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Potassium Organotrifluoroborates: Chemistry Beyond Cross-Coupling

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Potassium Organotrifluoroborates: Chemistry Beyond Cross-Coupling

Abstract
Over the years, organoboron species have been vastly utilized in synthetic organic chemistry. Traditional methods to synthesize these compounds, such as metal-halogen exchange, C-H activation and Miyaura borylation, often require the use of bisboronates as borylating partners [e.g., bis(pinacolato) diboron (B2Pin2), pinacolborane (HBPin) or neopentylglycolborane]. When the boronic acid is the target, the use of these reagents requires extra deprotection step, affording wasteful diol byproducts. Recently, the palladium-catalyzed synthesis of arylboronic acids employing the atom economical tetrahydroxydiboron (BBA) reagent has been reported. The high cost associated with palladium, combined with several limitations of both palladium and copper-catalyzed processes, prompted us to develop an alternative method. Thus, the nickel-catalyzed borylation of aryl and heteroaryl halides and pseudo-halides using tetrahydroxydiboron (BBA) has been formulated. The reaction proved to be widely functional group tolerant and applicable to a number of heterocyclic systems.

Because of their tetracoordinate nature, potassium organotrifluoroborates do not undergo undesirable side reactions with commonly employed organic reagents, and therefore the organic substructure of simple organotrifluoroborates can be functionalized to build molecular complexity while leaving the carbon-boron bond intact. This valuable bond can then be further converted into a variety of groups in a later synthetic step. Furthermore, in contrast to the corresponding aryl and heteroarylboronic acids, organotrifluoroborates are air and moisture stable and can be stored on the bench for months without appreciable decomposition. The major thrust of this thesis research has been the development of mild and metal-free methods for the hydrolysis, oxidation, chlorination and nitrosation of potassium organotrifluoroborates. All developed conditions were efficient for a variety of trifluoroborates containing diverse functional groups and especially heteroaryl units. Moreover, to explore the reactions of the unique nitrosoarenes synthesized, these species were used in a 1,3-dipolar cycloaddition with (trifluoromethyl)diazomethane and alkenes to afford trifluoromethylated isoxazolidines.

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CHEMISTRY BEYOND CROSS-COUPLING

Livia N. Cavalcanti

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POTASSIUM ORGANOTRIFLUOROBORATES: CHEMISTRY BEYOND CROSS-COUPLING

To my father Alirio Cavalcanti (in loving memory)

Dad, it was all because and for you.

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I would like to thank my family and friends in Brazil for their love and understanding of my professional choices. Although they complained a lot that I was too far away and missing so many special moments in their lives, they made the distance shorter by finding a way of sharing all those moments with me. I would like to especially thank my mother Maria for being the amazing human being she is. This strong woman took my education as the first priority in her life, and for all the sacrifices she did for me, I love her more than words can ever say.

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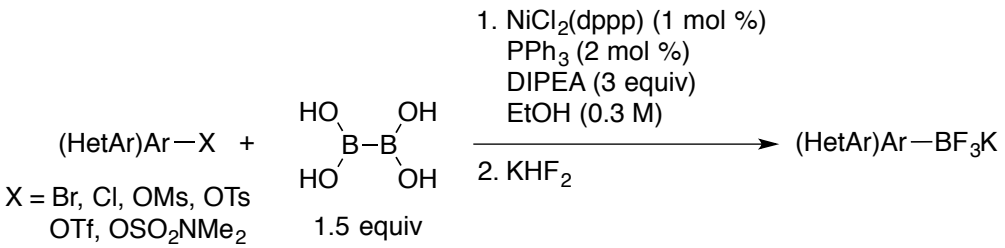
ABSTRACT

POTASSIUM ORGANOTRIFLUOROBORATES: CHEMISTRY BEYOND CROSS-COUPLING

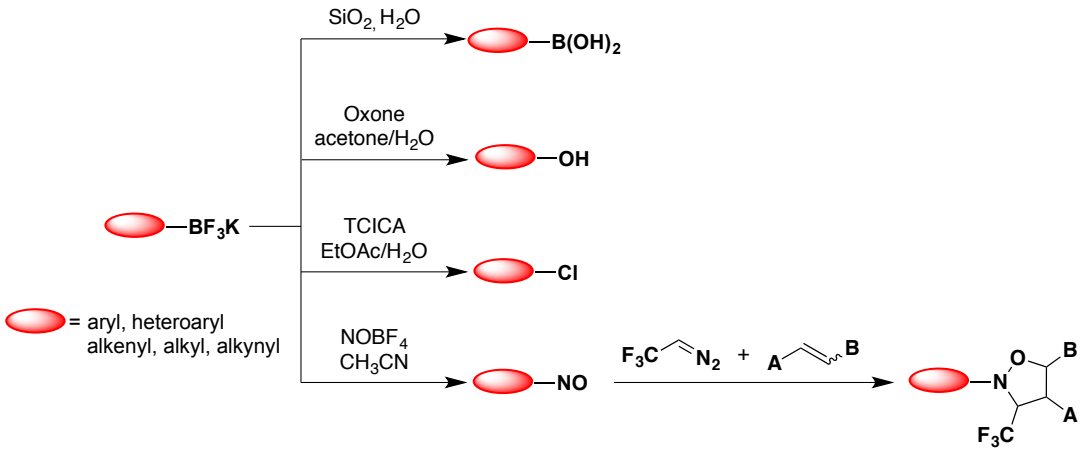
Livia N. Cavalcanti

Professor Gary A. Molander

Over the years, organoboron species have been vastly utilized in synthetic organic chemistry. Traditional methods to synthesize these compounds, such as metal-halogen exchange, C-H activation and Miyaura borylation, often require the use of bisboronates as borylating partners [e.g., bis(pinacolato) diboron (B_2Pin_2), pinacolborane (HBPin) or neopentylglycolborane]. When the boronic acid is the target, the use of these reagents requires extra deprotection step, affording wasteful diol byproducts. Recently, the palladium-catalyzed synthesis of arylboronic acids employing the atom economical tetrahydroxydiboron (BBA) reagent has been reported. The high cost associated with palladium, combined with several limitations of both palladium and copper-catalyzed processes, prompted us to develop an alternative method. Thus, the nickel-catalyzed borylation of aryl and heteroaryl halides and pseudo-halides using tetrahydroxydiboron (BBA) has been formulated. The reaction proved to be widely functional group tolerant and applicable to a number of heterocyclic systems.



Because of their tetracoordinate nature, potassium organotrifluoroborates do not undergo undesirable side reactions with commonly employed organic reagents, and therefore the organic substructure of simple organotrifluoroborates can be functionalized to build molecular complexity while leaving the carbon-boron bond intact. This valuable bond can then be further converted into a variety of groups in a later synthetic step. Furthermore, in contrast to the corresponding aryl and heteroarylboronic acids, organotrifluoroborates are air and moisture stable and can be stored on the bench for months without appreciable decomposition. The major thrust of this thesis research has been the development of mild and metal-free methods for the hydrolysis, oxidation, chlorination and nitrosation of potassium organotrifluoroborates. All developed conditions were efficient for a variety of trifluoroborates containing diverse functional groups and especially heteroaryl units. Moreover, to explore the reactions of the unique nitrosoarenes synthesized, these species were used in a 1,3-dipolar cycloaddition with (trifluoromethyl)diazomethane and alkenes to afford trifluoromethylated isoxazolidines.



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LIST OF ABBREVIATIONS

δ	Chemical shift in parts per million
(Ind)Ir(COD)	(1,5-Cyclooctadiene)-η^5-indenyl)iridium(I)
(*R*)-(*S*)-Josiphos	(1*R*)-1-[Bis(1,1-dimethylethyl)phosphino]-2-[(1*R*)-1-[bis(2-methylphenyl)phosphino]ethyl]ferrocene
$[Ir(OMe)COD]_2$	(1,5-Cyclooctadiene)(methoxy)iridium(I) dimer
$[Pd_2(dba)_3]_2$	Tris(dibenzylideneacetone)dipalladium(0)
^{11}B	Boron nuclear magnetic resonance
^{13}C	Carbon nuclear magnetic resonance
^{19}F	Fluorine nuclear magnetic resonance
^{1}H	Proton nuclear magnetic resonance
aq	Aqueous
B(dan)	2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
B_2Pin_2	Bis(pinacolato)diboron
BBA	Tetrahydroxydiboron
BHT	2,6-Di-*tert*-butyl-4-methylphenol
CPME	Cyclopentylmethylether
$CuBr•SMe_2$	Copper(I) bromide dimethyl sulfide complex

DAST	(Diethylamino)sulfur trifluoride
DCDMH	1,3-Dichloro-5,5-dimethylhydantoin
DIPEA	Diisopropylethylamine
DMDO	Dimethyldioxirane
DMF	*N,N*-Dimethylformamide
dmpe	1,2-Bis(dimethylphosphino)ethane
DMSO	Dimethyl sulfoxide
dppf	1,1′-Bis(diphenylphosphino)ferrocene
dtbpy	4,4′-Di-*tert*-butyl-2,2′-dipyridyl
EDG	Electron-donating group
equiv	Equivalent(s)
Et_3N	Triethylamine
EtOAc	Ethylacetate
EtOH	Ethanol
EWG	Electron-withdrawing group
g	Gram(s)
GC	Gas chromatography
GC/MS	Gas Chromatography/ Mass Spectrometry
h	Hour(s)
HBPin	Pinacolborane

HPLC	High performance liquid chromatography
HTE	High Throughput Experimentation
K_2CO_3	Potassium carbonate
KF	Potassium fluoride
KHF_2	Potassium hydrogen fluoride
KOAc	Potassium Acetate
KO*t*-Bu	Potassium *tert*-butoxide
M	Molar
MeCN	Acetonitrile
MeOH	Methanol
MeOH	Methanol
MIDA	*N*-Methyliminodiacetic acid
min	Minute(s)
mL	Milliliter
mmol	Milimol
n-Bu_3P	Tri-*n*-butylphosphine
NaO*t*-Bu	Sodium *tert*-butoxide
NCS	*N*-Chlorosuccinimide
$NiCl_2$(dppp)	[1,3-Bis(diphenylphosphino)propane]dichloronickel(II)
NMO	4-Methylmorpholine *N*-oxide

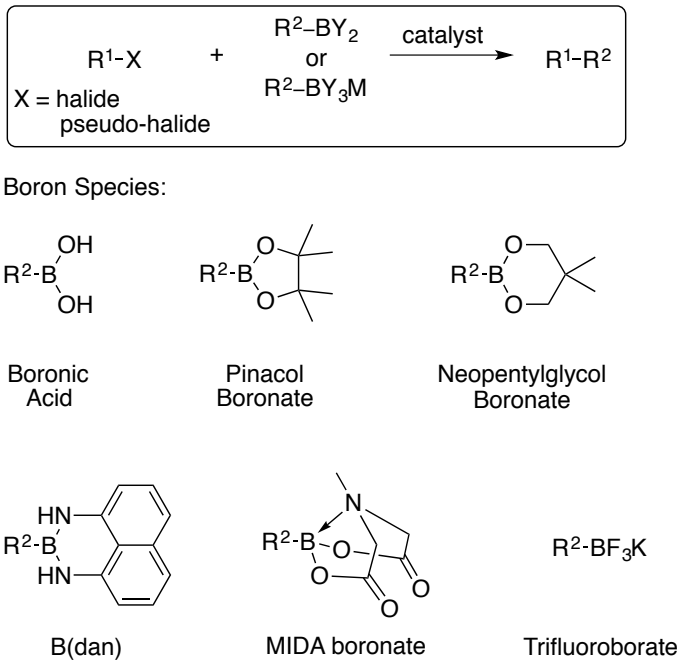
NMR	Nuclear magnetic resonance
Nuc	Nucleophile
ºC	Degrees Celcius
OMe	Methoxy
OMs	Mesylate
OTf	Triflate
PET	Positron emission tomography
Ph	Phenyl
PPh_3	Triphenylphosphine
rt	Room temperature
TCICA	Trichloroisocyanuric acid
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TMSCl	Trimethylchlorosilane
TPAP	Tetrapropylammonium perruthenate
XPhos	2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl

Chapter 1. Synthesis of Organoboranes and Potassium Organotrifluoroborates

1.1 Organoboron Species

Organoboron species have found great utility in synthetic organic chemistry.[1] They have been used in a variety of transformations such as 1,2-additions to aldehydes,[2] conjugate additions,[3] Petasis-borono Mannich reactions[4] and ether couplings.[5] However, their most predominant use is as the nucleophilic partners in Suzuki cross-coupling for formation of carbon-carbon bonds.[6] Over the years, a variety of boron species such as boronic acids, boronates esters, and trifluoroborates have been reported to undergo this important class of reactions (Scheme 1.1). Among all such species, the most utilized are boronic acids.[7] Although commercially available, these boron species are known to exist as dimers or trimeric cyclic anhydrides, making their stoichiometry uncertain. Consequently, boronic acids are often used in excess to ensure consumption of the electrophilic partner of the reaction. Furthermore, the empty p-orbital of boronic acids and boronate esters makes them susceptible to reactions with commonly employed reagents such as acids, bases, and oxidants. Thus, these species are rarely carried through synthetic steps, and are often made and utilized immediately.

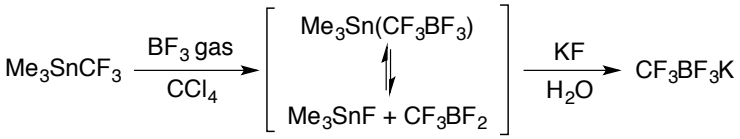
Scheme 1.1 Nucleophilic Partners in the Suzuki Cross-Coupling Reaction



1.2 Potassium Organotrifluoroborates

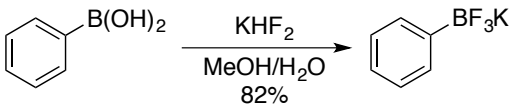
To overcome the limitations associated with tricoordinate boron species, organotrifluoroborates, have emerged as a viable alternative. These borate salts were synthesized for the first time in 1960 by Chambers and co-workers[8] and proved to be more robust than boronic acids. In this seminal paper the investigators were able to synthesize potassium trifluoromethylfluoroborate from the corresponding tin compound using BF_3 gas and potassium fluoride (eq 1.1).

Equation 1.1



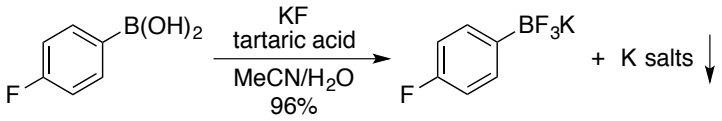
However, it was only in 1995 that a more general method for the synthesis of organotrifluoroborates was developed.[9] Vedejs and co-workers reported the synthesis of diverse potassium trifluoroborates from the corresponding boronic acid using inexpensive and widely available aqueous potassium hydrogen fluoride (KHF_2) (eq 1.2). Following this procedure a variety of potassium organotrifluoroborates have been synthesized through the years, and the chemistry of this stable tetracoordinate species has been extensively studied.[10]

Equation 1.2



Because the use of KHF_2 causes extensive etching of glassware, recently Lloyd-Jones and co-workers reported the preparation of potassium trifluoroborates under non-etching conditions (eq 1.3).[11] Using a mixture of KF and tartaric acid in acetonitrile, they were able to obtain the desired trifluoroborate along with potassium salt byproducts that could easily be removed from the mixture by simple filtration, yielding the desired aryltrifluoroborate in excellent yields after evaporation of the solvent.

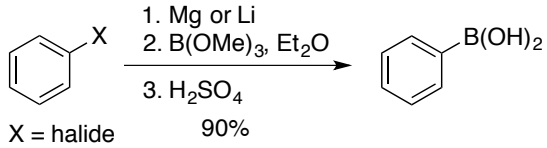
Equation 1.3



1.3 Synthesis of Organoboron Species

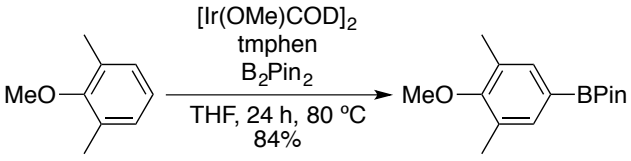
As aforementioned, potassium aryltrifluoroborates are commonly synthesized from the corresponding boronic acids. Traditional methods for the synthesis of arylboronic acids from the corresponding halides and trialkyl borates rely on a metal-halogen exchange approach and require the use of organolithium or organomagnesium reagents (eq 1.4).[12] Although widely utilized, this process presents limitations regarding functional group tolerability, being incompatible with molecules containing sensitive functional groups embedded within their structures.[13]

Equation 1.4



Transition metal-catalyzed borylation has emerged as a viable alternative to afford boron species containing a high degree of molecular complexity. Rh[14] and Ir-[15]catalyzed C-H borylation provides access to many aryl and heteroarylboron derivatives (eq 1.5). However, the selectivity of this reaction is determined by steric and electronic effects within the aryl system, making it limited to specific substitution patterns.

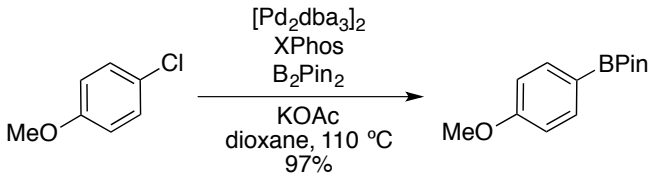
Equation 1.5



To overcome these limitations, Ni,[16] Cu[17] and Pd[18]-catalyzed Miyaura borylations of aryl and heteroaryl halides have been developed. Since Miyaura's first publication in 1995,[18a] a variety of catalysts and ligands have been developed for the Pd-catalyzed

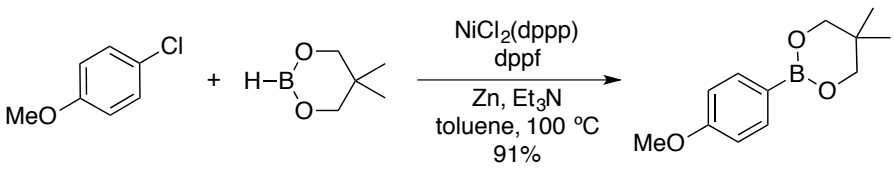
borylation of aryl halides. Nevertheless, the biggest advance in this area came with the development of Buchwald's air-stable ligands (eq 1.6),[18e] which allowed the successful borylation of many aryl halides that have failed in previous attempts, largely expanding the scope of these reactions.

Equation 1.6



In the field of Ni-catalyzed Miyaura borylation, the Percec group has made great contributions.[16a-f] The development of *in situ* prepared neopentylglycolborane in combination with a variety of nickel catalysts and simple non-proprietary ligands allowed the borylation of aryl halides and pseudo-halides in good yields (eq 1.7). However, these protocols usually requires the use of additives such as zinc,[16b,16e] and they proceed at high reaction temperatures (100 – 110 ºC).

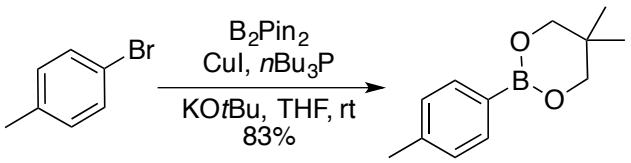
Equation 1.7



There are very few reports in the literature for copper-catalyzed borylation of aryl halides. In work published in 2006, Ma and co-workers reported the borylation of aryl iodides with pinacolborane, and moderate to good yields of the desired borylated product were obtained.[17a] In 2009, Marder and co-workers expanded the scope of this reaction to aryl bromides.[17b] Thus, the reaction of aryl iodides and bromides with bis(pinacolato)

diboron (B_2Pin_2), CuI, *n*-Bu_3P and KO*t*-Bu in THF at room temperature was developed (eq 1.8). Moreover, a recently reported copper borylation protocol of aryl iodides, bromides and benzyl halides has shown the conversion of these species into the corresponding pinacol boronates in moderate yields.[17c]

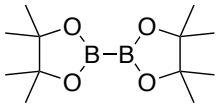
Equation 1.8



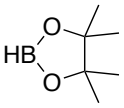
1.4 Borylating Agents

Regardless of the high selectivity and functional group compatibility, all published Miyaura borylation methods often require the use of bis(pinacolato) diboron (B_2Pin_2), pinacolborane (HBPin) or neopentylglycolborane as a boron source, thus resulting in the initial formation of boronates. To access the boronic acids, an additional deprotection step is required. Representative examples of deprotection conditions to unveil the desired boronic acid include acidic hydrolysis,[19] oxidation[20] or reduction[21] (Scheme 1.2). In addition to the requisite deprotection, all of the boronate-based reagents release diols on conversion to the desired arylboronic acids, and these diol-byproducts must be removed from the reaction mixture through often laborious procedures.[22] This, combined with the inherent lack of atom economy in these processes, greatly diminishes the appeal of these approaches.

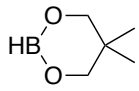
Scheme 1.2 Commonly Employed Borylating Agents and BBA



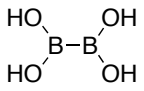
bis(pinacolato)diboron
(B_2Pin_2, BisPin)
MW = 254



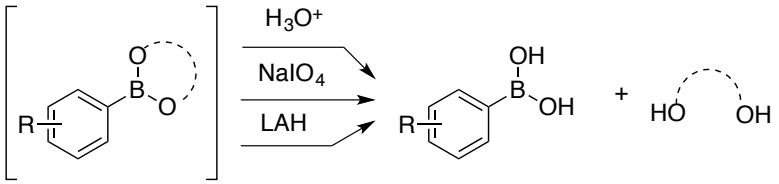
pinacolborane
(HBPin)
MW = 128



neopentylglycolborane
MW = 114



tetrahydroxydiboron
[$B_2(OH)_4$, BBA]
MW = 90



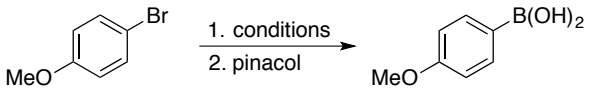
In an effort to devise a method to provide direct access to arylboronic acids, we recently developed a Pd-catalyzed borylation of aryl- and heteroaryl halides utilizing tetrahydroxydiboron (BBA).[23] Under the conditions that evolved, aryl and heteroaryl chlorides and bromides were efficiently borylated. The reaction required 0.1 – 5 mol % of a palladium-based pre-formed catalyst, 3 equivalents of BBA, and reaction temperatures of 80 ºC. Although highly effective in most cases, aryl halides containing ketones and aldehydes afforded the desired product along with undesired byproducts resulting from reduction of these embedded functional groups. Furthermore, the substrate scope for heteroaryl systems was restricted to nitrogen-containing molecules such as quinolines and indoles, and borylation of furans and thiophenes derivatives could not be achieved.

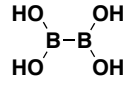
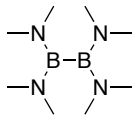
1.5 Copper-Catalyzed Borylation with BBA

Because of the high cost of palladium and the limitations associated with the developed nickel and copper methods, the search for a cost and chemical economical process for the borylation of aryl halides is still necessary. We started our investigation with inexpensive and less toxic copper catalysts. The previously reported copper-catalyzed borylations,[17] besides using the wasteful B_2Pin_2, have a very limited substrate scope for heteroaryl systems as well as a limited functional group compatibility. Furthermore, the majority of the examples are restricted to aryl iodides. Therefore, we were interested in a copper-catalyzed borylation of aryl bromides and chlorides with tetrahydroxydiboron.

Using microscale high throughput experimentation (HTE), we began the investigation for optimal reaction conditions using 4-bromoanisole. A variety of copper catalysts, ligands, bases, borylating agents [BBA and its precursor tetrakis(dimethylamino)diboron] and solvents was examined (Scheme 1.3).

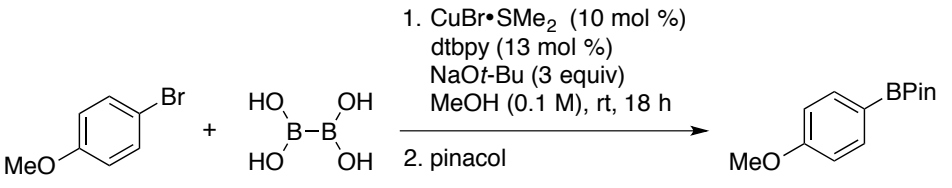
Scheme 1.3 Microscale HTE screening for copper-catalyzed borylation



Cu (10 mol%)	Ligands (15 mol%)	Borylating Agent (3 equiv)	Bases (3 equiv)	Solvents (0.1 M)
CuCl	PPh_3		KO*t*-Bu	THF : EtOH
CuI	nBu_3P		**NaO*t*-Bu**	**MeOH**
CuBr • SMe_2	tBu_3P		LiO*t*-Bu	EtOH
CuCN	$Cy_3P•HBF_4$		KOAc	*t*-BuOH
CuOTf • benzene	$tBu_3P•HBF_4$		K_2CO_3	THF
CuOAc	CyJohnPhos		K_3PO_4	CPME
$Cu(NCCH_3)_4PF_6$	XPhos		NaOTs	toluene
CuO_2	RuPhos		KOMe	ethylene glycol
$Cu(NO_3)(PPh_3)_2$	SPhos		Cs_2CO_3	THF : ethylene glycol
CuBr(phenanthroline)(PPh_3)	BrettPhos		NaH	EtOH : ethylene glycol
$CuNO_3$(phenanthroline)$(PPh_3)_2$	Catacxium A			
CuCl(IMs)	ICy			
CuBr	IAd			
CuOAc	IMes			
$Cu(Cp)_2(PEt_3)$	dppf			
$Cu(CF_3acac)_2$	dppe			
Cu(t-Bu-acetoacetato)$_2$	dppp			
$Cu(FOD)_2$	phenanthroline			
$Cu(TMHD)_2$	**dtbpy**			
Cu(II)phthalocyanine	dmbpy			
$Cu(OTf)_2$	cyclohexyldiamine			
$Cu(OAc)_2$	1,3-dicyclohexylimidazolium			
$CuCl_2$	Pybox			
$Cu(NO_3)_2$	no ligand			

Unfortunately, after more than 10 x 96 well plates, all the conditions tested were inefficient to ensure reaction completion as indicated by HPLC analysis. Because, some product formation was observed when BBA was used along with CuBr·SMe_2, dtbpy, NaO*t*Bu in MeOH, these conditions were chosen to be performed on a 1 mmol scale (eq 1.9). However, after more optimization, the product was obtained in only 10% yield.

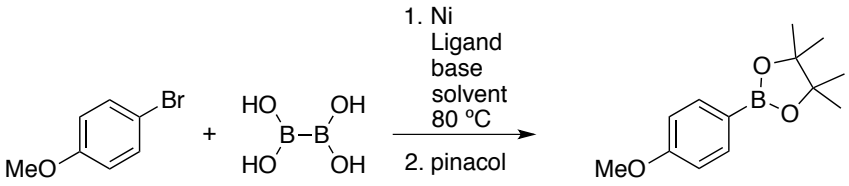
Equation 1.9



1.6 Nickel-Catalyzed Borylation with BBA[24]

Next, we pursued the optimization of the reaction conditions for the nickel-catalyzed borylation of aryl halides using BBA with 4-bromoanisole. Once again, using microscale high throughput experimentation (HTE), an array of nickel catalysts, ligands, bases and solvents was examined. In contrast with the copper-catalyzed reaction, for these reactions we were pleased to find that a combination of $NiCl_2$(dppp), PPh_3, and diisopropylethylamine (DIPEA) in ethanol at 80 ºC was efficient, affording the desired boronic acid in good yield as evidenced by conversion to the pinacol boronate and analysis by HPLC (Scheme 1.4).

Scheme 1.4 Microscale HTE screening for optimal reaction conditions with 4-bromoanisole

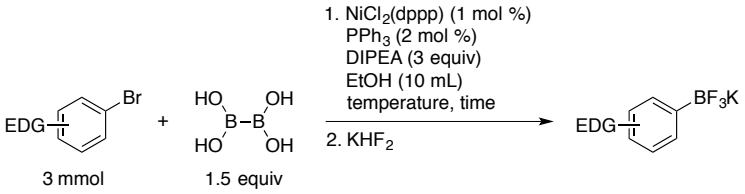


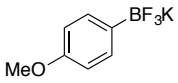
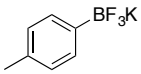
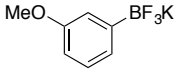
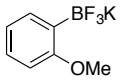
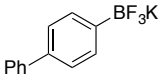
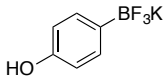
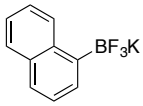
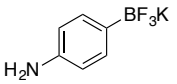
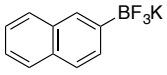
Ni	Ligand	Base	Solvent
$NiBr_2$•glyme	dppe	Et_3N	**EtOH**
$NiCl_2$(dppp)	dppf	**DIPEA**	MeOH
$NiCl_2(PCy_3)_2$	CyJohnPhos	Cy_2NMe	THF
$Ni(PPh_3)_4$	BrettPhos	Bu_3N	CPME
$Ni(COD)_2$	XPhos	KOAc	toluene
$NiCl_2$(dppf)	RuPhos	K_3PO_4	dioxane
$NiCl_2$(dppe)	**PPh_3**	KO*t*-Bu	
$NiCl_2$•glyme	SPhos	K_2CO_3	
$NiCl_2(PPh_3)_2$	AtaPhos		
$NiCl_2$	dtbpy		
$NiBr_2$	dmbpy		
	phenanthroline		
	cyclohexyldiamine		
	no ligand		

The optimal HTE conditions performed on microscale were scaled up and repeated on the benchtop. Because boronic acids are known to be relatively unstable tricoordinate boron species,[25] to determine the isolated yields the crude reaction mixture was treated with aqueous KHF_2 to afford the more robust potassium trifluoroborate salts without purification of the intermediate boronic acid. Thus, in a very straightforward and simple procedure the reaction of 4-bromoanisole (3 mmol) with BBA (1.5 equiv), 1 mol % of $NiCl_2$(dppp), 2 mol % of PPh_3, and 3 equivalents of DIPEA in 10 mL of degassed ethanol at 80 ºC, followed by aqueous KHF_2 addition, yielded potassium trifluoro(4-methoxyphenyl)borate (Table 1.1, entry 1) in 91% yield. Importantly, all reagents utilized in this method are inexpensive and bench stable, avoiding the use of glovebox techniques and dry solvents. Furthermore, when compared to other Ni-catalyzed borylations, the reaction occurs in only 2 h (as indicated by GC) without the use of metal additives. With optimal conditions in hand, the substrate scope for aryl bromides containing electron-donating and electron-neutral groups was subsequently investigated (Table 1.1). The indicated reaction time was determined by GC analysis. Aryl bromides containing a methyl ether group in the para (entry 1), meta (entry 2) and ortho (entry 3) position afforded the desired trifluoroborates in good yield in only 2 h at 80 ºC. The same trend was observed for simple methyl substituted arenes (entries 6 and 7). When the reaction of electron neutral aryl bromides was performed at 80 ºC, significant amounts of undesired homocoupled product was observed by GC/MS, leading to lower yields. Carrying out the reaction at room temperature diminished this problem, and excellent yields were achieved for those substrates (entries 8 – 10). The presence of alcohol or free amine functional groups in the molecule required the use of 3 mol % of the Ni catalyst. However, the

reactions proceeded at room temperature in only 6 h, and the desired trifluoroborates were obtained in good yields. Furthermore, the reaction of 2-bromonaphthalene was performed on a 48 mmol scale (~10 g), providing the product in 81% yield after 8 h at room temperature (entry 10). The catalyst loading for this large-scale reaction was reduced to 0.1 mol % $NiCl_2$(dppp), and 0.2 mol % of PPh_3 in 90 mL of ethanol (0.5 M). Unfortunately, sterically hindered 2,6-dimethylbromobenzene did not perform well under the reaction conditions, and only 16% conversion was observed by GC/MS (data not shown).

Table 1.1 Ni-catalyzed Borylation of Electron-Rich and Electron-Neutral Aryl Bromides with BBA



entry	product	time	temperature	yield (%)	entry	product	time	temperature	yield (%)
1		2 h	80 °C	91	6		4 h	80 °C	84
2		2 h	80 °C	89	7		3 h	80 °C	72
3		2 h	80 °C	77	8		6 h	rt	90
4[a]		6 h	rt	78	9		4 h	rt	93
5[a]		6 h	rt	67	10		4 h 8 h	rt	90 81[b]

[a] 3 mol % $NiCl_2$(dppp) and 6 mol % PPh_3
[b] 48 mmol scale using 0.1 mol % $NiCl_2$(dppp), 0.2 mol % PPh_3 in EtOH (90 mL)

Next, aryl bromides containing electron-withdrawing groups were tested using the developed borylation protocol (Table 1.2). The broad functional group compatibility of this method is illustrated with the set of substrates utilized. Aryl bromides containing nitrile, ketone, ester and aldehyde functional groups at the *para* and *meta* positions (entries 1 – 6) were efficiently borylated at room temperature, affording the corresponding trifluoroborates in good to excellent yields. Remarkably, because of the

very mild reaction conditions, compounds in entries 3 – 6 were obtained without reduction of the carbonyl group. Previously developed palladium-catalyzed borylations with BBA delivered up to 30% of the reduced alcohol side product.[23b] Of note, borylation of aryl halides containing aldehydes were not included in any previously reported nickel-catalyzed borylation methods. *para*- and *ortho*-Substituted fluorine-containing substrates were also borylated (entries 7 – 10). These molecules provide easy access to fluorinated aryl compounds via cross-coupling reactions and are of increasing interest in medicinal chemistry.[26] As a limitation of the method, ortho substituted aryl bromides containing electron-withdrawing groups other than fluorine and trifluoromethyl did not provide the desired borylated product, and only protodehalogenation was observed. Furthermore, aryl bromides containing nitro groups afforded only the reduced amine product (eq 1.10), along with unreacted starting material, as indicated by GC/MS analysis.

Equation 1.10

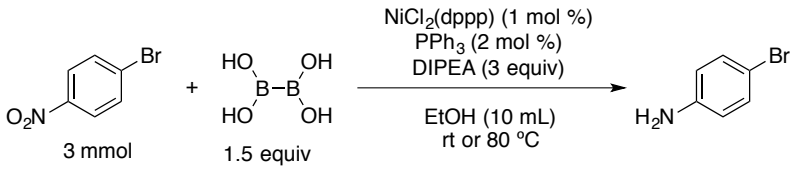
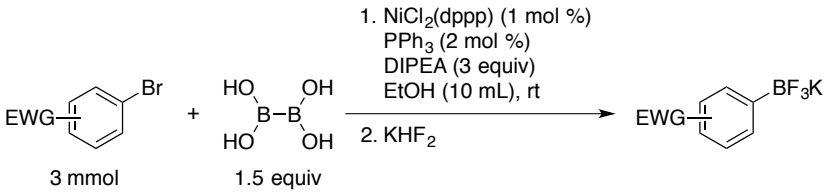
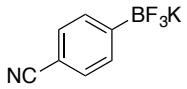
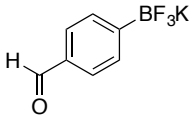
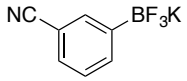
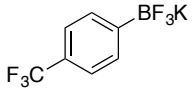
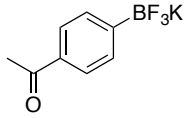
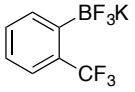
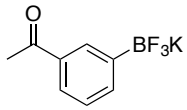
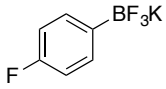
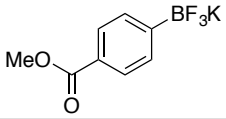
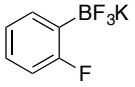


Table 1.2 Ni-catalyzed Borylation of Electron-Poor Aryl Bromides with BBA



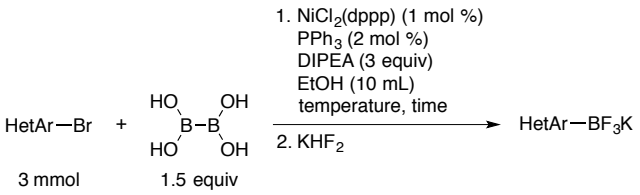
entry	product	time	yield (%)	entry	product	time	yield (%)
1		4 h	91	6		6 h	84
2		4 h	78	7		6 h	86
3		4 h	93	8		12 h	71
4		4 h	81	9		2 h	96
5		6 h	92[a]	10		12 h	75

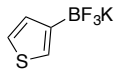
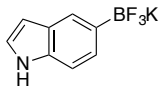
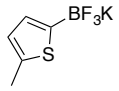
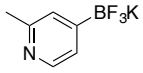
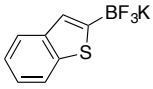
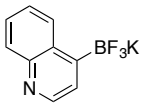
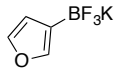
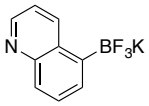
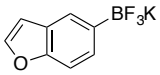
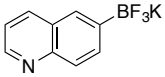
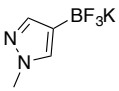
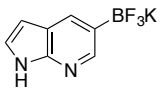
[a] reaction run at 50 ºC

The scope of the reaction was further expanded to heteroaryl bromides (Table 1.3). Under the developed reaction conditions, a variety of heteroaryl trifluoroborates such as thiophene, furan, benzofuran, benzothiophene, pyrazole, indole, pyridine, quinoline, and azaindole systems were successfully borylated in good to excellent yields. Nitrogen-containing heterocycles required higher catalyst loading and temperatures. Furthermore, after addition of KHF_2 a mixture of potassium and internal salt was obtained for these substrates, and full conversion to the potassium salt required treatment

of the crude mixture with K_2CO_3 in acetonitrile.[27] To the best of our knowledge, the examples illustrated in Table 1.3 represent the largest and most diverse substrate scope for borylation of heteroaryl systems in the current literature. As one limitation of the current method, heteroaryls such as pyrimidine, isoxazole and thiazole did not undergo borylation, and only halide starting material was recovered in these cases.

Table 1.3 Ni-catalyzed Borylation of Heteroaryl Bromides with BBA

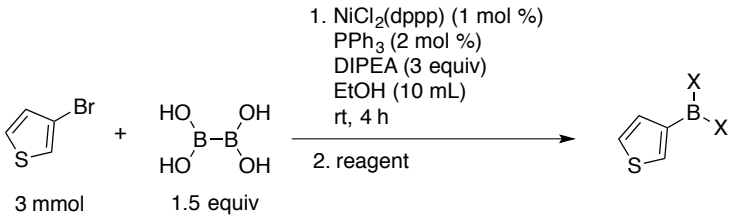


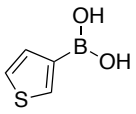
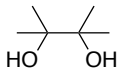
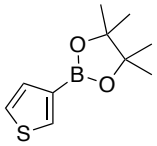
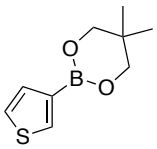
entry	product	time	temperature	yield (%)	entry	product	time	temperature	yield (%)
1		4 h	rt	94	7		6 h	rt	86
2[a]		4 h	rt	85	8[b]		4 h	80 ºC	72
3[a]		6 h	rt	74	9[b]		4 h	80 ºC	74
4		4 h	rt	92	10[b]		4 h	80 ºC	81
5		4 h	rt	91	11[b]		4 h	80 ºC	83
6[b]		12 h	rt	82	12[b]		4 h	80 ºC	83

[a] $NiCl_2$(dppp) (0.5 mol %), PPh_3 (1 mol %)
[b] $NiCl_2$(dppp) (5 mol %), PPh_3 (10 mol %)

As mentioned previously, one of the advantages in utilizing BBA as a borylating agent is that it provides direct access to boronic acids as well as a variety of boronate esters. Thus, 3-bromothiophene was subjected to the nickel-catalyzed borylation protocol with BBA followed by different workups to provide diverse boron derivatives (Table 1.4). Boronic acid was obtained in good yield after a simple hexane wash of the crude mixture. Various boronate esters were accessed after acid workup followed by addition of the corresponding diol reagent and purification by column chromatography.

Table 1.4 Direct Synthesis of Boron Derivatives

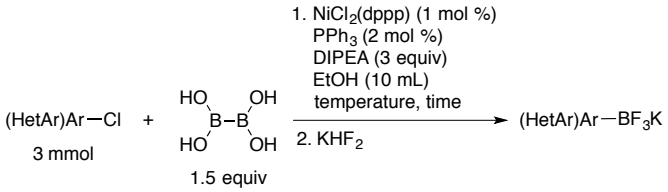


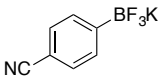
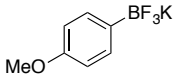
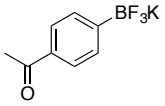
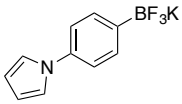
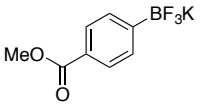
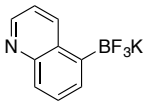
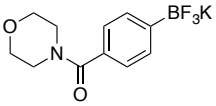
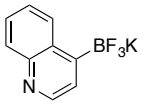
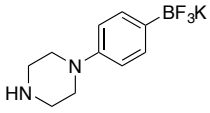
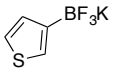
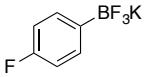
entry	reagent	product	yield (%)
1	hexane wash		87
2			90
3			96

Additionally, we were interested in utilizing the same developed set of conditions for the more commercially available aryl and heteroaryl chlorides (Table 1.5). Aryl chlorides containing nitrile, ester, ketone, morpholine, piperazine, ether, fluorine

and pyrrole subunits embedded within their structure provided the organotrifluoroborates in moderate to good yields. Heteroaryl chlorides such as quinolinyl and thienyl chloride were also borylated. The use of chlorides as the electrophile of choice required, in general, longer reaction times and higher temperatures than when the corresponding bromide was used. Nevertheless, the same set of conditions could be used for the borylation of both halides.

Table 1.5 Ni-catalyzed Borylation of Aryl and Heteroaryl Chlorides with BBA



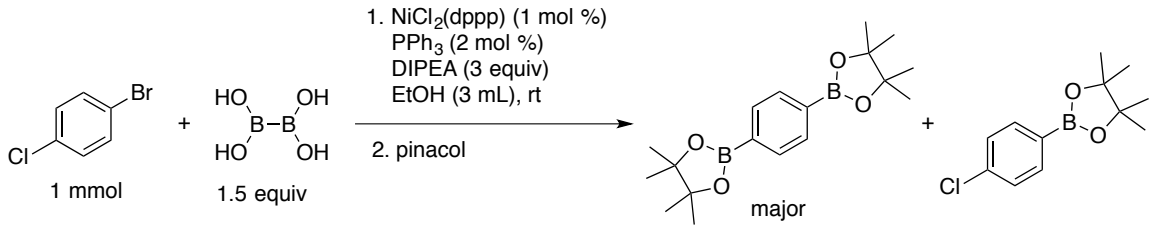
entry	product	time	temperature	yield (%)	entry	product	time	temperature	yield (%)
1		4 h	rt	92	7		12 h	80 °C	66
2		4 h	rt	89	8		2 h	80 °C	69
3		4 h	80 °C	89	9[a]		12 h	80 °C	75
4		12 h	rt	64	10[a]		12 h	80 °C	58
5[a]		8 h	80 °C	52	11		12 h	rt	86
6		12 h	rt	83					

[a] $NiCl_2(dppp)$ (5 mol %), PPh_3 (10 mol %)

Because aryl bromides generally reacted under milder conditions, we were interested in examining the selectivity of the method for molecules containing both bromide and chloride within the molecule (eq 1.11). Thus, 4-bromochlorobenzene was chosen as a test substrate. Unfortunately, after 30 minutes the major product obtained was the diborylated compound, as identified after addition of pinacol and GC/MS analysis.

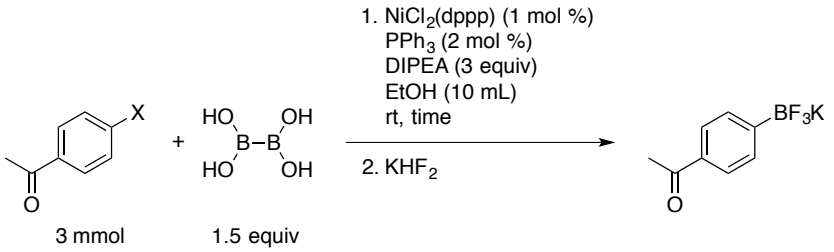
The remaining 1-bromo-4-chlorobenzene starting material was also recovered, along with small amounts of monoborylated product containing the chloride group. The result indicates that although the reaction should proceed slightly faster for bromides, this preference was insignificant under the developed conditions.

Equation 1.11



To compare the efficiency of the method for different borylation partners, the developed conditions were applied to the same aryl bromide, chloride, iodide, triflate, tosylate, mesylate, sulfamate, carbamate and pivalate (Table 1.6). When compared as a group, bromides are the best electrophilic partners for this reaction. The aryl iodide gave a lower yield compared to other halide electrophiles, mostly because of the large amount of homocoupling product observed. Aryl triflates, tosylates, mesylates and sulfamates were borylated in good yields (entries 4 – 7), while carbamates and pivalates failed to provide borylated product under this set of conditions, and only starting material was recovered.

Table 1.6 Ni-catalyzed Borylation of Different Electrophiles



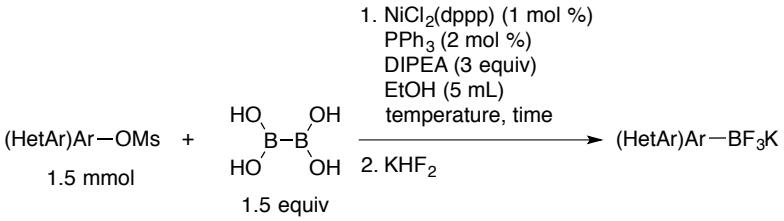
3 mmol 1.5 equiv

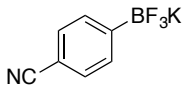
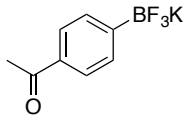
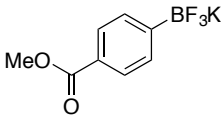
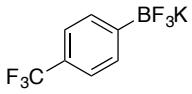
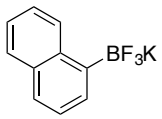
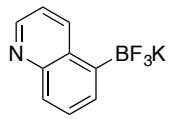
entry	X	time	yield (%)
1	Br	4 h	93
2	Cl	4 h	89
3	I	2 h	75
4	OTf	6 h	88
5[a]	OTs	2 h	76
6	OMs	12 h	81
7[a]	OSO_2NMe_2	12 h	71
8[a]	$OC(O)NEt_2$	24 h	0
9[a]	OPiv	24 h	0

[a] reaction run at 80 ºC

Because the palladium-catalyzed borylation with BBA failed to afford the desired borylated product when aryl mesylates were used,[23b] we were interested in investigating the scope of the reaction for this class of electrophiles (Table 1.7). Aryl mesylates containing electron-donating, electron-withdrawing and electron-neutral groups underwent borylation under the developed conditions. The products were obtained in good yields without the use of additives as required using previously developed nickel-catalyzed borylation methods.[16e]

Table 1.7 Ni-catalyzed Borylation of Aryl and Heteroaryl Mesylates with BBA



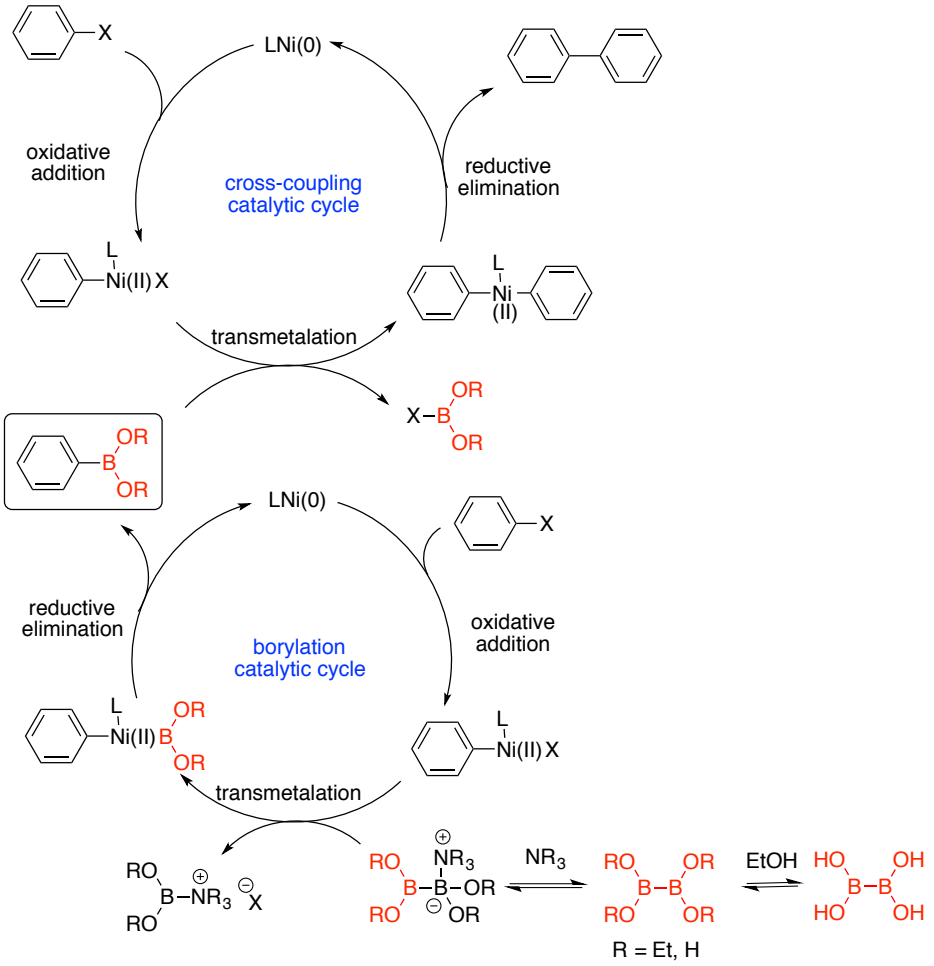
entry	product		time	temperature	yield (%)
1		**7a**	4 h	50 °C	82
2		**7b**	4 h	50 °C	88
3		**7c**	4 h	80 °C	71
4		**7d**	12 h	50 °C	81
5		**7e**	8 h	50 °C	87
6[a]		**7f**	8 h	80 °C	76

[a] $NiCl_2(dppp)$ (5 mol %), PPh_3 (10 mol %)

The proposed reaction mechanism is analogous to the one proposed for the Pd-catalyzed borylation BBA (Scheme 1.5). On the basis of this mechanism, PPh_3 is necessary to help stabilize the *in situ* formed Ni(0) catalyst. Because homocoupling products were observed

for some substrates, we envisioned the possibility of a catalytic cycle occurring parallel to the borylation cycle. The formed boronic acid can compete with BBA in transmetalation with the oxidative addition complex. As observed in our studies, lower catalyst loading and reaction temperature minimized the side product formation and afforded the desired boronic acid in good yields.

Scheme 1.5 Proposed Reaction Mechanism



1.7 Conclusions

In conclusion, the nickel-catalyzed borylation using tetrahydroxydiboron was developed. The same set of conditions was efficient to borylate a wide array of aryl and heteroaryl bromides, chlorides, mesylates, tosylates, triflates and sulfamates containing diverse functional groups. All reagents utilized in this method are stable and can be stored on the benchtop. The low cost of nickel compared to that of palladium, combined with the ability to use non-proprietary ligands, makes the method economically attractive for industrial purposes. The use of BBA allows access to different boron derivatives, and most importantly this approach provides direct access to boronic acids and also to the more robust trifluoroborates. To the best of our knowledge, the examples herein presented that proceeded at room temperature are the first effective Ni-catalyzed Miyaura-borylations to be carried out under such mild condition. Finally, the substrate scope for heteroaryls is the largest found in the currently available literature.

On the other hand, the copper-catalyzed version of this reaction failed to afford the desired borylated product in good yields. Extensive HTE optimization revealed very low conversion for all conditions investigated. The best yield obtained after scale up of the microscale reaction was no more than 10%.

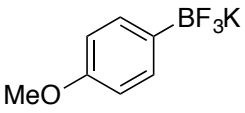
1.8 Experimental

General Procedure for Parallel Microscale Experimentation. In a glovebox, Ni catalysts (0.4 μmol) were dosed into the 96-well reactor vial as solutions (50 μL of a 0.008 M solution in CH_3CN or THF depending upon the solubility of the catalyst). Ligand (0.8 μmol, 50 μL of a 0.016 M solution in CH_3CN or THF depending upon the solubility of the catalyst) was then added to the reaction vials, and this was evacuated to dryness. In the case of solid bases, they were added to the ligand/catalyst mixture (60 μmol, 100 μL of a 0.6 M slurry solution in THF), and this was evacuated to dryness. A parylene stir-bar was then added to each reaction. The 4-bromoanisole (20 μmol/reaction), $(HO)_2B\text{-}B(OH)_2$ (30 μmol/reaction), liquid bases (60 μmol/reaction) and *tert*-butylbiphenyl (1 μmol/reaction, used as an internal standard to measure HPLC yield) were then dosed together in the desired reaction solvents using a single-tip pipettor. The reactions were then sealed, taken outside the glovebox, and heated at 80 ºC for 18 h. After cooling to ambient temperature, pinacol (100 μL of a 1.8 M solution in CH_3CN) was added to the reactions, and the plate was diluted with 500 μL of MeCN. A silicon-rubber storage mat was added, and the contents were shaken to homogenize. Into a separate 96-well-plate LC plate with 1 mL vials was then added 750 μL of MeCN, and then 20 μL of the diluted reaction mixtures. The 96-well plate LC block was then sealed with a silicon rubber storage mat. The reactions were then analyzed using an HPLC modified with a 96-well plate auto-sampler.

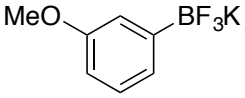
General Procedure for Ni-catalyzed Borylation of Aryl and Heteroaryl Halides and Mesylates : To a glass vessel capable of being sealed with a Teflon cap (for microwave vials) was added $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06

mmol, 2 mol %) and $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv). The vessel was capped and then evacuated and backfilled with Ar (process repeated 3 x). EtOH (10 mL, degassed) was added via syringe followed by the addition of DIPEA (1.6 mL, 9 mmol, 3 equiv) and the halide (3 mmol) in a similar manner (solid halides were added with the other solid reagents before sealing). The reaction was then heated at determined temperatures until the starting material was consumed (as monitored by GC). After the required time, the reaction was cooled to rt and transferred to a 250 mL round bottom flask and concentrated under reduced pressure. The concentrated crude reaction was taken up in MeOH (~ 15 mL or enough to make a free-flowing solution) and cooled to 0 ºC. To this solution was added 7.5 equivalents of a 4.5 M aqueous KHF_2 (5 mL), and the reaction was stirred for 10 min at 0 ºC. The ice bath was removed, and the reaction was stirred at rt for 20 min (or until full conversion to the corresponding trifluoroborate as determined by ^{11}B NMR). The resulting mixture was concentrated and then lyophilized overnight to remove any traces of H_2O. The compound was purified with continuous Soxhlet extraction (overnight) with acetone (150 mL). The collected solvent was concentrated until a minimal volume of acetone remained (~5 mL). The addition of Et_2O (~25 mL) led to the precipitation of the desired product. The collected solid was washed with Et_2O. In cases where the trifluoroborate was obtained with a trace amount of the protonated base and for nitrogen-containing trifluoroborates (internal salt formation), the crude mixture was concentrated after Soxhlet extraction and dissolved in acetonitrile (~ 15 mL). To this solution was added K_2CO_3 (4 g, 10 equiv) and the reaction was stirred for 4 h (quinoline and pyridine derivatives required 16 h). The slurry was concentrated, and acetone was added to the solid mixture followed by filtration (process repeated 3 x).

The collected solvent was concentrated until a minimal volume of acetone remained (~5 mL). The addition of Et_2O (~25 mL) led to the precipitation of the desired product. The collected solid was washed with Et_2O.

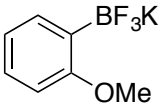


Potassium Trifluoro(4-methoxyphenyl)borate. Following the general procedure, a mixture of 4-bromoanisole (0.56 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at 80 ºC for 2 h. The title compound was obtained in 91% yield (0.58 g, 2.73 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.28 (d, J = 7.3 Hz, 2H), 6.69 (d, J = 7.3 Hz, 2H), 3.67 (s, 3H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 158.0, 132.9, 112.5, 55.1; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 138.2; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.6.

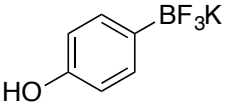


Potassium Trifluoro(3-methoxyphenyl)borate. [28] Following the general procedure, a mixture of 3-bromoanisole (0.56 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at 80 ºC for 2 h. The title compound was obtained in 89% yield (0.57 g, 2.67 mmol) as a white solid, mp 179 – 181 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.05 (t, J = 7.1 Hz, 1H), 6.97 (d, J = 6.6 Hz, 1H), 6.93 (s, 1H), 6.62 (d, J = 7.3 Hz, 1H) 3.69 (s, 3H); ^{13}C NMR

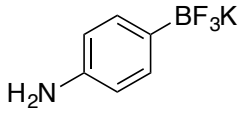
(125.8 MHz, DMSO-d_6) δ 158.5, 127.6, 124.2, 116.8, 111.1, 54.8; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 139.2; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.7.



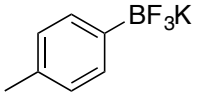
Potassium Trifluoro(2-methoxyphenyl)borate.[23b] Following the general procedure, a mixture of 2-bromoanisole (0.56 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at 80 ºC for 2 h. The title compound was obtained in 77% yield (0.44 g, 2.31 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.34 (d, J = 6.0 Hz, 1H), 7.07 (t, J = 7.0 Hz, 1H), 6.72 (d, J = 8.0 Hz, 2H), 3.65 (s, 3H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 162.8, 133.5, 127.2, 119.6, 110.0, 55.1; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 136.8; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.5.



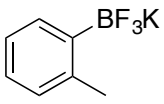
Potassium Trifluoro(4-hydroxyphenyl)borate.[23b] Following the general procedure, a mixture of 4-bromophenol (0.52 g, 3 mmol), $NiCl_2$(dppp) (48.8 mg, 0.09 mmol, 3 mol %), PPh_3 (47.2 mg, 0.18 mmol, 6 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 6 h. The title compound was obtained in 78% yield (0.47 g, 2.34 mmol) as light pink solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.56 (s, 1H), 7.10 (d, J = 8.1 Hz, 2H), 6.50 (d, J = 7.9 Hz, 2H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 155.2, 132.6, 113.7; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 138.0; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.6.



Potassium (4-Aminophenyl)trifluoroborate.[23b] Following the general procedure, a mixture of 4-bromoaniline (0.52 g, 3 mmol), $NiCl_2$(dppp) (48.8 mg, 0.09 mmol, 3 mol %), PPh_3 (47.2 mg, 0.18 mmol, 6 mol %), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 6 h. The title compound was obtained in 67% yield (0.40 g, 2.01 mmol) as a brown solid (treatment with K_2CO_3 needed), mp = 200 ºC (decomposed). ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.99 (d, *J* = 7.9 Hz, 2H), 6.35 (d, *J* = 7.7 Hz, 2H), 4.38 (s, 2H).; ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 145.8, 132.3, 113.3; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 137.7; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.7.

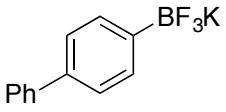


Potassium Trifluoro(*p*-tolyl)borate.[23b] Following the general procedure, a mixture of 4-bromotoluene (0.51 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at 80 ºC for 4 h. The title compound was obtained in 84% yield (0.50 g, 2.52 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.21 (d, *J* = 7.4 Hz, 2H), 6.89 (d, *J* = 7.3 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 158.0, 132.9, 112.5, 55.1; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 138.6; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.5.

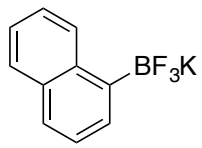


Potassium Trifluoro(*o*-tolyl)borate.[23b] Following the general procedure, a mixture of 2-bromotoluene (0.51 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol

%), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at 80 ºC for 3 h. The title compound was obtained in 72% yield (0.43 g, 2.16 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.32 (d, J = 6.8 Hz, 1H), 7.03 – 6.78 (m, 3H), 2.29 (s, 3H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 140.8, 132.0, 128.5, 125.4, 123.7, 22.0; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 137.5; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 4.4.

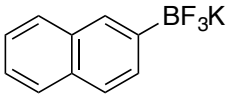


Potassium [1,1'-Biphenyl]-4-yltrifluoroborate.[11] Following the general procedure, a mixture of 4-bromo-1,1'-biphenyl (0.7 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 6 h. The title compound was obtained in 90% yield (0.70 g, 2.7 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.60 (d, J = 7.8 Hz, 2H), 7.45 – 7.40 (m, 6H), 7.29 (t, J = 7.3 Hz, 1H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 142.1, 137.5, 132.6, 129.4, 127.1, 126.9, 125.3; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 139.0; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.8.

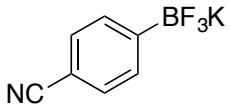


Potassium Trifluoro(naphthalen-1-yl)borate.[11] Following the general procedure, a mixture of 1-bromonaphthalene (0.62 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at

rt for 4 h. The title compound was obtained in 93% yield (0.65 g, 2.79 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.39 (d, *J* = 8.1 Hz, 1H), 7.70 (m, 1H), 7.58 – 7.53 (m, 2H), 7.36 – 7.18 (m, 3H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 137.0, 133.4, 130.7, 128.9, 127.8, 125.6, 125.3, 124.3, 123.8; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 135.2; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.6.

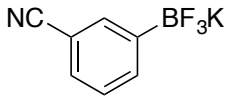


Potassium Trifluoro(naphthalen-2-yl)borate. [29] Following the general procedure, a mixture of 2-bromonaphthalene (10.0 g, 48.3 mmol), $NiCl_2$(dppp) (27 mg, 0.05 mmol, 0.1 mol %), PPh_3 (26 mg, 0.10 mmol, 0.2 mol %), $(HO)_2B\text{-}B(OH)_2$ (6.5 g, 72.5 mmol, 1.5 equiv) and DIPEA (25.2 mL, 144.9 mmol, 3 equiv) in EtOH (97 mL) was stirred at rt for 8 h. The title compound was obtained in 81% yield (9.2 g, 39.1 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.78 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.28 (m, 2H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 133.4, 132.5, 131.2, 130.1, 127.9, 127.6, 125.5, 125.0, 124.5; ^{19}F NMR (470.8 MHz, Acetone-d_6) δ – 141.9; ^{11}B NMR (128.4 MHz, Acetone -d_6) δ 4.4.

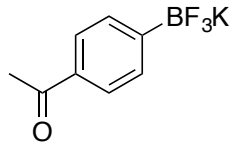


Potassium (4-Cyanophenyl)trifluoroborate.[23b] Following the general procedure, a mixture of 4-bromobenzonitrile (0.55 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 4 h. The title compound was obtained in 91% yield (0.57 g, 2.73 mmol) as a white

solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.53 (brs, 4 H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 132.4, 132.4, 130.4, 120.4, 108.2; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 140.5; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.9.

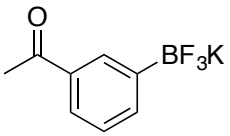


Potassium (3-Cyanophenyl)trifluoroborate.[23b] Following the general procedure, a mixture of 3-bromobenzonitrile (0.55 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 4 h. The title compound was obtained in 78% yield (0.49 g, 2.34 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.62 (d, J = 7.5 Hz, 1H), 7.58 (s, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 136.5, 135.1, 129.4, 127.9, 120.6, 109.9; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 140.3; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.8.

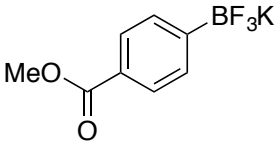


Potassium (4-Acetylphenyl)trifluoroborate.[23b] Following the general procedure, a mixture of 4'-bromoacetophenone (0.60 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 4 h. The title compound was obtained in 93 % yield (0.63 g, 2.79 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.74 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 7.7 Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 198.6, 134.7, 131.8,

126.7, 26.9; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 139.8; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.0.

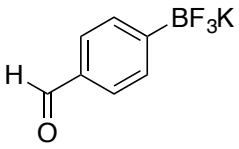


Potassium (3-Acetylphenyl)trifluoroborate.[30] Following the general procedure, a mixture of 3'-bromoacetophenone (0.60 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 4 h. The title compound was obtained in 81% yield (0.55 g, 2.43 mmol) as a white solid, mp 180 – 182 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.94 (s, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 7.1 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 199.5, 137.0, 135.8, 131.9, 127.2, 125.7, 27.2; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 139.5; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.2.

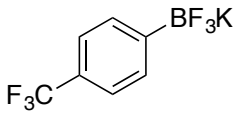


Potassium Trifluoro(4-(methoxycarbonyl)phenyl)borate.[23b] Following the general procedure, a mixture of methyl 4-bromobenzoate (0.65 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at 50 ºC for 6 h. The title compound was obtained in 92 % yield (0.67 g, 2.76 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.75 (d, J = 7.0 Hz, 2H), 7.50 (d, J = 6.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (125.8 MHz,

DMSO-d_6) δ 167.5, 131.8, 127.6, 126.9, 52.0; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 139.9; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.1.

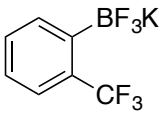


Potassium Trifluoro(4-formylphenyl)borate. [31] Following the general procedure, a mixture of 4-bromobenzaldehyde (0.56 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 6 h. The title compound was obtained in 84% yield (0.53 g, 2.52 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.91 (s, 1H), 7.67 (d, J = 7.3 Hz, 2H), 7.58 (d, J = 7.2 Hz, 2H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 193.8, 134.4, 132.2, 128.2; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 140.0; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.2.

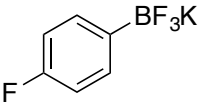


Potassium Trifluoro(4-(trifluoromethyl)phenyl)borate.[23b] Following the general procedure, a mixture of 4-bromobenzotrifluoride (0.68 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 6 h. The title compound was obtained in 86% yield (0.65 g, 2.58 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.57 (d, J = 7.5 Hz, 2H), 7.44 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ

132.1, 126.5, 125.3 (d, J = 238.6 Hz), 123.1 (d, J = 3.7 Hz); ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 60.6, – 140.0; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.0.

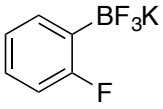


Potassium Trifluoro(2-(trifluoromethyl)phenyl)borate.[16f] Following the general procedure, a mixture of 2-bromobenzotrifluoride (0.68 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 12 h. The title compound was obtained in 71% yield (0.54 g, 2.13 mmol) as a white solid, mp 200 – 202 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.67 (d, J = 7.3 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 134.5 (d, J = 3.8 Hz), 130.1, 125.8, 124.7, 124.5 (d, J = 6.7 Hz); ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 57.5 (q, J = 9.3 Hz), –137.1; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.5.

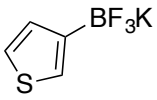


Potassium Trifluoro(4-fluorophenyl)borate.[23b] Following the general procedure, a mixture of 1-bromo-4-fluorobenzene (0.53 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 2 h. The title compound was obtained in 96% yield (0.58 g, 2.88 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.38 (t, J = 7.4 Hz, 2H), 6.90 (t, J = 9.0 Hz, 2H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 161.4 (d, J = 238.8 Hz), 133.2

(d, J = 6.5 Hz), 113.1 (d, J = 18.4 Hz); ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 118.3, – 138.8; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.2.

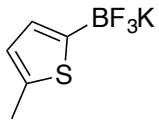


Potassium Trifluoro(2-fluorophenyl)borate.[16e] Following the general procedure, a mixture of 1-bromo-2-fluorobenzene (0.53 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 2 h. The title compound was obtained in 75% yield (0.45 g, 2.25 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.34 (dd, J = 12.0, 6.2 Hz, 1H), 7.07 (dd, J = 13.2, 5.9 Hz, 1H), 6.91 (t, J = 7.1 Hz, 1H), 6.79 (t, J = 8.6 Hz, 1H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 166.0 (d, J = 238.8 Hz), 134.5 (d, J = 10.9 Hz), 129.1 (d, J = 641.3 Hz), 127.5 (d, J = 8.0 Hz), 122.8, 114.0 (d, J = 25.9 Hz); ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 107.0, – 137.12 (dd, J = 92.8, 39.0 Hz); ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.51 (dd, J = 99.1, 49.2 Hz).

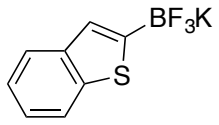


Potassium Trifluoro(thien-3-yl)borate.[25a] Following the general procedure, a mixture of 3-bromothiophene (0.49 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 4 h. The title compound was obtained in 94% yield (0.54 g, 2.82 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.18 (s, 1H), 7.11 – 6.88 (m, 2H);

^{13}C NMR (125.8 MHz, DMSO-d_6) δ 132.2, 124.7, 122.9; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ –135.5 (d, J = 58.2 Hz); ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.6 (d, J = 47.7 Hz).

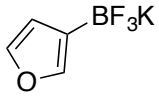


Potassium Trifluoro(5-methylthien-2-yl)borate. Following the general procedure, a mixture of 2-bromo-5-methylthiophene (0.53 g, 3 mmol), $NiCl_2$(dppp) (8.1 mg, 0.015 mmol, 0.5 mol %), PPh_3 (7.9 mg, 0.03 mmol, 1 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 4 h. The title compound was obtained in 85% yield (0.52 g, 2.55 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.58 – 6.53 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 137.2, 127.1, 125.2, 15.2; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 134.0 (m); ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.3; IR (neat) 1472, 1222, 1146, 960, 899, 879, 801 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_5H_5BSF_3$ $(M)^-$ 165.0157, found 165.0152.

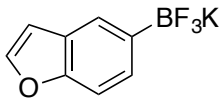


Potassium Benzo[*b*]thien-2-yltrifluoroborate.[25a] Following the general procedure, a mixture of 2-bromo-1-benzothiophene (0.64 g, 3 mmol), $NiCl_2$(dppp) (8.1 mg, 0.015 mmol, 0.5 mol %), PPh_3 (7.9 mg, 0.03 mmol, 1 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 6 h. The title compound was obtained in 74% yield (0.53 g, 2.22 mmol) as a white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ

7.83 (d, J = 7.9 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H), 7.19 – 7.17 (m, 2H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 141.9, 141.5, 123.9, 123.4, 122.6, 122.5, 122.3; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 134.8; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.4.

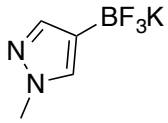


Potassium Trifluoro(furan-3-yl)borate.[32] Following the general procedure, a mixture of 3-bromofuran (0.44 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 4 h. The title compound was obtained in 92% yield (0.48 g, 2.76 mmol) as a light yellow tan solid, mp 175 – 177 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.35 (s, 1H), 7.09 (s, 1H), 6.19 (s, 1H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 143.0, 140.7, 114.1; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ –134.6 (d, J = 58.2 Hz); ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.1.

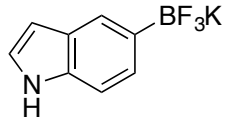


Potassium Benzofuran-5-yltrifluoroborate. Following the general procedure, a mixture of 5-bromobenzofuran (0.59 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 4 h. The title compound was obtained in 91% yield (0.61 g, 2.73 mmol) as an off white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.76 (m, 1H), 7.57 (m, 1H), 7.31 – 7.28 (m, 2H), 6.78 (m, 1H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 153.8, 144.3, 128.4, 126.1, 123.9, 109.1, 106.9; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ –138.1; ^{11}B NMR

(128.4 MHz, DMSO-d_6) δ 3.5; IR (neat) 1545, 1380, 1265, 1152, 904 cm^{-1}; HRMS (ESI) *m/z* calcd. For $C_8H_5BOF_3$ $(M)^-$ 185.0386, found 185.0381.

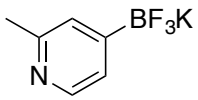


Potassium Trifluoro(1-methyl-1*H*-pyrazol-4-yl)borate. Following the general procedure, a mixture of 4-bromo-1-methyl-1*H*-pyrazole (0.48 g, 3 mmol), $NiCl_2$(dppp) (81.3 mg, 0.15 mmol, 5 mol %), PPh_3 (78.7 mg, 0.3 mmol, 10 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 12 h. The title compound was obtained in 82% yield (0.46 g, 2.46 mmol) as a white solid (treatment with K_2CO_3 needed), mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.06 (s, 1H), 7.04 (s, 1H), 3.69 (s, 3H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 142.4, 132.4, 38.1; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ –132.9; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.0. IR (neat) 1546, 1172, 944, 906, 830 cm^{-1}; HRMS (ESI) *m/z* calcd. For $C_4H_5BN_2F_3$ $(M)^-$ 149.0498, found 149.0491.

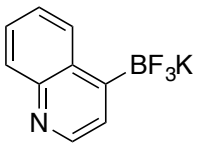


Potassium Trifluoro(1*H*-indol-5-yl)borate.[25a] Following the general procedure, a mixture of 5-bromo-1*H*-indole (0.59 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 6 h. The title compound was obtained in 86% yield (0.57 g, 2.58 mmol) as a white solid (treatment with K_2CO_3 needed), mp > 225 ºC. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.75 (s, 1H), 7.74 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.15 – 7.06 (m, 1H), 6.31 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (125.8 MHz, acetone-d_6) δ 135.5, 127.5,

125.7, 123.0, 122.6, 109.1, 101.0; ^{19}F NMR (470.8 MHz, Acetone -d_6) δ –140.5; ^{11}B NMR (128.4 MHz, acetone -d_6) δ 5.3.

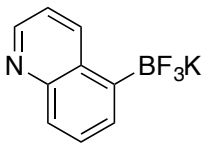


Potassium Trifluoro(2-methylpyridin-4-yl)borate. Following the general procedure, a mixture of 4-bromo-2-methylpyridine (0.52 g, 3 mmol), $NiCl_2$(dppp) (81.3 mg, 0.15 mmol, 5 mol %), PPh_3 (78.7 mg, 0.3 mmol, 10 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at 80 ºC for 4 h. The title compound was obtained in 72% yield (0.43 g, 2.16 mmol) as a light yellow tan solid (treatment with K_2CO_3 needed), mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.14 (d, J = 4.4 Hz, 1H), 7.14 (s, 1H), 7.05 (d, J = 4.2 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 155.3, 147.0, 126.6, 124.4, 24.4; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ –140.8; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.7; IR (neat) 1537, 1380, 1259, 1170, 966, 833 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_6H_6BNF_3$ $(M)^-$ 160.0545, found 160.0546.

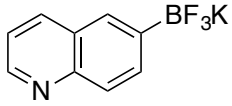


Potassium Trifluoro(quinolin-4-yl)borate. Following the general procedure, a mixture of 4-bromoquinoline (0.62 g, 3 mmol), $NiCl_2$(dppp) (81.3 mg, 0.15 mmol, 5 mol %), PPh_3 (78.7 mg, 0.3 mmol, 10 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at 80 ºC for 4 h. The title compound was obtained in 74% yield (0.52 g, 2.22 mmol) as a light yellow solid (treatment with K_2CO_3 needed), mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.64 (m, 1H), 8.39 (m, 1H), 7.86 (m, 1H), 7.57 (m, 1H), 7.50 – 7.33 (m,

2H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 149.5, 147.8, 132.4, 130.7, 129.1, 127.8, 124.5, 124.4; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 136.6; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.1; IR (neat) 1238, 1090, 1055, 998, 935, 846, 750 cm^{-1}; HRMS (ESI) *m/z* calcd. For $C_9H_6BNF_3$ $(M)^-$ 196.0545, found 196.0540.

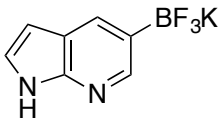


Potassium Trifluoro(quinolin-5-yl)borate. Following the general procedure, a mixture of 5-bromoquinoline (0.62 g, 3 mmol), $NiCl_2$(dppp) (81.3 mg, 0.15 mmol, 5 mol %), PPh_3 (78.7 mg, 0.3 mmol, 10 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at 80 ºC for 4 h. The title compound was obtained in 81% yield (0.57 g, 2.43 mmol) as a light yellow solid (treatment with K_2CO_3 needed), mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.74 – 8.71 (m, 2H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 6.5 Hz, 1H), 7.51 (m, 1H), 7.32 (m, 1H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 148.9, 148.5, 138.4, 131.5, 129.1, 128.7, 126.7, 119.7; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 135.0; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.3; IR (neat) 1546, 1172, 968, 906 cm^{-1}; HRMS (ESI) *m/z* calcd. For $C_9H_6BNF_3$ $(M)^-$ 196.0545, found 196.0538.

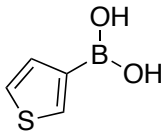


Potassium Trifluoro(quinolin-6-yl)borate. Following the general procedure, a mixture of 6-bromoquinoline (0.62 g, 3 mmol), $NiCl_2$(dppp) (81.3 mg, 0.15 mmol, 5 mol %), PPh_3 (78.7 mg, 0.3 mmol, 10 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at

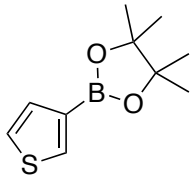
80 ºC for 4 h. The title compound was obtained in 83% yield (0.58 g, 2.49 mmol) as a light yellow solid (treatment with K_2CO_3 needed), mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.75 (m, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.88 (s, 1H), 7.85 – 7.76 (m, 2H), 7.38 (m, 1H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 148.9, 147.7, 135.9, 134.6, 130.0, 127.8, 126.5, 120.6; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 139.1; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.3; IR (neat) 1569, 1344, 1170, 984, 836, 650 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{14}H_{15}NO_5F_3$ $(M)^-$ 196.0545, found 196.0543.



Potassium Trifluoro(1*H*-pyrrolo[2,3-*b*]pyridin-5-yl)borate. Following the general procedure, a mixture of 5-bromo7-azaindole (0.59 g, 3 mmol), $NiCl_2$(dppp) (81.3 mg, 0.15 mmol, 5 mol %), PPh_3 (78.7 mg, 0.3 mmol, 10 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at 80 ºC for 4 h. The title compound was obtained in 83% yield (0.56 g, 2.49 mmol) as a yellow solid (treatment with K_2CO_3 needed), mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.05 (s, 1H), 8.17 (s, 1H), 7.79 (s, 1H), 7.22 (d, *J* = 3.3 Hz, 1H), 6.26 (d, *J* = 3.3 Hz, 1H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 148.1, 147.1, 131.0, 124.0, 119.3, 99.5; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ – 137.3; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 4.0; IR (neat) 1276, 1144, 903, 668 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_9H_6BNF_3$ $(M)^-$ 185.0498, found 185.0498.

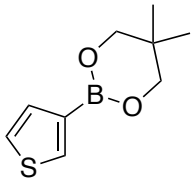


Thien-3-ylboronic acid.[33] Following the general procedure, a mixture of 3-bromothiophene (0.49 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 4 h. The crude reaction was transferred to a separatory funnel followed by the addition of EtOAc (10 mL) and then aq HCl (20 mL of a 1 M solution). The layers were separated, and the water layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were dried (Na_2SO_4), concentrated, and lyophilized overnight. The crude solid was washed with hexane to afford the title compound in 87% yield (0.33 g, 2.61 mmol) as a white solid, mp 125 – 127 ºC (lit. 126 – 128 ºC). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.96 (d, J = 2.5 Hz, 1H), 7.46 (dd, J = 4.7, 2.7 Hz, 1H), 7.41 (d, J = 4.8 Hz, 1H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 135.2, 132.8, 125.5; ^{11}B NMR (128.4 MHz, acetone-d_6) δ 27.8.



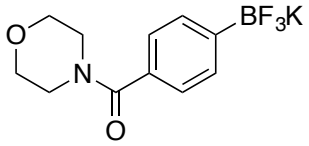
4,4,5,5-Tetramethyl-2-(thien-3-yl)-1,3,2-dioxaborolane. [34] Following the general procedure, a mixture of 3-bromothiophene (0.49 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 4 h. The crude reaction was transferred to a separatory funnel followed by the addition of EtOAc (10 mL) and then aq HCl (20 mL of a 1 M solution). The layers were separated and the water layer was extracted with EtOAc (2 x 10 mL). The combined

organic layers were dried (Na_2SO_4) and concentrated. To the crude mixture was added CH_2Cl_2 (10 mL) and pinacol (1.06 g, 9 mmol, 3 equiv). The reaction was stirred for 2 h. The crude mixture was transferred to a separatory funnel followed by the addition of H_2O (20 mL). The layers were separated, and the water layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The title compound was obtained after column chromatography (hexane/EtOAc, 3:1) in 90% yield (0.57 g, 2.7 mmol) as a colorless oil. ^{1}H NMR (500 MHz, acetone-d_6) δ 7.95 (m, 1H), 7.45 (m, 1H), 7.37 (m, 1H), 1.31 (s, 12H); ^{13}C NMR (125.8 MHz, acetone -d_6) δ 136.4, 132.1, 125.6, 83.6, 24.5; ^{11}B NMR (128.4 MHz, acetone-d_6) δ 28.8.

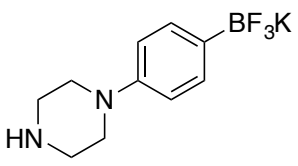


5,5-Dimethyl-2-(thien-3-yl)-1,3,2-dioxaborinane. [35] Following the general procedure, a mixture of 3-bromothiophene (0.49 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 4 h. The crude reaction was transferred to a separatory funnel followed by the addition of EtOAc (10 mL) and then aq HCl (20 mL of a 1 M solution). The layers were separated and the water layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. To the crude mixture was added CH_2Cl_2 (10 mL) and 2,2-dimethyl-1,3-propanediol (0.94 g, 9 mmol, 3 equiv). The reaction was stirred for 2 h. The crude mixture was transferred to a separatory funnel followed by the addition of H_2O (20 mL). The layers were separated, and the water layer

extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The title compound was obtained after column chromatography (hexane/ EtOAc, 3:1) in 96% yield (0.56 g, 2.88 mmol) as a white solid, mp 125 – 127 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (m, 1H), 7.39 (m, 1H), 7.32 (m, 1H), 3.76 (s, 4H), 1.03 (s, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 134.8, 131.6, 124.9, 72.1, 31.8, 21.8; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ 25.1.

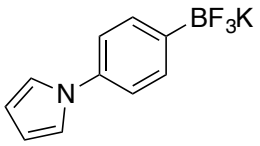


Potassium Trifluoro(4-(morpholine-4-carbonyl)phenyl)borate.[23b] Following the general procedure, a mixture of (4-chlorophenyl)(morpholino)methanone (0.68 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B$-$B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at rt for 12 h. The title compound was obtained in 64% yield (0.57 g, 1.92 mmol) as an off white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.41 (d, J = 7.0 Hz, 1H), 7.16 (d, J = 7.1 Hz, 1H), 3.58 (brs, 8H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 170.7, 132.5, 131.5, 125.6, 66.6; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ –139.6; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.2.



Potassium Trifluoro(4-(piperazin-1-yl)phenyl)borate. Following the general procedure, a mixture of 1-(4-chlorophenyl)piperazine (0.59 g, 3 mmol), $NiCl_2$(dppp) (81.3 mg, 0.15 mmol, 5 mol %), PPh_3 (78.7 mg, 0.3 mmol, 10 mol

%), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at 80 ºC for 8 h. The title compound was obtained in 52% yield (0.42 g, 1.56 mmol) as an off white solid (treatment with K_2CO_3 needed), mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.16 (d, *J* = 7.5 Hz, 2H), 6.66 (d, *J* = 7.5 Hz, 2H), 2.91 (brs, 4H), 2.80 (brs, 4H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 150.0, 132.2, 114.7, 50.8, 46.2; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ –138.2; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.6; IR (neat) 1545, 1173, 968, 906 cm^{-1}; HRMS (ESI) *m/z* calcd. For $C_{10}H_{13}BN_2F_3$ $(M)^-$ 229.1124, found 229.1129.



Potassium (4-(1*H*-Pyrrol-1-yl)phenyl)trifluoroborate.[23b]

Following the general procedure, a mixture of 1-(4-chlorophenyl)-1H-pyrrole (0.53 g, 3 mmol), $NiCl_2$(dppp) (16.3 mg, 0.03 mmol, 1 mol %), PPh_3 (15.7 mg, 0.06 mmol, 2 mol %), $(HO)_2B\text{-}B(OH)_2$ (0.4 g, 4.5 mmol, 1.5 equiv) and DIPEA (1.6 mL, 9 mmol, 3 equiv) in EtOH (10 mL) was stirred at 80 ºC for 2 h. The title compound was obtained in 69% yield (0.57 g, 2.28 mmol) as white solid, mp > 225 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.42 – 7.38 (m, 2H), 7.27 – 7.22 (m, 4H), 6.23 – 6.19 (m, 2H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 138.0, 132.8, 119.1, 118.1, 110.0; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ –139.0; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.5.

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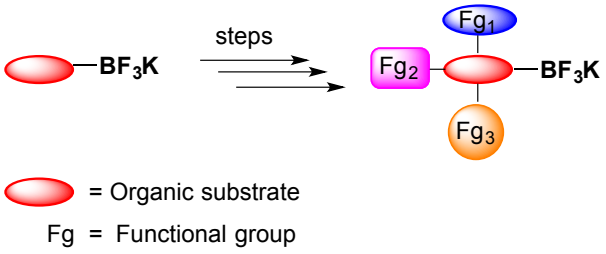
Chapter 2. Reactivity of Organotrifluoroborates: Chemistry Beyond Cross-Coupling

2.1 Organotrifluoroborates for molecular complexity

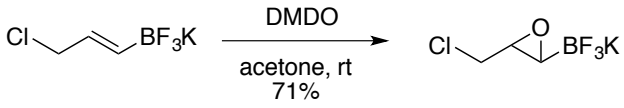
Over the last decade, organotrifluoroborates have received considerable attention as useful alternatives to tricoordinated boron species such as boronic acids and boronate esters.[1] Owing to their tetracoordinate nature, these organoboron species do not undergo undesirable side reactions with the commonly employed organic reagents. Consequently, the organic substructure of simple organotrifluoroborates can be functionalized to build molecular complexity, while leaving the boron-carbon bond intact (Scheme 2.1)

Scheme 2.1



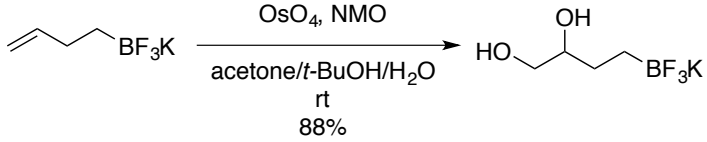
Through the years, the Molander group has largely contributed to illustrate this unique feature of organotrifluoroborates, and a variety of important transformations in molecules containing this important functional group were performed. In 2003, Molander and Ribagorda[2] reported the epoxidation of alkenyltrifluoroborates. The desired epoxide-containg trifluoroborate products were obtained in good yields by reacting alkenyltrifluoroborates with dimethyldioxirane (DMDO) in acetone (eq 2.1).

Equation 2.1



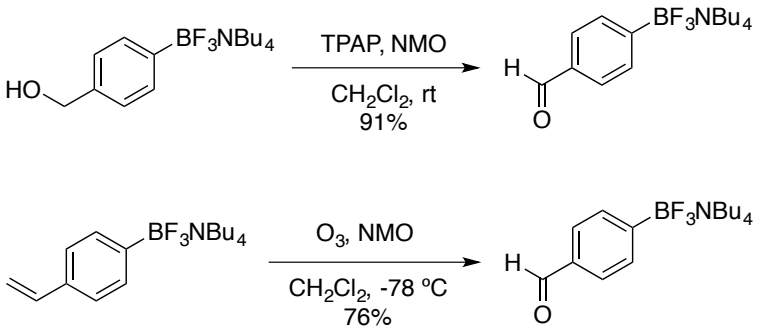
After this publication, other oxidations in molecules containing potassium organotrifluoroborates were also published by the group. Thus, the dihydroxylation of unsaturated potassium alkyl and aryltrifluoroborates was reported.[3] *cis*-Diols were obtained in moderate to excellent yields from the reaction of alkene-containing trifluoroborates with OsO_4, and NMO in a mixture of acetone/*t*-BuOH/H_2O at room temperature (eq 2.2).

Equation 2.2



Ozonolysis[4] and alcohol oxidations[5] in the presence of the trifluoroborate moiety have also been reported by Molander and co-workers (Scheme 2.2). In both cases, the use of tetrabutylammonium trifluoroborates were necessary to overcome solubility issues. Regardless, the oxidized products were obtained in good to excellent yields while keeping the appended borate group unaffected.

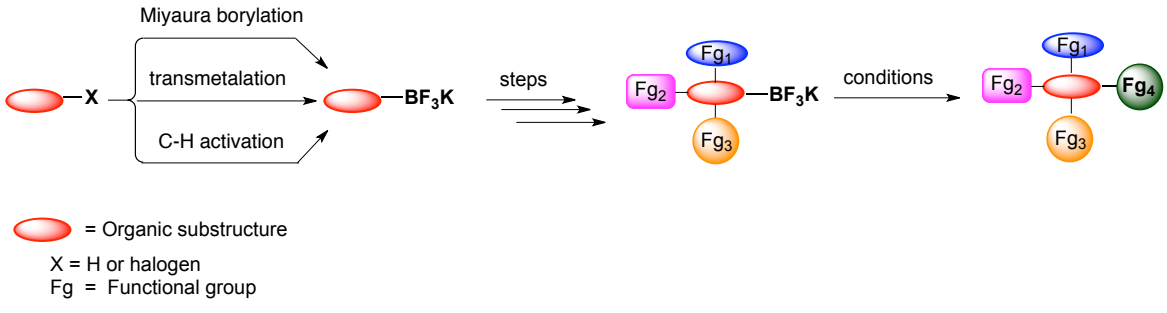
Scheme 2.2



The same group also reported many other reactions in the presence of the trifluoroborate functional group, such as Wittig and Horner-Wadsworth-Emmons olefination,[6] 1,3-dipolar cycloaddition of azides,[7] reductive amination,[8] nucleophilic substitutions [9] and oxidative condensations,[10] illustrating further the ability of organotrifluoroborates to undergo a wide range of reactions without affecting the remaining carbon-boron bond.

Because of the aforementioned resistance of organotrifluoroborates to a variety of reaction conditions, we envisaged the use of this species in the synthesis of complex molecules followed by late stage conversion into different groups such as boronic acids, alcohols, halogens and nitroso (Scheme 2.3).

Scheme 2.3



2.2 Hydrolysis of Organotrifluoroborates via Silica Gel[11]

2.2.1 Introduction

Because trifluoroborates are more robust boron species and can be used to build complexity on a molecule, they can be envisaged as protecting group of other organoboron compounds, especially boronic acids. In addition to their wide use as nucleophilic partners in cross-coupling reactions, boronic acids have also been utilized as biological inhibitors and sensors as well as drug delivery agents.[12] The recent FDA approval of the drug Velcade, a boronic acid-based proteasome inhibitor used in the treatment of multiple myeloma, has initiated immense interest in small molecules containing boronic acids in drug discovery efforts, wherein these agents can be screened for lead-like or drug-like properties (Figure 2.1).[13]

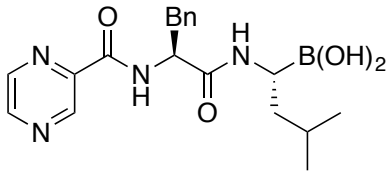
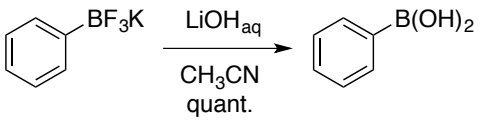


Figure 2.1 Velcade (bortemozib)

The deprotection of organotrifluoroborates to the corresponding boronic acids using fluorophiles (e.g., $SiCl_4$, TMSCl) has been previously reported.[14] However, these fluorophiles are either toxic, difficult to handle, or highly reactive, and therefore not ideal for use in complex molecule synthesis. Recently, Hutton and Yuen published a two-step procedure for the deprotection of boronate esters via the intermediate organotrifluoroborate, allowing access to boronic acids (eq 2.3).[15] For the deprotection of organotrifluoroborates, they employed either LiOH/acetonitrile or TMSCl/H_2O. Their

study was limited in substrate scope, as they only reported the deprotection of aryltrifluoroborates.

Equation 2.3

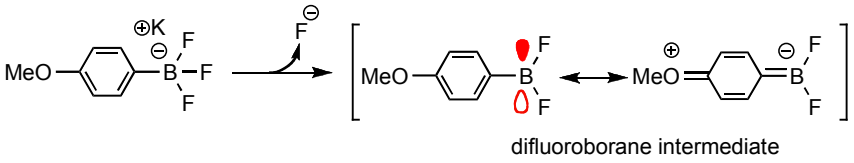


Current limitations associated with the deprotection of organotrifluoroborates, combined with the emerging importance of boronic acids in drug discovery efforts, prompted us to investigate a general, efficient, mild, and convenient method for the late stage deprotection of organotrifluoroborates. Of note, right after we published our results, a similar hydrolysis of organotrifluoroborates was reported by Kabalka and co-workers using aluminium oxide under microwave conditions.[16] Although good yields were reported, the substrate scope was restricted to aryltrifluoroborates and two isolated examples of alkenyl and alkyltrifluoroborates. Later, the same group reported an iron promoted version of this reaction.[17] Once again, the limited substrate scope, especially regarding heteroaryls, makes the method less than ideal for synthetic purposes.

2.2.2 – Results and Discussion

Perrin and coworkers have reported that the rate of organotrifluoroborate solvolysis is governed by substituent groups.[18] They pointed out that loss of a fluoride ion leads to a vacancy of the *p*-orbital on boron, providing a difluoroborane intermediate that should be stabilized by electron-rich substituent groups (Scheme 2.4) or destabilized by electron-withdrawing groups. Consequently, electron-rich organotrifluoroborates undergo solvolysis faster than those with electron-withdrawing groups.

Scheme 2.4

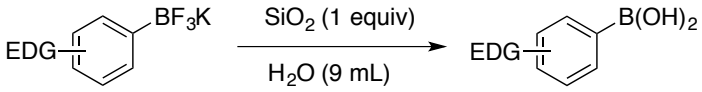


Because substituent groups play a key role in the deprotection, we independently investigated conditions for hydrolysis of the electron-rich potassium 4-methoxyphenyltrifluoroborate and the electron-poor potassium benzothiophen-2-yltrifluoroborate substrates. Silica gel[19] was employed as a convenient, inexpensive and readily available fluorophile. Various solvents were examined including acetonitrile, acetone, DMF, DMSO, and H_2O. The reactions were monitored via ^{11}B NMR spectroscopy. Of the solvents screened, H_2O proved to be the best solvent for the deprotection of potassium 4-methoxyphenyltrifluoroborate and benzothiophen-2-yltrifluoroborate, as the reactions were complete in 1 and 3 h, respectively. The efficacy of H_2O in these transformations can be attributed to the enhanced solubility of 4-methoxyphenyltrifluoroborate and benzothiophen-2-yltrifluoroborate in H_2O compared to the solvents mentioned above. Because silica gel proved to be a suitable fluorophile for this study, additional screening of fluorophiles was not necessary. The most efficient deprotection conditions employed 1 equivalent of silica gel in H_2O.

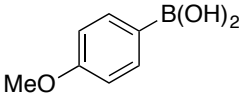
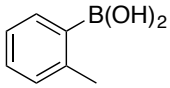
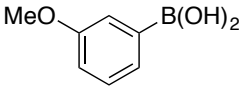
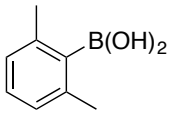
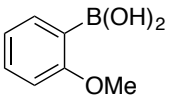
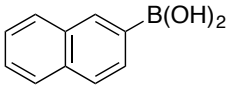
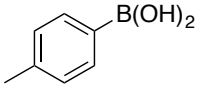
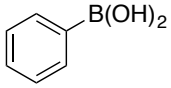
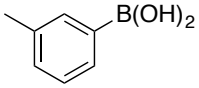
The requisite potassium organotrifluoroborates were readily prepared by previously reported procedures.[20] Initially, a broad range of electron-rich and electron-neutral aryltrifluoroborates were investigated (Table 2.1.1). In all cases, the deprotection was complete in 1 h, except for entries 2 and 9, which required reaction times of 3 and 4 h, respectively. The reactivity of *para*-, *meta*-, and *ortho*-methoxyphenyltrifluoroborate

and *para*-, *meta*-, and *ortho*-4-methylphenyltrifluoroborate were also examined. In both substrates, the para-derivatives provided the desired products in higher yields (Table 2.1.1, entries 1 and 4). Also, sterically hindered derivatives afforded the products in good yields (Table 2.1.1, entries 3, 6, and 7). We demonstrated that the reaction could be scaled to 5 mmol, providing 4-methoxyphenylboronic acid in 83% yield (Table 2.1.1, entry 1).

Table 2.1.1 Deprotection of Electron-rich and Electron-neutral Potassium Aryltrifluoroborates



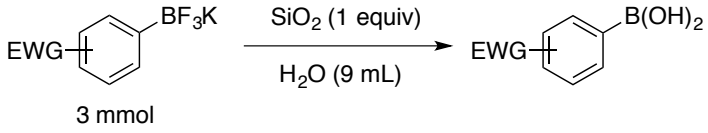
3 mmol

entry	product	time (h)	yield (%)	entry	product	time (h)	yield (%)
1		1	83[a]	6		1	61
2		3	83	7		1	81
3		1	67	8		1	63
4		1	76	9		4	65
5		1	67				

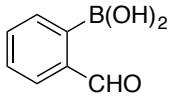
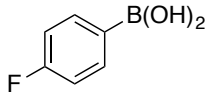
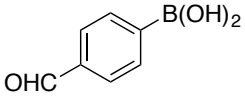
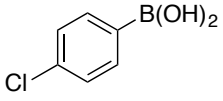
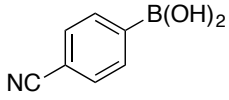
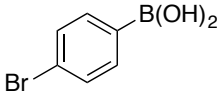
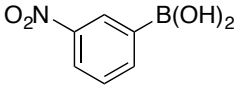
[s] 5 mmol scale

Next, attention was turned to electron-poor aryltrifluoroborates. The conditions developed worked equally well for these substrates, providing the arylboronic acids in good yields (Table 2.1.2). As expected, aldehyde-, nitrile-, and nitro-containing phenyltrifluoroborates required a longer time (24 h) for complete deprotection (Table 2.1.2, entries 1-4). As mentioned above, the slow deprotection is attributed to the destabilized difluoroborane intermediate. Of note, heating the reactions at 50 ^{o}C led to the formation of protodeboronation products (boric acid was detected by ^{11}B NMR at ~18 ppm). The reactivity of 4-halophenyltrifluoroborates was investigated, and it was determined that 4-fluorophenyltrifluoroborate required 4 h for full conversion, compared to only 1 h for 4-chloro- and 4-bromophenyltrifluoroborate (Table 2.1.2, entries 5-7). However, 4-fluorophenyltrifluoroborate provided the desired product in higher yield (Table 2.1.2, entry 5).

Table 2.1.2 Deprotection of Electron-poor Potassium Aryltrifluoroborates

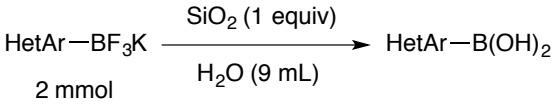


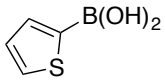
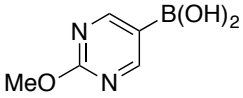
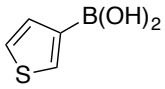
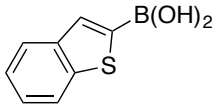
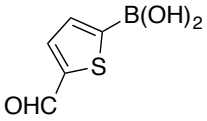
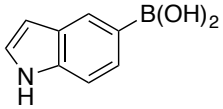
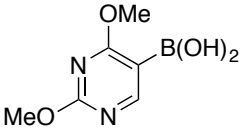
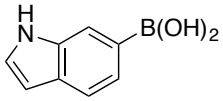
3 mmol

entry	product	time (h)	yield (%)	entry	product	time (h)	yield (%)
1		24	64	5		4	80
2		24	88	6		1	60
3		24	66	7		1	71
4		24	86				

To expand the utility of the developed conditions further, heteroaryl systems were investigated, including thienyl-, pyrimidinyl-, pyridinyl-, benzothioyl-, and indolyl derivatives (Table 2.1.3). The heteroaryls afforded the desired boronic acids in moderate to good yields, except for the electron-deficient 3-pyridyl- and 4-pyridyltrifluoroborates (data not shown). A few heteroaryls required a longer reaction time (24 h) for complete deprotection (Table 2.1.3, entries 2-5). Interestingly, thiophene-2-yltrifluoroborate was converted to the corresponding boronic acid in 3 h, while thiophene-3-yltrifluoroborate required 24 h for full conversion (Table 2.1.3, entries 1 and 2).

Table 2.1.3 Deprotection of Potassium Heteroaryltrifluoroborates

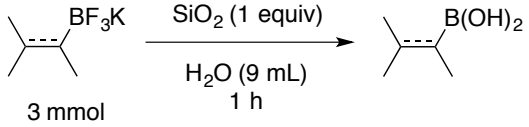


entry	product	time (h)	yield (%)	entry	product	time (h)	yield (%)
1		3	81	5		24	53
2		24	79[a]	6		3	79[a]
3		24	73	7		1	62
4		24	63	8		1	80

[s] 3 mmol scale

The scope of the general reaction conditions was extended to alkyl- and alkenyltrifluoroborates (Table 2.1.4). Alkylboronic acids are generally unstable species, and therefore readily undergo protodeboronation. Nonetheless, we were successful in obtaining both the 2-isobutylboronic acid and octylboronic acid in 73 and 67% yields, respectively (Table 2.1.4, entries 1 and 2). Alkenylboronic acids are more stable than the corresponding alkylboronic acids. The deprotection of alkenyltrifluoroborates was examined, and the conditions developed proved to be effective, providing the alkenylboronic acids in moderate to good yields (Table 2.1.4, entries 3-7). Also, both alkyl- and alkenyltrifluoroborates were deprotected in 1 h.

Table 2.1.4 Deprotection of Potassium Alkyl- and Alkenyltrifluoroborates



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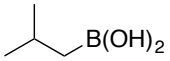
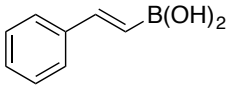
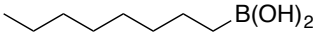
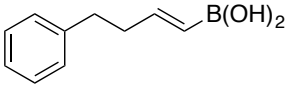
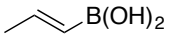
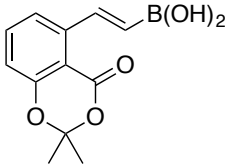
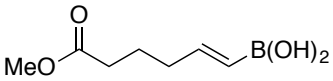
1		73	5		63
2		67	6		62
3		81	7		89[b]
4		82[a]			

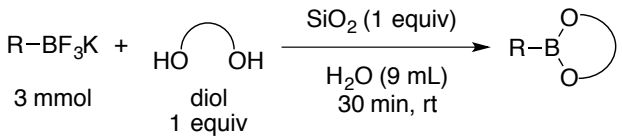
[a] 2 mmol scale [b] 1.5 mmol scale

Of special note, during the study we observed that arylboronic acids were more stable than the corresponding heteroaryl-, alkyl-, and alkenylboronic acid counterparts. In our hands, many of the heteroaryl-, alkyl-, and alkenylboronic acids decomposed readily (as observed by the emergence of byproducts appearing at ~18 ppm in the ^{11}B NMR spectrum), even when stored at low temperatures. To avoid extensive decomposition prior to recording of various spectra, these boronic acids were quickly isolated and dried in vacuo for several minutes. Immediate characterization was necessary to avoid contamination by various byproducts. Of the boronic acids examined, 5-indoleboronic acid was the most problematic substrate as it decomposed within minutes upon drying in vacuo. This study further verifies the advantages of robust potassium

organotrifluoroborates, as these species could be kept indefinitely without significant decomposition.

Boronates are more stable alternatives to boronic acids, and these species have found extensive use in organic synthesis.[21] Matteson and coworkers showed that organotrifluoroborates could be converted to boronate esters via the intermediate dichloroborane by treatment of organotrifluoroborates with $SiCl_4$ in the presence of MeOH followed by treatment with pinacol.[14a] Owing to the important complementary physical and chemical properties of organotrifluoroborates, we sought to determine whether the conditions developed herein would be applicable to their direct conversion to boronate esters (Table 2.1.4). Treatment of 4-trifluoroboratoanisole with silica gel, H_2O, and pinacol afforded the desired boronate in 81% yield (Table 2.1.4, entry 1). Encouraged by this result, other diols including chiral dimethyl D(-)- and L(+)-tartrates and neopentyl glycol were examined. In each case the products were obtained in good yields (Table 2.1.4, entries 2-4). Furthermore, octyltrifluoroborates and benzothiophene-2-yltrifluoroborate were successfully converted to boronate esters in good yields (Table 2.1.4, entries 6 and 7).

Table 2.1.4 Conversion of Potassium Organotrifluoroborates to Boronate



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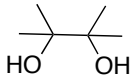
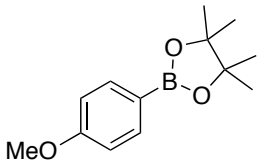
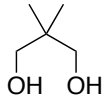
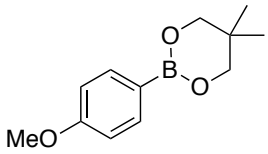
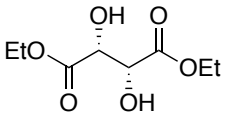
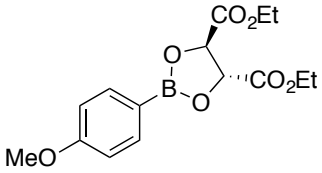
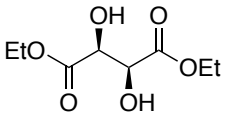
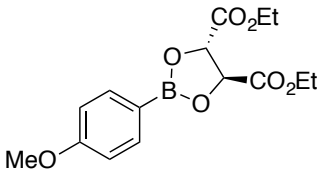
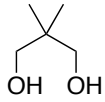
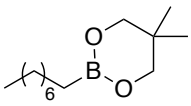
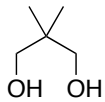
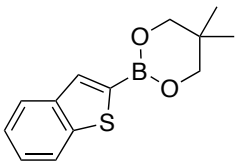
1			81
2			90
3			81
4			85
5			85
6			72

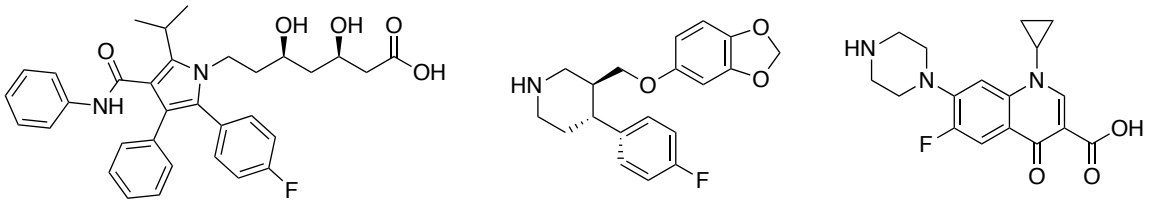
2.2.3 - Conclusions

In conclusion, a general, mild and efficient method was developed for the deprotection of aryl-, heteroaryl-, alkyl-, and alkenyltrifluoroborates to the corresponding boronic acids. The rate of deprotection was influenced by the substituent groups, wherein electron-rich substrates underwent deprotection faster than electron-poor substrates. We demonstrated that the method developed could be extended to the direct formation of boronate esters from organotrifluoroborates.

2.3 Metal-Free Fluorination of Potassium Organotrifluoroborates

2.3.1 Introduction

Functionalized aryl fluorides are found in a large number of pharmaceutical and agrochemical compounds (Figure 2.2).[22] The presence of one fluorine atom can enhance the solubility, bioavailability, and metabolic stability compared with non-fluorinated analogues. Additionally, ^{18}F-labeled aryl fluorides have been applied as contrasting agents in positron emission tomography (PET).



Lipitor Paxil Ciprofloxacin

Figure 2.2 Fluorine containing drugs

Traditional methods used to introduce a fluorine atom in a molecule usually require harsh conditions (e.g., F_2,[23] diazonium salts[24]), which are incompatible with many functional groups. Therefore, fluorine atoms are often introduced in an earlier step in the synthetic sequence, which increases the difficulty of accessing target molecules.

Recently, electrophilic fluorinating agents (Figure 2.3) have been used to promote selective fluorination of aryl compounds in a late synthetic stage.[25] Such reagents are commercially available, stable, safe, and easy to handle. Furthermore, some of these fluorinating agents show similar reactivity as established reagents (e.g., HF, F_2) with an increase in selectivity previously unattainable.

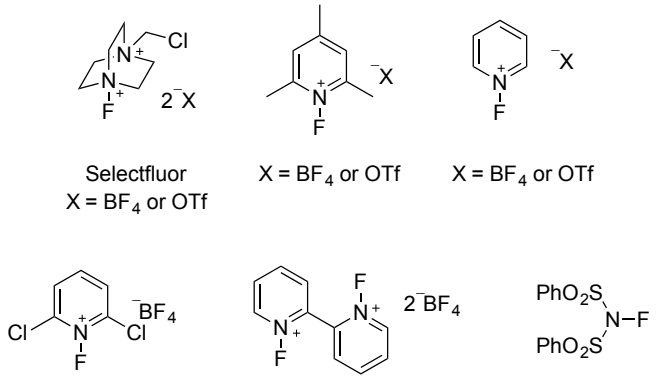
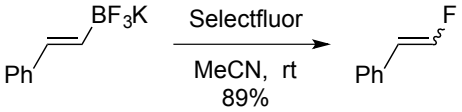


Figure 2.3 Common Electrophilic Fluorinating Agents

Electrophilic fluorination of organometallic species such as organomagnesium[26] and organotin[27] has been reported in the literature. Because of the low functional group tolerability of Grignard reagents and the toxicity associated with stanannes, the fluorination of organoboron species would provide a more desirable route to access fluorinated aryl compounds.

Many efforts have been made to access fluorinated compounds from boronic acids and trifluoroborates. In 1997, Olah and co-workers reported the direct fluorination of alkenyltrifluoroborates using Selectfluor in acetonitrile (eq 2.4).[28] Although moderate to good yields of the fluorinated products were obtained, the reaction was not selective giving a 1:1 mixture of *E* and *Z* isomers.

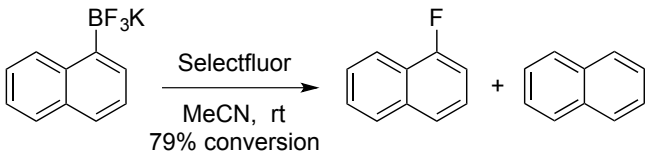
Equation 2.4



The more challenging fluorination of arylboronic acids and trifluoroborates has also been reported. Lemaire and co-workers reported a metal-free fluorination of these species with Selectfluor (eq 2.5).[29] In this paper, the authors showed very limited

substrate scope and no isolated yield was reported, only starting material conversion. Furthermore, the products were often obtained in a mixture with undesired protodeboronated arene.

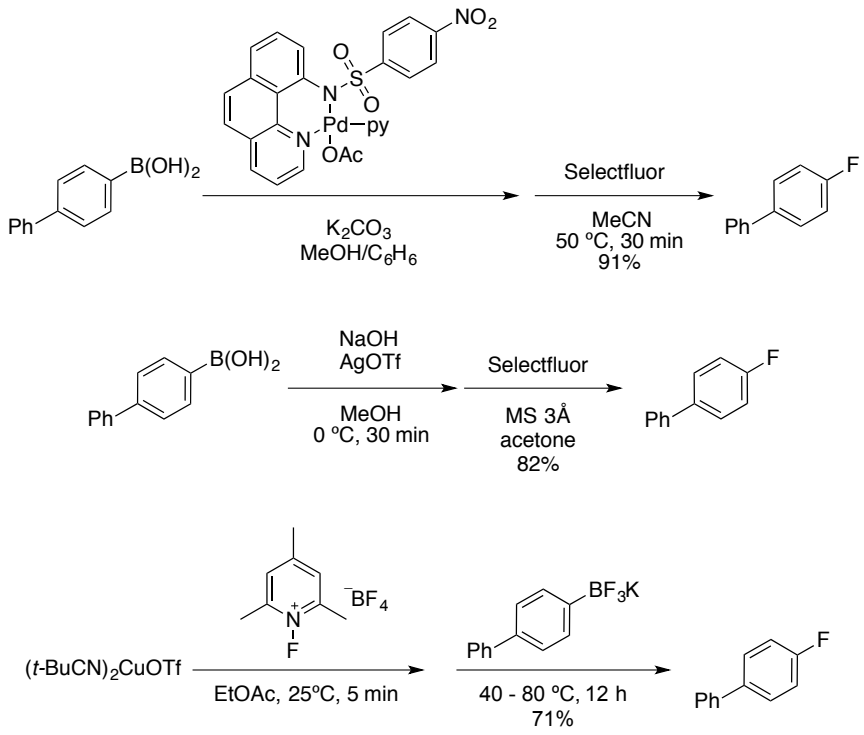
Equation 2.5



In an attempt to solve the selectivity issues associated with these reactions, the palladium,[30] silver,[31] and copper-mediated[32] fluorination of arylboronic acids and trifluoroborates have been reported (Scheme 2.5). Although highly selective and efficient in affording fluorinated arenes in good yields, these reactions use stoichiometric amounts of metal reagents (1 equivalent of Pd-complex and 3 equivalents of AgOTf), making it less than ideal for a late stage synthetic approach.

To overcome these limitations, an efficient and metal free route to convert arylmetallic species to the corresponding fluorinated compound is still an important goal to achieve.

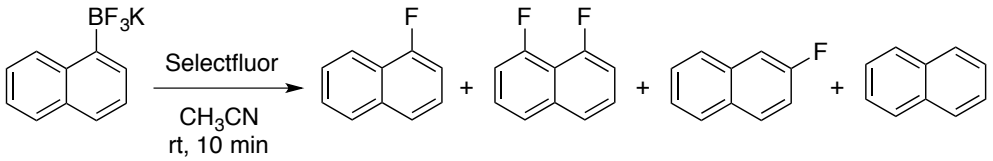
Scheme 2.5



2.3.2 Results and Discussion

We began our investigation for a metal free fluorination of organotrifluoroborates by repeating Lemaire's[29] reaction of potassium naphthalen-1-yltrifluoroborate and Selectfluor in acetonitrile. To our surprise, and contrary to the reported results that claimed that 24 h were needed to obtain a mixture of 1-fluoronaphthalene and naphthalene, the reaction was complete in less than 10 min (as monitored by ^{11}B NMR), and a mixture of 3 fluorinated products along with naphthalene was observed (eq 2.6).

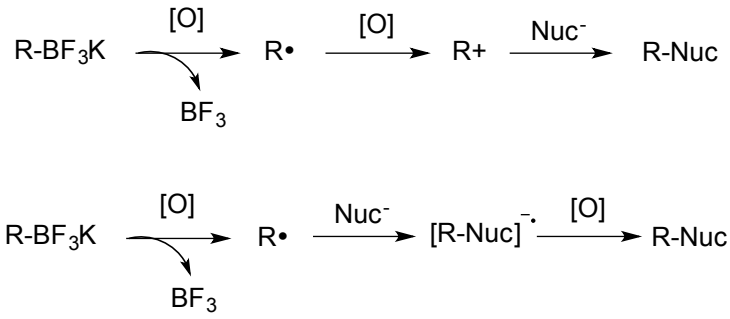
Equation 2.6



To improve the selectivity of this reaction, a variety of solvents, temperatures, concentrations, order of addition, electrophilic fluorinating agents, boron species, and additives (such as acids and bases) were investigated. However, in all cases either good selectivity or good yields, but not both, were achieved.

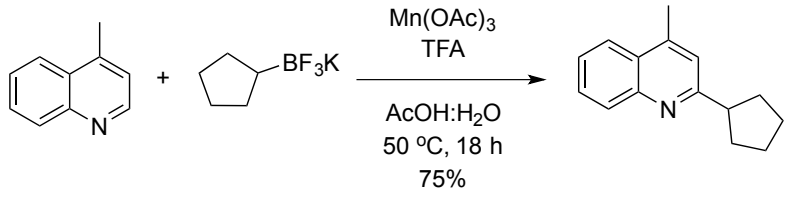
In the course of this investigation some important features of this reaction were observed. For example, when the reaction was set up in a glovebox atmosphere, no reaction took place. However, as soon as the flask was opened to air a pink solution was formed and the starting material consumed almost immediately. Furthermore, when Selectfluor was used with a triflate counterion instead of tetrafluoroborate or hexafluorophosphate, only naphthalene was observed, suggesting the need for a nucleophilic fluorine source. Based on this observations we hypothesized a possible radical mechanisms for these reactions (Scheme 2.6).[33]

Scheme 2.6 Proposed Radical Mechanism for Fluorination of Trifluoroborates



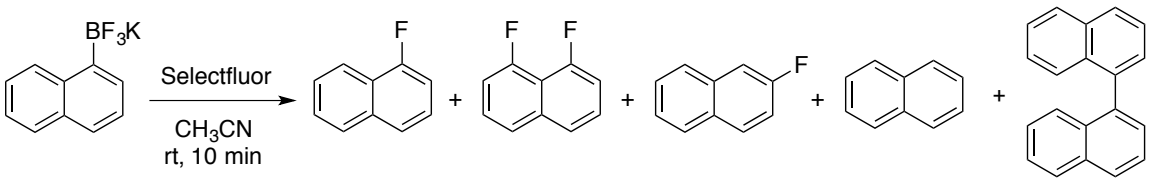
Radical formation from organoboron species is known in the literature.[34] Specifically, potassium organotrifluoroborates have been reported as radical surrogates in Minisci type reactions (eq 2.7),[34c, 35] Pschorr cyclizations,[36] and oxidation with TEMPO.[37]

Equation 2.7



To test the hypothesis of radical formation, we tried the fluorination reaction of potassium naphthalen-1-yltrifluoroborate and Selectfluor in the presence of a variety of radical initiators (such as peroxides) and inhibitors (such as TEMPO and BHT). Unfortunatelly, all conditions that were attempted failed to provide the desired product in good selectivity and yield. Interestingly, when radical initiators were used, the starting material would also dimerize, and the formation of binaphthalene was also observed, along with the other four products previously mentioned (eq 2.8).

Equation 2.8



To investigate the possibility of radical formation followed by nucleophilic attack further, we tried the reaction of potassium naphthalen-1-yltrifluoroborate with a variety of oxidants (such as peroxides and persulfates) and nucleophilic fluorine sources (such as HF, DAST and CsF). Once more, all the conditions failed to afford the desired fluorinated product. However, to our delight, the use of specific oxidants afforded undesired, but interesting, products. For example, the use of Oxone yielded 1-hydroxynaphthalene in quantitative yield, and when Chloramine-T was used, 1-

chloronaphthalene was obtained exclusively. These results initiated the oxidation and chlorination projects described below.

2.3.3 Conclusion

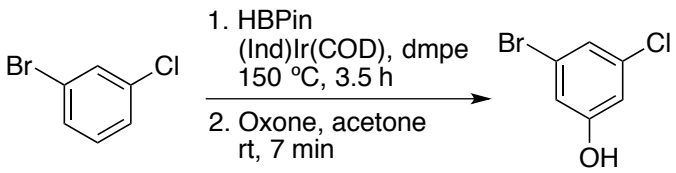
Despite all efforts, the metal free fluorination of potassium organotrifluoroborates remains a challenge. All reaction conditions tried during the course of this study failed to provide good selectivity or good yield of the desired fluorinated product. On a bright note, the observation of a possible radical mechanism for this reaction made possible the development of other projects, and opened the horizon for new types of chemistry involving organotrifluoroborates.

2.4 Oxidation of Organotrifluoroborates via Oxone[38]

2.4.1 Introduction

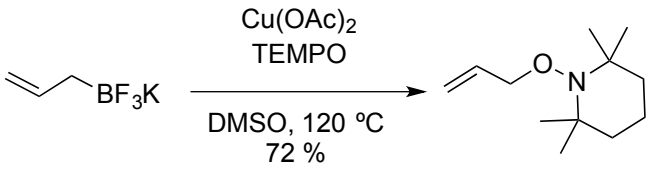
Phenols are found in numerous natural products, pharmaceuticals, and polymers and have been widely used as versatile synthetic intermediates.[39] Traditional methods for the synthesis of these compounds include various protocols for substitution of aryl halides. Unfortunately, the harsh reaction conditions required for direct nucleophilic substitution make this approach incompatible with a variety of common functional groups.[40] Copper- and palladium-catalyzed hydroxylation of aryl halides has been reported in the literature and offers an alternative to the former method.[41] In this case, however, the use of transition metals with attendant ligands and/or high reaction temperatures leads to processes that are less than ideal. Various boron species can be incorporated into aromatic and heteroaromatic systems in a variety of complementary ways, and recently the oxidation of boronic acids in a copper-catalyzed reaction has been reported.[42] Although perhaps useful on a small scale in the laboratory, the use of a copper reagent, ligand, and excess base significantly reduces its appeal on a larger scale. As an alternative to this method, several nonmetal-promoted oxidations of boronic acids and their derivatives have been described.[43] Among the oxidants used for this transformation, hydrogen peroxide,[31a,c,e,f] hydroxylamine,[31b] and Oxone[31d,g] are most often employed. The first two reagents require long reaction times, and the products are obtained in moderate yields for arylboronic acids containing electron-withdrawing groups. On the other hand, the use of Oxone provides an extremely rapid and generally efficient reaction (eq 2.9).[31d]

Equation 2.9



To the best of our knowledge, reports of the oxidation of organotrifluoroborates into the corresponding phenol, alcohol, or related derivatives are currently limited.[25,30,44] For example, phenyltrifluoroborate has been oxidized to phenol in a copper-catalyzed procedure requiring 8 h at room temperature.[30] In another isolated example, an alkyltrifluoroborate has been oxidized by utilizing an excess of a hypervalent iodonium complex to afford an excellent yield of the desired alcohol in 3 h.[32] Finally, during the preparation of this paper, Fensterbank et al. reported the 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO)-promoted oxidation of several alkyltrifluoroborates, which required high temperatures and long reaction times (120 ºC, 20 h) with excess TEMPO (1.2 equiv) and copper salts (1.2 equiv) in DMSO, or 3 equiv of TEMPO in the presence of Dess-Martin periodinane in Et_2O at room temperature for 1-2 days (eq 2.10).[25] The products isolated were the corresponding TEMPO derivatives, which were accessed in modest to good yields depending on the substrates.

Equation 2.10



Importantly, these reactions were demonstrated to proceed via radical intermediates, and thus they would not be expected to be stereospecific for enantiomerically enriched alkyltrifluoroborates, although this latter aspect was not specifically addressed in an unambiguous manner.

The lack of examples detailing a practical method for the oxidation of organotrifluoroborates and the limitations associated with other boron derivatives prompted us to investigate a general, efficient, mild, rapid, and convenient method for this transformation. Herein, we report the oxidation of a broad range of aryl-, heteroaryl-, alkenyl-, and alkyltrifluoroborates using Oxone at room temperature.

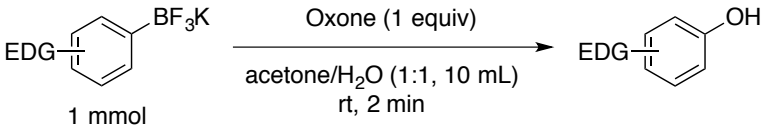
2.4.2 Results and Discussion

On the basis of previous research in which a variety of arylboronic acids and pinacol boronates were transformed to the corresponding phenols,[31d,g] investigations were initiated on the oxidation of potassium naphthalen-1-yltrifluoroborate. Very rapidly it was evident that the protocol developed by Maleczka and Smith for pinacol boronates,[31d] using 1 equiv of Oxone (as a 0.2 M solution in H_2O) in acetone at room temperature, open to the air, was also ideal for the rapid (<5 min) oxidation of organotrifluoroborates. The desired phenol was obtained by an aqueous workup and simple filtration in excellent yield (99%). Because Oxone is an inexpensive,[45] widely available, and industrially acceptable reagent, all subsequent reactions were performed using this material.

With optimal conditions in hand, the investigation continued to outline the full scope of this process. Initially, a broad range of electron-rich and electron-neutral aryltrifluoroborates were investigated (Table 2.4.1). In all cases, quantitative conversion to the desired products was accomplished in only 2 min. The reaction provided excellent

yields for all substrates containing para, meta, or ortho substituents (entries 3-5). Sterically hindered compounds also afforded the products in high yields (entry 7). Importantly, we demonstrated that the reaction could be scaled to 55 mmol, providing the product in 96% yield (Table 2.4.1, entry 1).

Table 2.4.1 Oxidation of Electron-Rich and Electron-Neutral Potassium Aryltrifluoroborates



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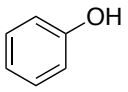
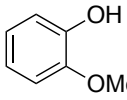
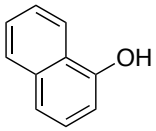
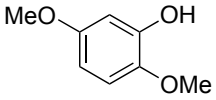
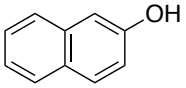
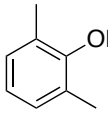
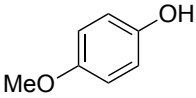
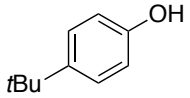
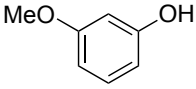
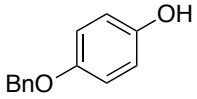
1		96[a]	6		97
2		99	7		95
3		97	8		94
4		98	9		99
5		93	10		97

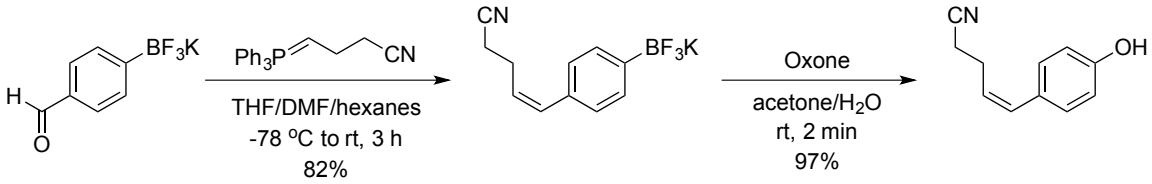
[s] 55 mmol scale

In contrast to the metal-catalyzed processes utilizing other organoboron species, the use of organotrifluoroborates and Oxone in every case afforded the desired products with little or no formation of organic side products. Therefore, a simple aqueous workup

followed, at most, by filtration through a short plug of silica with charcoal afforded the desired products in virtually quantitative yield. Throughout the course of this study, no chromatography was required to obtain pure products.

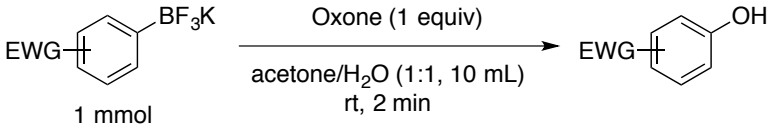
To demonstrate the ability of organotrifluoroborates of being carried through synthetic steps and then converted into a functional group in a late synthetic step, a functionalized substrate was elaborated and then converted into the phenol. Thus, potassium (*Z*)-(4-(4-cyanobut-1-en-1-yl)phenyl)trifluoroborate was synthesized through a Wittig reaction of (4-formylphenyl)trifluoroborate and the nitrile-containing ylide (Scheme 2.7).[3] The organotrifluoroborate was then converted into the phenol, using the oxidation protocol with Oxone. The desired product was obtained in excellent yield in only 2 min without affecting either the nitrile or the double bond of the molecule.[46]

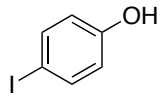
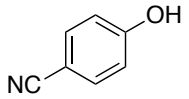
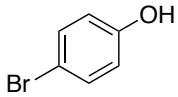
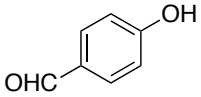
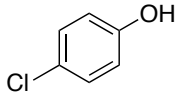
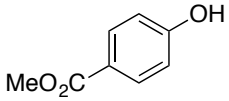
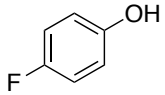
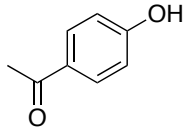
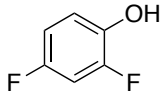
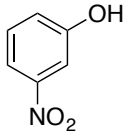
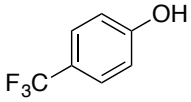
Scheme 2.7



Next, attention was turned to electron-poor aryltrifluoroborates. The conditions developed worked equally well for these substrates, providing the phenols in excellent yields (Table 2.4.2). Substrates such as aldehyde-, ester-, keto-, nitrile-, and nitro-containing aryltrifluoroborates afforded the hydroxylated product without affecting the pendant functional groups (entries 7-11). Halogenated trifluoroborates also provide the corresponding phenol in excellent yields (entries 1-6).

Table 2.4.2 Oxidation of Electron-Poor Potassium Aryltrifluoroborates

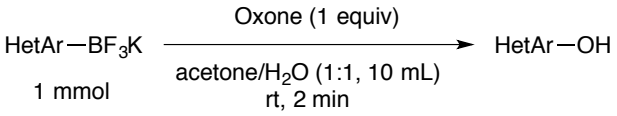


entry	product	yield (%)	entry	product	yield (%)
1		85	7		98
2		96	8		99
3		99	9		99
4		99	10		99
5		97	11		98
6		98			

To expand the utility of the developed conditions further, heteroaryl systems were investigated, including dibenzothio- phenyl, dibenzofuranyl, pyridinyl, benzothiophenyl, benzo- furanyl, thienyl, and furanyl derivatives (Table 2.4.3). Heteroaryls, such as dibenzo[b,d]furan-4-yl-, dibenzo[b,d]thiophen-4-yl-, 6-chloropyridin-3-yl-, and 6-fluoro-5-methylpyridin-3-yltrifluoroborate, afforded the desired phenol in excellent yields in only 5 min (entries 1-4). For substrates where the

most stable tautomers are the carbonyl isomers,[47] only the keto tautomer was observed (entries 5-8). 2-Trifluoroboratofuran afforded the β,γ-unsaturated lactone (entry 9), along with 10% of the α,β-unsaturated product. Interestingly, under the reaction conditions, no oxidation of the nitrogen or sulfur atom of these heterocycles was observed.[48]

Table 2.4.3 Oxidation of Potassium Heteroaryltrifluoroborates



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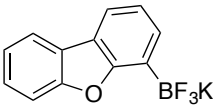
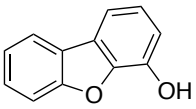
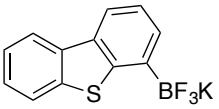
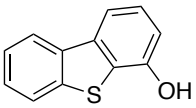
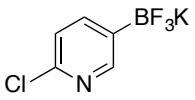
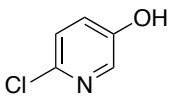
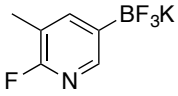
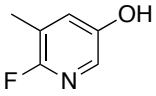
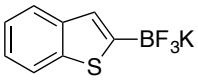
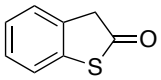
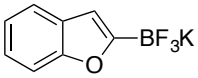
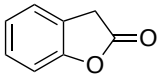
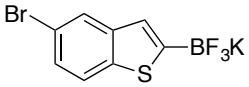
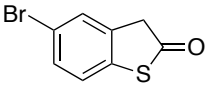
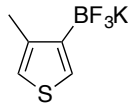
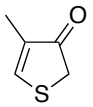
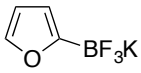
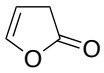
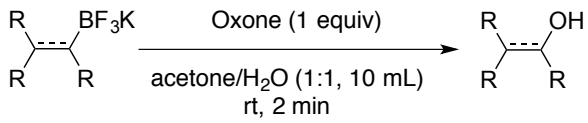
1			97
2			95
3			91
4			94
5			99
6			97
7			94
8			89
9			97

The scope of the general reaction conditions was further extended to alkyl- and alkenyltrifluoroborates (Table 2.4.4). We were pleased to find that the desired alcohol was obtained in excellent yields from primary, secondary, and benzylic alkyl-

trifluoroborates (entries 1-8). Primary alcohols containing halogens or ester groups were generated without affecting these incorporated functional groups. Alkenyltrifluoroborates were converted into the corresponding aldehydes, also in excellent yields (entries 9-11). However, under the reaction conditions, minor amounts of the hydrated aldehyde were observed (entries 9 and 10). Oxidation of both alkyltrifluoroborates and alkenyltrifluoroborates was complete in only 2 min.

Table 2.4.4 Hydroxylation of Potassium Alkyl- and Alkenyltrifluoroborates



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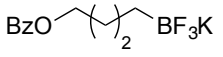
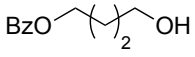
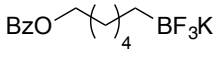
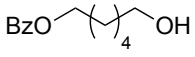
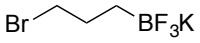
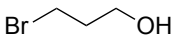
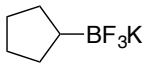
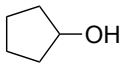
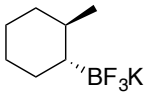
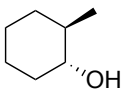
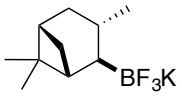
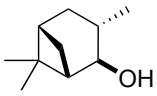
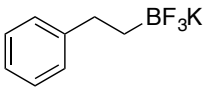
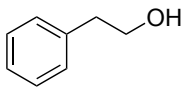
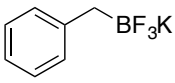
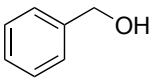
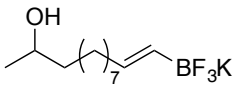
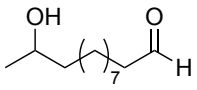
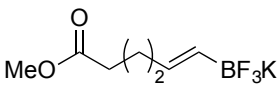
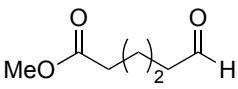
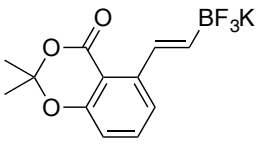
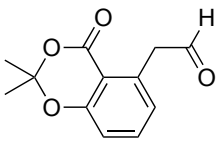
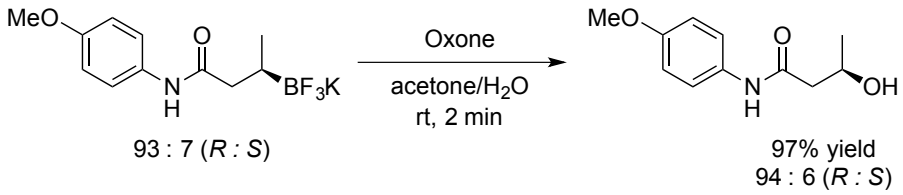
1			99
2			99
3			98
4			95
5			96
6			98
7			99
8			99
9			99
10			99
11			99

To investigate the stereochemical integrity of the process, the enantiomerically enriched β-trifluoroboratoamide was prepared from the corresponding α,β-unsaturated amide and bis(pinacolato)diboron in a copper-catalyzed process using (*R*)-(*S*)-Josiphos as the chiral ligand, according to the procedures previously reported by Yun et al. (eq 2.11).[49] With the enantioeriched organotrifluoroborate in hand, this material was subjected to the oxidation conditions with Oxone. We were pleased to observe that the transformation transpired with complete retention of configuration. The desired alcohol was obtained in 97% yield in only 2 min, in a 94:6 (*R*:*S*) ratio.

Equation 2.11



2.4.3 Conclusions

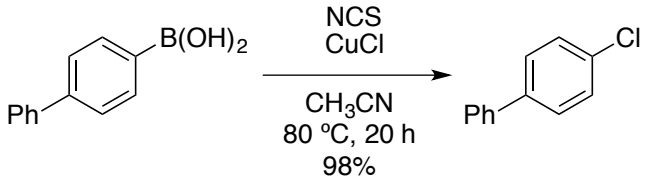
In summary, we have successfully developed a general, rapid, and efficient method for the oxidation of aryl-, heteroaryl-, alkyl-, and alkenyltrifluoroborates. The reactions were complete in only 2-5 min at room temperature, affording the desired products in virtually quantitative yield. The use of Oxone as the oxidant makes the process both economical and environmentally sound. Numerous attendant functional groups were tolerated in this process, and no chromatography was required a simple aqueous workup followed at most by filtration through a plug of silica gel afforded pure material. The oxidation of enantiomerically enriched secondary alkyltrifluoroborates affords the desired alcohols with complete retention of configuration.

2.5 – Metal-Free Chlorodeboronation of Organotrifluoroborates[50]

2.5.1 Introduction

Aryl chlorides are found in many pharmaceuticals and natural products and have been employed as important synthetic intermediates in carbon-carbon bond-forming reactions, such as Suzuki-Miyaura cross-couplings.[51] Among the methods utilized for the synthesis of chlorinated arenes, the Sandmeyer[52] reaction and direct electrophilic aromatic substitution[53] are the most utilized. The direct halogenation of aromatics with electrophilic halogenating agents via electrophilic aromatic substitution is the classic way to introduce chlorine into aromatic and heteroaromatic substrates.[54] However, this method has obvious limitations in terms of both chemoselectivity and regioselectivity. In particular, the site selectivity of these chlorinations relies on directing functional groups in the substrate, and certain regioisomers are often unattainable. The halogenation of boron compounds, particularly those synthesized by complementary methods such as C-H activation[55] and ortho metalation,[56] has emerged as an alternative to circumvent this problem.[57] Specifically, the chlorodeboronation of boronic acids and boronate esters has been described (eq 2.12).[58]

Equation 2.12



In the absence of a metal-based catalyst or promoter, the scope of these reactions appears limited, and moderate yields have been described for electron-deficient aryl substrates.[46d] The use of transition metal complexes, such as copper salts, as catalysts for

the chlorination of aromatic boronic acids and boronate esters improved the yield for electron-poor aromatic systems.[46a] To the best of our knowledge, no chlorodeboronation of organotrifluoroborates has been reported. Consequently, we were prompted to investigate a mild and convenient method for the synthesis of aryl chlorides. Herein we report a metal-free chlorodeboronation of organotrifluoroborates using trichloroisocyanuric acid (TCICA).

2.5.2 Results and Discussion

Electrophilic chlorinating agents have been reported as efficient reagents for the chlorination of boronic acids and boronate esters (Figure 2.4).[46]

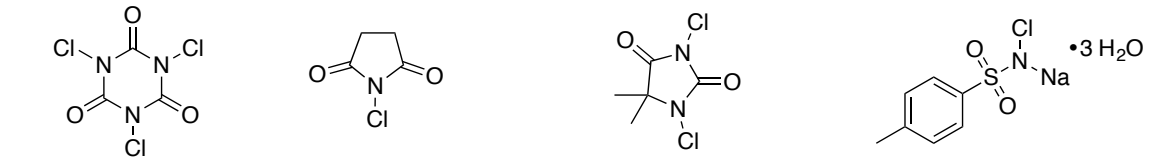
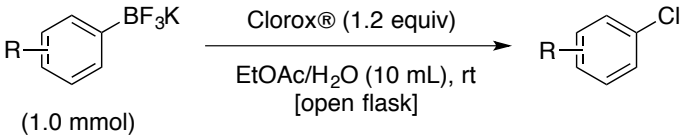


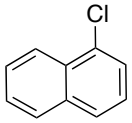
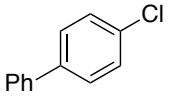
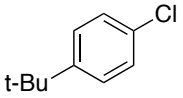
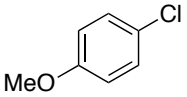
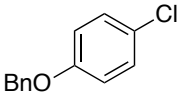
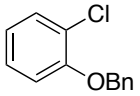
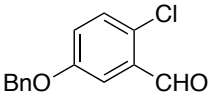
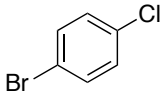
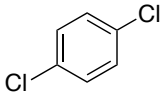
Figure 2.4 Common Electrophilic Chlorinating Reagents

Our investigations were initiated by exploring the chlorodeboronation of potassium naphthalen-1-yltrifluoroborate with sodium hypochlorite (NaOCl, 6.15%, Clorox), because this is a widely available and inexpensive chlorinating agent. A screening of common solvents revealed that EtOAc/H_2O (1:1) was a good solvent system. Thus, the reaction of potassium naphthalen-1-yltrifluoroborate and 1.2 equiv of NaOCl provided the desired product in 92% yield (Table 2.5.1) after 30 min (monitored by ^{11}B NMR). The scope of the reaction for various aryltrifluoroborates was investigated (Table 2.5.1).

Table 2.5.1 Chlorination of Potassium Aryltrifluoroborates Using Clorox

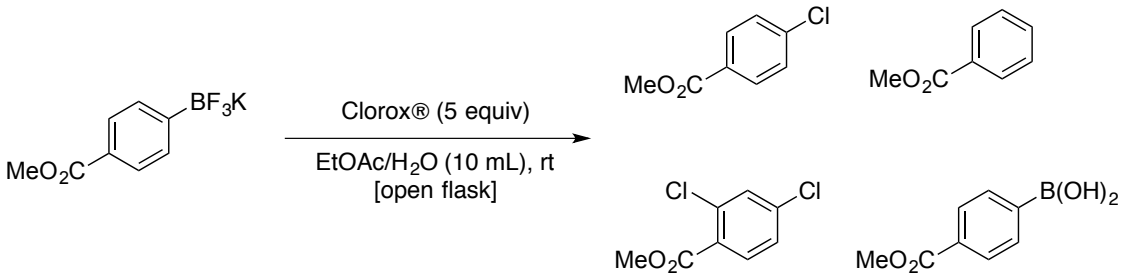


(1.0 mmol)

entry	product	reaction time	yield (%)
1		40 min	92
2		4 h	53
3		1 h	75
4		40 min	71
5		40 min	91
6		1 h	73
7		40 min	81
8		1 h	64
9		1 h	53

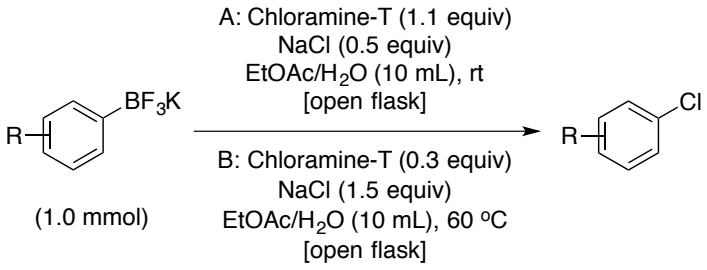
The reaction with electron-rich aryltrifluoroborates proceeded in good yields, and most transformations were complete in 40 min or 1 h (entries 1 – 7). Halogen-containing aryltrifluoroborates also underwent chlorodeboronation to afford the desired aryl chlorides in modest yields (entries 8 and 9). Unfortunately, electron-deficient aryltrifluoroborates were not reactive under these conditions, and the starting material was completely recovered. In an attempt to obtain complete reaction conversion, an excess of NaOCl was utilized (5 equiv); however, the use of a large amount of this reagent afforded a mixture of the desired chlorinated product along with protodeboronation, dichlorination, and boronic acid side products (eq 2.13). All efforts to optimize the conditions for aryltrifluoroborates containing electron-withdrawing groups (e.g., ester, ketone, or nitro) with NaOCl were unsuccessful.

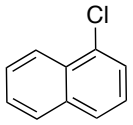
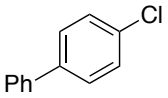
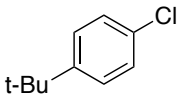
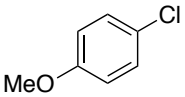
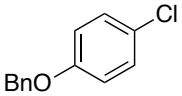
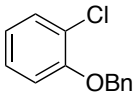
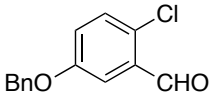
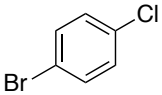
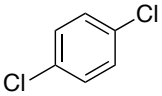
Equation 2.13



Next we investigated the use of Chloramine-T as the chlorinating reagent, because it has been used as an oxidant for the bromination[43c] and iodination[43d] of aryltrifluoroborates. After extensive optimization, we determined that the reaction of potassium naphthalen-1-yltrifluoroborate with 1.1 equiv of Chloramine-T and 0.5 equiv of NaCl in EtOAc/H_2O at rt (condition A) afforded the desired chlorinated product in 94% yield (Table 2.5.2).

Table 2.5.2 Chlorination of Potassium Aryltrifluoroborates Using Chloramine-T



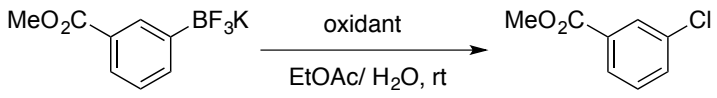
entry	product	reaction time	yield (%)
1		40 min	A: 94 B: 83
2		4 h	A: 72 B: 70
3		1 h	A: 71 B: 68
4		40 min	A: 78 B: 65
5		40 min	A: 87 B: 74
6		1 h	A: 82 B: 71
7		40 min	A: 85 B: 71
8		1 h	A: 54 B: 15
9		1 h	A: 57 B: 21

Importantly, the reactions with 0.3 equiv of Chloramine-T and 1.5 equiv of NaCl in EtOAc/H_2O at 60 ºC (condition B) also afforded the desired chlorinated product in 83% yield and 100% conversion.

As illustrated in Table 2.5.2, the reaction of electron-rich aryltrifluoroborates with Chloramine-T afforded the desired chlorinated products in good yield (entries 1 – 7). However, the chlorodeboronation of halogen-containing aryltrifluoroborates proceeded in low yields (entries 8 and 9). Once more, the chlorination of aryltrifluoroborates bearing electron-withdrawing groups (e.g., ester, ketone, or nitro) did not afford the desired product in good yield.

To improve the yield of this reaction for electron-withdrawing groups, other chlorinating agents were tested (Table 2.5.3).

Table 2.5.3 Chlorination of Potassium (3-Methoxycarbonyl)-phenyltrifluoroborate Using Various Chlorinating Agents

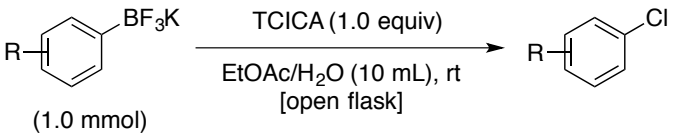


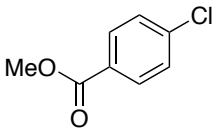
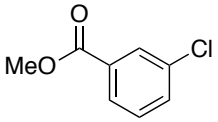
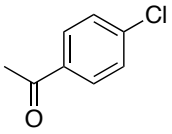
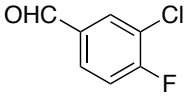
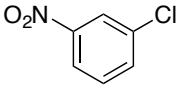
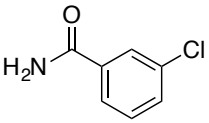
(1.0 mmol)

entry	oxidant	(mmol)	reaction time	yield (%)
1	NCS	1.2	24 h	21
2	Chloramine-T	1.2	24 h	30
3	DCDMH	1.2	24 h	only S.M. recovered
4	Clorox	1.2	2 h	15
5	TCICA	1.0	1 h	92

The chlorodeboronation of potassium (3-methoxycarbonyl)phenyltrifluoroborate with *N*-chlorosuccinimide (NCS) afforded the desired chlorinated product in only 21% yield. Chloramine-T improved the yield to only 30% after 24 h in a mixture with protodeboronation product, whereas 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) and sodium hypochlorite (NaOCl) were inefficient in this transformation. However, when 1.0 equiv of trichloroisocyanuric acid (TCICA) was utilized, we were pleased to find that methyl 3-chlorobenzoate was obtained in 92% yield in only 1 h at room temperature. Because TCICA is a widely available and inexpensive material ($11.00/mol catalog price), all subsequent reactions were carried out using this electrophilic chlorinating agent. With optimized conditions in hand, the scope of the reaction for aryltrifluoroborates containing electron-withdrawing groups was investigated (Table 2.5.4). The reaction with a variety of available electron-poor aryltrifluoroborates proceeded in good yields with 1 equiv of TCICA. 1-Chloro-3-nitrobenzene (entry 5) and 3-chlorobenzamide (entry 6) were obtained in high yields, although heating to 80 ºC was required. Furthermore, 3-chlorobenzamide was obtained in 89% yield with no observed chlorination at the nitrogen of the amide.[59] Importantly, the reaction with potassium (4-methoxycarbonyl)- phenyltrifluoroborate afforded the product (entry 1) in 87% yield. This regiochemistry was previously unattainable by the chlorination of simple arenes.[42]

Table 2.5.4 Chlorodeboronation of Electron-Poor Potassium Aryltrifluoroborates with TCICA

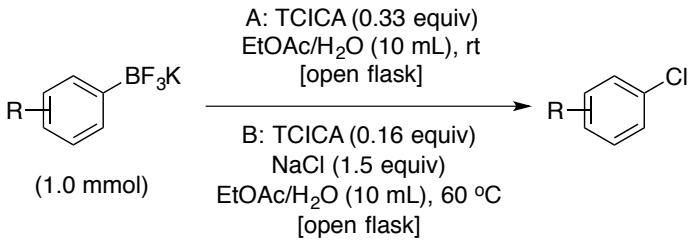


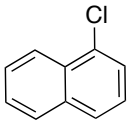
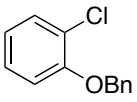
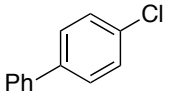
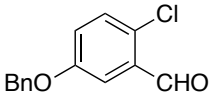
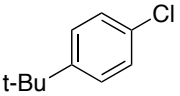
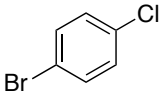
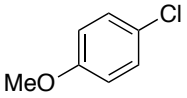
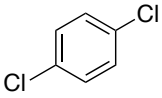
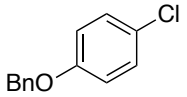
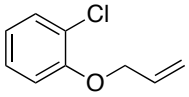
entry	product	reaction time	yield (%)
1		2 h	87
2		1 h	92
3		30 min	82
4		40 min	80
5[a]		4 h	85
6[a]		6 h	89

[a] reaction run at 80 °C.

Next, TCICA was applied as the chlorinating agent in the reaction with electron-rich aryltrifluoroborates (Table 2.5.5).

Table 2.5.5 Chlorodeboronation of Electron-Rich and Halogen-Containing Potassium Aryltrifluoroborates with TCICA



entry	product	reaction time	yield (%)	entry	product	reaction time	yield (%)
1		40 min	A: 95 B: 82	6		1 h	A: 91 B: 86
2		40 min	A: 89[a] B: 85	7		40 min	A: 92 B: 80
3		1 h	A: 94 B: 87	8		1 h	A: 81 B: 67
4		40 min	A: 98 B: 91	9		1 h	A: 86 B: 54
5		40 min	A: 92 B: 89	10		1 h	A: 84 B: 76

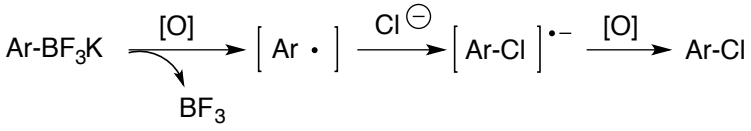
[a] 5 mmol scale

The reaction with electron-rich aryltrifluoroborates proceeded in good yields using only 0.33 equiv of TCICA at rt (condition A) or 0.16 equiv of TCICA and 1.5 equiv of

NaCl at 60 ºC (condition B), and all were complete in 1 h or less (entries 1 – 7). It is important to mention that the reaction with electron-donating groups in the para position (e.g., entries 2 – 5 and 7) can be run at higher concentrations (e.g., 0.33 M). However, for compounds such as the ones illustrated in entries 1 and 8 – 10, higher concentrations led to a mixture of regioisomers. Nonetheless, the reaction with potassium biphenyl-4-yltrifluoroborate was carried out on a 5 mmol scale (1.3 g) with 0.33 equiv of TCICA and 15 mL of solvent (0.33 M), providing product 4-chlorobiphenyl in 81% yield (entry 2). Halogen-containing aryltrifluoroborates also underwent chlorodeboronation to afford the desired aryl chloride in moderate to good yields (entries 8 and 9), depending on the condition utilized. Unfortunately, this method was unsuccessful for the chlorodeboronation of meta-substituted electron-rich aryl systems. Inexplicably, only starting material or protodeboronation products were obtained for the reactions of TCICA with potassium 3-methoxyphenyltrifluoroborate, potassium 3-(benzyloxy)phenyltrifluoroborate, and potassium 3,5-diisopropylphenyltrifluoroborate.

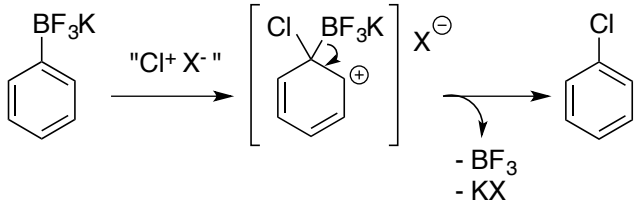
The mechanism of these transformations is enigmatic, particularly in view of the fact that less than 1 equiv of electrophilic chlorine can be employed along with NaCl in an oxygenated atmosphere. We considered the possibility that the reaction transpired via a version of the rare $S_{ON}1$ mechanism (Scheme 2.8),[33b, 60] where the various chlorinating agents initially served as oxidants of the trifluoroborate.

Scheme 2.8 Proposed Radical Mechanism



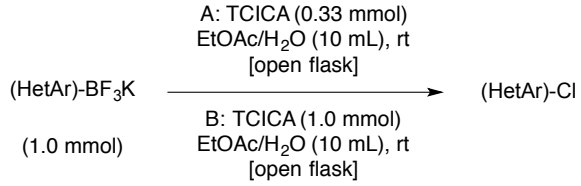
To investigate the possibility of radical intermediates, potassium [2-(allyloxy)phenyl]trifluoroborate was subjected to both reaction conditions (Table 2.5.5, entry 10). However, no cyclization product was observed, and the reaction afforded only the ortho-substituted chlorinated product in 84% or 76% yield, respectively. Therefore, it seems unlikely that the reaction proceeds by a radical mechanism,[61] and perhaps an electrophilic aromatic substitution with ipso attack is more likely (Scheme 2.9).[62]

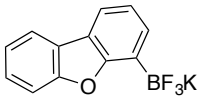
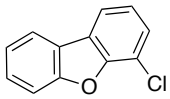
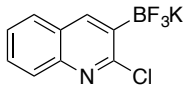
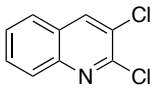
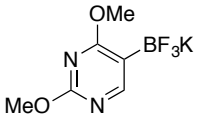
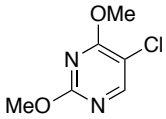
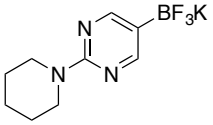
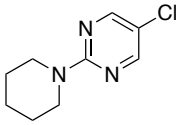
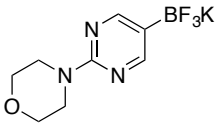
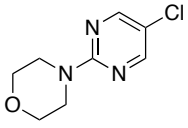
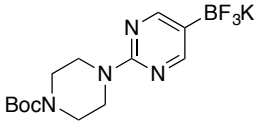
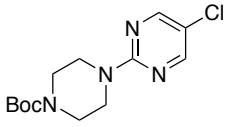
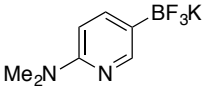
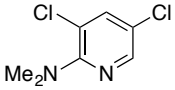
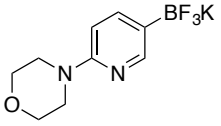
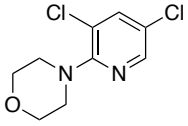
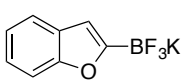
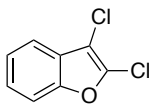
Scheme 2.9 Proposed Ipso Attack Mechanism



Moving forward, the scope of the reaction for heteroaryl systems was also examined. To the best of our knowledge, the chlorodeboronation of heteroarylboron compounds in the literature is limited to one example using stoichiometric copper(II) chloride as the chlorinating agent.[46b] Hence, diverse heteroaryltrifluoroborates were examined under two different reaction conditions with TCICA (Table 2.5.6).

Table 2.5.6 Chlorodeboronation of Potassium Heteroaryltrifluoroborates with TCICA

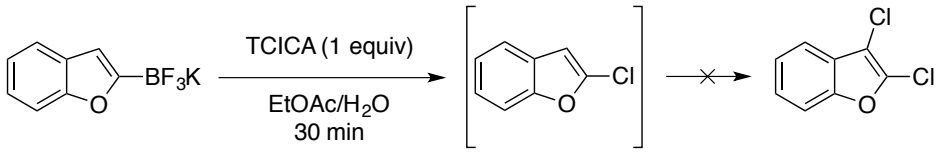


entry	(HetAr)-BF_3K	product	method	reaction time	yield (%)
1			A	40 min	95
2			A	6 h	80
3			A	2 h	91
4			A	2 h	90
5			A	2 h	89
6			A	2 h	95
7			B	1 h	88
8			B	1 h	91
9			B	30 min	86

The majority of the heteroaryl chlorides obtained were not commercially available or had limited commercial availability. Organotrifluoroborate derivatives containing the dibenzofuranyl, quinolinyl, benzofuranyl, pyrimidinyl, and pyridinyl subunits were successfully converted into the corresponding chlorinated product in good yields. However, the use of only 0.33 equiv of TCICA (method A) in the reaction with the pyridine and benzofuran derivatives (entries 7 – 9) afforded mixtures of mono and dichlorinated compounds (1: 1). The use of less than 0.33 equiv of TCICA with or without NaCl did not improve the selectivity of the reaction. When method B (1 equiv of TCICA) was applied to these substrates, only dichlorination products were observed in good yields. Under the developed conditions, heteroaryls such as thiophenes, furans, and indoles afforded complex product mixtures of monochlorinated regioisomers, as well as dichlorinated and protodeboronated compounds. The formation of dichlorinated compounds from monotrifluoroborato heteroaryls represented an unexpected reactivity.

To elucidate the source of these products, we examined the possibility of a chlorodeboronation and subsequent chlorination of the monochloride intermediate (eq 2.14).

Equation 2.14

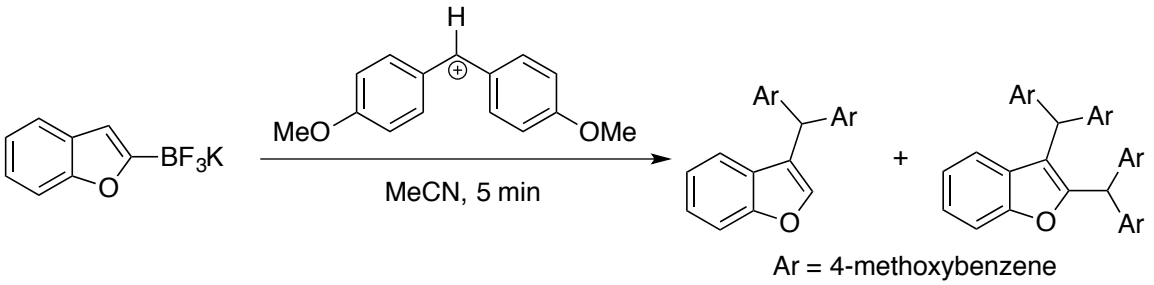


Thus, we applied our general method B (1 equiv of TCICA) in the reaction with 2-chlorobenzofuran. Surprisingly, none of the dichlorinated product was observed under these conditions, and only starting material was recovered. Although the developed

protocol is an efficient method for the synthesis of these dichlorinated heterocycles, the mechanistic pathway for their formation is again puzzling.

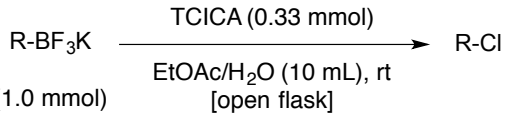
Interestingly, after our publication the Mayr group reported a study on electrophilic aromatic substitutions of aryltrifluoroborates.[63] In this work, they investigated the reactivity of heteroaryltrifluoroborates toward different electrophiles. The reaction is claimed to occur first at the vicinal position to the trifluoroborate group followed by ipso substitution to afford disubstituted products. Specifically, the reaction of potassium benzofuran-2-yltrifluoroborate with benzhydrylium ion afforded a mixture of mono and dibenzylated products (eq 2.15). These findings provide some insight into the dichlorination of the aforementioned compounds, wherein a vicinal substitution followed by ipso chlorination of those reagents (e.g., potassium benzofuran-2-yltrifluoroborate) can be proposed.

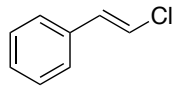
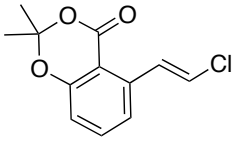
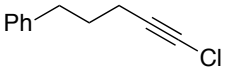
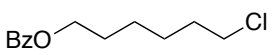
Equation 2.15



Encouraged by the results obtained with aryl- and heteroaryltrifluoroborates, we examined the feasibility of applying the process to alkyl-, alkenyl-, and alkynyltrifluoroborates (Table 2.5.7).

Table 2.5.7 Chlorodeboronation of Potassium Alkyl-, Alkenyl-, and Alkynyltrifluoroborates with TCICA



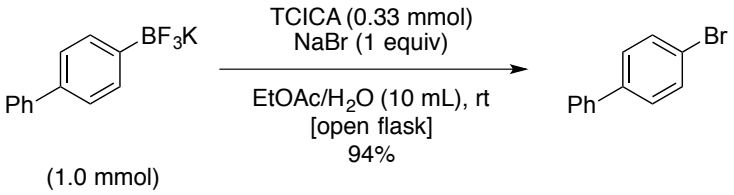
entry	product	reaction time	yield (%)
1		30 min	85
2		30 min	92
3		40 min	82
4		2 h	81

The use of only 0.33 equiv of TCICA was sufficient to afford the desired chlorinated products in good yields. Although for many substrates the process worked very well, the protocol is somewhat capricious, and thus attempts to promote the chlorodeboronation of secondary alkyltrifluoroborates as well as Z-alkenyltrifluoroborates were unsuccessful.

Finally, based on the work of Kabalka and co-workers[45c] where the bromination of aryltrifluoroborates was described by using Chloramine-T and sodium bromide, we

demonstrated that the use of 0.33 equiv of TCICA in the presence of 1 equiv of sodium bromide afforded the desired brominated product in 94% yield in only 30 min (eq 2.16).

Equation 2.16



2.5.3 Conclusions

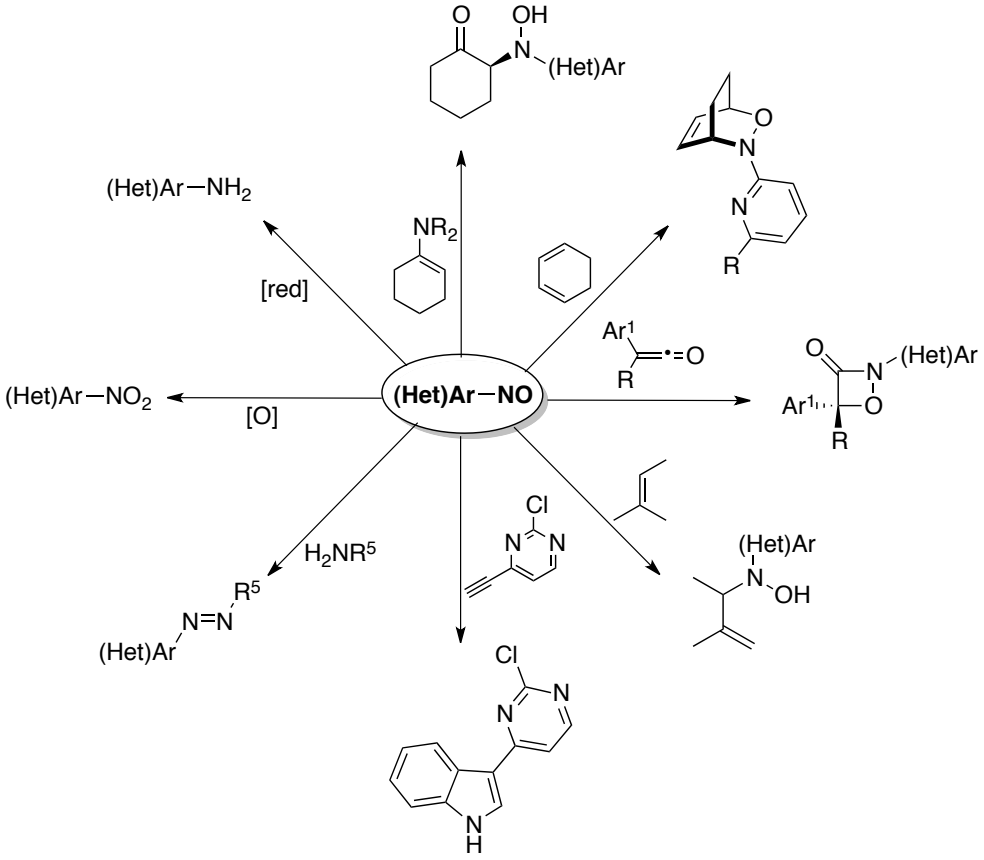
In conclusion, we have developed the first metal-free method for the chlorodeboronation of organotrifluoroborates utilizing commercially available TCICA. Under our mild conditions, aryl-, heteroaryl-, alkyl-, alkenyl-, and alkynyltrifluoroborates bearing a variety of functional groups afforded the corresponding chlorinated product in good yields. The mechanism of these reactions is unclear, leading to surprising and perplexing results in some cases. We are attempting to elucidate the nature of these and other reactions that transpire under oxidative conditions in our continuing studies of the organotrifluoroborates.

2.6 Nitrosation of Aryl- and Heteroaryltrifluoroborates with Nitrosonium Tetrafluoroborate[64]

2.6.1 Introduction

Nitroso compounds are versatile synthetic intermediates and have been utilized in a variety of transformations[65] such as nitroso aldol reactions,[66] [4+2],[67] [3+3],[68] and [2+2][69] cycloadditions, ene reactions,[70] addition of Grignard reagents,[71] reactions with alkynes to yield indoles,[72] coupling with amines to afford azo compounds,[73] oxidation to nitro compounds[74] and reduction to amines[75] (Scheme 2.10). Additionally, nitrosoarenes have shown some activity against HIV-1 infectivity.[76] Despite their potentially wide applications, many of these reported methods utilize a single or limited subset of nitroso aromatics, presumably because of the lack of synthetic methods available to synthesize a diverse set of functionalized nitrosoarenes.

Scheme 2.10

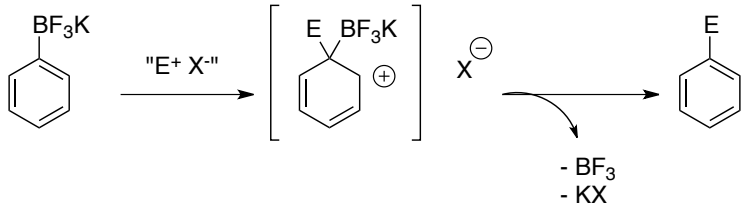


The first synthesis of nitrosobenzene was published by Baeyer over a century ago.[77] Since then, various methods have been published to afford nitrosoarenes.[78] Among them, the oxidation of anilines to the corresponding nitrosoarene is the most widely utilized.[79] Although many protocols for this conversion are reported in the literature, their reliance on the availability of anilines makes them somewhat limited in scope. Furthermore, the use of oxidants restricts the range of functional groups allowed in this transformation. As an example, aldehyde-containing nitrosoarenes cannot be made by this method. Another problem generally associated with this method is the formation of undesired side products such as azo and azoxy compounds.[66] Moreover, few heteroarylnitroso compounds have been obtained by this method, and those that have

been accessed have been confined to nitrogen-containing heterocycles.[80] Nitrosation of simple arenes[81] and arylmetallics (e.g., organotin,[82] -thallium[83] and -silicon[84] compounds) have also been reported in the literature using electrophilic nitrosonium reagents. For both of these types of transformations the reaction only works for aryl species containing electron-donating groups, which limits the breadth of nitroso products that can be accessed. Because of the limited examples using organometallic species and the drawbacks associated with oxidation reactions of aryl and heteroarylnitroso synthesis (e.g., functional group tolerance and side product formation), we were interested in finding a novel, rapid, and mild method to synthesize nitrosoarene derivatives.

The *ipso*-substitution of arylboron species, as previously demonstrated for halogenation[45] and nitration[50] of arylboronic acids, provides a potential means to accomplish this goal. This mechanism was also previously proposed for the chlorodeboronation of aryl and heteroaryltrifluoroborates (Scheme 2.11).[85]

Scheme 2.11

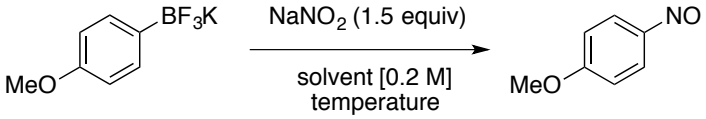


Because there are no examples for nitrosation of organoboron species in the literature, we were interested on develop a new method to synthsize this underrepresented class of molecules.

2.6.2 Results and Discussion

Based on the *ipso*-nitration of boronic acids with nitrate salts developed by Olah and co-workers,[74] we began the screening for nitrosation of organotrifluoroborates with sodium nitrite in different solvents (Table 2.6.1). The choice of this nitrite salt was made by the ready availability and low cost of this reagent. After optimization, we determined that the reaction of potassium trifluoro(4-methoxyphenyl)borate with $NaNO_2$ (1.5 equiv) in heptane/H_2O at 50 ºC afforded the desired nitrosated product in 89% isolated yield as determined by ^1H NMR and GC/MS analysis.

Table 2.6.1. Optimization with Sodium Nitrite



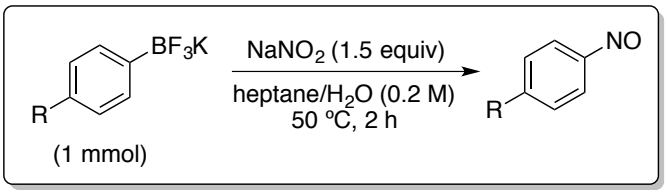
1a

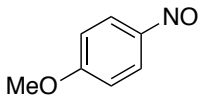
entry	solvent	temperature	reaction time (h)	^{11}B NMR / GC/MS
1	EtOAc	rt	48	S.M.
2	CH_3CN	rt	48	S.M.
3	heptane	rt	48	S.M.
4	H_2O	rt	4	**1a** : protodeboronation (1 : 1)
5	EtOAc/H_2O	rt	4	**1a** : protodeboronation (3 : 1)
6	CH_3CN/H_2O	rt	4	**1a** : protodeboronation (2 : 1)
7	heptane/H_2O	rt	4	**1a**
8	heptane/H_2O	50 ºC	2	**1a** (89% isolated yield)

With these conditions in hand, we began to examine the nitrosation of a variety of aryltrifluoroborates (Scheme 2.12). Phenyltrifluoroborates bearing electron-donating groups were successfully converted into the corresponding nitrosobenzene in good yields. Unfortunately, electron-neutral aryltrifluoroborates (e.g., biphenyl) and electron-

withdrawing (ester) groups inhibited this transformation, and only the protodeboronated products were obtained.

Scheme 2.12





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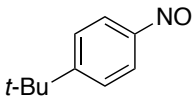

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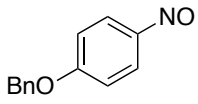

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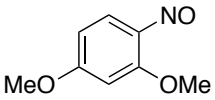
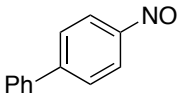
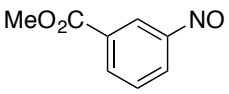


65%



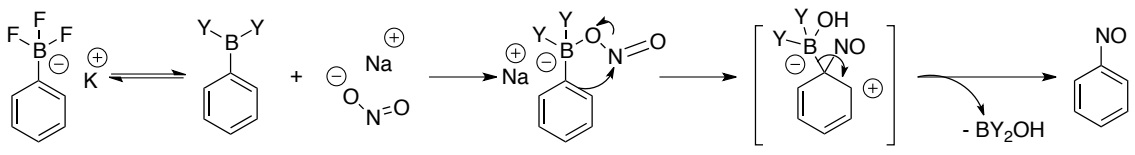
only protodeboronation



only protodeboronation

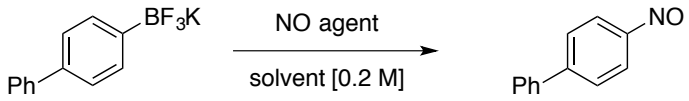
The results obtained further demonstrated that the reaction does not occur in the absence of water and that only electron-rich aryltrifluoroborates afforded the desired product. Thus, we hypothesized that aqueous conditions are necessary to form the tricoordinate boron species *in situ,*[18] and this species, now possessing a Lewis acidic boron moiety with an empty p-orbital, could then undergo attack of sodium nitrite to form an ate-complex and a more electrophilic NO^+, with subsequent *ipso*-substitution affording the nitroso product (Scheme 2.13).

Scheme 2.13



To improve the scope of this reaction, the nitrosation of potassium [1,1'-biphenyl]-4-yltrifluoroborate was further optimized. A variety of solvents, additives, nitrosating agents and temperatures were investigated. As illustrated in Table 2.6.2, the use of other nitrite salts, such as KNO_2 and $AgNO_2$ (entries 1–3), were inefficient for this transformation. The use of acid additives for *in situ* formation of NO^+ [69c,86] also did not afford the desired nitroso product, and only protodeboronation was observed (entries 4–7). Fortunately, the use of nitrosonium tetrafluoroborate (1.03 equiv) in CH_3CN (0.2 M) at room temperature in an open flask proved to be efficient for this transformation, affording the nitroso product in 90% isolated yield. Importantly, the reaction can be followed visually. The slurry formed by the trifluoroborate in CH_3CN becomes a bright green, homogeneous solution almost immediately. The crude reaction is then worked up by addition of water followed by dichloromethane extraction, with subsequent filtration through a plug of silica providing the product in high purity. A prolonged reaction time leads to oxidation of the formed nitroso product and affords a mixture of this compound along with the corresponding nitroaromatic. The use of more than 1.03 equivalents of nitrosonium tetrafluoroborate does not fully convert the nitroso into the nitro group. Instead, a mixture of nitroso, nitro and protodeboronation products is observed.

Table 2.6.2 Optimization of the Nitrosation of Potassium [1,1'-Biphenyl]-4-yltrifluoroborate

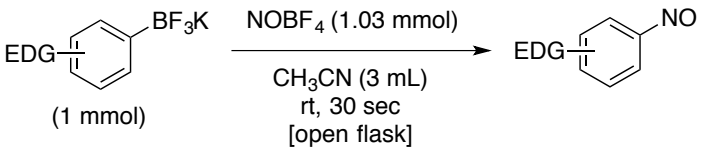


entry	NO agent	solvent	reaction time	GC/MS
1	$NaNO_2$	heptane/H_2O (1 : 1)	4 h	protodeboronation
2	KNO_2	heptane/H_2O (1 : 1)	4 h	protodeboronation
3	$AgNO_2$	heptane/H_2O (1 : 1)	2 h	protodeboronation
4	$NaNO_2$/HCl	heptane/H_2O (1 : 1)	1 h	protodeboronation
5	KNO_2/HCl	heptane/H_2O (1 : 1)	1 h	protodeboronation
6	$AgNO_2$/HCl	heptane/H_2O (1 : 1)	1 h	protodeboronation
7	$NaNO_2$/TMSCl	CH_2Cl_2/H_2O (1 : 1)	1 h	protodeboronation
8	$NOBF_4$	CH_3CN	30 sec	product (90% isolated yield)

With the optimal conditions in hand, the scope of the reaction for electron-donating and electron neutral aryltrifluoroborates was investigated (Table 2.6.3). In all cases, the reaction was complete in only 30 seconds and afforded the desired product in good to excellent yields. The method proved to be selective, and aryltrifluoroborates containing ortho, meta and para substituents were readily converted to the corresponding nitrosobenzene (Table 2.6.3, entries 1–3). This regioselectivity cannot be attained by the direct nitrosation of arenes. The reaction was scaled up to 1 g, and the product was obtained in excellent yield (Table 2.6.3, entry 1). Sterically hindered substrates also afforded the desired product in good yield. Importantly, potassium (3,5-diisopropylphenyl)trifluoroborate, made by direct C-H activation of arenes [87] was converted into 1,3-diisopropyl-5-nitrosobenzene in 88% yield (Table 2.6.3, entry 9). This

illustrates a unique substitution pattern, because the corresponding aryl chloride (necessary for preparation of the amine utilized for the oxidation method previously mentioned) has very limited availability.

Table 2.6.3. Nitrosation of Electron-rich and Electron-neutral Potassium Aryltrifluoroborates



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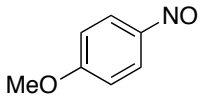
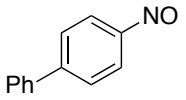
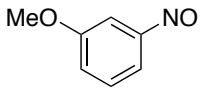
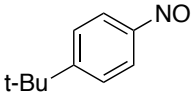
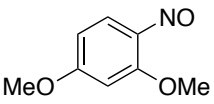
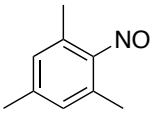
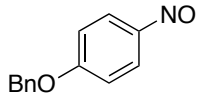
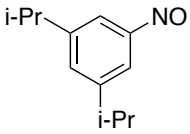
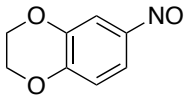
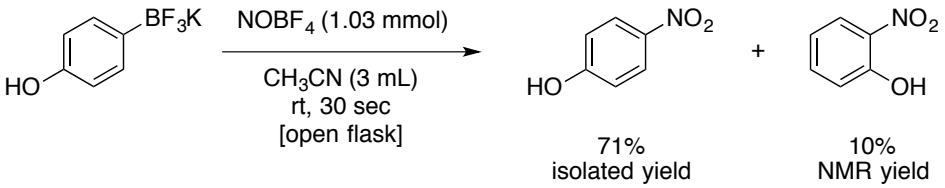
1		95[a]	6		90
2		89	7		93
3		91	8		92
4		92	9		88
5		91			

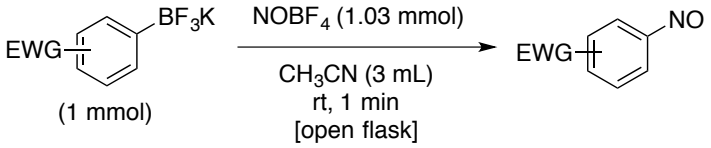
Surprisingly, the reaction of potassium trifluoro(4-hydroxyphenyl)borate yielded the corresponding nitrophenol as a mixture of regioisomers (eq 2.17).

Equation 2.17



Subsequently, the reaction of aryltrifluoroborates bearing electron-withdrawing groups was investigated (Table 2.6.4). Methods such as direct nitrosation of arenes and other organometallic species have proven inefficient in the production of nitrosobenzenes with electron-poor groups.[69-72] In our hands, aryltrifluoroborates containing ester, ketone, aldehyde, nitrile, amide, nitro and carboxylic acid groups (Table 2.6.4, entries 1-9) were converted into the corresponding nitroso compounds in good yields without affecting the aforementioned, embedded functional groups. The reaction was regiospecific, and ortho, meta, and para substituted nitrosobenzenes were obtained. Importantly, aldehyde-containing aryltrifluoroborates afforded the corresponding nitrosobenzaldehyde in good yields and high regioselectivity without oxidation of the aldehyde group (Table 2.6.4, entries 4–6). These aldehyde-containing nitroso products were previously obtained only by a four-step procedure from the corresponding nitroarene.[88] As illustrated previously with potassium (3,5-diisopropylphenyl)trifluoroborate (Table 2.6.3, entry 9), we were able to synthesize methyl 3-methyl-5-nitrosobenzoate and 1-methoxy-3-nitroso-5-(trifluoromethyl)benzene (Table 2.6.4, entries 10 and 11) from trifluoroborates made by C-H activation. Furthermore, the conversion of aryltrifluoroborates containing halogens into the corresponding nitroso product was accomplished in good yields (Table 2.6.4, entries 12–15).

Table 2.6.4. Nitrosation of Electron-poor Potassium Aryltrifluoroborates



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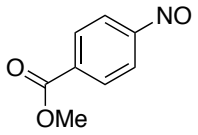
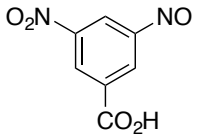
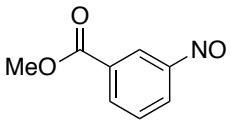
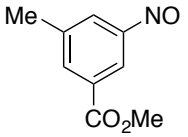
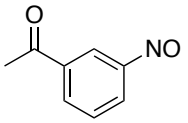
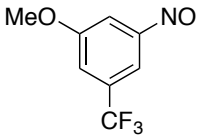
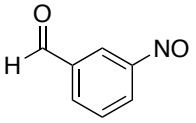
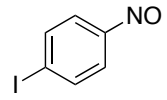
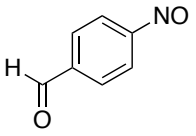
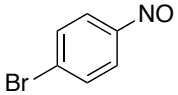
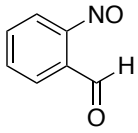
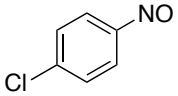
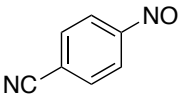
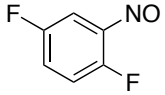
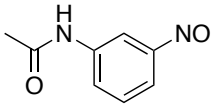
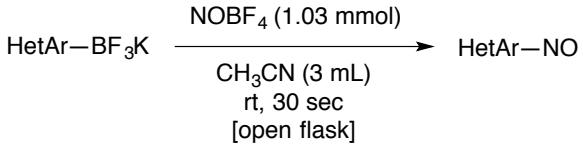
1		96	9		90
2		95	10		91
3		94	11		81
4		91	12		92
5		94	13		94
6		78	14		92
7		89	15		79
8		91			

To expand the scope of this reaction further we turned our attention to the reaction of heteroaryltrifluoroborates. Once more, this transformation was accomplished for a variety of substrates, including dibenzofuranyl, dibenzothienyl, benzothienyl, indolyl, pyrimidinyl and pyridinyl derivatives, affording the nitrosoheteroaryl products in good yields (Table 2.6.5). Furthermore, nitrogen-containing heterocycles (Table 2.6.5 entries 5– 6) were obtained with no observed nitrosation of the heterocyclic nitrogen.[89] To the best of our knowledge, all compounds illustrated in Table 2.6.5 were never before synthesized by any other method.

Table 2.6.5. Nitrosation of Potassium Heteroaryltrifluoroborates



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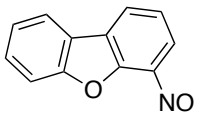
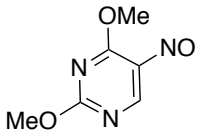
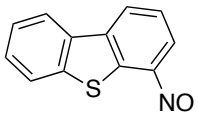
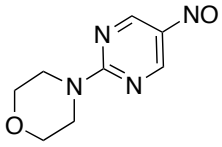
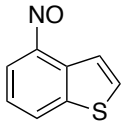
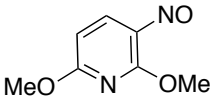
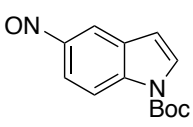
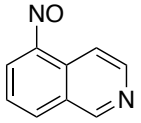
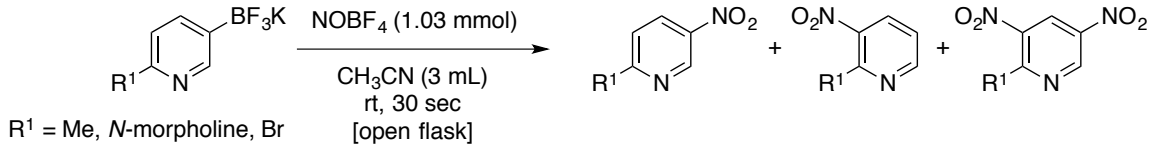
1		85	5		82
2		80	6		76
3		81	7		72
4		73	8		62[a]

[a] NMR yield using EtOAc as internal standard

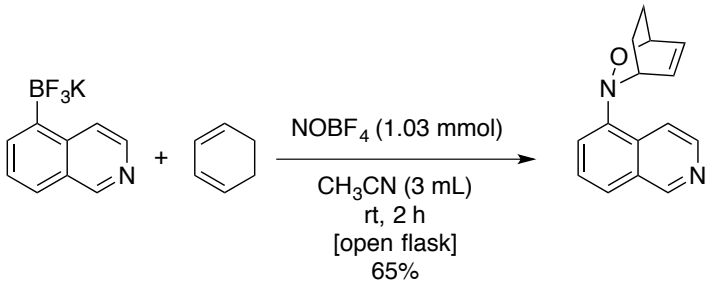
However, for 5-membered heteroaryltrifluoroborates (e.g., thienyl, furanyl, pyrrolyl, isoxazolyl and pyrazolyl) and fused system with the trifluoroborate substituent within the 5-membered heterocycle (e.g., 2- or 3-substituted dibenzofuranyl, dibenzothienyl and indolyl), the reaction was inefficient, and only protodeboronated product was recovered. Moreover, the reaction with 3-trifluoroboratopyridines containing a substituent at the 6 position afforded a mixture of nitro and dinitro products, and no nitroso derivatives were observed (eq 2.18). The use of more than 1 equivalent of $NOBF_4$ did not give the dinitro product; instead a mixture of products along with protodeboronation was observed. The same pattern was observed for quinolines bearing trifluoroborates at the 2, 3 and 4 positions, where a mixture of nitro and dinitro derivatives was obtained.

Equation 2.18



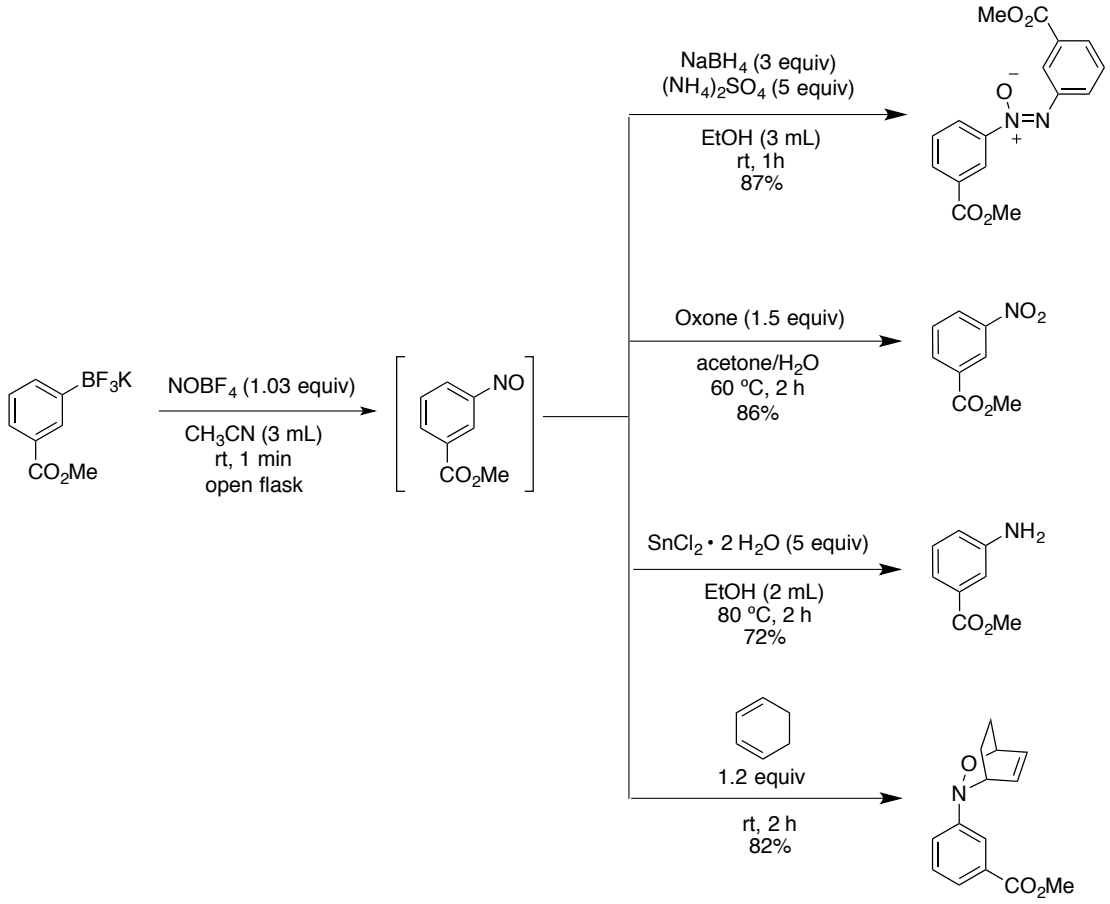
Interestingly, 5-nitrosoisoquinoline (Table 2.6.5, entry 8) was obtained as a yellow solid that upon exposure to air would turn black and could not be further purified. The crude material appeared to be very pure by ^{1}H NMR, which led to the conclusion that the nitroso product obtained is not stable. To circumvent this problem, a one-pot nitrosation of potassium trifluoro(isoquinolin-5-yl)borate, followed by Diels-Alder reaction with cyclohexa-1,3-diene, was investigated (eq 2.19).[65] The reaction afforded the Diels-Alder adduct in 65% yield over two steps.

Equation 2.19



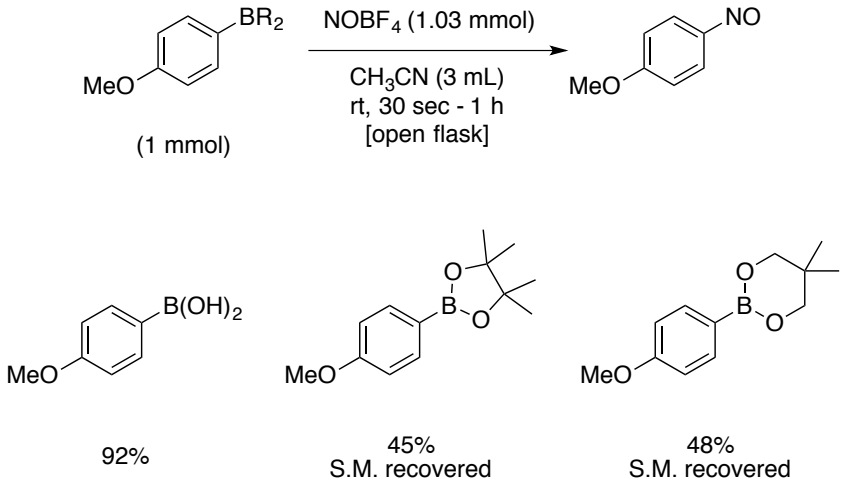
With the success of the nitroso one-pot Diels-Alder reaction, we were interested in illustrating other reactions that potentially unstable arylnitroso compounds can undergo (Scheme 2.15). Nitrogen-containing compounds are found in a variety of pharmaceuticals and are also the building blocks for important synthetic transformations.[90] Therefore, potassium methyl 3-trifluoroboratobenzoate was subjected to the nitrosation protocol followed by different transformations, and diverse nitrogen-containing products were obtained. The one-pot reaction of the aforementioned trifluoroborate with $NOBF_4$ followed by addition of $NaBH_4$ afforded the corresponding azoxy product, in 87% overall yield. Methyl 3-nitrobenzoate was also obtained by a two-step procedure from the corresponding trifluoroborate. In this case, a minimal work-up of the nitrosation reaction was necessary before addition of the oxidant. Nevertheless, the desired product was obtained in 86% yield over the two steps. The one-pot nitrosation-reduction of the *in situ* formed methyl 3-nitrosobenzoate was performed, and the methyl 3-aminobenzoate, was obtained in 72% overall yield. The one-pot nitrosation/Diels-Alder reaction was also accomplished, with the oxazabicyclo benzoate being isolated in 82% yield.

Scheme 2.15



Finally, as illustrated in Scheme 2.16, different boron derivatives were tested under the same reaction conditions. 4-Methoxyphenylboronic acid afforded the product in nearly the same yield as the trifluoroborates, while the boronate esters were not successful in this transformation, instead providing the nitroso product in moderate yields after 1 h with starting material being recovered.

Scheme 2.16



2.6.3 Conclusions

In summary, it has been demonstrated that the nitrosation of a broad range of aryl and heteroaryltrifluoroborates can be carried out under extraordinarily mild reaction conditions. Aryltrifluoroborates containing different functional groups, such as esters, ketones, aldehydes, nitriles and amides were successfully converted into the nitroso product, while leaving the aforementioned groups intact. Furthermore, nitrogen-containing heteroaryltrifluoroborates underwent nitrosation selectively, and no nitrosation of the nitrogen atom was observed. Despite their simplicity, most of the nitroso compounds prepared were previously unknown, highlighting the lack of synthetic methods available for this important class of molecules. The versatility of the nitroso products obtained has been illustrated by converting these intermediates in a variety of one-pot transformations, demonstrating that even those nitrosoarenes that may have limited stability can be employed as useful substrates for further synthetic applications.

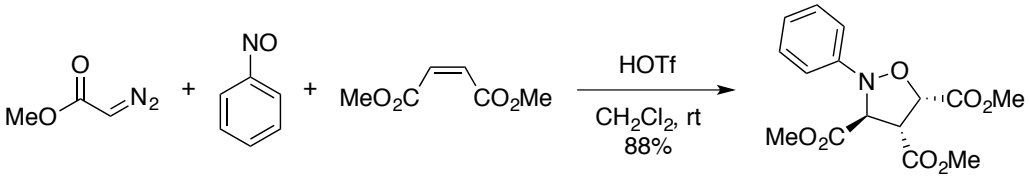
2.7 Synthesis of Trifluoromethylated Isoxazolidines: 1,3-Dipolar Cycloaddition of Nitrosoarenes, (Trifluoromethyl)diazomethane, and Alkenes[91]

2.7.1 Introduction

Having developed this unique protocol to access nitrosoarenes, we became interested in applying these newly synthesized molecules, especially the nitrosoheteroarenes, into new and chemically relevant reactions. In our search we found that there are limited examples of nitroso compounds undergoing 1,3-dipolar cycloadditions, and therefore we sought to develop a new method to use aryl and heteroarylnitroso species in these reactions.

Isoxazolidines are important building blocks in organic synthesis.[92] Their valuable nitrogen-oxygen bond provides easy access to 1,3-amino alcohols and lactams. The most common method to access these structures is the 1,3-dipolar cycloaddition of nitrones and alkenes.[93] Although an effort has been made to improve reaction conditions and substrate scope,[94] the synthesis of diverse *N*-functionalized nitrones remains a challenge, and multistep synthetic steps are often required. Zhong and co-workers developed an alternative to the use of nitrones by using diazo reagents and nitrosobenzene in the acid catalyzed 1,3-dipolar cycloaddition with electron-deficient alkenes (eq 2.20).[95]

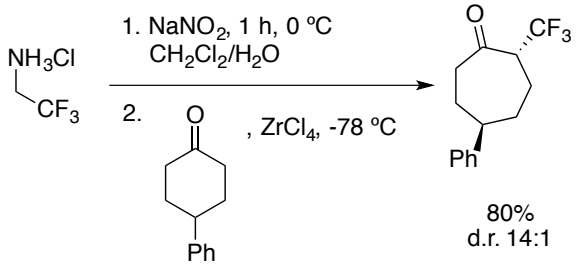
Equation 2.20



The method proved to be efficient for a variety of alkenes. However, the scope of the nitrosoarenes was limited to a few aryl systems. Moreover, although many

isoxazolidines have proven to be of biological importance, the trifluoromethylated version of these compounds remains somewhat limited.[96] Trifluoromethylated molecules figure prominently among pharmacologically active compounds.[97] The trifluoromethyl group adds, among other features, stability and lipophilicity to a molecule. Thus, the need for the development of methods to afford compounds containing a CF_3 group has increased. Recently, Carreira and co-workers reported an easy method to access trifluoroethyl-substituted ketones.[98] In this elegant protocol they were able to generate 2-diazo-1,1,1-trifluoroethane *in situ* by reacting inexpensive and widely available 2,2,2-trifluoroethylamine hydrochloride with sodium nitrite in a mixture of dichloromethane and water (eq 2.21).

Equation 2.21



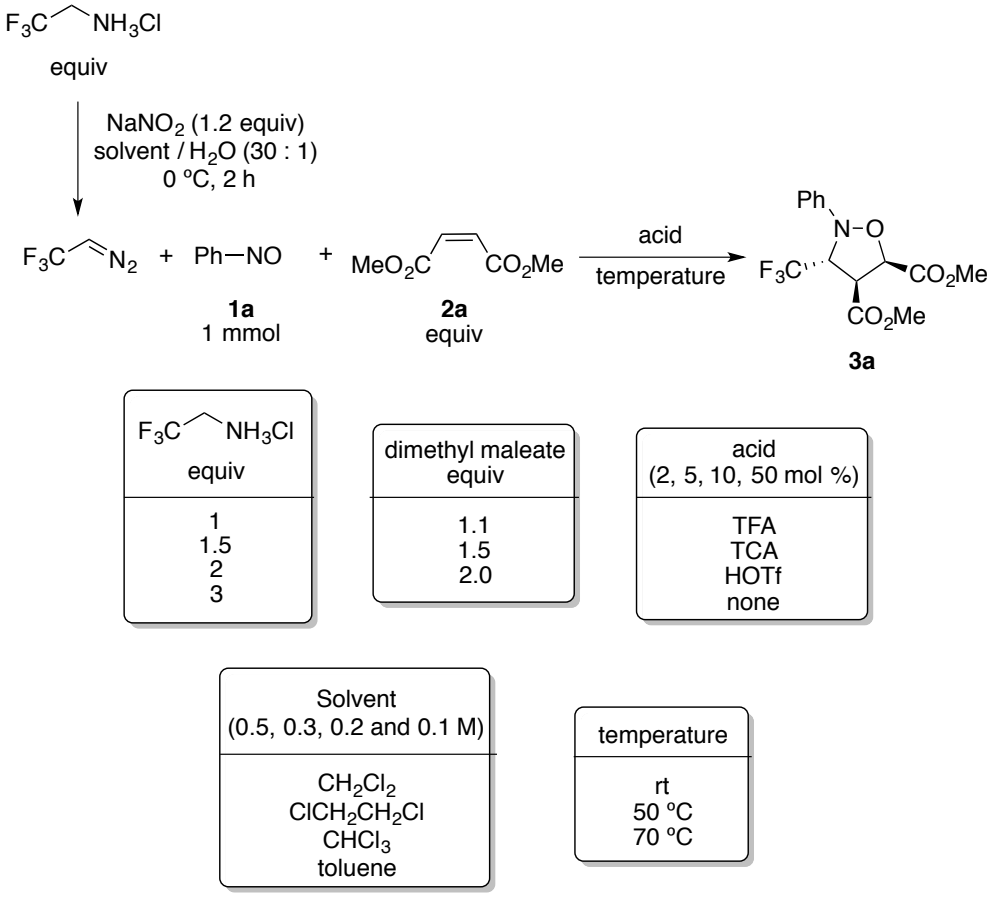
Inspired by this work in combination with our previously developed method to access aryl and heteroaryl nitrosoarenes from organotrifluoroborates,[99] we became interested in a three component 1,3-dipolar cycloaddition of nitrosoarenes, (trifluoromethyl)diazomethane, and alkenes to afford trifluoromethylated isoxazolidines.

2.7.1 Results and Discussion

We began the optimization of the reaction conditions by combining the procedures developed by Carreira and Zhong. Thus, to a solution of *in situ* formed (trifluoromethyl)diazomethane were added nitrosobenzene, dimethyl maleate, and triflic

acid in dichloromethane/H_2O at room temperature. Although some isoxazolidine was observed, the reaction afforded azoxybenzene and dimethyl 3-(trifluoromethyl)cyclopropane-1,2-dicarboxylate as major side products. Therefore, further optimization of the reaction conditions (Scheme 2.17) was necessary.

