

Electronic Supplementary Information

Cu-catalysed carboxylation of aryl boronic acids with CO₂

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1. General Information

1.1 Materials

All required fine chemicals were purchased from available commercial sources in China and used directly without purification. All the reactions were carried out under nitrogen atmosphere using standard Schlenk tubes (See Figure S1). Dry solvents (99.7%) were purchased and stored in glove box under N₂ atmosphere and were transferred into the Schlenk tubes under N₂.

1.2 Reaction apparatus

Schlenk Tube, magnetic stirring beads, silicon oil bath, reaction hot plate etc.

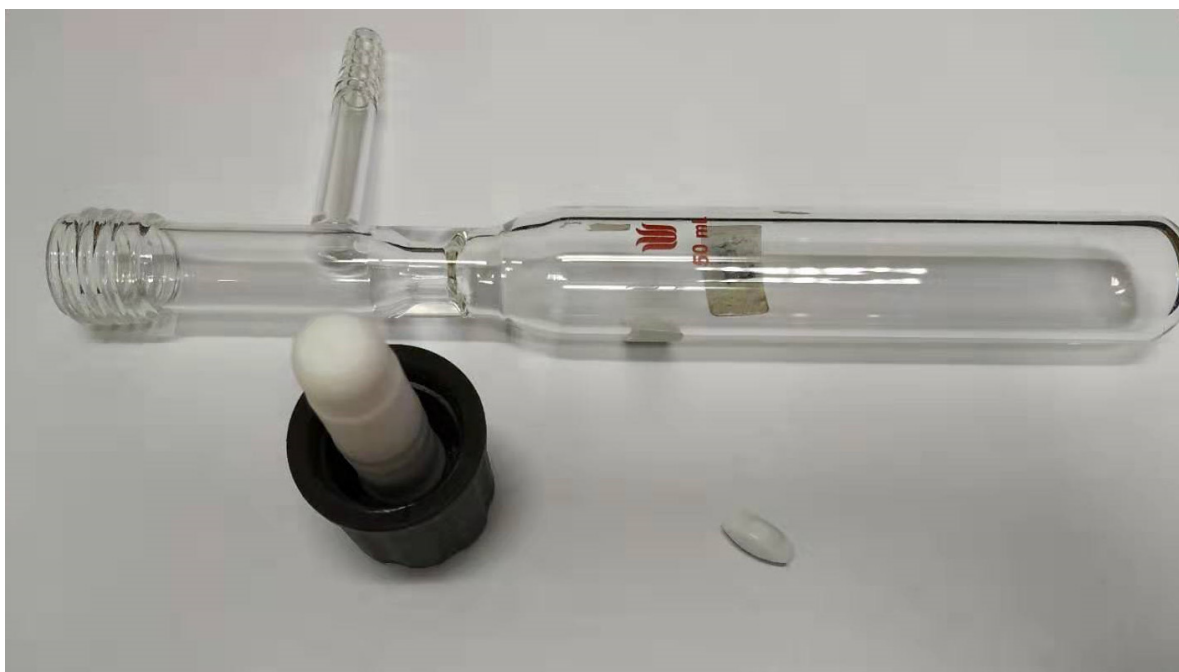


Figure S1. The reaction Schlenk tube, Schlenk tube cap and magnetic stirring bead used for current study.

1.3 Preliminary detection of the carboxylated product

For the preliminary detection of the carboxylated product, Thin layer chromatography (TLC) was performed on TLC Silica gel prefabricated Plate [HSGF 254 (size 75 x 25)]. Visualization of the developed chromatogram was performed by bromocresol green solution.

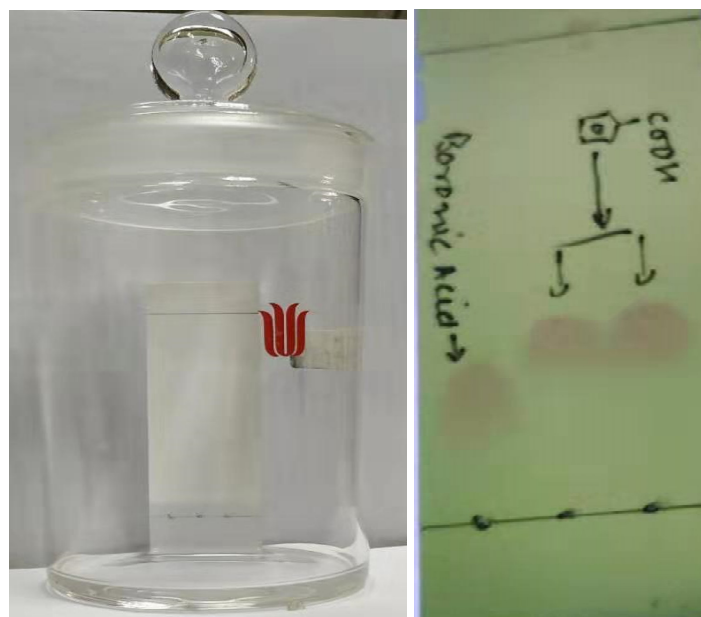


Figure S2. TLC image of phenylboronic acid and benzoic acid

1.3.1 Preliminary detection of the carboxylated product through TLC staining agent

Visualization of the developed chromatogram was performed by bromocresol green solution.

1.3.1.1 Preparation of Bromocresol green (BCG) solution

To 100 ml of absolute ethanol is added 0.04 g of bromocresol green. Then a 0.1 M solution of aqueous NaOH is added dropwise until a blue colour just appears in solution (the solution should be colourless prior to addition). Ideally, these stains may be stored in 100 mL wide mouth jars. The lifetime of such a solution typically depends upon solvent evaporation. Thus, it would be advantageous to tightly seal such jars in between uses.

Bromocresol green is yellow below pH 3.8 and blue above pH 5.4. When an acidic compound is spotted on the plate, the acid lowers the pH and causes the indicator to shift to the lower pH yellow form.

Note: Carboxylic acids stain yellow on a blue background.

This stain provides an excellent means of selectively visualizing carboxylic acids. These will appear as **bright yellow spots on either a dark or light blue background** and typically, it is not necessary to heat the TLC plate following immersion. This TLC visualization method has a fairly long lifetime (usually weeks).



Figure S3. Bromocresol Green Solution (Left) and stained TLC with BCG for the detection of carboxylic acid (yellow spot).

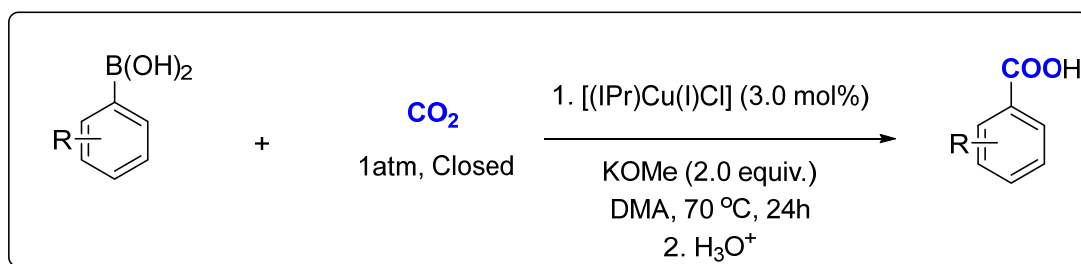
1.4 Procedure for isolation of synthesized compounds

For the isolation of synthesized compounds, the column chromatography was performed on silica gel (Particle size 230-400 mesh) and eluted with appropriate mixture of *n*-hexane/ethyl acetate or ethyl acetate /methanol.

1.5 Characterization of isolated compounds (Instruments)

For the characterization of isolated compounds, NMR spectra were measured on a Bruker ARX400 (^1H at 400 MHz, ^{13}C at different MHz) magnetic resonance spectrometer. Chemical shifts (δ) are reported in ppm using tetramethylsilane as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), and coupling constants (J) were reported in Hertz (Hz).

2. General procedure for carboxylation of boronic acids with CO₂:



A mixture of aryl boronic acid (1.0 mmol), KOMe (2.0 equiv.) and catalyst $[(\text{IPr})\text{CuCl}]$ (14.4 mg, 3.0 mol%) was stirred for 5-10 minutes under N_2 at room temperature. After that the Schlenk tube was filled with carbon dioxide by applying four-five cycles of evacuation and filling with CO_2 . The Schlenk tube was tightly sealed and stirred at $70\text{ }^\circ\text{C}$ for 24 hours after which it was quenched by careful addition of 2.0 M aq. HCl sol. The reaction mixture was diluted with water and extracted three times with EtOAc . The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The solvent was then removed under reduced pressure and it was purified by manual column chromatography.

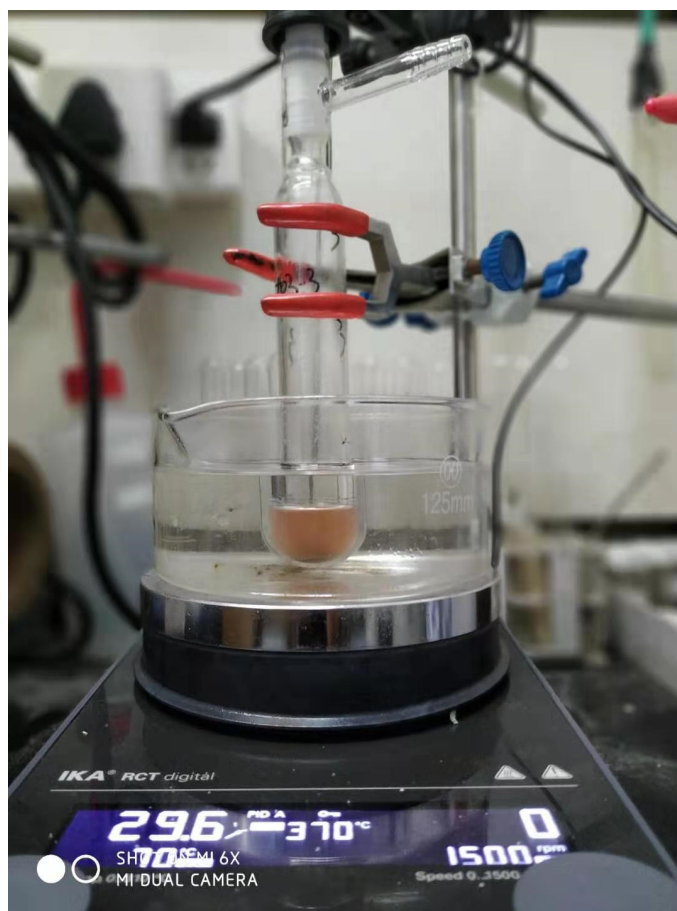


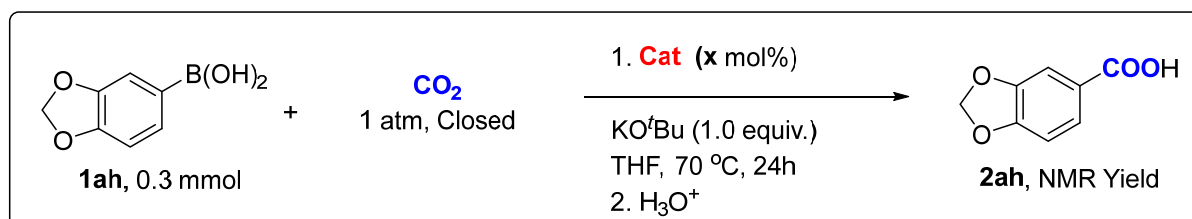
Figure 4. Reaction setup

3. Optimization of standard reaction conditions

benzo[d][1,3]dioxol-5-ylboronic acid (**1ah**) was selected as the starting materials for optimization of the reaction conditions of carboxylation reaction with CO₂

3.1 Optimization of catalyst

Table S1. Optimization of catalyst.^a



Entry	catalyst	Cat. loading	Ligand	Base (1.0 equiv.)	Yield (%) ^b
1	[Rh(COD)(OH)] ₂	5 mol%	Dppe	KO ^t Bu	Trace
2	[Rh(COD)(OMe)] ₂	5 mol%	dppp	KO ^t Bu	Trace
3	[Rh(COD)Cl] ₂	5 mol%	Pcy ₃	KO ^t Bu	N.R.
4	[Ir(COD)Cl] ₂	5 mol%	Dppe	KO ^t Bu	N.R.
5 ^c	NiBr ₂ + Mn	5 mol%	1,10-phenan	KO ^t Bu	N.R.
6	Cu(IPr)Cl	5 mol%	none	KO ^t Bu	10%
7 ^c	Co(acac) ₂	5 mol%	dppb	KO ^t Bu	N.R.
8	Cu(IPr)Cl	3 mol%	none	KO ^t Bu	9 %
9	Cu(IPr)Cl	1 mol%	none	KO ^t Bu	Trace
10	---	KO ^t Bu	N.R.

^aReaction performed on 0.30 mmol scale. ^bYield was determined by ¹H NMR with benzyl alcohol as an internal standard. ^cMn (1.0 equiv.) used as reductant. N.R. = no reaction

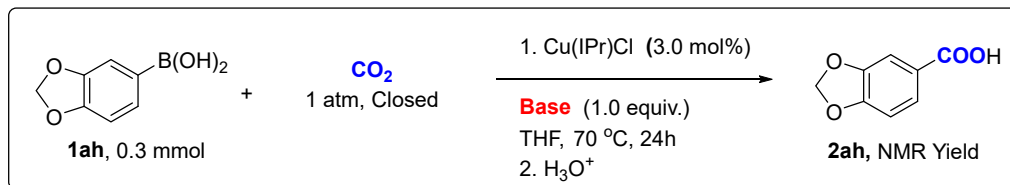
We chose a series of metal salts for the optimization of catalyst with and without ligand for the carboxylation of benzo[d][1,3]dioxol-5-ylboronic acid (**1ah**) with CO₂ in presence of THF as a solvent (Table S1). Cu(IPr)Cl complex was found to be active catalyst as compared to other transition metal salts (Table S1, entries 1-10).

3.2 Optimization of Base

Further to improve the outcome of carboxylated product, we moved our attention towards the base optimization. Base plays key role in the trans-metalation step in the carboxylation reaction

which already know for this. Interestingly, potassium methoxide (KOMe) was found to be more active base as compared to other bases (Table S2, entries 1-5).

Table S2. Optimization of base.^a

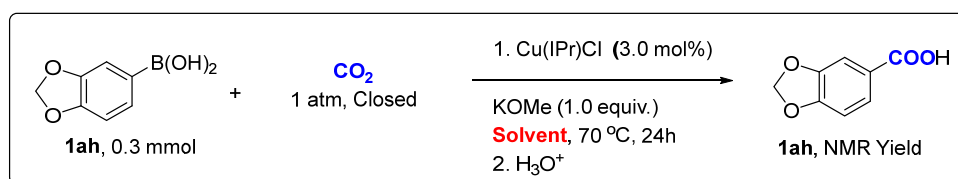


Entry	Catalyst	Cat. loading	Base (1.0 equiv.)	Yield (%) ^b
1	$\text{Cu}(\text{iPr})\text{Cl}$	3 mol%	KO^tBu	10
2	$\text{Cu}(\text{iPr})\text{Cl}$	3 mol%	LiO^tBu	trace
3	$\text{Cu}(\text{iPr})\text{Cl}$	3 mol%	KOMe	20 %
4	$\text{Cu}(\text{iPr})\text{Cl}$	3 mol%	LiOMe	trace
5	$\text{Cu}(\text{iPr})\text{Cl}$	3 mol%	NaO^tBu	trace

^aReaction performed on 0.30 mmol scale. ^bYield was determined by ^1H NMR with benzyl alcohol as an internal standard.

3.3 Optimization of solvent.^a

Table S3. Optimization of solvent.^a



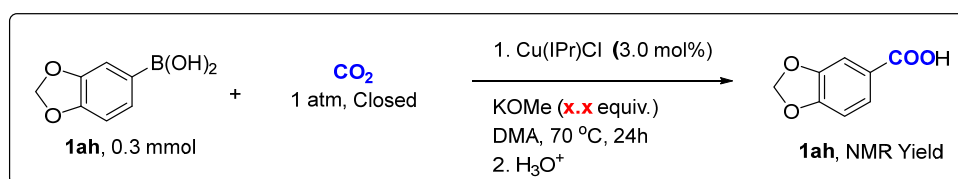
Entry	Catalyst	Base	Base loading	Solvent	Yield (%) ^b
1	$\text{Cu}(\text{iPr})\text{Cl}$	KOMe	1.0 equiv	DMF	38
2	$\text{Cu}(\text{iPr})\text{Cl}$	KOMe	1.0 equiv.	DMA	67
3	$\text{Cu}(\text{iPr})\text{Cl}$	KOMe	1.0 equiv.	DMSO	33
4	$\text{Cu}(\text{iPr})\text{Cl}$	KOMe	1.0 equiv.	ACN	23
5	$\text{Cu}(\text{iPr})\text{Cl}$	KOMe	1.0 equiv.	THF	20
6	$\text{Cu}(\text{iPr})\text{Cl}$	KOMe	1.0 equiv.	Dioxane	NR

^aReaction performed on 0.30 mmol scale. ^bYield was determined by ^1H NMR with benzyl alcohol as an internal standard.

Further to more enhance the outcome of carboxylated product, we moved our attention towards the solvent. In the carboxylation reactions, solubility of carbon dioxide is one of important factor. Therefore, keeping this point in mind, different solvents were screened, and DMA was found to be more efficient solvent as compared to others (Table S3, entries 1-6)

3.4 Optimization of base loading.

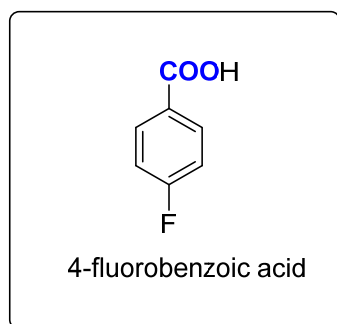
Table S4. Optimization of quantity of base.^a



Entry	catalyst	Base	Base loading	Yield (%) ^b
1	Cu(IPr)Cl	KOMe	1.0 equiv	67
2	Cu(IPr)Cl	KOMe	1.5 equiv.	75
3	Cu(IPr)Cl	KOMe	2.0 equiv.	82
4	Cu(IPr)Cl	----	----	NR

^aReaction performed on 0.30 mmol scale. ^bYield was determined by ¹H NMR with benzyl alcohol as an internal standard.

4.0 Characterization data of synthesized compounds

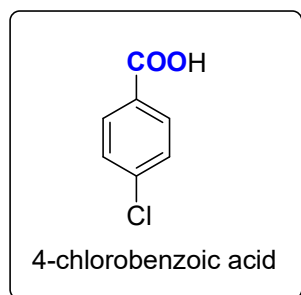


From 4-fluorophenyl boronic acid: General procedure was followed using 4-fluorophenyl boronic acid (254 mg, 1.81 mmol), affording **2a** (136 mg, 73% yield). White solid.

¹H NMR (400 MHz, CDCl₃) δ 12.02 (dd, *J* = 8.9, 5.5 Hz, 2H), 11.13 (t, *J* = 8.8 Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.28, 169.71 (d, $J = 251.9$ Hz), 136.01 (d, $J = 9.4$ Hz), 130.91 (d, $J = 2.9$ Hz), 118.92 (d, $J = 22.3$ Hz).

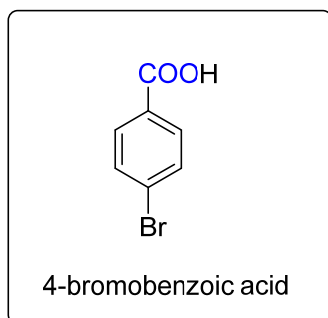
Characterization data matched that reported in the literature: Zhang, X. Zhang, W. Shi, L. Guo, C. Zhang, L. Lu X. Silver(I)-catalyzed carboxylation of arylboronic esters with CO_2 . *Chem. Commun.* **2012**, 48, 6292–6294.



From 4-Chlorophenyl boronic acid: General procedure was followed using benzene-1,4-diboronic acid (156 mg, 1.0 mmol), affording **2b** (117 mg, 75% yield). White solid
 ^1H NMR (400 MHz, DMSO) δ 7.96 (d, $J = 8.0$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 171.68, 143.02, 136.34, 134.85, 133.93.

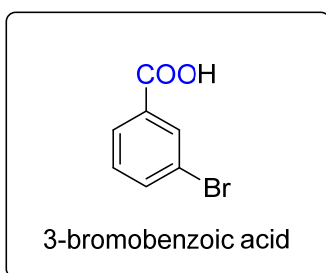
Characterization data matched that reported in the literature: Zhang, X. Zhang, W. Shi, L. Guo, C. Zhang, L. Lu X. Silver(I)-catalyzed carboxylation of arylboronic esters with CO_2 . *Chem. Commun.* **2012**, 48, 6292–6294.



From 4-bromophenyl boronic acid: General procedure was followed using 4-bromophenyl boronic acid (200 mg, 1.0 mmol), affording **2c** (150 mg, 75% yield). White solid
 ^1H NMR (400 MHz, DMSO) δ 13.21 (s, 1H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 8.0$ Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 167.08, 132.17, 131.76, 130.49, 127.34.

Characterization data matched that reported in the literature: Zhang, X. Zhang, W. Shi, L. Guo, C. Zhang, L. Lu X. Silver(I)-catalyzed carboxylation of arylboronic esters with CO_2 . *Chem. Commun.* **2012**, 48, 6292–6294.

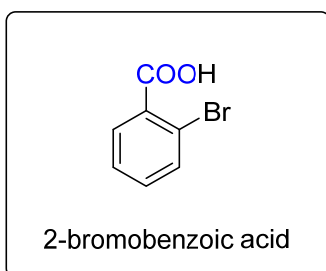


From 3-bromophenyl boronic acid: General procedure was followed using 3-bromophenyl boronic acid (200 mg, 1.00 mmol), affording **2d** (158 mg, 79% yield). White solid

¹H NMR (400 MHz, MeOD) δ 8.13 (t, $J = 1.6$ Hz, 1H), 7.98 (d, $J = 7.8$ Hz, 1H), 7.74 (ddd, $J = 8.0, 1.9, 0.9$ Hz, 1H), 7.40 (t, $J = 7.9$ Hz, 1H).

¹³C NMR (101 MHz, MeOD) δ 166.75, 135.46, 132.79, 132.15, 129.98, 128.04, 121.90.

Characterization data matched that reported in the literature: Mukhopadhyay S. Batra S. Direct transformation of arylamines to aryl halides via sodium nitrite and *N*-halosuccinimide. *Chem. Eur. J.* **2018**, *24*, 14622 – 14626.

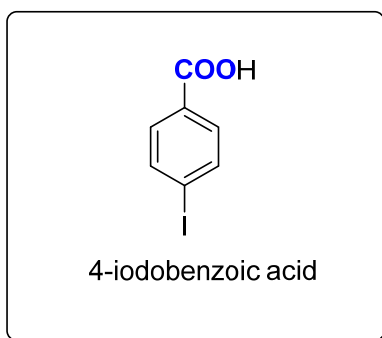


From 2-bromophenyl boronic acid: General procedure was followed using 2-bromophenyl boronic acid (200 mg, 1.00 mmol), affording **2e** (130 mg, 65% yield). White solid

¹H NMR (400 MHz, MeOD) δ 7.79 (dd, $J = 7.5, 1.9$ Hz, 1H), 7.68 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.45 – 7.34 (m, 2H).

¹³C NMR (101 MHz, MeOD) δ 168.20, 133.85, 133.27, 132.14, 130.68, 127.04, 120.56.

Characterization data matched that reported in the literature; Han, W. Jin, F. Zhou, Q. Ligand-free palladium-catalyzed hydroxycarbonylation of aryl halides under ambient conditions: synthesis of aromatic carboxylic acids and aromatic esters. *Synthesis* **2015**, *47*, 1861-1868.

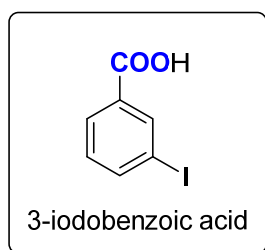


From 4-iodophenyl boronic acid: General procedure was followed using 4-iodophenyl boronic acid (248 mg, 1.0 mmol), affording **2f** (171.12 mg, 69% yield). White solid.

¹H NMR (400 MHz, DMSO) δ 13.15 (s, 1H, COOH), 7.90 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H).

¹³C NMR (101 MHz, DMSO) δ 167.38, 138.05, 131.53, 130.73, 101.69.

Characterization data matched that reported in the literature: Zhang, X. Zhang, W. Shi, L. Guo, C. Zhang, L. Lu X. Silver(I)-catalyzed carboxylation of arylboronic esters with CO₂. *Chem. Commun.* **2012**, 48, 6292–6294.

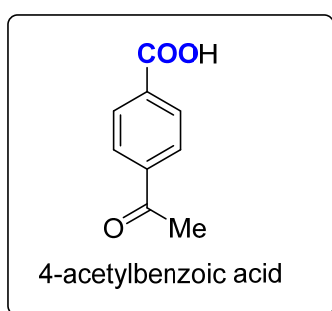


From 3-Iodophenyl boronic acid: General procedure was followed using 3-iodophenyl boronic acid (240 mg, 1.0 mmol), affording **2g** (179 mg, 72% yield). White solid

¹H NMR (400 MHz, DMSO) δ 13.27 (s, 1H, COOH), 8.23 (t, J = 1.5 Hz, 1H), 7.99 (ddd, J = 7.8, 1.7, 1.1 Hz, 1H), 7.97 – 7.93 (m, 1H), 7.32 (t, J = 7.8 Hz, 1H).

¹³C NMR (101 MHz, DMSO) δ 166.40, 141.82, 138.08, 133.33, 131.27, 129.05, 95.16.

Characterization data matched that reported in the literature: Mukhopadhyay S. Batra S. Direct transformation of arylamines to aryl halides via sodium nitrite and *N*-halosuccinimide. *Chem. Eur. J.* **2018**, 24, 14622 – 14626.

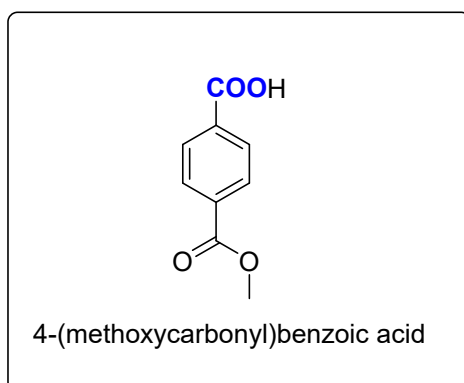


From 4-(acetyl)phenyl boronic acid: General procedure was followed using 4-(acetyl)phenyl boronic acid (164 mg, 1.0 mmol), affording **2h** (125 mg, 76% yield). White solid.

¹H NMR (400 MHz, DMSO) δ 8.07 (s, 4H), 2.64 (s, 3H).

¹³C NMR (101 MHz, DMSO) δ 198.21, 167.10, 140.28, 134.96, 130.01, 128.78, 27.46.

Characterization data matched that reported in the literature: Ukai, K. Aoki, M. Takaya, J. Iwasawa, N. Rhodium(I)-catalyzed carboxylation of aryl- and alkenylboronic esters with CO₂. *J. Am. Chem. Soc.* **2006**, 128, 27, 8706-8707.

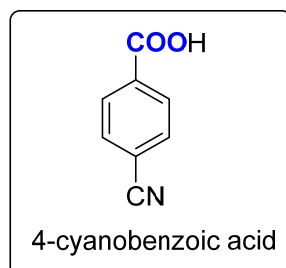


From 4-(methoxycarbonyl)phenyl boronic acid: General procedure was followed using 4-(methoxycarbonyl)phenyl boronic acid (180 mg, 1.0 mmol), affording **2i** (112 mg, 62% yield). White solid.

¹H NMR (400 MHz, MeOD) δ 8.10 (d, *J* = 1.0 Hz, 4H), 3.93 (s, 3H).

¹³C NMR (101 MHz, MeOD) δ 167.30, 166.27, 134.66, 133.70, 129.39, 129.10, 51.51.

Characterization data matched that reported in the literature: Ukai, K. Aoki, M. Takaya, J. Iwasawa, N. Rhodium(I)-catalyzed carboxylation of aryl- and alkenylboronic esters with CO₂. *J. Am. Chem. Soc.* **2006**, 128, 27, 8706-8707.

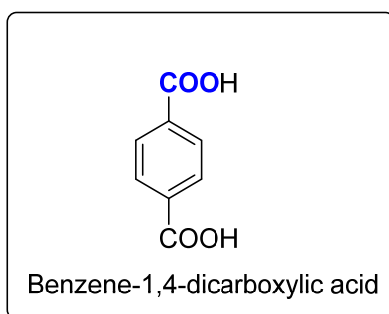


From 4-Cyanophenyl boronic acid: General procedure was followed using 4-cyanophenyl boronic acid (147 mg, 1.0 mmol), affording **2j** (67 mg, 45% yield). White solid.

¹H NMR (400 MHz, MeOD) δ 8.16 (d, *J* = 8.6 Hz, 2H), 7.85 (d, *J* = 8.6 Hz, 2H).

¹³C NMR (101 MHz, MeOD) δ 166.47, 135.01, 132.07, 129.95, 117.62, 115.87.

Characterization data matched that reported in the literature: Zhang, X. Zhang, W. Shi, L. Guo, C. Zhang, L. Lu X. Silver(I)-catalyzed carboxylation of arylboronic esters with CO₂. *Chem. Commun.* **2012**, 48, 6292–6294.

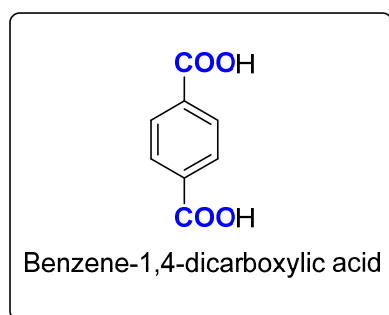


From 4-boronobenzoic acid: General procedure was followed using 4-boronobenzoic acid (166 mg, 1.0 mmol), affording **2k** (121 mg, 73% yield). White solid.

$^1\text{H NMR}$ (400 MHz, DMSO) δ 13.33 (s, 2H), 8.08 (s, 4H).

$^{13}\text{C NMR}$ (101 MHz, DMSO) δ 167.14, 134.90, 129.91.

Characterization data matched that reported in the literature. Yang, D., Yanga H. Fu H. Copper-catalyzed aerobic oxidative synthesis of aromatic carboxylic acids. *Chem. Commun.* **2011**, 47, 2348-2350.

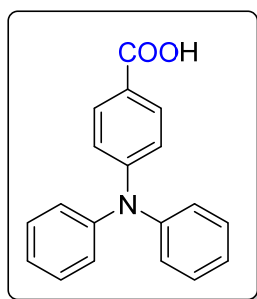


From benzene-1,4-diboronic acid: General procedure was followed using benzene-1,4-diboronic acid (166 mg, 1.0 mmol), affording **2l** (146 mg, 88% yield). White solid

$^1\text{H NMR}$ (400 MHz, DMSO) δ 13.34 (s, 2H), 8.10 (s, 4H).

$^{13}\text{C NMR}$ (101 MHz, DMSO) δ 167.15, 134.89, 129.90.

Characterization data matched that reported in the literature. Yang, D., Yanga H. Fu H. Copper-catalyzed aerobic oxidative synthesis of aromatic carboxylic acids. *Chem. Commun.* **2011**, 47, 2348-2350.



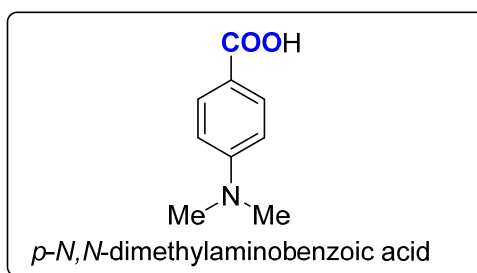
4-(Diphenylamino)benzoic acid (**3m**)

From 4-(diphenylamino)phenylboronic acid: General procedure was followed using 4-(diphenylamino)phenylboronic acid (289 mg, 1.0 mmol), affording **2m** (246 mg, 85% yield). White solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.8$ Hz, 2H), 7.32 (t, $J = 7.8$ Hz, 4H), 7.14 (dd, $J = 13.0, 7.4$ Hz, 6H), 6.99 (d, $J = 8.8$ Hz, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.08, 152.77, 146.48, 131.62, 129.66, 126.09, 124.74, 120.89, 119.52.

Characterization data matched that reported in the literature: Akintola, O. Böhme, M., Rudolph M. Buchholz, A. Görls, H. Plass, W. Metal-bonded redox-active triarylamines and their interactions: synthesis, structure, and redox properties of paddle-wheel copper complexes. *ChemistryOpen* **2019**, 8, 271–284.

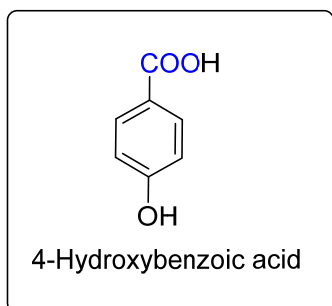


From *p*-*N,N*-dimethylaminophenyl boronic acid: General procedure was followed using 4-(dimethylamino)phenylboronic acid (165 mg, 1.0 mmol), affording **2n** (129 mg, 78% yield). White solid.

$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 12.10 (s, 1H), 7.75 (d, $J = 8.7$ Hz, 2H), 6.70 (d, $J = 8.7$ Hz, 2H), 2.99 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 167.99, 153.54, 131.39, 117.37, 111.24, 39.43.

Characterization data matched that reported in the literature: Pietrzak, M. Jedrzejewska, B. Madrzejewska, D. and Bajorek, A. Convenient synthesis of *p*-aminobenzoic acids and their methyl esters. *Organic Preparations and Procedures International*. **2017**, 49, 45–52.

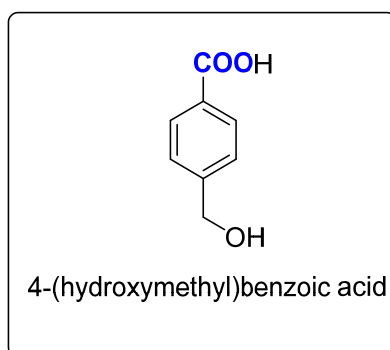


From 4-hydroxyphenyl boronic acid: General procedure was followed using 4-hydroxyphenyl boronic acid (138 mg, 1.0 mmol), affording **2o** (94 mg, 68% yield). White solid.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.45 (s, 1H), 10.24 (s, 1H, -OH), 7.82 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H).

¹³C NMR (101 MHz, DMSO) δ 167.65, 162.07, 132.01, 121.82, 115.59.

Characterization data matched that reported in the literature. Nakamura, A. Kanou, H. Tanaka, J. Imamiya, A. Maegawa, T. Miki, Y. A mild method for synthesizing carboxylic acids by oxidation of aldoximes using hypervalent iodine reagents. *Org. Biomol. Chem.* **2018**, *16*, 541–544.

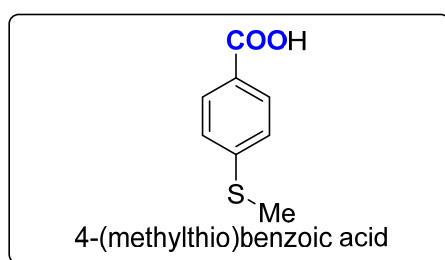


From 4-(hydroxymethyl)phenyl boronic acid: General procedure was followed using 4-(hydroxymethyl)phenyl boronic acid (152 mg, 1.0 mmol), affording **2p** (111 mg, 73% yield). White solid.

¹H NMR (400 MHz, MeOD) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 4.67 (s, 2H).

¹³C NMR (101 MHz, MeOD) δ 168.43, 146.89, 129.45, 126.14, 63.19.

Characterization data matched that reported in the literature. Huy, P. H. Filbrich I. General catalytic method for highly cost- and atom-efficient nucleophilic substitutions. *Chem. Eur. J.* **2018**, *24*, 7410 – 7416.

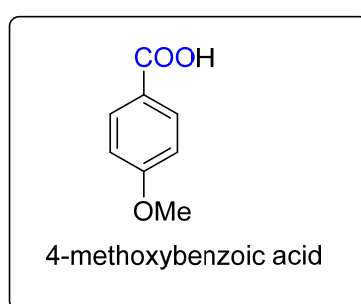


From 4-(methylthio) phenyl boronic acid: General procedure was followed using (4-methylthiophenyl boronic acid (168 mg, 1.0 mmol), affording **2q** (142 mg, 85% yield). White solid.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.85 (s, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 2.53 (s, 3H).

¹³C NMR (101 MHz, DMSO) δ 167.51, 145.25, 130.17, 127.18, 125.33, 14.42.

Characterization data matched that reported in the literature: Friis, S. D. Andersen, T. L. Skrydstrup, T. Palladium-catalyzed synthesis of aromatic carboxylic acids with silacarboxylic acids. *Org. Lett.* **2013**, *15*, 1378-1381.

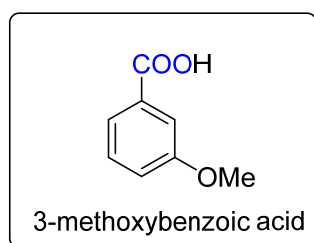


From 4-methoxyphenyl boronic acid: General procedure was followed using 4-methoxyphenyl boronic acid (152 mg, 1.0 mmol), affording **2r** (126 mg, 83% yield). White solid.

¹H NMR (400 MHz, DMSO) δ 12.65 (s, 1H), 7.92 (d, *J* = 8.9 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H).

¹³C NMR (101 MHz, DMSO) δ 167.49, 163.30, 131.81, 123.44, 114.24, 55.85.

Characterization data matched that reported in the literature: Zhang, X. Zhang, W. Shi, L. Guo, C. Zhang, L. Lu X. Silver(I)-catalyzed carboxylation of arylboronic esters with CO₂. *Chem. Commun.* **2012**, *48*, 6292–6294.

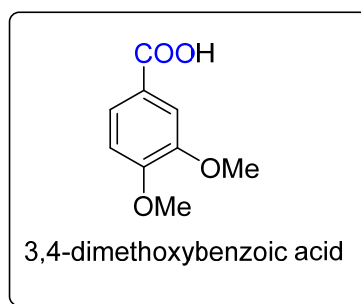


From 3-methoxyphenylboronic acid: General procedure was followed using 4-methoxyphenyl boronic acid (152 mg, 1.0 mmol), affording **2s** (127 mg, 83% yield). White solid.

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 13.00 (s, 1H), 7.54 (dt, $J = 7.7, 1.3$ Hz, 1H), 7.46 – 7.39 (m, 2H), 7.19 (ddd, $J = 8.2, 2.7, 1.0$ Hz, 1H), 3.81 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, DMSO) δ 167.59, 159.71, 132.80, 130.19, 122.05, 119.36, 114.39, 55.71.

Characterization data matched that reported in the literature: Hazra, S. Kushawaha, A. K. Yadav, D. Dolui, P. Deb, M. Elias, A. Table salt as a catalyst for the oxidation of aromatic alcohols and amines to acids and imines in aqueous medium: effectively carrying out oxidation reactions in sea water. *J. Green Chem.* **2019**, *21*, 1929-1934.

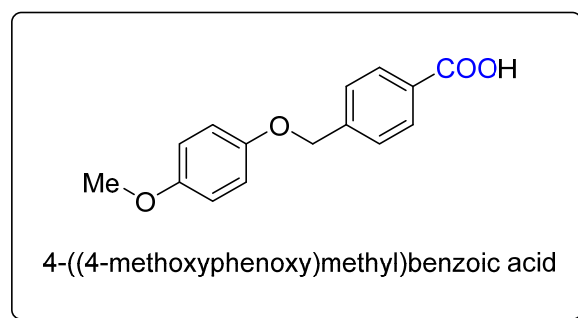


From 3,4-dimethoxyphenyl boronic acid: General procedure was followed using 2-methoxyphenyl boronic acid (182 mg, 1.0 mmol), affording **2t** (125.8 mg, 69% yield). White solid.

