Synthesis and Applications of biscyclopropenium phosphines as ancillary ligands in catalysis

Synthese und Anwendung von Biscyclopropenium Phosphinen als Liganden in der Katalyse

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Prof. Dr. M. Alcarazo

unter Aufsicht von

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vorgelegt von Dipl. Chem. P. M. Linowski

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Inhaltsangabe

Die Entwicklung neuer Phosphane und ihre Anwendung in der Katalyse sind ein wichtiger Forschungsschwerpunkt in den letzten Jahrzehnten gewesen. Trotz der strukturellen Vielfalt der heutzutage bekannten und verfügbaren Phosphane kann man die meisten dieser Liganden im besten Falle als moderate π-Akkzeptoren klassifizieren. Solange solche elektronischen Eigenschaften für die jeweiligen Anwendungen ausreichend sind, sind mehr als genug Beispiele für (solche) P-zentrierte Verbindungen mit unterschiedlichen sterischen Eigenschaften, verfügbar.

Allerdings existieren einige katalytische Reaktionen, die die Gegenwart von Liganden mit sehr starkem π-Akkzeptor Charakter erfordern. In diesen Fällen gibt es nur wenige kommerziell verfügbare, neutrale P-zentrierte Liganden mit solchen Eigenschaften (PF_3, $P(CF_3)_3$ und PCl_3). Unglücklicherweise sind diese Verbindungen in der Regel toxisch und feuchtigkeitsempfindlich, was problematisch für ihre Anwendung in der Katalyse ist.

Aus diesem Grund bleibt die Entwicklung neuer π-Akkzeptor Liganden eine Herausforderung. In unserer Herangehensweise wurden zwei Cyclopropenium-Substituenten an das Phosphoratom des hergestellten Phosphins gebunden, um einen verstärkten π-Akkzeptor Charakter einzuführen. Diese synthetisierten Biscyclopropeniumphosphine waren luftstabil im Gegensatz zu ihren polyhalogenierten Analogen. Die Variation des dritten (nicht-kationischen) Substituenten, der an das Phosphoratom des dikationischen Phosphins gebunden ist, erlaubt die Modifikation der elektronischen Eigenschaften der jeweiligen Verbindung. Die Anbringung längerer aliphatischer Ketten an die Cyclopropeniumeinheit ermöglicht die vollständige Lösung des dikationischen Phosphins in nicht-polaren Lösungsmitteln wie Toluol. Außerdem wurde für einige der hergestellten Phosphine das BF_4^- Gegenion für SbF_6^- ausgetauscht, um später seinen Einfluss auf die Reakivität in der Katalyse zu untersuchen.

Die anschließende Koordinierung dieser dikationischen Phosphine an Übergangsmetalle resultierte in der Isolation der jeweiligen Au(I)-, Pt(II)-, Ir(I)- und Ag(I)- Komplexe.

Die Reaktivität der hergestellten Au(I)-präkatalysatoren wurde in der Cycloisomerisierung von Biphenyl-Alkinen mit zwei Substituenten in internen Postionen zu den jeweiligen Phenanthrenderivaten untersucht. Nach erfolgreicher Optimierung wurde diese Methodik in der Synthese von *Calanchinon C* angewendet.

Schließlich wurde der Anwendungsbereich der verwendeten Au(I)-präkatalysatoren von der Synthese von Phenanthrenderivaten zur Herstellung von Naphto-furanen erweitert.

Abstract

The development of new phosphines and their application in catalysis has been a major research topic during the last decades. Despite the structural variety of the known and available phosphines, nowadays, most of these ligands can be classified as moderate π-acceptors at best. As long as such electronic properties are sufficient for the derived applications, more than enough examples depicting different steric parameters are available.

However, some catalytic reactions require the presence of ancillary ligands with very strong π-acceptor character. In these cases only few commercially available neutral P-centered ligands exist (PF_3, $P(CF_3)_3$ and PCl_3). Unforunately, these compounds are usually both toxic and moisture sensitive, which represents a strong limitation for their application in catalysis.

Therefore, the design of new π-acceptor ligands is still a challenge. In our approach two cyclopropenium substituents were attached to the phosphorus atom of the phosphine in order to introduce enhanced π-acceptor character. These biscyclopropenium phosphines, unlike their polyhalogenated analogues, were air stable. While the variation of the third (non-cationic) substituent attached to the phosphorus of the dicationic phosphine allowed further modification of its electronic properties, the decoration of one cyclopropenium unit with longer aliphatic chains facilitated the solution of the charged species in non-polar solvents like toluene. Furthermore, the BF_4^- counter-ion of some of the prepared phosphines was exchanged for SbF_6^- in order to investigate its influence on the reactivity in catalysis later on.

Subsequent coordination of these dicationic phosphines to various transition metals afforded the corresponding Au(I), Pt(II), Ir(I) and Ag(I) complexes.

The reactivity of the prepared dicationic Au(I)-precatalysts was investigated in the *6-endo-dig* cycolisomerization of biphenyl-alkynes with two substituents in internal positions to their corresponding phenanthrene derivatives. After successful optimization, this methodology was applied in the synthesis *Calanquinone C*.

Finally, the substrate scope of the utilized Au(I)-precatalysts was expanded from the synthesis of phenanthrene derivatives to the preparation of naphto-furans.

Experience is the teacher of all things.

-Julius Caesar

Abbreviations

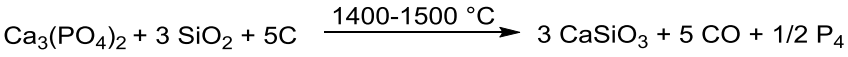
Å	Angstrom
Ac	Acetyl
Ad	Adamantyl
aq	Aqueous
atm	Pressure in atmospheres
[BMIM][BF_4]	1-Butyl-3-methylimidazolium tetrafluoroborate
Bu	Butyl
COD	1,5-Cyclooctadiene
Cpr	Cyclopropenium
Cy	Cyclohexyl
dba	Dibenzylideneacetone
DCE	1,2-Dichloroethane
DCM	Dichloromethane
dipp	2,6-Diisopropylphenyl
DMF	Dimethylformamide
DFT	Density functional theory
δ	Chemical shift (NMR)
Ep(Ox)	oxidation potential
Et	Ethyl
equiv.	Equivalent
EtOAc	Ethyl acetate
eV	Electronvolt

GC-MS	Gas chromatography – mass spectrometry
h	Hour
Hex	Hexyl
HOMO	Highest occupied molecular orbital
HPLC	High-performance liquid chromatography
HRMS	High-resolution mass spectrometry
Hz	Hertz
IR	Infrared
J	Coupling constant
KHMDS	Potassium hexamethyldisilazane
L	Generalized ligand
L_nM	Generalized metal fragment with *n* ligands
LDA	Lithium diisopropylamide
LUMO	Lowest unoccupied molecular orbital
m	Meta
M	Generalized metal
Me	Methyl
MeO	Methoxy
Mes	Mesityl
min	Minutes
MO	Molecular orbital
MS	Mass spectrometry
MTBE	Methyl *tert*-butyl ether

n	Normal
NHC	*N*-Heterocyclic carbenes
NHP	*N*-Heterocyclic phosphines
NMR	Nuclear magnetic resonance
ῡ	Frequency
o	Ortho
p	Para
Ph	Phenyl
Pr	Propyl
Py	Pyridine
r.t.	Room temperature
t	Tertiary
Tf	Triflate
THF	Tetrahydrofurane
TLC	Thin layer chromatography
TMS	Trimethylsilyl
vs	Versus
X	Anion

1 Introduction

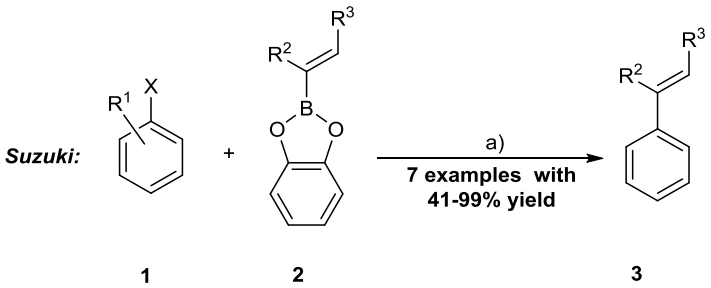
Phosphorus does not exist in nature in its elemental form as it is easily oxidized. It can be found in the earth crust in form of the salts derived from phosphoric acid, such as *apatite* (3 $Ca_3(PO_4)_2{\cdot}Ca(OH, F, Cl)_2$), or in the biosphere as derivatives of phosphoric esters and phosphates. Overall, its natural occurrence sums up to 0.1% (m/w%) of the total mass of the litho- and biosphere.[1] Elemental phosphorus is accessible in industrial scale by the reduction of the afore mentioned apatite with coke in the presence of silica at 1400-1500 °C in an arc furnace affording elemental P_2, which dimerizes to P_4 (white phosphorus) upon cooling.



Scheme 1-1: Reductions of phosphates to elemental phosphorus.

White phosphorus has a tetrahedral structure with P-P bond lengths in between 2.20 and 2.21 Å. It is extremely reactive, up to the point that it spontaneously ignites at room temperatures upon exposure to oxygen in a highly exothermic reaction.[1] Despite of that, white phosphorus is the key starting material for the preparation of bulk phosphorus chemicals like PCl_3, PH_3 and their commercial derivatives, which in turn, are used to access most of the known P-ligands in organometallic chemistry such as phosphines, phosphites and phosphoramidites.[1]

Phosphorus derived ligands have found a wide range of applications, in particular in coordination chemistry and catalysis. Examples for this privileged use as ligands can be found in many coupling (Scheme 1-2), [2,3,4] metathesis or hydrogenation reactions, among others.



Scheme 1-2: *Suzuki*-cross coupling in the presence of **PPh_3** as ligand. a) 0.1 equiv. mol% Pd(**PPh_3**)$_4$, 2 equiv. NaOEt, benzene, 70 °C, 2 h.

For example, in order to improve all relevant reaction parameters of cross-couplings, such as selectivity, conversion-rate, functional group tolerance and catalyst loading, a lot of effort was

invested mainly into the design of new phosphorus based ligands modifying their structural and electronic properties. Thus, the evolution of P-based ligands in this area led to the synthesis of biphenylphosphines, which were first developed by *S. L. Buchwald et al.* for coupling reactions and later have been applied in a broad range of different reactions including *Suzuki-Miyaura* couplings (**4** and **5**),[5a, 5b] α-arylations of aldehydes (**4** and **5**),[5c] *Negishi*-couplings (**6**),[5d] fluorination reactions (**7**),[5e] arylations of hindered primary amines (**8**),[5f] hydroxylations of aryl/hetereoaryl halides (**9**)[5g] and cyanation of aryl/heteroaryl halides (**10**, Figure 1-1).[5h]

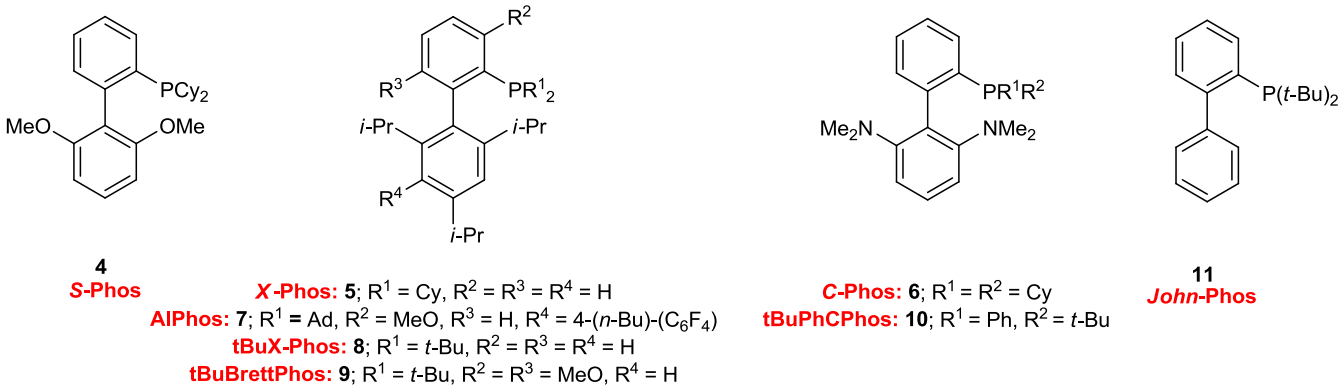
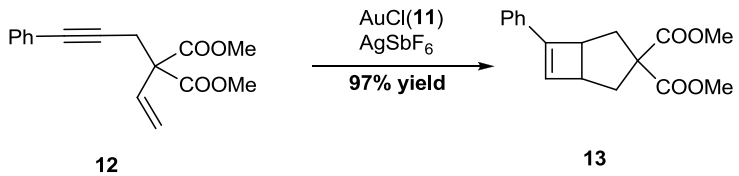


Figure 1-1: *Lewis*-structures of biphenyl phosphines developed by *S. L. Buchwald et al* and *John*-Phos **11**.

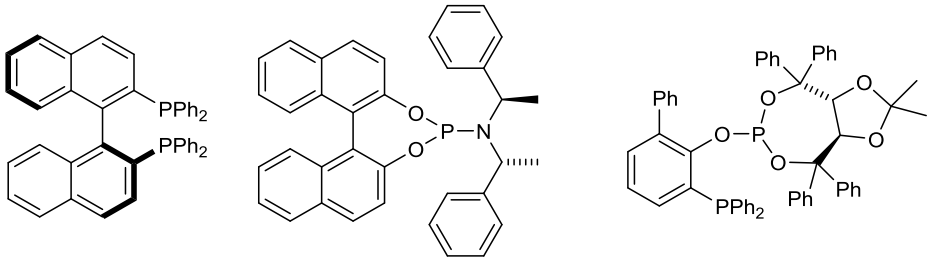
Despite of the fact that cross-couplings are one of the prominent fields for the application of phosphorus ligands like phosphines, there are many other catalytic reactions where such compounds are applied. *John*-Phos **11,** one of the simplest *Buchwald* type phosphines, has been also successfully used in Au(I)-catalyzed processes. The cycloisomerization of enyne **12** to cyclobutene **13** reported by *R. A. Widenhöfer et al.* (Scheme 1-3) can be used as an illustrative example for this chemistry.[6]



Scheme 1-3: Au(I)-catalyzed cycloisomerization of enyne **12**. a) 0.05 equiv. AuCl(**11**), 0.05 equiv. $AgSbF_6$, DCM r.t..

Another interesting advantage of the utilization of phosphines as ancillary ligands derives from the relative facility to prepare chiral, enantiopure derivatives that expand the scope of their use to asymmetric synthesis. BINAP **14**,[7] chiral phosphoramidite **15**[8] and chiral

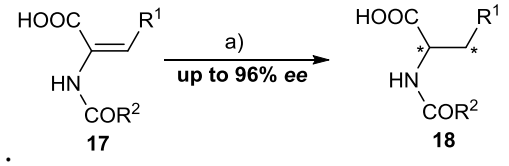
phosphine phosphite[9] such as **16** are excellent examples of chiral P-based ligands (Figure 1-3), which have demonstrated extraordinary levels of enantioinduction in several interesting processes.



R. Noyori et al. **14** | *B. L. Feringa et al.* **15** | *H.-G. Schmalz et al.* **16**

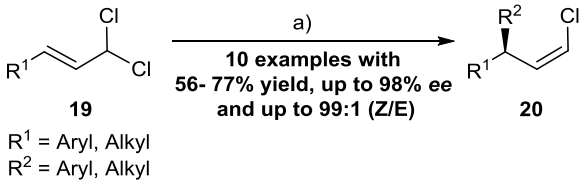
Figure 1-2: Examples for chiral P-centered pro-ligands.

BINAP **14** has been utilized with great success in the asymmetric Ru-catalyzed hydrogenation of α,β-unsaturated carboxylic acids,[7b] allylic alcohols,[7c] enamides[7d] and ketones [7e] by *R. Noyori* et al. For example, the use of *(R)*-BINAP in the Ru(II)-catalyzed enantioselective hydrogenation of substituted enamides **17** provided the corresponding enantioenriched (protected) α-or β-amino acids **18** with up to 96% *ee* (Scheme 1-4).[7d]



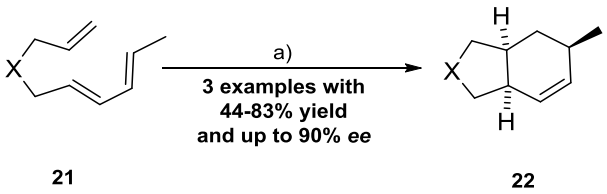
Scheme 1-4: *Noyori*-reduction of enamides **17** to their respective α-or β-amino acids **18**. a) 0.005 equiv. $Rh(OAc)_2$(**14**), H_2 (1 atm), MeOH, r.t..

Additionally, chiral phosphoramidite **15** was used by *B. L. Feringa et al.* with great success, for example, as a ligand in the Cu(I)-catalyzed asymmetric 1,4-addition of *Grignard* reagents to allylic gem-dichlorides **19**. The desired 1,4-addition products **20** were obtained in good yields (up to 74%), remarkable *ees* (up to 98%) and almost complete Z-selectivity (Scheme 1-5).[8]



Scheme 1-5: Asymmetric 1,4-addition of *Grignard* reagents to allylic gem-dichlorides **19** by *B. L. Feringa*. a) 0.05 equiv. Cu(I)TC, 0.055 equiv. **15**, 1.5 equiv. R-MgBr, DCM, -78 °C, 4 h (TC = tiophene-2-carboxylate**)**.

Another type of asymmetric reaction, which in this case was made possible by employing TADDOL-derived phosphine-phosphite ligand **16**, is the enantioselective Rh(I)-catalyzed [4+2] cycloaddition of trienes of type **21**. The enanatioenriched bicyclic products of type **22** were obtained in good yields (up to 83%) and up to 90% *ee* (Scheme 1-6).[9]



Scheme 1-6: [4+2] Cycloaddtion of trienes **21** to their respective bicyclic products **22** by *H.-G. Schmalz et al.*. a) 0.03 equiv. $[RhCl(NBD)]_2$(NBD = norbornadiene), 0.06 equiv. $AgSbF_6$, 0.072 equiv. **16**, EtOAc, 50 °C (microwave), 1-3 days.

While this is only a brief survey on the different P-centered ligands employed in catalysis, it clearly demonstrates the incredible power of ligand design. However, it has to be noted that most of the known P-based compounds, which were mentioned afore can be classified as poor-to-moderate π-acceptors and good-to-moderate σ-donors. As long as such electronic properties are sufficient, additional modification of the ligands remains unnecessary.

However, when strong π-acceptor properties become necessary to facilitate a certain reaction, only PCl_3, PF_3 and $P(CF_3)_3$ are readily available as these are the only phosphorus compounds possessing stronger π-acceptor properties than phosphites (e.g. $P(OPh)_3$). These phosphines and their respective transition metal complexes are unfortunately highly air and moisture-sensitive, which makes them not the most adequate choices as ligands for catalysis.[10] For this reason, the development of new strategies to improve π-acceptor properties of the P-center of phosphines is still necessary.

1.1 Phosphines with peripheral charges

Homogenous transition-metal catalysis has grown in importance in both, academic and in industrial applications. Asymmetric hydrogenation, cross-couplings and hydroformylation are good examples for noteworthy applications with organophosphorus compounds playing a key role as ligands. However, the use of homogenous catalysts presents a challenge in their implementation on industrial scale. The separation of the catalyst from the product after the reaction is finished may not be straightforward. An elegant solution to this problem consists of the use water as a solvent for the reaction, if non-polar products are fromed that are easy to separate from this solvent due to their hydrophobic nature. In order to facilitate this separation even more, the catalyst should ideally remain in the aqueous phase after the reaction is

finished. A trick often used to increase the hydrophilicity of the catalyst consists of the introduction a positive or negative charge on the periphery of the ligand. This charge should be placed at a relative distance from the phosphorus to avoid changes on the electronic properties of the respective phosphine. Several phosphines containing positively charged moieties on their periphery have been developed with this objective in mind, and a selection of them is illustrated in Figure 1-3.[11]

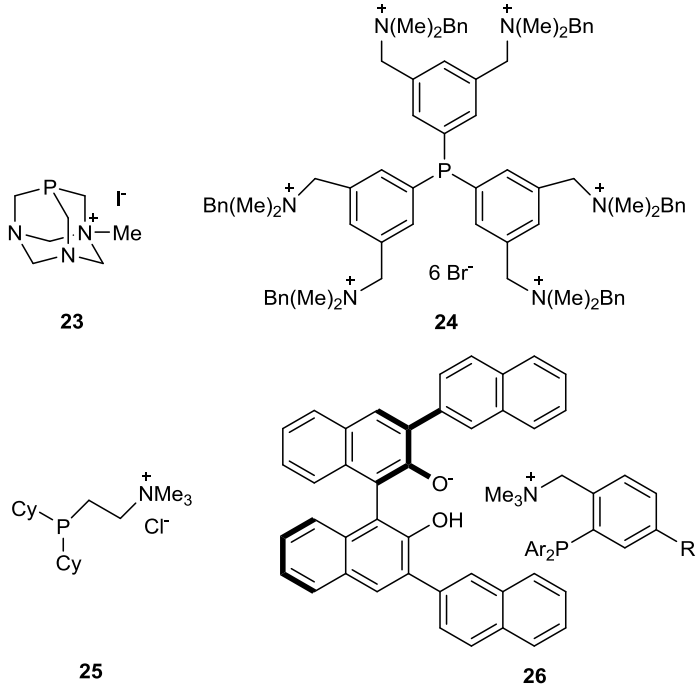
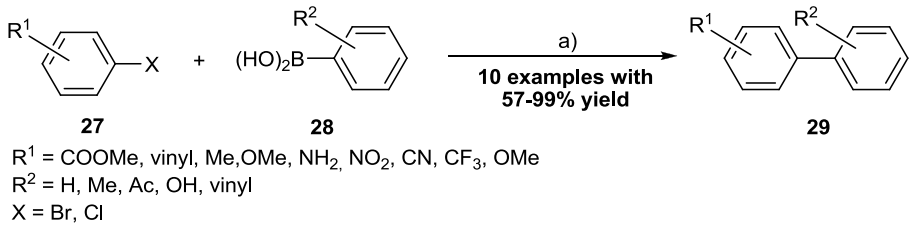


Figure 1-3: Examples for phosphines possessing peripheral charges.

A good example for such a hydrophilic P-centered ligand with a peripheral positive charge is 1-Methyl-1,3,5-triaza-7-phosphaadamantan-1-ium iodide **23** (Figure 1-3), which was prepared by the methylation of the corresponding amine. By treatment of **23** with $[(RhCl(CO)_2]_2$ and $[(Rh(I)(CO)_2]_2$, complexes of type $RhX(CO)L_2$ (X = Cl, I) were obtained and utilized in the hydroformylation of alkenes or in the reduction of aldehydes.[12]

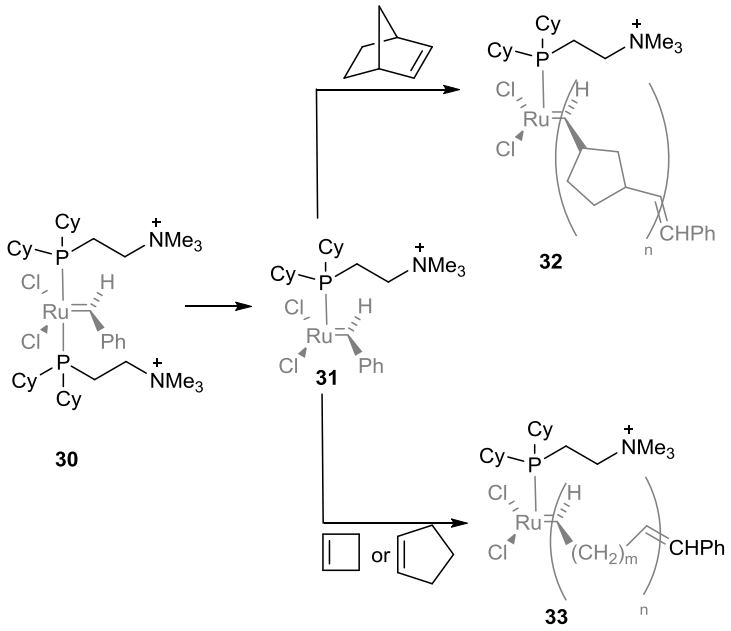
Another example for such a charged phosphine is ben-*Dendriphos* **24** (Figure 1-3), which was used successfully by *G. van Koten et al.* in a *Suzuki-Miyaura* cross-coupling of various aryl bromides **27** with the corresponding boronic acids **28** in aqueous media, affording the coupling products **29** in moderate to good yields (57-99%, Scheme 1-7). A broad range of different functional groups (Scheme 1-7) is tolerated by this protocol, and the employed hexacationic ligand shows even higher reactivity than PPh_3 under the evaluated conditions (aqueous media). Furthermore, it could be concluded that ben-*Dendriphos* **24** stabilizes the Pd(0)-intermediate without inhibiting the reactivity. This was rationalized by suggesting that

ligand **24** favors the formation of a coordinatively unsaturated 16e$^-$-complex, which is probably facilitated by a combination of steric and *Coulombic* repulsions of the charged ammonium groups that avoids the coordination of a second phosphine to the metal center.[13]



Scheme 1-7: *Suzuki*-coupling in the presence of ben-*Dendriphos* **24** by *G. van Koten et al*. a) 0.01 equiv. $Pd(dba)_2$, 0.04 equiv. **24**, $MeOH/H_2O$, 65 °C.

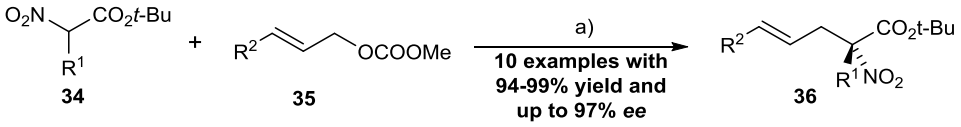
Olefin metathesis has also benefitted from the use of cationic phosphines such as **25**. In particular, this ligand has been useful in the evaluation of the ring-opening metathesis mechanism *via* ESI-MS spectrometry (Scheme 1-8). [14] The inactive precatalyst **30**, the active monocationic species **31** as well as intermediates **32** and **33** were detectable in the MS-spectrometry utilizing this methodology.



Scheme 1-8: Intermediates **32** and **33** formed in the ring opening metathesis polymerization of cyclic alkenes in the gas-phase.

A very original additional application of the use of organophosphorus compounds with peripheral charges was recently reported by *T. Ooi et al*. (Scheme 1-9). He described a Pd(0)-catalyzed asymmetric allylation of α-nitrocarboxylate derivatives **34** with allyl carbonates **35** utilizing the ion-paired chiral ligand **26** (Figure 1-4 and Scheme 1-9).

The developed methodology delivered the enantio-enriched products **36** in excellent yields (up to 99%) and remarkable enantioselectivity of up to 97% *ee*. According to the authors, the *Coulomb* interactions between the charged phosphine and a chiral counter-anion, in this case binaphtolate, induce the observed enantioselectivity.[15]



Scheme 1-9: Pd(0)-catalyzed asymmetric allylation of α-nitrocarboxylate derivatives **34** with 2-en-1-yl derivatives **35** by *T. Ooi*. a) 0.0125 equiv. $Pd_2(dba)_3$, 0.05 equiv. **26**, toluene/H_2O, r.t.

The reaction itself follows a pattern similar to the *Tsuji-Trost* reaction as the initial steps is suggested to be the insertion of the [Pd(0)(**26**)$_2$] species on the allylic carbonate resulting in the formation of π-allyl-Pd(II) complex. This structure would be maintained as the deprotonated nitro-ester is delivered *via* a hydrogen-bonding interaction to the phenolic proton of the binaphtolate anion. The organization of this intermediate through *Coulombic* interactions would be essential to produce the obtained enantioselectivity during addition of the pro-chiral nucleophile to the formed π-allyl-Pd(II) complex (Figure 1-4).[15]

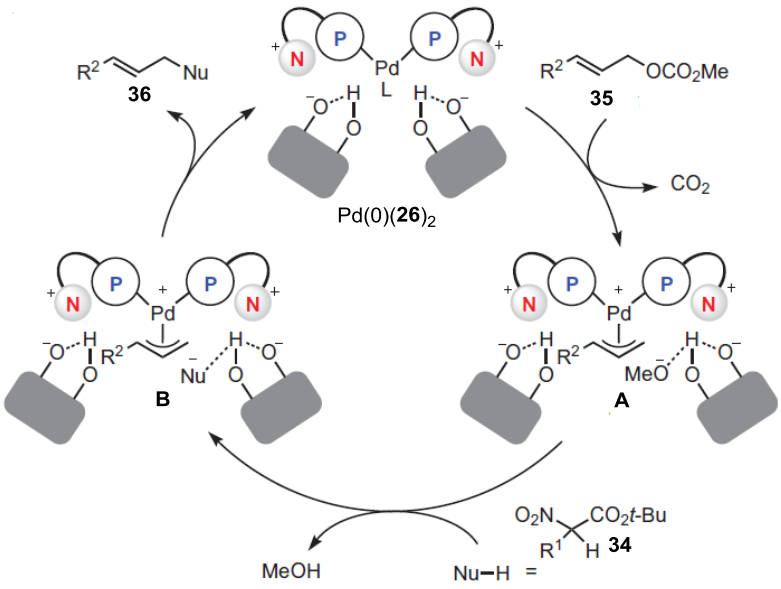


Figure 1-4: Proposed catalytic cycle for enantioselective alkylation catalyzed by an ion-pair catalyst.

1.2 Phosphines with charges directly attached to the P-center.

1.2.1 Introduction

It was already mentioned in section 1.1, that the variety of neutral P-centered compounds, which can act as strong π-acceptor ligands is very limited and mainly restricted to halogenated

phosphines. However, these halogenated compounds are usually labile, air/moisture-sensitive and therefore difficult to handle. An alternative approach to obtain the desired π-acceptor properties consists of the introduction of positively charged moieties in close proximity to the P-center. In contrast to compounds where the charge is attached on the periphery of the ligand, the new charges would not only result in a significant change of their solubility, but also in a modification of their electronic properties.

It is well known that in phosphines, the electron pair located on the P-center accounts for the σ-donor ability of the respective compound, while the σ*(P-C) orbitals govern its π-acceptor properties. A strong electron-withdrawing and positively charged group R' attached to the P-atom, will decrease the energy of all molecular orbitals of the corresponding phosphine, including those responsible for its π-acceptor properties. For this reason, the resulting cationic phosphine should depict poorer electron donor and improved π-acceptor character when compared to their neutral counterparts.[16]

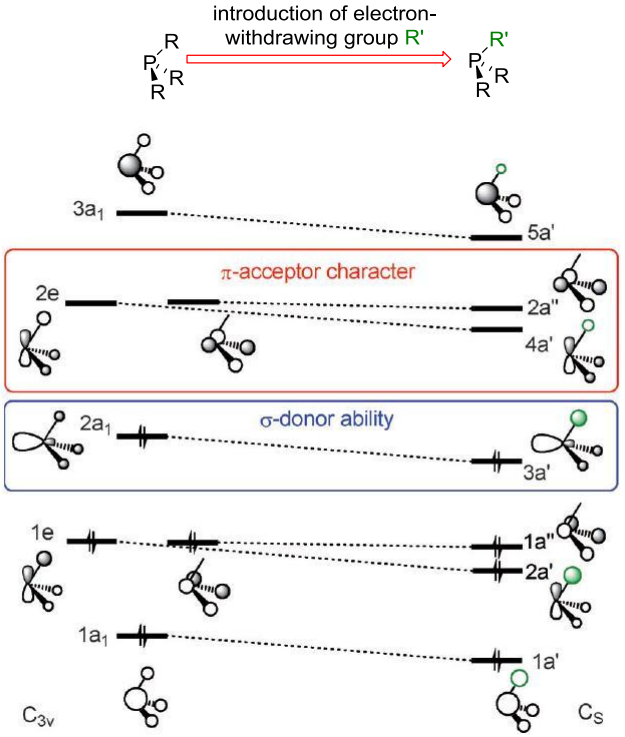


Figure 1-5: simplified molecular orbital diagram for PR_3 diagram and the perturbation occasioned when one R group is substituted with one electron-withdrawing group R'.[16a, 16b]

Additionally, it has to be taken into consideration that most organic cationic substituents that can be introduced as electron-withdrawing groups R' are aromatic rings, which already possess empty low lying π* orbitals. These π*-orbitals are also able to overlap with occupied orbitals on the P-center of suitable symmetry. Two of these secondary interactions are of high relevance for the evaluation of the electronic properties of the respective phosphines.

First, the orbital responsible for the σ-component of the P-M bond may delocalize electron density on the π-system of the aromatic ring, if the π system of the aromatic system is in plane with orbital containing the electron lone pair located on the P-center (Figure 1-6, **A**). As this interaction stabilizes the electron pair, it decreases the interaction with the orbitals of the metal. Due to this effect the σ-component of the P-M bond is weakened.

Second, an empty π-system which could interact with the orbital of 2a'' symmetry of the phosphine, lowers the energy of that orbital additionally, as a consequence, it leads to an amplification of the π-acceptor properties of the respective ligand (Figure 1-6, **B**).[16a]

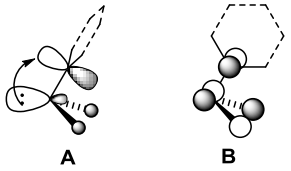


Figure 1-6: Secondary interactions **A** and **B** between phosphines and positively charged aromatic substituents,

The strength of both interactions depends on the relative energy level of the LUMO of the charged fragment as well as its orientation. As a result, different cationic substituents will have different effects. It can be concluded that the cationic substituent with the lowest LUMO should be able to maximize these secondary interactions and therefore, enhance the π-acceptor properties of the respective ligand significantly.

Our theoretical department calculated the LUMOs of the most common charged aromatic substituents at the B3LYP/6-31G* level (Figure 1-7). A comparison of the respective energy values, illustrates that the tropylium cation **37** possesses the lowest LUMO with -0.2817 eV while the cyclopropenium cation **38** possesses the highest one with -0.1388 eV. Therefore, phosphines with tropylium **37** as an electron-withdrawing substituent should possess the strongest π-acceptor properties and the weakest σ-donor abilities.[16a]

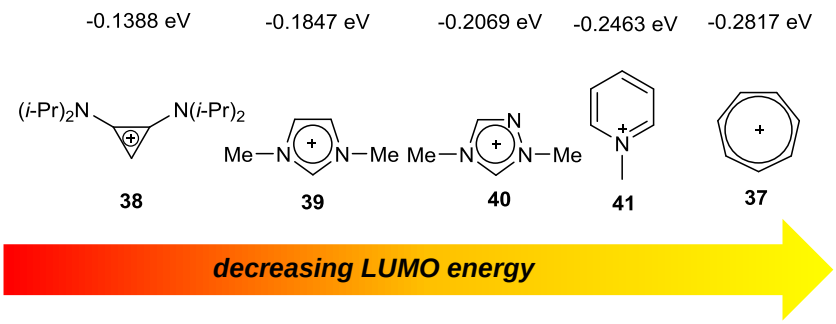


Figure 1-7: Calculated energy levels of the LUMOs of the most common cations, which can be used as substituents of phosphorus on theB3LYP/6-31G* level.[16a]

Finally, there are two more factors, which have to be considered. First, the reduction of the σ-donation from the P atom to the metal due to the attachment of a positive charge is not completely compensated by the back-donation, resulting in a weaker M-P bond. This can lead to a complete disappearance of the coordinating properties of the ligand. Second, the presence of charged moieties on the coordinated ligand, results in *Coulomb* interactions between the respective ligand moieties and also between the ligand and the metal if both are charged. This will also drastically influence the stability of the complex.[16]

1.2.1.1 Evaluation of electronic properties

The traditional method to obtain information about the π-acceptor character of a ligand consists of the measurement of the carbonyl stretching frequency ($\tilde{\upsilon}_{CO}$) of a metal-carbonyl complex, which is coordinated to the ligand under study. This is done normally using $[Ni(CO)_3L]$ complexes (*Tolman* method). Carbonyl ligands possess an empty, low lying π*-orbital (LUMO), which is capable of accepting electron density from an occupied metal d-orbital of suitable symmetry. If the phosphine coordinated to the same metal is a good σ-donor, the metal has more electron density to back-donate into the aforementioned LUMO of the CO-ligand. As a consequence the carbonyl triple bond is weakened, resulting in a decreased wavenumber for the stretching frequency measured *via* infrared spectroscopy (Figure 1-8). The opposite can be observed, if the ligand under study is a good π-acceptor ligand. In such a case, back-donation from the filled metal d-orbital to the empty σ*(P-R)-orbital of the phosphine increases and, as a consequence, the metal has less electron density to share with the π*-orbital of the CO ligand. Due to this, the strength of the carbonyl triple bond does not diminish strongly and as a consequence the measured $\tilde{\upsilon}_{CO}$ value is similar to the one of free CO.

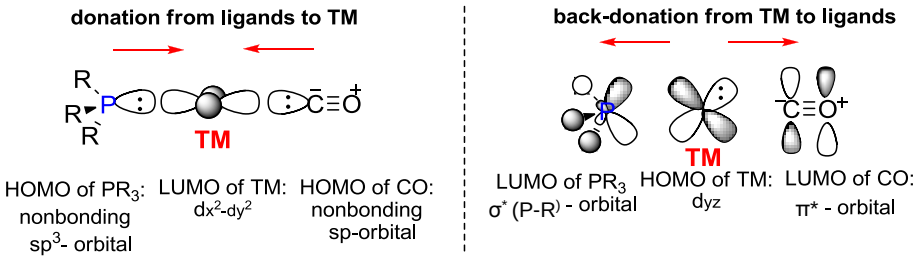


Figure 1-8: Relevant orbital interactions between the CO and PR_3 Ligands of a **$Ni(CO)_3L$**

While it is also possible to use other metal fragments like $[(L)Rh(Cl)(CO)_2]$ or $[(L)_2Rh(Cl)CO]$ to determine this value, it must be considered that for complexes of type $[(L)_2Rh(Cl)CO]$ a tetrahedral distortion of the square-planar geometry is often observed, especially when bulky ligands are employed. This makes the comparison of $\tilde{\upsilon}_{CO}$ for the

different $[(L)_2Rh(Cl)CO]$ compounds increasingly difficult.[16b] As an alternative, the σ-donor properties of P-centered ligands can also be determined by the measurement of the oxidation potential $E_p(Ox)$ by cyclic voltammetry. The electron richness on the P-center (where the ligand-HOMO is preferentially located) is inversely proportional to this value.[16b]

1.2.2 Monocationic phosphines

1.2.2.1 Synthesis of monocationic phosphines

Apart from the covalent description used up to now, most α-cationic phosphines can be additionally described as *Lewis*-acid-base adducts between a phosphenium cation and an appropriate *Lewis* base. The *Lewis* base can be another phosphine, a heteroaromatic ring or, as discussed in this thesis, a carbene (Figure 1-9). From this point of view, the synthetic approaches developed to prepare these compounds are obvious.

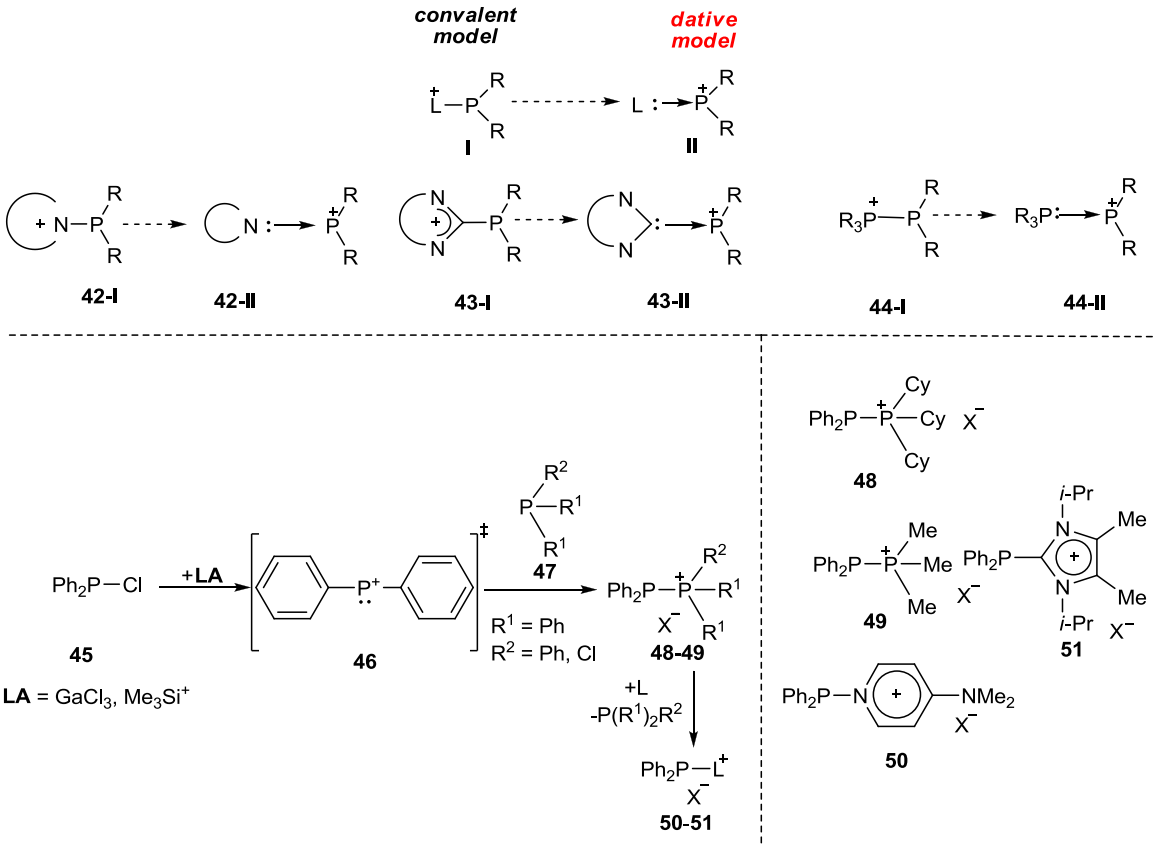


Figure 1-9: Up: Covalent model for phosphenium cation stabilized by a *Lewis* base as well the dative model. **Down Left:** Preparation of phosphino-phosphenium compounds **48-49** and possible subsequent ligand exchange reactions. **Down Right:** Accessible products **48-51** through ligand-exchange.

Hence, *N. Burford et al.* developed a synthesis of phosphino-phosphenium compounds **48-49** starting with the abstraction of one chloride from a chlorophosphine **45**, this leads to the *in situ* formation of a phosphenium cation **46**, which was stabilized by the mesomeric delocalization of the positive charge, when aromatic groups like phenyls were attached to the P-center (Figure 1-9). Addition of an equivalent amount of a phosphine **47** leads to the formation of the corresponding *Lewis*-acid-base adduct **48-49** in good yield (77-88%), which

highlights the synthetic use of this procedure in the P-P bond formation.[17] Compounds **48**-**49** can be submitted to a subsequent ligand exchange using other ligands with better σ-donor properties (compounds **50**-**51**, Figure 1-9). It has to be highlighted that it is possible to prepare the monocationic imidazolium phosphine **51** as well as the pyridine-phosphenium complex **50** following this route.[18]

Imidazolium phosphine **51** was prepared for the first time by *N. Kuhn et al.* in 1999, by a condensation of an N-heterocyclic carbene of type **52** (R^1 = *i*-Pr, R^2 = Me) with chlorodiphenylphosphine **45**, affording the desired product **51** in very good yield (87%, Scheme 1-10).[19] The carbene itself was prepared from the corresponding thioureas in a two-step sequence.

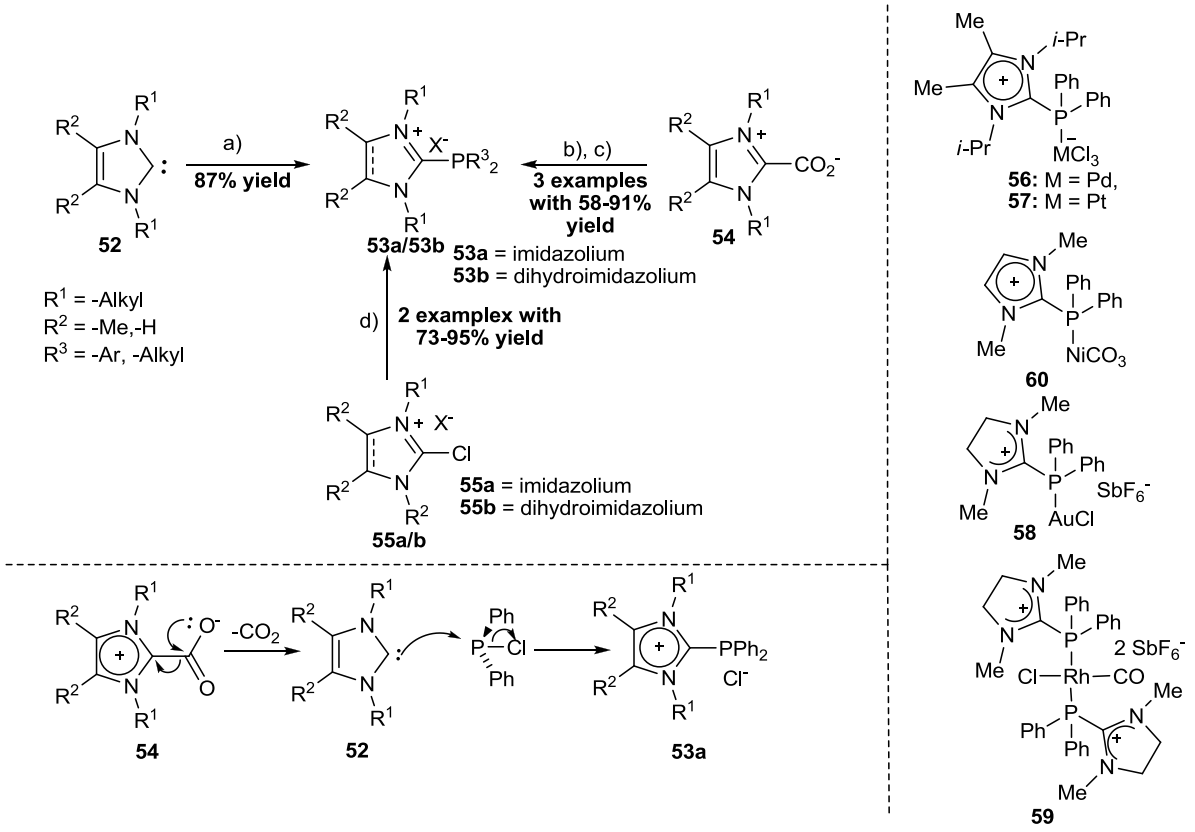
While the protocol for the preparation of imidazolium phosphines **51** is quite reproducible, it requires careful handling of free carbenes, which are air sensitive species. In order to avoid this problem *M. Azouri et al.* devised an alternative route to access imidazolium phosphines of type **53a** employing carboxylate derivative **54** as starting material (Scheme 1-10). In the presence of chlorodiphenylphosphine, **45** eliminates CO_2 and the free carbene formed *in situ* reacts with chlorophosphines to afford imidazolium phosphine **53** in moderate to excellent yield after ion-exchange (58-91% yield).[20]

Another possible route to monocationic phosphines of type **53** involves the condensation of dihydroimidazolium chlorides **55b** with the respective secondary phosphines (Scheme 1-10, route d). This methodology has been successfully applied in our work-group for the preparation of dihydroimidazolium **53b** and formamidinium substituted phosphines.[21]

N. Kuhn et al. also managed to prepare the first transition metal complexes of these imidazolium phosphines in 1999 using $PtCl_2(MeCN)_2$ and $PdCl_2(MeCN)_2$ as a metal-sources, which gave the Pd(II)-complex **56** and Pt(II)-complex **57**.[22]

Furthermore, the synthesis and coordination chemistry of dihydroimidazolium phosphines was also first described in our work-group. Coordination of Au(I) and Rh(I) to those α-cationic phosphines afforded Au(I)-complex **58** and Rh(I)-complex **59** (Scheme 1-10).[22]

The measurement of the CO-stretching frequency ($\tilde{\upsilon}_{CO}$) of the $Ni(CO)_3L$ complex **60** provided a value of $\tilde{\upsilon}_{CO}$ =2082 cm^{-1}, which classifies imidazolium phosphines of type **53a** as moderate π-acceptors, similarly to phosphites, with $\tilde{\upsilon}_{CO}$ around 2085 cm^{-1}.[16a]



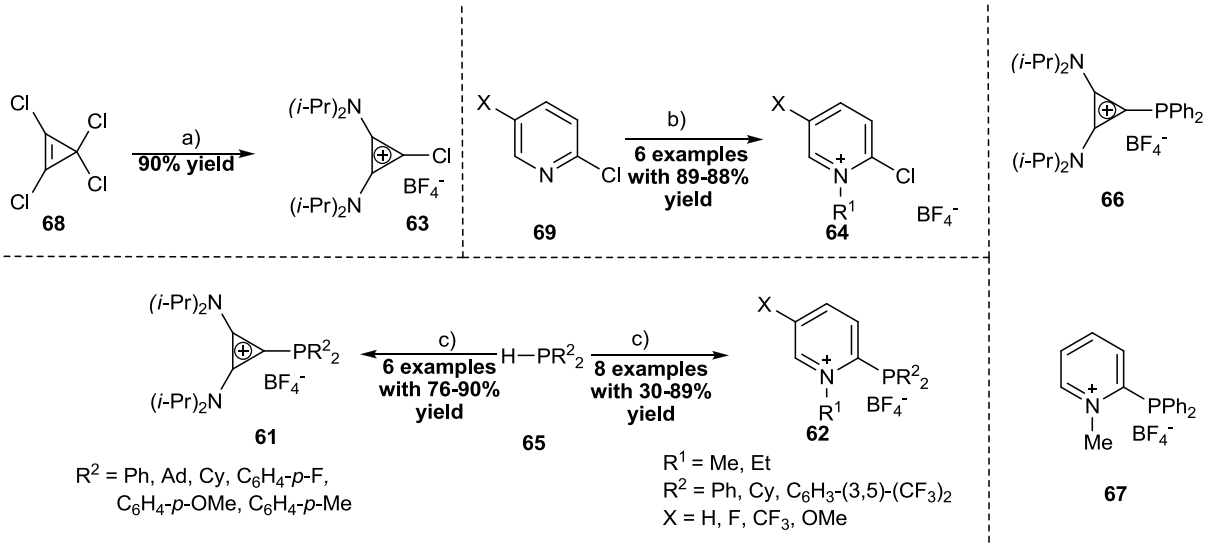
Scheme 1-10: Left up: Possible pathways for the synthesis of diimidazolium phosphines **53a/53b**. **Left down**: Possible mechanism for the formation of imidazolium phosphine **53a** from the carboxylate **54** upon addition of PPh_2Cl according to *M. Azouri et al.*. **Right:** Metal complexes of diimidazolium phosphines **53a/53b**. a) 1.0 equiv. PPh_2Cl, Et_2O, r.t, 1 h .; b) 1.0 equiv. PPh_2Cl, DCM, r.t., 4 h; c) 1.25 equiv. KPF_6, acetone, r.t., 2 days; d) 2.0 equiv. $R^3{}_2PH$, THF, reflux, 24 h.

Our work-group has also recently developed two additional families of monocationic phosphines with intersting π-acceptor properties: cyclopropenium phosphines of type **61**[23] and pyridinium phosphines of type **62**[24] (Scheme 1-11), both prepared by condensation of the corresponding chloro cyclopropenium **63**[25] or chloro pyridinium salt **64** respectively, with secondary phosphines (Scheme 1-11). The pyridinium phosphines **62** showed stronger π-acceptor and weaker σ-donor character as deduced from the carbonyl-stretching frequencies ($\tilde{\upsilon}_{CO}$) of the corresponding $Ni(CO)_3L$ complexes and the oxidation potentials *Ep(Ox)* of the free ligands (**66** and **67**):

$\tilde{\upsilon}_{CO}$ ($Ni(CO)_3$(**67**)) = 2094 cm^{-1}> $\tilde{\upsilon}_{CO}$ ($Ni(CO)_3$(**66**)) = 2082;

Ep(Ox, **67***)* = 1.398 V >*Ep(Ox*, **66***)* = 1.207 V.

The increase of the π-acceptor properties of the pyridinium phosphines **62** compared to the cyclopropenium phosphines **61** was expected since the LUMO of the pyrdinium moiety lies much lower in energy than the LUMO of the cyclopropenium ring.



Scheme 1-11: Left up: Synthesis of chloro cyclopropenium salt **63** by *Weiss et al.* **Right up:** Synthesis of chloro pyridnium salts **64** by *M. Alcarazo et al*. **Middle down:** Synthesis of cyclopropenium phosphines **61**/ pyridinium phosphines **62** by *M. Alcarazo et al.* **Right:** Examples for both ligand types. a) 4 equiv. $(i\text{-Pr})_2NH$, DCM, r.t., overnight; b) 1.0 equiv. $R^1{}_3OBF_4$, DCM, r.t. c) 2.0 equiv. H-$PR^2{}_2$, 1.0 equiv. **63**/**64**, THF, reflux, 24-72 h.

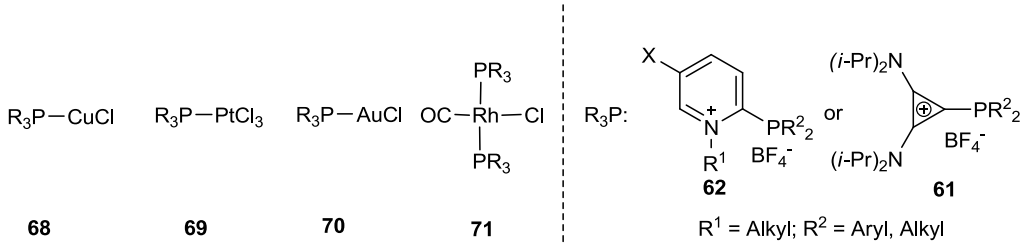
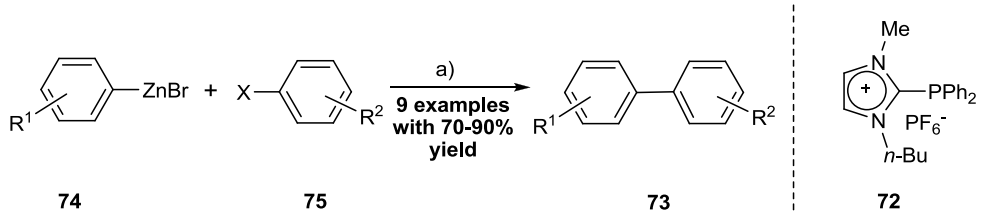


Figure 1-10: Transition metal complexes prepared from monocationic phosphines **67** and **68.**

Phosphines **61** and **62** were successfully coordinated to Pt(II), Au(I), Rh(I) and Cu(I) (only **61**), affording the corresponding metal complexes **68-71** (Figure 1-10).[26, 27] The chemistry and applications of monocyclopropenium phosphines is described in detail in the Ph.D. theses of *J. Petšukova* and *Á. Kozma* and only a short summary is given here.

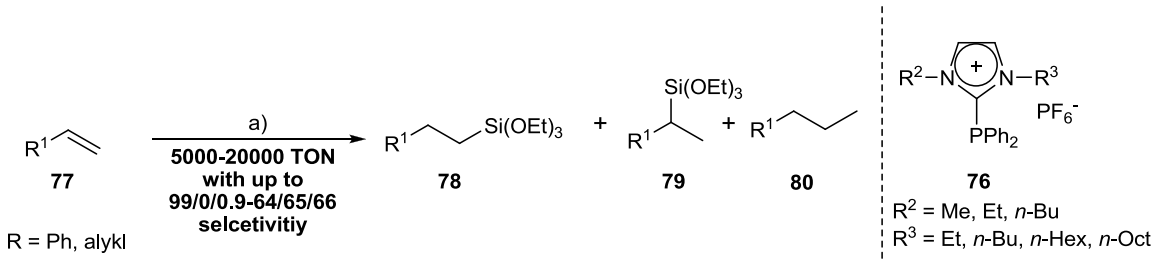
1.2.2.2 Applications of monocationic phosphines

A good example for the application of imidazolium phosphines like **72** as ligands in catalysis is the Pd-catalyzed *Negishi* cross-coupling reaction developed by *P. Knochel et al.* The reaccion tolerates a broad range of different functional groups (R^1 = COOMe, OMe, OTIPS, Cl, CN, thiophene-ZnBr, (C_6H_5)-CH_2-ZnBr; R^2 = COOEt, NO_2, OAc, OMe). Furthermore, the utilization of a ([bdmim][BF_4])/toluene solvent mixture allowed an easy separation of the synthesized biphenyls **73** from the catalyst, thus allowing the re-use of the catalyst in further catalytic cycles (Scheme 1-12).[28]



Scheme 1-12: *Negishi* cross-coupling in an ionic liquid utilizing ligand **72**. a) 0.02 equiv. $Pd(dba)_2$, 0.04 equiv. **72**; toluene/[bdmim][BF_4], r.t..

A second application reported by *X. Li et al.* describes the Rh(I)-catalyzed hydrosilation of alkenes. The authors demonstrated that [RhCl(**76**)$_3$] (Scheme 1-13) show a significantly higher activity and β-selectivity in the hydrosilation of terminal alkenes **77** ([bmim][PF_6] as a solvent) than $RhCl(PPh_3)_3$. TONs of up to 20000 were measured. It is suggested in their publication that the close proximity of the positive charge to the P-atom greatly enhances the catalytic activity. Moreover, it was possible to re-use the ionic liquid containing the Rh(I)-catalyst for at least four cycles without a significant drop in activity.[29]

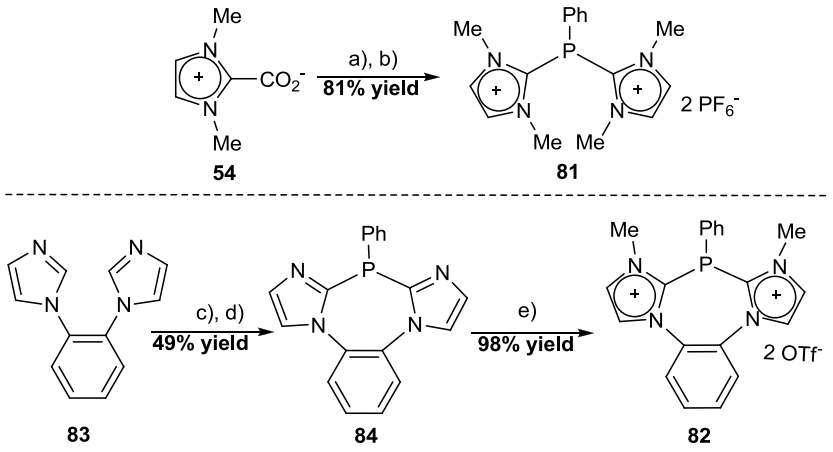


Scheme 1-13: Rh(I)-catalyzed Hydrosilation of Alkenes in ([bmim][PF_6]) utilizing ligand **76** by *X. Li et al*. a) 0.00005-0.0002 equiv. Rh(I)(**76**)$_3$Cl, ([bmim][PF_6]), 70 °C.

1.3 Dicationic phosphines

The list of dicationic phosphines that are known in literature is significantly shorter than that of the monocationic analogues. One example is bisimidazolium phosphine **81**, which was prepared from carboxylate **54** using the same protocol, which was employed for the synthesis of the monocationic analogues **53a**. In this case two equivalents of **54** and only one of dichlorophenylphosphine afforded the desired dicationic phosphine **81** in very good yield (81%; Scheme 1-14; for the mechanism Scheme 1-10).[30]

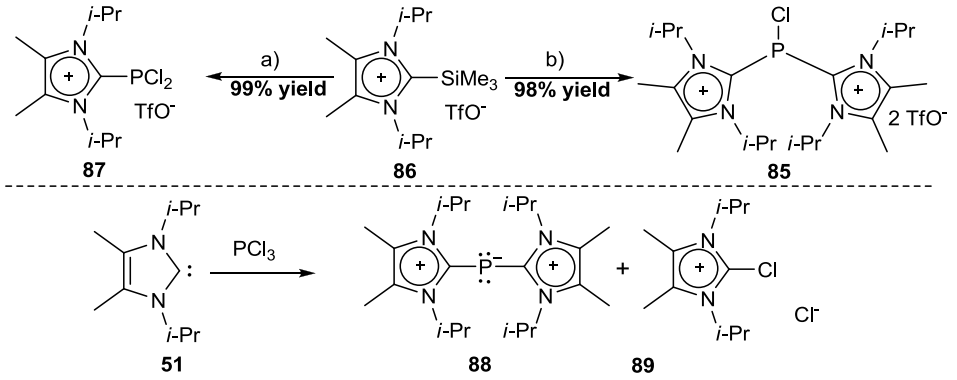
Another bisimidazolium phosphine, which is accessible from dichlorophenylphosphine, is compound **82**. This phosphine was prepared by *R. Chauvin et al.* from 1,2-di(1H-imidazol-1-yl)benzene **83** in a three step sequence (Scheme 1-14), which includes deprotonation of the bisimidazol species, followed by a condensation with dichlorophenylphosphine, and selective methylation at both N-atoms.[31] While the calculated carbonyl stretching frequency $\tilde{\upsilon}_{CO}$ = 2115 cm^{-1} of compound **81** implies that it is an extreme π-acceptor ligand, the measured oxidation potential *Ep(Ox)* = 2.330 V of compound **82** shows that bisimidazolium phosphines should be extremely poor σ-donors. Due to this, it is not surprising that no metal complex derivatives from **81** and **82** are known.[16,30,31]



Scheme 1-14: Up: Synthesis of diimidazoliumphosphine **81** by *M. Azouri et al.*. **Down:** Synthesis of diimidazoliumphosphines **82** by *R. Chauvin et al.* a) 0.5 equiv. $PPhCl_2$, DCM, r.t. 18 h; b) 2.5 equiv. KPF_6, EtOH, 24 h; c) 2.0 equiv. *n*-BuLi, THF, -78 °C, -78 °C to r.t., r.t., 4 h; d) 0.5 equiv. $PPhCl_2$, THF, - 78 °C, -78 °C to 60 °C, 60 °C, 2 h; e) 2.0 equiv. MeOTf, DCM, r.t.

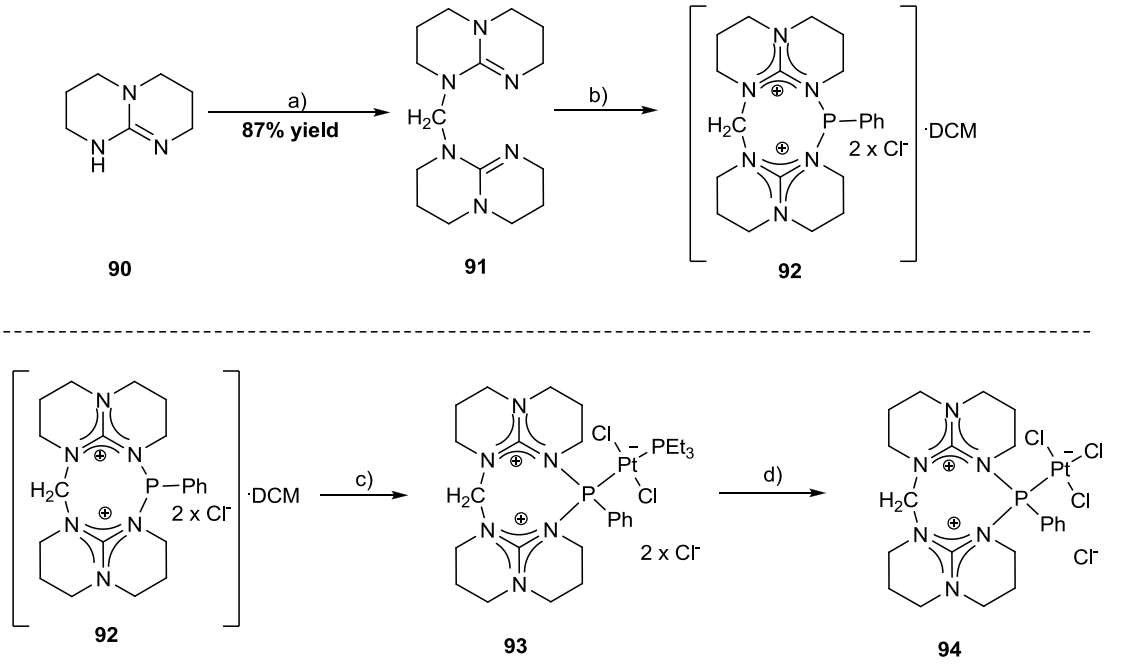
Dicationic chlorobisimidazoliumphosphine salt **85** has been prepared by a protocol published by *J. J. Weigand et al.* The key step in this reaction was the nucleophilic substitution of two chlorides in trichlorophosphine by the silyl protected carbene **86**. Depending on the stoichiometry, either dichloroimidazoliumphosphine **87** or chlorodiimidazoliumphosphine **85**

were accessible in quantitative yields (**85**: 99%; **87**: 98%; Scheme 1-15). These compounds could be used as $[PCl_2]^+$ and $[PCl]^{2+}$ synthons, in fact, it was possible to exchange the chloride substituent by either CN^- or N_3^- groups.[32] Silyl imidazolium **86** itself was prepared by silylation of the free carbene. It has to be highlighted that the utilization of silyl protected carbenes was essential to obtain compounds **85**/**87** without undesired side reactions. It is known that the treatment of trichlorophosphine with NHC **51** results in the formation of **88** and **89** through a redox process besides the expected condensation (Scheme 1-15).



Scheme 1-15: Up: Synthesis dichloroimidazoliumphosphine **87** or chlorodiimidazoliumphosphine **85** by *J. J. Weigand et al*. **Down:** Possible side reaction in the condensation of carbene **51** and PCl_3. a) 1.5 equiv. PCl_3, fluorobenzene, 50 °C, ultrasound bath, 10 h; b) 2.0 equiv. PCl_3, fluorobenzene, 50 °C, ultrasound bath, 24 h.

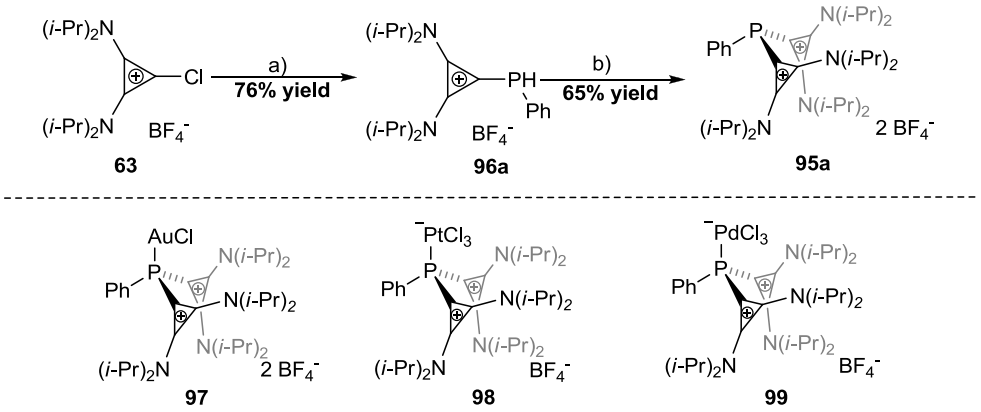
The first and only dicationic phosphine capable of coordinating transition metals prior to this work was prepared by *M. P. Coles et al.* from the bicyclic guanidine **90** in a two-step sequence (Scheme 1-16). First, 1,3,4,6,7,8-hexa-hydro-2H-pyrimido[1,2-a]pyrimidine **90** was submitted to deprotonation generating an amide, which reacted with DCM to yield the CH_2 bridged species **91**. Secondly, the condensation of **91** with chlorodiphenylphospane afforded the desired dionium-phosphine **92**. Interestingly, it was possible to treat this charged phosphine **92** with $[PtCl_2(PEt_3)\text{-}\mu\text{-}(Cl)]_2$ to form the Pt(II)-complex **93**, which upon heating to 50 °C, exchanged the PEt_3 ligand by one of the Cl^- counter ions affording the desired complex **94**. A structural confirmation of the constitution of the free phosphine **92**, as well as Pt-complex **94,** was achieved via XRD-analysis.[33]



Scheme 1-16: Up: Synthesis of dionio-substituted phosphines **92** by *M. P. Coles et al*. **Down:** Formation of corresponding Pt-complexes **93** and **94.** a) 1.1 equiv. NaH, 0.5 equiv. DCM, THF, r.t.; b) 1.0 equiv. Ph_2P-CL, DCM c) 1.0 equiv. $[PtCl_2(PEt_3)$-µ-$(Cl)]_2$, DCM, r.t.; d) 50 °C, 24h (yields were not described by the authors for steps b-d).

Finally, another example of a dicationic phosphine capable of coordinating transition metals was prepared by *J. Petuškova* in our work-group. A cyclopropenium unit was utilized as a positively charged moiety in these compounds. Biscyclopropenium phosphine **95a** was accessed in moderate yield (Scheme 1-17) over two steps from the chloro cyclopropenium salt **63**.[34] The synthetic sequence included a condensation with a primary phosphine to first yield monocationic phosphine **96a**. Subsequent deprotonation with a strong base afforded a phosphaalkene, which was then reacted *in situ* with a second equivalent of the chloro cyclopropenium salt **63**. Interestingly, it was possible to coordinate phosphine **95a** to Au(I), Pt(II) and Pd(II), resulting in the formation of complexes **97-99** (Scheme 1-17).

The use of these dicationic phosphines as ancillary ligands in catalysis is the main topic of this thesis. Therefore, their stereoelectronic attributes will be evaluated in more detail in the discussion part of this work.



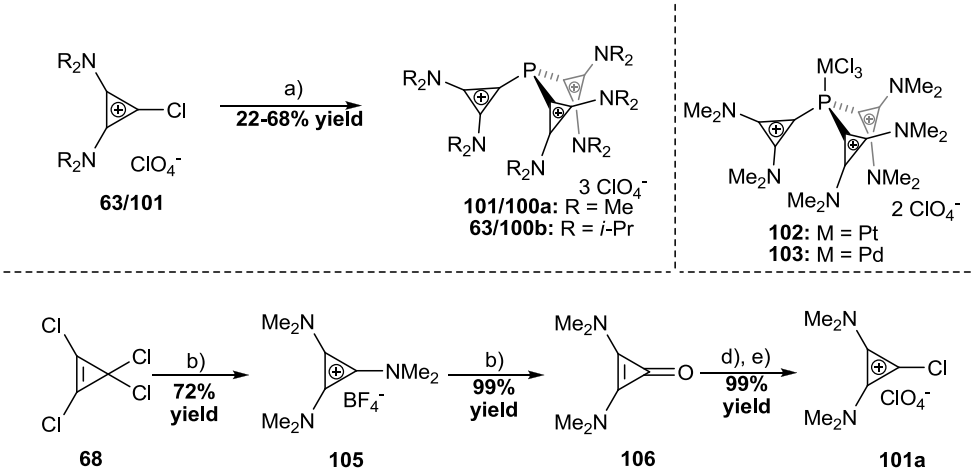
Scheme 1-17: Up: Synthesis of biscyclopropenium phosphine **95a** by *M. Alcarazo et al.*. **Down:** Transition-metal complexes of dicationic phosphine **95a**. a) 2.5 equiv. $PhPH_2$, THF, 24 h; b) 1.0 equiv. KHMDS, -40°C, 2h, 1.0 equiv. **63**, -40°C to r.t., overnight.

1.4 Tricationic phosphines

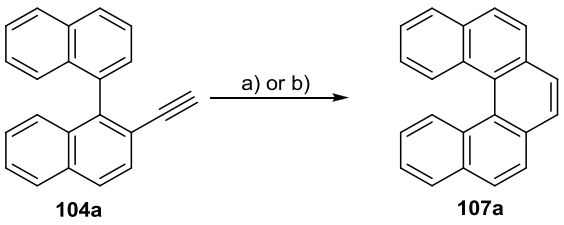
The first tricationic phosphines **100a/b** capable of coordinating transition metals were also prepared in our work group by *J. Petuškova* by condensation of tris(trimethylsilylphosphine) with the corresponding cyclopropenium salts **63**/**101** in poor to moderate yields (22-68%, Scheme 1-18). When the steric demand of the alkyl residues attached to the N-atoms of the cyclopropenium moieties was small enough, coordination of these compounds to Pt(II) and Pd(II) (**102**, **103**, Scheme 1-18) was possible. However, all of them all failed to coordinate Au(I) or Rh(I)-centers at room temperature.[35] The calculated carbonyl stretching frequency of the $Ni(CO)_3L$ complex of tricationic phosphine **100a** has a value of value of $\tilde{\upsilon}_{CO}$(**100a**) = 2111 cm^{-1} and the measured oxidation potential is *Ep(Ox)* = 2.062 V.[16a] While the carbonyl stretching frequency shows that the tricationic phosphine is indeed a very strong π-acceptor (comparable with PF_3), it is easier to oxidize than the bisimidazolium phosphines **81/82**, which can be explained by the fact that the LUMO (-0.1388 eV) of one cyclopropenium cation lies much higher in energy than the corresponding LUMO of an imidazolium unit (-0.1847 eV). As a result, the electron withdrawing effect of the respective cationic moieties is more pronounced for phosphines bearing imidazolium rings as substituents, than for those with cyclopropenium units.

Furthermore, Pt-complex **102** has been successfully used as a precatalyst for the *6-endo-dig* cycloisomerization of binaphtyl alkyne **104a** (Scheme 1-19) by *J. Carreras* in our working-group.[36] This reaction had been already discovered by *A. Fürstner et al.*,[37] but the levels of reactivity achieved using ligand **100a** clearly surpassed those previously reported (Scheme 1-19, Figure 1-11). Using precatalyst **102**, 22 different substrates were submitted to the optimized cycloisomerization conditions, affording the desired *6-endo-dig* product in good to

excellent yields (75-97%). Furthermore, the functional group tolerance of this reaction was also remarkable and functionalities such as -CF_3, -F, -alkyl,-naphtyl, thiophene, -OMe, -$SiMe_3$ and –COOMe were tolerated.



Scheme 1-18: Left up: Synthesis of tricyclopropenium phosphine **101a/b** by *M. Alcarazo et al*. **Right up:** Isolated metal complexes of tricyclopropenium phosphine **101a**. D**own**: Synthesis of chloro cyclopropenium salt **102** by *M. Alcarazo et al.* a) 0.33 equiv. $P(SiMe_3)_3$, fluorobenzene, 60 °C, 3 days; b) 3.6-4.0 equiv. H-NMe_2, DCM, -78 °C, 5 h, -78 °C to 0 °C, 1 h, 0 °C to r.t., overnight, reflux, 3 h; c) 10 equiv. $KOH_{(aq)}$, 65 °C, 2 h; d) 3.2 equiv. $(COCl)_2$, DCM, 0 °C, r.t., 15 min; e) 0.5 equiv. $Mg(ClO_4)_2$, CH_3CN, r.t., overnight.



Scheme 1-19: Cycloisomerization of binaphtyl alkyne **104b** by *M. Alcarazo et al*. a) 0.05 equiv. $PtCl_3L$ (L: **66/95a/100a**), 0.05 equiv. $Ag(CB_{11}H_6Cl_6)$, 1,2-DCE, 80 °C; b) 0.05 equiv. $PtCl_2$, 0.05 equiv. PR_3, 1,2-DCE, 80 °C.

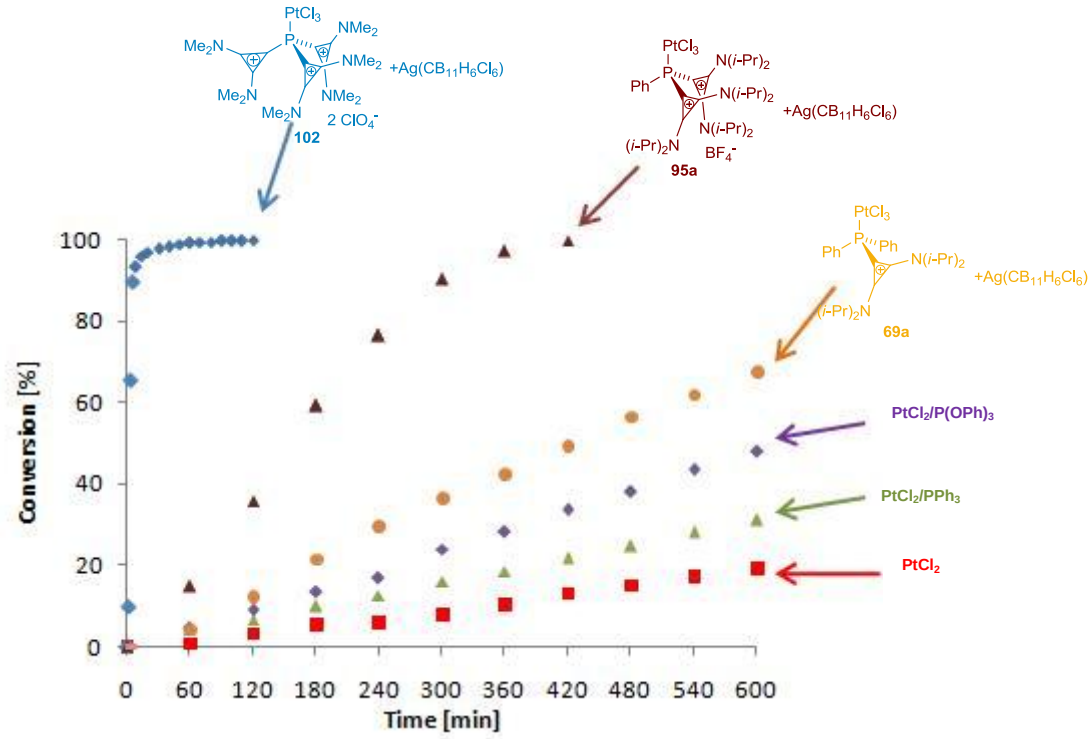
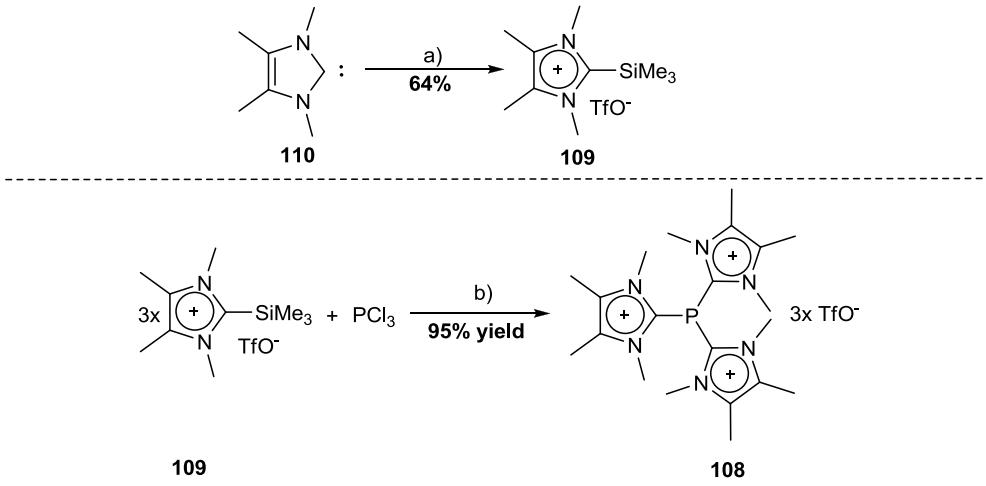


Figure 1-11: Ligand effect on the cycloisomerization of binaphtyl alkyne **104a**.[36]

A more recent example for a tricationic phosphine was provided by *J. J. Weigand et al*. in the form of trisimidazolium phosphine **108**. This compound was prepared from the silyl carbenoid **109** and PCl_3 in excellent yield (95%, Scheme 1-20). In order to force the reaction to full conversion a temperature of 140 °C was required. The silyl carbenoid **109** itself was accessible in moderate yield (64%, Scheme 1-20) from the respective free carbene **110** upon reaction with Me_3Si-OTf. While structurally quite interesting no coordination compounds of this tricharged phosphine have been described.[38]

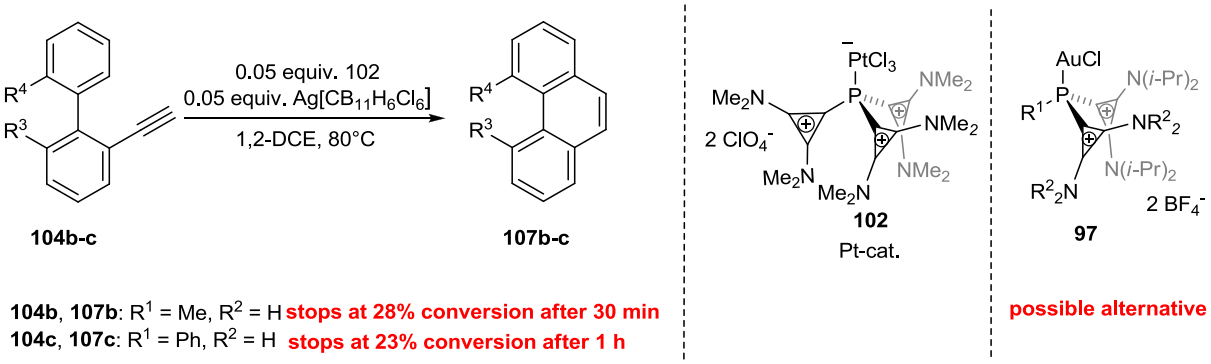


Scheme 1-20: Up: Preparation of silyl carbenoid. Down: Synthesis of triimidazolium phosphine **108** *by J. J. Weigand et al.*. a) 1.3 equiv. Me_3Si-OTf fluorobenzene, 1h, r.t.; b) 140 °C, 3 h.

.

2 Motivation

It was mentioned in the previous section that the utilization of tricationic phosphines of type **100a** in the Pt(II)-catalyzed *6-endo-dig* cycloisomerization of biphenyl/binaphtyl-alkynes provided high reactivity as well as a broad substrate scope. Despite of this, the employed cycloisomerization methodology presented several drawbacks. For example, the presence of (two) substituents in C-6 (R^3) and C-2' (R^4) positions on a biphenyl-alkyne substrate resulted often in an incomplete conversion to the desired product (R^1, R^2 in Scheme 2-1).



Scheme 2-1: Left: Cycloisomerization of biphenyl-alkynes **104b** and **104** in the presence of Pt-cat. **102**; **Middle:** Pt-precatalyst **102**; **Right:** possible alternative Au(I)-precatalyst **97**.

In order to solve this problem, we first decided to utilize a more π-acidic metal center like Au(I) in combination with **100a**. However as already mentioned, tricationic phosphine **100a** did not form a stable Au(I) complex.[35, 39] For this reason we decided to test if the use of Au(I)-complexes of biscyclopropenium phosphines such as **95a** could solve the problem. It has to be mentioned here that Au(I)-complex **97a** is stable in solution at room temperature. As a consequence several Au-precatalysts of type **97** were prepared and evaluated for the cycloisomerization of these problematic substrates (**104b**, **104c**).

Another key issue, which is addressed in this thesis is the improvement of the solubility of the prepared dicationic phosphines as well as their respective Au(I)-complexes. Polycationic catalysts are usually only soluble in polar solvents like acetonitrile, DCM or 1,2-DCE. It was envisioned that the utilization of halide-free solvents like toluene would be beneficial in terms of environmental reasons. Moreover, solvents such as toluene could possibly stabilize the activated Au-complex by π-coordination to the vacant site of the catalyst. This should result in an extended stability of the catalytic system and may allow the use of lower catalyst loading.

In order to increase the solubility of dicationic phosphines and their corresponding complexes in apolar solvents, it was decided to exchange the aliphatic residues (R^2) on the N-atoms of the cyclopropenium by longer aliphatic chains. Moreover, the effect of the counter ion has also been studied (Figure 2-1).

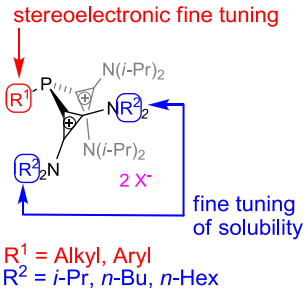


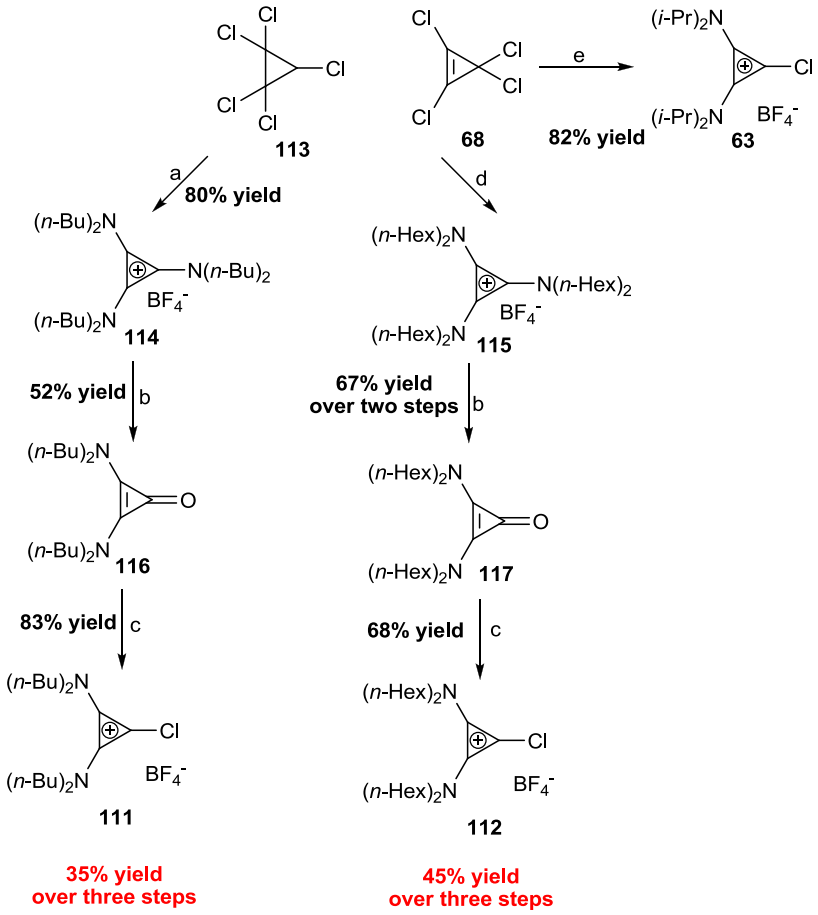
Figure 2-1: General Scheme of a dicationic cyclopropenium phosphine.

After establishing an optimized catalytic system for the cycloisomerization of biphenyl-alkynes **104** with two internal substituents, the synthetic value of the developed methodology will be demonstrated in the preparation of a natural product, which depicts a phenanthrene architecture.

3 Synthesis and Evaluation of dicationic phosphines

3.1 Synthesis of dicationic phosphines

Dicationic phosphines of the general formula **95** were prepared from the respective cyclopropenium salts **63**, **111 or 112** (Scheme 3-1), which are accessible from either tetrachlorocyclopropene **68** or pentachlorocyclopropane **113**, both commercially available compounds. Reaction of those starting materials with an excess of HNR_2 yielded either **63** (82% yield) or the triaminocyclopropenium salts **114** and **115** respectively, depending on the steric bulk of the used amine. In order to transform **114** and **115** to the synthetically more useful chloro cyclopropenium salts **111** and **112,** controlled hydrolysis of **114** and **115** under basic conditions was carried out to afford the lipophilic ketones **116** and **117** in moderate yield over two steps (40-67%). Subsequently, these compounds were treated with 3.1 equivalents of oxalyl chloride to obtain the corresponding chloro cyclopropenium salts **111** and **112** in good yields (68-83%).[39,40]

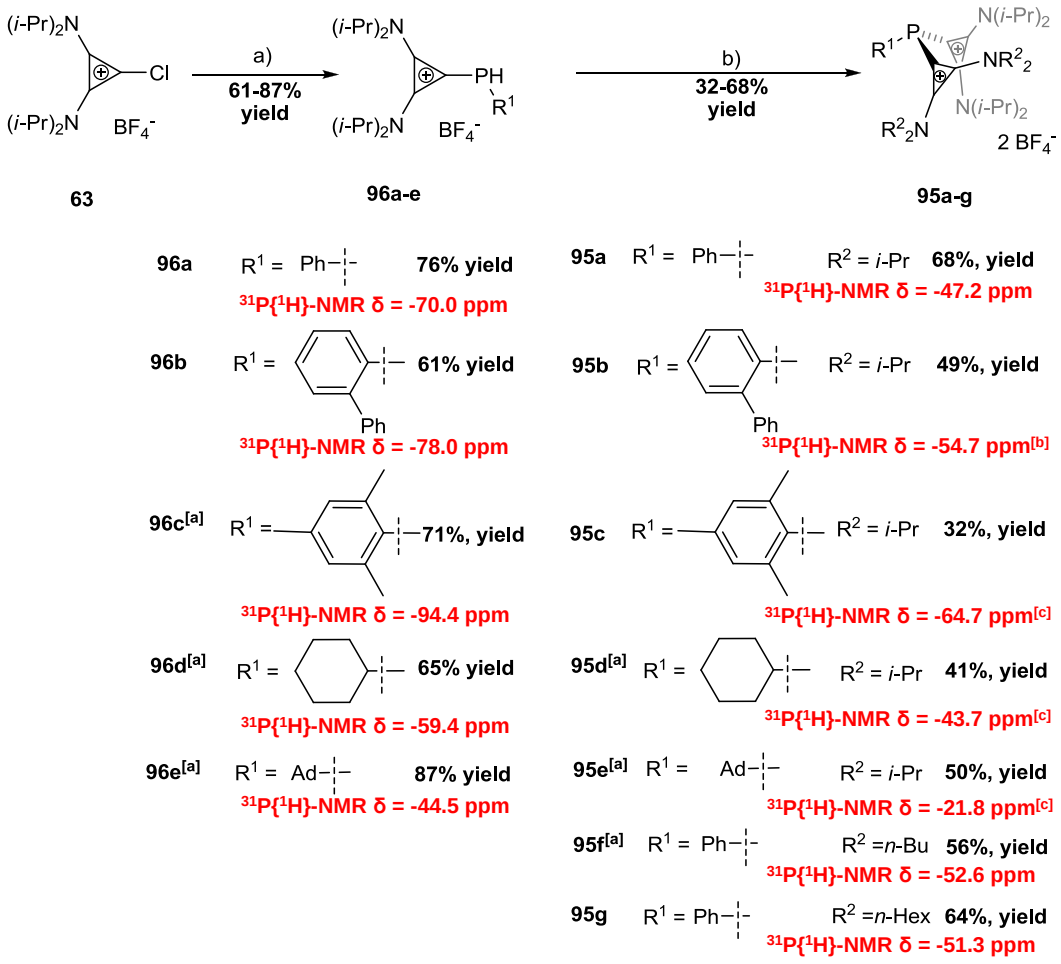


Scheme 3-1: Synthesis of cyclopropenium salts **63**, **111**, **112**. a) 7.8 equiv. HN(*n*-Bu)$_2$, 0 °C, 4 h, RT, 18 h, reflux, 5 h, DCM;[40] b) 10 equiv. KOH, MeOH, H_2O, 60°C, 16 h; c) 3.1 equiv. $(COCl)_2$, 0°C, 0°C to r.t., r.t., 1 h; d) 4.0 equiv. HN(*n*-Hex)$_2$, -78 °C, 1h, 0 °C, 4 h, r.t., 18 h, DCM; e) 4.0 eqiv. HN(*i*-Pr)$_2$, -78 °C, r.t., 18 h, DCM.[25]

With these cyclopropenium salts in hand, the dicationic phosphines of type **95** were prepared, in collaboration with *G. Mehler,* in low to moderate isolated yields (22-52%) following the already described two steps sequence from the corresponding primary phosphines (Scheme 3-2). Thus, condensation of the cyclopropenium salt **63** and the desired primary phosphine afforded the monocationic secondary phosphine intermediate **96**, which was subsequently condensed with a second equivalent of the chloro cyclopropenium salt under basic conditions to yield **95**.

Successful formation of intermediate **96** could be confirmed by measuring the $^{31}P\{^1H\}$-NMR resonance, which experienced a considerable downfield shift compared to the measured values of the corresponding primary phosphines. All $^{31}P\{^1H\}$-NMR signals are in the range of -94 ppm to -45 ppm (Scheme 3-2).[41] Furthermore, signals of aromatic protons (if present) also shifted downfield in the ^1H-NMR spectrum when the first condensation product **96** is

compared with the free phosphine. A final confirmation of the general structure of monocationic intermediates **96** was achieved by successful XRD analysis of compound **96a** (section 3.2).

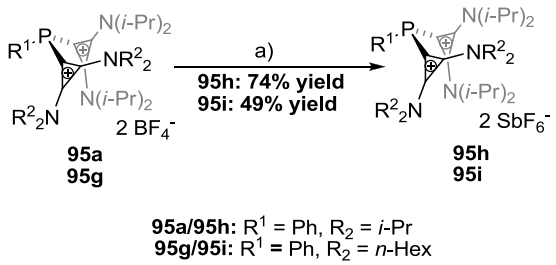


Scheme 3-2: Modular synthesis of dicationic cyclopropenium phosphines **95a-g**. All NMR spectra were measured in $CDCl_3$ unless stated otherwise. [a]: provided by *G. Mehler*; [b]: measured in CD_3CN; [c]:measured in CD_2Cl_2. a) 2.5 equiv. R^1-PH_2, THF (or diglyme), 60 °C (or 100 °C), 24 h; b) 1.0 equiv. KHMDS, -40 °C, 2h, 1.0 equiv. of **63**, **111** or **112** -40 °C to r.t., overnight.

The isolated secondary phosphines were deprotonated by a strong base (KHMDS) generating a phosphalkene *in situ*, which then reacted with a second equivalent of the desired cyclopropenium salt (**63**, **111** or **112**) affording the desired dicationic phosphines **95a-g** in moderate yields (32-68%). The attachment of a second cyclopropenium unit displaces the chemical shift of the $^{31}P\{^1H\}$-NMR resonance further downfield into the range of -65 ppm to -21 ppm (Scheme 3-2).[41] These observed chemical shifts of the $^{31}P\{^1H\}$-resonance were in line with the corresponding values which were measured for the bisimidazolium phosphines **81** and **82** (δ = -54 and -76 ppm respectively).[30, 31]

Dicationic phosphines thus prepared are slightly soluble in THF. As this solvent proved to be indispensable to wash the crude product to obtain pure materials, the moderate yields are not surprising. Furthermore, it should be mentioned that the solubility of the prepared biscyclopropenium phosphines **95** is highly dependent on the aliphatic residues R^2 attached to the N-atoms of the cyclopropenium moieties (Scheme 3-2). All dicationic phosphines, which have exclusively *i*-Pr substituents, are only soluble in polar solvents such as DCM or acetonitrile. However, as soon as the R^2 residues on one of the cyclopropenium units are exchanged for *n*-Bu or *n*-Hex, the resulting dicationic ligands become soluble in non-polar solvents such as toluene or diethyl ether. Due to this remarkable solubility the work-up of phosphines **95f** and **95g** had to be adjusted. In the case of **95f** the crude material was repeatedly washed with pentane, while **95g** had to be purified by column chromatography, because no precipitation was observed in THF.

Finally, an ion exchange was performed for two of the prepared phosphines using an excess of $NaSbF_6$ in acetonitrile (Scheme 3-3, **95h**, **95i**). While the absence of BF_4^- was easily confirmed by ^{19}F-NMR and ^{11}B-NMR spectroscopy, the presence of the SbF_6^- counter ion was also proven by $^{19}F\{^1H\}$-NMR spectrum ($\delta = 124$ (sext., $J_{F\text{-}Sb(I=5/2)} = 1930.5$ Hz, $J_{F\text{-}Sb(I=7/2)} = 1054.7$ Hz) and negative MS spectrometry (m/z = 234.9 [SbF_6^-]) and IR (strong band at 652 cm^{-1}). Final confirmation of the successful ion-exchange was achieved by XRD-analysis of **95i**. (Scheme 3-3).



95a **95g** **95h** **95i**

95a/95h: R^1 = Ph, R_2 = *i*-Pr
95g/95i: R^1 = Ph, R_2 = *n*-Hex

Scheme 3-3: Ion exchange**.** a) 7.0 equiv. $NaSbF_6$, CH_3CN, r.t., overnight.

3.2 Structural properties of dicationic phosphines

Single crystals suitable for XRD analysis were obtained for secondary phosphine **96a**, the dicationic phosphine **95b** (R^1 = *o*-biPh, R^2 = *i*-Pr, X = BF_4) and the lipophilic analogue **95i** (R^1 = Ph, R^2 = *n*-Hex, X = SbF_6^-). These structures could be compared among them and with the already known dicationic phosphine **95a** (R^1 = Ph, R^2 = *i*-Pr, X = BF_4^-, Figure 3-1, Table 3-1).[41a, ,42]

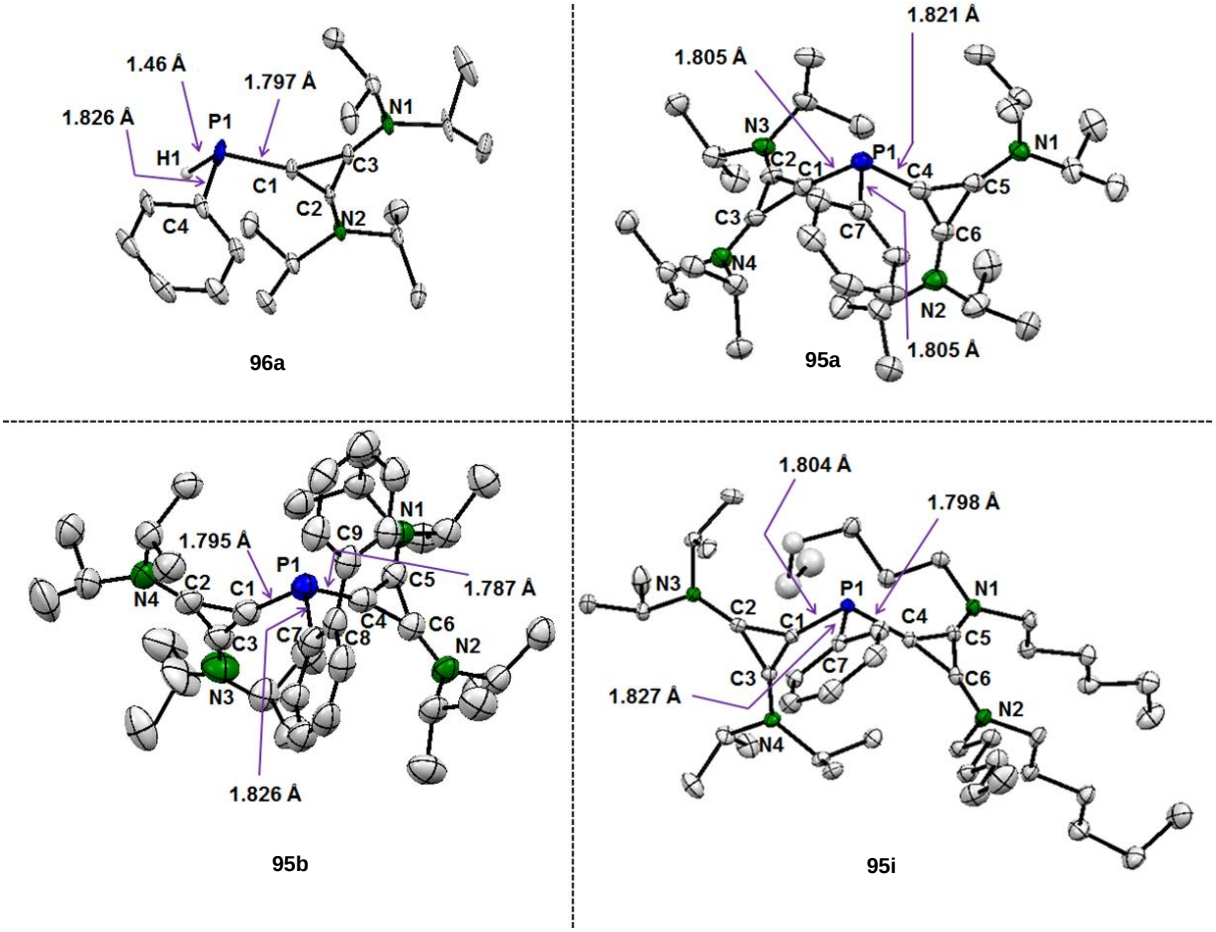


Figure 3-1: X-Rays of monocationic secondary phosphine **96a**, dicationic Phosphine **95a, 95b** and **95i**. For **96a**: α(H1-P1-C1) = 104(2)°, β(C1-P1-C4) = 103.04(11)°, γ (C4-P1-H1) = 100(2)°. For **95a**: α(C1-P1-C2) = 98.38(11), β(C2-P1-C3) = 100.53(11)°, γ(C3-P1-C1) = 102.36(11)°. For **95b**: α(C1-P1-C4) = 100.68(18)°, β(C4-P1-C7) = 104.09(18)°, γ(C7-P1-C1) = 103.21(18)°. For **95i**: α(C1-P1-C4) = 102.23(11)°, β(C4-P1-C7) = 100.59(11)°, γ(C7-P1-C1) = 103.17(11)°. Anisotropic displacements shown at 50% probability level, counter-ions and hydrogens (except the one the P-center of **96a**) omitted for clarity purposes.

Table 3-1: Comparison of bond lengths *d* and pyramidalization degrees [PD][43] for different charged and neutral phosphines.

Entry	phosphine	d (P-H) [Å]	d (C_{Ph}-P) [Å]	d (C_{Cpr}-P)[a] [Å]	d ((C-C)$_{CPr}$)[b] [Å]	PD [%][c]
1	**95b**	-	1.826(3)	1.787(4)-1.795(4)	1.383(6)-1.409(6)	57.8
2	**95i**	-	1.827(3)	1.798(2)-1.804(3)	1.377(3)-1.415(3)	60.0
3	**95a**[42]	-	1.821(4)	1.805(3)	1.374(5)-1.414(4)	65.3
4	**96a**	1.46(6)	1.826(2)	1.797(3)	1.377(3)-1.405(3)	58.2
5	PPh_3[44]	-	1.828(2)-1.834(2)	-	1.370(3)-1.395(3)[d]	56.7
6	Ph_2P-H[45]	1.42	1.830(6)-1.831(6)	-	1.402(3)[d]	/

[a]: ***d*(C$_{Cpr}$-P)** refers to the bond length in between the P-center and cyclopropenium C-atom directly attached to this P-atom. [b]: ***d*((C-C)$_{Cpr}$)** refers to the C-C bond distance between two neighboring C-atoms in the cyclopropenium ring [c]: PD refers to the calculated pyramidalization degree. [d]: As these compounds do not possess a cyclopropenium moiety, the given values refer to C-C bond distances in between the aromatic carbons of the phenyl residues.

The measured P-C_{CPr} bond-distances in **95b** of (1.787(4)-1.795(4) Å), **95i** (1.798(2)-1.804(3) Å) and **95a** (1.805(3) Å) are shorter than the respective P-C_{Ph} bonds in the same molecule. This can be rationalized by the electron-withdrawing nature of the cyclopropenium moieties and the resulting back-donation form the P-center to these charged units. However, these distances are still by far longer than a true P=C double bond (i.e. d(C=P) =1.662(8) Å in an unstabilized ylide $Ph_3P{=}CH_2$)[46] and indicate mainly single-bond character.[41]

The bond lengths in between the P-center and the aromatic carbon (Table 3-1, d(C_{Ph}-P); Figure 3-1) of the aryl group bound to the phosphorus are virtually identical for the intermediate **96a** and all dicationic phosphines (**95a**, **95b**, **95i**) with values around 1.821(4)-1.827(3) Å. These are in line with the measured C_{Ph}-P distances of PPh_3 (c.f. 1.828(2)-1.834(2) Å) or Ph_2P-H (c.f. 1.830(6)-1.831(6) Å).

