Metal-Isonitriles

Synthesis, Characterization and Application in Catalysis

Dissertation

zur Erlangung des Doktorgrades

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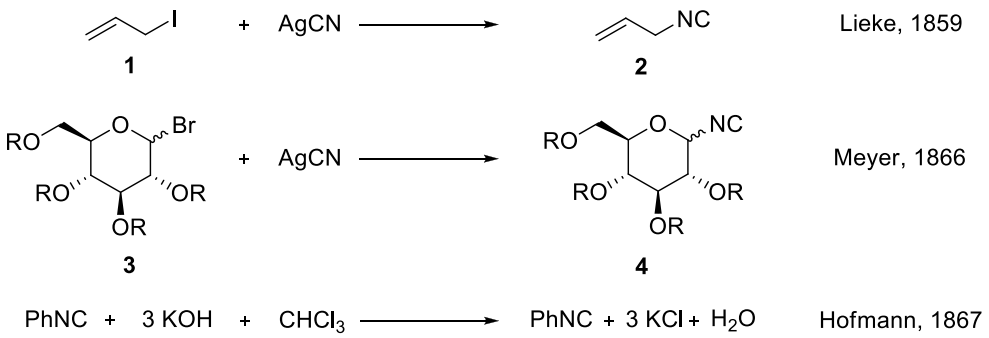
A Isonitrile Synthesis

1. Introduction

The history of isonitriles began 1859 when *Lieke* tried to prepare allyl cyanide (**2**) by reacting allyl iodide (**1**) with silver cyanide[1] (Scheme 1). Unwittingly, he isolated the first isonitrile instead. He was surprised that the acidic hydrolysis of the obtained compound did not yield crotonic but formic acid. Further studies of this "anomalous" hydrolysis were canceled since *Lieke* performed all experiments outdoors due to the "horrifying" odor of the compound which led to "continuing complaints in the neighborhood".[1]

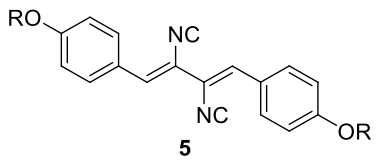
Several years later, *Meyer* produced 1-isocyano-1-desoxy-glucose (**4**)[2] and *Gautier* prepared alkylisonitriles[3] using the same procedure. In 1867, *Hofmann* reported a new strategy for the formation of isonitriles by the addition of primary amines to chloroform and potassium hydroxide[4] (Scheme 1). During this period, *Gautier's* fundamental work identified these novel compounds as isomers of the ordinary nitriles and finally as a distinct compound class.[5]

Scheme 1. First synthetic appoaches towards isonitriles.



At this time, only 12 different isonitriles were prepared, due to their cumbersome preparation and their disagreeable smell.[6] Also, their further investigation proceeded slowly. In 1910, *Oliveri-Mandala* and *Alagna* reported the formation of tetrazoles using isonitriles and hyrdazoic acid.[7] In the following years, *Passerini* introduced the first three component reactions applying isonitriles (P-3-CRs).[8]

The first naturally occurring isonitrile was discovered 1948 by *Rothe* in *Penicillum notatum Westling* and in the *Penicillum chrysogenum*.[9] This compound and its *O*,*O'*-dimethylether were used as the antibiotic *xanthocillin* later[10] (Figure 1).



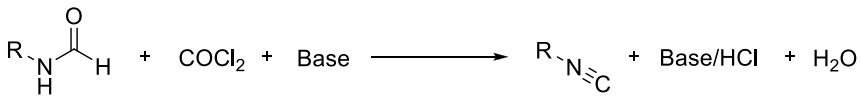
5

R = H, CH_3

Figure 1. The first discovered naturally occurring isonitrile *xanthocillin* and its *O*,*O*'-dimethylether.

Considering the hydrolysis products, *Gautier* already suggested the dehydration of formamides with phosphorous pentoxide as a possible route towards isonitriles.[11] However, not realizing that acidic media destroy isonitriles, he did not succeed in developing such a synthetic route. Finally a new era began in 1958, when *Ugi* introduced the dehydration of formamides with phosgene in the presence of a base as a general method for the preparation of isonitriles[12] (Scheme 2). In particular, the popularity of isonitriles began, when *Ugi* introduced the four component reaction of isonitriles, amines, carbonyl compounds and acids (U-4CR).[13]

Scheme 2. First general method for the preparation of isonitriles by *Ugi* in 1958.



6 **7**

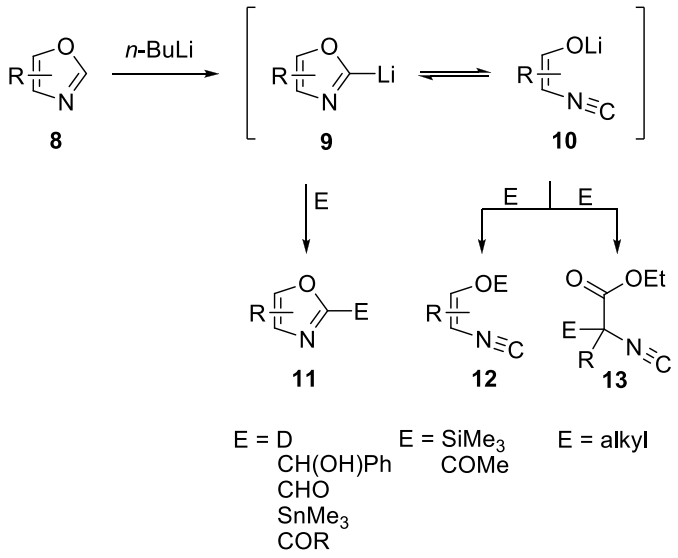
To circumvent the use of phosgene, a systematic search for a more suitable dehydration reagent followed. Adressing this matter, the dehydration of *N*-formamides was achieved by $POCl_3$,[12b] chlorodimethylformiminium chloride,[14] DABCO,[15] aryl chlorothionoformate,[16] and under microwave irradiation with supported sulfonyl chlorides[17] or 2,4,6-trichloro[1,3,5]-

triazine (cyanuric chloride, TCT).[18] Although other methods have been reported, the dehydration of *N*-formamides is still considered as the most commonly used method for the preparation of isonitriles.

2. Oxazole-derived Isonitriles

A less common route towards isonitriles starts with the metalation of oxazole derivatives. In oxazoles the 2-H is generally the most acidic, having pK_a values in the range of 20.[19] Hence, lithiation of these heterocycles furnishes 2-lithiooxazoles. By a ring chain tautomerism, the 2-lithiooxazoles equilibrate with the open-chain lithio-α-isocyanide species.[20]

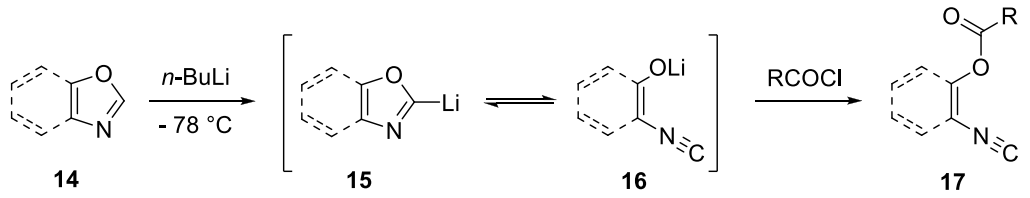
Scheme 3. The chemistry of 2-metalated oxazoles.



The application of appropriate electrophiles allows a selective trapping of these anions. Substituted oxazoles (**11**) were obtained[20-21] by trapping the anions with D_2O, benzaldehyde, *N*-alkylated formamides, trimethyltin chloride, or carboxamide acylate. In contrast, quenching with hard electrophiles like chloro trimethylsilane or acyl chlorides led to open-chain isonitriles[20,21d,22] **12**, while the application of alkyl halides yielded products of type **13** (Scheme 3).[21a]

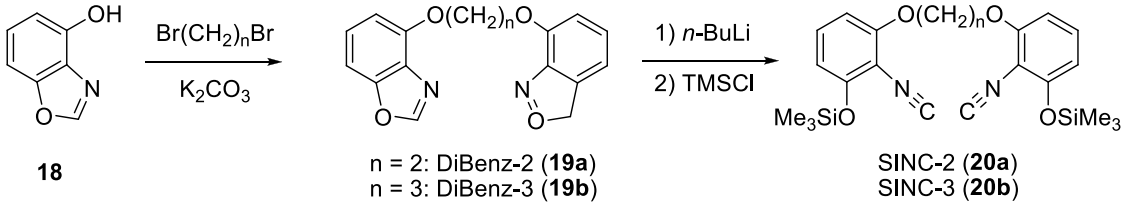
Using this methodology, *Pirrung* and co-workers reported the synthesis of surprisingly fragrant isonitriles starting from oxazoles.[22c] Upon metalation and subsequent entrapment of the resulting anion using various acyl chlorides, oxazole or benzoxazole was converted into (*Z*)-isocyanovinyl respectively 2-isocyanophenyl esters **17** (Scheme 4).

Scheme 4. Conversion of oxazoles into fragrant isonitriles.



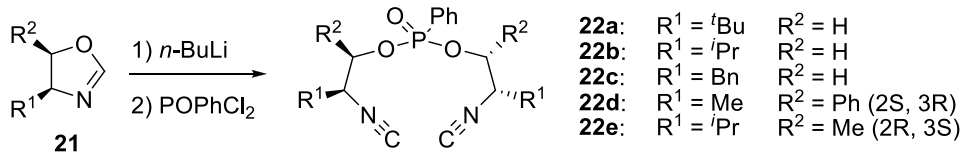
The preparation of bidentate isonitriles, originating from 4-hydroxy benzoxazole (**18**), was already introduced by *Angelici et al.* in 1984.[22d] They reported a two-step synthesis starting with the connection of two benzoxazoles via an ethylene bridge, followed by the opening of the benzoxazoles with trimethylsilane chloride (Scheme 5).

Scheme 5. Peparation of **SINC-2** (**20a**) and **SINC-3** (**20b**) in a two-step process by *Angelici et al.*



A more direct access to bisisonitriles was developed in our labs. By choosing an appropriate electrophile various sterically and electronically different chiral bisisonitrile ligands **22** could be obtained in a single step reaction[23] (Scheme 6).

Scheme 6. Synthesis of various chiral bisisonitrile ligands.

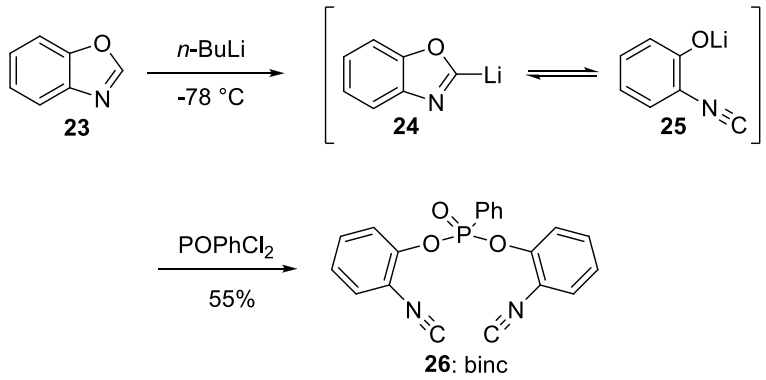


Here, lithiation of chiral oxazolines **21** was followed by the addition of phenyl phosphonic dichloride as electrophile. The ability of **22** to form chelates was proven by the successful preparation of their bidentate complexes with various transition-state metals.[24]

3. Preparation of a New Bis(isonitrile) Ligand and its $PdCl_2$-Complex

In the context of this thesis, the latter methodology was further expanded to the commercially available benzoxazole (**23**) to obtain the more rigid aromatic bisisonitrile **26** in a single step reaction (Scheme 7).

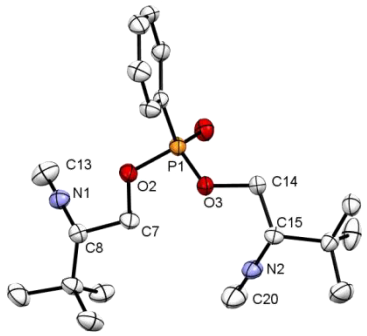
Scheme 7. Synthesis of binc (**26**) (bis(2-isocyanophenyl) phenylphosphonate).



Conditions: benzoxazole (**23**) (0.91 g, 7.63 mmol, 1.0 equiv.), *n*-BuLi (1.6 M in hexane, 5.0 ml, 8.0 mmol, 1.05 equiv.), THF (20 ml), -78 °C, 1.5 h; $POPhCl_2$ (0.57 ml, 4.04 mmol, 0.53 equiv.), -78°C- rt, 2 h.

Parallel to our research, compound **26** and its Pt(II)-complex together with various other benzoxazole derived carbonyl-bridged bisisonitrile ligands were published by *Sgarbossa* and *Tubaro*.[25] In our group we investigated the structure of this easy to prepare, odorless and bench-stable compound by X-ray analysis[26] (Table 1). The solid state structure of **26** revealed that both isonitrile moieties are already pre-oriented for the chelation of a metal. In contrast, in the X-ray structure of bis(isonitrile) **22a**[23a] both isonitriles point away from each other, thus coordination of **22a** to a metal center must be realized by rearrangement of the two diastereotopic isonitrile arms

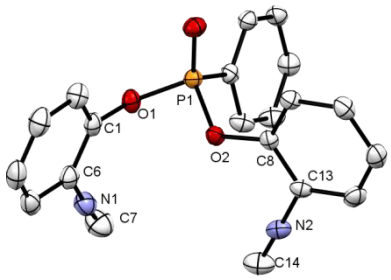
Table 1. Solid-state structure and selected bond angles and length of the bisisonitrile ligands **22a** and **26**.



22a[23a]

Bond angles [deg]: C13-N1-C8: 177.1; N1-C8-C7: 108.7; C8-C7-O2: 107.7; O3-C14-C15: 108.2; C14-C15-N2: 108.8; C15-N2-C20: 179.1.

Bond length [Å]: C13-N1. 1.152; C20-N2: 1.148; N1-C8: 1.446; N2-C15: 1.444.

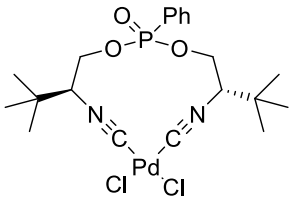


26

Bond angles [deg]: C7-N1-C6: 176.6; N1-C6-C1: 118.7; C6-C1-O1: 117.2; O2-C8-C13: 117.0; C8-C13-N2: 119.5; C13-N2-C14: 178.3.

Bond length [Å]: C7-N1: 1.159; C14-N2: 1.153; N1-C6: 1.398; N2-C13: 1.399.

Having the new bisisonitrile in hand, its palladium(II) complex was prepared by using one equivalent of $Pd(MeCN)_2Cl_2$ to probe its applicability as a bidentate ligand (Figure 2). Similar to the known chiral palladium-bisisonitrile **27**,[23] the more rigid complex **28** was obtained in DCM after two hours at room temperature by a ligand exchange reaction.



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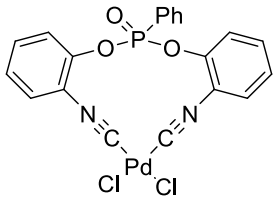

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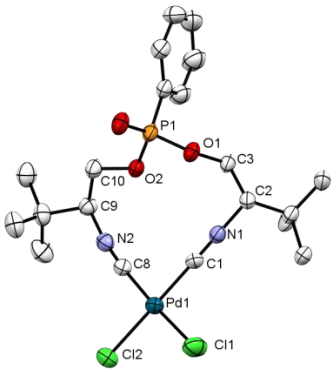
Figure 2. The $PdCl_2$-bisisonitrile complexes **27** and **28**.

The solid-state structure of complex **28** is shown in Table 2. With 88°, the ligands bite-angle stays within the scope of square-planar d8 complexes. This value is in agreement with the previous discussed Pd(bisisonitrile)Cl_2 complex **27**.[23a]

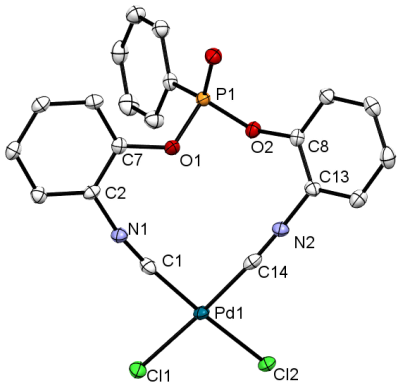
Table 2. Solid-state structure and selected bond angles and length of the Pd(bisisonitrile)Cl_2 complexes **27** and **28**.



27[23a]

Bond angles [deg]: C8-Pd1-C1: 88.2; Cl1-Pd1-Cl2: 93.7; N1-C1-Pd1: 177.2; N2-C8-Pd1: 174.4; C1-N1-C2: 177.6; C8-N2-C9: 171.8; N1-C2-C3: 106.4; N2-C9-C10: 107.0; C2-C3-O1: 106.1; C9-C10-O2: 108.5.

Bond length [Å]: Pd1-C1: 1.943; Pd1-C8: 1.935; Pd1-Cl1: 2.296; Pd1-Cl2: 2.299; C1-N1: 1.128; C8-N2: 1.136; N1-C2: 1.457; N2-C9: 1.453.



28

Bond angles [deg]: C1-Pd-C14: 88.1; Cl1-Pd-Cl2: 92.9; Pd-C1-N1: 174.3; Pd-C14-N2: 175.8; C1-N1-C2: 170.2; C14-N2-C13: 176.8; N1-C2-C7: 117.3; N2-C13-C8: 118.4; C2-C7-O1: 116.2; C13-C8-O2: 118.3.

Bond length [Å]: Pd-C1: 1.932; Pd-C14: 1.937; Pd-Cl1: 2.295; Pd-Cl2: 2.302; C1-N1: 1.148; C14-N2: 1.145; N1-C2: 1.391; N2-C13: 1.400.

Similar to **27**, the bond distances between the palladium and the isonitrile carbon (1.932 and 1.937 Å) determined for compound **28** were shorter than the Pd-Cl bonds (2.295 and 2.302 Å). Additionally, the metal back bonding to the π*-orbitals of the isonitrile ligand is reflected in the deviation of the linear coordination of the isonitriles to the palladium center (174.3 and 175.8°). However, the structure of **28** shows a significant widening of the other angles at the isonitrile arms, rationalized by the minor flexibility of the sp^2-carbon moieties (Table 2).

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(26) CCDC-1064132 (**26**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

B Metal-Isonitriles in Catalysis

1. Introduction

After *Lieke's* discovery of isonitriles in 1859,[1] it took almost one century until *Ugi* published the first multicomponent reaction (U-4CR),[2] and thus made isonitriles popular in organic chemistry.[3] The development of this and other isocyanide-based multicomponent reactions (MCRs) enabled the generation of extensive compound libraries by efficient and economic single-step combinatorial synthesis. Isonitriles readily react with electrophiles, nucleophiles and even radicals, which is why they still represent popular and versatile building blocks in modern organic chemistry.

Besides their application in organic chemistry, isonitriles also serve as ligands in various metal complexes.[4] The first metal coordinated isonitriles were prepared by *Gautier* in 1869.[5] He reacted silver cyanide with different alkylating reagents and thus yielded isonitrile-adducts with the composition RNC-AgCN. Soon, the analogy between carbon monoxide and isonitriles became apparent and in 1959 *Malatesta* published a first general review, where he describes a huge variety of transition state metal isonitriles.[4a]

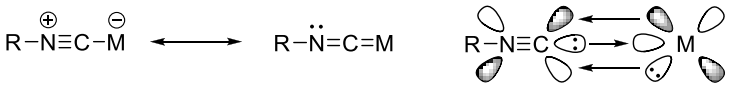


Figure 1. Metal isonitrile in valence-bond and molecular-orbital view.

Compared to carbon monoxide, isonitriles are quite polar substances (e.g. PhNC 3.44 Debye, CO 0.12 Debye).[6] Additionally, isonitrile ligands exhibit stronger σ–donor but weaker π–acceptor qualities than carbon monoxide. The lone electron pair of the isonitrile carbon forms a σ-type donor bond to coordinate the metal. In addition, a second π -bond can be formed, if the fully occupied d-orbital of the metal overlaps with the empty, low-lying antibonding orbitals of the isonitrile ligand (Figure 1).

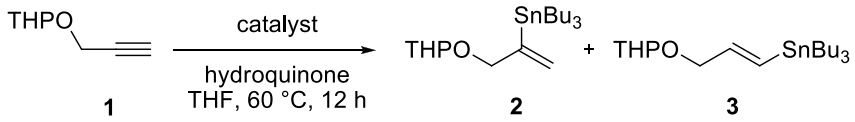
In general, the properties of RNCs heavily depend on the steric and electronic properties of their organic rest R. Thus, metal catalysis with isonitrile complexes can be optimized by the design of innovative ligands combined with effective ligand variation. This review is focused on the molecular structure and catalytic activity of various isonitrile complexes of the Cr, Mn, Fe, Co, Ni and Cu triads that were successfully applied in metal catalysis.

2. Group 6-Isonitriles: Molybdenum, Tungsten

Hydro- and Bis-stannation of Functionalized Alkynes

The application of (isonitrile)molybdenum cabonmonoxide complexes for hydrostannations was studied by *Kazmaier el al*.. While the use of $Mo(CO)_6$ led to moderate yields and selectivites, the subsequent substitution of carbonmonoxide with *tert*-butylisonitrile ligands resulted in a dramatic increase of both, with best results obtained using $Mo(CO)_3(^tBuNC)_3$[7] (Table 1). Several advantages of the isonitrile were stated: 1) The bulky *tert*-butyl group may influence the regioselectivity; 2) Since the π-backdonation of the isonitrile to the metal center is weaker compared to CO, the isonitrile could easily dissociate form the metal and thus open a free coordination site for the substrate; 3) In contrast to CO, the isonitrile ligand stays in solution after dissociation form the metal, which may lead to a prolonged lifetime of the catalyst.

Table 1. Catalytic hydrostannation of THP-propargylether (**1**) (THP = tetrahydropyranyl) using different molybdenum catalysts.



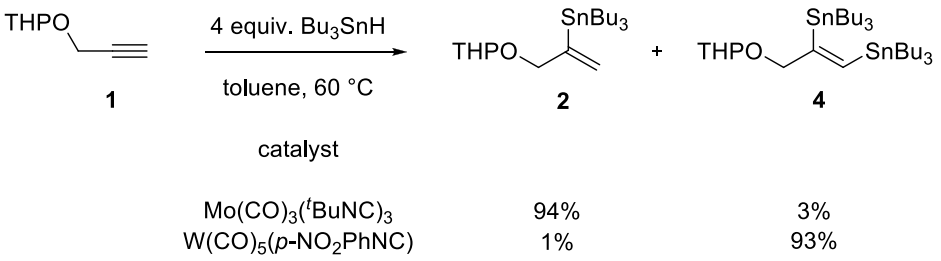
1 **2** **3**

Entry	Catalyst	Yield [%]	Selectivity α:β
1	$Mo(CO)_6$	35	28 : 72
2	$Mo(CO)_5(^tBuNC)$	64	62 : 38
3	$Mo(CO)_4(^tBuNC)_2$	89	87 : 13
4	$Mo(CO)_3(^tBuNC)_3$	91	>95:5
5	$Mo(CO)_2(^tBuNC)_4$	85	>95:5

Hence, $Mo(CO)_3(^tBuNC)_3$ proved to be a highly active and selective catalyst for the preparation of α-stannylated products by hydrostannation of functionalized alkyens, such as propargylic esters or protected propargyl alcohols.[7-8] The products obtained could be further transformed e.g. in Pd(0)-catalyzed coupling reactions,[9] towards substituted Morita-Baylis-Hillman products[10] or vinyliodides,[11] and into stannylated amino acids[12] which again could be processed in Stille couplings.[13] Furthermore, it was found, that both, the reactivity and the regionselectivity towards the α-products increases by substitution of the substrates triple bond with electron-withdrawing groups. This shows, that propargylic esters are more reactive and more selective than propargylic ethers,[14] sulfones[15] or phosphonates.[16]

While $Mo(CO)_3(^tBuNC)_3$ provided mainly the α-stannylated products, application of $Wo(CO)_5(p\text{-}NO_2PhNC)$ only yielded traces of the hydrostannylated compounds, but gave excellent yield of the distannylated allyl products under the same reaction condition[17] (Scheme 1). Further studies revealed that by carrying out the reaction under a CO atmosphere or microwave irradiation, side reactions could be suppressed which led to better yields and selectivities.[18]

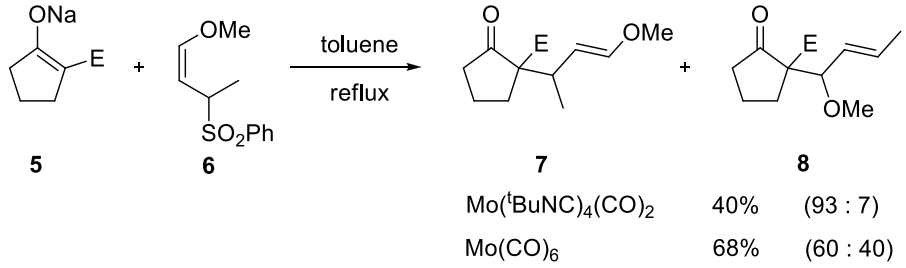
Scheme 1. Hydro- and distannylations of propargyl alcohol derivatives.



Allylic Alkylation

Trost et al. used Mo(^{t}BuNC)$_4$(CO)$_2$ as highly reactive catalysts for allylic alkylations.[19] The complex showed good catalytic activity towards a broad range of allyl acetates and especially allyl sulfones. In addition, the catalyst showed improved chemo-, regio- and stereoselectivity compared to Mo(CO)$_6$ (Scheme 2).

Scheme 2. Molybdenum-isonitrile catalyzed alkylation.



5 **6** **7** **8**

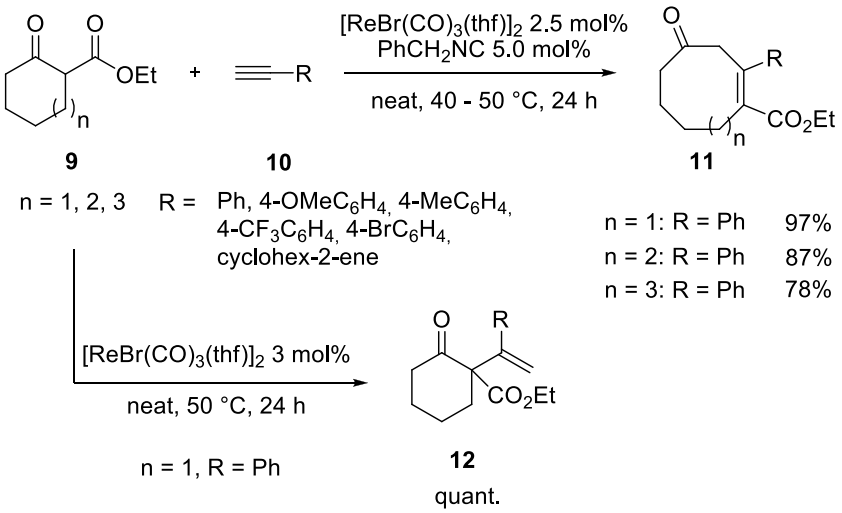
Mo(^{t}BuNC)$_4$(CO)$_2$	40%	(93 : 7)
Mo(CO)$_6$	68%	(60 : 40)

3. Group 7-Isonitriles: Rhenium

Insertion of Acetylenes in Cyclic Compounds

The insertion of acetylenes into a carbon-carbon single bond of non-strained cyclic compounds in presence of $[ReBr(CO)_3(thf)]_2$ and benzyl isocyanide as additional ligand under solvent free conditions was reported by *Takai et al.*.[20] While this system led to the formation of the ring insertion products **11**, alkenyl derivative **12** was formed in the absence of the isonitrile (Scheme 3).

Scheme 3. Insertion of acetylenes using a rhenium-isonitrile system as catalyst.

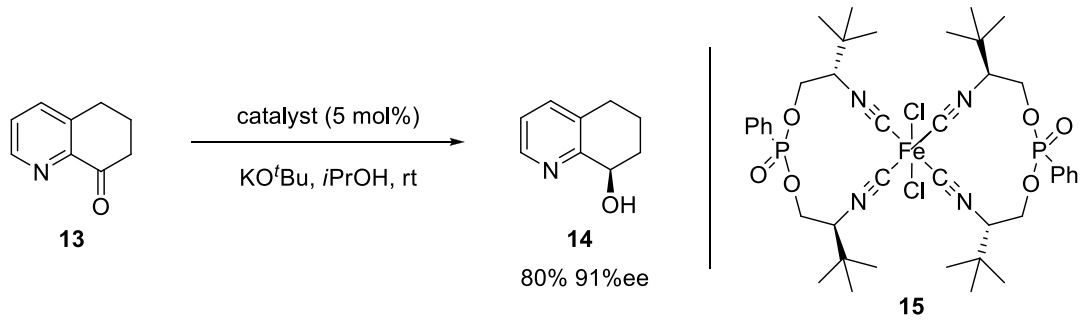


4. Group 8-Isonitriles: Iron, Ruthenium

Transfer Hydrogenation

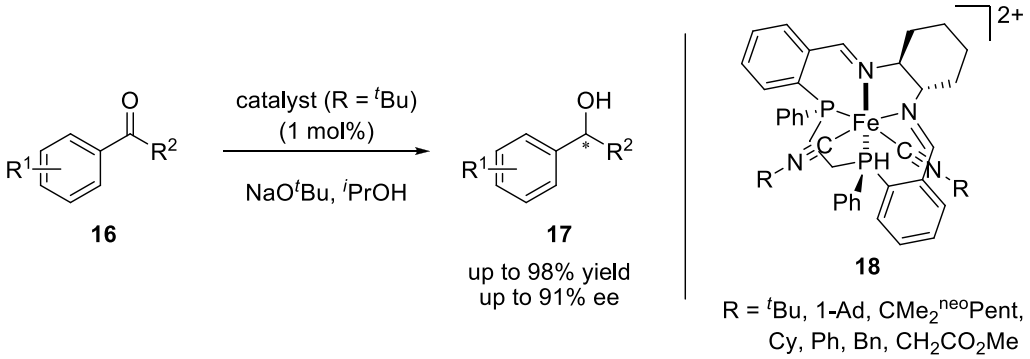
In 2010, *Reiser et al*. demonstrated for the applicability of isonitriles as chiral inductors in asymmetric catalysis.[21] They reported the preparation of a chiral iron(II)-bis(isonitrile) complex (**15**) which catalyzes the transfer hydrogenation of aromatic ketones with enantioselectivities up to 91% ee (Scheme 4). The reaction proceeds most likely via hydride transfer through imine intermediates which were generated by the reduction of the isonitrile ligands while the metal center acts as Lewis acid to activate the ketone.

Scheme 4. Transfer hydrogenation of 6,7-dihydroquinolin-8(*5H*)-one using an chiral iron(II)-bis(isonitrile).



A different class of iron(II)-isonitriles for the enantioselective transfer hydrogenation was introduced by *Mezzetti* and coworkers.[22] Complexes bearing a chiral N_2P_2 macrocycle ligand were prepared from the corresponding bis(acetonitrile) analogues and could transform a huge variety of aromatic ketons to enantioenriched alcohols (Scheme 5). Screening of the complexes identified the *tert*-butylisonitrile complex to be superior to carbonyl, acetonitrile or other isonitrile analogues concerning yield and chiral induction.

Scheme 5. Enantioselective transfer hydrogenation using iron(II)-isonitriles with a chiral N_2P_2 macrocycle ligand



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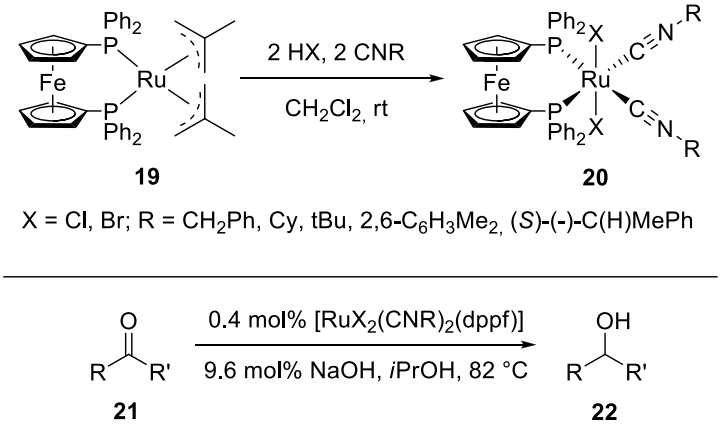
The transfer hydrogenation of ketones catalyzed by the bis(isocyanide)-ruthenium(II) complexes *trans*,*cis*,*cis*-[$RuX_2(CNR)_2$(dppf)] (X = Cl, Br; R = CH_2Ph, Cy, ^{t}Bu, 2,6-$C_6H_3Me_2$, (*S*)-(-)-C(H)MePh; dppf = 1,1′-bis(diphenylphosphino)ferrocene) (**20**) was reported by *Cadierno* and coworkers.[23]

Scheme 6. Transfer hydrogenation of ketones, catalyzed by bis(isocyanide)-ruthenium(II) complexes.



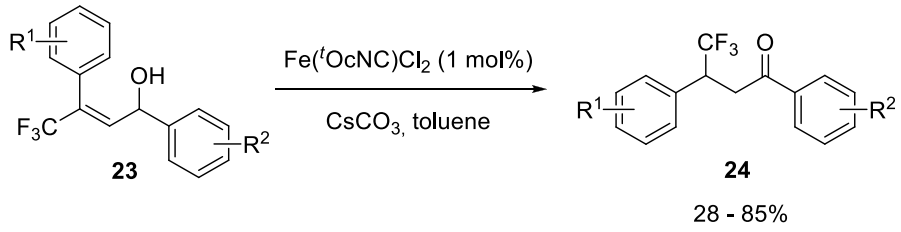
The complexes were prepared by the reaction of the bis(allyl)-Ru(II) derivative [Ru(η^3-2-$C_3H_4Me)_2$(dppf)] (**19**) with isocyanide ligands and hydrogen halides and *trans*,*cis*,*cis*-[$RuCl_2(CNCH_2Ph)_2$(dppf)] proved to be the most active catalyst for the transfer hydrogenation of various ketones (Scheme 6). In addition, the hydride complexes *cis*,*cis*-[RuHCl(CN-2,6-$C_6H_3Me_2)_2$(dppf)] and *cis*,*cis*,*cis*-[RuH_2(CN-2,6-$C_6H_3Me_2)_2$(dppf)] could be isolated. These

complexes were able to perform the transfer hydrogenation of acetophenone in the absence of base, thus leading to the assumption to be the real active species.

Isomerization of γ-Trifluoromethylated Allylic Alcohols into β-Trifluoromethylated Ketones

The synthesis of trifluoromethylated dihydrochalcones **24** by the isomerization of the corresponding γ-trifluoromethylated allylic alcohols **23** using iron(II)-isonitriles was reported by *Cahard et al.*.[24] By the screening of different catalytic system, $Fe(^{t}OcNC)_4Cl_2$ (^{t}OcNC = 1,1',3,3'-tetramethylbutylisonitrile) proved to be the most efficient catalyst for this transformation (Scheme 7). This catalyst is considered as cost-effective replacement of platinum compounds.

Scheme 7. Synthesis of trifluoromethylated dihydrochalcones using $Fe(^{t}Oc)_4Cl_2$ as catalyst.



5. Group 9-Isonitriles: Rhodium

Hydrogenation

The hydrogenation and isomerization of 1-hexene using an insoluble matrix of $[RhCl(CO)(1,4\text{-}(CN)_2C_6H_4)]_n$ was reported by *Efraty el al.*.[25] The heterogeneous catalyst was prepared by the reaction of $[Rh(CO)_2Cl]_2$ with an equimolar amount of 1,4-diisocyanobenzene as non-chelating bidentate linker between the metal nuclei. The geometry of this matrix was suggested as tetranuclear cyclic oligomer (**27**), linear (**25**) or non-linear (**26**) polymers units with regular or irregular Rh-Rh intrachain interactions of 3.2 – 3.5 Å (Figure 2).

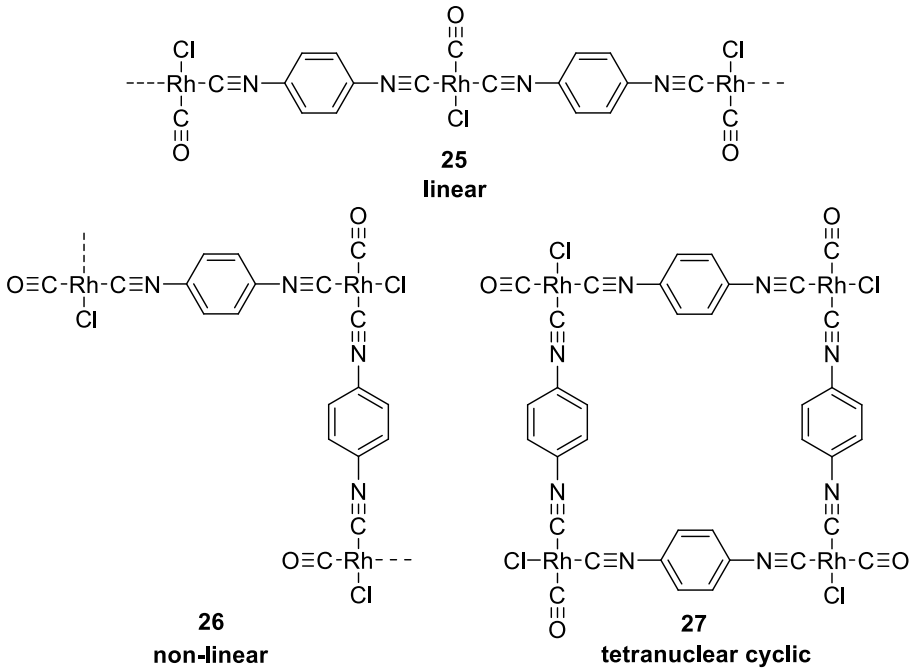


Figure 2. Different geometries of $[RhCl(CO)(1,4\text{-}(CN)_2C_6H_4)]_n$.

The rhodium catalyzed hydrogenation and isomerization of 1-hexene was observed by applying a hydrogen pressure of 0.5 atm at room temperature to the reaction mixture. In the dark, isomerization of *trans*- and *cis*-hexenes was followed by the hydrogenation to *n*-hexane, whereas under UV irradiation no hydrogenation of the isomers was observed.

The preparation and catalytic activity of rhodium(I) complexes of isonitrile-functionalized silica was investigated by *Howell* and coworkers.[26] By condensation of $(EtO)_3Si(CH_2)_3NC$ with Aerosil® 200, they prepared silica with an isonitrile content in the range of 0.10 – 0.15 mmol NC/g. The heterogenized Rh(I) complex was synthesized the addition of $[RhCl(COD)]_2$ or $[RhCl(CO)_2]_2$ to this functionalized silica. The obtained material showed catalytic activity towards the hydrogenation of cyclo- and 1-hexene at 60 °C under 1 atm of hydrogen in toluene. However, it is suggested, that the catalysis proceed via reduction to metallic rhodium accompanied by metal crystallite formation.

Angelici et al. studied the combination of homogeneous and heterogeneous catalysts by tethering rhodium and platinum isocyanide complexes on silica supported metal catalysts[27] (Figure 3). Theses catalysts were prepared by the immobilization of $RhCl(CO)[CN(CH_2)_3Si(OEt)_3]_2$ (Rh-CNR_2), $RhCl[CN(CH_2)_3Si(OEt)_3]_3$ (Rh-CNR_3) or $PtCl_2[CN(CH_2)_3Si(OEt)_3]_2$ (Pt-CNR_2) on M-SiO_2 (M = Pd, Pt, Ru). The resulting TCSM (tethered complex on supported metal) compounds Rh-CNR_2/Pd-SiO_2 and Rh-CNR_3/M-SiO_2 (M = Pd, Pt, Ru) were used to catalyze the hydrogenation of arenes and Pt-CNR_2/Pd-SiO_2 for the hydrogenation of cyclohexanone under mild conditions of at 40 °C and 1 atm.

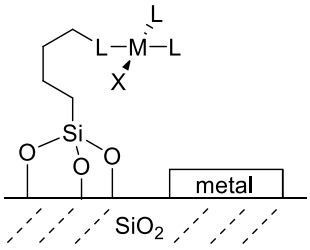


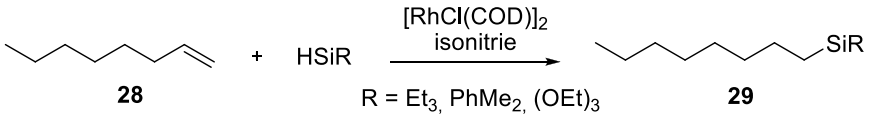
Figure 3. Conceptual illustration of a homogeneous complex tethered on a heterogeneous supported metal catalyst.

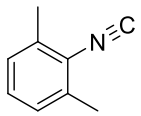
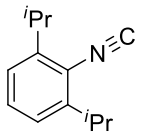
Comparison of the catalytic activity of the TCSM catalysts with the separate homogeneous rhodium or platinum isonitrile complexes, the heterogeneous silica supported metal catalysts and the rhodium or platinum complexes tethered on just silica, exhibit the superior activity of the TCSMs. In addition, DRIFT-IR spectroscopy showed that the isocyanide ligands remained coordinated to the metal centers after the catalytic experiments.

Hydrosilylation

In their study towards the catalytic activity of various sterically hindered isonitrile complexes of transition state metals *Nile* and coworkers reported hydrosilylations of different unsaturated molecules.[28] The active species was prepared *in situ* from $[RhCl(COD)]_2$ and an appropriate amount of 2,6-dimethylphenylisocyanide (**30**) or 2,6-diisopropylphenylisocyanide (**31**).

Table 2. Hydrosilylation of 1-octene (**28**) using Rh/isonitrile as catalytic system.

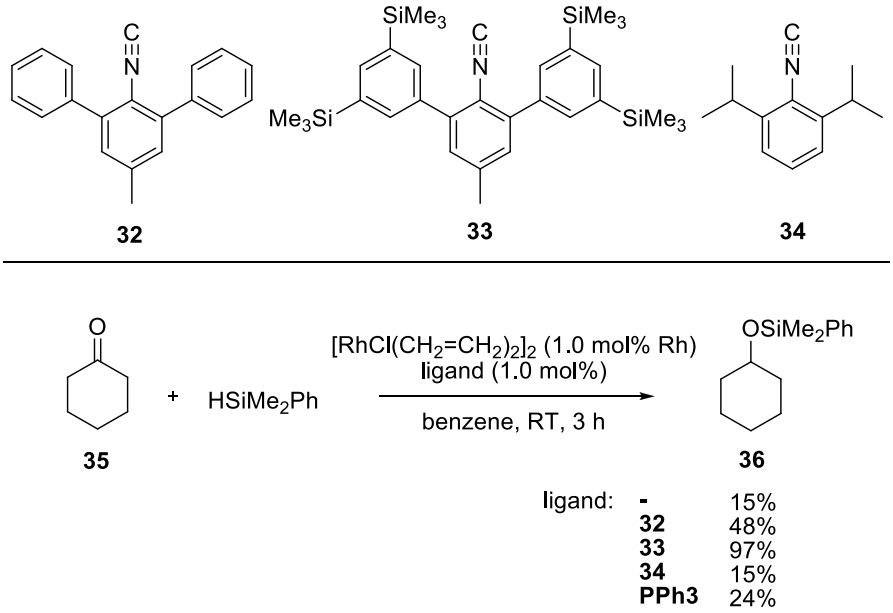


Entry	Isonitrile ligand	Silane	Isonitrile/Rh	Temp. [°C]	Yield
1	 **30**	$HSiEt_3$	1:1	100	69
2			2:1		82
3			3:1		61
4			4:1		0
5	 **31**	$HSiPhMe_2$	2:1	20	81
6		$HSiEt_3$			66
7		$HSi(OEt)_3$			40

It was shown that the best results for the hydrosilylation of 1-octene (**28**) could be obtained with a **30**/Rh-ratio of 2:1. By application of the more sterically demanding **31** good activity was observed even at an **31**/Rh ratio of 10:1. Furthermore, this system showed higher activity towards alkylsilanes as compared to alkoxysilanes (Table 2). In addition, they reported group 6 zero-valent complexes $M(2,6\text{-}{}^{i}PrC_6H_3NC)_n(CO)_{6-n}$ (M = Cr, Mo, W; n = 1 or 2) which were active catalysts for the hydrosilylation of 1,3-dienes.

Sawamura and coworkers investigated new bulky isocyanide ligands with *meta*-terphenyl backbones in the rhodium catalyzed hydrosilylation of ketones. These ligands showed higher activity compared to other isocyanide or phosphine ligands (Scheme 8).

Scheme 8. Hydrosilylation in the presence of a neutral rhodium complex with various isocyanides or PPh_3.



They proposed that the formation of the catalytically active monoisocyanide-rhodium species was facilitated by the high affinity of the ligand to the metal in combination with the bulkiness of the isocyanide.

Hydrosilylation was also reported using $MCl_2(2,6\text{-}Me_2C_6H_3NC)_2$ (M = Pt, Pd, Ni) with decreasing activity in the order Pt>Ni>Pd for the reaction of α-methylstyrene with dimethyphenylsilane. These group 10 isonitriles as well as the rhodium isocyanide complexes provided 1,4-addition products of α,β-unsaturated ketones and 1,2-addition to an olefinic position to give silylketons with α,δ-unsaturated ketones.[29]

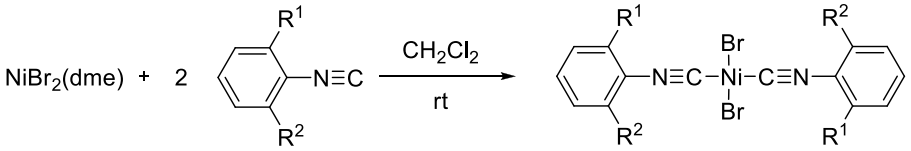
6. Group 10-Isonitriles: Nickel, Palladium, Platinum

The synthesis and structural characterization of nickel-isonitrile clusters and their use as catalysts for a variety of reactions was reported by *Muetterties et al.*.[30] The tetrahedral cluster $Ni_4[^tBuNC]_7$ catalyzed e.g. the trimerization of acetylenes to benzenes, butadiene to 1,5-cyclooctadienes, the polymerization of allene, the hydrogen-deuterium exchange reaction between H_2 and D_2, the hydrogenation of isoyanides and nitriles as well as the selective hydrogenation of acetylenes to *cis* olefins.

Polymerization of Ethylene

Nagashima and coworkers studied nickel(II) isocyanide complexes as catalysts for the polymerization of ethylene in the presence of methylaluminoxane (MAO).[31] Various $NiBr_2(CNAr)_2$ (**38**) complexes were prepared having substituents at the 2- and/or 6-position using $NiBr_2$(dme) (dme = 1,2-dimethoxyethane) as precursor. (Scheme 9) Depending on the substitution pattern, these compounds furnished polyethylenes of different molecular weights.

Scheme 9. Different $NiBr_2(CNAr)_2$ complexes used for the polymerization of ethylene.



37 **38**

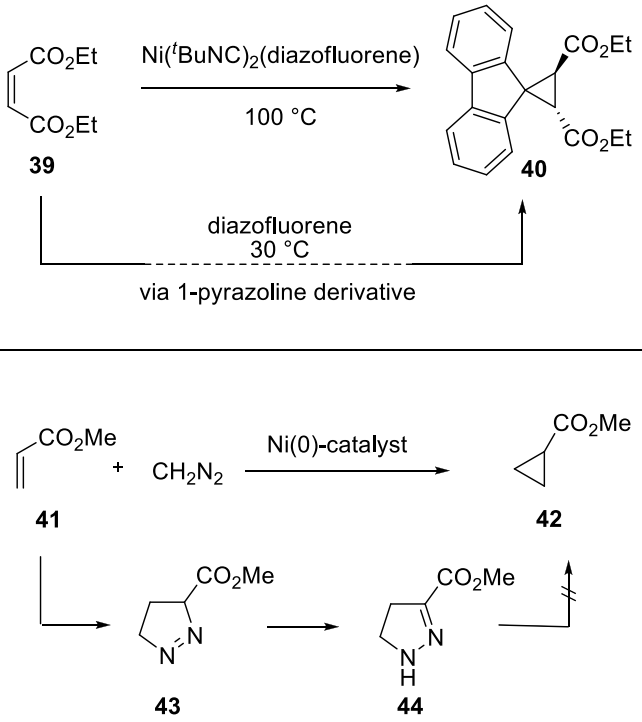
R^1 = ^{i}Pr, Ph, 4-^{t}BuC$_6$H$_4$, 2-MeC$_6$H$_4$, 2,6-Me$_2$C$_6$H$_3$; R^2 = H
R^1 = R^2 = Me, Et, ^{i}Pr, Ph, 4-^{t}BuC$_6$H$_4$, 2,6-Me$_2$C$_6$H$_3$

Cyclopropanation of Olefins

Diazofluorene reacts with Ni(0) and Pd(0) complexes of the constitution $M(^tBuNC)_2$ or $M(PPh_3)_2(C_2H_4)$ to the corresponding ML_2(diazofluorene) compounds.[32] By the reaction of $Ni(^tBuNC)_2$(diazofluorene) with methyl acrylate or diethyl maleate (**39**) at 100 °C cyclopropane derivatives were obtained. However, in absence of the metal catalyst, diazofluorene reacts

with the olefin directly to the corresponding 1-pyrazoline derivative, which subsequently converts to the cyclopropane by nitrogen elimination (Scheme 10). Therefore, the formation of the cyclopropane may result from the thermal reaction of free diazofluorene after dissociation of the diazofluorene form the nickel complex.

Scheme 10. Cyclopropanation reactions with diazoalkanes with substituted olefines using Ni(0) catalysts.

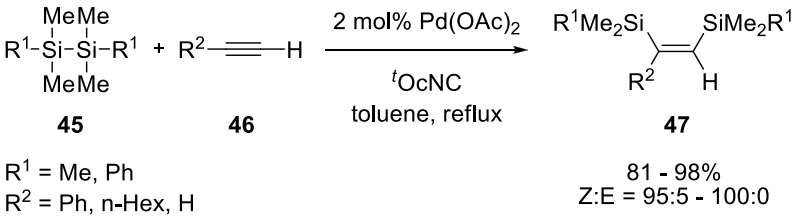


In contrast, diazomethane does not form stable complexes with these metals. The cyclopropaneted product **42** was readily formed in presence of a Ni(0) complex (e.g. ($Ni(tBuNC)_2$, $Ni(PPh_3)_4$). In absence of the catalyst, pyrazoline derivatives were formed, which did not undergo ring contraction, even after subsequent addition of Ni(0) or Pd(0) catalysts (Scheme 10). This leads to the assumption, that with diazomethane the product is formed via a carbene pathway.

Bis-silylation of Unsaturated C-C Bonds

With the introduction of palladium(II) acetate-*tert*-alkyl isocyanide a new highly active catalytic system for bis-silylations of alkynes, which enables the application of otherwise unreactive disilanes, was established by *Ito* and coworkers[33] (Scheme 11). In these reactions, the catalytic active species is formed by the addition of excess of isonitrile ligand (4 – 15 equivalents) to palladium precursors like $Pd(OAc)_2$, $Pd(acac)_2$ or PdCp(π-allyl). The obtained $Pd(0)(RNC)_n$-species (n = 2 – 4) is converted into a bis(organosilyl)palladium(II) complex by oxidative addition and subsequent insertion of the alkyne into the Pd-Si bond followed by a reductive elimination of the Pd(0)-species completed the catalytic cycle. The excess of isonitrile is mandatory to prevent the decomposition of the Pd(0)-species, however, the free isonitriles did not interfere with the bis-silylation reaction.

Scheme 11. Intermolecular bis-silylation of alkynes with disilanes.



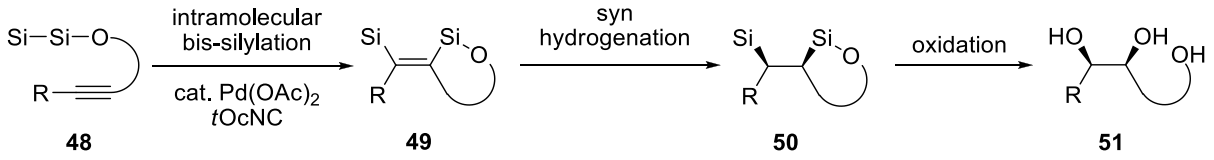
45 **46** **47**

R^1 = Me, Ph
R^2 = Ph, n-Hex, H

81 - 98%
Z:E = 95:5 - 100:0

Unlike conventional phosphine ligands, this system could also be applied in the intramolecular bis-silylation of carbon-carbon double and triple bonds. The resulting cyclic products could be transferred into 1,2,4-trioles[34] and polyols[35] by stereoselective hydration followed by oxidation (Scheme 12). The intramolecular bis-silylation was further applied to vicinally disubstituted alkenes leading to 5-*exo* ring closure products by stereospecific *cis* addition of both, (*Z*)- and (*E*)- disilanyl alkenes.[36]

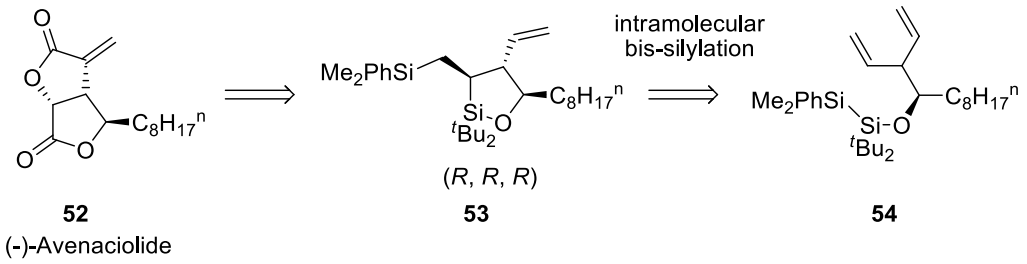
Scheme 12. Stereoselective synthesis of trioles by intramolecular bis-silylation of alkynes, followed by *syn* hydrogenation and oxidation.



Furthermore, *Ito* reported the stereocontrolled synthesis of (-)-avenaciolide (**52**) applying intramolecular bis-silylation as key-step.[37] In presence of bulky *tert*-butyl groups at the disilanyl ether, high yields (92%) and good diastereoselectivity (90:10) of the silylated product could be obtained (

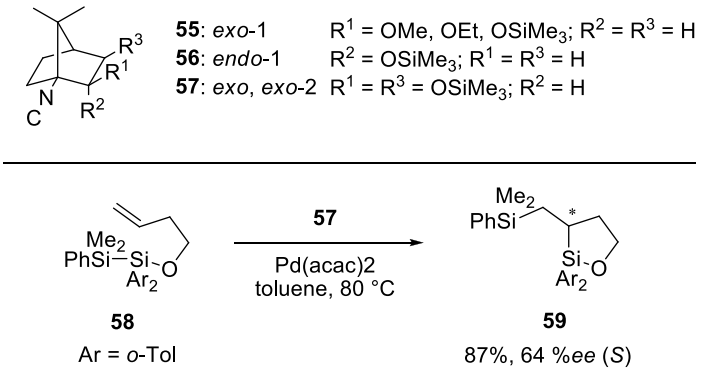
Scheme 13).

Scheme 13. Retrosynthetic analysis for (-)-avenaciolide.



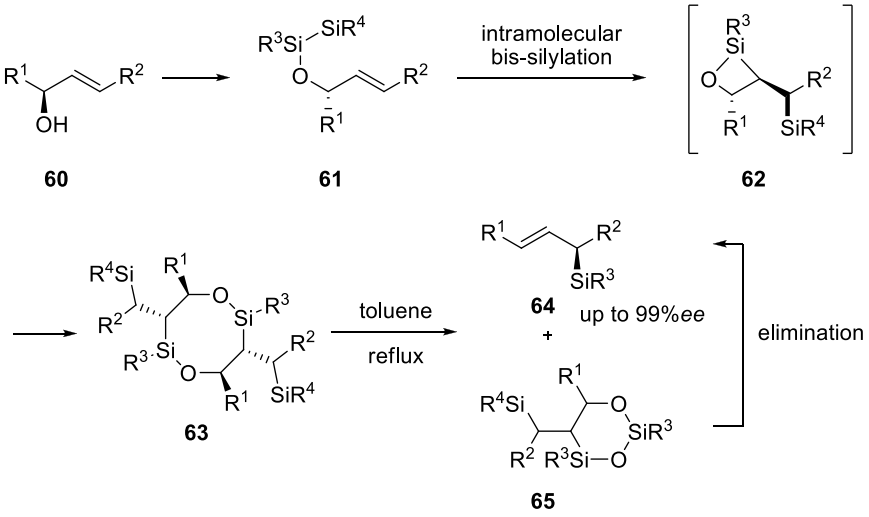
The application of the optically active *tert*-alkyl isocyanides **55-57** towards the intramolecular bis-silylation of carbon-carbon double bonds furnished the corresponding cyclic products with moderate *ee*'s.[38] Here, the best result was obtained by the ligand **57** bearing two *exo*-siloxy groups (Scheme 14).

Scheme 14. The application of optically active isonitriles as ligands for the intramolecular bis-silylation.



The bis-silylations of propargylic alcohols using palladium-isonitrile as catalytic system furnished chiral allenylsilanes[39] and the synthesis of highly enantioenriched (*E*)-allylsilanes (**64**) starting from optically active allylic alcohols (**60**) was reported by *Suginome et al.*.[40] In the latter example, *O*-disilylation of the allylic alcohol was followed by a intramolecular bis-silylation using 1,1,3,3-tetramethylbutyl isocyanide/$Pd(acac)_2$ as catalyst led to cyclodimerization of the oxasilethan yielding an eight membered ring. Nearly complete stereoconversion of the starting material was obtained by subsequent heating of the reaction mixture in toluene and finally addition of organolithium reagents (Scheme 15).

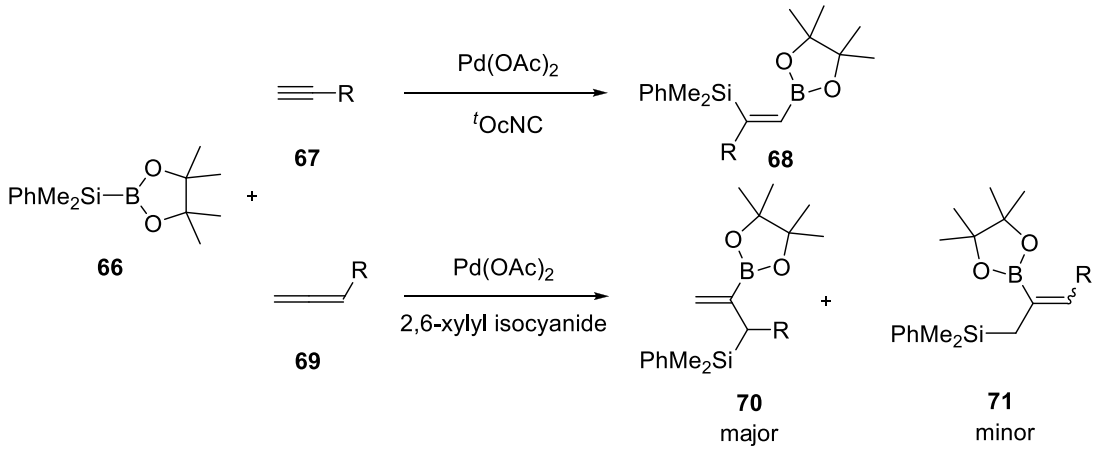
Scheme 15. Preparation of allylsilanes (**64**) in three steps: 1) *O*-Disilylation of allylic alcohols; 2) intramolecular bis-silylation. 3) Treatment of the reaction mixture with organolithium reagents.



Silaboration

The addition of a silicon-boron bond by reaction of (dimethylphenylsilyl)pinacolborane (**66**) to carbon-carbon triple bonds furnished (*Z*)-1-boryl-2-silyl alkenes (**68**) with high region- and stereoselectivity and was found to be most effectively catalyzed by the palladium(0)-*tert*-alkyl isocyanide system.[41] In contrast, 2,6-xylyl isocyanide proved to be the best ligand for the palladium catalyzed silaboration of 3-substituted 1,2-dienes (**69**) (Scheme 16). With one exception, all 3-substituted 1,2-dienes (R = CH_2CH_2Ph, Cy, ^tBu, Ph, OMe) furnished the major product (**70**) in good yields (88 – 99%) with selectivities >86:14. Only the C_6F_{13} substituted diene led to the minor product (**71**) as single isomer with 94%.[42]

Scheme 16. Silaboration of alkynes and 1,2-dienes using (dimethylphenylsilyl)pinacolborane.

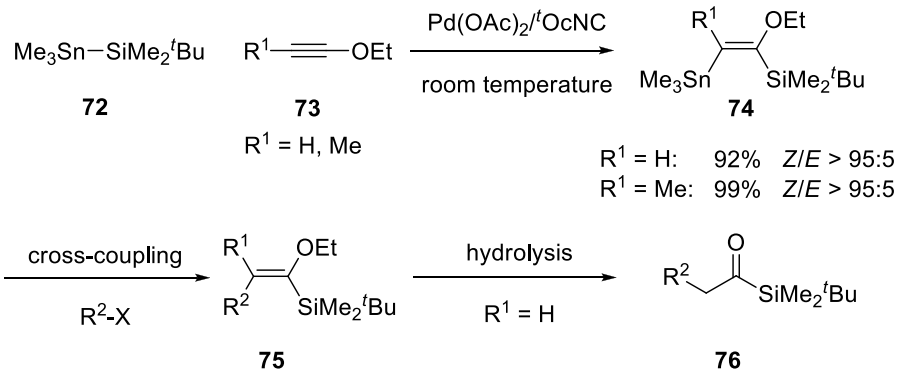


This methodology was further exploited to (dimethylphenylsilyl)boranes having catechol and diethylamnio groups on the boron.[43]

Silastannation

The silastannation of alkoxyalkynes (**73**) was promoted by $Pd(OAc)_2/^tOcNC$. Further cross-coupling of the obtained products (**74**) with organohalides followed by acid-catalyzed hydrolysis gave access to a variety of acyl silanes (**76**)[44] (Scheme 17).

Scheme 17. Synthesis of acylsilanes via silastanation of alkynes.



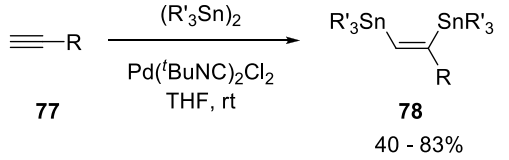
In addition, the superior catalytic activity of $Pd(OAc)_2$/isocyanide compared to $Pd(PPh_3)_4$ could be observed in the silastannation of 1-hexyne. While the isonitrile system catalyzed the reaction at room temperature, employment of $Pd(PPh_3)_4$ as catalyst required heating at around 70 °C.[45]

This silastannation strategy was further investigated to ethyne, leading to (*Z*)-1-silyl-2-stannylethene which could be transformed in various *cis*-disubstituted alkenes.[46]

Bis-stannylation of Alkynes

A mild and atom-efficient bis-stannylation of terminal alkynes using hexaalkylditin and a palladium-isonitrile as catalyst was developed in *Lautens* group[47] (Scheme 18). This methodology could be applied to a variety of terminal alkynes using $Pd(^tBuNC)_2Cl$ as catalyst. In addition, the catalysts tolerance towards sterically more hindered substrates was investigated using dimethyl propargylic alcohol. Furthermore, activated internal alkynes could be converted into their corresponding bis-stannylated products (**78**).

Scheme 18. Bis-stannylation of alkynes using $Pd(^tBuNC)_2Cl$ as catalyst

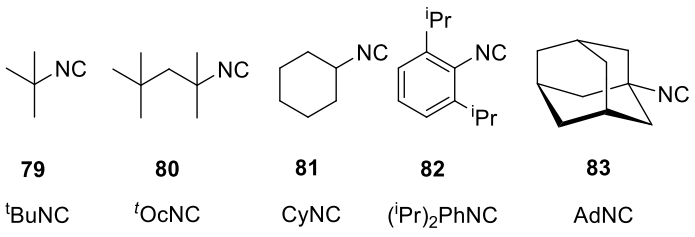


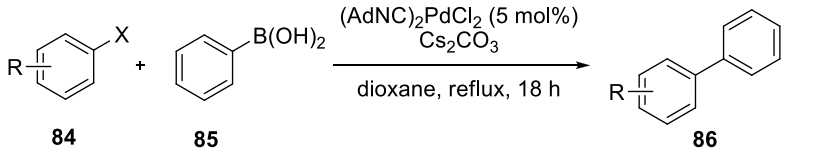
R = NHBoc, NHTs, OCH_3, CO_2CH_3, OH, OTBDMS

Suzuki-Miyaura Cross-Coupling

The isoelectric analogy between isonitriles and *Arduengo's* carbenes was exploited by *Villemin* and coworkers in the palladium-isonitrile catalyzed Suzuki-Miyaura cross coupling[48] (Scheme 19). They prepared $PdCl_2$-complexes of five hindered isonitrile ligands: *tert*-butylisonitrile (^tBuNC) (**79**), 1,1,3,3-tetramethylbutylisonitrile (^tOcNC) (**80**), cyclohexylisonitrile (CyNC) (**81**), 2,6-diisopropylphenylisonitrile ($(^iPr)_2PhNC$) (**82**) and adamantylisonitrile (AdNC) (**83**). Moderate to excellent yields were obtained by the reaction of various phenylboronic acids (**85**) and aryl halides (**84**) using $(AdNC)_2PdCl_2$. In addition, the coupling of heteroaromatic substrates was investigated with this complex. Compared to Arduengo's carbene or hindered alkylphosphine palladium complexes similar activity was observed.

Scheme 19. Different isonitrile ligands employed in palladium catalyzed Suzuki-Miyaura cross coupling.



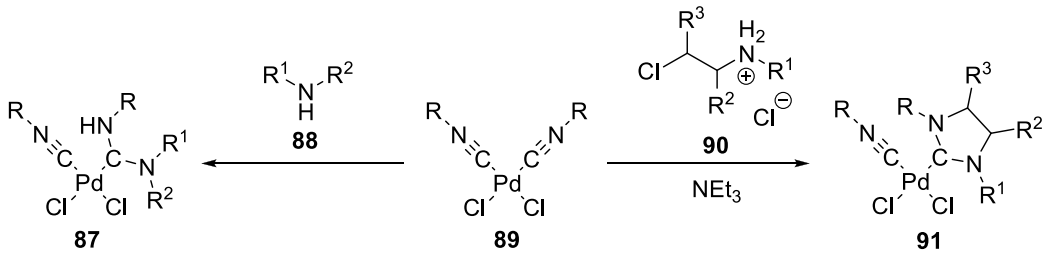


X = Cl, Br, I
R = *p*-OCH_3, *p*-CHO, *p*-$COCH_3$, *p*-CO_2CH_3, *p*-CN

X = Br, R = *p*-OCH_3, 81%

Palladium-isonitriles (**89**) can be converted into their corresponding acyclic amino- (**87**) and *N*-heterocyclic carbene (NHC) (**91**) complexes by the metal-mediated nucleophilic attack of amines to the activated isonitrile carbon (Scheme 20). In this regard, the catalytic activity of mixed ligand complexes bearing one carbene ligand and a second isonitrile ligand was investigated in the Suzuki-Miyaura cross coupling.

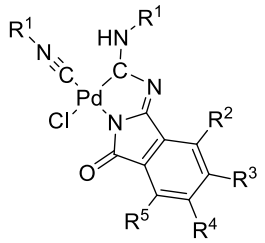
Scheme 20. Preparation of acyclic and *N*-heterocyclic palladium(II) carbenes from palladium-isonitriles.



Various palladium aminocarbene complexes, derived by the addition of 3-iminoisoondoin-1-ones[49] or benzophenone hydrazone[50] (Scheme 21) to their corresponding palladium-isonitriles were prepared and showed good to excellent activity towards the Suzuki-Miyaura cross coupling of aryl bromides and iodides with phenylboronic acids. In addition, the reactions were performed under air using non-dried EtOH which underlines the stability of the new complexes.

In a related study, different aminocarbene/isonitrile-palladium(II) complexes (**94**), derived from the reaction of and 1,3-diiminoisoindoline with the corresponding isonitrile complexes, were compared to bis-aminocarbene- (**95**) and aminocarbene/phosphine-palladium(II) (**96**) complexes in the Suzuki-Miyaura cross coupling.[51]

Scheme 21. Mixed ligand palladium aminocarbene/isonitrile complexes prepared by the reaction of 3-iminoisoindolin-1-ones or benzophenone hydrazones with a isonitrile complex



92

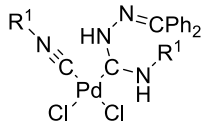
R^1 = Cy, ^{t}Bu, Xyl, 2-Cl-6-MeC_6H_3

R^2 - R^5 = H

R^2, R^4, R^5 = H, R^3 = Me / R^2, R^3, R^5 = H, R^4 = Me (isomeric mixture)

R^2, R^5 = H, R^3, R^4 = Cl

R^2 - R^5 = F

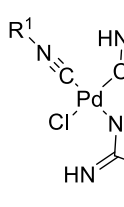


93

R^1 = Cy, ^{t}Bu, Xyl, 4-MeO-C_6H_4

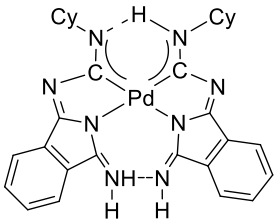
Here, best results were obtained by mixed aminocarbene/phosphine complexes (**96**) rationalized by a synergetic effect of two catalytically important ligands. Nevertheless, bis-aminocarbene (**95**) and the mixed aminocarbene/isonitrile (**94**) complexes showed reasonable activity (Table 3).