$^1\text{H NMR}$ (400 MHz, DMSO) δ 12.68 (s, 1H), 7.58 (dd, $J = 8.4, 1.9$ Hz, 1H), 7.45 (d, $J = 1.9$ Hz, 1H), 7.05 (d, $J = 8.5$ Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, DMSO) δ 167.58, 153.06, 148.76, 123.63, 123.40, 112.32, 111.43, 56.10, 55.89.

Characterization data matched that reported in the literature. Nair, V. Varghese V. Paul R., R. Jose, A. Sinu, C. R. Menon, R. S. NHC catalyzed transformation of aromatic aldehydes to acids by carbon dioxide: An unexpected reaction. *Org. Lett.* **2010**, *12*, 11, 2653-2655

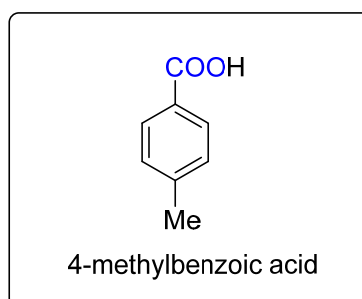


From 4-[(4-methoxyphenoxy)methyl]phenyl boronic acid: General procedure was followed using [4-[(4-methoxyphenoxy)methyl]phenyl]boronic acid (258 mg, 1.0 mmol), affording **2u** (163 mg, 63% yield). White solid.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.64 (s, 1H), 7.93 – 7.86 (m, 2H), 7.43 – 7.36 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 5.09 (s, 2H), 3.76 (s, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.46, 162.47, 159.59, 131.78, 130.15, 128.83, 123.50, 115.07, 114.33, 69.72, 55.57.

Characterization data matched that reported in the literature: Manos-Turvey, A. Watson, E. E. Sykes, M. L. Jones, A. J. Baell, J. B. Kaiser, M. Avery, V. M. Payne, R. J. Synthesis and evaluation of phoxymethylbenzamide analogues as anti-trypanosomal agents. *Med. Chem. Commun.* **2015**, *6*, 403-406.



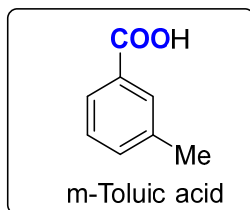
From 4-methylphenyl boronic acid: General procedure was followed using 4-methylphenyl boronic acid (136 mg, 1.0 mmol), affording **2v** (129 mg, 93% yield). White solid.

Note: THF solvent was used instead of DMA

¹H NMR (400 MHz, MeOD) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H).

¹³C NMR (101 MHz, MeOD) δ 168.65, 143.57, 129.44, 128.71, 127.67, 20.24.

Characterization data matched that reported in the literature: Zhang, X. Zhang, W. Shi, L. Guo, C. Zhang, L. Lu X. Silver(I)-catalyzed carboxylation of arylboronic esters with CO₂. *Chem. Commun.* **2012**, *48*, 6292–6294.



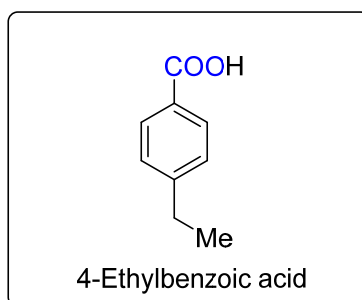
From 3-methylphenyl boronic acid: General procedure was followed using 3-methylphenyl boronic acid (136 mg, 1.0 mmol), affording **2w** (102 mg, 75% yield). White solid.

Note: THF solvent was used instead of DMA

¹H NMR (400 MHz, CDCl₃) δ 12.52 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 2.41 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.83, 138.33, 134.64, 130.74, 129.30, 128.41, 127.42, 21.28.

Characterization data matched that reported in the literature: You, T. Wang, Z. Chen, J. Xia, Y. Transfer hydro-dehalogenation of organic halides catalyzed by ruthenium(II) complex. *J. Org. Chem.* **2017**, 82 (3), 1340-1346.



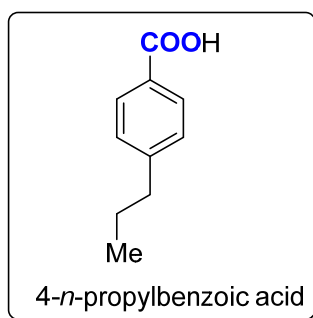
From 4-ethylphenyl boronic acid: General procedure was followed using 4-ethylphenyl boronic acid (150 mg, 1.0 mmol), affording **2x** (143 mg, 95% yield). Pale yellowish white solid.

Note: THF solvent was used instead of DMA.

¹H NMR (400 MHz, DMSO) δ 12.82 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.51, 150.84, 130.45, 128.07, 124.24, 29.07, 15.20.

Characterization data matched that reported in the literature: Urgoitia, G. SanMartin, R. Herrero, M. T. Domínguez, E. An outstanding catalyst for the oxygen-mediated oxidation of arylcarbinols, arylmethylene and arylacetylene compounds. *Chem. Commun.* **2015**, 51, 4799-4802.

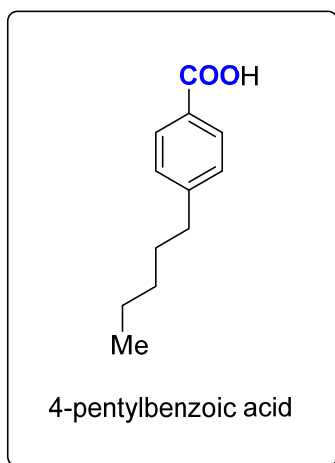


From 4-*n*-propylphenylboronic acid: General procedure was followed using 4-propylphenylboronic acid (164 mg, 1.0 mmol), affording **2y** (131 mg, 80% yield). White solid. Note: THF solvent was used instead of DMA.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.81 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.61 (h, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.79, 147.96, 129.80, 128.96, 128.78, 37.60, 24.22, 14.02.

Characterization data matched that reported in the literature: Song, S. Zhang, J. Gözaydın, G. Yan, N. Production of Terephthalic Acid from Corn Stover lignin. *Angew. Chem. Int. Ed.* **2019**, 58, 4934.



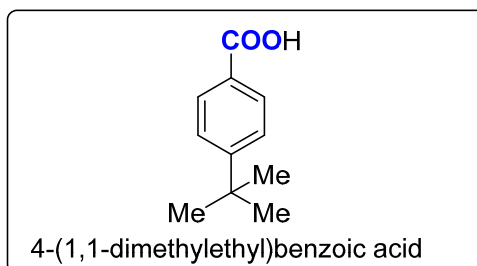
From 4-pentylphenyl boronic acid: General procedure was followed using (4-pentylphenyl) boronic acid (192 mg, 1.0 mmol), affording **2z** (136 mg, 71% yield). White solid.

Note: THF solvent was used instead of DMA

¹H NMR (400 MHz, CDCl₃) δ 12.43 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 1.64 (t, *J* = 7.5 Hz, 2H), 1.40 – 1.21 (m, 4H), 0.89 (t, *J* = 6.7 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.74, 149.63, 130.33, 128.59, 126.85, 36.11, 31.48, 30.82, 22.54, 14.02.

Characterization data matched that reported in the literature: Kraus, G. A. Riley, S. Cordes, T. Aromatics from pyrones: para-substituted alkyl benzoates from alkenes, coumalic acid and methyl coumalate. *Green Chem.* **2011**, *13*, 2734-2736.



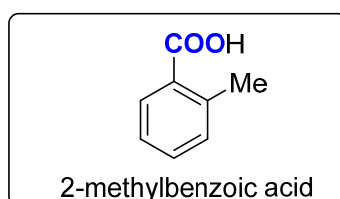
From 4-(1,1-dimethylethyl)phenyl boronic acid: General procedure was followed using 4-*tert*-butylphenylboronic acid (178 mg, 1.0 mmol), affording **2aa** (133 mg, 75% yield). White solid.

Note: THF solvent was used instead of DMA

¹H NMR (400 MHz, CDCl₃) δ 12.56 (s, 1H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 1.35 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 172.70, 157.62, 130.19, 126.65, 125.52, 35.22, 31.13.

Characterization data matched that reported in the literature: Chuan-Qi Zhao, C. M. Xu, X. Li, Z. Wang, X. Zhang, K. Mei, T. Nickel-catalyzed carboxylation of aryl and heteroaryl fluorosulfates using carbon dioxide. *Org. Lett.* **2019**, *21*, 2464-2467.



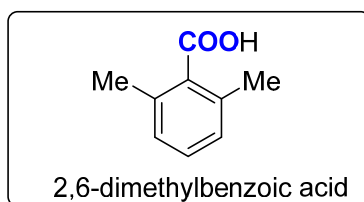
From 2-methylphenyl boronic acid: General procedure was followed using 2-methylphenyl boronic acid (136 mg, 1.0 mmol), affording **2ab** (122 mg, 75% yield). White solid.

Note: THF solvent was used instead of DMA

¹H NMR (400 MHz, CDCl₃) δ 12.69 (s, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 2H), 2.66 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 173.86, 141.46, 133.04, 132.00, 131.70, 128.40, 125.92, 22.21.

Characterization data matched that reported in the literature: Zhao, C. M. Xu, X. Li, Z. Wang, X. Zhang, K. Mei, T. Nickel-catalyzed carboxylation of aryl and heteroaryl fluorosulfates using carbon dioxide. *Org. Lett.* **2019**, *21*, 2464-2467.



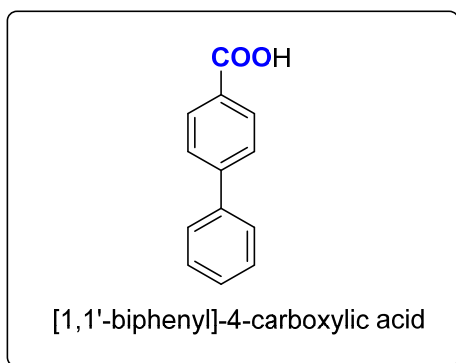
From 2,6-dimethylbenzoic acid: General procedure was followed using 2,6-dimethylbenzene boronic acid (150 mg, 1.0 mmol), affording **2ac** (133 mg, 88% yield). White solid.

Note: THF solvent was used instead of DMA

¹H NMR (400 MHz, DMSO-*d*₆) δ 13.12 (s, 1H), 7.24 – 7.15 (m, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 2.27 (s, 6H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 171.18, 135.92, 133.88, 129.09, 127.77, 19.71.

Characterization data matched that reported in the literature: Joseph, J. T. Sajith, A. M. Ningegowda, R. C. Shashikanth, S. Room temperature carbonylation of (hetero) aryl pentafluorobenzenesulfonates and triflates using palladium-cobalt bimetallic catalyst: dual role of cobalt carbonyl. *Adv. Synth. Catal.* **2017**, 359, 419.



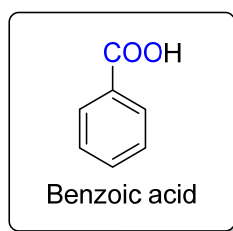
From [1,1'-biphenyl]-4-ylboronic acid: General procedure was followed using [1,1'-biphenyl]-4-ylboronic acid (198 mg, 1.0 mmol), affording **2ad** (164 mg, 83% yield). White solid.

Note: THF solvent was used instead of DMA

¹H NMR (400 MHz, DMSO) δ 13.02 (s, 1H), 8.05 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H).

¹³C NMR (101 MHz, DMSO) δ 167.62, 144.78, 139.50, 130.44, 130.10, 129.55, 128.76, 127.43, 127.28.

Characterization data matched that reported in the literature: Zhang, X. Zhang, W. Shi, L. Guo, C. Zhang, L. Lu X. Silver(I)-catalyzed carboxylation of arylboronic esters with CO₂. *Chem. Commun.* **2012**, 48, 6292–6294.



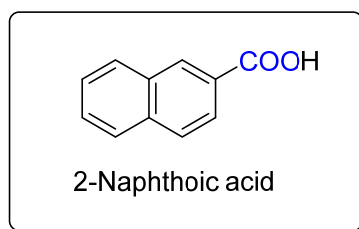
From phenyl boronic acid: General procedure was followed using phenylboronic acid (122 mg, 1.0 mmol), affording **2ae** (113 mg, 92% yield). White solid.

Note: THF solvent was used instead of DMA

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 13.13 (s, 1H), 8.12 (d, $J = 7.5$ Hz, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.83, 133.90, 130.29, 129.39, 128.54.

Characterization data matched that reported in the literature: Zhang, X. Zhang, W. Shi, L. Guo, C. Zhang, L. Lu X. Silver(I)-catalyzed carboxylation of arylboronic esters with CO_2 . *Chem. Commun.* **2012**, 48, 6292–6294.



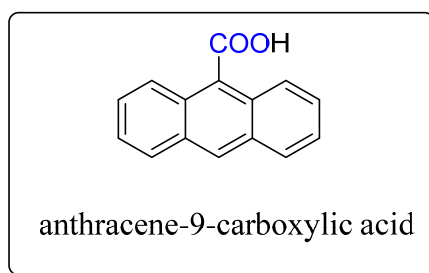
From 2-Naphthylboronic acid: General procedure was followed using 2-naphthylboronic acid (172 mg, 1.0 mmol), affording **2af** (148 mg, 86% yield). White solid.

Note: THF solvent was used instead of DMA

$^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 13.14 (s, 1H), 8.66 (s, 1H), 8.18 – 8.12 (m, 1H), 8.04 (s, 2H), 8.01 (s, 1H), 7.65 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, DMSO) δ 167.94, 135.40, 132.62, 131.00, 129.74, 128.77, 128.62, 128.57, 128.11, 127.25, 125.65.

Characterization data matched that reported in the literature: Ghalehshahi, H. G. Madsen, R. Silver-catalyzed dehydrogenative synthesis of carboxylic acids from primary alcohols. *Chem. Eur. J.* **2017**, 23, 11920 – 11926.



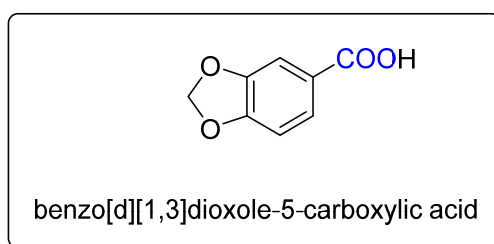
From anthracen-9-ylboronic acid: General procedure was followed using 2-naphthylboronic acid (222 mg, 1.0 mmol), affording **3ag** (182 mg, 82% yield). Yellow solid.

Note: THF solvent was used instead of DMA

¹H NMR (400 MHz, DMSO-*d*₆) δ 13.94 (s, 1H), 8.74 (s, 1H), 8.16 (dd, *J* = 8.2, 1.4 Hz, 2H), 8.07 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.61 (dddd, *J* = 22.6, 8.0, 6.6, 1.3 Hz, 4H).

¹³C NMR (101 MHz, DMSO) δ 170.68, 131.00, 130.15, 129.07, 128.80, 127.55, 127.41, 126.19, 125.35.

Khatana, A. K. Singh, V. Gupta, M. K. Tiwari, B. A highly efficient NHC-catalyzed aerobic oxidation of aldehydes to carboxylic acids. *Synthesis* **2018**, *50*, 4290-4294.

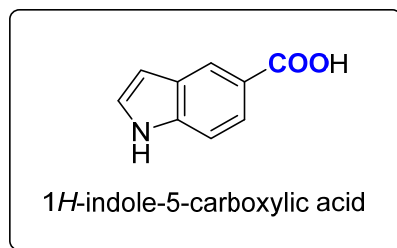


From benzo[d][1,3]dioxol-5-ylboronic acid: General procedure was followed using benzo[d][1,3]dioxol-5-ylboronic acid (166 mg, 1.0 mmol), affording **2ah** (133 mg, 80% yield). White solid

¹H NMR (400 MHz, MeOD) δ 7.63 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.40 (d, *J* = 1.6 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.04 (s, 2H).

¹³C NMR (101 MHz, MeOD) δ 167.84, 151.79, 147.86, 125.14, 124.39, 108.89, 107.45, 101.93.

Characterization data matched that reported in the literature: Zhang, X. Zhang, W. Shi, L. Guo, C. Zhang, L. Lu X. Silver(I)-catalyzed carboxylation of arylboronic esters with CO₂. *Chem. Commun.* **2012**, *48*, 6292–6294

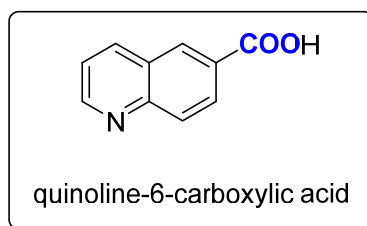


From (1H-indol-5-yl)boronic acid: General procedure was followed using (1H-indol-5-yl)boronic acid (161 mg, 1.0 mmol), affording **2ai** (85 mg, 53% yield). White solid

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.39 (s, 1H), 11.43 (s, 1H), 8.25 (d, *J* = 1.6 Hz, 1H), 7.72 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.50 – 7.40 (m, 2H), 6.58 (t, *J* = 2.6 Hz, 1H).

¹³C NMR (101 MHz, DMSO) δ 168.91, 138.80, 127.65, 127.39, 123.28, 122.69, 121.89, 111.57, 102.96.

Characterization data matched that reported in the literature: Gadakh, A. V. Chikanna, D. Rindhe, S. S. Karale, B. K. Heteroaryl hydroxycarbonylation: an efficient, robust, practically scalable approach using formyl acetate as the CO source. *Synthetic Communications* **2012**, *42*, 658-666.



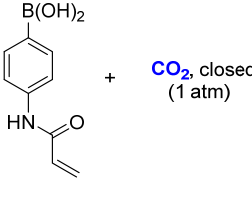
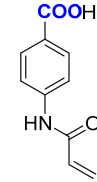
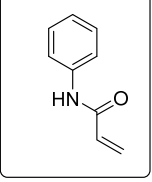
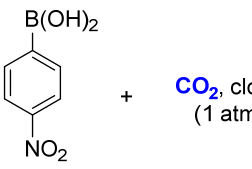
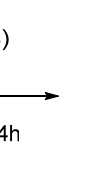
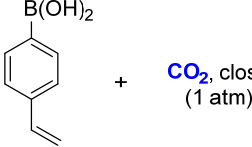
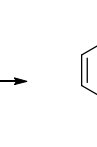
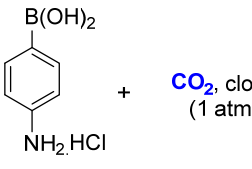
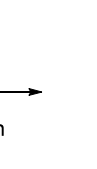
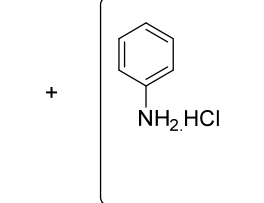
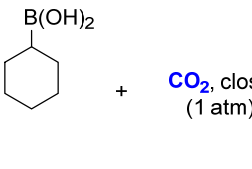
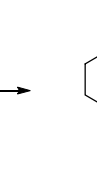
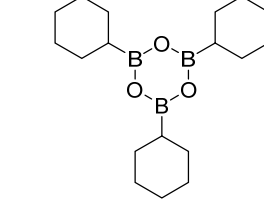
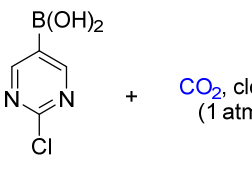
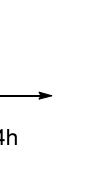
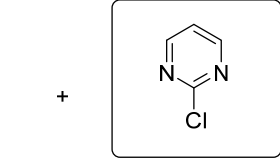
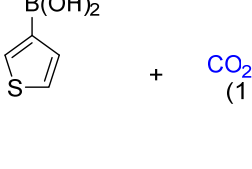
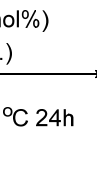

From quinolin-6-ylboronic acid: General procedure was followed using quinolin-6-ylboronic acid (173 mg, 1.0 mmol), affording **2aj** (102 mg, 59% yield). White solid

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.05 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.71 (d, *J* = 1.9 Hz, 1H), 8.60 (dd, *J* = 8.3, 2.0 Hz, 1H), 8.25 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.65 (dd, *J* = 8.3, 4.2 Hz, 1H).

¹³C NMR (101 MHz, DMSO) δ 167.45, 153.14, 149.78, 137.98, 131.42, 129.76, 129.24, 129.06, 127.65, 122.69.

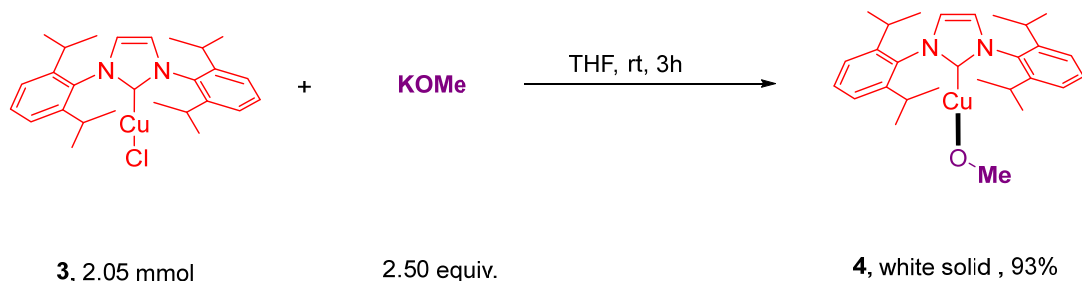
Characterization data matched that reported in the literature: Joseph, J. T. Sajith, A. M. Ningegowda, R. C. Shashikanth, S. Room temperature carbonylation of (hetero) aryl pentafluorobenzenesulfonates and triflates using palladium-cobalt bimetallic catalyst: dual role of cobalt carbonyl. *Adv. Synth. Catal.* **2017**, *359*, 419 – 425.

5.0 Substrate scope limitation of developed method

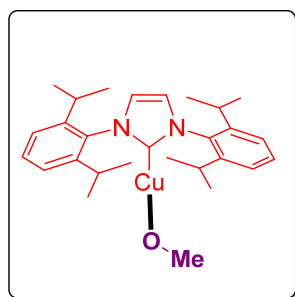
<p>1</p>		<p>1. Cu Cat. (3.0 mol%) KOMe (2.0 equiv.) DMA (5 mL), 70 °C 24h 2. H₃O⁺</p>	 <p>Not Obtained</p>	 <p>Obtained</p>
<p>2</p>		<p>1. Cu Cat. (3.0 mol%) KOMe (2.0 equiv.) DMA (5 mL), 70 °C 24h 2. H₃O⁺</p>	 <p>Not Obtained</p>	
<p>3</p>		<p>1. Cu Cat. (3.0 mol%) KOMe (2.0 equiv.) DMA (5 mL), 70 °C 24h 2. H₃O⁺</p>	 <p>Not Obtained</p>	<p>Various side product obtained</p>
<p>4</p>		<p>1. Cu Cat. (3.0 mol%) KOMe (2.0 equiv.) DMA (5 mL), 70 °C 24h 2. H₃O⁺</p>	 <p>Not Obtained</p>	 <p>Obtained</p>
<p>5</p>		<p>1. Cu Cat. (3.0 mol%) KOMe (2.0 equiv.) DMA (5 mL), 70 °C 24h 2. H₃O⁺</p>	 <p>Not Obtained</p>	 <p>Obtained</p>
<p>6</p>		<p>1. Cu Cat. (3.0 mol%) KOMe (2.0 equiv.) DMA (5 mL), 70 °C 24h 2. H₃O⁺</p>	 <p>Not Obtained</p>	
<p>7</p>		<p>1. Cu Cat. (3.0 mol%) KOMe (2.0 equiv.) DMA (5 mL), 70 °C 24h 2. H₃O⁺</p>	 <p>Not obtained</p>	

6.0 Mechanistic study

6.1 Synthesis of intermediate (1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-imidazol-2-yl)(methoxy)copper [Cu(IPr)(OMe)]



Procedure: In a glove box a 100 mL Schenk flask was charged with 1000.0 mg (2.05 mmol) of Chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) [(IPr)CuCl] and 30 mL anhydrous THF and then 2.50 equivalent of potassium methoxide (KOMe) was added. The resulting mixture was stirred at room temperature for 3 hours. The solvent was reduced to dryness under vacuum and 20 ml of benzene was added to extract the compound. The colourless solution was filtered, and the solvent was removed under vacuum to give an off-white solid. The complex was washed with *n*-pentane and dried under vacuum. Yield: 898.4 mg (93 %).

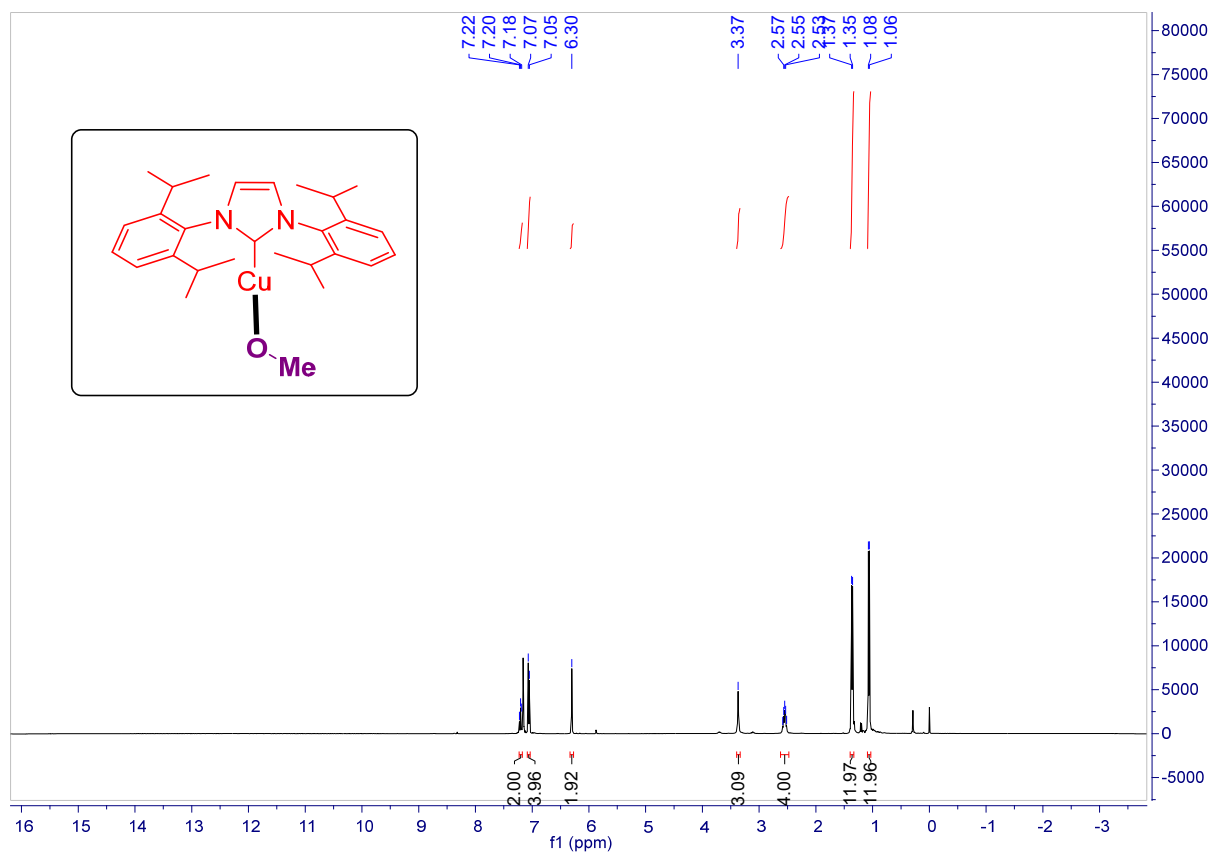


$^1\text{H NMR}$ (400 MHz, C_6D_6) δ 7.20 (t, $J = 7.7$ Hz, 2H), 7.06 (d, $J = 7.8$ Hz, 4H), 6.30 (s, 2H), 3.37 (s, 3H), 2.55 (dt, $J = 13.5, 6.7$ Hz, 4H), 1.36 (d, $J = 6.8$ Hz, 12H), 1.07 (d, $J = 6.9$ Hz, 12H).

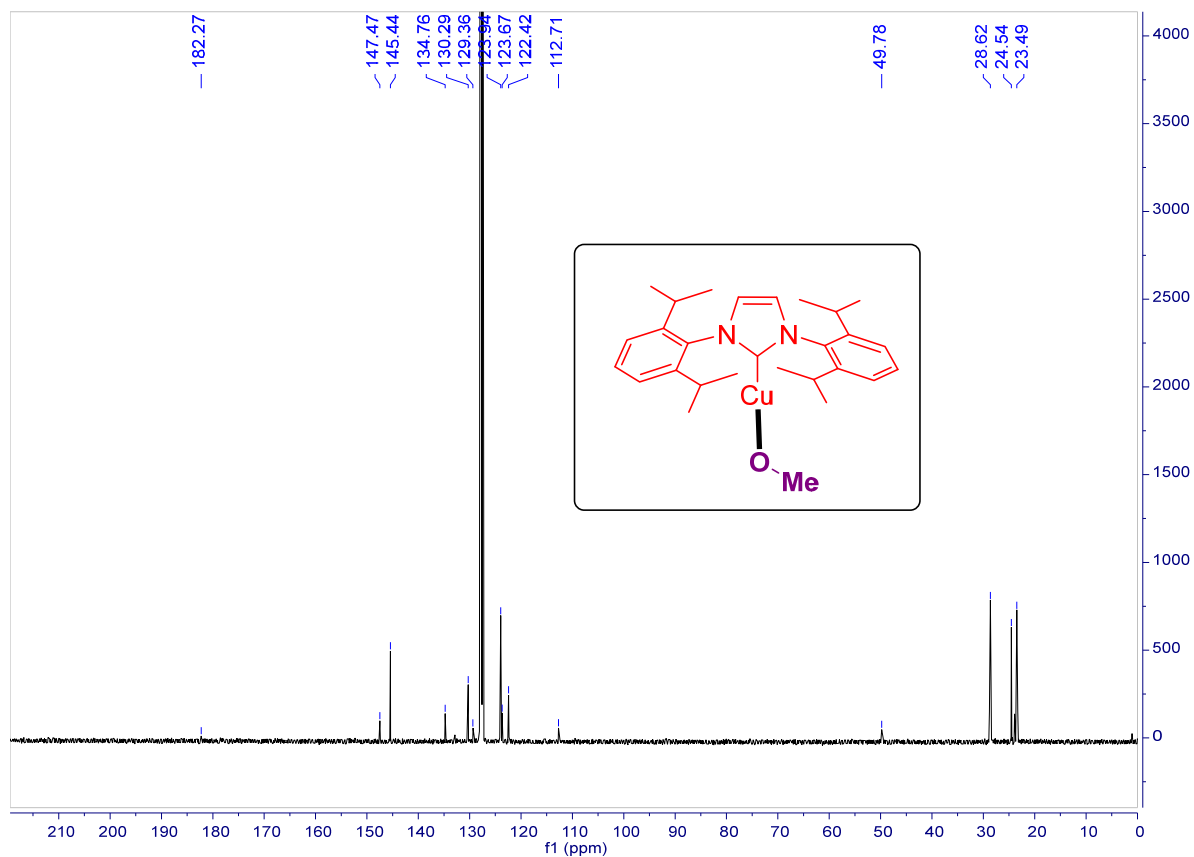
$^{13}\text{C NMR}$ (101 MHz, C_6D_6) δ 182.27, 147.47, 145.44, 134.76, 130.29, 129.36, 123.94, 123.67, 122.42, 112.71, 49.78, 28.62, 24.54, 23.49.

Characterization data matched that reported in the literature: Bonet, A. Lillo, V. Ramirez, J. Diaz-Requejo M. M. Fernandez E. The selective catalytic formation of β -boryl aldehydes through a base-free approach. *Org. Biomol. Chem.* **2009**, 7, 1533–1535.

^1H NMR of $[\text{Cu}(\text{IPr})(\text{OMe})]$ complex in C_6D_6

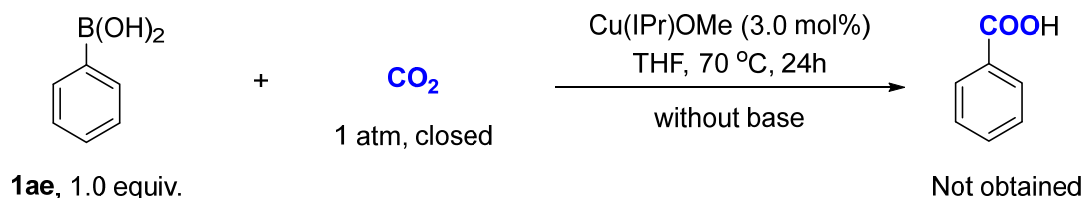


^{13}C NMR of $[\text{Cu}(\text{IPr})(\text{OMe})]$ complex in C_6D_6

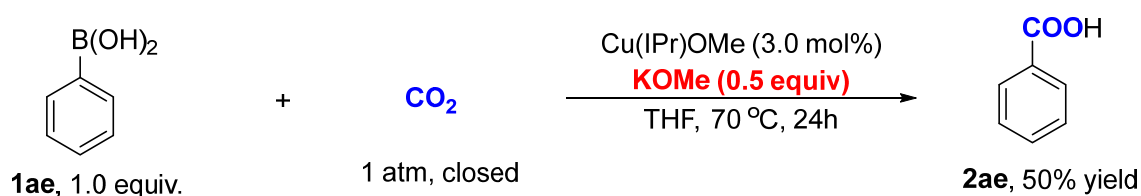


6.2 Carboxylation reaction of phenyl boronic acid with intermediate Cu-complex 4 using CO₂ as C1 source.

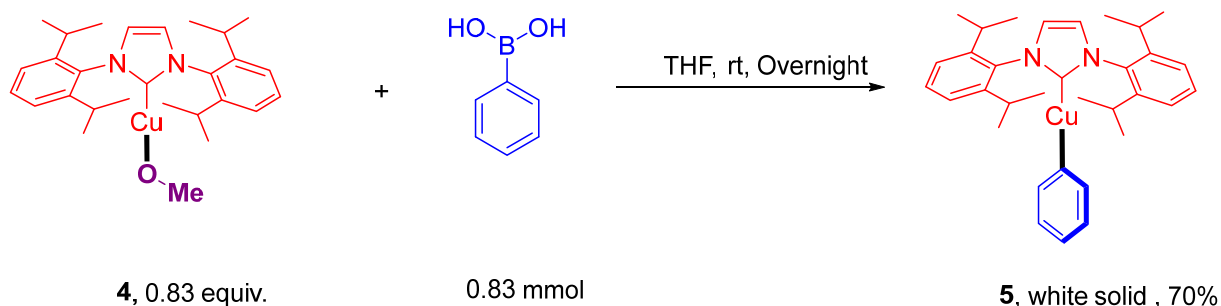
a) In the absence of base KOMe



b) In the presence of base KOMe



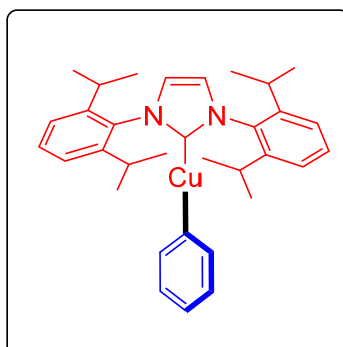
6.3 Synthesis of intermediate (1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-imidazol-2-yl)(phenyl)copper [Cu(IPr)Ph]



Procedure:

Phenylboronic acid (105 mg, 0.83 mmol) was added to a solution of Cu(OMe)(IPr) (400 mg, 0.83 mmol) in THF (10 mL) at room temperature. The reaction mixture was stirred for overnight at room temperature, and the solvent was removed under vacuum. The residue was

washed with cold *n*-pentane and recrystallized from dry benzene/*n*-pentane to afford compound Cu(IPr)(Ph) as a white solid (332 mg, 0.63 mmol; 70% yield).

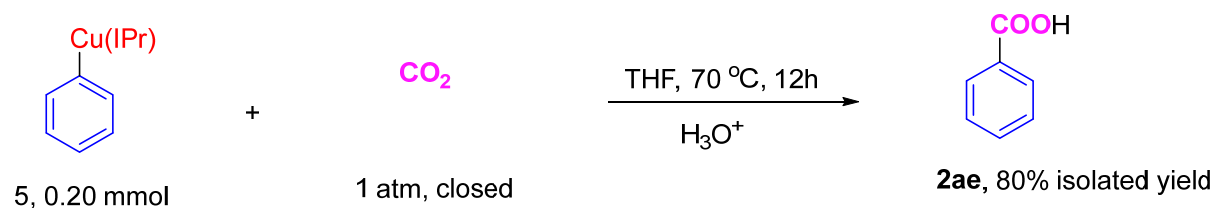


$^1\text{H NMR}$ (400 MHz, THF- d_8) δ 7.49 – 7.37 (m, 4H), 7.27 (d, J = 7.8 Hz, 4H), 7.19 (s, 1H), 6.44 (t, J = 6.9 Hz, 2H), 5.96 (t, J = 7.2 Hz, 1H), 5.71 (s, 1H), 2.56 (p, J = 6.9 Hz, 4H), 1.19 (d, J = 6.9 Hz, 12H), 1.13 (d, J = 6.9 Hz, 12H).

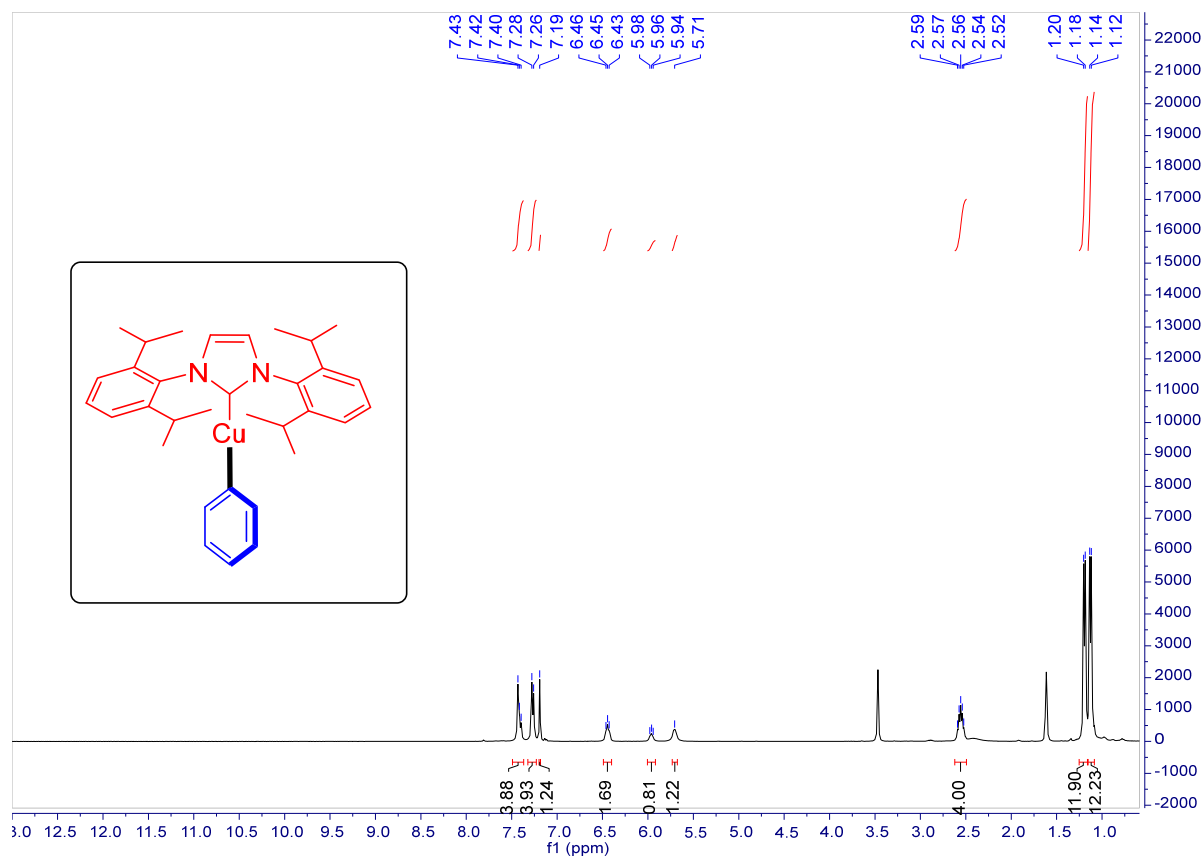
$^{13}\text{C NMR}$ (101 MHz, C_6D_6) δ 181.65, 168.86, 147.48, 145.52, 134.63, 130.44, 128.84, 128.23, 127.82, 127.73, 127.58, 124.10, 122.47, 113.64, 28.65, 24.58, 23.44.