The C-C bond-distances *d*(C-C)$_{Cpr}$ (1.370(3)-1.415(5) Å) between the neighboring C-atoms constituting the cyclopropenium rings of the analyzed cationic phosphines (**96a, 95a**, **95b**, **95i**) have similar values. Because these bond-lengths are significantly shorter than the typical

C-C single bond (1.54 Å),[47] but slightly longer than a true C=C (1.34 Å)[47] double bond, they indicate aromaticity in these three membered rings (Table 3-1).

Finally, the pyramidalization degree [PD] on the P-center depends on the overall charge and sterical demand of the residues attached to the P-atom. On the one hand, the pyramidalization is augmented with increasing charge as it can be observed in the comparison of monocationic intermediate **96a** with the dicationic phosphine **95a**. The [PD] value increases from 57.8% (**96a**) to 65.3% (**95a**) by exchanging the proton bound to phosphorus (**96a**) for one additional cyclopropenium unit (**95a**).

On the other hand, an enhancement of the steric bulk lowers the [PD] value. By increasing the steric demand of the aliphatic substituents R^2 (Scheme 3-3, Figure 3-1, Table 3-1) bound to the N-atoms of the cyclopropenium units a slight decrease of the pyramidalization can be observed, which becomes apparent when the [PD] value of dicationic phosphine **95a** (R^2 = *i*-Pr, [PD] = 65.3°) is compared with the corresponding value of **95i** (R^2 = *n*-Hex, [PD] = 60.0°). A similar effect is noticed when the steric demand of the aryl-residue R^1 (Scheme 3-3), bound to the P-atom of the respective dicationic phosphine, is increased (**95a**: R^1 = Ph, [PD] = 65.3%; **95i**: R^1 = *o*-biPh, [PD] = 58.2%).

Overall, the pyramidalization degrees [PD] of the analyzed dicationic phosphines are similar to the known value for PPh_3 ([PD] = 56.7°), which is in agreement with the conclusion that the back-donation from the P-atom to the cationic moieties is marginal. Otherwise an increased flattening of the structure should have been observed after sequential addition of new charged cyclopropenium moieties to the phosphorus. The weak back-donation form the P-atom to the charged moieties can be rationalized by an inefficient orbital-overlap between occupied non-bonding sp^3 orbital of the phosphine and the π*-orbitals of the bound cyclopropenium unit.

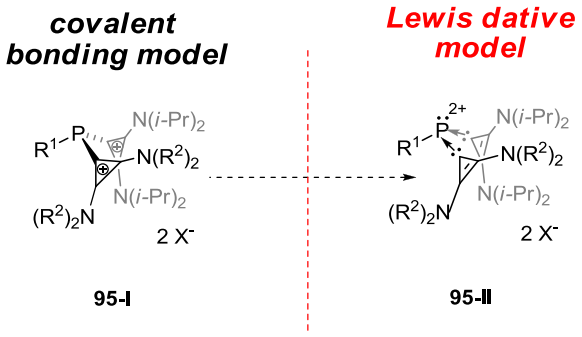
These results could be reproduced by the DFT calculations (B3LYP/6-31G*) performed for dicationic phosphine **95a** and carried out at our department of theoretical chemistry (Table 3-2).[34] Because the prepared dicationic phosphine **95i** is almost identical with the dicationic phosphine **95a** from an electronic as well as from a structural standpoint, the calculated data for **95a** can be considered also valid for **95i**. The calculated *Wiberg* index for the C_{CPr}-P bond of 0.909 supports the conclusion that the back-donation from the P-center to the cyclopropenium moiety is negligible. Furthermore, the calculated bond lengths for P-C_{CPr}-

and C_{Ph}-P of **95a** are in agreement with obtained experimental data for **95b** and **95i** (Table 3-2).[34]

Due to the experimental results the covalent model structure **95-I** (Scheme 3-4) seems to be more suitable to describe the bonding situation in these dicationic phosphines, but a natural population analysis (B3LYP/6-311+G**//6-31G*) reveals a charge Q of +0.88 assigned to the P-center of **95a**.[34] Due to this, the true nature of ligand **95a** (as well **95i**) lies in between structures **95-I** and **95-II** (Scheme 3-4), with a slight emphasis on model **95-I**.

Table 3-2: Comparison of experimental and calculated bond lengths and corresponding *Wiberg* bond orders at (B3LYP/6-31G*).[34]

	Bond length d [Å]			**Bond order**
	experimental		**calculated**	**95a**
	95i	**95a**	**95a**	
C_{CPr}-P	1.798(2)-1.804(3)	1.805(3)	1.83	0.909
C_{Ph}-P	1.827(3)	1.821(4)	1.84	0.911



Scheme 3-4: Possible model structures for dicationic phosphines **95**.

3.3 Evaluation of π-acceptor properties

A frontier orbital analysis (B3LYP/6-311+G**//6-31G*, calculations performed at our department of theoretical chemistry) of **95a** showed that its HOMO is lowered in energy (E (HOMO) =-11.50 eV) when compared to that of the monocationic phosphine **66** (E (HOMO)=-9.02 eV). However the shape of both oribtals is nearly identical and it depicts significant lone pair character centered on the phosphorus with an orbital occupancy of 1.87e (Figure 3-2). This allows the ligand to display some *Lewis*-basicity despite of the two positive charges that it bears. The calculated LUMO (E(LUMO)= -6.79 eV) lies considerably lower in energy than the LUMO of commercially available electron poor phosphines (e.g. $P(C_6F_5)_3$, (E(LUMO)= -2.44 eV)) or phosphites (e.g. $P(OMe)_3$, (E(LUMO)= -0.03 eV), which should result in a great enhancement of its π-acceptor properties.[34, 36]

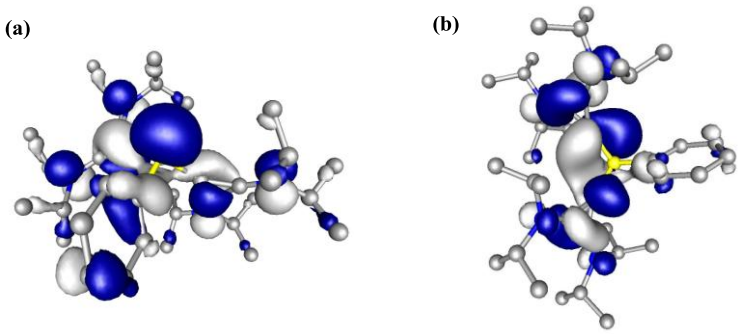


Figure 3-2: Representation of the calculated HOMO (left) and LUMO (right) for **95a**.

Overall, the calculations confirm that the successive attachment of electron withdrawing substituents directly to a phosphorus center leads to a decrease of the σ-donating properties and an increase the of π-acceptor properties of the resulting phosphine. (Figure 3-3).[34, 36]

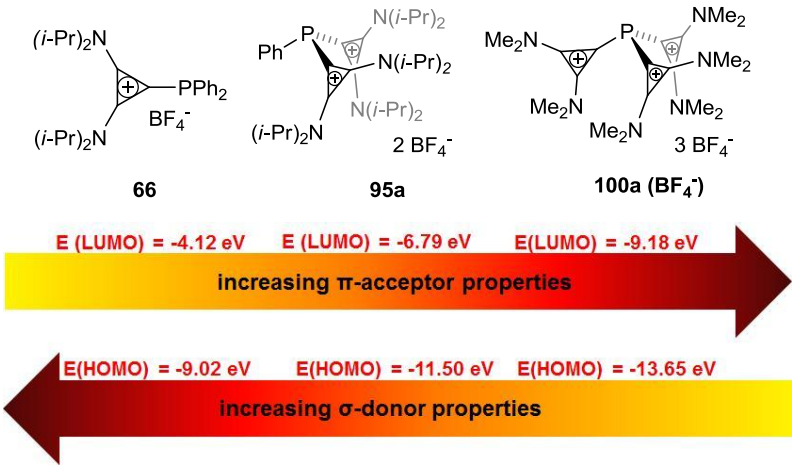


Figure 3-3: Increasing π-acceptor properties among cationic cyclopropenium phosphines with increasing charge. The LUMOs for **66**, **95a**, **100a** were calculated by B3LYP/6-311+G**//6-31G*.[34, 36]

3.4 Evaluation of steric properties

One of the most common ways to determine the steric as well as the electronic properties of a P-centered compound, is the *Tolman* analysis, which studies the CO-stretching frequency ($\tilde{\upsilon}_{CO}$) of [Ni(CO)$_3$L] complexes and the cone angles of the ligands (L).[16a, 48] As it was already explained in section 1.2.1.1 the CO-stretching frequency of the [Ni(CO)$_3$L] complex increases with rising π-acceptor/decreasing σ-donor properties of the used ligand. Due to this, it is a good indicator for the electronic nature of the investigated ligand.

The *Tolman* cone angle (Θ) is defined as the apex angle of a cylindrical cone centered 2.28 Å away from the center of the P-atom, which just touches the *van-der-Waals radii* of the outermost atoms of the substituents attached to the P-center (Figure 3-4). Due to the fact that the three substituents of the phosphine might not be identical, half-angles Θ_i are utilized for the determination of the aforementioned cone angles Θ employing equation 3-1.[48]

$$\theta = \frac{2}{3}\sum_{i=1}^{3}\frac{\theta_i}{2}$$ **Equation 3-1**

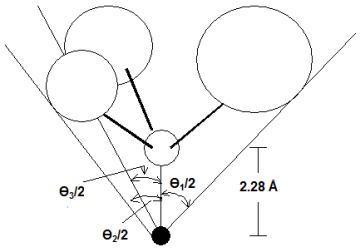


Figure 3-4: Representation of the *Tolman* cone for and unsymmetrical P-centered ligand.

By depicting $\tilde{\upsilon}_{CO}$ of the Ni(CO)$_3$L complexes against the cone angle Θ of the corresponding P-centered ligand a map is obtained, which provides information about the electronic nature of the used ligand as well as its sterical demand (Figure 3-5). The main disadvantage of this method is the preparation of the necessary metal complexes using the highly toxic and volatile Ni(CO)$_4$. For this reason *Tolman* electronic parameters (TEP) of strong π-acceptor ligands are not always available. Complementary data can be obtained in these cases with the help of theoretical chemistry. *Gusev* has implemented a method to determine these values.[49] This methodology is capable of reproducing the known values accurately and, therefore, it seems reasonable to accept that the predicted values for those phosphorus compounds, whose *Tolman* electronic parameters has not been measured, are correct.[16a, 49]

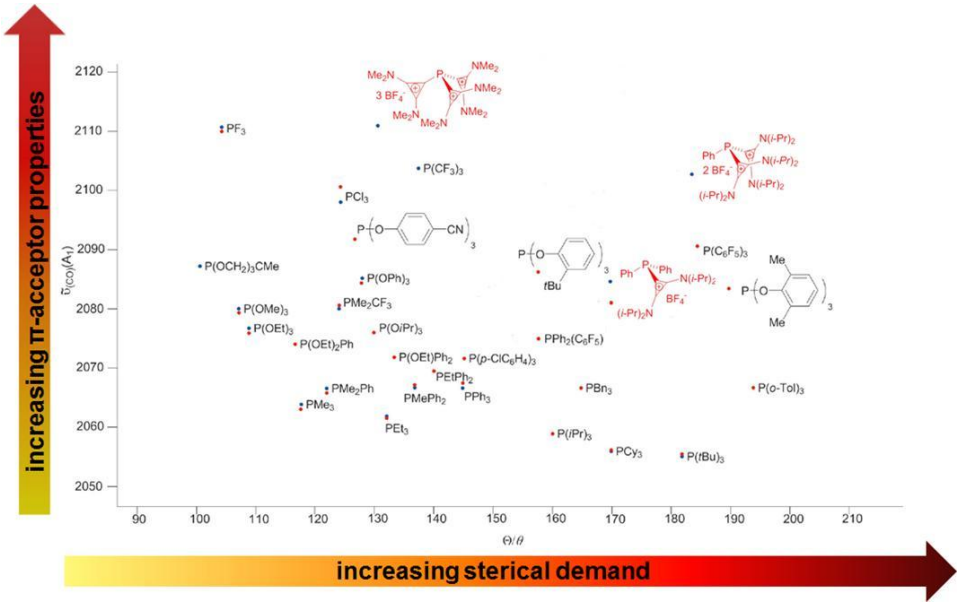


Figure 3-5: Comparison of *Tolman* angles for different P-centered ligands (experimental values are shown in red and calculated values in blue).[16a, 48a, 49]

Representation of the aforementioned values in the stereoelectronic map demonstrates the significant effect of an additional positive charge attached to the P-center. The monocationic cyclopropenium phosphine **66** has a wavenumber in the range of phosphites, being a moderate π-acceptor ligand with a TEP of 2082 cm^{-1}. However, if one of the phenyl groups is exchanged for an additional cyclopropenium moiety, the resulting dicationic phosphine **95a** is elevated into the range of strong π-acceptor ligands (i.e. $P(CF)_3$ and PF_3) with a wavenumber of 2101 cm^{-1}. In fact, **95a** is only surpassed in its π-acceptor properties by a tricyclopropenium phosphine **100a** with a carbonyl stretching frequency of $\tilde{\upsilon}_{CO}$ = 2111 cm^{-1}.[16a]

An alternative method to evaluate the σ-donor properties of P-centered ligands is the measurement of their oxidation potential $E_p(Ox)$ by cyclic voltammetry since the donor ability of a phosphine is inversely proportional to this value.

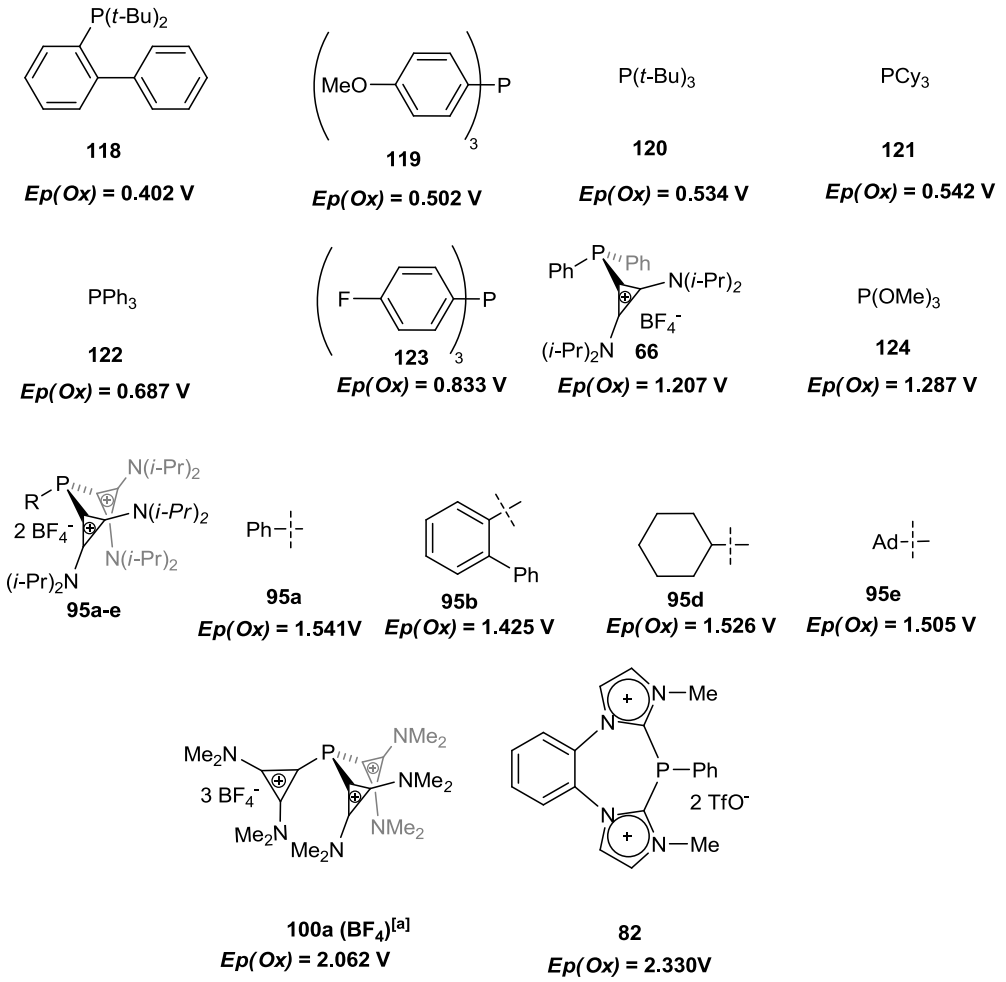


Figure 3-6: Structures of phosphines evaluated by cyclic voltammetry. Oxidation peak potential reported in V. Calibrated versus ferrocene/ferrocenium (E1/2 = 0), Bu_4NPF_6 (0.1 M) in DCM. [a]measured in acetonitrile. Credits for measurements go to *C. Wille.*[16]

The measured oxidation potentials (Figure 3-6) are in agreement with the results obtained from the *Tolman* stereoelectronic map and further confirm the decrease of the σ-donating abilities by introduction of an additional cyclopropenium unit on the phosphorus center. Furthermore, the oxidation potentials ($E_p(Ox)$) of the prepared biscyclopropenium phosphines **95a-e** show that they are even weaker σ-donors than phosphites, but at the same time, they provide σ-donor capabilities which are significantly greater than the bisimidazolium ligand **82**, which is not capable to coordinate metals.[16a, 31]

When the oxidation potentials of dicationic phosphines of similar structure are compared with each other, the influence of the residue R on the electronic properties becomes evident. In general, alkyl phosphines are more electron-donating than aryl-phosphines, because of the

possibility of the electron lone pair at the P-center to be delocalized on the π-system of the aryl group.[50]

Moreover, when two aryl-phosphines are compared with each other, the effect of the substitution pattern on the aromatic ring attached to the P-atom can be evaluated. For example, when the *Ep(Ox)* = 1.541 V of **95a** (R = Ph,) is compared with *Ep(Ox)* = 1.425 V of **95b** (R = *o*-biPh), it becomes evident that the presence of an additional phenyl group on the primary phenyl group attached to the P-center leads to an increase of the electron density on the phosphorus and an augmentation of the σ-donor properties of **95a.** A possible rationalization of this observation is the positive mesomeric effect of the secondary phenyl group.[51]

For alkyl phosphines the σ-donor character of the phosphorus increases with the number of alkyl substituents attached to the C-atom, which is bound to the P-center due the positive inductive effect of alkyl groups. Due to this, the following hierarchy among the donor-ability of the measured dicationic phosphines is found: **95b** (*o*-biPh) > **95e** (R = Ad) > **95d** (R = Cy) > **95a** (R = Ph) (Figure 3-6).[16a]

3.5 Summary

The synthesis of seven different dicationic phosphines (**95a-95g**) was accomplished in 22-49% yield over two steps in a modular fashion from the respective chloro cyclopropenium salts (**63**, **111**, **112**)**.** Subsequent ion-exchange was performed for two of those compounds in order to obtain the analogues of those dicationic phosphines with SbF_6^- as a counter-ion. The structure of these ligands was confirmed by full characterization and in addition, XRD-analysis of **96a**, **95a** and **95i**.

All C_{Cpr}-P bond lengths,[52] the aromatic nature of the C-C bond lengths within the cyclopropenium moiety and the pyramidalization at P suggest that the lone pair of electrons is still localized on the phosphorus.

Finally, the *Tolman* electronic parameters (TEP) fit the expectations. Enhanced π-acceptor properties are obtained by increasing the number of charged moieties attached to the P-center. Cyclic voltammetry measurements of the oxidation potential of the prepared dicationic phosphines **95a-95e** showed that the nature of R^1 influences this value and thus, the electron releasing properties of the corresponding phosphine **95** (Scheme 3-3).

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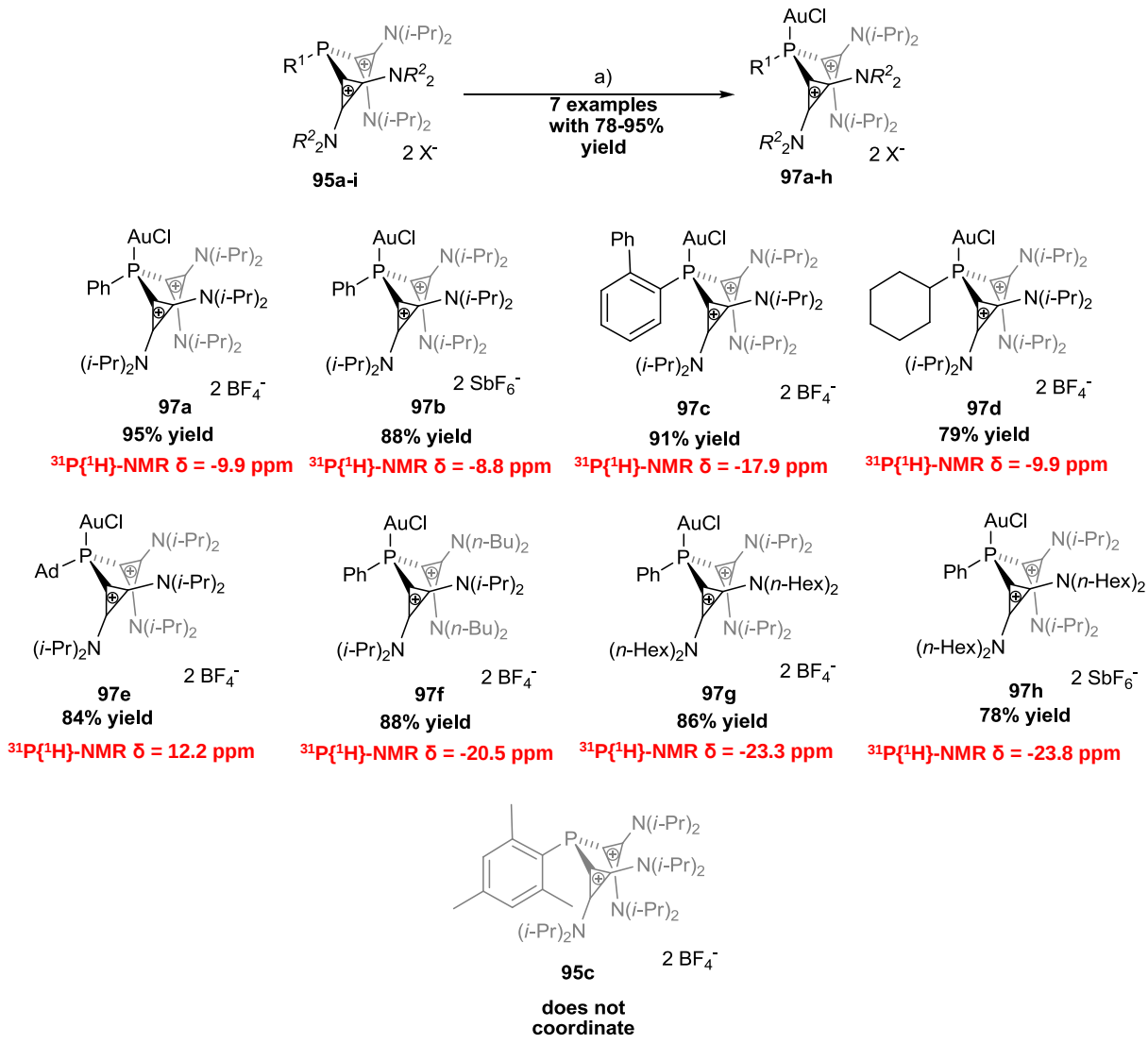
4 Coordination chemistry

4.1 Coordination to Au(I)

In order to check the coordinative properties of the dicationic phosphines (**95a-g**) they were treated with one equivalent of $AuCl(SMe_2)$ at -20 °C in DCM. The corresponding Au(I)-complexes **97a-h** were obtained as air stable solids in good to excellent yields (78-95%, Scheme 4-1). Moreover, all these compounds were stable in solid state as well as in solution at room temperature. Complexes **97a-e** were only soluble in polar solvents such as DCM, DMSO or acetonitrile, while compounds **97f**, **97g** and **97h** bearing *n*-butyl and *n*-hexyl chains (for R^2) were soluble in diethyl ether and toluene. This proved to be useful to avoid halogenated solvents in our catalytic systems.

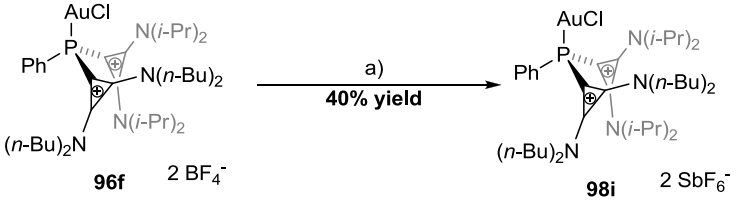
The formation of the desired Au(I)-complexes was easily confirmed by $^{31}P\{^1H\}$-NMR spectroscopy. After coordination to Au(I) the ^{31}P-resonance of the corresponding dicationic phosphines undergo a significant downfield shift in the $^{31}P\{^1H\}$-NMR spectrum appearing in the range between -23.8 ppm (**97h**, R^1 = Ph, R^2 = *n*-Hex, SbF_6, $CDCl_3$) and 12.2 ppm (**97e**, R^1 = Ad, R^2 = *i*-Pr, BF_4^-, CD_3CN).

Despite the generality of this coordination procedure (Scheme 4-1), the mesitylene substituted phosphine **95c** did not coordinate to the Au(I)-center under the reported conditions. Probably, the steric demand of the mesitylene group hinders the formation of the desired complex.



Scheme 4-1: Coordination of different dicationic ligands **95a-i** to Au(I). a) 1.0 equiv. $AuCl{\cdot}SMe_2$, DCM, -20 °C, 30 min, -20 °C to r.t., r.t., 30 min.

In order to study the counter ion-effect on catalysis, which will be discussed in detail in section 5, an ion exchange was performed for Au(I)-complex **97f** (Scheme 4-2). 5 equivalents of $NaSbF_6$ per equivalent of BF_4^- were needed to ensure that no signals corresponding to BF_4^- were detectable in the $^{19}F\{^1H\}$-NMR spectrum of the product.



Scheme 4-2: Ion exchange for compound **96f**. a) 10.0 equiv. $NaSbF_6$, CH_3CN, r.t., overnight.

A final confirmation for the coordination of Au(I) to our dicationic ligands was achieved by the XRD-analysis of single crystals of compounds **97b** (Figure 4-1) and **97c** (Figure 4-2), which were obtained by diffusion of diethyl ether in acetonitrile solutions of these compounds.

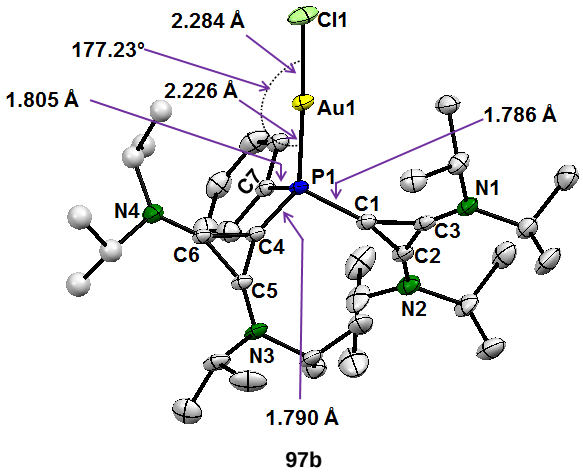


Figure 4-1: X-Ray of Au-complex **97b.** Anisotropic displacements shown at 50% probability level, counter-ions and hydrogens omitted for clarity purposes.

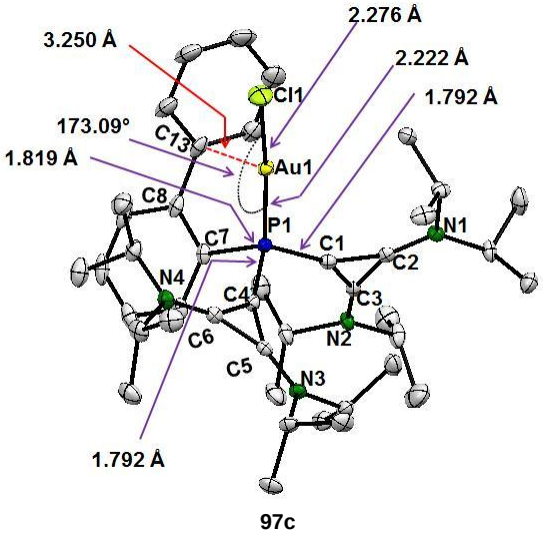


Figure 4-2: X-Ray of Au-complex **97c.** Anisotropic displacements shown at 50% probability level, counter-ions and hydrogens omitted for clarity purposes.

Table 4-1: Comparison of bond lengths of **97b** and **97c** to $AuCl(PPh_3)$ and $AuCl(P(OPh)_3)$.[53, 54]

Entry	AuCl(L)	d (P-Au) [Å]	d (Au-Cl) [Å]	d (C_{Ph}-P) [Å][a]	d(C_{CPr}-P) [Å][b]
1	**97b**	2.2257(14)	2.2835(15)	1.805(6)	1.786(6)-1.789(6)
2	**97c**	2.2224(10)	2.2763(10)	1.819(4)	1.791(4)-1.794(4)
3	PPh_3[53]	2.2308(5)	2.2915(5)	1.8091(15)-1.8116(15)	none
4	$P(OPh)_3$[54]	2.192(5)	2.273(5)	none	none

[a]: d(C_{Ph}-P) refers to the bond distance in between the P-center and the quaternary C-atom of the Aryl residue bound to the phosphorus;[b]: d(C_{CPr}-P) refers to the bond distance in between the P-center and C-atom of the cyclopropenium moiety bound to the P-center.

Both complexes **97b** (R = Ph, X = SbF_6^-) and **97c** (R = *o*-biPh, X = BF_4^-) have a linear coordination sphere around the Au-atom with only a slight distortion in the solid state. The P1-Au1-Cl1 angle in **97b** is 177.23°, while in **97c** the same parameter shows a value of 173.0°. The enhanced distortion in the case of **97c** is probably the result of the increased steric bulk of the biphenyl residue attached to the P-center, when compared with **97b**.

Both P-Au bond lengths (**97b:** *d*(P-Au) = 2.2257(14) Å; **97c:** *d*(P-Au) = 2.2224(10) Å) are crystallographically indistinguishable and in the same range of typical P-Au(I) bonds.

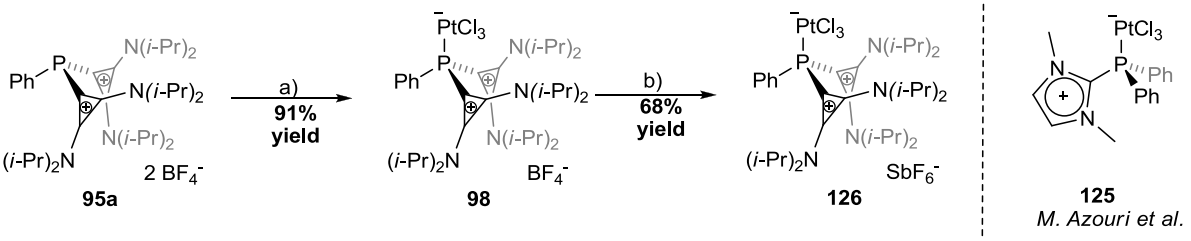
Compound **97c** depicts however an interesting feature. The carbon C13 (Figure 4-2) shows a short contact with the Au(I)-atom (d(C13-Au1) = 3.250 Å). This could be beneficial for future catalytic applications as such an interaction could stabilize the Au(I) center after the Cl atom is abstracted to form the active catalyst. As a consequence a longer lifetime of the catalyst in solution might be possible.

4.2 Coordination to Pt(II)

The coordination of monocationic imidazolium phosphines to Pt(II) utilizing K_2PtCl_4 as a metal source was reported for the first time by *N. Kuhn* as mentioned in section 1.2.[19] Prior to the preparation of biscyclopropenium phosphine **95a** (R^1 = Ph, R^2 = *i*-Pr, X = BF_4^-) by *J. Petuškova* in our work-group the only dicationic phosphine capable of coordinating Pt(II) was the guanidine derived species **92** synthesized by *M. P. Coles* in 2004[33] (section 1.3).

As in the case of the Au(I)-compounds, the $^{31}P\{^1H\}$-NMR signal of the dicationic phosphine experiences a significant downfield shift to -23.4 ppm ($^1J_{Pt\text{-}P}$ = 3997 Hz) upon coordination to Pt(II), which is consistent with the formation of the platinum complex.[41] Moreover, the Pt-P satellites of **98** provide a larger coupling constant than those reported for Pt-complex **125** ($^1J_{Pt\text{-}P}$ = 3425 Hz),[20] which can be explained by a stronger back-donation from the Pt-center to the P-atom in our case, probably due to the increased charge of the ligand (Scheme 4-3).

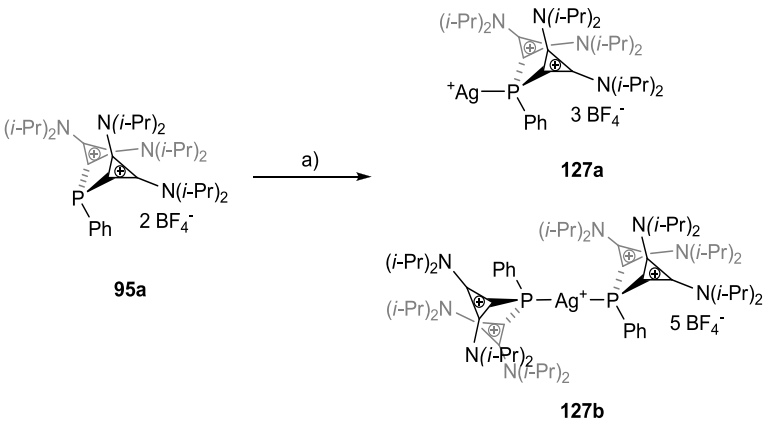
Precatalyst **98** was submitted to ion-exchange and gave the desired product **126** with SbF_6^- as a counter anion in good yield (68%). The ion exchange had to be performed at this stage as previous attempts to react K_2PtCl_4 with the biscyclopropenium phosphine **95h** (R^1 = Ph, R^2 = *i*-Pr, X = SbF_6^-) already bearing the SbF_6^- counter ion failed, probably due to the low solubility of the ligand.



Scheme 4-3: Left: Coordination of Pt(II) by dicationic ligand **95a** with subsequent ion exchange. **Right:** Pt(II)-complex **1325** by *M. Azouri et al.*, a) 1.0 equiv. K_2PtCl_4, CH_3CN, r.t., overnight; b) 3.5 equiv. $NaSbF_6$, CH_3CN, r.t., overnight.

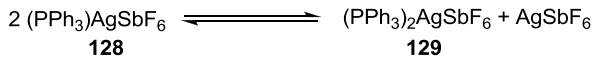
4.3 Coordination to Ag(I)

The coordination of dicationic phosphine **95a** to $AgBF_4$ in DCM at -25 °C resulted in the formation of a new Ag(I)-complex **127**, whose structure could not be unambiguously determined. *A priori* two possible structures (monocoordinated or biscoordinated Ag(I) complexes) can be proposed for **127** as shown in Scheme 4-4.



Scheme 4-4: Coordination of Ag(I) by dicationic ligand **95a**. a) 1.0 equiv. $AgBF_4$, DCM, -25 °C, 30 min, -25 °C to r.t., 1.5 h.

Coordination of Ag(I) is evident by the appearance of a new $^{31}P\{^1H\}$-NMR signal at -32.6 ppm as a broad singlet (Figure 4-3). Because Ag possesses two NMR active isotopes, namely ^{107}Ag and ^{109}Ag both with l=1/2, two doublets should be expected in the $^{31}P\{^1H\}$-NMR spectrum for the respective resonance. However, it is also known from literature that most ^{31}P-NMR resonances of unhindered Ag(I)-phosphine complexes appear as broad singlets as a result of fast ligand exchange, which is in agreement with the observed $^{31}P\{^1H\}$-NMR spectrum.[55] While HRMS spectrometry confirmed the presence of a Ag(I)-complex with one attached phosphine (m/z = 861.373040 $[M\text{-}BF_4^-]^+$), it does not exclude the possibility that the monocoordinated species was formed during the measurement *via* dissociation of the biscoordinated analogue, especially, since it is known that monocoordinated Ag(I)-complexes like **128** are in equilibrium with their biscoordinated analogues **129** (Scheme 4-5), which makes a clear statement on the structure of the compound **127a/b** difficult.[56]



Scheme 4-5: Equilibrium between monocoordinated Ag(I) complex **128** and biscoordinated Ag(I) complex **129**.[56]

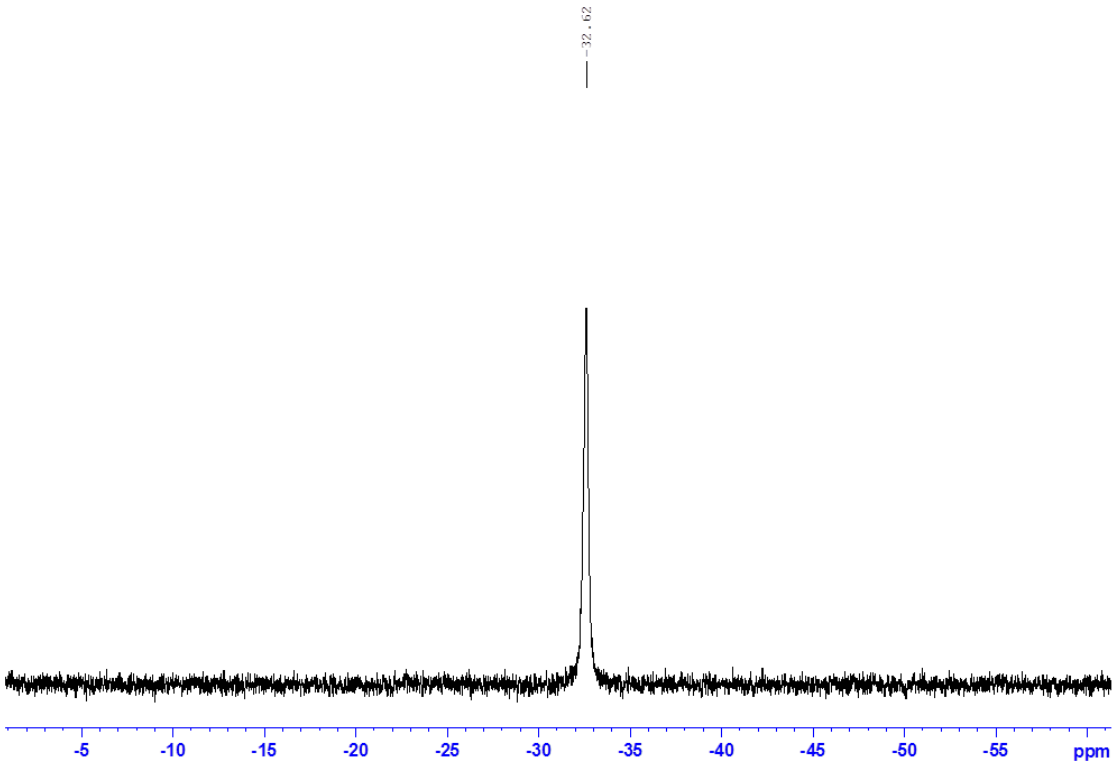


Figure 4-3: $^{31}P\{^{1}H\}$-NMR of compound **127** (measured in CD_2Cl_2).

4.4 Coordination to Cu(I) and Rh(I)

It has been known from the work of *J. Petuškova* that it is possible to coordinate monocationic cyclopropenium substituted phosphine **66** to Cu(I) and Rh(I) (Figure 4-4).[34, 41b] However, the coordination ability of the analogous dicationic phosphines towards these two metals had not been evaluated so far.

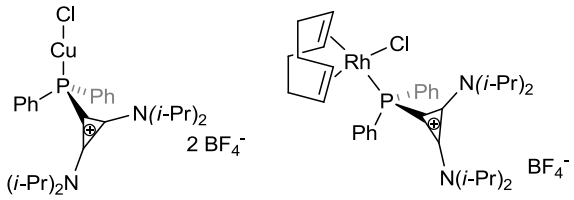
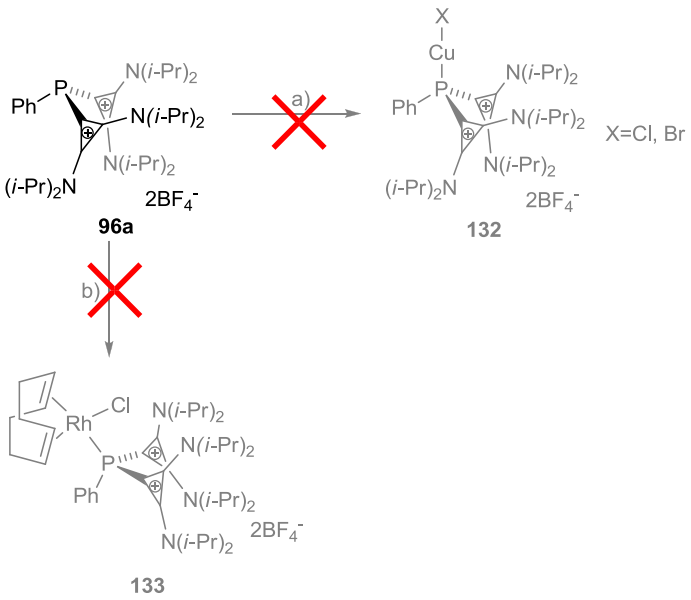


Figure 4-4: Prepared monocationic Cu(I) (**130**) and Rh(I) (**131**) complexes by *J. Petuškova*.

After the successful coordination of dicationic phosphine **95a** to Au(I) and Pt(II) we attempted to coordinate the very same ligand to Cu(I) and Rh(I) under similar conditions. However, the measurement of the $^{31}P\{^{1}H\}$-NMR spectrum showed only the ^{31}P-resonance of the free ligand **95a** even when several Cu(I) salts (i.e. $CuCl{\cdot}SMe_2$, CuCl and CuBr) and $[RhCl(COD)]_2$ were used. Since steric repulsion should not be an issue, at least in the case of

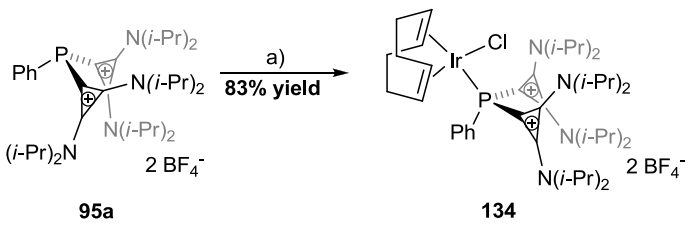
Cu(I) complexes, it has to be concluded that the utilized dicationic phosphine **95a** is probably too electron deficient to coordinate these metals.



Scheme 4-6: Attempted coordination of dicationic cyclopropenium phosphine **95a** to Cu(I) and Rh(I). a) 1.0 equiv. CuX, DCM (or THF) , -20 °C, 30 min, -20 °C to r.t. and then r.t., 1h. b) 0.5 equiv. $[RhCl(COD)]_2$, DCM, -20 °C, 30 min, -20 °C to r.t. and then r.t., 1h.

4.5 Coordination to Ir(I)

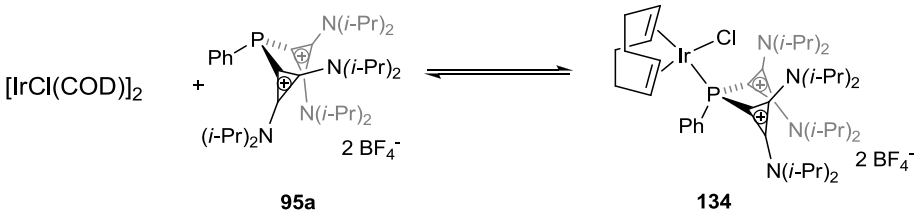
In contrast to the Rh(I) analogue **133**, the dicationic Ir(I)-complex **134** could be prepared in good yield (84%) from the dicationic phosphine **95a** and $[IrCl(COD)]_2$ at -25 °C in DCM (Scheme 4-7). However, **134** is thermally labile and dissociates into the starting materials at room temperature even in the solid state (Scheme 4-8).



Scheme 4-7: Coordination of dicationic cyclopropenium phosphine **95a** to $[IrCl(COD)]_2$. a) 0.5 equiv. $[IrCl(COD)]_2$, DCM, -25 °C, 1 h.

For this reason the complete work-up, including the solvent removal as well as subsequent NMR measurements, had to be performed at -20 °C. As usual, a confirmation of the coordination was achieved by measuring a ^{31}P-NMR spectrum at -20 °C. The ^{31}P resonance of the dicationic phosphine experiences a downfield shift to -18.7 ppm (Figure 4-5) upon coordination. The significant peak broadening observed for this signal at -20 °C can be

attributed to the hindered P-Ir rotation at this temperature (resulting in a loss of symmetry) and also to a coordination-decoordination equilibrium (Scheme 4-8) of compound **134** in solution.



Scheme 4-8: Observed equilibrium for compound **134.**

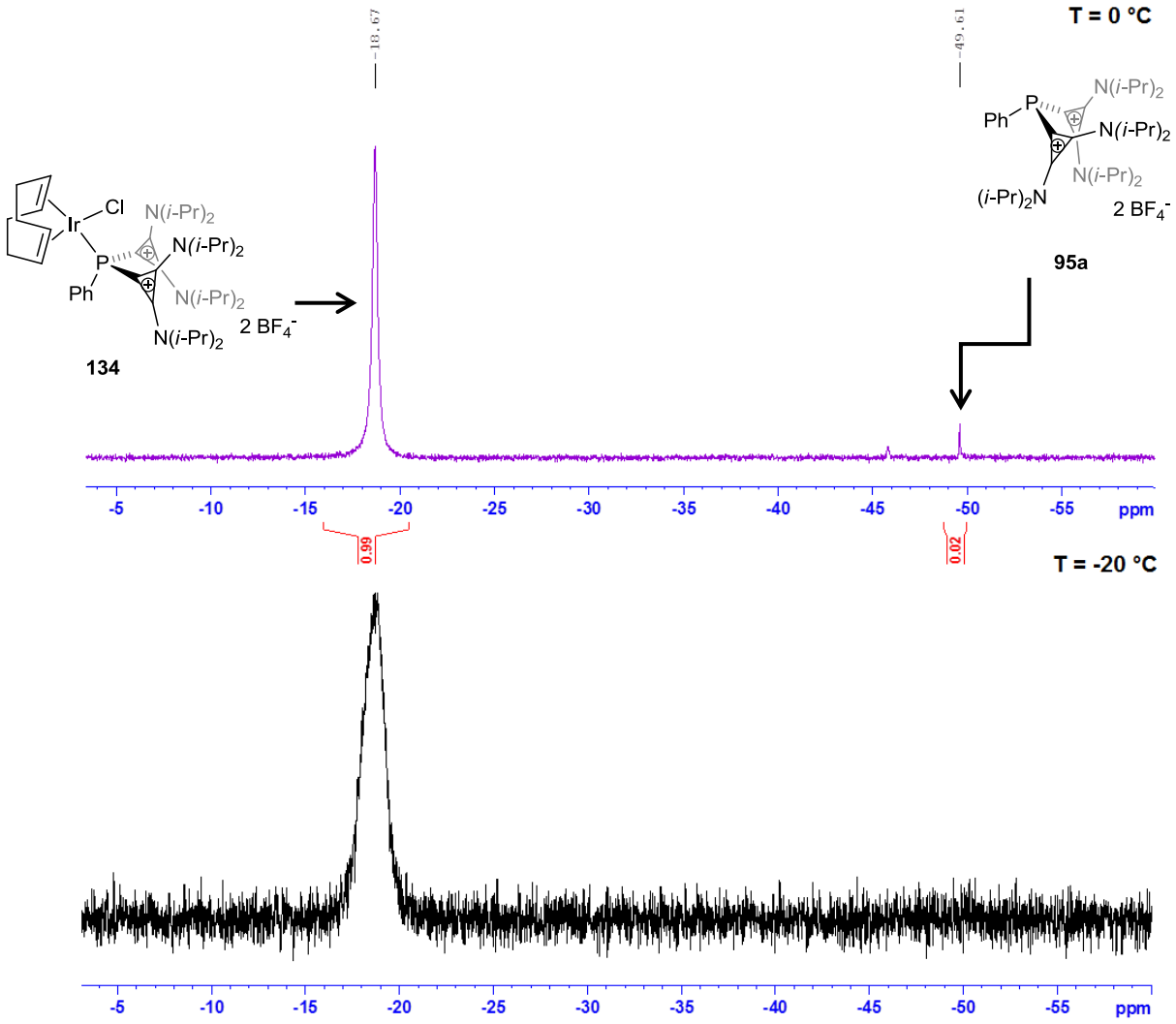


Figure 4-5: ^{31}P-NMR of compound **134** (measured at 0 °C and -20 °C in $CDCl_3$).

The identity of compound **134** was confirmed by ^{1}H-NMR, ^{13}C-NMR (one quaternary C-signal is missing due to peak broadening) and HRMS spectrometry (m/z = 1003.491794 [M-BF_4^-]$^+$). However, the observed thermal instability of compound **134** precludes its use as a catalyst.

Unfortunately, it was not possible to coordinate **95a** to $[Cp^*IrCl_2]_2$ under similar conditions possibly due to a combination of electronic and steric reasons (steric repulsion with Cp* could be a problem).

4.6 Summary

After successful synthesis of biscyclopropenium phosphines **95a-g**, those compounds were treated with $AuCl{\cdot}(SMe_2)$ in order gain access to the corresponding dicationic Au(I)-complexes. With the exception of **95c** (R^1 = Mes, R^2 = *i*-Pr, X = BF_4^-), all employed phosphines **95a**/**95b**/**95d-h** were successfully coordinated to Au(I) affording the desired coordination compounds **97a-h** in good to excellent yields. The solid-state structure of Au(I)-complexes **97b** and **97c** was confirmed by XRD analysis.

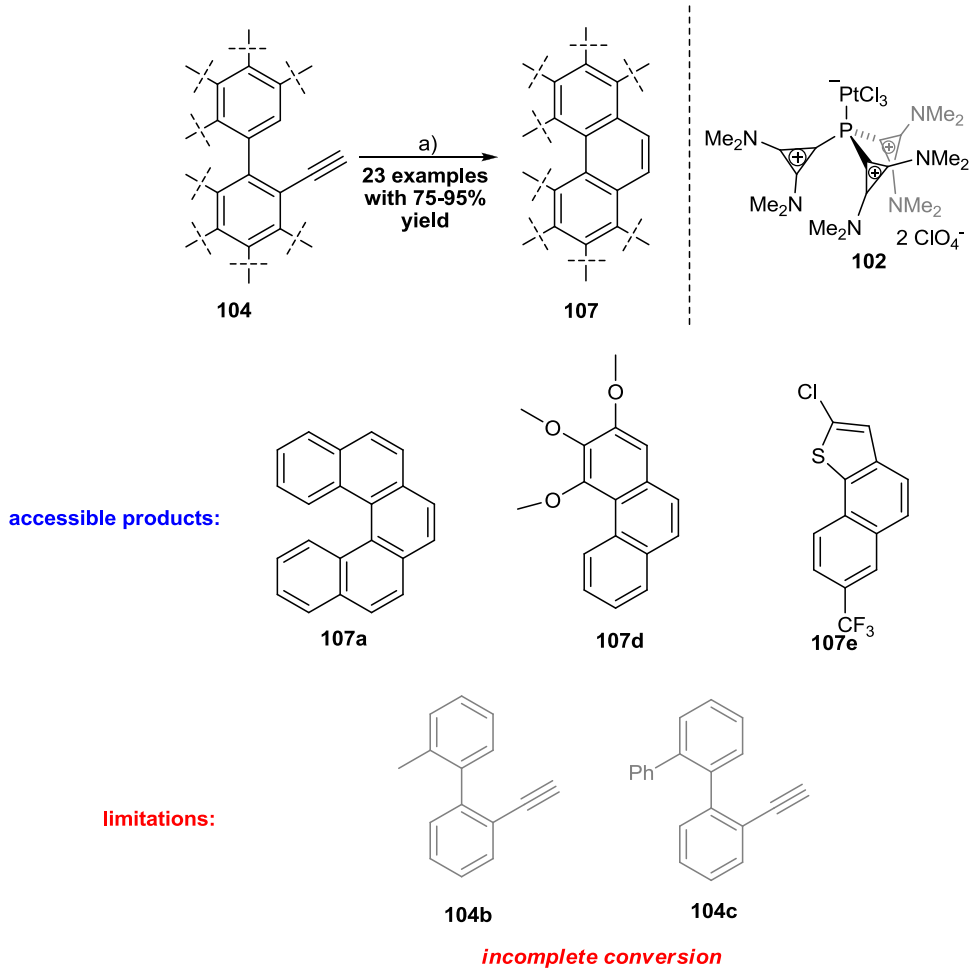
Additionally, it was possible to coordinate phosphine **95a** (R^1 = Ph, R^2 = *i*-Pr, X = BF_4^-) to Pt(II) as well as Ir(I) under similar conditions affording compounds **98** and **134** in good yields. It has to be highlighted that the isolated Ir(I)-complex **134** is only stable at -20 °C and decomposes even in solid state at room temperature.

Interestingly, treatment of $AgBF_4$ with **95a** resulted in a downfield shift of the ^{31}P-signal in the corresponding spectrum, which indicates a successful coordination. This is supported by HRMS spectrometry, as the m/z ratio is in agreement with the coordination to Ag(I). However, without XRD-analysis of the isolated compound **127** no definitive statement concerning the structure of the isolated Ag(I)-complex is possible.

Finally, no complexation was observed for the treatment of the utilized Rh(I), Cu(I) and Ir(III) sources with dicationic phosphine **95a** as a result of steric and probably also electronic reasons.

5 Applications in catalysis

5.1 Introduction



Scheme 5-1: Scope and limitations of the Pt(II)-precatalyst **102** on the *6-endo-dig* cycloisomerization of biphenyl alkynes. a) 0.05 equiv. **102,** 0.05 equiv. $Ag(CB_{11}H_6Cl_6)$, 1,2-DCE, 80 °C.

It has been already mentioned in section 1.4 that Pt(II)-complex **102** containing the tricationic phosphine **100a** was successfully applied as catalyst in our work-group on the *6-endo-dig* cyclization of biphenyl/binaphtyl-alkynes **104a/d/e** (Scheme 5-1).[36] Although 22 different substrates were prepared with a remarkable tolerance towards different functional groups, this methodology still had limitations as previously mentioned (section 2). The presence of (two) substituents in C-6 (R^3) and C-2' (R^4) positions of the substrate resulted in low conversion of the starting material to the desired product (**104b**, **104c**) or no reaction at all. In order test the reactivity profile of Au(I)-complexes **97a-h** in the same process, alkynes **104c**, **104f** and **104g**, all of which are difficult substrates for **100a**, were prepared as test substrates (Figure 5-1).

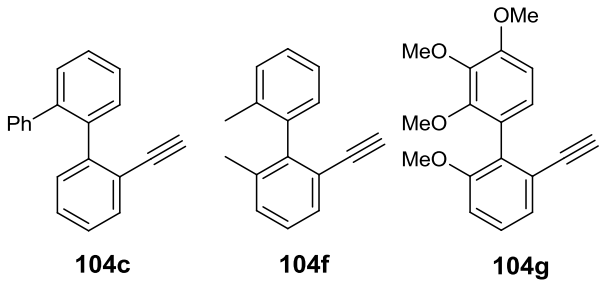


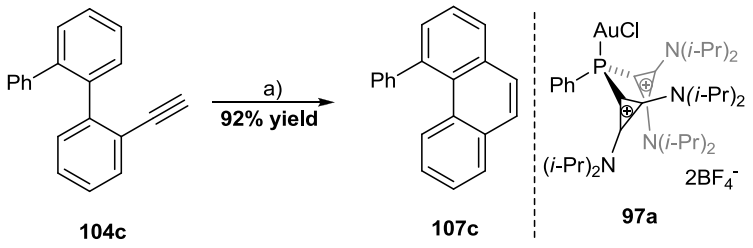
Figure 5-1: Employed model substrates for the investigation of the cycloisomerization of biphenyl-alkynes.

5.2 Synthesis of phenanthrene derivatives

5.2.1 Preliminary Studies

At the beginning 2-ethynyl-2'-phenyl-biphenyl **104c** was used as a model substrate. This alkyne could be transformed to the phenanthrene **107c** in only 23% yield in the presence of the Pt(II)-tricationic phosphine complex **102** (section 2, Scheme 2-1).

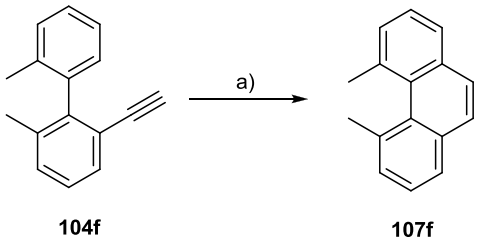
However, after optimization experiments of the solvent and the Ag(I)-salt screening, the desired cycloisomerization of 2-ethynyl-2'-phenyl-biphenyl **104c** could be performed in excellent yield in only 10-15 minutes employing 2 mol% **97a** and 2 mol% $AgSbF_6$ in DCM at room temperature (substrate concentration of 0.05 M, Scheme 5-2).



Scheme 5-2: Cycloisomerization of 2-ethynyl-2'-phenyl-biphenyl **104c** into **107c** in the presence of precatalyst **97a**. a) 0.02 equiv. Au-cat., 0.02 equiv. $AgSbF_6$, DCM, r.t.

5.2.2 Investigating the ligand effect

Once the optimal reaction conditions for this difficult cycloisomerization were established, traditional ligands were also used in this transformation in order to better understand the effect of our ligands. 2-Ethynyl-2',6-dimethylbiphenyl **104f** was employed as substrate, because its two methyl groups in C-6 and C-2' postions make the cycloisomerization more difficult. Therefore, this substrate is an ideal candidate to demonstrate the performance of our catalysts in comparison to traditional ones (Scheme 5-3).



Scheme 5-3: Cycloisomerization of 2-ethynyl-2',6-dimethylbiphenyl **104f** in the presence of different Au(I)-precatalysts. a) 0.02 equiv. Au-cat., 0.02 equiv. $AgSbF_6$, DCM, r.t.

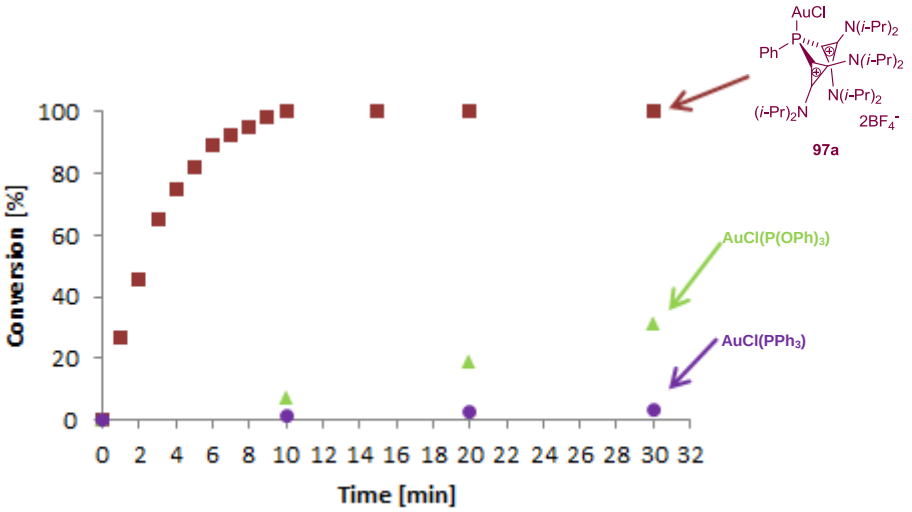
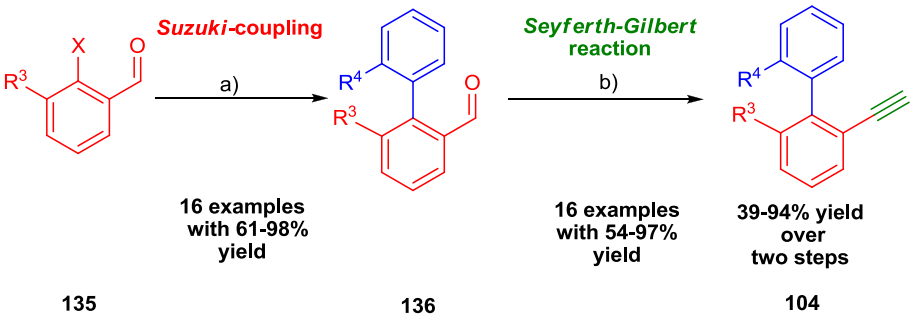


Figure 5-2: Ligand effect on the conversion rate for the cycloisomerization of 2-ethynyl-2',6-dimethylbiphenyl **104f**.

Figure 5-2 shows that the reaction rate is highly dependent on the π-acceptor properties of the phosphine attached to the Au(I)-center of the corresponding catalyst, it increased when strong π-acceptor ligands are coordinated to Au(I). Precatalyst **97a** performs much better in this reaction than any Au-precatalysts derived from commercial P-centered compounds. Thus, it was possible to transform the alkyne **104f** to the *6-endo*-product **107f** within 10 to 15 minutes. These results make us believe that the attack of the upper aryl-ring on the activated alkyne is probably the rate-determing step.

5.2.3 Investigating the substrate scope

In order to evaluate the substrate scope and the functional group tolerance of the new catalytic system, substrates of type **104** were synthesized (in collaboration with *Dr. J. Carreras*) in a two-step sequence from the appropriate aryl-(pseudo)halides **135**. This sequence included a *Suzuki*-coupling and a subsequent *Seyferth-Gilbert* alkynylation (Scheme 5-4, Figure 5-3).[57] Overall, 16 different biphenyl-alkynes of general structure **104** were prepared with different success (27-94%, Figure 5-3) over two steps.



Scheme 5-4: General scheme for the synthesis of biphenyl-alkynes **104**. a) *Suzuki*-coupling; b) 1.5 equiv. *Ohira-Bestmann* reagent, 2.0 equiv. K_2CO_3, MeOH, r.t., overnight.

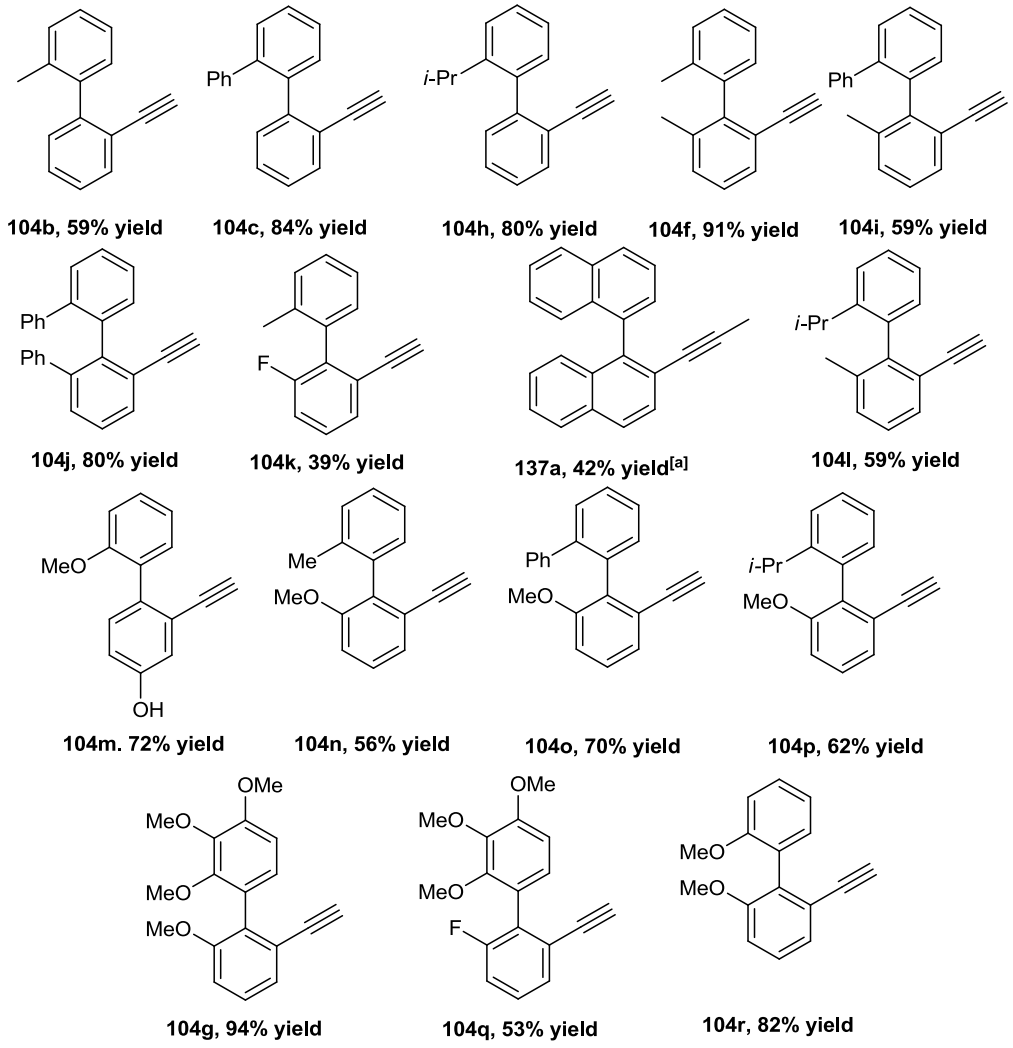


Figure 5-3: List of prepared substrates. All of the reported yields are over two steps. [a]: The displayed yield represents an isolated yield over three steps as it includes the methylation of the primary alkyne **104a**.

Submission of these compounds to the optimized cycloisomerization conditions afforded the desired phenanthrenes of type **107** in good to excellent yields (Figure 5-4). Filtration over a

short pad of Celite® was enough in most of the cases to obtain the desired products in analytical purity.

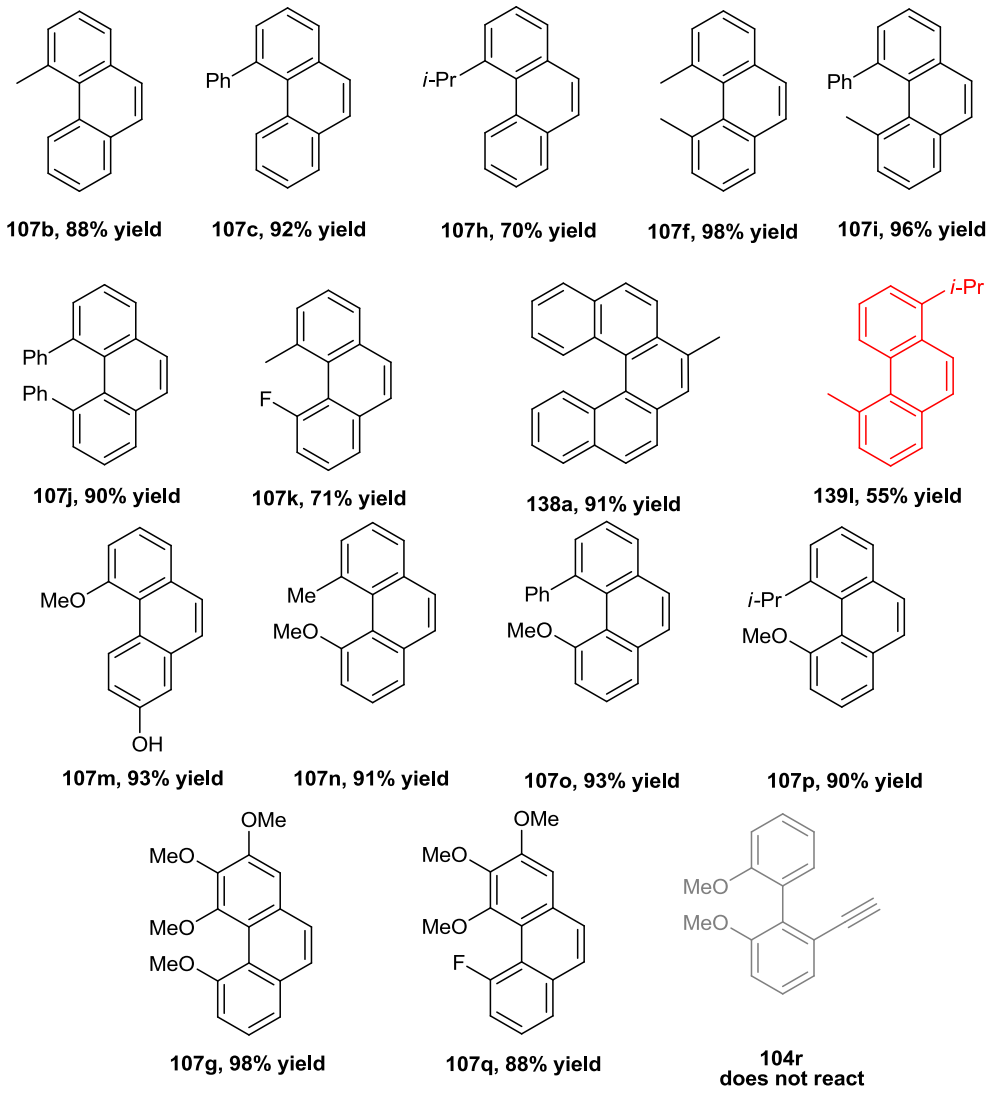


Figure 5-4: Substrate scope of the cycloisomerization under optimized conditions. Conditions: 0.02 equiv. Au-cat. **97a**, 0.02 equiv. $AgSbF_6$, DCM, r.t..

It can be concluded that the developed catalyst allows the introduction of up to two groups at the internal positions of the phenanthrene (C-4 for R^3, C-5 for R^4) with good tolerance towards functional groups of different steric and electronic nature (H, Me, *i*-Pr, Ph, F, OH, OMe). The catalyst is active enough to enable the ring-closing of biphenyl-alkynes, whose reaction is hindered (i.e.: **104f**: R^3 = Me, R^4 = Me; **104j**: R^3 = Ph, R^4 = Ph; **107p**: R^3 = OMe, R^4 = *i*-Pr) by steric repulsion between R^1 and R^2 (Figure 5-3, Figure 5-4). Furthermore, it has to be highlighted that it was possible to convert free phenols (**104m**) to the corresponding phenanthrenes (**107m**). Competitive coordination of the oxygen to the activated Au(I)-center does not seem to be a problem.

The X-Ray structures of compounds **107f** and **107j** (Figure 5-5) further emphasize the strained nature of the obtained products as well as the remarkable reactivity of the established catalytic system in the synthesis of such sterically strained phenanthrene derivatives. The clash between substituents on the C-4 and C-5 atoms generates destabilizing twists of up to 31.6° within the phenanthrene moiety. Despite this strain the ring-closing takes place quickly and cleanly.

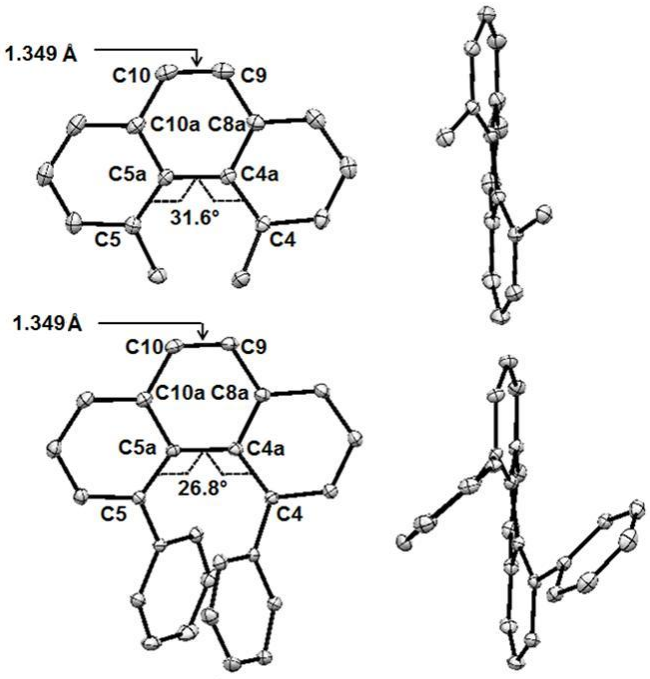


Figure 5-5: X-Ray crystal structures of **107f (up)** and **107j (down)**. Dihedral angles between the two terminal rings are defined in terms of torsion angle C4-C4a-C5a-C5. Hydrogen atoms are omitted for clarity and ellipsoids are shown for 50% probability.

5.2.4 Limitations

The steric limits of the procedure were reached when the cycloisomerization of 2-ethynyl-2'-*iso*-propyl-6-methylbiphenyl **104l** (R^3 = Me, R^4 = *i*-Pr) was attempted. Although, full consumption of the starting material was confirmed *via* GC-MS after 10-15 min reaction time, the recorded GC-chromatogramm (Figure 5-6) showed six new compounds. A careful analysis of the mixture *via* HPLC allowed the isolation of four main products (**139l**, **107l**, **140l**, **107b**), whose identity was confirmed by measurement of the ^{1}H-NMR and ^{13}C-NMR spectra as well as the ^{1}H/^{1}H-COESY, ^{1}H/^{1}H-NOESY and ^{1}H/^{13}C-HMBC 2D experiments.

Compound **107l**, which was isolated in 22% yield corresponds to the expected product, where the –Me and -*i*-Pr groups occupy C-4 and C-5 positions. The structures of products **139l** and **140l** reveal a migration of the *iso*-propyl group to adjacent positions after or during the ring-

closure, while in the case of **107b** the *i*-Pr has been cleaved off. Therefore, it seems that a migration of an *iso*-propyl cation over the π-system is possible if enough steric strain is present. In addition, the formation of **139l** suggests that the activated alkyne might be attacked by carbon C-6' of the aryl ring that bears the *i*-Pr group, followed by migration of the *i*-Pr cation to the adjacent position.

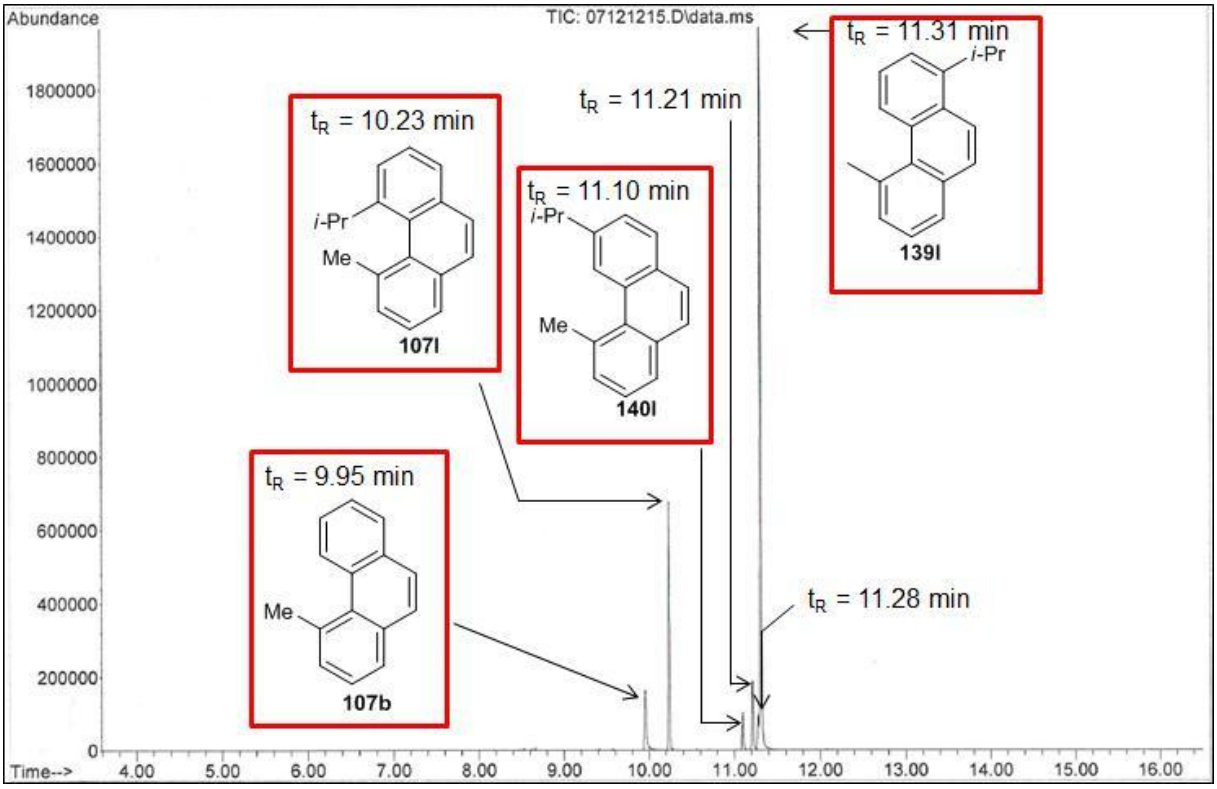


Figure 5-6: GC-Chromatogram of the cycloisomerization of **104b** after 10 minutes.

At this point it has been shown that the established cycloisomerization protocol tolerates substituents of different steric demand at the C-6 carbon (R^3) and C-2' carbon (R^4) of the evaluated biphenyl alkyne up to the aforementioned limitation (**104l**, R^3 = Me, R^4 = *i*-Pr). However, there are also electronic limitations, because as soon as the C-2' atom is bound to a methoxy-group the cycloisomerization may cease to work like in the case of 2-ethynyl-2',6-dimethoxybiphenyl **104r**. The methoxy group in this substrate is in meta position to the carbon, which has to attack the activated alkyne. Therefore, the negative inductive effect of this substituent, and not its positive mesomeric one, dominates the situation and reduces the overall reactivity. Additionally, steric repulsion between both –OMe groups raises the energy barrier for the cyclization of **104r** further (Figure 5-7).[51, 58] However, it is possible to compensate the presence of one –OMe at this postion through additional -OMe substituents on the same aryl ring, which increase the electron density at the correct carbon and facilitate

the *6-endo-dig* cyclization as shown in the case of 2'-ethynyl-2,3,4,6'-tetramethoxybiphenyl **104g** (Figure 5-7).

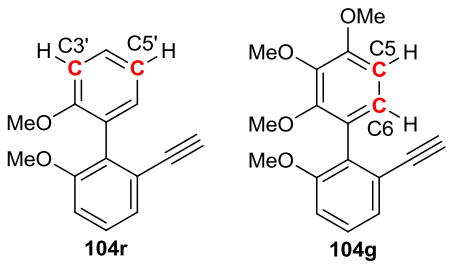


Figure 5-7: Carbons activated towards an electrophilic attack (highlighted in red) in substrates **104r**/**104g**.

5.2.5 Exchanging the solvents

At this point the prepared Au-precatalyst **97a-b/f-i** were tested in the cycloisomerization of biphenyl-alkynes in non-polar solvents, using 2-ethynyl-2',6-dimethylbiphenyl **104f** as a model substrate. Thus, we planned to determine the effect of R^2 and the counter-ion X^- on the reactivity.

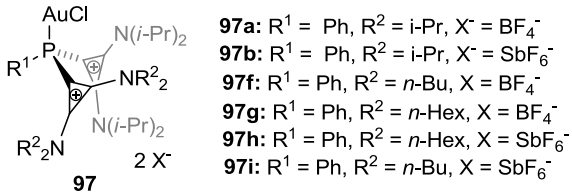


Figure 5-8: General structure of applied Au(I)-precatalysts **97**.

Interestingly, precatalysts **97f** (R^1 = Ph, R^2 = *n*-Bu, X = BF_4^-) and **97g** (R^1 = Ph, R^2 = *n*-Hex, X = BF_4^-) were completely soluble at 50 °C in toluene. Note however, that the substrate concentration had to be raised from 0.05 M to 0.25 M in order to achieve complete conversion of **104f** to **107f** under these conditions.

Figure 5-9 clearly depicts the effect of decorating the ancillary ligands with longer aliphatic chains. Because dicationic phosphines (**95f**, **95g**), which are coordinated to the Au(I)-center of precatalysts **97f** and **97g**, are virtually identical to phosphine **95a** (R^1 = Ph, R^2 = *i*-Pr, X = BF_4^-) from an electronic standpoint, the increased conversion and rate can be ascribed to a better solubility of the respective Au-complexes with longer chains lengths in toluene. This observation is supported by the fact, that precatalyst **97a** (R^1 = Ph, R^2 = *i*-Pr, X = BF_4^-) is completely insoluble in toluene.

Furthermore, ion-exchange from BF_4^- to the less coordinating SbF_6^- also leads to a clear improvement of the reaction rate. Probably, the SbF_6^- counter-ion increases additionally the

solubility of the corresponding active Au(I)-catalysts. Moreover, the less coordinating SbF_6^- surely minimizes a possible competition for the vacant site of the Au(I)-catalyst between the substrate and the counter-ion. This explains the increased conversion and rate obtained for precatalyst **97h** (R^1 = Ph, R^2 = *n*-Hex, X = SbF_6^-) in comparison to those obtained for **97g**. When **97h** was utilized, full conversion was achieved after 15 minutes without any significant loss of catalytic activity throughout this time frame.

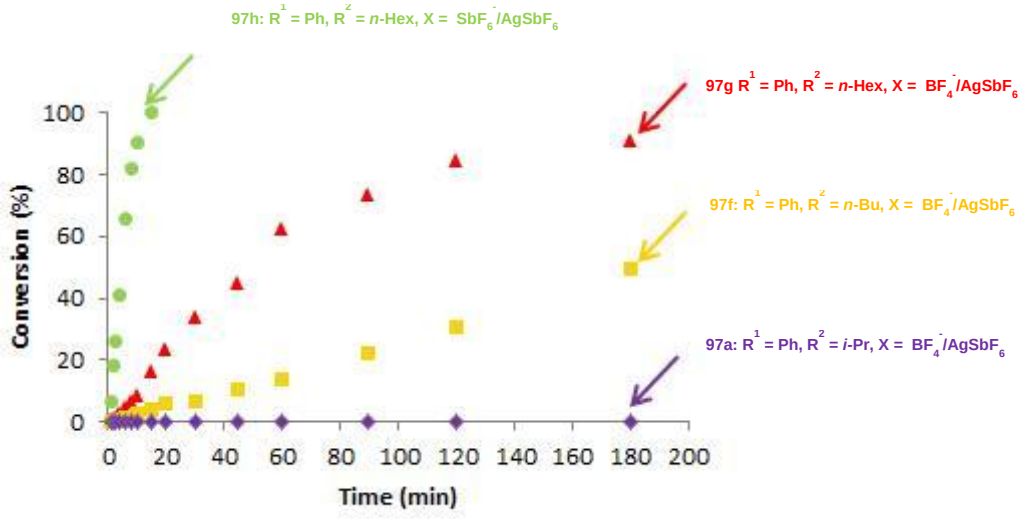


Figure 5-9: Cycloisomerization of 2-ethynyl-2',6-dimethylbiphenyl **104f** in the presence of different Au(I) precatalysts. Conditions: 0.02 equiv. Au-cat.; 0.02 equiv. $AgSbF_6$, toluene (c(**104b**) = 0.25 M), 50 °C.

5.2.6 Theoretical studies on the catalytic system

In order to get more insight into the actual catalyst **97a-Cl** (Figure 5-10), its electronic structure was evaluated by a fragment molecular orbital (MO) analysis employing the Amsterdam Density Functional (ADF) program package (details in section 6.6, calculations were performed at our department of theoretical chemistry).[59] In **97a-Cl**, the LUMO corresponds to a low-lying antibonding σ*-orbital (P−Au), which exhibits a strong contribution from the Au 6s-orbital (46%) (Figure 5-10, left). Comparison of this MO with the LUMO of $[(MeO)_3PAu]^+$ **141-Cl** shows that the shapes of the respective LUMOs (σ* P−Au) are similar. However, the LUMO of **97-Cl** lies much lower in energy (-11.89 eV) than the corresponding one of **141-Cl** (-8.03 eV). This probably explains the enhanced reactivity of **97a-Cl** since the energy of these orbitals dictates the π-acidity of both catalysts.[41a]

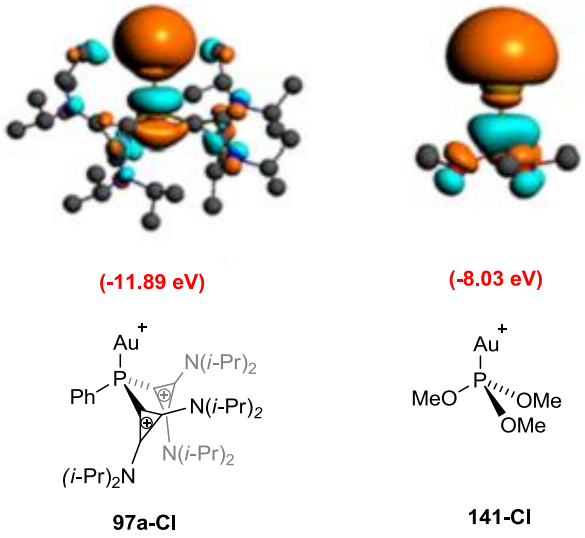


Figure 5-10: Calculated LUMOs of active tricationic Au(I)-catalyst **97a-Cl** and active monocationic Au(I)-catalyst **141-Cl** (ADF approach).

The possible reaction pathways for the cycloisomerization of 2-ethynyl-2',6-dimethylbiphenyl **104f** in the presence of either tricationic Au(I)-catalyst **98a-Cl** (green) or the monocationic Au(I)-catalyst **142-Cl** (red) in DCM were investigated by DFT calculations at our department of theoretical chemistry (Figure 5-11, exact conditions for these calculations are given in section 6.6).

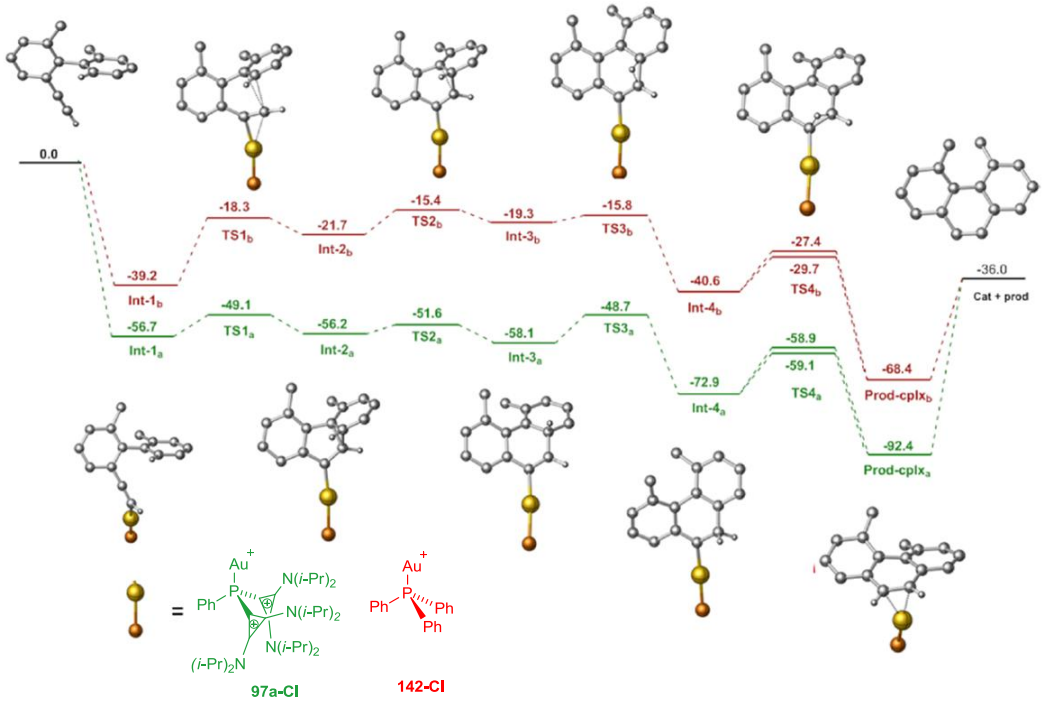


Figure 5-11: Free energy profiles (kcal/mol) for the cycloisomerization 2-ethynyl-2',6-dimethylbiphenyl **104f** to 4,5-dimethylphenanthrene **107f** in DCM. The green line represents the calculated profile for catalyst **97a-Cl**. The red line represents the calculated profile for catalyst **142-Cl**. Both diastereomeric protons were considered in the calculations of **TS4$_a$** and **TS4$_b$**.

In both cases the catalytic cycle starts with coordination of alkyne to the Au(I)-center generating the catalyst-substrate complex **Int1**, which is more exergonic when the dicationic phosphine is used (catalyst **97a-Cl**), **Int1$_a$**. The increased thermodynamic stability of **Int1$_a$** is a direct result of the very low lying LUMO of the Au(I)-catalyst **97a-Cl**. The subsequent step of this reaction involves the nucleophilic attack of the aryl-system on the activated alkyne for both catalytic species (**97a-Cl** and **142-Cl**) forming the cyclopropyl intermediates **Int2$_{a/b}$**. According to the calculated relative free energies this intermediate is generated more easily when the strongly activating catalyst **97a-Cl** is employed, since the free energy of activation (relative to the preceding intermediate) is only 7.6 kcal/mol compared with 20.9 kcal/mol when using the catalyst **142-Cl** derived from PPh_3. Cyclopropane ring-opening and subsequent 1,2-H shift to **Int4$_{a/b}$** occur in both cases readily as they have free energy barriers of less than 10 kcal/mol. Therefore, these steps are not strongly influenced by the nature of the ancillary ligand. Both intermediates **Int4$_{a/b}$** are more stable than intermediates **Int3$_{a/b}$** by 14.8 and 21.3 kcal/mol respectively. Furthermore, the energies of the subsequent transition states **TS4$_a$** (−59.1 kcal/mol) and **TS4$_b$** (−29.7 kcal/mol) leading to protodemetalation are much lower in energy than those determined for **TS3$_a$** (−48.7 kcal/mol) and **TS3$_b$** (−15.8 kcal/mol), respectively. Due to this, the formation of the Au-carbenes **Int4$_{a/b}$** is probably irreversible. Then, a 1,2-hydrogen shift occurs, which involves one of the diastereomeric H atoms, affording the phenanthrene-Au(I) complexes **Prod-cplx$_a$/Prod-cplx$_b$**. As might be expected, this step is more difficult when dicationic phosphines are employed as ligands. Finally, dissociation of the Au(I)-olefin complexes liberates the product and regenerates the catalyst. It should be noted, that the calculated interaction between the tricationic catalytic species **97a-Cl** and the phenanthrene **142-Cl** is very strong (92.4 kcal/mol). This might explain why the catalyst deactivation is observed at high substrate conversion once the phenanthrene product accumulates (in DCM as a solvent).[41a]

5.2.7 Synthesis of *Calanquinone C*

5.2.7.1 Introduction

There are many natural products like *Bulbophylatrin* **143**[60], *Calanquinone C* **144**[61], *Orcholide* **145**[62], *Angustatin A* **146**[63] or *epimedoicarisoside A* **147**[64], which are derived from phenanthrenes with at least one oxygenated group in C-4 or C-5 position (Figure 5-12). Therefore, these natural products could be ideal candidates to test the synthetic potential of the new catalyst prepared.

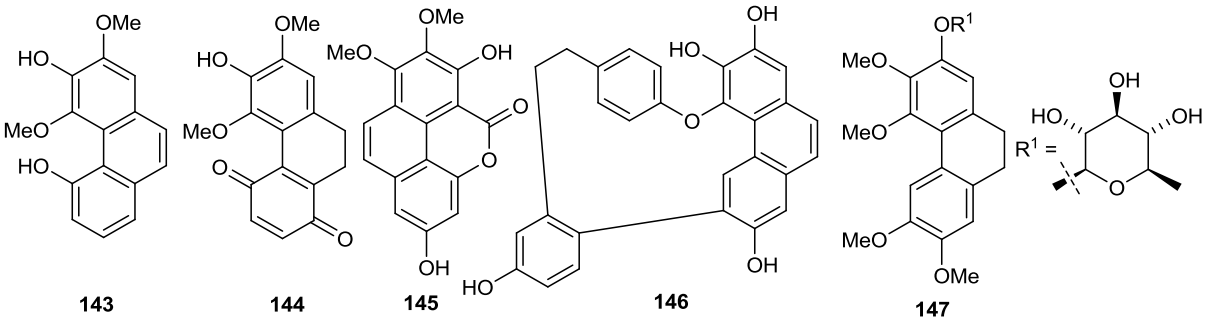
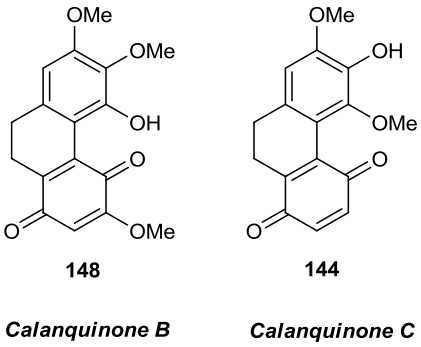


Figure 5-12: Examples for phenanthrene derived natural products with at least one internal methoxy group.

In this regard, *Calanquinone C* **144** was chosen as a synthetic target. *Calanquinone C* **144** is a phenanthrenequinone, which was isolated alongside *Calanquinone B* **148** from *Calanthe Arisanensis*, a plant belonging to the *Orchidaceae* family, (Figure 5-13) by *C.-L. Lee et al.* in 2009. Moreover, C*alanquinone C* **144** shows significant cytotoxic activity (EC_{50}<4µg/mL) against certain breast cancer cell lines.[61] This work was performed in cooperation with *Dr. A. Zanardi* and *Dr. J. Carreras*.

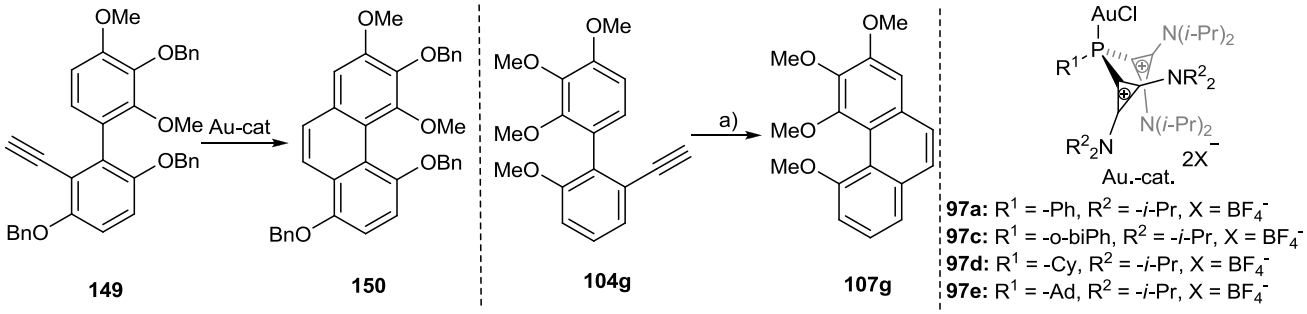


Calanthe arisanensis

Figure 5-13: Left: Structures of *Calanquinone B* **148** and *Calanquinone C* **144**. **Right:** *Calanthe arisanensis*.

5.2.7.2 Optimization Studies

Our synthetic approach towards *Calanquinone C* included the cyclization of alkyne **149** to phenanthrene derivative **150** as the key-step (section 5.2.7.3). It was decided to optimize the reaction conditions of this transformation by using the 2'-ethynyl-2,3,4,6'-tetramethoxybiphenyl **104g** as a test substrate, due to its similar substitution pattern to **149** (Scheme 5-5). This investigation was first initialized with 2 mol% Au(I)-precatalyst **97a** and 2 mol% $AgSbF_6$, before the catalyst amount was reduced to the smallest amount possible to afford complete conversion.



Scheme 5-5: Left Key-step in the Synthesis of *calanquinone C*. **Right:** Model System for the screening of possible precatalysts. Conditions: 0.02 equiv. Au-cat. **97a**/**97c-e**, 0.02 equiv. $AgSbF_6$, DCM, r.t..

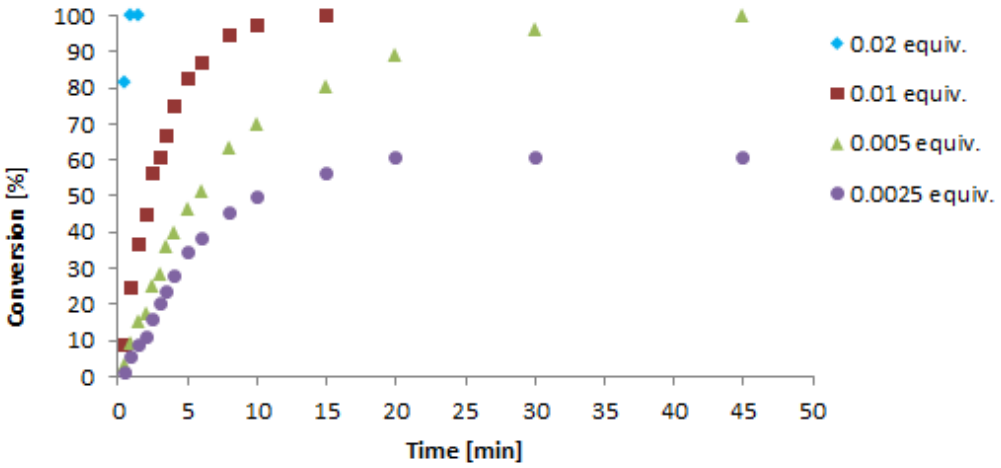


Figure 5-14: Effect of the catalyst amount on the cycloisomerization of 2'-ethynyl-2,3,4,6'-tetramethoxybiphenyl **104g** to 2,3,4,5-tetramethoxyphenanthrene **107g**. Conditions: amount of **97a** and $AgSbF_6$ shown in the figure above, DCM (c(**104g**) = 0.05 M), r.t..

Figure 5-14 illustrates the conversion vs. time profile for the cycloisomerization of 2'-ethynyl-2,3,4,6'-tetramethoxybiphenyl **104g**. As it can be seen, it proceeds much faster under standard conditions than the cycloisomerization of 2-ethynyl-2',6-dimethylbiphenyl **104f**. The reaction was finished within 60 seconds (for **104f**: full coversion after 10-15 min, Figure 5-2). This high reactivity can be rationalized by the presence of three –OMe groups on the upper aryl system, which increase the electron density in C-6 position through a strong mesomeric effect (Scheme 5-3, Figure 5-2). As a consequence of this high reactivity, full conversion was still achieved with a catalyst loading of 0.5 mol% within 45 minutes. A further decrease of the catalyst amount to 0.25 mol% leads to a maximum conversion of 60% after 20 minutes before the reaction stops, likely due to catalyst decomposition.

In order to determine the most effective precatalyst for the desired cycloisomerization, the different precatalysts **97a/c-e** were tested in the cyclization of **104g** in DCM at a catalyst

loading of 0.25 mol%. As the substrate was shown to be highly reactive, the reduced catalyst loading was essential to illustrate the activity difference of the Au(I)-catalysts (Figure 5-15).

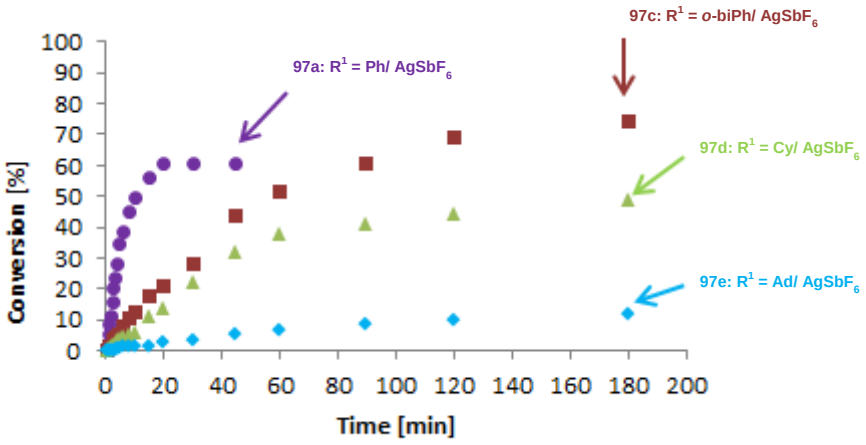


Figure 5-15: Effect of R on the cycloisomerization of 2'-ethynyl-2,3,4,6'-tetramethoxybiphenyl **104g** to 2,3,4,5-tetramethoxyphenanthrene **107g**. Conditions: 0.025 equiv. **97a/97c-e**, 0.025 eqiv. $AgSbF_6$, DCM (c(**104g**) = 0.05 M), r.t..

Comparison of the different precatalysts shows that the conversion and rate both increase with rising π-acidity of the Au(I)-catalysts (Figure 5-15): **97a** (R^1= Ph) >**97c** (R^1 = *o*-biPh) >**97d** (R^1 = Cy) > **97e** (R^1 = Ad). This is in agreement with the results discussed in section 5.2.2. Precatalyst **97a** (R^1 = Ph) provided the highest conversion and rate upon activation, affording approximately 63% product within 20 min before the catalyst was decomposed. While precatalyst **97c** (R^1 = *o*-biPh) provided the second best results with 74% conversion after 3 hours, the active species derived from **97c** was stable for 60 minutes before decomposition became an issue. The enhanced stability of the active species derived from **97c** can be probably attributed to the secondary phenyl group in *ortho* position, which could stabilize the Au(I)-center *via* π-coordination. In light of these results, it was decided to investigate, if the utilization of toluene as a solvent in this reaction led to a similar stabilizing effect.

At this point it was known that full conversion of **104g** to the desired product **107g** can be achieved with 0.5 mol% catalyst loading as long as R^1 = Ph. Furthermore, it was also known that full solution of dicationic Au(I)–precatalyst **97h** in toluene at 50 °C is possible, if R^2 = *n*-Hex and X = SbF_6^- (section 5.2.5). Under those conditions **97h** (2 mol%) provided a similar catalytic activity for the cyclization of **104f** to **107f** to the one of **97a** (2 mol%) in DCM.

With this information in hand, it was possible to establish optimal reaction conditions for the cycloisomerization of **104g**. These cyclizations were performed at 0.5 mol% catalyst loading

in toluene at 0.25 M substrate concentration and 50 °C using precatalyst **97h** (R^1 = Ph, R^2 = *n*-Hex, X = SbF_6^-). Full conversion of **104g** to **107g** was achieved within 120 seconds under these optimized conditions. This is comparable with the results obtained at 2 mol% catalyst loading (**97a**) in DCM. Due to the lowered loading, the TON for this reaction increased from 50 (for 2 mol%) to 200 (for 0.5 mol%). A slight delay of the reaction was also observed, which probably can be attributed to the time needed for the activation of the Au(I)-catalyst *via* halide-abstraction. Furthermore, an exchange of the solvent for anisole resulted in a slight decrease of the rate as the reaction time was extended to 180 seconds to achieve full conversion. Because anisole is more electron rich than toluene, this observation might indicate π-coordination of the activated Au(I)-catalyst by the solvent molecules.

In order to check, if the utilized precatalyst **97h** was applicable for less reactive substrates like 2-ethynyl-2',6-dimethylbiphenyl **104f** under the same conditions, the reaction was repeated for this substrate.