Scheme 2.17

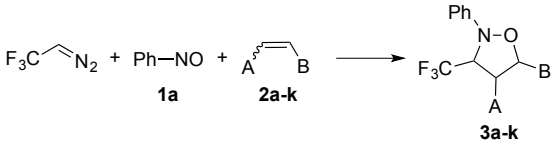


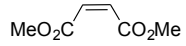
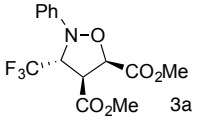
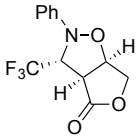
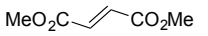
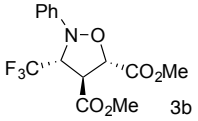
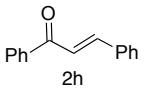
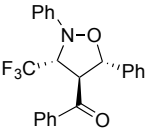
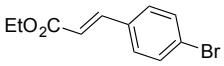
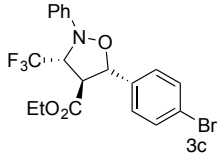
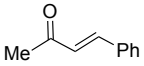
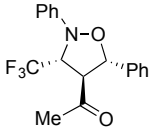
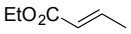
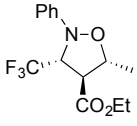
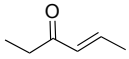
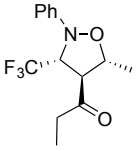
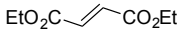
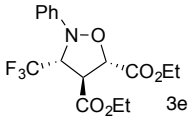
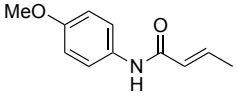
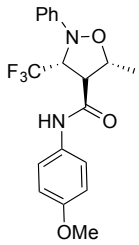
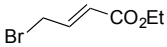
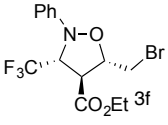
After extensive screening, it was determined that nitrosobenzene reacts with 2 equivalents of 2,2,2-trifluoroethylamine hydrochloride, 1.1 equivalents of dimethyl maleate in dichloroethane/H_2O at 70 ºC to afford the desired trifluoromethylated isoxazolidine **3a** in 94% isolated yield. The reaction proved to be diastereoselective,

providing **3a** in a diastereomeric ratio higher than 30:1 as determined by crude NMR, with the stereochemistry confirmed by X-ray single crystal structure analysis.

With optimal conditions in hand, we further investigated the scope of the reaction for diverse alkenes (Table 2.7.1).

Table 2.7.1 Scope of Electron-Deficient Alkenes



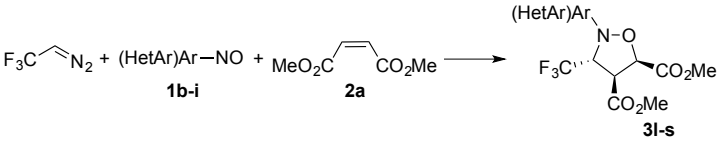
entry	alkene	product	yield (%)	entry	alkene	product	yield (%)
1	 2a	 3a	91[a]	7	 2g	 3g	78
2	 2b	 3b	80[b]	8	 2h	 3h	55
3	 2c	 3c	78	9	 2i	 3i	62
4	 2d	 3d	85	10	 2j	 3j	80
5	 2e	 3e	75[b]	11	 2k	 3k	71
6	 2f	 3f	81				

Conditions: 2,2,2-trifluoroethylamine hydrochloride (2 equiv), $NaNO_2$ (2.4 equiv), dichloroethane / H_2O (30 : 1, 0.2 M), 2 h at 0 ºC, then **1a** (1 mmol) and alkene (1.1 equiv), 16 h at 70 ºC.
[a] 1 g scale. [b] Along with a small amount of side product impurity.

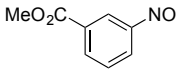
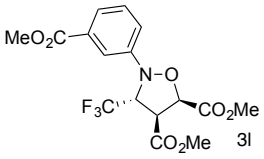
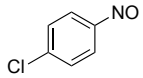
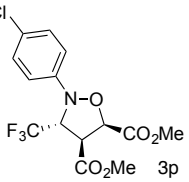
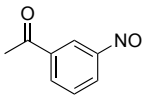
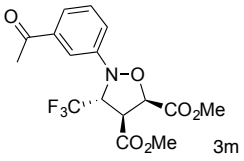
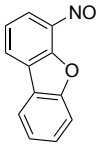
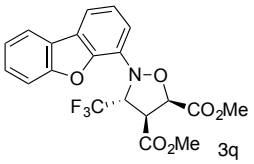
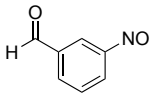
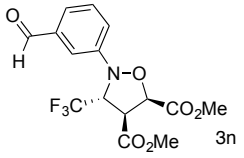
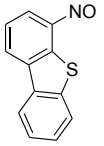
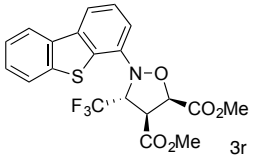
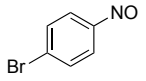
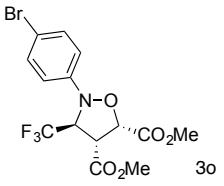
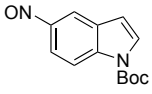
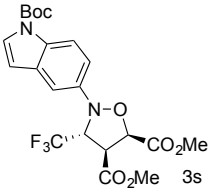
Dipolarophiles containing esters, ketones and amides were efficiently reacted, providing the desired trifluoromethylated isoxazolidine in moderate to excellent yields. As previously reported,[85,86] the reaction proceeded with transfer of the dipolarophile geometry to the product. For example, when *cis*-alkenes, such as **2a**, were used, the 4,5-*cis* isoxazolidine product **3a** was observed. The same trend was noticed with *trans*-alkenes, such as **2h**, and 4,5-*trans* cycloadduct **3h** was obtained in a diastereomeric ratio higher than 30:1 as determined by crude NMR, with the structure again being confirmed by X-ray analysis. Lactone **2g** was also utilized, providing access to the bicyclic trifluoromethylated isoxazolone **3g** in 78% yield. The reactions using dimethyl and diethyl fumarate (**2b** and **2e**) afforded the isoxazolidine product along with cyclopropanation side product.[100] Of note, the reaction of alkene **2a** was performed on a gram scale open to the atmosphere to yield trifluoromethylated product **3a** in 91% yield.

Next, we were interested in expanding the scope of the reaction with diverse nitrosoarenes. As previously mentioned, our recently developed method to synthesize nitroso compounds from organotrifluoroborates provides easy access to a variety of aryl and heteroaryl nitroso reagents.[90] As illustrated on Table 2.7.2, nitrosoarenes containing ester, ketone, aldehyde and halide functional groups were successful, affording the desired trifluoromethylated 1,3-dipolar cycloaddition products in excellent yields. Importantly, heteroarylnitroso species were also utilized, and the isoxazolidines containing trifluoromethyl and heteroaryl functional units were obtained in good yields. None of the isoxazolidines obtained by this protocol have been previously reported.

Table 2.7.2 Scope of Aryl and Heteroaryl Nitroso Compounds



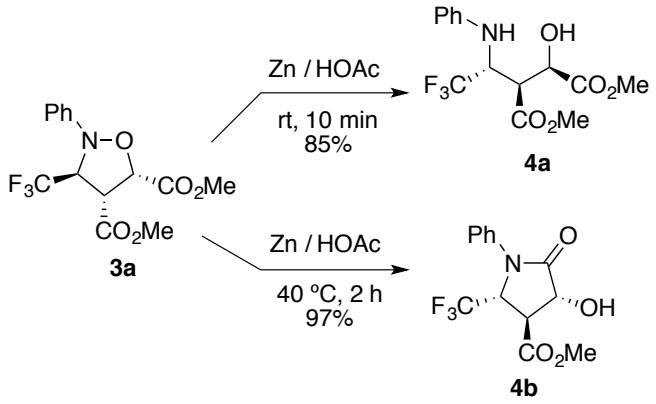
1b-i 2a 3l-s

entry	(HetAr)Ar—NO	product	yield (%)	entry	(HetAr)Ar—NO	product	yield (%)
1	 1b	 3l	94	5	 1f	 3p	91
2	 1c	 3m	90	6	 1g	 3q	81
3	 1d	 3n	85	7	 1h	 3r	71
4	 1e	 3o	96	8	 1i	 3s	76

Conditions: 2,2,2-trifluoroethylamine hydrochloride (2 equiv), $NaNO_2$ (2.4 equiv), dichloroethane / H_2O (30:1, 0.2 M), 2 h at 0 ºC, then **1** (1 mmol) and **2a** (1.1 equiv), 16 h at 70 ºC.

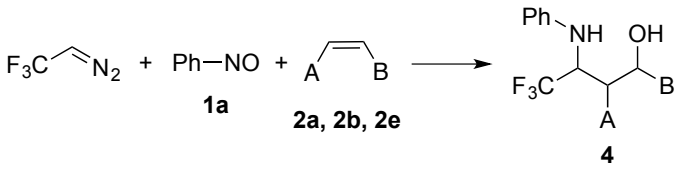
To illustrate the utility of the isoxazolidines herein obtained, we subjected product **3a** to a ring opening reaction using zinc powder in acetic acid[101] (Scheme 2.18). Interestingly, when **3a** reacts with zinc for only 10 minutes at room temperature, the desired trifluoromethylated 1,3-amino alcohols **4a** was obtained, while heating the reaction at 40 ºC for 2 h provided the trifluoromethylated lactam.

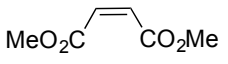
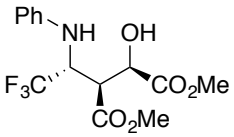
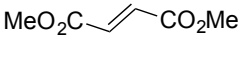
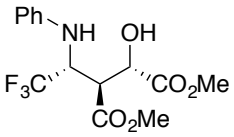
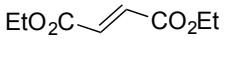
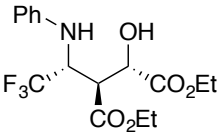
Scheme 2.18



Because alkenes such as dimethyl and diethyl fumarate (**2b** and **2e**) provided a mixture of products that could not be further purified, we turned our attention to carry out a one-pot/two-step 1,3-dipolar cycloaddition followed by ring cleavage to provide direct access to the desired amino alcohol. Thus, alkenes **2a**, **2b** and **2c** were tested in this one-pot reaction, and the desired trifluoromethylated 1,3-amino alcohols were obtained as pure products after column chromatography in good yields (Table 2.7.3).

Table 2.7.3 One-pot 1,3-Dipolar Cycloaddition/Ring Cleavage



entry	alkene	product		yield (%)
1	 2a		4a	80
2	 2b		4c	82
3	 2e		4d	78

Conditions: 2,2,2-trifluoroethylamine hydrochloride (2 equiv), $NaNO_2$ (2.4 equiv), dichloroethane / H_2O (30:1, 0.2 M), 2 h at 0 ºC, then **1** (1 mmol) and **2** (1.1 equiv), 16 h at 70 ºC. After reaction time, Zn (10 equiv) and HOAc (1 mL) were added at rt for 10 min.

2.7.3 Conclusions

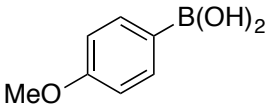
In conclusion, *in situ* formed trifluoromethyl diazomethane was successfully used on a 1,3-dipolar cycloaddition with nitrosoarenes and alkenes. A broad range of electron-deficient alkenes can be used as well as aryl and heteroaryl nitroso substrates, providing access to very unique, previously unreported structures. The cycloadducts were reduced to yield trifluoromethylated hydroxyamines or lactams.

2.8 Experimental

2.8.1 Experimental for section 2.2

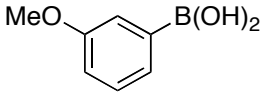
General Considerations: All of the reagents and HPLC grade MeOH were used as received. Melting points (^{o}C) are uncorrected. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 500.4, 125.8, and 470.8 MHz, respectively. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). ^{11}B NMR spectra at 128.4 MHz were obtained on a spectrometer equipped with the appropriate decoupling accessories. All ^{11}B NMR chemical shifts were referenced to external $BF_3 \cdot OEt_2$ (0.0 ppm) with a negative sign indicating an upfield shift.

General Experimental Procedure for the Preparation of Organoboronic Acids.

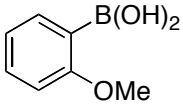


Preparation of 4-Methoxyphenylboronic Acid.[102] To a 50 mL round bottom flask containing a mixture of potassium 4-methoxyphenyltrifluoroborate (456 mg, 3.0 mmol) and silica gel (180 mg, 3.0 mmol) under N_2 was added H_2O (9 mL) in one portion. The reaction was stirred at rt until ^{11}B NMR indicated completion of the reaction (~1 h). The reaction mixture was filtered tom remove silica gel, and the filter cake was thoroughly rinsed with EtOAc. For the extraction of sensitive substrates, a low boiling solvent (Et_2O) was employed to facilitate rapid isolation of the product at low temperatures and thereby avoid decomposition. The aqueous and organic layers were separated, and the aqueous layer was extracted with EtOAc (2 x 15 mL) (Table 2.1.2, electron-deficient arylboronic acids were washed with brine). The combined organic layers were dried ($MgSO_4$), filtered, concentrated, and dried *in vacuo* overnight to afford the desired pure product in 83% yield (0.38 g, 2.49 mmol) as a white solid. ^{1}H NMR (500

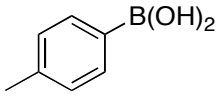
MHz, DMSO-d_6) δ 7.82 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.5 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 161.6, 137.6, 136.0, 114.0, 55.8.



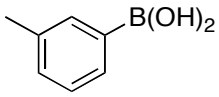
3-Methoxyphenylboronic Acid.[103] The general procedure was employed using potassium 3-methoxyphenyltrifluoroborate, and the reaction was complete in 3 h. The desired pure product was obtained in 83% yield (0.37 g, 2.46 mmol) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.03 (brs, 2H), 7.38–7.32 (m, 2H), 7.24 (t, J = 8.0 Hz, 1H), 6.94 (m, 1H), 3.74 (s, 3H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 159.5, 137.6, 129.5, 127.3, 119.9, 116.7, 55.8. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 27.6.



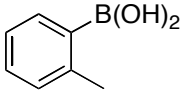
2-Methoxyphenylboronic Acid.[106] The general procedure was employed using potassium 2-methoxyphenyltrifluoroborate, and the reaction was complete in 1 h. The desired pure product was obtained in 67% yield (0.30 g, 1.98 mmol) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.68 (brs, 2H), 7.55 (m, 1H), 7.37 (m, 1H), 7.00–6.88 (m, 2H), 3.80 (s, 3H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 164.4, 137.6, 136.3, 132.5, 121.2, 111.2, 56.2. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 28.1.



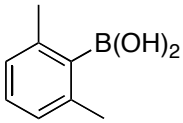
4-Methylphenylboronic Acid.[104] The general procedure was employed using potassium 4-methylphenyltrifluoroborate, and the reaction was complete in 1 h. The desired pure product was obtained in 76% yield (0.31 g, 2.3 mmol) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.76 (d, J = 7.6 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 139.6, 135.2, 134.5, 129.1, 22.2.



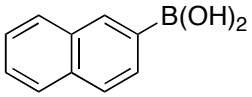
3-Methylphenylboronic Acid. The general procedure was employed using potassium 3-methylphenyltrifluoroborate, and the reaction was complete in 1 h. The desired pure product was obtained in 67% yield (0.27 g, 2.0 mmol) as a white solid. mp: 159-160 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–7.64 (m, 2H), 7.25 (t, J = 7.5 Hz, 1H), 7.19 (m, 1H), 2.34 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 137.6, 137.0, 135.0, 131.6, 131.0, 128.3, 22.2. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 28.6. FT-IR (neat) 3260, 1344, 725 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_{10}BO_2$ (MH^+) 137.0774, found 137.0773.



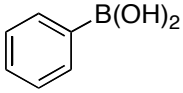
2-Methylphenylboronic Acid.[105] The general procedure was employed using potassium 2-methylphenyltrifluoroborate, and the reaction was complete in 1 h. The desired pure product was obtained in 61% yield (0.25 g, 1.8 mmol) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 7.3 Hz, 1H), 7.25 (m, 1H), 7.18–7.12 (m, 2H), 2.65 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 144.2, 137.6, 135.6, 130.7, 130.1, 125.5, 23.2. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 30.1.



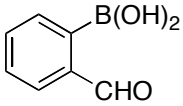
2,6-Dimethylphenylboronic Acid. [106] The general procedure was employed using potassium 2,6-dimethylphenyltrifluoroborate, and the reaction was complete in 1 h. The desired pure product was obtained in 81% yield (0.36 g, 2.43 mmol) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.11 (s, 2H), 7.06 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 7.6 Hz, 2H), 2.26 (s, 6H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 139.3, 137.6, 128.3, 126.5, 22.9. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 30.7. FT-IR (neat) 3306, 2360, 1342, 827 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_{11}BO_2$ (M^+)150.0852, found 150.0855.



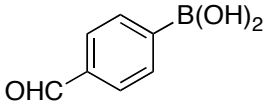
2-Naphthalenylboronic Acid. [107] The general procedure was employed using potassium 2-naphthalenytrifluoroborate, and the reaction was complete in 1 h. The desired pure product was obtained in 63% yield (0.33 g, 1.90 mmol) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.57 (s, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.05 (m, 1H), 7.98–7.88 (m, 2H), 7.56–7.48 (m, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 134.4, 134.3, 133.1, 130.9, 128.8, 127.9, 126.9, 126.6, 126.0. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 29.2. FT-IR (neat) 3047, 1354, 755 cm^{-1}.



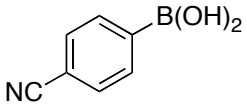
Phenylboronic Acid.[105] The general procedure was employed using potassium phenyltrifluoroborate, and the reaction was complete in 4 h. The desired pure product was obtained in 65% yield (0.24 g, 1.97 mmol) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.93–7.87 (m, 2H), 7.42–7.34 (m, 3H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 137.6, 134.4, 130.4, 128.4.



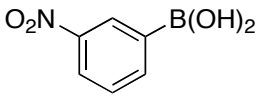
2-Formylphenylboronic Acid.[108] The general procedure was employed using potassium 2-formylphenyltrifluoroborate, and the reaction was stirred for 24 h (based on ^{11}B NMR, incomplete reaction, prolonged heating resulted in protodeboronation). The desired pure product was obtained in 64% yield (0.26 g, 1.93 mmol) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.13 (s, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.66–7.58 (m, 2H), 7.55 (m, 1H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 195.2, 140.1, 134.1, 134.0, 131.8, 130.3, 129.7. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 29.4.



4-Formylphenylboronic Acid. [109] The general procedure was employed using potassium 4-formylphenyltrifluoroborate, and the reaction was stirred for 24 h (based on ^{11}B NMR, incomplete reaction, prolonged heating resulted in protodeboronation). The desired pure product was obtained in 88% yield (0.39 g, 2.64 mmol) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.03 (s, 1H), 8.38 (brs, 2H), 7.99 (d, J = 7.7 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 194.6, 138.2, 135.6, 129.5, 129.4. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 28.2.

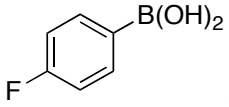


4-Cyanophenylboronic Acid.[106] The general procedure was employed using potassium 4-cyanophenyltrifluoroborate, and the reaction was stirred for 24 h (based on ^{11}B NMR, incomplete reaction, prolonged heating resulted in protodeboronation). The desired pure product was obtained in 66% yield (0.29 g, 1.98 mmol) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.93 (d, J = 7.7 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 135.6, 132.2, 132.0, 120.0, 113.4. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 28.3.

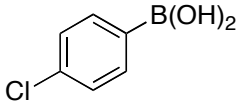


3-Nitrophenylboronic Acid. The general procedure was employed using potassium 3-nitrophenyltrifluoroborate, and the reaction was complete in 24 h. The desired pure product was obtained in 86% yield (0.43 g, 2.57 mmol) as a white solid. mp: > 200 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.62 (m, 1H), 8.25 (m, 1H), 8.19 (m, 1H), 7.64 (t, J = 7.6 Hz, 1H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 148.4, 141.6, 130.0, 129.2, 125.8. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 27.5. FT-IR (neat) 3085, 1613, 1525, 1344,

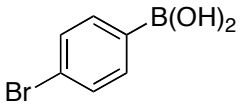
707 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_7BNO_4$ $((M\text{-}H_2O+CH_3O\cdot)^-)$ 180.0468, found 180.0465.



4-Fluorophenylboronic Acid.[110] The general procedure was employed using potassium 4-fluorophenyltrifluoroborate, and the reaction was complete in 4 h. The desired pure product was obtained in 80% yield (0.34 g, 2.40 mmol) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.10 (brs, 2H), 7.87–7.82 (m, 2H), 7.17–7.12 (m, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 165.1, 163.2, 136.9, 114.7. ^{19}F NMR (470.8 MHz, DMSO-d_6) δ -110.9. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 27.8. FT-IR (neat) 3046, 1589, 830, 735 cm^{-1}.

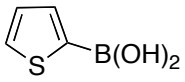


4-Chlorophenylboronic Acid.[106] The general procedure was employed using potassium 4-chlorophenyltrifluoroborate, and the reaction was complete in 1 h. The desired pure product was obtained in 60% yield (0.28 g, 1.8 mmol) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.17 (brs, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 137.0, 136.1, 128.5. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 27.8.

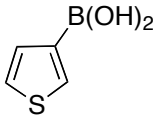


4-Bromophenylboronic Acid. [111] The general procedure was employed using potassium 4-bromophenyltrifluoroborate, and the reaction was complete in 1 h. The desired pure product was obtained in 71% yield (0.43 g, 2.12 mmol) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.17 (brs, 2H), 7.71 (d, J = 8.3 Hz, 2H),

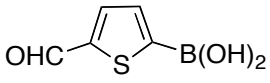
7.52 (d, J = 8.3 Hz, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 136.6, 130.7, 124.5. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 27.9. FT-IR (neat) 3043, 1592, 732 cm^{-1}.



Thiophen-2-ylboronic Acid.[112] The general procedure was employed using potassium thiophen-2-yltrifluoroborate, and the reaction was complete in 3 h. The desired pure product was obtained in 84% yield (0.32 g, 2.49 mmol) as a white solid. ^{1}H NMR (500 MHz, Acetone-d_6) δ 8.02 (m, 1H), 7.97 (m, 1H), 7.35 (m, 1H). ^{13}C NMR (125.8 MHz, Acetone-d_6) δ 140.7, 136.3, 130.4. ^{11}B NMR (128.4 MHz, Acetone-d_6) δ 27.1. FT-IR (neat) 3270, 1516, 1170, 717 cm^{-1}.

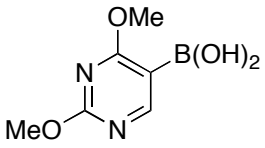


Thiophen-3-ylboronic Acid.[113] The general procedure was employed using potassium thiophen-3-yltrifluoroborate, and the reaction was complete in 24 h. The desired pure product was obtained in 79% yield (0.30 g, 2.35 mmol) as a white solid. ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.99 (m, 1H), 7.48 (m, 1H), 7.43 (m, 1H), 7.16 (s, 2H). ^{13}C NMR (125.8 MHz, Acetone-d_6) δ 136.3, 134.0, 133.8, 126.5. ^{11}B NMR (128.4 MHz, Acetone-d_6) δ 27.3. FT-IR (neat) 3206, 1513, 1015, 789 cm^{-1}.

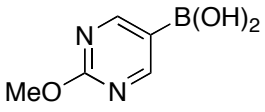


5-Formylthiophen-2-ylboronic Acid.[114] The general procedure was employed using potassium 5-formylthiophen-2-yltrifluoroborate, and the reaction was complete in 24 h. The desired pure product was obtained in 76% yield (0.36 g, 2.29 mmol) as a brown solid. mp: > 200 °C dec. ^{1}H NMR (500 MHz, Acetone-d_6) δ 10.00 (s, 1H), 7.95 (m, 1H), 7.76 (m, 1H). ^{13}C NMR (125.8 MHz, Acetone-d_6) δ 185.02, 150.0,

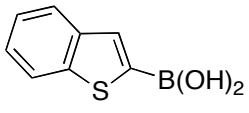
138.6, 137.8. ^{11}B NMR (128.4 MHz, Acetone-d_6) δ 26.5. FT-IR (neat) 3243, 1659, 819, 765 cm^{-1}.



2,4-Dimethoxypyrimidin-5-ylboronic Acid. [115] The general procedure was employed using 1 mmol of potassium 2,4-dimethoxypyrimidin-5-yltrifluoroborate and 1 mmol of SiO_2, and the reaction was complete in 24 h. The desired pure product was obtained in 52% yield (0.09 g, 0.51 mmol) as a white solid. ^{1}H NMR (500 MHz, Acetone-d_6) δ 8.62 (s, 1H), 6.99 (s, 2H), 4.02 (s, 3H), 3.97 (s, 3H). ^{13}C NMR (125.8 MHz, Acetone-d_6) δ 176.7, 168.8, 55.7, 55.0. ^{11}B NMR (128.4 MHz, Acetone-d_6) δ 28.5. FT-IR (neat) 3369, 1589, 1391, 1017, 806 cm^{-1}.

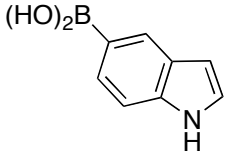


2-Methoxypyrimidin-5-ylboronic Acid.[116] The general procedure was employed using 1 mmol of potassium 2-methoxypyrimidin-5-yltrifluoroborate and 1 mmol of SiO_2, and the reaction was complete in 24 h. The desired pure product was obtained in 52% yield (0.09 g, 0.51 mmol) as a white solid. ^{1}H NMR (500 MHz, Acetone-d_6) δ 8.88 (s, 2H), 3.97 (s, 3H). ^{13}C NMR (125.8 MHz, Acetone-d_6) δ 164.9, 53.9. ^{11}B NMR (128.4 MHz, Acetone-d_6) δ 28.5. FT-IR (neat) 3338, 1590, 1031, 808 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_5H_8BN_2O_3$ (MH^+) 155.0628, found 155.0634.

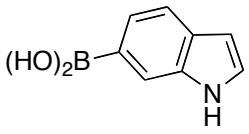


Benzothiophen-2-ylboronic Acid. The general procedure was employed using potassium benzothiophen-2-yltrifluoroborate, and the reaction was complete in 3 h. The desired pure product was obtained in 79% yield (0.42 g, 2.35 mmol)

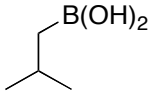
as a white solid. mp: > 200 °C. ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.99–7.93 (m, 2H), 7.91 (m, 1H), 7.59 (s, 2H), 7.41–7.33 (m, 2H). ^{13}C NMR (125.8 MHz, Acetone-d_6) δ 143.4, 140.8, 132.6, 124.8, 124.0, 123.8, 122.2. ^{11}B NMR (128.4 MHz, Acetone-d_6) δ 27.2. FT-IR (neat) 3060, 1513, 747 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_9H_8BO_2S$ ((M-H_2O+$CH_3O\cdot$)$^-$) 191.0338, found 191.0331.



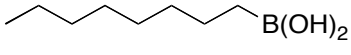
1*H*-Indol-5-ylboronic Acid. The general procedure was employed using 1 mmol of potassium 1*H*-indol-5-yltrifluoroborate and 1 mmol of SiO_2, and the reaction was complete in 1 h. The desired pure product was obtained in 62% yield (0.1 g, 0.62 mmol) as a yellow solid. mp: > 200 °C. ^{1}H NMR (500 MHz, Acetone-d_6) δ 10.46 (brs, 1H), 8.68 (s, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.42 (m, 1H), 6.70 (m, 1H). ^{13}C NMR (125.8 MHz, Acetone-d_6) δ 140.8, 131.1, 129.8, 129.8, 126.8, 126.7, 112.5, 104.1. ^{11}B NMR (128.4 MHz, Acetone-d_6) δ 29.4. FT-IR (neat) 3400, 1693, 1359, 738 cm^{-1}. HRMS (ESI) *m/z* calcd. for C_8H_8N (M-BO_2) 118.0657, found 118.0653.



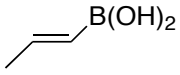
1*H*-Indol-6-ylboronic Acid. The general procedure was employed using 1 mmol of potassium 1*H*-indol-6-yltrifluoroborate and 1 mmol of SiO_2, and the reaction was complete in 1 h. The desired pure product was obtained in 80% yield (0.13 g, 0.79 mmol) as a yellow solid. mp: > 200°C. ^{1}H NMR (500 MHz, Acetone-d_6) δ 10.47 (brs, 1H), 8.47 (s, 1H), 8.00 (m, 1H), 7.76 (m, 1H), 7.51 (m, 1H), 6.59 (m, 1H). ^{13}C NMR (125.8 MHz, Acetone-d_6) δ 136.2, 131.6, 127.0, 125.5, 119.6, 119.3, 101.8. ^{11}B NMR (128.4 MHz, Acetone-d_6) δ 29.6. FT-IR (neat) 3409, 1504, 1336, 720 cm^{-1}.



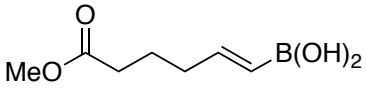
Isobutylboronic Acid. The general procedure was employed using potassium isobutyltrifluoroborate, and the reaction was complete in 1 h. The desired pure product was obtained in 73% yield (0.24 g, 2.3 mmol) as a white solid. mp: 107-109 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.73 (m, 1H), 0.84 (d, J = 6.7 Hz, 6H), 0.43 (d, J = 6.9 Hz, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 29.8, 26.6, 25.6. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 31.4. FT-IR (neat) 3203, 2950, 1360, 780 cm^{-1}.



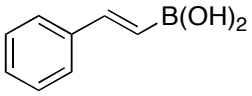
Octylboronic Acid. The general procedure was employed using potassium octyltrifluoroborate, and the reaction was complete in 1 h. The desired pure product was obtained in 67% yield (0.45 g, 2 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.96–3.64 (m, 2H), 1.65–1.45 (m, 2H), 1.40–1.18 (m, 10H), 0.88 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 32.3, 31.9, 29.5, 29.3, 25.9, 23.3, 22.7, 14.1. ^{11}B NMR (128.4 MHz, $CDCl_3$) δ 32.9. FT-IR (neat) 3217, 2255, 1486, 798 cm^{-1}. HRMS (ESI) *m/z* calcd. for C_8H_{17} (M-$B(OH)_2$) 113.1330, found 113.1327.



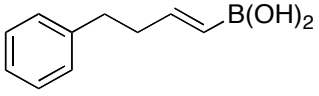
(*E*)-Propenylboronic Acid.[117] The general procedure was employed using potassium (*E*)-propenyltrifluoroborate, and the reaction was complete in 1 h. The desired pure product was obtained in 81% yield (0.21 g, 2.45 mmol) as a white solid. ^{1}H NMR (500 MHz, Acetone-d_6) δ 6.61 (s, 2H), 6.55 (m, 1H), 5.44 (m, 1H), 1.79–1.76 (m, 3H). ^{13}C NMR (125.8 MHz, Acetone-d_6) δ 147.0, 118.4, 22.3. ^{11}B NMR (128.4 MHz, Acetone-d_6) δ 27.1. FT-IR (neat) 3193, 1648, 1165, 796 cm^{-1}.



(*E*)-6-Methoxy-6-oxohex-1-enylboronic Acid. The general procedure was employed using 1 mmol of potassium (*E*)-6-methoxy-6-oxohex-1-enyltrifluoroborate and 1 mmol of SiO_2, and the reaction was complete in 1 h. The desired pure product was obtained in 60% yield (0.10 g, 0.59 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (m, 1H), 5.56 (m, 1H), 3.69 (s, 3H), 2.38–2.31 (m, 2H), 2.30–2.22 (m, 2H), 1.86–1.76 (m, 2H). ^{13}C NMR (125.8 MHz, Acetone-d_6) δ 174.6, 157.6, 151.1, 52.3, 36.1, 34.4, 24.9. ^{11}B NMR (128.4 MHz, Acetone-d_6) δ 28.2. FT-IR (neat) 3412, 2953, 1719, 1369, 997 cm^{-1}.

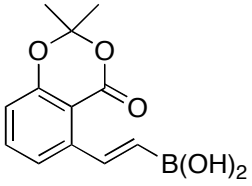


(*E*)-Styrylboronic Acid.[118] The general procedure was employed using potassium (*E*)-styryltrifluoroborate, and the reaction was complete in 1 h. The desired pure product was obtained in 63% yield (0.28 g, 1.87 mmol) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 18.1 Hz, 1H), 7.62 (d, J = 7.2 Hz, 2H), 7.44–7.34 (m, 3H), 6.36 (d, J = 18.1 Hz, 1H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 144.0, 138.4, 129.0, 128.4, 127.0, 126.8. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 28.5. FT-IR (neat) 3351, 1620, 1360, 744 cm^{-1}.

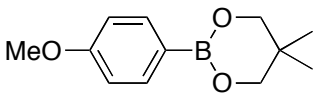


(*E*)-4-Phenylbut-1-enylboronic Acid. The general procedure was employed using potassium (*E*)-4-phenylbut-1-enyltrifluoroborate, and the reaction was complete in 1 h. The desired pure product was obtained in 62% yield (0.33 g, 1.87 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.21 (m, 2H), 7.19–7.12 (m, 3H), 7.00 (m, 1H), 5.58 (m, 1H), 2.78–2.69 (m, 2H), 2.55–2.46 (m, 2H). ^{13}C NMR

(125.8 MHz, $CDCl_3$) δ 156.5, 151.6, 141.6, 128.4, 125.9, 37.2, 34.5. ^{11}B NMR (128.4 MHz, $CDCl_3$) δ 28.3. FT-IR (neat) 3233, 1354, 703 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{10}H_{11}$ (M-$B(OH)_2$) 131.0861, found 131.0860.

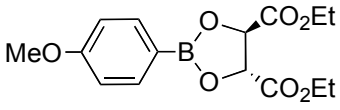


(*E*)-2-(2,2-Dimethyl-4-oxo-4H-benzo[d][1,3]dioxin-5-yl)vinylboronic Acid. The general procedure was employed using 1.5 mmol of potassium (*E*)-2-(2,2-dimethyl-4-oxo-4H-benzo[d][1,3]dioxin-5-yl)vinyltrifluoroborate and 1.5 mmol of SiO_2, and the reaction was complete in 1 h. The desired pure product was obtained in 90% yield (0.33 g, 1.34 mmol) as a yellow solid. mp: 116-119 °C. ^1H NMR (500 MHz, DMSO-d_6) δ 8.05 (d, *J* = 18.2 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.07 (d, *J* = 18.2 Hz, 1H), 1.66 (s, 6H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 160.4, 157.2, 144.7, 143.2, 137.1, 122.7, 118.0, 111.6, 106.4, 26.1. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 27.3. FT-IR (neat) 3427, 1731, 1575, 1046, 800 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_{13}BO_5Na$ $(M+Na)^+$ 271.0761, found 271.0754.

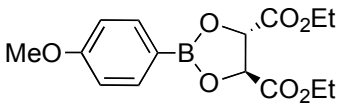


2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane. The general procedure was employed using potassium 4-methoxyphenyltrifluoroborate and neopentyl glycol, and the reaction was complete in 30 min. The desired pure product was obtained in 90% yield (0.59 g, 2.70 mmol) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 3.76 (s, 3H), 3.71 (s, 4H), 0.97 (s, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 161.74, 135.53, 113.09, 72.16, 54.93, 31.80,

21.85. ^{11}B NMR (128.4 MHz, $CDCl_3$) δ 25.71. FT-IR (neat) 2965, 1604, 1246, 837 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_{18}BO_3$ (MH^+) 221.1336, found 221.1341.

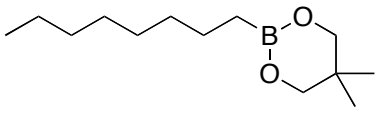


(4*S*,5*S*)-Diethyl 2-(4-Methoxyphenyl)-1,3,2-dioxaborolane-4,5-dicarboxylate. The general procedure was employed using potassium 4-methoxyphenyltrifluoroborate and diethyl **L**-tartrate, and the reaction was complete in 30 min. The desired pure product was obtained in 81% yield (0.71 g, 2.44 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 5.03 (s, 2H), 4.29 (q, *J* = 7.0 Hz, 4H), 3.83 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.49, 162.76, 137.05, 113.43, 77.84, 71.93, 62.08, 55.02, 14.01. ^{11}B NMR (128.4 MHz, $CDCl_3$) δ 30.74. FT-IR (neat) 3498, 2983, 1748, 1605, 1368, 1029 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{15}H_{19}BO_7$ (M^+Na) 345.1122, found 345.1124. $[\alpha]_D$= +20.9 (*c* = 1 in CH_2Cl_2).

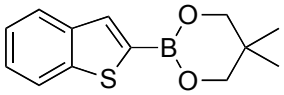


(4*R*,5*R*)-Diethyl 2-(4-Methoxyphenyl)-1,3,2-dioxaborolane-4,5-dicarboxylate. The general procedure was employed using potassium 4-methoxyphenyltrifluoroborate and diethyl **D**-tartrate, and the reaction was complete in 30 min. The desired pure product was obtained in 85% yield (0.75 g, 2.56 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 5.03 (s, 2H), 4.30 (q, *J* = 7.3 Hz, 4H), 3.84 (s, 3H), 1.33 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.49, 162.76, 137.05, 113.43, 77.84, 71.93, 62.08, 55.02, 14.01. ^{11}B NMR (128.4 MHz, $CDCl_3$) δ 30.77. FT-IR (neat) 3500, 2983, 1755, 1605,

1368, 1030 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{15}H_{20}BO_7$ (MH^+) 323.1302, found 323.1277. $[\alpha]_D$= -14.7 (c=1 in CH_2Cl_2).



5,5-Dimethyl-2-octyl-1,3,2-dioxaborinane. The general procedure was employed using potassium octyltrifluoroborate and neopentyl glycol, and the reaction was complete in 30 min. The desired pure product was obtained in 67% yield (0.46 g, 2.01 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.58 (s, 4H), 1.37–1.33 (m, 2H), 1.28–1.24 (m, 10H), 0.95 (s, 6H), 0.89–0.85 (m, 3H), 0.69 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 71.8, 36.3, 32.5, 31.9, 31.5, 29.3, 29.2, 24.0, 22.6, 21.7, 21.3, 14.0. ^{11}B NMR (128.4 MHz, $CDCl_3$) δ 28.8. FT-IR (neat) 3369, 2925, 1477, 1250, 813 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{13}H_{27}BO_2$ (M^+) 226.2104, found 226.2099.

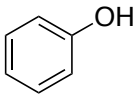


2-(Benzo[b]thiophen-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane. The general procedure was employed using potassium benzothiophen-2-yltrifluoroborate and neopentyl glycol, and the reaction was complete in 3 h. The desired pure product was obtained in 72% yield (0.53 g, 2.17 mmol) as a white solid. mp: 136-137 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.98 (m, 1H), 7.91 (m, 1H), 7.83 (s, 1H), 7.39–7.36 (m, 2H), 3.77 (s, 4H), 0.96 (s, 6H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 142.9, 140.6, 133.2, 125.6, 124.7, 124.6, 122.9, 71.9, 32.0, 21.7. ^{11}B NMR (128.4 MHz, $CDCl_3$) δ 24.8. FT-IR (neat) 3428, 1657, 1026, 762 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_{13}H_{16}BO_2S$ (MH^+) 247.0964, found 247.0979.

2.8.2 Experimental for section 2.4

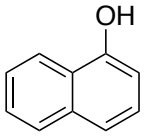
General Considerations: All of the reagents and HPLC grade acetone were used as received. Melting points (^{o}C) are uncorrected. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 500.4, 125.8, and 470.8 MHz, respectively. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm).

General Experimental Procedure for the Preparation of Phenols (55 mmol scale).

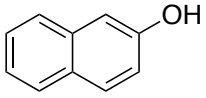


Preparation of Phenol.[42] To a 50 mL round bottom flask containing a mixture of potassium phenyltrifluoroborate (10.12 g, 55.0 mmol) and acetone (275 mL, 0.2 M) was added Oxone® (275 mL of a 0.2 M solution in H_2O, 1 equiv) in one portion. The reaction was stirred at rt until ^{11}B NMR indicated completion of the reaction (~2 min). To the crude mixture was added H_2O (30 mL) and aqueous HCl (0.1 M, 20 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried (Na_2SO_4), filtered, concentrated, and dried *in vacuo*. The crude extract was filtered through a small plug of silica topped with charcoal, eluting with CH_2Cl_2 to afford the desired pure product in 96% yield (5.0 g, 53 mmol) as a light yellow solid, mp 41 – 43 ^{o}C (lit. 40 – 42 ^{o}C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, J = 7.5 Hz, 2H), 6.93 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 8.5 Hz, 2H), 4.88 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.4, 129.7, 120.8, 115.3.

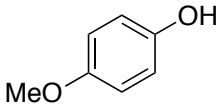
General Experimental Procedure for the Preparation of Phenols (1 mmol scale).



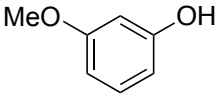
Preparation of Naphthalen-1-ol.[42] To a 50 mL round bottom flask containing a mixture of potassium naphthalen-1-yltrifluoroborate (0.23 g, 1.0 mmol) and acetone (5 mL, 0.2 M) was added Oxone® (5 mL of a 0.2 M solution in H_2O, 1 equiv) in one portion. The reaction was stirred at rt until ^{11}B NMR indicated completion of the reaction (~2 min). To the crude mixture was added H_2O (5 mL) and aqueous HCl (0.1 M, 3 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried (Na_2SO_4), filtered, concentrated, and dried *in vacuo*. The crude extract was filtered through a small plug of silica topped with charcoal, eluting with CH_2Cl_2 to afford the desired pure product in 99% yield (0.14 g, 0.99 mmol) as a white solid, mp 91 – 93 °C (lit.[41a] 92 – 94 °C). ^1H NMR (500 MHz, $CDCl_3$) δ 8.17 (m, 1H), 7.81 (m, 1H), 7.50–7.48 (m, 2H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 5.21 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 151.3, 134.8, 127.7, 126.4, 125.8, 125.2, 124.3, 121.5, 120.7, 108.6.



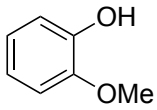
Naphthalen-2-ol.[42] The general procedure was employed using potassium naphthalen-2-yltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 97% yield (0.14 g, 0.97 mmol) as a white solid, mp 121–123 °C (lit. 122–124 °C). ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 (t, *J* = 8.9 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.42 (m, 1H), 7.32 (m, 1H), 7.13 (m, 1H), 7.08 (m, 1H), 5.01 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 134.4, 134.3, 133.1, 130.9, 128.8, 127.9, 126.9, 126.6, 126.0



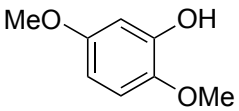
4-Methoxyphenol.[42] The general procedure was employed using potassium 4-methoxyphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield (0.12 g, 0.98 mmol) as a white solid, mp 57–58 ^{o}C (lit 57–58 ^{o}C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.79 – 6.75 (m, 4H), 5.31 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 161.6, 137.6, 136.0, 114.0, 55.8.



3-Methoxyphenol.[42] The general procedure was employed using potassium 3-methoxyphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 93% yield (0.11 g, 0.93 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (m, 1H), 6.50 (m, 1H), 6.44 – 6.41 (m, 2H), 5.62 (brs, 1H), 3.75 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 160.8, 156.6, 130.2, 107.9, 106.5, 101.6, 55.3.

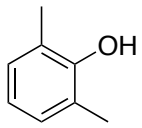


2-Methoxyphenol.[42] The general procedure was employed using potassium 2-methoxyphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 97% yield (0.12 g, 0.97 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (m, 1H), 6.88 – 6.84 (m, 3H), 5.61 (brs, 1H), 3.89 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 146.6, 145.7, 121.5, 120.1, 114.5, 110.7, 55.9.

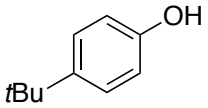


2,4-Dimethoxyphenol.[119] The general procedure was employed using potassium 2,4-dimethoxyphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 95% yield (0.15 g, 0.95 mmol) as a light yellow

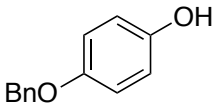
oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (d, J = 9.0 Hz, 1H), 6.56 (d, J = 3.0 Hz, 1H), 6.37 (m, 1H), 5.78 (brs, 1H), 3.81 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 154.5, 146.4, 141.0, 111.5, 104.5, 101.8, 56.5, 55.6.



2,6-Dimethylphenol.[42] The general procedure was employed using potassium 2,6-dimethyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 94% yield (0.11 g, 0.94 mmol) as a white solid, mp 43–45 °C (lit. 42–43 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (d, J = 7.5 Hz, 2H), 6.75 (t, J = 7.5 Hz, 1H), 4.61 (brs, 1H), 2.23 (s, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 152.1, 128.6, 123.0, 120.2, 15.8.

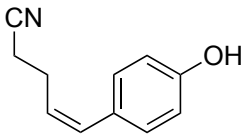


4-*tert*-Butylphenol.[41d] The general procedure was employed using potassium 4-*tert*-butylphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.15 g, 0.99 mmol) as a white solid, mp 97–99 °C (lit. 96–99 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, J = 6.5 Hz, 2H), 7.17 (d, J = 6.5 Hz, 2H), 4.66 (brs, 1H), 1.29 (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 153.1, 143.6, 126.4, 114.7, 34.1, 31.5.

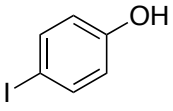


4-(Benzyloxy)phenol.[120] The general procedure was employed using potassium 4-(benzyloxy)phenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 97% yield (0.19 g, 0.97 mmol) as a light yellow solid, mp 117–121 °C (lit. 118 – 122 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.36 (m,

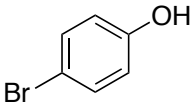
4H), 7.32 (m, 1H), 6.85 (d, J = 9 Hz, 2H), 6.75 (d, J = 9 Hz, 2H) 5.00 (s, 2H), 4.46 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 149.6, 137.2, 128.5, 127.9, 127.5, 116.1, 116.0, 70.8.



(*Z*)-5-(4-Hydroxyphenyl)pent-4-enenitrile. The general procedure was employed using potassium (*Z*)-4-(4-cyanobut-1-enyl)phenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield (0.17 g, 0.98 mmol) as a white solid. mp 67-69 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H) 6.52 (d, J = 11.5 Hz, 1H), 5.55 (m, 1H), 5.00 (brs, 1H), 2.69 – 2.65 (m, 2H), 2.44 (t, J = 7.0 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 154.8, 131.6, 130.1, 129.2, 126.0, 119.2, 115.2, 24.4, 17.6. IR (neat) 3325, 2257, 1608, 1514, 1228, 836 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{11}H_{11}NONa$ $(M+Na)^+$ 196.0738, found 196.0741.

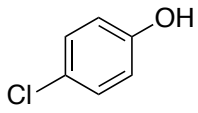


4-Iodophenol.[121] The general procedure was employed using potassium 4-iodophenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 85% yield (0.19 g, 0.85 mmol) as a light yellow solid mp 90-93 ºC (lit. 92-95 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 9.0 Hz, 2H), 6.61 (d, J = 9.0 Hz, 2H), 5.00 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.2, 138.4, 117.8, 82.8.

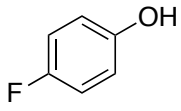


4-Bromophenol. [122] The general procedure was employed using potassium 4-bromophenyltrifluoroborate, and the reaction was complete in 2 min. The

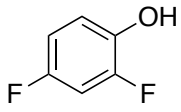
desired pure product was obtained in 98% yield (0.17 g, 0.98 mmol) as a light yellow solid mp 55-58 ^{o}C (lit. 54–64 ^{o}C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, J = 8.5 Hz, 2H), 6.70 (d, J = 9.0 Hz, 2H), 5.64 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 154.4, 132.5, 117.2, 112.9.



4-Chlorophenol.[42] The general procedure was employed using potassium 4-chlorophenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.13 g, 0.99 mmol) as a white solid, mp 43–46 ºC (lit. 44–45 ºC) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, J = 9.0 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 5.52 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 153.9, 129.5, 125.7, 116.7.

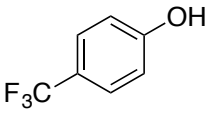


4-Fluorophenol.[42] The general procedure was employed using potassium 4-fluorophenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.11 g, 0.99 mmol) as a white solid, mp 45–47 ºC (lit. 46–47 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 – 6.90 (m, 2H), 6.79 – 6.74 (m, 2H), 4.88 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 157.2 (d, J = 235.9 Hz), 151.4, 116.2 (d, J = 10.0 Hz, 2C), 116.0 (d, J = 22.9, 2C). ^{19}F NMR (470.8 MHz, $CDCl_3$) δ -124.3.

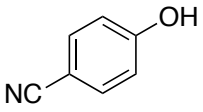


2,4-Difluorophenol.[43f] The general procedure was employed using potassium 2,4-difluorophenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 97% yield (0.13 g, 0.97 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (m, 1H), 6.85 (m, 1H), 6.76 (m, 1H), 5.75 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.9 (dd, J = 240.9, 10.3 Hz), 150.4 (dd, J =

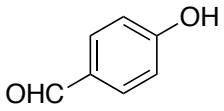
240.1, 12.2 Hz), 139.9 (dd, J = 14.1, 3.5 Hz), 117.3 (d, J = 6.4 Hz), 111.7 – 110.6 (m), 104.5 – 103.3 (m). ^{19}F NMR (470.8 MHz, $CDCl_3$) δ -121.0, -135.7.



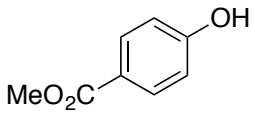
4-(Trifluoromethyl)phenol.[123] The general procedure was employed using potassium 4-(trifluoromethyl)phenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield (0.16 g, 0.98 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 9 Hz, 2H) 5.45 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 158.1, 127.2 (q, J = 3.8 Hz), 125.4, 123.7 – 122.7 (m), 115.4. ^{19}F NMR (470.8 MHz, $CDCl_3$) δ -61.5.



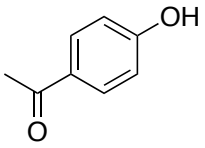
4-Hydroxybenzonitrile.[43f] The general procedure was employed using potassium 4-cyanophenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield (0.12 g, 0.98 mmol) as a light yellow solid mp 107–109 ºC (lit. 108–109 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 9.0 Hz, 2H), 6.94 (d, J = 8.5 Hz, 2H), (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 160.0, 134.3, 119.2, 116.4, 103.3.



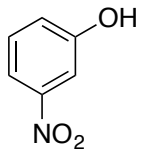
4-Hydroxybenzaldehyde.[42] The general procedure was employed using potassium 4-formylphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.12 g, 0.99 mmol) as a white solid, mp 114–117 ºC (lit. 114–116 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.82 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 6.73 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 191.1, 161.4, 132.4, 129.9, 115.9.



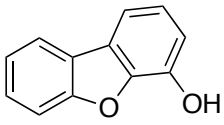
Methyl 4-Hydroxybenzoate. [124] The general procedure was employed using potassium 4-(methoxycarbonyl)phenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.15 g, 0.99 mmol) as a white solid, mp 121-123 ºC (lit. 127-129 ºC). ^{1}H NMR (500 MHz, acetone-d_6) δ 9.12 (brs, 1H), 7.89 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 167.8, 163.4, 133.2, 123.3, 116.8, 52.6.



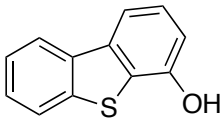
1-(4-Hydroxyphenyl)ethanone.[126] The general procedure was employed using potassium 4-acetylphenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.13 g, 0.99 mmol) as a white solid , mp 105-107 ^{o}C (lit. 108-109 ^{o}C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (brs, 1H), 7.92 (d, J = 9.0 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 2.59 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 199.0, 161.6, 131.3, 129.4, 115.6, 26.3.



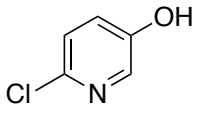
3-Nitrophenol.[42] The general procedure was employed using potassium 3-nitrophenyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield (0.14 g, 0.98 mmol) as a light yellow solid mp 96-99 ºC (lit. 98-99 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (m, 1H), 7.71 (t, J = 2.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.19 (m, 1H), 5.61 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 156.3, 130.3, 122.0, 115.9, 110.6.



Dibenzo[*b*,*d*]furan-4-ol. The general procedure was employed using potassium dibenzo[*b*,*d*]furan-4-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 97% yield (0.18 g, 0.97 mmol) as a white solid, mp 98-100 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.23 (m, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 5.39 (s, 1H).^{13}C NMR (125.8 MHz, $CDCl_3$) δ 156.1, 144.0, 141.1, 127.3, 125.7, 124.6, 123.7, 123.0, 121.0, 113.6, 112.8, 111.8. IR (neat) 3277, 1603, 1437, 1249, 744 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_7O_2$ $(M-H)^-$ 183.0446, found 183.0454.

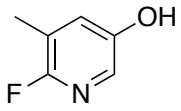


Dibenzo[*b*,*d*]thiophen-4-ol. The general procedure was employed using potassium dibenzo[*b*,*d*]thiophen-4-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 97% yield (0.18 g, 0.97 mmol) as a white solid. mp 158-160 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (m, 1H), 7.89 (m, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 5.35 (s, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 150.5, 139.6, 137.9, 135.9, 126.9, 126.5, 125.7, 124.4, 123.1, 122.0, 114.5, 111.7. IR (neat) 3230, 1569, 1444, 1253, 744 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_7OS$ $(M-H)^-$ 199.0218, found 199.0222.

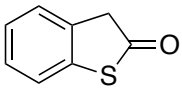


6-Chloropyridin-3-ol. The general procedure was employed using potassium 6-chloropyridin-3-yltrifluoroborate, and the reaction was complete in 5 min.

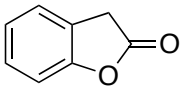
The desired pure product was obtained in 91% yield (0.12 g, 0.97 mmol) as a white solid, mp 155-157 ºC. ^{1}H NMR (500 MHz, acetone-d_6) δ 9.04 (brs, 1H), 7.99 (d, J = 2.9 Hz, 1H), 7.40 – 7.14 (m, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 154.9, 142.5, 138.9, 127.6, 126.1. IR (neat) 3004, 1573, 1464, 1278, 1228, 826 cm^{-1}. HRMS (ESI) *m/z* calcd. for C_5H_3NOCl $(M-H)^-$ 127.9903, found 127.9902.



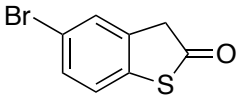
6-Fluoro-5-methylpyridin-3-ol. The general procedure was employed using potassium 6-chloropyridin-3-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 94% yield (0.12 g, 0.94 mmol) as a white solid. mp 120-122 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (brs, 1H), 7.61 (s, 1H), 7.22 (m, 1H), 2.25 (s, 3H).^{13}C NMR (125.8 MHz, $CDCl_3$) δ 157.1, 155.2, 151.1, 129.8 (dd, J = 44.4, 9.5 Hz), 120.7 (d, J = 34.1 Hz), 14.4. ^{19}F NMR (470.8 MHz, $CDCl_3$) δ -83.9. IR (neat) 3048, 1471, 1232, 770 cm^{-1}. HRMS (ESI) *m/z* calcd. for C_6H_7NOF $(M+H)^+$ 128.0512, found 128.0510.



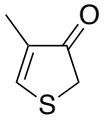
Benzo[*b*]thiophen-2(3*H*)-one.[125] The general procedure was employed using potassium benzothiophen-2-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 99% yield (0.15 g, 0.99 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, acetone-d_6) δ 7.44 (m, 1H), 7.38 (d, J = 7.5 Hz, 1H), 7.33 (m, 1H), 7.25 (m, 1H), 4.09 (s, 2H). ^{13}C NMR (125.8 MHz, acetone-d_6) δ 203.7, 138.3, 134.7, 129.8, 127.7, 126.7, 124.5, 48.4.



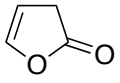
Benzofuran-2(3*H*)-one.[126] The general procedure was employed using potassium benzofuran-2-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 97% yield (0.13 g, 0.97 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.13 (m, 1H), 7.08 (d, J = 8.1 Hz, 1H), 3.71 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 174.0, 154.6, 128.8, 124.5, 123.9, 123.0, 110.6, 32.8.

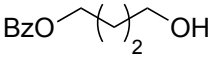


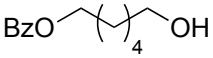
5-Bromobenzo[*b*]thiophen-2(3*H*)-one. The general procedure was employed using potassium 5-bromobenzo[*b*]thiophen-2-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 94% yield (0.21 g, 0.94 mmol) as a light yellow solid. mp 117-120 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 2H), 7.21 (d, J = 8.9 Hz, 1H), 3.97 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 201.5, 136.1, 133.9, 131.4, 127.9, 124.3, 119.7, 47.1. FT- IR (neat) 1711, 1017, 819 cm^{-1}. HRMS (ESI) *m/z* calcd. for C_8H_4OSBr $(M-H)^-$ 226.9166, found 226.9158.

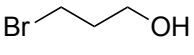


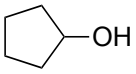
4-Methylthiophen-2(3*H*)-one. The general procedure was employed using potassium 4-methylthiophen-2-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 89% yield (0.10 g, 0.89 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.09 (m, 1H), 3.97 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 199.7, 167.7, 129.0, 40.8, 18.9. FT- IR (neat) 2918, 1676, 1096, 653 cm^{-1}. HRMS (ESI) *m/z* calcd. for C_5H_7OS $(M+H)^+$ 115.0218, found 115.0215.

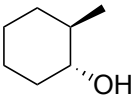
 **Furan-2(3*H*)-one.**[127] The general procedure was employed using potassium thiophen-3-yltrifluoroborate, and the reaction was complete in 5 min. The desired pure product was obtained in 98% yield (0.10 g, 0.98 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (m, 1H), 5.55 (m, 1H), 3.14 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 176.5, 143.8, 105.4, 32.3.

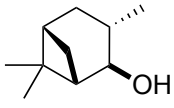
 **4-Hydroxybutyl Benzoate.**[44] The general procedure was employed using potassium 4-(benzoyloxy)butyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.19 g, 0.99 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 8.02 (m, 2H), 7.53 (m, 1H), 7.44 – 7.40 (m, 2H), 4.35 (t, *J* = 6.5 Hz, 2H), 3.70 (t, *J* = 6.5 Hz, 2H), 2.60, (brs, 1H), 1.88 – 1.83 (m, 2H), 1.74 – 1.69 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.7, 132.8, 130.2, 129.4, 128.3, 64.8, 62.0, 29.1, 25.1.

 **6-Hydroxyhexyl Benzoate.**[128] The general procedure was employed using potassium 7-(benzoyloxy)hexyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.23 g, 0.99 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 8.03 (m, 2H), 7.53 (m, 1H), 7.44 – 7.41 (m, 2H), 4.31 (t, *J* = 6.5 Hz, 2H), 3.63 (t, *J* = 6.5 Hz, 2H), 2.38, (brs, 1H), 1.80 – 1.75 (m, 2H), 1.62 – 1.56 (m, 2H), 1.48 – 1.43 (m, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.6, 132.7, 130.2, 129.4, 128.2, 64.8, 62.4, 32.4, 28.5, 25.7, 25.3.

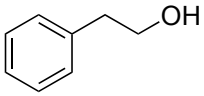
 **3-Bromopropan-1-ol.**[129] The general procedure was employed using potassium 3-bromopropyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield (0.14 g, 0.98 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.78 (t, J = 6.0 Hz, 2H), 3.54 (t, J = 6.5 Hz, 2H), 2.69 (brs, 1H), 2.11 – 2.07 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 60.1, 34.9, 30.3.

 **Cyclopentanol.**[130] The general procedure was employed using potassium cyclopentyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.09 g, 0.99 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.33 (m, 1H), 1.78 – 1.76 (m, 4H), 1.59 (brs, 1H), 1.58 – 1.56 (m, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 74.0, 35.5, 23.2.

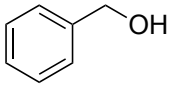
 **2-Methylcyclohexanol.**[131] The general procedure was employed using potassium 2-methylcyclohexyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 96% yield (0.11 g, 0.96 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.11 (m, 1H), 1.95 – 1.93 (m, 1H), 1.75 – 1.59 (m, 4H), 1.36 – 1.18 (m, 4H), 1.01 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 76.5, 40.2, 35.5, 33.6, 25.7, 25.2, 18.5.

 **3,6,6-Trimethylbicyclo[3.1.1]heptan-2-ol.**[132] The general procedure was employed using potassium 3,6,6-trimethylbicyclo[3.1.1]heptan-2-yltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 98% yield (0.15 g, 0.98 mmol) as a white solid, mp 49 – 52 ºC (lit. 51-53 ºC). ^{1}H NMR (500 MHz,

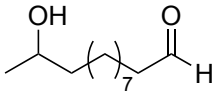
$CDCl_3$) δ 4.05 (m, 1H), 2.64 (brs, 1H), 2.50 (m, 1H), 2.37 (m, 1H), 2.00 – 1.90 (m, 2H), 1.79 (m, 1H), 1.73 (m, 1H), 1.21 (s, 3H), 1.13 (d, J = 7.4 Hz, 3H), 1.06 (d, J = 9.7 Hz, 1H), 0.92 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 71.3, 47.7, 47.4, 41.67, 38.8, 38.1, 34.2, 27.6, 23.6, 20.6. IR (neat) 3260, 2905, 1469, 1043, 1006, 923 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{10}H_{17}$ $(M\text{-}OH)^+$ 137.1330, found 137.1326.



2-Phenylethanol.[133] The general procedure was employed using potassium phenethyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.12 g, 0.99 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 7.21 – 7.18 (m, 3H), 3.78 (t, J = 6.5 Hz, 2H), 2.81 (t, J = 6.5 Hz, 2H), 2.20 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 138.6, 129.0, 128.5, 126.4, 63.5, 39.1.

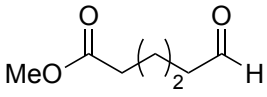


Phenylmethanol.[133] The general procedure was employed using potassium benzyltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.11 g, 0.99 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 5H), 4.56 (s, 2H), 2.90 (brs, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 140.8, 128.4, 127.4, 126.9, 64.9.

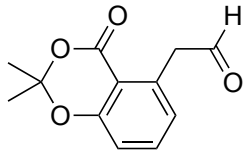


11-Hydroxydodecanal.[134] The general procedure was employed using potassium (*E*)-11-hydroxydodec-1-en-1-yltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.2 g, 0.99 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (t, J = 1.9 Hz, 1H), 3.79 (m, 1H), 2.44 –

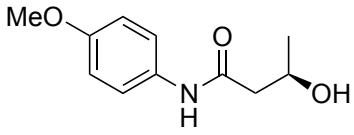
2.40 (m, 2H), 1.69 – 1.50 (m, 2H), 1.41 (d, J = 14.2 Hz, 2H), 1.29 (s, 12H), 1.19 (d, J = 6.2 Hz, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 68.2, 43.9, 39.3, 29.6, 29.3, 29.1, 25.7, 22.1.



Methyl 6-Oxohexanoate.[135] The general procedure was employed using potassium (*E*)-6-methoxy-6-oxohex-1-en-1-yltrifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.14 g, 0.99 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (t, J = 1.2 Hz, 1H), 3.67 (s, 3H), 2.55 – 2.25 (m, 4H), 1.67 (m, 4H).^{13}C NMR (125.8 MHz, $CDCl_3$) δ 202.0, 174.0, 173.7, 51.5, 43.5, 33.7, 24.3, 21.5.



2-(2,2-Dimethyl-4-oxo-4*H*-benzo[*d*][1,3]dioxin-5-yl)acetaldehyde. The general procedure was employed using potassium (*E*)-(2-(2,2-dimethyl-4-oxo-4*H*-benzo[*d*][1,3]dioxin-5-yl)vinyl)trifluoroborate, and the reaction was complete in 2 min. The desired pure product was obtained in 99% yield (0.22 g, 0.99 mmol) as a light yellow solid, mp 55 – 57 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.50 (t, J = 8 Hz, 1H), 6.96 (d, J = 8.3 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 4.22 (s, 2H), 1.75 (s, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 198.1, 160.8, 157.1, 137.0, 135.6, 126.4, 117.0, 112.6, 105.7, 49.0, 25.6. IR (neat) 1722, 1292, 1052 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_{12}O_4Na$ $(M+Na)^+$ 243.0633, found 243.0633.



(*R*)-3-Hydroxy-*N*-(4-methoxyphenyl)butanamide.[49] The general procedure was employed using 0.1 mmol of potassium (*R*)-(4-((4-methoxyphenyl)amino)-4-oxobutan-2-yl)trifluoroborate (*R* : *S*) (97 : 3), and the reaction was complete in 2 min. The desired pure product was obtained in 97% yield (0.020 g, 0.097 mmol) as a white solid, mp 136-138 ºC (lit. 135 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (brs, 1H), 7.39 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 4.28 (m, 1H), 3.78 (s, 3H), 3.43 (d, *J* = 2.9 Hz, 1H), 2.52 – 2.41 (m, 2H), 1.27 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.3, 156.5, 130.5, 122.0, 114.1, 64.9, 55.5, 44.8, 22.9.

2.8.2 Experimental for section 2.5

General Procedure for Chlorination of Organotrifluoroborates with NaOCl: To a 50 mL round bottom flask containing a solution of potassium organotrifluoroborate (1 mmol) in EtOAc/H_2O (1:1, 10 mL, 0.1 M) was added NaOCl [1.5 mL of Clorox® Ultra (6.15% NaOCl), 1.2 mmol, 1.2 equiv] in one portion. The reaction was stirred open to air at rt until ^{11}B NMR indicated completion of the reaction. The reaction was quenched with 10% aq. Na_2SO_3 (10 mL). The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with 1 N NaOH (3 x 10 mL) to remove any unreacted starting material. The Et_2O layer was dried (Na_2SO_4), filtered, concentrated, and dried *in vacuo*. In general the product obtained was pure. Trace impurities were removed by column chromatography using Et_2O/pentanes to afford the desired pure product.

General Procedure for Chlorination of Organotrifluoroborates with Stoichiometric Chloramine-T: To a 50 mL round bottom flask containing a solution of potassium organotrifluoroborate (1 mmol) in EtOAc/H_2O (1:1, 10 mL, 0.1 M) was added NaCl (1M in H_2O, 0.5 mL, 0.5 mmol, 0.5 equiv) and Chloramine-T · 3 H_2O (310 mg, 1.1 mmol, 1.1 equiv) in one portion. The reaction was stirred open to air at rt until ^{11}B NMR indicated completion of the reaction. The reaction was quenched with 10% aq. Na_2SO_3 (10 mL). The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with 1 N NaOH (3 x 10 mL) to remove any unreacted starting material. The Et_2O layer was dried (Na_2SO_4), filtered, concentrated, and dried *in vacuo*. In general the product obtained was pure. Trace impurities were removed by column chromatography using Et_2O/pentanes to afford the desired pure product.

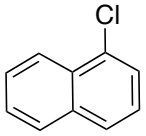
General Procedure for Chlorination of Organotrifluoroborates with Substoichiometric Chloramine-T: To a 50 mL round bottom flask containing a solution of potassium organotrifluoroborate (1 mmol) in EtOAc/H_2O (1:1, 10 mL, 0.1 M) was added NaCl (1M in H_2O, 1.5 mL, 1.5 mmol, 1.5 equiv) and Chloramine-T · 3 H_2O (85 mg, 0.3 mmol, 0.3 equiv) in one portion. The reaction was stirred open to air at rt until ^{11}B NMR indicated completion of the reaction. The reaction was quenched with 10% aq. Na_2SO_3 (10 mL). The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with 1 N NaOH (3 x 10 mL) to remove any unreacted starting material. The Et_2O layer was dried (Na_2SO_4), filtered, concentrated, and dried *in vacuo*. In general the product obtained was pure. Trace impurities were removed by column chromatography using Et_2O/pentanes to afford the desired pure product.

General Procedure for Chlorination of Organotrifluoroborates with Trichloroisocyanuric acid:

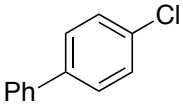
General Procedure A: To a 50 mL round bottom flask containing a solution of potassium organotrifluoroborate (1 mmol) in EtOAc/H_2O (1:1, 10 mL, 0.1 M) was added trichloroisocyanuric acid (76.7 mg, 0.33 mmol, 0.33 equiv) in one portion. The reaction was stirred open to air at rt until ^{11}B NMR indicated completion of the reaction. The reaction was quenched with 10% aq. Na_2SO_3 (10 mL). The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with 1 N NaOH (3 x 10 mL) to remove any unreacted starting material. The Et_2O layer was dried (Na_2SO_4), filtered, concentrated, and dried *in vacuo*. In general the product obtained was pure. Trace impurities were removed by column chromatography using Et_2O/pentanes to afford the desired pure product.

General Procedure B: To a 50 mL round bottom flask containing a solution of potassium organotrifluoroborate (1 mmol) in EtOAc/H_2O (1:1, 10 mL, 0.1 M) was added NaCl (1M in H_2O, 1.5 mL, 1.5 mmol, 1.5 equiv) and trichloroisocyanuric acid (37 mg, 0.16 mmol, 0.16 equiv) in one portion. The reaction was stirred open to air at rt until ^{11}B NMR indicated completion of the reaction. The reaction was quenched with 10% aq. Na_2SO_3 (10 mL). The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with 1 N NaOH (3 x 10 mL) to remove any unreacted starting material. The Et_2O layer was dried (Na_2SO_4), filtered, concentrated, and dried *in vacuo*. In general the product obtained was pure. Trace impurities were removed by column chromatography using Et_2O/pentanes to afford the desired pure product.

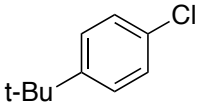
General Procedure C: To a 50 mL round bottom flask containing a solution of potassium organotrifluoroborate (1 mmol) in EtOAc/H_2O (1:1, 10 mL, 0.1 M) was added trichloroisocyanuric acid (232.4 mg, 1 mmol, 1 equiv) in one portion. The reaction was stirred open to air at rt until ^{11}B NMR indicated completion of the reaction. The reaction was quenched with 10% aq. Na_2SO_3 (10 mL). The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with 1 N NaOH (3 x 10 mL) to remove any unreacted starting material. The Et_2O layer was dried (Na_2SO_4), filtered, concentrated, and dried *in vacuo*. In general the product obtained was pure. Trace impurities were removed by column chromatography using Et_2O/pentanes to afford the desired pure product.



1-Chloronaphthalene. [136] General procedure **A** was employed using potassium naphthalen-1-yltrifluoroborate (0.23 g, 1 mmol), and the reaction was complete in 40 min. The desired pure product was obtained in 95% yield (0.15 g, 0.94 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.48 (m, 1H), 7.31 (t, J = 8.0 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 134.8, 132.1, 131.0, 128.4, 127.4, 127.2, 126.9, 126.4, 125.9, 124.6.

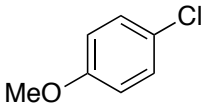


4-Chlorobiphenyl. [137] General procedure **A** was employed using potassium biphenyl-4-yltrifluoroborate (1.3 g, 5 mmol), and 15 mL of the solvent mixture, and the reaction was complete in 40 min. The desired pure product was obtained in 81% yield (0.76 g, 4.05 mmol) as a white solid, mp 75 – 77 ºC (lit. 76 – 78 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.43 – 7.40 (m, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.34 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 140.2, 139.8, 133.6, 129.1, 129.0, 128.6, 127.8, 127.2.

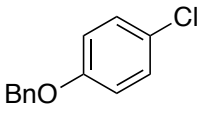


1-*tert*-Butyl-4-chlorobenzene.[138] General procedure **A** was employed using potassium 4-*tert*-butylphenyltrifluoroborate (0.24 g, 1 mmol), and the reaction was complete in 1 h. The desired pure product was obtained in 94% yield (0.16 g, 0.94 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 9 Hz, 2H), 7.27 (d, J

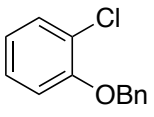
= 8.5 Hz, 2H), 1.32 (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 149.7, 131.3, 128.2, 126.9, 34.6, 31.4.



1-Chloro-4-methoxybenzene.[139] General procedure **A** was employed using potassium 4-methoxyphenyltrifluoroborate (0.21 g, 1 mmol), and the reaction was complete in 40 min. The desired pure product was obtained in 98% yield (0.14 g, 0.98 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J = 9.0 Hz, 2H), 6.81 (d, J = 9.0 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 158.3, 129.4, 125.7, 115.3, 55.6.

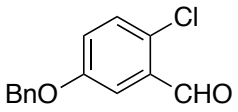


1-(Benzyloxy)-4-chlorobenzene.[140] General procedure **A** was employed using potassium 4-(benzyloxy)phenyltrifluoroborate (0.25 g, 1 mmol), and the reaction was complete in 40 min. The desired pure product was obtained in 92% yield (0.20 g, 0.92 mmol) as a light yellow solid, mp 65 – 67 ºC (lit. 65 – 67 ºC).[141] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 4H), 7.31 (m, 1H), 7.19 (d, J = 9 Hz, 2H) 6.85 (d, J = 9.0 Hz, 2H), 4.98 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 157.3, 136.6, 129.3, 128.6, 128.1, 127.4, 125.8, 116.1, 70.2.

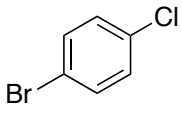


1-(Benzyloxy)-2-chlorobenzene (1f).[146] General procedure **A** was employed using potassium 2-(benzyloxy)phenyltrifluoroborate (0.25 g, 1 mmol), and the reaction was complete in 1 h. The desired pure product was obtained in 94% yield (0.21 g, 0.94 mmol) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 4H), 7.31 (m, 1H), 7.19 (d, J = 9 Hz, 2H) 6.85 (d, J = 9.0 Hz, 2H), 4.98 (s, 2H). ^{13}C NMR (125.8

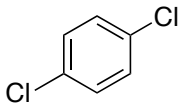
MHz, $CDCl_3$) δ 154.3, 136.6, 130.4, 128.7, 128.0, 127.8, 127.1, 123.3, 121.7, 114.1, 70.8.



5-(Benzyloxy)-2-chlorobenzaldehyde. General procedure **A** was employed using potassium (4-(benzyloxy)-2-formylphenyl)trifluoroborate (0.32 g, 1 mmol), and the reaction was complete in 40 min. The desired pure product was obtained in 91% yield (0.22 g, 0.91 mmol) as a light yellow solid, mp 55 – 57 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.49 (d, J = 3 Hz, 1H), 7.43 – 7.38 (m, 4H), 7.39 – 7.34 (m, 2H), 7.16 (m, 1H) 5.09 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 189.7, 157.7, 135.9, 132.9, 131.5, 129.9, 128.7, 128.3, 127.5, 123.4, 113.0, 70.5. FT – IR (neat) 1696, 1230, 1004, 748 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{14}H_{11}O_2NaCl$ $(M+Na)^+$ 269.0345, found 269.0347.

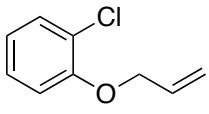


1-Bromo-4-chlorobenzene.[57b] General procedure **A** was employed using potassium (4-bromophenyl)trifluoroborate (0.26 g, 1 mmol), and the reaction was complete in 1 h. The desired pure product was obtained in 81% yield (0.15 g, 0.81 mmol) as a colorless solid, mp 64 – 66 ºC (lit. 65 – 66 ºC).[142] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 133.2, 132.7, 130.2, 120.2.

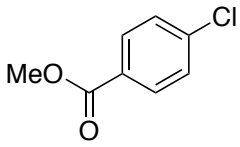


1,4-Dichlorobenzene.[143] General procedure **A** was employed using potassium (4-chlorophenyl)trifluoroborate (0.22 g, 1 mmol), and the reaction was complete in 1 h. The desired pure product was obtained in 86% yield (0.13 g, 0.86 mmol)

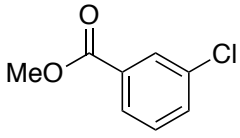
as a colorless solid, mp 47 – 50 ºC (lit. 46 – 49 ºC).[144] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (s, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 132.5, 129.8.



1-(Allyloxy)-2-chlorobenzene.[145] General procedure **A** was employed using potassium (2-(allyloxy)phenyl)trifluoroborate (0.24 g, 1 mmol), and the reaction was complete in 1 h. The desired pure product was obtained in 84% yield (0.14 g, 0.84 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (m, 1H), 7.19 (m, 1H), 6.93 – 6.88 (m, 2H), 6.08 (m, 1H), 5.47 (m, 1H), 5.31 (m, 1H), 4.63 – 4.61 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 154.1, 132.7, 130.3, 127.6, 123.1, 121.5, 117.8, 113.8, 69.7.

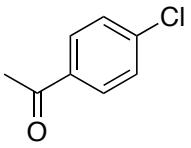


Methyl 4-Chlorobenzoate.[146] General procedure **C** was employed using potassium (4-methoxycarbonyl)phenyltrifluoroborate (0.24 g, 1 mmol), and the reaction was complete in 2 h. The desired pure product was obtained in 87% yield (0.15 g, 0.87 mmol) as a light yellow solid mp 40 – 43 ºC (lit. 40 – 42 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.2, 139.4, 131.0, 128.7, 128.6, 52.3.

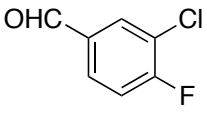


Methyl 3-Chlorobenzoate.[147] General procedure **C** was employed using potassium (3-methoxycarbonyl)phenyltrifluoroborate (0.24 g, 1 mmol), and the reaction was complete in 1 h. The desired pure product was obtained in 92% yield (0.16 g, 0.92 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (m, 1H), 7.92 (m,

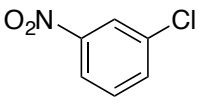
1H), 7.52 (m, 1H), 7.38 (m, 1H), 3.92 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.8, 134.5, 132.9, 131.8, 129.6, 129.6, 127.6, 52.3.



1-(4-Chlorophenyl)ethanone.[148] General procedure **C** was employed using potassium (4-acetylphenyl)trifluoroborate (0.23 g, 1 mmol), and the reaction was complete in 30 min. The desired pure product was obtained in 82% yield (0.13 g, 0.82 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 196.7, 139.5, 135.4, 129.6, 128.8, 26.5.

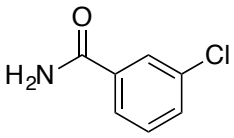


3-Chloro-4-fluorobenzaldehyde. General procedure **A** was employed using potassium 2-fluoro-5-formylphenyltrifluoroborate (0.23 g, 1 mmol), and the reaction was complete in 40 min. The desired pure product was obtained in 80% yield (0.13 g, 0.80 mmol) as a colorless solid, mp 83 – 85 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.97 (m, 1H), 7.81 (m, 1H), 7.32 (t, J = 8.5 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 189.3, 161.8 (d, J = 7.3 Hz), 133.5, 132.1, 130.0 (d, J = 8.9 Hz), 122.7 (d, J = 18.9 Hz), 117.4 (d, J = 22.1 Hz). ^{19}F NMR (470.8 MHz, $CDCl_3$) δ -104.7. FT – IR (neat) 1698, 1264, 1058, 708 cm^{-1}. HRMS (ESI) *m/z* calcd. for C_7H_4OFCl $(M)^+$ 157.9935, found 157.9941.

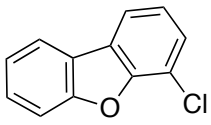


1-Chloro-3-nitrobenzene.[58a] General procedure **C** was employed using potassium 3-nitrophenyltrifluoroborate (0.23 g, 1 mmol), the reaction was run at 80 ºC

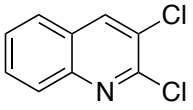
and it was complete in 4 h. The desired pure product was obtained in 85% yield (0.13 g, 0.85 mmol) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (t, *J* = 2.1 Hz, 1H), 8.14 (m, 1H), 7.69 (m, 1H), 7.52 (t, *J* = 8.1 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 148.7, 135.3, 134.6, 130.3, 123.8, 121.6.



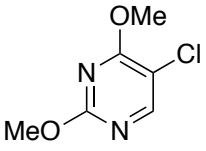
3-Chlorobenzamide.[58a] General procedure **C** was employed using potassium (3-carbamoylphenyl)trifluoroborate (0.23 g, 1 mmol), the reaction was run at 80 ºC and it was complete in 6 h. The desired pure product was obtained in 89% yield (0.14 g, 0.89 mmol) as a white solid, mp 125 – 127 ºC (lit.[143] 125 – 128 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (t, *J* = 2.0 Hz, 1H), 7.68 (m, 1H), 7.51 (m, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 6.02 (brs, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.9, 135.1, 134.9, 132.0, 129.9, 127.7, 125.4.



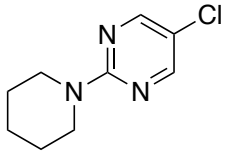
4-Chlorodibenzo[*b*,*d*]furan. General procedure **A** was employed using potassium dibenzo[*b*,*d*]furan-4-yltrifluoroborate (0.27 g, 1 mmol), and the reaction was complete in 2 h. The desired pure product was obtained in 95% yield (0.19 g, 0.95 mmol) as a white solid, mp 64 – 66 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 156.1, 151.9, 127.8, 127.1, 125.9, 124.0, 123.6, 123.2, 120.9, 119.0, 117.1, 112.1. FT – IR (neat) 1420, 1197, 1040, 870, 744, 683 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_8OCl$ $(M+H)^+$ 203.0264, found 203.0263.



2,3-Dichloroquinoline. General procedure **A** was employed using potassium (2-chloroquinolin-3-yl)trifluoroborate (0.27 g, 1 mmol), and the reaction was complete in 6 h. The desired pure product was obtained in 80% yield (0.16 g, 0.80 mmol) as a white solid, mp 97 – 99 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.00 (m, 1H), 7.75 – 7.71 (m, 2H), 7.59 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 148.2, 145.8, 137.2, 130.6, 128.5, 127.9, 127.6, 127.1, 126.6. FT – IR (neat) 1150, 975, 757, 655 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_9H_5NCl_2$ $(M)^+$ 196.9799, found 196.9799.

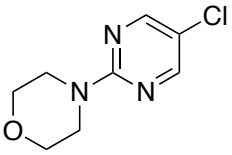


5-Chloro-2,4-dimethoxypyrimidine. General procedure **A** was employed using potassium (2,4-dimethoxypyrimidin-5-yl)trifluoroborate (0.25 g, 1 mmol), and the reaction was complete in 2 h. The desired pure product was obtained in 91% yield (0.16 g, 0.91 mmol) as a white solid, mp 70 – 72 ºC (lit.[149] 72 – 73 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 4.07 (s, 3H), 3.99 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.0, 163.4, 156.4, 110.3, 55.2, 54.7. FT – IR (neat) 1560, 1400, 1275, 1004, 780, 690 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_6H_8N_2O_2Cl$ $(M+H)^+$ 175.0274, found 175.0281.

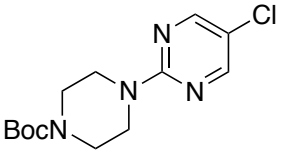


5-Chloro-2-(piperidin-1-yl)pyrimidine. General procedure **A** was employed using potassium 2-(piperidin-1-yl)pyrimidin-5-yltrifluoroborate (0.27 g, 1 mmol), and the reaction was complete in 2 h. The desired pure product was obtained in 90% yield (0.18 g, 0.90 mmol) as a white solid, mp 45 – 47 ºC. ^{1}H NMR (500 MHz,

$CDCl_3$) δ 8.19 (s, 2H), 3.75 (t, *J* = 5.5 Hz, 4H), 1.67 – 1.66 (m, 2H), 1.61 – 1.58 (m, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 159.9, 155.7, 117.3, 45.1, 25.6, 24.7. FT – IR (neat) 1584, 1508, 1441 1256, 782 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_9H_{13}N_3Cl$ $(M+H)^+$ 198.0798, found 198.0792.

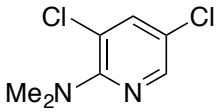


4-(5-Chloropyrimidin-2-yl)morpholine. General procedure **A** was employed using potassium 2-morpholinopyrimidin-5-yltrifluoroborate (0.27 g, 1 mmol), and the reaction was complete in 2 h. The desired pure product was obtained in 89% yield (0.18 g, 0.89 mmol) as a white solid, mp 70 – 72 ºC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 2H), 3.76 – 3.75 (m, 8H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 160.0, 155.9, 118.6, 66.7, 44.4. FT – IR (neat) 2922, 1585, 1494, 1253, 1112, 953, 787, 667 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_{11}N_3OCl$ $(M+H)^+$ 200.0591, found 200.0589.

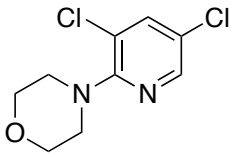


***tert*-Butyl 4-(5-Chloropyrimidin-2-yl)piperazine-1-carboxylate.** General procedure **A** was employed using potassium (2-(4-(*tert*-butoxycarbonyl)piperazin-1-yl)pyrimidin-5-yl)trifluoroborate (0.37 g, 1 mmol), and the reaction was complete in 2 h. The desired pure product was obtained in 95% yield (0.28 g, 0.95 mmol) as a white solid, mp 102 – 105 ºC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 2H), 3.77 (t, *J* = 5.0 Hz, 4H), 3.49 (t, *J* = 5.0 Hz, 4H), 1.49 (s, 9H).^{13}C NMR (125.8 MHz, $CDCl_3$) δ 159.9, 156.0, 118.7, 80.2, 44.0, 28.6. FT – IR (neat) 1677, 1585, 1514,

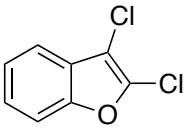
1249, 1131, 993, 784 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{13}H_{19}N_4O_2NaCl$ $(M+Na)^+$ 321.1094, found 321.1099.



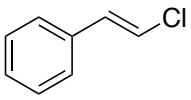
3,5-Dichloro-*N*,*N*-dimethylpyridin-2-amine. General procedure **C** was employed using potassium (6-(dimethylamino)pyridin-3-yl)trifluoroborate (0.23 g, 1 mmol), and the reaction was complete in 1 h. The desired pure product was obtained in 88% yield (0.17 g, 0.88 mmol) as a white solid, mp 24 – 26 ºC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2 Hz, 1H), 7.54 (d, *J* = 2 Hz, 1H), 2.98 (s, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 157.5, 143.9, 138.3, 122.7, 120.9, 41.5. FT – IR (neat) 1491, 1414, 1176, 1049, 837, 753 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_{10}N_2Cl$ $(M+H)^+$ 157.0533, found 157.0533.



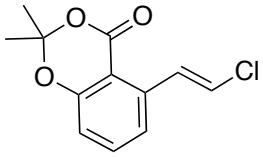
4-(3,5-Dichloropyridin-2-yl)morpholine. General procedure **C** was employed using potassium 6-morpholinopyridin-3-yltrifluoroborate (0.27 g, 1 mmol), and the reaction was complete in 1 h. The desired pure product was obtained in 91% yield (0.21 g, 0.91 mmol) as a white solid, mp 83 – 85 ºC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.5 Hz, 1H), 7.60 (d, *J* = 2.5 Hz, 1H), 3.85 (t, *J* = 5.0 Hz, 4H), 3.33 (t, *J* = 5.0 Hz, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 156.6, 144.3, 138.3, 124.5, 122.6, 66.8, 49.5. FT – IR (neat) 1435, 1243, 1111, 944, 823, 709 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_9H_{11}N_2OCl_2$ $(M+H)^+$ 233.0248, found 233.0257.



2,3-Dichlorobenzofuran. General procedure **C** was employed using potassium benzofuran-*2*-yltrifluoroborate (0.22 g, 1 mmol), and the reaction was complete in 30 min. The desired pure product was obtained in 86% yield (0.16 g, 0.86 mmol) as a white solid, mp 25 – 27 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 1H), 7.42 (m, 1H), 7.35 – 7.29 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 152.3, 137.7, 126.5, 125.4, 123.9, 118.4, 111.3, 108.4. FT – IR (neat) 1449, 1155, 1034, 742 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_5OCl_2$ $(M+H)^+$ 186.9717, found 186.9721.

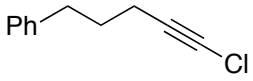


(*E*)-(2-Chlorovinyl)benzene.[150] General procedure **A** was employed using potassium (*E*)-styryltrifluoroborate (0.21 g, 1 mmol), and the reaction was complete in 40 min. The desired pure product was obtained in 85% yield (0.12 g, 0.85 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 5H), 6.81 (d, *J* = 13.5 Hz, 1H), 6.61 (d, *J* = 13.5 Hz, 1H).^{13}C NMR (125.8 MHz, $CDCl_3$) δ 134.8, 133.2, 128.7, 128.1, 126.1, 118.6.

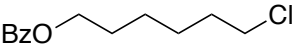


(*E*)-5-(2-Chlorovinyl)-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one. General procedure **A** was employed using potassium (*E*)-(2-(2,2-dimethyl-4-oxo-4H-benzo[d][1,3]dioxin-5-yl)vinyl)trifluoroborate (0.18 g, 0.5 mmol), and the reaction was complete in 30 min. The desired pure product was obtained in 92% yield (0.11 g, 0.92 mmol) as a light yellow solid, mp 86–88 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 13.5, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H),

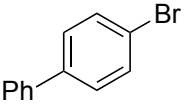
6.63 (d, J = 13.5 Hz, 1H), 1.71 (s, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 134.8, 133.2, 128.7, 128.1, 126.1, 118.6. FT – IR (neat) 1722, 1273, 1042, 924, 780, 691 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_{11}O_3NaCl$ $(M+Na)^+$ 261.0294, found 261.0297.



(5-Chloropent-4-yn-1-yl)benzene. General procedure **A** was employed using potassium 5-phenylpent-1-yn-1-yltrifluoroborate (0.25 g, 1 mmol), and the reaction was complete in 40 min. The desired pure product was obtained in 82% yield (0.15 g, 0.82 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.31 – 7.27 (m, 3H), 2.80 (t, J = 8 Hz, 2H), 2.30 – 2.26 (m, 2H), 1.95 – 1.90 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 141.6, 128.7, 128.6, 126.2, 69.5, 57.8, 34.9, 30.2, 18.4. FT – IR (neat) 1496, 1082, 744, 698 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{11}H_{11}Cl$ $(M)^+$ 178.0549, found 178.0553.



6-Chlorohexyl Benzoate.[151] General procedure **A** was employed using potassium (6-(benzoyloxy)hexyl)trifluoroborate (0.31 g, 1 mmol), and the reaction was complete in 2 h. The desired pure product was obtained in 81% yield (0.19 g, 0.82 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 - 803 (m, 2H), 7.54 (m, 1H), 7.45 – 7.42 (m, 2H), 4.32 (t, J = 6.5 Hz, 2H), 3.65 (t, J = 6.5 Hz, 2H), 1.81 – 1.76 (m, 2H), 1.63 – 1.59 (m, 2H), 1.49 – 1.43 (m, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.9, 133.0, 130.6, 129.7, 128.5, 65.1, 62.9, 32.7, 28.9, 26.0, 25.6.



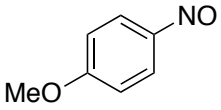
4-Bromobiphenyl (5a).[152] To a 50 mL round bottom flask containing a mixture of trichloroisocyanuric acid (76.7 mg, 0.33 mmol, 1 equiv) and NaBr (103 mg, 1 mmol, 1 equiv) in EtOAc : H_2O (1:1, 10 mL, 0.1 M) was added potassium biphenyl-4-

yltrifluoroborate (260 mg, 1 mmol) in one portion. The reaction was stirred open to air at rt until ^{11}B NMR indicated completion of the reaction (30 min). The reaction was quenched with 10% aq. Na_2SO_3 (10 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with 1 N NaOH (3 x 10 mL) to remove any unreacted starting material. The EtOAc layer was dried (Na_2SO_4), filtered, concentrated, and dried *in vacuo*. The desired pure product was obtained in 94% yield (0.84 g, 4.45 mmol) as a white solid, mp 88 – 90 ºC (lit. 89 ºC)[151]. ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 4H), 7.46 – 7.42 (m, 4H), 7.36 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 140.1, 140.0, 131.8, 128.9, 128.7, 127.6, 126.9, 121.5.

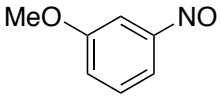
2.8.2 Experimental for section 2.6

General Procedure A: Nitrosation of Aryltrifluoroborates with $NaNO_2$: To a 20 mL glass microwave vial containing a solution of potassium organotrifluoroborate (1 mmol) in heptane/H_2O (1:1, 5 mL, 0.2 M) was added $NaNO_2$ (104 mg, 1.5 mmol, 1.5 equiv) in one portion. The reaction was stirred open to air at 50 ºC until the trifluoroborate was consumed (as indicated by ^{11}B NMR). To the crude mixture was added H_2O (20 mL) and CH_2Cl_2 (10 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The products were obtained in high purity after filtration through a small plug of silica topped with Celite, eluting with CH_2Cl_2.

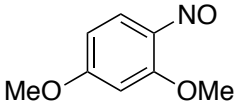
General Procedure B: Nitrosation of Aryl and Heteroaryltrifluoroborates with $NOBF_4$: To a 20 mL glass microwave vial containing a solution of potassium organotrifluoroborate (1 mmol) in CH_3CN (3 mL, 0.33 M) was added $NOBF_4$ (120 mg, 1.03 mmol, 1.03 equiv) in one portion. The reaction was stirred open to air at rt until the reaction became homogeneous. The reaction changed from a white slurry to a green or black solution. To the crude mixture was added H_2O (20 mL) and CH_2Cl_2 (10 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. In general the product was obtained in high purity after filtration through a small plug of silica topped with Celite, eluting with CH_2Cl_2/hexanes. In specific cases trace impurities were removed by column chromatography using CH_2Cl_2/hexanes or EtOAc/hexanes to afford the desired pure product.



1-Methoxy-4-nitrosobenzene.[72a] General procedure B was employed using potassium 4-methoxyphenyltrifluoroborate (214 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 95% yield (130 mg, 0.95 mmol) as a green oil after filtration through a short plug of silica topped with Celite using hexanes/CH_2Cl_2 (3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 6.5 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.6, 163.9, 124.3, 113.8, 55.9. IR (neat) 1598, 1504, 1411, 1263, 1020, 837 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_8NO_2$ $(M+H)^+$ 138.0555, found 138.0558.

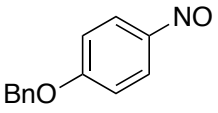


1-Methoxy-3-nitrosobenzene. General procedure B was employed using potassium 3-methoxyphenyltrifluoroborate (214 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 89% yield (122 mg, 0.89 mmol) as a green oil after column chromatography with hexanes/CH_2Cl_2 (3:1) as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (m, 1H), 7.60 (t, *J* = 8 Hz, 1H), 7.28 (m, 1H), 6.89 (t, *J* = 2 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.9, 160.5, 130.5, 122.9, 119.8, 99.8, 55.8. IR (neat) 1604, 1483, 1384, 1041, 789 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_8NO_2$ $(M+H)^+$ 138.0555, found 138.0558.

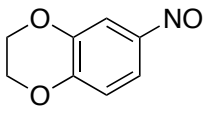


2,4-Dimethoxy-1-nitrosobenzene. General procedure B was employed using potassium (2,4-dimethoxyphenyl)trifluoroborate (244 mg, 1 mmol) and

$NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 91% yield (152 mg, 0.91 mmol) as a green solid, mp 93–95 ºC, after filtration through a short plug of silica topped with Celite using hexanes/CH_2Cl_2 (3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.65 (d, J = 2.5 Hz, 1H), 6.50 (d, J = 9 Hz, 1H) 6.34 (m, 1H), 4.22 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.5, 164.4, 157.1, 112.1, 105.8, 98.5, 56.9, 56.2. IR (neat) 1600, 1397, 1246, 1014, 837 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_{10}NO_3$ $(M+H)^+$ 168.0661, found 168.0664.

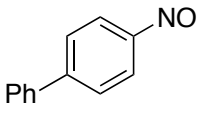


1-(Benzyloxy)-4-nitrosobenzene. General procedure B was employed using potassium (4-(benzyloxy)phenyl)trifluoroborate (290 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 92% yield (196 mg, 0.92 mmol) as a blue solid, mp 81–83 ºC, after filtration through a short plug of silica topped with Celite using hexanes/CH_2Cl_2 (3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (brs, 2H), 7.45 – 7.37 (m, 5H), 7.10 (t, J = 8 Hz, 2H), 5.21 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.9, 164.1, 135.6, 129.0, 128.7, 127.7, 114.9, 70.8. IR (neat) 1598, 1502, 1262, 1117, 844, 730 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{13}H_{11}NO_2$ $(M)^+$ 213.0790, found 213.0797.

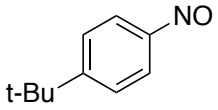


6-Nitroso-2,3-dihydrobenzo[b][1,4]dioxine. General procedure B was employed using potassium (2,3-dihydrobenzo[b][1,4]dioxin-6-yl)trifluoroborate (242 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 91% yield (150 mg, 0.91 mmol) as a green solid, mp 88–90 ºC, after column chromatography with hexanes/CH_2Cl_2 (3:1) as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 1H), 7.13 (s, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 4.38 – 4.36 (m, 2H), 4.33 – 4.31 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 163.6, 150.9, 143.9, 120.8, 117.6, 107.7, 65.1, 64.2. IR (neat) 1591, 1495, 1280, 1054, 913 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_8NO_3$ $(M+H)^+$ 166.0504, found 166.0504.

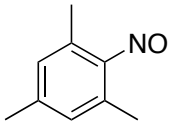


4-Nitrosobiphenyl. [153] General procedure B was employed using potassium biphenyl-4-yltrifluoroborate (260 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 90% yield (165 mg, 0.90 mmol) as an orange solid, mp 72–74 ºC (lit. 73–74 ºC), after filtration through a short plug of silica topped with Celite using hexanes/CH_2Cl_2 (3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8 Hz, 2H), 7.68 – 7.66 (m, 2H), 7.52 – 7.49 (m, 2H), 7.45 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.12, 148.2, 139.3, 129.3, 129.1, 128.0, 127.6, 121.8. IR (neat) 1483, 1249, 760, 695 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_{10}NO$ $(M+H)^+$ 184.0762, found 184.0758.

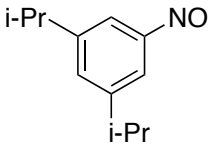


1-*tert*-Butyl-4-nitrosobenzene. General procedure B was employed using potassium (4-*tert*-butylphenyl)trifluoroborate (240 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 93% yield (152 mg, 0.93 mmol) as a green oil after filtration through a short plug of silica topped with Celite using hexanes/CH_2Cl_2 (3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 9 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.3, 159.9, 126.2, 121.1, 35.7, 31.1. IR (neat) 1601, 1509, 1453, 1124,

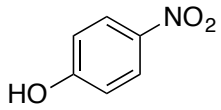
1099, 840, 710 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{10}H_{14}NO$ $(M+H)^+$ 164.1075, found 164.1082.



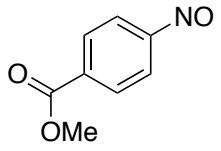
1,3,5-Trimethyl-2-nitrosobenzene.[81a] General procedure B was employed using potassium trifluoro(mesityl)borate (260 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 92% yield (137 mg, 0.90 mmol) as a white solid, mp 120–122 ºC (lit. 121–122 ºC), after filtration column chromatography with hexanes/CH_2Cl_2 (3:1) as eluent. ^1H NMR (500 MHz, $CDCl_3$) δ 6.99 (s, 2H), 2.62 (s, 2H), 2.41 (s, 4H), 2.34 (s, 1H), 2.33 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 140.7, 139.3, 132.7, 129.9, 21.2, 18.7. IR (neat) 1603, 1475, 1245, 807 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_9H_{12}NO$ $(M+H)^+$ 150.0919, found 150.0919.



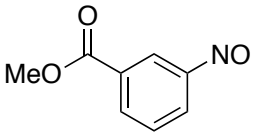
1,3-Diisopropyl-5-nitrosobenzene. General procedure B was employed using potassium (3,5-diisopropylphenyl)trifluoroborate (268 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 88% yield (168 mg, 0.88 mmol) as a green oil after filtration through a short plug of silica topped with Celite using hexanes/CH_2Cl_2 (3:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 2H), 7.46 (s, 1H), 3.07 – 3.01 (m, 2H), 1.32 (d, J = 7 Hz, 12 H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.4, 150.5, 132.7, 117.0, 34.1, 24.0. IR (neat) 1608, 1493, 1096, 886, 694 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_{18}NO$ $(M+H)^+$ 192.1388, found 192.1384.



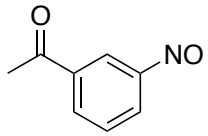
4-Nitrophenol.[154] General procedure B was employed using potassium trifluoro(4-hydroxyphenyl)borate (200 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. In this case no nitroso product was observed and a mixture of 4-nitrophenol and 2-nitrophenol (10% NMR yield) was obtained. The pure 4-nitrophenol product was obtained in 71% yield (99 mg, 0.71 mmol) as a yellow solid, mp 108–110 ºC (lit.[155] 109–110 ºC), after column chromatography with hexanes/CH_2Cl_2 (2:1) as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, J = 9.5 Hz, 2H), 6.92 (d, J = 9 Hz, 2H), 5.72 (s, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 161.6, 141.7, 126.5, 115.9. IR (neat) 3359, 1592, 1488, 1331, 1113, 844 cm^{-1}.



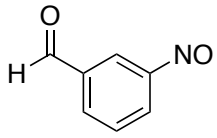
Methyl 4-Nitrosobenzoate.[156] General procedure B was employed using potassium trifluoro(4-(methoxycarbonyl)phenyl)borate (242 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 95% yield (157 mg, 0.95 mmol) as a light yellow solid, mp 123–125 ºC (lit.[157] 129.5 ºC), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, J = 8 Hz, 2H), 7.92 (d, J = 8 Hz, 2H), 3.97 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.9, 164.5, 135.3, 131.2, 120.5, 52.9. IR (neat) 1727, 1441, 1266, 766, 694 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_8NO_3$ $(M+H)^+$ 166.0504, found 166.0510.



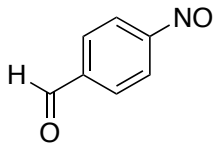
Methyl 3-Nitrosobenzoate.[79b] General procedure B was employed using potassium trifluoro(3-(methoxycarbonyl)phenyl)borate (242 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 96% yield (158 mg, 0.96 mmol) as a light yellow solid, mp 91–93 ºC (lit.[158] 93 ºC), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (t, J = 1.5 Hz, 1H), 8.39 (m, 1H), 8.01 (m, 1H), 7.71 (t, J = 7.5 Hz, 1H), 4.01 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.8, 164.9, 135.8, 131.9, 129.7, 123.9, 122.6, 52.8. IR (neat) 1727, 1433, 1259, 754, 685 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_8NO_3$ $(M+H)^+$ 166.0504, found 166.0510.



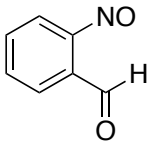
1-(3-Nitrosophenyl)ethanone. General procedure B was employed using potassium (3-acetylphenyl)trifluoroborate (226 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 94% yield (140 mg, 0.94 mmol) as a light yellow solid, mp 78–80 ºC (lit.[161] 81.5 ºC), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (t, J = 1.5 Hz, 1H), 8.33 (m, 1H), 8.05 (m, 1H), 7.75 (t, J = 8 Hz, 1H), 2.73 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 196.8, 165.0, 138.2, 134.3, 130.0, 124.3, 121.0, 26.9. IR (neat) 1691, 1248, 800, 676 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_8H_8NO_2$ $(M+H)^+$ 150.0555, found 150.0557.



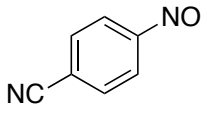
3-Nitrosobenzaldehyde. General procedure B was employed using potassium trifluoro(3-formylphenyl)borate (212 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 88% yield (119 mg, 0.88 mmol) as a light yellow solid, mp 106–108 ºC (lit.[159] 106.5–107 ºC), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^1H NMR (500 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.38 (s, 1H), 8.26 (m, 1H), 8.15 (m, 1H), 7.83 (t, *J* = 8 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 190.9, 164.7, 137.4, 135.0, 130.5, 125.7, 121.7. IR (neat) 1689, 1257, 1121, 678 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_6NO_2$ $(M+H)^+$ 136.0399, found 136.0402.



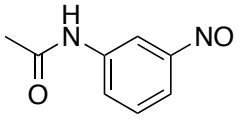
4-Nitrosobenzaldehyde.[91a] General procedure B was employed using potassium trifluoro(4-formylphenyl)borate (212 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 94% yield (127 mg, 0.94 mmol) as a light yellow solid, mp 135–137 ºC (lit.[164] 135–136 ºC), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^1H NMR (500 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 8 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 191.4, 163.9, 139.6, 131.2, 121.2. IR (neat) 1691, 1259, 789 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_7H_5NO_2$ $(M)^+$ 135.0320, found 135.0322.



2-Nitrosobenzaldehyde.[160] General procedure B was employed using potassium trifluoro(2-formylphenyl)borate (212 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 78% yield (105 mg, 0.78 mmol) as a light yellow solid, mp 110–112 ºC (lit.[76] 110 ºC), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.1 (s, 1H), 8.22 (m, 1H), 7.91 (t, *J* = 7.5 Hz, 1H), 7.69 (m, 1H), 6.44 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 193.5, 162.2, 136.6, 134.2, 132.8, 127.8, 106.7. IR (neat) 1702, 1248, 1196, 768 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_6NO_2$ $(M+H)^+$ 136.0399, found 136.0404.

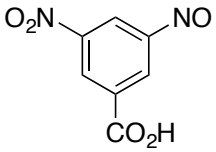


4-Nitrosobenzonitrile.[161] General procedure B was employed using potassium (4-cyanophenyl)trifluoroborate (209 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 89% yield (117 mg, 0.94 mmol) as a light yellow solid, mp 128–130 ºC (lit.[165] 128–129 ºC), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 4 H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 162.3, 134.1, 120.9, 118.5, 117.6. IR (neat) 2239, 1499, 1252, 868 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_4N_2O$ $(M)^+$ 132.0324, found 132.032.

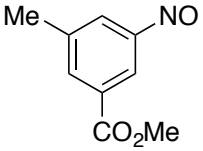


***N*-(3-Nitrosophenyl)acetamide.** General procedure B was employed using potassium (3-acetamidophenyl)trifluoroborate (241 mg, 1 mmol) and $NOBF_4$ (120

mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 91% yield (149 mg, 0.91 mmol) as a light yellow solid, mp 118–120 ºC, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8 Hz, 1H), 7.84 (d, *J* = 8 Hz, 1H), 7.79 (s, 1H), 7.61 (t, *J* = 8 Hz, 1H), 7.55 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.9, 165.9, 139.2, 130.2, 126.5, 118.8, 110.3, 24.8. IR (neat) 1672, 1598, 1492, 1076, 800 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_9N_2O_2$ $(M+H)^+$ 165.0664, found 165.0659.

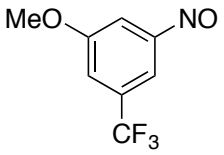


3-Nitro-5-nitrosobenzoic Acid. General procedure B was employed using potassium (3-carboxy-5-nitrophenyl)trifluoroborate (273 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 92% yield (180 mg, 0.92 mmol) as a green solid, mp 148–150 ºC, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (t, *J* = 2 Hz, 1H), 9.10 (s, 1H), 8.78 (t, *J* = 1.5 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.6, 162.5, 149.5, 132.8, 129.6, 128.0, 118.2. IR (neat) 3095, 1700, 1545, 1294, 1177, 918, 736 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_3N_2O_5$ $(M–H)^-$ 195.0042, found 195.0045.

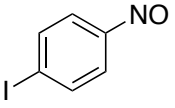


Methyl 3-Methyl-5-nitrosobenzoate. General procedure B was employed using potassium trifluoro(3-(methoxycarbonyl)-5-methylphenyl)borate (256 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 91% yield (163 mg, 0.91 mmol) as a yellow solid,

mp 68–70 ºC, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.20 (s, 1H), 7.73 (s, 1H), 3.99 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.9, 165.3, 140.1, 136.3, 131.6, 123.9, 120.6, 52.7, 21.2. IR (neat) 1726, 1445, 1253, 1134, 760 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_9H_{10}NO_3$ $(M+H)^+$ 180.0661, found 180.0667.

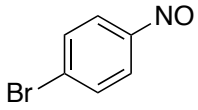


1-Methoxy-3-nitroso-5-(trifluoromethyl)benzene. General procedure B was employed using potassium trifluoro(3-methoxy-5-(trifluoromethyl)phenyl)borate (282 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 10 min. The desired pure product was obtained in 81% yield (166 mg, 0.81 mmol) as a green oil after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.50 (s, 1H), 7.21 (m, 1H), 3.93 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.2, 161.0, 133.4 (d, J = 34 Hz), 123.3 (m), 118.4 (d, J = 3.5 Hz), 114.0 (d, J = 3.5 Hz), 104.8, 56.3. ^{19}F NMR (470.8 MHz, $CDCl_3$) δ –62.9. IR (neat) 1507, 1325, 1131, 1046, 873, 688 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_7NO_2F_3$ $(M+H)^+$ 206.0429, found 206.0431.

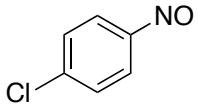


1-Iodo-4-nitrosobenzene.[162] General procedure B was employed using potassium trifluoro(4-iodophenyl)borate (310 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 92% yield (214 mg, 0.92 mmol) as a green solid, mp 100–102 ºC (lit.[163] 104 –106 ºC), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR

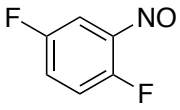
(500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.3, 138.9, 122.0, 105.6. IR (neat) 1579, 1481, 1113, 822 cm^{-1}.



1-Bromo-4-nitrosobenzene.[72a] General procedure B was employed using potassium (4-bromophenyl)trifluoroborate (263 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 94% yield (175 mg, 0.94 mmol) as a light yellow solid, mp 92–94 ºC (lit. 99–101 ºC), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.0, 132.9, 131.8, 122.3. IR (neat) 1478, 1257, 1011, 856 cm^{-1}. HRMS (ESI) *m/z* calcd. for C_6H_5NOBr $(M+H)^+$ 185.9554, found 185.9555.

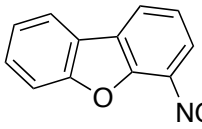


1-Chloro-4-nitrosobenzene.[79d] General procedure B was employed using potassium (4-chlorophenyl)trifluoroborate (219 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 92% yield (130 mg, 0.92 mmol) as a light yellow solid, mp 87–89 ºC (lit.[164] 88–89 ºC), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9 Hz, 2H), 7.60 (d, *J* = 9 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.0, 142.6, 129.8, 122.3. IR (neat) 1481, 1256, 1089, 857 cm^{-1}. HRMS (CI) *m/z* calcd. for C_6H_5NOCl $(M+H)^+$ 142.0060, found 142.0056.

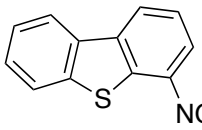


1,4-Difluoro-2-nitrosobenzene. General procedure B was employed using potassium (2,5-difluorophenyl)trifluoroborate (220 mg, 1 mmol) and $NOBF_4$ (120 mg,

1.03 mmol). The reaction was complete in 10 min. The desired pure product was obtained in 81% yield (116 mg, 0.81 mmol) as a white solid, mp 35–37 ºC, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (m, 1H), 6.87 (m, 1H), 6.61 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.9 (d, J = 12 Hz), 166.9 (m), 164.8 (d, J = 13 Hz), 153.3 (d, J = 4 Hz), 112.0 (m), 106.4 (m). ^{19}F NMR (470.8 MHz, $CDCl_3$) δ –94.4, –123.7. IR (neat) 1613, 1501, 1241, 845 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_6H_4NOF_2$ $(M+H)^+$ 144.0261, found 144.0260.

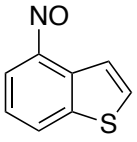


4-Nitrosodibenzo[*b*,*d*]furan. General procedure B was employed using potassium dibenzo[*b*,*d*]furan-4-yltrifluoroborate (274 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 85% yield (168 mg, 0.85 mmol) as a green solid, mp 84–86 ºC, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (m, 1H), 8.01 (m, 1H), 7.78 (d, J = 8 Hz, 1H), 7.59 – 7.56 (m, 2H), 7.49 – 7.44 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 157.4, 153.3, 148.8, 128.7, 128.5, 128.4, 124.1, 122.6, 122.5, 121.0, 116.3, 112.7. IR (neat) 1456, 1417, 1174, 1107, 830, 744 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_{12}H_8NO_2$ $(M+H)^+$ 198.0555, found 198.0553.

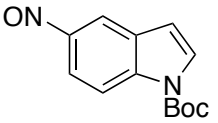


4-Nitrosodibenzo[*b*,*d*]thiophene. General procedure B was employed using potassium dibenzo[*b*,*d*]thiophen-4-yltrifluoroborate (290 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 80% yield (171 mg, 0.80 mmol) as a green solid, mp 115–117 ºC, after

filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^1H NMR (500 MHz, $CDCl_3$) δ 9.56 (m, 1H), 8.46 (m, 1H), 8.15 (m, 1H), 7.93 – 7.89 (m, 2H), 7.53 – 7.50 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 162.9, 142.1, 138.1, 137.9, 132.4, 128.2, 127.8, 125.9, 125.5, 123.7, 121.7, 120.1. IR (neat) 1421, 1190, 1086, 920, 750 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_8NOS$ $(M+H)^+$ 214.0327, found 214.0336.

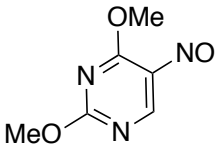


4-Nitrosobenzo[*b*]thiophene. General procedure B was employed using potassium benzo[*b*]thiophen-4-yltrifluoroborate (240 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 81% yield (132 mg, 0.81 mmol) as a yellow solid, mp 76–78 ºC, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^1H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8 Hz, 1H), 8.31 (m, 1H), 8.22 (d, *J* = 8 Hz, 1H), 7.86 (d, *J* = 5.5 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 160.6, 142.8, 134.1, 130.2, 127.0, 126.8, 124.2, 121.7. IR (neat) 1450, 1265, 861, 746 cm^{-1}. HRMS (ESI) *m/z* calcd. for C_8H_6NOS $(M+H)^+$ 164.0170, found 164.0168.

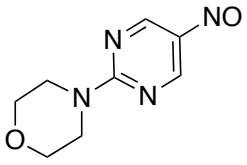


***tert*-Butyl 5-Nitroso-1*H*-indole-1-carboxylate.** General procedure B was employed using potassium (1-(*tert*-butoxycarbonyl)-1*H*-indol-5-yl)trifluoroborate (323 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 73% yield (180 mg, 0.73 mmol) as a green solid, mp 101–103 ºC, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^1H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 7.72

(d, J = 4 Hz, 1H), 7.61 (d, J = 8.5 Hz, 1H), 6.83 (d, J = 3.5 Hz, 1H), 1.70 (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.8, 149.2, 139.0, 130.6, 128.8, 119.7, 115.3, 115.1, 109.3, 85.2, 28.2. IR (neat) 1743, 1467, 1325, 1155, 1071, 721 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{13}H_{13}N_2O_3$ $(M-H)^-$ 245.0926, found 245.0932.

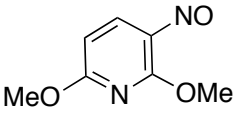


2,4-Dimethoxy-5-nitrosopyrimidine. General procedure B was employed using potassium (2,4-dimethoxypyrimidin-5-yl)trifluoroborate (246 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 82% yield (139 mg, 0.82 mmol) as a green solid, mp 78–80 ºC, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 4.33 (s, 3H), 4.16 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.6, 166.3, 149.6, 149.2, 56.5, 55.4. IR (neat) 1594, 1547, 1474, 1314, 1054, 796 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_6H_8N_3O_3$ $(M+H)^+$ 170.0566, found 170.0570.

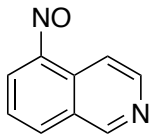


4-(5-Nitrosopyrimidin-2-yl)morpholine. General procedure B was employed using potassium trifluoro(2-morpholinopyrimidin-5-yl)borate (271 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 76% yield (148 mg, 0.76 mmol) as a green solid, mp 151–153 ºC, after column chromatography with CH_2Cl_2 as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 2H), 4.00 (t, J = 5 Hz, 4H), 3.79 (t, J = 5 Hz, 4H). ^{13}C NMR

(125.8 MHz, $CDCl_3$) δ 161.5, 154.8, 133.6, 66.6, 44.8. IR (neat) 2359, 1601, 1548, 1329, 1109, 790 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_{11}N_4O_2$ $(M+H)^+$ 195.0882, found 195.0884.

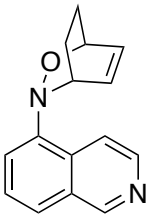


2,6-Dimethoxy-3-nitrosopyridine. General procedure B was employed using potassium (2,6-dimethoxypyridin-3-yl)trifluoroborate (245 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 72% yield (121 mg, 0.72 mmol) as a green solid, mp 95–97 ºC, after column chromatography with CH_2Cl_2 as eluent. ^1H NMR (500 MHz, $CDCl_3$) δ 6.87 (d, *J* = 8.5 Hz, 1H), 6.23 (d, *J* = 8.5 Hz, 1H), 4.37 (s, 3H), 4.11 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.3, 165.6, 151.2, 122.1, 103.3, 54.8. IR (neat) 1588, 1384, 1286, 1001, 825 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_9N_2O_3$ $(M+H)^+$ 169.0613, found 169.0618.



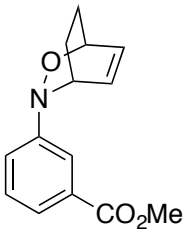
5-Nitrosoisoquinoline. General procedure B was employed using potassium trifluoro(isoquinolin-5-yl)borate (235 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 62% yield (NMR yield) as a yellow solid that upon exposure to air becomes black after column chromatography with EtOAc/CH_2Cl_2 (1:1) as eluent. ^1H NMR (500 MHz, $CDCl_3$) δ 9.49 (s, 1H), 9.41 (d, *J* = 6 Hz, 1H), 8.97 (d, *J* = 6 Hz, 1H), 8.40 (d, *J* = 8 Hz, 1H), 7.73 (t, *J* = 8 Hz, 1H), 7.14 (q, *J* = 1 and 8 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 157.7, 152.6, 147.2, 136.4, 131.5, 129.6, 126.2, 116.2, 114.0.

General Procedure C: One-pot Nitrosation / Diels-Alder: Adapted from a previously reported method.[79a] To a 20 mL glass microwave vial containing a solution of potassium organotrifluoroborate (1 mmol) in CH_3CN (3 mL, 0.33 M) was added 1,3-cyclohexadiene (114 μL, 1.2 mmol, 1.2 equiv). To the mixture was added $NOBF_4$ (120 mg, 1.03 mmol, 1.03 equiv) in one portion. The flask was then capped (exothermic reaction) and stirred for 2 h. To the crude mixture was added H_2O (20 mL) and EtOAc (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The product was purified by column chromatography using EtOAc/hexanes.

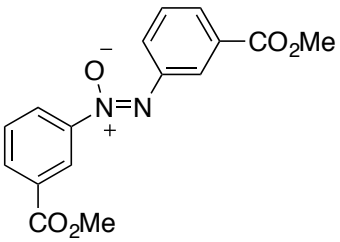


3-(Isoquinolin-5-yl)-2-Oxa-3-azabicyclo[2.2.2]oct-5-ene. General procedure C was employed using potassium trifluoro(isoquinolin-5-yl)borate (235 mg, 1 mmol), 1,3-cyclohexadiene (114 μL, 1.2 mmol, 1.2 equiv), and $NOBF_4$ (120 mg, 1.03 mmol). The desired pure product was obtained in 65% yield (155 mg, 0.65 mmol) as a yellow solid, mp 68–70 ºC, after column chromatography with EtOAc/hexanes (1:1) as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.51 (d, J = 6 Hz, 1H), 7.91 (d, J = 6 Hz, 1H), 7.64 (d, J = 8 Hz, 1H), 7.45 (t, J = 8 Hz, 1H), 7.37 (m, 1H), 6.75 (d, J = 2 and 6.5 Hz, 1H), 5.96 (t, J = 6.5 Hz, 1H), 4.82 (m, 1H), 4.34 (m, 1H), 2.51 (m, 1H), 2.36 (m, 1H), 1.60 (m, 1H), 1.50 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 152.6, 146.1, 142.5, 132.1, 129.1, 129.1, 128.9, 126.8, 123.1, 120.5, 116.0, 69.5, 56.9, 23.7, 22.0. IR (neat)

1579, 1371, 1271, 932, 838, 768 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{15}H_{15}N_2O$ $(M+H)^+$ 239.1184, found 239.1183.

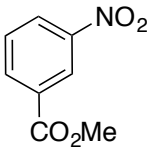


Methyl 3-(-2-oxa-3-azabicyclo[2.2.2]oct-5-en-3-yl)benzoate. General procedure C was employed using potassium trifluoro(3-(methoxycarbonyl)phenyl)borate (242 mg, 1 mmol), 1,3-cyclohexadiene (114 μL, 1.2 mmol, 1.2 equiv), and $NOBF_4$ (120 mg, 1.03 mmol). The desired pure product was obtained in 82% yield (201 mg, 0.82 mmol) as a yellow solid, mp 87–89 ºC, after column chromatography with EtOAc/hexanes (5:1) as eluent. ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.58 (m, 1H), 7.26 (t, *J* = 8 Hz, 1H), 7.19 (m, 1H), 6.57 (m, 1H), 6.12 (m, 1H), 4.73 (m, 1H), 4.48 (m, 1H), 3.88 (s, 3H), 2.29 – 2.22 (m, 2H), 1.57 (m, 1H), 1.38 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.3, 152.7, 131.9, 130.5, 129.9, 128.6, 123.3, 122.1, 118.4, 69.5, 56.6, 52.2, 24.0, 21.4. IR (neat) 1719, 1439, 1270, 944, 759 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{14}H_{16}NO_3$ $(M+H)^+$ 246.1130, found 246.1130.



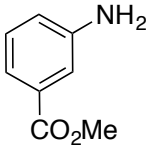
One-pot Procedure for Formation of Azoxy Compound: Synthesis of 1,2-Bis(3-(methoxycarbonyl)phenyl)diazene Oxide:[165] Adapted from a previously reported method.[166] To a 20 mL glass microwave vial containing potassium trifluoro(3-(methoxycarbonyl)phenyl)borate (242 mg, 1 mmol) in CH_3CN (3 mL, 0.33

M) was added $NOBF_4$ (120 mg, 1.03 mmol, 1.03 equiv) in one portion. After 30 sec the solvent was removed and EtOH was added (3.5 mL, 0.3M), followed by $(NH_4)_2SO_4$ (1 g, 5 mmol, 5 equiv) and $NaBH_4$ (661 mg, 3 mmol, 3 equiv). The flask was then capped (exothermic reaction) and stirred at rt for 30 min. The reaction mixture changed from green to yellow. To the crude mixture was added H_2O (20 mL) and EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by filtration through a short plug of silica topped with Celite using EtOAc afforded the pure product in 87% yield (137 mg, 0.44 mmol) as a yellow solid, mp 135–137 ºC (lit.[169] 135 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (d, J = 2 Hz, 1H), 8.77 (t, J = 2 Hz, 1H), 8.51 (m, 1H), 8.42 (m, 1H), 8.25 (d, J = 7.5 Hz, 1H), 8.07 (d, J = 7.5 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 3.99 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.5, 165.8, 148.4, 143.9, 132.9, 131.4, 131.1, 130.8, 129.6, 129.3, 129.0, 127.2, 126.7, 123.7, 52.7, 52.5. IR (neat) 1726, 1466, 1301, 1267, 1083, 753 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}N_2O_5$ $(M+H)^+$ 315.0981, found 315.0981.



Procedure for Formation of Nitro Compounds: Synthesis of Methyl 3-Nitrobenzoate:[167] Adapted from a previously reported method.[79b] To a 20 mL glass microwave vial containing potassium trifluoro(3-(methoxycarbonyl)phenyl)borate (242 mg, 1 mmol), in CH_3CN (3 mL, 0.33 M) was added $NOBF_4$ (120 mg, 1.03 mmol, 1.03 equiv) in one portion. After 30 sec the crude mixture was filtered through a plug of silica

topped with Celite using CH_2Cl_2, the solvent was removed, and acetone : H_2O (1:1, 5 mL) was added. To the solution was then added Oxone (461 mg, 1.5 mmol, 1.5 equiv). The flask was then capped and stirred at 60 ºC for 2 h. The reaction solution changed from green to yellow. To the crude mixture was added H_2O (20 mL) and EtOAc (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by filtration through a short plug of silica topped with Celite using EtOAc afforded the pure product in 86% yield (156 mg, 0.86 mmol) as a yellow solid, mp 75–77 ºC (lit.[171] 77–79 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (t, J = 1.5 Hz, 1H), 8.42 (m, 1H), 8.37 (m, 1H), 7.67 (t, J = 8.5 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.9, 148.3, 135.2, 131.9, 129.6, 127.4, 124.6, 52.8. IR (neat) 3098, 1718, 1527, 1350, 1290, 1269, 1134, 720 cm^{-1}.



One-pot Procedure for Formation of Aniline Compounds: Synthesis of Methyl 3-Aminobenzoate:[168] Adapted from a previously reported method.[169] To a 20 mL glass microwave vial containing potassium trifluoro(3-(methoxycarbonyl)phenyl)borate (242 mg, 1 mmol) in CH_3CN (3 mL, 0.33 M) was added nitrosonium tetrafluoroborate (120 mg, 1.03 mmol, 1.03 equiv) in one portion. EtOH (2 mL) and $SnCl_2$•$2H_2O$ (1.13 g, 5 mmol, 5 equiv) were added after 30 sec. The flask was then capped, and the reaction was stirred at 80 ºC for 2 h. To the crude mixture was added 5% $NaHCO_3$ (3 mL, or enough to make the pH slightly basic, 7–9). The resulting emulsion was filtered, and the solid was washed with H_2O (10 mL) and EtOAc

(10 mL). The layers of the filtrate were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by filtration through a short plug of silica topped with Celite using EtOAc afforded the pure product as a yellow oil in 72% yield (109 mg, 0.72 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (m, 1H), 7.35 (t, J = 2 Hz, 1H), 7.21 (t, J = 8 Hz, 1H), 6.85 (m, 1H), 3.89 (s, 3H), 3.79 (brs, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.4, 146.6, 131.3, 129.4, 119.8, 119.5, 115.9, 52.2. IR (neat) 3372, 2951, 1710, 1603, 1239, 753 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_{10}NO_2$ $(M+H)^+$ 152.0712, found 152.0713.

2.8.3 Experimental for section 2.7

General Considerations

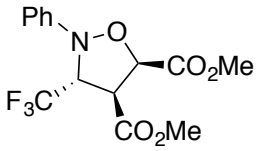
Reagents: Trifluoroethylamine hydrochloride was purchased from Matrix Scientific and used as received. Nitrosobenzene was purchased from TCI America and used without purification. Dichloroethane, sodium nitrite, and alkene reagents were purchased from commercial sources and used as received. Nitrosoarene starting materials were prepared by our previously reported method. All products were purified using Combiflash chromatography with gradient hexanes : EtOAc as eluent (the gradient consisted of 5 min hexanes, 5 min 10 % EtOAc , 5 min 20% EtOAc, and 5 min 100% EtOAc)

Analytical Methods: Melting points (^{o}C) are uncorrected. All pure compounds were characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectra, IR spectroscopy, high-resolution mass spectrometry (HRMS) and melting point determination (for solids). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 500.4, 125.8, and 470.8 MHz, respectively. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm).

General procedure A: To a glass vessel capable of being sealed with a Teflon cap (for microwave vials) was added trifluoroethylamine hydrochloride (0.27 g, 2 mmol, 2 equiv) and $NaNO_2$ (0.17 g, 2.4 mmol, 2.4 equiv). The vessel was sealed and cooled in an ice bath. $ClCH_2CH_2Cl$ (5 mL, 0.2 M) and H_2O (0.17 mL) were added via syringe. The reaction was stirred for 2 h at 0 ºC. After this time, the yellow mixture was cooled to -78 ºC. The vial was opened and the corresponding nitrosoarene (1 mmol, 1 equiv) and alkene (1.1 mmol, 1.1 equiv) were added. The vial was sealed, and the reaction was stirred at 70 ºC. After 16 h, the reaction was cooled to rt. The pressure was released through a needle insertion and the vial was opened. H_2O (10 mL) was added, and the

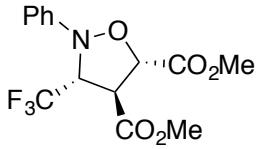
contents of the vial were transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude mixture was purified to afford the desired pure product.

Procedure for 1 g Scale Reaction:



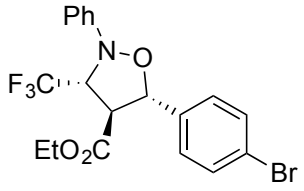
3a **Dimethyl 2-Phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3a)**. To a 200 mL round bottom flask was added trifluoroethylamine hydrochloride (2.71 g, 20 mmol, 2 equiv) and $NaNO_2$ (1.70 g, 24 mmol, 2.4 equiv). The flask was capped with a rubber septum and cooled in an ice bath. $ClCH_2CH_2Cl$ (50 mL) and H_2O (1.7 mL) were added via syringe. The reaction was stirred for 3 h at 0 ºC. After this time, the yellow mixture was cooled to -78 ºC. The flask was opened, and nitrosobenzene (1.07 g, 10 mmol, 1 equiv) and dimethyl maleate (1.56 g, 11 mmol, 1.1 equiv) were added. The flask was connected to a reflux condenser, and the reaction was stirred at 70 ºC. After 24 h, the reaction was cooled to rt. H_2O (100 mL) was added, and the contents of the flask were transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude mixture was purified to afford the desired pure product in 91% yield (3.0 g, 9.1 mmol) as a light yellow solid, mp 73 – 74 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.07 (m, 2H), 7.00 – 6.95 (m, 1H), 5.00 (d, J = 7.4 Hz, 1H), 4.96 – 4.87 (m, 1H),

4.00 (dd, J = 7.3, 6.1 Hz, 1H), 3.66 (s, 3H), 3.40 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.0, 167.58, 149.9, 129.1, 124.8 (d, J = 279.4 Hz), 123.0, 113.7, 78.5, 67.0 (q, J = 32.0 Hz), 53.1, 52.6, 52.2; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.8; IR (neat) 1752, 1732, 1595, 1491, 1228, 1165, 757 cm^{-1}; HRMS (ESI) *m/z* calcd. For $C_{14}H_{15}NO_5F_3$ $(M + H)^+$ 334.0902, found 334.0913.



3b

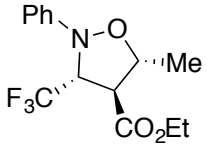
Dimethyl 2-Phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3b). The general procedure A was followed using nitrosobenzene (0.11 g, 1 mmol) and dimethyl fumarate (0.16 g, 1.1 mmol, 1.1 equiv). The product was obtained in 80% yield (0.26 g, 0.80 mmol), along with ~10% of a side product impurity (by ^{1}H NMR), as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 2H), 7.12 – 7.07 (m, 3H), 4.97 (d, J = 7.7 Hz, 1H), 4.75 (m, 1H), 4.11 (dd, J = 7.7, 4.2 Hz, 1H), 3.87 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.7, 167.0, 148.4, 129.4, 124.2 (d, J = 276.8), 123.8, 114.5, 78.9, 69.9 (q, J = 32.2 Hz), 53.2, 53.1, 52.7; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.6; IR (neat) 1759, 1742, 1599, 1493, 1284, 1229, 1171, 1134, 758 cm^{-1}; HRMS (ESI) *m/z* calcd. For $C_{14}H_{15}NO_5F_3$ $(M + H)^+$ 334.0902, found 334.0897.



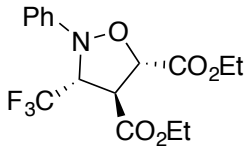
3c

Ethyl 5-(4-Bromophenyl)-2-phenyl-3-(trifluoromethyl)isoxazolidine-4-carboxylate (3c). The general procedure A was followed using nitrosobenzene (0.11 g, 1 mmol) and ethyl (*E*)-3-(4-bromophenyl)acrylate

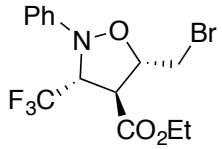
(0.28 g, 1.1 mmol, 1.1 equiv). The pure product was obtained in 78% yield (0.34 g, 0.78 mmol) as a light yellow solid, mp 96 – 98 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.54 (m, 2H), 7.37 – 7.32 (m, 4H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 5.15 (d, *J* = 9.1 Hz, 1H), 4.85 (qd, *J* = 7.5, 5.2 Hz, 1H), 4.14 – 4.07 (m, 2H), 3.64 (dd, *J* = 9.1, 5.0 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.9, 149.4, 134.4, 132.2, 129.7, 128.9, 125.0 (d, *J* = 279.3 Hz), 123.6, 123.3, 114.1, 83.0, 70.7 (q, *J* = 31.9 Hz), 62.4, 58.4, 14.1; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.6; IR (neat) 1720, 1596, 1488, 1282, 1218, 1161, 1138, 756 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{19}H_{18}NO_3F_3Br$ $(M + H)^+$ 444.0422, found 444.0418.



3d **Ethyl 5-Methyl-2-phenyl-3-(trifluoromethyl)isoxazolidine-4-carboxylate (3d).** The general procedure A was followed using nitrosobenzene (0.11 g, 1 mmol) and ethyl (*E*)-but-2-enoate (0.13 g, 1.1 mmol, 1.1 equiv). The pure product was obtained in 85% yield (0.26 g, 0.85 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 2H), 7.11 – 7.04 (m, 2H), 7.00 (m, 1H), 4.76 (m, 1H), 4.25 (dt, *J* = 15.1, 5.9 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.29 (dd, *J* = 9.2, 5.4 Hz, 1H), 1.55 (d, *J* = 5.9 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.1, 149.9, 129.5, 125.1 (d, *J* = 279.0 Hz), 122.8, 114.0, 78.3, 70.4 (q, *J* = 31.9 Hz), 62.2, 57.3, 17.1, 14.1; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.9; IR (neat) 1737, 1598, 1490, 1283, 1171, 1135, 757 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{14}H_{17}NO_3F_3$ $(M + H)^+$ 304.1161, found 304.1165.

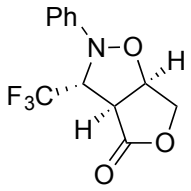


3e **Diethyl 2-Phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3e).** The general procedure A was followed using nitrosobenzene (0.11 g, 1 mmol) and diethyl fumarate (0.19, 1.1 mmol, 1.1 equiv). The product was obtained in 75% yield (0.27 g, 0.75 mmol), along with ~5% of a side product impurity (by ^{1}H NMR), as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.7 Hz, 2H), 7.13 – 7.10 (m, 2H), 7.07 (m, 1H), 4.95 (d, *J* = 7.6 Hz, 1H), 4.74 (m, 1H), 4.38 – 4.31 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 4.07 (dd, *J* = 7.6, 4.1 Hz, 1H), 1.36 (td, *J* = 7.1, 0.7 Hz, 3H), 1.16 (td, *J* = 7.1, 0.7 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.3, 166.7, 148.6, 129.3, 124.2 (d, *J* = 279.3 Hz), 123.7, 114.6, 79.1, 70.1 (q, *J* = 32.2 Hz), 62.4, 62.4, 53.0, 13.9, 13.7; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.5; IR (neat) 1741, 1595, 1491, 1372, 1280, 1220, 1170, 1136, 758 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{16}H_{19}NO_5F_3$ $(M + H)^+$ 362.1215, found 362.1206.

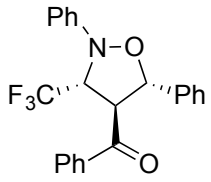


3f **Ethyl 5-(Bromomethyl)-2-phenyl-3-(trifluoromethyl)isoxazolidine-4-carboxylate (3f).** The general procedure A was followed using nitrosobenzene (0.11 g, 1 mmol) and ethyl (*E*)-4-bromobut-2-enoate (151 μL, 1.1 mmol, 1.1 equiv). After column chromatography the pure product was obtained in 81% yield (0.31 g, 0.81 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, J = 8.7, 7.4 Hz, 2H), 7.13 – 6.98 (m, 3H), 4.79 (qd, *J* = 7.5, 5.1 Hz, 1H), 4.46 (m, 1H), 4.14 (m, 2H), 3.82 (dd, *J* = 11.4,

3.5 Hz, 1H), 3.67 (dd, *J* = 11.4, 6.3 Hz, 1H), 3.58 (dd, *J* = 9.0, 5.0 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.1, 149.1, 129.4, 124.5 (d, *J* = 279.4 Hz), 123.2, 113.9, 80.3, 70.3 (q, *J* = 32.1 Hz), 62.4, 53.9, 29.3, 13.8; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.6; IR (neat) 1736, 1593, 1490, 1281, 1169, 1133, 757 cm^{-1}; HRMS (ESI) *m/z* calcd. For $C_{14}H_{16}NO_3F_3Br$ $(M + H)^+$ 382.0266, found 382.0264.

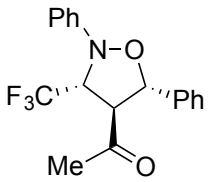


3g **2-Phenyl-3-(trifluoromethyl)tetrahydrofuro[3,4-*d*]isoxazol-4(2*H*)-one (3g).** The general procedure A was followed using nitrosobenzene (0.11 g, 1 mmol) and furan-2(5*H*)-one (92.5 mg, 1.1 mmol, 1.1 equiv). The pure product was obtained in 78% yield (0.21 g, 0.71 mmol) as a light yelow solid, mp 93 – 94 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 4.91 (d, *J* = 8.6 Hz, 1H), 4.51 – 4.46 (m, 2H), 4.01 (dd, *J* = 10.2, 4.2 Hz, 1H), 3.87 (m, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 172.3, 147.9, 129.4, 124.9, 123.8, 122.6, 114.2, 99.9, 77.5, 73.2 (q, *J* = 31.2 Hz), 69.7, 44.5; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 75.0; IR (neat) 2359, 2337, 1770, 1597, 1488, 1391, 1278, 1203, 1174, 1138, 753, 644 cm^{-1}; HRMS (ESI) *m/z* calcd. For $C_{12}H_{11}NO_3F_3$ $(M + H)^+$ 274.0691, found 274.0692.



3h

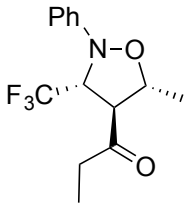
(2,5-Diphenyl-3-(trifluoromethyl)isoxazolidin-4-yl)(phenyl)methanone (3h). The general procedure A was followed using nitrosobenzene (0.11 g, 1 mmol) and chalcone (0.23 g, 1.1 mmol, 1.1 equiv). The pure product was obtained in 55% yield (0.22 g, 0.55 mmol) as a light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 3H), 7.38 – 7.33 (m, 7H), 7.25 – 7.21 (m, 2H), 7.20 – 7.16 (m, 2H), 7.07 (m, 1H), 5.11 (m, 1H), 5.01 (d, *J* = 9.2 Hz, 1H), 4.75 (dd, *J* = 9.2, 5.2 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 194.6, 149.7, 135.1, 134.7, 134.1, 129.5, 129.4, 128.9, 128.9, 128.5, 127.1, 126.3, 122.8, 113.9, 85.8, 71.1 (q, *J* = 31.5 Hz), 61.4; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.0; IR (neat) 1682, 1595, 1492, 1284, 1221, 1166, 1129, 757, 692 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{23}H_{19}NO_2F_3$ $(M + H)^+$ 398.1368, found 398.1366.



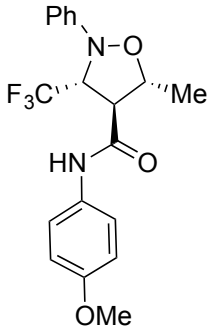
3i

1-(-2,5-Diphenyl-3-(trifluoromethyl)isoxazolidin-4-yl)ethan-1-one (3i). The general procedure A was followed using nitrosobenzene (0.11 g, 1 mmol) and (*E*)-4-phenylbut-3-en-2-one (0.16 g, 1.1 mmol, 1.1 equiv). After column chromatography the pure product was obtained in 62% yield (0.21 g, 0.62 mmol) as a light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.50 (m, 2H), 7.47 – 7.44 (m, 3H), 7.34 – 7.31 (m, 2H), 7.11 – 7.10 (m, 2H), 7.03 (m, 1H), 4.96 (d, *J* = 9.5 Hz, 1H), 4.88 (m, 1H), 3.94 (dd,

J = 9.5, 5.4 Hz, 1H), 1.96 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 201.8, 149.7, 134.8, 130.1, 129.6, 129.4, 127.7, 125.3 (d, *J* = 279.1 Hz), 123.1, 114.1, 84.1, 69.7 (q, *J* = 31.5 Hz), 66.4, 30.52; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.4; IR (neat) 1720, 1597, 1492, 1282, 1220, 1167, 1130, 757, 694 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{18}H_{17}NO_2F_3$ $(M + H)^+$ 336.1211, found 336.1212.

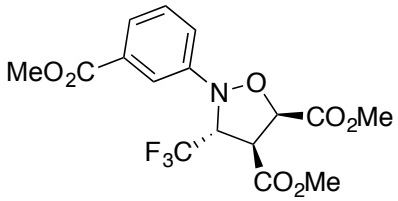


3j **1-(5-Methyl-2-phenyl-3-(trifluoromethyl)isoxazolidin-4-yl)propan-1-one (3j).** The general procedure A was followed using nitrosobenzene (0.11 g, 1 mmol) and (*E*)-hex-4-en-3-one (0.11 g, 1.1 mmol, 1.1 equiv). The pure product was obtained in 80% yield (0.23 g, 0.80 mmol) as a light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 2H), 7.06 – 7.03 (m, 2H), 7.00 (t, *J* = 7.3 Hz, 1H), 4.70 (qd, *J* = 7.6, 5.5 Hz, 1H), 4.15 (dq, *J* = 11.8, 5.9 Hz, 1H), 3.44 (dd, *J* = 9.2, 5.3 Hz, 1H), 2.55 – 2.41 (m, 2H), 1.54 (d, *J* = 5.9 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 204.9, 149.6, 129.2, 125.0 (q, *J* = 278.9 Hz) 122.6, 113.8, 78.1, 70.08 (q, *J* = 31.5 Hz), 63.9, 36.4, 17.1, 7.2; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.7; IR (neat) 1720, 1595, 1489, 1284, 1135, 908, 731, 694 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{14}H_{17}NO_2F_3$ $(M + H)^+$ 288.1211, found 288.1215.



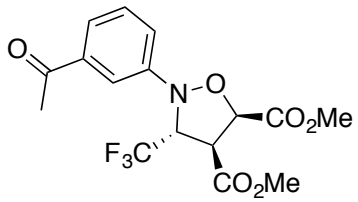
3k

***N*-(4-Methoxyphenyl)-5-methyl-2-phenyl-3-(trifluoromethyl)isoxazolidine-4-carboxamide (3k).** The general procedure A was followed using nitrosobenzene (0.11 g, 1 mmol) and (*E*)-*N*-(4-methoxyphenyl)but-2-enamide (0.21 g, 1.1 mmol, 1.1 equiv). The pure product was obtained in 71% yield (0.27 g, 0.71 mmol) as a white solid, mp 168 – 170 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.9 Hz, 2H), 4.73 (m, 1H), 4.36 (dq, *J* = 11.9, 5.9 Hz, 1H), 3.77 (s, 3H), 3.15 (dd, *J* = 9.3, 6.0 Hz, 1H), 1.43 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.9, 157.1, 150.0, 129.7, 129.3, 125.1 (d, *J* = 278.7 Hz), 122.8, 122.3, 114.3, 114.1, 113.8, 79.2, 71.6 (q, *J* = 31.3 Hz), 60.1, 55.4, 16.0; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.4; IR (neat) 3261, 1653, 1602, 1551, 1512, 1280, 1239, 1170, 1136, 760, 686 cm^{-1}; HRMS (ESI) *m/z* calcd. For $C_{19}H_{20}N_2O_3F_3$ $(M + H)^+$ 381.1426, found 381.1438.



3l

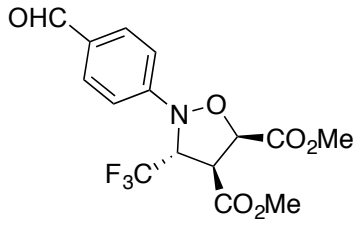
Dimethyl 2-(3-(Methoxycarbonyl)phenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3l). The general procedure A was followed using methyl 3-nitrosobenzoate (0.16 g, 1 mmol) and dimethyl maleate (0.16 g, 1.1 mmol, 1.1 equiv). The pure product was obtained in 94% yield (0.37 g, 0.94 mmol) as a light yellow solid, mp 88 – 89 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 1.3 Hz, 1H), 7.64 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.22 (m, 1H), 5.02 (d, *J* = 7.5 Hz, 1H), 4.93 (m, 1H), 4.02 (m, 1H), 3.88 (s, 3H), 3.65 (s, 3H), 3.42 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.8, 167.1, 166.5, 149.9, 130.8, 129.0, 124.5 (d, *J* = 279.4 Hz), 123.7, 117.6, 114.0, 78.3, 66.7 (q, *J* = 32.4 Hz), 52.9, 52.4, 52.0, 51.9; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.8; IR (neat) 1755, 1724, 1586, 1438, 1258, 1221, 1172, 1137, 756 cm^{-1}; HRMS (ESI) *m/z* calcd. For $C_{16}H_{17}NO_7F_3$ $(M + H)^+$ 392.0957, found 392.0954.



3m

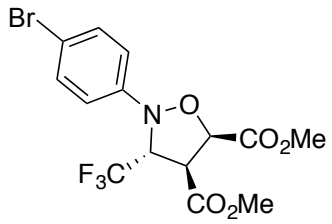
Dimethyl 2-(3-Acetylphenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3m). The general procedure A was followed using 1-(3-nitrosophenyl)ethan-1-one (0.15 g, 1 mmol) and dimethyl maleate (0.16 g, 1.1 mmol, 1.1 equiv). The pure product was obtained in 90% yield (0.34 g, 0.90 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (m, 1H), 7.55 (dd, *J* =

7.6, 0.8 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.22 (dd, *J* = 8.2, 2.5 Hz, 1H), 5.03 (d, *J* = 7.5 Hz, 1H), 4.92 (dd, *J* = 12.7, 6.3 Hz, 1H), 4.02 (dd, *J* = 7.4, 6.0 Hz, 1H), 3.65 (s, 3H), 3.43 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 197.5, 167.8, 167.1, 150.1, 137.7, 129.2, 124.4 (d, *J* = 279.7 Hz), 122.7, 117.8, 112.7, 78.3, 66.8 (q, *J* = 32.2 Hz), 52.9, 52.5, 51.9, 26.5; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.8; IR (neat) 1754, 1686, 1583, 1438, 1252, 1217, 1171, 1137, 788 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{16}H_{17}NO_6F_3$ (M + H)$^+$ 376.1008, found 376.1013.



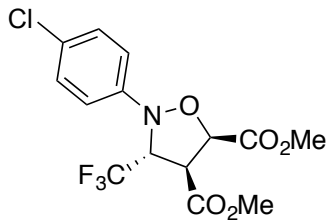
3n

Dimethyl 2-(4-Formylphenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3n). The general procedure A was followed using 4-nitrosobenzaldehyde (0.13 g, 1 mmol) and dimethyl maleate (0.16 g, 1.1 mmol, 1.1 equiv). The pure product was obtained in 85% yield (0.26 g, 0.85 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.81 (d, *J* = 8.9 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 5.06 (d, *J* = 7.6 Hz, 1H), 5.00 (m, 1H), 4.06 (dd, *J* = 7.4, 6.2 Hz, 1H), 3.70 (s, 3H), 3.45 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 190.6, 167.5, 166.9, 154.2, 131.2, 130.8, 124.3 (d, *J* = 279.7 Hz), 112.4, 78.4, 65.8 (q, *J* = 32.8 Hz), 53.1, 52.7, 51.9; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.8; IR (neat) 1740, 1696, 1600, 1507, 1440, 1268, 1217, 1168, 1127, 817 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{15}H_{15}NO_6F_3$ (M + H)$^+$ 362.0851, found 362.0848.



3o

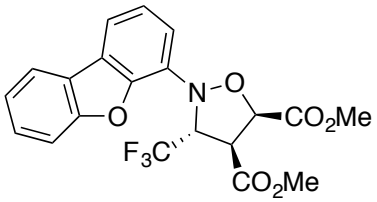
Dimethyl 2-(4-Bromophenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3o). The general procedure A was followed using 1-bromo-4-nitrosobenzene (0.19 g, 1 mmol) and dimethyl maleate (0.16 g, 1.1 mmol, 1.1 equiv). The pure product was obtained in 96% yield (0.39 g, 0.96 mmol) as a light yellow solid, mp 99 – 100 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 9.0 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 5.00 (d, J = 7.5 Hz, 1H), 4.83 (m, 1H), 3.99 (dd, J = 7.4, 5.9 Hz, 1H), 3.70 (s, 3H), 3.49 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.6, 167.1, 148.8, 131.7, 124.4 (q, J = 279.4 Hz), 115.3, 78.3, 66.8 (q, J = 32.1 Hz), 52.9, 52.5, 51.9; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.7; IR (neat) 1747, 1730, 1487, 1354, 1224, 1168, 1128, 648 cm^{-1}; HRMS (ESI) *m/z* calcd. For $C_{14}H_{13}NO_5F_3NaBr$ $(M + Na)^+$ 433.9827, found 433.9833.



3p

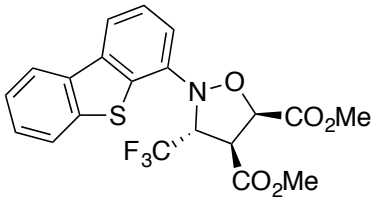
Dimethyl 2-(4-Chlorophenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3p). The general procedure A was followed using 1-chloro-4-nitrosobenzene (0.14 g, 1 mmol) and dimethyl maleate (0.16 g, 1.1 mmol, 1.1 equiv). The pure product was obtained in 91% yield (0.33 g, 0.91 mmol) as a light yellow solid, mp 103 – 104 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 9.1

Hz, 2H), 7.00 (d, J = 9.1 Hz, 2H), 5.00 (d, J = 7.4 Hz, 1H), 4.83 (m, 1H), 3.99 (dd, J = 7.4, 5.9 Hz, 1H), 3.68 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.6, 167.2, 148.3, 128.8, 124.4 (d, J = 279.4 Hz), 123.3, 115.0, 78.3, 66.9 (q, J = 32.1 Hz), 52.9, 52.5, 51.9; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.7; IR (neat) 1746, 1732, 1490, 1352, 1225, 1168, 1128, 648 cm^{-1}; HRMS (ESI) m/z calcd. For $C_{14}H_{13}NO_5F_3NaCl$ $(M + Na)^+$ 390.0332, found 390.0331.



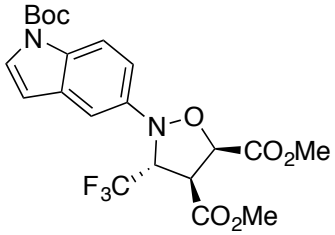
3q

Dimethyl 2-(Dibenzo[*b*,*d*]furan-4-yl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3q). The general procedure A was followed using 4-nitrosodibenzo[*b*,*d*]furan (0.20 g, 1 mmol) and dimethyl maleate (0.16 g, 1.1 mmol, 1.1 equiv). The pure product was obtained in 81% yield (0.34 g, 0.81 mmol) as a light yellow solid, mp 85 – 87 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, J = 7.7, 0.5 Hz, 1H), 7.67 (dd, J = 7.7, 1.0 Hz, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.50 (dd, J = 8.0, 0.9 Hz, 1H), 7.45 (m, 1H), 7.33 (m, 1H), 7.27 (dd, J = 15.8, 8.0 Hz, 1H), 5.63 (m, 1H), 5.10 (d, J = 7.7 Hz, 1H), 4.06 (dd, J = 7.7, 4.4 Hz, 1H), 3.64 (s, 3H), 3.50 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.9, 167.8, 155.9, 145.1, 133.7, 127.3, 125.4, 124.30 (d, J = 280.4 Hz), 123.2, 123.0, 122.9, 120.6, 116.7, 115.9, 111.9, 78.5, 66.0 (q, J = 31.5 Hz), 52.9, 52.4, 51.8; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.4; IR (neat) 1760, 1735, 1452, 1347, 1218, 1190, 1133, 758 cm^{-1}; HRMS (ESI) m/z calcd. For $C_{20}H_{17}NO_6F_3$ $(M + H)^+$ 424.1008, found 424.1006.



3r

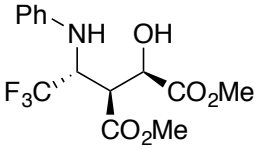
Dimethyl 2-(Dibenzo[*b*,*d*]thiophen-4-yl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3r). The general procedure A was followed using 4-nitrosodibenzo[*b*,*d*]thiophene (0.21 g, 1 mmol) and dimethyl maleate (0.16 g, 1.1 mmol, 1.1 equiv). After column chromatography the pure product was obtained in 71% yield (0.31 g, 0.71 mmol) a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (m, 1H), 7.99 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.88 (m, 1H), 7.53 – 7.40 (m, 4H), 5.24 – 5.16 (m, 1H), 5.09 (d, *J* = 7.6 Hz, 1H), 4.09 (dd, *J* = 7.6, 5.0 Hz, 1H), 3.76 (s, 3H), 3.46 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.0, 167.4, 142.8, 140.1, 137.4, 135.0, 132.9, 126.9, 125.0, 124.2 (d, *J* = 279.8 Hz), 124.2, 122.4, 121.6, 119.1, 115.8, 78.4, 66.0 (q, *J* = 31.3 Hz), 53.1, 52.4, 51.9; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 73.9; IR (neat) 1738, 1443, 1399, 1243, 1172, 1137, 753 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{20}H_{17}NO_5F_3S$ $(M + H)^+$ 440.0780, found 440.0784.



3s

Dimethyl 2-(1-(*tert*-Butoxycarbonyl)-1*H*-indol-5-yl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3s). The general procedure A was followed using *tert*-butyl 5-nitroso-1*H*-indole-1-carboxylate (0.25 g, 1 mmol) and

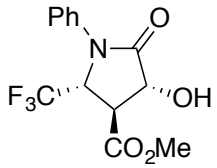
dimethyl maleate (0.16 g, 1.1 mmol, 1.1 equiv). The pure product was obtained in 76% yield (0.36 g, 0.76 mmol) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 3.2 Hz, 1H), 7.35 (d, *J* = 2.3 Hz, 1H), 7.15 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.52 (d, *J* = 3.7 Hz, 1H), 5.03 (d, *J* = 7.3 Hz, 1H), 4.90 (m, 1H), 4.00 (dd, *J* = 7.3, 5.5 Hz, 1H), 3.71 (s, 3H), 3.49 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.8, 167.8, 149.6, 145.2, 132.0, 130.9, 126.9, 124.6 (d, *J* = 279.4 Hz), 115.4, 113.0, 107.3, 107.2, 83.7, 78.2, 68.0 (q, *J* = 31.2 Hz), 53.0, 52.5, 52.1, 28.1; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.4; IR (neat) 1733, 1469, 1372, 1249, 1167, 1134, 767 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{21}H_{24}N_2O_7F_3$ $(M + H)^+$ 473.1536, found 473.1538.



4a

Dimethyl 2-Hydroxy-3-(2,2,2-trifluoro-1-(phenylamino)ethyl)succinate (4a). Based on literature procedure,[92] to a 25 mL round bottom flask was added dimethyl-2-phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate, **3a** (0.1 g, 0.3 mmol) and H_2O (3 mL). To the suspension was added zinc powder (0.79 g, 12 mmol, 40 equiv) and AcOH (3 mL). The reaction was stirred at rt for 10 min. The crude reaction mixture was then diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude mixture was purified by combiflash chromatography (using the previously described hexane/EtOAc gradient) to afford the desired pure product in 85% yield (85 mg, 0.26 mmol) as a white solid, mp 90 – 91 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.9 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 2H), 4.84 (m, 2H), 4.72 (dd, *J* = 6.3, 2.5 Hz, 1H), 3.79

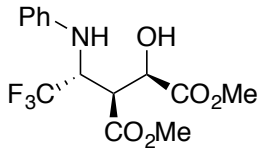
(s, 3H), 3.60 (d, J = 6.4 Hz, 1H), 3.58 (s, 3H), 3.50 (dd, J = 5.2, 2.6 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 172.7, 169.4, 146.0, 129.2, 125.4 (d, J = 284.3 Hz), 119.2, 113.8, 68.8, 55.9 (q, J = 29.9 Hz), 53.0, 52.4, 46.8; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 73.2; IR (neat) 3505, 3391, 1730, 1724, 1608, 1440, 1258, 1109, 1133, 636 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{14}H_{16}NO_5F_3Na$ $(M + Na)^+$ 358.0878, found 358.0870.



4b

Methyl 4-Hydroxy-5-oxo-1-phenyl-2-(trifluoromethyl)pyrrolidine-3-carboxylate (4b). To a 25 mL round bottom flask was added dimethyl-2-phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate, **3a** (0.1 g, 0.3 mmol) and H_2O (3 mL). To the suspension was added zinc powder (0.79 g, 12 mmol, 40 equiv) and AcOH (3 mL). The reaction was stirred at 40 ºC for 2 h. The crude reaction mixture was then diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude mixture was purified by Combiflash chromatography (using the previously described hexane/EtOAc gradient) to afford the desired pure product in 97% yield (88 mg, 0.29 mmol) as a white solid, mp 158 – 159 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (t, J = 7.6 Hz, 2H), 7.39 – 7.31 (m, 3H), 4.98 (m, 1H), 4.66 (m, 1H), 4.22 (s, 1H), 3.88 (s, 3H), 3.32 (t, J = 6.4 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 172.2, 170.6, 135.3, 129.3, 128.2, 125.6, 123.6 (d, J = 282.6 Hz), 71.8, 60.2 (q, J = 31.5 Hz), 53.3, 46.1; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 73.2; IR (neat) 3301, 1732, 1709, 1692, 1440, 1243, 1109, 1137, 646 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{13}H_{13}NO_4F_3$ $(M + H)^+$ 304.0797, found 304.0799.

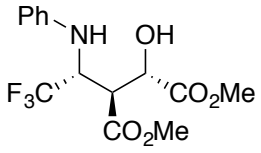
General procedure B: One-pot 1,3-dipolar cycloaddition / N–O bond cleavage: To a 50 mL round bottom flask was added 2,2,2-trifluoroethylamine hydrochloride (0.27 g, 2 mmol, 2 equiv) and $NaNO_2$ (0.17 g, 2.4 mmol, 2.4 equiv). The vessel was sealed and cooled in an ice bath. $ClCH_2CH_2Cl$ (5 mL, 0.2 M) and H_2O (0.17 mL) were added via syringe. The reaction was stirred for 2 h at 0 ºC. After this time, the yellow mixture was then cooled to -78 ºC. The flask was opened and nitrosobenzene (0.11 g, 1 mmol) and the corresponding alkene (0.11 mmol, 1.1 equiv) were added. The flask was connected to a reflux condenser and the reaction was stirred at 70 ºC. After 16 h, the reaction was cooled to rt, and the solvent was removed under reduced pressure and H_2O (3 mL) was added to the crude mixture. To the suspension was added zinc powder (0.79 g, 12 mmol, 40 equiv) and AcOH (3 mL). The reaction was stirred at room temperature for 10 min. The crude reaction mixture was then diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude mixture was purified by Combiflash chromatography (using the previously described hexane/EtOAc gradient).



4a

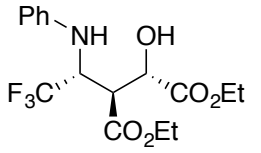
Dimethyl 2-Hydroxy-3-(2,2,2-trifluoro-1-(phenylamino)ethyl)succinate (4a). The general procedure B was followed using dimethyl maleate (0.16 g, 1.1 mmol, 1.1 equiv). The product was obtained in 80% yield (0.27 g, 0.80 mmol) as a white solid, mp 90 – 91 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.9 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 2H), 4.84 (m, 2H), 4.72 (dd, *J* = 6.3, 2.5 Hz, 1H), 3.79 (s, 3H), 3.60 (d, *J* = 6.4 Hz, 1H), 3.58 (s, 3H), 3.50 (dd, *J*

= 5.2, 2.6 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 172.7, 169.4, 146.0, 129.2, 125.4 (d, *J* = 284.3 Hz), 119.2, 113.8, 68.8, 55.9 (q, *J* = 29.9 Hz), 53.0, 52.4, 46.8; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 73.2; IR (neat) 3505, 3391, 1730, 1724, 1608, 1440, 1258, 1109, 1133, 636 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{14}H_{16}NO_5F_3Na$ $(M + Na)^+$ 358.0878, found 358.0870.



4c

Dimethyl 2-Hydroxy-3-(2,2,2-trifluoro-1-(phenylamino)ethyl)succinate (4c). The general procedure B was followed using dimethyl fumarate (0.16 g, 1.1 mmol, 1.1 equiv). The product was obtained in 82% yield (0.27 g, 0.82 mmol) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.9 Hz, 2H), 6.82 (m, 1H), 6.74 – 6.71 (m, 2H), 4.85 (m, 1H), 4.65 (s, 1H), 3.97 (d, *J* = 11.2 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.44 (dd, *J* = 8.9, 3.1 Hz, 1H), 3.35 (s, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 172.7, 170.6, 145.6, 129.6, 125.7 (d, *J* = 284.6 Hz), 120.0, 114.2, 69.6, 54.4 (q, *J* = 29.5 Hz), 53.2, 52.9, 48.6; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.1; IR (neat) 3497, 3369, 1733, 1719, 1605, 1437, 1242, 1122, 752 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{14}H_{17}NO_5F_3$ $(M + H)^+$ 336.1059, found 336.1051.



4d

Diethyl 2-hydroxy-3-(2,2,2-trifluoro-1-(phenylamino)ethyl)succinate (4d). The general procedure B was followed using

Diethyl fumarate (0.19 g, 1.1 mmol, 1.1 equiv). The product was obtained in 78% yield (0.28 g, 0.78 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.74 – 6.70 (m, 2H), 4.85 (m, 1H), 4.66 (d, *J* = 2.8 Hz, 1H), 4.34 – 4.15 (m, 4H), 4.01 (d, *J* = 11.0 Hz, 1H), 3.43 (dd, *J* = 8.5, 3.0 Hz, 1H), 3.27 (s, 1H), 1.29 – 1.22 (m, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 172.3, 170.0, 145.7, 129.5, 125.7 (d, *J* = 284.4 Hz), 119.9, 114.2, 69.7, 62.7, 62.1, 54.6 (q, *J* = 29.8 Hz), 48.6, 14.2, 14.1; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 74.0; IR (neat) 3399, 1732, 1604, 1499, 1249, 1127, 749 cm^{-1}; HRMS (ESI) *m/ z* calcd. For $C_{16}H_{21}NO_5F_3$ $(M + H)^+$ 364.1372, found 364.1368.

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Appendix A1. ^{1}H, ^{13}C, ^{19}F and ^{11}B Spectra Relevant to Chapter 1

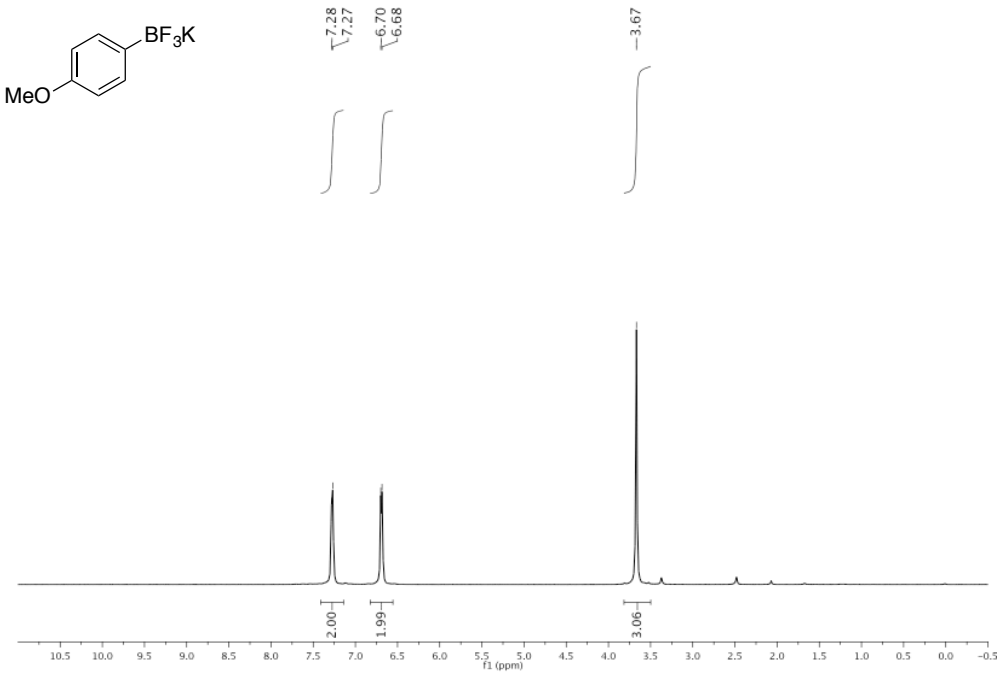


Figure A1.1 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-methoxyphenyl)borate

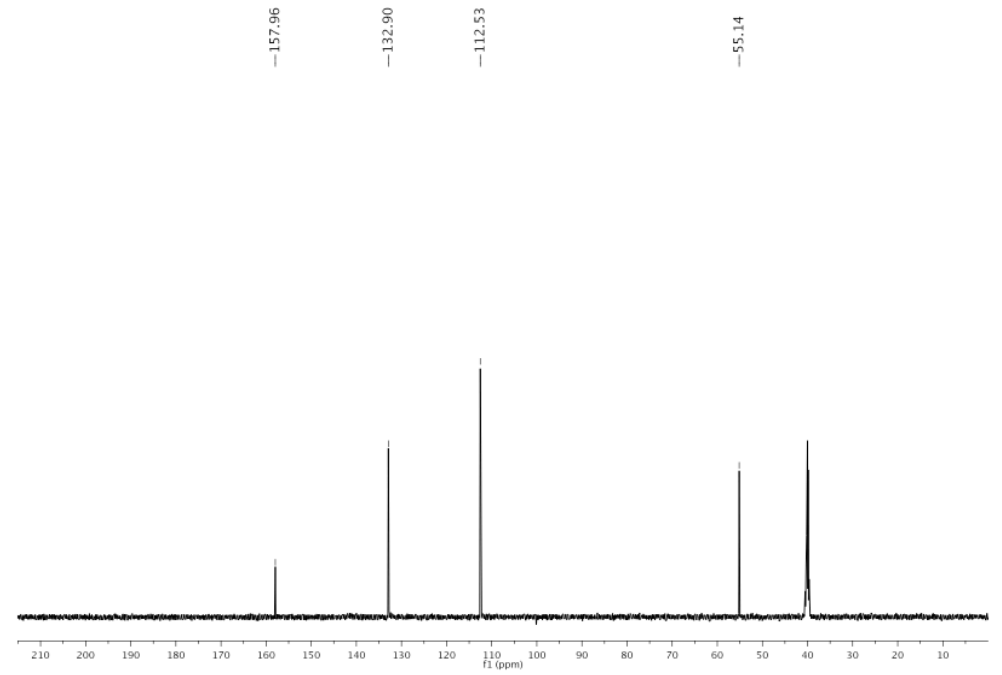


Figure A1.2 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-methoxyphenyl)borate

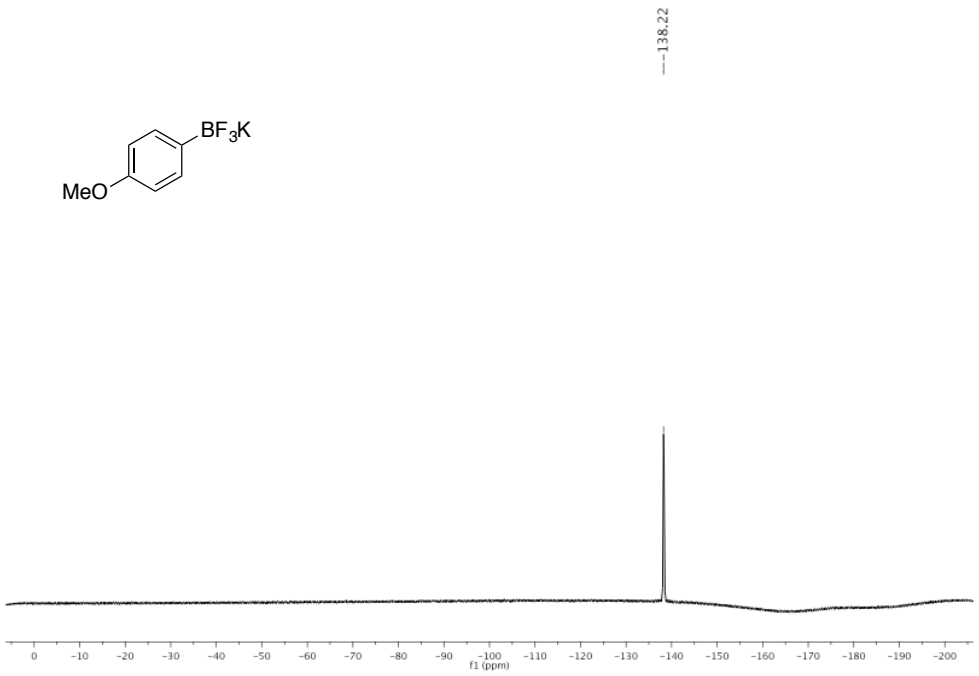


Figure A1.3 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-methoxyphenyl)borat

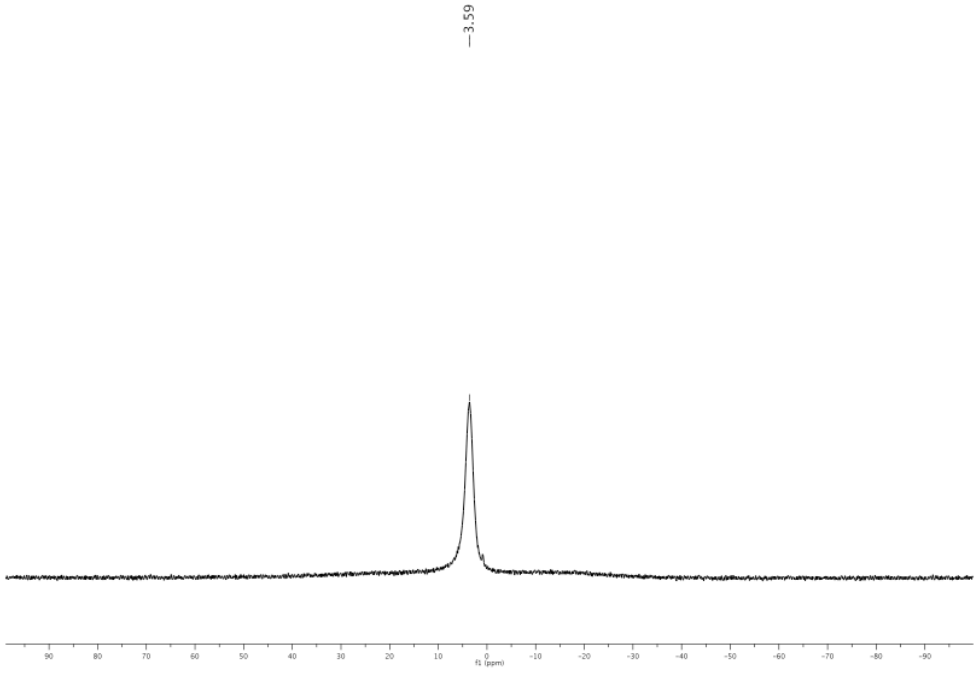


Figure A1.4 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-methoxyphenyl)borate

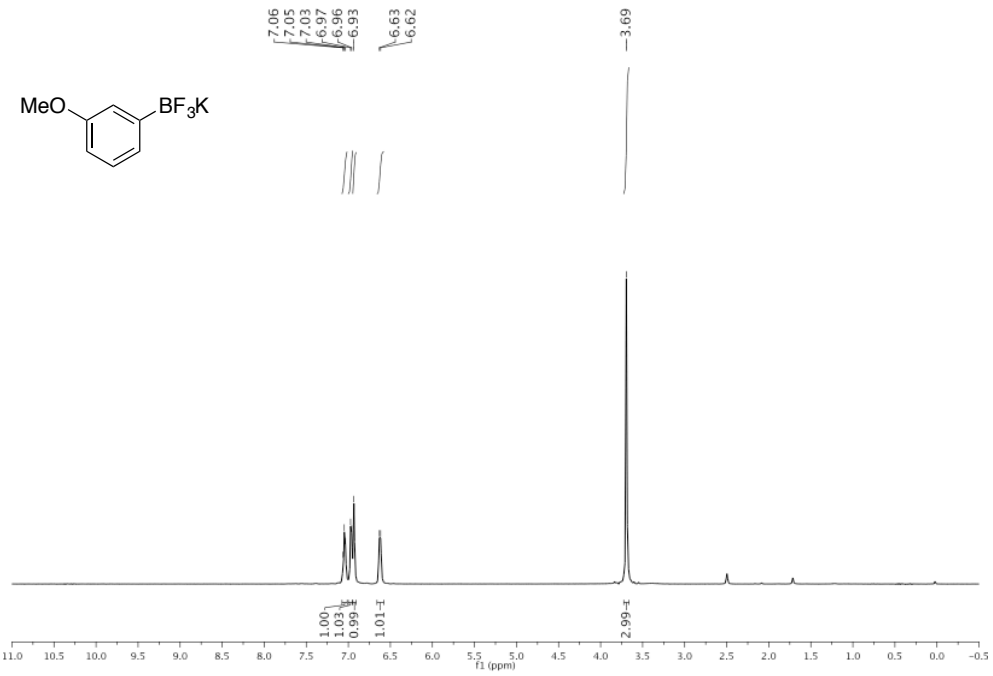


Figure A1.5 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(3-methoxyphenyl)borate

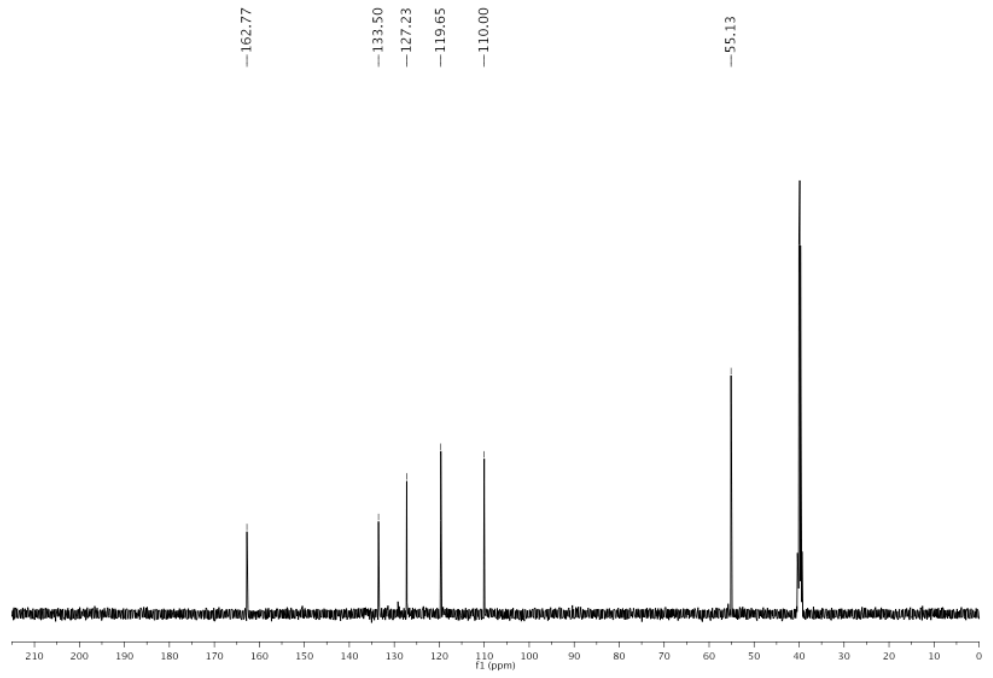


Figure A1.6 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(3-methoxyphenyl)borate

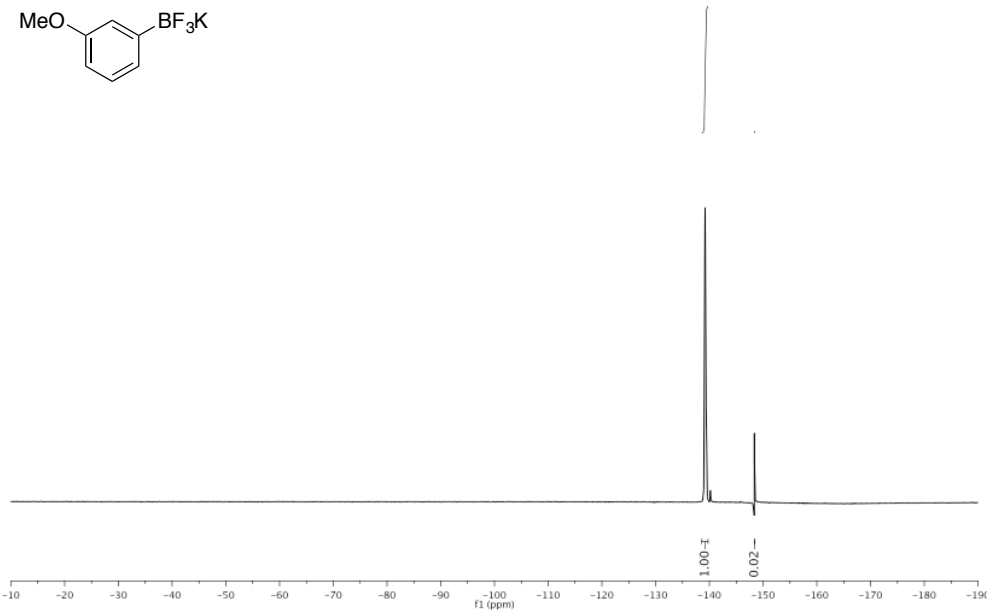


Figure A1.7 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(3-methoxyphenyl)borate

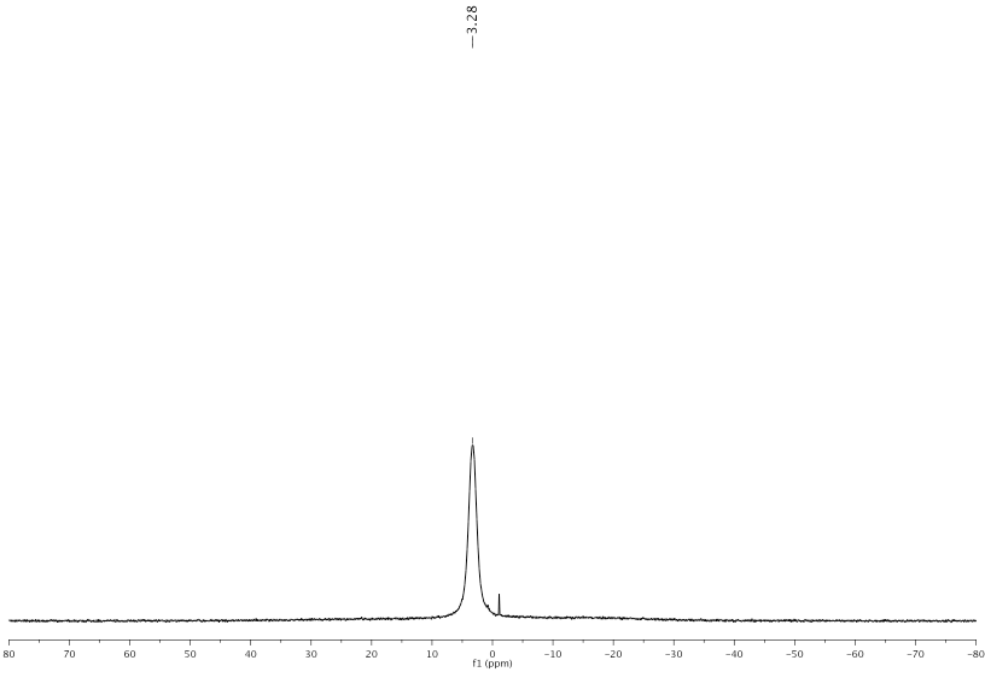


Figure A1.8 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(3-methoxyphenyl)borate

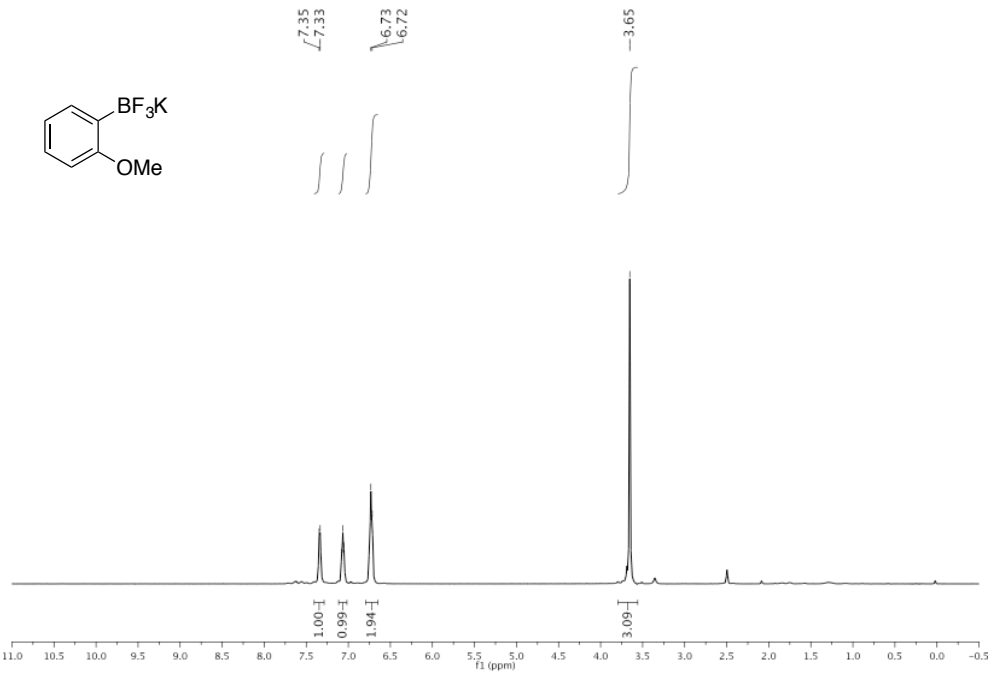


Figure A1.9 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(2-methoxyphenyl)borate

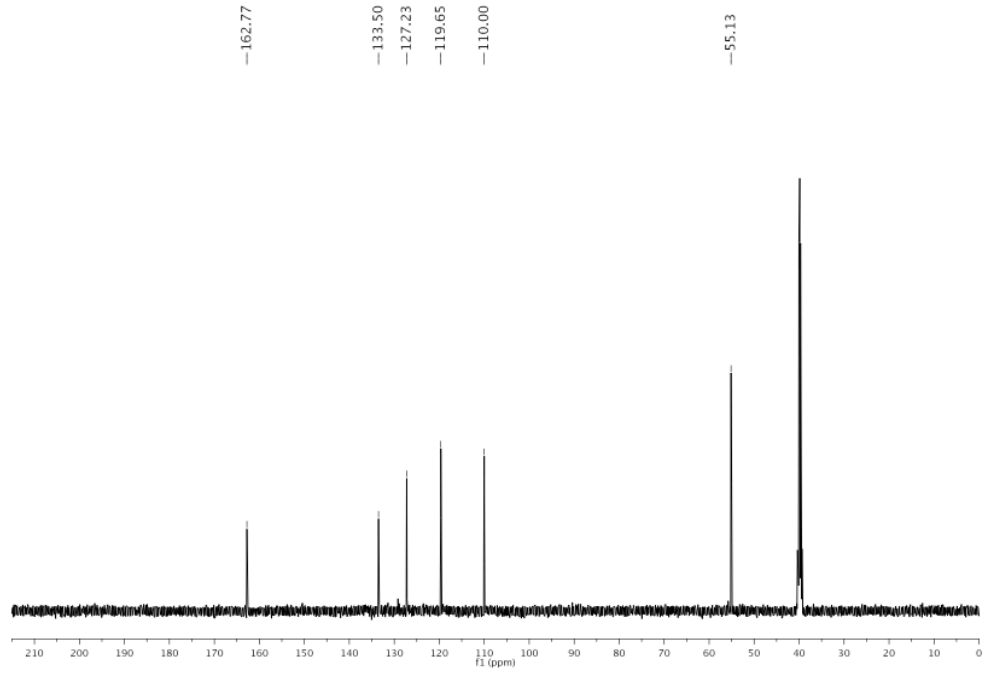


Figure A1.10 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(2-methoxyphenyl)borate

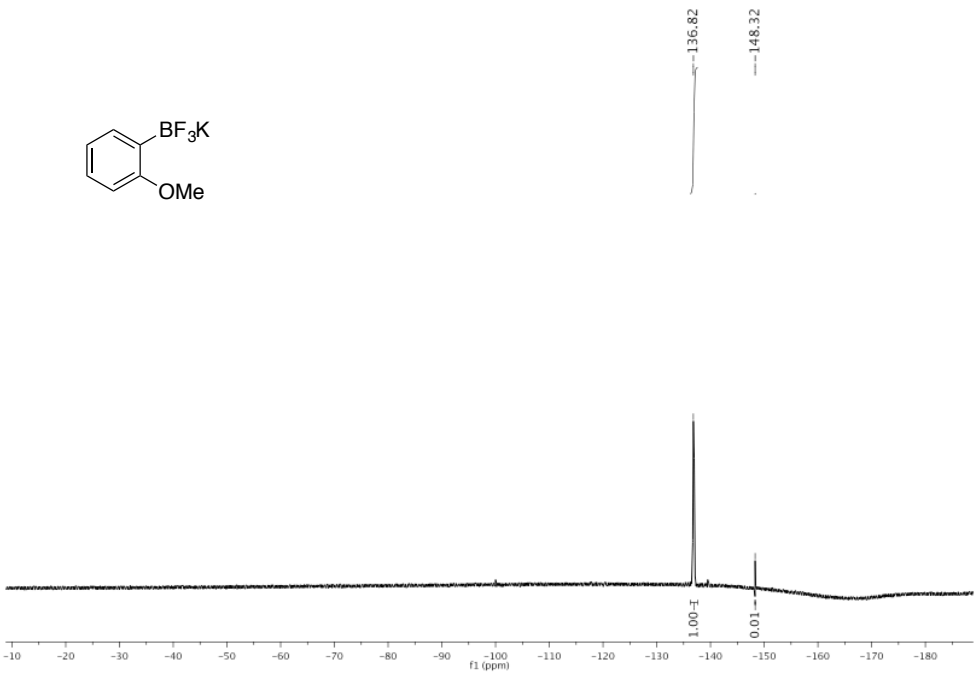


Figure A1.11 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(2-methoxyphenyl)borate

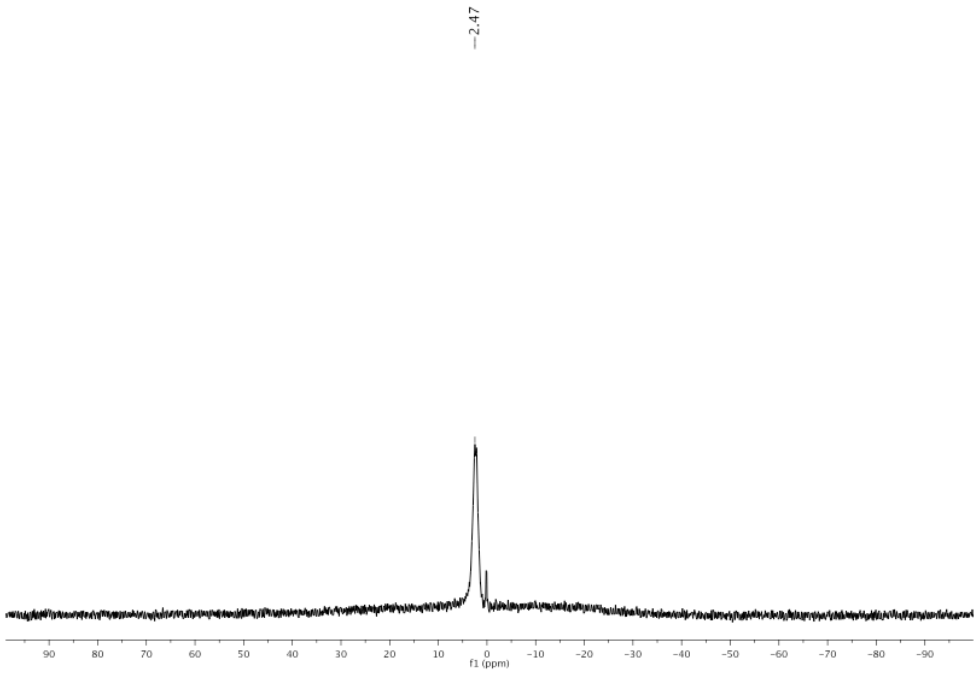


Figure A1.12 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(2-methoxyphenyl)borate

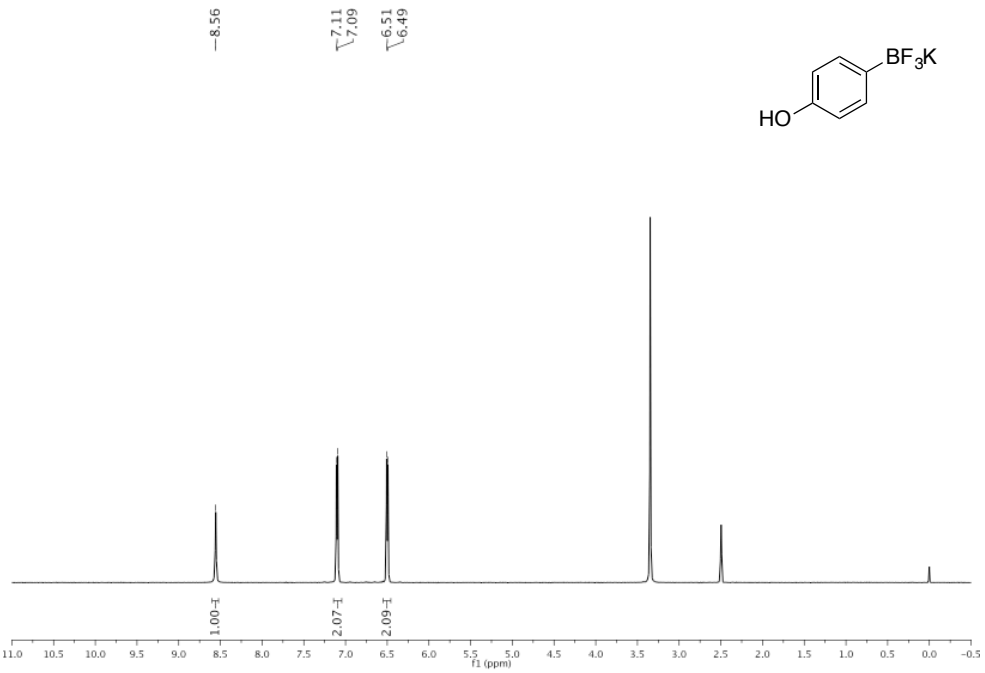


Figure A1.13 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-hydroxyphenyl)borate

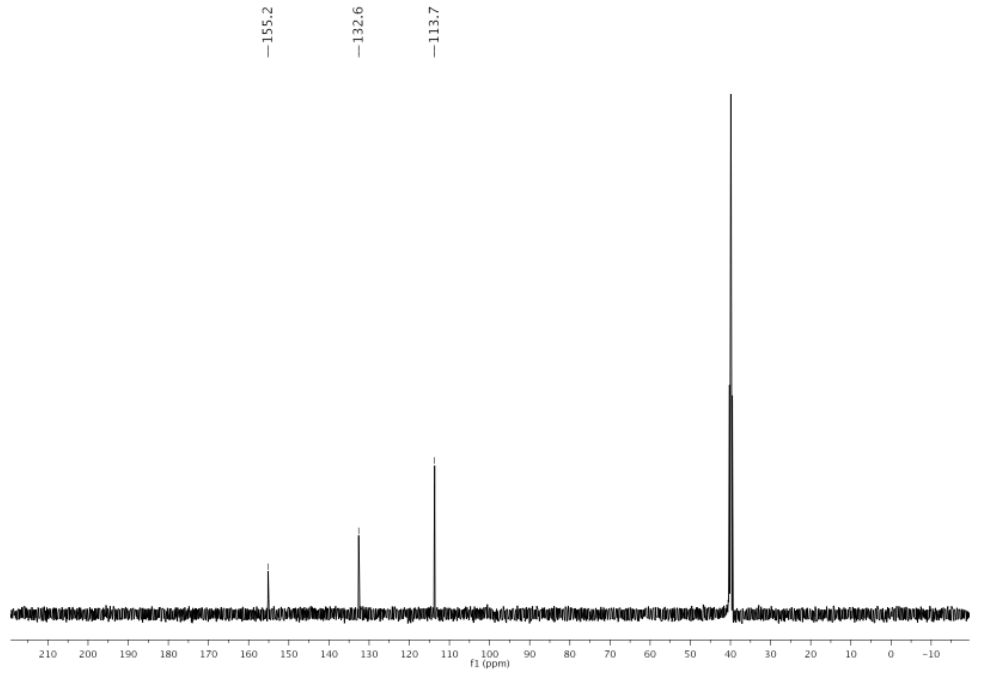


Figure A1.14 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-hydroxyphenyl)borate

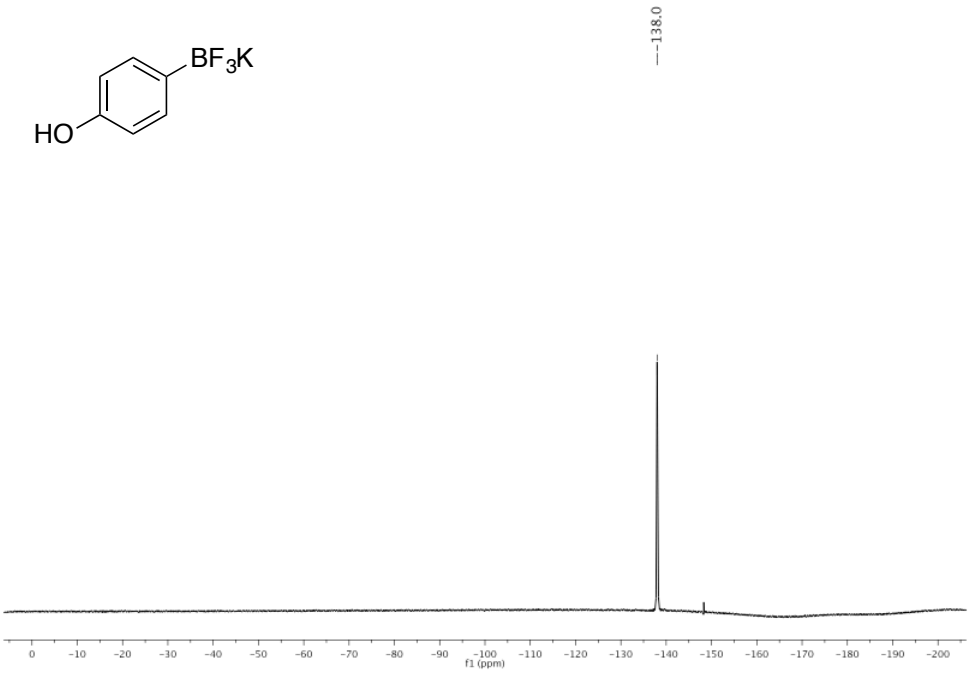


Figure A1.15 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-hydroxyphenyl)borate

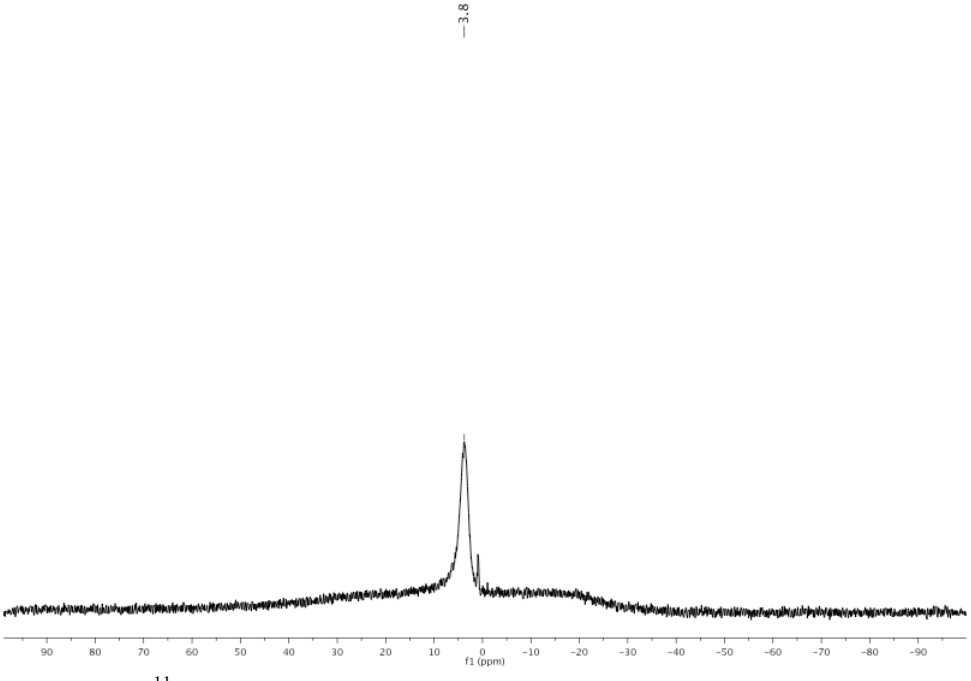


Figure A1.16 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-hydroxyphenyl)borate