Table 3. Catalytic activtiy of aminocarbene/isonitrile (**94**), bis-amiocarbene (**95**) and amino-carbene/phosphine-palladium(II) (**96**) complexes in Suzuki-Miyaura cross-coupling.

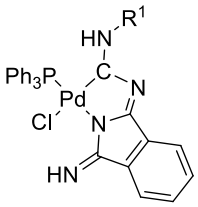


94

R^1 = ^{t}Bu, Xyl, $CMe_2CH_2CMe_3$

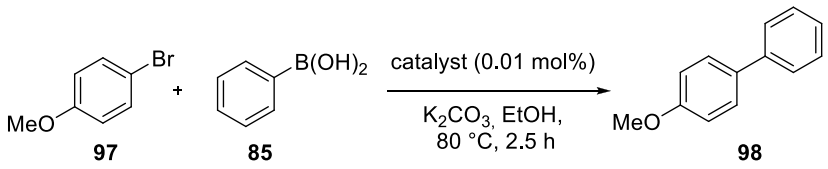


95



96

R^1 = Cy, ^{t}Bu, $CMe_2CH_2CMe_3$



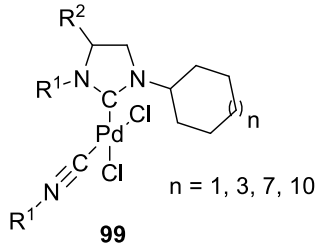
97 **85** **98**

Entry	Catalyst	Yield
1	aminocarbene/isonitrile-Pd(**II**)	27 - 77
2	bis-aminocarbene-Pd(**II**)	70
3	aminocarbene/phosphine-Pd(**II**)	67 - 86

The preparation of imidazolidene based NHC/isonitrile complexes of palladium(II), platinum(II) and gold(I), accessible from the easily available isonitrile complexes was reported by *Hashmi et al.* in 2010.[52]. Even aryl chlorides could be converted by the obtained palladium complexes in Suzuki-Miyaura cross coupling reactions at room temperature in technical grad solvent.

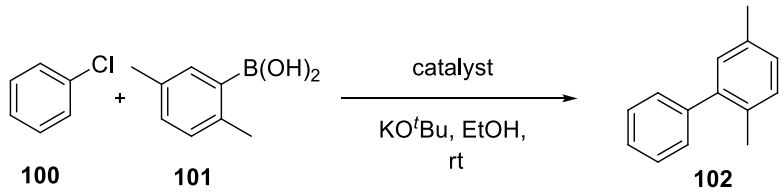
A further study revealed that the NHC/isonitrile compounds have much higher activity compared to their related acyclic representatives. Furthermore, a series of NHC/isonitrile palladium(II) complexes bearing an aryl at one nitrogen of the heterocycle and different 6-15 membered cycloalkyl rings were introduced.

Table 4. Relationship between ring size and backbone substitution of the palladium-complex and the TON in Suzuki-Miyaura cross coupling.



99

R^1 = 2,6-diisopropylphenyl
R^2 = H, Ph



100 **101** **102**

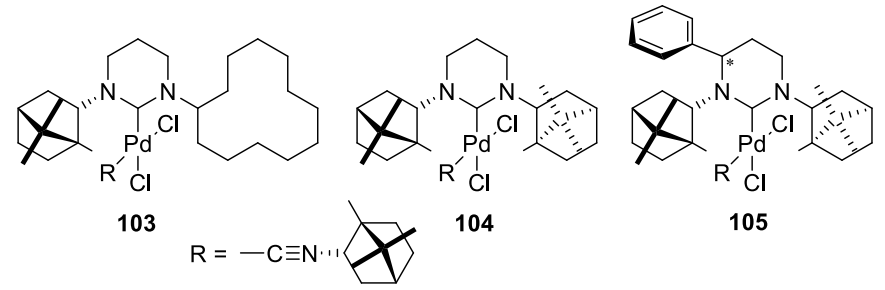
Entry	R^2	n	TON
1	H	1	62
2	Ph	1	64
3	Ph	3	57
4	H	7	330
5	Ph	7	450
6	Ph	10	660

Especially the complexes with larger rings showed excellent TONs in the coupling of phenyl chloride (**100**) with 2,5-dimethylphenyl boronic acid (**101**) (Table 4). This was explained by a hydrophobic effect of the aliphatic ring and further steric effects of the phenyl groups, which facilitate the reductive elimination. Furthermore, the increased conformational freedom by the cyclohexyl groups allows simplified oxidative addition.[53]

Asymmetric Oxindole Synthesis

Three chiral six-membered NHC/isonitrile-palladium(II) complexes, derived from a chiral bornylisonitrile-palladium(II) complex, were reported by *Trapp* and coworkers.[54] The catalysts were applied in the asymmetric oxindole synthesis and showed good conversion of bromo as well as chloro substrates.

Table 5. Selected results of the asymmetric oxindole synthesis, catalyzed by different chiral NHC/isonitrile complexes.



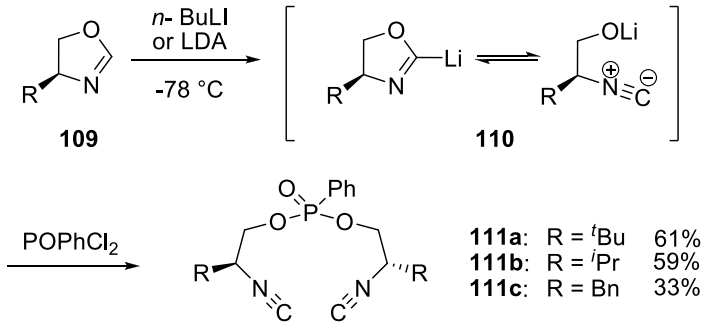
Entry	Catalyst	X	R^1	Ar	107	108	Yield	ee [A; %]
1	**103**	Br	Me	1-naphthyl	100	-	quant.	rac
2	**104**	Cl	Me	Ph	100	-	98	63
3	**105**	Br	Me	1-naphthyl	36	64	89	8

While the catalysts **103** and **104** led to the oxindole (**107**) solely, the sterical more demanding complex **105** furnished both, the arylated (**107**) and the dehalogenated (**108**) product. Concerning the chiral induction, catalyst **104** proved to be more effective than complex **103**, leading to an enantiomeric excess of 55 – 72%ee depending on the substrate (Table 5).

Aerobic Wacker Oxidation

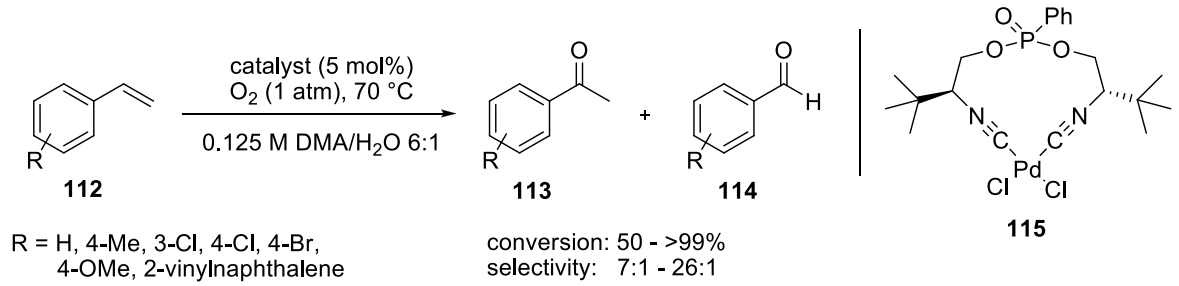
A new class of palladium(II)-complexes was introduced by *Reiser* and coworkers in 2010.[55] They prepared various chiral bis(isonitrile) ligands (**111a-c**) by metalation of chiral oxazoles (**109**) followed by trapping of the resulting anions (**110**) with phenylphosphonic dichloride (Scheme 22).

Scheme 22. The synthesis of bis(isonitriles) from chiral oxazoles.



The corresponding palladium(II)-bis(isonitrile) complexes proved to be highly active catalysts for the aerobic Wacker oxidation of alkenes and especially styrenes in the absence of further co-catalysts (Scheme 23).

Scheme 23. Wacker oxidation of aromatic alkenes using $PdCl_2$(bis(isonitrile)) (**115**).



Alkyne Hydroarylation

In 2013, *Sgarbossa* and *Tubaro* introduced a series of novel platinum(II) diisocyanide complexes for alkyne hydrolations.[56] The ligands were synthesized via the reaction of various diacylic and phosphonic dichlorides with 2-lithiated benzoxazoles, and their $PtCl_2$- and $PtMe_2$-complexes were prepared by using cis-[PtX_2(COD)] (COD = cyclooctadiene). In addition, the dinuclear complex **120** was prepared by application of $PtCl_2(PPh_3)$ (Figure 4).

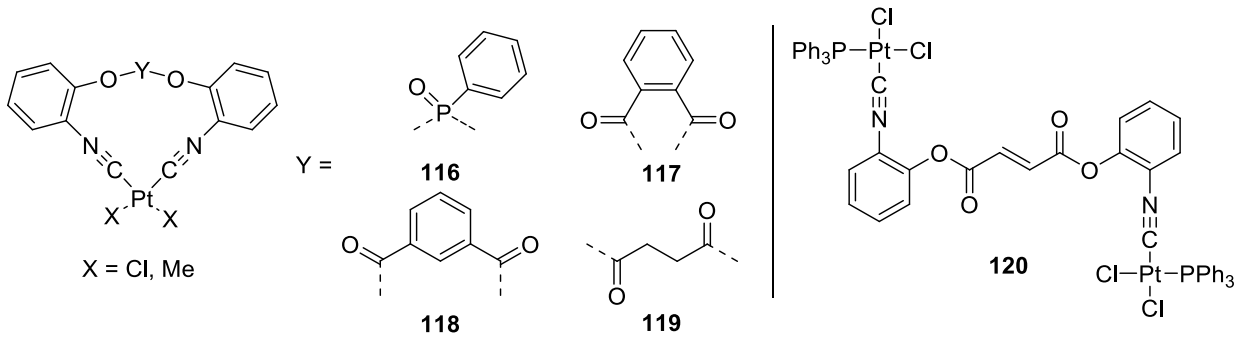
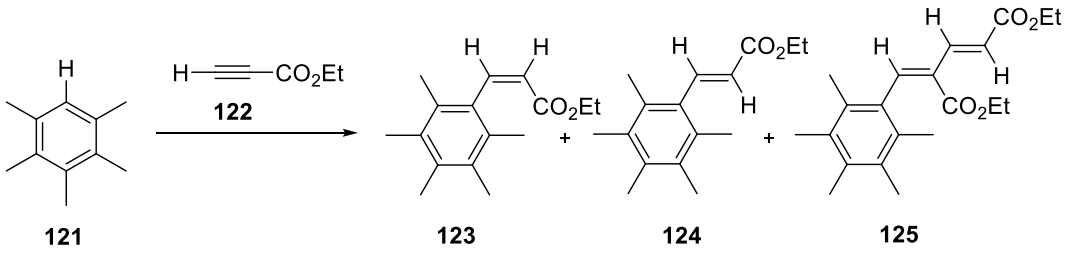


Figure 4. Various platinum(II)-bis(isonitrile complexes (**116**-**119**) and the dinuclear complex **120**.

These complexes were converted to the catalytic species by Cl^-/TFA^- (TFA = trifluoroacetate) or Me^-/TFA^- exchange with AgTFA or HTFA respectively. Especially the mononuclear compounds showed good activity and selectivity towards the *trans*-hydroarylation products (**123**) (Scheme 24). In contrast, the application of *N*-methylindole furnished a heterocycle:alkyne 2:1 adduct as major product.

Scheme 24. Hydroarylation of ethyl propiolate and pentamethylbenzene.



121 **123** **124** **125**

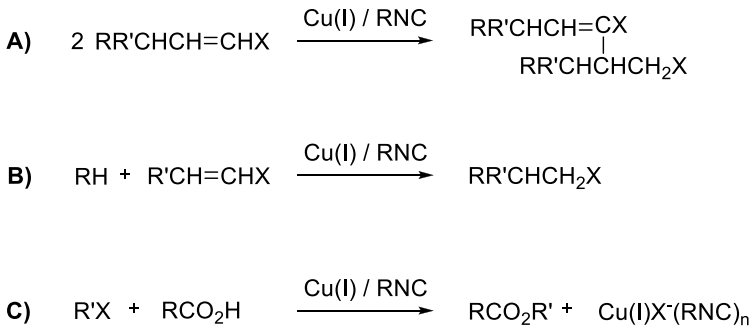
116 - 119: 76 - 91%
120: 58%

7. Group 11-Isonitriles: Copper

Reactions Involving Active Hydrogen Compounds

Since 1967, *Saegusa* and co-worker explored copper-isonitrile systems in homogenous catalysis.[57] Complexes applied were Cu_2O/isonitriles, Cu(0)/isonitriles and different copper(I) salt/isonitrile complexes like Cu(I)Cl/$(RNC)_n$ and Cu(I)CN/$(RNC)_n$ (n = 1 – 4).

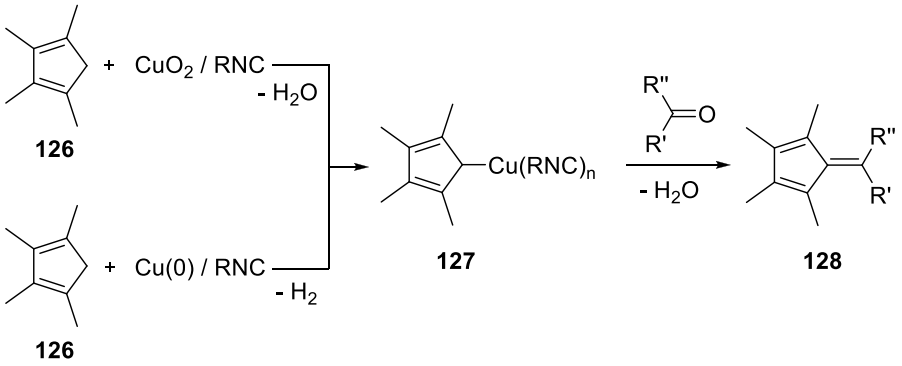
Scheme 25. Reactions catalyzed by copper-isonitrile complexes: A) Dimerization of α,β-unsaturated carbonyl and nitrile compounds; B) Michael-type addition; C) Esterification.



These complexes were able to catalyze various reactions with active hydrogen or halogen compounds.[57a] In this regard the dimerization of α,β-unsaturated carbonyl and nitrile compounds was shown.[57b,57c] (Scheme 25) While Cu_2O and Cu(0) in combination with excess of aliphatic isonitriles showed good activity, the use of cupric oxide, cupric and cuprous chloride or copper(II) acetylacetonate systems afforded only traces of the dimer. In a related way, Michael-type additions[57c] and esterifications[57d,57e] were reported (Scheme 25).

In addition, the complexes could catalyze the reaction between cyclopentadiene homologs and carbonyl compounds leading to fulvene derivatives (**128**)[57f] (Scheme 26). The latter reaction, involves the activation of a methylene compound which further reacts with a carbonyl compound to fulvene-type products (**128**).

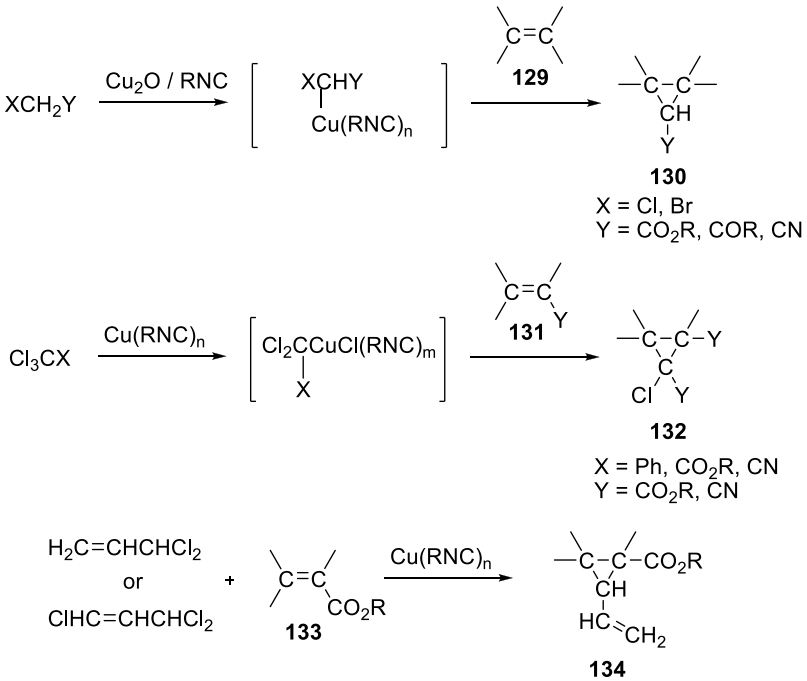
Scheme 26. Reaction between cyclopentadienes and carbonyl compounds catalyzed by copper-isonitriles.



Preparation of Cyclic Compounds

By further investigation of the copper-isonitriles, *Saegusa et al*. introduced the preparation of cyclopropanes. The products were formed by the reaction of polyhalomethane derivatives with electron deficient olefins and the copper-isonitrile system[57g,57h] (Scheme 27).

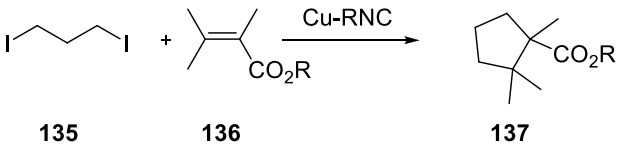
Scheme 27. Various copper-isonitrile catalyzed reactions towards cyclopropanes.



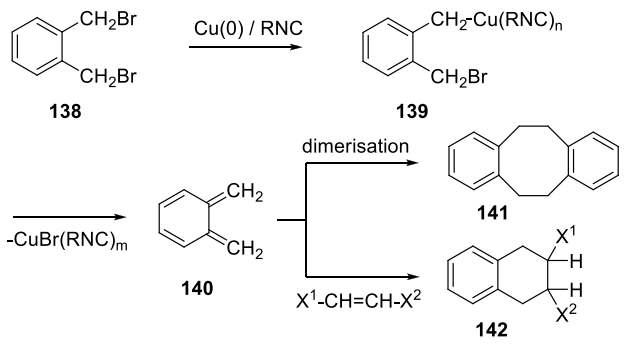
The reaction may be explained by the formation of a copper carbenoid-isonitrile complex. Formation of the cyclopropane ring was finally achieved by treating this intermediate with α,β-unsaturated carbonyl compounds followed by 1,3 elimination of copper halide. In addition, the synthesis of vinyl cyclopropanes (**134**) was reported by the reaction of allylidene dichloride or 1,3 dichloropropene[57k] (Scheme 27).

In a similar way, five membered rings were obtained by trapping of an 3-iodopropylcopper-isonitrile complex, formed by the reaction of 1,3-diiodopropane (**135**) and Cu-RNC, with α,β-unsaturated esters[57i] (Scheme 28).

Scheme 28. Reaction between 1,3-diiodopropane and α,β-unsaturated esters with copper-isonitriles.



The reaction of *o*-xylylene halides (**138**) with copper(0)-isonitrile complexes affords dibenzocyclooctadiene (**141**) as major product.[57j] However, in the presence of electron deficient alkenes such as acrylate or fumarate, tetrahydronaphthalenes (**142**) were produced selectively (Scheme 29).

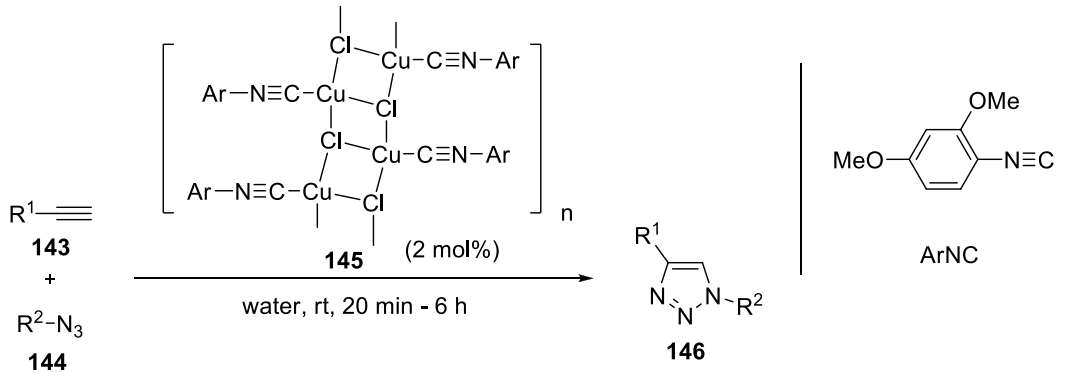


Scheme 29. The reaction of *o*-xylene halides with copper(0)-isonitriles.

Huisgen Azide-Alkyne 1,3-Cycloaddition

More recently, a different class of copper-isonitriles were introduced by *Reiser el al.*.[58] Upon treatment of 2,4-dimethoxyphenyl isonitrile with CuCl in THF $(Cu(ArNC)Cl)_n$ (**145**) was obtained. X-ray crystallography revealed the structure as one dimensional chain polymer which showed to be an efficient heterogeneous catalyst for the Huisgen azide-alkyne 1,3-cycloaddition. The reaction was carried out under mild condition in water. (Scheme 30) In addition, the complex could also catalyze the formation of 1,4-disubstituted 1,2,3-triazoles (**146**) by the three-component reaction of a halide, sodium azide and alkynes. Owing its heterogeneous nature, the catalyst could be readily recovered and recycled without significant loss of activity.

Scheme 30. Copper(I)-isonitrile as heterogeneous catalyst for the azide-alkyne cycloaddition in water.



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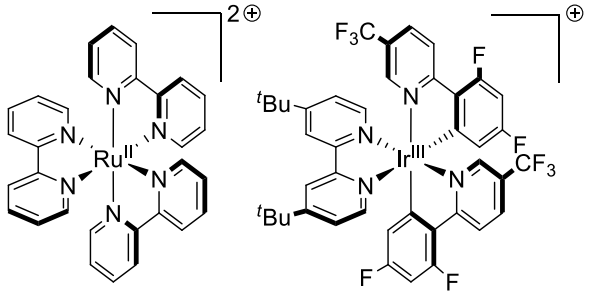
C Copper-Isonitriles as Visible-Light Photoredox Catalysts

This chapter is based upon the Journal Article "*[Copper(phenanthroline)(bisisonitrile)]$^+$-Complexes for the Visible-Light-Mediated Atom Transfer Radical Addition and Allylation Reactions*". Adapted with permission from M. Knorn, T. Rawner, R. Czerwieniec and O. Reiser, *ACS Catal.* **2015**, 5, 5186-5193. Copyright 2015 American Chemical Society.

1. Introduction

In the last years, visible-light mediated photoredox catalysis developed rapidly. Besides the search for new applications, the continuous design of highly active catalysts promotes this green technology. The most commonly employed visible-light photoredox catalysts are metal complexes based on ruthenium or iridium (Figure 1),[1] owing to their excellent stability and catalytic activity manifested in long life times of their excited states combined with suitable redox potentials to initiate electron transfer events with organic compounds. However, these metals are scarce in nature, and hence the use of copper complexes can be considered as an attractive alternative, since copper is less expensive, safer and environmentally more benign.



$[Ru(bpy)_3]^{2+}$ $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]^+$

Figure 1. Two examples of metal complexes based on ruthenium ($[Ru(bpy)_3]^{2+}$ (bpy: 2,2′-bipyridyl)) or itidium ($[Ir(dF(CF_3)\ ppy)_2(dtbbpy)]^+$ ($dF(CF_3)ppy$: 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine; dtbbpy: 4,4′-di-tert-butyl-2,2′-dipyridyl)) used in visible-light photoredoxcatalysis.

However, there are only few reports in literature on copper based photoactive complexes used for visible-light driven organic synthesis.[2] In particular, the excited-state properties of

copper(I) diimine complexes attracted attention since long. As a major drawback, such materials often suffer from short excited state lifetimes, caused by an excited-state reorganization from a tetrahedral to a square-planar complex geometry. The introduction of bulky substituents, e.g. in 2,9-position of the phenanthroline moiety, thus preventing such a structural relaxation that facilitates the non-radiative relaxation to the ground state, has been attempted to overcome this problem.[3] Accordingly, $[Cu(dpp)_2]^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) could be used as catalyst for the photocatalytic hydrogen production from water[4] as well as for the generation of aryl radicals derived from diaryliodonium salts under visible-light photoredox catalysis conditions.[5] Recently, we succeeded in the application of $[Cu(dap)_2]^+$ (**1**) (*Sauvage's* catalyst, dap = 2,9-di(p-anisyl)-1,10-phenanthroline)[6] as photoredox catalyst (Figure 2), utilizing its oxidative quenching cycle for intermolecular atom transfer radical addition (ATRA) and allylation reactions under irradiation with green LEDs (λ = 530 nm) or even sunlight.[7]

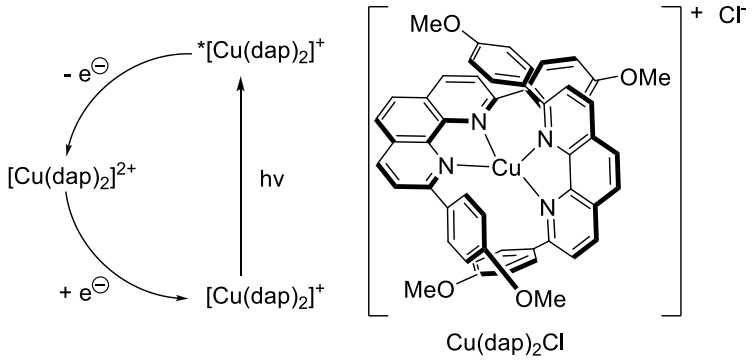


Figure 2. $[Cu(dap)_2]^+$ (**1**) (Sauvage's catalyst, dap: 2,9-di(p-anisyl)-1,10-phenanthroline) and its oxidative quenching cycle.

Very recently, fluoroalkylsulfonyl chlorides were introduced as reagents for the $[Cu(dap)_2]Cl$ (**1-Cl**) catalyzed visible light ATRA reaction.[8] Similar to Ru and Ir based photocatalysts, net CF_3Cl addition was observed by the reaction of triflyl chloride with heteroatom containing alkenes. In contrast, an inner sphere mechanism which suppresses SO_2 extrusion was described for inactivated alkenes, leading to the trifluoromethylsulfonylated products, pointing to special opportunities copper based photocatalysts might offer beyond acting as electron transfer reagents.[8b]

Nevertheless, with sub-microsecond (~ 300 ns) luminescence decay times,[5,6] these two copper complexes still are disadvantageous with respect to their short excited-state lifetime compared to related Ru or Ir complexes, (e.g.: $[Ru(bpy)_3]^{2+}$ (bpy: 2,2′-bipyridyl): 1.1 µs[9a], $[Ir(dF(CF_3)\ ppy)_2(dtbbpy)]^+$ ($dF(CF_3)$ppy: 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine; dtbbpy: 4,4′-di-tert-butyl-2,2′-dipyridyl): 2.3 µs[9b]) which limits their application in photocatalysis.

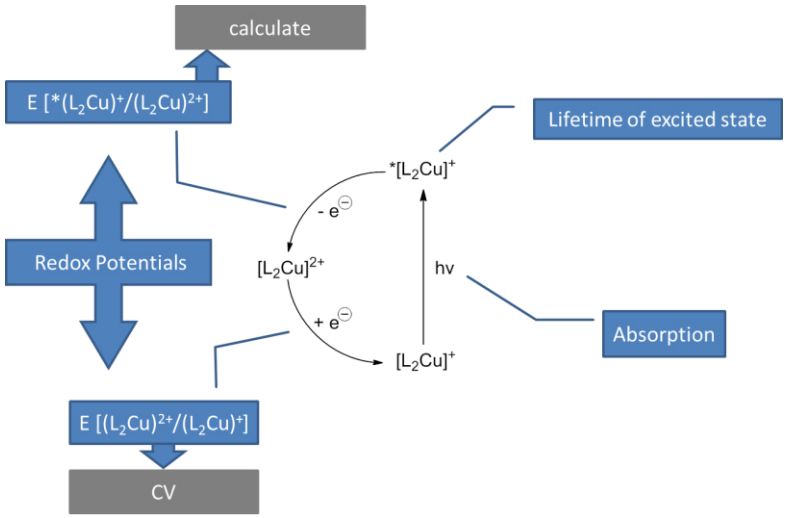
To increase the excited-state lifetime, specially designed copper(I)bisphenanthroline complexes using cooperative steric hindrance with reported excited state lifetimes in the range of one microsecond were developed.[10] As an alternative approach, mixed ligand copper(I) complexes with a phenanthroline (NN) and a wide-bite-angle bidentate phosphine (PP) ligand have been proposed.[11] With reported room temperature lifetimes in the order of several microseconds (e.g. $[Cu(dmp)(pop)]^+$ (dmp: neocuproine, 2,9-dimethyl-1,10-phenanthroline; pop: bis(2-(diphenylphosphanyl)phenyl)ether): 14.3 µs[11c]), these complexes were extensively studied as sensitizers for the nobel-metal free photocatalytic water reduction.[12] Moreover, *Collins* and co-workers reported the visible-light mediated synthesis of helicenes and carbazoles,[13] using different $[Cu(NN)(PP)]^+$-complexes. Very recently, a remarkable study by *Chen et al.* appeared in which heteroleptic copper(I) complexes containing phenanthroline and a monoanionic nido-carborane-diphosphine ligand with excited-state lifetimes of 10-20 µs at ambient temperature were applied for photoinduced cross-dehydrogenative couplings.[14]

Following our interest in photocatalysis[15] and the further improvement and investigation of copper-complexes for visible-light photoredox catalysis,[7,8b] we were intrigued by a study of *Mann et al.*,[43] in which emission lifetimes up to milliseconds were reported for specially designed heteroleptic copper(I) complexes having phenanthroline and monodentate isonitrile ligands that were applied for oxygen gas sensing.

Concerning the design of new copper based photocatalysts, one has to consider three key properties. As first intrinsic feature, the compound has to absorb visible-light to form an excited species. Here, an elongated lifetime help to transfer one electron to form the Cu(II)-species effectively. This mean lifetime is accessible by measuring the complex decay time. In addition, non-radiative quenching to the ground-state should be prevented at this stage. Third, the redox-potentials, which indicate the "strength" of the catalyst, should be

considered. Here, the oxidation potential could be directly obtained by cyclometric experiments. The reduction potential of the excited state has to be estimated combining the values obtained by cyclic voltammetry and spectroscopic data (Scheme 1).

Scheme 1. The key features of photoredox catalysts: a) Absorption, b) Lifetime of the excited state, c) Redoxpotentials.

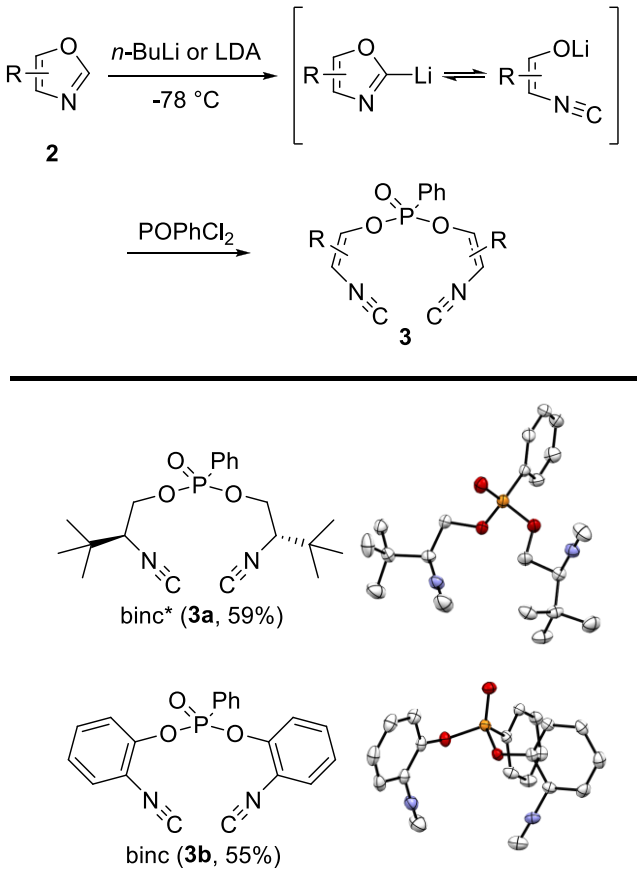


We envisioned that copper(I) phen-anthroline complexes bearing chelating bis(isonitrile) ligands further impede structural reorganization upon irradiation and thus extend the lifetimes of the excited state, which might lead to improved photoredox catalysts. Indeed, here we report the synthesis and characterization of new heteroleptic [Cu(phenanthroline)-(bisisonitrile)]$^{+}$-complexes. The new compounds have significantly improved photophysical characteristics and can be used under mild visible-light conditions for a variety of atom transfer radical additions (ATRAs) and allylation reactions with trimethylallylsilane, the latter being particularly challenging with previously known catalysts.

2. Synthesis and Characterization

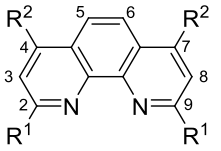
Aiming at heteroleptic [Cu(phenanthroline)(bisisonitrile)]$^+$ complexes, bisisonitrile ligands **3a**[17] and **3b**[18] were synthesized, following the methodology introduced by us[17] by treating oxazoles with *n*-BuLi or LDA and trapping the resulting anion with phenylphosphonic dichloride (Scheme 2). Bisisonitrile **3b** was further characterized by X-ray analysis (Scheme 2, also cf. Chapter A).[19]

Scheme 2. Synthesis[a] of bis(isonitriles) (bis((*S*)-2-isocyano-3,3-dimethylbutyl) phenylphosphonate) (binc*, **3a**) and (bis(2-isocyanophenyl) phenylphosphonate) (binc, **3b**) and their crystal structures.



[a] Conditions: Oxazole 2 (1.0 equiv.), n-BuLi (1.6 M in hexane, 1.05 equiv.), THF (0.4 M), –78 °C, 1.5 h; POPhCl2 (0.53 equiv.), –78°C to rt, 2 h.

As counterparts, commercially available phenanthroline ligands **4a-c** and readily synthesized 2,9-di(p-anisyl)-1,10-phenanthroline[6,7a] (**4d**) were employed in this study (Figure 3).

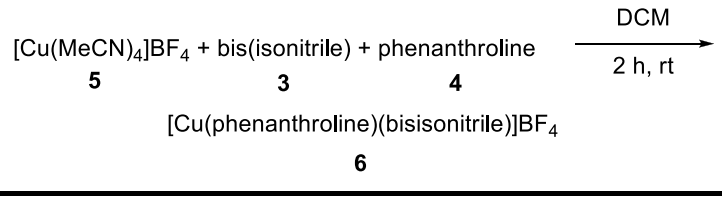


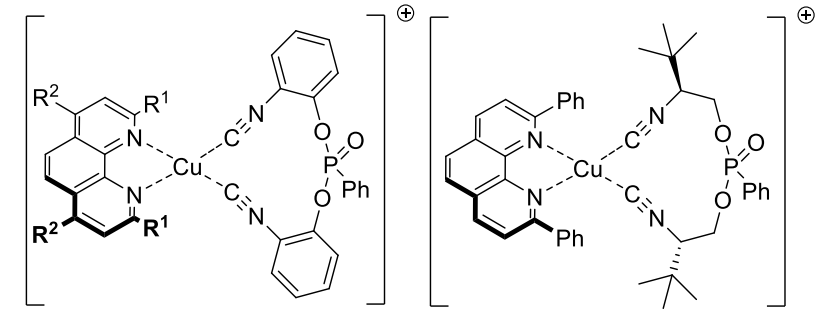
4a: dpp R^1 = Ph R^2 = H
4b: dmp R^1 = Me R^2 = H
4c: dpdmp R^1 = Me R^2 = Ph
4d: dap R^1 = *p*-MeO-Ph R^2 = H

Figure 3. 2,9-diphenyl-1,10-phenanthroline (dpp, **4a**); 2,9-dimethyl-1,10-phenanthroline (dmp, **4b**); 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (dpdmp, **4c**); 2,9-di(*p*-anisyl)-1,10-phenanthroline (dap, **4d**).

Besides the known $[Cu(dap)_2]Cl$ (**1-Cl**) the novel heteroleptic copper(I)-complexes **6a-e** were investigated that were obtained in quantitative yield by reacting an equimolar solution of two different ligands in dichloromethane with $[Cu(MeCN)_4]BF_4$ (Scheme 2).[20] After precipitation in diethyl ether, the light-brown to brown colored complexes **6** could be stored for extended periods without any sign of decomposition.

Scheme 2. Preparation of the [Cu(phenanthroline)(bisisonitrile)]$^+$-complexes **6a-e**.





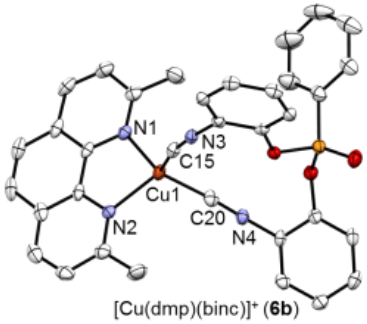
6a: phen = dpp [Cu(dpp)(binc)]$^+$
6b: phen = dmp [Cu(dmp)(binc)]$^+$
6c: phen = dpdmp [Cu(dpdmp)(binc)]$^+$
6d: phen = dap [Cu(dap)(binc)]$^+$

6e: [Cu(dpp)(binc*)]$^+$

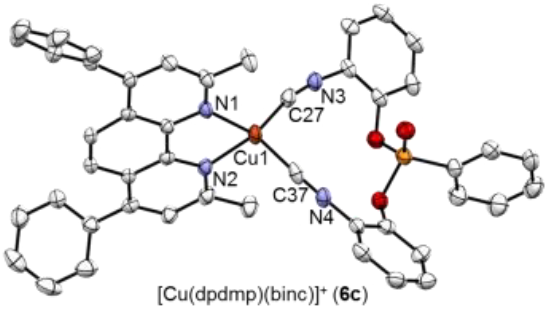
Single crystals suitable for X-ray analysis of **6b** and **6c**[19] were obtained by vapor diffusion of diethyl ether into dichloromethane solution, which revealed a tetrahedral coordination set up by the two different ligands around Cu(I) with little distortion (Table 1). While the bond

distances of Cu to either the phenanthroline or the bisisonitrile ligands are almost the same and in the expected range, the bite angle of the bisisonitrile ligands in both copper complexes are significantly larger (101° and 103°) than the bite angle of a phenanthroline ligand (81-82° in agreement with other literature reports.[11c,14,16])

Table 1. X-ray structures of $[Cu(dmp)(binc)]^+$ (**6b**) and $[Cu(dpdmp)(binc)]^+$ (**6c**).



$[Cu(dmp)(binc)]^+$ (**6b**)



$[Cu(dpdmp)(binc)]^+$ (**6c**)

Bond Angle [deg]			
N1-Cu1-N2	81.9	N1-Cu1-N2	80.8
C15-Cu1-C20	101.2	C27-Cu1-C37	103.1
Cu1-C15-N3	164.2	Cu1-C27-N3	166.8
Cu1-C20-N4	161.3	Cu1-C37-N4	166.5
Dieder Angle [deg]			
N1Cu1N2/C15Cu1C20	80.0	N1Cu1N2/C15Cu1C20	84.2
Bond Length [Å]			
Cu1-N1	2.045	Cu1-N1	2.066
Cu1-N2	2.053	Cu1-N2	2.050
Cu1-C15	1.903	Cu1-C27	1.912
Cu1-C20	1.910	Cu1-C37	1.906

This should result in increased steric interactions between both ligands upon planarization, which corroborates our hypothesis that the lifetime of the excited state in Cu(I) complexes can be increased by substituting one phenanthroline by one bisisonitrile ligand.

The UV-Vis absorption spectrum of $[Cu(dpp)(binc)]^+$ (**6a**) (Figure 4) displays below 350 nm intense absorptions (e.g. $\varepsilon(299nm) = 3.9 \cdot 10^4$ mol dm^3 cm^{-1}), which are assigned to $\pi \rightarrow \pi^*$ transitions of the ligands. At longer wavelengths, a much weaker tail ($\varepsilon(450\ nm) = 5 \cdot 10^2$ mol dm^3 cm^{-1}) is observed, which is attributed to metal-to-ligand charge-transfer (MLCT)

transitions involving an occupied 3d orbital of the copper ion and an empty π* orbital of the dpp ligand (singlet-singlet d → π* transitions). This analysis is in line with other Cu(I) complexes with phenathroline ligands,[11a,21] moreover, the MLCT character of the lowest singlet excited state in $[Cu(dpp)(binc)]^+$ (**6a**) is also supported by the results of TD-DFT calculations (Figure 5).

Luminescence of $[Cu(dpp)(binc)]^+$ (**6a**) was studied in poly(methyl methacrylate) (PMMA). At ambient temperature the complex shows a broad unstructured emission spectrum centered at λ_{em} = 560 nm, with a quantum yield Φ_{PL} of 3 %, accompanied by a decay time τ of 17 µs, which is higher compared to $[Cu(dap)_2]^+$ (**1**) (τ = 560 ns in PMMA) by a factor of about 30.[6]

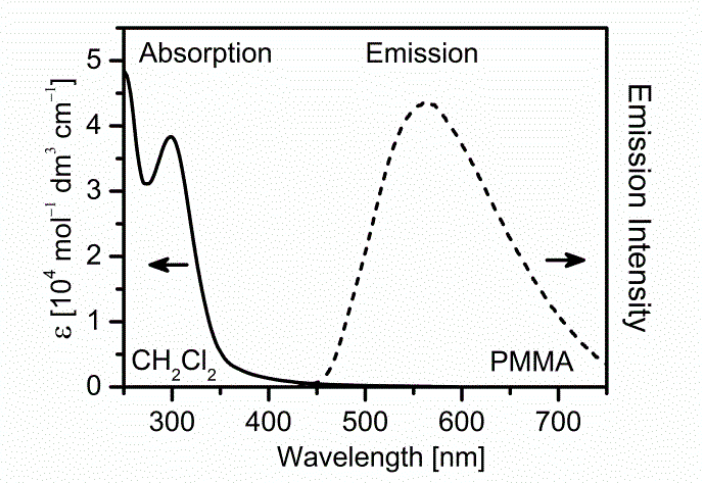


Figure 4. Electronic absorption and luminescence spectra of $[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**) at ambient temperature. Absorption spectrum was recorded in CH_2Cl_2 and emission was measured in poly(methyl methacrylate) (PMMA) respectively. The emission quantum yield Φ_{PL} and lifetime τ (mean lifetime resulting from a biexponential fit of the measured transient) are 3 % and 17 µs, respectively.

To gain a deeper understanding of the radiative processes of $[Cu(dpp)(binc)]^+$ (**6a**), we determined the radiative rate $k^r = \Phi_{PL}/\tau \approx 1.8 \times 10^3\ s^{-1}$ from the measured values Φ_{PL} and τ (Figure 3), which corresponds to a radiative lifetime of $\tau^r = 1/k^r \approx 570$ µs. This large value points to a forbidden character of the emission. Thus, the emitting state is assigned to the lowest triplet state T_1 and the emission of $[Cu(dpp)(binc)]^+$ (**6a**) at ambient temperature represents $S_0 \leftarrow T_1$ phosphorescence. Such an assignment of the emitting state as a triplet state T_1 is, at first glance, surprising, since the ambient temperature emission of numerous

copper(I) complexes with phenanthroline-type ligands was demonstrated to represent thermally activated delayed fluorescence (TADF).[11a,21f,22] The latter process involves an emission from the lowest excited singlet state S_1, which is thermally populated from the long-lived triplet state T_1. Since the $S_0 \leftarrow S_1$ transition is spin allowed, the TADF decay times (radiative) of such materials are usually in the order of few to several microseconds, i.e. the TADF lifetimes are much shorter than 570 µs determined for $[Cu(dpp)(binc)]^+$ (**6a**).

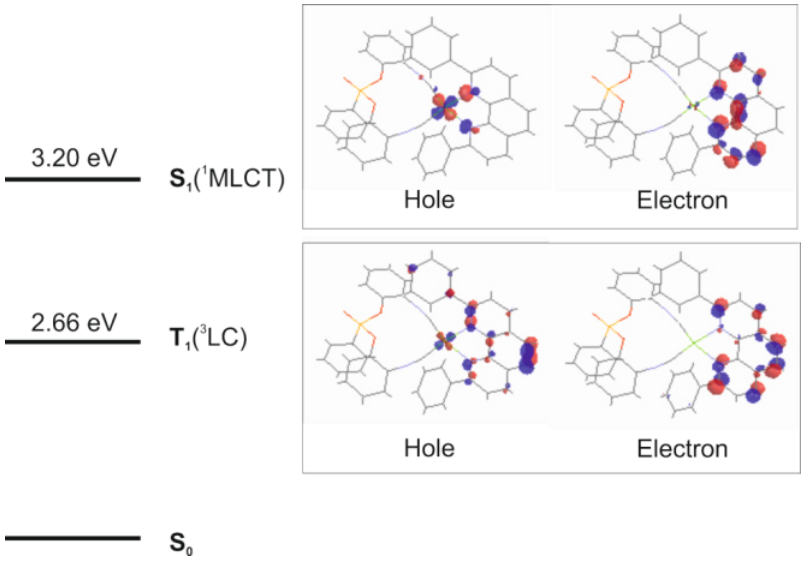


Figure 5. Energy level diagram of the lowest energy excited states of $[Cu(dpp)(binc)]^+$ (**6a**) resulting from the TD-DFT calculations and natural transition orbitals for the lowest excited singlet (S_1) and triplet (T_1) states. Results obtained for the ground-state molecular geometry.

This discrepancy can be rationalized by a relatively high energy separation between the lowest triplet and singlet excited states $\Delta E(S_1\text{-}T_1)$. Indeed TD-DFT calculations predict the S_1 state (= ^{1}MLCT) at 3.20 eV and the T_1 state, being a ligand-centered (^{3}LC) excited state localized mainly at the dpp ligand, at 2.66 eV (Figure 5). Thus, the calculated energy difference $\Delta E(S_1\text{-}T_1)$ = 0.54 eV, being much larger than the singlet-triplet splitting typically found (0.05 – 0.2 eV) for compounds showing TADF at ambient temperature, is not adequate for efficient S_1 population at 300 K. Accordingly, the excited state behavior of $Cu(dpp)(binc)^+$ (**6a**), in particular luminescence as well as light-induced energy/charge-transfer reactions, is related to the T_1 properties of this compound.

Electrochemical measurements reveal the reversible redox behavior at 0.69 V (vs SCE) for the Cu(I)/Cu(II) (A) couple in $[Cu(dpp)(binc)]^+$ (**6a**) (Figure 6). The second redox wave (B) corresponds to the reduction of the dpp ligand. Considering this and the spectroscopic data, a reduction potential Cu(I)*/Cu(II) of -1.88 V (vs SCE) could be appraised. Both values are higher compared to $[Cu(dap)_2]^+$ (**1**) (0.62 and -1.43 V vs SCE),[6] and especially the latter in combination with the long decay time makes **6a** promising for applications in photoredoxcatalysis.

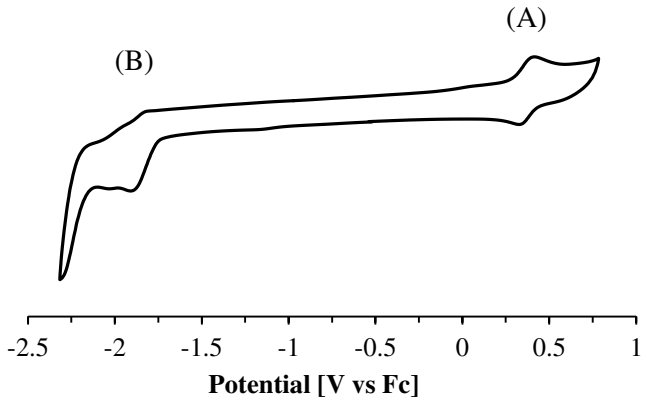


Figure 6. Cyclic voltammogram of $[Cu(dpp)(binc)]BF_4$ (**6a-BF_4**) in MeCN using tetrabutyl ammonium tetrafluoroborate as supporting electrolyte at a scan rate of 50 $mV \cdot s^{-1}$. Redox potentials were referenced against ferrocene as internal standard. (A) $Cu^{I/II}$: 0.31 V vs Fc (= 0.69 V vs SCE). (B) $dpp^{0/-I}$.

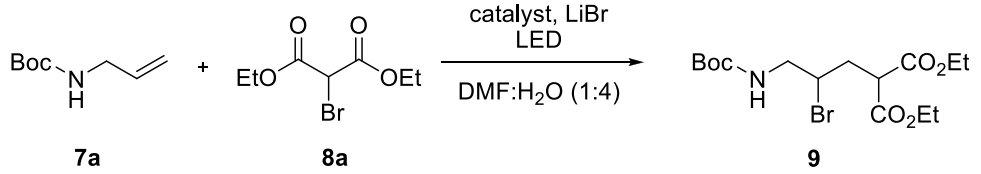
3. Catalysis

3.1 Atom Transfer Radical Addition

Having addressed the synthesis and characterization of the complexes, as well as the spectroscopic and electrochemical properties of $[Cu(dpp)(binc)]^+$ (**6a**), we started to investigate their catalytic activity for visible-light mediated photoredoxcatalysis. As model system we choose the visible-light induced atom transfer radical addition (ATRA) between *N*-boc-allylamine (**7a**) and diethyl-2-bromomalonate (**8a**), for which we previously demonstrated that $[Cu(dap)_2]^+$ (**1**) is a capable catalyst upon irradiation at 530 nm (Table 2, entry 1).[7a] Employing only half the catalyst amount (0.5 mol%) of $[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**) under otherwise identical conditions gave 87% of the ATRA-product **9** after 20 h, however, shortening the reaction time resulted in a significant decrease of yield (entry 3). Further optimization indicated that the reaction proceeds faster upon irradiation at 455 nm (blue LED), which reduces the reaction time to 7.5 h (entry 4), while also under these conditions $[Cu(dap)_2]^+$ (**1**) gave inferior results (entry 2). It should be noted that the absorption spectra of $[Cu(dap)_2]^+$ (**1**) and $[Cu(dpp)(binc)]^+$ (**6a**) are very similar (see supporting information) with slightly larger extinction coefficients found for **1** both at 455 and 530 nm. Thus, the higher activity of **6a** with respect to **1** is not a reflection of a more efficient absorption of light. No conversion in the presence of **6a-BF$_4$** was observed in the dark (entry 5), and further control experiments omitting catalyst or ligands did not lead to appreciable conversion (entry 6,7). As reported for dap **4d**[7a], employing the dpp **4a** alone promotes the reaction, but to a less extend than $[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**) (entry 8). The bisisonitrile ligand **3b**, however, shows no significant catalytic effect (entry 9).

Subsequently, we applied the heteroleptic $[Cu(phenanthroline)(bisisonitrile)]BF_4$ complexes **6b-6e** to this reaction using the optimized conditions from entry 3. While the yield was slightly reduced employing dap **4d** as NN-ligand (**6d-BF$_4$**, entry 12), the crucial role of the aryl moiety in 2,9-position of the phenanthroline can clearly be seen by comparing the low yields of product that were obtained with complexes **6b-BF$_4$** and **6c-BF$_4$** (entry 10,11). In contrast, the exchange of binc **3b** with its more flexible, chiral version binc* **3a** did not affect the catalytic performance. No asymmetric induction was observed in this reaction (entry 12), albeit **3a** had been proven to be a capable chiral promoter in iron complexes.[17a]

Table 2. Optimization and control experiment for the visible-light mediated ATRA between boc-allylamine (**7a**) and diethyl-bromomalonate (**8a**).[a]



7a **8a** **9**

Entry	Catalyst (mol%)	λ [nm]	Time [h]	Yield [%]
1[b]	$[Cu(dap)_2]Cl$ (**1-Cl**) (1.0)	530	24	75
2	$[Cu(dap)_2]Cl/BF_4$ (**1-Cl or BF$_4$**) (0.5)	455	7.5	45 / 46
3	$[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**) (0.5)	530	7.5 / 20	30 / 87
4	$[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**) (0.5)	455	7.5 / 20	88 / 89
5	$[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**) (1.0)	–	20	n.r.
6	no catalyst	455	20	3
7	$CuBF_4$ (1.0)	455	7.5	2
8	dpp (**4a**) (0.5)	455	7.5	45
9	binc (**3b**) (0.5)	455	7.5	5
10	$[Cu(dmp)(binc)]BF_4$ (**6b-BF$_4$**) (0.5)	455	7.5	13
11	$[Cu(dpdmp)(binc)]BF_4$ (**6c-BF$_4$**) (0.5)	455	7.5	12
12	$[Cu(dap)(binc)]BF_4$ (**6d-BF$_4$**) (0.5)	455	7.5	78
13	$[Cu(dpp)(binc^*)]BF_4$ (**6e-BF$_4$**) (0.5)	455	7.5	88[c]

[a] Conditions: *tert*-butyl allylcarbamate (157 mg, 1.0 equiv., 1.0 mmol), diethyl 2-bromomalonate (0.34 ml, 2.0 equiv., 2.0 mmol), LiBr (174 mg, 2.0 equiv., 2.0 mmol), catalyst, DMF:H_2O (1:4) 1 ml, LED-Stick, freeze-pump-thaw (3x), rt; n.r.= no reaction; [b] see ref. [7a]; [c] $[\alpha]_D^{20}$ 0 ° (c = 1 g/100 ml, $CHCl_3$)

The higher activity of the heteroleptic complex $[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**) compared to the homoleptic copper $[Cu(dap)_2]Cl$ (**1-Cl**) was further confirmed by a kinetic study of the title reaction. In addition, we tested $[Cu(dap)(pop)]BF_4$ (pop: 2,2'-oxybis(2,1-phenylene)bis(di-phenylphosphine) (**10-BF$_4$**) for our model reaction to quantify the effect of the bisphophine vs. the bisisonitrile substitution (Figure 7). Mixed ligand [Cu(phenanthroline)(bisphosphine)]$^+$-complexes have excited state lifetimes of several microseconds and promote photocatalytic reactions effectively.[12,13] Indeed, $[Cu(dap)(pop)]BF_4$ (**10-BF$_4$**) is more active than $[Cu(dap)_2]Cl$ (**1-Cl**), but did not reach the rate measured for $[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**).

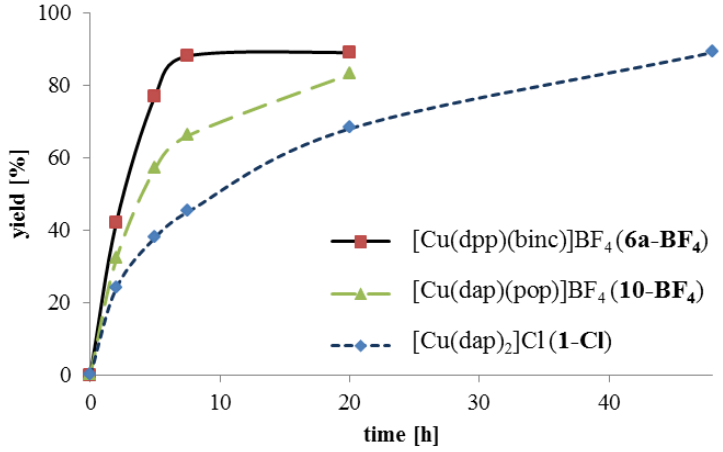


Figure 7. Kinetic study of the visible-light mediated ATRA between boc-allylamine (**7a**) and diethyl-bromomalonate (**8a**). Conditions: *tert*-butyl allylcarbamate (157 mg, 1.0 equiv., 1.0 mmol), diethyl 2-bromomalonate (0.34 ml, 2.0 equiv., 2.0 mmol), LiBr (174 mg, 2.0 equiv., 2.0 mmol), catalyst (0.5 mol%), DMF:H_2O (1:4) 1 ml, LED-Stick (455 nm), freeze-pump-thaw (3x), rt, 7.5 h.

The lower activity of **10-BF_4** could be a consequence of the known[23] tendency of heteroleptic copper(I) complexes combining biphosphine with sterically more demanding phenanthroline ligands to form equilibria with their homoleptic representatives in solution that was also observed by NMR for **10** (Figure 8). In contrast, NMR studies revealed a low susceptibility of **6a** to undergo ligand exchange. In conclusion, [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) was identified as the most active catalyst, and especially outperforming the up to now best catalyst [Cu(dap)$_2$]Cl (**1-Cl**) by a factor of at least two, which we attribute to the increased lifetime as well as to the higher reduction potential of its excited state.

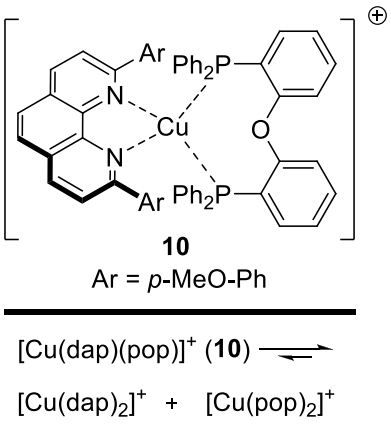
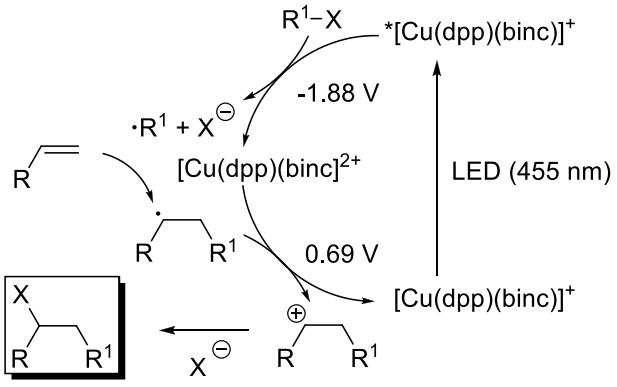


Figure 8. $[Cu(dap)(pop)]^+$ (**10**) in equilibrium with its homoleptic representatives in solution.

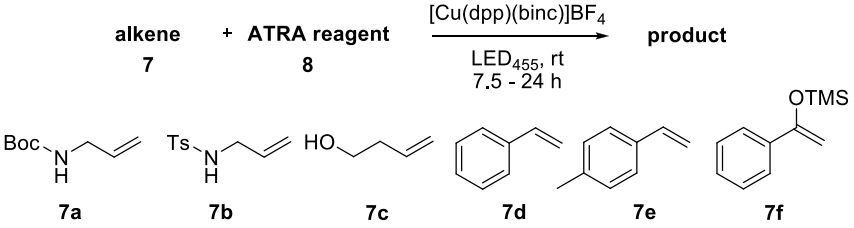
The data obtained suggest a mechanistic picture for $[*Cu(dpp)(binc)]^+$ (**6a**) (Scheme 3) that is in agreement with the previously reported mechanism for copper(I)-catalyzed ATRA reactions under visible light irradiation.[16,17] The excited catalyst species transfers an electron to the ATRA reagent following the oxidative quenching cycle. The generated radical adds to the alkene, forming an intermediate which transfers its electron to the Cu(II) species to regenerate the catalyst in a thermodynamically favored process.

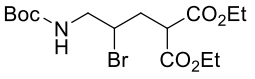
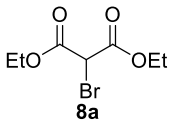
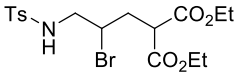
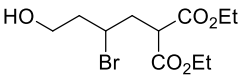
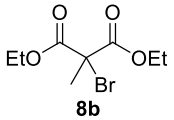
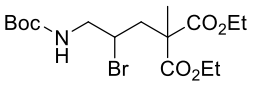
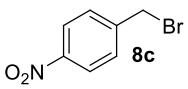
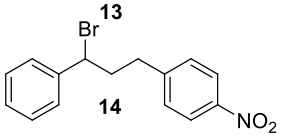
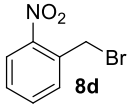
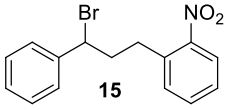
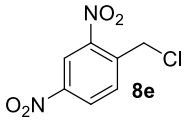
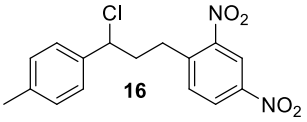
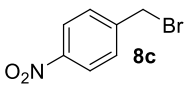
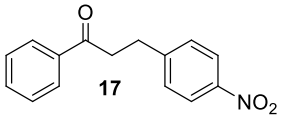
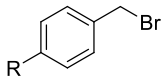
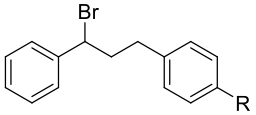
Scheme 3. Mechanistic concept of the Cu(I) catalyzed ATRA under visible-light photocatalysis.



The scope of ATRA reactions was evaluated using $[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**) as catalyst. The addition of bromomalonate **8a** to different olefins **7a-c** proceeded smoothly with the exception of the sterically more hindered diethyl-2-bromo-2-methylmalonate (**8b**) (Table 3, entry 1-4).

Table 3. Visible-light induced ATRA reactions with [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) as photoredox catalyst.



entry	ATRA reagent	alkene	product	Yield [%]
1		7a	 **9**	88
2	 **8a**	7b	 **11**	68
3		7c	 **12**	80
4	 **8b**	7a	 **13**	29
5	 **8c**	7d	 **14**	80
6	 **8d**	7d	 **15**	42
7	 **8e**	7e	 **16**	70
8	 **8c**	7f	 **17**	85
9	 **8f** R = CN	7d		n.r.
10	**8g** R = SO_2Me			n.r.

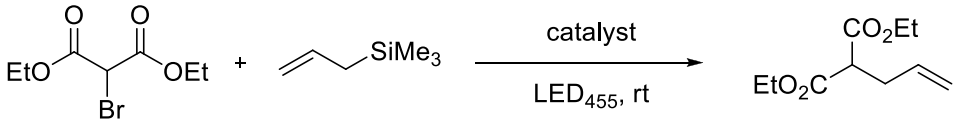
Conditions: entry 1-4: alkene (1.0 mmol, 1.0 equiv.), ATRA reagent (2.0 mmol, 2.0 equiv.), LiBr (2.0 mmol, 2.0 equiv.), [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (0.5 mol%), DMF/H_2O mixture (0.2 ml / 0.8 ml), blue LED (455 nm), freeze-pump-thaw (3x), rt; entry 5-10: benzyl halide (1.0 mmol, 1.0 equiv.), alkene (5.0 mmol, 5.0 equiv.), Cu(dpp)(binc)BF_4 (**6a-BF_4**) (1.0 mol%), MeCN (1.0 ml), blue LED (455 nm), freeze-pump-thaw (3x), rt.

Nitro substituted benzylhalides (**8c-e**) cleanly reacted with styrenes **7d,e** or silylenol ether **7f** giving rise to the ATRA products **14-17** in respectable yields (entry 5-8). Attempts to utilize 4-cyano (**8f**) (entry 9) or 4-methylsulfonyl-benzyl bromide (**8g**) (entry 10) resulted in no conversion of the starting material. The higher reduction potential of the benzyl bromides with less electron withdrawing groups ($E_{1/2}$ = -0.95 V for **8c**, -1.39 V for **8f** and -1.43 V for **8g**; vs SCE in MeCN) apparently prevented the turnover with these substrates, although based on the estimated reduction potential of **6a** (vide supra) we had assumed that this catalyst should be able to activate these substrate.

3.2 Alkylation using Allyltrimethylsilane

While the utilization of allyltrimethylsilanes under visible-light photoredox conditions was impressively shown in trifluoromethylation reactions,[24] its use in allylation reactions of organohalides remains challenging. In our previous report we could demonstrate the reaction of allyltributyltin with organohalides under visible light photoredoxcatalyzed conditions, but our attempts using allyltrimethylsilane as ecologically more viable alternative, was met with success only in one example.[7a] We questioned, whether the new copper(I) catalysts could engage in this barley investigated process.

Table 4. Optimization of the alkylation of diethyl bromomalonate (**8a**) using allyltrimethyl-silane (**18a**).



8a **18a** **19**

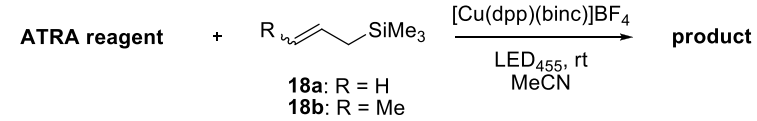
Entry	Catalyst (mol%)	8a : 18a	Solvent	Time [h]	Yield [%]
1	$[Cu(dap)_2]Cl$ (**1-Cl**) (1.0)	1:1		16	5 / 6[a]
2	$[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**) (0.5)	1:1	DMF:H_2O (1:4)	19	30
3	$[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**) (1.5)[b]	1:1		27	39
4	$[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**) (0.5)	1:1		19	45
5	$[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**) (1.0)	1:10	MeCN	72	77
6	$[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**) (0.5)	1:3		24	77 (64[c])

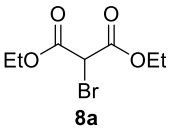
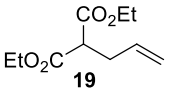
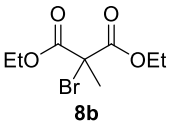
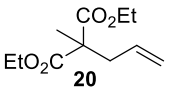
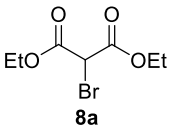
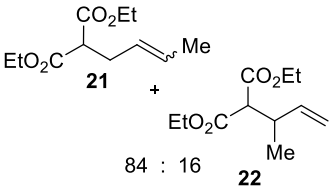
[a] LED530; [b] stepwise addition of catalyst; [c] isolated Yield;.

Conditions: diethyl 2-bromomalonate (**8a**) (171 µl, 1.0 equiv., 1.0 mmol), allyltrimethylsilane (**18a**) (159 µl, 1.0 equiv., 1.0 mmol), entry 1-4: LiBr (87 mg, 1.0 equiv., 1.0 mmol), $[Cu(dpp)(binc)]BF_4$ (**6a-BF$_4$**), solvent 1 ml, LED (455 nm), freeze-pump-thaw (3x), rt. Yield determined with dicyanobenzene as internal standard.

Indeed, we found that 0.5 mol% [Cu(dpp)(binc)]BF_4 (**6a-BF_4**), 3 equivalents of allyltrimethylsilane (**18a**) in MeCN and irradiation with blue LED for 24 h furnishes the allylated product **19** in 64% yield (Table 4, entry 6; Table 5, entry 1).

Table 5. Visible-light mediated allylation of organohalides with allyltrimethylsilan and [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) as photoredox catalyst.[a]



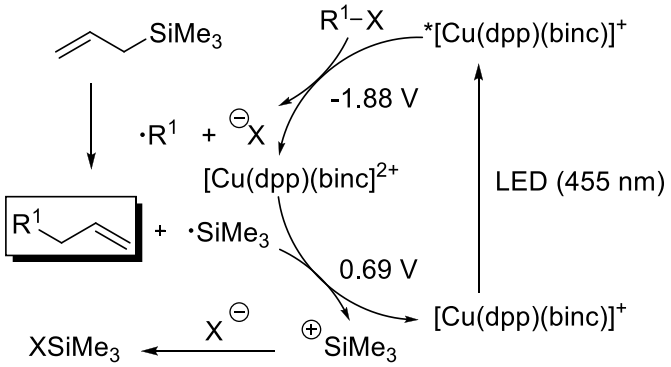
entry	ATRA reagent	allylsilane	product	Yield [%]
1[b] 2[c] 3[d]	 **8a**	**18a**	 **19**	64 n.r. n.r.
4	 **8b**	**18a**	 **20**	82
5	 **8a**	**18b**	 **21** + **22** 84 : 16	80

[a] Conditions: halide (0.5 mmol, 1.0 equiv.), allyltrimethylsilane (1.5 mmol, 3.0 equiv.), [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (1.0 mol%), MeCN (1.0 ml), blue LED (455 nm), freeze-pump-thaw (3x), rt. [b] 0.5 mol% [Cu(dpp)(binc)]BF_4 (**6a-BF_4**); [c] dark reaction; [d] without catalyst.

The necessity of both, catalyst and irradiation with visible light was shown by control experiments (entry 2-3). An even higher yield could be obtained for the 2-methyl substituted malonate **8b** (entry 4). Furthermore, we successfully applied 2-butenyltrimethylsilane (**18b**) in this reaction (entry 5), which gave rise to a 84:16 mixture of the linear and the branched isomer **21** and **22** in good yield.