Characterization data matched that reported in the literature: Takatsu, K. Shintani, R. Hayashi T. Copper-catalyzed 1,4-addition of organoboronates to alkylidene cyanoacetates: mechanistic insight and application to asymmetric catalysis. *Angew. Chem. Int. Ed.* **2011**, *50*, 5548 –5552.

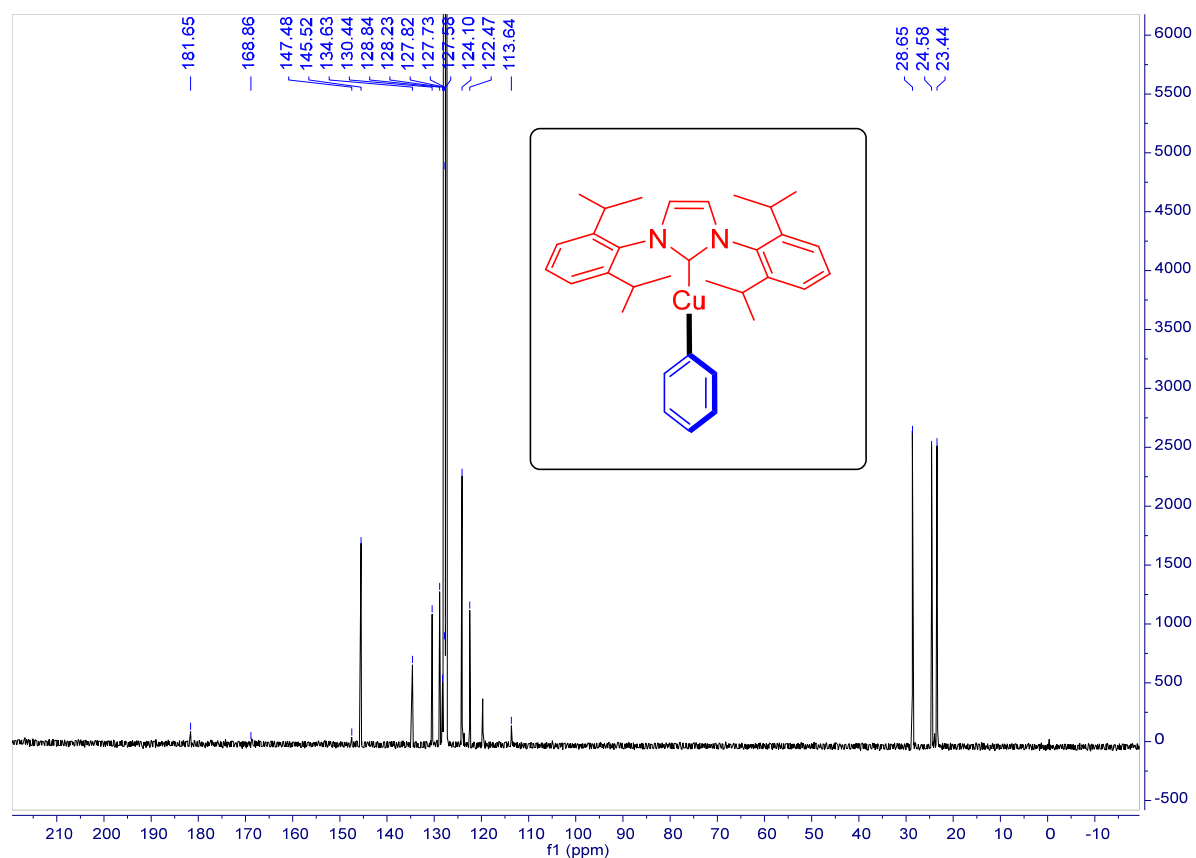
6.4 Carboxylation reaction with Cu-aryl complex



^1H NMR of $[\text{Cu}(\text{IPr})(\text{Ph})]$ complex in $\text{THF-}D_8$

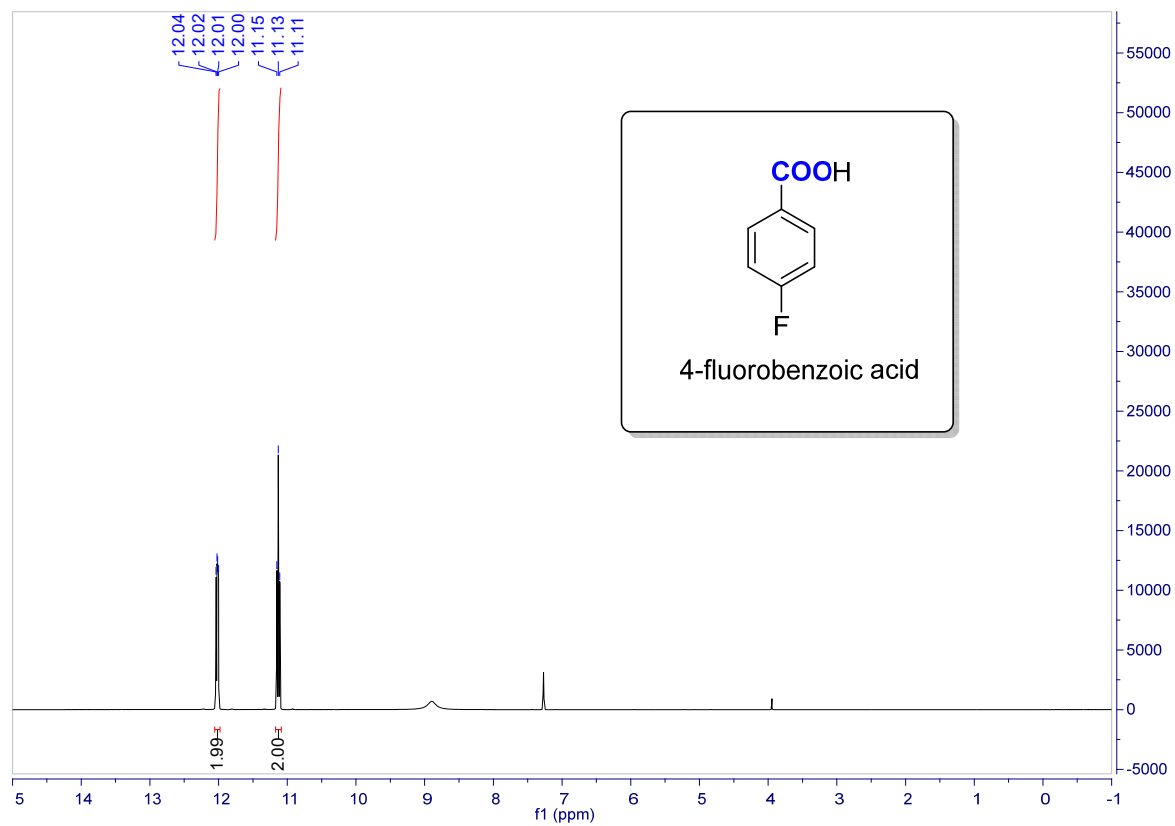


^{13}C NMR of $[\text{Cu}(\text{IPr})(\text{Ph})]$ complex in C_6D_6

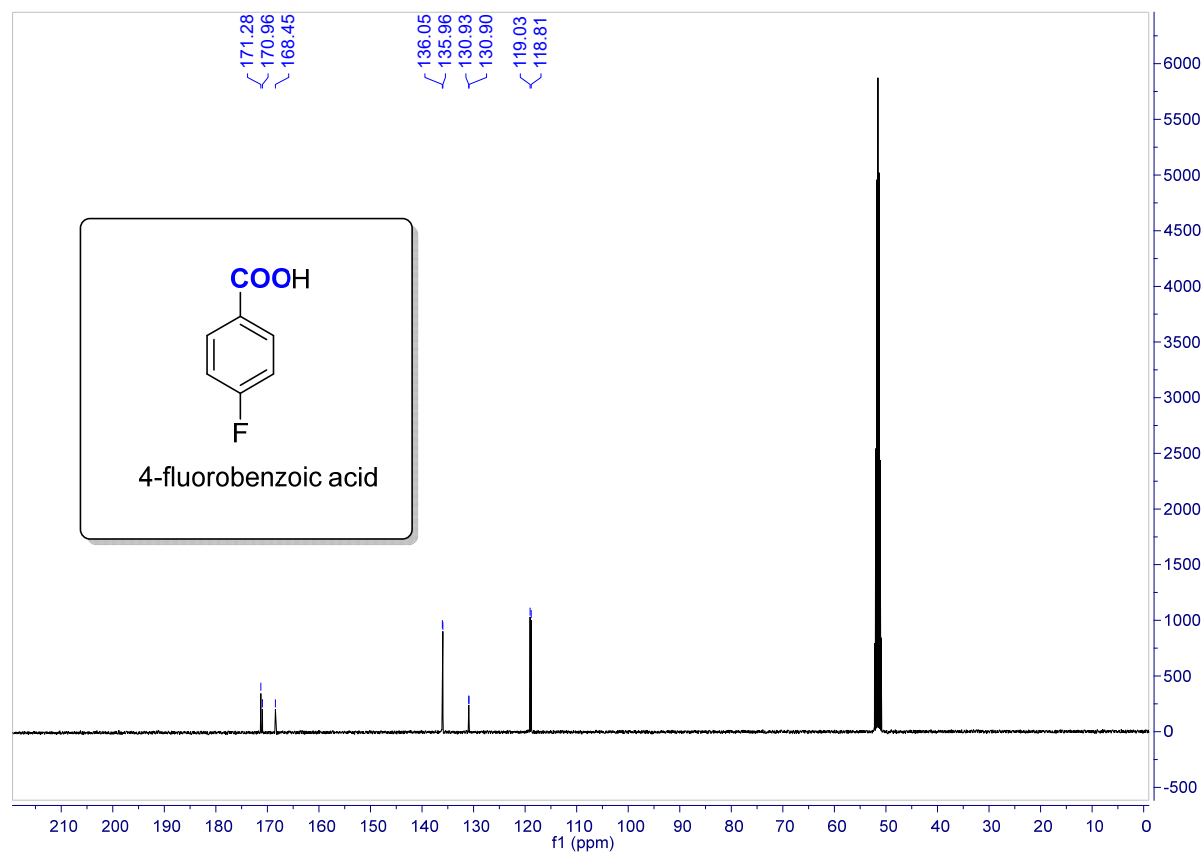


7.0 ^1H and ^{13}C NMR spectra copy of synthesized compounds

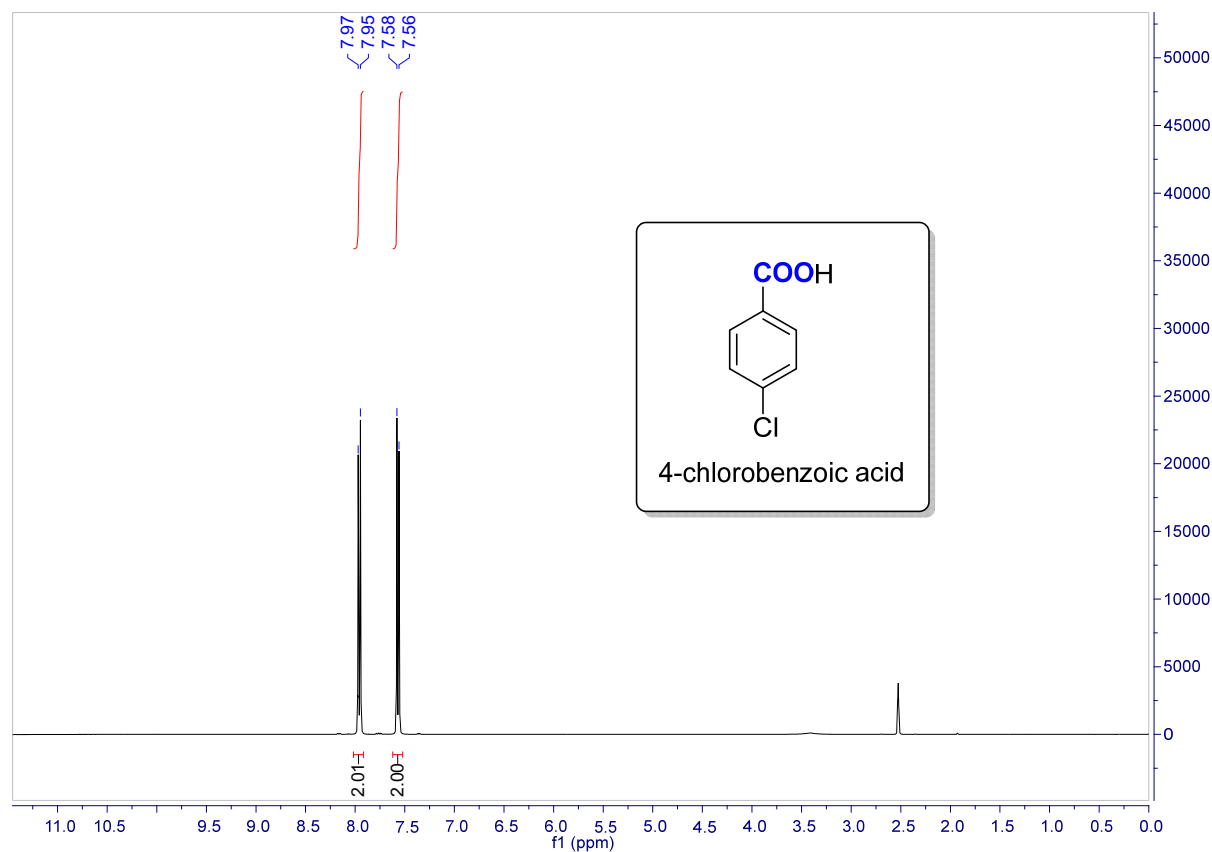
^1H NMR of 4-fluorobenzoic acid (2a)



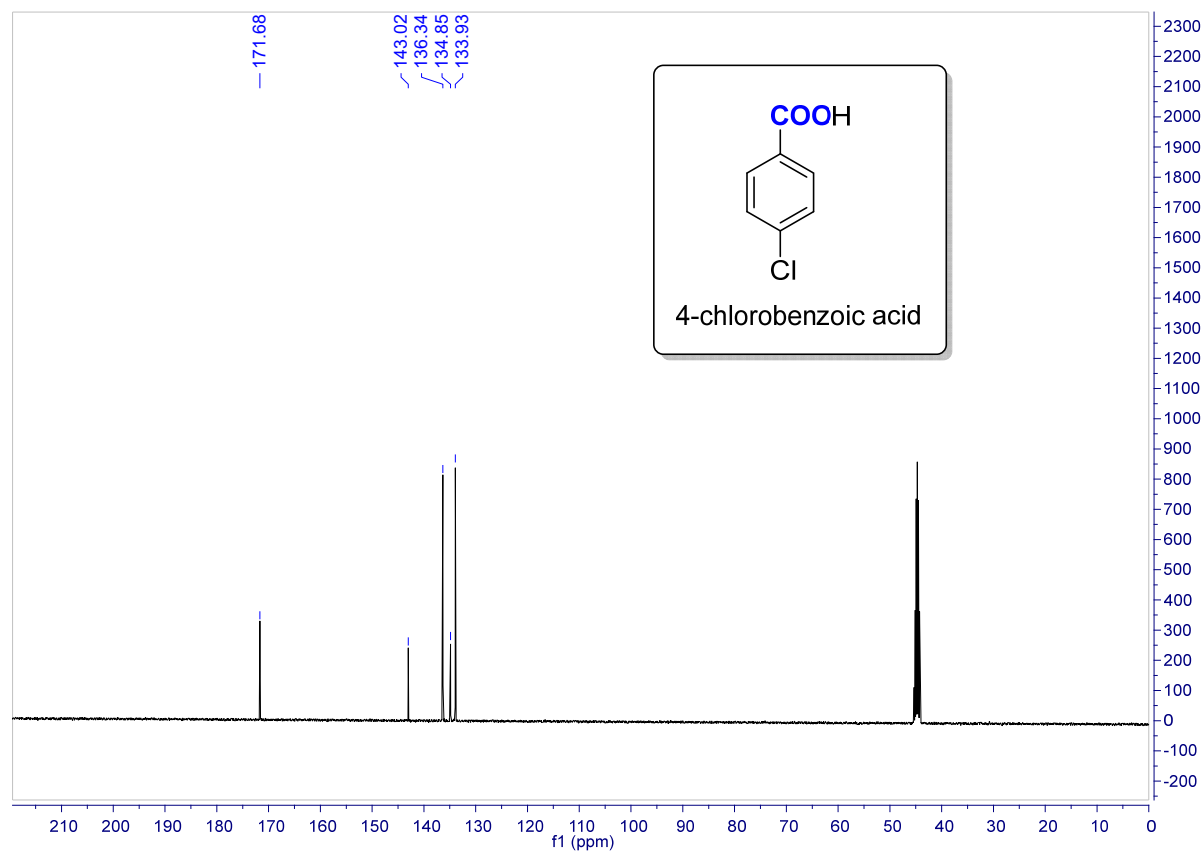
^{13}C NMR of 4-fluorobenzoic acid (2a)



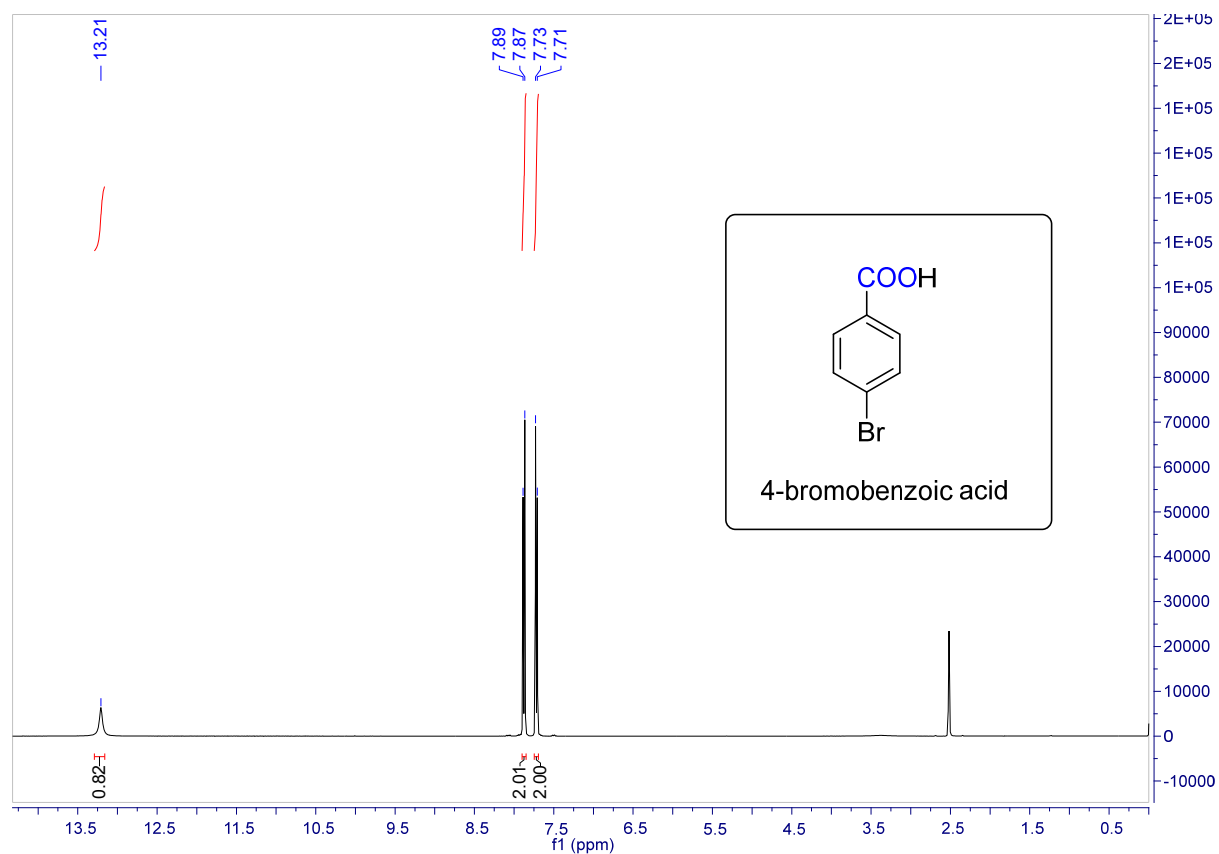
¹H NMR of 4-chlorobenzoic acid (2b)



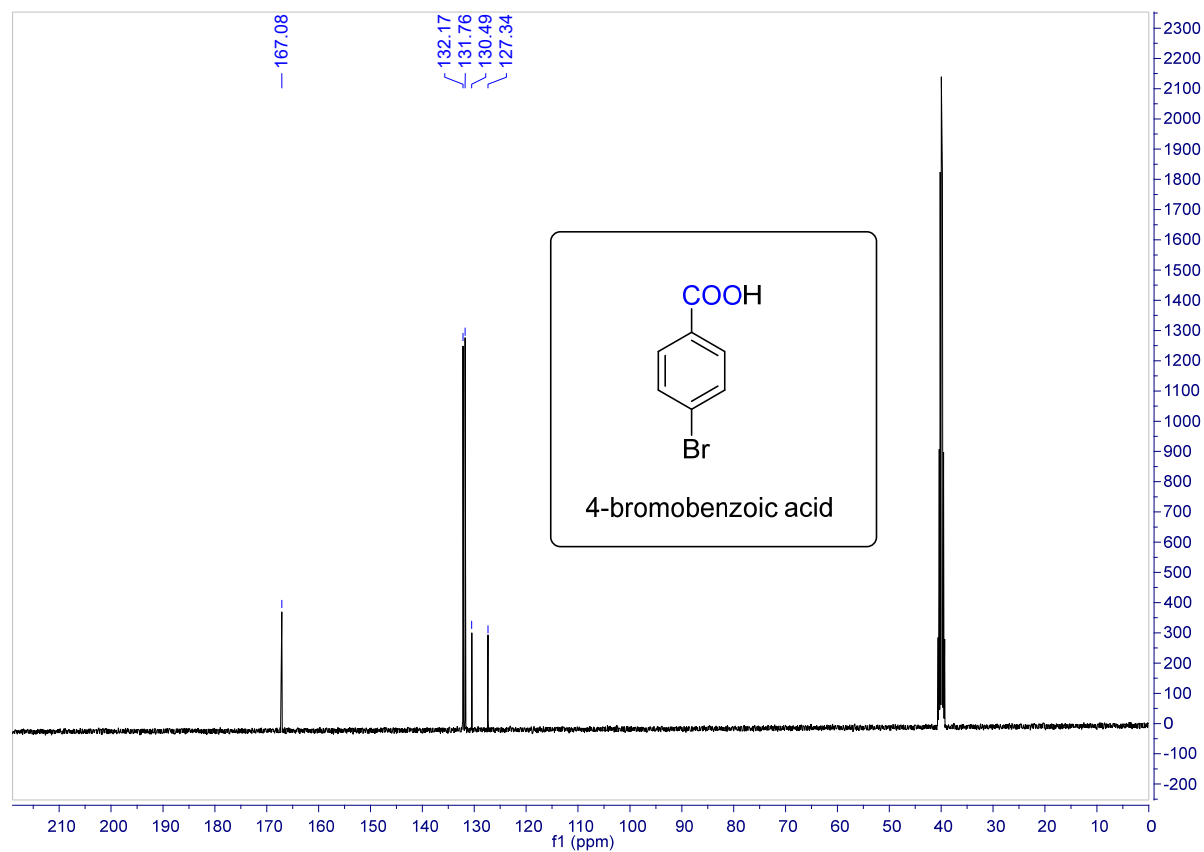
¹³C NMR of 4-chlorobenzoic acid (2b)



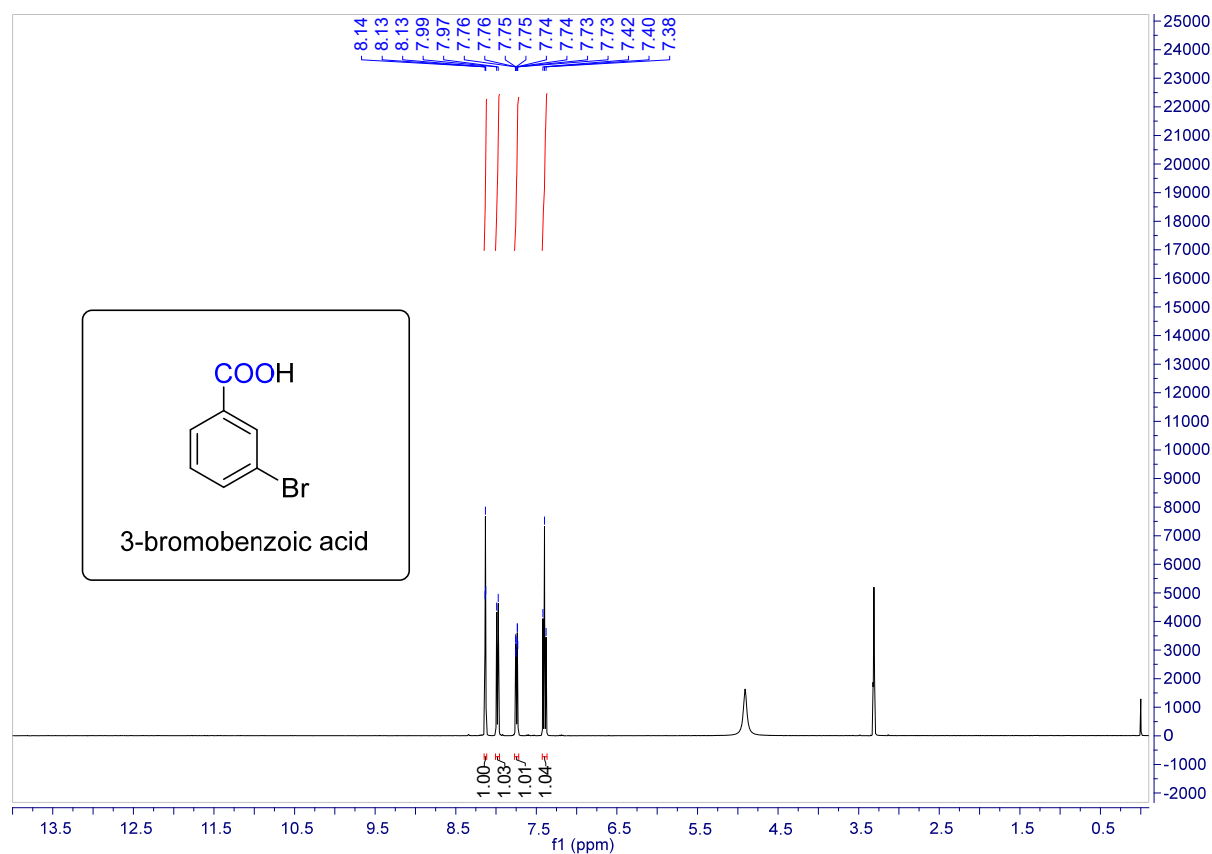
¹H NMR of 4-bromobenzoic acid (2c)



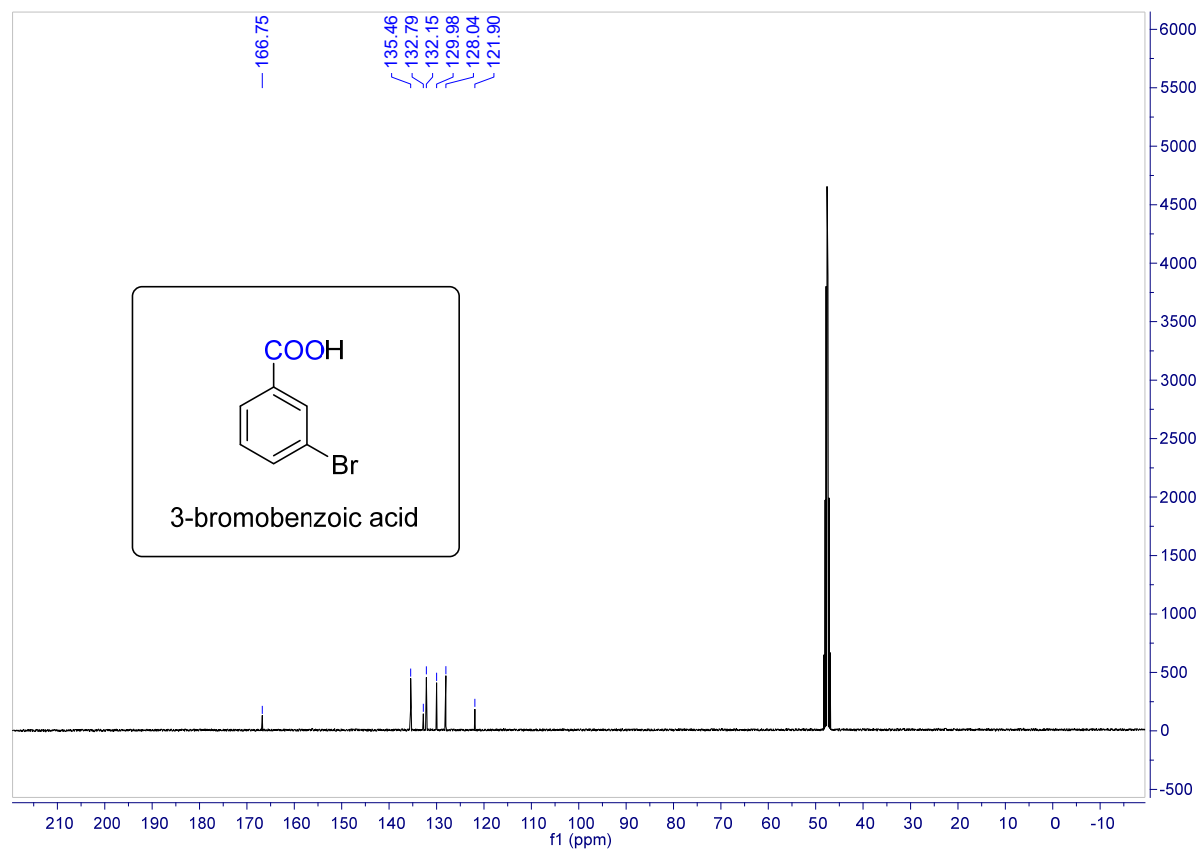
¹³C NMR of 4-bromobenzoic acid (2c)



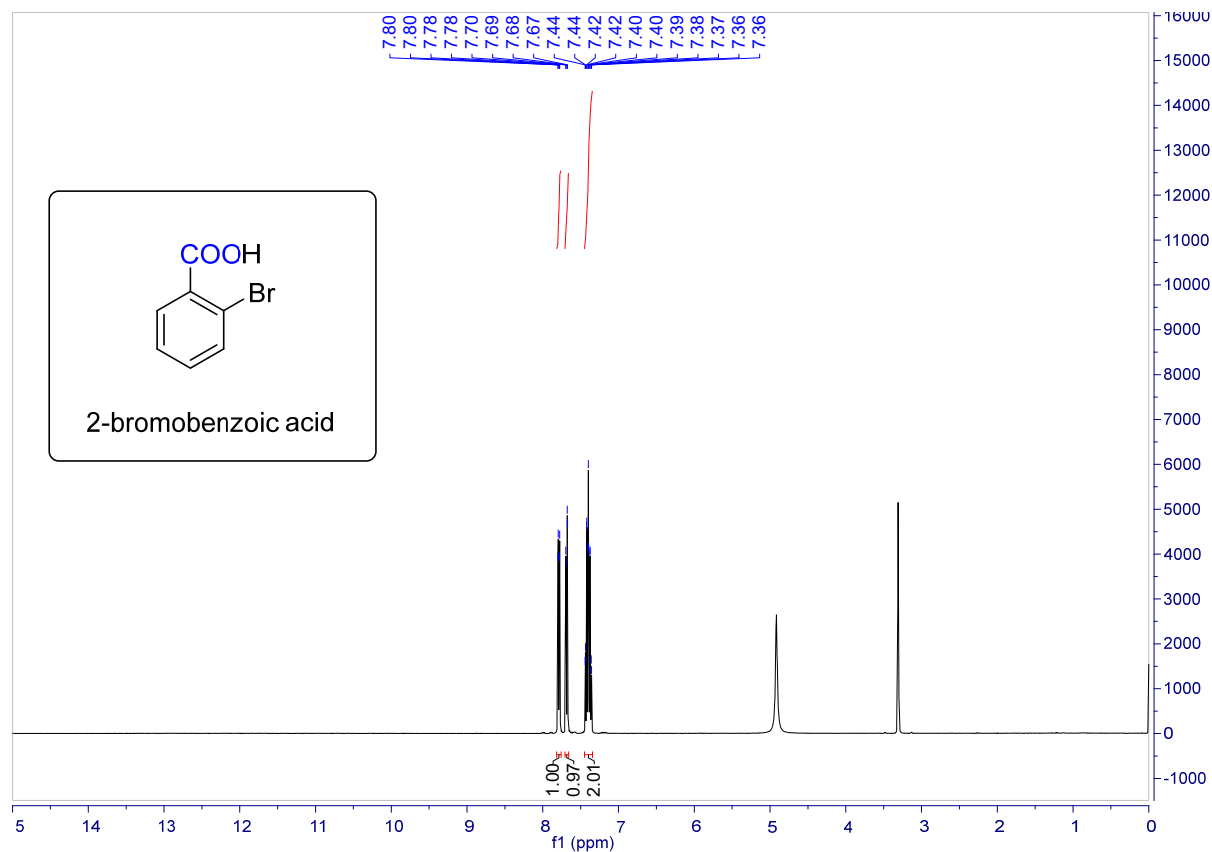
¹H NMR of 3-bromobenzoic acid (2d)



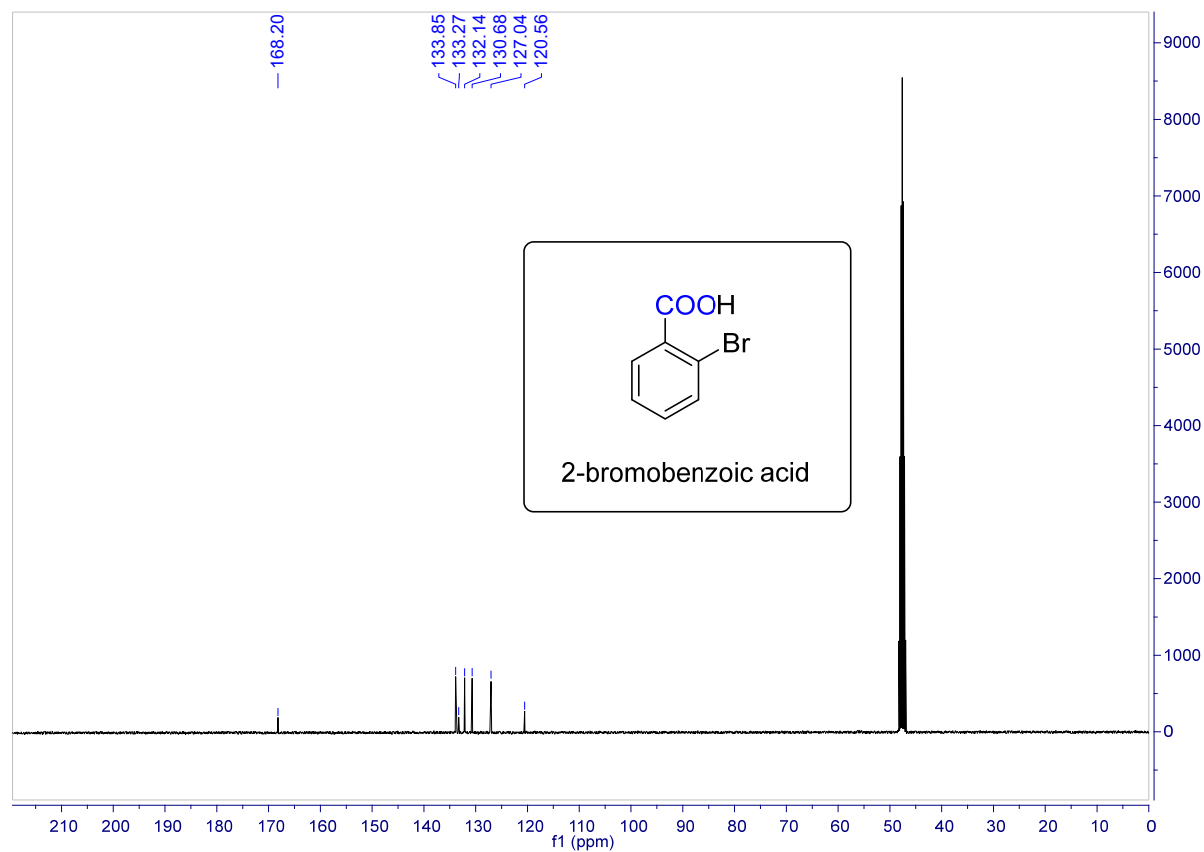
¹³C NMR of 3-bromobenzoic acid (2d)



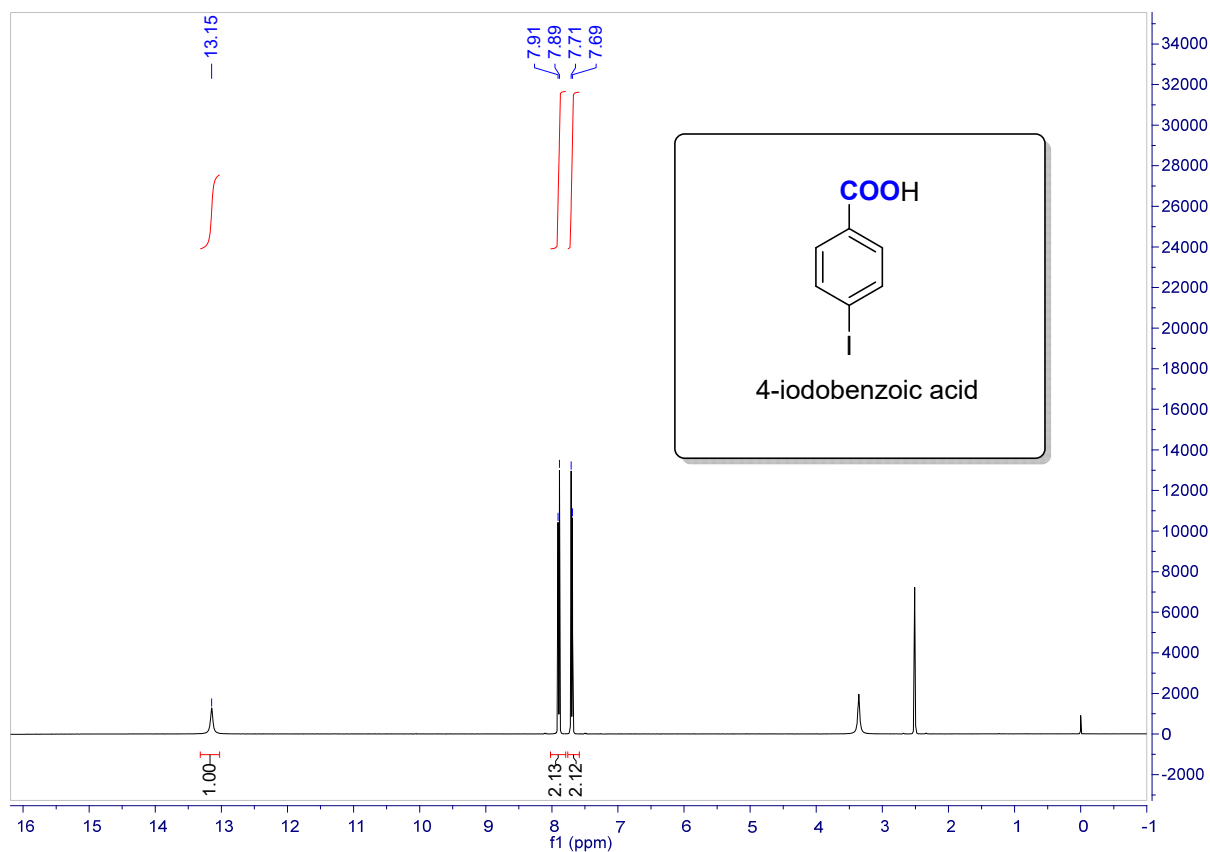
¹H NMR of 2-bromobenzoic acid (2e)