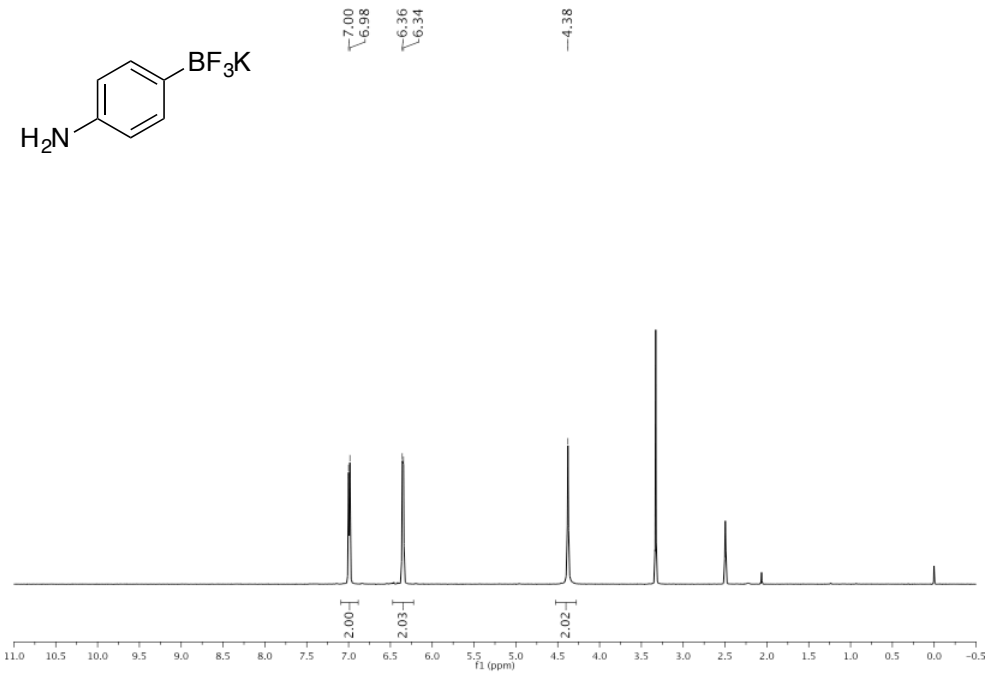


Figure A1.17 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium (4-Aminophenyl)trifluoroborate

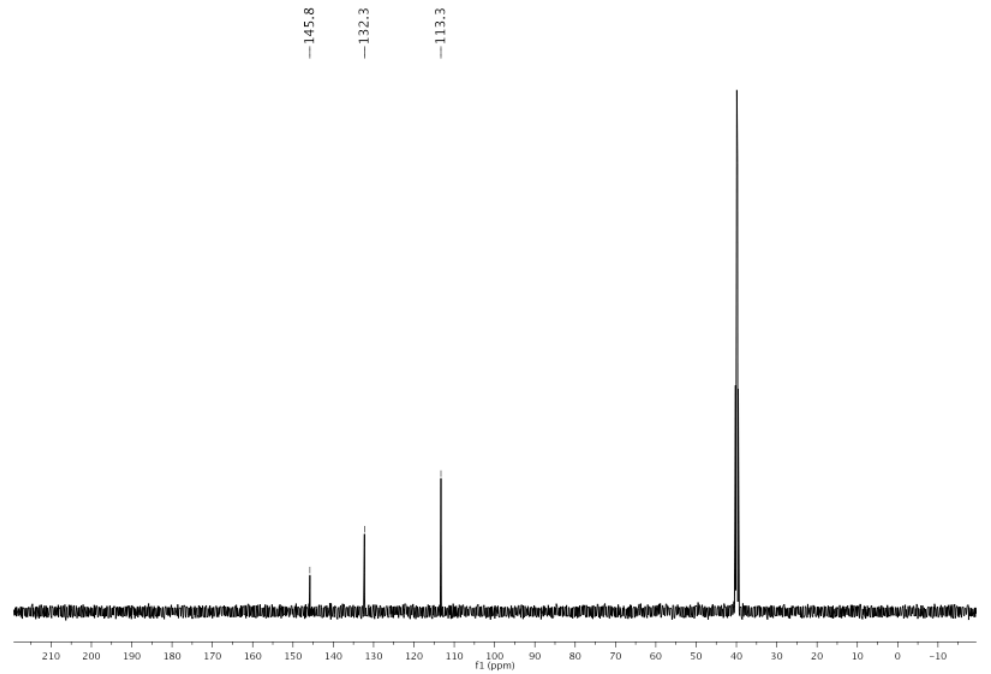


Figure A1.18 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium (4-Aminophenyl)trifluoroborate

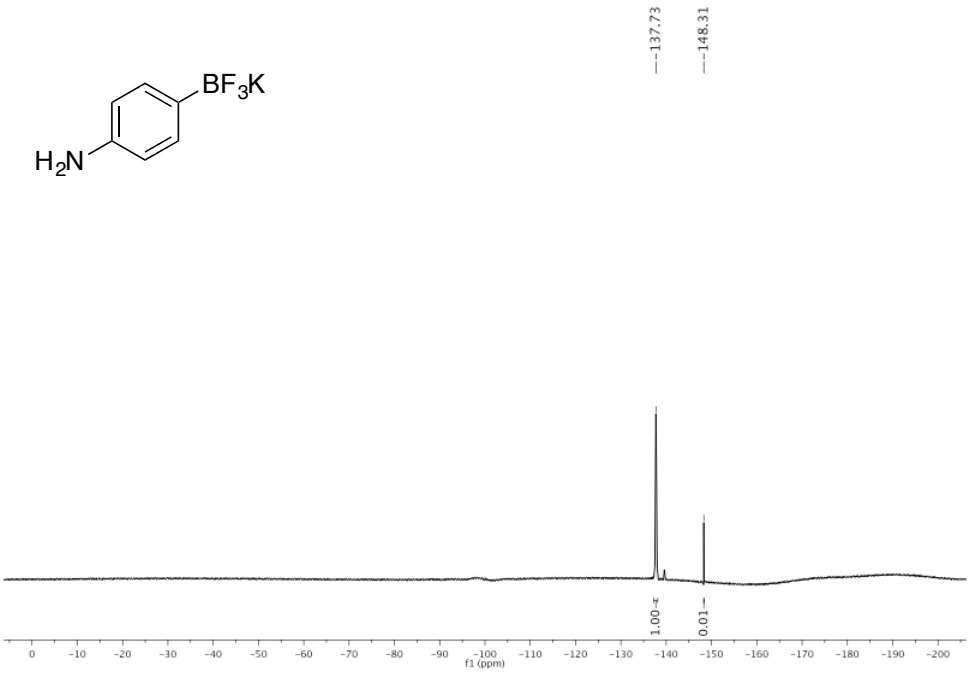


Figure A1.19 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium (4-Aminophenyl)trifluoroborate

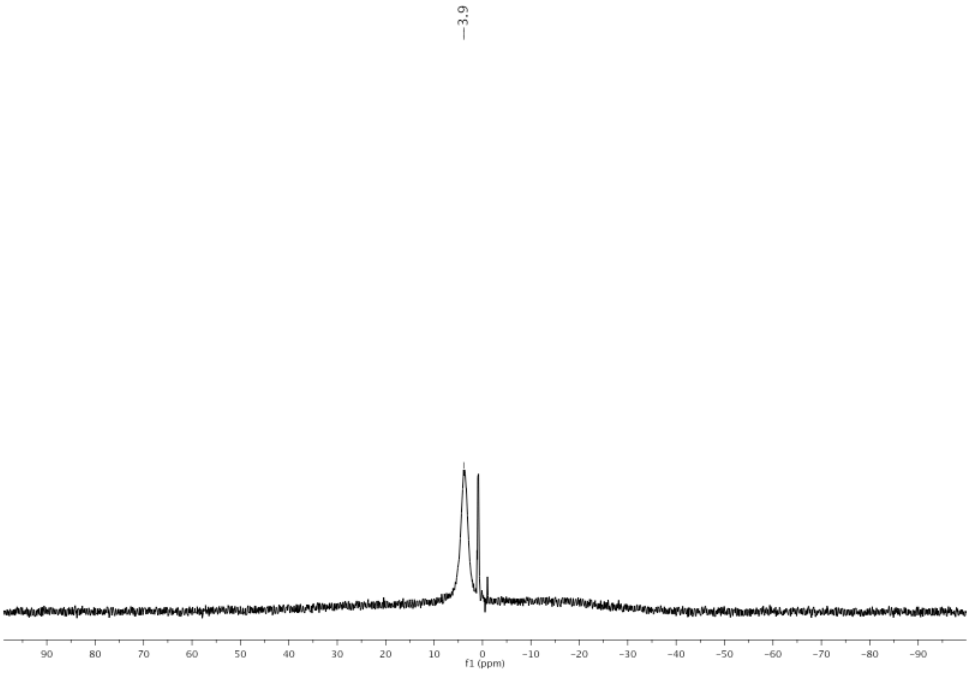


Figure A1.19 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium (4-Aminophenyl)trifluoroborate

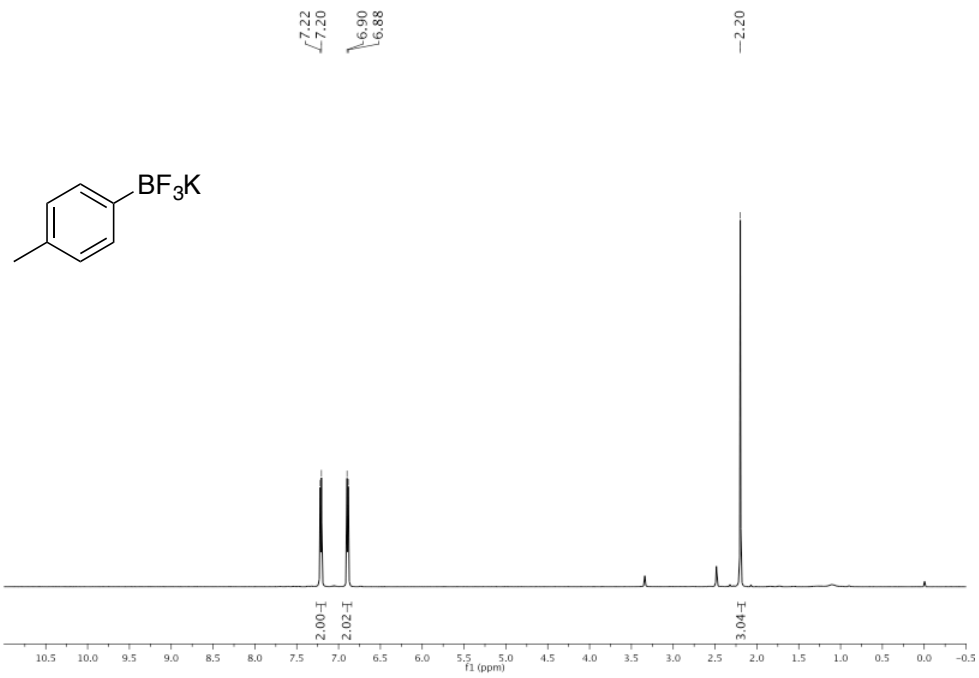


Figure A1.20 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(*p*-tolyl)borate

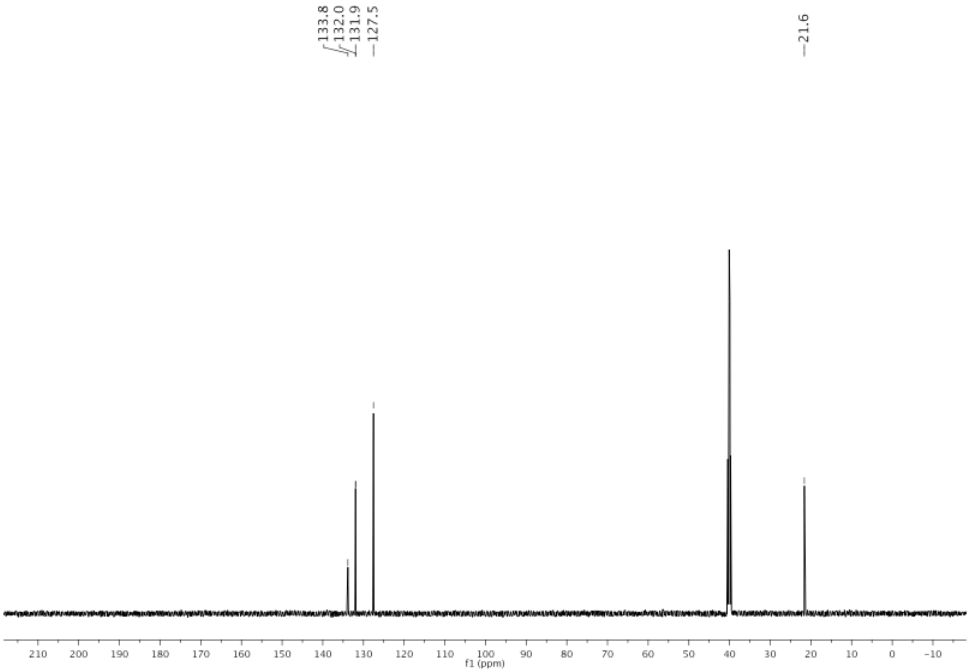


Figure A1.21 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(*p*-tolyl)borate

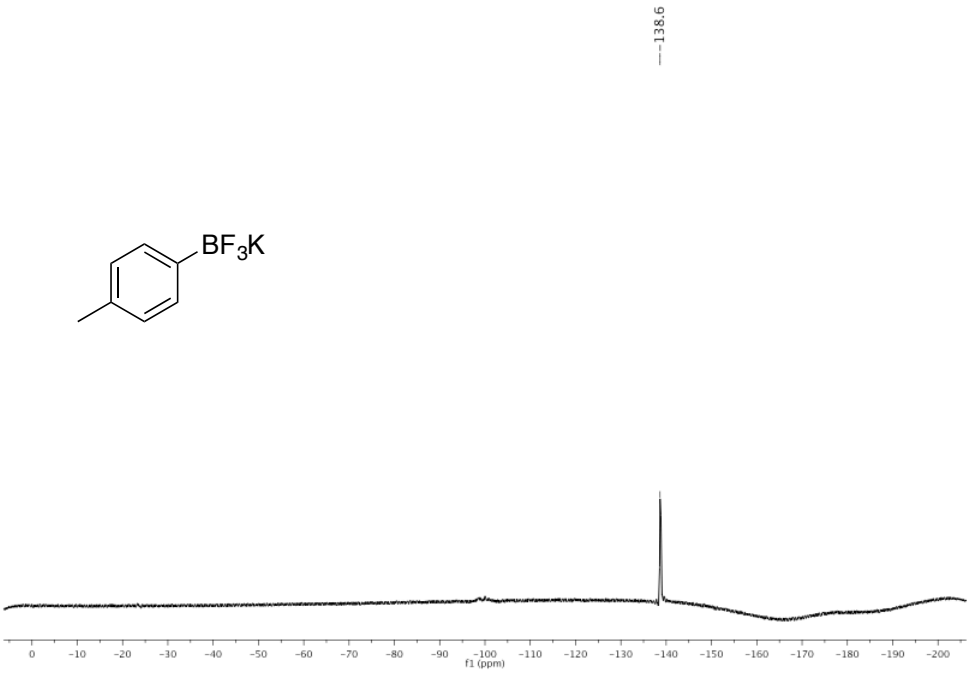


Figure A1.22 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(*p*-tolyl)borate

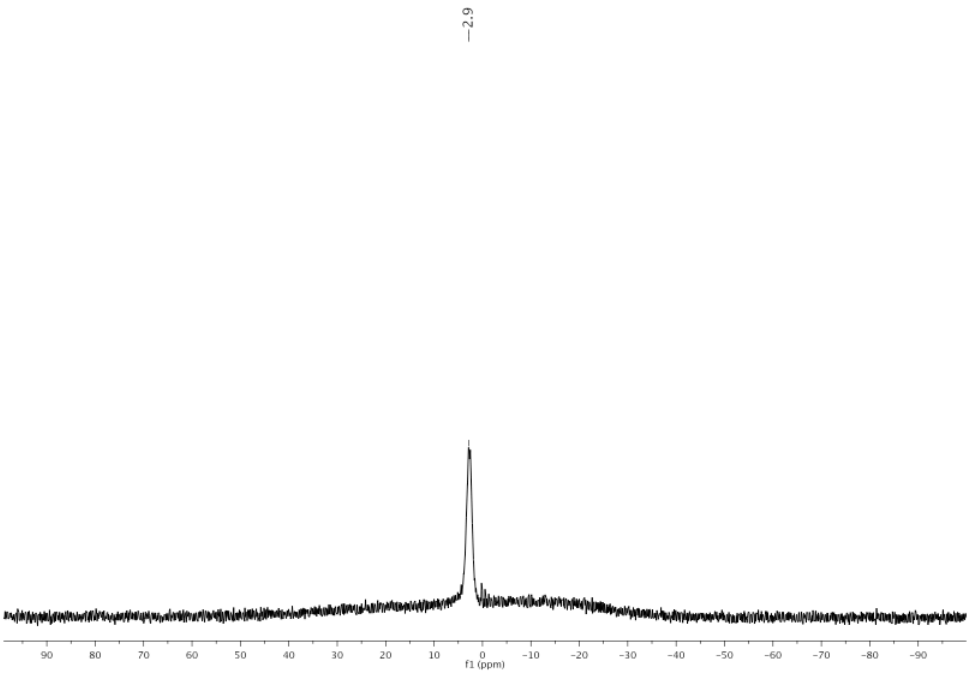


Figure A1.23 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(*p*-tolyl)borate

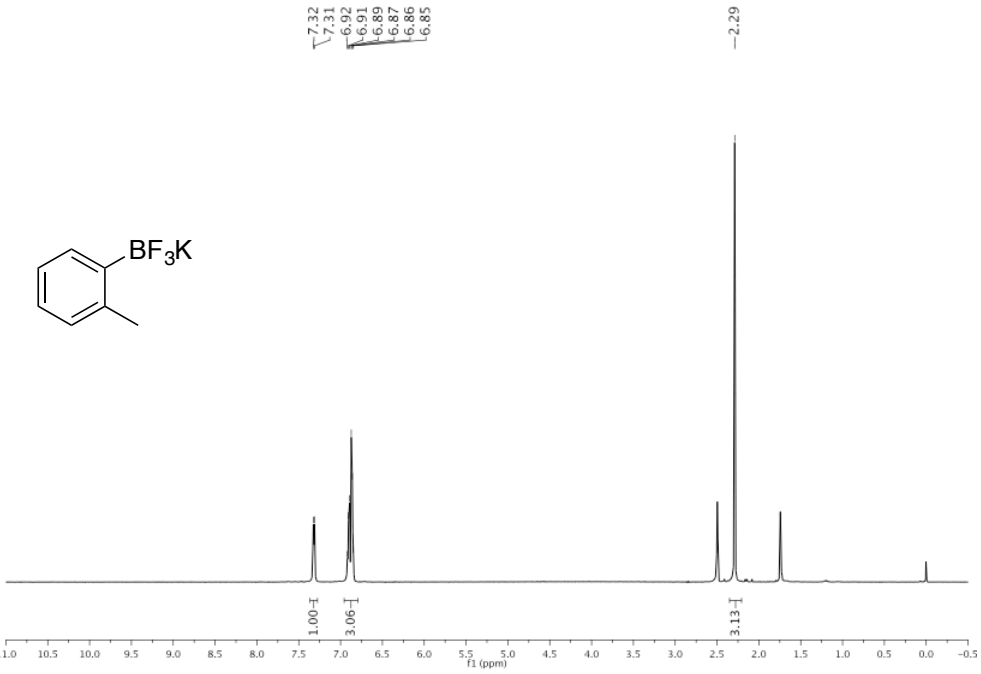


Figure A1.24 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(*o*-tolyl)borate

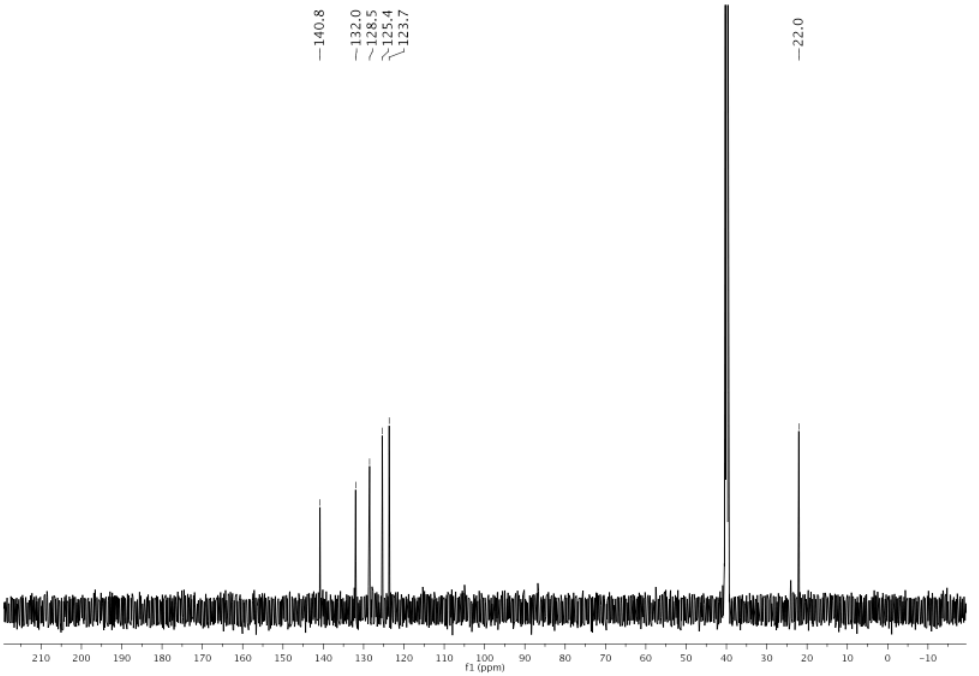


Figure A1.25 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(*o*-tolyl)borate

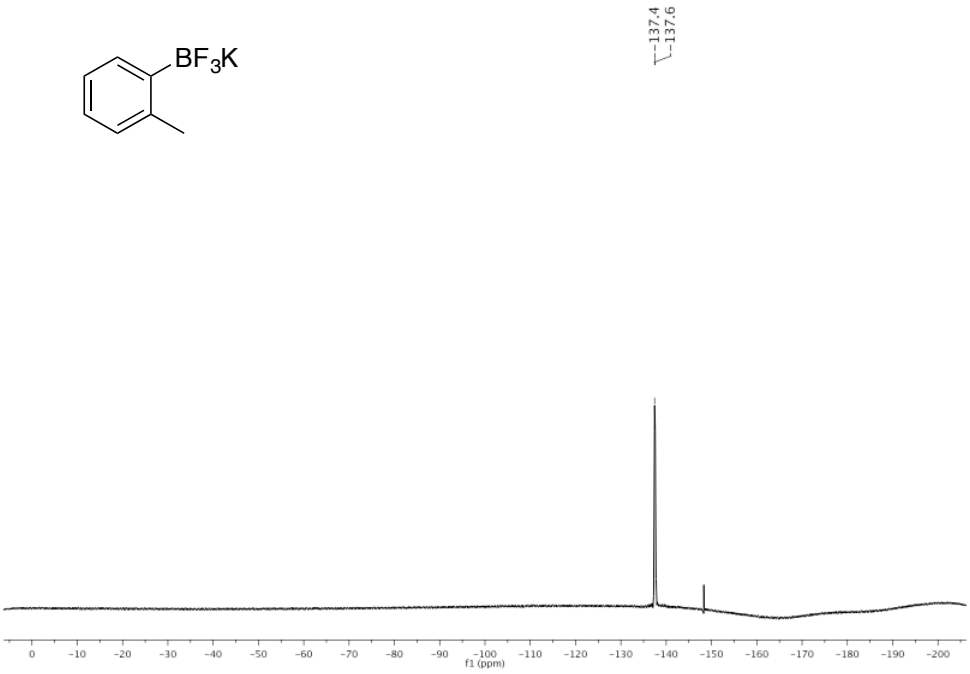


Figure A1.26 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(*o*-tolyl)borate

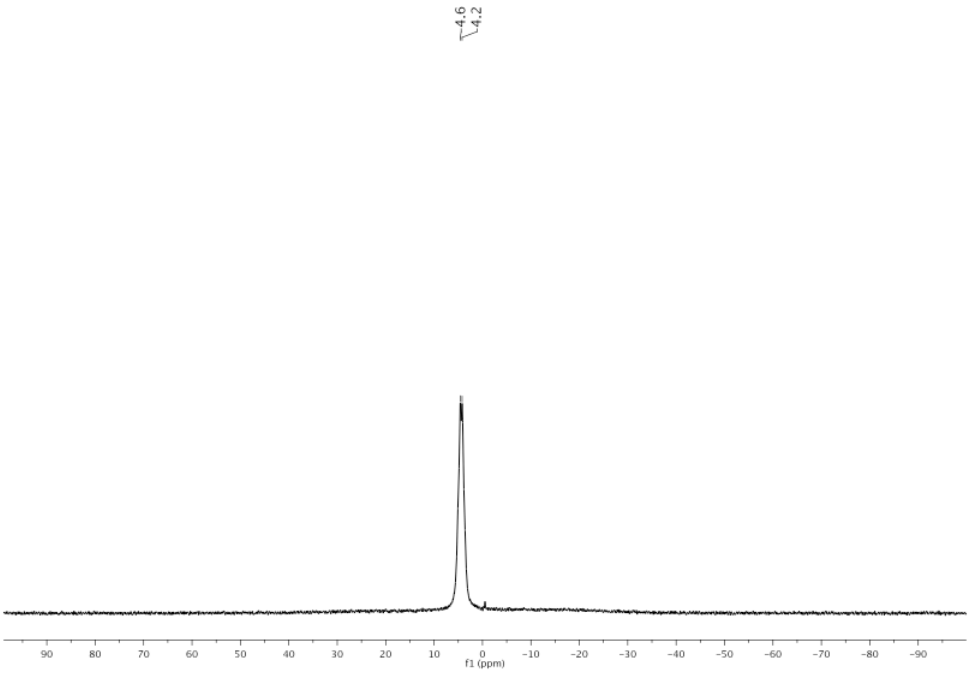


Figure A1.27 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(*o*-tolyl)borate

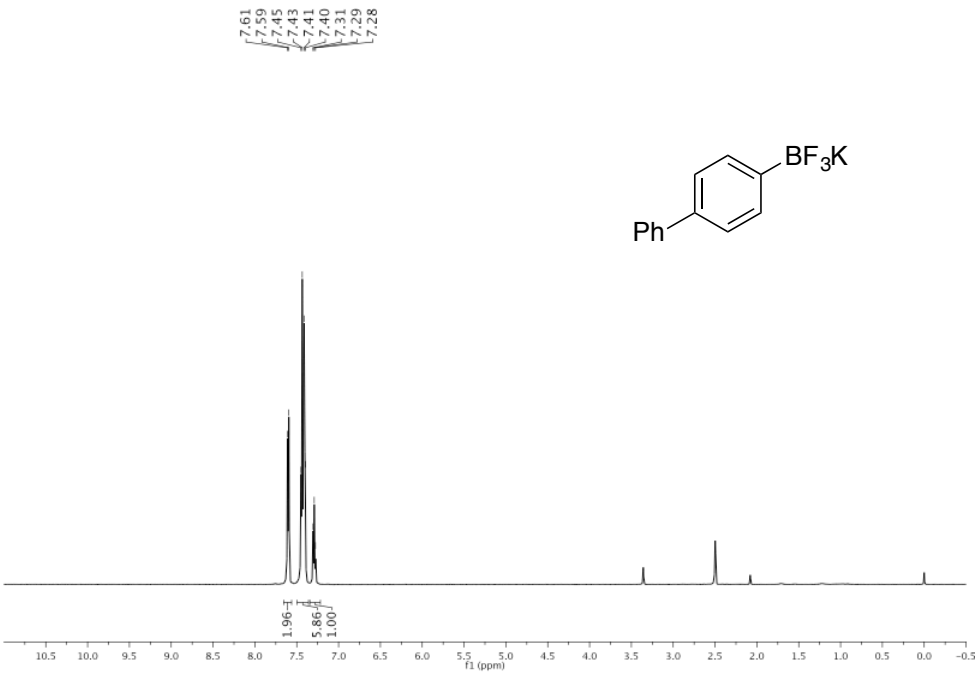
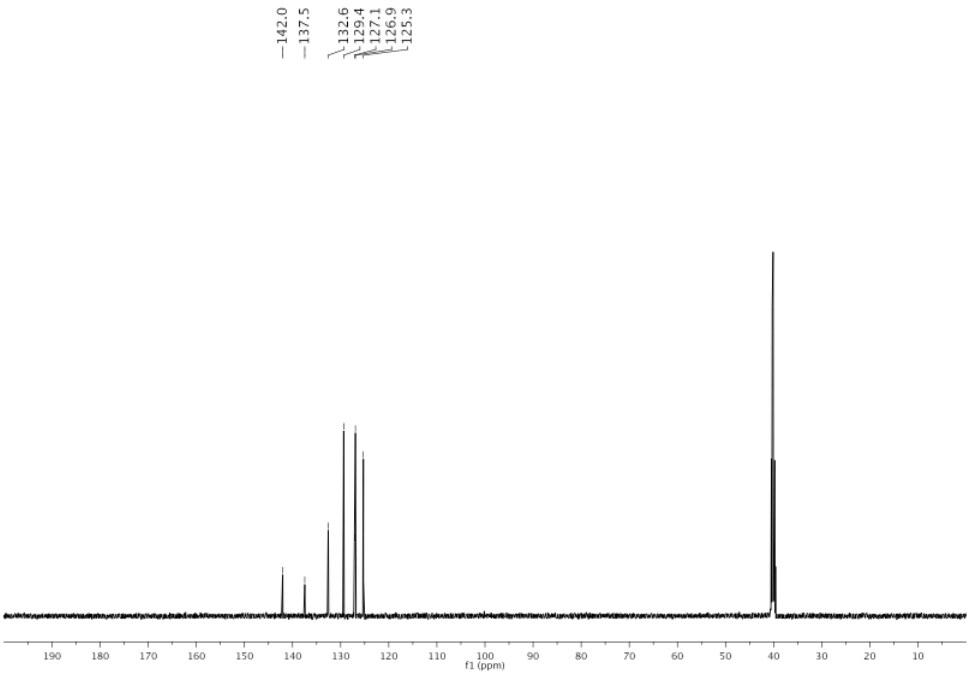


Figure A1.28 [1]H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium [1,1'-Biphenyl]-4-yltrifluoroborate



[1] **Figure A1.29** [3]C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium [1,1'-Biphenyl]-4-yltrifluoroborate

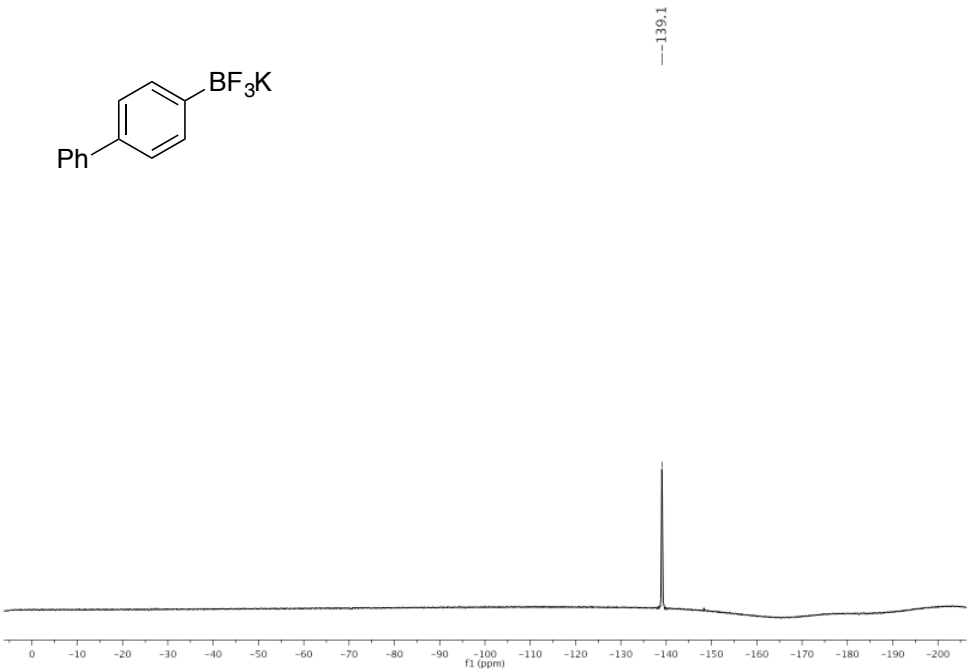


Figure A1.30 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium [1,1'-Biphenyl]-4-yltrifluoroborate

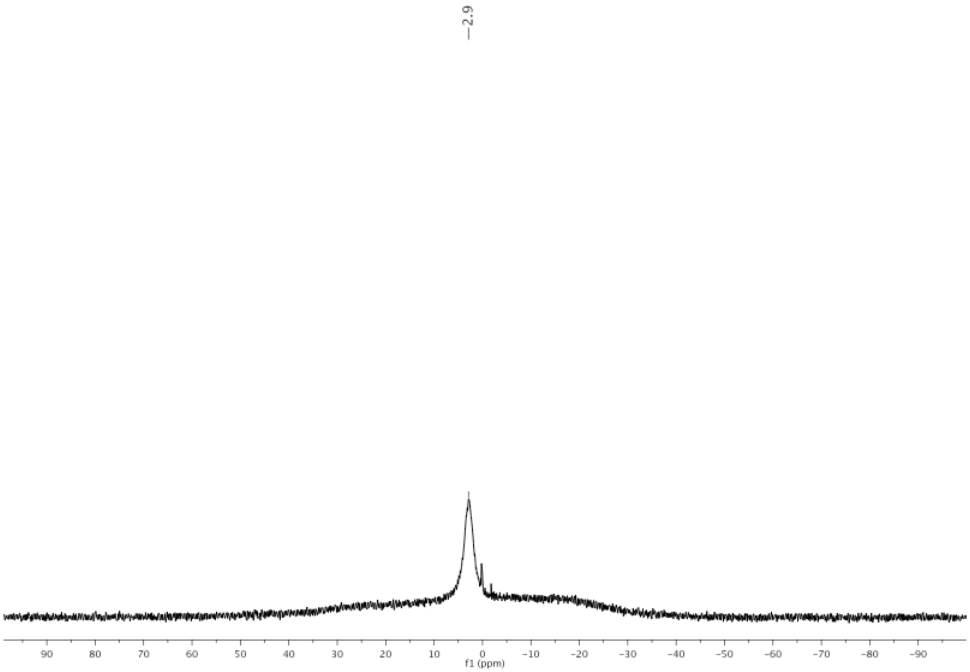


Figure A1.31 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium [1,1'-Biphenyl]-4-yltrifluoroborate

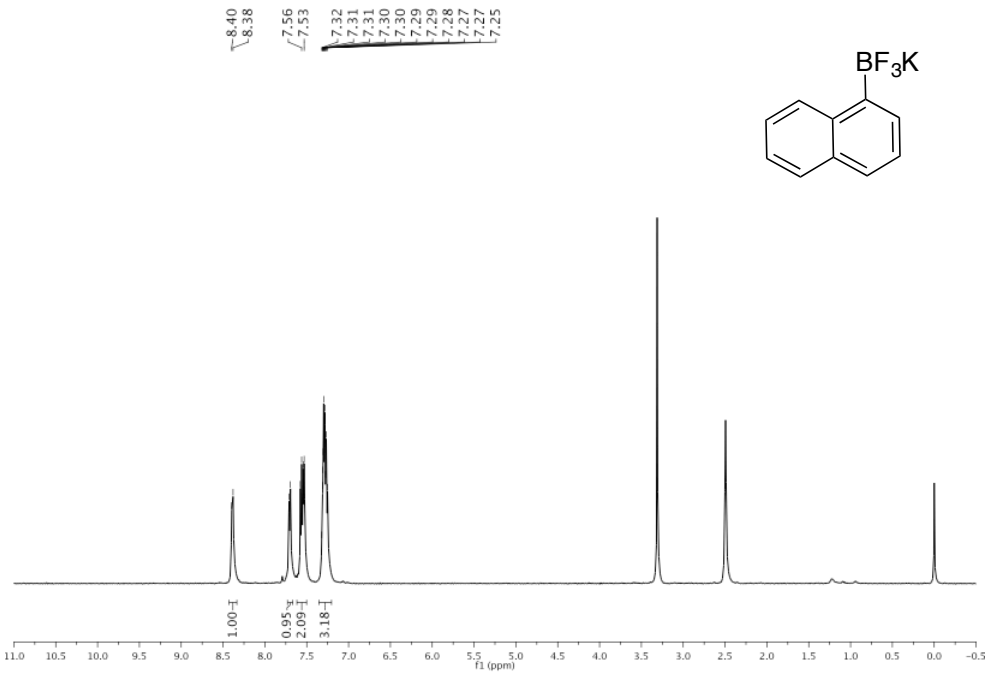
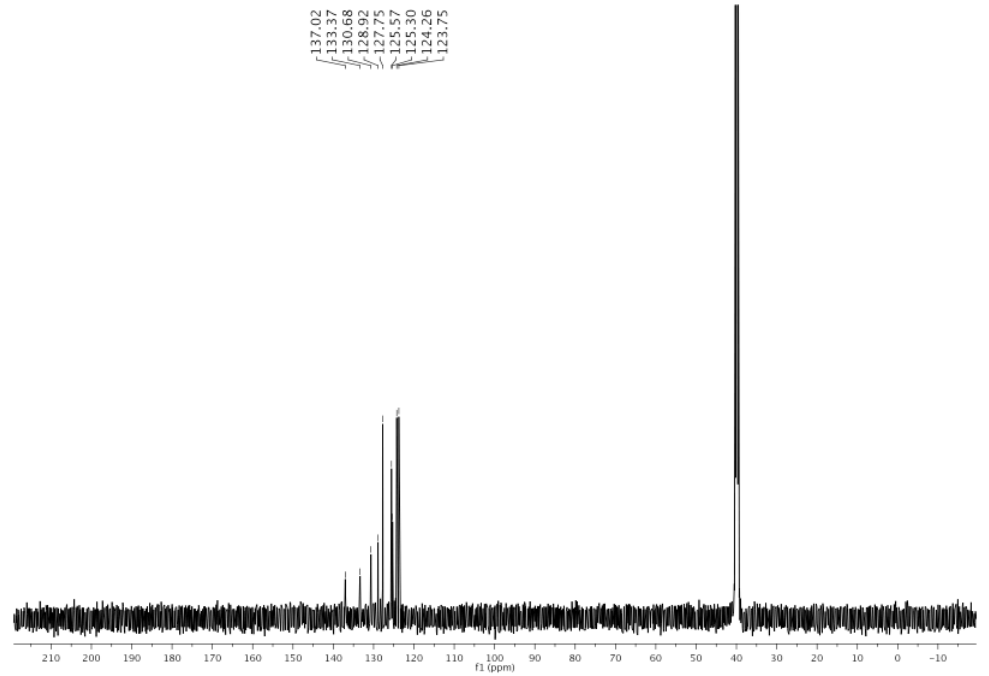


Figure A1.32 [1]H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(naphthalen-1-yl)borate



[1] **Figure A1.33** [3]C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(naphthalen-1-yl)borate

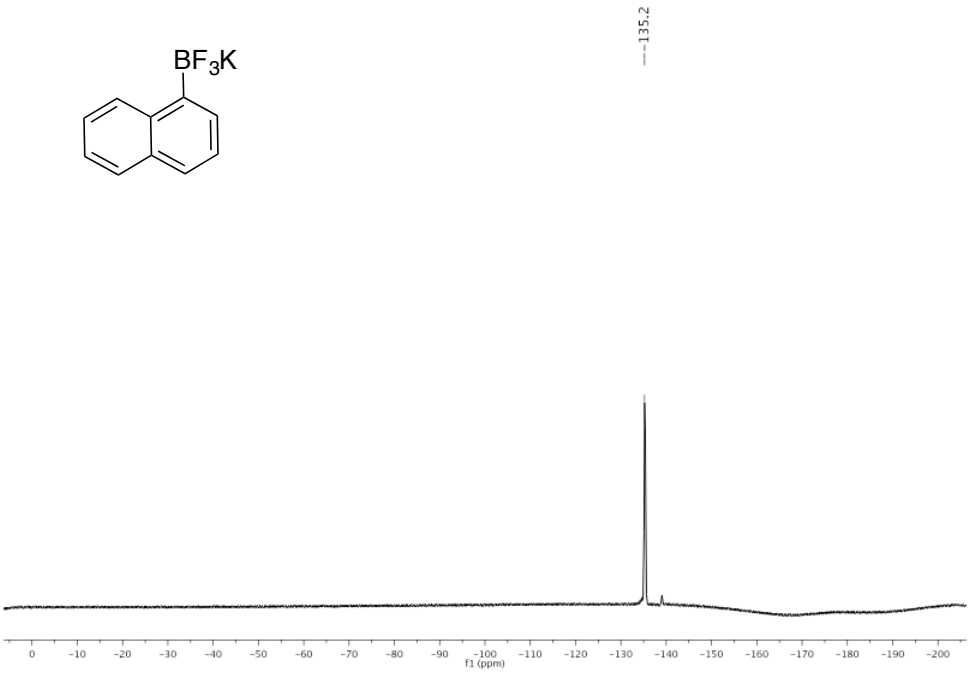


Figure A1.34 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(naphthalen-1-yl)borate

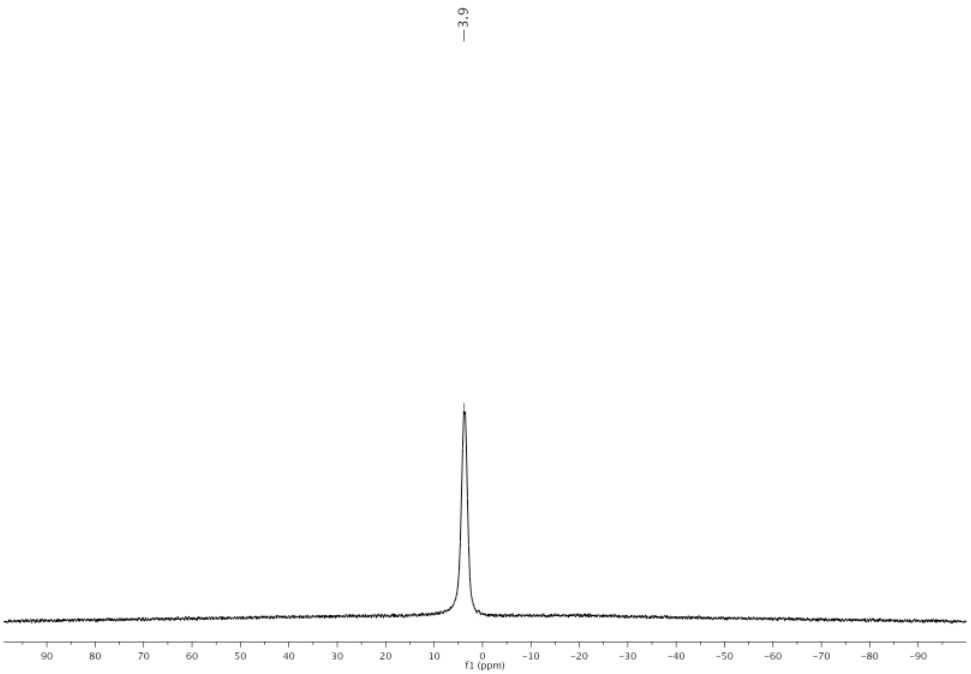


Figure A1.35 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(naphthalen-1-yl)borate

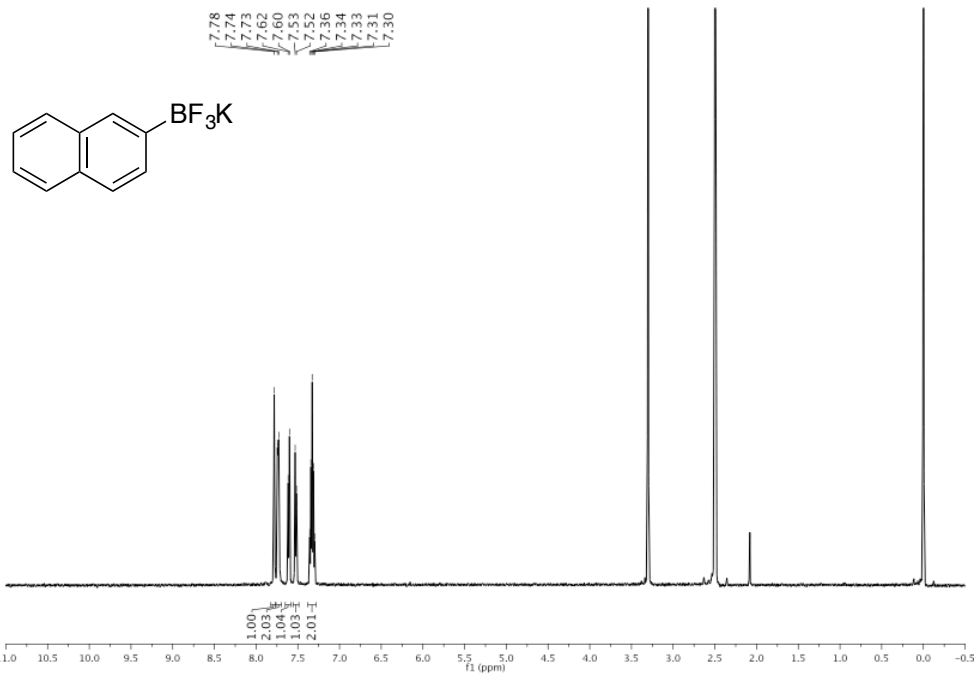


Figure A1.36 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(naphthalen-2-yl)borate

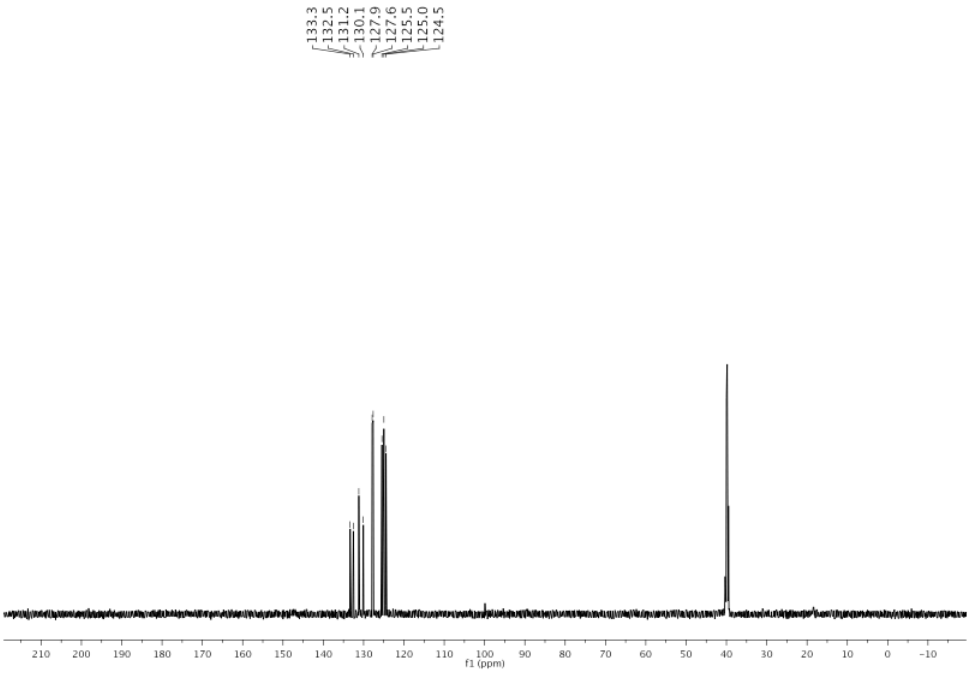


Figure A1.37 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(naphthalen-2-yl)borate

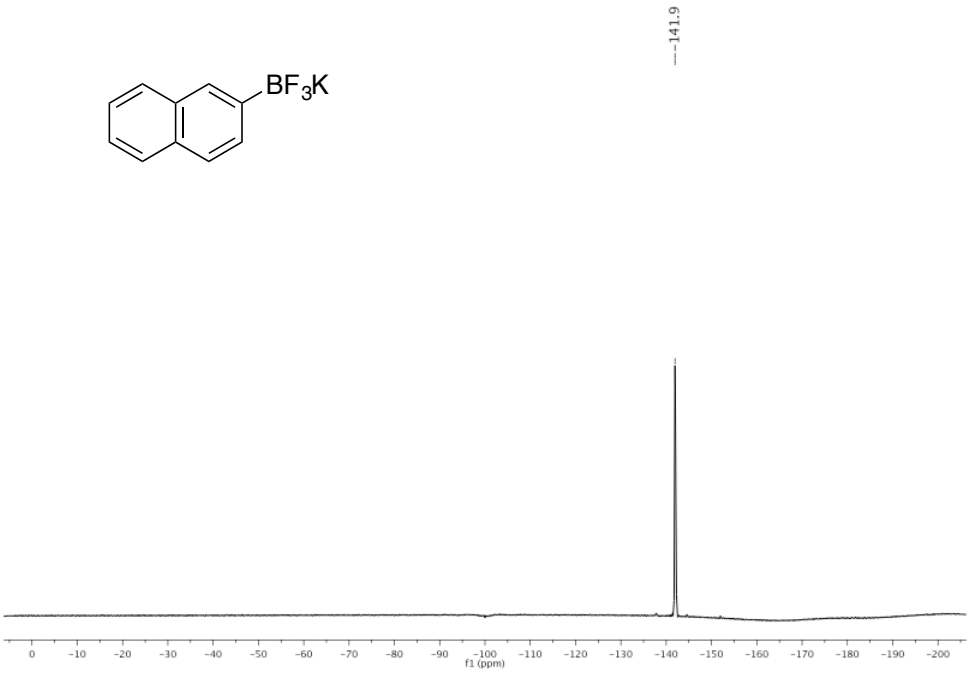


Figure A1.38 ^{19}F NMR (470.8 MHz, acetone-d_6) Spectrum of Potassium Trifluoro(naphthalen-2-yl)borate

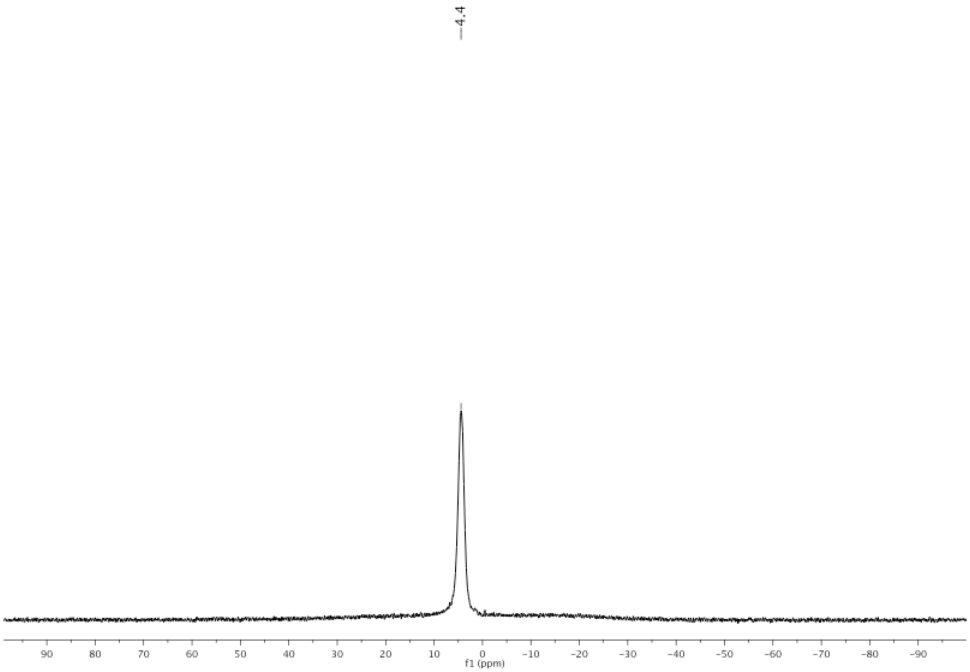


Figure A1.39^{11}B NMR (128.4 MHz, acetone-d_6) Spectrum of Potassium Trifluoro(naphthalen-2-yl)borate

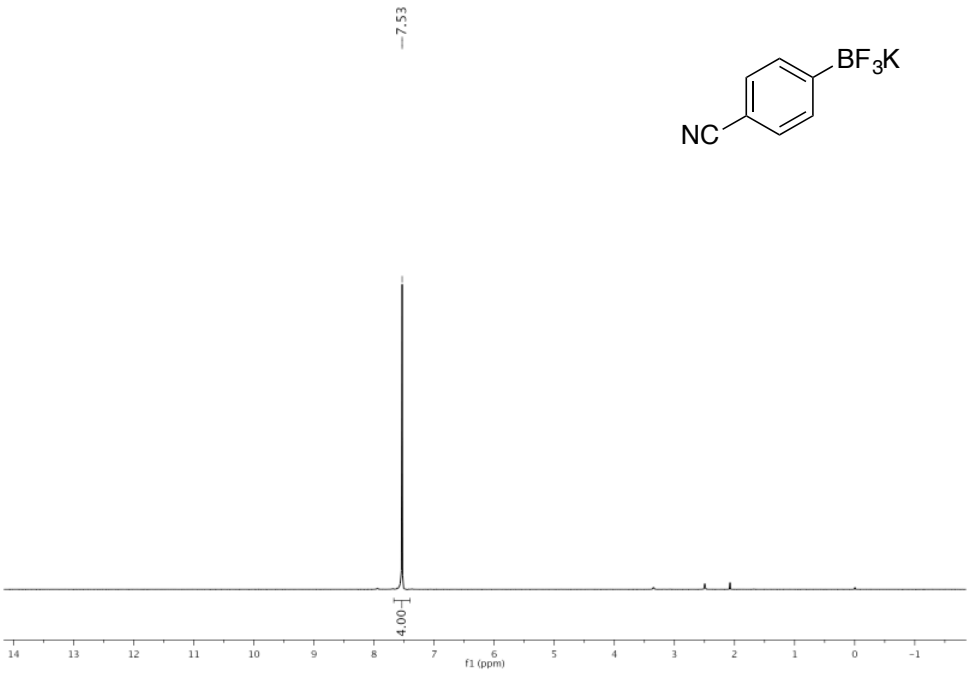
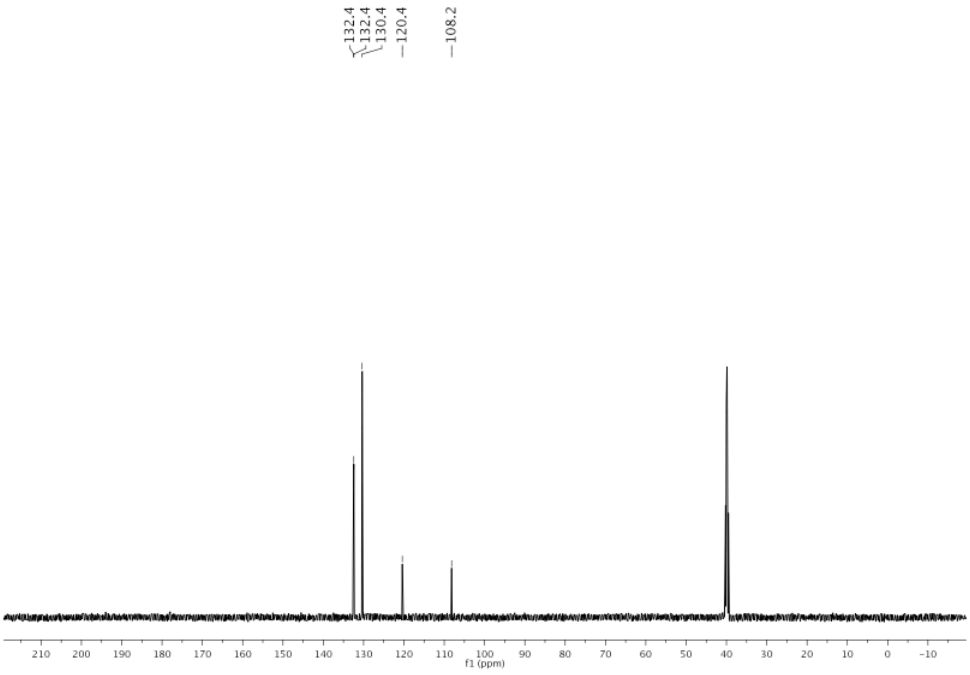


Figure A1.40 [1]H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium (4-Cyanophenyl)trifluoroborate



[1] **Figure A1.41** [3]C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium (4-Cyanophenyl)trifluoroborate

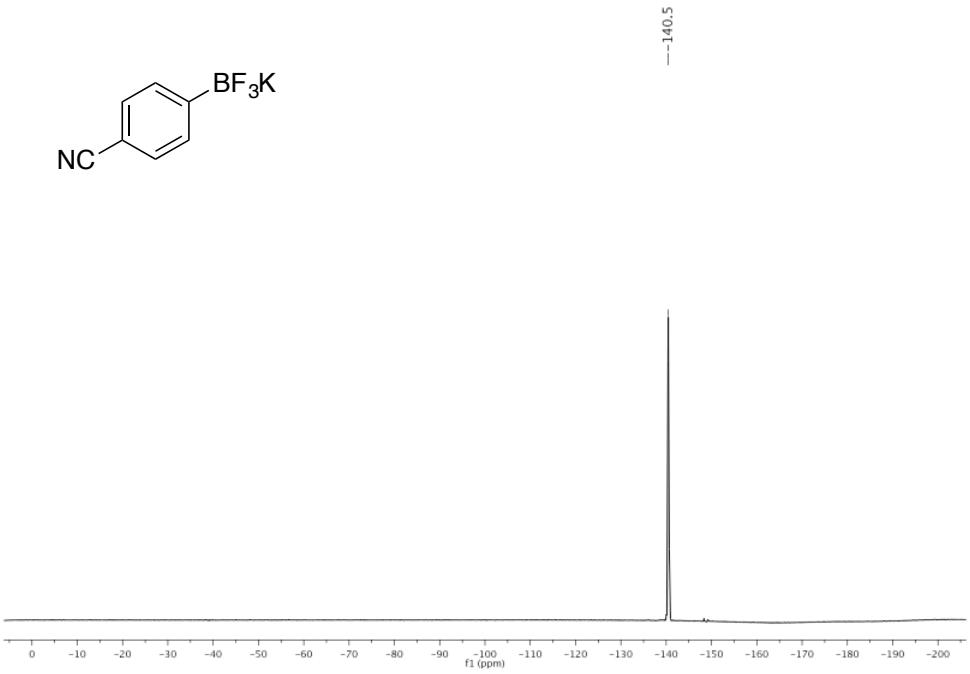


Figure A1.42 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium (4-Cyanophenyl)trifluoroborate

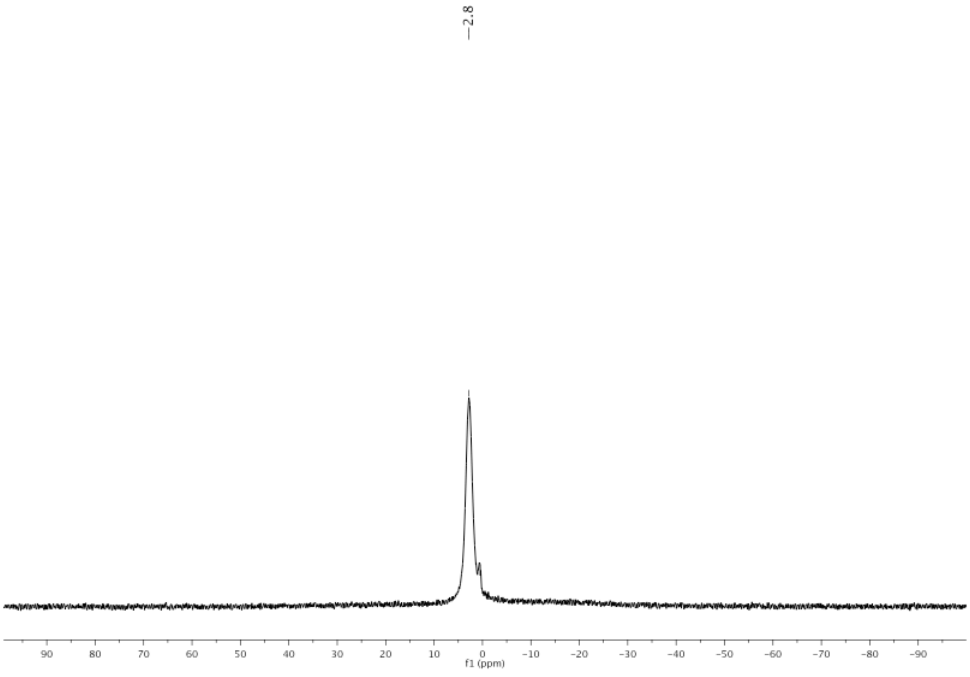


Figure A1.43 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium (4-Cyanophenyl)trifluoroborate

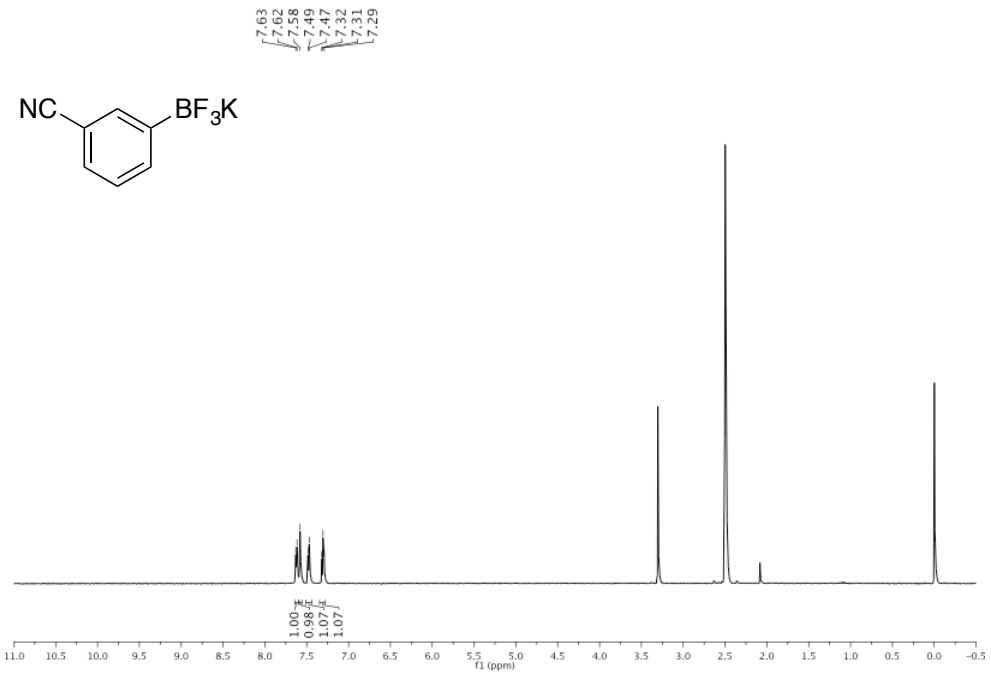


Figure A1.44 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium (3-Cyanophenyl)trifluoroborate

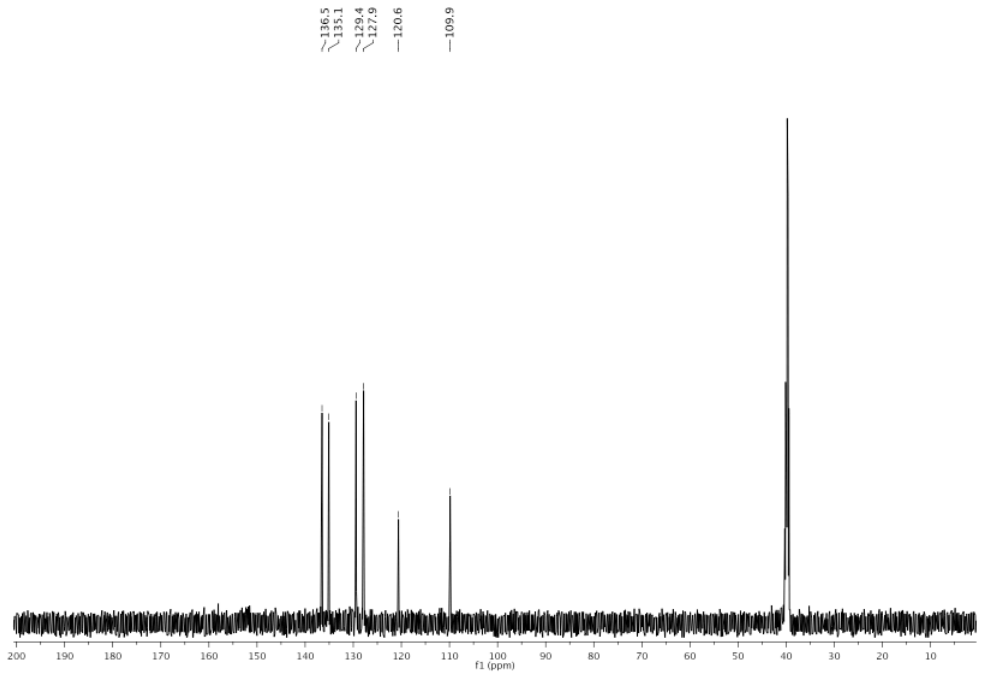


Figure A1.45 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium (3-Cyanophenyl)trifluoroborate

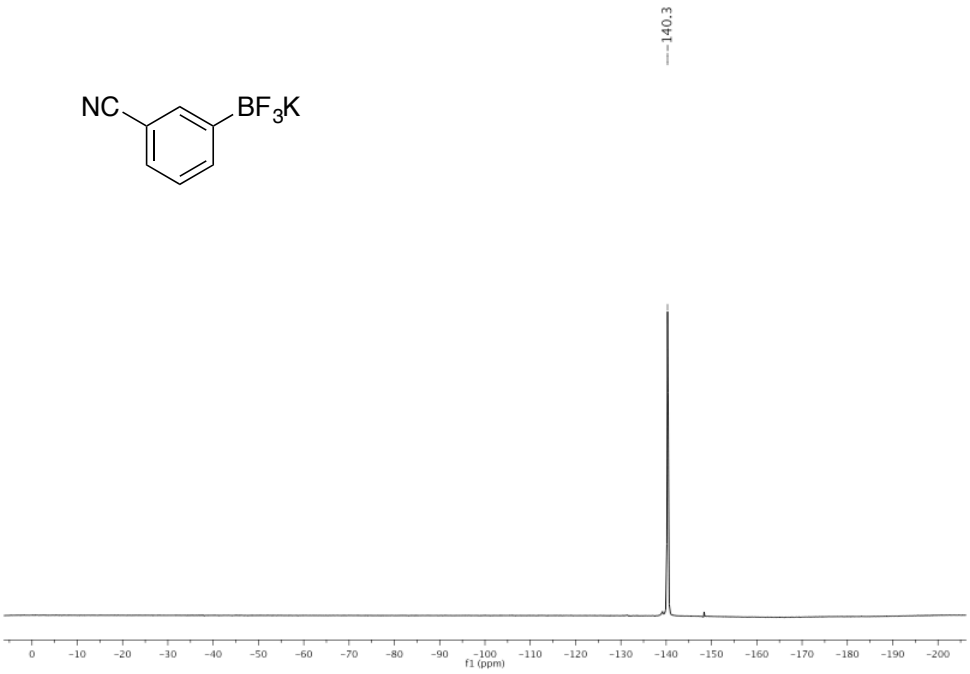


Figure A1.46 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium (3-Cyanophenyl)trifluoroborate

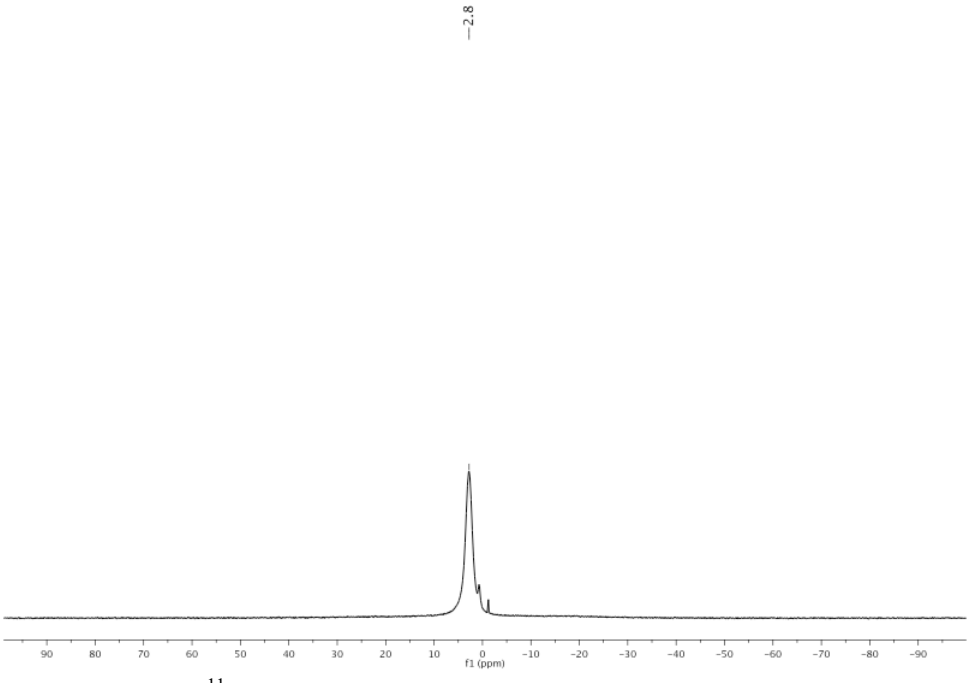


Figure A1.47 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium (3-Cyanophenyl)trifluoroborate

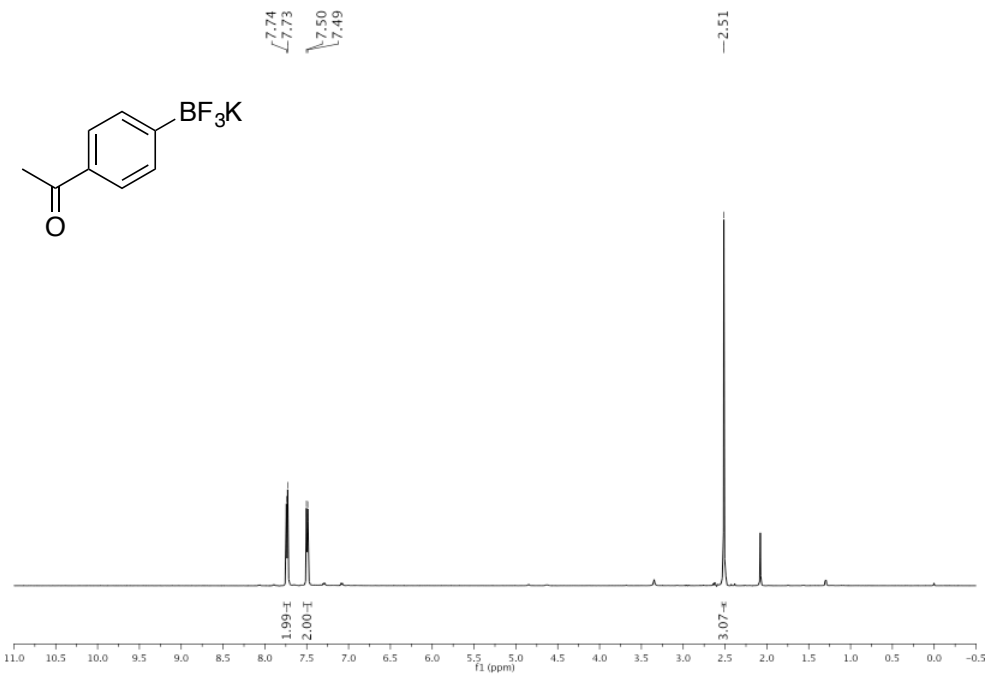


Figure A1.48 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium (4-Acetylphenyl)trifluoroborate

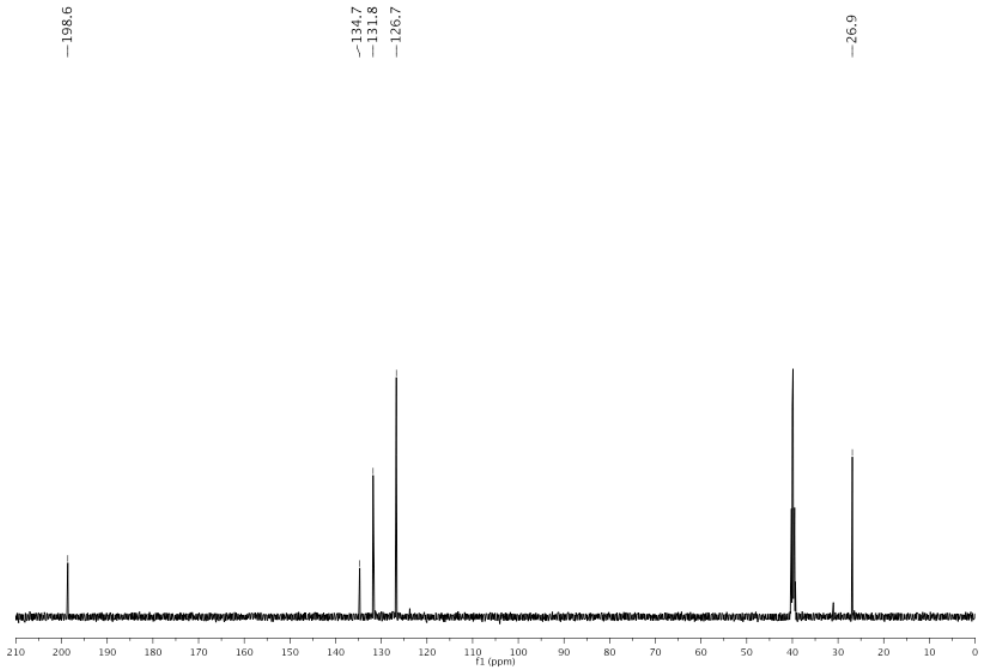


Figure A1.49 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium (4-Acetylphenyl)trifluoroborate

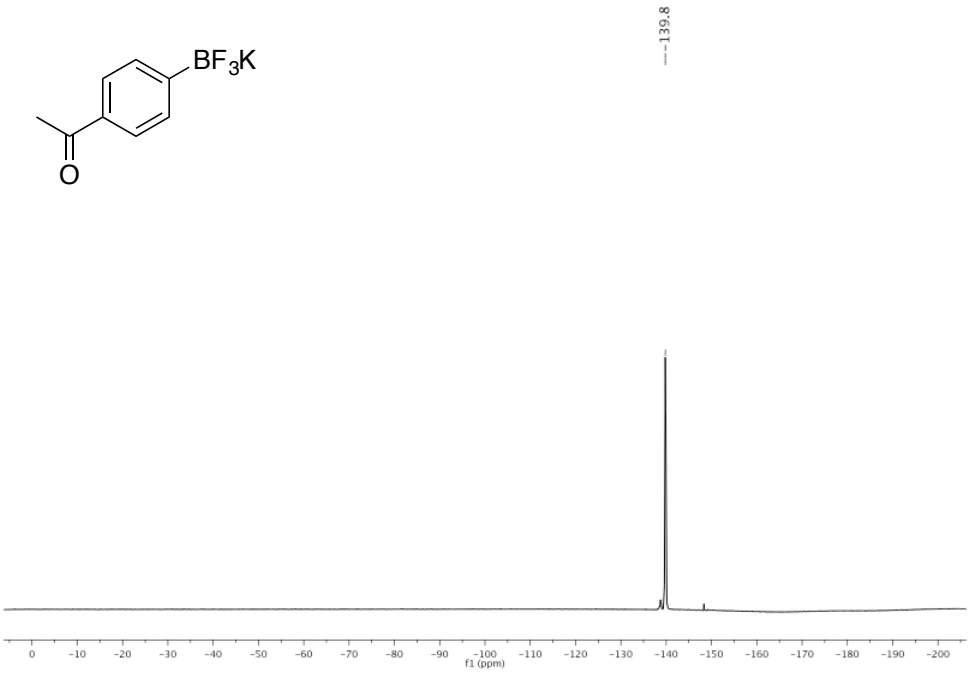


Figure A1.50 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium (4-Acetylphenyl)trifluoroborate

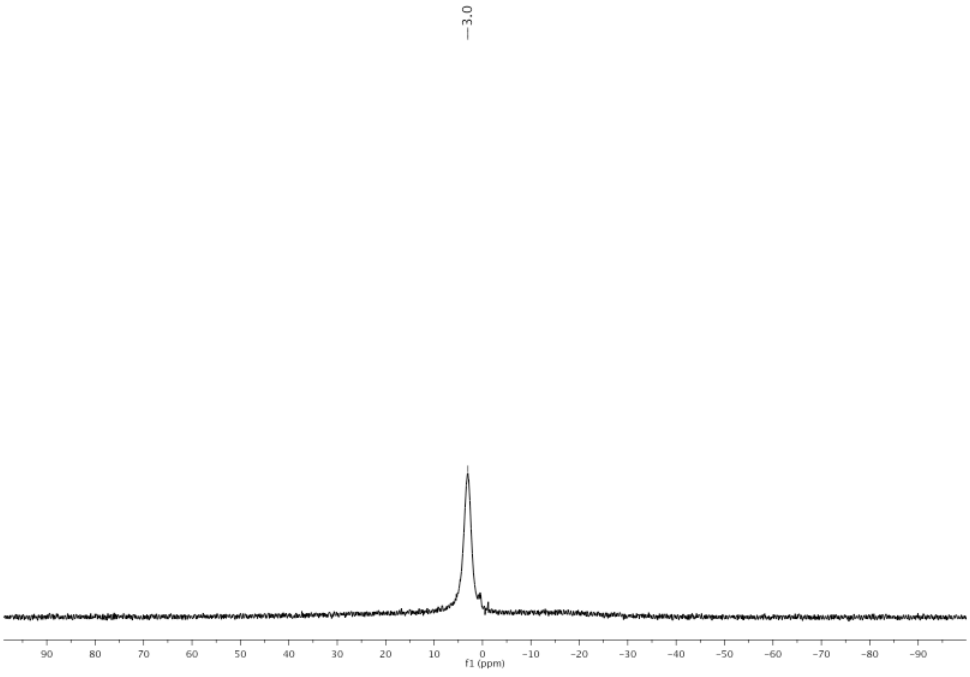


Figure A1.51 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium (4-Acetylphenyl)trifluoroborate

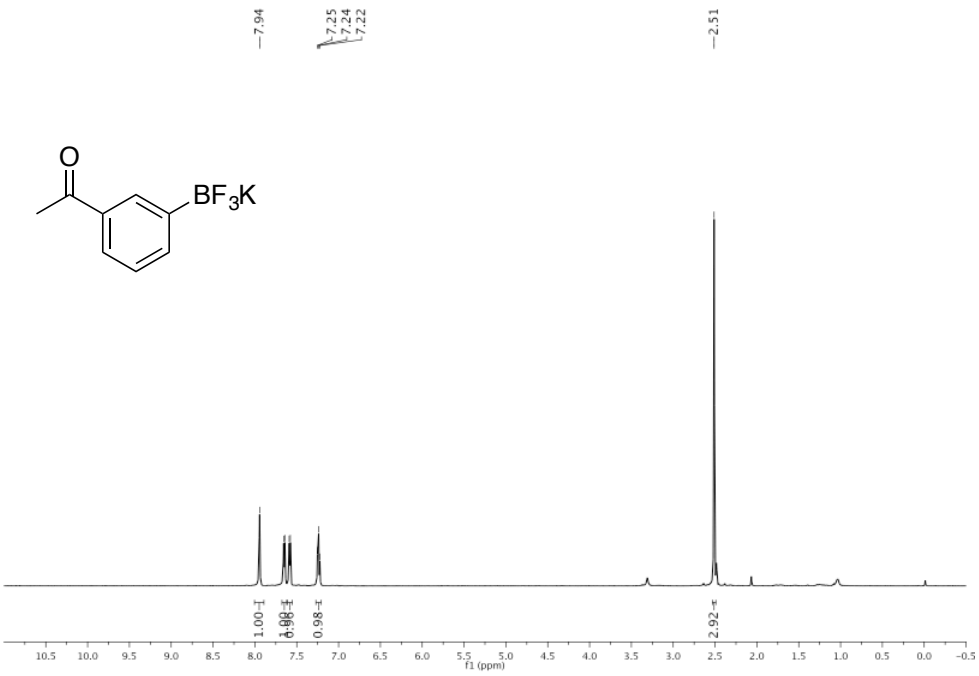


Figure A1.52 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium (3-Acetylphenyl)trifluoroborate

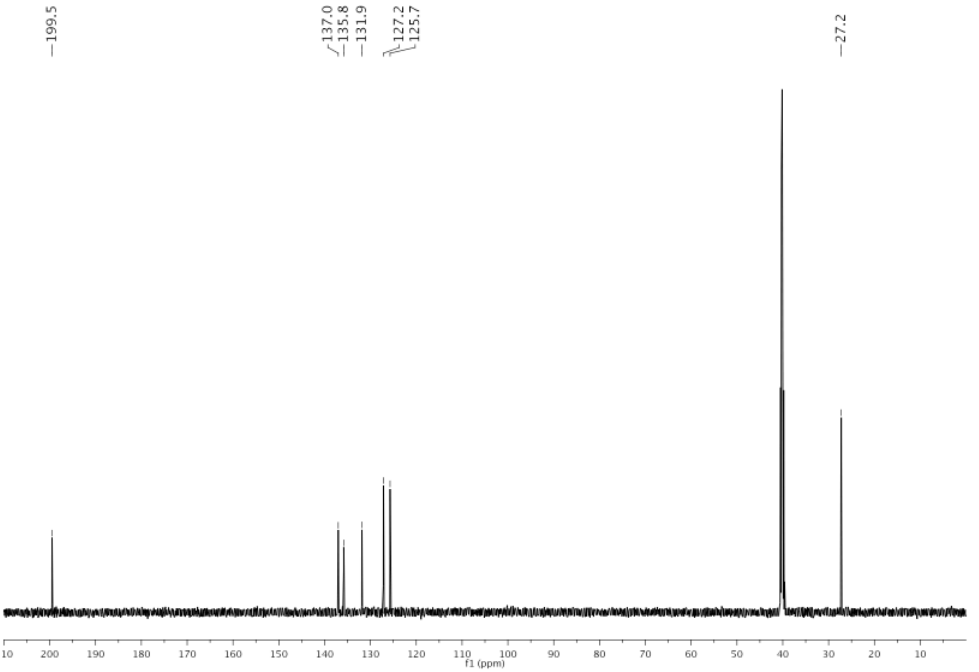


Figure A1.53 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium (3-Acetylphenyl)trifluoroborate

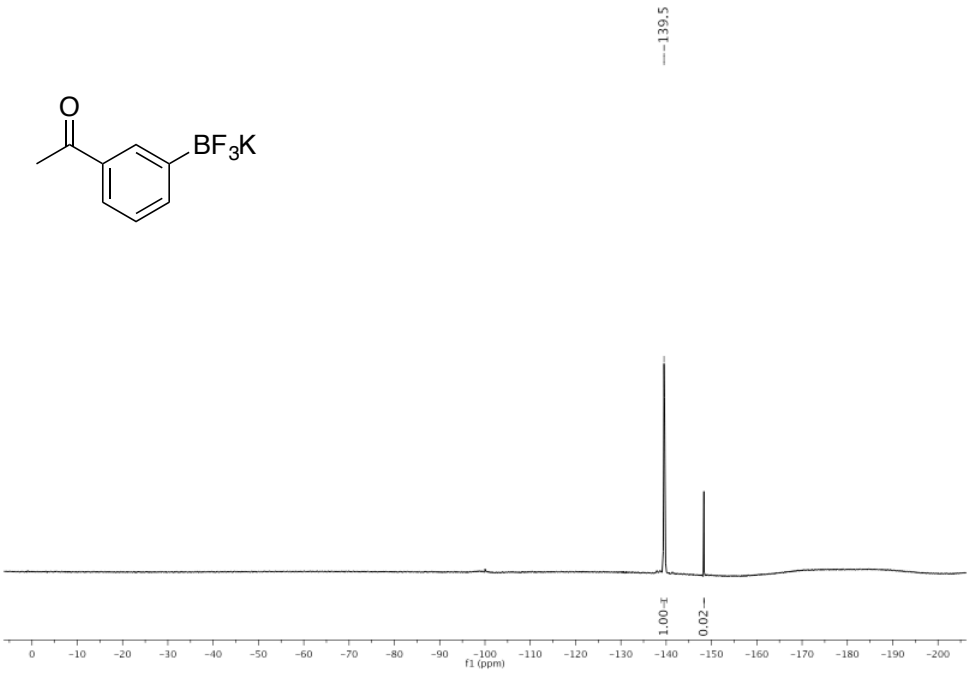


Figure A1.54 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium (3-Acetylphenyl)trifluoroborate

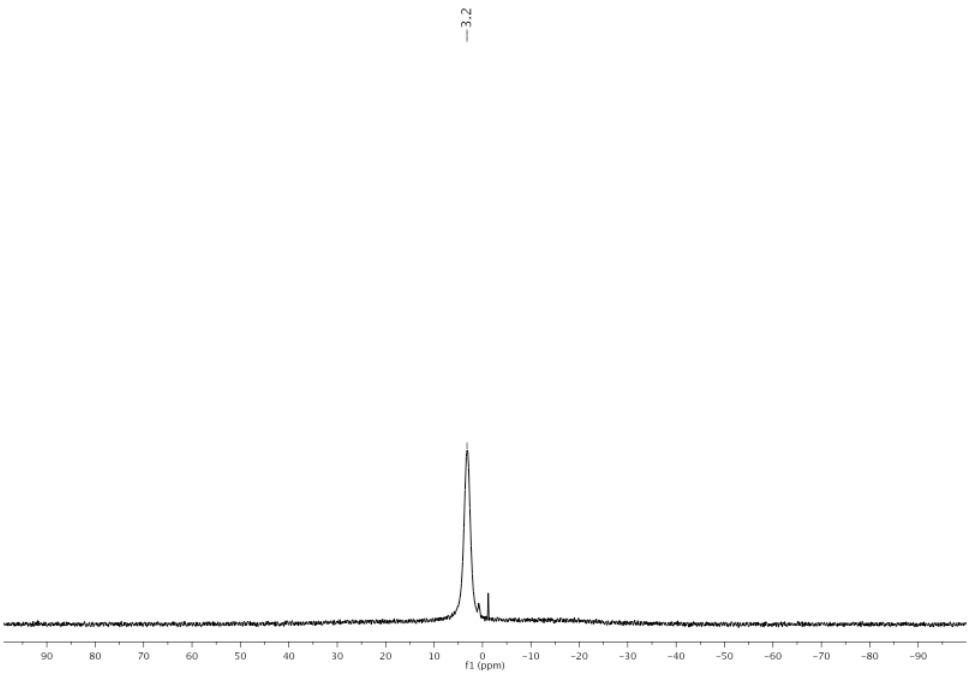


Figure A1.55 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium (3-Acetylphenyl)trifluoroborate

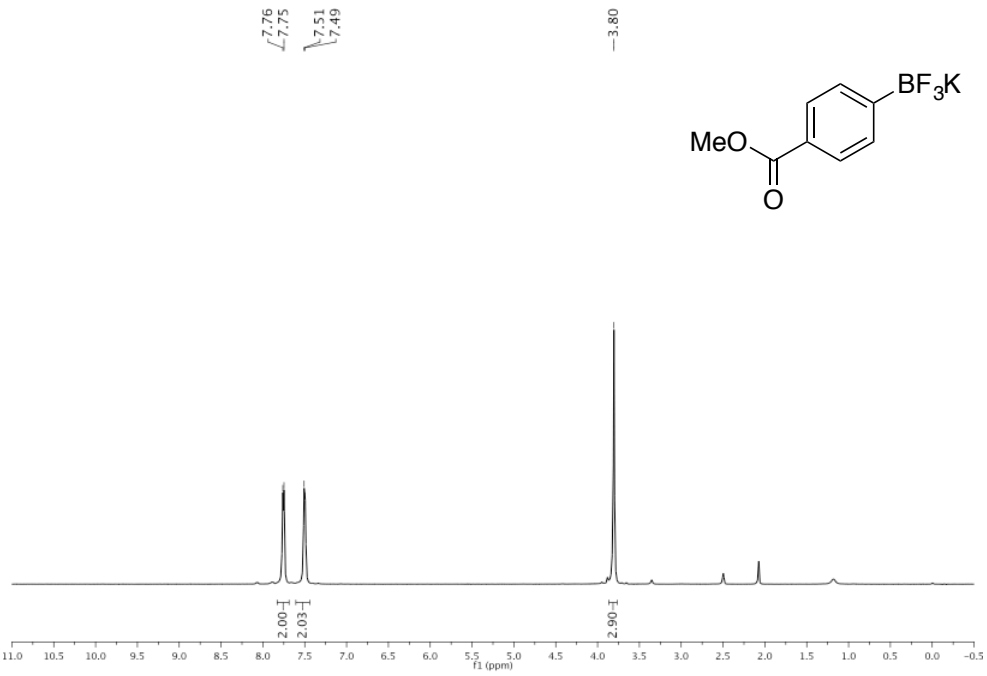


Figure A1.56 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-(methoxycarbonyl)phenyl)borate

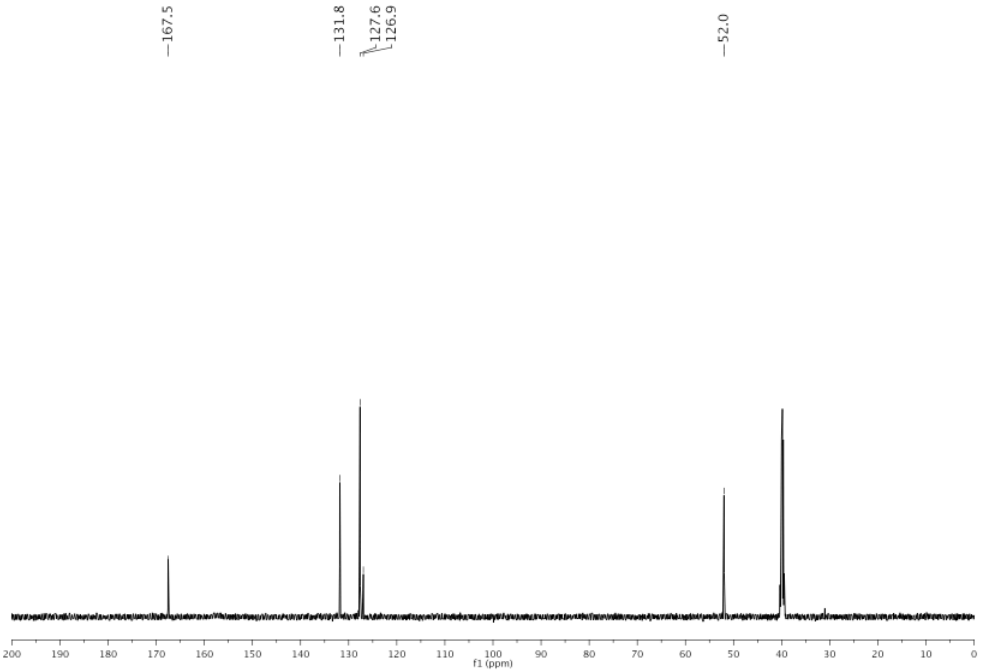


Figure A1.57 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-(methoxycarbonyl)phenyl)borate

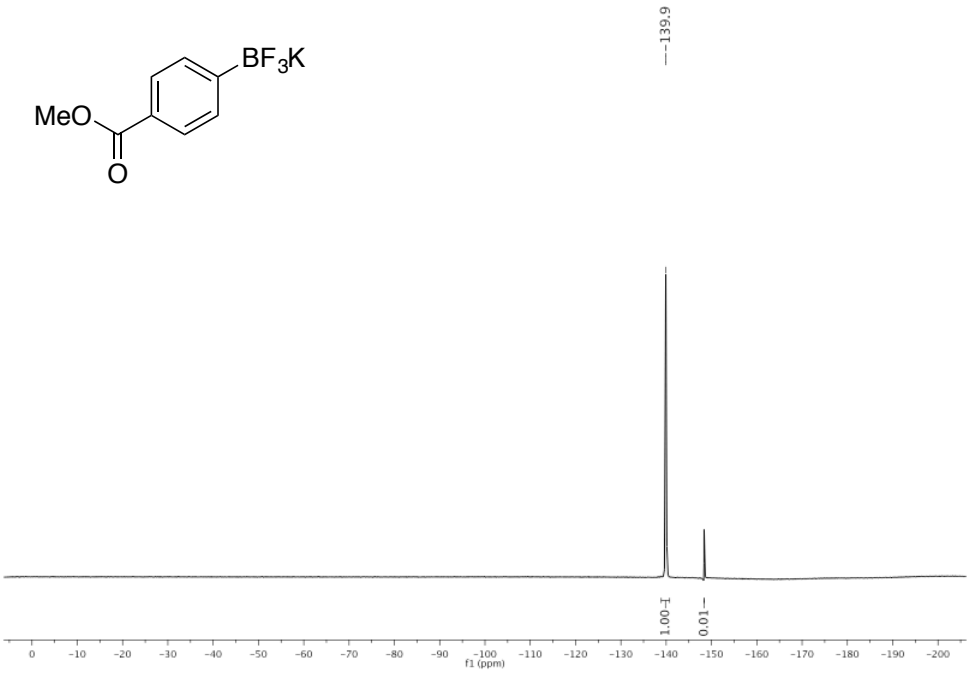


Figure A1.58 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-(methoxycarbonyl)phenyl)borate

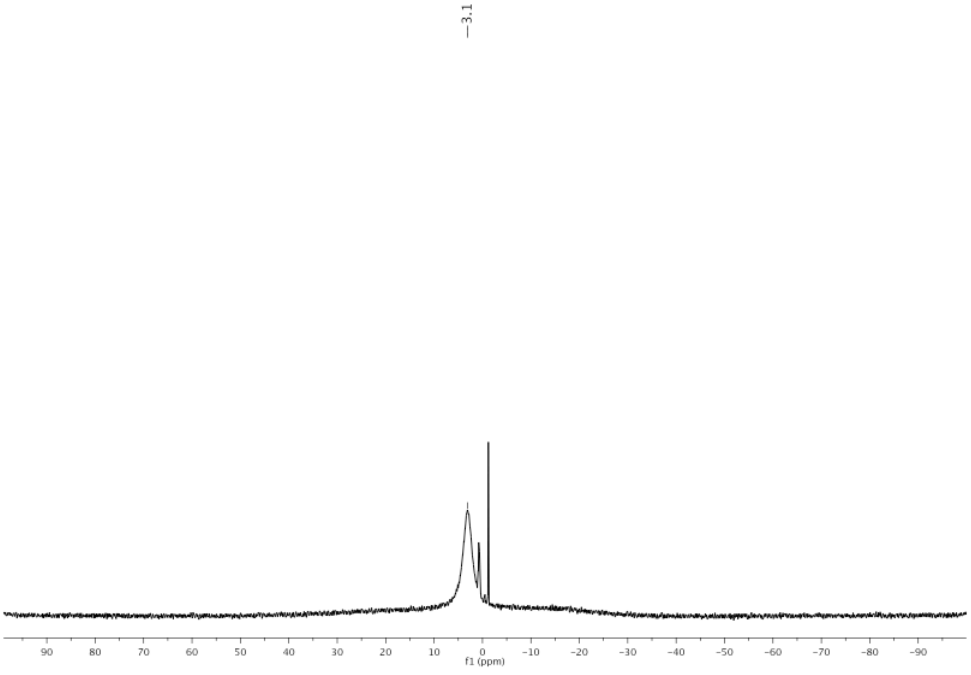


Figure A1.59 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-(methoxycarbonyl)phenyl)borate

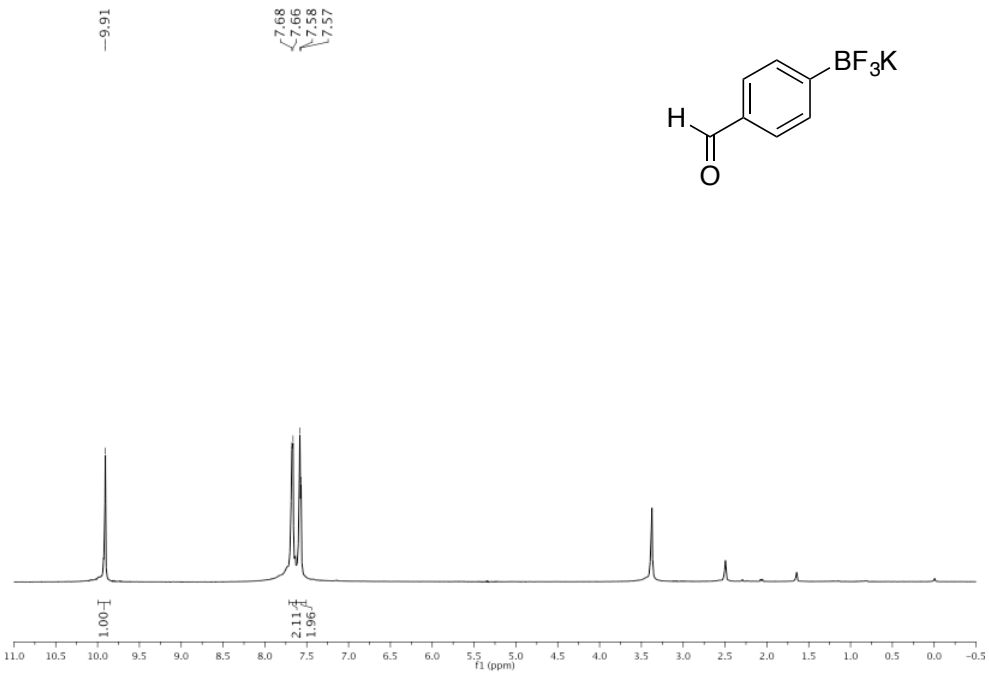


Figure A1.60 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-formylphenyl)borate

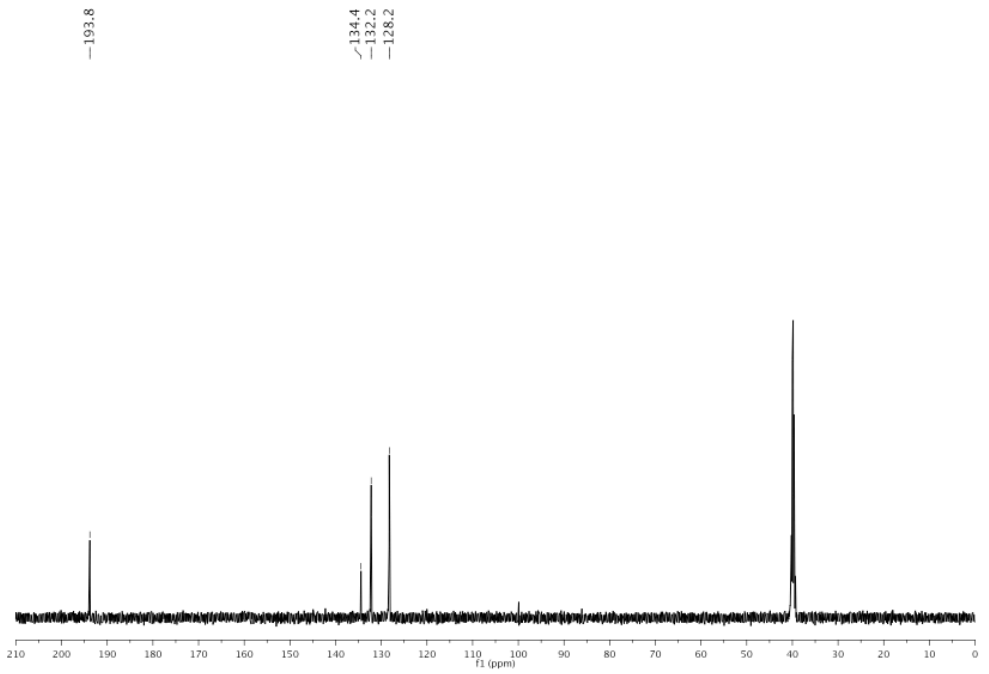


Figure A1.61 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-formylphenyl)borate

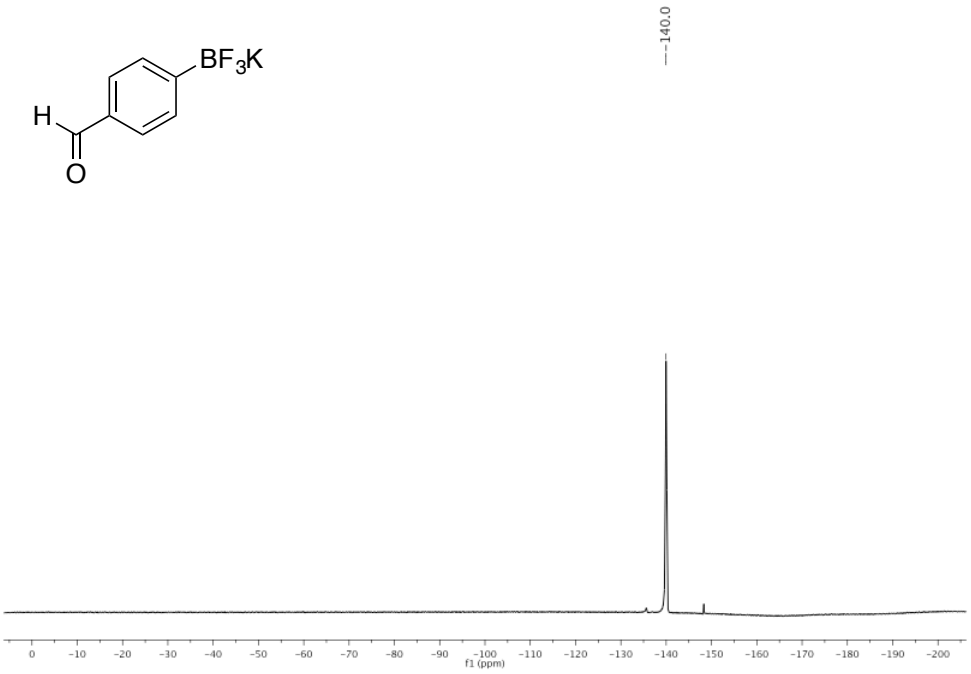


Figure A1.62 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-formylphenyl)borate

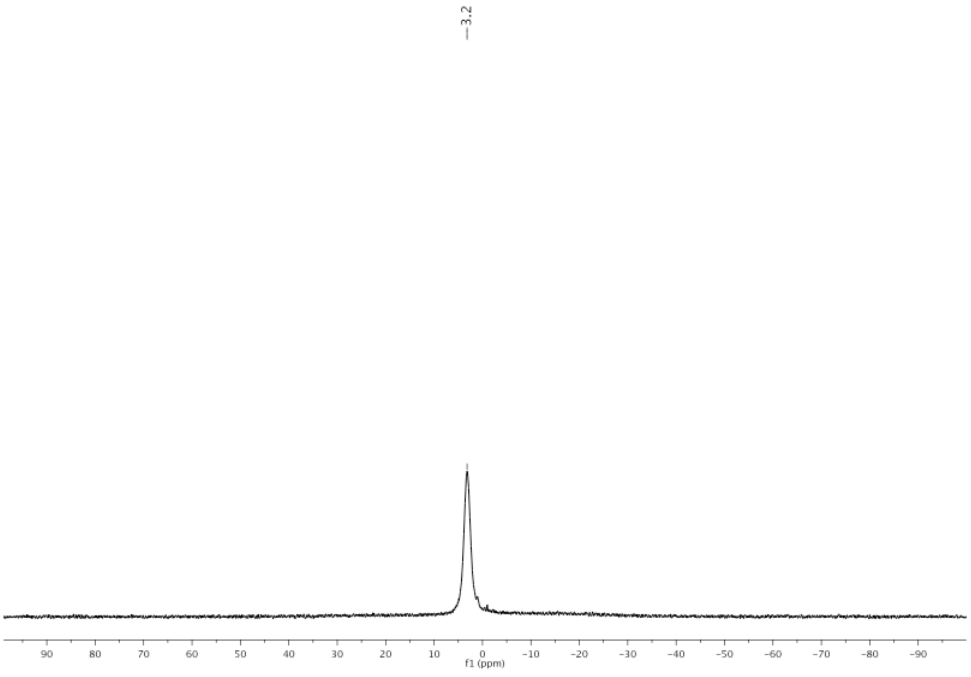


Figure A1.63 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-formylphenyl)borate

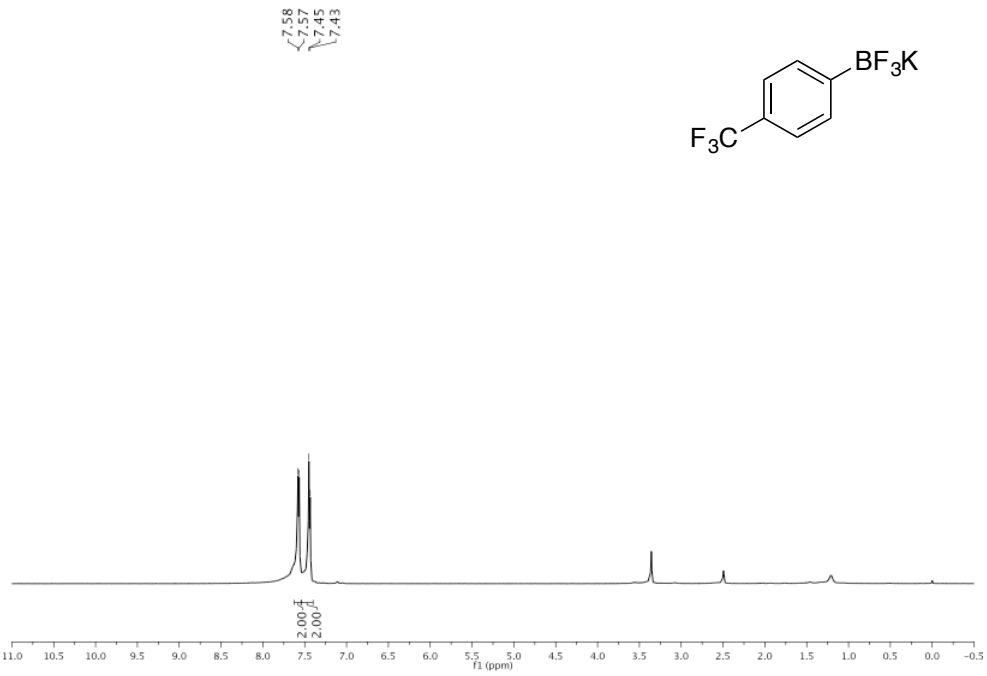


Figure A1.64 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-(trifluoromethyl)phenyl)borate

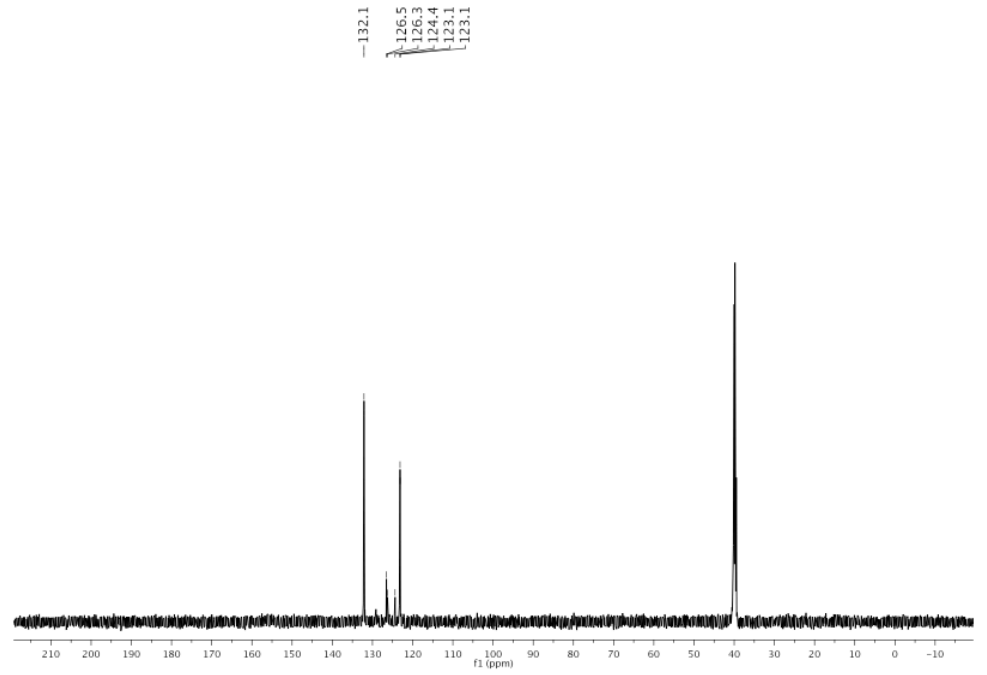


Figure A1.65 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-(trifluoromethyl)phenyl)borate

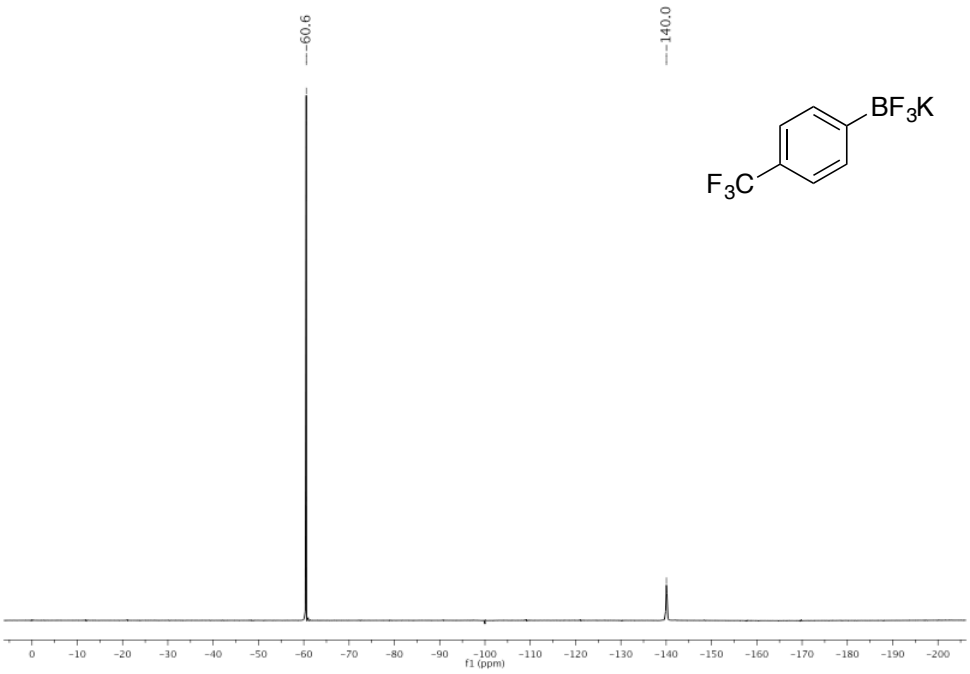


Figure A1.66 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-(trifluoromethyl)phenyl)borate

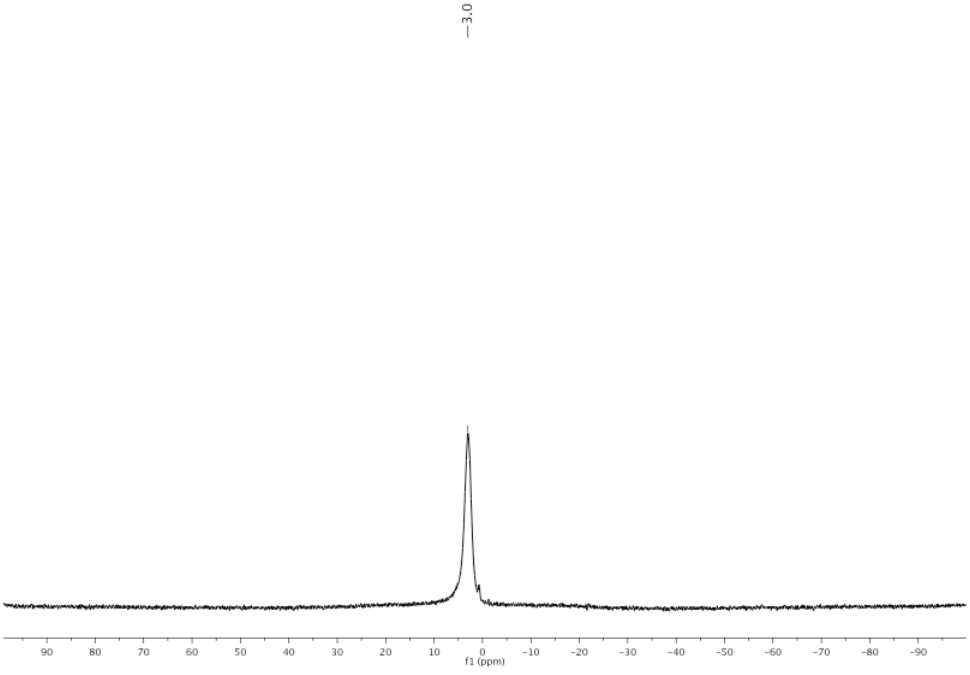


Figure A1.67 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-(trifluoromethyl)phenyl)borate

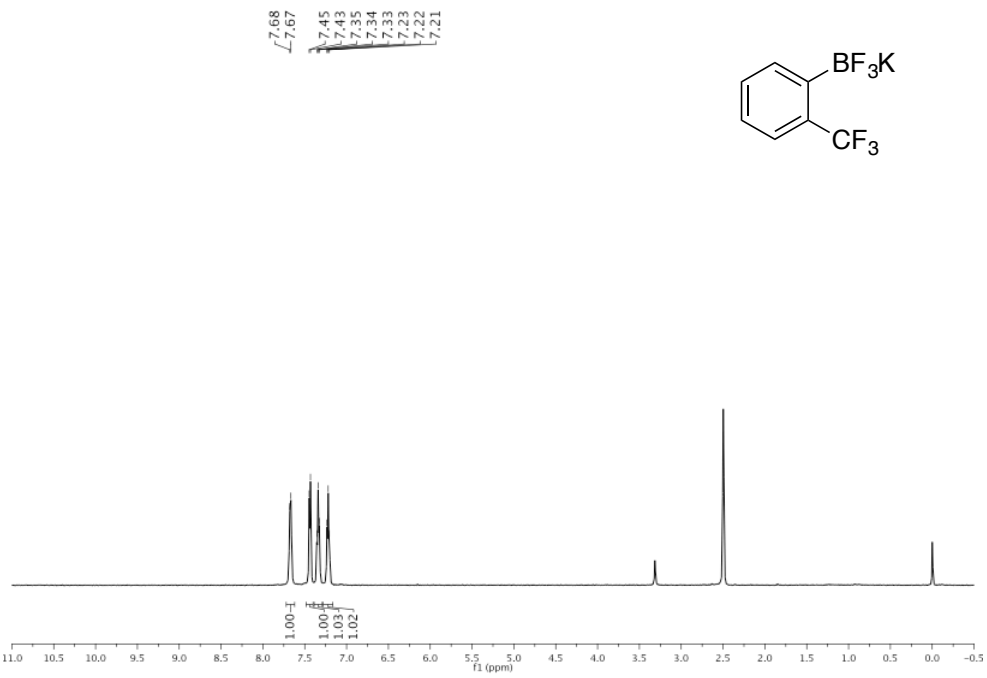


Figure A1.68 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(2-(trifluoromethyl)phenyl)borate

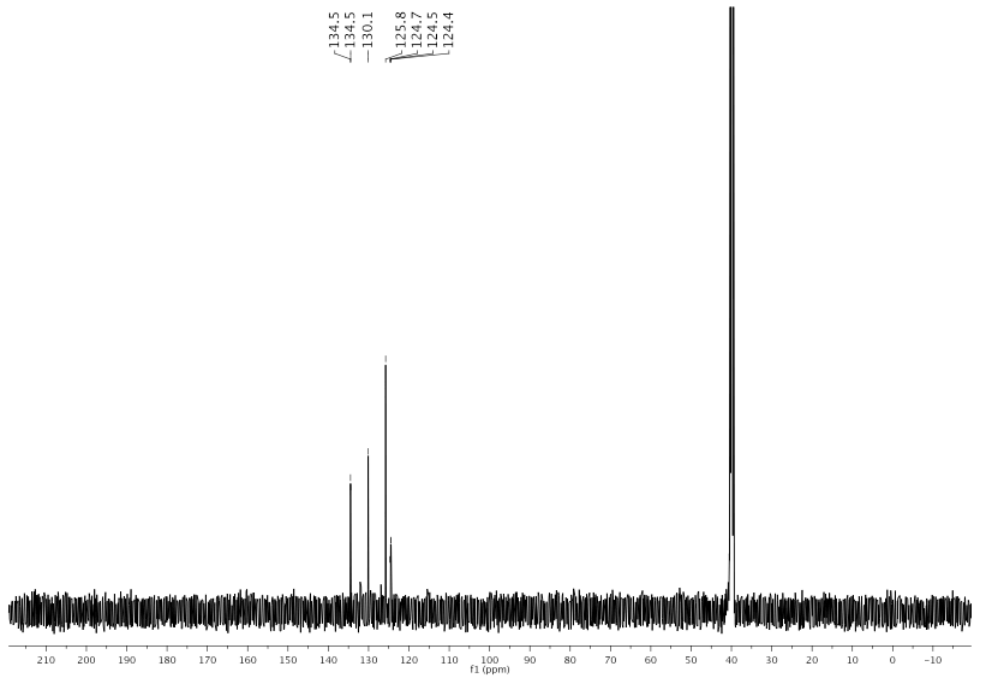


Figure A1.69 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(2-(trifluoromethyl)phenyl)borate

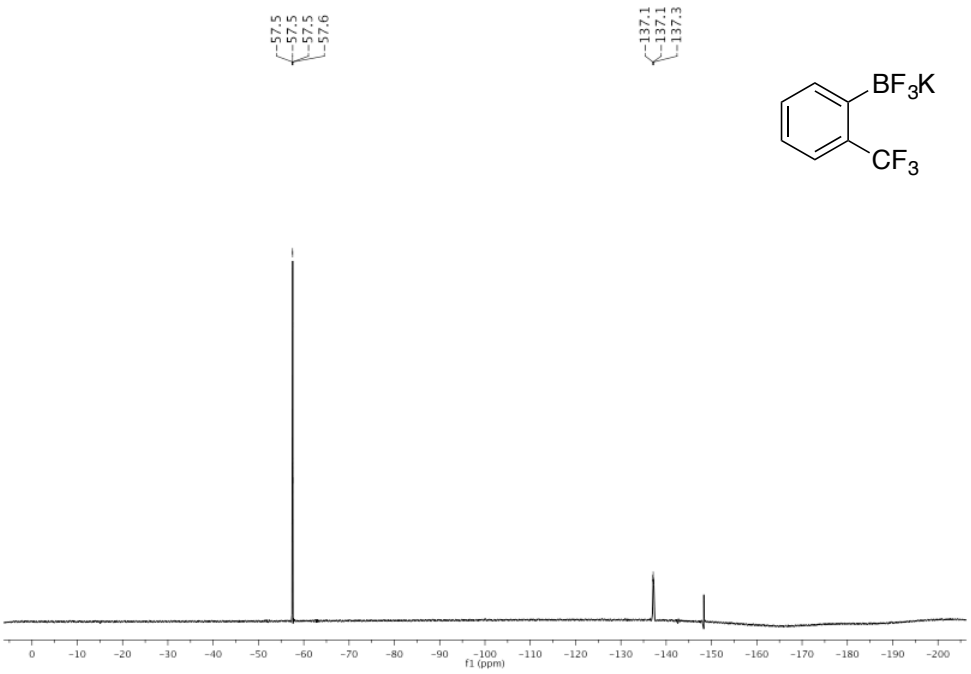


Figure A1.70 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(2-(trifluoromethyl)phenyl)borate

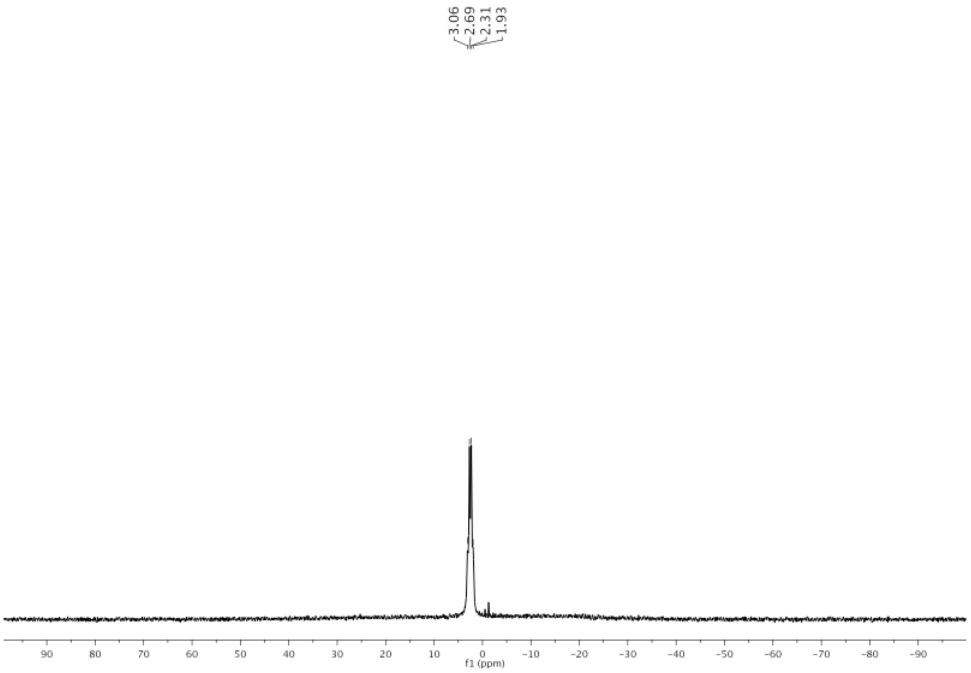


Figure A1.71 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(2-(trifluoromethyl)phenyl)borate

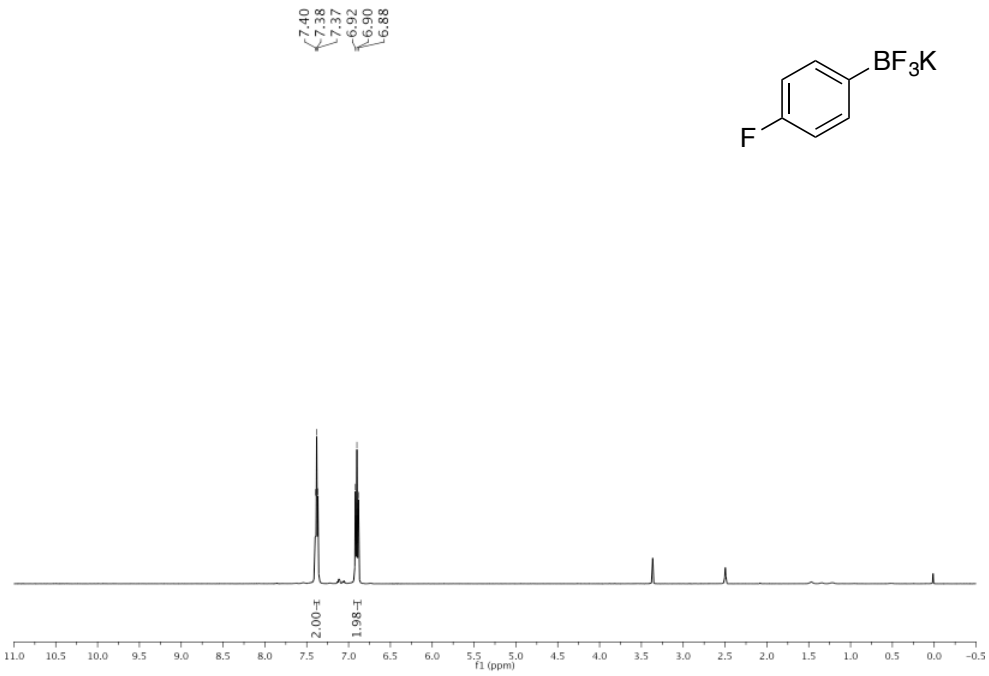


Figure A1.72 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-fluorophenyl)borate

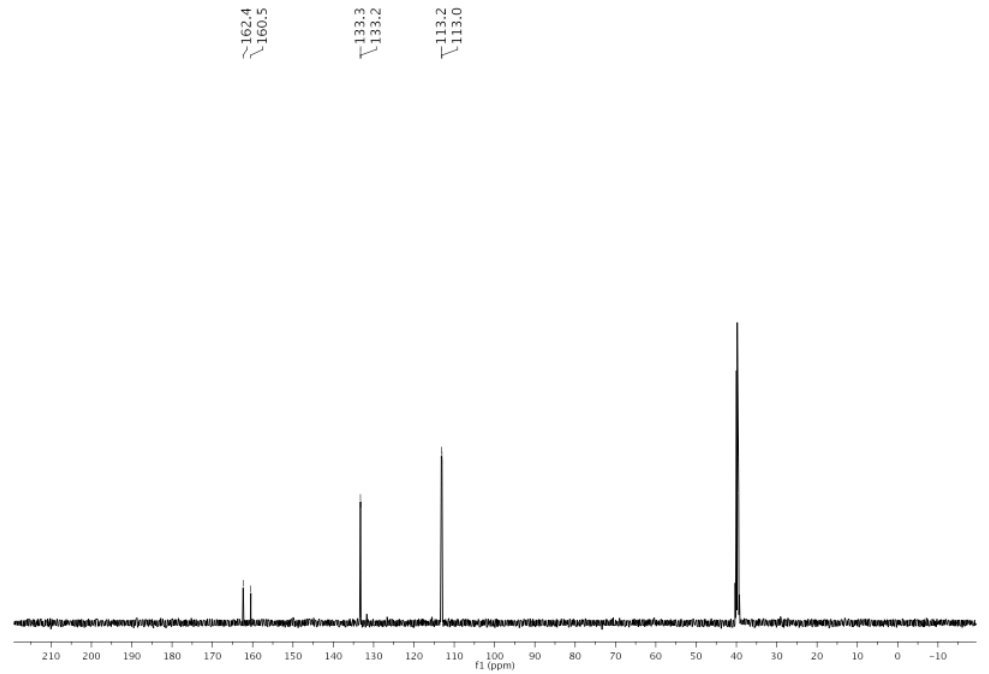


Figure A1.73 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-fluorophenyl)borate

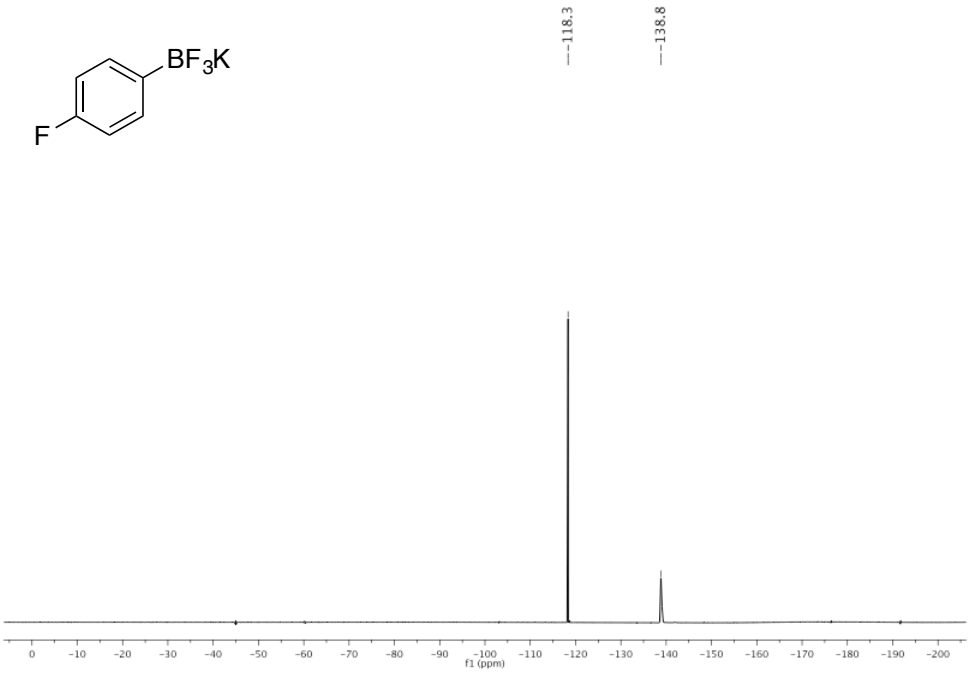


Figure A1.74 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-fluorophenyl)borate

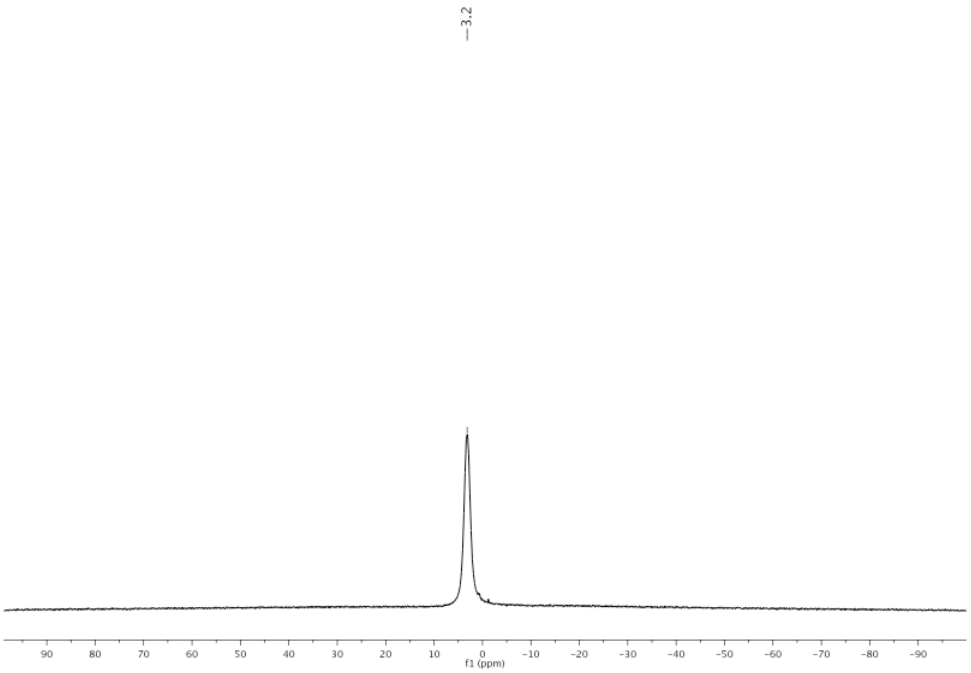


Figure A1.75 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-fluorophenyl)borate

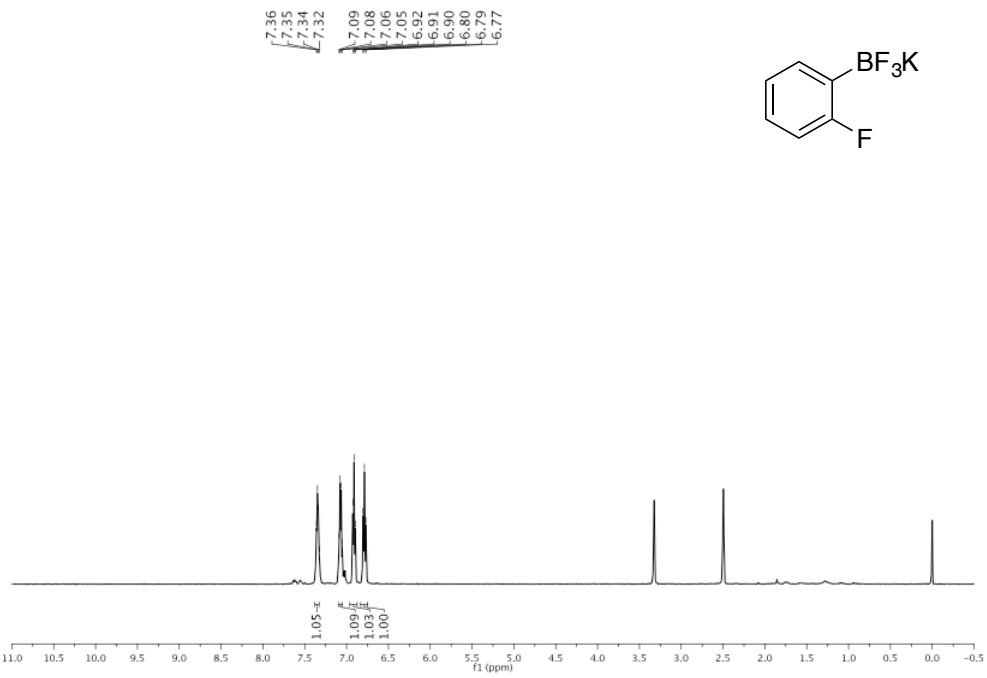


Figure A1.76 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(2-fluorophenyl)borate

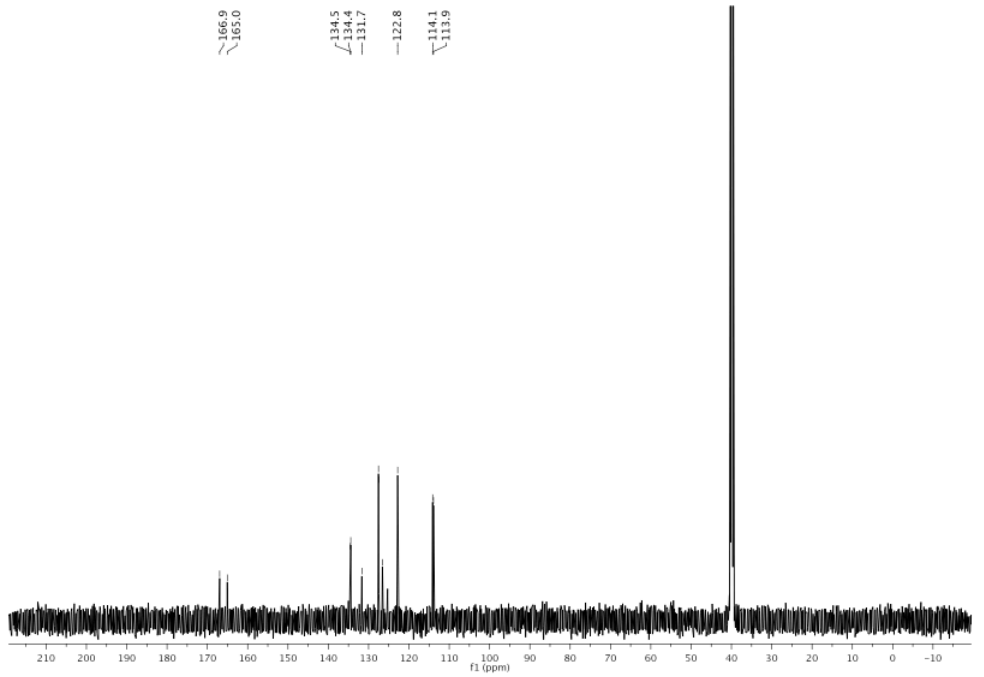


Figure A1.77 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(2-fluorophenyl)borate

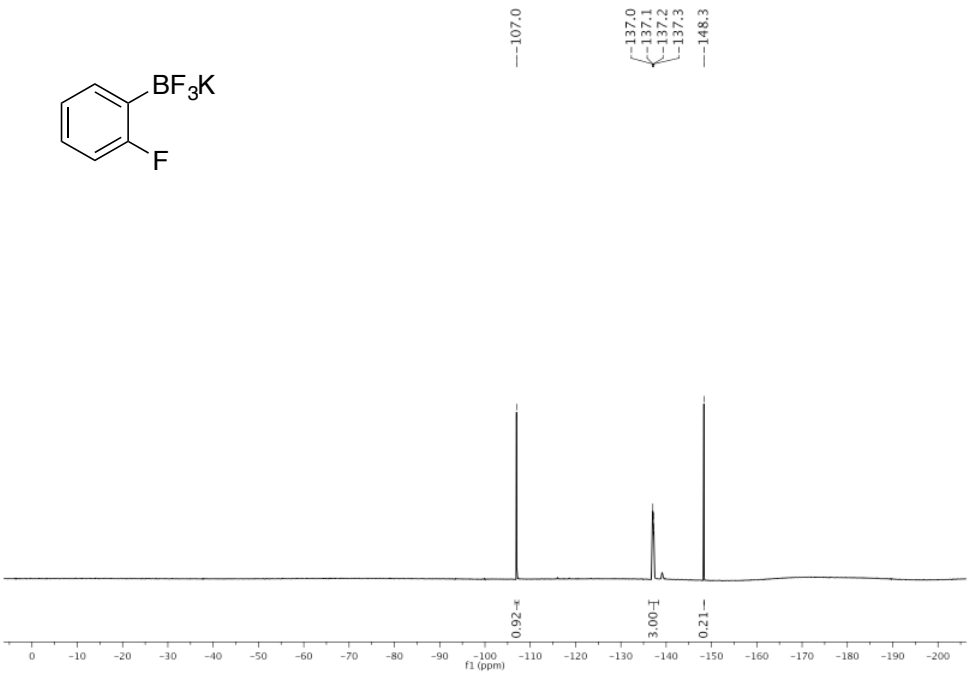


Figure A1.78 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(2-fluorophenyl)borate

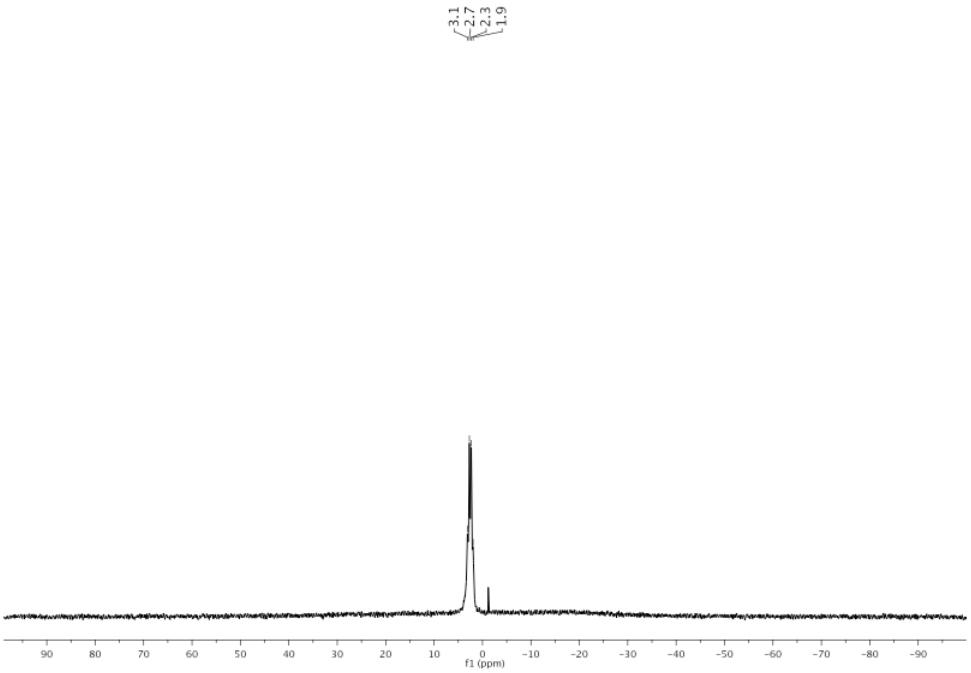


Figure A1.79 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(2-fluorophenyl)borate

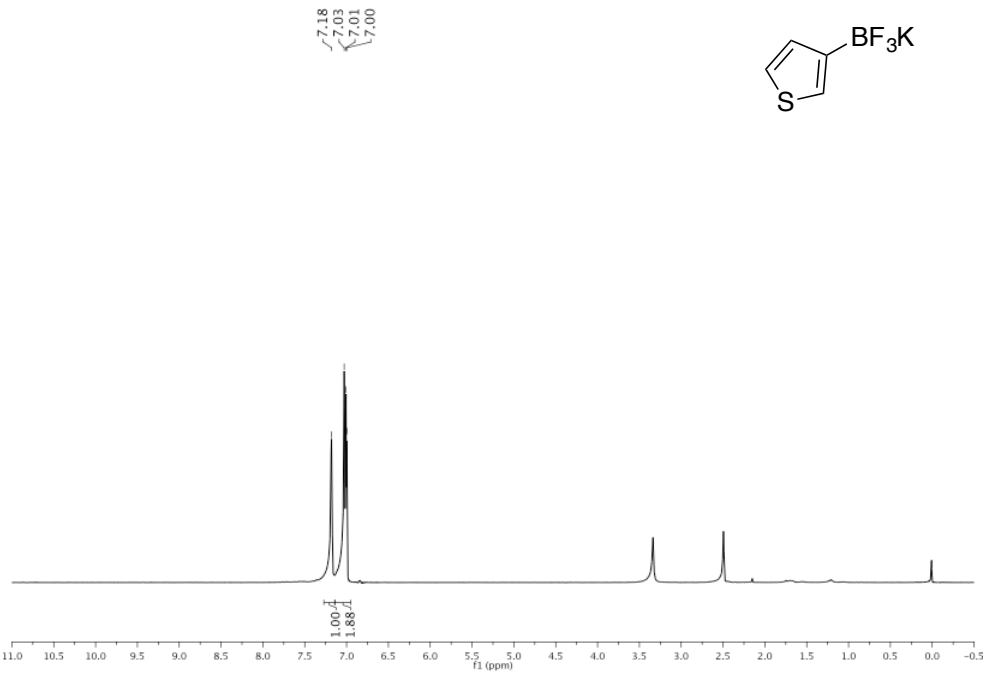


Figure A1.80 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(thien-3-yl)borate

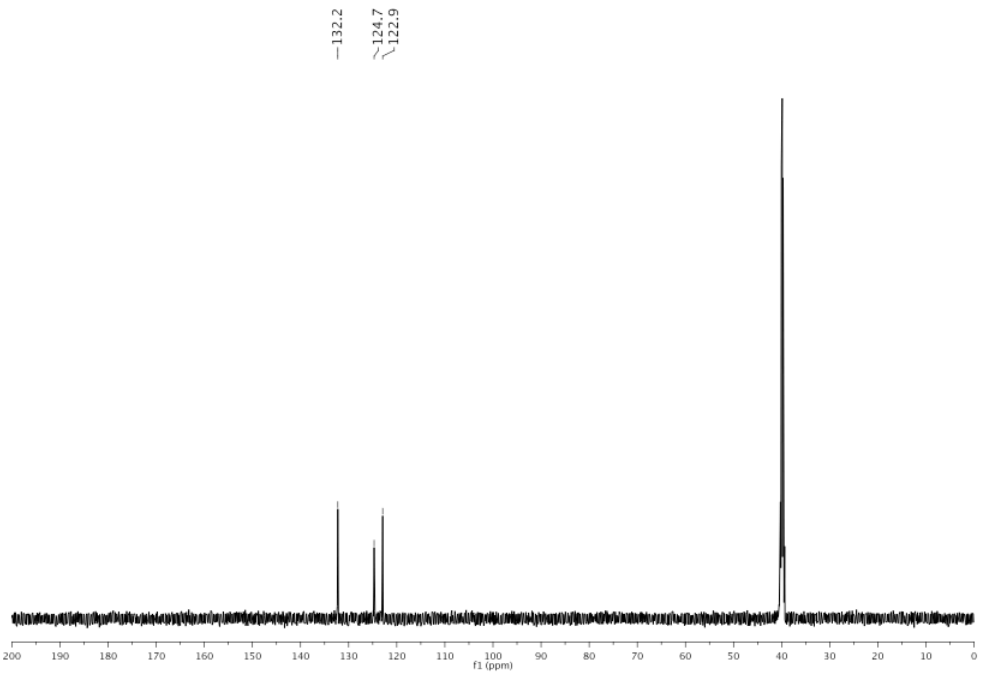


Figure A1.81 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(thien-3-yl)borate

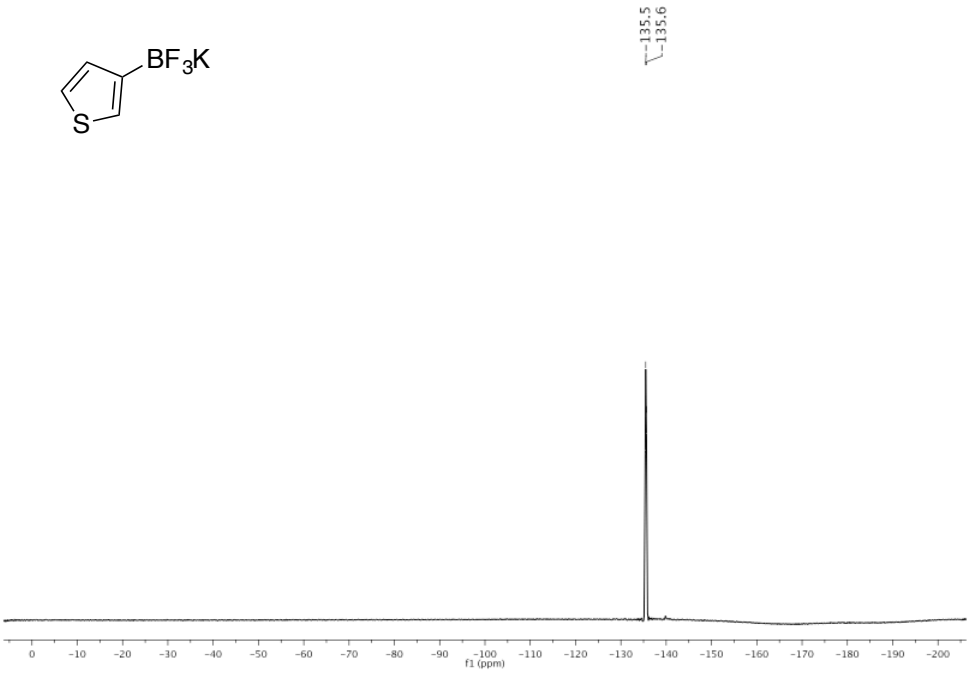


Figure A1.82 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(thien-3-yl)borate

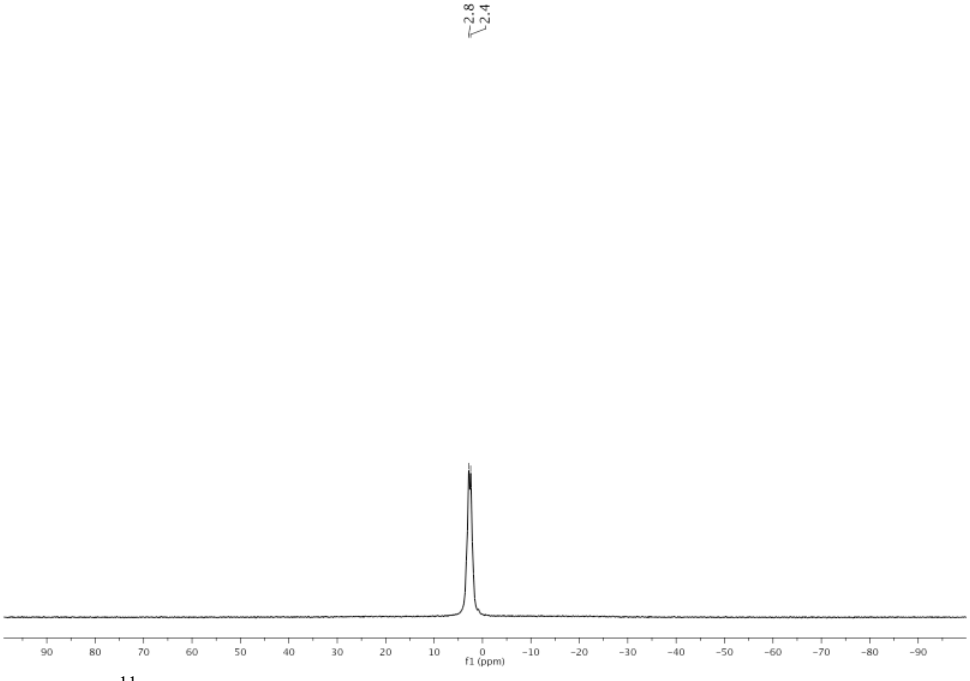


Figure A1.83 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(thien-3-yl)borate

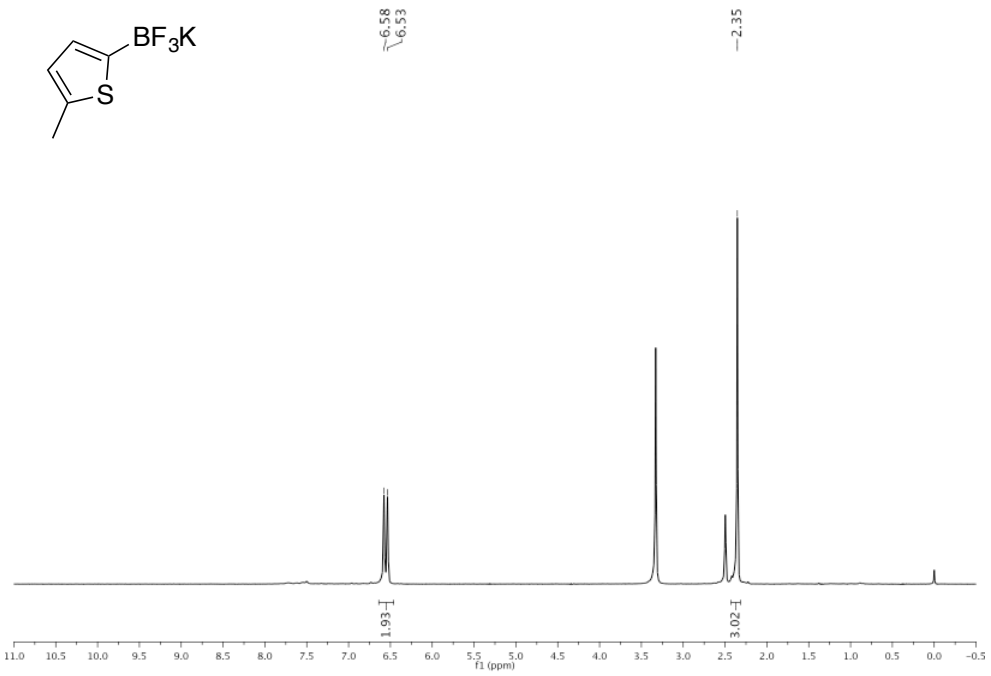


Figure A1.84 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(5-methylthien-2-yl)borate

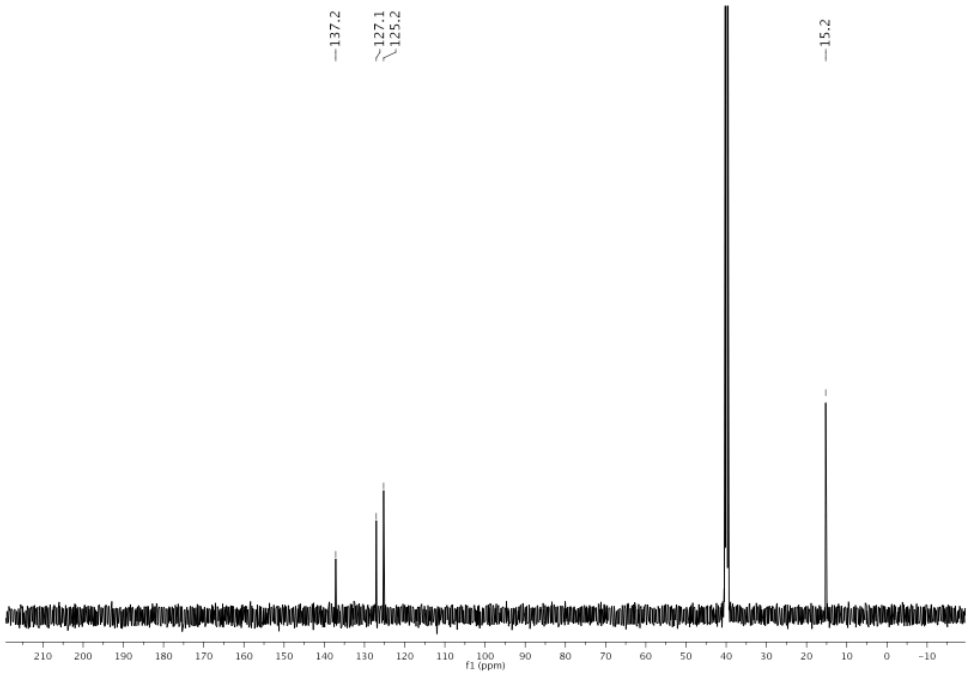


Figure A1.85 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(5-methylthien-2-yl)borate

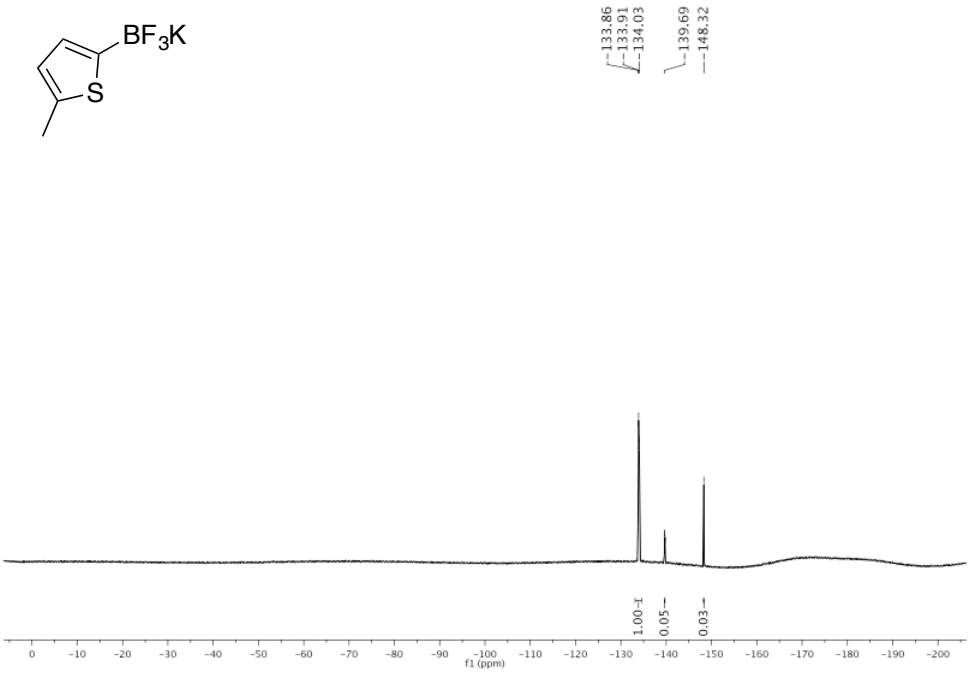


Figure A1.86 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(5-methylthien-2-yl)borate

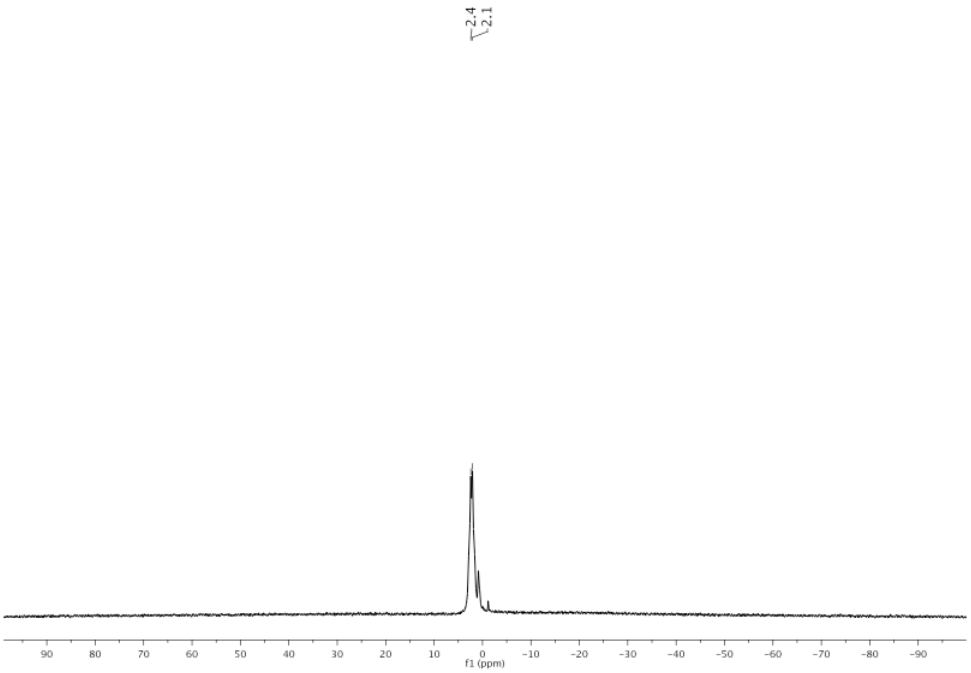


Figure A1.87 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(5-methylthien-2-yl)borate

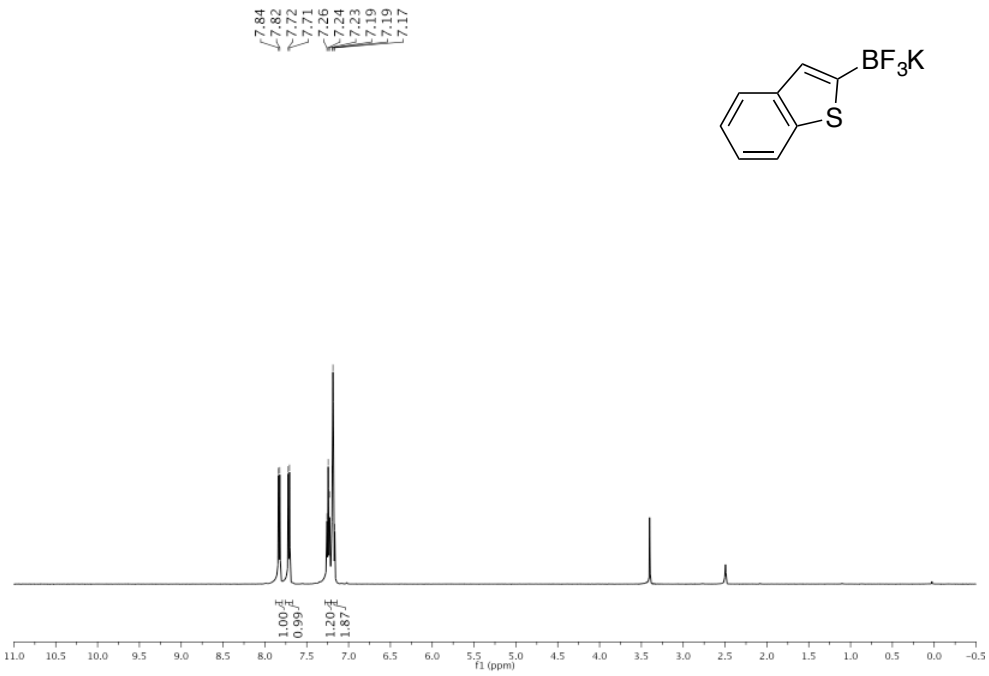


Figure A1.88 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Benzo[*b*]thien-2-yltrifluoroborate

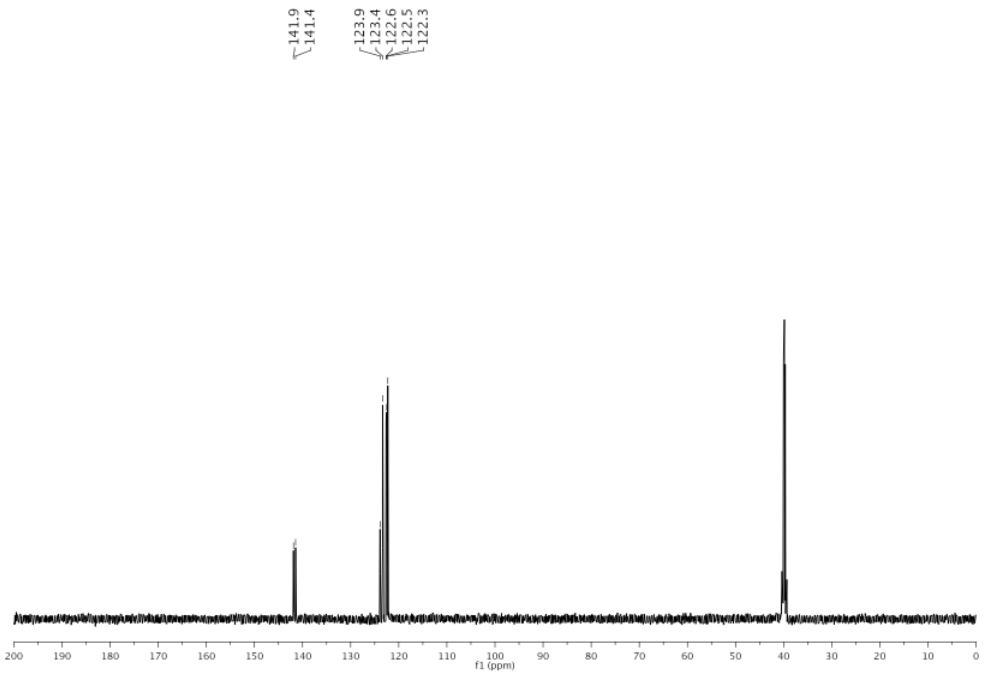


Figure A1.89 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Benzo[*b*]thien-2-yltrifluoroborate

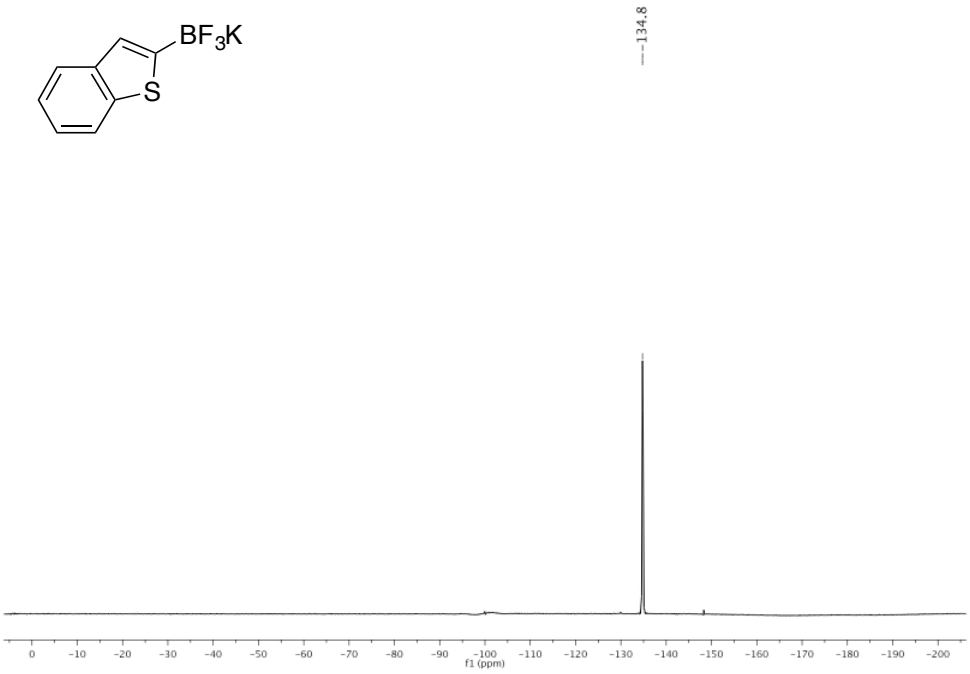


Figure A1.90 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Benzo[*b*]thien-2-yltrifluoroborate

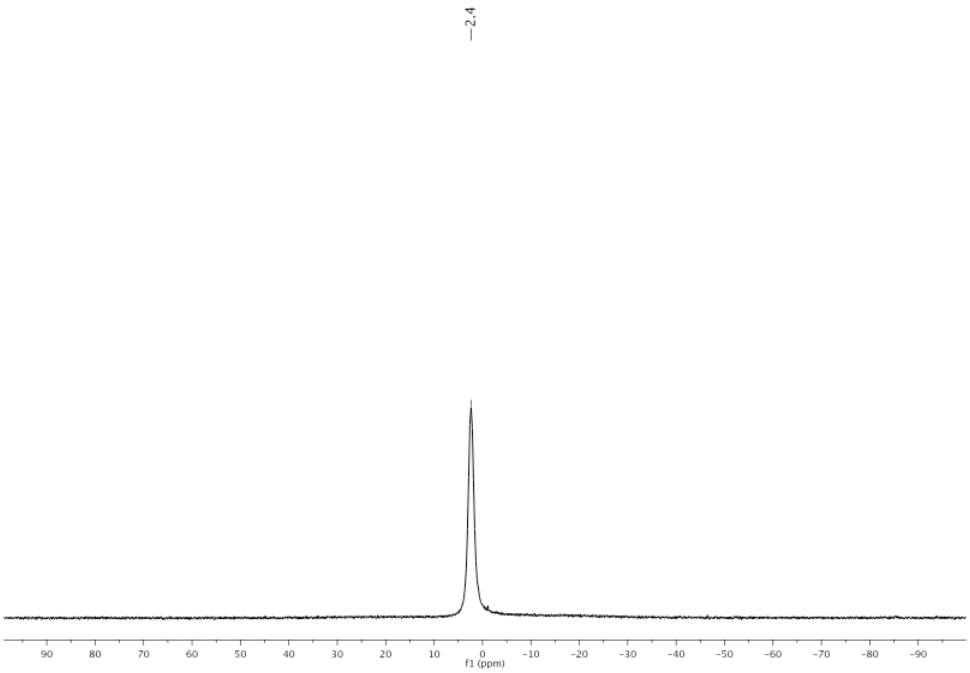


Figure A1.91 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Benzo[*b*]thien-2-yltrifluoroborate

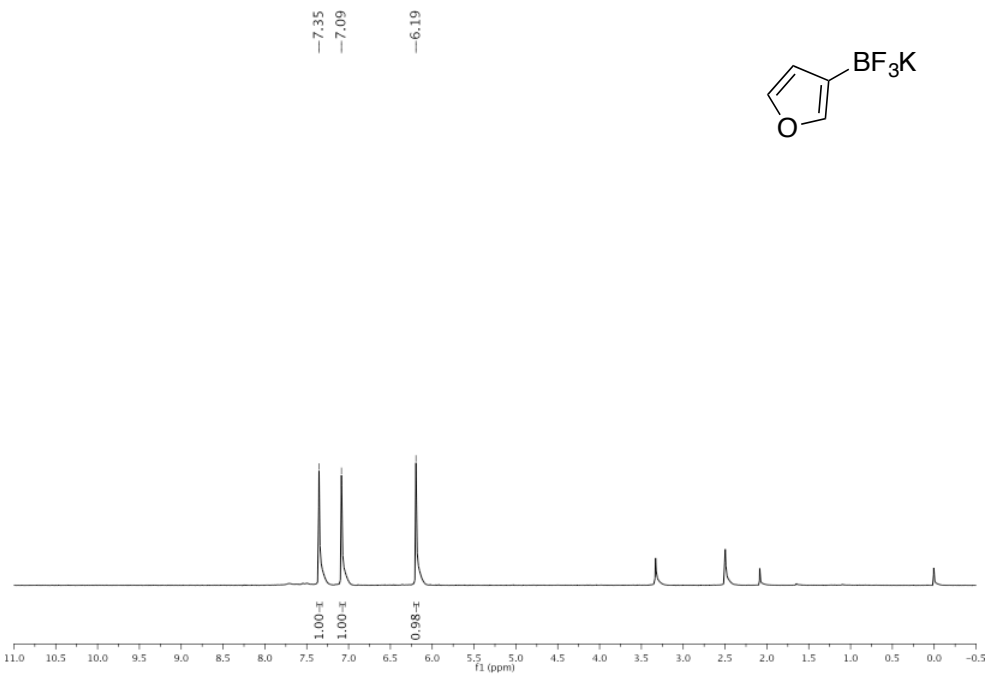


Figure A1.92 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(furan-3-yl)borate

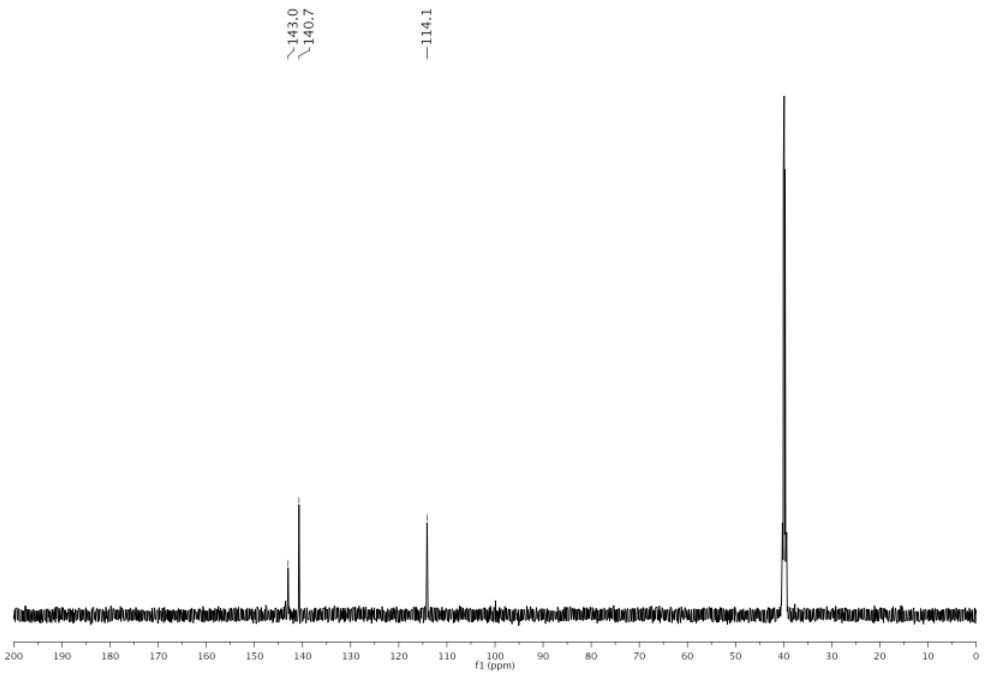


Figure A1.93 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(furan-3-yl)borate

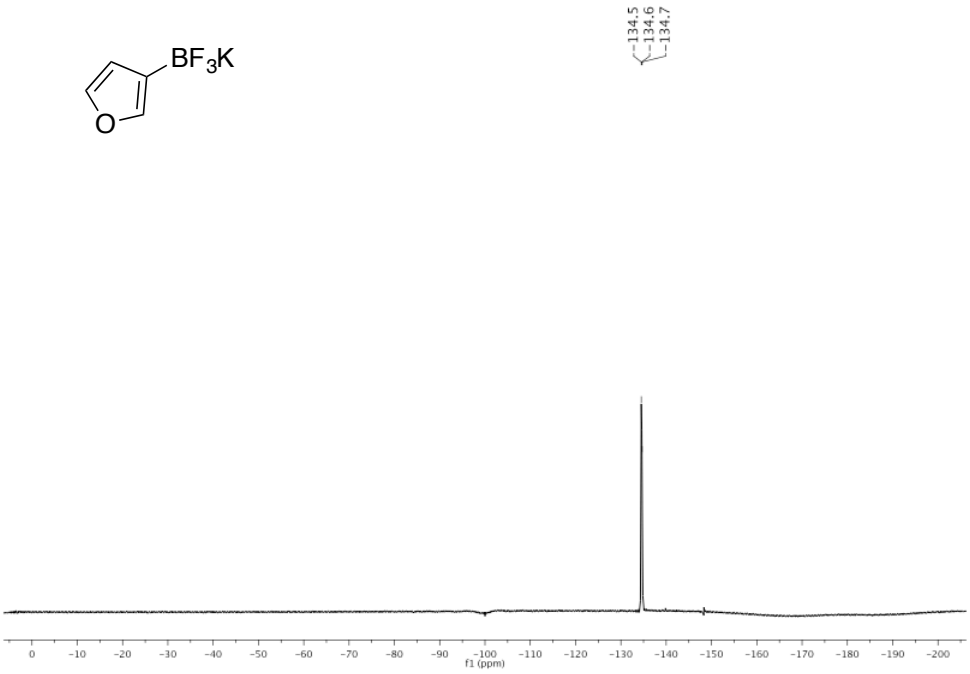


Figure A1.94 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(furan-3-yl)borate

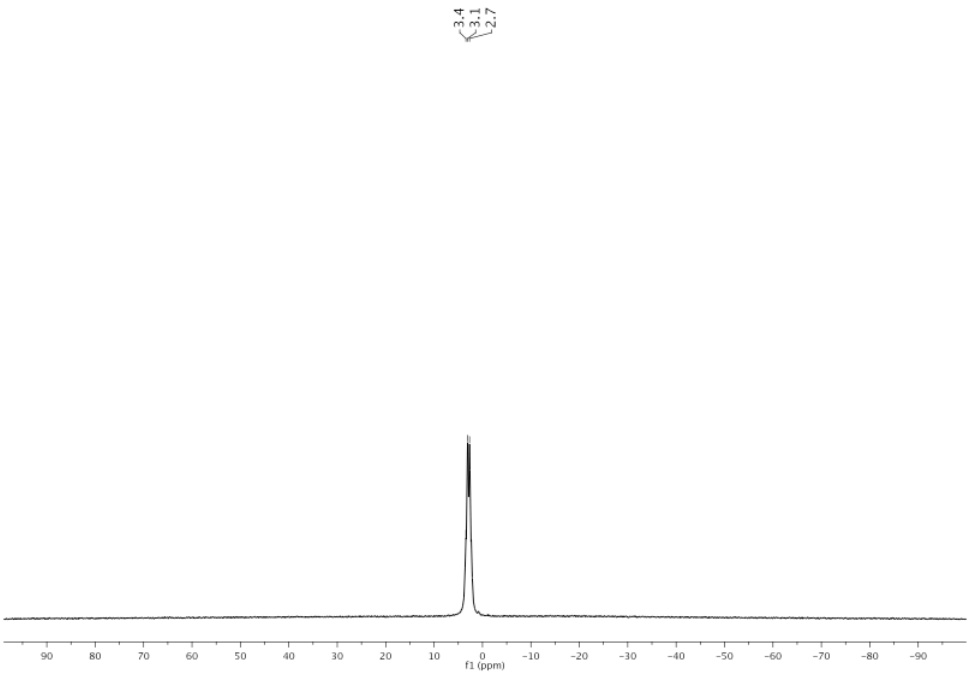


Figure A1.95 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(furan-3-yl)borate

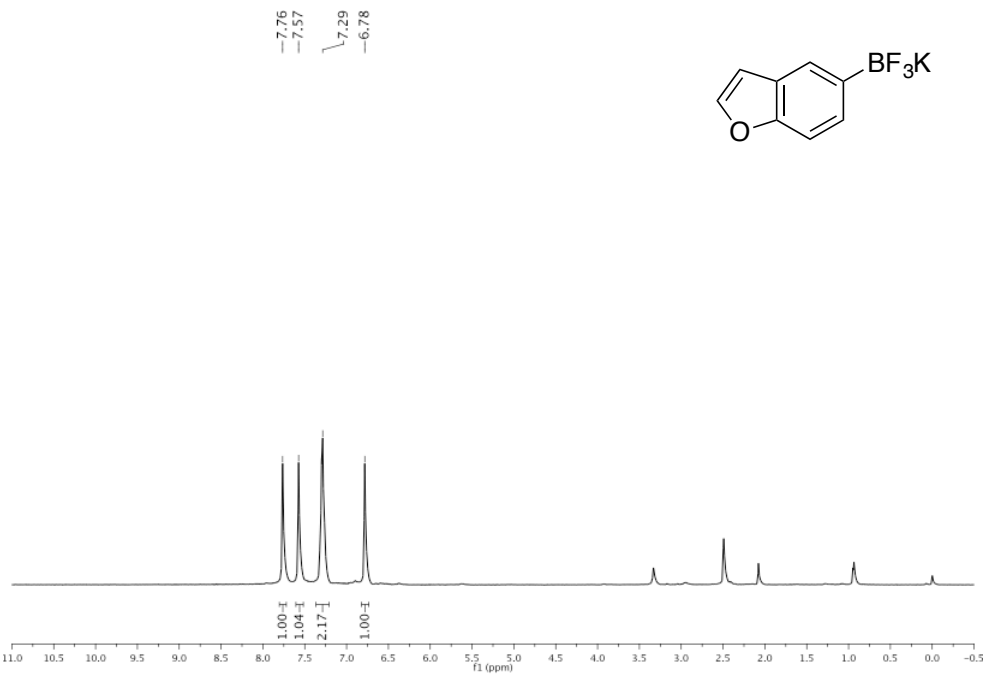


Figure A1.96 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Benzofuran-5-yltrifluoroborate

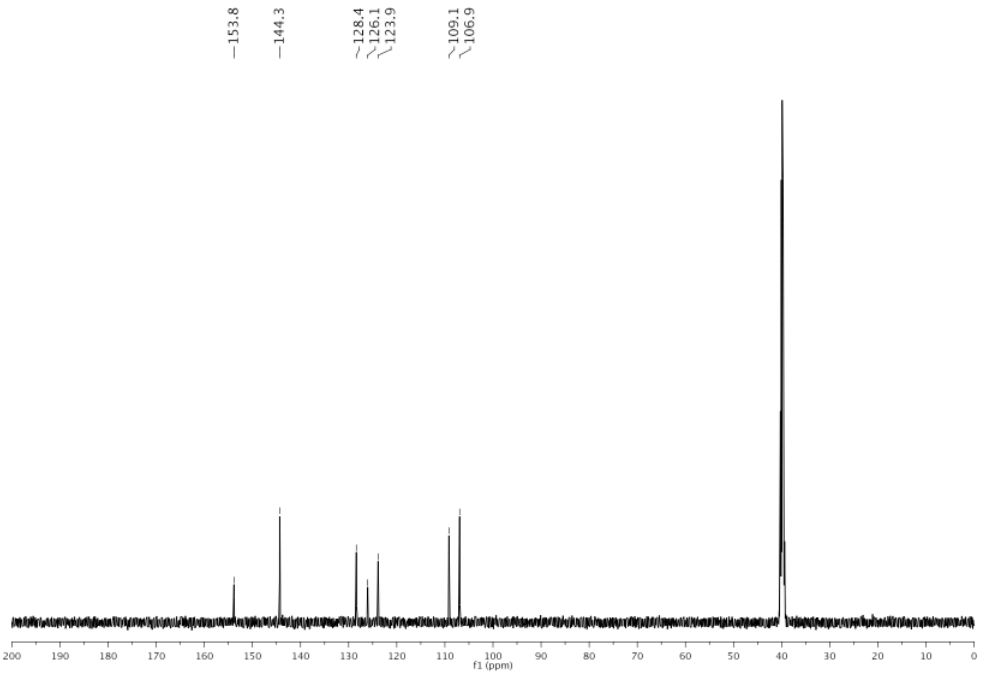


Figure A1.97 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Benzofuran-5-yltrifluoroborate

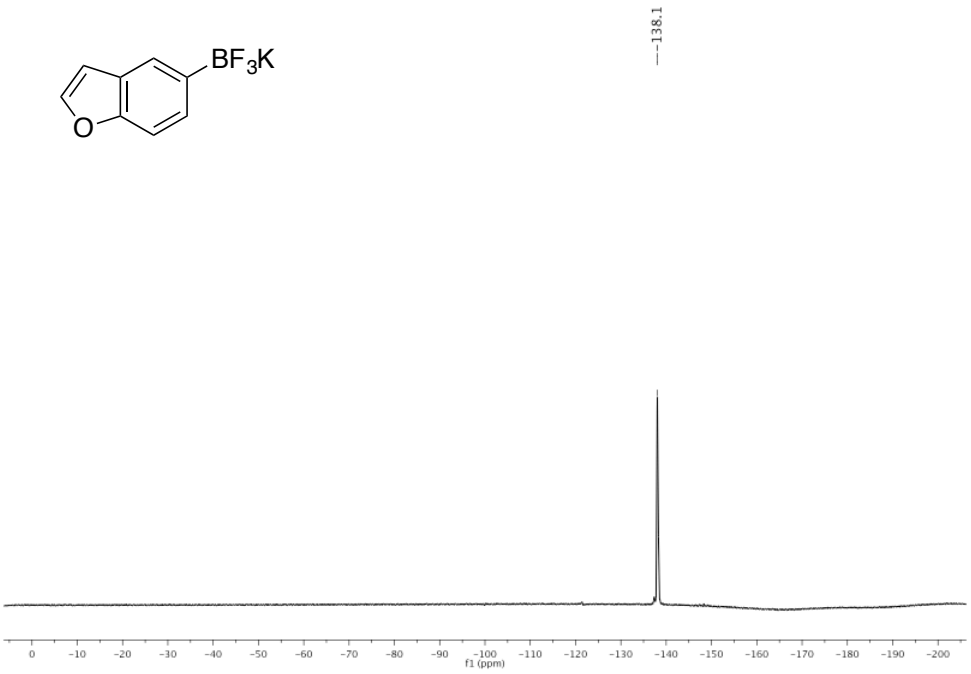


Figure A1.98 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Benzofuran-5-yltrifluoroborate

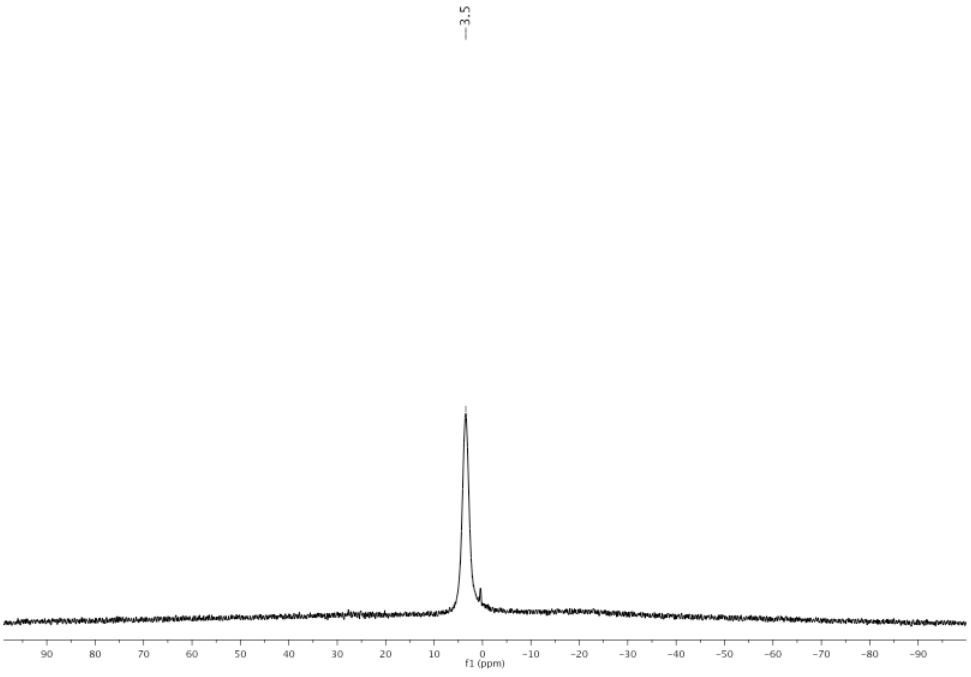


Figure A1.99 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Benzofuran-5-yltrifluoroborate

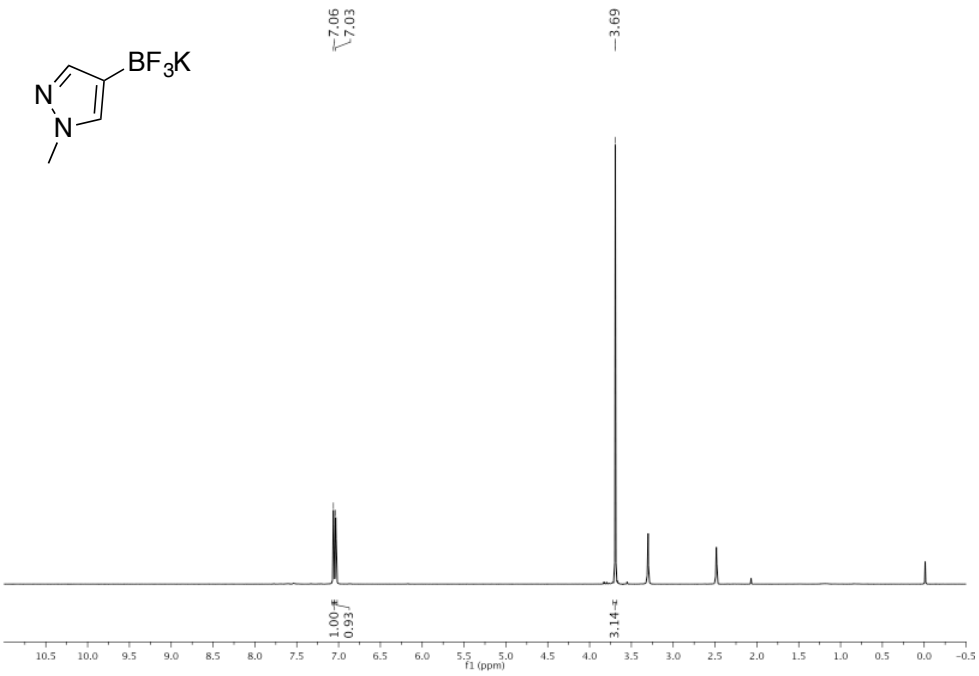


Figure A1.100 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(1-methyl-1*H*-pyrazol-4-yl)borate

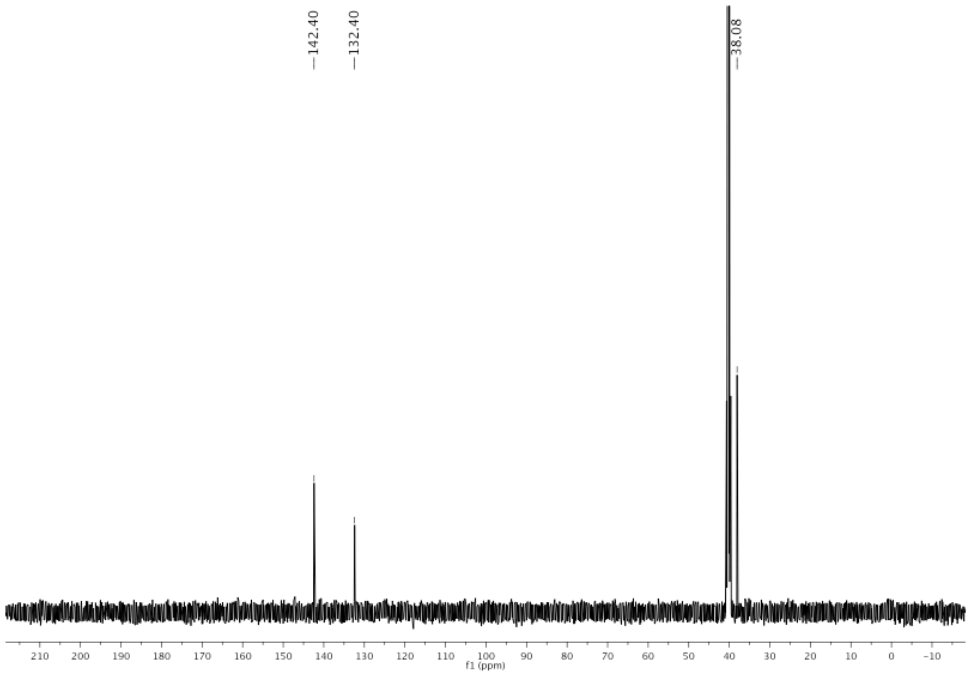


Figure A1.101 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(1-methyl-1*H*-pyrazol-4-yl)borate

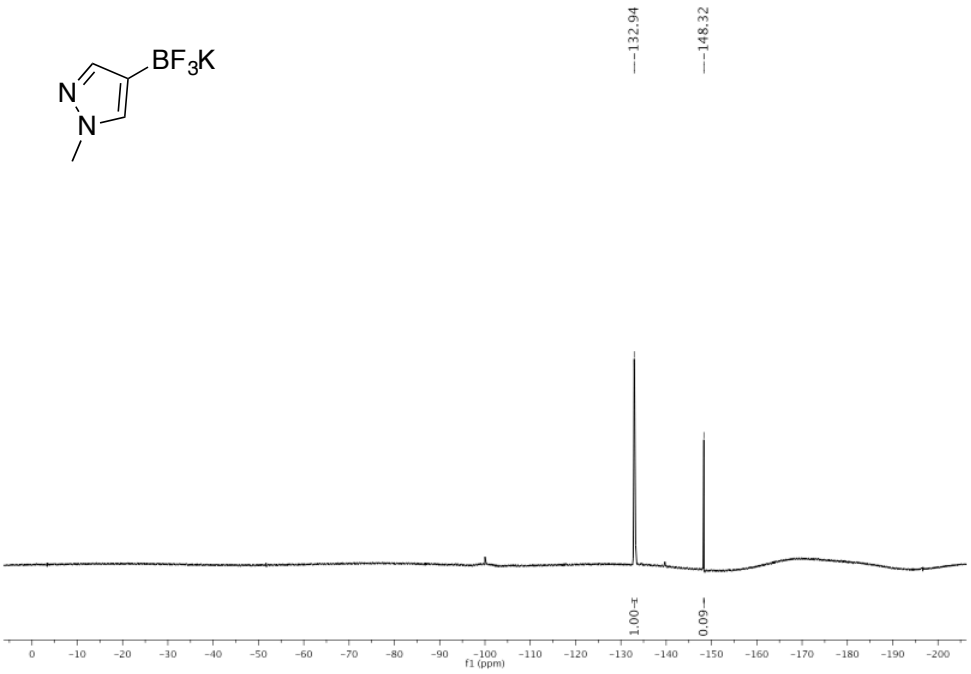


Figure A1.102 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(1-methyl-1*H*-pyrazol-4-yl)borate

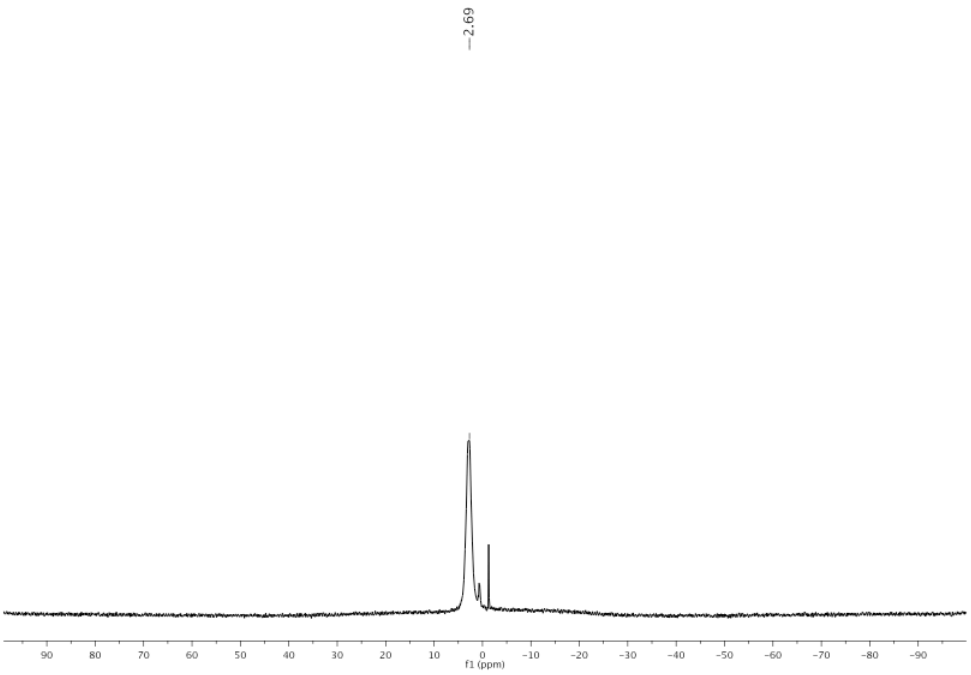


Figure A1.103 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(1-methyl-1*H*-pyrazol-4-yl)borate

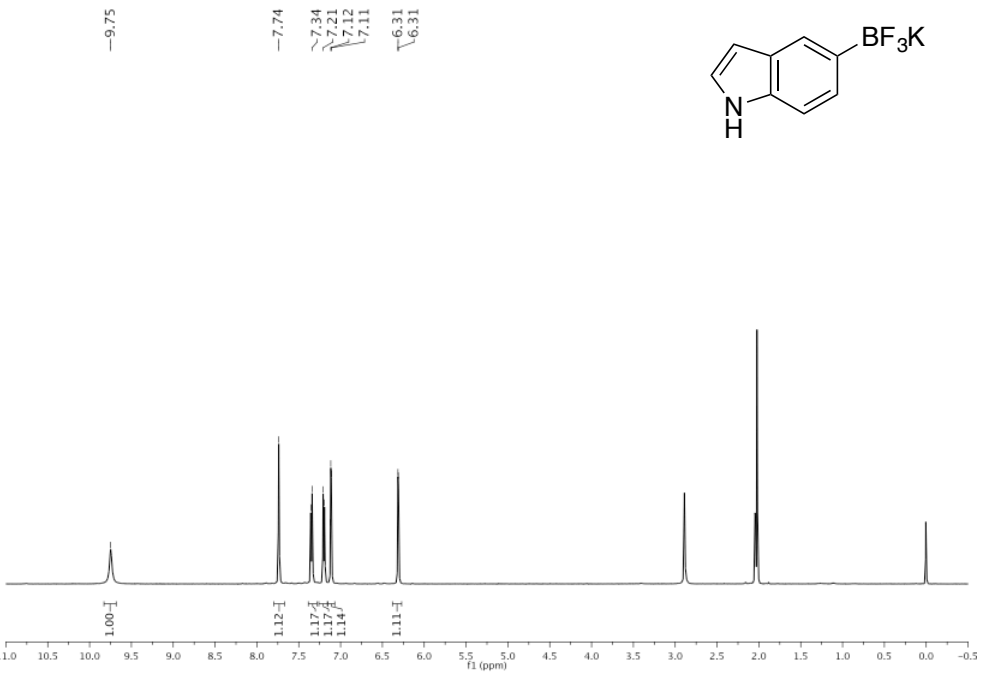


Figure A1.104 ^{1}H NMR (500 MHz, acetone-d_6) Spectrum of Potassium Trifluoro(1*H*-indol-5-yl)borate

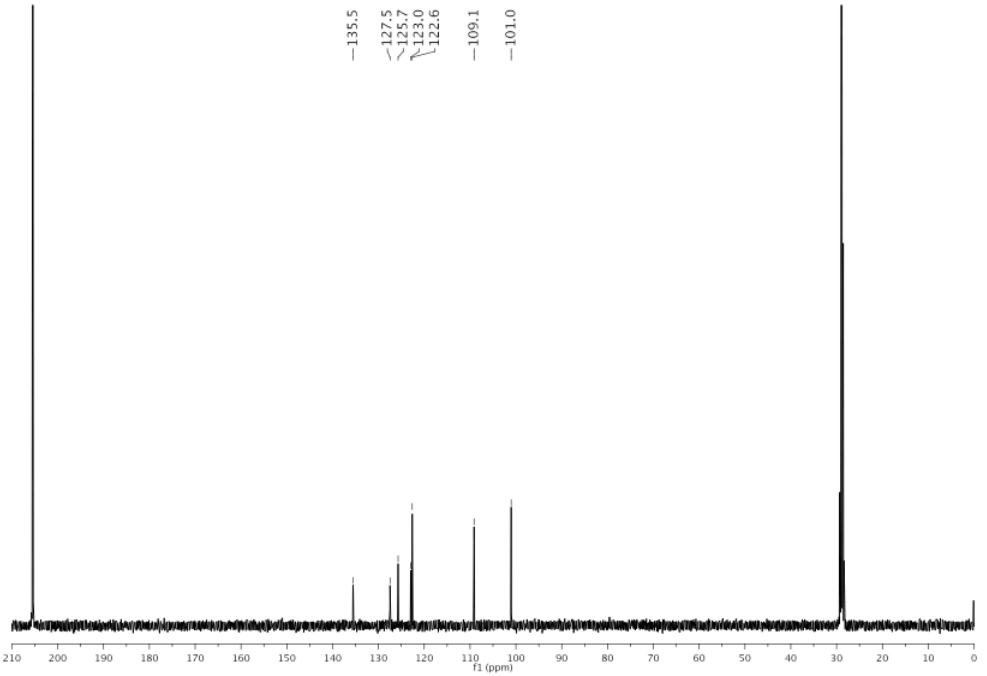


Figure A1.105 ^{13}C NMR (128.5 MHz, acetone -d_6) Spectrum of Potassium Trifluoro(1*H*-indol-5-yl)borate

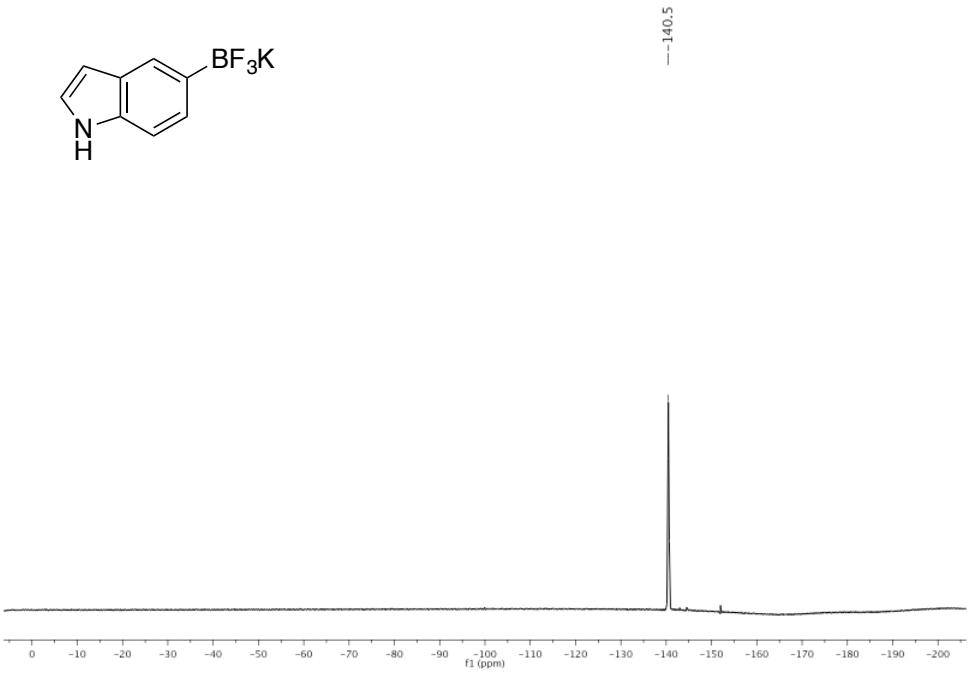


Figure A1.106 ^{19}F NMR (470.8 MHz, acetone -d_6) Spectrum of Potassium Trifluoro(1*H*-indol-5-yl)borate