Again, we assume an oxidative quenching cycle, where the copper catalyst acts as electron shuttle. After irradiation, the excited Cu(I) catalyst **6a** is transformed to its Cu(II) species generating the reactive radical from the organohalide. Upon forming the product, a trimethylsilylradical is released which re-oxidases the catalyst (Scheme 4).

Scheme 4. Proposed mechanism for the visible-light mediated allylation of organohalides with [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) as photoredox catalyst.



4. Summary

In conclusion, we showed the synthesis and characterization of a series of new, bench-stable heteroleptic copper(phenanthroline)(bisisonitrile)$^+$-complexes. Referring its applicability in visible light-mediated photoredox catalysis we analyzed the spectroscopic and electrochemical properties of [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (Figure 9).

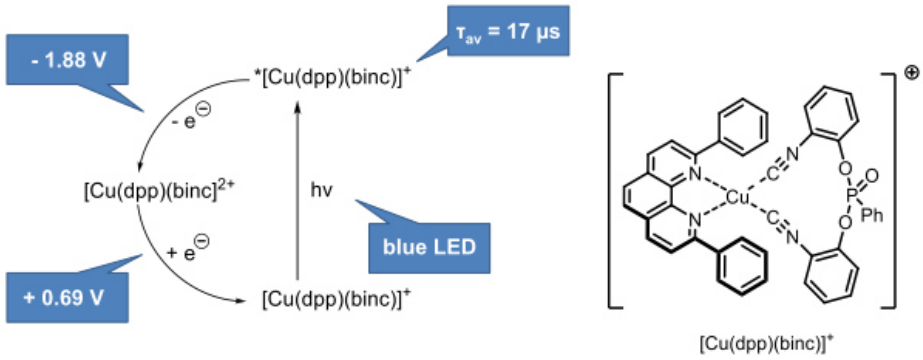


Figure 9. Spectroscopic and electrochemical properties of [Cu(dpp)(binc)]$^+$ (**6a**).

The correlation between its enhanced excited state lifetime compared to the known [$Cu(dap)_2$]Cl (**1-Cl**) and its catalytic activity could be investigated by a kinetic study. The new complex showed excellent activity in the visible light-mediated atom transfer radical addition as well as in the so far scarcely investigated allylation with trimethylallylsilane under mild visible light conditions.

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D Isonitrile-Acyclic Diaminocarbene Palladium(II) Compounds in Catalysis

This chapter is based upon the Journal Article "*Synthesis of New Chiral Bidentate Isonitrile-Acyclic Diaminocarbene Palladium(II) Compounds and Their Catalytic Activity*". Adapted with permission from M. Knorn, E. Lutsker and O. Reiser, *Organometallics* **2015**, DOI: 10.1021/acs.organomet.5b00516. Copyright 2015 American Chemical Society.

1. Introduction

While metal complexes of *N*-heterocyclic carbenes (NHCs) have attracted much attention in the field of organometallic chemistry and homogenous catalysis,[1] the corresponding complexes of acyclic diaminocarbenes (ADCs) are less explored in their long history (Figure 1).

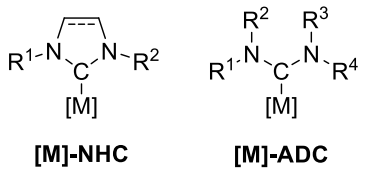
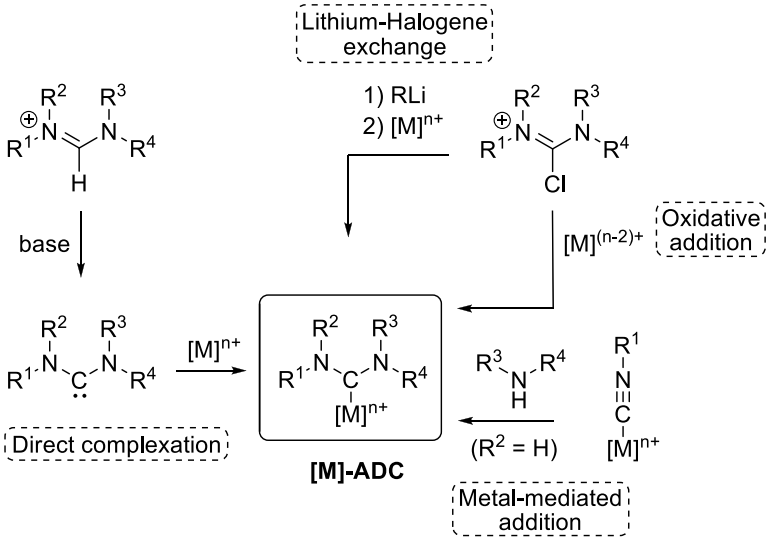


Figure 1. Metal complexes of a *N*-Heterocyclic carbene (NHC) and an acyclic diaminocarbene (ADC).

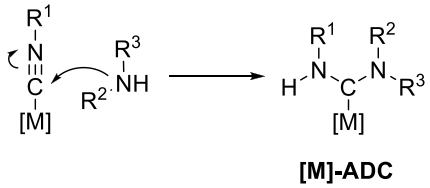
The first ADC-metal complex reported was synthesized by Tschugajeff *et al.* in 1915, but spuriously perceived as dimeric hydrazine-bridged complex.[2] Its correct structure was identified much later by Badley and co-workers.[3] However, only recently ADCs started to be recognized as attractive ligands in metal catalysis.[4] Being strong electron donors, ADC ligands increase the electron density at the metal center in their corresponding complexes. Such donor properties facilitate the oxidative addition of transition metal complexes that have been utilized in many cross coupling reactions. Compared to *N*-heterocyclic carbenes, ADC-ligands possess a wider N-C-N carbene angle, which increases the stability of their complexes and provides better steric control as well as favors the reductive elimination in many metal catalyzed reactions.[4b,4d]

Scheme 1. Synthetic routes towards metal-ADCs.



ADC-metal complexes can be synthesized by the direct complexation of deprotonated carbene precursors, for example *N*,*N*,*N*',*N*'-tetraalkylformamidinium salts,[5] or starting from *C*-chloro iminium and –formamidinium salts via oxidative addition to electron-rich metals[4d,6] or by lithium-halogen exchange followed by transmetalation (Scheme 1).[7] Alternatively, metal-isonitrile complexes can be directly transformed to their corresponding acyclic carbene complexes in a highly atom-economic procedure by the addition of amines (Scheme 2). Especially late transition metals such as Pt(II), Pd(II) or Au(I) provide sufficient electrophilic activation, which is required for the addition of amine nucleophiles to the isonitriles carbon, to form metal-ADCs.[4a-c,8] In addition, a facile addition of the nucleophile allows the employment of only stoichiometric amounts of the latter and alleviates the work-up of the reaction mixture. Moreover, this route is versatile for the generation of libraries or fine-tuning of electronic and steric properties of the target complexes. In recent years, this methodology was especially applied to palladium(II) compounds, being arguably the most prominent carbene complexes.[4a,8b,8c,9] Combination of both, their straightforward synthesis from easy accessible isonitrile precursors as well as their key properties makes palladium ADC-compounds an attractive alternative to the well-studied *N*-heterocyclic carbene complexes. Relevant to our study, mixed isonitrile/ADC palladium(II) compounds were also recently synthesized and employed in Heck and Suzuki-Miyaura cross-coupling reactions.[8c,9a-d]

Scheme 2. Preparation of a metal-ADC complex via metal-mediated nucleophilic addition of an amine to an isonitrile complex.

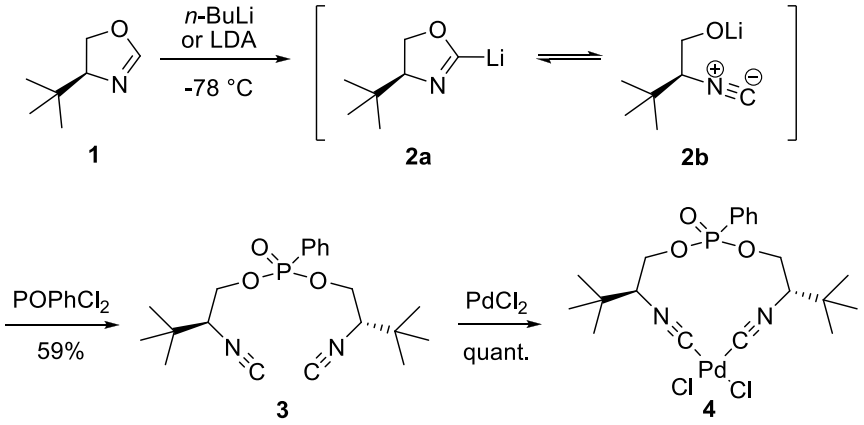


We wondered if the steric prerequisites of bidentate isonitrile complexes, being so far unexplored in this context, allow the synthesis of metal-ADC complexes as well. Moreover, we were interested in the effect of introducing asymmetry at the carbene center in the target molecule imposed by α-chiral isonitrile precursors. We report here the synthesis of two new chiral bidentate mixed isonitrile/ADC as well as one chiral bis-ADC-palladium(II) complex prepared from the corresponding chiral bisisonitrile complex. All complexes were fully characterized by 1D- and 2D-NMR experiments, ESI-MS, IR. In addition, X-ray structures of all new complexes were obtained, which allowed us to analyze the geometry changes imposed by the nucleophile addition in detail. Finally, we employed the new complexes as catalyst in the Suzuki-Miyaura coupling, the intermolecular asymmetric Heck and in the asymmetric allylic alkylation (AAA) to study both, the correlation between their structure and their reactivity as well as their ability to transfer chiral information to the substrate molecules.

2. Synthesis and Characterization

We recently introduced bidentate isonitrile ligands bridged by a phenylphosphonyl linker and metal complexes derived thereof for various applications in catalysis.[10] As a starting point for this study, the bisisonitrile ligand **3** and its corresponding palladium complex **4** was readily prepared from the chiral oxazoline **1** as previously reported by us[11] (Scheme 3).

Scheme 3. Synthesis of the bisisonitrile ligand **3**[a] and its corresponding $PdCl_2$-complex.

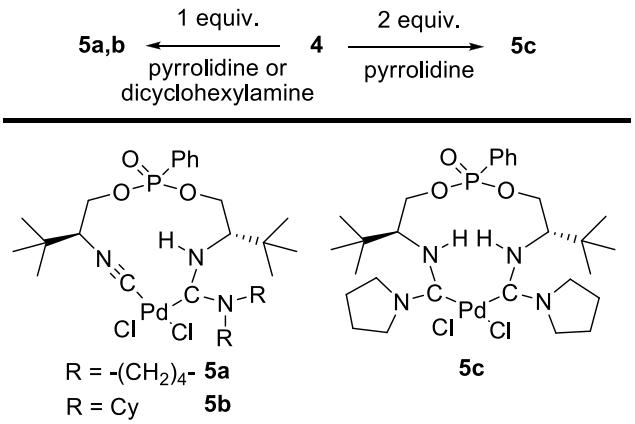


[a] Conditions: (*S*)-4-*tert*-Butyl-4,5-dihydrooxazole (**1**) (1.0 equiv.), *n*-BuLi (1.6 M in hexane, 1.05 equiv.), THF (0.4 M), –78 °C, 1.5 h; $POPhCl_2$ (0.53 equiv.), –78 °C to rt, 2 h.

The hypsochromic shift of the isonitriles IR stretching frequency of around 100 cm^{-1} to 2237 cm^{-1} upon transforming **3** to **4** indicates the complexation to this 12-membered chelate. In comparison to its iron analog $Fe(\mathbf{3})_2Cl_2$[10a] showing an isonitrile IR frequency at 2165 cm^{-1} it also become evident that **4** is activated for a nucleophilic attack to the isonitrile carbon, being in line with literature precedent for monodentate isonitrile metal complexes.[4a,9,12] Indeed, the addition of one equivalent of pyrrolidine or dicyclohexyl amine to **4** led to a new type of chiral bidentate palladium(II)-isonitrile/acyclic diaminocarbene complexes **5a** and **5b** (Scheme 4). In both cases, the formation of the carbene was validated by the typical peak in the ^{13}C-NMR at around 180 ppm as compared to the shifts of the isonitrile carbons in **4** which are found around 120 ppm. The formation of the bidentate ADC complex **5c** was achieved using two equivalents of pyrrolidine, evidenced by the vanishing of the NC isonitrile stretching frequency in the infrared spectrum at 2237 cm^{-1}. As consequence of the non-C2-symmetrical geometry of **5c**, two different signals at 187.3 and 186.6 ppm could be observed

in the ^{13}C resonance spectrum for the carbene carbons. Attempts to synthesize a biscarbene complex with dicyclohexylamine analogous to **5c** failed, most probably being a consequence to severe steric crowding as can be judged from the X-ray structure of the monocarbene complex **5b** *(vide infra*). Single crystals, suitable for X-ray diffraction analysis,[13] could be obtained by vapor diffusion for all carbene complexes **5a**-**5c** and compared to the structure of **4** that was already previously reported (Table 1).[11]

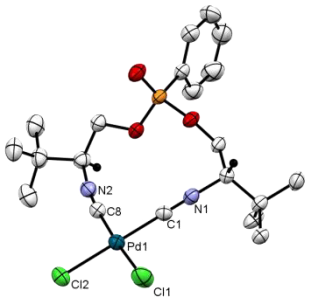
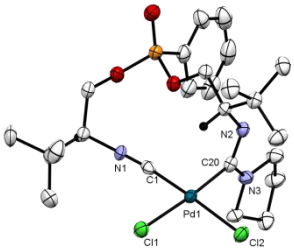
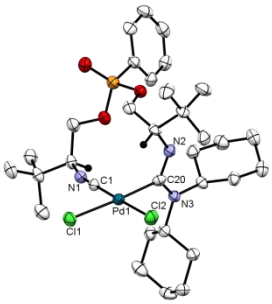
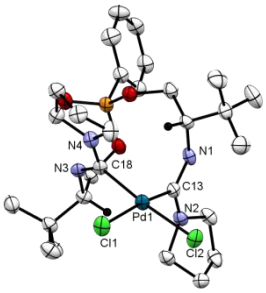
Scheme 4. Preparation of the palladium(II)-isonitrile/ADC complexes **5a** and **5b**, and the bidentate palladium(II)-bis-ADC Complex **5c** from the chiral palladium(II)-bisisonitrile complex **4**.



The realization of a square-planar environment around palladium is the dominating factor in all structures, which causes a substantial reorganization of the ligand backbone as can be seen from the dihedral torsion angle between the $(N\text{-}C)_{carbene}$-Pd-C (**5a** (86°), **5b** (98°), **5c** (63 and 64°)). The bond distances between the palladium and the isonitrile carbon (1.909 – 1.943 Å) were shorter compared to those with the carbene carbon centers (1.994 – 2.018 Å), suggesting the strong susceptibility of an isonitrile ligand for metal back bonding to its π^*-orbitals which is also reflected in the deviation of the linear coordination of the isonitriles to the palladium center (174 – 177°).

As a consequence, the chloro-palladium bond lengths trans to the isonitrile moieties were shorter (2.296 – 2.319 Å) than trans to the carbene carbons (2.352 – 2.378 Å) which is in agreement with values reported for monodentate palladium and platinum isonitrile-carbene complexes.[9a,9c,9n,12b,14]

Table 1. Solid-state molecular structures and selected bond angles [deg] and length [Å] of the palladium(II) complexes **4**[11], **5a**, **5b** and **5c**.

			
4[11]	**5a**	**5b**	**5c**
Angles [deg]: C8-Pd1-C1: 88.2; Cl1-Pd1-Cl2: 93.7; N1-C1-Pd1: 177.2; N2-C8-Pd1: 174.4.	Angles [deg]: C1-Pd1-C20: 90.8; Cl1-Pd1-Cl2: 93.3; N1-C1-Pd1: 173.8; N2-C20-N3: 118.2; N2-C20-Pd1-C1: 85.6.	Angles [deg]: C1-Pd1-C20: 87.8; Cl1-Pd1-Cl2: 94.0; N1-C1-Pd1: 175.4; N2-C20-N3: 119.0; N2-C20-Pd1-C1: 97.9.	Angles [deg]: C18-Pd1-C13: 94.8; Cl1-Pd1-Cl2: 92.6; N1-C13-N2: 116.6; N3-C18-N4: 114.8; N1-C13-Pd1-C18: 64.3; N3-C18-Pd1-C13: 62.6.
Length [Å]: Pd1-C1: 1.943; Pd1-C8: 1.935; Pd1-Cl1: 2.296; Pd1-Cl2: 2.299.	Length [Å]: Pd1-C1: 1.927; Pd1-C20: 1.993; Pd1-Cl1: 2.377; Pd1-Cl2: 2.319.	Length [Å]: Pd1-C1: 1.909; Pd1-C20: 2.018; Pd1-Cl1: 2.352; Pd1-Cl2: 2.319.	Length [Å]: Pd1-C13: 2.012; Pd1-C18: 1.984; Pd1-Cl1: 2.373; Pd1-Cl2: 2.378.

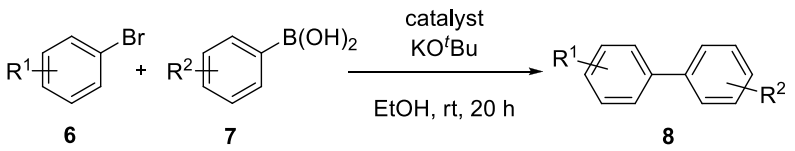
While in the bisisonitrile complex a bite-angle of 88° to palladium by dissymmetric arrangement of its isonitrile arms is realized[11], in the structures of **5a** and **5c** a significant widening of the ligands bite-angle to 91° and 95° is observed due to the higher steric demand of the amine moieties. Surprisingly, **5b** does not follow this trend (bite angle C-Pd-C = 88°) which appears to be a consequence of a significant reorganization of the somewhat flexible ligand backbone. The amine groups are oriented opposite to the *tert*-butyl groups, thus conferring the chiral environment imposed by the *tert*-butyl groups closer to the metal centers (gearing effect). With 115-119°, wide N-C-N angles being characteristic for acyclic carbenes were observed, which are significantly wider than most typical angles for cyclic carbene ligands (~100-108°)[1e].

3. Catalysis

3.1 Suzuki-Miyaura Cross Coupling

Having analyzed the structural characteristics of **5**, we were especially interested in the correlation between their structure and their catalytic performance. We started with the Suzuki-Miyaura cross coupling of 4-methoxybromobenzene with 4-methyl phenylboronic acid as model system (Table 2). In terms of practicability, we used technical grade solvent without prior degassing. In all cases, a loading of 1 mol% of catalyst, was sufficient to perform this reaction. While most protocols using palladium-ADCs require elevated temperatures or environmentally unfavorable solvents for such transformations,[5h,8b,8c,9a,9b,15] we were able to perform the reaction at room temperature in ethanol with KO^{t}Bu as base to cope with more user-friendly conditions.[9c,9d]

Table 2. Suzuki-Miyaura cross coupling using complexes **5a**-**5c** as catalyst.[a]



6 **7** **8**

Entry	R^1	R^2	Catalyst	Yield[b] [%]
1			**5a**	76
2	4-OMe	4-Me	**5b**	84
3			**5c**	33
4	H	4-OMe	**5a**	75
5	4-OMe	4-^{t}Bu	**5a**	83
6	4-NO_2	4-Me	**5b**	77
7	H	2-OMe	**5b**	81

[a] Conditions: Bromo benzene (1.0 equiv., 1.0 mmol), boronic acid (1.2 equiv., 1.2 mmol), KO^{t}Bu (1.0 equiv., 1.2 mmol), 1 mol% catalyst, 2 mL EtOH, rt, 20 h. [b] entry 1-3: NMR-yield; entry 4-7: isolated yield.

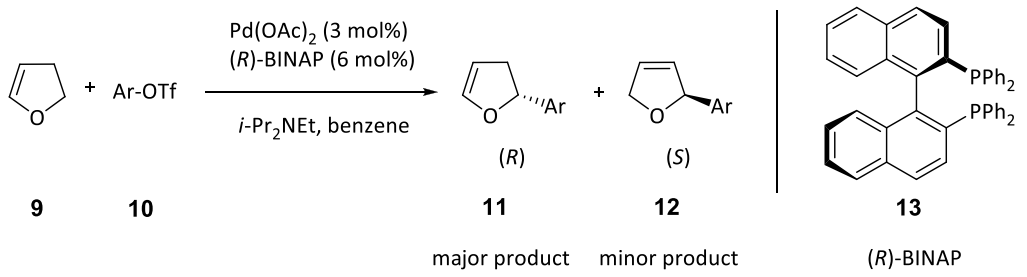
The isonitrile/acyclic diaminocarbene complexes **5a** and **5b** gave the product in good yields without significant differences (entry 1-2). However, it became evident, that the bis-ADC

complex **5c** showed only minor activity (entry 3). A possible explanation could be the steric shielding of the palladium(II) metal center by the amine moieties, which prevents an effective oxidative addition of the bromobenzene. Similar to related monodentate palladium isonitrile-ADC complexes, none of the complexes was able to activate the more challenging chlorobenzenes under these conditions.[9c] Application of different substrates confirmed the excellent activity of **5a** and **5b** to bromo benzenes (entry 4-7).

3.2 Intermolecular Asymmetric Heck

As second process, we investigated the intermolecular asymmetric Heck reaction[16], first reported by Hayashi and co-workers using 2,3-dihydrofuranes and aryl triflates.[17] Here, the application of $Pd(OAc)_2$ in combination with BINAP (**13**) resulted in the formation of two arylated products – the 2-aryl-2,3-dihydrofuran (**11**) as major and 2-aryl-2,5-dihydrofuran (**12**) as minor product (Scheme 5).

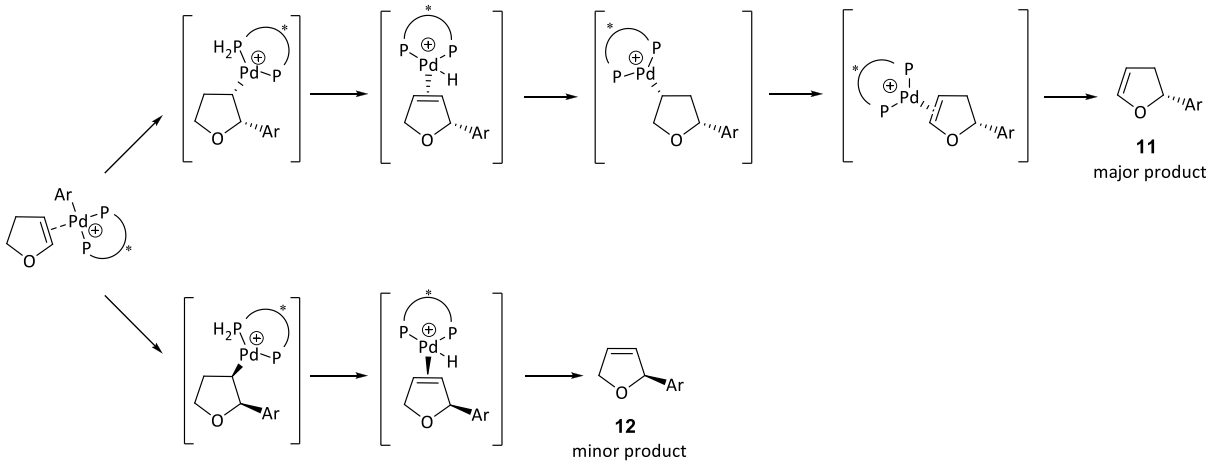
Scheme 5. Asymmetric arylation of 2,3-dihydrofurane using $Pd(OAc)_2$/BINAP as catalytic system.



This finding can be rationalized considering the catalysts coordination to either face of the substrate. Hereby, a sterical unfavorable conformation could arise, which leads to the direct dissociation of the catalyst, thus forming the minor product. By coordination on the other side, the palladium-species is able to reinsert and perform a second β-hydride elimination to furnish the 2,5-dihydrofuran isomer[17a,18] (Scheme 6).

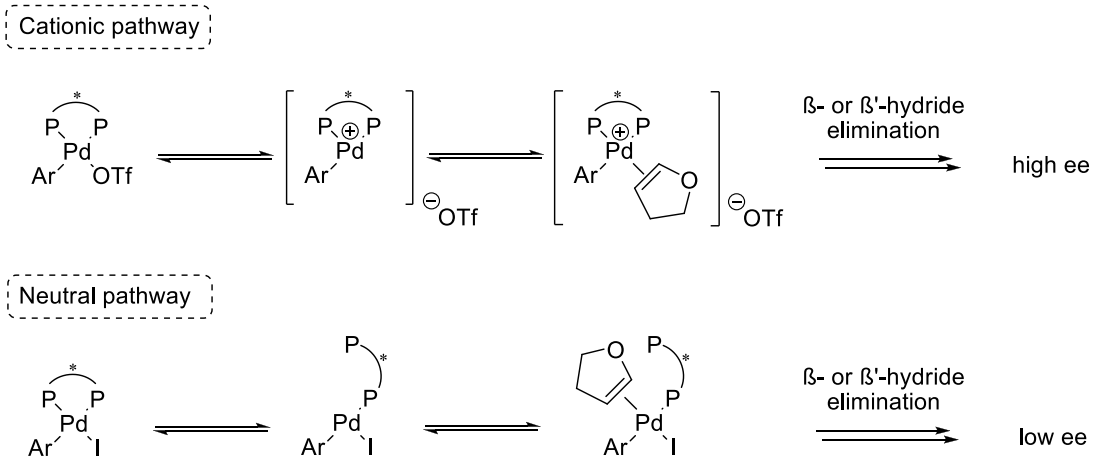
Regarding the chiral induction, it was found that the application of aryl iodides compared to aryl triflates, lead to a dramatic reduction of the ee.[19] This restriction could be explained by the strength of the Pd-I bond which prevent the dissociation of the halide to expose a vacant site. Thus the coordination of the substrate could force the dissociation of one arm of the ligand. However, this geometry does not allow an effective asymmetric induction

Scheme 6. Mechanistic rational of Hayashi's reaction leading to two different products.



In the case of the triflate anion, the chiral ligand stays fully chelated throughout all important steps for the chiral induction. Here, the dissociation of the triflate anion[20] leads to the vacant site by generation of a tricoordinated cationic species. Therefore, the substrate molecule could coordinate to the palladium, while the ligand could transfer its chirality effectively (Scheme 7).

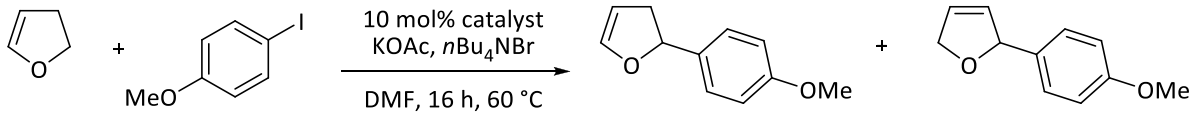
Scheme 7. Two possible pathways for the coordination of 2,3-dihydrofurane to the catalyst species.



Unfortunately, even by variation of all reaction parameters like temperature, solvent, reaction time or the application of different bases, none of the catalysts was able to perform the

reaction with aryl triflates. Nevertheless, we screened our catalysts using of 4-iodo anisole (Table 3).

Table 3. Coupling of 4-iodo anisole with 2,3-dihydrofurane.[a]



9 **13** **14** **15**

Entry	Catalyst	Yield[b] 14 [%]	ee[c] 14 [%]	Yield[b] 15 [%]	ee[c] 15 [%]	14/15[d]
1	$Pd(OAc)_2$	56	0	14	0	80:20
2	**4**	49 (44)	0	17 (14)	0	74:26
3	**5a**	51 (47)	0	18 (14)	0	74:26
4	**5b**	44 (39)	0	16 (15)	0	73:27
5	**5c**	56 (50)	0	19 (14)	0	75:25

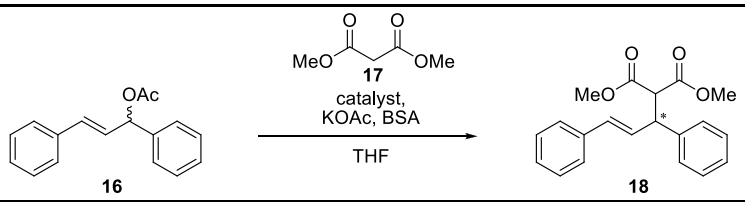
[a] Conditions: 2,3-dihydrofuran (4.0 equiv., 2 mmol, 151 µl), 4-methoxy-anisol (1.0 equiv., 0.5 mmol, 117 mg), KOAc (15 mol%, 75 µmol, 7 mg), nBu$_4$NBr (2 equiv., 1.0 mmol, 332 mg), catalyst (10 mol%), DMF (3 ml), 16 h, 60 °C; [b] NMR-Yield (isolated Yield); [c] determined by chiral HPLC; [d] calculated from NMR-Yields.

All catalysts were able to perform the reaction within 16 hours in 60-75% yield, (entry 2-5) which is in the same range as by the use of $Pd(OAc)_2$ (entry 1). However, a moderate change in the ratio of the product isomers could be observed. By using $Pd(OAc)_2$ without any additional ligand, the formation of the major substrate is favored by a ratio of 80:20. Application of our catalysts softens this preference to a ratio around 75:25, indicating a weak influence of the ligands sterical hindrance only. Also, chiral HPLC revealed the fully racemic nature of the isolated products. For this finding, one could consider the strength of the Pd-I bond and the consequential following of the neutral pathway as additional explanation.

3.3 Asymmetric Allylic Alkylation

In order to evaluate the capability of complexes **5**, we investigated the asymmetric allylic alkylation (AAA)[21] as third process. In contrast to the Heck, Suzuki-Miyaura or Negishi cross-coupling, the mechanism of this reaction involves a controlled nucleophilic attack to a metal coordinated allylic substrate, to yield optically active products. By the design of new catalysts for this reaction, a wide bite-angle of the ligand, which creates a chiral cavity for the allyl system, was identified as decisive feature for a successful transformation with an effective chiral induction.[21c,21g,22] While the most common ligands for this reaction are bidentate donor ligands which contain phosphorous, nitrogen and sulfur or a combination of these atoms,[21e-h,22b] the use of NHC-ligand systems has been explored only recently.[23] So far, there were no reports on the palladium-isonitrile or acyclic carbene catalysis for this transformation.

Table 4. Optimization of the reaction conditions for the AAA between *rac*-(*E*)-1,3-diphenyl allylacetate (**16**) and dimethyl malonate (**17**) using **4** as catalyst.[a]



Entry	mol% of catalyst	Time [min]	Temperature [°C]	Yield [%]
1	1			9
2	5	60	60	42
3	10			100
4		30	60	51
5	10	60	40	27
6[b]		60	60	83

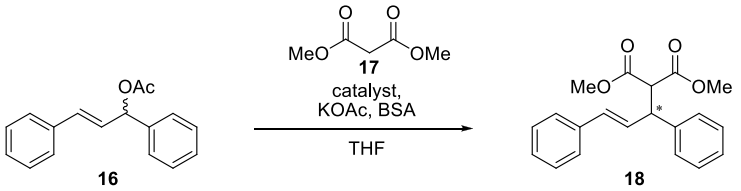
[a] Conditions: *rac*-(*E*)-1,3-diphenyl allylacetate (1.0 equiv., 0.5 mmol, 126 mg), dimethyl malonate (3.0 equiv., 1.5 mmol, 172 µL), BSA (3.0 equiv., 1.5 mmol, 370 µL), KOAc (20 mol%, 0.1 mmol, 10 mg), catalyst **4**, 3 mL THF.

[b] 1.0 equiv. dimethyl malonate.

Using optimized conditions (Table 4) we found **4** to be a capable catalyst, albeit 10 mol% were necessary to full conversion within 60 min (Table 5, entry 1). Application of **5a-5c** revealed substantial differences in the catalytic activity. While complex **5b** leads to quantitative yield after 120 minutes (entry 3), the pyrrolidine containing complex **5a** reaches 87% yield after a prolonged reaction time of 18 h (entry 2). However, similar to the Suzuki-

Miyaura coupling, catalyst **5c** led to poor results only (entry 4). Here again, an increase of steric crowding seems to be responsible for the observed differences. In agreement with this reasoning, only **5b** showed moderate enantioselecion in the reaction.

Table 5. The Asymmetric Allylic Alkylation using complexes **4** and **5a**-**5c** as catalysts.[a]



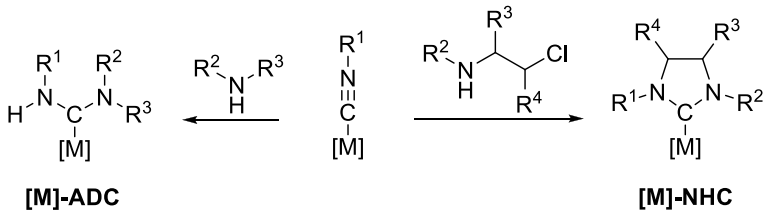
Entry	Catalyst	Time	Yield [%]	%ee[b]
1	**4**	60 min	100 (89)[c]	8 (R)[d]
2	**5a**	18 h	87	6 (S)
3	**5b**	120 min	100	45 (S)[e]
4	**5c**	18 h	5	n.d.

[a] Conditions: *rac*-(*E*)-1,3-diphenyl allylacetate (1.0 equiv., 0.5 mmol, 126 mg), dimethyl malonate (3.0 equiv., 1.5 mmol, 172 µL), BSA (3.0 equiv., 1.5 mmol, 370 µL), KOAc (20 mol%, 0.1 mmol, 10 mg), 10 mol% Catalyst, 3 mL THF, 60 °C.[b] enantiomeric excess determined by chiral HPLC (Chiralcel OJ-H), absolute configuration in brackets; [c] isolated yield in brackets; [d] $[\alpha]_D^{20}$ +5.0 °; [e] $[\alpha]_D^{20}$ -10.2 °.

4. Excursus: Synthesis of a Chiral Bidentate NC/NHC-Palladium(II) Complex

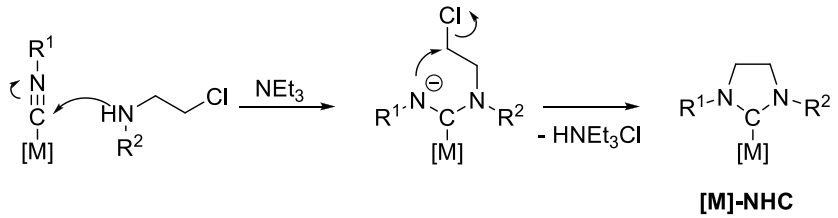
Using the metal mediated addition pathway on metal isonitriles could not only lead to the corresponding ADC-complexes. By the application to nucleophiles, bearing an electrophilic center (e.g. 2-(chloroethyl)amines), NHC-metal compounds are easy accessible within one step[4a,9c,9k,14,24] (Scheme 8).

Scheme 8. Synthesis of ADC and NHC-complexes applying the metal mediated addition pathway on isonitrile precursors.



From the mechanistic point of view, the first attack of the amine leads to the formation of a secondary nucleophilic nitrogen. The following nucleophilic substitution of this nitrogen towards the electrophilic center causes the closing of the heterocycle, and thus, leading to the metal-NHC compound[9c] (Scheme 9).

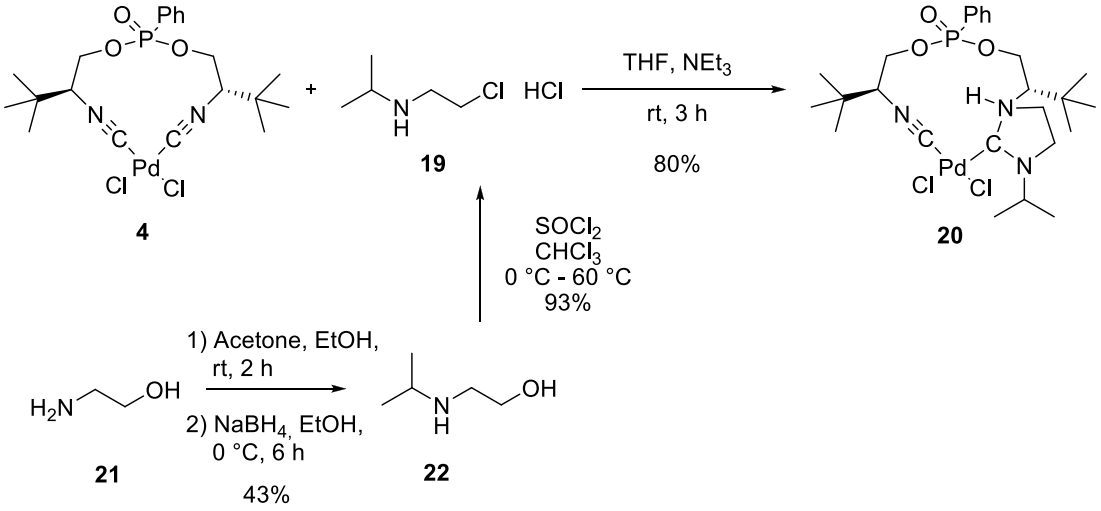
Scheme 9. Mechanistic view on the formation of metal-NHCs using 2-(chloroethyl)amines and an isonitrile complex.



Having successfully shown the formation of isonitrile/ADCs applying metal mediated addition of simple amines to the bisisonitrile complex **4**, we now used the *N*-(2-chloroethyl)propan-2-amine as nucleophile. The ammonium salt of this compound was prepared by a literature known route in two steps.[25] By applying this β-ammonium salt to **4** in presence of a weak

base, we could synthesize the corresponding bidentate isonitrile/NHC-palladium(II) complex, which was characterized by ESI-MS (Scheme 10).

Scheme 10. Synthesis of a chiral bidentate isonitrile/NHC-palladium(II) complex.



5. Summary

In conclusion, the metal-mediated synthesis of ADCs was successfully applied to the chiral bisisonitrile complex **4**. This straight forward synthesis led to three novel palladium complexes **5a**-**5c** (two bidentate isonitrile-ADCs and one bis-ADC complex) which were characterized by NMR, IR and ESI-MS. Their solid-state structure could be compared with the known bisisonitrile complex and finally their catalytic activity was investigated. While the bis-ADC complex showed only weak activity in the Suzuki-Miyaura cross coupling and the intermolecular AAA, the mixed ligand compounds led to excellent results. In addition, a moderate enantiomeric excess was obtained using complex **5b** in the AAA. However, a clear correlation between their structure and their ability for chiral induction could be observed. In addition, a chiral bidentate isonitrile/*N*-heterocyclic carbene palladium(II) complex could be synthesized.

6. References

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E Synthesis and Characterization of New Platinum(biphenyl)(isonitrile)$_n$ (n = 1,2) Compounds

1. Introduction

Starting at the end of the last century, the structure and luminescent properties of various platinum(II)-biphenyl complexes were examined extensively. For instance, the photophysical properties of various Pt(bph)L_n (n=1,2) complexes have been investigated in which bph is the biphenyl di-anion and the other ligands (L) are either carbonmonoxide,[1] diethylsulfane,[2] bipyridine,[2] acetonitrile,[2-3] pyridine (py),[4] ethylenediamine (en)[2] or 1,5-cyclooctadiene (COD)[5]. However, none of these reports analyzed the emission properties of platinum-biphenyl compounds bearing isonitrile ligands.

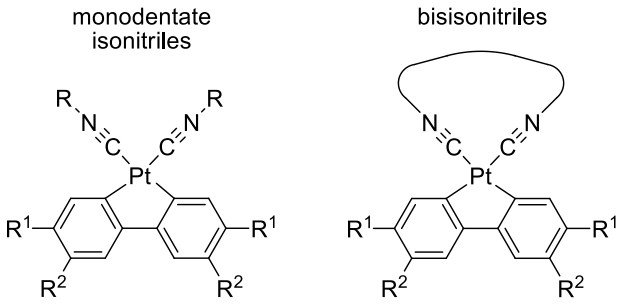


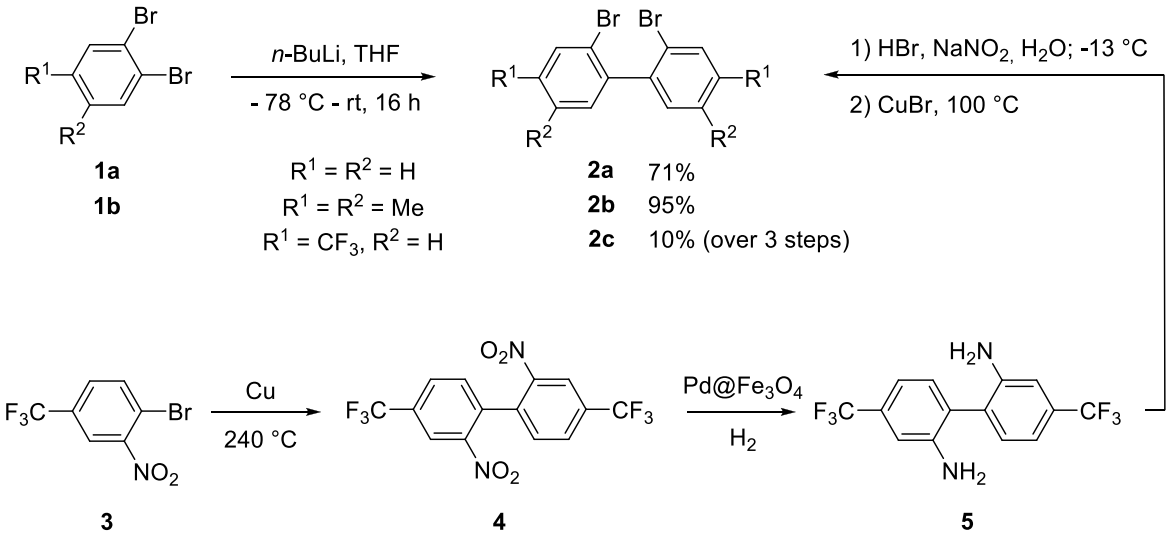
Figure 1. Different platinum(II)-complexes with various biphenyl and isonitrile ligands.

Having different isonitriles in hand, we prepared a matrix of twelve different cyclometallated platinum(II)-compounds. Additionally, two modifications were realized, which may provide some interesting photophysical properties: On the one hand four different ancillary isonitrile ligands were applied, furthermore three alternations of the cyclometallated ring systems were introduced (Figure 1).

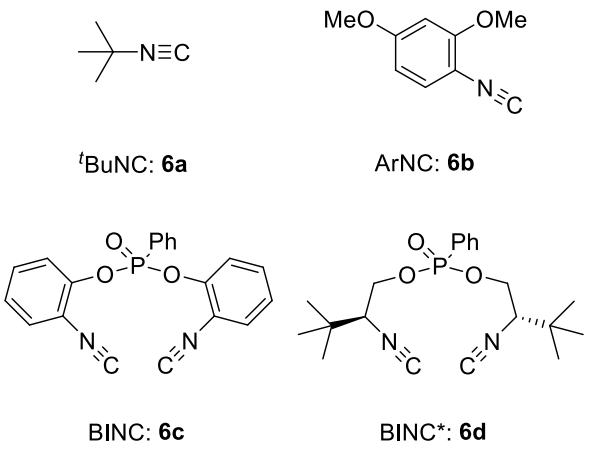
2. Synthesis and Characterization

The 2,2′-biphenyl scaffolds were prepared using standard reaction methods (Scheme 1). While 2,2′-dibromobiphenyl (**2a**) and 2,2′-dibromo-4,4′,5,5′-tetramethylbiphenyl (**2b**) could be obtained in a single step reaction from their corresponding 1,2-dibromobenzenes,[6] the CF_3-derivative 2,2'-dibromo-4,4'-bis(trifluoromethyl)biphenyl (**2c**) was prepared in a three-step sequence which starts with the construction of the biphenyl backbone by applying **3** to classical Ullmann conditions.[7] Finally, the 2,2′-dibromo-compound **2c** could be obtained upon hydrolysis of the nitro group, followed by Sandmeyer's reaction. The low yield resulted from the parallel formation of benzo[*c*]cinnoline[8] as a side product.

Scheme 1. Synthesis of the 2,2′-dibromo-biphenyls **2a**-**c**.



We applied both, mono- and bidentate isonitrile ligands with one aliphatic and one aromatic representative each (Figure 2). More precise, *tert*-Butyl isonitrile (^{t}BuNC) (**6a**) and 2,4-dimethoxy phenylisonitrile (ArNC) (**6b**)[9] represent the monodentate ligands, while bis(2-isocyanophenyl) phenylphosphonate (BINC) (**6c**) and bis((*S*)-2-isocyano-3,3-dimethylbutyl) phenylphosphonate (BINC*) (**6d**)[9-10] were applied as bidentate ligands. Seen from a different perspective, two of the ligands exhibit an aliphatic nature (**6a** and **6c**), while the ligands **6b** and **6d** possess an aromatic nature.



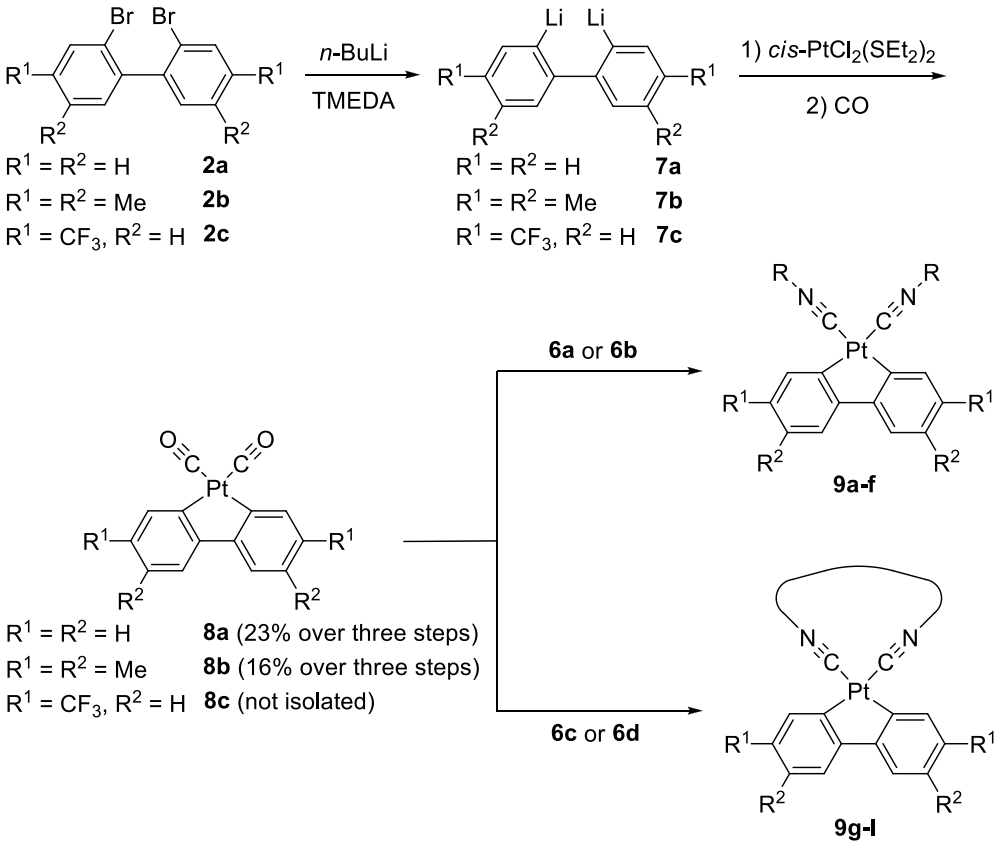
^{t}BuNC: **6a** ArNC: **6b**

BINC: **6c** BINC*: **6d**

Figure 2. Isonitrile-ligands applied in this study.

The platinum complex **9a** is already known in literature, however its synthesis starts from either tin biphenyls[11] or is carried out indirectly using Pt(dtbpm)(bph) (dtbpm = di(*tert*-butyl-phosphino)methane).[11-12] In contrast to these reports we prepared our platinum(biphenyl)(isonitrile)-complexes by a straight-forward ligand exchange reaction utilizing the irreversible loss of CO from platinum(biphenyl)$(CO)_2$ precursors **8a**-**c** which were prepared from the corresponding 2,2′-dibromo biphenyls **2a**-**c**. The synthesis of Pt(bph)$(CO)_2$ (**8a**) is known[1b] and starts with the metalation of the 2,2′-dibromo-biphenyl (**2a**), followed by the addition of *cis*-$PtCl_2(SEt_2)_2$. Following this route, **8a** could be isolated as green crystals by precipitation from the crude reaction mixture using CO gas. This procedure could also be adopted to **2b** and furnished the insoluble Pt(4,4′,5,5′-tetramethyl-bph)$(CO)_2$ (**8b**) as red crystals which could be directly analyzed by X-ray diffraction (Table 2). Hence, **8a** and **8b** could be quantitatively transferred into their isonitrile complexes by the stoichiometric addition of the appropriate isonitrile ligand. However, this facile isolation of the CO-species was not possible for the trifluoromethyl biphenyl-species **2c**. Therefore, an excess of the isonitrile ligand was directly added to the crude reaction mixture of **8c** to obtain the corresponding complexes **9c, 9f, 9i** and **9l** by chromatographic separation (Scheme 2).

Scheme 2. Synthetic route towards platinum(biphenyl)(isonitrile) complexes.



Altogether, a matrix of twelve complexes could be synthesized following this methodology (Table 1). All complexes **9** were obtained from the corresponding biphenyl **2** with an overall yield between 5-23%. A first evaluation of the emission properties of **9** was performed in poly(methyl methacrylate) (PMMA) at ambient temperature. Upon irradiation, structured emissions with maxima in the range of 508 – 580 nm, quantum yields of 15-39% and lifetimes in the range of 6-17 µs could be observed.[13] Further, a complete characterization by ^{1}H- and ^{13}C-NMR, IR and HR-ESIMS could be realized for all complexes with the exception of **9f** and **9i** as a result of their poor solubility. However, their constitution could be unambiguously proven by X-ray analysis. Overall, the solid-state structures of complexes **9b**-**i** could be successfully analyzed.[13]

The structure of Pt(4,4′,5,5′-tetramethylbiphenyl)$(CO)_2$ (**8b**)[14] (Table 2) is closely related to the known structure of **8a**.[1b] Similar to **8a**, the comparatively long Pt-C(CO) bond distances (1.976 and 1.988 Å) indicate the influence of the competitive π-backbonding between the empty π*-

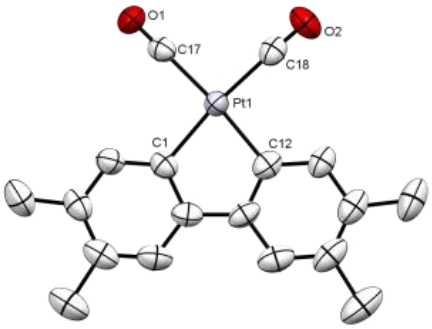
orbitals of CO and bph for electrons from the filled metal d-orbital which weakens the Pt-C(CO) bond.

Table 1. Matrix of 12 platinum(II)-complexes bearing one biphenyl and one or two isonitrile ligands.

	$R^1 = R^2 = H$	$R^1 = R^2 = Me$	$R^1 = CF_3$, $R^2 = H$
^{t}BuNC (**6a**)	**9a**	**9b**	**9c**
ArNC (**6b**)	**9d**	**9e**	**9f**
BINC (**6c**)	**9g**	**9h**	**9i**
BINC* (**6d**)	**9j**	**9k**	**9l**

Also, the Pt-C(bph) bond distances and the small bite angle of the biphenyl (80.2°) which leads to a deviation from the ideal square-planar geometry around the metal center have already been described for compound **8a**. However, the monomeric units of **8a** are arranged in planar superimposed stacked columns with a Pt-Pt distance of 3.24 Å which is – despite all analogies – not observed for **8b**.

Table 2. Solid-state structures and selected bond angles [deg] and length [Å] of **8b**.[14]



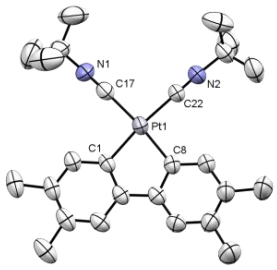
8b[14]

Angles [deg]: C17-Pt1-C18: 92.3; C1-Pt1-C12: 80.2; O1-C17-Pt1: 177.4; O2-C18-Pt1: 177.7.

Length [Å]: Pt1-C1: 2.078; Pt1-C12: 2.057; Pt1-C17 1.976; Pt1-C18: 1.988; O1-C17: 1.092; O2C18: 1.106.

The solid-state structures of the complexes with 4,4′,5,5′-tetramethyl substituted biphenyls (**9b**,[14] **9e** and **9h**) are depicted in Table 3. For all complexes, the typical biphenyl bite-angle of around 81° which lead to a distorted square-planar geometry was obtained. The bite-angle of the bisisonitrile in **9h** (91.5°) is in between the isonitrile C-Pt-C angles of the monodentate isonitriles (**9b**: 93.8°; **9e**: 90.9°) which indicates the privileged geometry of BINC (**6d**) to form chelates. As a result of the metals π-backbonding to the isonitrile carbon, the coordination of the isonitrile to the platinum center (172.2 – 179.3°) deviates from its linear geometry. The bond distances of the coordinating biphenyl carbons to the platinum(II) center (2.043 – 2.060 Å) are slightly smaller compared to the carbonmonoxide complex **8b** (2.057 and 2.078 Å), however, the bond distances of the platinum center to the isonitrile carbons are with 1.965 - 2.008 Å in the same range compared to Pt-C(CO) distances in **8b** (1.976 and 1.988 Å) which underlines the analogy of carbonmonoxide and isonitriles.

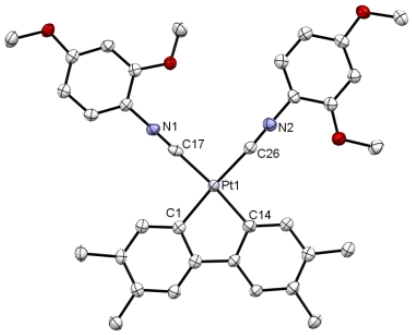
Table 3. Solid-state structures and selected bond angles [deg] and length [Å] of **9b**, **9e** and **9h**.



9b[14]

Angles [deg]: C17-Pt1-C22: 93.8; C1-Pt1-C8: 80.5; N1-C17-Pt1: 173.6; N2-C22-Pt1: 179.3.

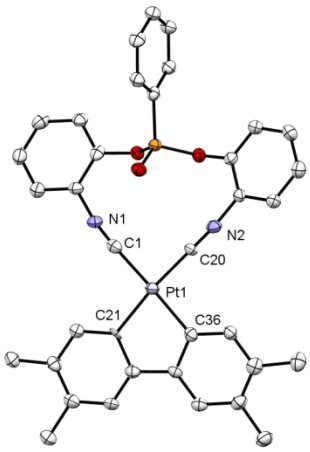
Length [Å]: Pt1-C1: 2.060; Pt1-C8: 2.053; Pt1-C17: 2.008; Pt1-C22: 2.008; N1-C17: 1.131; N2-C22: 1.136.



9e

Angles [deg]: C17-Pt1-C26: 90.9; C1-Pt1-C14: 81.1; N1-C17-Pt1: 178.8; N2-C26-Pt1: 176.0.

Length [Å]: Pt1-C1: 2.046; Pt1-C14: 2.043; Pt1-C17: 1.965; Pt1-C26: 1.986; N1-C17: 1.163; N2-C16: 1.143.



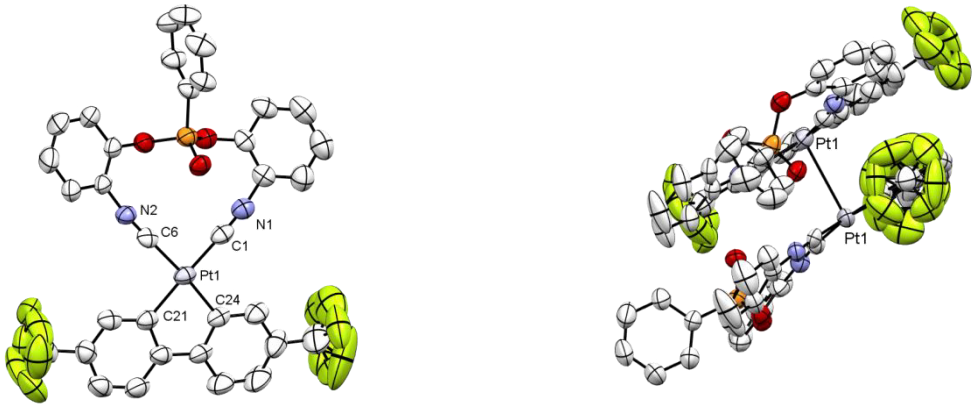
9h

Angles [deg]: C1-Pt1-C20: 91.5; C21-Pt1-C36: 81.2; N1-C1-Pt1: 172.2; N2-C20-Pt1: 178.2.

Length [Å]: Pt1-C21: 2.058; Pt1-C36: 2.052; Pt1-C1: 1.983; Pt1-C20: 1.965; N1-C1: 1.139; N2-C20: 1.153.

The structures of all other complexes showed similar geometries with the exception of **9i** which forms dimers of mirrored, 75° twisted monomeric units with an Pt-Pt distance of 3.216 Å which is in the range of most stacking square-planar platinum(II) complexes (Table 4).

Table 4. Solid-state structure and selected bond angles [deg] and length [Å] of the dimer **9i**.



9i

One molecule of the dimer

Angles [deg]: C6-Pt1-C1: 90.3; C21-Pt1-C24: 80.9; N2-C6-Pt1: 175.6; N1-C1-Pt1: 174.5.

Site-view of the dimer.

Length [Å]:Pt1-C21: 2.021; Pt1-C24: 2.038; Pt1-C6: 1.973; Pt1-C1: 1.955; N2-C6: 1.148; N1-C1: 1.167.

3. Summary

In conclusion, a full matrix of twelve platinum(II) complexes of the structure Pt(biphenyl)(isonitrile)$_n$ (n = 1,2) was synthesized. The alternations were introduced by using four different isonitriles (^{t}BuNC (**6a**), ArNC (**6b**), BINC (**6c**) and BINC* (**6d**)) and by the modification of the biphenyl backbone (2,2′-dibromo biphenyl (**2a**), 2,2′-dibromo-4,4′,5′5-tetramethyl-biphenyl (**2b**) and 2,2′-dibromo-4,4′- bis(trifluoromethyl)-biphenyl (**2c**)). The final complexes were prepared by a ligand exchange reaction from their corresponding Pt(biphenyl)(CO)$_2$ precursors. The route towards Pt(bph)(CO)$_2$ (**8a**) is known and its tetramethyl derivative **8b** could be synthesized in a similar way. Hence, the isonitrile complexes **9a,b,d,e,g,h,j,k** could be obtained in crystalline form. However, the CF_3-subsituted **8c** analogue could not be isolated by this method, hence, its isonitrile complexes **9c,f,i,l** had to be prepared from the crude reaction mixture and were obtained after purification. The complexes were characterized by NMR, IR, ESI-MS and X-Ray analysis. In addition, a first examination of their emission properties was done.

4. References

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(13) see experimental section.

(14) X-ray structure of **8b** and **9b** were kindly provided by Rafal Czerwieniec (AK Yersin).

F Summary / Zusammenfassung

1. Summary

After a short introduction on the history of isonitriles, *chapter A* describes the preparation of oxazole-derived isonitriles. Based upon previous investigations in our group, bis(2-isocyanophenyl) phenylphosphonate (binc) could be prepared by the metalation of benzoxazole followed by subsequent trapping of the resulting anion with phenylphosphonic dichloride. Further the solid-state structure of this ligand and its $PdCl_2$-complex was investigated.

Chapter B gives an overview on the molecular structure and catalytic activity of various isonitrile complexes of the Cr, Mn, Fe, Co, Ni and Cu triads that were, so far, successfully applied in metal catalysis.

In *Chapter C*, the synthesis of a series of heteroleptic [Cu(phenantroline)(bisisonitrile)]$^+$-complexes and the investigation of their structural, spectroscopic and electrochemical properties is described. The new copper(I) complexes were employed as photoredox-catalysts in the visible light-mediated atom transfer radical addition (ATRA). Especially $[Cu(dpp)(binc)]BF_4$ (dpp = 2,9-diphenyl-1,10-phenanthroline) proved to be highly active owing to an enhanced excited state lifetime compared to the commonly employed $[Cu(dap)_2]Cl$ (dap = 2,9-di(*p*-anisyl)-1,10-phenanthroline). Furthermore, the catalyst could be applied to allylation reactions with trimethylallylsilane under mild visible-light photoredox conditions.

In *Chapter D*, the preparation of two new chiral bidentate isonitrile-diaminocarbene palladium(II) complexes as well as one bis-diaminocarbene complex by metal-mediated nucleophilic addition of amines to the corresponding bisisonitrile-palladium(II) compound is described. The new chelates were fully characterized by 1D- and 2D-NMR experiments, IR, ESI-MS and X-ray structure analysis. Showing different sterical properties we furthermore investigated the relationship between their structure and their catalytic activity. The mixed ligand complexes showed both excellent activity in Suzuki-Miyaura cross coupling and the intermolecular asymmetric allylic alkylation (AAA) as well as moderate chiral induction in the

AAA. In addition, the synthesis of a chiral bidentate isonitrile/*N*-heterocyclic carbene-palladium(II) complex is described.

Chapter E finally, covers the preparation and structural discussion of a full matrix of twelve platinum(II) complexes of the structure Pt(biphenyl)(isonitrile)$_n$ (n = 1,2) derived from their corresponding Pt(biphenyl)(CO)$_2$-precursors. The modifications were introduced by the combination of three different 2,2′-biphenyls with four different isonitrile ligands. In addition, a first evaluation of their emission properties was performed.

2. Zusammenfassung

Nach einer kurzen Abhandlung über die Geschichte der Isonitrile, wird in *Kapitel A* die Herstellung von Isonitrilen aus Oxazolen beschrieben. Anschließend wird die Synthese von Bis(2-isocyanophenyl) phenylphosphonat (binc) beschrieben. Dieser zweizähnige Ligand konnte mit Hilfe einer in unserer Gruppe entwickelten Methode, über die Metallierung von Benzoxazol und dem Abfangen des dadurch entstehenden Anions mit Phenylphosphonsäure dichlorid hergestellt werden. Desweitern wurde die Kristallstruktur dieses Liganden sowie seines $PdCl_2$-Komplexes diskutiert.

Kapitel B thematisiert die Anwendung von Isonitril-Metal-Komplexen in der Katalyse und vermittelt so einen Überblick über die Struktur und die katalytische Aktivität verschiedener Isonitrilekomplexe der Cr, Mn, Fe, Co, Ni und Cu Triaden.

Die Synthese verschiedener heteroleptischer [Cu(phenanthrolin)(bisisonitril)]$^+$-Komplexe und ihre strukturellen, spektroskopischen und elektrochemischen Eigenschaften werden in *Kapitel C* beschrieben. Die neuen Komplexe konnten als Photoredoxkatalysatoren für mit sichtbarem Licht induzierte atom transfer radical additions (ATRAs) verwendet werden. Verglichen mit dem für diese Reaktionen etablierten Katalysator $[Cu(dap)_2]Cl$ (dap = 2,9-Di(*p*-anisyl)-1,10-phenanthrolin) zeigte insbesondere $[Cu(dpp)(binc)]BF_4$ (dpp = 2,9-Diphenyl-1,10-phenanthrolin) eine deutlich verlängerte Lebenszeit des angeregten Zustandes und somit auch eine höhere katalytische Aktivität. Zusätzlich wurde dieser Katalysator für milde licht-induzierte Allylierungen mit Trimethylallylsilan verwendet.

Kapitel D beschreibt die Synthese und Charakterisierung von zwei neuartigen chiralen zweizähnigen Isonitril-Diaminocarben Palladium(II)-Komplexen sowie eines neuen Bis-Diaminocarben Komplexes. Die neuen Verbindungen wurden ausgehend von $Pd(binc)Cl_2$ durch eine metall-vermittelte nukleophile Aminaddition hergestellt. Mithilfe von 1D- und 2D-NMR, IR, ESI-MS und Kristallstrukturanalyse konnten die neuen Komplexe vollständig charakterisiert werden. Da sich die Komplexe stark bezüglich ihrer sterischen Eigenschaften unterschieden, wurde zusätzlich der Zusammenhang zwischen ihrer Struktur und ihrer katalytischen Aktivität untersucht. Die Isonitril-Diaminocarbenkomplexe zeigten hierbei nicht nur eine hohe Aktivität in der Suzuki-Miyaura Kreuzkupplung und der intermolekularen asymmetrischen allylischen Alkylierung (AAA), sondern auch eine moderate chirale Induktion

in der AAA. Des Weiteren wird die Synthese eines chiralen zweizähnigen Isonitril/*N*-heterocyclischen-Carben Palladium(II)-Komplex beschrieben.

Die Synthese von Platin(II) Komplexen der Struktur Pt(biphenyl)(isonitril)$_n$ (n = 1,2) wird in *Kapitel E* beschrieben. Die Komplexe wurden ausgehend von den entsprechenden Pt(biphenyl)(CO)$_2$ Verbindungen hergestellt und ihre strukturellen Eigenschaften konnten anhand von Kristallstrukturen diskutiert werden. Durch die Modifikation der Biphenyle (Biphenyl, 4,4‘,5,5‘-Tetramethyl-biphenyl und 4,4‘-Bis(trifluoromethyl)-biphenyl) sowie der Verwendung vier verschiedener Isonitrilliganden konnte eine komplette Matrix aus zwölf Komplexen synthetisiert werden. Zusätzlich wurde eine erste Untersuchung der Emissionseigenschaften durchgeführt.

G Experimental

1. General

All photo-reactions were carried out in oven-dried glassware applying three consecutive freeze-pump-thaw cycles. All solvents were dried and distilled prior to use. Thin layer chromatography (TLC) was performed using silica gel 60 F254 aluminium plates (Merck). Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable stain followed by heating. Column chromatography was performed on silica gel 60 (0.063–0.200 mm, Merck).

1H- and 13C-NMRspectra were recorded on a Bruker Avance 300 (300 MHz for 1H, 75 MHz for 13C), Bruker Avance II 400"Nanobay"(400 MHz for 1H, 101 MHz for 13C) or Avance III 600 (600 MHz for 1H, 151 MHz for 13C) FT-NMR-spectrometer. Chemical shifts are reported in parts per million (ppm). ATR-IR spectroscopy was carried out on a Biorad Excalibur FTS 3000 spectrometer equipped with a Specac Golden Gate Diamond Single Reflection ATR-system. Mass spectrometry was performed on a Varian MAT 311A, Finnigan MAT 95, Thermoquest Finnigan TSQ 7000 or Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS.

UV-Vis absorption spectra were recorded with a Varian Cary 300 double beam spectrometer. Luminescence and excitation spectra were measured with a Horiba Jobin Yvon Fluorolog 3 steady-state fluorescence spectrometer. For decay time measurements a PicoQuant LDH-P-C-375 pulsed diode laser (λexc = 372 nm, pulse width 100 ps) was applied as the excitation source. The emission signal was detected with a cooled photomultiplier attached to a FAST ComTec multichannel scalar card with a time resolution of 250 ps. Photoluminescence quantum yields were determined with a Hamamatsu C9920-02 system equipped with a Spectralon® integrating sphere.

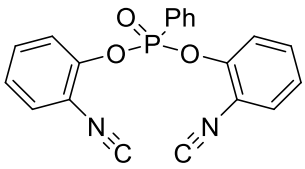
Molecular geometry of $[Cu(dpp)(binc)]^+$ (**6a**) was optimized using the density functional theory (DFT) with the hybrid gradient corrected correlation functional B3LYP.[1] Electronic excitations were calculated for the DFT optimized ground-state geometry using the time-dependent density functional theory (TD-DFT). Six lowest triplet and singlet excitations were

computed. The Ahlrichs split-valence basis set SVP^2 was applied for all atoms. All computations were carried out using the Gaussian 09 (Version 8.0) program package.

Cyclic voltammetry measurements were carried out on an Autolab PGSTAT 302N set-up at 20 °C in the stated solvent containing tetrabutyl ammonium tetrafluoroborate as the supporting electrolyte under an argon atmosphere with use of a conventional undivided electrochemical cell, a glassy carbon working electrode, platinum wire as the counter electrode and silver wire as the reference electrode. The solvent was degassed by vigorous argon bubbling prior to the measurements. Redox potentials were referenced against ferrocene as an internal standard. For better comparison all values are reported in reference to the SCE electrode.