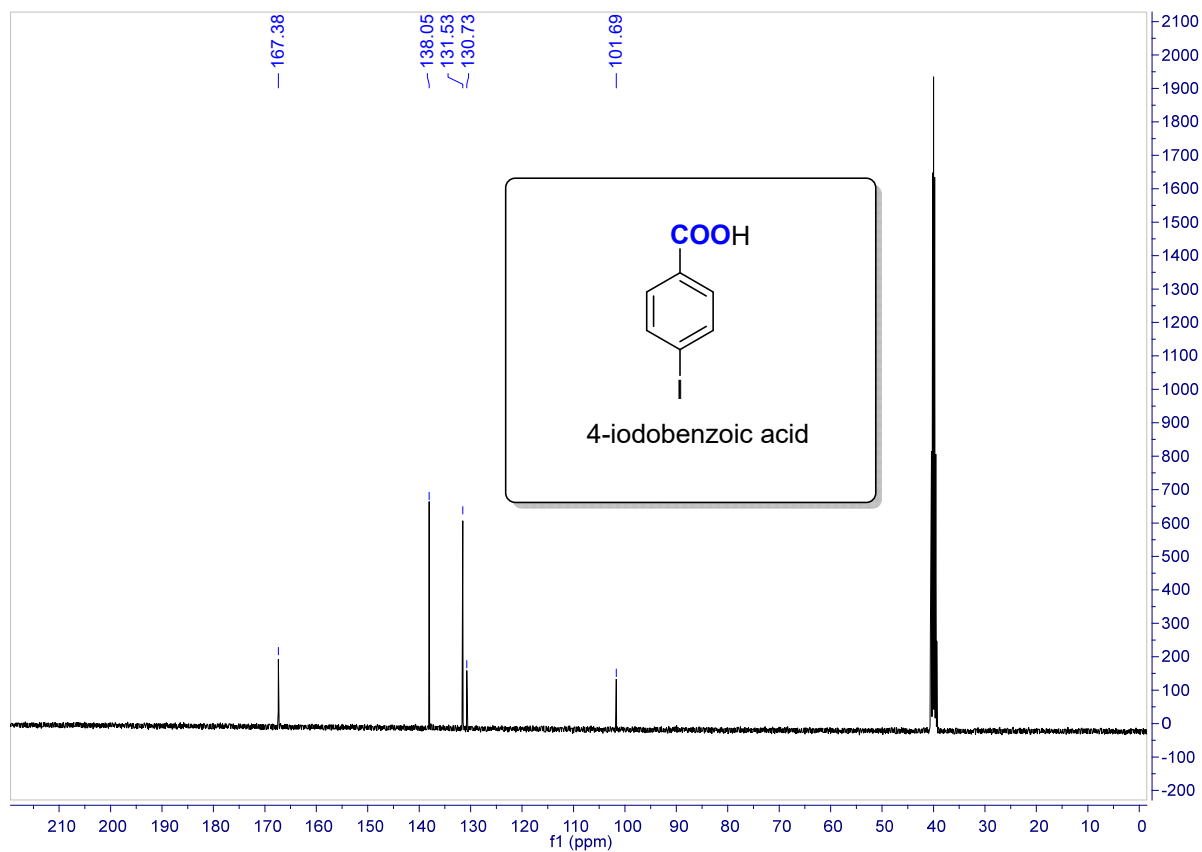
¹³C NMR of 2-bromobenzoic acid (2e)



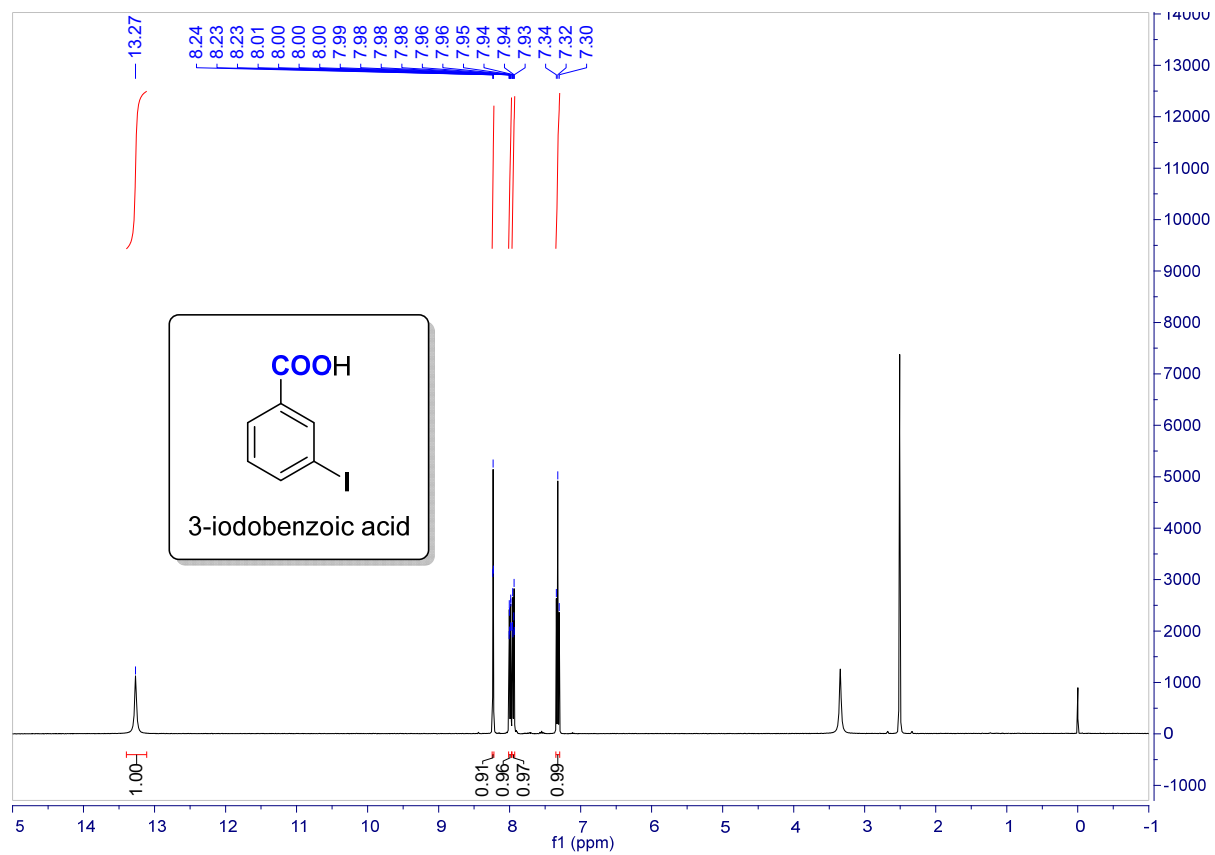
¹H NMR of 4-iodobenzoic acid (2f)



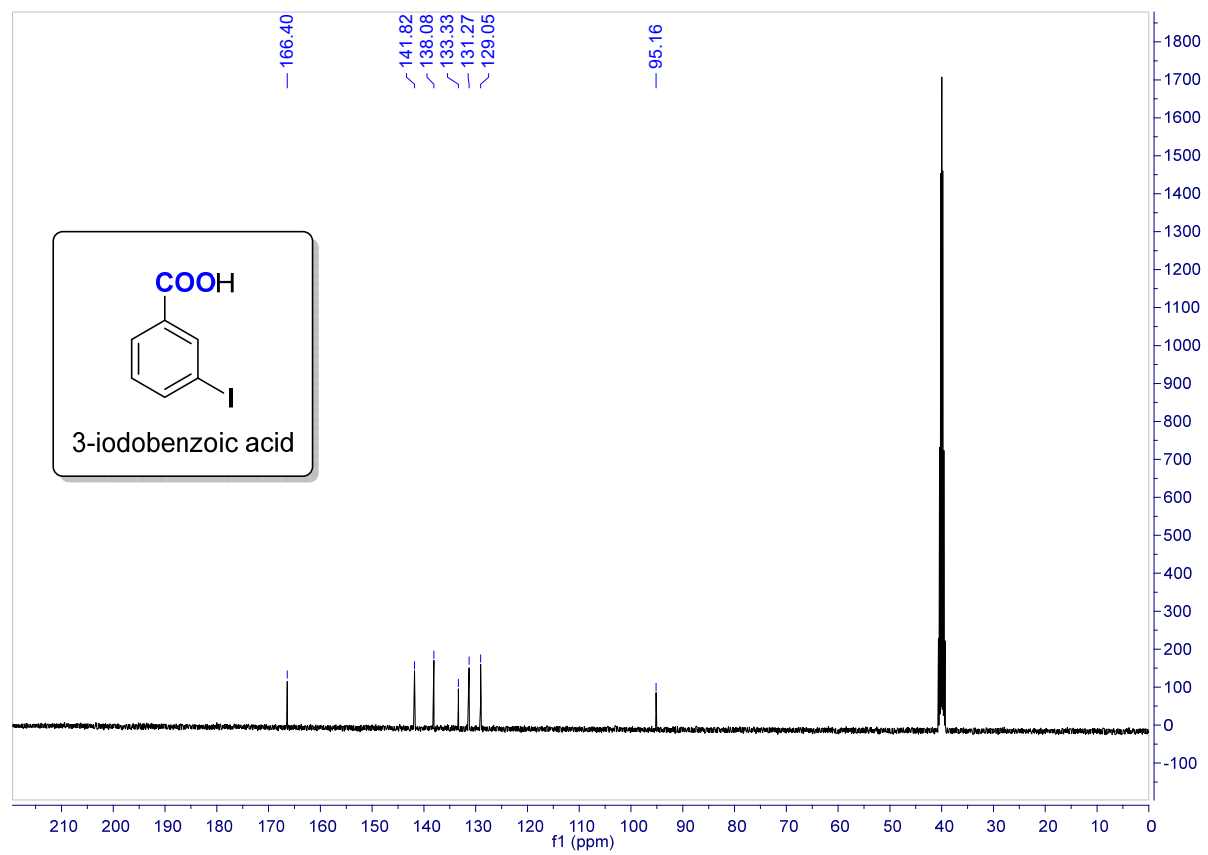
¹³C NMR of 4-iodobenzoic acid (2f)



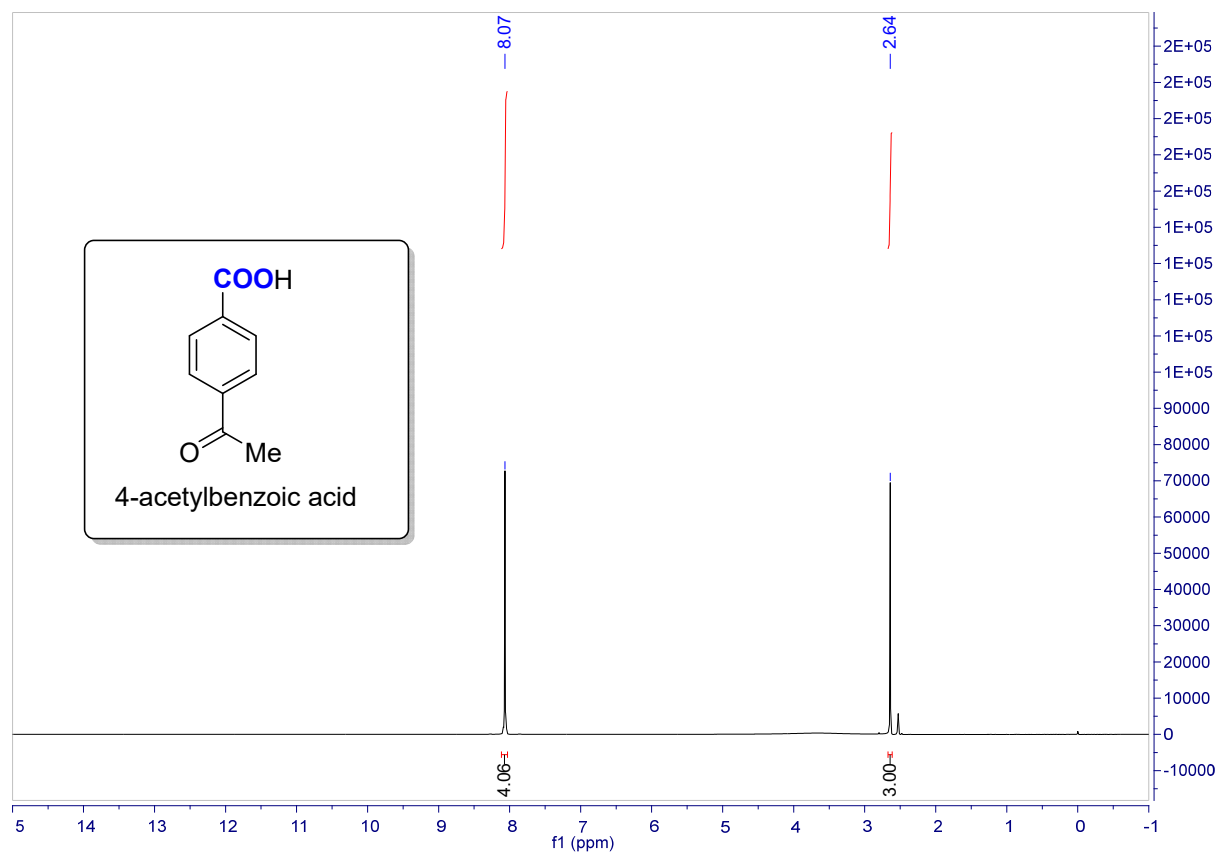
¹H NMR of 3-iodobenzoic acid (2g)



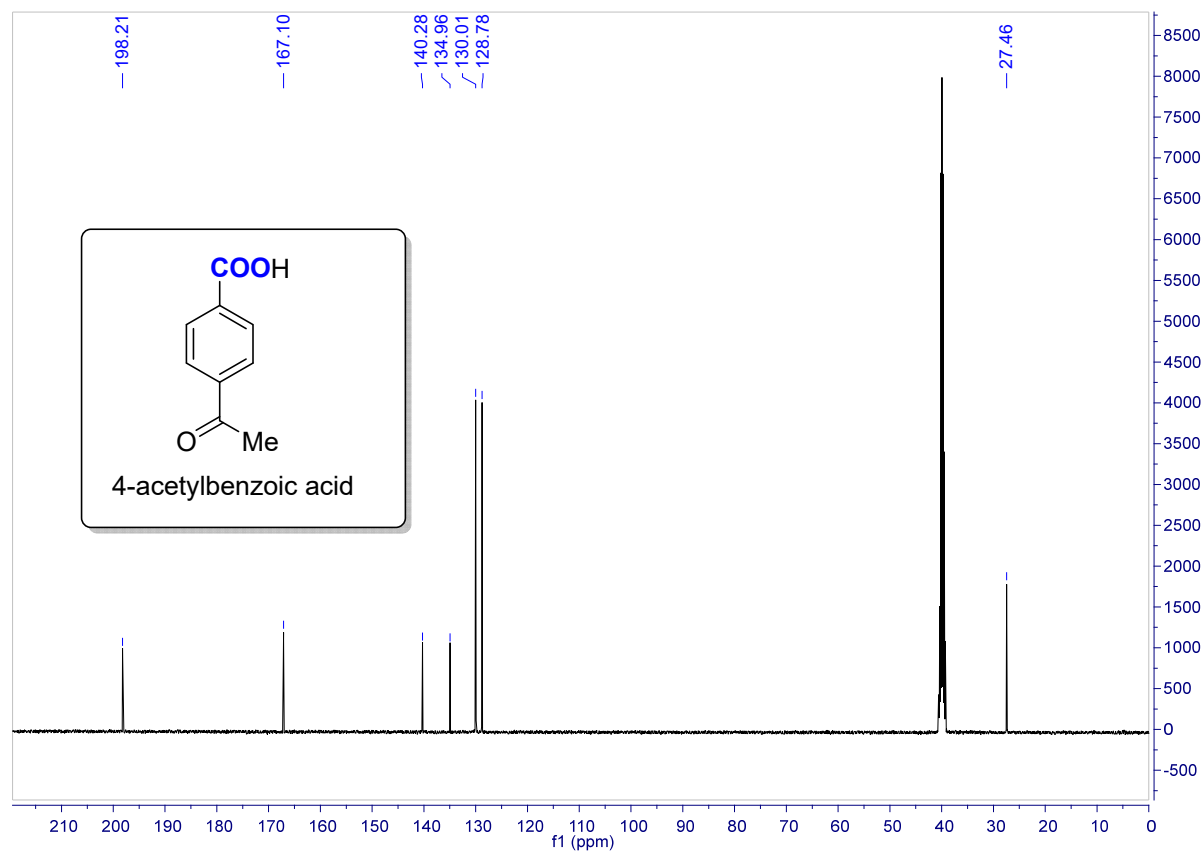
¹³C NMR of 3-iodobenzoic acid (2g)



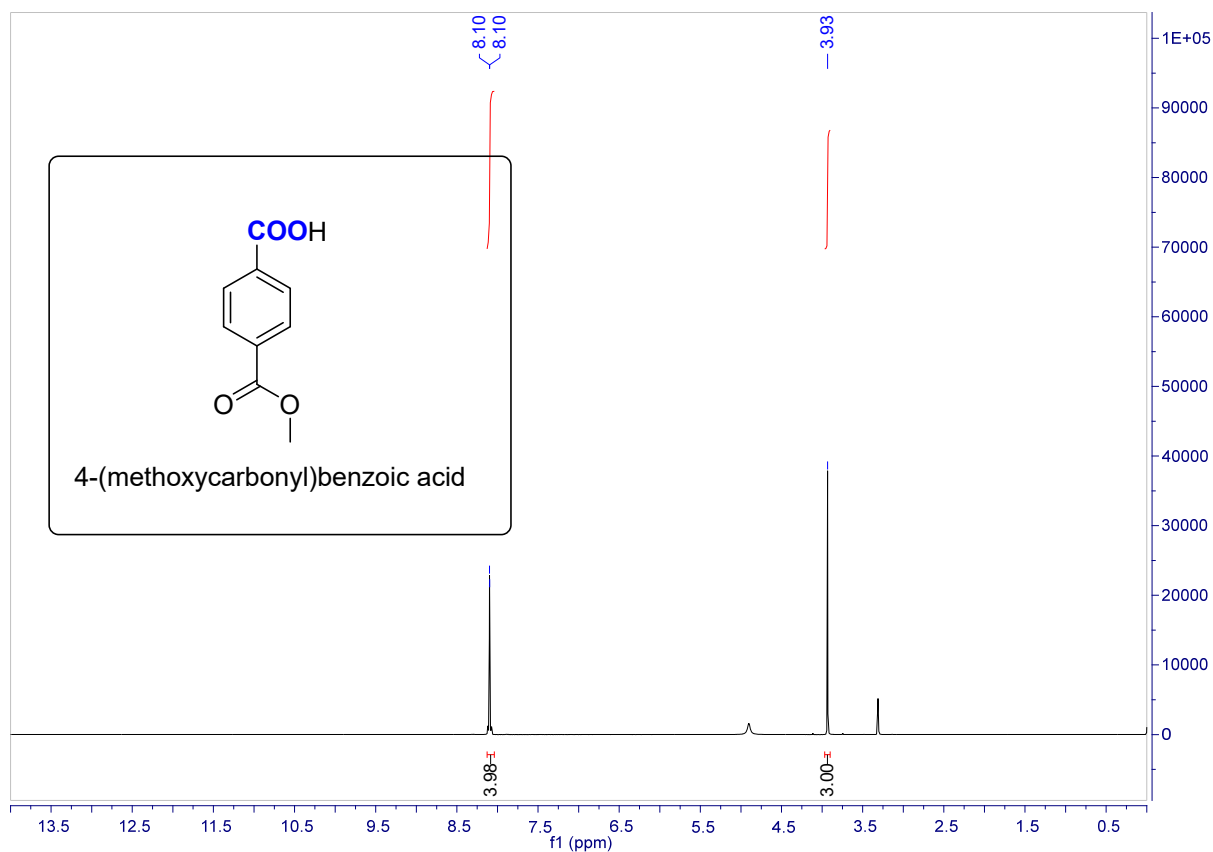
¹H NMR of 4-acetylbenzoic acid (2h)



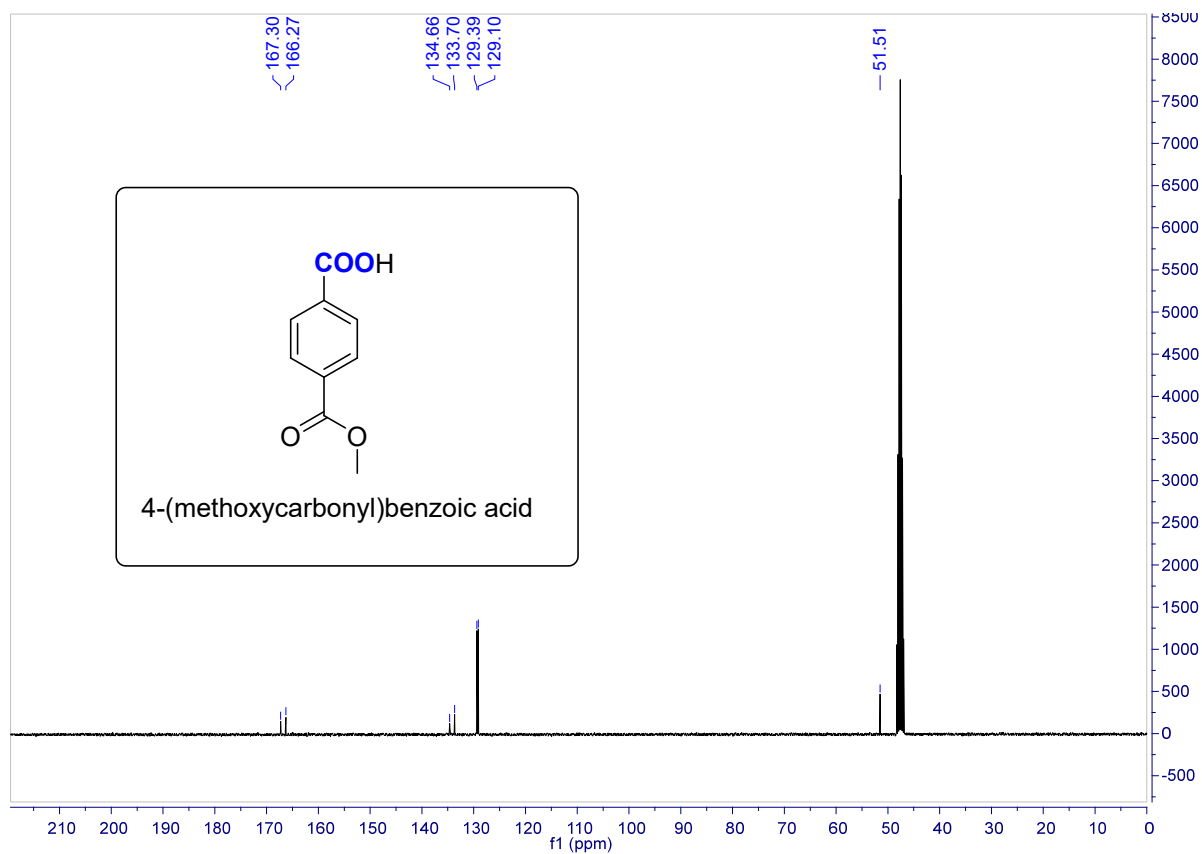
¹³C NMR of 4-acetylbenzoic acid (2h)



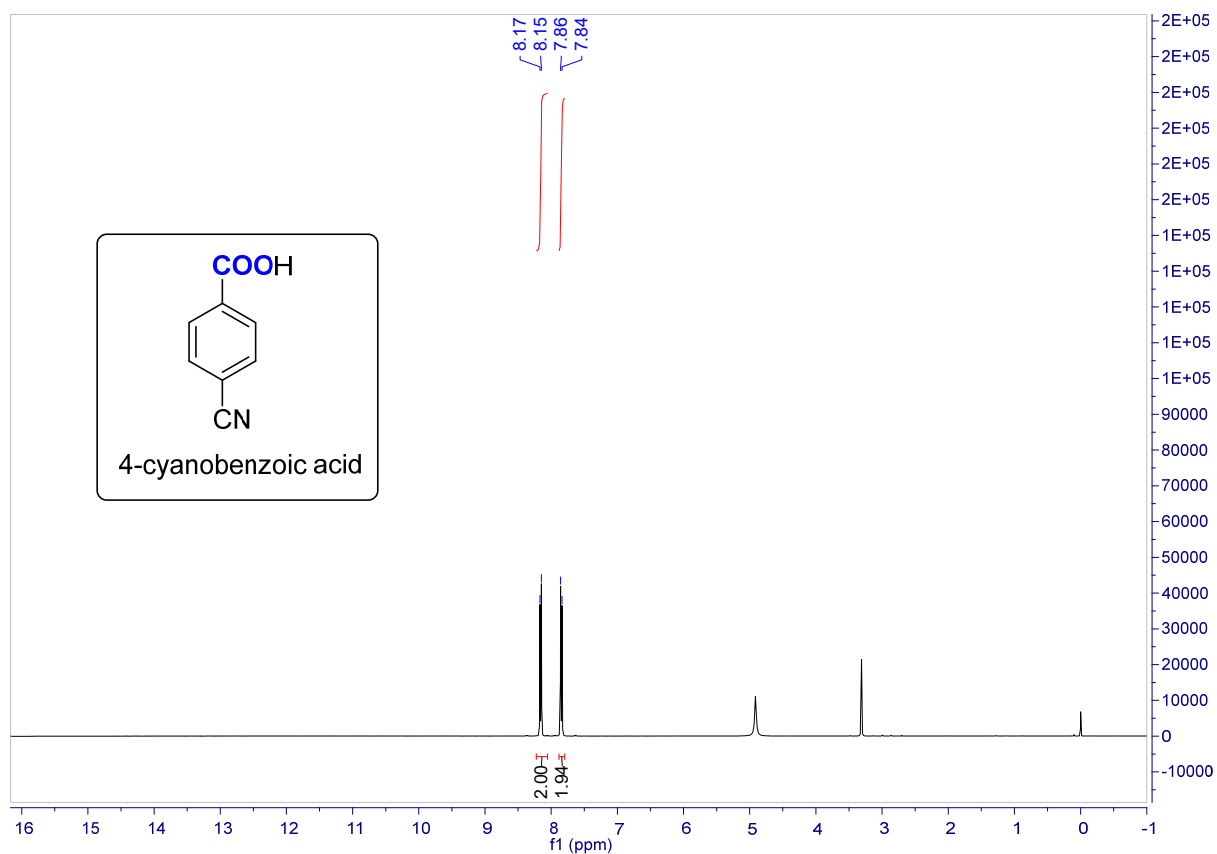
¹H NMR of 4-(methoxycarbonyl)benzoic acid (2i)



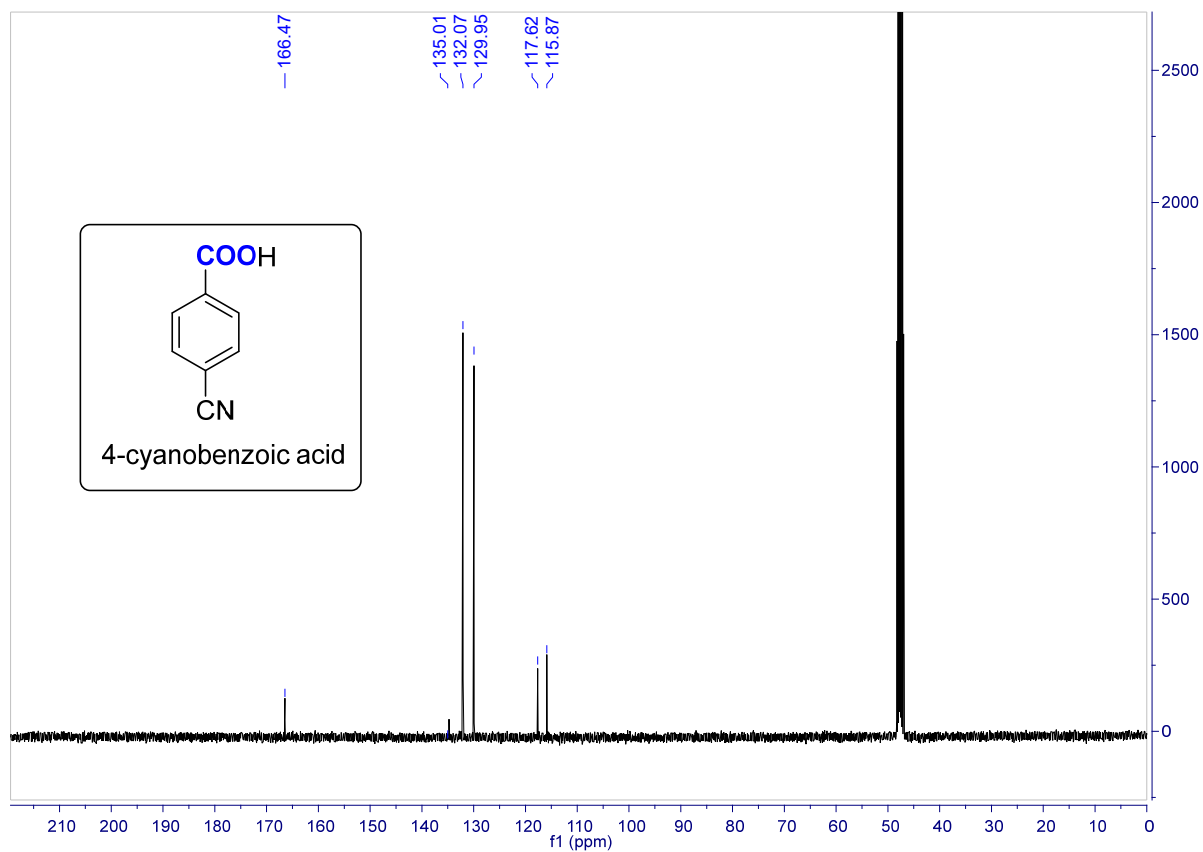
¹³C NMR of 4-(methoxycarbonyl)benzoic acid (2i)



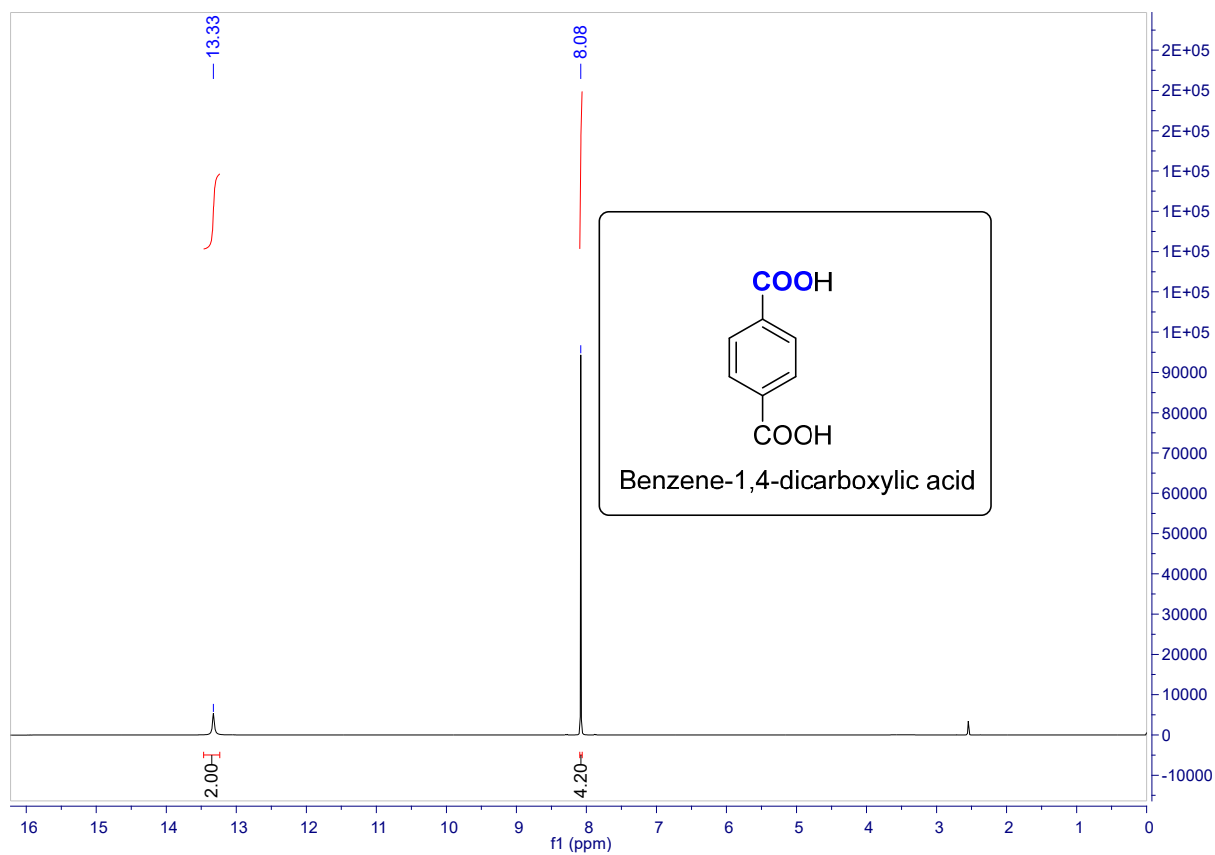
¹H NMR of 4-cyanobenzoic acid (2j)



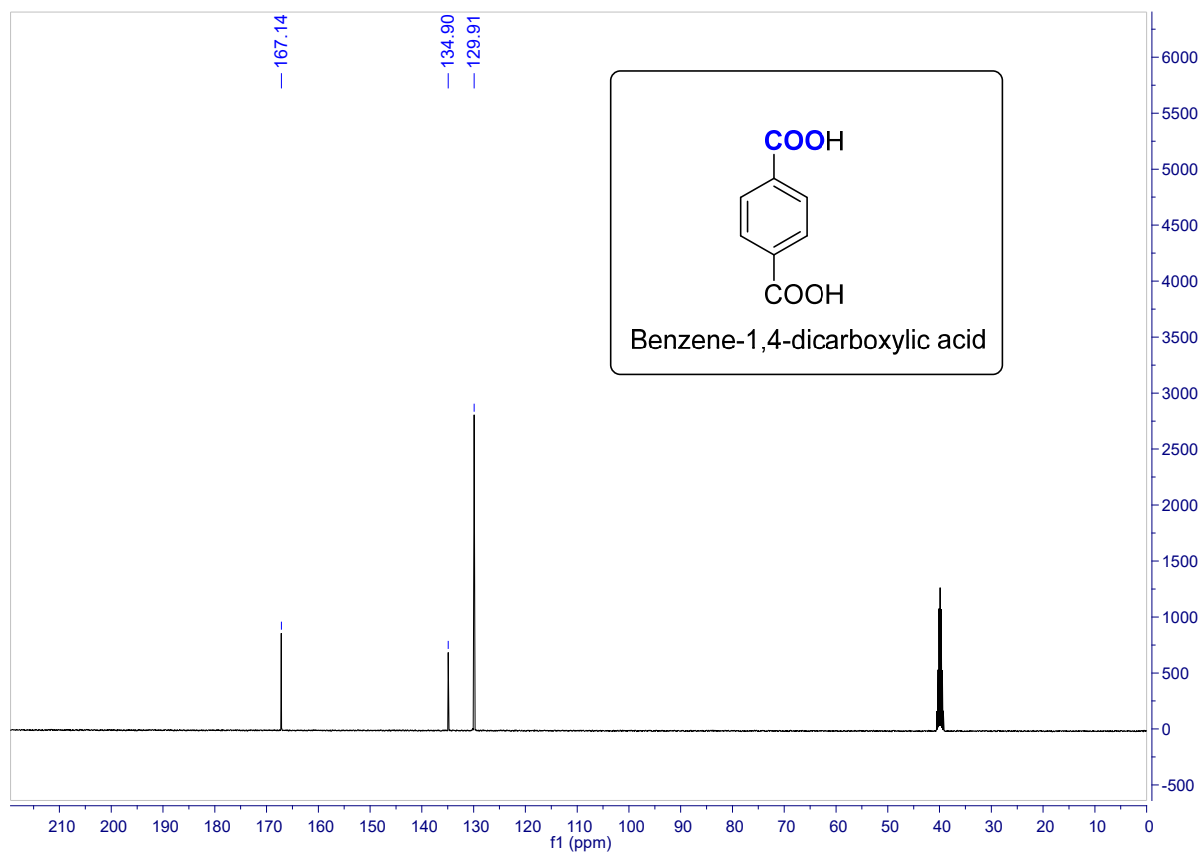
¹³C NMR of 4-cyanobenzoic acid (2j)