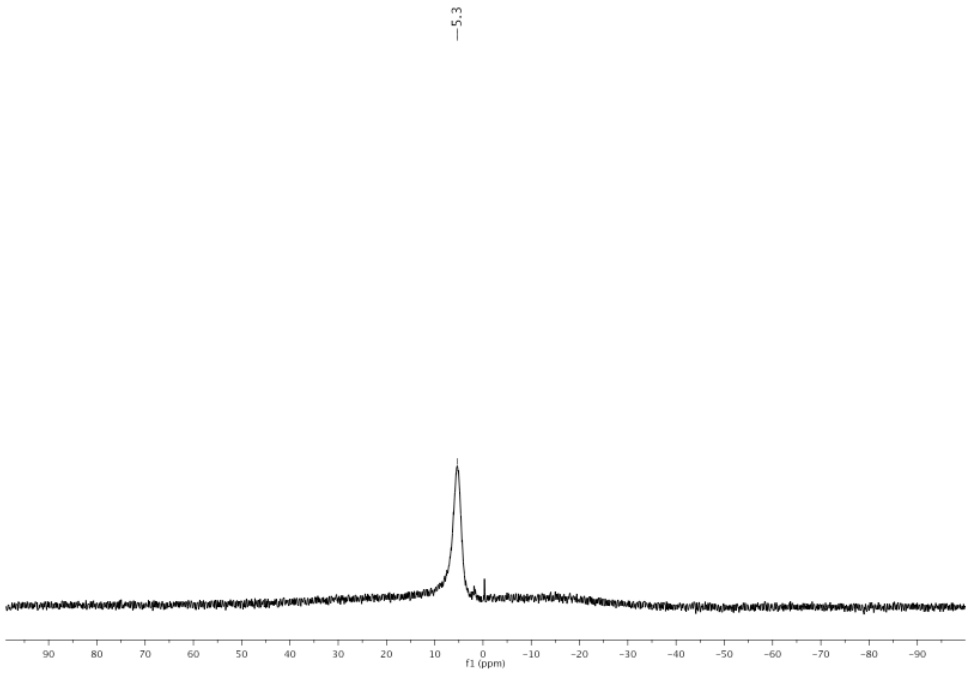


Figure A1.107 ^{11}B NMR (128.4 MHz, acetone-d_6) Spectrum of Potassium Trifluoro(1*H*-indol-5-yl)borate

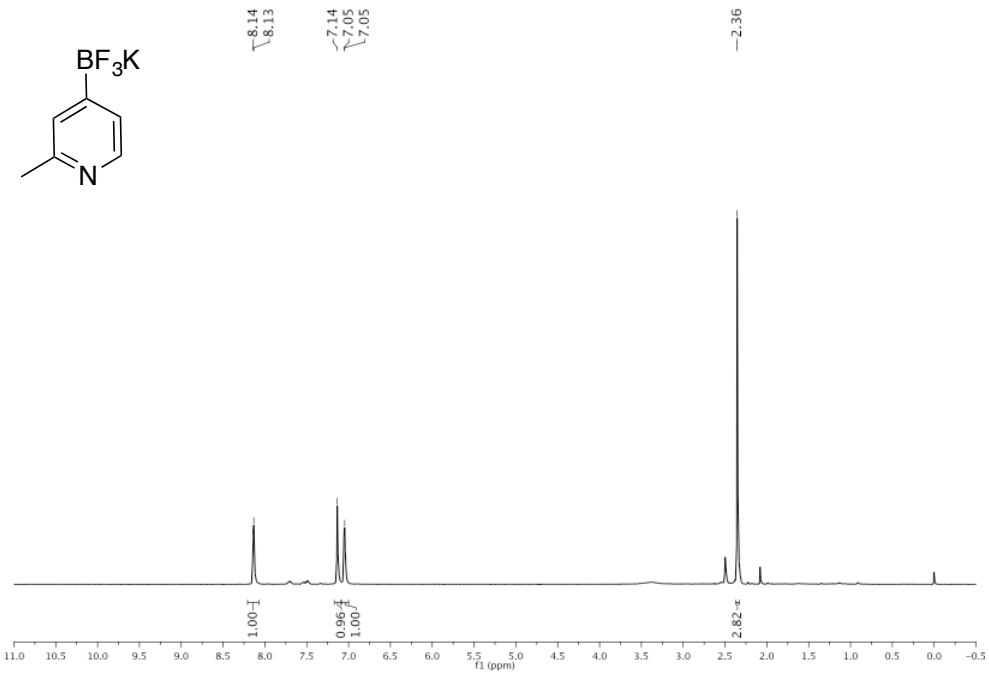


Figure A1.108 ^{1}H NMR (500 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(2-methylpyridin-4-yl)borate

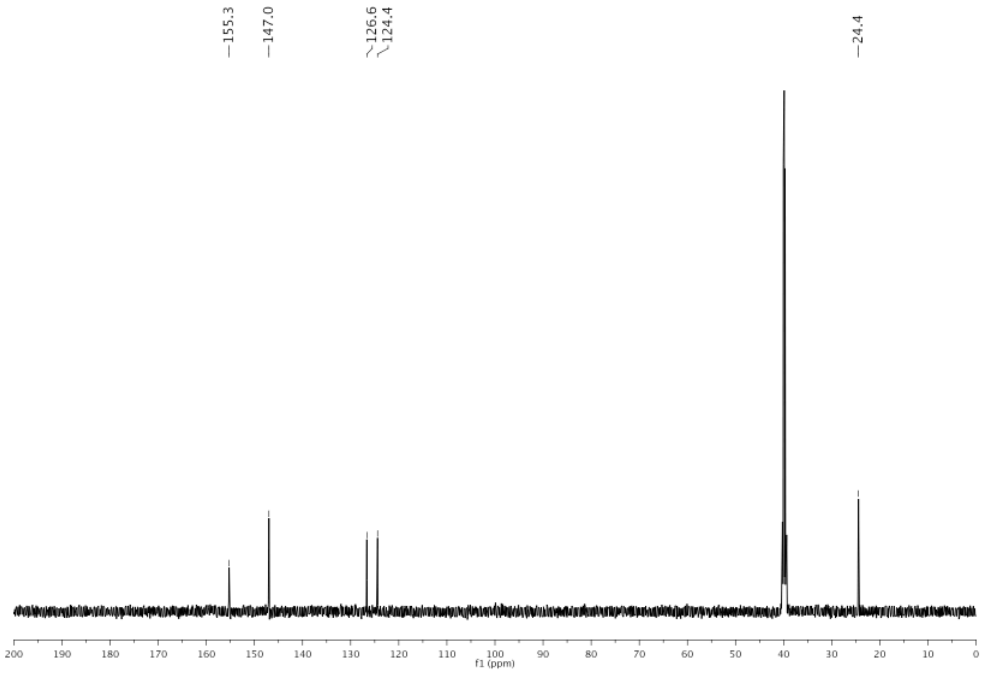


Figure A1.109 ^{13}C NMR (128.5 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(2-methylpyridin-4-yl)borate

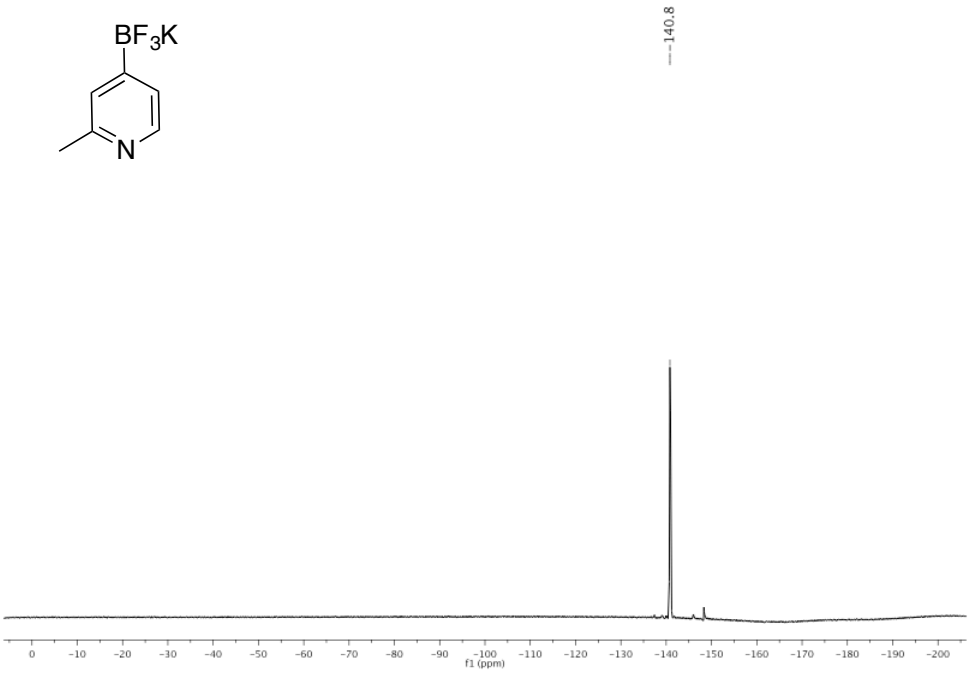


Figure A1.110 ^{19}F NMR (470.8 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(2-methylpyridin-4-yl)borate

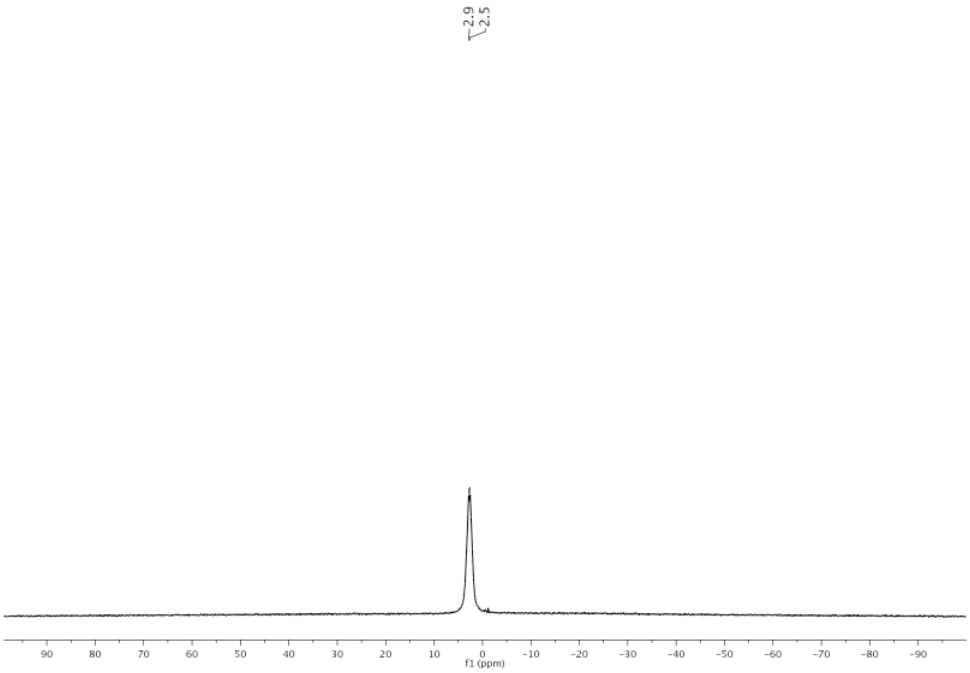


Figure A1.111 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(2-methylpyridin-4-yl)borate

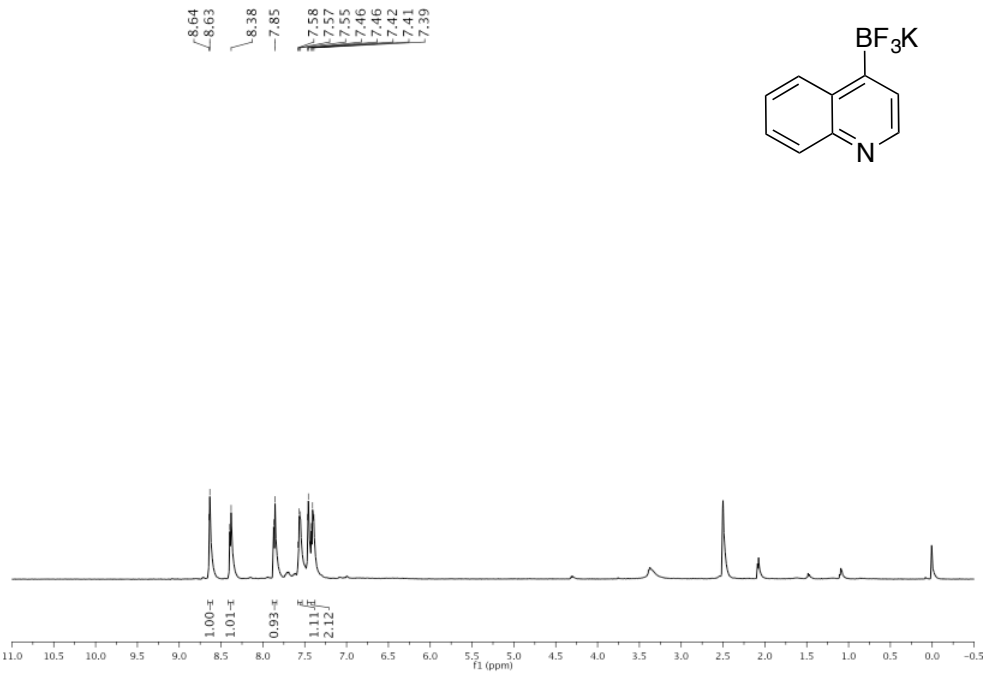


Figure A1.112 ^{1}H NMR (500 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(quinolin-4-yl)borate

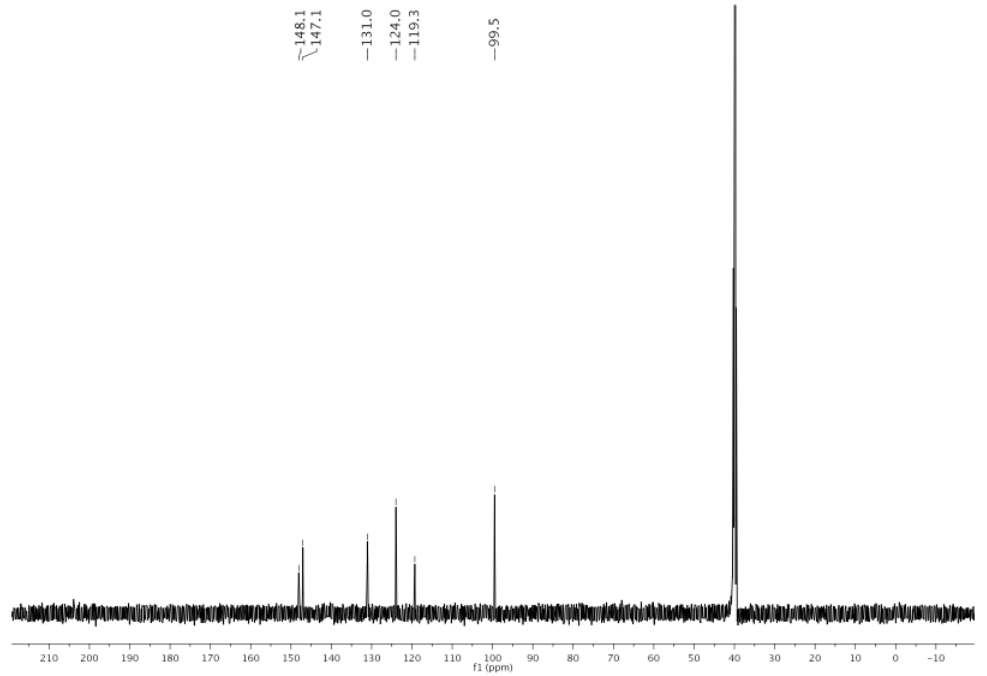


Figure A1.113 ^{13}C NMR (128.5 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(quinolin-4-yl)borate

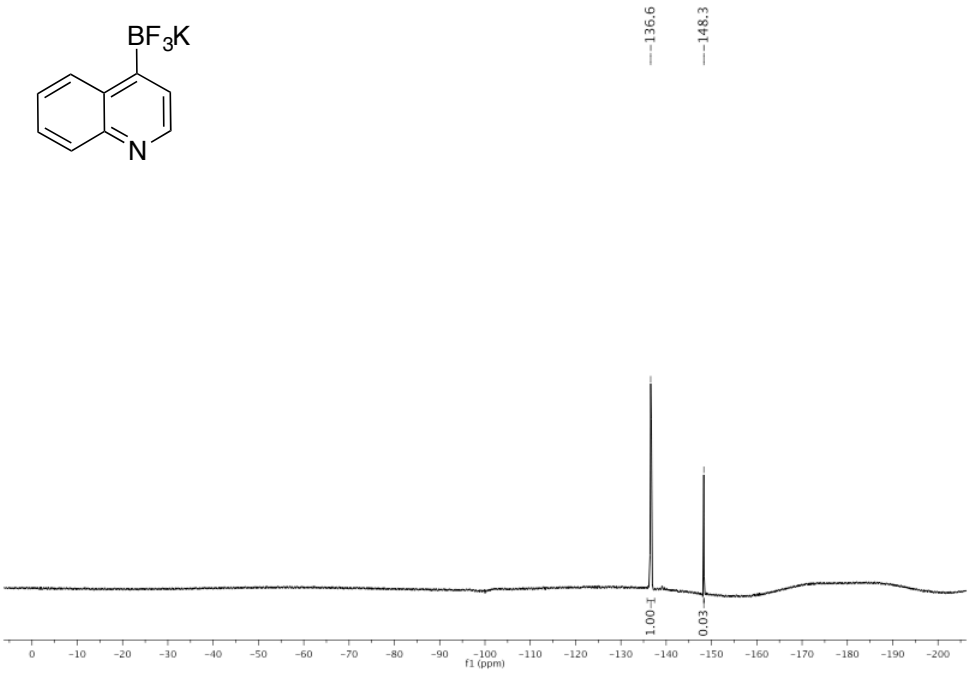


Figure A1.114 ^{19}F NMR (470.8 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(quinolin-4-yl)borate

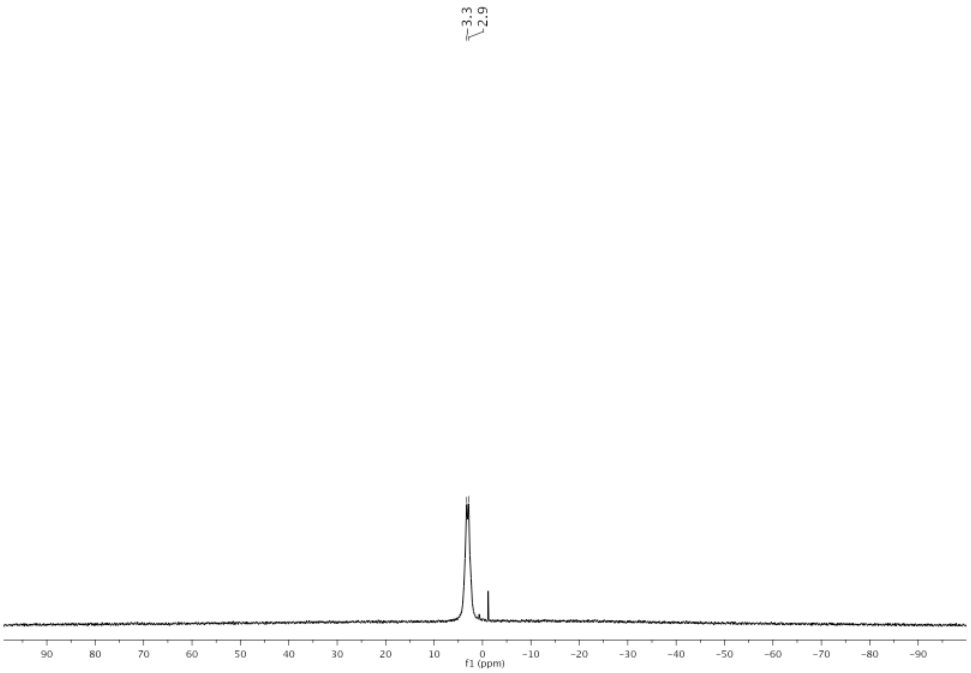


Figure A1.115 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(quinolin-4-yl)borate

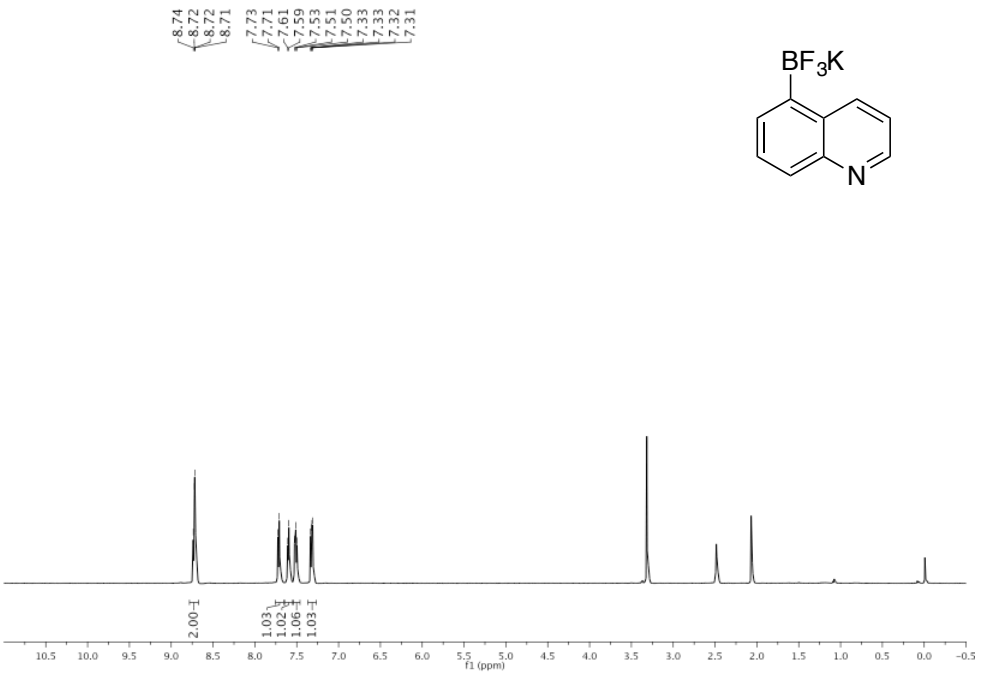


Figure A1.116 ^{1}H NMR (500 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(quinolin-5-yl)borate

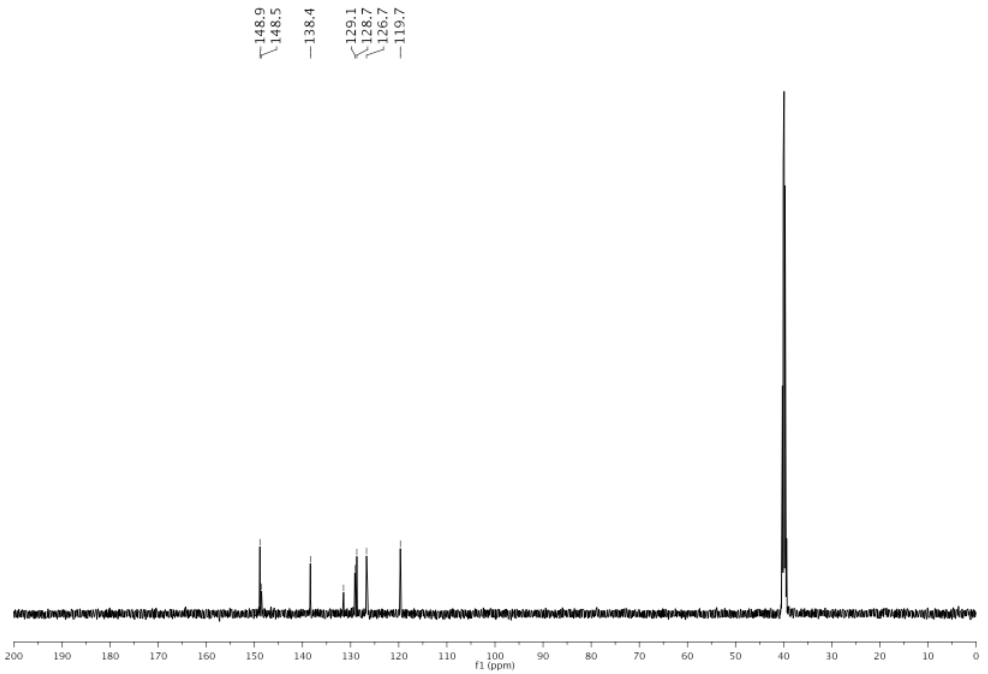


Figure A1.117 ^{13}C NMR (128.5 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(quinolin-5-yl)borate

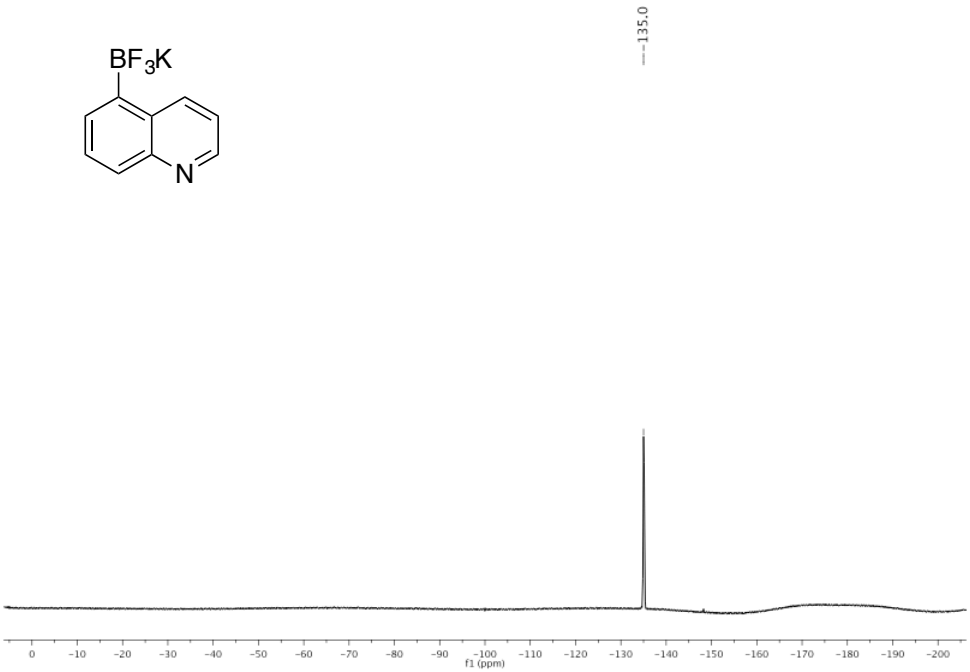


Figure A1.118 ^{19}F NMR (470.8 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(quinolin-5-yl)borate

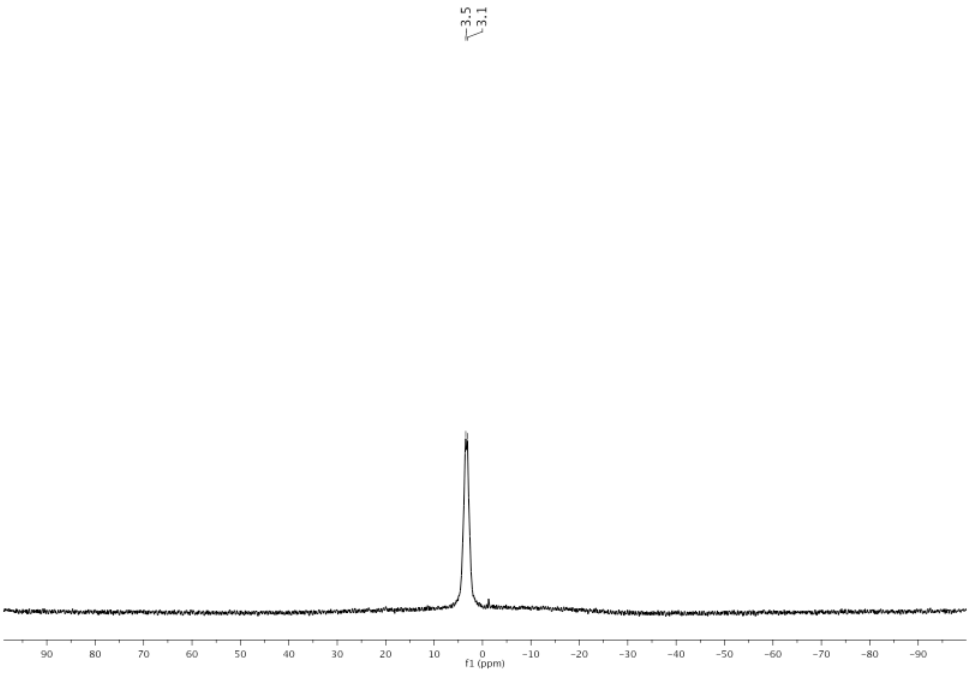


Figure A1.119 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(quinolin-5-yl)borate

Figure A1.120 ^{1}H NMR (500 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(quinolin-6-yl)borate

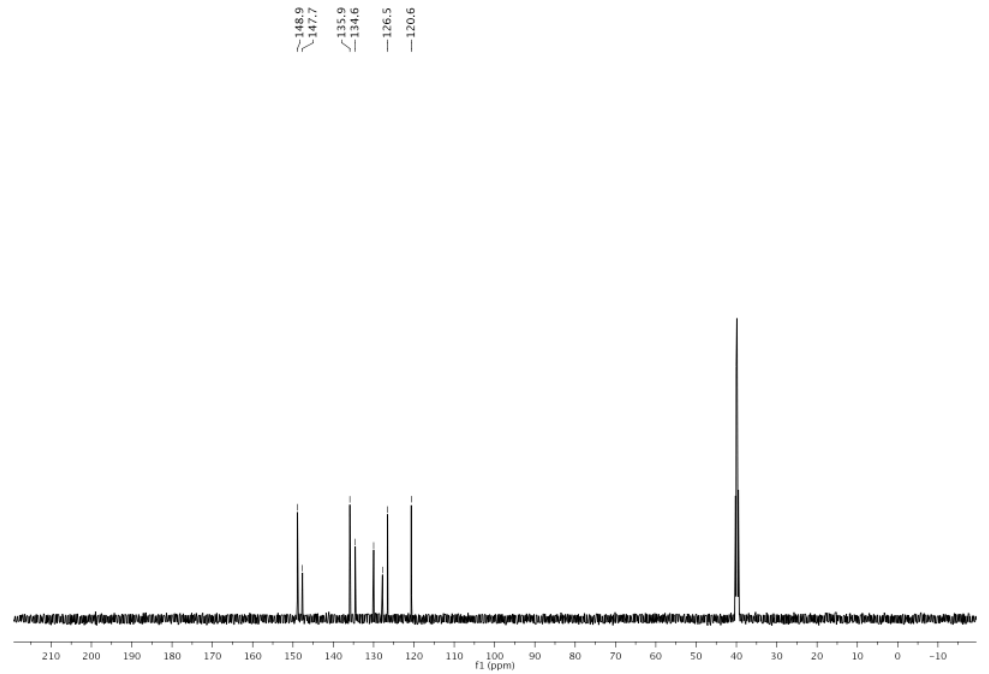


Figure A1.121 ^{13}C NMR (128.5 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(quinolin-6-yl)borate

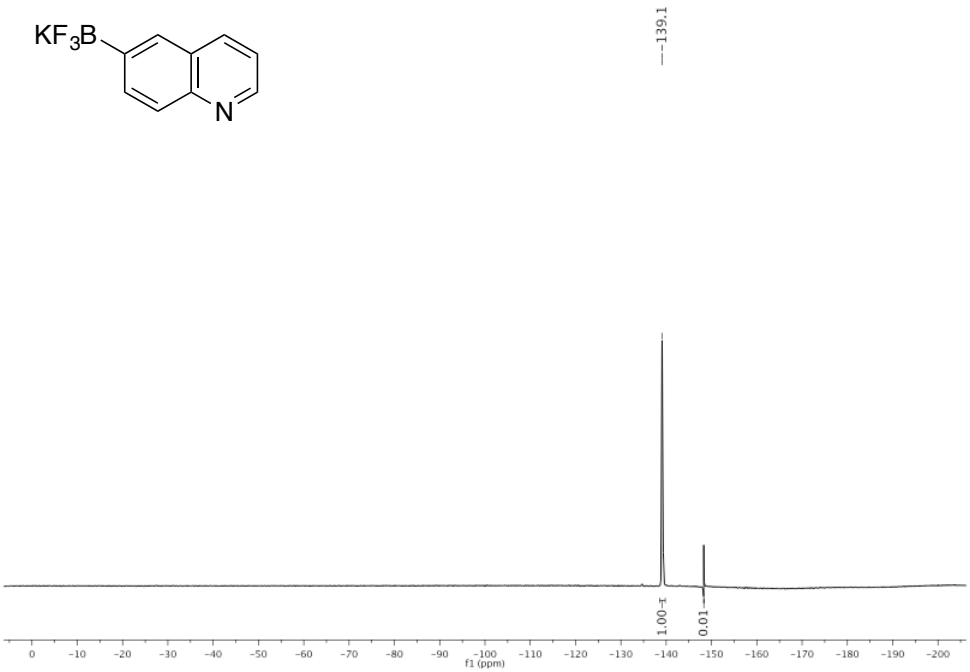


Figure A1.122 ^{19}F NMR (470.8 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(quinolin-6-yl)borate

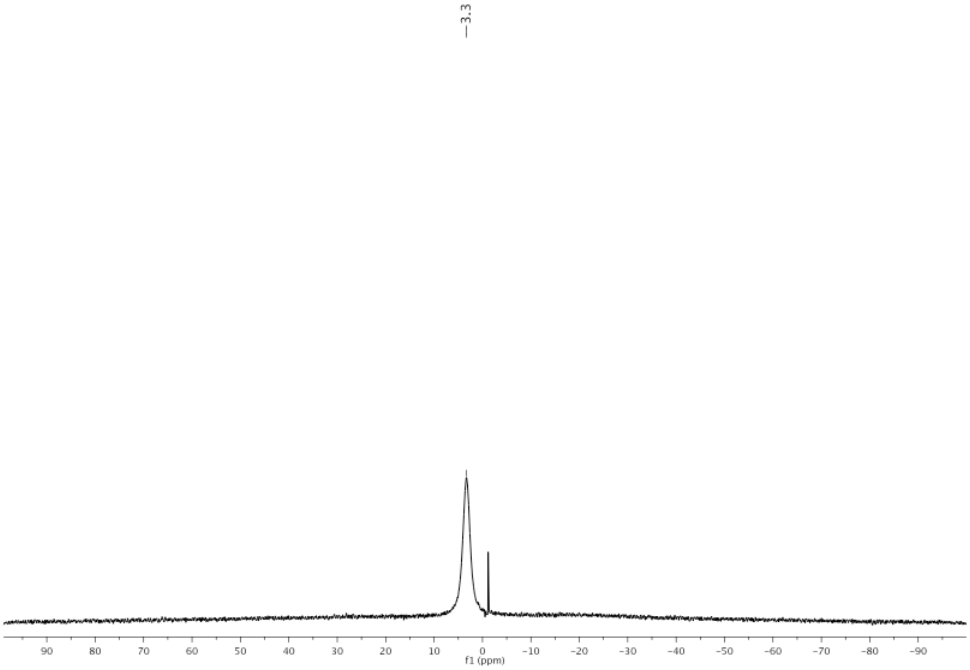


Figure A1.123 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(quinolin-6-yl)borate

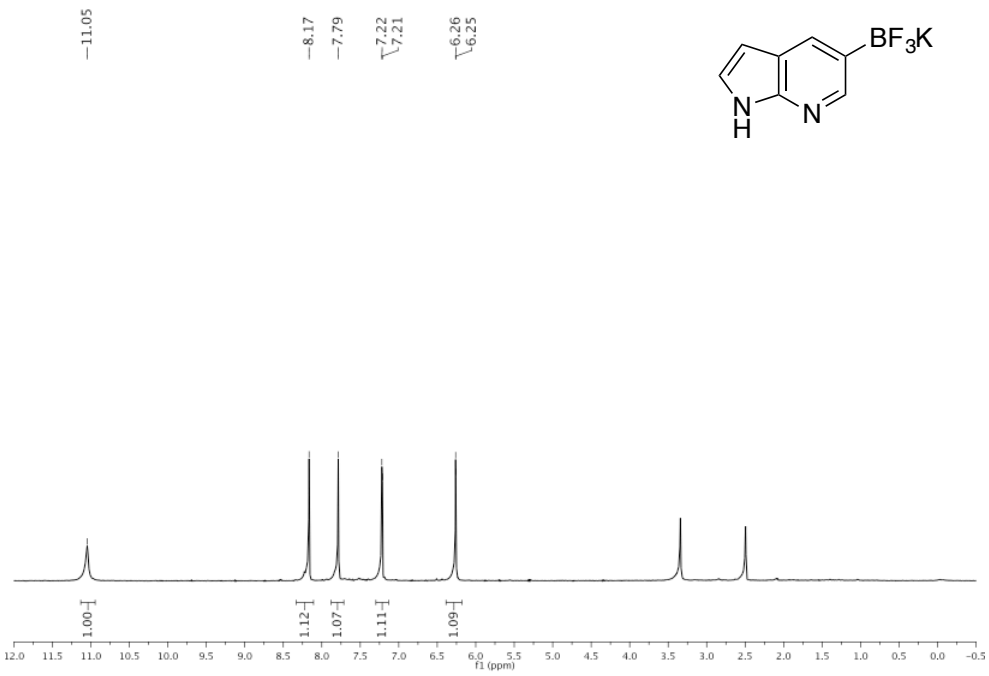


Figure A1.124 ^{1}H NMR (500 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(1*H*-pyrrolo[2,3-*b*]pyridin-5-yl)borate

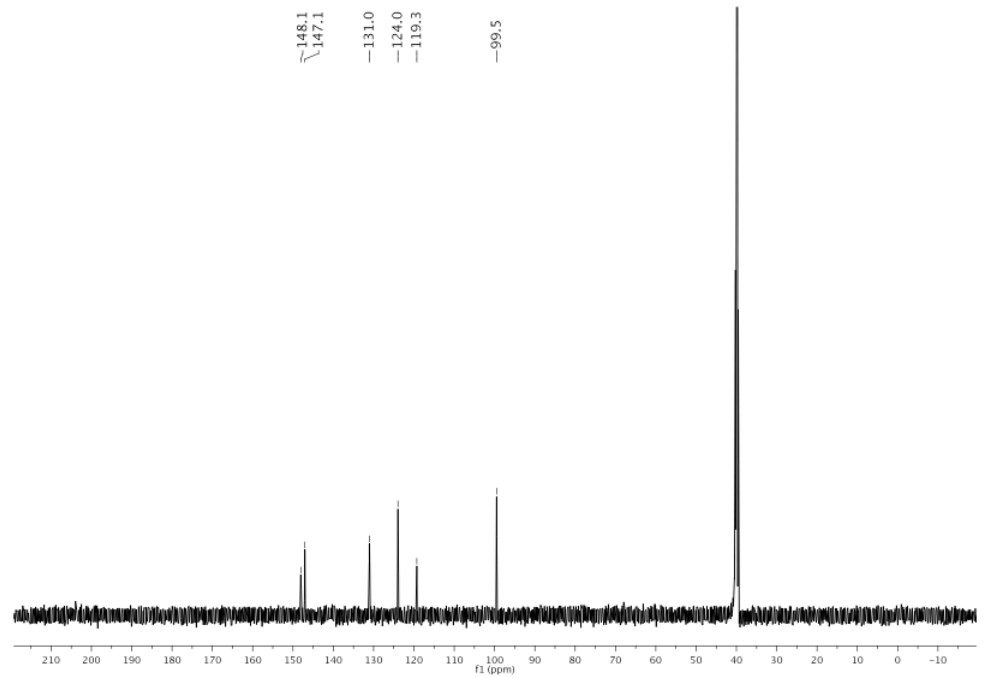


Figure A1.125 ^{13}C NMR (128.5 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(1*H*-pyrrolo[2,3-*b*]pyridin-5-yl)borate

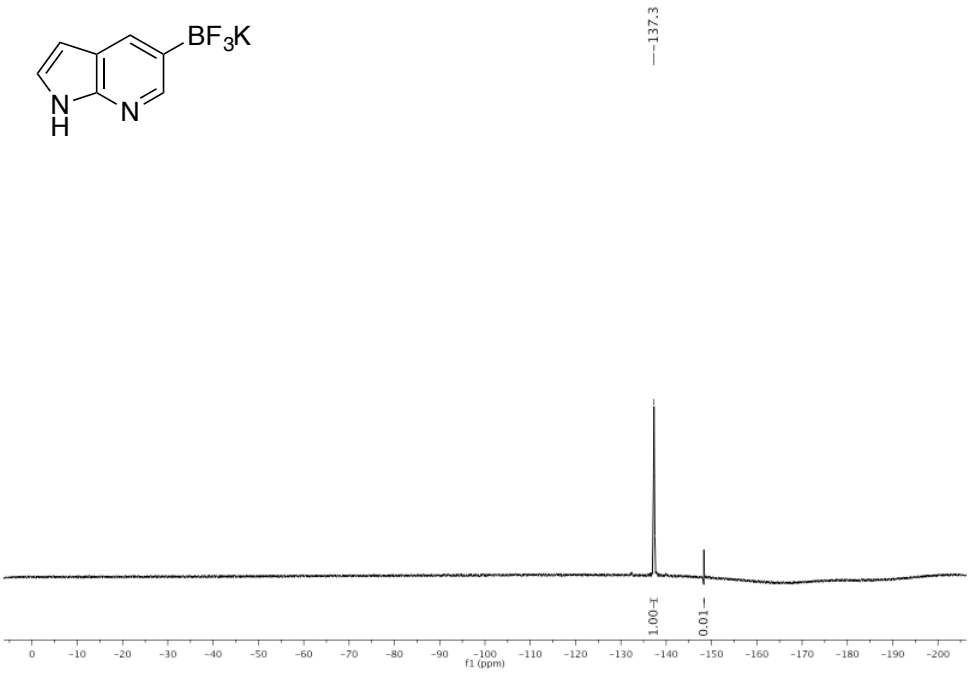


Figure A1.126 ^{19}F NMR (470.8 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(1*H*-pyrrolo[2,3-*b*]pyridin-5-yl)borate

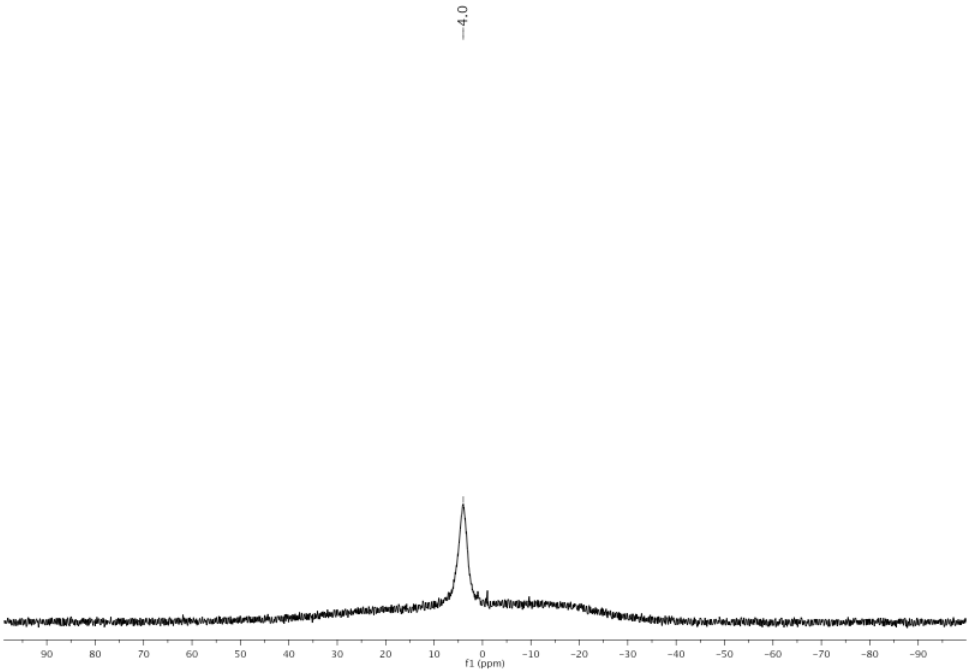


Figure A1.127 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(1*H*-pyrrolo[2,3-*b*]pyridin-5-yl)borate

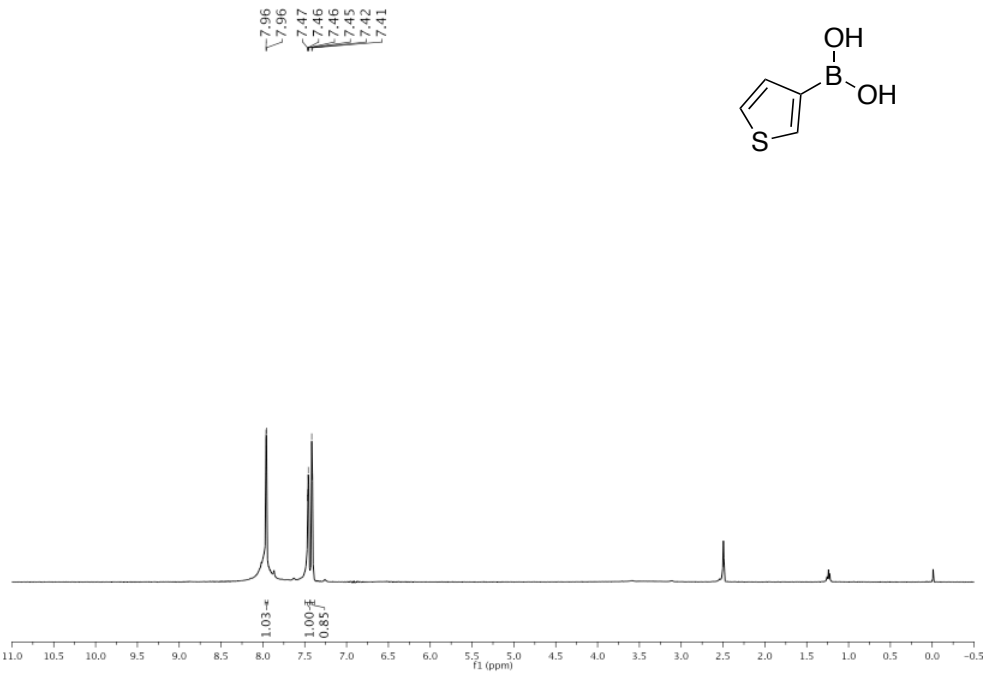


Figure A1.128 ^{1}H NMR (500 MHz, DMSO -d_6) Spectrum of Thien-3-ylboronic acid

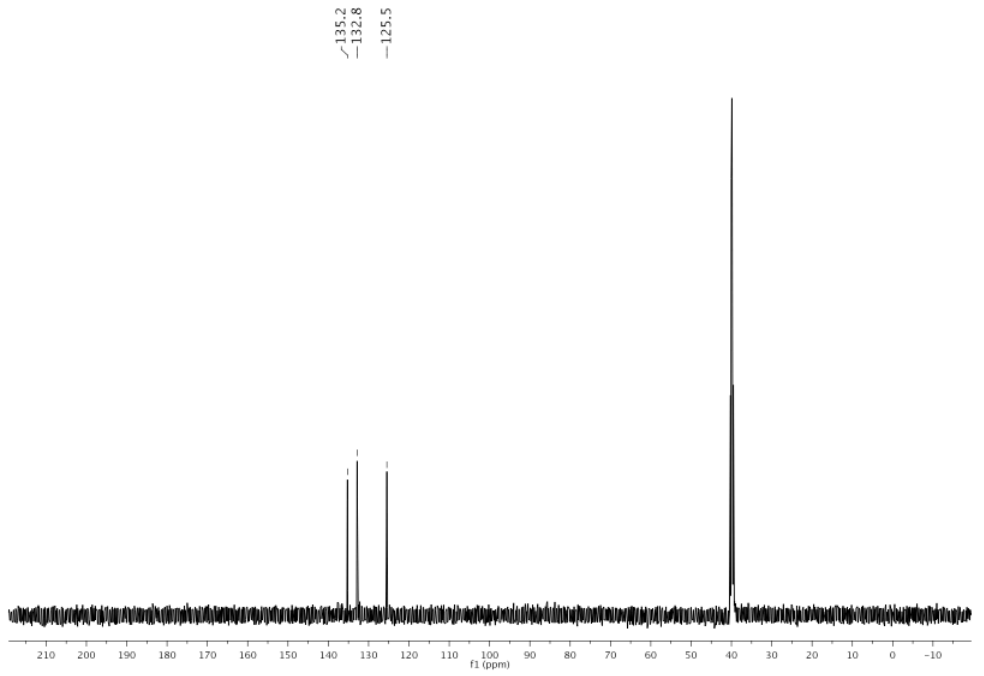


Figure A1.129 ^{13}C NMR (128.5 MHz, DMSO -d_6) Spectrum of Thien-3-ylboronic acid

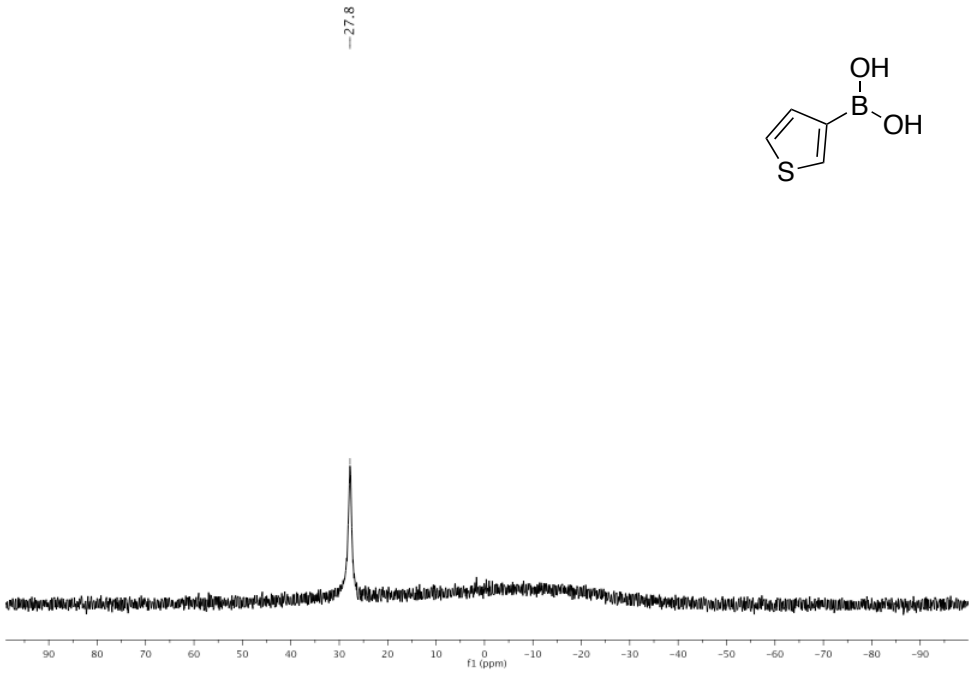


Figure A1.130 ^{11}B NMR (128.4 MHz, acetone-d_6) Spectrum of Thien-3-ylboronic acid

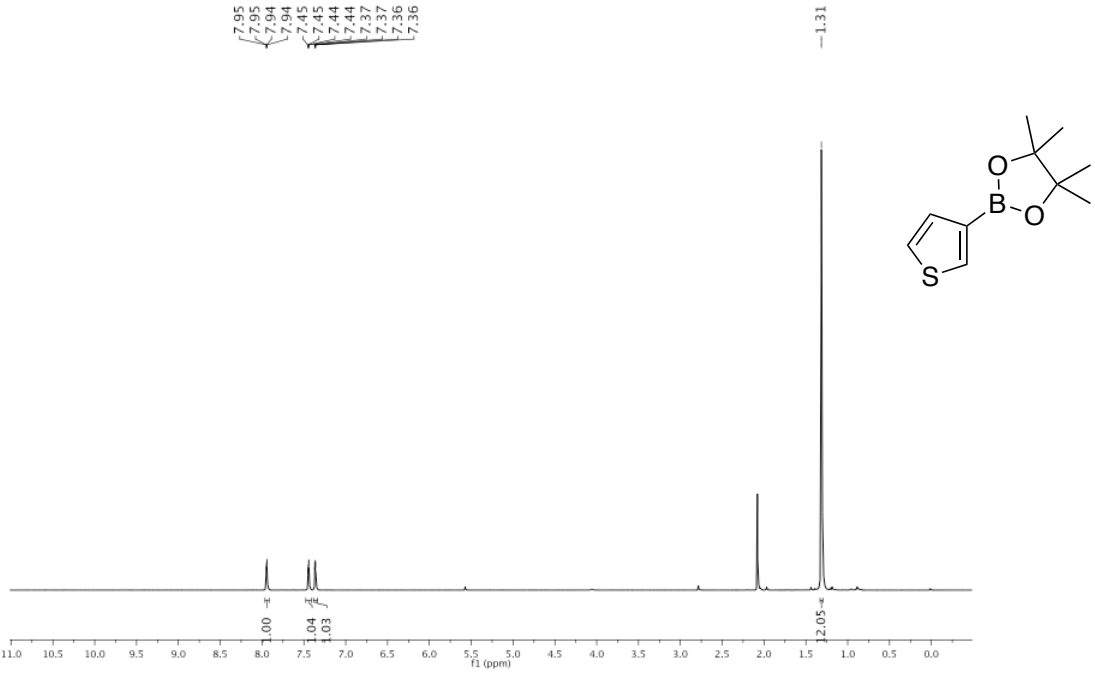


Figure A1.131 ^{1}H NMR (500 MHz, acetone -d_6) Spectrum of 4,4,5,5-Tetramethyl-2-(thien-3-yl)-1,3,2-dioxaborolane

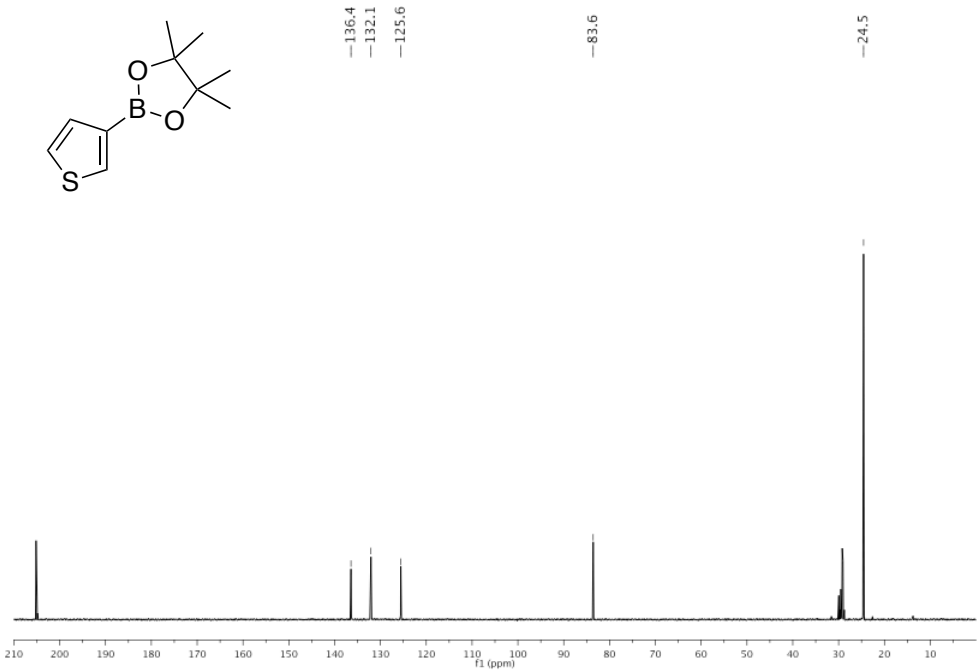


Figure A1.132 ^{13}C NMR (128.5 MHz, acetone -d_6) Spectrum of 4,4,5,5-Tetramethyl-2-(thien-3-yl)-1,3,2-dioxaborolane

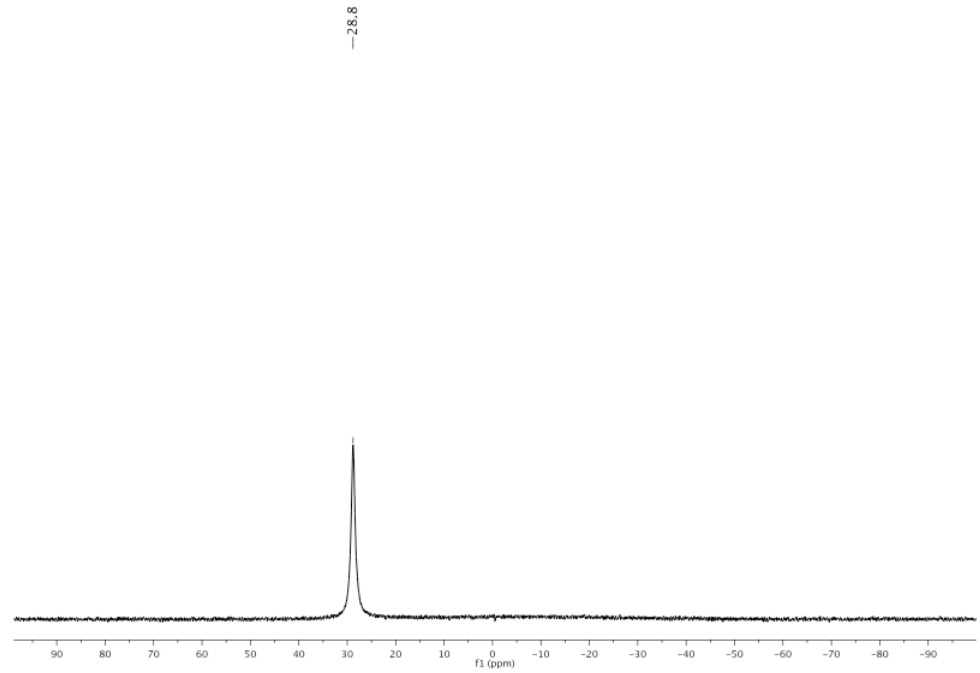


Figure A1.133 ^{11}B NMR (128.4 MHz, acetone-d_6) Spectrum of 4,4,5,5-Tetramethyl-2-(thien-3-yl)-1,3,2-dioxaborolane

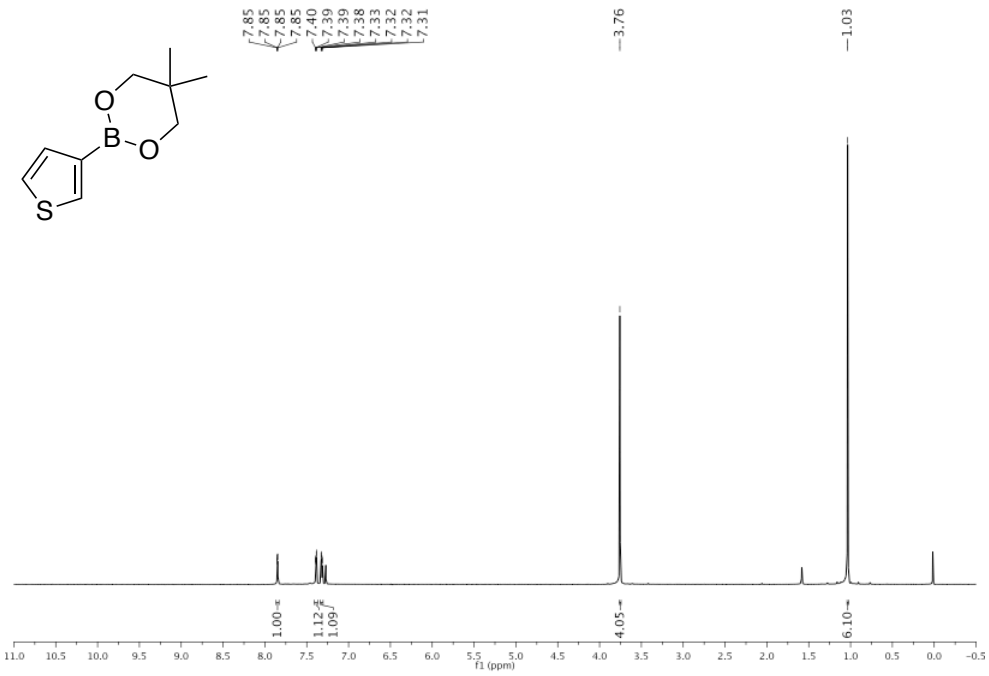


Figure A1.134 ^{1}H NMR (500 MHz, acetone -d_6) Spectrum of 5,5-Dimethyl-2-(thien-3-yl)-1,3,2-dioxaborinane

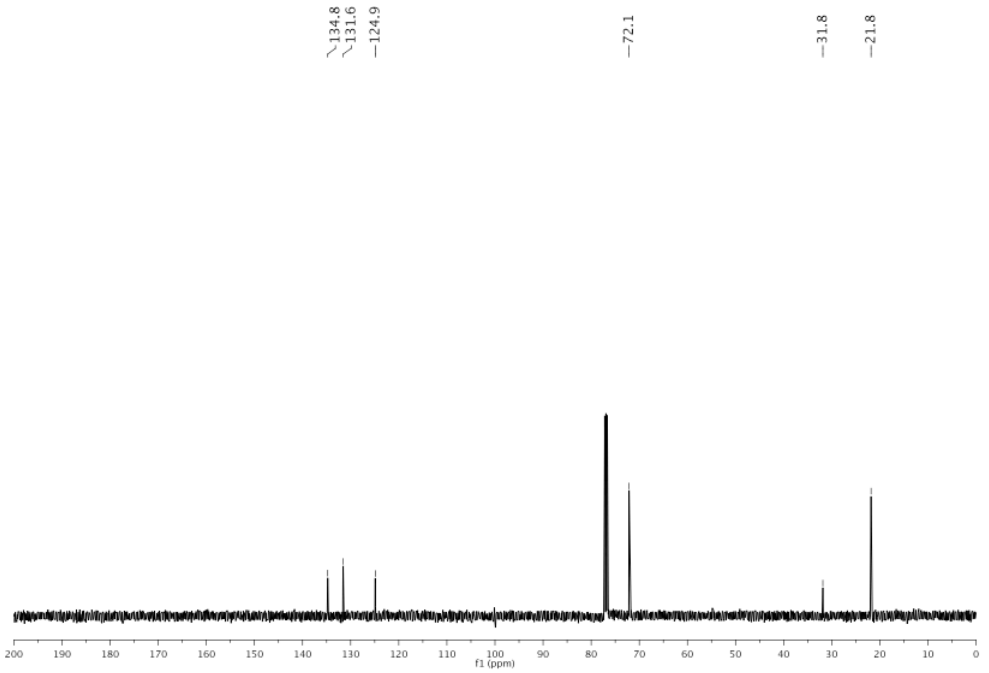


Figure A1.135 ^{13}C NMR (128.5 MHz, acetone -d_6) Spectrum of 5,5-Dimethyl-2-(thien-3-yl)-1,3,2-dioxaborinane

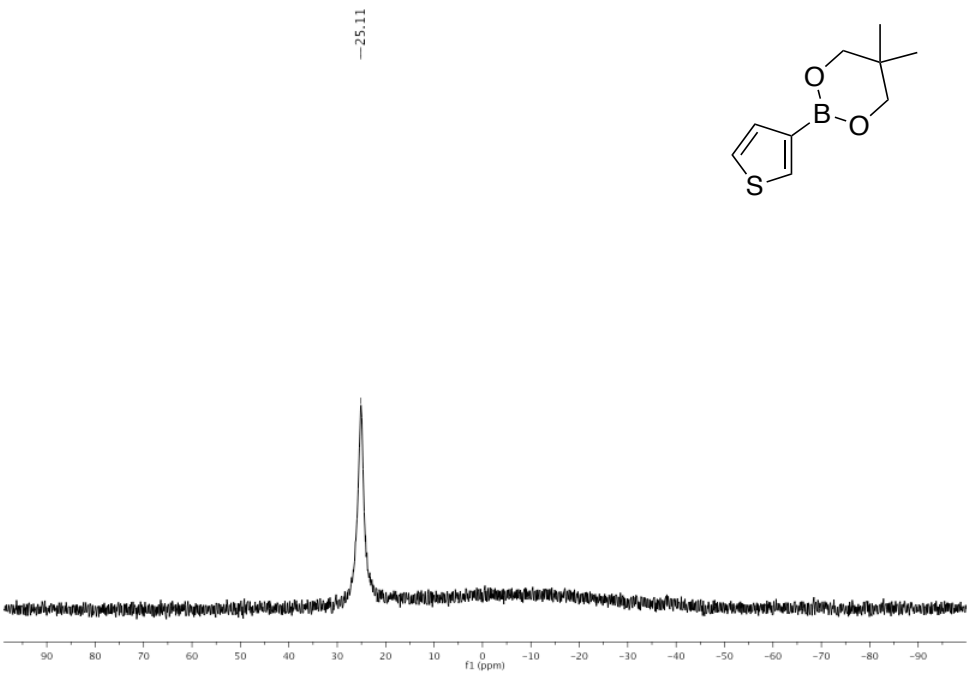


Figure A1.136 ^{11}B NMR (128.4 MHz, acetone-d_6) Spectrum of 5,5-Dimethyl-2-(thien-3-yl)-1,3,2-dioxaborinane

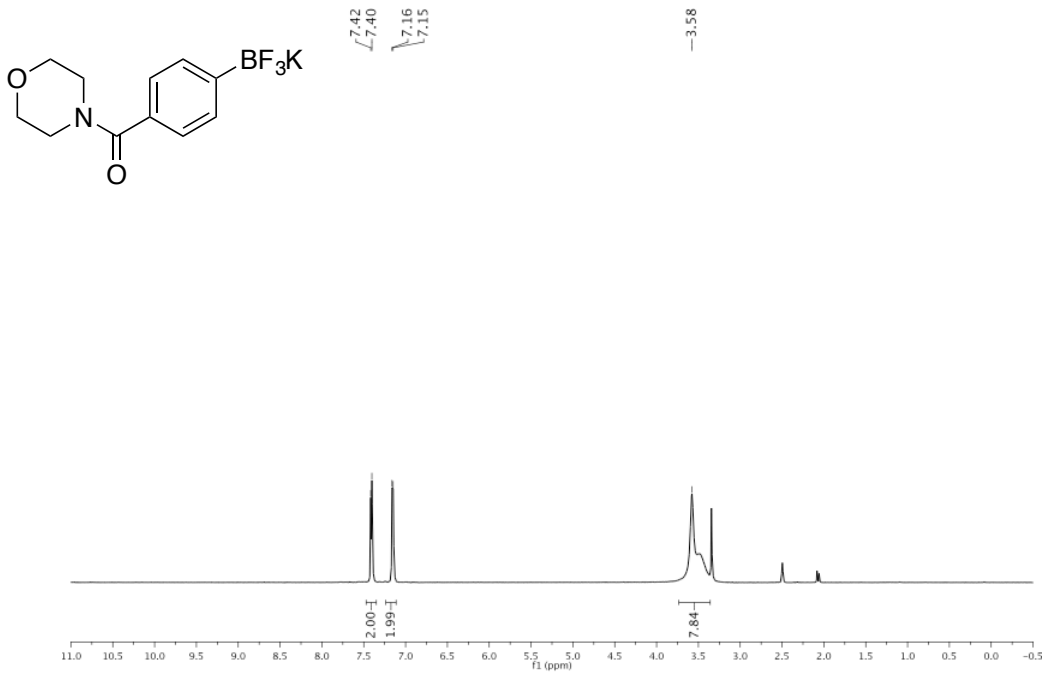


Figure A1.137 ^{1}H NMR (500 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(4-(morpholine-4-carbonyl)phenyl)borate

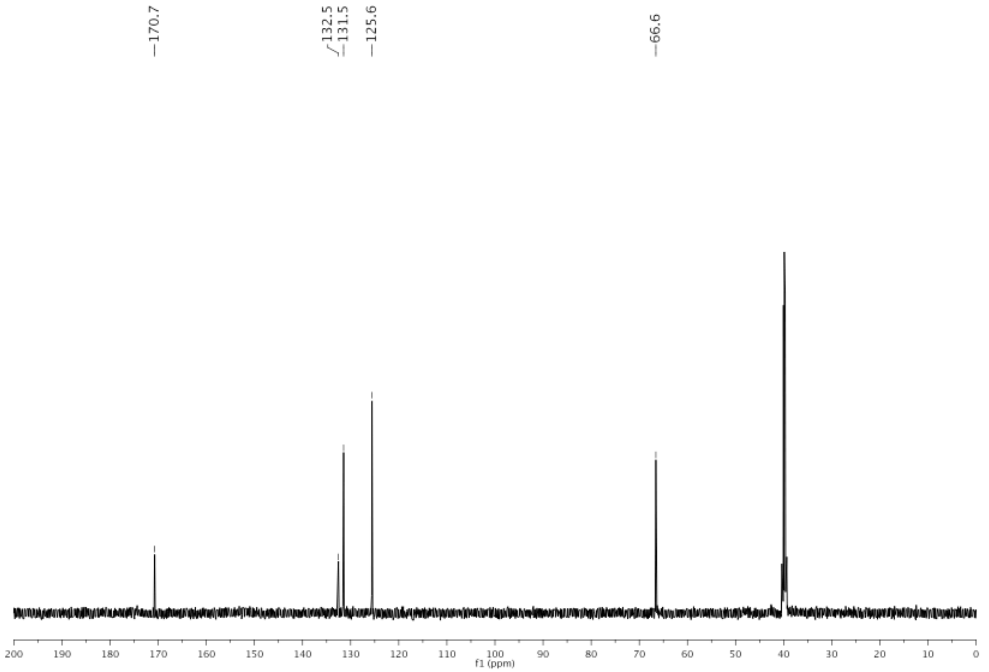


Figure A1.138 ^{13}C NMR (128.5 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(4-(morpholine-4-carbonyl)phenyl)borate

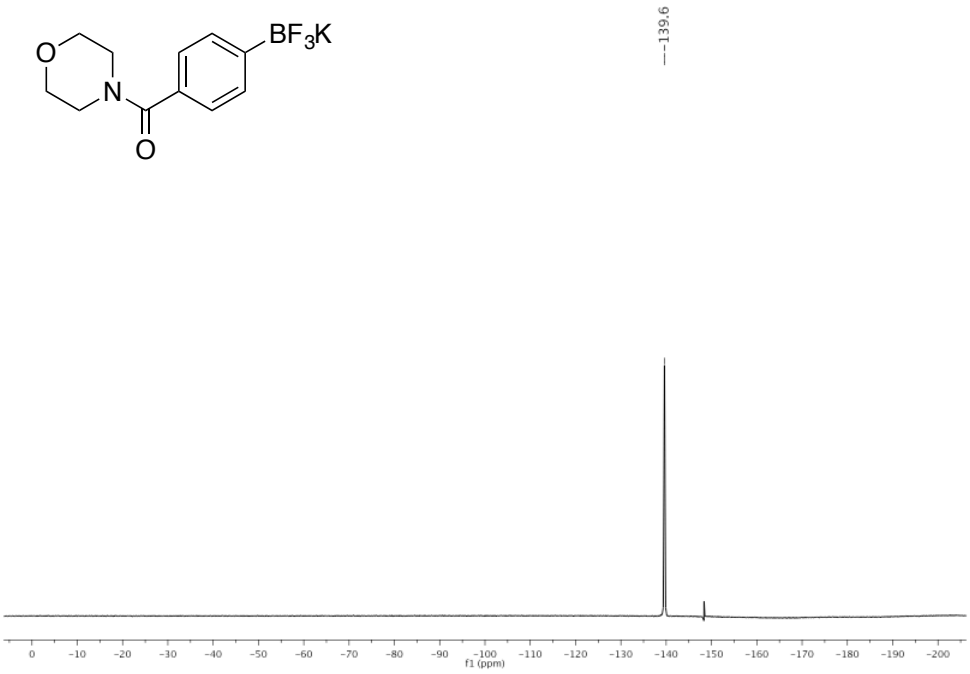


Figure A1.139 ^{19}F NMR (470.8 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(4-(morpholine-4-carbonyl)phenyl)borate

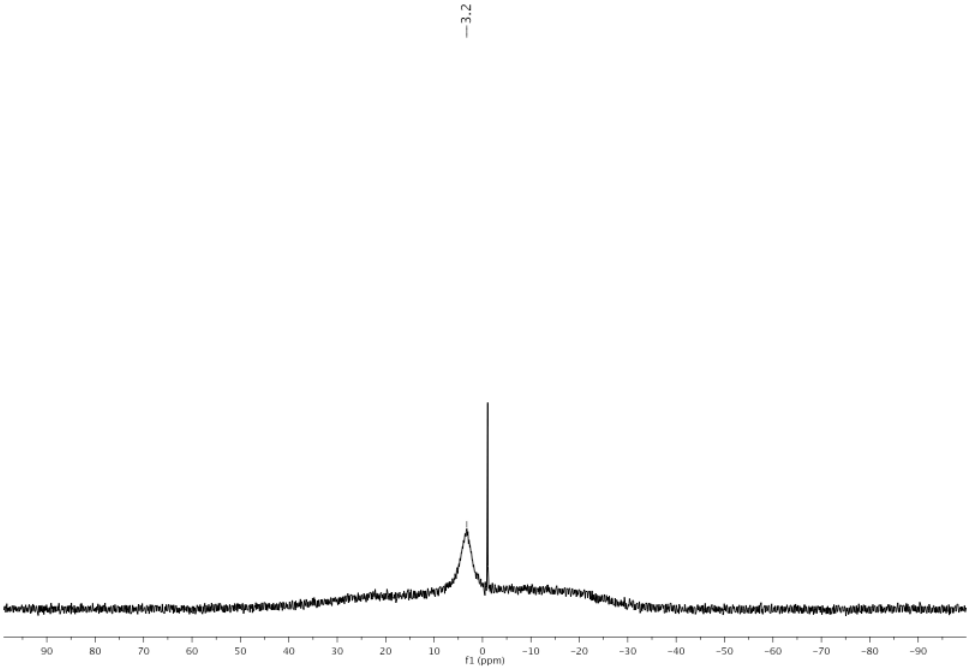


Figure A1.140 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-(morpholine-4-carbonyl)phenyl)borate

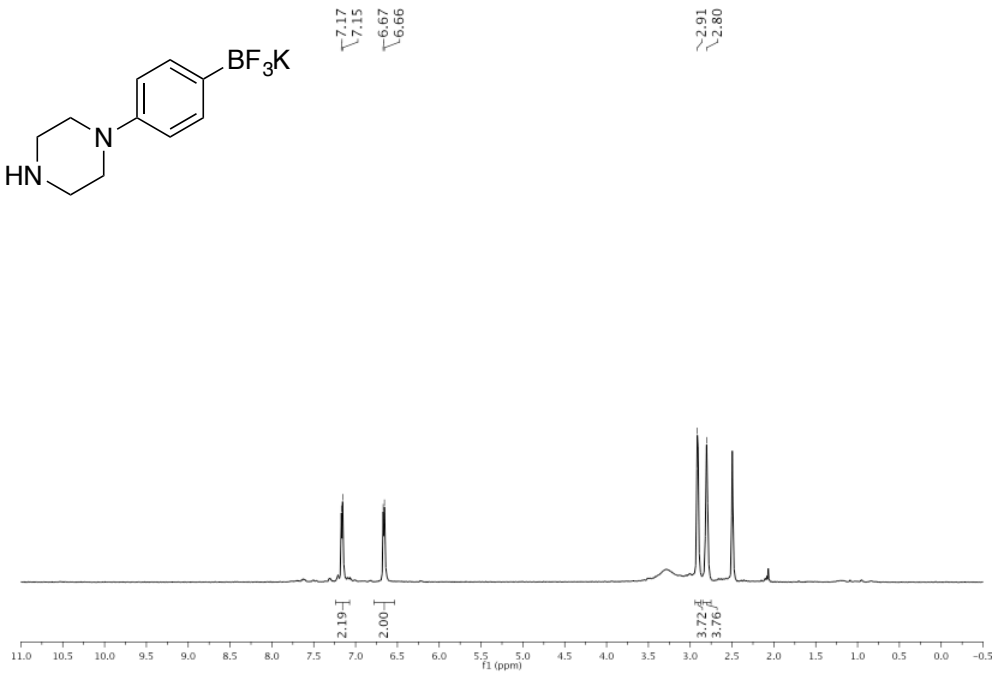


Figure A1.141 ^{1}H NMR (500 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(4-(piperazin-1-yl)phenyl)borate

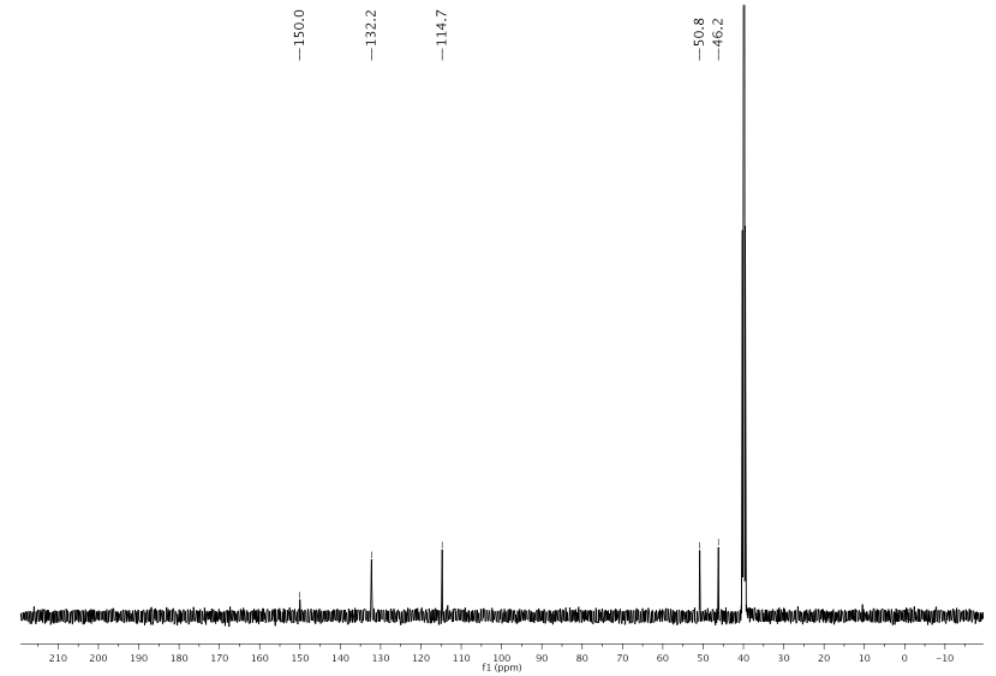


Figure A1.142 ^{13}C NMR (128.5 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(4-(piperazin-1-yl)phenyl)borate

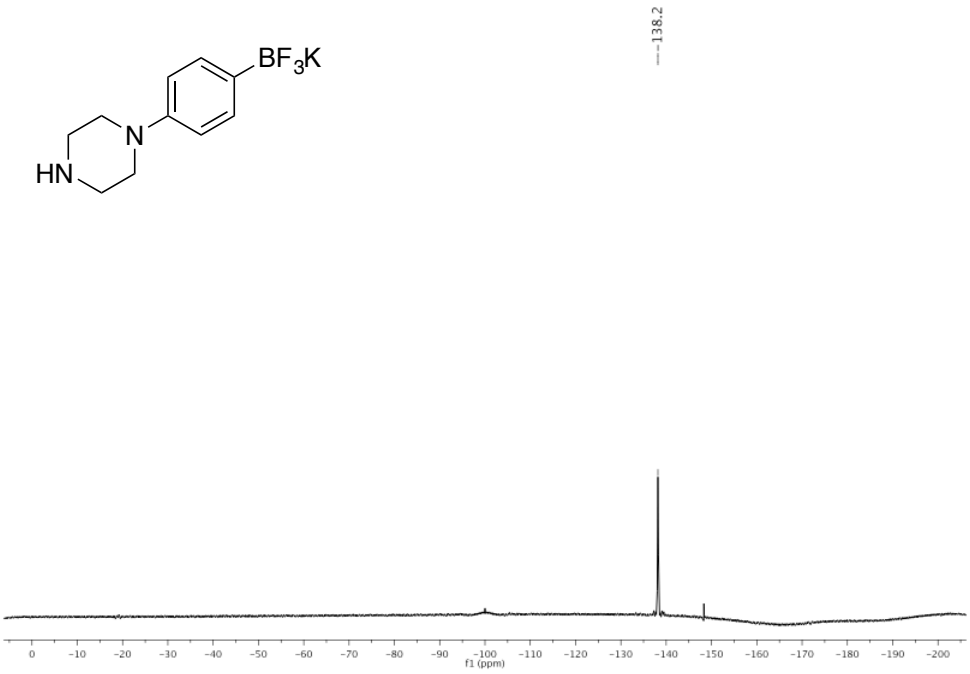


Figure A1.143 ^{19}F NMR (470.8 MHz, DMSO -d_6) Spectrum of Potassium Trifluoro(4-(piperazin-1-yl)phenyl)borate

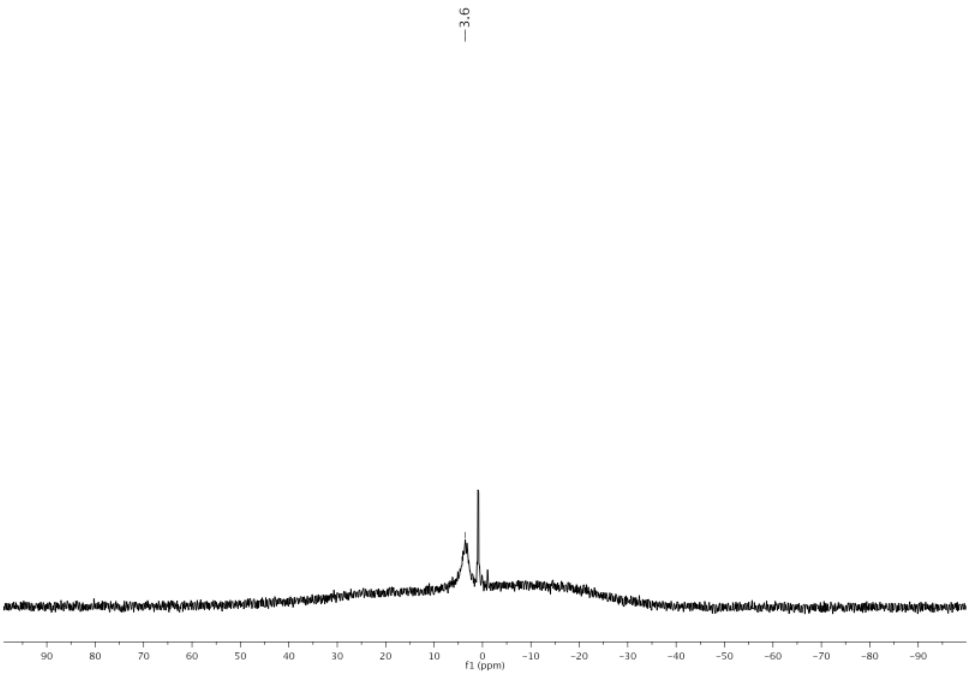


Figure A1.144 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium Trifluoro(4-(piperazin-1-yl)phenyl)borate

Figure A1.145 ^{1}H NMR (500 MHz, DMSO -d_6) Spectrum of Potassium (4-(1*H*-Pyrrol-1-yl)phenyl)trifluoroborate

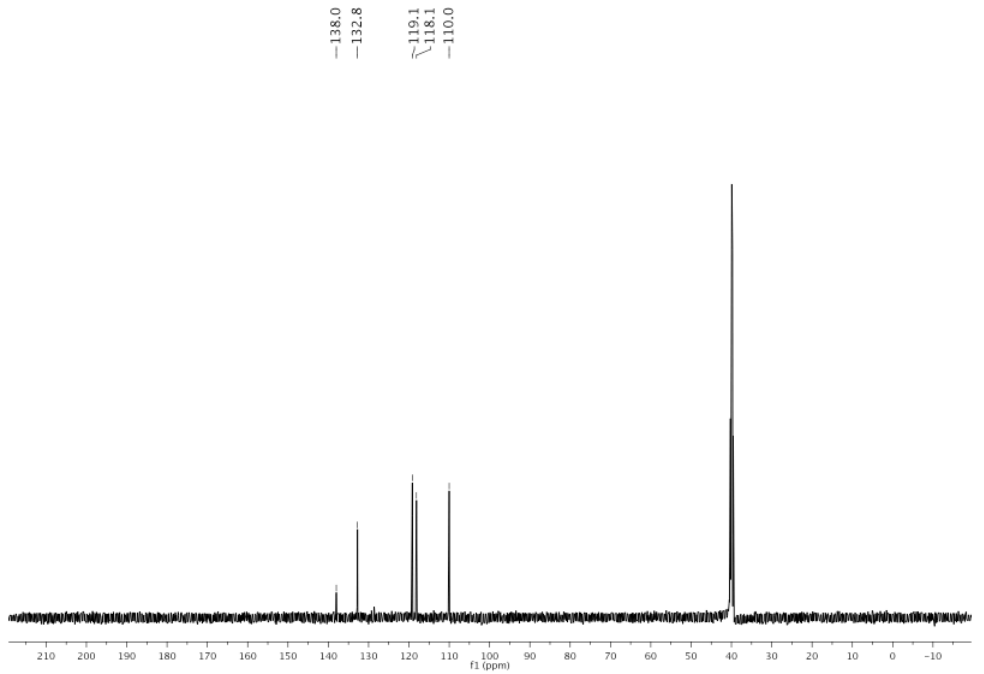


Figure A1.146 ^{13}C NMR (128.5 MHz, DMSO -d_6) Spectrum of Potassium (4-(1*H*-Pyrrol-1-yl)phenyl)trifluoroborate

Figure A1.147 ^{19}F NMR (470.8 MHz, DMSO -d_6) Spectrum of Potassium (4-(1*H*-Pyrrol-1-yl)phenyl)trifluoroborate

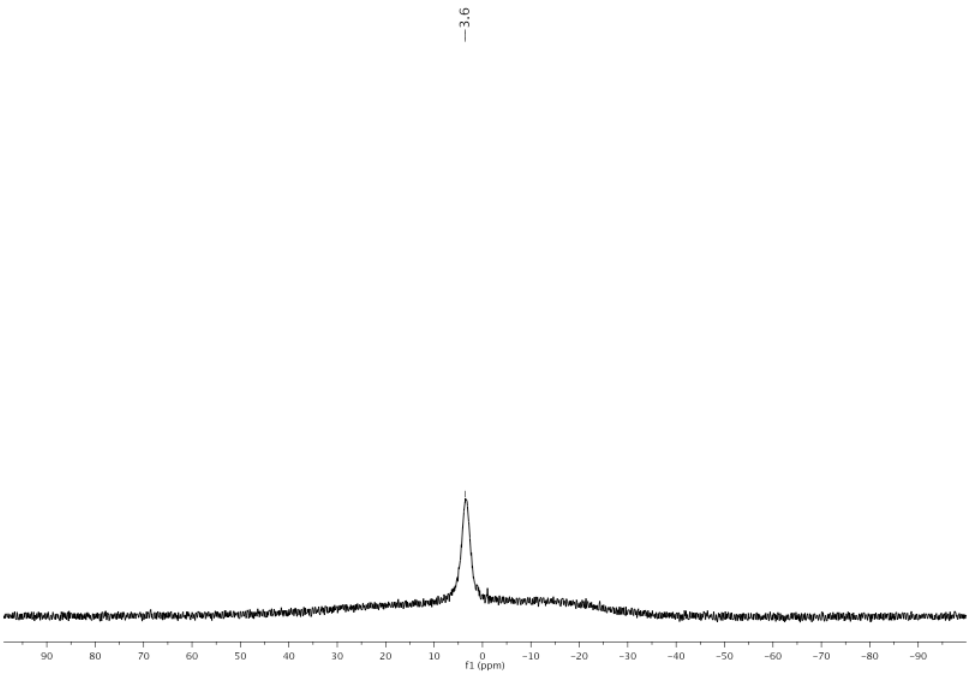


Figure A1.148 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Potassium (4-(1*H*-Pyrrol-1-yl)phenyl)trifluoroborate

Appendix A2. ^{1}H, ^{13}C, ^{19}F and ^{11}B Spectra Relevant to Chapter 2.2

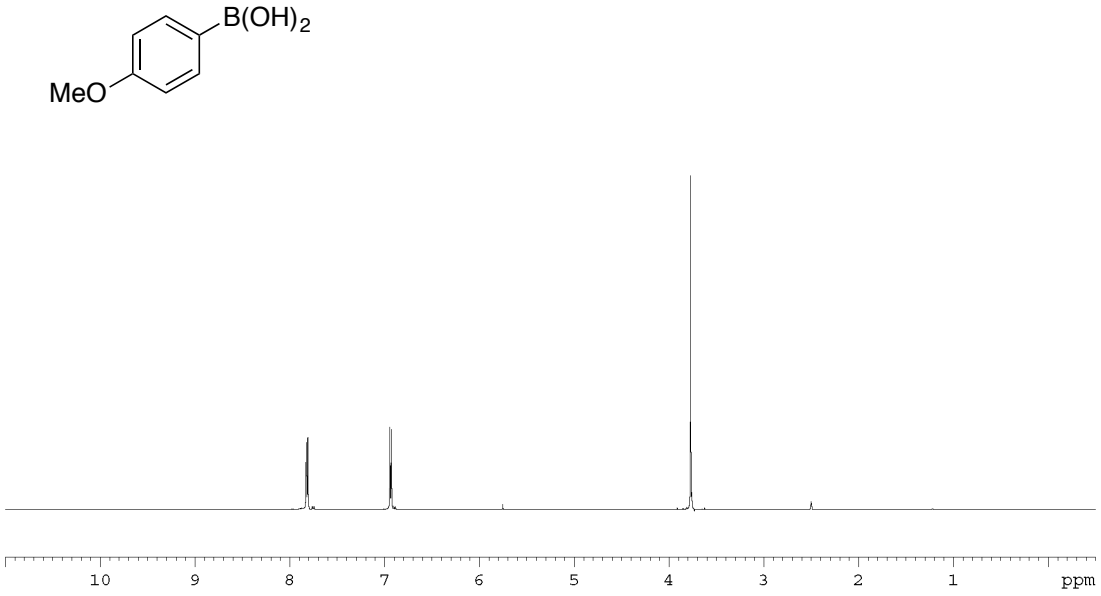


Figure A2.1 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 4-Methoxyphenylboronic Acid

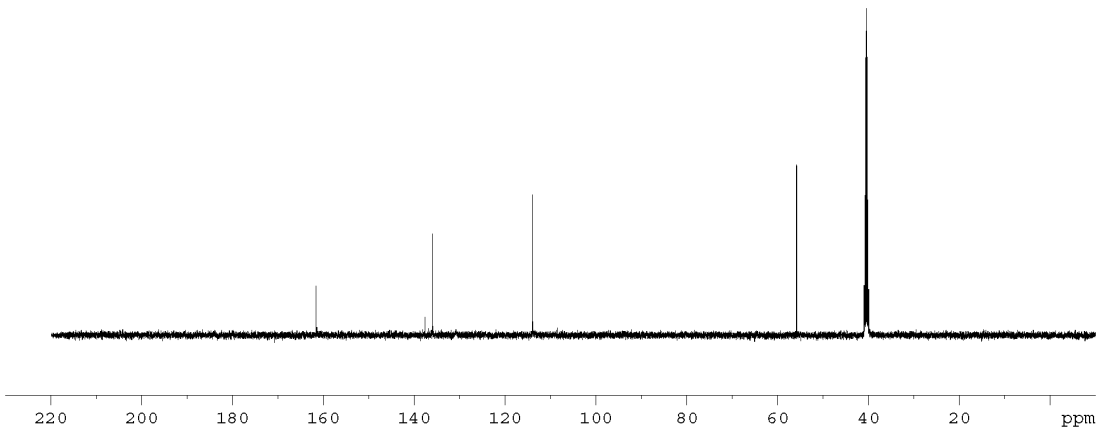


Figure A2.2 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 4-Methoxyphenylboronic Acid

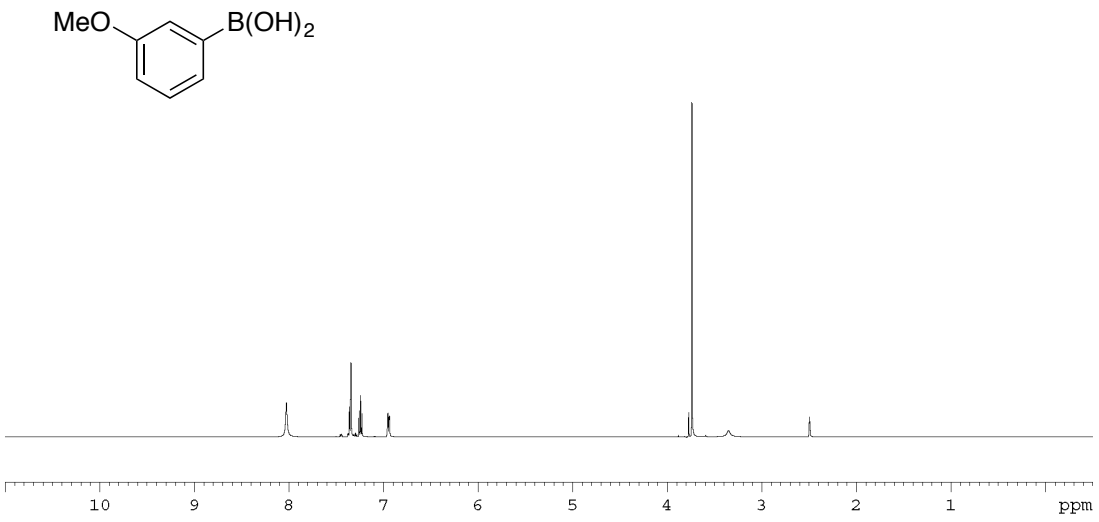


Figure A2.3 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 3-Methoxyphenylboronic Acid

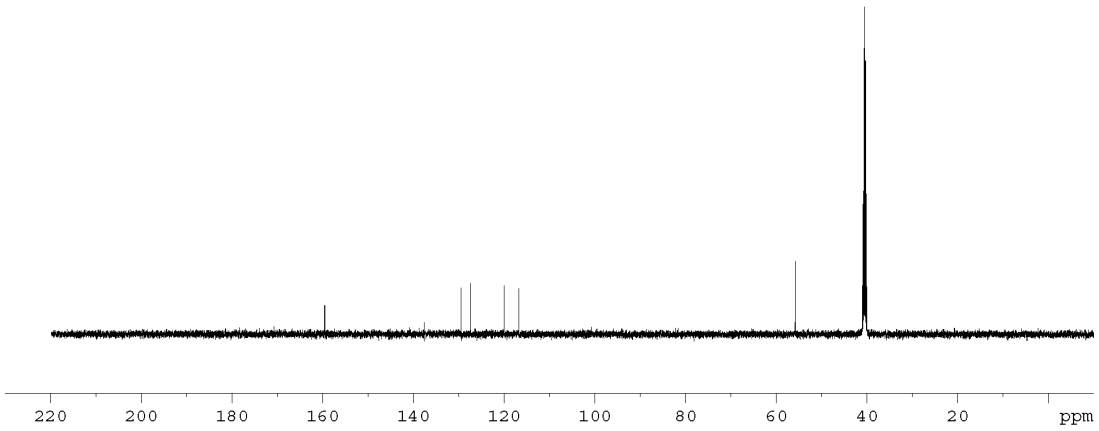


Figure A2.4 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 3-Methoxyphenylboronic Acid

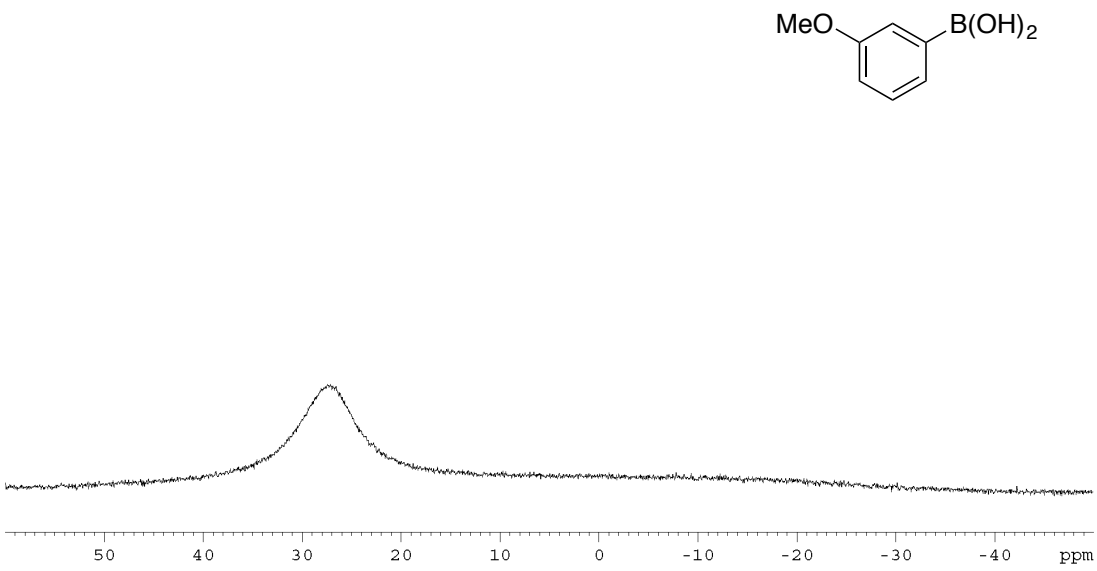


Figure A2.5 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 3-Methoxyphenylboronic Acid

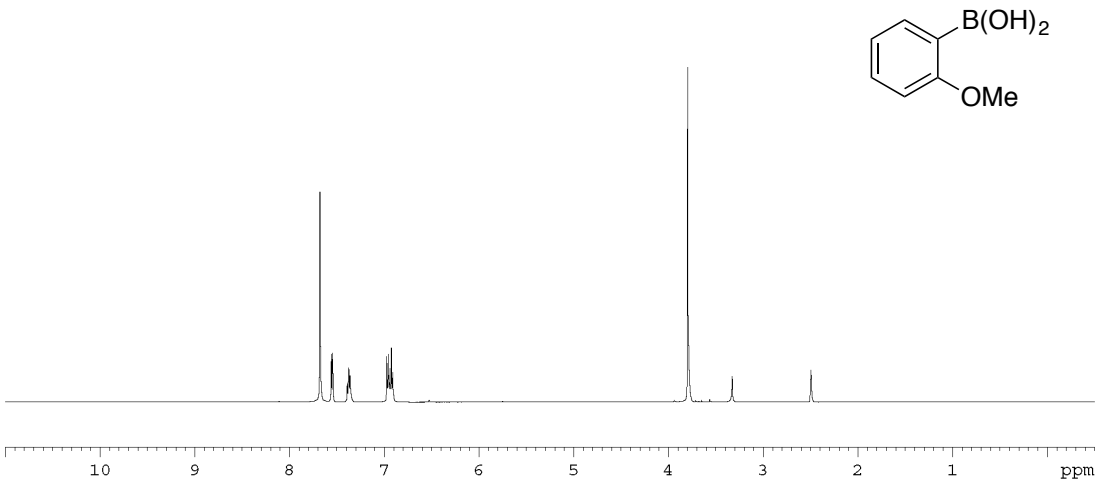


Figure A2.6 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 2-Methoxyphenylboronic Acid

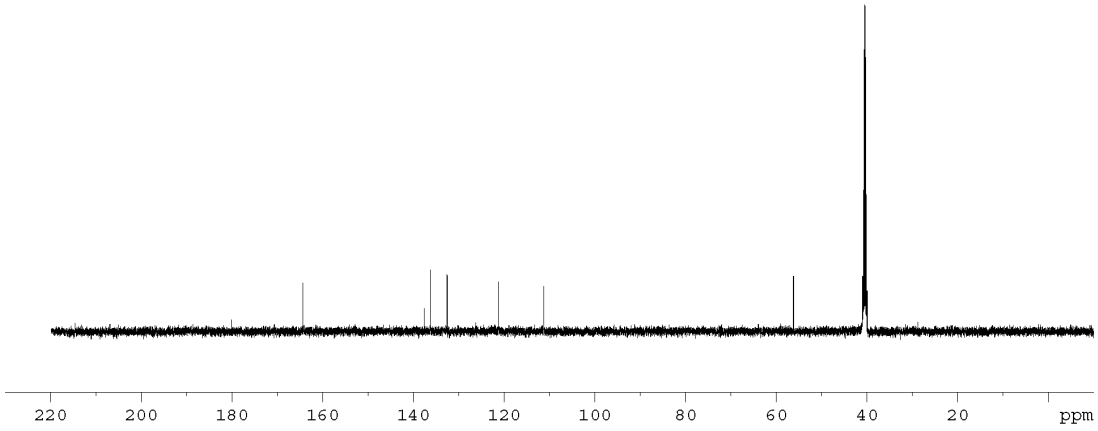


Figure A2.7 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 2-Methoxyphenylboronic Acid

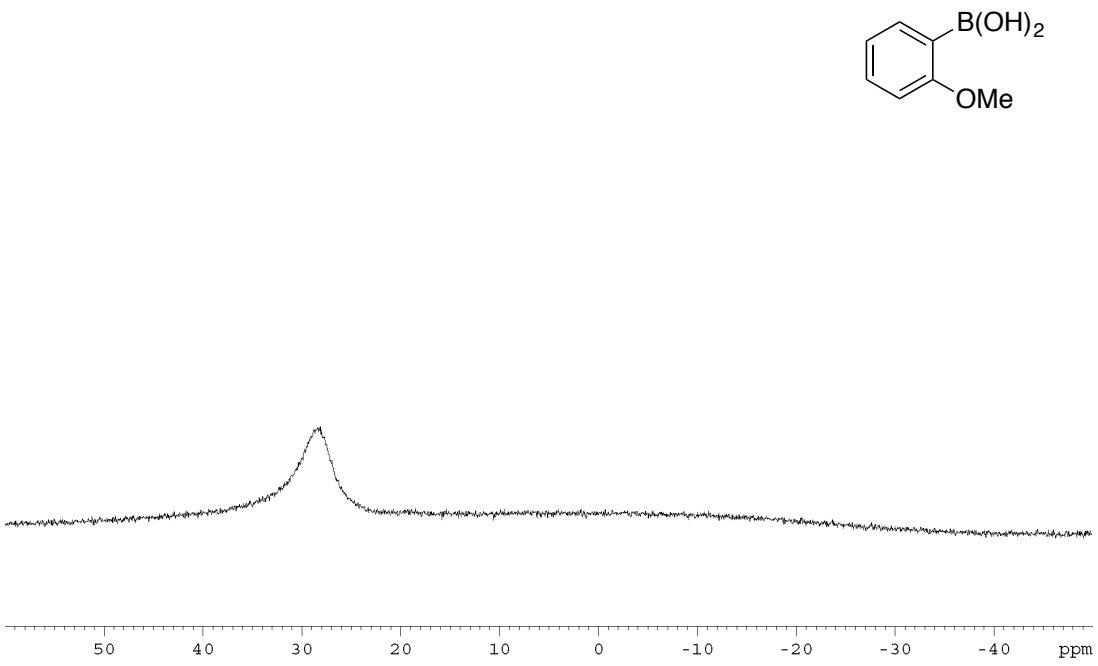


Figure A2.8 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 2-Methoxyphenylboronic Acid

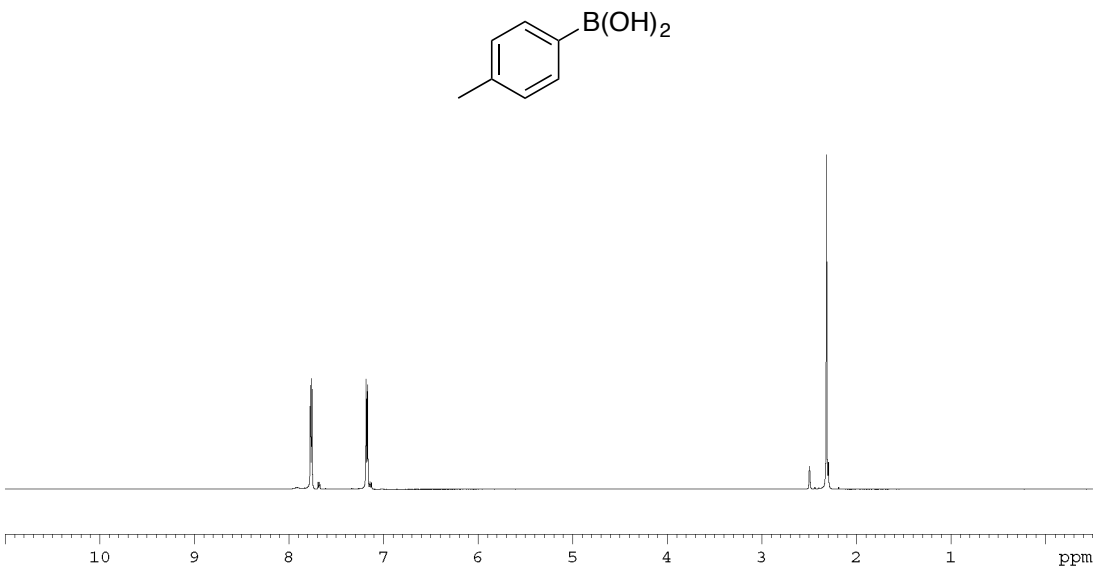


Figure A2.9 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 4-Methylphenylboronic Acid

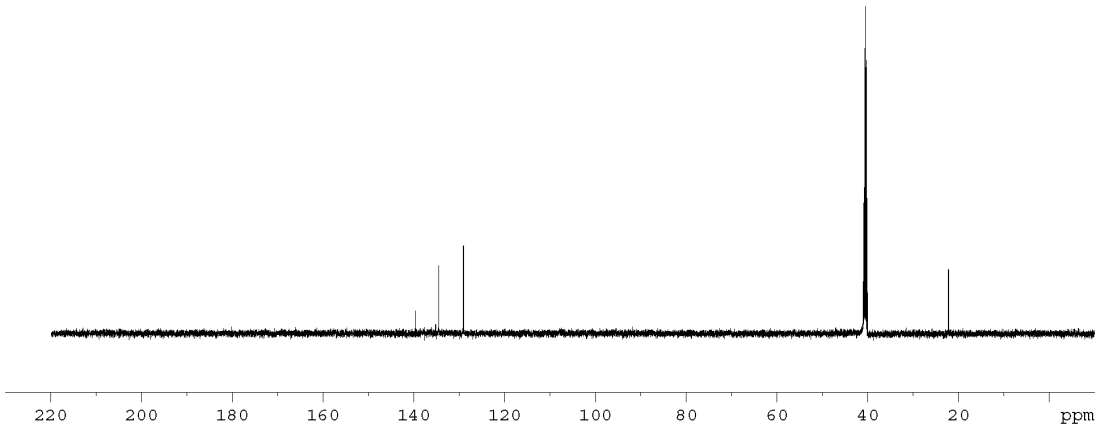


Figure A2.10 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 4-Methylphenylboronic Acid

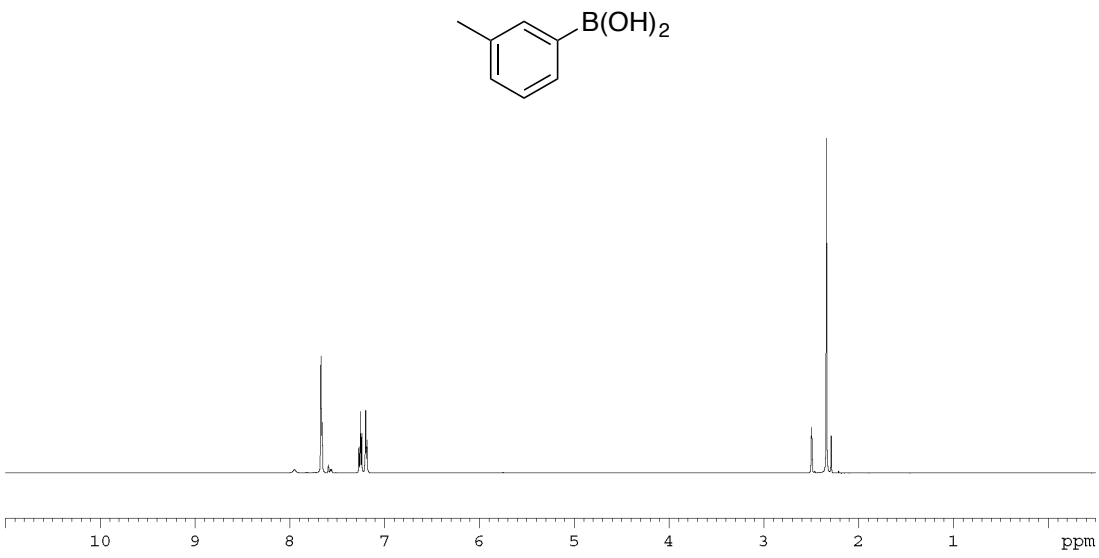


Figure A2.11 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 3-Methylphenyllboronic Acid

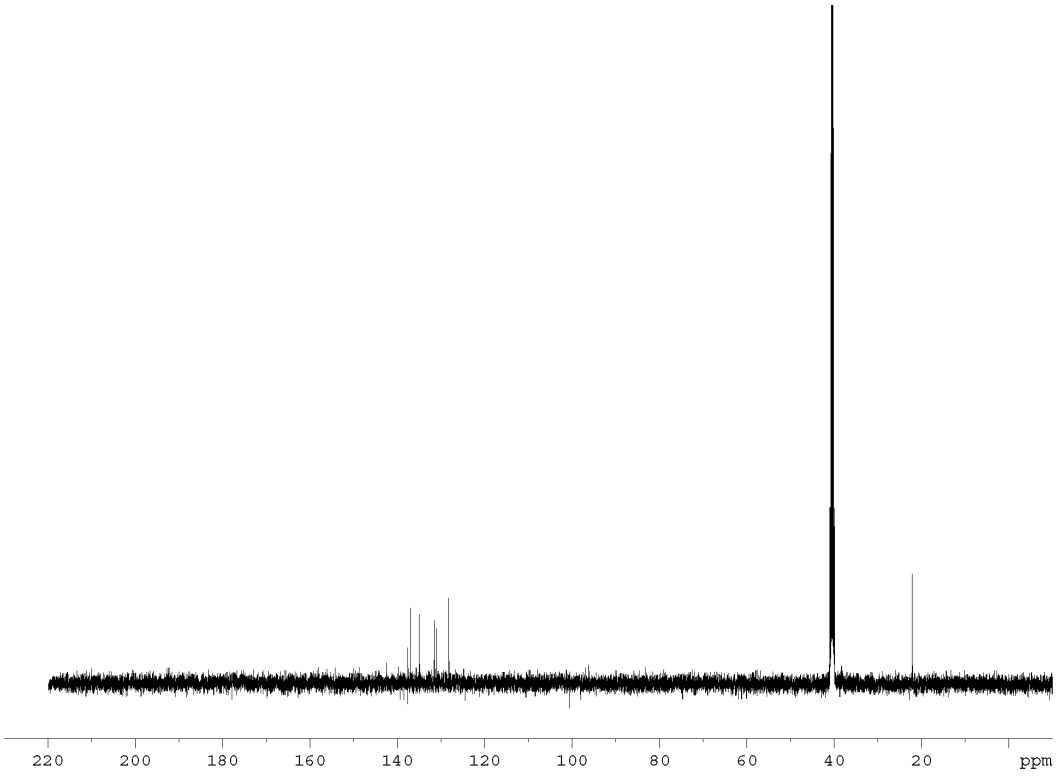


Figure A2.12 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of *3*-Methylphenyllboronic Acid

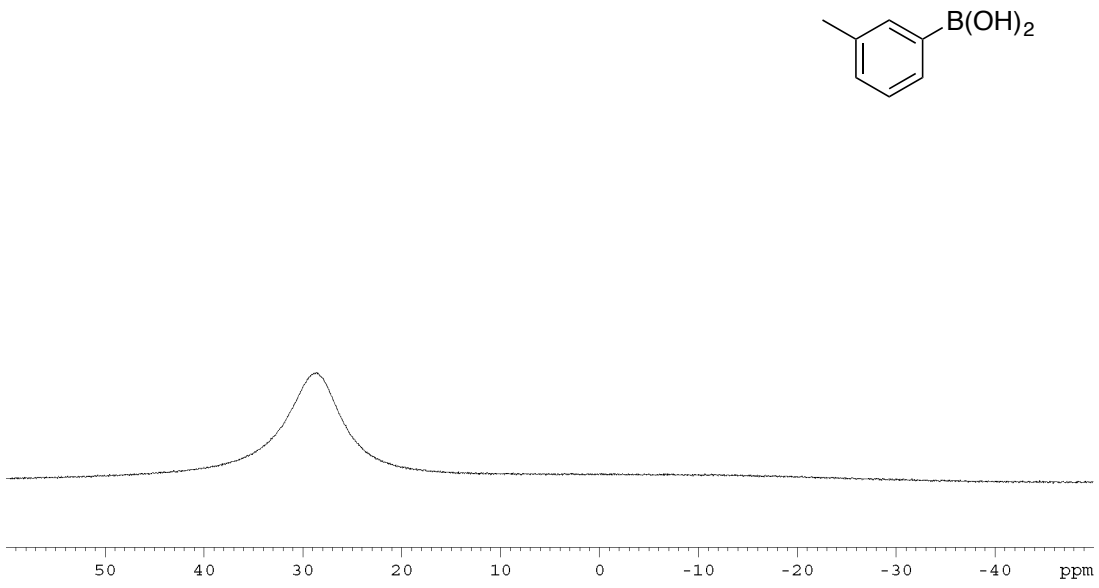


Figure A2.13 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 3-Methylphenyllboronic Acid

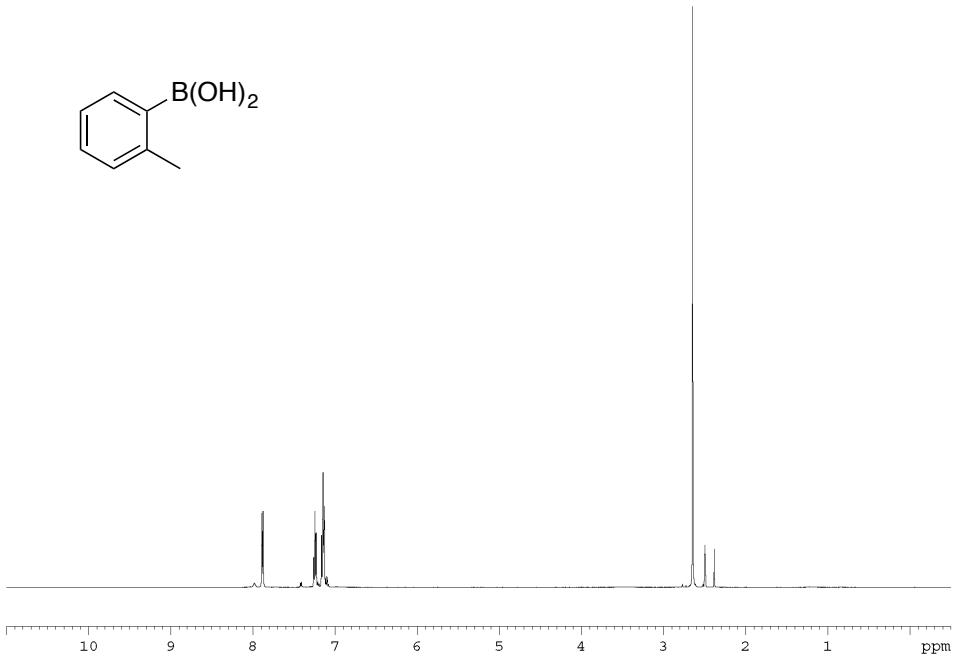


Figure A2.14 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 2-Methylphenyllboronic Acid

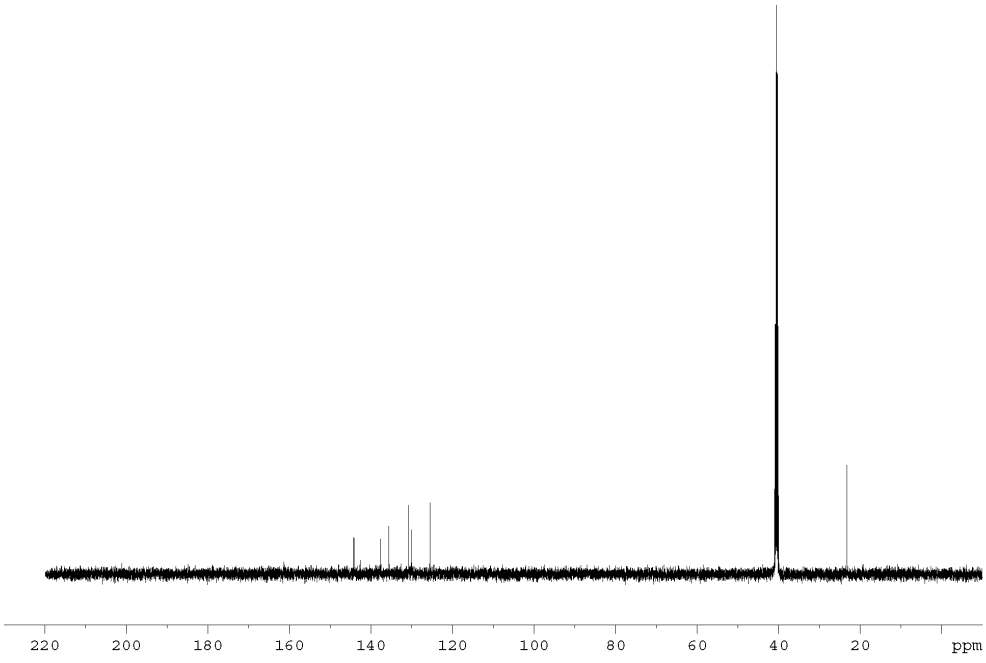


Figure A2.15 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 2-Methylphenyllboronic Acid

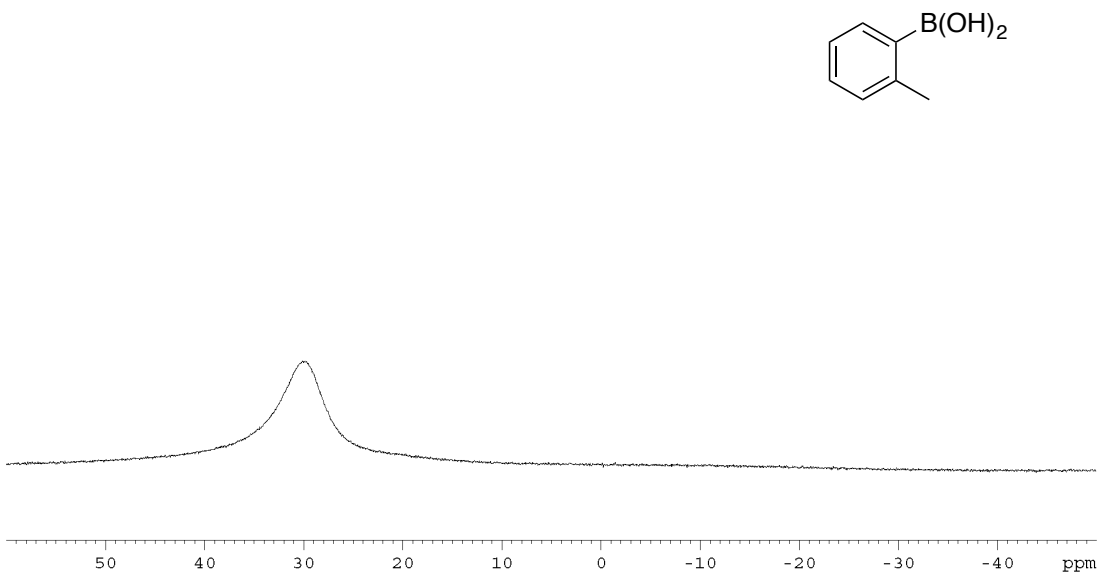


Figure A2.16 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 2-Methylphenyllboronic Acid

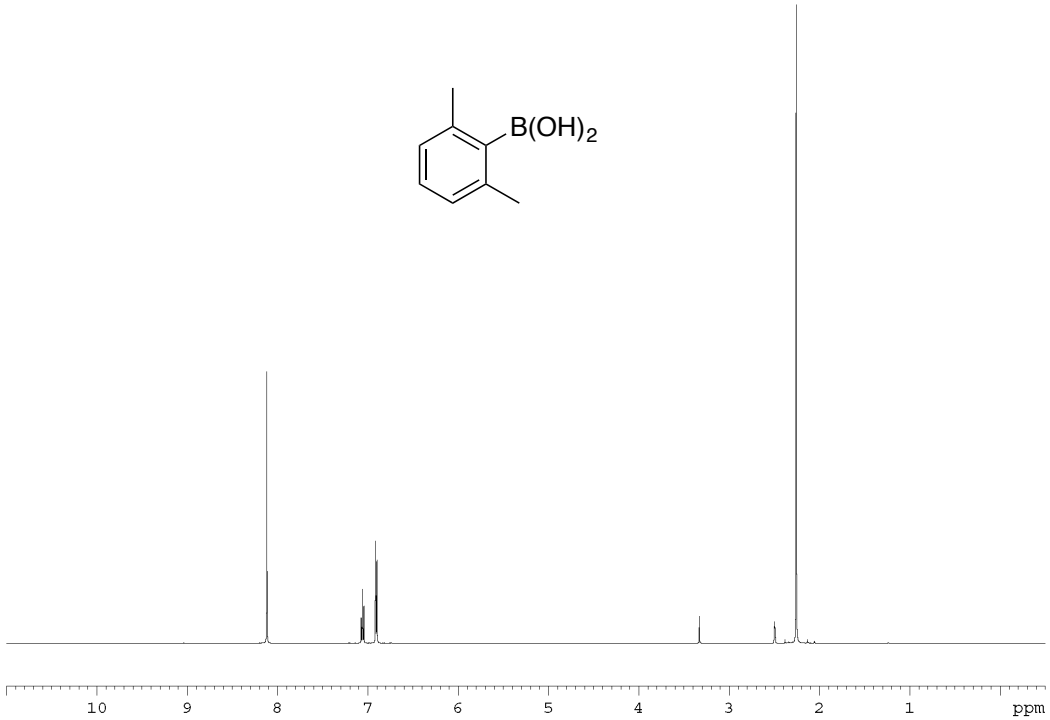


Figure A2.17 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 2,6-Dimethylphenylboronic Acid

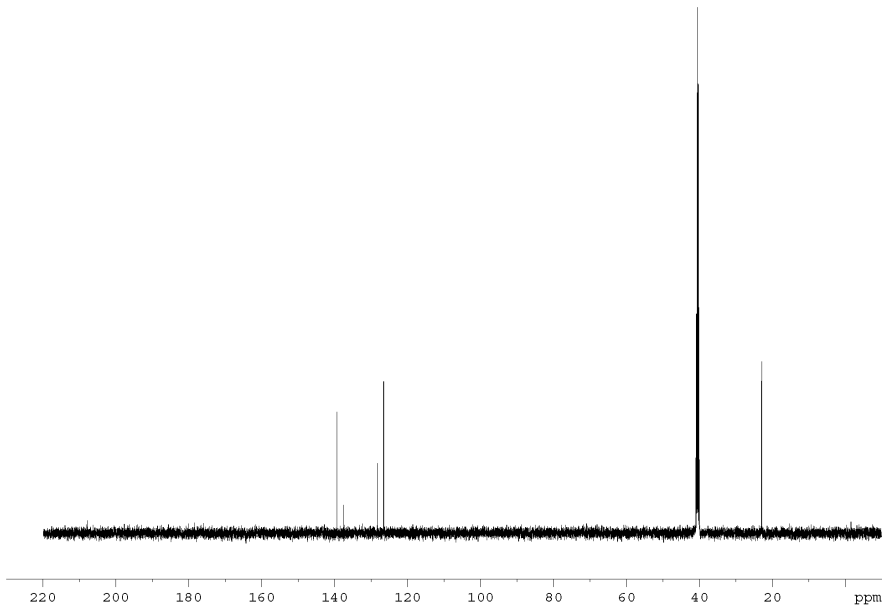


Figure A2.18 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 2,6-Dimethylphenylboronic Acid

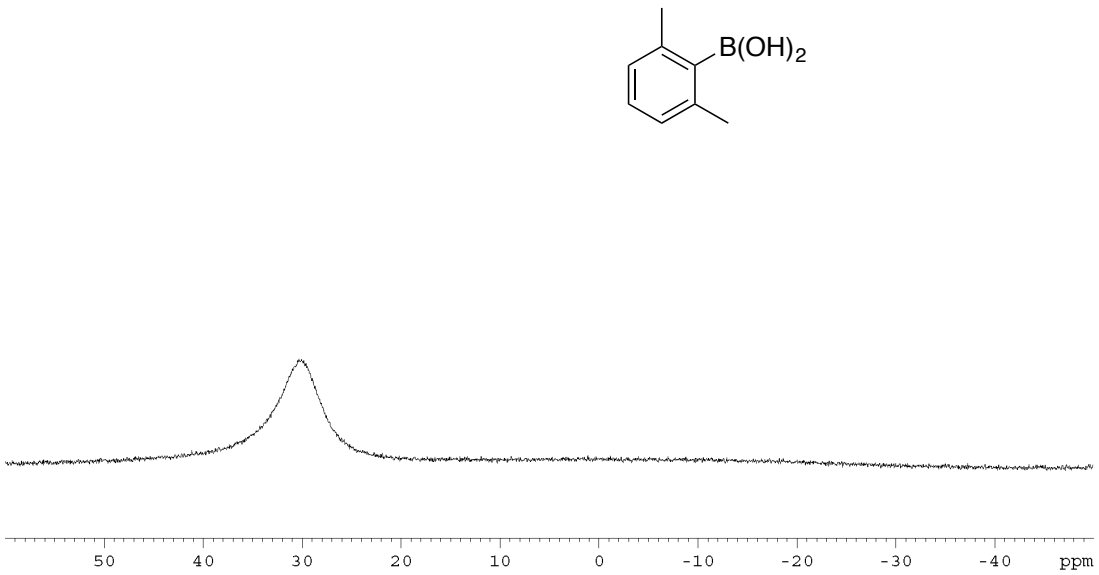


Figure A2.19 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 2,6-Dimethylphenylboronic Acid

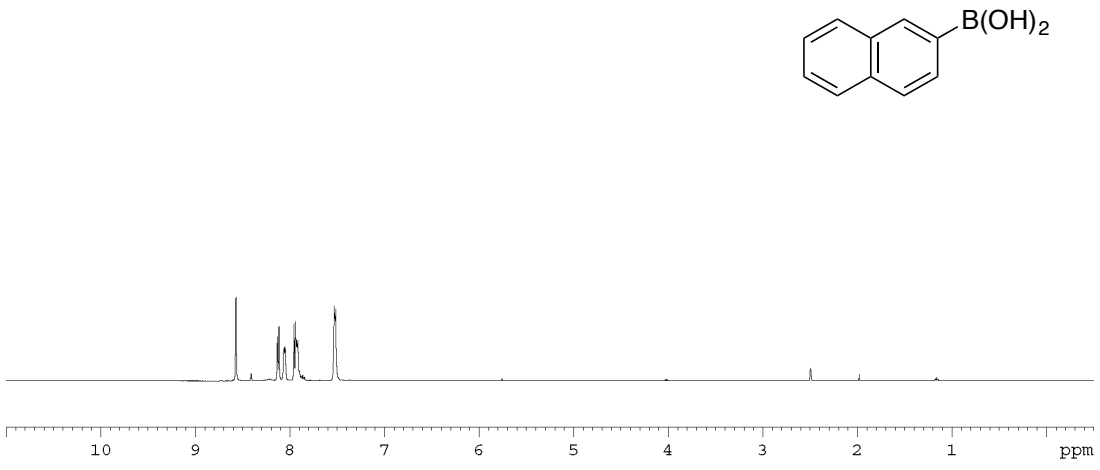


Figure A2.20 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 2-Naphthalenylboronic Acid

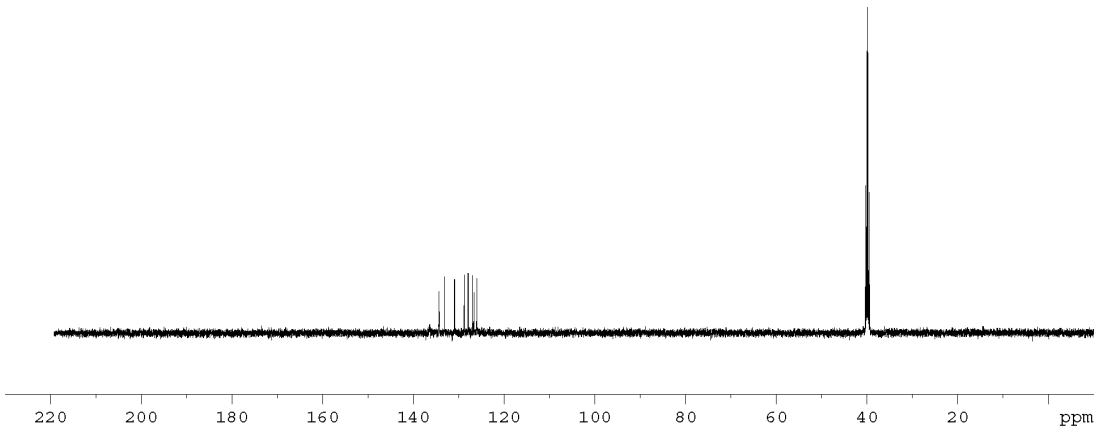


Figure A2.21 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 2-Naphthalenylboronic Acid

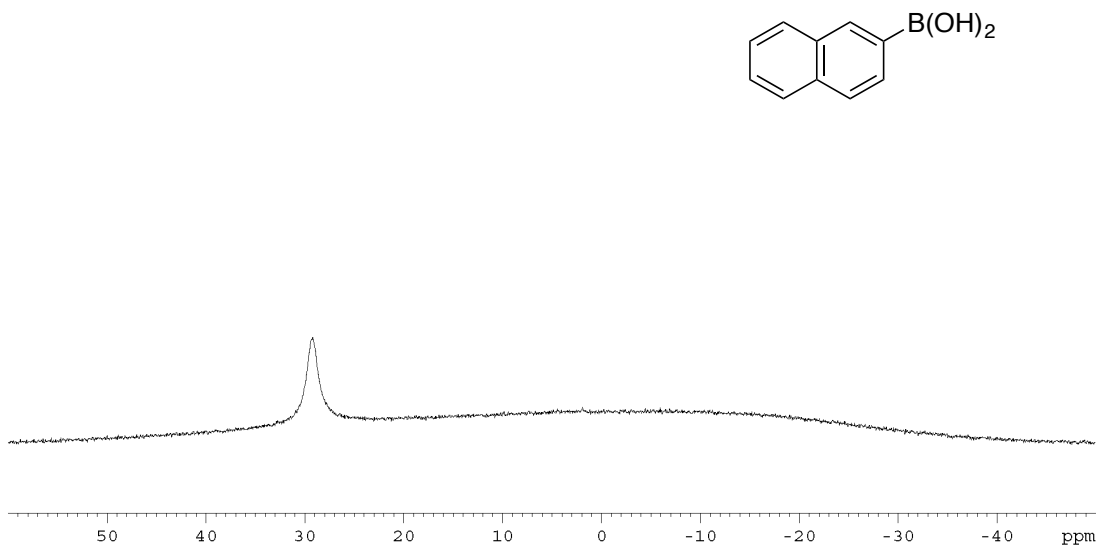


Figure A2.22 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 2-Naphthalenylboronic Acid

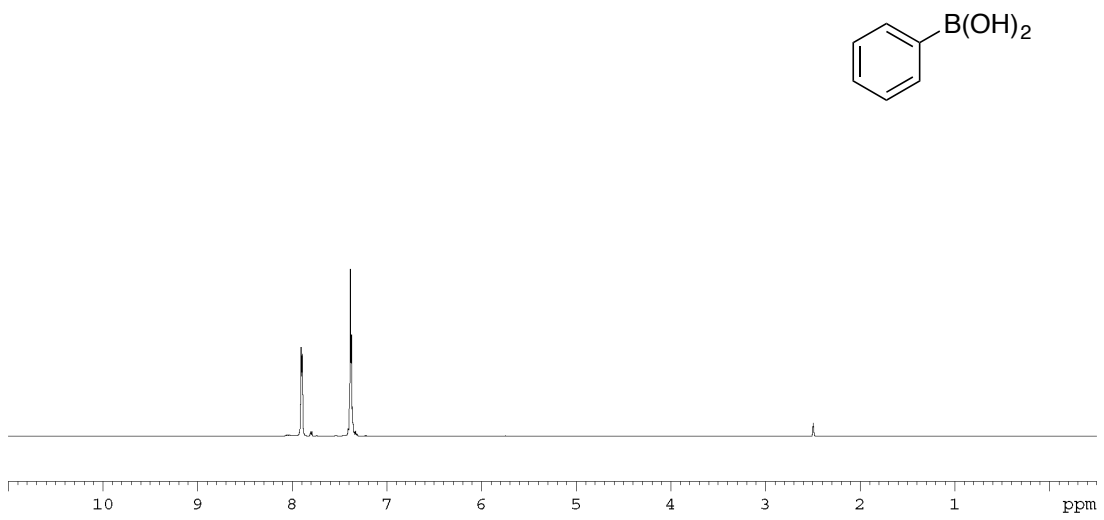


Figure A2.23 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Phenylboronic Acid

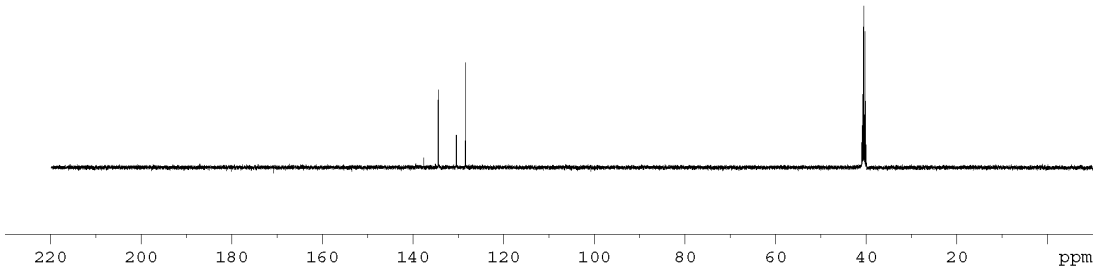


Figure A2.24 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Phenylboronic Acid

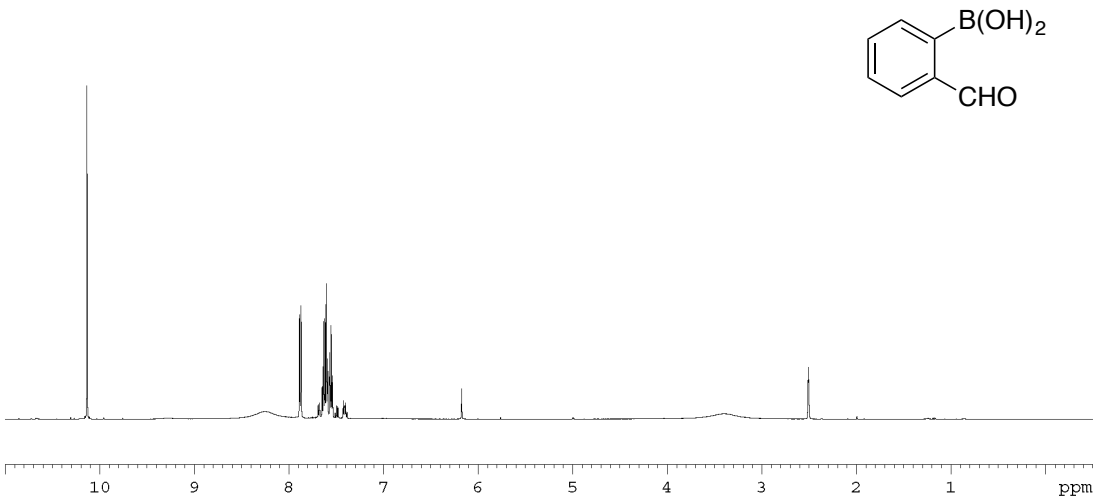


Figure A2.25 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 2-Formylphenylboronic Acid

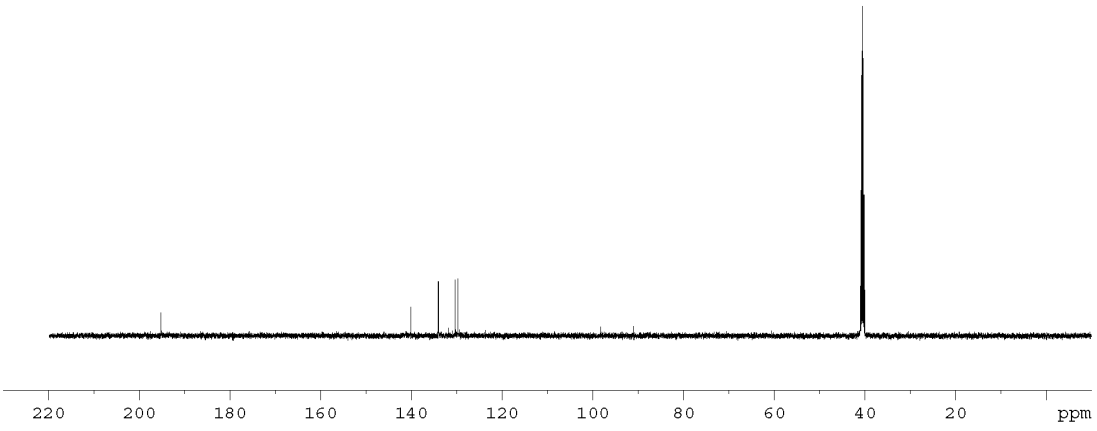


Figure A2.26 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 2-Formylphenylboronic Acid

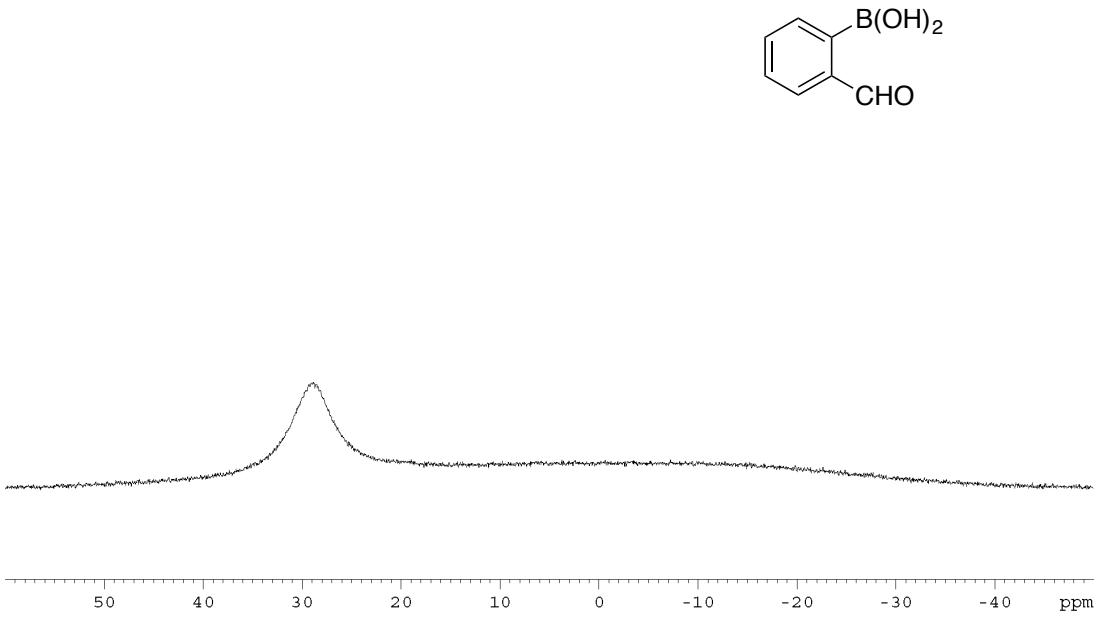


Figure A2.27 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 2-Formylphenylboronic Acid

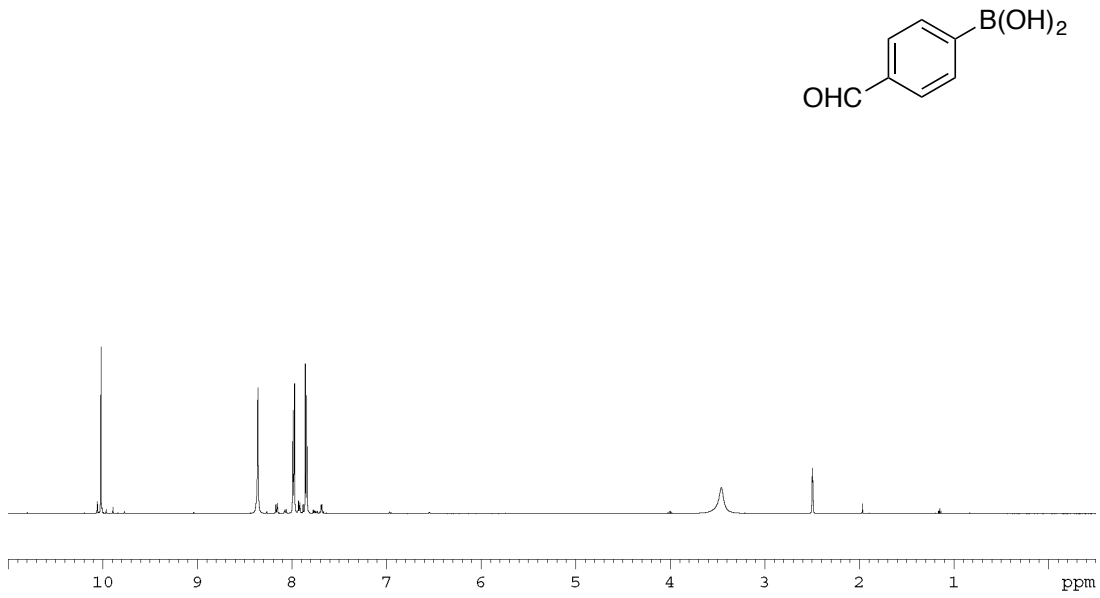


Figure A2.28 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 4-Formylphenylboronic Acid

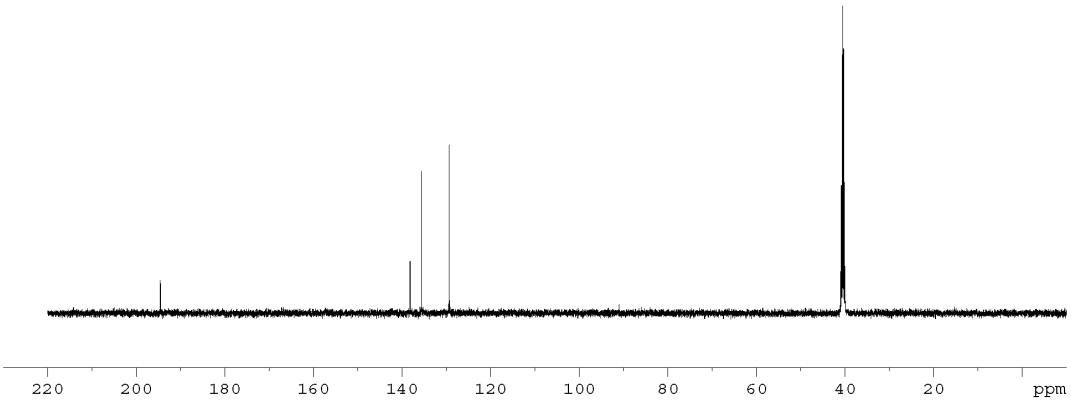


Figure A2.29 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 4-Formylphenylboronic Acid

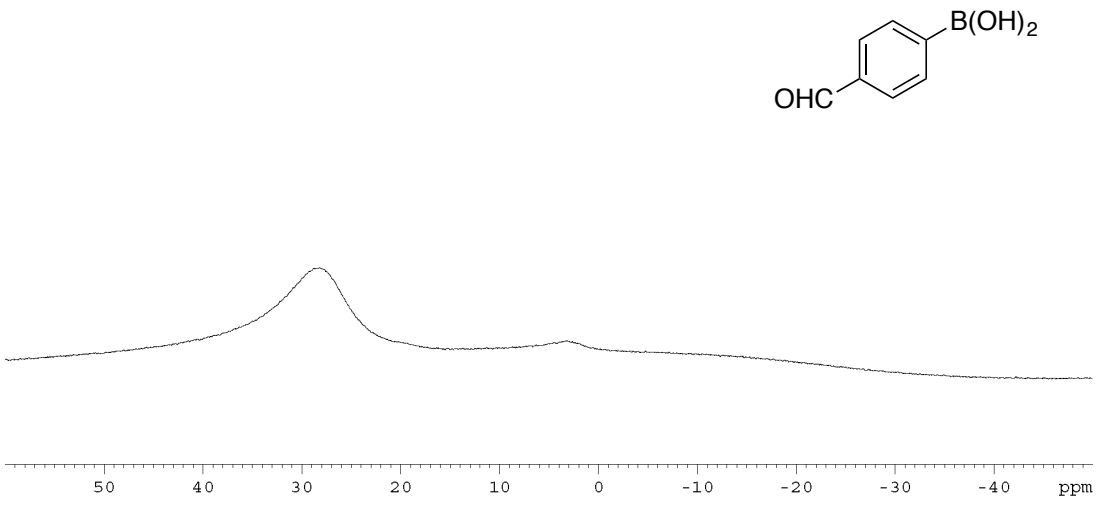


Figure A2.30 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 4-Formylphenylboronic Acid

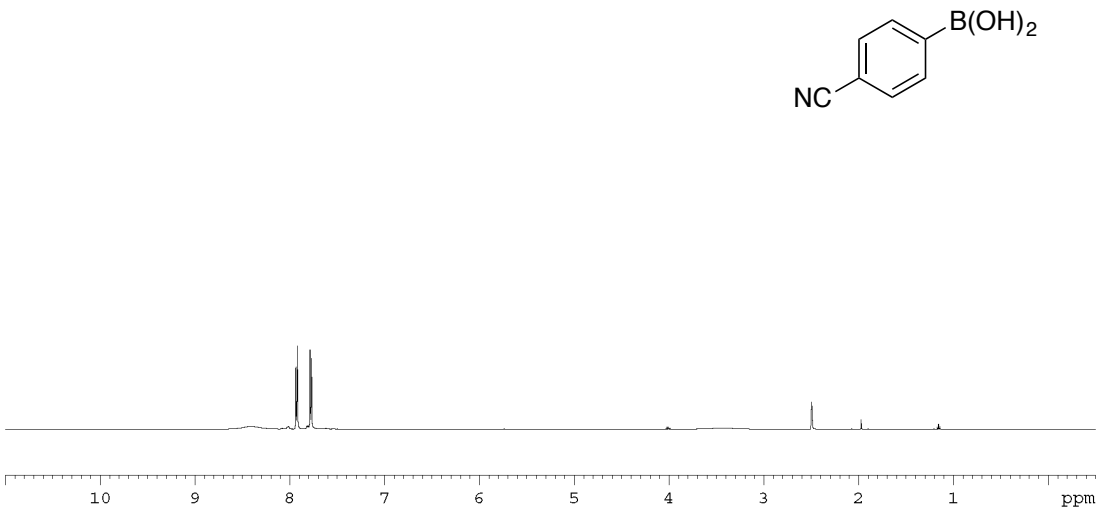


Figure A2.31 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 4-Cyanophenylboronic Acid

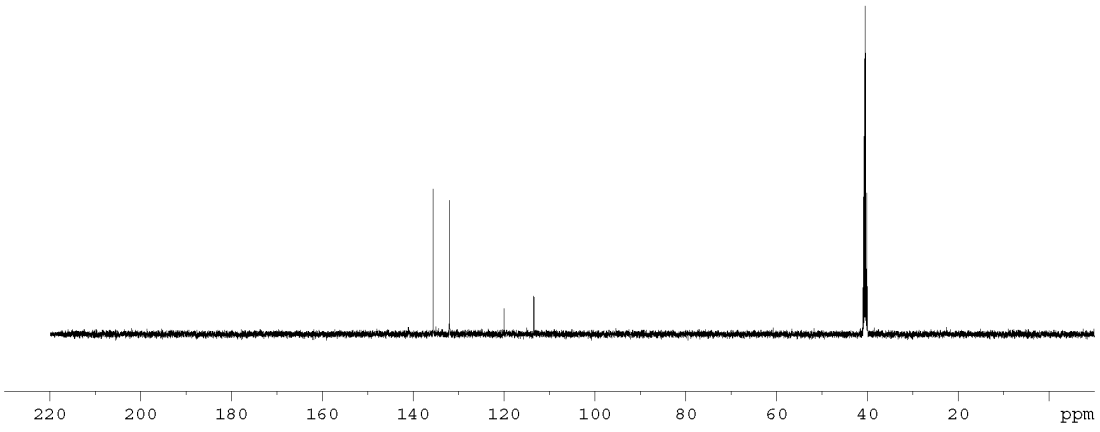


Figure A2.32 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 4-Cyanophenylboronic Acid

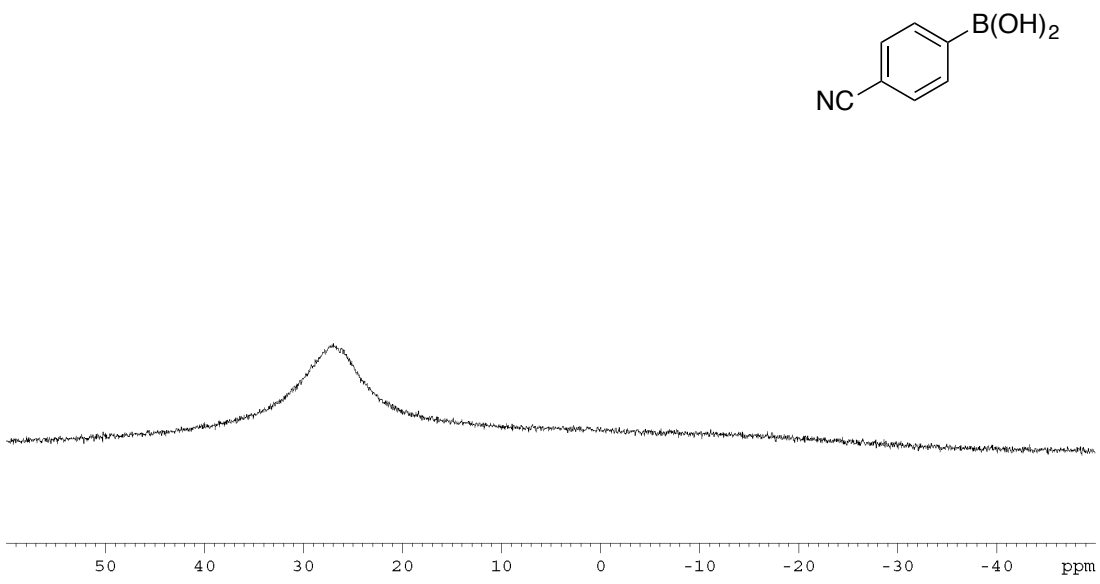


Figure A2.33 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 4-Cyanophenylboronic Acid

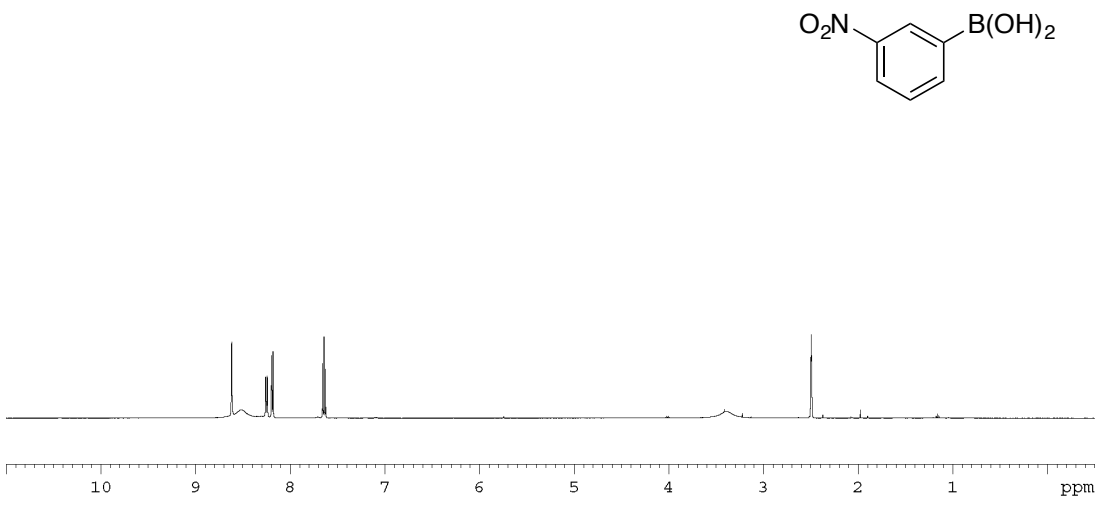


Figure A2.34 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 3-Nitrophenylboronic Acid

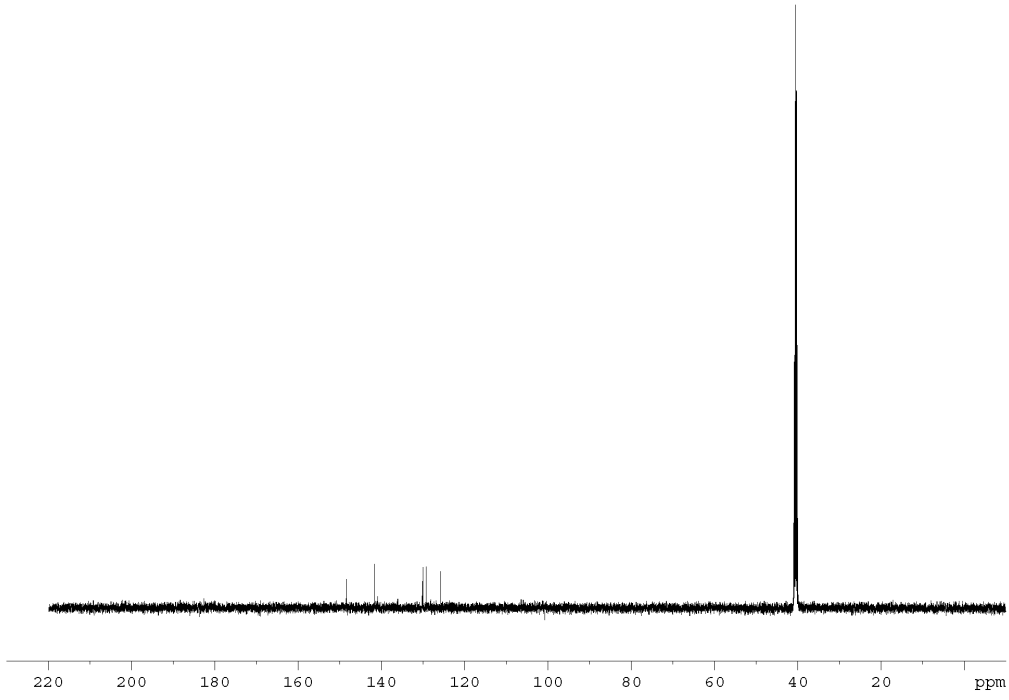


Figure A2.35 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 3-Nitrophenylboronic Acid

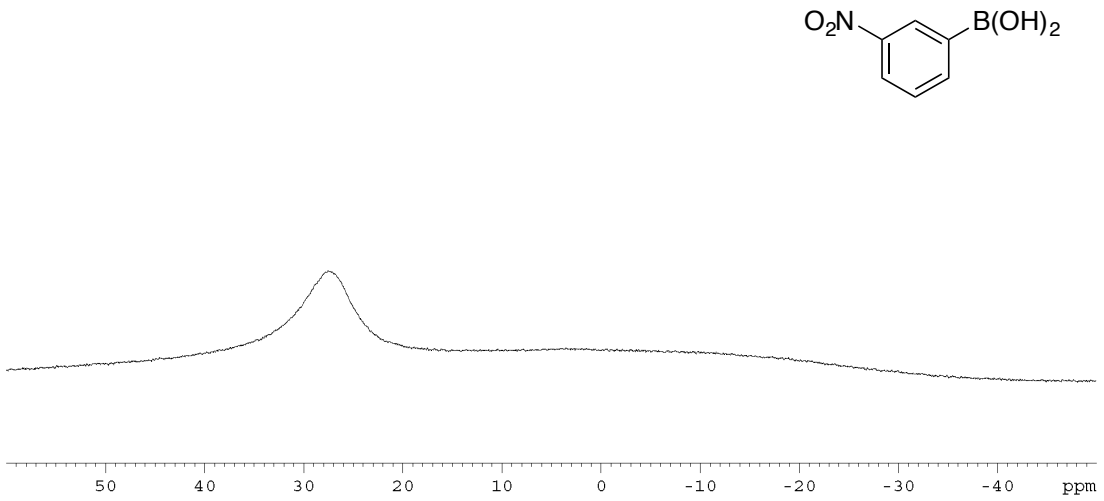


Figure A2.36 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 3-Nitrophenylboronic Acid

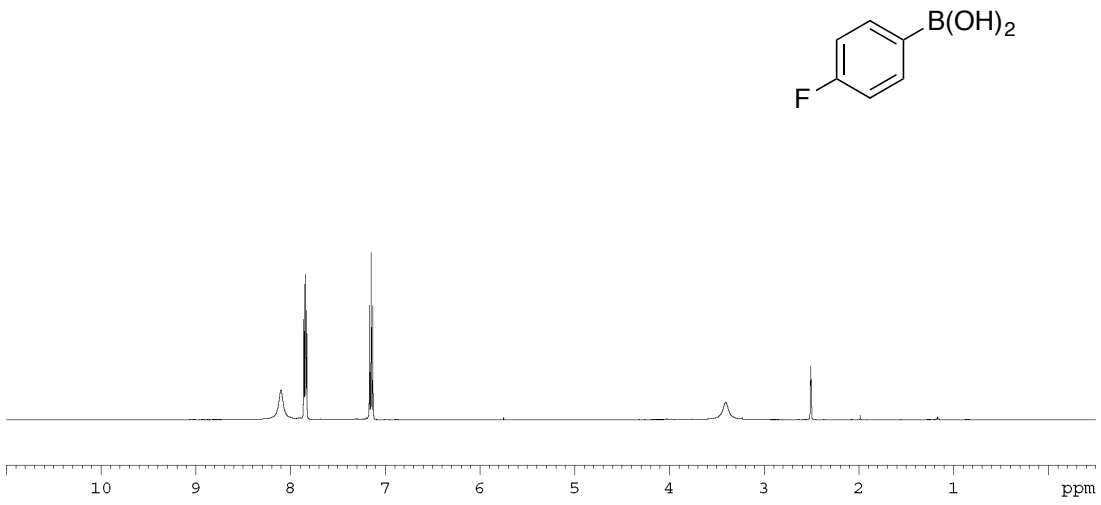


Figure A2.37 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 4-Fluorophenylboronic Acid

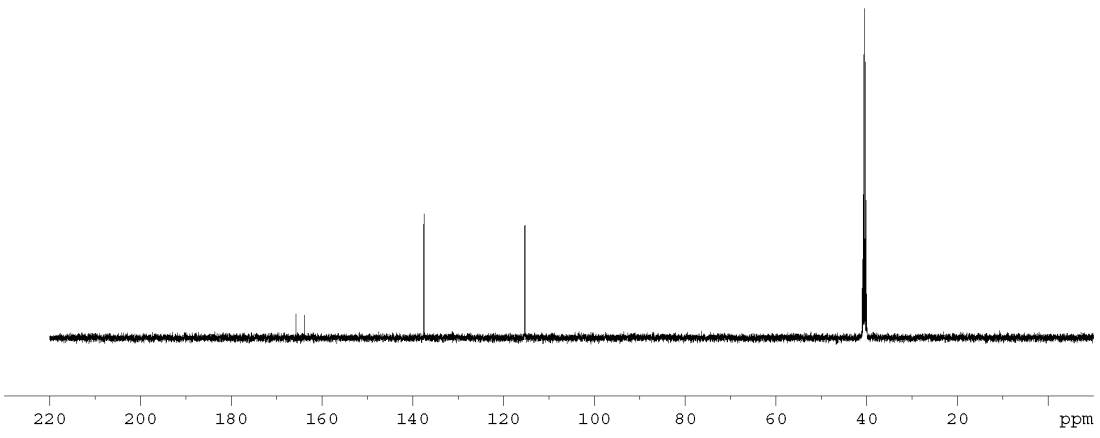


Figure A2.38 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 4-Fluorophenylboronic Acid

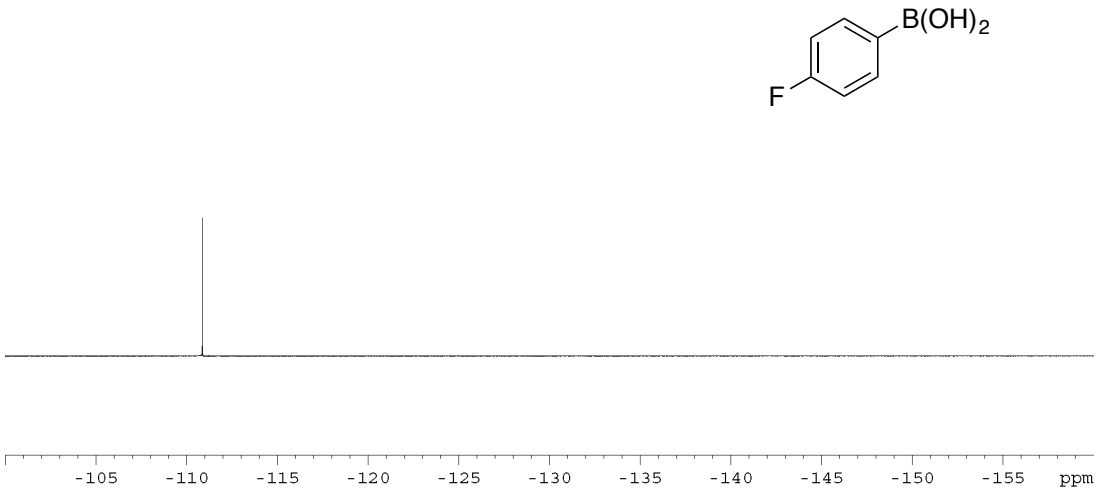


Figure A2.39 ^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of 4-Fluorophenylboronic Acid

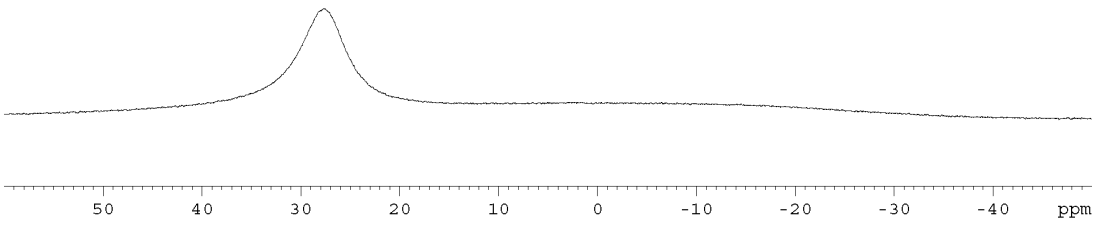


Figure A2.40 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 4-Fluorophenylboronic Acid

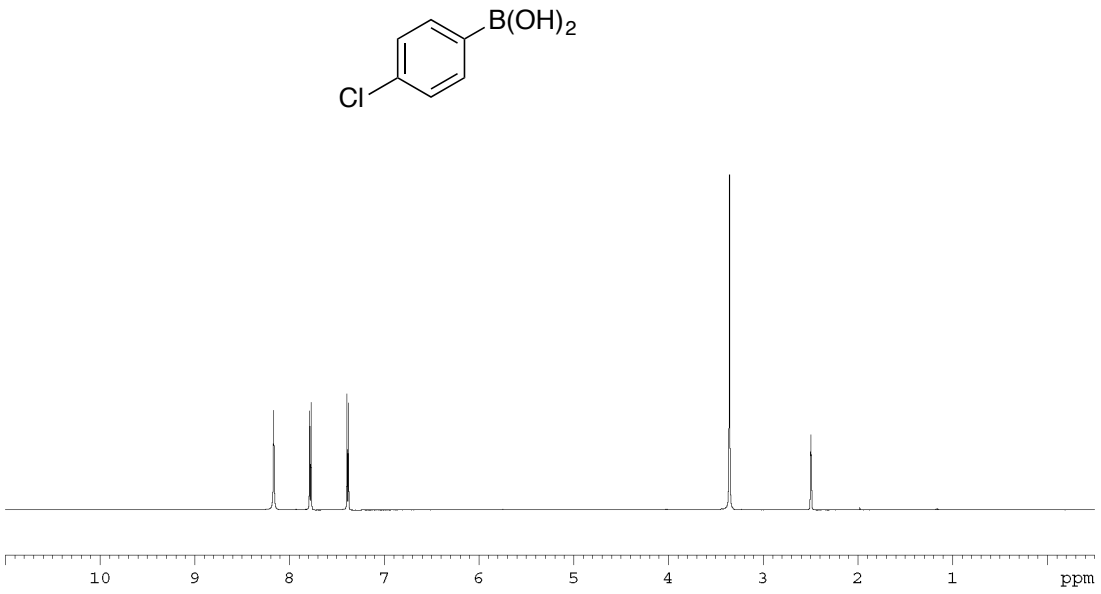


Figure A2.41 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 4-Chlorophenylboronic Acid

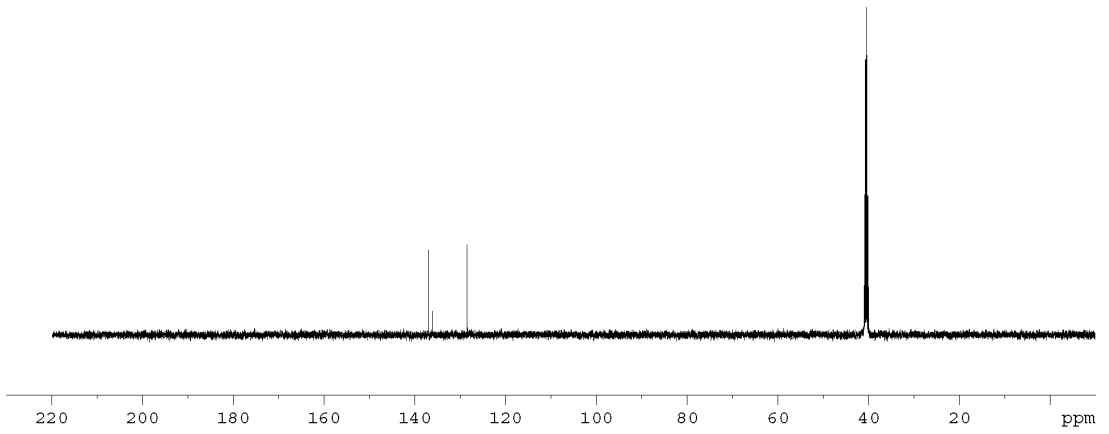


Figure A2.42 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 4-Chlorophenylboronic Acid

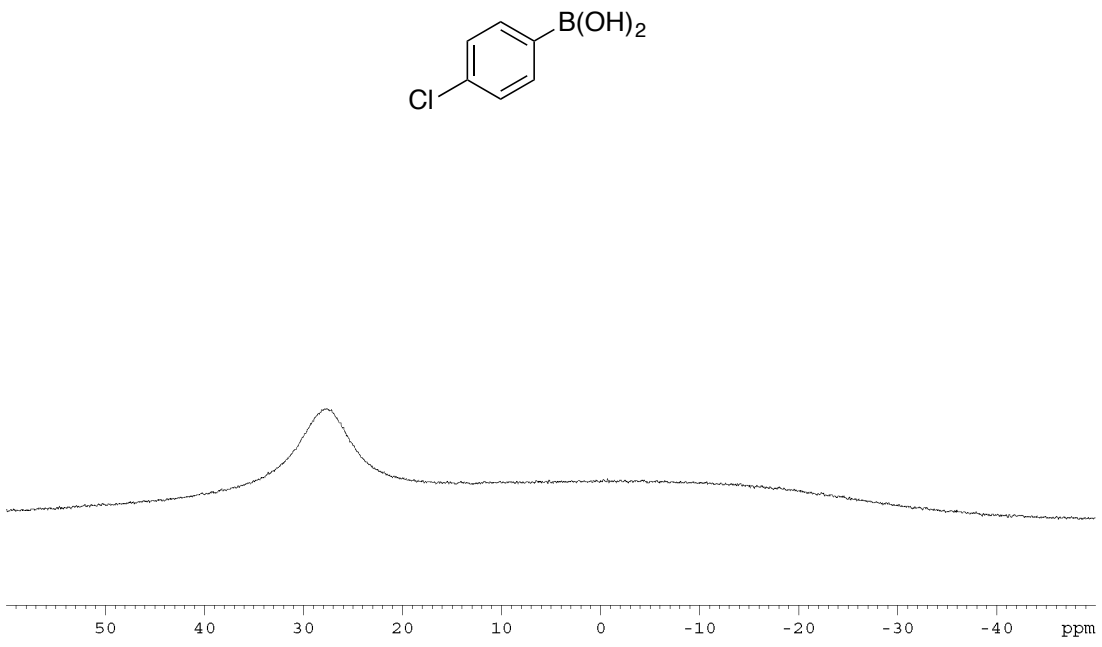


Figure A2.43 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 4-Chlorophenylboronic Acid

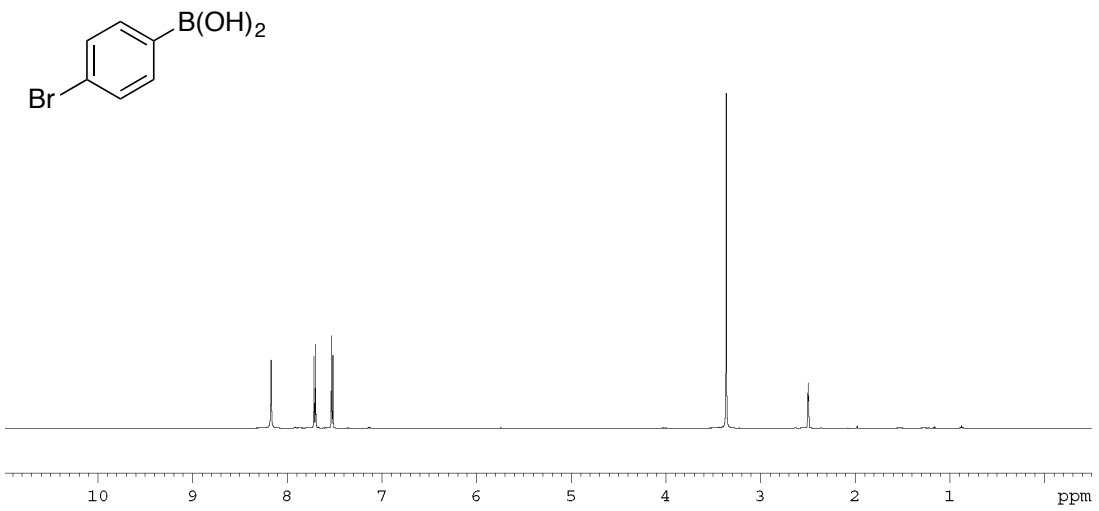


Figure A2.44 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 4-Bromophenylboronic Acid

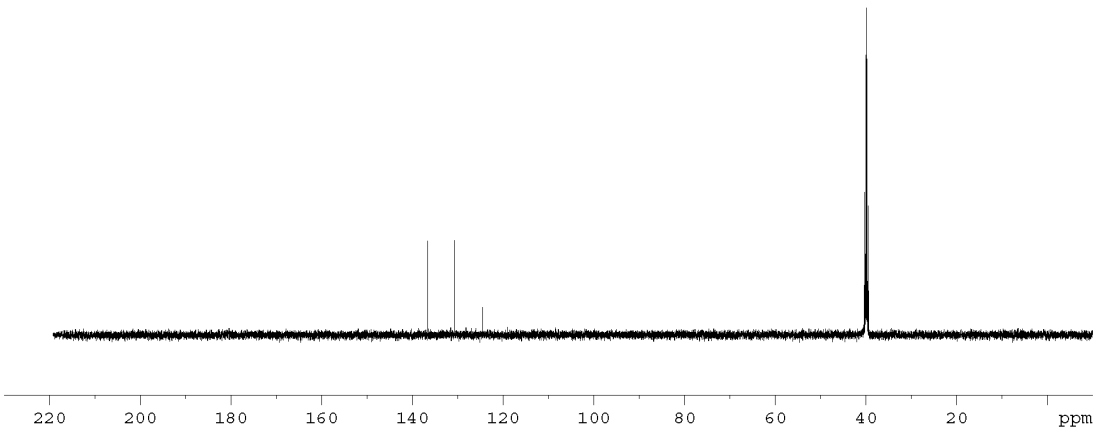


Figure A2.45 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 4-Bromophenylboronic Acid

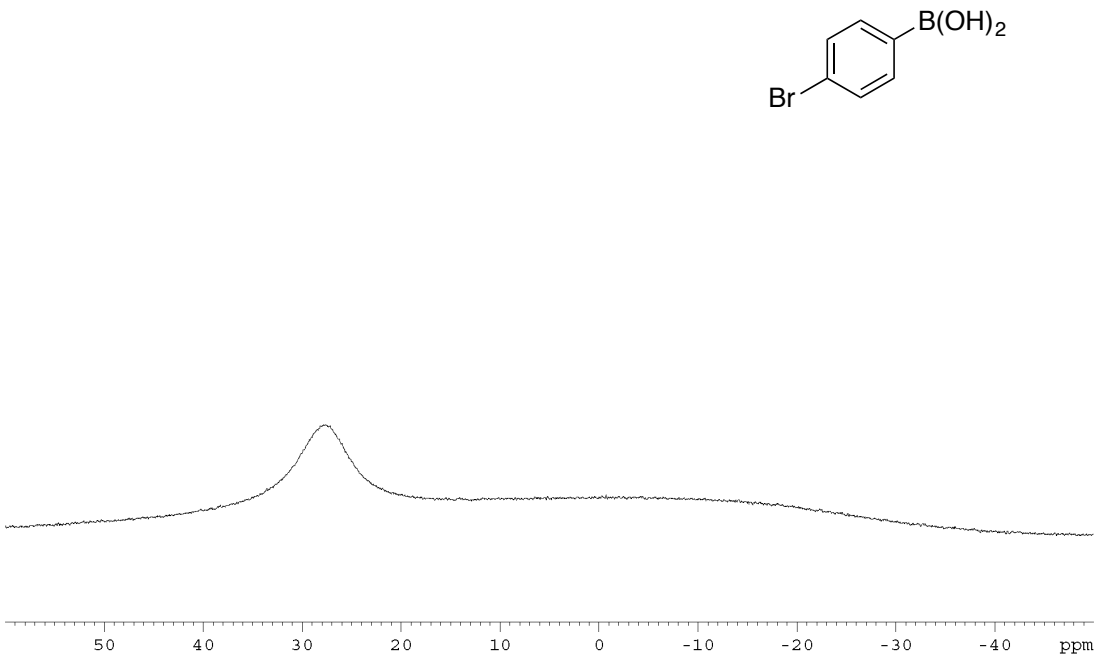


Figure A2.46 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 4-Bromophenylboronic Acid

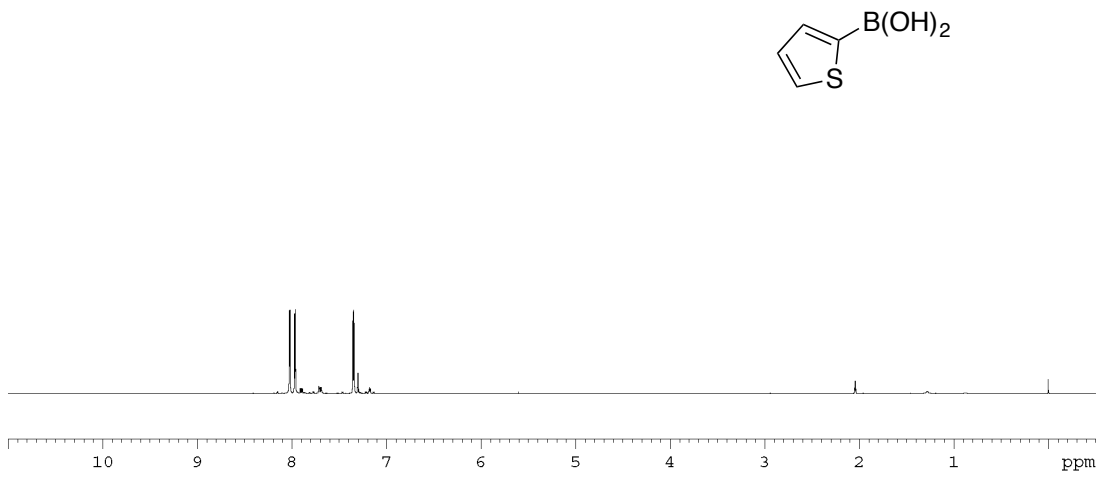


Figure A2.47 ^{1}H NMR (500 MHz, Acetone-d_6) Spectrum of Thiophen-2-ylboronic Acid

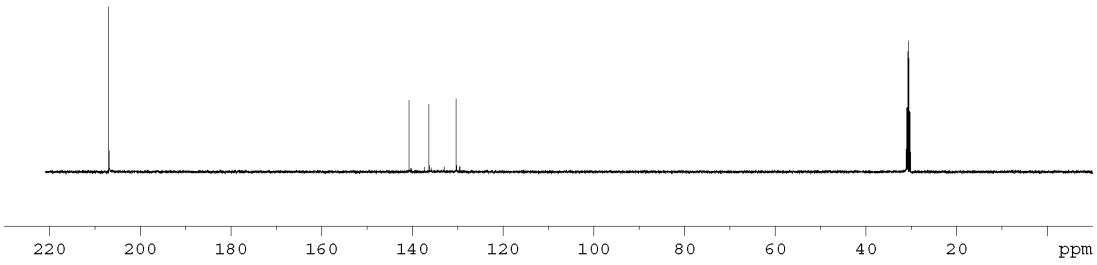


Figure A2.48 ^{13}C NMR (128.5 MHz, Acetone-d_6) Spectrum of Thiophen-2-ylboronic Acid

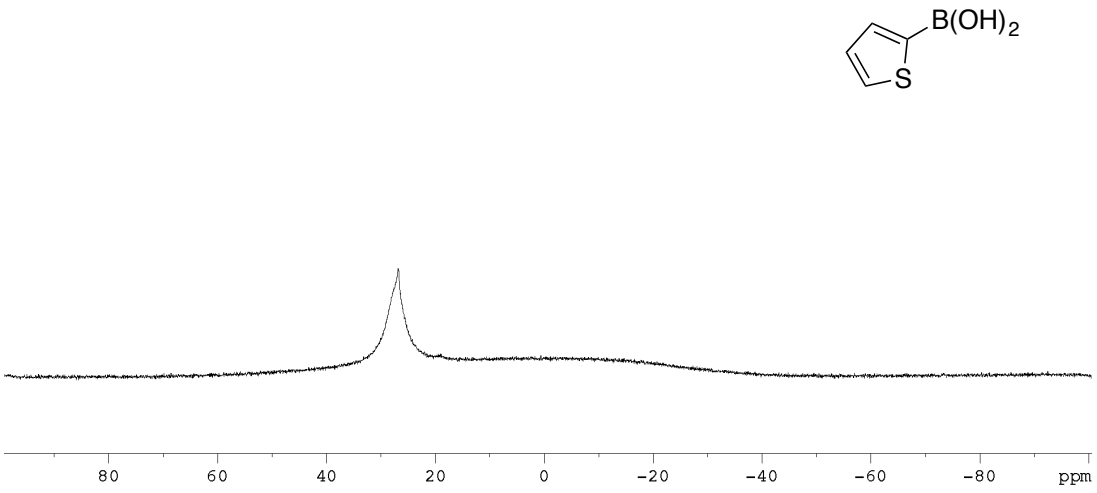


Figure A2.49 ^{11}B NMR (128.4 MHz, Acetone-d_6) Spectrum of Thiophen-2-ylboronic Acid

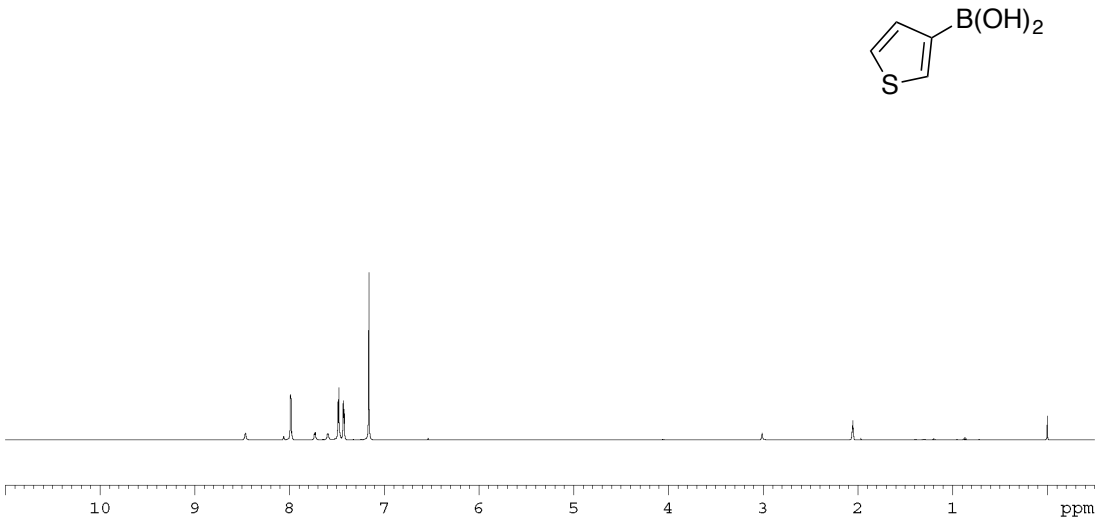


Figure A2.50 ^{1}H NMR (500 MHz, Acetone-d_6) Spectrum of Thiophen-3-ylboronic Acid

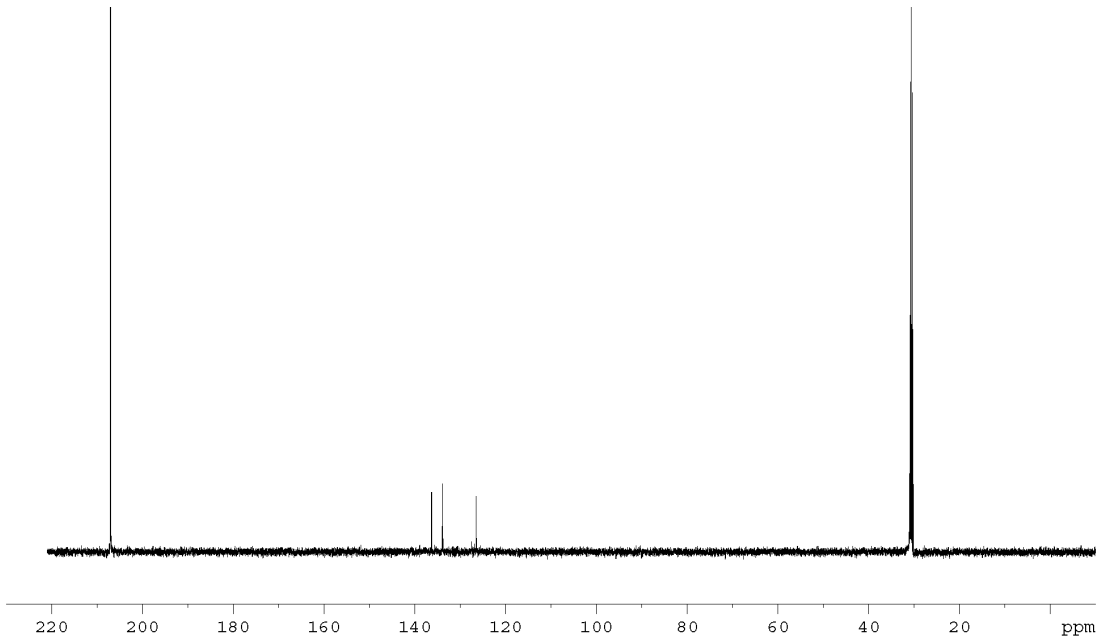


Figure A2.51 ^{13}C NMR (128.5 MHz, Acetone-d_6) Spectrum of Thiophen-3-ylboronic Acid

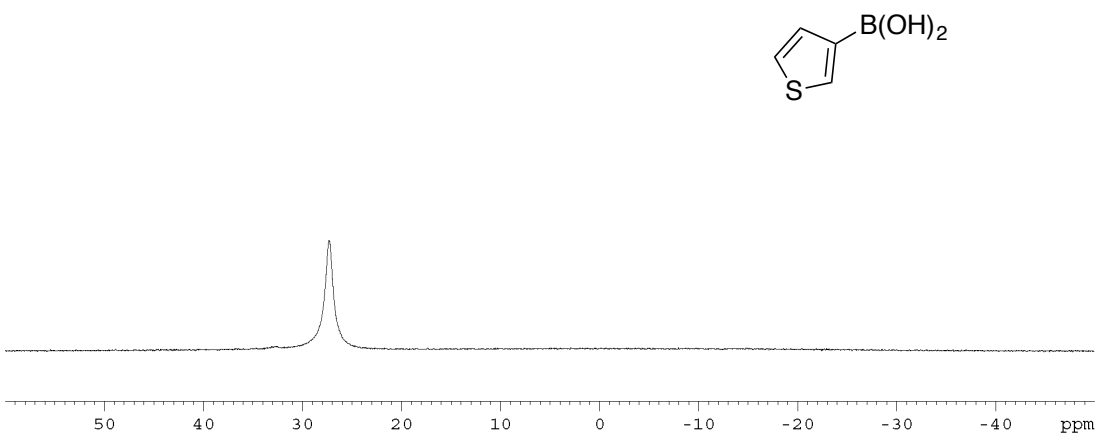


Figure A2.52 ^{11}B NMR (128.4 MHz, Acetone-d_6) Spectrum of Thiophen-3-ylboronic Acid

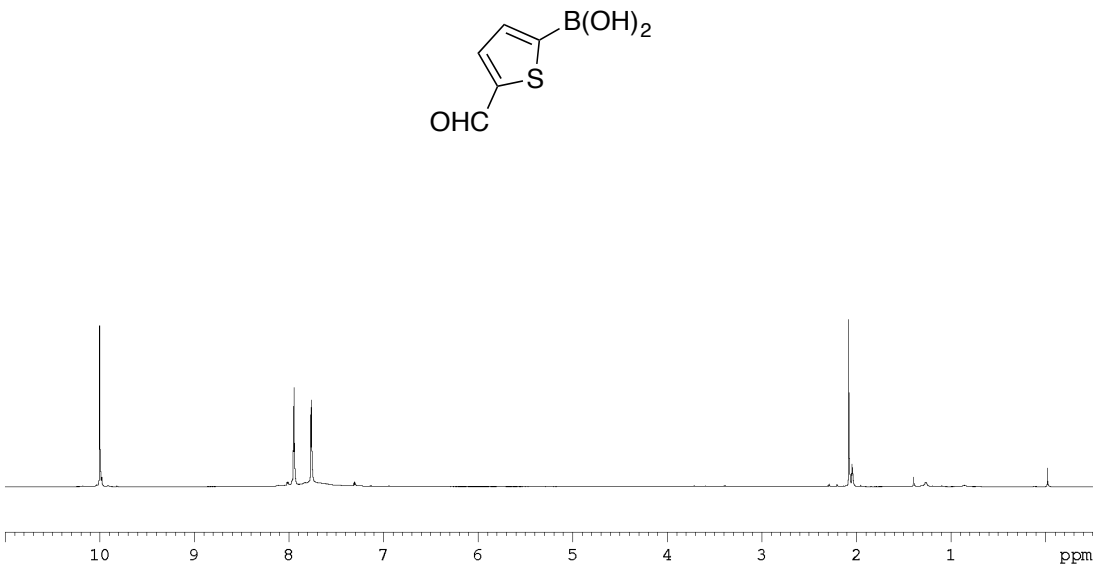


Figure A2.53 ^{1}H NMR (500 MHz, Acetone-d_6) Spectrum of 5-Formylthiophen-2-ylboronic Acid

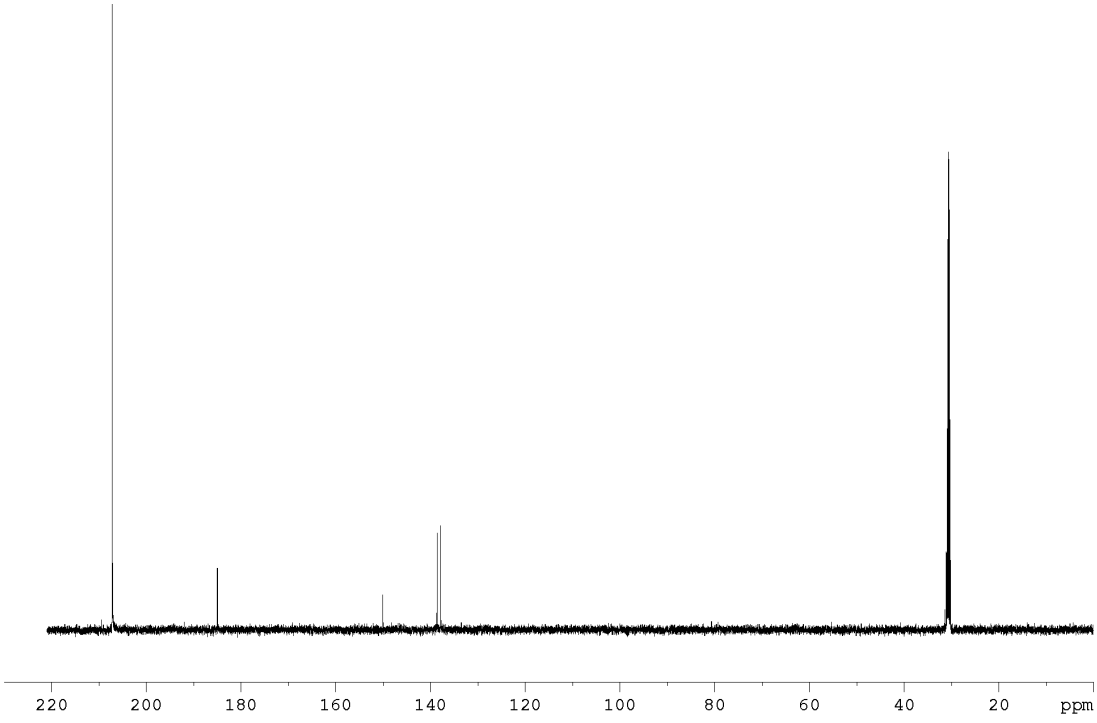


Figure A2.54 ^{13}C NMR (128.5 MHz, Acetone-d_6) Spectrum of 5-Formylthiophen-2-ylboronic Acid

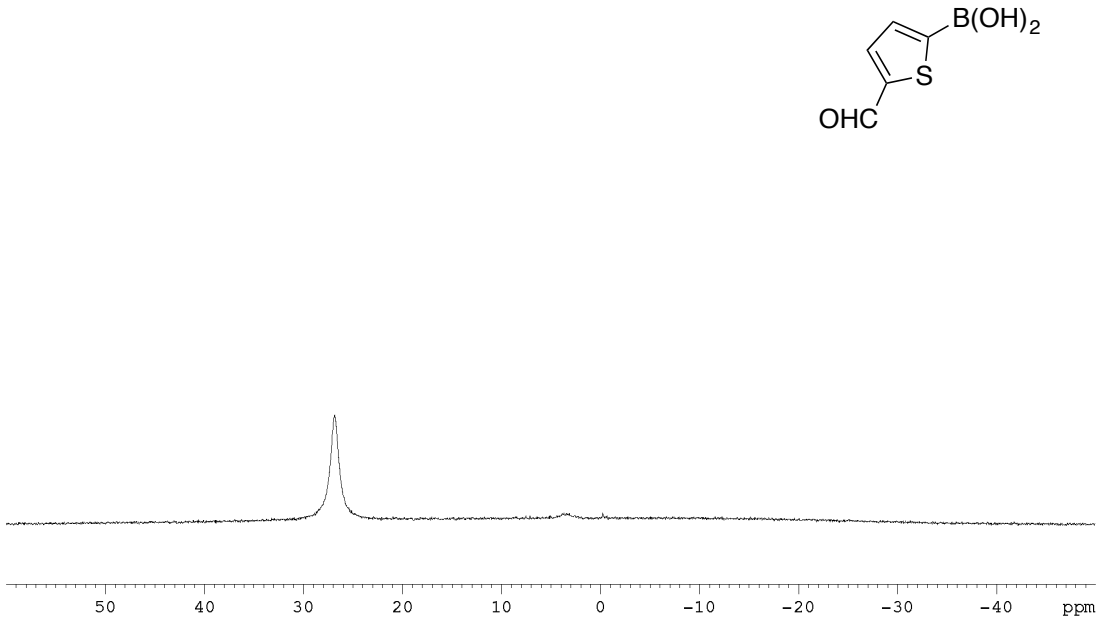


Figure A2.55 ^{11}B NMR (128.4 MHz, Acetone-d_6) Spectrum of 5-Formylthiophen-2-ylboronic Acid

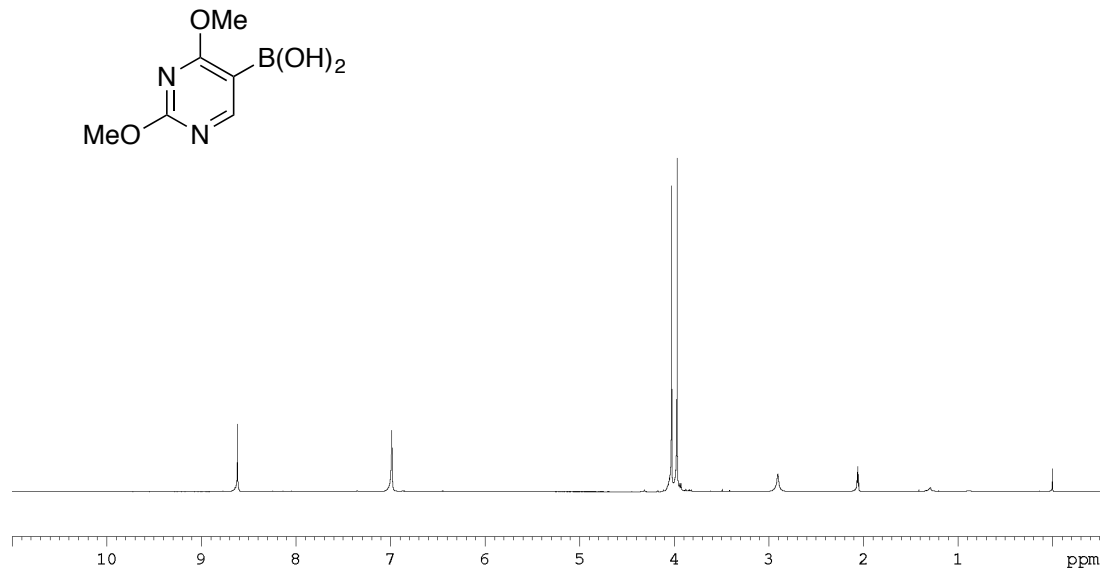


Figure A2.56 ^{1}H NMR (500 MHz, Acetone-d_6) Spectrum of 2,4-Dimethoxypyrimidin-5-ylboronic Acid

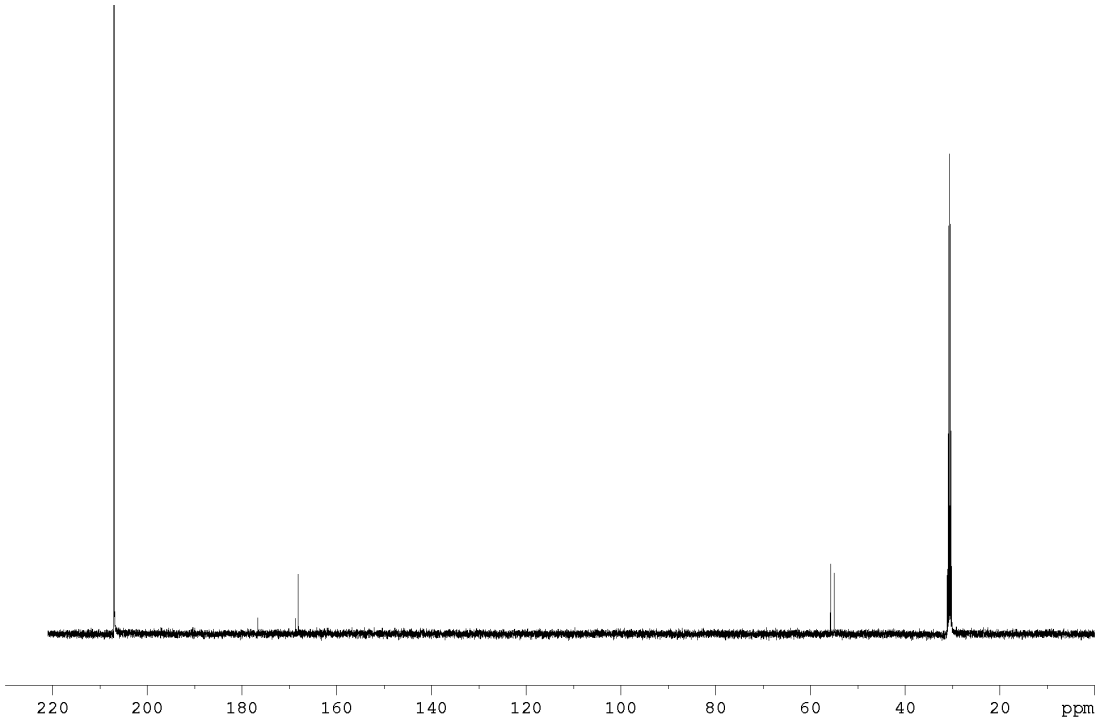


Figure A2.57 ^{13}C NMR (128.5 MHz, Acetone-d_6) Spectrum of 2,4-Dimethoxypyrimidin-5-ylboronic Acid

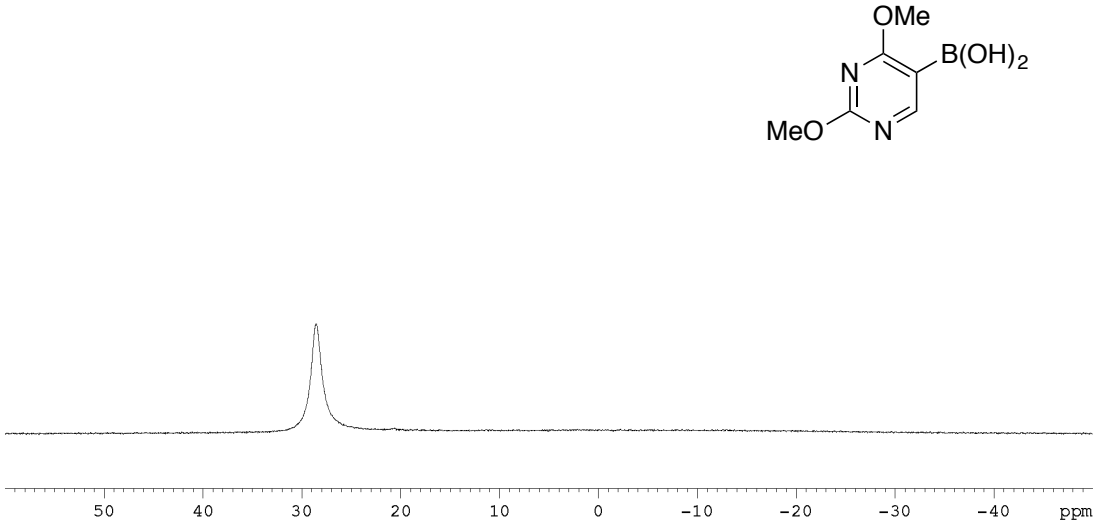


Figure A2.58 ^{11}B NMR (128.4 MHz, Acetone-d_6) Spectrum of 2,4-Dimethoxypyrimidin-5-ylboronic Acid