2. Chapter A: Isonitrile-Synthesis

2.1 Compound Characterization

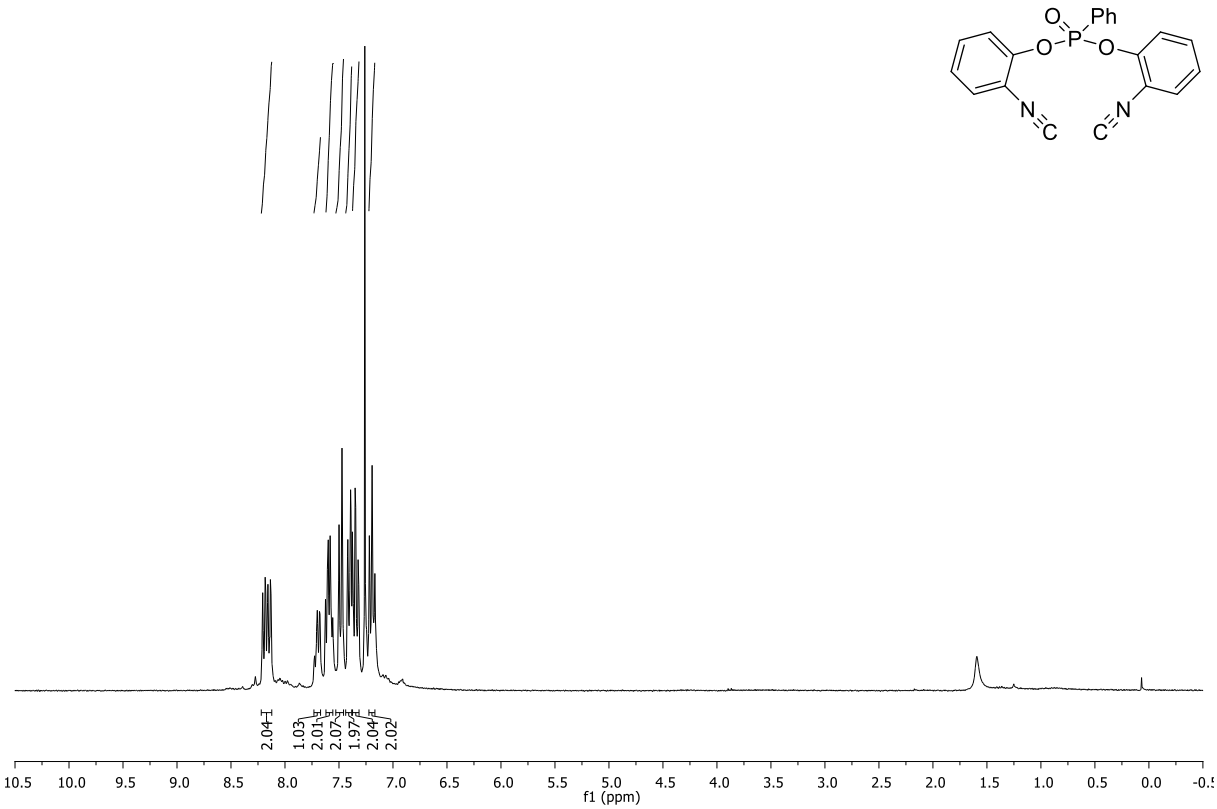


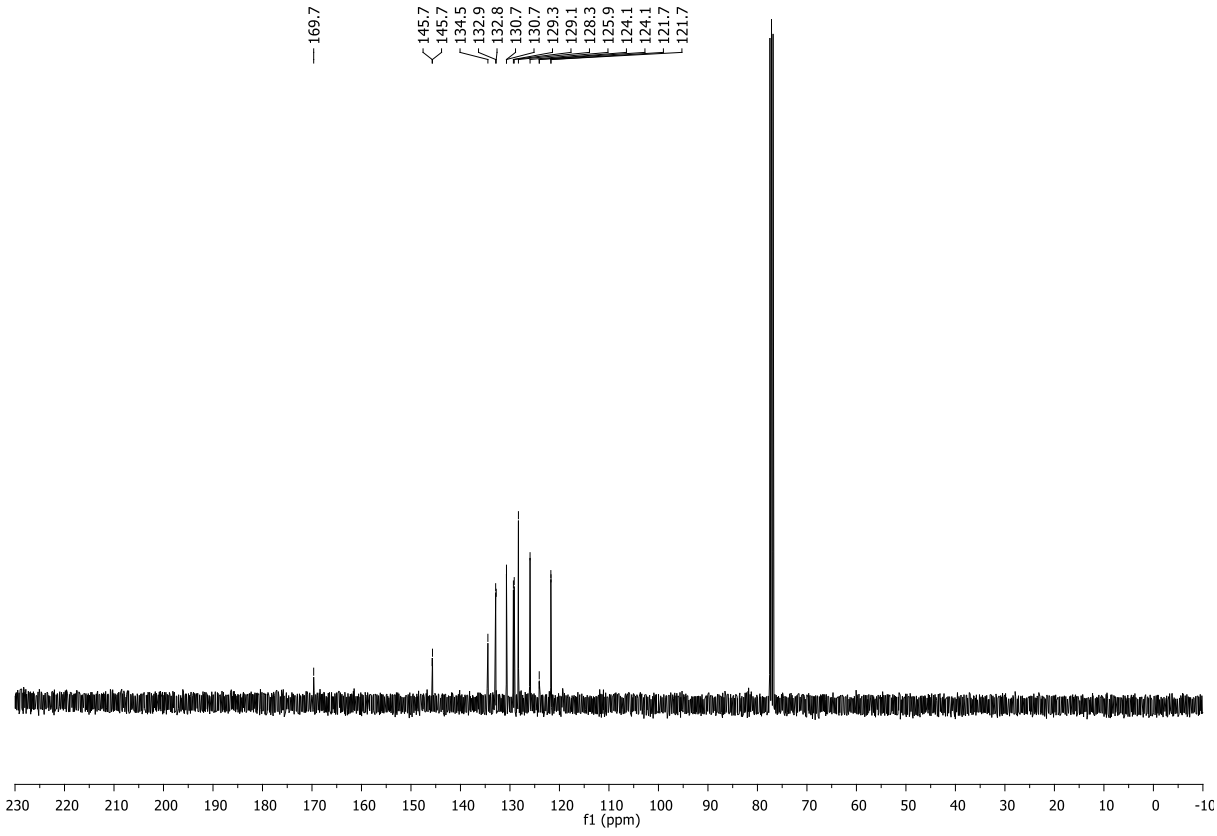
bis(2-isocyanophenyl) phenylphosphonate (binc) (**26**)

A flame-dried 50 ml round-bottom flask equipped with a magnetic stir bar was charged with benzoxazole (0.91 g, 7.63 mmol, 1.0 equiv.) and dry THF (20 ml). n-BuLi (1.6 M in hexane, 5.0 ml, 8.0 mmol, 1.05 equiv.) was added dropwise at -78 °C resulting in an immediate colorchange of the reaction mixture (light brown to black). The reation mixture was allowed to stir at -78 °C for 1.5 h. The phenylphosphonic dichloride (0.57 ml, 4.04 mmol, 0.53 equiv.) was slowly added dropwise to the solution which turned yellow. The solution was allowed to warm to room temperature and stirred for 2 h. After quenching the reaction by pouring the mixture into Et_2O:$NaHCO_3$ (2:1, 150 ml), the organic layer was washed with water (2x 50 ml), dried and concentrated in vacuo. The resulting residue was purified by silica gel flash column chromatography (PE: EA = 4:1 – 1:1) to provide the binc ligand **26** (755 mg, 2.1 mmol, 55%) as light brown solid. R_f (PE:EA = 1:1) = 0.66; 1H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.11 (m, 2 H), 7.74 – 7.66 (m, 1 H), 7.63 – 7.54 (m, 2 H), 7.48 (dt, J = 8.3, 1.3 Hz, 2 H), 7.40 (d, J = 7.9 Hz, 2 H), 7.38 – 7.30 (m, 2 H), 7.23 – 7.15 (m, 2 H); 13C NMR (101 MHz, $CDCl_3$) δ 169.7, 145.7, 145.7, 134.5, 132.9, 132.8, 130.7, 130.7, 129.3, 129.1, 128.3, 125.9, 124.1, 124.1, 121.7, 121.7. (isonitrile carbons not detected); IR (neat): 2127, 1590, 1487, 1442, 1285, 1263, 1232, 1172, 1157, 1132, 1100, 1035, 920, 788, 763, 750, 708, 688 cm^{-1}; ESI-HRMS: calcd. for $C_{20}H_{13}N_2O_3P$ [MH^+]: 361.0739. Found: 361.0737.

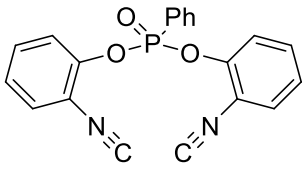
2.2 NMR-Spectra

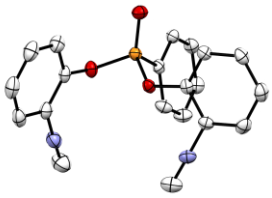
bis(2-isocyanophenyl) phenylphosphonate (binc) (**26**)





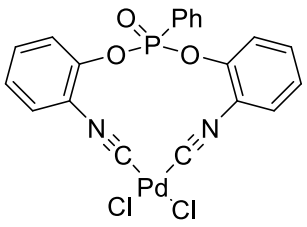
2.3 Solid-State Structures

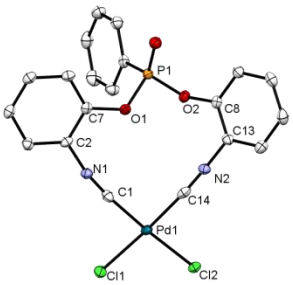




bis(2-isocyanophenyl) phenylphosphonate (**26**)

CCDC-Code	1064132
Formula	C42H28Cl10N4O6P2Pd2
Dcalc./ g cm-3	1.807
□/mm-1	12.161
Formula Weight	1313.92
Colour	colourless
Shape	prism
Max Size/mm	0.13
Mid Size/mm	0.06
Min Size/mm	0.03
T/K	123(2)
Crystal System	triclinic
Space Group	P-1
a/Å	10.5194(5)
b/Å	11.3050(6)
c/Å	12.8486(6)
□/°	64.026(5)
□/°	86.154(4)
□/°	63.035(5)
V/Å3	1207.70(12)
Z	1
Z'	0.5
□min/°	3.880
□max/°	73.637
Measured Refl.	10562
Independent Refl.	4668
Reflections Used	4260
Rint	0.0369
Parameters	301
Restraints	0
Largest Peak	0.680
Deepest Hole	-0.829
GooF	1.056
wR2 (all data)	0.0660
wR2	0.0644
R1 (all data)	0.0293
R1	0.0258





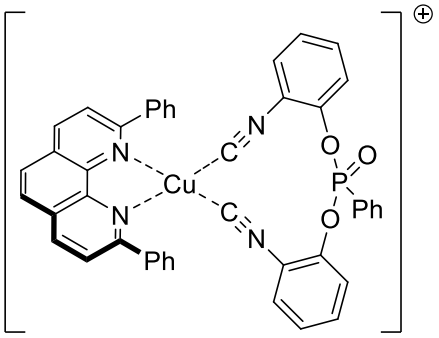
28

Formula	C42H28Cl10N4O6P2Pd2
Dcalc./ g cm-3	1.807
m/mm-1	12.161
Formula Weight	1313.92
Colour	colourless
Shape	prism
Max Size/mm	0.13
Mid Size/mm	0.06
Min Size/mm	0.03
T/K	123(2)
Crystal System	triclinic
Space Group	P-1
a/Å	10.5194(5)
b/Å	11.3050(6)
c/Å	12.8486(6)
a/°	64.026(5)
b/°	86.154(4)
g/°	63.035(5)
V/Å3	1207.70(12)
Z	1
Z'	0.5
Qmin/°	3.880
Qmax/°	73.637
Measured Refl.	10562
Independent Refl.	4668
Reflections Used	4260
Rint	0.0369
Parameters	301
Restraints	0
Largest Peak	0.680
Deepest Hole	-0.829
GooF	1.056
wR2 (all data)	0.0660
wR2	0.0644
R1 (all data)	0.0293
R1	0.0258

3. Chapter C: Copper-Isonitriles

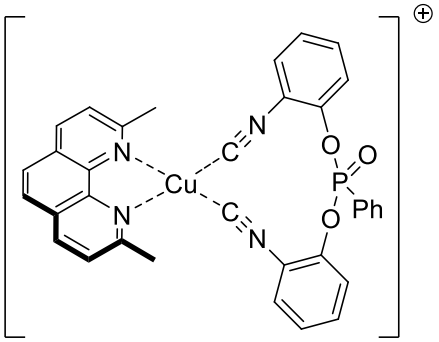
3.1 Compound Characterization

General procedure for the preparation of heteroleptic phenanthroline bisisonitrile copper(I) complexes 6a-e: To a stirred solution of the phenanthroline (0.5 mmol, 1.0 equiv.) and the bisisonitrile (0.5 mmol, 1.0 equiv.) in DCM (50 ml), $Cu(MeCN)_4BF_4$ (157 mg, 0.5 mmol, 1.0 equiv.) was added. After 2 h, the reaction mixture was concentrated to a minimum of DCM. The complexes were obtained by precipitation in diethyl ether as brown solids in quantitative yield.



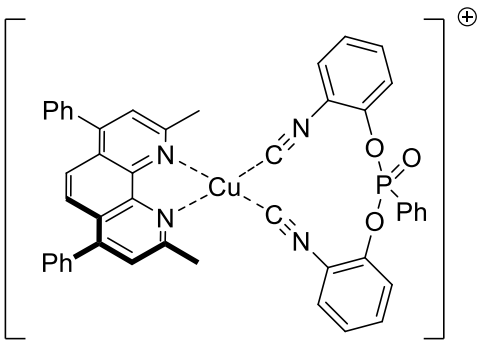
[Cu(dpp)(binc)]BF_4 (**6a-BF_4**)

1H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 8.3 Hz, 2H), 8.19 – 8.11 (m, 4H), 8.02 – 7.93 (m, 4H), 7.90 – 7.12 (m, 19H); IR (neat): 3072, 2142, 1589, 1488, 1443, 1361, 1271, 1236, 1056, 1037, 921, 863, 806, 758, 742, 698, 654, 600 cm^{-1}; ESI-HRMS: calcd. for $C_{34}H_{29}CuN_4O_3P$ [M^+]: 775.1268. Found: 775.1263.



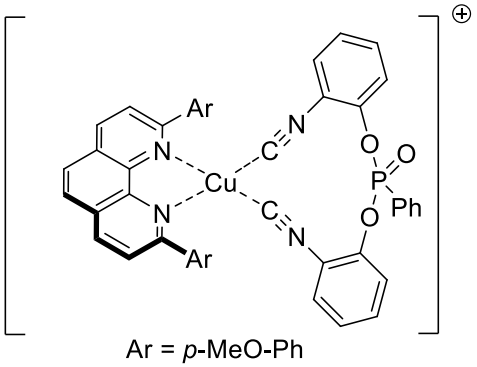
[Cu(dmp)(binc)]BF_4 (**6b-BF_4**)

Crystals suitable for x-ray analysis were obtained by ether diffusion in a DCM solution of **6b-BF_4**; 1H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, J = 8.0 Hz, 2H), 8.10 (dd, J = 14.2, 7.5 Hz, 2H), 7.95 (s, 2H), 7.88 (d, J = 7.4 Hz, 2H), 7.77 (t, J = 7.2 Hz, 1H), 7.65 (dd, J = 12.6, 7.4 Hz, 2H), 7.44 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.35 (s, 2H), 7.27 – 7.23 (m, 2H), 3.18 (s, 6h); 13C NMR (151 MHz, $CDCl_3$) δ 159.2, 146.7, 143.1, 138.4, 135.3, 132.7, 132.1, 129.8, 127.7, 127.3, 126.6, 126.1, 125.7, 124.7, 123.5, 121.3, 119.0, 27.1; IR (neat): 3125, 2159, 2136, 1591, 1487, 1441, 1235, 1104, 1052, 942, 909, 853, 800, 793, 766, 755, 730, 695 cm^{-1}; ESI-HRMS: calcd. for $C_{34}H_{25}CuN_4O_3P$ [M^+]: 631.0955. Found: 631.0960.



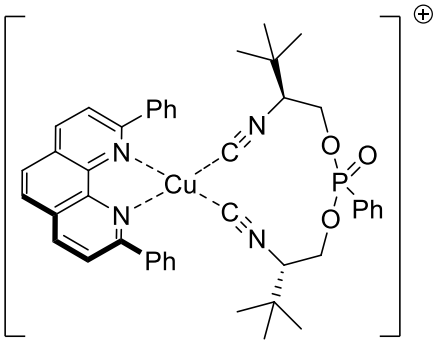
[Cu(dpdmp)(binc)]BF_4 (**6c-BF_4**)

Crystals suitable for x-ray analysis were obtained by ether diffusion in a DCM solution of **6c-BF_4**; 1H NMR (600 MHz, $CDCl_3$) δ 8.10 (dd, J = 14.2, 7.5 Hz, 2H), 7.94 (s, 2H), 7.81 (s, 2H), 7.78 (t, J = 7.6 Hz, 1H), 7.66 (dd, J = 12.4, 7.2 Hz, 2H), 7.61 – 7.53 (m, 10H), 7.48 (d, J = 7.7 Hz, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.27 (d, J = 9.0 Hz, 2H), 3.25 (s, 2H); 13C NMR (151 MHz, $CDCl_3$) δ 158.6, 150.9, 146.7, 143.9, 136.6, 135.3, 132.7, 132.0, 129.8, 129.7, 129.4, 129.1, 127.4, 126.7, 125.9, 125.8, 124.7, 123.9, 123.5, 121.5, 119.1, 27.2; IR (neat): 3093, 3042, 2160, 2135, 1488, 1440, 1281, 1232, 1099, 1051, 1035, 911, 829, 703, 610 cm_{-1}; ESI-HRMS: calcd. for $C_{46}H_{33}CuN_4O_3P$ [M^+]: 738.1586. Found: 738.1583.



[Cu(dap)(binc)]BF_4 (**6d-BF_4**)

1H NMR (300 MHz, $CDCl_3$) δ 8.59 – 8.52 (m, 2H), 8.51 – 8.32 (m, 2H), 8.11 – 7.08 (m, 19H), 6.94 (t, J = 8.2 Hz, 2H), 6.87 (d, J = 8.2 Hz, 2H), 3.63 (s, 3H), 3.48 (s, 3H). IR (neat): 3100, 2160, 1691, 1605, 1489, 1358, 1252, 1178, 1055, 1025, 926, 864, 838, 801, 754, 692, 649 cm^{-1}; ESI-HRMS: calcd. for $C_{46}H_{33}CuN_4O_5P$ [M^+]: 815.1479. Found: 815.1472.



[Cu(dpp)(binc*)]BF_4 (**6e-BF_4**)

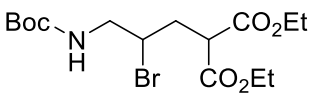
1H NMR (300 MHz, $CDCl_3$) δ 8.66 (d, J = 8.3 Hz, 2H), 8.18 – 7.82 (m, 10H), 7.74 – 7.48 (m, 9H), 4.21 – 3.61 (m, 6H), 1.13 – 0.62 (m, 18H); IR (neat): 2967, 2871, 2178, 1647, 1488, 1373, 1240, 1020, 995, 865, 742, 697 cm^{-1}; ESI-MS: 771.4 [M^+].

General procedure for ATRAs with bromomalonates (table 3, entry 1-4) (GPA): A solution of alkene (1.0 mmol, 1.0 equiv.), ATRA reagent (2.0 mmol, 2.0 equiv.), LiBr (2.0 mmol, 2.0 equiv.) and Cu(dpp)(binc)BF_4 (**6a-BF_4**)(0.5 mol%) in DMF/H2O mixture (0.2 ml / 0.8 ml)

was degassed using three freeze-pump-thaw cycles, set under nitrogen and irradiated with a blue LED (455 nm) at room temperature. After completion of the reaction (judged by TLC) water (5 ml) was added and the reaction mixture was extracted with dichloromethane (1 x) and water (3 x), dried over $MgSO_4$ and concentrated in vacuo. The residue was purified on silica gel.

General procedure for ATRAs with benzylbromides (table 3, entry 5-10) (GPB): A solution of benzyl halide (1.0 mmol, 1.0 equiv.), alkene (5.0 mmol, 5.0 equiv.) and Cu(dpp)(binc)BF_4 (**6a-BF_4**) (1.0 mol%) in MeCN (1.0 ml) was degassed using three freeze-pump-thaw cycles, set under nitrogen and irradiated with a blue LED (455 nm) at room temperature. After completion of the reaction (judged by TLC) the reaction mixture was concentrated in vacuo. The residue was purified on silica gel.

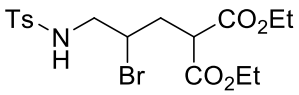
General procedure for the allylation with allyltrimethylsilane (table 5) (GPC): A solution of halide (0.5 mmol, 1.0 equiv.) and Cu(dpp)(binc)BF_4 (**6a-BF_4**) (1.0 mol%) in MeCN (1.0 ml) was degassed using three freeze-pump-thaw cycles. Allyltrimethylsilane (1.5 mmol, 3.0 equiv.) was added under nitrogen and the reaction mixture was irradiated with a blue LED (455 nm) at room temperature. After completion of the reaction (judged by TLC) water (5 ml) was added and the reaction mixture was extracted with dichloromethane (1 x) and water (3 x), dried over $MgSO_4$ and concentrated in vacuo. The residue was purified on silica gel.



Diethyl 2-(2-bromo-3-(tert-butoxycarbonylamino)propyl)malonate (**9**)[3]

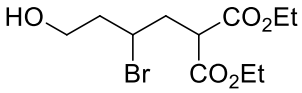
According to GPA, *tert*-butyl allylcarbamate (**7a**) (157 mg, 1.0 mmol, 1.0 equiv.), diethyl 2-bromomalonate (**8a**) (0.34 ml, 2.0 mmol, 2.0 equiv.), LiBr (174 mg, 2.0 mmol, 2.0 equiv.) and [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (0.5 mol%) afforded **9** (347 mg, 0.88 mmol, 88%) after irradiation for 7.5 h as yellow oil by column purification on silica gel. R_f (PE:EA = 4:1) = 0.44. 1H NMR

(300 MHz, $CDCl_3$) δ 5.12 – 4.86 (m, 1H), 4.27 – 4.01 (m, 5H), 3.68 (dd, J = 9.5, 4.9 Hz, 1H), 3.46 (t, J = 5.9 Hz, 2H), 2.43 (ddd, J = 14.8, 9.6, 3.7 Hz, 1H), 2.20 (ddd, J = 15.0, 10.2, 5.0 Hz, 1H), 1.38 (s, 9H), 1.21 (td, J = 7.1, 1.6 Hz, 6H). 13C NMR (75 MHz, $CDCl_3$) δ 168.8, 168.5, 155.7, 79.8, 61.8, 61.7, 53.2, 50.2, 47.1, 34.6, 28.3, 14.0, 14.0. ESI-MS (rel. int.): MH^+-Boc 296.1 (100), 297.1 (10), 298.1 (97), 299.1 (10); MNa^+ 418.1 (57), 419.1 (10), 420.1 (60), 421.1 (9).



Diethyl 2-(2-bromo-3-(4-methylphenylsulfonamido)propyl)malonate (**11**)[3]

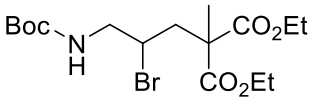
According to GPA, *N*-allyl-4-methylbenzenesulfonamide (**7b**) (211 mg, 1.0 mmol, 1.0 equiv.), diethyl 2-bromomalonate (**8a**) (0.34 ml, 2.0 mmol, 2.0 equiv.), LiBr (174 mg, 2.0 mmol, 2.0 equiv.) and [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (0.5 mol%) afforded **11** (308 mg, 0.68 mmol, 68%) after irradiation for 15.5 h as colorless oil by column purification on silica gel. R_f (PE:EA = 4:1) = 0.15. 1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.12 (t, J = 6.6 Hz, 1H), 4.24 – 4.12 (m, 4H), 4.08 – 4.01 (m, 1H), 3.64 (dd, J = 9.5, 4.9 Hz, 1H), 3.36 – 3.20 (m, 2H), 2.48 – 2.43 (m, 1H), 2.41 (s, J = 4.0 Hz, 3H), 2.24 (ddd, J = 15.0, 10.1, 4.9 Hz, 1H), 1.28 – 1.22 (m, 6H). 13C NMR (101 MHz, $CDCl_3$) δ 168.7, 168.4, 143.9, 136.9, 130.0, 127.2, 62.0, 61.9, 51.9, 50.0, 49.5, 34.6, 21.6, 14.1, 14.1. ESI-MS (rel. int.): MH^+ 450.0 (97), 451.0 (19), 452.0 (100), 453.0 (18); MNH_4^+ 467.1 (60), 468.1 (11), 469.1 (60), 470.1 (12).



Diethyl 2-(2-bromo-4-hydroxybutyl)malonate (**12**)[3]

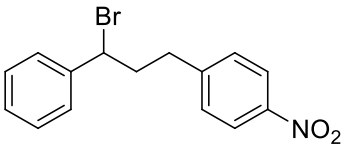
According to GPA, but-3-en-1-ol (**7c**) (86 µl, 1.0 mmol, 1.0 equiv.), diethyl 2-bromomalonate (**8a**) (0.34 ml, 2.0 mmol, 2.0 equiv.), LiBr (174 mg, 2.0 mmol, 2.0 equiv.) and [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (0.5 mol%) afforded **12** (249 mg, 0.80 mmol, 80%) after irradiation for 15.5 h as colorless oil by column purification on silica gel. R_f (PE:EA = 4:1) = 0.66. 1H NMR (300 MHz, $CDCl_3$) δ 4.28 – 4.11 (m, 5H), 3.88 – 3.70 (m, 3H), 2.48 (ddd, J = 14.9, 10.1, 3.2 Hz, 1H), 2.28

(ddd, J = 14.9, 10.6, 4.4 Hz, 1H), 2.16 – 1.95 (m, 3H), 1.25 (td, J = 7.1, 2.1 Hz, 6H). 13C NMR (75 MHz, $CDCl_3$) δ 169.1, 168.9, 61.9, 61.9, 60.4, 51.2, 50.6, 41.7, 38.0, 14.1, 14.1. ESI-MS (rel. int.): MH^+ 311.0 (99), 312.1 (13), 313.0 (100), 314.1 (12); MNa^+ 333.0 (49), 334.0 (6), 335.0 (49), 336.0 (6).



Diethyl 2-(2-bromo-3-(tert-butoxycarbonylamino)propyl)-2-methylmalonate (**13**)

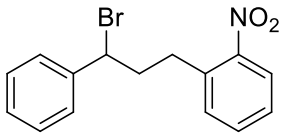
According to GPA, *tert*-butyl allylcarbamate (**7a**) (157 mg, 1.0 mmol, 1.0 equiv.), diethyl 2-bromo-2-methylmalonate (**8b**) (0.38 ml, 2.0 mmol, 2.0 equiv.), LiBr (174 mg, 2.0 mmol, 2.0 equiv.) and [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (0.5 mol%) afforded **13** (119 mg, 0.29 mmol, 29%) after irradiation for 24 h as yellow oil by column purification on silica gel. 1H NMR (300 MHz, $CDCl_3$) δ 5.01 (s, 1H), 4.22 – 4.01 (m, 5H), 3.57 – 3.43 (m, 1H), 3.30 (ddd, J = 14.4, 7.4, 5.6 Hz, 1H), 2.53 – 2.37 (m, 2H), 1.43 (s, J = 6.8 Hz, 3H), 1.38 (s, 9H), 1.19 (td, J = 7.1, 1.8 Hz, 6H). 13C NMR (75 MHz, $CDCl_3$) δ 171.6, 171.5, 155.7, 79.8, 61.8, 61.7, 52.9, 50.4, 48.4, 41.4, 28.4, 19.9, 14.0. IR (neat): 2981, 1726, 1507, 1450, 1366, 1248, 1164, 1111, 1018, 860 cm^{-1}. ESI-HRMS: calcd. for $C_{16}H_{29}BrNO_6$ [MH^+]: 410.1173. Found: 410.1176.



1-(3-Bromo-3-phenylpropyl)-4-nitrobenzene (**14**)[4]

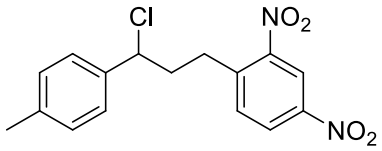
According to GPB, 1-(bromomethyl)-4-nitrobenzene (**8c**) (216 mg, 1.0 mmol, 1.0 equiv.), styrene (**7d**) (0.57 ml, 5.0 mmol, 5.0 equiv.) and [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (1 mol%) afforded **14** (257 mg, 0.80 mmol, 80%) after irradiation for 15.5 h as colorless oil by column purification on silica gel R_f (PE:EA = 4:1) = 0.66. 1H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.14 (m, 2H), 7.40 – 7.30 (m, 7H), 4.87 (dd, J = 8.7, 6.1 Hz, 1H), 2.99 – 2.90 (m, 1H), 2.86 – 2.77 (m, 1H),

2.68 – 2.57 (m, 1H), 2.50 – 2.39 (m, 1H). 13C NMR (101 MHz, $CDCl_3$) δ 148.4, 146.8, 141.6, 129.5, 129.0, 128.8, 127.4, 124.0, 54.1, 40.9, 34.3.



1-(3-Bromo-3-phenylpropyl)-2-nitrobenzene (**15**)[4]

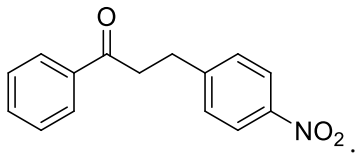
According to GPB, 1-(bromomethyl)-2-nitrobenzene (**8d**) (216 mg, 1.0 mmol, 1.0 equiv.), styrene (**7d**) (0.57 ml, 5.0 mmol, 5.0 equiv.) and [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (1 mol%) afforded **15** (134 mg, 0.42 mmol, 42%) after irradiation for 24 h as light yellow liquid by column purification on silica gel R_f (PE:EA = 4:1) = 0.66. 1H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.5, 1.3 Hz, 1H), 7.54 (td, J = 7.6, 1.3 Hz, 1H), 7.45 – 7.25 (m, 7H), 5.00 (dd, J = 8.5, 6.3 Hz, 1H), 3.12 (ddd, J = 13.4, 10.0, 5.2 Hz, 1H), 2.94 (ddd, J = 13.3, 9.9, 6.0 Hz, 1H), 2.69 – 2.47 (m, 2H). 13C NMR (101 MHz, $CDCl_3$) δ 149.3, 141.6, 135.8, 133.3, 132.3, 128.9, 128.7, 127.6, 127.4, 125.1, 54.7, 40.6, 32.2. EI-MS (rel. int.): 319.0 (10), 240.1 (42), 194.1 (29), 134.1 (24), 104.2 (34), 91.0 (100).



1-(3-Chloro-3-p-tolylpropyl)-2,4-dinitrobenzene (**16**)[4]

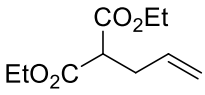
According to GPB, 1-(chloromethyl)-2,4-dinitrobenzene (**8e**) (108 mg, 0.5 mmol, 1.0 equiv.), 1-methyl-4-vinylbenzene (**7e**) (0.20 ml, 3.0 mmol, 1.5 equiv.) and [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (1 mol%) afforded **16** (117 mg, 0.35 mmol, 70%) after irradiation for 18 h as light yellow oil by column purification on silica gel R_f (PE:EA = 4:1) = 0.5. 1H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 2.4 Hz, 1H), 8.37 (dd, J = 8.5, 2.4 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 4.89 (dd, J = 8.5, 5.8 Hz, 1H), 3.24 (ddd, J = 13.5, 9.8, 5.4 Hz, 1H), 3.06 (ddd, J = 13.5, 9.7, 6.3 Hz, 1H), 2.54 – 2.39 (m, 2H), 2.35 (s, J = 4.1 Hz, 3H). 13C NMR (101 MHz, $CDCl_3$) δ 149.2, 146.7, 143.1, 138.8, 137.8, 133.6, 129.6, 127.2, 126.9, 120.6, 62.7, 40.2,

31.2, 21.3 EI-MS (rel. int.): 334.1 (44), 299.1 (5), 281.2 (10), 207.1 (20), 179.1 (23), 141.1 (26), 139.1 (76), 134.2 (55), 119.1 (100), 105.1 (96).



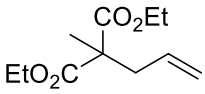
3-(4-Nitrophenyl)-1-phenylpropan-1-one (**17**)[5]

According to GPB, 1-(bromomethyl)-4-nitrobenzene (**8c**) (216 mg, 1.0 mmol, 1.0 equiv.), trimethyl((1-phenylvinyl)oxy)silane (**7f**) (0.62 ml, 3.0 mmol, 3.0 equiv.) and [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (1 mol%) afforded **17** (217 mg, 0.85 mmol, 85%) after irradiation for 15.5 h as light yellow solid by column purification on silica gel R_f (PE:EA = 9:1) = 0.3. 1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.7 Hz, 2H), 7.95 (dd, J = 8.4, 1.3 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.51 – 7.40 (m, 4H), 3.36 (t, J = 7.4 Hz, 2H), 3.19 (t, J = 7.3 Hz, 2H). 13C NMR (101 MHz, $CDCl_3$) δ 198.3, 149.3, 146.7, 136.7, 133.5, 129.5, 128.9, 128.1, 123.9, 39.5, 29.9. EI-MS (rel. int.): 255.1 (22), 105.0 (100), 77.1 (35).



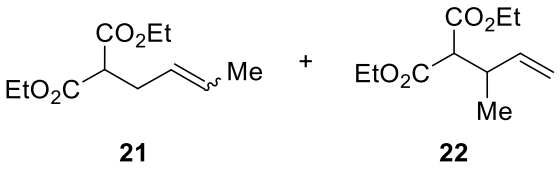
Diethyl 2-allylmalonate (**19**)[6]

According to GPC, diethyl 2-bromomalonate (**8a**) (86 µL, 0.5 mmol, 1.0 equiv.), allyltrimethylsilane (**18a**) (0.24 ml, 1.5 mmol, 3.0 equiv.), and [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (0.5 mol%) afforded **19** (64 mg, 0.32 mmol, 64%) after irradiation for 24 h as colorless liquid by column purification on silica gel R_f (PE:EA = 4:1) = 0.6. 1H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddt, J = 17.0, 10.2, 6.8 Hz, 1H), 5.09 (ddq, J = 21.7, 10.2, 1.3 Hz, 2H), 4.19 (qd, J = 7.1, 1.6 Hz, 4H), 3.42 (t, J = 7.6 Hz, 1H), 2.68 – 2.60 (m, 2H), 1.26 (t, J = 7.1 Hz, 6H). 13C NMR (101 MHz, $CDCl_3$) δ 169.1, 134.2, 117.7, 61.6, 51.8, 33.0, 14.2. APCI-MS (rel. Int.): MH^+ 201.1 (100), 202.1 (11); MH^+-C_2H_4 173.1 (12), 174.1 (1).



Diethyl 2-allyl-2-methylmalonate (**20**)[7]

According to GPC, diethyl 2-bromo-2-methylmalonate (**8b**) (90 µL, 0.5 mmol, 1.0 equiv.), allyltrimethylsilane (**18a**) (0.24 ml, 1.5 mmol, 3.0 equiv.), and [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (1.0 mol%) afforded **20** (88 mg, 0.41 mmol, 82%) after irradiation for 40 h as colorless liquid by column purification on silica gel R_f (PE:EA = 4:1) = 0.6. 1H NMR (300 MHz, $CDCl_3$) δ 5.77 – 5.61 (m, 1H), 5.15 – 5.09 (m, 1H), 5.08 – 5.06 (m, 1H), 4.18 (q, J = 7.1 Hz, 4H), 2.61 (d, J = 7.4 Hz, 2H), 1.38 (s, 3H), 1.24 (t, J = 7.1 Hz, 6H). 13C NMR (75 MHz, $CDCl_3$) δ 172.1, 132.8, 119.2, 61.4, 40.2, 19.9, 14.2. APCI-HRMS: calcd. for $C_{11}H_{19}O_4$ [MH^+]: 215.1278. Found: 215.1279.



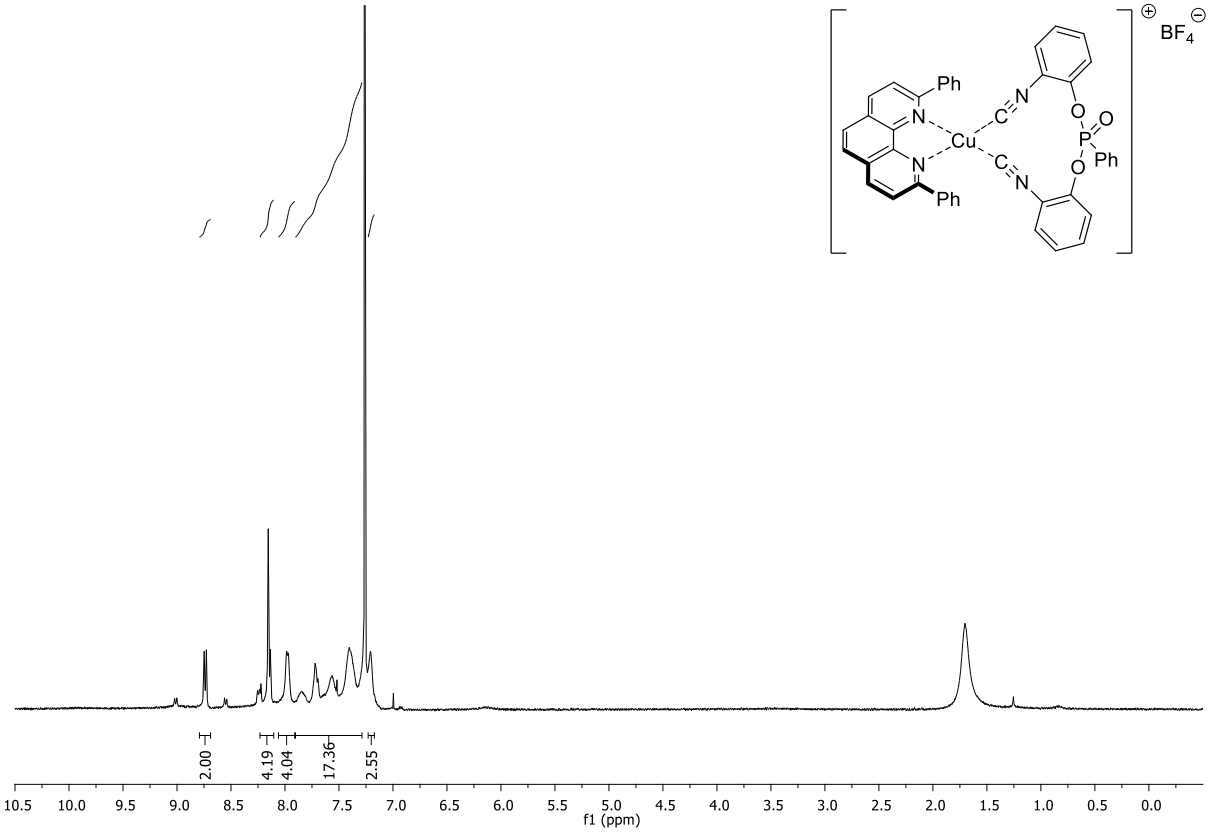
21 **22**

Diethyl 2-(but-2-en-1-yl)malonate (**21**)[8] and Diethyl 2-(but-2-en-1-yl)malonate (**22**)[9]

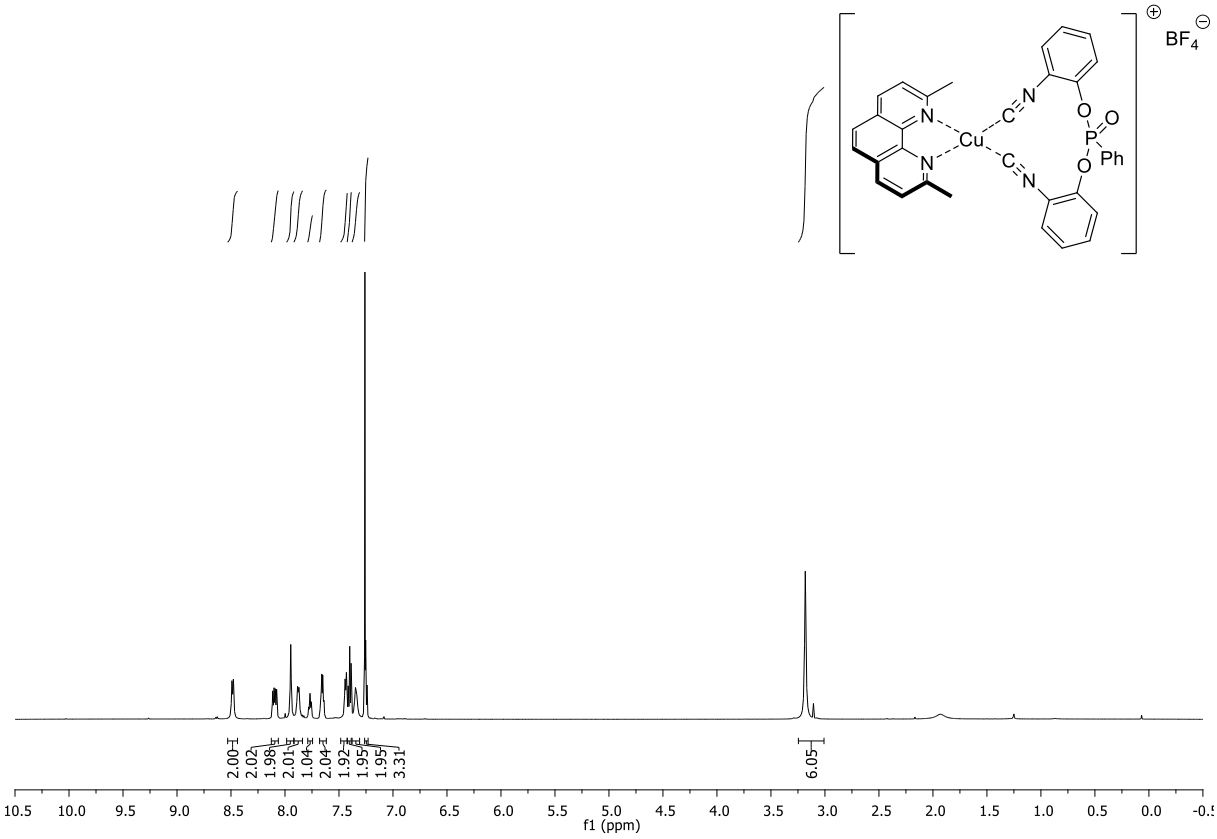
According to GPC, diethyl 2-bromomalonate (**8a**) (86 µL, 0.5 mmol, 1.0 equiv.), but-2-en-1-yltrimethylsilane (**18b**) (384 mg, 1.5 mmol, 3.0 equiv.), and [Cu(dpp)(binc)]BF_4 (**6a-BF_4**) (1.0 mol%) afforded an unseparable mixture of **21** : **22** = 84 : 16 (87 mg, 0.40 mmol, 80% overall yield) after 24 h as colourless oil by column purification on silica gel. R_f (PE:EA = 5:1) = 0.48.
Diethyl 2-(but-2-en-1-yl)malonate (**21**)[8] 1H NMR (300 MHz, $CDCl_3$) δ = 5.59 – 5.24 (m, 2H), 4.16 (q, J = 7.2 Hz, 4H), 3.33 (t, J = 7.6 Hz, 1H), 2.67 – 2.48 (m, 2H), 1.63 – 1.58 (m, 3H), 1.23 (ddd, J = 7.1, 4.8, 1.6 Hz, 6H). 13C NMR (75 MHz, CDCl3) δ = 169.2, 169.2, 128.4, 126.6, 125.6, 61.4, 61.4, 57.8, 31.9, 26.4, 18.0, 18.0, 14.2, 14.1, 12.9. APCI-HRMS: calcd. for $C_{11}H_{18}O_4$ [MH^+]: 214.1209. Found: 214.1205.
Diethyl 2-(but-2-en-1-yl)malonate (**22**)[9] 1H NMR (300 MHz, $CDCl_3$) δ = 5.74 (ddd, J = 17.2, 10.3, 8.0 Hz, 1H), 5.10 – 4.91 (m, 2H), 4.12 – 4.07 (m, 4H), 3.22 (d, J = 8.9 Hz, 1H), 2.90 (m, 1H), 1.19 (m, 6H), 1.06 (d, J = 6.8 Hz, 3H). 13C NMR (75 MHz, $CDCl_3$) δ = 168.4, 168.4, 139.9, 115.5, 61.3, 52.3, 52.0, 38.1, 18.0, 14.2. APCI-HRMS: calcd. for $C_{11}H_{18}O_4$ [MH^+]: 214.1209. Found: 214.1205.

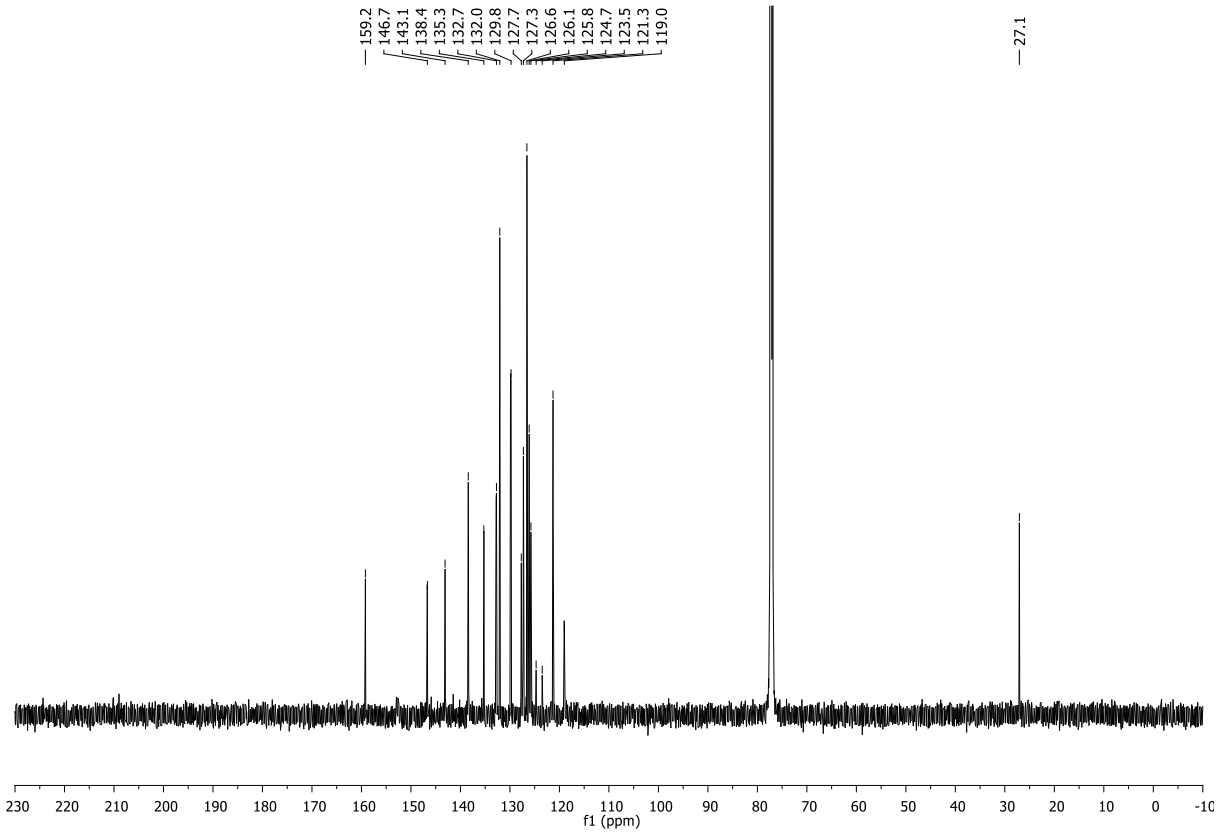
3.2 NMR-Spectra

[Cu(dpp)(binc)]BF_4 (**6a-BF_4**)

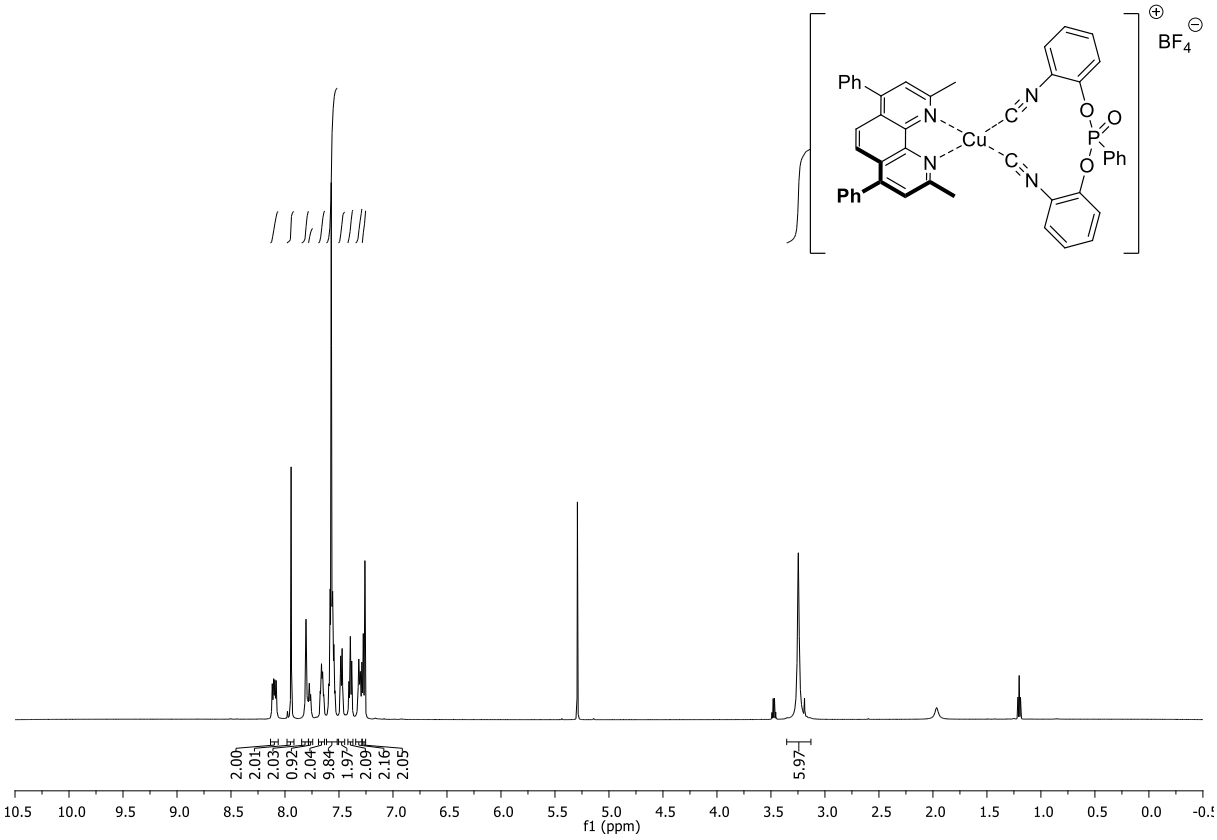


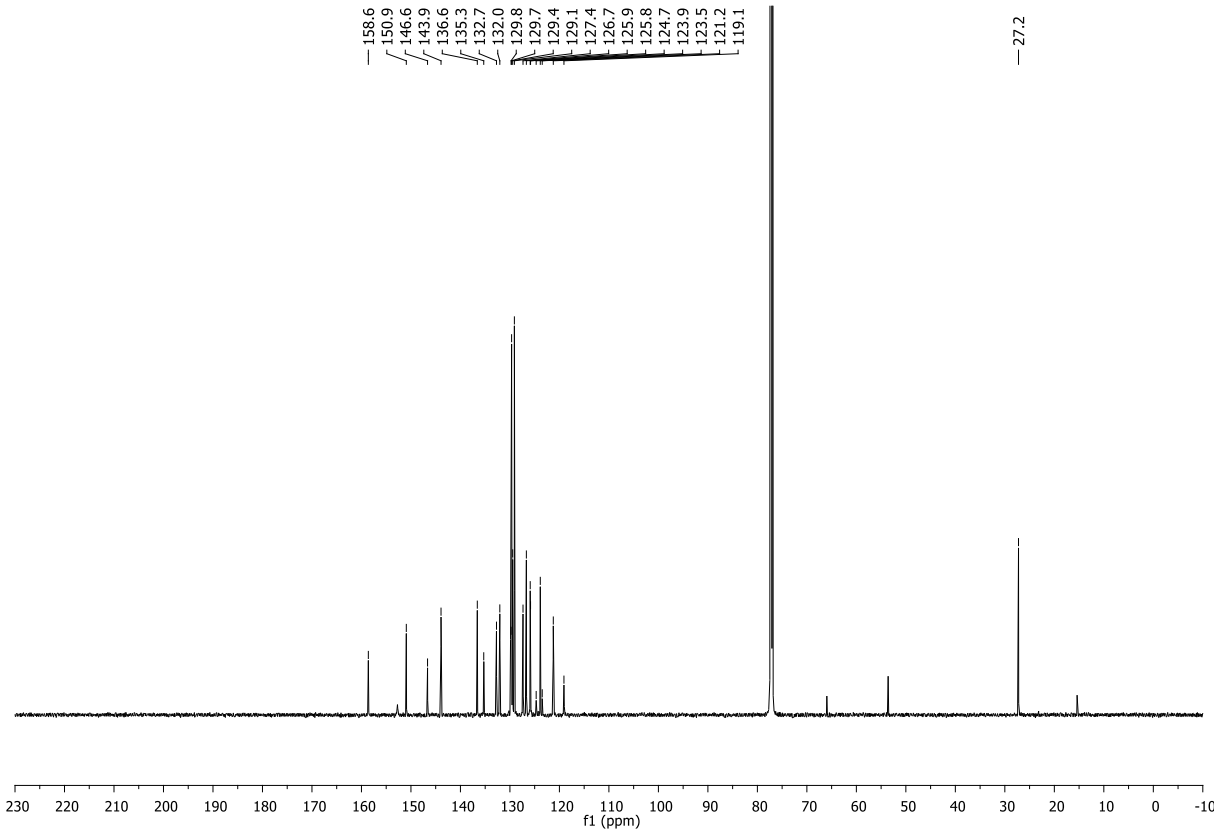
[Cu(dmp)(binc)]BF_4 (**6b-BF_4**)



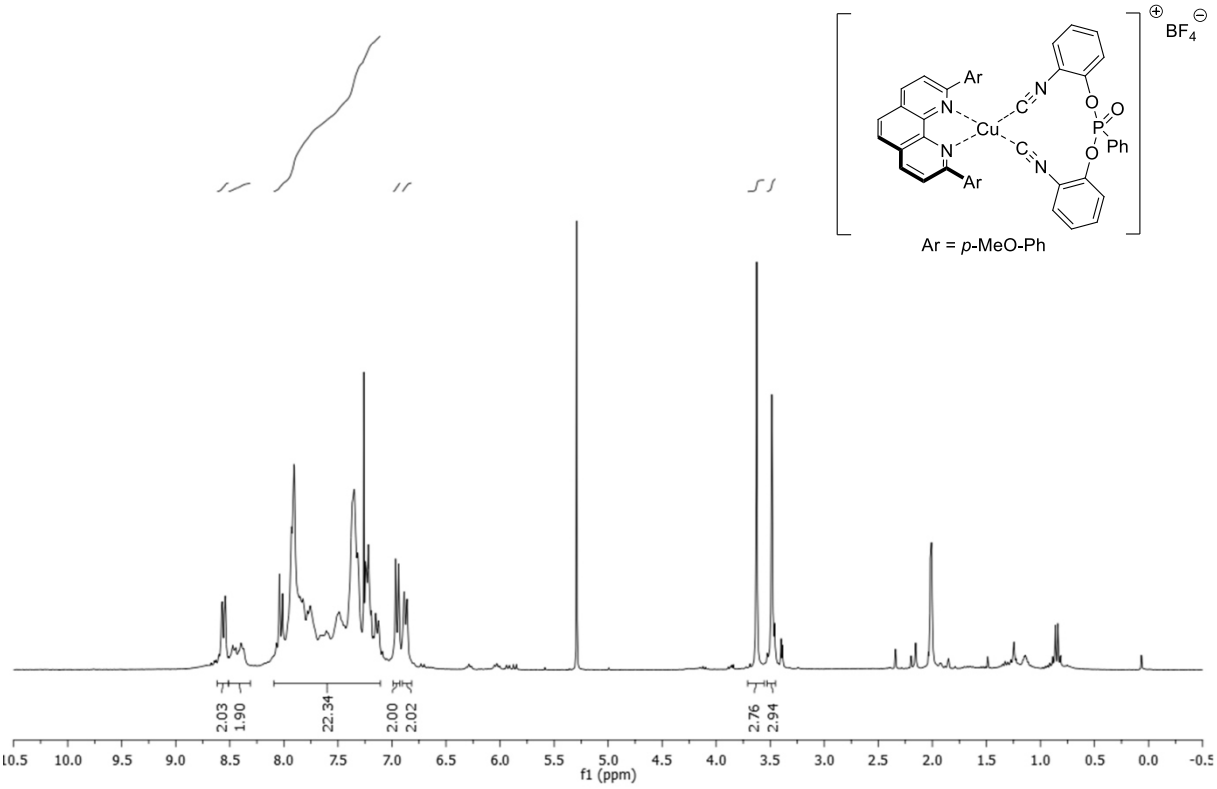


[Cu(dpdmp)(binc)]BF_4 (**6c-BF_4**)

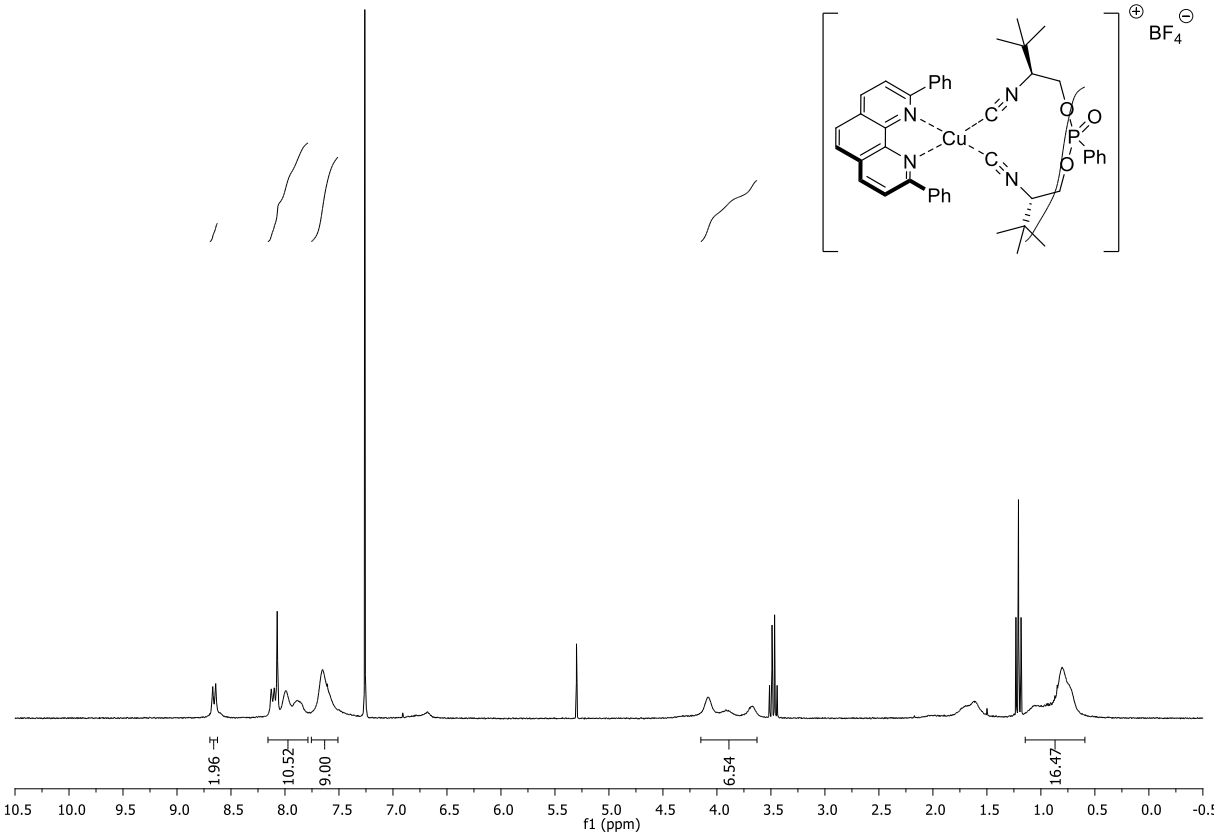




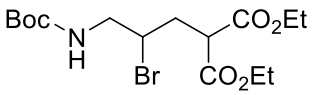
[Cu(dap)(binc)]BF_4 (**6d-BF_4**)

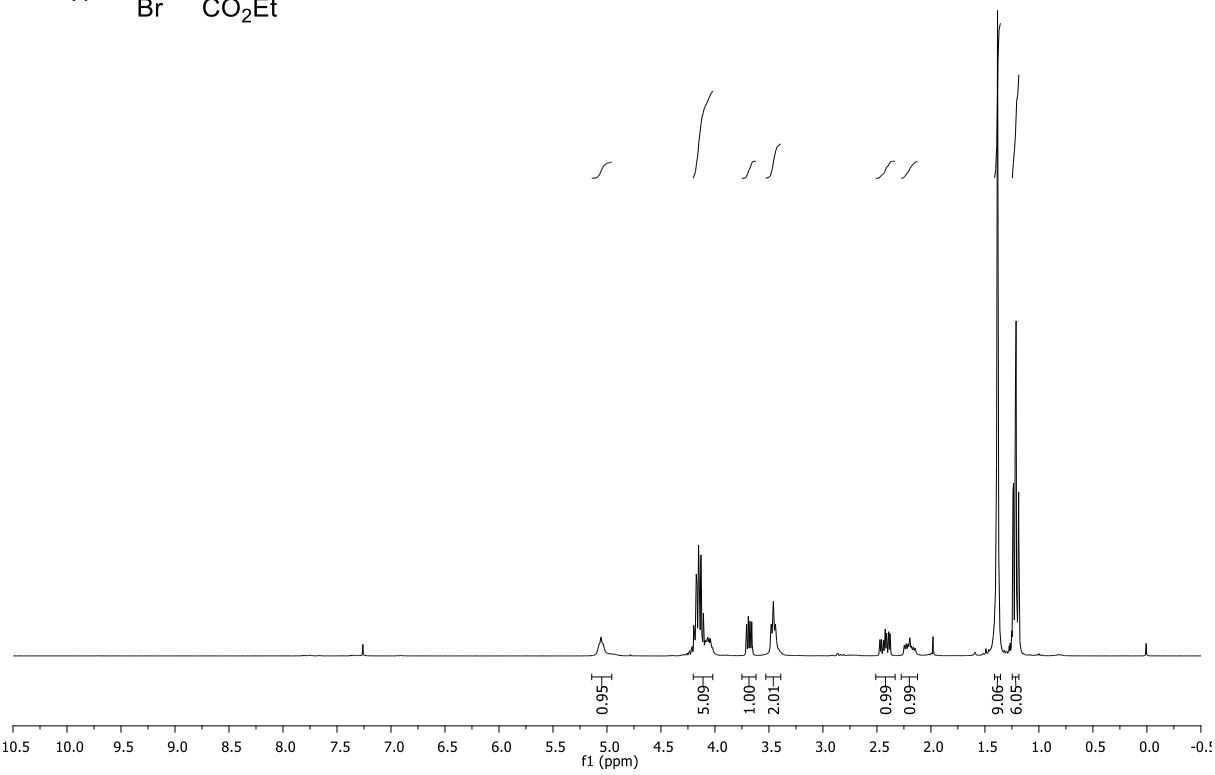


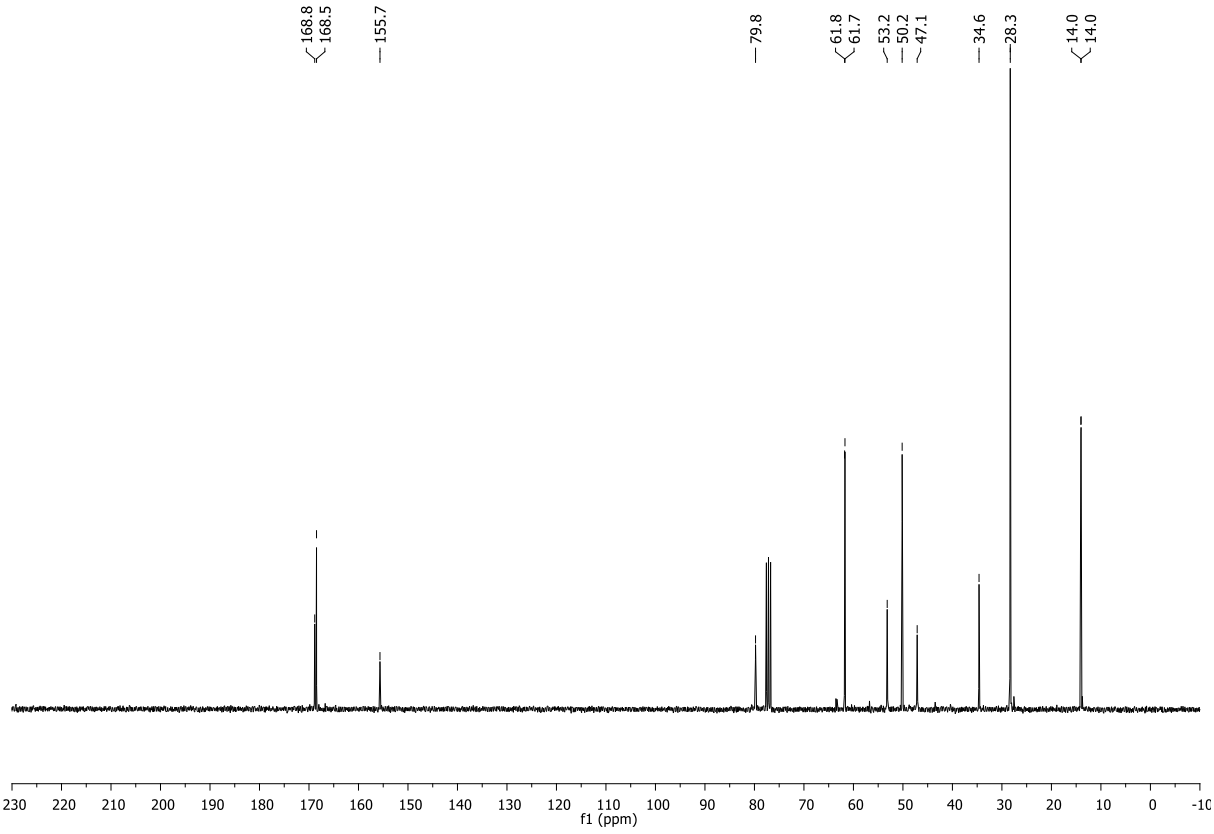
[Cu(dpp)(binc*)]BF_4 (**6e-BF_4**)



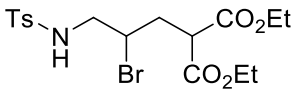
diethyl 2-(2-bromo-3-(tert-butoxycarbonylamino)propyl)malonate (**9**)