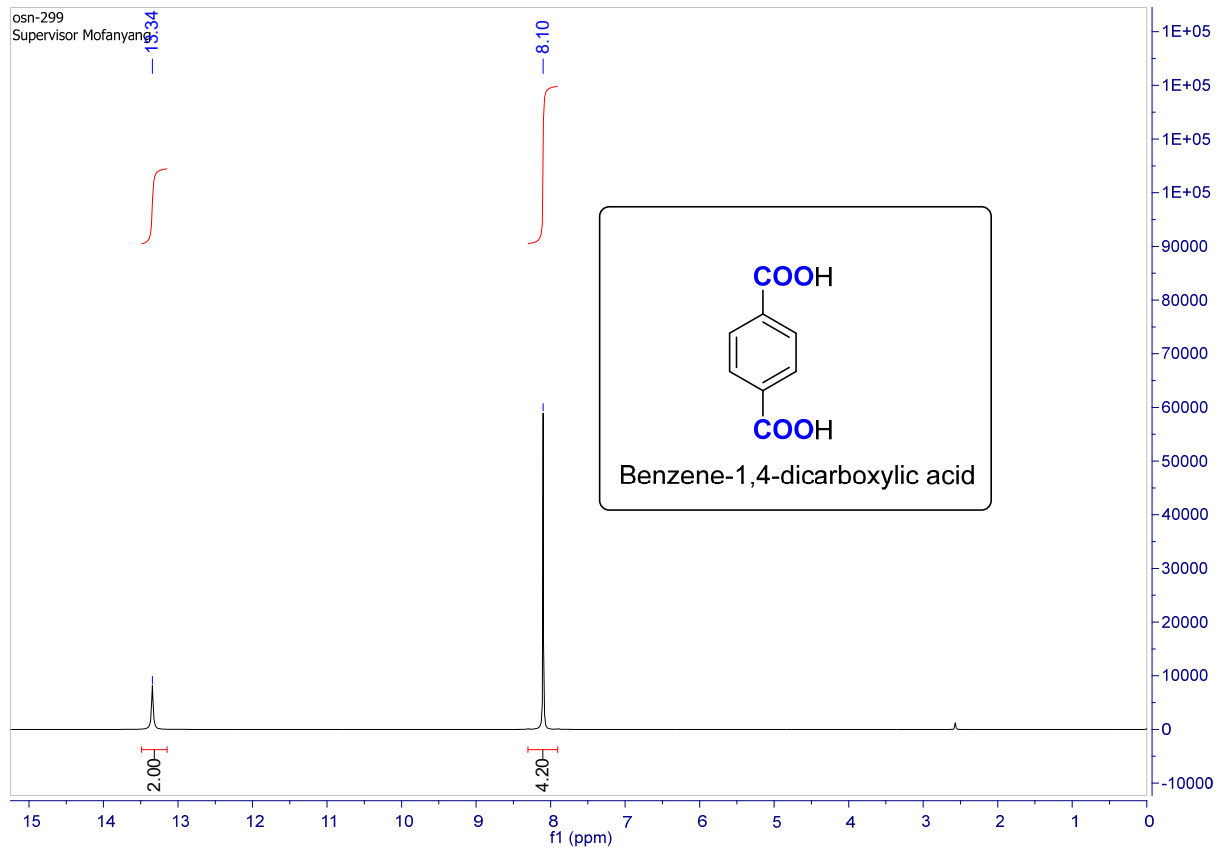
¹H NMR of Benzene-1,4-dicarboxylic acid (2k)



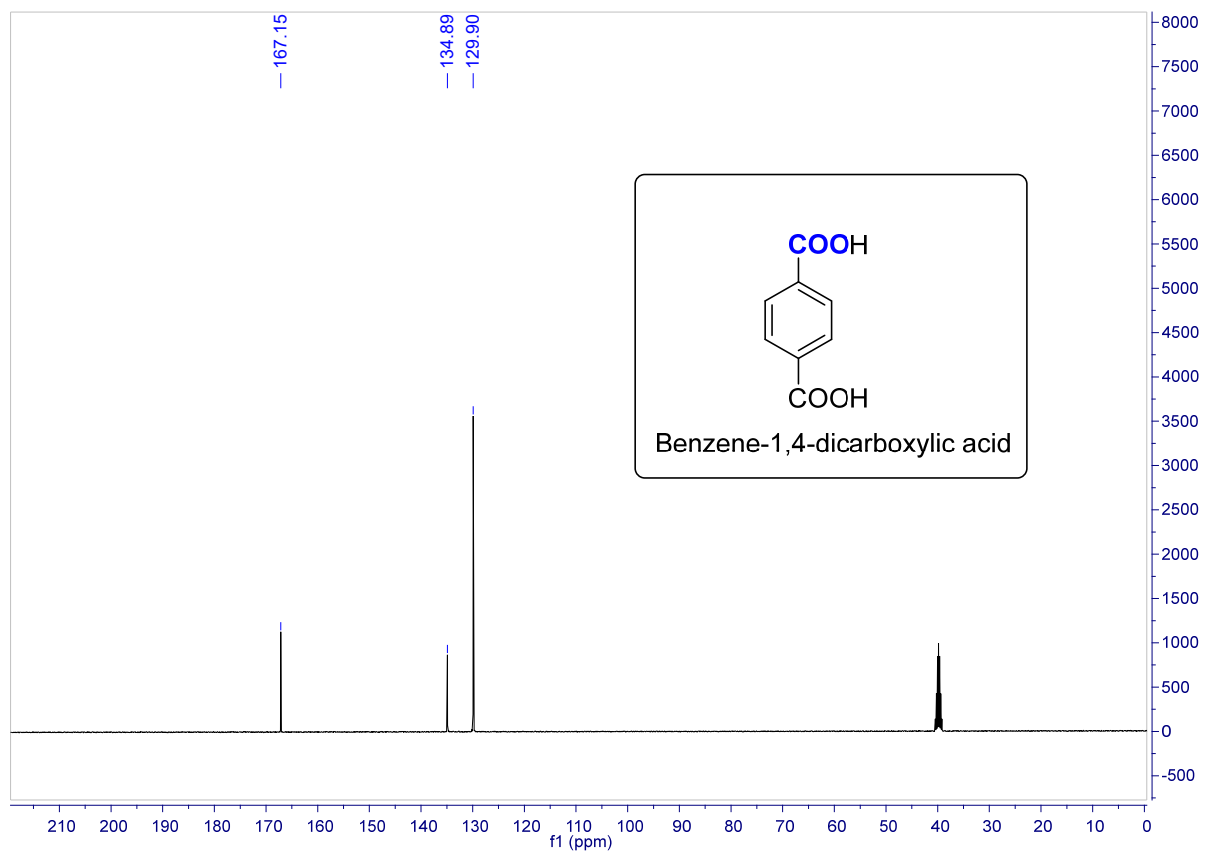
¹³C NMR of Benzene-1,4-dicarboxylic acid (2k)



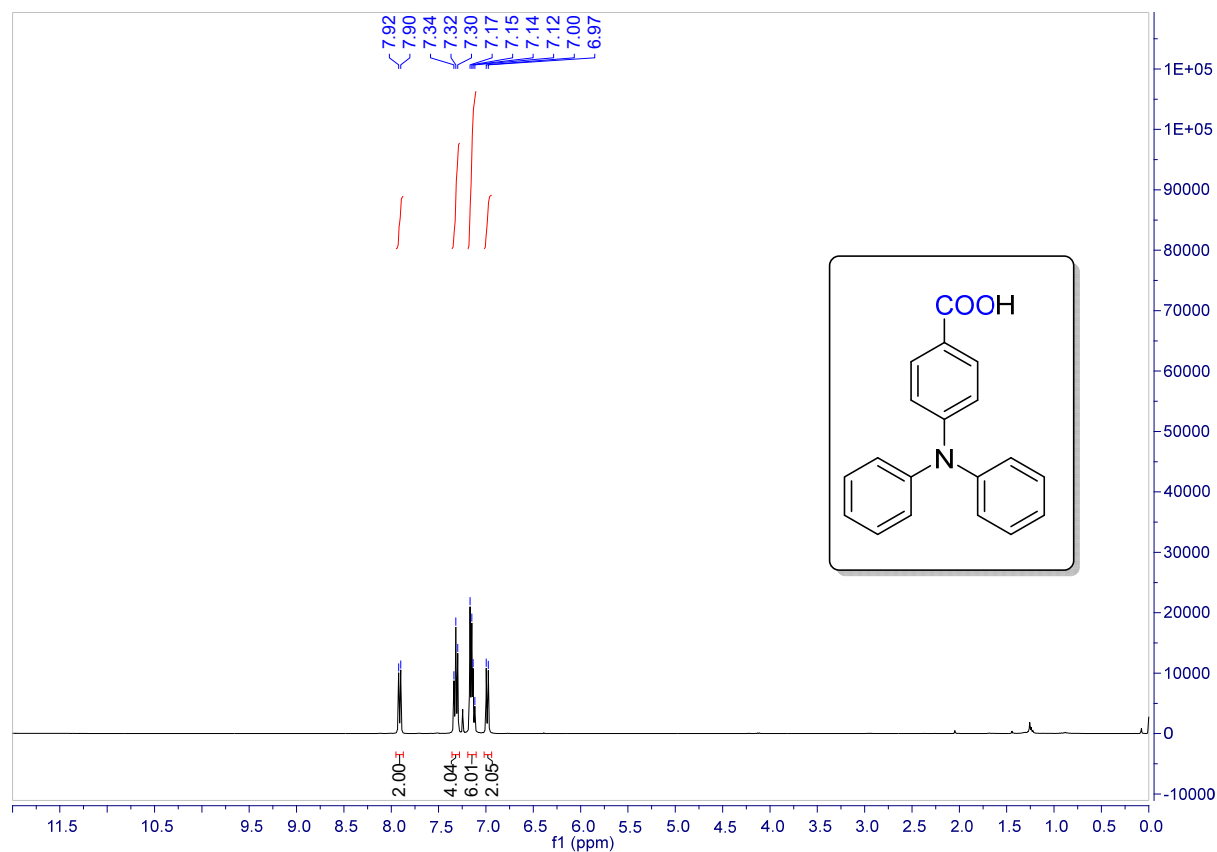
¹H NMR of Benzene-1,4-dicarboxylic acid (2I)



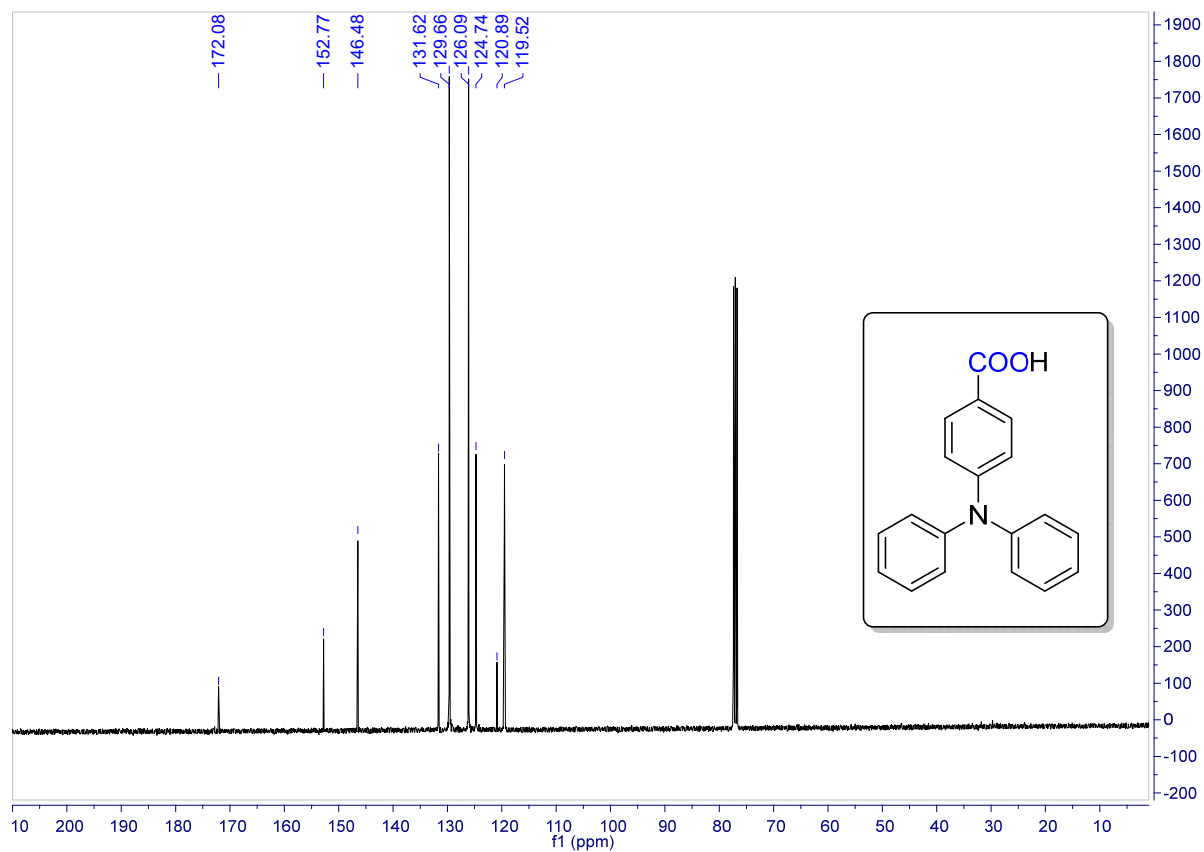
¹³C NMR of Benzene-1,4-dicarboxylic acid (2I)



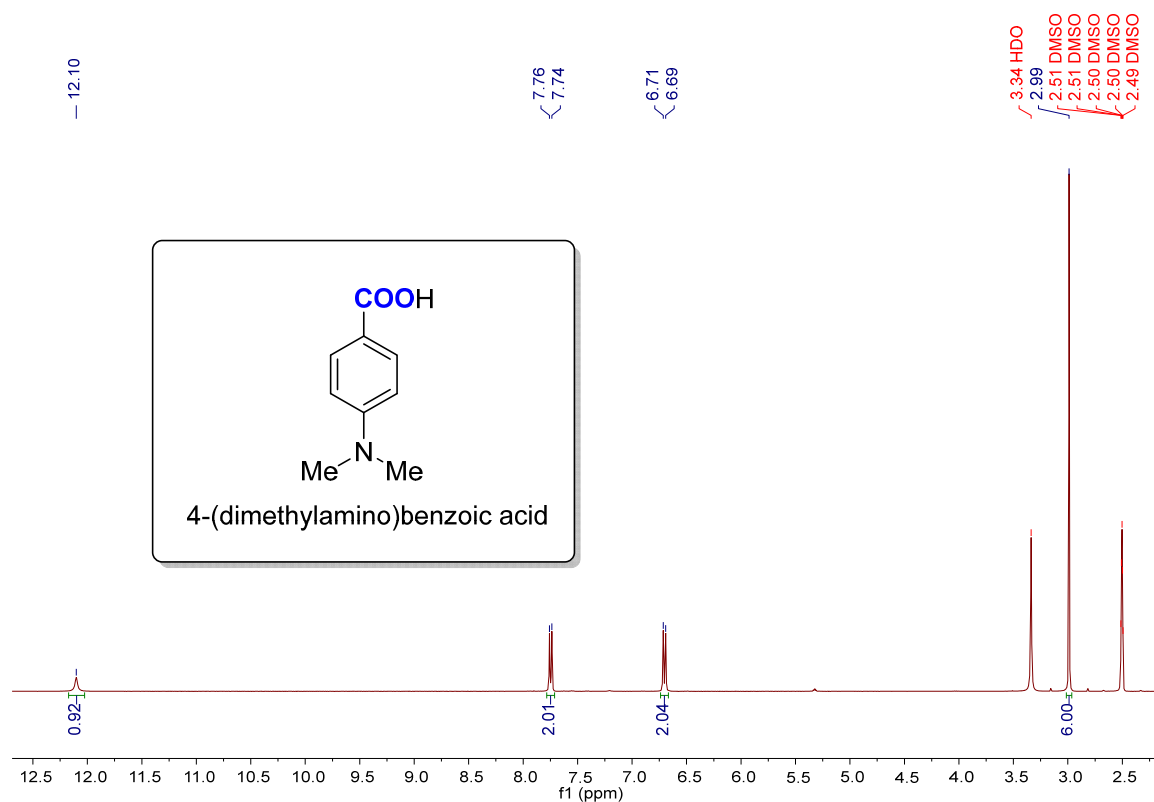
¹H NMR of 4-(Diphenylamino)benzoic acid (2m)



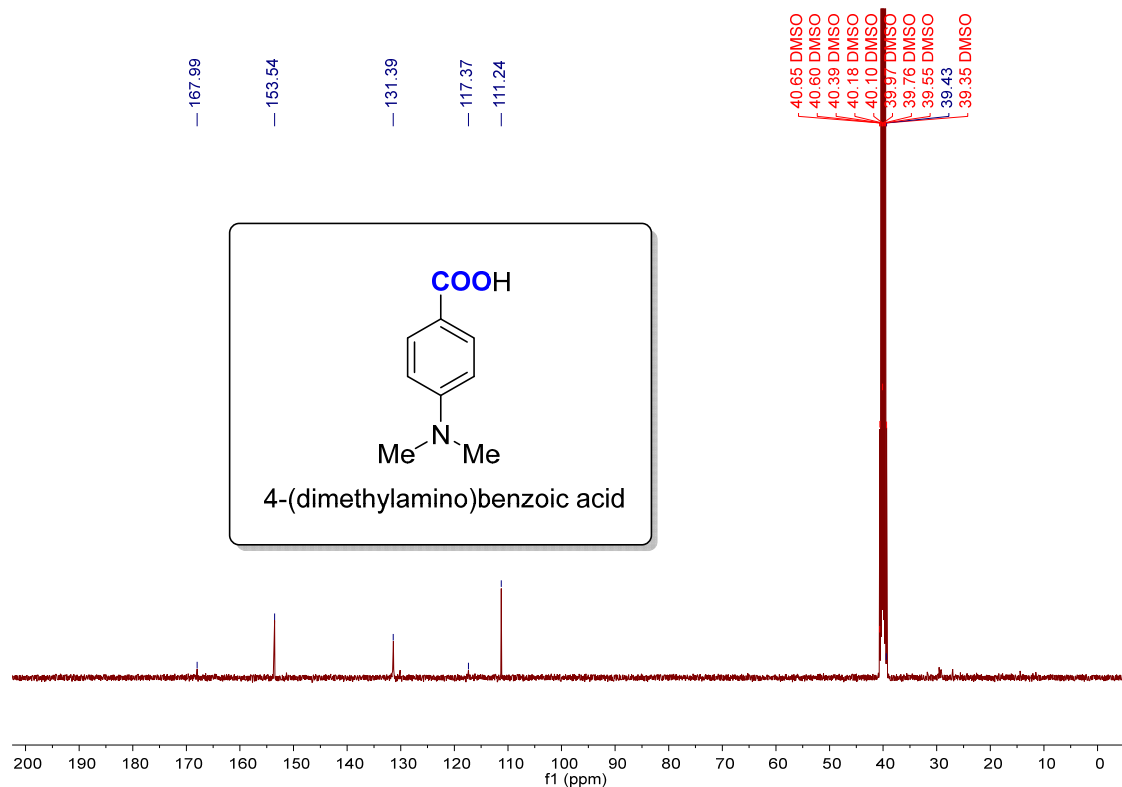
¹³C NMR of 4-(Diphenylamino)benzoic acid (2m)



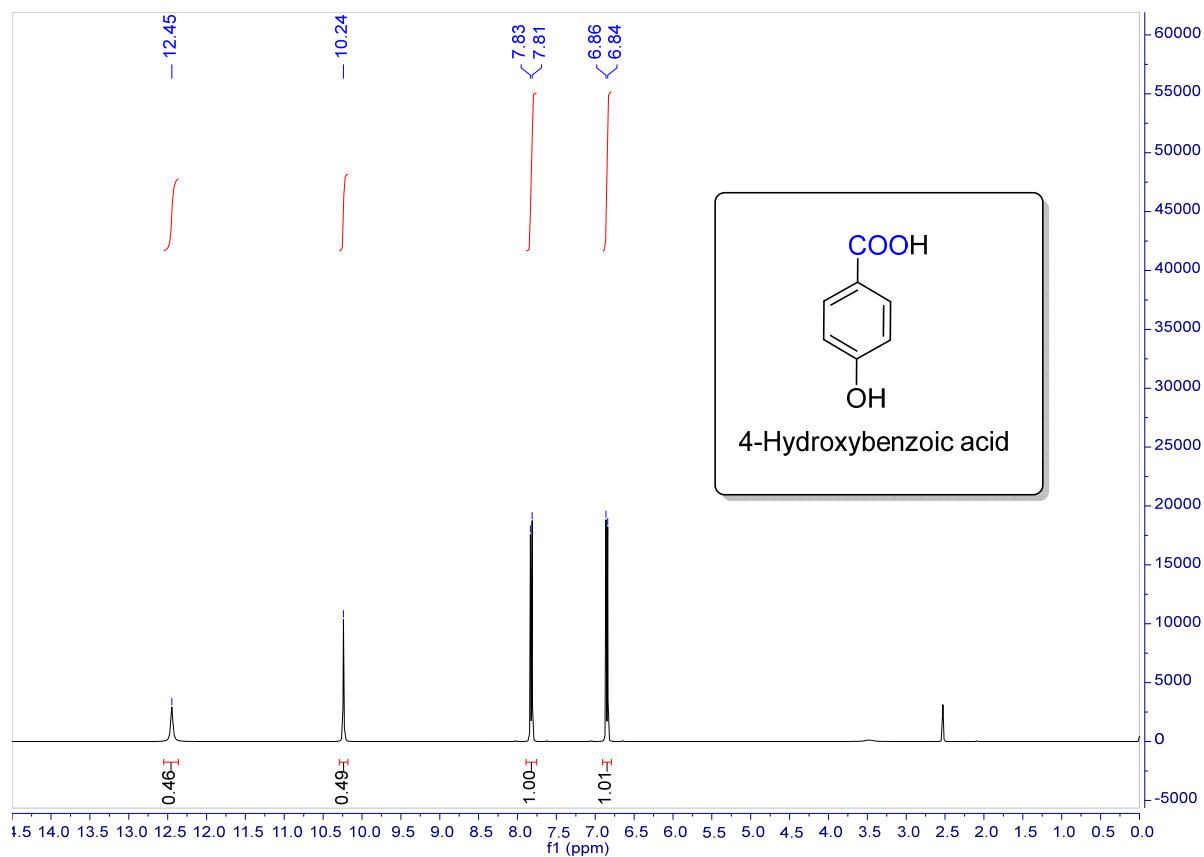
^1H NMR of *p*-*N,N*-dimethylaminobenzoic acid (2n)



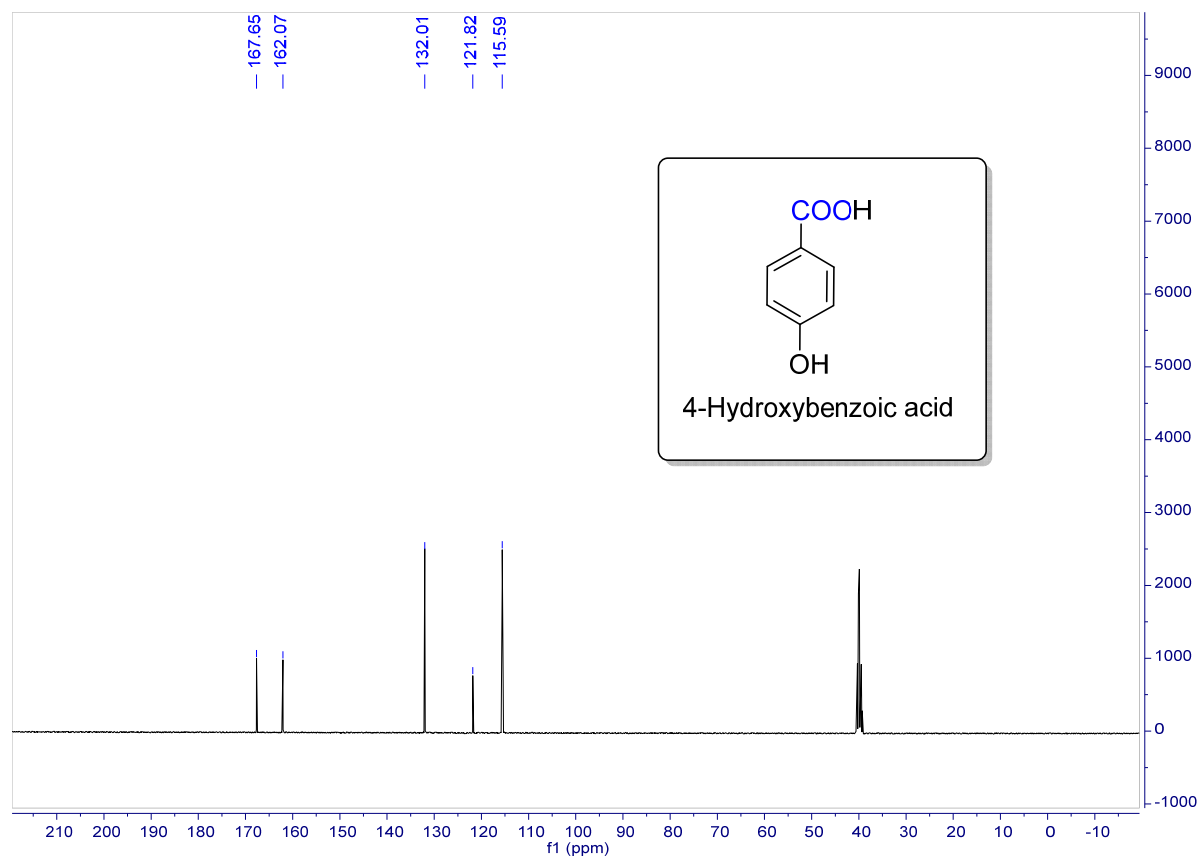
^{13}C NMR of *p*-*N,N*-dimethylaminobenzoic acid (2n)



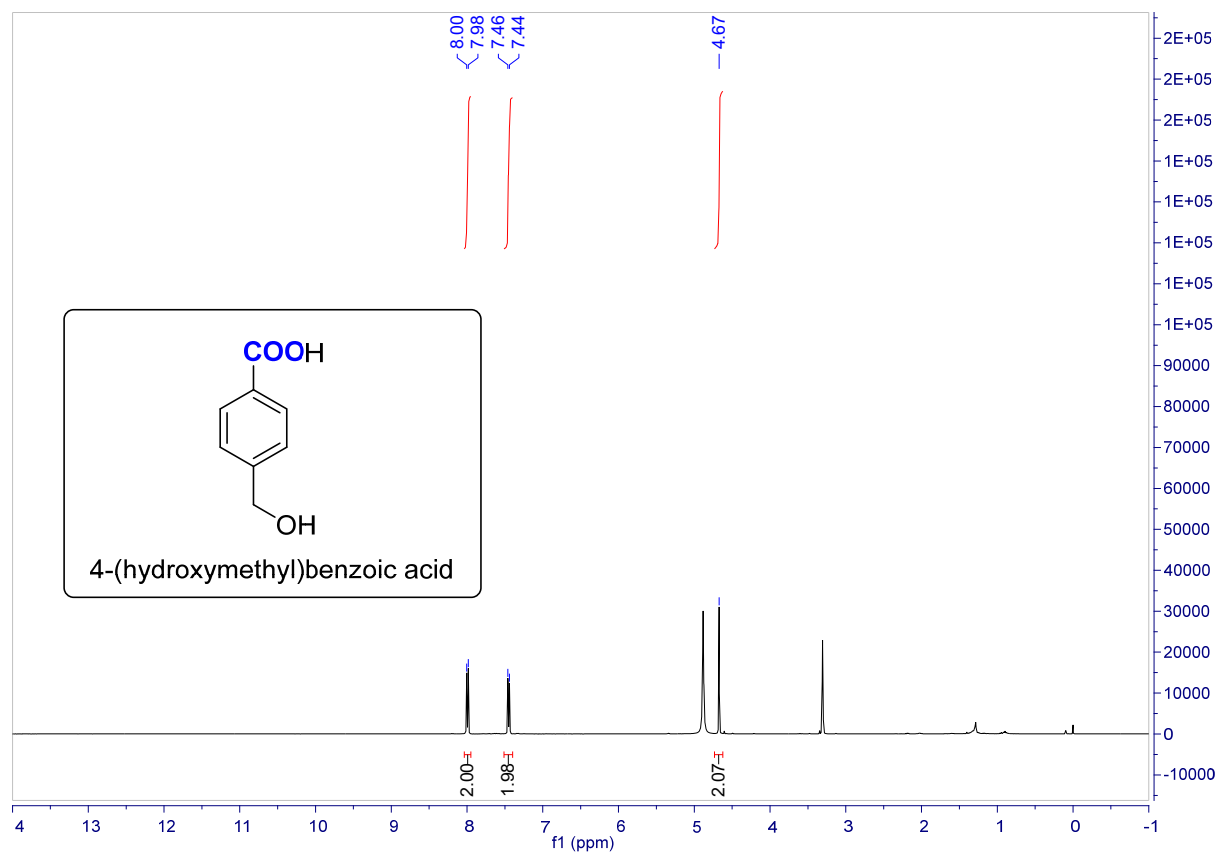
¹H NMR of 4-hydroxybenzoic acid (2o)



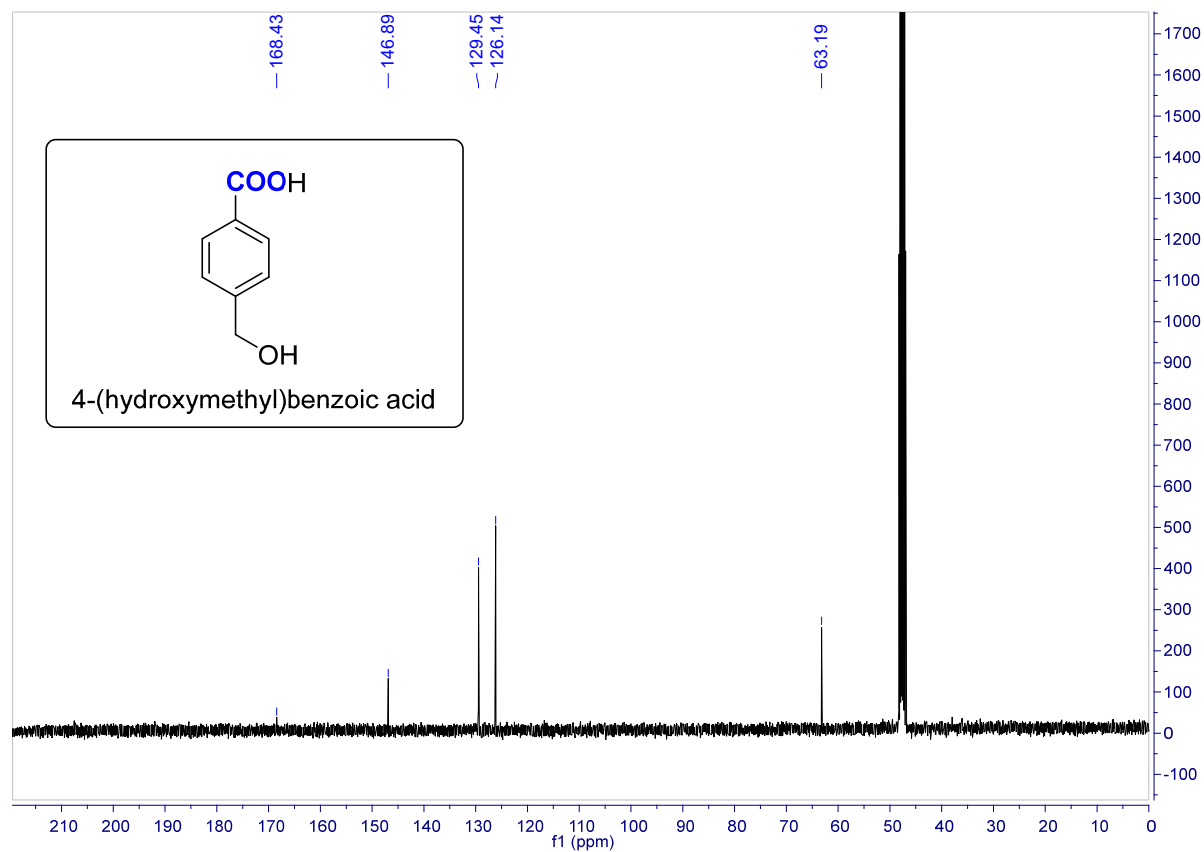
¹³C NMR of 4-hydroxybenzoic acid (2o)



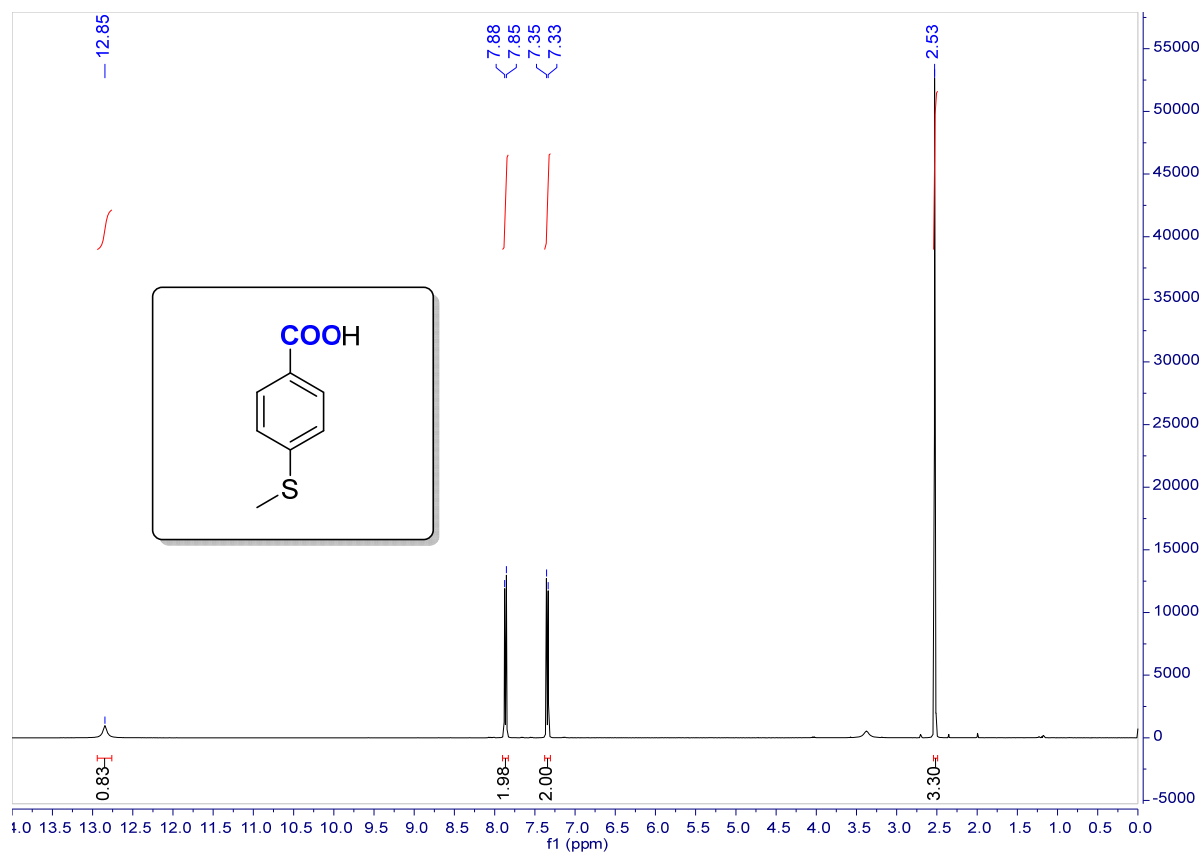
¹H NMR of 4-(hydroxymethyl) benzoic acid (2p)



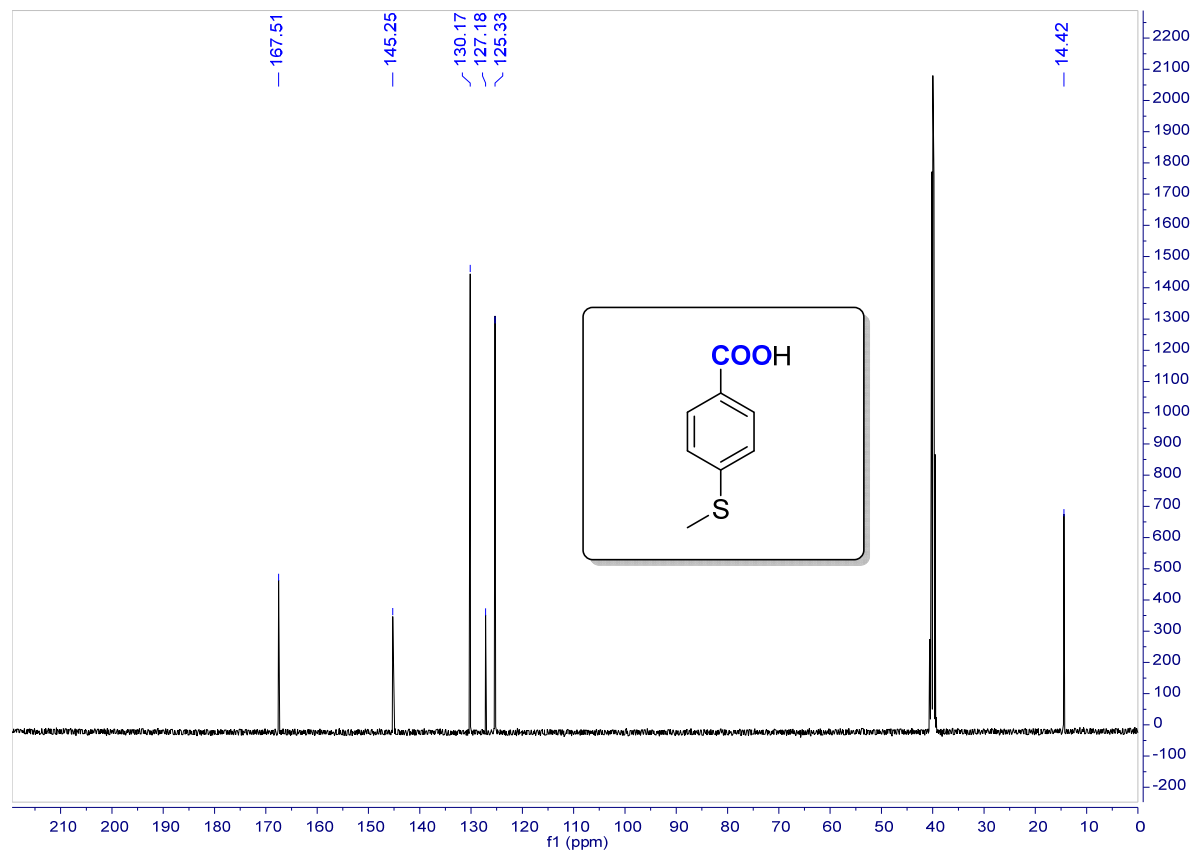
¹³C NMR of 4-(hydroxymethyl) benzoic acid (2p)



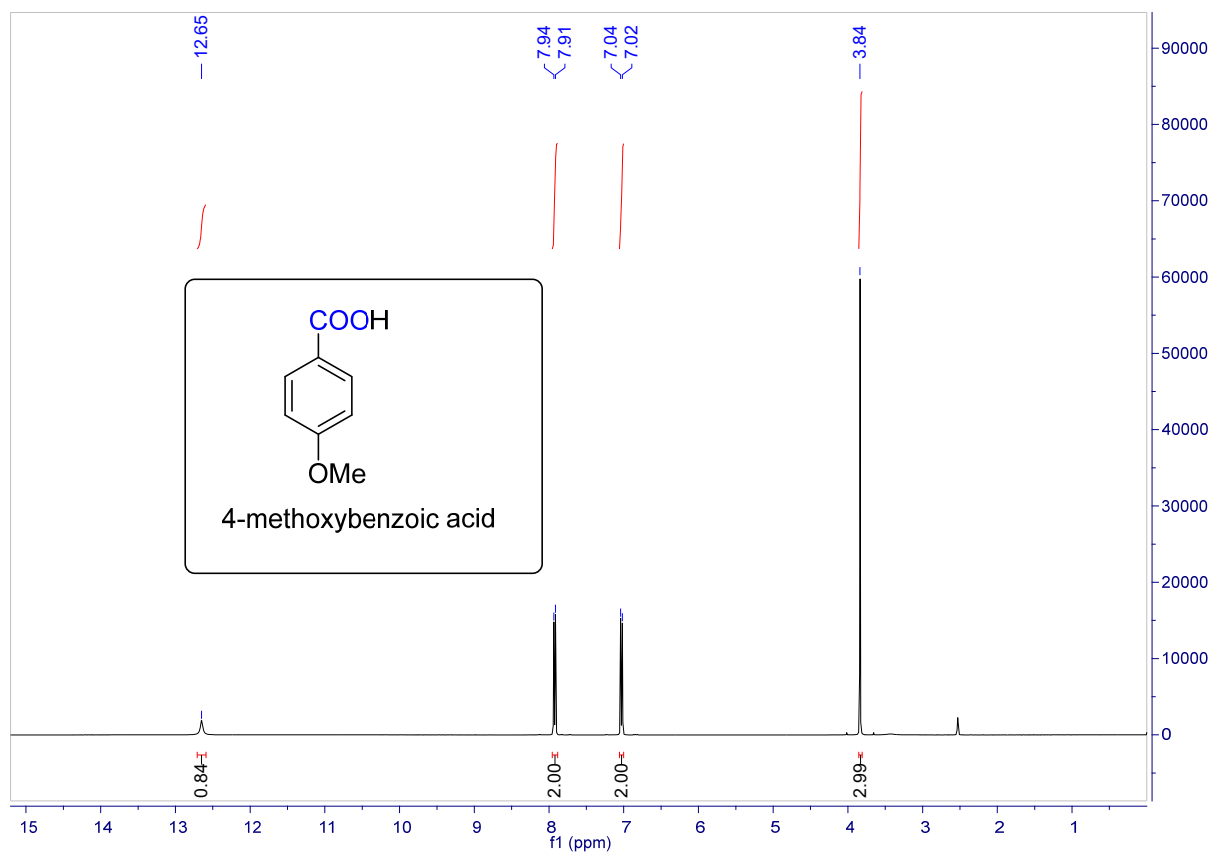
¹H NMR of 4-(thiomethyl) benzoic acid (2q)