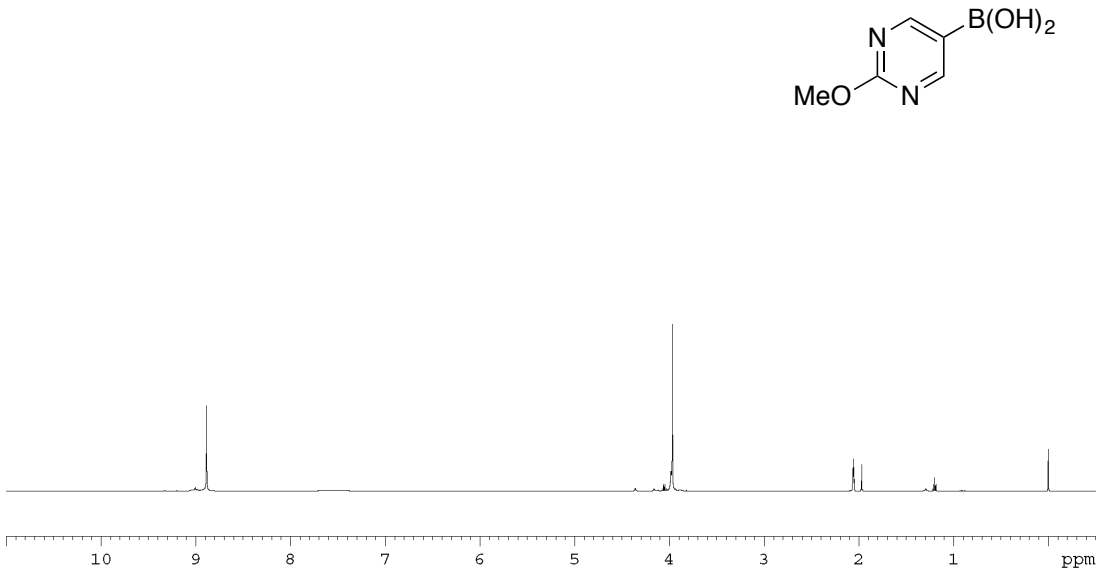


Figure A2.59 ^{1}H NMR (500 MHz, Acetone-d_6) Spectrum of 2-Methoxypyrimidin-5-ylboronic Acid

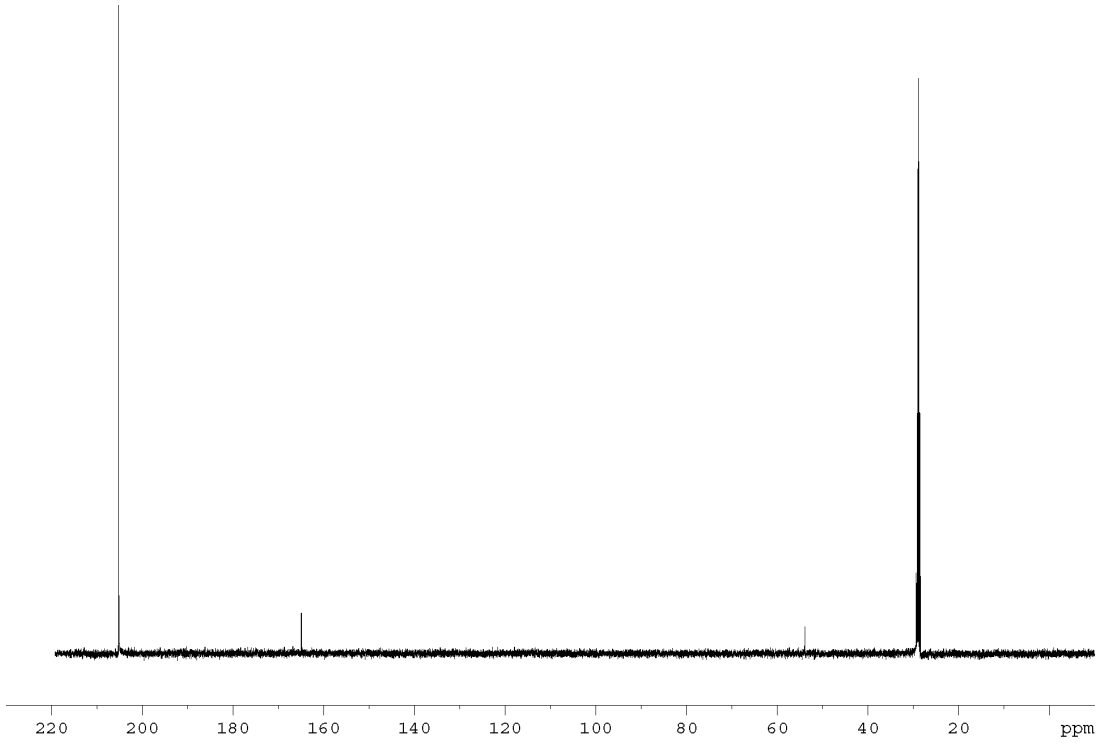


Figure A2.60 ^{13}C NMR (128.5 MHz, Acetone-d_6) Spectrum of 2-Methoxypyrimidin-5-ylboronic Acid

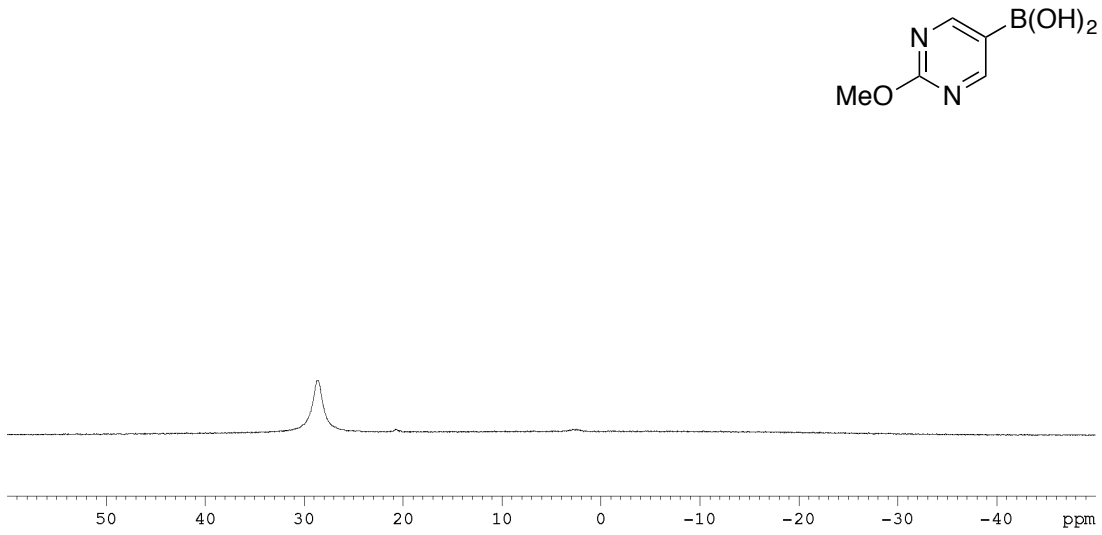


Figure A2.61 ^{11}B NMR (128.4 MHz, Acetone-d_6) Spectrum of 2-Methoxypyrimidin-5-ylboronic Acid

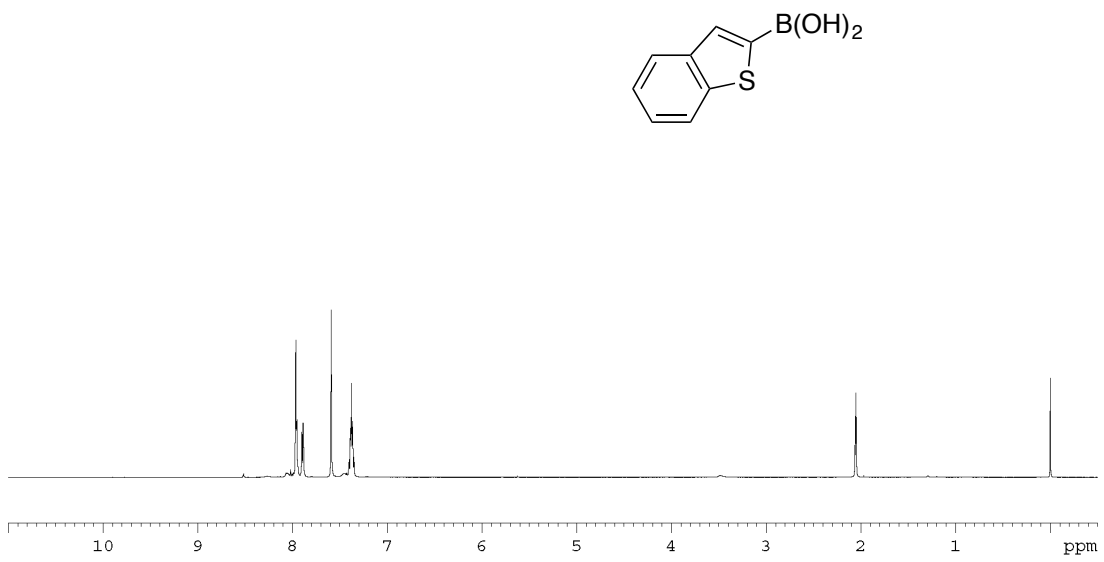


Figure A2.62 ^{1}H NMR (500 MHz, Acetone-d_6) Spectrum of Benzothiophen-2-ylboronic Acid

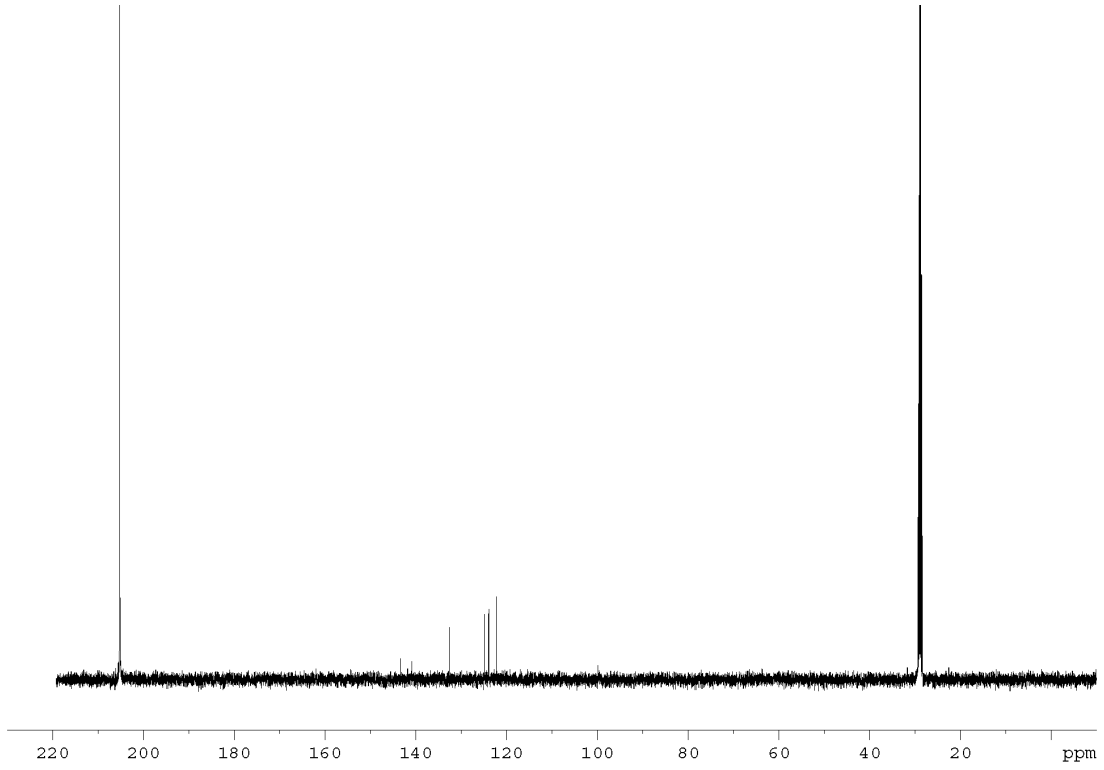


Figure A2.63 ^{13}C NMR (128.5 MHz, Acetone-d_6) Spectrum of Benzothiophen-2-ylboronic Acid

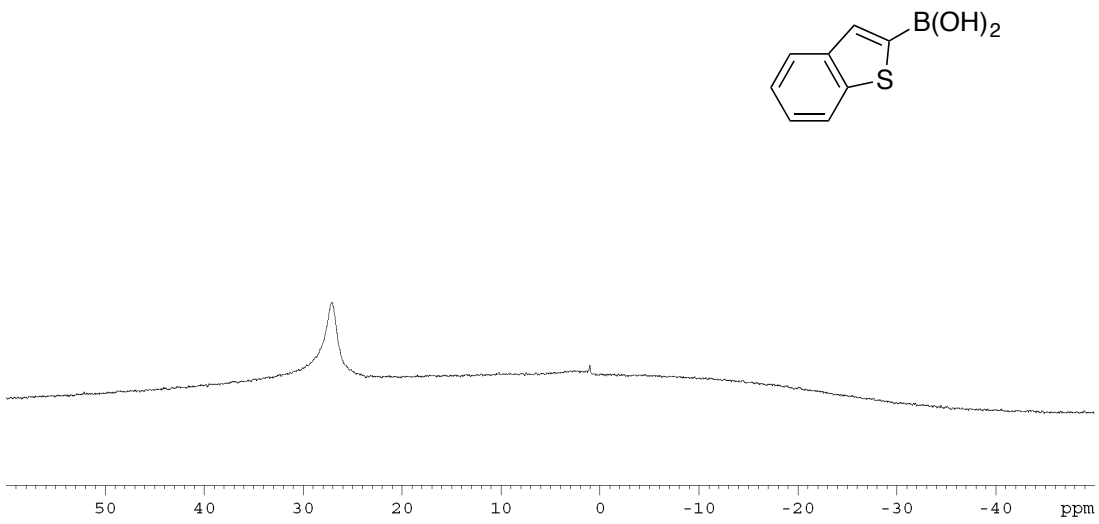


Figure A2.64 ^{11}B NMR (128.4 MHz, Acetone-d_6) Spectrum of Benzothiophen-2-ylboronic Acid

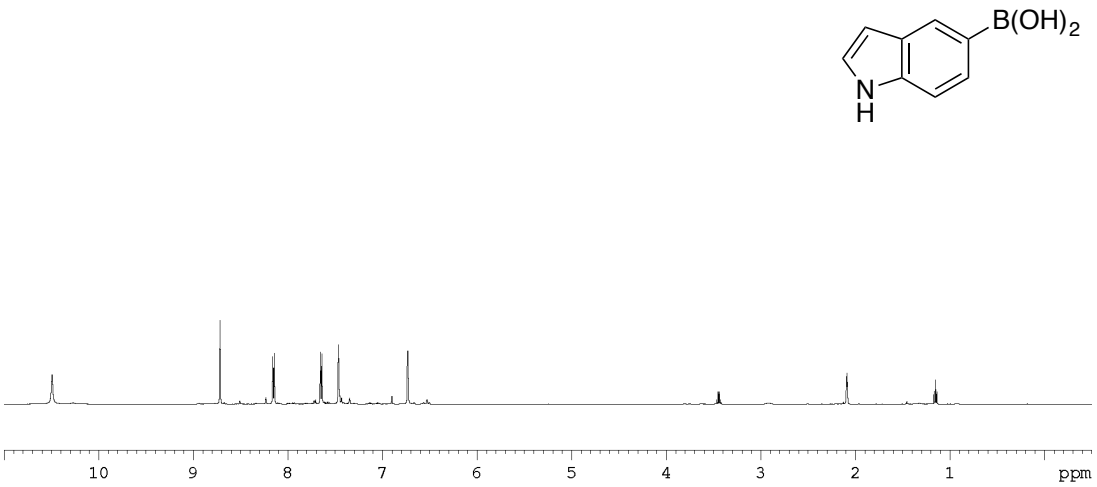


Figure A2.65 ^{1}H NMR (500 MHz, Acetone-d_6) Spectrum of 1*H*-Indol-5-ylboronic Acid

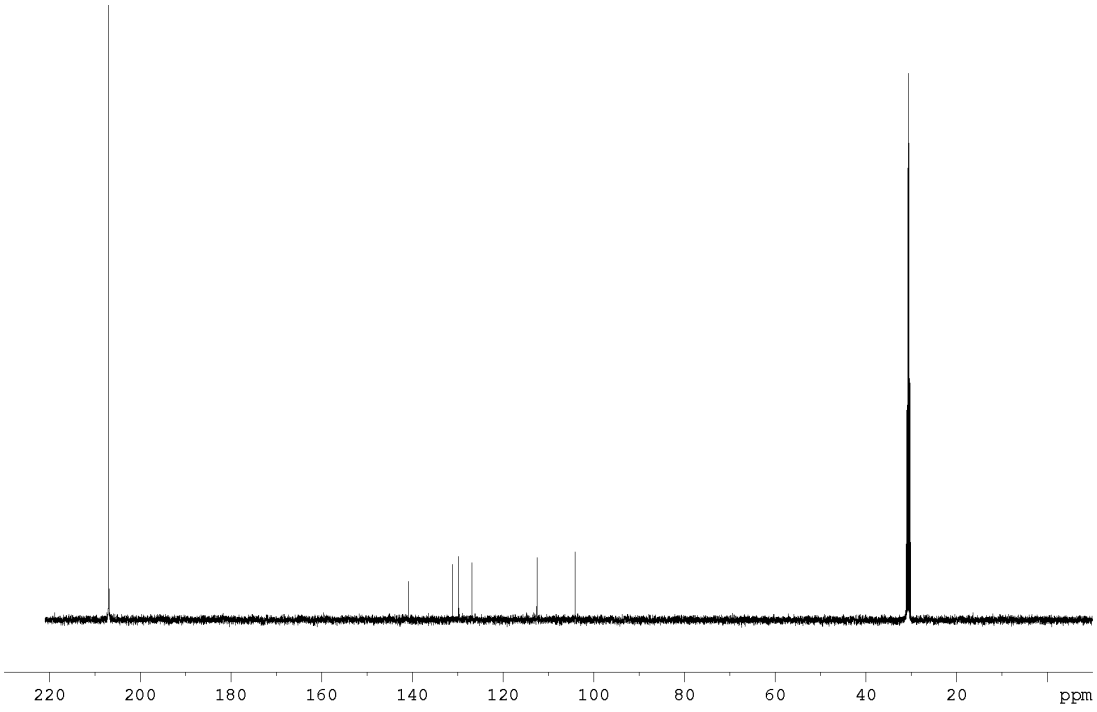


Figure A2.66 ^{13}C NMR (128.5 MHz, Acetone-d_6) Spectrum of 1*H*-Indol-5-ylboronic Acid

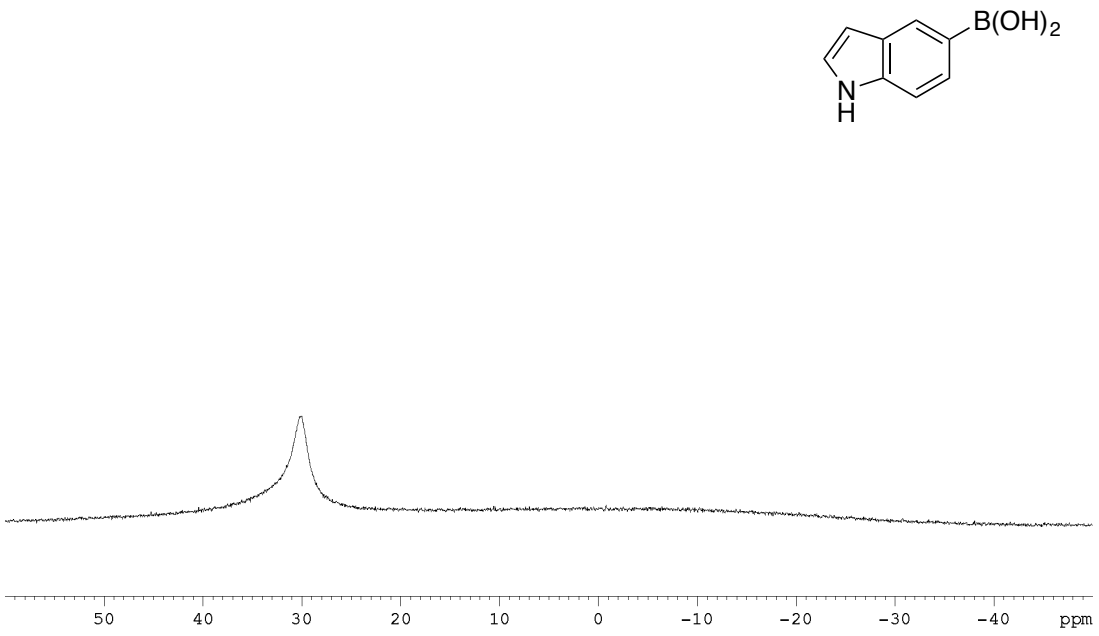


Figure A2.67 ^{11}B NMR (128.4 MHz, Acetone-d_6) Spectrum of 1*H*-Indol-5-ylboronic Acid

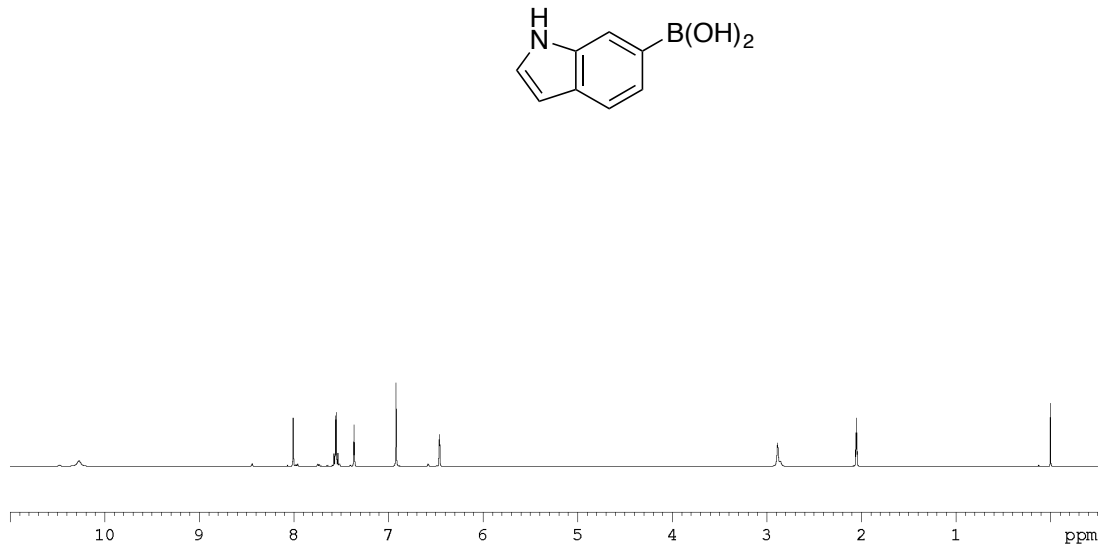


Figure A2.68 ^{1}H NMR (500 MHz, Acetone-d_6) Spectrum of 1*H*-Indol-6-ylboronic Acid

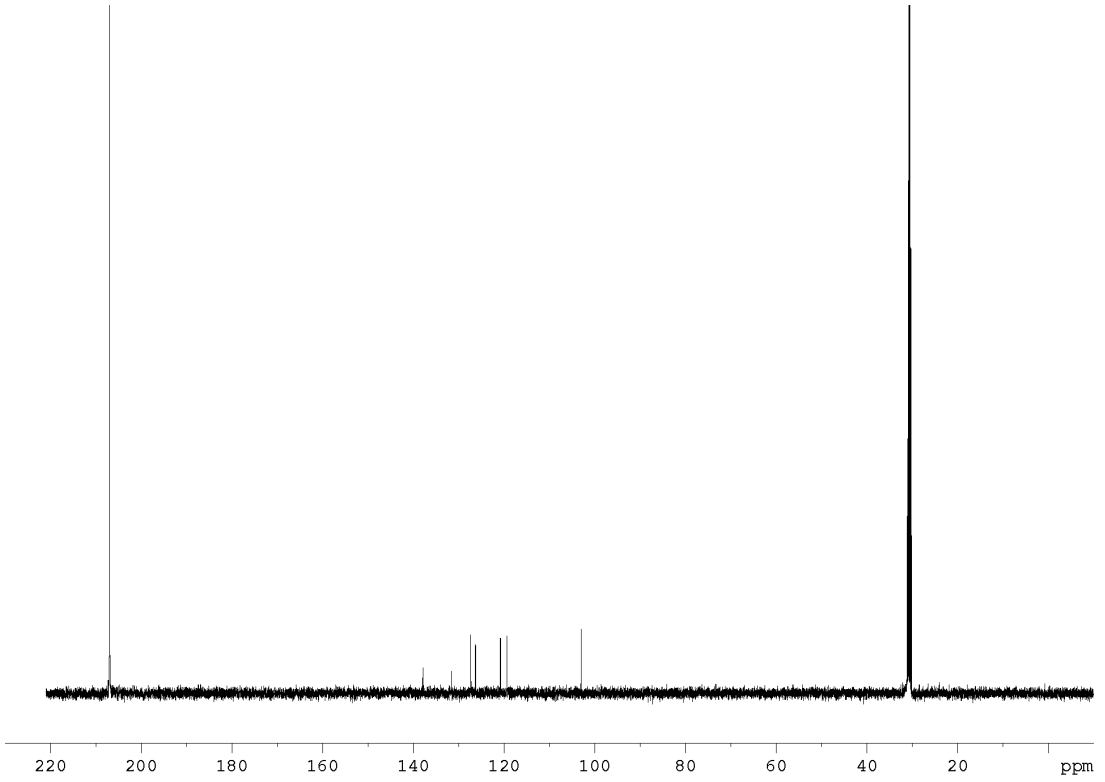


Figure A2.69 ^{13}C NMR (128.5 MHz, Acetone-d_6) Spectrum of 1*H*-Indol-6-ylboronic Acid

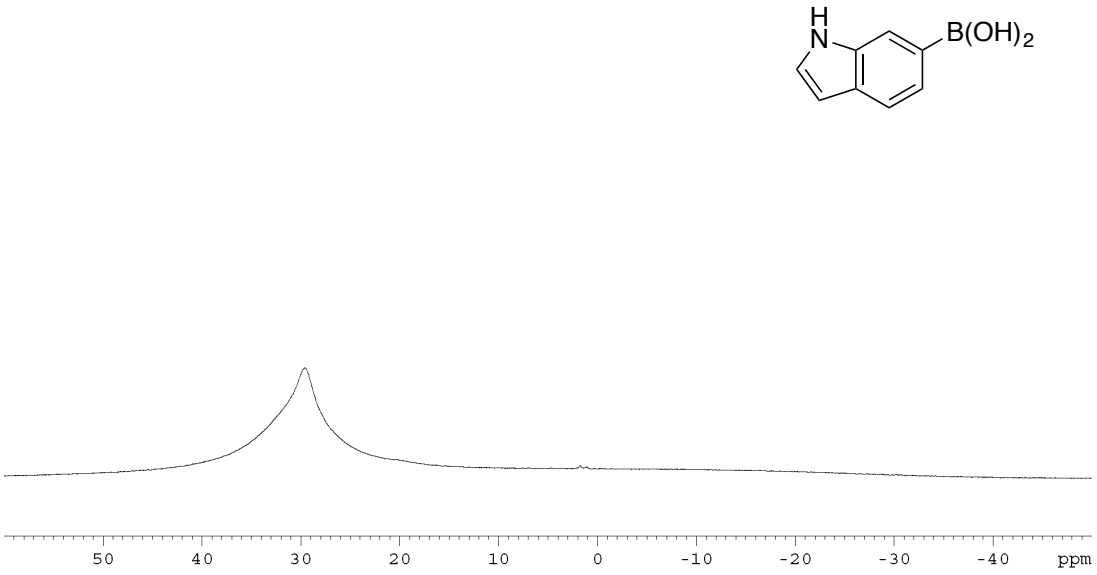


Figure A2.70 ^{11}B NMR (128.4 MHz, Acetone-d_6) Spectrum of 1*H*-Indol-6-ylboronic Acid

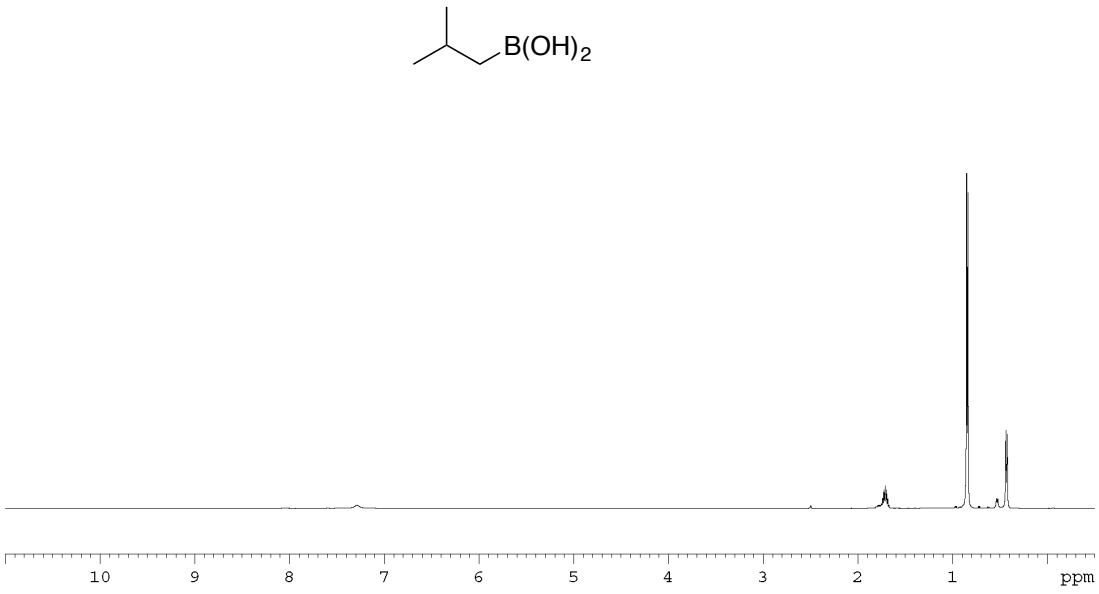


Figure A2.71 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of Isobutylboronic Acid

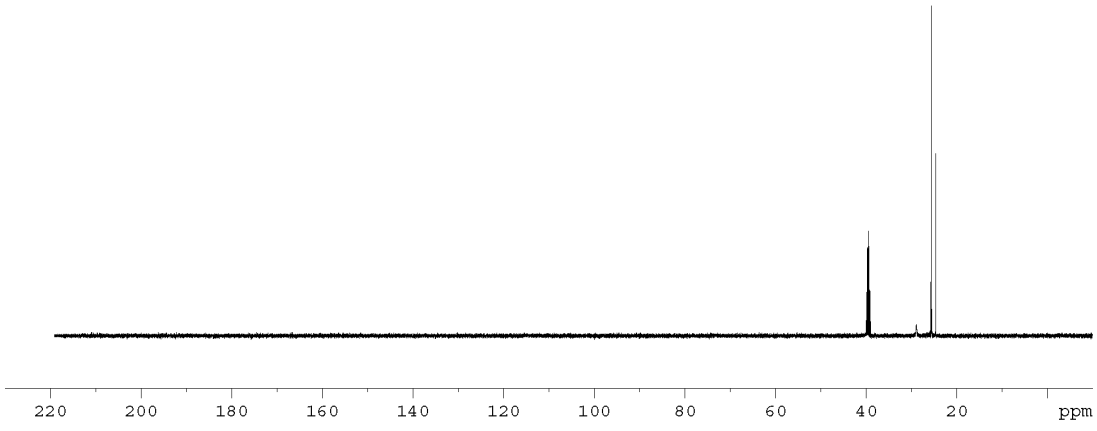


Figure A2.72 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of Isobutylboronic Acid

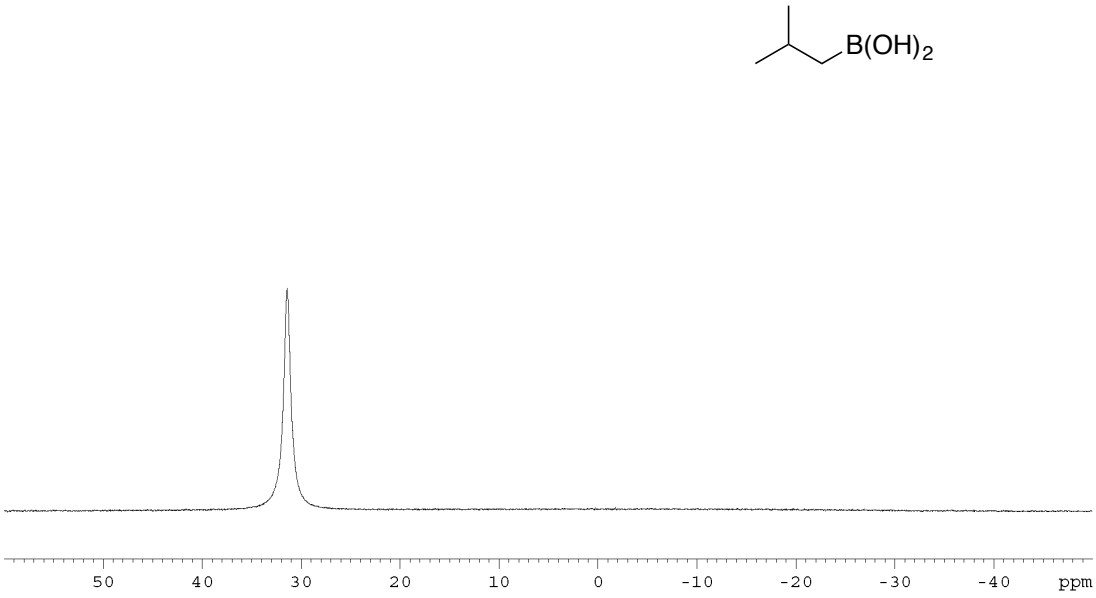


Figure A2.73 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of Isobutylboronic Acid

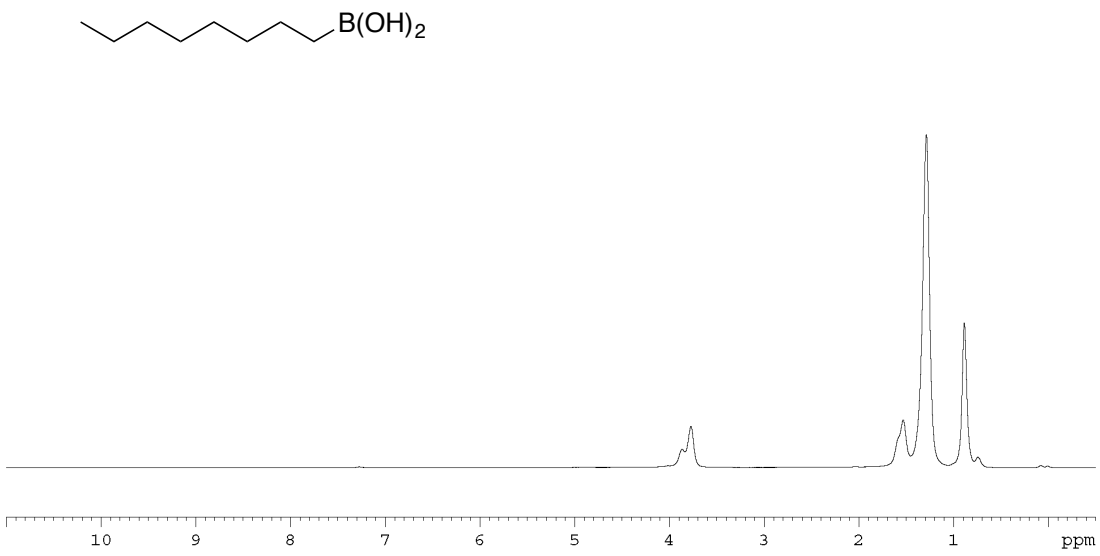


Figure A2.74 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Octylboronic Acid

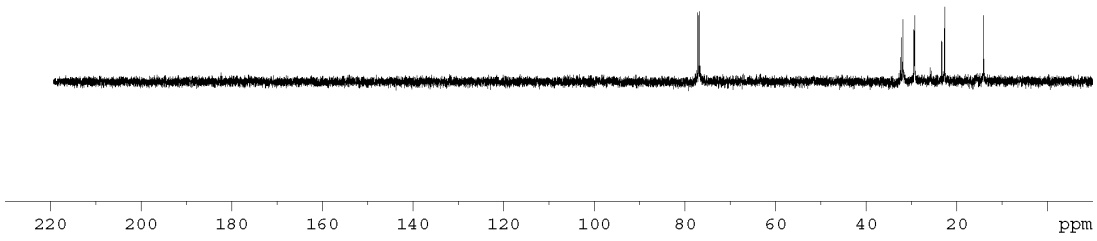


Figure A2.75 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Octylboronic Acid

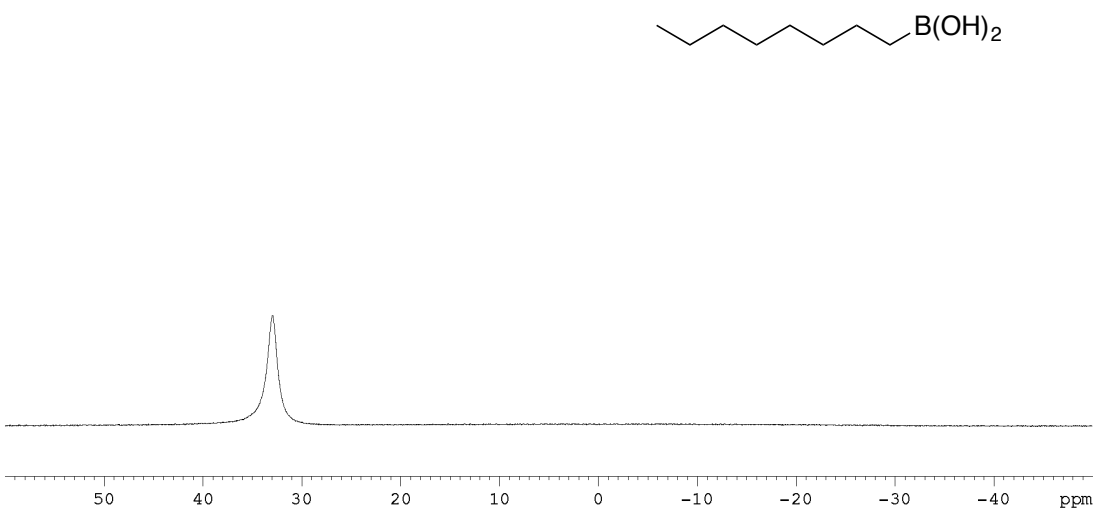


Figure A2.76 ^{11}B NMR (128.4 MHz, $CDCl_3$) Spectrum of Octylboronic Acid

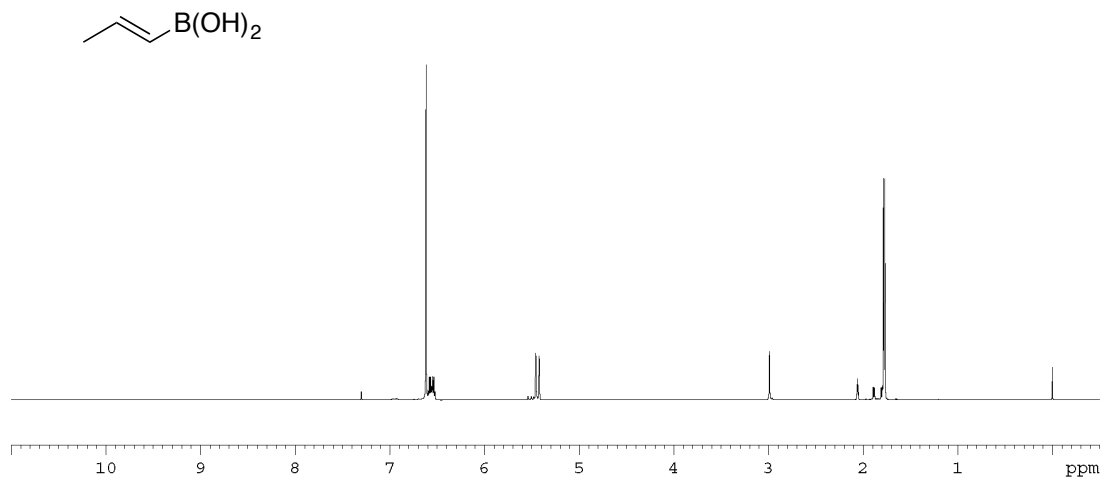


Figure A2.77 ^{1}H NMR (500 MHz, Acetone-d_6) Spectrum of (*E*)-Propenylboronic Acid

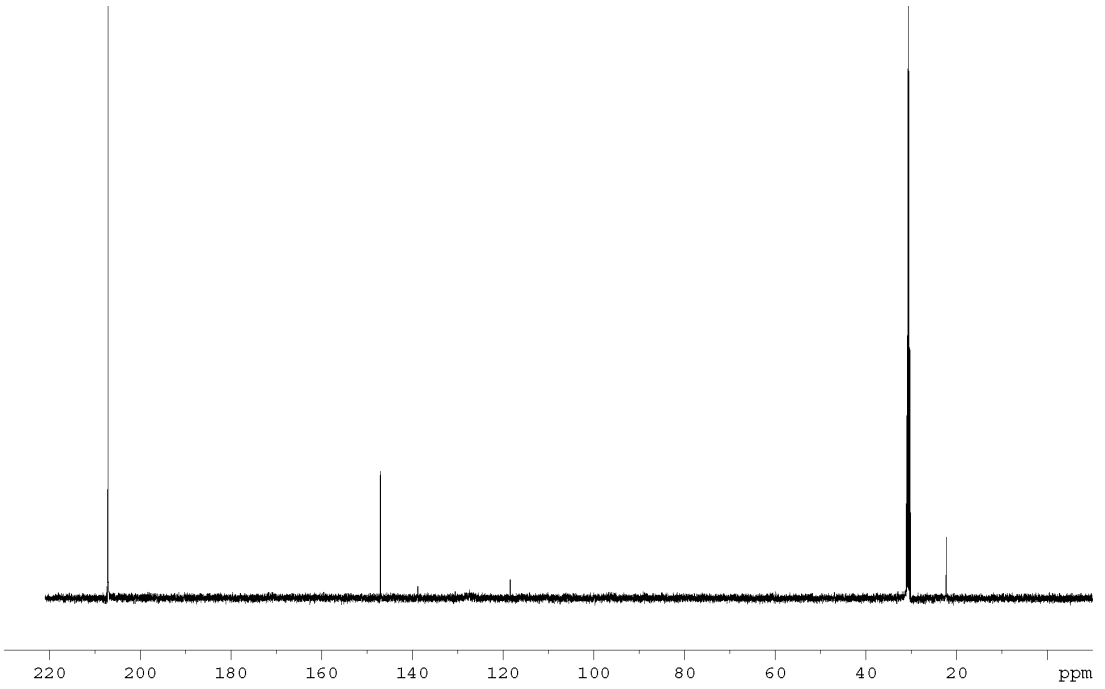


Figure A2.78 ^{13}C NMR (128.5 MHz, Acetone-d_6) Spectrum of (*E*)-Propenylboronic Acid

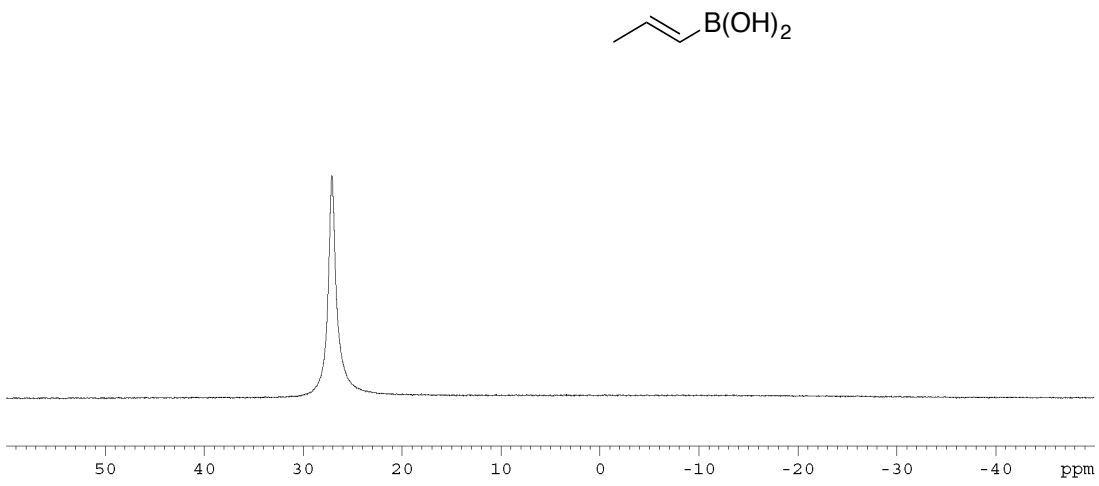


Figure A2.79 ^{11}B NMR (128.4 MHz, Acetone-d_6) Spectrum of (*E*)-Propenylboronic Acid

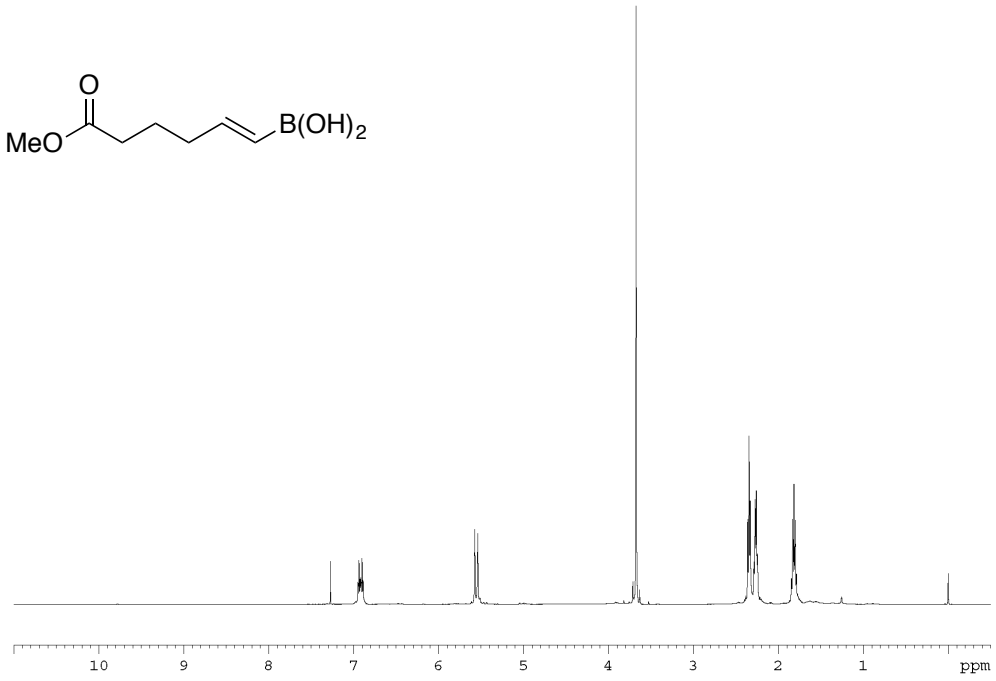


Figure A2.80 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of (*E*)-6-Methoxy-6-oxohex-1-enylboronic Acid

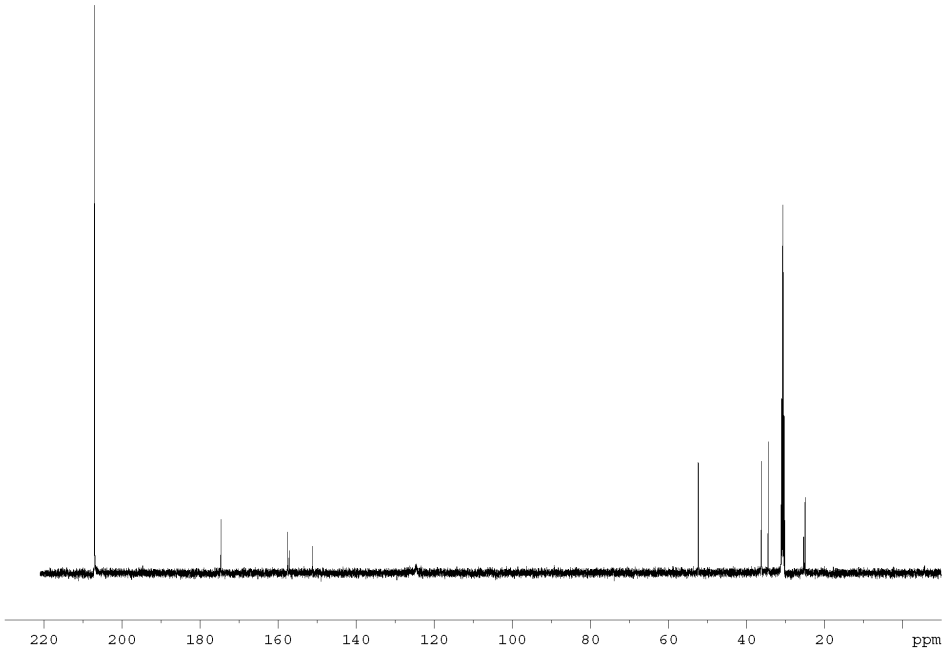


Figure A2.81 ^{13}C NMR (128.5 MHz, Acetone-d_6) Spectrum of (*E*)-6-Methoxy-6-oxohex-1-enylboronic Acid

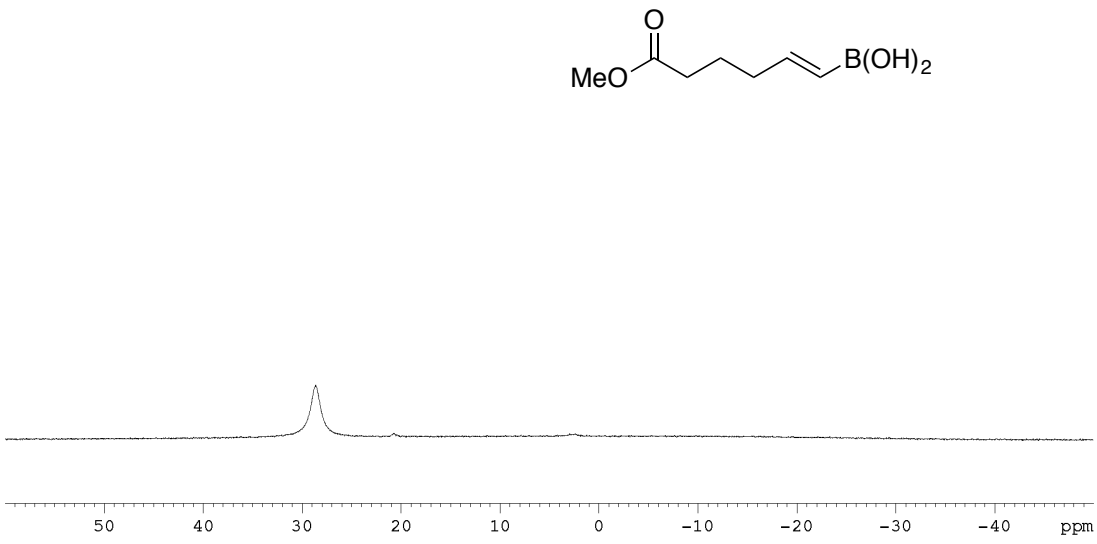


Figure A2.82 ^{11}B NMR (128.4 MHz, Acetone-d_6) Spectrum of (*E*)-6-Methoxy-6-oxohex-1-enylboronic Acid

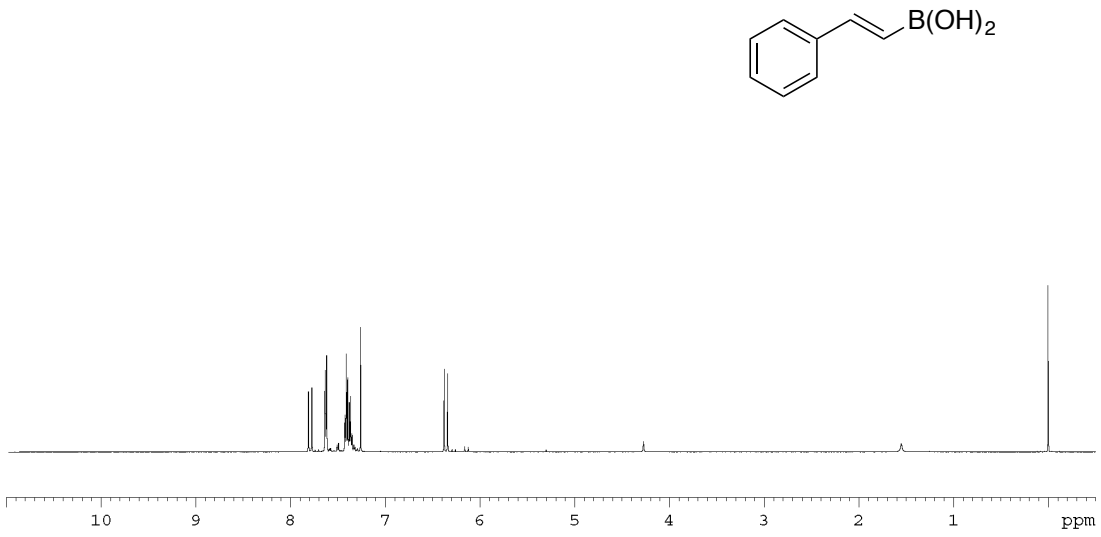


Figure A2.83 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of (*E*)-Styrylboronic Acid

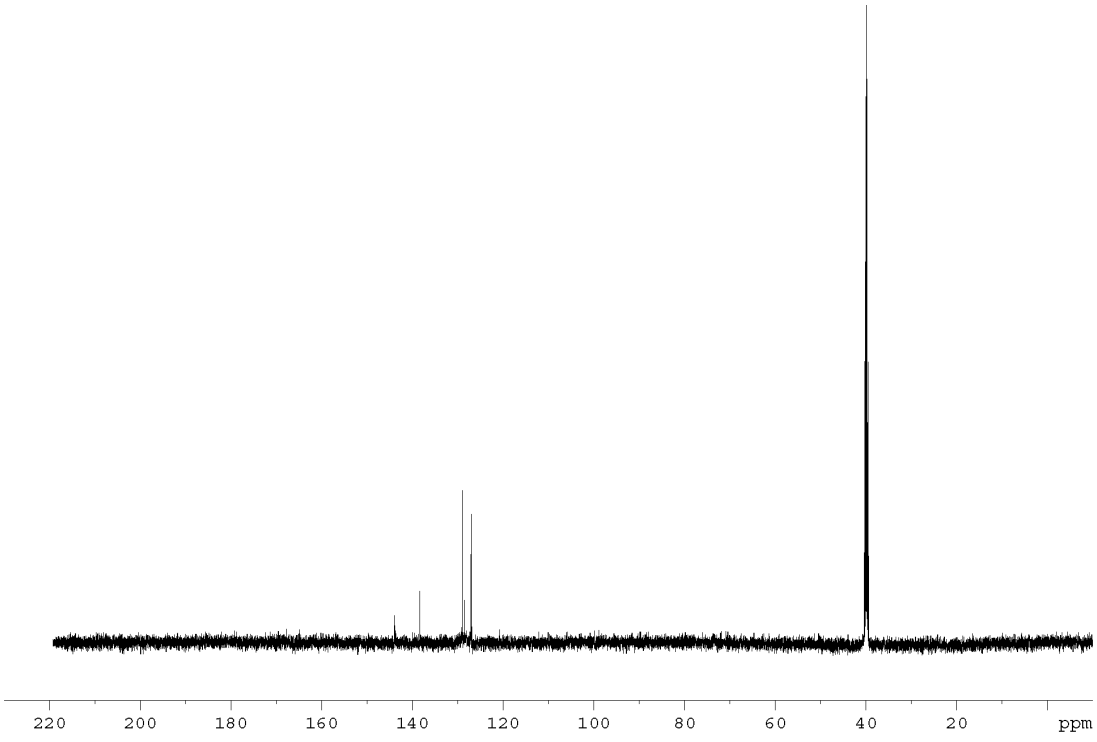


Figure A2.84 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of (*E*)-Styrylboronic Acid

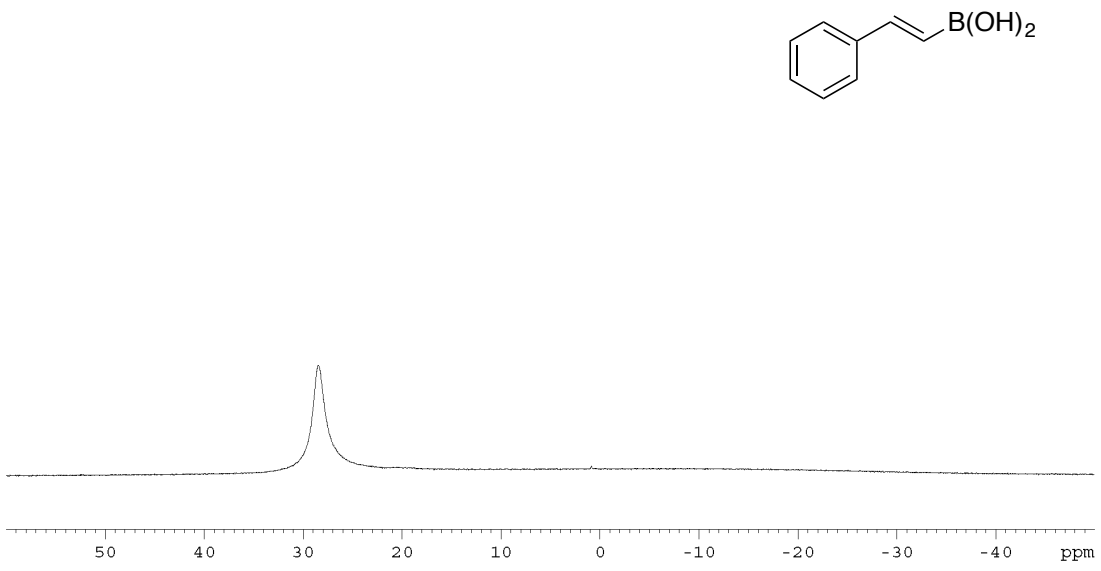


Figure A2.85 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of (*E*)-Styrylboronic Acid

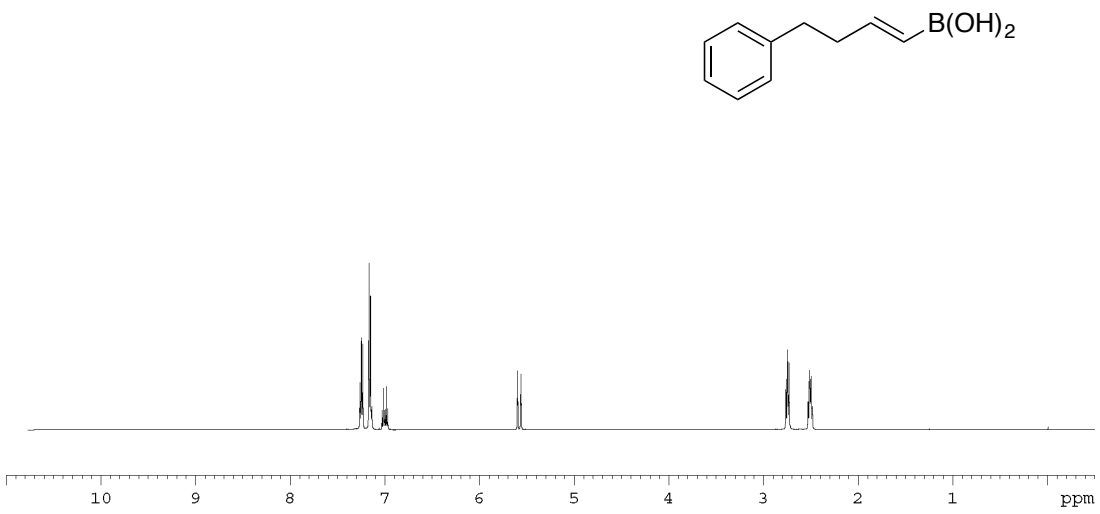


Figure A2.86 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of (*E*)-4-Phenylbut-1-enylboronic Acid

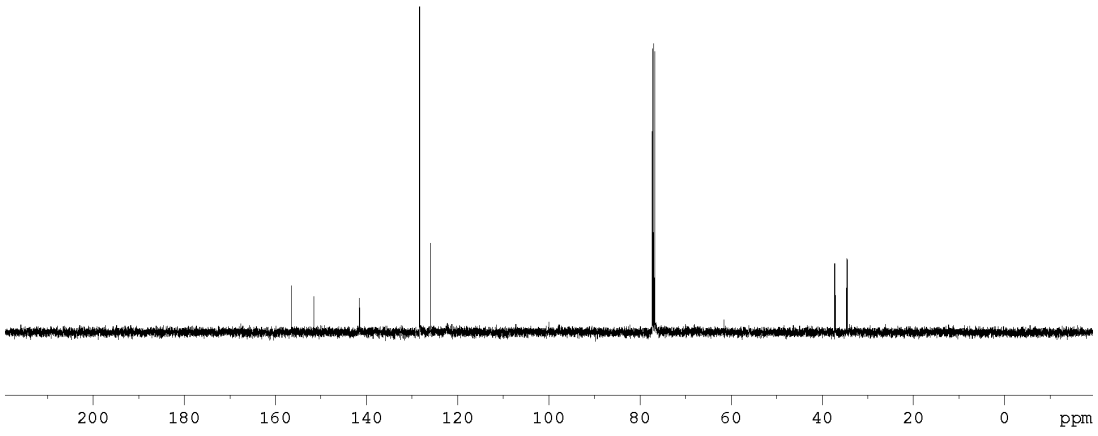


Figure A2.87 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of (*E*)-4-Phenylbut-1-enylboronic Acid

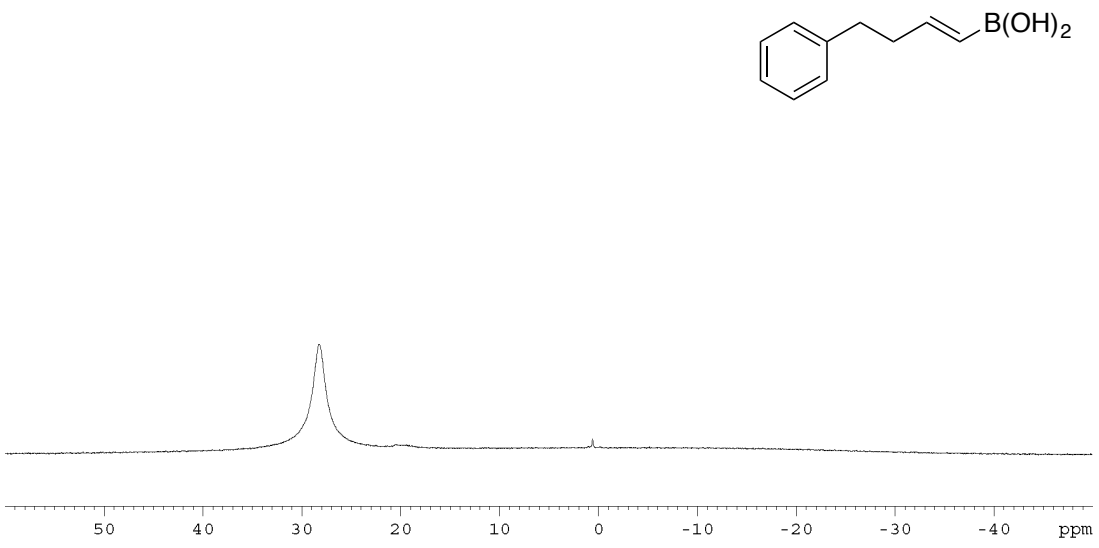


Figure A2.88 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of (*E*)-4-Phenylbut-1-enylboronic Acid

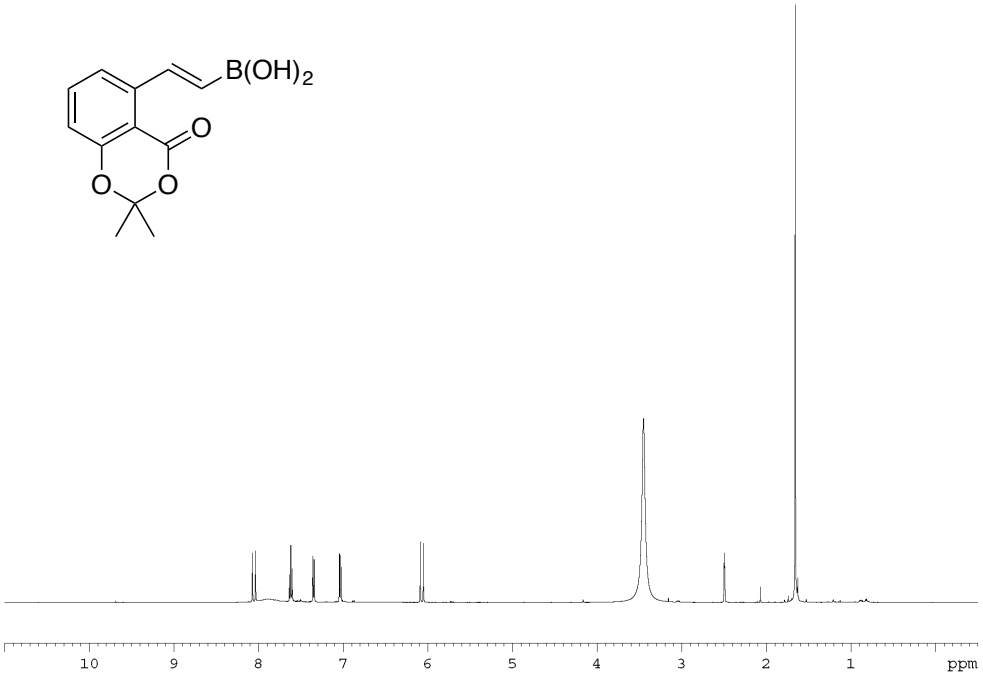


Figure A2.89 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of (*E*)-2-(2,2-Dimethyl-4-oxo-4H-benzo[d][1,3]dioxin-5-yl)vinylboronic Acid

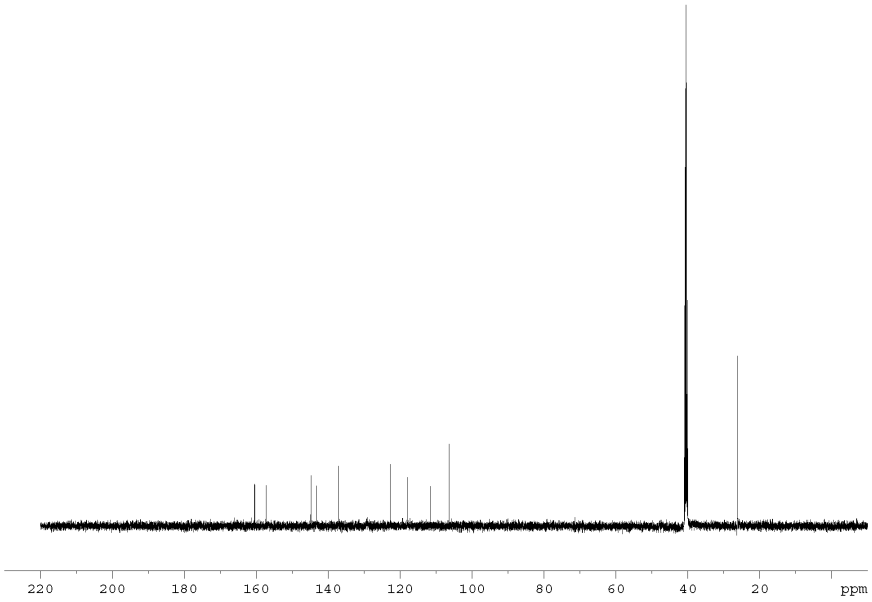


Figure A2.90 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of (*E*)-2-(2,2-Dimethyl-4-oxo-4H-benzo[d][1,3]dioxin-5-yl)vinylboronic Acid

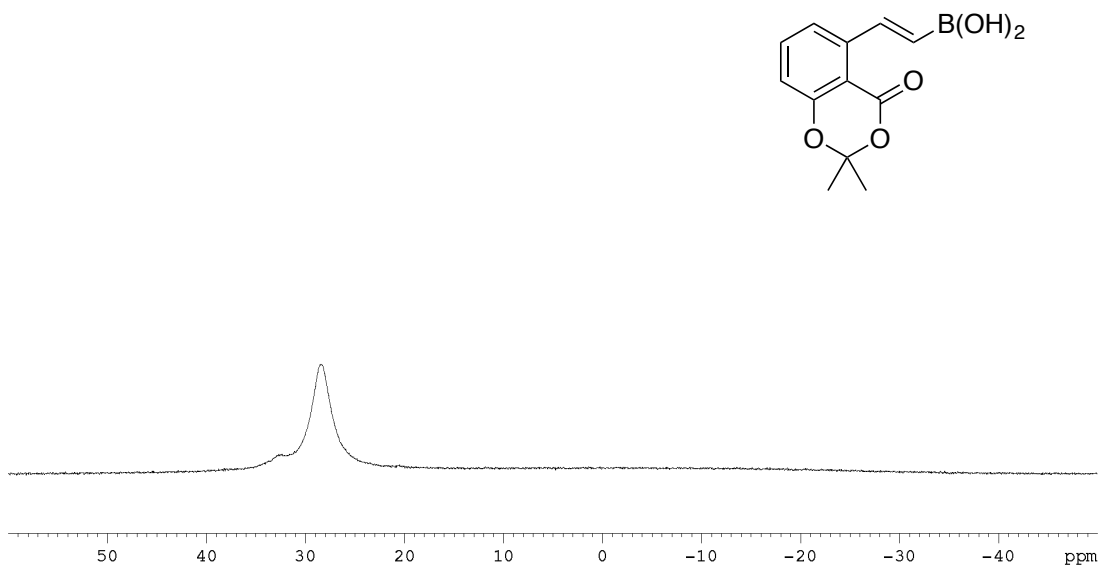


Figure A2.91 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of (*E*)-2-(2,2-Dimethyl-4-oxo-4H-benzo[d][1,3]dioxin-5-yl)vinylboronic Acid

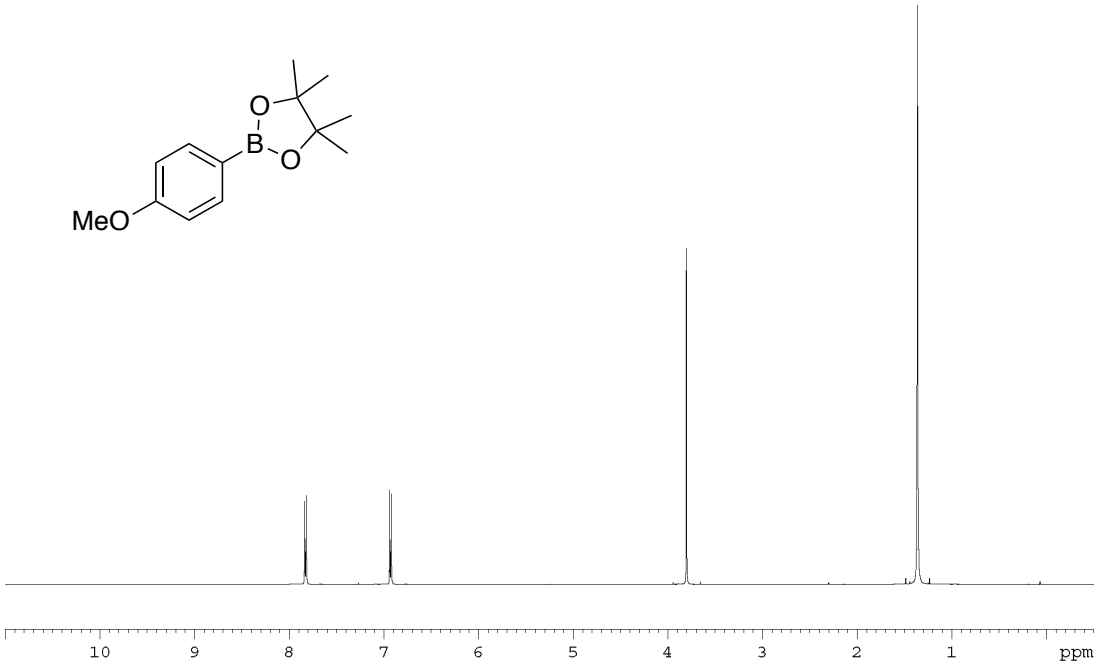


Figure A2.92 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

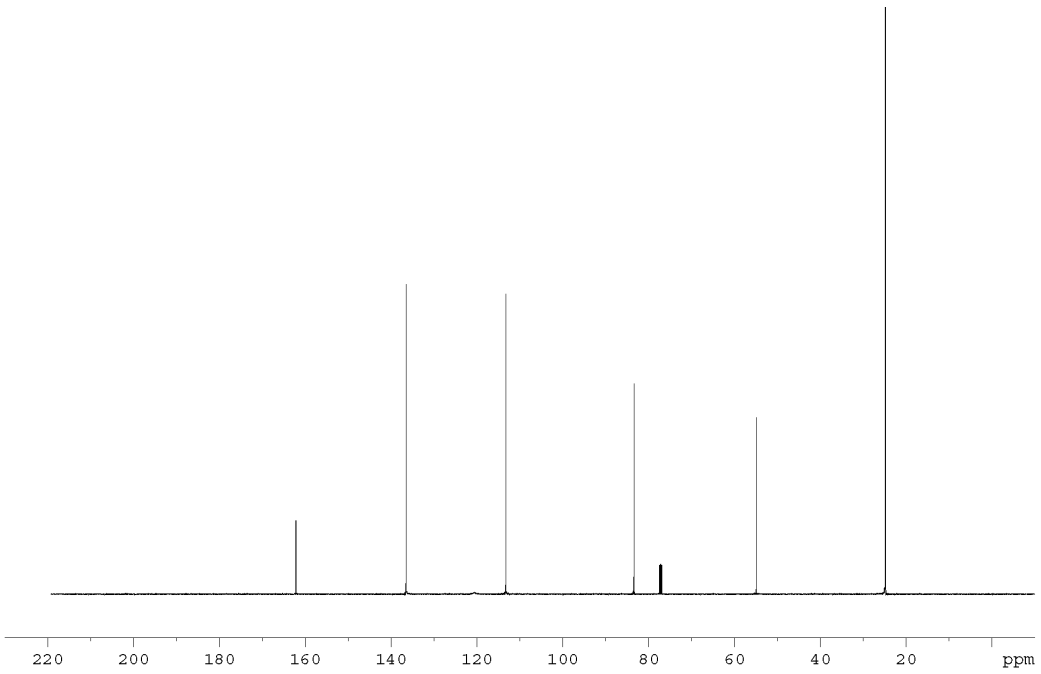


Figure A2.93 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

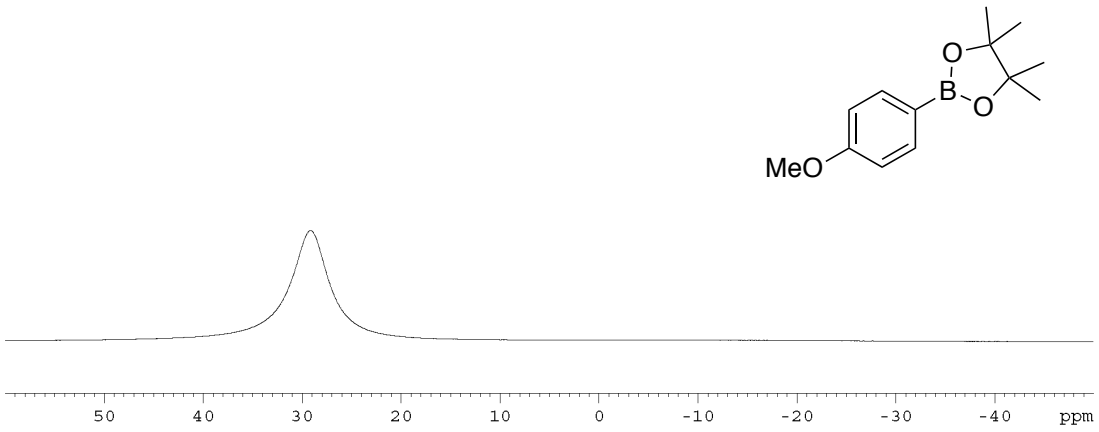


Figure A2.94 ^{11}B NMR (128.4 MHz, $CDCl_3$) Spectrum of 2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

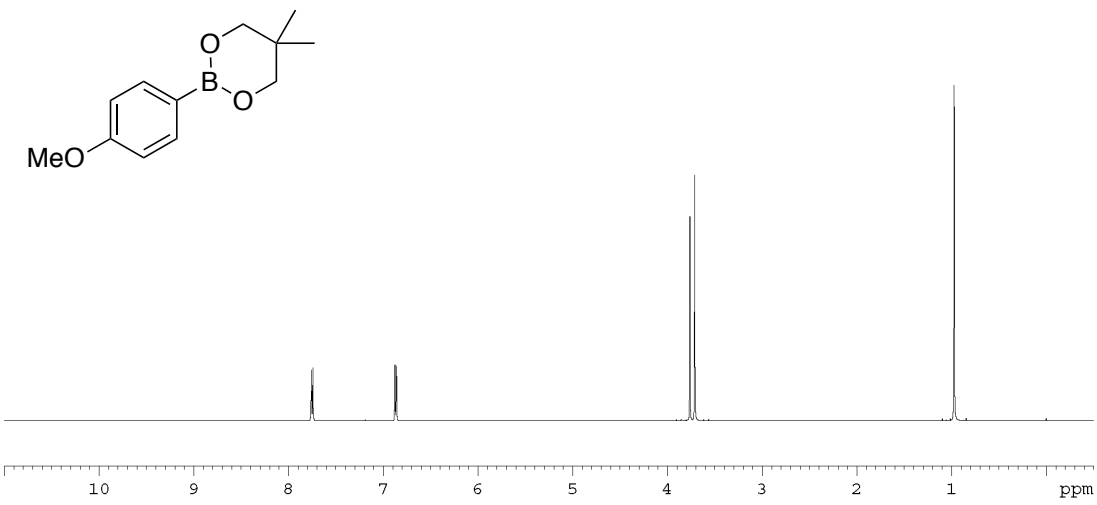


Figure A2.95 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane

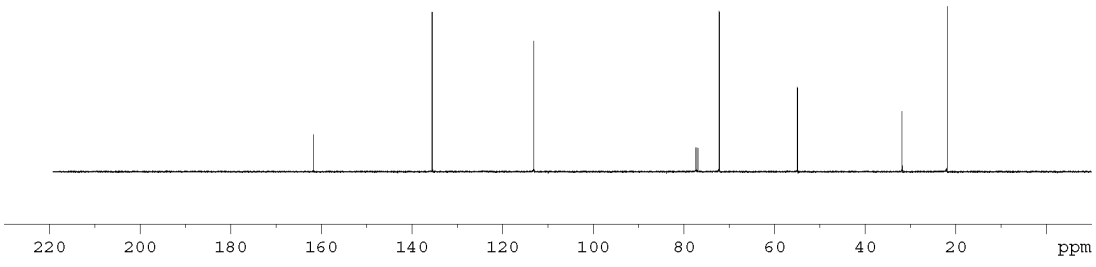


Figure A2.96 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane

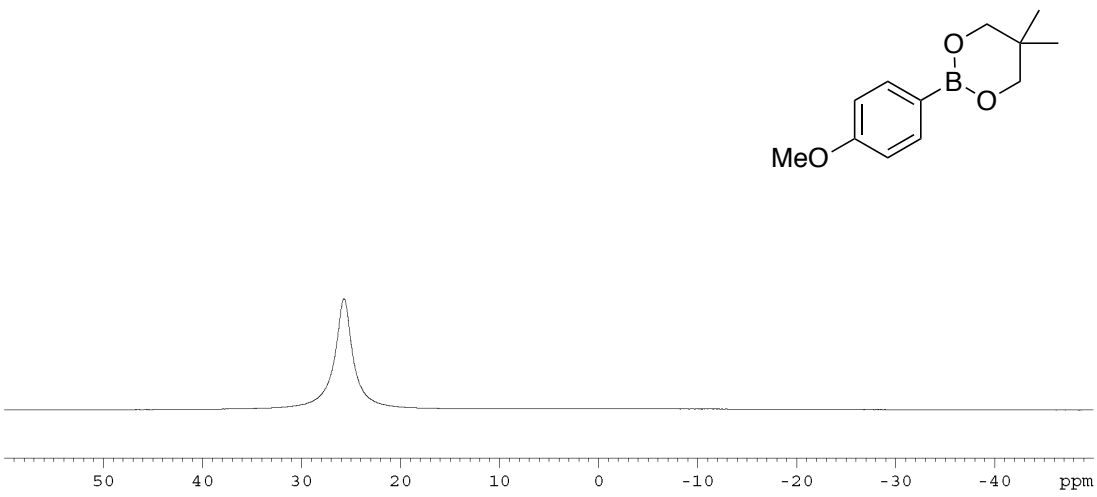


Figure A2.97 ^{11}B NMR (128.4 MHz, $CDCl_3$) Spectrum of 2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane

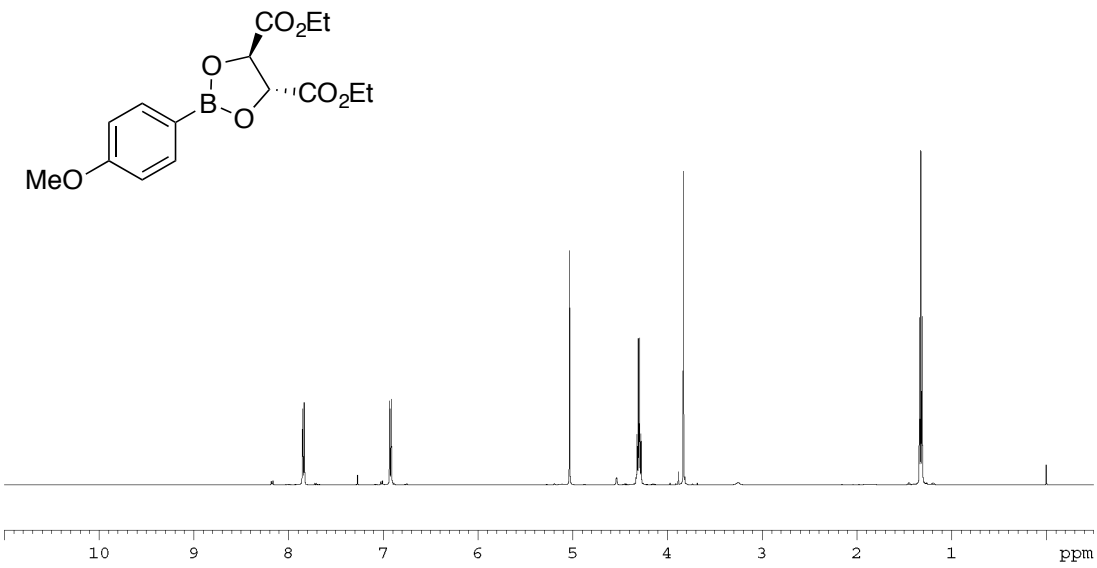


Figure A2.98 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of (4*S*,5*R*)-Diethyl 2-(4-Methoxyphenyl)-1,3,2-dioxaborolane-4,5-dicarboxylate

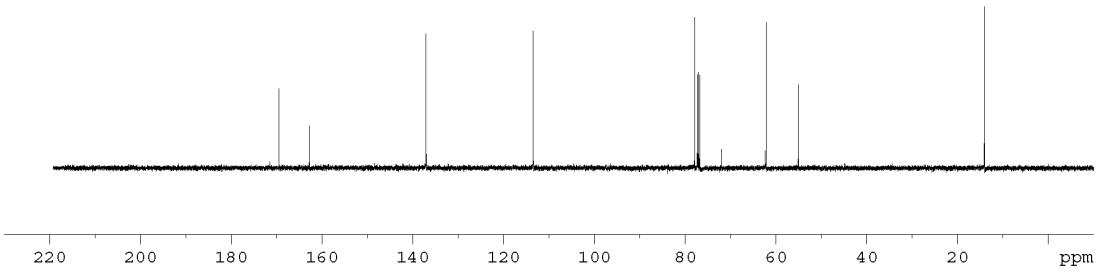


Figure A2.99 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of (4*S*,5*R*)-Diethyl 2-(4-Methoxyphenyl)-1,3,2-dioxaborolane-4,5-dicarboxylate

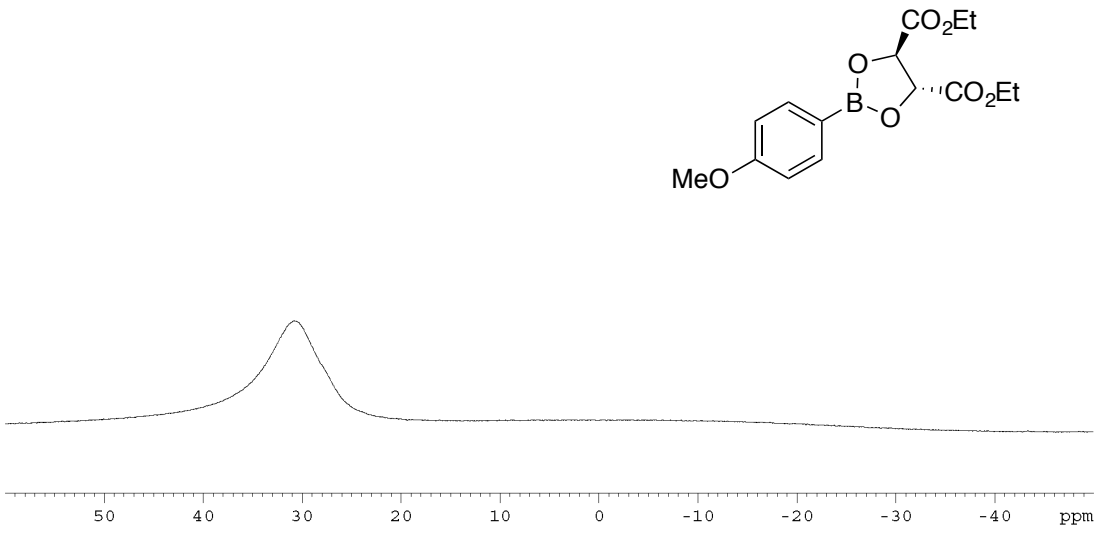


Figure A2.100 ^{11}B NMR (128.4 MHz, $CDCl_3$) Spectrum of (4*S*,5*R*)-Diethyl 2-(4-Methoxyphenyl)-1,3,2-dioxaborolane-4,5-dicarboxylate

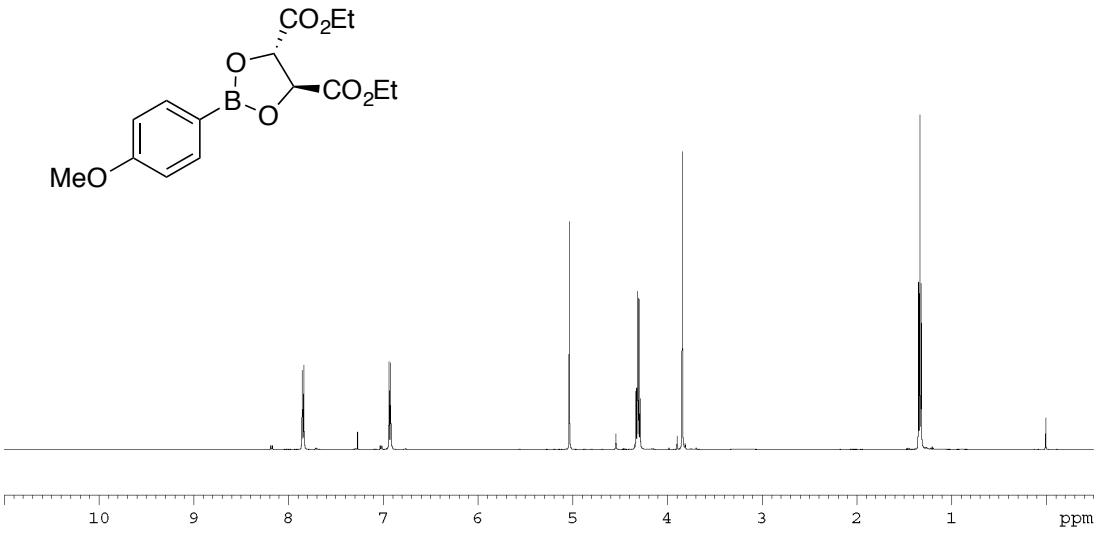


Figure A2.101 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of (4*R*,5*S*)-Diethyl 2-(4-Methoxyphenyl)-1,3,2-dioxaborolane-4,5-dicarboxylate

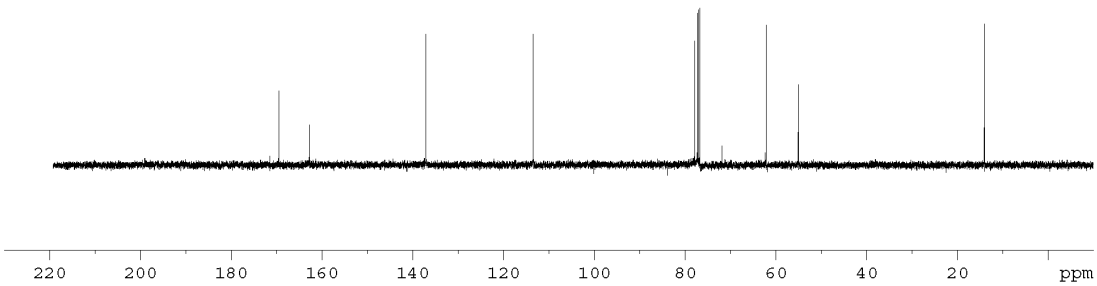


Figure A2.102 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of (4*R*,5*S*)-Diethyl 2-(4-Methoxyphenyl)-1,3,2-dioxaborolane-4,5-dicarboxylate

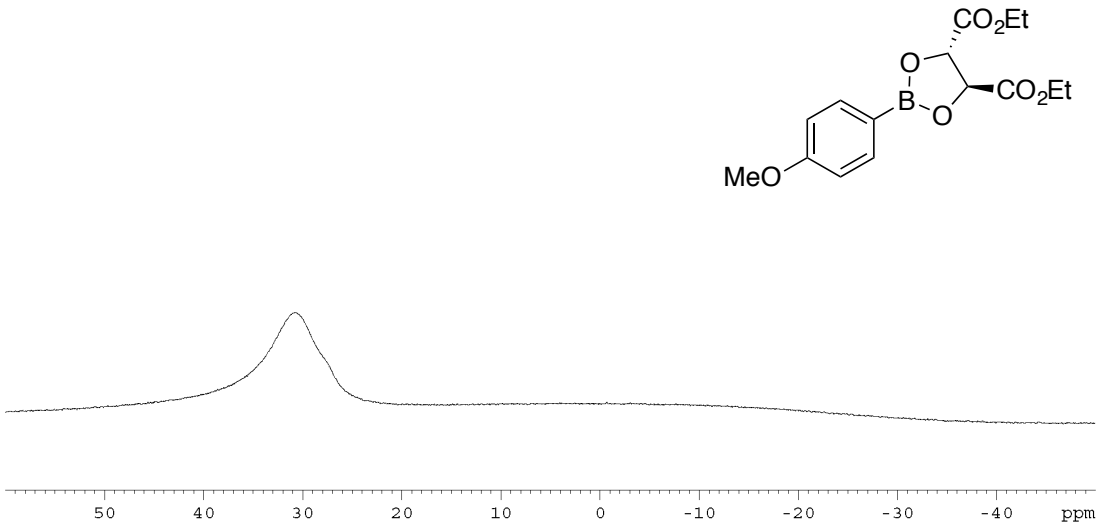


Figure A2.103 ^{11}B NMR (128.4 MHz, $CDCl_3$) Spectrum of (4*R*,5*S*)-Diethyl 2-(4-Methoxyphenyl)-1,3,2-dioxaborolane-4,5-dicarboxylate

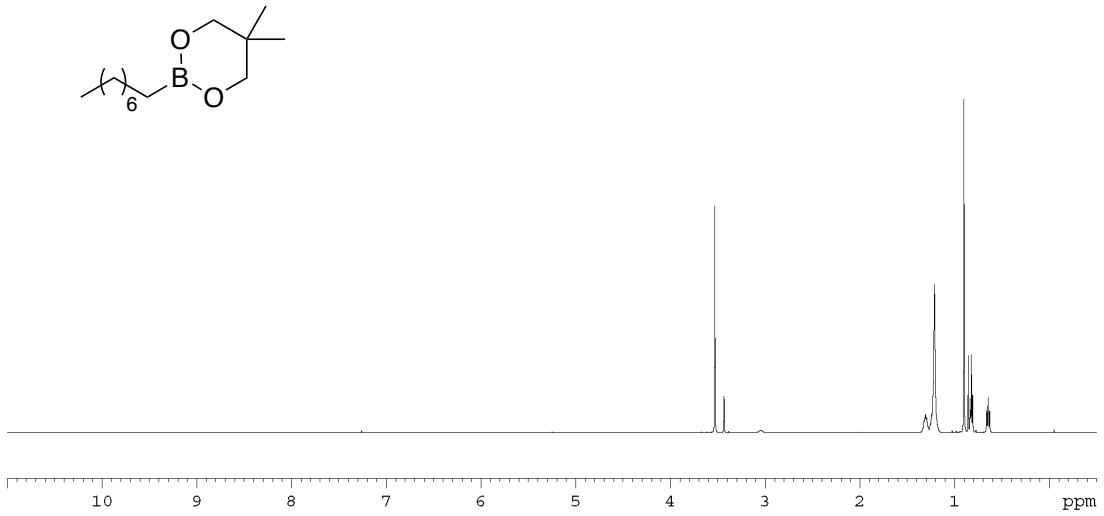


Figure A2.104 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 5,5-Dimethyl-2-octyl-1,3,2-dioxaborinane

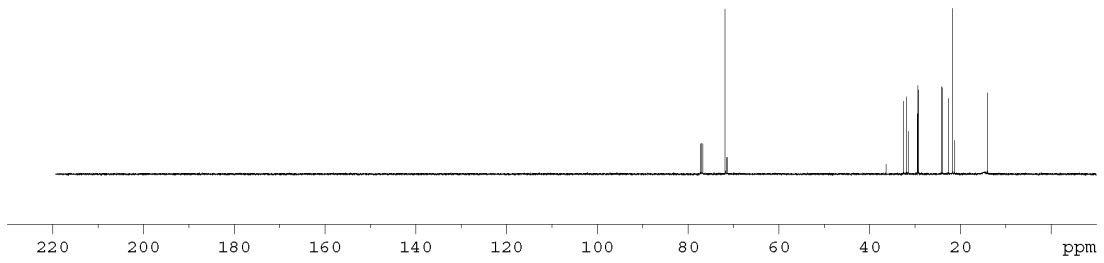


Figure A2.105 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 5,5-Dimethyl-2-octyl-1,3,2-dioxaborinane

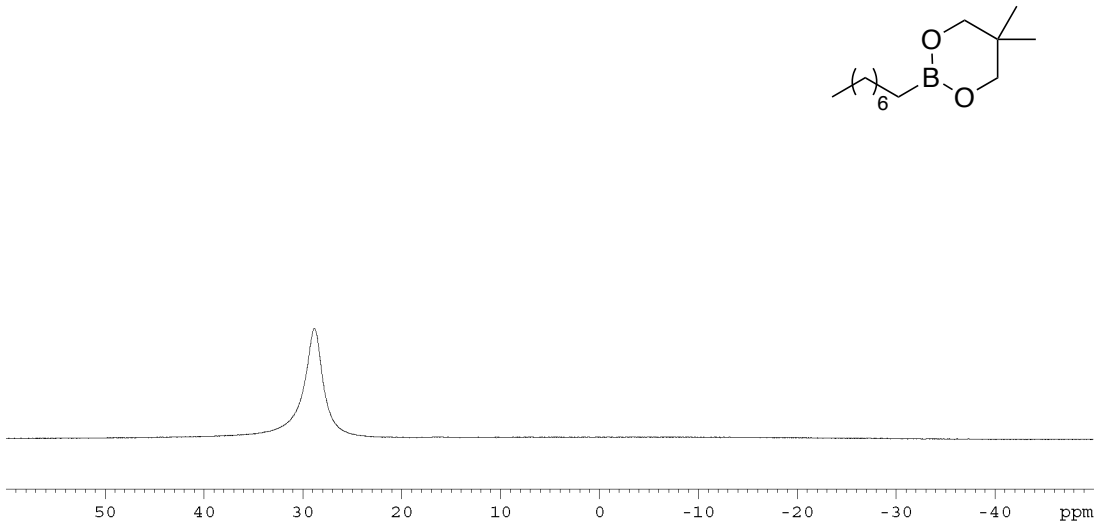


Figure A2.106 ^{11}B NMR (128.4 MHz, $CDCl_3$) Spectrum of 5,5-Dimethyl-2-octyl-1,3,2-dioxaborinane

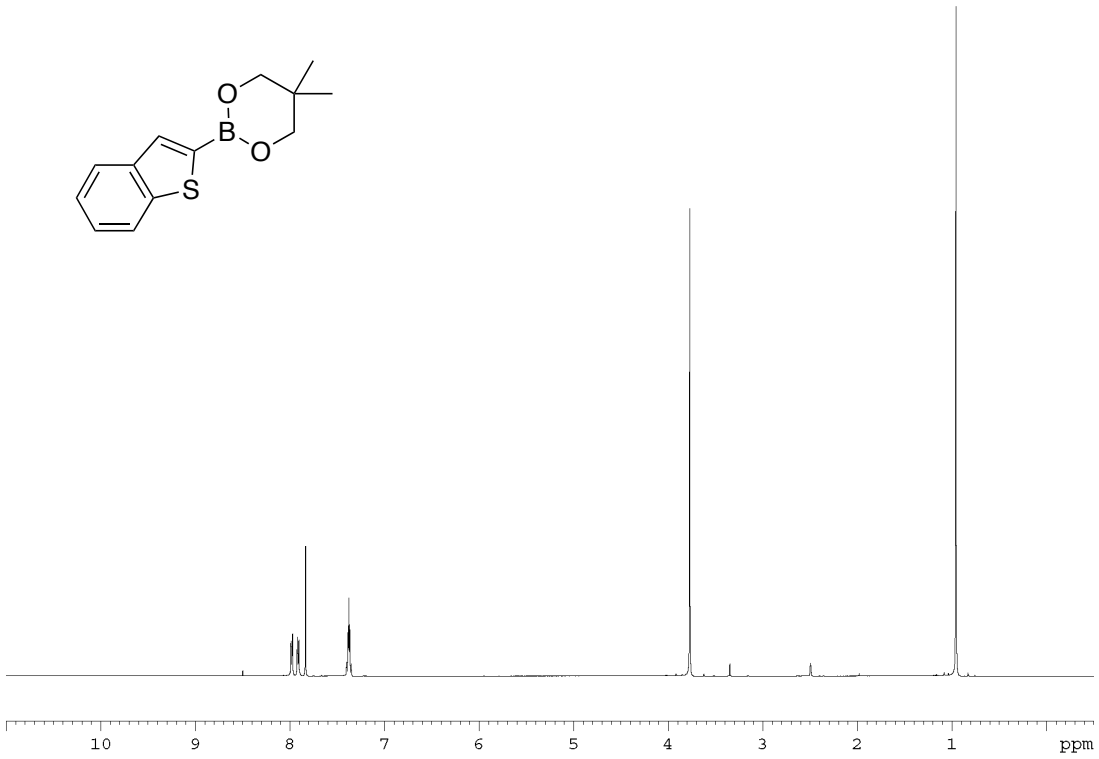


Figure A2.107 ^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of 2-(Benzo[b]thiophen-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane

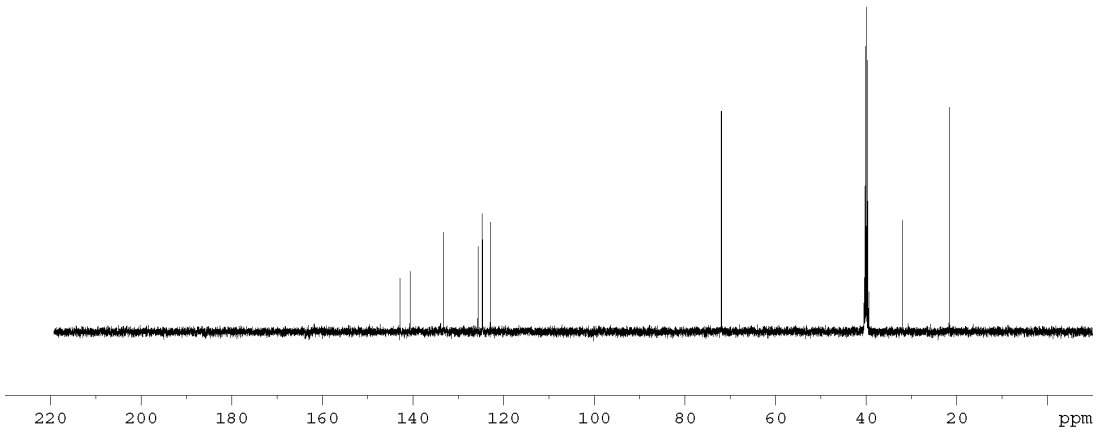


Figure A2.108 ^{13}C NMR (128.5 MHz, DMSO-d_6) Spectrum of 2-(Benzo[b]thiophen-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane

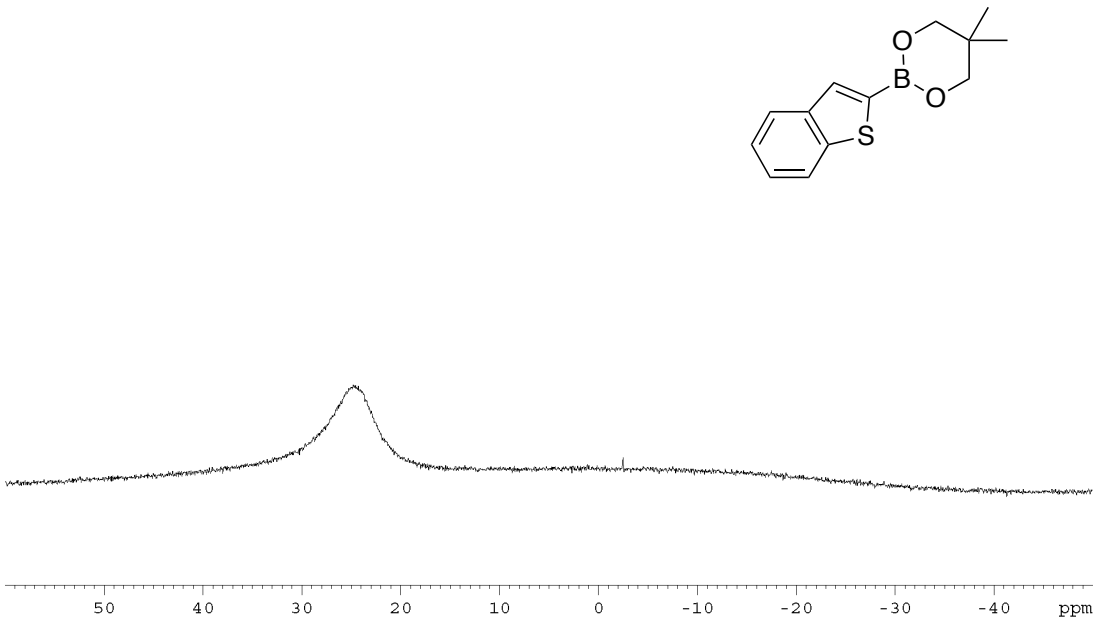


Figure A2.109 ^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of 2-(Benzo[b]thiophen-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane

Appendix A3. ^{1}H, ^{13}C and ^{19}F Spectra Relevant to Chapter 2.4

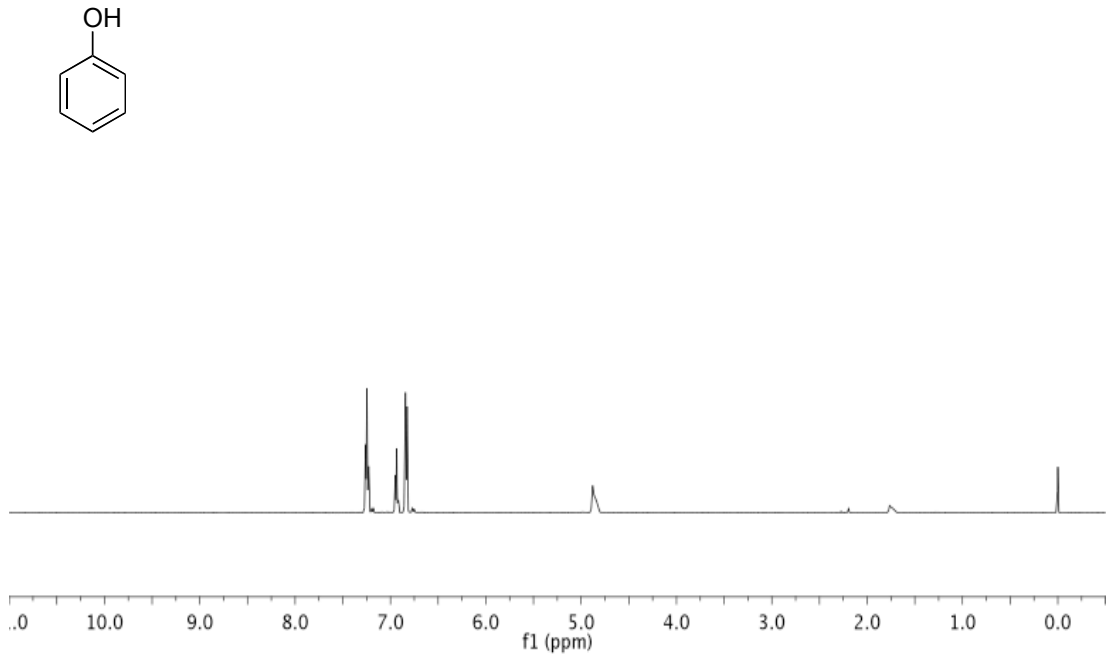


Figure A3.1 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of phenol

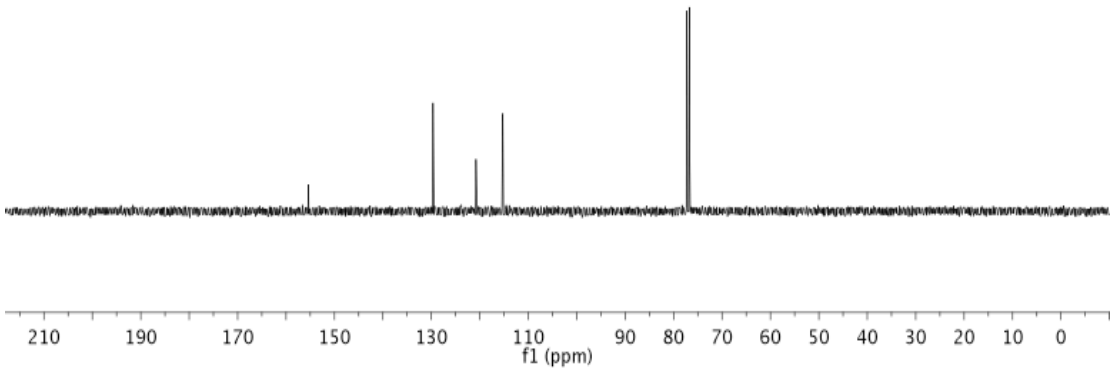


Figure A3.2 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of phenol

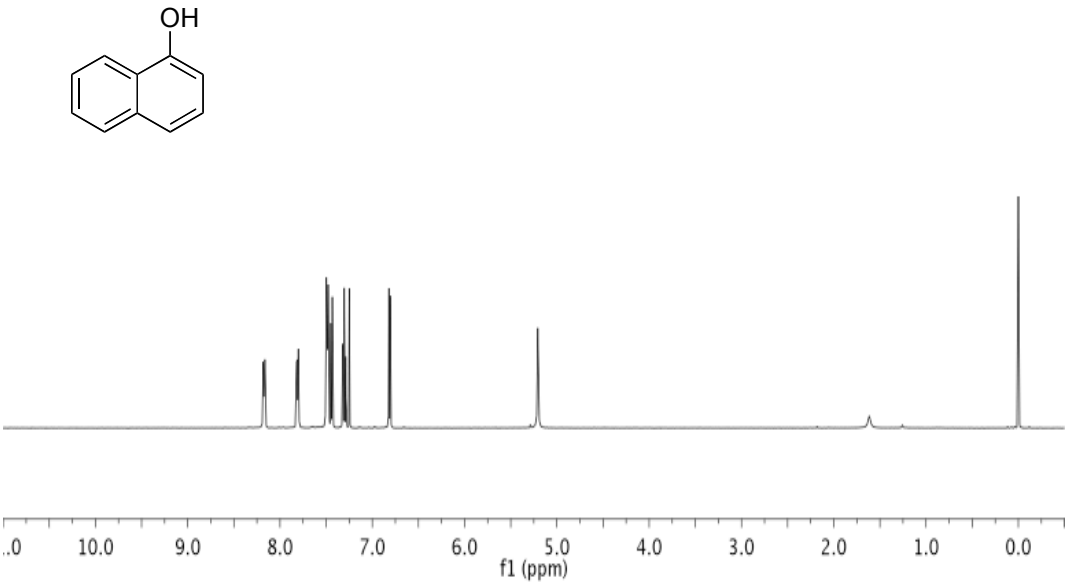


Figure A3.3 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of naphthalen-1-ol

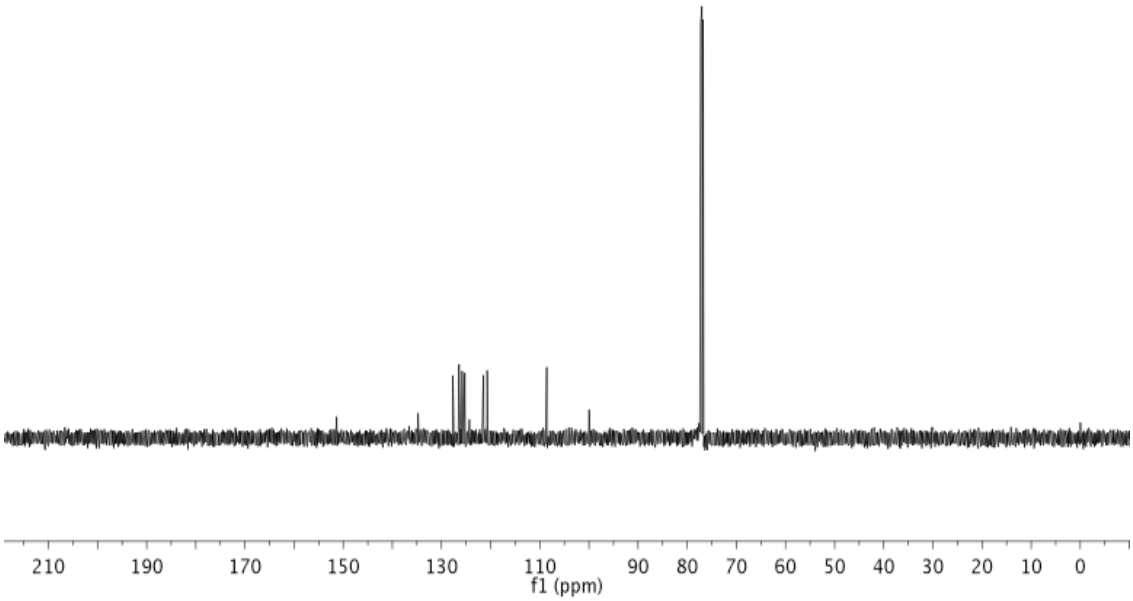


Figure A3.4 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of naphthalen-1-ol

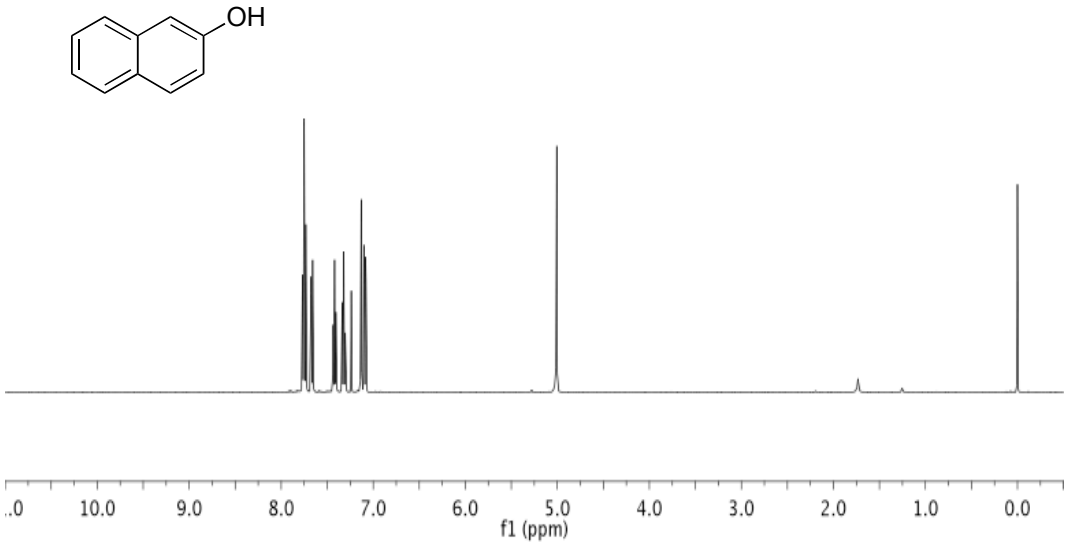


Figure A3.5 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of naphthalen-2-ol

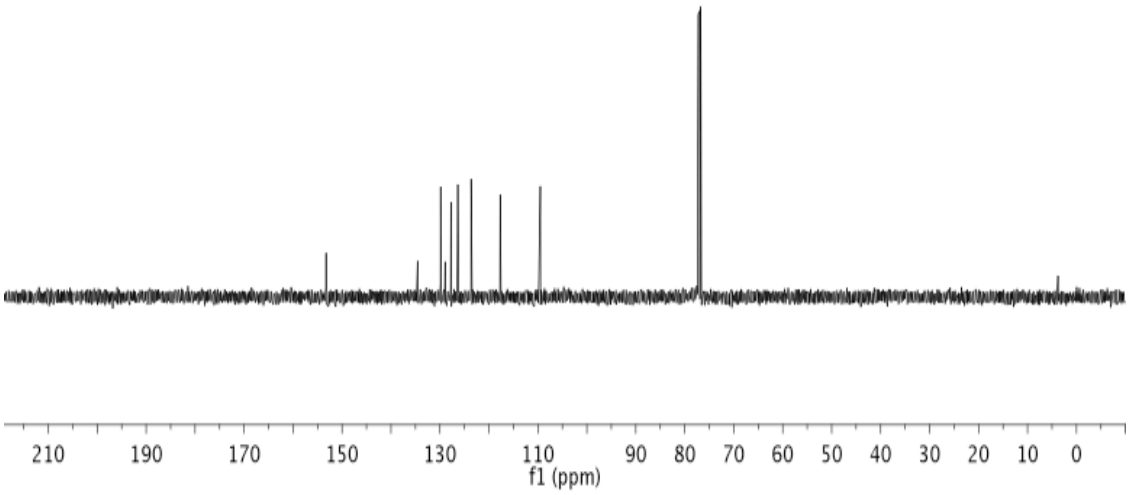


Figure A3.6 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of naphthalen-2-ol

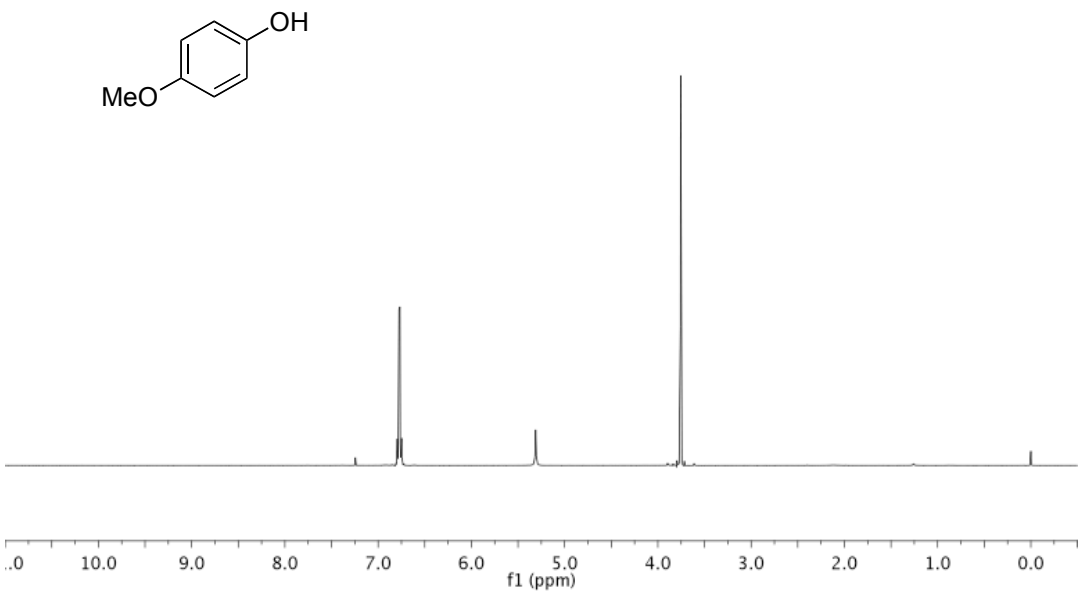


Figure A3.7 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-methoxyphenol

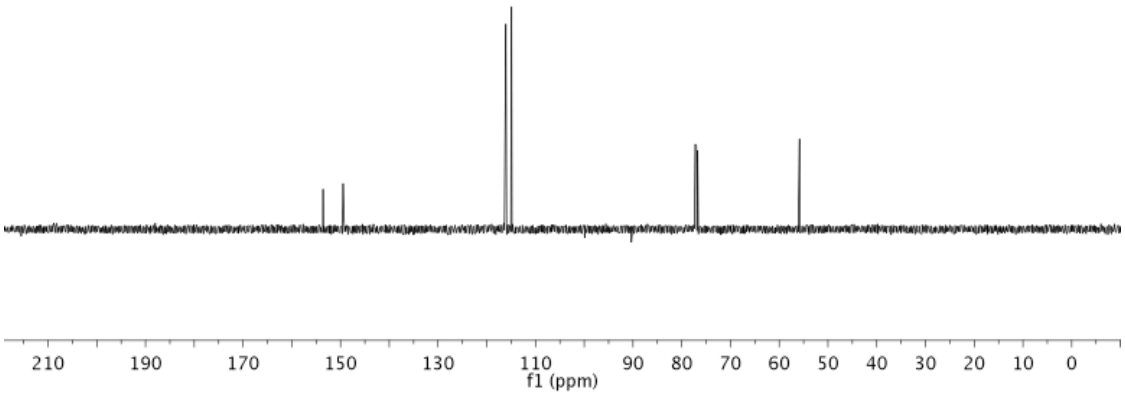


Figure A3.8 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-methoxyphenol

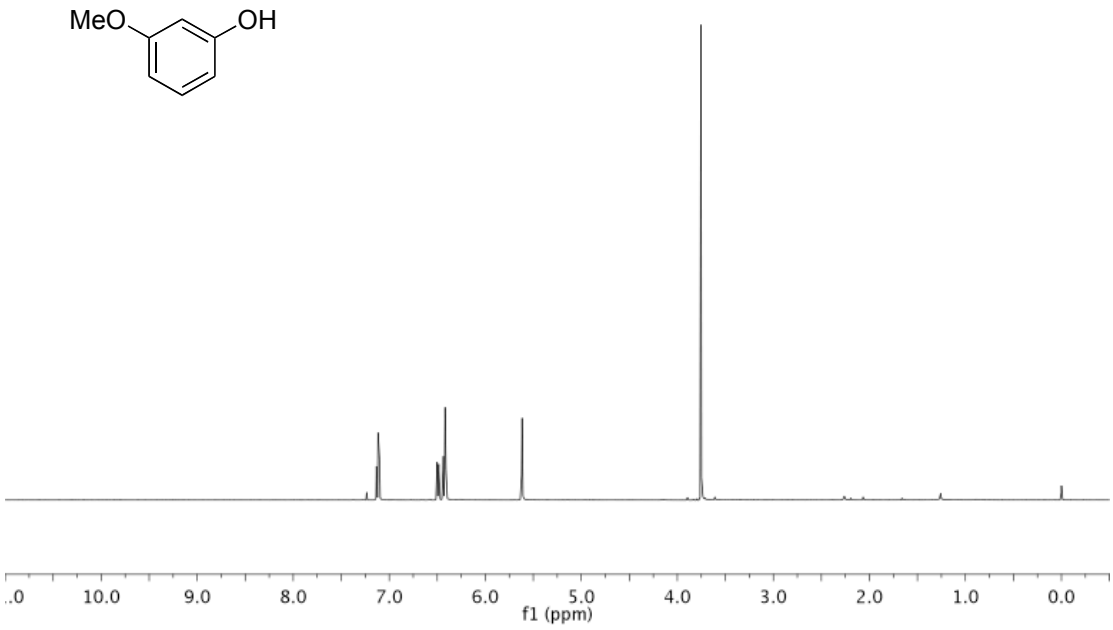


Figure A3.9 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 3-methoxyphenol

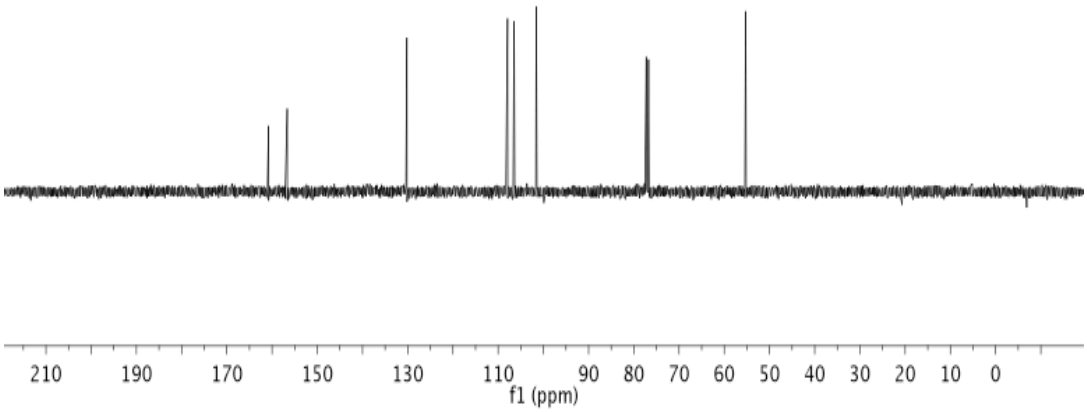


Figure A3.10 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 3-methoxyphenol

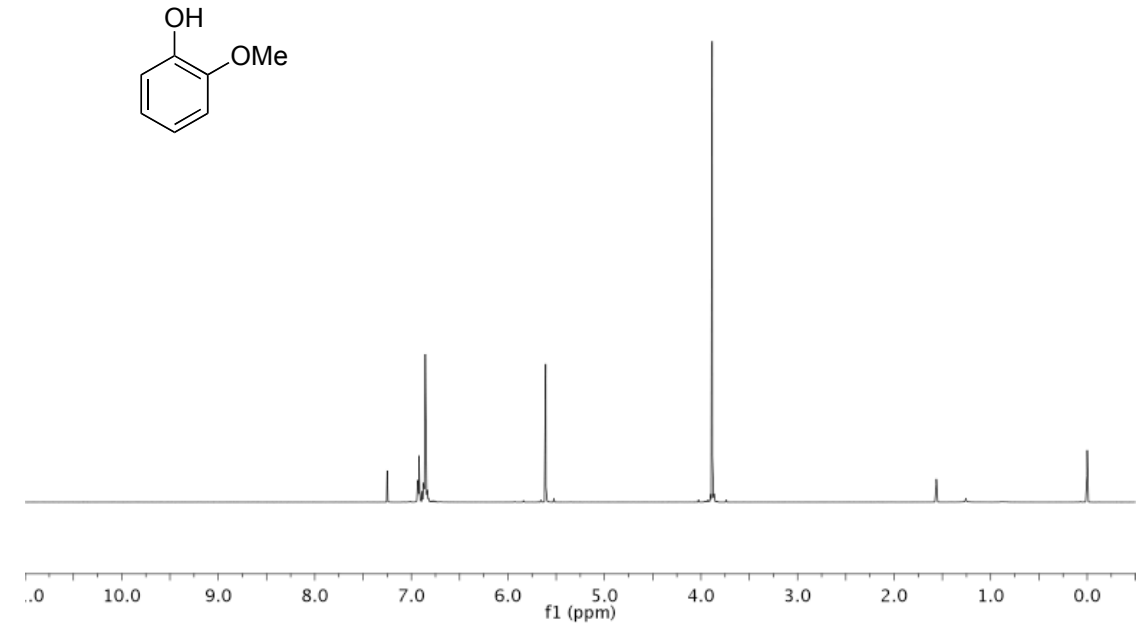


Figure A3.11 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-methoxyphenol

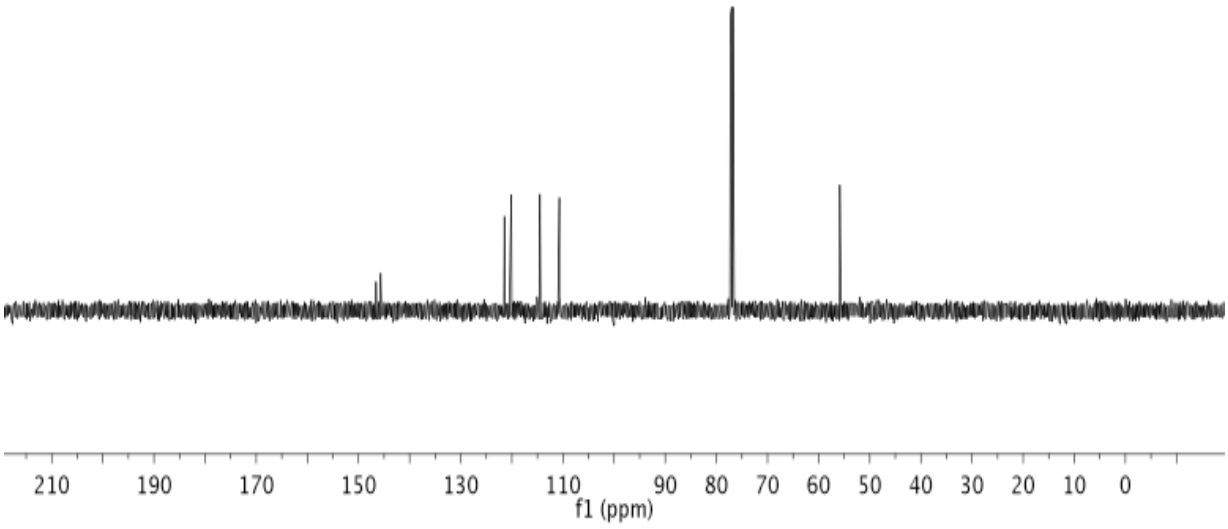


Figure A3.12 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2-methoxyphenol

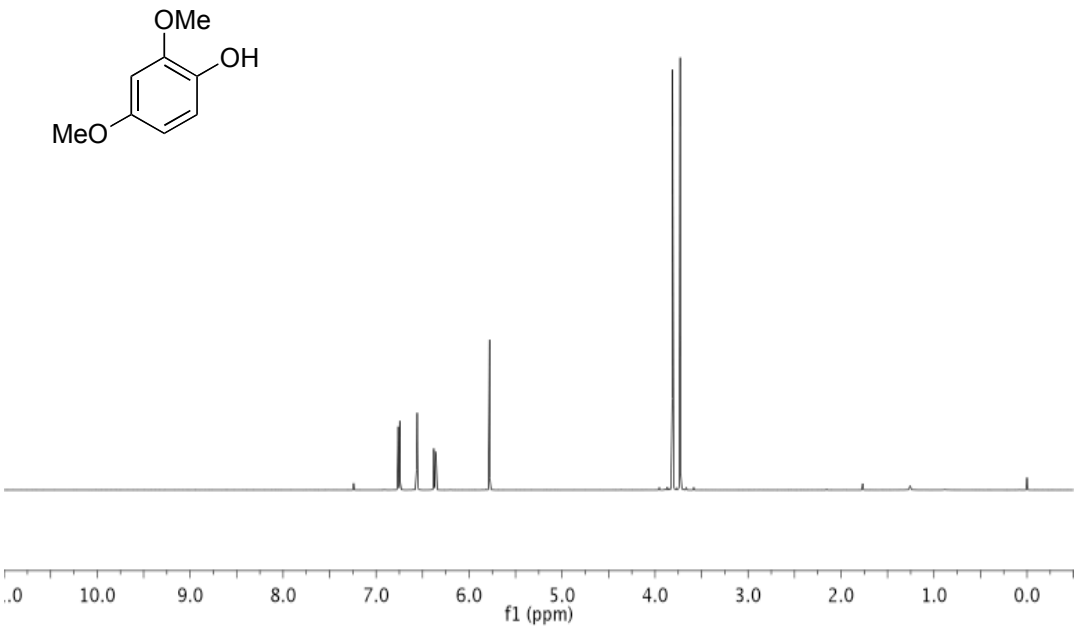


Figure A3.13 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,4-dimethoxyphenol

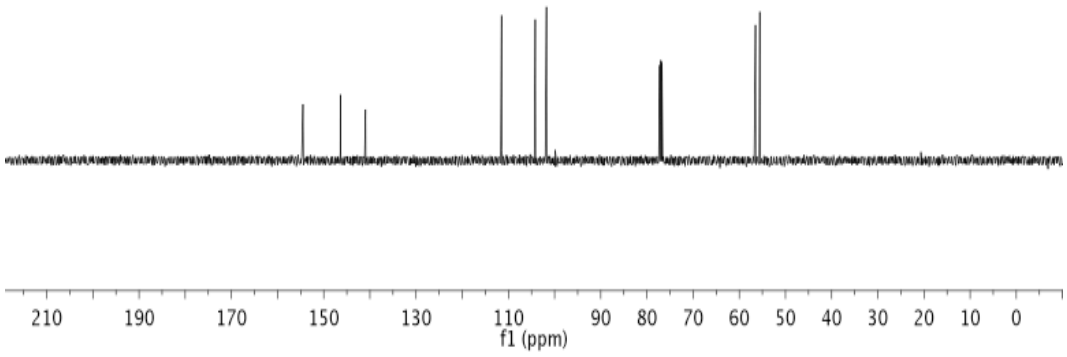


Figure A3.14 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2,4-dimethoxyphenol

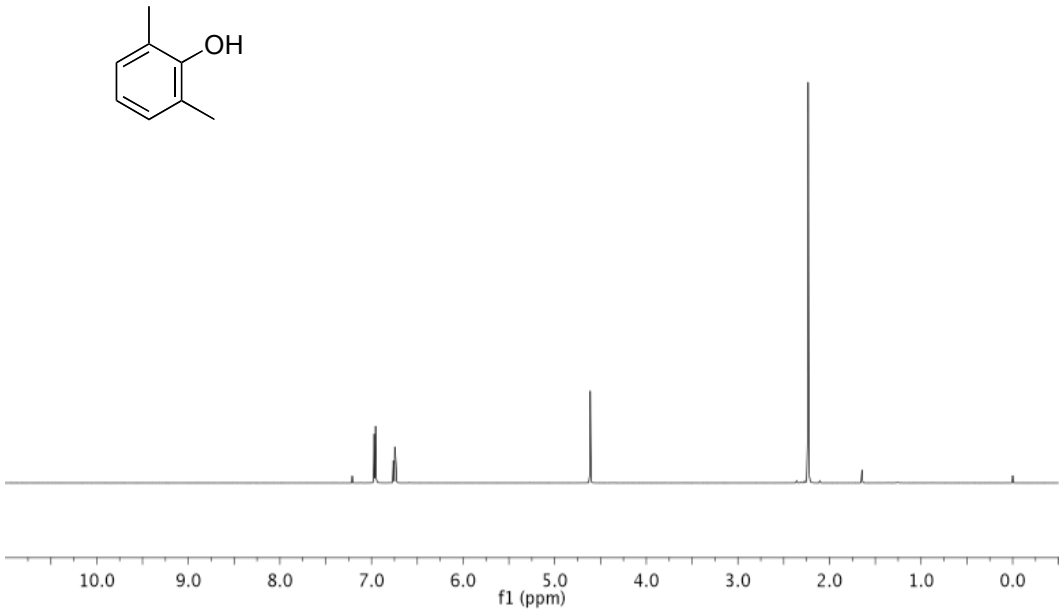


Figure A3.15 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,6-dimethylphenol

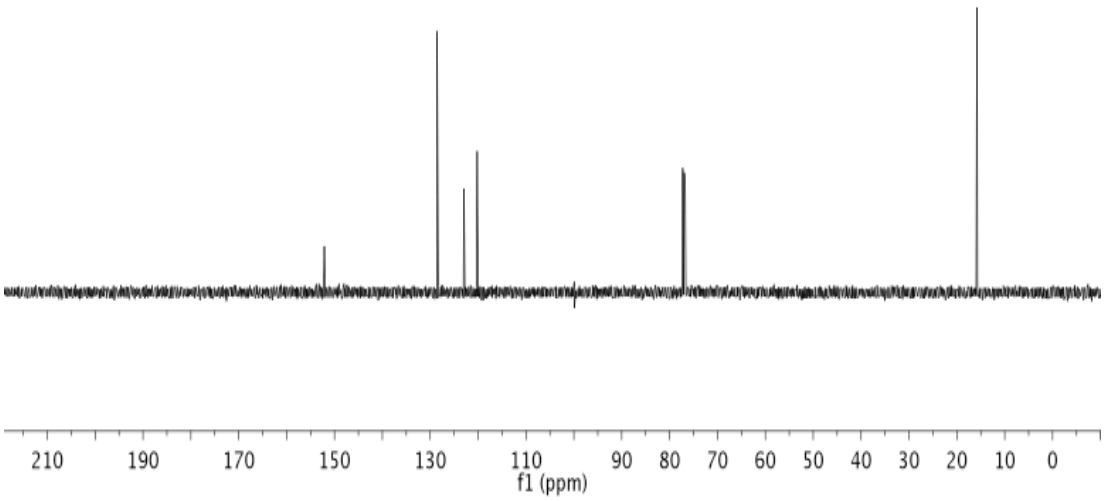


Figure A3.16 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2,6-dimethylphenol

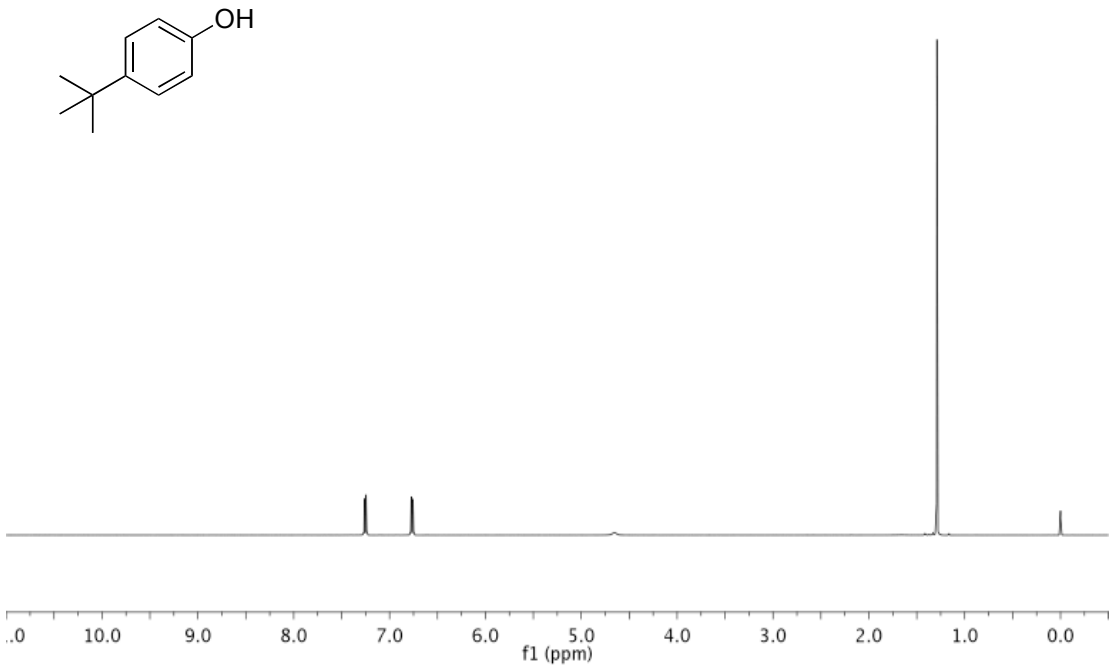


Figure A3.17 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-(*t*-butyl)phenol

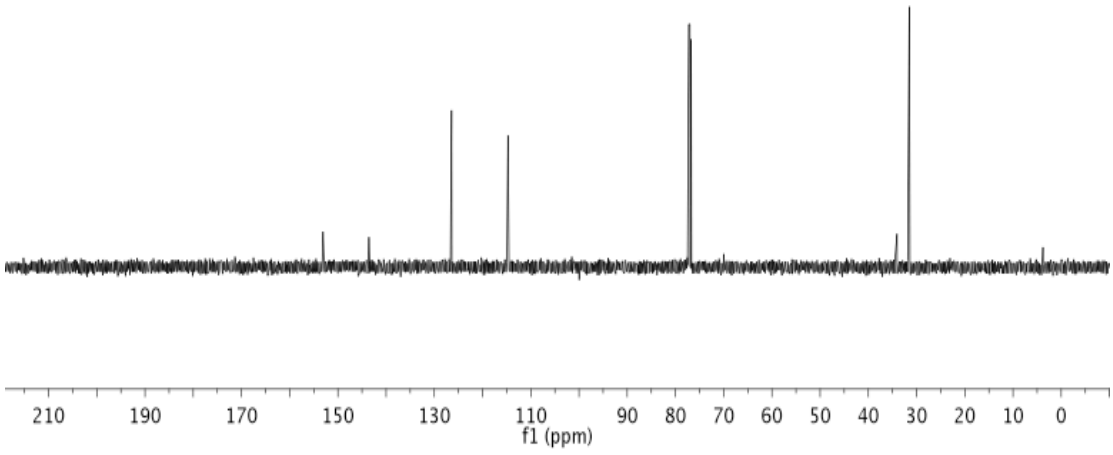


Figure A3.18 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-(*t*-butyl)phenol

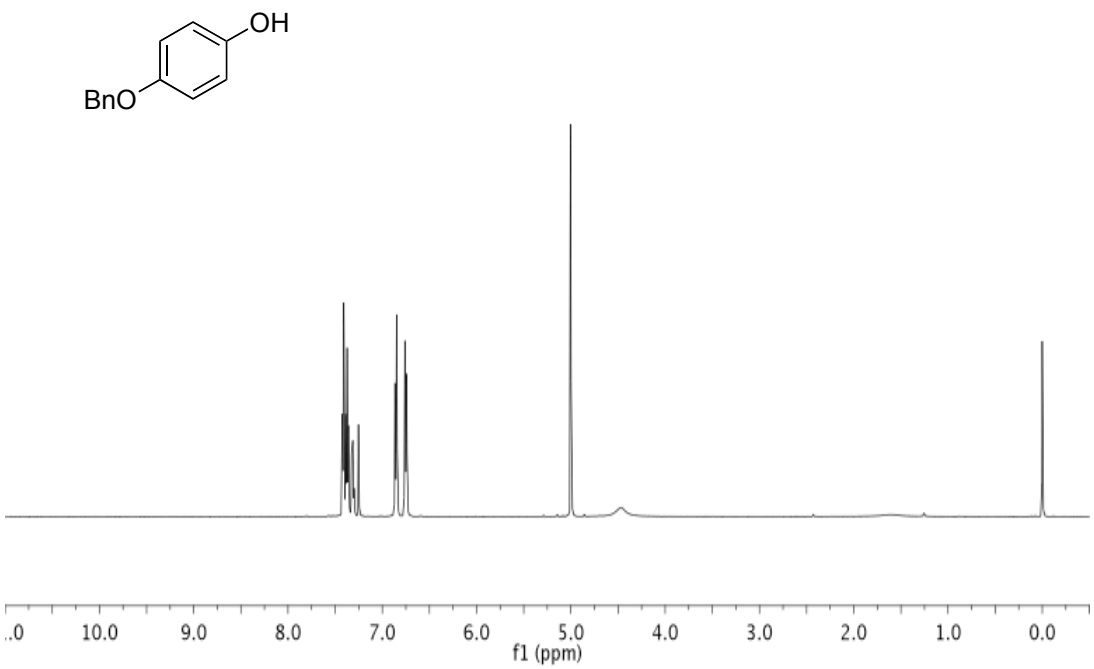


Figure A3.19 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-(benzyloxy)phenol

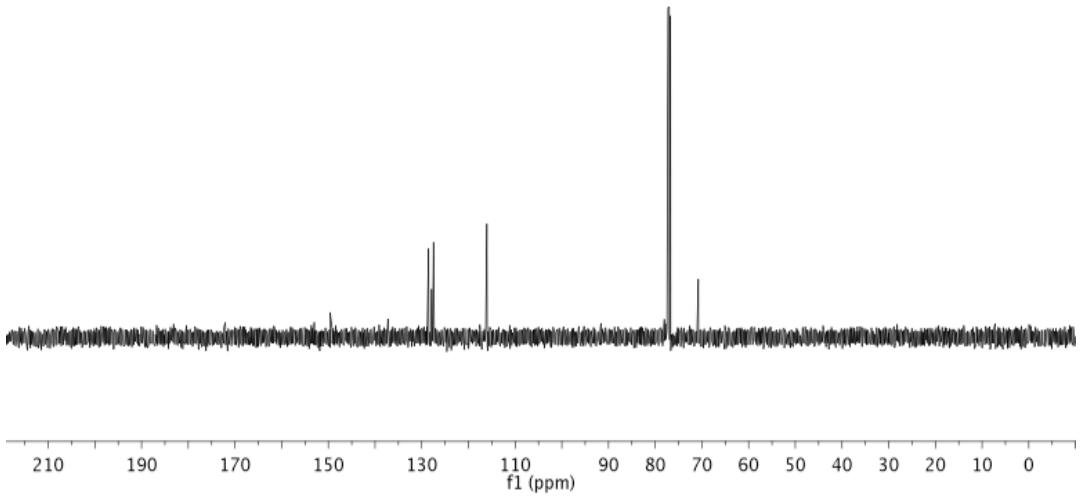


Figure A3.20 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-(benzyloxy)phenol

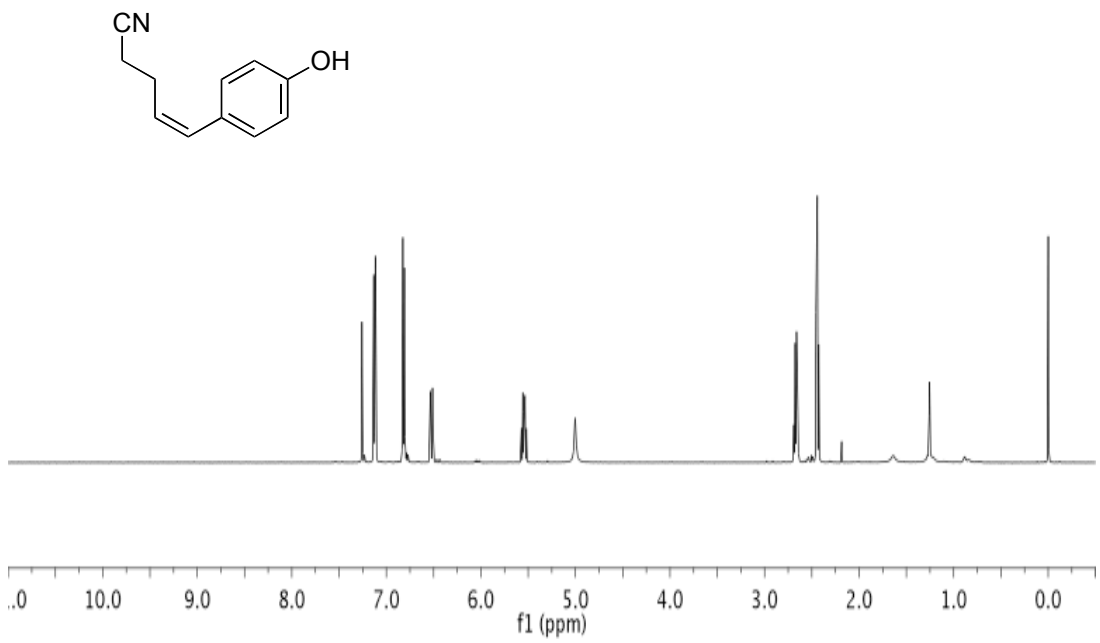


Figure A3.21 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of (*Z*)-5-(4-hydroxyphenyl)pent-4-enenitrile

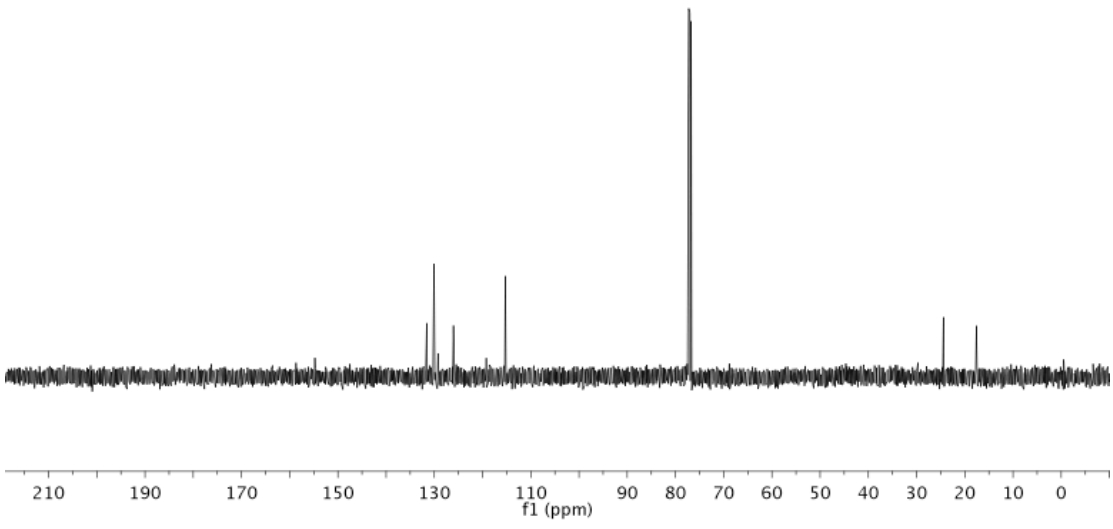


Figure A3.22 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of (*Z*)-5-(4-hydroxyphenyl)pent-4-enenitrile

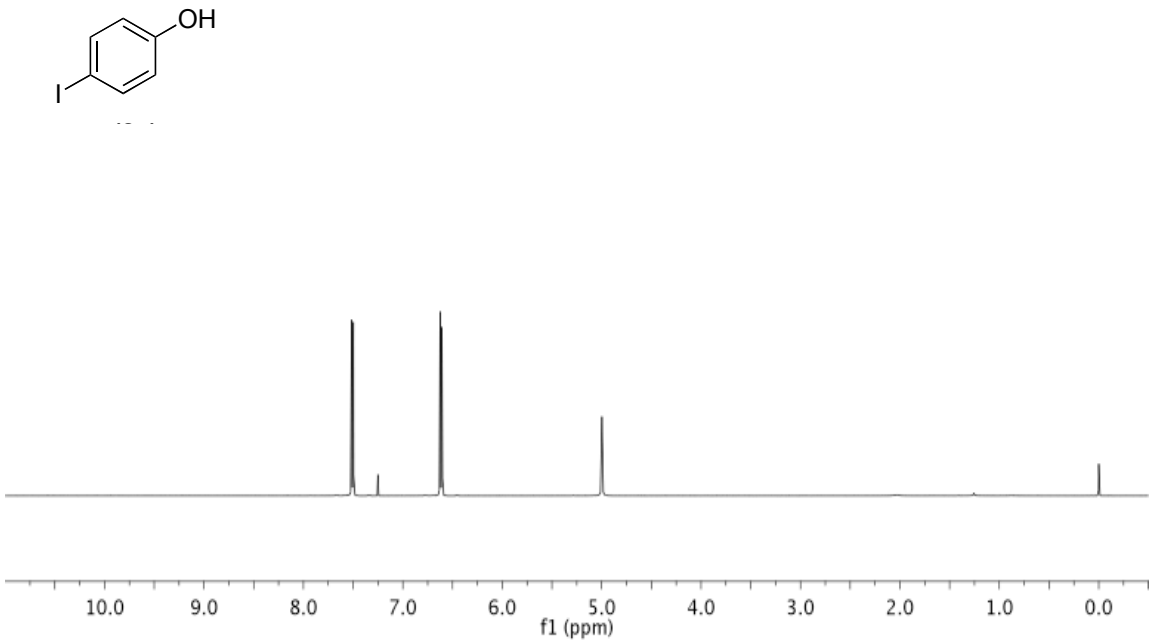


Figure A3.23 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-iodophenol

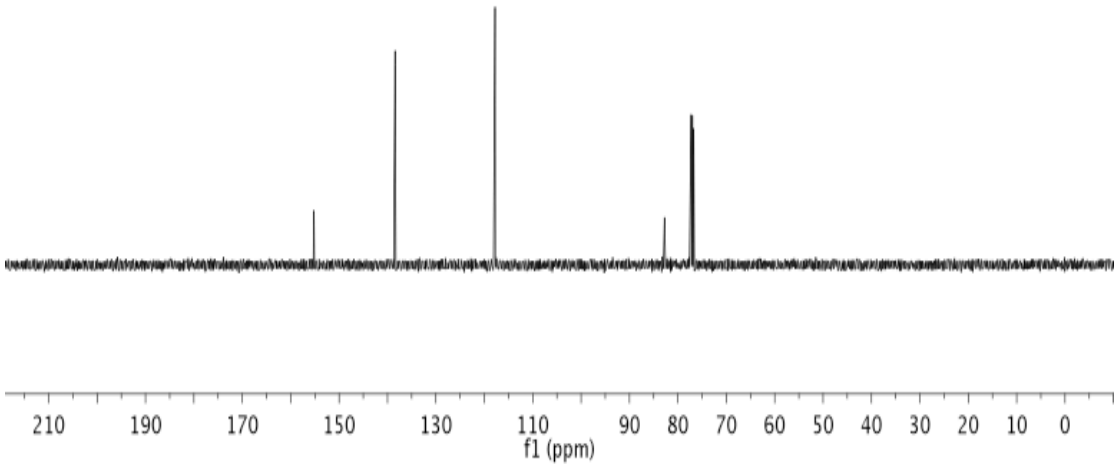


Figure A3.24 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-iodophenol

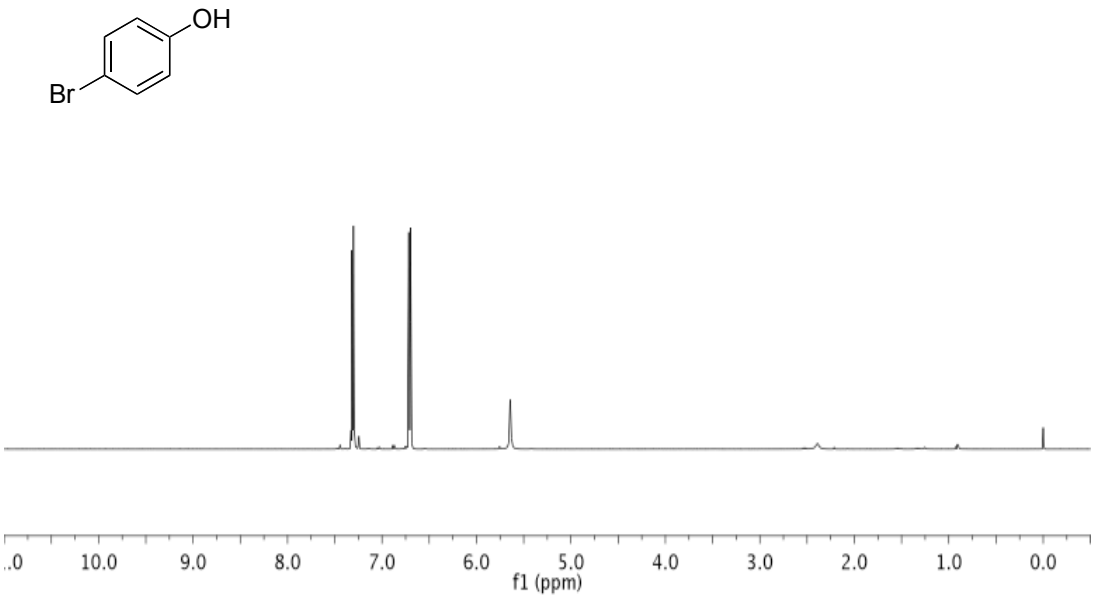


Figure A3.25 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-bromophenol

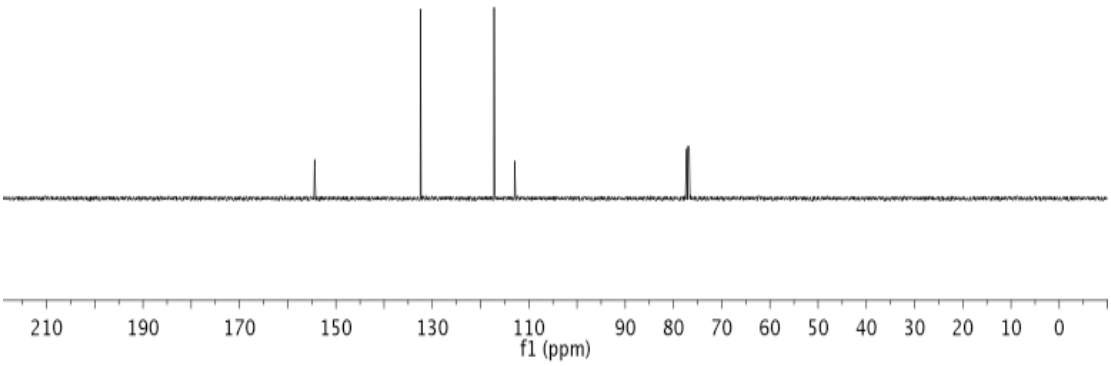


Figure A3.26 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-bromophenol

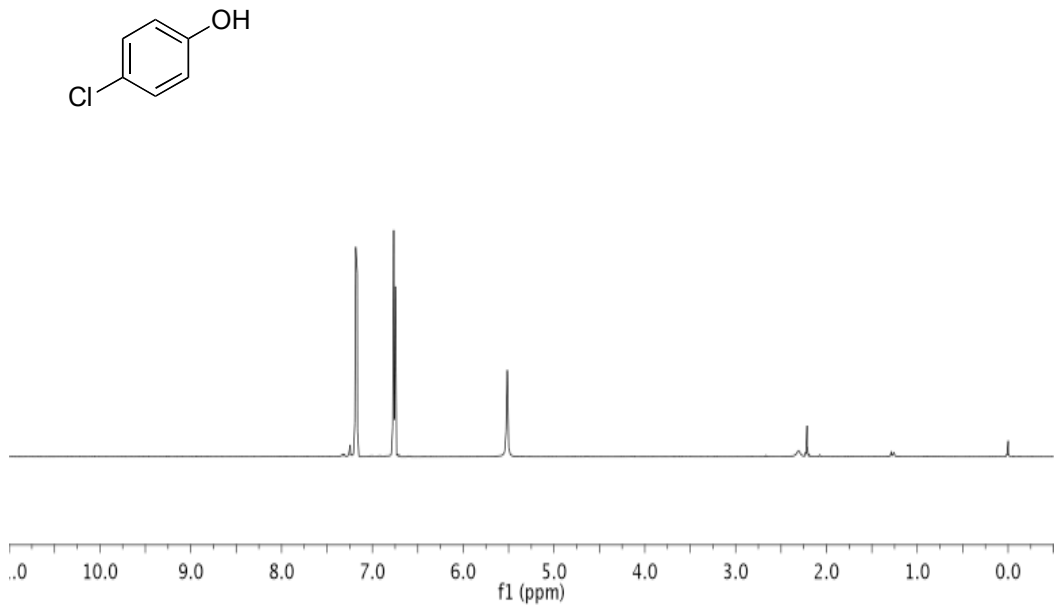


Figure A3.27 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-chlorophenol

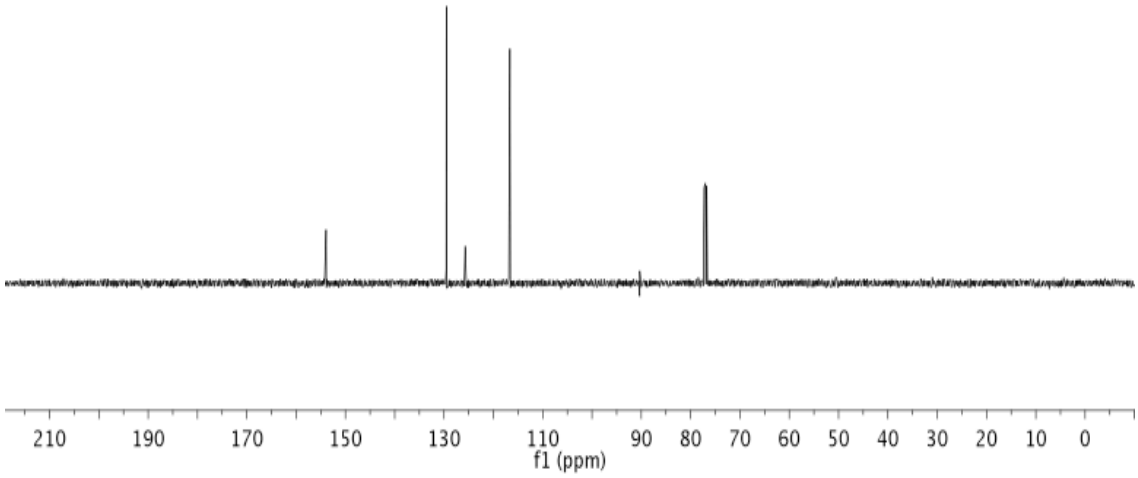


Figure A3.28 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-chlorophenol

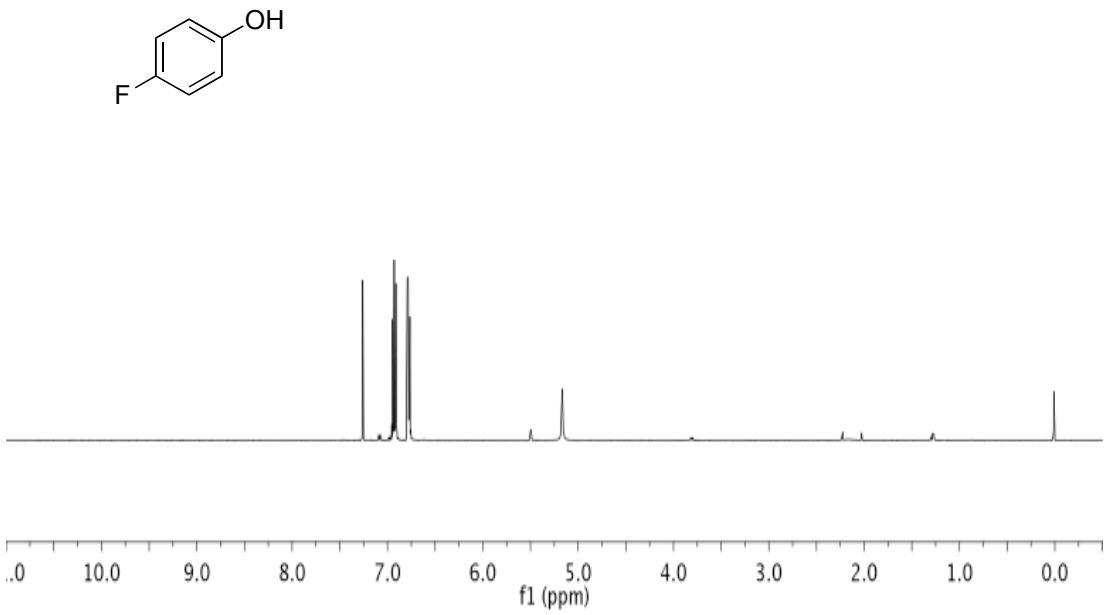


Figure A3.29 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-Fluorophenol

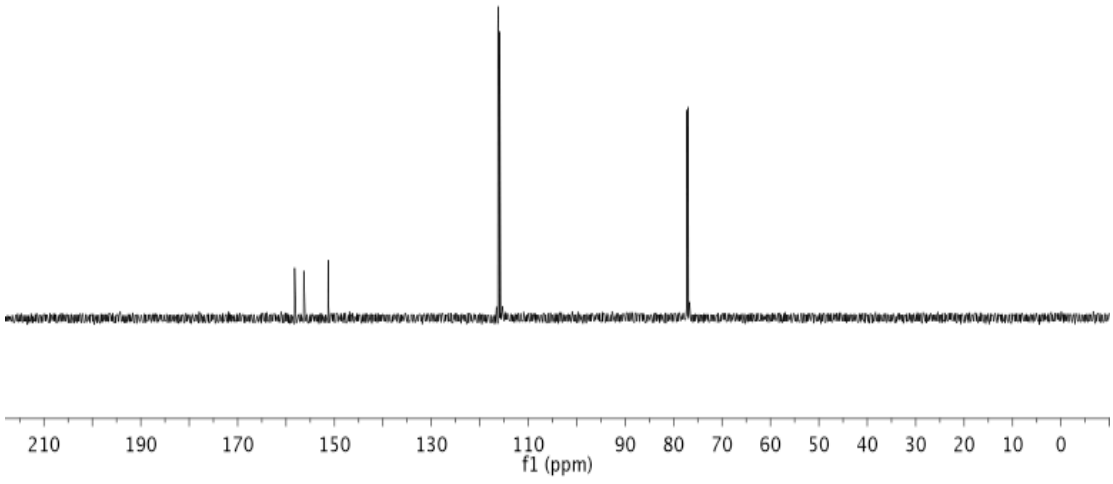


Figure A3.30 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-Fluorophenol

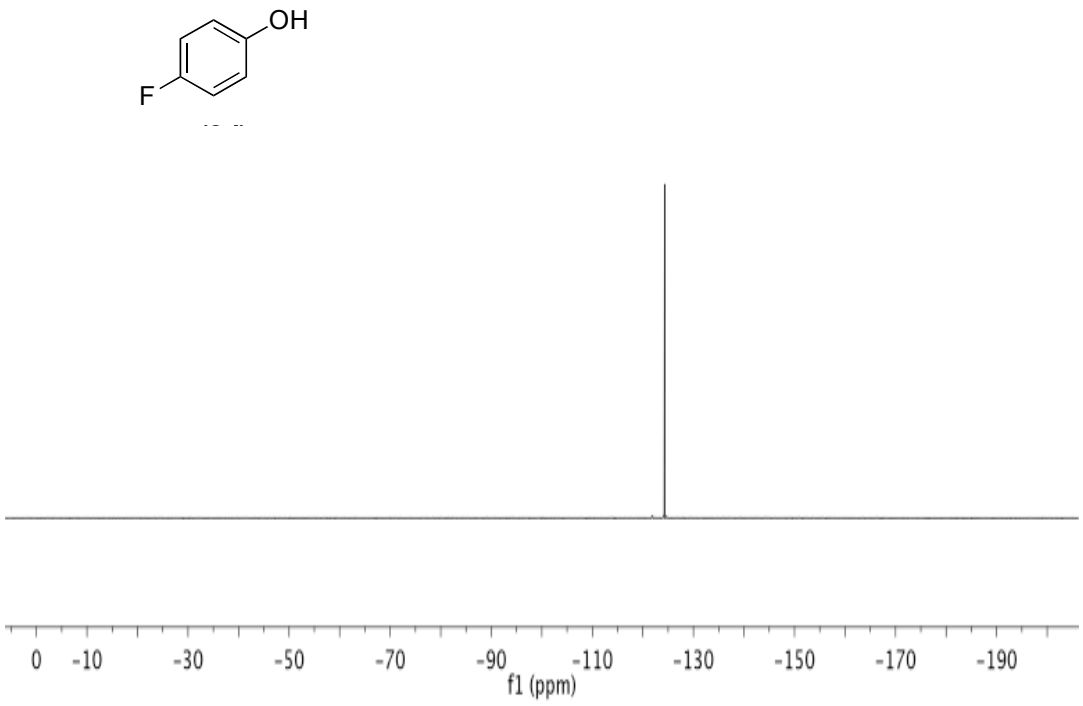


Figure A3.31 ^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of 4-Fluorophenol

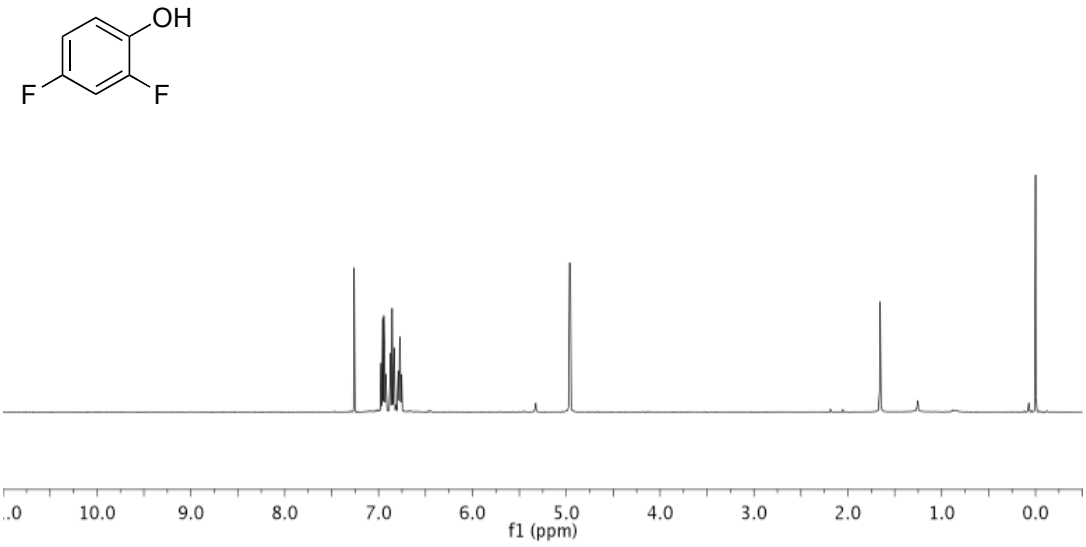


Figure A3.32 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,4-Difluorophenol

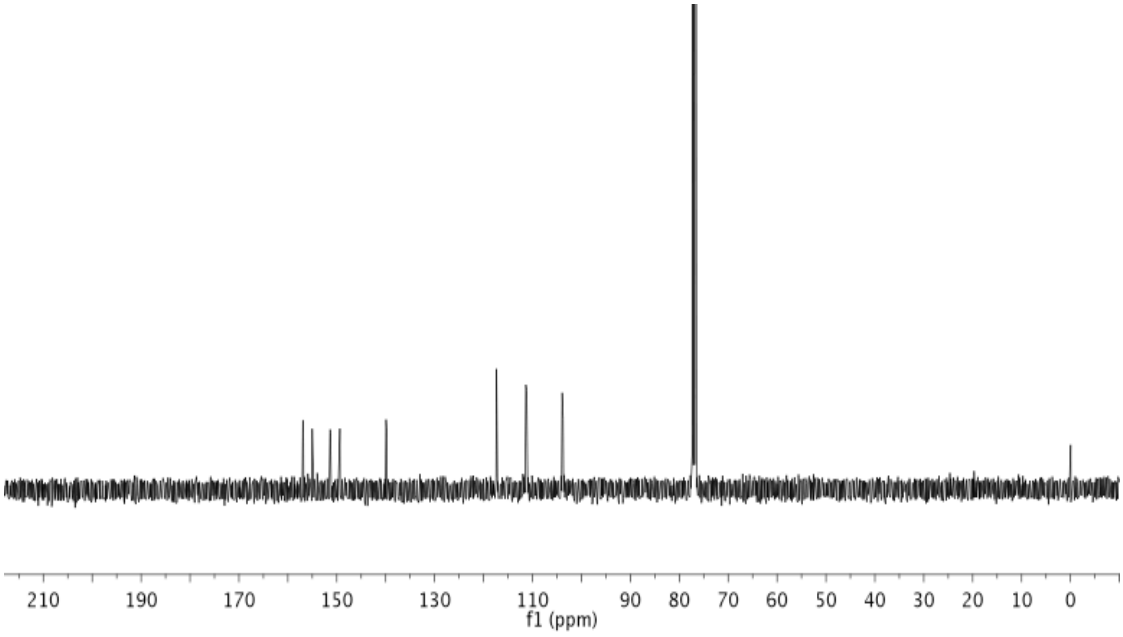
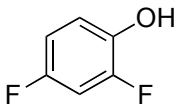


Figure A3.33 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2,4-Difluorophenol



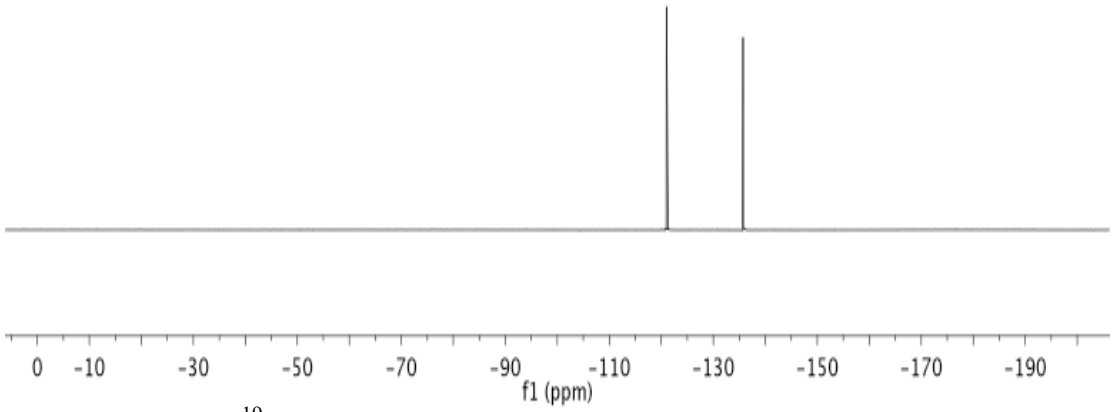
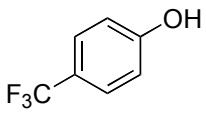


Figure A3.34 ^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of 2,4-diFluorophenol



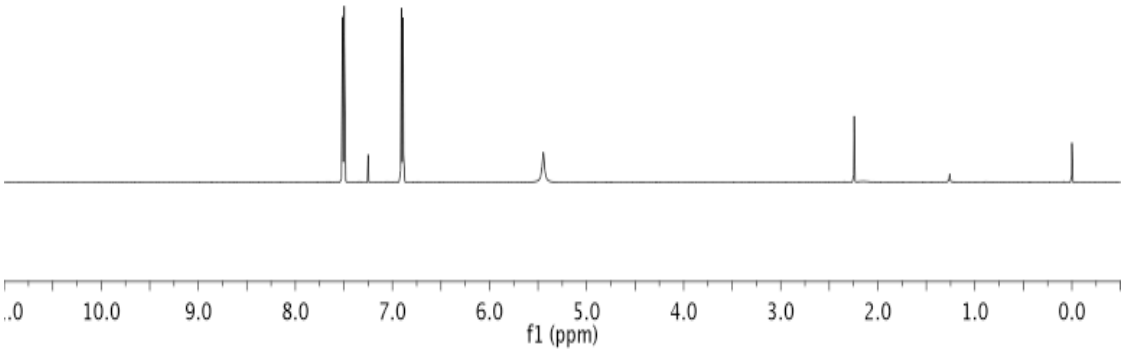


Figure A3.35 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-(trifluoromethyl)phenol

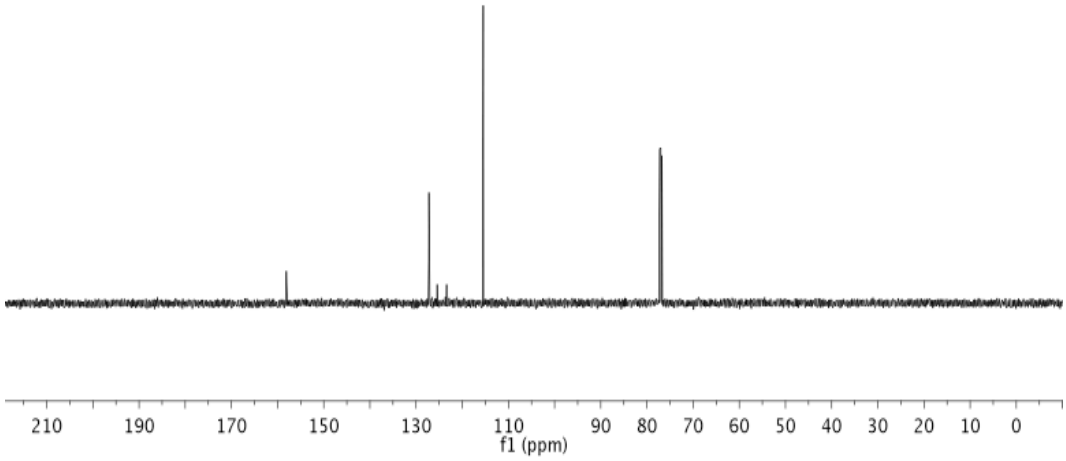


Figure A3.36 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-(trifluoromethyl)phenol

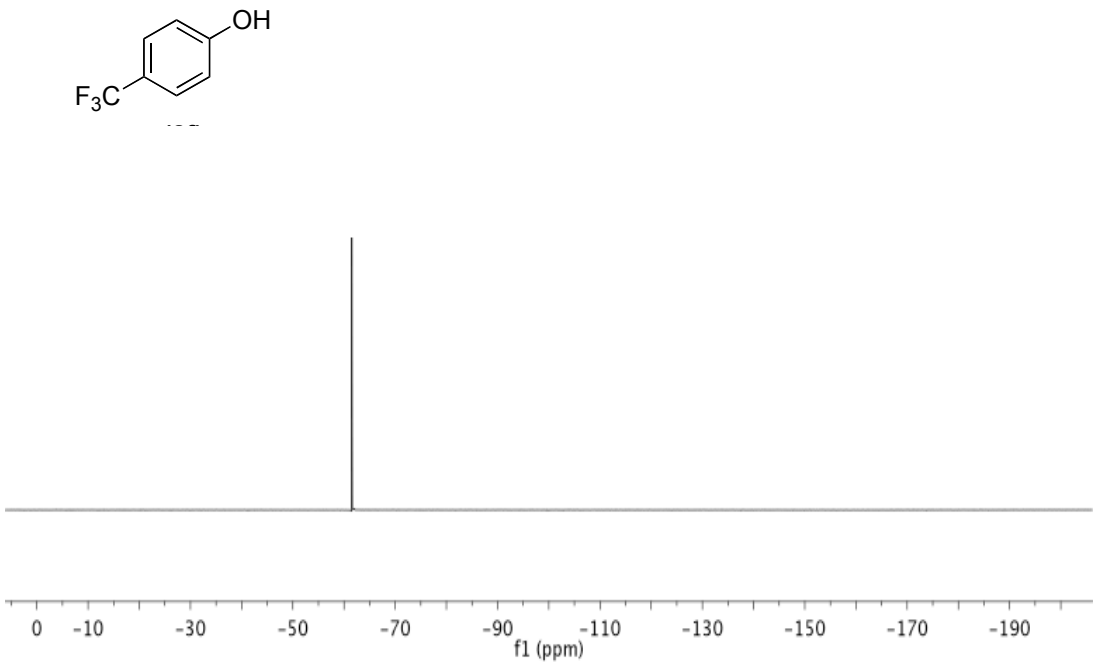


Figure A3.37 ^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of 4-(trifluoromethyl)phenol

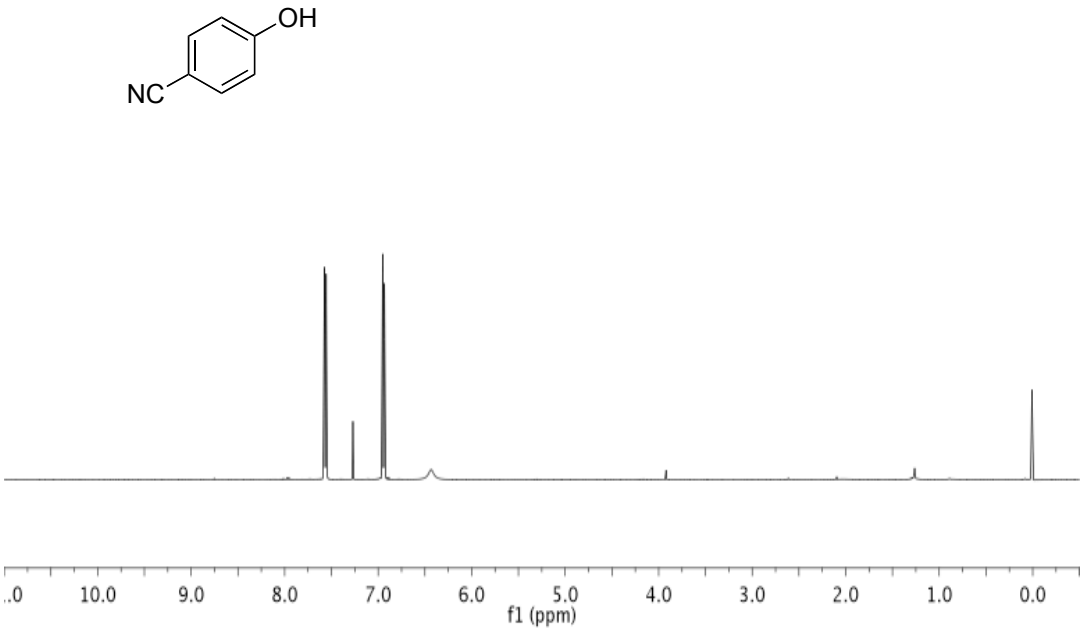


Figure A3.38 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-hydroxybenzonitrile

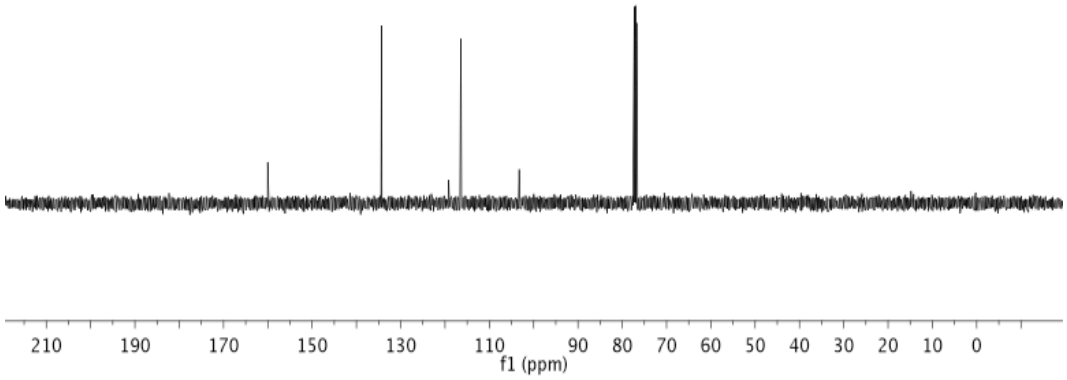


Figure A3.39 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-hydroxybenzonitrile

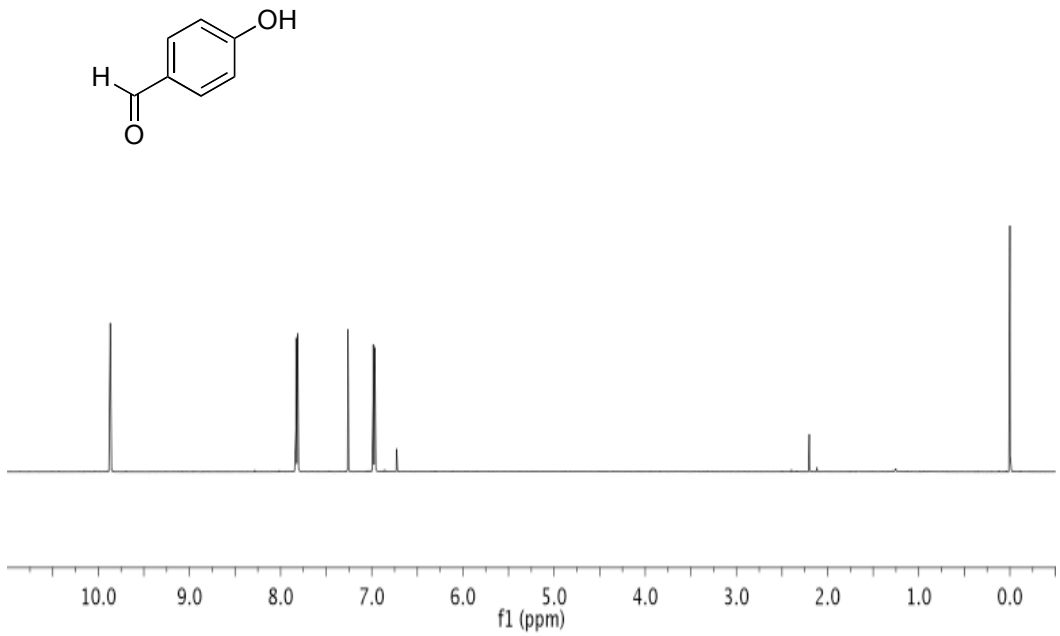


Figure A3.40 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-hydroxybenzaldehyde

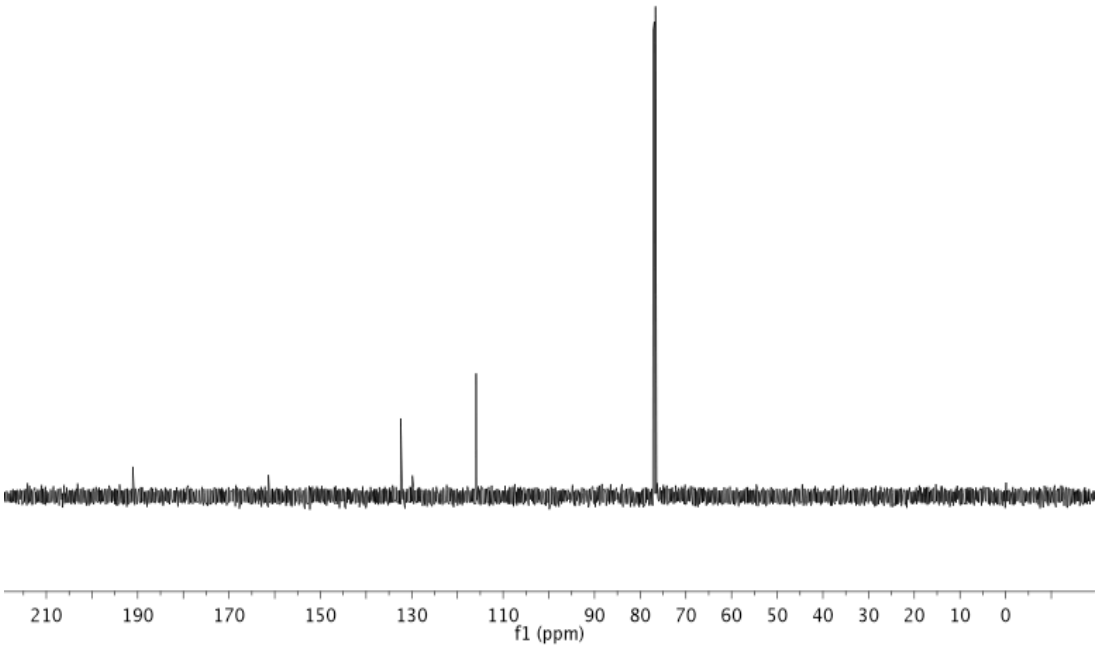


Figure A3.41 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-hydroxybenzaldehyde

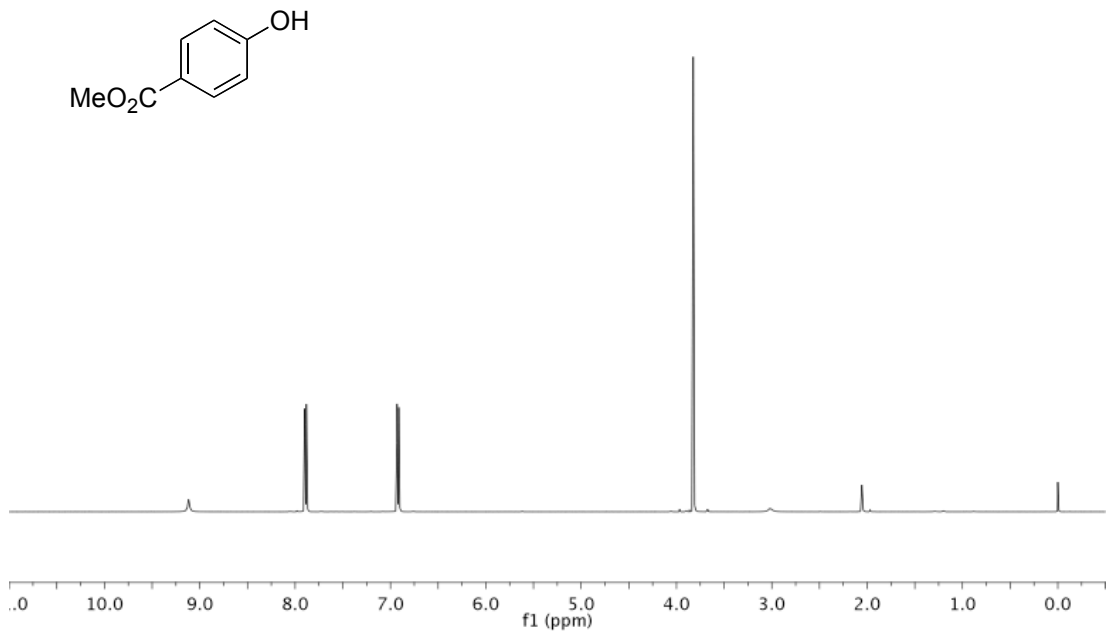


Figure A3.41 ^{1}H NMR (500 MHz, acetone- d_6) Spectrum of methyl 4-hydroxybenzoate

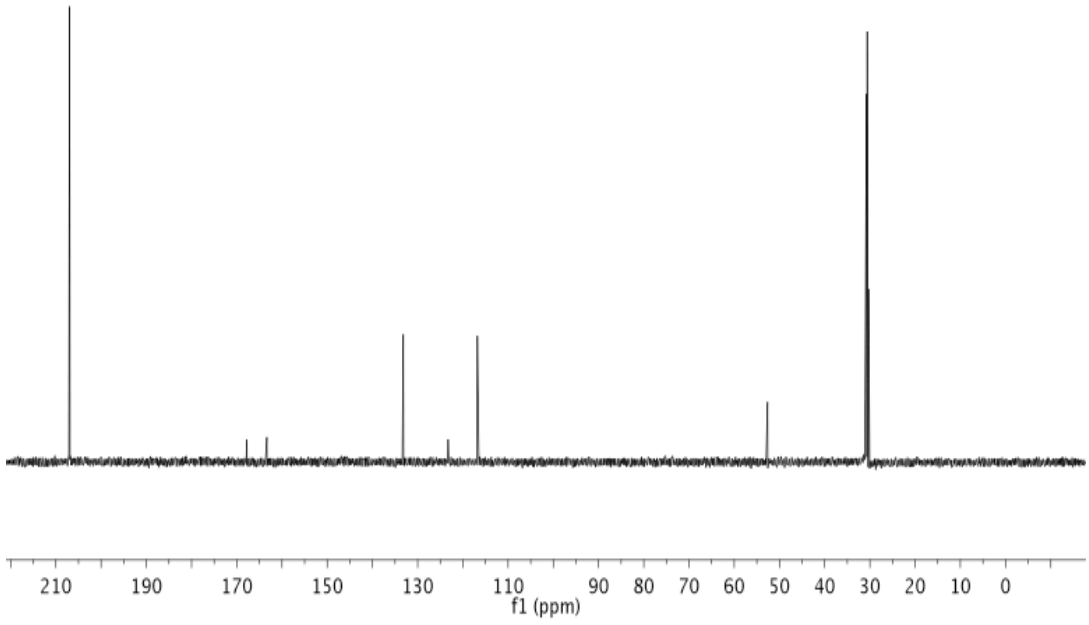


Figure A3.42 ^{13}C NMR (128.5 MHz, acetone- d_6) Spectrum of methyl 4-hydroxybenzoate

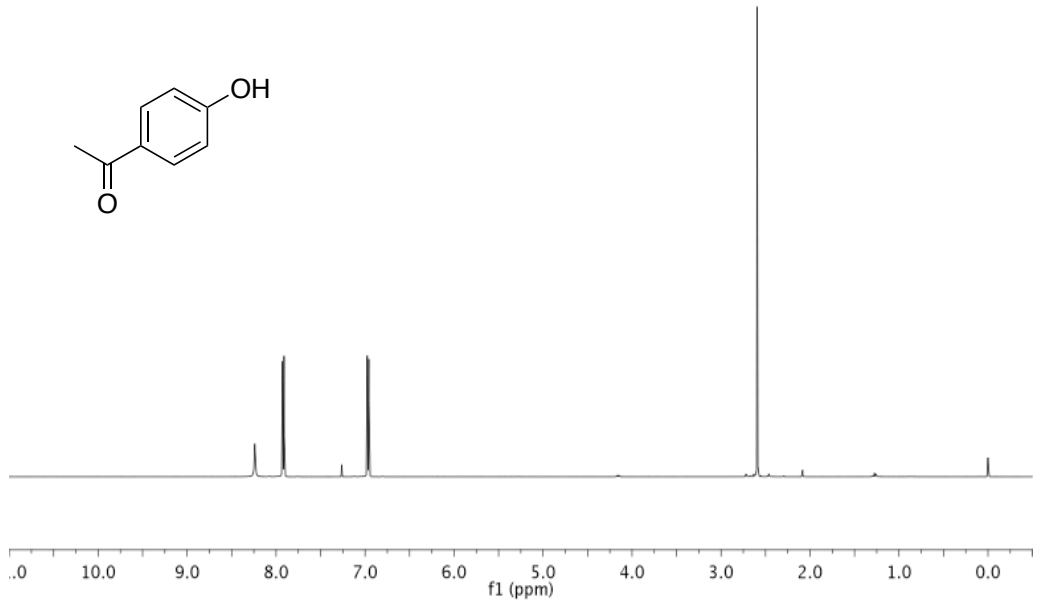


Figure A3.43 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(4-hydroxyphenyl)ethanone

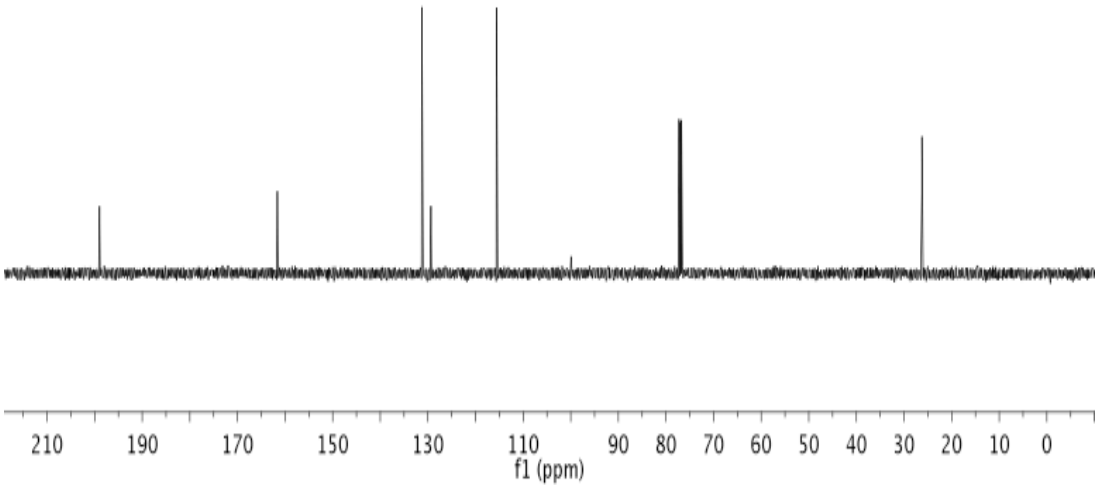


Figure A3.44 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-(4-hydroxyphenyl)ethanone

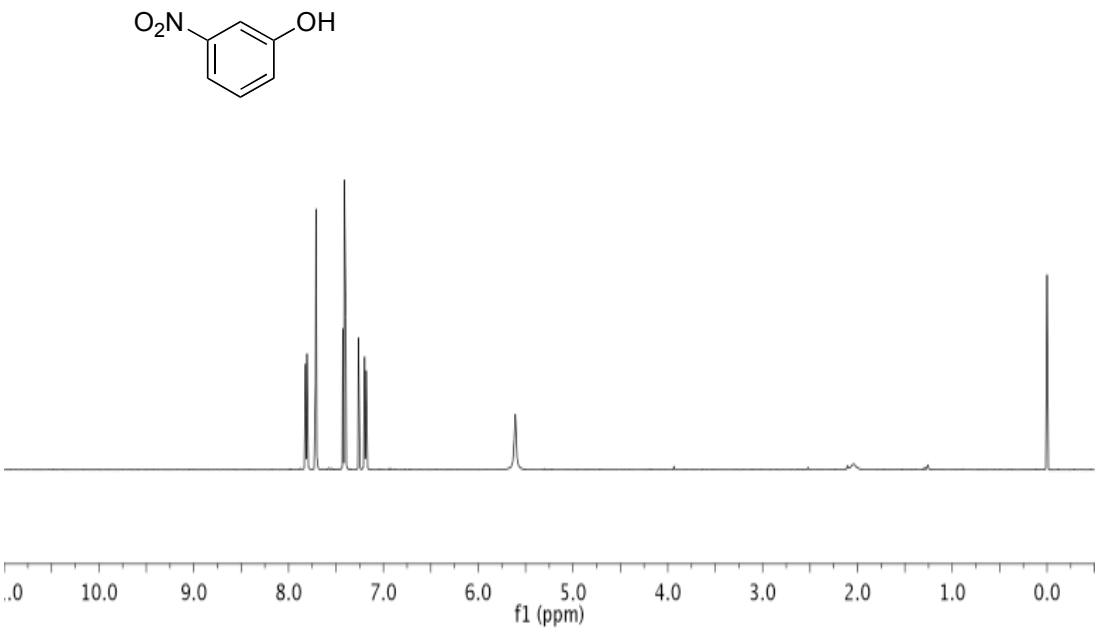


Figure A3.45 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 3-nitrophenol

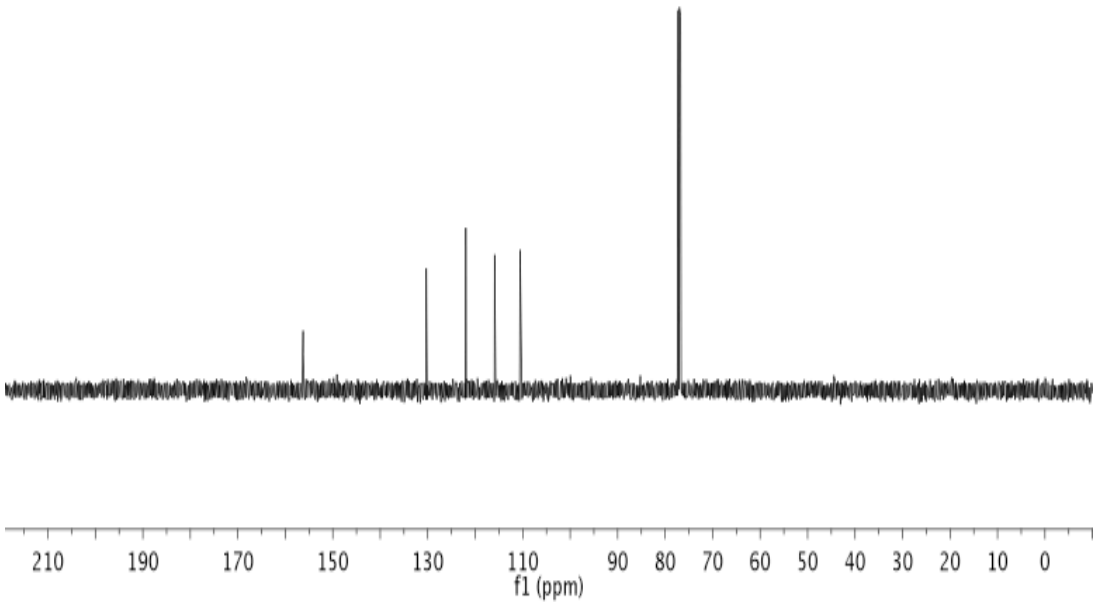


Figure A3.46 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 3-nitrophenol

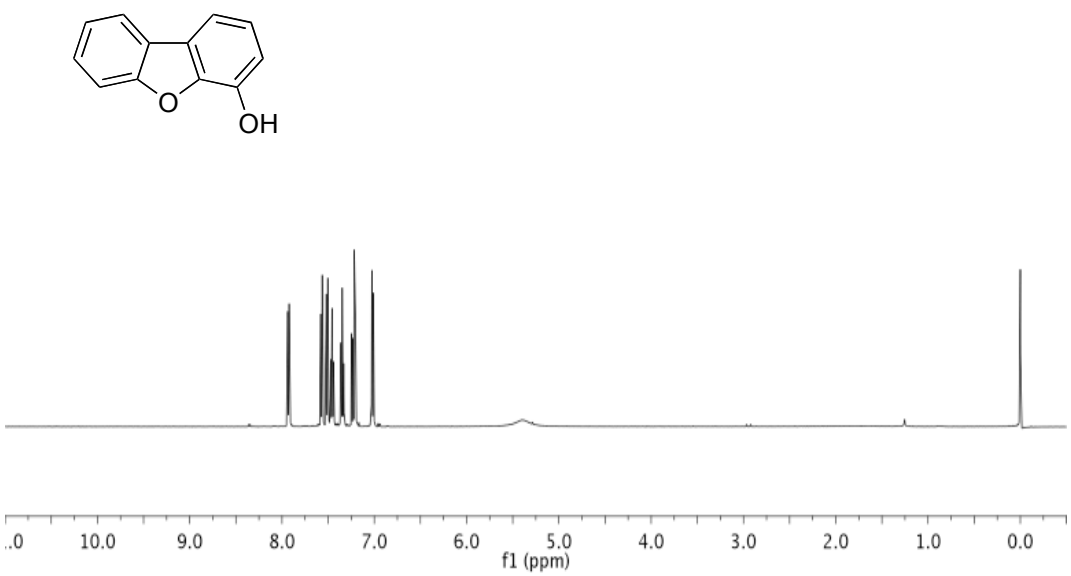


Figure A3.47 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of dibenzo[*b*,*d*]furan-4-ol