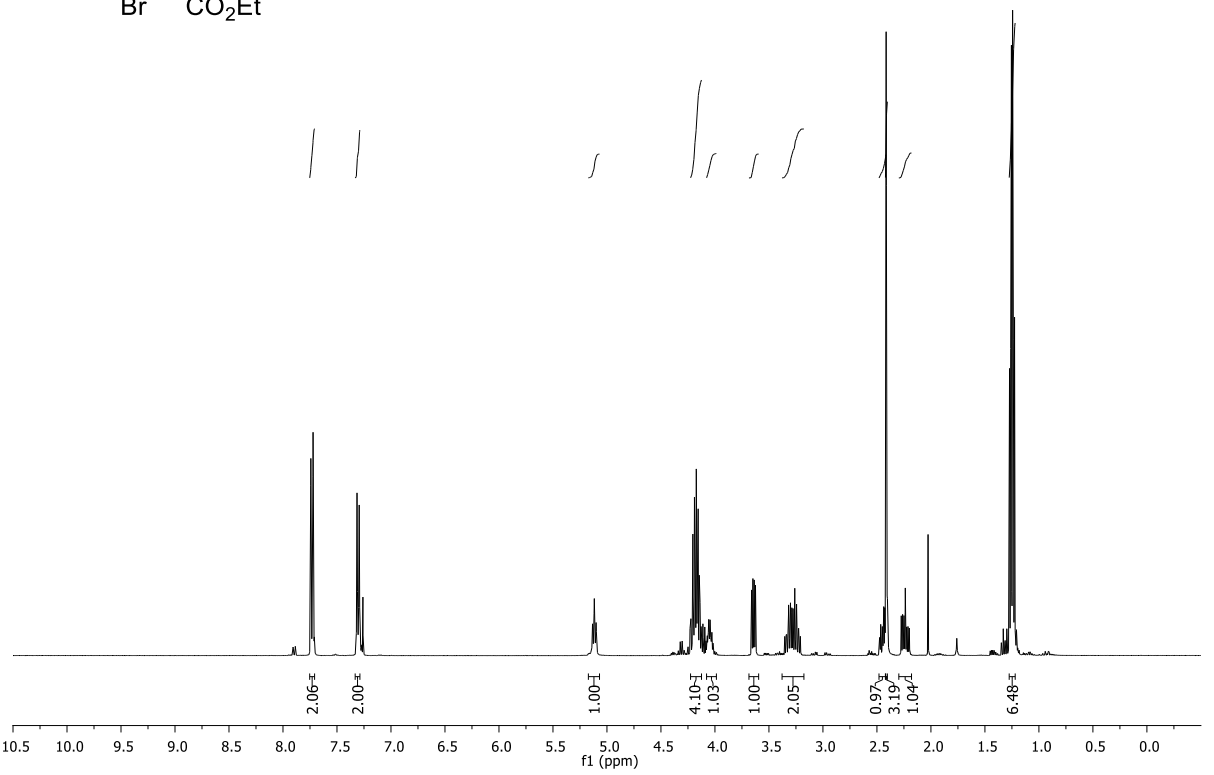


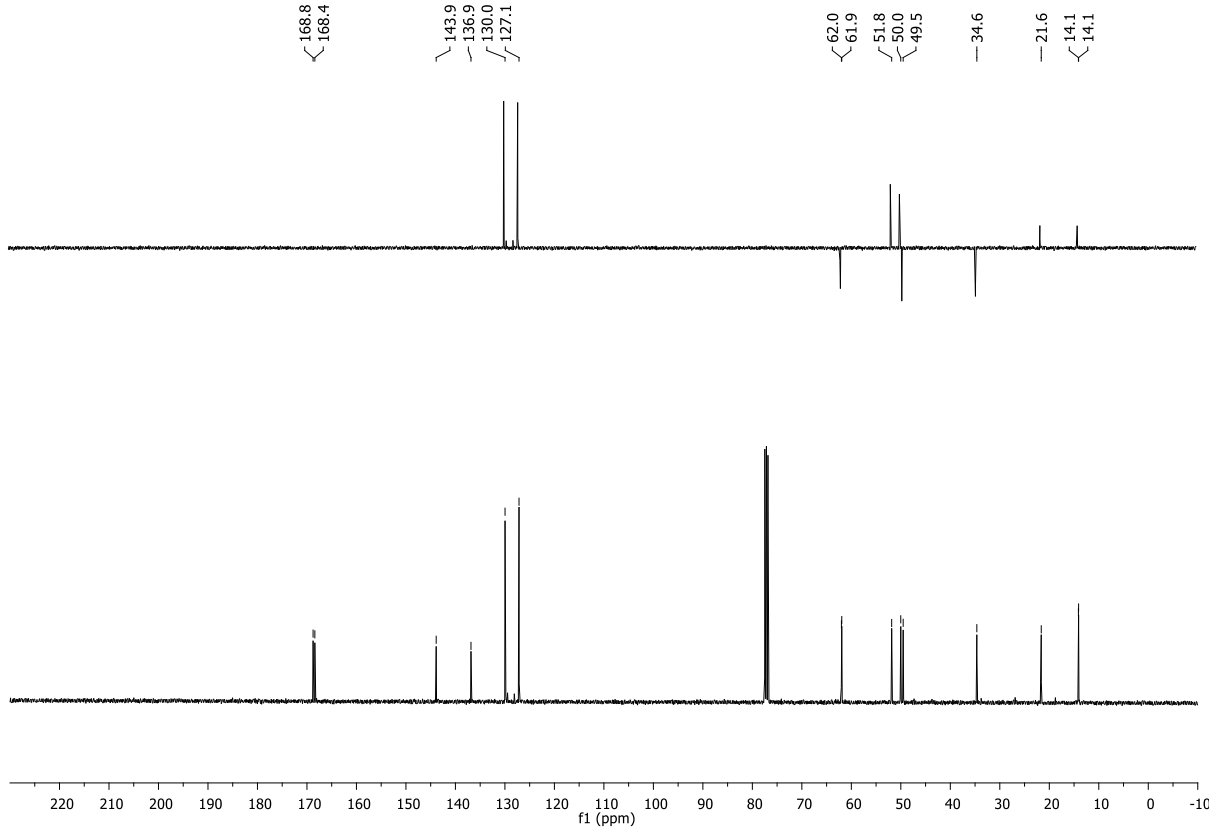




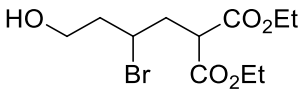
diethyl 2-(2-bromo-3-(4-methylphenylsulfonamido)propyl)malonate (**11**)

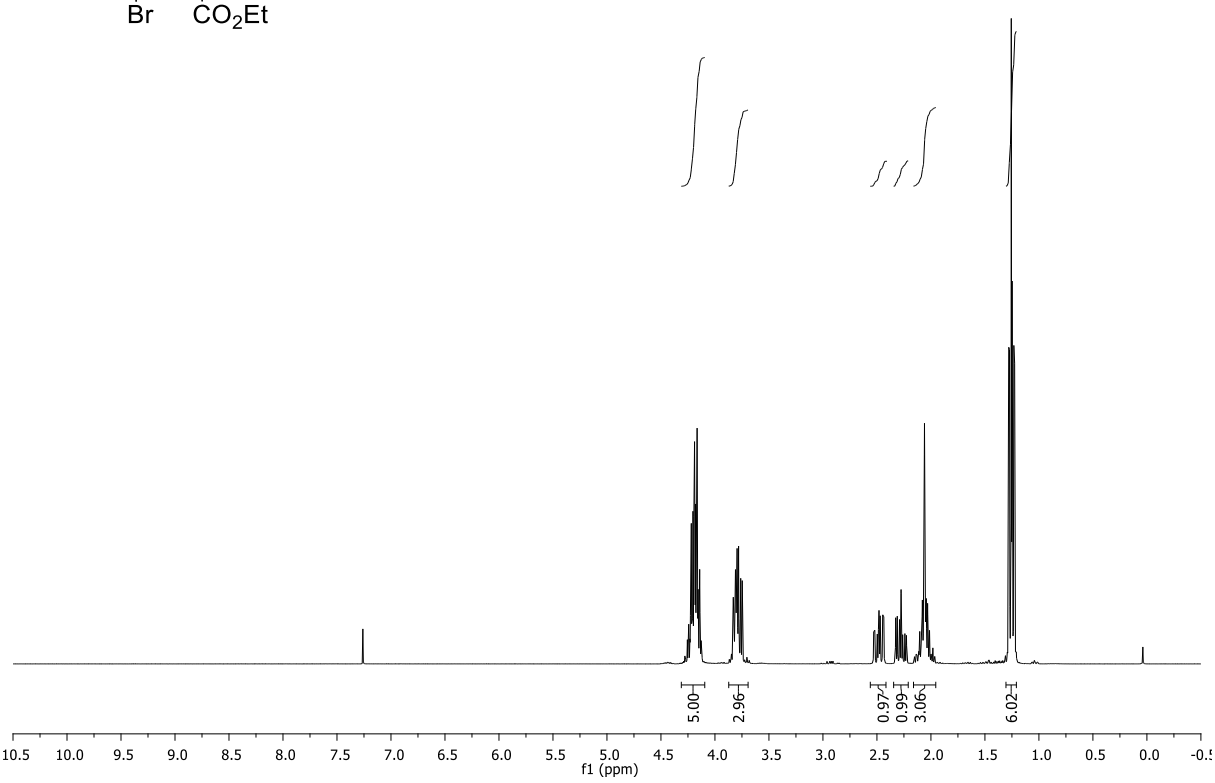


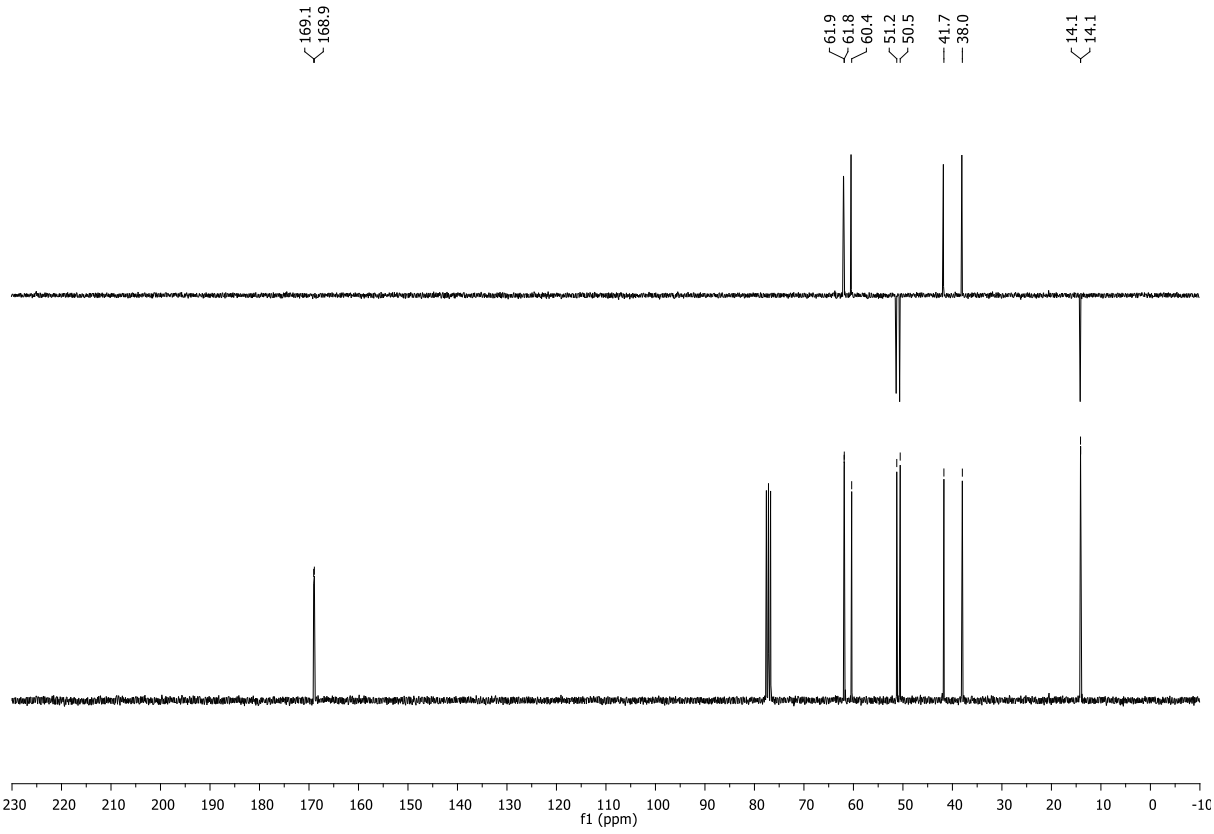




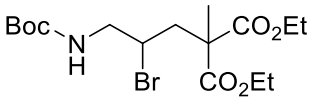
diethyl 2-(2-bromo-4-hydroxybutyl)malonate (**12**)

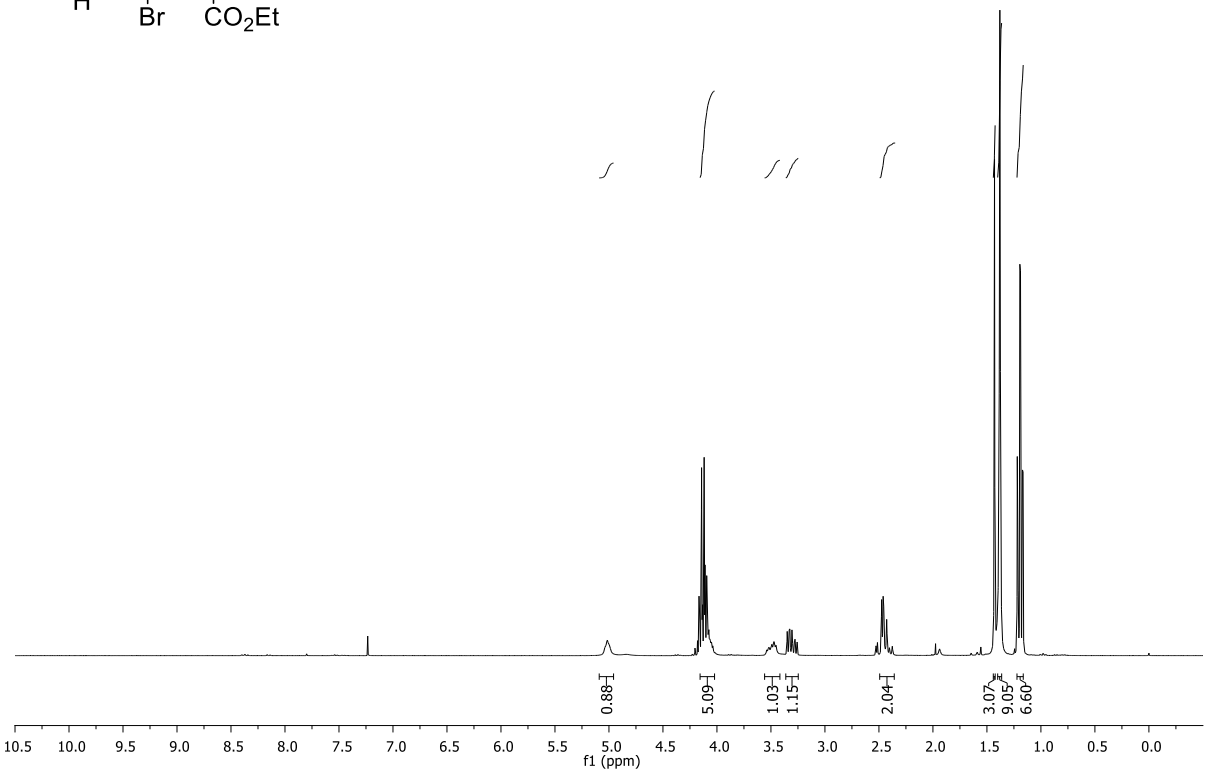


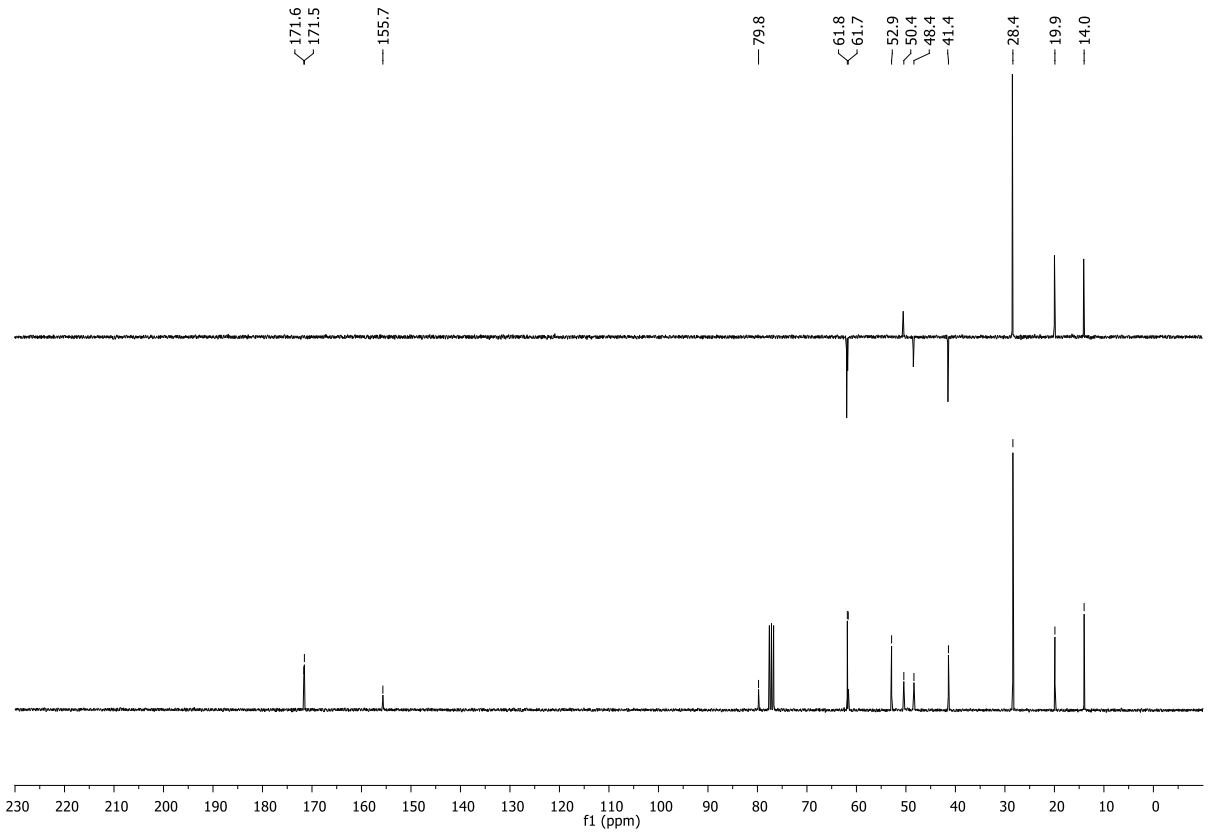




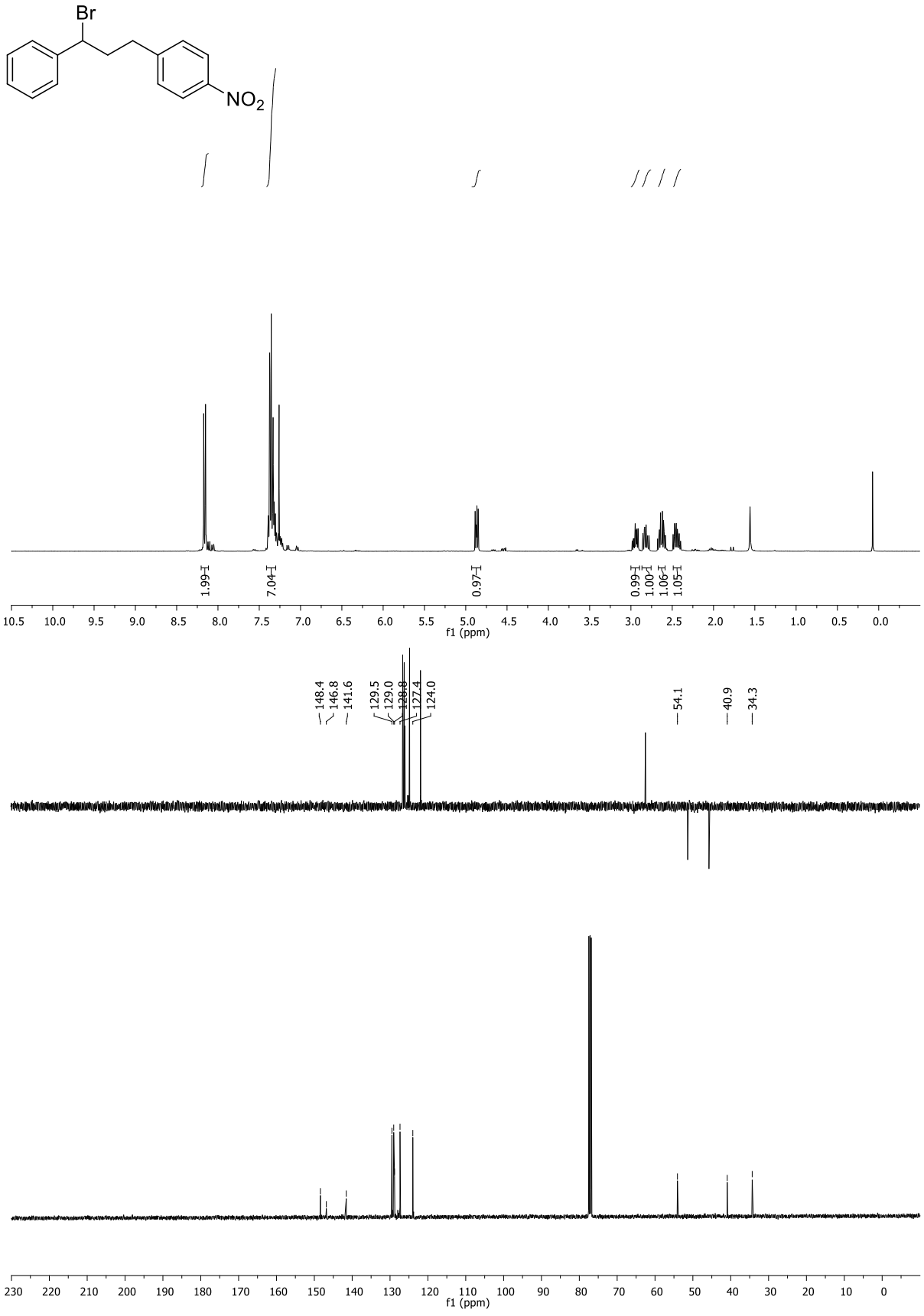
diethyl 2-(2-bromo-3-(tert-butoxycarbonylamino)propyl)-2-methylmalonate (**13**)



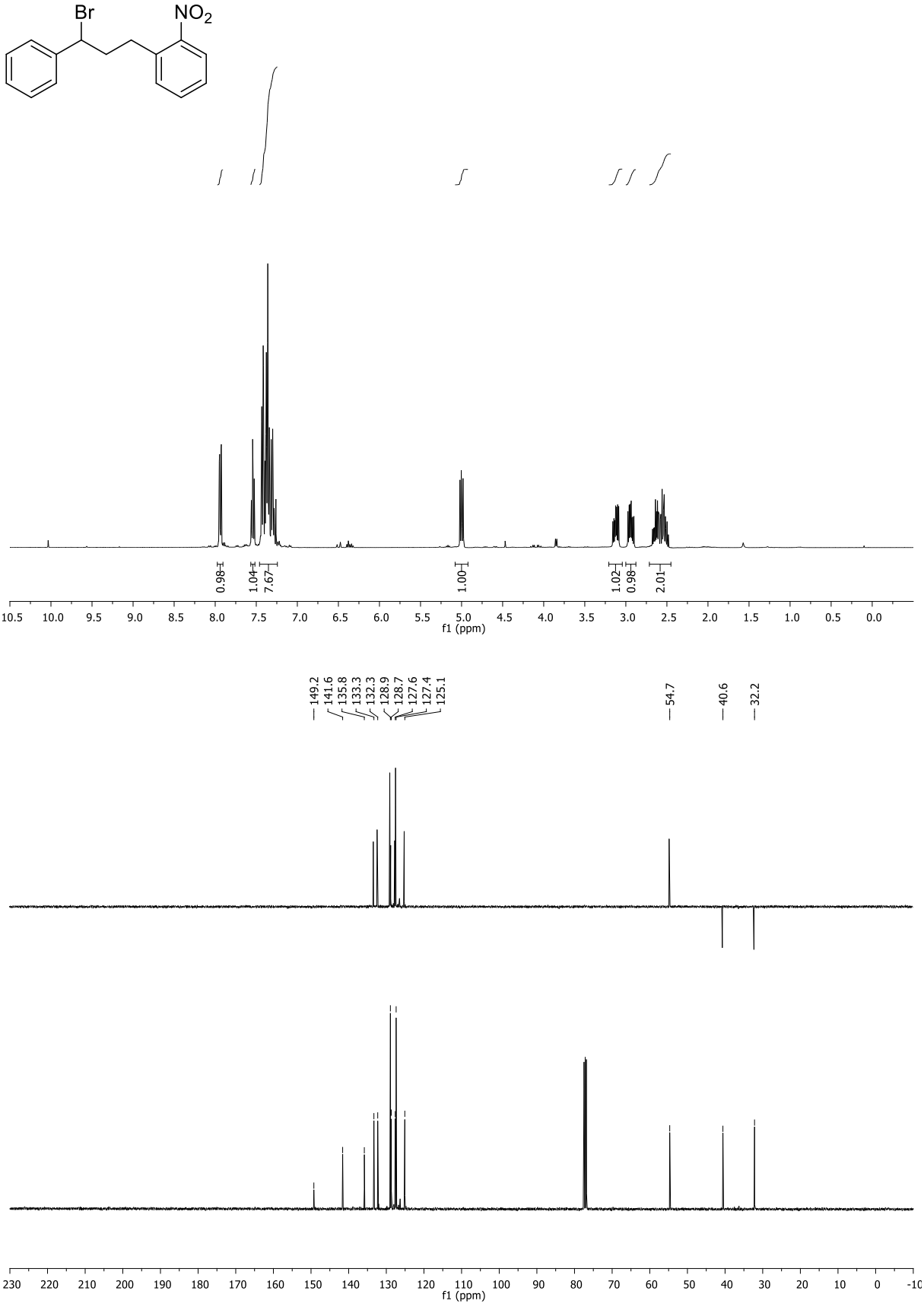




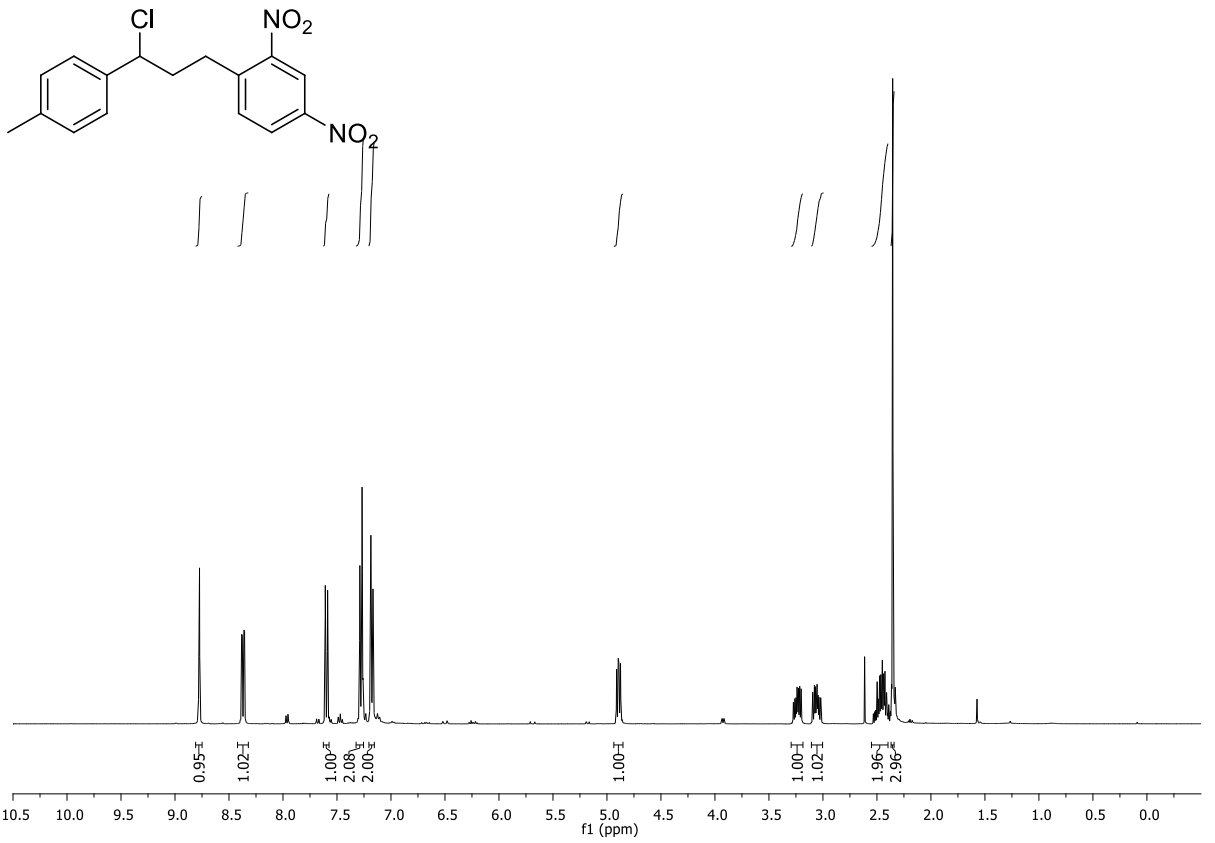
1-(3-bromo-3-phenylpropyl)-4-nitrobenzene (**14**)

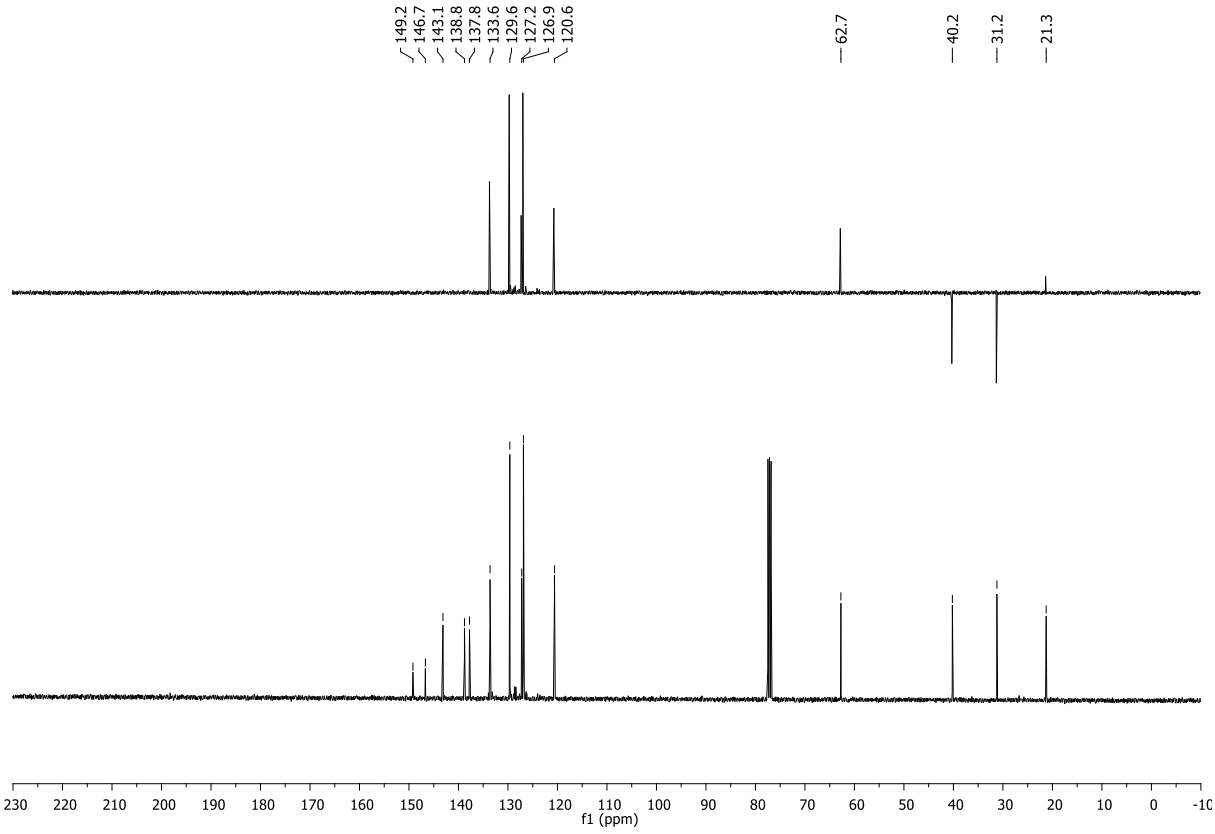


1-(3-bromo-3-phenylpropyl)-2-nitrobenzene (**15**)

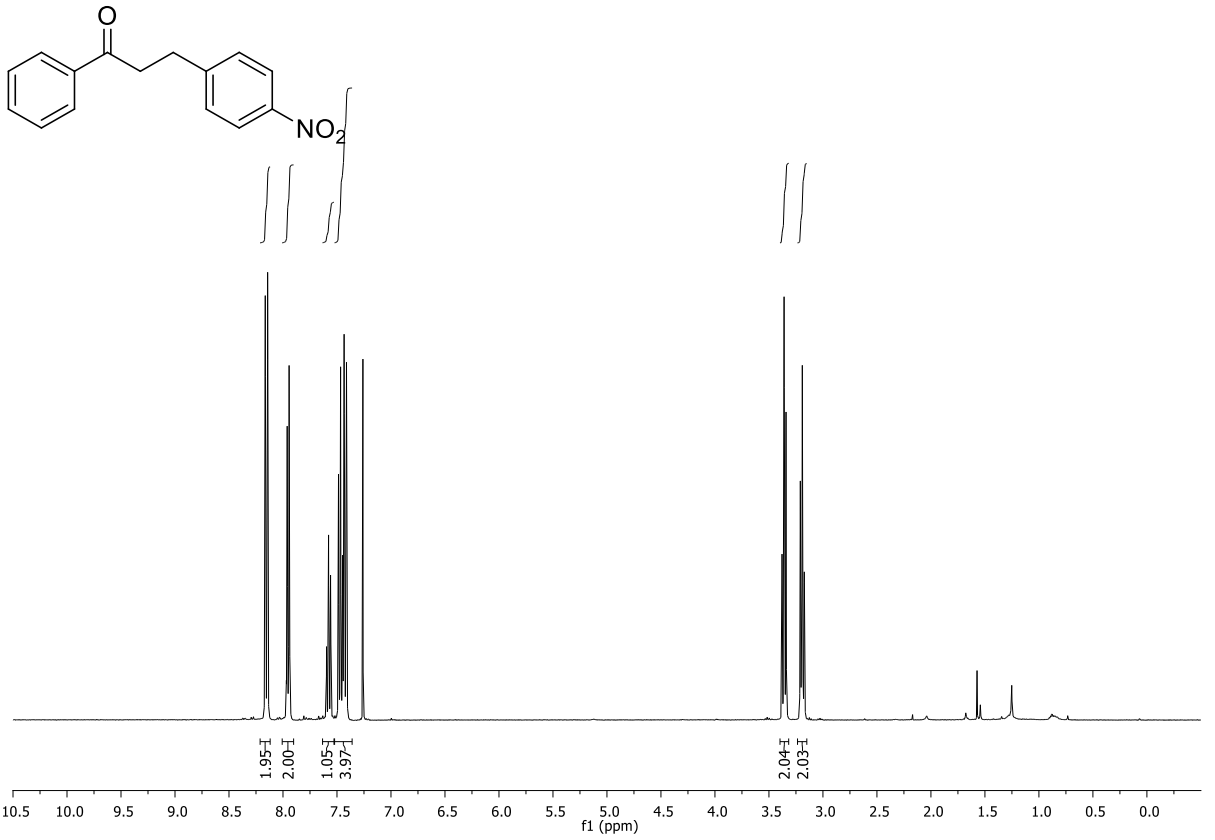


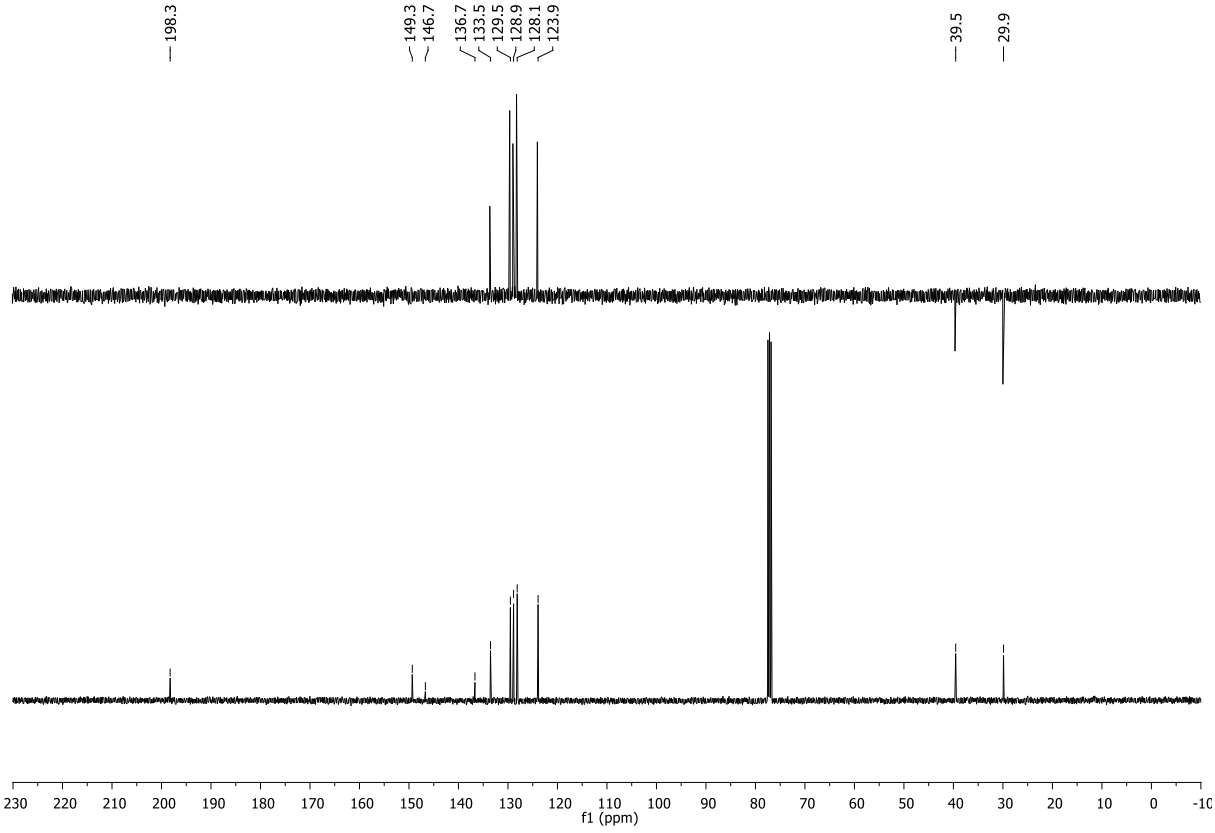
1-(3-chloro-3-p-tolylpropyl)-2,4-dinitrobenzene (**16**)



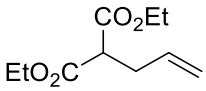


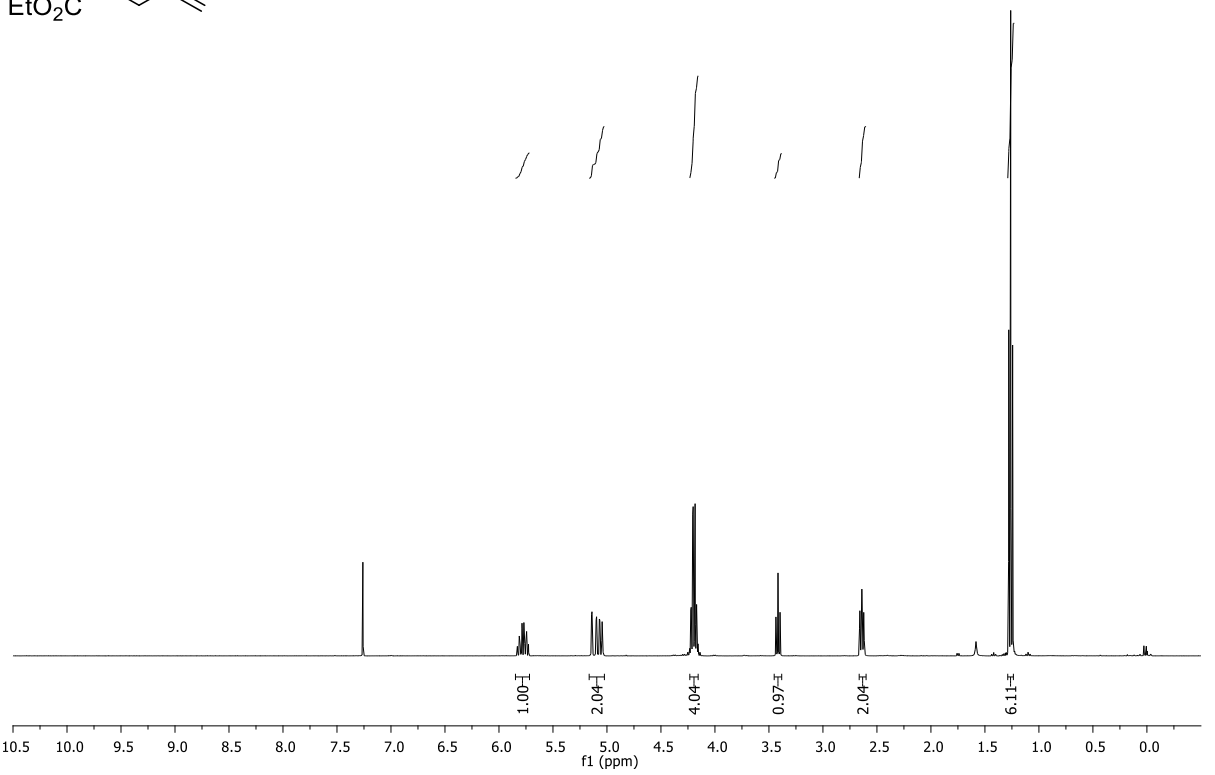
3-(4-nitrophenyl)-1-phenylpropan-1-one (**17**)

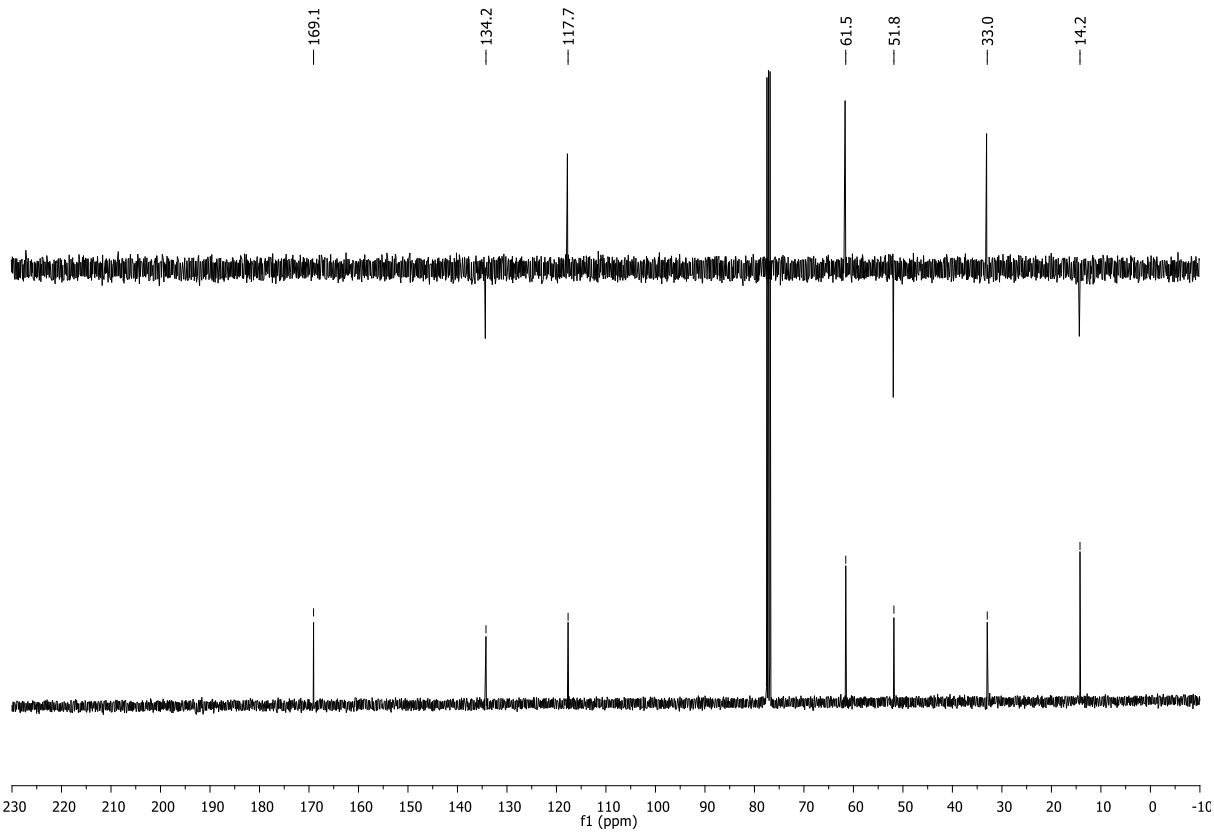




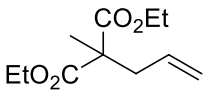
diethyl 2-allylmalonate (**19**)

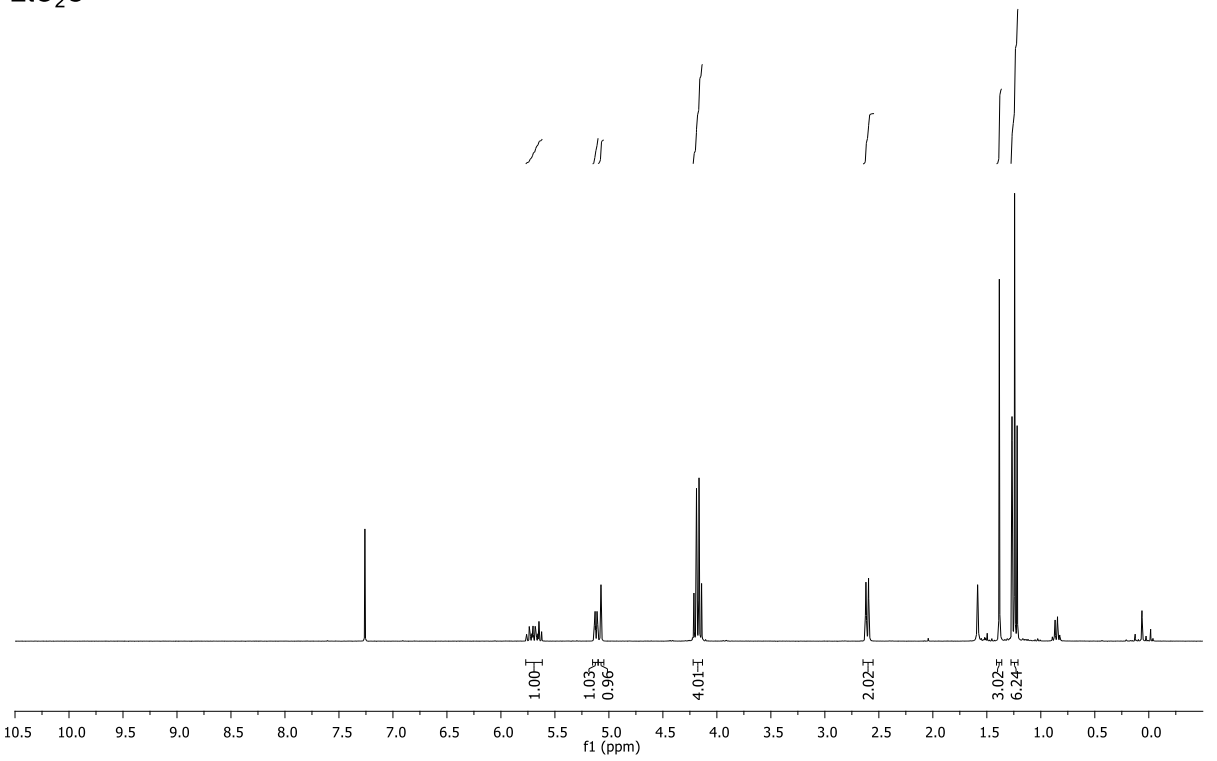


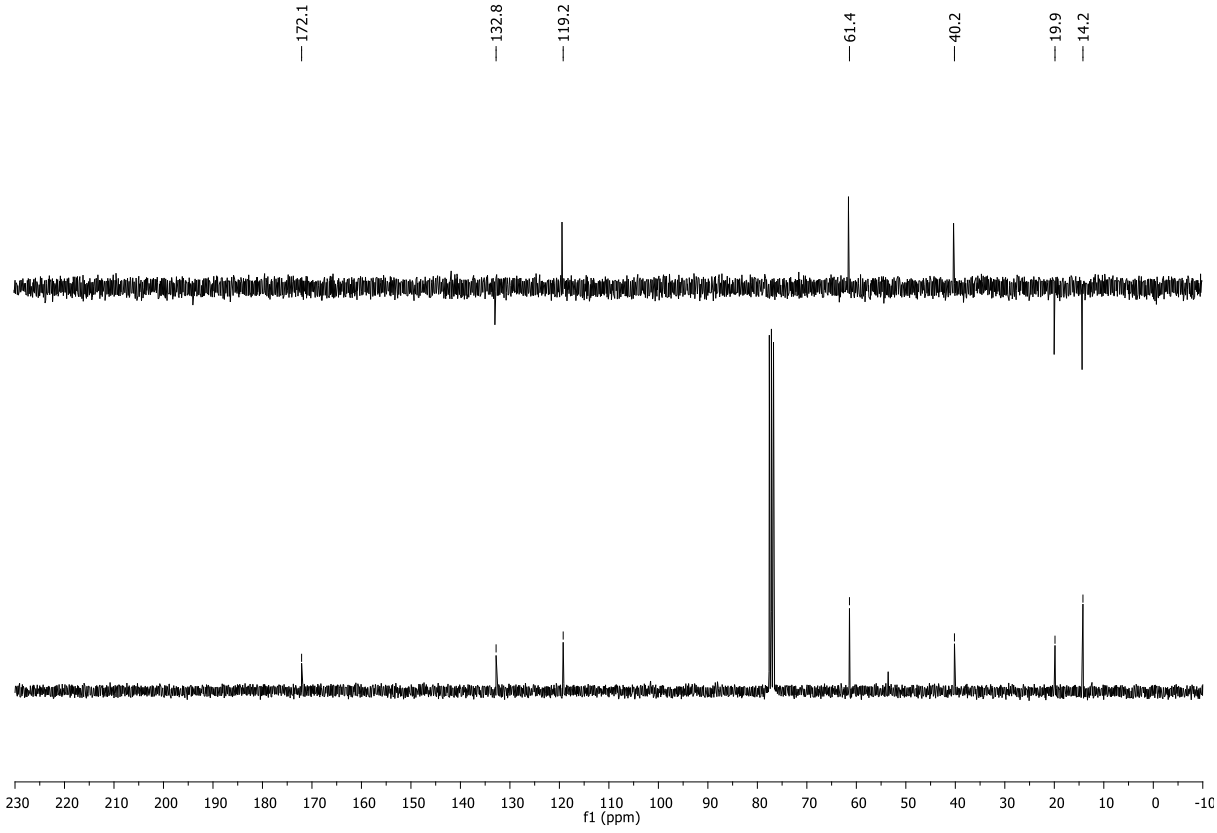




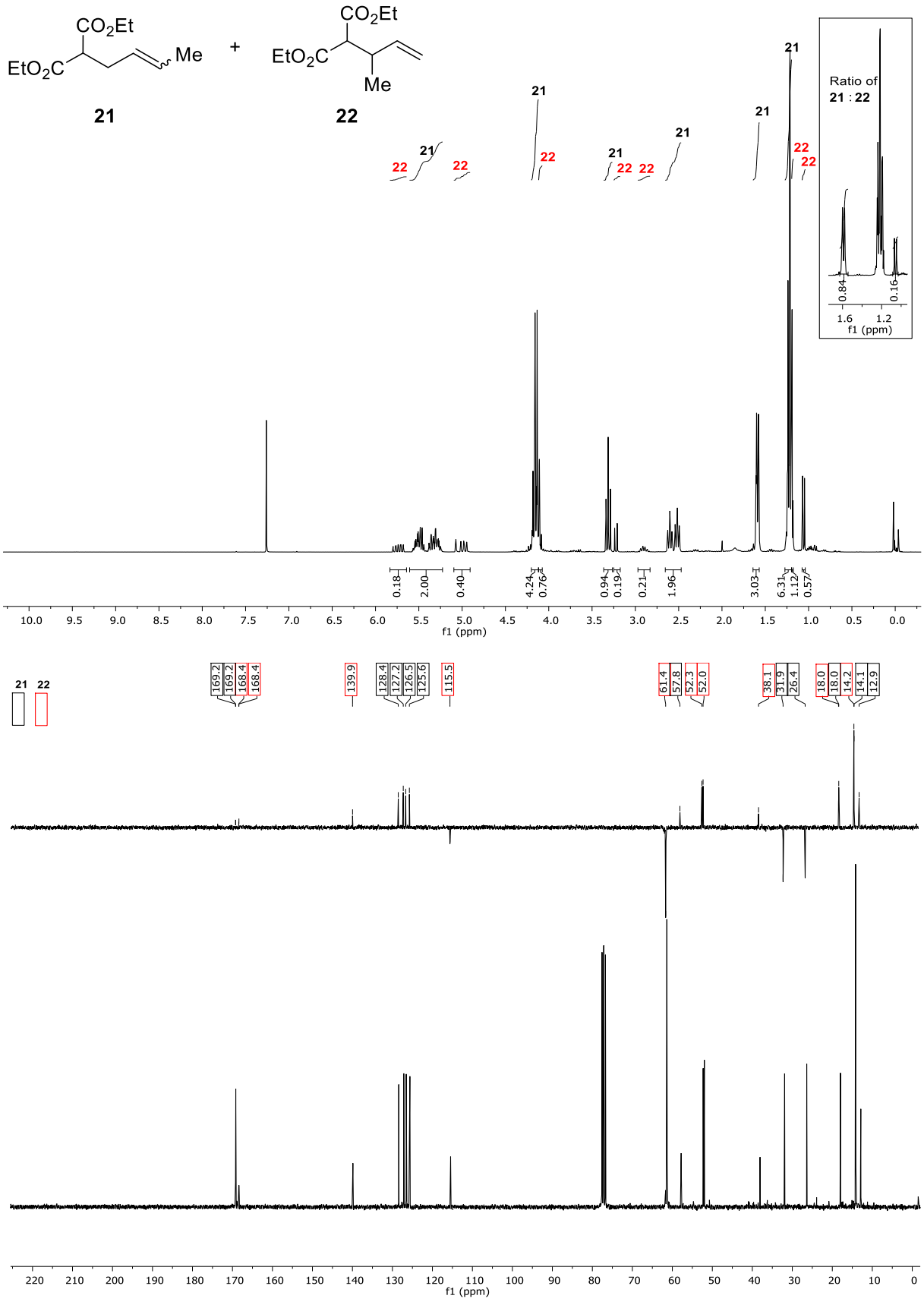
diethyl 2-allyl-2-methylmalonate (**20**)



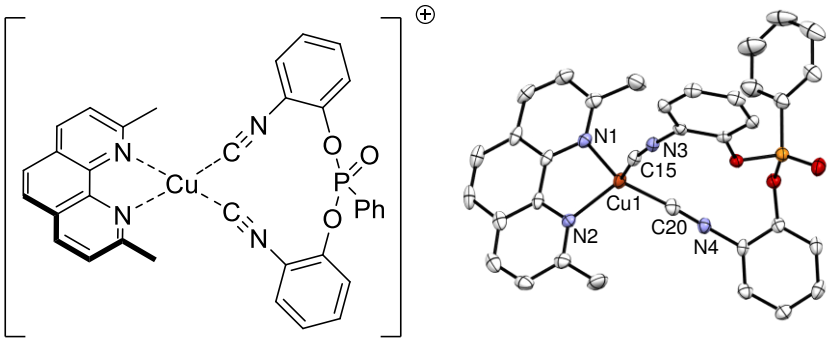




diethyl 2-(but-2-en-1-yl)malonate (**21**) and diethyl 2-(but-3-en-2-yl)malonate (**22**)

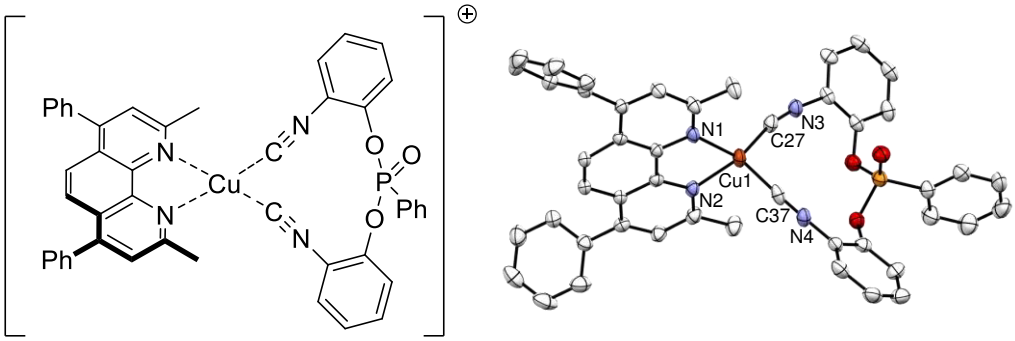


3.3 Solid-State Structures



$[Cu(dmp)(binc)]^+$ (**6b**)

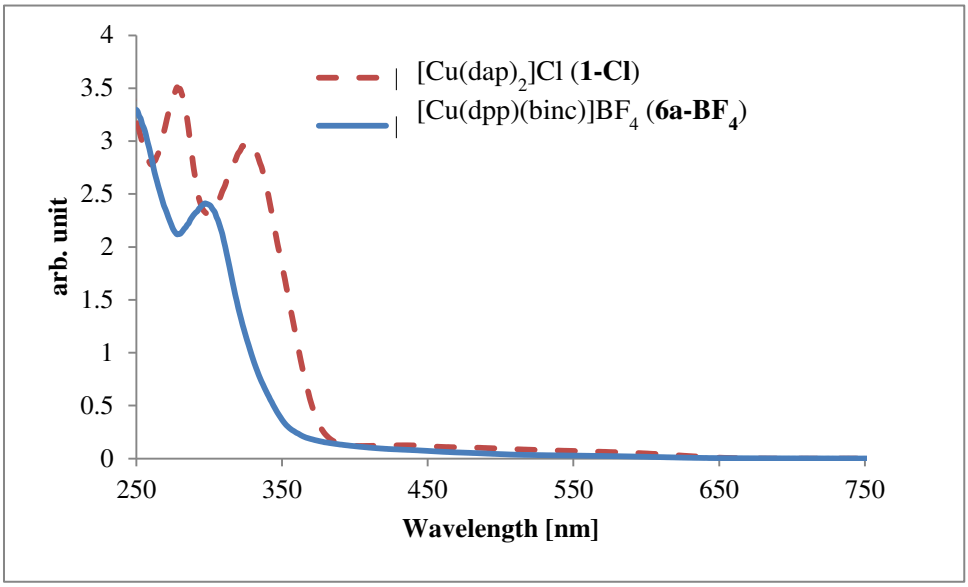
CCDC-Code	1400153
Formula	C34H25BCuF4N4O3P
Dcalc./ g cm-3	1.547
•/mm-1	0.827
Formula Weight	718.90
Colour	colourless
Shape	plate
Max Size/mm	0.51
Mid Size/mm	0.34
Min Size/mm	0.14
T/K	123(1)
Crystal System	monoclinic
Space Group	P21/n
a/Å	12.5021(3)
b/Å	13.6073(3)
c/Å	19.1227(4)
•/°	90
•/°	108.373(2)
•/°	90
V/Å3	3087.32(12)
Z	4
Z'	1
•min/°	3.263
•max/°	26.787
Measured Refl.	10587
Independent Refl.	5822
Reflections Used	5065
Rint	0.0181
Parameters	471
Restraints	0
Largest Peak	0.932
Deepest Hole	-0.424
GooF	1.060
wR2 (all data)	0.0894
wR2	0.0852
R1 (all data)	0.0437
R1	0.0360

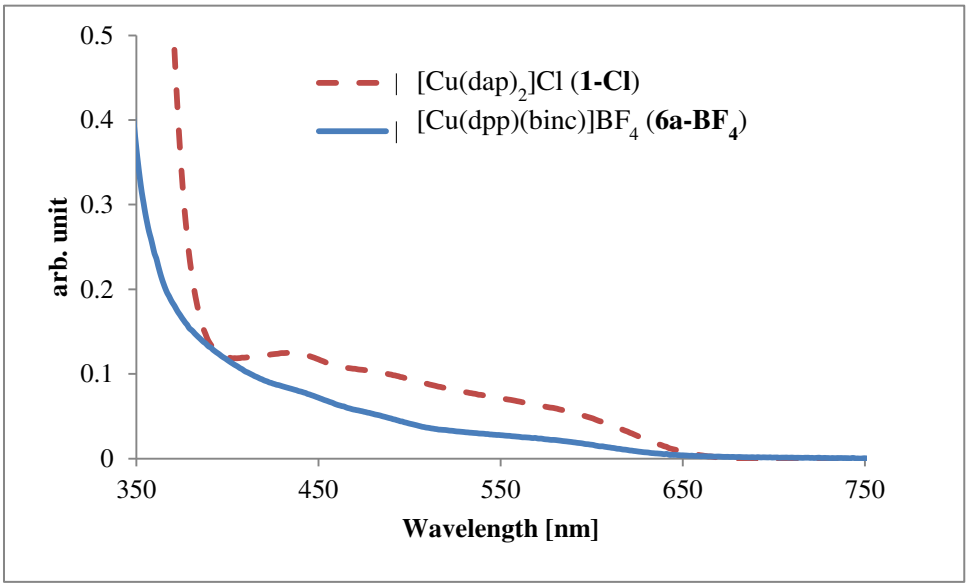


[Cu(dpdmp)(binc)]$^{+}$ (**6c**)

CCDC-Code	1400154
Formula	C47H35BCl2CuF4N4O3P
Dcalc./ g cm-3	1.485
•/mm-1	2.779
Formula Weight	956.01
Colour	colourless
Shape	stick
Max Size/mm	0.94
Mid Size/mm	0.13
Min Size/mm	0.04
T/K	122.99(16)
Crystal System	orthorhombic
Space Group	Pbcn
a/Å	30.0446(6)
b/Å	11.56203(18)
c/Å	24.6258(4)
•/°	90
•/°	90
•/°	90
V/Å3	8554.4(3)
Z	8
Z'	1
•min/°	3.880
•max/°	63.579
Measured Refl.	23903
Independent Refl.	6670
Reflections Used	5457
Rint	0.0428
Parameters	596
Restraints	0
Largest Peak	0.464
Deepest Hole	-0.455
GooF	1.034
wR2 (all data)	0.1180
wR2	0.1099
R1 (all data)	0.0597
R1	0.0461

3.4 UV-Spectra of 1-Cl and 6a-BF_4

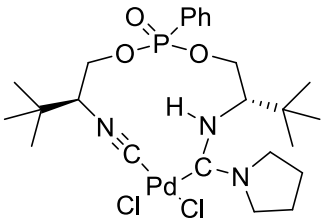




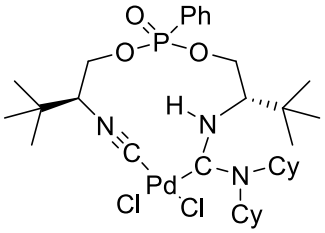
4. Chapter D: Palladium-Isonitriles

4.1 Compound Characterization

General procedure for the preparation of 5a-5c: Stoichiometric addition of amine (1.0 or 2.0 equiv.) to a stirred solution of palladium(II)-bisisonitrile complex **4** (0.5 mmol, 1.0 equiv.) in 50 ml DCM, furnished the desired complex by evaporation of the solvent as yellow solid. Crystals, suitable for x-ray analysis were obtained by vapor diffusion of Et_2O in a DCM solution of the complex.

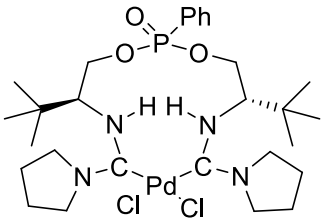


5a: 1H NMR (300 MHz, CD_3CN) δ 7.76 – 7.63 (m, 3H), 7.59 – 7.49 (m, 2H), 5.46 (d, J = 10.1 Hz, 1H), 4.71 (td, J = 10.5, 3.2 Hz, 1H), 4.64 (dd, J = 22.1, 11.4 Hz, 1H), 4.45 – 4.38 (m, 1H), 4.36 (dd, J = 9.0, 5.2 Hz, 1H), 4.27 – 4.11 (m, 2H), 3.92 (dd, J = 10.4, 2.7 Hz, 1H), 3.74 (td, J = 10.5, 3.9 Hz, 1H), 3.20 – 3.08 (m, 1H), 3.03 – 2.86 (m, 1H), 2.11 – 1.96 (m, 4H), 1.13 (s, 9H), 1.02 (s, 9H). 13C NMR (75 MHz, CD_3CN) δ 180.8, 134.1, 133.1, 129.7, 129.5, 69.8, 69.2, 66.2, 64.6, 56.7, 49.5, 34.9, 34.4, 28.1, 26.2, 25.9, 25.6 (isonitrile carbon not detected). IR (neat): 2963, 2876, 2228, 1567, 1451, 1373, 1242, 1131, 996, 862, 751, 695 cm-1. ESI-MS, m/z: $[M\text{-}2Cl^-+HCOO^-]^+$ 598.17.



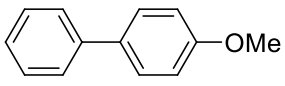
5b: 1H NMR (600 MHz, $CDCl_3$) δ 7.73 (dd, J = 13.6, 7.5 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.48 (td, J = 7.5, 4.7 Hz, 2H), 5.74 (t, J = 11.7 Hz, 1H), 5.57 (d, J = 9.8 Hz, 1H), 5.08 – 5.01 (m, 1H), 4.74 – 4.62 (m, 2H), 4.22 – 4.15 (m, 1H), 3.91 – 3.84 (m, 1H), 3.77 (d, J = 9.9 Hz, 1H), 3.33 (t, J = 11.6 Hz, 1H), 2.30 (d, J = 10.6 Hz, 1H), 1.92 – 1.46 (m, 10H), 1.39 – 1.22 (m, 5H), 1.16 (s, 9H),

1.19 – 1.04 (m, 2H), 1.08 (s, 9H), 0.93 – 0.79 (m, 2H). 13C NMR (151 MHz, $CDCl_3$) δ 182.9, 133.3, 131.3, 128.8, 125.8, 70.2, 68.4, 66.7, 65.1, 64.4, 57.4, 34.4, 34.1, 31.6, 31.0, 30.6, 29.7, 27.6, 26.3, 25.6, 25.2 (isonitrile carbon not detected). IR (neat): 2967, 2934, 2860, 2235, 1552, 1467, 1439, 1406, 1373, 1347, 1250, 1131, 1095, 1037, 1019, 995, 825, 752, 735, 695 cm-1. ESI-MS, m/z: $[M–2Cl+HCOO^-]^+$ 708.28.



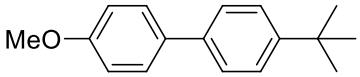
5c: 1H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 3H), 7.54 – 7.49 (m, 2H), 5.50 (d, J = 10.2 Hz, 1H), 5.22 (d, J = 9.6 Hz, 1H), 5.14 – 5.10 (m, 1H), 5.01 – 4.96 (m, 1H), 4.91 – 4.86 (m, 1H), 4.67 – 4.61 (m, 1H), 4.42 – 4.37 (m, 1H), 4.30 (dd, J = 22.2, 11.1 Hz, 1H), 4.19 – 4.12 (m, 2H), 4.09 – 3.98 (m, 2H), 3.96 – 3.91 (m, 1H), 3.74 – 3.68 (m, 1H), 3.44 – 3.36 (m, 2H), 3.26 (dd, J = 15.8, 8.1 Hz, 1H), 2.19 – 2.00 (m, 5H), 1.95 – 1.76 (m, 3H), 1.11 (s, 9H), 1.06 (s, 9H). 13C NMR (151 MHz, $CDCl_3$) δ 187.3, 186.6, 133.4, 130.9, 129.2, 125.2, 66.4, 66.4, 65.3, 63.1, 57.3, 56.9, 47.4, 46.8, 34.5, 33.9, 29.9, 27.4, 27.2, 25.4, 25.0, 24.9. IR (neat): 2955, 2879, 1554, 1439, 1375, 1316, 1241, 1129, 1089, 1050, 1025, 989, 912, 841, 805, 749, 694, 662 cm-1. ESI-MS, m/z: $[M–2Cl-H]^+$ 623.23.

General procedure for the Suzuki-Miyaura cross coupling: To a stirred solution of bromo benzene (1.0 mmol, 1.0 equiv.), boronic acid (1.2 mmol, 1.2 equiv.) and catalyst (1 mol%) in 2 ml of EtOH, KO^tBu (1.0 mmol, 1.2 equiv.) was added at room temperature. The reaction mixture was stirred for 20 hours, extracted with DCM (3x 10 ml) and dried over $MgSO_4$. The biphenyls were obtained by column chromatography as white solids.



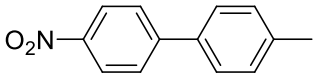
4-Methoxybiphenyl (table 2, entry 4)

According to the general procedure, bromo benzene (105 µl, 1.0 mmol, 1.0 equiv.), 4-methoxy phenylboronic acid (182 mg, 1.2 mmol, 1.2 equiv.), KO^{t}Bu (112 mg, 1.0 mmol, 1.0 equiv.) and **5a** (1 mol%) afforded 4-methoxybiphenyl (138 mg, 0.75 mmol, 75 %) as white solid. NMR- data are in agreement with those reported in literature.[10] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 4H), 7.47 – 7.40 (m, 2H), 7.36 – 7.29 (m, 1H), 7.04 – 6.97 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 139.8, 132.7, 127.7, 127.1, 125.7, 125.6, 113.1, 54.3.



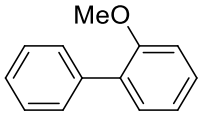
4-*tert*-Butyl-4'-methoxybiphenyl (table 2, entry 5)

According to the general procedure, 4-methoxybromo benzene (120 µl, 1.0 mmol, 1.0 equiv.), 4-*tert*-butyl phenylboronic acid (214 mg, 1.2 mmol, 1.2 equiv.), KO^{t}Bu (112 mg, 1.0 mmol, 1.0 equiv.) and **5a** (1 mol%) afforded 4- *tert*-butyl-4'-methoxybiphenyl (200 mg, 0.83 mmol, 83 %) as white solid. NMR- data are in agreement with those reported in literature.[11] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.38 (m, 5H), 7.02 – 6.91 (m, 2H), 3.85 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 149.6, 137.9, 133.6, 128.0, 126.4, 125.7, 114.1, 55.4.