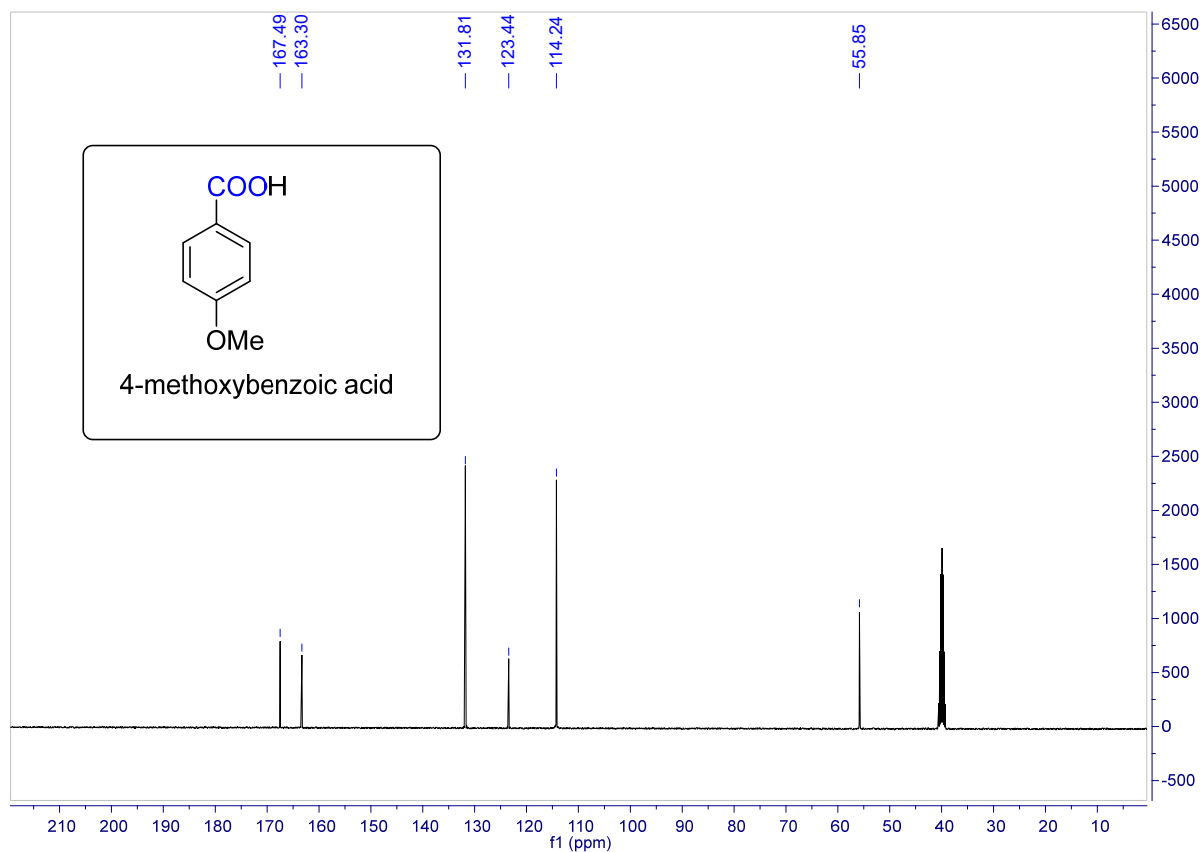
¹³C NMR of 4-(thiomethyl) benzoic acid (2q)



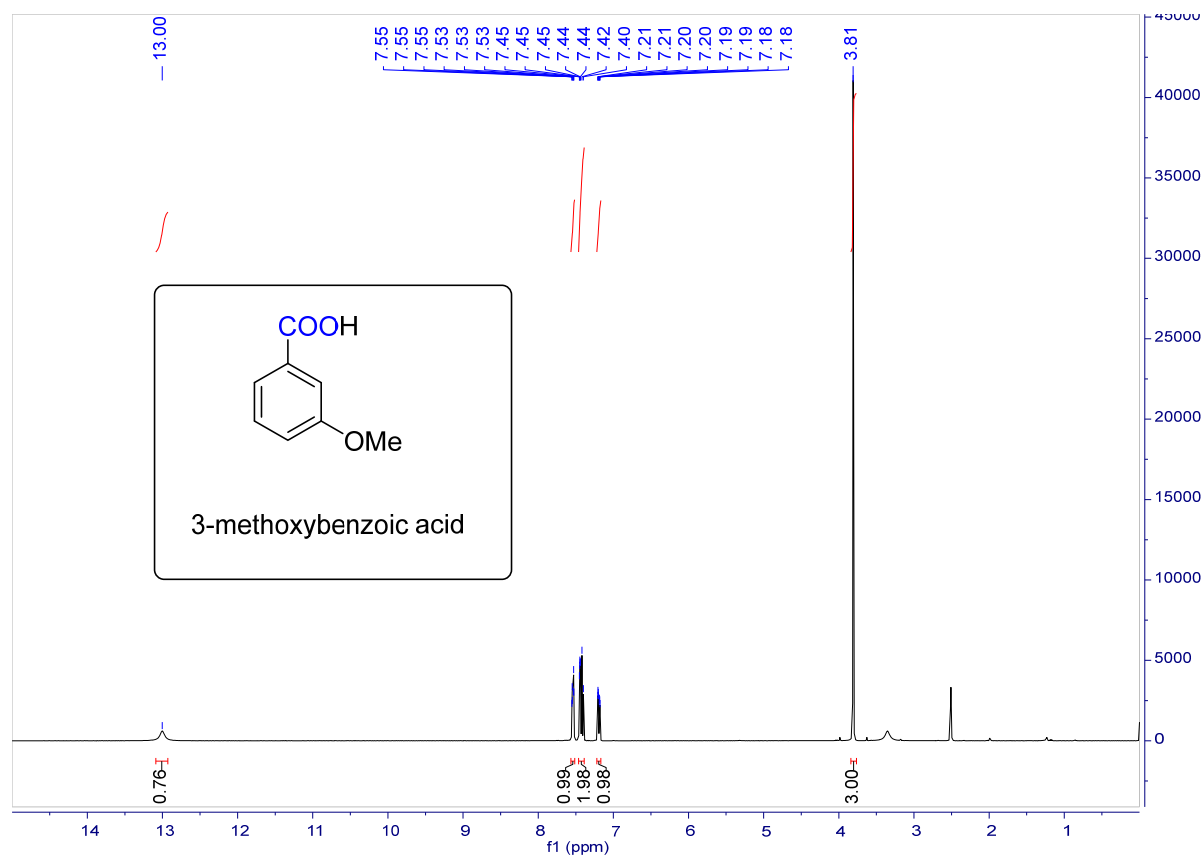
¹H NMR of 4-methoxybenzoic acid (2r)



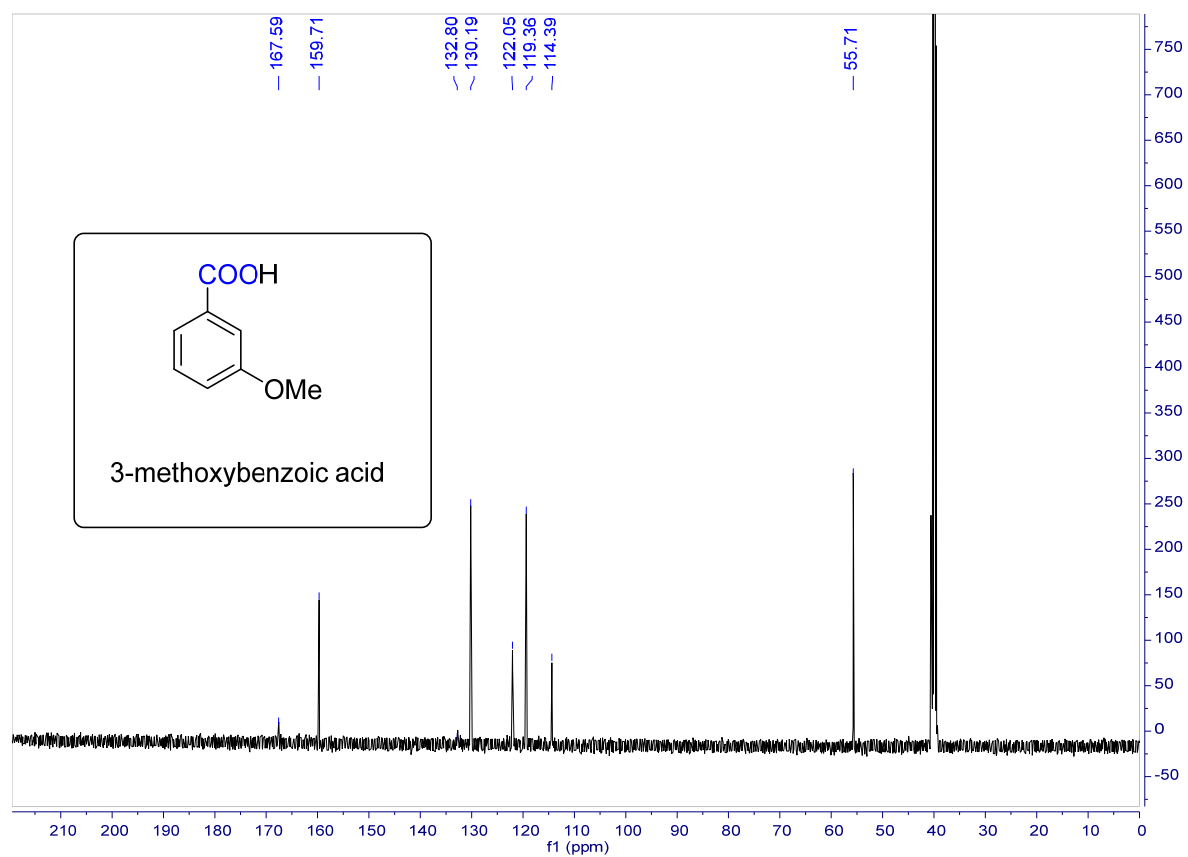
¹³C NMR of 4-methoxybenzoic acid (2r)



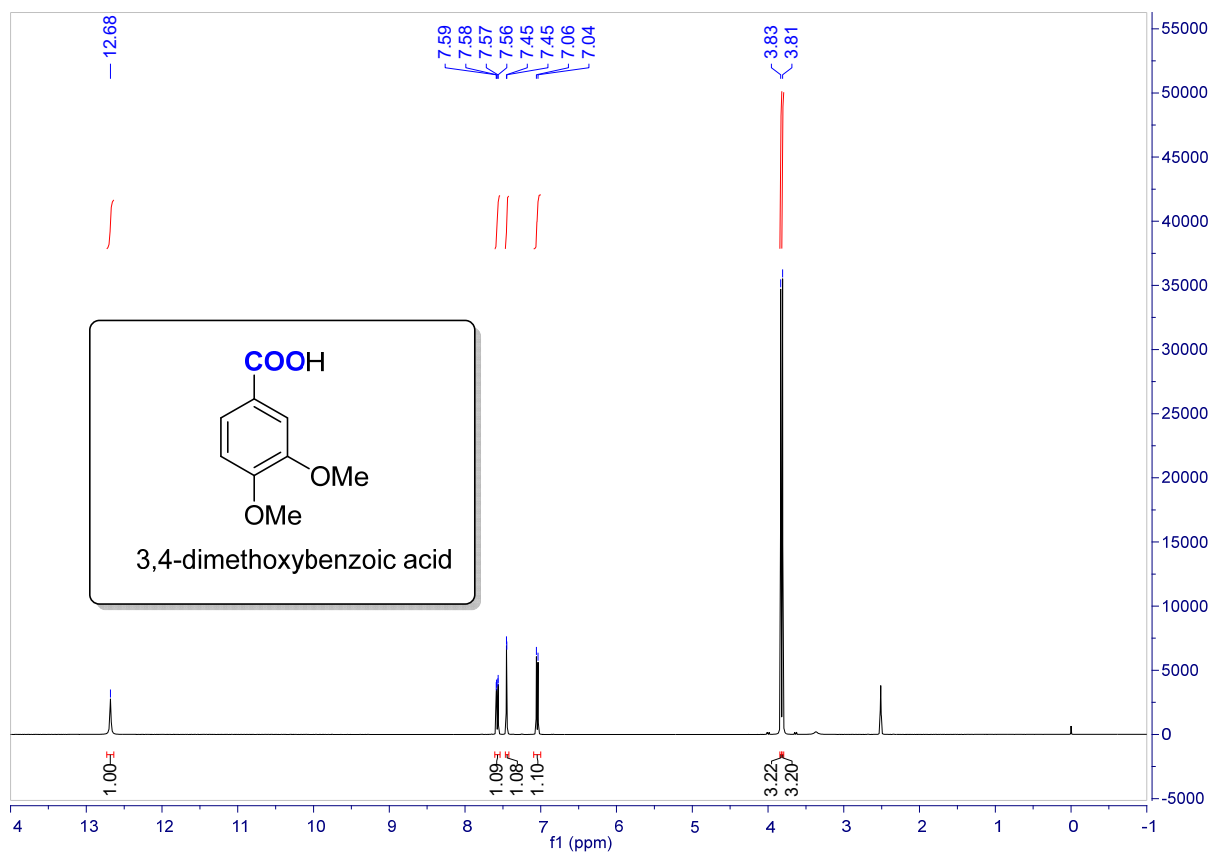
^1H NMR of 3-methoxybenzoic acid (2s)



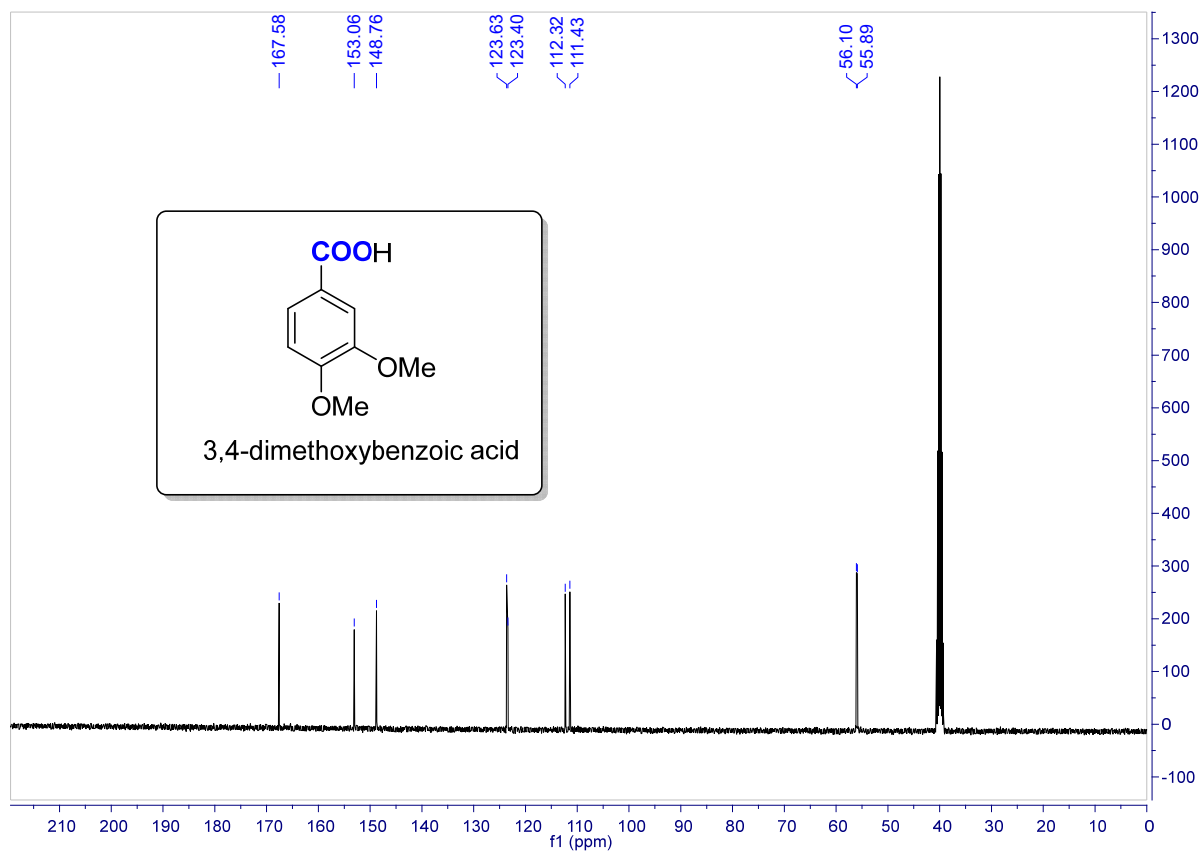
^{13}C NMR of 3-methoxybenzoic acid (2s)



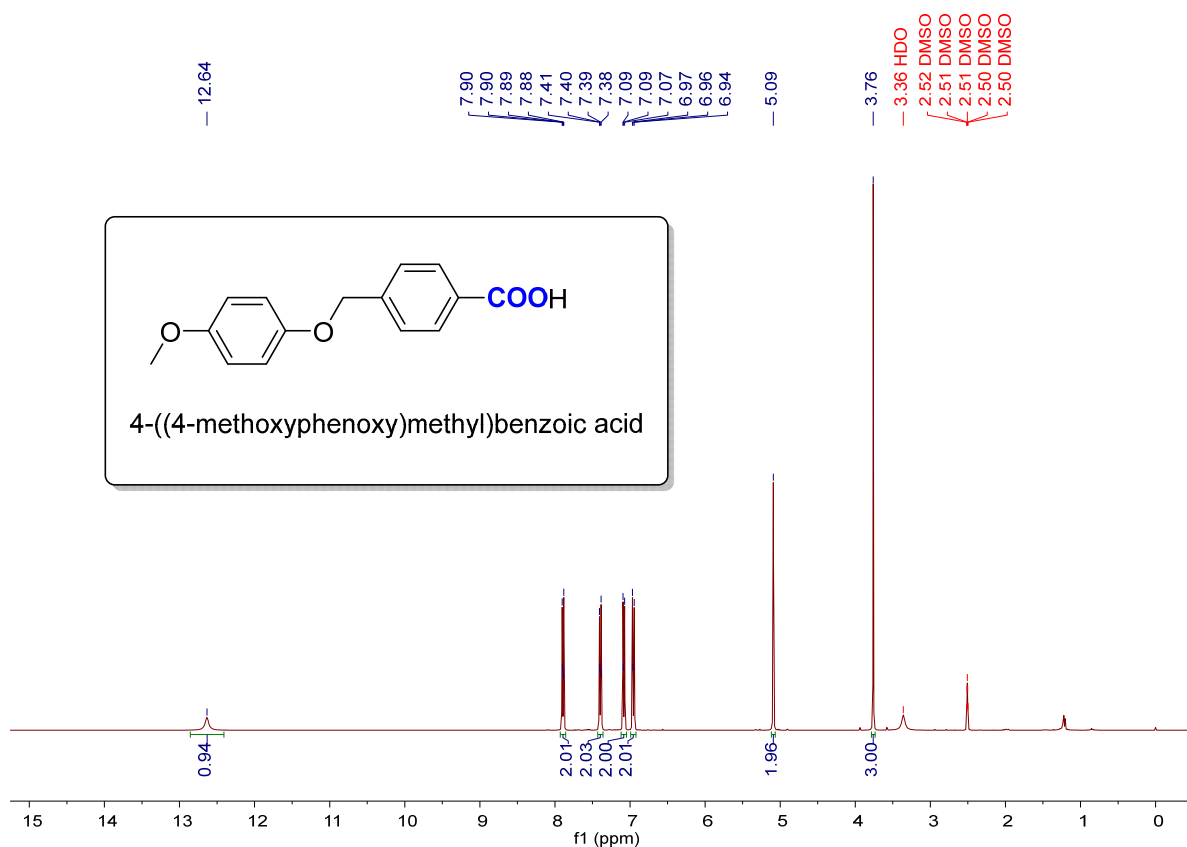
¹H NMR of 3,4-dimethoxybenzoic acid (2t)



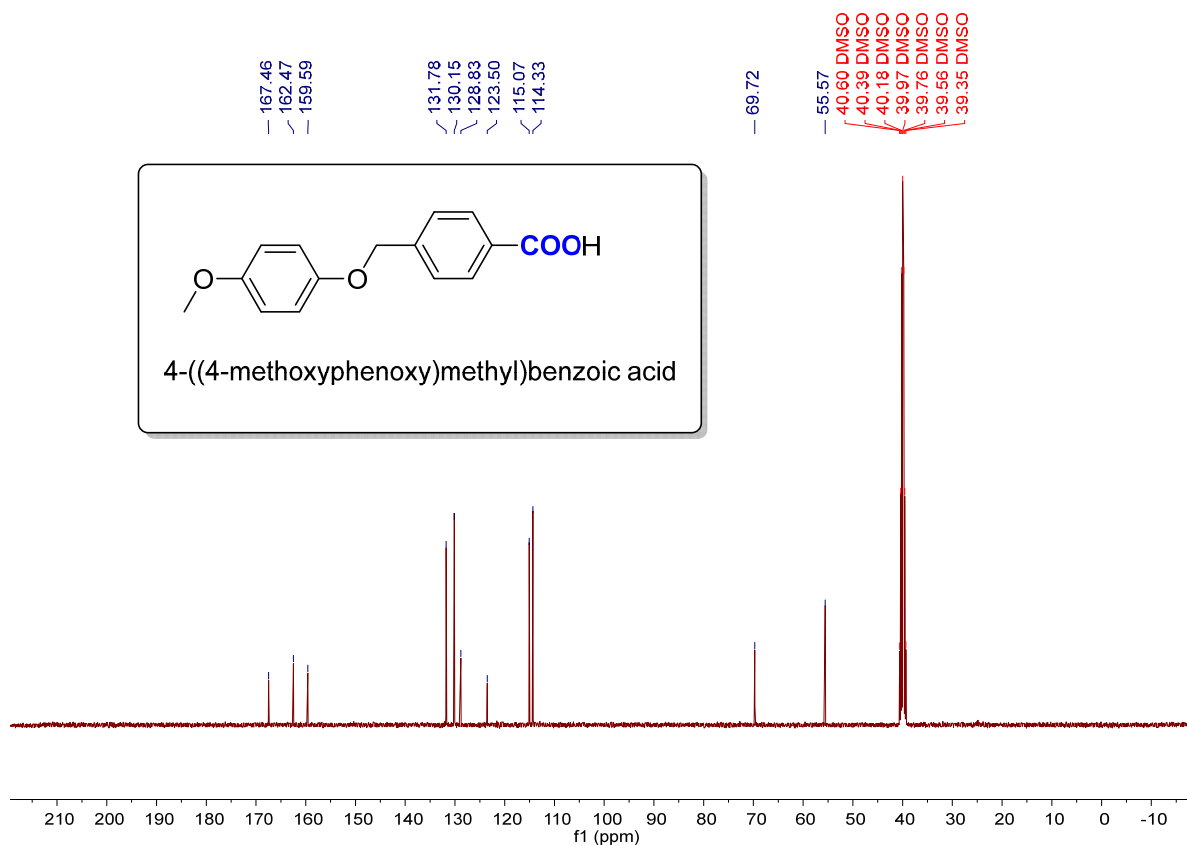
¹³C NMR of 3,4-dimethoxybenzoic acid (2t)



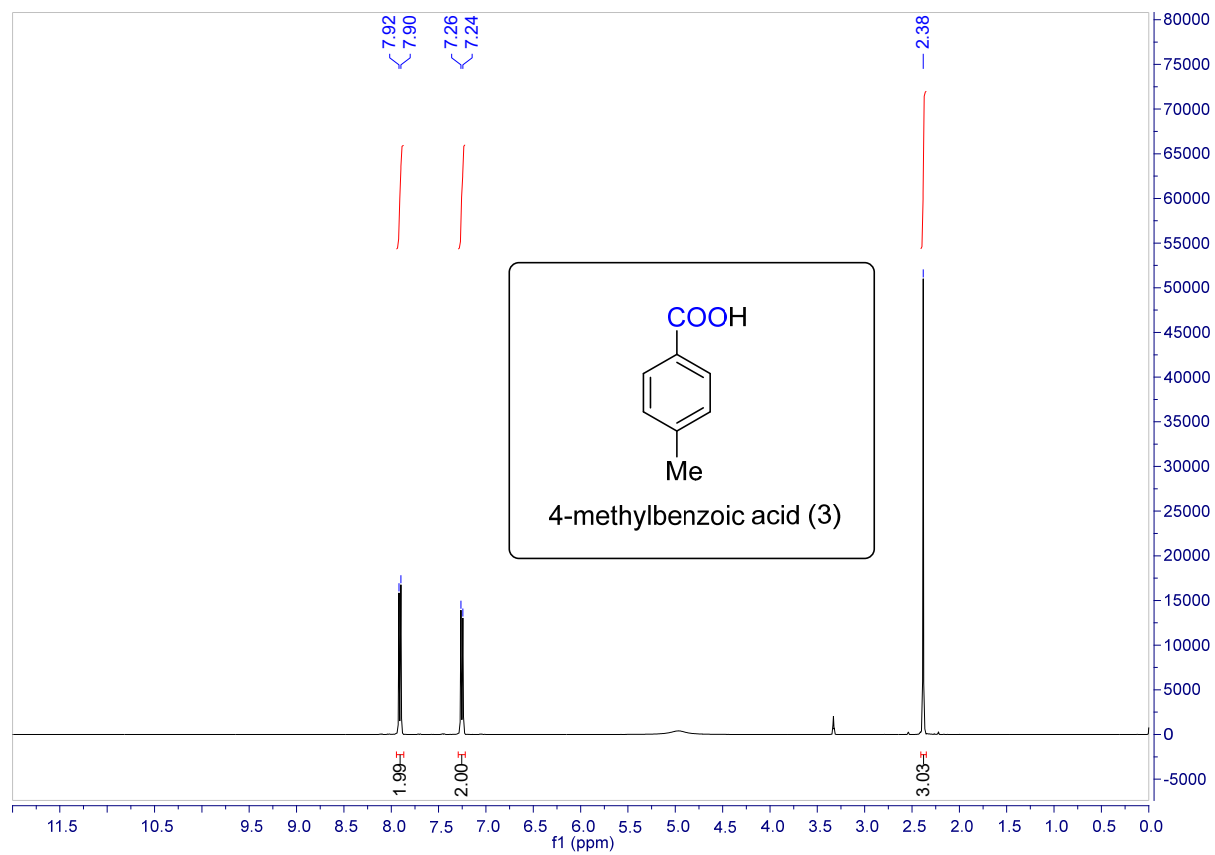
^{13}C NMR of 4-((4-methoxyphenoxy)methyl)benzoic acid (2u)



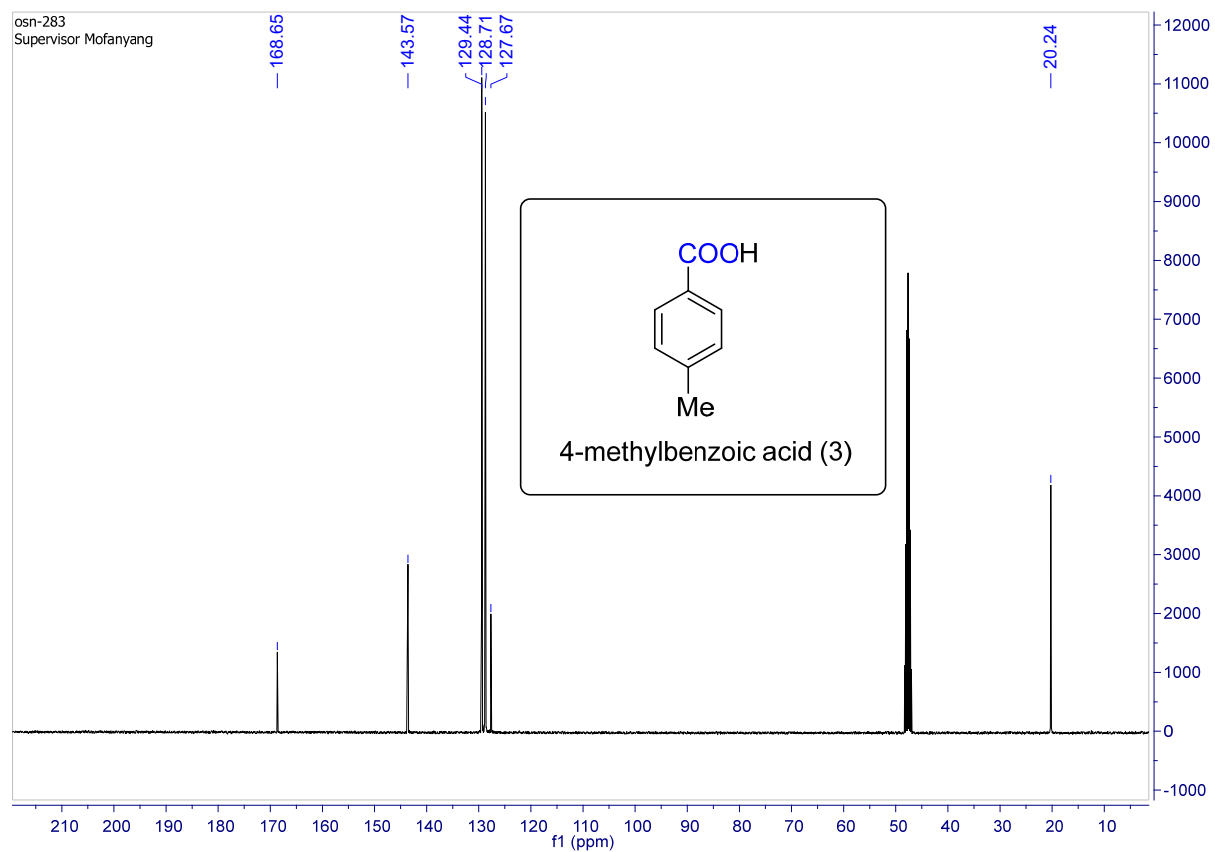
^{13}C NMR of 4-((4-methoxyphenoxy)methyl)benzoic acid (2u)



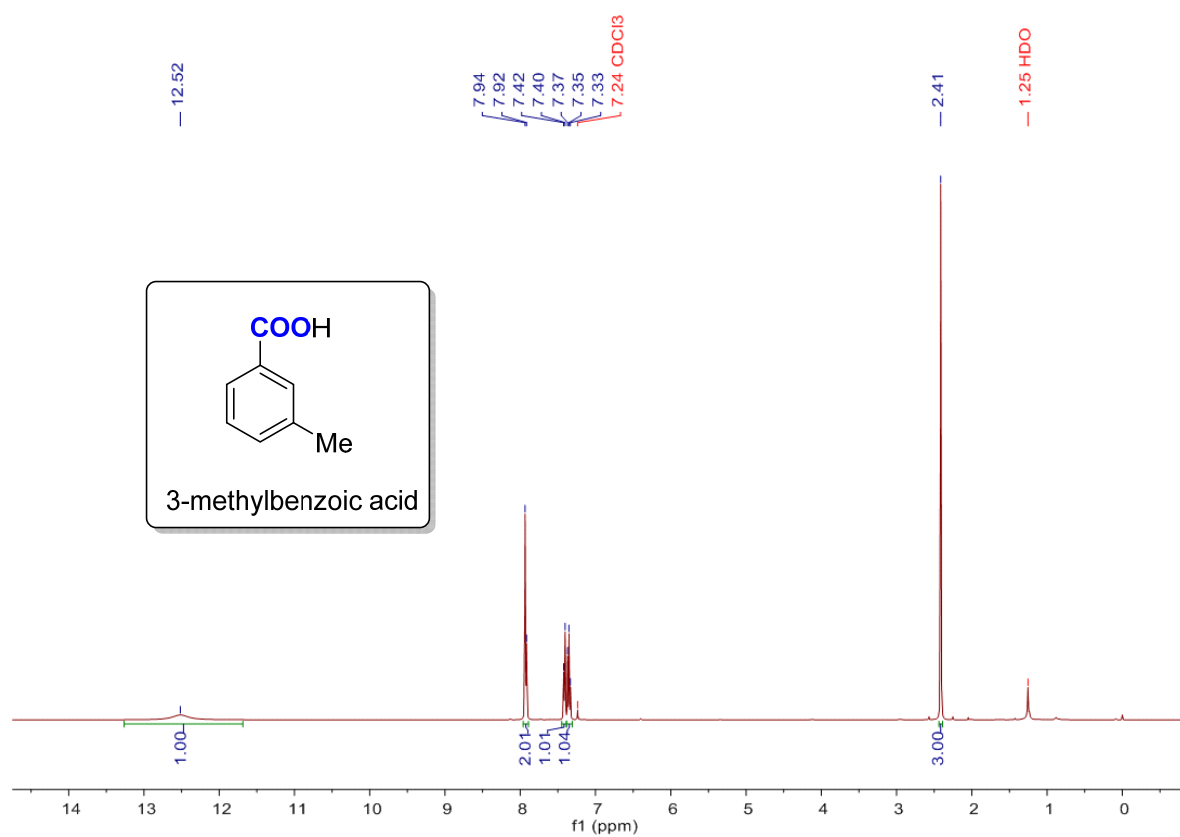
¹H NMR of 4-methylbenzoic acid (2v)



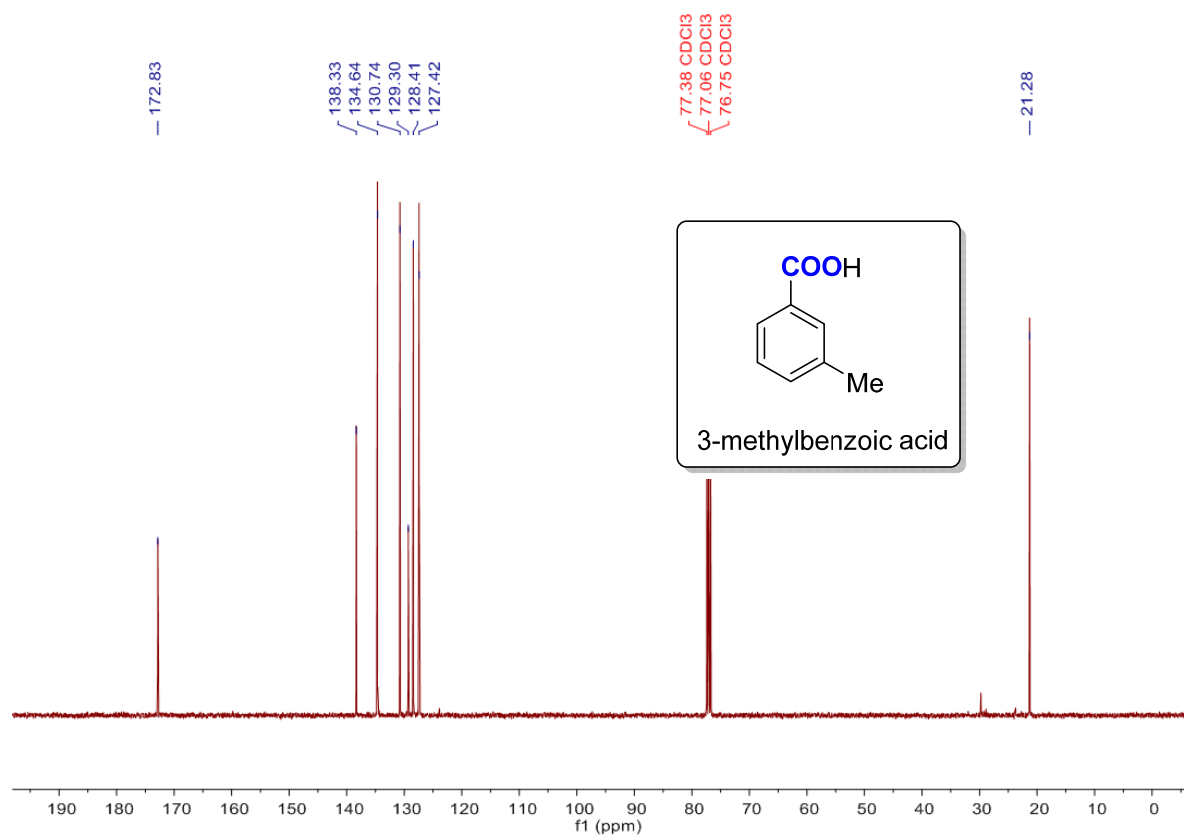
¹³C NMR of 4-methylbenzoic acid (2v)



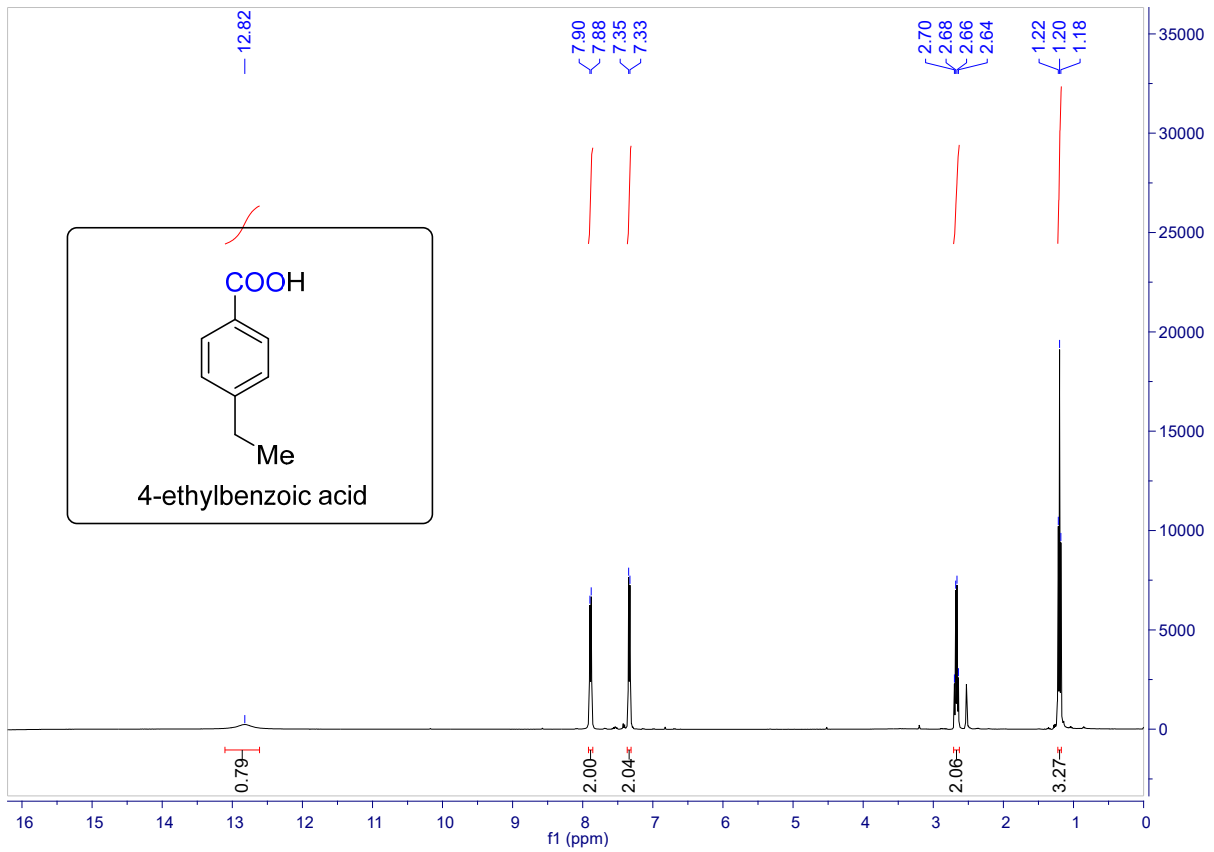
¹H NMR of 3-methylbenzoic acid (2w)