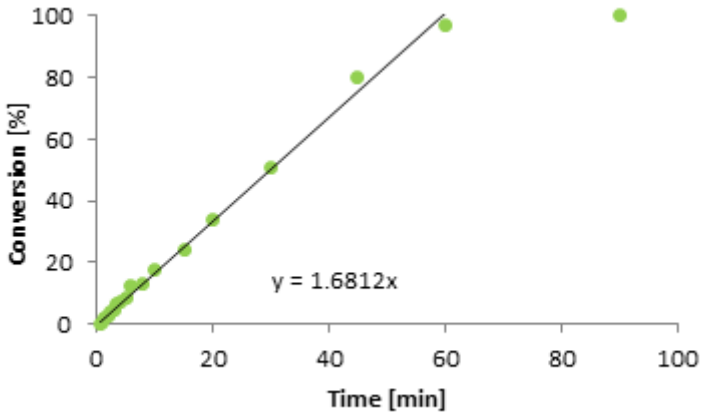


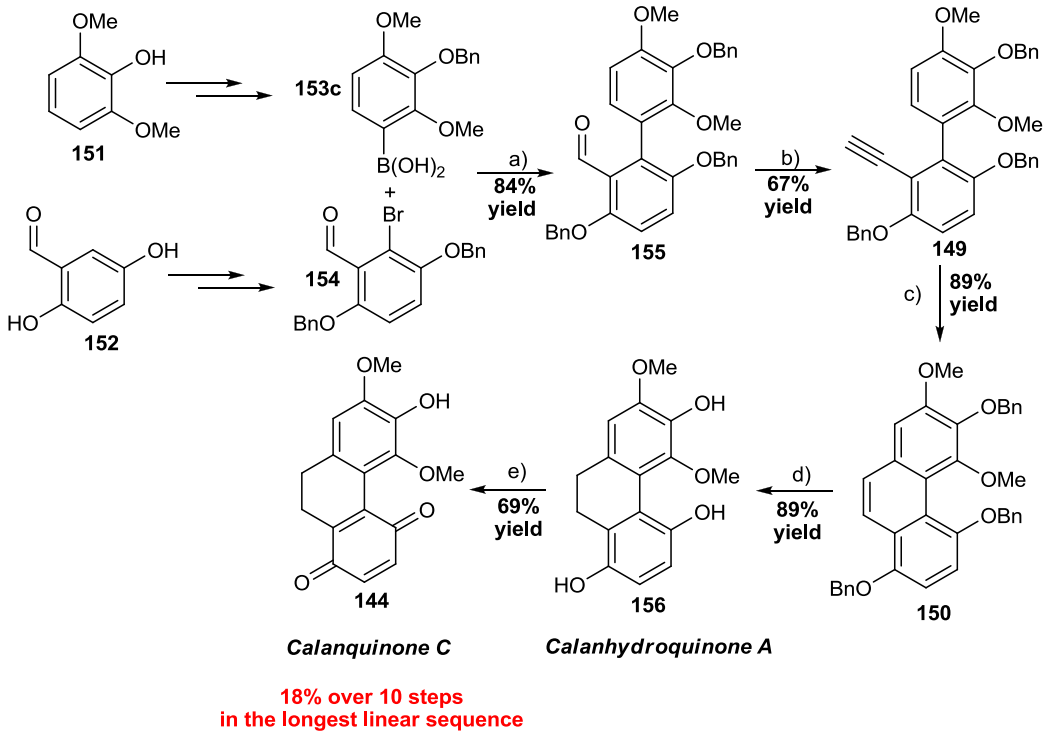
Figure 5-16: Cycloisomerization of 2-ethynyl-2',6-dimethylbiphenyl **104f** under optimized conditions in the presence of precatalyst **97h** (R^1 = Ph, R^2 = *n*-Hex, X = SbF_6^-). Conditions: 0.005 equiv. **97h**, 0.005 equiv. $AgSbF_6$, toluene, 50 °C, (c(**104f**) = 0.25 M).

To our delight, full conversion to the desired *6-endo-dig* **107f** product was detected after 60 minutes under optimized conditions. Throughout the duration of the reaction, the activated Au(I)-catalyst remained stable without any significant decrease of activity, which might support the formation of a π-complex with toluene (Figure 5-16).

These conditions were then applied in the synthesis of *Calanquinone C* **144**.

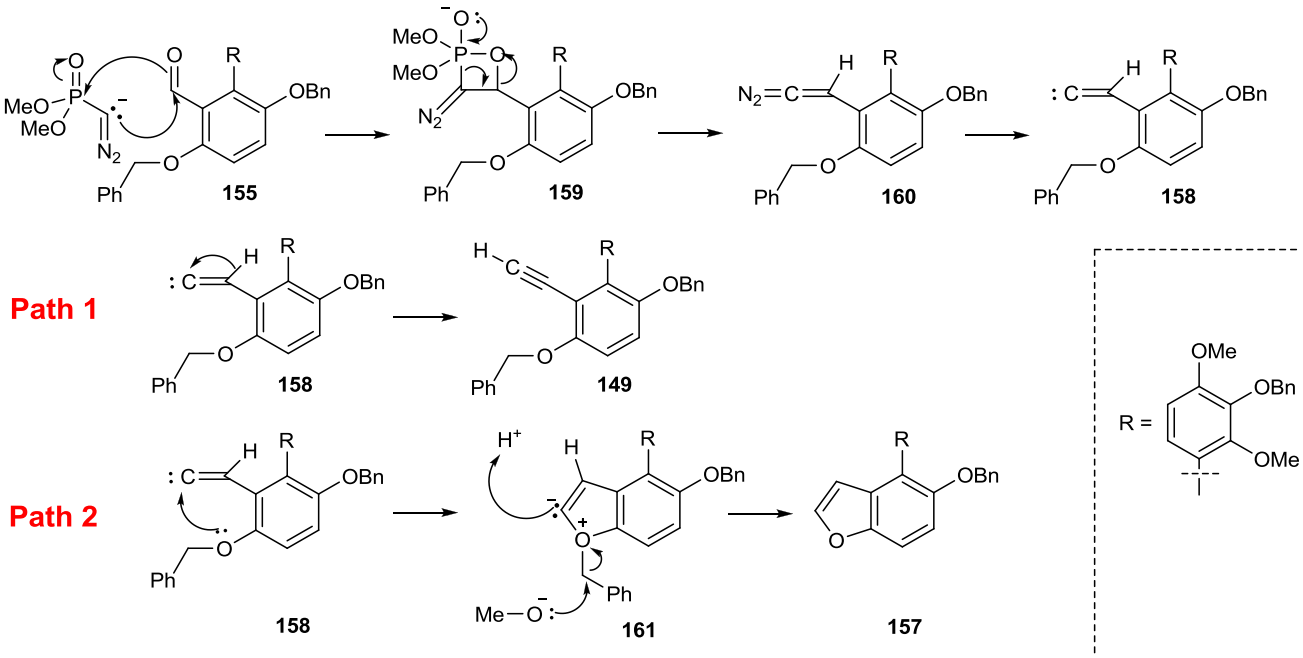
5.2.7.1 Synthesis

Our synthetic route towards *Calanquinone C* **144** commences with the *Suzuki*-coupling of **153c**[65] and the aryl bromide **154**[66] (Scheme 5-6). This reaction was facilitated by utilizing 5 mol% $Pd_2(dba)_3$ as precatalyst to afford 3,3',6-tris(benzyloxy)-2',4'-dimethoxybiphenyl-2-carbaldehyde **155** in 84% yield.



Scheme 5-6: Synthetic sequence for the preparation of *Calanquinone C* **144**. a) *Suzuki*-coupling, b) *Seyferth-Gilbert* homologation, c) Au(I)-catalyzed cycloisomerization, d) Pd-catalyzed reduction/deprotection, e) oxidation.

According to our expectations the exposure of the carbaldeyde **155** to *Seyferth-Gilbert* alkynylation conditions afforded 3,3',6'-tris(benzyloxy)-2'-ethynyl-2,4-dimethoxybiphenyl **149** in 67% yield as the main product. However, 5-(benzyloxy)-4-(3-(benzyloxy)-2,4-dimethoxyphenyl)benzofuran **157** was also obtained as a side-product of this reaction in 23% yield. The formation of **157** can be explained by a nucleophilic attack of the oxygen-lone pair of the benzyloxy group adjacent to the C-2 atom on the carbene-C-atom of the transcent vinylidencarbene **158**, which is formed as an intermediate during the alkynylation reaction (Scheme 5-7).[67]



Scheme 5-7: Established mechanism for the formation of the Alkyne **149** *via Seyferth-Gilbert* reaction (Path 1) and proposed mechanism for the formation of side-product **191**(Path 2).

The successful cycloisomerization of **149** into **150** was achieved by utilizing 0.5 mol% of precatalyst **97h** (Figure 5-17) and 0.5 mol% $AgSbF_6$ under the already optimized conditions. After purification by column chromatography 1,4,6-tris(benzyloxy)-5,7-dimethoxy-phenanthrene **150** was isolated in 89% yield. The identity of the product was confirmed by full NMR analysis (including the measurements of the following spectra: ^{1}H-NMR, ^{13}C{^{1}H}-NMR,^{1}H/^{1}H-COSY, ^{1}H/^{1}H-NOESY, ^{1}H/^{13}C{^{1}H}-HMQC, ^{1}H/^{13}C{^{1}H}-HMBC), HRMS spectrometry and IR-spectroscopy.

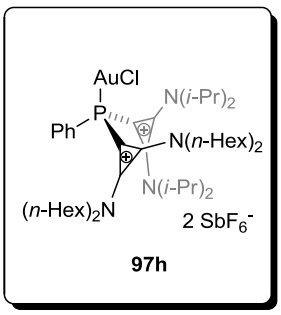


Figure 5-17: Successful precatalysts **97h** in the formation of 1,4,6-tris(benzyloxy)-5,7-dimethoxyphenanthrene **150**.

Subsequently, compound **150** was deprotected to *Calanhydroquinone A* **156** in 89% yield by hydrogenation (20 bar) using Pd/C as catalyst. The structure of **156** was also proven by XRD-analysis confirming the expected connectivity (Figure 5-18).

Finally, the oxidation of *Calanhydroquinone A* **156** to *Calanquinone C* **144** was performed using $(NH_4)_2Ce(NO_3)_6$ as oxidant in THF at room temperature (69% yield). The connectivity of **144** was again confirmed by XRD analysis. The decrease of the C4-O4 and C1-O5 bond lengths from 1.375(1)-1.388(1) Å in **156** to 1.288(3)-1.239(4) Å in **144** supports the formation of the quinone moiety ($d(R_2C{=}O)$ = 1.20 Å). This is in agreement with the two new signals in the ^{13}C-NMR spectrum with chemical shifts of 185.3 ppm and 185.6 ppm, as well as the presence of a CO-band at 1664 cm^{-1}.

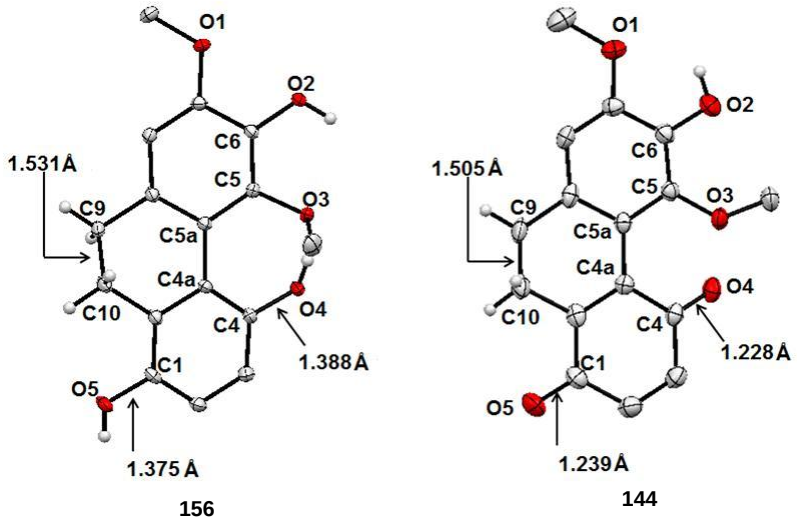


Figure 5-18: X-Ray structures of *Calanhydroquinone A* **156** and *Calanquinone C* **144**. Hydrogen atoms are omitted (exceptions are Hydrogens on –OH groups and C9/C10 atoms) for clarity and ellipsoids are shown for 50% probability.

5.2.8 Summary

After an initial optimization it was possible to establish a cycloisomerization protocol for biphenyl-alkynes with (two) substituents in C-6 (R^3) and C-2' (R^4) positions using the prepared Au(I)-precatalyst **97a** (R^1 = Ph, R^2 = *i*-Pr, X = BF_4^-) and $AgSbF_6$. Kinetic studies of the cyclization of 2-ethynyl-2',6-dimethylbiphenyl **104f** revealed that rate and conversion increase with rising π-acceptor properties of the employed ligand. This indicated that the nucleophilic attack of the activated alkyne is the rate-determing step.

Subsequently, this methodology was used for the cyclization of 16 different biphenyl-alkynes, which were prepared in a two-step procedure. The utilized conditions gave access to 15 different phenanthrene derivatives with substituents of varying steric and electronic properties (R^3 = H, Me, OMe, Ph, F; R^4 = Me, *i*-Pr, OMe, Ph, OH).

While this method is powerful, there are limits how much steric strain can be tolerated during the cyclization as a migration of a *i*-Pr group was detected for the ring-closing of **104l** (R^3 = Me, R^4 = *i*-Pr). Furthermore, no reaction at all was observed for **104r** (R^3 = OMe, R^4 = OMe).

The exchange of the aliphatic residues R^2 for more lipophilic groups like *n*-Hexyl and the counter-ion for SbF_6^- on the Au-precatalysts **97** (i.e.: **97h**: R^1 = Ph, R^2 = *n*-Hex, X = SbF_6^-) facilitated the cycloisomerization of 2-ethynyl-2',6-dimethylbiphenyl **104f** in toluene avoiding the use of chlorinated solvents.

Finally, the synthesis of *Calanquinone* C **144** proved the scope of our catalysts. After optimization, *Calanquinone C* **144** was accessed in a sequence of 10 steps from 2,6-dimethoxyphenol **151** and gentisaldehyde **152** in 18% overall yield for the longest linear sequence. The key step of this sequence involved a late stage Au(I)-catalyzed cycloisomerization utilizing precatalyst **97h** with a catalyst loading of 0.5 mol%.

5.3 Synthesis of naphto-furans

5.3.1 Initial Evaluations

At this point, it was decided to extend the substrate scope of our methodology to the synthesis of heterocycles such as, for example, naphto-furans. This is of interest, because the naphto-furan architecture is often present in nature. *Balsaminone A* **162**[68], *Furomullugin* **163**[69] and *Senarguine B* **164**[70] are examples for such natural products (Figure 5-19).

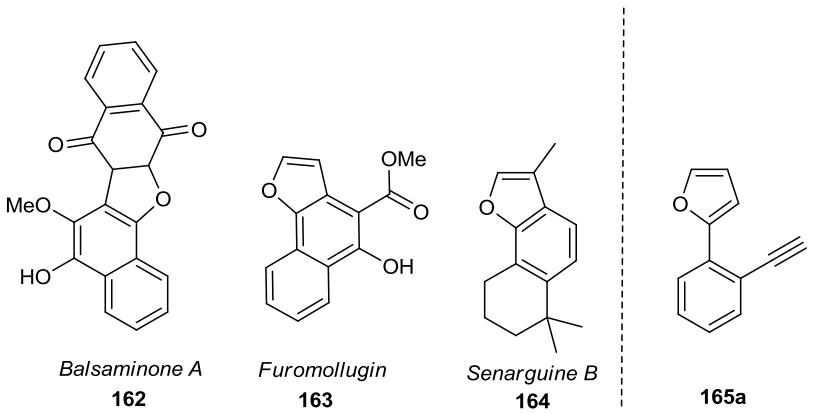
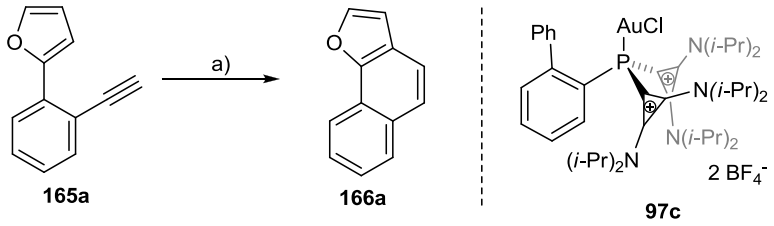


Figure 5-19: Examples for naphto-furan derived natural products (**162**, **163**, **164**) and model substrate **165** prepared for the evaluation of the cycloisomerization of 2-(ethynylaryl)furans.

Thus, we started to investigate whether the cycloisomerization of 2-(2-ethynylphenyl)furan **165a** into the corresponding naphtofuran **166a** could be possible in the presence of precatalyst **97a.** After some optimization, full conversion of **165a** into the desired product **166a** was

achieved after 10-15 minutes employing 2 mol% precatalyst **97c** (or **97a** alternatively) and 2 mol% $AgSbF_6$ in 1,2-DCE at 50 °C (Scheme 5-8).



Scheme 5-8: Cycloisomerization of 2-(2-ethynylphenyl)furan **165a** to naphtha[1,2-b]furan **166a.** a) 0.02 equiv. Au-cat. **97c**, 0.02 equiv. $AgSbF_6$, DCE, 50 °C.

5.3.2 Ligand Effect

5.3.2.1 Comparison with commercial phosphines

After determing the necessary reaction conditions, the performance of precatalysts **97a** (R^1 = Ph, R^2 = *i*-Pr, X = BF_4^-) and **97c** (R^1 = *o*-biPh, R^2 = *i*-Pr, X = BF_4^-) in the cycloisomerization of 2-(2-ethynylphenyl)furan **165a** was compared with other Au(I)-catalysts derived from commercial P-centered compounds ($(PhO)_3PAuCl$, Ph_3PAuCl, $Ph_2(C_6F_5)PAuCl$; Figure 5-20).

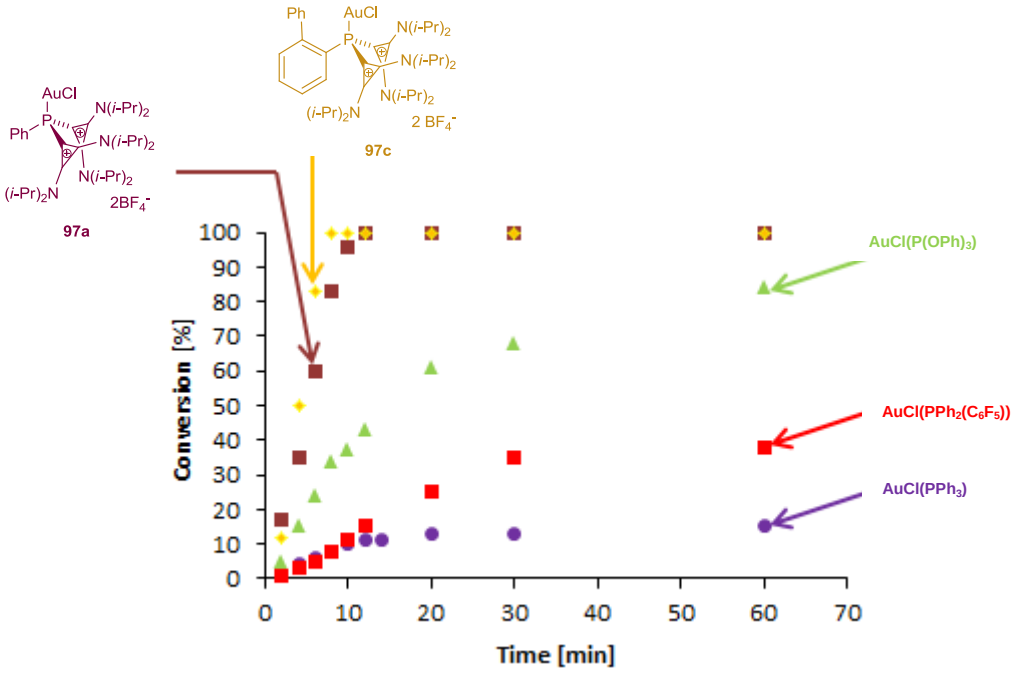


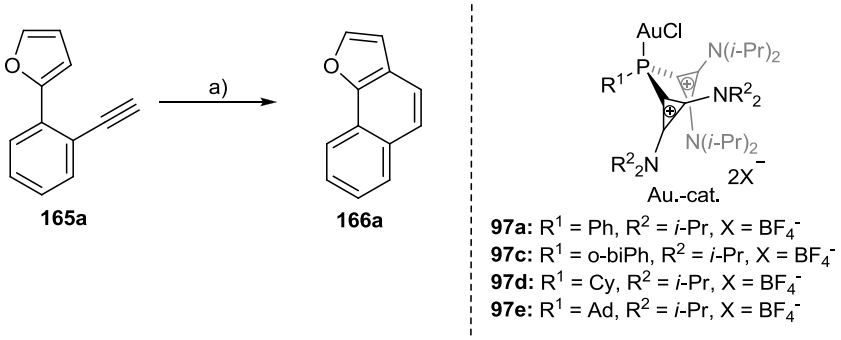
Figure 5-20: Ligand effect for the cycloisomerization of 2-(2-ethynylphenyl)furan **165a** to naphtha[1,2-b]furan **166a**. Conditions: 0.02 equiv. Au-cat. **97a**, 0.02 equiv. $AgSbF_6$, DCE, 50 °C.

It can be concluded that the reaction rate of the cycloisomerization of **165a** is directly related to the π-acidity of the catalyst. Like in the case of biphenyl-alkyne **104f** it becomes evident

that an increased reaction rate can be observed with increasing π-acceptor properties of the phosphine bound to the Au(I)-center (Figure 5-20). While no notable difference between the results for precatalyst **97a** and **97c** was detected at this catalyst loading, the general trend remains the same and results in the following activity hierarchy: $Ph_3PAuCl < Ph_2(C_6F_5)PAuCl < (PhO)_3PAuCl <$ **97c** = **97a**. These results are also in agreement with the known TEP-values of the employed ligands.

5.3.2.2 Comparison with other dicationic phosphines

Again it is clear, that the catalyst derived from Au(I)-complexes **97a/97c** are superior to other Au(I)-catalysts derived from the typical neutral P-centered compounds. Subsequently, the influence of different residues R^1 attached to the P-center of those dicationic phosphines on the reactivity of their corresponding Au(I)-catalysts was evaluated (Scheme 5-9, Figure 5-21).



Scheme 5-9: Effect of R on the cycloisomerization of 2-(2-ethynylphenyl)furan **165a** to naphtha[1,2-b]furan **166a**. a) 0.02 equiv. [Au]-cat. **97a/1c-e**, 0.02 equiv. $AgSbF_6$, 1,2-DCE, 50 °C.

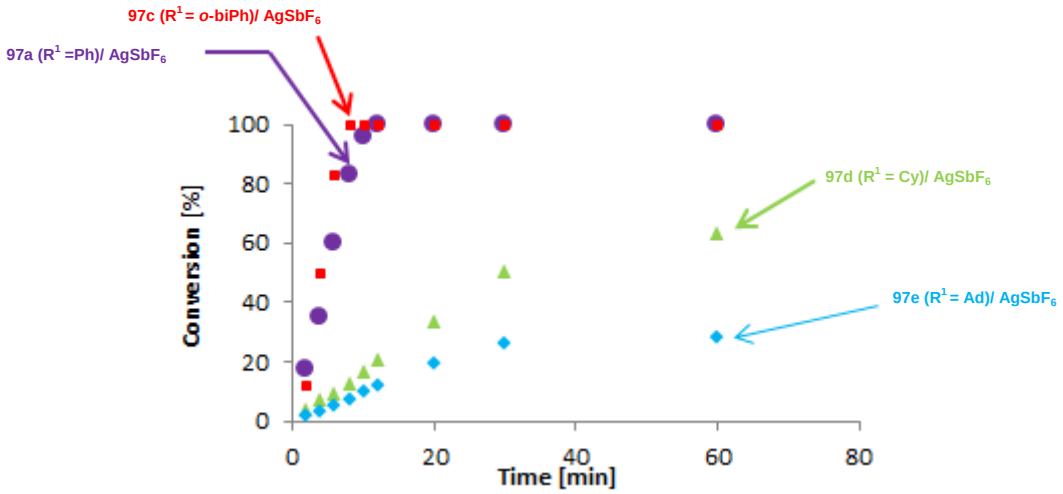


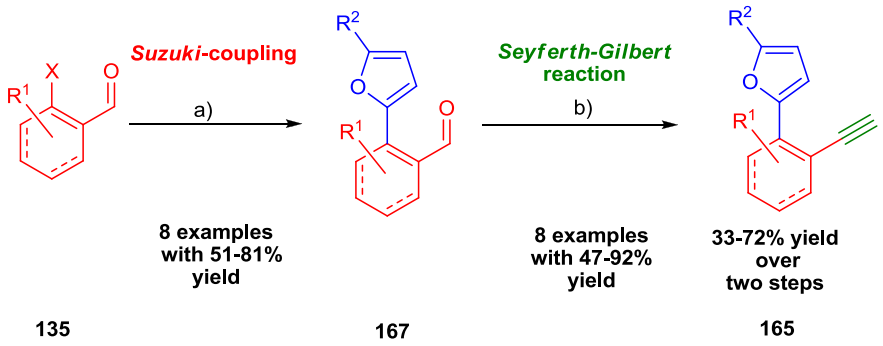
Figure 5-21: Effect of R on the cycloisomerization of 2-(2-ethynylphenyl)furan **165a** to naphtha[1,2-b]furan **166a**.

From Figure 5-21 it becomes evident that the reactivity of the catalyst decreases when the π-acidity of ligands diminishes (**97d**, **97e**), resulting in the following order of activity (Scheme 5-16, Figure 5-21): **97a** (R^1 = Ph) = **97c** (R^1 = *o*-biPh) > **97d** (R^1 = Cy) > **97e** (R^1 = Ad).

This observation, which is in agreement with the determined TEP and the oxidation potentials of the free dicationic phosphines, makes us think that the rate determing step in this reaction is again the attack of the furan ring on the activated alkyne.

5.3.3 Substrate scope

After the initial evaluations of the cycloisomerization of **165a** to **166a** the substrate scope of this reaction was evaluated. Hence, 2-(ethynylaryl)furans of general structure **165** were prepared in a two-step sequence (Scheme 5-10, Figure 5-22). This sequence included a *Suzuki*-reaction, which converted the corresponding aryl-halide **135** to the desired carbaldehyde **167** in moderate to good yield (51-81%) while a subsequent *Seyferth-Gilbert* homologation yielded the desired products of type **165** in moderate to good yield (47-92%). Once prepared, these furans were submitted to the cycloisomerization conditions (precatalyst **97c**, Scheme 5-9).



Scheme 5-10: General scheme for the synthesis of 2-(ethynylaryl)furans **165**. a) *Suzuki*-coupling; b) 1.5 equiv. *Ohira-Bestmann* reagent, 2.0 equiv. K_2CO_3, MeOH, r.t., overnight.

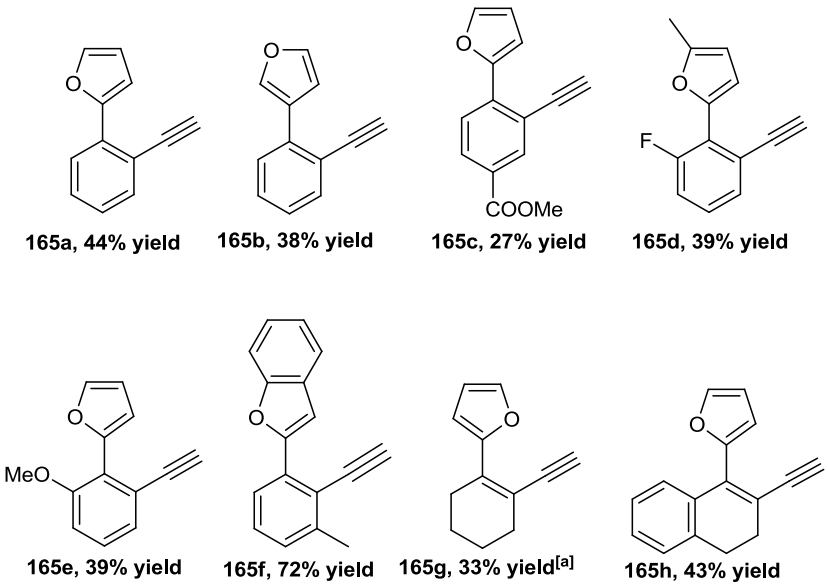


Figure 5-22: List of prepared furan-phenyl/cyclohexene-alkynes **200b.** All reported yields are over two steps.[a]: modified *Seyferth-Gilbert* conditions: 1.5 equiv. *Ohira-Bestmann* reagent, 2.0 equiv. K_2CO_3, MeOH, -40 °C, 1.0 equiv. aldehyde **206a**, -40 °C to 0 °C, 40 min, 0 °C, overnight.

As can be seen from figure 5-23, products containing -OMe, -F, -COOMe and methyl substituents on the aryl residue were formed. Moreover, derivatization of the 2-furan group by introduction of methyl substituents and benzannulation is possible. The structure of the isolated naphto-furans was confirmed not only by spectroscopic techniques, but also by an exemplary XRD-analysis of methyl naphtho[1,2-b]furan-9-carboxylate **166c** (Figure 5-24).

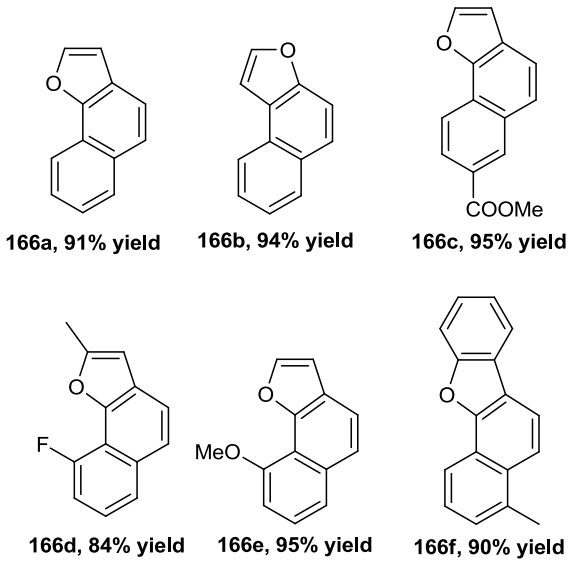


Figure 5-23: Substrate scope for cycloisomerization 2-(ethynylaryl)furans of type **165** to naphto-furans of type **166.** Conditions: 0.02 equiv. Au-cat. **97c**, 0.02 equiv. $AgSbF_6$, 1,2-DCE (c(substrate) =0.05M), 50 °C.

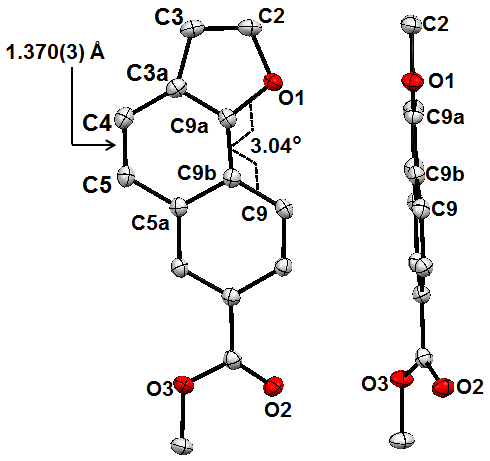


Figure 5-24: X-Ray crystal structure of **166c**. Dihedral angles between the two terminal rings are defined in terms of torsion angle 01-C9a-C9b-C9. Hydrogen atoms are omitted for clarity and ellipsoids are shown for 50% probability.

5.3.4 Limitations

The procedure reached its limit when the aromatic ring was exchanged by a partially hydrogenated one. In the cases of **165g** and **165h** (Figure 5-25) either no reaction (**165g**) or polymerization (**165h**) was observed. Indicative for the polymerization of **165h** was the signal broadening in the aromatic region of the ^{1}H-NMR spectrum, which was measured from the residue of the reaction after filtration and solvent removal.

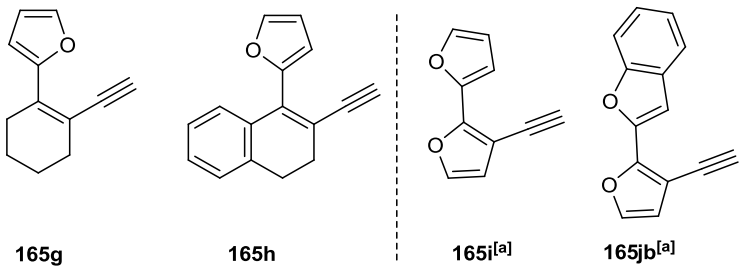


Figure 5-25: Substrates, which failed to cyclize. [a]: Prepared and attempted to cyclize by *G. Mehler*.

Further difficulties were encountered, when the phenyl-residue was exchanged for a furan (**165i**, **165j**, Figure 5-25). In these cases the cycloisomerization does not proceed at all. Probably, the longer distance **d** between the activated alkyne and the C3-atom of the upper furan ring, which is a consequence of the geometry of the furan ring, exceeds the capabilities of the employed catalyst (Figure 5-26).

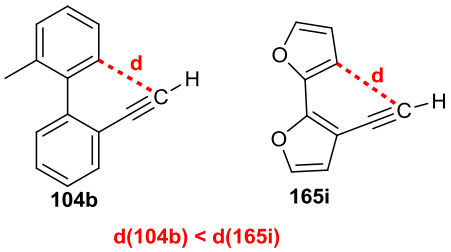


Figure 5-26: Distances between the activated alkyne and the C6-carbon of **104b** or the C3-carbon of **165i.**

5.3.5 Summary

In the initial optimization of the cyclization of 2-(2-ethynylphenyl)furan **165a** to naphto-furan **166a**, full conversion to the desired product was afforded employing 2 mol% precatalyst (**97a** or **97c**) and 2 mol% $AgSbF_6$ in 1,2-DCE at 50 °C. Furthermore it was demonstrated, that the the conversion and rate of this reaction improve with increasing π-acceptor properties of the employed ligands, which leads to the conclusion that the rate-determing step is the nucleophilic attack of the furan on the alkyne.

8 alkynes of type **165** were prepared in the same two step sequence as the biphenyl-alkynes. The applied cycloisomerization protocol tolerated the presence of -OMe, -F, -COOMe and methyl substituents on the aryl rings as well as the derivatization of the furan group by methyl substituents. The exchange of the 2-furan for a benzofuran/3-furan residue was also tolerated. Despite this promising behavior under the same conditions substrates **165g** and **165h** (as well as **165i** and **165j**) did not yield the desired products.

6 Experimental Part

6.1 General remarks

Working techniques

All moisture- and oxidation-sensitive reactions were performed in dried glassware under an argon atmosphere. Argon was obtained from *Air Liquide* with higher than 99.5% purity.

Solvents and reagents

All solvents were purified by distillation before use following standard procedures. Dry solvents were obtained by distillation over the appropriate drying agent and then kept under an atmosphere of argon: diethyl ether, tetrahydrofuran, toluene and pentane (sodium, benzophenone as indicator); *N*,*N*'-dimethylformamide (dried over molecular sieves 4 Å); dichloromethane, 1,2-dichloroethane, acetone, acetonitrile, triethylamine (calcium hydride); anisole (calcium chloride and molecular sieves 4 Å), methanol (magnesium) and 1,1,2,2-tetrachloroethane (potassium carbonate and molecular sieves 4 Å). *Ohira-Bestmann* reagent was prepared according to literature procedure.[57b] Unless specified commercial reagents were used as received from commercial sources.

Chromatographic methods

Reactions were monitored by thin layer chromatography (TLC) using silica gel pre-coated polyester sheets (40 × 80 mm, Polygram® SIL G/UV254 from Macherey-Nagel). The spots were visualized with UV-light (λ = 254 nm) and/or by staining with phosphomolybdic acid or potassium permanganate stains.

Flash column chromatography

Column chromatography was performed using silica gel 60 (Merck, 60 Å, 230-400 mesh 0.040-0.063 mm) and separations were conducted at slight overpressure in a glass column.

6.2 Analytical methods

Nuclear magnetic resonance spectroscopy (NMR)

Spectra were recorded on a *Bruker AV400, AV500, AV600* or a *DPX 300*; ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS and coupling constants (*J*) in Hz. All spectra were measured at room temperature unless stated otherwise. The solvent signals were used as reference and the chemical shifts converted to the TMS scale. Multiplicities are assigned as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), sextet (sext), septet (sept), octet (oct), multiplet (m), pseudo (p) and broad ($_{br}$). The signals have been assigned using 1D and 2D experiments.

Infrared spectroscopy

IR spectra were recorded using ATR-techniques (attenuated total reflection) on a *Nicolet* FT-7199 and a *Bruker Alpha Platinum ATR* spectrometer at room temperature. The characteristic absorption bands are given in wavenumbers [cm^{-1}].

Analytical gas chromatography

GC-MS couplings were performed on an *Agilent Technology* GC 6890 Series and MSD 5973 (carrier gas: helium) with HP6890 Series Injector, employing an MN Optima®5 column (30 m x 0.25 mm x 0.25 mm). Mass spectra were recorded with an *Agilent Technology* 5973 Network MSD spectrometer. Qualitative evaluation of the integration was based on the substance peaks without considering response factors, unless stated otherwise.

Mass spectrometry (MS)

Mass spectra were measured on a *Finnigan MAT 8200* (70 eV) or *MAT 8400* (70 eV) spectrometer by electron ionization, chemical ionization, or fast atom/ion bombardment techniques. For electron-spray ionization a Finnigan MAT 95 was used. High resolution masses were determined on a *Bruker APEX III FT-MS* spectrometer (7 T magnet). All masses are given in atomic units per elementary charge (*m/z*) and reported in percentage relative to the basic peak.

X-ray crystal structure analysis

The crystal structures were measured in the X-ray department of the *"Max Planck Institut für Kohleforschung"* in Mülheim an der Ruhr, under the direction of *Prof. C. W. Lehmann*. The measurements were made using a *Bruker-AXS Kappa* CCD diffractometer.

6.3 Provided Chemicals

The following chemicals were provided by co-workers of our work-group (Figure 6-1):

- Chloro cyclopropenium salt **111**/**112** (provided by *G. Mehler*),
- tertiary biscyclopropenium phosphines **95c, 95d, 95e** and **95f** (provided by *G. Mehler*),
- Aryl ester **135i** (provided by *T. Deden*). [71]

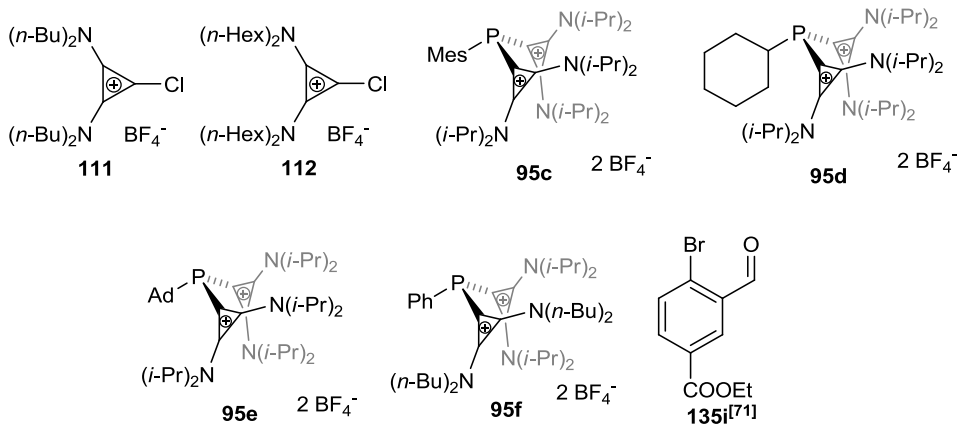


Figure 6-1: Structures of of provided chemicals**.**

The experimental results of the provided chemicals and their respective precursors are shown in section 6.5 in order to provide a comprehensive overview over the relevant data as the provided dicationic phosphines were utilized for coordination purposes (section 4) and catalysis (section 5).

6.4 Literature known compounds

The following chemicals were prepared according to known literature procedures (Figure 6-2): [25, 37b, 41b, 65, 66,72, 73, 74, 75, 76,77, 78, 79, 80, 81]

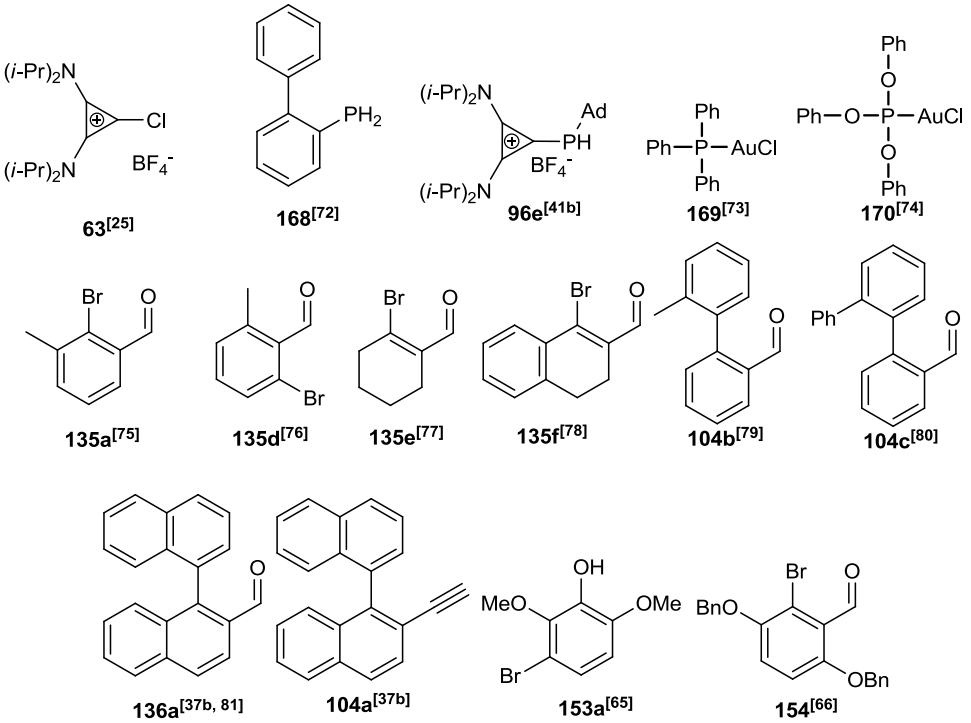
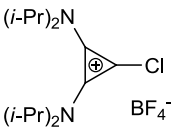


Figure 6-2: Compounds prepared according to literature procedures.

6.5 Synthesis

6.5.1 Synthesis of Cyclopropenium salts

Chlorocyclopropenium salt 63



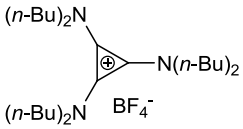
63

Compound **63** was prepared in 82% yield according to literature procedure.[25]

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.42 (d, *J* = 1.5 Hz, 12H), 1.43 (d, *J* = 1.6 Hz, 12H), 3.87 (sept, *J* = 6.8 Hz, 2H), 4.16 ppm (sept, *J* = 6.7 Hz, 2H).

The measured spectral data were in agreement with those found in the literature.[25]

Triaminocyclopropenium salt 114



114

Pentachlorocyclopropane **113** (10.0 g, 47.7 mmol) was dissolved in DCM (150 mL) and the resulting solution was cooled down to -78 °C. Then HN(*n*-Bu)$_2$ (48.3 g, 373 mmol) was added over 1 hour and the solution stirred at 0 °C for 4 additional hours. Subsequently, the reaction mixture was allowed to warm to room temperature during 18 hours. Afterwards this mixture was refluxed for 5 hours, which resulted in the formation of a light brown liquid. The DCM was removed *in vacuo* and acetone was added to precipitate the secondary ammonium salt, which was filtered from the solution comprising the triaminocyclopropenium salt **114**. Once the aqueous phase was extracted with DCM (3x), the organic phases were combined and the solvent removed *in vacuo*. Then the crude was washed with pentane (4x) to remove residual amine and the residue was redissolved in DCM. HBF_4 (50 mL, 48%) in water (50 mL) was added. Extraction of the product with DCM yielded an organic phase, which was washed with HBF_4 (20 mL, 35%) and with water (until the pH was neutral). The combined extracts were dried over Na_2SO_4 before the solvent was removed *in vacuo* in affording **114** as an orange liquid (19.0 g, 80.2%).[40]

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.32 Hz, 18H), 1.23-1.33 (m, 12H), 1.52-1.60 (m, 12H), 3.22-3.26 ppm (m, 12H).

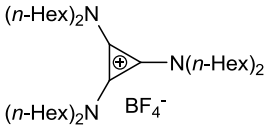
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 13.4, 19.5, 30.5, 52.4, 116.4 ppm.

HRMS *calcd.* for $C_{27}H_{54}N_3^+$: 420.431220 $[M\text{-}BF_4]^+$; *found*: 420.431380.

IR: ϑ̃ = 519, 654, 763, 891,1048, 1194, 1375, 1528, 1853, 2958, 2973 cm^{-1}.

The measured spectral data were in agreement with those found in the literature.[40]

Triaminocyclopropenium salt 115



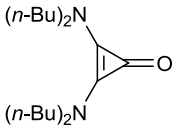
115

Tetrachlorocyclopropene **68** (5.0g, 28.1 mmol) was dissolved in DCM (100 mL) and the resulting solution was cooled down to -78 °C. Then HN(*n*-Hex)$_2$ (20.85 g, 112.5 mmol) was added over 1 hour and the solution stirred at 0 °C for 4 additional hours. Subsequently, the reaction mixture was allowed to warm to room temperature during 18 hours. Then it was cooled to 0 °C and HBF_4 (50 mL, 48%) in water (50 mL) was added. The mixture thus obtained was extracted with DCM (3x) and the combined organic phases were washed with HBF_4 (20 mL, 48%) and water (until the pH was neutral) before being dried over sodium sulfate. Removal of the solvents *in vacuo* yielded an orange liquid, which was resolved in dry DCM. From this solution the product **115** was precipitated with *n*-pentane (13.4 g). Small impurities of dihexylammonium salt could not be removed. The mixture was used for the next step in this state.

^{1}H-NMR(400 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 6.7 Hz, 18H), 1.24 (m_{br}, 36H), 1.55 (m_{br}, 12H), 3.21 (pt, *J* = 7.9 Hz, 12H) ppm.

HRMS *calcd.* for $C_{39}H_{78}N_3^+$: 588.619021 $[M\text{-}BF_4]^+$; *found*: 588.619280.

Ketone 116



116

To an aqueous KOH solution (19.64 g, 350 mmol, in 68.5 mL water) cyclopropenium salt **114** (17.76 g, 35.0 mmol) was added dissolved in MeOH (30.0 mL). The reaction mixture was heated to 60°C for 16 hours and then cooled to room temperature. Then the obtained reaction crude was extracted with DCM (4x), the combined organic phases dried over sodium sulfate and the solvent evaporated. Finally, the obtained residue was purified by column chromatography on silica gel (DCM/Acetone, 9/1) affording **116** as a transparent oil (5.63 g, 52.1%).

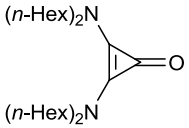
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.26 Hz, 12H), 1.22-1.31 (m, 8H), 1.48-1.56 (m, 8H), 3.08 ppm (pt, *J* = 7.5 Hz, 8H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ =13.5, 19.6, 30.5, 52.3, 119.1, 133.3 ppm.

HRMS *calcd.* for $C_{19}H_{37}N_2O^+$: 309.290036 $[M+H]^+$; *found*: 309.290250.

IR: ῡ= 518, 643, 747, 1052, 1192, 1347, 1454, 1590, 1899, 2872, 2957 cm^{-1}.

Ketone 117



117

To an aqueous KOH solution (15.6 g, 277 mmol, in 100 mL water) cyclopropenium salt **115** (18.75 g, 27.7 mmol) was added dissolved in MeOH (15.0 mL). The reaction mixture was heated to 60°C for 16 hours and then cooled to room temperature. Then the obtained reaction crude was extracted with DCM (4x), the combined organic phases dried over sodium sulfate and the solvent evaporated. Finally, the obtained residue was purified by column chromatography on silica gel (DCM/Acetone, 15/1) affording **117** as a transparent oil (11.1 g, 95.0%).

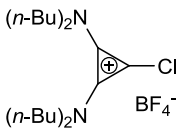
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 6.88 Hz, 12H), 1.22 (ps_{br}, 24H), 1.52 (m_{br}, 8H), 3.06-3.09 ppm (m, 8H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 13.2, 21.8, 25.7, 27.9,31.0, 51.1, 118.7, 132.8 ppm.

HRMS *calcd.* for $C_{27}H_{53}N_2O^+$: 421.415237 $[M+H]^+$; *found*: 421.415390.

IR: ῡ = 726, 1105, 1261, 1375, 1420, 1463, 1597, 1893, 2856, 2925, 2955 cm^{-1}.

Chlorocyclopropenium salt 111



111

Oxalyl chloride (5.0 mL, 58.2 mmol) was added dropwise to ketone **116** (5.6 g, 18.2 mmol) at 0 °C. Strong gas evolution was observed. After the addition was finished, the reaction mixture was stirred at room temperature for an additional hour and then the excess of oxalyl chloride was removed *in vacuo*. The residue obtained was dissolved in DCM and the solution washed with a saturated solution of $NaBF_{4(aq)}$ (3x). Finally, the organic phase was dried over sodium sulfate, the solvent removed *in vacuo* and the crude obtained was purified by column chromatography on silica gel (DCM/acetone, 9/1) to afford **111** as a red liquid (6.27 g, 83.1%).

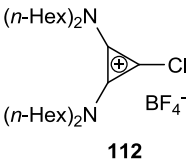
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.26 Hz, 6H), 0.91 (t, *J* = 7.40 Hz, 6H), 1.23-1.30 (m, 4H), 1.30-1.38 (m, 4H), 1.56-1.62 (m, 4H), 1.64-1.69 (m, 4H), 3.39 (t, *J* = 7.7 Hz, 4H), 3.42 ppm (t, *J* = 7.8 Hz, 4H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 13.2, 13.3, 19.3, 19.6, 29.6, 30.2, 52.3, 53.6, 92.1, 133.4 ppm.

HRMS *calcd.* for $C_{19}H_{36}N_2Cl^+$: 327.256151 $[M-BF_4]^+$; *found*: 327.256220.

IR: ῡ= 519, 647, 734, 1048, 1239, 1376, 1455, 1605, 1903, 2875, 2960 cm^{-1}.

Chloro cyclopropenium salt 112



112

Oxalyl chloride (3.5 mL, 41.1 mmol) was added dropwise to ketone **117** (5.4 g, 12.8 mmol) at 0 °C. Strong gas evolution was observed. After the addition was finished, the reaction mixture was stirred at room temperature for an additional hour and then the excess of oxalyl chloride was removed *in vacuo.* The residue obtained was dissolved in DCM and the solution washed with a saturated solution of $NaBF_{4(aq)}$ (3x). Finally, the organic phase was dried over sodium sulfate, the solvent removed *in vacuo* and the crude obtained was purified by column chromatography on silica gel (DCM/acetone, 15/1) to afford **112** as a red liquid (4.57 g, 67.6%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.86-0.89 (m, 12H), 1.28-1.36 (m, 24H), 1.63 (m_{br}, 4H), 1.78-1.74 (m, 4H), 3.41-3.45 (m, 4H), 3.46-3.49 (m 4H) ppm.

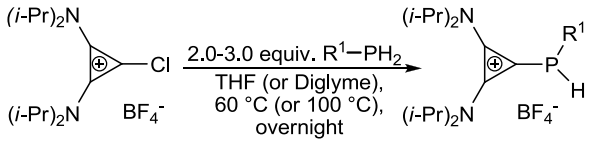
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.5, 22.6, 26.3, 26.5, 28.0, 28.7, 31.3, 31.6, 53.1, 54.4, 92.5, 133.9 ppm.

HRMS *calcd.* for $C_{27}H_{52}N_2Cl^+$: 439.381351 $[M\text{-}BF_4]^+$; *found*: 439.380970.

IR: ῡ = 520, 731, 1048, 1269, 1377, 1414, 1604, 1933, 2858, 2927, 2955 cm^{-1}.

6.5.2 Synthesis secondary phosphines bearing one cyclopropenium substituent

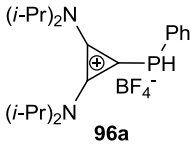
General procedure A



63 **96a-e**

A dry *Schlenk*-flask was charged with a primary phosphine (2.0-3.0 equiv.), chloro cyclopropenium salt **63** (1.0 equiv.) and THF (or diglyme) and the resulting mixture was heated overnight (in THF: 60 °C; in diglyme: 100 °C). After cooling the reaction mixture to room temperature, the solvent was removed *in vacuo*, the residue dissolved in DCM and the organic phase thus obtained was washed with a saturated aqueous solution of $NaBF_4$. Once the combined organic phases were dried over sodium sulfate, removal of the solvent *in vacuo* afforded a residue that was further purified by column chromatography on silica gel (DCM/Acetone, 9/1) affording the desired product as a white solid.

Monocationic phosphine 96a



96a

A dry *Schlenk*-flask was charged with a solution of phenylphosphine (7.4 mL, 5.3 mmol, 10% in hexane) and the solvent was concentrated *in vacuo* to approximately 1/3 of its starting volume. Then, chloro cyclopropenium salt **63** (630.0 mg, 1.8 mmol) and THF (6.0 mL) were added and the resulting mixture heated to 60 °C overnight. After cooling the reaction mixture to room temperature, the solvent was removed *in vacuo*, the residue dissolved in DCM and the organic phase thus obtained was washed with a saturated aqueous solution of $NaBF_4$. Once the combined organic phases were dried over sodium sulfate, removal of the solvent *in vacuo* afforded a residue that was further purified by column chromatography on silica gel (DCM/Acetone, 9/1). Thus the desired compound **96a** was obtained as a white solid (575 mg, 76%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 6.8 Hz, 6H), 1.32 (d, *J* = 6.9 Hz, 6H), 1.37 (d, *J* = 6.8 Hz, 6H), 1.40 (d, *J* = 6.8 Hz, 6H), 3.71 (sept d, *J* = 6.8, 2.0 Hz, 2H), 4.13 (sept, *J* =6.8 Hz, 2H), 5.63 (d, *J* =233.3 Hz, 1H), 7.45-7.47 (m, 3H), 7.64-7.69 ppm (m, 2H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 21.0, 21.1, 21.3, 21.4, 22.4, 22.5, 49.6, 56.5, 103.4 (d, J_{P-C} = 56.4 Hz), 125.4 (d, J_{P-C} = 6.3 Hz), 129.7 (d, J_{P-C} = 8.5 Hz), 131.3 (d, J_{P-C} = 0.9 Hz), 136.2 (d, J_{P-C} = 20.5 Hz), 138.5 (d, J_{P-C} = 3.9 Hz) ppm.

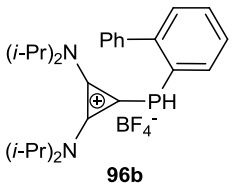
^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$): δ = -70.2 ppm.

HRMS *calcd*. for $C_{21}H_{34}N_2P^+$: 345.245415 $[M\text{-}BF_4]^+$; *found*: 345.245568.

IR: ϑ̃ = 729, 1032, 1349, 1558, 1872, 2984 cm^{-1}.

The measured spectral data were in agreement with those found in the literature.[41]

Secondary monocationic phosphine 96b



96b

Compound **96b** was prepared according to general procedure **A** from 1,1'-(biphenyl-2-yl)-phosphine **168** (2.24 g, 12.0 mmol) and chloro cyclopropenium salt **63** (2.15 g, 6.0 mmol) in diglyme (20.0 mL). White solid (1.86 g, 61.0%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.08 (d, *J* = 6.8 Hz, 6H), 1.16 (d, *J* = 6.8 Hz, 6H), 1.34 (d, *J* = 6.8 Hz, 6H), 1.37 (d, *J* = 6.8 Hz, 6H), 3.65 (sept d, *J* = 6.8, 1.8 Hz, 2H), 4.12 (sept, *J* = 6.9

Hz, 2H), 5.39 (d, *J* = 233.3 Hz, 1H), 7.22-7.23 (m, 1H), 7.26 (m, 1H, overlaps with solvent) 7.31-7.51 (m, 6H), 7.69-7.75 (m, 1H) ppm.

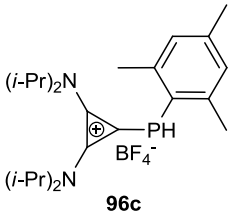
$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 21.0, 21.0, 21.5, 21.5, 22.1, 22.2, 49.4, 56.5, 103.4 (d, J_{P-C} = 58.4 Hz), 124.9 (d, J_{P-C}= 8.1 Hz), 128.2, 128.7, 128.9 (d, J_{P-C} = 4.4 Hz), 129.1 (d, J_{P-C} = 3.0 Hz), 130.6 (d, J_{P-C} = 4.0 Hz), 131.0, 136.8 (d, J_{P-C} = 9.3 Hz), 138.9 (d, J_{P-C} = 2.0 Hz), 141.0 (d, J_{P-C} = 4.0 Hz), 147.9 (d, J_{P-C} = 20.2 Hz) ppm.

$^{31}P\{^1H\}$-NMR (161 MHz, $CDCl_3$): δ = -79.1 ppm.

HRMS *calcd.* for $C_{27}H_{38}N_2P^+$: 421.276711 $[M\text{-}BF_4]^+$; *found*: 421.276383.

IR: ϑ = 702, 762, 861, 884, 1029, 1152, 1340, 1458, 1562, 1874, 2297, 2984 cm^{-1}.

Secondary monocationic phosphine 96c



96c

Compound **96b** was prepared according to general procedure **A** from mesitylphsophine (2.44 g, 17.7 mmol) and chloro cyclopropenium salt **63** (3.1g, 8.64 mmol) in diglyme (20.0 mL). White solid (2.9 g, 70.7%).

^1H-NMR (400 MHz, $CDCl_3$): δ = 1.08 (d, *J* = 6.9 Hz, 6H), 1.19 (d, *J* = 6.9 Hz, 6H), 1.35 (d, *J* = 6.9 Hz, 6H), 1.37 (d, *J* = 6.9 Hz, 6H), 2.30 (s, 3H), 2.48 (s, 6H), 3.58 (sept., *J* = 6.4 Hz, 2H), 4.08 (sept., *J* = 6.4 Hz, 2H), 5.44 (d, *J* = 240 Hz, 1H), 7.00 ppm (d, *J* = 2.6 Hz, 2H).

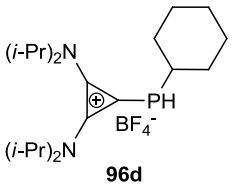
$^{13}C\{^1H\}$-NMR (101 MHz, CD_2Cl_2): δ = 21.0, 21.1, 21.4 (d, J_{P-C} = 5.6 Hz), 22.3, 23.4, 23.5, 49.9, 54.7, 105.4 (d, J_{P-C} = 62.5 Hz), 120.5 (d, *J* = 9.6 Hz), 129.7 (d, J_{P-C} = 5.0 Hz), 137.9, 142.2, 144.7 ppm (d, J_{P-C} = 8.1 Hz).

$^{31}P\{^1H\}$-NMR (161 MHz, $CDCl_3$): δ = -94.4 ppm.

HRMS *calcd.* for $C_{24}H_{40}N_2P^+$: 387.292359$[M\text{-}BF_4]^+$; *found*: 387.292161.

IR: ϑ = 520, 562, 658, 803, 1050, 1093, 1155, 1345, 1538, 1868, 2982 cm^{-1}.

Secondary monocationic phosphine 96d



96d

Compound **96d** was prepared according to general procedure **A** from cyclohexylphosphine (2.44 g, 21.0 mmol) and chloro cyclopropenium salt **63** (2.5 g, 7.0 mmol) in THF (30.0 mL). White solid (2.0 g, 65%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.07-1.23, (m, 4H), 1.30 (d, *J* = 6.6 Hz, 6H), 1.33 (d, *J* = 6.6 Hz, 12H), 1.38 (d, *J* = 6.6 Hz, 6H), 1.65-1.90 (7H), 3.85 (sept, *J* = 6.4 Hz, 2H), 4.07 (dd, *J* = 220 Hz, *J* = 9.5 Hz, 1H),4.09 (sept, *J* = 6.4 Hz, 2H) ppm.

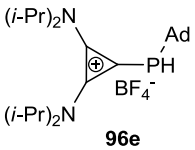
^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ = 20.6 (d, J_{P-C} = 2.9 Hz), 21.0 (d, J_{P-C} = 1.7 Hz), 22.2 (d, J_{P-C} = 3.7 Hz), 25.2, 26.5, 26.6 (d, *J* = 1.7 Hz), 31.0 (d, J_{P-C} = 19.8 Hz), 32.3 (d, J_{P-C} = 10.8 Hz), 35.1, 49.2, 56.1, 103.0 (d, J_{P-C} = 62.2 Hz), 138.9 (d, J_{P-C} = 3.4 Hz) ppm.

^{31}P{^{1}H}-NMR (161 MHz, $CDCl_3$): δ = -59.4 ppm.

HRMS *calcd.* for $C_{21}H_{40}N_2P^+$: 351.292360 $[M\text{-}BF_4]^+$; *found*: 351.292146.

IR: ϑ = 732, 891, 1033, 1142, 1348, 1542, 1859, 2933 cm^{-1}.

Secondary monocationic phosphine 96e[82]



96e

Compound **96e** was prepared in 87% yield according to a literature procedure.[41b]

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.35 (d, *J* = 6.8 Hz, 18H), 1.41 (d, *J* = 6.8 Hz, 6H), 1.67 (m, 6H), 1.81-1.82 (m, 6H), 1.97 (m, 3H), 3.96 (sept, *J* = 6.8 Hz, 2H), 3.99 (d, *J* = 221.3 Hz, 1H), 4.13 (sept, *J* = 6.8 Hz, 2H) ppm.

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 20.6, 20.9, 21.0, 21.4, 28.4 (d, J_{P-C} = 8.6 Hz), 35.5, 36.7 (d, J_{P-C} = 11.2 Hz), 42.7 (d, J_{P-C} = 9.5 Hz), 51.4, 53.6, 101.9 (d, J_{P-C} = 67.7 Hz), 140.3 ppm.

^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$): δ = -44.5 ppm.

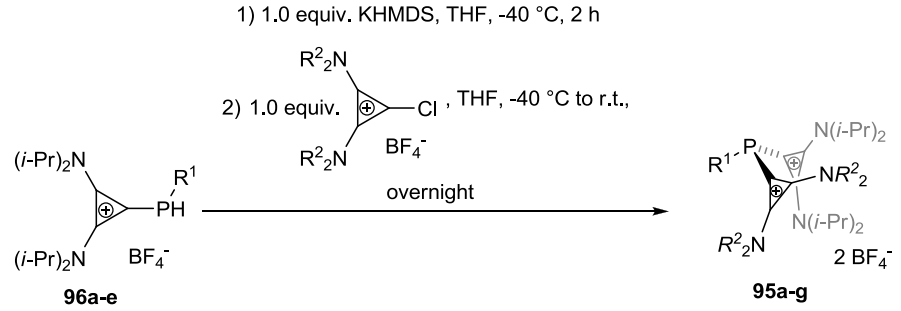
HRMS *calcd*. for $C_{25}H_{44}N_2P^+$: 403.323658 $[M\text{-}BF_4]^+$; *found:* 403.323727.

IR: ϑ = 607, 1045, 1153, 1376, 1543, 1863, 2903 cm^{-1}.

The measured spectral data were in agreement with those found in the literature.[41b]

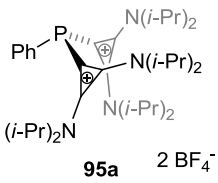
6.5.3 Synthesis of biscyclopropenium phosphines

General procedure B



Dry THF was added to a cooled (-40°C) solid mixture of KHMDS (1.0 equiv.) and phosphines **96a-e** (1.0 equiv.) and the resulting suspension was stirred at this temperature for 2 hours. Then, the desired chloro cyclopropenium salt **63**/**111**/**112** (1.0 equiv.) was added, and the reaction warmed to room temperature overnight. Removal of the solvent *in vacuo* afforded a residue that was redissolved in DCM and washed with an aqueous saturated solution of $NaBF_4$ (3x). Once dried over sodium sulfate, the organic phase was concentrated and the obtained residue (oil or solid) washed with THF to afford the desired compounds **95a-g** as a solid.

Biscyclopropenium phosphine 95a



Compound **95a** was prepared according to general procedure **B,** employing KHMDS (230.1 mg, 1.16 mmol), phosphine **96a** (500 mg, 1.16 mmol) and chloro cyclopropenium salt **63** (414.8 mg, 1.16 mmol) in dry THF (7 mL). White solid (598.2 mg, 68.2%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 6.9 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 12H), 1.38 (d, *J* = 6.9 Hz, 12H), 1.44 (d, *J* = 6.9 Hz, 12H), 3.64 (sept, *J* = 6.9 Hz, 4H), 4.17 (sept d, *J* = 6.8, 1.4 Hz, 4H), 7.62-7.68 (m, 3H), 7.73-7.80 ppm (m, 2H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 21.2, 21.5, 21.6, 21.7, 53.4, 54.8, 98.2 (d, $J_{P\text{-}C}$ = 59.5 Hz), 125.0 (d, $J_{P\text{-}C}$ = 4.6 Hz), 131.1 (d, $J_{P\text{-}C}$ = 8.9 Hz), 133.0, 134.8 (d, $J_{P\text{-}C}$ = 22.9 Hz), 140.0 ppm.

^{31}P{^{1}H}-NMR (400 MHz, $CDCl_3$): δ = -47.2 ppm.

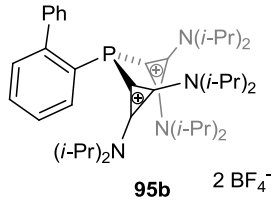
^{19}F-NMR (282 MHz, $CDCl_3$): δ = -152.2 ppm.

HRMS *calcd*. for $C_{36}H_{61}BF_4N_4P^+$: 667.467509 $[M\text{-}BF_4]^+$; *found*: 667.467401.

IR: ϑ = 694, 1029, 1151, 1357, 1555, 1858, 2974 cm^{-1}.

The measured spectral data were in agreement with those found in the literature.[41]

Biscyclopropenium phosphine 95b



95b 2 BF_4^-

Compound **95b** was prepared according to general procedure **B,** employing KHMDS (325 mg, 1.63 mmol), phosphine **96b** (830 mg, 1.63 mmol) and chloro cyclopropenium salt **63** (580 mg, 1.63 mmol) in dry THF (20 mL). White solid (660 mg, 48.7%).

^{1}H-NMR (400 MHz, CD_3CN): δ = 0.97 (d, *J* = 6.8 Hz, 12H), 1.16 (d, *J* = 6.8 Hz, 12H), 1.32 (d, *J* = 6.8 Hz, 12H), 1.35 (d, *J* = 6.8 Hz, 12H), 3.68-3.71 (m_{br}, 4H), 4.13 (sept, *J* = 6.8 Hz, 4H), 7.17-7.19 (m, 2H), 7.44-7.50 (m, 3H), 7.52-7.56 (m, 1H), 7.60-7.64 (m, 1H) 7.67-7.70 (m, 1H), 7.73 ppm (td, *J* = 7.5 Hz, 1.3 Hz, 1H).

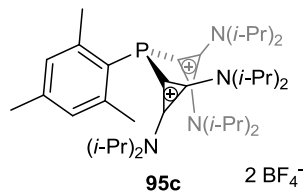
^{13}C{^{1}H}-NMR (101 MHz, CD_3CN): δ = 21.1, 21.2, 21.5, 21.6, 21.6, 21.7, 53.2, 56.0, 98.7 (d, $J_{P\text{-}C}$ = 60.6 Hz), 125.7, 129.7, 129.8, 129.9 (d, $J_{P\text{-}C}$ = 4.0 Hz), 130.2, 132.4 (d, $J_{P\text{-}C}$ = 6.5 Hz), 134.0, 136.2(d, $J_{P\text{-}C}$ = 3.1 Hz), 140.6 (d, $J_{P\text{-}C}$ = 2.0 Hz), 140.7, 150.0 ppm (d, $J_{P\text{-}C}$ = 36.1 Hz).

^{31}P{^{1}H}-NMR (162 MHz, CD_3CN): δ = -54.7 ppm.

HRMS *calcd.* for $C_{42}H_{65}BF_4N_4P^+$: 743.497053 $[M\text{-}BF_4]^+$; *found*: 743.498110.

IR: ϑ = 440, 519, 549, 578, 616, 640, 666, 688, 705, 740, 761, 891, 1028, 1048, 1150, 1182, 1204, 1283, 1353, 1376, 1457, 1552, 1852, 2879, 2939, 2976 cm^{-1}.

Biscyclopropenium phosphine 95c



95c 2 BF_4^-

Compound **95c** was prepared according to general procedure **B,** employing KHMDS (69.0 mg, 0.35 mmol), phosphine **96c** (164.0 mg, 0.35 mmol) and chloro cyclopropenium salt **63** (125.5 mg, 0.35 mmol) in dry THF (10 mL). White solid (88.0 mg, 31.6%).

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.08 (d, *J* = 6.6 Hz, 12H), 1.26 (d, *J* = 6.8 Hz, 12H), 1.32 (d, *J* = 6.8 Hz, 12H), 1.33 (d, *J* = 6.8 Hz, 12H), 2.26 (s, 3H), 2.40 (s, 6H),3.71 (sept, *J* = 6.6 Hz, 4H), 4.13 (sept, *J* = 6.6 Hz, 4H), 7.03 ppm (d, *J* = 3.9 Hz, 2H).

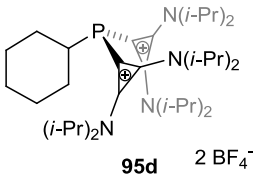
$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 21.2, 21.4, 21.4, 21.5, 21.5, 21.6, 21.8, 53.7, 54.3, 99.1 (d, J_{P-C} = 58.0 Hz), 118.9 (d, J_{P-C} = 9.6 Hz), 131.1, 131.2, 139.2, 144.2 ppm.

$^{31}P\{^1H\}$-NMR (161 MHz, CD_2Cl_2): δ = -64.7 ppm.

HRMS *calcd.* for $C_{39}H_{67}BF_4N_4P^+$: 709.512703 $[M\text{-}BF_4]^+$; *found*: 709.513703.

IR: ῡ= 520, 579, 645, 689, 893, 1034, 1051, 1151, 1362, 1455, 1551, 1852, 2974 cm^{-1}.

Biscyclopropenium phosphine 95d



95d 2 BF_4^-

Compound **95d** was prepared according to general procedure **B,** employing KHMDS (49.9 mg, 0.25 mmol), phosphine **96d** (109.6 mg, 0.25 mmol) and chloro cyclopropenium salt **63** (89.7 mg, 0.25 mmol) in dry THF (6 mL). White solid (80.0 mg, 42%).

^1H-NMR (400 MHz, CD_2Cl_2): δ = 1.26-1.37 (m, 4H), 1.28 (d, *J* = 6.9 Hz, 12H), 1.30 (d, *J* = 6.9 Hz, 12H), 1.35 (d, *J* = 6.9 Hz, 12H), 1.37 (d, *J* = 6.9 Hz, 12H), 1.71-1.84 (m, 6H), 2.59 (m, 1H), 3.90 (sept, *J* = 6.9 Hz, 4H), 4.13 (sept, *J* = 6.9 Hz, 4H) ppm.

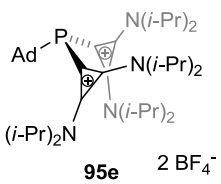
$^{13}C\{^1H\}$-NMR (101 MHz, CD_2Cl_2): δ = 21.2, 21.4, 21.4, 21.6, 21.6, 21.8, 25.3, 26.6 (d, J_{P-C} = 13.0 Hz), 30.5 (d, J_{P-C} = 16.1 Hz), 36.6 (d, J_{P-C} = 10.5 Hz), 53.0, 54.1, 98.5 (d, J_{P-C} = 70.1 Hz), 140.4 ppm.

$^{31}P\{^1H\}$-NMR (161 MHz, CD_2Cl_2): δ = -43.7 ppm.

HRMS *calcd.* for $C_{36}H_{67}BF_4N_4P^+$: 673.512703 $[M\text{-}BF_4]^+$; *found*: 673.512360.

IR: ῡ= 519, 576, 684, 892, 1030, 1049, 1151, 1355, 1455, 1547, 1851, 2937 cm^{-1}.

Biscyclopropenium phosphine 95e



95e 2 BF_4^-

Compound **95e** was prepared according to general procedure **B**, employing KHMDS (49.9 mg, 0.25 mmol), phosphine **96e** (122.6 mg, 0.25 mmol) and chloro cyclopropenium salt **63** (89.7 mg, 0.25 mmol) in dry THF (6.0 mL). White solid (102.0 mg, 50%).

^1H-NMR (400 MHz, CD_2Cl_2): δ = 1.32 (d, *J* = 6.8 Hz, 12H), 1.30 (d, *J* = 6.9 Hz, 12H), 1.46 (dd, *J* = 6.8, 4.0 Hz, 24H), 1.76-1.85 (m, 6H), 2.04 (m, 6H), 2.17 (m, 3H), 4.15-4.28 ppm (m, 8H).

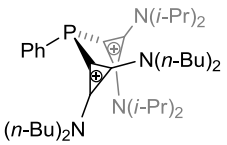
$^{13}C\{^1H\}$-NMR (101 MHz, CD_2Cl_2): δ = 21.4, 21.7, 21.8, 28.6 (d, J_{P-C} = 10.3 Hz), 35.8, 39.4 (d, J_{P-C} = 16.5 Hz), 40.0 (d, J_{P-C} = 11.2 Hz), 53.0-55.0 (broad **C**$H_{i\text{-}Pr}$signal covered by CD_2Cl_2), 98.2 (d, J_{P-C} = 76.1 Hz), 140.5 ppm.

$^{31}P\{^1H\}$-NMR (161 MHz, CD_2Cl_2): δ = -21.8 ppm.

HRMS *calcd.* for $C_{40}H_{71}BF_4N_4P^+$: 725.544003 $[M\text{-}BF_4]^+$; *found:* 725.544080.

IR: ῡ = 520, 575, 685, 893, 1033, 1051, 1151, 1358, 1458, 1555, 1845, 2910, 2978 cm^{-1}.

Biscyclopropenium phosphine 95f



95f 2 BF_4^-

Compound **95f** was prepared according to general procedure **B**, employing KHMDS (115.6 mg, 0.78 mmol), phosphine **96a** (338.0 mg, 0.78 mmol) and chloro cyclopropenium salt **111** (414.8 mg, 0.78 mmol) in dry THF (20 mL). After the reaction was finished the work-up was performed as described and the obtained crude product was washed with pentane (4x, instead of THF), affording the desired compound **95f** as a dark red oil of high viscosity (353.0g, 56%).

^1H-NMR (400 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 7.4 Hz, 6H), 0.93 (t, *J* = 7.4 Hz, 6H), 0.99-1.09 (m, 4H), 1.20 (d, *J* = 6.8 Hz, 6H), 1.28-1.33 (m, 4H), 1.37(d, *J* = 6.8 Hz, 6H), 1.40 (d, *J* = 6.8 Hz, 6H), 1.42 (d, *J* = 6.8 Hz, 6H), 1.46-1.54 (m, 4H), 1.56-1.65 (m, 4H), 3.16-3.20 (m, 4H), 3.46-3.50 (m, 4H), 3.84 (sept d, *J* = 6.8 Hz, 1.5 Hz, 2H), 4.18 (sept, *J* = 6.8 Hz, 2H), 7.50-7.59 (m, 3H), 7.7.70-7.75 ppm (m, 2H).

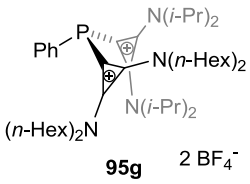
$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 13.3, 19.4, 19.6, 20.6, 20.7, 20.8, 20.8, 29.5, 30.2, 51.6, 53.4, 53.5, 55.1, 96.6 (d, J_{P-C} = 55.6 Hz), 98.4 (d, J_{P-C} = 61.8 Hz), 126.0 (d, J_{P-C} = 4.2 Hz), 130.0 (d, J_{P-C} = 8.7 Hz), 131.7, 133.5 (d, J_{P-C} = 22.4Hz), 139.3 (d, J_{P-C} = 3.7 Hz), 141.1 ppm (d, J_{P-C} = 1.8 Hz).

$^{31}P\{^1H\}$-NMR (162 MHz, $CDCl_3$): δ = -51.5 ppm.

HRMS *calcd.* for $C_{40}H_{69}BF_4N_4P^+$: 723.528353 $[M\text{-}BF_4]^+$; *found*: 723.528140.

IR: ῡ = 519, 696, 753, 892, 1031, 1046, 1152, 1377, 1437, 1460, 1563, 1862, 1897, 2874, 2936, 2961 cm^{-1}.

Biscyclopropenium phosphine 95g



95g

Compound **95g** was prepared according to general procedure **B**, employing KHMDS (521 mg, 2.61 mmol), phosphine **96a** (1.11 g, 2.56 mmol) and chloro cyclopropenium salt **112** (1.35 g, 2.56 mmol) in dry THF (15.5 mL). After the reaction was finished the work-up was performed as described and the obtained crude product purified by column chromatography on silica gel (DCM/Acetone, 2/1) to afford **95g** as a dark red solid (1.53 g, 65%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.84-0.91 (m, 12H), 0.99-1.06 (m, 4H), 1.23 (d, *J* = 6.8 Hz, 10H), 1.26-1.30 (m, 15H), 1.37-1.46 (m, 19H), 1.51-1.56 (m, 4H), 1.60-1.68 (m_{br}, 4H), 3.17-3.22 (m, 4H), 3.46-3.51 (m, 4H), 3.85 (sept, *J* = 6.8 Hz, 2H), 4.19 (sept, *J* = 6.8 Hz, 2H), 7.49-7.62 (m, 3H), 7.73-74 (m, 1H), 7.76-7.77 ppm (m, 1H).

^{13}C{^{1}H}-MR (101 MHz, $CDCl_3$): δ = 14.1, 14.1, 21.1, 21.1, 21.2, 21.3, 21.3, 22.6, 22.7, 26.3, 26.5, 27.9, 28.7, 31.4, 31.5, 51.9, 54.0, 54.2, 55.6, 96.8 (d, J_{P-C} = 57.4 Hz), 98.1 (d, J_{P-C} = 54.9 Hz), 126.5 (d, J_{P-C} = 4.1 Hz), 130.5 (d, J_{P-C} = 8.2 Hz), 132.1, 133.9 (d, J_{P-C}= 22.2Hz), 139.7 (d, J_{P-C} = 2.9 Hz), 141.5 ppm (d, J_{P-C} = 2.02 Hz).

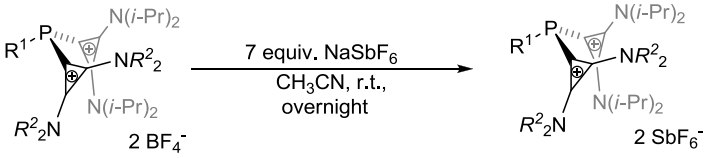
^{31}P{^{1}H}-NMR (122 MHz, $CDCl_3$): δ = -52.6 ppm.

^{19}F{^{1}H}-NMR (282 MHz, $CDCl_3$): δ = -152.4 ppm.

HRMS *calcd.* for $C_{48}H_{85}BF_4N_4P^+$: 835.653553 $[M\text{-}BF_4]^+$; *found*: 835.654050.

IR: ῡ = 411, 441, 583, 646, 695, 725, 751, 892, 1031, 1041, 1153, 1182, 1207, 1282, 1315, 1351, 1377, 1437, 1460, 1563, 1864, 1897, 2859, 2930, 2956 cm^{-1}.

General procedure C: **Anion exchange of the BF_4^- counter ion for SbF_6^-**

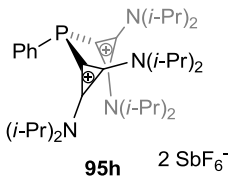


95a/g **95h/i**

A suspension of the desired dicationic phosphine **95a/g** (1.0 equiv.) and sodium hexafluoroantimonate (7.0 equiv.) in acetonitrile (c(phosphine) = 0.1M) was stirred overnight at room temperature. After filtration the solvent was removed *in vacuo* and the remaining

residue dissolved in DCM causing the precipitation of inorganic salts, which were discarded by filtration. Removal of the solvent *in vacuo* afforded the desired product **95h/i**.

Biscyclopropenium phosphine 95h



95h 2 SbF_6^-

Compound **95h** was prepared according to general procedure **C** employing dicationic phosphine **95a** (110 mg, 0.14 mmol) and sodium hexafluoroantimonate (264 mg, 1.0 mmol) in acetonitrile (1.4 mL). However, in this case the inorganic salts had to be separated from the product by precipitation *via* addition of DCM to a solution of crude **95h** in CH_3CN. Removal of the solvents *in vacuo* afforded compound **95h** as a white solid (114 mg, 74%).

^{1}H-NMR (300 MHz, CD_3CN): δ = 1.14 (d, *J* = 6.8 Hz, 12H), 1.21 (d, *J* = 6.8 Hz, 12H), 1.38 (pt, *J* = 7.2 Hz, 24H), 3.67 ($sept_{br}$, *J* = 6.8 Hz, 4H), 4.18 (sept, *J* = 6.9 Hz, 4H), 7.68-7.70 ppm (m, 5H).

^{13}C{^{1}H}-NMR (101 MHz, CD_3CN): δ = 21.3, 21.4, 21.6, 21.7, 21.8, 21.9, 53.6(s_{br}), 55.6(s_{br}), 98.2 (d, $J_{P\text{-}C}$ = 57.2 Hz), 126.1 (d, $J_{P\text{-}C}$ = 4.0 Hz), 131.5 (d, $J_{P\text{-}C}$ = 8.8 Hz), 133.8, 135.2 (d, $J_{P\text{-}C}$ = 23.0 Hz), 140.6 ppm.

^{31}P{^{1}H}-NMR (122 MHz, CD_3CN): δ = -48.7 ppm.

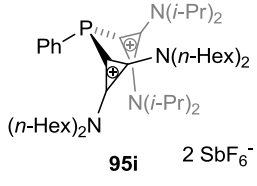
^{19}F{^{1}H}-NMR (282 MHz, CD_3CN): δ = -124.0 ppm (sext, $J_{F\text{-}Sb(I=5/2)}$ = 1930.5 Hz, oct, $J_{F\text{-}Sb(I=7/2)}$ = 1054.7 Hz).

ESI-MS (negative): m/z = 234.9 [SbF_6^-].

HRMS *calcd.* for $C_{36}H_{61}F_6N_4PSb^+$: 815.357003 $[M\text{-}SbF_6]^+$; *found*: 815.357470.

IR: ϑ = 499, 549, 579, 653, 752, 892, 1012, 1038, 1148, 1182, 1204, 1352, 1377, 1438, 1458, 1552, 1854, 2883, 2939 cm^{-1}.

Biscyclopropenium phosphine 95i



95i 2 SbF_6^-

Compound **95i** was prepared according to general procedure **C** employing dicationic phosphine **95g** (194 mg, 0.21 mmol) and sodium hexafluoroantimonate (381 mg, 1.47 mmol) in acetonitrile (2.1 mL). Clean **95i** was obtained by precipitation from 1,2-DCE/ diethyl ether. White solid (127 mg, 49%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.83-0.89 (m, 12H), 0.98-1.02 (m, 4H), 1.17 (d, *J* = 6.8 Hz, 6H), 1.19-1.24 (m, 7H), 1.28 (m, 13H), 1.34 (d, *J* = 6.8 Hz, 6H), 1.41 (d, *J* = 3.2 Hz, 6H), 1.42 (d, *J* = 3.2 Hz, 6H), 1.48-1.54 (m, 4H), 1.61 (m_{br}, 4H), 3.11-3.23 (m, 4H), 3.43 (d, *J* = 6.8 Hz, 2H), 3.45 (d, *J* =6.8 Hz, 2H), 3.77-3.84 (m, 2H), 4.14 (sept., *J* = 6.8 Hz, 2H), 7.51-7.55 (m, 1H), 7.58-7.65 (m, 4H) ppm.

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ =14.0, 14.1, 21.1, 21.1, 21.3, 21.3, 22.6, 22.7, 26.4, 26.6, 27.9, 28.6, 31.4, 31.5, 52.1 (s_{br}), 54.0, 54.1, 55.8 (s_{br}), 97.4 (d, $J_{P\text{-}C}$ = 62.3 Hz), 98.0 (d, $J_{P\text{-}C}$ = 58.0 Hz), 126.3 (d, $J_{P\text{-}C}$ = 4.2 Hz), 130.8 (d, $J_{P\text{-}C}$ = 8.4 Hz), 132.3, 133.6 (d, $J_{P\text{-}C}$ = 22.6 Hz), 139.6 (d, $J_{P\text{-}C}$ = 2.7 Hz), 141.5 (d, $J_{P\text{-}C}$ =1.1 Hz) ppm.

^{31}P{^{1}H}-NMR (162 MHz, $CDCl_3$): δ = -52.3 ppm.

ESI-MS (negative): m/z = 234.9 [SbF_6^-].

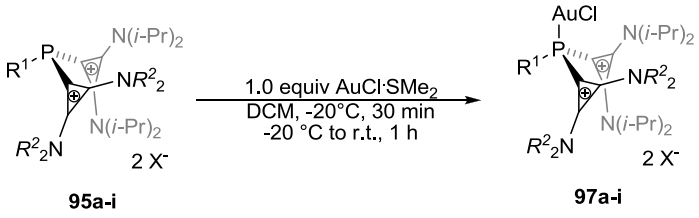
HRMS *calcd.* for $C_{48}H_{85}F_6N_4PSb$: 983.544803 $[M\text{-}SbF_6]^+$; found*:* 983.545350.

IR: ῡ = 583, 652, 694, 721, 750, 891, 1015, 1098, 1151, 1180, 1207, 1268, 1314, 1349, 1377, 1436, 1463, 1565, 1586, 1865, 1893, 2859, 2930, 2956 cm^{-1}.

6.5.4 Coordination chemistry of dicationic phosphines

6.5.4.1 Coordination to Au(I)

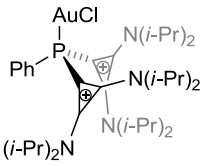
General Procedure D: **Synthesis of Au(I)-complexes**



95a-i **97a-i**

[$AuCl(Me_2S)$] (1.0 equiv.) was added to a precooled (-20°C) solution of biscyclopropenium phosphine **95a-i** (1.0 equiv.) in dry DCM (c = 0.033 M). The reaction mixture was stirred at this temperature for 30 minutes, warmed to room temperature and stirred for an additional hour at this temperature. Removal of the solvent *in vacuo* afforded the desired products **97a-i** as white solids.

Au(I)-complex 97a



Synthesized according to general procedure **D** from [AuCl(Me$_2$S)] (17.9 mg, 0.061 mmol) and biscyclopropenium phosphine **95a** (45.8 mg, 0.061 mmol) in DCM (1.8 mL). White solid (54 mg, 90%).

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.25 (d, *J* = 7.0 Hz, 12H), 1.34 (d, *J* = 7.0 Hz, 12H), 1.45 (d, *J* = 7.0 Hz, 24H), 3.86 (sept, *J* = 7.0 Hz, 4H), 4.24 (sept, *J* = 7.0 Hz, 4H), 7.72-7.78 (m, 3H), 8.08-8.17 ppm (m, 2H).

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ = 21.5, 21.7, 21.9, 55.5, 56.0, 90.9 (d, J_{P-C} = 53.2 Hz), 121.9 (d, J_{P-C} = 69.4 Hz), 131.5 (d, J_{P-C} = 14.2 Hz), 135.4, 135.4 (d, J_{P-C} =17.9 Hz), 138.9 (d, J_{P-C} = 6.3 Hz) ppm.

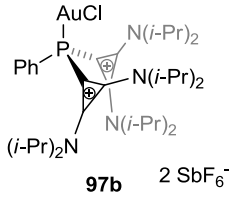
^{31}P{^{1}H}-NMR (161 MHz, CD_2Cl_2): δ = -9.9 ppm.

HRMS *calcd*. for $C_{36}H_{61}AuBClF_4N_4P^+$: 899.401161 $[M\text{-}BF_4]^+$; *found* 899.401924.

IR: ϑ = 694, 1030, 1151, 1358, 1556, 1858, 2973 cm^{-1}.

The found spectral data are in agreement with those previously reported by our workgroup.[41]

Au(I)-complex 97b (SbF_6)



Synthesized according to general procedure **D** from [AuCl(Me$_2$S)] (11.2 mg, 0.038 mmol) and biscyclopropenium phosphine **95h** (40 mg, 0.038 mmol). Acetonitrile was employed as a solvent (1.2 mL, since the ligand is NOT soluble in DCM). White solid (43 mg, 88%).

^{1}H-NMR (400 MHz, CD_3CN): δ = 1.21 (d, *J* = 6.6 Hz, 12H), 1.26 (d, *J* = 6.6 Hz, 12H), 1.37-1.39 (dd, *J* = 6.9, 2.3 Hz, 24 H), 3.81 (m_{br}, 4H), 4.21-4.25 (m_{br}, 4H), 7.75-7.80 (m, 2H), 7.84-7.88 (m, 1H), 7.92-7.95 (m, 1H), 7.97-7.99 ppm (m, 1H).

^{13}C{^{1}H}-NMR (101 MHz, CD_3CN): δ = 21.4, 21.8, 22.0, 55.9 (s_{br}), 90.5 (d, J_{P-C} = 57.2 Hz), 122.4 (d, J_{P-C} = 69.7 Hz), 131.9 (d, J_{P-C} = 14.0 Hz), 135.8 (d, J_{P-C} = 17.5 Hz), 136.6 (d, J_{P-C} = 2.7 Hz), 139.3 ppm.

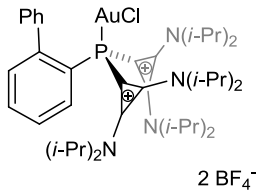
^{31}P{^{1}H}-NMR (162 MHz, CD_3CN): δ = -8.8 ppm.

^{19}F{^{1}H}-NMR (282 MHz, CD_3CN): δ = -123.9 ppm (sext, $J_{F-Sb(I=5/2)}$ = 1936.3 Hz, oct, $J_{F-Sb(I=7/2)}$ = 1096.4 Hz).

HRMS *calcd*. for $C_{36}H_{61}AuClF_6N_4PSb^+$: 1047.292408 $[M\text{-}SbF_6]^+$; *found*: 1047.292180.

IR: ϑ = 447, 522, 582, 654, 759, 870, 893, 1008, 1035, 1098, 1146, 1179, 1201, 1319, 1350, 1377, 1441, 1456, 1568, 1855, 2881, 2944, 2988, 3063 cm^{-1}.

Au(I)-complex 97c



97c

Synthesized according to general procedure **D** from $[AuCl(Me_2S)]$ (17.7 mg, 0.06 mmol) and biscyclopropenium phosphine **95b** (50 mg, 0.06 mmol) in DCM (1.8 mL). White solid (58 mg, 91%).

^{1}H-NMR (400 MHz, CD_3CN): δ = 1.12 (d, *J* = 6.8 Hz, 12H), 1.22 (d, *J* = 7.4 Hz, 12H), 1.41 (d, *J* = 6.9 Hz, 24H), 3.91 (sept, *J* = 6.8 Hz, 4H), 4.25 (sept, *J* = 6.8 Hz, 4H), 7.24-7.25 (m, 2H), 7.51-7.56 (m, 3H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.78-7.81 (m, 1H), 7.89 (td, *J* = 7.7, 0.9 Hz, 1H), 7.94-8.00 ppm (m, 1H).

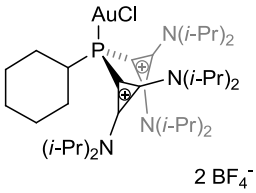
^{13}C{^{1}H}-NMR (101 MHz, CD_3CN): δ = 21.5, 21.6, 22.2, 56.2(s_{br}), 92.0 (d, $J_{P\text{-}C}$ = 54.1 Hz), 121.5 (d, $J_{P\text{-}C}$ = 71.7 Hz), 130.2, 130.6, 130.7, 130.8, 134.4 (d, $J_{P\text{-}C}$ = 9.4 Hz), 135.9, 136.1 (d, $J_{P\text{-}C}$ = 2.0 Hz), 139.1, 140.3 (d, $J_{P\text{-}C}$ = 10.1 Hz), 149.3 ppm (d, $J_{P\text{-}C}$ = 21.2 Hz).

^{31}P{^{1}H}-NMR (162 MHz, CD_3CN): δ = -17.9 ppm.

HRMS *calcd.* for $C_{42}H_{65}AuBClF_4N_4P^+$: 975.432459 $[M\text{-}BF_4]^+$; *found*: 975.432440.

IR: ϑ = 447, 498, 519, 552, 582, 617, 644, 685, 704, 737, 760, 891, 1029, 1048, 1147, 1180, 1201, 1355, 1377, 1459, 1565, 1848, 2878, 2941, 2977 cm^{-1}.

Au(I)-complex 97d



97d

Synthesized according to general procedure **D** from $[AuCl(Me_2S)]$ (31 mg, 0.11 mmol) and biscyclopropenium phosphine **95d** (80 mg, 0.11 mmol) in DCM (3.2 mL). White solid (82.0 mg, 79%).

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.34-1.39 (m, 2H), 1.47 (dd, *J* = 7.0 Hz, 2.0 Hz, 24H), 1.55 (pt, *J*= 7.0 Hz, 24H), 1.61-1.67 (m, 3H), 1.81-1.84 (m_{br}, 1H), 1.98-2.00 (m_{br}, 4H), 2.93 (m, 1H), 4.13-4.20 ppm (m, 8H).

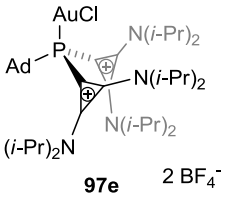
^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2): δ = 21.9, 22.0, 22.5, 25.2 (d, $J_{P\text{-}C}$ = 2.0 Hz), 25.7 (d, $J_{P\text{-}C}$ = 18.2 Hz), 30.6 (d, $J_{P\text{-}C}$ = 6.1 Hz), 38.5 (d, $J_{P\text{-}C}$ = 37.0 Hz), 57.8 (s_{br}), 89.9 (d, $J_{P\text{-}C}$ = 42.2Hz), 139.7 ppm (d, $J_{P\text{-}C}$ = 8.6 Hz).

$^{31}P\{^{1}H\}$-NMR (162 MHz, CD_2Cl_2): δ = -9.92 ppm.

HRMS *calcd.* for $C_{36}H_{67}AuBClF_4N_4P^+$: 905.448109 $[M\text{-}BF_4]^+$; *found*: 905.449040.

IR: ῡ = 457, 519, 557, 581, 645, 664, 684, 892, 1026, 1047, 1148, 1180, 1358, 1377, 1453, 1561, 1848, 2858, 2936, 2978 cm^{-1}.

Au(I)-complex 97e



Synthesized according to general procedure **D** from $[AuCl(Me_2S)]$ (22.1 mg, 0.075 mmol) and biscyclopropenium phosphine **95e** (61.0 mg, 0.075 mmol) in DCM (2.0 mL). White solid (66.2 mg, 84%).

^{1}H-NMR (400 MHz, CD_3CN): δ = 1.37-1.41(m, 21H), 1.43 (d, *J* = 7.0 Hz, 12H), 1.48 (d, *J* = 6.5 Hz, 12H), 1.76-1.86 (m, 6H), 2.12-2.14 (m, 6H), 2.18 (s, 3H), 2.22 (s, 3H) 4.21 (sept, *J* = 6.8 Hz, 4H), 4.30 ppm (m_{br}, 4H).

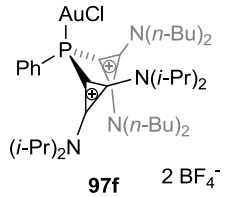
$^{13}C\{^{1}H\}$-NMR (101 MHz, CD_3CN): δ = 21.3, 22.0, 22.3 (s_{br}, overlaps with former signal), 28.9 (d, $J_{P\text{-}C}$ = 12.5 Hz), 35.7, 39.6 (d, $J_{P\text{-}C}$ = 3.4 Hz), 56.4 (s_{br}), 139.9 ppm (C_q signals for $C_{Ad\text{-}P}$ and $C_{Cpr\text{-}P}$ are missing due to signal broadening even if extended measurements were done (amount of scans increased from 800 to 60000)).

$^{31}P\{^{1}H\}$-NMR (162 MHz, CD_3CN): δ = 12.2 (s_{br}) ppm.

HRMS *calcd.* for $C_{40}H_{71}AuBClF_4N_4P^+$: 957.479409 $[M\text{-}BF_4]^+$; *found:* 957.479480.

IR: ῡ = 453, 520, 557, 586, 641, 684, 801, 893, 1029, 1051, 1149, 1182, 1357, 1377, 1454, 1556, 1846, 2858, 2915, 2972 cm^{-1}.

Au(I)-complex 97f



Synthesized according to general procedure **D** from $[AuCl(Me_2S)]$ (39.2 mg, 0.13 mmol) and biscyclopropenium phosphine **95f** (107 mg, 0.13 mmol) in DCM (3.9 mL). Red solid (121 mg, 87%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.3 Hz, 6H), 0.93 (t, *J* = 7.3 Hz, 6H), 0.98-1.06 (m_{br}, 2H), 1.12-1.20 (m_{br}, 2H), 1.26-1.32 (m, 4H), 1.34-1.36 (m, 8H), 1.41 (d, *J* = 6.5 Hz, 6H), 1.46 (dd, *J* = 6.9 Hz, *J* =1.7 Hz, 12H), 1.61-1.70 (m, 6H), 3.20-3.28 (m, 2H), 3.46-3.52 (m, 6H), 3.84 (sept, *J* = 6.6 Hz, 2H), 4.22 (m_{br}, 2H), 7.57-7.61 (m, 2H), 7.65-7.69 (m 1H), 7.86-7.88 (m, 1H), 7.92 ppm (m, 1H).

$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 13.7, 13.9, 19.8, 20.0, 21.2, 21.3, 21.4, 21.8, 29.6, 30.2, 53.7, 54.9, 55.0(s_{br}), 88.5 (d, J_{P-C} = 60.6 Hz), 88.5 (d, J_{P-C} = 59.6 Hz), 121.8 (d, J_{P-C} = 72.8 Hz), 130.9 (d, J_{P-C} = 13.8 Hz), 132.3 (d, J_{P-C} = 15.5 Hz), 134.7, 139.0 (d, J_{P-C} = 5.4 Hz), 140.5 ppm (d, J_{P-C} = 7.1 Hz).

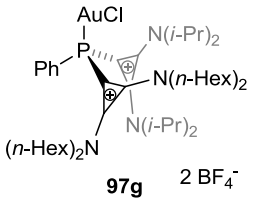
$^{31}P\{^1H\}$-NMR (162 MHz, $CDCl_3$): δ = -20.51 ppm.

$^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = -151.1 ppm.

HRMS *calcd.* for $C_{40}H_{69}AuBClF_4N_4P^+$: 955.463759 $[M\text{-}BF_4]^+$; *found*: 955.46400.

IR: ῡ = 454, 520, 554, 586, 652, 690, 727, 754, 798, 893, 1031, 1042, 1148, 1316, 1355, 1377, 1439, 1458, 1573, 1607, 1863, 1898, 2874, 2934, 2961cm^{-1}.

Au(I)-complex 97g



Synthesized according to general procedure **D** from [AuCl(Me_2S)] (58.4 mg, 0.2 mmol) and biscyclopropenium phosphine **95g** (183.0 mg, 0.2 mmol) in DCM (6.0 mL). Orange solid (177.8 mg, 86%).

^1H-NMR (400 MHz, $CDCl_3$): δ = 0.81-0.85 (m, 12H), 0.96 (m_{br}, 2H), 1.10 (m_{br}, 2H), 1.21-1.26 (m, 19H), 1.32-1.35 (m, 7H), 1.39 (d, *J* = 6.7 Hz, 6H), 1.44 (dd, *J* = 6.8 Hz, 2.0 Hz, 12H), 1.51-1.58 (m_{br}, 2H), 1.65-1.74 (m, 6H), 3.20-3.27 (m, 2H), 3.41-3.53 (m, 6H), 3.80-3.83 (m_{br}, 2H), 4.19 (m_{br}, 2H), 7.53-7.57 (m, 2H), 7.62-7-65 (m, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.88 ppm (d, *J* = 7.6 Hz, 1H).

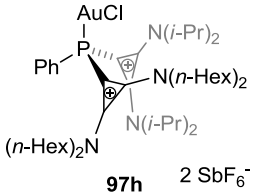
$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 14.1, 14.2, 21.3, 21.4, 21.6, 22.1, 22.7, 22.7, 26.3, 26.6, 27.7, 28.4, 31.4, 31.5, 54.0, 55.2, 55.3 (s_{br}), 88.5 (d, J_{P-C} = 58.0 Hz), 88.7 (d, J_{P-C} = 60.4 Hz), 121.8 (d, J_{P-C} = 71.8 Hz), 131.0 (d, J_{P-C} = 13.5 Hz), 132.2 (d, J_{P-C} = 15.5 Hz), 134.8 (d, J_{P-C} = 2.0 Hz), 139.1 (d, J_{P-C} = 6.3 Hz), 140.5 ppm (d, J_{P-C} = 7.1 Hz).

$^{31}P\{^1H\}$-NMR (162 MHz, $CDCl_3$): δ = -23.3 ppm.

IR: ῡ = 448, 520, 586, 652, 690, 726, 752, 797, 863, 1049, 1149, 1377, 1463, 1573, 1607, 1863, 1898, 2859, 2930 cm^{-1}.

HRMS *calcd.* for: $C_{48}H_{85}N_4AuBClF_4P^+$: 1067.588959 $[M\text{-}BF_4]^+$; *found*: 1067.588230.

Au(I)-complex 97h



Synthesized according to general procedure **D** from [AuCl(Me$_2$S)] (7.3 mg, 0.025 mmol) and biscyclopropenium phosphine **95i** (30 mg, 0.025 mol) in DCM (0.75 mL). White solid (28 mg, 78%).

^{1}H-NMR (400 MHz, CDCl$_3$): δ = 0.85-0.90 (m, 12H), 0.95 (m_{br}, 2H), 1.13 (m_{br}, 2H), 1.26-1.29 (m, 21H), 1.37-1.39 (m, 11H), 1.46 (d, *J* = 6.8 Hz, 12H), 1.51-1.56 (m, 2H), 1.68-1.71 (m_{br}, 6H), 3.26-3.30 (m, 2H), 3.42-3.60 (m, 6H), 3.84 (m_{br}, 2H), 4.20 (m_{br}, 2H), 7.58-7.64 (m, 3H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.76 ppm (d, *J* = 7.3 Hz, 1H).

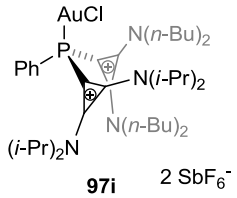
^{13}C{^{1}H}-NMR (150 MHz, CDCl$_3$):δ = 14.0, 14.1, 21.2, 21.3, 21.6, 22.3, 22.6, 22.7, 26.4, 26.6, 27.5, 28.2, 31.4, 31.5, 54.2, 55.1, 55.6, 87.9, (d, J_{P-C} =55.6 Hz), 88.4 (d, J_{P-C} =56.9 Hz), 121.8 (d, J_{P-C} = 71.8 Hz), 131.3 (d, J_{P-C} = 13.6 Hz), 132.0 (*J* = 15.9 Hz), 135.0, 138.8 (d, J_{P-C} = 6.2 Hz), 140.6 ppm (d, J_{P-C} = 6.7 Hz).

^{31}P{^{1}H}-NMR (162 MHz, CDCl$_3$): δ = -23.8 ppm.

HRMS *calcd.* for $C_{48}H_{85}AuClF_6N_4PSb^+$: 1215.480208 $[M\text{-}SbF_6]^+$; *found:* 1215.480400.