4-Methyl-4'-nitrobiphenyl (table 2, entry 6)

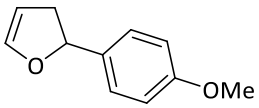
According to the general procedure, 4-nitrobromo benzene (202 mg, 1.0 mmol, 1.0 equiv.), 4-methyl phenylboronic acid (163 mg, 1.2 mmol, 1.2 equiv.), KO^{t}Bu (112 mg, 1.0 mmol, 1.0 equiv.) and **5b** (1 mol%) afforded 4-methyl-4'-nitrobiphenyl (164 mg, 0.77 mmol, 77 %) as off-white solid. NMR- data are in agreement with those reported in literature.[12] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 – 8.25 (m, 2H), 7.76 – 7.69 (m, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6, 146.8, 139.1, 135.9, 129.9, 127.5, 127.3, 124.1, 21.3.



2-Methoxybiphenyl (table 2, entry 7)

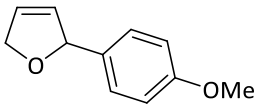
According to the general procedure, bromo benzene (105 µl, 1.0 mmol, 1.0 equiv.), 2-methoxy phenylboronic acid (182 mg, 1.2 mmol, 1.2 equiv.), KO^{t}Bu (112 mg, 1.0 mmol, 1.0 equiv.) and **5b** (1 mol%) afforded 2-methoxy biphenyl (150 mg, 0.81 mmol, 81 %) as off-white solid. NMR- data are in agreement with those reported in literature.[13] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.49 – 7.40 (m, 2H), 7.40 – 7.31 (m, 2H), 7.23 – 7.10 (m, 2H), 6.96 – 6.87 (m, 1H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 142.8, 141.1, 129.8, 128.8, 127.4, 127.2, 119.7, 112.9, 112.7, 55.3.

General procedure for the asymmetric Heck reaction: A pressure-tube filled with DMF (3 ml), KOAc (15 mol%, 75 µmol, 7 mg) and catalyst (10 mol%) was stirred for 30 min. 2,3-Dihydrofuran (4.0 equiv., 2 mmol, 151 µl), 4-methoxy-anisol (1.0 equiv., 0.5 mmol, 117 mg) and *n*Bu_4NBr (2 equiv., 1.0 mmol, 332 mg) was added and the reaction mixture war stirred for 16 h. The mixture was diluted with ethyl acetate, filtered and the washed with water. Products **14** and **15** were obtained by chromatographic purification (hexanes : ethyl acetate = 19:1).



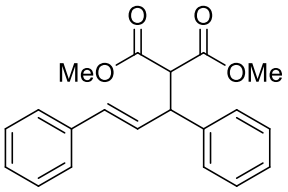
2-(4-methoxyphenyl)-2,3-dihydrofuran (**14**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 6.94 – 6.87 (m, 2H), 6.44 (dd, *J* = 5.1, 2.4 Hz, 1H), 5.48 (dd, *J* = 10.6, 8.5 Hz, 1H), 4.97 (q, *J* = 2.6 Hz, 1H), 3.81 (s, 3H), 3.04 (ddt, *J* = 15.3, 10.6, 2.4 Hz, 1H), 2.62 (ddt, *J* = 15.2, 8.5, 2.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 145.3, 135.2, 127.6, 127.2, 114.0, 99.2, 82.3, 55.4, 37.8.



2-(4-methoxyphenyl)-2,5-dihydrofuran (**15**)

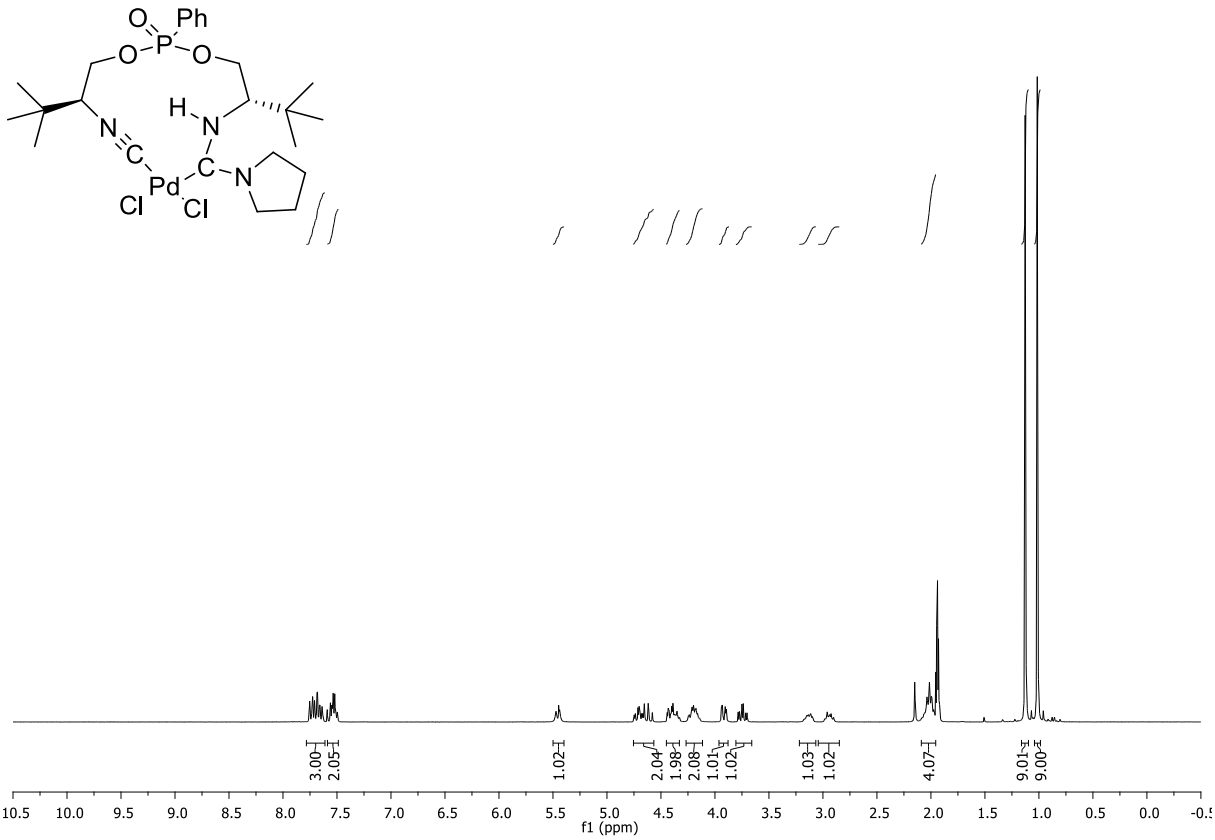
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 6.91 – 6.85 (m, 2H), 6.08 – 6.01 (m, 1H), 5.90 – 5.84 (m, 1H), 5.79 – 5.72 (m, 1H), 4.92 – 4.81 (m, 1H), 4.79 – 4.68 (m, 1H), 3.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 134.2, 130.1, 128.0, 126.8, 114.0, 87.7, 75.7, 55.4.

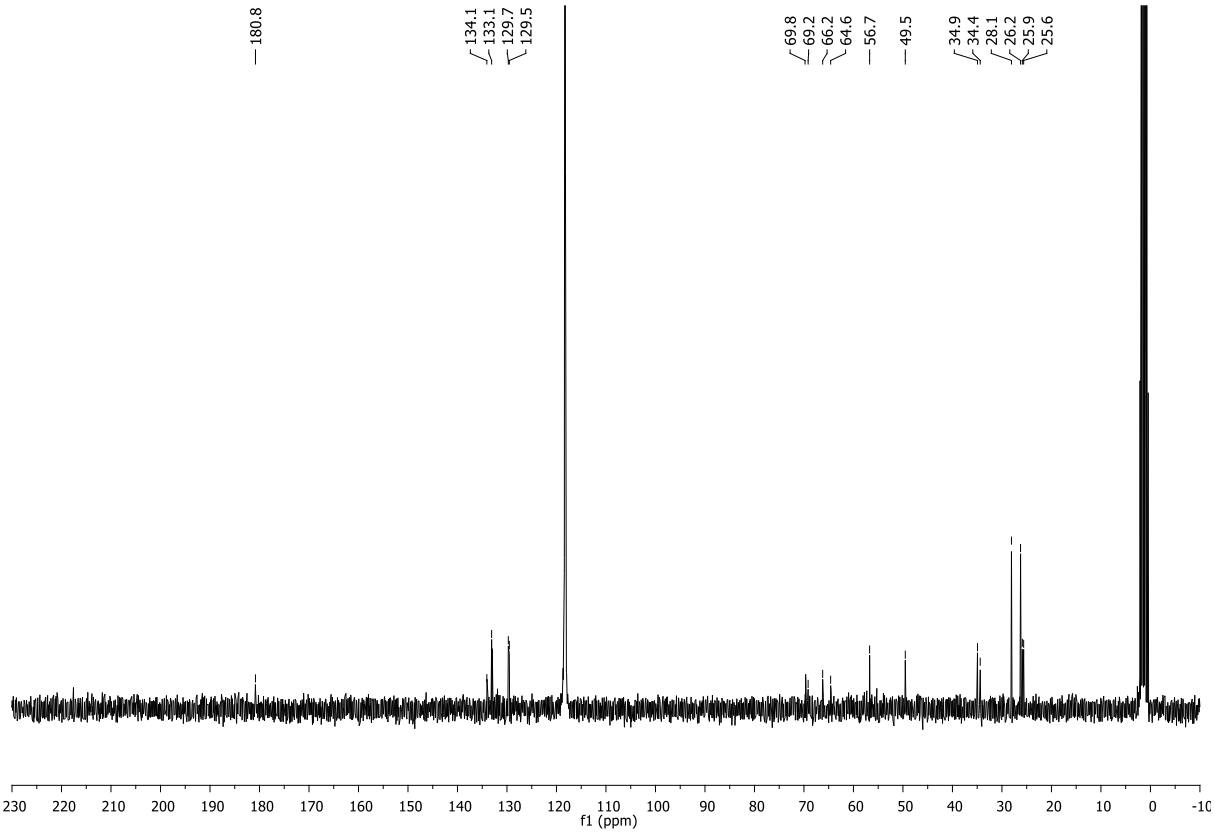


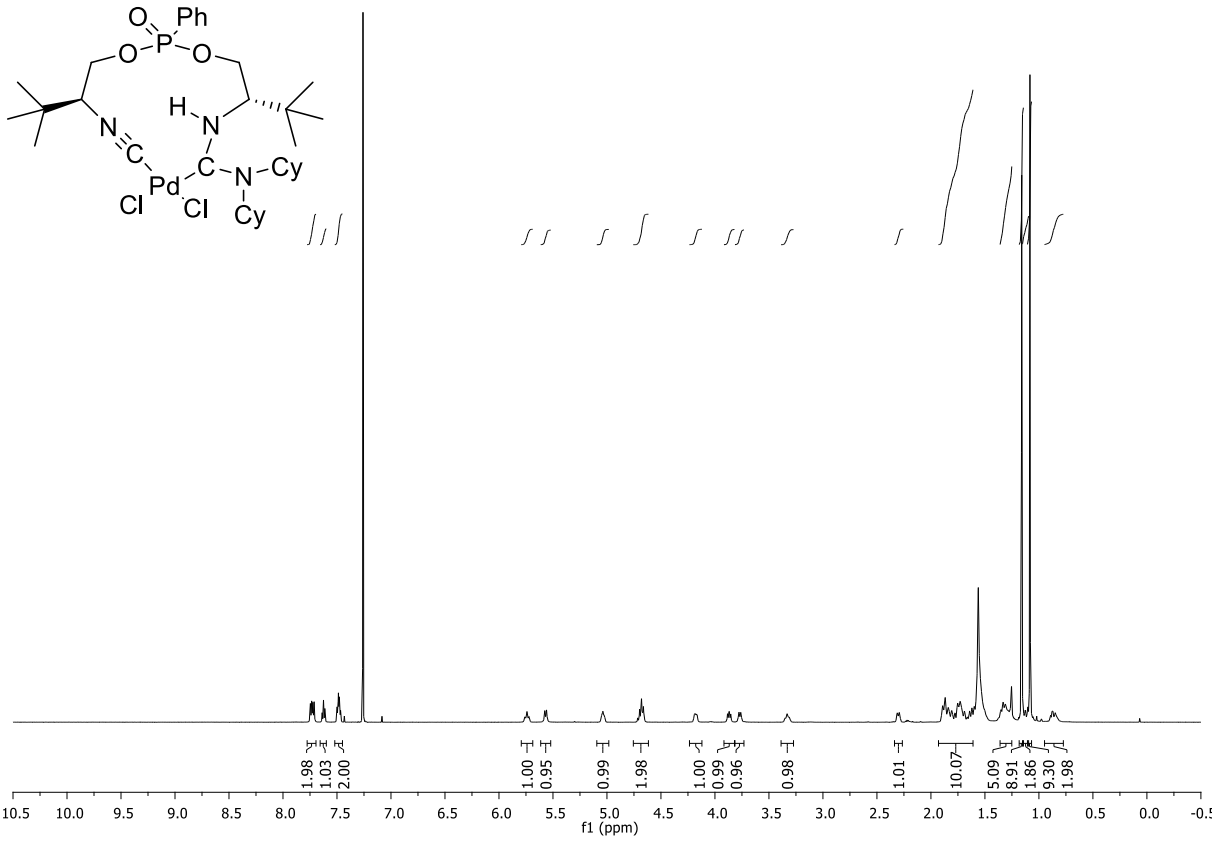
(*E*)-Dimethyl 2-(1,3-diphenylallyl)malonate (**11**) (table 5)

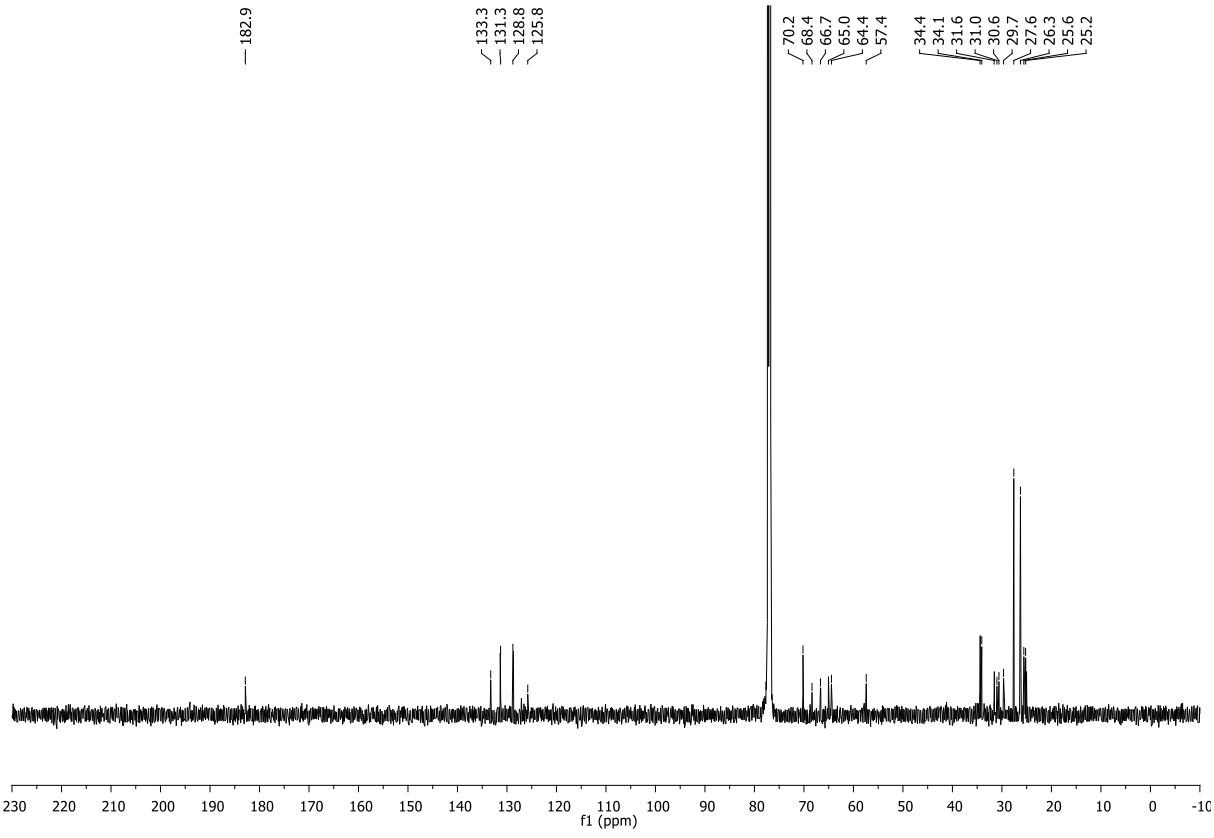
To a stirred solution of *rac*-(*E*)-1,3-diphenyl allylacetate (126 mg, 0.5 mmol, 1.0 equiv.), dimethyl malonate (172 µl, 1.5 mmol, 3.0 equiv.) and catalyst (10 mol%) in 3 ml THF, BSA (370 µL, 1.5 mmol, 3.0 equiv.) and KOAc (10 mg, 0.1 mmol, 20 mol%) was added. The reaction mixture was heated to 60 °C and stirred for the indicated time. After dilution with Et_2O (5 ml), the reaction was quenched with NH_4Cl (sat.) (25 ml), extracted with Et_2O (3x 25 ml), dried over $MgSO_4$. (*E*)-Dimethyl 2-(1,3-diphenylallyl)malonate (**11**) was obtaind by column chromatography as colorless oil. NMR- data are in agreement with those reported in literature.[14] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.16 (m, 10H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.34 (dd, *J* = 15.7, 8.5 Hz, 1H), 4.28 (dd, *J* = 10.9, 8.5 Hz, 1H), 3.97 (d, *J* = 10.9 Hz, 1H), 3.71 (s, 3H), 3.53 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 167.9, 140.3, 136.9, 131.9, 129.2, 128.9, 128.6, 128.0, 127.7, 127.3, 126.5, 57.8, 52.8, 52.6, 49.3. ESI-MS, m/z: [MH^+-$C_5H_8O_4$] 193.10, [MNH_4^+] 342.17, [2M+Na^+] 671.26.

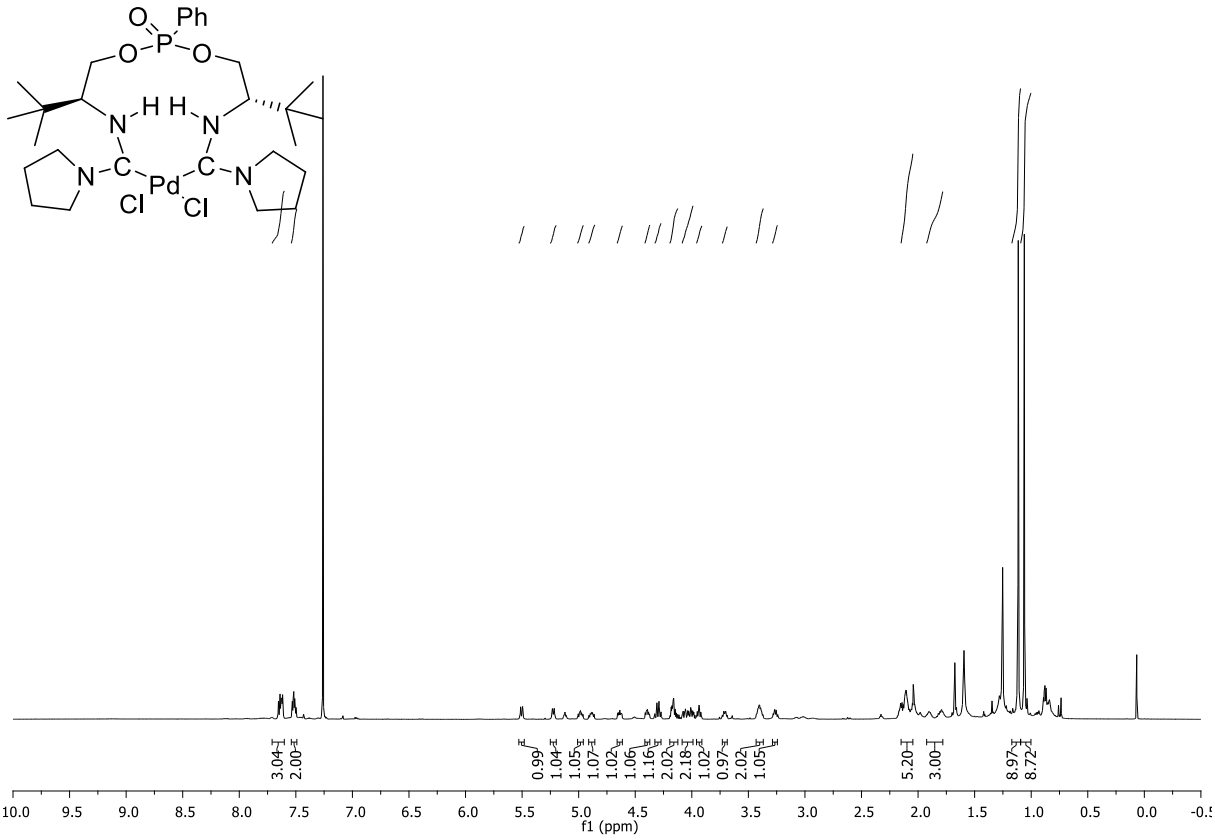
4.2 NMR-Spectra

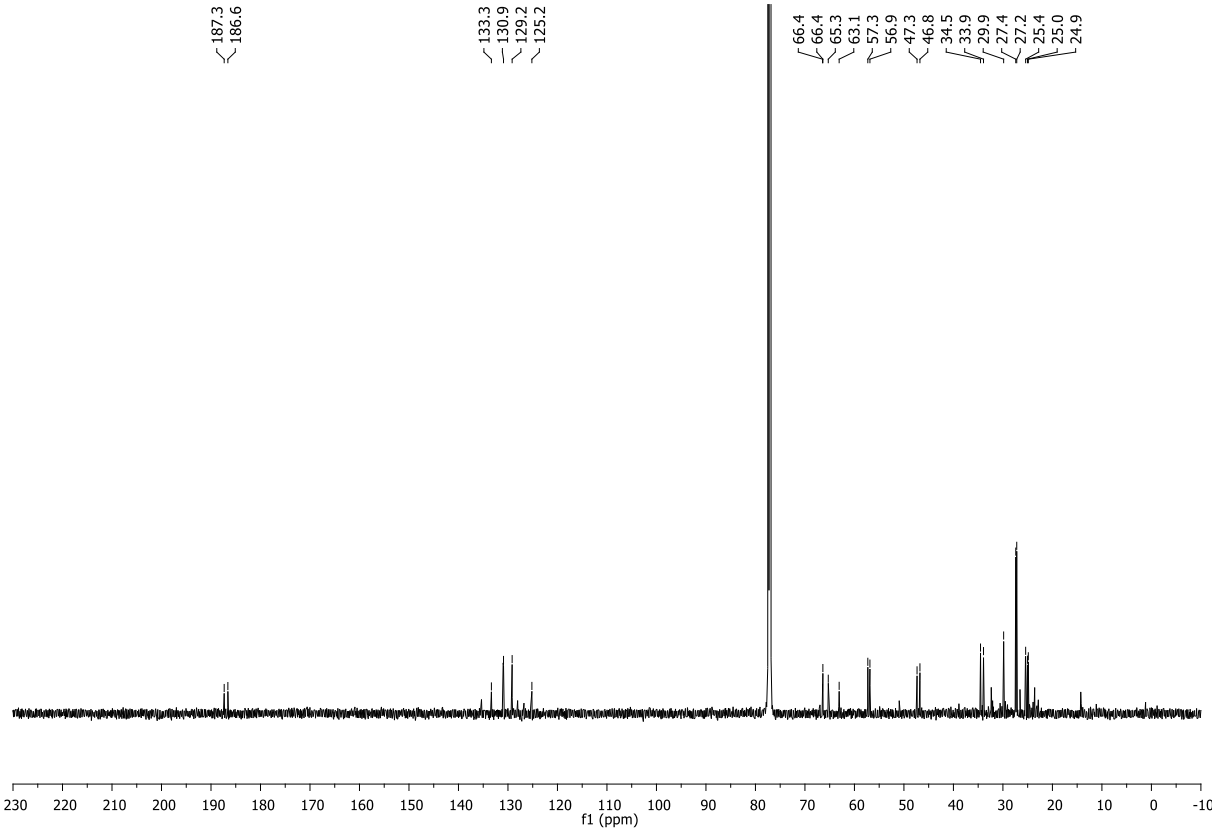


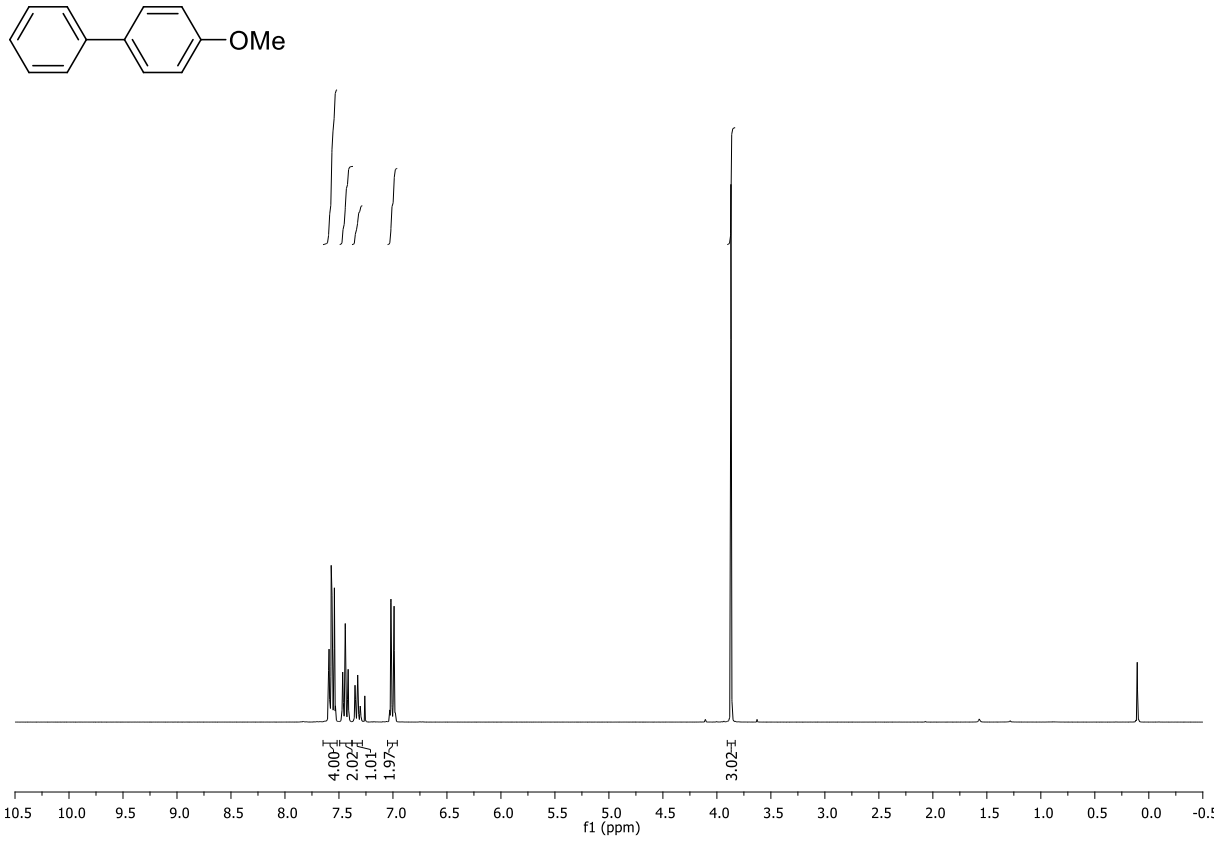


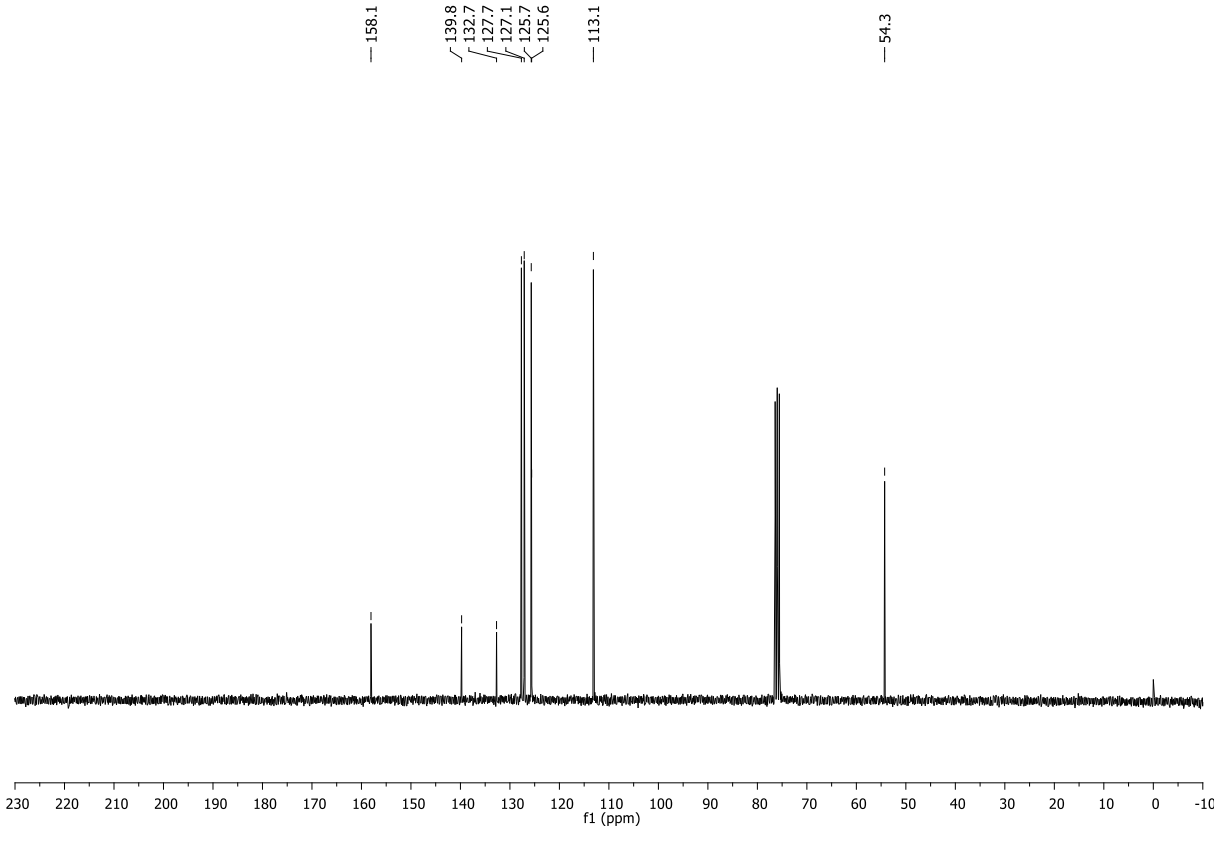

O
Ph
O
P
O
H
N
N
C
Pd
C
N
Cy
Cl
Cl
Cy
1.98
1.03
2.00
1.00
0.95
0.99
1.98
1.00
0.99
0.96
0.98
1.01
10.07
5.09
8.91
1.86
9.30
1.98
f1 (ppm)

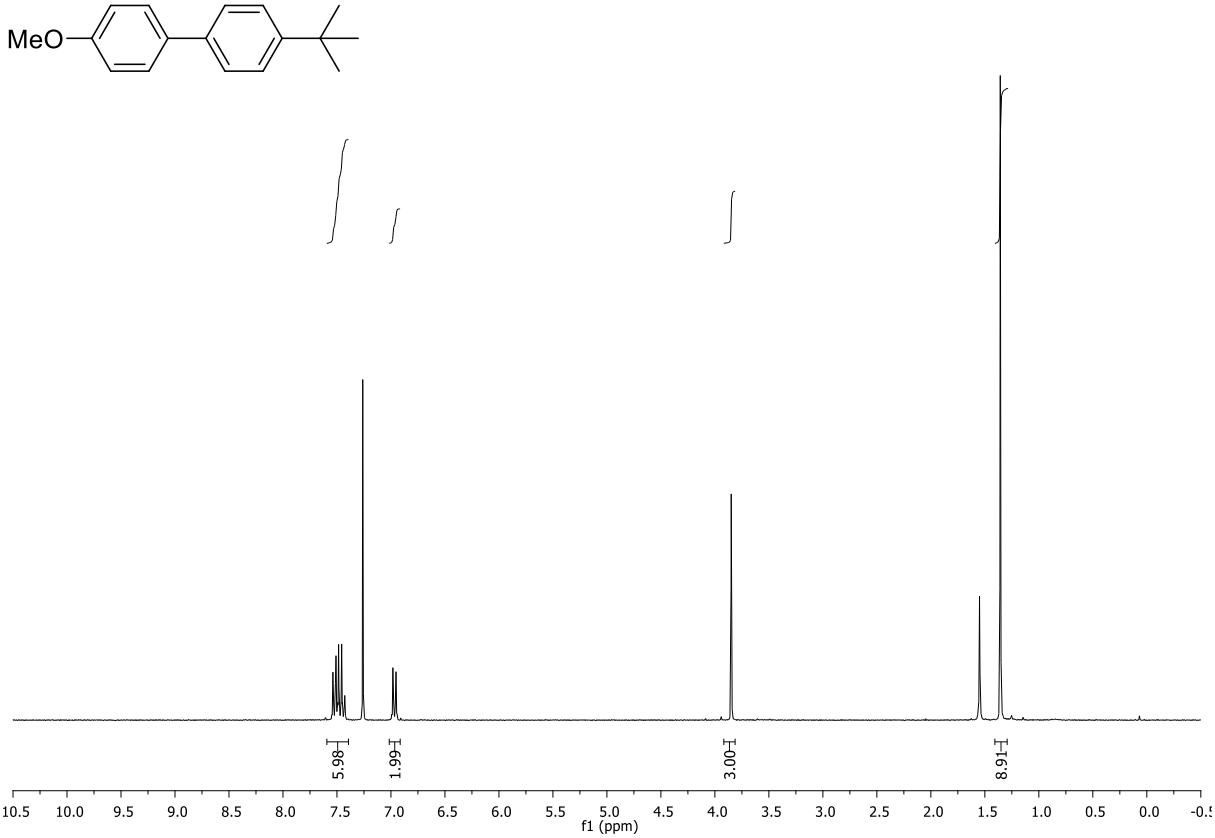

182.9
133.3
131.3
128.8
125.8
70.2
68.4
66.7
65.0
64.4
57.4
34.4
34.1
31.6
31.0
30.6
29.7
27.6
26.3
25.6
25.2
f1 (ppm)

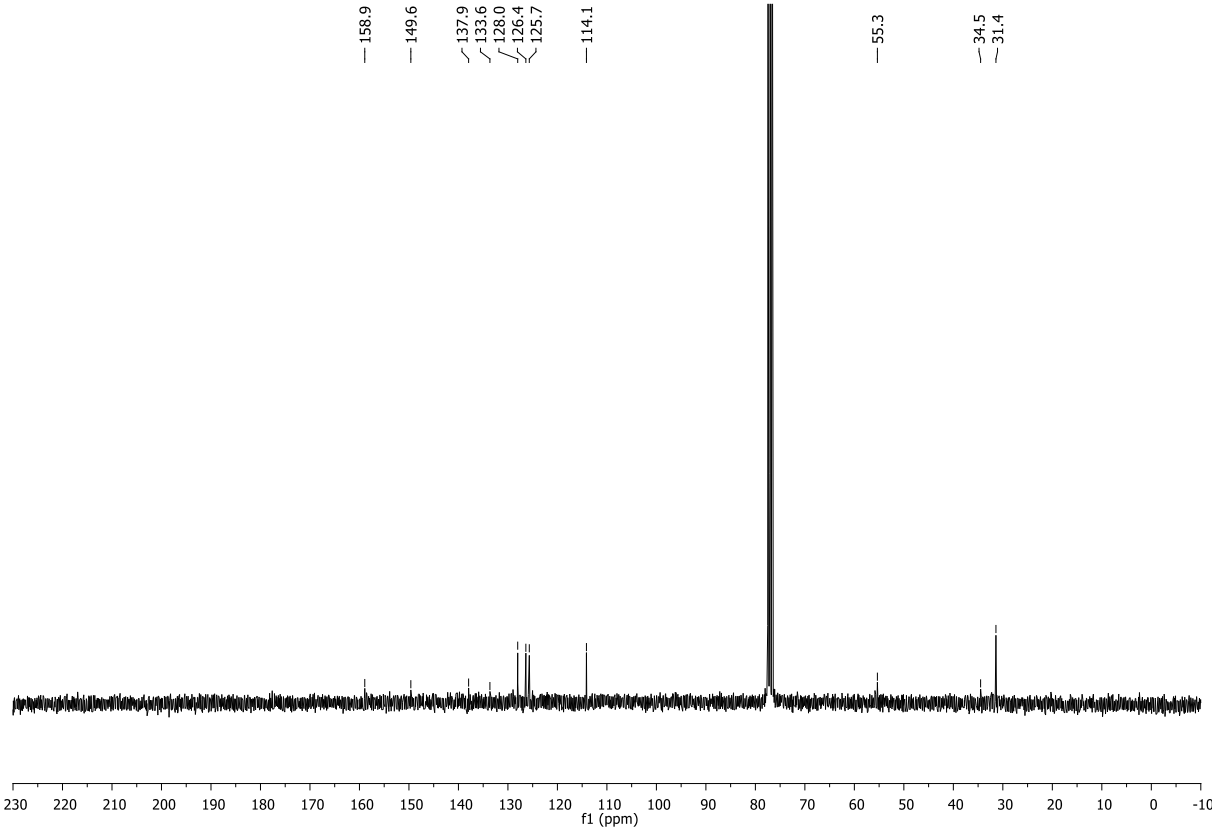

O
Ph
O
P
O
N
H
H
N
N
C
Pd
C
N
Cl
Cl
3.04
2.00
0.99
1.04
1.05
1.07
1.02
1.06
1.16
2.02
2.18
1.02
0.97
2.02
1.05
5.20
3.00
8.97
8.72
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

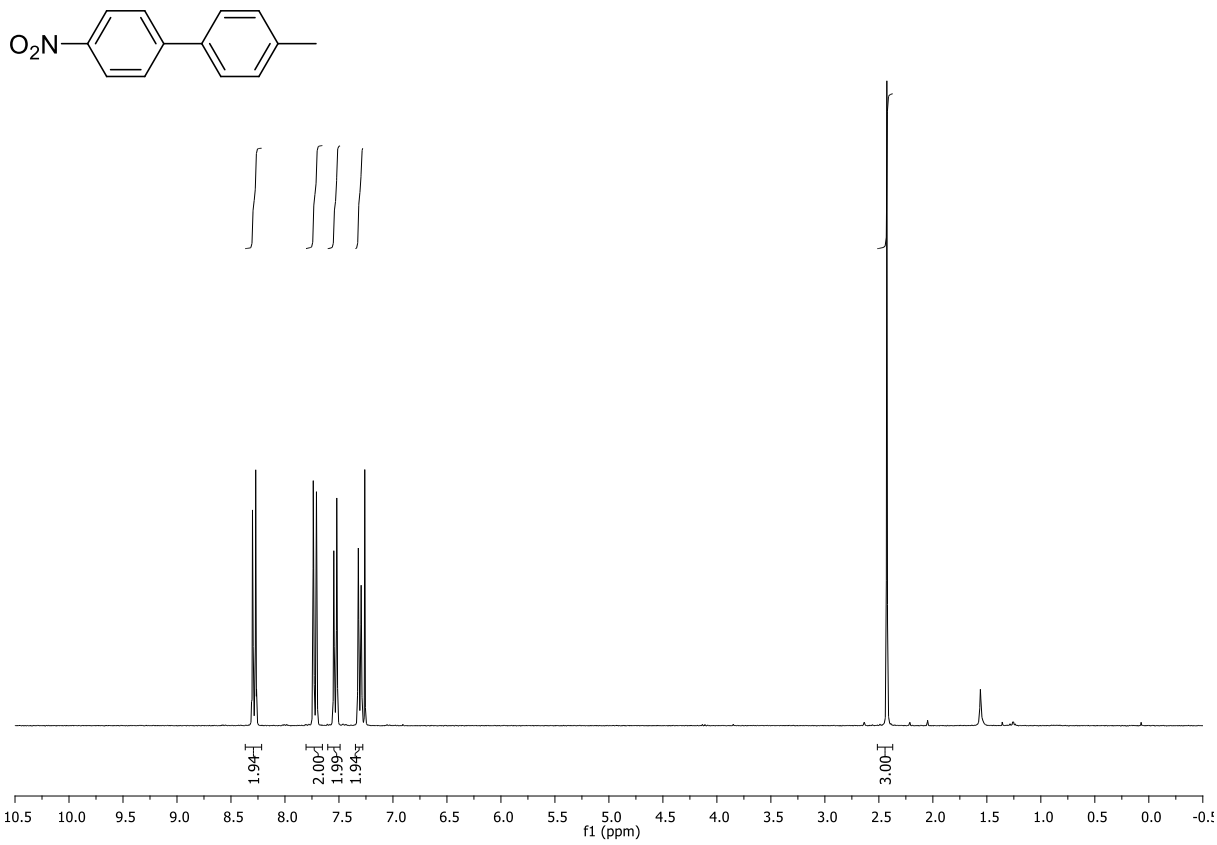

187.3
186.6
133.3
130.9
129.2
125.2
66.4
66.4
65.3
63.1
57.3
56.9
47.3
46.8
34.5
33.9
29.9
27.4
27.2
25.4
25.0
24.9
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

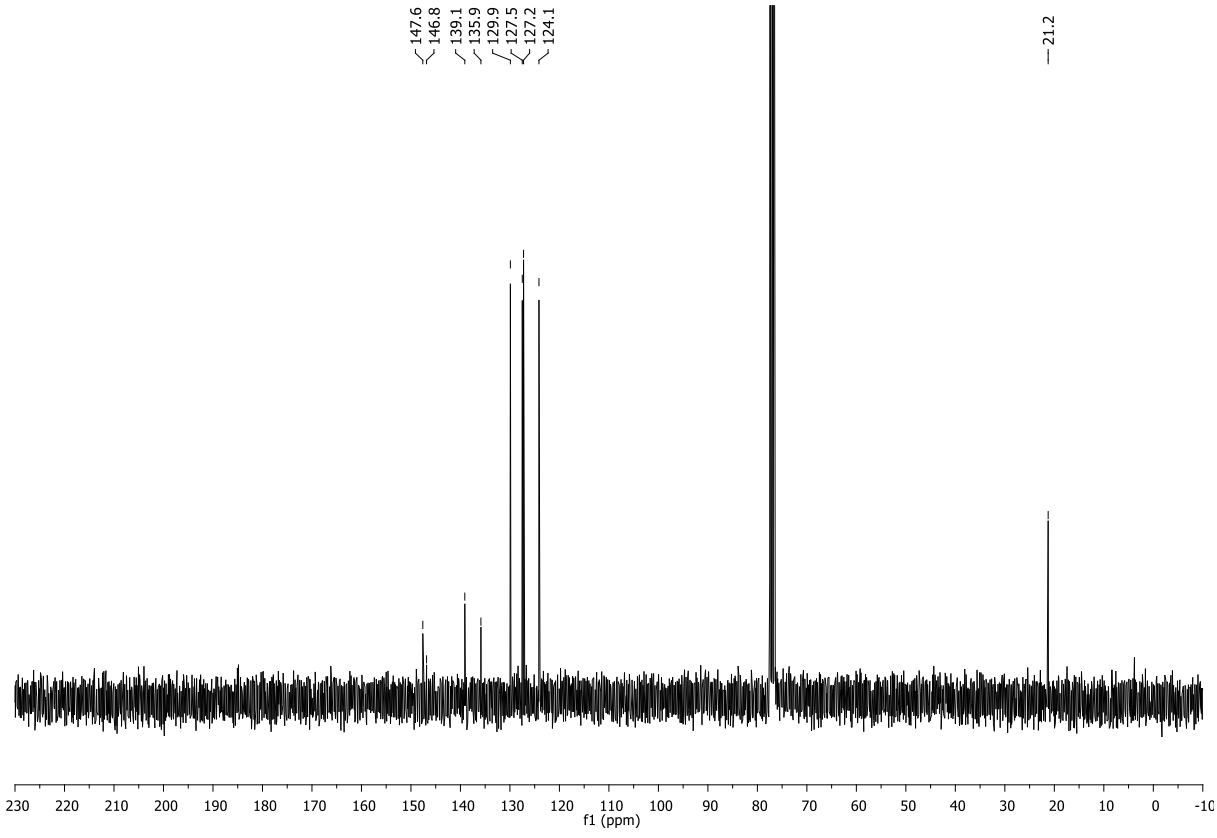

OMe
4.00
2.02
1.01
1.97
3.02
f1 (ppm)

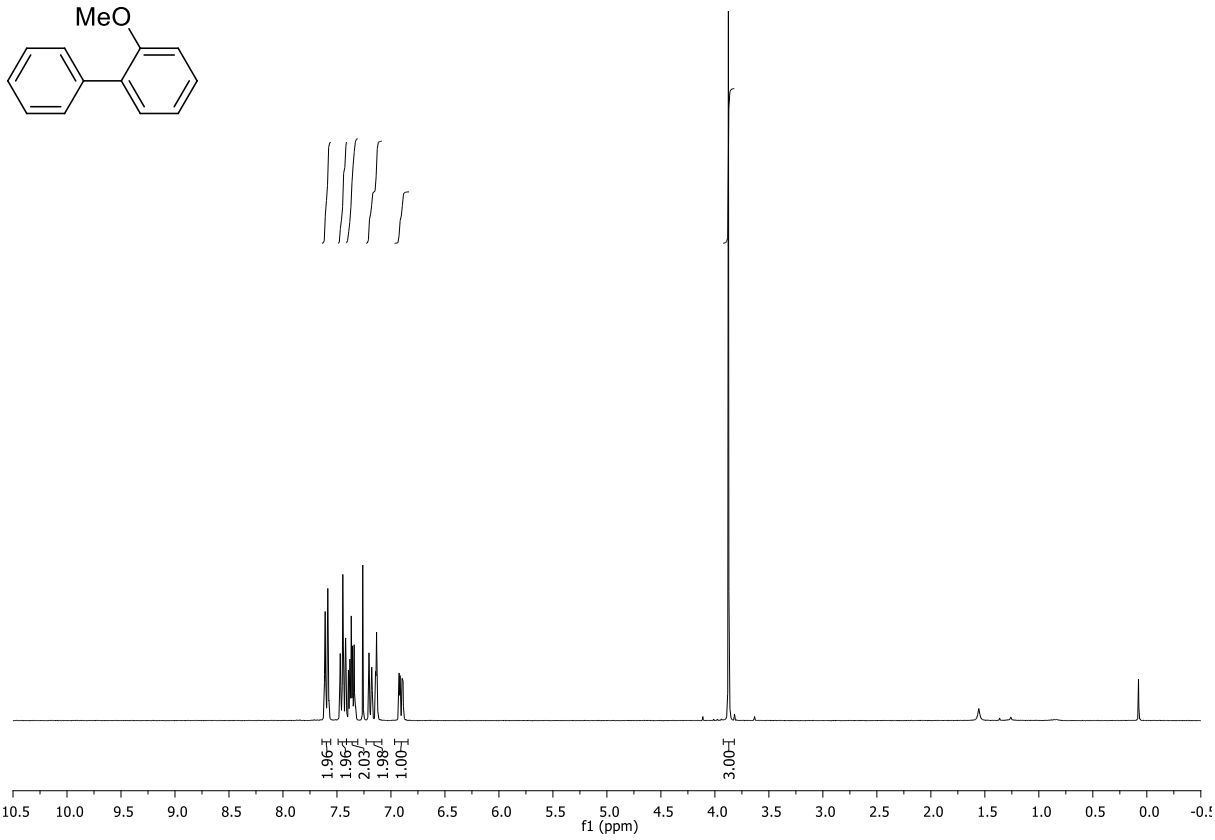

158.1
139.8
132.7
127.7
127.1
125.7
125.6
113.1
54.3
f1 (ppm)

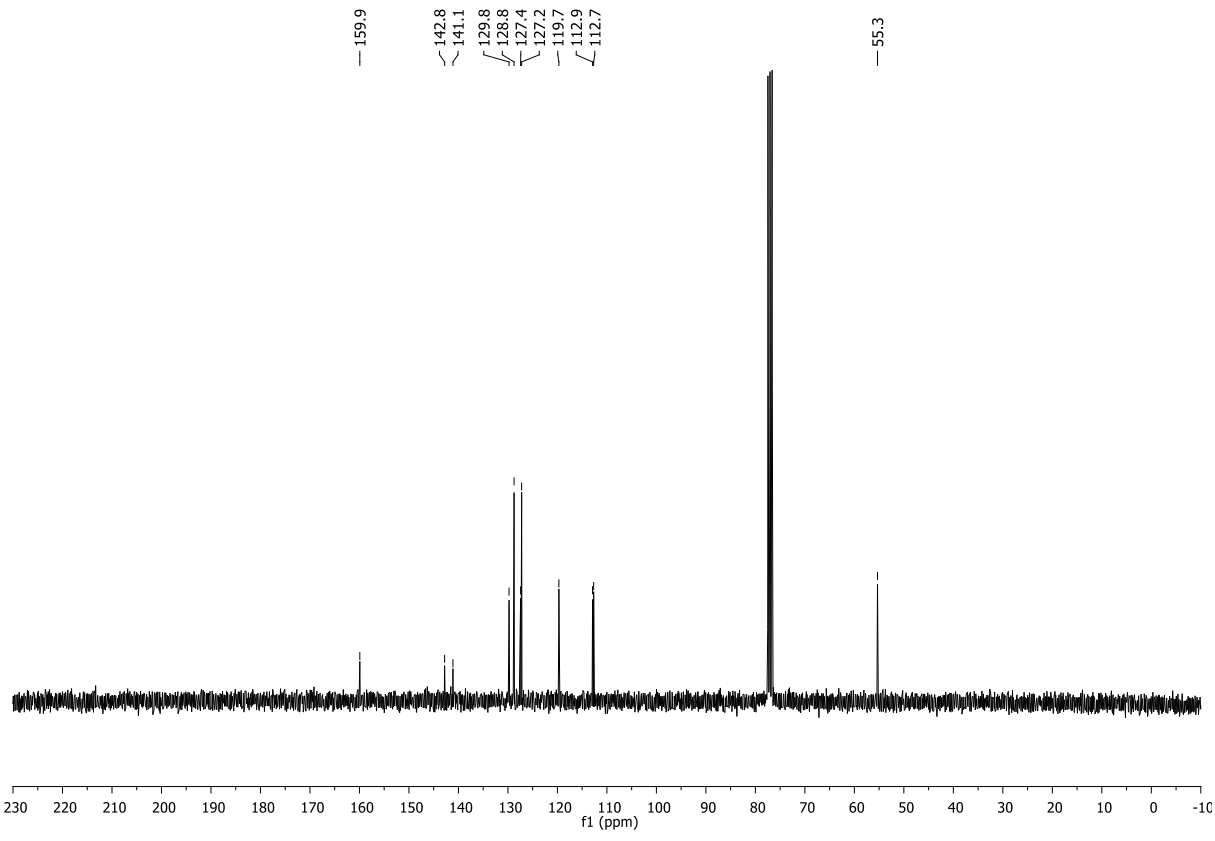

MeO
5.98
1.99
3.00
8.91
f1 (ppm)

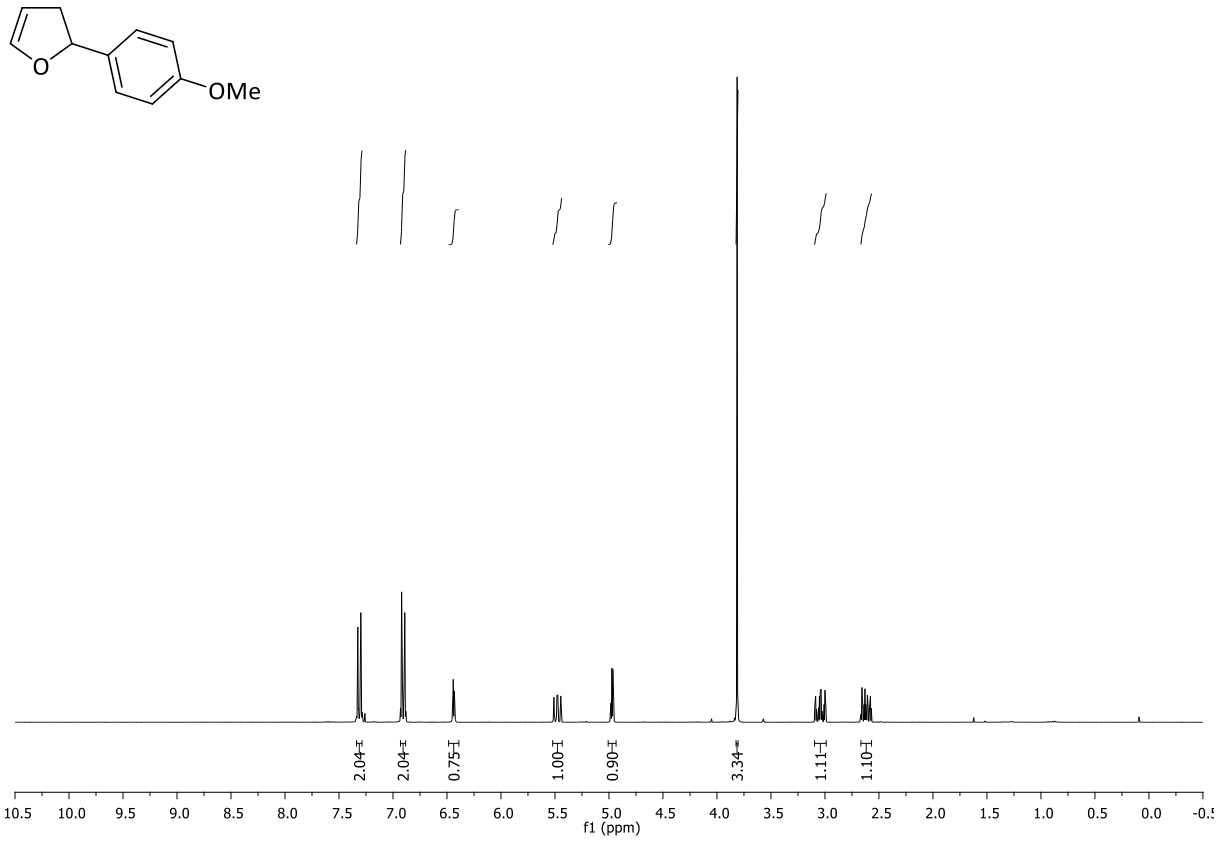

158.9
149.6
137.9
133.6
128.0
126.4
125.7
114.1
55.3
34.5
31.4
f1 (ppm)


O2N
1.94
2.00
1.99
1.94
3.00
f1 (ppm)


147.6
146.8
139.1
135.9
129.9
127.5
127.2
124.1
21.2
f1 (ppm)


MeO
1.96
1.96
2.03
1.98
1.00
3.00
f1 (ppm)


159.9
142.8
141.1
129.8
128.8
127.4
127.2
119.7
112.9
112.7
55.3
f1 (ppm)


O
OMe
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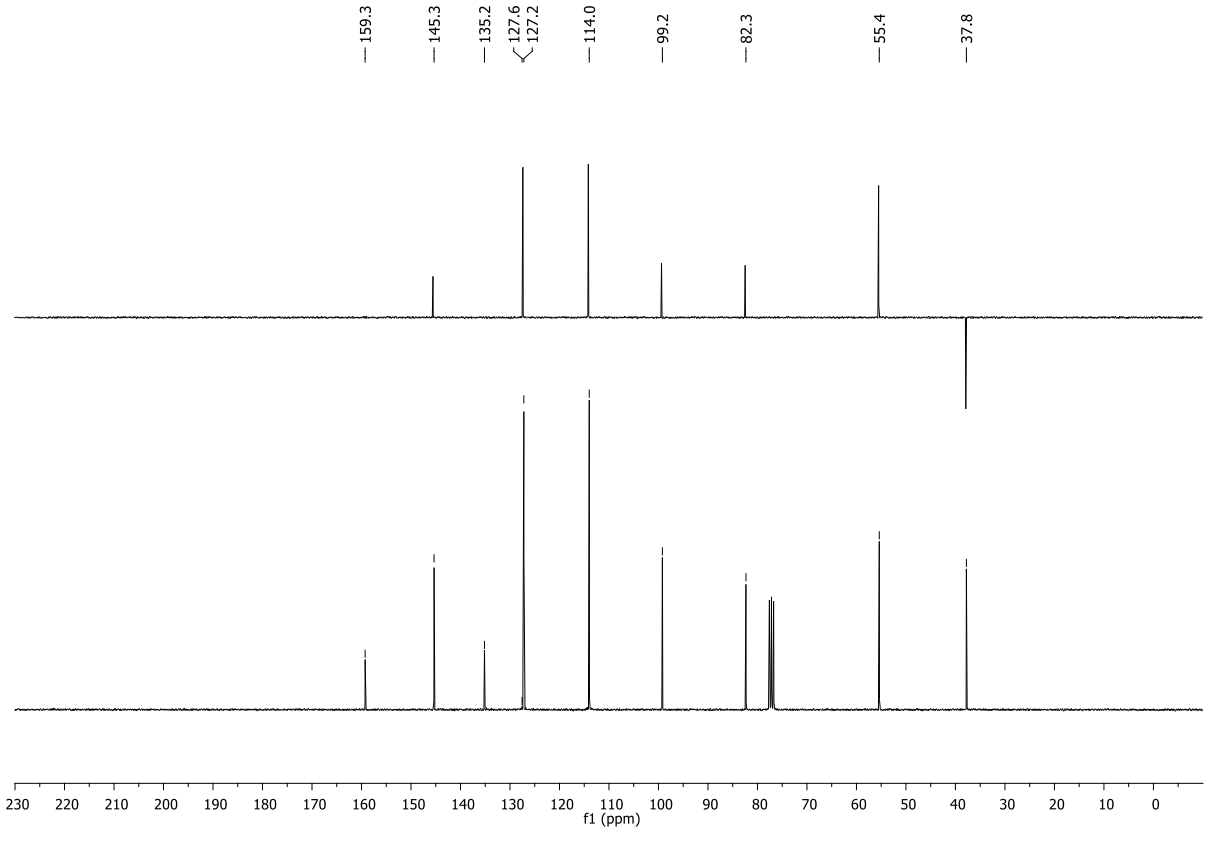
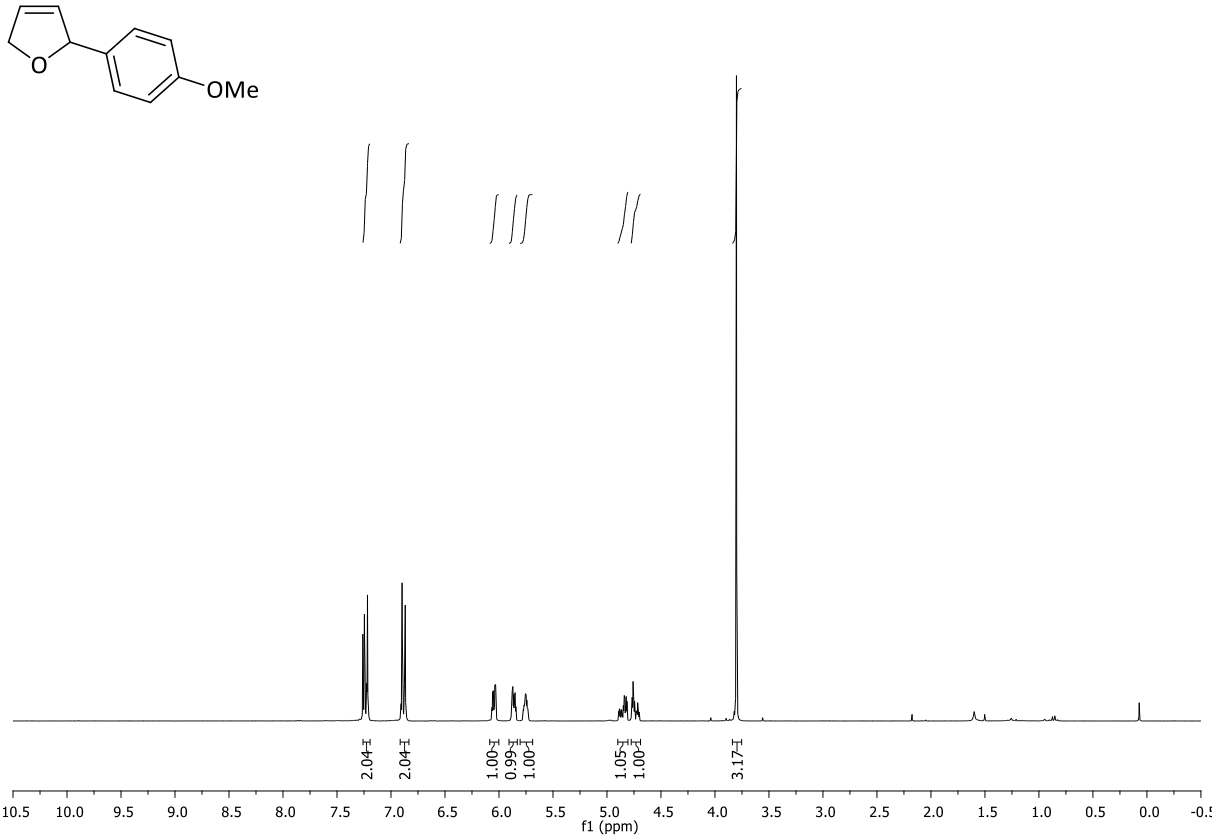
2.04
0.75
1.00
0.90
3.34
1.11
1.10
f1 (ppm)


159.3
145.3
135.2
127.6
127.2
114.0
99.2
82.3
55.4
37.8
f1 (ppm)


O
OMe
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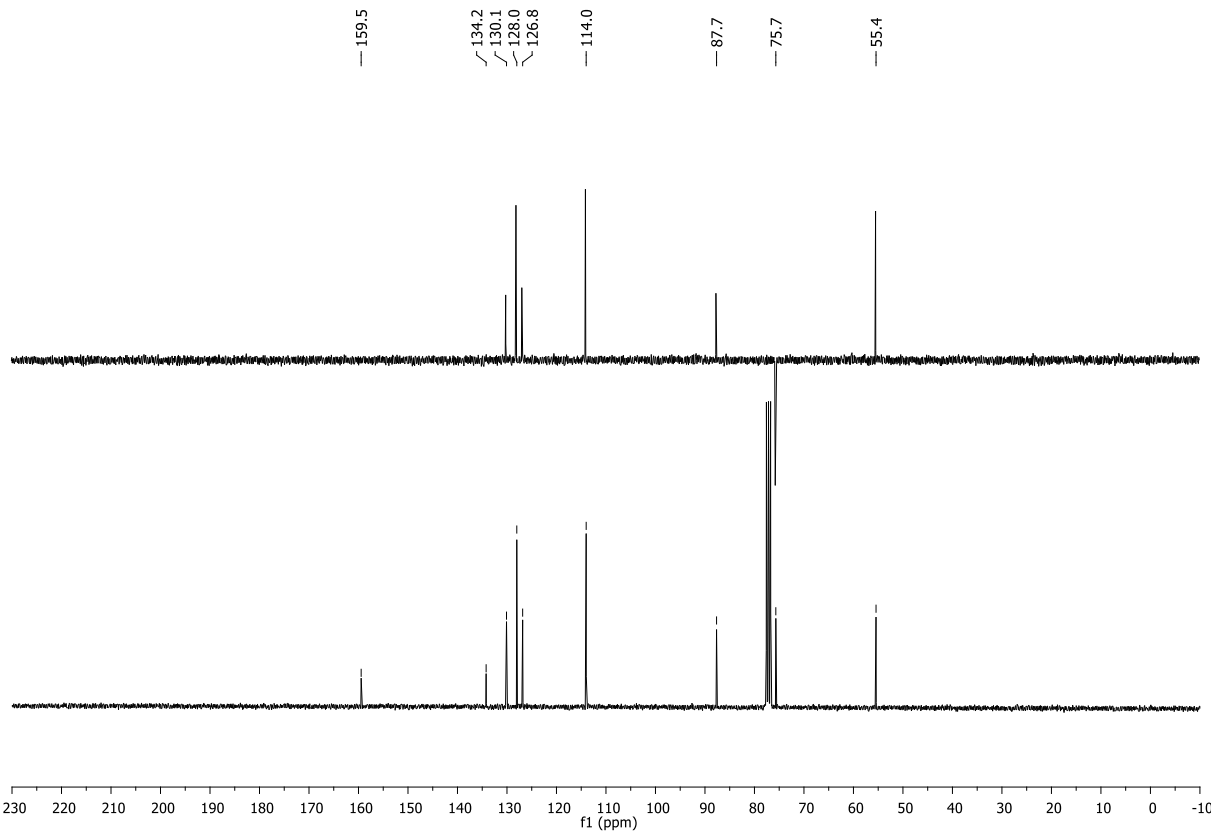
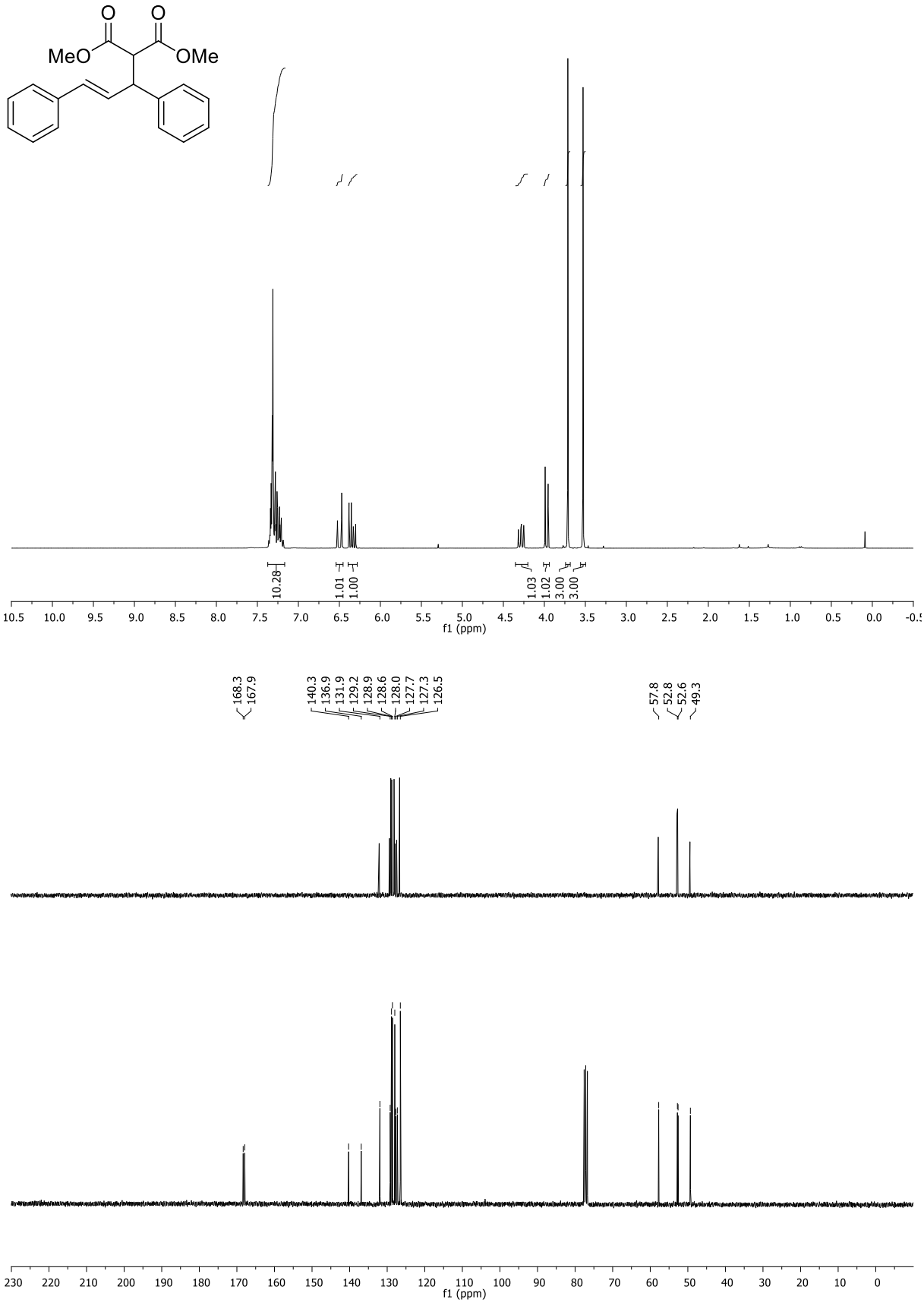
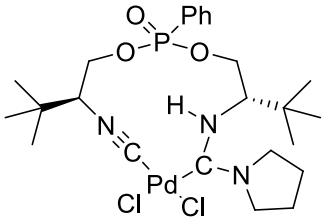
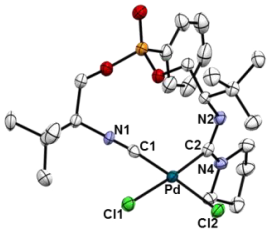
2.04
1.00
0.99
1.00
1.05
1.00
3.17
f1 (ppm)