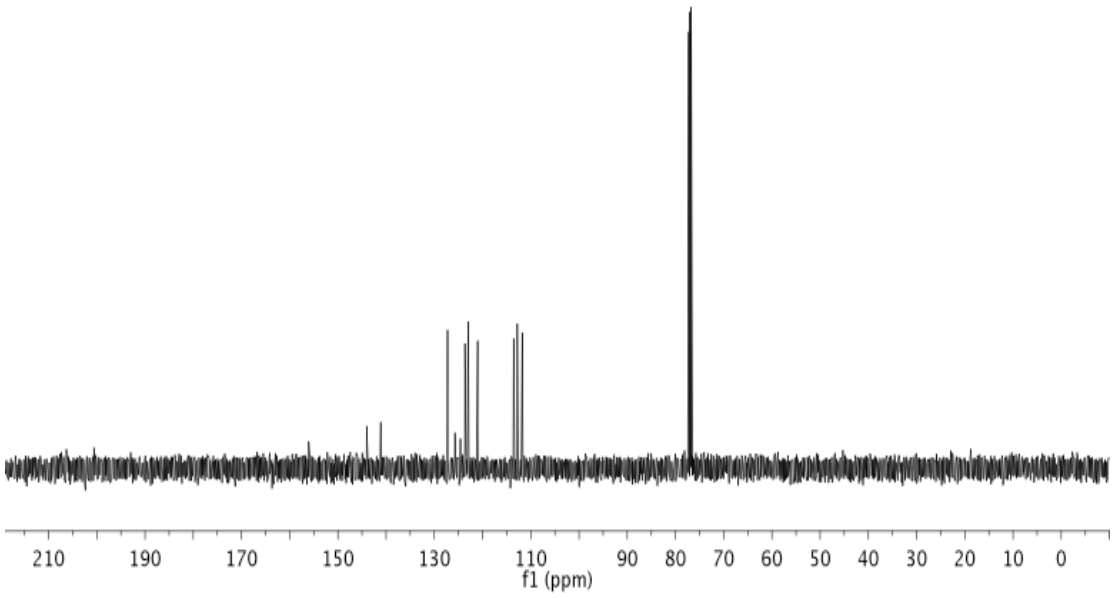


Figure A3.48 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of dibenzo[*b*,*d*]furan-4-ol

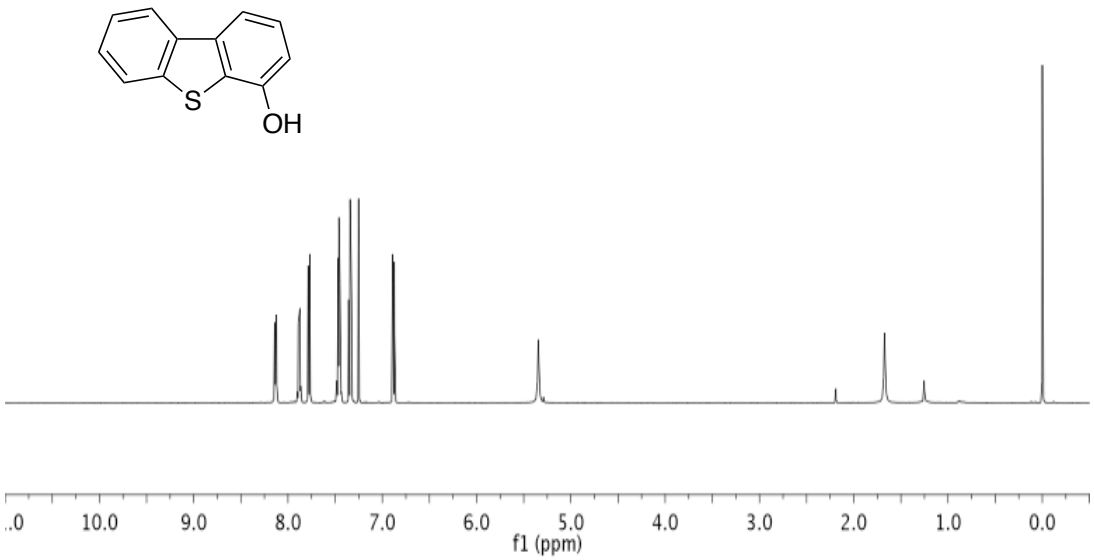


Figure A3.49 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of dibenzo[*b*,*d*]thiophen-4-ol

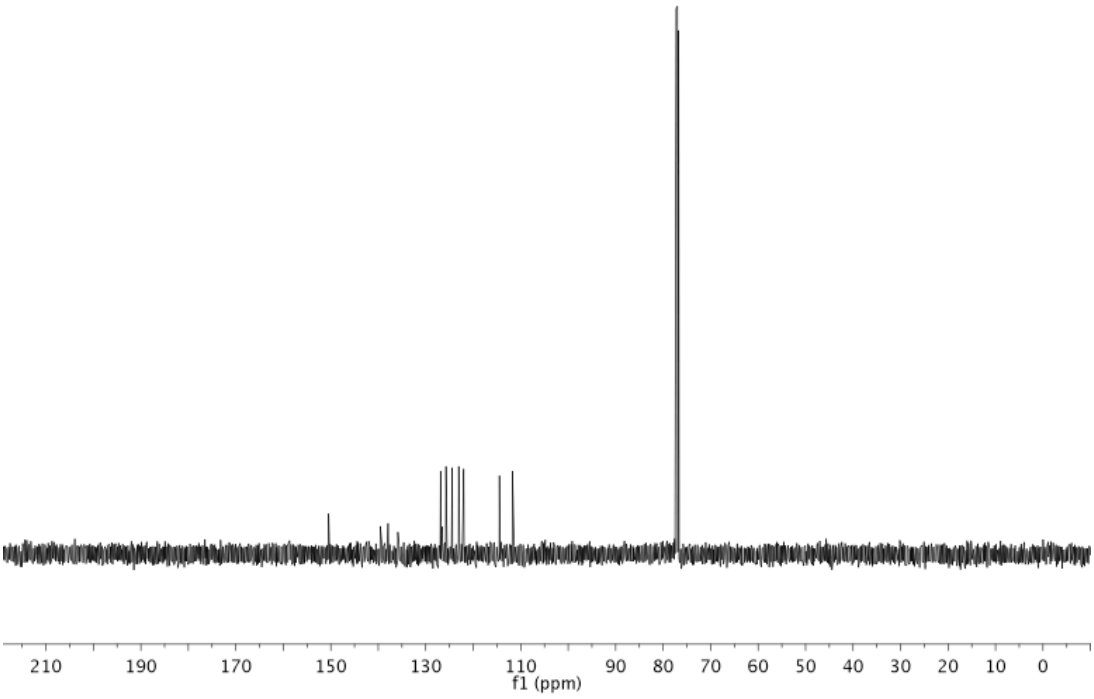


Figure A3.50 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of dibenzo[*b*,*d*]thiophen-4-ol

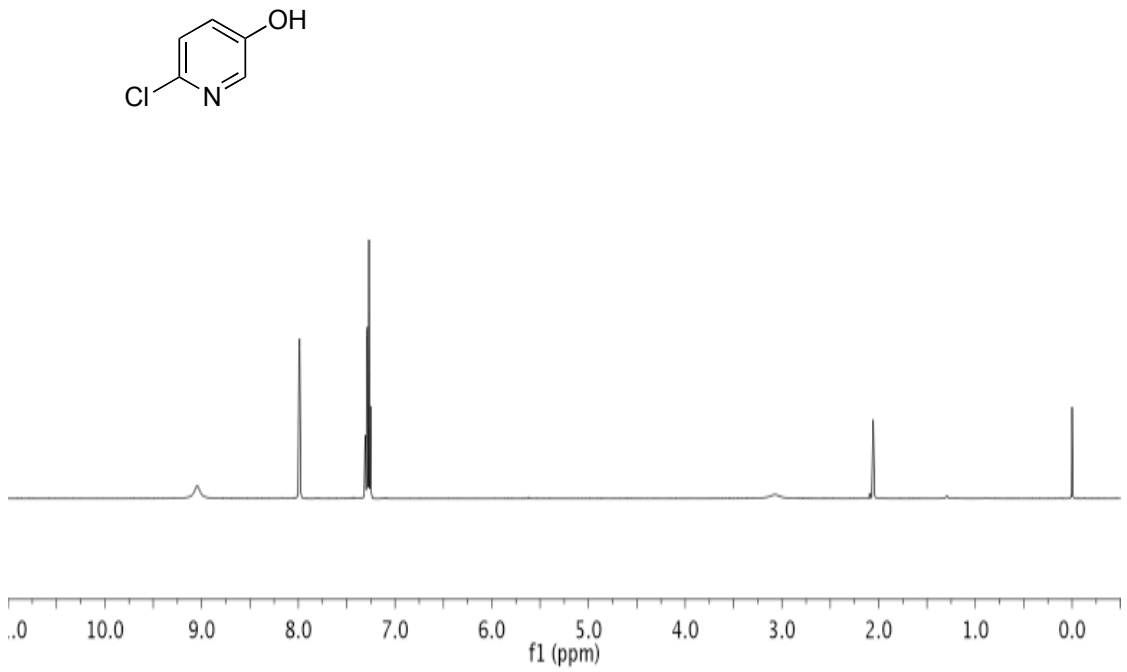


Figure A3.51 ^{1}H NMR (500 MHz, acetone-d_6) Spectrum of 6-chloropyridin-3-ol

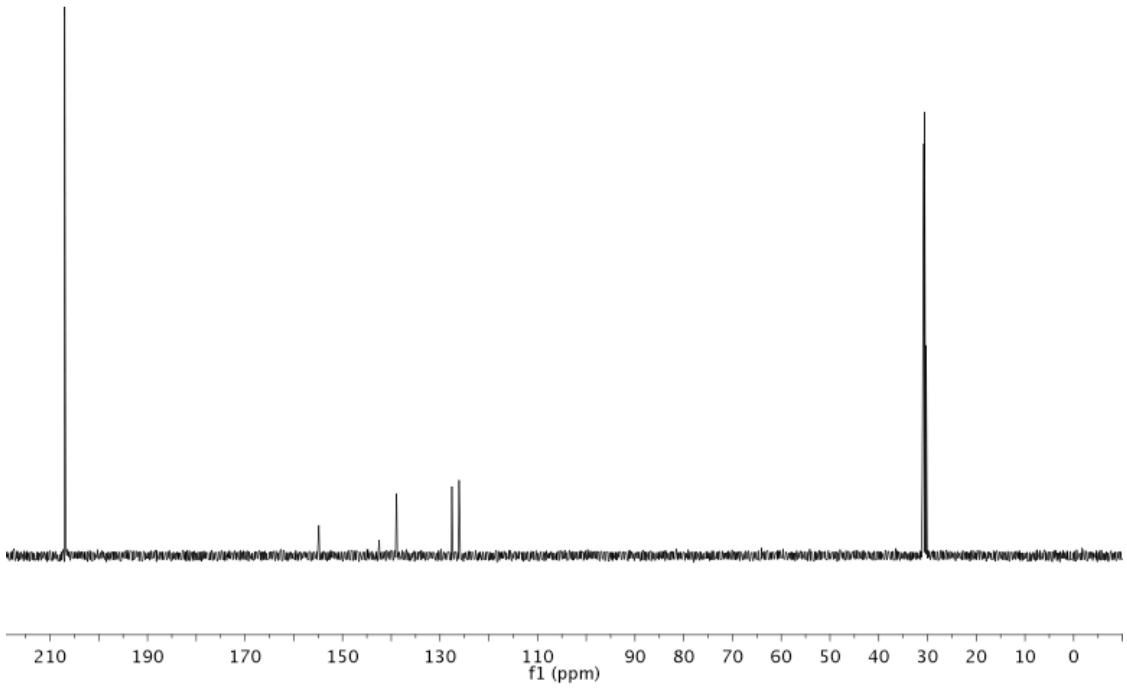


Figure A3.52 ^{13}C NMR (128.5 MHz, acetone-d_6) Spectrum of 6-chloropyridin-3-ol

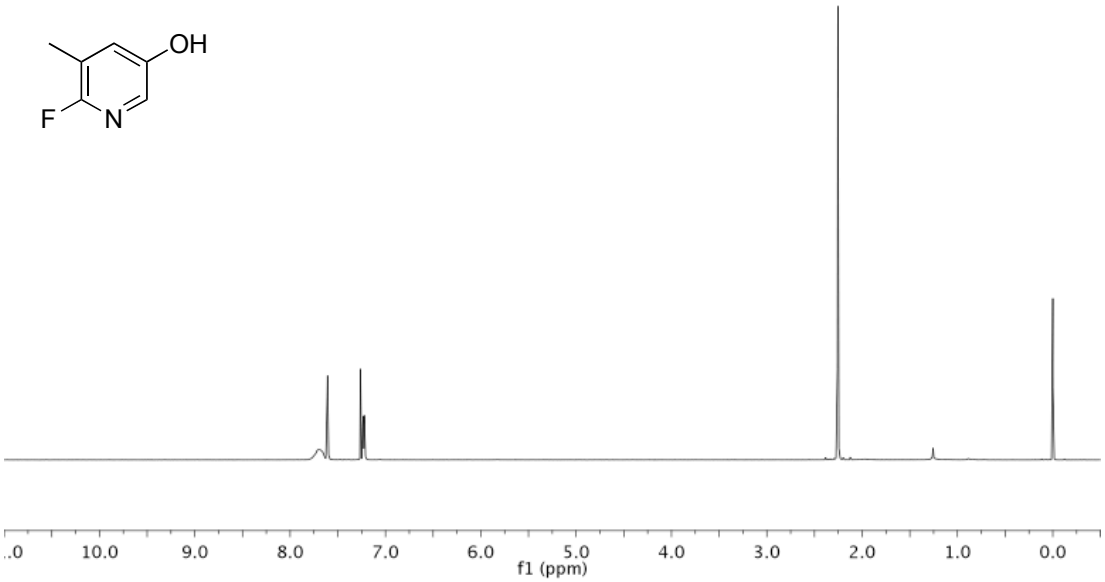


Figure A3.53 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 6-fluoro-5-methylpyridin-3-ol

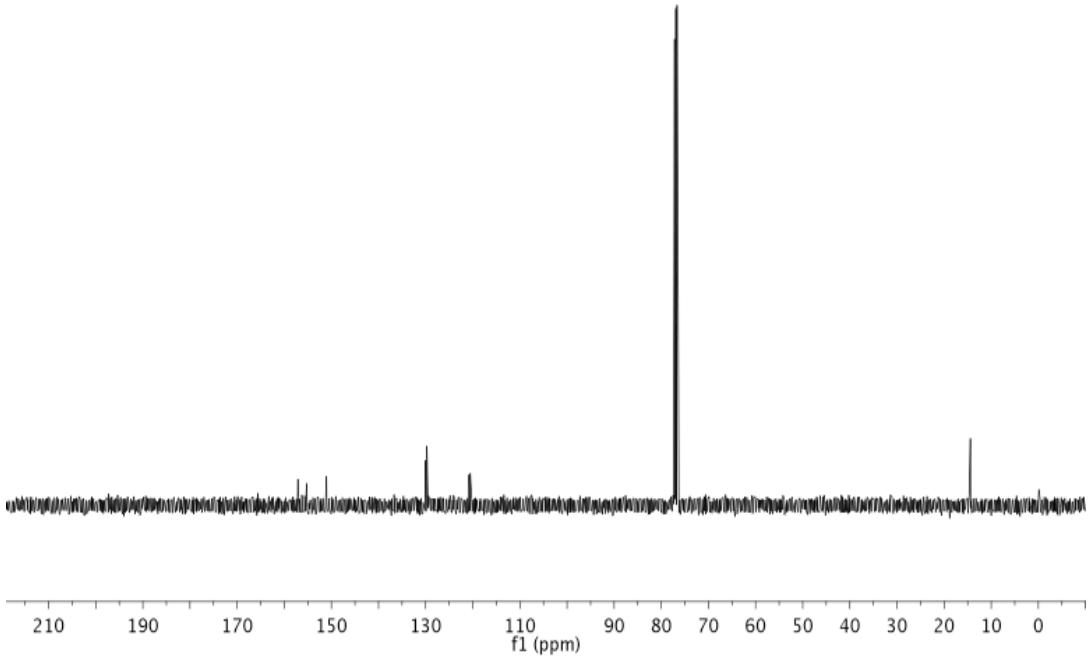


Figure A3.54 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 6-fluoro-5-methylpyridin-3-ol

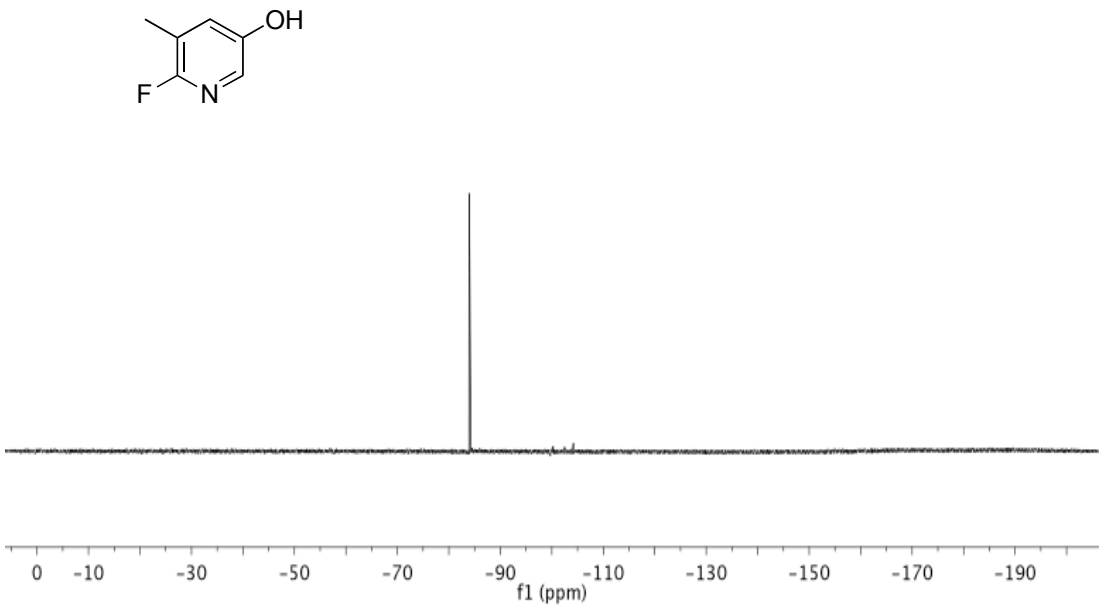


Figure A3.55 ^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of 6-fluoro-5-methylpyridin-3-ol

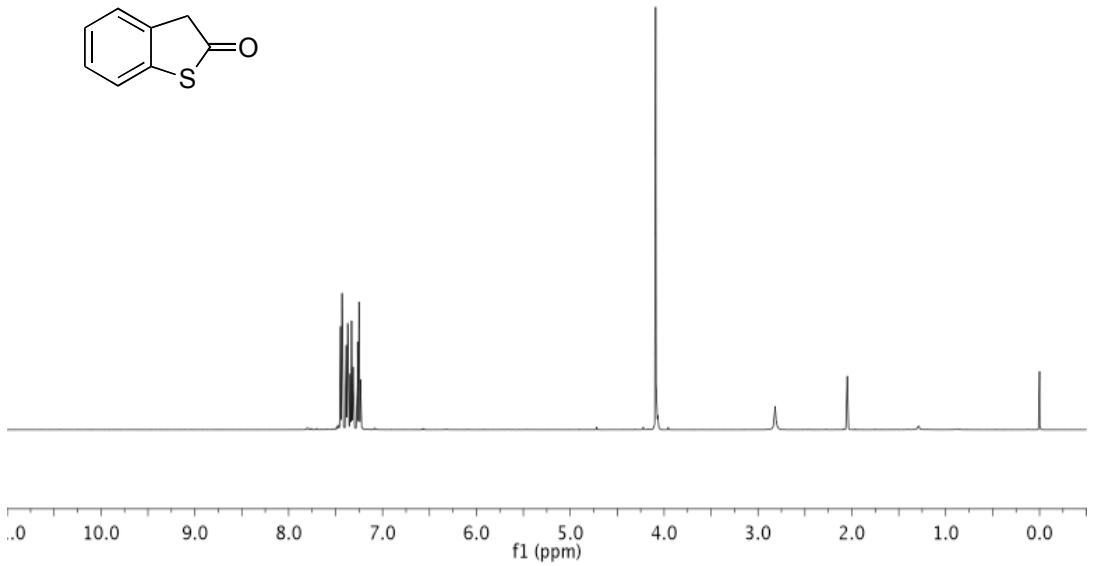


Figure A3.56 ^{1}H NMR (500 MHz, acetone-d_6) Spectrum of benzo[*b*]thiophen-2(3*H*)-one

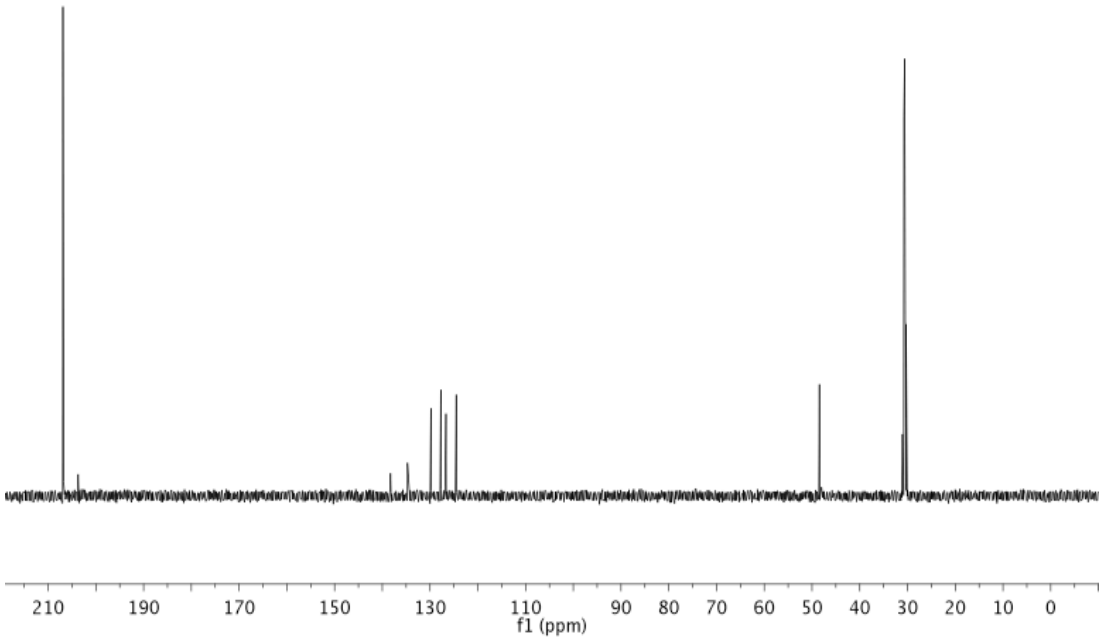


Figure A3.57 ^{13}C NMR (128.5 MHz, acetone-d_6) Spectrum of benzo[*b*]thiophen-2(3*H*)-one

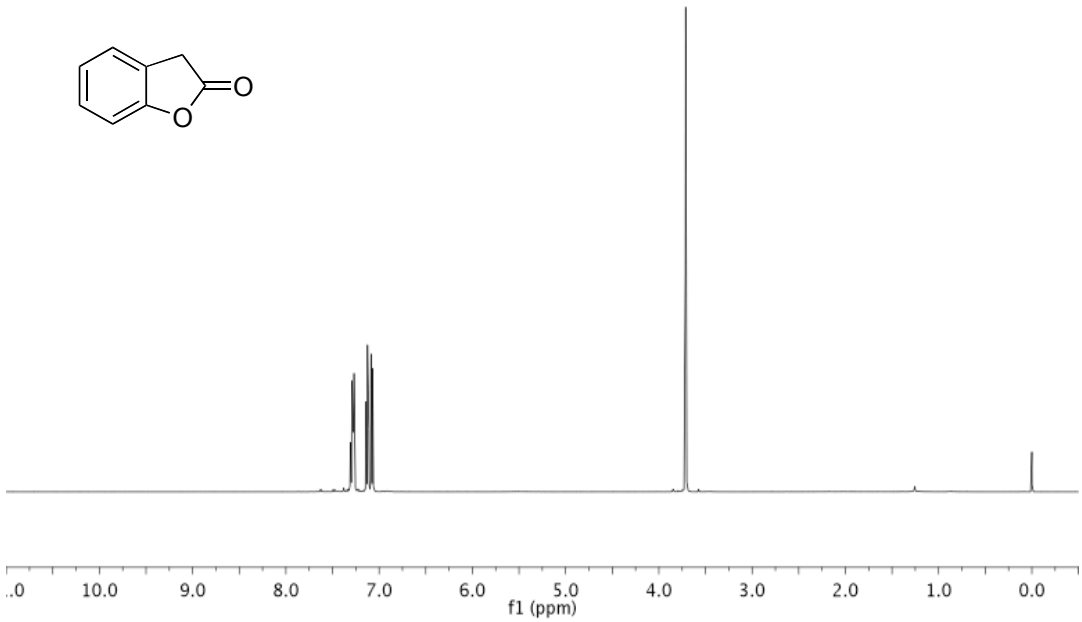


Figure A3.58 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of benzofuran-2(3*H*)-one

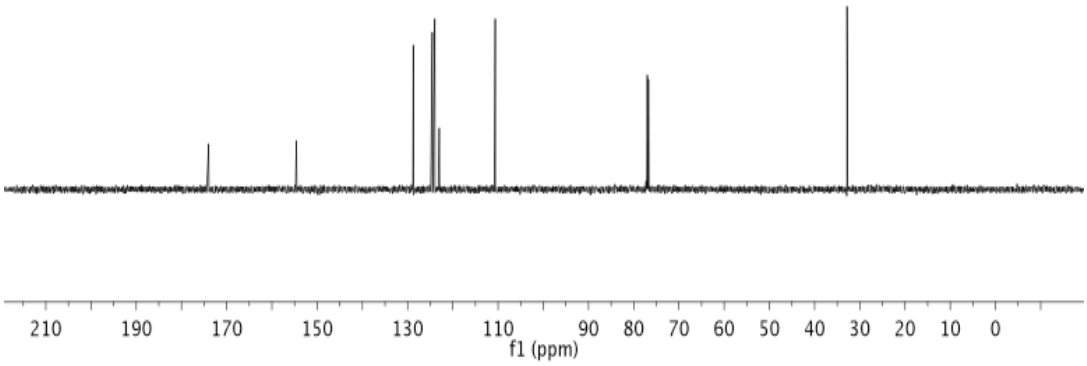


Figure A3.59 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of benzofuran-2(3*H*)-one

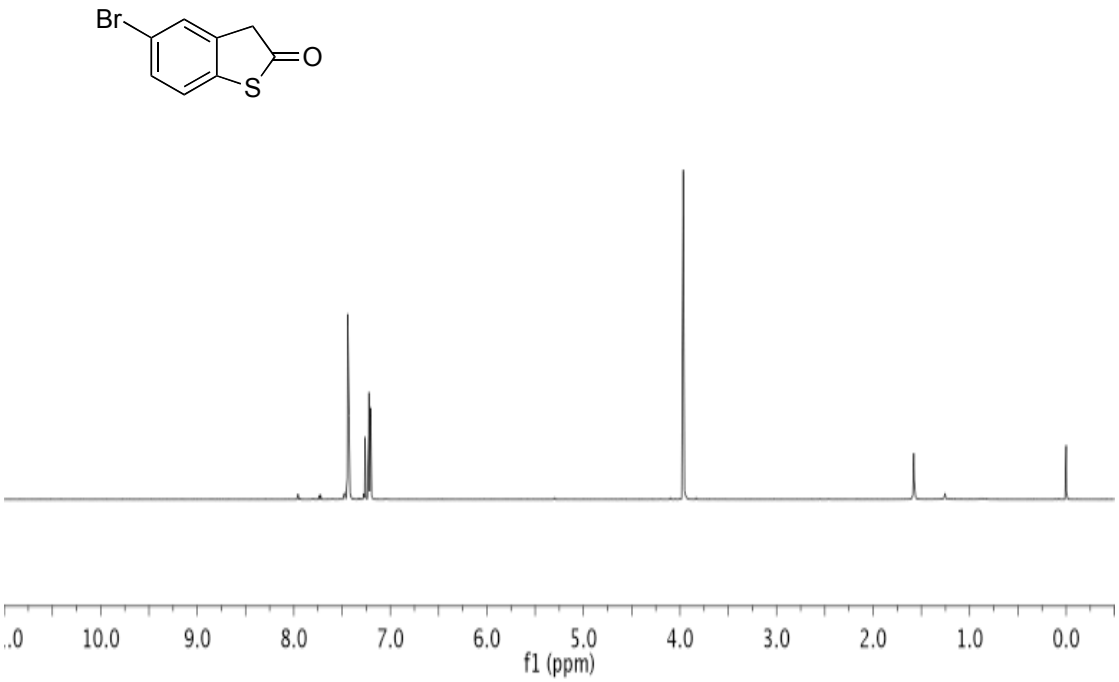


Figure A3.60 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 5-bromobenzo[*b*]thiophen-2(3*H*)-one

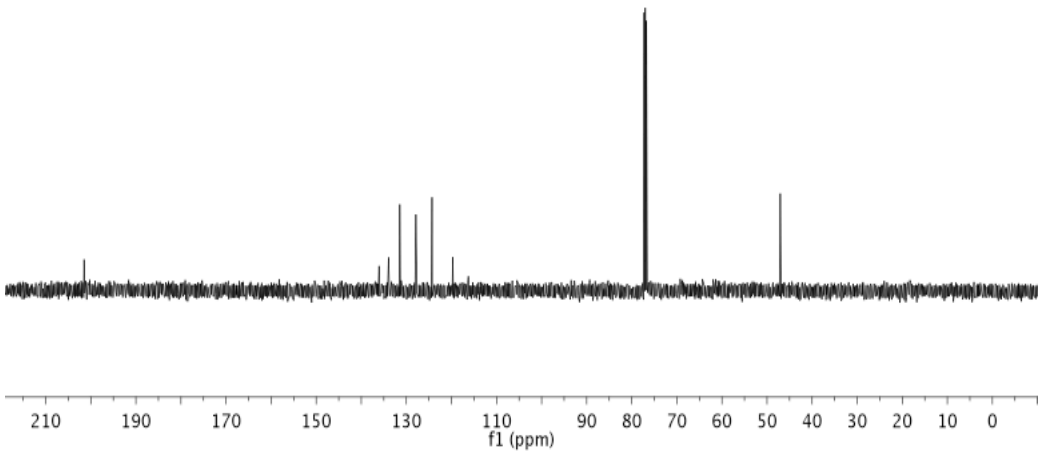


Figure A3.61 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 5-bromobenzo[*b*]thiophen-2(3*H*)-one

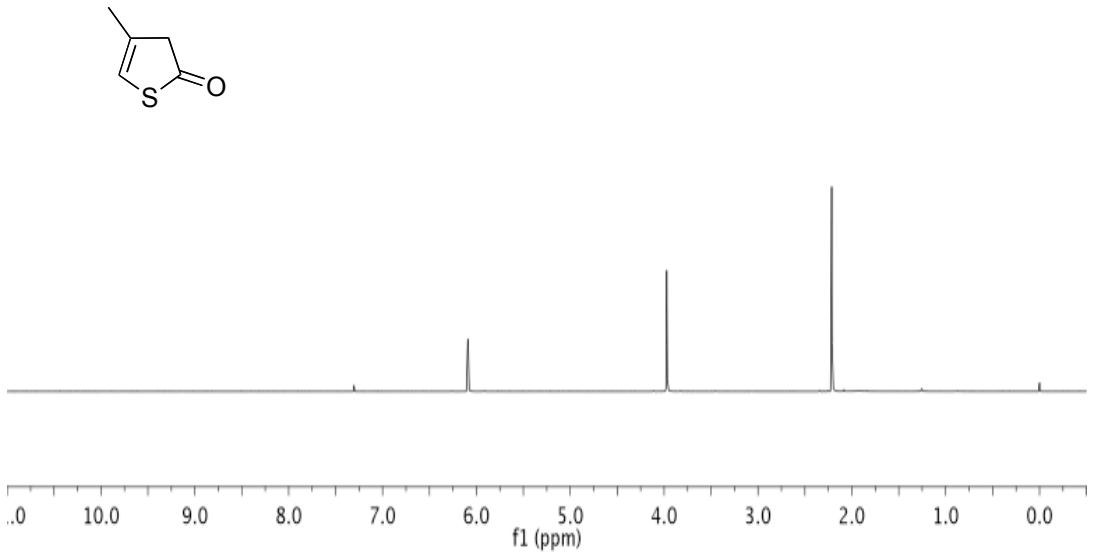


Figure A3.62 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-methylthiophen-2(3*H*)-one

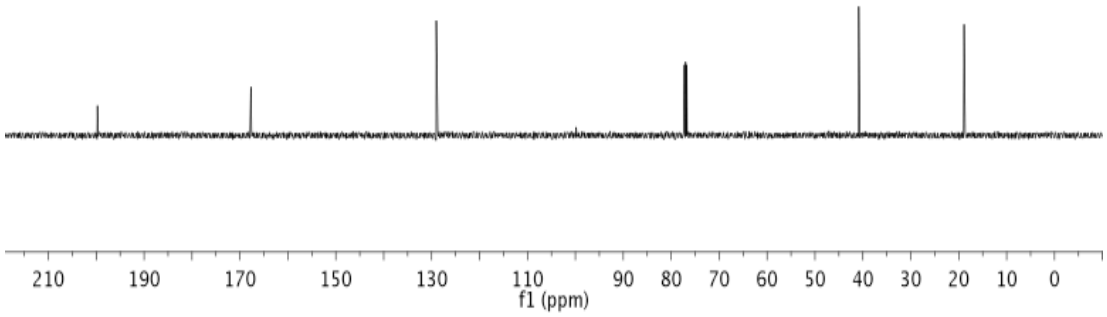


Figure A3.63 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-methylthiophen-2(3*H*)-one

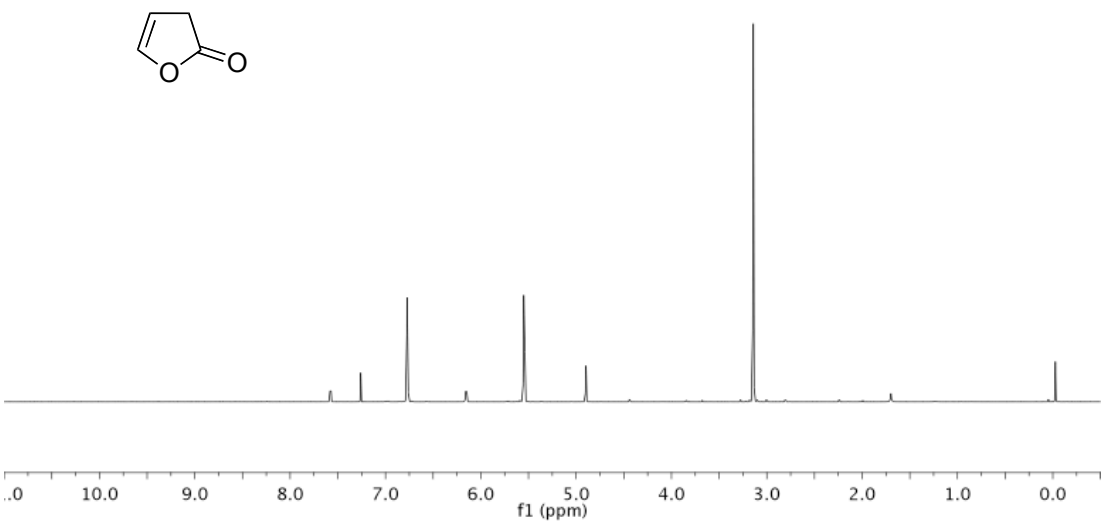


Figure A3.64 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of furan-2(3*H*)-one

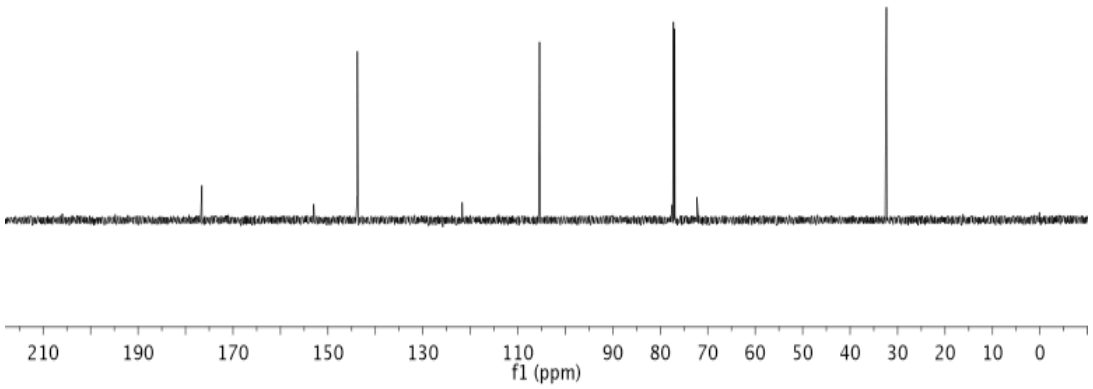


Figure A3.65 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of furan-2(3*H*)-one

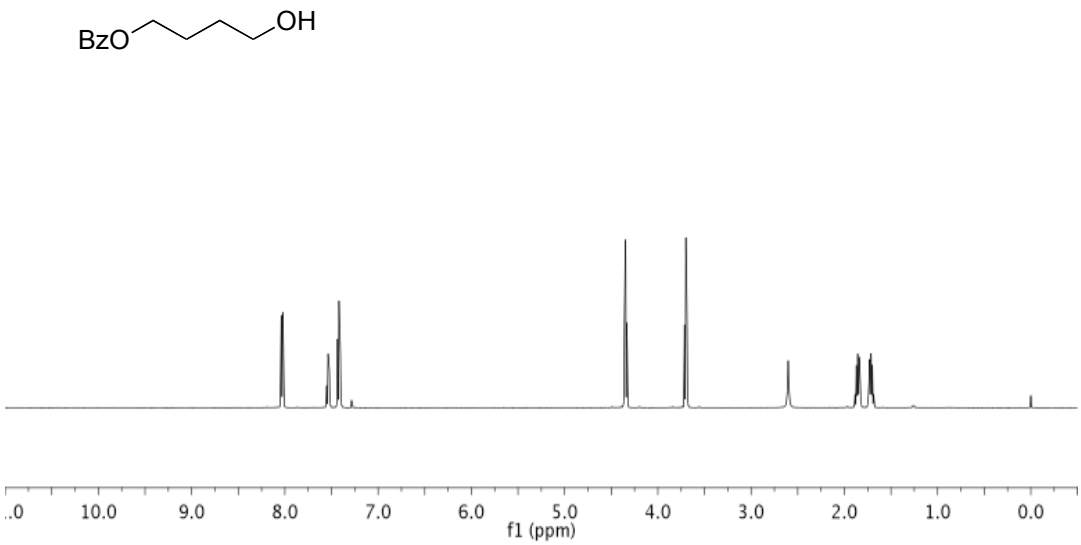


Figure A3.66 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-hydroxybutyl benzoate

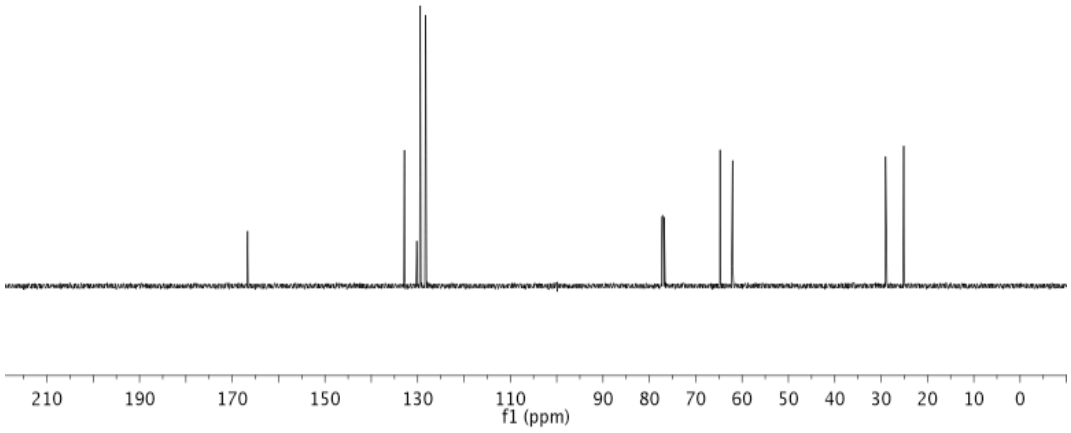


Figure A3.67 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-hydroxybutyl benzoate

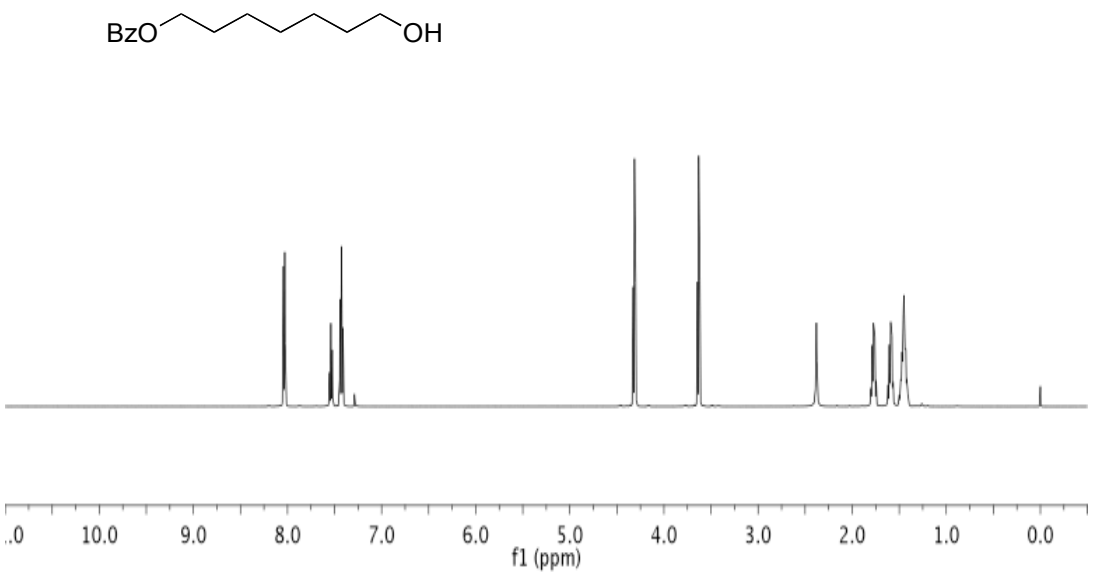


Figure A3.68 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 7-hydroxyheptylbenzoate

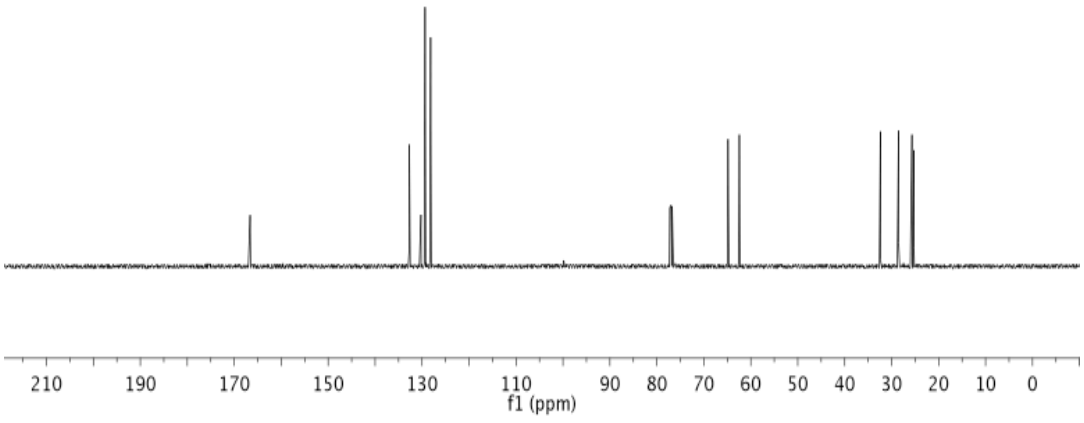


Figure A3.69 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 7-hydroxyheptylbenzoate

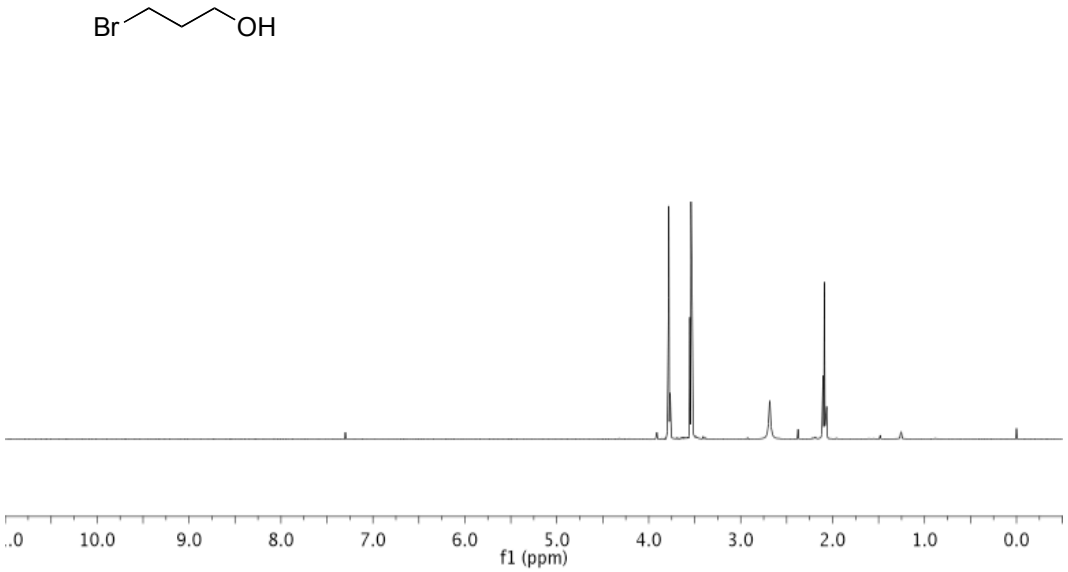


Figure A3.70 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 3-bromopropan-1-ol

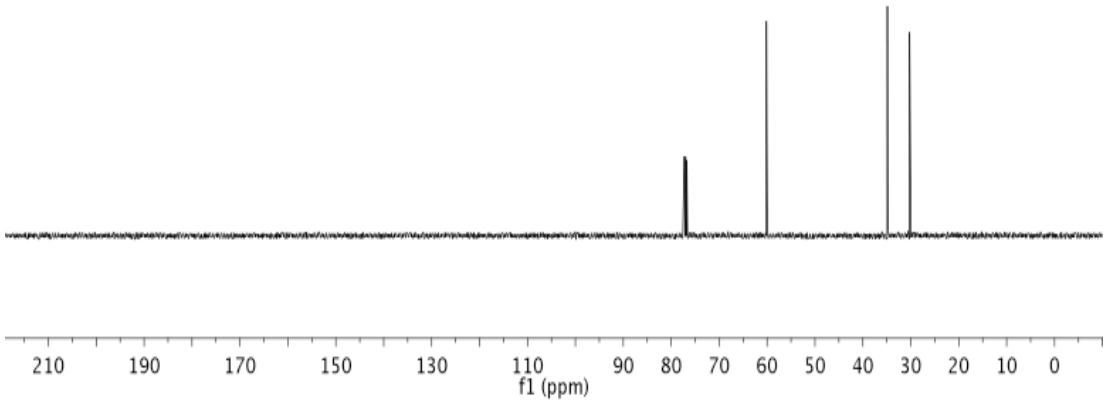


Figure A3.71 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 3-bromopropan-1-ol

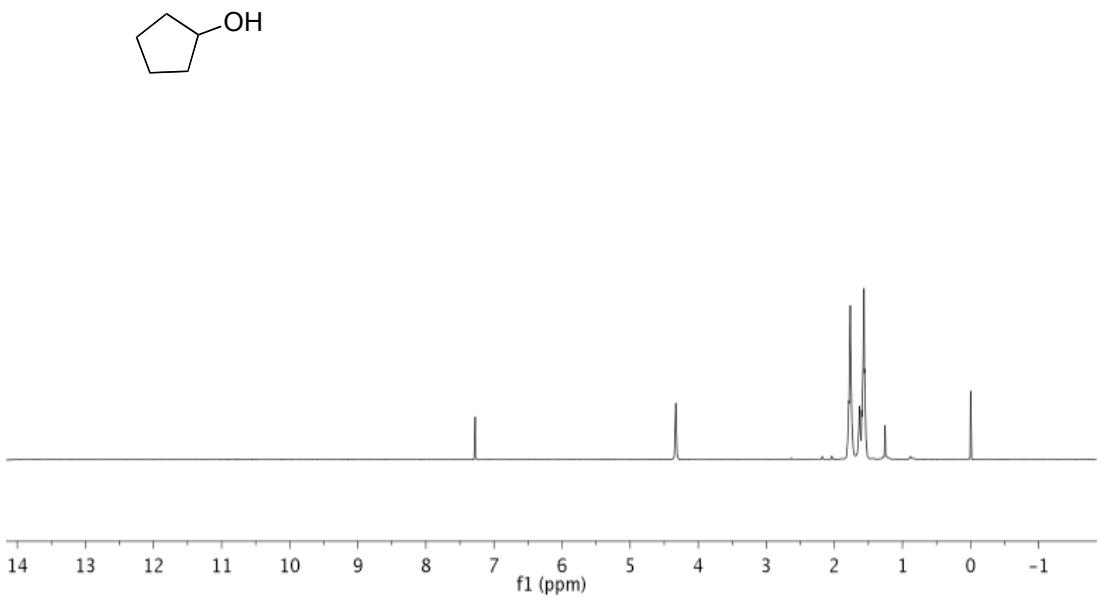


Figure A3.72 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of cyclopentanol

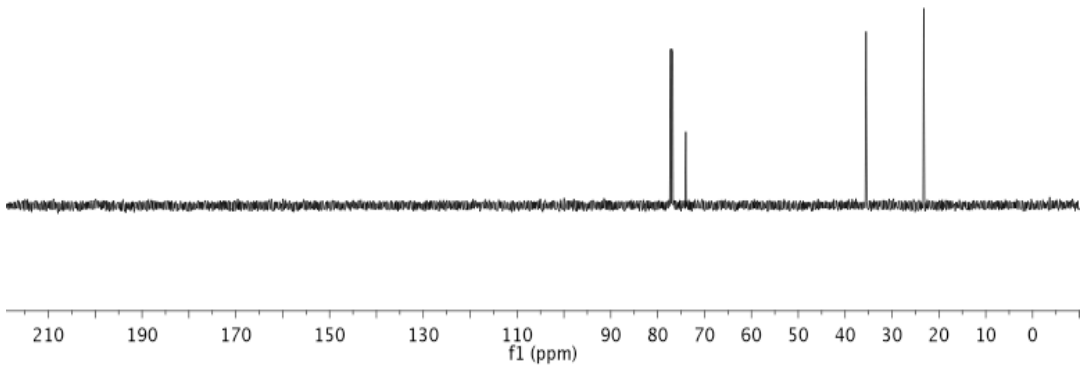


Figure A3.73 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of cyclopentanol

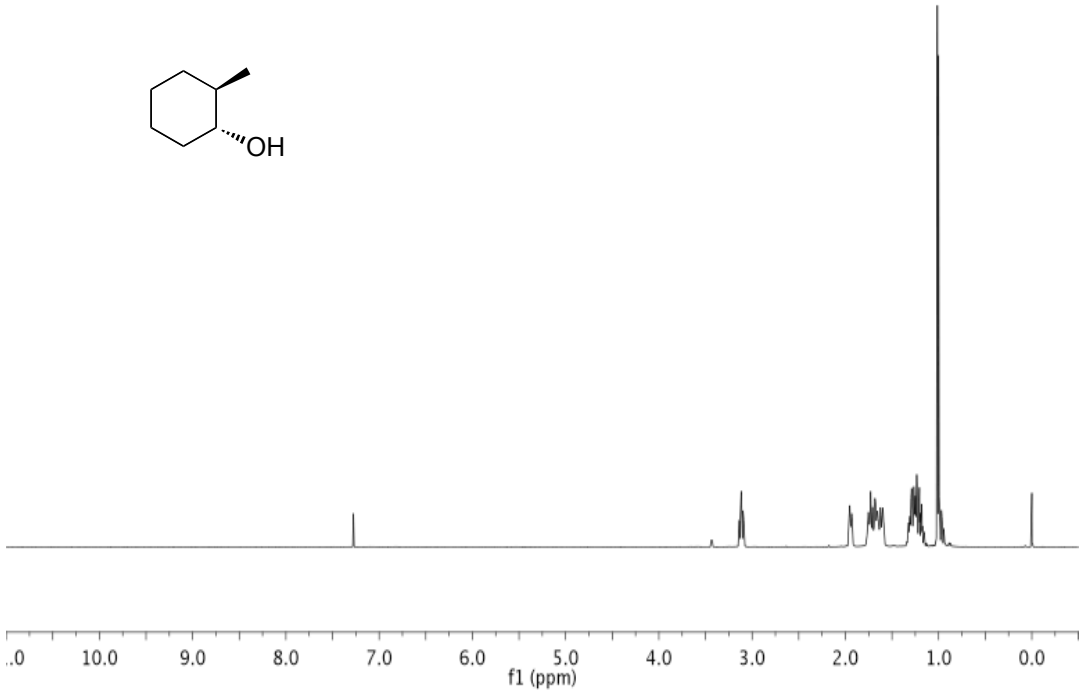


Figure A3.74 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-methylcyclohexanol

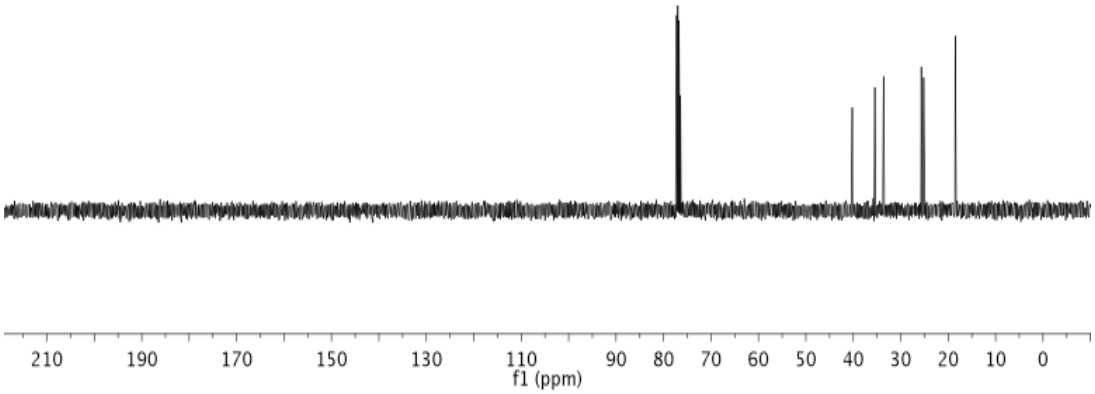


Figure A3.75 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2-methylcyclohexanol

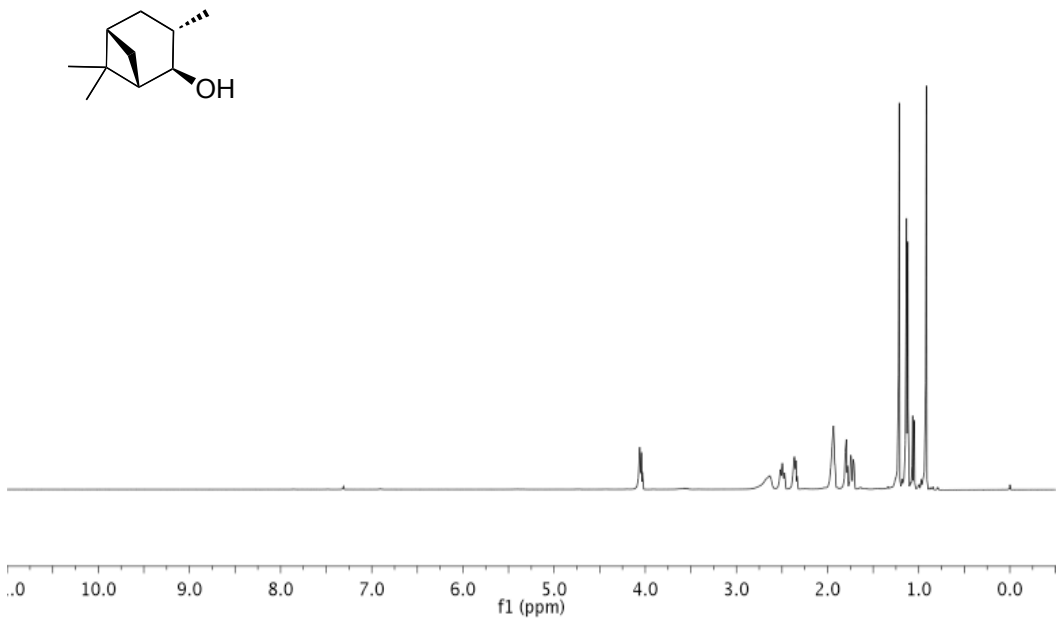


Figure A3.76 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 3,6,6-trimethylbicyclo[3.1.1]heptan-2-ol

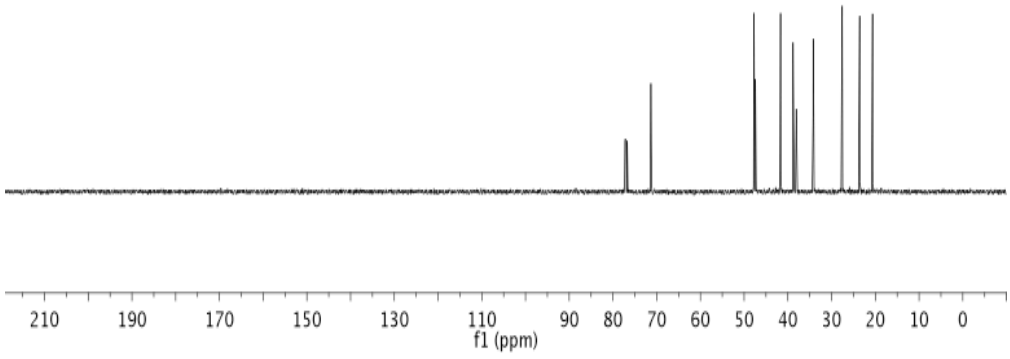


Figure A3.77 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 3,6,6-trimethylbicyclo[3.1.1]heptan-2-ol

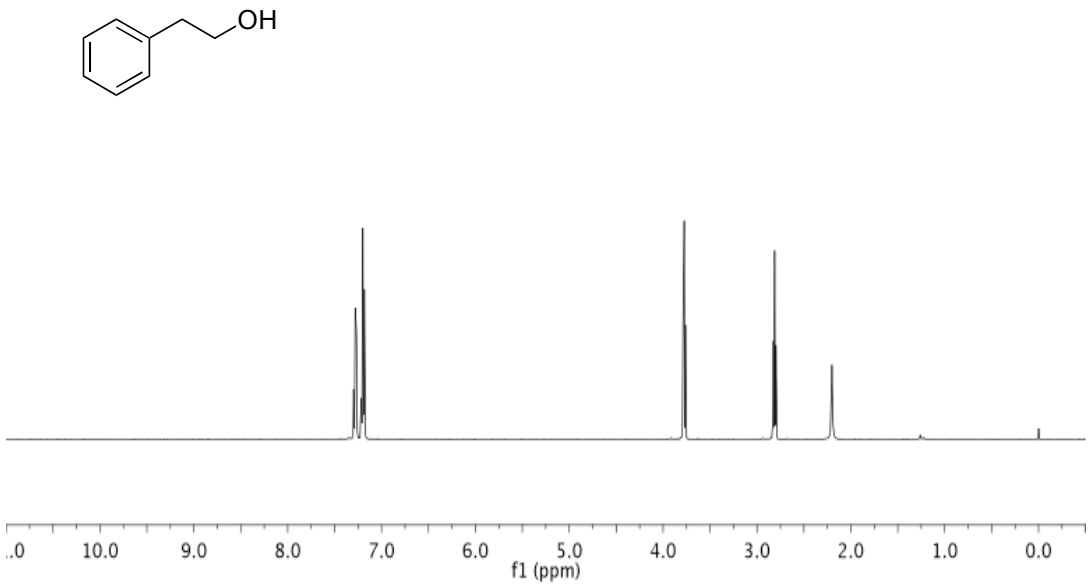


Figure A3.78 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-phenylethanol

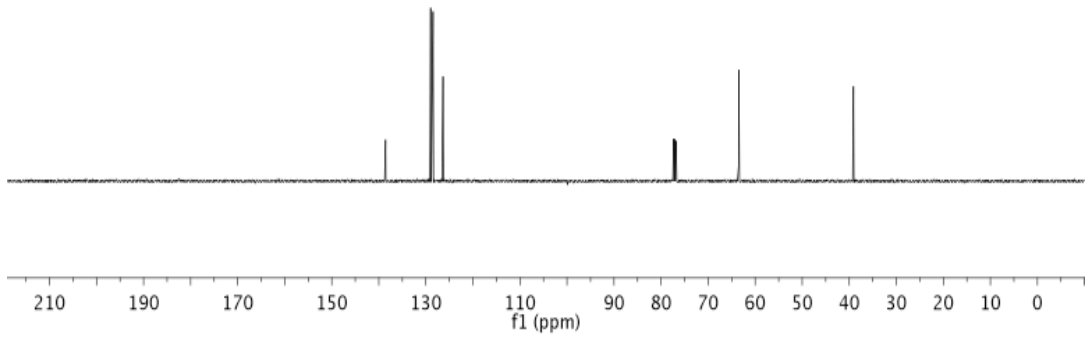


Figure A3.79 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2-phenylethanol

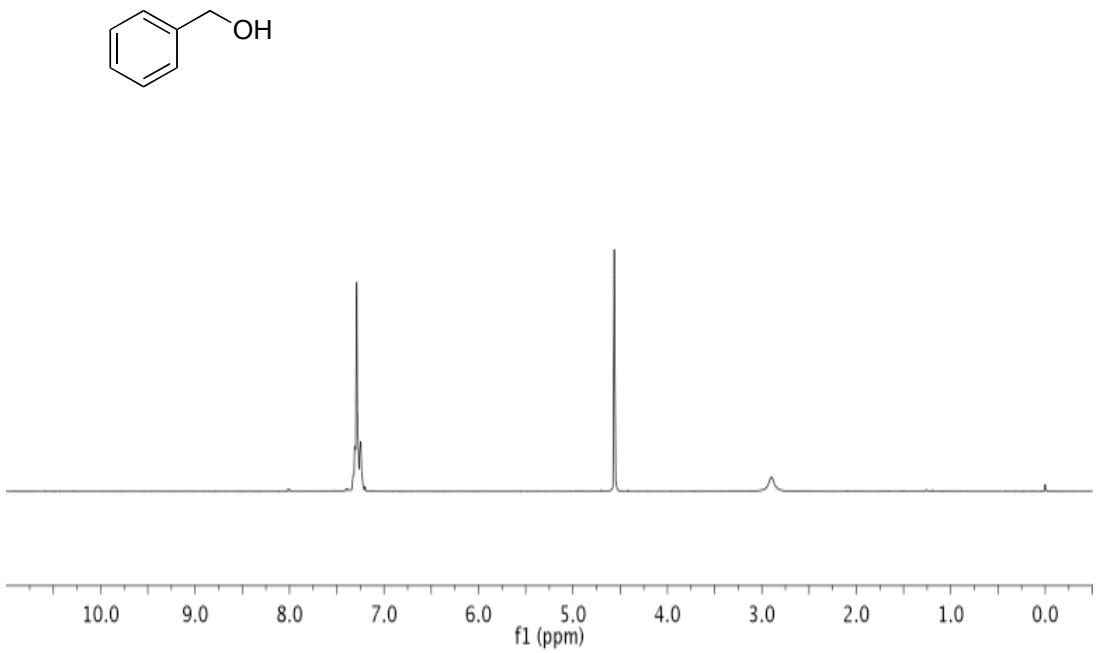


Figure A3.80 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of phenylmethanol

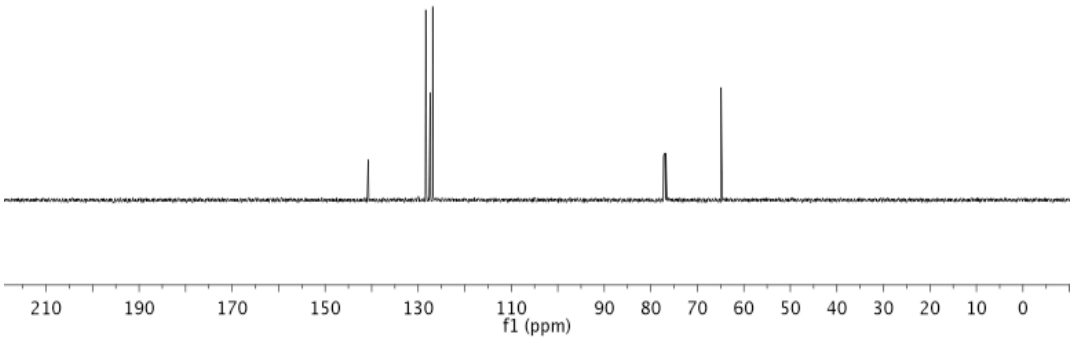


Figure A3.81 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of phenylmethanol

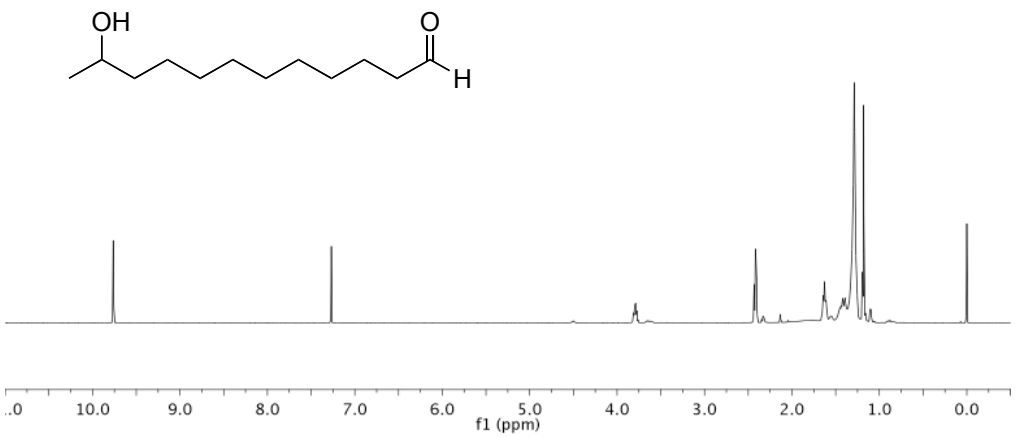


Figure A3.82 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 11-hydroxydodecanal

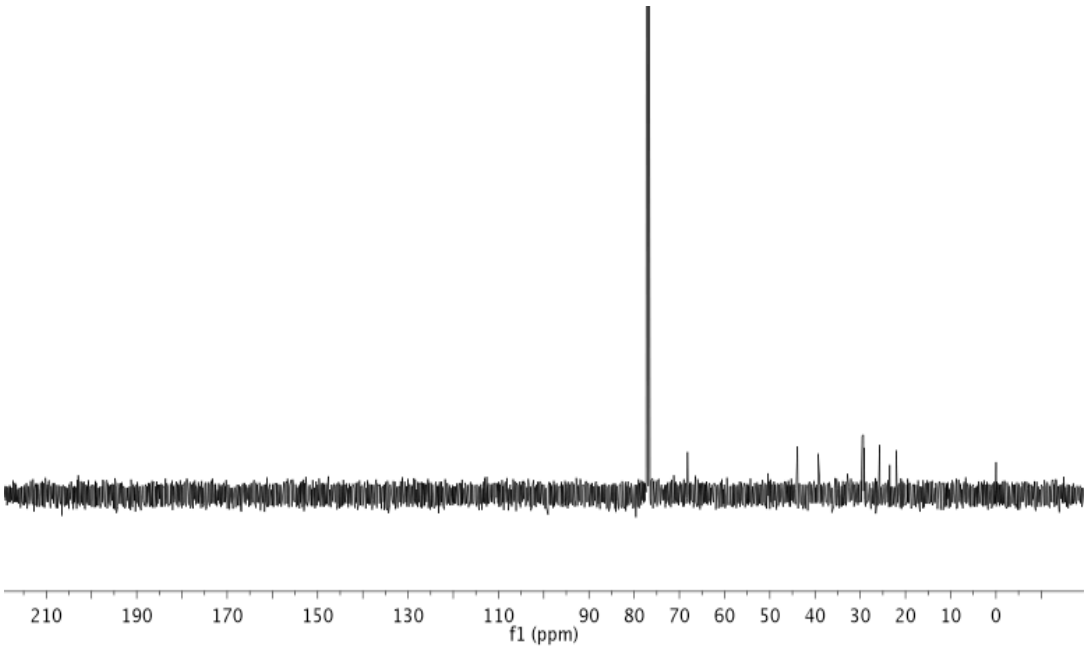


Figure A3.83 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 11-hydroxydodecanal

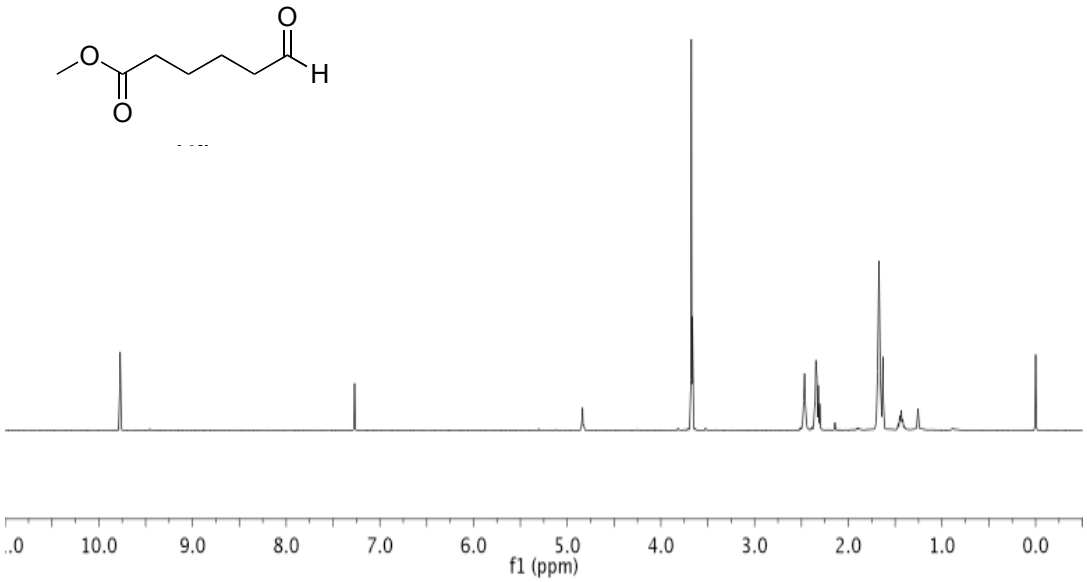


Figure A3.84 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of methyl 6-oxohexanoate

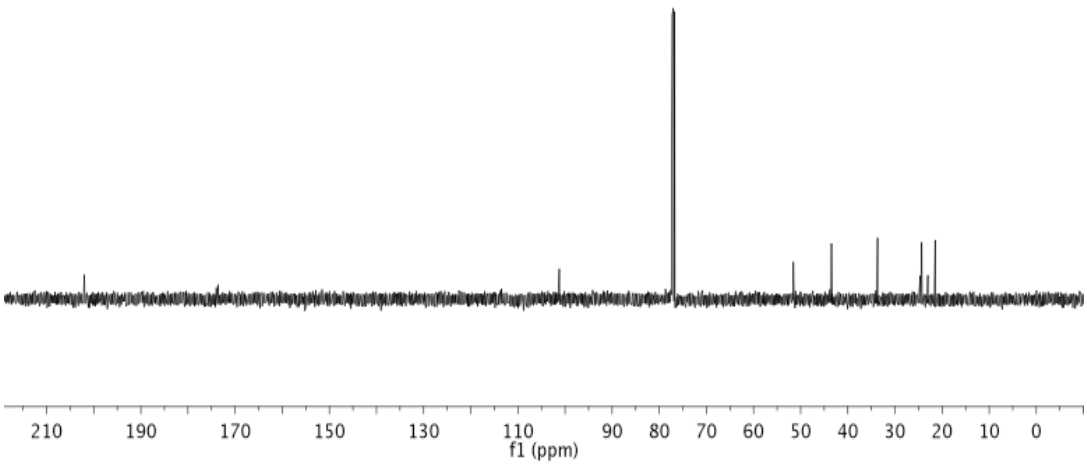


Figure A3.85 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of methyl 6-oxohexanoate

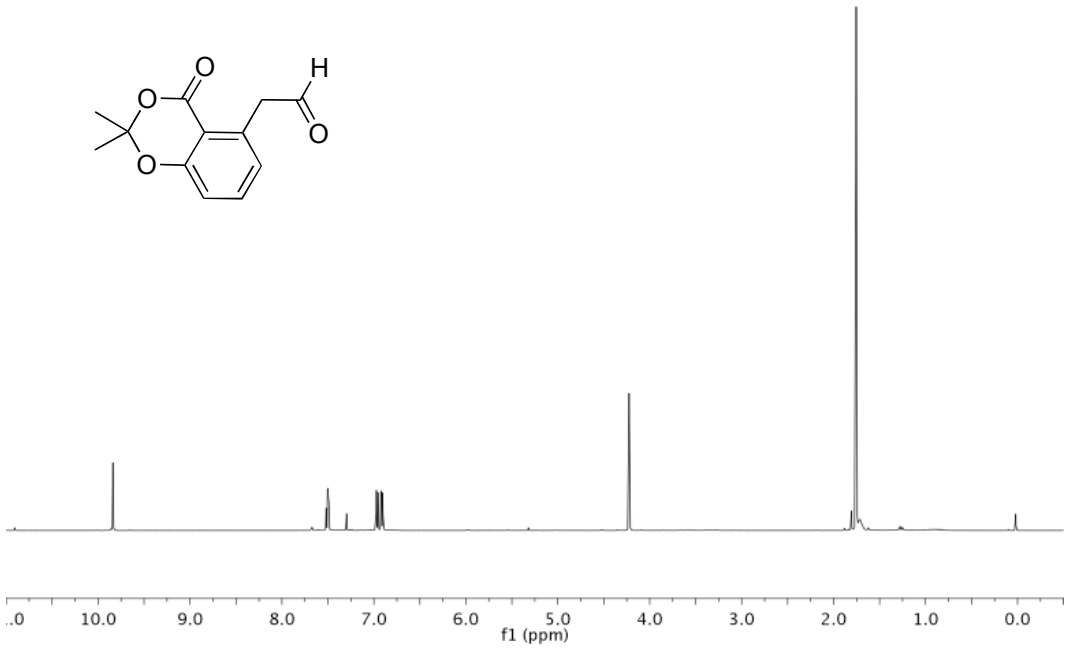


Figure A3.86 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-(2,2-dimethyl-4-oxo-4*H*-benzo[*d*][1,3]dioxin-5-yl)acetaldehyde

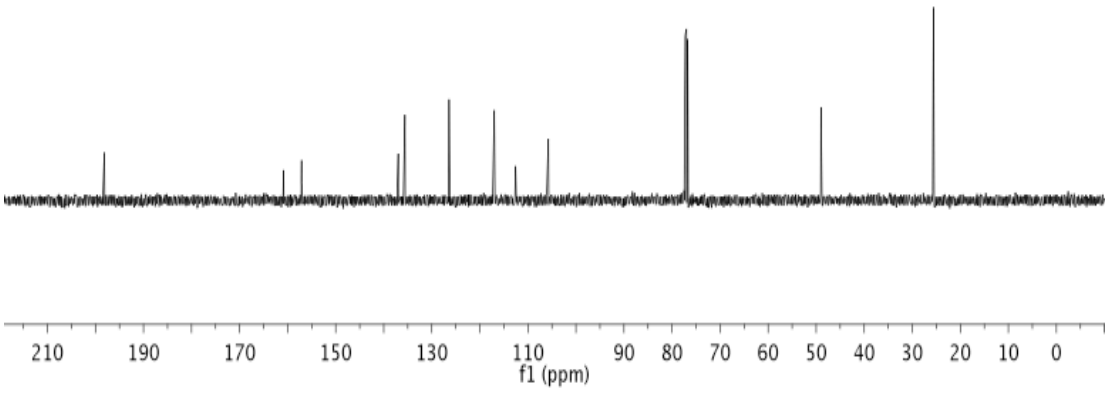


Figure A3.87 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2-(2,2-dimethyl-4-oxo-4*H*-benzo[*d*][1,3]dioxin-5-yl)acetaldehyde

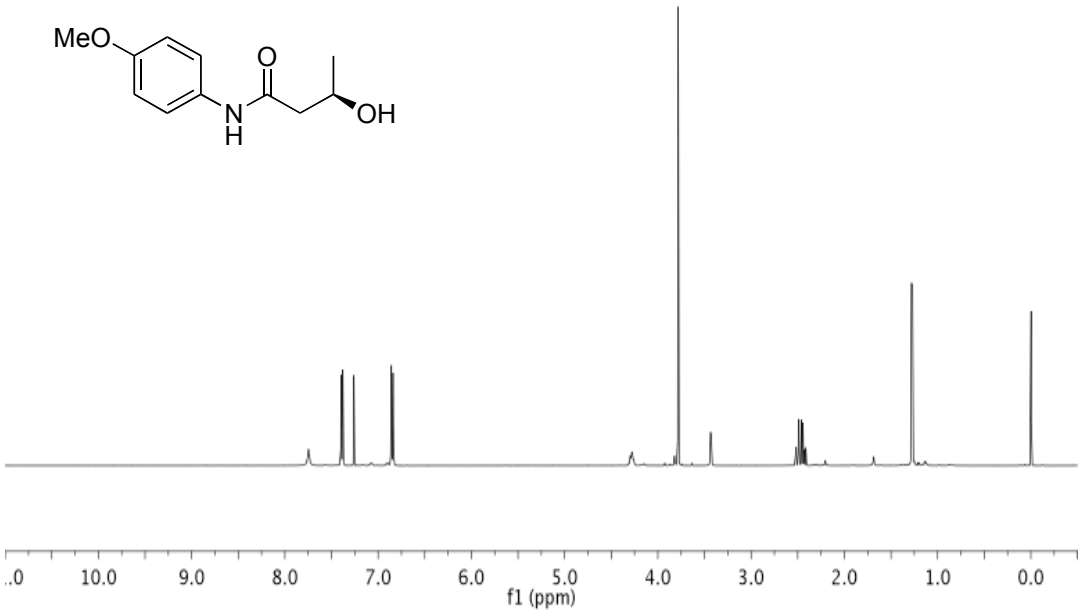


Figure A3.88 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of (*R*)-3-hydroxy-*N*-(4-methoxyphenyl)butanamide

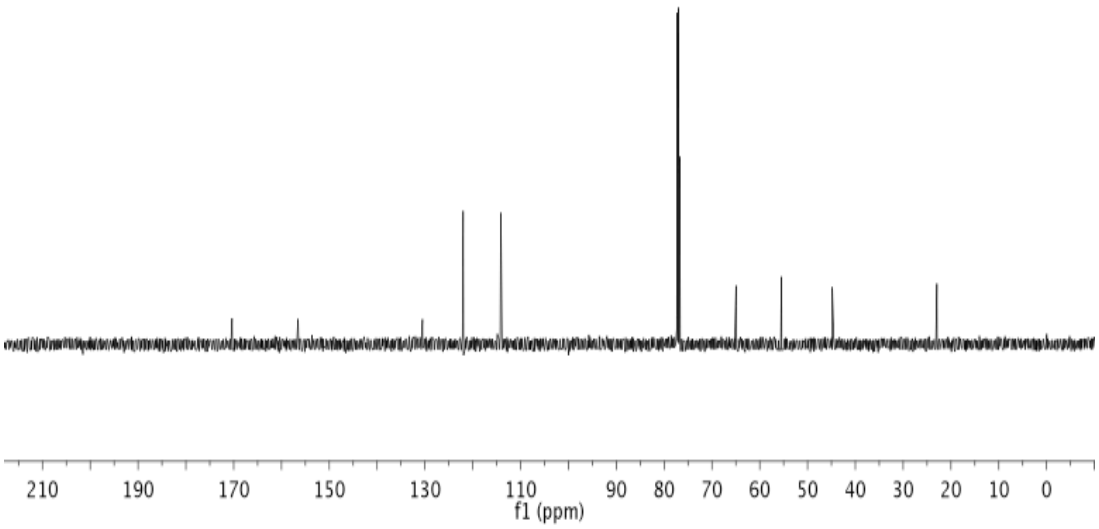
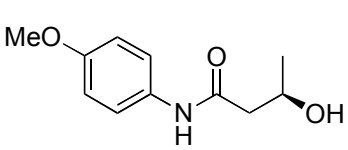


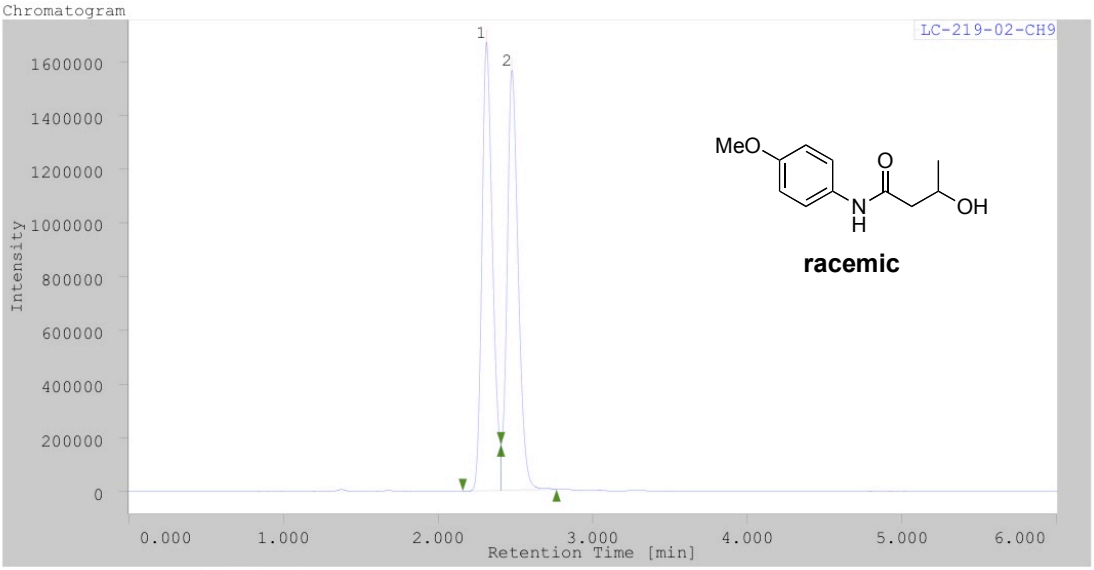
Figure A3.89 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of (*R*)-3-hydroxy-*N*-(4-methoxyphenyl)butanamide



Analysis of 3-Hydroxy-*N*-(4-methoxyphenyl)butanamide using SFC. Analysis was performed using Column OD-H, 20% *i*-PrOH, 4 mL, 12MPa.

(*S*) – isomer t_r = 2.3 min and (*R*) – isomer t_r = 2.4 min.

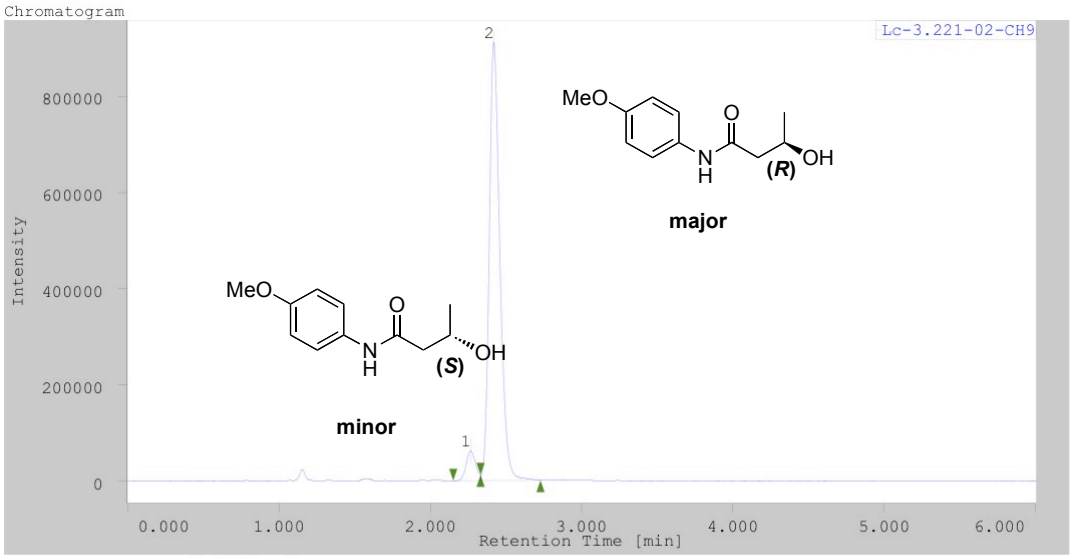
Chromatogram of racemic 3-Hydroxy-*N*-(4-methoxyphenyl)butanamide product:



Peak Information

#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Quantity	Symmetry Factor
1	9	2.312	7997572	1669395	50.914	N/A	N/A
2	9	2.477	7710444	1562457	49.086	N/A	N/A

Chromatogram of enantioenriched 3-Hydroxy-*N*-(4-methoxyphenyl)butanamide product:



Peak Information

#	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Quantity	Symmetry Factor
1	9	2.267	270816	61808	5.749	N/A	N/A
2	9	2.420	4440056	911449	94.251	N/A	1.251

Appendix A4. ^{1}H, ^{13}C and ^{19}F Spectra Relevant to Chapter 2.5

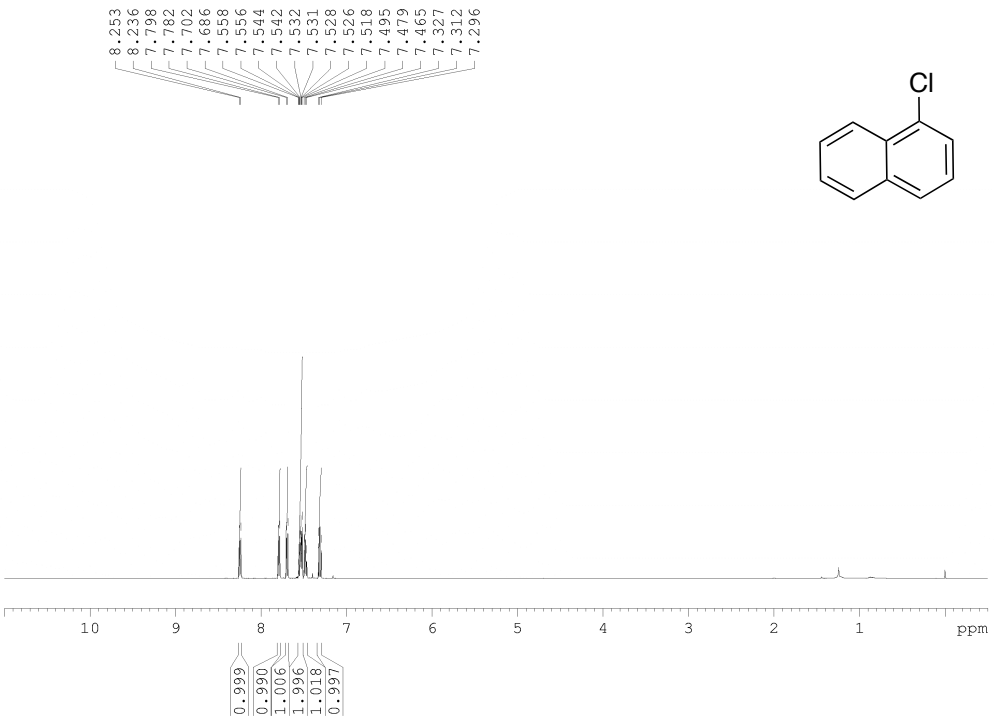


Figure A4.1 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-Chloronaphthalene

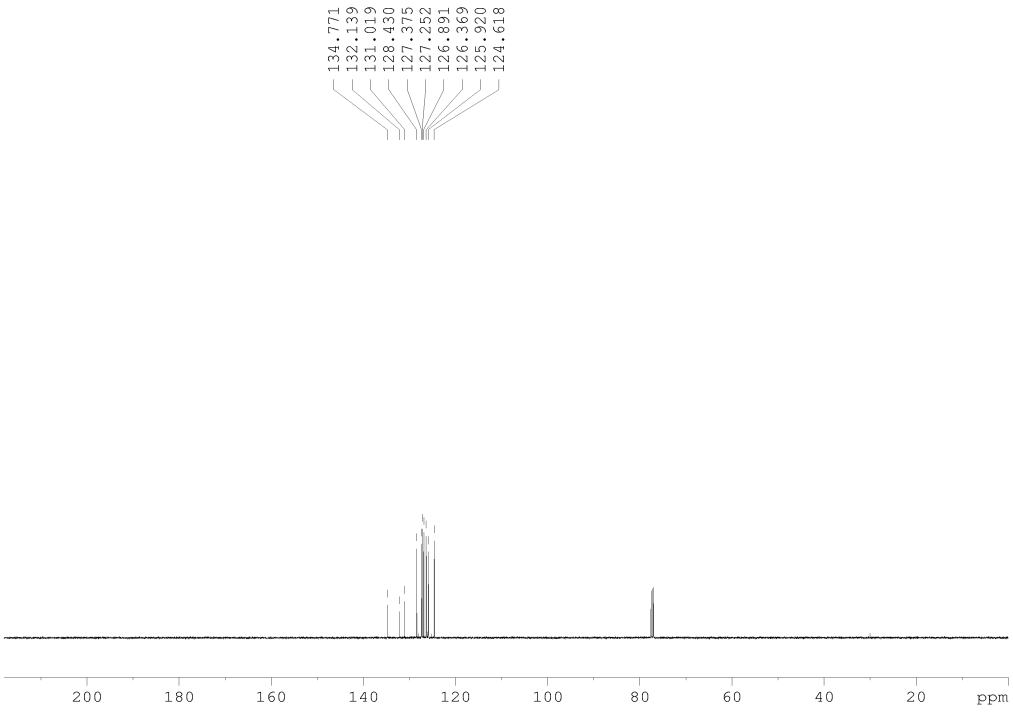


Figure A4.2 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-Chloronaphthalene

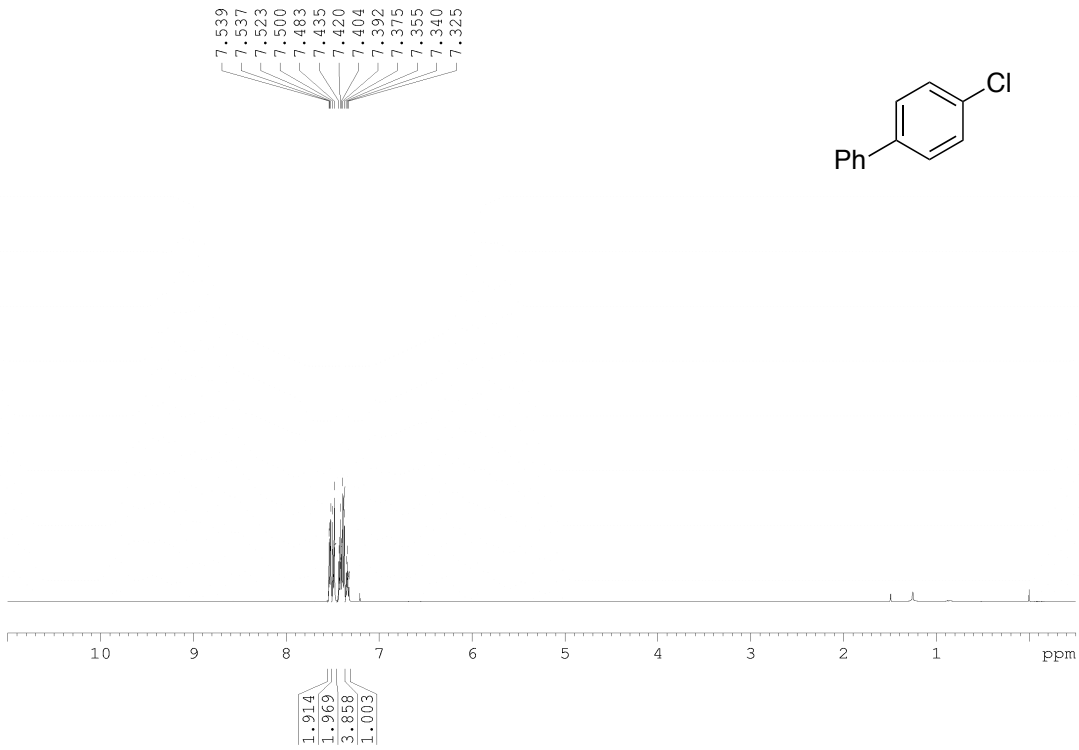


Figure A4.3 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-Chlorobiphenyl

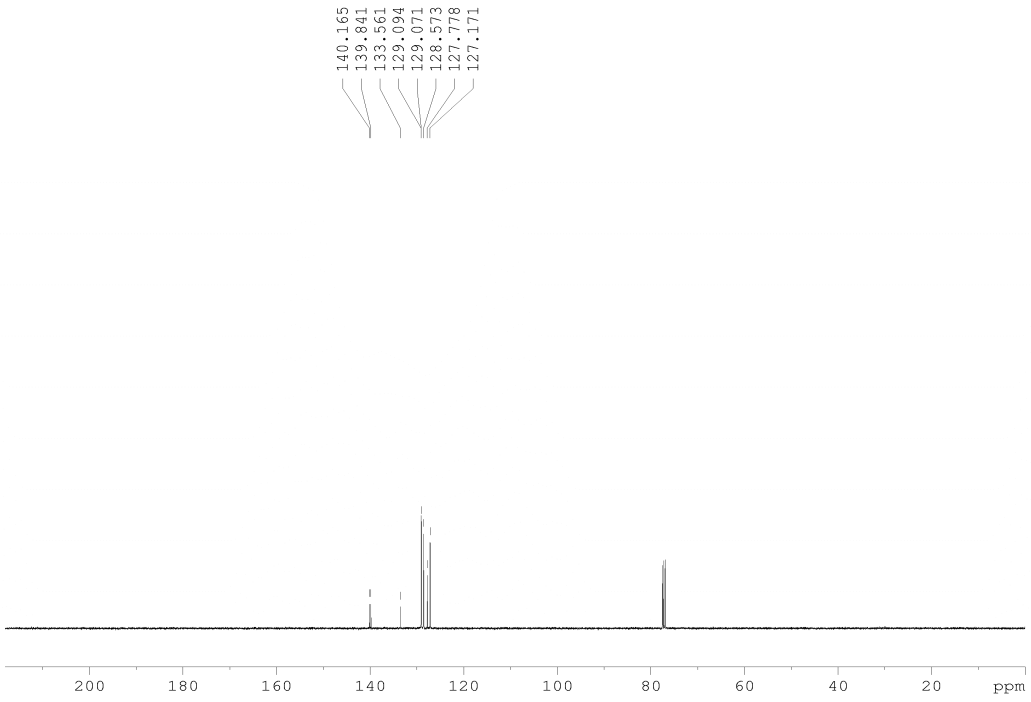


Figure A4.4 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-Chlorobiphenyl

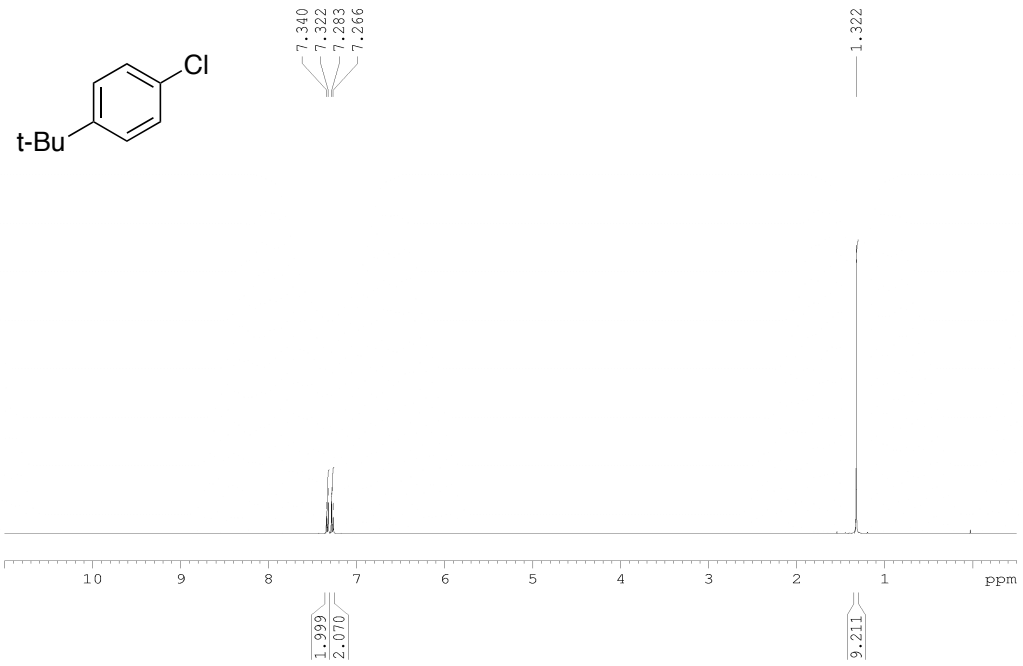


Figure A4.5 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-*tert*-butyl-4-chlorobenzene

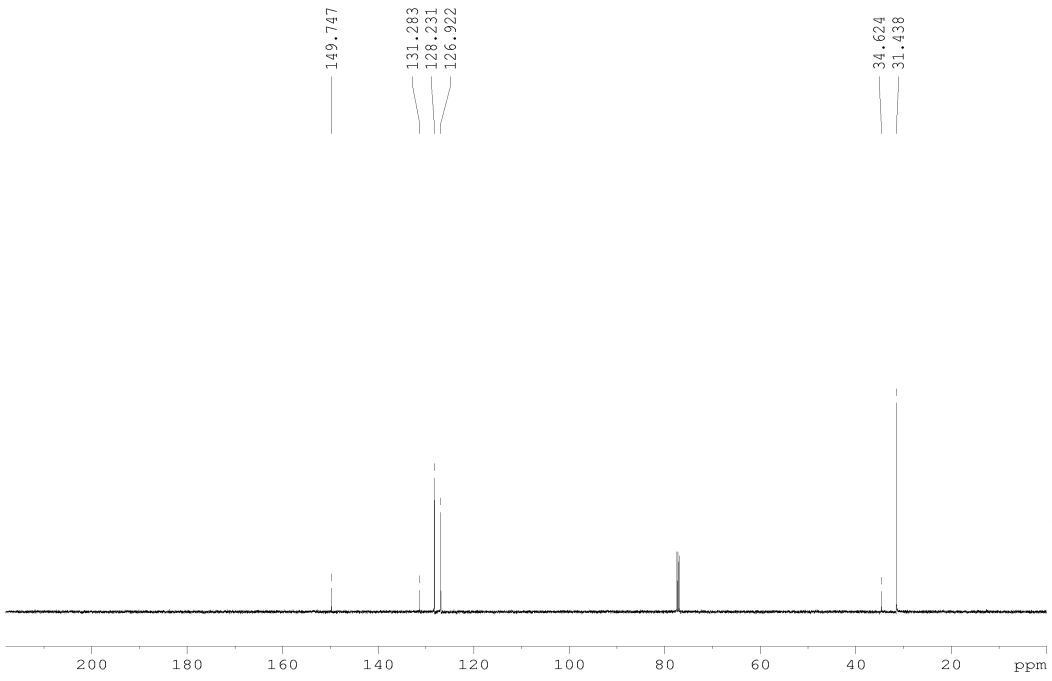


Figure A4.6 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-*tert*-butyl-4-chlorobenzene

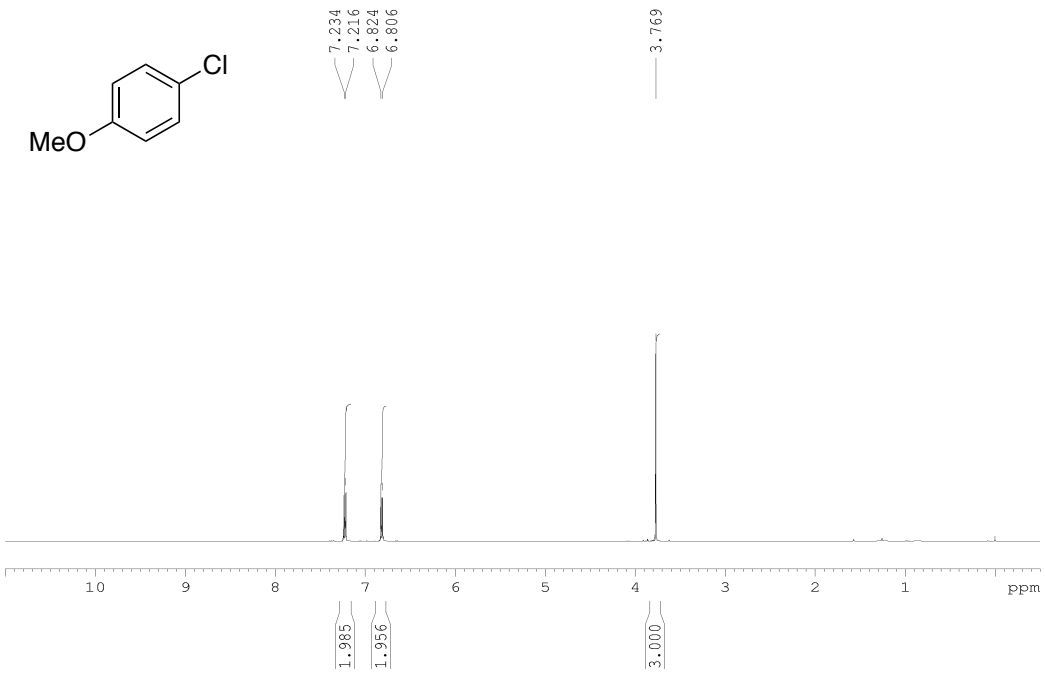


Figure A4.7 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-chloro-4-methoxybenzene

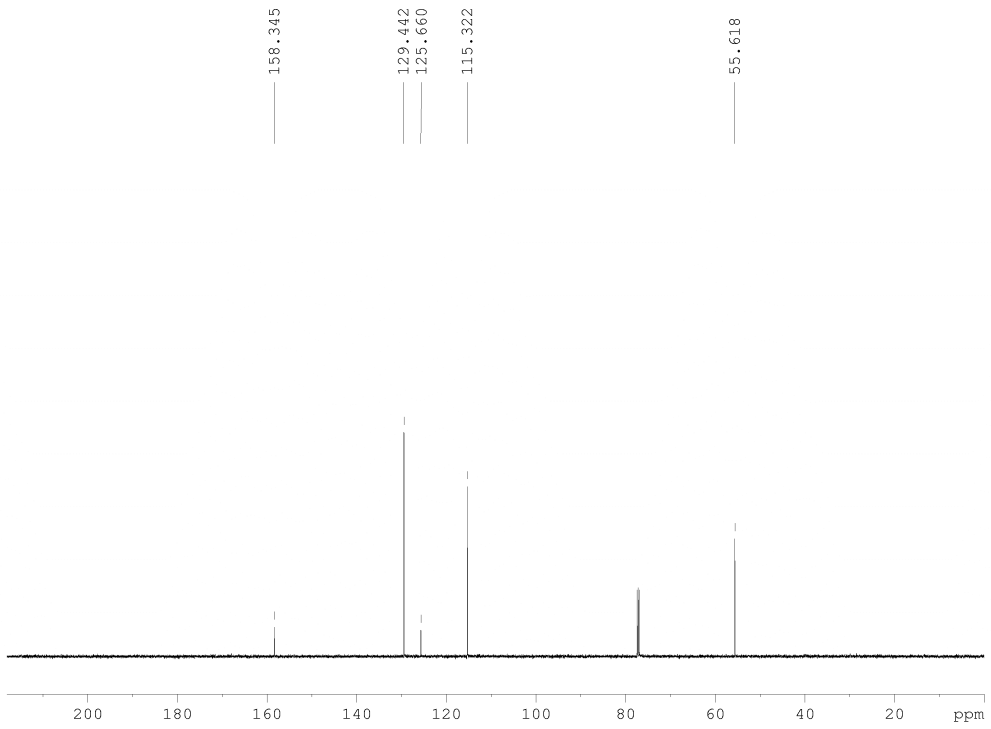


Figure A4.8 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-chloro-4-methoxybenzene

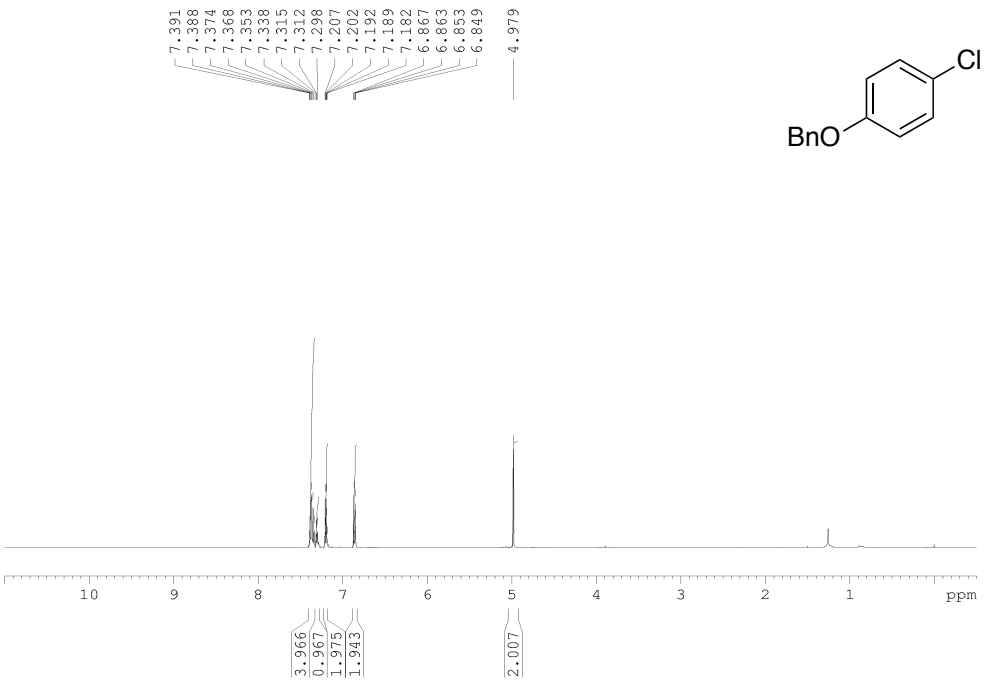


Figure A4.9 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(benzyloxy)-4-chlorobenzene

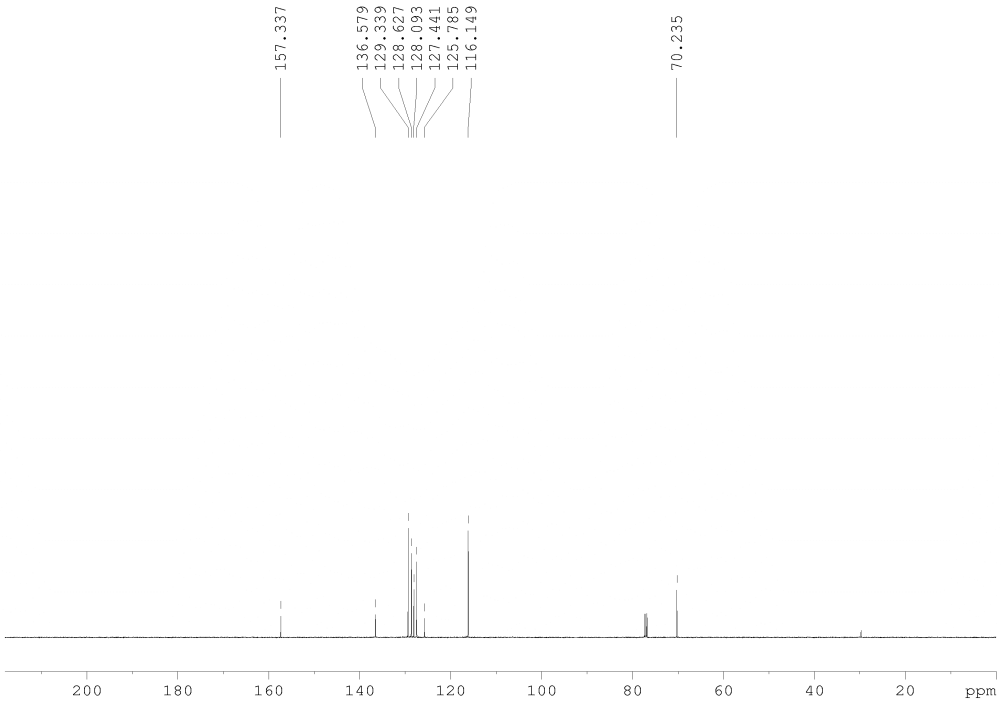


Figure A4.10 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-(benzyloxy)-4-chlorobenzene

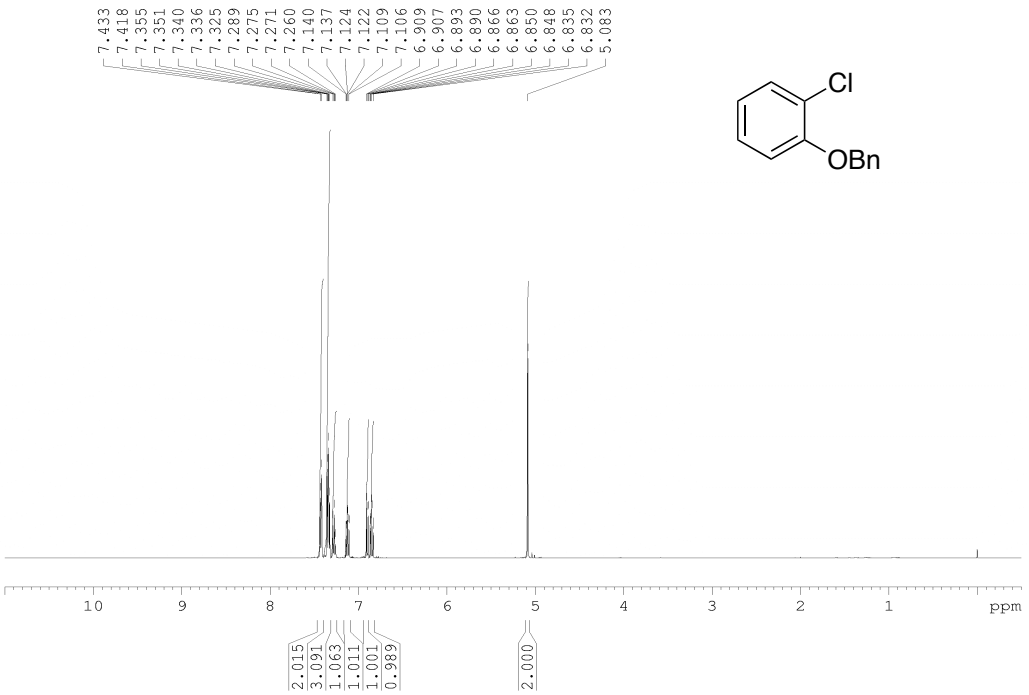


Figure A4.11 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(benzyloxy)-2-chlorobenzene

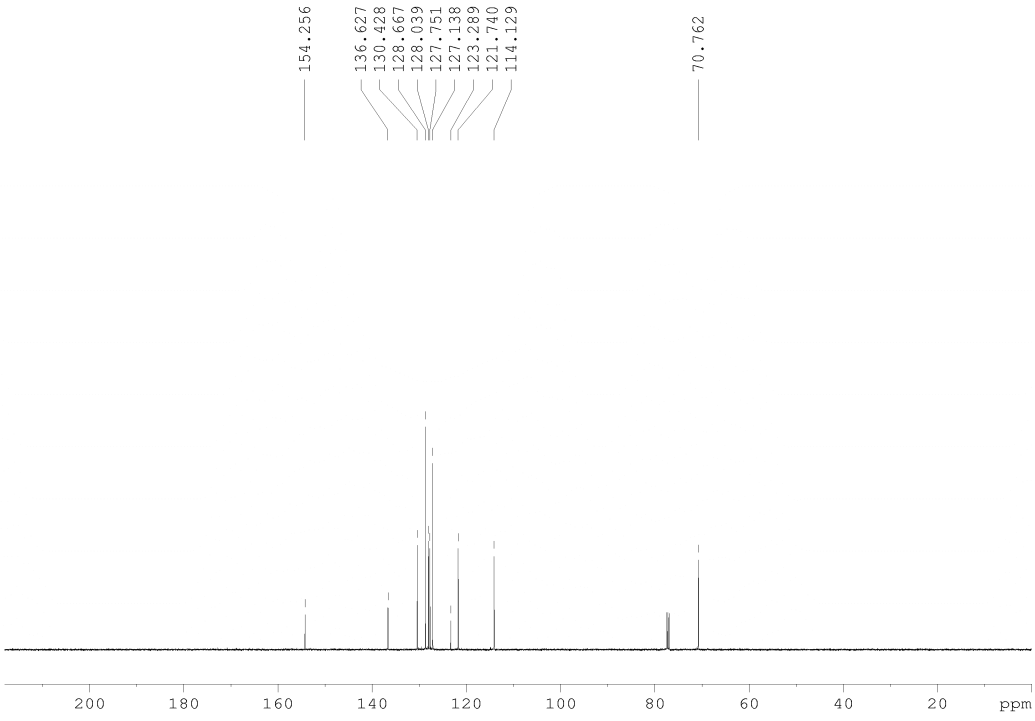


Figure A4.12 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-(benzyloxy)-2-chlorobenzene

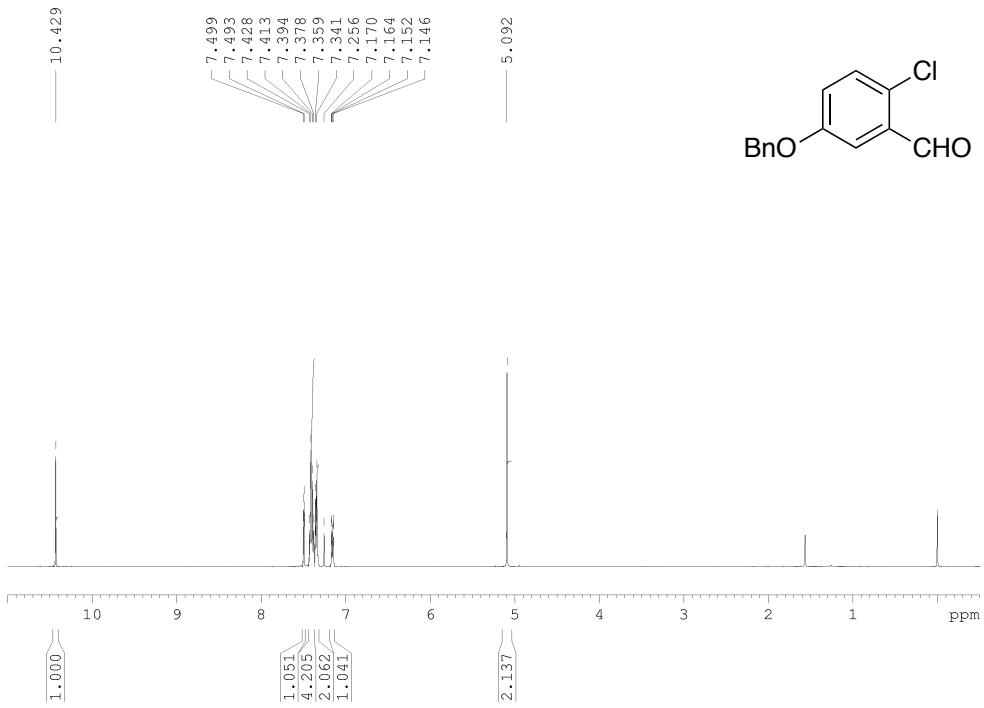


Figure A4.13 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 5-(benzyloxy)-2-chlorobenzaldehyde

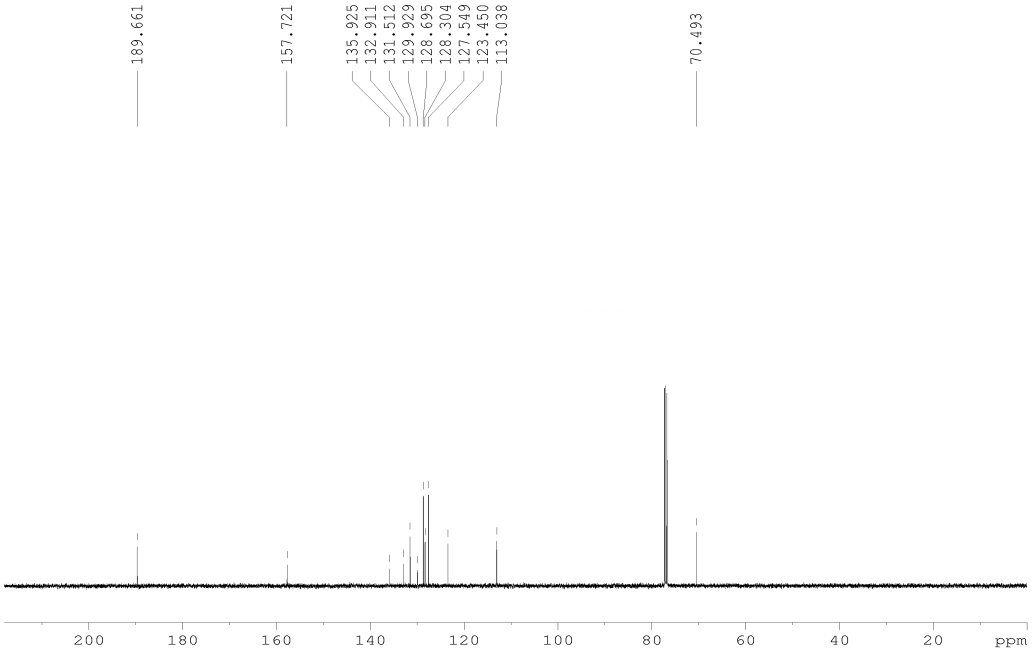


Figure A4.14 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 5-(benzyloxy)-2-chlorobenzaldehyde

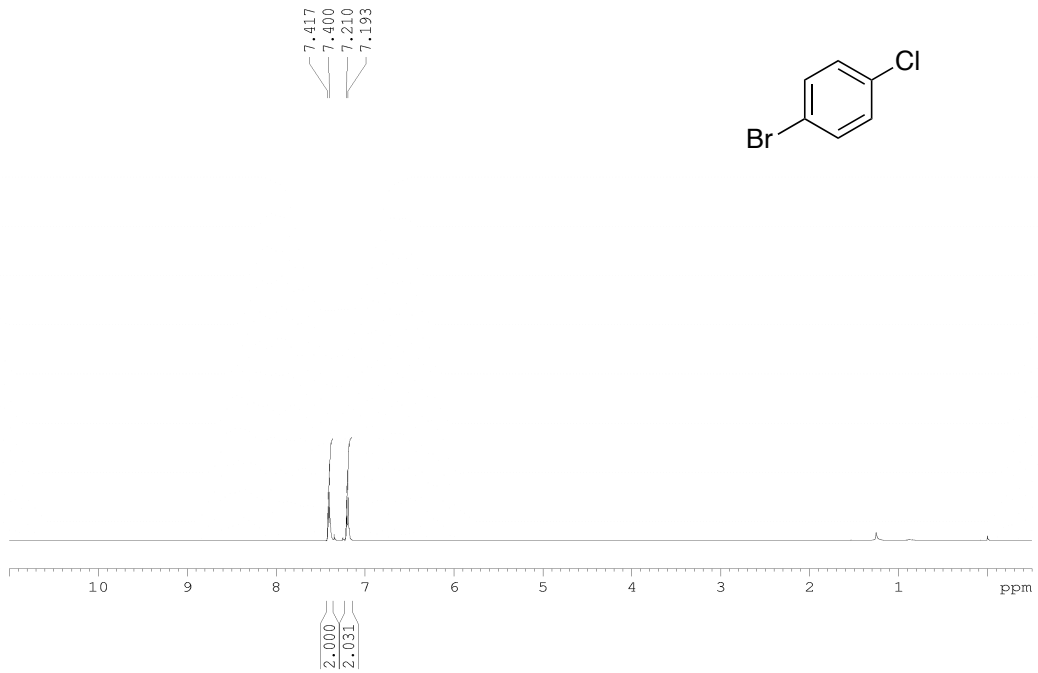


Figure A4.15 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-bromo-4-chlorobenzene

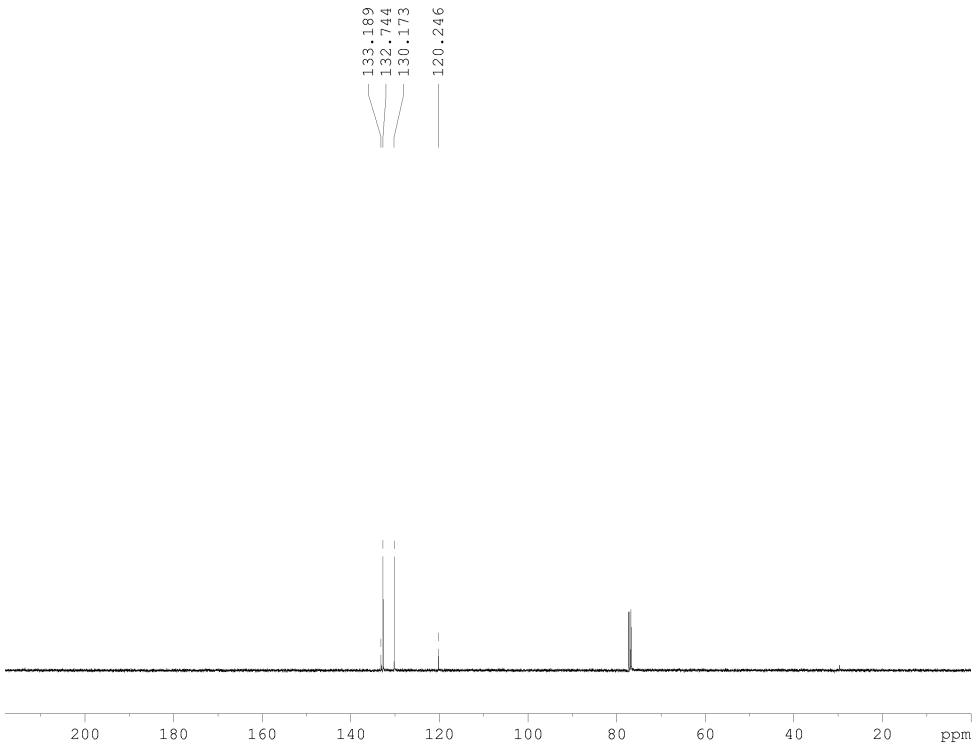


Figure A4.16 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-bromo-4-chlorobenzene

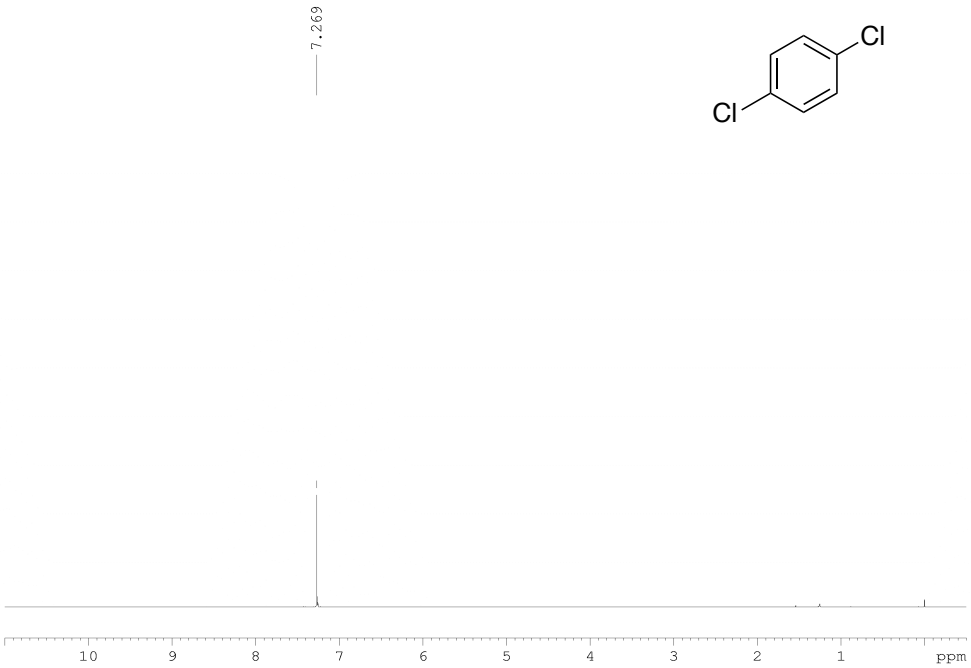


Figure A4.17 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1,4-dichlorobenzene

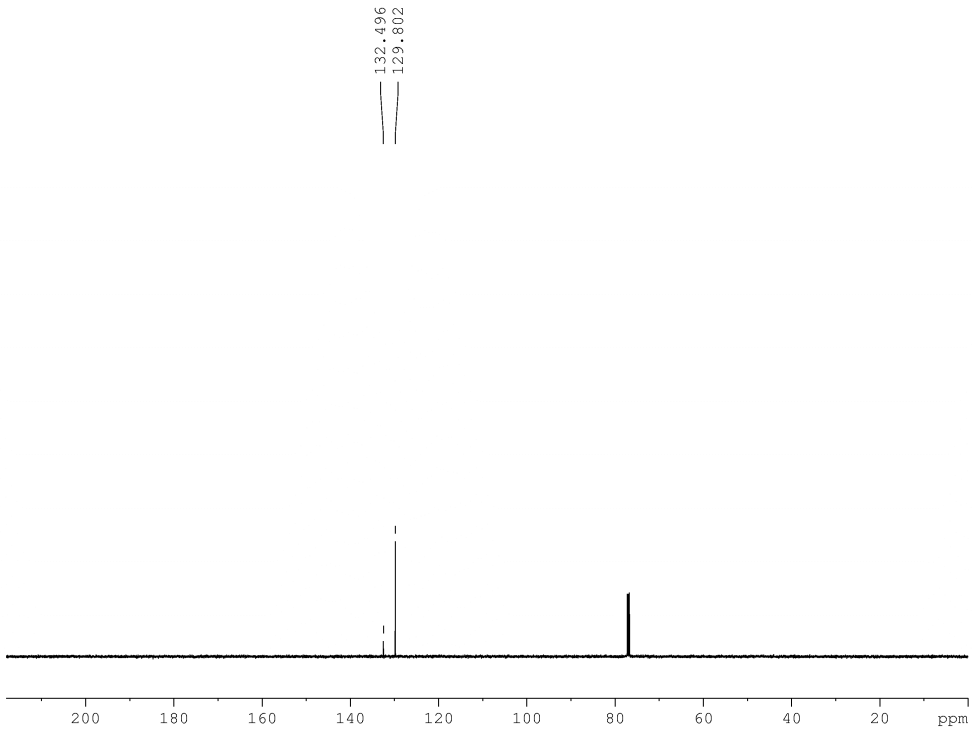


Figure A4.18 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1,4-dichlorobenzene

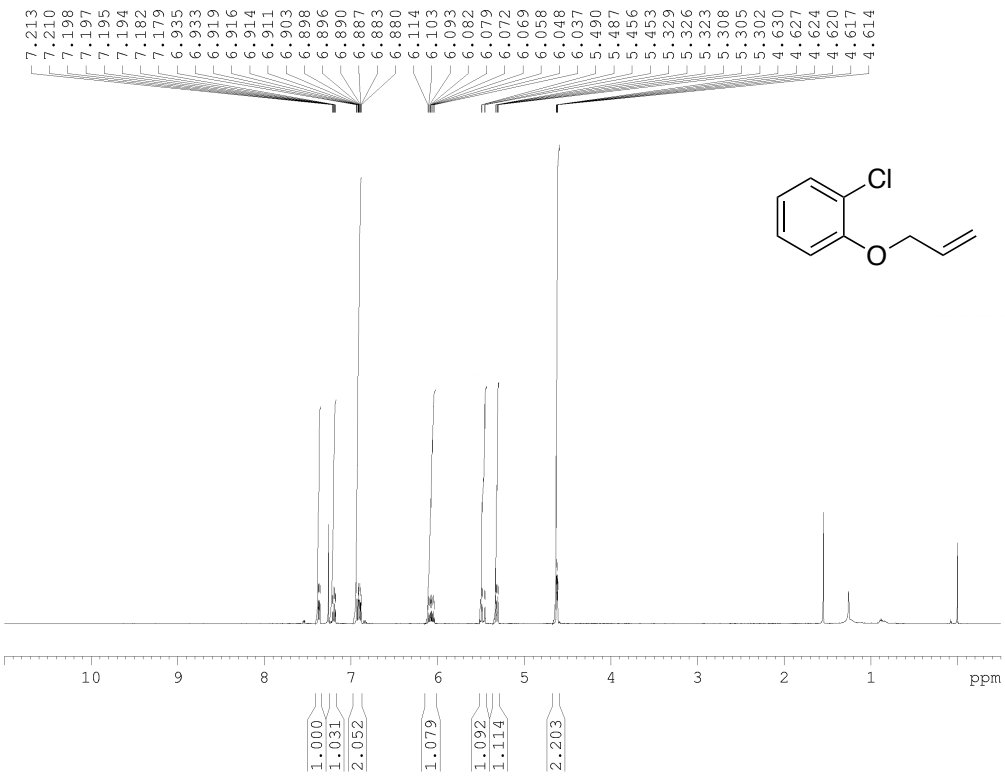


Figure A4.19 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(allyloxy)-2-chlorobenzene

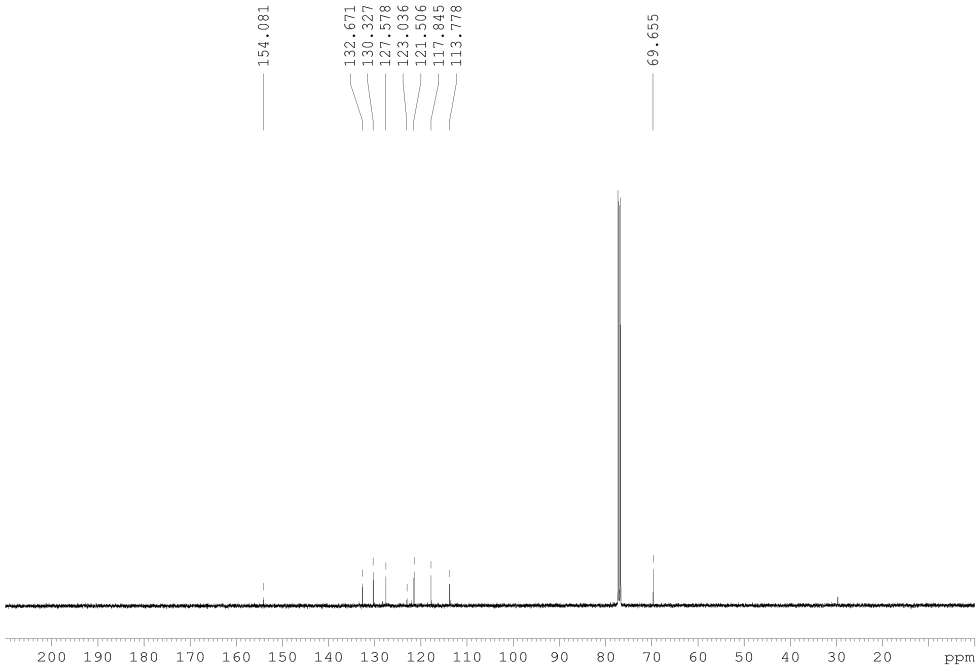


Figure A4.20 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-(allyloxy)-2-chlorobenzene

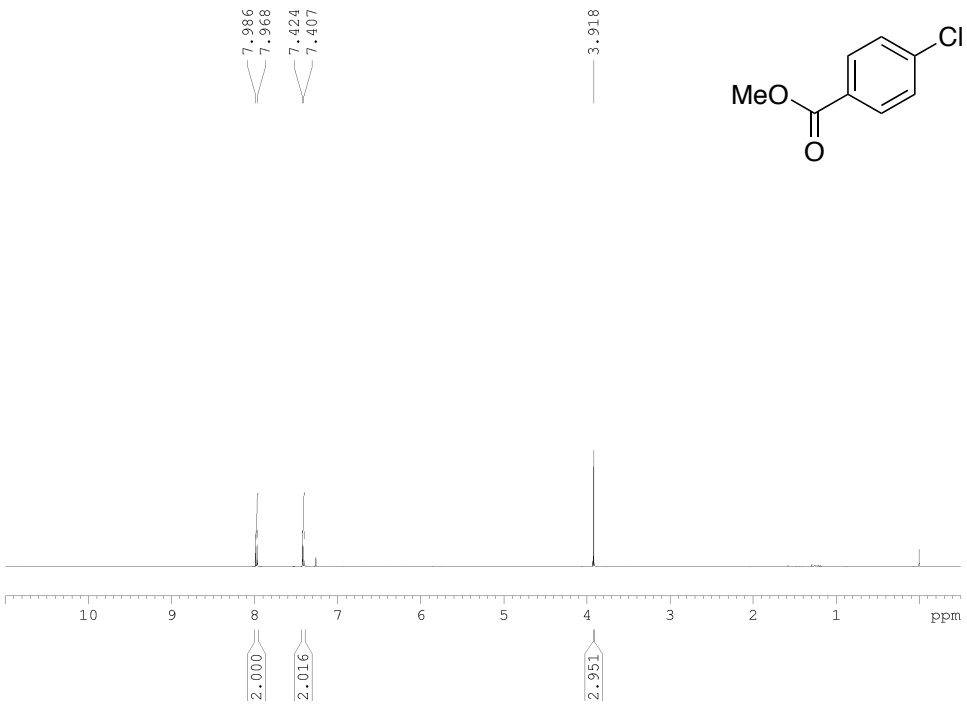


Figure A4.21 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of methyl 4-chlorobenzoate

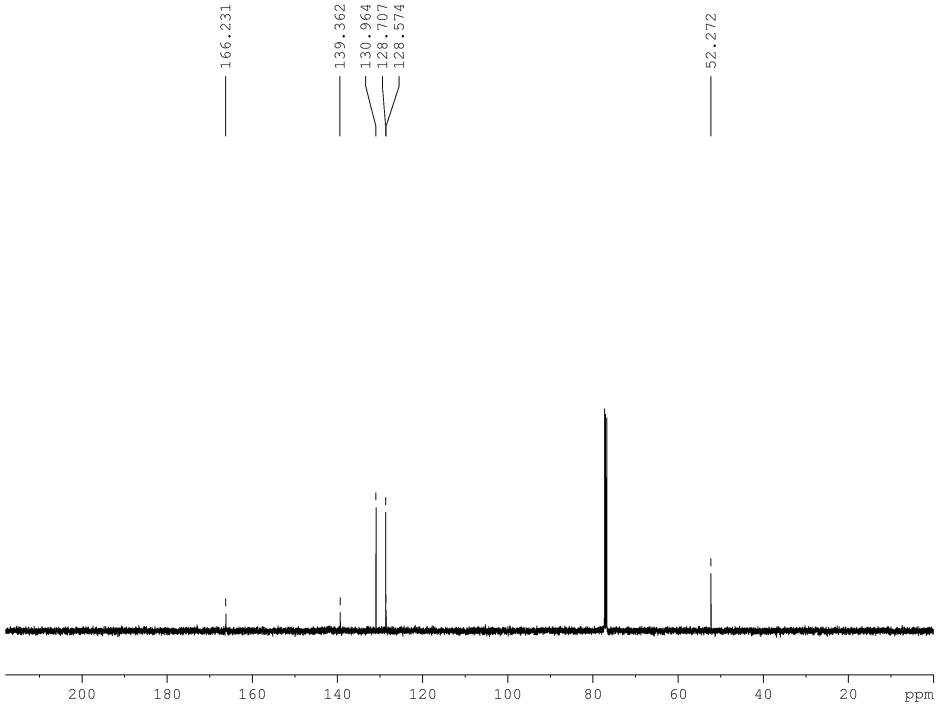


Figure A4.22 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of methyl 4-chlorobenzoate

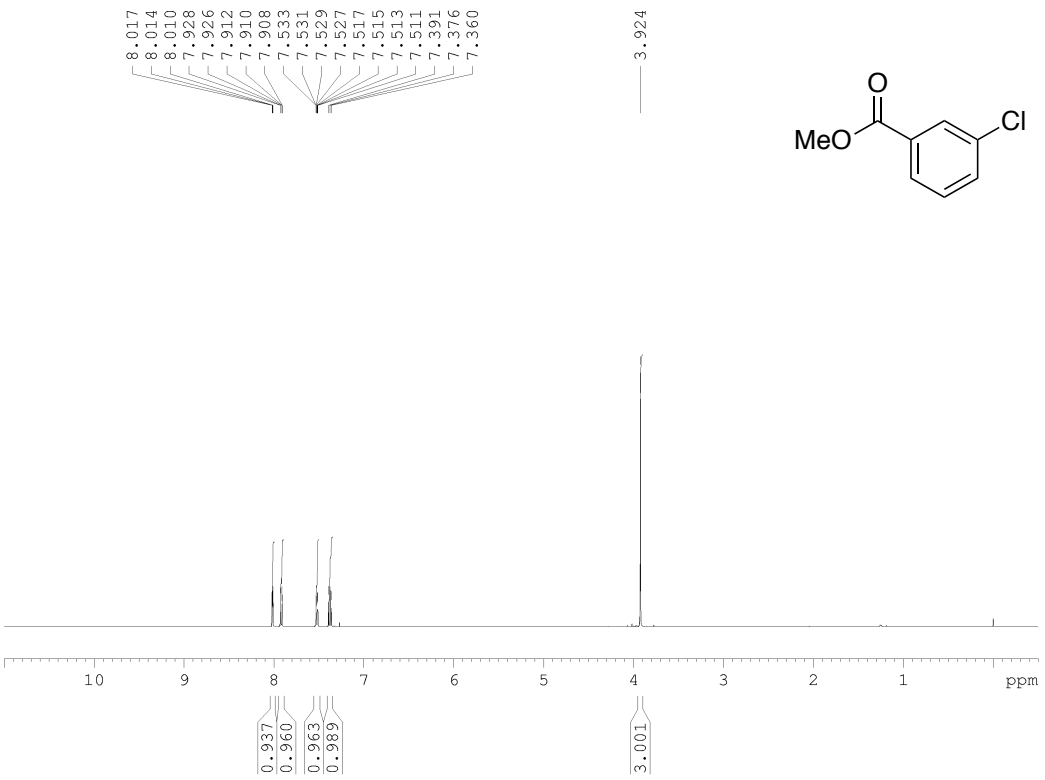


Figure A4.23 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of methyl 3-chlorobenzoate

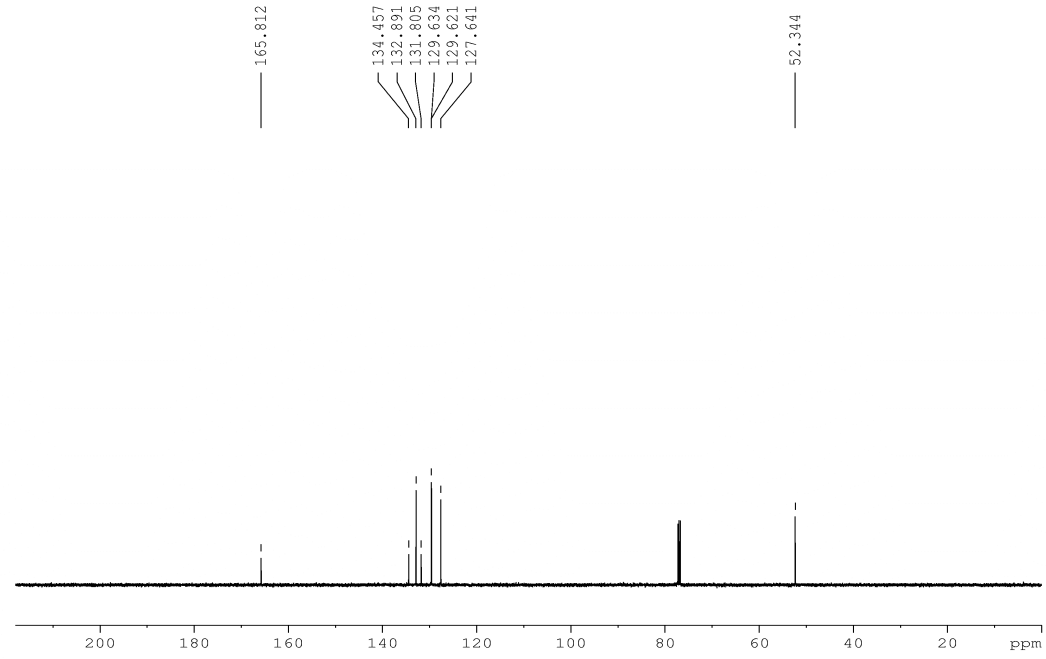


Figure A4.24 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of methyl 3-chlorobenzoate

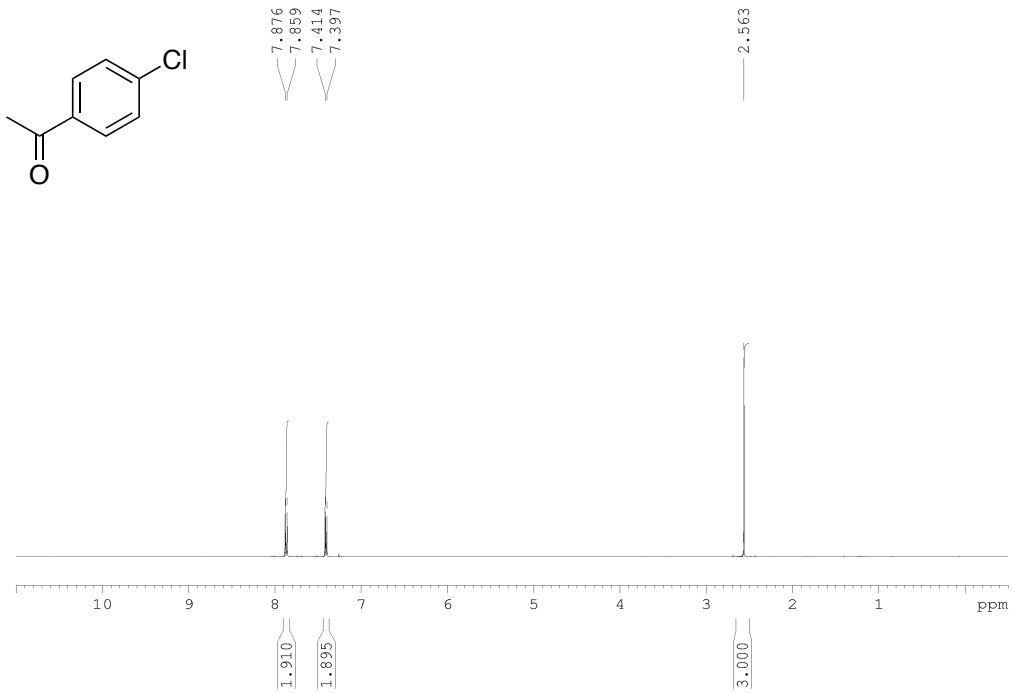


Figure A4.25 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(4-chlorophenyl)ethanone

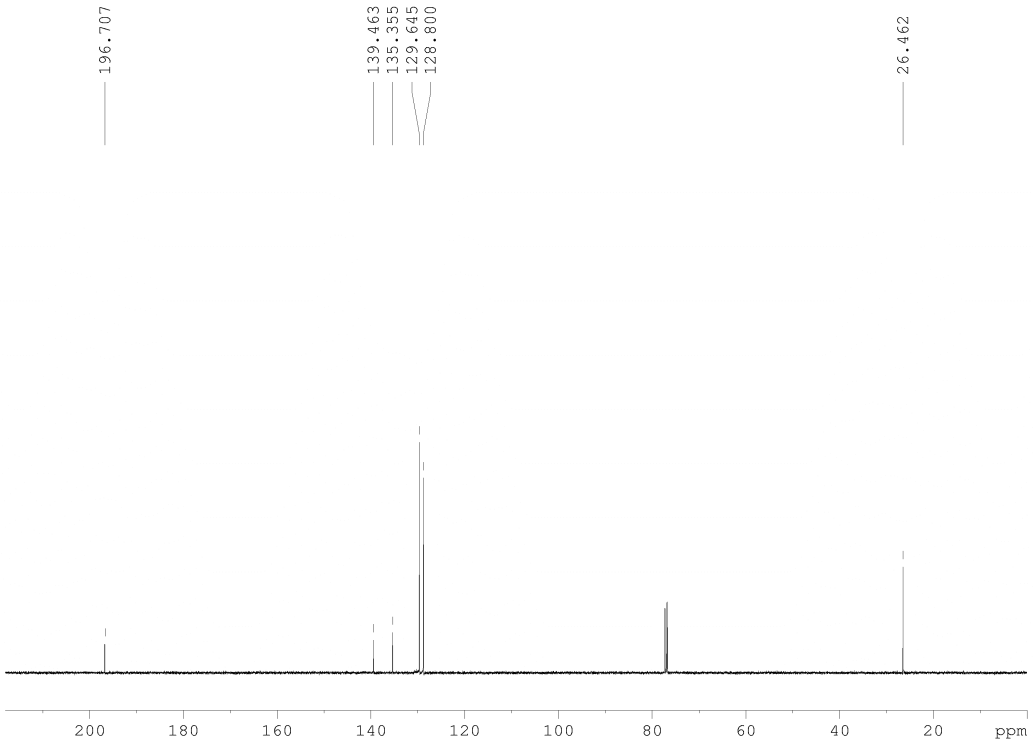


Figure A4.26 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-(4-chlorophenyl)ethanone

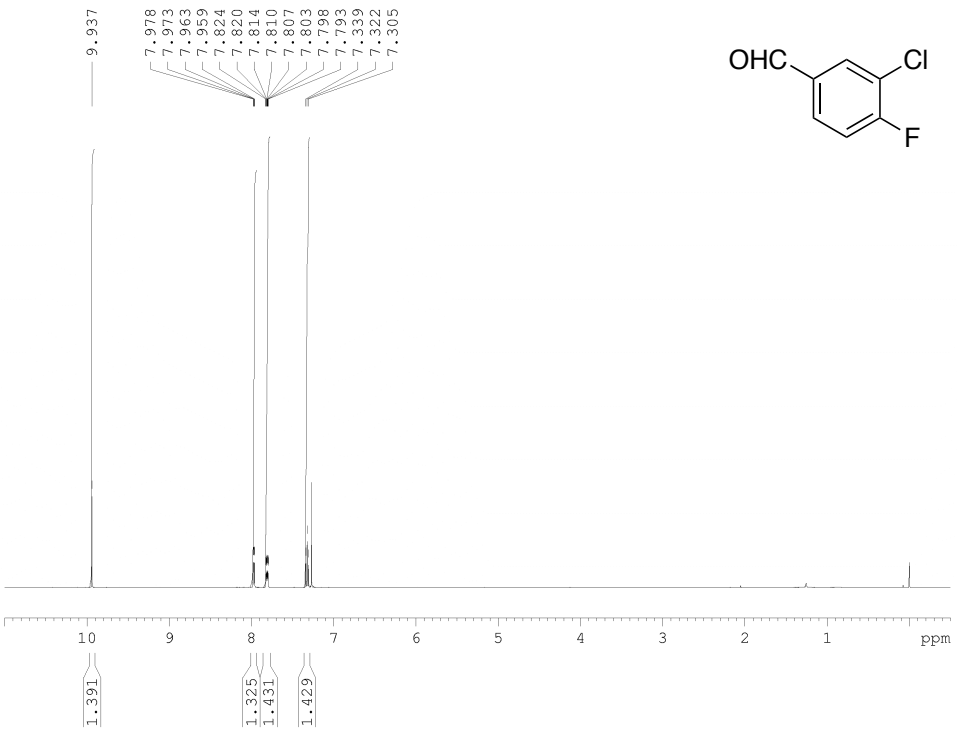


Figure A4.27 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 3-chloro-4-fluorobenzaldehyde

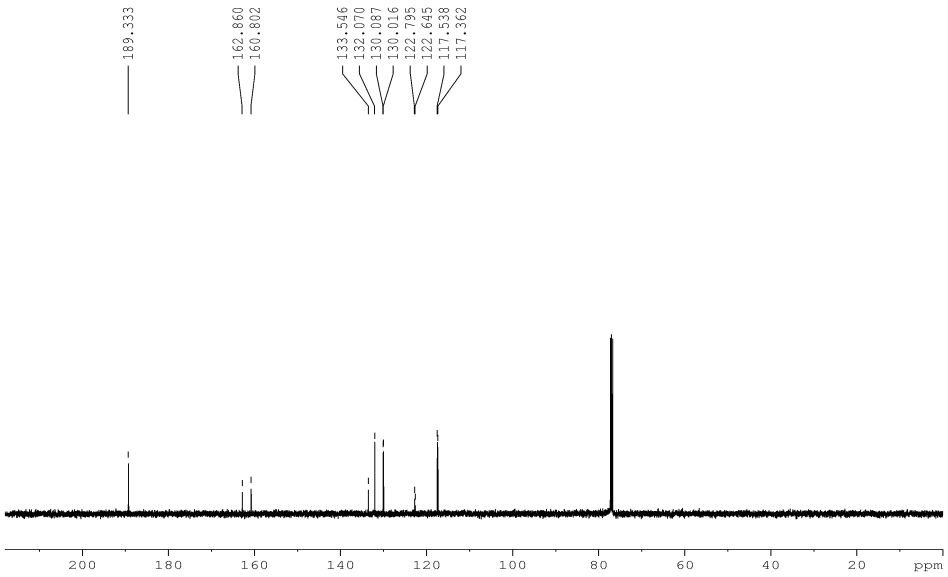


Figure A4.28 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 3-chloro-4-fluorobenzaldehyde

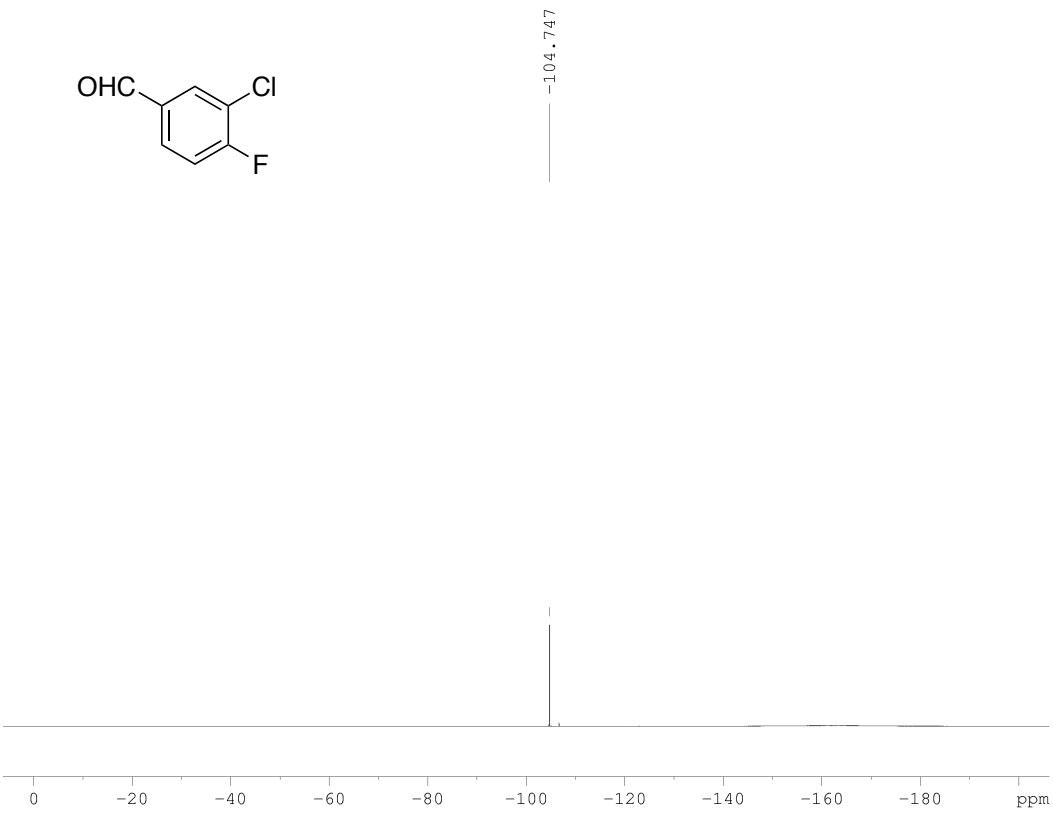


Figure A4.29 ^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of 3-chloro-4-fluorobenzaldehyde

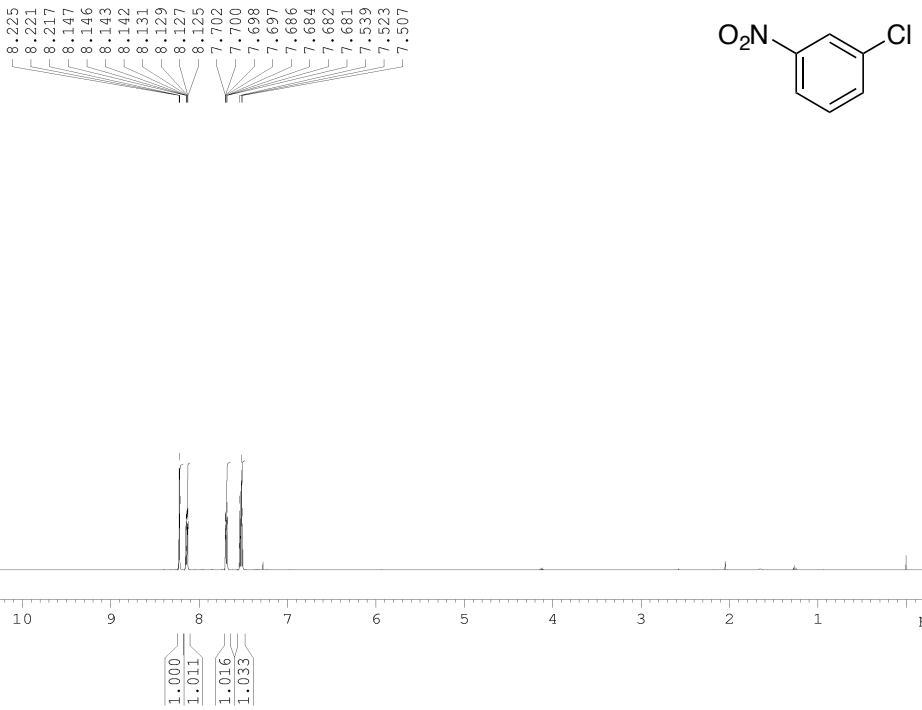


Figure A4.30 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-chloro-3-nitrobenzene

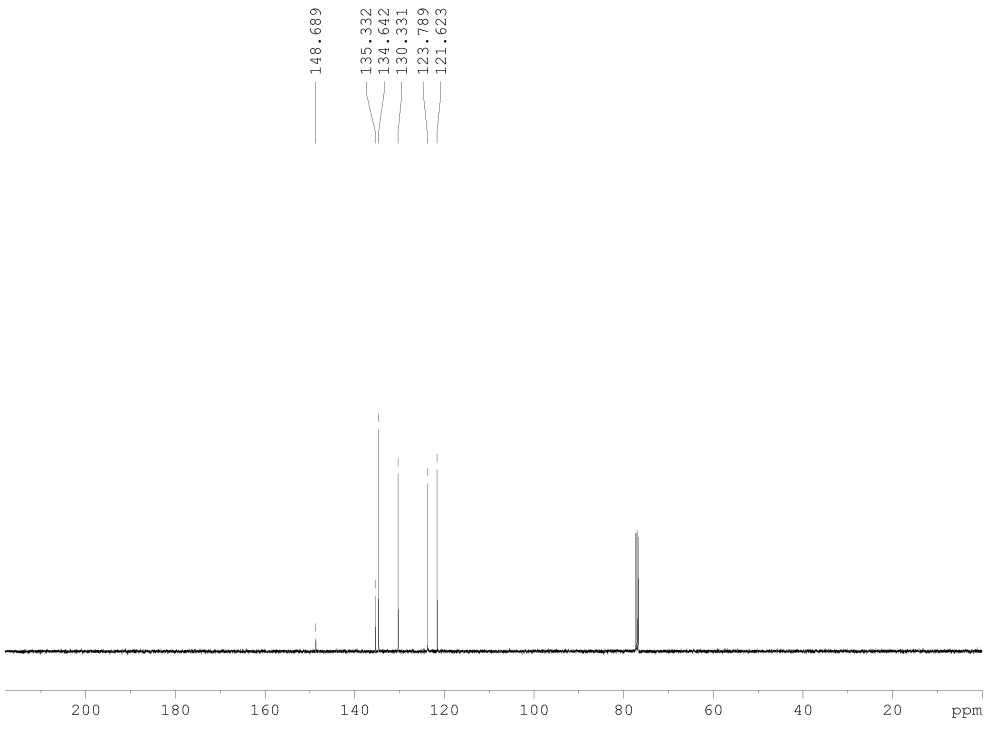


Figure A4.31 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-chloro-3-nitrobenzene

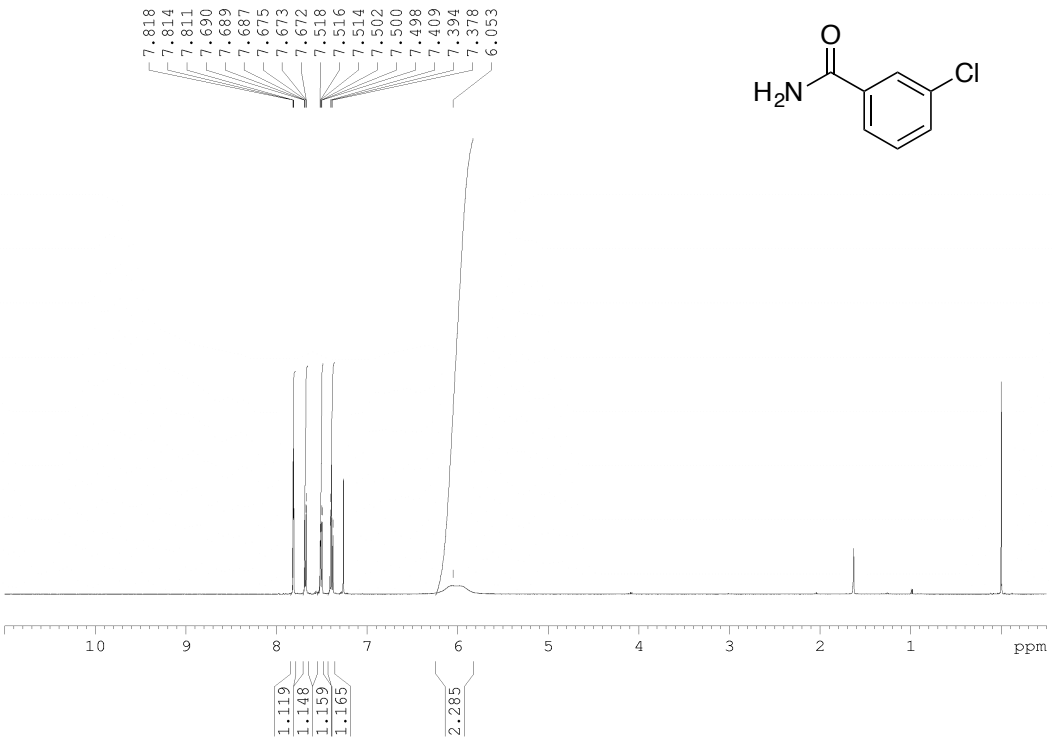


Figure A4.32 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 3-chlorobenzamide

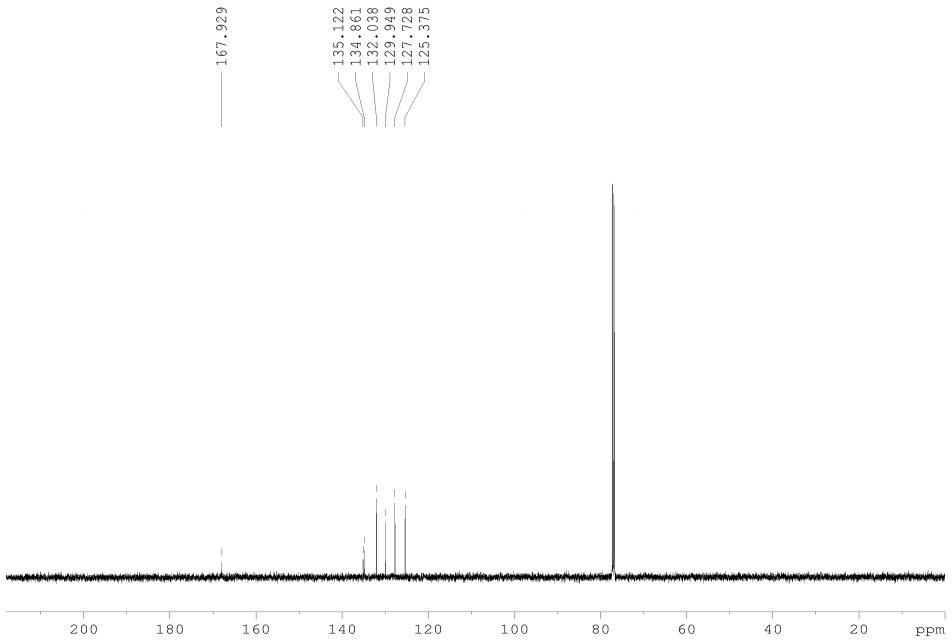


Figure A4.33 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 3-chlorobenzamide

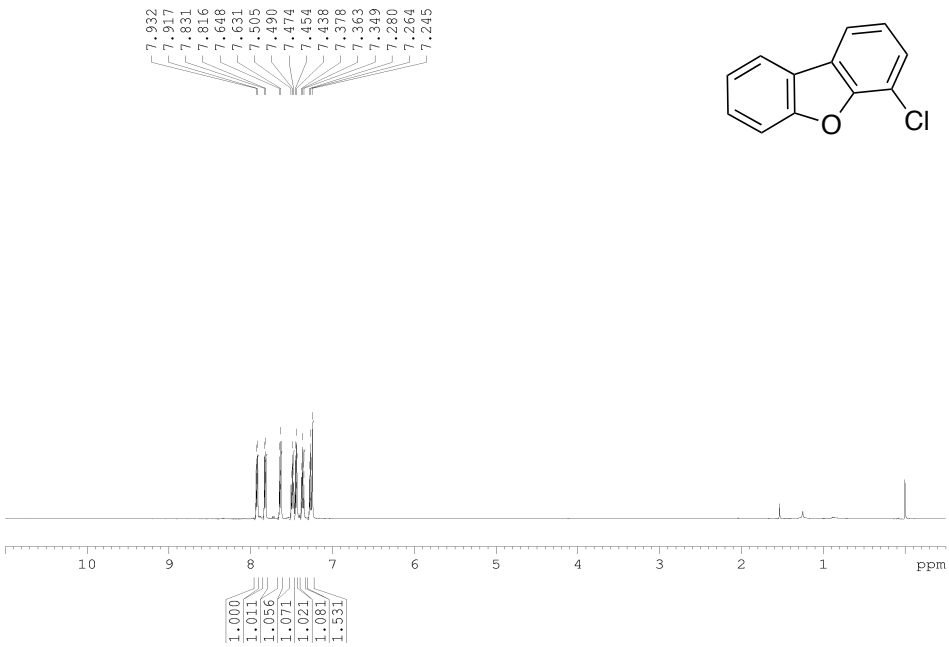


Figure A4.34 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-chlorodibenzo[*b*,*d*]furan

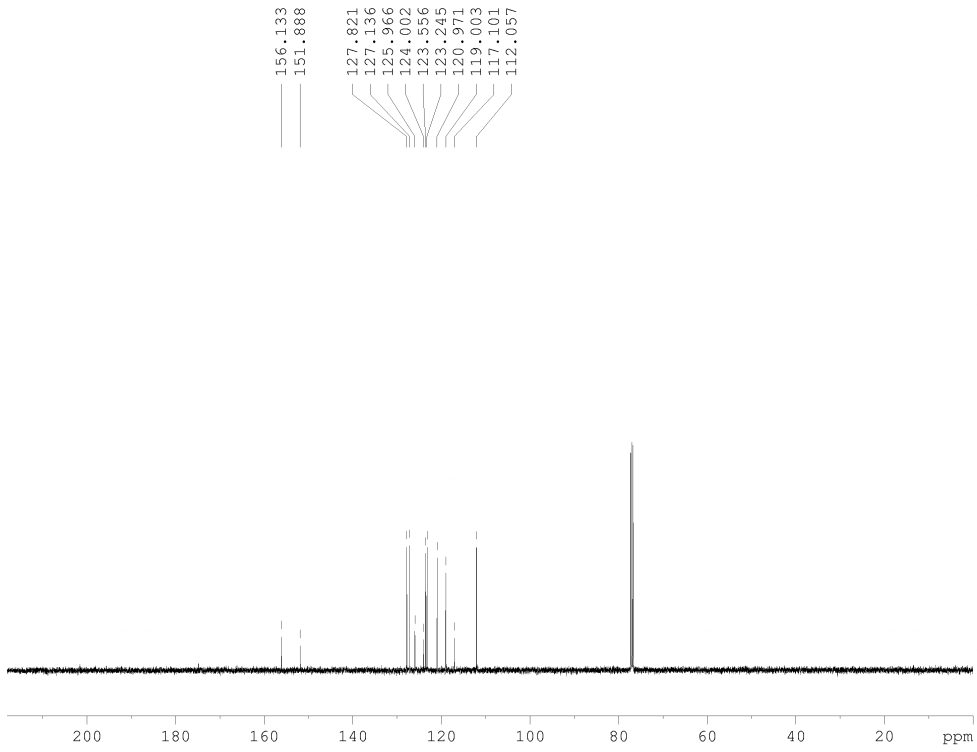


Figure A4.35 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-chlorodibenzo[*b*,*d*]furan

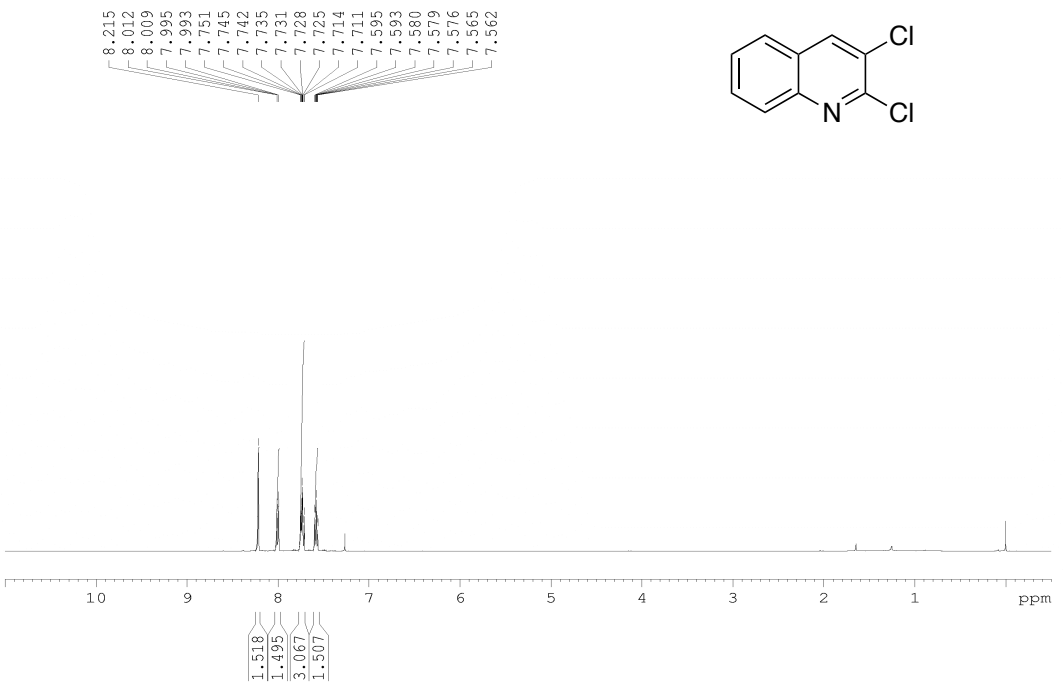


Figure A4.36 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-dichloroquinoline

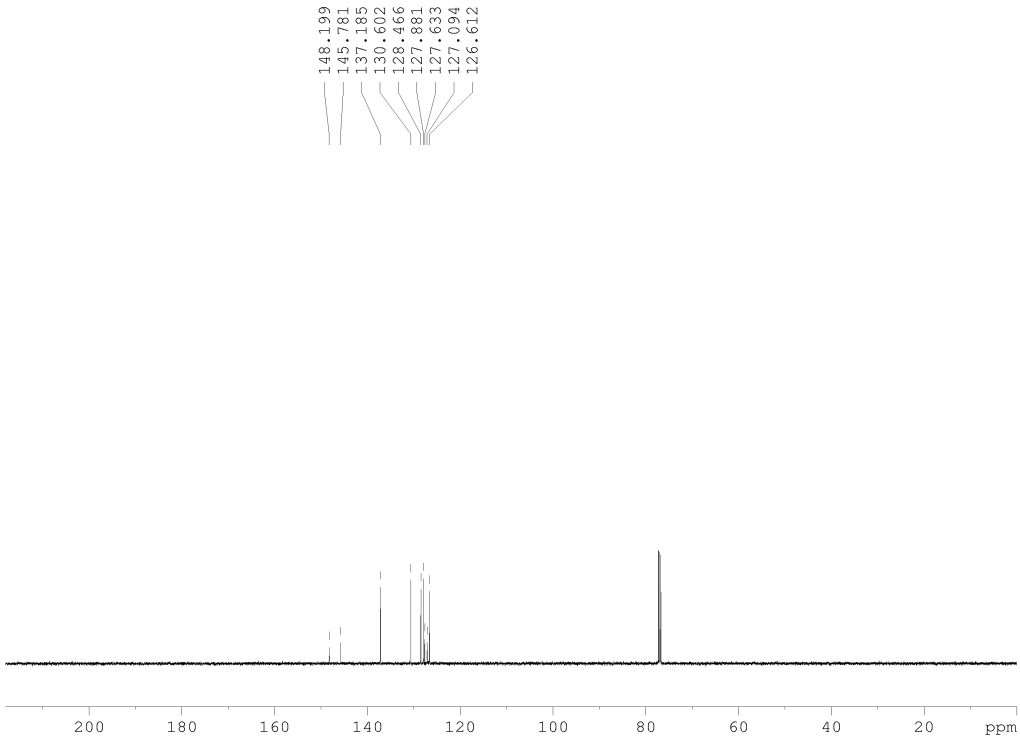


Figure A4.37 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2,3-dichloroquinoline

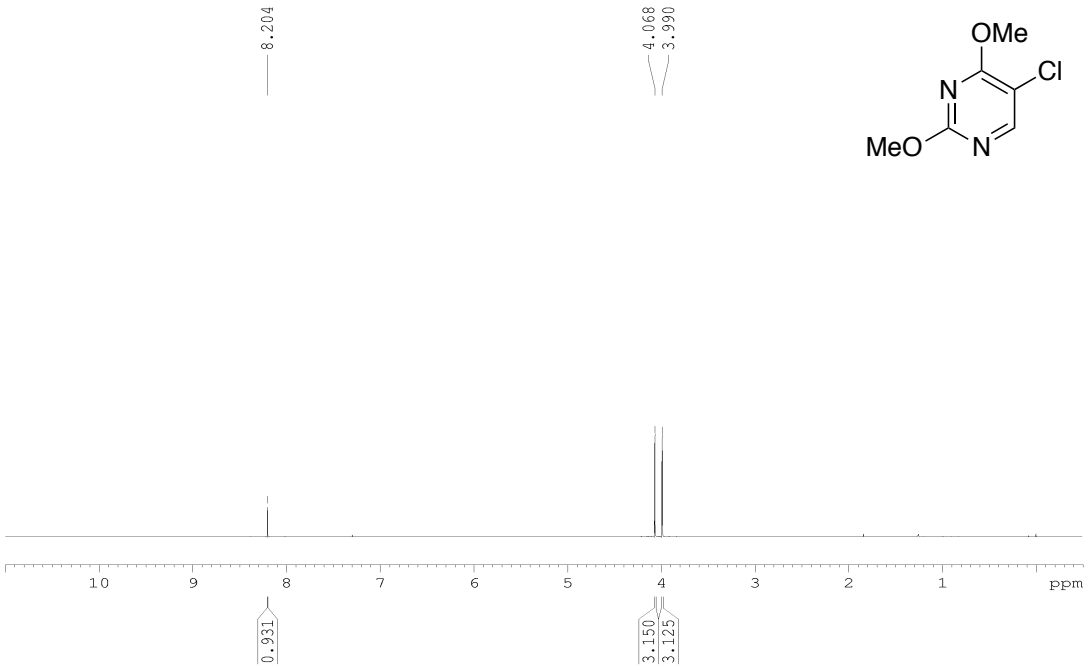


Figure A4.38 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 5-chloro-2,4-dimethoxypyrimidine

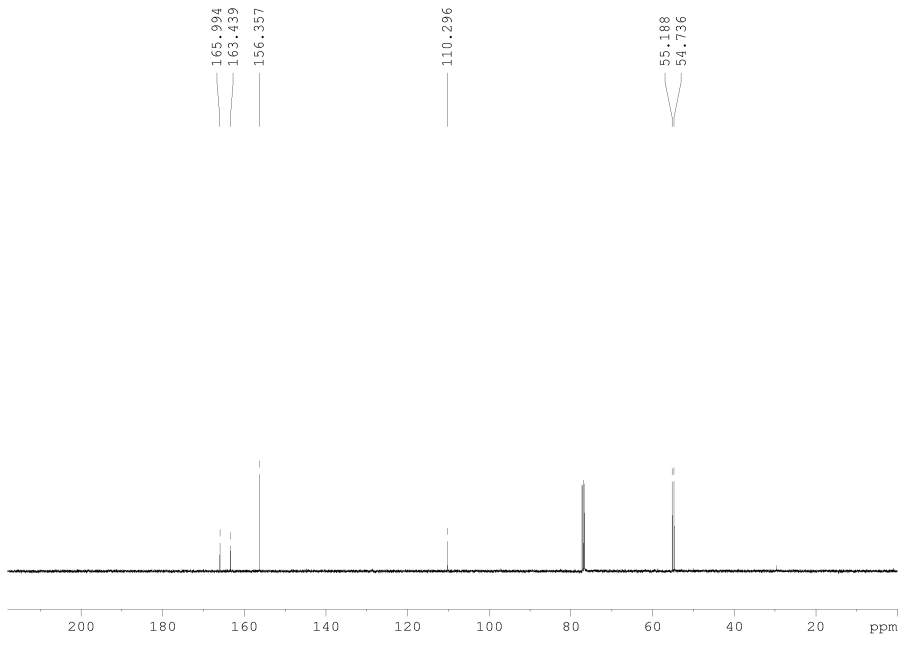


Figure A4.39 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 5-chloro-2,4-dimethoxypyrimidine

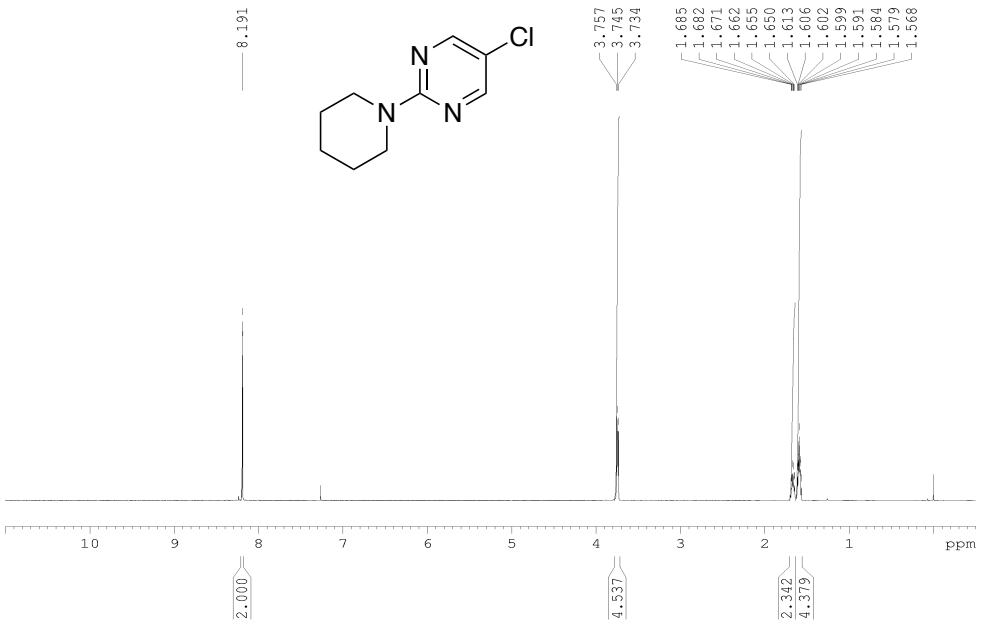


Figure A4.40 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 5-chloro-2-(piperidin-1-yl)pyrimidine

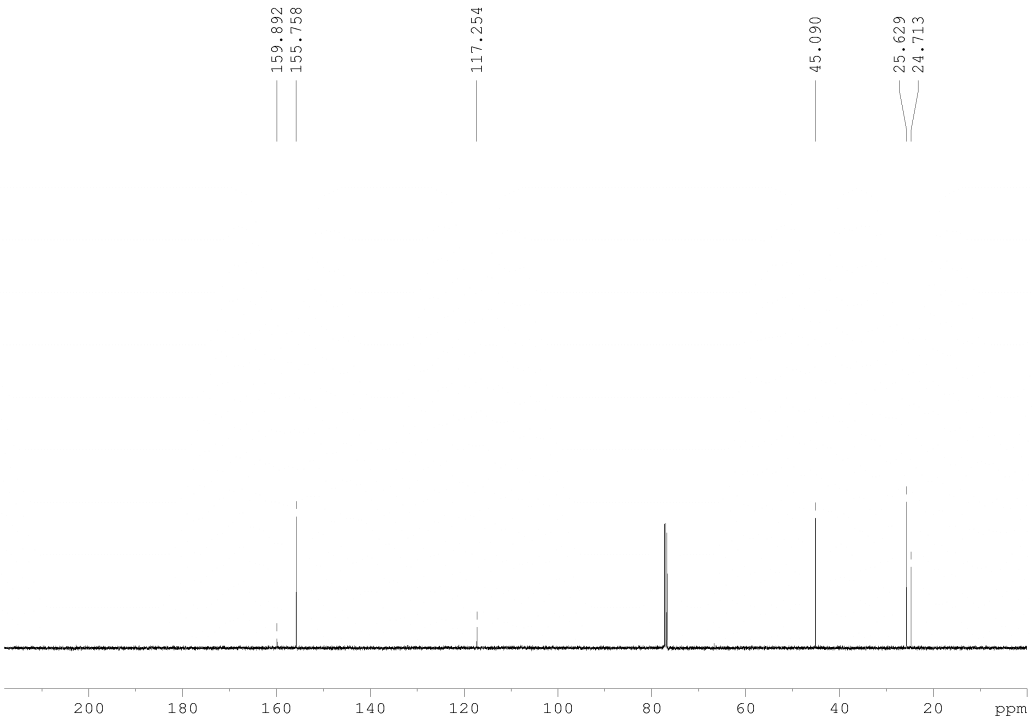


Figure A4.41 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 5-chloro-2-(piperidin-1-yl)pyrimidine

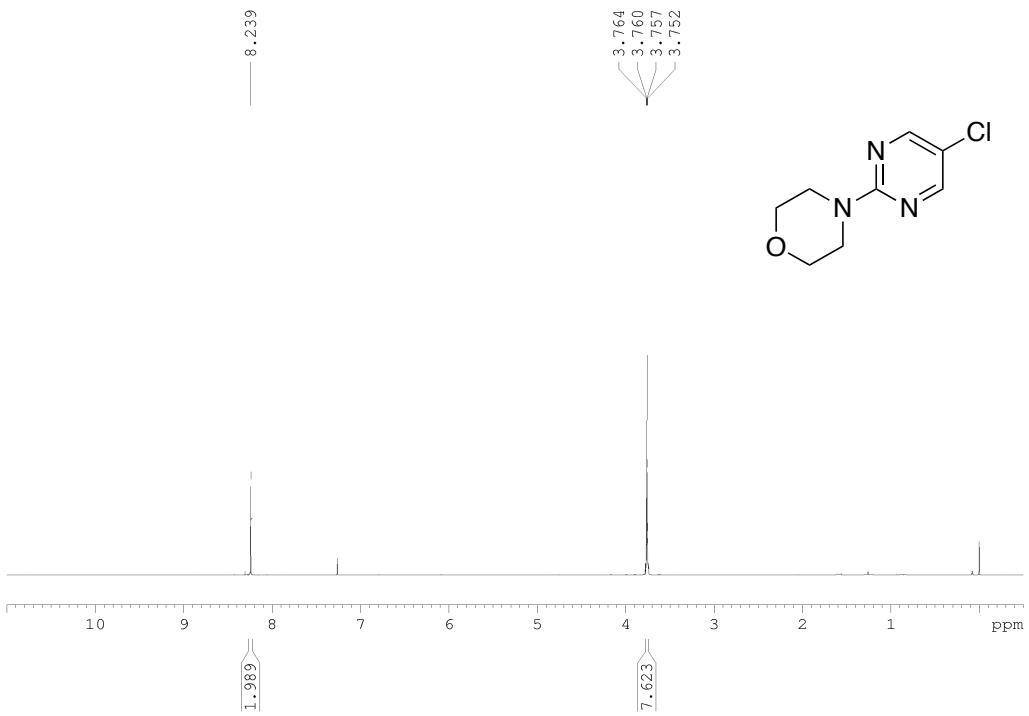


Figure A4.42 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-(5-chloropyrimidin-2-yl)morpholine

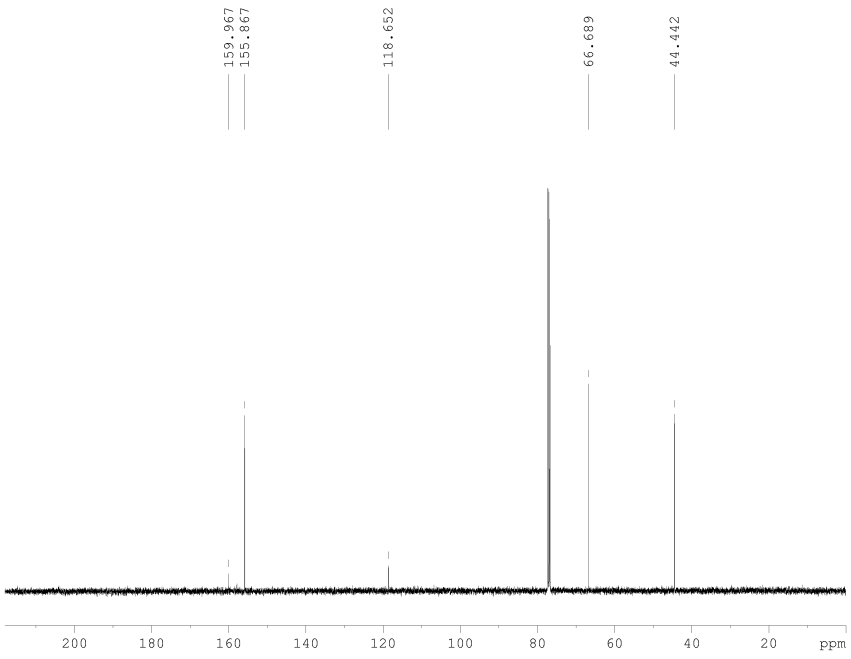


Figure A4.43 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-(5-chloropyrimidin-2-yl)morpholine

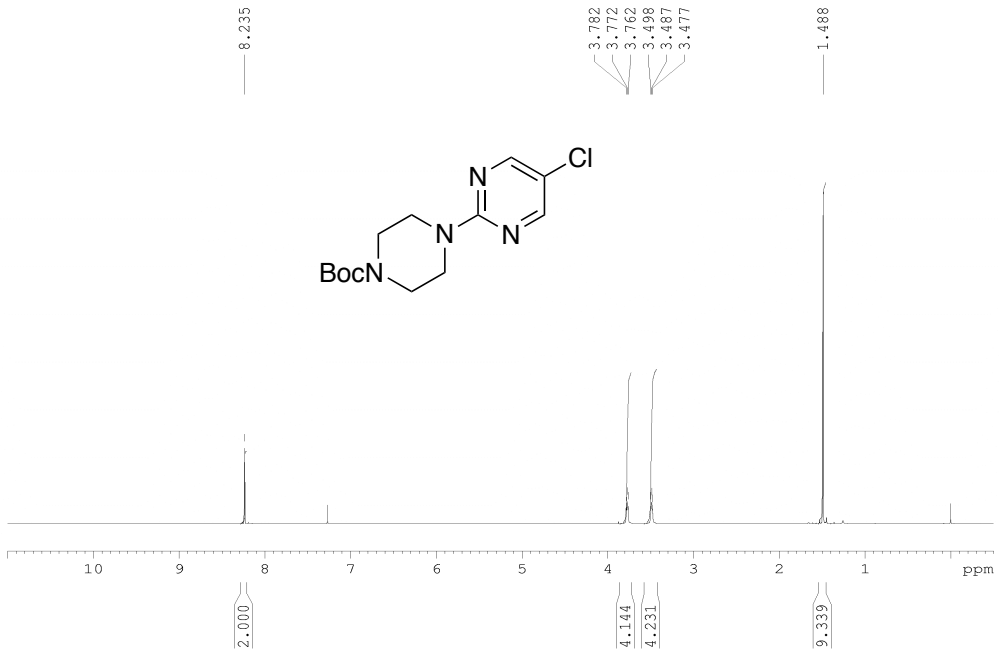


Figure A4.44 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of *tert*-butyl 4-(5-chloropyrimidin-2-yl)piperazine-1-carboxylate

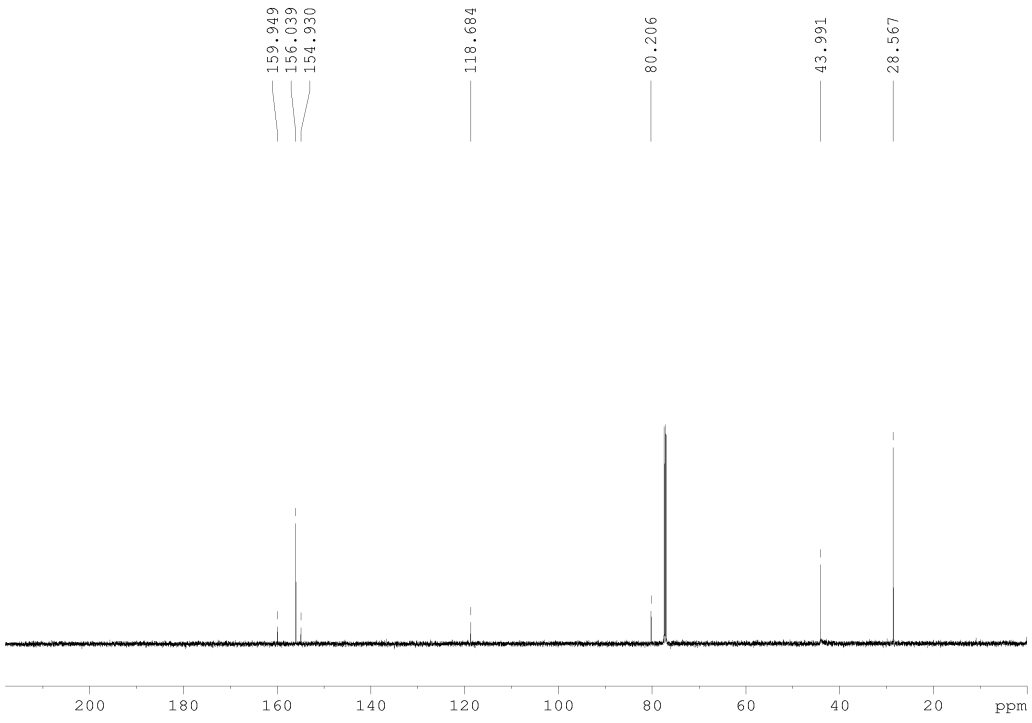


Figure A4.45 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of *tert*-butyl 4-(5-chloropyrimidin-2-yl)piperazine-1-carboxylate

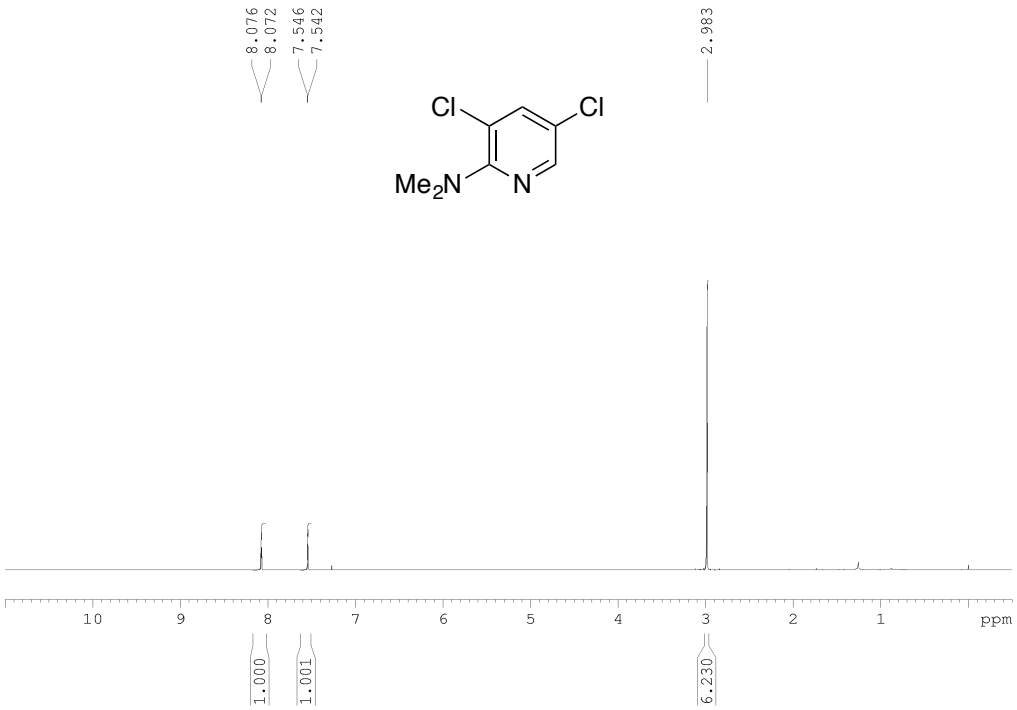


Figure A4.46 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 3,5-dichloro-*N*,*N*-dimethylpyridin-2-amine

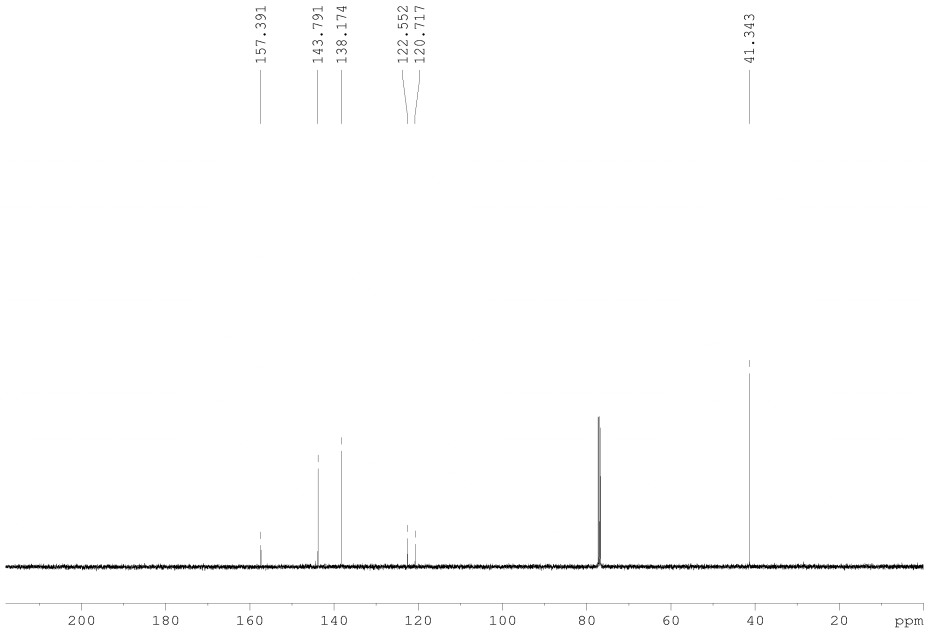


Figure A4.47 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 3,5-dichloro-*N*,*N*-dimethylpyridin-2-amine

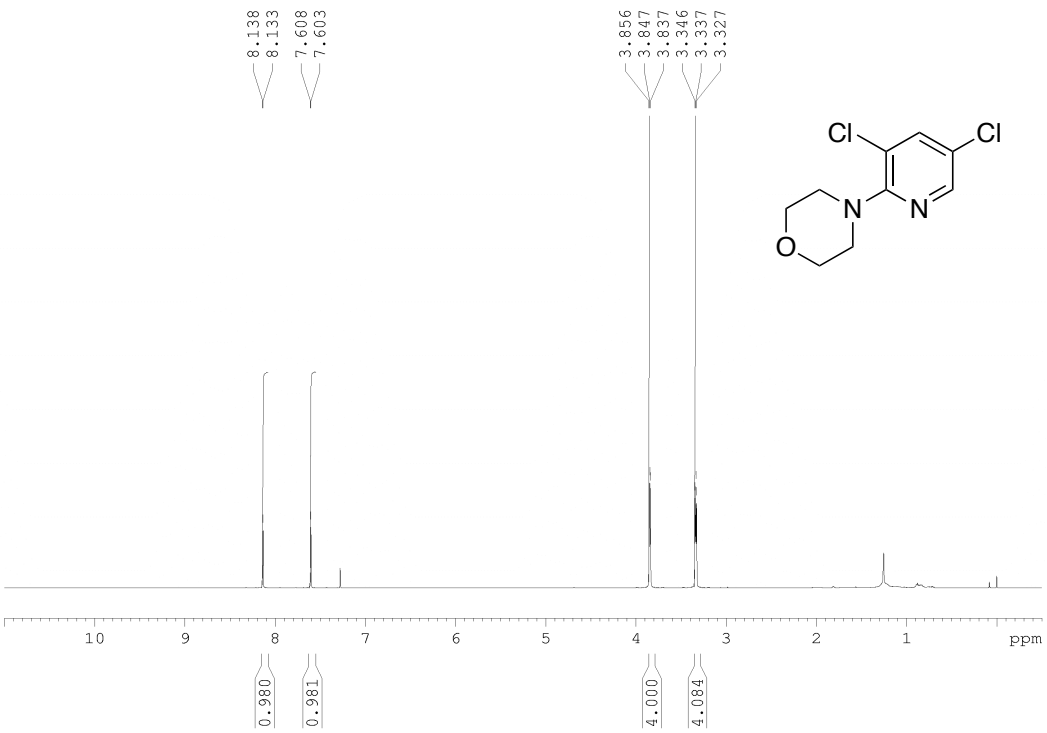


Figure A4.48 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-(3,5-dichloropyridin-2-yl)morpholine

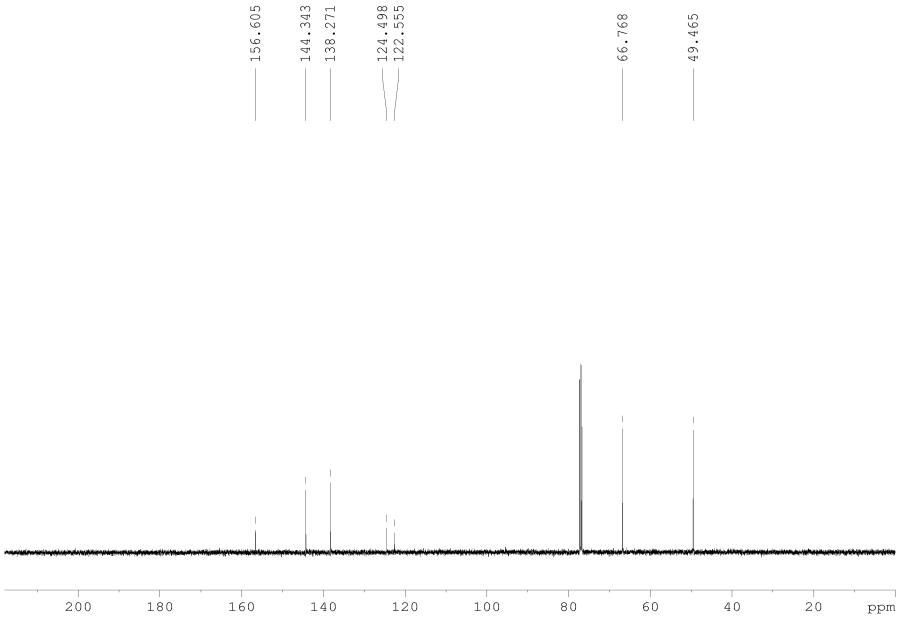


Figure A4.49 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-(3,5-dichloropyridin-2-yl)morpholine