IR: ῡ = 453, 525, 587, 652, 691, 726, 751, 892, 1009, 1036, 1098, 1148, 1180, 1202, 1269, 1315, 1354, 1378, 1439, 1457, 1573, 1606, 1859, 1894, 2859, 2930, 2956 cm^{-1}.

Au(I)-complex 97i



Au(I)-complex **97f** (40.9 mg, 0.039 mmol) and sodium hexafluoroantimonate (101.4 mg, 0.39 mmol) were stirred in acetonitrile (0.39 mL) overnight at room temperature. After this time, the solvent was removed *in vacuo*, the residue washed with DCM (3x) and the combined organic phases were concentrated to 1/3 of their original volume. Addition of diethyl ether caused a separation of an oily phase that was solidified at -78 °C. The crude product thus obtained was dried *in vacuo* affording product **97i** as a yellow solid (21 mg, 40%).

^{1}H-NMR (400 MHz, CD$_2$Cl$_2$): δ = 0.89 (t, *J* = 7.2 Hz, 6H), 0.99 (t, *J* = 7.3 Hz, 6H), 1.09-1.21 (m, 4H), 1.31 (d, *J* = 6.5 Hz, 6H), 1.34 (d, *J* = 6.9 Hz, 6H), 1.36-1.40 (m, 6H), 1.46 (d, *J* = 6.9 Hz, 6H), 1.49 (d, *J* = 6.6 Hz, 6H) 1.58-1.71 (m, 6H), 3.33-3.43 (m, 2H), 3.48-3.57 (m, 6H), 3.90 (sept, *J* = 6.7 Hz, 2H), 4.24 (sept, *J* = 6.7 Hz, 2H), 7.80 (m_{br}, 3H), 7.91-7.93 (m, 1H), 7.97-7.99 ppm (m, 1H).

$^{13}C\{^1H\}$-NMR (101 MHz, CD_2Cl_2): δ = 13.7, 13.8, 20.0, 20.2, 21.0, 21.3, 21.4, 21.6, 29.9, 30.8, 54.4, 55.3, 55.9(s_{br}), 88.5 (d, J_{P-C} = 53.6 Hz), 90.1 (d, 57.6 Hz), 121.8 (d, J_{P-C} = 69.8 Hz), 131.7 (d, J_{P-C} = 14.7 Hz), 134.0 (d, J_{P-C} = 16.5 Hz), 135.6, 137.8, 140.4 ppm (d, J_{P-C} = 6.1 Hz).

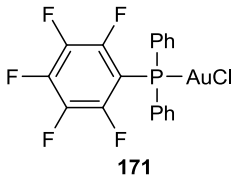
$^{31}P\{^1H\}$-NMR (162 MHz, CD_2Cl_2): δ = -14.7 ppm.

ESI-MS (negative): m/z = 234.9 [SbF_6^-].

HRMS *calcd.* for $C_{40}H_{69}AuClF_6N_4PSb^+$: 1103.355009 [M-$SbF_6$]$^+$; *found:* 1103.355960.

IR: ῡ = 524, 587, 652, 726, 754, 799, 892, 935, 1012, 1035, 1097, 1147, 1181, 1201, 1242, 1261, 1315, 1354, 1378, 1459, 1573, 1607, 1860, 1895, 2875, 2936, 2963 cm^{-1}.

(Pentafluorophenyl)diphenylphosphine gold chloride 171



171

Synthesized according to general procedure **D** from [AuCl(Me_2S)] (21.2 mg, 0.072 mmol) and pentafluorophenyl diphenyl-phosphine (25.5 mg, 0.072 mmol) in DCM (2.1 mL). White solid (34.7 mg, 88%).

^1H-NMR (400 MHz, $CDCl_3$): δ = 7.46-7.51 (m, 4H), 7.55-7.60 (m, 2H), 7.62-7.70 (m 4H) ppm.

$^{13}C\{^1H\}$-NMR(101 MHz, $CDCl_3$): δ = 104.9 (m), 126.4 (d, J_{P-C}= 64.4 Hz), 129.7 (d, J_{P-C} = 13.0 Hz), 133.0 (d, J_{P-C} = 2.8 Hz), 133.8 (d, J_{P-C} = 15.7 Hz), 138.2 (m), 144.3 (m), 147.5 ppm (m).

$^{31}P\{^1H\}$-NMR (122 MHz, $CDCl_3$): δ = 15.4 ppm (m).

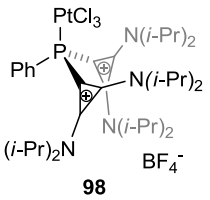
$^{19}F\{^1H\}$-NMR (282 MHz, $CDCl_3$): δ = -157.9-(-157.7) (m), -144.8-(-144.6) (m), -125.6-(-125.4) ppm (m).

HRMS *calcd*. for $C_{36}H_{20}Au_2ClF_{10}P_2^+$: 1132.989472 [$M_2$-Cl]$^+$; *found*: 1132.991070.

IR: ῡ = 419, 429, 478, 519, 534, 631, 688, 709, 724, 744, 799, 848, 979, 998, 1024, 1093, 1260, 1295, 1390, 1436, 1477, 1518, 1644, 2852, 2920, 3055, 3074 cm^{-1}.

6.5.4.2 Coordination to Pt(II)

Pt(II)-complex 98



98

Biscyclopropenium phosphine **95a** (40 mg, 0.053 mmol), K_2PtCl_4 (24.2 mg, 0.058 mmol) and acetonitrile (1 mL) were stirred overnight at room temperature. After that, the solvent was removed *in vacuo* and the residue obtained redissolved in dry DMSO (3 mL). Slow addition of DCM (6 mL) caused the precipitation of the inorganic salts, which were subsequently discarded after filtration. Removal of the solvents *in vacuo* afforded product **98** as a yellow solid (47 mg, 91%).

^{1}H-NMR (400 MHz, CD_3CN): δ = 1.12 (d, *J* = 6.7 Hz, 12H), 1.22 (d, *J* = 6.7 Hz, 12H), 1.39 (d, *J* = 6.8 Hz, 24H), 4.24 (sept, *J* = 6.9 Hz, 4H), 4.41 (m_{br}, 4H), 7.65-7.78 (m, 3H), 8.31 (d, *J* = 7.7 Hz, 1H), 8.36 (d, *J* = 7.7 Hz, 1H) ppm.

^{13}C{^{1}H}-NMR (100 MHz, CD_2Cl_2): δ = 17.5, 18.1, 18.5, 53.4, 90.6 (d, J_{P-C} = 51.5 Hz), 118.9 (d, J_{P-C} = 70.8 Hz), 126.8 (d, J_{P-C} = 12.9 Hz), 130.9 (d, J_{P-C} = 2.3 Hz), 133.5 (d, J_{P-C} = 13.5 Hz), 134.7 ppm (d, J_{P-C} = 8.6 Hz).

^{31}P{^{1}H}-NMR (162 MHz, CD_3CN): δ = -23.6 (J_{Pt-P}=3997.8 Hz).

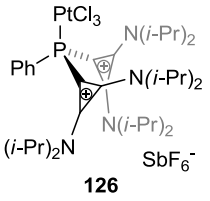
^{19}F{^{1}H}-NMR (282 MHz, CD_3CN): δ = -152.1 ppm.

HRMS *calcd.* for $C_{36}H_{61}Cl_3N_4PPt^+$: 880.333066 $[M\text{-}BF_4]^+$; *found* 880.333903.

IR: ῡ= 679, 1050, 1148, 1376, 1557, 1850, 2977 cm^{-1}.

The found spectral data are in agreement with those previously reported by our workgroup.[41b]

Pt(II)-complex 126



126

Pt(II)-complex **98** (48 mg, 0.050 mmol, 1.0 equiv.) and sodium hexafluoroantimonate (44.8 mg, 0.173 mmol, 3.5 equiv.) were stirred in acetonitrile (5 ml) overnight at room temperature. Then, the solvents were removed *in vacuo* and the resulting solid extracted with DCM. The combined organic phases thus obtained were dried over sodium sulfate and after solvent removal the afforded crude material was redissolved in acetonitrile (3 mL). Slow addition of diethyl ether (5 mL) caused the separation of an oily phase which solidified at -30 °C. Yellow solid (38 mg, 69%).

^{1}H-NMR (400 MHz, CD_3CN): δ = 1.11 (d, *J* = 6.8 Hz, 12H), 1.21 (d, *J* = 6.8 Hz, 12H), 1.39 (dd, *J* = 7.0 Hz, 24H), 4.24 (sept, *J* = 7.0 Hz, 4H), 4.41 (m_{br}, 4H), 7.65-7.79 (m, 3H), 8.29-8.32 (m, 1H), 8.34-8.37 ppm (m, 1H).

^{13}C{^{1}H}-NMR (101 MHz, CD_3CN): δ = 21.3, 21.4, 22.0, 22.1, 54.4 (s_{br}), 57.4 (s_{br}), 94.2 (d, J_{P-C} = 51.5 Hz), 123.7 (d, J_{P-C} = 71.1 Hz), 130.9 (d, J_{P-C} = 12.6 Hz), 135.4 (d, J_{P-C} = 2.9 Hz), 137.4 (d, J_{P-C} = 14.8 Hz), 139.1 ppm.

^{31}P{^{1}H}-NMR (122 MHz, CD_3CN): δ = -23.4 (J_{Pt-P} = 3995.9 Hz) ppm.

^{19}F{^{1}H}-NMR (282 MHz, CD_3CN): δ = -124.1 (sext, $J_{F-Sb(I=5/2)}$ = 1939.8 Hz, oct, $J_{F-Sb(I=7/2)}$ = 1045.5 Hz) ppm.

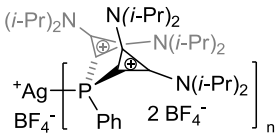
ESI-MS (negative): m/z = 234.9 [SbF_6^-].

HRMS *calcd*. for $C_{36}H_{61}Cl_3N_4Pt^+$: 880.334520 [M-SbF_6]$^+$; *found*: 880.334206.

IR: ῡ = 449, 496, 578, 655, 894, 1036, 1112, 1146, 1180, 1354, 1377, 1454, 1555, 1848, 2886, 2941, 2980 cm^{-1}.

6.5.4.3 Coordination to Ag(I)

Ag(I)-complex 127a/b (proposed structures)



127a: n = 1
127b: n = 2

Biscyclopropenium phosphine **95a** (49.2 mg, 0.065 mmol) and silver tetrafluoroborate (12.7 mg, 0.065 mmol) were stirred in dry DCM (1.3 mL) for 30 minutes at -25 °C. Then, the reaction mixture was warmed to room temperature and stirred for additional 1.5 hours. Subsequently, the yellow solution was filtered over a glass fiber filter and the solvent was removed *in vacuo* affording a yellow solid **127a/b** (52 mg).

As previously mentioned in section 4.3, a definitive structure assignment of the isolated species is difficult without XRD-analysis. Structures **127a** and **127b** represent just two possible structures.

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.25 (d, *J* = 6.8 Hz, 12H), 1.28 (d, *J* = 6.9 Hz, 12H), 1.42 (d, *J* = 7.0 Hz, 12H), 1.45 (d, *J* = 7.0 Hz, 12H), 3.73 (sept, J = 6.6 Hz, 4H), 4.21 (sept, *J* = 6.7 Hz, 4H), 7.72-7.75 (m, 3H), 8.03-8.05 (m, 1H), 8.06-8.09 ppm (m, 1H).

$^{13}C\{^1H\}$-NMR (101 MHz, CD_2Cl_2): δ = 21.4, 21.5, 21.6, 21.7, 54.5 (s_{br}), 55.6 (s_{br}), 93.0 (d, J_{P-C} = 7.6 Hz), 121.3 (d, J_{P-C} = 37.7 Hz), 131.4 (d, J_{P-C} = 12.7 Hz), 134.9, 135.7 (d, J_{P-C} = 21.1 Hz) 139.0 ppm (d, J_{P-C} = 5.0 Hz).

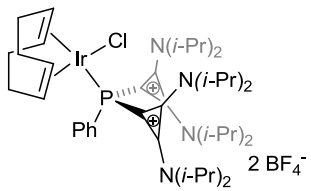
$^{31}P\{^1H\}$-NMR (162 MHz, CD_2Cl_2): δ = -32.6 ppm.

HRMS *calcd.* for. $C_{36}H_{61}AgB_2F_8N_4P$: 861.373640 $[M\text{-}BF_4]^+$; *found*: 861.373040.

IR: ῡ = 427, 442, 483, 519, 553, 580, 644, 689, 733, 754, 892, 1025, 1148, 1182, 1202, 1285, 1355, 1378, 1440, 1455, 1561, 1628, 1855, 2884, 2941, 2988, 3078, 3527 cm^{-1}.

6.5.4.4 Coordination to Ir(I)

Ir(I)-complex 134



134

Biscyclopropenium phosphine **95a** (45 mg, 0.06 mmol) and $[IrCl(COD)]_2$ (20 mg, 0.03 mmol) were stirred in DCM (1.5 mL) at -25 °C for 1 hour. Removal of solvent *in vacuo* at this temperature afforded a residue, which was washed with pentane (3x) and dried *in vacuo* at -25 °C overnight. Yellow solid (83%, 54 mg). The compound slowly decomposes over time already at 0 °C.

^1H-NMR (500 MHz, $CDCl_3$, 0 °C): δ = 1.20-1.49 (m_{br}, 48H), 1.80 (m_{br}, 2H), 1.96 (m_{br}, 2H), 2.21 (m_{br}, 4H), 2.29-5.12 (m_{br}, 10H), 5.39 (m_{br}, 2H), 7.50-7.53 (m_{br}, 1H), 7.70 (m_{br}, 1H), 7.78-7.81 (m_{br}, 3H) ppm.

$^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$, -20 °C): δ = 21.8 (s_{br}), 29.0 (s_{br}), 33.6 (s_{br}), 54.4-63.0 (s_{br}), 102.6 (m_{br}), 130.9 (m_{br}), 131.0, 131.8-132.4 (m_{br}), 133.0 (m_{br}), 140.2 ppm (m_{br}) (C_q signal for C_{Ph}-P is missing due to signal broadening).

$^{31}P\{^1H\}$-NMR (202 MHz, $CDCl_3$, -20 °C): δ = -18.8 (s_{br}) ppm.

$^{31}P\{^1H\}$-NMR (202 MHz, $CDCl_3$, 0 °C): δ = -18.7 (s_{br}) ppm.

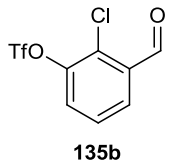
HRMS *calcd.* for $C_{44}H_{73}BClF_4IrN_4P^+$: 1003.491794 $[M\text{-}BF_4]^+$; *found*: 1003.492010.

IR: ῡ = 427, 519, 578, 646, 675, 753, 871, 895, 1032, 1044, 1149, 1181, 1376, 1454, 1551, 1849, 2840, 2881, 2975 cm^{-1}.

6.5.5 Preparation and cycloisomerization of biphenyl-alkynes

6.5.5.1 Synthesis of precursors

2-Chloro-3-formylphenyl trifluoromethanesulfonate 135b



135b

2-Chloro-3-hydroxybenzaldehyde (522 mg, 3.33 mmol) and an aqueous potassium phosphate solution (1.93 g, 9.1 mmol, in 6.5 mL water) were stirred at room temperature until a clear solution was formed. Then toluene was added (6.5 mL) and the mixture was cooled down to 0 °C. Subsequently, trifluoromethanesulfonic anhydride (0.67 mL, 1.1 g, 4.00 mmol) was added slowly over 10 minutes while keeping the reaction temperature below 6 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature and then stirred for additional 40 minutes. The organic phase was separated and the remaining aqueous phase extracted with toluene (2x). The combined organic phases were washed with brine (2x) and dried over sodium sulfate. Removal of the solvents *in vacuo* afforded the desired product **135b** as a colorless oil (904 mg, 94%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.48 - 7.52 (m, 1H), 7.61 (dd, *J* = 8.2 Hz, 1.6 Hz, 1H), 7.97 (dd, *J* = 7.8 Hz,1.6 Hz, 1H), 10.48 ppm (s, 1H).

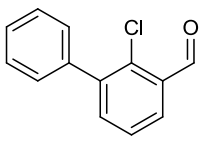
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 118.8 (d, J_{F-C} = 320.6 Hz, CF_3), 128.2, 128.4, 131.1, 129.1, 134.7, 146.4, 188.0 ppm.

^{19}F{^{1}H}-NMR (282 MHz, $CDCl_3$): δ = -73.2 ppm.

HRMS *calcd.* for $C_8H_4Cl_1F_3O_4S^+$: 287.947094 $[M]^+$; *found:* 287.947140.

IR: ϑ = 708, 745, 774, 798, 826, 949, 1052, 1134, 1165, 1209, 1388, 1427, 1460, 1568, 1594, 1702, 1777, 2877, 3091 cm^{-1}.

2-Chlorobiphenyl-3-carbaldehyde 135c



135c

A two neck-flask equipped with a reflux condenser was charged with 2-Chloro-3-formylphenyl trifluoromethanesulfonate **135b** (400 mg, 1.39 mmol), phenylboronic acid (169 mg, 1.39 mmol), potassium phosphate (588 mg, 2.72 mmol) and palladium(II) acetate as catalyst (15. 6 mg, 0.069 mmol). A THF/water solution (9 mL/6.2 µL) was subsequently added. Then, the mixture was heated to 80 °C for 20 hours. After this time, the crude reaction was filtered over a short pad of silica and rinsed with ethyl acetate. Removal of the solvents and

purification of the crude material by column chromatography on silica gel (gradient hexane to hexane/ethyl acetate (15/1)) afforded **135c** as a white solid (75 mg, 25 %).

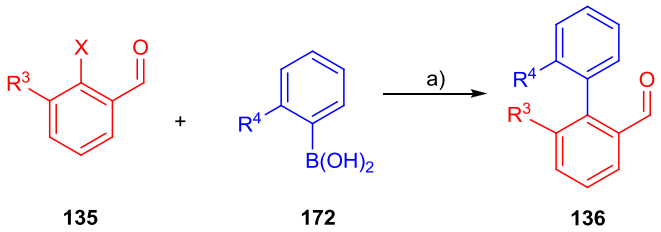
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.42-7.50 (m, 6H), 7.57 (dd, *J* = 7.5 Hz, 1.8 Hz, 1H), 7.94 (dd, *J* = 7.7 Hz,1.8 Hz, 1H), 10.60 ppm (s, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 127.1, 128.3, 128.4, 128.6 , 129.6, 133.4 , 136.4, 136.8, 138.4, 142.5, 190.6 ppm.

HRMS *calcd.* for $C_{13}H_9ClO^+$: 216.034192 $[M]^+$; *found:* 216.033995.

IR: ῡ = 698, 726, 757, 768, 800, 918, 972, 1028, 1042, 1072, 1109, 1159, 1173, 1239, 1268, 1301, 1336, 1380, 1421, 1447, 1457, 1479, 1569, 1603, 1682, 1710, 1728, 1813, 1979, 2884, 3015, 3056 cm^{-1}.

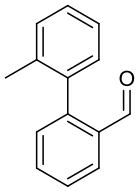
6.5.5.2 Synthesis of Biphenyl-carbaldehydes



General procedure E: A suspension of the aldehyde **135**, boronic acid **172** (1.1 equiv.), palladium acetate (0.02 equiv.) and potassium carbonate (2.5 equiv.) was prepared in a THF/water mixture (9/1, c(aldehyde) = 0.16 M) and was stirred overnight at room temperature. After that, the mixture was diluted with water and ethyl acetate was added to extract (3x) the aqueous phase. The combined organic phases were washed with brine (1x) and dried over sodium sulfate. Removal of the solvents *in vacuo* yielded a residue, which was purified by column chromatography on silica gel affording the desired product **136**.

General procedure F: A two neck flask equipped with a reflux condenser was charged with the corresponding aldehyde **135** (1.0 equiv.), boronic acid **172** (1.5 equiv.), tris(dibenzylideneaceton)dipalladium (0.032 equiv.), tricyclohexylphosphine (0.074 equiv.), cesium carbonate (1.7 equiv.) and a toluene/1,4-dioxane mixture (3/2, c(aldehyde) = 0.5 M). The suspension thus obtained was heated to 85°C for 24 hours and after that time it was filtered through a pad of Celite®. Removal of the solvents *in vacuo* afforded a crude material that was purified by column chromatography.

2'-Methylbiphenyl-2-carbaldehyde 136b



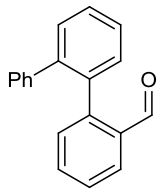
136b

Compound **136b** was prepared according to general procedure **E** from 2-bromo-benzaldehyde **135g** (0.31 mL, 2.65 mmol) and *o*-tolylboronic (400 mg, 2.94 mmol. The crude material thus obtained was purified by column chromatography on silica gel (hexanes/EtOAc, 9/1) affording **136b** as a yellow oil (327 mg, 63%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 3H), 7.19 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.25 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.28-7.36 (m, 3H), 7.470-7.52 (m, 1H), 7.64 (td, *J* = 7.5, 1.5 Hz, 1H), 8.03 (dd, *J* = 7.7, 1.2 Hz, 1H), 9.74 ppm (d, J = 0.8 Hz, 1H).

The found spectral data were in agreement with those reported in the literature.[79]

2'-Phenyl-biphenyl-2-carbaldehyde 136c



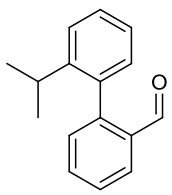
136c

Compound **136c** was prepared according to general procedure **E** from 2-bromo-benzaldehyde **135g** (0.19 mL, 300 mg, 1.62 mmol) and 2-biphenyl boronic acid (353 mg, 1.78 mmol). In this case a N,N-DMF/water solvent mixture (5/1, 10 mL) was employed. The crude material thus obtained was purified by column chromatography on silica gel (hexanes/ethyl acetate, 95/5) affording **136c** as a pale yellow solid (370 mg, 88%).

^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 7.04-7.12 (m, 2H), 7.15-7.23 (m, 3H), 7.29-7.59 (m, 7H), 7.73-7.80 (m, 1H), 9.76 ppm (d, *J*= 0.9 Hz, 1H).

The found spectral data were in agreement with those reported in the literature.[80]

2'-Isopropyl-[1,1'-biphenyl]-2-carbaldehyde 136h



136h

Compound **136h** was prepared according to general procedure **E** from 2-bromo-benzaldehyde **135g** (222 mg, 1.2 mmol) and (2-*iso*-propylphenyl)boronic acid (216 mg, 1.32 mmol). The crude material thus obtained was purified by column chromatography on silica gel (hexanes) affording **136h** as a colorless oil (254 mg, 94%).

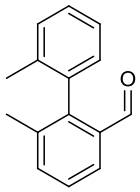
^{1}H-NMR (300 MHz, $CDCl_3$):δ = 1.02 (d, *J* = 6.9 Hz, 3H), 1.05 (d, *J* = 6.8 Hz, 3H), 2.67 (hept, *J* = 6.9 Hz, 1H), 7.07 (dt, *J* = 7.4, 0.9 Hz, 1H), 7.12 - 7.20 (m, 1H), 7.24 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.31 - 7.38 (m, 2H), 7.43 (tt, *J* = 7.5, 1.1 Hz, 1H), 7.55 (td, *J* = 7.5, 1.5 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.2 Hz, 1H), 9.69 (d, *J* = 0.7 Hz, 1H) ppm.

$^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$):δ = 23.5, 24.5, 30.2, 125.4, 125.7, 127.1, 127.9, 128.8, 130.4, 131.1, 133.6, 134.3, 136.3, 145.8, 147.2, 192.4 ppm.

HRMS *calcd.* for $C_{17}H_{16}NaO^+$: 247.108915 $[M+Na]^+$; *found*: 247.109335.

IR: ῡ = 715, 755, 825, 1004, 1033, 1193, 1251, 1389, 1442, 1473, 1596, 1692, 2747, 2868, 2927, 2961, 3023, 3060 cm^{-1}.

2',6-Dimethylbiphenyl-2-carbaldehyde 136f



136f

A microwave vial was charged with 2-bromo-3-methylbenzaldehyde **135a** (250 mg, 1.26 mmol), 2-tolyl boronic acid (187.9 mg, 1.39 mmol), tetrakis(triphenylphosphine)palladium (14.6 mg, 1.26 µmol), sodium carbonate (267.1 mg, 2.52 mmol) and a 1,4-dioxane/water mixture (3/2, 1.4 mL). The vessel was sealed with a Teflon crimp top and the suspension was heated to 120 °C under microwave irradiation for 25 minutes. After this time the mixture was diluted with water and ethyl acetate was added to extract (4x) the aqueous phase. Then, the combined organic phases were washed with brine (1x), dried over sodium sulfate and the solvent removed *in vacuo*. The crude material thus obtained was purified by column chromatography on silica gel (pentane/MTBE, 30/1) affording **136f** as a colorless oil (97%, 257.3 mg).

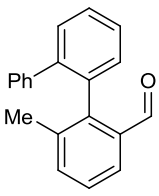
^1H-NMR (300 MHz, $CDCl_3$): δ = 1.93 (s, 3H), 1.98 (s, 3H), 7.04 (d, *J* = 7.2 Hz, 1H), 7.18 - 7.28 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.45 - 7.58 (m, 1H), 7.80 (dd, *J* = 7.7, 0.7 Hz, 1H), 9.55 ppm (d, *J* = 0.8 Hz, 1H).

$^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): δ = 19.6, 20.0, 124.8, 126.1, 127.8, 128.3, 129.8, 130.2, 134.2, 135.7, 136.3, 136.5, 137.4, 145.2, 192.8 ppm.

HRMS *calcd.* for $C_{15}H_{14}O^+$: 210.104454 $[M]^+$; *found:* 210.104462.

IR: ῡ = 730, 759, 781, 918, 1006, 1120, 1214, 1235, 1381, 1458, 1491, 1591, 1684, 1739, 2856, 2921, 3017 cm^{-1}.

6-Methyl-2'-phenyl-biphenyl-2-carbaldehyde 136i



136i

A microwave vial was charged with 2-bromo-3-methylbenzaldehyde **135a** (200 mg, 1.0 mmol), 2-biphenylboronic acid (218.9 mg, 1.1 mmol), tetrakis(triphenyl-phosphine)palladium (11.6 mg, 0.01 mmol), sodium carbonate (212 mg, 2.0 mmol) and a 1,4-dioxane/water mixture (3/2, 1.1 mL)

was added. The vessel was sealed with a Teflon crimp top and the suspension was heated to 120 °C under microwave irradiation for 25 minutes. After this time, the mixture was diluted with water and ethyl acetate was added (4x) to extract the aqueous phase. The combined organic phases were then washed with brine (1x), dried over sodium sulfate and the solvents removed *in vacuo*. The crude material thus obtained was purified by column chromatography on silica gel (hexanes) affording **136i** as a colorless oil (204 mg, 75%).

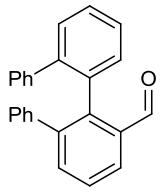
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.90 (s, 3H), 6.86-6.93 (m, 2H), 6.96-7.02 (m, 3H), 7.09-7.16 (m, 2H), 7.21 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.26-7.33 (m, 1H), 7.34-7.38 (m, 2H), 7.59 (dd, *J* = 7.7, 0.8 Hz, 1H), 9.63 ppm (d, *J* = 0.7 Hz, 1H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 20.0, 124.8, 126.9, 127.3, 127.6, 128.0, 128.6, 129.0, 130.2, 131.0, 134.3, 135.0, 135.4, 137.4, 140.6, 141.8, 144.6, 192.4 ppm.

HRMS *calcd.* for $C_{20}H_{16}O^+$: 272.119921 $[M]^+$; *found*: 272.120111.

I**R:** ϑ = 699, 715, 747, 781, 921, 1008, 1074, 1116, 1162, 1239, 1448, 1459, 1480, 1591, 1686, 2744, 2852, 3058 cm^{-1}.

6-Phenyl-2'-phenyl-biphenyl-2-carbaldehyde 136j



136j

Compound **136j** was prepared according to general procedure **F** from 2-chlorobiphenyl-3-carbaldehyde **135c** (190 mg, 0.87 mmol) and 2-biphenylboronic acid (260.5 mg, 1.31 mmol). The crude material thus obtained was purified by column chromatography on silica gel (hexanes/ethyl acetate, 15/1) affording **136j** as a white solid (179 mg, 61%).

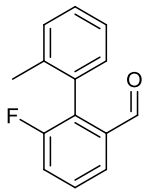
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.60 - 6.65 (m, 4H), 7.01-7.16 (m, 6H), 7.24-7.27 (m, 1H), 7.31 - 7.50 (m, 5H), 7.98 (dd, *J* = 7.3, 1.8 Hz, 1H), 9.97 ppm (s, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 126.5, 126.7, 126.8, 127.7, 127.7, 128.1, 128.7, 129.4, 129.6, 130.4, 133.3, 134.3, 135.2, 135.7, 139.9, 140.3, 142.1, 142.5, 143.5, 192.9 ppm.

HRMS *calcd.* for $C_{25}H_{18}O^+$: 334.135767 $[M]^+$; *found*: 334.135729.

IR: ϑ = 696, 715, 745, 764, 807, 866, 910, 951, 982, 1008, 1026, 1075, 1117, 1158, 1181, 1231, 1263, 1294, 1329, 1386, 1425, 1434, 1448, 1456, 1480, 1497, 1570, 1584, 1687, 1731, 1805, 1903, 1954, 2746, 2803, 2852, 3029, 3057 cm^{-1}.

6-Fluoro-2'-methylbiphenyl-2-carbaldehyde 136k



136k

A microwave vial was charged with 2-bromo-3-fluorobenzaldehyde (150 mg, 0.72 mmol), 2-methyl-phenyl boronic acid (126.8 mg, 0.93 mmol), tetrakis(triphenylphosphine)palladium(0) (49.7 mg, 0.043 mmol) as catalyst, potassium carbonate (240.8 mg, 1.8 mmol) and a 1,4-dioxan/water mixture (4/1, 3.0 mL). The vessel was sealed with a Teflon crimp top and the suspension heated to 110 °C under microwave irradiation for 2.5 hours. After this time, the suspension was filtered over a short pad of silica gel and rinsed with DCM. Removal of the solvents *in vacuo* gave a crude residue which was purified by column chromatography on silica gel (hexanes) affording **136k** as a yellow oil (113 mg, 71%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 3H), 7.19 (dd, *J* = 7.4 Hz, 1.1 Hz, 1H), 7.29 (td, *J* = 7.3 Hz, 7.3, 1.6 Hz, 1H), 7.33-7.38 (m, 2H), 7.40-7.42 (m, 1H), 7.47-7.53 (m, 1H), 7.84 (dd, *J* = 7.7 Hz, 1.1 Hz, 1H), 9.68 ppm (dd, *J* = 0.92 Hz, 1H).

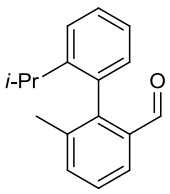
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 20.3, 121.1 (d, J_{F-C} = 22.6 Hz), 123.2 (d, J_{F-C} = 3.0 Hz), 125.9, 129.1, 129.4 (d, J_{F-C} = 8.2 Hz), 130.4, 130.4, 132.7 (d, J_{F-C} = 21.6 Hz), 131.0, 135.9 (d, J_{F-C} = 2.0 Hz), 137.4, 159.9 (d, J_{F-C} = 247.6 Hz), 191.2 ppm (d, J_{F-C} = 3.9 Hz).

^{19}F{^{1}H}-NMR(282 MHz, $CDCl_3$): δ = -114.3 ppm.

HRMS *calcd.* for $C_{14}H_{11}FO^{+}$: 214.079396 $[M]^{+}$; *found*: 214.079586.

IR: ϑ̃ = 695, 729, 739, 761, 782, 796, 870, 907, 942, 959, 1007, 1036, 1073, 1120, 1158, 1240, 1258, 1288, 1389, 1458, 1496, 1569, 1609, 1693, 2750, 2858, 2928, 3012, 3064 cm^{-1}.

2'-*Iso*-propyl-6-methylbiphenyl-2-carbaldehyde 136l



136l

Compound **136l** was prepared according to general procedure **E** from 2-bromo-3-methylbenzaldehyde **135a** (100 mg, 0.5 mmol) and 2-*iso*-propyl-phenyl boronic acid (90.2 mg, 0.55 mmol). The crude material thus obtained was purified by column chromatography on silica gel (hexanes) affording **136l** as a white solid (98 mg, 66%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.92 (d, *J* = 6.9 Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 3H), 1.97 (s, 3H), 2.44 (hept, *J* = 6.9 Hz, 1H), 6.96 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.16 (ddd, *J* = 7.6, 6.7, 2.0

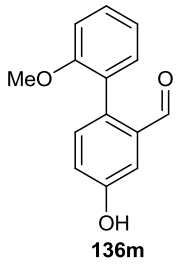
Hz, 1H), 7.26 - 7.39 (m, 3H), 7.43 (dd, *J* = 7.5, 0.4 Hz,1H), 7.78 (dd, *J* = 7.7, 0.4 Hz, 1H), 9.56 ppm (d, *J* = 0.6 Hz, 1H).

$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 20.0, 23.6, 24.1, 30.3, 124.7, 125.9, 127.7, 128.7, 129.8, 134.6, 135.0, 135.5, 137.7, 145.1, 147.1, 192.8, 192.8 ppm.

HRMS *calcd.* for $C_{17}H_{18}O^+$: 238.135875 $[M]^+$; *found*: 238.135768.

IR: ῡ = 716, 756, 787, 920, 1004, 1034, 1127, 1216, 1234, 1362, 1382, 1443, 1460, 1591, 1687, 1740, 2867, 2960 cm^{-1}.

4-Hydroxy-2'-methoxybiphenyl-2-carbaldehyde 136m



136m

Compound **136m** was prepared according to general procedure **E** from 2-bromo-5-hydroxybenzaldehyde (387 mg, 1.92 mmol) and 2-methoxyphenylboronic acid (380 mg, 2.50 mmol). In this case a DMF/water solvent mixture (5/1, 12.0 mL) was employed instead. Heating to 50 °C was necessary to achieve full conversion. The crude material thus obtained was purified by column chromatography on silica gel (hexanes/ethyl acetate, 7/3) affording **136m** as a pale yellow solid (328 mg, 75%).

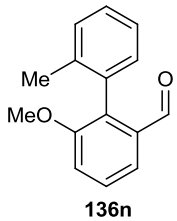
^1H-NMR (400 MHz, $CDCl_3$): δ = 3.74 (s, 3H), 5.88 (s, *J* = 2.8 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 7.07 (td, *J* = 7.73, 0.3 Hz, 1H), 7.18 (dd, *J* = 9.7, 1.4 Hz, 1H), 7.26 (1xCH_{Ar} under solvent signal), 7.28 (s, 1H), 7.38-7.42 (m, 1H), 7.52 (d, *J* = 2.8 Hz, 1H), 9.70 ppm (s, 1H).

$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 55.5, 110.7, 112.5, 121.1, 121.6, 126.4, 129.9, 131.7, 132.9, 134.6, 134.8, 155.6, 156.6, 193.2 ppm.

HRMS *calcd.* for $C_{14}H_{12}NaO_3^+$: 251.067864 $[M+Na]^+$; *found*: 251.067890.

IR: ῡ = 441, 458, 503, 529, 544, 574, 586, 615, 703, 719, 772, 798, 828, 859, 875, 928, 955, 977, 1020, 1052, 1091, 1124, 1162, 1178, 1225, 1272, 1311, 1347, 1413, 1430, 1446, 1469, 1486, 1504, 1600, 1674, 2848, 2921, 2951, 3010, 3057, 3343 cm^{-1}.

6-Methoxy-2'-methylbiphenyl-2-carbaldehyde 136n



136n

Compound **136n** was prepared according to general procedure **F** from 2-chloro-3-methoxy-benzaldehyde (200 mg, 1.17 mmol) and 2-methyl-phenylboronic acid (239 mg, 1.76 mmol. The crude material thus obtained

was purified by column chromatography on silica gel (hexanes/ethyl acetate 15/1) affording **136n** as a yellow solid (182 mg, 69%).

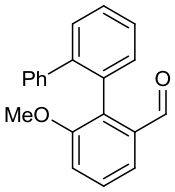
^{1}H-NMR (300 MHz, $CDCl_3$): δ= 2.06 (s, 3H), 3.78 (s, 3H), 7.11-7.14 (m, 1H), 7.20 (dd, *J* = 8.1 Hz, 0.8 Hz, 1H), 7.23 - 7.36 (m, 3H), 7.47 (td, *J* = 8.0 Hz, 8.0 Hz, 0.6 Hz, 1H), 7.63 (dd, *J* = 7.8 Hz, 1H), 9.62 ppm (d, *J* = 0.7 Hz, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 20.2, 56.4, 116.3, 119.1, 125.7, 128.4, 128.9, 130.0, 131.0, 133.3, 134.9, 135.4, 137.5, 157.5, 192.6 ppm.

HRMS *calcd.* for $C_{15}H_{14}NaO_2^+$: 249.088595 $[M+Na]^+$; *found*: 249.088542.

IR: ῡ =729, 744, 762, 794, 911, 943, 983, 1003, 1067, 1119, 1185, 1240, 1262, 1298, 1389, 1467, 1494, 1575, 1592, 1682, 1697, 2341, 2742, 2837, 2948, 3011, 3067 cm^{-1}.

6-Methoxy-2'-phenyl-biphenyl-2-carbaldehyde 136o



136o

Compound **136o** was prepared according to general procedure **F** from 2-chloro-3-methoxy-benzaldehyde (713 mg, 4.18 mmol) and 2-biphenylboronic acid (1.2 g, 6.27 mmol). The crude material thus obtained was purified by column chromatography on silica gel (hexanes/ethyl acetate 7/1) affording **136o** as a yellow solid (1.18 g, 98%).

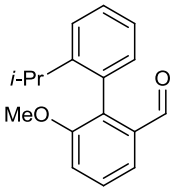
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.60 (s, 3H), 6.99-7.15 (m, 6H), 7.15-7.27 (m, 2H), 7.41-7.49 (m, 4H), 9.74 ppm (m, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 55.8, 115.9, 119.2, 126.9, 127.1, 127.9, 128.6, 128.9, 129.0, 129.9, 132.0, 132.1, 134.7, 135.2, 141.3, 143.0, 157.2, 192.2 ppm.

HRMS *calcd.* for $C_{20}H_{16}NaO_2^+$: 311.104249 $[M+Na]^+$; *found*: 311.103990.

IR: ῡ = 699, 715, 748, 778, 798, 880, 912, 1000, 1009, 1066, 1114, 1156, 1185, 1239, 1260, 1301, 1387, 1437, 1463, 1483, 1574, 1592, 1684, 1947, 2750, 2837, 2857, 2938, 2960, 3011, 3055 cm^{-1}.

2'-Isopropyl-6-methoxybiphenyl-2-carbaldehyde 136p



136p

Compound **136p** was prepared according to general procedure **F** from 2-chloro-3-methoxy-benzaldehyde (200 mg, 1.17 mmol) and 2-*iso*-propyl-phenyl boronic acid (288 mg, 1.76 mmol. The crude material thus obtained

was purified by column chromatography on silica gel (hexanes/ethyl acetate 15/1) affording **136p** as a yellow solid (208 mg, 70%).

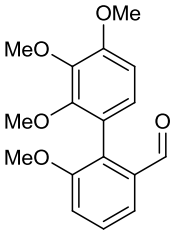
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.01 (d, *J* = 6.9 Hz, 3H), 1.17 (d, *J* = 6.9, 3H), 2.61 (hept., *J* = 6.9 Hz, 1H), 3.76 (s, 3H), 7.05-7.08 (m, 1H), 7.18 (dd, *J* = 8.1 Hz, 1.0 Hz, 1H), 7.19-7.26 (m, 1H), 7.40-7.41 (m, 1H), 7.41(d, *J* = 1.0 Hz, 1H), 7.46 (td, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.62 (dd, *J* = 7.9 Hz, 1.2 Hz, 1H), 9.64 ppm (d, *J* = 0.8 Hz, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 23.6, 24.1, 30.7, 56.0, 115.8, 119.0, 125.5, 125.6, 128.8, 130.9, 131.9, 134.9, 135.7, 148.2, 157.4, 192.5 ppm.

HRMS *calcd*. for $C_{17}H_{18}O_2^+$: 254.130677 $[M]^+$; *found:* 254.130555.

IR: ϑ = 666, 716, 744, 755, 784, 794, 872, 912, 949, 1002, 1035, 1066, 1098, 1168, 1186, 1201, 1240, 1259, 1301, 1345, 1362, 1389, 1436, 1467, 1492, 1576, 1592, 1688, 1925, 1948, 1979, 2837, 2867, 2961, 3018, 3064 cm^{-1}.

2',3',4',6-Tetramethoxybiphenyl-2-carbaldehyde 136g



136g

Compound **136g** was prepared according to general procedure **F** from 2-chloro-3-methoxy-benzaldehyde (226 mg, 1.32 mmol) and 2,3,4-tri-methoxy-phenyl boronic acid (421 mg, 1.98 mmol). The crude material was purified by column chromatography on silica gel (hexanes/ethyl acetate, 2/1) affording **136g** as a yellow solid (386 mg, 97%).

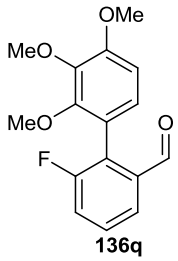
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3H), 3.80 (s, 3H), 3.91 (s, 3H), 3.92 (s, 3H), 6.76 (d, *J* = 8.7 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 1H), 7.20 (dd, *J* = 8.3 Hz, 0.9 Hz, 1H) 7.44 (td, *J* = 8.0, 0.7 Hz, 1H), 7.61 (dd, *J* = 7.8 Hz, 1.1 Hz, 1H), 9.70 ppm (d, *J* = 0.8 Hz, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 56.1, 56.1, 60.7, 61.0, 107.1, 115.9, 119.0, 119.8, 126.5, 128.7, 131.2, 135.6, 142.3, 152.1, 154.0, 157.6, 192.6 ppm.

HRMS *calcd.* for $C_{17}H_{18}NaO_4^+$: 325.104643 $[M+Na]^+$; *found:* 325.104246.

IR: ϑ = 667, 689, 719, 744, 771, 788, 795, 815, 867, 916, 1001, 1012, 1071, 1091, 1111, 1167, 1181, 1203, 1242, 1257,1289, 1395, 1409,1428, 1462, 1501, 1578, 1592, 1681, 1693, 1874, 1977, 2163, 2761, 2838, 2868, 2939, 2977 cm^{-1}.

6-Fluoro-2',3',4'-trimethoxybiphenyl-2-carbaldehyde 136q



136q

A microwave vial was charged with 2-bromo-3-fluorobenzaldehyde (150 mg, 0.72 mmol), 2,3,4-tri-methoxy-phenylboronic acid (197.8 mg, 0.93 mmol), tetrakis(triphenylphosphine)palladium (49.7 mg, 0.043 mmol), potassium carbonate (240.8 mg, 1.8 mmol) and a 1,4-dioxan/water mixture (4/1, 3.0 mL). The vessel was sealed with a Teflon crimp top and the suspension was heated to 110 °C under microwave irradiation for 2.5 hours. After this time, the suspension was filtered over a short pad of silica gel and rinsed with DCM. Removal of the solvent *in vacuo* afforded a crude residue, which was purified by column chromatography on silica gel (pentane/MTBE, 6/1) affording **136q** as a yellow oil (200 mg, 95%).

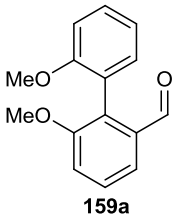
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.67 (s, 3H), 3.91 (s, 3H), 3.92 (s, 3H), 6.78 (d, *J* = 8.6 Hz, 1H), 6.95 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.34-7.49 (m, 2H), 7.81 (ddd, *J* = 7.7, 1.3, 0.3 Hz, 1H), 9.77 ppm (d, *J* = 0.8 Hz, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ =56.3, 61.0, 61.2, 107.4, 117.0, 120.8 (d, $_{JF\text{-}C}$ = 23.4 Hz), 123.0 (d, $J_{F\text{-}C}$ = 3.6 Hz), 126.5 (d, $J_{F\text{-}C}$ = 1.5 Hz), 129.2 (d, $J_{F\text{-}C}$ = 8.3 Hz), 130.2, 136.2 (d, $J_{F\text{-}C}$ = 2.3 Hz), 142.6, 152.2, 154.6, 160.3 (d, $J_{F\text{-}C}$ = 242.3 Hz), 191.3 ppm (d, $J_{F\text{-}C}$ = 4.2 Hz).

^{19}F{^{1}H}-NMR(282 MHz, $CDCl_3$): δ = -114.6 ppm.

HRMS *calcd*. for $C_{16}H_{15}FNaO_4^+$: 313.0084461 $[M+Na]^+$; *found*: 313.084409.

2',6-Di-methoxy-biphenyl-2-carbaldehyde 136r



159a

Compound **136r** was prepared according to general procedure **F** from 2-chloro-3-methoxy-benzaldehyde (713 mg, 4.18 mmol) and 2-methoxyphenylboronic acid (952.8 mg, 6.27 mmol). The crude material thus obtained was purified by column chromatography on silica gel (hexanes/ethyl acetate 10/1) affording **136r** as a yellow solid (890 mg, 88%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.73 (s, 3H), 3.78 (s, 3H), 7.00 (d, *J* = 8.6 Hz, 1H), 7.05 (td, *J* = 7.6, 0.9 Hz, 1H), 7.20-7.25 (m, 2H), 7.39-7.44 (m, 1H), 7.46 (dd, *J* = 7.8, 0.4 Hz, 1H), 7.63 (dd, *J* = 7.8, 1.1 Hz, 1H), 9.70 ppm (d, *J* = 0.8 Hz, 1H).

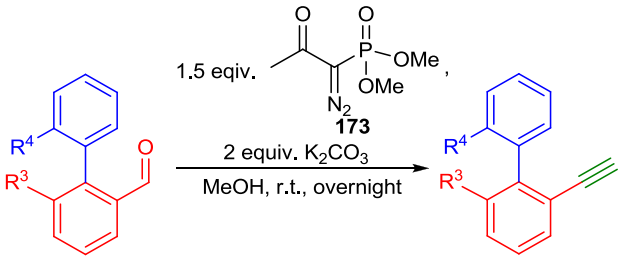
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 55.6, 56.2, 111.0, 116.4, 118.9, 120.5, 122.1, 128.8, 129.9, 131.4, 132.6, 135.4, 157.3, 157.4, 192.9 ppm.

HRMS *calcd*. for $C_{15}H_{14}NaO_3^+$: 265.083511 $[M+Na]^+$; *found*: 265.083381.

IR: ϑ = 725, 756, 793, 852, 908, 939, 975, 1000, 1023, 1050, 1061, 1093, 1122, 1162, 1178, 1230, 1248, 1260, 1290, 1395, 1432, 1460, 1495, 1574, 1591, 1677, 1965, 2048, 2835, 2934, 2958, 3005, 3023, 3083 cm^{-1}.

6.5.5.3 Peparation of the corresponding alkynes

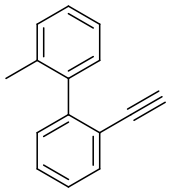
General procedure G: Ohira-Bestmann variant of the Seyferth-Gilbert alkynylation



136 **104**

Dimethyl (1-diazo-2-oxopropyl)phosphonate *(Ohira-Bestmann* reagent) **173** (1.5 equiv.), potassium carbonate (2 equiv.) and the corresponding aldehyde **136** (1.0 equiv.) were suspended in methanol (c(aldehyde) = 0.13 M) and stirred overnight at room temperature. Subsequently, the solvent was removed *in vacuo* and the residue obtained dissolved in ethyl acetate and washed with brine (3x). Then, the organic phase was dried over sodium sulfate and the solvent was removed *in vacuo* yielding the crude product **104**. Purification of this material by column chromatography on silica gel afforded **104**.

2-Ethynyl-2'-methyl-biphenyl 104b



104b

Compound **104b** was prepared according to general procedure **G** from carbaldehyde **136b** (327 mg, 1.67 mmol). Purification of the crude product was performed by column chromatography on silica gel (hexanes/ethyl acetate, 12/1) afforded **104b** as a white solid (223 mg, 94%).

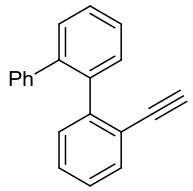
^{1}H -NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 3H), 2.96 (s, 1H), 7.23-7.36 (m, 5H), 7.38 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.66 ppm (dd, *J* = 7.6, 1.3 Hz, 1H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 20.1, 79.9, 82.8, 121.9, 125.5, 127.1, 127.8, 128.7, 129.7, 129.8, 129.9, 133.0, 136.3, 140.6, 145.1 ppm.

HRMS *calcd*. for $C_{15}H_{12}^{+}$: 192.093896 $[M]^{+}$; *found*: 192.094011.

IR: ῡ = 725, 745, 755, 875, 950, 1005, 1042, 1101, 1122, 1159, 1264, 1378, 1438, 1456, 1472, 1495, 1595, 3019, 3060, 3283 cm^{-1}.

2-Ethynyl-2'-phenyl-biphenyl 104c



104c

Compound **104c** was prepared according to general procedure **G** from carbaldehyde **136c** (370 mg, 1.43 mmol). Purification of the crude product was performed by column chromatography on silica gel (hexanes/ethyl acetate, 95/5) afforded **104c** as a white solid (350 mg, 96%).

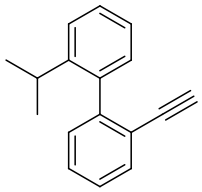
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.95 (s, 1H), 6.99-7.02 (m, 1H), 7.13-7.21 (m, 7H), 7.38-7.49 ppm (m, 5H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 80.4, 83.1, 122.0, 126.6, 126.8, 126.9, 127.8, 128.1, 128.3, 129.9, 130.2, 131.0, 131.1, 133.1, 139.2, 141.4, 141.4, 144.8 ppm.

HRMS *calcd*. for $C_{20}H_{14}^{+}$: 254.109546 $[M]^{+}$; *found*: 254.109501.

IR: ῡ = 698, 742, 756, 770, 913, 948, 1008, 1073, 1159, 1240, 1265, 1429, 1449, 1467, 1488, 1597, 1735, 3020, 3057, 3283 cm^{-1}.

2-Ethynyl-2'-*iso*-propyl-biphenyl 104h


104h

Compound **104h** was prepared according to general procedure **G** from carbaldehyde **136h** (200 mg, 0.89 mmol Purification of the crude product was performed by column chromatography on silica gel (hexanes/ethyl acetate, 95/5) afforded **104h** as a white solid (167 mg, 85%).

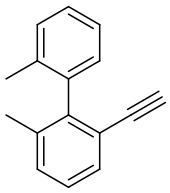
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.00 (d, *J* = 6.9 Hz, 3H), 1.12 (d, *J* = 6.9 Hz, 3H), 2.73 (hept, *J* = 6.9 Hz, 1H), 2.82 (s, 1H), 7.03-7.10 (m, 1H), 7.10-7.20 (m, 2H), 7.20-7.38 (m, 4H), 7.51 (dd, *J* = 7.6, 1.4 Hz, 1H) ppm.

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 23.6, 24.6, 30.1, 80.3, 82.9, 122.2, 125.2, 125.3, 127.0, 128.2, 128.5, 129.8, 130.0, 132.9, 139.6, 145.2, 146.9 ppm.

HRMS *calcd.* for $C_{17}H_{16}$: 220.125307 $[M]^{+}$; *found:*220.125200.

IR: ῡ = 665, 747, 757, 1004, 1031, 1043, 1089, 1105, 1203, 1257, 1330, 1364, 1385, 1433, 1446, 1470, 2867, 2961, 3020, 3057, 3267 cm^{-1}.

2-Ethynyl-2',6-dimethylbiphenyl 104f


104f

Compound **104f** was prepared according to general procedure **G** from carbaldehyde **136f** (228.6 mg, 1.09 mmol). Purification of the crude product was performed by column chromatography on silica gel (pentane) afforded **104f** as a colorless oil (210.7 mg, 94%).

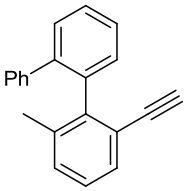
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.91 (s, 3H), 1.96 (s, 3H), 2.72 (s, 1H), 6.96-7.02 (m, 1H), 7.09-7.20 (m, 5H), 7.35 ppm (dd, *J* = 7.3, 1.3 Hz, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 19.6, 20.4, 79.5, 82.9, 122.1, 125.8, 127.1, 127.6, 129.1, 129.9, 130.5, 130.6, 136.0, 136.6, 139.8, 144.5 ppm.

HRMS *calcd*. for $C_{16}H_{14}^{+}$: 206.109326 $[M]^{+}$; *found*: 206.109547.

IR: ϑ =727, 746, 756, 785, 915, 1006, 1120, 1268, 1379, 1454, 1489, 1574, 2921, 3016, 3061, 3286 cm^{-1}.

2-Ethynyl-6-methyl-2'-phenyl-biphenyl 104i



104i

Compound **104i** was prepared according to general procedure **G** from carbaldehyde **136i** (204 mg, 0.75 mmol). Purification of the crude product was performed by column chromatography on silica gel (hexanes) affording **104i** as a white solid (158 mg, 78%).

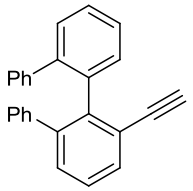
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.88 (s, 3H), 2.96 (s, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.19 - 7.25 (m, 5H), 7.29-7.32 (m, 1H), 7.40-7.47 (m, 2H), 7.49-7.51 ppm (m, 2H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 20.5, 80.3, 83.6, 122.8, 126.7, 127.0, 127.2, 127.7, 127.9, 129.2, 130.0, 130.3, 130.4, 130.6, 136.6, 138.4, 141.4, 141.4, 144.3 ppm.

HRMS *calcd*. for $C_{21}H_{16}^{+}$: 268.125101 $[M]^{+}$; *found*: 268.125200.

IR: ϑ = 668, 698, 742, 749, 757, 772, 915, 952, 1008, 1074, 1105, 1159, 1262, 1428, 1449, 1468, 1488, 1598, 1967, 3059, 3270 cm^{-1}.

2-Ethynyl-2',6-diphenyl-biphenyl 104j



104j

Compound **104j** was prepared according to general procedure **G** from carbaldehyde **136j** (135 mg, 0.40 mmol). Purification of the crude product was performed by column chromatography on silica gel (hexanes/ethyl acetate, 20/1) affording **104j** as a white solid (115 mg, 85%).

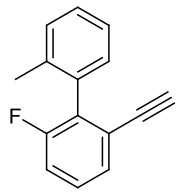
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.99 (s, 1H), 6.48-6.52 (m, 2H), 6.58-6.61 (m, 2H); 6.93-7.14 (m, 8H), 7.24 (d, *J* = 1.6 Hz, 1H), 7.28-7.38 (m, 2H), 7.49-7.52 (m, 1H), 7.58 ppm (dd, *J* = 7.5 Hz, 1.4 Hz, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 80.9, 83.6, 123.6, 126.3, 126.4, 126.4, 127.3, 127.4, 127.4, 128.0, 129.4, 129.6, 129.9, 130.7, 132.1, 132.7, 137.6, 140.5, 141.0, 141.5, 142.0, 143.1 ppm.

HRMS *calcd.* for $C_{26}H_{18}^{+}$: 330.140849 $[M]^{+}$; *found*: 330.140613.

IR: ῡ = 654, 671, 697, 730, 741, 749, 760, 810, 854, 910, 966, 979, 1008, 1027, 1073, 1092, 1115, 1157, 1182, 1253, 1284, 1419, 1434, 1455, 1481, 1496, 1578, 1597, 1748, 1804, 1819, 1881, 1900, 1947, 3029, 3056, 3278 cm^{-1}.

2-Ethynyl-6-fluoro-2'-methylbiphenyl 104k



104k

Compound **104k** was prepared according to general procedure **G** from carbaldehyde **136k** (61.7 mg, 0.29 mmol). Purification of the crude product was performed by column chromatography on silica gel (hexanes/ethylacetate, 40/1) affording **104k** as a white solid (33 mg, 54%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ =2.10 (s, 3H), 2.86 (s, 1H), 7.06-7.25 (m, 6H), 7.35 (d, *J* = 7.5 Hz, 1H) ppm.

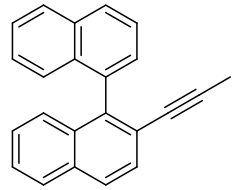
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ =19.8, 80.9, 81.5 (d, J_{F-C} = 4.6 Hz), 116.4 (d, J_{F-C} = 23.1 Hz), 124.3 (d, J_{F-C} = 5.0 Hz), 125.6, 128.4, 128.8 (d, J_{F-C} = 9.0 Hz), 128.9 (d, J_{F-C} = 3.4 Hz), 130.0, 130.2, 132.3 (d, J_{F-C} = 19.5 Hz), 133.7, 137.0, 159.7 (d, J_{F-C} = 246.1 Hz) ppm.

^{19}F{^{1}H}-NMR (282 MHz, $CDCl_3$):δ = -113.2 ppm.

HRMS *calcd*. for $C_{15}H_{11}F$: 210.084479 $[M]^{+}$; *found*: 210.084303.

IR: ϑ = 724, 737, 760, 794, 940, 960, 1008, 1034, 1074, 1120, 1159, 1250, 1379, 1452, 1494, 1564, 1601, 1608, 2861, 2928, 3019, 3063, 3293 cm^{-1}.

2-(Prop-1-ynyl)-1,1'-binaphthyl 137a


137a

To a solution of 2-ethynyl-1,1'-binaphthyl **104a** (250 mg, 0.90 mmol) in THF (5.8 mL) at -10 °C, *n*-BuLi (1.4 mL, 2.25 mmol, c = 1.6 M in hexane) was added dropwise over 30 minutes. The mixture was then stirred for 1.5 h at this temperature and then iodomethane (0.15 mL, 331.5 mg, 2.33 mmol) was added dropwise over 30 minutes at -20 °C. After 2 hours under these conditions, the solution was warmed to room temperature and stirred for an additional hour. Then, the solvents were removed *in vacuo* and the crude product purified by column chromatography on silica gel (hexanes) affording **136a** as a colorless solid (185 mg, 70%).

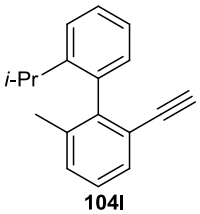
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.66 (s, 3H), 7.22-7.24 (m, 2H), 7.28-7.30 (m, 2H), 7.44-7.49 (m, 3H), 7.61-7.67 (m, 2H), 7.87-7.91 (m, 2H), 7.95-7.98 ppm (m, 2H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 4.5, 79.5, 90.2, 122.1, 125.5, 125.8, 126.0, 126.2, 126.4, 126.5, 126.9, 127.8, 128.0, 128.0, 128.2, 128.3, 129.2, 132.7, 132.7, 133.1, 133.6, 137.1, 140.6 ppm.

HRMS *calcd.* for $C_{23}H_{16}^{+}$: 292.125200 $[M]^{+}$; *found*: 292.125095.

IR: ϑ = 432, 442, 508, 536, 569, 584, 614, 633, 659, 679, 689, 747, 779, 801, 818, 866, 943, 1017, 1032, 1049, 1079, 1132, 1144, 1157, 1205, 1260, 1332, 1366, 1427, 1501, 1559, 1592, 1617, 1703, 1769, 1814, 1923, 2226, 2846, 2912, 2962, 3053 cm^{-1}.

2-Ethynyl-2'-isopropyl-6-methyl-1,1'-biphenyl 104l



104l

Compound **104l** was prepared according to general procedure **G** from carbaldehyde **136l** (123 mg, 0.52 mmol). Purification of the crude product was performed by column chromatography on silica gel (hexanes/ethyl acetate, 20/1) affording **104l** as a white solid (107 mg, 89%).

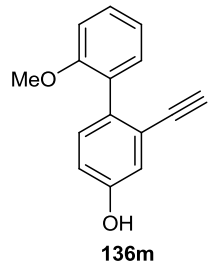
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.18 (d, *J* = 6.9 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H), 2.08 (s, 3H), 2.65 (hept, *J* = 6.9 Hz, 1H), 2.89 (s, 1H), 7.09 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.27-7.35 (m, 3H), 7.40-7.48 (m, 2H), 7.50 ppm (dd, *J* = 7.4, 0.9 Hz, 1H).

$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 20.7, 23.9, 24.4, 30.4, 80.1, 83.3, 122.5, 125.4, 125.7, 127.0, 128.0, 129.2, 130.4, 130.4, 136.9, 138.5, 144.5, 146.8 ppm.

HRMS *calcd.* for $C_{18}H_{18}^+$: 234.140849 $[M]^+$; *found*: 234.140643.

IR: ῡ =756, 786, 1005, 1035, 1085, 1258, 1362, 1381, 1456, 1575, 2867, 2960, 3286 cm^{-1}.

2-Ethynyl-2'-methoxybiphenyl-4-ol 104m



136m

Compound **104m** was prepared according to general procedure **G** from carbaldehyde **136m** (328 mg, 1.43 mmol). Purification of the crude product was performed by column chromatography on silica gel (hexanes/ethyl acetate, 7/3) affording **104m** as a white solid (227 mg, 96%).

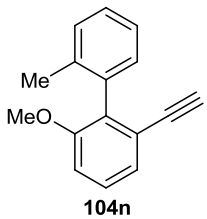
^1H-NMR (400 MHz, $CDCl_3$): δ = 2.91 (s, 1H), 3.79 (s, 3H), 4.83 (s, 1H), 6.87 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 7.01 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.05 (d, *J* = 2.7 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.26-7.29 (m, 1H), 7.34 ppm (ddd, *J* = 8.2, 7.5, 1.8 Hz, 1H).

$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 55.7, 79.3, 82.9, 111.3, 116.3, 119.6, 120.4, 123.2, 129.0, 129.3, 131.6, 131.8, 134.5, 154.4, 157.0 ppm.

HRMS (negative) *calcd.* for $C_{15}H_{11}O_2^-$: 223.076455 $[M-H]^-$; *found*: 223.076432.

IR: ῡ = 675, 700, 719, 760, 793, 829, 868, 936, 946, 1004, 1015, 1050, 1101, 1122, 1160, 1181, 1227, 1266, 1283, 1306, 1432, 1463, 1477, 1507, 1578, 1596, 2840, 3241, 3408 cm^{-1}.

2-Ethynyl-6-methoxy-2'-methylbiphenyl 104n



104n

Compound **104n** was prepared according to general procedure **G** from carbaldehyde **136n** (140 mg, 0.62 mmol). Purification of the crude product was performed by column chromatography on silica gel (hexanes/ethyl acetate, 20/1) affording **104n** as a white solid (113 mg, 82%).

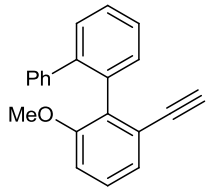
^1H-NMR (300 MHz, $CDCl_3$): δ= 2.04 (s, 3H), 2.79 (s, 1H), 3.67 (s, 3H), 6.90 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.07-7.23 ppm (m, 6H).

$^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): δ = 19.8, 56.0, 79.9, 82.5, 111.7, 123.4, 125.3, 125.4, 127.7, 128.4, 129.7, 130.2, 133.9, 136.6, 136.9, 157.0 ppm.

HRMS *calcd.* for $C_{16}H_{14}O^+$: 222.104464 $[M]^+$; *found:* 222.104228.

IR: ϑ = 667, 729, 758, 795, 810, 909, 945, 967, 1004, 1068, 1120, 1159, 1171, 1186, 1260, 1292, 1378, 1436, 1462, 1566, 1589, 1602, 1672, 1701, 1842, 1931, 2836, 2934, 2956, 3018, 3063, 3277 cm^{-1}.

2-Ethynyl-6-methoxy-2'-phenyl-biphenyl 104o



104o

Compound **104o** was prepared according to general procedure **G** from carbaldehyde **136o** (179 mg, 0.62 mmol). Purification of the crude product was performed by column chromatography on silica gel (hexanes/ethyl acetate, 15/1) affording **104o** as a white solid (125 mg, 71%).

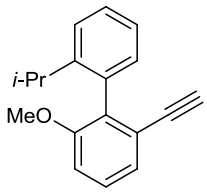
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.94 (s, 1H), 3.41 (s, 3H), 6.70 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.11-7.18 (m, 7H), 7.35-7.45 ppm (m, 4H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 55.5, 80.5, 83.0, 111.5, 123.7, 125.1, 126.5, 127.0, 127.4, 128.0, 128.3, 129.0, 129.5, 131.2, 134.0, 135.3, 142.0, 142.4, 156.7 ppm.

HRMS *calcd.* for $C_{21}H_{16}O^{+}$: 284.120115 $[M]^{+}$; *found:* 284.120047.

IR: ϑ= 672, 698, 742, 759, 779, 794, 845, 911, 948, 1008, 1065, 1117, 1159, 1187, 1265, 1292, 1427, 1435, 1449, 1460 , 1484, 1503, 1565, 1597, 1634, 1927, 1950, 1970, 2837, 2934, 2967, 3014, 3051, 3262 cm^{-1}.

2-Ethynyl-2'-isopropyl-6-methoxybiphenyl 104p



104p

Compound **104p** was prepared according to general procedure **G** from carbaldehyde **136p** (158 mg, 0.62 mmol). Purification of the crude product was performed by column chromatography on silica gel (hexanes/ethyl acetate, 10/1) affording **104p** as a white solid (139 mg, 89%).

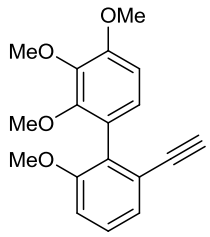
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.04 (d, *J* = 3.3 Hz, 3H), 1.06 (d, *J* = 3.3 Hz, 3H), 2.56 (sept, *J* = 6.9 Hz, 1H), 2.77 (s, 1H), 3.64 (s, 3H), 6.88 (d, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.1 Hz, 1H), 7.12-7.21 (m, 3H), 7.30-7.32 ppm (m, 2H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 23.7, 24.2, 30.7, 55.7, 80.3, 82.6, 111.4, 123.8, 125.0, 125.2, 125.4, 128.1, 128.2, 130.2, 134.1, 135.4, 147.6, 157.2 ppm.

HRMS *calcd*. for $C_{18}H_{18}O^{+}$: 250.135768 $[M]^{+}$; *found*: 250.135996.

IR: ϑ = 660, 731, 739, 758, 789, 909, 948, 1004, 1034, 1069, 1098, 1169, 1187, 1201, 1253, 1293, 1343, 1361, 1381, 1431, 1461, 1493, 1569, 1591, 2834, 2863, 2958, 3019, 3060, 3263, 3314 cm^{-1}.

2'-Ethynyl-2,3,4,6'-tetramethoxybiphenyl 104g



104g

Compound **104g** was prepared according to general procedure **G** from carbaldehyde **136g** (187 mg, 0.62 mmol). Purification of the crude product was performed by column chromatography on silica gel (hexanes/ethyl acetate, 3/1) affording **104g** as a white solid (180 mg, 97%).

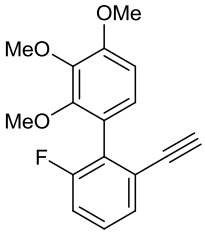
^{1}H-NMR (300 MHz, $CDCl_3$): δ= 2.90 (s,1H), 3.69 (s, 3H), 3.75 (s, 3H), 3.90 (s, 3H), 3.91 (s, 3H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.9 (d, *J* = 9.1 Hz, 1H), 6.95-6.98 (m, 1H), 7.19-7.29 ppm (m, 2H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 56.0, 56.0, 61.0, 61.0, 80.0 , 82.9, 106.9, 111.7, 123.7, 124.0, 125.2, 125.6, 128.3, 131.0, 142.2, 152.1, 153.5, 157.5 ppm.

HRMS *calcd*. for $C_{18}H_{18}NaO_4^+$: 321.109730 $[M+Na]^+$; *found*: 321.109738.

IR: ϑ = 690, 746, 795, 872, 920, 1004, 1070, 1092, 1115, 1169, 1206, 1261, 1296, 1410, 1432, 1462, 1501, 1568, 1590, 2102, 2837, 2936, 3000, 3278 cm^{-1}.

2'-Ethynyl-6'-fluoro-2,3,4-trimethoxybiphenyl 104q



104q

Compound **104q** was prepared according to general procedure **G** from carbaldehyde **136q** (132.0 mg, 0.45 mmol). Once the reaction was finished, the crude material was purified by column chromatography on silica gel (hexanes/ethyl acetate, 15/1). Additional purification HPLC (Nucleodur, 15 cm x 4.8 cm, methanol/H_2O 70/30, 50 mL/min; 91.1 mg in 6 mL methanol and 1 mL H_2O) was necessary to afford **104q** in analytical purity as a white solid (72.7 mg, 56%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.00 (s, 1H), 3.73 (s, 3H), 3.91 (s, 3H), 3.92 (s, 3H), 6.75 (d, *J* = 8.6 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 7.11-7.16 (m, 1H), 7.25-7.30 (m, 1H), 7.39 ppm (dd, *J* = 7.6, 0.98 Hz, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 54.9, 59.9, 60.07, 79.6, 80.8 (d, J_{F-C} = 5.3 Hz), 105.8, 115.1 (d, J_{F-C} = 23.2 Hz), 119.5, 123.5 (d, J_{F-C} = 4.3 Hz), 124.6, 127.5 (d, J_{F-C} = 9.1 Hz),

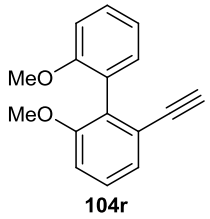
127.6 (d, J_{F-C} = 3.5 Hz), 128.0 (d, J_{F-C} = 19.2), 141.1, 150.9, 153.0, 159.1 ppm (d, J_{F-C} = 245.6).

^{19}F{^{1}H}-NMR (282 MHz, $CDCl_3$): δ = -112.6 ppm.

HRMS *calcd.* for $C_{17}H_{15}FNaO_3^+$: 309.089746 $[M+Na]^+$; *found*: 309.089731.

IR: ῡ = 662, 691, 741, 797, 874, 921, 960, 1005, 1064, 1089, 1113, 1170, 1209, 1235, 1251, 1272, 1298, 1411, 1432, 1454, 1470, 1503, 1564, 1597, 2839, 2938, 3000, 3283 cm^{-1}.

2-Ethynyl-2',6-dimethoxybiphenyl 104r



104r

Compound **104r** was prepared according to general procedure **G** from carbaldehyde **136r** (150 mg, 0.62 mmol). Purification of the crude product was performed by column chromatography on silica gel (hexanes/ethyl acetate, 15/1) affording the desired product **104r** as a white solid (136 mg, 93%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.81 (s, 1H), 3.69 (s, 3H), 3.72 (s, 3H), 6.92-6.96 (m, 2H), 6.99 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.16 (d, *J* = 1.8 Hz, 1H), 7.19 (d, *J* = 1.5 Hz, 1H), 7.21 (d, *J* = 1.8 Hz, 1H), 7.29-7.34 ppm (m, 1H).

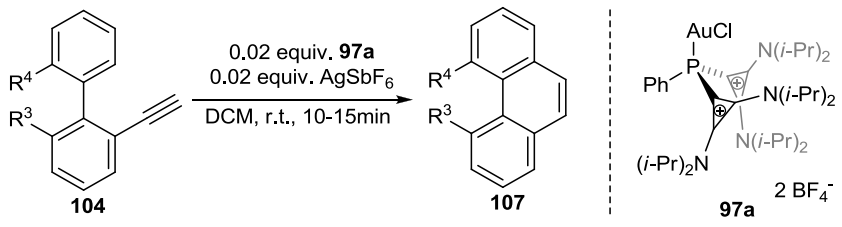
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 56.0, 56.1, 79.4, 82.9, 111.4, 112.0, 120.4, 123.8, 125.3, 126.0, 128.3, 129.1, 131.1, 131.7, 157.4, 157.4 ppm.

HRMS *calcd.* for $C_{16}H_{14}NaO_2^+$: 261.088596 $[M+Na]^+$; *found*: 261.088337.

IR: ῡ= 676, 745, 754, 793, 801, 907, 935, 1001, 1022, 1049, 1067, 1119, 1159, 1182, 1232, 1258, 1295, 1434, 1462, 1497, 1568, 1600, 1694, 1934, 2838, 2939, 3011, 3263, 3279 cm^{-1}.

6.5.5.4 Cycloisomerization

General procedure H: **Cycloisomerization of biphenyl alkynes**

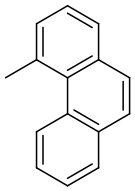


104 **107** **97a**

A solution of the desired biphenyl alkyne **104** (1.0 equiv.) in DCM (c = 0.05 M) solution was transferred *via* cannula to a *Schlenk*-flask previously charged with Au(I)-precatalyst **97a** (0.02

equiv) and silver hexafluoroantimonate (0.02 equiv.). The mixture was stirred at room temperature until full consumption of the starting material was detected *via* GC-MS (10-15 minutes unless stated otherwise) and then filtered over a short pad of Celite®. If necessary, further purification of the isolated compound was performed *via* column chromatography on silica gel and/or HPLC in order to afford phenanthrene **107** in analytical purity.

4-Methylphenanthrene 107b


107b

Alkyne **104b** (28.0 mg, 0.15 mmol) was treated with precatalyst **97a** (2.87 mg, 2.91 µmol) and silver hexafluoroantimonate (1.0 mg, 2.91 µmol) in DCM (3.0 mL) according to general procedure **H**. The crude material thus obtained was purified by column chromatography on silica gel (hexanes/ethyl acetate, 20/1) affording **107b** as a white solid (24.7 mg, 88%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.18 (s, 3H), 7.49 - 7.55 (m, 2H), 7.58-7.63 (m, 1H), 7.63-7.68 (m, 1H), 7.74 (s, 2H), 7.77-7.83 (m, 1H), 7.91-7.96 (m, 1H), 8.95 ppm (dd, *J* = 9.3, 8.2 Hz, 1H).

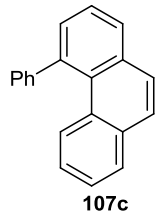
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 27.5, 125.7, 125.9, 126.0, 127.2, 127.6, 127.7, 128.1, 128.9, 130.2, 131.4, 131.8, 133.6, 133.9, 135.7 ppm.

HRMS *calcd*. for $C_{15}H_{12}$: 192.093898 $[M]^+$; *found*:192.093722.

IR: ϑ̃ = 666, 709, 735, 793, 820, 862, 895, 943, 957, 993, 1027, 1106, 1165, 1215, 1295, 1315, 1376, 1438, 1449, 1497, 1597, 2875, 2963, 3048 cm^{-1}.

The spectral data measured were in agreement with those reported in the literature.[83]

4-Phenylphenanthrene 107c



107c

Alkyne **104c**(33.3 mg, 0.13 mmol) was treated with precatalyst **97a** (2.6 mg, 2.62 µmol) and silver hexafluoroantimonate (0.9 mg, 2.62 µmol) in DCM (2.6 mL) according to general procedure **H**. Pale yellow solid (30.6 mg, 92%).

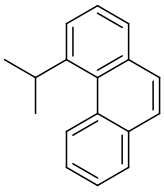
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.12 (ddd, *J* = 8.6, 7.0, 1.5 Hz, 1H), 7.38-7.54 (m, 7H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 9.4 Hz, 1H), 7.77 (q, *J* = 8.6 Hz, 2H), 7.84 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.90 ppm (dd, *J* = 7.9, 1.4 Hz, 1H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 125.0, 125.8, 126.1, 127.2, 127.5, 127.7, 128.4, 128.5, 128.6, 128.7, 129.1, 129.2, 130.5, 130.9, 133.6, 133.8, 140.7, 145.5 ppm.

HRMS *calcd*. for $C_{20}H_{14}^{+}$: 254.109551 $[M]^{+}$; *found*: 254.109307.

IR: ϑ = 673, 698, 721, 738, 765, 779, 799, 826, 872, 910, 948, 957, 1024, 1040, 1072, 1091, 1164, 1178, 1254, 1305, 1393, 1434, 1491, 1521, 1599, 2851, 2922, 3052 cm^{-1}.

4-*Iso*-propylphenanthrene 107h


107h

Alkyne **104h** (32.4 mg, 0.15 mmol) was treated with precatalyst **97a** (2.9 mg, 2.94 µmol) and silver hexafluoroantimonate (1.0 mg, 2.94µmol) in DCM (3.0 mL) according to general procedure **H**. The crude material thus obtained was purified by semi-preparative HPLC (YMC, 2 cm x 15 cm, CH_3CN/H_2O 75/25, 15 mL/min; 32.4 mg in 1.0 mL of CH_3CN) affording **107h** as a colorless oil (22.7 mg, 70%).

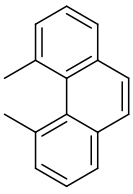
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.54 (d, *J* = 6.7 Hz, 6H), 4.34 (hept, *J* = 6.7 Hz, 1H), 7.56-7.63 (m, 3H), 7.68 (d, *J* = 1.3 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.88-7.95 (m, 1H), 8.60-8.67 ppm (m, 1H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ= 25.5, 31.2, 125.4, 125.7, 126.0, 126.2, 126.7, 126.8, 128.0, 128.1, 128.6, 129.4, 130.5, 133.5, 133.7, 147.0 ppm.

HRMS *calcd*. for $C_{17}H_{16}$: 220.125282 $[M]^{+}$; found: 220.125198.

IR: ϑ = 666, 713, 723, 740, 771, 797, 827, 865, 965, 1040, 1162, 1176, 1261, 1324, 1363, 1384, 1436, 1452, 1495, 1594, 1714, 2866, 2961, 3048 cm^{-1}.

4,5-Dimethylphenanthrene 107f


107f

Alkyne **104f** (20.6 mg, 0.10 mmol) was treated with precatalyst **97a** (2.0 mg, 1.99 µmol) and silver hexafluoroantimonate (0.7 mg, µmol 1.99 µmol) in DCM (2.0 mL) according to general procedure **H**. White solid (20.1 mg, 98%).

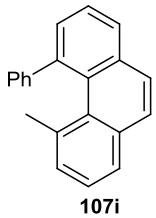
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.62 (s, 6H), 7.43 (dd, *J* = 7.2, 0.6 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.51 (s, 2H), 7.66 ppm (dd, *J* = 7.6, 0.8 Hz, 2H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 22.9, 124.8, 126.0, 126.6, 128.6, 130.5, 134.0, 135.9 ppm.

HRMS *calcd*. for $C_{16}H_{14}^{+}$: 206.109638 $[M]^{+}$; *found*: 206.109547.

IR: ϑ = 697, 718, 748, 756, 773, 814, 887, 1160, 1234, 1372, 1436, 1457, 2853, 2924, 2951, 3044 cm^{-1}.

4-Methyl-5-phenylphenanthrene 107i



107i

Alkyne **104i** (30.0 mg, 0.12 mmol) was treated with precatalyst **97a** (2.2 mg, 2.24 µmol) and silver hexafluoroantimonate (0.8 mg, 2.24 µmol) in DCM (2.4 mL) according to general procedure **H**. The crude material thus obtained was purified by column chromatography on silica gel (hexanes) affording **107i** as a colorless oil (28.8 mg, 96%).

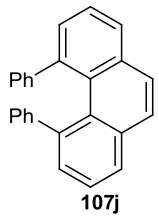
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.85 (s, 3H), 6.35-8.30 (m, 4H), 7.06 (d, *J* = 6.9 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.58-7.70 (m, 5H), 7.79 ppm (dd, *J* = 6.3, 2.8 Hz, 1H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 23.3, 125.0, 126.3, 126.4, 126.4, 126.7, 126.8, 127.5, 128.3, 128.7 (s_{br}), 128.8, 129.5, 130.6, 133.9, 135.0, 136.8, 141.6, 144.9 ppm.

HRMS *calcd*. for $C_{21}H_{16}^{+}$: 268.125017 $[M]^{+}$; *found*: 268.125200.

IR: ϑ = 696, 722, 749, 766, 813, 826, 882, 916, 965, 1030, 1074, 1115, 1164, 1176, 1244, 1263, 1302, 1376, 1412, 1437, 1493, 1568, 1596, 1927, 2851, 2922, 3044 cm^{-1}.

4,5-Diphenylphenanthrene 107j



107j

Alkyne **104j** (47.9 mg, 0.14 mmol) was treated with **97a** (2.9 mg, 2.90 µmol) and silver hexafluoroantimonate (1.0 mg, 2.90 µmol) in DCM (2.9 mL) according to general procedure **H**. White solid (43.0 mg, 90%).

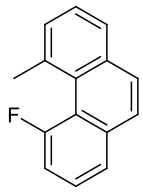
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.51-6.60 (m, 4H); 6.93-6.98 (m, 4H), 7.06 (tt, *J* = 7.4, 1.2 Hz, 2H), 7.13 (dd, *J* = 7.3, 1.2 Hz, 2H), 7.50 (t, *J* = 7.44 Hz, 2H), 7.69 (s, 2H), 7.76 ppm (dd, *J* = 7.8, 1.5 Hz, 2H).

^{13}C{^{1}H}-NMR (101MHz, $CDCl_3$): δ = 125.6, 126.7, 126.9, 127.2, 128.0, 128.3, 129.6, 129.7, 134.8, 142.2, 143.7 ppm.

HRMS *calcd*. for $C_{26}H_{18}^{+}$: 330.140852 $[M]^{+}$; *found*: 330.140898.

IR: ϑ =693, 726, 744, 771, 828, 868, 909, 943, 961, 1025, 1075, 1130, 1155, 1176, 1260, 1278, 1307, 1410, 1437, 1491, 1596, 1666, 1799, 1871, 1934, 2849, 2923, 3027, 3047, 3075 cm^{-1}.

4-Fluoro-5-methylphenanthrene 107k



107k

Alkyne **104k** (20.0 mg, 0.10 mmol) was treated with precatalyst **97a** (1.9 mg, 1.90 µmol) and silver hexafluoroantimonate (0.8 mg, 1.90 µmol) in DCM (1.9 mL) according to general procedure **H**. The crude material thus obtained was purified first by column chromatography on silica gel (hexanes/ethyl acetate, 35/1) and then by HPLC (YMC, 2 cm x 15 cm, methanol/H_2O 90/10, 10 mL/min; 18.2 mg in 1 mL methanol) affording **107k** as an orange oil (13.1 mg, 71%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.73 (d, *J* = 12.3 Hz, 3H), 7.25-7.32 (m, 1H), 7.51-7.58 (m, 3H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.63-7.70 ppm (m, 3H).

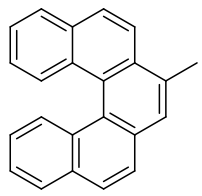
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ =23.7 (d, J_{F-C} = 24.1 Hz), 112.9 (d, J_{F-C} = 25.4 Hz), 119.4 (d, J_{F-C} = 14.0 Hz), 123.4 (d, J_{F-C} = 3.1 Hz), 125.6 (d, J_{F-C} = 3.1 Hz), 126.7, 127.1 (d, J_{F-C} = 9.7 Hz), 127.3 (d, J_{F-C} = 2.0 Hz), 128. 5 (d, J_{F-C} = 1.3 Hz), 128.5, 130.2, 133.5 (d, J_{F-C} = 0.8 Hz), 135.6 (d, J_{F-C} = 4.93 Hz), 137.1 (d, J_{F-C} = 1.0 Hz), 159.6 ppm (d, J_{F-C} = 252.2 Hz).

^{19}F{^{1}H}-NMR (282 MHz, $CDCl_3$): δ = -101.0 ppm.

HRMS *calcd*. for $C_{15}H_{11}F^+$: 210.084482 $[M]^+$; *found*: 210.084528.

IR: ϑ = 696, 713, 753, 780, 797, 819, 879, 892, 936, 960, 996, 1057, 1079, 1106, 1146, 1165, 1202, 1252, 1277, 1308, 1378, 1397, 1417, 1441, 1492, 1523, 1569, 1590, 1609, 1621, 1714, 1776, 1840, 1917, 2876, 2934, 2981, 3050 cm^{-1}.

Pentahelicene 138a


138a

Alkyne **137a** (35.0 mg, 0.12 mmol) was treated with precatalyst **97a** (2.8 mg, 2.39 µmol) and silver hexafluoroantimonate (0.8 mg, 2.39 µmol) in DCM (2.4 mL) according to general procedure **H**. The crude material thus obtained was purified by column chromatography on silica gel (pentane/DCM, 80/1) affording **138a** as a pale yellow oil of high viscosity (32 mg, 91%).

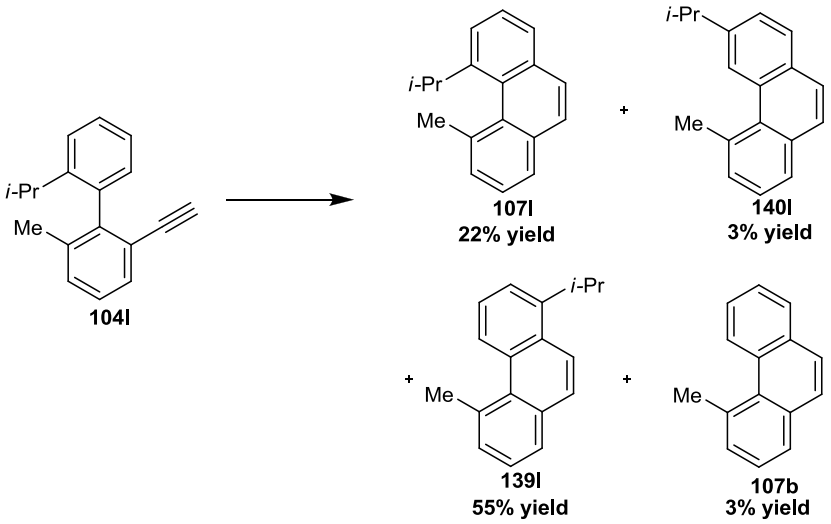
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.84 (s, 3H), 7.22-7.28 (m, overlaps with solvent signal, 2H), 7.46-7.54 (m, 2H), 7.72 (s, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.88-7.99 (m, 4H), 8.09 (d, *J* = 8.8 Hz, 1H), 8.39 (dd, *J* = 8.5, 3.8 Hz, 1H), 8.48 ppm (dd, *J* = 8.5, 3.8 Hz, 1H).

$^{13}C\{^1H\}$-NMR (400 MHz, $CDCl_3$): δ = 20.2, 122.3, 124.4, 124.5, 125.7, 125.9, 126.1, 126.3, 127.3, 127.5, 127.7, 127.8, 128.0, 129.0, 129.1, 129.6, 130.9, 131.0, 131.8, 132.0, 132.1, 132.3, 133.2 ppm.

HRMS *calcd*. for $C_{23}H_{16}^+$: 292.125200 $[M]^+$; *found*: 292.125095.

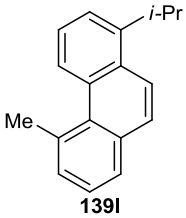
IR: ϑ = 416, 449, 478, 505, 521, 589, 630, 655, 695, 741, 803, 875, 947, 958, 1030, 1083, 1126, 1159, 1243, 1320, 1338, 1375, 1432, 1515, 1601, 1749, 1835, 1898, 1916, 3855, 2914, 3015, 3052 cm^{-1}.

4-*Iso*-propyl-5-methylphenanthrene 107l, 3-*iso*-propyl-5-methylphenanthrene 140l, 1-*iso*-propyl-5-methylphenanthrene 139l



Alkyne **104l** (95.7 mg, 0.41 mmol) was treated with precatalyst **97a** (8.1 mg, 8.17 µmol) and silver hexafluoroantimonate (2.8 mg, 8.17 µmol) in DCM (8.2 mL) according to general procedure **H**. The crude material thus obtained was purified by semi-preparative HPLC (YMC, 2 cm x 15 cm, CH_3CN/H_2O 75/20, 10 mL/min; 19.5 mg in 1.4 mL of CH_3CN and 0.1 mL of H_2O) obtaining four different products (three isomers).

1-*Iso*-propyl-5-methylphenanthrene 139l



White solid (52.6 mg, 55%).

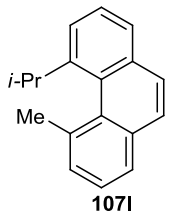
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.50 (dd, *J* = 6.9, 2.2 Hz, 6H), 3.19 (s, 3H), 3.90 (sept, *J* = 6.7 Hz, 1H), 7.50-7.54 (m, 2H), 7.62-7.66 (m, 2H), 7.78 -7.82 (m, 2H), 8.13 (d, *J* = 9.2, 1.3 Hz, 1H), 8.80-8.82 ppm (m, 1H).

$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 24.0, 27.6, 29.2, 121.9, 122.2, 125.0, 125.7, 125.9, 127.2, 127.8, 131.0, 131.1, 131.4, 132.0, 133.2, 135.6, 144.9 ppm.

HRMS *calcd*. for $C_{18}H_{18}^+$: 234.140849 $[M]^+$; *found*: 234.140628.

IR: ϑ = 721, 747, 774, 819, 829, 893, 960, 1054, 1102, 1164, 1190, 1216, 1275, 1310, 1359, 1377, 1410, 1434, 1448, 1594, 1784, 1922, 2867, 2923, 2959, 3047 cm^{-1}.

4-*Iso*-propyl-5-methylphenanthrene 107l



107l

White solid (21.0 mg, 22%).

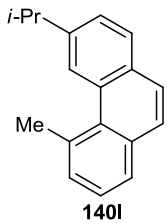
^1H-NMR (400 MHz, $CDCl_3$): δ = 0.57 (d, *J* = 6.6 Hz, 3H), 1.69 (d, *J* = 6.8 Hz, 3H), 2.68 (s, 3H), 3.78 (sept, *J* = 6.7 Hz, 1H), 7.37-7.39 (m, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.49 (m, 2H), 7.52-7.57 (m, 2H), 7.61-7.66 ppm (m, 2H).

$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 21.2, 23.2, 28.3, 32.1, 123.0, 124.9, 125.1, 125.8, 126.5, 126.6, 126.8, 128.1, 128.2, 130.2, 134.0, 134.2, 135.8, 147.9 ppm.

HRMS *calcd*. for $C_{18}H_{18}^+$: 234.140848 $[M]^+$; *found*: 234.140779.

IR: ϑ = 699, 725, 751, 768, 792, 813, 824, 862, 891, 925, 961, 979, 995, 1037, 1044, 1090, 1114, 1172, 1216, 1230, 1265, 1300, 1361, 1383, 1418, 1438, 1459, 1565, 1594, 1716, 1772, 2865, 2924, 2952, 3044 cm^{-1}.

3-*Iso*-propyl-5-methylphenanthrene 140l



140l

White solid (2.9 mg, 3%).

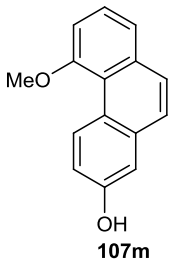
^1H-NMR (300 MHz, $CDCl_3$): δ = 1.41 (d, *J* = 6.8 Hz, 6H), 3.17-3.22 (m, 4H), 7.47-7.52 (m, 3H), 7.65-7.70 (m, 2H), 7.75-7.77 (m, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 8.78 ppm (s, 1H).

$^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): δ = 24.3, 27.5, 34.8, 125.0, 125.2, 125.8, 127.0, 127.3, 127.6, 128.7, 130.3, 131.2, 131.9, 131.9, 134.0, 135.5, 146.2 ppm.

HRMS *calcd*. for $C_{18}H_{18}^+$: 234.140848 $[M]^+$; *found*: 234.140779.

IR: ϑ = 716, 757, 791, 812, 838, 893, 957, 1018, 1032, 1052, 1078, 1104, 1133, 1149, 1193, 1216, 1234, 1292, 1312, 1359, 1378, 1407, 1431, 1450, 1459, 1500, 1522, 1569, 1595, 1615, 2869, 2928, 2957, 3047 cm^{-1}.

5-Methoxyphenanthren-2-ol 107m



107m

Alkyne **104m** (32.6 mg, 0.15 mmol) was treated with precatalyst **97a** (2.9 mg, 2.90 µmol) and silver hexafluoroantimonate (1.0 mg, 2.90 µmol) in DCM (2.9 mL) according to general procedure **H**. The crude material thus obtained was purified by column chromatography on silica gel (hexanes/ethyl acetate, 7/3) affording **107m** as a white solid (30.2 mg, 93%).

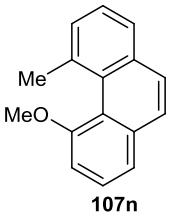
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.12 (s, 3H), 5.10 (s, 1H), 7.14 (dd, *J* = 6.9, 2.2 Hz, 1H), 7.20 (dd, *J* = 9.2, 2.9 Hz, 1H), 7.23 (d, *J* = 2.8 Hz, 1H), 7.45-7.54 (m, 2H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 9.59 ppm (d, *J* = 9.2 Hz, 1H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 55.8, 108.5, 111.8, 116.2, 121.1, 121.8, 124.9, 125.7, 127.2, 128.0, 130.8, 133.7, 134.7, 153.4, 158.3 ppm.

HRMS *calcd*. for $C_{15}H_{12}O_2^+$: 224.083727 $[M]^+$; *found*: 224.083483.

IR: ϑ = 708, 752, 788, 805, 827, 859, 877, 943, 966, 994, 1073, 1098, 1139, 1154, 1220, 1256, 1266, 1312, 1336, 1352, 1429, 1449, 1529, 1573, 1614, 2833, 2934, 3192 cm^{-1}.

4-Methoxy-5-methylphenanthrene 107n



107n

Alkyne **104n** (32.2 mg, 0.14 mmol) was treated with precatalyst **97a** (2.9 mg, 2.89 µmol) and silver hexafluoroantimonate (1.0 mg, 2.89 µmol) in DCM (2.9 mL) according to general procedure **H**. White solid (29.0 mg, 91%).

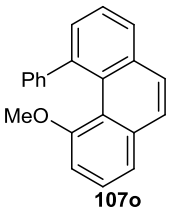
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.61 (s, 3H), 3.97 (s, 3H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.46-7.67 ppm (m, 7 H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 24.2, 55.0, 107.5, 120.0, 120.9, 124.9, 125.8, 125.9, 127.0, 127.9, 128.8, 129.3, 133.5, 135.2, 137.4, 157.0 ppm.

HRMS *calcd*. for $C_{16}H_{14}O^+$: 222.104467 $[M]^+$; *found*: 222.104643.

IR: ϑ =698, 716, 750, 793, 817, 860, 888, 921, 977, 994, 1020, 1096, 1145, 1164, 1185, 1240, 1261, 1311, 1332, 1374, 1414, 1432, 1450, 1491, 1522, 1568, 1600, 1777, 1907, 2832, 2926, 2956, 2992, 3048 cm^{-1}.

4-Methoxy-5-phenylphenanthrene 107o



107o

Alkyne **104o** (42.6 mg, 0.15 mmol) was treated with precatalyst **97a** (3.0 mg, 2.99 µmol) and silver hexafluoroantimonate (1.0 mg, 2.99 µmol) in DCM (3.0 mL) according to general procedure **H**. White solid (40.0 mg, 93%).

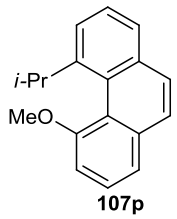
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.06 (s, 3H), 6.67 (quin, *J* = 4.5 Hz, 1H), 7.16-7.22 (m, 1H), 7.30-7.31 (m, 4H), 7.45 (d, *J* = 4.6 Hz, 2H), 7.59 (d, *J* = 4.9 Hz, 2H) 7.64 (d, *J* = 8.7 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.76-7.81 ppm (m, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 53.4, 107.0, 119.8, 120.8, 125.9, 126.1, 126.1, 126.3, 126.7, 126.8, 127.3, 127.6, 128.4, 129.9, 134.3, 135.1, 141.8, 146.8, 156.0 ppm.

HRMS *calcd*. for $C_{21}H_{16}O$: 284.120116 $[M]^+$; *found*: 284.120169.

IR: ῡ = 667, 689, 719, 744, 771, 788, 815, 867, 916, 1001, 1062, 1091, 1111, 1167, 1181, 1203, 1242, 1257, 1289, 1395, 1409, 1428, 1462, 1501, 1578, 1592, 1681, 1693, 2761, 2869, 2939, 2977 cm^{-1}.

4-*Iso*-propyl-5-methoxyphenanthrene 107p



107p

Alkyne **104p** (36.2 mg, 0.15 mmol) was treated with precatalyst **97a** (2.9 mg, 2.91 µmol) and silver hexafluoroantimonate (1.0 mg, 2.91 µmol) in DCM (2.9 mL) according to general procedure **H**. White solid (32.9 mg, 91%)

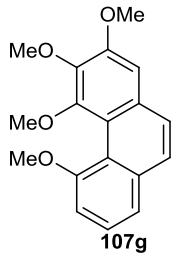
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.23 (s_{br}, 6H), 3.59 (sept, *J* = 6.7 Hz, 1H), 3.91 (s, 3H), 7.01 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.45 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.48-7.63 ppm (m, 6H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 33.2, 38.2, 55.4, 107.2, 120.0, 120.7, 124.0, 124.9, 125.9, 126.4, 126.5, 126.7, 127.8, 133.4, 135.3, 149.2, 156.7 ppm.

HRMS *calcd*. for $C_{18}H_{18}O^+$: 250.135764 $[M]^+$; *found*: 250.135535.

IR: ῡ= 699, 723, 757, 815, 824, 860, 891, 920, 988, 1043, 1085, 1151, 1171, 1221, 1235, 1259, 1302, 1328, 1359, 1379, 1416, 1431, 1451, 1491, 1521, 1567, 1601, 1613, 1726, 1777, 1912, 2867, 2932, 2951, 2984, 3047 cm^{-1}.

2,3,4,5-Tetramethoxyphenanthrene 107g



107g

Alkyne **104g** (44.7 mg, 0.15 mmol) was treated with precatalyst **97a** (3.0 mg, 3.00 µmol) and silver hexafluoroantimonate (1.0 mg, 3.00 µmol) in DCM (3.0 mL) according to general procedure **H**. White solid (44.0 mg, 98%).

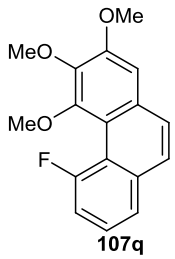
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 3H), 4.01 (s, 6H), 4.02 (s, 3H), 7.00 (s, 1H), 7.06 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.40 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.49-7.53 ppm (m, 2H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 56.1, 56.2, 60.9, 61.4, 103.6, 108.1, 117.1, 119.7, 119.9, 126.2, 126.3, 126.7, 130.5, 133.9, 142.5, 152.5, 152.8, 157.6 ppm.

HRMS *calcd*. for $C_{18}H_{18}NaO_4^+$: 321.109729 $[M+Na^+]^+$; *found*: 321.109738.

IR: ϑ =688, 728, 766, 782, 814, 835, 908, 925, 953, 1003, 1048, 1079, 1096, 1111, 1138, 1197, 1229, 1342, 1386, 1423, 1465, 1496, 1510, 1560, 1602, 2249, 2832, 2853, 2932, 2996, 3047 cm^{-1}.

5-Fluoro-2,3,4-trimethoxyphenanthrene 107q



107q

Alkyne **104q** (40.0 mg, 0.14 mmol) was treated with precatalyst **97a** (2.8 mg, 2.79 µmol) and silver hexafluoroantimonate (1.0 mg, 2.79 µmol) in DCM (1.9 mL) according to general procedure **H**. The crude material thus obtained was purified by column chromatography on silica gel (pentane/MTBE, 5/1) affording **171** as a yellow oil (35 mg, 88%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.16 (d, *J* = 0.9 Hz, 3H), 4.24 (d, *J* = 1.2 Hz, 6H), 7.26 (C**H**$_{Ar}$ hidden under solvent signal), 7.46-7.53 (m, 1H), 7.65-7.73 (m, 1H), 7.76-7.77 (m, 2H), 7.81 ppm (dd, *J* = 8.4, 0.8 Hz, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ =56.1, 61.3, 60.4 (d, J_{F-C} = 4.8 Hz), 104.2, 113.3 (d, J_{F-C} = 25.9 Hz) 116.2 (d,J_{F-C} = 4.3 Hz), 117.8 (d, J_{F-C} = 14.9 Hz), 123.5 (d, J_{F-C} = 3.2 Hz), 126.2, 126.2 (d, J_{F-C} = 7.3 Hz), 127.2 (d, J_{F-C} = 1.2 Hz), 130.5, 134.5 (d, J_{F-C} = 4.9 Hz), 143.1, 152.2, 153.5, 159.9 ppm (d, J_{F-C} = 255.7 Hz).

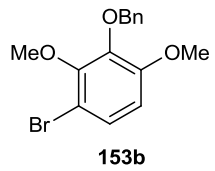
^{19}F{^{1}H}-NMR(282 MHz, $CDCl_3$): δ = -97.9 ppm.

HRMS *calcd*. for $C_{17}H_{15}FNaO_3^+$: 309.089743 $[M+Na]^+$; *found*: 309.089110.

IR: ϑ = 679, 738, 748, 783, 816. 838, 882, 910, 927, 968, 999, 1069, 1104, 1139, 1169, 1192, 1206, 1231, 1243, 1275, 1345, 1388, 1425, 1444, 1466, 1496, 1514, 1561, 1595, 1608, 2834, 2857, 2936, 2988, 3055 cm^{-1}.

6.5.5.5 Synthesis of *Calanquinone C*

2-(Benzyloxy)-4-bromo-1,3-dimethoxybenzene 153b



153b

To a suspension of 3-bromo-2,6-dimethoxyphenol **153a (**1.8 g, 7.72 mmol) and potassium carbonate (1.6 g 11.59 mmol) in acetone (40 mL), benzyl bromide (0.96 mL, 1.38 g, 8.07 mmol) was added and the reaction mixture stirred overnight at room temperature. Removal of the solvents *in vacuo* afforded a crude material, which was purified by column chromatography on silica gel (hexane/ethyl acetate, 9/1) affording **153b** as a colorless oil (2.2 g, 88%).

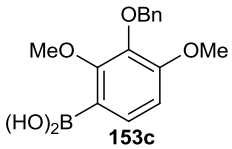
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3H), 3.90 (s, 3H), 5.03 (s, 2H), 6.59 (d, *J* = 9.0 Hz, 1H), 7.22 (d, *J* = 8.9 Hz, 1H), 7.32-7.39 (m, 3H), 7.48-7.53 ppm (m, 2H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 56.3, 61.3, 75.6, 108.6, 108.9, 127.1, 128.2, 128.5, 137.5, 142.7, 151.5, 153.8 ppm.

HRMS *calcd*. for $C_{15}H_{15}BrNaO_3^+$: 345.009358 $[M+Na]^+$; *found*: 345.009358.

IR: ϑ = 694, 734, 791, 876, 915, 980, 1008, 1088, 1179, 1214, 1226, 1271, 1293, 1371, 1413, 1438, 1460, 1473, 1574, 2837, 2937 cm^{-1}.

3-(Benzyloxy)-2,4-dimethoxyphenylboronic acid 153c



153c

2-(Benzyloxy)-4-bromo-1,3-dimethoxybenzene **153b** (1.6 g, 4.95 mmol) was dissolved in diethyl ether (40 mL) and cooled to -78 °C. *n*-Butyl lithium (1.98 mL, 4.95 mmol, c = 2.5 M in hexanes) was then added dropwise over 30 minutes and the resulting solution was stirred for 1 hour at -78 °C. Then trimethylborate (1.69 mL, 14.85 mmol) was added and the mixture allowed to warm to room temperature overnight. After quenching the reaction with $HCl_{(aq)}$ (20 mL, c = 3 M), the aqueous phase was extracted with MTBE (3x) and dried over sodium sulfate. Removal of the solvent *in vacuo* afforded crude **153c**, which was purified by column chromatography on silica gel (hexane/ethyl acetate, 6/4). White solid (935 mg, 66%). The compound should be stored at -20 °C under argon as it decomposes slowly over time at room temperature.