159.5
134.2
130.1
128.0
126.8
114.0
87.7
75.7
55.4
f1 (ppm)


MeO
OMe
10.28
1.01
1.00
1.03
1.02
3.00
3.00
f1 (ppm)
168.3
167.9
140.3
136.9
131.9
129.2
128.9
128.6
128.0
127.7
127.3
126.5
57.8
52.8
52.6
49.3
f1 (ppm)

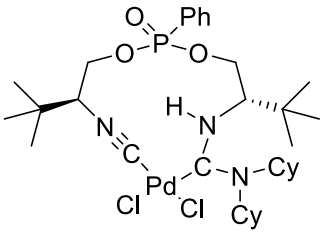
4.3 Solid-State Structures

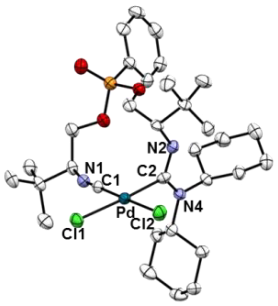




5a

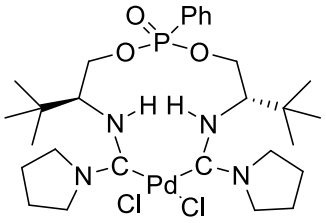
CCDC-Code	1400874
Formula	$C_{24}H_{38}N_3O_3PCl_2Pd$
$D_{calc.}$/ g cm^{-3}	1.398
•/mm^{-1}	7.436
Formula Weight	624.84
Colour	colourless
Shape	prism
Max Size/mm	0.30
Mid Size/mm	0.19
Min Size/mm	0.06
T/K	123
Crystal System	orthorhombic
Flack Parameter	-0.026(5)
Hooft Parameter	-0.014(3)
Space Group	$P2_12_12_1$
a/Å	12.91450(9)
b/Å	18.83710(10)
c/Å	24.40150(13)
•/°	90
•/°	90
•/°	90
V/Å^3	5936.19(6)
Z	8
Z'	2
•$_{min}$/°	3.623
•$_{max}$/°	66.636
Measured Refl.	41098
Independent Refl.	10287
Reflections Used	10116
R_{int}	0.0645
Parameters	619
Restraints	0
Largest Peak	0.633
Deepest Hole	-1.093
GooF	1.029
wR_2 (all data)	0.0888
wR_2	0.0882
R_1 (all data)	0.0353
R_1	0.0349

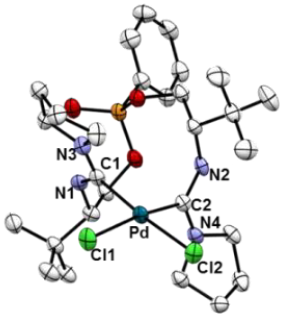




5b

CCDC-Code	1400876
Formula	$C_{32}H_{52}Cl_2N_3O_3PPd$
$D_{calc.}$/ g cm^{-3}	1.386
•/mm^{-1}	6.350
Formula Weight	735.03
Colour	colourless
Shape	needle
Max Size/mm	0.18
Mid Size/mm	0.02
Min Size/mm	0.01
T/K	122.98(17)
Crystal System	monoclinic
Flack Parameter	0.005(9)
Hooft Parameter	0.013(9)
Space Group	$P2_1$
a/Å	9.56244(16)
b/Å	17.2200(3)
c/Å	10.7458(2)
•/°	90
•/°	95.6935(15)
•/°	90
V/Å^3	1760.73(5)
Z	2
Z'	1
•$_{min}$/°	4.134
•$_{max}$/°	70.857
Measured Refl.	7961
Independent Refl.	4862
Reflections Used	4555
R_{int}	0.0458
Parameters	379
Restraints	1
Largest Peak	1.044
Deepest Hole	-1.041
GooF	1.012
wR_2 (all data)	0.1008
wR_2	0.0983
R_1 (all data)	0.0430
R_1	0.0396





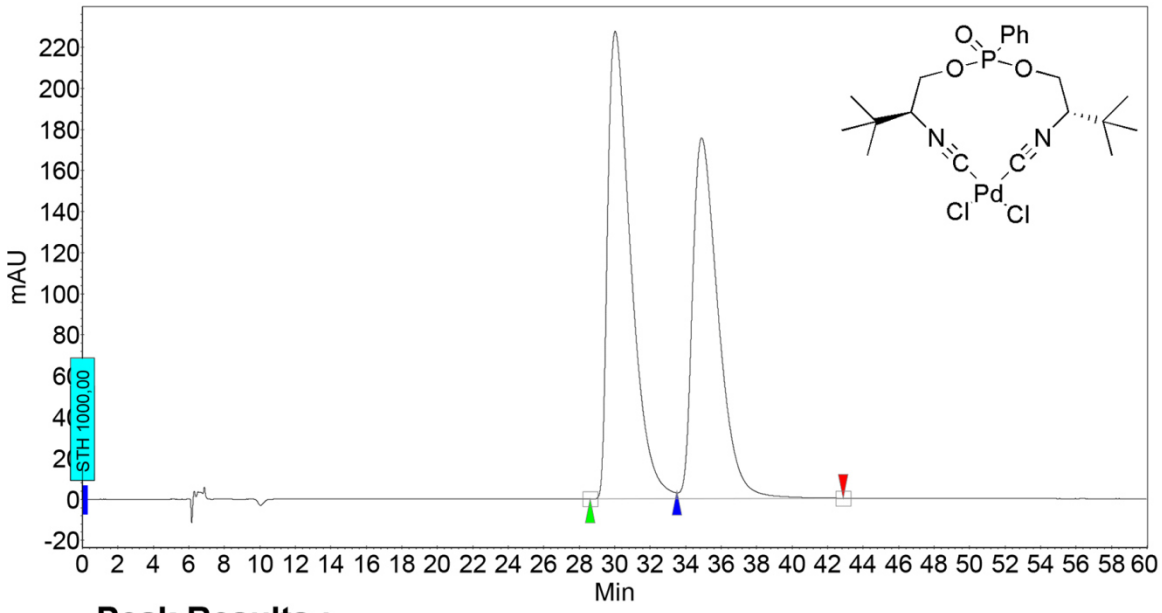
5c

CCDC-Code	1400875
Formula	$C_{32}H_{57}N_4O_4PCl_2Pd$
$D_{calc.}$/ g cm^{-3}	1.372
•/mm^{-1}	6.048
Formula Weight	770.08
Colour	colourless
Shape	needle
Max Size/mm	0.41
Mid Size/mm	0.07
Min Size/mm	0.05
T/K	123.00(10)
Crystal System	orthorhombic
Flack Parameter	-0.038(9)
Hooft Parameter	-0.018(7)
Space Group	$P2_12_12_1$
a/Å	13.9031(3)
b/Å	16.1632(4)
c/Å	16.5945(4)
•/°	90
•/°	90
•/°	90
V/Å^3	3729.10(14)
Z	4
Z'	1
•$_{min}$/°	3.818
•$_{max}$/°	74.046
Measured Refl.	17492
Independent Refl.	6887
Reflections Used	6375
R_{int}	0.0694
Parameters	403
Restraints	0
Largest Peak	1.385
Deepest Hole	-1.018
GooF	1.034
wR_2 (all data)	0.1342
wR_2	0.1296
R_1 (all data)	0.0529
R_1	0.0487

4.4 HPLC-Spectra

Enantiomeric excess was determined by chiral HPLC (Chiralcel OJ-H, n-Heptan/iPrOH 90/10, 0.5 ml/min, 254 nm)

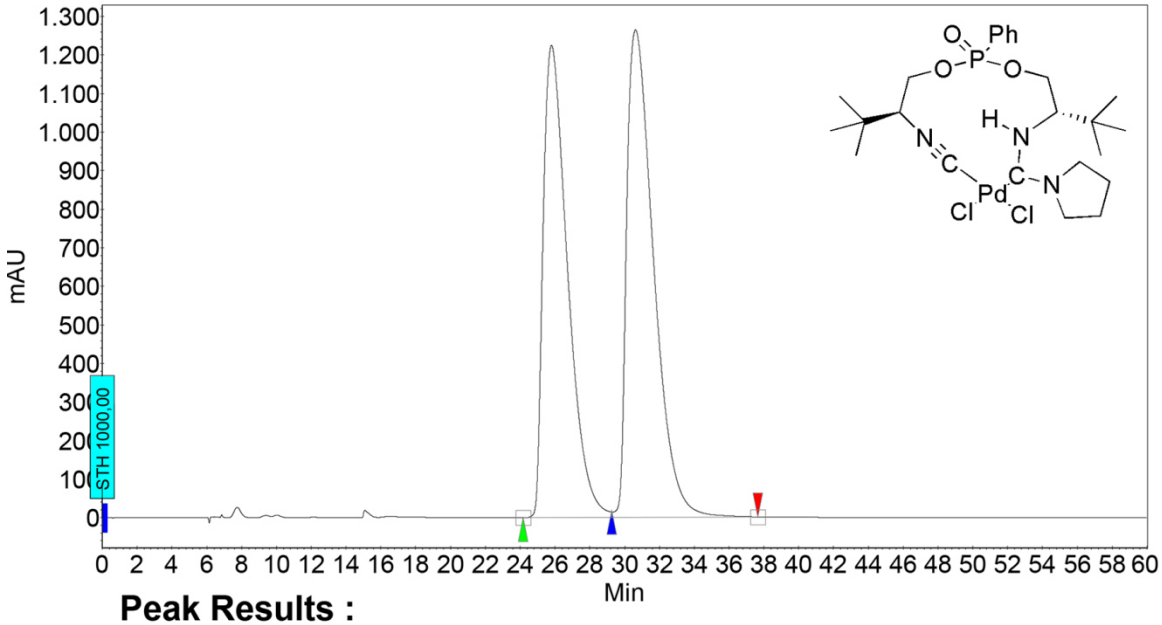
Table 5, Entry 1:



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	30,03	53,85	227,6	344,2	53,850
2	UNKNOWN	34,90	46,15	175,6	295,0	46,150
Total			100,00	403,2	639,2	100,000

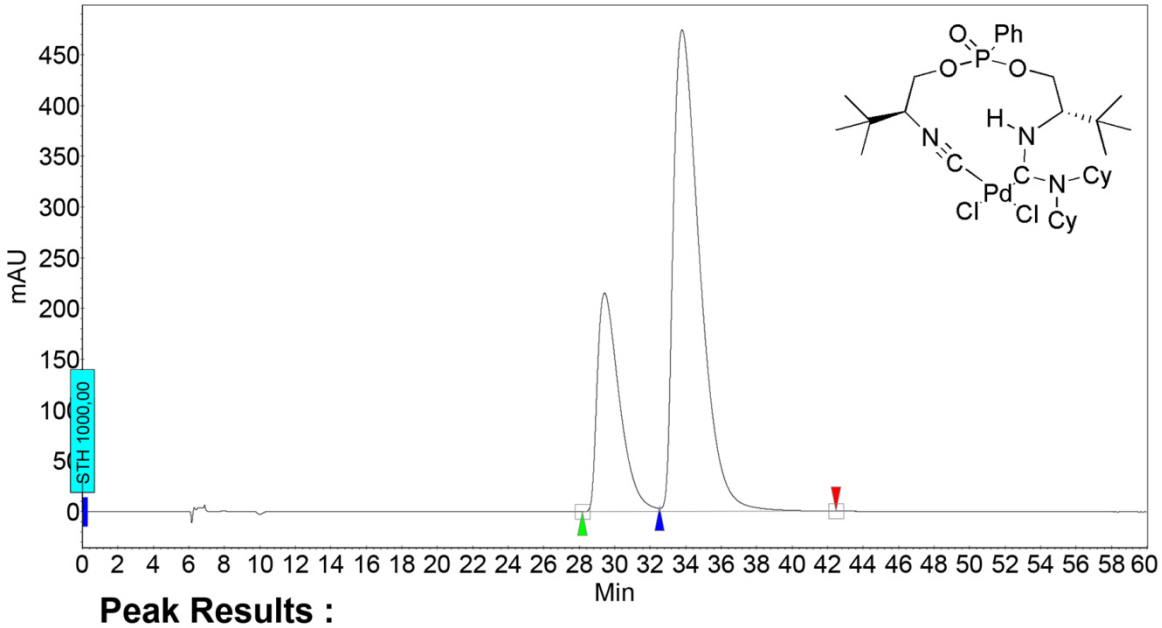
Table 5, Entry 2:



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	25,80	46,84	1224,7	1994,7	46,842
2	UNKNOWN	30,63	53,16	1264,1	2263,6	53,158
Total			100,00	2488,8	4258,3	100,000

Table 5, Entry 3:

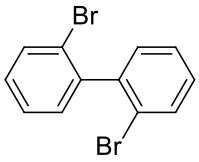


Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	29,43	27,45	215,5	311,8	27,454
2	UNKNOWN	33,80	72,55	474,5	823,9	72,546
Total			100,00	690,0	1135,7	100,000

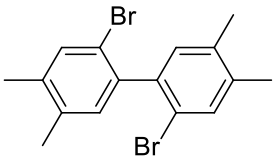
5. Platinum-Isonitriles

5.1 Compound Characterization



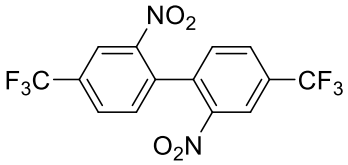
2,2'-dibromo biphenyl (**2a**)[15]

To a stirred solution of 1,2-dibromobenzene (1.0 equiv., 20 mmol, 2.4 ml) in 50 ml anhydrous tetrahydrofuran was added *n*-BuLi (0.5 equiv. 10 mmol, 1.6 M in hexane, 6.3 ml) at -78 °C. The reaction mixture was stirred for 2 h. After quenching with water, extraction with DCM (3x) and washing with NaCl (sat.) **2a** was obtained in 71 % (14.2 mmol, 4.43 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 1H), 7.41 – 7.35 (m, 1H), 7.30 – 7.23 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 132.6, 131.0, 129.4, 127.1, 123.5. IR (neat): 3057, 1584, 1561, 1454, 1422, 1266, 1120, 1075, 1025, 1002, 754, 723, 677 cm^{-1}.



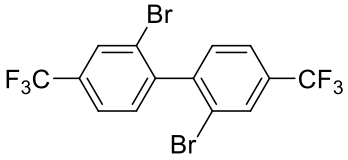
2,2'-dibromo 4,4',5,5'-tetramethyl biphenyl (**2b**)[16]

To a stirred solution of 1,2-dibromo-4,5-dimethylbenzene (1.0 equiv., 7.6 mmol, 2.0 g) in 50 ml anhydrous tetrahydrofuran was added *n*-BuLi (0.5 equiv. 3.8 mmol, 1.6 M in hexane, 2.4 ml) at -78 °C. The reaction mixture was stirred for 2 h. After quenching with water, extraction with DCM (3x) and washing with NaCl (sat.) **2b** was obtained in 95 % (7.2 mmol, 2.65 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (s, 2H), 6.99 (s, 2H), 2.29 (s, 6H), 2.23 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 138.1, 135.6, 133.1, 132.1, 120.2, 19.3, 19.3. IR (neat): 3022, 2971, 2917, 2956, 1474, 1443, 1379, 1255, 1153, 1097, 968, 870 cm^{-1}. EI-HRMS: calcd. for $C_{16}H_{16}{}^{79}Br_2$ [$M^{+\cdot}$]: 365.9619. Found: 365.9615 .



2,2'-dinitro-4,4'-bis(trifluoromethyl)biphenyl (**4**)[17]

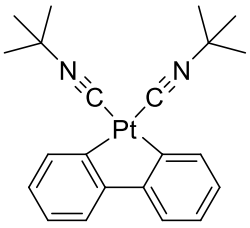
1-Bromo-2-nitro-4-(trifluoromethyl)benzene (1.0 equiv., 3.26 mmol, 880mg) and copper-powder (1.5 equiv., 4.89 mmol, 311 mg) stirred at 240 °C for 16 h. After dilution of the reaction mixture with ethyl acetate followed by filtration pure **4** (89%, 16.3 mmol, 554 mg) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.1 Hz, 2H), 8.01 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.5. IR (neat): 3102, 1629, 1537, 1320, 1265, 1180, 1133, 1082, 1008, 917, 886, 852, 802, 768, 700 cm^{-1}. EI-MS (rel. Int.): 361.1 [$(M-F^{\cdot})^{+}$] (14), 334.0 (100), 304.1 (33.5).



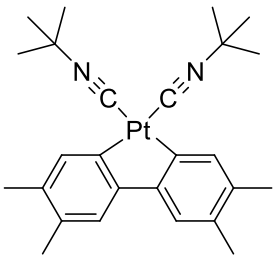
2,2'-dibromo 4,4'-bis(trifluoromethyl) biphenyl (**2c**)

2,2'-Dinitro-4,4'-bis(trifluoromethyl)biphenyl (**4**) (1.0 equiv., 16 mmol, 554 mg) was hydrogenated using a hydrogen balloon with Pd@Fe_3O_4 in EtOH. The reaction mixture was filtered, evaporated and the crude product was directly dissolved in an 50:50 mixture of water and HBr(aq.) (1.4 ml) at 0 °C. A solution of $NaNO_2$ (2.0 equiv., 33 mmol, 225 mg) in 2 ml water was added dropwise and the reaction was stirred for 15 min, followed be the addition of CuBr (2.7 equiv., 44 mmol, 631 mg) and HBr(aq.). The reaction mixture was stirred for 2 h at 100 °C. **2c** (11%, 1.6 mmol, 80 mg) was obtained after extraction (ethyl acetate 2x, water 1x, Na_2CO_3(sat.) 1x) and column chromatography (hexanes : ethyl acetate = 9:1 – 2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.72 – 7.63 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.7. EI-MS (rel. Int.): 447.8 (33), 367.0 (57), 288.1 (100), 219.1 (49).

General procedure for the preparation of 9: In a flame-dried Schlenk-flask **2** (1.0 equiv., 1.0 mmol) was dissolved in 150 ml of anhydrous diethyl ether. The mixture was cooled to -78 °C and *n*-BuLi (1.6 M in hexane, 2.4 equiv., 2.4 mmol, 1.5 ml) was added dropwise. After 4 h *cis*-$Pt(SEt)_2Cl_2$ (1.0 equiv., 1.0 mmol, 446 mg) was added at -78 °C and the reaction was allowed to warm to room temperature overnight. The mixture was evaporated and re-dissolved in DCM. After filtration, CO gas was bubbled through the solution to yield **8a** (23%) and **8b** (16%) as green or red crystals which could quantitatively be transformed into their corresponding isonitrile complexes **9a,b,d,e,g,h,k,l** by stoichiometric addition of the isonitrile ligand. **8c** could not be isolated using CO gas, therefore **9c**, **9f**, **9i** and **9l** were obtained by the direct addition of isonitrile ligand to the crude reaction mixture followed by chromatographic separation in 5-12% yield.

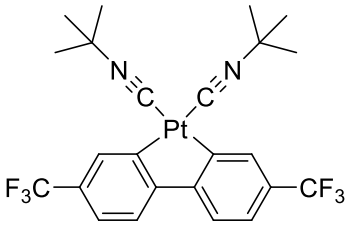


9a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.47 (m, 2H), 7.40 – 7.33 (m, 2H), 7.01 (td, *J* = 7.4, 1.4 Hz, 2H), 6.90 (td, *J* = 7.3, 1.4 Hz, 2H), 1.63 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 156.0, 139.7, 138.3, 126.4, 125.3, 119.9, 57.5, 30.4. IR (neat): 3044, 2980, 2926, 2199, 2173, 1452, 1419, 1359, 1232, 1195, 1024, 743 cm^{-1}. ESI-HRMS: calcd. for $C_{22}H_{27}N_2{}^{194}Pt$ [MH^+]: 513.1795. Found: 513.1794.

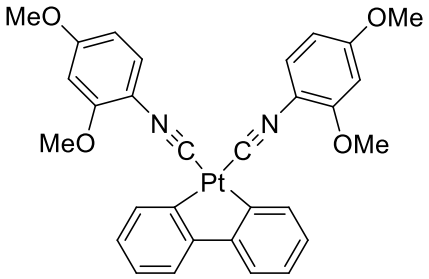


9b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 2H), 7.09 (s, 2H), 2.20 (s, 6H), 2.16 (s, 6H), 1.64 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 153.2, 139.8, 133.2, 132.7, 121.1, 57.3, 30.4, 20.0, 19.8 (one quaternary carbon not detected). IR (neat): 2981, 2920, 2857, 2187, 2153, 1445,

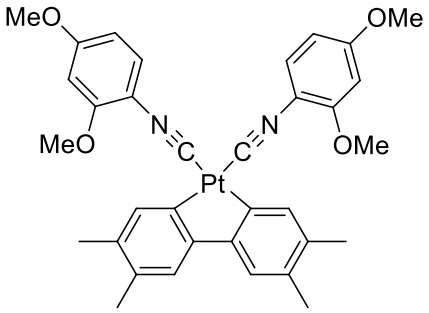
1370, 1193, 1018, 952, 908, 866, 726 cm^{-1}. ESI-HRMS: calcd. for $C_{26}H_{35}N_2{}^{194}Pt$ [MH^+]: 569.2421. Found: 569.2417.



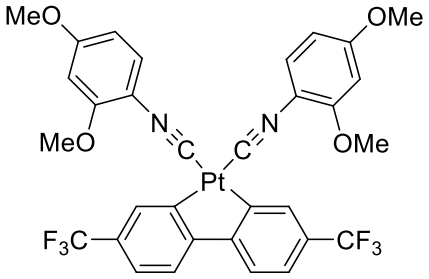
9c: ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.71 (m, 2H), 7.49 – 7.41 (m, 2H), 7.30 – 7.26 (m, 2H), 1.66 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.4, 122.5, 120.3, 30.3 (quarternary peaks not detected). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.7. IR (neat): 2988, 2943, 2204, 2184, 1373, 1316, 1253, 1165, 1101, 1074, 1056, 895, 831, 730 cm^{-1}. ESI-HRMS: calcd. for $C_{24}H_{25}F_6N_2{}^{194}Pt$ [MH^+]: 649.1543. Found: 649.1544.



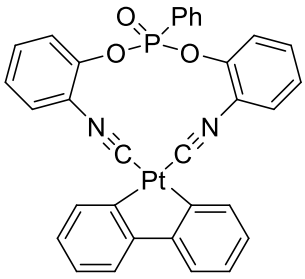
9d: ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.75 (m, 2H), 7.46 – 7.35 (m, 4H), 7.03 (td, *J* = 7.4, 1.4 Hz, 2H), 6.92 (td, *J* = 7.3, 1.4 Hz, 2H), 6.58 – 6.42 (m, 4H), 3.93 (s, 6H), 3.84 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8, 158.1, 156.7, 156.7, 139.4, 128.1, 126.5, 126.2, 125.4, 119.9, 110.2, 105.1, 99.4, 56.2, 55.9. IR (neat): 3031, 2926, 2923, 2155, 1500, 1506, 1469, 1323, 1290, 1215, 1158, 1106, 1025, 939, 812, 736 cm^{-1}. ESI-HRMS: calcd. for $C_{30}H_{27}N_2O_3P^{194}Pt$ [MH^+]: 673.1592. Found: 673.1578.



9e: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.13 (s, 2H), 6.56 – 6.45 (m, 4H), 3.94 (s, 6H), 3.85 (s, 6H), 2.22 (s, 6H), 2.18 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.6, 156.6, 156.3, 153.9, 151.6, 140.8, 133.4, 132.8, 128.2, 121.1, 110.7, 105.1, 99.5, 56.2, 55.9, 20.1, 19.9. IR (neat): 2928, 2864, 2191, 1738, 1600, 1505, 1454, 1290, 1261, 1214, 1108, 1024, 802, 751 cm^{-1}. ESI-HRMS: calcd. for $C_{34}H_{35}N_2O_4P^{194}Pt$ [MH^+]: 729.2218. Found: 729.2180.

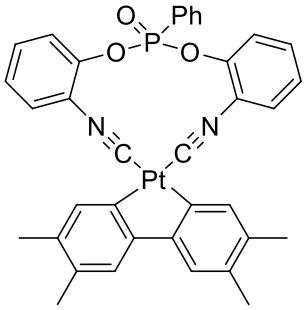


9f: IR (neat): 2191, 2168, 1582, 1506, 1506, 1459, 1314, 1289, 1118, 1101, 1026, 832, 815, 796 cm^{-1}. ESI-HRMS: calcd. for $C_{32}H_{24}F_6N_2O_4{}^{194}Pt$ [MH^+]: 810.1364. Found: 810.1348.

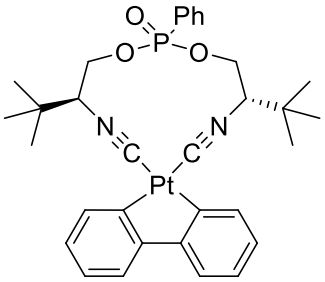


9g: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 2H), 7.82 (dd, *J* = 7.1, 1.1 Hz, 2H), 7.64 – 7.60 (m, 3H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.54 – 7.50 (m, 2H), 7.48 – 7.44 (m, 2H), 7.43 (dd, *J* = 7.6, 1.0 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.07 (td, *J* = 7.5, 1.2 Hz, 2H), 6.97 (td, *J* = 7.2, 1.2 Hz, 2H). ^{13}C NMR

(151 MHz, $CDCl_3$) δ 158.1, 157.0, 154.5, 146.4, 139.8, 134.8, 132.8, 131.3, 129.4, 127.0, 126.7, 126.3, 126.2, 124.3, 123.0, 121.8, 120.3. ^{31}P NMR (121 MHz, $CDCl_3$) δ 14.8. IR (neat): 3058, 2932, 2180, 1668, 1593, 1487, 1439, 1244, 1201, 1132, 1103, 923, 808 cm^{-1}. ESI-HRMS: calcd. for $C_{32}H_{22}N_2O_3P^{194}Pt$ [MH^+]: 708.0989. Found: 708.0978.

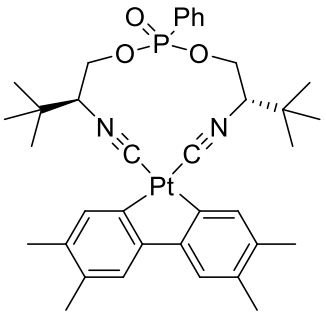


9h: ^1H NMR (600 MHz, $CDCl_3$) δ 8.15 – 8.09 (m, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.60 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.56 – 7.49 (m, 6H), 7.47 – 7.43 (m, 2H), 7.28 – 7.24 (m, 2H), 7.15 (s, 2H), 2.24 (s, 6H), 2.21 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.3, 155.0, 154.4, 146.4, 141.3, 134.7, 133.7, 132.8, 131.0, 129.4, 126.6, 126.3, 124.2, 123.0, 121.8, 121.5, 120.4, 20.1, 19.8. ^{31}P NMR (121 MHz, $CDCl_3$) δ 14.7. IR (neat): 2918, 2858, 2163, 2127, 1488, 140, 1262, 1102, 1026, 933, 864 cm^{-1}. ESI-HRMS: calcd. for $C_{36}H_{30}N_2O_3P^{194}Pt$ [MH^+]: 763.1615. Found: 763.1595.

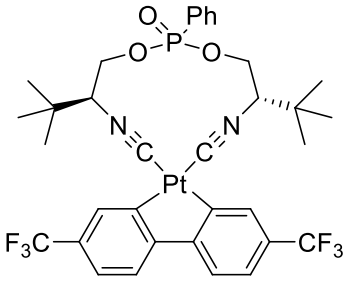


9j: ^1H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.76 – 7.63 (m, 3H), 7.57 – 7.53 (m, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.02 (t, *J* = 7.2 Hz, 2H), 6.92 – 6.87 (m, 2H), 4.52 – 4.45 (m, 1H), 4.37 (ddd, *J* = 10.6, 6.7, 4.1 Hz, 1H), 4.30 (dt, *J* = 10.4, 2.9 Hz, 1H), 4.01 (dd, *J* = 8.6, 4.1 Hz, 1H), 3.92 – 3.86 (m, 1H), 3.76 (dd, *J* = 10.2, 2.9 Hz, 1H), 1.17 (s, 9H), 1.11 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1, 156.6, 139.6, 133.9, 132.3, 129.3, 126.6, 126.1, 125.6, 124.8, 120.1, 67.7, 67.0, 64.8, 63.4, 33.7, 33.6, 26.7, 26.6. ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.8. IR (neat): 3056, 2966, 2870,

2199, 1549, 1471, 1371, 1339, 1252, 1132, 1096, 1021, 989, 858, 823 cm^{-1}. ESI-HRMS: calcd. for $C_{32}H_{38}N_2O_3P^{194}Pt$ [MH^+]: 723.2241. Found: 723.2236.

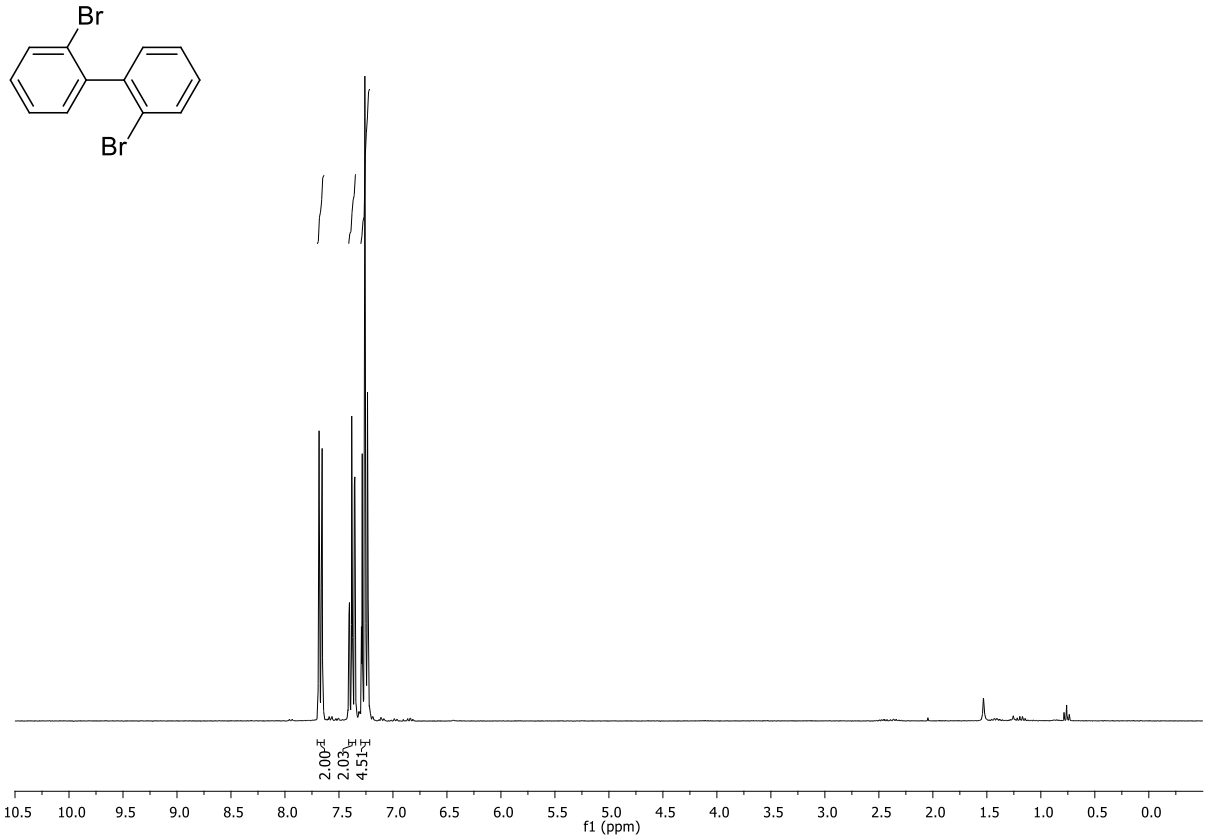


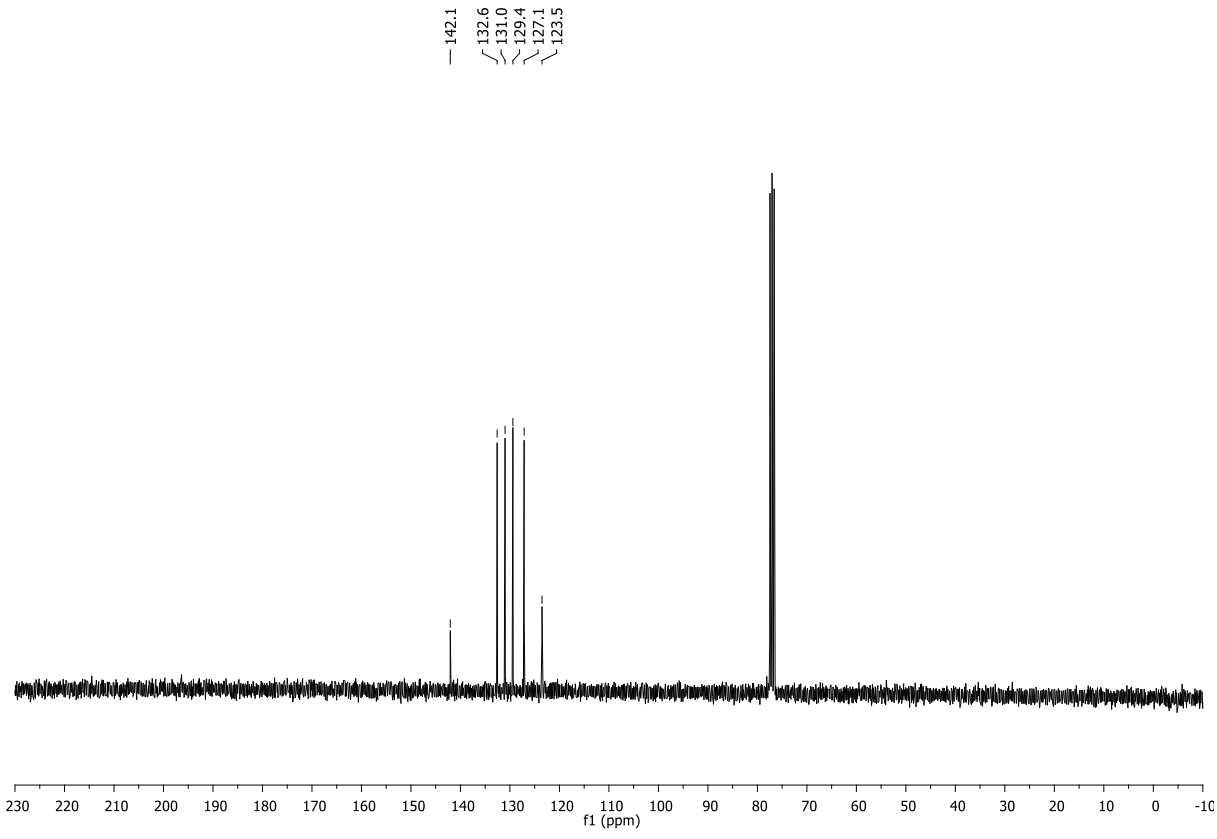
9k: ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.84 (m, 2H), 7.69 – 7.61 (m, 1H), 7.59 – 7.50 (m, 2H), 7.49 – 7.35 (m, 2H), 7.13 – 7.07 (m, 2H), 4.48 (td, *J* = 10.3, 7.9 Hz, 1H), 4.38 – 4.27 (m, 2H), 4.00 (dd, *J* = 8.7, 4.0 Hz, 1H), 3.93 – 3.82 (m, 1H), 3.75 (dd, *J* = 10.2, 3.0 Hz, 1H), 2.20 (s, 6H), 2.14 (s, 6H), 1.18 (s, 9H), 1.11 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 133.7, 132.0, 129.2, 121.1, 67.4, 66.5, 64.8, 63.2, 26.5, 26.6, 20.0, 19.6 (quaternary carbons not detected). ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.7. IR (neat): 2963, 2920, 2201, 1672, 1593, 1464, 1440, 1464, 1440, 1371, 1336, 1251, 1132, 1092, 1018, 984, 865, 812, 734 cm^{-1}. ESI-HRMS: calcd. for $C_{36}H_{46}N_2O_3P^{194}Pt$ [MH^+]: 779.2867. Found: 779.2858.

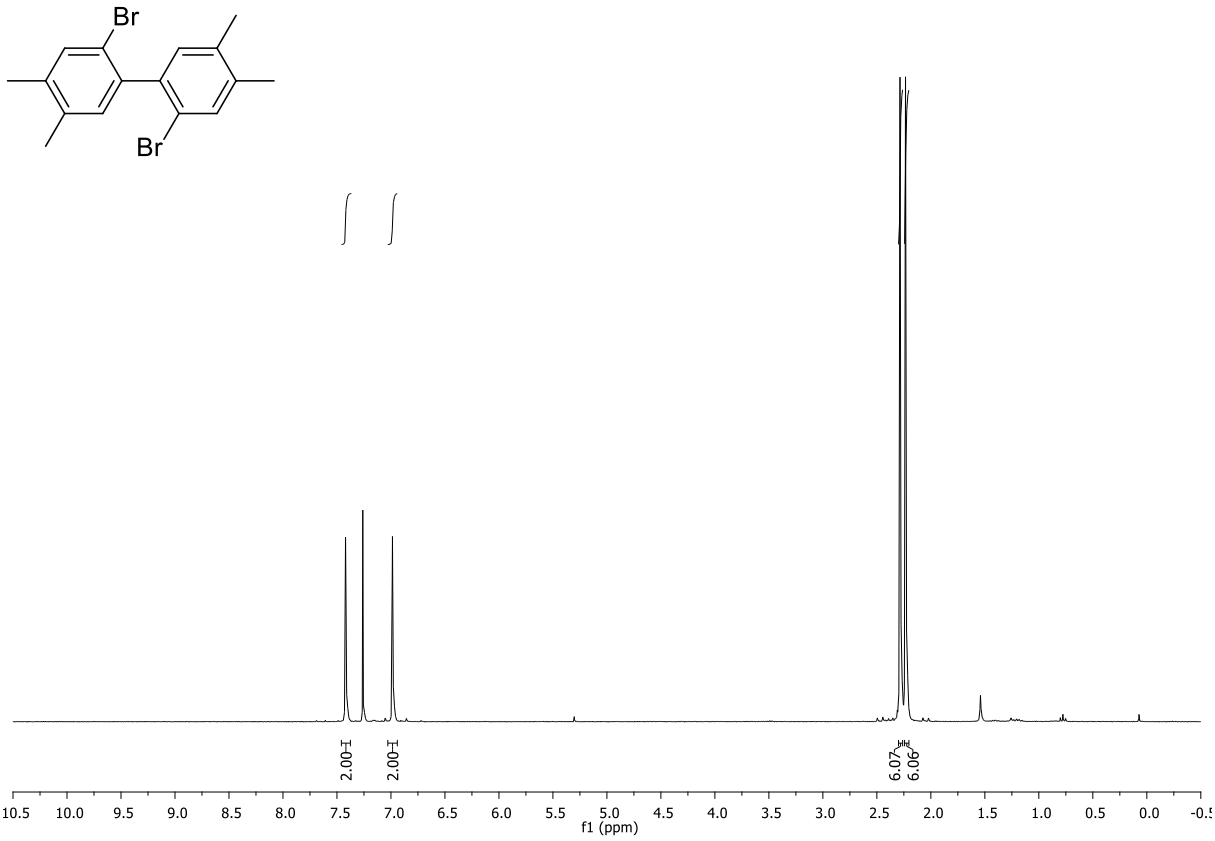


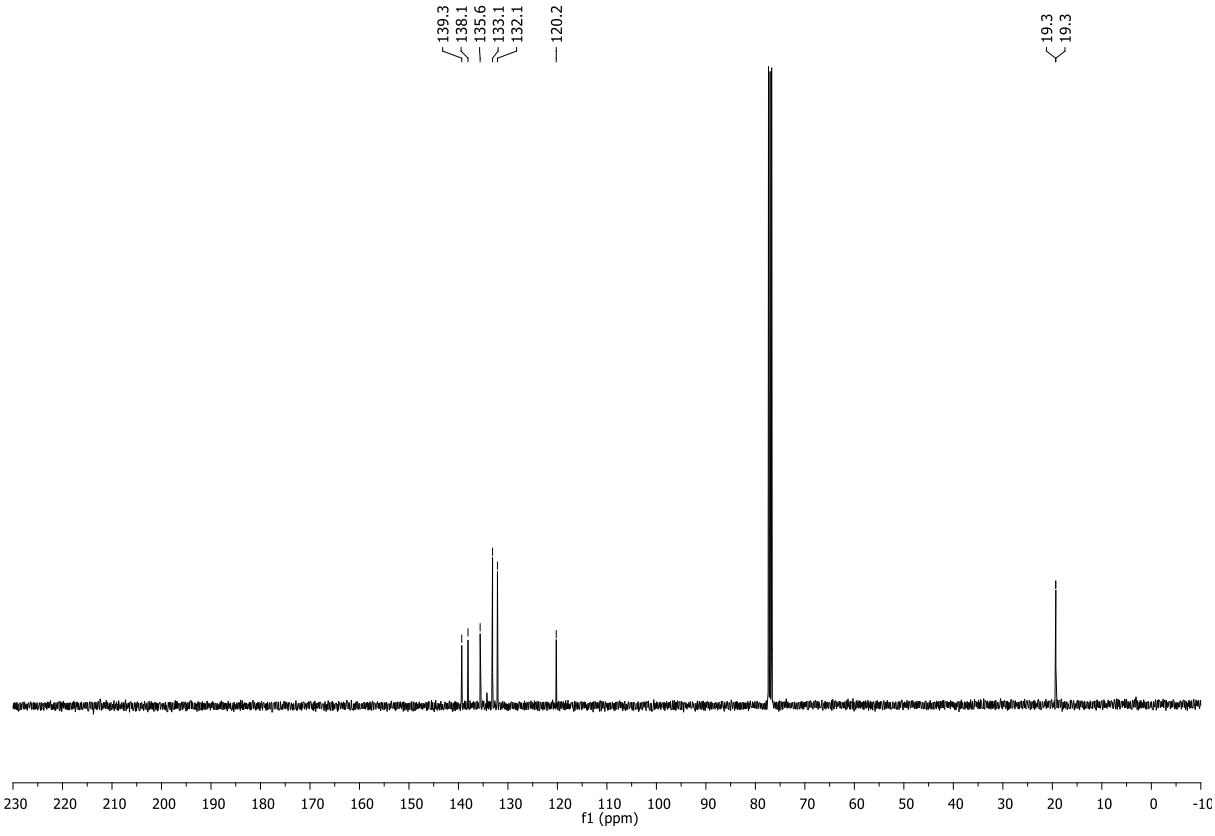
9l: ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 – 7.82 (m, 4H), 7.71 – 7.63 (m, 1H), 7.60 – 7.52 (m, 2H), 7.49 – 7.42 (m, 2H), 7.28 (dd, *J* = 6.5, 5.6 Hz,2H), 4.52 (td, *J* = 10.4, 7.9 Hz, 1H), 4.40 – 4.26 (m, 2H), 4.14 – 4.07 (m, 1H), 3.97 – 3.82 (m, 2H), 1.18 (s, 9H), 1.12 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 156.4, 156.1, 135.9, 133.9, 132.1, 129.2, 126.8, 124.3, 122.7, 120.3, 67.9, 67.1, 64.8, 63.2, 33.7, 26.5, 26.4. ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.8 (d, *J* = 20.7 Hz). IR (neat): 2976, 2202, 2180, 1316, 1252, 1166, 1106, 1056, 1020, 984, 820, 686 cm^{-1}. ESI-HRMS: calcd. for $C_{34}H_{36}N_2O_3P^{194}Pt$ [MH^+]: 859.1989. Found: 859.1989.

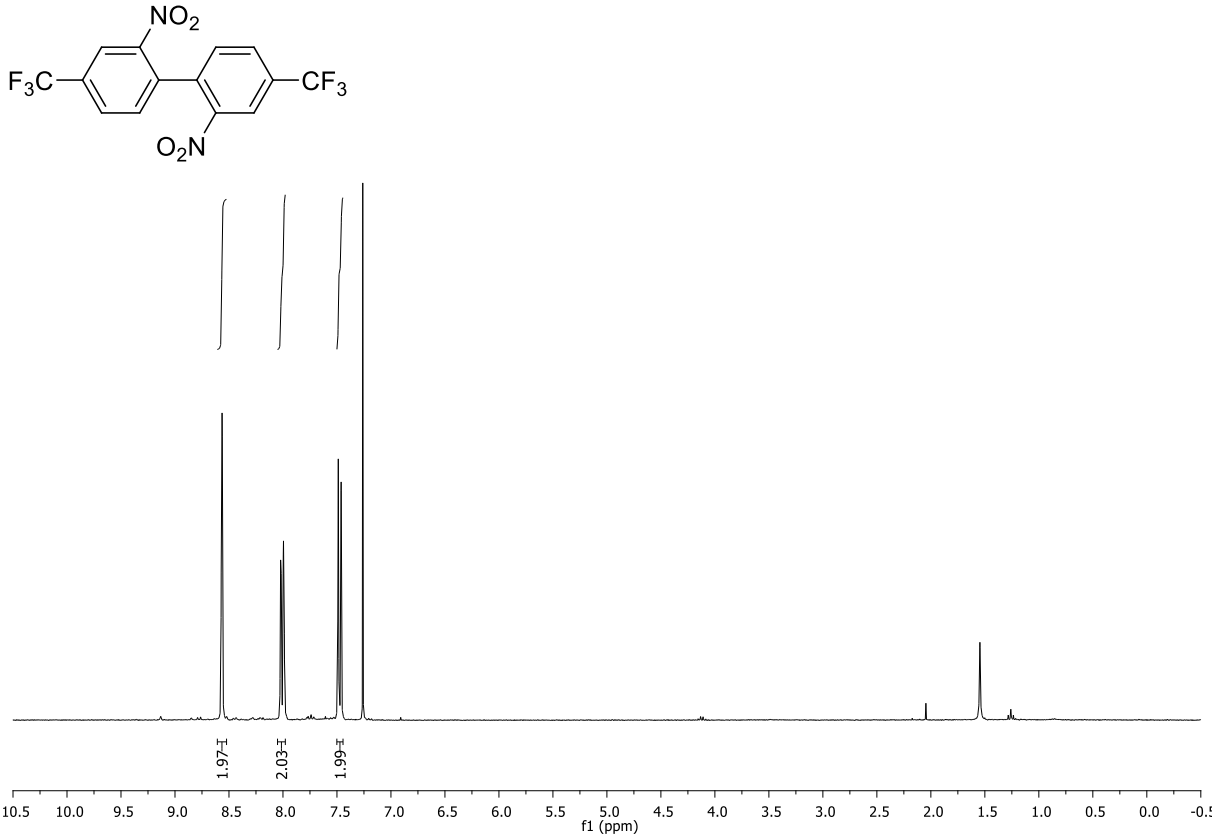
5.2 NMR-Spectra

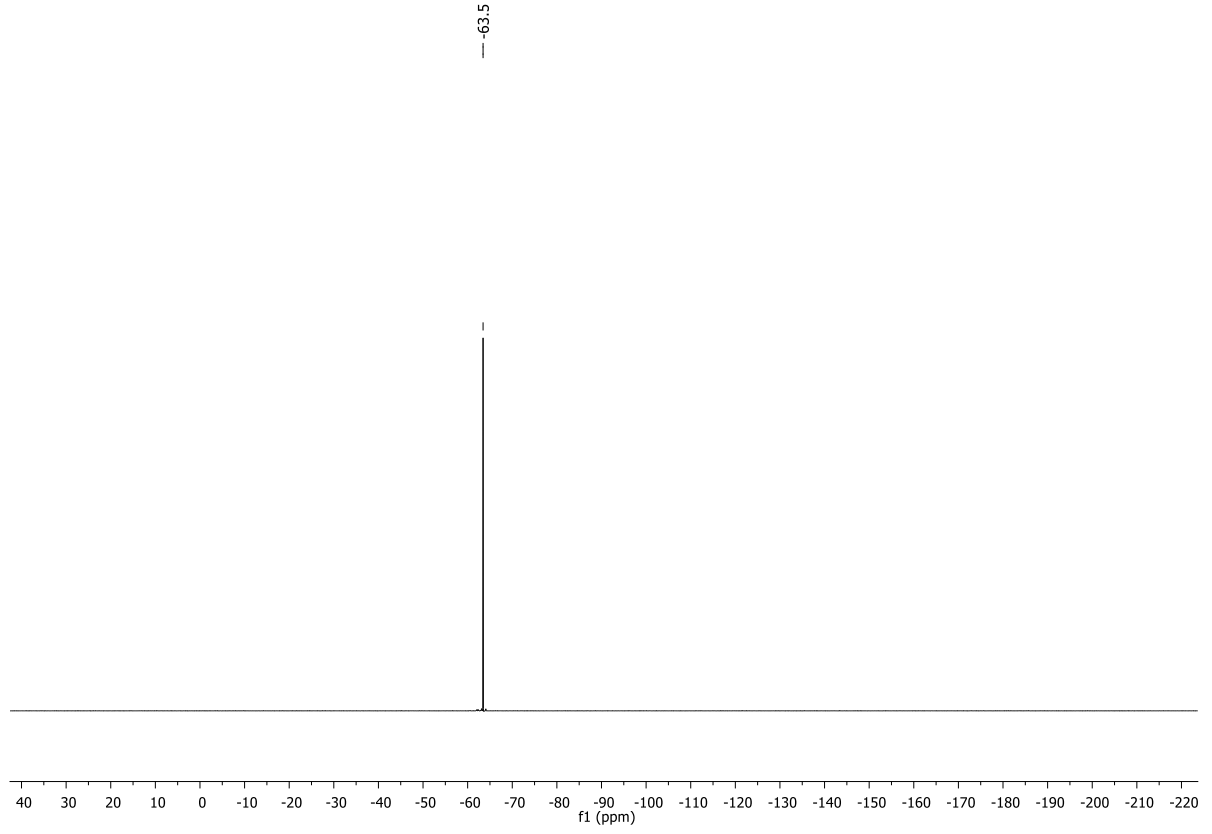


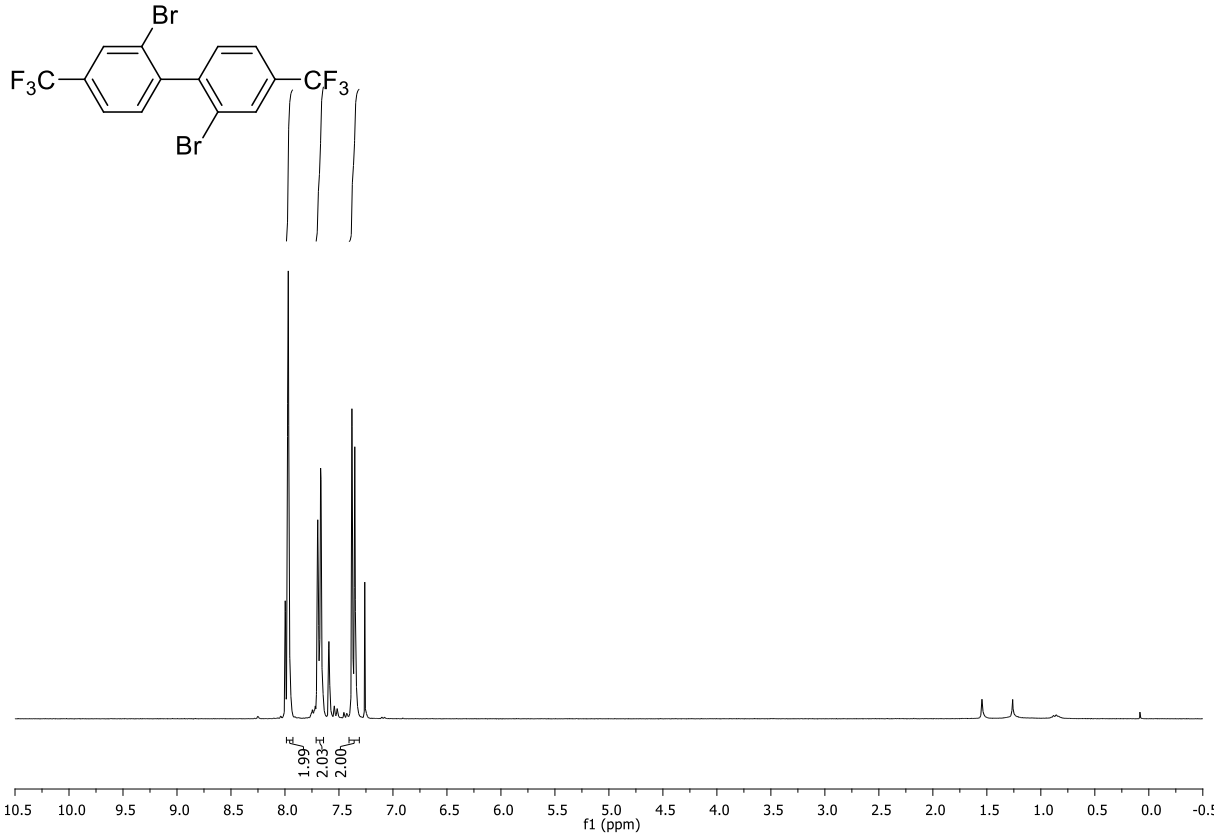


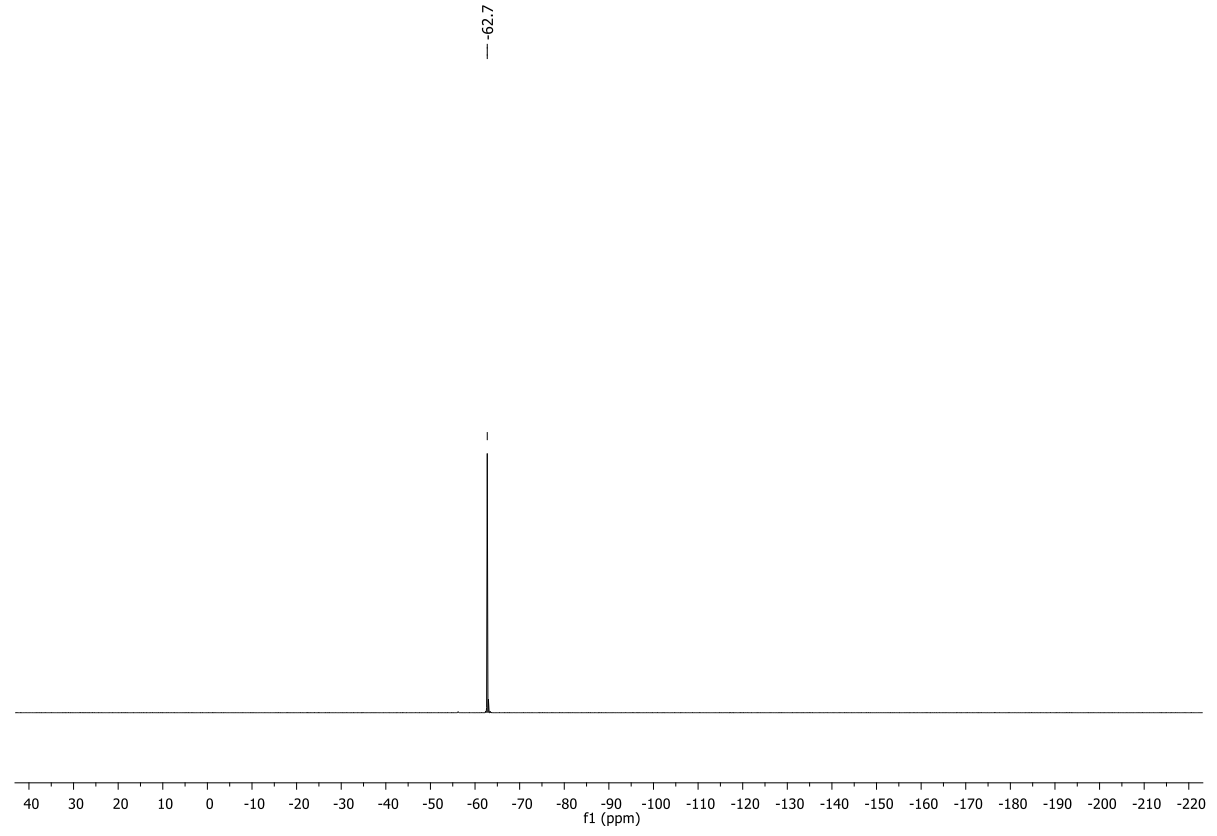

Br
Br
2.00
2.00
6.07
6.06
f1 (ppm)

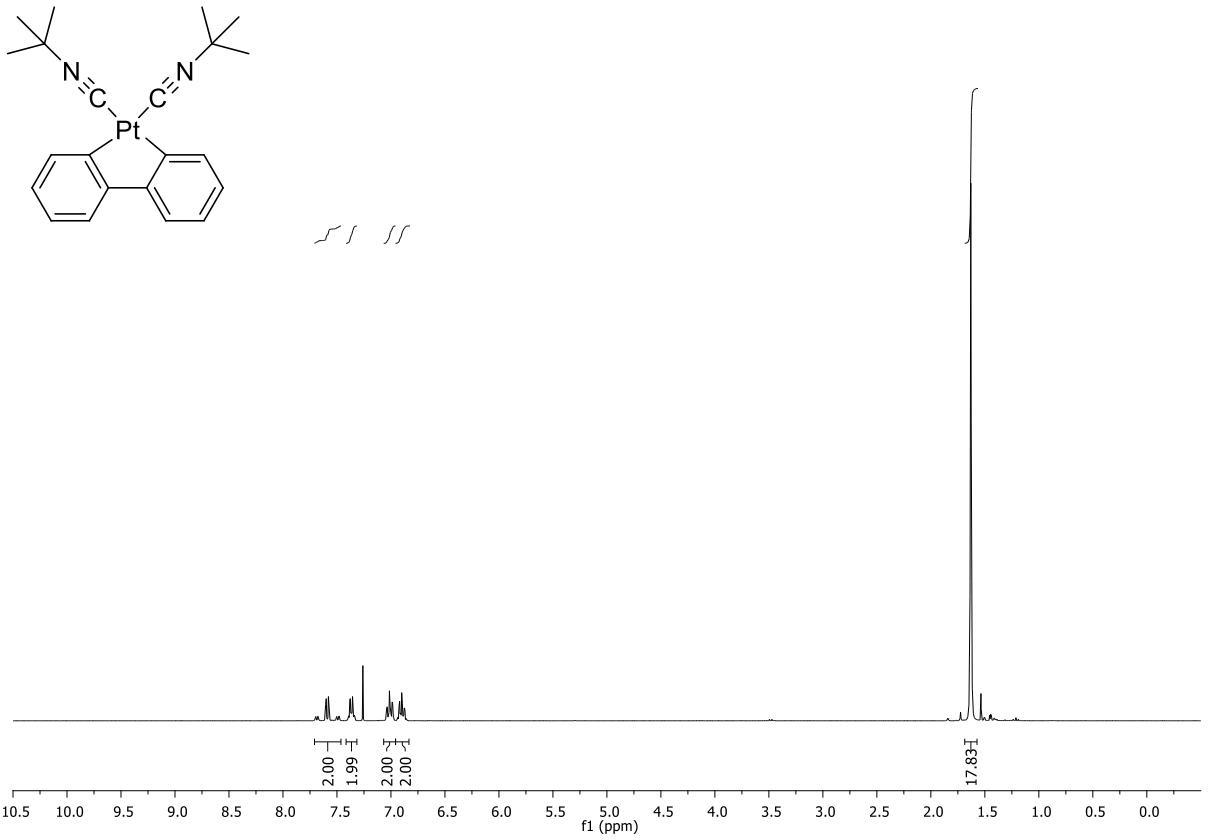

139.3
138.1
135.6
133.1
132.1
120.2
19.3
19.3
f1 (ppm)

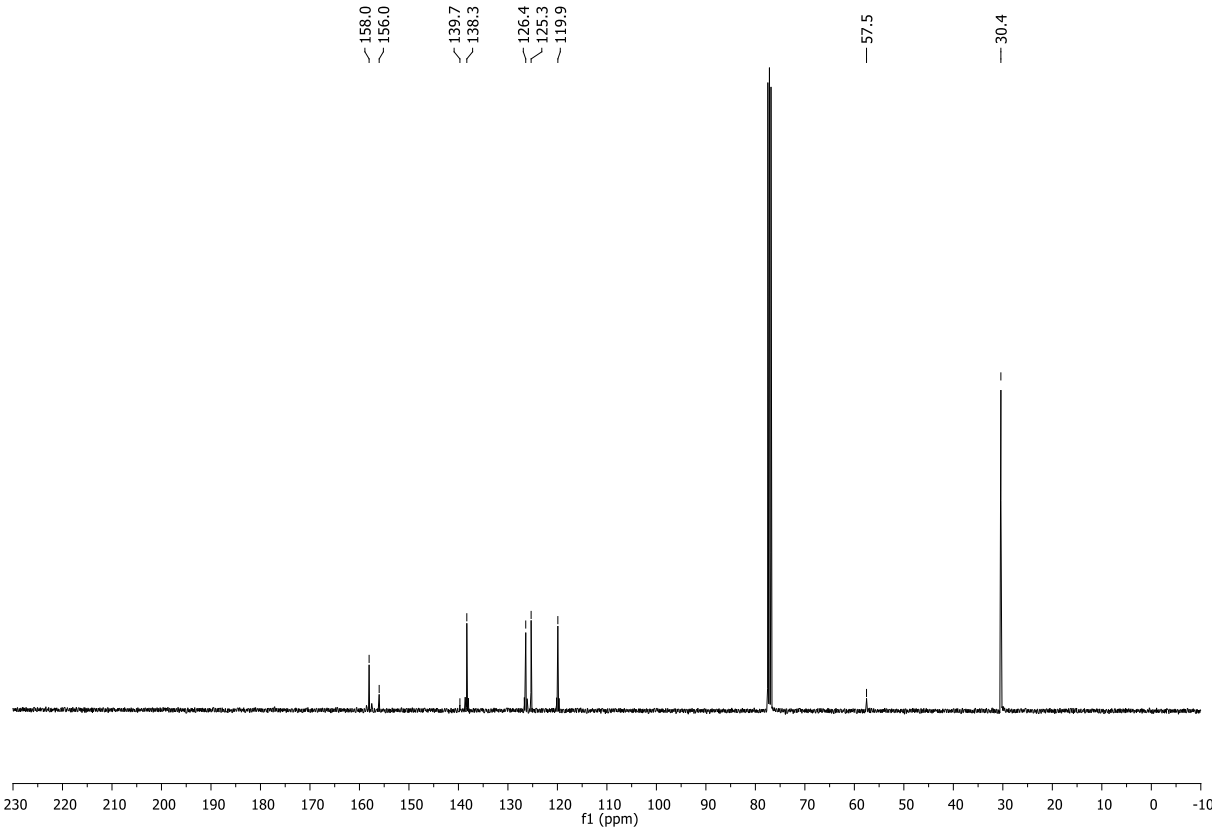

NO2
F3C
CF3
O2N
1.97
2.03
1.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