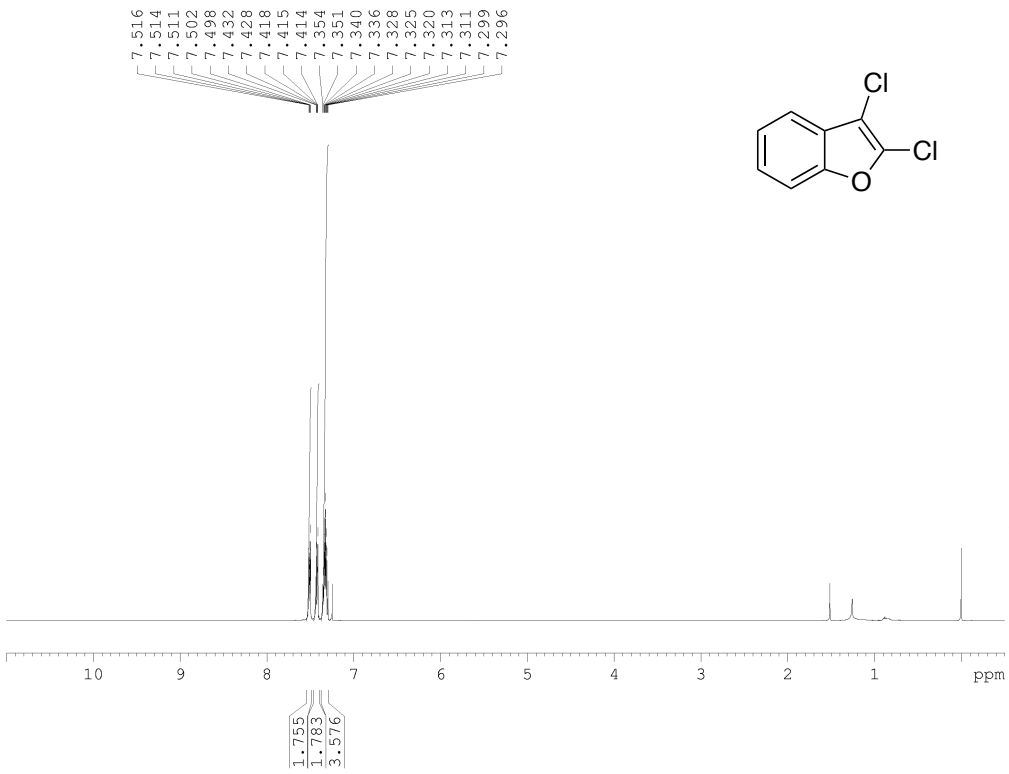


Figure A4.50 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-dichlorobenzofuran

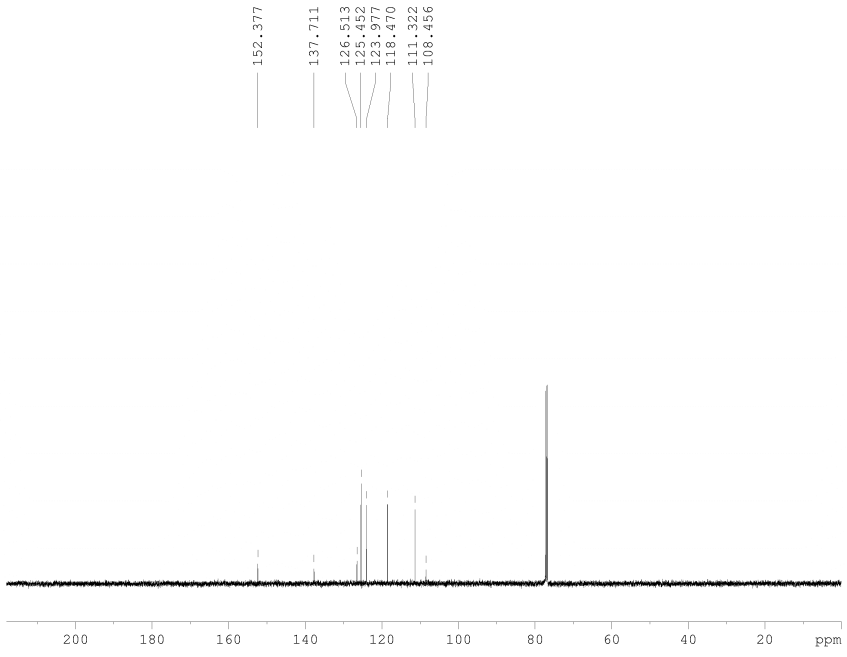


Figure A4.51 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2,3-dichlorobenzofuran

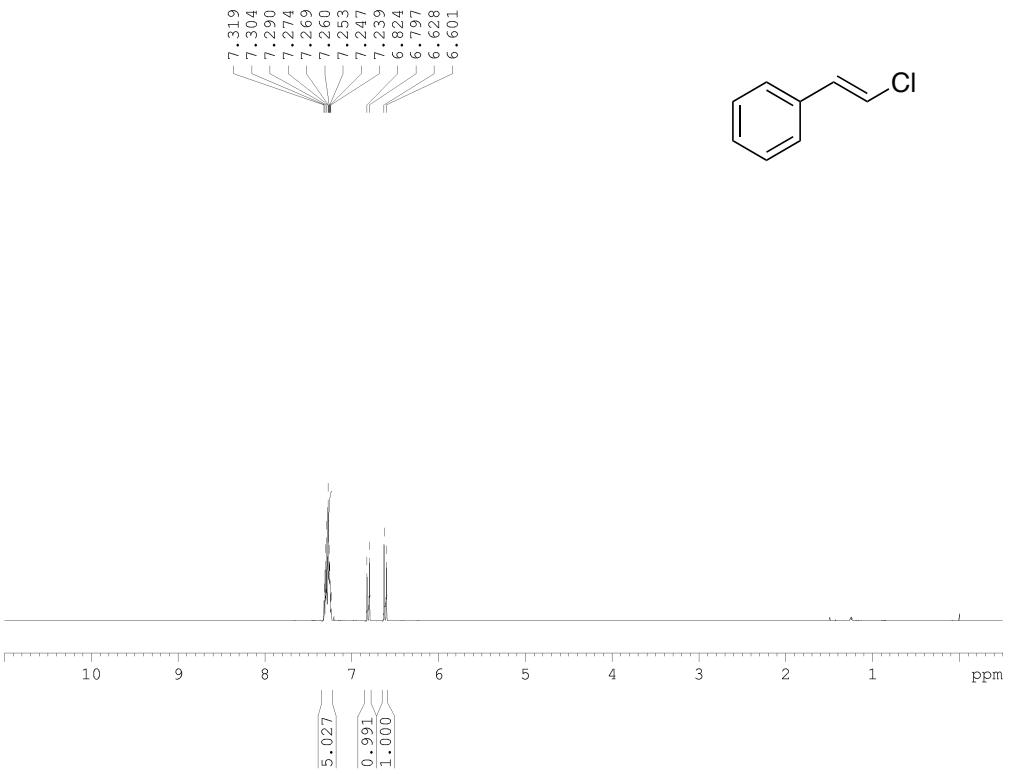


Figure A4.52 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of (*E*)-(2-chlorovinyl)benzene

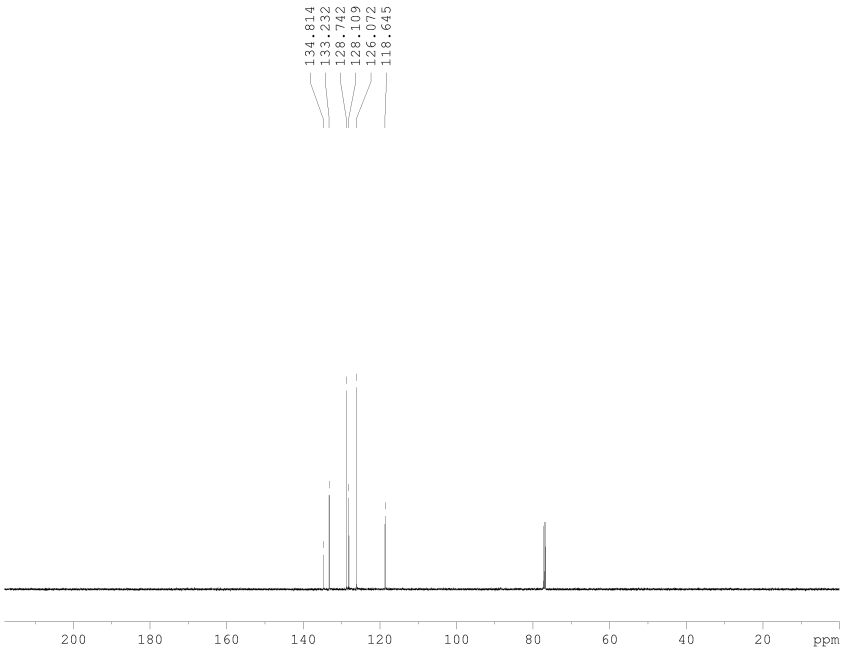


Figure A4.53 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of (*E*)-(2-chlorovinyl)benzene

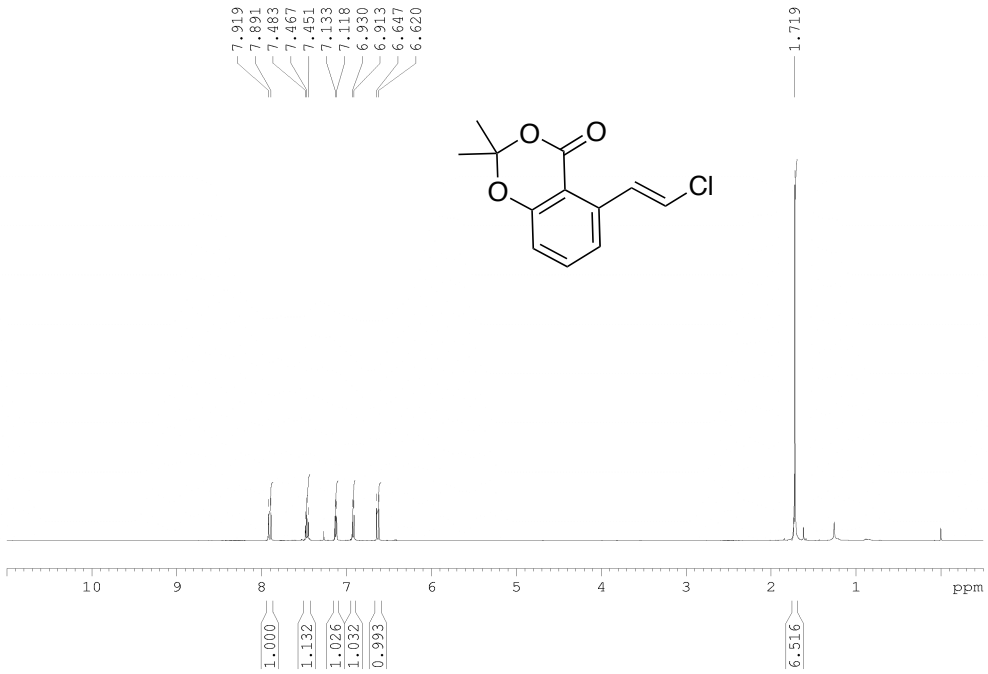


Figure A4.54 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of (*E*)-5-(2-chlorovinyl)-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one

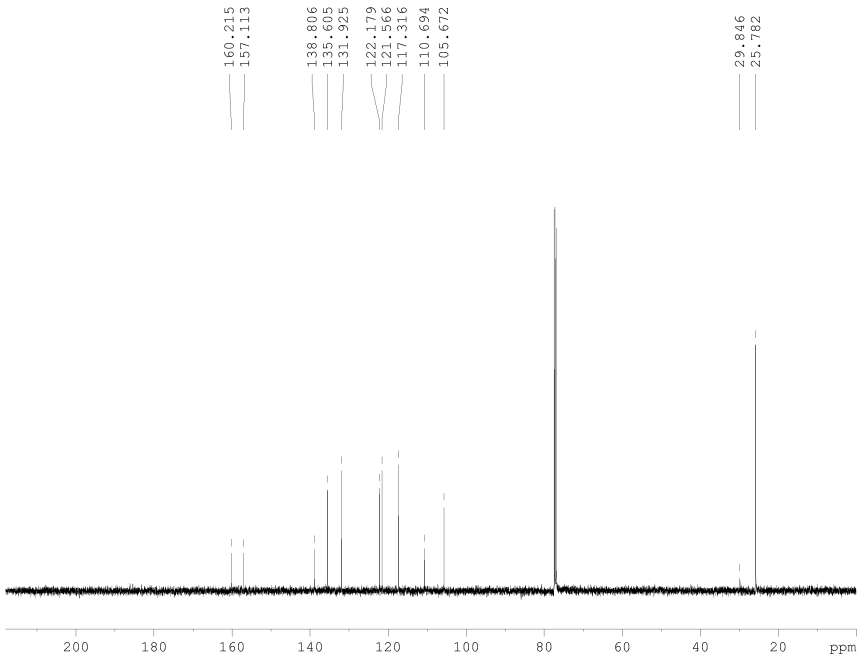


Figure A4.55 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of (*E*)-5-(2-chlorovinyl)-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one

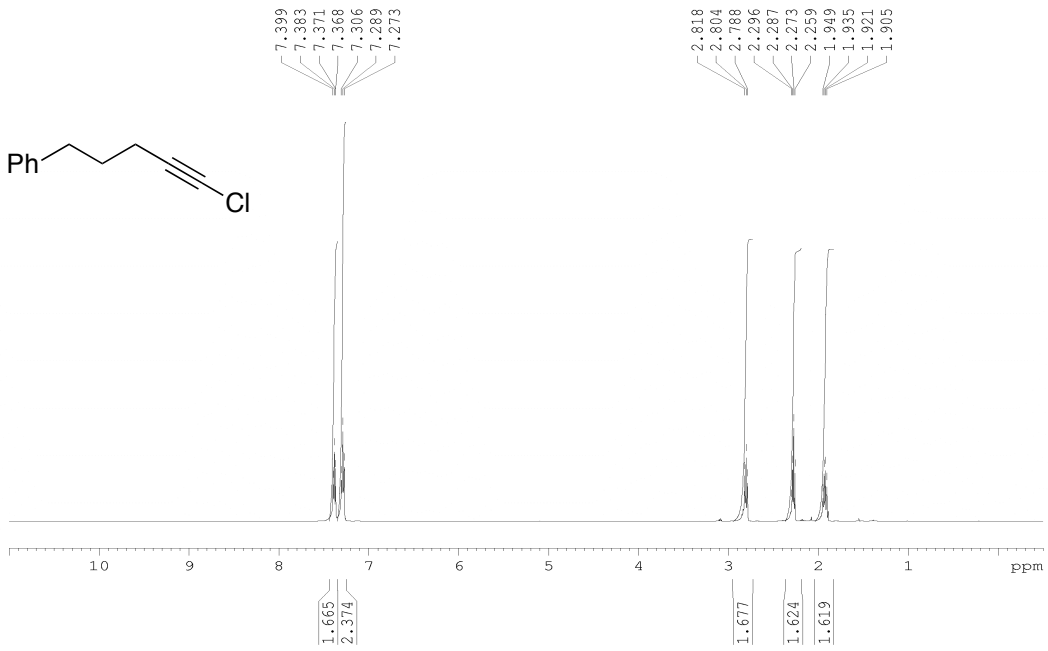


Figure A4.56 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of (5-chloropent-4-yn-1-yl)benzene

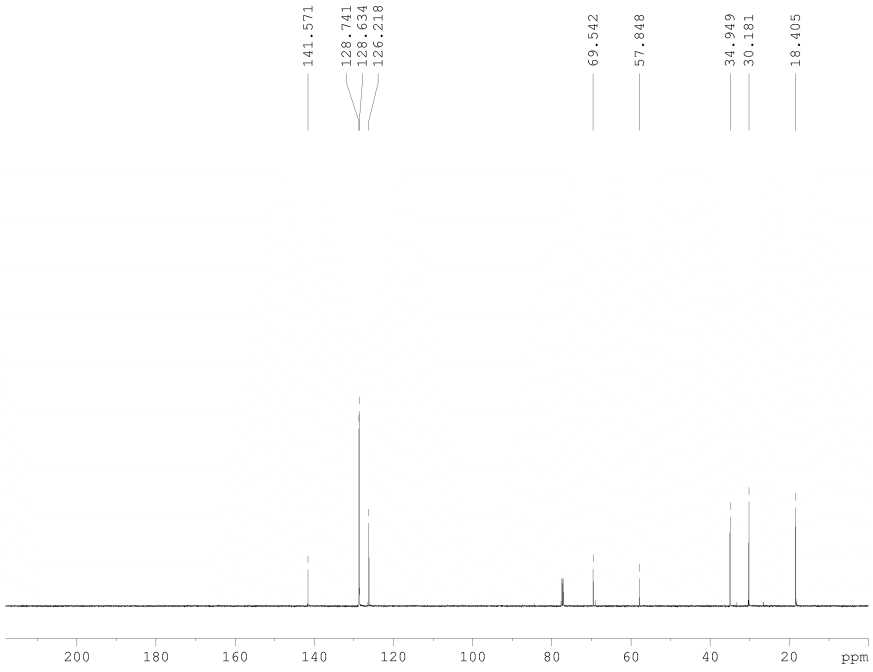


Figure A4.57 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of (5-chloropent-4-yn-1-yl)benzene

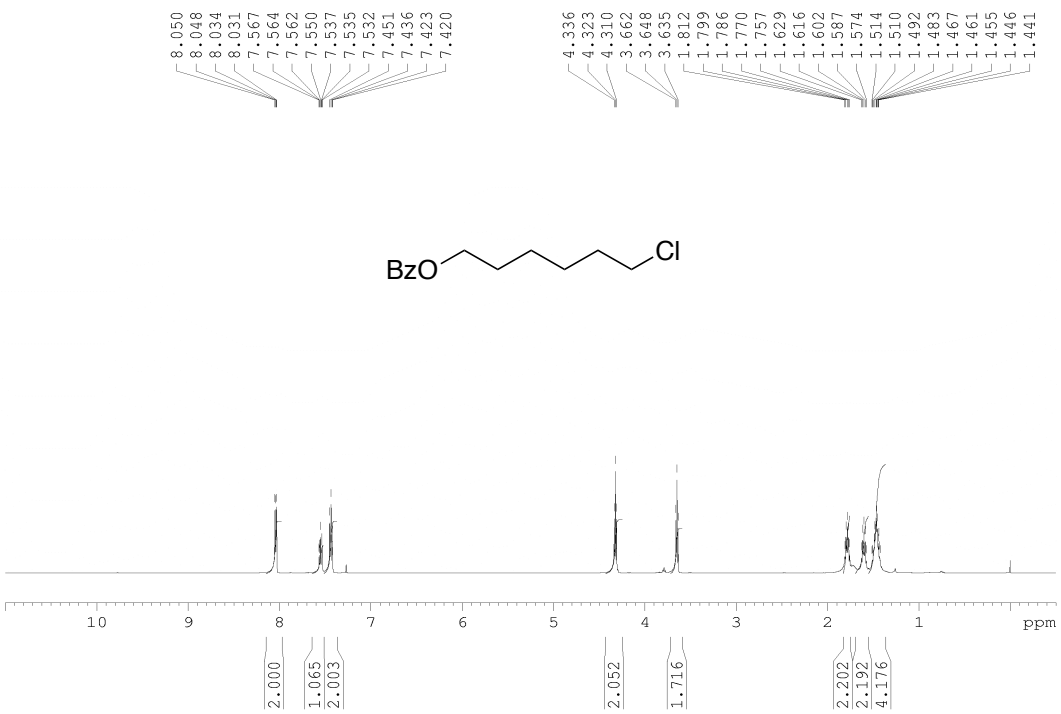


Figure A4.58 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 6-chlorohexyl benzoate

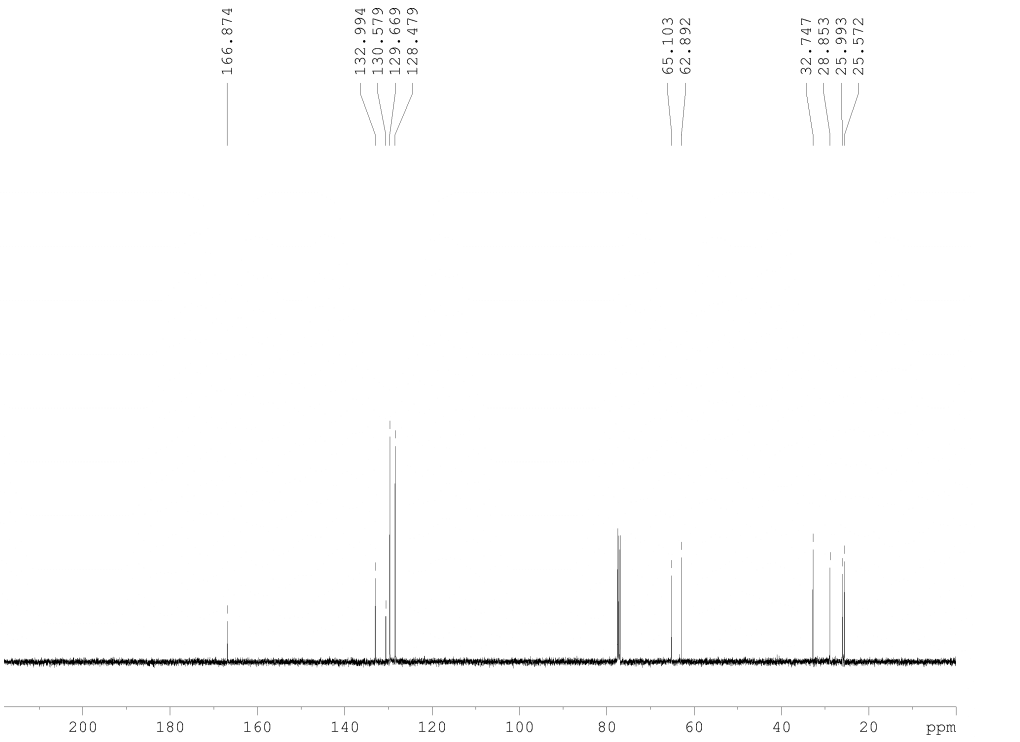


Figure A4.59 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 6-chlorohexyl benzoate

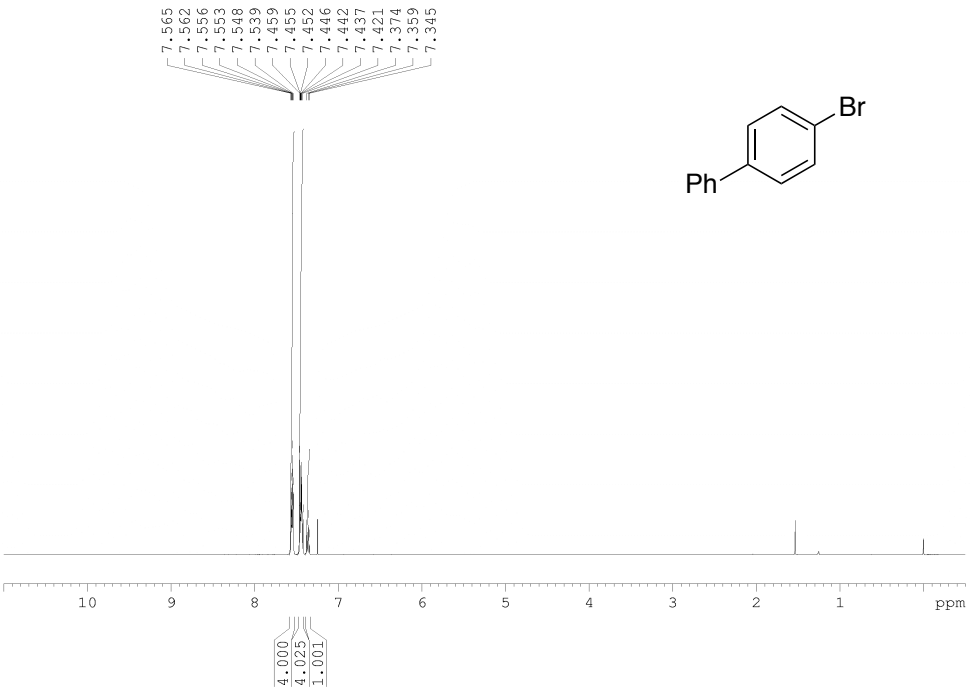


Figure A4.60 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-Bromobiphenyl

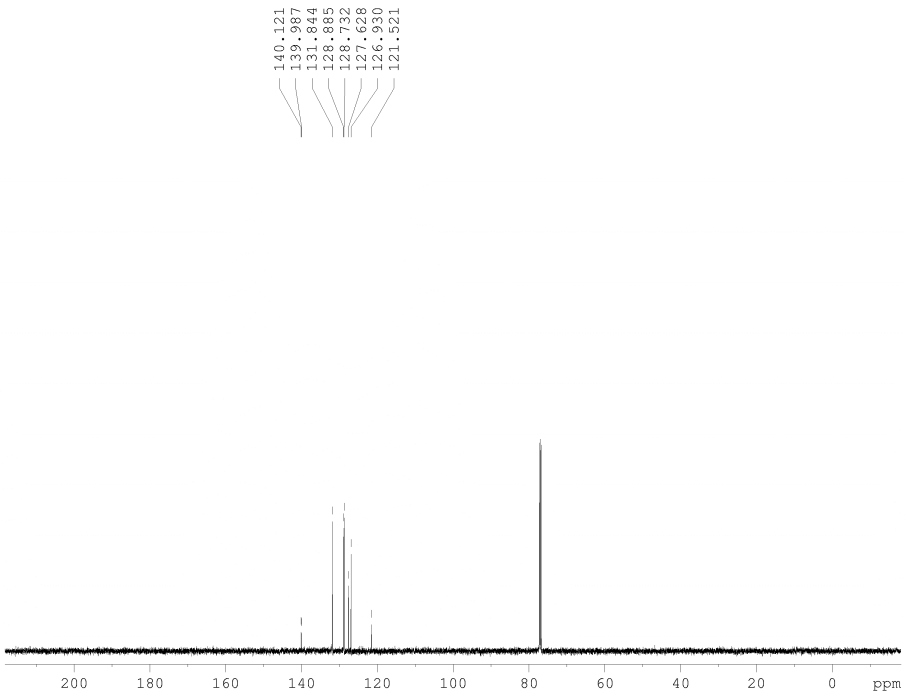


Figure A4.61 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-Bromobiphenyl

Appendix A5. ^{1}H, ^{13}C and ^{19}F Spectra Relevant to Chapter 2.6

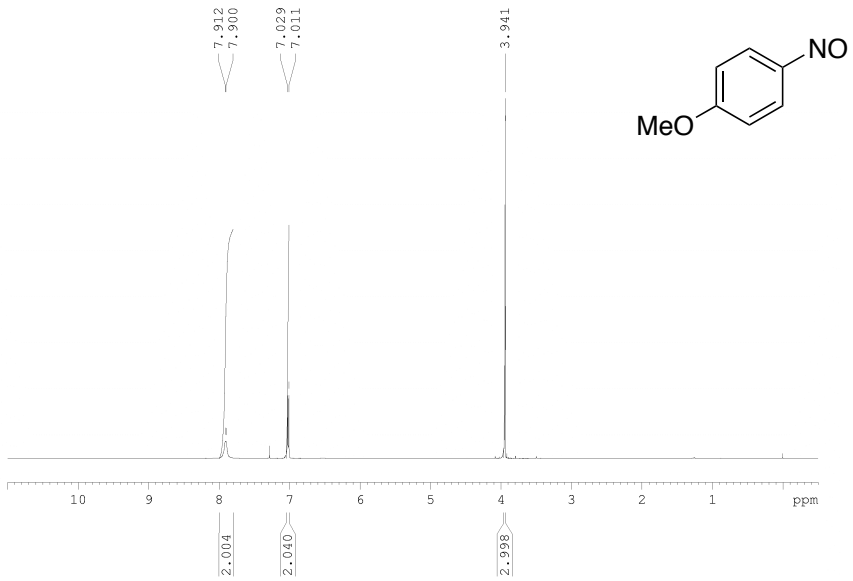


Figure A5.1 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-methoxy-4-nitrosobenzene

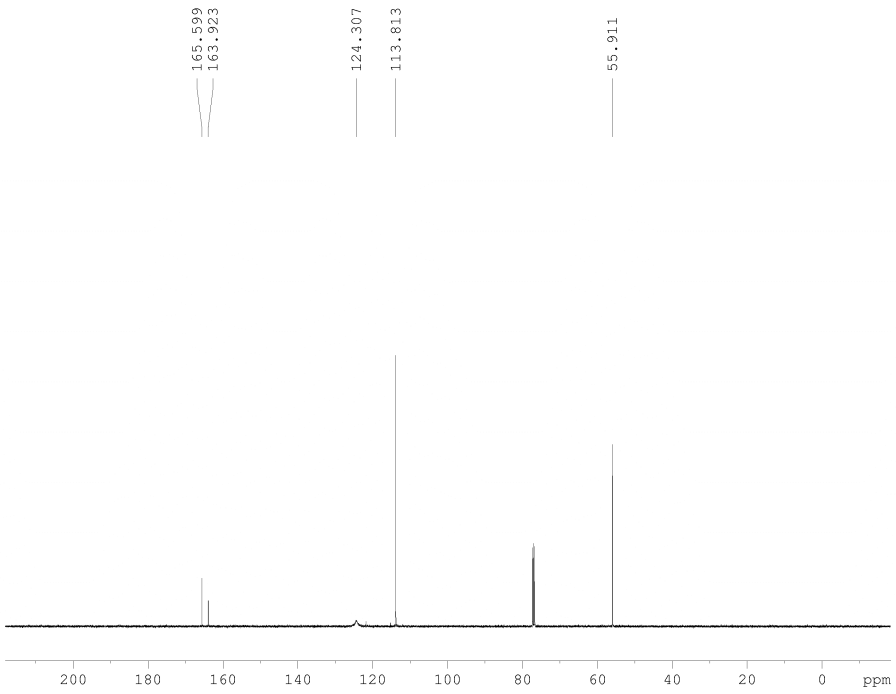


Figure A5.2 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-methoxy-4-nitrosobenzene

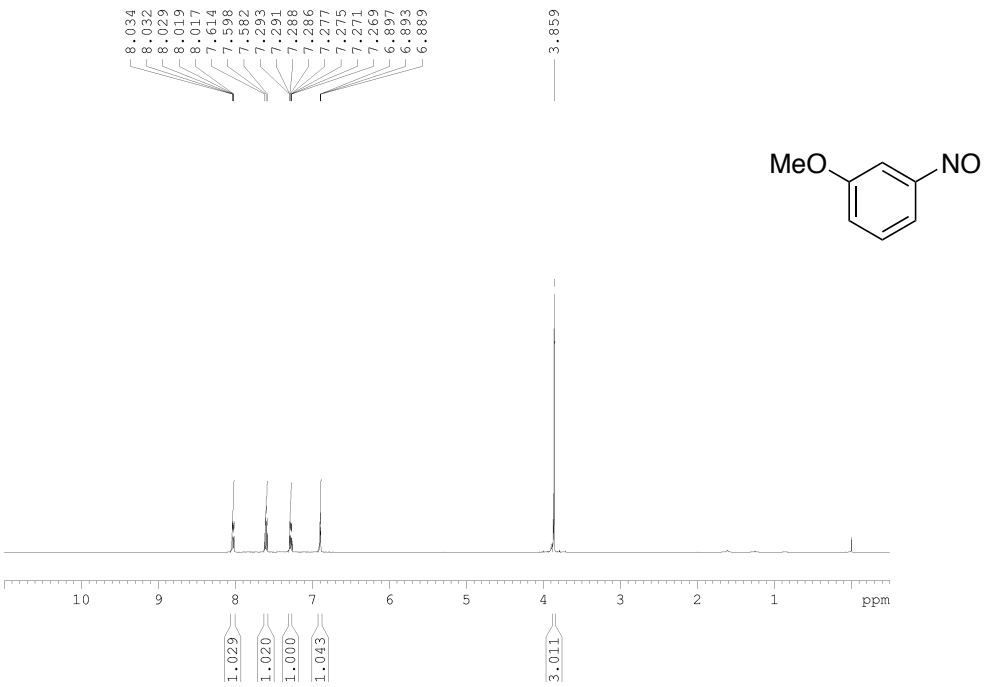


Figure A5.3 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-methoxy-3-nitrosobenzene

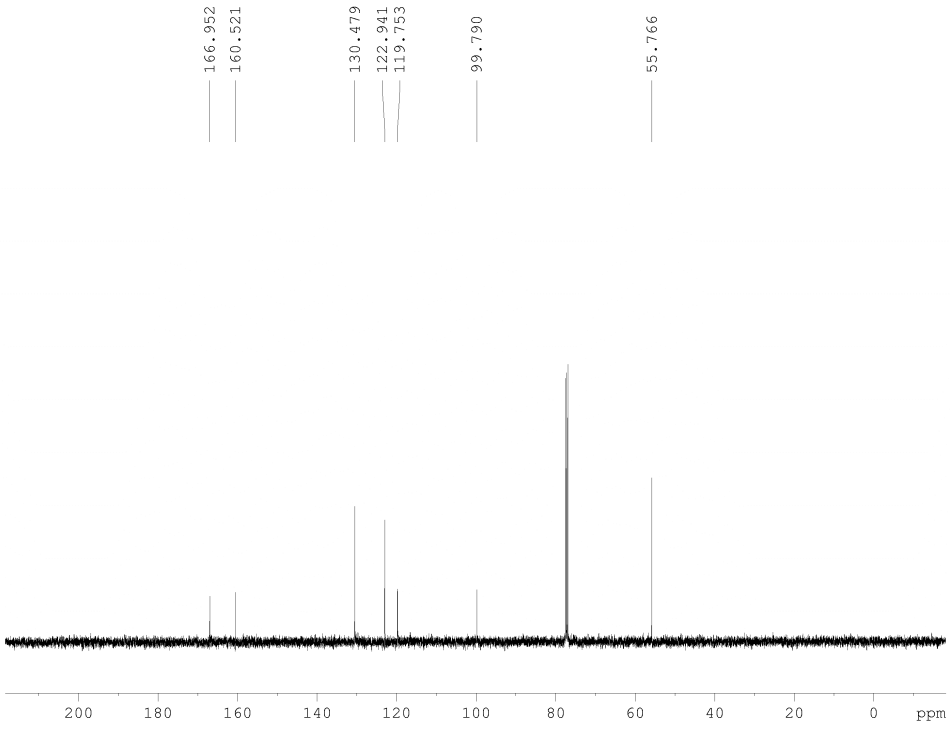


Figure A5.4 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-methoxy-3-nitrosobenzene

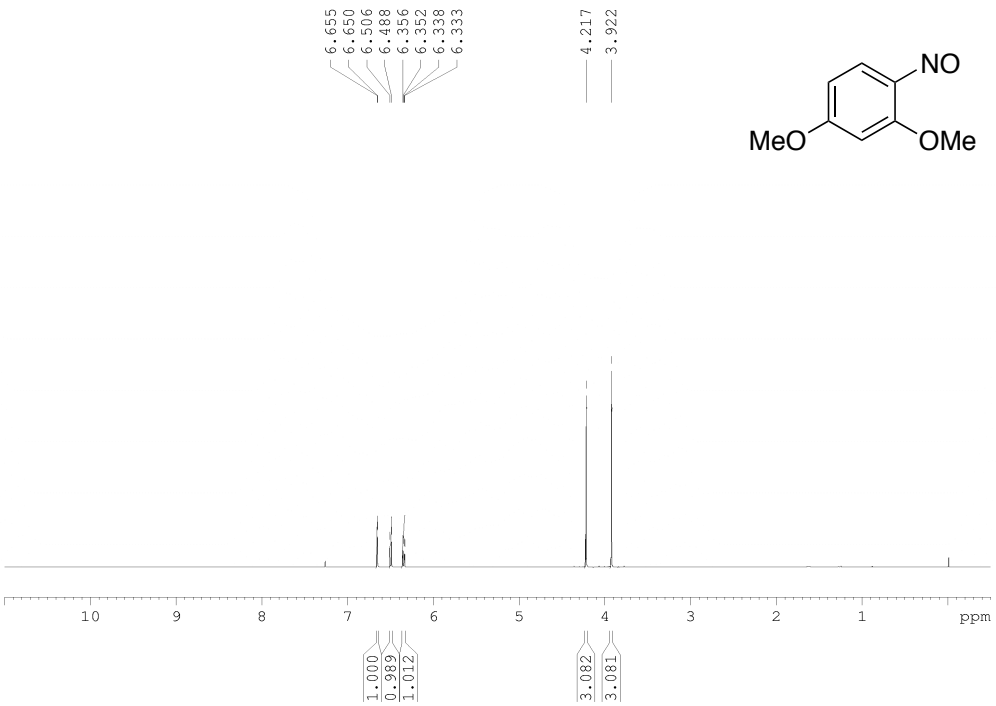


Figure A5.5 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,4-dimethoxy-1-nitrosobenzene

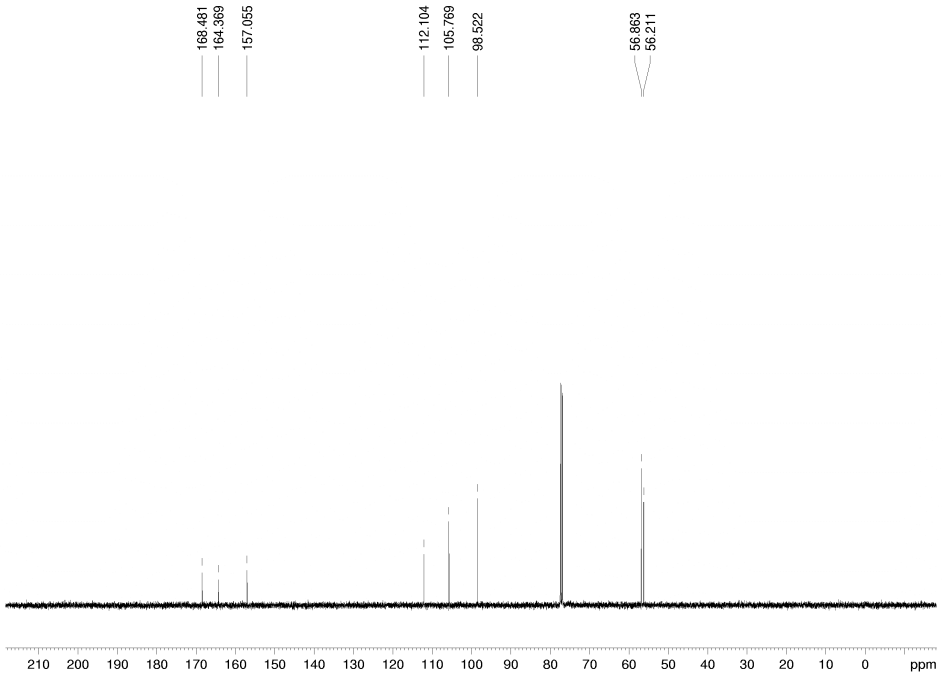


Figure A5.6 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2,4-dimethoxy-1-nitrosobenzene

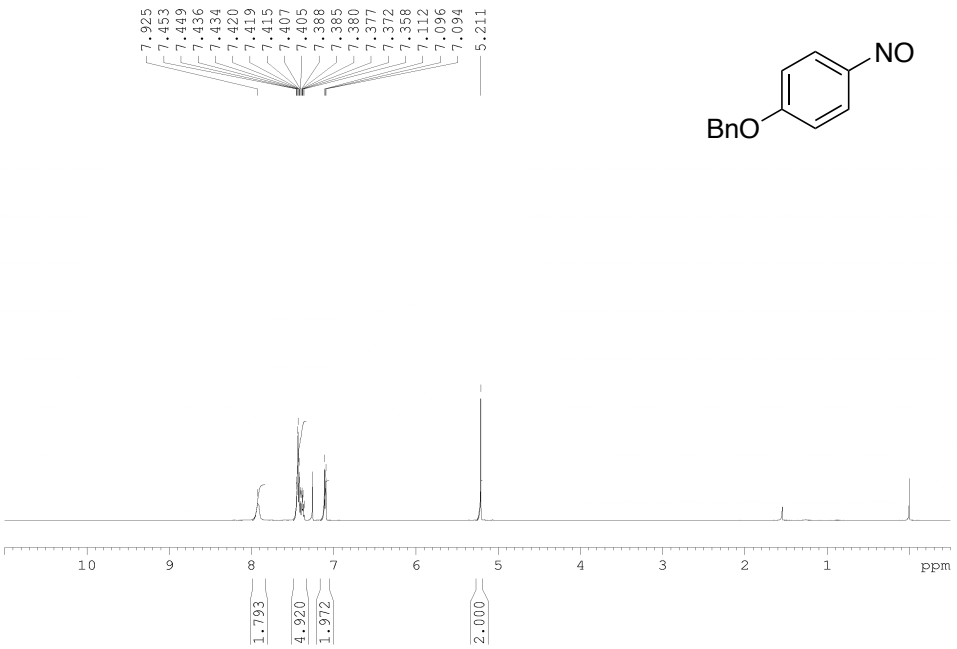


Figure A5.7 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(benzyloxy)-4-nitrosobenzene

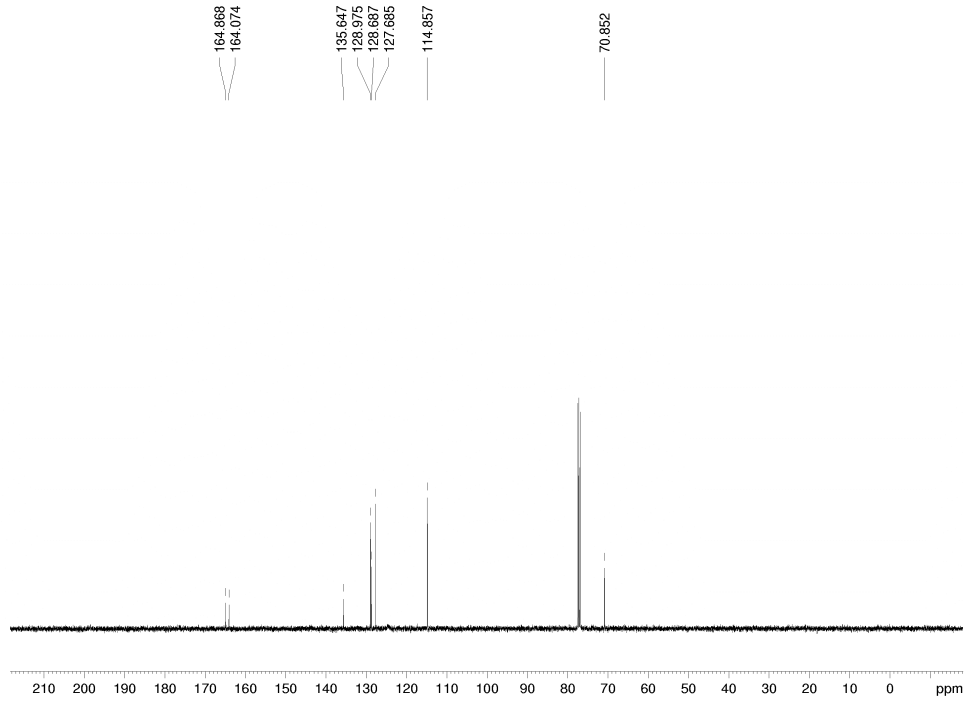


Figure A5.8 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-(benzyloxy)-4-nitrosobenzene

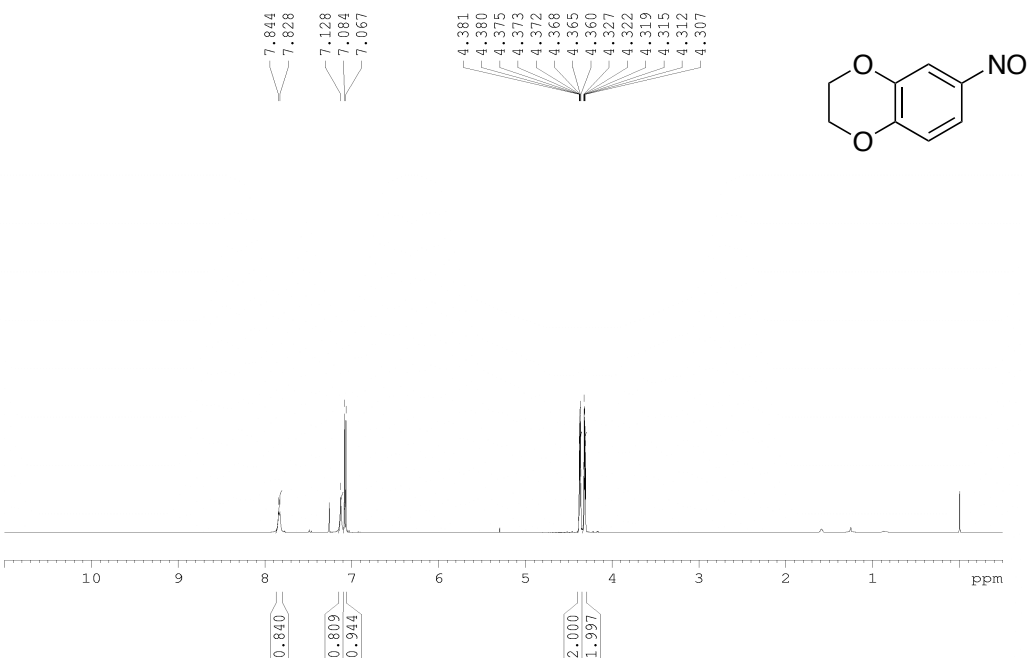


Figure A5.9 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 6-nitroso-2,3-dihydrobenzo[b][1,4]dioxine

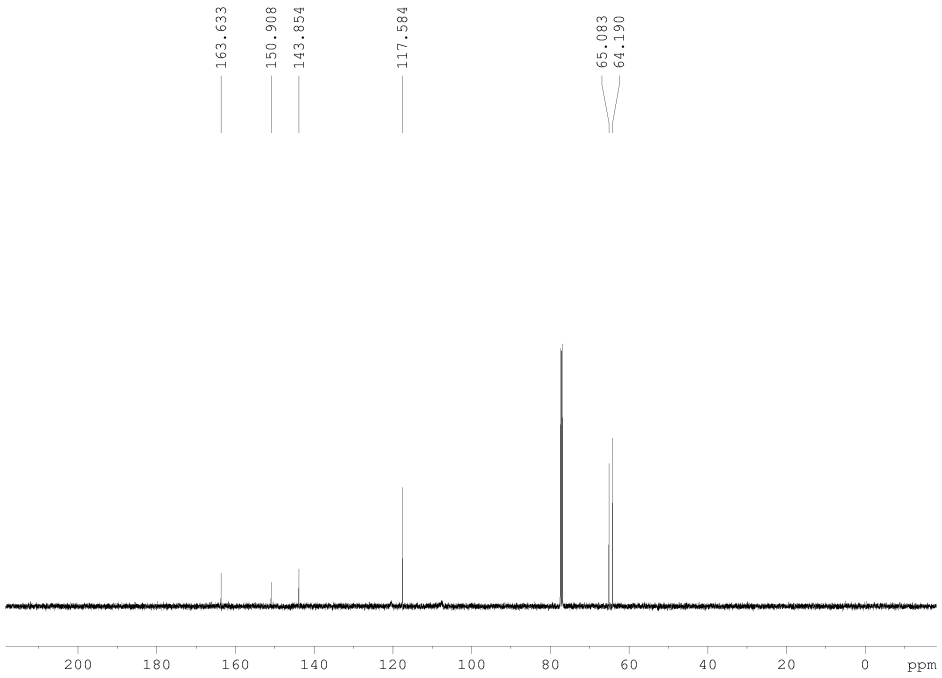


Figure A5.10 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 6-nitroso-2,3-dihydrobenzo[b][1,4]dioxine

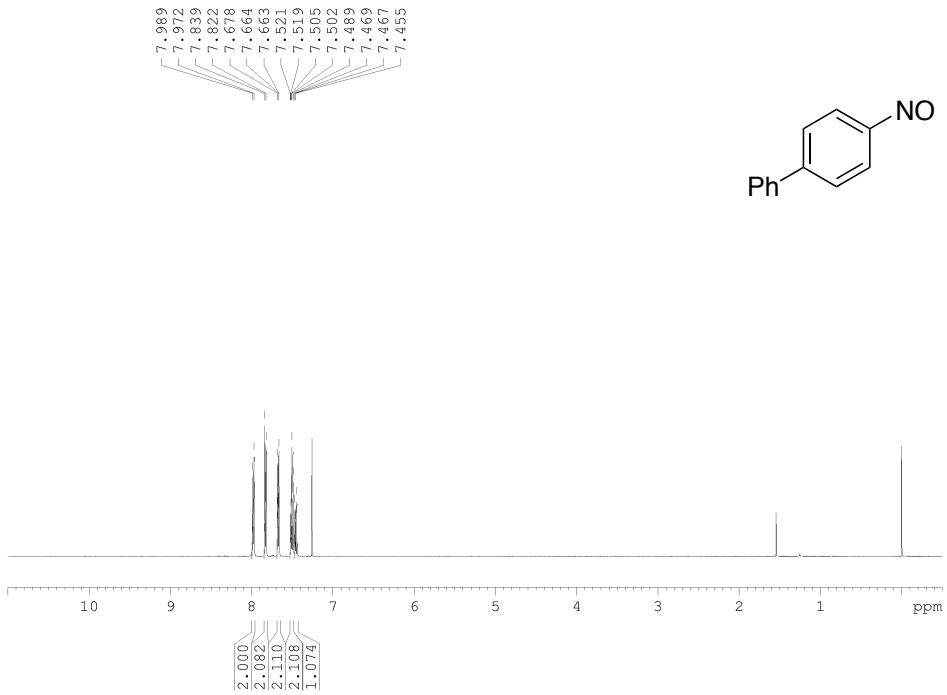


Figure A5.11 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-nitrosobiphenyl

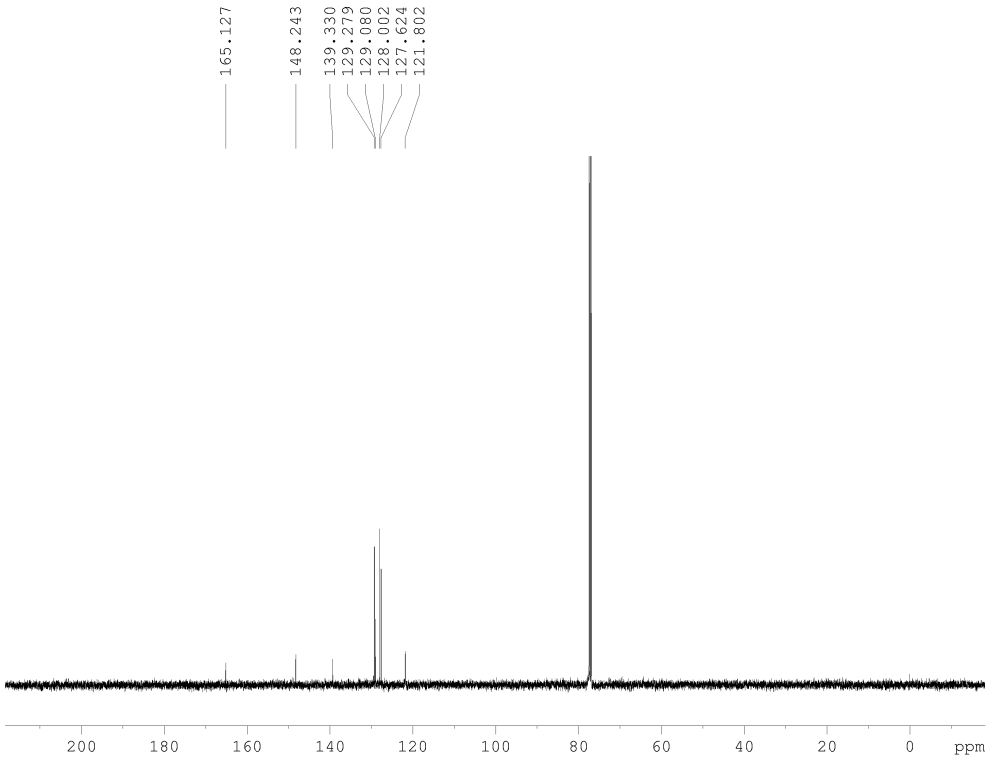


Figure A5.12 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-nitrosobiphenyl

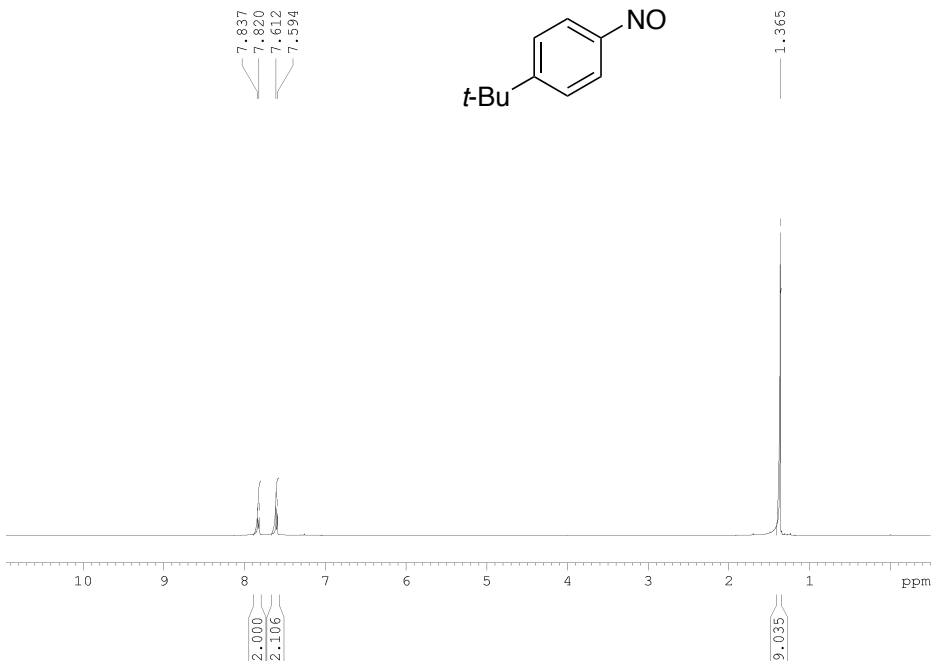


Figure A5.13 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-tert-butyl-4-nitrosobenzene

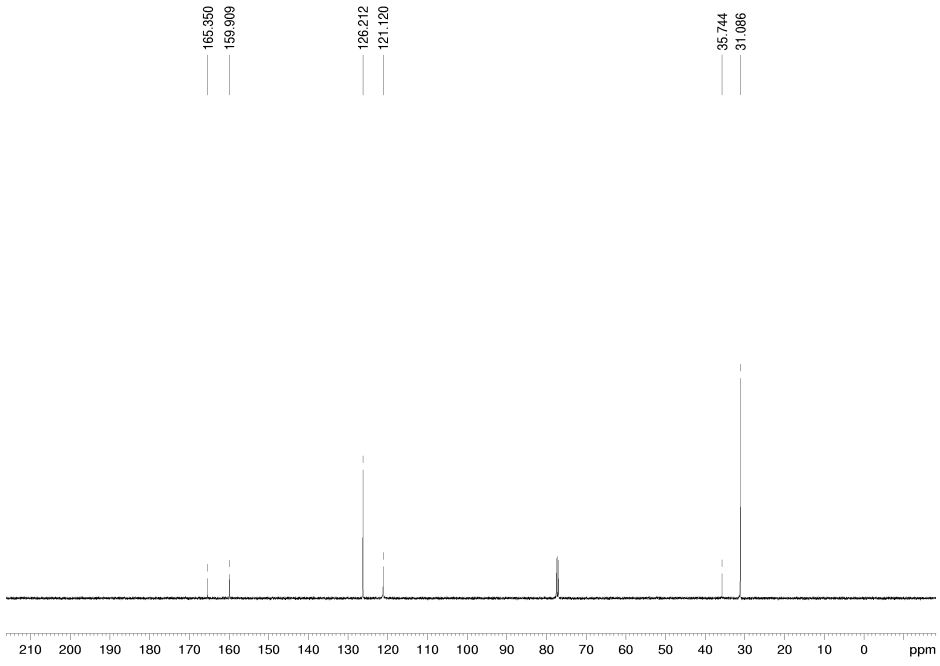


Figure A5.14 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-tert-butyl-4-nitrosobenzene

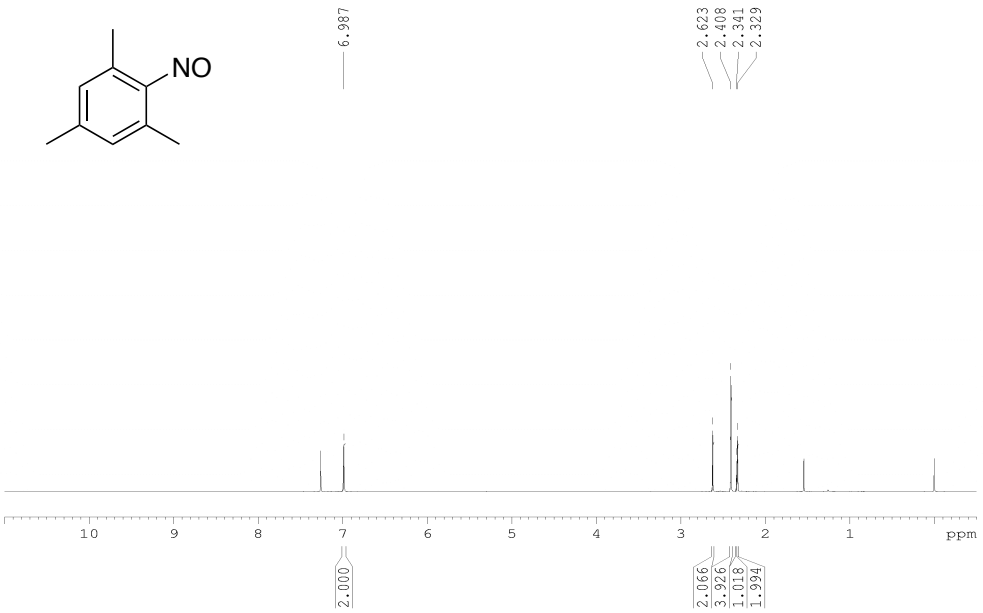


Figure A5.15 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1,3,5-trimethyl-2-nitrosobenzene

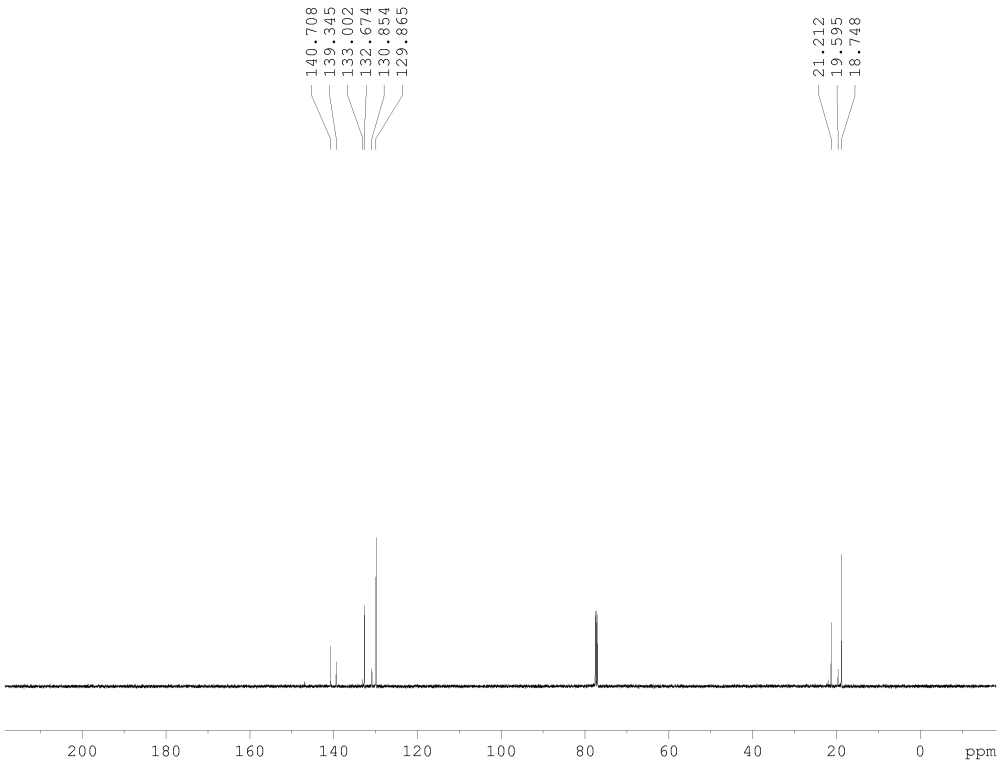


Figure A5.16 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1,3,5-trimethyl-2-nitrosobenzene

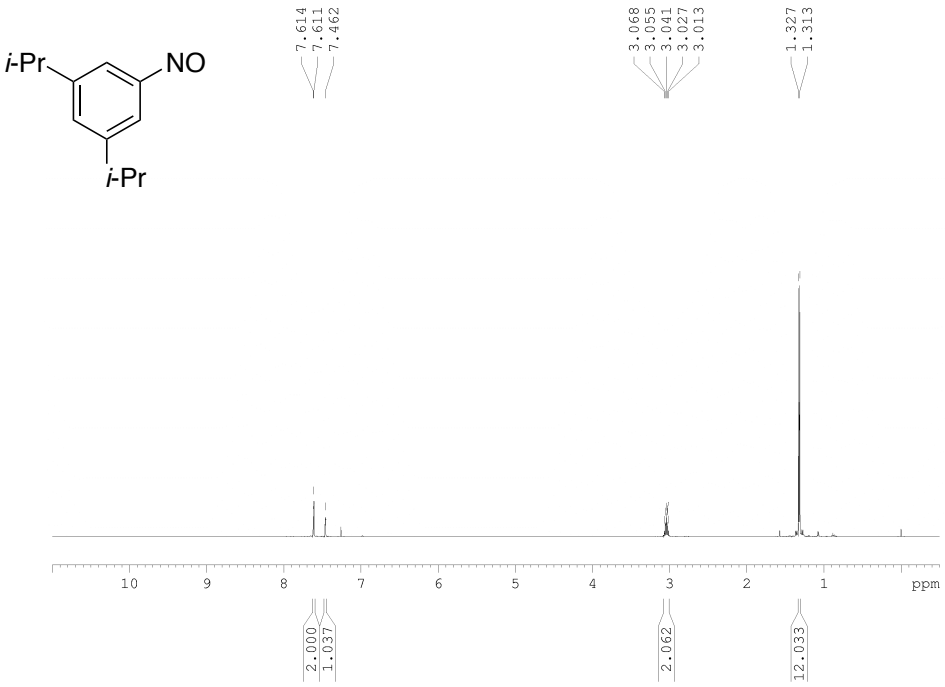


Figure A5.17 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1,3-diisopropyl-5-nitrosobenzene

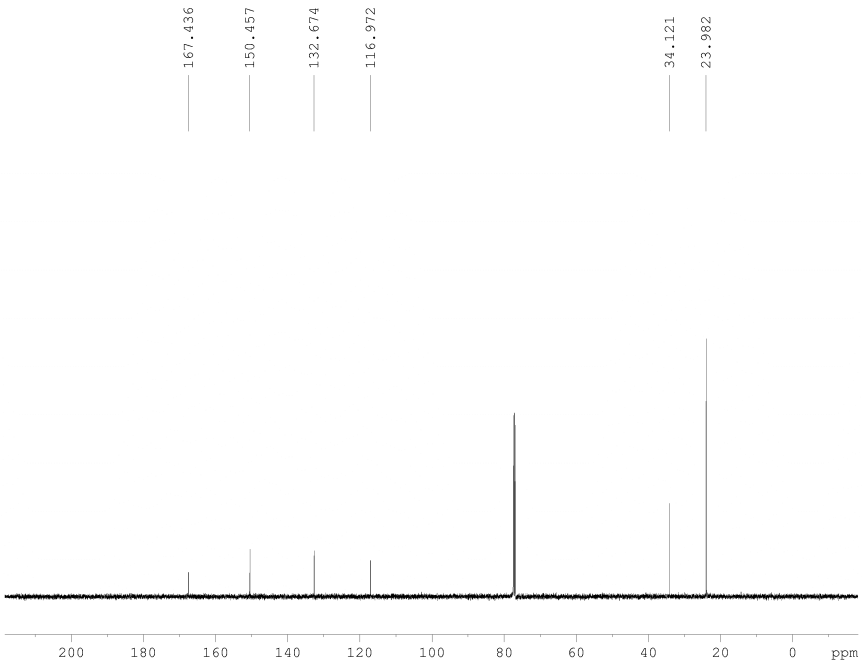


Figure A5.18 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1,3-diisopropyl-5-nitrosobenzene

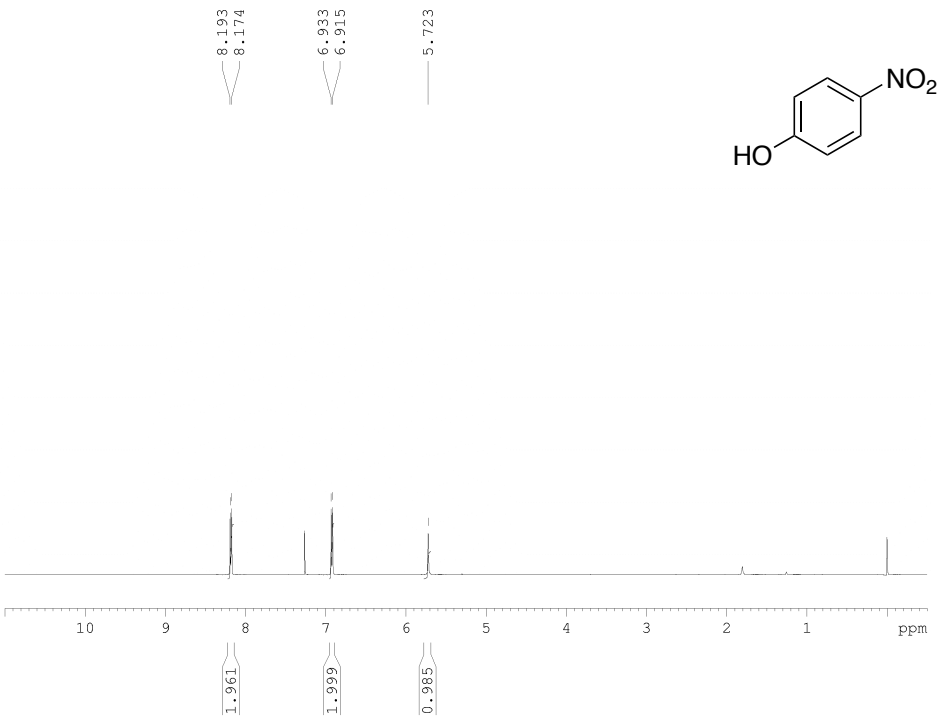


Figure A5.19 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-nitrophenol

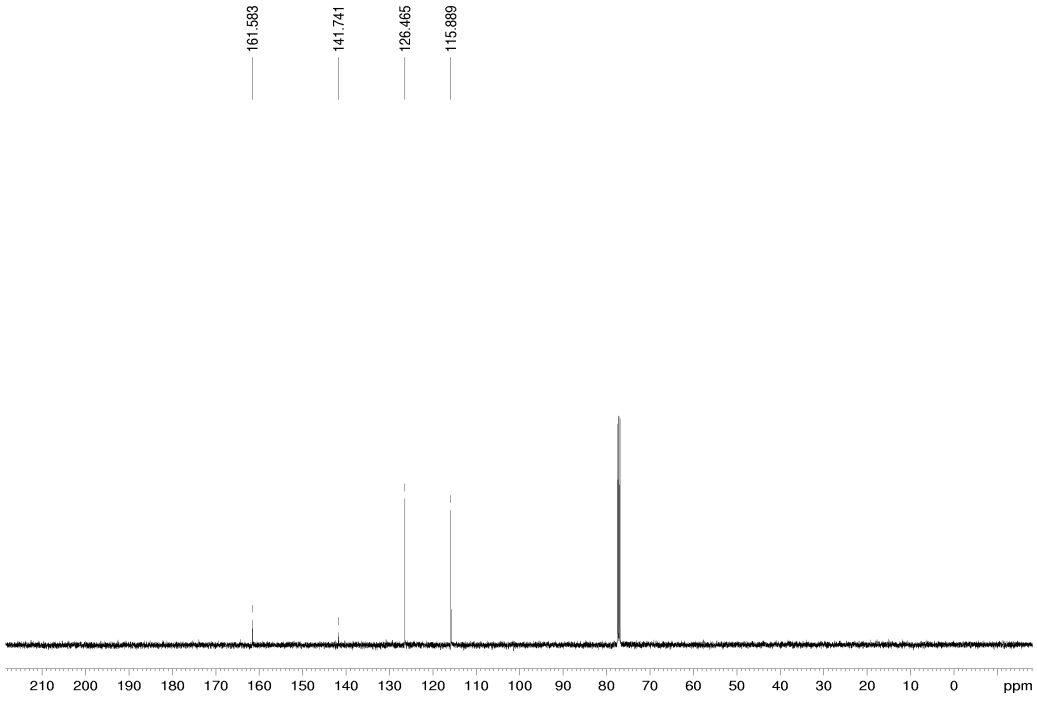


Figure A5.20 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-nitrophenol

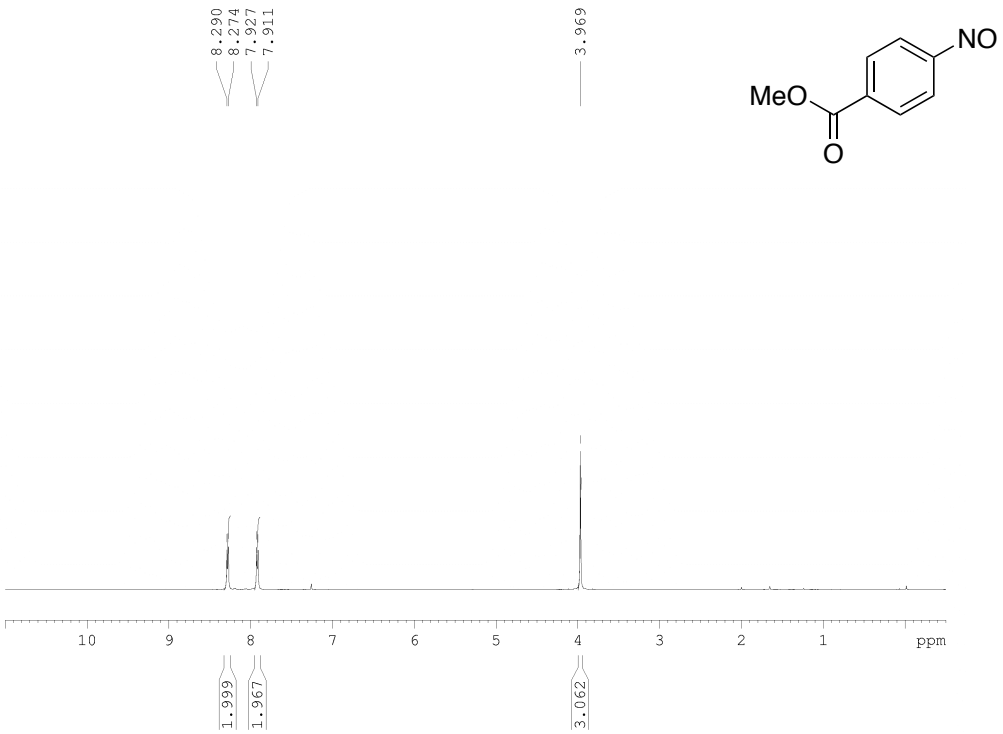


Figure A5.21 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of methyl 4-nitrosobenzoate

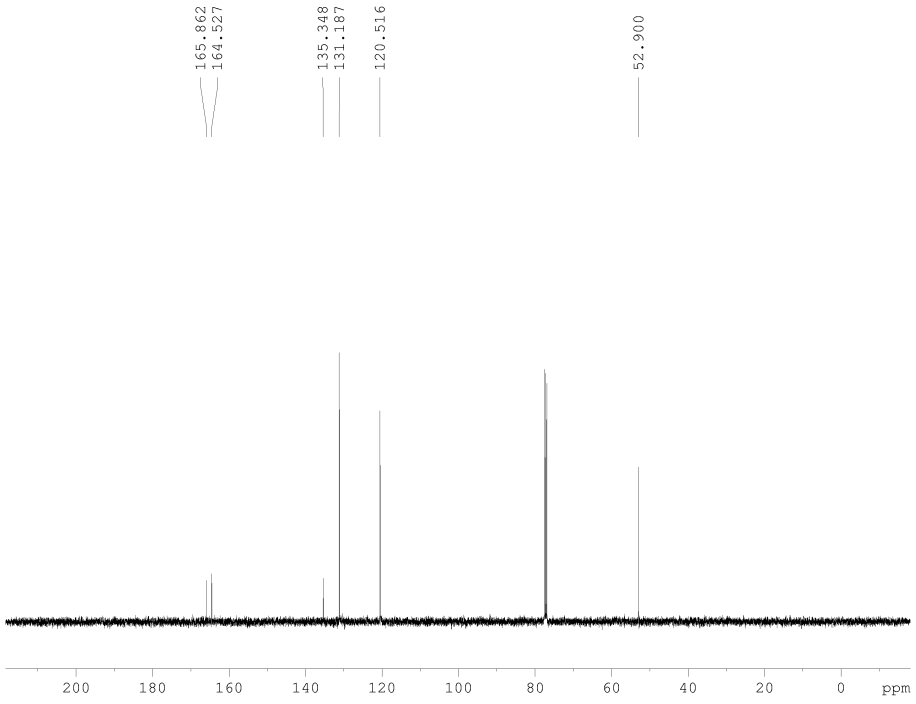


Figure A5.22 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of methyl 4-nitrosobenzoate

Figure A5.23 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of methyl 3-nitrosobenzoate

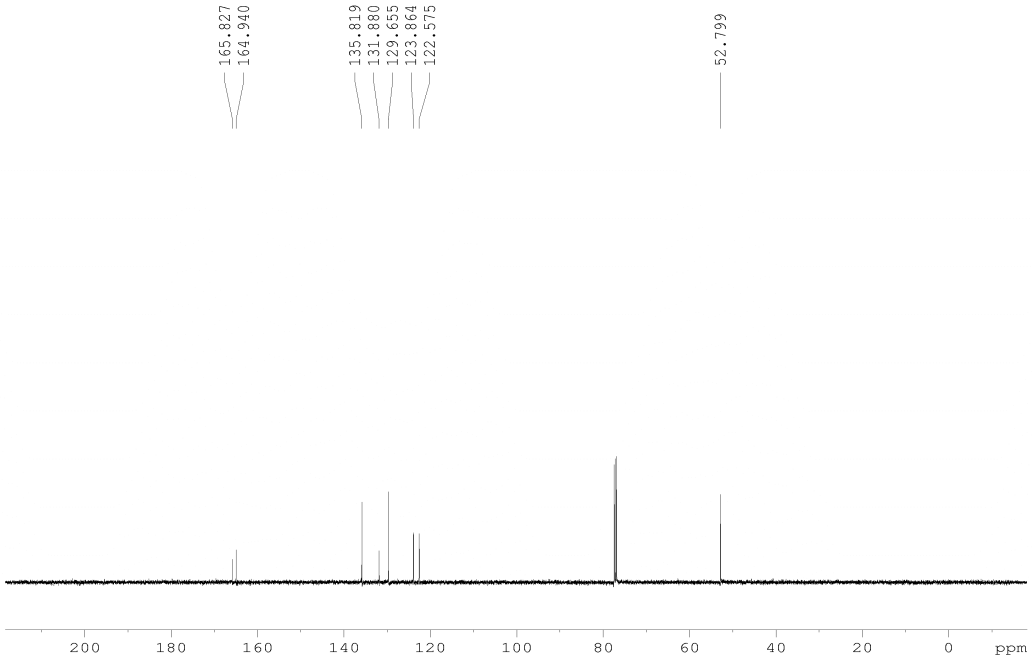


Figure A5.24 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of methyl 3-nitrosobenzoate

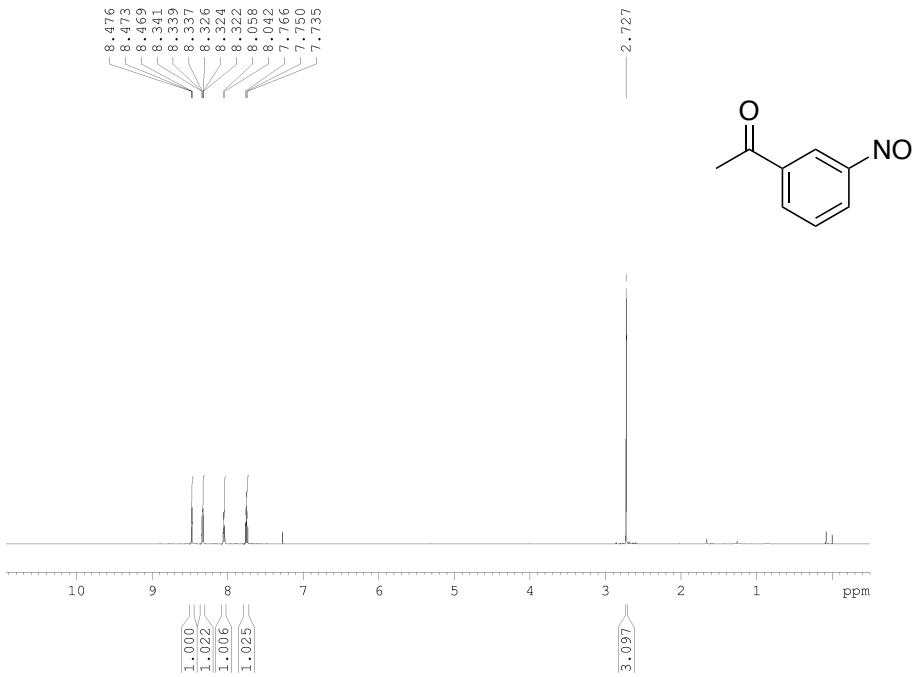


Figure A5.25 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(3-nitrosophenyl)ethanone

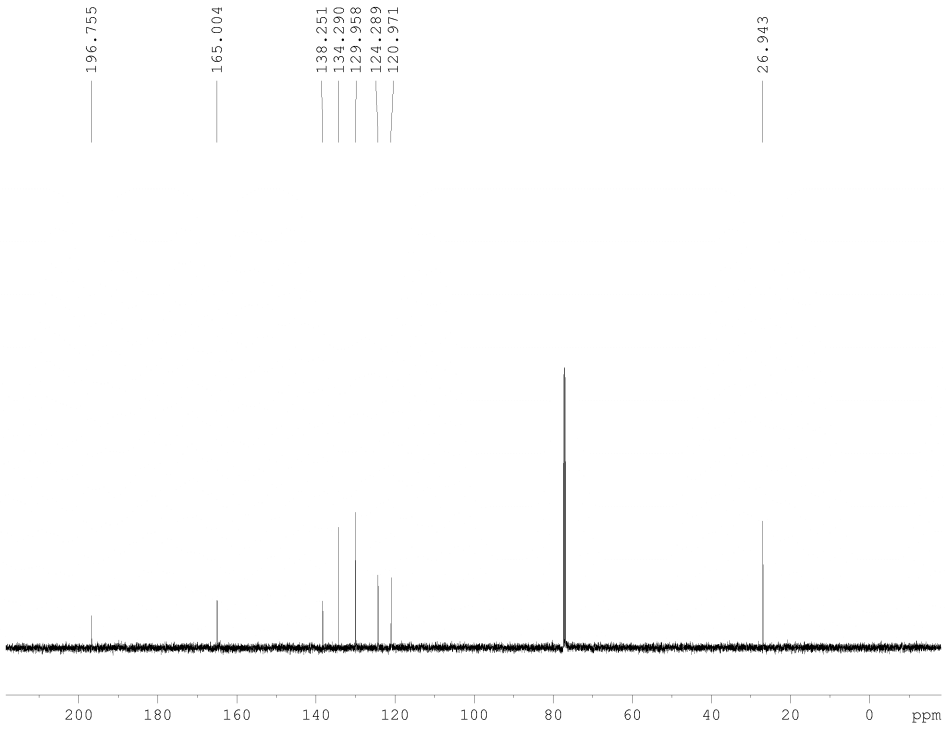


Figure A5.26 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-(3-nitrosophenyl)ethanone

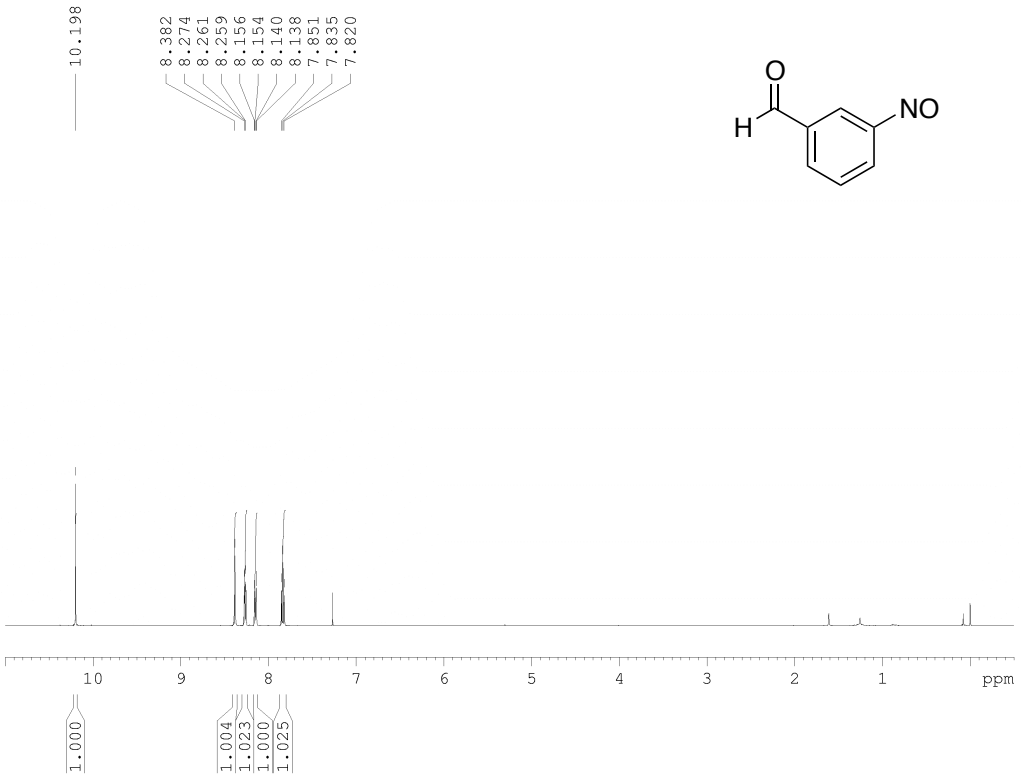


Figure A5.27 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 3-nitrosobenzaldehyde

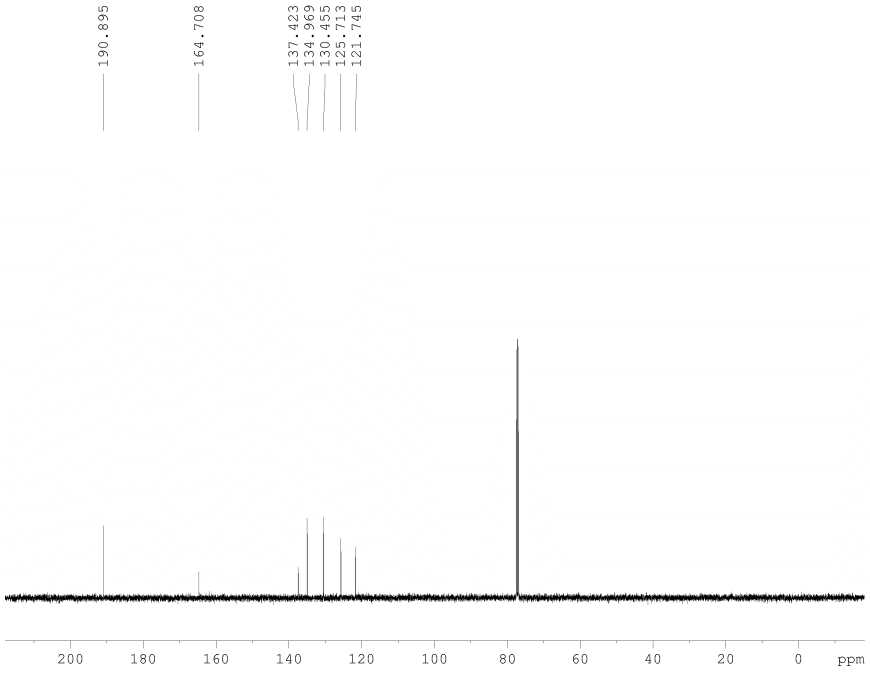


Figure A5.28 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 3-nitrosobenzaldehyde

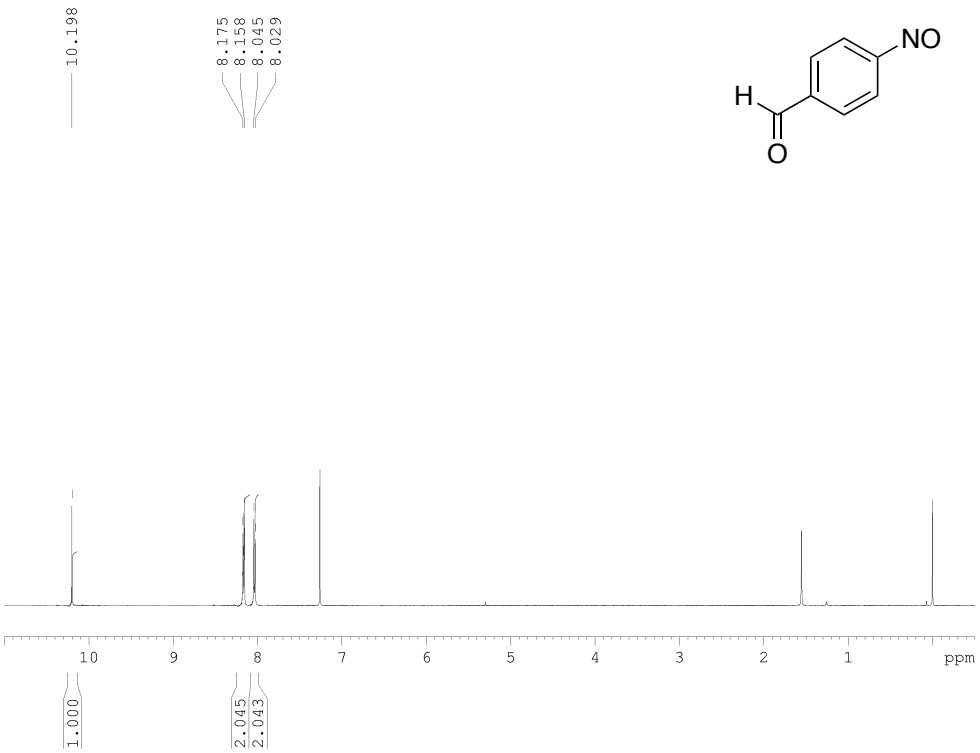


Figure A5.29 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-nitrosobenzaldehyde

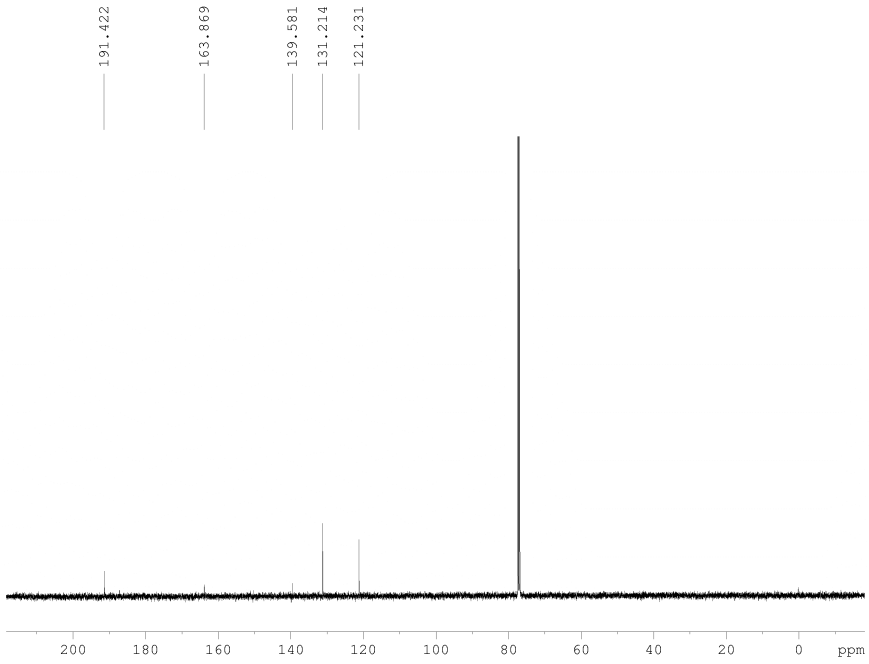


Figure A5.30 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-nitrosobenzaldehyde

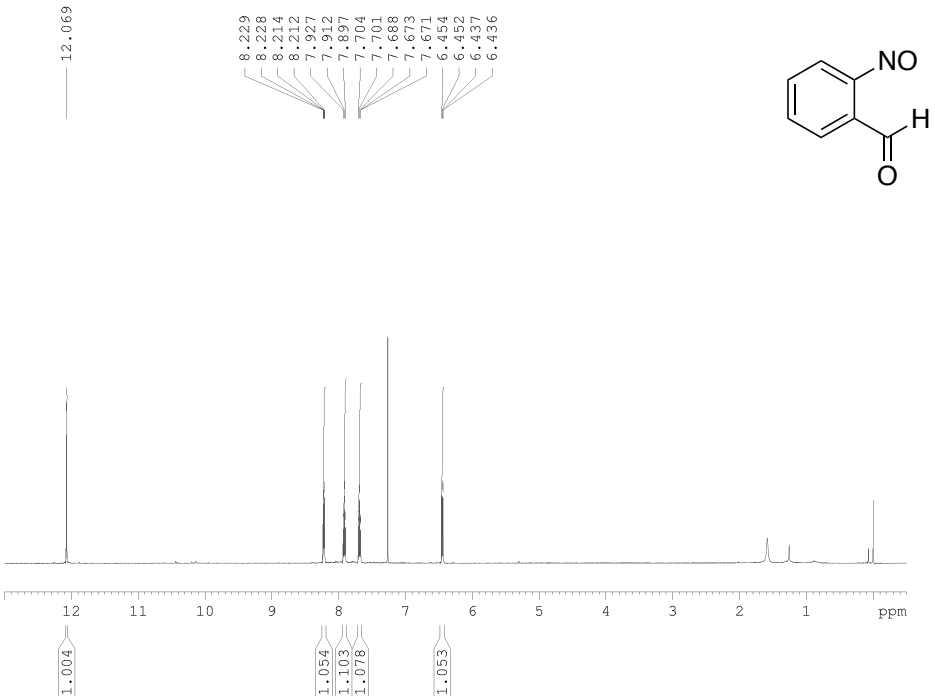


Figure A5.31 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-nitrosobenzaldehyde

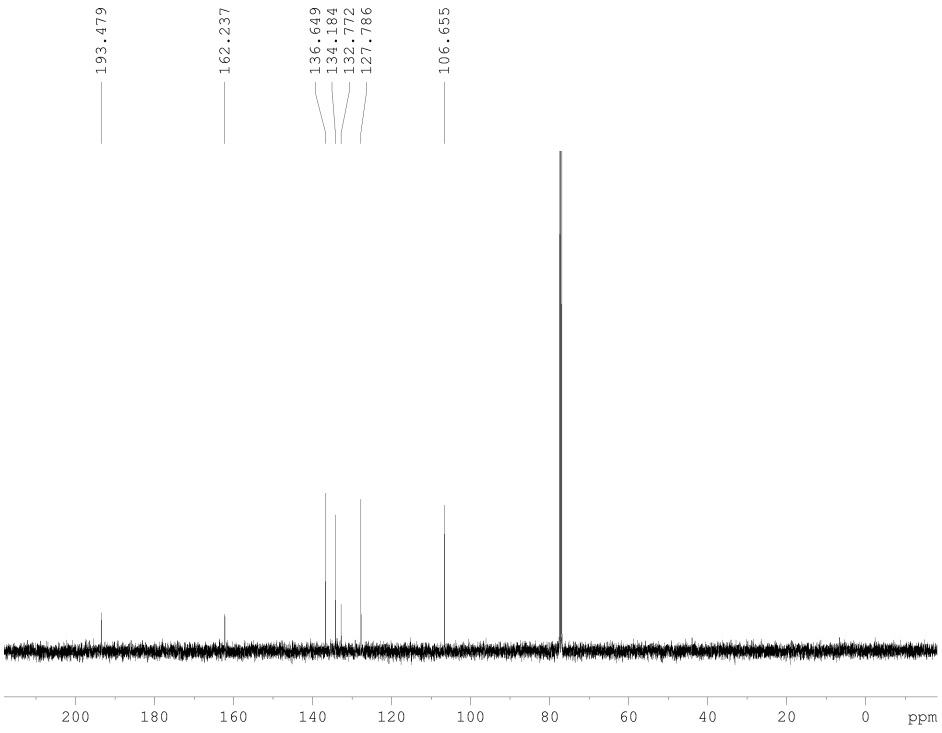


Figure A5.32 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2-nitrosobenzaldehyde

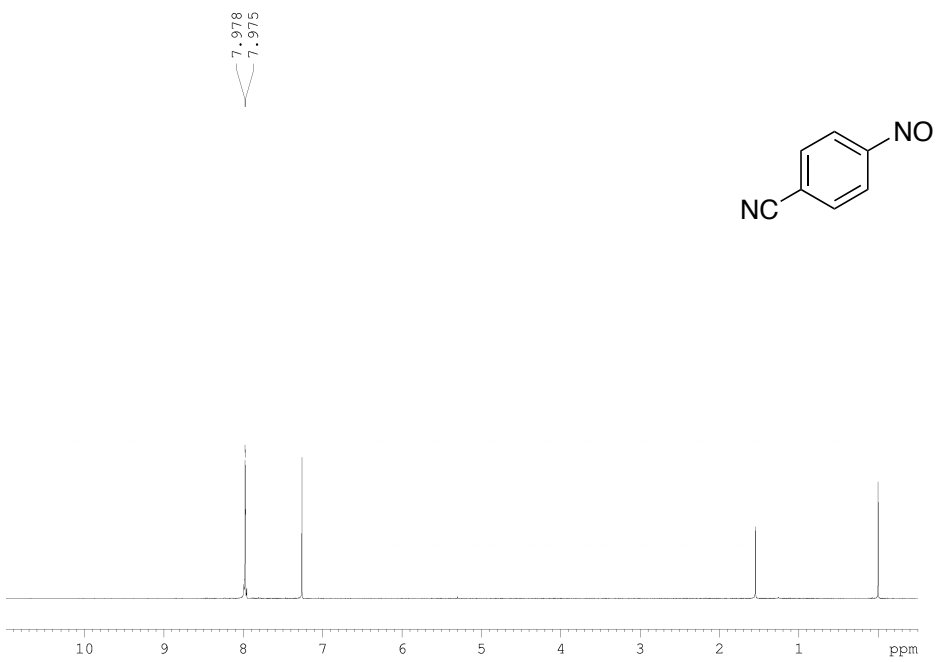


Figure A5.33 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-nitrosobenzonitrile

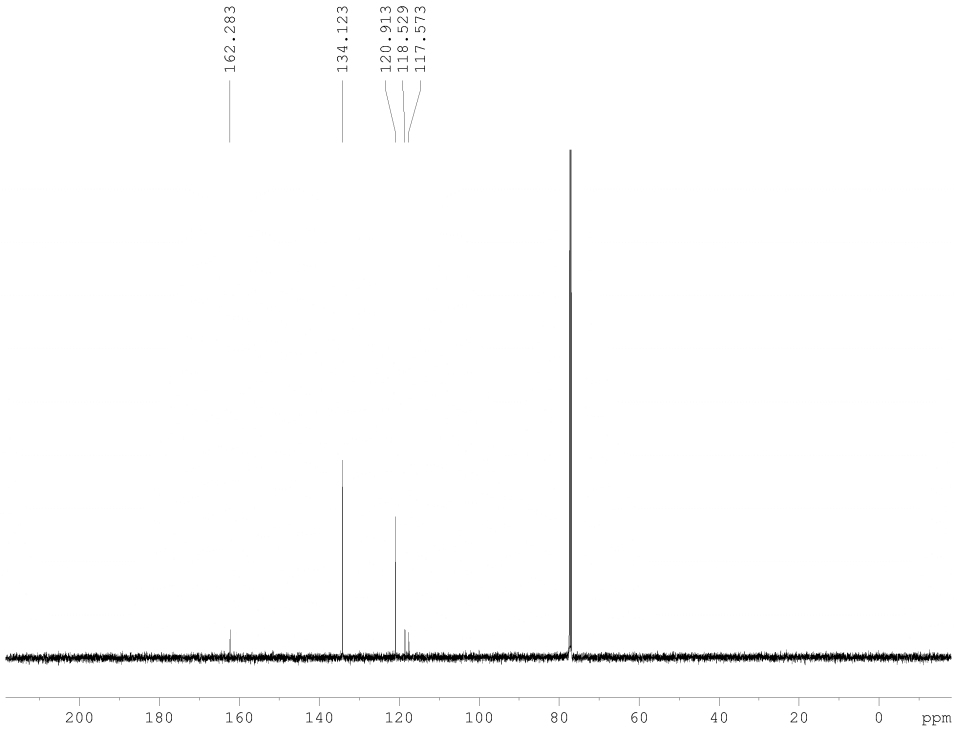


Figure A5.34 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-nitrosobenzonitrile

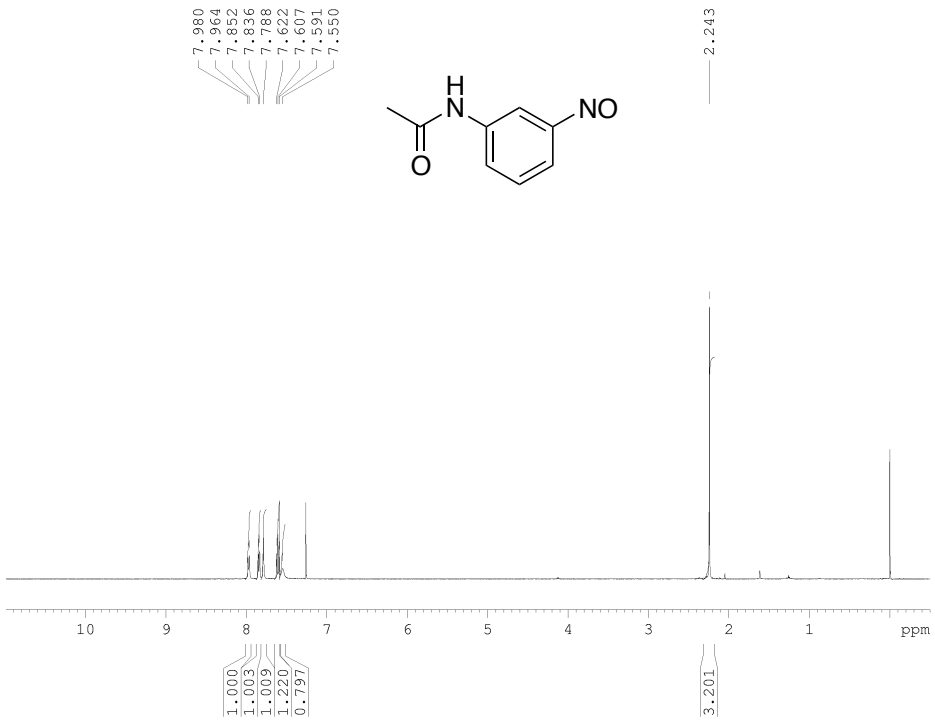


Figure A5.35 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of *N*-(3-nitrosophenyl)acetamide

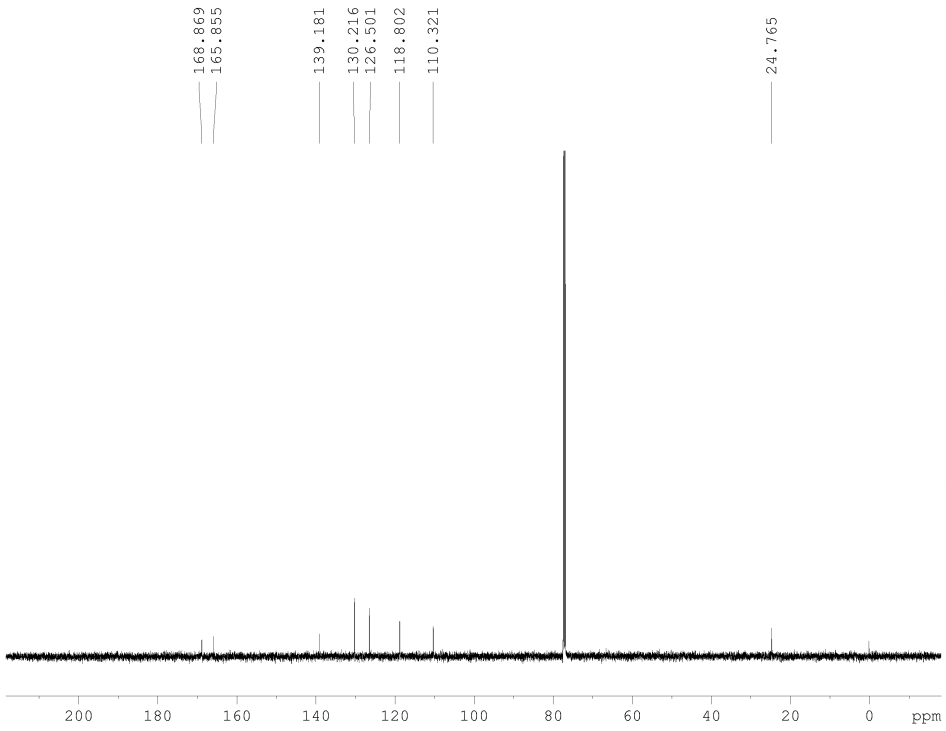


Figure A5.36 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of *N*-(3-nitrosophenyl)acetamide

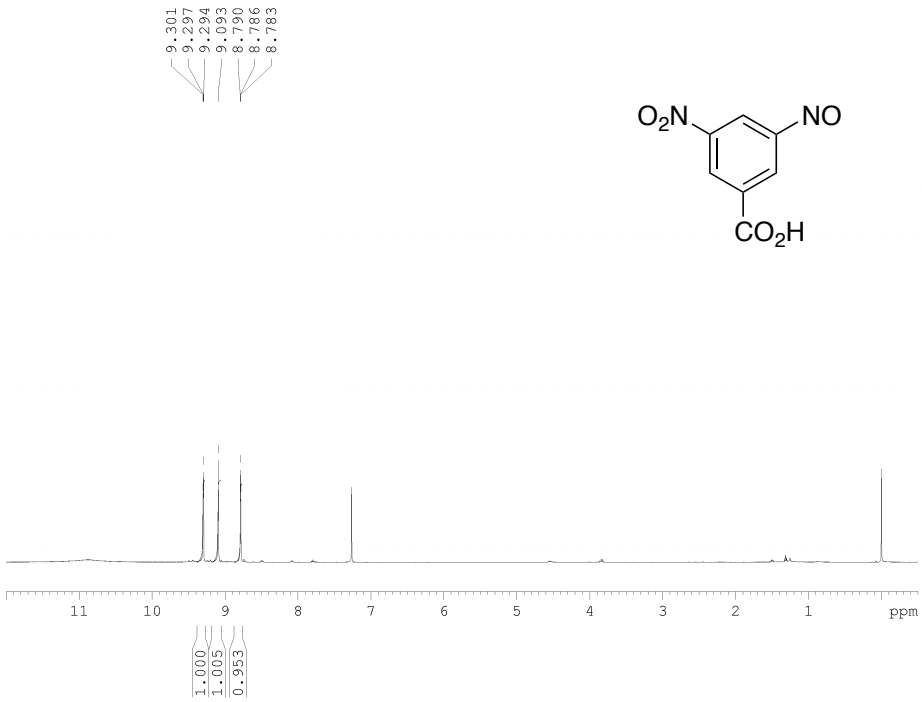


Figure A5.37 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 3-nitro-5-nitrosobenzoic acid

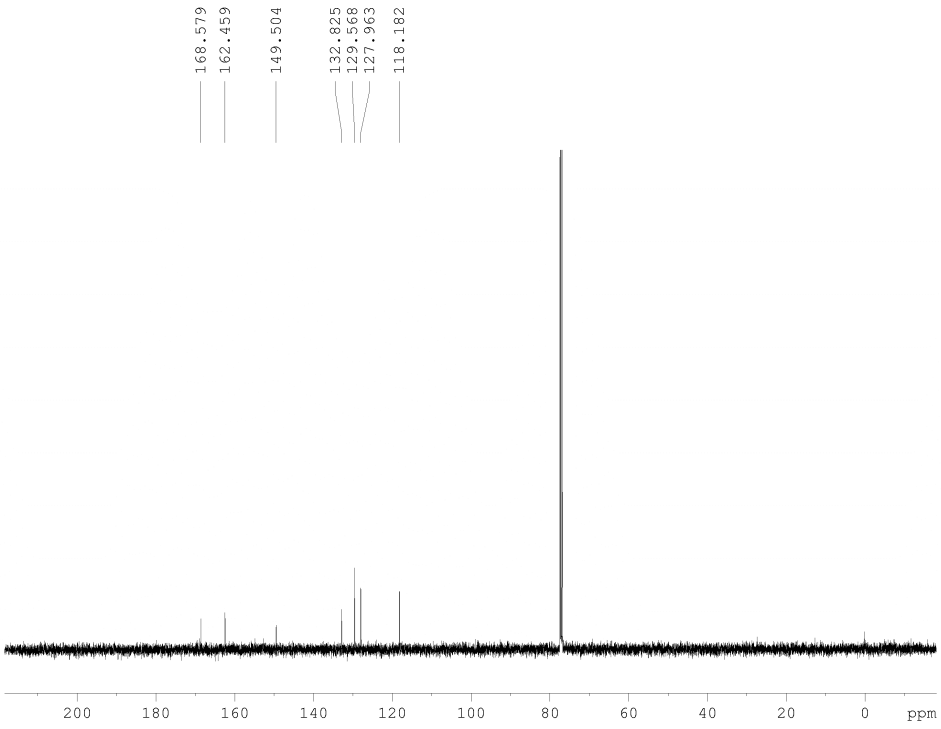


Figure A5.38 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 3-nitro-5-nitrosobenzoic acid

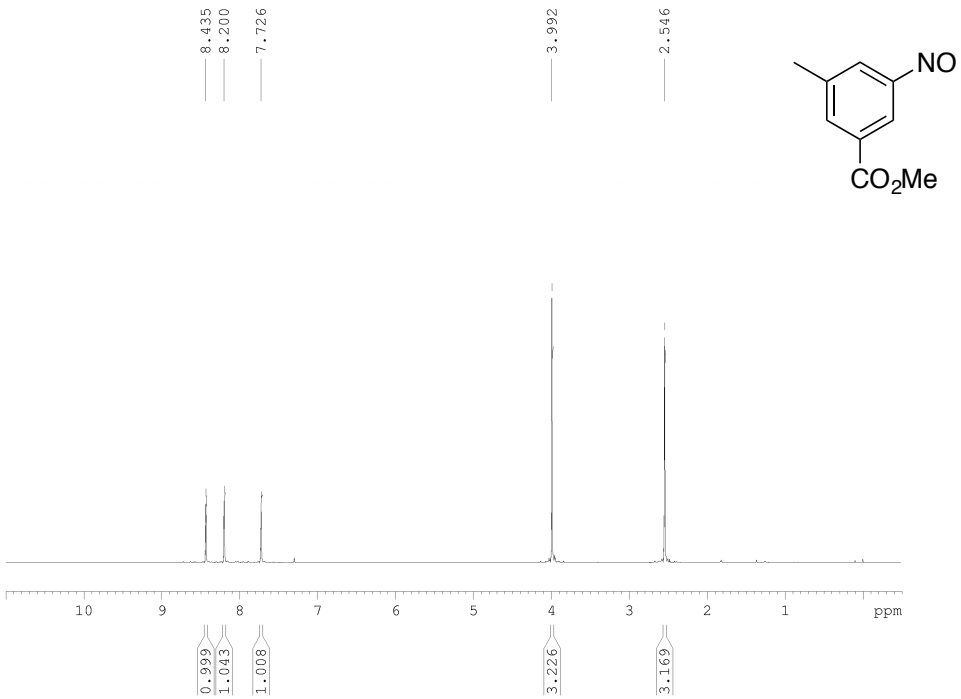


Figure A5.39 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of methyl 3-methyl-5-nitrosobenzoate

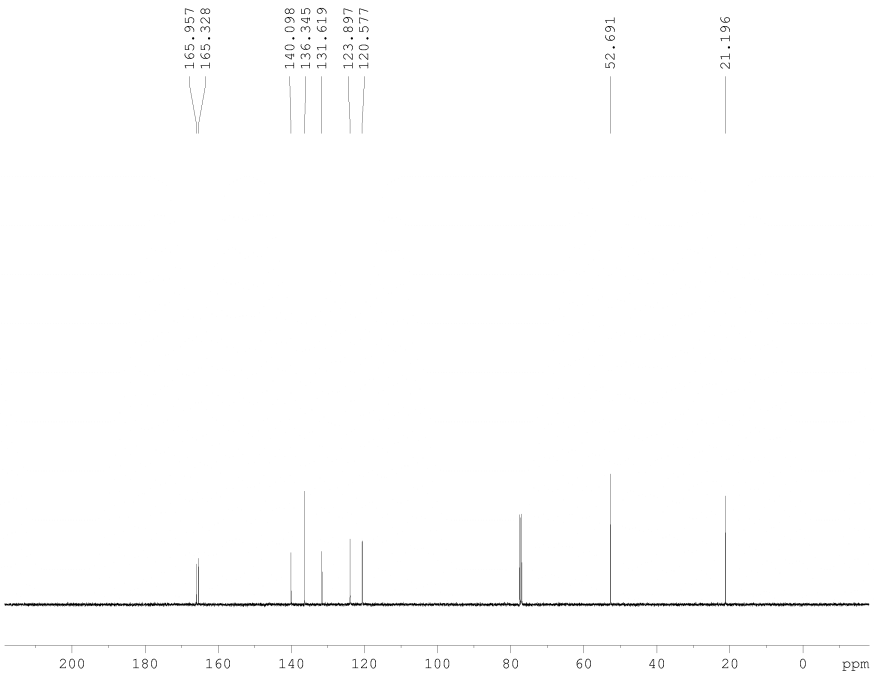


Figure A5.40 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of methyl 3-methyl-5-nitrosobenzoate

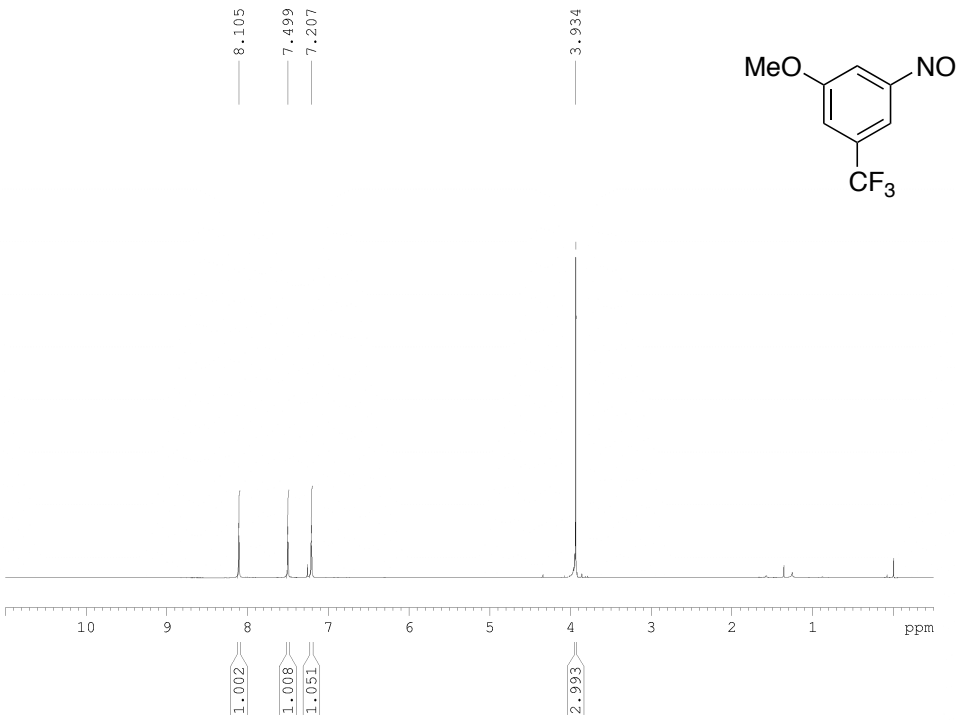


Figure A5.41 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-methoxy-3-nitroso-5-(trifluoromethyl)benzene

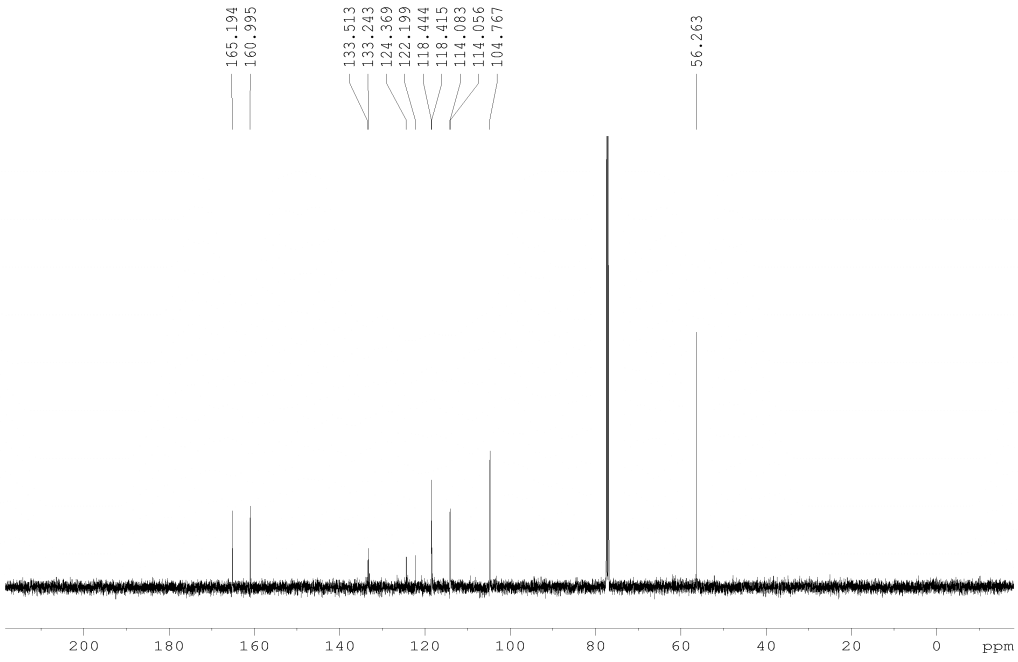


Figure A5.42 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-methoxy-3-nitroso-5-(trifluoromethyl)benzene

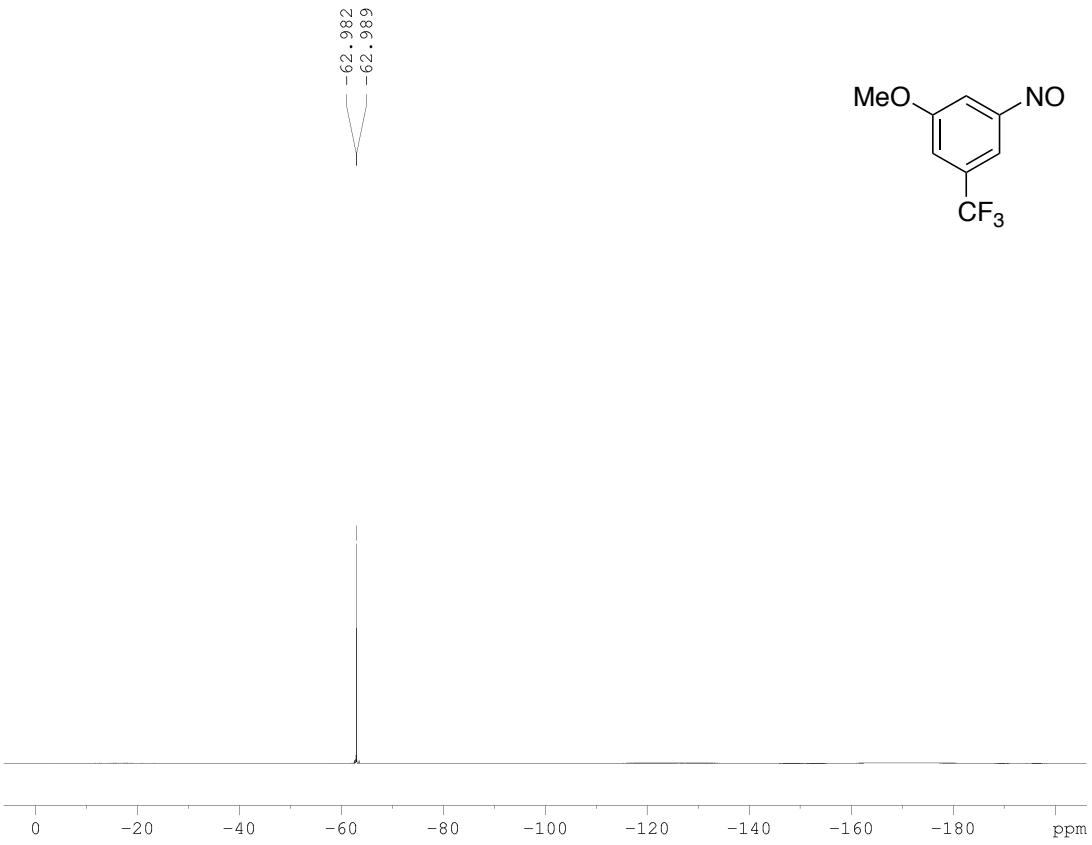


Figure A5.43 ^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of 1-methoxy-3-nitroso-5-(trifluoromethyl)benzene

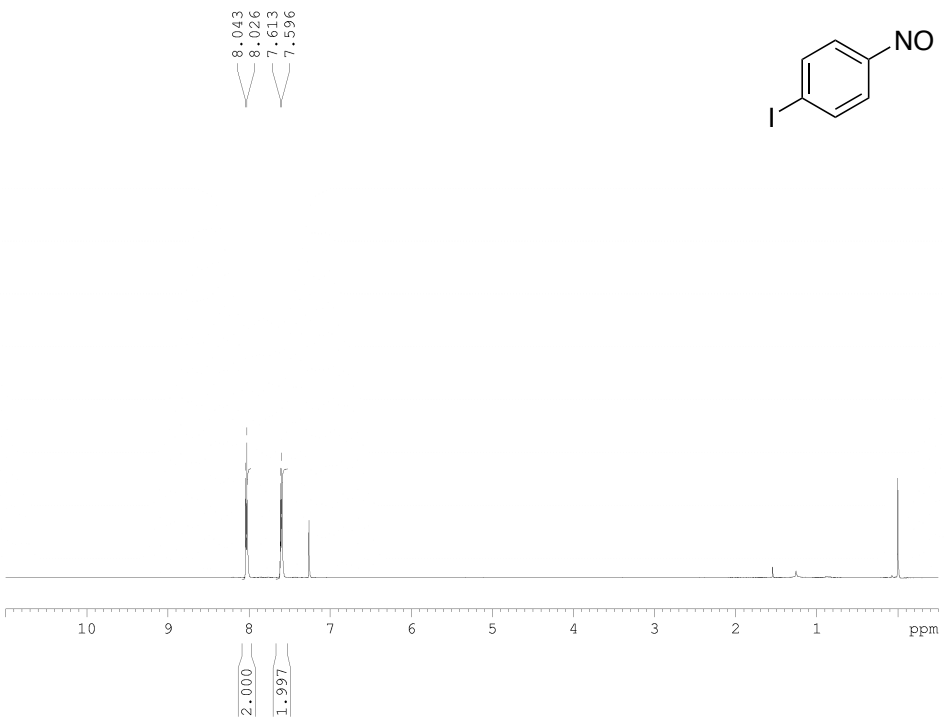


Figure A5.44 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-iodo-4-nitrosobenzene

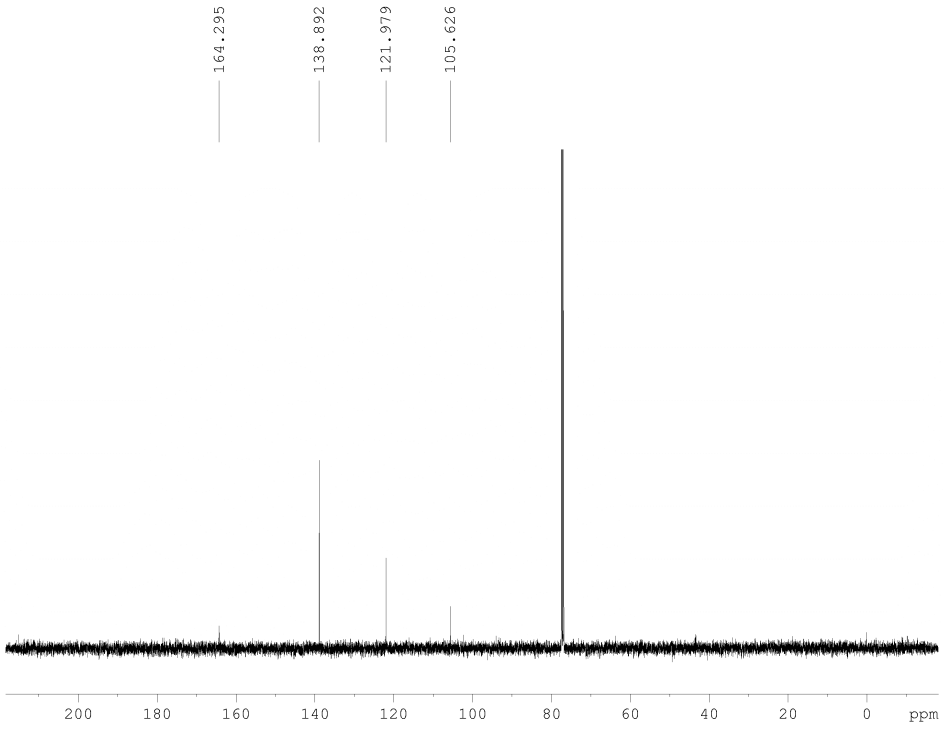


Figure A5.45 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-iodo-4-nitrosobenzene

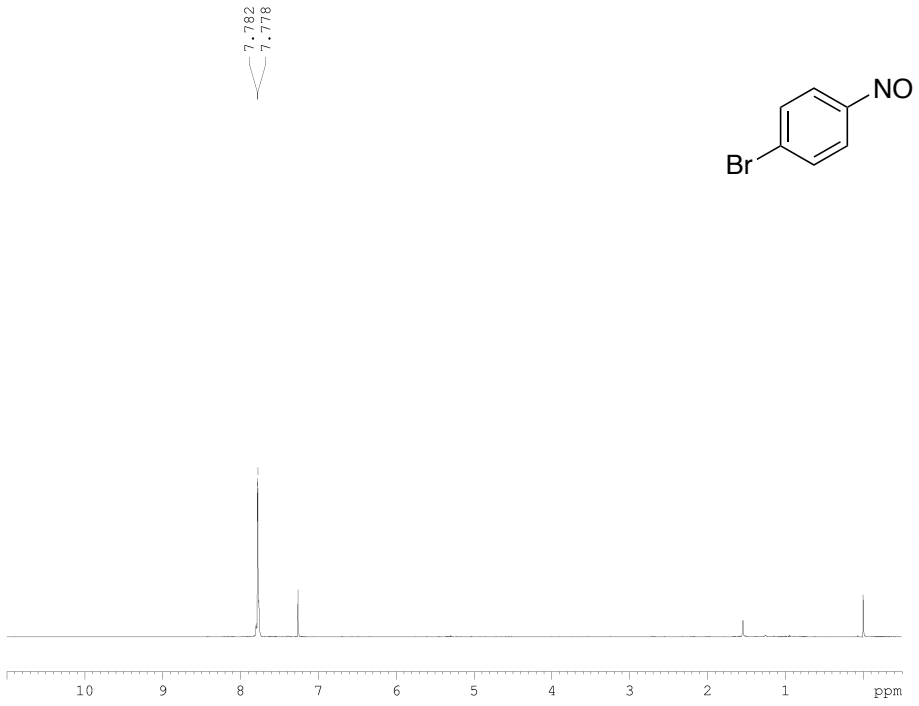


Figure A5.46 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-bromo-4-nitrosobenzene

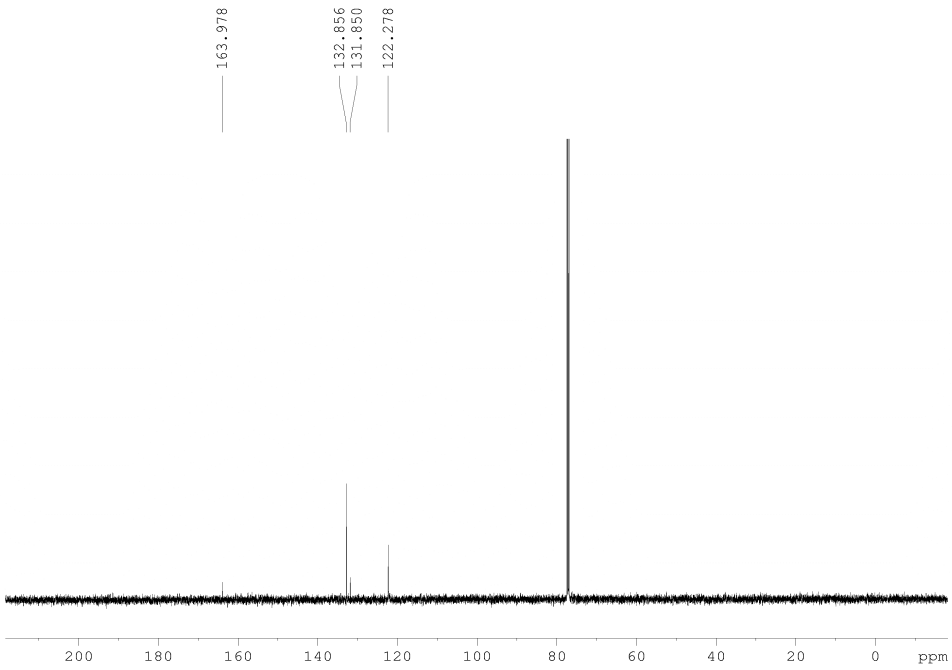


Figure A5.47 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-bromo-4-nitrosobenzene

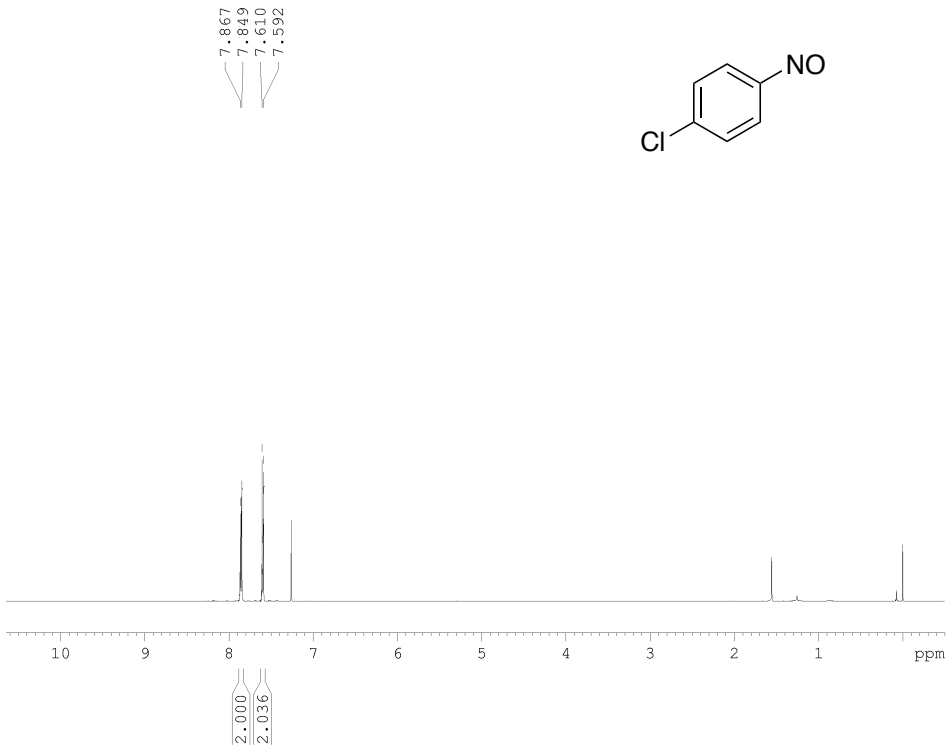


Figure A5.48 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-chloro-4-nitrosobenzene

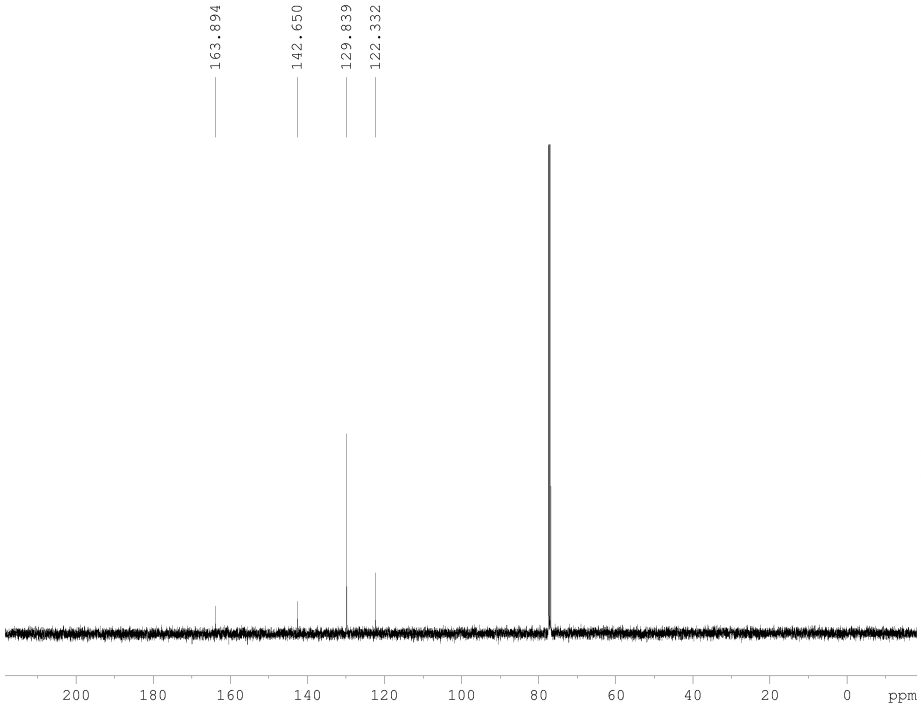


Figure A5.49 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-chloro-4-nitrosobenzene

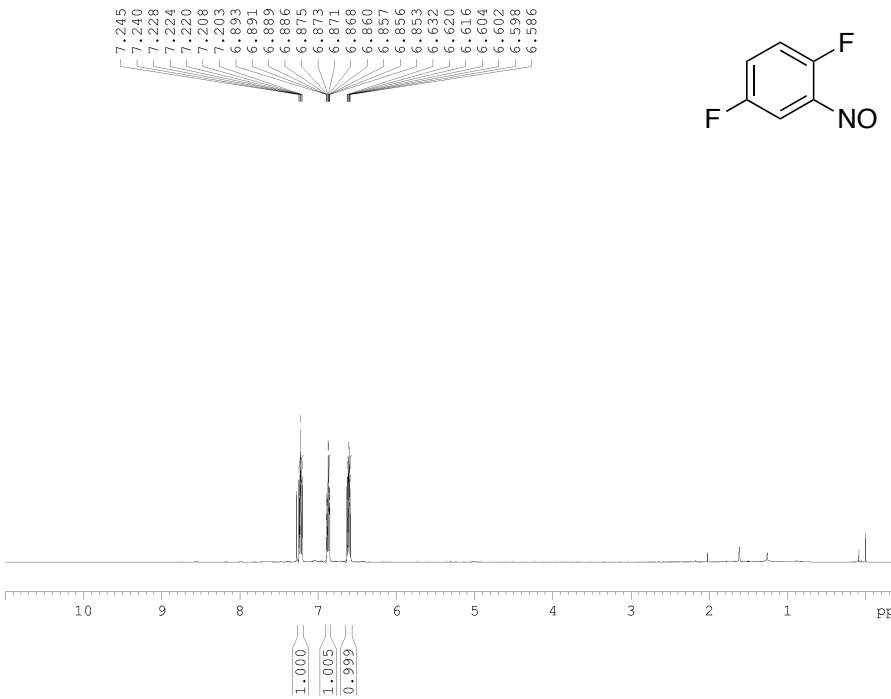


Figure A5.50 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1,4-difluoro-2-nitrosobenzene

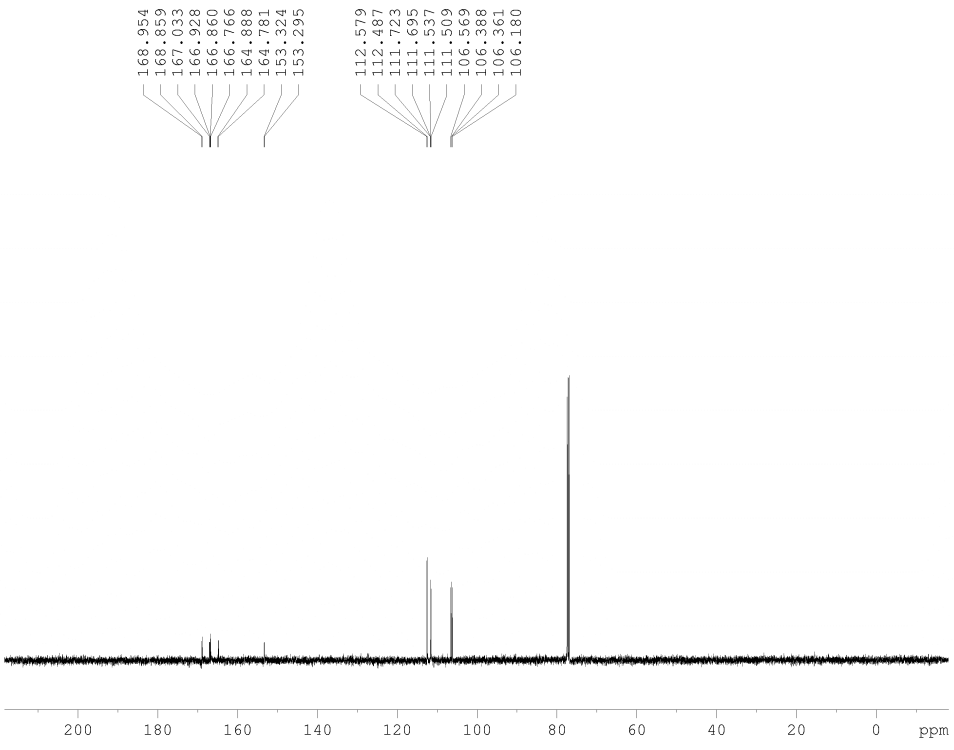


Figure A5.51 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1,4-difluoro-2-nitrosobenzene

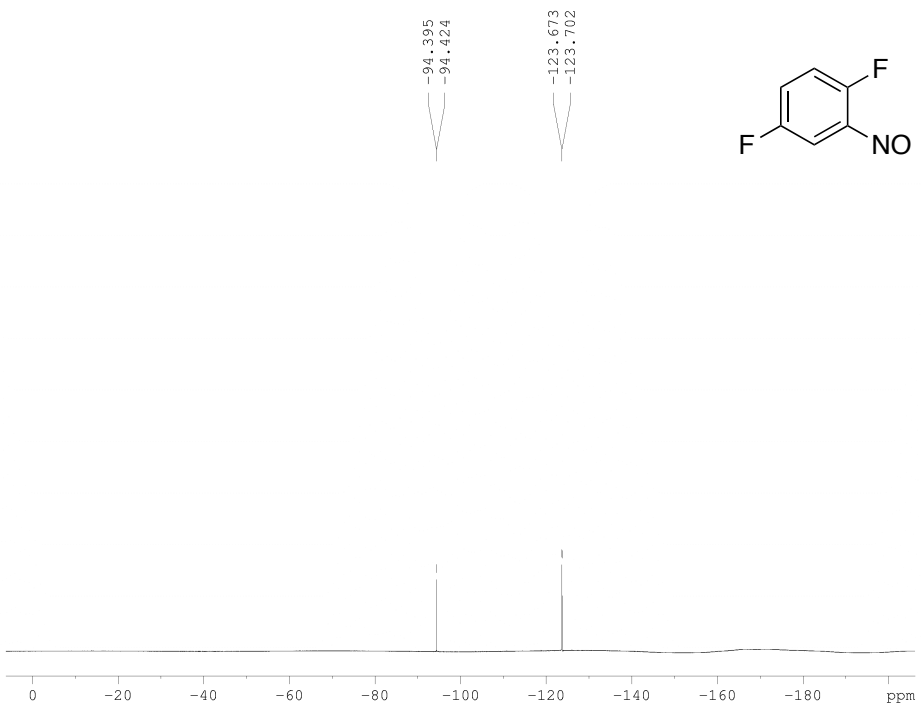


Figure A5.52 ^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of 1,4-difluoro-2-nitrosobenzene

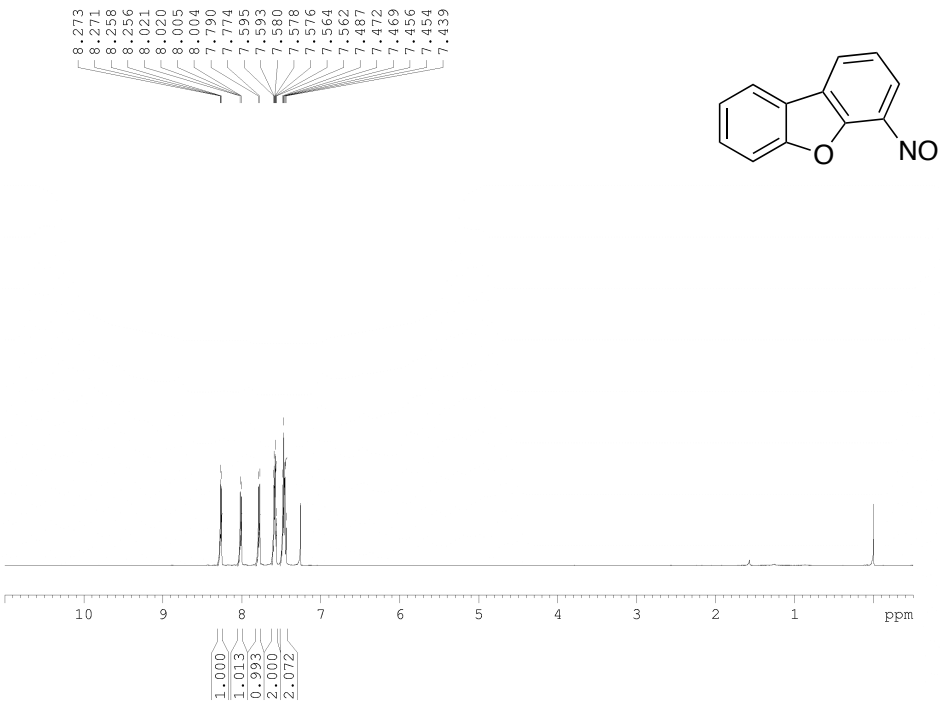


Figure A5.53 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-nitrosodibenzo[*b*,*d*]furan

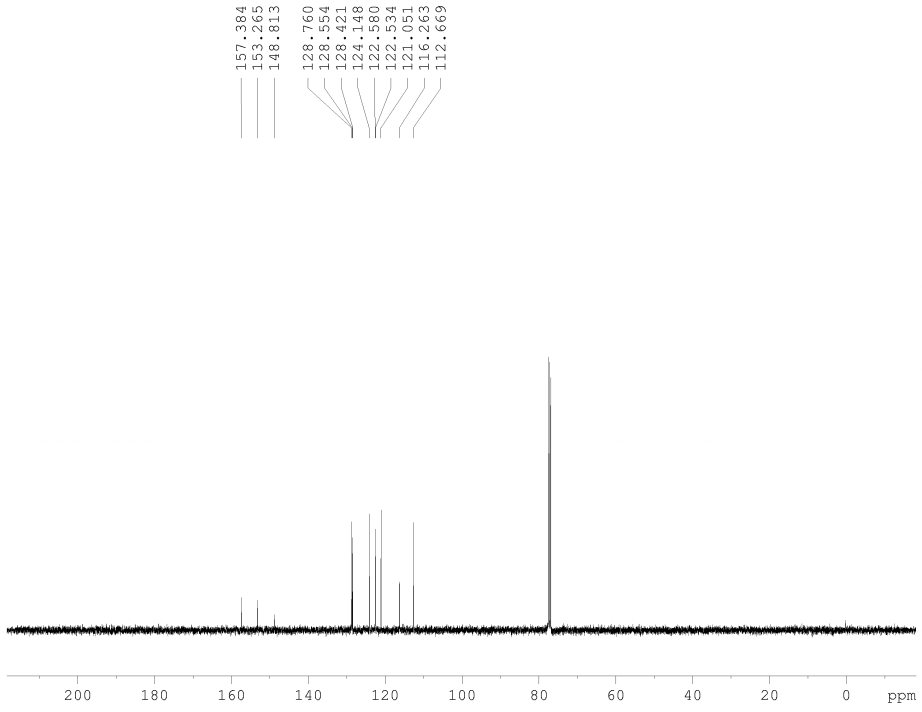


Figure A5.54 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-nitrosodibenzo[*b*,*d*]furan

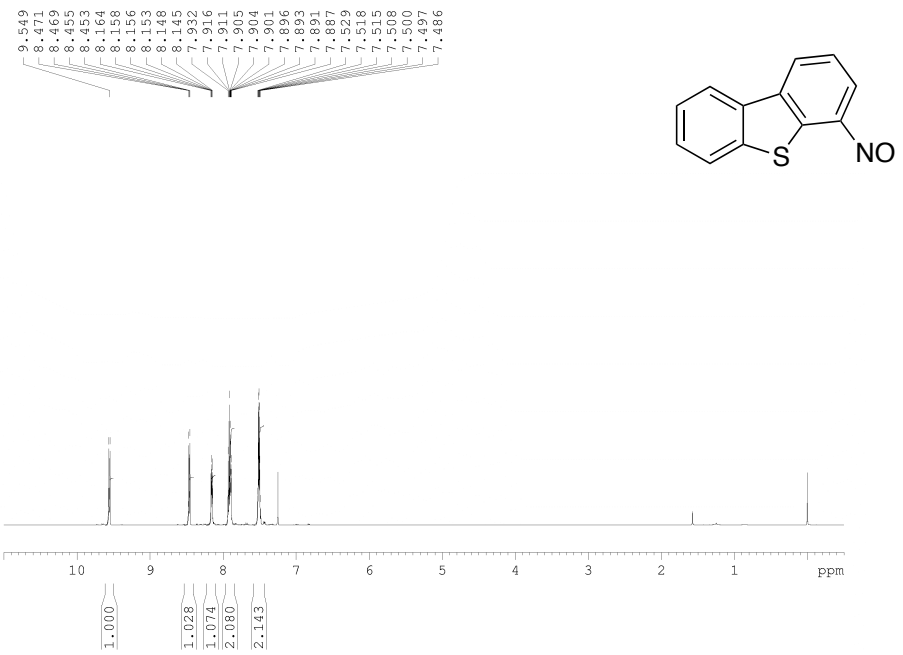


Figure A5.55 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-nitrosodibenzo[*b*,*d*]thiophene

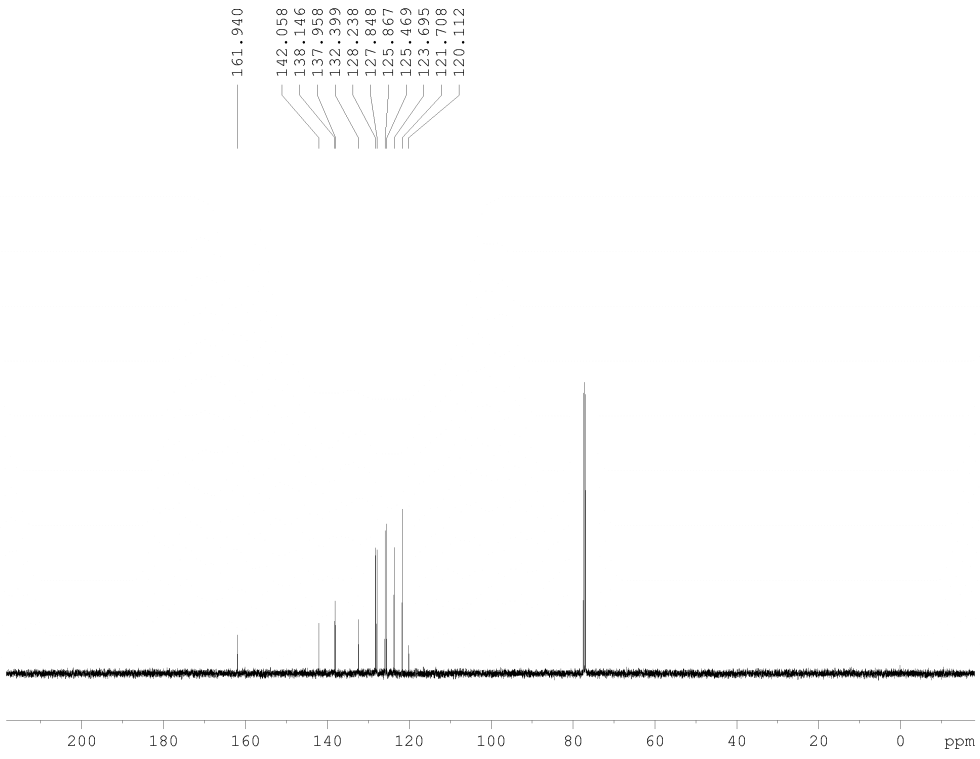


Figure A5.56 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-nitrosodibenzo[*b*,*d*]thiophene

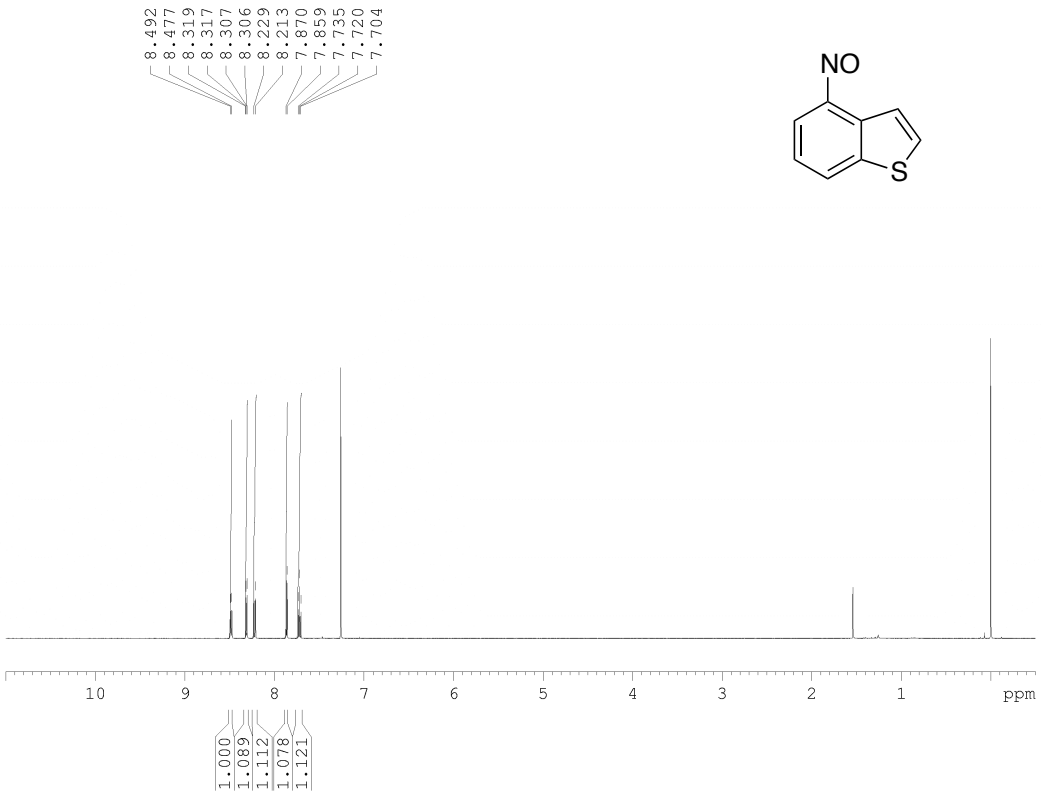


Figure A5.57 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-nitrosobenzo[*b*]thiophene

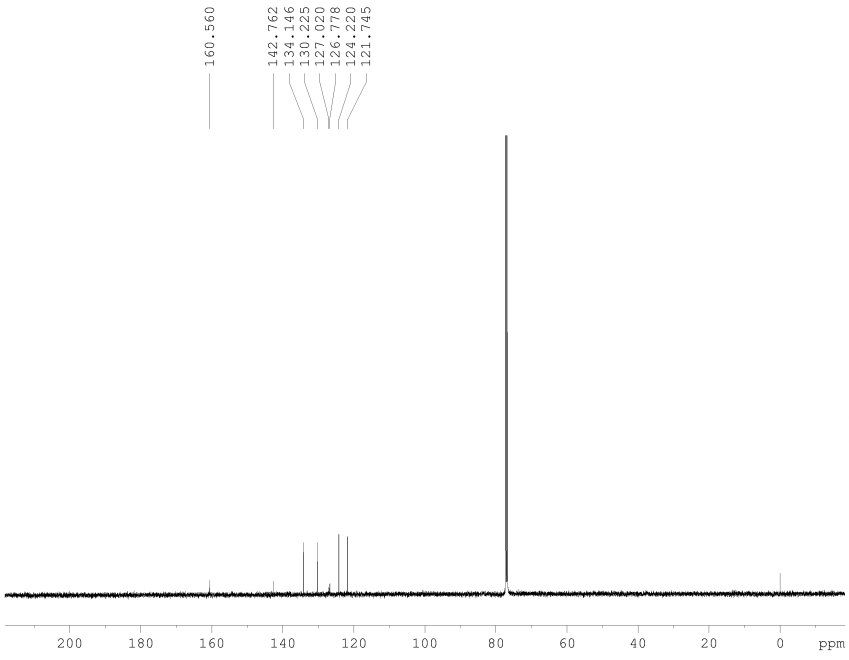


Figure A5.58 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-nitrosobenzo[*b*]thiophene

Figure A5.59 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of *tert*-butyl 5-nitroso-1*H*-indole-1-carboxylate

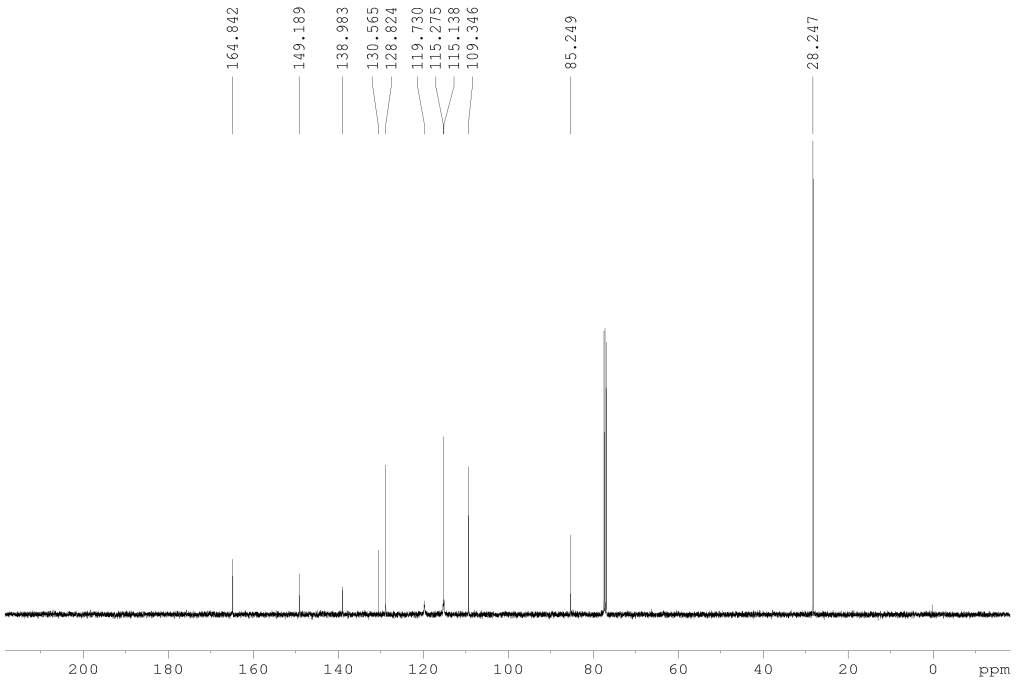


Figure A5.60 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of *tert*-butyl 5-nitroso-1*H*-indole-1-carboxylate

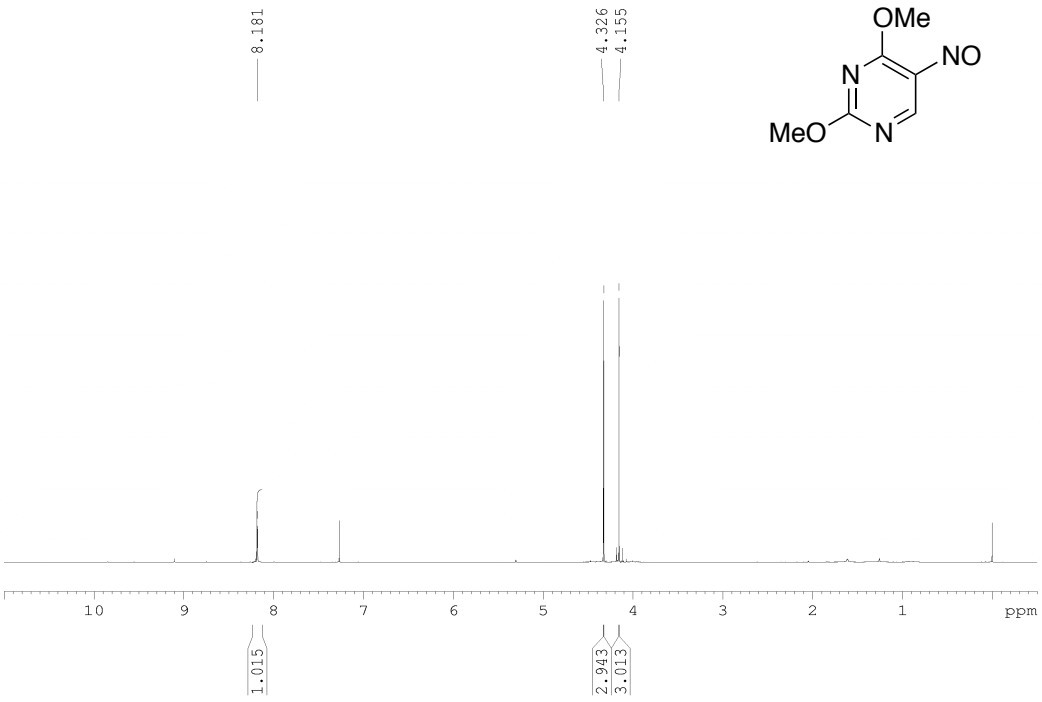


Figure A5.61 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,4-dimethoxy-5-nitrosopyrimidine

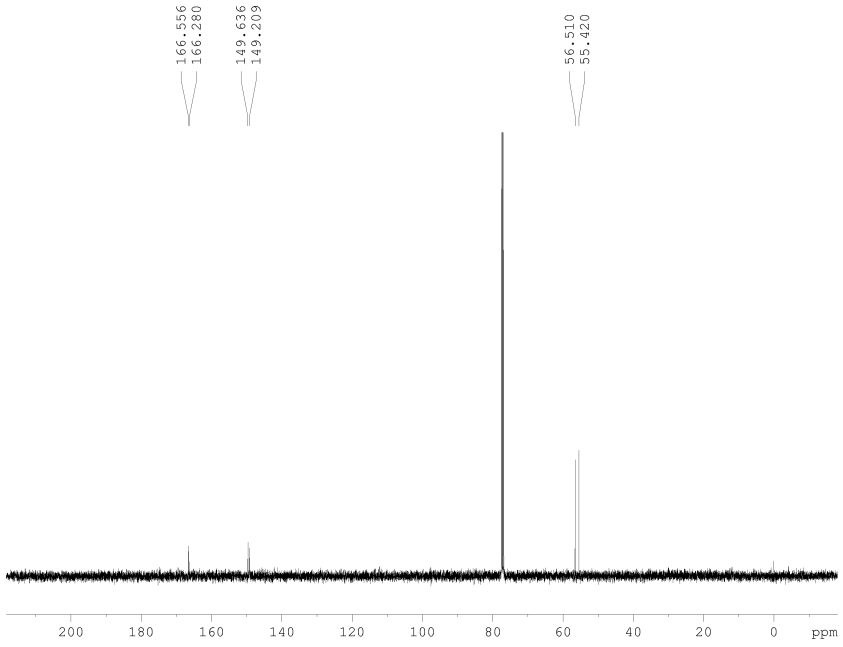


Figure A5.62 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2,4-dimethoxy-5-nitrosopyrimidine

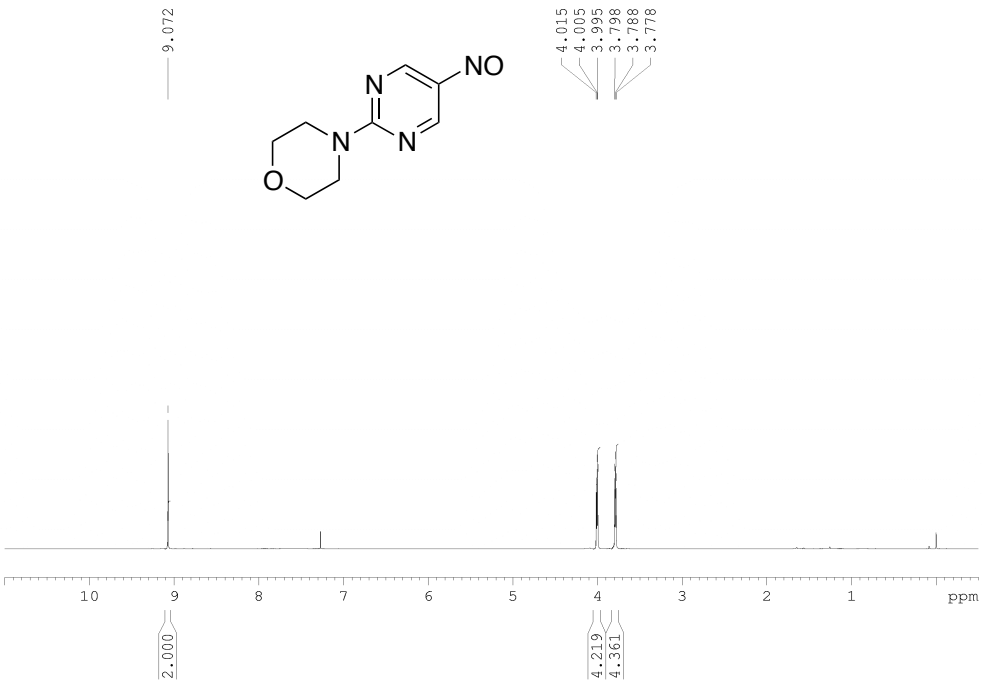


Figure A5.63 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-(5-nitrosopyrimidin-2-yl)morpholine

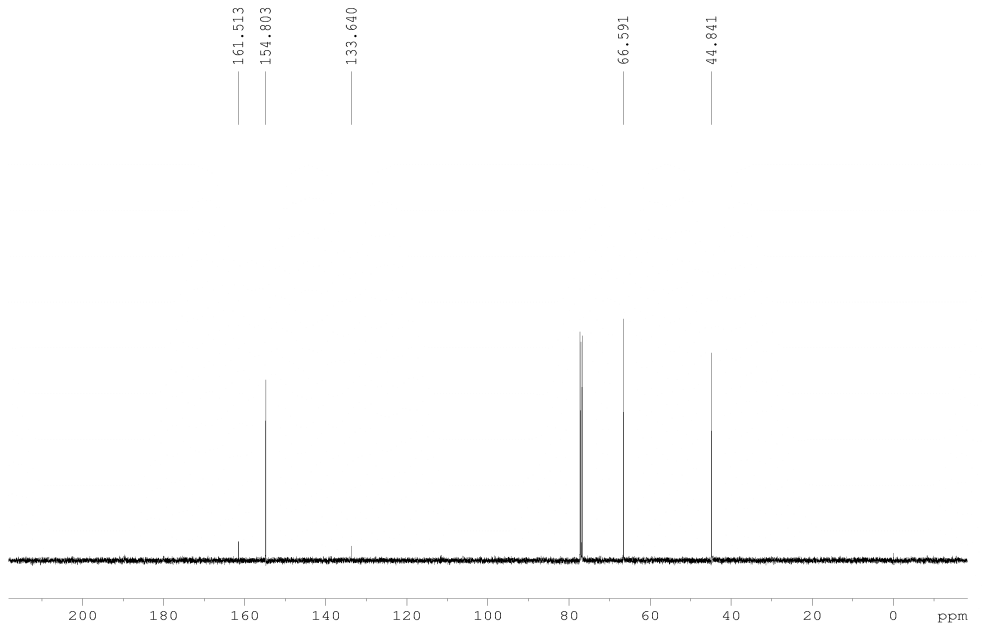


Figure A5.64 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 4-(5-nitrosopyrimidin-2-yl)morpholine

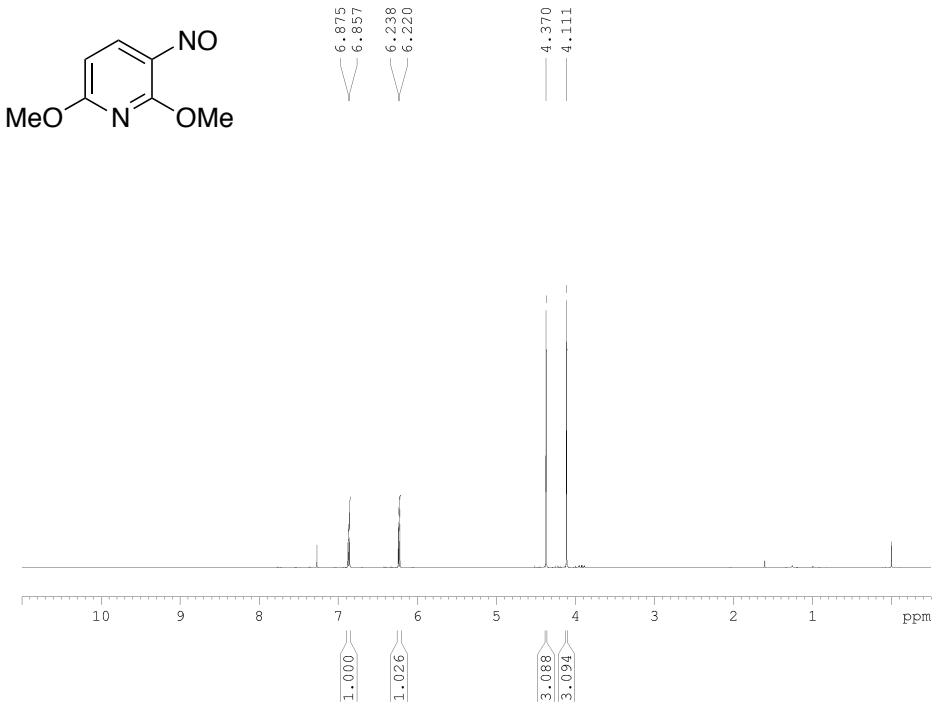


Figure A5.65 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,6-dimethoxy-3-nitrosopyridine

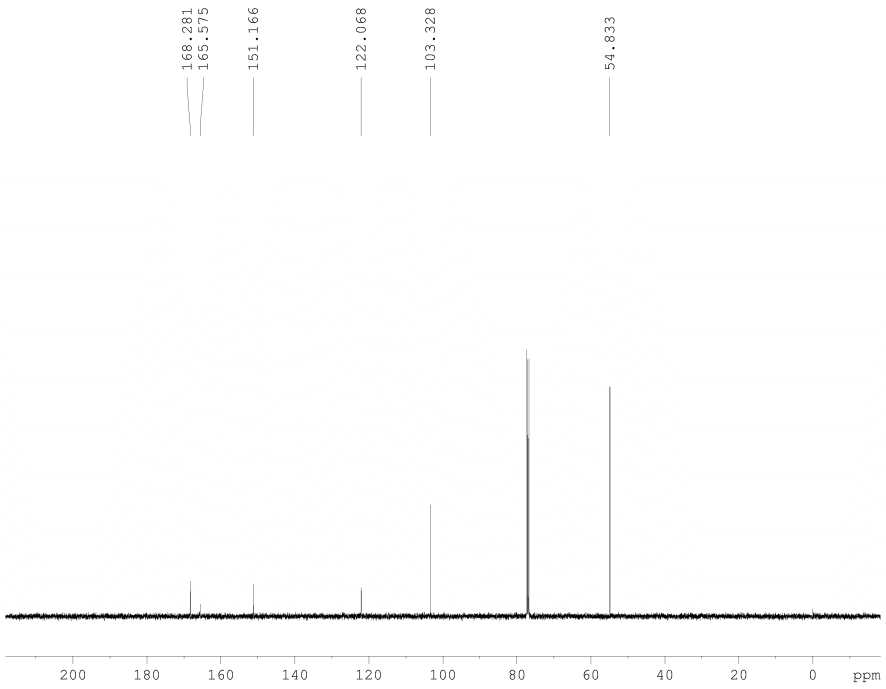


Figure A5.66 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2,6-dimethoxy-3-nitrosopyridine

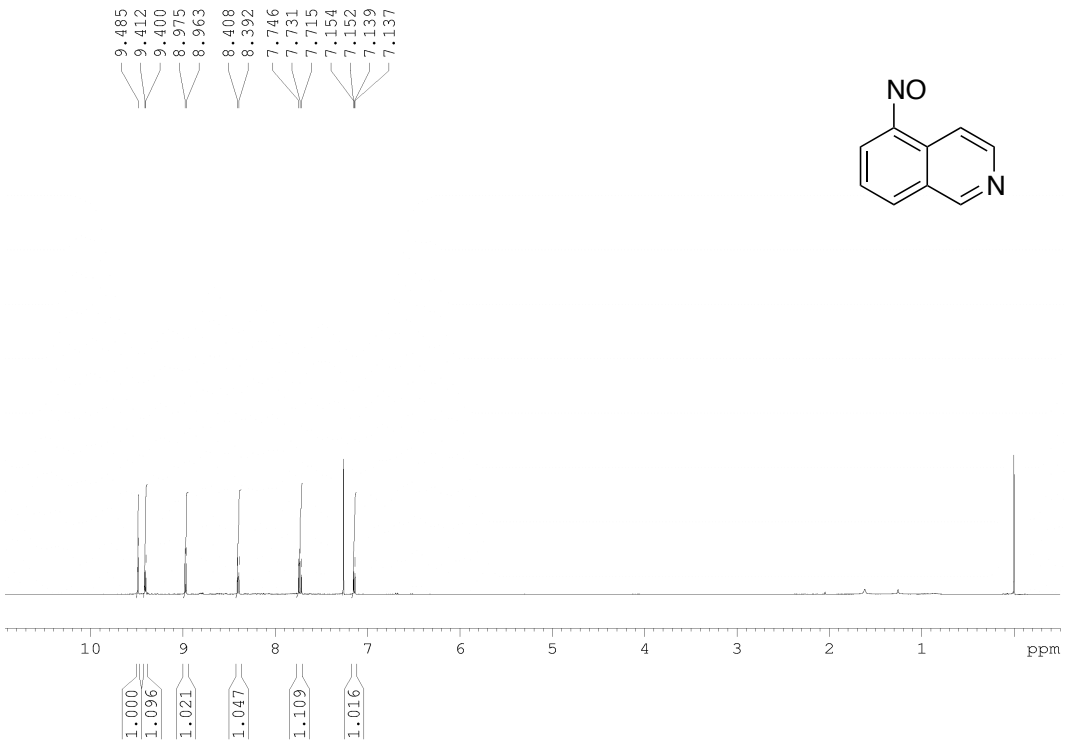


Figure A5.67 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 5-nitrosoisoquinoline

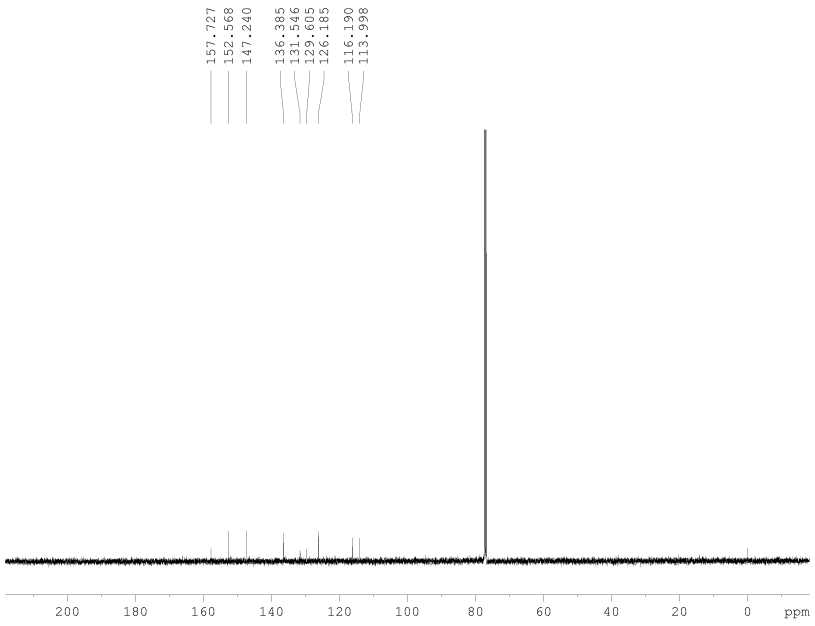


Figure A5.68 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 5-nitrosoisoquinoline

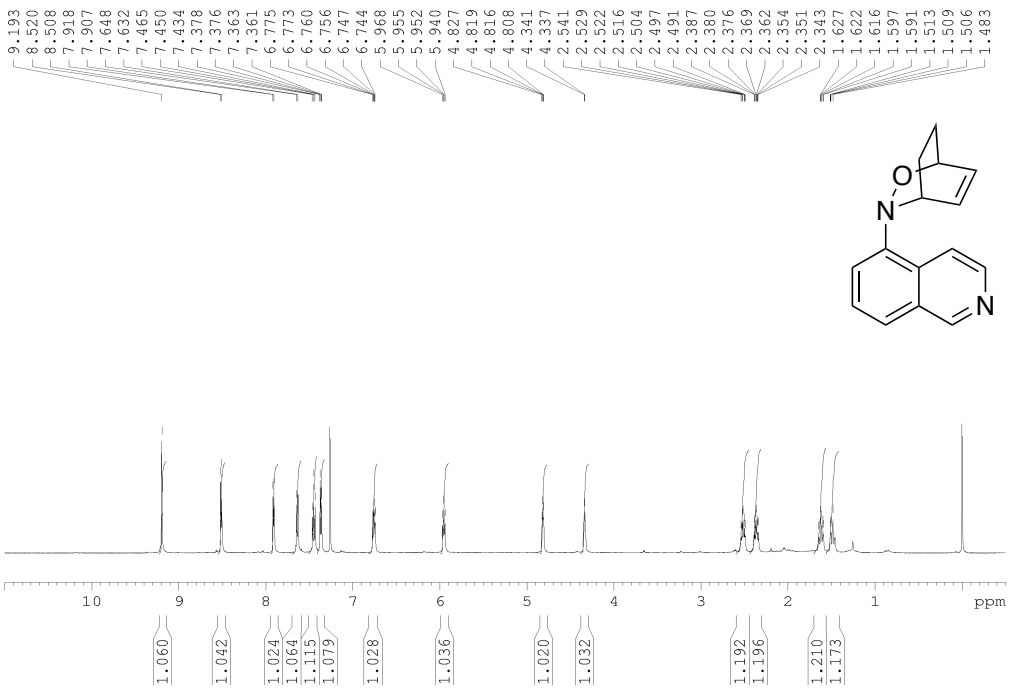


Figure A5.69 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 3-(isoquinolin-5-yl)-2-oxa-3-azabicyclo[2.2.2]oct-5-ene

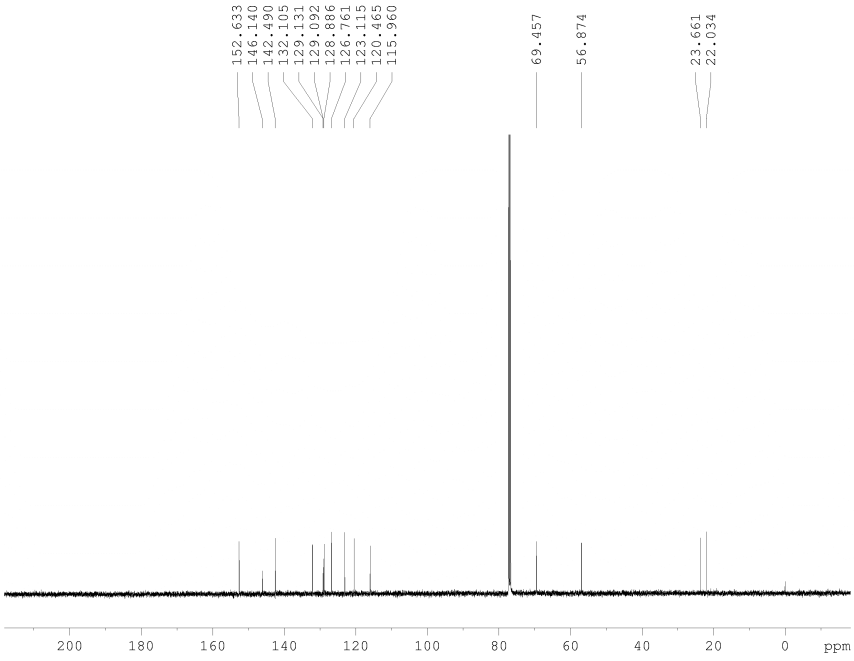


Figure A5.70 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 3-(isoquinolin-5-yl)-2-oxa-3-azabicyclo[2.2.2]oct-5-ene

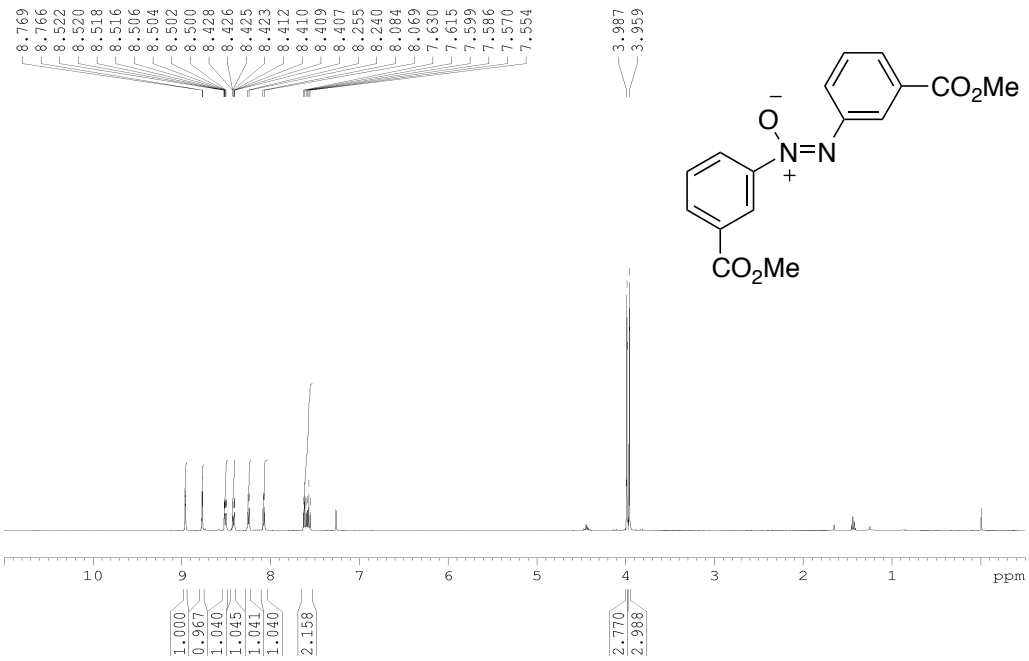


Figure A5.71 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1,2-bis(3-(methoxycarbonyl)phenyl)diazene oxide

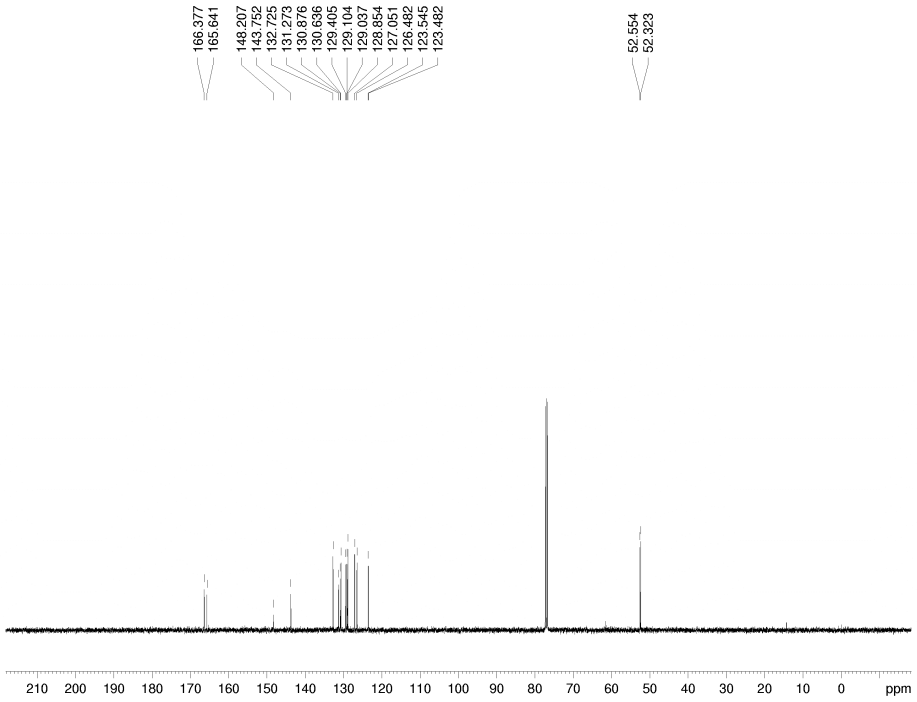


Figure A5.72 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1,2-bis(3-(methoxycarbonyl)phenyl)diazene oxide

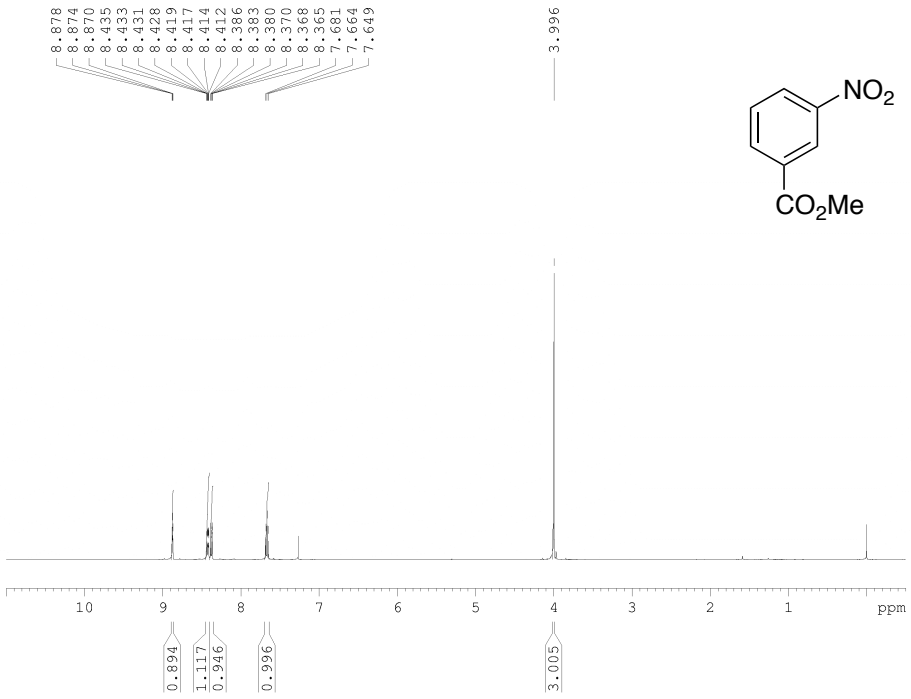


Figure A5.73 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of methyl 3-nitrobenzoate

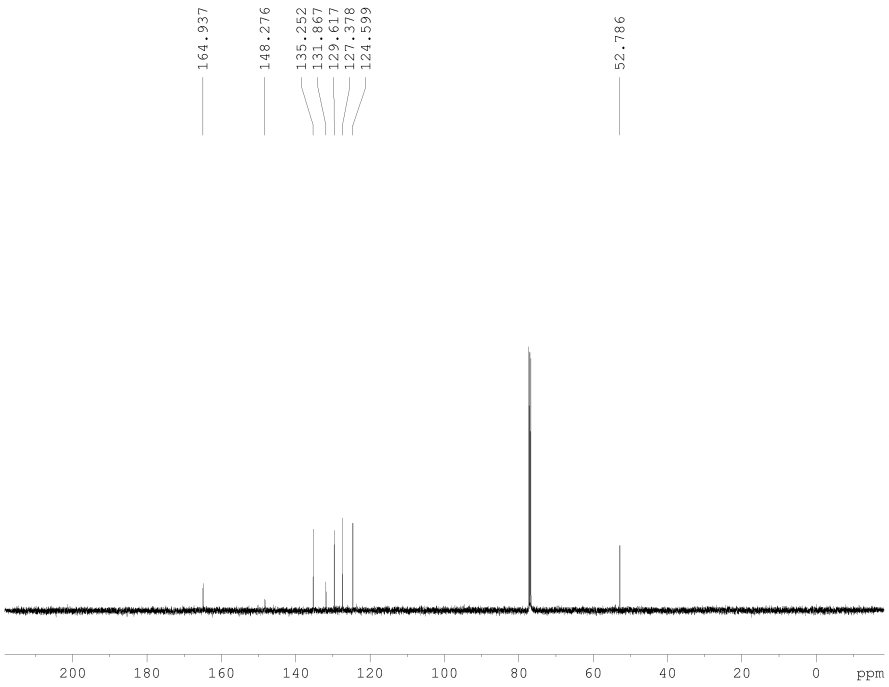


Figure A5.74 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of methyl 3-nitrobenzoate

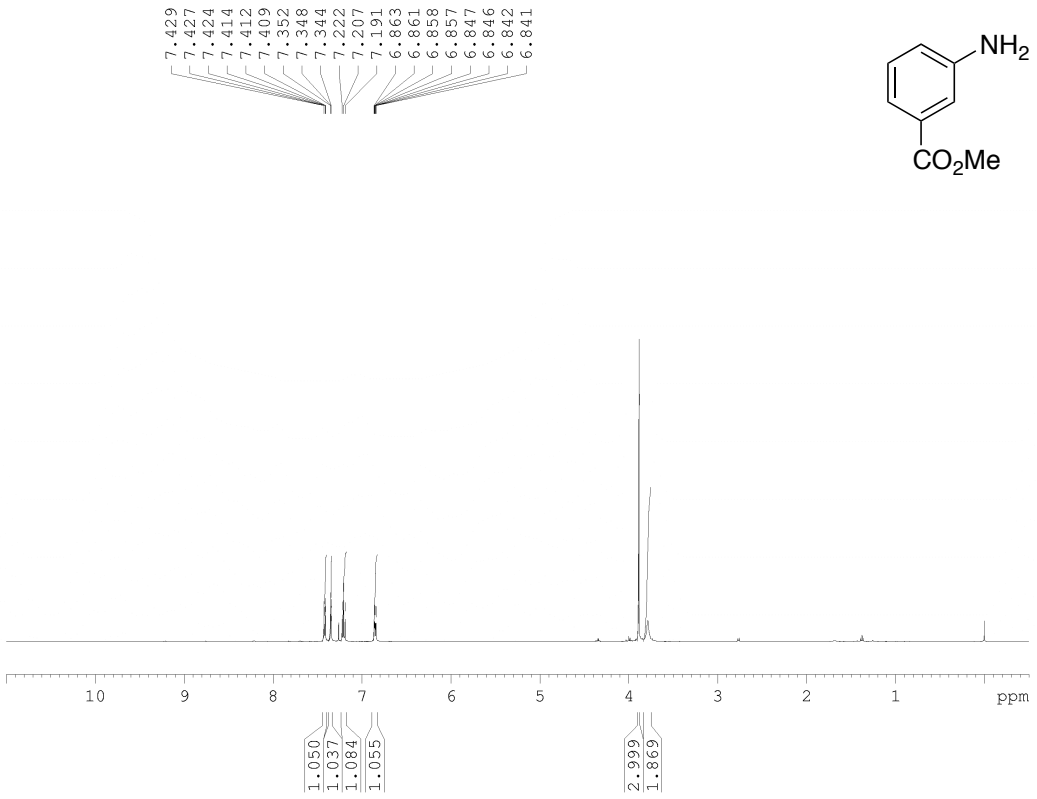


Figure A5.75 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of methyl 3-aminobenzoate

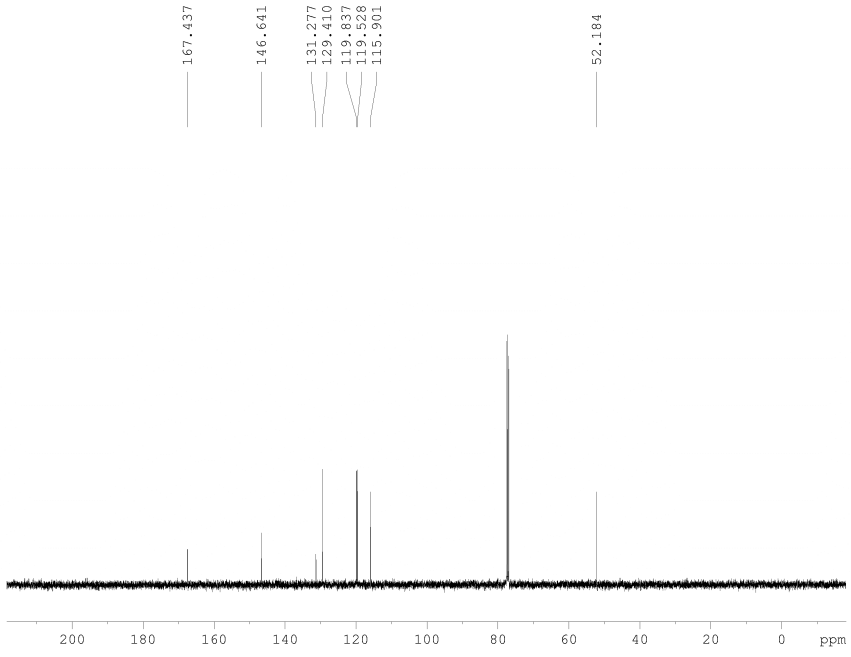


Figure A5.76 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of methyl 3-aminobenzoate

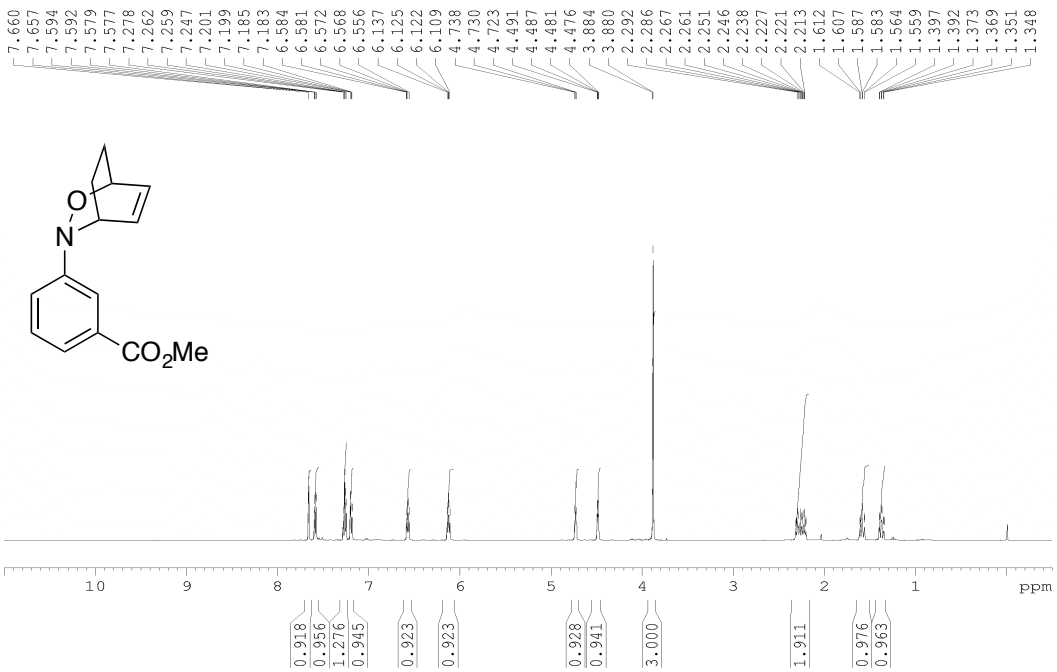


Figure A5.77 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of methyl 3-(-2-oxa-3-azabicyclo[2.2.2]oct-5-en-3-yl)benzoate

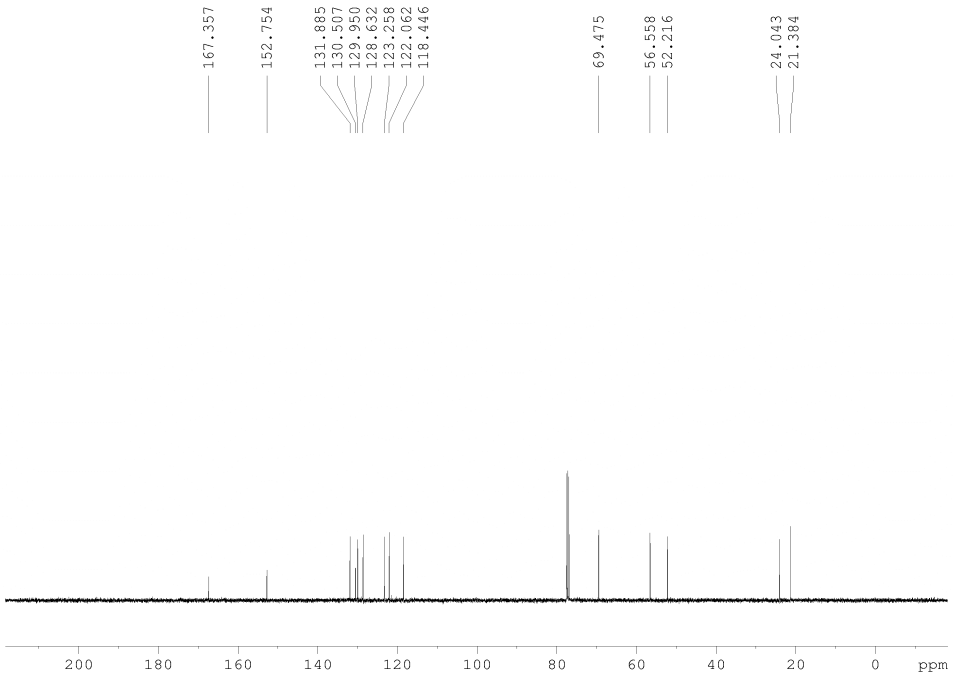
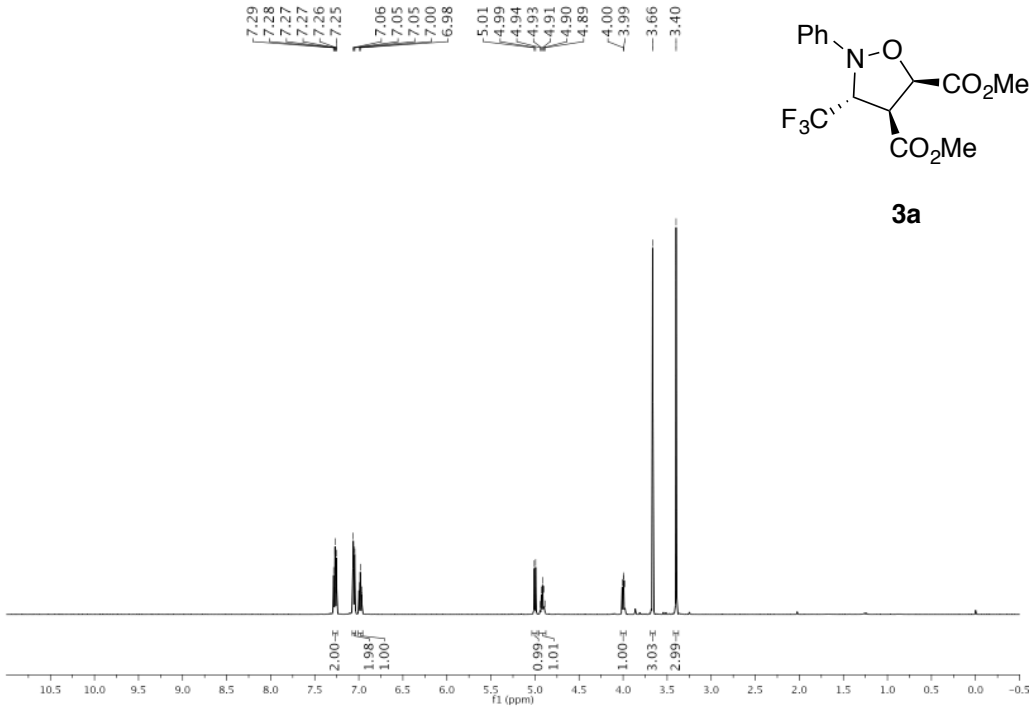


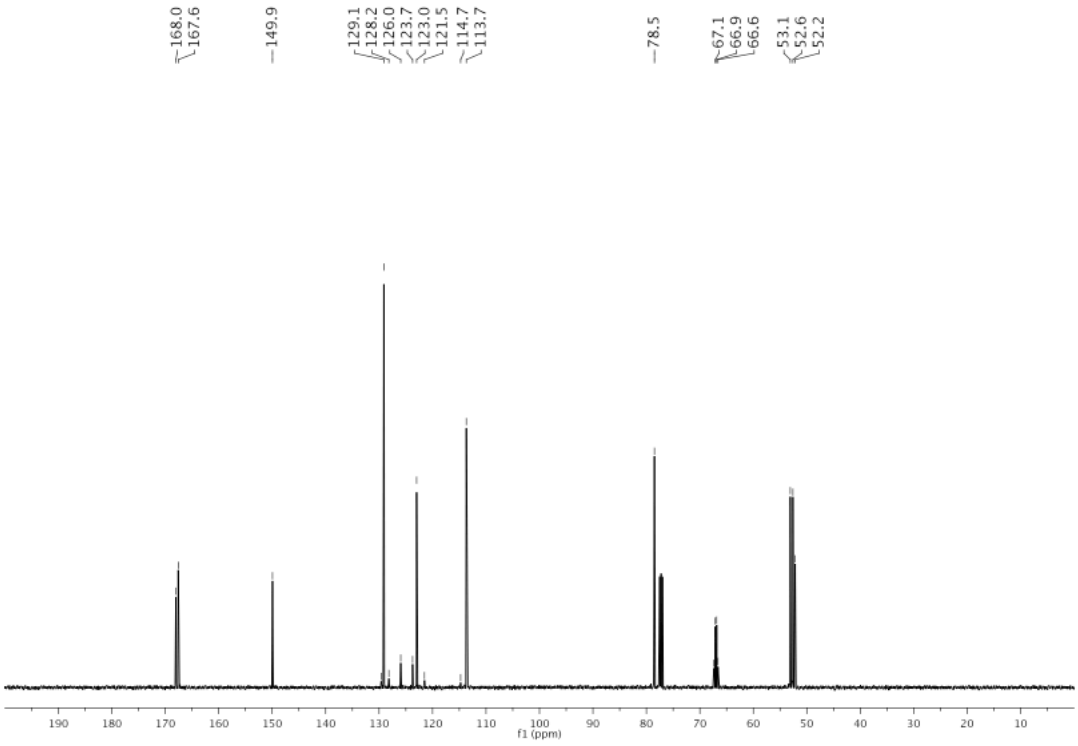
Figure A5.78 ^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of methyl 3-(-2-oxa-3-azabicyclo[2.2.2]oct-5-en-3-yl)benzoate