^{1}H-NMR (300 MHz, CD_3CN): δ = 3.86 (s, 3H), 3.94 (s, 3H), 4.99 (s, 2H), 6.32 (s, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 7.33-7.42 (m, 3H), 7.46 (d, *J* = 8.4, 1H),7.48-7.51 ppm (m, 2H).

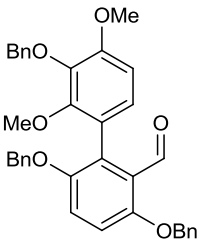
^{13}C{^{1}H}-NMR (75 MHz, CD_3CN): δ = 56.7, 62.5, 75.7, 109.3, 129.0, 129.3, 129.3, 132.1, 138.9, 141.0, 157.7, 160.2 ppm.

^{11}B{^{1}H}-NMR (96 MHz, CD_3CN): δ = 28.7 ppm.

HRMS *calcd*. for $C_{15}H_{17}BNaO_5^+$: 311.107456 $[M+Na]^+$; *found*: 311.107270.

IR: ῡ = 693, 725, 751, 805, 896, 981, 1004, 1063, 1089, 1185, 1225, 1278, 1342, 1377, 1434, 1457, 1498, 1596, 2838, 2929, 3000, 3358 cm^{-1}.

3,3',6-Tris(benzyloxy)-2',4'-dimethoxybiphenyl-2-carbaldehyde 155



155

Compound **155** was prepared according to general procedure **F** from 3,6-dibenzyloxy-2-bromobenzaldehyde **154** (110 mg, 0.28 mmol) and 3-(benzyl-oxy)-2,4-dimethoxyphenylboronic acid **153c** (120 mg, 0.42 mmol) employing 5 mol% of tris(dibenzylidenaceton)dipalladium and 10 mol% of tricyclohexylphosphine as a catalytic mixture. Once the reaction was finished the work-up was performed as described and the crude material purified by column chromatography on silica gel (hexane/ethyl acetate, 4/1) affording **155** as a pale yellow solid (130 mg, 84%).

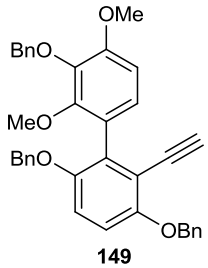
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.61 (s, 3H), 3.81 (s, 3H), 4.86 (d, *J* = 12.2 Hz, 1H), 4.90 (d, *J* = 12.2 Hz, 1H), 4.99 (s, 2H), 5.11 (s, 2H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.93 (d, *J* = 9.1 Hz, 1H), 7.07- 7.11 (m, 3H), 7.16- 7.22 (m, 3H), 7.24- 7.36 (m, 6H), 7.43- 7.45 (m, 4H), 10.11 ppm (s, 1H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 56.3, 61.1, 71.6, 71.9, 75.4, 107.4, 113.8, 120.0, 121.8, 126.0, 126.2, 127.1, 127.4, 127.8, 128.0, 128.2, 128.4, 128.5, 128.6, 128.8, 132.0, 136.9, 137.3, 138.0, 141.3, 151.0, 152.2, 154.1, 154.4, 191.4 ppm.

HRMS *calcd*. for $C_{36}H_{32}NaO_6^+$: 583.209108 $[M+Na]^+$; *found*: 583.208933.

IR: ῡ= 692, 731, 744, 767, 800, 810, 841, 906, 965, 991, 1088, 1130, 1171, 1197, 1262, 1286, 1374, 1382, 1411, 1452, 1477, 1497, 1586, 1683, 2863, 2935, 3032, 3064 cm^{-1}.

3,3',6'-Tris(benzyloxy)-2'-ethynyl-2,4-dimethoxybiphenyl 149



149

Compound **149** was prepared according to general procedure **G** from carbaldehyde **155** (130 mg, 0.23 mmol). Purification of the crude material thus obtained was performed by column chromatography on silica gel (pentane/ethyl acetate, 10/1) affording **149** as a pale yellow solid (86 mg, 67%).

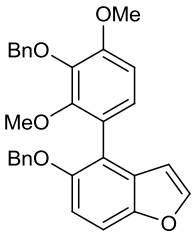
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.20 (s, 1H), 3.74 (s, 3H), 3.89 (s, 3H), 4.92 (d, *J* = 12.1 Hz, 1H), 4.98 (d, *J* = 12.2 Hz, 1H), 5.08 (s, 2H), 5.19 (s, 2H), 6.76 (d, *J* = 8.6 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.93- 6.97 (m, 2H), 7.19- 7.28 (m, 5H), 7.31- 7.42 (m, 6H),7.51- 7.54 ppm (m, 4H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 56.1, 61.3, 71.3, 71.6, 75.3, 79.0, 85.0, 107.1, 112.8, 114.3, 115.4, 123.8, 125.9, 127.0, 127.1, 127.6, 127.8, 127.9, 128.3, 128.4, 128.4, 128.6, 133.9, 137.3, 137.5, 138.1, 141.1, 151.0, 152.4, 153.8, 154.8 ppm.

HRMS *calcd*. for $C_{37}H_{32}NaO_5^+$: 579.214195 $[M+Na]^+$; *found*: 579.214523.

IR: ῡ = 691, 726, 808, 852, 913, 970, 1007, 1065, 1094, 1137, 1172, 1203, 1222, 1265, 1288, 1376, 1413, 1447, 1475, 1497, 1588, 1604, 2931, 3027, 3067, 3255 cm^{-1}.

5-(Benzyloxy)-4-(3-(benzyloxy)-2,4-dimethoxyphenyl)benzofuran 157



157

Compound **157** was isolated as byproduct from the previous alkynylation reaction. Yellow oil (25 mg, 23%).

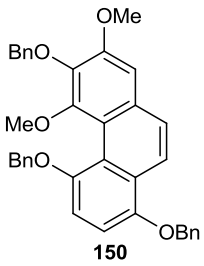
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.59 (s, 3H), 3.92 (s, 3H), 5.01 (d, *J* = 11.9 Hz; 1H), 5.05 (d, *J* = 12.0 Hz; 1H), 5.10 (s, 2H), 6.47 (dd, *J* = 2.1, 0.8 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 7.07 (d, *J* = 9.0 Hz, 1H), 7.23-7.27 (m, 3H), 7.30-7.38 (m, 5H), 7.41 (d, *J* = 8.9, 0.8 Hz, 1H),7.52-7.54 (m, 2H), 7.58 ppm (d, *J* = 2.3 Hz, 1H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 56.2, 61.3, 72.8, 75.4, 106.8, 107.3, 110.6, 112.9, 121.1, 123.0, 126.3, 127.4, 127.6, 128.0, 128.4, 128.4, 128.5, 129.1, 137.9, 138.0, 141.3, 145.8, 150.3, 152.1, 152.7, 153.7 ppm.

HRMS *calcd*. for $C_{30}H_{26}NaO_5^+$: 489.167248 $[M+Na]^+$; *found*: 489.167179.

IR: ϑ = 696, 733, 796, 843, 911, 994, 1028, 1044, 1081, 1112, 1150, 1194, 1216, 1262, 1346, 1370, 1439, 1464, 1497, 1510, 1602, 1659, 2848, 2931, 3032 cm^{-1}.

1,4,6-Tris(benzyloxy)-5,7-dimethoxyphenanthrene 150



150

A solution of **149** (78.0 mg, 0.12 mmol) in toluene (0.48 mL) was heated to 50 °C and transferred *via* cannula to a *Schlenk*-flask charged with Au(I)-precatalyst **97h** (0.9 mg, 0.61 µmol) and silver hexafluoroantimonate (0.22 mg, 0.61 µmol)[84]. The reaction was stirred at 50 °C until full consumption of the starting material could be detected by TLC (4 hours). Then, the reaction mixture was filtered over a short pad of silica gel and the residue rinsed with ethyl acetate. Solvent removal *in vacuo* afforded a crude material, which was purified by column chromatography on silica gel (pentane/ethyl acetate, 9/1). White solid (69 mg, 89%).

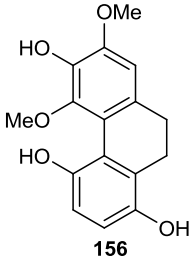
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.61 (s, 3H), 3.96 (s, 3H), 5.00 (s, 2H), 5.14 (s, 2H), 5.24 (s, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.99 (s, 1H), 7.08 (d, *J* = 8.6 Hz, 1H), 7.17-7.27 (m, overlaps with solvent signal, 3H), 7.29-7.38 (m, 4H), 7.41-7.56 (m, 9H), 8.11 ppm (d, *J* = 8.8 Hz, 1H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 56.1, 61.1, 71.2, 71.9, 75.9, 103.2, 107.6, 110.0, 117.3, 120.0, 121.2, 124.9, 126.2, 127.6, 127.7, 127.8, 127.9, 128.0, 128.3, 128.3, 128.4, 128.7, 130.8, 137.7, 138.2, 138.3, 141.4, 148.8, 151.4, 153.2, 152.2 ppm.

HRMS *calcd*. for $C_{37}H_{32}NaO_5^+$: 579.214196 $[M+Na]^+$; *found*: 579.214280 .

IR: ϑ = 696, 733, 796, 843, 911, 994, 1028, 1044, 1081, 1112, 1150, 1194, 1216, 1262, 1346, 1370, 1439, 1464, 1497, 1510, 1602, 1659, 2848, 2931, 3032 cm^{-1}.

***Calanhydroquinone A* 156**



156

Compound **150** (140 mg, 0.25 mmol) and (10% m/w) Pd/C (26.5 mg, 0.025 mmol) were suspended in an ethanol/DCM mixture (3/1, 8 mL) in an autoclave and stirred overnight at room temperature under hydrogen atmosphere (20 bar). Then, the suspension was filtered over a short pad of Celite®, the residue rinsed with acetone (80 mL) and the solvent removed *in vacuo*. The crude material thus obtained was purified by column

chromatography on silica gel (pentane/ethyl acetate, 6/4) affording **156** as an orange solid (65 mg, 89%).

^{1}H-NMR (400 MHz, CD_3CN): δ = 2.54-2.57 (m, 2H), 2.65 (m, 2H), 3.62 (s, 3H), 3.88 (s, 3H), 6.49 (s, 1H), 6.54 (s, 1H), 6.72 (d, *J* = 8.6 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 6.83 (s, 1H), 8.10 ppm (s, 1H).

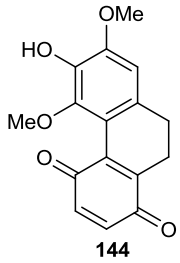
^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 22.7, 30.2, 56.5, 62.1, 107.8, 116.2, 117.8, 119.2, 121.4, 125.8, 132.3, 137.3, 142.8, 145.2, 146.5, 147.9 ppm.

HRMS *calcd*. for $C_{16}H_{16}NaO_5^+$: 311.088993 $[M+Na]^+$; *found*: 311.089100.

IR: ϑ = 731, 800, 834, 899, 929, 978, 1014, 1032, 1050, 1093, 1147, 1191, 1231, 1258, 1282, 1329, 1356, 1385, 1455, 1499, 1559, 1609, 1646, 2851, 2925, 3226, 3408 cm^{-1}.

The spectral data measured were in agreement with those reported in the literature.[61]

***Calanquinone C* 144**



144

Cerium ammoniumnitrate (140 mg, 0.255 mmol) was dissolved in water (2 mL) and added to a solution of *calanhydroquinone A* **156** (37 mg, 0.128 mmol) in THF (6 mL) over 30 minutes at room temperature. After extracting the reaction mixture with diethyl ether (20 mL), the organic phase was washed with saturated $NaHCO_{3(aq)}$ (2x) and water (1x). Then, the organic phase was dried over sodium sulfate. Subsequent solvent removal afforded **144** as a crude product. The crude material was purified by column chromatography on silica gel (pentane/ethyl acetate, 7/3). Deep red solid (25.3 mg, 69%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.51-2.57 (m, 2H), 2.60-1.66 (m, 2H), 3.89 (s, 3H), 3.92 (s, 3H), 5.52 (s_{br}, 1H), 6.55 (s, 1H), 6.72 (d, *J* = 10.1 Hz, 1H), 6.83 ppm (d, *J* = 10.1 Hz, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 20.5, 28.5, 56.5, 60.9, 105.6, 116.3, 131.9, 135.5, 137.4, 137.5, 140.5, 141.0, 145.5, 149.3, 185.6, 185.9 ppm.

HRMS *calcd*. for $C_{16}H_{14}NaO_5^+$: 309.073341 $[M+Na]^+$; *found*: 309.073410.

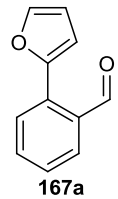
IR: ϑ = 834, 915, 1061, 1095, 1138, 1283, 1358, 1385, 1465, 1497, 1558, 1607, 1646, 1664, 2848, 2927, 3402 cm^{-1}.

The spectral data measured were in agreement with those reported in the literature.[61]

6.5.6 Cycloisomerization of 2-(ethynylaryl)furans

6.5.6.1 Synthesis Carbaldehydes

2-(Furan-2-yl)benzaldehyde 167a


167a

A microwave vial was charged with 2-bromobenzaldehyde **135g** (316 µL, 500.0 mg, 2.70 mmol), furan-2-boronic acid (393.1 mg, 3.51 mmol), sodium carbonate (429.6 mg, 4.15mmol), bis(triphenylphosphine)palladium chloride (94.8 mg, 0.135 mmol) and an acetonitrile/water mixture (1/1, 16.2 mL). The vessel was sealed with a Teflon crimp top and the suspension heated to 150 °C under microwave irradiation for 1.5 hours. Then brine was added and the aqueous phase was extracted with ethyl acetate (3x). The combined organic phases were dried over sodium sulfate and the solvent was removed *in vacuo* to afford a crude material, which was purified by column chromatography on silica gel (pentane/MTBE, 30/1).Yellow oil (302.7 mg, 65%).

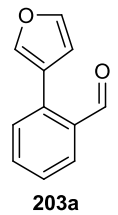
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.56 (dd, *J* = 3.5, 1.9 Hz, 1H), 6.63 (dd, *J* = 3.3, 0.6 Hz, 1H), 7.41-7.46 (m, 1H), 7.58-7.70 (m, 3H), 7.98 (dd, *J* = 7.7, 1.3 Hz, 1H), 10.38 ppm (d, *J* = 0.8 Hz, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 111.4, 112.1, 128.2, 128.7, 128.6, 133.4, 133.6, 133.7, 144.2, 151.4, 192.5 ppm.

HRMS *calcd.* for $C_{11}H_8O_2^+$: 172.052432 $[M]^+$; *found*: 172.052257.

IR: ϑ = 671, 692, 740, 761, 823, 885, 905, 960, 1006, 1028, 1078, 1105, 1156, 1194, 1217, 1254, 1277, 1300, 1343, 1375, 1397, 1439, 1461, 1476, 1498, 1598, 1683, 1774, 2759, 2854, 3067, 3120, 3146 cm^{-1}.

2-(Furan-3-yl)benzaldehyde 167b


203a

A microwave vial was charged with 2-bromobenzaldehyde (148 µl, 234.3 mg, 1.27 mmol), furan-3-boronic acid (170 mg, 1.52 mmol), triethylamine (529 µL, 385 mg, 3.80 mmol), tetrakis(triphenylphosphine)palladium (117.1 mg, 0.101 mmol) and DMF (9 mL). The vessel was sealed with a Teflon crimp top and the suspension was heated to 130 °C under microwave irradiation for 5 hours. Then the reaction was diluted with an equal amount of water, and extracted with MTBE (4x). The combined organic phases were washed with saturated $NH_4Cl_{(aq)}$ (1x), brine (3x), and dried over sodium sulfate. Finally, the solvent was removed *in vacuo* and the crude material

was purified by column chromatography on silica gel (pentane/MTBE, 30/1) to afford **203a** as a yellow oil (132.2 mg, 60%).

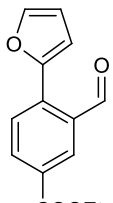
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.59 (dd, *J* = 1.8, 1.0 Hz, 1H), 7.43-7.49 (m, 2H), 7.54-7.56 (m, 2H), 7.59-7.64 (m, 1H), 7.98-8.01 (m, 1H), 10.23 ppm (d, *J* = 0.7 Hz, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 112.4, 122.7, 128.0, 128.0, 130.8, 134.0, 134.2, 136.6, 141.4, 143.7, 192.8 ppm.

HRMS *calcd.* for $C_{11}H_8O_2^+$: 172.052433 $[M]^+$; *found*: 172.052273.

IR: ῡ = 659, 690, 762, 798, 824, 873, 923, 961, 1015, 1035, 1055, 1116, 1161, 1197, 1238, 1262, 1290, 1312, 1356, 1394, 1447, 1474, 1506, 1585, 1600, 1649, 1686, 1775, 2759, 2852, 3067, 3130, 3146 cm^{-1}.

Ethyl 3-formyl-4-(furan-2-yl)benzoate 167c



167c

A microwave vial was charged with ethyl 4-bromo-3-formylbenzoate **135i** (234.0 mg, 0.91 mmol), furan-2-boronic acid (122.1 mg, 0.109 mmol), triethylamine (381 µL, 276.2 mg, 2.73 mmol), tetrakis(triphenyl-phosphine)palladium (84.1 mg, 0.073 mmol) and DMF (6.5 mL). The vessel was sealed with a Teflon crimp top and the suspension heated to 130 °C under microwave irradiation for 5 hours. After this time, the reaction mixture was diluted with an equal amount of water and extracted with MTBE (4x). The combined organic phases were washed with saturated $NH_4Cl_{(aq)}$ (1x), brine (3x), and dried over sodium sulfate. Removal of the solvents *in vacuo* afforded a residue, which was purified by column chromatography on silica gel (pentane/MTBE, 20/1). Yellow solid (113 mg, 51%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.42 (t, *J* = 7.2 Hz, 3H), 4.41 (q, *J* = 7.2 Hz, 2H), 6.60-6.61 (m, 1H), 6.78 (d, *J* = 3.6 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 8.25 (dd, *J* = 8.2, 1.9 Hz, 1H), 8.61 (d, *J* = 1.8 Hz, 1H), 10.46 ppm (s, 1H).

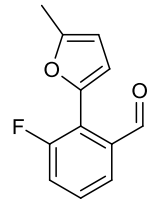
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 14.5, 61.7, 112.6, 113.1, 128.3, 129.9, 131.5, 133.0, 134.2, 136.5, 145.0, 150.7, 165.7, 191.8 ppm.

HRMS *calcd.* for $C_{14}H_{12}O_4^+$: 244.075362 $[M]^+$; *found*: 244.073364.

IR: ῡ = 3147, 3119, 2996, 2974, 2910, 1772, 1707, 1677, 1602, 1577, 1550, 1499, 1476, 1458, 1448, 1398, 1367, 1302, 1279, 1244, 1229, 1183, 1159, 1128, 1116, 1097, 1074, 1043, 1017, 951, 928, 905, 887, 869, 858, 820, 765, 746, 710, 679 cm^{-1}.

3-Fluoro-2-(5-methylfuran-2-yl)benzaldehyde 167d

Compound **167d** was prepared according to literature procedure in a two-step one pot reaction.[85]



167d

A THF suspension (2 mL) of 2-methylfuran (86.3 µl, 78.5 mg, 0.96 mmol), bispinacoldiboron (121.5 mg, 0.48 mmol), $[Ir(OMe)(COD)]_2$ (1.58 mg, 2.39 µmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (1.28 mg, 4.78 µmol) was heated to 80 °C. After the reaction was complete (18 hours, GC-MS monitoring), the solvent was removed *in vacuo* affording the literature known 4,4,5,5-tetramethyl-2-(5-methylfuran-2-yl)-1,3,2-dioxaborolane **174**.[86] Then, 2-bromo-3-fluoro-benzaldehyde (176.0 mg, 0.84 mmol), bis(dibenzylideneacetone)palladium (9.68 mg, 0.0168 mmol), tri(*o*-tolyl)phosphine (10.25 mg, 0.0337 mmol), sodium carbonate (356.9 mg, 3.36 mmol) and a THF/water mixture (9/1, 3.3 mL) were added to the crude boronic ester **174** and the suspension was stirred for 20 h at room temperature. Filtration of the suspension over a short pad of Avicel® and subsequent removal of solvents *in vacuo* gave a crude material, which was purified by column chromatography on silica gel (pentane/MTBE, 30/1) affording **167d** as an orange oil (117 mg, 60% over two steps).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 6.19-6.20 (m, 1H), 6.74 (t, J = 3.3 Hz, 1H), 7.33-7.41 (m, 2H), 7.75-7.77 (m, 1H), 10.33 ppm (s, 1H).

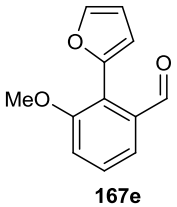
^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$): δ = 13.9, 108.3, 115.4 (d, J_{F-C} = 8.1 Hz), 120.7, 120. 9, 123.8 (d, J_{F-C} = 3.0 Hz), 128.7 (d, J_{F-C} = 9.1 Hz), 135.4, 143.1, 154.8, 159.4 (d, J_{F-C} = 251.6), 192.1 ppm (d, J_{F-C} = 3.5 Hz).

^{19}F{^{1}H}-NMR (282 MHz, $CDCl_3$): δ = -113.1 ppm.

HRMS *calcd.* for $C_{12}H_{10}O_2F^+$: 204.058657 $[M+H]^+$; *found*: 204.058680.

IR: ϑ = 707, 734, 778, 852, 920, 939, 1025, 1047, 1088, 1135, 1160, 1201, 1235, 1249, 1352, 1394, 1446, 1462, 1480, 1543, 1569, 1602, 1689, 1784, 2753, 2876, 2923, 3079, 3416 cm^{-1}.

2-(Furan-2-yl)-3-methoxylbenzaldehyde 167e



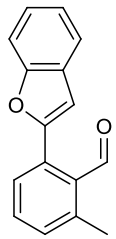
167e

2-Chloro-3-methoxy-benzaldehyde (150 mg, 0.879 mmol), furane-2-boronic acid (147.6 mg, 1.319 mmol), tris(dibenzylideneacetone)dipalladium(0) (64.4 mg, 0.070 mmol), *S*-Phos (57.8 mg, 0.141 mmol) and cesium carbonate (487.0 mg, 1.490 mmol) were suspended in a degassed toluene/1,4-dioxane

mixture (1.1/1, 2.1 mL). The vessel was sealed with a Teflon crimp top and the suspension heated to 115 °C under microwave irradiation for 7 hours. Then, the crude material was filtrated over a short pad of silica and the residue rinsed with a pentane/MTBE mixture (2/1, 50 mL). Removal of the solvents *in vacuo* afforded a crude product, which was purified by column chromatography on silica gel (pentane/MTBE, 50/1) to give **167e** (118.0 mg). While residues of dibenzylideneacetone were still present in this material, it was used for the next step without further purification attempts.

HRMS *calcd*. for $C_{12}H_{10}O_3^+$: 202.062997 $[M]^+$; *found*: 202.063172.

2-(Benzofuran-2-yl)-6-methylbenzaldehyde167f



167f

A microwave vial was charged with 2-bromo-6-methylbenzaldehyde **135d** (215 mg, 1.08 mmol), benzofuran-2-ylboronic acid (227 mg, 1.40 mmol), sodium carbonate (172 mg, 1.62 mmol), bis(triphenylphosphine)-palladium chloride (38.9 mg, 0.054 mmol) and an acetonitrile/water mixture (1/1, 6.4 mL). The vessel was sealed with a Teflon crimp top and the mixture heated to 150 °C under microwave irradiation for 1.5 hours. Then, brine was added and the aqueous phase extracted with ethyl acetate (3x). The combined organic phases were then dried over sodium sulfate and the solvent was removed *in vacuo*. The crude material thus obtained was purified by column chromatography on silica gel (pentane/MTBE, 15/1) affording **167f** as a yellow solid (201 mg, 79%).

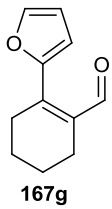
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.63 (s, 3H), 6.87 (d, *J* = 0.9 Hz, 1H), 7.29 (td, *J* = 7.5, 7.5, 1.0 Hz, 1H), 7.33-7.37 (m, 2H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.54-7.56 (m, 1H), 7.63-7.65 (m, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 10.31 ppm (s, 1H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 21.3, 108.4, 111.5, 121.4, 123.4, 125.2, 127.2, 128.7, 132.2, 132.4, 133.1, 133.9, 139.7, 153.1, 155.5, 194.1 ppm.

HRMS *calcd.* for $C_{16}H_{12}NaO_2^+$: 259.072950 $[M+Na]^+$; *found*: 259.072988.

IR: ϑ = 688, 733, 747, 760, 783, 818, 836, 855, 873, 905, 939, 975, 1009, 1034, 1076, 1098, 1112, 1141, 1167, 1183, 1238, 1259, 1298, 1309, 1349, 1382, 1408, 1425, 1444, 1456, 1474, 1566, 1597, 1686, 2925, 2968, 3062, 3104 cm^{-1}.

2-(Furan-2-yl)cyclohex-1-ene-1-carbaldehyde 167g


167g

A microwave vial was charged with 2-bromocyclohex-1-ene-1-carbaldehyde **135e** (227 mg, 1.19 mmol), furane-2-boronic acid (268 mg, 2.40 mmol), cesium carbonate (1.17 g, 3.60 mmol), ammonium bromide (117 mg, 1.20 mmol), tetrakis(triphenyl-phosphine)palladium (416 mg 0.36 mmol) and a 1,4-dioxane/water mixture (9/1, 10 mL). The vessel was sealed with a Teflon crimp top and the suspension heated to 70 °C under microwave irradiation for 7 hours. Then, brine was added and the aqueous phase extracted with ethyl acetate (3x). Afterwards, the combined organic phases were dried over sodium sulfate and the solvents were removed *in vacuo*. The crude material thus obtained was purified by column chromatography on silica gel (pentane/MTBE, 70/1) affording **167g** as a yellow oil (144 mg, 68%).

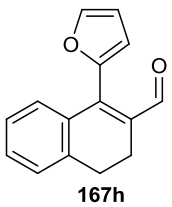
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.64-1.69 (m, 2H), 1.71-1.77 (m, 2H), 2.36-2.40 (m, 2H), 2.58-2.62 (m, 2H), 6.47-6.48 (m, 1H), 6.51 (d, *J* = 3.4 Hz, 1H), 7.52 (d, *J* = 1.3 Hz, 1H), 10.11 (s, 1H) ppm.

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 21.5, 22.2, 23.2, 29.3, 111.6, 113.2, 136.0, 143.9, 144.2, 152.1, 193.6 ppm.

HRMS *calcd.* for $C_{11}H_{12}O_2$: 176.083730 $[M]^+$; *found*: 176.083570.

IR: ῡ = 513, 541, 594, 675, 712, 744, 802, 813, 885, 910, 962, 991, 1025, 1062, 1093, 1155, 1198, 1228, 1245, 1277, 1395, 1431, 1450, 1486, 1608, 1656, 2859, 2932, 3119, 3296 cm^{-1}.

1-(Furan-2-yl)-3,4-dihydronaphthalene-2-carbaldehyde 167h


167h

A microwave vial was charged with 2-bromo-3,4-dihydronaphthalene-2-carbaldehyde **135f** (350 mg, 1.48 mmol), furane-2-boronic acid (330 mg, 2.95 mmol), cesium carbonate (1.44 g, 4.49 mmol), ammonium bromide (144 mg, 1.48 mmol), tetrakis(triphenylphosphine)palladium (512 mg 0.44 mmol) and a 1,4-dioxane/water mixture (9/1, 15 mL). The vessel was sealed with a Teflon crimp top and the suspension heated to 70 °C under microwave irradiation for 7 hours. Then, brine was added and the aqueous phase was extracted with ethyl acetate (3x). Afterwards, the combined organic phases were dried over sodium sulfate and the solvents removed *in vacuo*. The crude material thus obtained was purified by column chromatography on silica gel (pentane/MTBE, 50/1) affording **167h** as a yellow solid (270 mg, 81%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.66-2.70 (m, 2H), 2.84-2.88 (m, 2H), 6.55-6.57 (m, 1H), 6.61 (dd, *J* = 3.6, 0.4 Hz, 1H), 7.13 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.19-7.26 (m, 2H), 7.32 (td, *J* = 7.4, 7.4, 1.4 Hz, 1H), 7.62 (dd, *J* = 1.9, 0.8 Hz, 1H), 9.88 ppm (s, 1H).

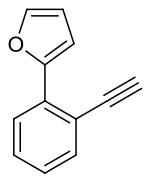
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 21.2, 27.7, 111.3, 115.5, 126.9, 128.1, 128.3, 130.5, 133.4, 137.1, 139.0, 142.7, 144.2, 147.9, 193.0 ppm.

HRMS *calcd.* for $C_{15}H_{12}NaO_2^+$: 247.072949 $[M+Na]^+$; *found:* 247.073002.

IR: ϑ = 678, 724, 734, 757, 803, 833, 845, 881, 889, 906, 920, 972, 1000, 1014, 1034, 1072, 1105, 1143, 1176, 1192, 1205, 1226, 1235, 1295, 1333, 1359, 1378, 1436, 1454, 1477, 1543, 1557, 1601, 1655, 2748, 2836, 2857, 2882, 2952, 3069, 3129 cm^{-1}.

6.5.6.2 Synthesis of the corresponding alkynes

2-(2-Ethynylphenyl)furan 165a


165a

Compound **165a** was prepared according to general procedure **G** from carbaldehyde **167a** (220.0 mg, 1.03 mmol). Purification of the crude material was performed by column chromatography on silica gel (pentane) afforded **165a** as a yellow oil (115 mg, 66%).

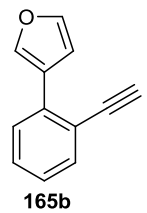
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.41 (s, 1H), 6.52 (dd, *J* = 3.4, 1.8 Hz, 1H), 7.22 (td, *J* = 7.7, 1.3 Hz, 1H), 7.38-7.42 (m, 2H), 7.50 (d, *J* = 1.5 Hz, 1H), 7.58 (dd, *J* = 8.3, 0.6 Hz, 1H), 7.85 ppm (dd, *J* = 8.1, 1.0 Hz, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 82.2, 83.9, 109.9, 111.9, 117.3, 125.8, 127.0, 129.3, 132.6, 135.0, 142.4, 151.9 ppm.

HRMS *calcd.* for $C_{12}H_8O^+$: 168.057516 $[M]^+$; *found:* 168.057600.

IR: ϑ = 660, 735, 756, 781, 814, 886, 901, 952, 1006, 1029, 1050, 1082, 1114, 1158, 1189, 1214, 1255, 1276, 1288, 1378, 1430, 1478, 1498, 1561, 1599, 1631, 1735, 3065, 3119, 3146, 3285 cm^{-1}.

3-(2-Ethynylphenyl)furan 165b


165b

Compound **165b** was prepared according to general procedure **G** from carbaldehyde **167b** (99.6 mg, 0.58 mmol. Purification of the crude material by

column chromatography on silica gel (pentane) afforded **165b** as a yellow oil (63 mg, 64%).

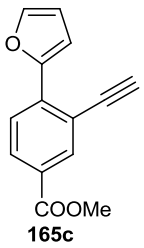
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.27 (s, 1H), 6.84 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.23 (td, *J* = 7.6, 7.6, 1.4 Hz, 1H), 7.37 (td, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.44 (ddd, *J* = 7.9, 1.4, 0.5 Hz , 1H), 7.48 (t, *J* = 1.7 Hz, 1H), 7.58 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.06 ppm (dd, *J* = 1.5, 0.9 Hz, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 81.4, 83.9, 110.6, 119.8, 124.7, 126.8, 128.2, 129.3, 134.6, 134.9, 141.3, 142.8 ppm.

HRMS *calcd.* for $C_{12}H_8O^+$: 168.057513 $[M]^+$; *found*: 168.057368.

IR: ῡ = 561, 596, 617, 657, 728, 753, 793, 871, 923, 950, 1015, 1032, 1055, 1086, 1162, 1233, 1306, 1356, 1438, 1474, 1509, 1566, 1585, 1599, 2852, 2924, 3025, 3063, 3151, 3285 cm^{-1}.

Methyl 3-ethynyl-4-(furan-2-yl)benzoate 165c



165c

Compound **165c** was prepared according to general procedure **G** from carbaldehyde **167c** (60.0 mg, 0.24 mmol). Purification of the crude material by column chromatography on silica gel (pentane/MTBE, 50/1) afforded **165c** as a white solid (31.8 mg, 54%).

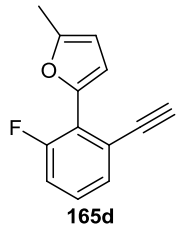
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.46 (s, 1H), 3.92 (s, 3H), 6.54 (d, *J* = 3.5, 1.8 Hz, 1H), 7.53-7.54 (m, 1H), 7.56 (dd, *J* = 3.5, 0.6 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 8.02 (dd, *J* = 8.4, 1.9 Hz, 1H), 8.25 ppm (d, *J* = 1.8 Hz, 1H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 52.3, 82.9, 83.1, 112.0, 112.2, 116.9, 125.4, 128.2, 130.1, 135.8, 136.2, 143.2, 151.0, 166.2 ppm.

HRMS *calcd.* for $C_{14}H_{10}O_3^+$: 226.062994 $[M]^+$; *found*: 226.063200.

IR: ῡ = 655, 671, 677, 691, 733, 746, 767, 817, 848, 886, 918, 970, 1007, 1032, 1106, 1128, 1159, 1220, 1254, 1267, 1296, 1373, 1389, 1434, 1476, 1500, 1555, 1600, 1711, 1834, 2960, 3087, 3247 cm^{-1}.

2-(2-Ethynyl-6-fluorophenyl)-5-methylfuran 165d



165d

Compound **165d** was prepared according to general procedure **G** from carbaldehyde **167d** (70.0 mg, 0.34 mmol. Purification of the crude material by column chromatography on silica gel (pentane) afforded **165d** as a white solid (45 mg, 65%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3H), 3.23 (s, 1H), 6.12-6.14 (m, 1H), 6.82 (dd, J = 2.9, 2.3 Hz 1H), 7.08-7.21 (m, 2H), 7.36-7.39 ppm (m, 1H).

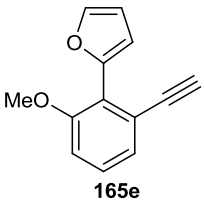
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 14.1, 81.3, 82.5 (d, J_{C-F} = 4.9 Hz), 107.5 (d, J_{C-F} = 0.8 Hz), 113.6 (d, J_{C-F} = 5.6 Hz), 116.9 (d, J_{C-F} = 23.0 Hz), 121.3 (d, J_{C-F} = 4.5 Hz), 121.9 (d, J_{C-F} = 14.6 Hz), 128.0 (d, J_{C-F} = 9.4 Hz), 130.4 (d, J_{C-F} = 3.3 Hz), 144.8 (d, J_{C-F} = 1.8 Hz), 152.9 (d, J_{C-F} = 1.6 Hz), 159.4 ppm (d, J_{C-F} = 250.2 Hz).

^{19}F{^{1}H}-NMR (282 MHz, $CDCl_3$): δ = -112.74 ppm.

HRMS *calcd*. for. $C_{13}H_9FO^+$: 200.063743 $[M]^+$; *found*: 200.063560.

IR: ῡ = 664, 735, 791, 857, 922, 946, 973, 1025, 1045, 1090, 1161, 1201, 1222, 1229, 1252, 1282, 1355, 1382, 1438, 1459, 1537, 1567, 1603, 1677, 1785, 2857, 2924, 2956, 2992, 3075, 3292 cm^{-1}.

2-(2-Ethynyl-6-methoxyphenyl)furan 165e



165e

Compound **165e** was prepared according to general procedure **G** from the crude carbaldehyde **167e** (118.0 mg, 0.58 mmol). Purification of the crude material by column chromatography on silica gel (pentane/MTBE, 30/1) afforded the desired product **165e** as a white solid (70 mg, 40% over two steps).

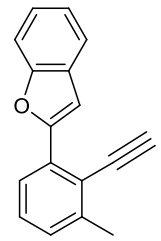
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.12 (s, 1H), 3.86 (s, 3H), 6.52-6.53 (m, 1H), 6.72 (d, *J* = 3.6 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 7.20-7.28 (m, 2H, overlaps with solvent signal), 7.56 ppm (s, 1H).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 56.3, 80.3, 83.1, 110.9, 111.7, 112.2, 122.8, 123.1, 126.5, 129.0, 142.1, 148.6, 157.4 ppm.

HRMS *calcd*. for $C_{13}H_{10}O_2^+$: 198.068079 $[M]^+$; *found*: 198.068225.

IR: ϋ = 736, 789, 812, 885, 901, 1003, 1028, 1066, 1098, 1155, 1186, 1210, 1231, 1265, 1290, 1376, 1432, 1463, 1500, 1567, 1609, 2838, 2939, 2963, 3005, 3069, 3118, 3142, 3285 cm^{-1}.

2-(2-Ethynyl-3-methylphenyl)benzofuran 165f


165f

Compound **165f** was prepared according to general procedure **G** from carbaldehyde **167f** (50.0 mg, 0.21 mmol). Purification of the crude material by column chromatography on silica gel (pentane/MTBE, 60/1) afforded **165f** as a white solid (45 mg, 92%).

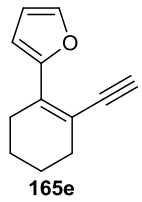
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.55 (s, 3H), 3.74 (s, 1H), 7.22-7.27 (m, 2H, overlaps with solvent signal), 7.29-7.33 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.52 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.62-7.64 (d, 1H), 7.79 (d, *J* = 0.9 Hz 1H), 7.89 ppm (d, *J* = 8.6 Hz, 1H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 21.6, 81.8, 87.8, 106.2, 111.1, 118.5, 121.5, 122.9, 124.5, 124.8, 128.7, 129.3, 132.5, 142.8, 154.0, 154.4 ppm.

HRMS *calcd*. for $C_{17}H_{12}O^{+}$: 232.088816 $[M]^{+}$; *found*: 232.088602.

IR: ϋ = 738, 749, 784, 814, 854, 888, 936, 1009, 1036, 1074, 1088, 1110, 1146, 1172, 1220, 1242, 1259, 1307, 1347, 1379, 1443, 1455, 1565, 1571, 2916, 2952, 3035, 3063, 3289 cm^{-1}.

2-(2-Ethynylcyclohex-1-en-1-yl)furan 165g


165e

To a solution of potassium carbonate (253.7 mg, 1.84 mmol) in methanol (5.6 mL) at -40 °C, the *Ohira-Bestmann* reagent **173** (282.1 mg, 1.47 mmol) and **167g** (129.4 mg, 0.73 mmol) in methanol (1 mL) were added. The reaction was subsequently warmed to 0 °C and stirred overnight at this temperature. After that, the solvent was removed *in vacuo* and the obtained residue dissolved in ethyl acetate and washed with brine (4x). Finally, the organic phase was dried over sodium sulfate, and the crude material purified by column chromatography on silica gel (pentane/MTBE, 30/1) affording **165g** as a violet oil (60 mg, 47%). The compound was stored under argon at -20 °C and had to be used within 3 days to avoid decomposition.

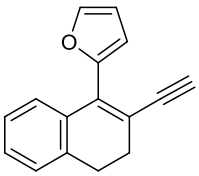
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.64-1.74 (m, 4H), 2.35-2.39 (m, 2H), 2.53-2.56 (m, 2H), 3.34 (s, 1H), 6.42 (dd, *J* = 3.5, 1.8 Hz, 1H), 7.08 (d, *J* = 3.5 Hz, 1H), 7.37 ppm (d, *J* = 1.4 Hz, 1H).

$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 21.1, 22.3, 26.4, 31.6, 82.6, 85.8, 109.1, 111.3, 113.1, 134.1, 141.1, 154.3 ppm.

HRMS *calcd*. for $C_{12}H_{13}O^+$: 173.096090 $[M+H]^+$; *found*: 173.096170.

IR: ῡ = 459, 516, 594, 609, 655, 800, 871, 876, 904, 962, 989, 1021, 1084, 1154, 1211, 1247, 1278, 1336, 1354, 1436, 1450, 1487, 1547, 1604, 2084, 2838, 2860, 2882, 2933, 3118, 3145, 3291 cm^{-1}.

2-(2-Ethynyl-3,4-dihydronaphthalen-1-yl)furan 165h



165h

Compound **165h** was prepared according to general procedure **G** from carbaldehyde **167h** (200.0 mg, 0.89 mmol). Purification of the crude material by column chromatography on silica gel (pentane/MTBE, 30/1) afforded **165h** as a dark red oil (131 mg, 66%). The compound was stored under argon at -20 °C and had to be used within 3 days to avoid decomposition.

^1H-NMR (400 MHz, $CDCl_3$): δ = 2.54-2.58 (m, 2H), 2.83-2.87 (m, 2H), 3.38 (s, 1H), 6.52 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.82 (d, *J* = 2.8 Hz, 1H), 7.09-7.20 (m, 4H), 7.49 ppm (dd, *J* = 1.8, 0.7 Hz, 1H).

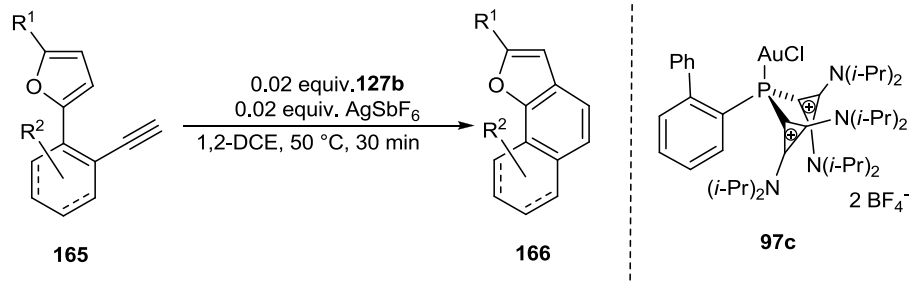
$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ =27.9, 29.5, 84.5, 84.7, 110.9, 112.3, 119.0, 126.6, 126.8, 127.6, 128.1, 133.5, 134.8, 136.7, 142.1, 151.0 ppm.

HRMS *calcd*. for $C_{16}H_{12}O^+$: 220.088816 $[M]^+$; *found*: 220.088747.

IR: ῡ = 736, 766, 810, 868, 884, 925, 943, 965, 985, 1016, 1042, 1078, 1101, 1149, 1183, 1216, 1294, 1329, 1349, 1429, 1448, 1485, 1553, 1597, 1625, 1668, 1724, 2841, 2888, 2945, 3031, 3071, 3280 cm^{-1}.

6.5.6.3 Cycloisomerization

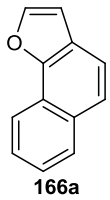
General procedure I: **Formation of naphto-furan derivatives**



165 **166** **97c**

A solution of the desired Alkyne **165** (1.0 equiv.) in 1,2-DCE (c = 0.05 M) at 50 °C was transferred *via* cannula to a prewarmed *Schlenk*-flask, which was already charged with Au(I)-precatalyst **97c** (0.02 equiv) and silver hexafluoroantimonate (0.02 equiv.). The reaction mixture was stirred at 50 °C until the reaction was finished (30 minutes) and then filtered over a short pad of silica gel. The residue was then rinsed with DCM and purified by column chromatography on silica gel affording **166.**

Naphtho[1,2-b]furan 166a


166a

Alkyne **165a** (24.9 mg, 0.15 mmol) was treated with precatalyst **97c** (3.1 mg, 2.9 µmol) and silver hexafluoroantimonate (1.0 mg, 2.9 µmol) in 1,2-DCE (3.0 mL) according to general procedure **I**. The crude material thus obtained was purified by column chromatography on silica gel (pentane) affording **166a** as a white solid (21 mg, 91%).

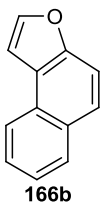
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.92 (d, *J* = 1.8 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.67 (s, 2H), 7.78 (d, *J* = 1.9 Hz, 1H), 7.95 (d, *J* = 9.9 Hz, 1H), 8.33 ppm (d, *J* = 8.20 Hz, 1H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 107.8, 119.9, 120.2, 121.7, 123.1, 123.6, 125.3, 126.5, 128.5, 131.6, 144.3, 150.8 ppm.

HRMS *calcd*. for $C_{12}H_8O^+$: 168.057518 $[M]^+$; *found*: 168.057388.

IR: ϑ̃ = 685, 736, 785, 806, 869, 881, 945, 955, 1002, 1021, 1039, 1068, 1127, 1169, 1208, 1268, 1321, 1391, 1438, 1454, 1468, 1511, 1592, 1700, 1748, 1807, 2857, 2932, 3019, 3055, 3146 cm^{-1}.

Naphtho[2,1-b]furan 166b


166b

Alkyne **165b** (32.6 mg, 0.19 mmol) was treated with precatalyst **97c** (4.1 mg, 3.8 µmol) and silver hexafluoroantimonate (1.3 mg, 3.8 µmol) in 1,2-DCE (3.9 mL) according to general procedure **I**. The crude material thus obtained was purified by column chromatography on silica gel (pentane) affording **166b** as a pale yellow solid (31 mg, 94%).

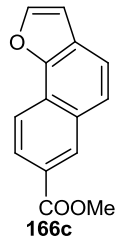
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 1.1 Hz, 1H), 7.50 (t,*J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.78 (d, *J* = 1.8 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 8.16 ppm (d, *J* = 8.2 Hz, 1H).

$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$): δ = 105.8, 112.7, 122.8, 123.6, 124.7, 125.4, 126.5, 128.0, 128.9, 130.5, 144.4, 152.7 ppm.

HRMS *calcd*. for $C_{12}H_8O$: 168.057515 $[M]^+$; *found*: 168.057385.

IR: ϑ = 683, 727, 787, 803, 860, 905, 952, 972, 1022, 1047, 1071, 1133, 1165, 1206, 1245, 1269, 1320, 1347, 1385, 1448, 1515, 1584, 1628, 1734, 2849, 2926, 3059, 3115, 3146 cm^{-1}.

Methyl naphto[1,2-b]furan-7-carboxylate 166c



166c

Alkyne **165c** (27.9 mg, 0.11 mmol) was treated with precatalyst **97c** (2.5 mg, 2.3 µmol) and silver hexafluoroantimonate (0.8 mg, 2.3 µmol) in 1,2-DCE (2.3 mL) according to general procedure **I**. The crude material thus obtained was purified by column chromatography on silica gel (pentane/MTBE, 20/1) affording the desired product **166c** as a white solid (27 mg, 95%).

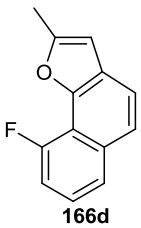
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.00 (s, 3H), 6.94 (d, *J* = 2.1 Hz, 1H), 7.75 (q, *J* = 8.7 Hz, 2H), 7.84 (d, *J* = 2.0 Hz, 1H), 8.19 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.35 (d, *J* = 8.6 Hz, 1H), 8.71 ppm (d, *J* = 1.3 Hz, 1H).

$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$): δ = 52.4, 108.0, 120.4, 120.8, 123.6, 124.8, 125.3, 126.2, 126.7, 130.6, 131.5, 145.4, 150.4, 167.4 ppm.

HRMS *calcd*. for $C_{14}H_{10}O_3^+$: 226.06299 $[M]^+$; *found*: 226.062770.

IR: ϑ = 426, 442, 505, 546, 585, 605, 624, 684, 750, 791, 808, 843, 883, 917, 974, 1002, 1044, 1067, 1104, 1130, 1194, 1263, 1292, 1320, 1369, 1402, 1421, 1437, 1464, 1502, 1576, 1635, 1702, 1762, 1805, 2848, 2924, 2950, 2998, 3114, 3144 cm^{-1}.

9-Fluoro-2-methylnaphtho[1,2-b]furan 166d



166d

Alkyne **165d** (13.9 mg, 0.069) was treated with precatalyst **97c** (1.5 mg, 1.39 µmol) and silver hexafluoroantimonate (0.5 mg, 1.39 µmol) in 1,2-DCE (1.4 mL) according to general procedure **I**. The crude material thus obtained was purified by column chromatography on silica gel (pentane/MTBE, 20/1) affording the desired product **166d** as a white solid (12 mg, 84%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.61 (s, 3H), 6.53-6.53 (m, 1H), 7.20-7.27 (m, 1H), 7.32-7.37 (m, 1H), 7.63-7.63 (m, 2H), 7.69 ppm (dd, *J* = 8.7, 0.5 Hz, 1H).

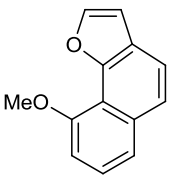
$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 14.5, 103.5, 110.9 (d, J_{F-C} = 19.1 Hz), 120.6 (d, J_{F-C} = 1.4 Hz), 122.8 (d, J_{F-C} = 2.9 Hz), 124.1 (d, J_{F-C} = 4.3 Hz), 124.3 (d, J_{F-C} = 7.6 Hz), 126.2 (d, J_{F-C} = 0.9 Hz), 126.8, 133.2 (d, J_{F-C} = 5.2 Hz), 147.4 (d, J_{F-C} = 1.8 Hz), 155.8 (d, J_{F-C} =2.4 Hz), 157.1 ppm (d, J_{F-C} = 251.4 Hz).

$^{19}F\{^1H\}$-NMR (282 MHz, $CDCl_3$): δ = -117.69 ppm.

HRMS *calcd*. for $C_{13}H_9OF^+$: 200.063741 $[M]^+$; *found*: 200.063635.

IR: ϑ = 688, 733, 747, 760, 783, 818, 836, 855, 873, 905, 939, 975, 1009, 1034, 1076, 1112, 1141, 1167, 1183, 1**239**, 1259, 1298, 1309, 1349, 1382, 1408, 1425, 1444, 1456, 1474, 1566, 1597, 1686, 2925, 2968, 3062, 3104 cm^{-1}.

9-Methoxynaphto[1,2-b]furan 166e



166e

Alkyne **165e** (42.1 mg, 0.21 mmol) was treated with precatalyst **97c** (4.5 mg, 4.25 µmol) and silver hexafluoroantimonate (1.5 mg, 4.25 µmol) in 1,2-DCE (4.3 mL) according to general procedure **I**. The crude material thus obtained was purified by column chromatography on silica gel (pentane/MTBE, 20/1) affording **166e** as a white solid (40 mg, 95%).

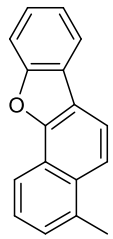
^1H-NMR (400 MHz, $CDCl_3$): δ =4.13 (s, 3H), 6.91 (d,*J* = 2.1 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H). 7.41 (t, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.85 ppm (d, *J* = 2.0 Hz, 1H).

$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 56.3, 105.9, 107.1, 114.1, 120.7, 121.0, 123.6, 124.2, 125.3, 133.7, 144.5, 149.9, 154.9 ppm.

HRMS *calcd*. for $C_{13}H_{10}O^+$: 198.068083 $[M]^+$; *found*: 198.067909.

IR: ϑ = 434, 475, 504, 527, 589, 626, 660, 691, 733, 754, 799, 810, 867, 881, 950, 997, 1021, 1061, 1087, 1134, 1162, 1200, 1216, 1254, 1268, 1257, 1377, 1404, 1431, 1461, 1515, 1536, 1575, 1622, 1743, 1815, 1907, 2839, 2961, 3011, 3058, 3123, 3147 cm^{-1}.

4-Methylbenzo[d]naphto[1,2-b]furan 166f



166f

Alkyne **165f** (31.0 mg, 0.13 mmol) was treated with precatalyst **97c**[87] (2.8 mg, 2.66 µmol) and silver hexafluoroantimonate (0.9 mg, 2.66 µmol) in 1,2-DCE (2.6 mL) according to general procedure **I**. The crude material thus obtained was

purified by column chromatography on silica gel (pentane/MTBE, 50/1) affording the desired product **166f** as a white solid (28 mg, 90%).

^{1}H-NMR(400 MHz, $CDCl_3$): δ = 2.79 (s, 3H), 7.39-7.43 (m, 2H), 7.46-7.50 (m, 1H), 7.53-7.57 (m, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.94 (dd, *J* = 8.7, 0.7 Hz, 1H), 8.01-8.04 (m, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 8.35 ppm (d, *J* = 8.3 Hz, 1H).

^{13}C{^{1}H}-NMR(101 MHz, $CDCl_3$): δ = 20.3, 111.9, 118.3, 119.0, 119.3, 119.6, 120.4, 121.5, 123.0, 125.1, 126.3, 127.2, 132.2, 135.2, 152.7, 156.1 ppm.

HRMS *calcd*. for $C_{17}H_{12}O^{+}$: 232.088815 $[M]^{+}$; *found*: 232.088643.

IR: ῡ = 436, 489, 565, 607, 682, 747, 767, 813, 909, 1010, 1032, 1069, 1088, 1118, 1150, 1183, 1201, 1268, 1306, 1343, 1378, 1397, 1441, 1460, 1529, 1583, 2860, 2928, 2946, 2968, 3063 cm^{-1}.

6.6 Computational Methods

6.6.1 General

All calculations were performed at our department of theoretical chemistry under the direction of *Prof. Dr. W. Thiel.*

Geometry optimizations were carried out using BP86[88] functional in combination with def2-SVP basis sets.[89] In the case of gold, the 60 inner-shell core electrons were replaced by an effective core potential (ECP) generated for the neutral atom using quasi-relativistic methods, and the explicitly treated electrons were described by the standard def2-ECP basis set.[90] The resolution-of-identity (RI) approximation[91] was applied in conjunction with the appropriate auxiliary basis sets to speed up the calculations. This approach is computationally efficient and has been employed successfully in our previous computations on gold chemistry.[92] All low-energy conformations of the substrate and the catalyst were considered during initial screening, and all relevant stationary points were characterized as minima or first-order transition states by evaluating the harmonic vibrational frequencies at the same level (RI-BP86/def2-SVP) that had been applied for geometry optimization.

The influence of the solvent environment (dichloromethane, dielectric constant $\varepsilon = 8.93$) on the relative energies was investigated through single-point calculations with the conductor-like screening model (COSMO)[93] at the RI-BP86/def2-SVP level. In order to evaluate the best estimate of the total energies, all located stationary points were re-optimized at the RI-BP86 level employing the def2-TZVPP basis set.[89b] Empirical Grimme-type dispersion corrections were also incorporated during this step using the latest parameterization (DFT-D3).[94] Relative free energies (ΔG) at standard pressure (1 bar) and 273.15K were determined at the RI-BP86/def2-SVP level. The required thermal and entropic contributions were evaluated within the rigid-rotor harmonic-oscillator approximation. All geometry optimizations were carried out using the TURBOMOLE (version 6.4) suite of programs.[95]

To gain insight into the electronic structure of the complexes, a fragment molecular orbital (MO) analysis was performed for selected molecules using the *Amsterdam Density Functional* (ADF) package.[60] The MOs were expanded in terms of Slater-type orbitals (STO) employing a triple-ζ basis set (TZP) with one polarization function. Relativistic effects were taken into account by the zero-order regular approximation (ZORA) approach,[96] as implemented in ADF.

6.6.2 Computational Results

Figures 6-4 sketches the frontier orbital interactions in complexes **97a-Cl** and **141-Cl**.

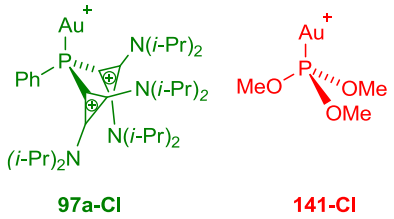


Figure 6-3: Evaluated active catalysts.

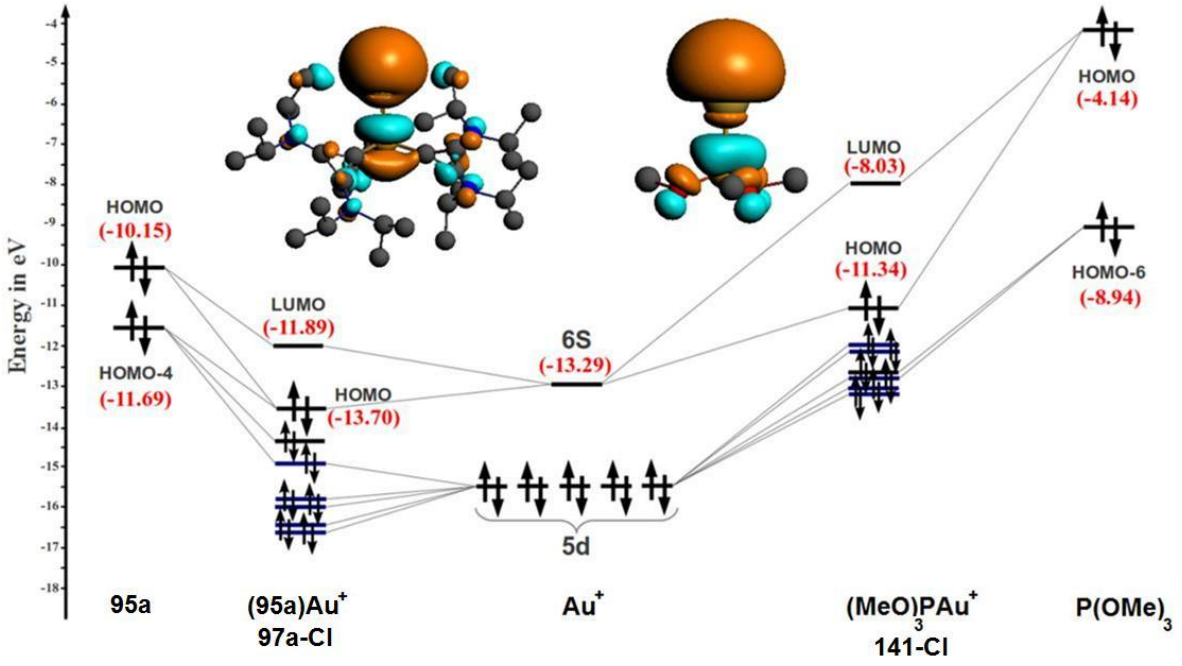


Figure 6-4: Frontier orbitals interactions in complexes **97a-Cl** (left) and **141-Cl** (right). Shown are the LUMOs that are mainly responsible for the catalyst-substrate interaction and contain a very strong 6s(Au) contribution. The fragments **95a** and $(MeO)_3P$ (left and right) were calculated at their geometries in the complexes **97-Cl** and **141-Cl**.

7 Appendix

7.1 X-Ray

Compound 96a

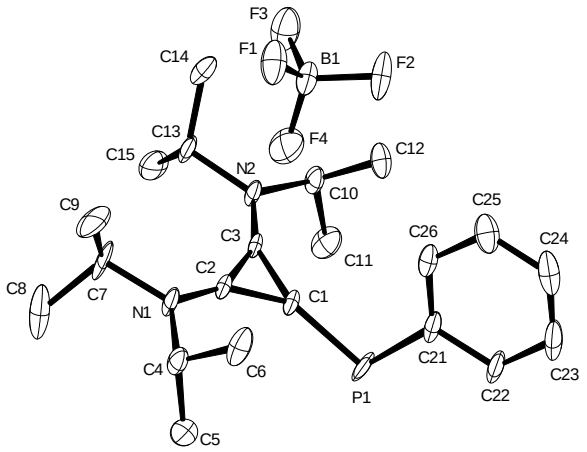
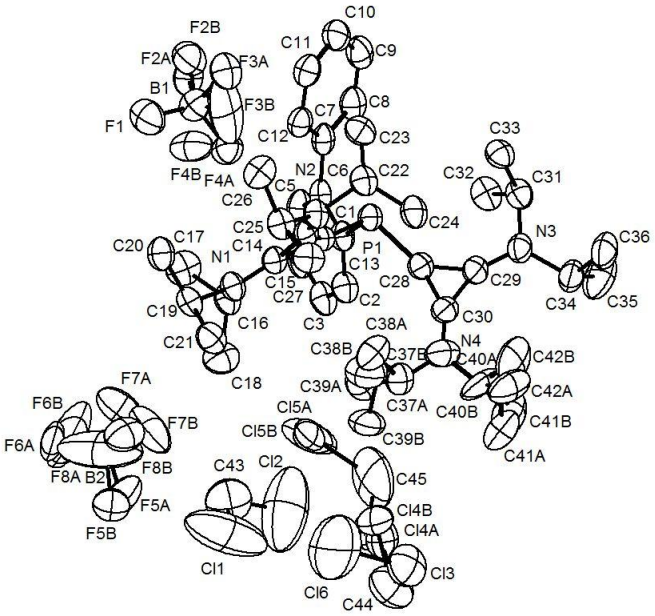


Table 7-1: Crystal data and structure refinement of compound **96a**.

Empirical formula	$C_{21}H_{34}BF_4N_2P$	
Color	colorless	
Formula weight	432.28 g mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	**Cc, (no. 9)**	
Unit cell dimensions	a = 11.811(5) Å	α = 90°.
	b = 15.362(6) Å	β = 101.797(8)°.
	c = 13.008(5) Å	γ = 90°.
Volume	2310.3(16) Å^3	
Z	4	
Density (calculated)	1.243 Mg m^{-3}	
Absorption coefficient	0.160 mm^{-1}	
F(000)	920 e	
Crystal size	0.10 x 0.04 x 0.02 mm^3	
Θ range for data collection	2.20 to 31.15°.	
Index ranges	$-17 \le h \le 17$, $-22 \le k \le 22$, $-18 \le l \le 17$	
Reflections collected	19071	
Independent reflections	6768 [R_{int} = 0.0889]	
Reflections with I>2σ(I)	4970	
Completeness to Θ = 31.15°	99.2 %	
Absorption correction	Empirical	
Max. and min. transmission	1.00 and 0.50	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6768 / 2 / 274	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2σ(I)]	R_1 = 0.0542	wR^2 = 0.1318

R indices (all data)	R_1 = 0.0837	wR^2 = 0.1632
Absolute structure parameter	0.20(10)	
Largest diff. peak and hole	0.461 and -0.675 e $Å^{-3}$	

Compound 95b



Comment: Two of the isopropyl groups and both tetrafluoroborate anions are disordered. In addition, the crystal contains badly disordered dichloromethane. The dichloromethane was modelled by C, H and Cl atoms. The refined occupancies summed up to C 2.28, H 4.55 and Cl 4.36. This approximates to 2.25 (CH_2Cl_2) per mole. Nether the less $R_1 = 0.0906 < 0.1$, which means that the structure is possibly publishable. Out of 6 attempts to obtain suitable crystals this was the best result, which could be obtained.

Table 7-2: Crystal data and structure refinement of compound **95b**.

Empirical formula	$C_{44.28}H_{69.55}B_2Cl_{4.36}F_8N_4P$	
Color	colourless	
Formula weight	1016.90 g·mol^{-1}	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	orthorhombic	
Space group	**P b c a, (no. 61)**	
Unit cell dimensions	a = 15.3679(7) Å	α= 90°.
	b = 21.1957(10) Å	β= 90°.
	c = 32.9485(16) Å	γ = 90°.
Volume	10732.4(9) Å^3	
Z	8	
Density (calculated)	1.259 Mg·m^{-3}	
Absorption coefficient	2.970 mm^{-1}	
F(000)	4274 e	
Crystal size	0.33 x 0.24 x 0.07 mm^3	
Θ range for data collection	2.682 to 67.845°.	
Index ranges	$-17 \leq h \leq 16$, $-25 \leq k \leq 25$, $-39 \leq l \leq 39$	
Reflections collected	240324	
Independent reflections	9610 [R_{int} = 0.1195]	
Reflections with I>2σ(I)	7562	
Completeness to Θ = 67.679°	99.0 %	
Absorption correction	Gaussian	

Max. and min. transmission	0.90807 and 0.67634	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9610 / 0 / 756	
Goodness-of-fit on F^2	1.103	
Final R indices [I>2σ(I)]	R_1 = 0.0906	wR^2 = 0.2460
R indices (all data)	R_1 = 0.1077	wR^2 = 0.2598
Extinction coefficient	0.00196(14)	
Largest diff. peak and hole	0.443 and -0.768 e·$Å^{-3}$	

Compound 95i

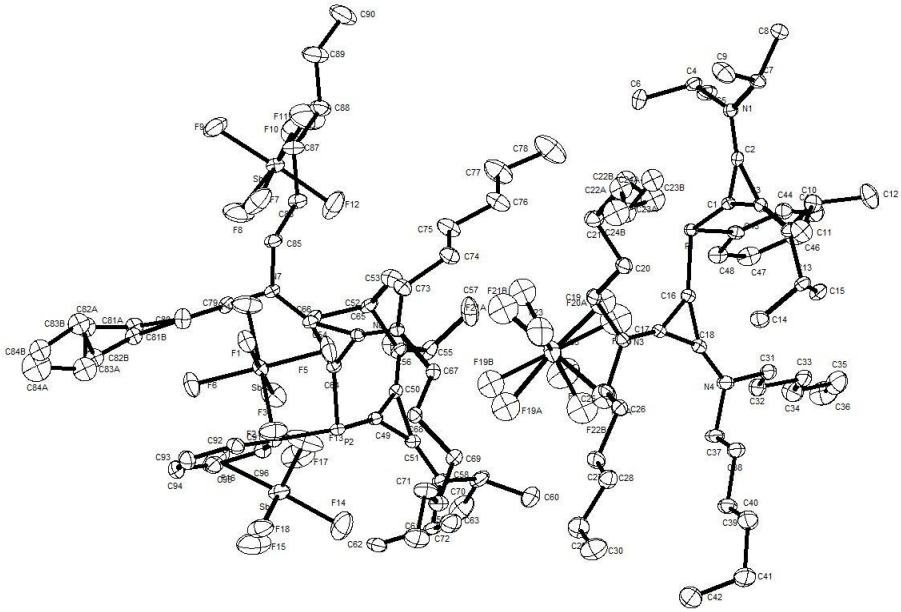


Table 7-3: Crystal data and structure refinement of compound **95i.**

Empirical formula	$C_{48}H_{85}F_{12}N_4PSb_2$	
Color	colourless	
Formula weight	1220.66 g·mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**p 21/n, (no. 14)**	
Unit cell dimensions	a = 14.879(2) Å	α= 90°.
	b = 30.262(5) Å	β= 95.646(3)°.
	c = 27.205(5) Å	γ = 90°.
Volume	12191(3) Å^3	
Z	8	
Density (calculated)	1.330 Mg·m^{-3}	
Absorption coefficient	0.981 mm^{-1}	
F(000)	5008 e	
Crystal size	0.29 x 0.08 x 0.07 mm^3	
Θ range for data collection	1.346 to 31.024°.	
Index ranges	$-21 \leq h \leq 21$, $0 \leq k \leq 43$, $0 \leq l \leq 39$	
Reflections collected	38745	
Independent reflections	38745 [R_{int} = 0.0451]	
Reflections with I>2σ(I)	31443	
Completeness to Θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.94595 and 0.77201	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	38745 / 0 / 1222	
Goodness-of-fit on F^2	1.115	
Final R indices [I>2σ(I)]	R_1 = 0.0435	wR^2 = 0.1141
R indices (all data)	R_1 = 0.0565	wR^2 = 0.1197
Extinction coefficient	n/a	
Largest diff. peak and hole	1.340 and -1.212 e·Å^{-3}	

Compound 97b

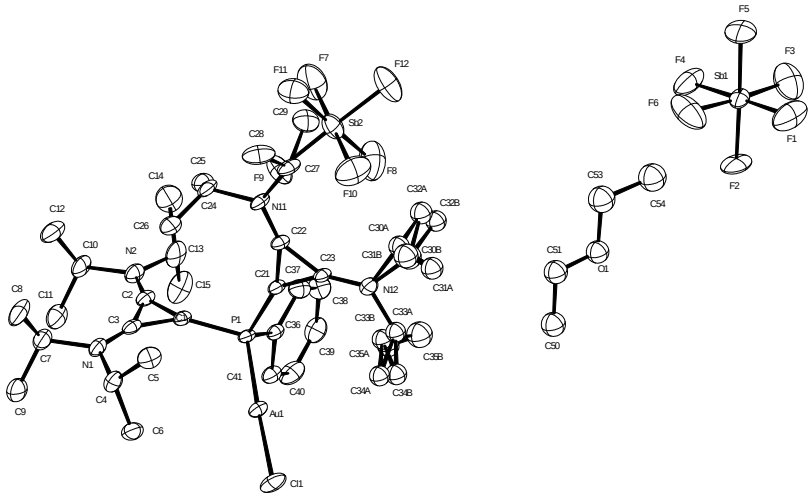


Table 7-4: Crystal data and structure refinement of compound **97b**.

Empirical formula	$C_{76}H_{132}Au_2Cl_2F_{24}N_8O\,P_2Sb_4$ (cell contains two molecules of **97b** and one ether molecule)	
Color	colorless	
Formula weight	2643.66 g mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 18.222(3) Å	α = 90°.
	b = 10.6242(15) Å	β = 92.535(3)°.
	c = 27.563(4) Å	γ = 90°.
Volume	5330.9(13) $Å^3$	
Z	2	
Density (calculated)	1.647 Mg m^{-3}	
Absorption coefficient	3.903 mm^{-1}	
F(000)	2588 e	
Crystal size	0.22 x 0.04 x 0.02 mm^3	
Θ range for data collection	2.055 to 28.363°.	
Index ranges	$-24 \le h \le 24$, $-14 \le k \le 14$, $-36 \le l \le 36$	
Reflections collected	126469	
Independent reflections	13286 [R_{int} = 0.0855]	
Reflections with I>2σ(I)	10302	
Completeness to Θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.93 and 0.61	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13286 / 0 / 554	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2σ(I)]	R_1 = 0.0501	wR^2 = 0.1197
R indices (all data)	R_1 = 0.0724	wR^2 = 0.1307

Largest diff. peak and hole 3.5 and -2.1 e $Å^{-3}$

Compound 97c

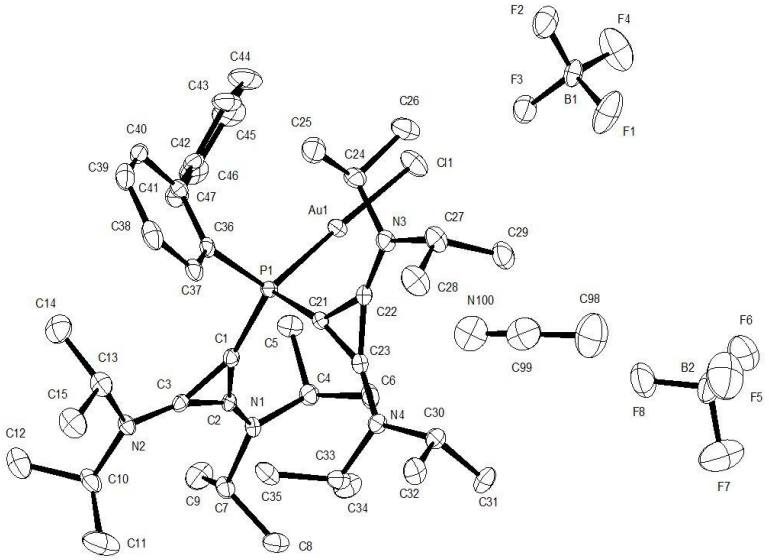


Table 7-5: Crystal data and structure refinement of compound **97c**.

Empirical formula	$C_{44}H_{68}AuB_2ClF_8N_5P$	
Color	colourless	
Formula weight	1104.04 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	**P b c a, (no. 61)**	
Unit cell dimensions	a = 14.720(2) Å	α= 90°.
	b = 17.611(3) Å	β= 90°.
	c = 38.084(6) Å	γ = 90°.
Volume	9872(3) $Å^3$	
Z	8	
Density (calculated)	1.486 $Mg \cdot m^{-3}$	
Absorption coefficient	3.133 mm^{-1}	
F(000)	4480 e	
Crystal size	0.11 x 0.09 x 0.07 mm^3	
Θ range for data collection	1.069 to 26.439°.	
Index ranges	$-18 \leq h \leq 18$, $-22 \leq k \leq 22$, $-47 \leq l \leq 46$	
Reflections collected	204020	
Independent reflections	10150 [R_{int} = 0.0510]	
Reflections with I>2σ(I)	8558	
Completeness to Θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.82715 and 0.70856	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10150 / 0 / 576	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2σ(I)]	R_1 = 0.0313	wR^2 = 0.0723
R indices (all data)	R_1 = 0.0406	wR^2 = 0.0774
Extinction coefficient	0	

Largest diff. peak and hole	3.207 and -1.089 e·Å^{-3}

Compound 107f

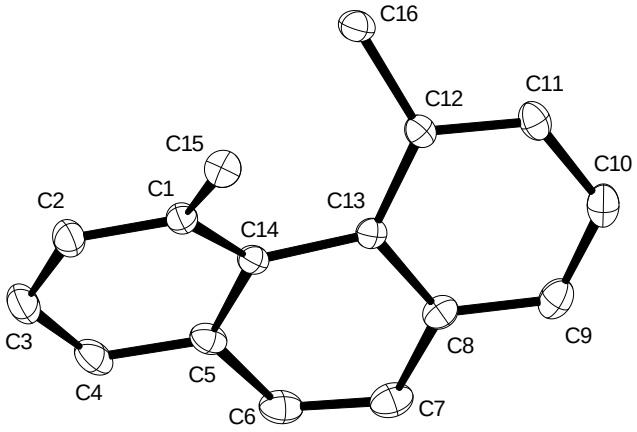


Table 7-6: Crystal data and structure refinement for compound **107f**.

Empirical formula	$C_{16}H_{14}$	
Color	colourless	
Formula weight	206.27 g mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**P 2_1, (no. 4)**	
Unit cell dimensions	a = 8.3090(8) Å	α = 90°.
	b = 8.0817(7) Å	β = 108.2270(10)°.
	c = 8.7050(8) Å	γ = 90°.
Volume	555.22(9) Å^3	
Z	2	
Density (calculated)	1.234 Mg m^{-3}	
Absorption coefficient	0.069 mm^{-1}	
F(000)	220 e	
Crystal size	0.39 x 0.36 x 0.16 mm^3	
Θ range for data collection	2.46 to 34.97°.	
Index ranges	-13 ≤ h ≤ 13, -12≤ k ≤ 13, -14 ≤ l ≤ 14	
Reflections collected	19639	
Independent reflections	4809 [R_{int} = 0.0396]	
Reflections with I>2σ(I)	4635	
Completeness to Θ = 34.97°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.97	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4809 / 1 / 147	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2σ(I)]	R_1 = 0.0360	wR^2 = 0.1003
R indices (all data)	R_1 = 0.0381	wR^2 = 0.1029
Absolute structure parameter	0(8)	
Largest diff. peak and hole	0.438 and -0.194 e Å^{-3}	

Compound 107j

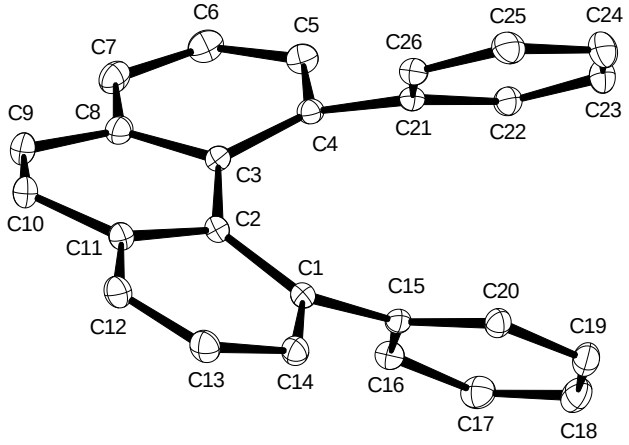


Table 7-7: Crystal data and structure refinement for compound **107j**.

Empirical formula	$C_{26}H_{18}$	
Color	colourless	
Formula weight	330.40 g mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/n$, (no. 14)**	
Unit cell dimensions	a = 8.9259(3) Å	α = 90°.
	b = 12.5274(11) Å	β = 105.646(5)°.
	c = 16.0569(10) Å	γ = 90°.
Volume	1728.93(19) Å^3	
Z	4	
Density (calculated)	1.269 Mg m^{-3}	
Absorption coefficient	0.072 mm^{-1}	
F(000)	696 e	
Crystal size	0.46 x 0.30 x 0.25 mm^3	
Θ range for data collection	2.63 to 33.10°.	
Index ranges	$-13 \leq h \leq 13$, $-19 \leq k \leq 19$, $-24 \leq l \leq 24$	
Reflections collected	35362	
Independent reflections	6570 [R_{int} = 0.0302]	
Reflections with I>2σ(I)	5307	
Completeness to Θ = 33.10°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98and 0.96	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6570 / 0 / 235	
Goodness-of-fit on F^2	1.115	
Final R indices [I>2σ(I)]	R_1 = 0.0460	wR^2 = 0.1293
R indices (all data)	R_1 = 0.0600	wR^2 = 0.1381
Largest diff. peak and hole	0.577 and -0.594 e Å^{-3}	

Compound 156

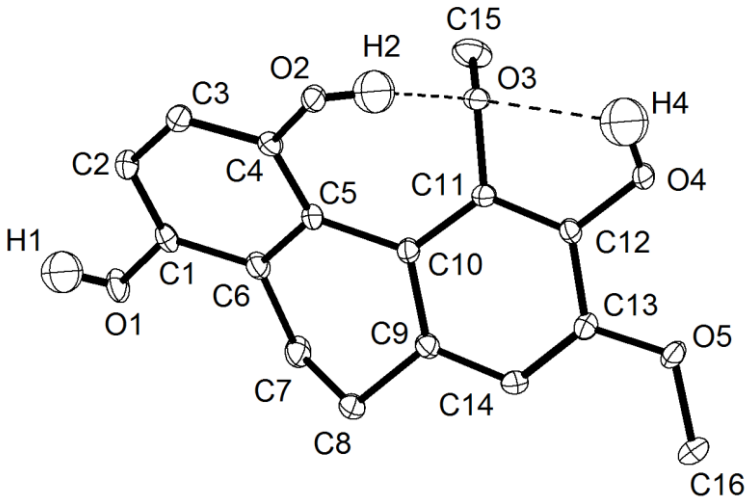


Table 7-8: Crystal data and structure refinement for compound **156**.

Empirical formula	$C_{16}H_{16}O_5$	
Color	colourless	
Formula weight	288.29 g·mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	**p 2_1/n, (no. 14)**	
Unit cell dimensions	a = 7.4040(11) Å	α = 90°.
	b = 9.3488(14) Å	β = 90.669(3)°.
	c = 20.526(3) Å	γ = 90°.
Volume	1420.7(4) Å^3	
Z	4	
Density (calculated)	1.348 Mg·m^{-3}	
Absorption coefficient	0.100 mm^{-1}	
F(000)	608 e	
Crystal size	0.473 x 0.146 x 0.080 mm^3	
Θ range for data collection	1.984 to 28.538°.	
Index ranges	-9 ≤ h ≤ 9, -12≤ k ≤ 12, -27≤ l ≤ 27	
Reflections collected	32312	
Independent reflections	3606 [R_{int} = 0.0389]	
Reflections with I>2σ(I)	3017	
Completeness to Θ = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99236 and 0.96919	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3606 / 0 / 204	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2σ(I)]	R_1 = 0.0378	wR^2 = 0.1026
R indices (all data)	R_1 = 0.0475	wR^2 = 0.1089
Extinction coefficient	0	
Largest diff. peak and hole	0.489 and -0.227 e·Å^{-3}	

Compound 144

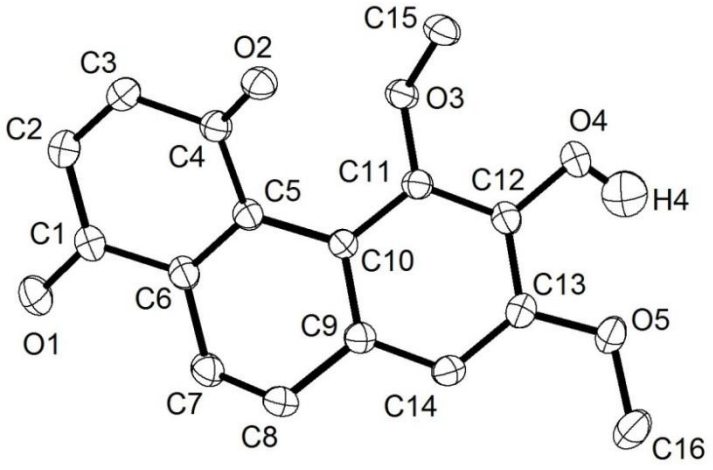


Table 7-9: Crystal data and structure refinement for compound **144**.

Empirical formula	$C_{16}H_{14}O_5$	
Color	orange	
Formula weight	286.27 g·mol^{-1}	
Temperature	100 K	
Wavelength	0.61992 Å	
Crystal system	orthorhombic	
Space group	**P b c a, (no. 61)**	
Unit cell dimensions	a = 16.566(3) Å	α = 90°.
	b = 7.5009(15) Å	β = 90°.
	c = 21.041(4) Å	γ = 90°.
Volume	2614.5(9) Å^3	
Z	8	
Density (calculated)	1.455 Mg·m^{-3}	
Absorption coefficient	0.109 mm^{-1}	
F(000)	1200 e	
Crystal size	0.032 x 0.025 x 0.005 mm^3	
Θ range for data collection	2.730 to 28.551°.	
Index ranges	$-22 \leq h \leq 25$, $-11 \leq k \leq 11$, $-32 \leq l \leq 32$	
Reflections collected	108289	
Independent reflections	4979 [R_{int} = 0.0617]	
Reflections with I>2σ(I)	3900	
Completeness to Θ = 21.836°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0 and 0.3142	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4979 / 0 / 195	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2σ(I)]	R_1 = 0.0477	wR^2 = 0.1316
R indices (all data)	R_1 = 0.0641	wR^2 = 0.1466
Extinction coefficient	0	
Largest diff. peak and hole	0.369 and -0.317 e·Å^{-3}	

Diffraction data were collected at the P11 beamline of the Petra III synchrotron facility Hamburg.

Compound 166c

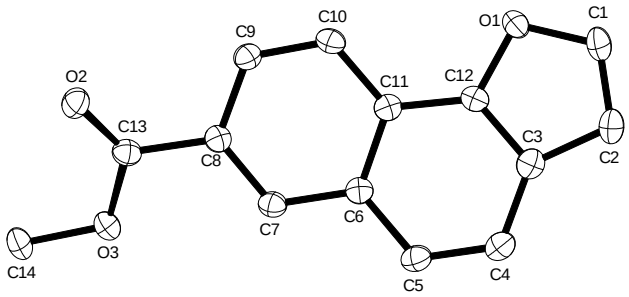
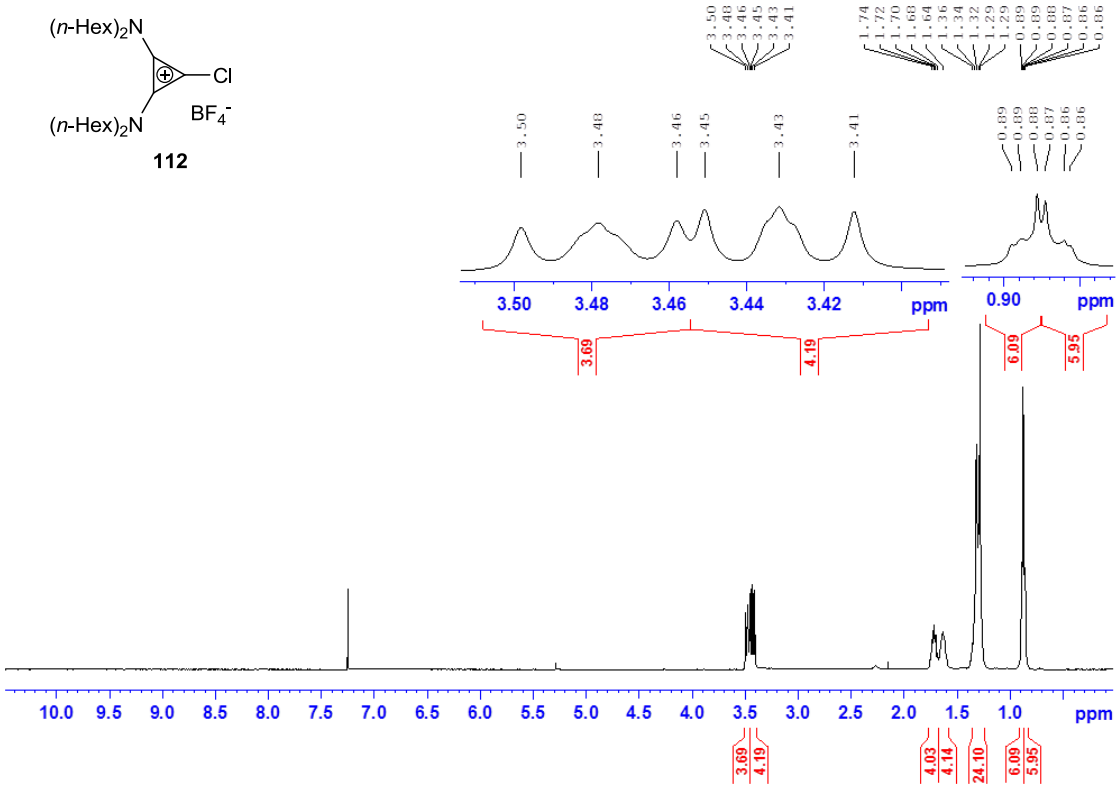


Table 7-10: Crystal data and structure refinement for compound **166c**.

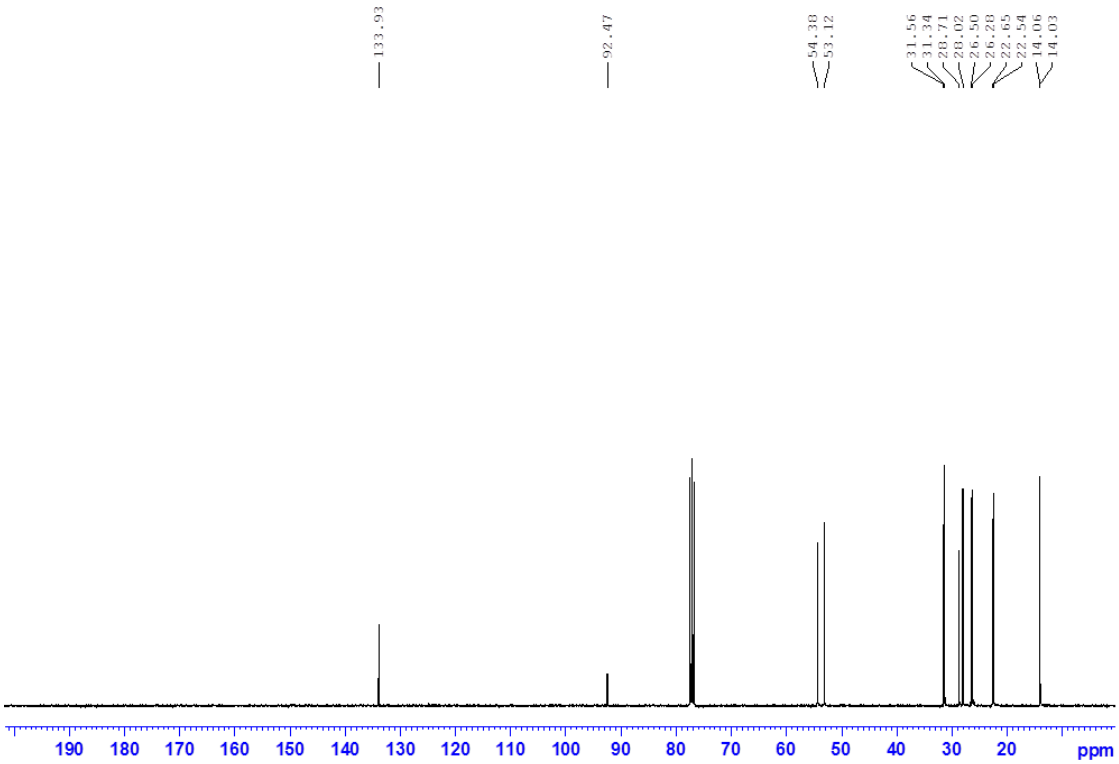
Empirical formula	$C_{14}H_{10}O_3$	
Color	colourless	
Formula weight	226.22 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	MONOCLINIC	
Space group	**p 21, (no. 4)**	
Unit cell dimensions	a = 7.6215(3) Å	α = 90°.
	b = 6.1218(2) Å	β = 104.1171(15)°.
	c = 11.6856(4) Å	γ = 90°.
Volume	528.75(3) $Å^3$	
Z	2	
Density (calculated)	1.421 $Mg \cdot m^{-3}$	
Absorption coefficient	0.824 mm^{-1}	
F(000)	236 e	
Crystal size	0.30 x 0.07 x 0.06 mm^3	
Θ range for data collection	3.900 to 67.297°.	
Index ranges	$-9 \leq h \leq 9$, $-7 \leq k \leq 6$, $-13 \leq l \leq 13$	
Reflections collected	12502	
Independent reflections	1771 [R_{int} = 0.0379]	
Reflections with I>2σ(I)	1684	
Completeness to Θ = 67.297°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.95884 and 0.83568	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1771 / 1 / 156	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2σ(I)]	R_1 = 0.0422	wR^2 = 0.1081
R indices (all data)	R_1 = 0.0441	wR^2 = 0.1099
Absolute structure parameter	-0.1(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.173 and -0.229 $e \cdot Å^{-3}$	

7.2 NMR-Spectra

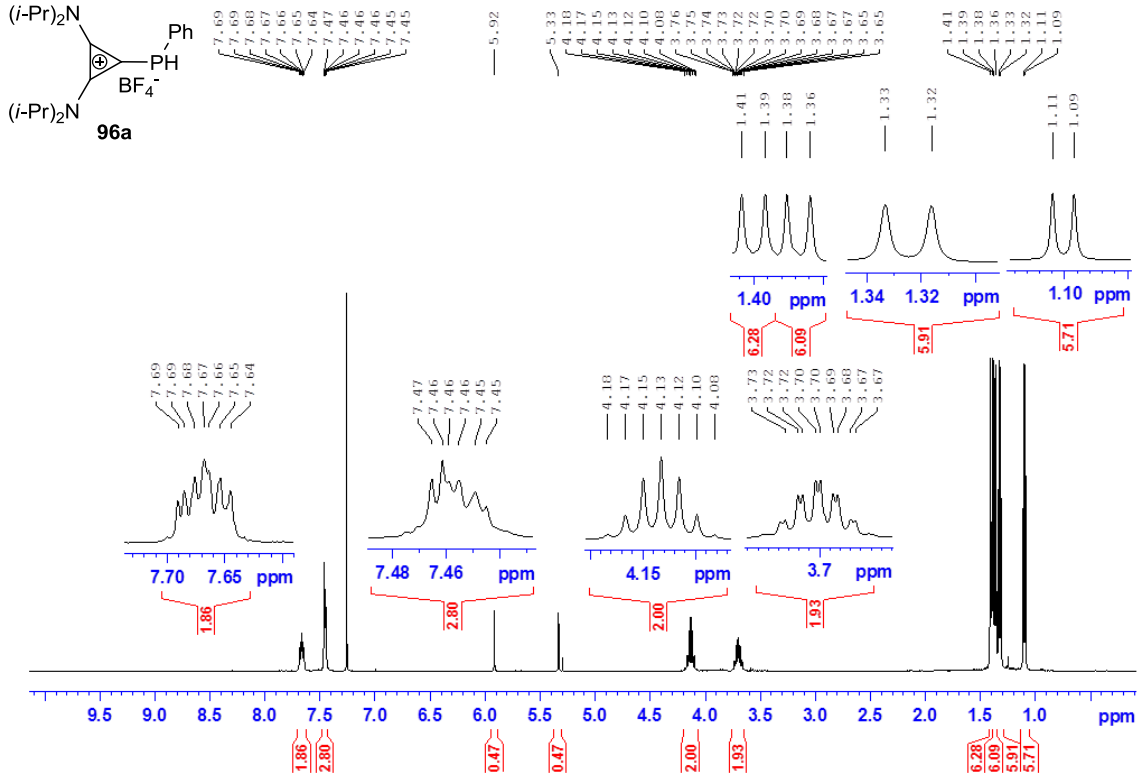
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **112**



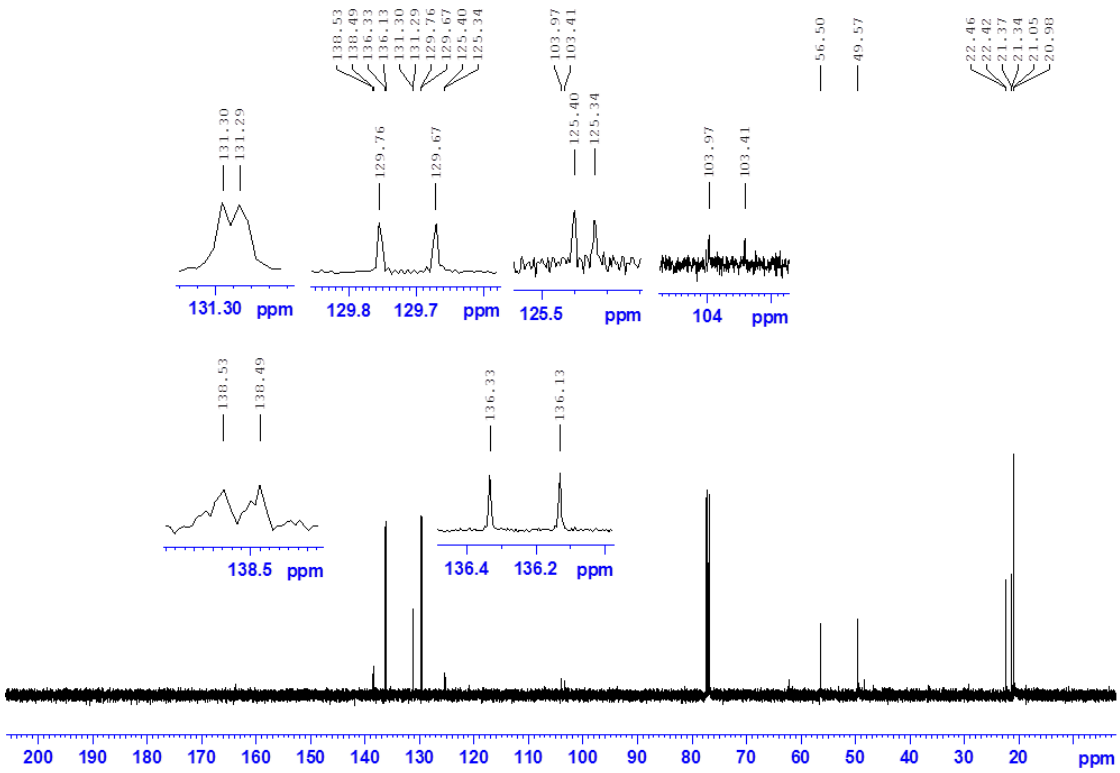
^{13}C-NMR (101 MHz, $CDCl_3$): Compound **112**



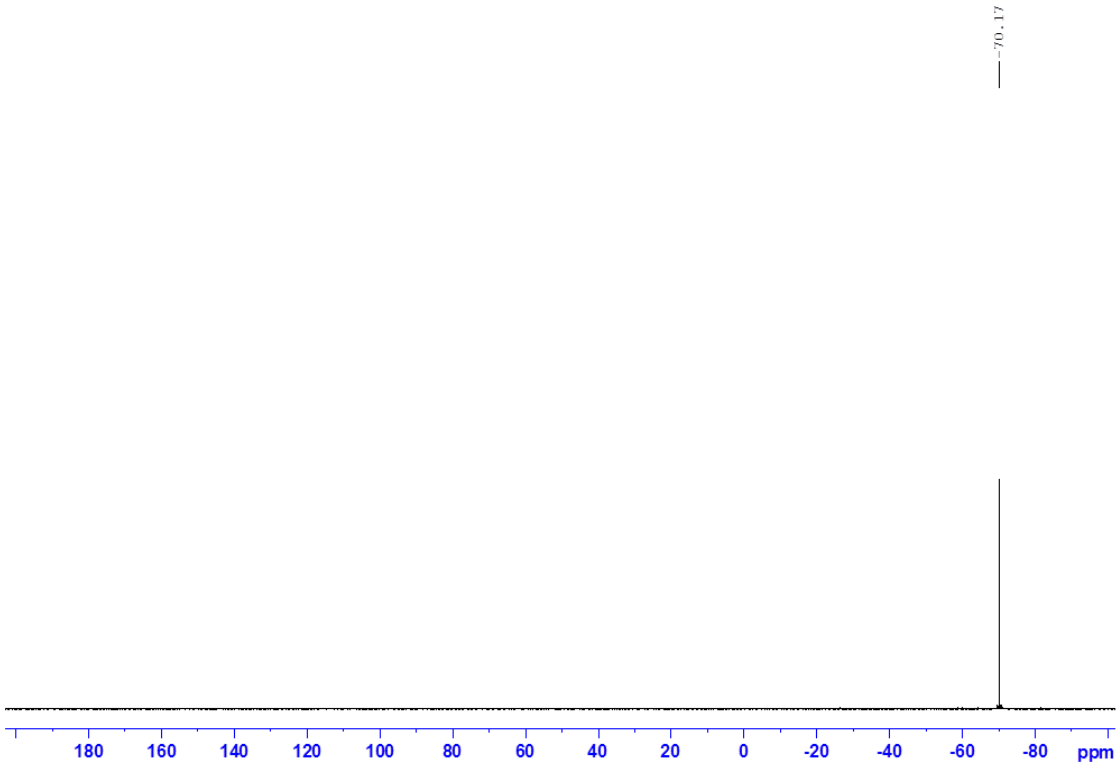
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **96a**



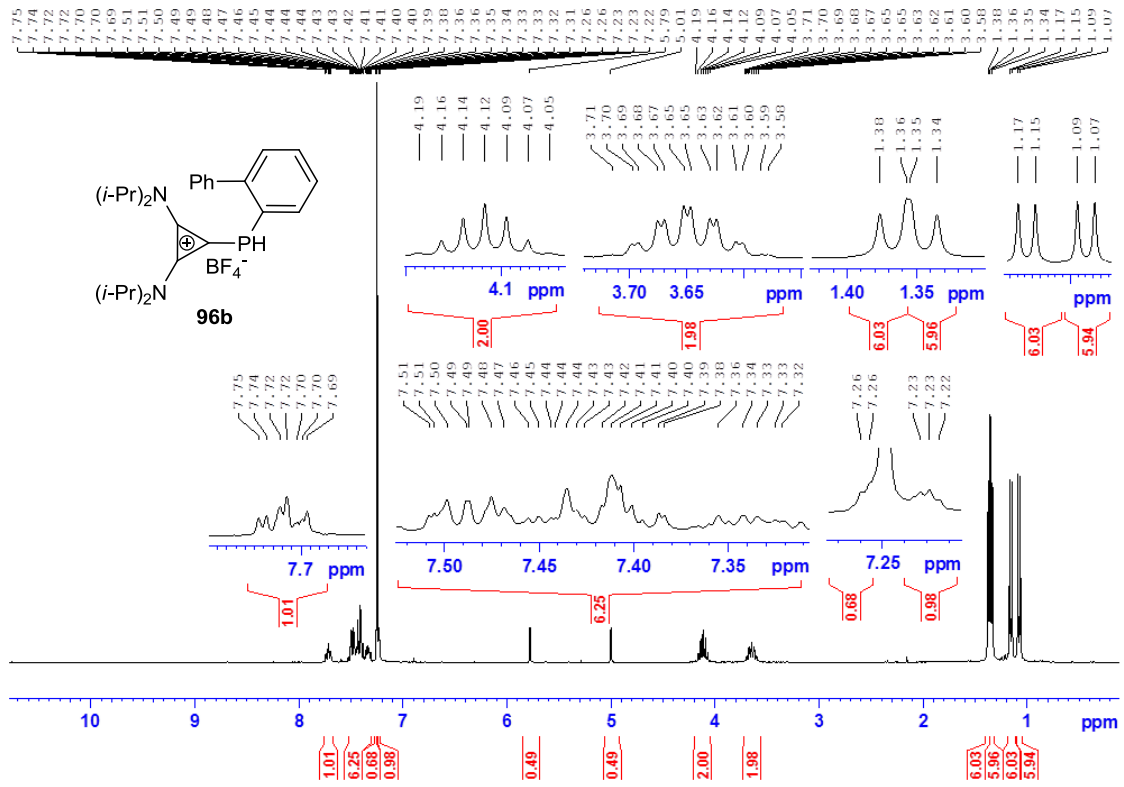
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): Compound **96a**



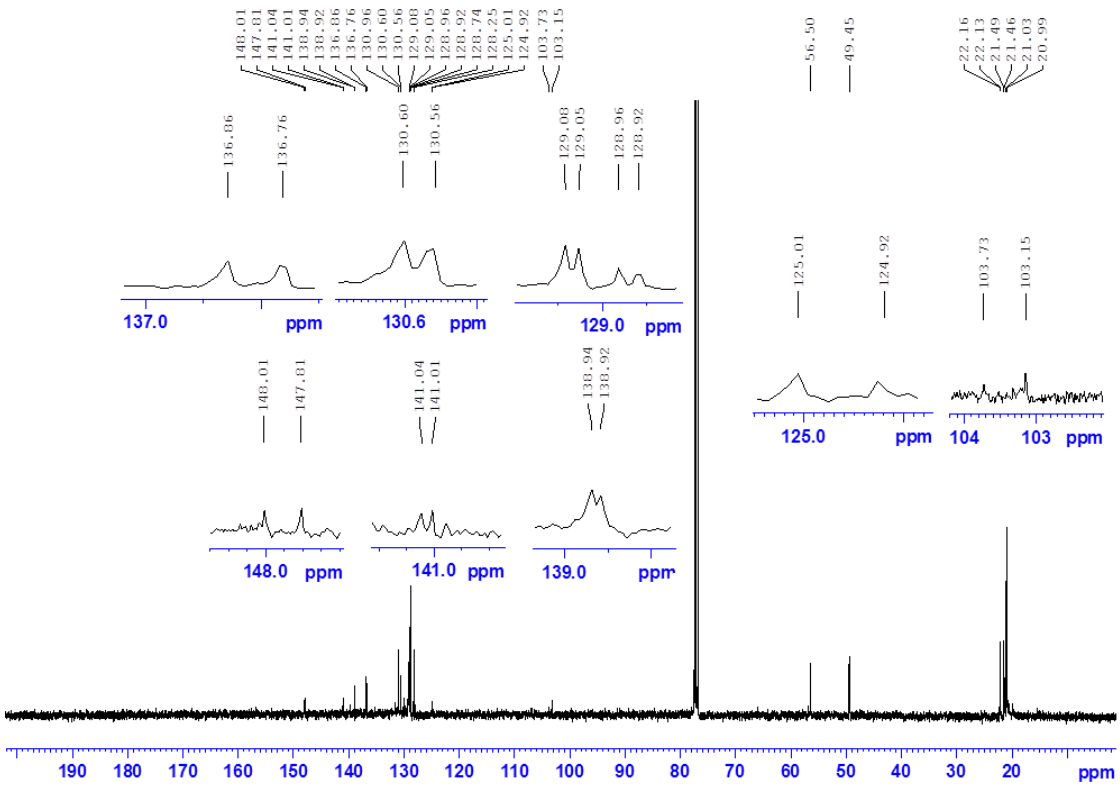
$^{31}P\{^{1}H\}$-NMR (162 MHz, $CDCl_3$): Compound **96a**