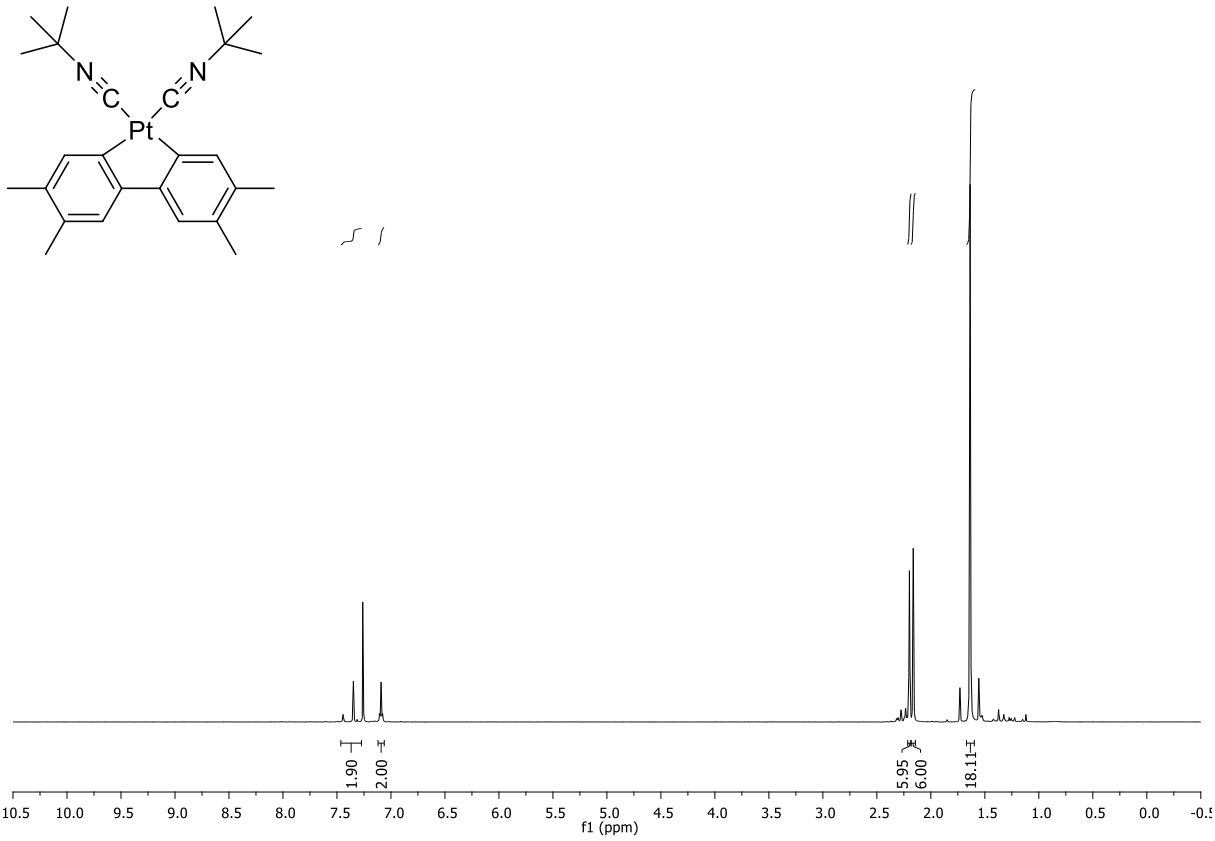

-63.5
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

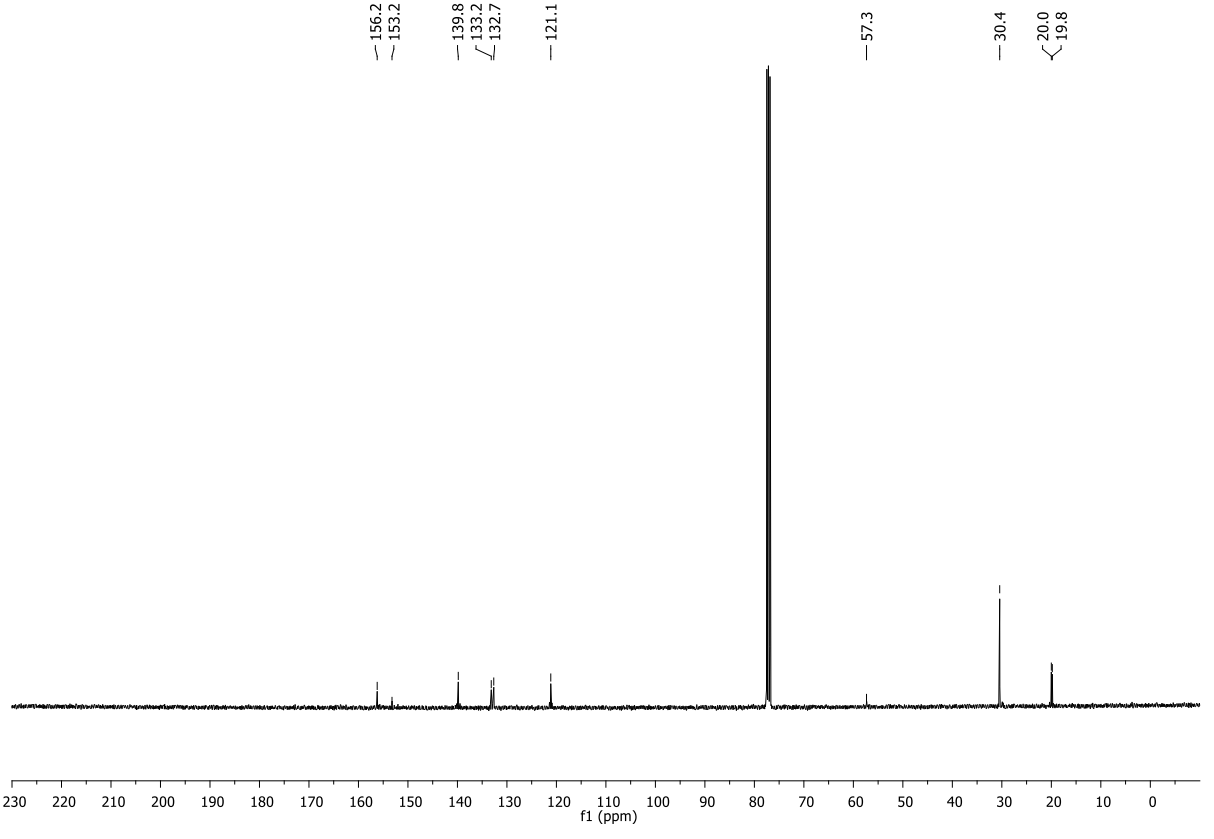

Br
F3C
CF3
Br
1.99
2.03
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

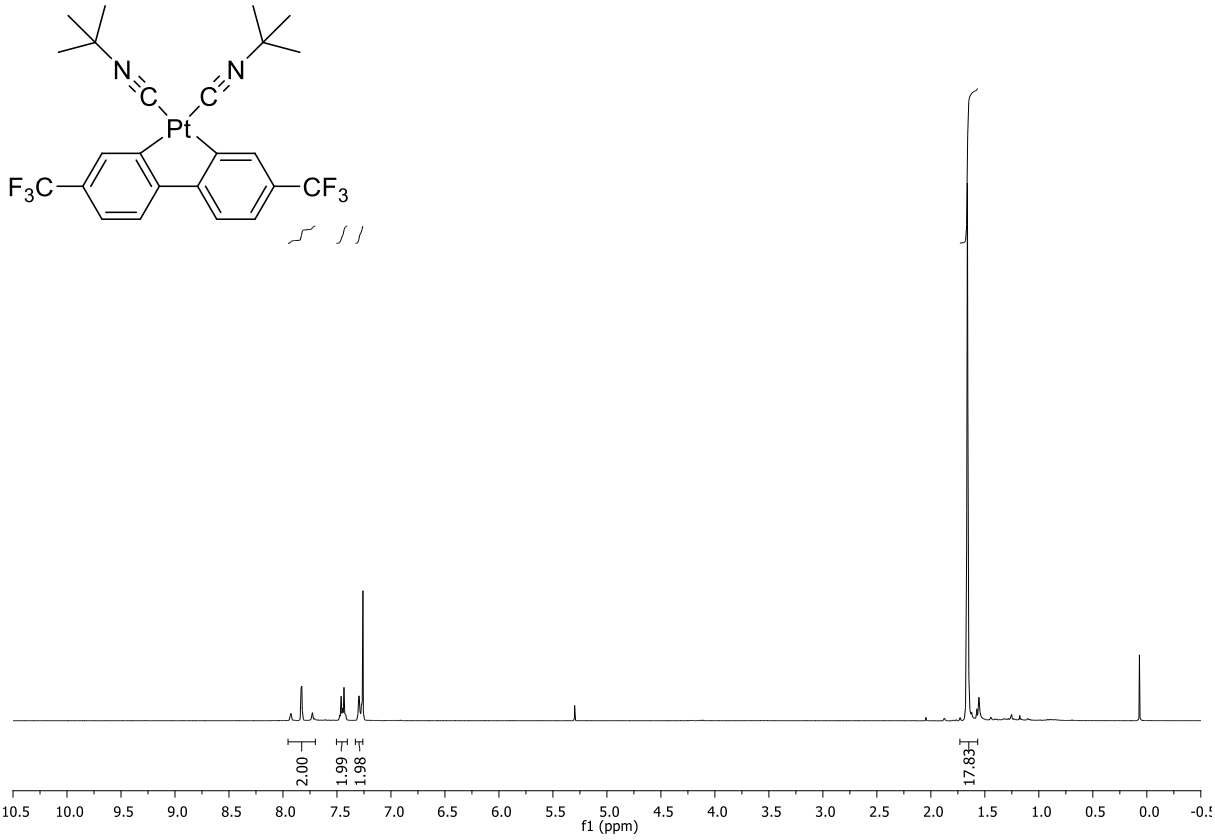

-62.7
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

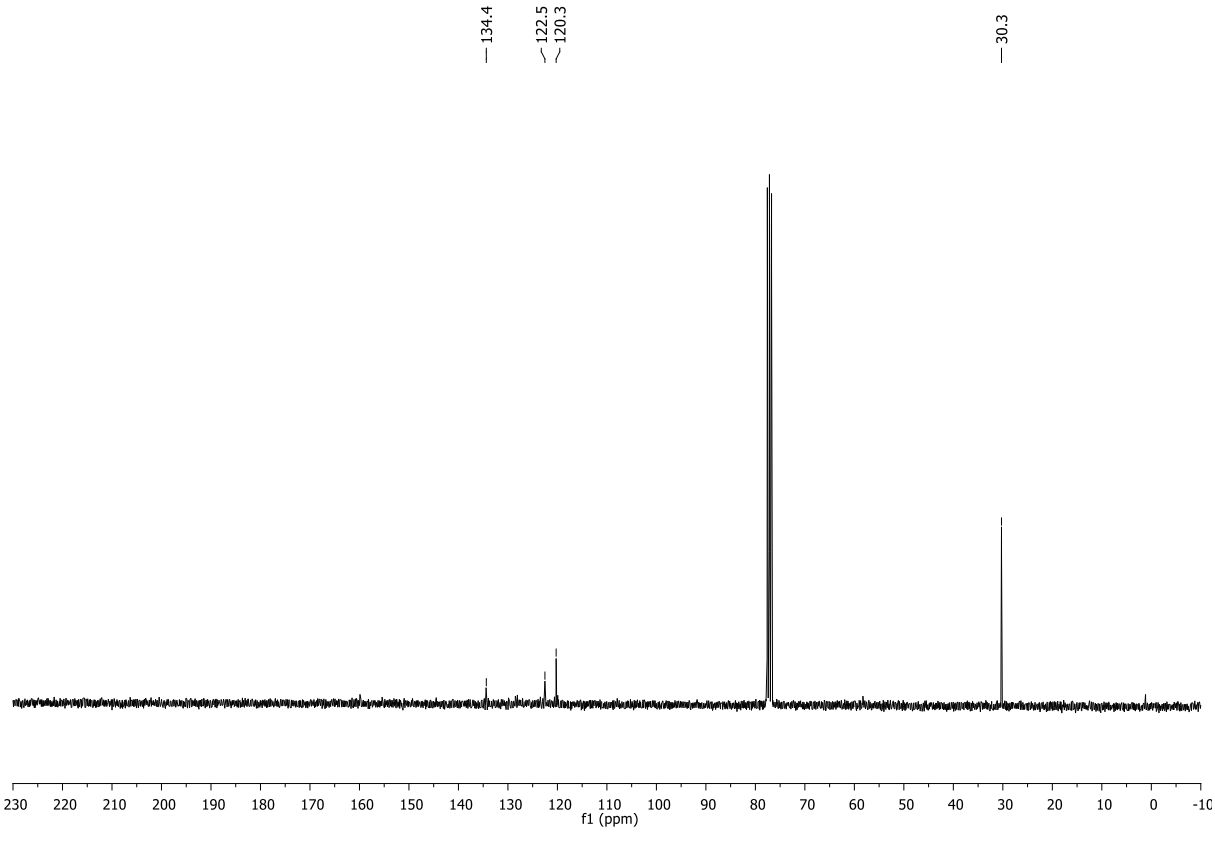

N
C
C
N
Pt
2.00
1.99
2.00
2.00
17.83
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

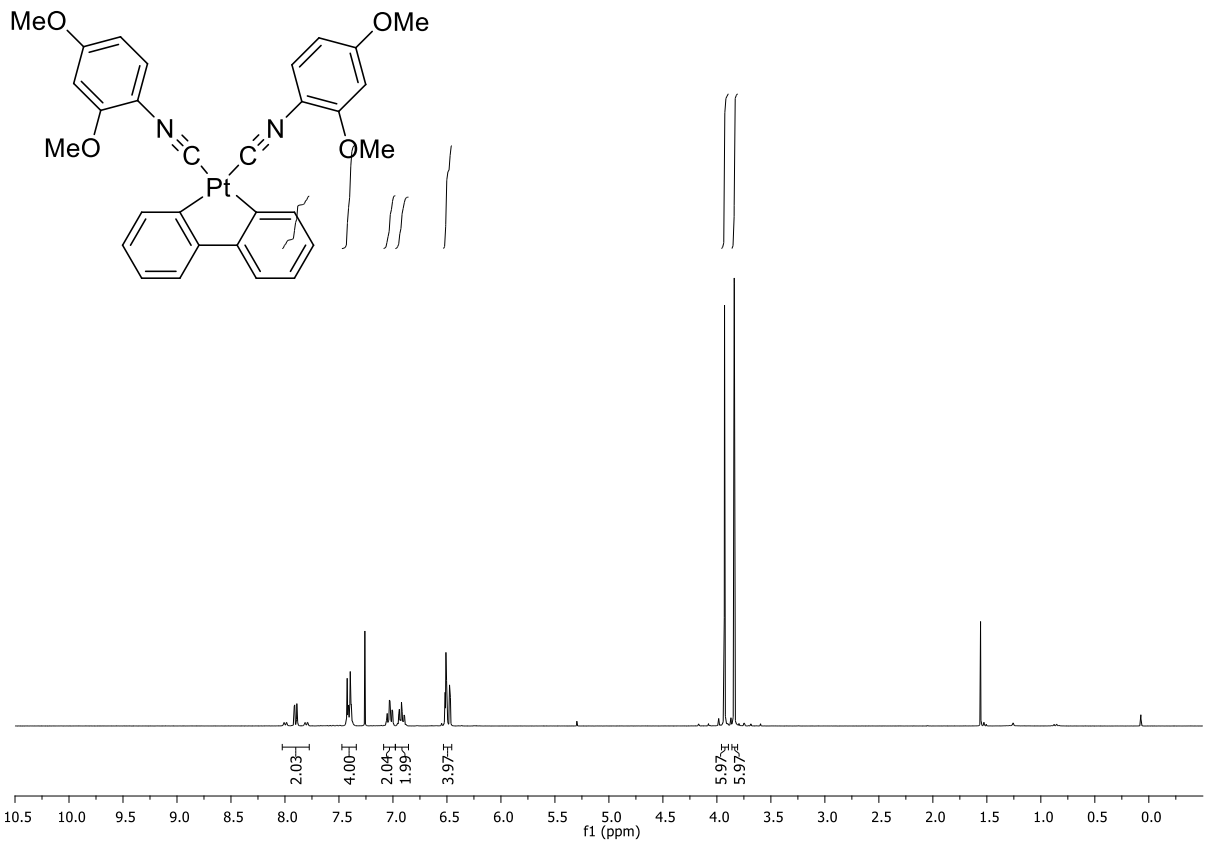

158.0
156.0
139.7
138.3
126.4
125.3
119.9
57.5
30.4
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

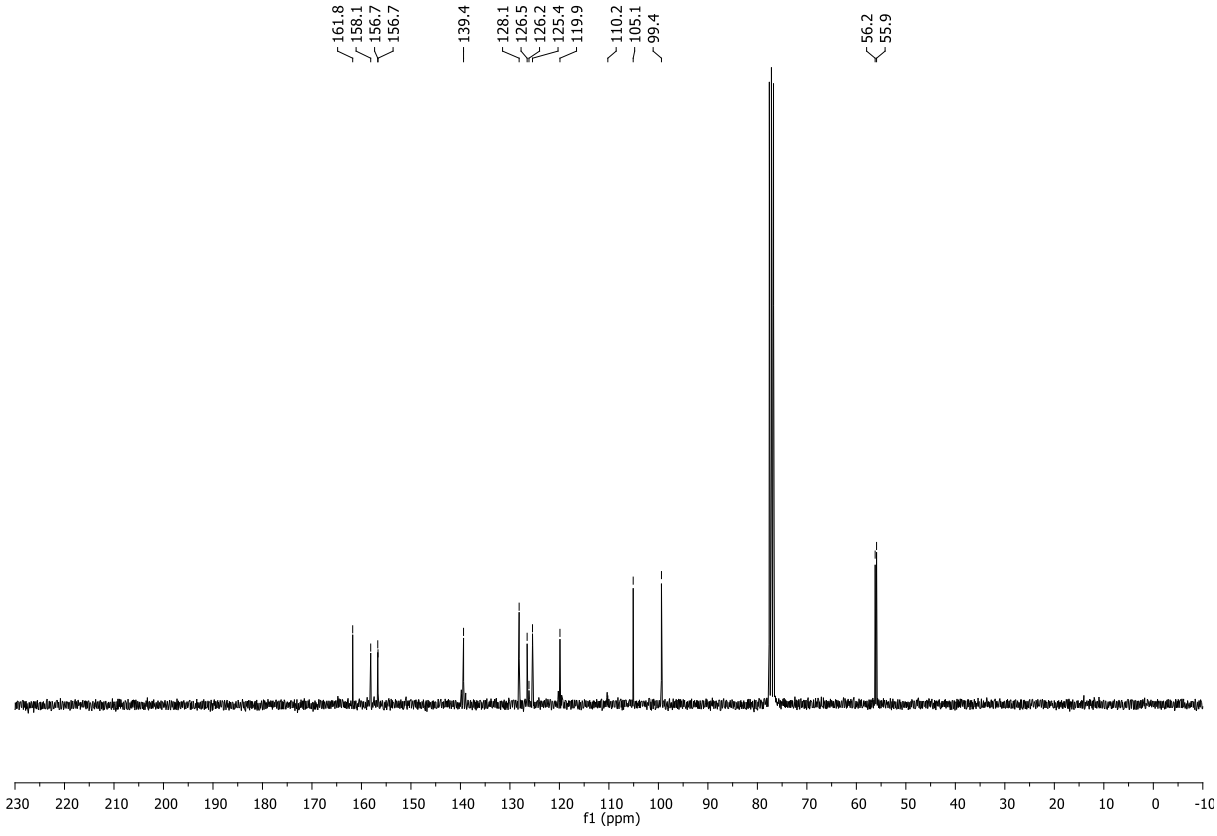

N
C
C
N
Pt
1.90
2.00
5.95
6.00
18.11
f1 (ppm)

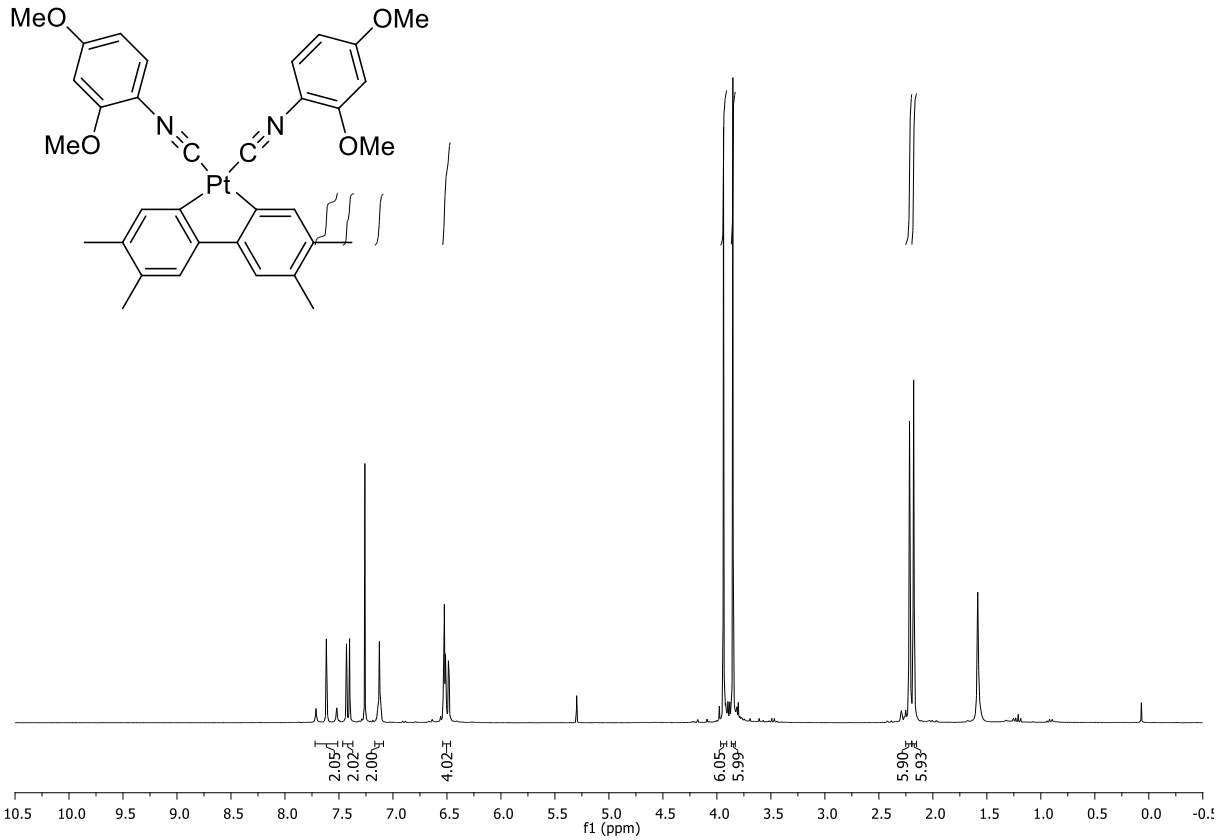

156.2
153.2
139.8
133.2
132.7
121.1
57.3
30.4
20.0
19.8
f1 (ppm)

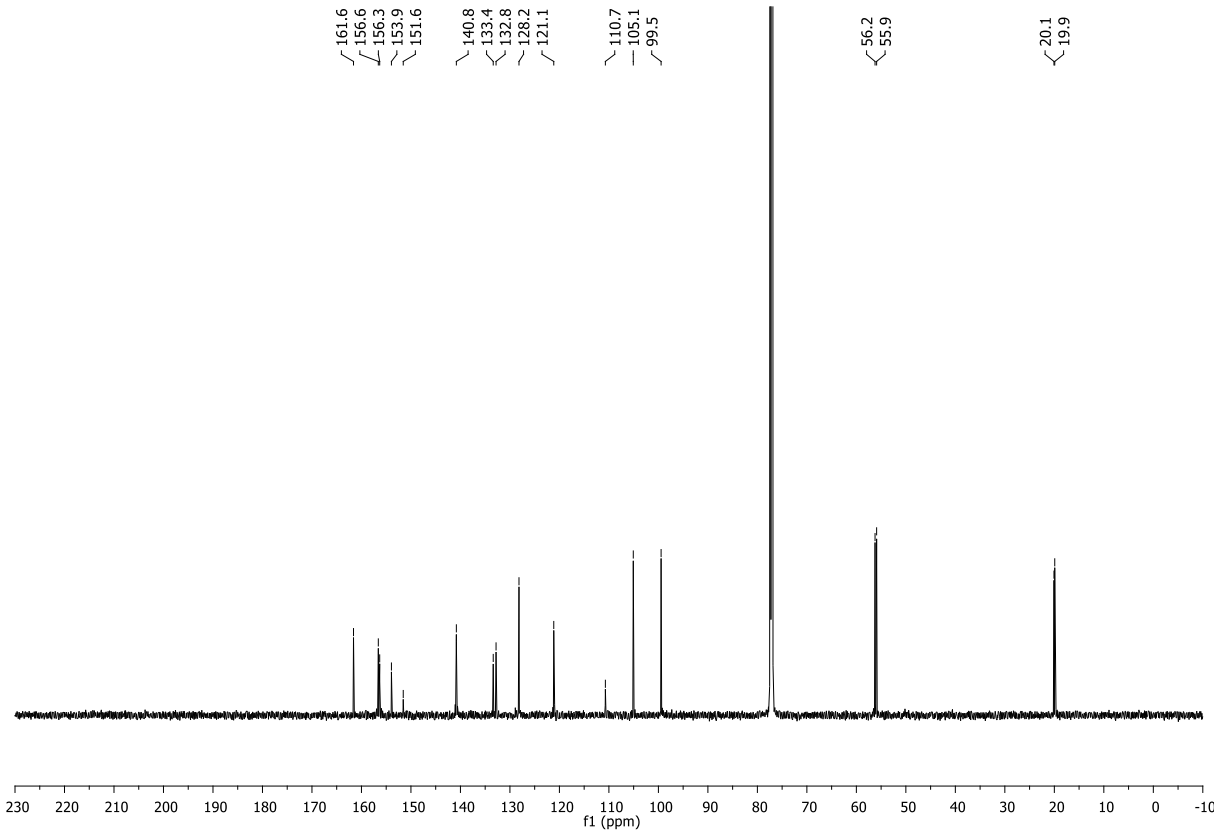

N
C
C
N
Pt
F3C
CF3
2.00
1.99
1.98
17.83
f1 (ppm)

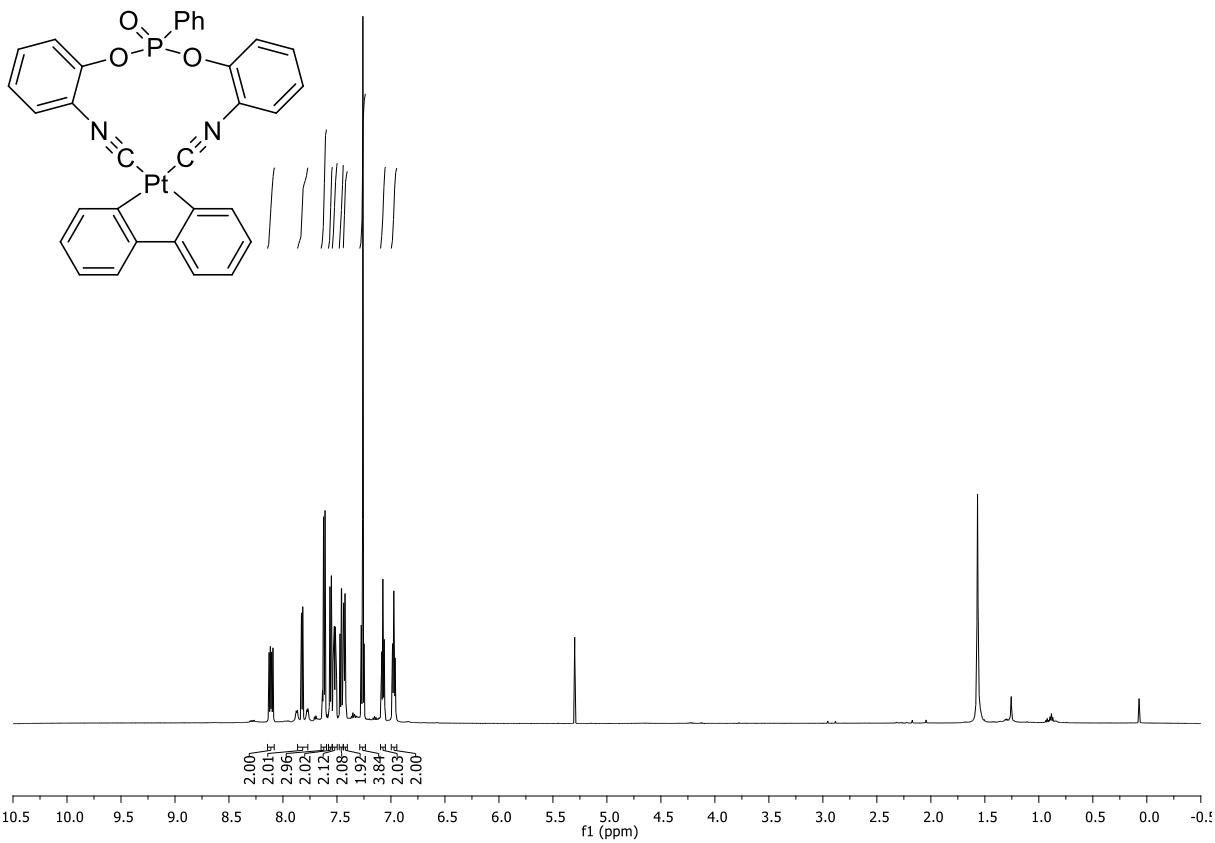

134.4
122.5
120.3
30.3
f1 (ppm)

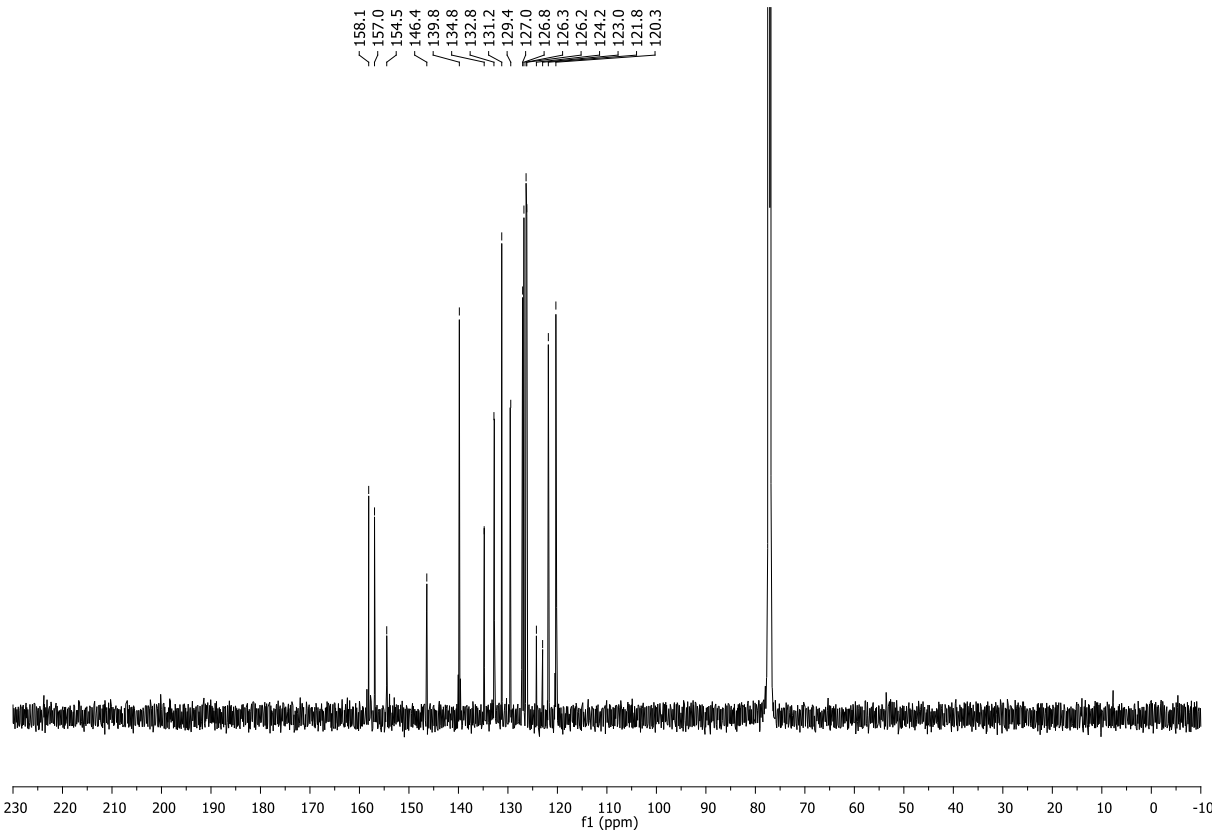

MeO
OMe
MeO
OMe
N
C
C
N
Pt
2.03
4.00
2.04
1.99
3.97
5.97
5.97
f1 (ppm)

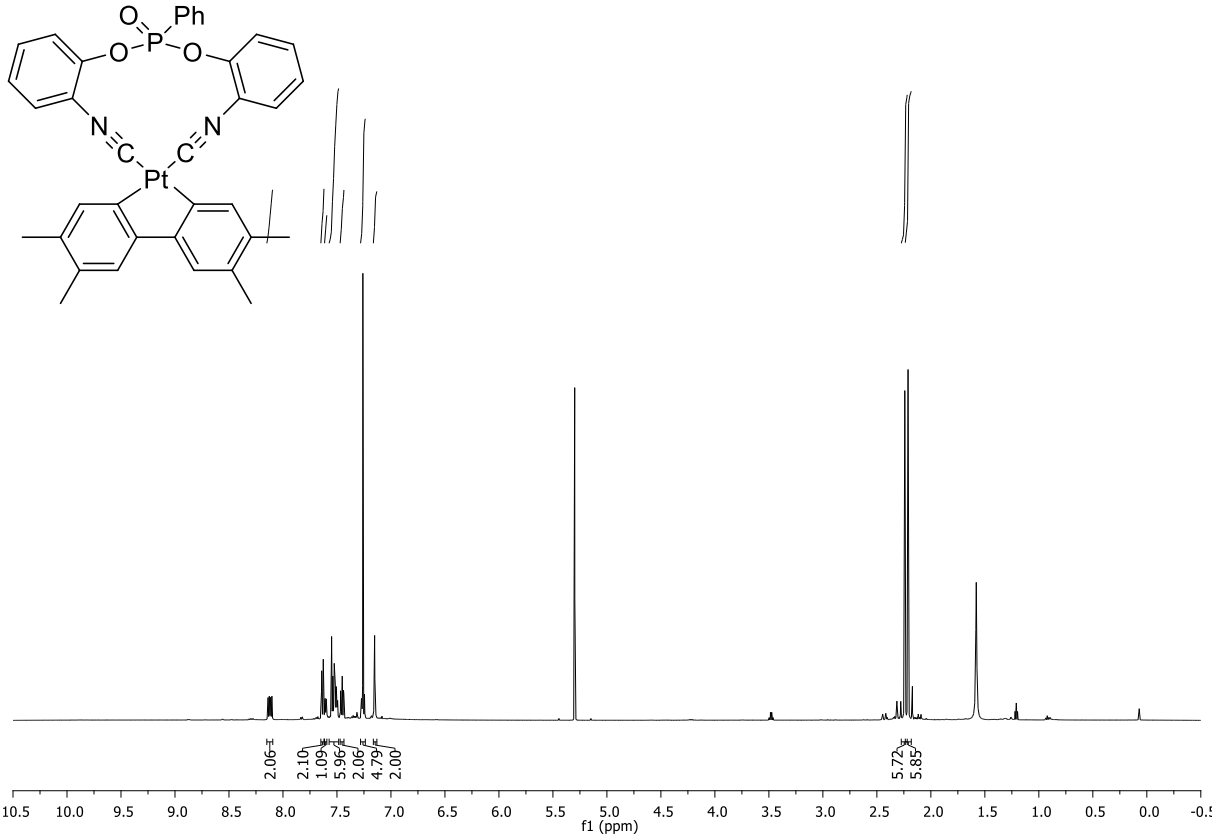

161.8
158.1
156.7
156.7
139.4
128.1
126.5
126.2
125.4
119.9
110.2
105.1
99.4
56.2
55.9
f1 (ppm)

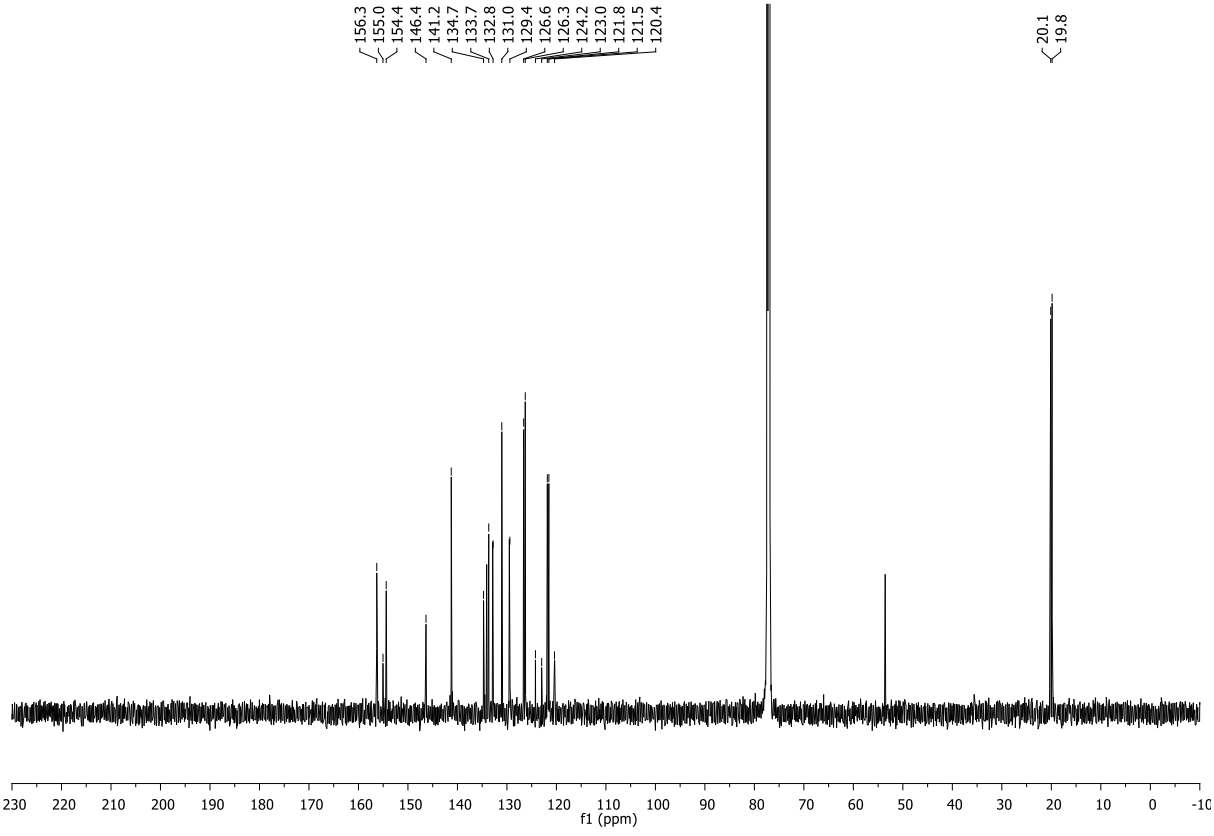

MeO
OMe
MeO
OMe
N
C
C
N
Pt
2.05
2.02
2.00
4.02
6.05
5.99
5.90
5.93
f1 (ppm)

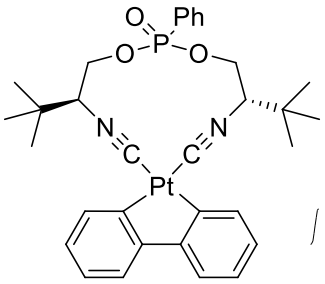

161.6
156.6
156.3
153.9
151.6
140.8
133.4
132.8
128.2
121.1
110.7
105.1
99.5
56.2
55.9
20.1
19.9
f1 (ppm)


O
Ph
P
O
O
N
C
C
N
Pt
2.00
2.01
2.96
2.02
2.12
2.08
1.92
3.84
2.03
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

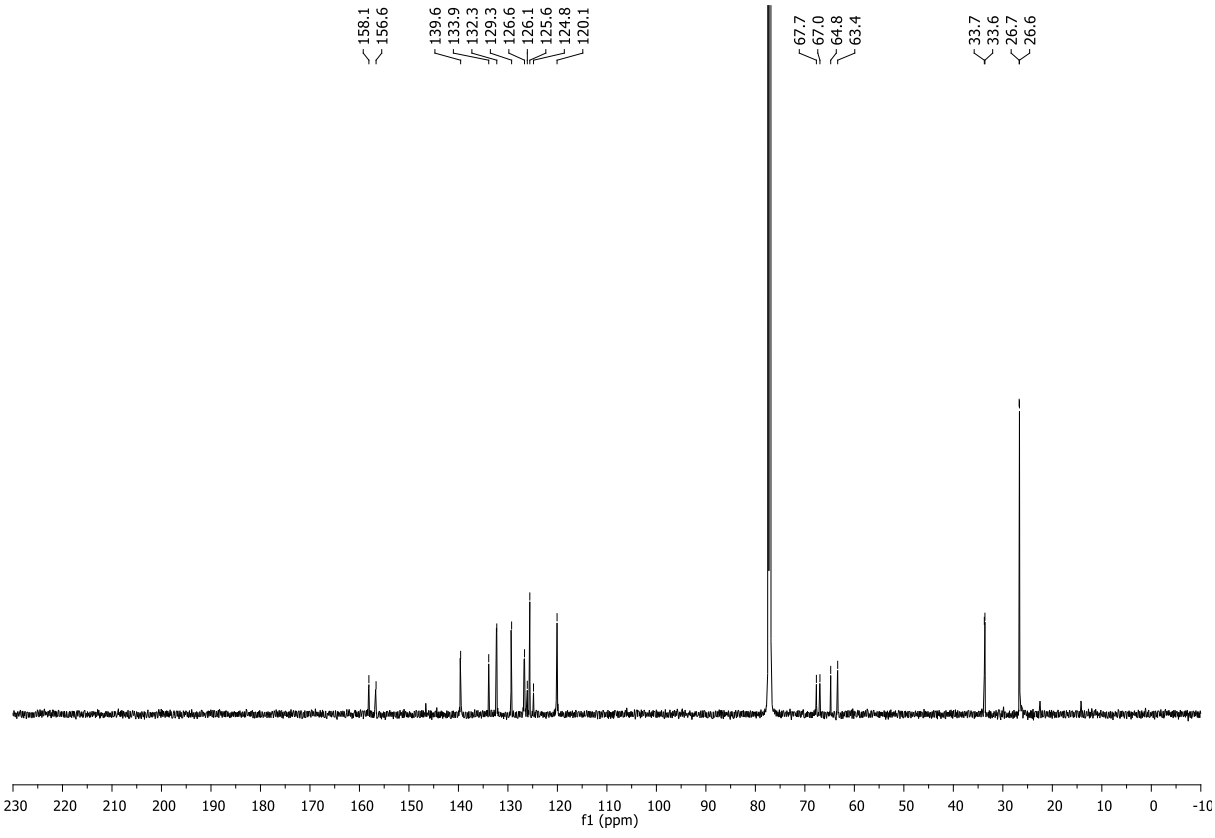

158.1
157.0
154.5
146.4
139.8
134.8
132.8
131.2
129.4
127.0
126.8
126.3
126.2
124.2
123.0
121.8
120.3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

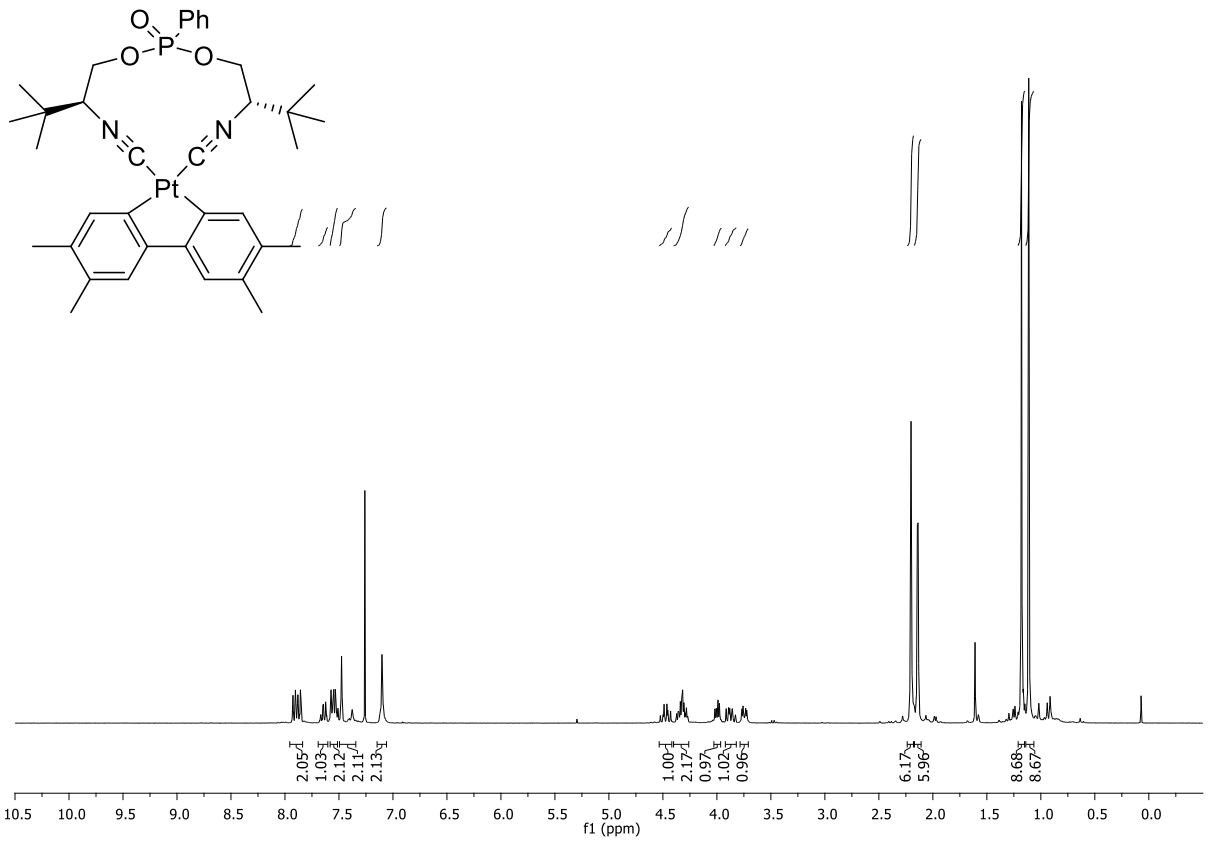

O
Ph
O
P
O
N
C
C
N
Pt
2.06
2.10
1.09
5.96
2.06
4.79
2.00
5.72
5.85
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

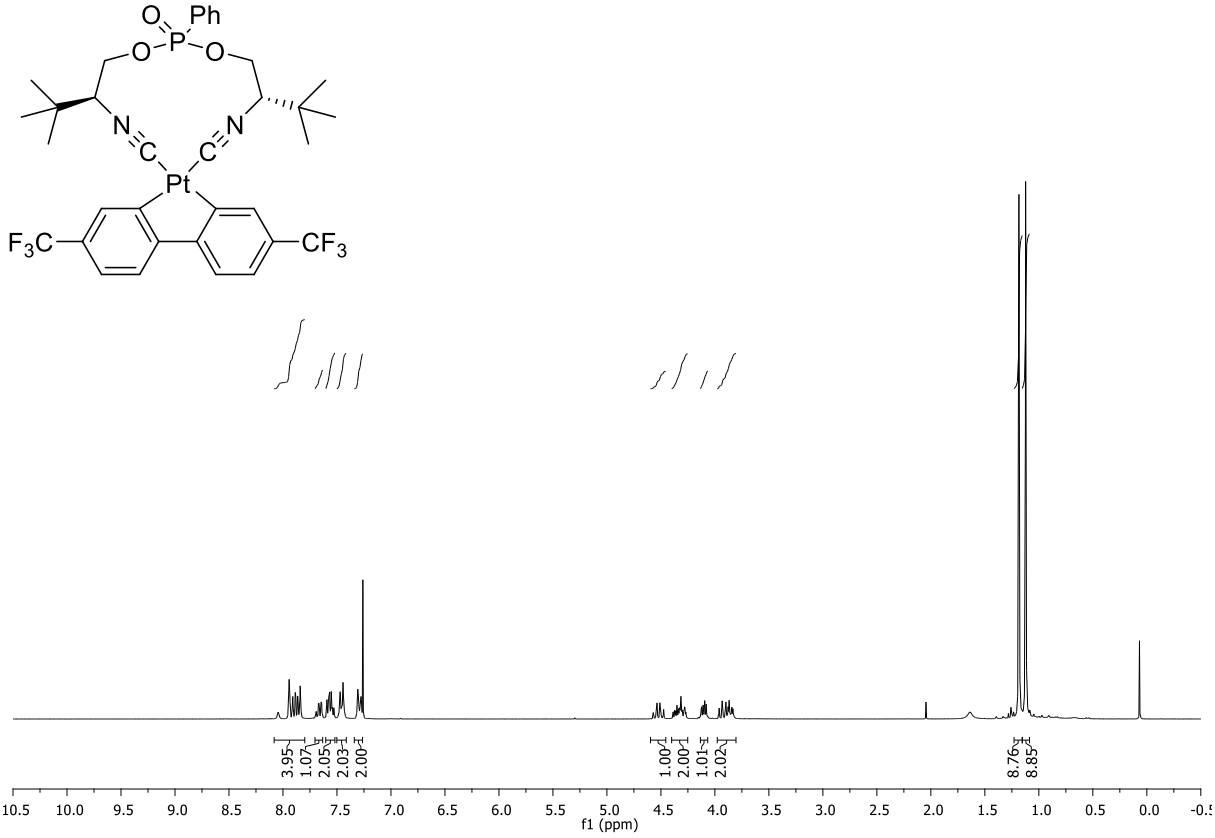

156.3
155.0
154.4
146.4
141.2
134.7
133.7
132.8
131.0
129.4
126.6
126.3
124.2
123.0
121.8
121.5
120.4
20.1
19.8
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

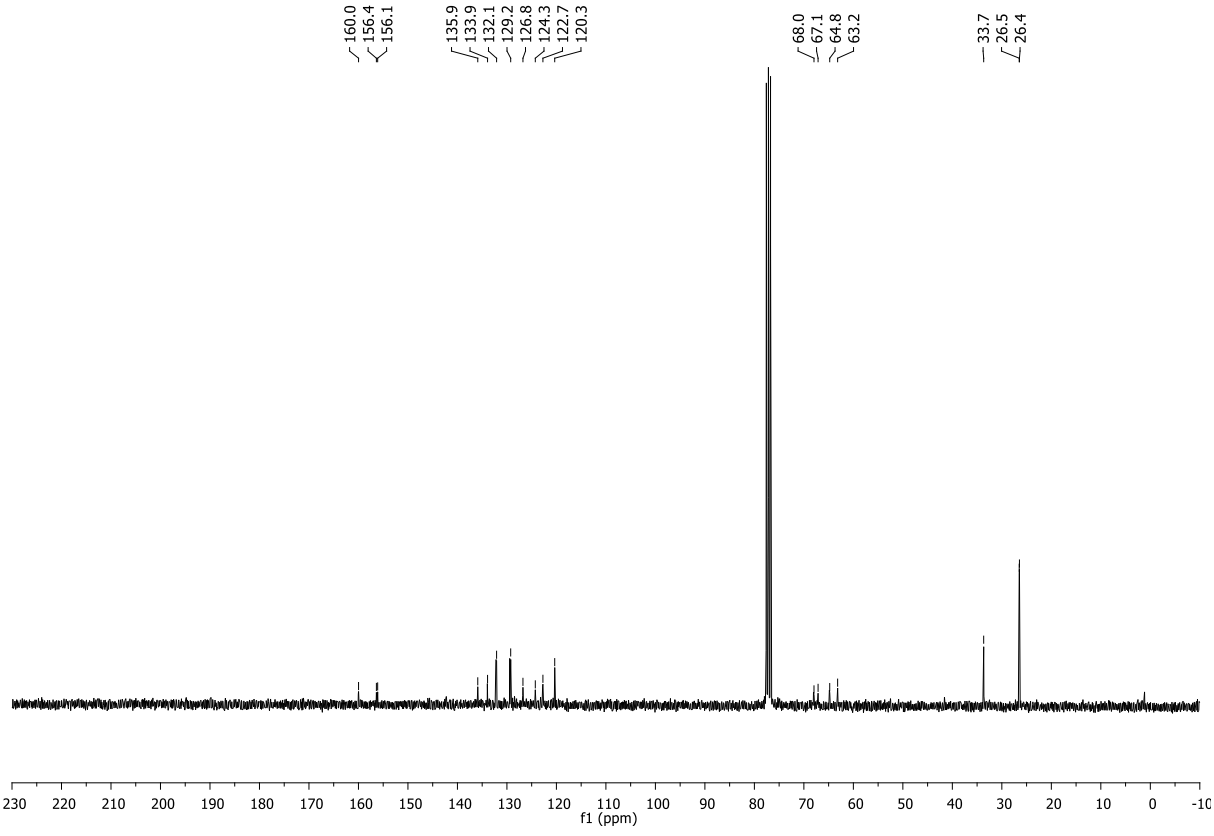

O
Ph
O
P
O
N
C
C
N
Pt

2.05
3.10
2.04
2.16
2.08
2.01
1.05
1.02
1.01
1.00
1.06
1.06
8.85
8.73
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

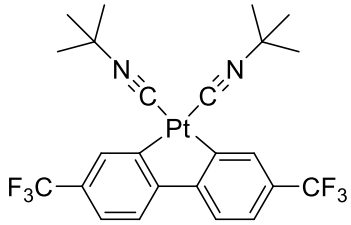

158.1
156.6
139.6
133.9
132.3
129.3
126.6
126.1
125.6
124.8
120.1
67.7
67.0
64.8
63.4
33.7
33.6
26.7
26.6
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Ph
O
P
O
N
C
C
N
Pt
2.05
1.03
2.12
2.11
2.13
1.00
2.17
0.97
1.02
0.96
6.17
5.96
8.68
8.67
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

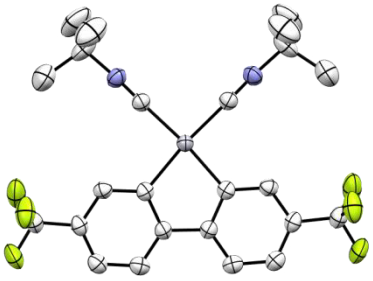

O
Ph
O
P
O
N
C
C
N
Pt
F3C
CF3
3.95
1.07
2.05
2.03
2.00
1.00
2.00
1.01
2.02
8.76
8.85
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


160.0
156.4
156.1
135.9
133.9
132.1
129.2
126.8
124.3
122.7
120.3
68.0
67.1
64.8
63.2
33.7
26.5
26.4
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

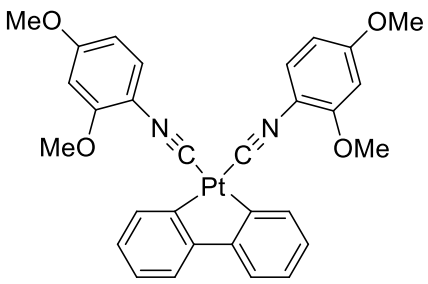
5.3 Solid-State Structures



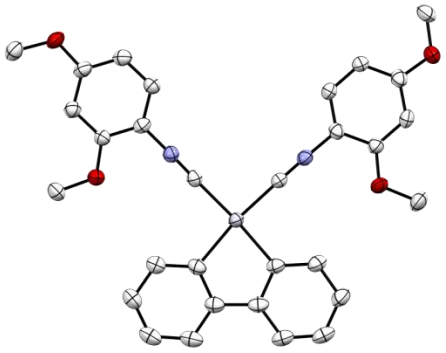
9c



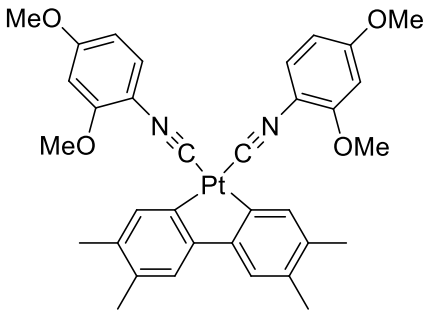
Formula	$C_{24}H_{24}F_6N_2Pt$
$D_{calc.}$/ g cm^{-3}	1.692
m/mm^{-1}	5.560
Formula Weight	649.54
Colour	faint yellow
Shape	prism
Max Size/mm	0.21
Mid Size/mm	0.12
Min Size/mm	0.07
T/K	123.00(10)
Crystal System	orthorhombic
Space Group	Pnma
a/Å	10.3298(5)
b/Å	24.6705(7)
c/Å	10.0050(4)
a/°	90
b/°	90
g/°	90
V/Å^3	2549.69(18)
Z	4
Z'	0.5
Q_{min}/°	3.207
Q_{max}/°	27.393
Measured Refl.	13066
Independent Refl.	2830
Reflections Used	2379
R_{int}	0.0331
Parameters	151
Restraints	0
Largest Peak	4.001
Deepest Hole	-1.905
GooF	1.208
wR_2 (all data)	0.1159
wR_2	0.1130
R_1 (all data)	0.0537
R_1	0.0454



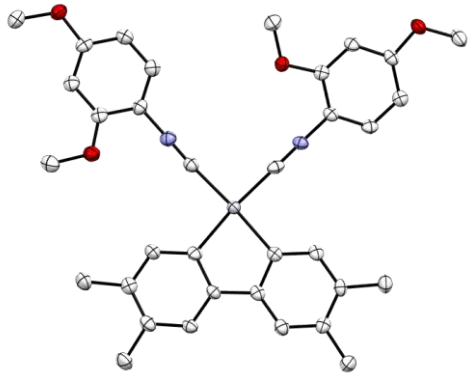
9d



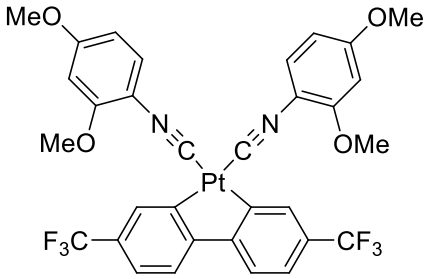
Formula	$C_{31}H_{27}Cl_3N_2O_4Pt$
$D_{calc.}$/ g cm^{-3}	1.742
m/mm^{-1}	11.444
Formula Weight	792.98
Colour	clear yellow
Shape	prism
Max Size/mm	0.25
Mid Size/mm	0.24
Min Size/mm	0.15
T/K	123(2)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	14.9446(2)
b/Å	15.11788(20)
c/Å	13.46944(18)
a/°	90
b/°	96.6033(12)
g/°	90
V/Å^3	3022.98(7)
Z	4
Z'	1
Q_{min}/°	2.977
Q_{max}/°	73.715
Measured Refl.	19089
Independent Refl.	5917
Reflections Used	5367
R_{int}	0.0378
Parameters	373
Restraints	0
Largest Peak	1.294
Deepest Hole	-3.387
GooF	1.087
wR_2 (all data)	0.1022
wR_2	0.0997
R_1 (all data)	0.0400
R_1	0.0365



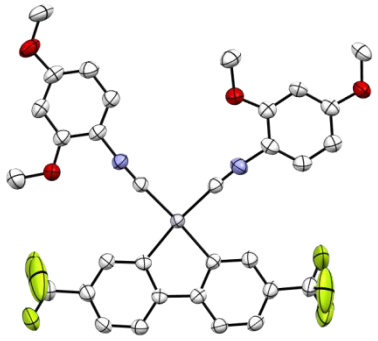
9e



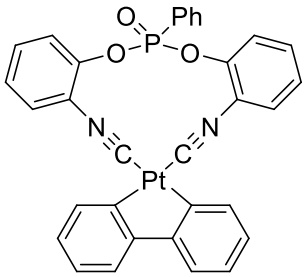
Formula	$C_{34}H_{34}N_2O_4Pt$
$D_{calc.}$/ g cm^{-3}	1.661
m/mm^{-1}	9.326
Formula Weight	729.72
Colour	clear intense yellow
Shape	trapezoid
Max Size/mm	0.32
Mid Size/mm	0.30
Min Size/mm	0.19
T/K	123.01(13)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	11.83280(16)
b/Å	9.04490(12)
c/Å	27.5935(4)
a/°	90
b/°	98.8100(13)
g/°	90
V/Å^3	2918.39(7)
Z	4
Z'	1
Q_{min}/°	3.241
Q_{max}/°	73.604
Measured Refl.	9697
Independent Refl.	5607
Reflections Used	5252
R_{int}	0.0251
Parameters	371
Restraints	0
Largest Peak	1.411
Deepest Hole	-2.058
GooF	1.037
wR_2 (all data)	0.0818
wR_2	0.0800
R_1 (all data)	0.0334
R_1	0.0313



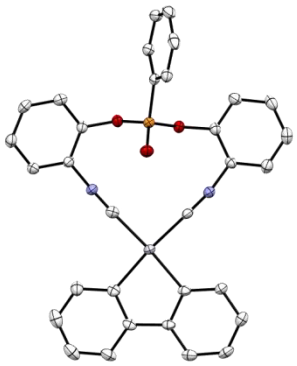
9f



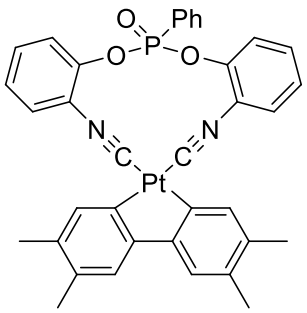
Formula	$C_{32}H_{24}N_2O_4F_6Pt$
$D_{calc.}$/ g cm^{-3}	1.788
m/mm^{-1}	4.743
Formula Weight	809.62
Colour	yellow
Shape	stick
Max Size/mm	0.42
Mid Size/mm	0.09
Min Size/mm	0.05
T/K	293(2)
Crystal System	monoclinic
Space Group	C2/c
a/Å	30.4338(5)
b/Å	7.70688(15)
c/Å	25.6556(5)
a/°	90
b/°	91.7798(15)
g/°	90
V/Å^3	6014.62(19)
Z	8
Z'	1
Q_{min}/°	3.072
Q_{max}/°	27.595
Measured Refl.	40585
Independent Refl.	6471
Reflections Used	5468
R_{int}	0.0510
Parameters	406
Restraints	0
Largest Peak	0.748
Deepest Hole	-0.652
GooF	1.046
wR_2 (all data)	0.0656
wR_2	0.0602
R_1 (all data)	0.0358
R_1	0.0262



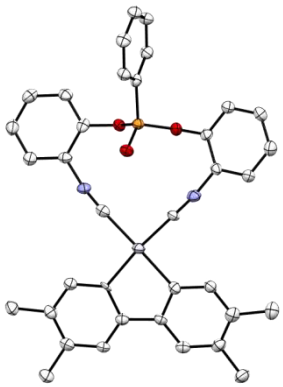
9g



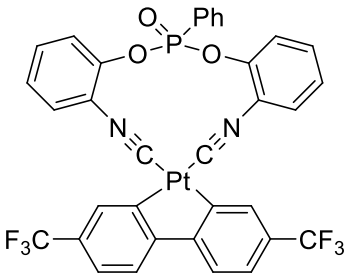
Formula	$C_{32}H_{21}N_2O_3PPt$
$D_{calc.}$/ g cm^{-3}	1.800
m/mm^{-1}	10.945
Formula Weight	707.57
Colour	yellow
Shape	plate
Max Size/mm	0.14
Mid Size/mm	0.07
Min Size/mm	0.03
T/K	123(2)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	8.53643(12)
b/Å	14.4198(2)
c/Å	21.2606(3)
a/°	90
b/°	94.0610(12)
g/°	90
V/Å^3	2610.47(7)
Z	4
Z'	1
Q_{min}/°	3.707
Q_{max}/°	73.747
Measured Refl.	12937
Independent Refl.	5048
Reflections Used	4509
R_{int}	0.0247
Parameters	352
Restraints	0
Largest Peak	0.503
Deepest Hole	-0.881
GooF	1.027
wR_2 (all data)	0.0496
wR_2	0.0478
R_1 (all data)	0.0245
R_1	0.0202



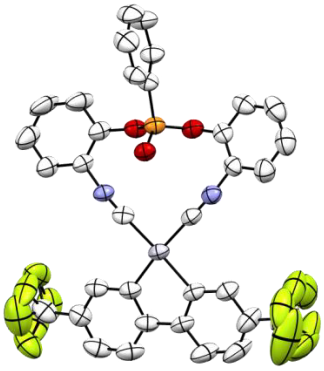
9h



Formula	$C_{75}H_{61}N_4O_6P_2Pt_2Cl_9$
$D_{calc.}$/ g cm^{-3}	1.689
m/mm^{-1}	10.792
Formula Weight	1885.44
Colour	yellow
Shape	rod
Max Size/mm	0.12
Mid Size/mm	0.07
Min Size/mm	0.04
T/K	123
Crystal System	triclinic
Space Group	P-1
a/Å	12.2372(7)
b/Å	13.0892(6)
c/Å	23.6083(10)
a/°	86.566(4)
b/°	85.687(4)
g/°	79.787(4)
V/Å^3	3706.8(3)
Z	2
Z'	1
Q_{min}/°	3.678
Q_{max}/°	73.811
Measured Refl.	27518
Independent Refl.	14426
Reflections Used	11965
R_{int}	0.0401
Parameters	892
Restraints	3
Largest Peak	2.028
Deepest Hole	-2.172
GooF	1.085
wR_2 (all data)	0.1181
wR_2	0.1118
R_1 (all data)	0.0561
R_1	0.0449



9i



Formula	$C_{34}H_{19}F_6N_2O_3PPt$
$D_{calc.}$/ g cm^{-3}	1.817
m/mm^{-1}	4.678
Formula Weight	843.57
Colour	yellow
Shape	needle
Max Size/mm	0.17
Mid Size/mm	0.03
Min Size/mm	0.02
T/K	293(2)
Crystal System	monoclinic
Space Group	C2/c
a/Å	20.9167(4)
b/Å	16.0129(3)
c/Å	18.4104(4)
a/°	90
b/°	90.016(2)
g/°	90
V/Å^3	6166.3(2)
Z	8
Z'	1
Q_{min}/°	3.187
Q_{max}/°	28.159
Measured Refl.	20902
Independent Refl.	6534
Reflections Used	3723
R_{int}	0.0353
Parameters	478
Restraints	0
Largest Peak	0.526
Deepest Hole	-0.454
GooF	0.737
wR_2 (all data)	0.0403
wR_2	0.0377
R_1 (all data)	0.0629
R_1	0.0253

5.4 Photophysical Properties

Emission maxima, quantum yield and lifetime of **9a** – **9l** at ambient temperature was measured in poly(methyl methacrylate) (PMMA).

	$\lambda_{em,max}$ [nm]	Φ_{PL} [%]	τ [µs]
9a	508, 547	31	
9b	531, 571	19	14
9c	509, 548	28	17
9d	515, 554	37	13
9e	543, 582	28	11
9f	512, 550	39	15
9g	527, 556	38	11
9h	580	21	6
9i	521, 561	47	12
9j	543	29	13
9k	537, 573	15	14
9l	508, 546	29	15

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H Appendix

1. List of Publications

[11] M. Knorn and O. Reiser,
"*Metal-Isonitriles in Catalysis*",
ChemCatChem, in manuscript.

[10] M. Knorn, E. Lutsker and O. Reiser,
"*Synthesis of New Chiral Bidentate Isonitrile-Acyclic Diaminocarbene-Palladium(II) Compounds and Their Catalytic Activity*",
Organometallics **2015**, DOI: 10.1021/acs.organomet.5b00516.

[9] M. Knorn, T. Rawner, R. Czerwieniec and O. Reiser,
"*[Copper(phenanthroline)(bisisonitrile)]$^{+}$-Complexes for the Visible-Light-Mediated Atom Transfer Radical Addition and Allylation Reactions*",
ACS Catal. **2015**, *5*, 5186-5193.

[8] D. B. Bagal, G. Kachkovski, M. Knorn, T. Rawner, B. M. Bhanage and O. Reiser,
"*Trifluoromethylchlorosulfonylation of alkenes - evidence for an inner sphere mechanism by a copperphenanthroline photoredox catalyst*",
Angew. Chem. Int. Ed. **2015**, *54*, 6999 - 7002; *Angew. Chem*. **2015**, *127*, 7105 - 7108.

[7] A. P. G. Macabeo, P. Y. M. Rubio, G. J. D. Alejandro and M. Knorn,
"*An α-Glucosiase Inhibitor from Drepananthus philippinensis*",
Procedia Chemistry **2015**, *14*, 36 - 39.

[6] J. L. A. Covarrubias, A. P. G. Macabeo, O. B. Villaflores, M. Knorn, P. Kohls and A. V. Bayquen,
"*Antibacterial Activity and Concentration Dependent Modulation of Angiogenesis of the Saponins of Schefflera Iuzoniensis*",
Res. J. Pharm., Biol. Chem. Sci. **2015**, *6*, 418 - 422.

[5] A. P. G. Macabeo, F. P. A. Martinez, T. Kurtán, L. Tóth, A. Mándi, S. Schmidt, J. Heilmann, G. J. D. Alejandro, M. Knorn, H.-M. Dahse and S. G. Franzblau, "*Tetrahydroxanthene-1,3(2H)-dione Derivatives from Uvaria valderramensis*", *J. Nat. Prod*. **2014**, *77*, 2711 - 2715.

[4] S. B. Lirio., A. P. G. Macabeo, E. M. Paragas, M. Knorn, P. Kohls, S. G. Franzblau, Y. Wang and A. M. Aguinaldo, "*Antitubercular constituents from Premna odorata Blanco*", *J. Ethnopharmacol*. **2014**, *154*, 471 - 474.

[3] A. Suresh Kumar, M. Amarnath Reddy, M. Knorn, O. Reiser and B. Sreedhar, **"***Magnetically Recoverable $CuFe_2O_4$ Nanoparticles: Catalyzed Synthesis of Aryl Azides and 1,4-Diaryl-1,2,3-triazoles from Boronic Acids in Water*", *Eur. J. Org. Chem*. **2013**, *21*, 4674 - 4680.

[2] W. S. Vidar, A. P. G. Macabeo, M. Knorn, P. Kohls and A. M. Aguinaldo, "*Polymethoxylated flavones from Micromelum compressum*", *Biochem. Syst. Ecol*. **2013**, *50*, 48 - 50.

[1] B. G. Panlilioa, A. P. G. Macabeo, M. Knorn, P. Kohls, P. Richomme, S. F. Kouam, D. Gehle, K. Krohn, S. G. Franzblau, Q. Zhang and A. M. Aguinaldo, "*A lanostane aldehyde from Momordica charantia*", *Phytochem. Lett*. **2012**, *5*, 682 - 684.

2. Congresses and Scientific Meetings

[5] M. Knorn, T. Rawner and Oliver Reiser
"*New Phenanthroline-Isonitrile-Copper(I) Complexes as Visible-Light Photoredox Catalysts*",
5th EuCheMS Chemistry Congress 2014, Istanbul, Turkey

[4] M. Knorn and O. Reiser
"*New Bidentate Isonitrile/NAC-Pd(II) Complexes for the Asymmetric Allylic Alkylation*"
GDCh-Wissenschaftsforum 2013, Darmstadt, Germany

[3] M. Knorn and O. Reiser
"*New Chiral Bidentate Isonitrile/NAC-Pd(II) Complexes*"
Forum of Molecular Catalysis 2013, Heidelberg, Germany

[2] M. Knorn, A. S. Kumar, B. Sreedhar and O. Reiser
„*Magnetically Recoverable $CuFe_2O_4$ Nanoparticles: Catalyzed Synthesis of Aryl Azides and 1,4-Diaryl-1,2,3-triazoles from Boronic Acids*"
4th EuCheMS Chemistry Congress 2012, Prague, Czech Republic

[1] M. Knorn and O. Reiser
"*Immobilization of Catalysts on Nanomagnets*"
3rd INDIGO Conference 2012, Chennai, India

3. Curriculum Vitae

Matthias Korbinian Christian Knorn

PERSONAL DETAILS

Date of birth	3rd April 1986
Place of birth	Pfaffenhofen a. d. Ilm, Germany
Nationality	German

EDUCATION

10/2011 – 09/2015	**PhD Thesis**, University of Regensburg, Germany "*Metal-Isonitriles – Synthesis, Characterization and Application in Catalysis*" (Institute of Organic Chemistry: Prof. Oliver Reiser) Including a three month research project at the IICT Hyderabad, India (Inorganic and Physical Chemistry: Dr. Bojja Sreedhar)
10/2009 – 09/2011	**Master of Science** Chemistry, University of Regensburg Master Thesis: "*Synthesis and Characterization of Gold-Isonitriles and Their Use in Catalysis*" (Institute of Organic Chemistry: Prof. Oliver Reiser)
10/2006 – 09/2009	**Bachelor of Science** Chemistry, University of Regensburg Bachelor Thesis: "*Untersuchung neuer Ausgangsverbindungen für die stereoselektive Synthese von Paeonilid*" (Institute of Organic Chemistry: Prof. Oliver Reiser)
10/2005 – 06/2006	**Basic Military Service** Führungsunterstützungsbatallion 292, Dillingen/Donau
09/1995 – 06/2005	**University Entrance Diploma** Schyren-Gymnasium, Pfaffenhofen/Ilm

ADVANCED EDUCATION / CERTIFICATES

09/2014 – 02/2015	*Business Studies for Developer,* Strategischen Partnerschaft Sensorik
11/2014	*Quality Systems GMP und GLP - An Overview,* GDCh-Education
05/2014	*Introduction in Business Studies for Chemists,* GDCh-Education
09/2009	Umfassende Sachkunde nach § 5, i. V. m. § 2 der Chemikalien-Verbotsordnung
Language Skills	German (native), English (fluent)

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J Declaration

Herewith I declare that this present thesis is a presentation of my original work prepared single-handed. Wherever contributions from other are involved all of them are marked clearly, with reference to the literature, license, and acknowledgement of collaborative research.

Regensburg, 08.07.2015

Matthias Knorn