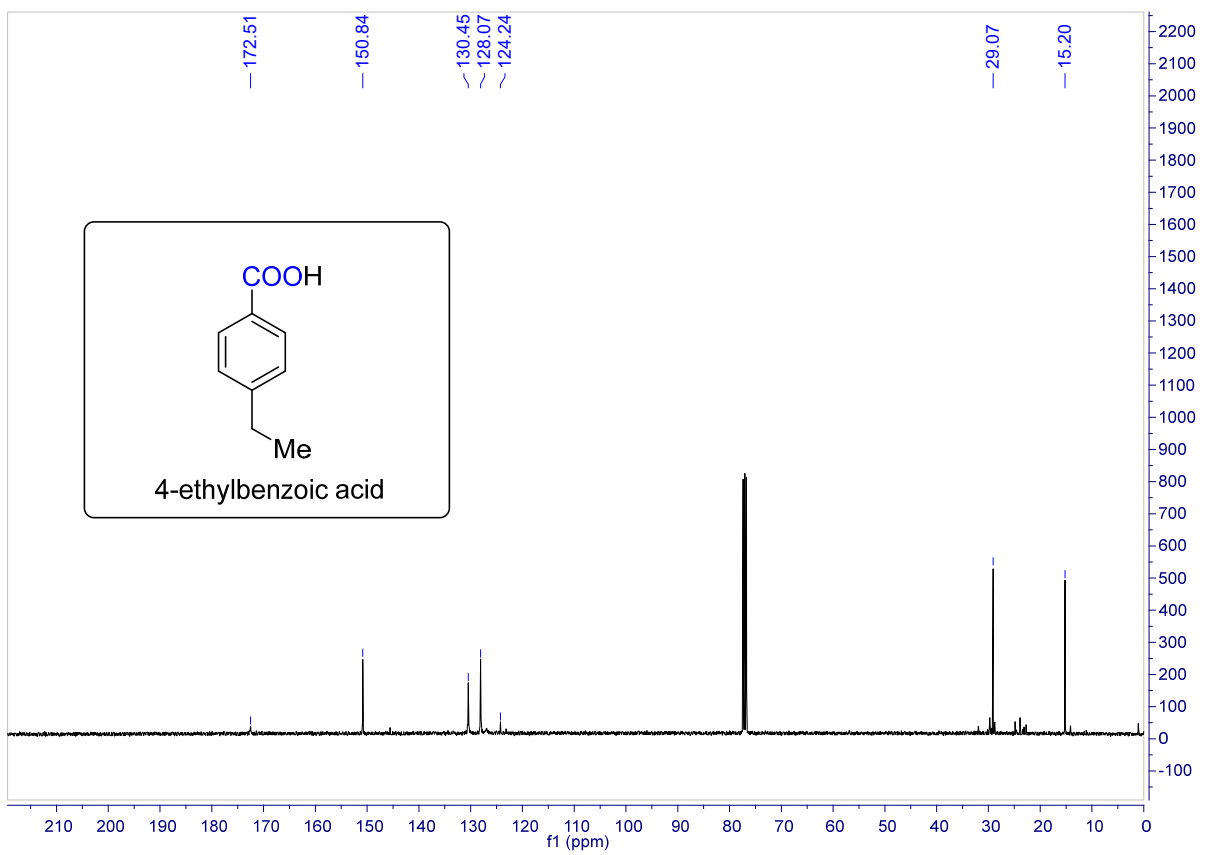
¹³C NMR of 3-methylbenzoic acid (2w)



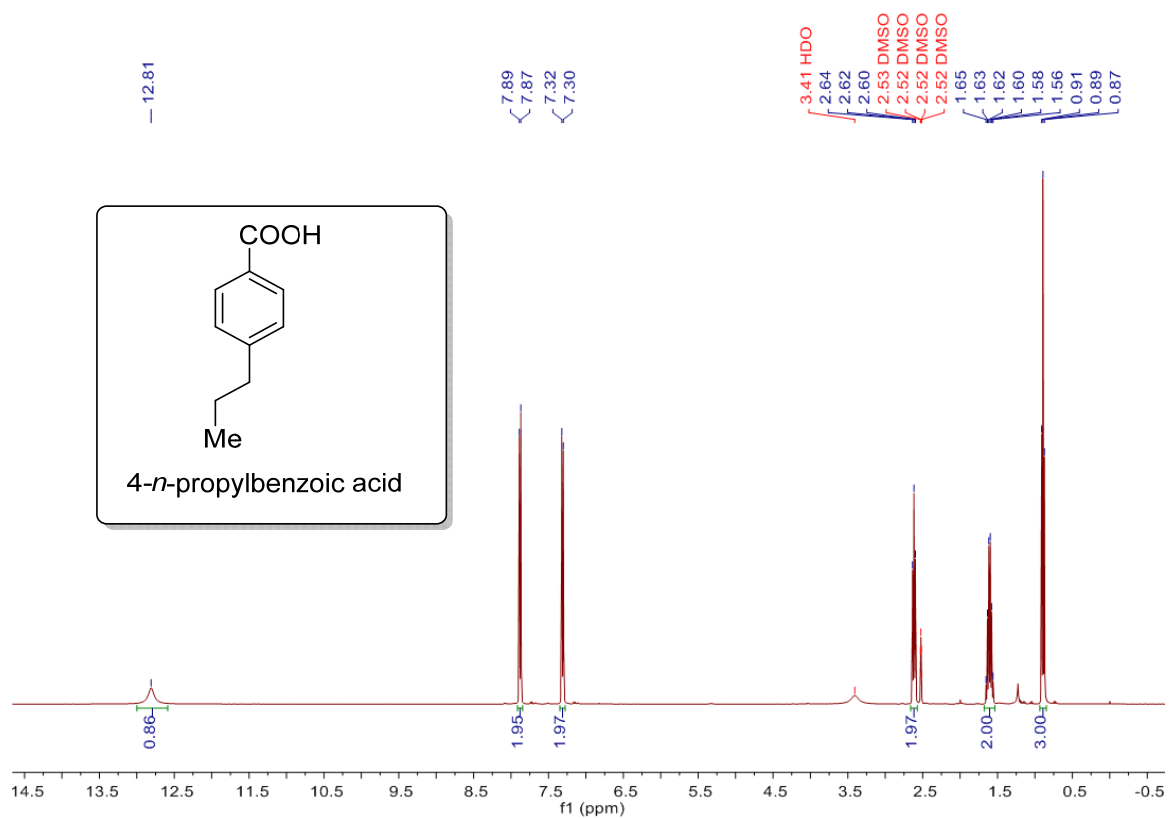
¹H NMR of 4-ethylbenzoic acid (2x)



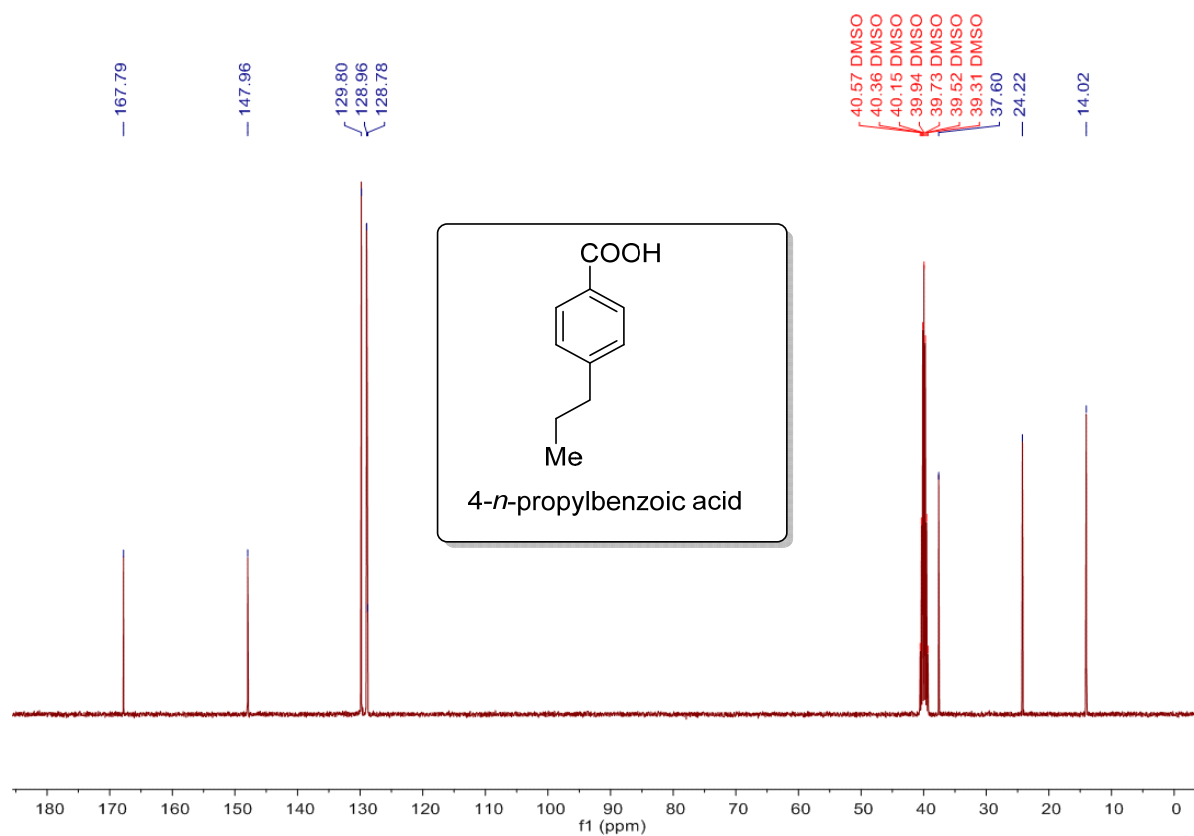
¹³C NMR of 4-ethylbenzoic acid (2x)



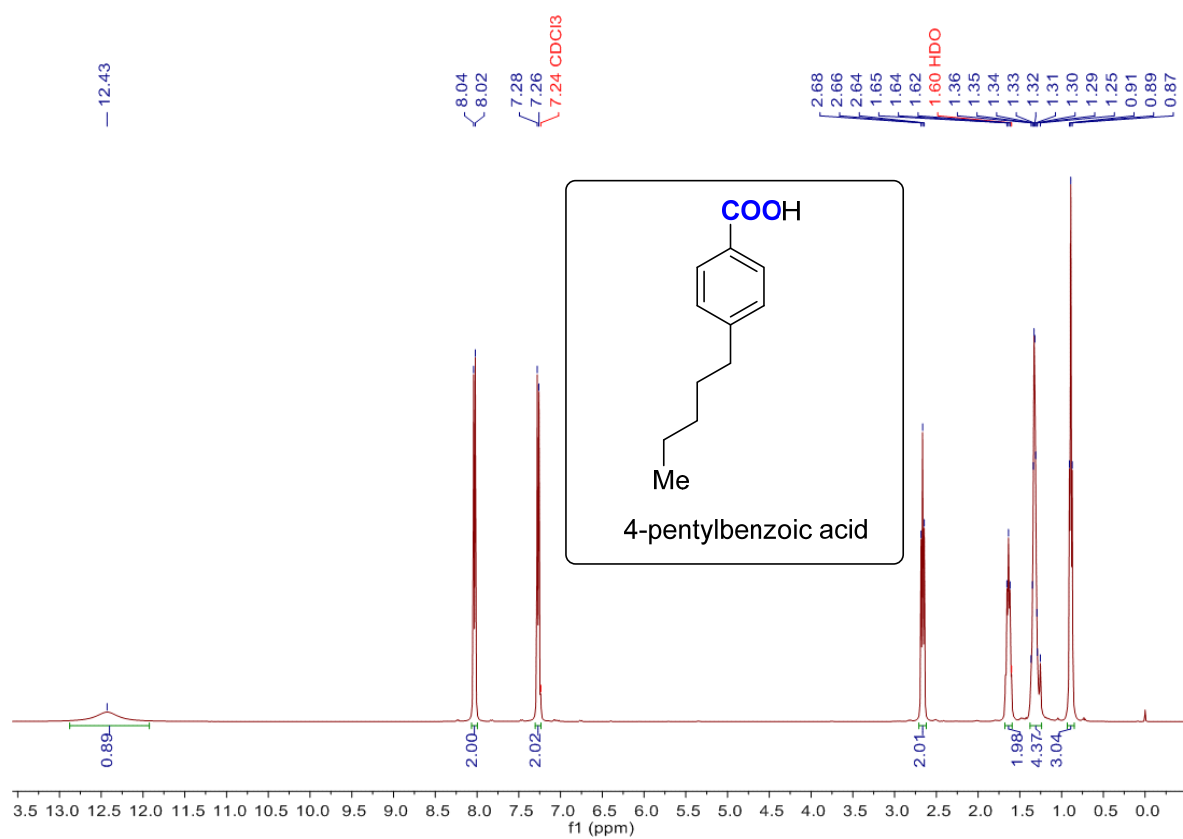
¹H NMR of 4-*n*-propylbenzoic acid (2y)



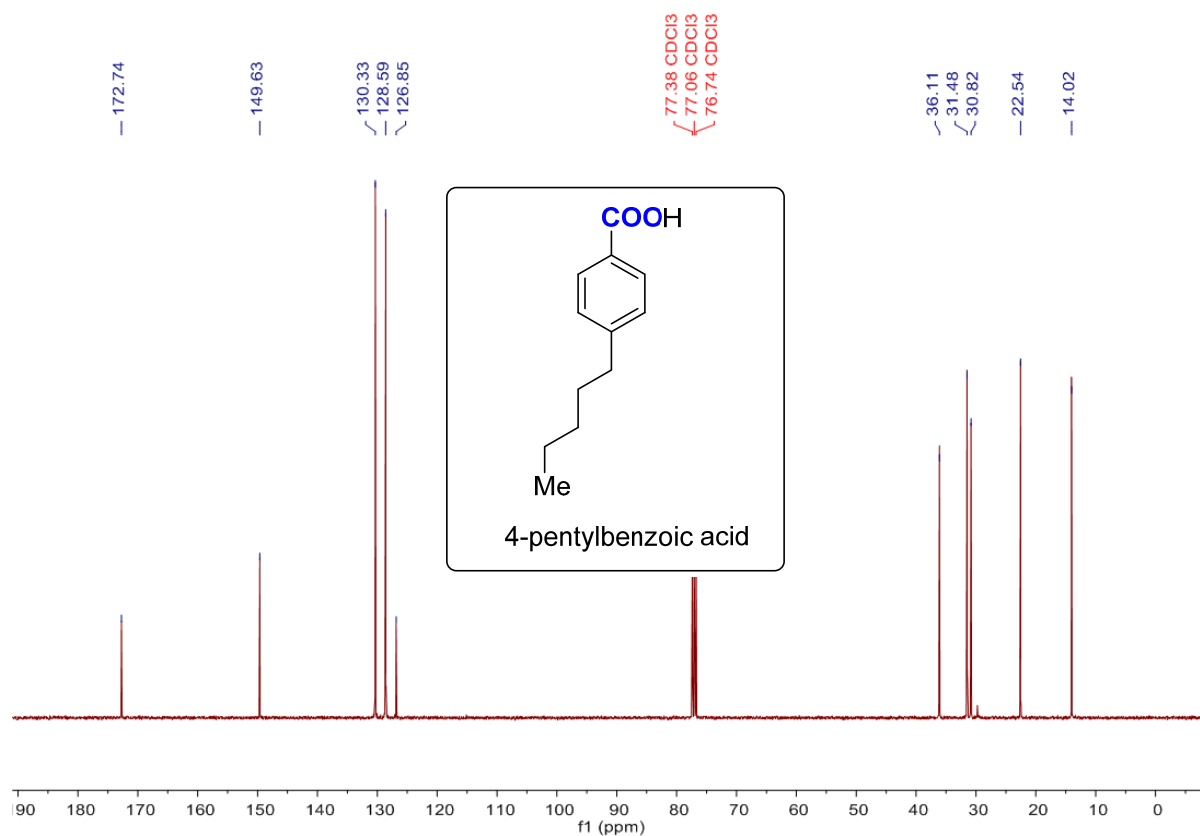
¹³C NMR of 4-*n*-propylbenzoic acid (2y)



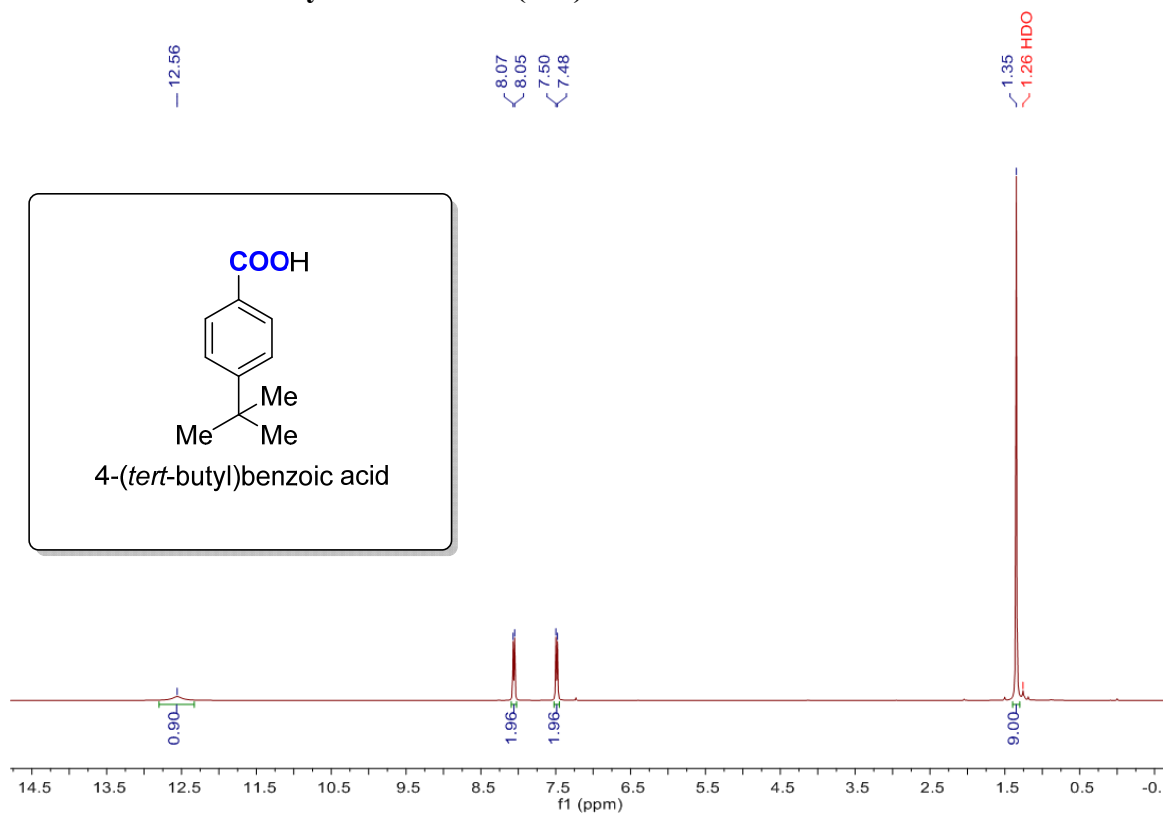
¹H NMR of 4-pentylbenzoic acid (2z)



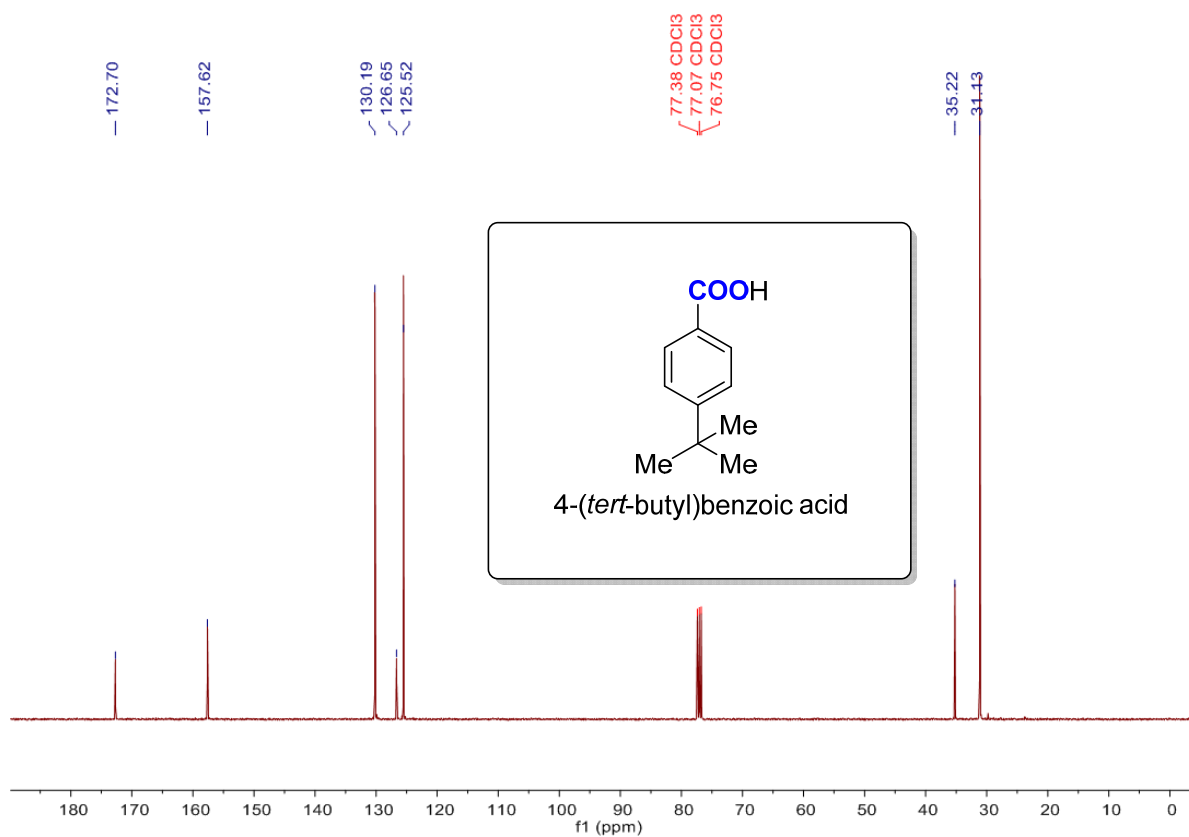
¹³C NMR of 4-pentylbenzoic acid (2z)



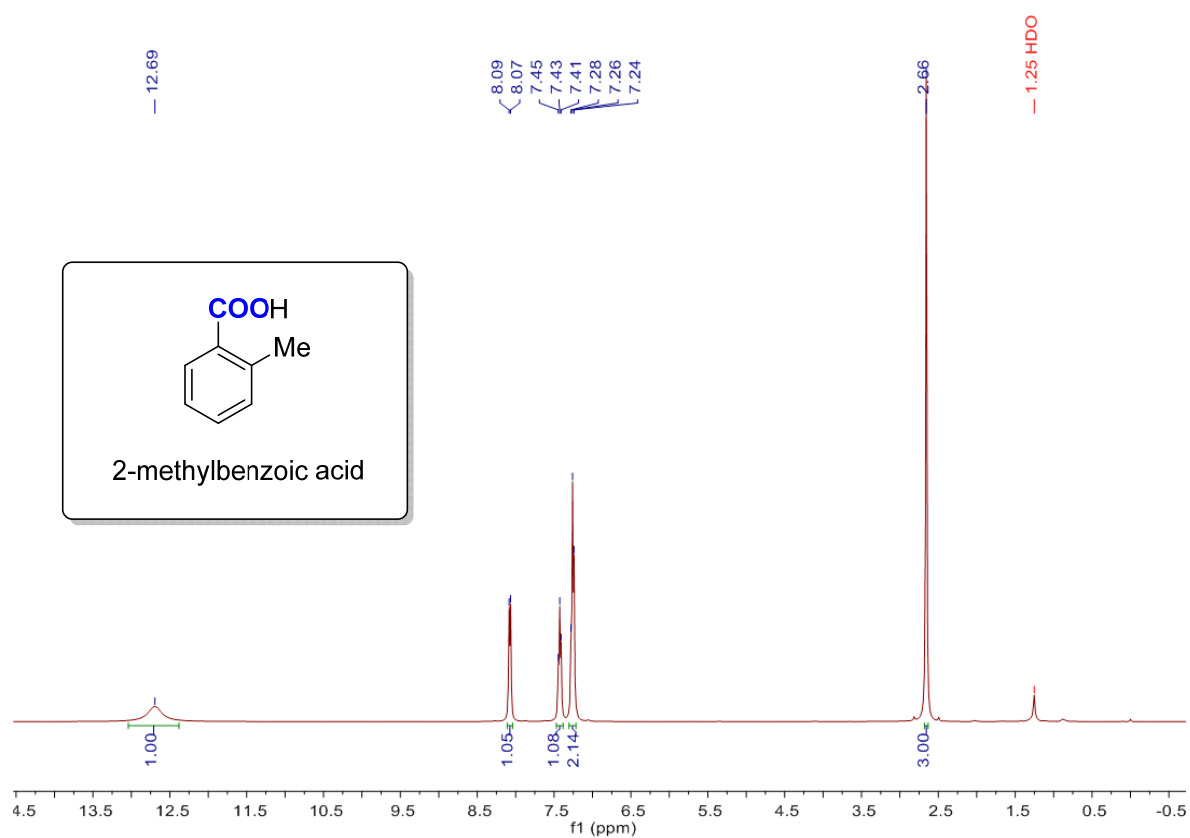
¹H NMR of 4-*tert*-butyl benzoic acid (2aa)



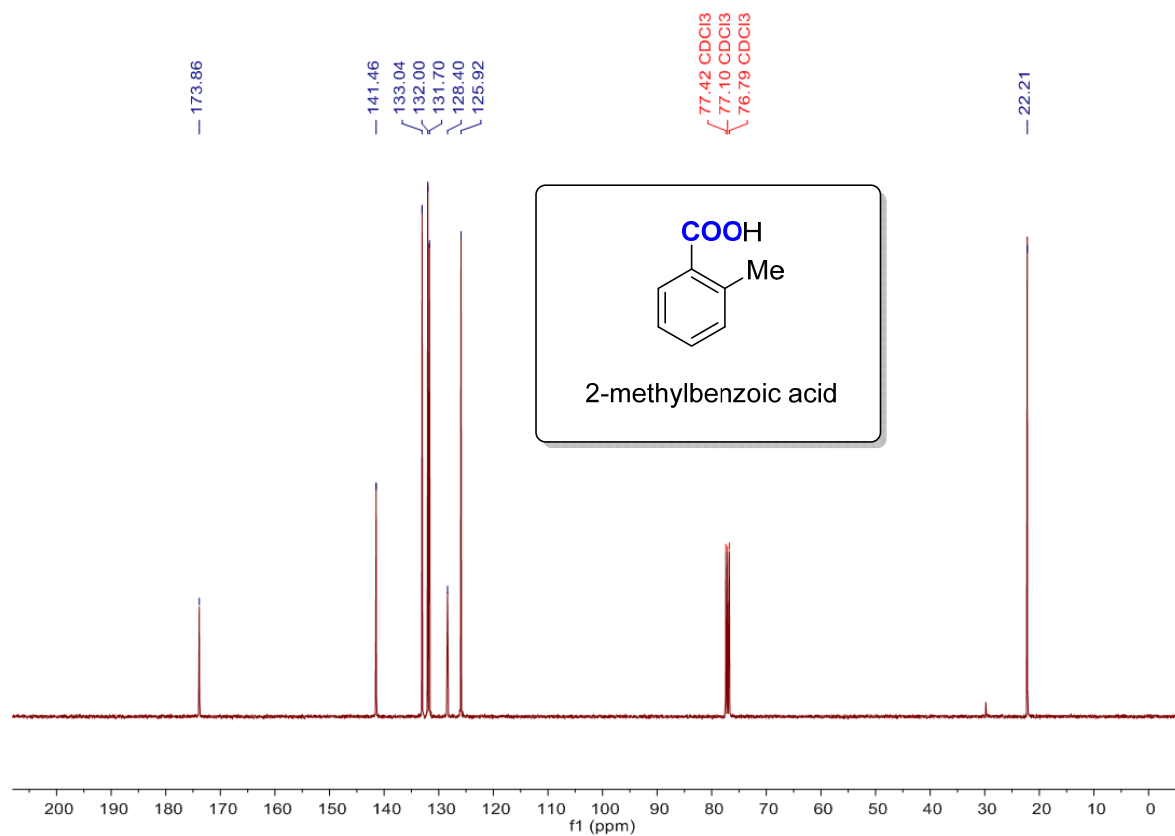
¹³C NMR of 4-*tert*-butyl benzoic acid (2aa)



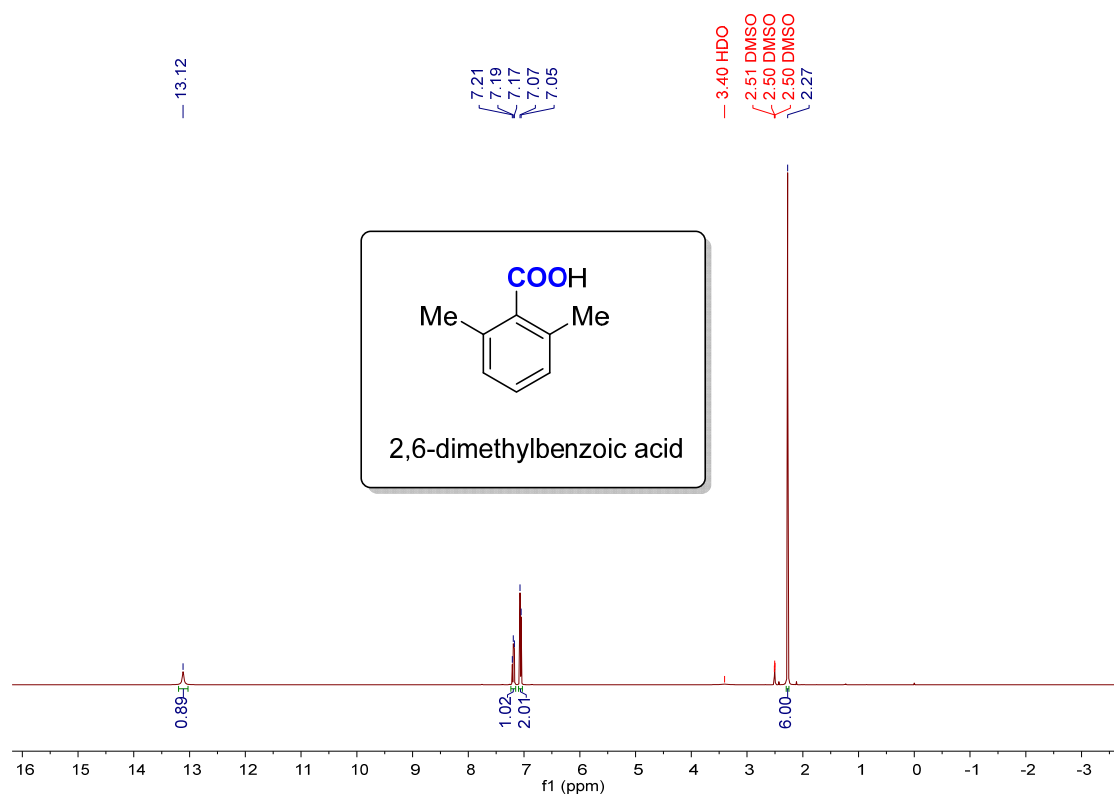
¹H NMR of 2-methylbenzoic acid (2ab)



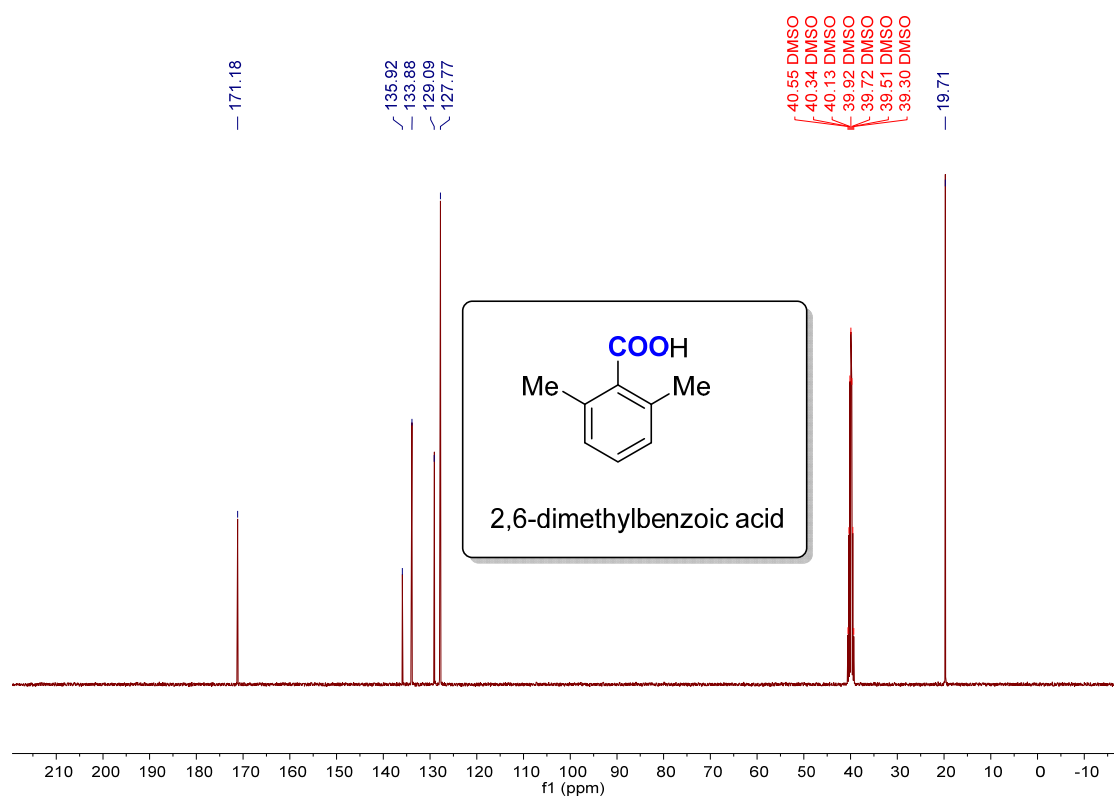
¹³C NMR of 2-methylbenzoic acid (2ab)



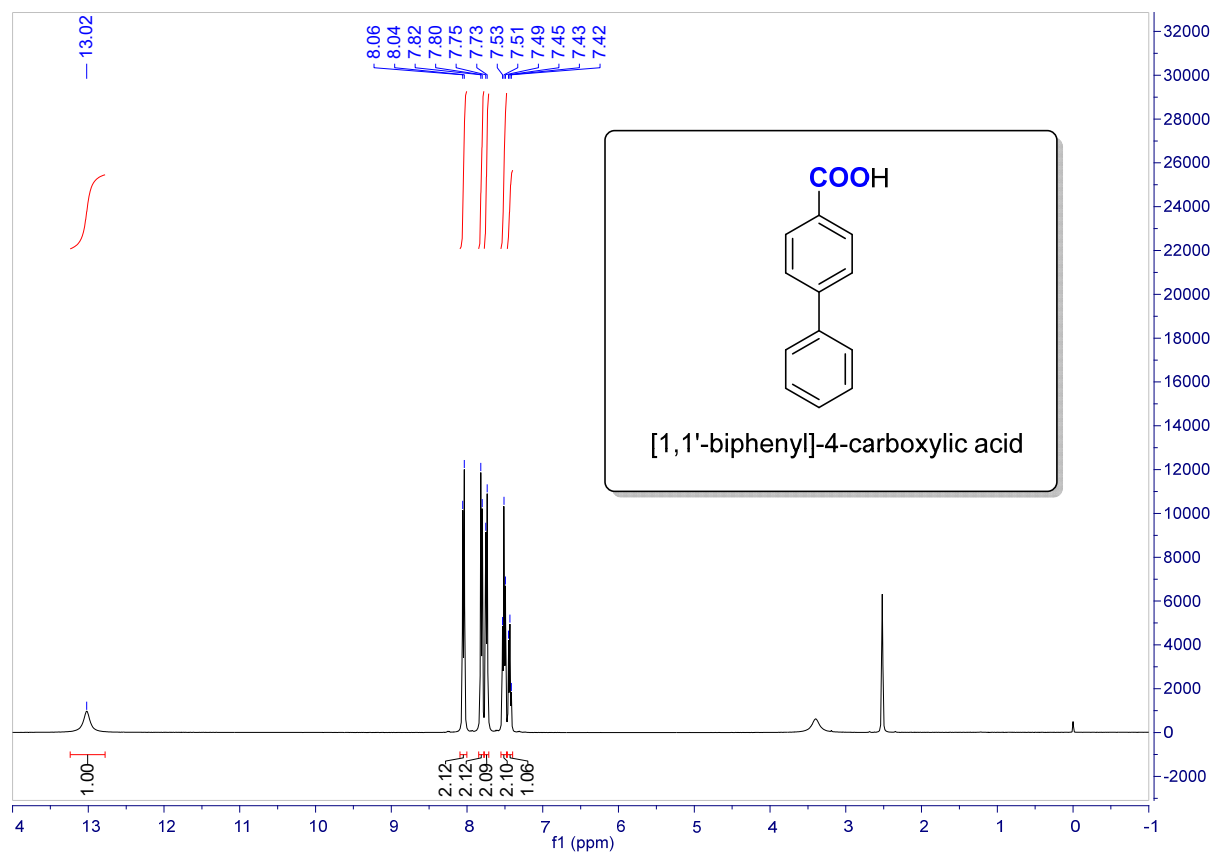
¹H NMR of 2,6-dimethylbenzoic acid (2ac)