Appendix A6. ^{1}H, ^{13}C and ^{19}F Spectra Relevant to Chapter 2.7

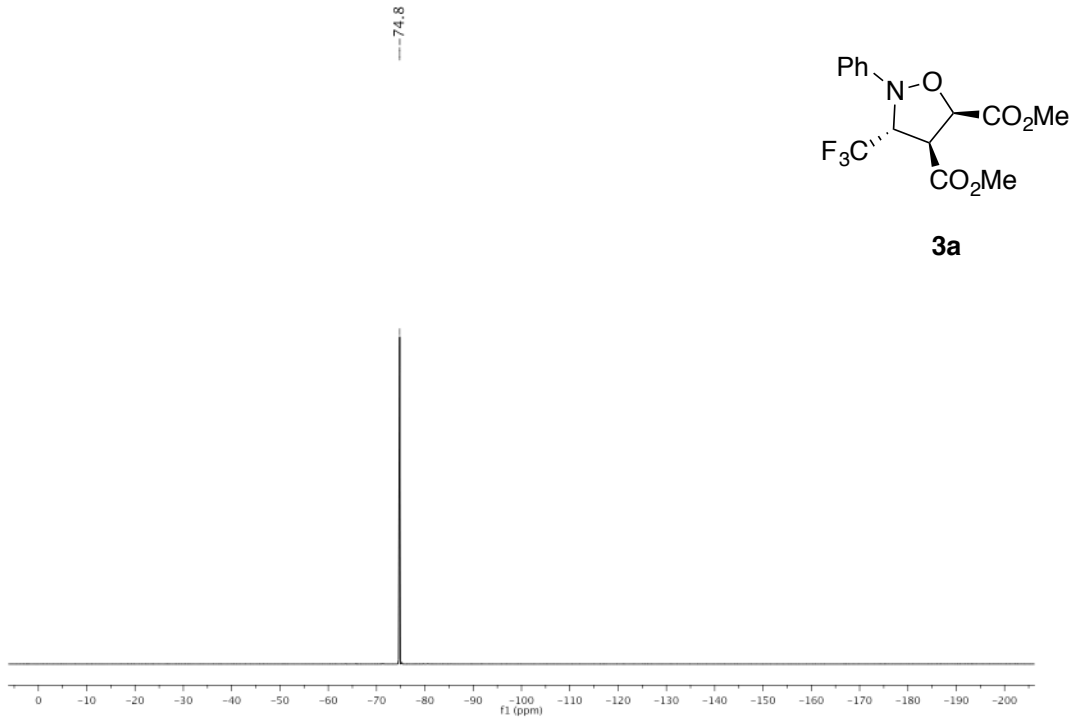


3a

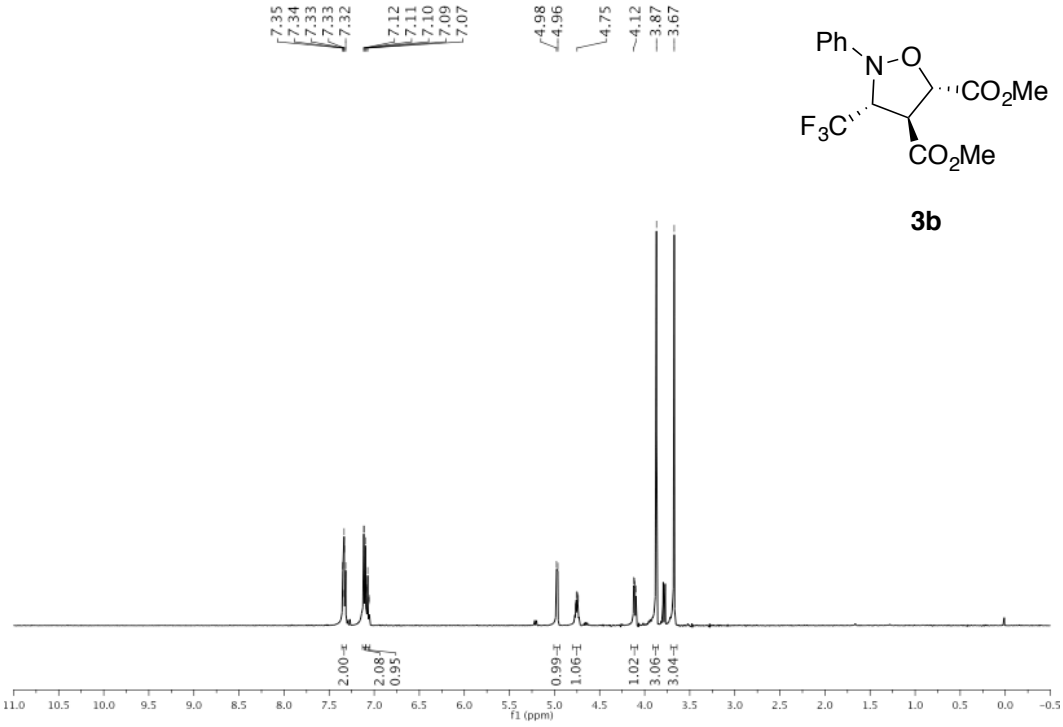
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Dimethyl 2-phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3a)



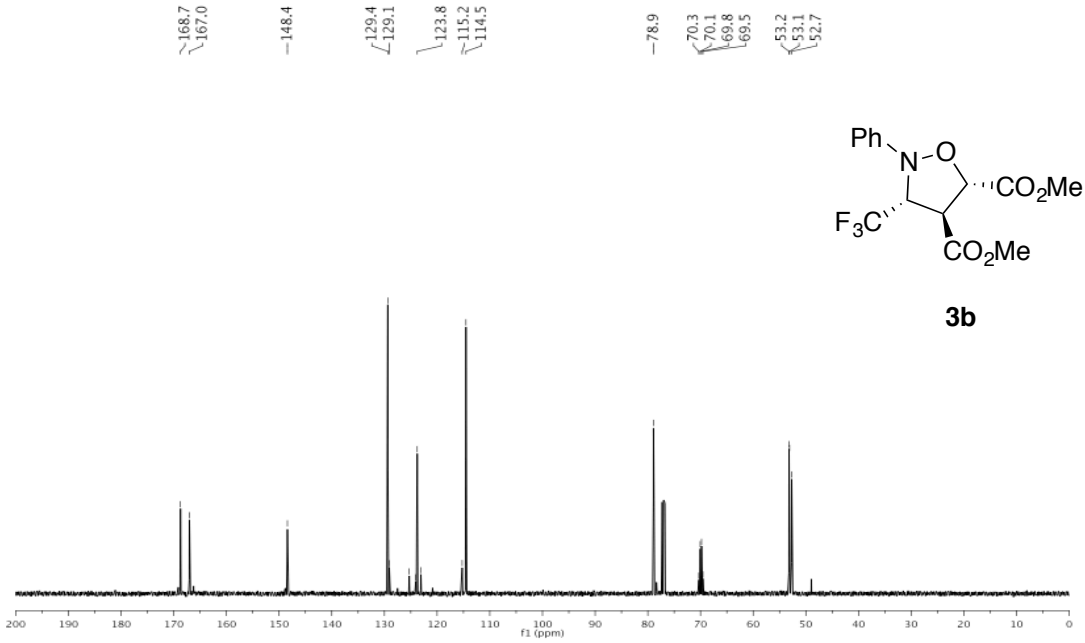
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Dimethyl 2-phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3a)



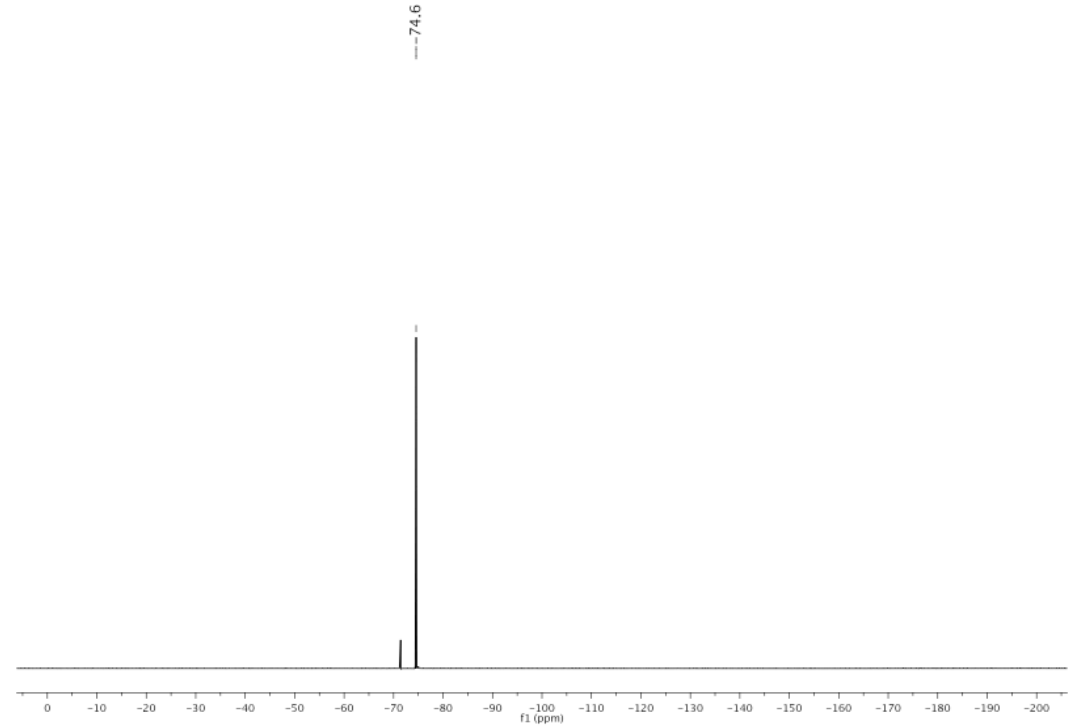
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Dimethyl 2-phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3a)



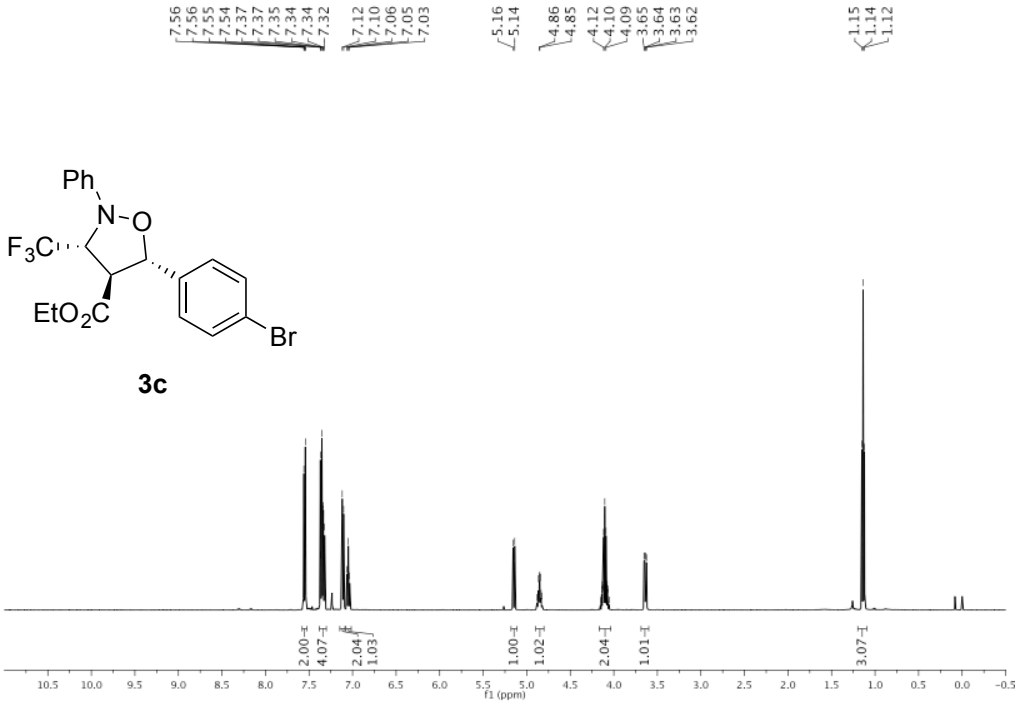
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Dimethyl 2-phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3b)



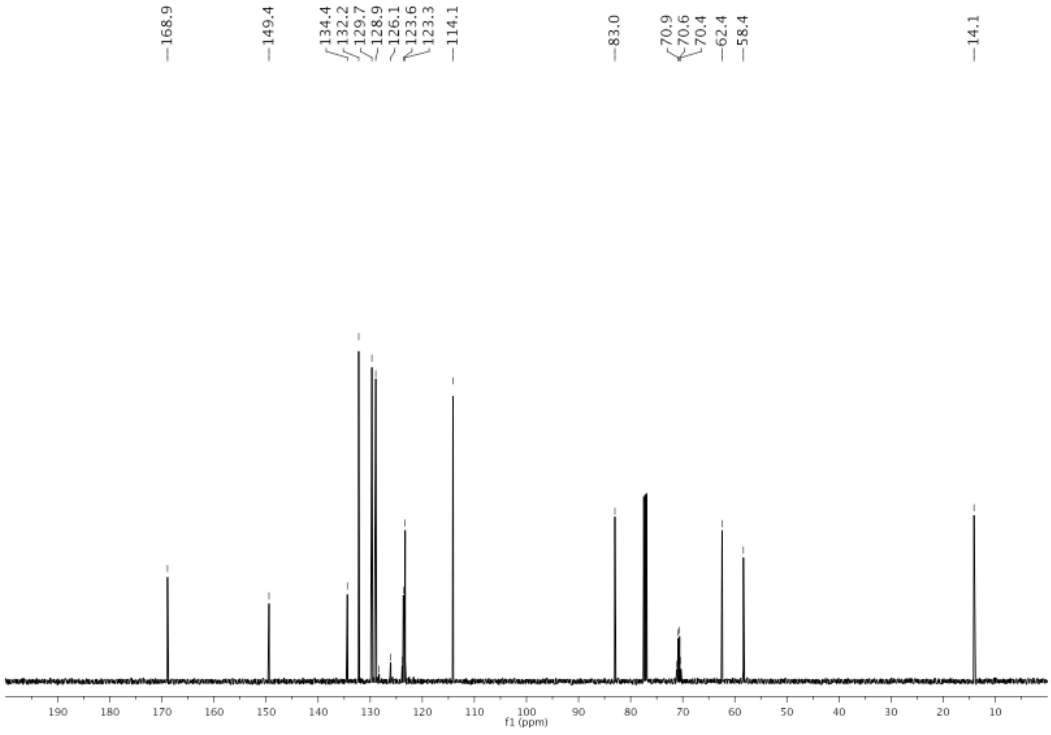
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Dimethyl 2-phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3b)



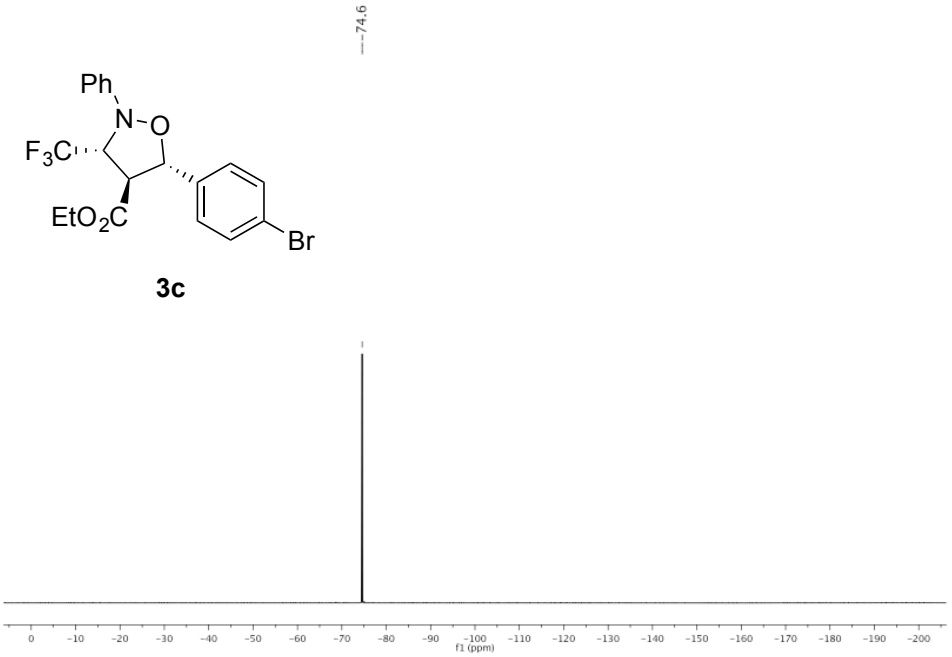
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Dimethyl 2-phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3b)



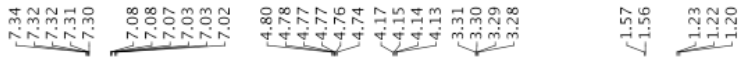
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Ethyl 5-(4-bromophenyl)-2-phenyl-3-(trifluoromethyl) isoxazolidine-4-carboxylate (3c)

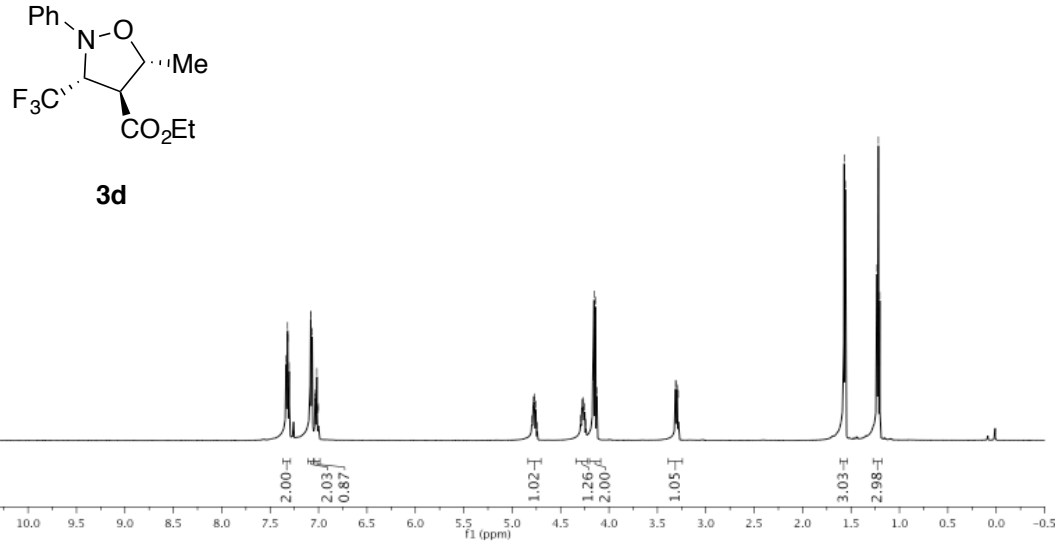


^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Ethyl 5-(4-bromophenyl)-2-phenyl-3-(trifluoromethyl) isoxazolidine-4-carboxylate (3c)

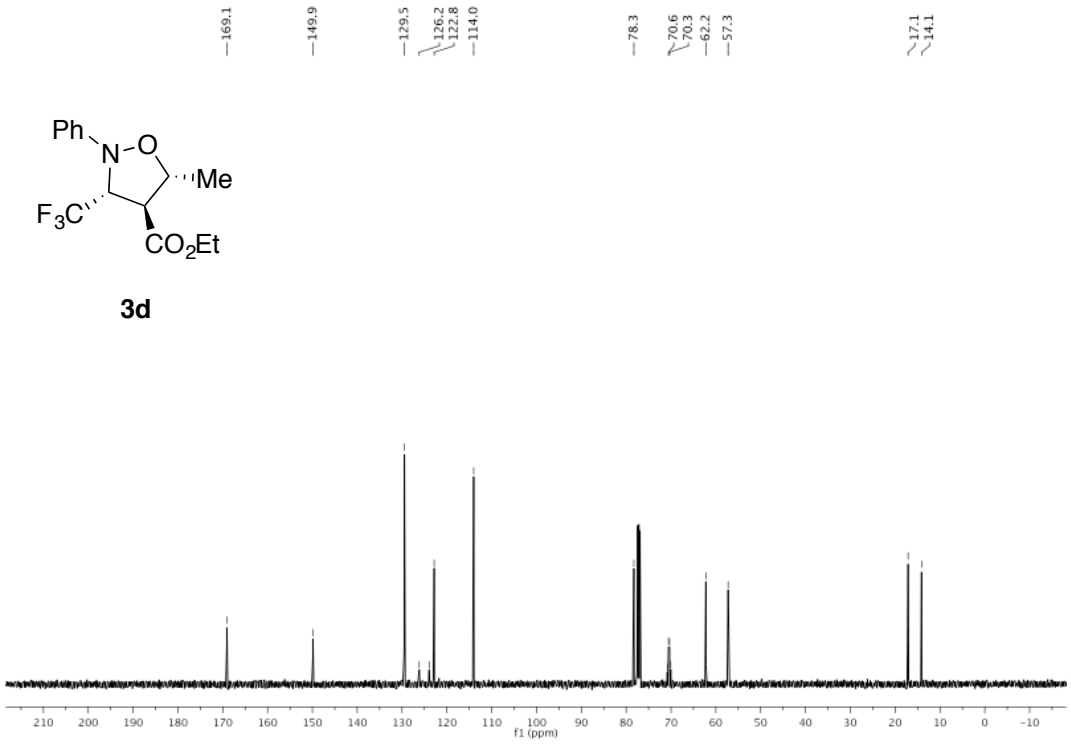


^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Ethyl 5-(4-bromophenyl)-2-phenyl-3-(trifluoromethyl) isoxazolidine-4-carboxylate (3c)



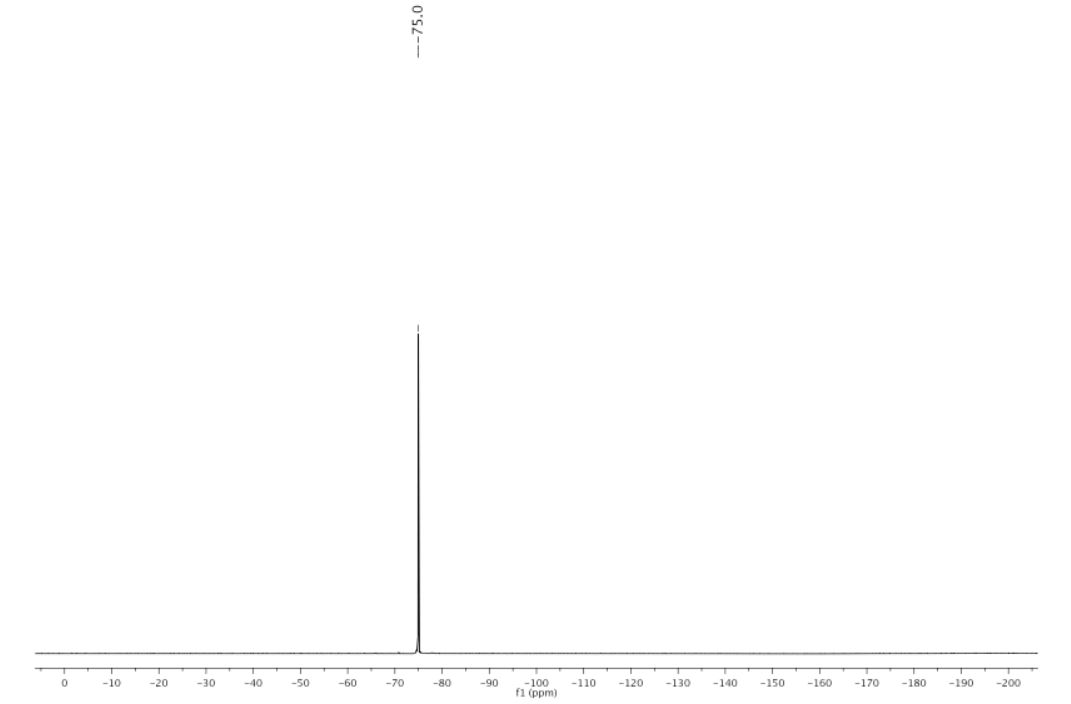


^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Ethyl 5-methyl-2-phenyl-3-(trifluoromethyl)isoxazolidine-4-carboxylate (3d)

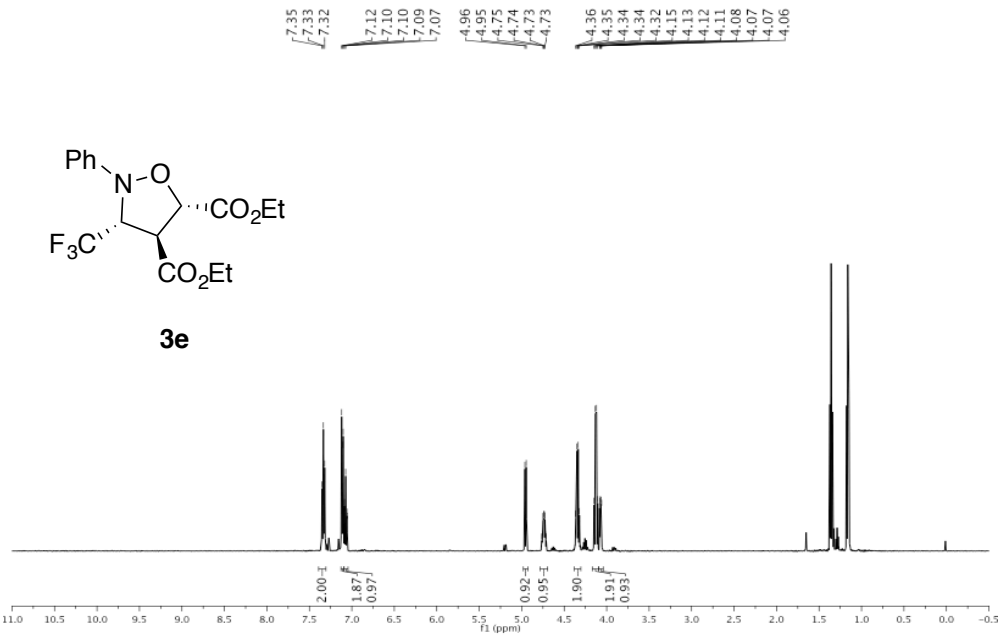


3d

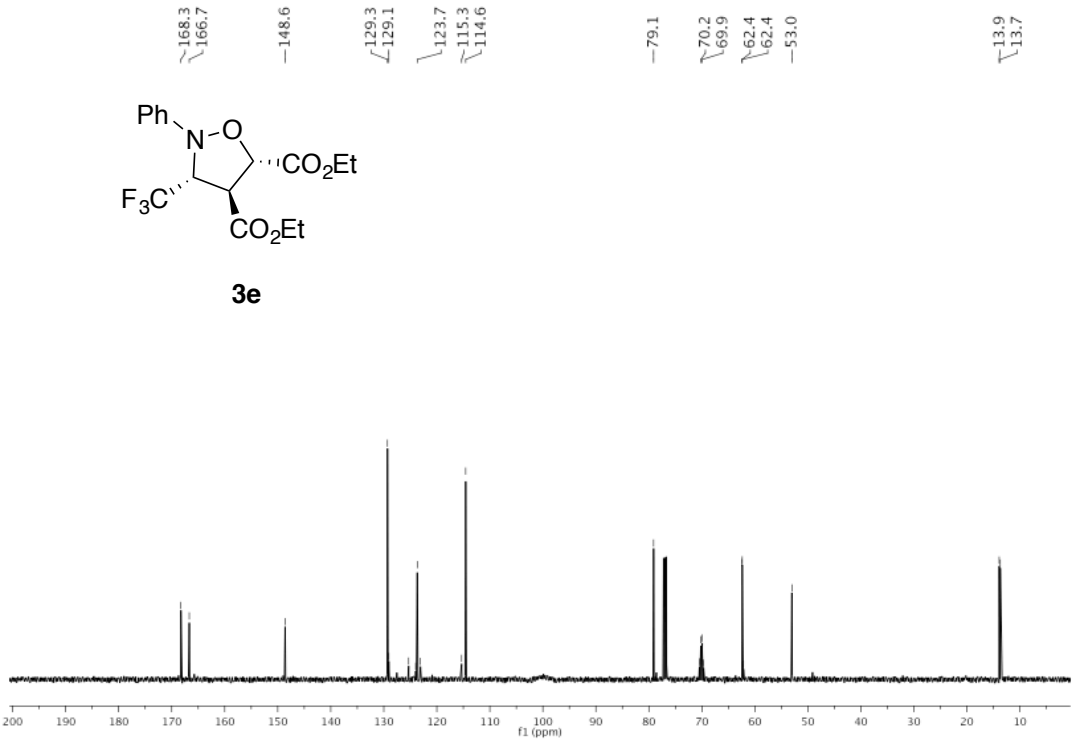
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Ethyl 5-methyl-2-phenyl-3-(trifluoromethyl)isoxazolidine-4-carboxylate (3d)



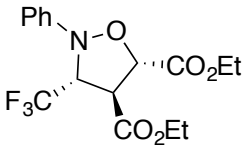
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Ethyl 5-methyl-2-phenyl-3-(trifluoromethyl)isoxazolidine-4-carboxylate (3d)



^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Diethyl 2-phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3e)



^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Diethyl 2-phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3e)

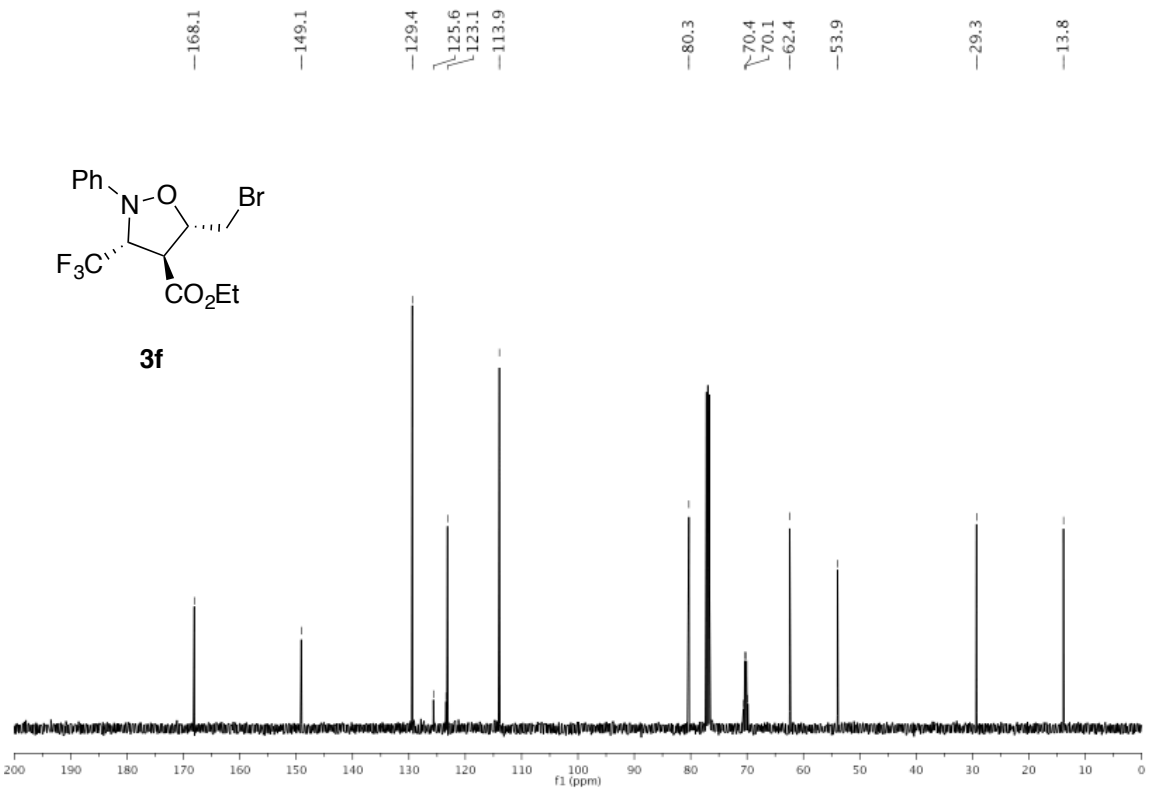


3e

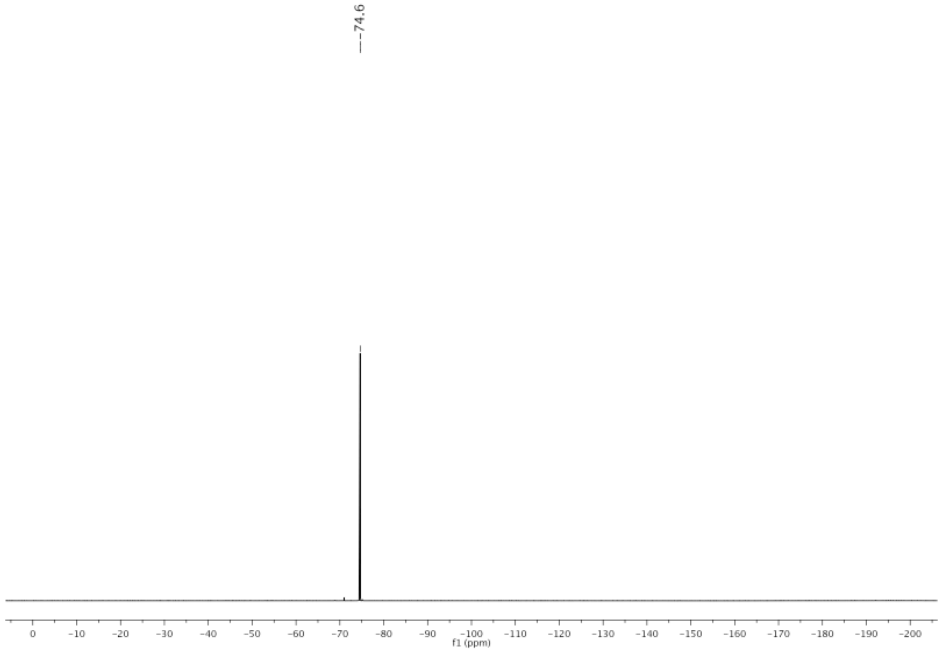
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Diethyl 2-phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3e)

3f

^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Ethyl 5-(bromomethyl)-2-phenyl-3-(trifluoromethyl)isoxazolidine-4-carboxylate (3f)

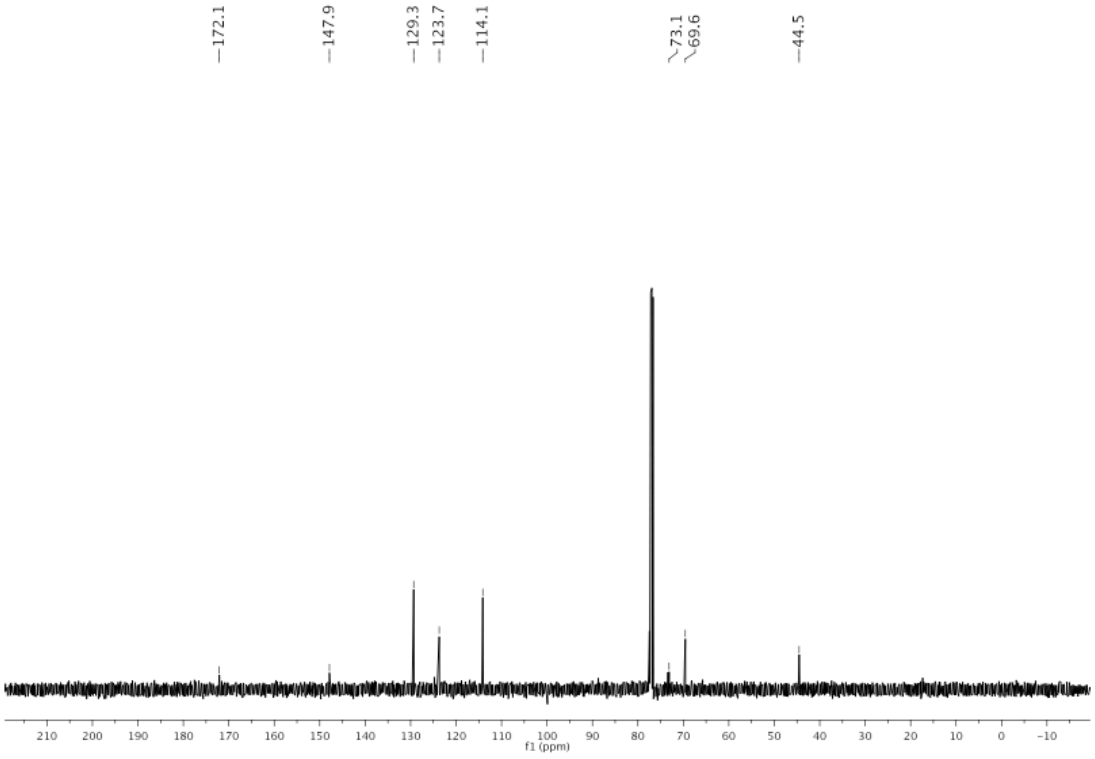


^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Ethyl 5-(bromomethyl)-2-phenyl-3-(trifluoromethyl)isoxazolidine-4-carboxylate (3f)

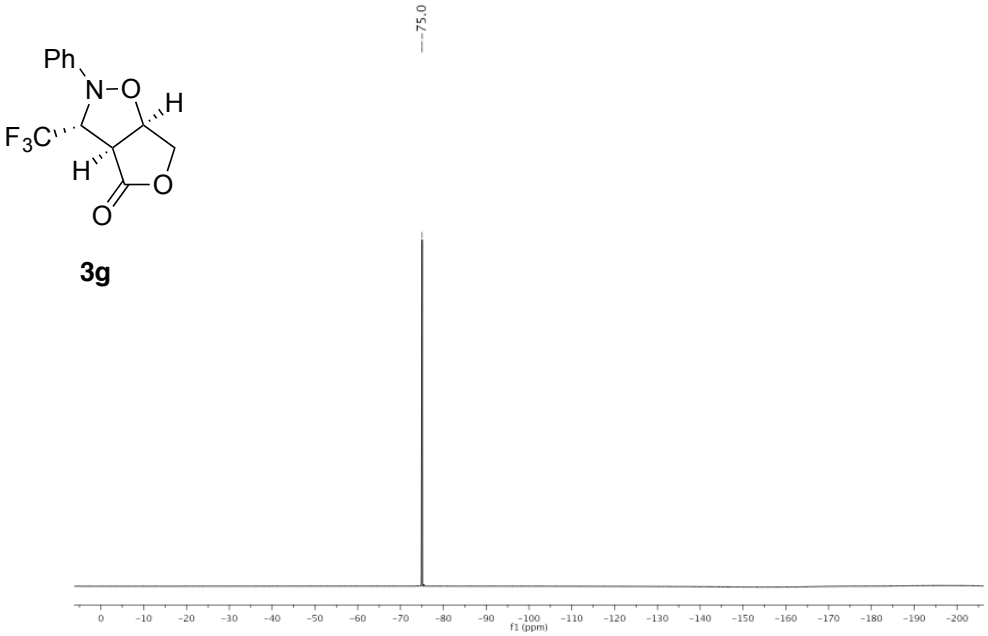


^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Ethyl 5-(bromomethyl)-2-phenyl-3-(trifluoromethyl)isoxazolidine-4-carboxylate (3f)

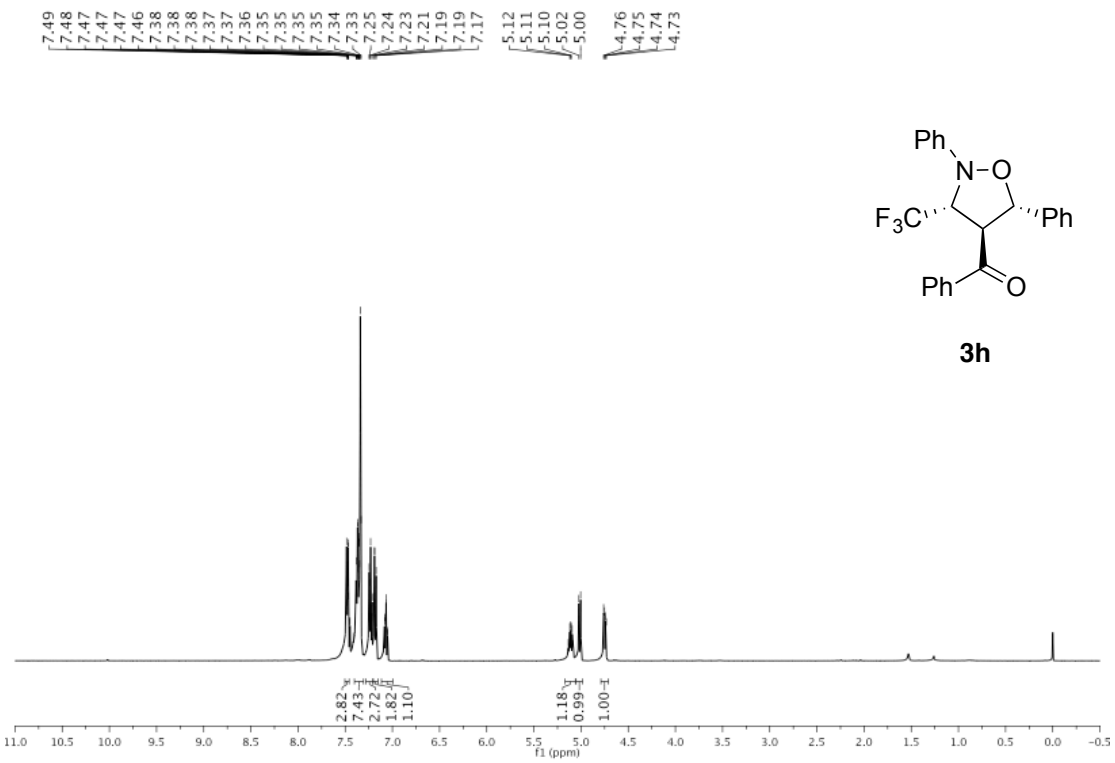
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-Phenyl-3-(trifluoromethyl)tetrahydrofuro[3,4-*d*]isoxazol-4(2*H*)-one (3g)



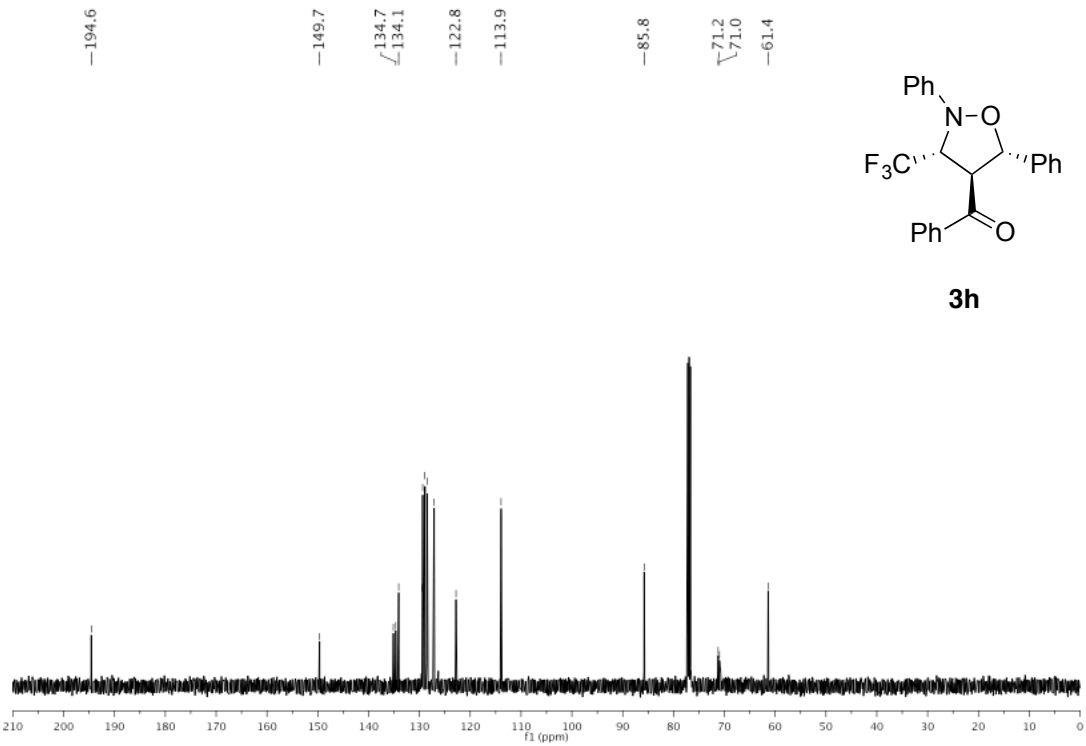
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 2-Phenyl-3-(trifluoromethyl)tetrahydrofuro[3,4-*d*]isoxazol-4(2*H*)-one (3g)



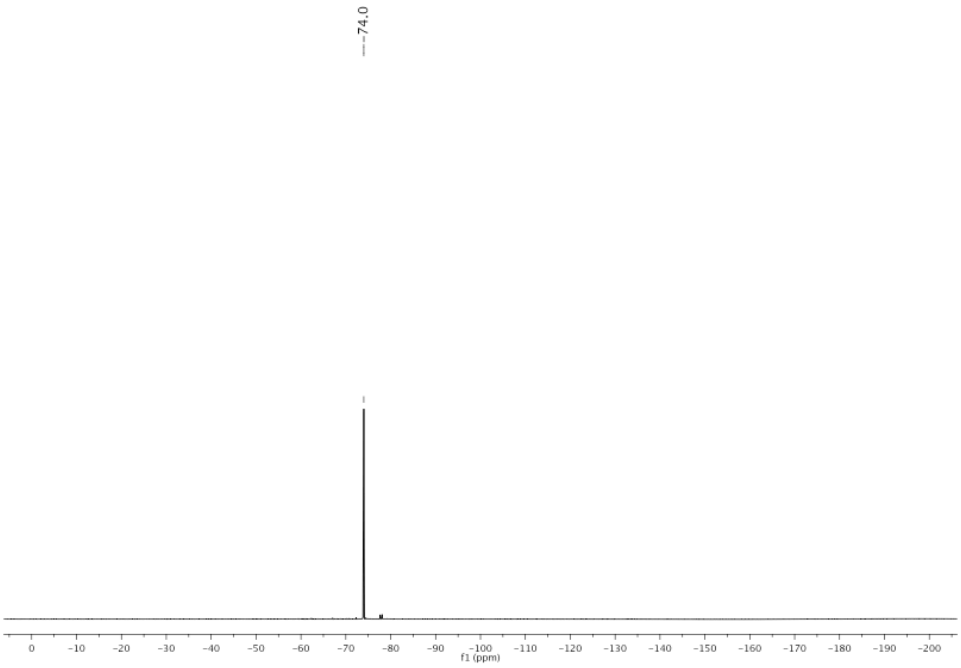
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of 2-Phenyl-3-(trifluoromethyl)tetrahydrofuro[3,4-*d*]isoxazol-4(2*H*)-one (3g)



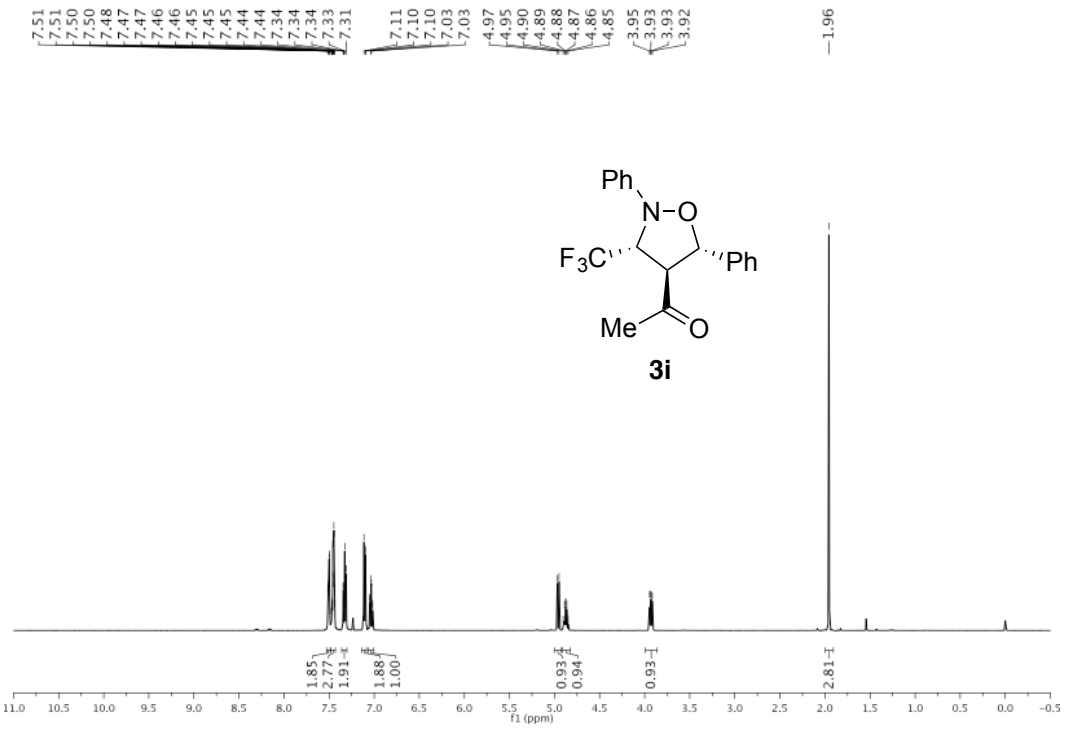
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of (2,5-Diphenyl-3-(trifluoromethyl)isoxazolidin-4-yl)(phenyl)methanone (3h)



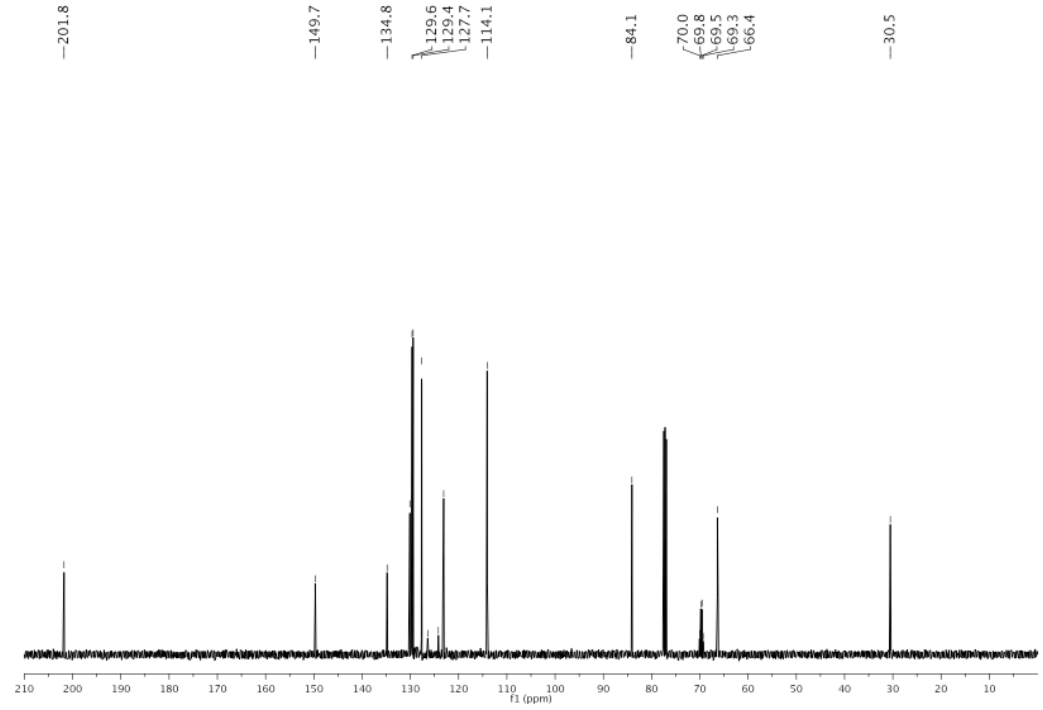
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of (2,5-Diphenyl-3-(trifluoromethyl)isoxazolidin-4-yl)(phenyl)methanone (3h)



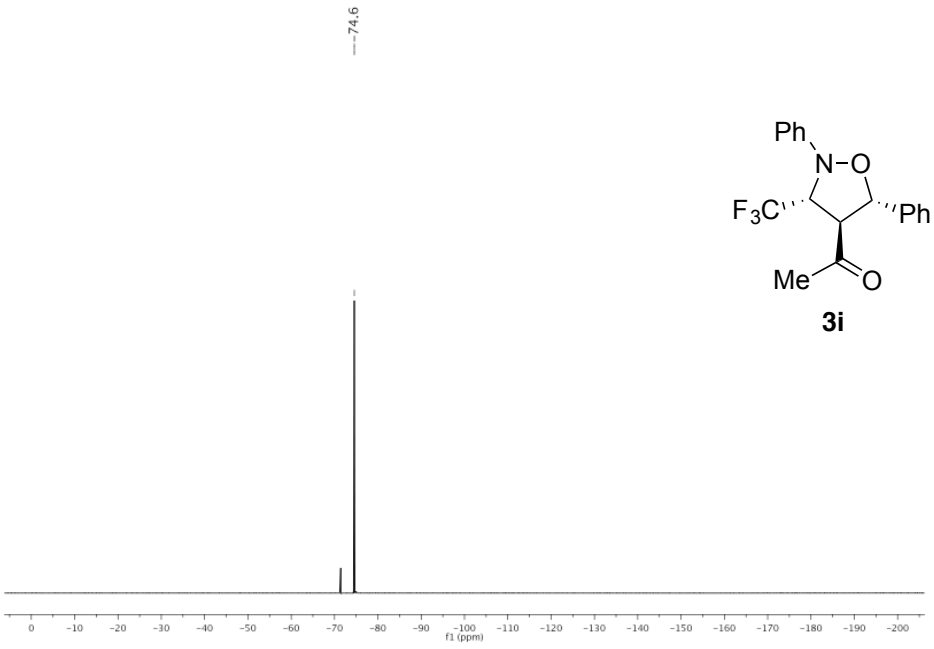
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of (2,5-Diphenyl-3-(trifluoromethyl)isoxazolidin-4-yl)(phenyl)methanone (3h)



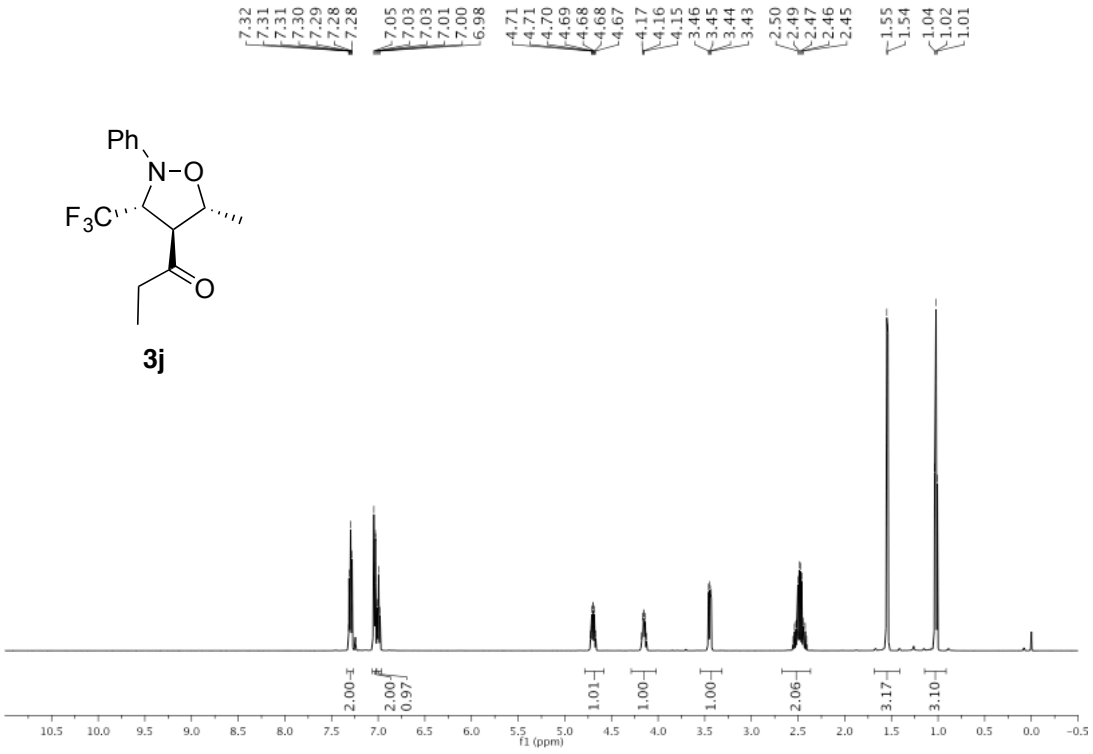
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(-2,5-Diphenyl-3-(trifluoromethyl)isoxazolidin-4-yl)ethan-1-one (3i)



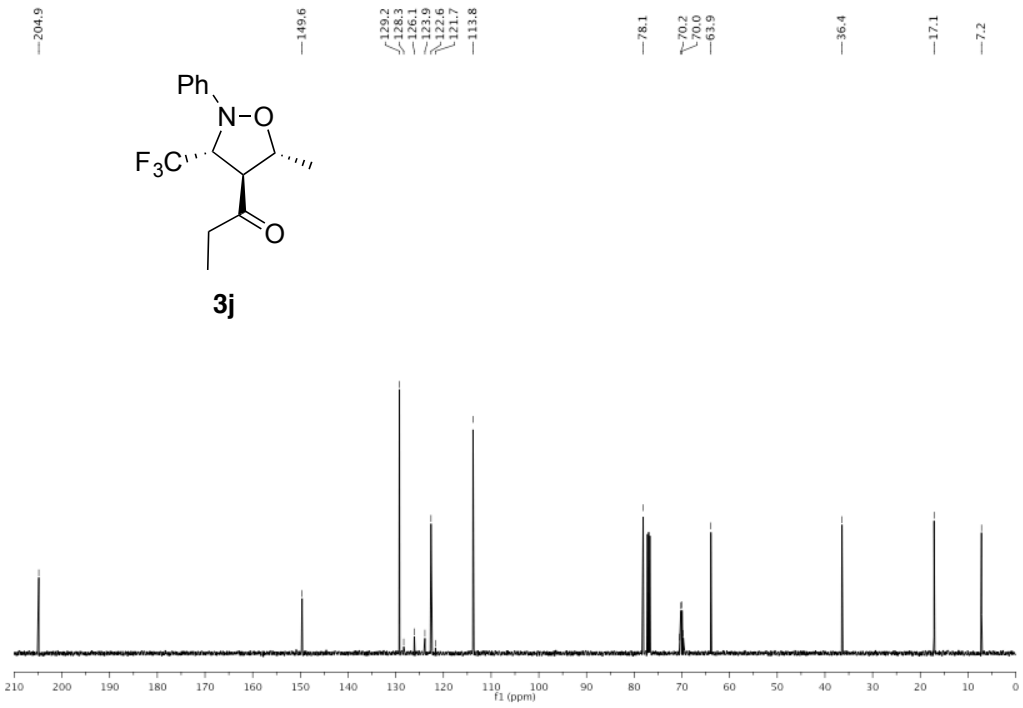
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-(-2,5-Diphenyl-3-(trifluoromethyl)isoxazolidin-4-yl)ethan-1-one (3i)



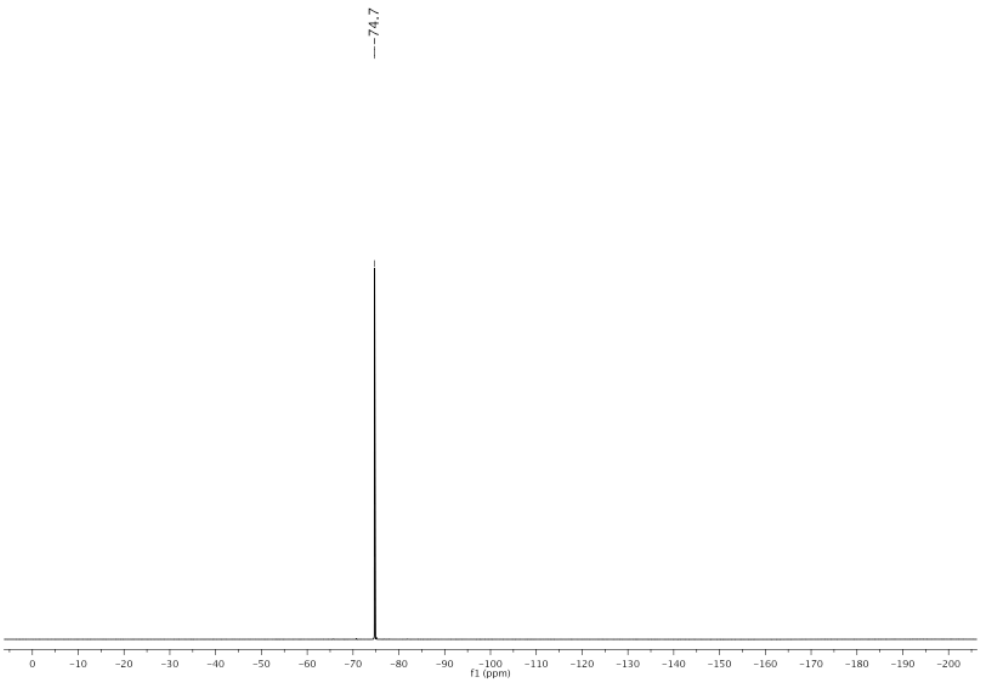
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of 1-(-2,5-Diphenyl-3-(trifluoromethyl)isoxazolidin-4-yl)ethan-1-one (3i)



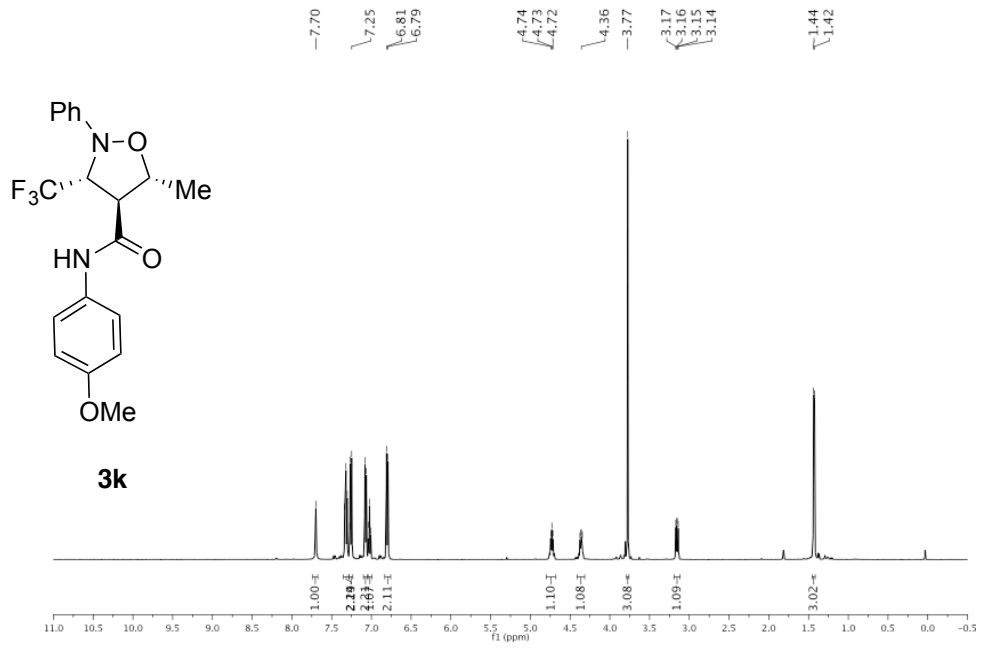
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(5-Methyl-2-phenyl-3-(trifluoromethyl)isoxazolidin-4-yl)propan-1-one (3j)



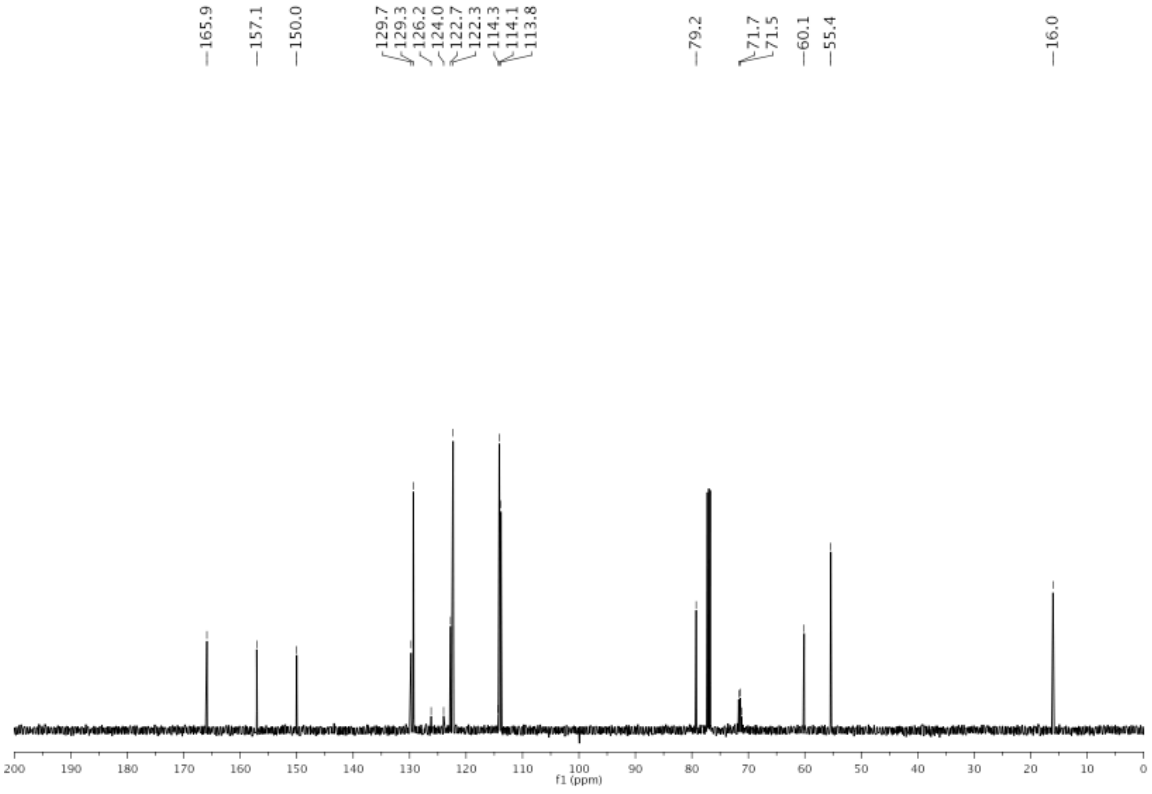
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of 1-(5-Methyl-2-phenyl-3-(trifluoromethyl)isoxazolidin-4-yl)propan-1-one (3j)



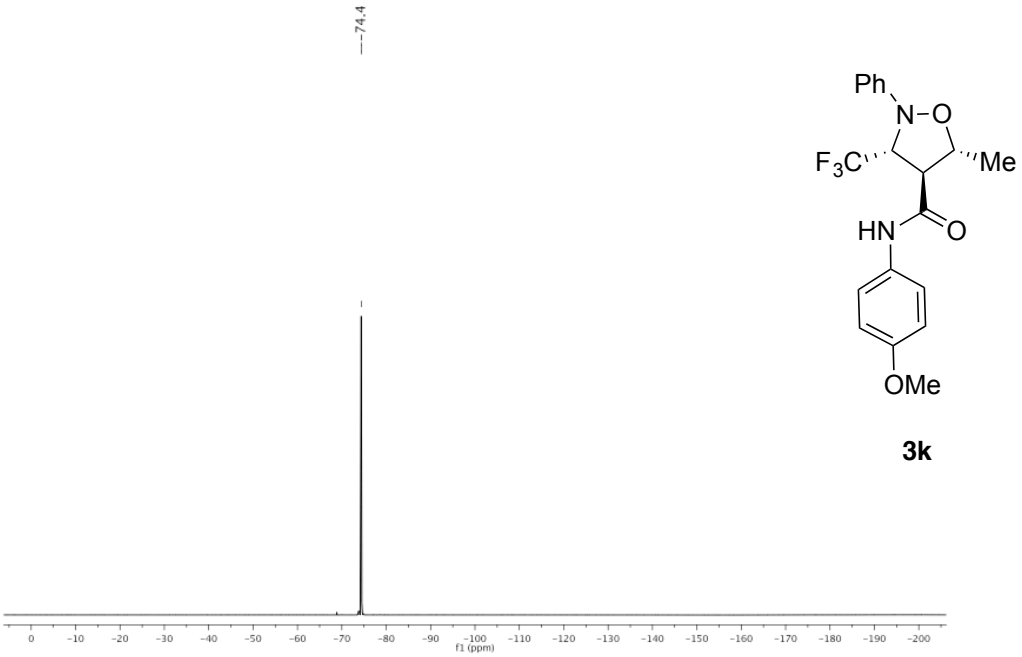
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of 1-(5-Methyl-2-phenyl-3-(trifluoromethyl)isoxazolidin-4-yl)propan-1-one (3j)



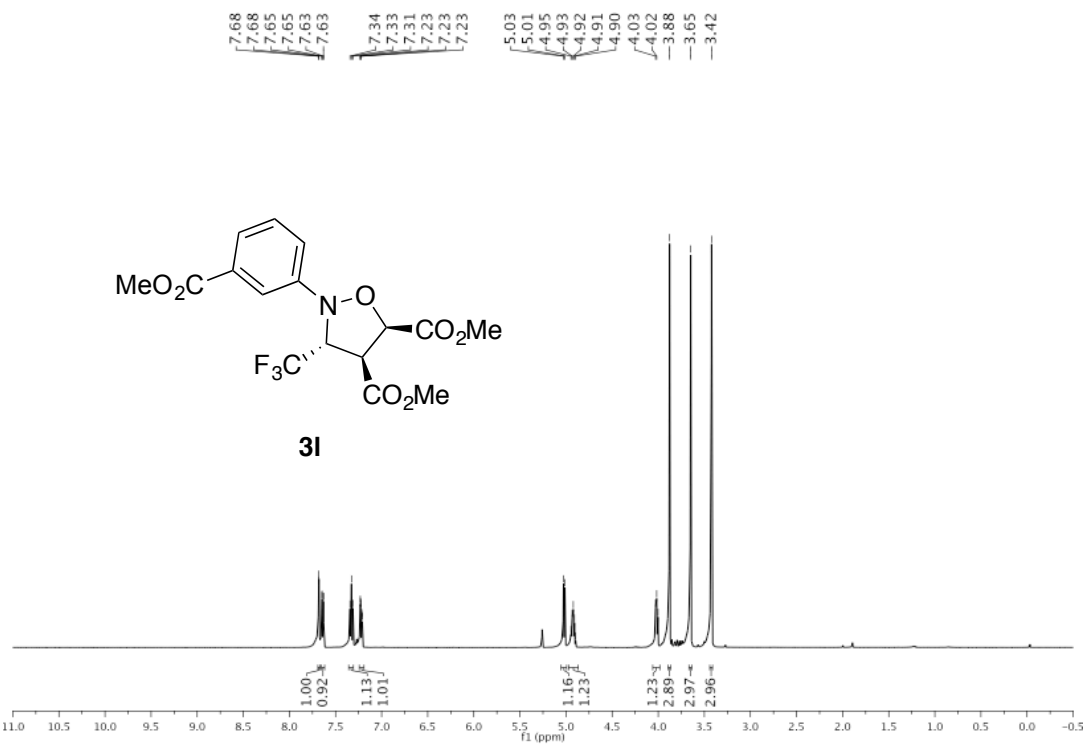
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of *N*-(4-Methoxyphenyl)-5-methyl-2-phenyl-3-(trifluoromethyl)isoxazolidine-4-carboxamide (3k)



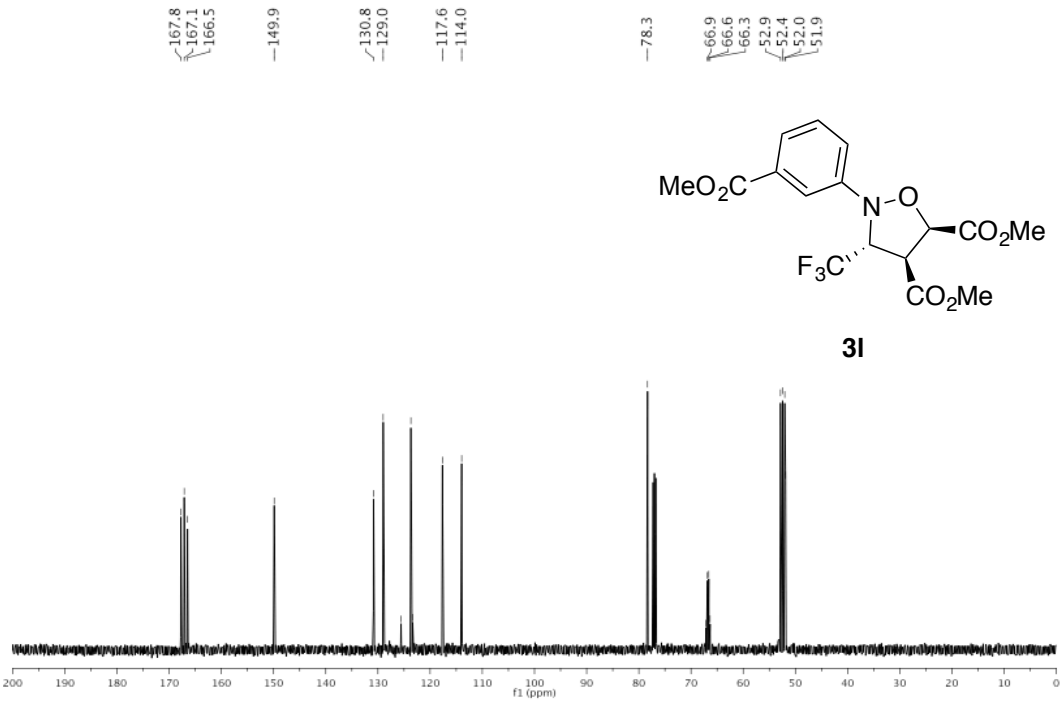
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of *N*-(4-Methoxyphenyl)-5-methyl-2-phenyl-3-(trifluoromethyl)isoxazolidine-4-carboxamide (3k)



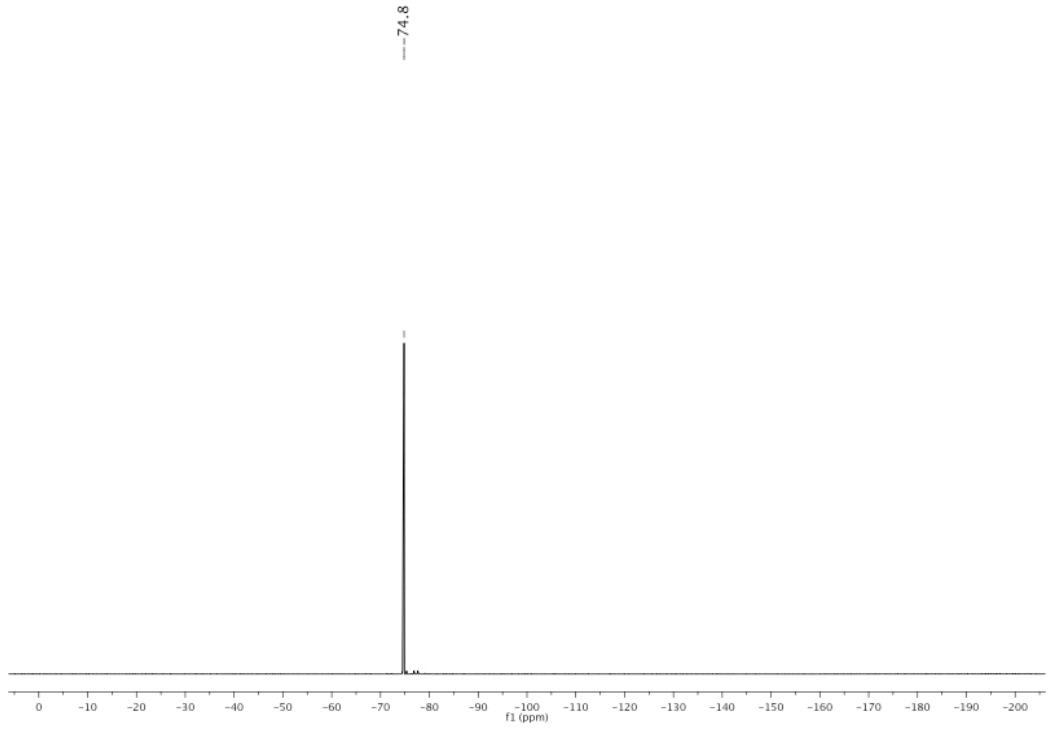
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of *N*-(4-Methoxyphenyl)-5-methyl-2-phenyl-3-(trifluoromethyl)isoxazolidine-4-carboxamide (3k)



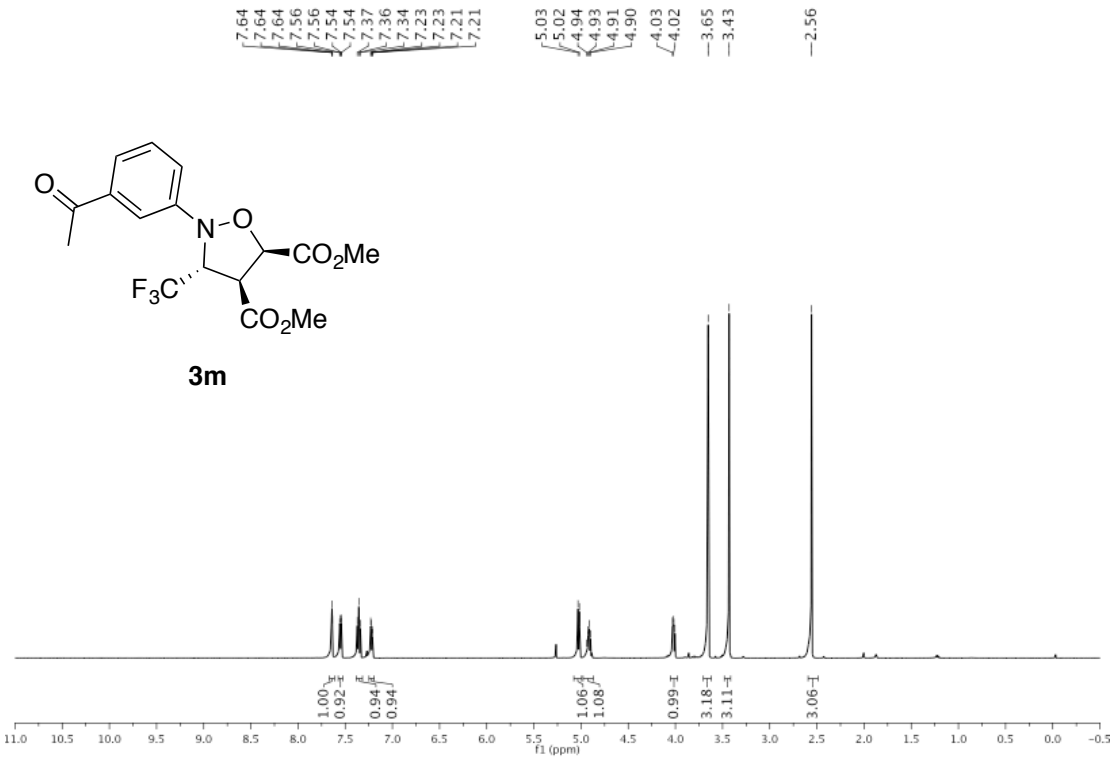
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(3-(methoxycarbonyl)phenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3l)



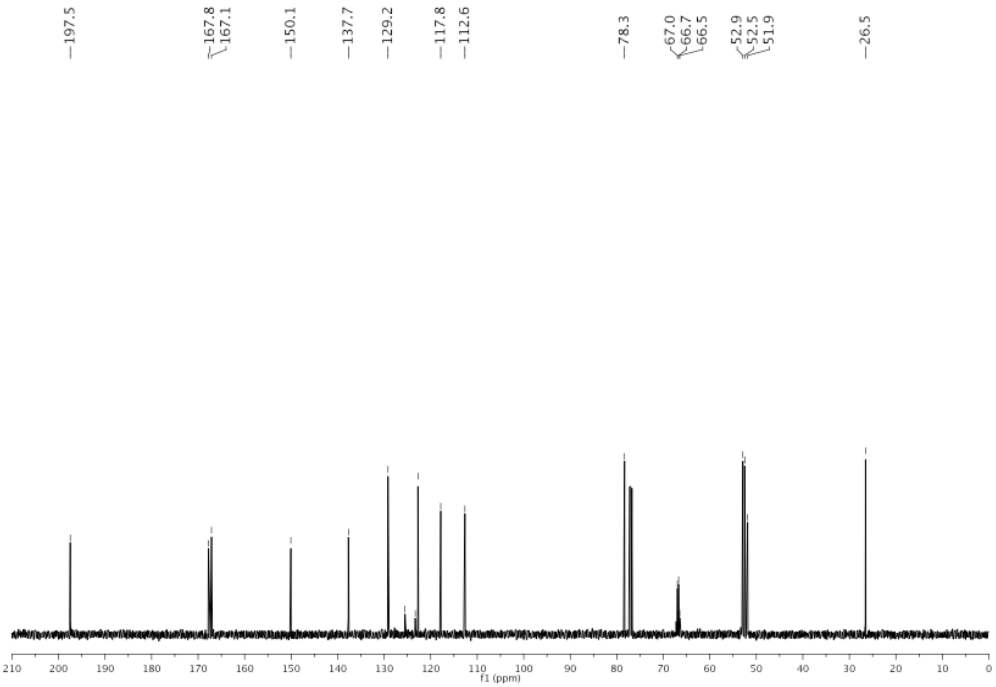
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(3-(methoxycarbonyl)phenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3l)



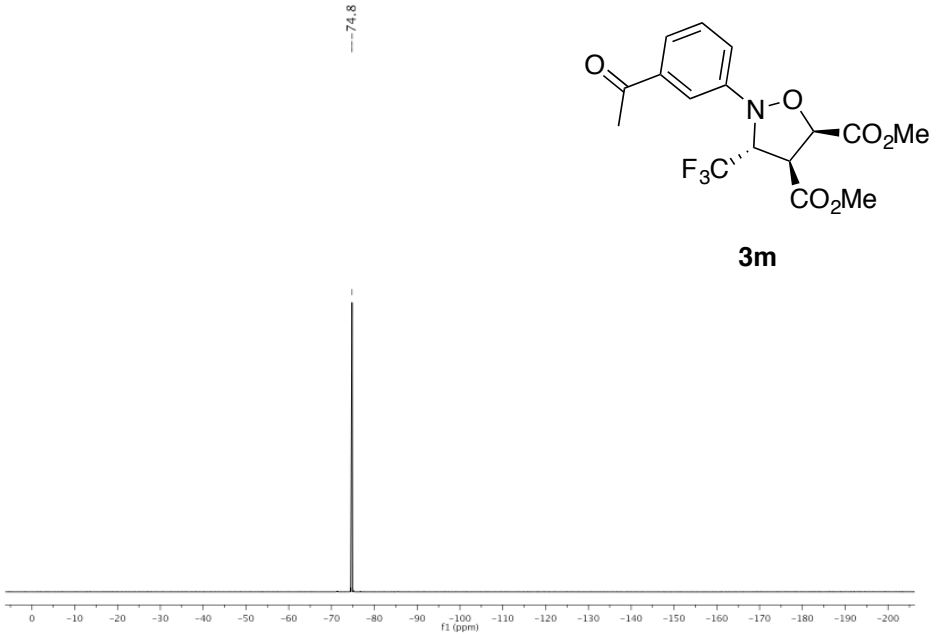
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(3-(methoxycarbonyl)phenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3l)



^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(3-acetylphenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3m)

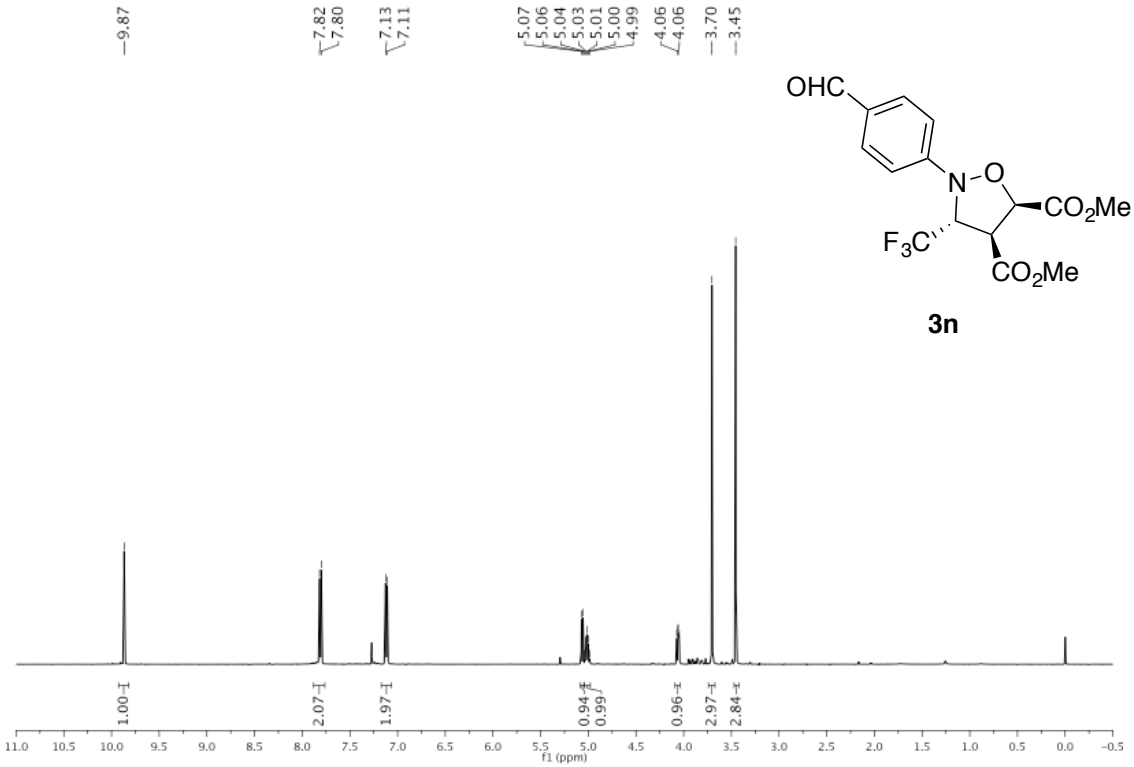


^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(3-acetylphenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3m)



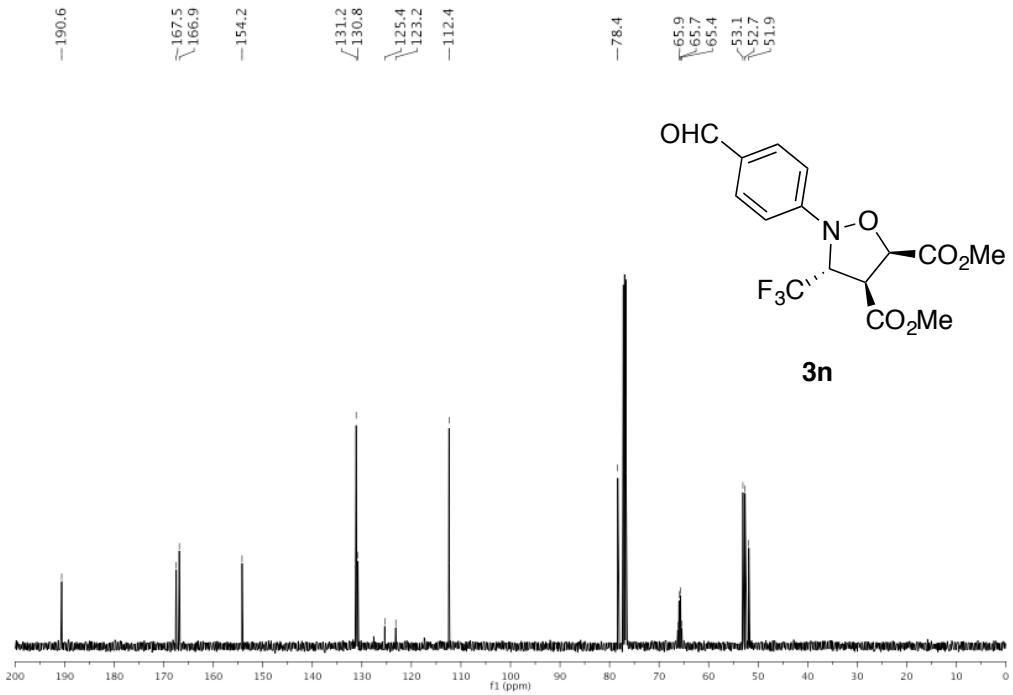
3m

^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(3-acetylphenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3m)

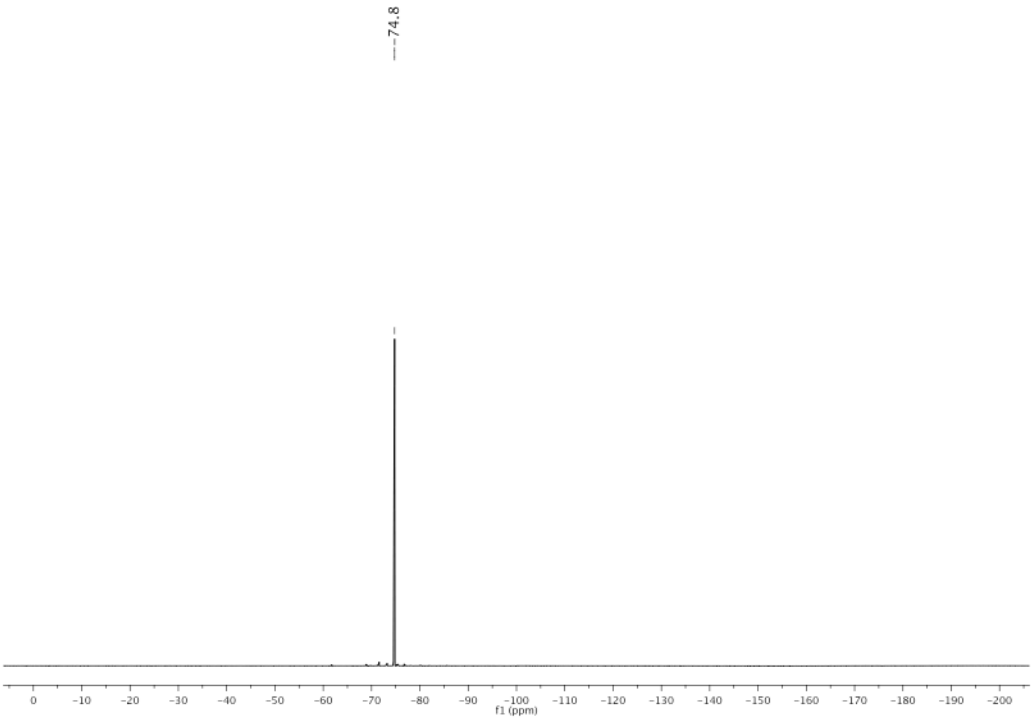


3n

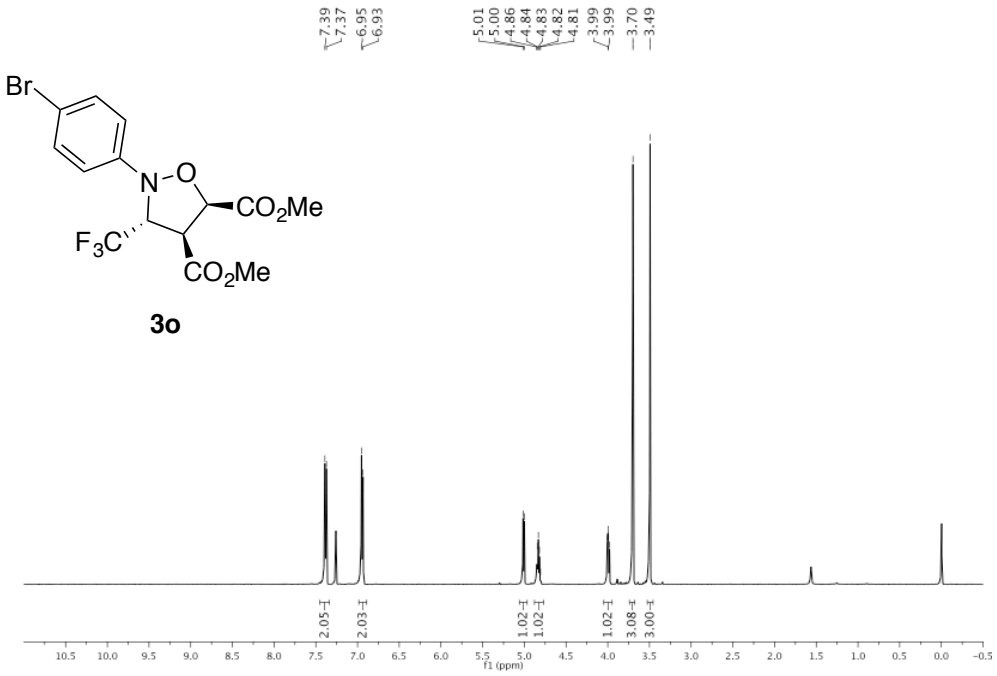
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(4-formylphenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3n)



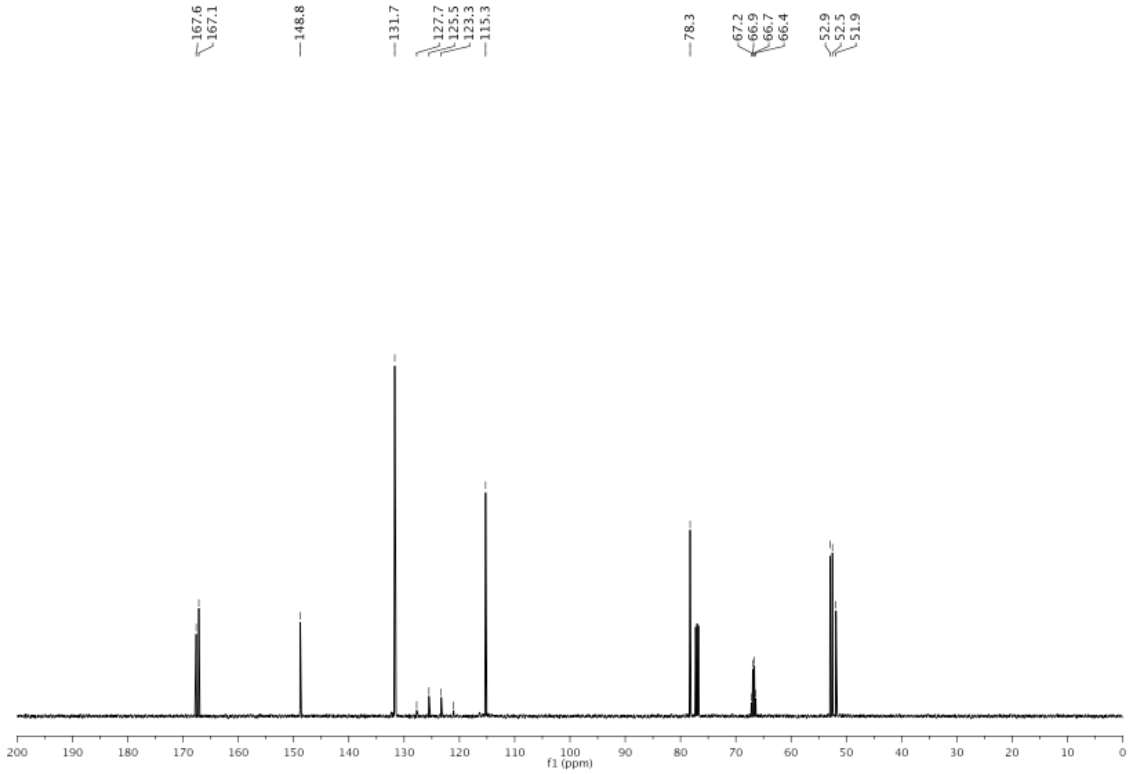
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(4-formylphenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3n)



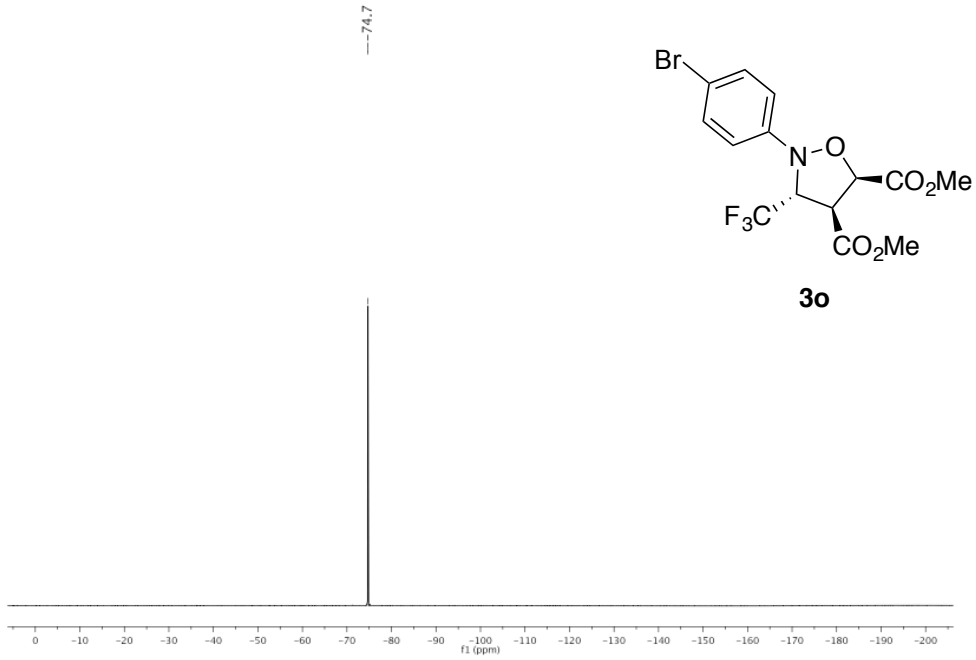
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(4-formylphenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3n)



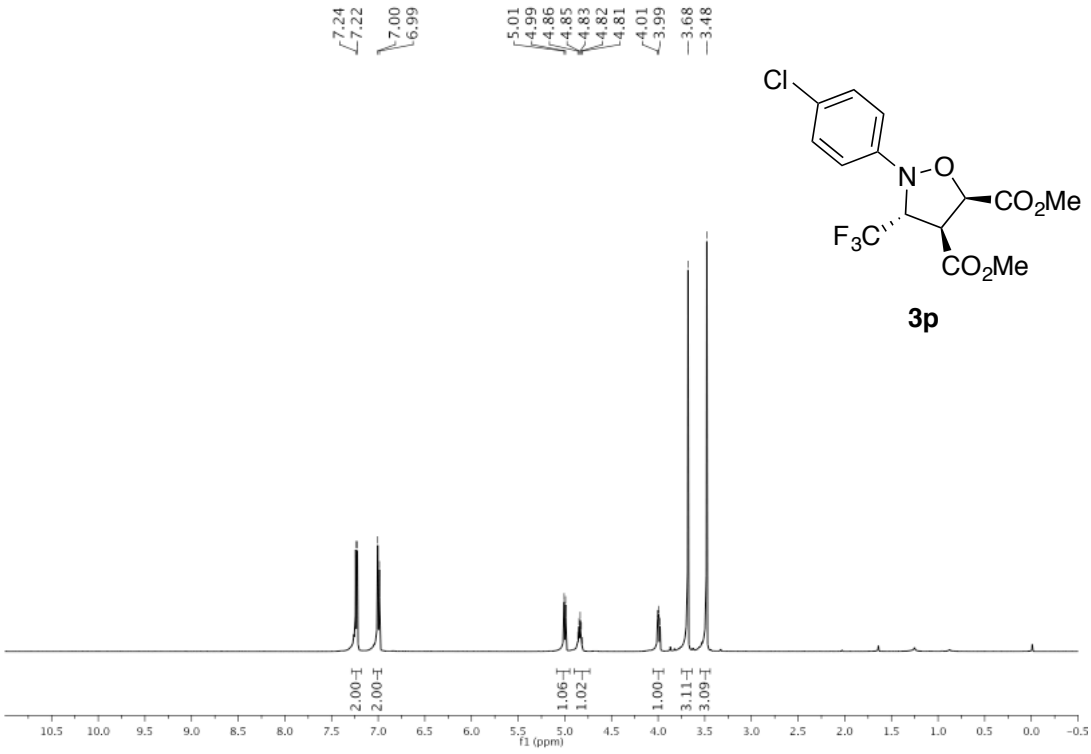
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(4-bromophenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3o)



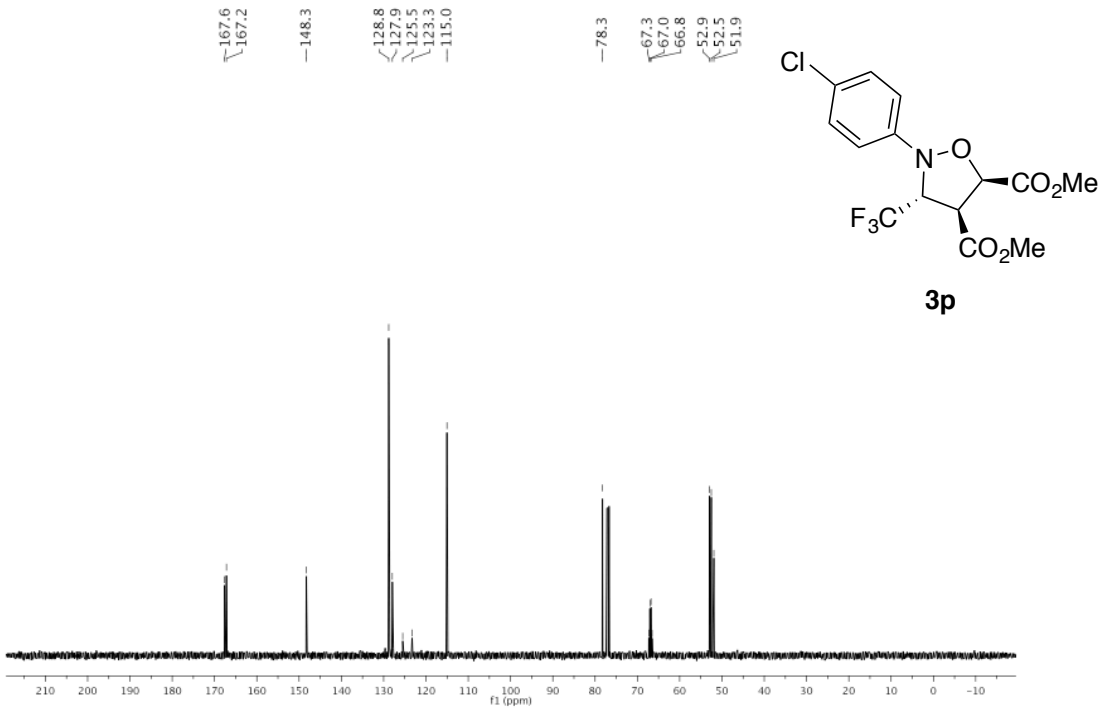
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(4-bromophenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3o)



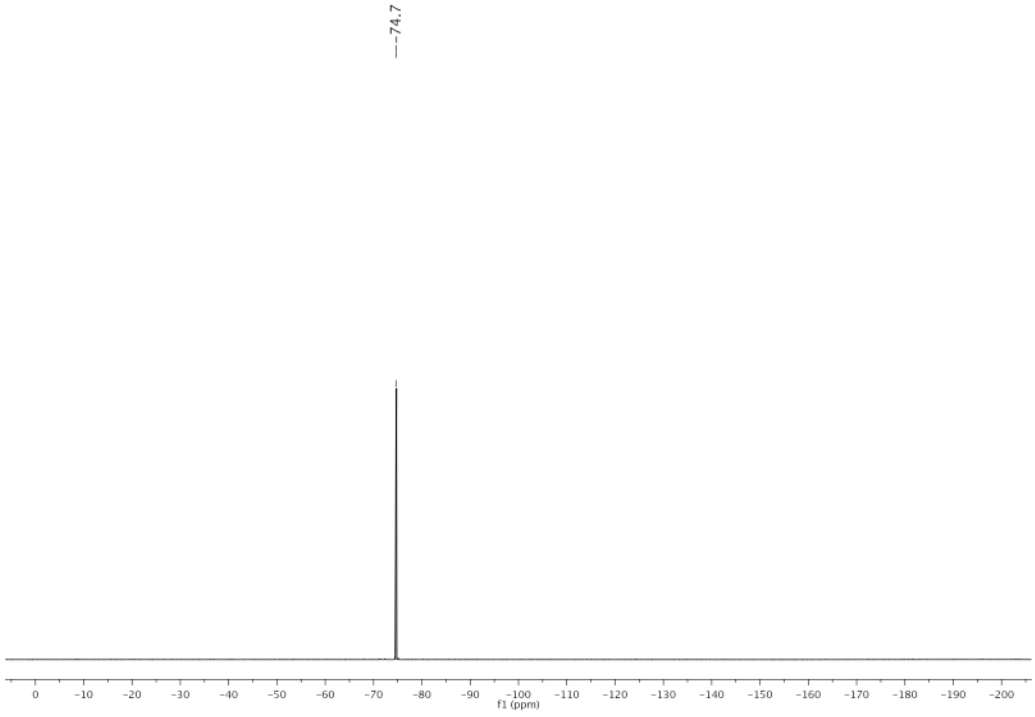
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(4-bromophenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3o)



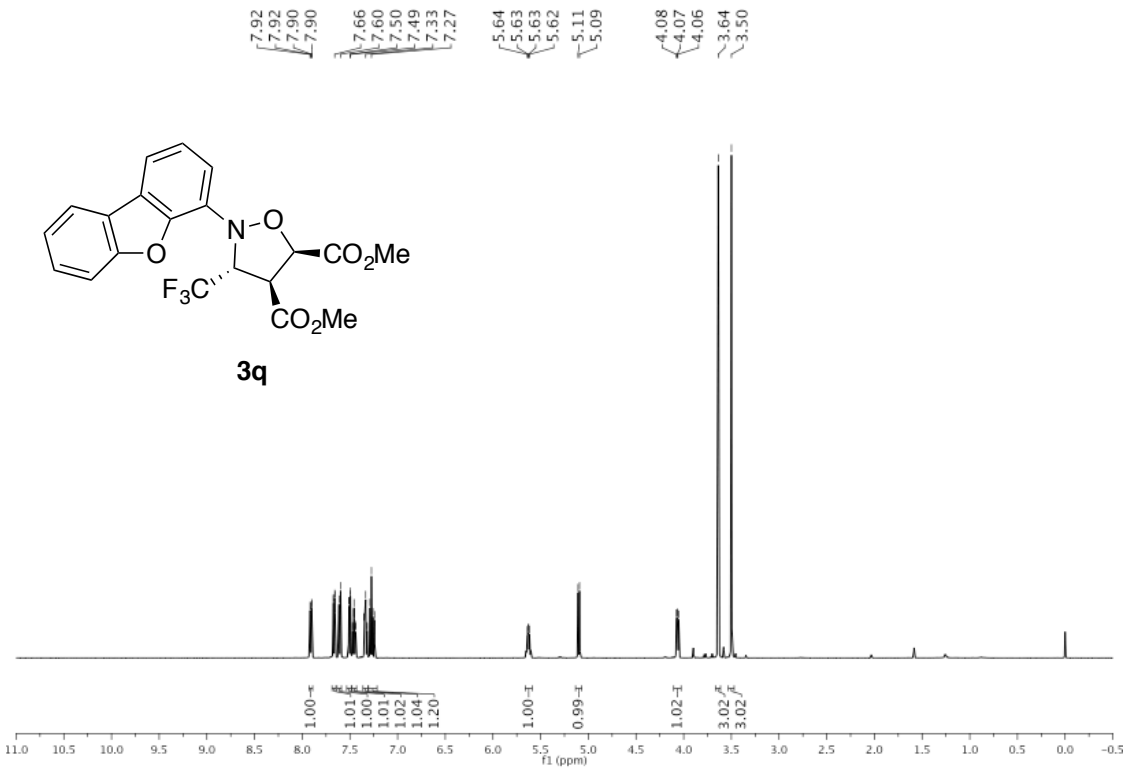
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(4-chlorophenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3p)



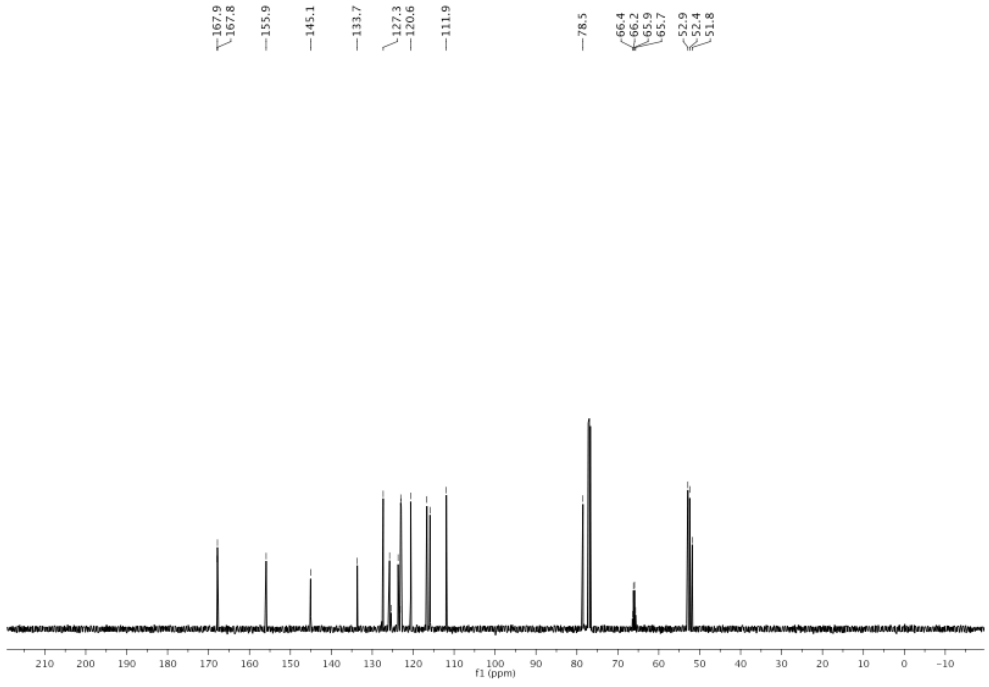
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(4-chlorophenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3p)



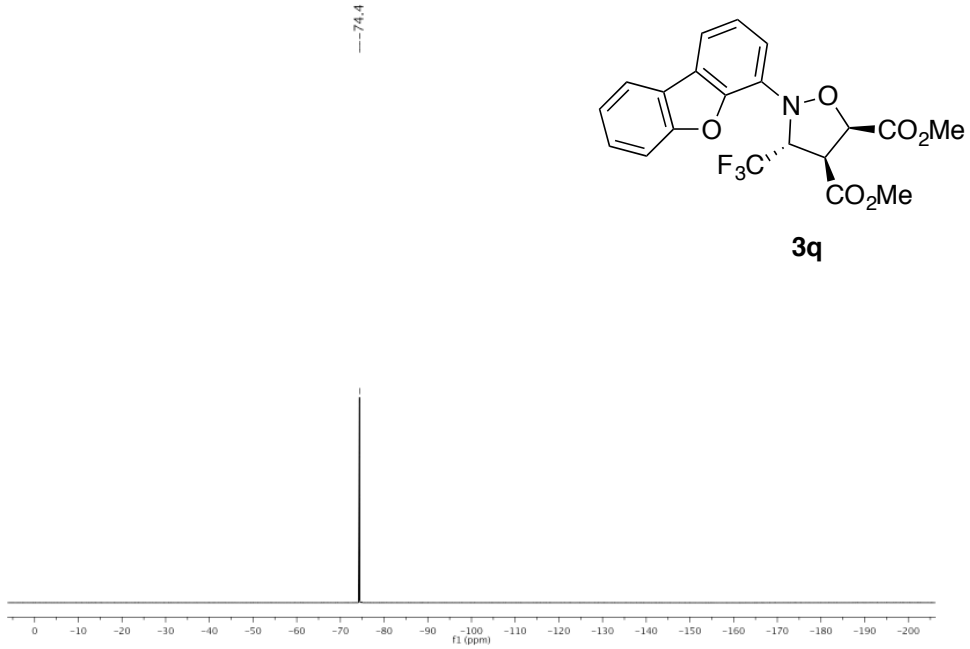
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(4-chlorophenyl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3p)



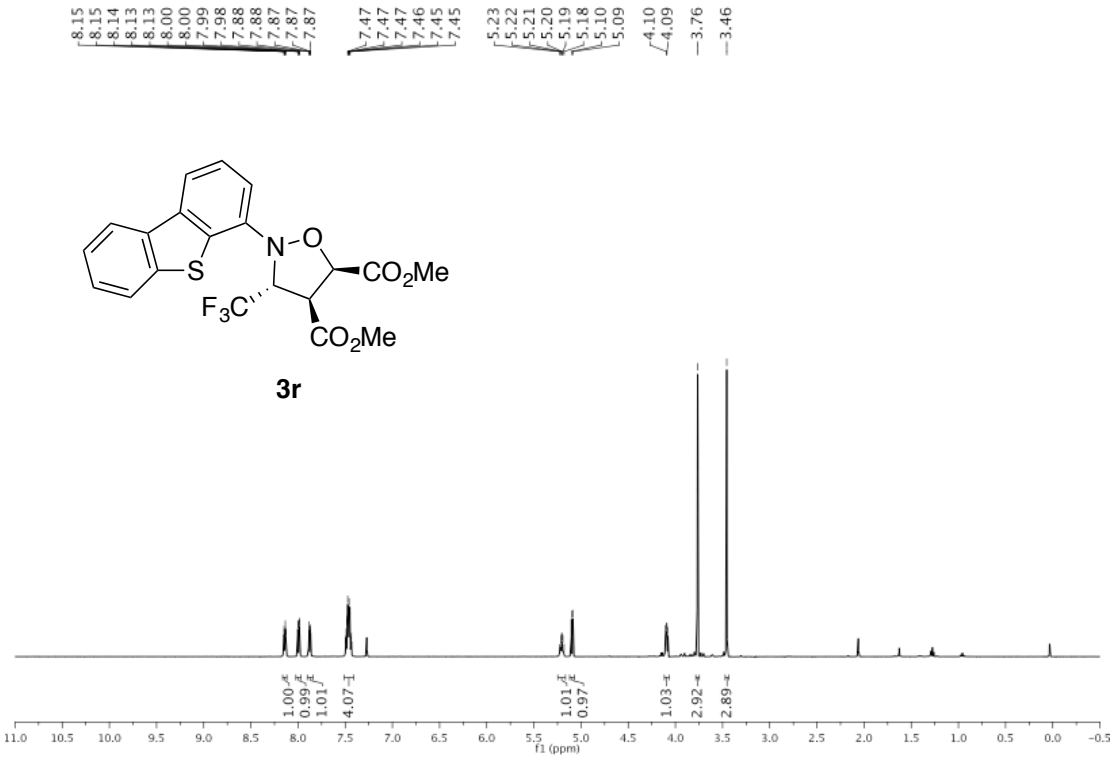
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(dibenzo[*b*,*d*]furan-4-yl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3q)



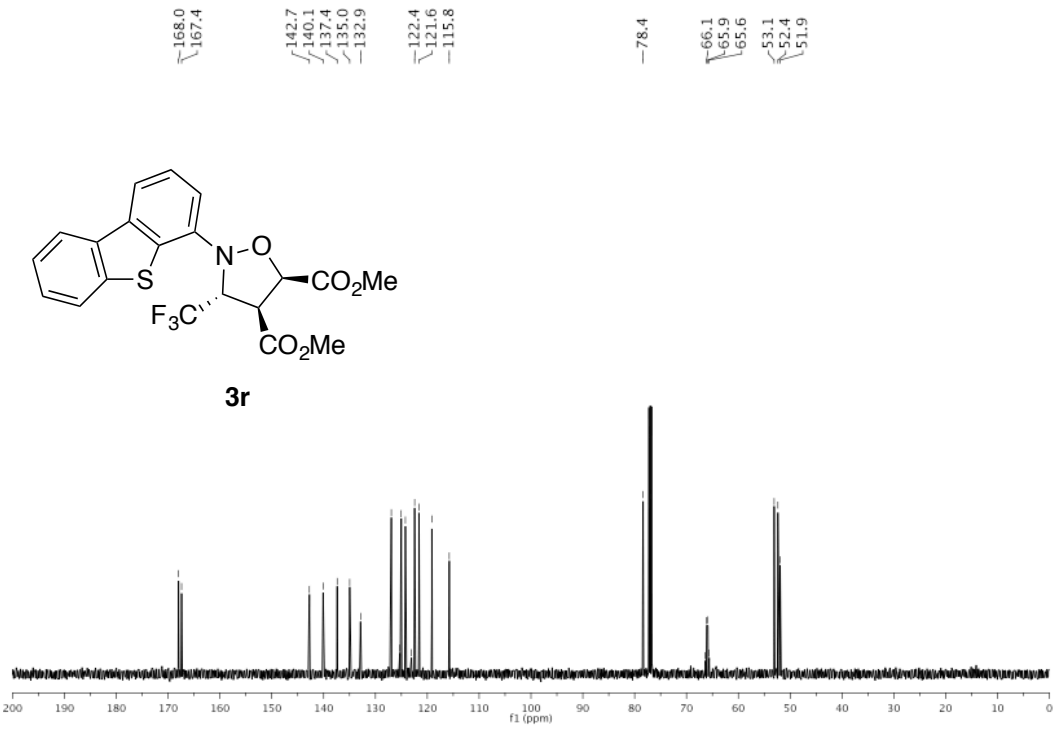
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(dibenzo[*b*,*d*]furan-4-yl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3q)



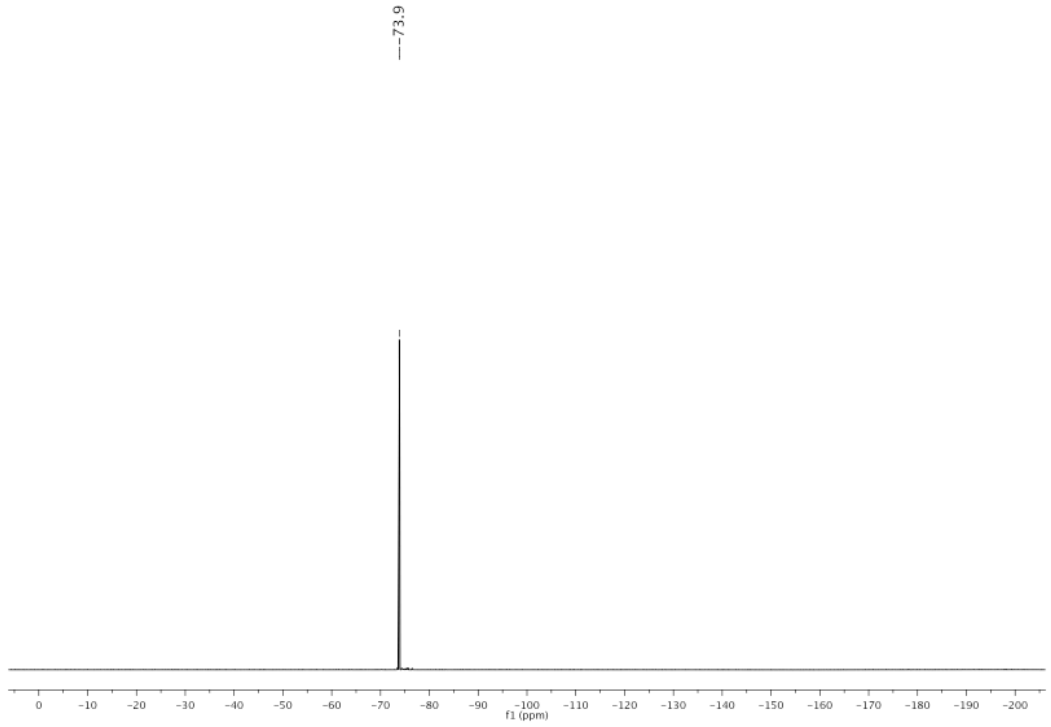
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(dibenzo[*b*,*d*]furan-4-yl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3q)



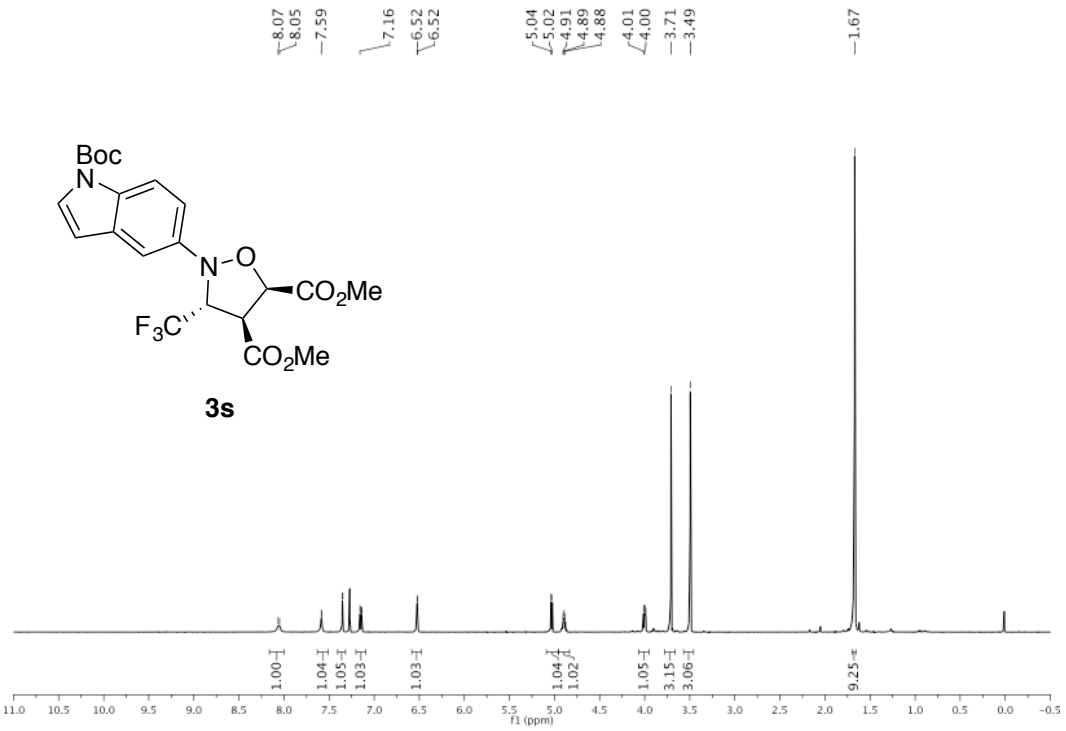
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(dibenzo[*b*,*d*]thiophen-4-yl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3r)



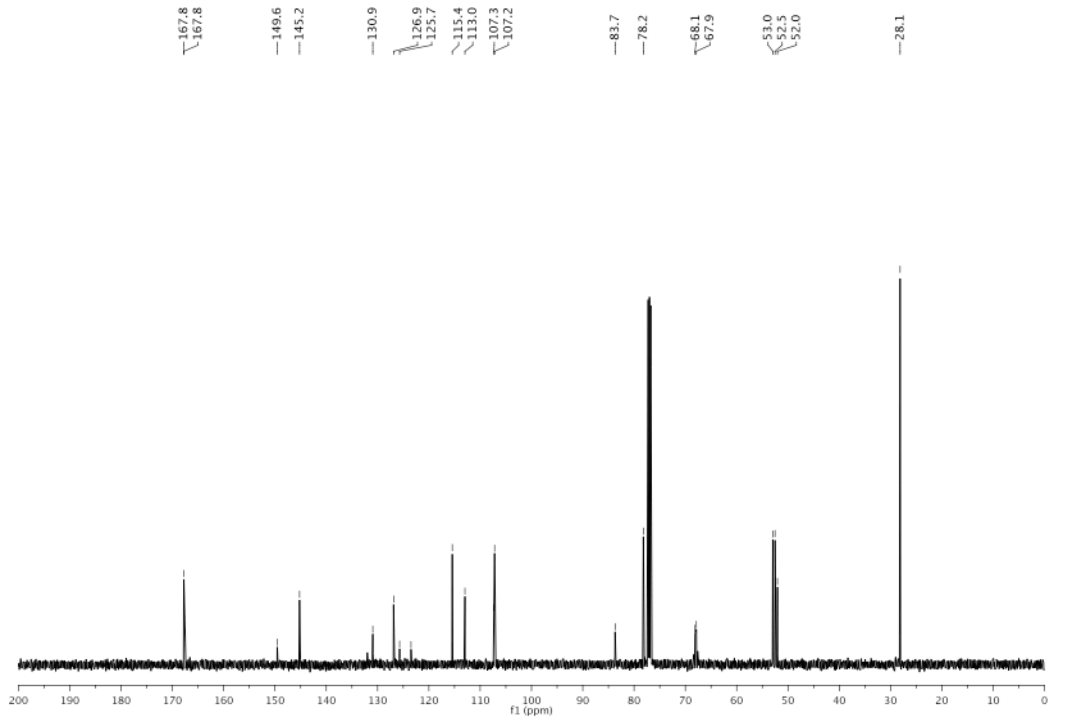
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(dibenzo[*b*,*d*]thiophen-4-yl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3r)



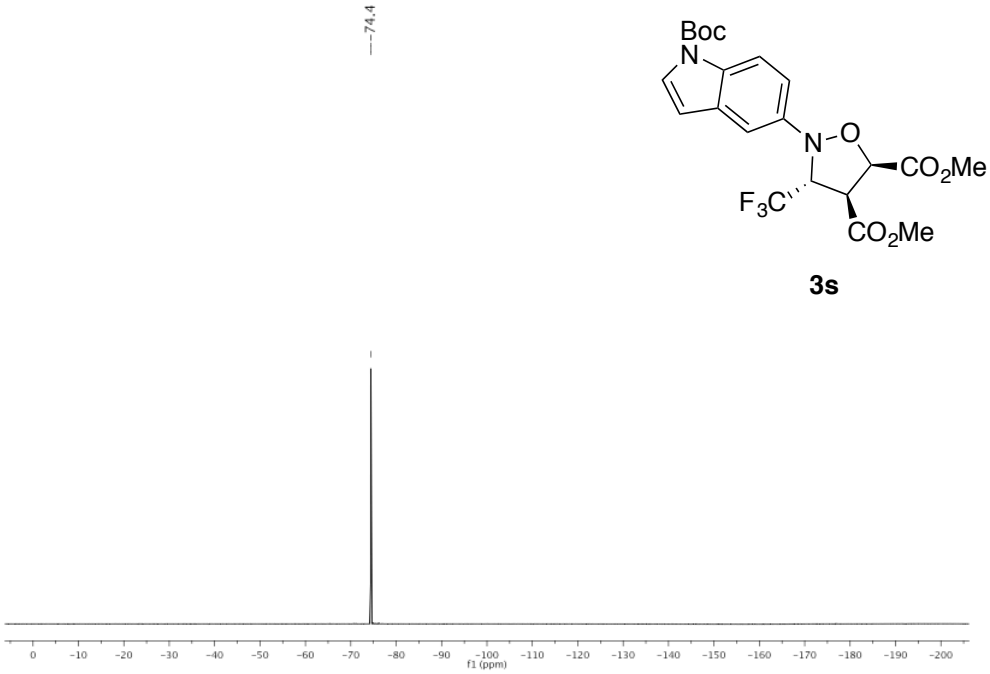
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(dibenzo[*b*,*d*]thiophen-4-yl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3r)



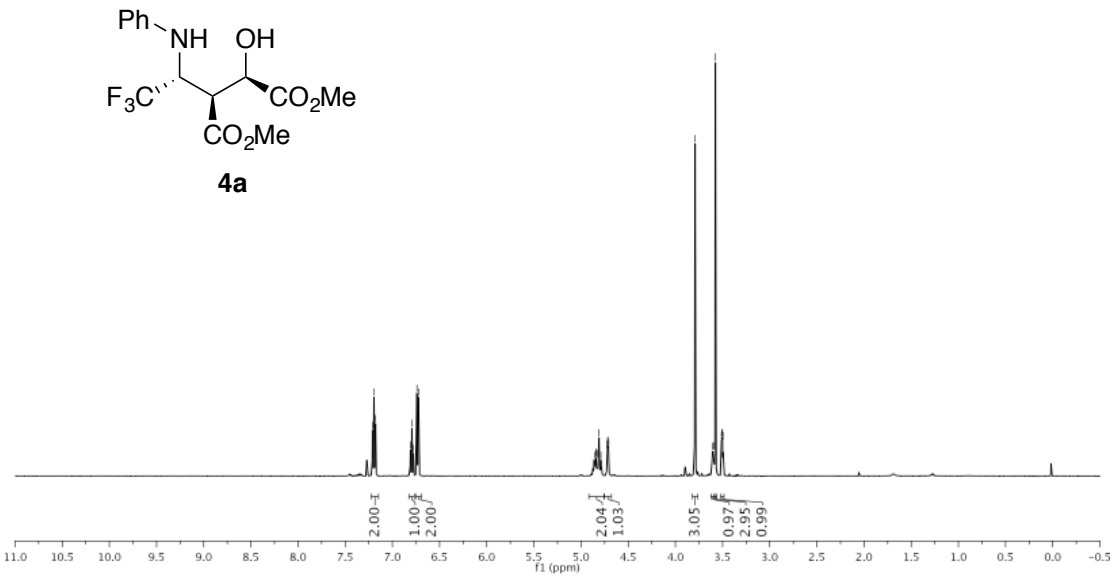
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(1-(*tert*-butoxycarbonyl)-1*H*-indol-5-yl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3s)



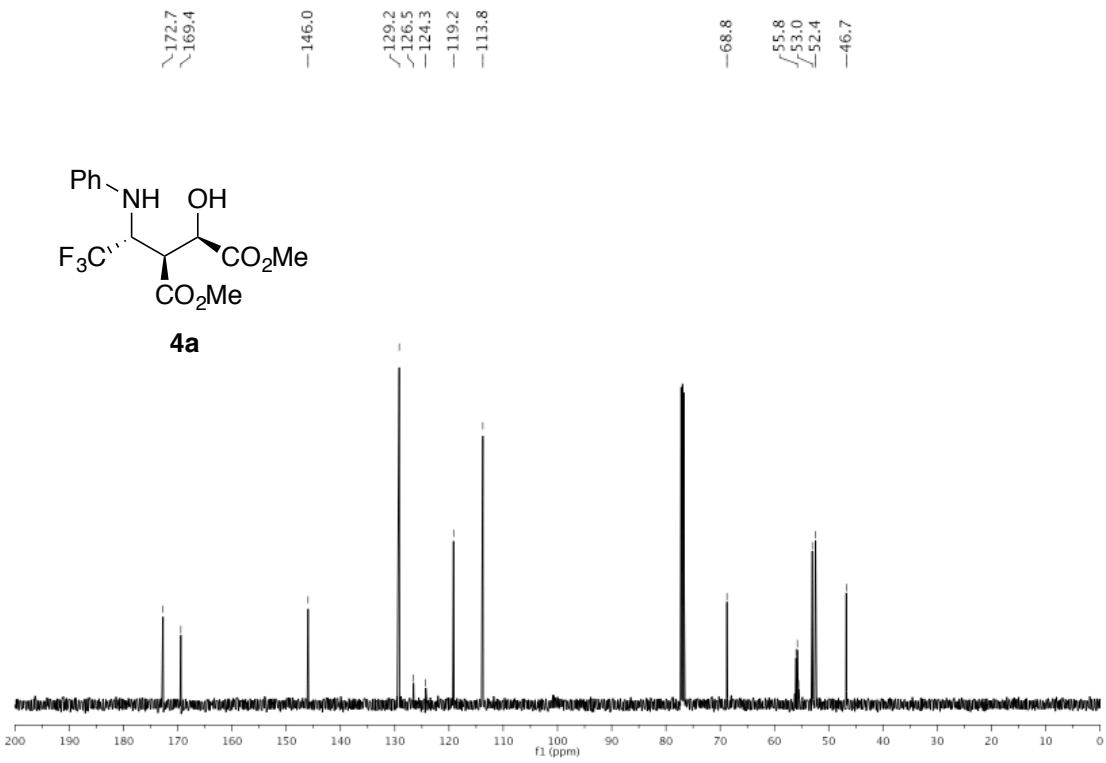
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(1-(*tert*-butoxycarbonyl)-1*H*-indol-5-yl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3s)



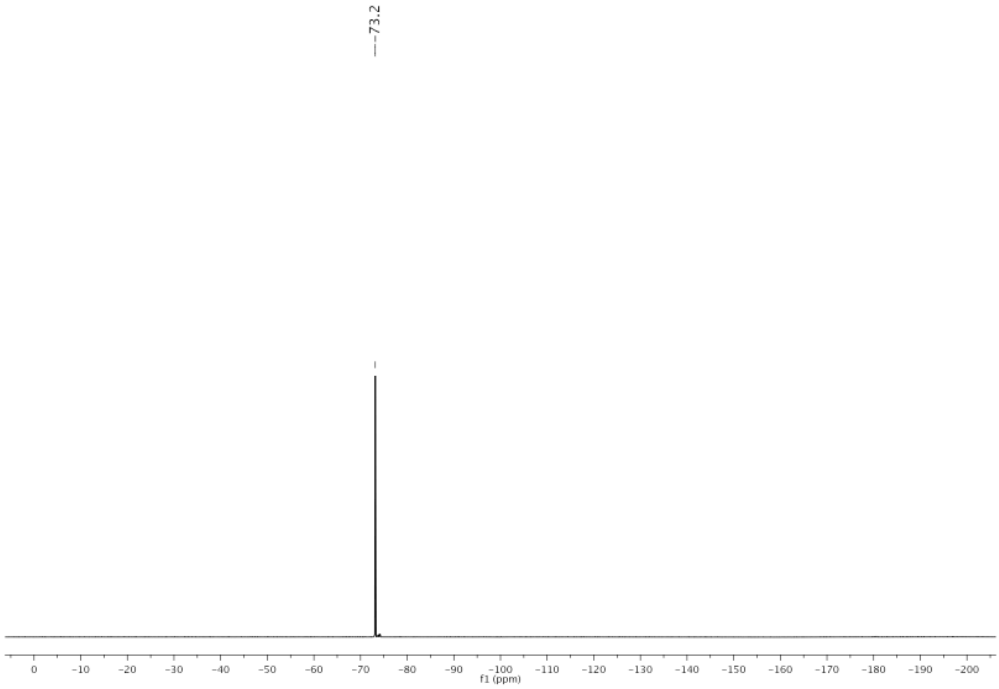
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Dimethyl 2-(1-(*tert*-butoxycarbonyl)-1*H*-indol-5-yl)-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3s)



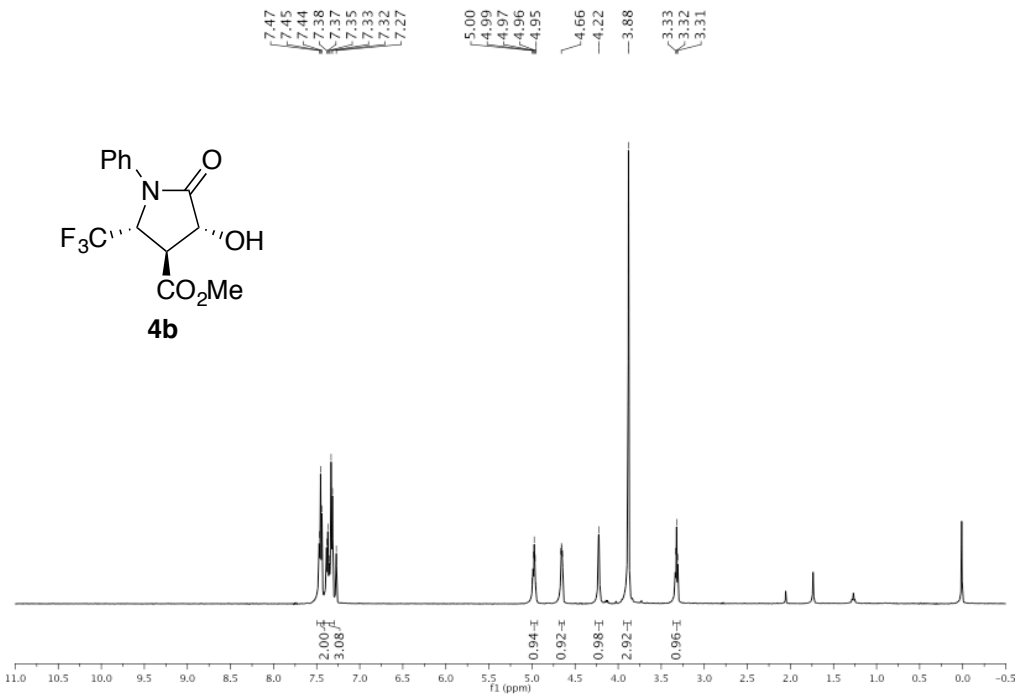
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Dimethyl 2-hydroxy-3-(2,2,2-trifluoro-1-(phenylamino)ethyl)succinate (4a)



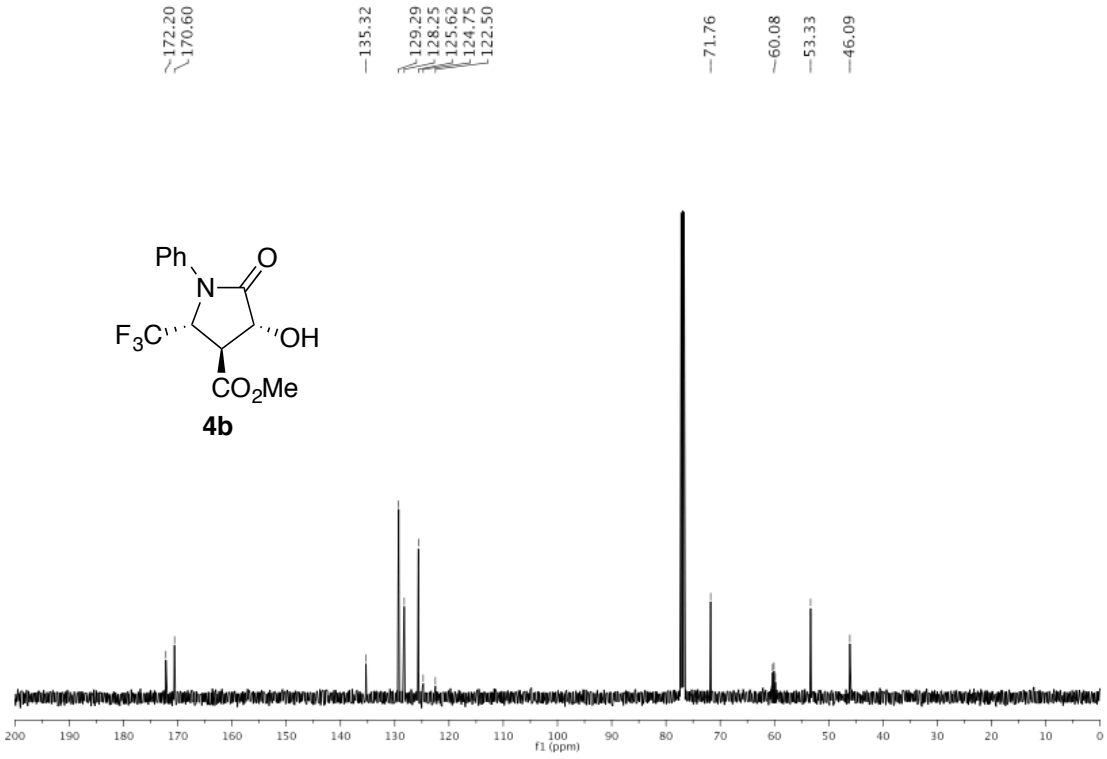
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Dimethyl 2-hydroxy-3-(2,2,2-trifluoro-1-(phenylamino)ethyl)succinate (4a)



^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Dimethyl 2-hydroxy-3-(2,2,2-trifluoro-1-(phenylamino)ethyl)succinate (4a)

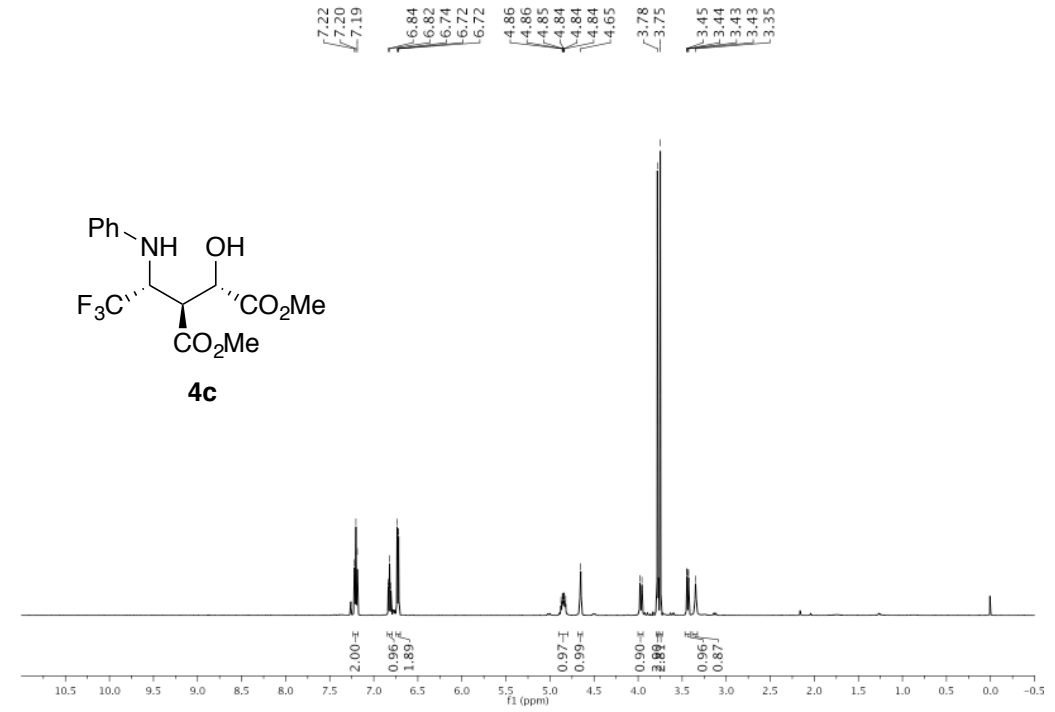


^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Methyl 4-hydroxy-5-oxo-1-phenyl-2-(trifluoromethyl)pyrrolidine-3-carboxylate (4b)

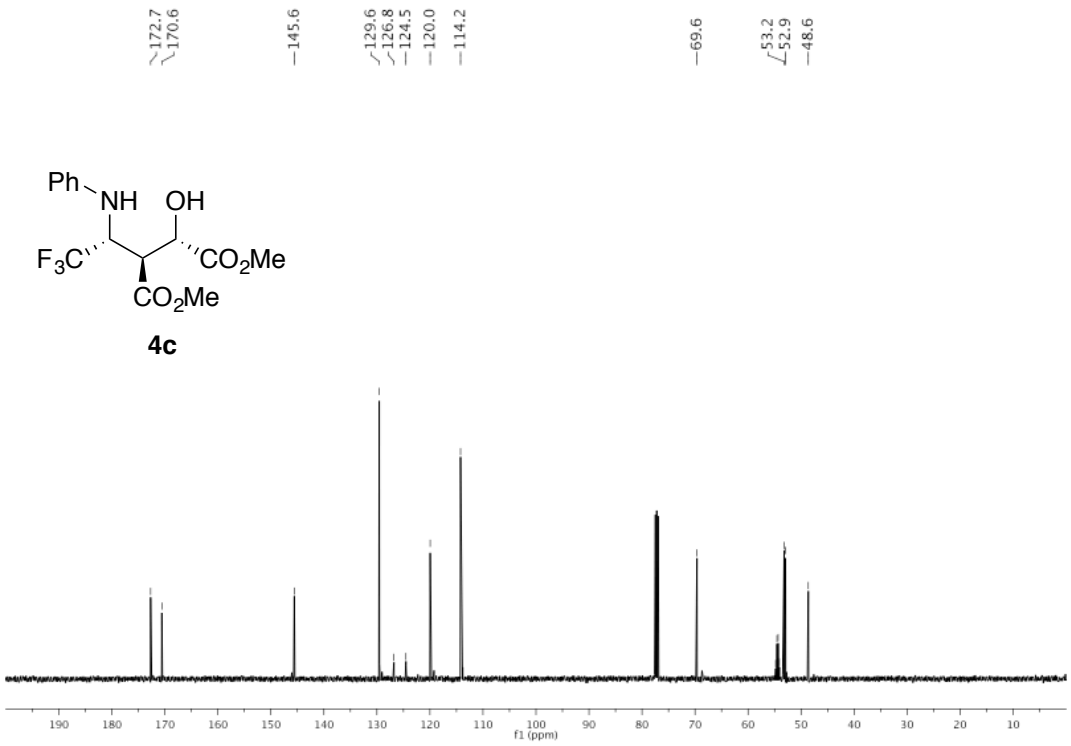


^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Methyl 4-hydroxy-5-oxo-1-phenyl-2-(trifluoromethyl)pyrrolidine-3-carboxylate (4b)

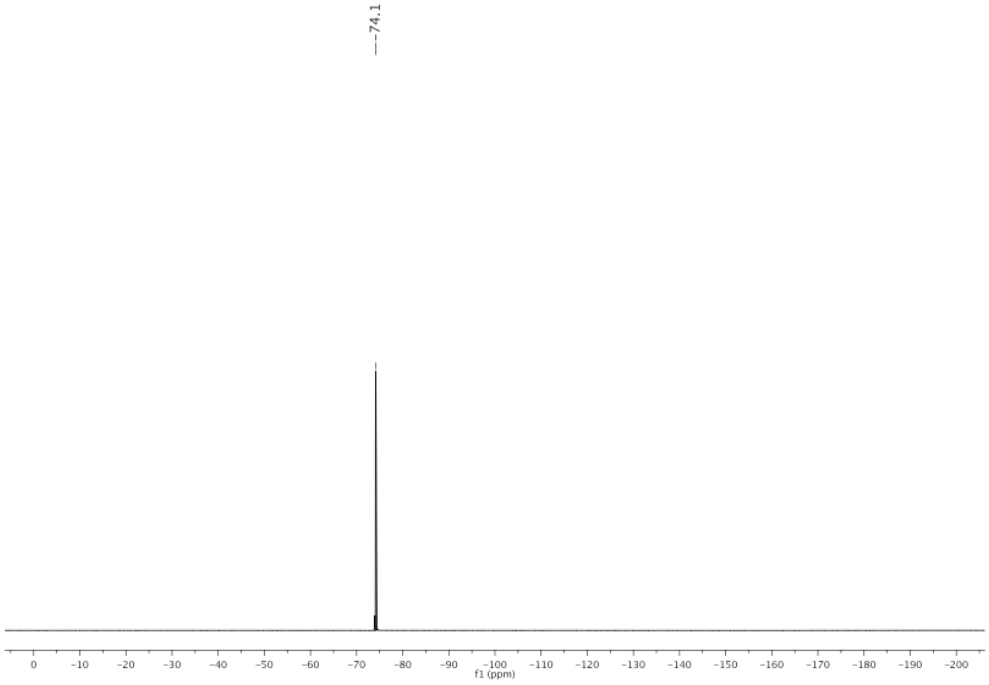
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Methyl 4-hydroxy-5-oxo-1-phenyl-2-(trifluoromethyl)pyrrolidine-3-carboxylate (4b)



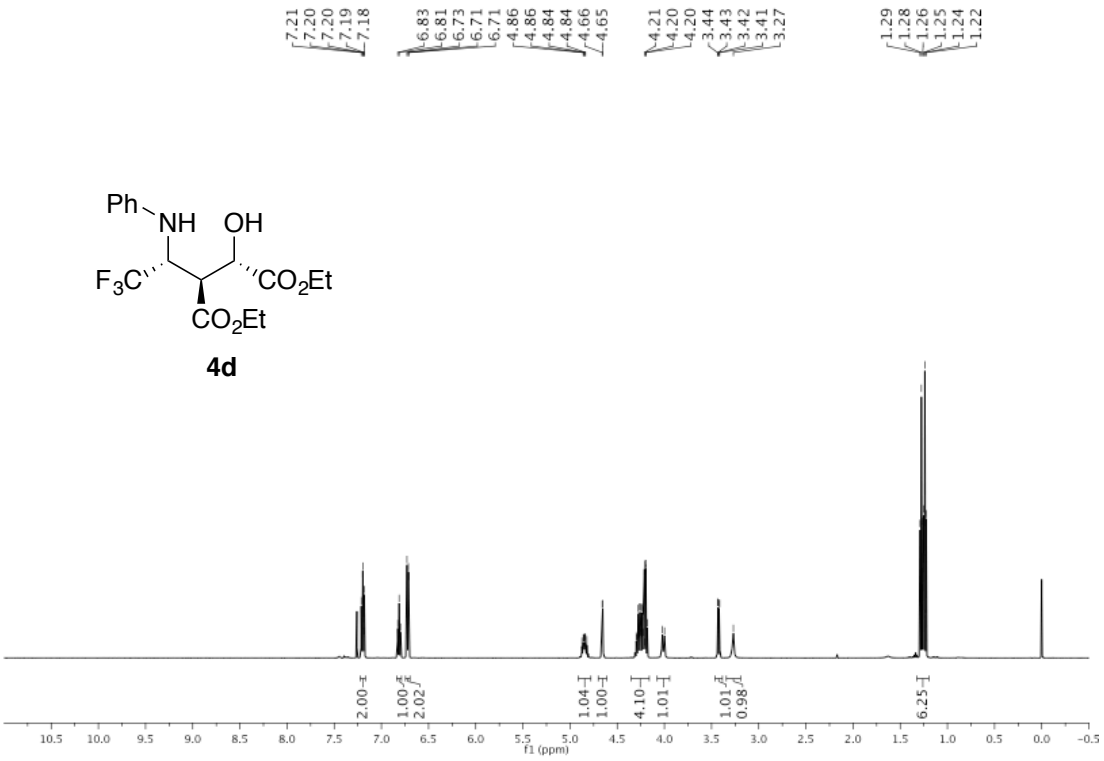
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Dimethyl 2-hydroxy-3-(2,2,2-trifluoro-1-(phenylamino)ethyl)succinate (4c)



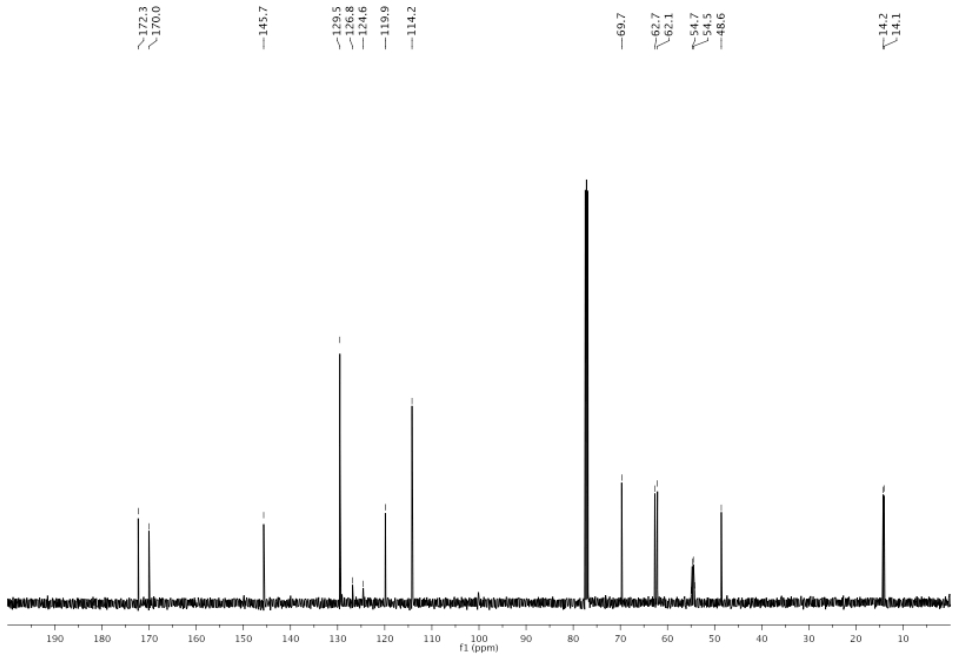
^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Dimethyl 2-hydroxy-3-(2,2,2-trifluoro-1-(phenylamino)ethyl)succinate (4c)



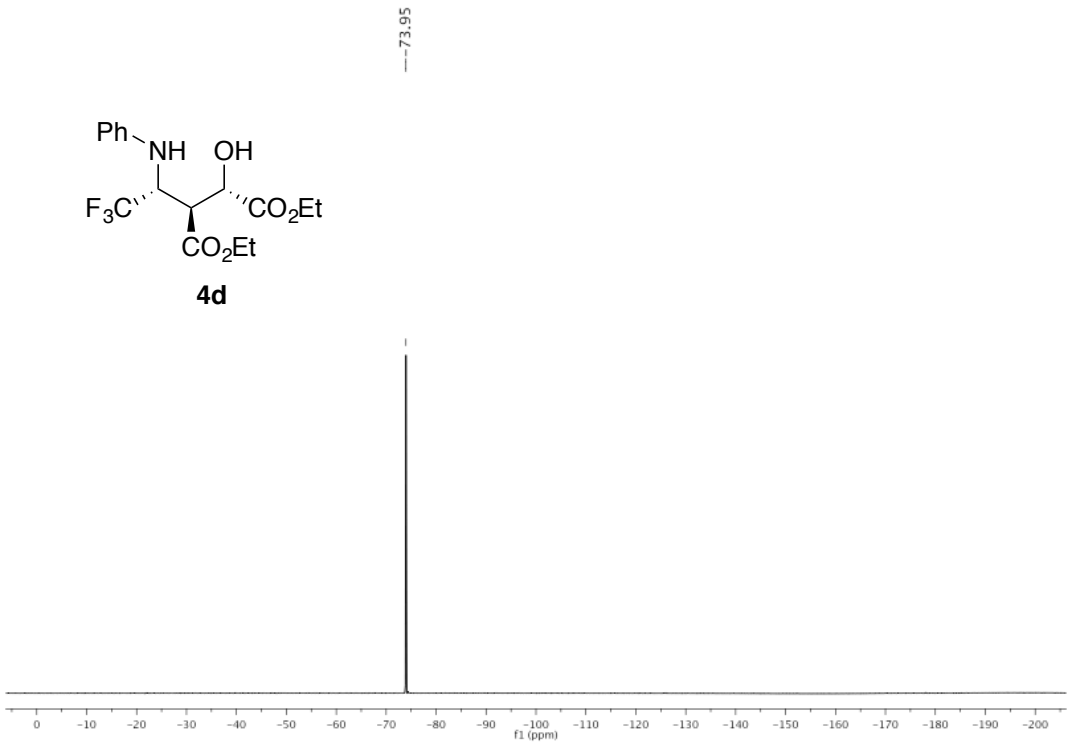
^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Dimethyl 2-hydroxy-3-(2,2,2-trifluoro-1-(phenylamino)ethyl)succinate (4c)



^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Diethyl 2-hydroxy-3-(2,2,2-trifluoro-1-(phenylamino)ethyl)succinate (4d)

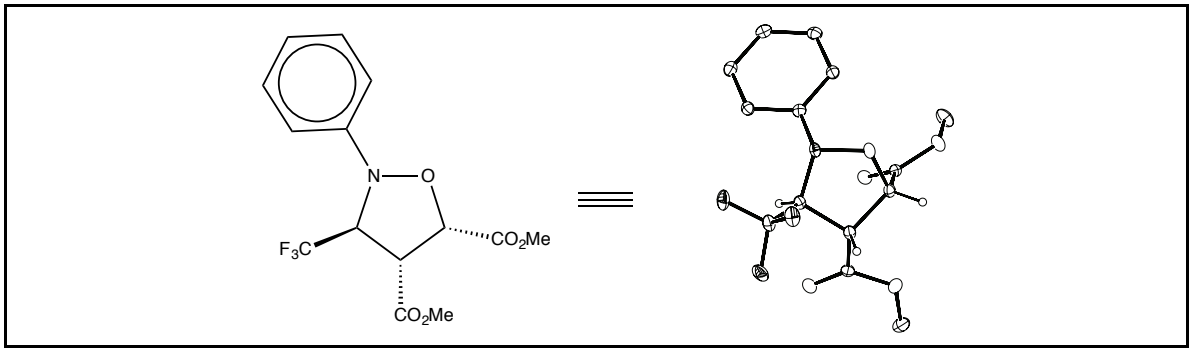


^{13}C NMR (128.5 MHz, $CDCl_3$) Spectrum of Diethyl-2 hydroxy-3-(2,2,2-trifluoro-1-(phenylamino)ethyl)succinate (4d)



^{19}F NMR (470.8 MHz, $CDCl_3$) Spectrum of Diethyl 2-hydroxy-3-(2,2,2-trifluoro-1-(phenylamino)ethyl)succinate (4d)

X-ray Structure Determination of Compound 9202 – Dimethyl 2-Phenyl-3-(trifluoromethyl)isoxazolidine-4,5-dicarboxylate (3a).



Compound 9202, $C_{14}H_{14}NO_5F_3$, crystallizes in the monoclinic space group $P2_1/c$ (systematic absences 0k0: k=odd and h0l: l=odd) with a=9.0022(5)Å, b=12.1545(7)Å, c=13.6525(8)Å, b=101.948(2)°, V=1461.46(14)Å^3, Z=4, and d_{calc}=1.515 g/cm^3 . X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Ka radiation (l=0.71073 Å) at a temperature of 100(1)K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. A total of 4407 frames were collected with a crystal to detector distance of 37.6 mm, rotation widths of 0.5° and exposures of 1seconds:

scan type	2q	w	f	c	frames
f	-13.00	-15.40	-16.81	-39.24	704
w	-5.50	0.24	18.26	-42.87	191
w	-15.50	-117.02	18.69	41.79	212
f	-3.00	-3.88	-4.68	-31.86	344
f	-23.00	315.83	-257.25	28.88	442
f	-15.50	258.48	-341.11	19.46	704
f	-23.00	-25.79	-321.05	73.66	739
w	-10.50	-47.52	-87.93	99.72	68
f	12.00	23.21	-227.82	-99.82	264
f	-23.00	316.70	-281.19	98.89	739

Rotation frames were integrated using SAINT[i], producing a listing of unaveraged F^2 and $s(F^2)$ values which were then passed to the SHELXTL[ii] program package for further processing and structure solution. A total of 55106 reflections were measured over the ranges 2.27 £ q £ 25.45°, -10 £ h £ 10, -14 £ k £ 14, -16 £ l £ 16 yielding 2690 unique reflections (Rint = 0.0243). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS[iii] (minimum and maximum transmission 0.7032, 0.7452).

The structure was solved by direct methods (SHELXS-97[iv]). Refinement was by full-matrix least squares based on F^2 using SHELXL-97.[v] All reflections were used during refinement. The weighting scheme used was $w=1/[s^2(F_o^2)+ (0.0358P)^2 + 0.6070P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0280 and wR2=0.0723 for 2562 observed reflections for which F > 4s(F) and R1=0.0291 and wR2=0.0736 and GOF =1.059 for all 2690 unique, non-zero reflections and 211 variables.[vi] The maximum D/s in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.298 and -0.258 e/$Å^3$.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2. and 3. Anisotropic thermal parameters are in Table 4. Tables 5. and 6. list bond distances and bond angles. Figure 1. is an ORTEP[vii] representation of the molecule with 30% probability thermal ellipsoids displayed.

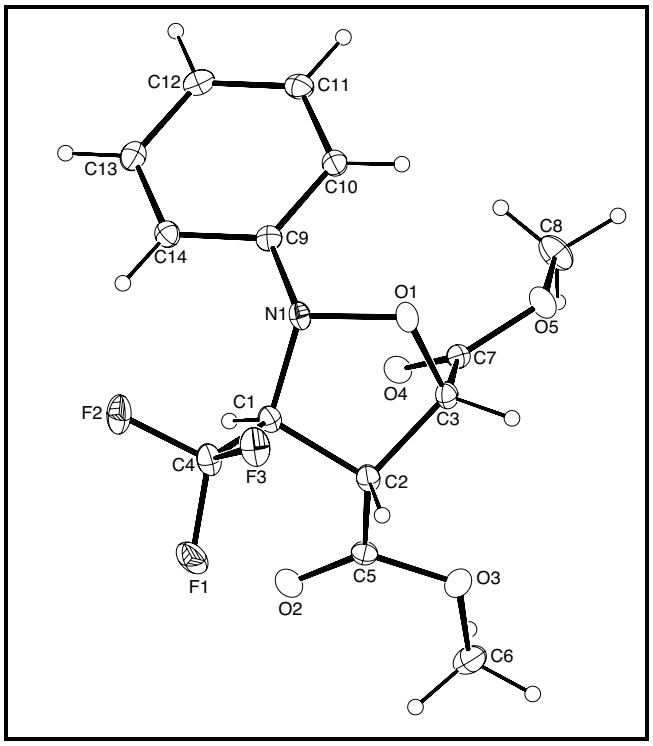


Figure 1. ORTEP drawing of the title compound with 30% probability thermal ellipsoids.

Table 1. Summary of Structure Determination of Compound 9202

Empirical formula	$C_{14}H_{14}NO_5F_3$
Formula weight	333.26
Temperature	100(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Cell constants:	
a	9.0022(5) Å
b	12.1545(7) Å
c	13.6525(8) Å
b	101.948(2)°
Volume	1461.46(14) $Å^3$
Z	4
Density (calculated)	1.515 Mg/m^3
Absorption coefficient	0.139 mm^{-1}
F(000)	688
Crystal size	0.32 x 0.22 x 0.12 mm^3
Theta range for data collection	2.27 to 25.45°
Index ranges	-10 £ h £ 10, -14 £ k £ 14, -16 £ l £ 16
Reflections collected	55106
Independent reflections	2690 [R(int) = 0.0243]

Completeness to theta = 25.45°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.7032
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2690 / 0 / 211
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0280, wR2 = 0.0723
R indices (all data)	R1 = 0.0291, wR2 = 0.0736
Largest diff. peak and hole	0.298 and -0.258 e.$Å^{-3}$

Table 2. Refined Positional Parameters for Compound 9202

Atom	x	y	z	U_{eq}, Å^2
C1	0.42777(12)	0.24107(9)	0.35892(8)	0.0187(2)
C2	0.41847(12)	0.12693(10)	0.30901(8)	0.0199(2)
C3	0.39625(12)	0.15537(9)	0.19787(8)	0.0196(2)
C4	0.56198(14)	0.24945(10)	0.44646(9)	0.0245(3)
C5	0.30067(13)	0.05129(9)	0.33763(8)	0.0209(2)
C6	0.17579(15)	-0.11942(10)	0.29327(10)	0.0305(3)
C7	0.22980(13)	0.17256(9)	0.14750(8)	0.0188(2)
C8	0.06188(14)	0.19830(13)	-0.00782(9)	0.0327(3)
C9	0.33462(12)	0.40246(9)	0.25200(8)	0.0184(2)
C10	0.28019(13)	0.42909(9)	0.15151(8)	0.0201(2)
C11	0.17524(13)	0.51366(10)	0.12695(9)	0.0227(2)
C12	0.12667(13)	0.57376(10)	0.20078(9)	0.0242(3)
C13	0.18443(13)	0.54886(10)	0.30062(9)	0.0238(3)
C14	0.28774(13)	0.46362(9)	0.32689(8)	0.0206(2)
N1	0.44751(10)	0.32032(8)	0.28160(7)	0.0193(2)
O1	0.47756(9)	0.25734(7)	0.19859(6)	0.02107(19)
O2	0.24128(10)	0.06419(7)	0.40798(6)	0.0260(2)
O3	0.27881(10)	-0.03396(7)	0.27450(6)	0.0267(2)
O4	0.12952(9)	0.18908(7)	0.19172(6)	0.02183(19)
O5	0.21283(9)	0.17093(7)	0.04778(6)	0.0254(2)
F1	0.55856(8)	0.16824(7)	0.51219(5)	0.03318(19)
F2	0.56179(8)	0.34507(7)	0.49581(5)	0.03251(19)
F3	0.69581(8)	0.24337(6)	0.41845(5)	0.03083(19)

$U_{eq}=^{1}/_{3}[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos g+2U_{13}aa^*cc^*\cos b+2U_{23}bb^*cc^*\cos a]$

Table 3. Positional Parameters for Hydrogens in Compound 9202

Atom	x	y	z	U_{iso}, Å^2
H1	0.3334	0.2566	0.3814	0.025
H2	0.5179	0.0915	0.3295	0.026
H3	0.4418	0.0985	0.1626	0.026
H6a	0.1874	-0.1299	0.3641	0.046
H6b	0.1987	-0.1869	0.2629	0.046
H6c	0.0732	-0.0980	0.2652	0.046
H8a	-0.0100	0.1465	0.0081	0.049
H8b	0.0604	0.1955	-0.0783	0.049
H8c	0.0354	0.2711	0.0099	0.049
H10	0.3139	0.3906	0.1014	0.027
H11	0.1370	0.5302	0.0600	0.030
H12	0.0562	0.6301	0.1836	0.032
H13	0.1536	0.5897	0.3505	0.032
H14	0.3255	0.4473	0.3940	0.027

Table 4. Refined Thermal Parameters (U's) for Compound 9202

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0165(5)	0.0232(6)	0.0163(5)	-0.0007(4)	0.0032(4)	0.0030(4)
C2	0.0180(5)	0.0241(6)	0.0166(5)	-0.0012(4)	0.0012(4)	0.0063(4)
C3	0.0194(5)	0.0224(6)	0.0172(5)	-0.0022(4)	0.0042(4)	0.0035(4)
C4	0.0214(6)	0.0322(6)	0.0190(6)	-0.0040(5)	0.0025(5)	0.0045(5)
C5	0.0221(6)	0.0207(6)	0.0174(5)	0.0028(4)	-0.0019(4)	0.0065(4)
C6	0.0312(7)	0.0210(6)	0.0354(7)	0.0000(5)	-0.0020(5)	0.0001(5)
C7	0.0213(6)	0.0174(5)	0.0171(5)	-0.0002(4)	0.0024(4)	0.0001(4)
C8	0.0233(6)	0.0510(8)	0.0204(6)	0.0045(6)	-0.0036(5)	0.0019(6)
C9	0.0149(5)	0.0188(5)	0.0215(6)	-0.0007(4)	0.0037(4)	-0.0045(4)
C10	0.0206(5)	0.0203(5)	0.0198(6)	-0.0014(4)	0.0047(4)	-0.0047(4)
C11	0.0230(6)	0.0214(6)	0.0223(6)	0.0025(5)	0.0011(5)	-0.0050(5)
C12	0.0220(6)	0.0187(6)	0.0312(6)	0.0020(5)	0.0037(5)	-0.0002(4)
C13	0.0242(6)	0.0213(6)	0.0270(6)	-0.0041(5)	0.0076(5)	-0.0020(5)
C14	0.0206(5)	0.0220(6)	0.0192(5)	-0.0013(4)	0.0038(4)	-0.0034(4)
N1	0.0183(5)	0.0246(5)	0.0158(5)	-0.0032(4)	0.0053(4)	0.0011(4)
O1	0.0193(4)	0.0277(4)	0.0177(4)	-0.0038(3)	0.0072(3)	0.0008(3)
O2	0.0301(5)	0.0291(5)	0.0189(4)	0.0012(3)	0.0048(3)	-0.0012(4)
O3	0.0309(5)	0.0210(4)	0.0269(5)	-0.0030(3)	0.0031(4)	0.0028(3)
O4	0.0191(4)	0.0256(4)	0.0212(4)	0.0018(3)	0.0049(3)	0.0011(3)
O5	0.0221(4)	0.0369(5)	0.0157(4)	-0.0002(3)	0.0002(3)	0.0034(3)
F1	0.0345(4)	0.0436(5)	0.0184(4)	0.0048(3)	-0.0018(3)	0.0070(3)
F2	0.0291(4)	0.0396(4)	0.0255(4)	-0.0143(3)	-0.0018(3)	0.0037(3)
F3	0.0166(4)	0.0455(5)	0.0282(4)	-0.0074(3)	-0.0002(3)	0.0047(3)

The form of the anisotropic displacement parameter is:

$\exp[-2p^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$

Table 5. Bond Distances in Compound 9202, Å

C1-N1	1.4668(15)	C1-C4	1.5167(16)	C1-C2	1.5403(15)
C2-C5	1.5146(16)	C2-C3	1.5284(15)	C3-O1	1.4384(14)
C3-C7	1.5281(15)	C4-F1	1.3387(15)	C4-F3	1.3394(14)
C4-F2	1.3436(14)	C5-O2	1.2022(14)	C5-O3	1.3361(14)
C6-O3	1.4501(15)	C7-O4	1.2023(14)	C7-O5	1.3383(14)
C8-O5	1.4514(14)	C9-C10	1.3960(16)	C9-C14	1.3981(16)
C9-N1	1.4222(15)	C10-C11	1.3894(17)	C11-C12	1.3869(17)
C12-C13	1.3879(17)	C13-C14	1.3888(17)	N1-O1	1.4389(12)

Table 6. Bond Angles in Compound 9202, °

N1-C1-C4	109.12(9)	N1-C1-C2	106.06(9)	C4-C1-C2	111.75(9)
C5-C2-C3	116.02(9)	C5-C2-C1	114.17(9)	C3-C2-C1	102.67(9)
O1-C3-C7	109.60(9)	O1-C3-C2	103.08(9)	C7-C3-C2	113.10(9)
F1-C4-F3	107.31(10)	F1-C4-F2	107.40(9)	F3-C4-F2	106.59(10)
F1-C4-C1	110.71(10)	F3-C4-C1	112.84(10)	F2-C4-C1	111.70(9)
O2-C5-O3	125.87(11)	O2-C5-C2	125.30(11)	O3-C5-C2	108.77(9)
O4-C7-O5	125.02(10)	O4-C7-C3	124.41(10)	O5-C7-C3	110.52(9)
C10-C9-C14	119.85(11)	C10-C9-N1	121.79(10)	C14-C9-N1	118.13(10)
C11-C10-C9	119.44(11)	C12-C11-C10	121.02(11)	C11-C12-C13	119.24(11)

C12-C13-C14	120.73(11)	C13-C14-C9	119.68(11)	C9-N1-O1	112.92(8)
C9-N1-C1	118.66(9)	O1-N1-C1	106.74(8)	C3-O1-N1	106.58(8)
C5-O3-C6	117.11(10)	C7-O5-C8	115.21(9)		

[i]Bruker (2009) SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.

[ii]Bruker (2009) SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.

[iii]Sheldrick, G.M. (2007) SADABS. University of Gottingen, Germany.

[iv]Sheldrick, G.M. (2008) Acta Cryst. A64,112-122.

[v]Sheldrick, G.M. (2008) Acta Cryst. A64,112-122.

[vi]$R1 = \Sigma||F_o| - |F_c|| / \Sigma |F_o|$

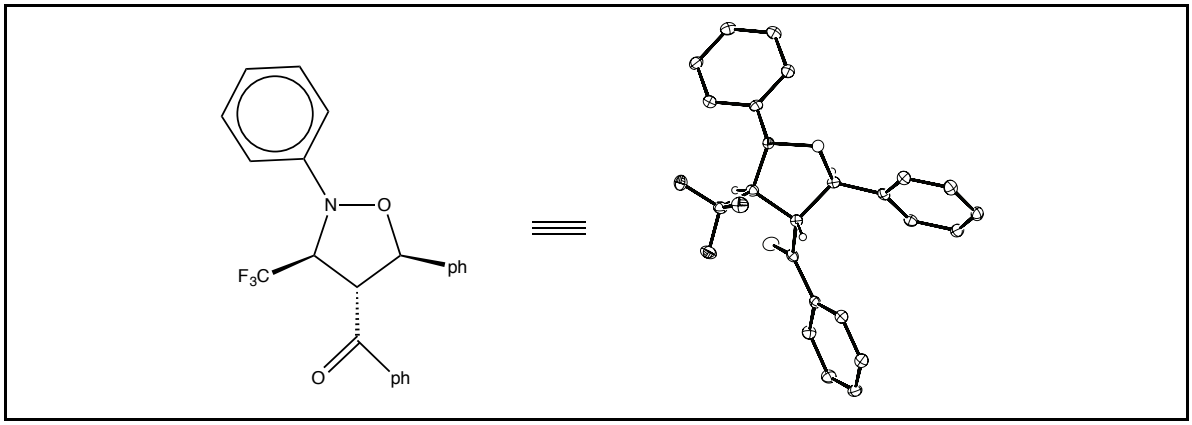
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$

$GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{½}$

where n = the number of reflections and p = the number of parameters refined.

[vii]"ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations". C.K. Johnson (1976) ORNL-5138.

X-ray Structure Determination of Compound 9203 - (2,5-Diphenyl-3-(trifluoromethyl)isoxazolidin-4-yl)(phenyl)methanone (3h)



Compound 9203, $C_{23}H_{18}NO_2F_3$, crystallizes in the monoclinic space group $P2_1/c$ (systematic absences 0k0: k=odd and h0l: l=odd) with a=20.4457(8)Å, b=19.4232(8)Å, c=9.4746(4)Å, b=90.583(2)°, V=3762.4(3)Å^3, Z=8, and d_{calc}=1.403 g/cm^3 . X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Ka radiation (l=0.71073 Å) at a temperature of 100(1)K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. A total of 2123 frames were collected with a crystal to detector distance of 37.628 mm, rotation widths of 0.5° and exposures of 30 seconds:

scan type	2q	w	f	c	frames
f	19.50	59.55	348.71	-26.26	739
w	-15.50	242.98	18.69	41.79	212
f	-13.00	335.42	287.46	64.29	138
w	-5.50	323.80	133.99	70.63	65
w	-3.00	1.94	217.86	-28.13	139
f	-15.50	349.33	342.90	-77.44	415
f	-10.50	300.13	140.28	39.97	415

Rotation frames were integrated using SAINT[vii], producing a listing of unaveraged F^2 and $s(F^2)$ values which were then passed to the SHELXTL[vii] program package for further processing and structure solution. A total of 69598 reflections were measured over the ranges 1.99 £ q £ 25.42°, -24 £ h £ 24, -23 £ k £ 23, -11 £ l £ 11 yielding 6930 unique reflections (Rint = 0.0547). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS [vii] (minimum and maximum transmission 0.6385, 0.7452).

The structure was solved by direct methods (SHELXS-97[vii]). Refinement was by full-matrix least squares based on F^2 using SHELXL-97.[vii] All reflections were used during refinement. The weighting scheme used was $w=1/[s^2(F_o^2)+ (0.0554P)^2 + 1.9351P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0447 and wR2=0.1044 for 5414 observed reflections for which F > 4s(F) and R1=0.0636 and wR2=0.1137 and GOF =1.057 for all 6930 unique, non-zero reflections and 524 variables.[vii] The maximum D/s in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were +0.324 and -0.232 e/$Å^3$.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2. and 3. Anisotropic thermal parameters are in Table 4. Tables 5. and 6. list bond distances and bond angles. Figures 1. and 2. are ORTEP[vii] representations of the molecule with 30% probability thermal ellipsoids displayed.

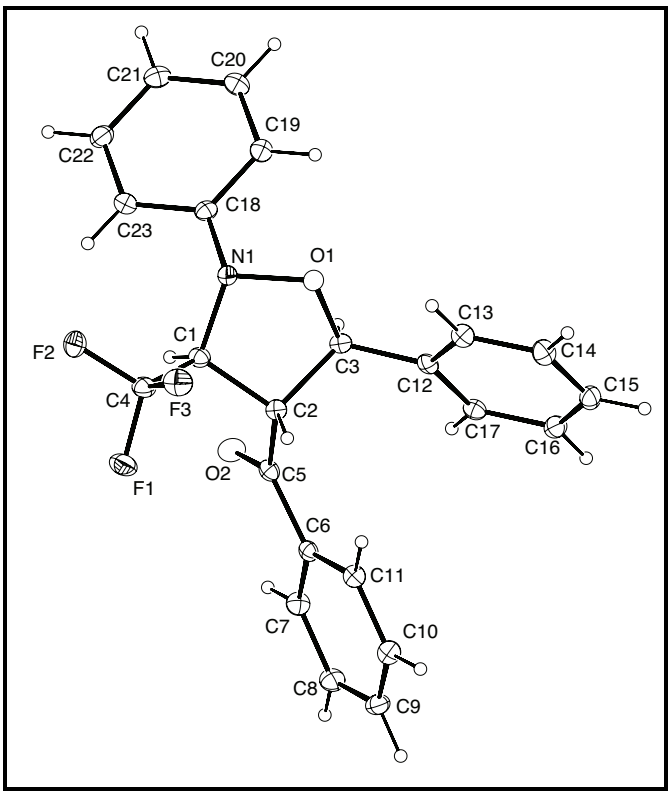


Figure 1. ORTEP drawing of molecule no. 1 of the asymmetric unit with 30% probability thermal ellipsoids.

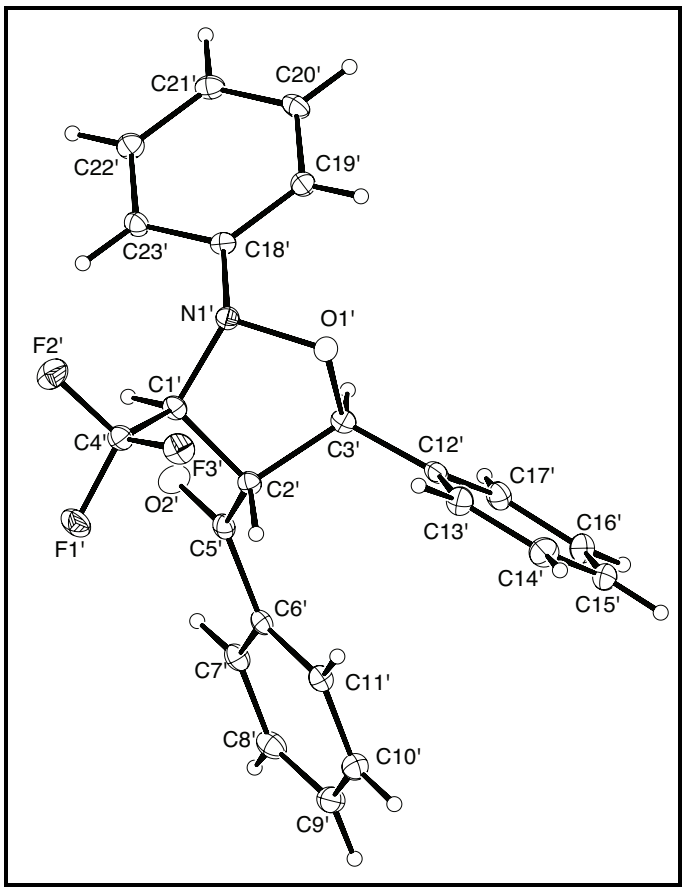


Figure 2. ORTEP drawing of molecule no. 2 of the asymmetric unit with 30% probability thermal ellipsoids.

Table 1. Summary of Structure Determination of Compound 9203

Empirical formula	$C_{23}H_{18}NO_2F_3$
Formula weight	397.38
Temperature	100(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$

Cell constants:

a	20.4457(8) Å
b	19.4232(8) Å
c	9.4746(4) Å
b	90.583(2)°
Volume	3762.4(3) $Å^3$
Z	8
Density (calculated)	1.403 Mg/m^3
Absorption coefficient	0.109 mm^{-1}
F(000)	1648
Crystal size	0.48 x 0.04 x 0.02 mm^3
Theta range for data collection	1.99 to 25.42°
Index ranges	-24 £ h £ 24, -23 £ k £ 23, -11 £ l £ 11
Reflections collected	69598
Independent reflections	6930 [R(int) = 0.0547]
Completeness to theta = 25.42°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6385
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6930 / 0 / 524
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.1044

R indices (all data)	R1 = 0.0636, wR2 = 0.1137
Largest diff. peak and hole	0.324 and -0.232 e.Å^{-3}

Table 2. Refined Positional Parameters for Compound 9203

Atom	x	y	z	U_{eq}, Å^2
C1	0.09823(9)	0.35577(10)	0.5843(2)	0.0206(4)
C2	0.16697(9)	0.38260(10)	0.6214(2)	0.0190(4)
C3	0.16727(9)	0.45019(10)	0.5353(2)	0.0192(4)
C4	0.06485(10)	0.32490(11)	0.7111(2)	0.0262(5)
C5	0.22017(9)	0.33173(10)	0.5771(2)	0.0197(4)
C6	0.28137(9)	0.32510(10)	0.6612(2)	0.0186(4)
C7	0.32704(10)	0.27671(10)	0.6163(2)	0.0244(4)
C8	0.38490(10)	0.26730(11)	0.6899(2)	0.0272(5)
C9	0.39807(10)	0.30642(11)	0.8090(2)	0.0256(5)
C10	0.35350(10)	0.35493(11)	0.8538(2)	0.0242(4)
C11	0.29505(9)	0.36423(10)	0.7815(2)	0.0216(4)
C12	0.21393(9)	0.50579(10)	0.58353(19)	0.0192(4)
C13	0.19152(10)	0.56201(10)	0.6604(2)	0.0231(4)
C14	0.23464(10)	0.61406(11)	0.6990(2)	0.0271(5)
C15	0.29982(10)	0.61040(11)	0.6637(2)	0.0269(5)
C16	0.32265(10)	0.55414(11)	0.5889(2)	0.0253(5)
C17	0.27967(9)	0.50234(10)	0.5482(2)	0.0220(4)
C18	0.03297(9)	0.41343(10)	0.3951(2)	0.0203(4)
C19	0.03372(9)	0.47080(10)	0.3090(2)	0.0227(4)

C20	0.00086(10)	0.46977(11)	0.1803(2)	0.0257(5)
C21	-0.03312(10)	0.41209(11)	0.1368(2)	0.0258(5)
C22	-0.03429(10)	0.35478(11)	0.2229(2)	0.0276(5)
C23	-0.00156(10)	0.35499(11)	0.3523(2)	0.0262(5)
N1	0.06073(7)	0.41531(8)	0.53361(17)	0.0200(4)
O1	0.10162(6)	0.47421(7)	0.55378(14)	0.0210(3)
O2	0.21118(7)	0.29787(7)	0.47016(15)	0.0277(3)
F1	0.10101(6)	0.27437(6)	0.76820(14)	0.0360(3)
F2	0.00642(6)	0.29813(6)	0.67679(14)	0.0346(3)
F3	0.05399(6)	0.37108(7)	0.81363(12)	0.0327(3)
C1'	0.42121(9)	0.58103(10)	0.11061(19)	0.0182(4)
C2'	0.34732(9)	0.56729(10)	0.11170(19)	0.0177(4)
C3'	0.32319(9)	0.62492(10)	0.2123(2)	0.0184(4)
C4'	0.44730(9)	0.59041(10)	-0.0371(2)	0.0216(4)
C5'	0.33171(9)	0.49559(10)	0.16855(19)	0.0195(4)
C6'	0.26896(9)	0.46120(10)	0.13155(19)	0.0191(4)
C7'	0.25716(10)	0.39633(10)	0.1887(2)	0.0226(4)
C8'	0.19949(10)	0.36230(11)	0.1604(2)	0.0264(5)
C9'	0.15246(10)	0.39227(11)	0.0742(2)	0.0279(5)
C10'	0.16378(10)	0.45643(11)	0.0147(2)	0.0261(5)
C11'	0.22172(9)	0.49108(10)	0.0429(2)	0.0220(4)
C12'	0.25579(9)	0.65190(10)	0.1844(2)	0.0197(4)
C13'	0.24232(10)	0.69369(11)	0.0681(2)	0.0246(4)
C14'	0.17906(10)	0.71538(11)	0.0410(2)	0.0292(5)
C15'	0.12846(10)	0.69485(11)	0.1278(2)	0.0287(5)
C16'	0.14158(10)	0.65374(11)	0.2437(2)	0.0275(5)

C17'	0.20494(10)	0.63290(11)	0.2723(2)	0.0240(4)
C18'	0.45783(9)	0.63760(10)	0.33278(19)	0.0176(4)
C19'	0.43887(9)	0.68433(10)	0.4359(2)	0.0199(4)
C20'	0.46755(10)	0.68158(10)	0.5694(2)	0.0229(4)
C21'	0.51501(10)	0.63305(10)	0.6006(2)	0.0228(4)
C22'	0.53407(10)	0.58705(10)	0.4972(2)	0.0232(4)
C23'	0.50577(9)	0.58917(10)	0.3633(2)	0.0206(4)
N1'	0.43289(7)	0.64475(8)	0.19059(16)	0.0180(3)
O1'	0.37042(6)	0.67893(7)	0.18888(13)	0.0193(3)
O2'	0.37092(7)	0.46810(7)	0.24846(15)	0.0275(3)
F1'	0.43404(6)	0.53434(6)	-0.11603(12)	0.0297(3)
F2'	0.51206(5)	0.59884(7)	-0.03684(12)	0.0316(3)
F3'	0.42100(6)	0.64444(6)	-0.10427(11)	0.0275(3)

$U_{eq}=1/3[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos g+2U_{13}aa^*cc^*\cos b+2U_{23}bb^*cc^*\cos a]$

Table 3. Positional Parameters for Hydrogens in Compound 9203

Atom	x	y	z	U_{iso}, Å^2
H1	0.1011	0.3213	0.5092	0.027
H2	0.1705	0.3925	0.7226	0.025
H3	0.1746	0.4399	0.4355	0.026
H7	0.3184	0.2505	0.5360	0.032
H8	0.4150	0.2347	0.6596	0.036
H9	0.4370	0.3000	0.8590	0.034
H10	0.3628	0.3815	0.9330	0.032

H11	0.2649	0.3965	0.8130	0.029
H13	0.1478	0.5647	0.6858	0.031
H14	0.2194	0.6518	0.7492	0.036
H15	0.3283	0.6455	0.6900	0.036
H16	0.3667	0.5511	0.5660	0.034
H17	0.2950	0.4650	0.4968	0.029
H19	0.0563	0.5101	0.3373	0.030
H20	0.0017	0.5085	0.1226	0.034
H21	-0.0550	0.4118	0.0503	0.034
H22	-0.0571	0.3157	0.1942	0.037
H23	-0.0027	0.3163	0.4101	0.035
H1'	0.4442	0.5428	0.1569	0.024
H2'	0.3285	0.5734	0.0170	0.024
H3'	0.3266	0.6090	0.3102	0.024
H7'	0.2886	0.3758	0.2466	0.030
H8'	0.1921	0.3191	0.1993	0.035
H9'	0.1133	0.3694	0.0561	0.037
H10'	0.1324	0.4762	-0.0442	0.035
H11'	0.2292	0.5341	0.0029	0.029
H13'	0.2760	0.7070	0.0086	0.033
H14'	0.1704	0.7439	-0.0359	0.039
H15'	0.0858	0.7087	0.1081	0.038
H16'	0.1078	0.6401	0.3024	0.037
H17'	0.2136	0.6059	0.3513	0.032
H19'	0.4071	0.7173	0.4155	0.026
H20'	0.4547	0.7127	0.6384	0.030

H21'	0.5340	0.6313	0.6902	0.030
H22'	0.5661	0.5544	0.5176	0.031
H23'	0.5189	0.5582	0.2943	0.027

Table 4. Refined Thermal Parameters (U's) for Compound 9203

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0196(10)	0.0208(10)	0.0216(10)	0.0012(8)	0.0015(8)	0.0025(8)
C2	0.0191(10)	0.0207(10)	0.0171(10)	-0.0001(8)	0.0017(8)	0.0007(8)
C3	0.0181(9)	0.0231(10)	0.0165(10)	0.0007(8)	0.0013(8)	0.0021(8)
C4	0.0193(10)	0.0263(11)	0.0330(12)	0.0066(9)	0.0017(9)	0.0038(9)
C5	0.0224(10)	0.0186(10)	0.0182(10)	0.0022(8)	0.0041(8)	0.0001(8)
C6	0.0190(10)	0.0187(10)	0.0182(10)	0.0033(8)	0.0044(8)	-0.0012(8)
C7	0.0255(11)	0.0237(11)	0.0241(11)	-0.0024(9)	0.0016(8)	0.0022(8)
C8	0.0213(10)	0.0267(12)	0.0338(12)	0.0001(9)	0.0043(9)	0.0061(9)
C9	0.0193(10)	0.0329(12)	0.0247(11)	0.0066(9)	-0.0007(8)	0.0008(9)
C10	0.0247(10)	0.0287(11)	0.0192(10)	-0.0003(9)	0.0025(8)	-0.0015(9)
C11	0.0216(10)	0.0227(11)	0.0206(10)	-0.0004(8)	0.0039(8)	0.0012(8)
C12	0.0248(10)	0.0202(10)	0.0126(9)	0.0039(8)	0.0009(8)	-0.0006(8)
C13	0.0246(10)	0.0256(11)	0.0192(10)	0.0003(8)	0.0041(8)	0.0002(9)
C14	0.0349(12)	0.0245(11)	0.0220(11)	-0.0036(9)	0.0001(9)	-0.0020(9)
C15	0.0314(12)	0.0265(11)	0.0228(11)	0.0024(9)	-0.0053(9)	-0.0075(9)
C16	0.0218(10)	0.0309(12)	0.0230(11)	0.0052(9)	0.0003(8)	-0.0026(9)
C17	0.0246(10)	0.0221(11)	0.0192(10)	0.0030(8)	0.0014(8)	0.0022(8)

C18	0.0165(9)	0.0221(11)	0.0223(10)	-0.0024(8)	0.0011(8)	0.0043(8)
C19	0.0228(10)	0.0215(11)	0.0240(11)	-0.0031(8)	0.0020(8)	0.0018(8)
C20	0.0305(11)	0.0244(11)	0.0223(11)	0.0024(9)	0.0022(9)	0.0038(9)
C21	0.0244(11)	0.0300(12)	0.0230(11)	-0.0042(9)	-0.0011(8)	0.0063(9)
C22	0.0230(11)	0.0251(11)	0.0347(12)	-0.0041(9)	-0.0066(9)	0.0014(9)
C23	0.0261(11)	0.0220(11)	0.0305(12)	0.0038(9)	-0.0032(9)	0.0012(9)
N1	0.0186(8)	0.0178(9)	0.0237(9)	0.0005(7)	-0.0015(7)	-0.0006(7)
O1	0.0188(7)	0.0184(7)	0.0258(7)	-0.0013(6)	-0.0008(6)	0.0007(5)
O2	0.0303(8)	0.0303(8)	0.0225(8)	-0.0073(6)	-0.0022(6)	0.0060(6)
F1	0.0271(7)	0.0363(7)	0.0446(8)	0.0202(6)	0.0042(6)	0.0047(5)
F2	0.0219(6)	0.0355(7)	0.0464(8)	0.0112(6)	0.0036(5)	-0.0062(5)
F3	0.0329(7)	0.0413(8)	0.0239(6)	0.0030(6)	0.0081(5)	0.0032(6)
C1'	0.0221(10)	0.0197(10)	0.0129(9)	0.0007(7)	0.0008(7)	0.0007(8)
C2'	0.0204(10)	0.0193(10)	0.0135(9)	0.0002(8)	-0.0004(7)	0.0013(8)
C3'	0.0217(10)	0.0189(10)	0.0146(9)	0.0014(8)	0.0006(8)	-0.0007(8)
C4'	0.0224(10)	0.0254(11)	0.0171(10)	-0.0012(8)	0.0010(8)	-0.0004(8)
C5'	0.0221(10)	0.0221(10)	0.0142(9)	-0.0019(8)	0.0021(8)	0.0035(8)
C6'	0.0215(10)	0.0204(10)	0.0153(9)	-0.0035(8)	0.0039(8)	0.0016(8)
C7'	0.0278(11)	0.0239(11)	0.0161(10)	-0.0022(8)	0.0034(8)	0.0017(9)
C8'	0.0335(12)	0.0241(11)	0.0216(11)	-0.0028(9)	0.0058(9)	-0.0050(9)
C9'	0.0241(11)	0.0324(12)	0.0274(11)	-0.0076(9)	0.0049(9)	-0.0054(9)
C10'	0.0236(10)	0.0301(12)	0.0246(11)	-0.0033(9)	-0.0012(8)	0.0023(9)
C11'	0.0240(10)	0.0213(11)	0.0208(10)	-0.0017(8)	0.0016(8)	0.0015(8)
C12'	0.0238(10)	0.0185(10)	0.0168(10)	-0.0056(8)	-0.0011(8)	0.0014(8)
C13'	0.0257(11)	0.0277(11)	0.0206(10)	0.0021(9)	0.0016(8)	0.0019(9)
C14'	0.0329(12)	0.0295(12)	0.0251(11)	0.0022(9)	-0.0065(9)	0.0061(9)

C15'	0.0241(11)	0.0304(12)	0.0314(12)	-0.0081(10)	-0.0057(9)	0.0080(9)
C16'	0.0229(11)	0.0313(12)	0.0284(11)	-0.0044(9)	0.0044(9)	0.0023(9)
C17'	0.0272(11)	0.0253(11)	0.0197(10)	-0.0013(8)	0.0026(8)	0.0035(9)
C18'	0.0184(9)	0.0206(10)	0.0137(9)	0.0015(8)	0.0012(7)	-0.0041(8)
C19'	0.0192(10)	0.0196(10)	0.0209(10)	-0.0002(8)	0.0018(8)	-0.0015(8)
C20'	0.0284(11)	0.0229(11)	0.0174(10)	-0.0054(8)	0.0045(8)	-0.0047(9)
C21'	0.0250(10)	0.0276(11)	0.0157(10)	0.0010(8)	-0.0016(8)	-0.0043(9)
C22'	0.0250(10)	0.0250(11)	0.0194(10)	0.0015(8)	-0.0024(8)	0.0009(8)
C23'	0.0230(10)	0.0225(11)	0.0164(10)	-0.0023(8)	0.0014(8)	0.0010(8)
N1'	0.0188(8)	0.0210(8)	0.0141(8)	-0.0001(6)	-0.0003(6)	0.0013(6)
O1'	0.0189(7)	0.0186(7)	0.0205(7)	0.0014(5)	-0.0004(5)	0.0013(5)
O2'	0.0268(8)	0.0279(8)	0.0275(8)	0.0074(6)	-0.0058(6)	-0.0009(6)
F1'	0.0368(7)	0.0335(7)	0.0187(6)	-0.0085(5)	0.0036(5)	0.0004(5)
F2'	0.0222(6)	0.0526(8)	0.0203(6)	-0.0002(6)	0.0056(5)	-0.0035(6)
F3'	0.0351(7)	0.0318(7)	0.0158(6)	0.0057(5)	0.0011(5)	0.0005(5)

The form of the anisotropic displacement parameter is:
$\exp[-2p^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$

Table 5. Bond Distances in Compound 9203, Å

C1-N1	1.466(2)	C1-C4	1.512(3)	C1-C2	1.536(3)
C2-C5	1.531(3)	C2-C3	1.546(3)	C3-O1	1.433(2)
C3-C12	1.509(3)	C4-F1	1.340(2)	C4-F2	1.340(2)
C4-F3	1.342(2)	C5-O2	1.220(2)	C5-C6	1.482(3)
C6-C7	1.394(3)	C6-C11	1.396(3)	C7-C8	1.379(3)
C8-C9	1.384(3)	C9-C10	1.380(3)	C10-C11	1.383(3)

C12-C17	1.390(3)	C12-C13	1.393(3)	C13-C14	1.388(3)
C14-C15	1.379(3)	C15-C16	1.386(3)	C16-C17	1.388(3)
C18-C19	1.381(3)	C18-C23	1.395(3)	C18-N1	1.425(3)
C19-C20	1.386(3)	C20-C21	1.379(3)	C21-C22	1.380(3)
C22-C23	1.391(3)	N1-O1	1.429(2)	C1'-N1'	1.469(2)
C1'-C4'	1.514(3)	C1'-C2'	1.534(3)	C2'-C5'	1.528(3)
C2'-C3'	1.554(3)	C3'-O1'	1.445(2)	C3'-C12'	1.495(3)
C4'-F2'	1.334(2)	C4'-F3'	1.337(2)	C4'-F1'	1.347(2)
C5'-O2'	1.220(2)	C5'-C6'	1.485(3)	C6'-C7'	1.393(3)
C6'-C11'	1.400(3)	C7'-C8'	1.376(3)	C8'-C9'	1.384(3)
C9'-C10'	1.388(3)	C10'-C11'	1.386(3)	C12'-C17'	1.389(3)
C12'-C13'	1.394(3)	C13'-C14'	1.382(3)	C14'-C15'	1.387(3)
C15'-C16'	1.381(3)	C16'-C17'	1.381(3)	C18'-C23'	1.387(3)
C18'-C19'	1.391(3)	C18'-N1'	1.442(2)	C19'-C20'	1.390(3)
C20'-C21'	1.383(3)	C21'-C22'	1.384(3)	C22'-C23'	1.390(3)
N1'-O1'	1.4394(19)				

Table 6. Bond Angles in Compound 9203, °

N1-C1-C4	109.54(15)	N1-C1-C2	106.35(15)	C4-C1-C2	111.83(16)
C5-C2-C1	111.66(16)	C5-C2-C3	113.38(15)	C1-C2-C3	100.13(14)
O1-C3-C12	108.67(15)	O1-C3-C2	101.74(14)	C12-C3-C2	117.01(16)
F1-C4-F2	107.50(16)	F1-C4-F3	107.00(17)	F2-C4-F3	106.35(16)
F1-C4-C1	111.08(16)	F2-C4-C1	111.68(17)	F3-C4-C1	112.92(17)
O2-C5-C6	121.26(17)	O2-C5-C2	118.29(17)	C6-C5-C2	120.44(16)

C7-C6-C11	119.14(18)	C7-C6-C5	117.30(17)	C11-C6-C5	123.56(17)
C8-C7-C6	120.56(19)	C7-C8-C9	119.88(19)	C10-C9-C8	120.09(19)
C9-C10-C11	120.45(19)	C10-C11-C6	119.87(18)	C17-C12-C13	119.20(18)
C17-C12-C3	120.17(17)	C13-C12-C3	120.61(17)	C14-C13-C12	119.83(19)
C15-C14-C13	120.8(2)	C14-C15-C16	119.73(19)	C15-C16-C17	119.86(19)
C16-C17-C12	120.62(19)	C19-C18-C23	119.59(18)	C19-C18-N1	121.10(17)
C23-C18-N1	118.95(17)	C18-C19-C20	119.97(19)	C21-C20-C19	120.84(19)
C20-C21-C22	119.36(19)	C21-C22-C23	120.49(19)	C22-C23-C18	119.74(19)
C18-N1-O1	111.77(14)	C18-N1-C1	118.92(15)	O1-N1-C1	106.53(13)
N1-O1-C3	105.69(13)	N1'-C1'-C4'	108.57(15)	N1'-C1'-C2'	107.33(14)
C4'-C1'-C2'	112.54(15)	C5'-C2'-C1'	111.73(15)	C5'-C2'-C3'	111.81(15)
C1'-C2'-C3'	101.40(14)	O1'-C3'-C12'	109.56(15)	O1'-C3'-C2'	102.25(14)
C12'-C3'-C2'	116.24(15)	F2'-C4'-F3'	107.40(15)	F2'-C4'-F1'	107.13(15)
F3'-C4'-F1'	107.03(15)	F2'-C4'-C1'	111.83(15)	F3'-C4'-C1'	112.98(16)
F1'-C4'-C1'	110.18(16)	O2'-C5'-C6'	120.67(18)	O2'-C5'-C2'	118.64(17)
C6'-C5'-C2'	120.65(16)	C7'-C6'-C11'	119.15(18)	C7'-C6'-C5'	117.88(17)
C11'-C6'-C5'	122.97(18)	C8'-C7'-C6'	120.68(19)	C7'-C8'-C9'	120.1(2)
C8'-C9'-C10'	119.97(19)	C11'-C10'-C9'	120.2(2)	C10'-C11'-C6'	119.82(19)
C17'-C12'-C13'	119.07(18)	C17'-C12'-C3'	119.69(18)	C13'-C12'-C3'	121.19(17)
C14'-C13'-C12'	120.09(19)	C13'-C14'-C15'	120.3(2)	C16'-C15'-C14'	119.83(19)
C17'-C16'-C15'	120.0(2)	C16'-C17'-C12'	120.71(19)	C23'-C18'-C19'	119.84(18)
C23'-C18'-N1'	120.15(16)	C19'-C18'-N1'	119.64(17)	C20'-C19'-C18'	119.74(18)
C21'-C20'-C19'	120.63(18)	C20'-C21'-C22'	119.38(18)	C21'-C22'-C23'	120.61(19)

C18'-C23'-C22'	119.80(18)	O1'-N1'-C18'	111.11(13)	O1'-N1'-C1'	104.07(13)
C18'-N1'-C1'	117.04(15)	N1'-O1'-C3'	104.94(13)		

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Having living in the United States for five years, Livia enjoined learning a new culture and has become passionate about travel and meet new people from all over the world. Upon graduation she will return to her country and post-doc for Dr. Luiz Silva at University of Sao Paulo, where she wishes to return the knowledge obtained in an effort to help improve the education in her country.