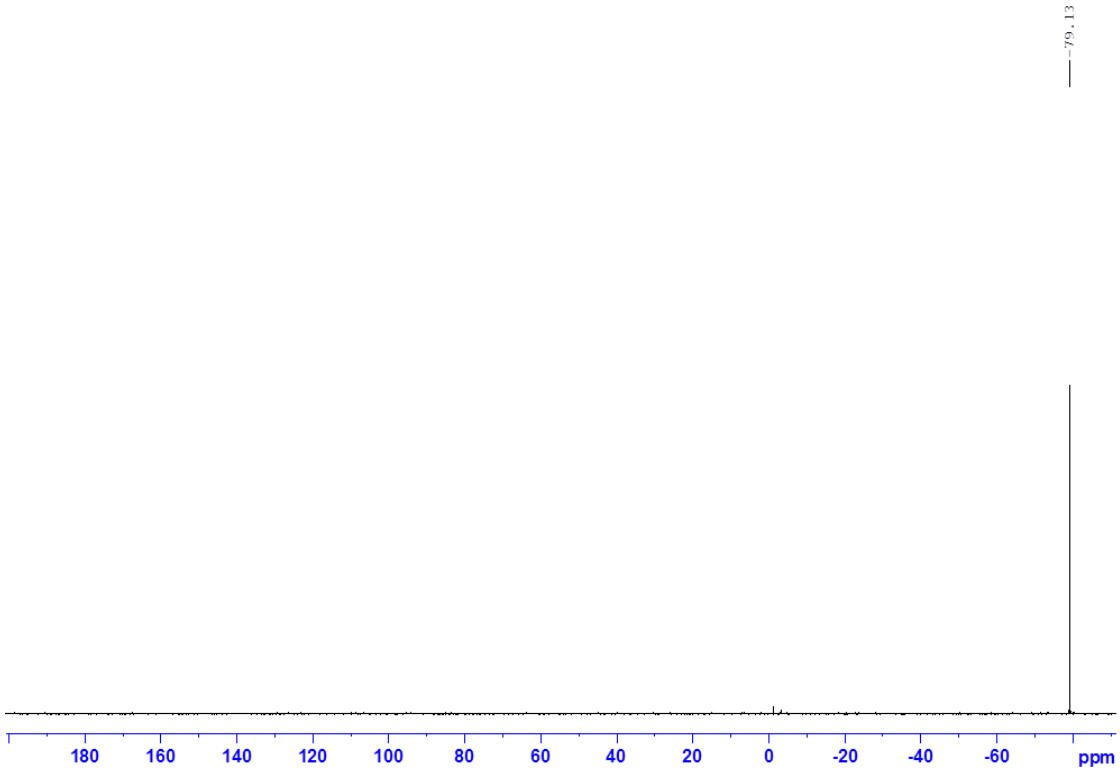
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **96b**



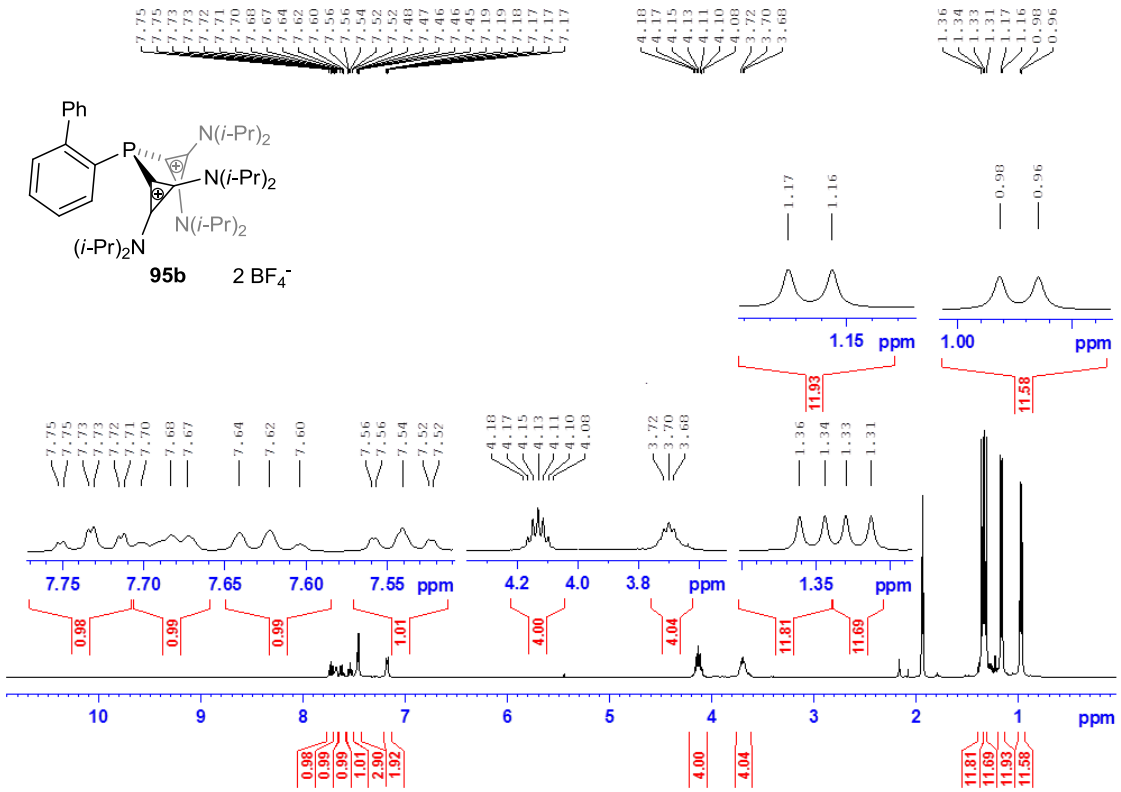
$^{13}C\{^1H\}$-NMR ($CDCl_3$, 101 MHz): Compound **96b**



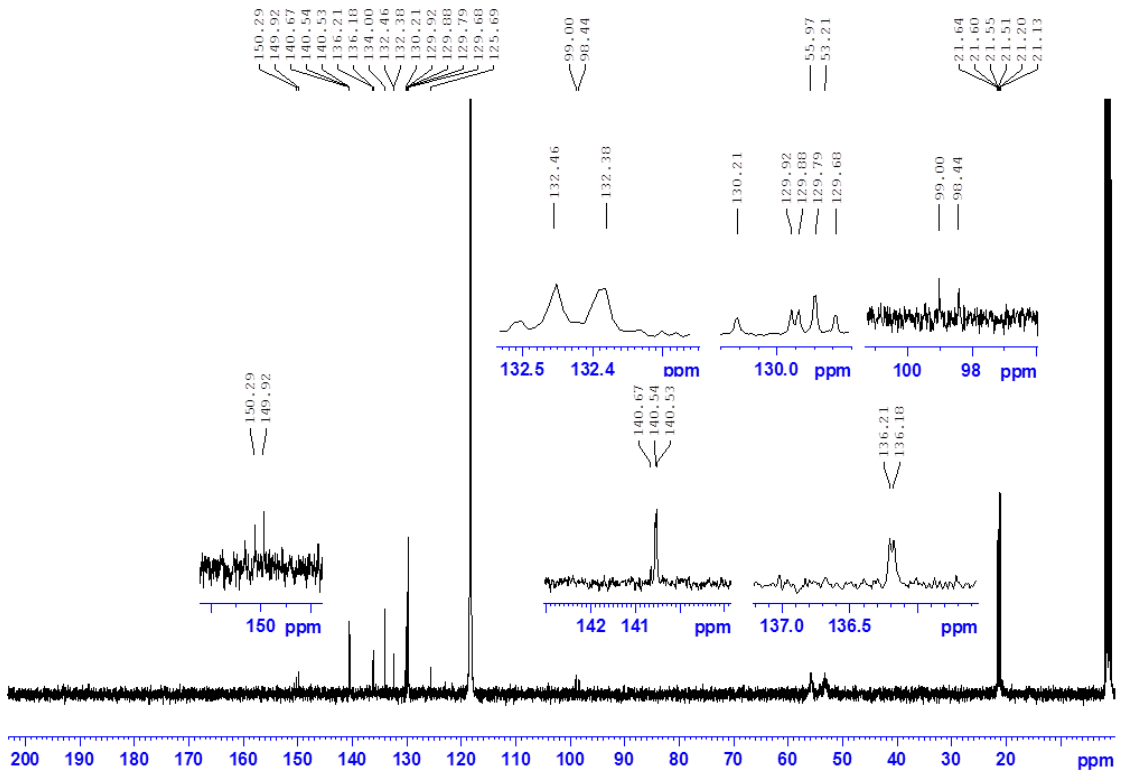
$^{31}P\{^1H\}$-NMR ($CDCl_3$, 162 MHz): Compound **96b**



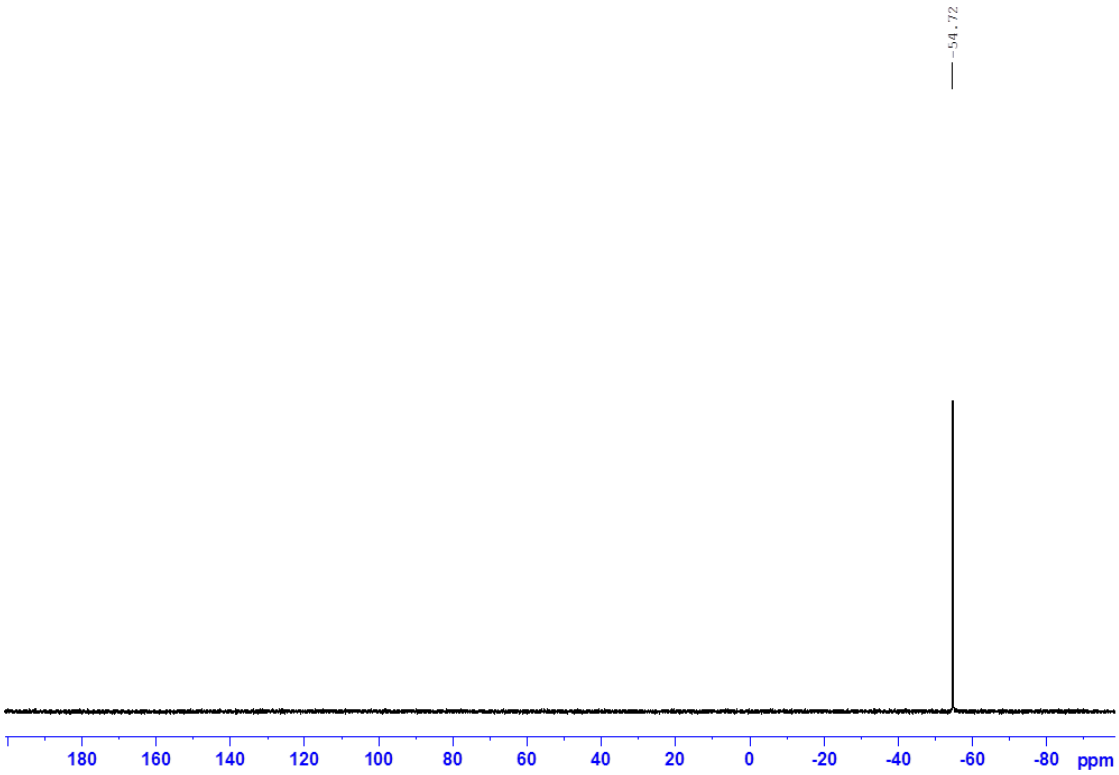
^{1}H-NMR (400 MHz, CD_3CN): Compound **95b**



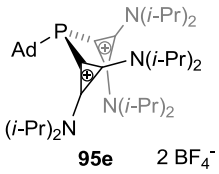
^{13}C{^{1}H}-NMR (101 MHz, CD_3CN): Compound **95b**



$^{31}P\{^{1}H\}$-NMR (CD_3CN, 162 MHz): Compound **95b**

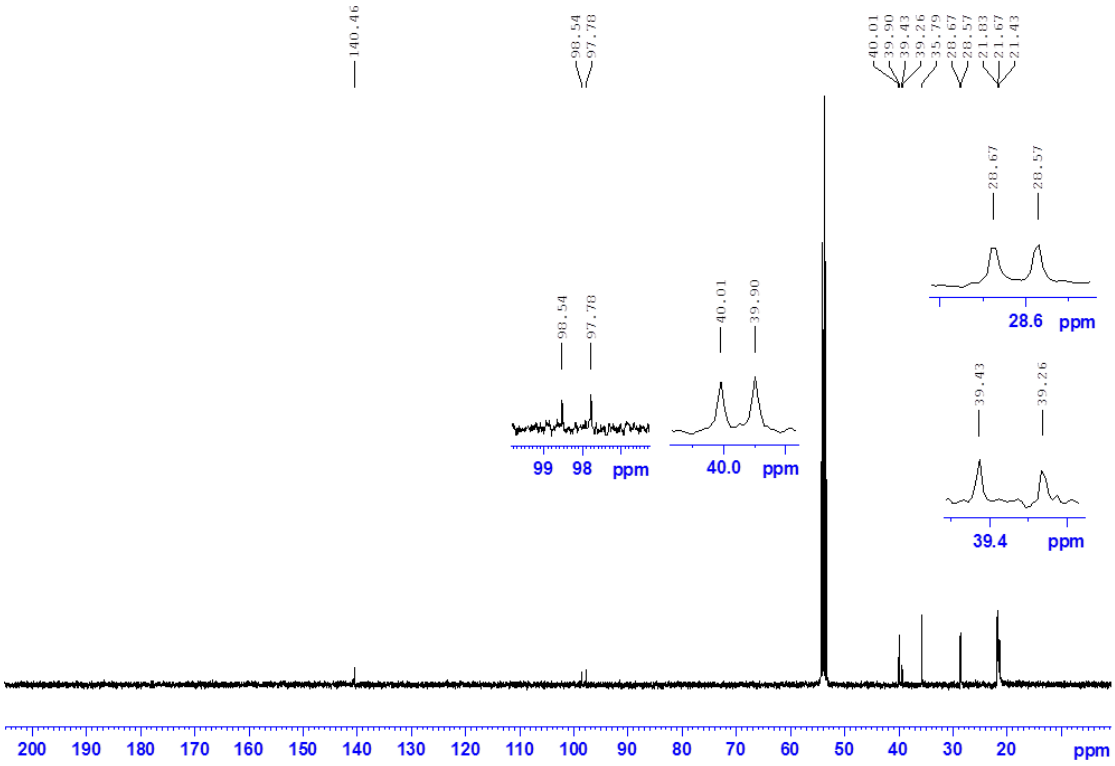


^{1}H-NMR (400 MHz, CD_2Cl_2): Compound **95e**

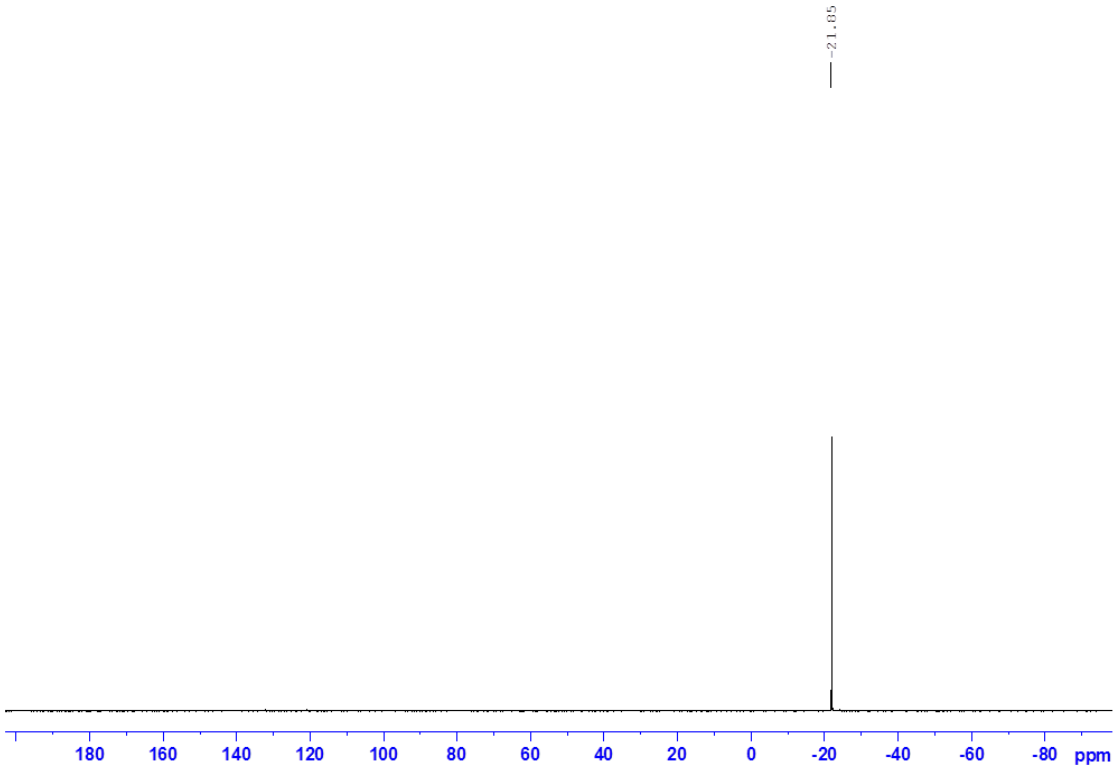


95e 2 BF_4^-

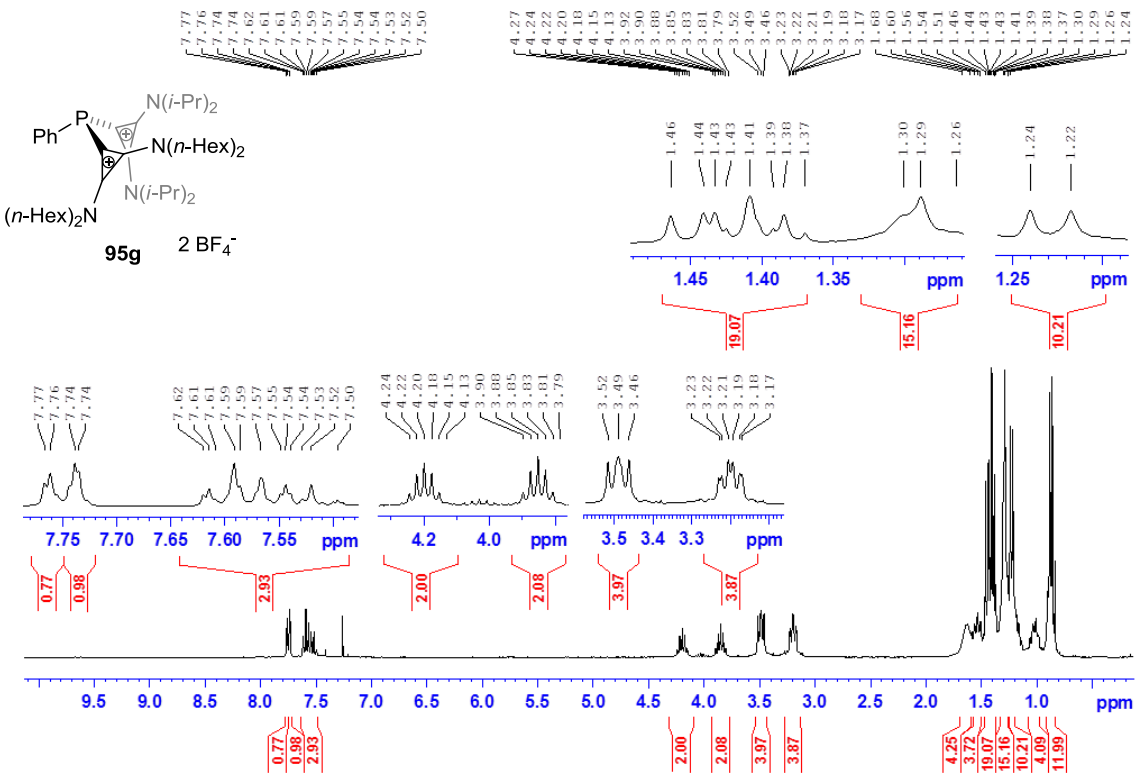
$^{13}C\{^1H\}$-NMR (101 MHz, CD_2Cl_2): Compound **95e**



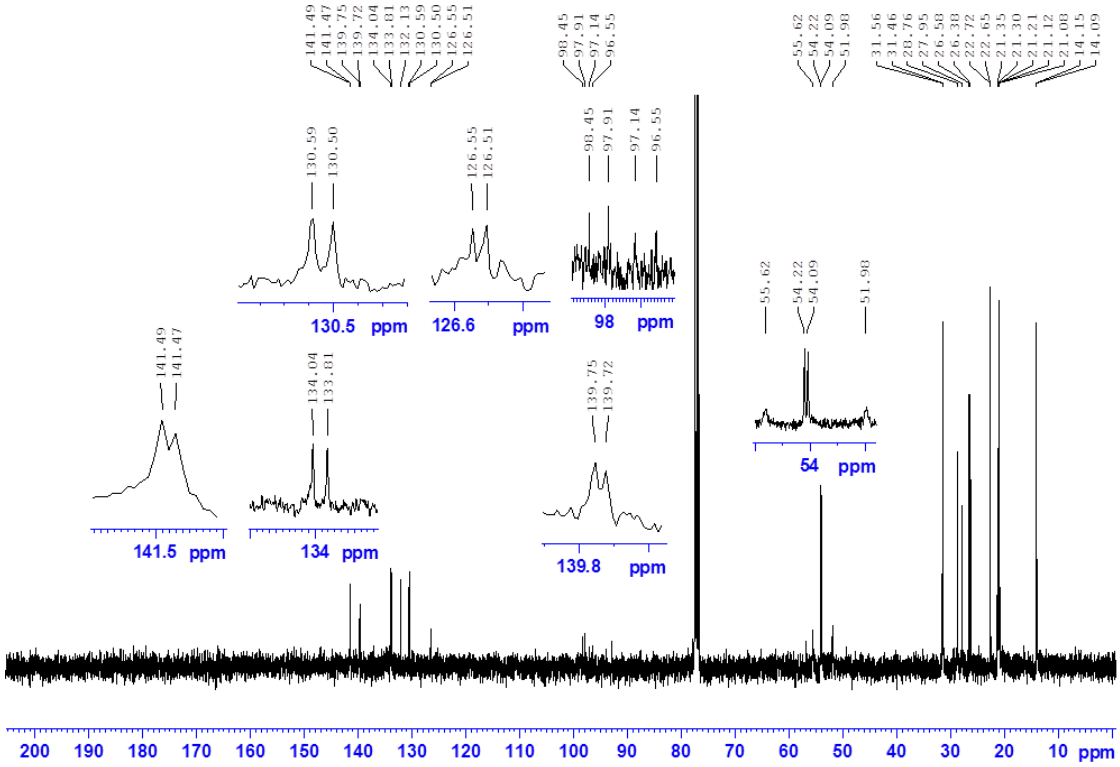
$^{31}P\{^1H\}$-NMR (162 MHz, CD_2Cl_2): Compound **95e**



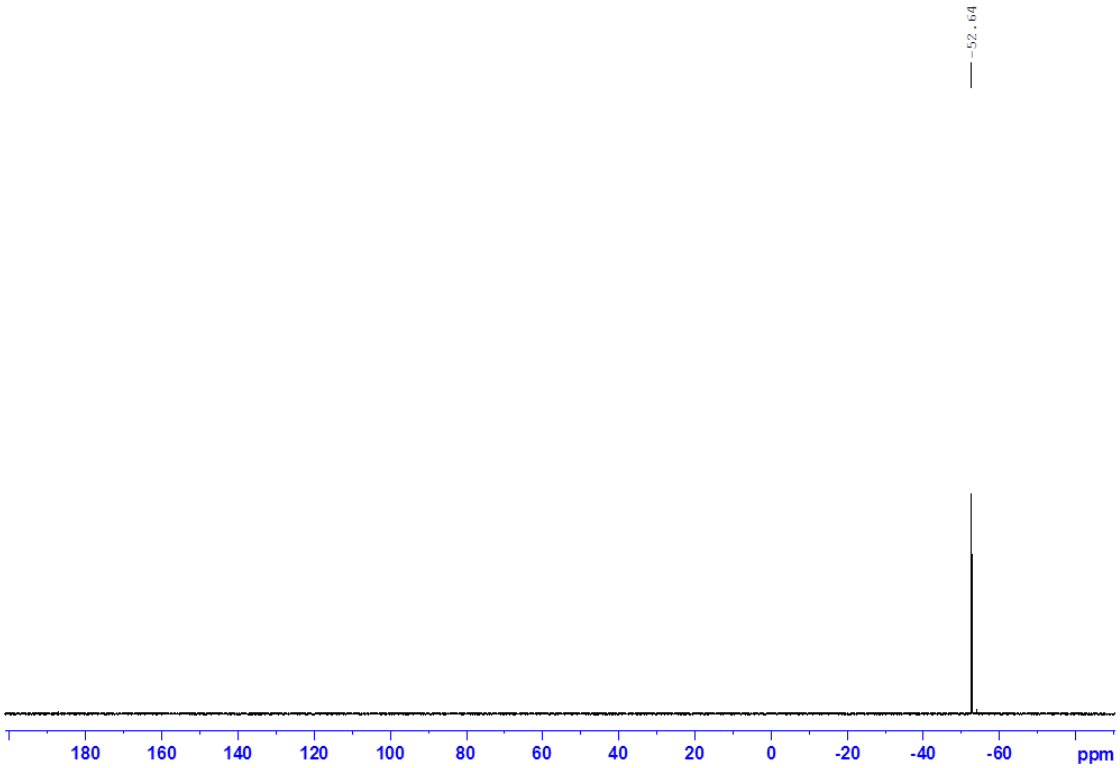
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **95g**



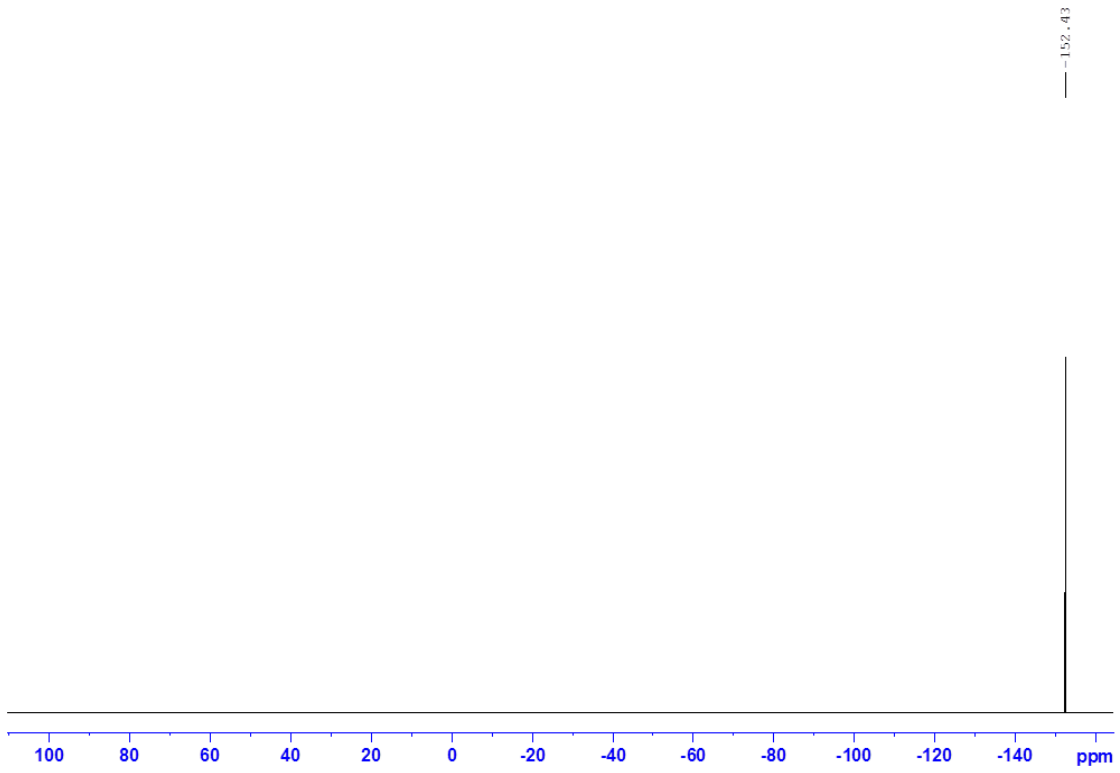
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): Compound **95g**



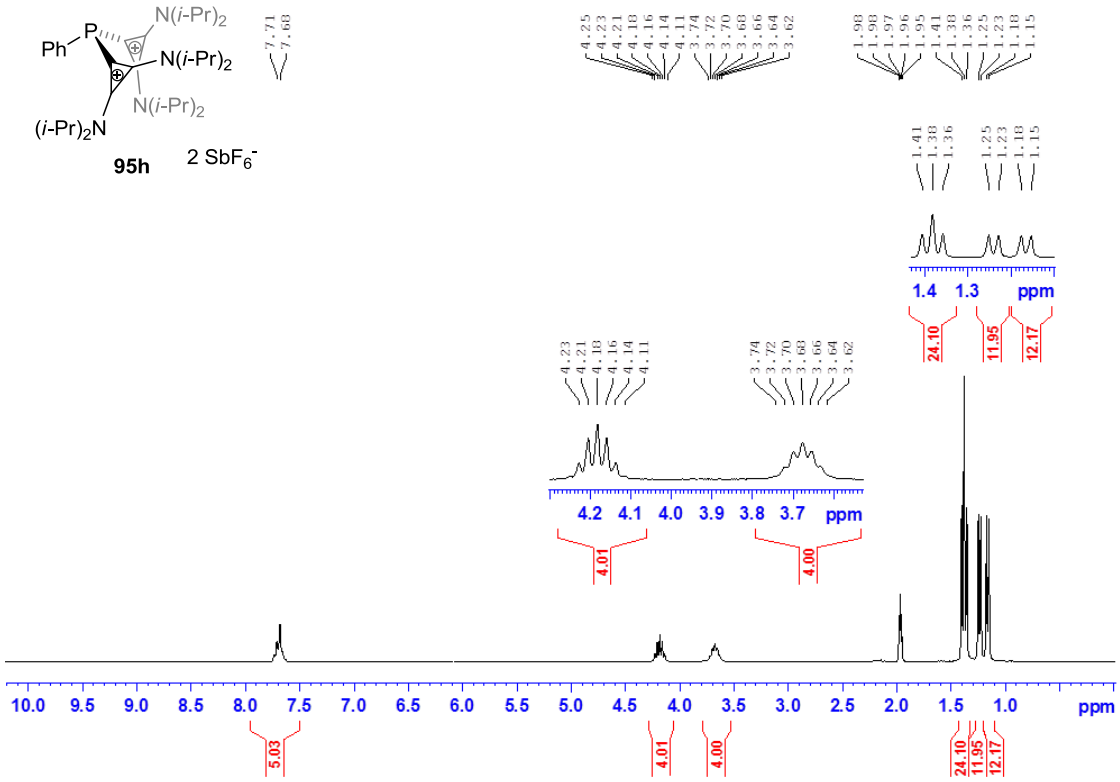
$^{31}P\{^{1}H\}$-NMR (122 MHz, $CDCl_3$): Compound **95g**



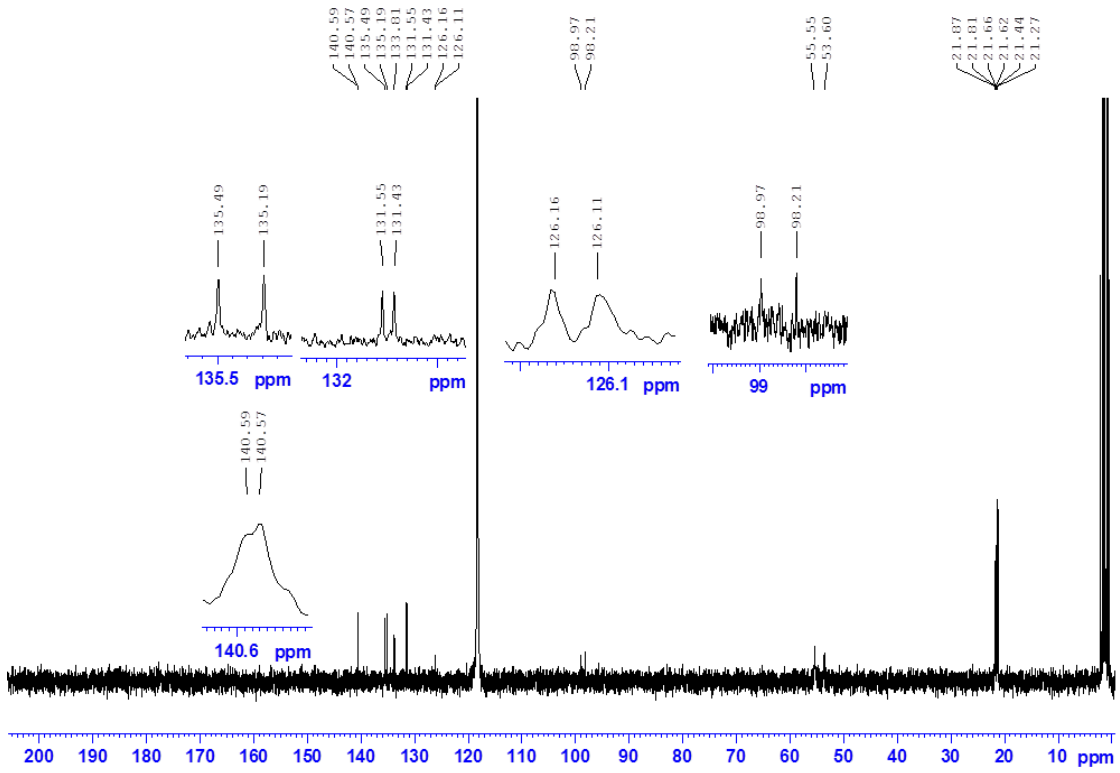
$^{19}F\{^{1}H\}$-NMR (282 MHz, $CDCl_3$): Compound **95g**



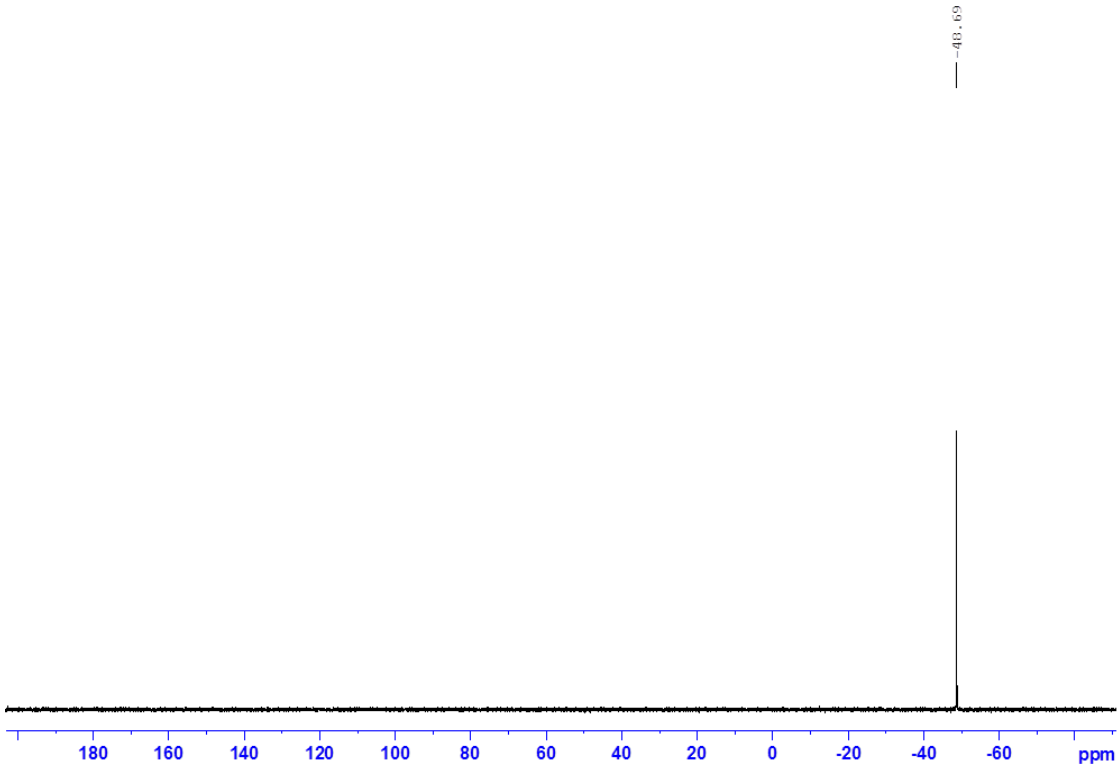
^{1}H-NMR (300 MHz, CD_3CN): Compound **95h**



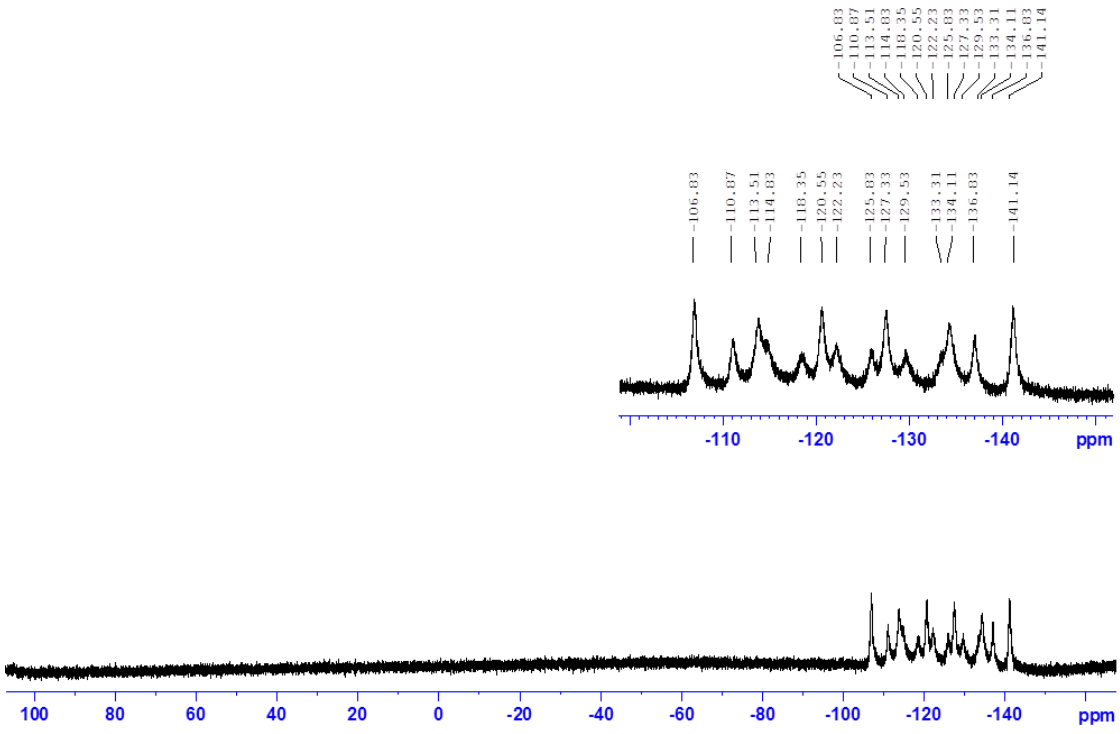
^{13}C{^{1}H}-NMR (CD_3CN, 75 MHz): Compound **95h**



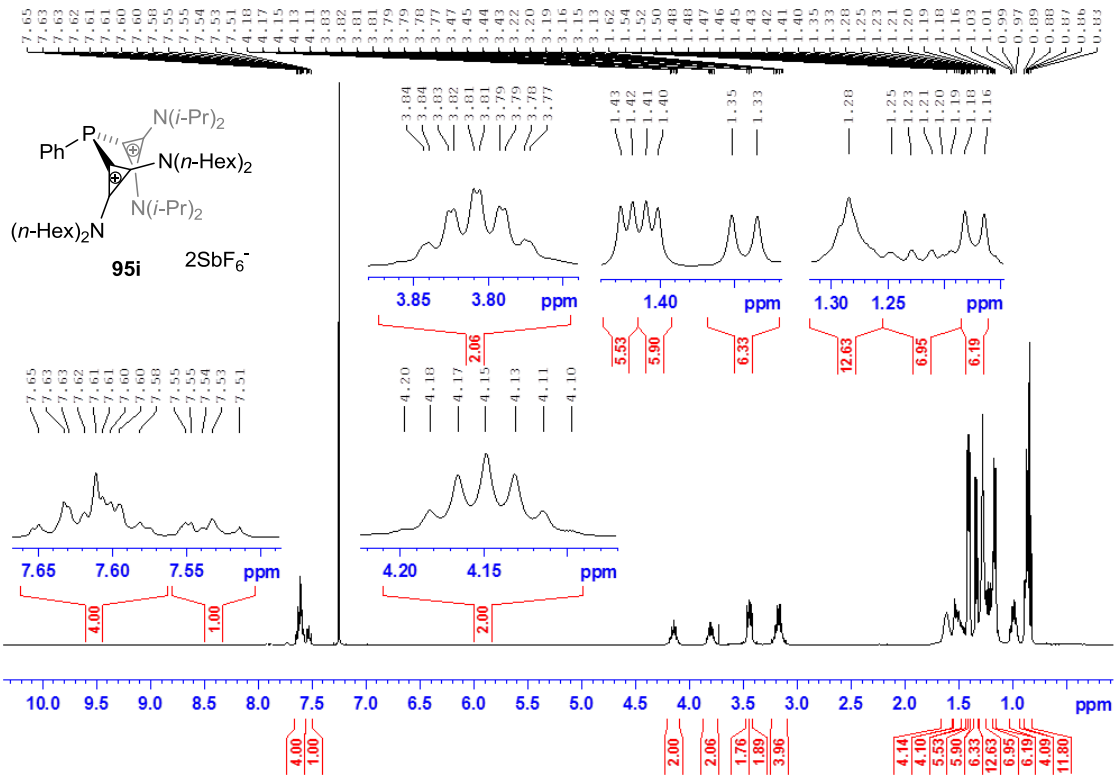
$^{31}P\{^{1}H\}$-NMR (CD_3CN, 122 MHz): Compound **95h**



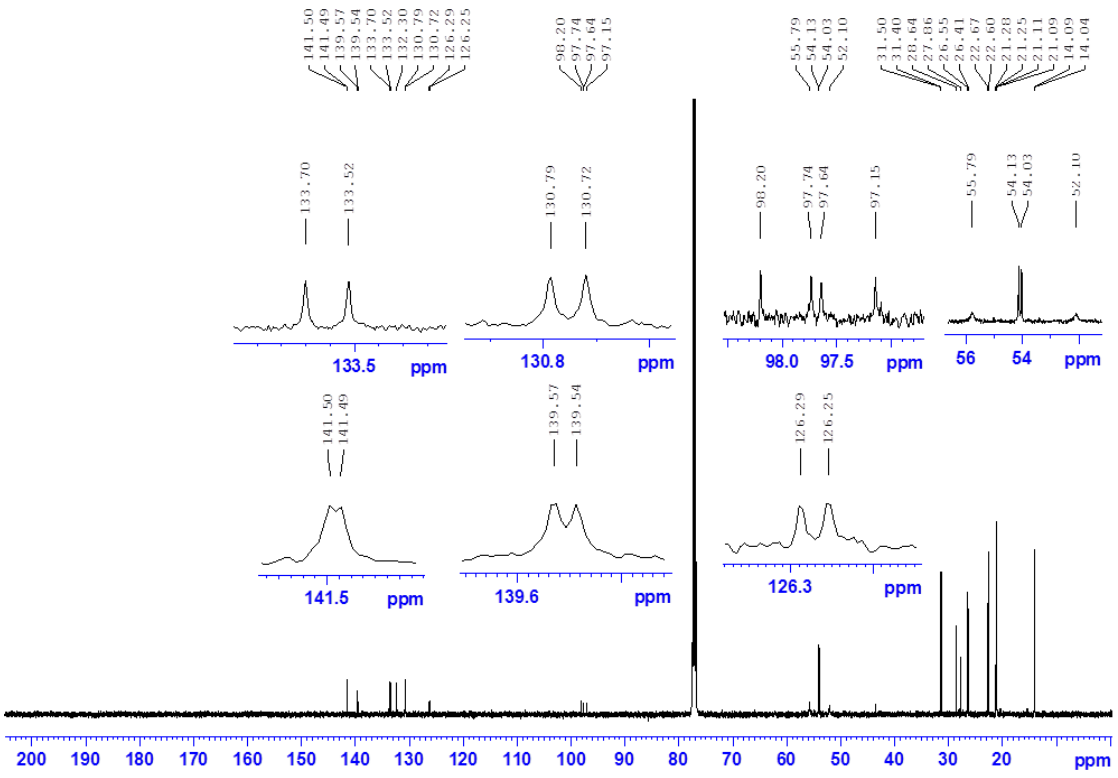
$^{19}F\{^{1}H\}$-NMR (CD_3CN, 282 MHz): Compound **95h**



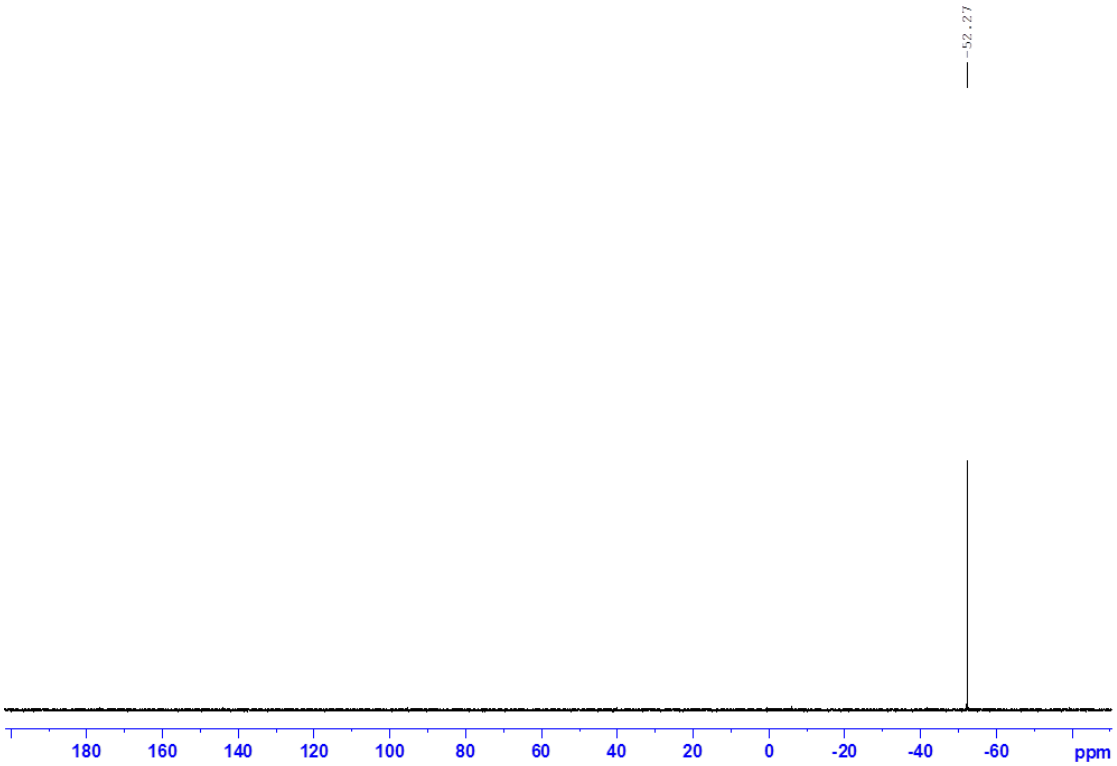
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **95i**



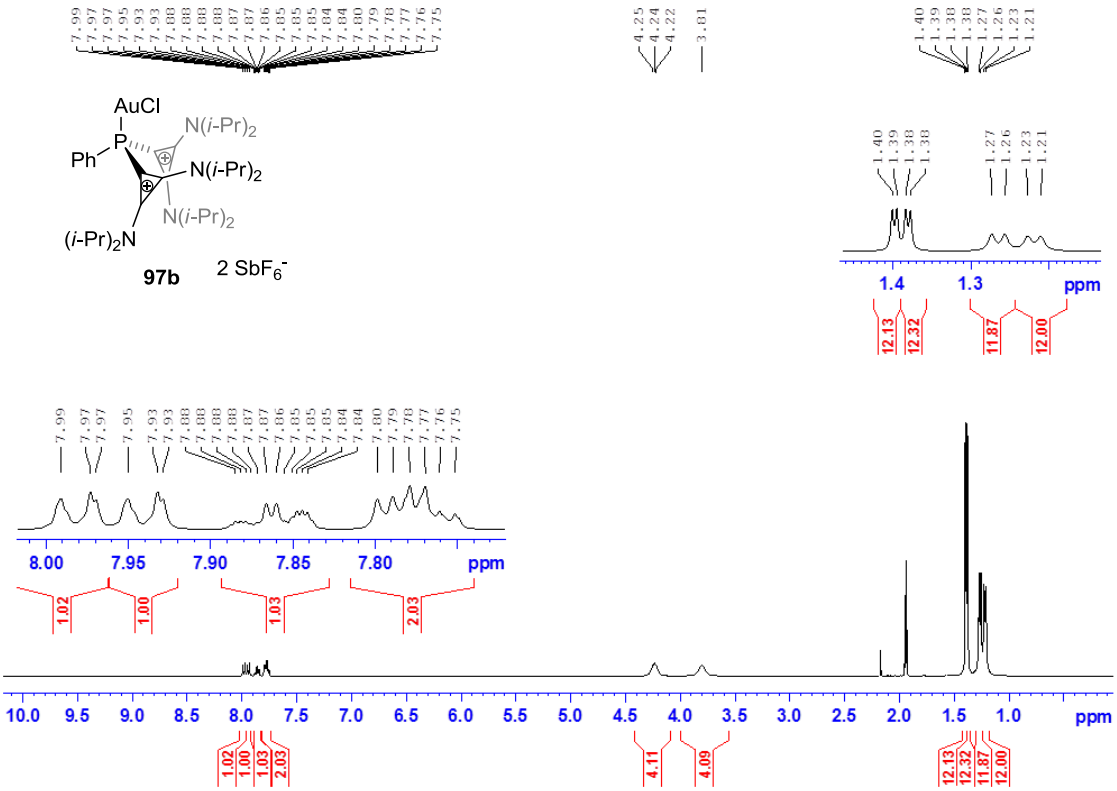
^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): Compound **95i**



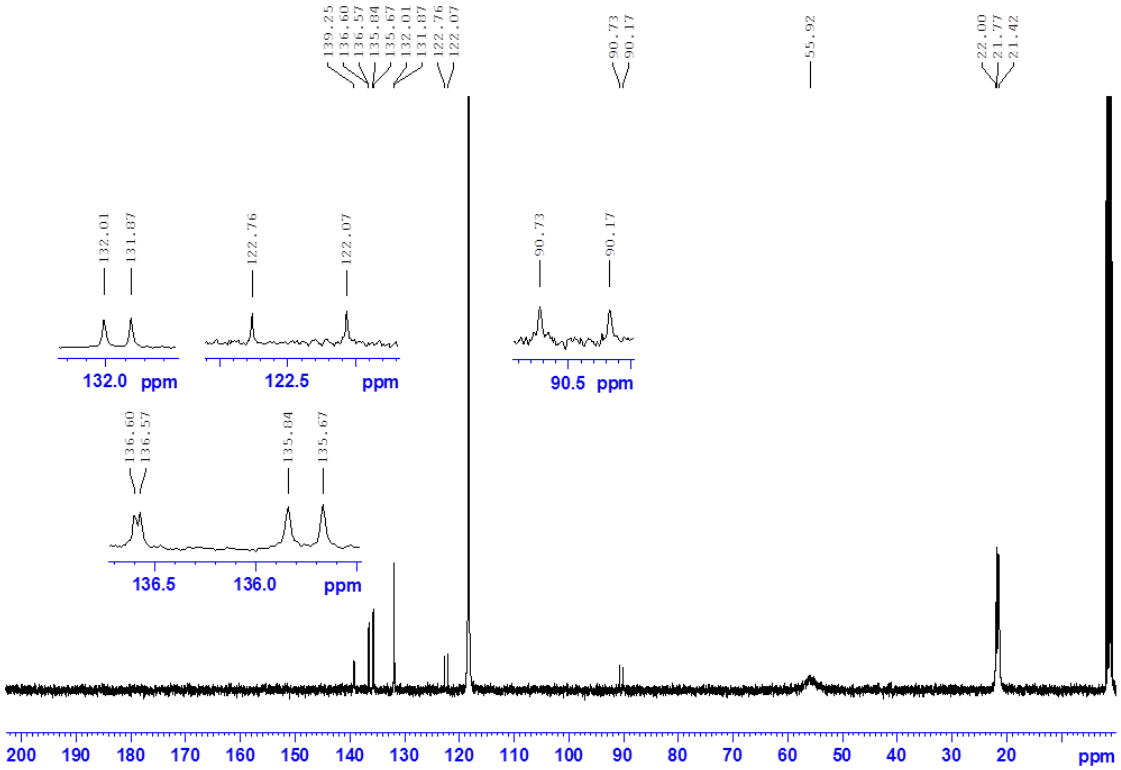
$^{31}P\{^{1}H\}$-NMR (122 MHz, $CDCl_3$): Compound **95i**



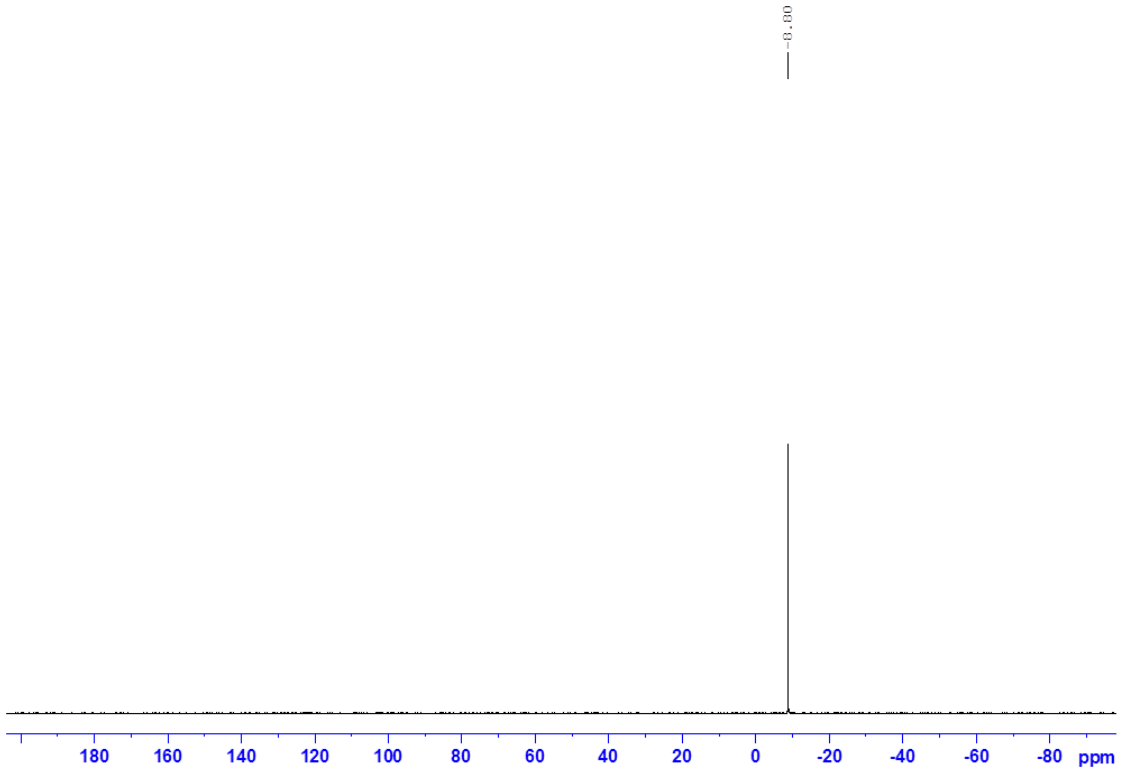
^{1}H-NMR (400 MHz, CD_3CN): Compound **97b**



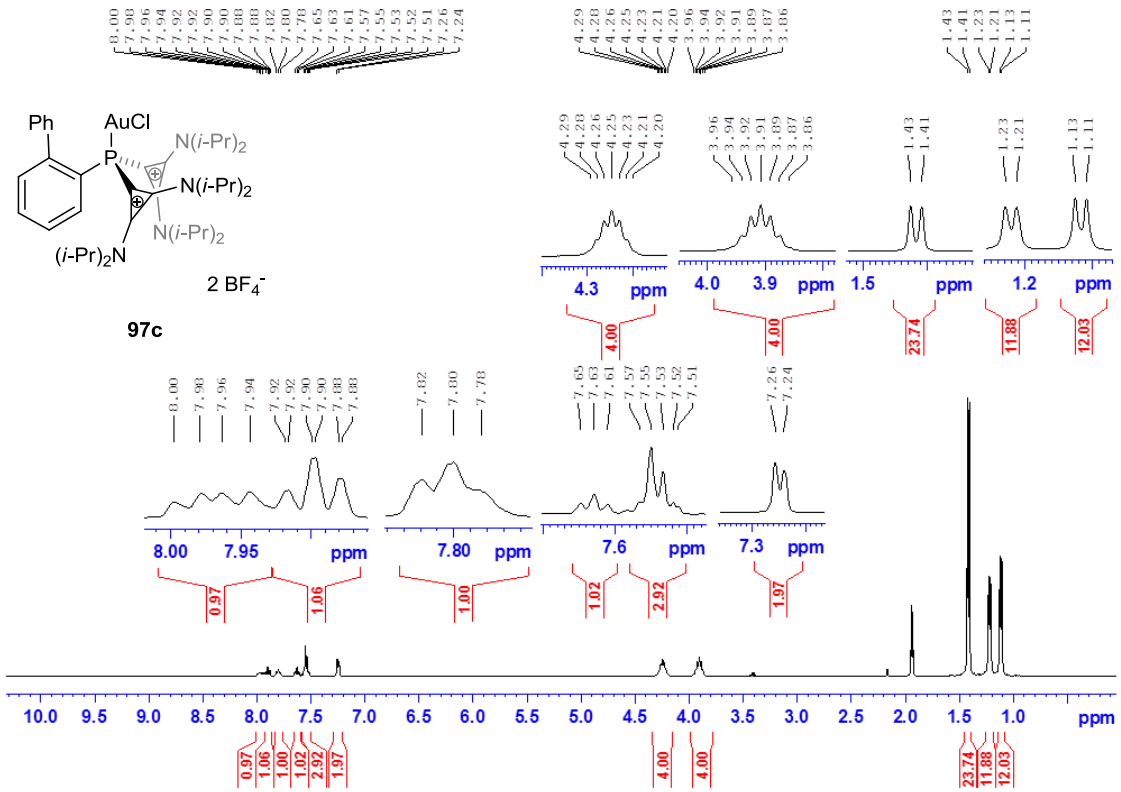
$^{13}C\{^{1}H\}$-NMR (125 MHz, CD_3CN): Compound **97b**



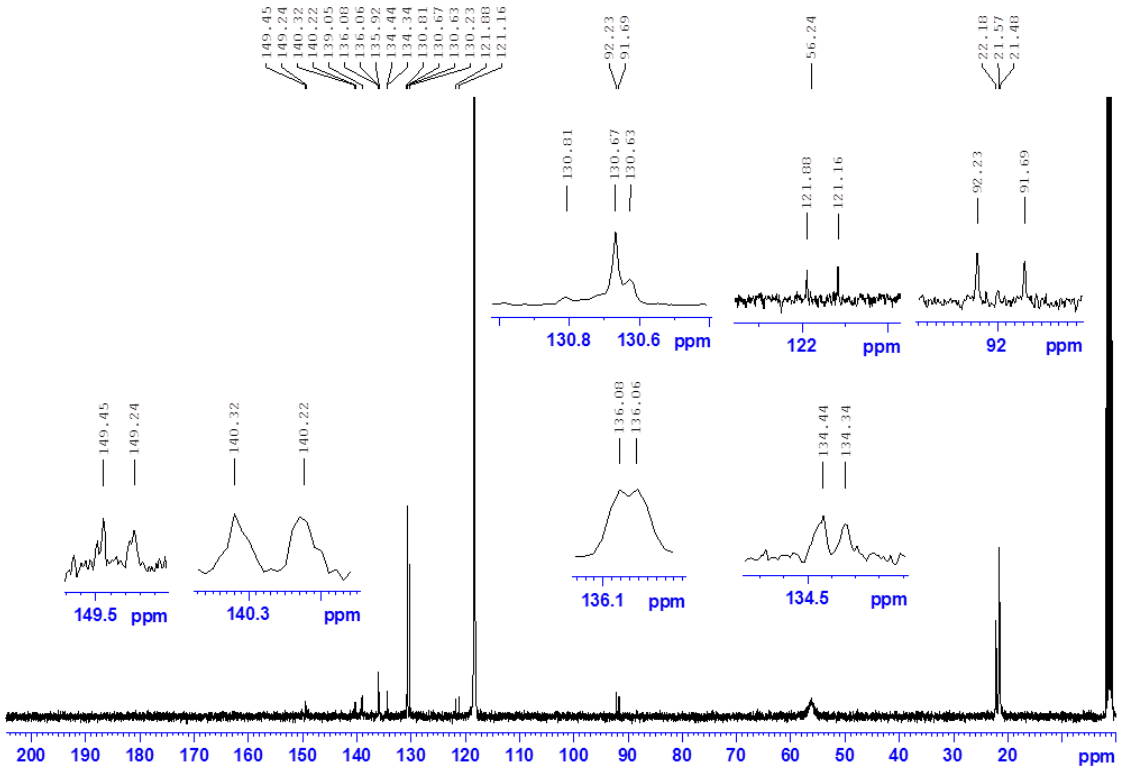
$^{31}P\{^{1}H\}$-NMR (162 MHz, CD_3CN): Compound **97b**



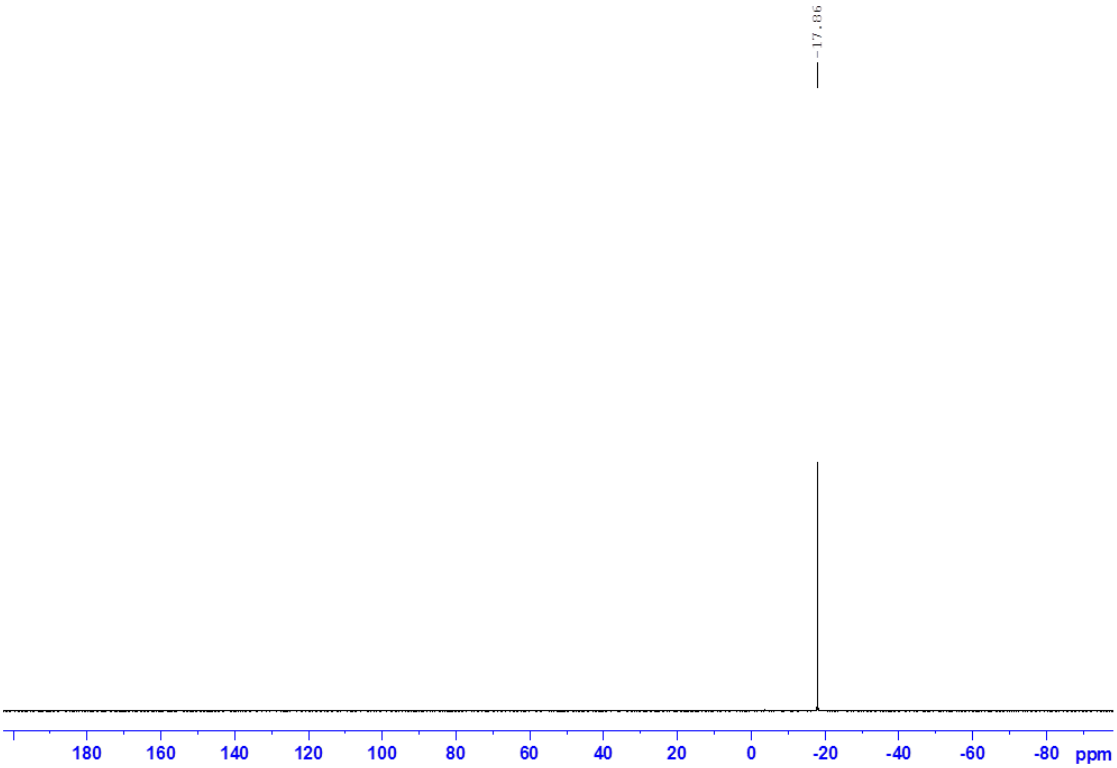
^{1}H-NMR (400 MHz, CD_3CN): Compound **97c**



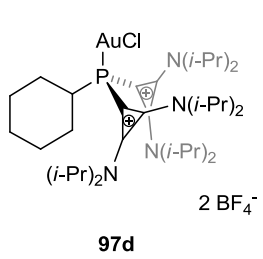
^{13}C{^{1}H}-NMR (125 MHz, CD_3CN): Compound **97c**



$^{31}P\{^{1}H\}$-NMR (162 MHz, CD_3CN): Compound **97c**

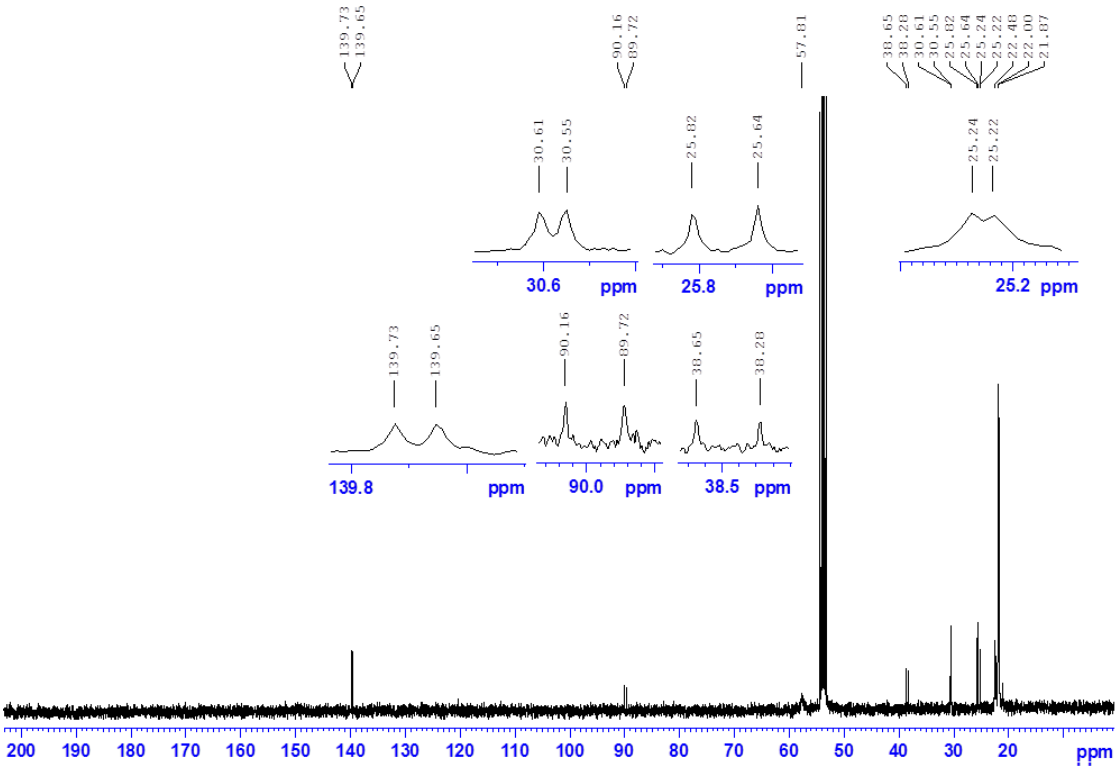


^{1}H-NMR (400 MHz, CD_2Cl_2): Compound **97d**

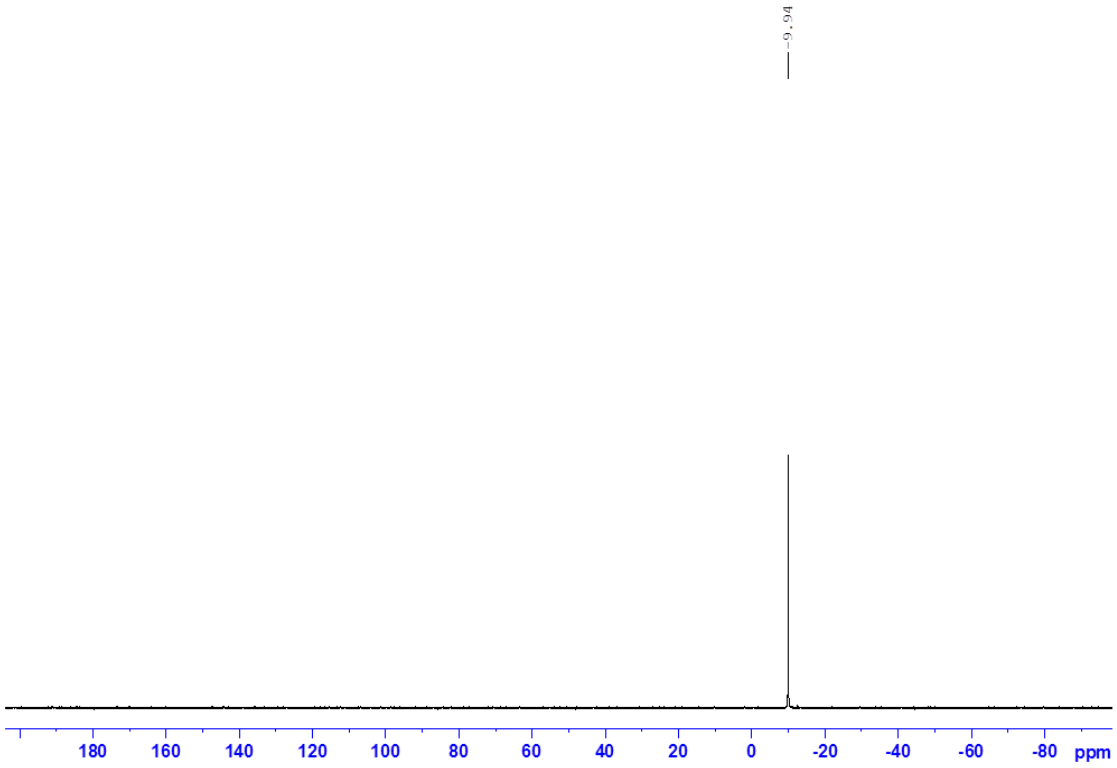


97d

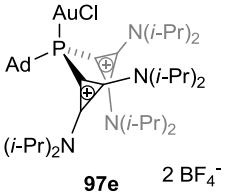
$^{13}C\{^1H\}$-NMR (400 MHz, CD_2Cl_2): Compound **97d**



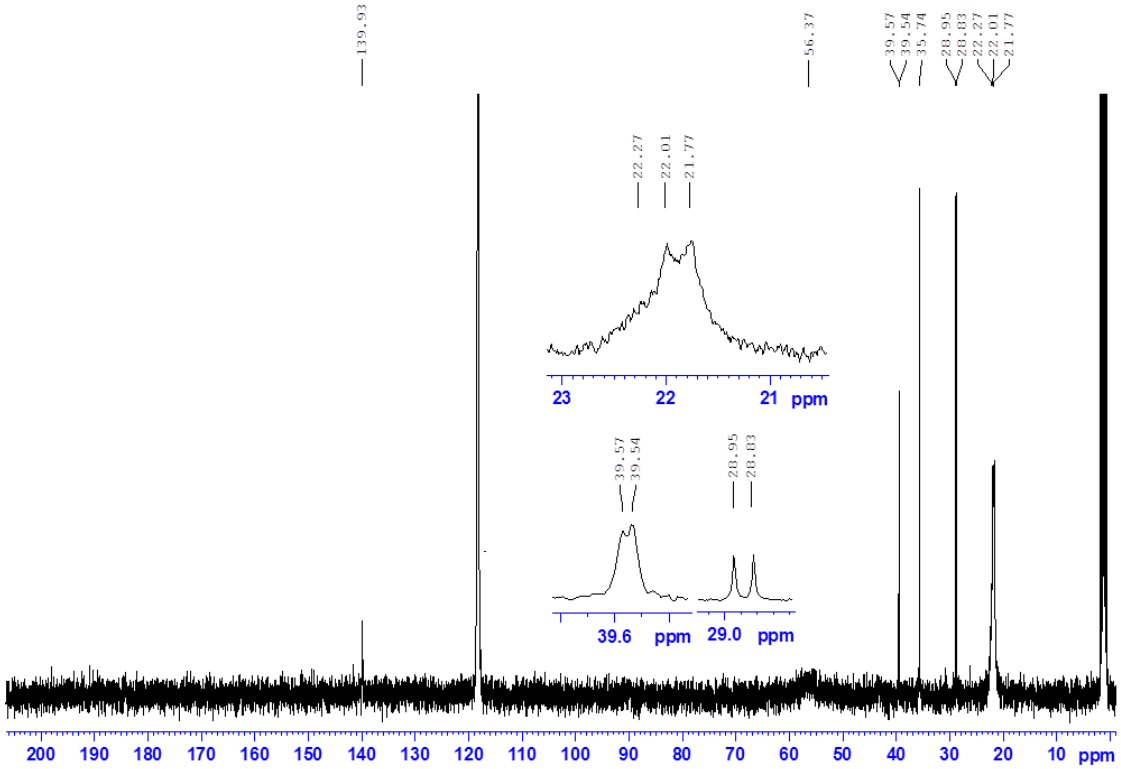
$^{31}P\{^1H\}$-NMR (400 MHz, CD_2Cl_2): Compound **97d**



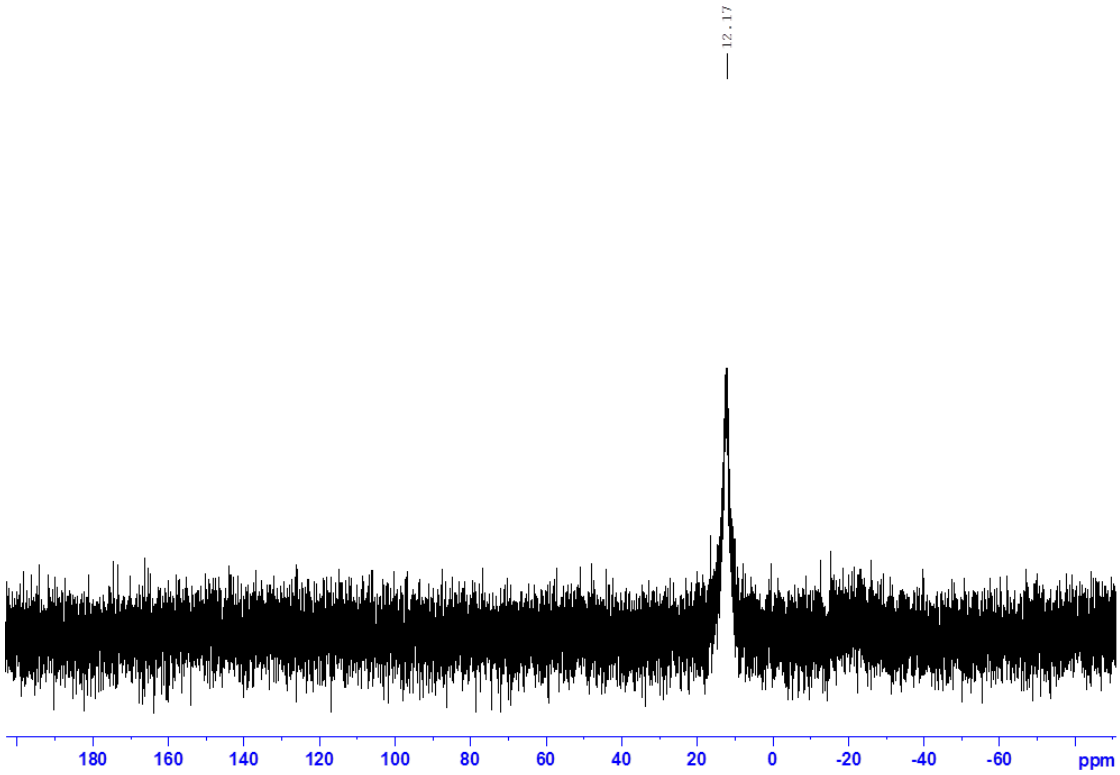
^{1}H-NMR (400 MHz, CD_3CN): Compound **97e**



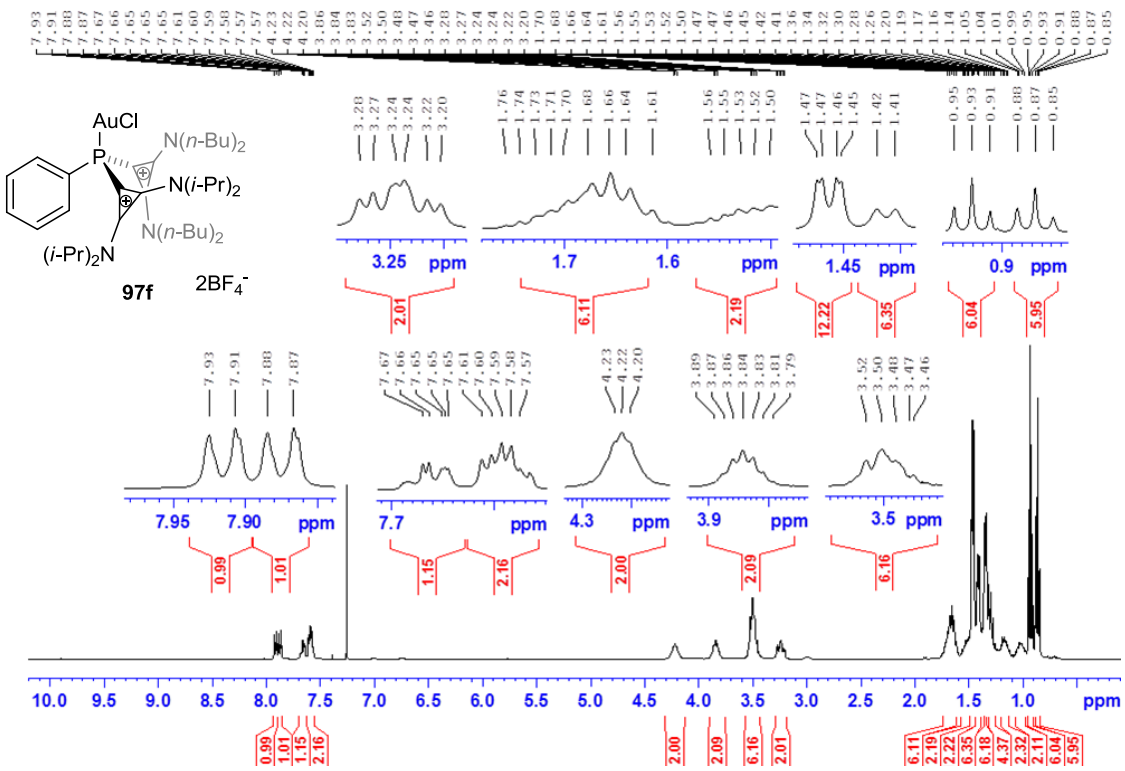
^{13}C{^{1}H}-NMR (101 MHz, CD_3CN): Compound **97e**[97]



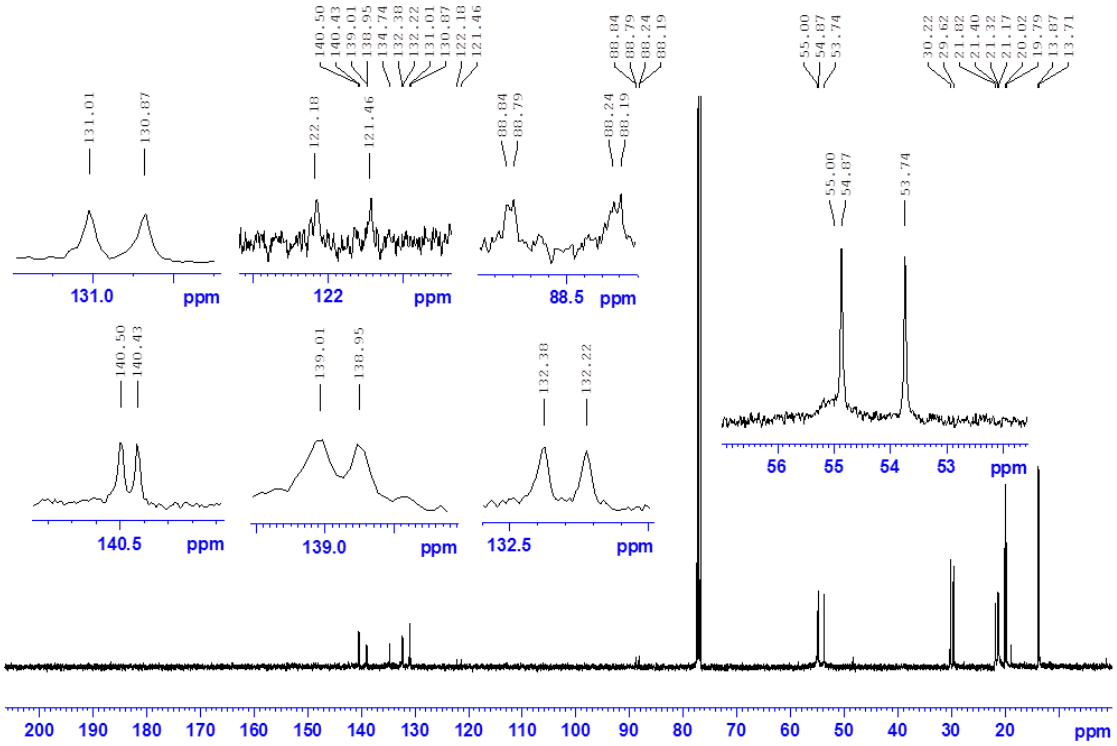
$^{31}P\{^{1}H\}$-NMR (162 MHz, CD_3CN): Compound **97e**



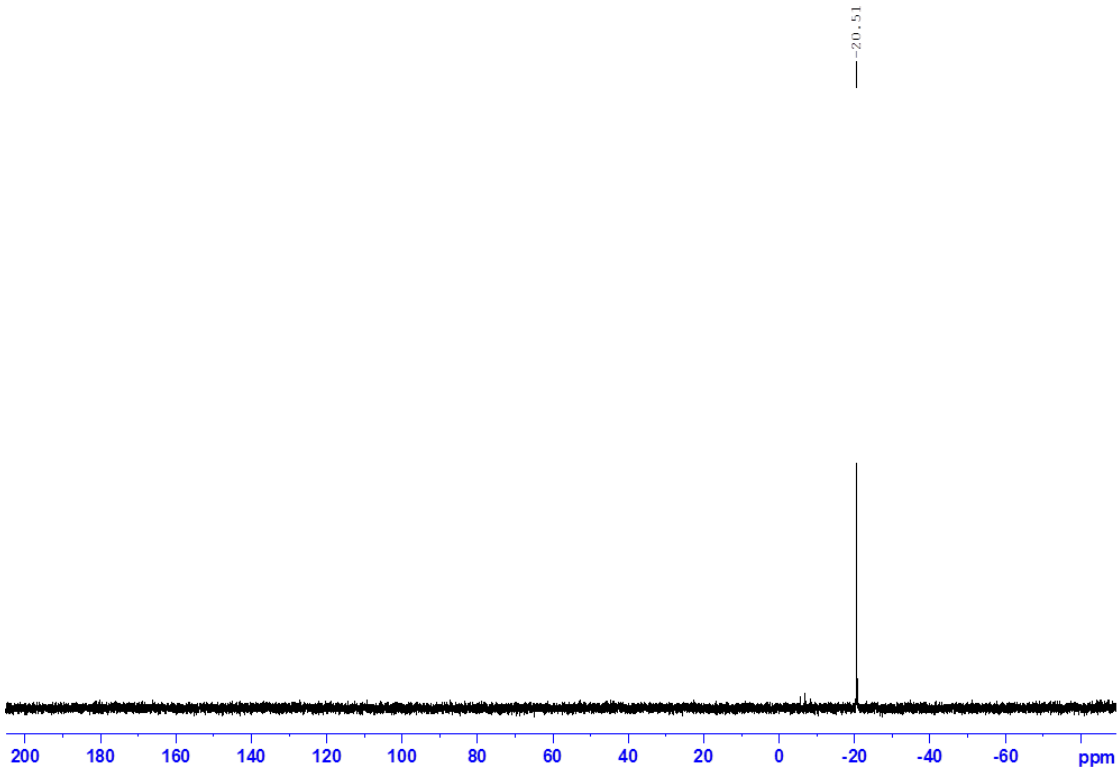
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **97f**



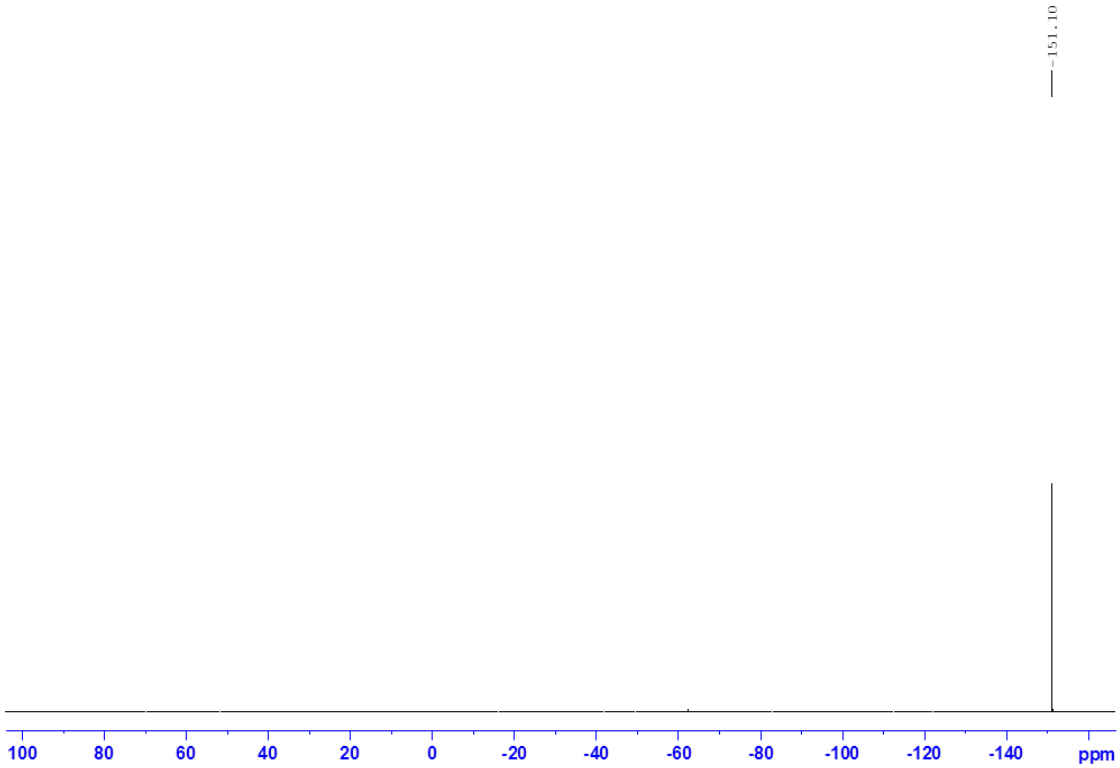
$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$): Compound **97f**



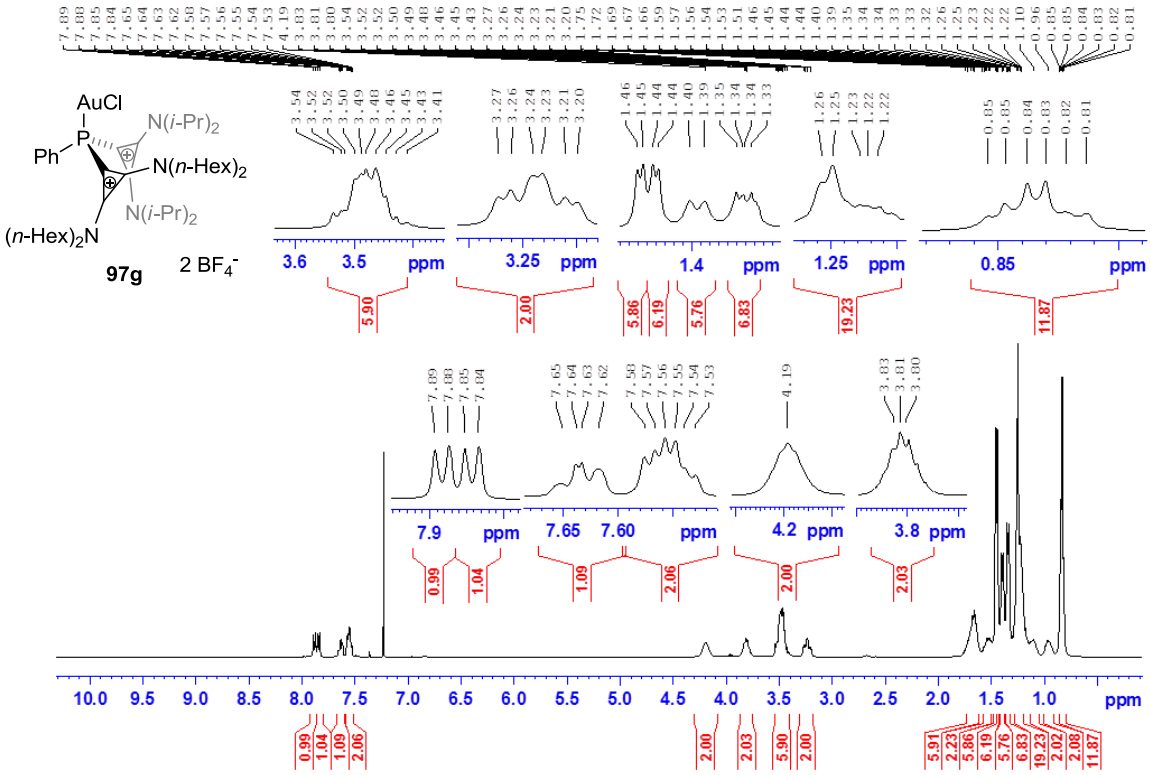
$^{31}P\{^{1}H\}$-NMR (122 MHz, $CDCl_3$): Compound **97f**



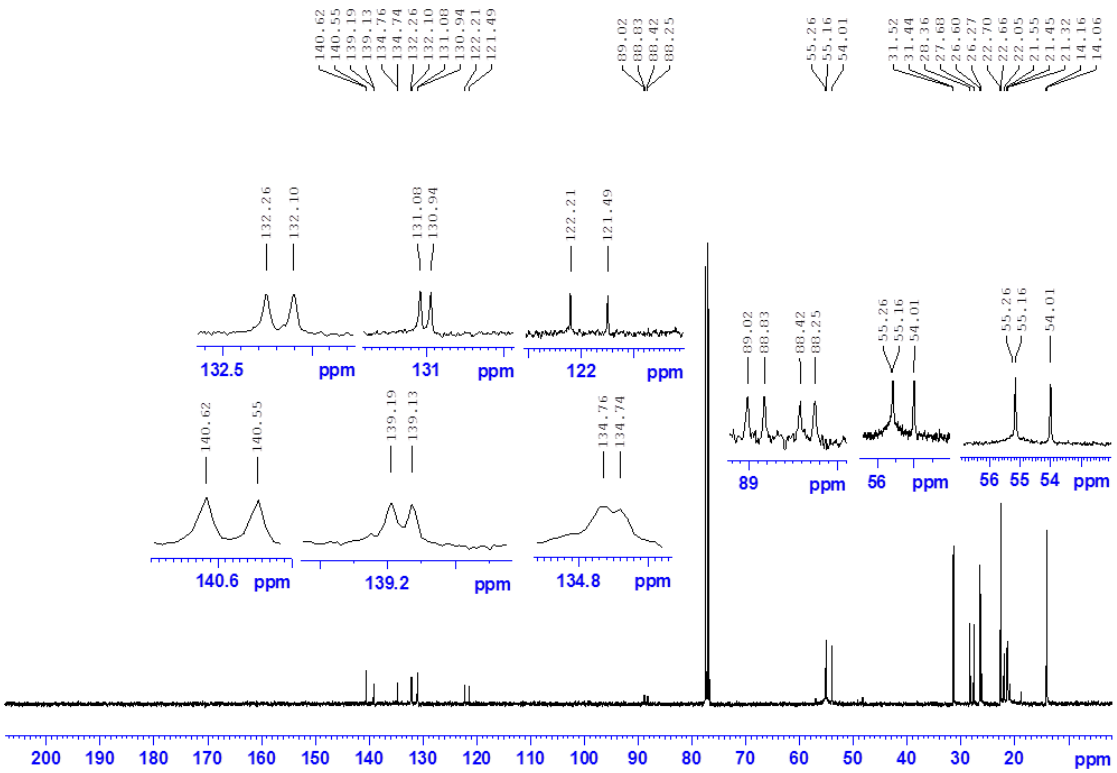
$^{19}F\{^{1}H\}$-NMR (470 MHz, $CDCl_3$): Compound **97f**



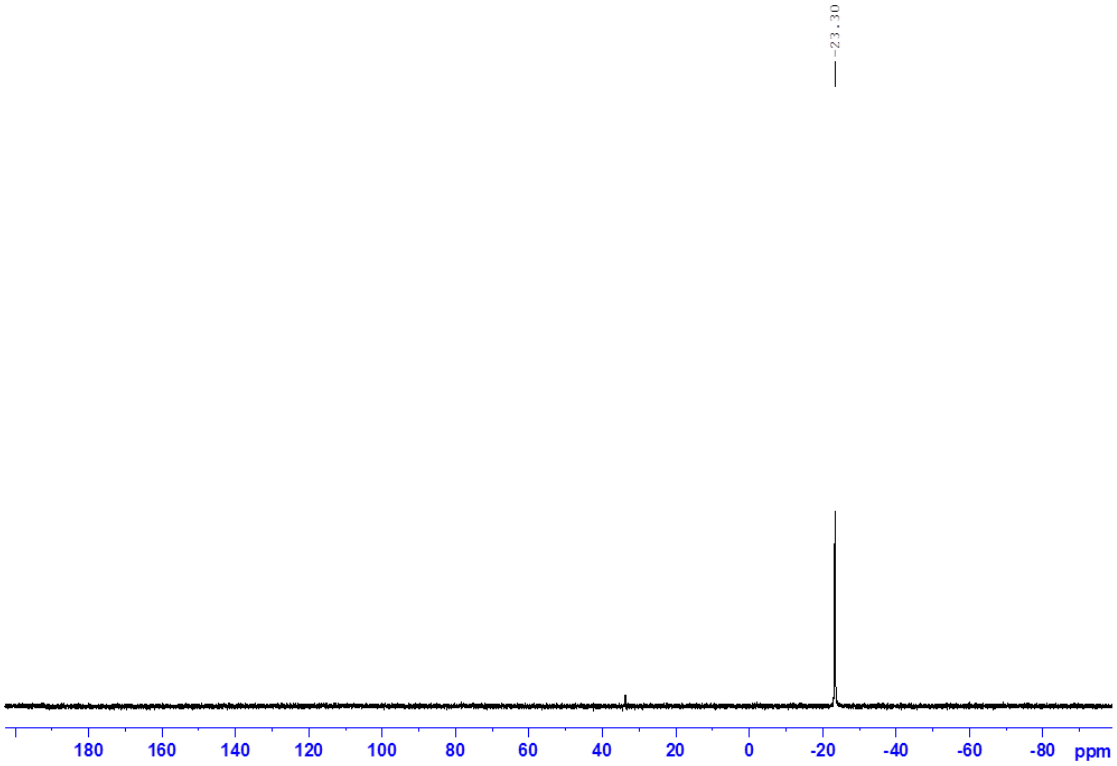
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **97g**



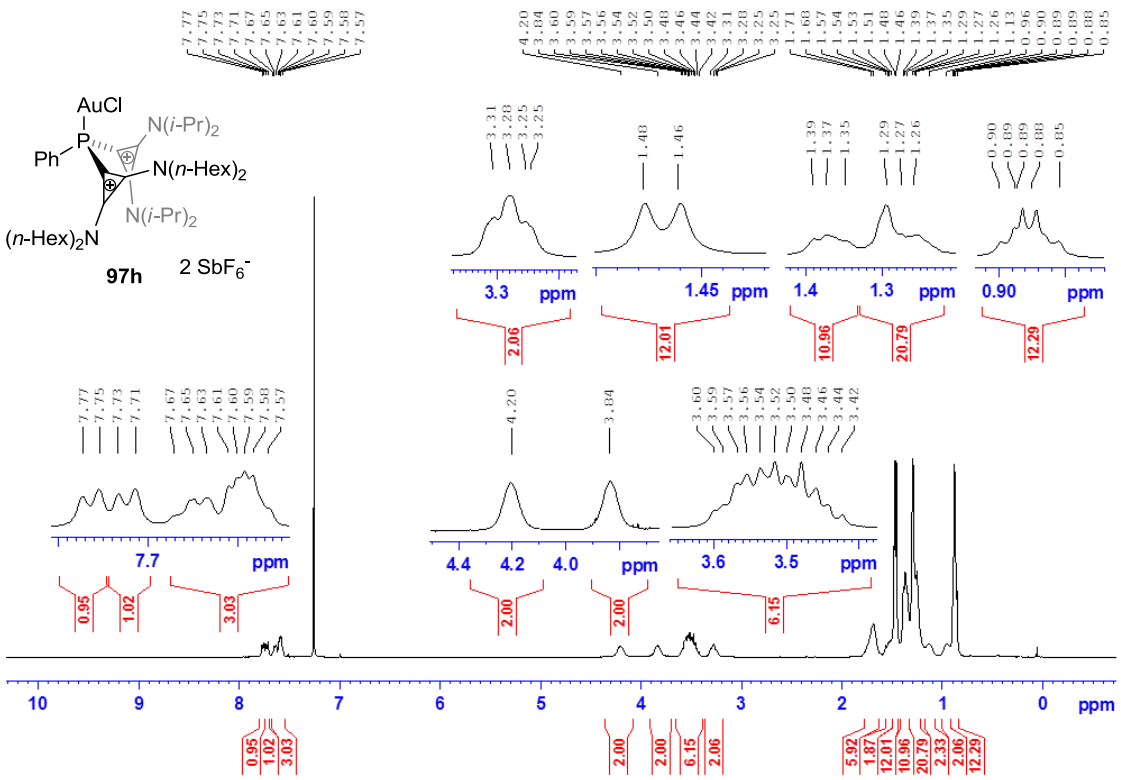
$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): Compound **97g**



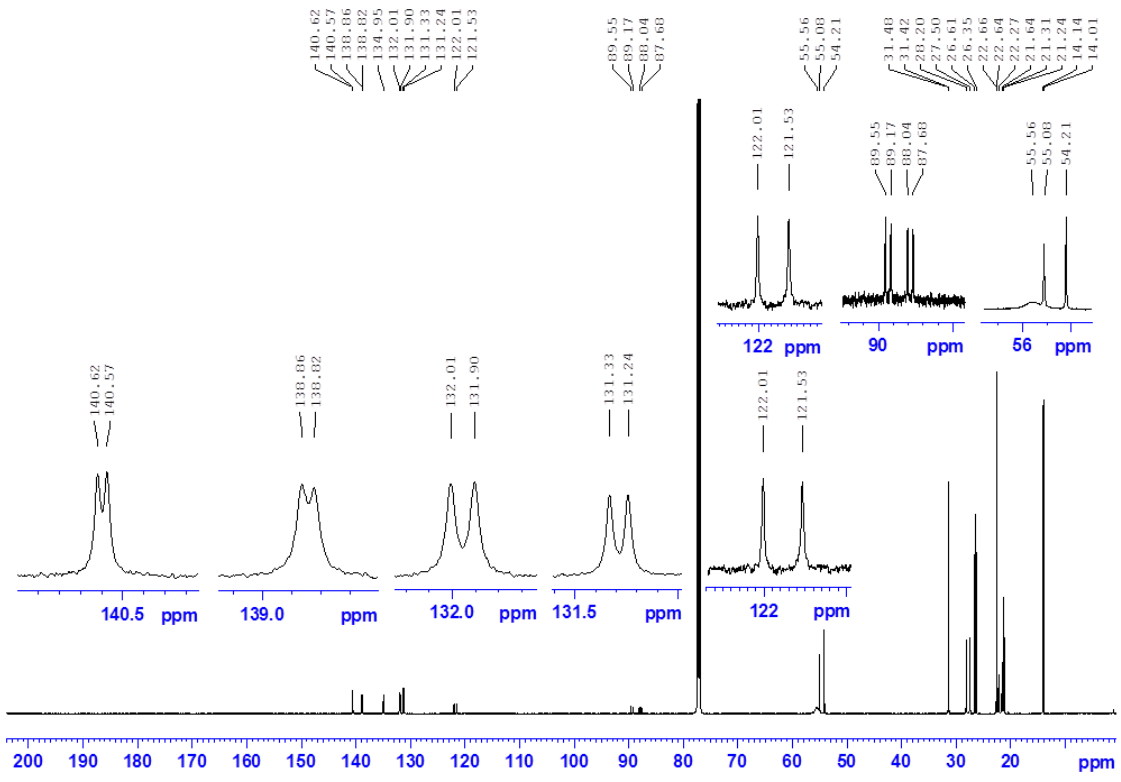
$^{31}P\{^1H\}$-NMR (162 MHz, $CDCl_3$): Compound **97g**



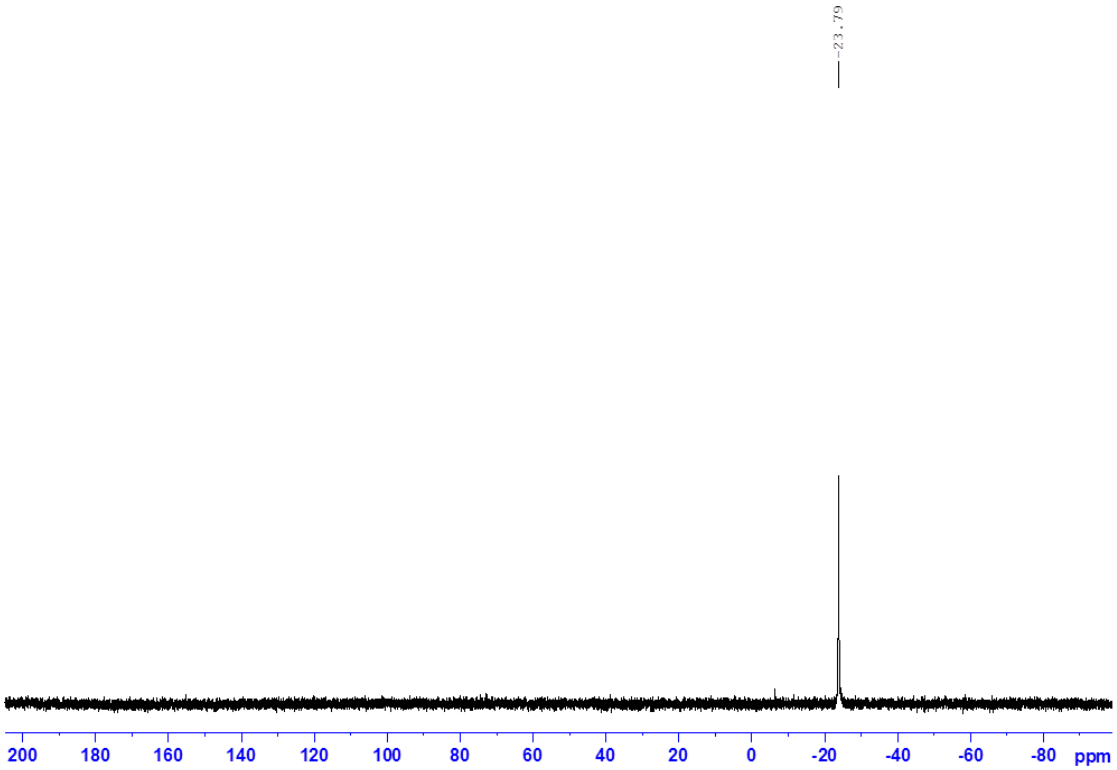
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **97h**