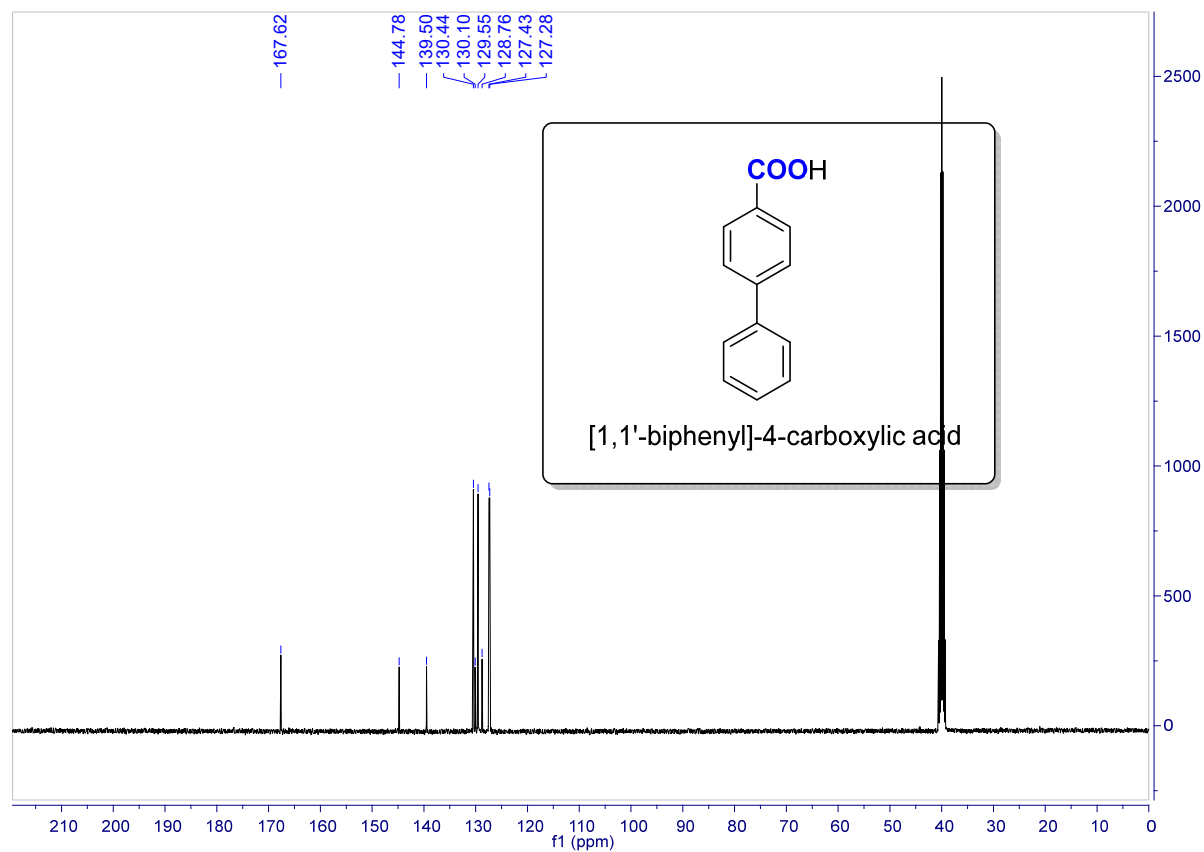
¹³C NMR of 2,6-dimethylbenzoic acid (2ac)



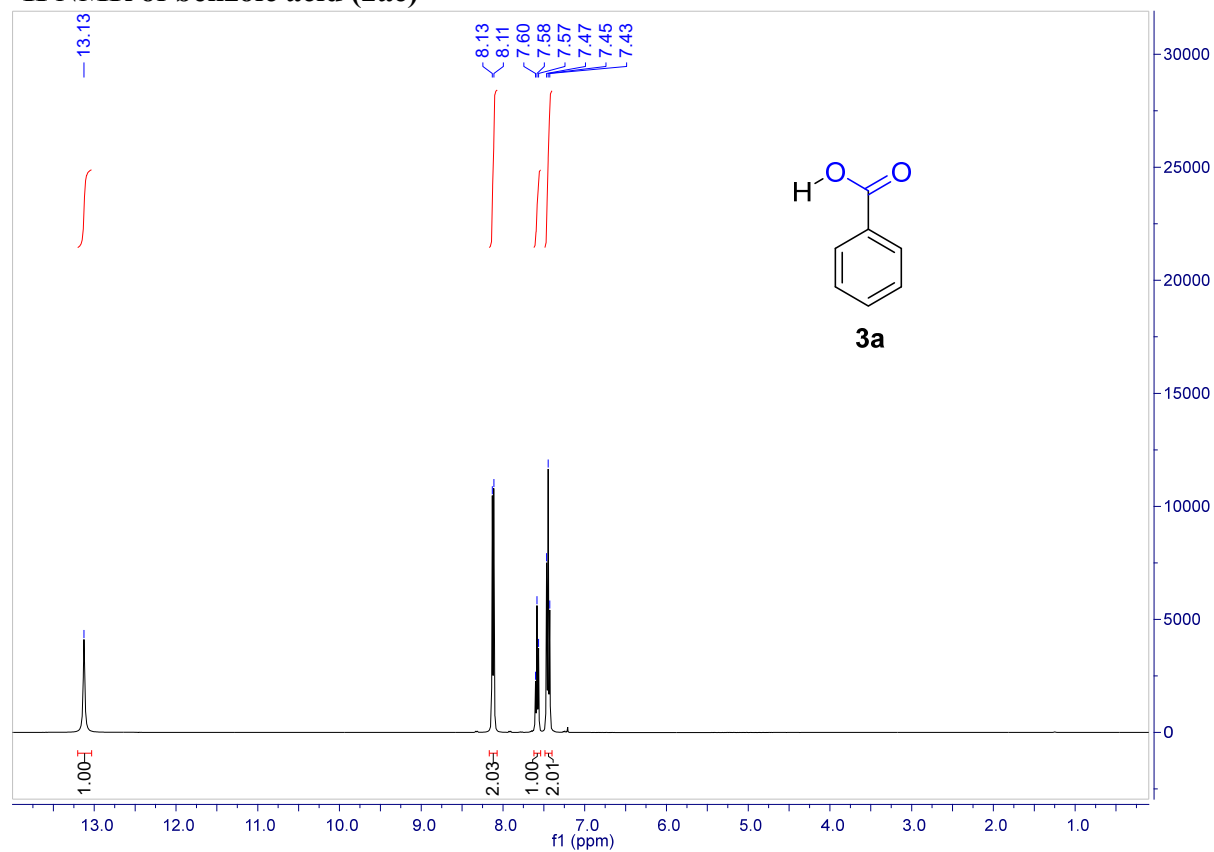
¹H NMR of [1,1'-biphenyl]-4-carboxylic acid (2ad)



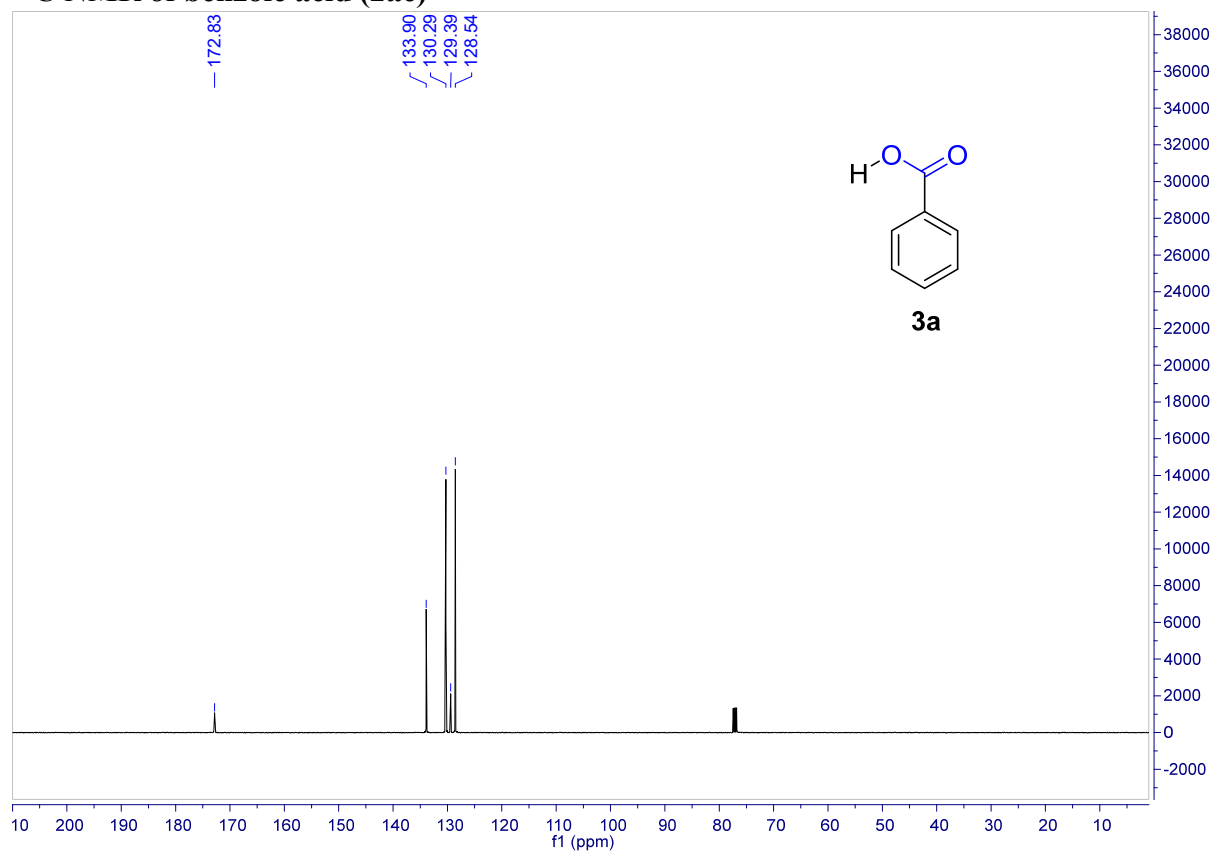
¹³C NMR of [1,1'-biphenyl]-4-carboxylic acid (2ad)



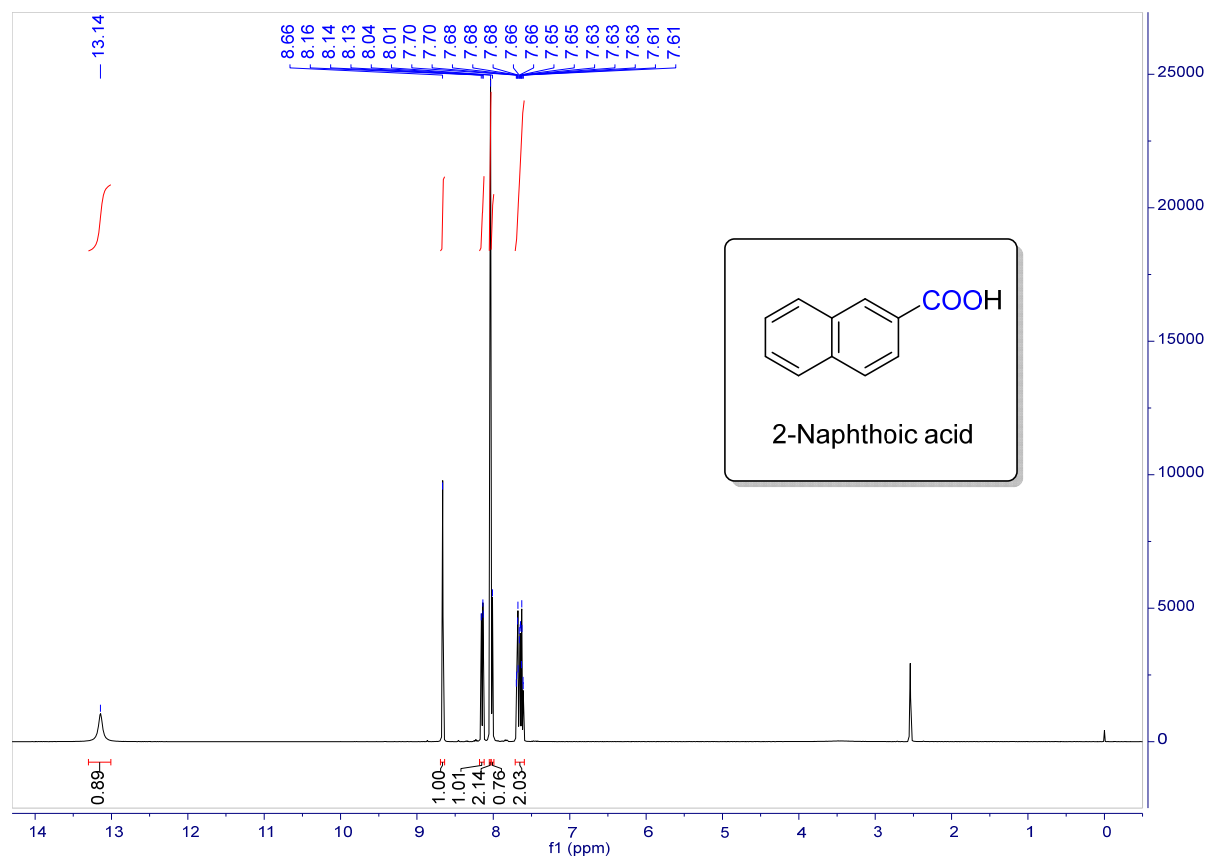
¹H NMR of benzoic acid (2ae)



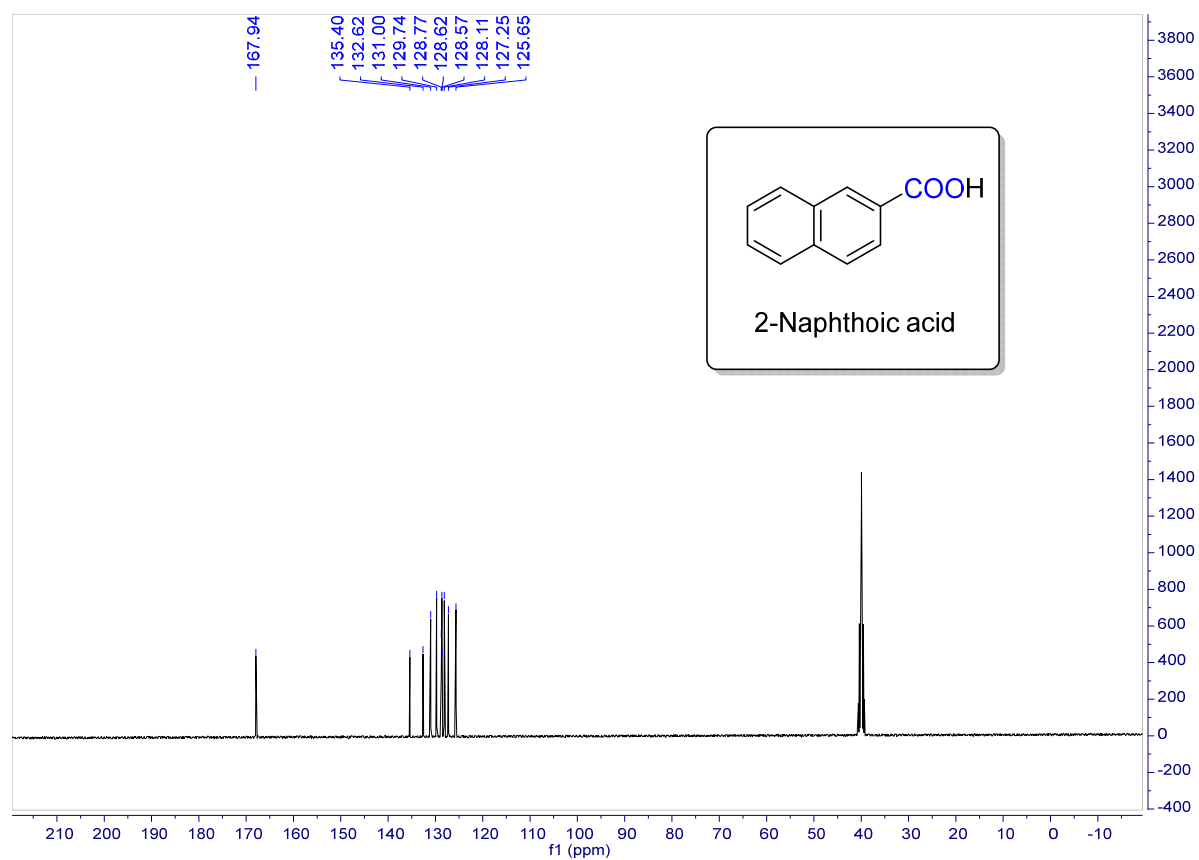
¹³C NMR of benzoic acid (2ae)



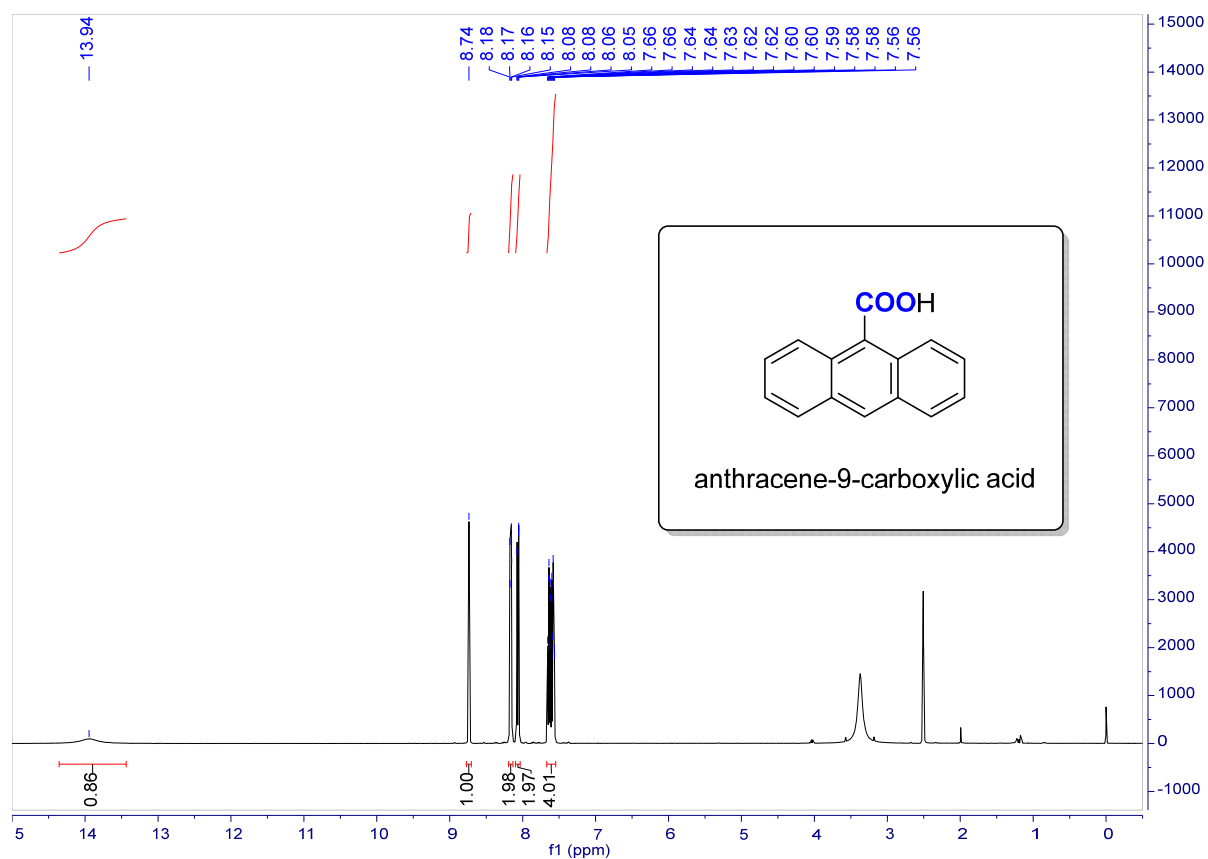
¹H NMR of 2-Naphthoic acid (2af)



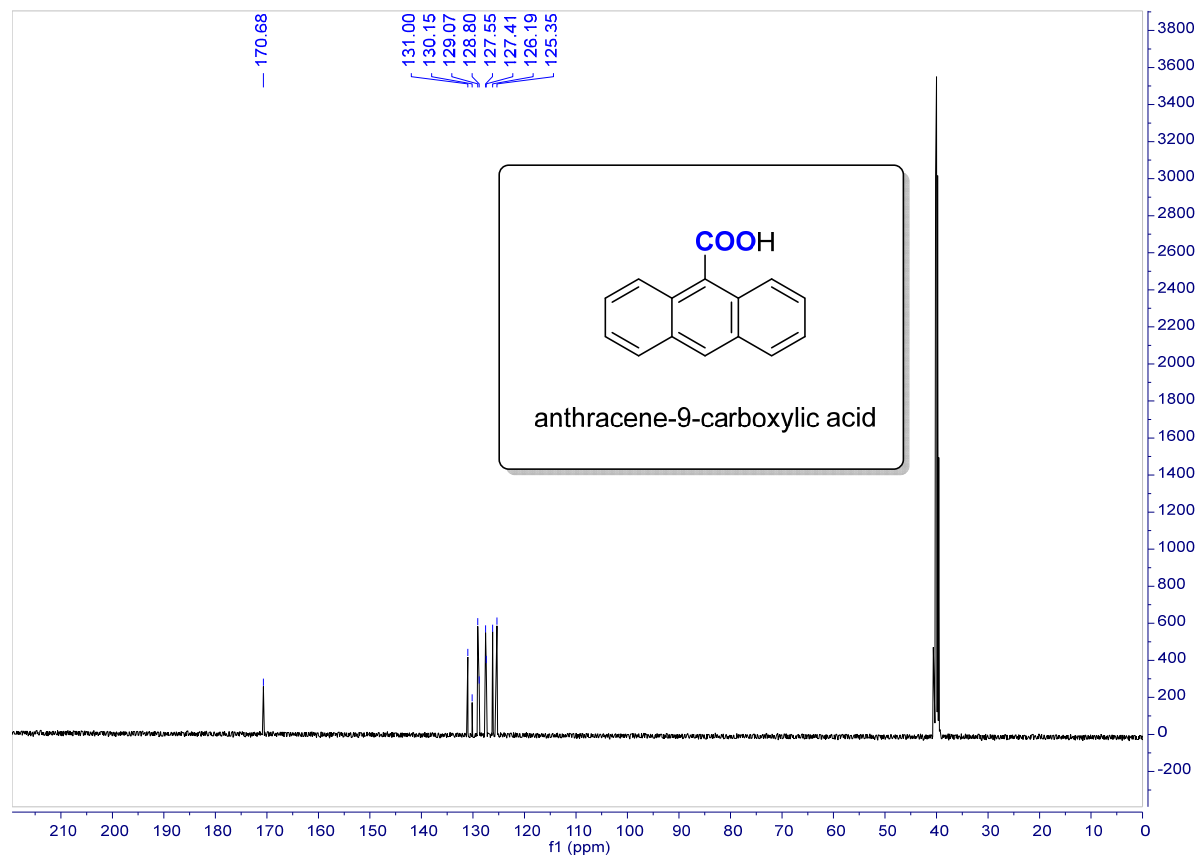
¹³C NMR of 2-Naphthoic acid (2af)



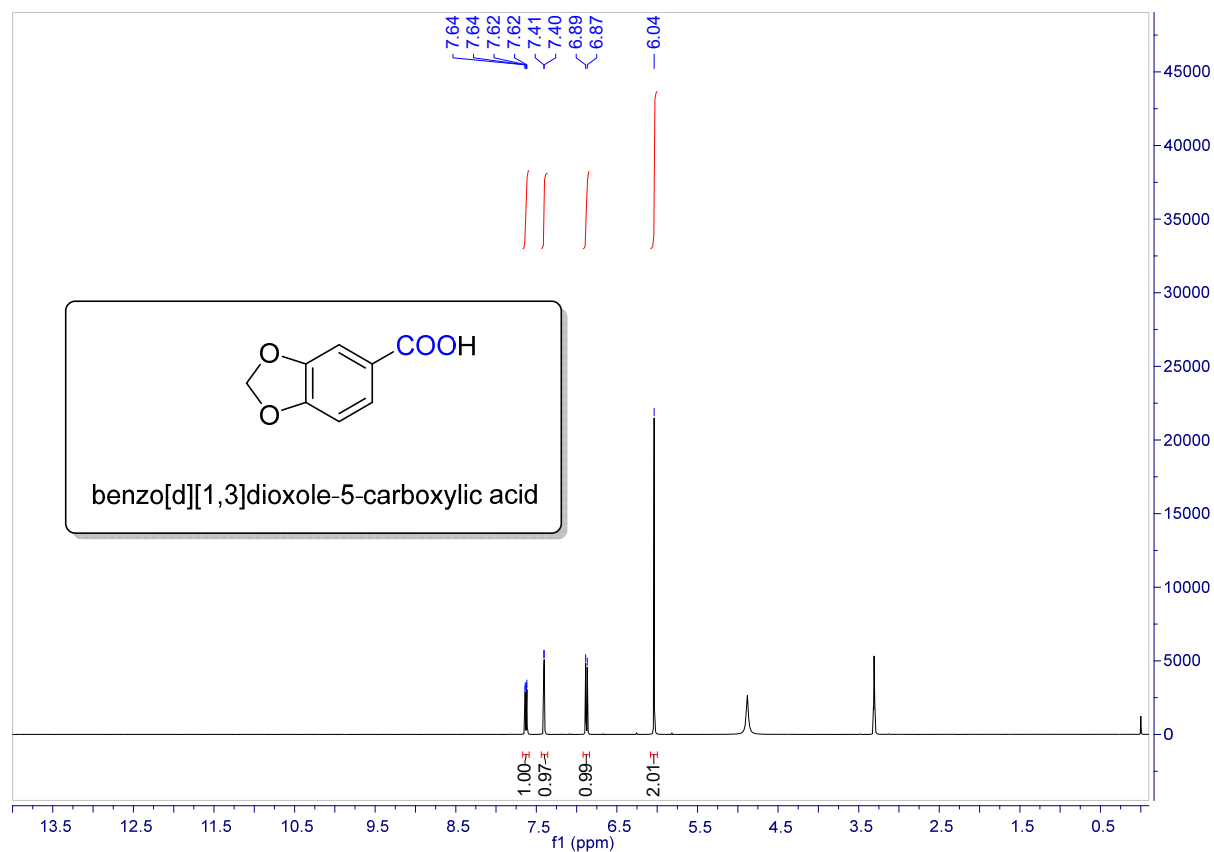
¹H NMR of anthracene-9-carboxylic acid (2ag)



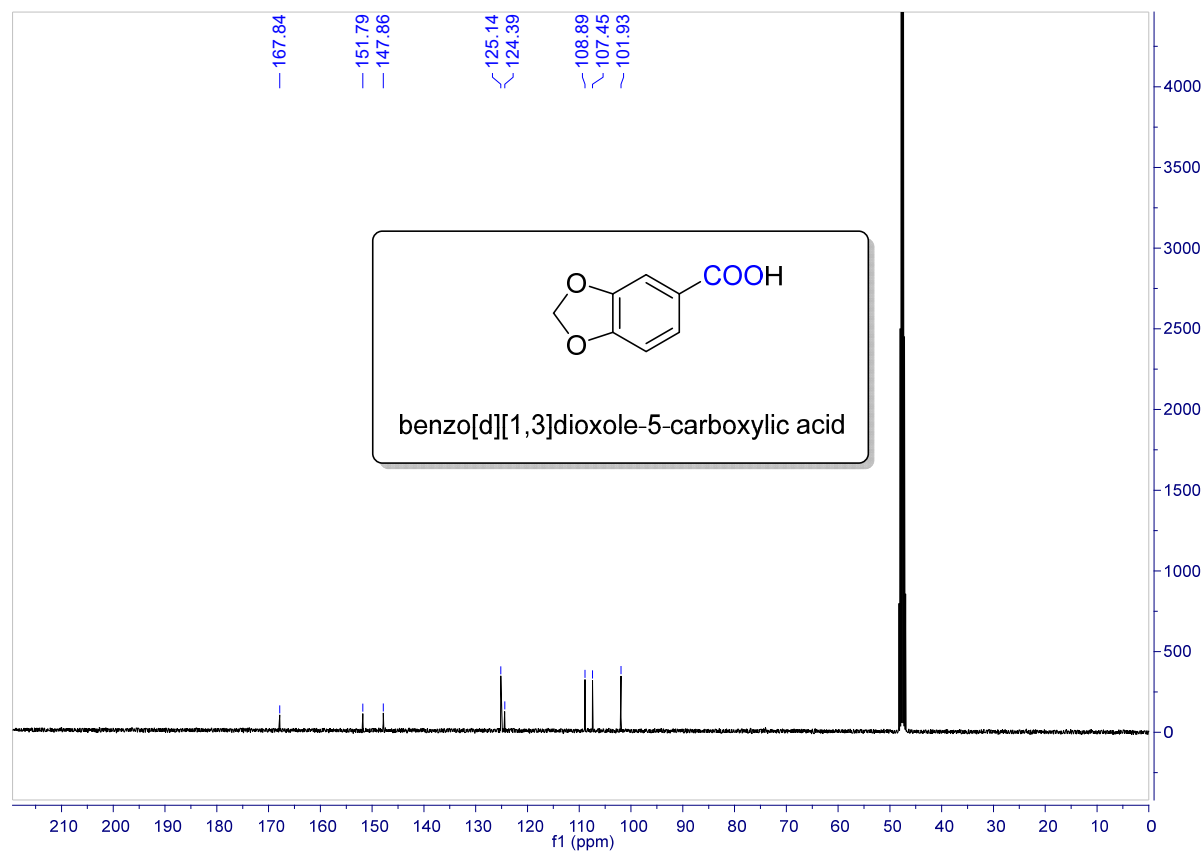
¹³C NMR of anthracene-9-carboxylic acid (2ag)



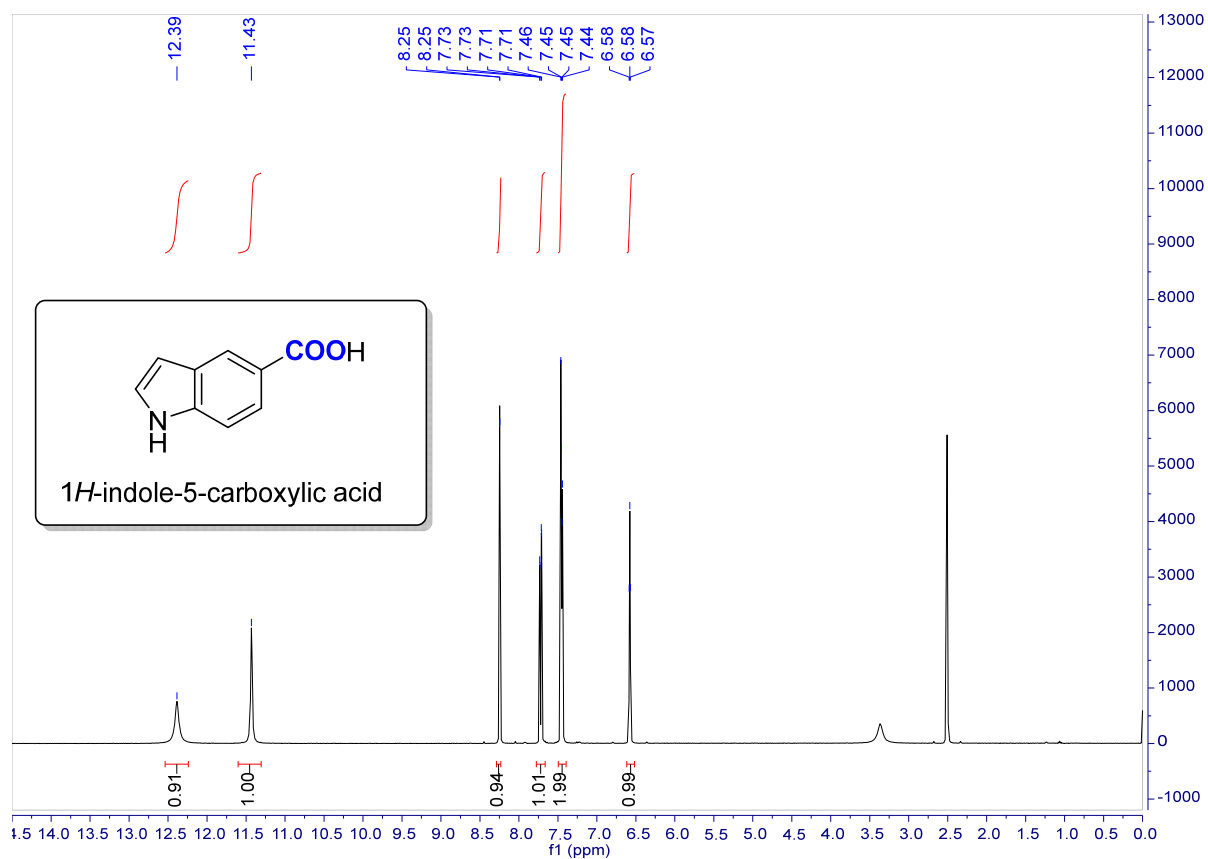
¹H NMR of benzo[d][1,3]dioxole-5-carboxylic acid (2ah)



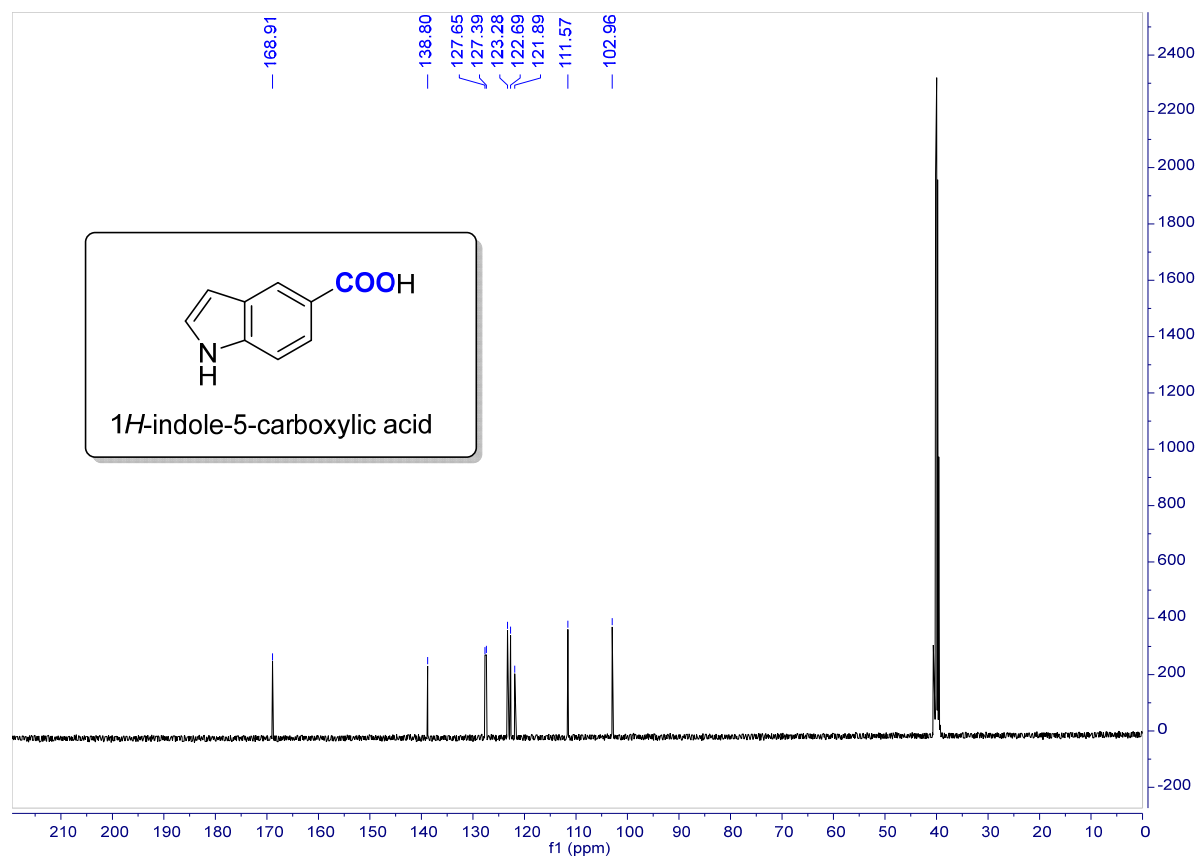
¹³C NMR of benzo[d][1,3]dioxole-5-carboxylic acid (2ah)



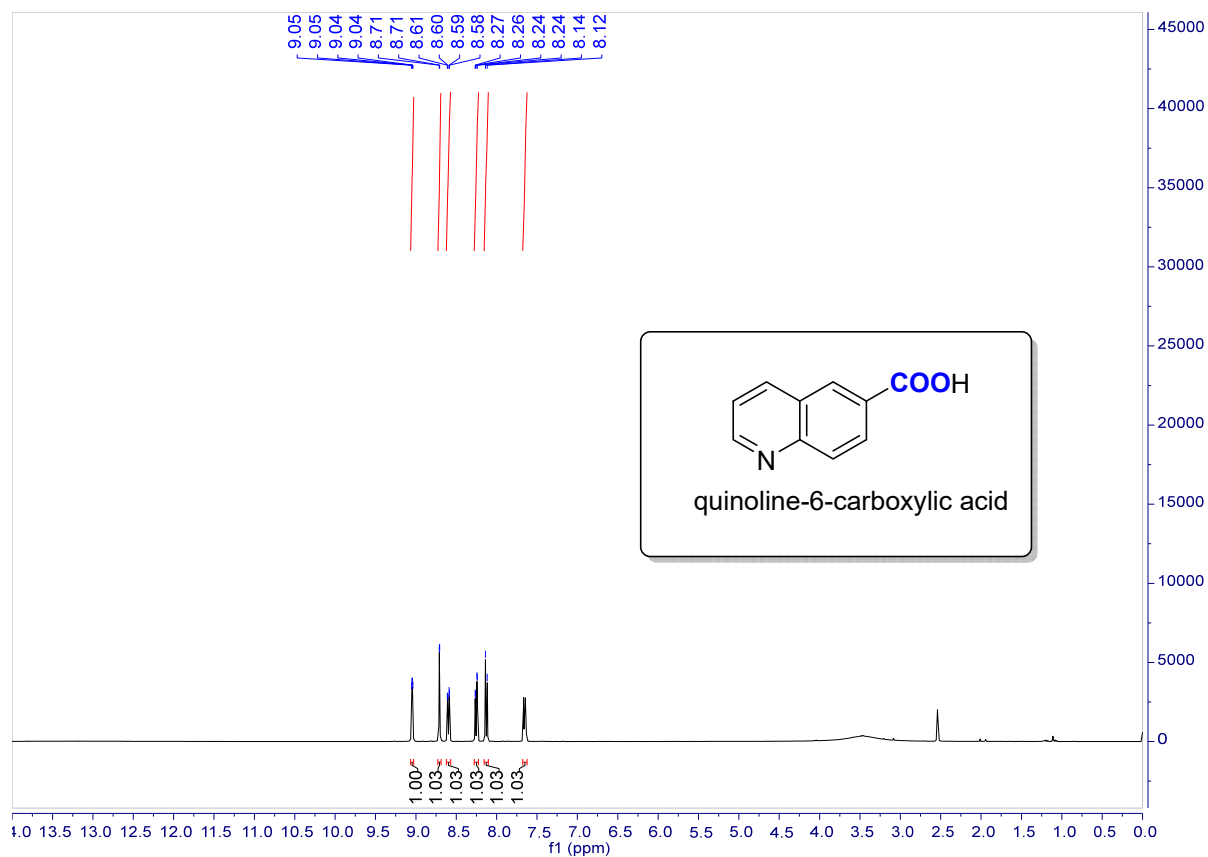
¹H NMR of 1H-indole-5-carboxylic acid (2ai)



¹³C NMR of 1H-indole-5-carboxylic acid (2ai)



¹H NMR of quinoline-6-carboxylic acid (2aj)



¹³C NMR of quinoline-6-carboxylic acid (2aj)