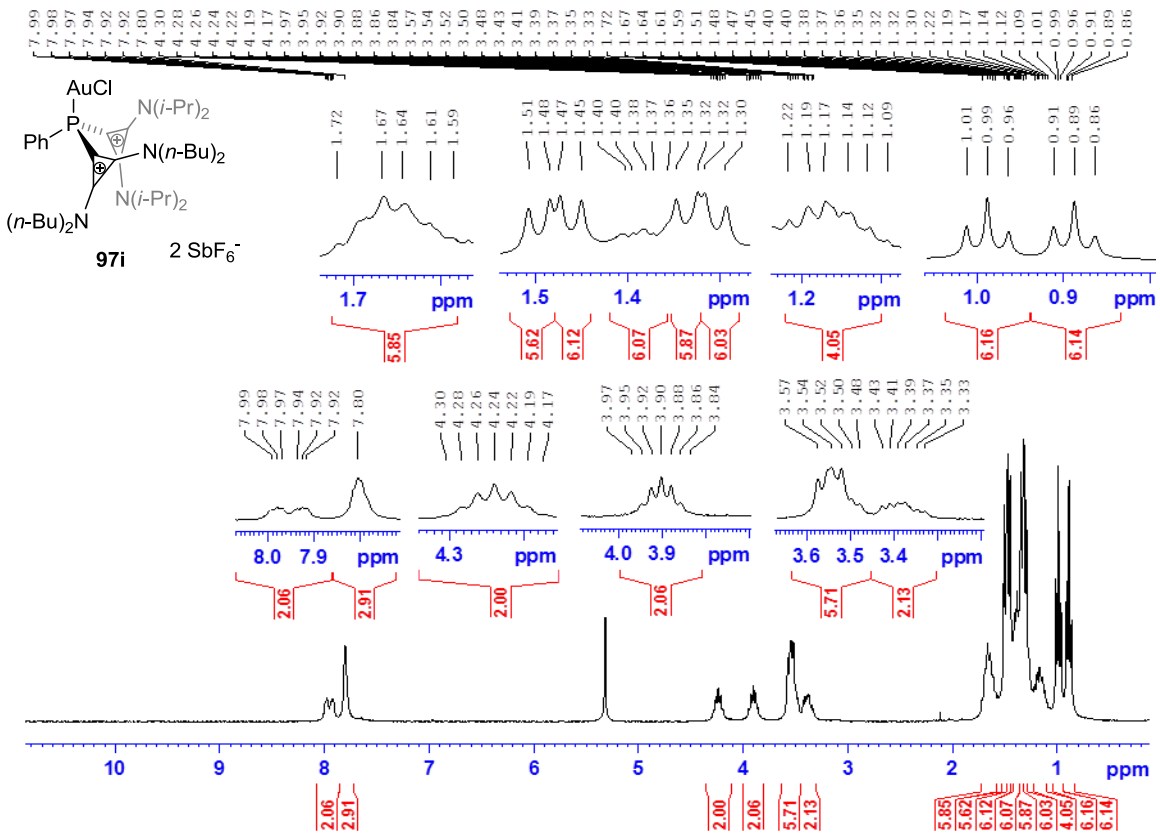
^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): Compound **97h**



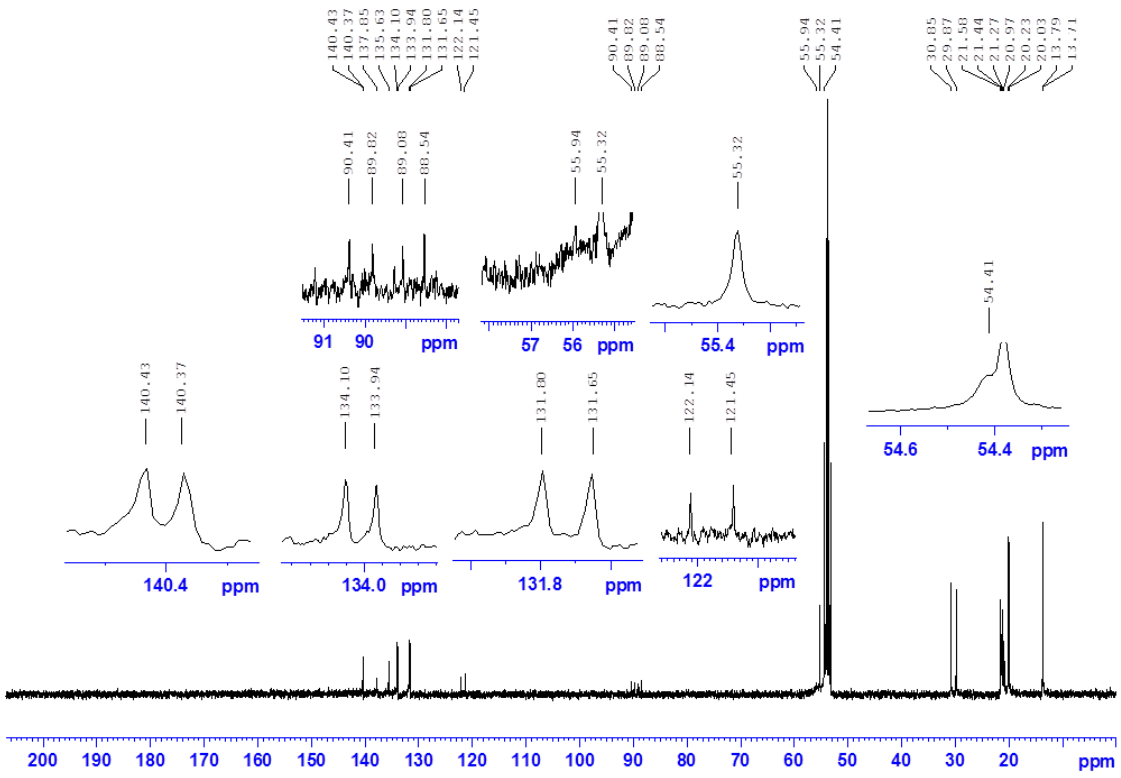
$^{31}P\{^{1}H\}$-NMR (162 MHz, $CDCl_3$): Compound **97h**



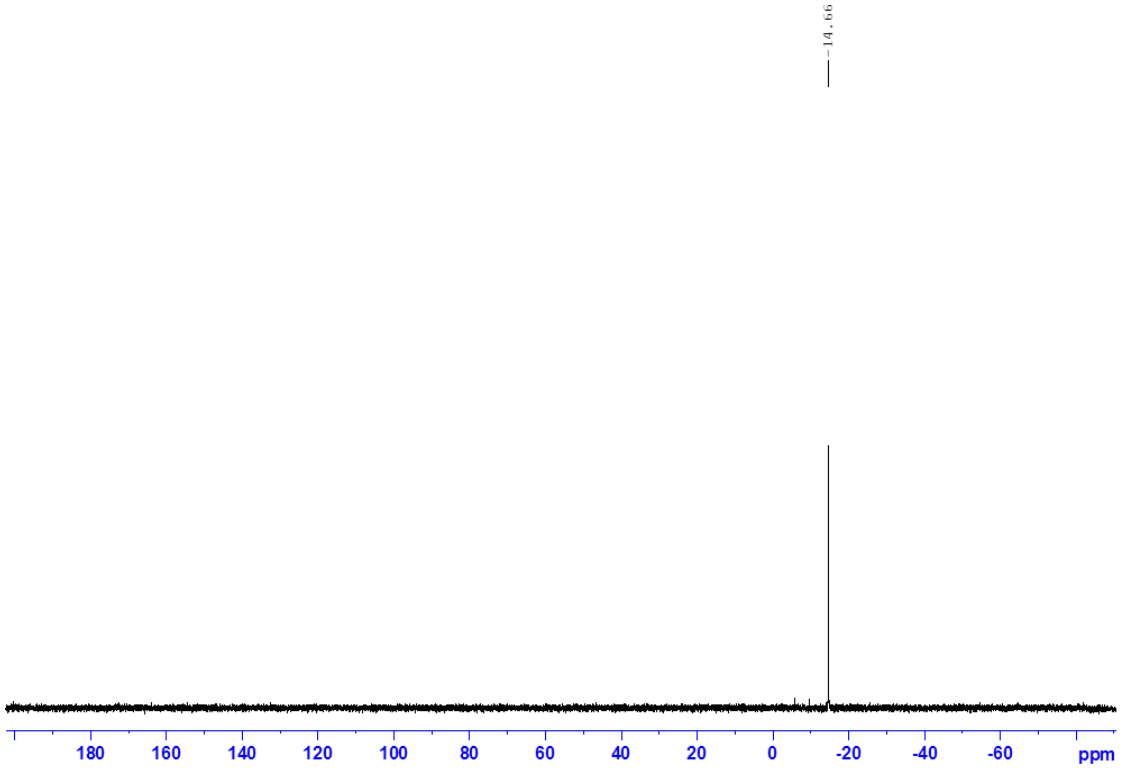
^{1}H-NMR (400 MHz, CD_2Cl_2): Compound **97i**



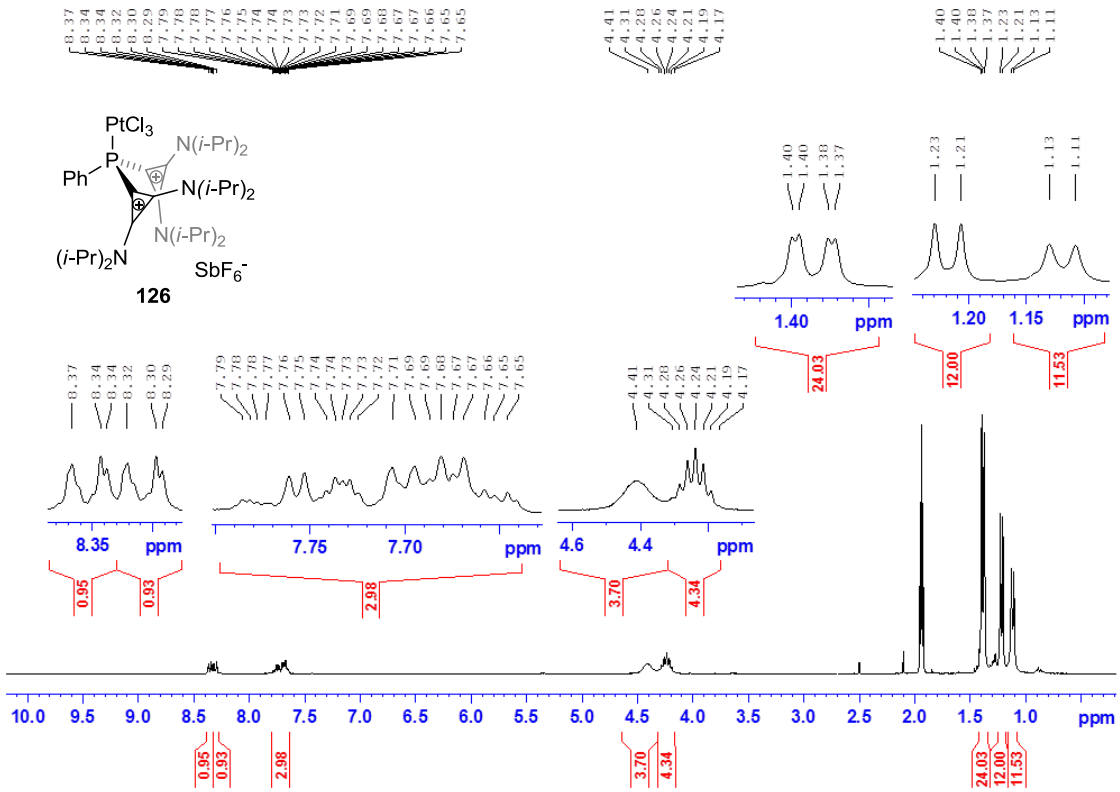
$^{13}C\{^1H\}$-NMR (101 MHz, CD_2Cl_2): Compound **97i**



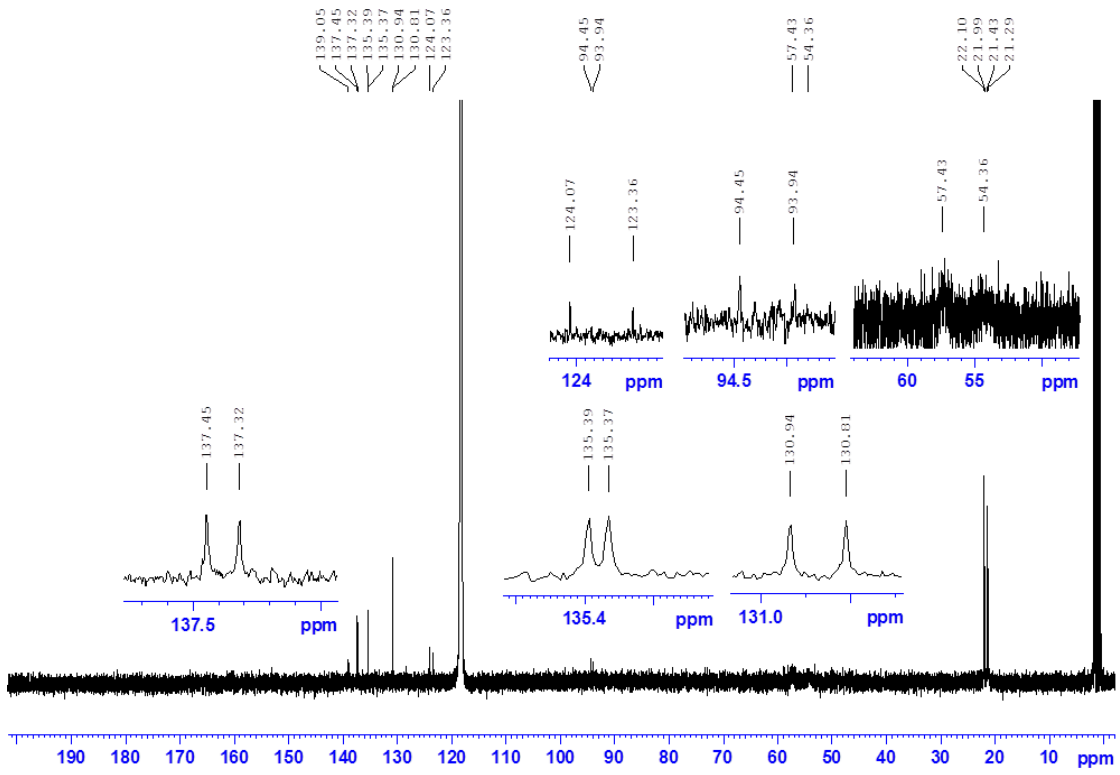
$^{31}P\{^1H\}$-NMR (162 MHz, CD_2Cl_2): Compound **97i**



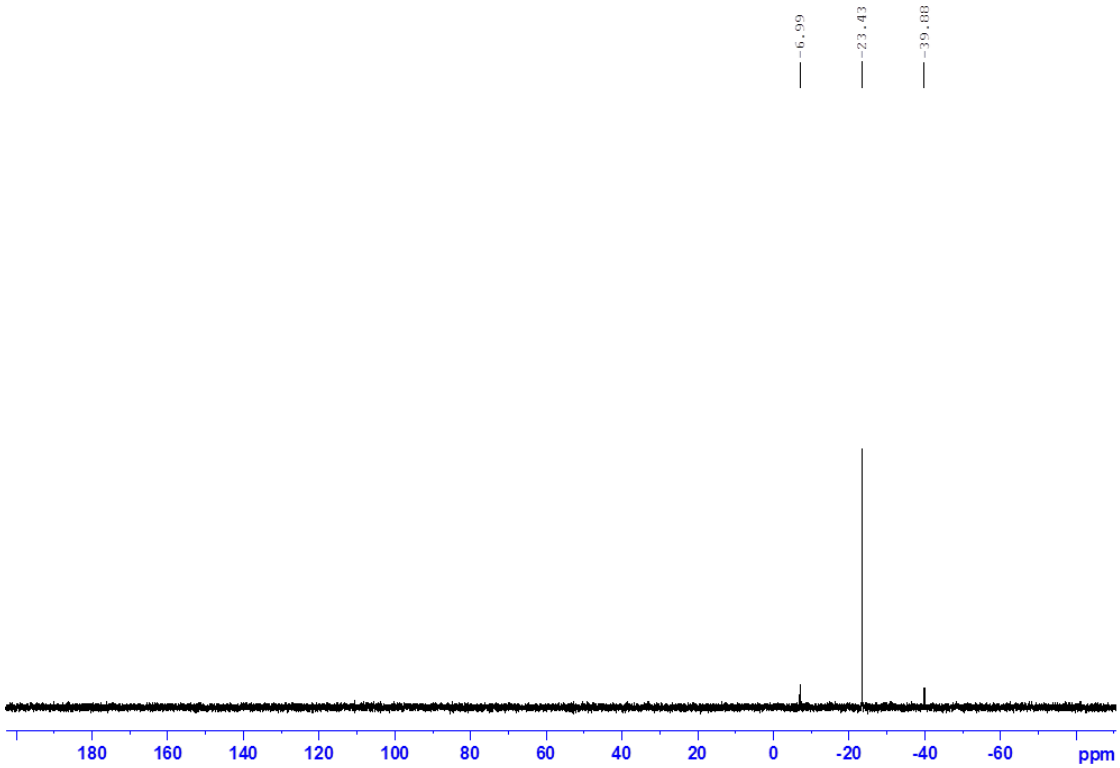
^{1}H-NMR (300 MHz, CD_3CN): Compound **126**



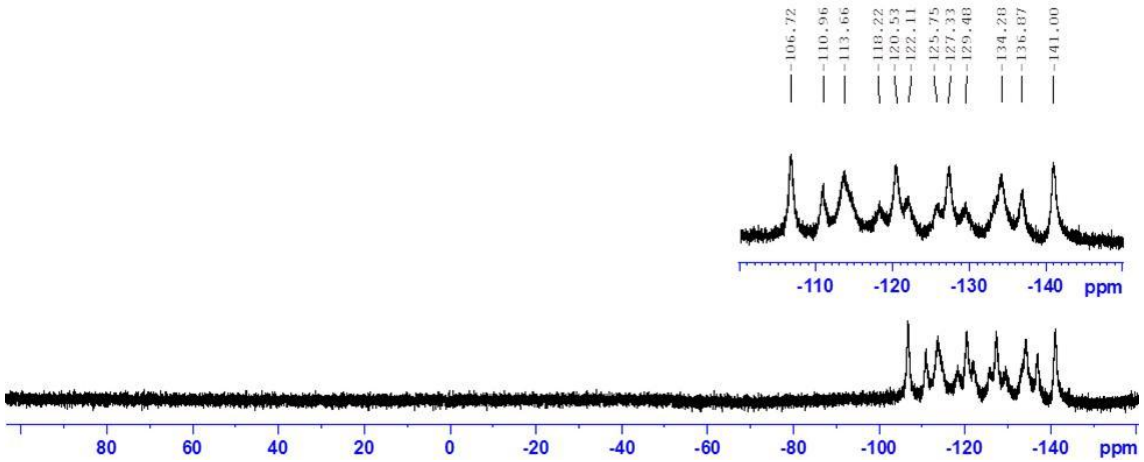
^{13}C{^{1}H}-NMR (101 MHz, CD_3CN): Pt(II)- Compound **126**



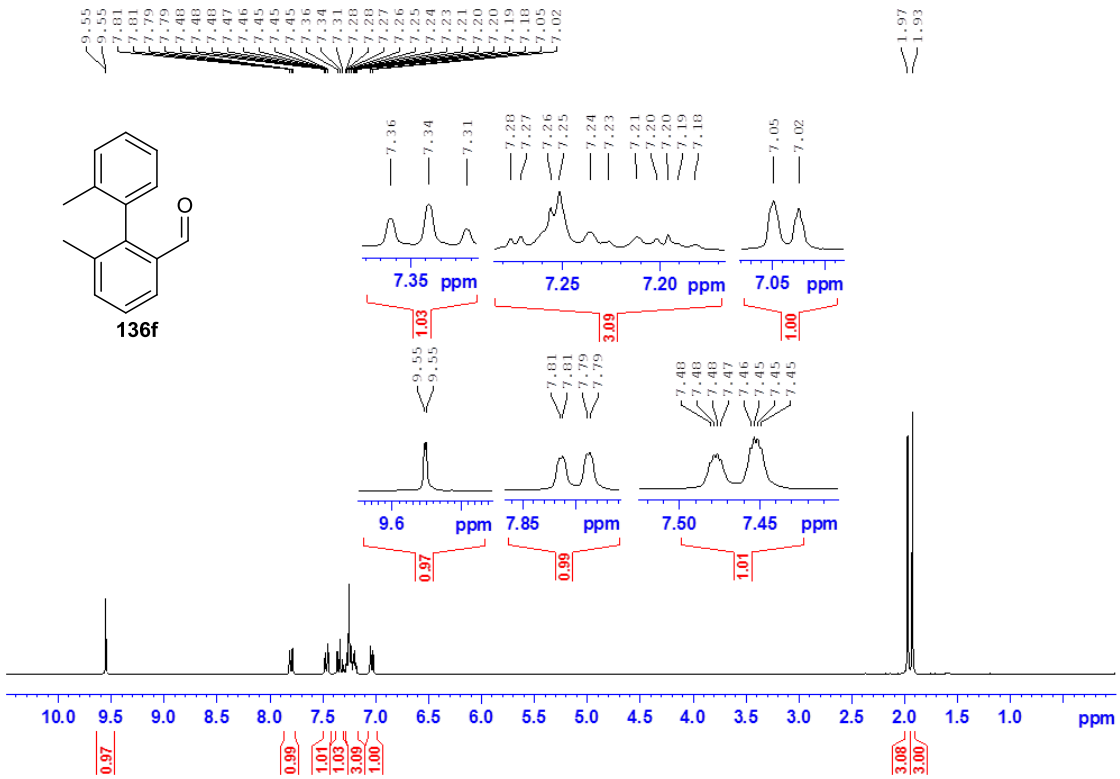
$^{31}P\{^{1}H\}$-NMR (122 MHz, CD_3CN): Compound **126**



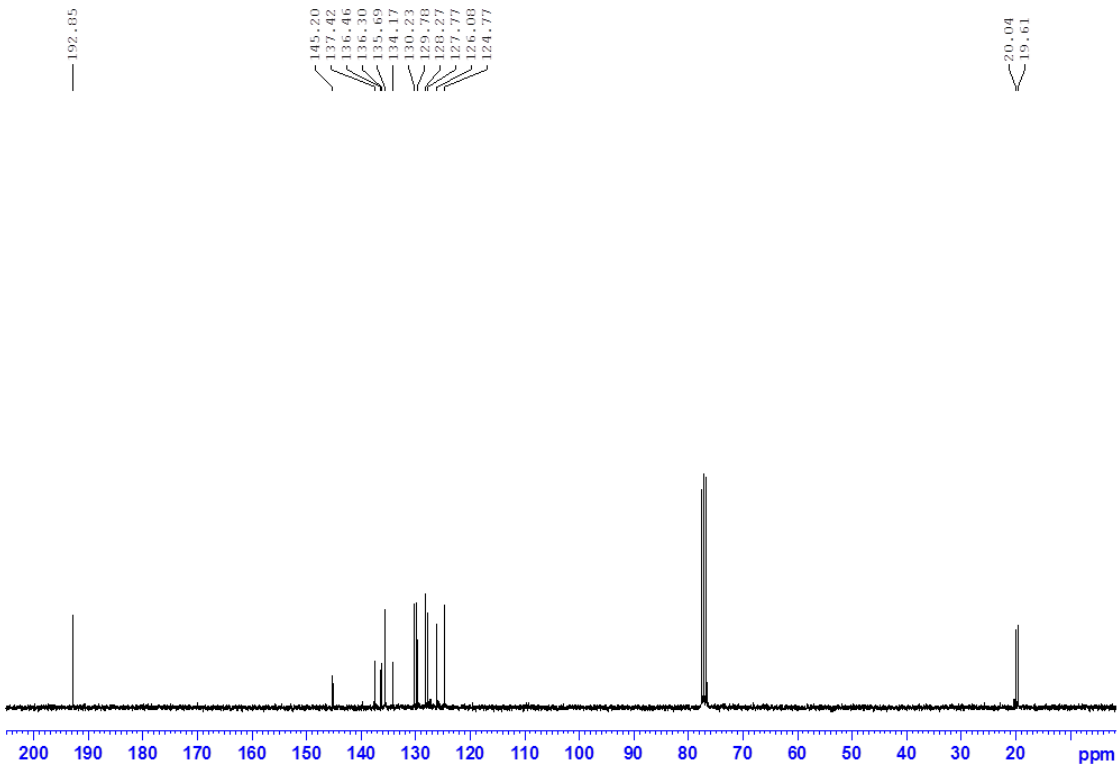
$^{19}F\{^{1}H\}$-NMR (282 MHz, CD_3CN): Pt(II)- Compound **126**



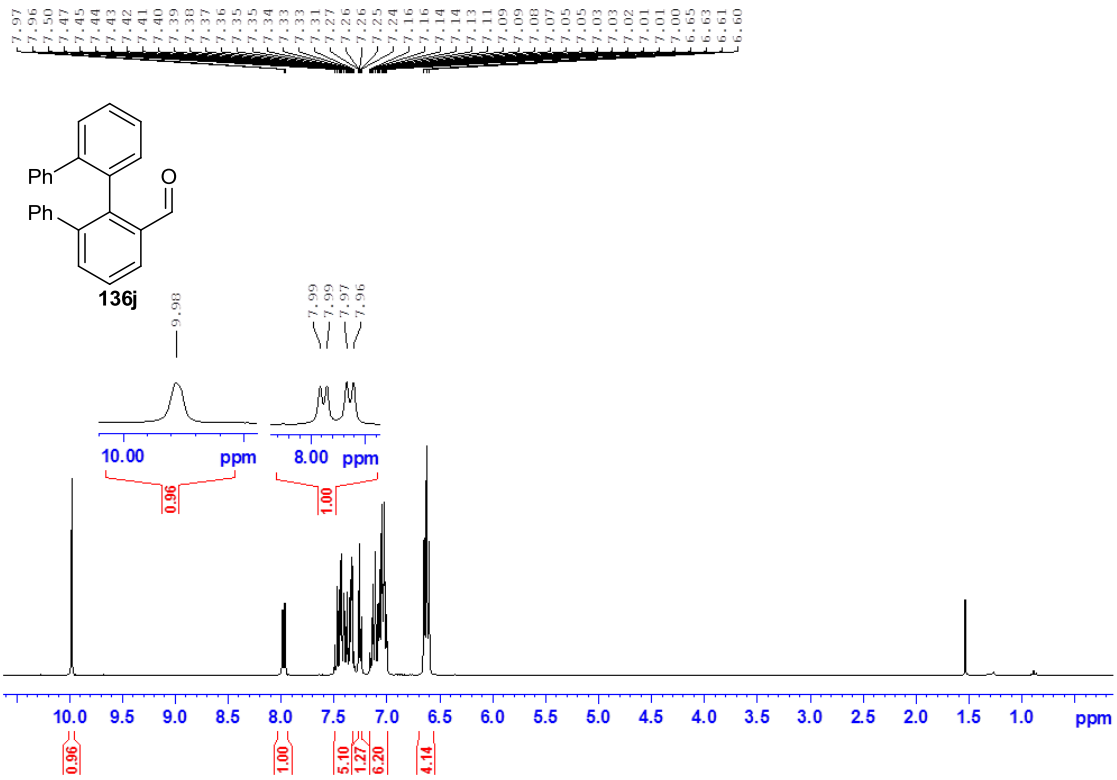
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **136f**



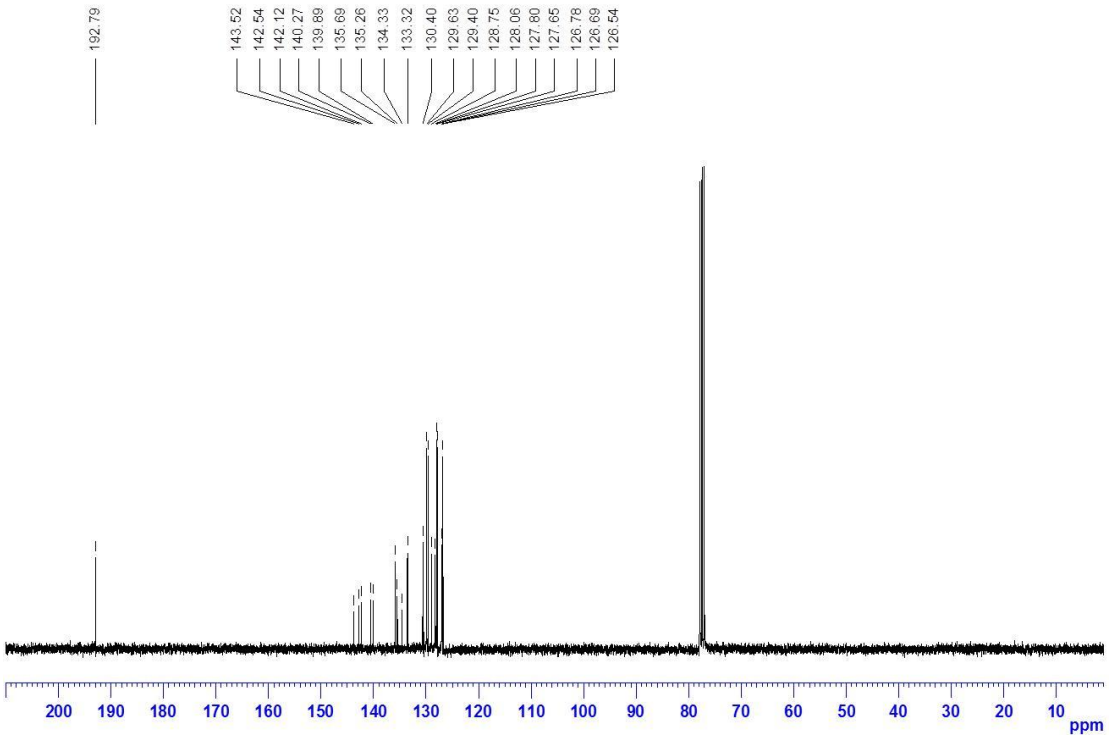
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): Compound **136f**



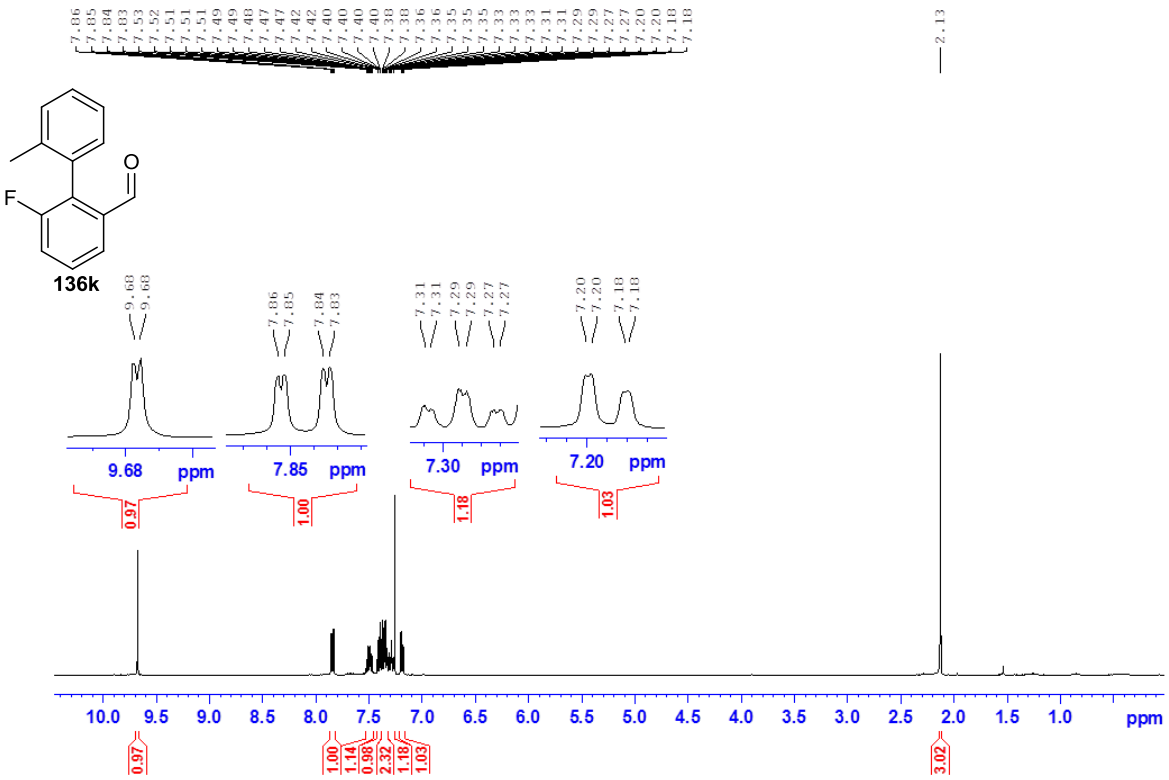
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **136j**



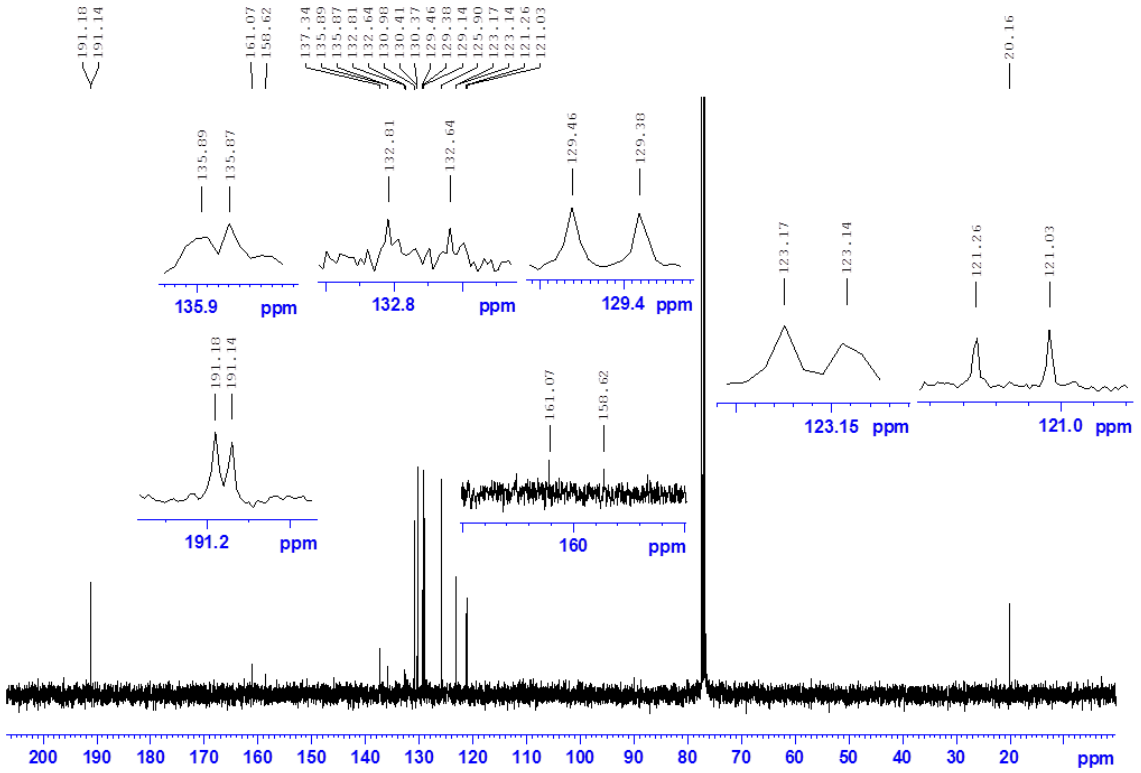
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): Compound **136j**



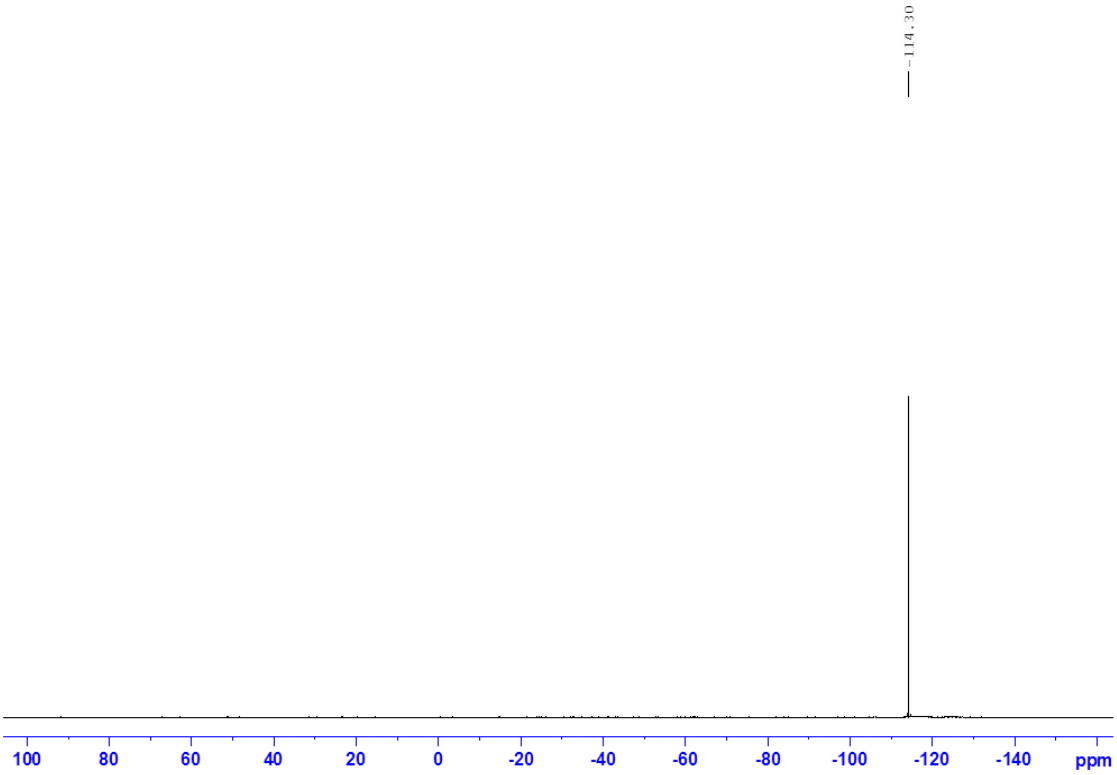
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **136k**



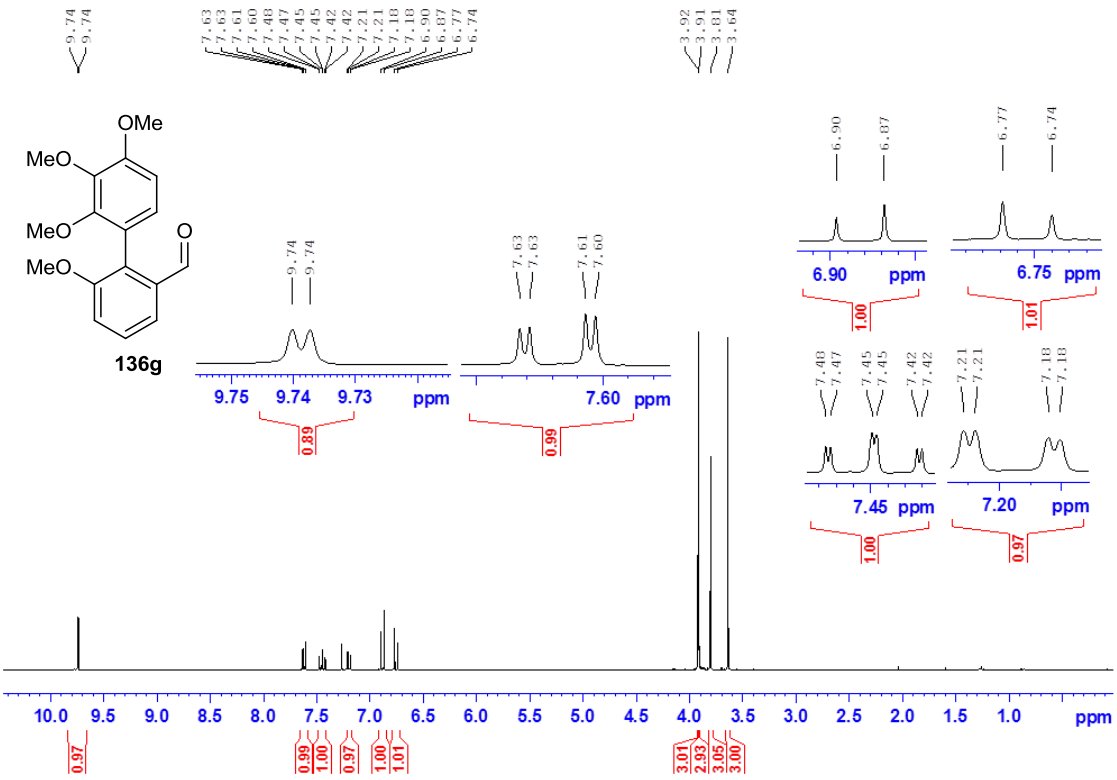
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): Compound **136k**



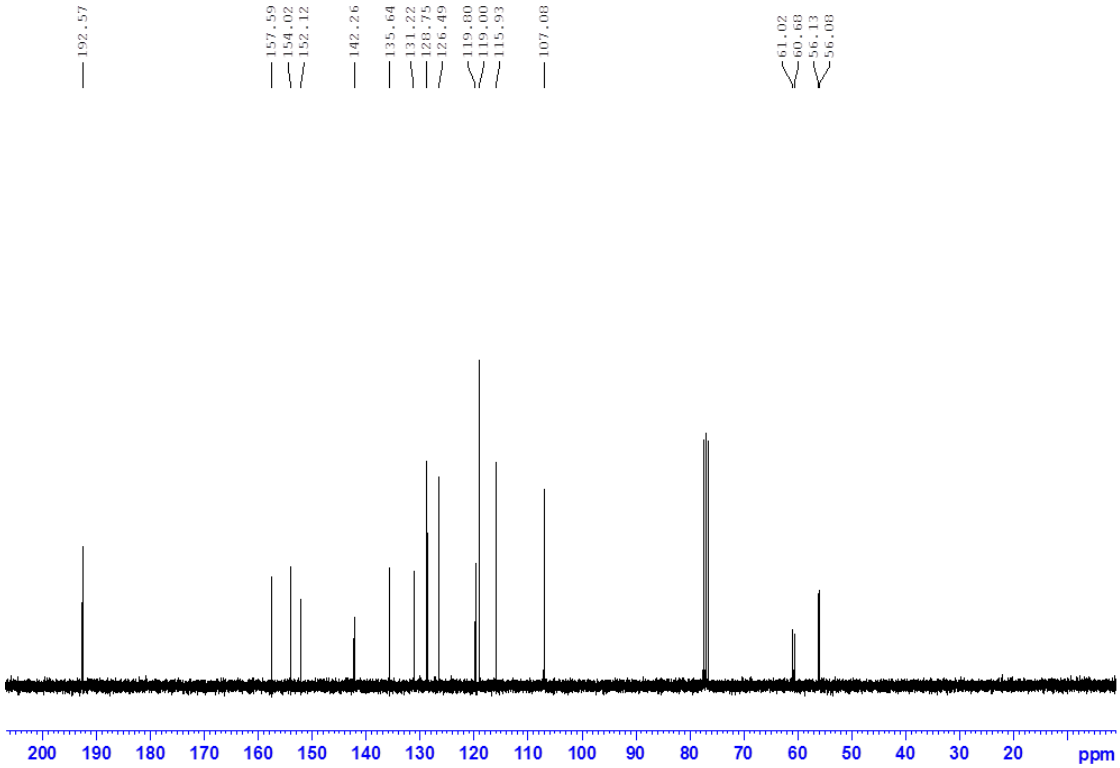
$^{19}F\{^{1}H\}$-NMR (282 MHz, $CDCl_3$): Compound **136k**



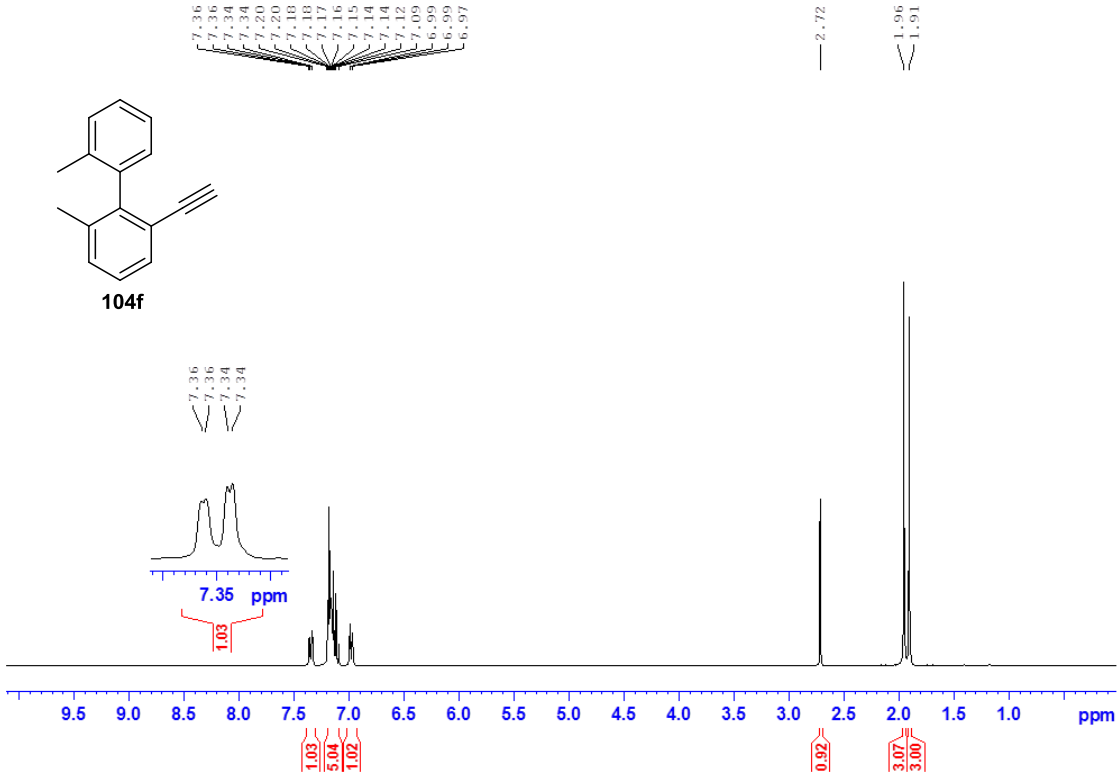
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **136g**



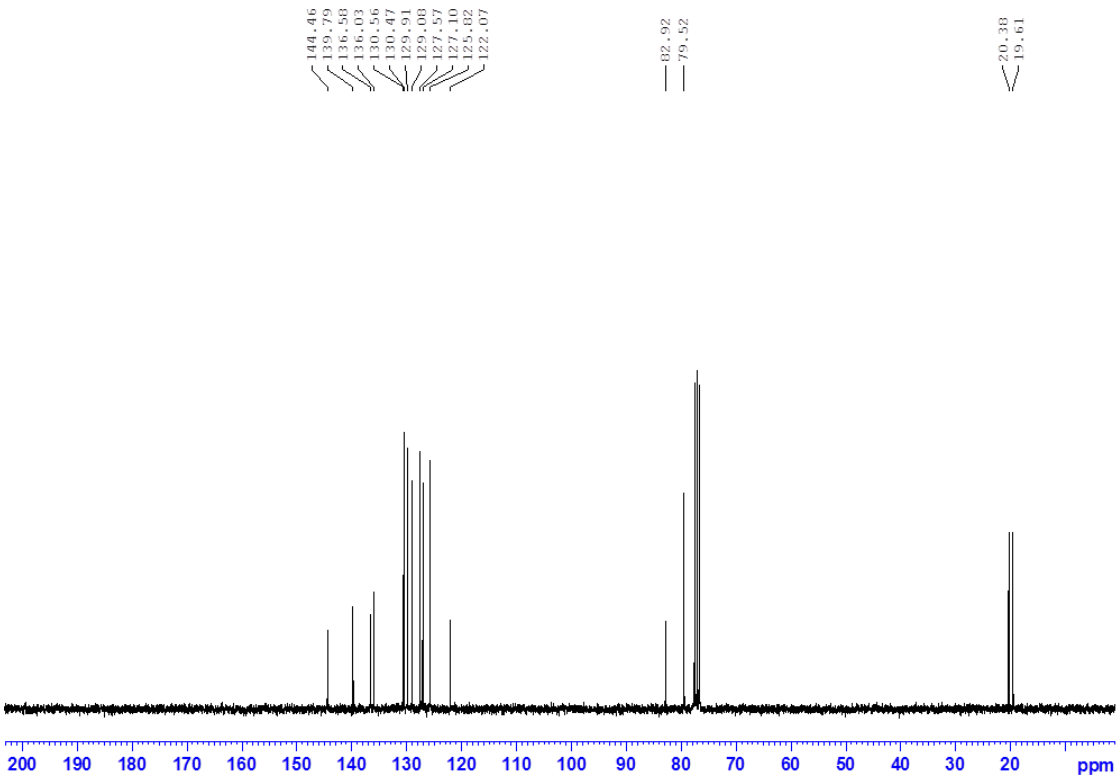
$^{13}C\{^{1}H\}$-NMR (75 MHz, $CDCl_3$): Compound **136g**



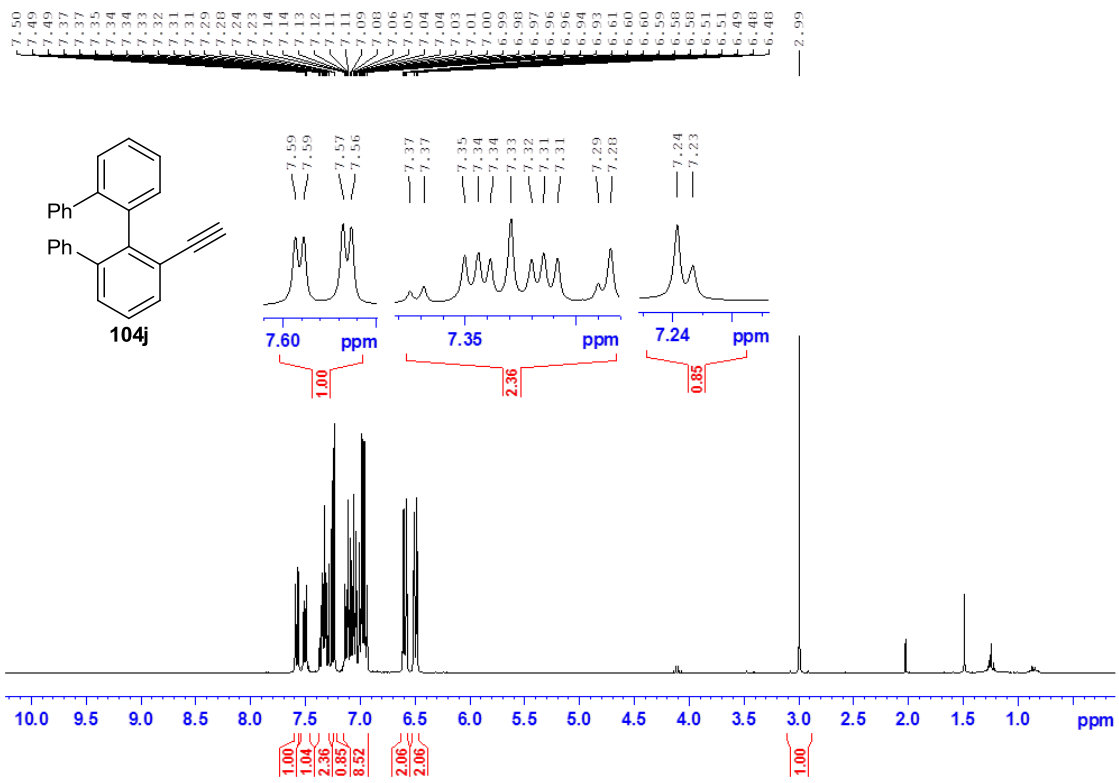
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **104f**



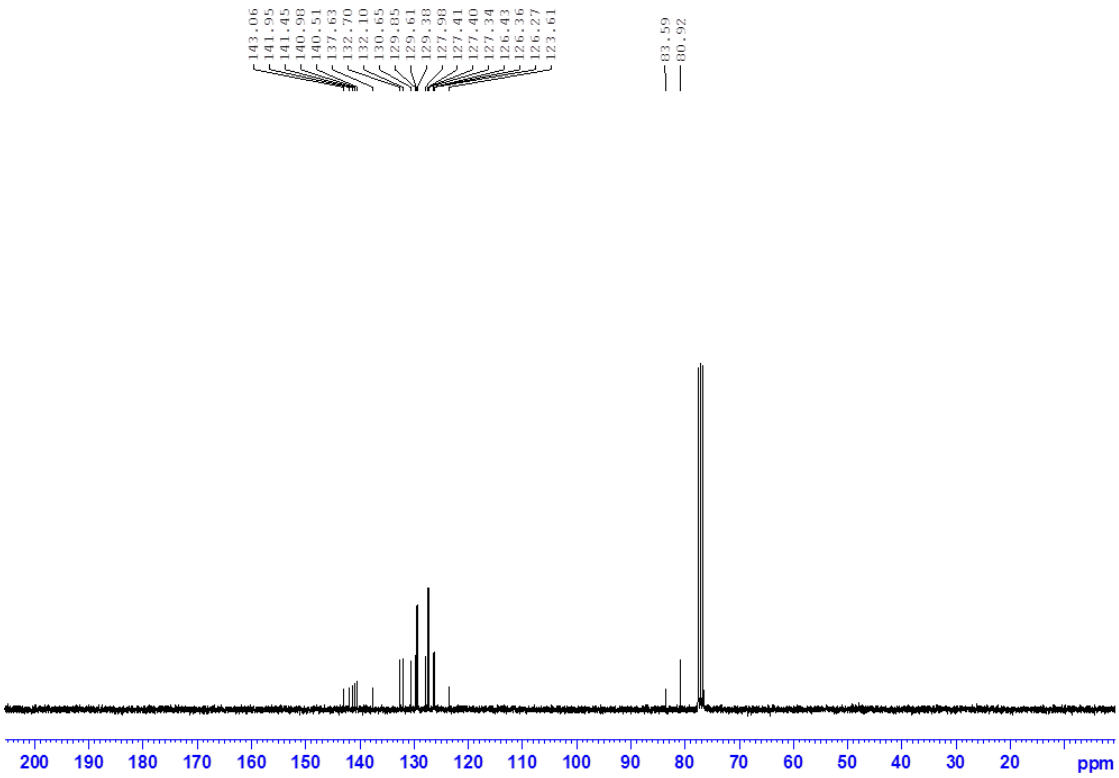
$^{13}C\{^{1}H\}$-NMR (75 MHz, $CDCl_3$): Compound **104f**



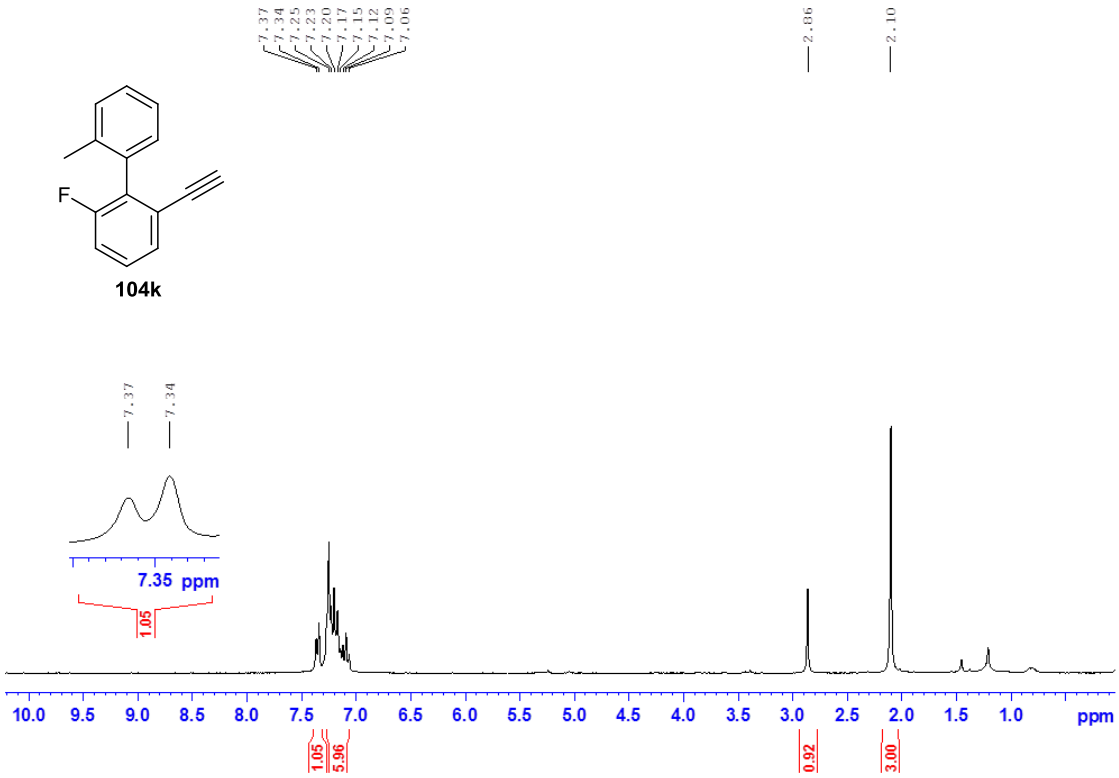
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **104j**



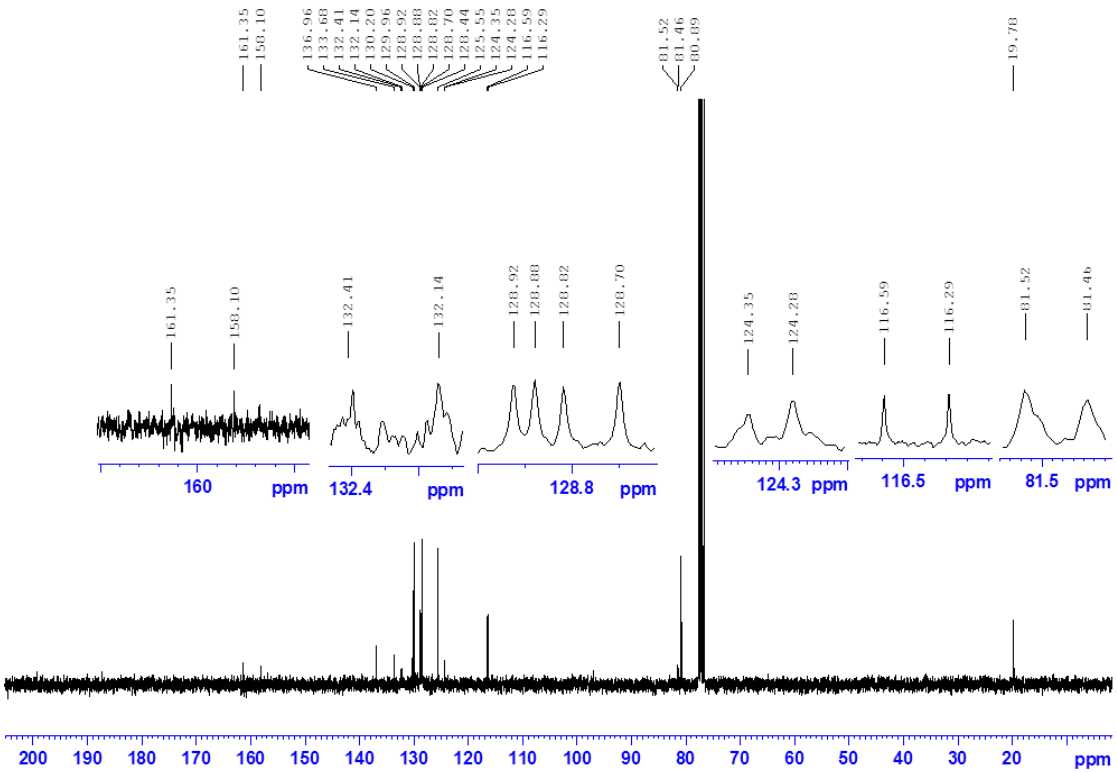
$^{13}C\{^{1}H\}$-NMR (75 MHz, $CDCl_3$): Compound **104j**



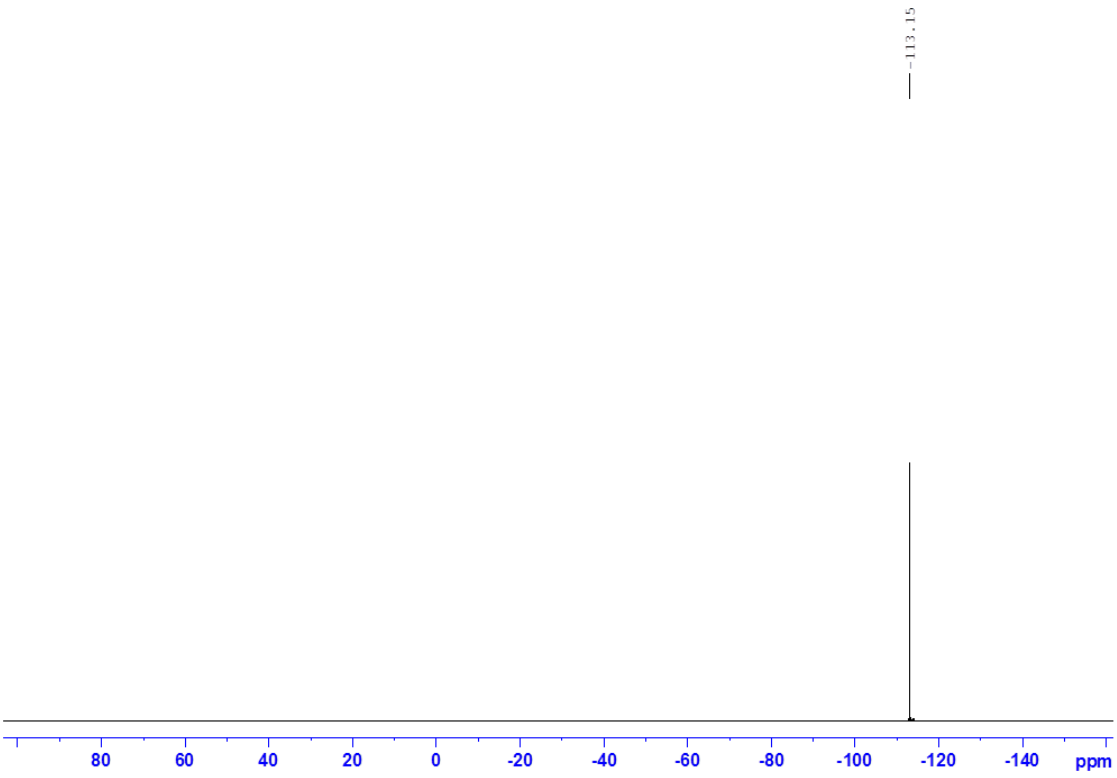
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **104k**



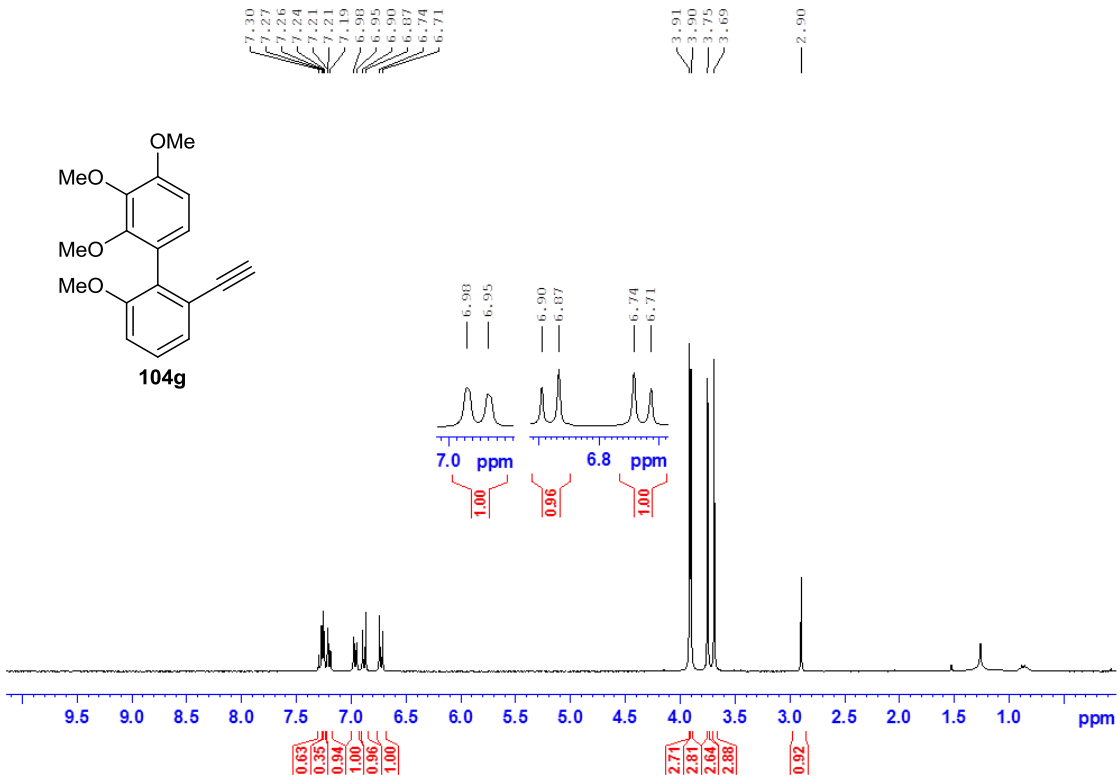
$^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): Compound **104k**



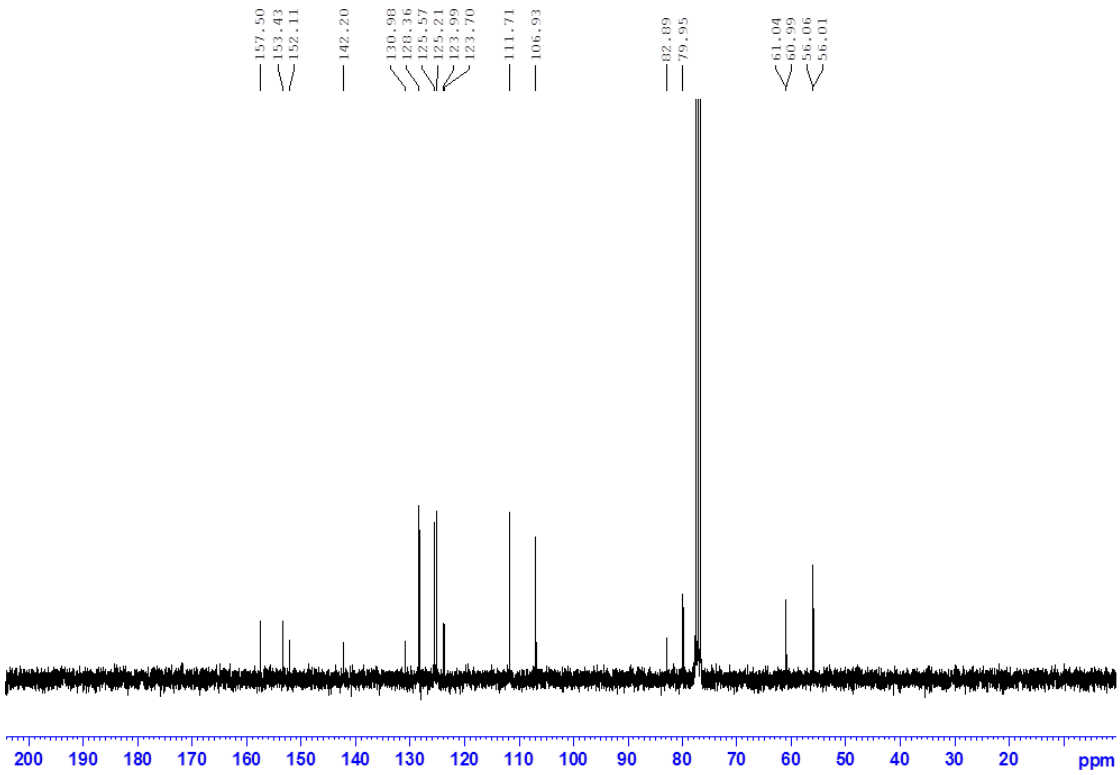
$^{19}F\{^1H\}$-NMR (282 MHz, $CDCl_3$): Compound **104k**



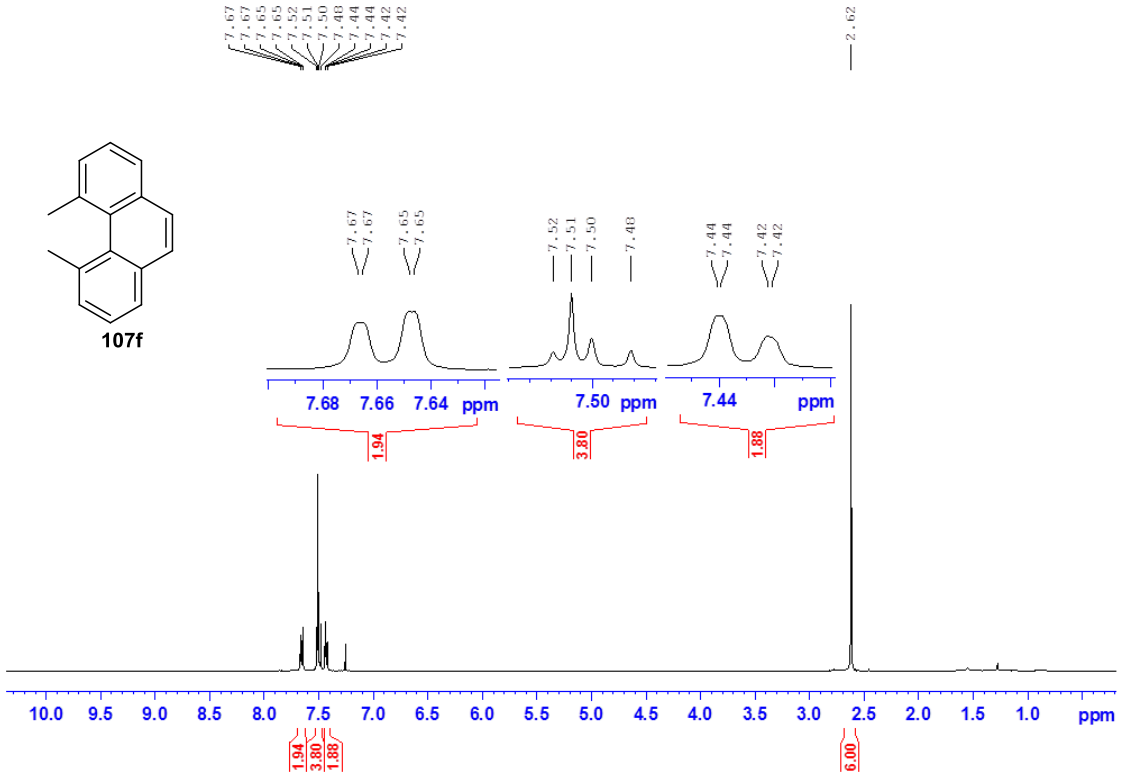
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **104g**



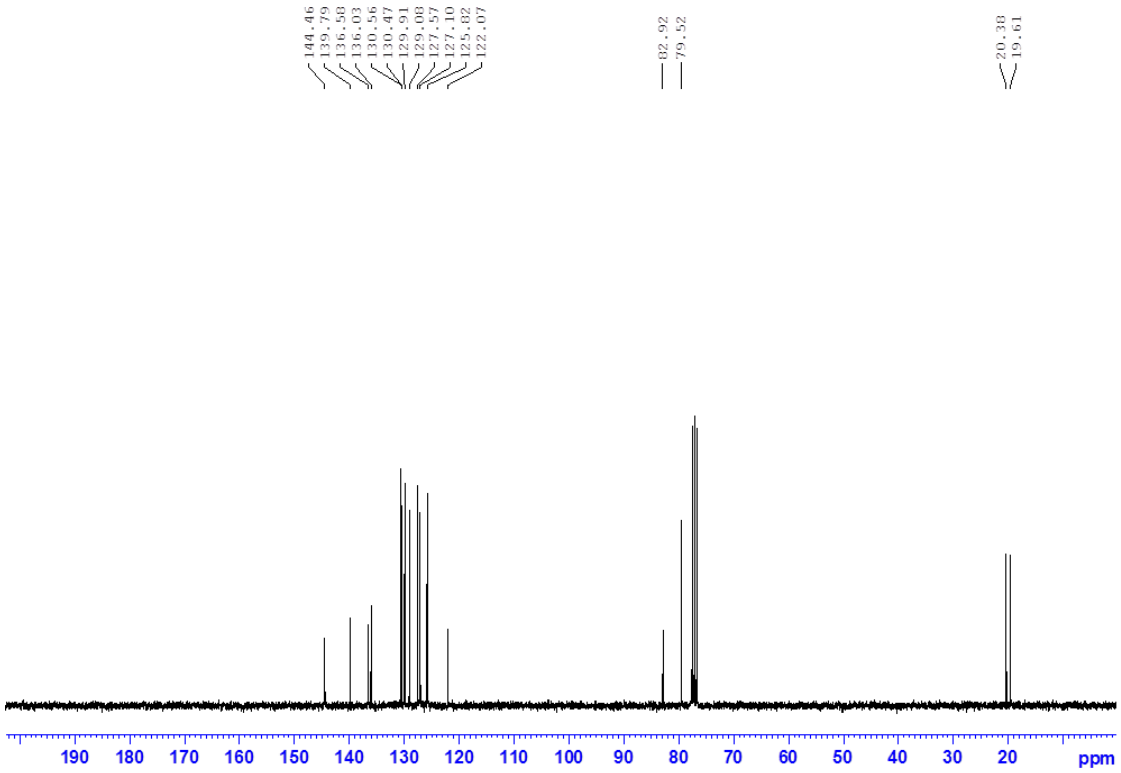
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): Compound **104g**



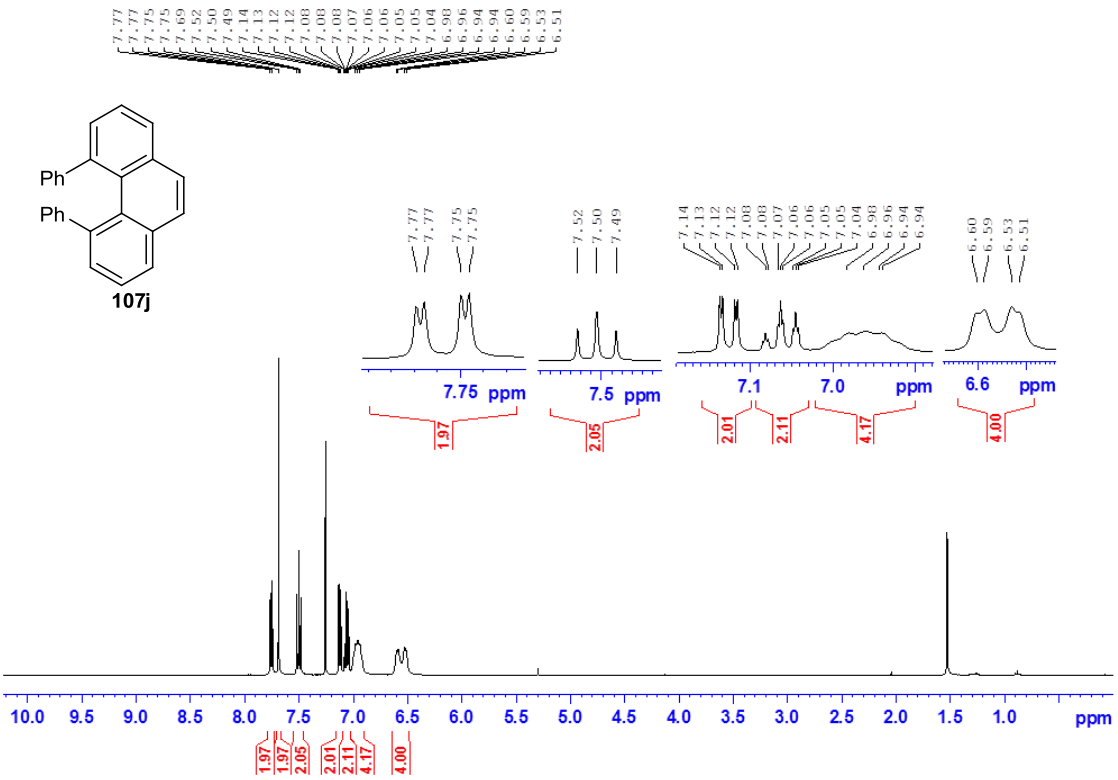
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **107f**



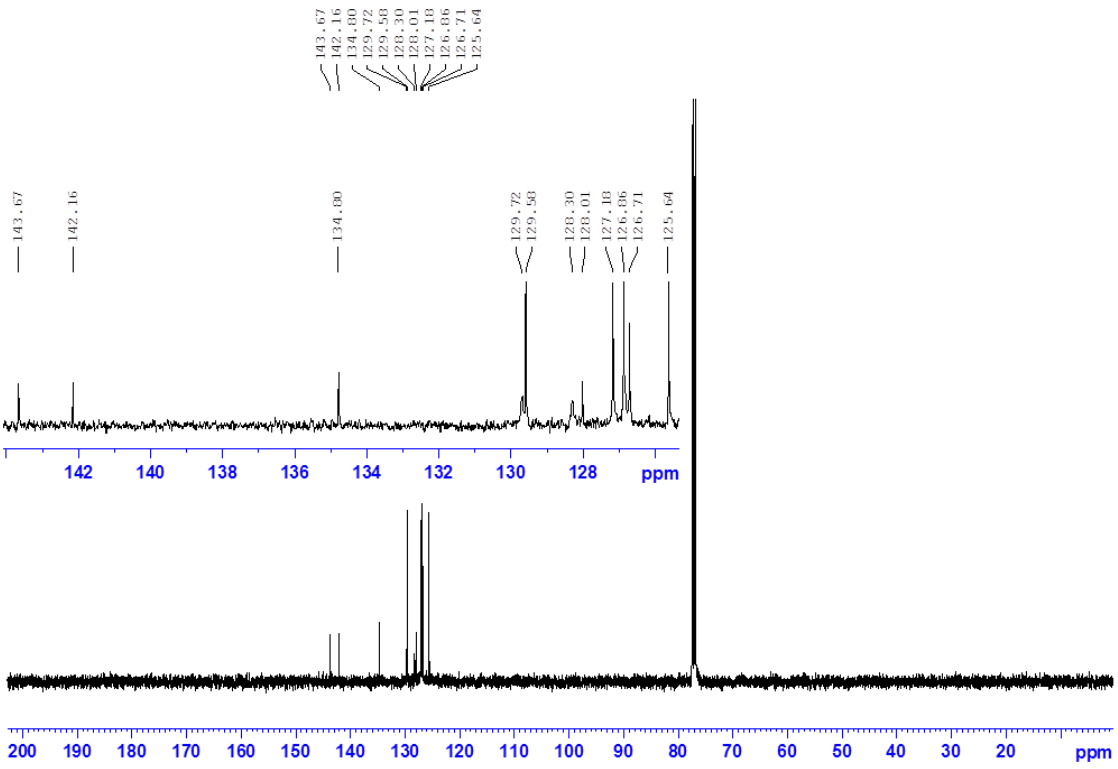
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): Compound **107f**



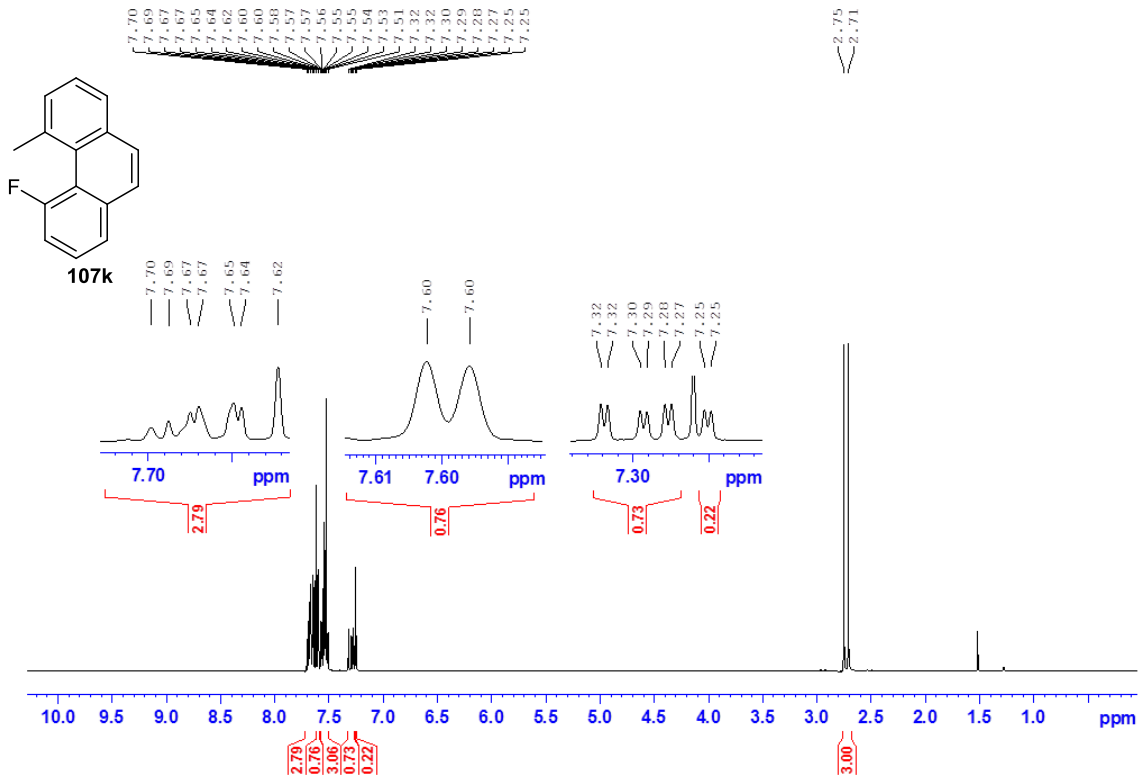
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **107j**



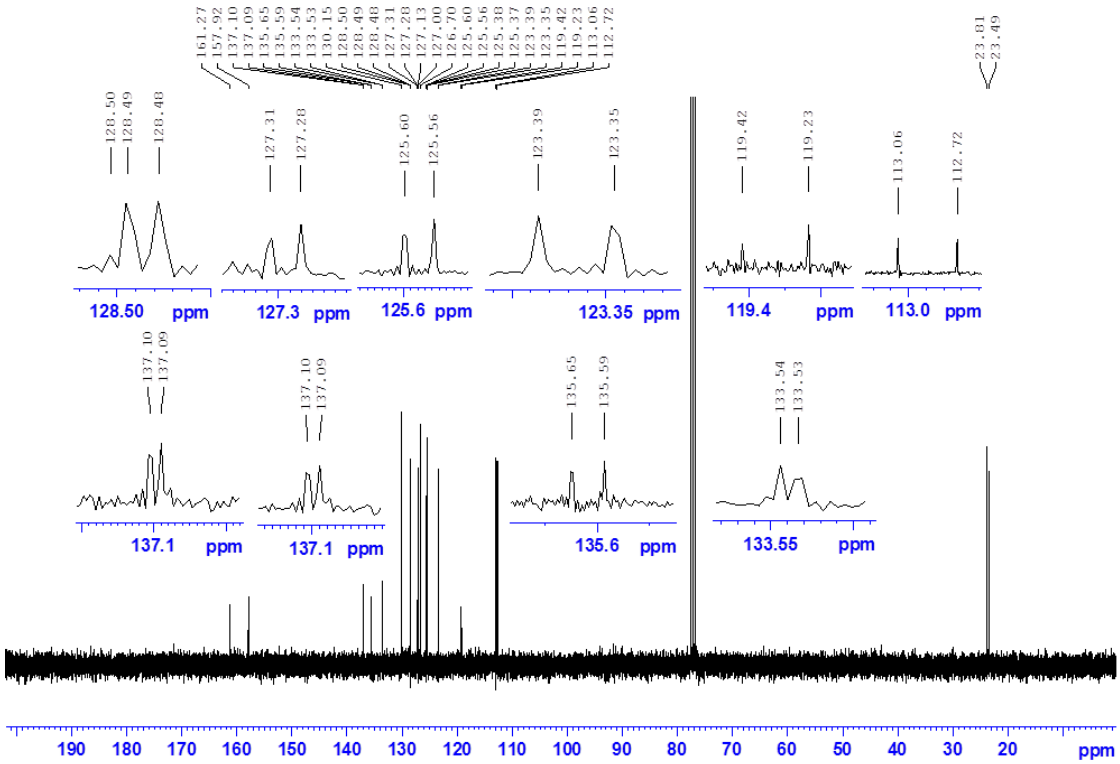
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): Compound **107j**



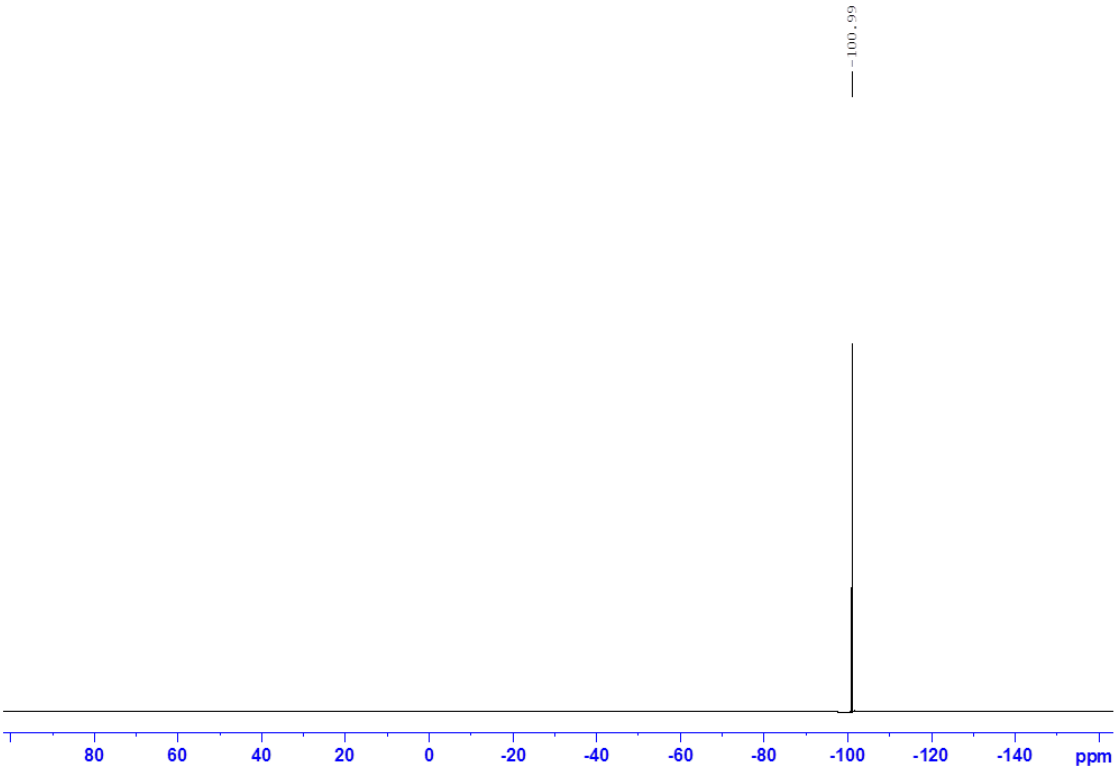
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **107k**



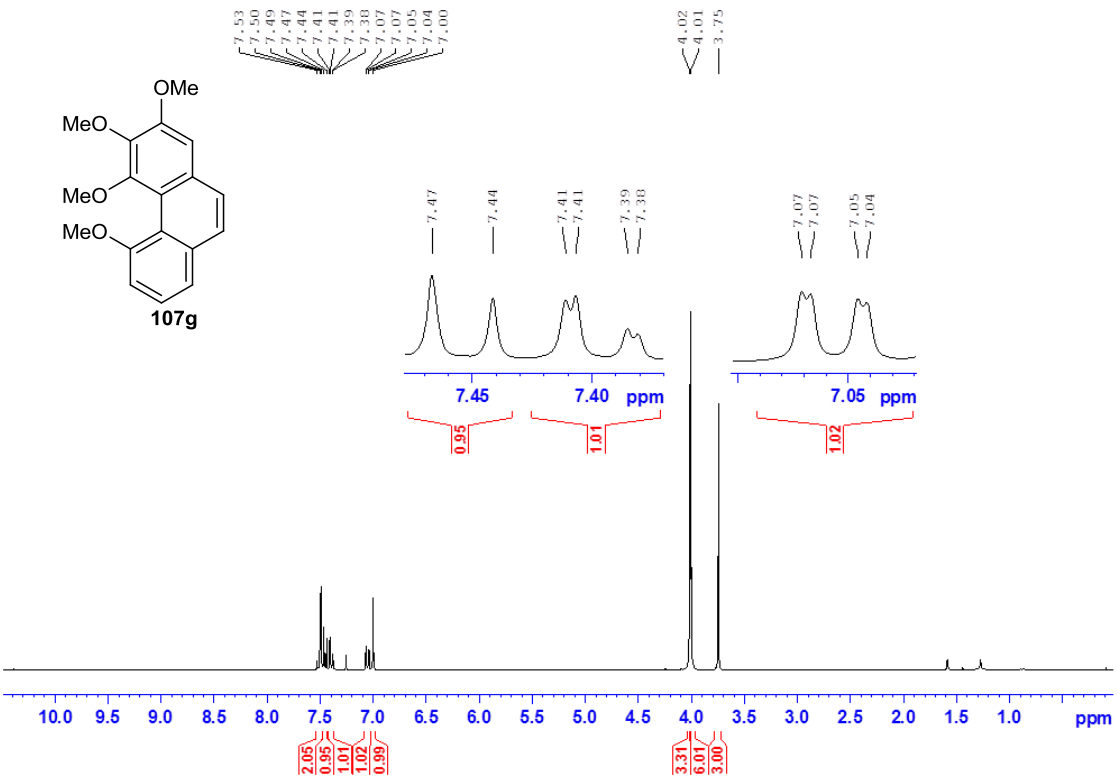
^{13}C{^{1}H}-NMR (75MHz, $CDCl_3$): Compound **107k**



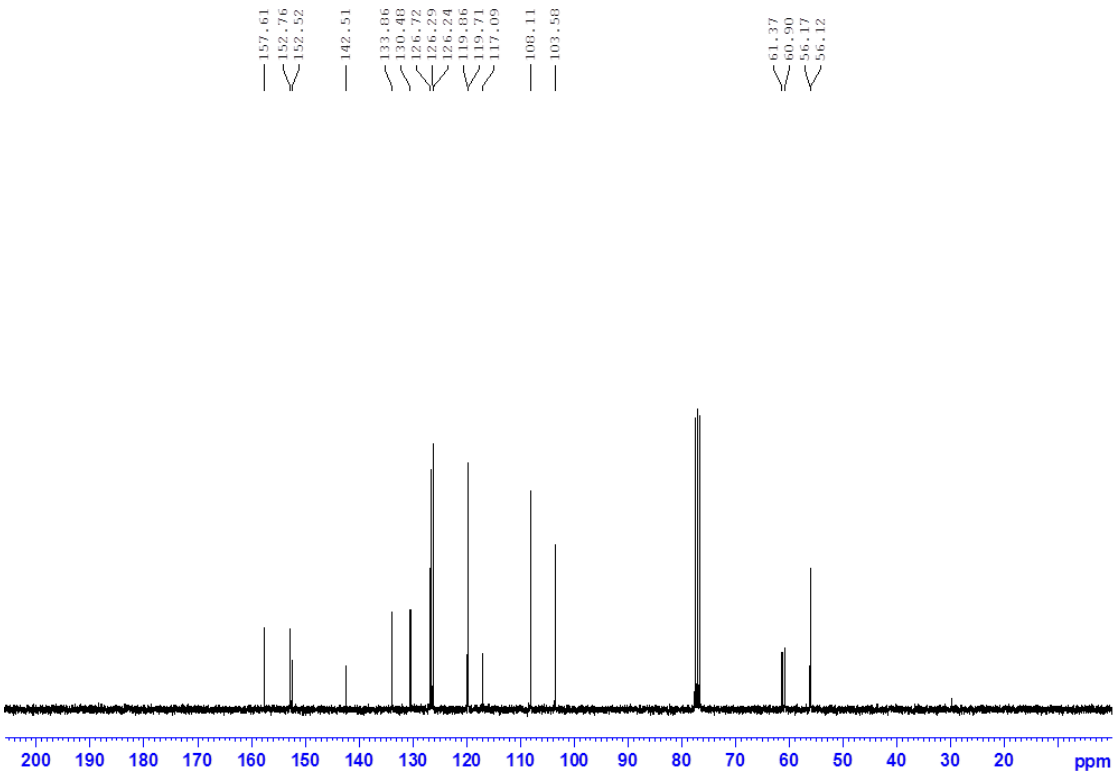
$^{19}F\{^{1}H\}$-NMR (282MHz, $CDCl_3$): Compound **107k**



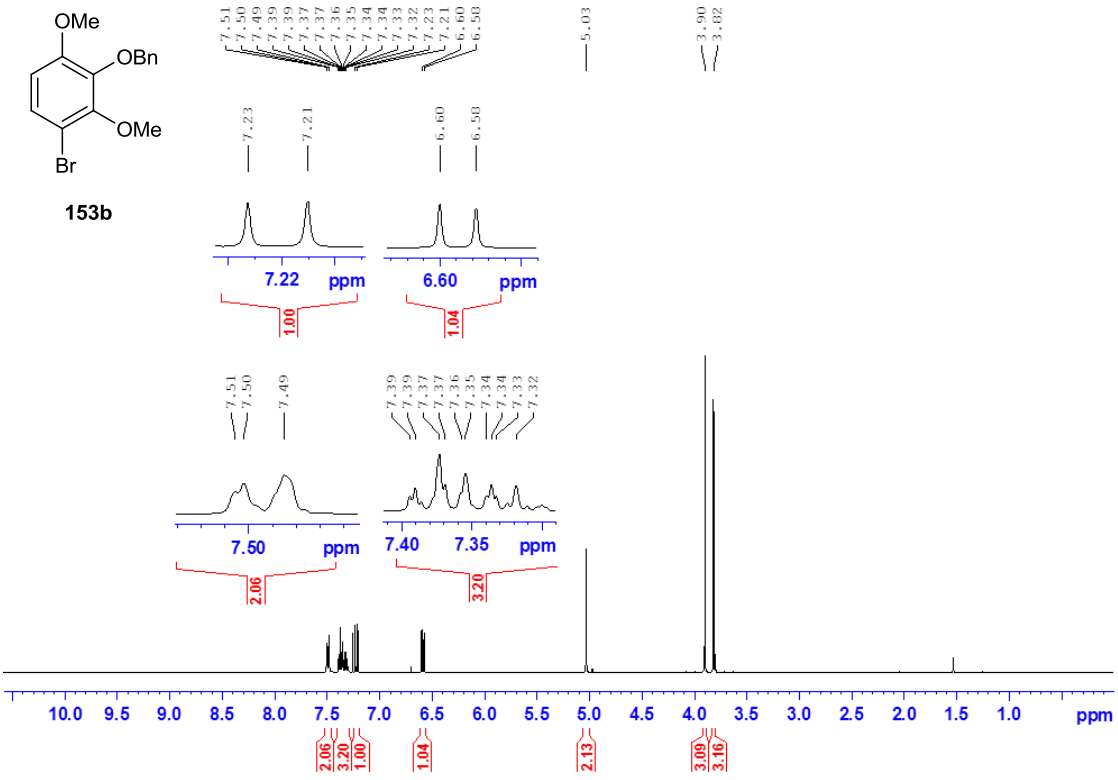
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **107g**



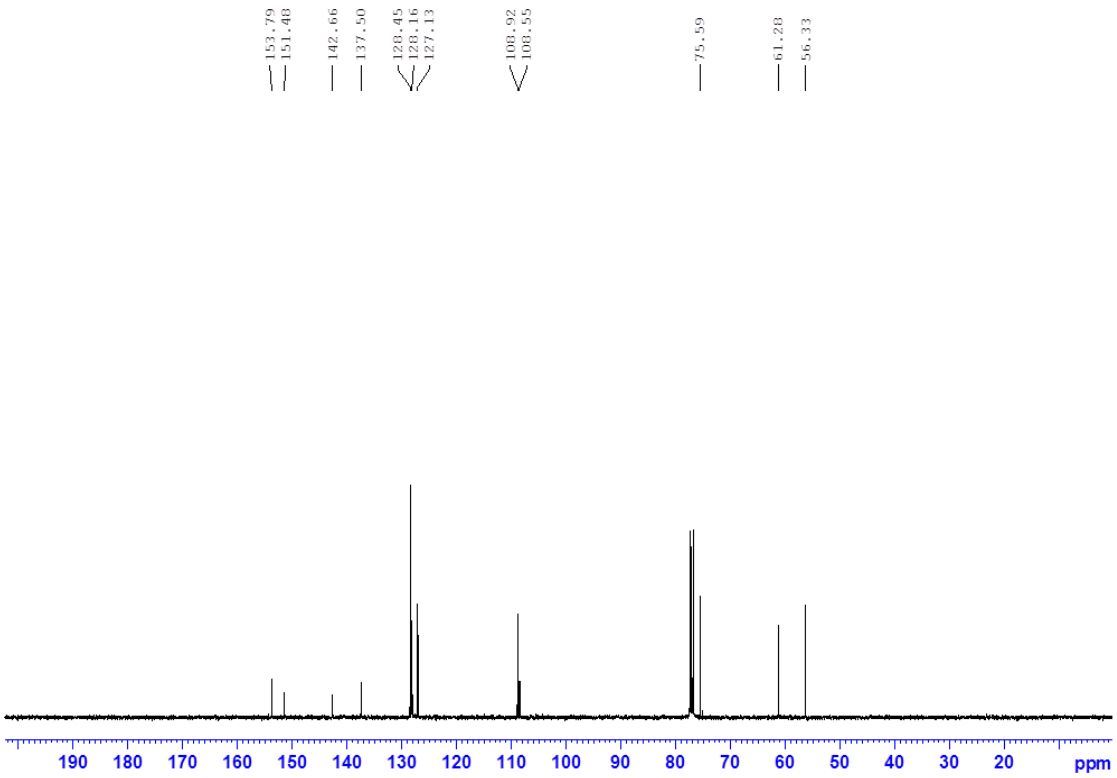
$^{13}C\{^{1}H\}$-NMR (75MHz, $CDCl_3$): Compound **107g**



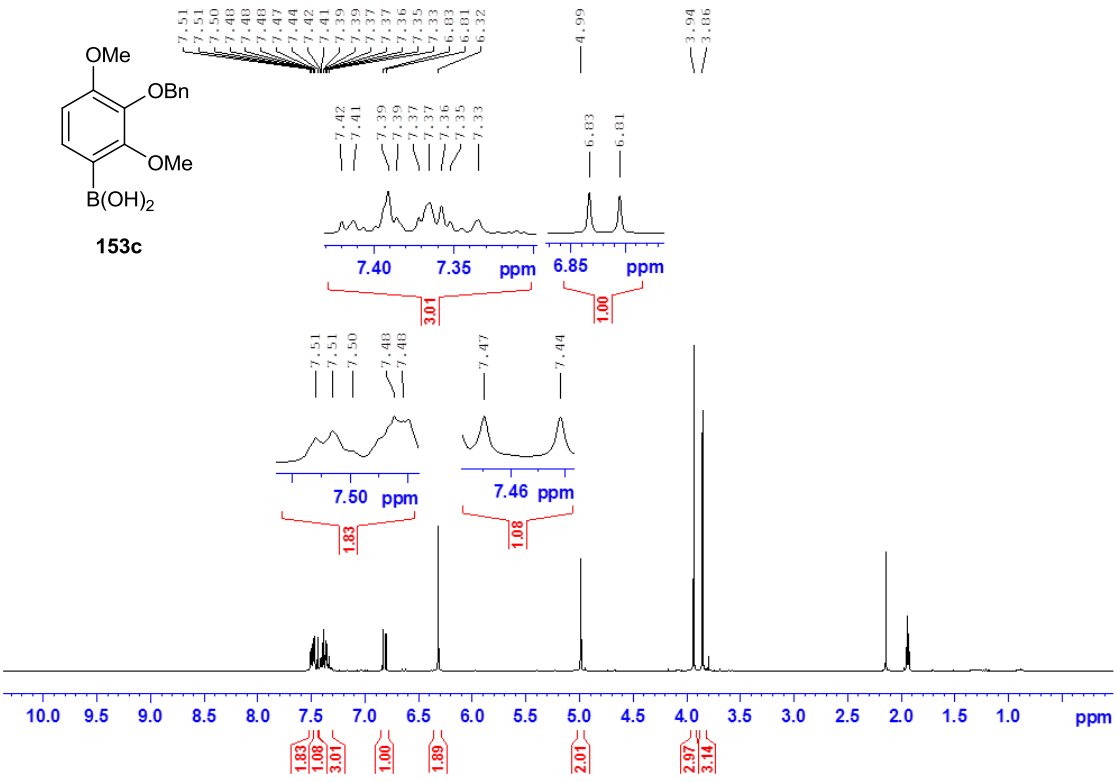
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **153b**



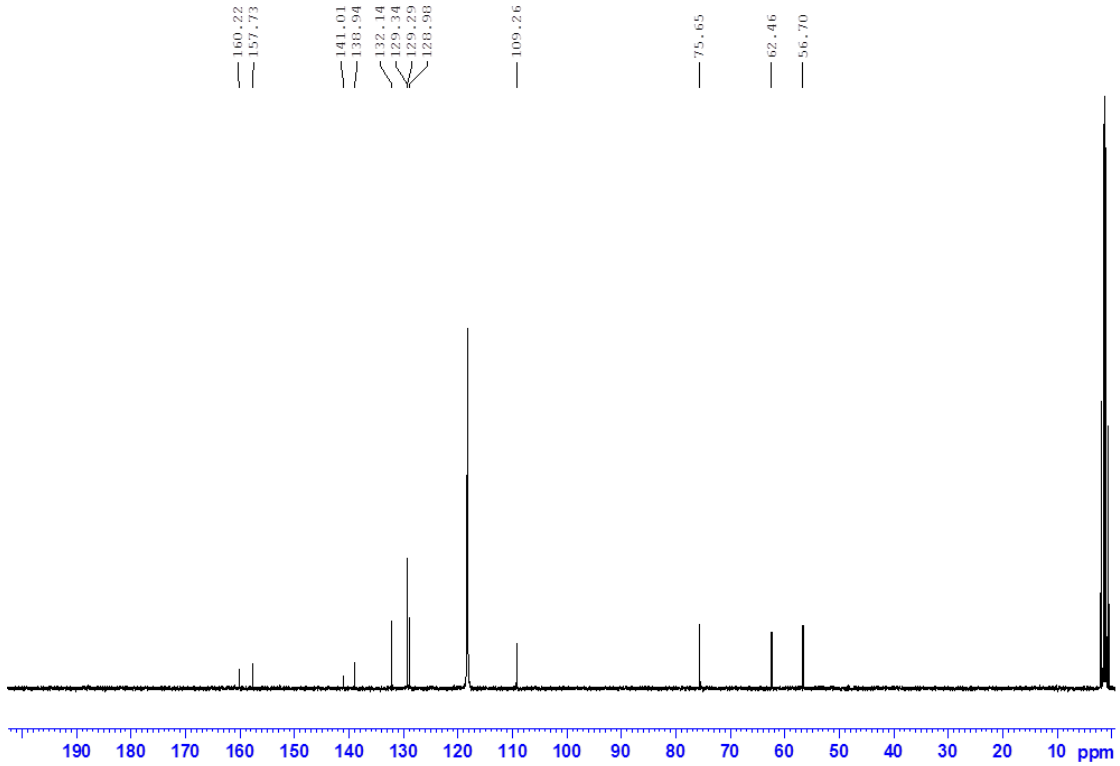
$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$): Compound **153b**



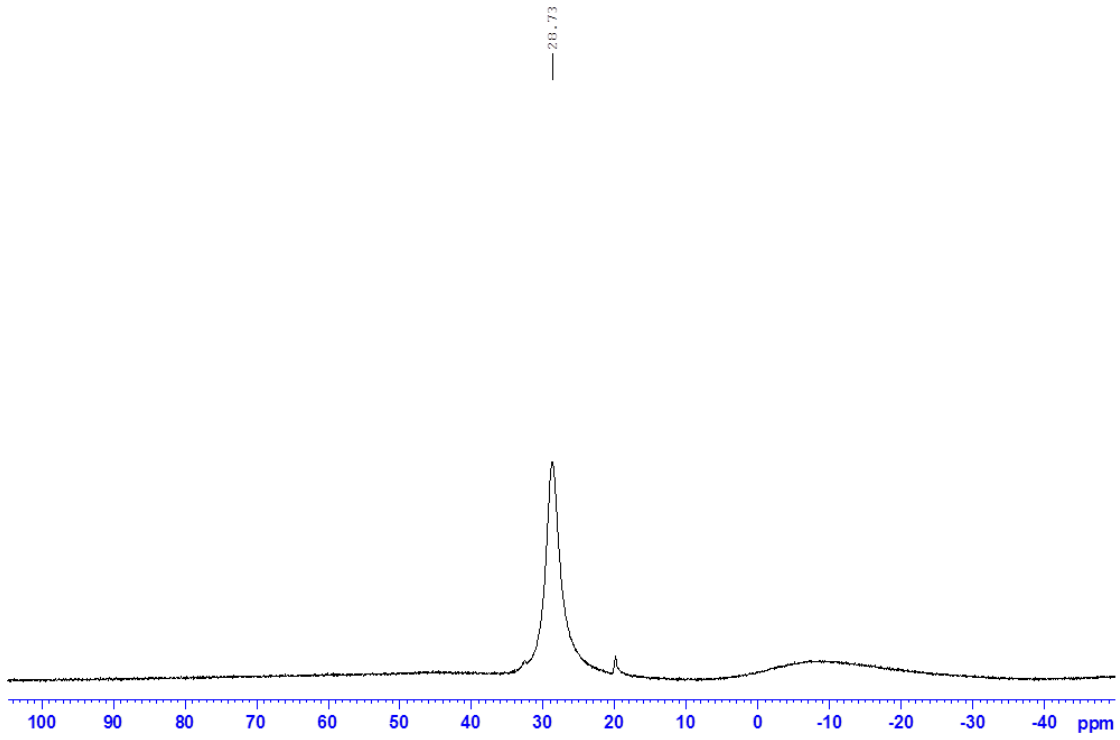
^{1}H-NMR (300 MHz, CD_3CN): Compound **153c**



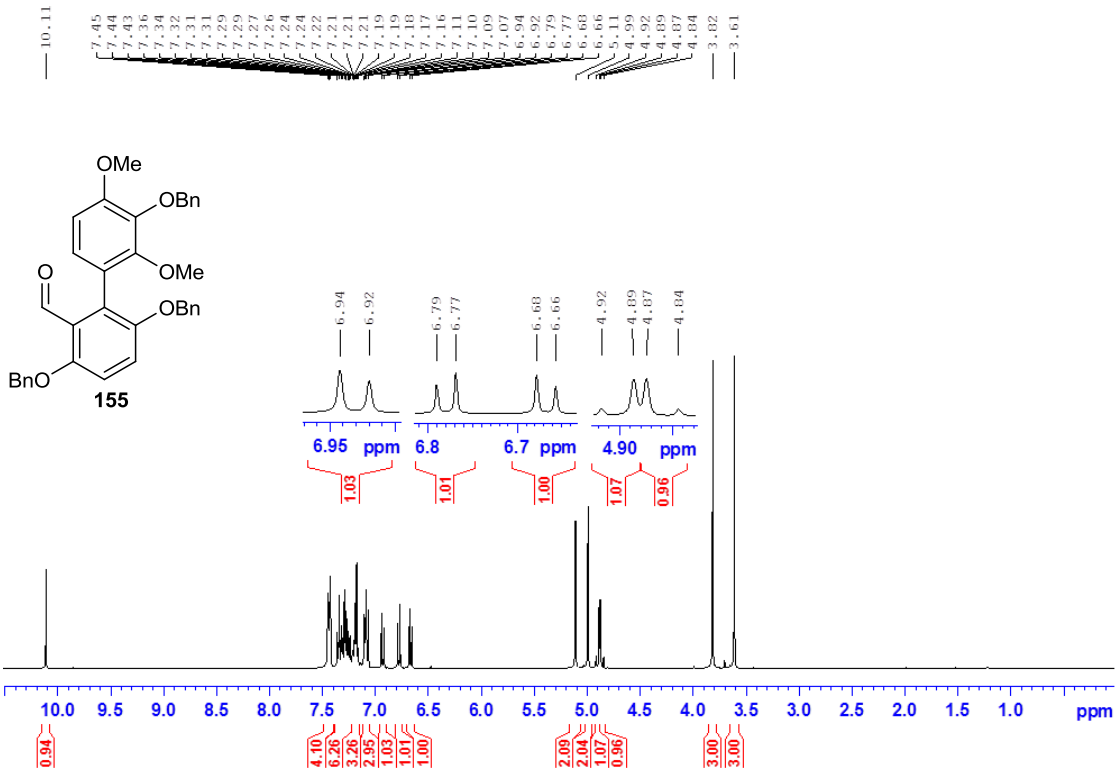
$^{13}C\{^1H\}$-NMR (75 MHz, CD_3CN): Compound **153c**



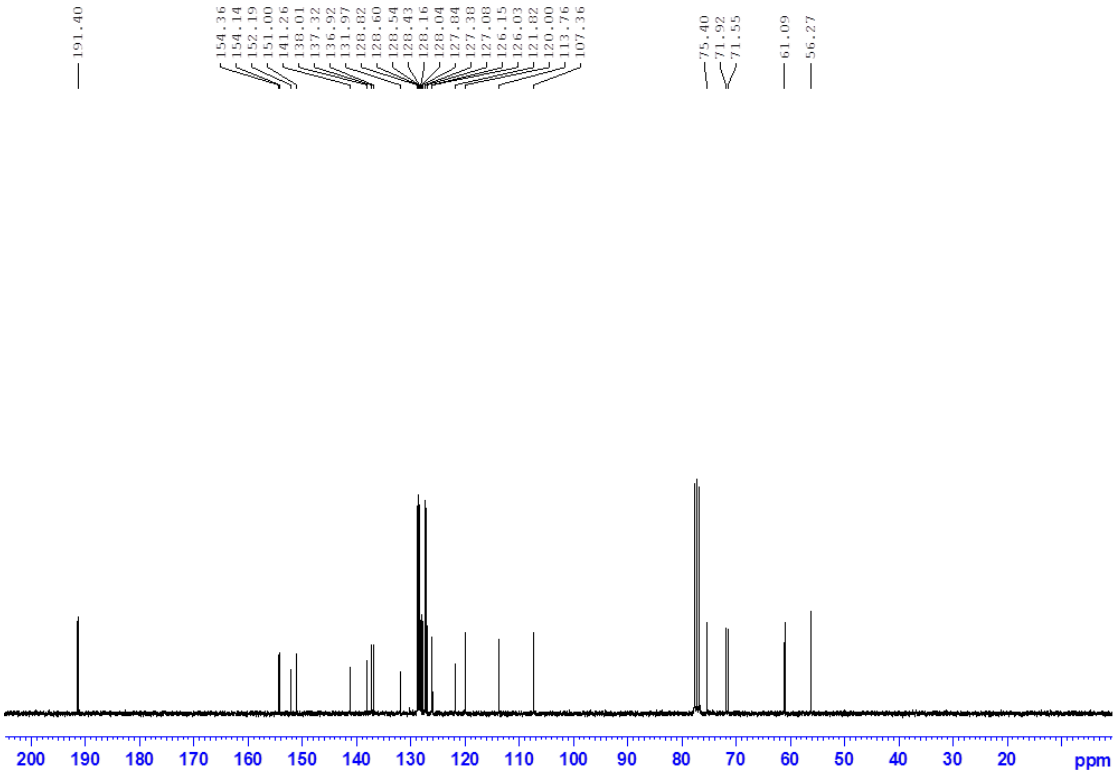
$^{11}B\{^1H\}$-NMR (96 MHz, CD_3CN): Compound **153c**



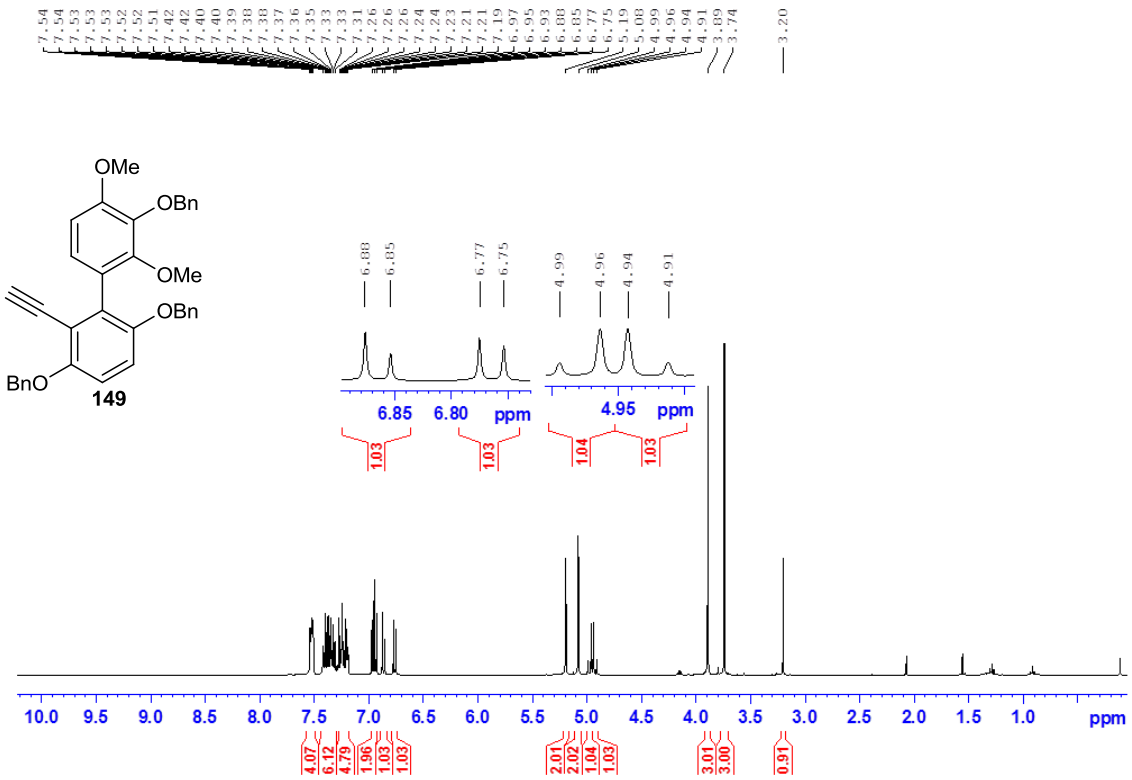
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **155**



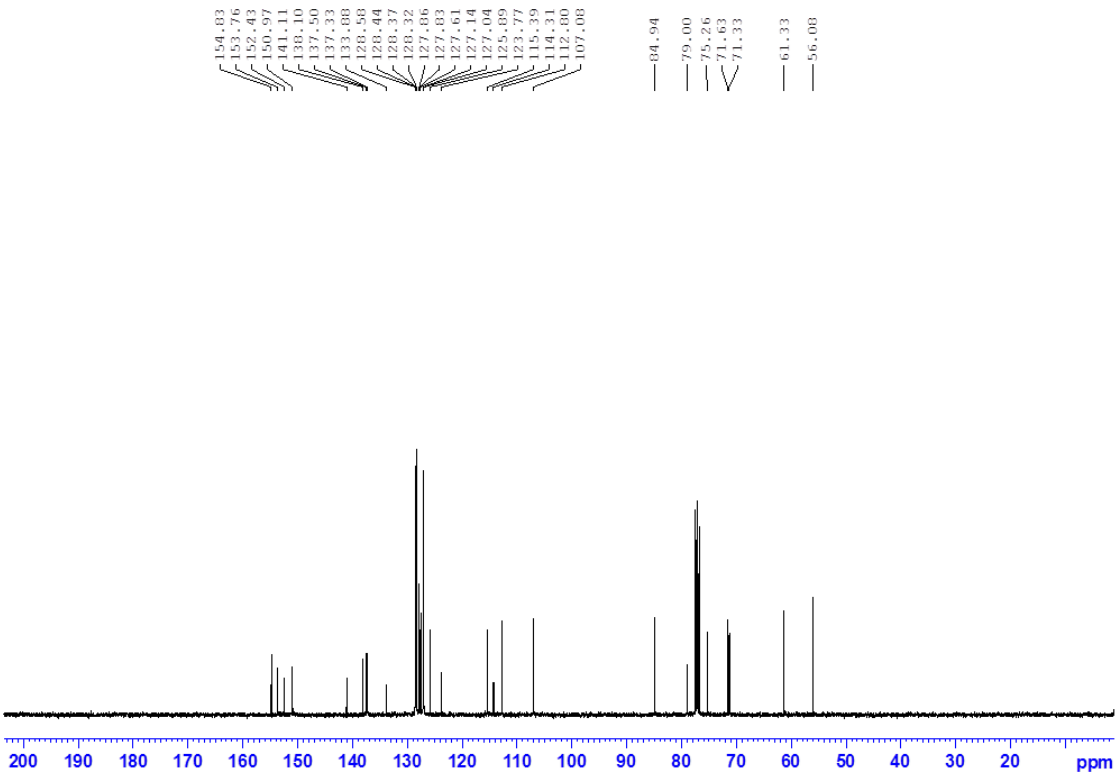
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): Compound **155**



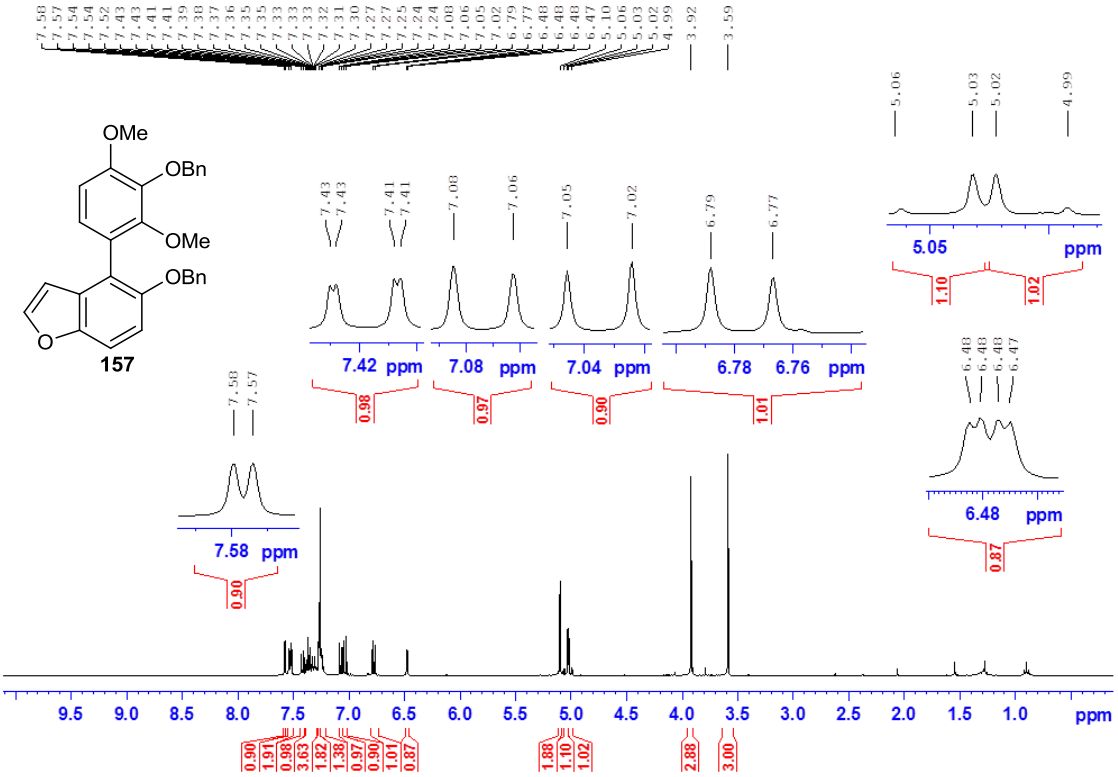
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **149**



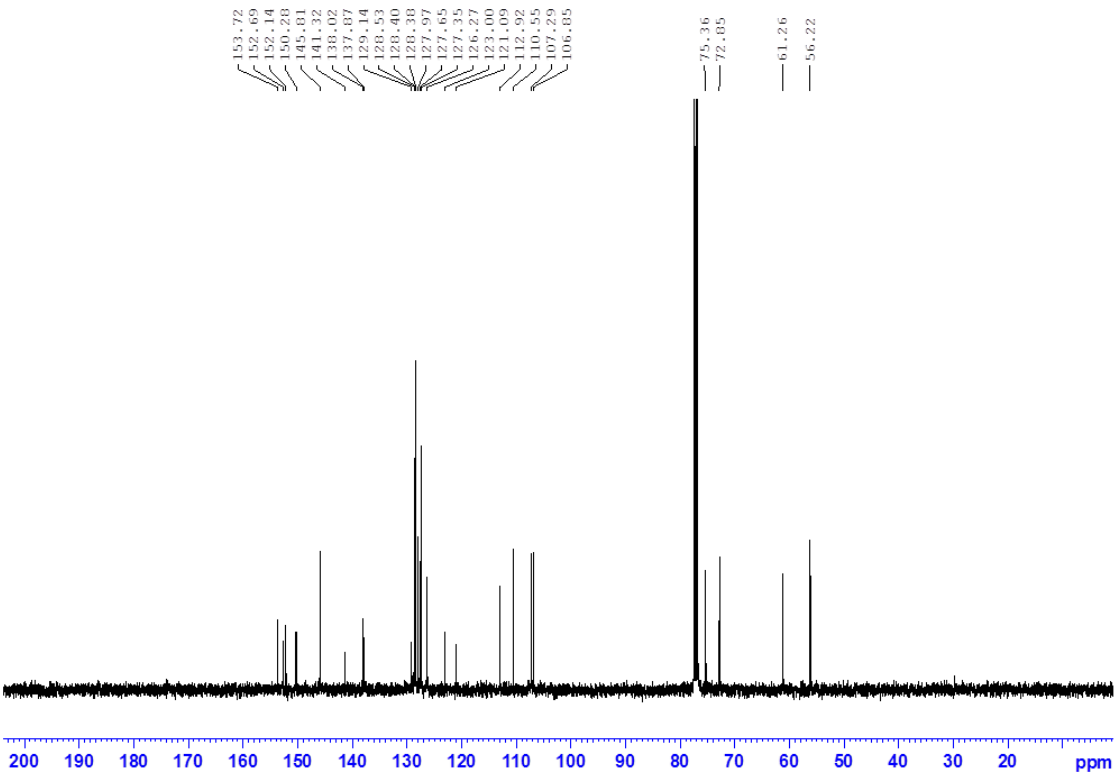
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): Compound **149**



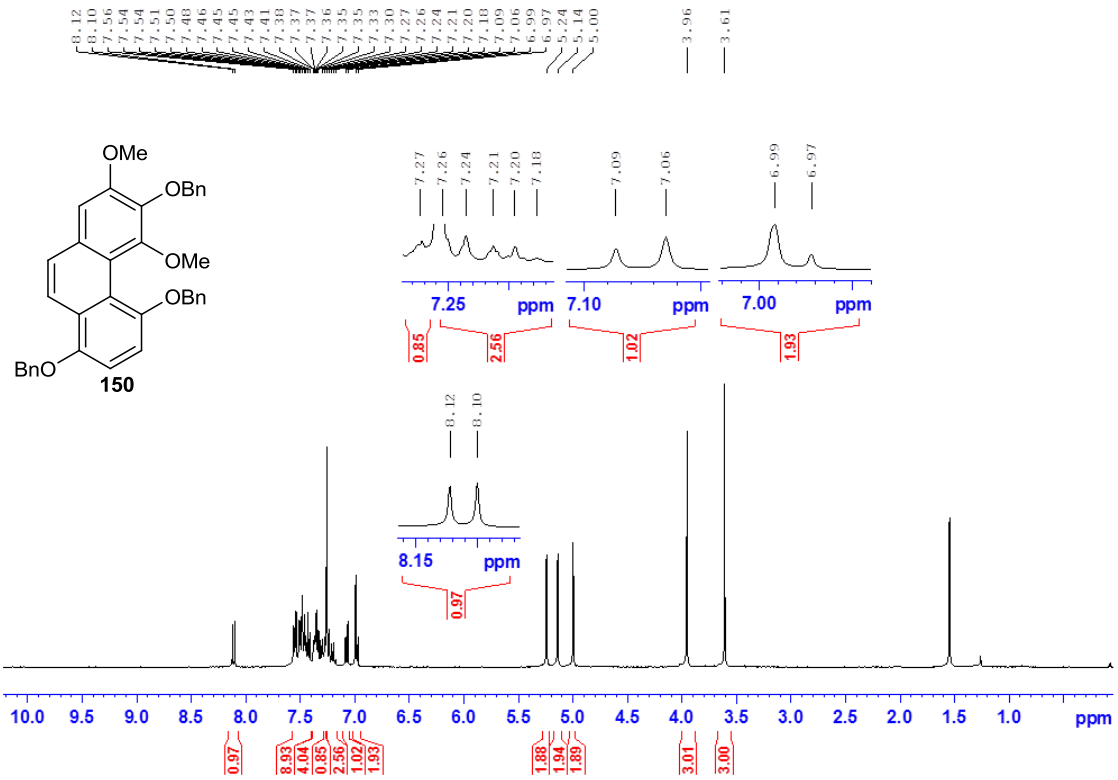
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **157**



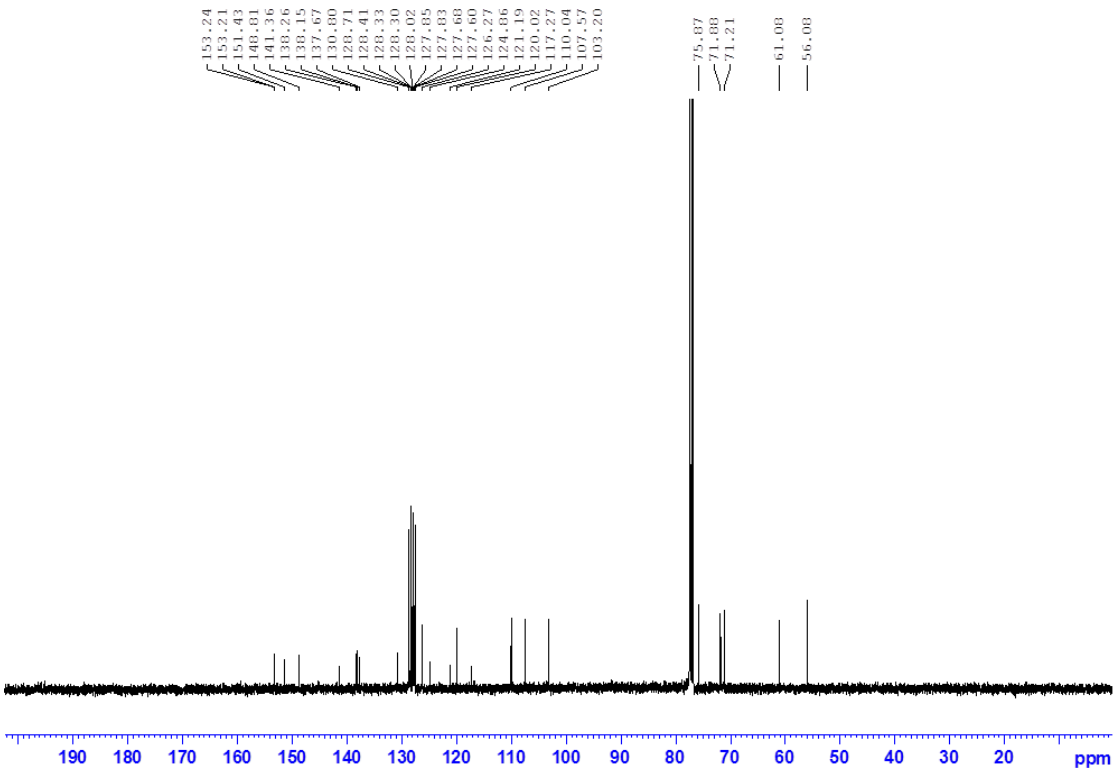
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): Compound **157**



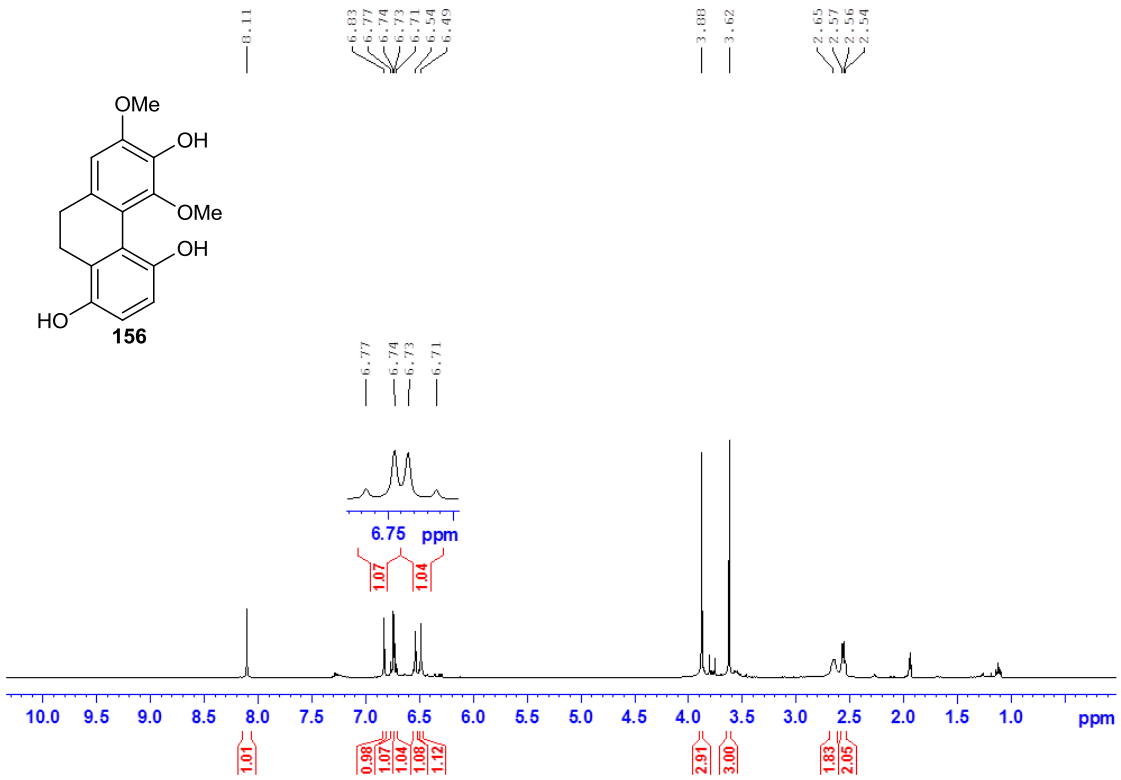
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **150**



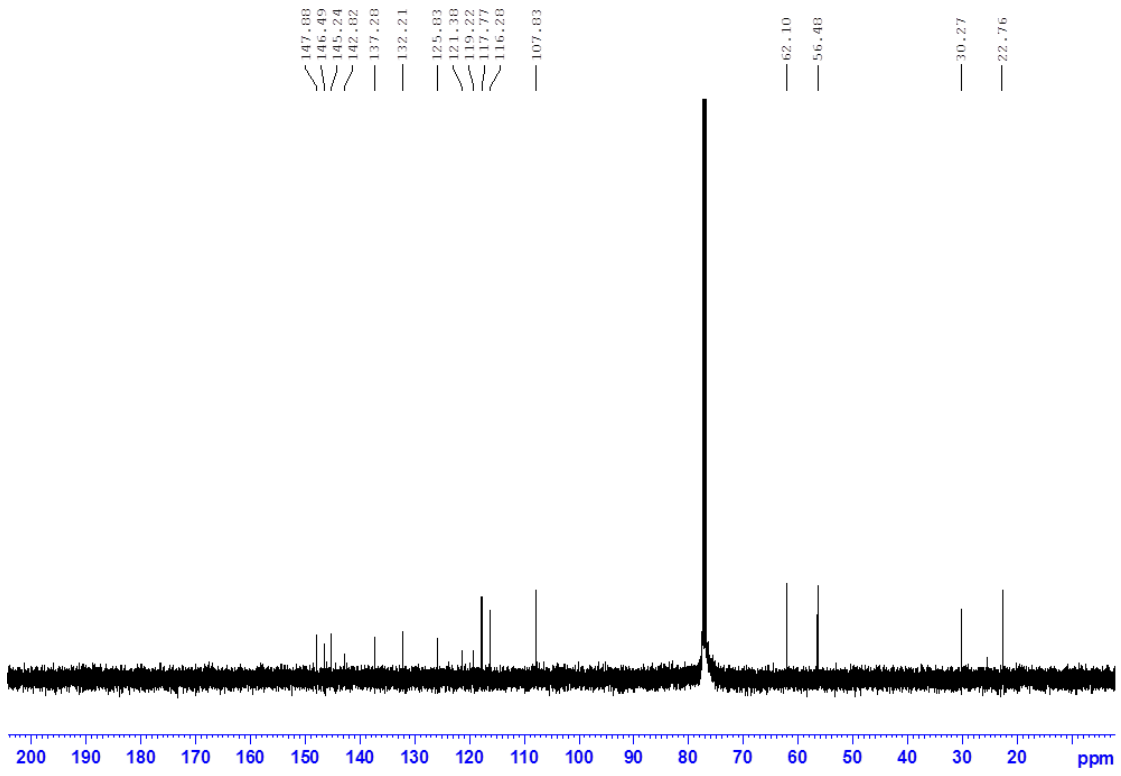
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): Compound **150**



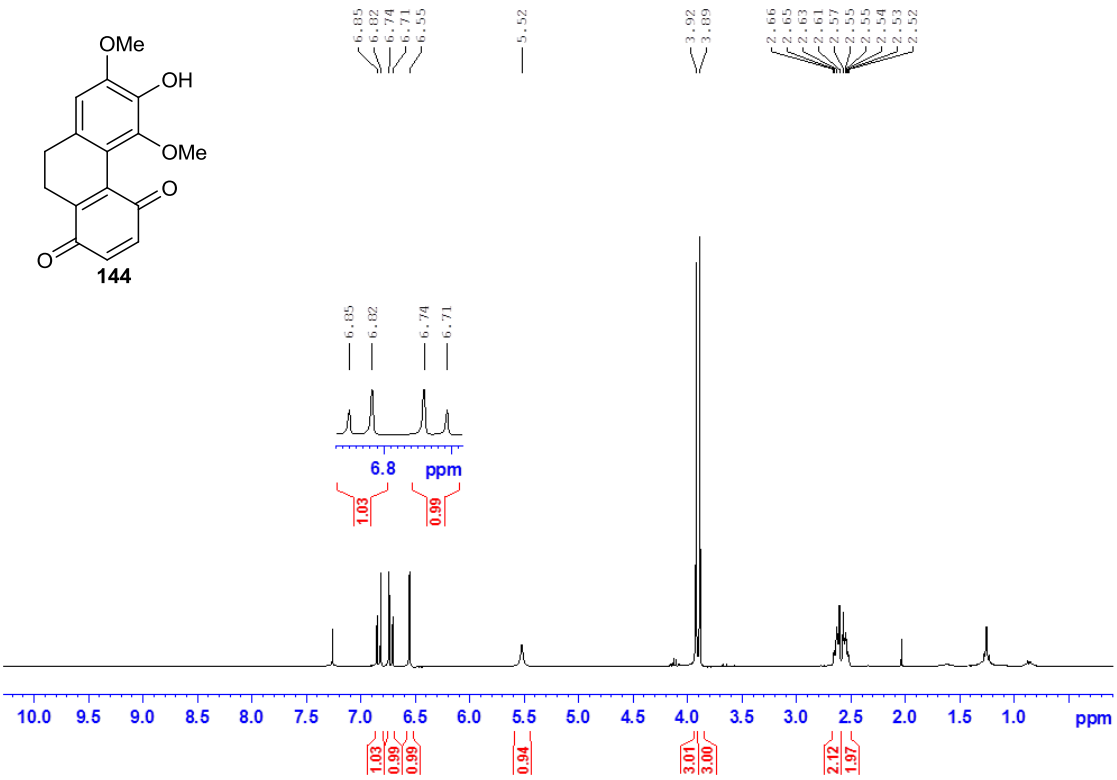
^{1}H-NMR (400 MHz, CD_3CN): *Calanhydroquinone A* **156**



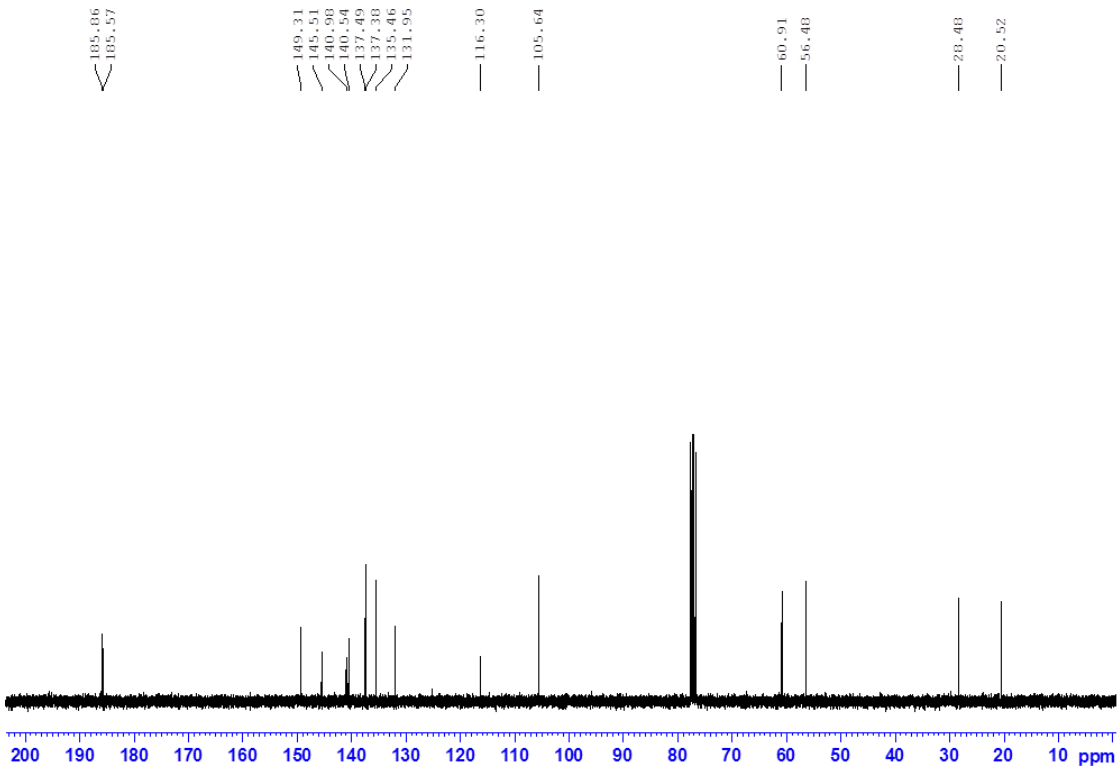
^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): *Calanhydroquinone A* **156**



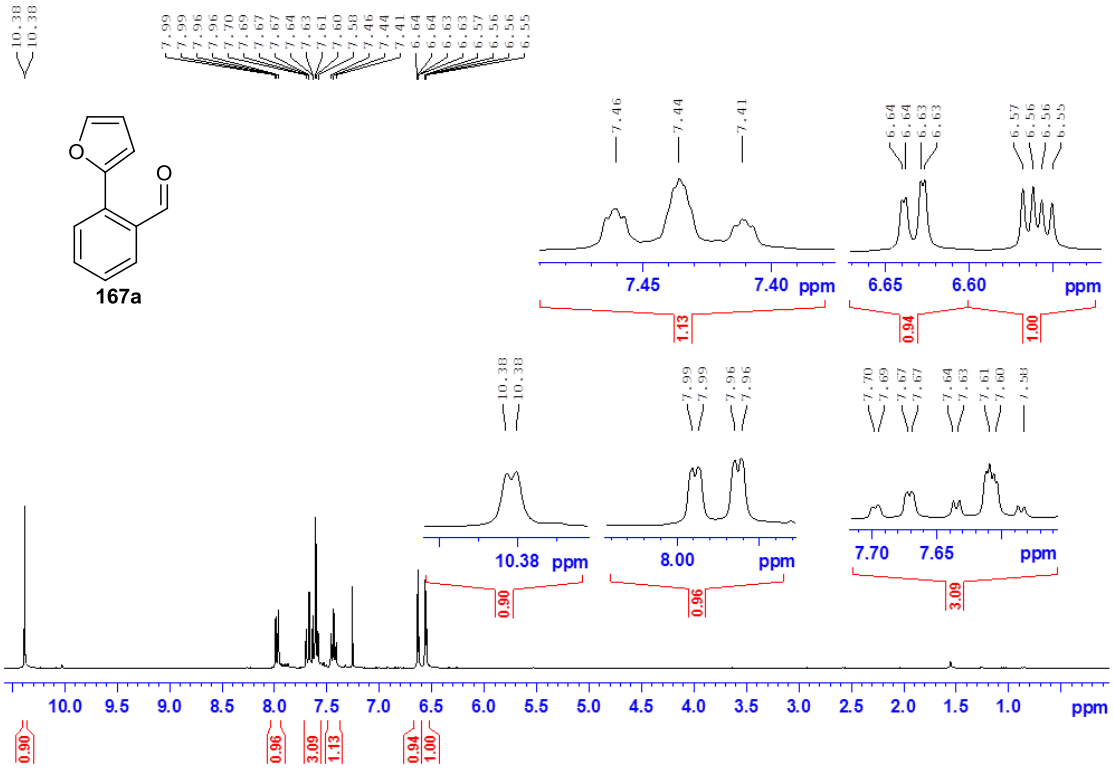
^{1}H-NMR (300 MHz, $CDCl_3$): *Calanquinone C* **144**



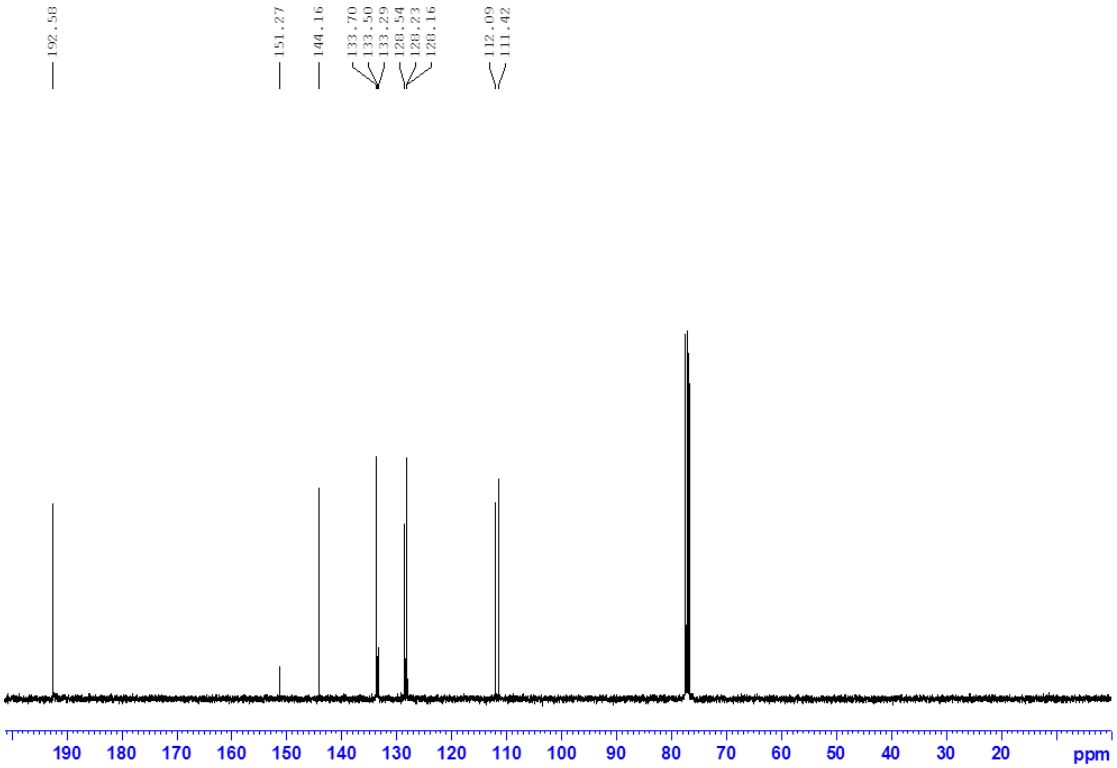
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): *Calanquinone C* **144**



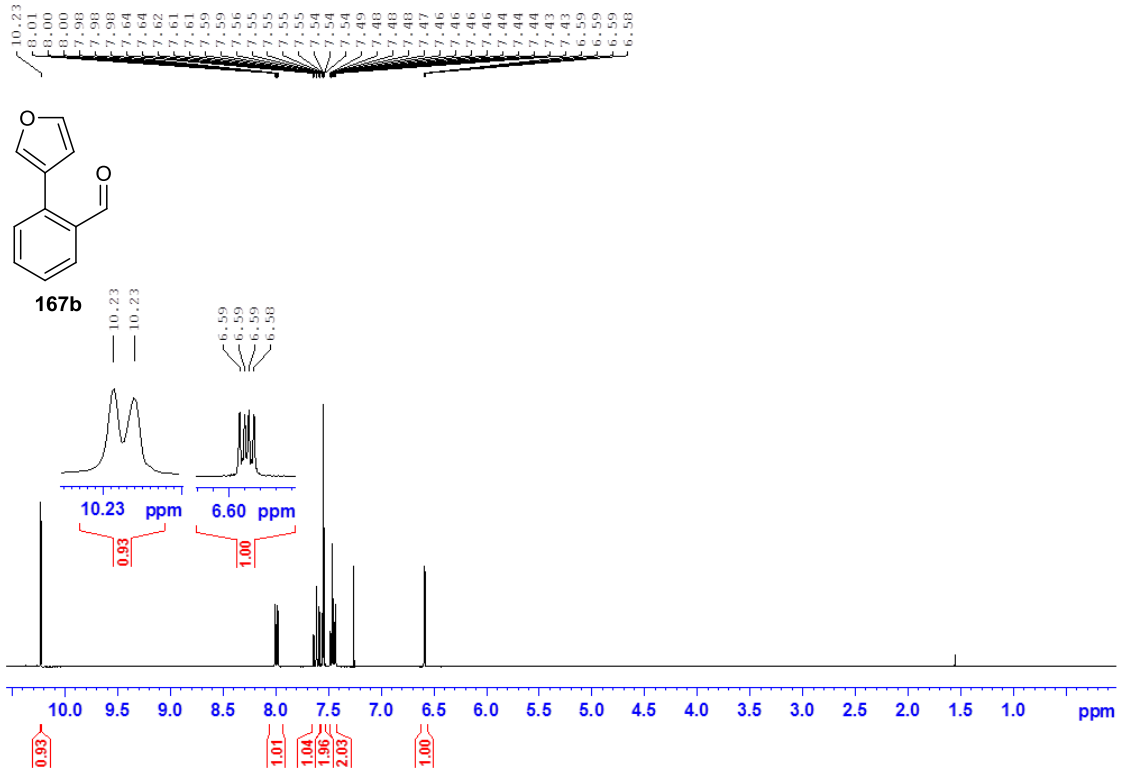
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **167a**



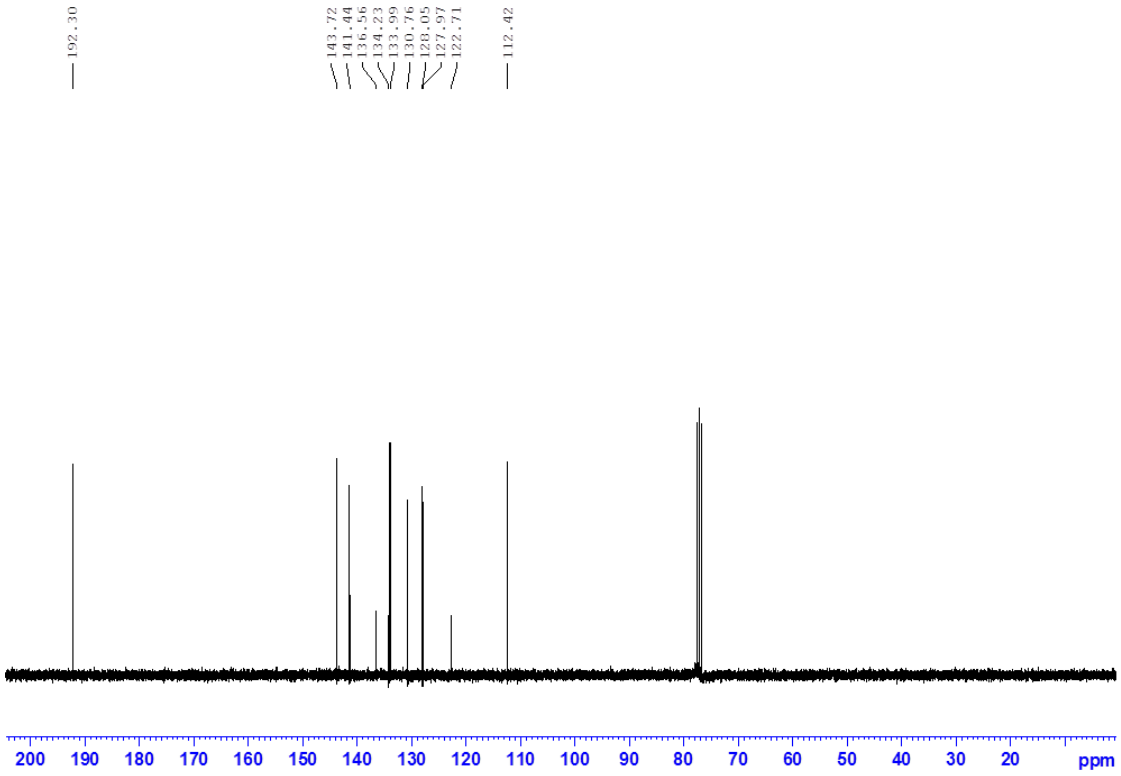
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): Compound **167a**



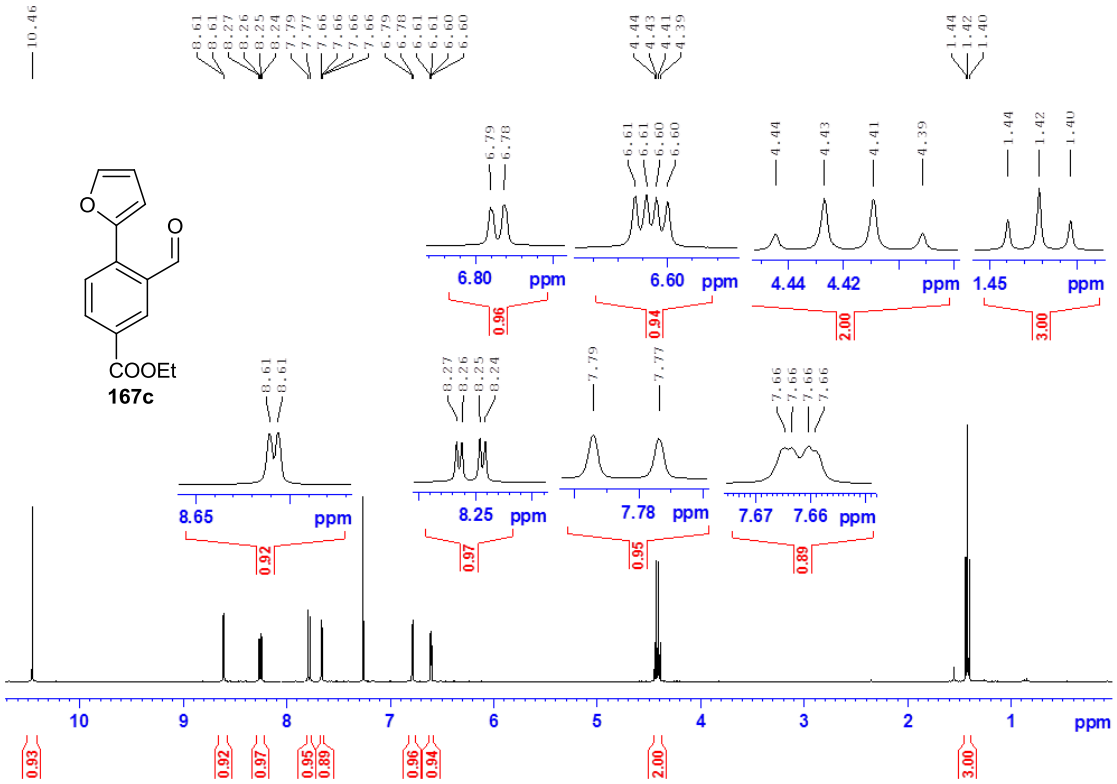
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **167b**



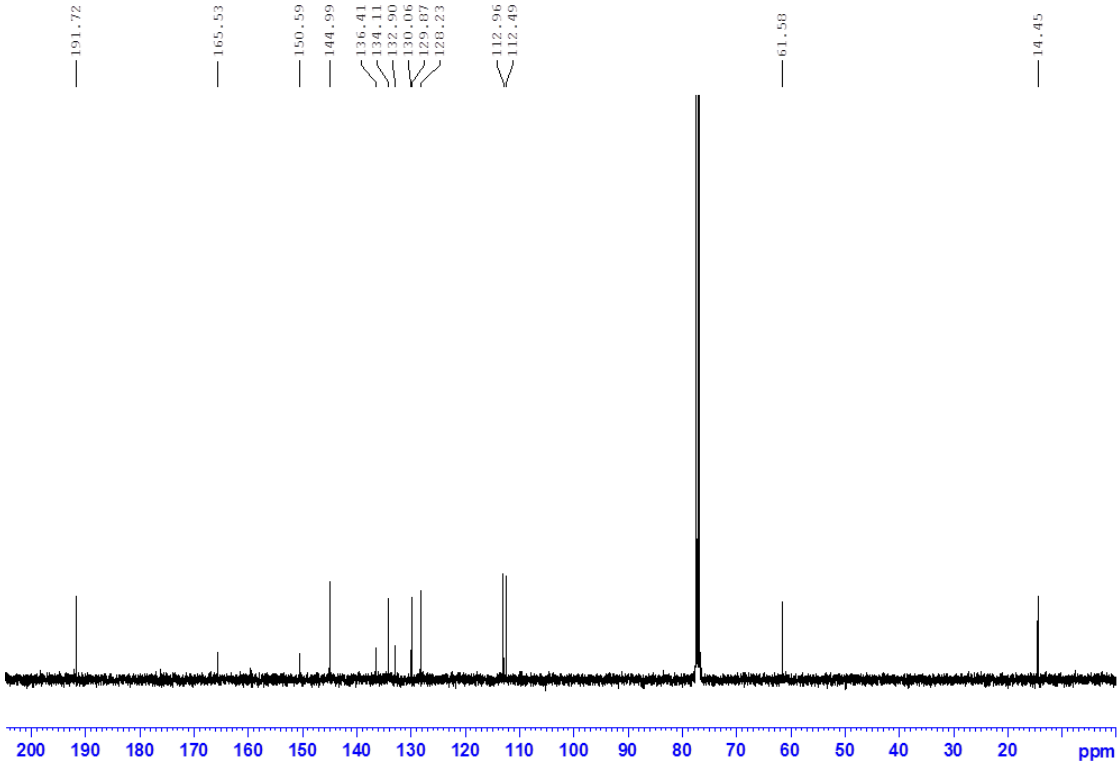
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): Compound **167b**



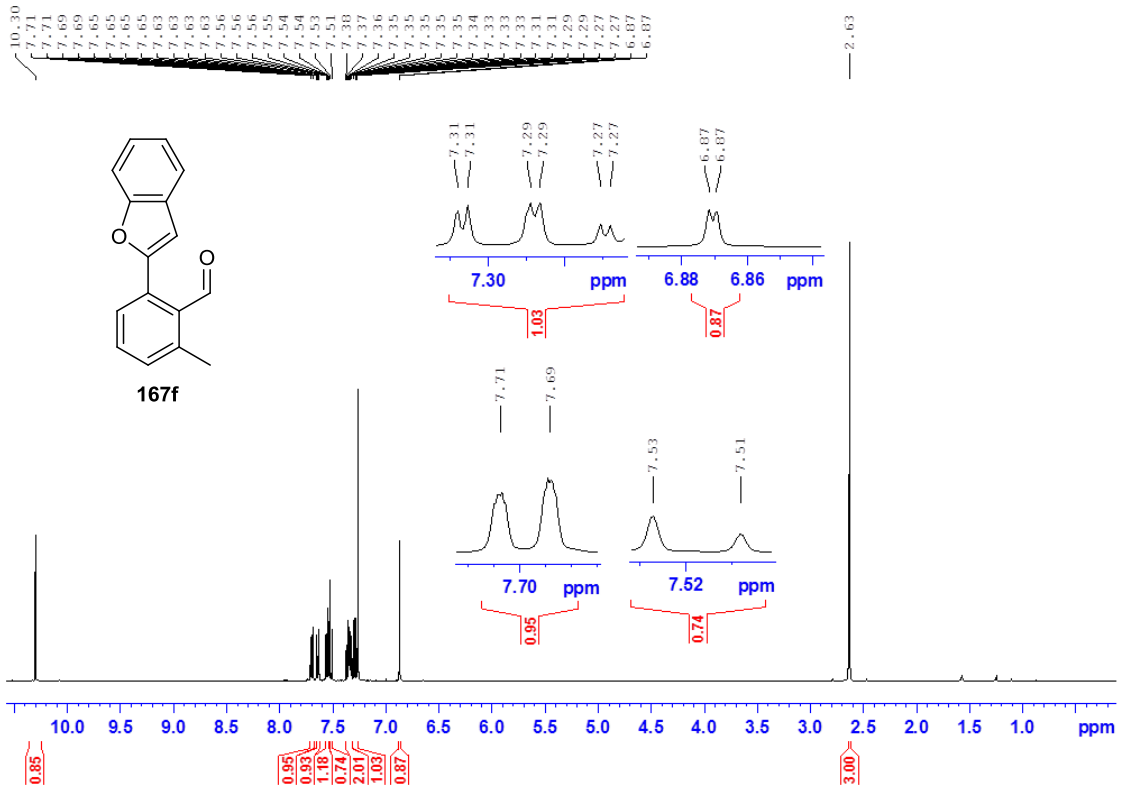
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **167c**



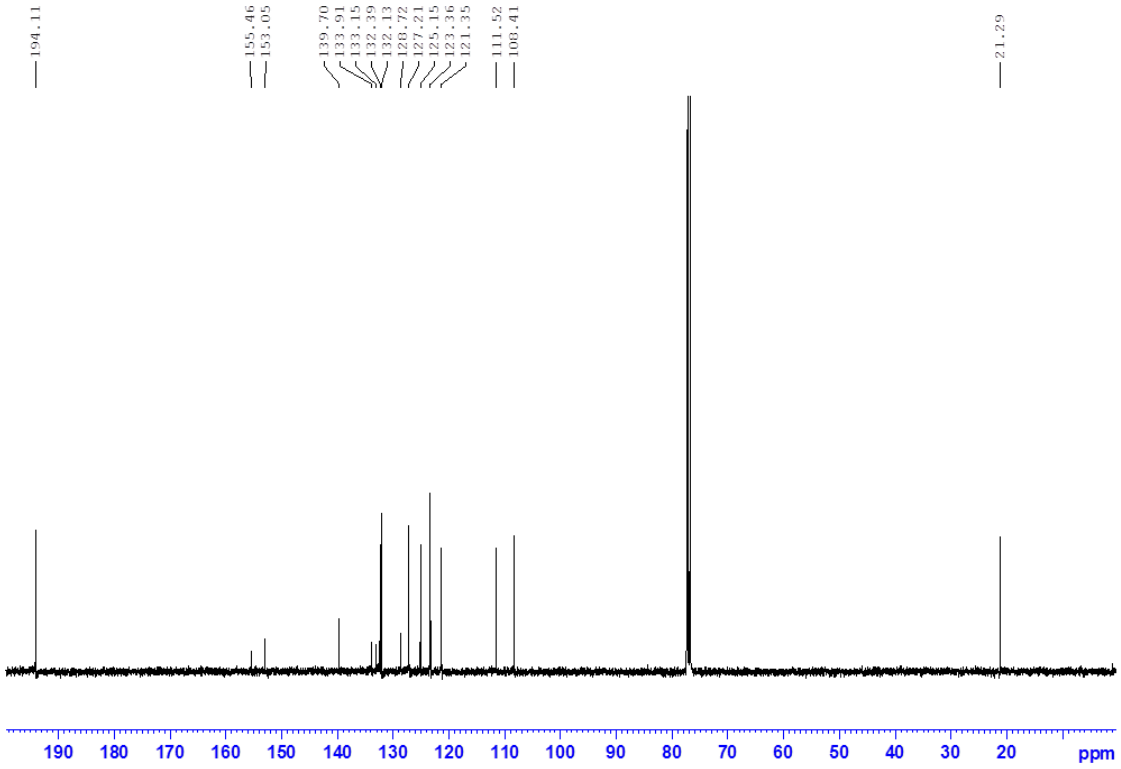
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): Compound **167c**



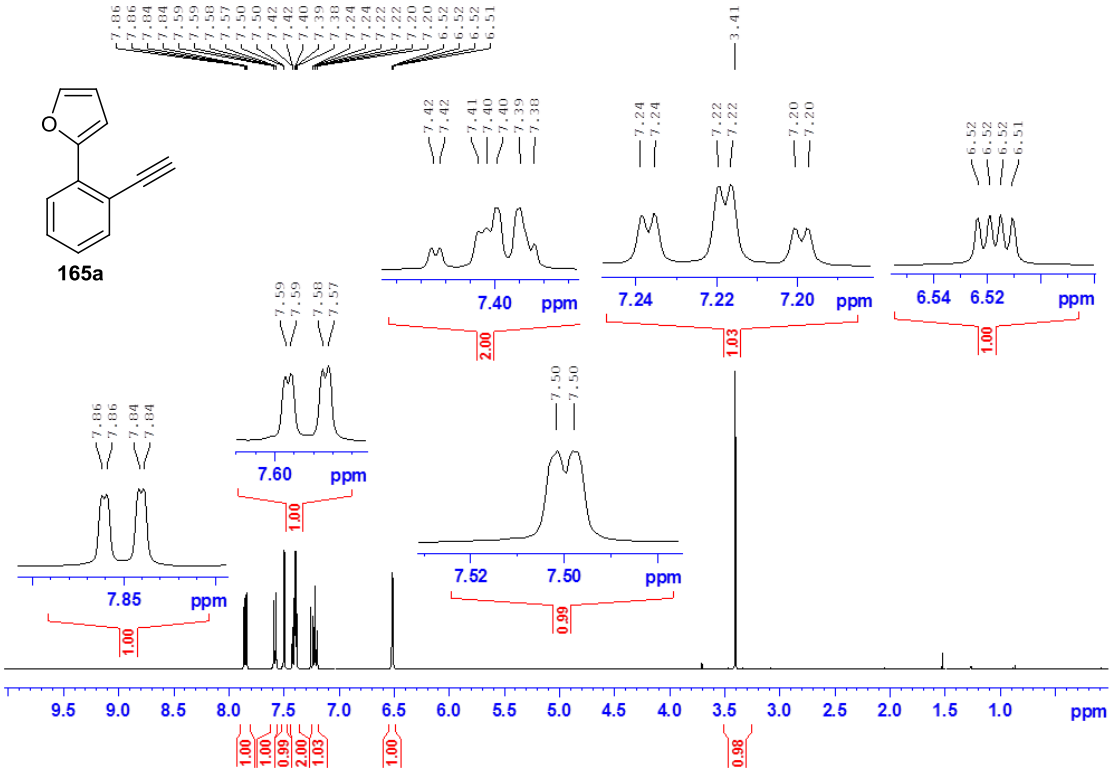
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **167f**



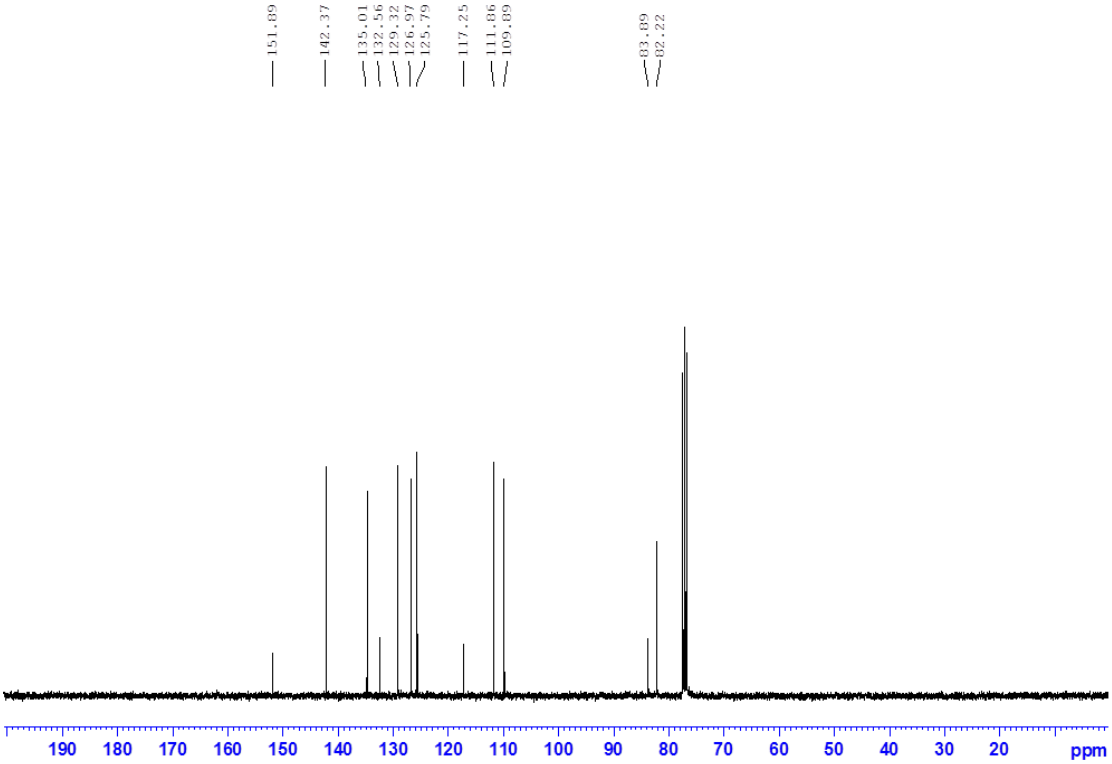
^{13}C{^{1}H}-NMR (101MHz, $CDCl_3$): Compound **167f**



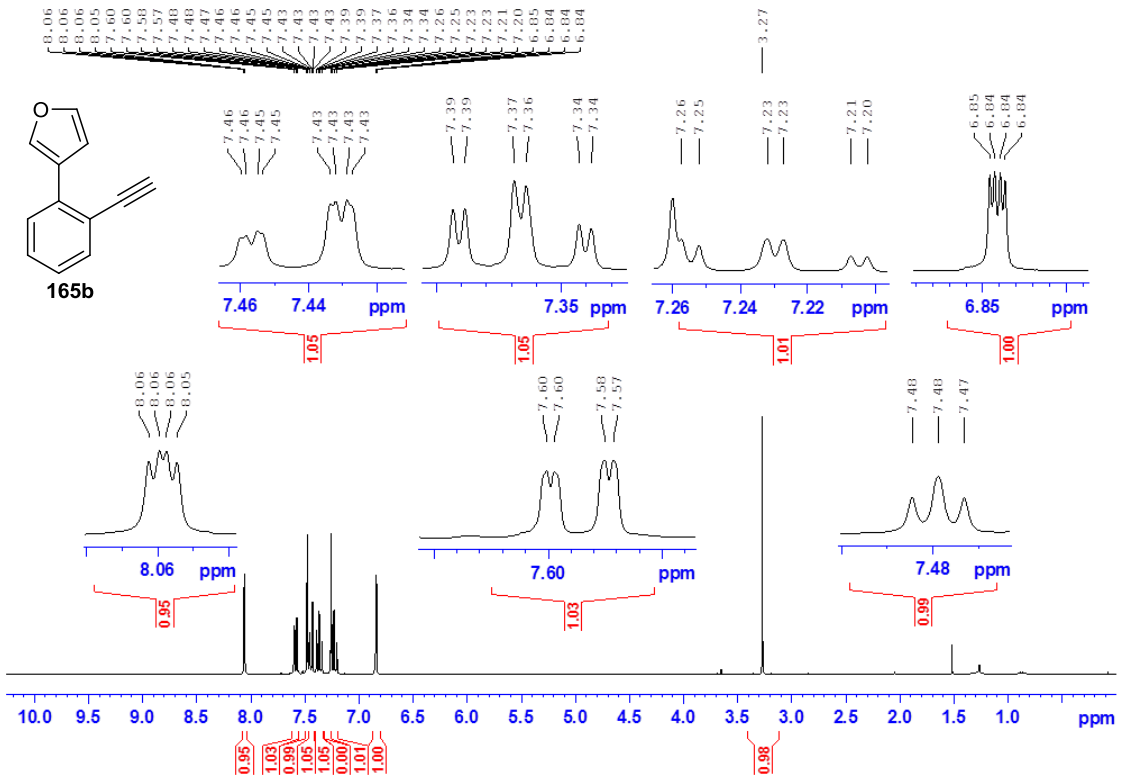
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **165a**



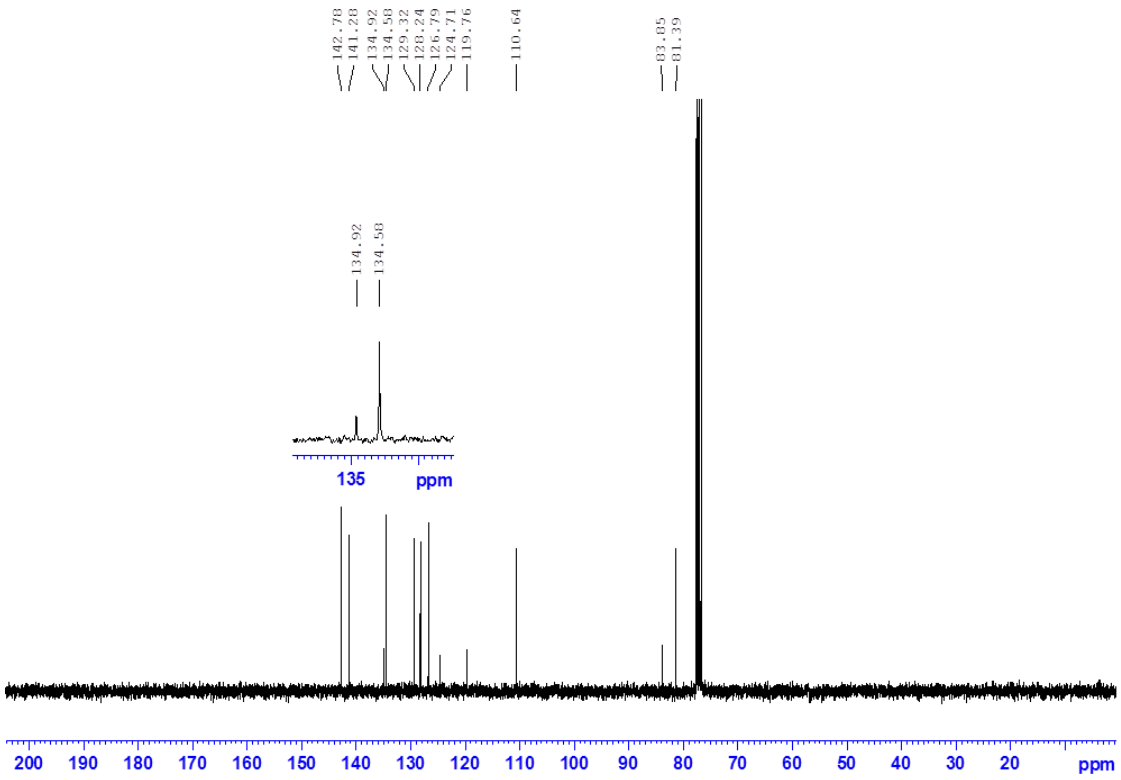
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): Compound **165a**



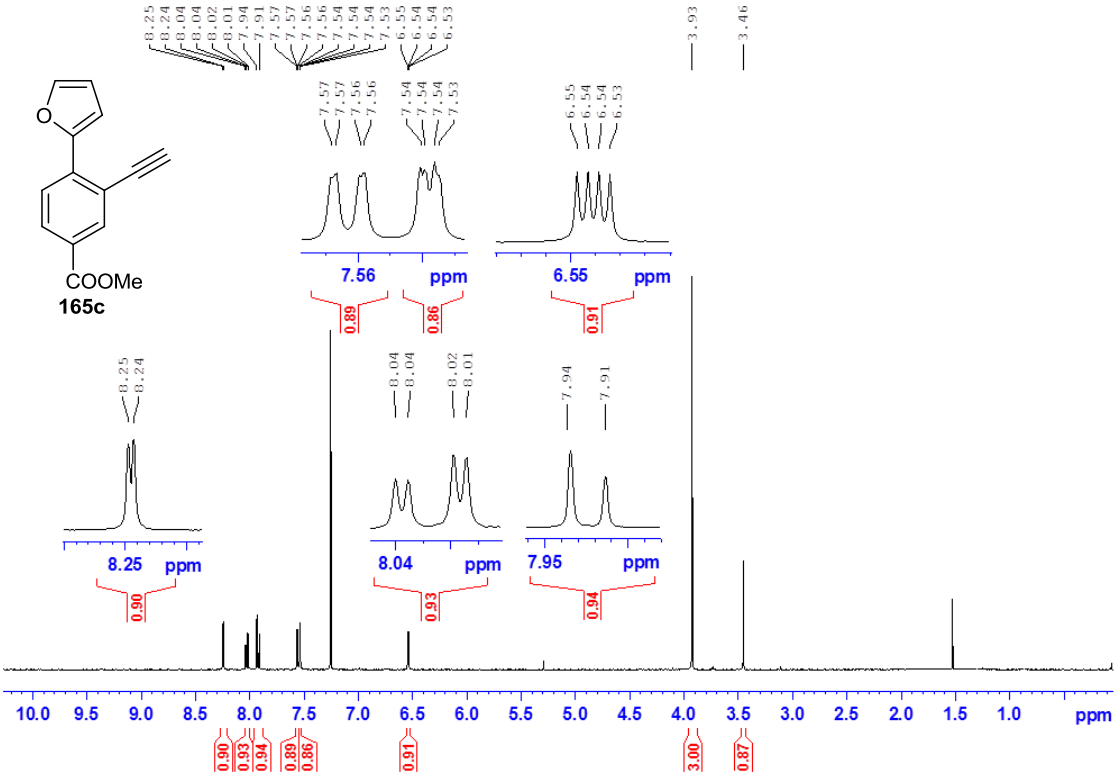
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **165b**



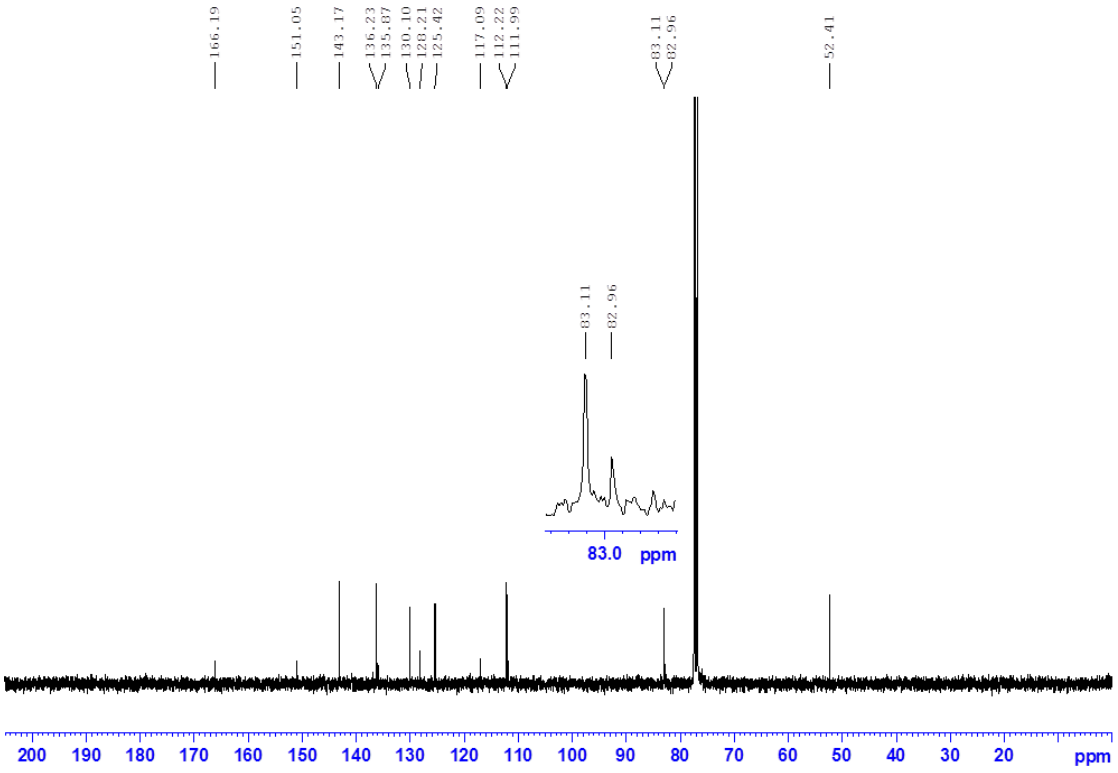
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): Compound **165b**



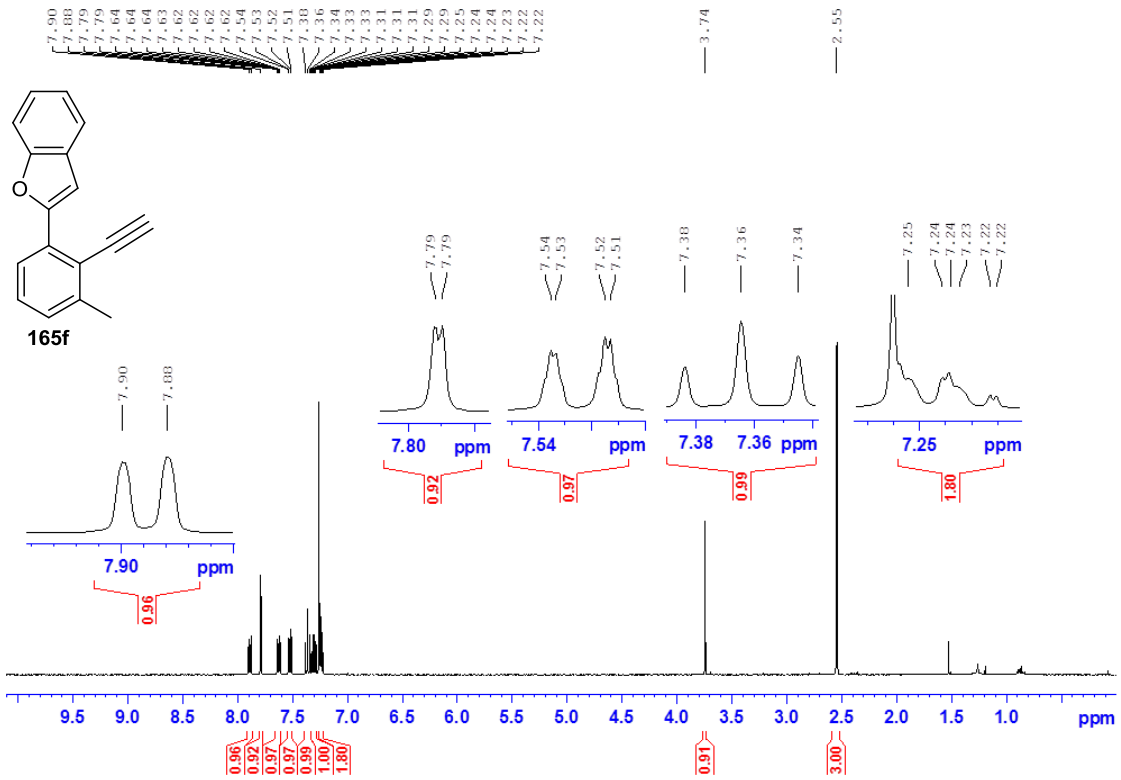
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **165c**



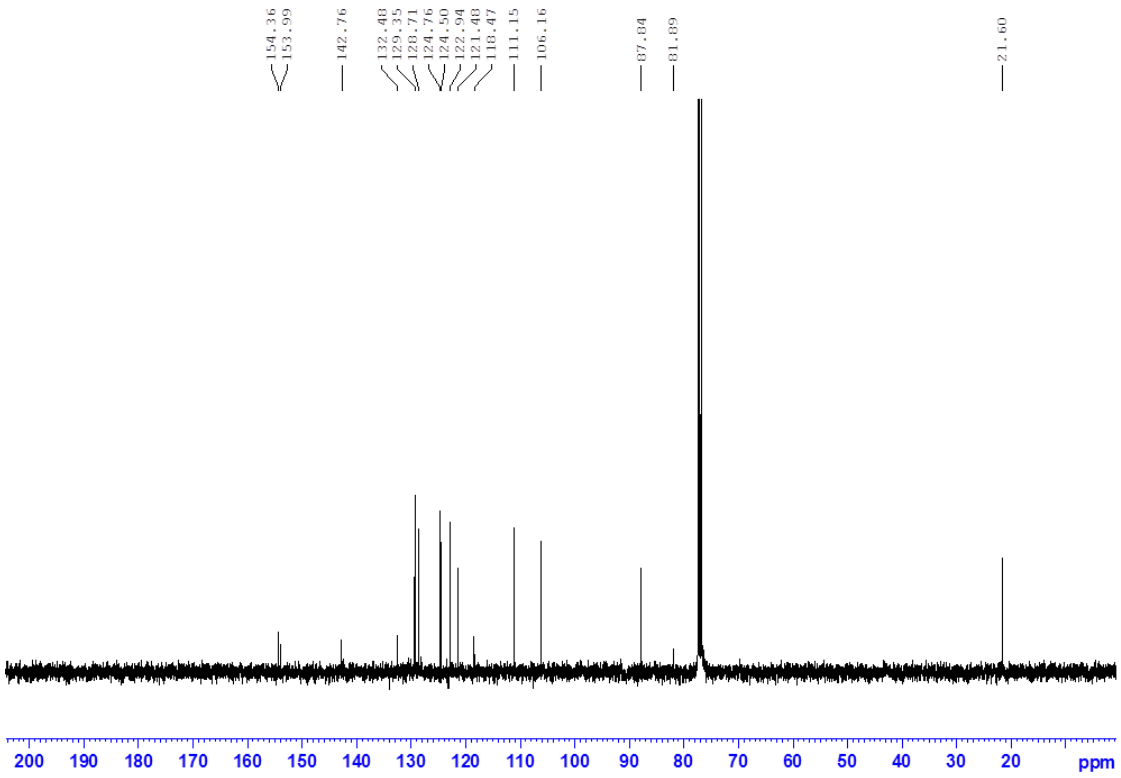
^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): Compound **165c**



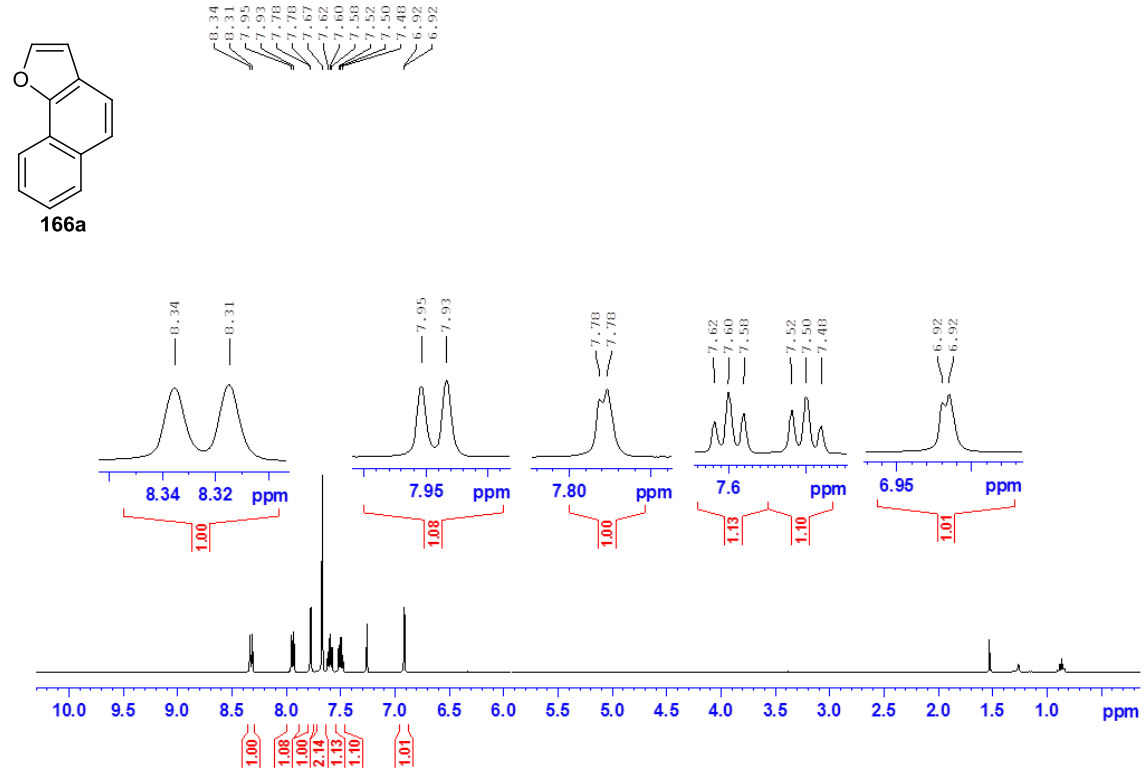
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **165f**



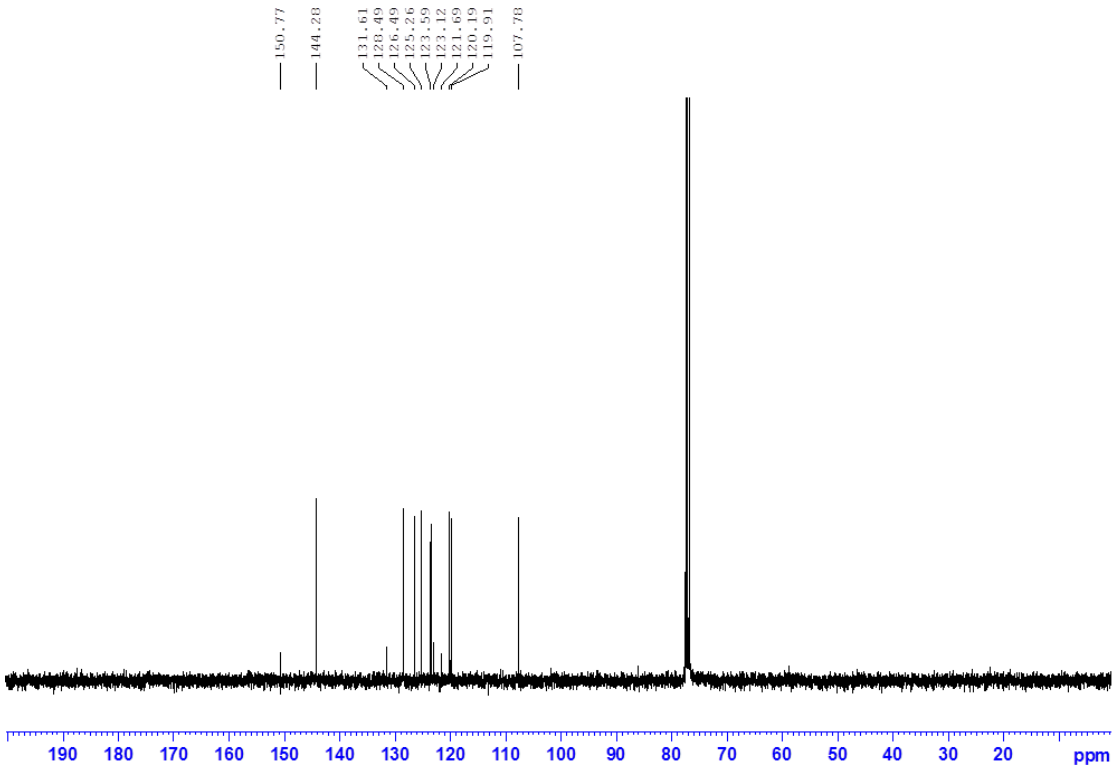
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): Compound **165f**



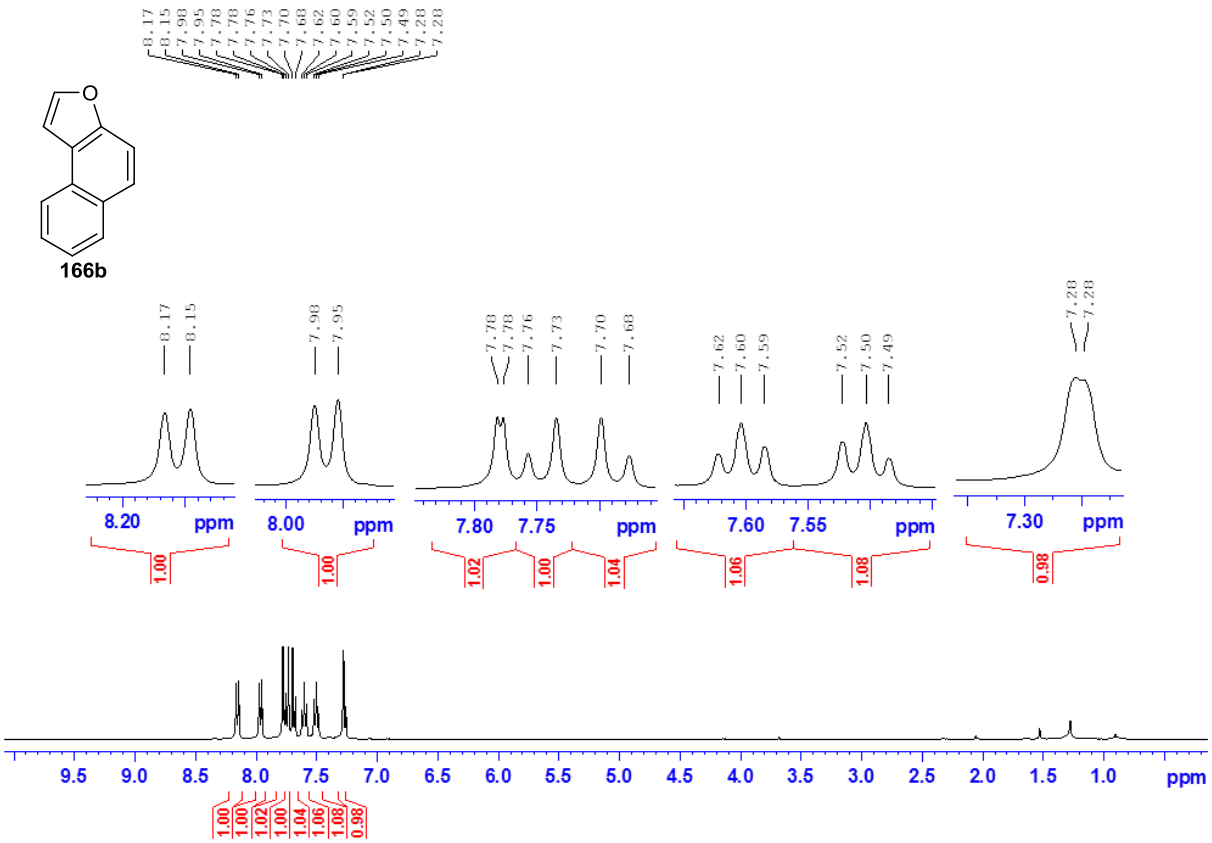
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **166a**



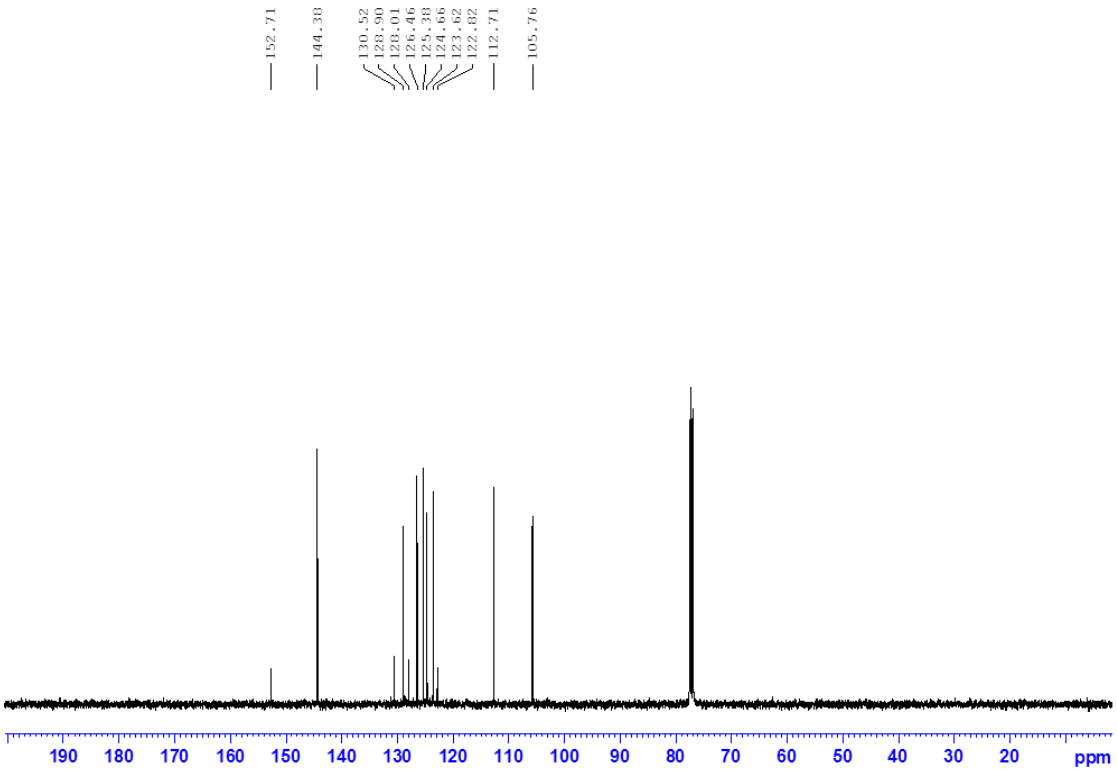
^{13}C{^{1}H}-NMR (75MHz, $CDCl_3$): Compound **166a**



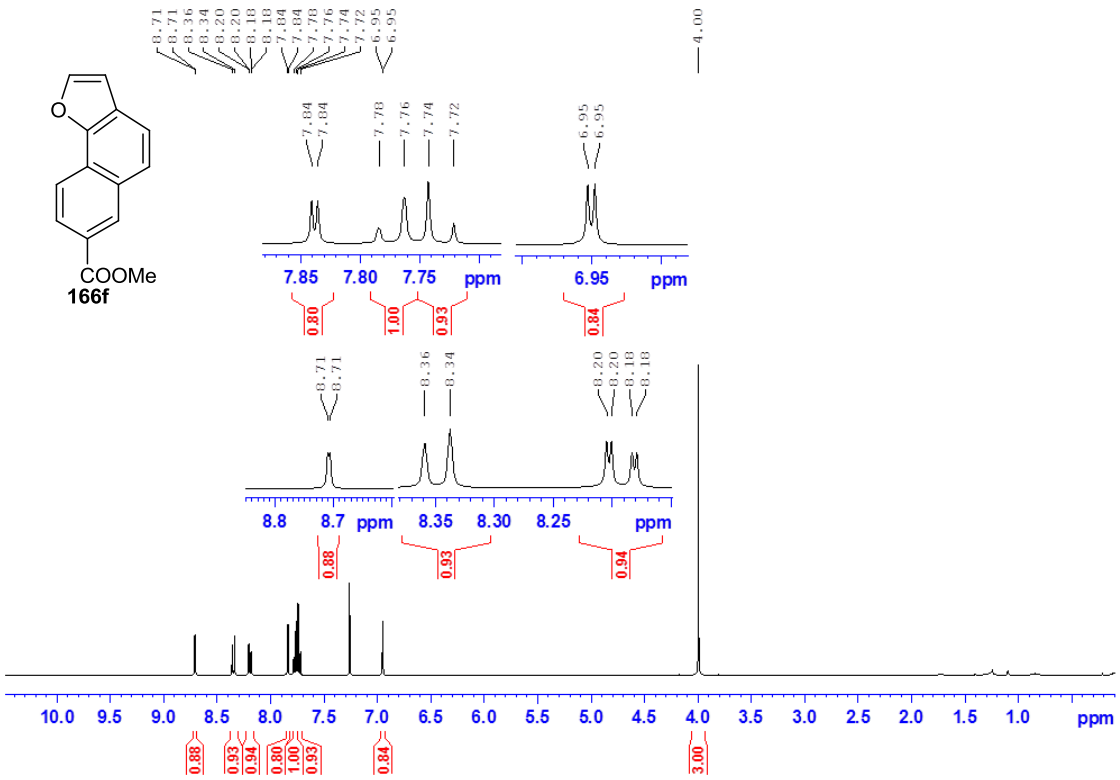
^{1}H-NMR (300 MHz, $CDCl_3$): Compound **166b**



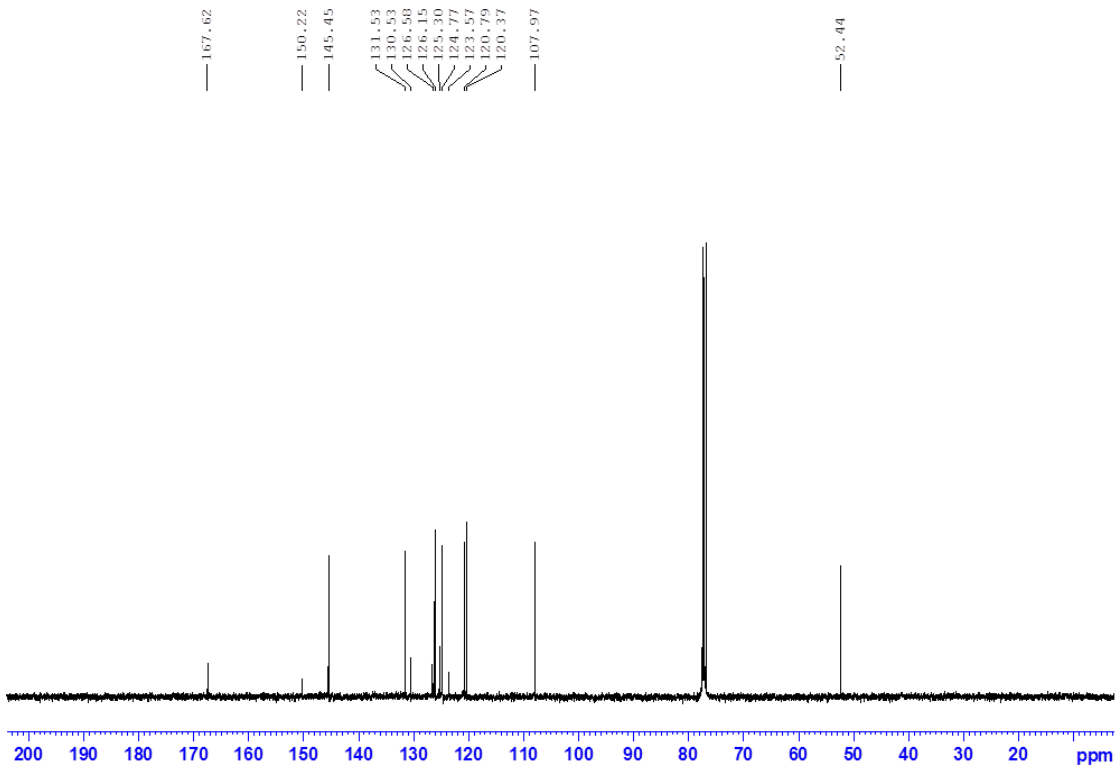
^{13}C{^{1}H}-NMR (75MHz, $CDCl_3$): Compound **166b**



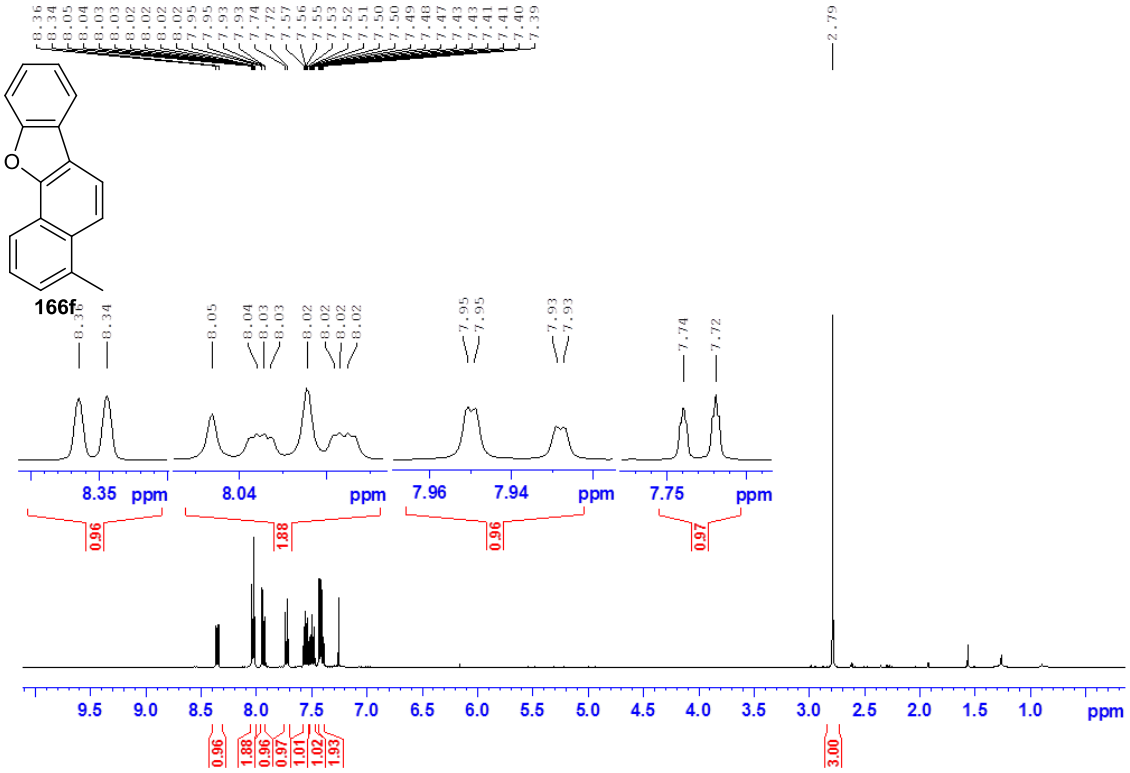
^{1}H-NMR (400 MHz, $CDCl_3$): Compound **166c**



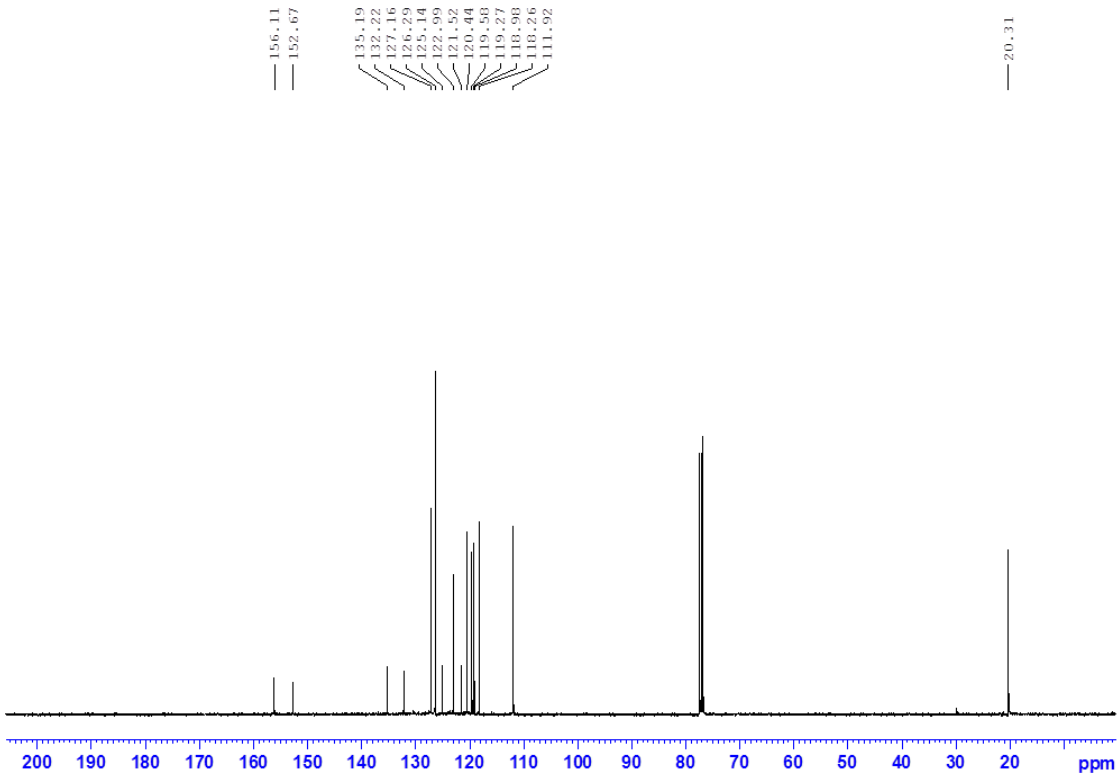
^{13}C{^{1}H}-NMR (101MHz, $CDCl_3$): Compound **166c**



^{1}H-NMR (400 MHz, $CDCl_3$): Compound **166f**



^{13}C{^{1}H}-NMR (101MHz, $CDCl_3$): Compound **166f**



8 References and endnotes

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