VILNIAUS UNIVERSITETAS
CHEMIJOS IR GEOMOKSLŲ FAKULTETAS
CHEMIJOS INSTITUTAS
ORGANINĖS CHEMIJOS KATEDRA

Tomas Paškevičius
Chemija
Magistro baigiamasis darbas

NAUJŲ FOSFININIŲ LIGANDŲ Pd(0)/Pd(II) KATALIZUOJAMAM (HETERO)AROMATINIŲ JUNGINIŲ FLUORINIMUI KŪRIMAS

Darbo vadovas
Vrs. m.d. dr. Linas Labanauskas

Vilnius 2023

VILNIUS UNIVERSITY
FACULTY OF CHEMISTRY AND GEOSCIENCES
INSTITUTE OF CHEMISTRY
DEPARTMENT OF ORGANIC CHEMISTRY

Tomas Paškevičius

Chemistry

Master thesis

DEVELOPMENT OF NEW PHOSPHINE LIGANDS FOR Pd(0)/Pd(II) CATALYZED (HETERO)ARYL FLUORINATIONS

Scientific adviser
Chief researcher dr. Linas Labanauskas

Vilnius 2023

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

2-MeTHF – 2-methyltetrahydrofuran
AcO – acetoxy
Ad – 1-adamantyl
BINAP – (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl)
Boc- – *tert*-butyloxycarbonyl
ca. – circa
CAM – cerium ammonium molybdate
CgPH – 1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphaadamantane (CagePhos)
Cy – cyclohexyl
CNC – (*N*,*N*-dimethylimidazolidino)-tetramethylguanidinium chloride
COD – 1,5-cyclooctadiene
DBU – 1,8-diazabicyclo[5.4.0]undec-7-ene
DCM – dichloromethane
DFT – density functional theory
DiPPF – 1,1-bis(diisopropylphosphino)-ferrocene
DME – 1,2-dimethoxyethane
DMEDA – 1,2-dimethylethylenediamine
DMF – *N*,*N*-dimethylformamide
DMSO – dimethylsulphoxide
dppe – 1,2-bis(diphenylphosphino)ethane
DPPF – 1,1′-bis(diphenylphosphino)-ferrocene
dppp – 1,2-bis(diphenylphosphino)propane
EtOAc – ethyl acetate
FG – functional group
GC-MS – gas chromatography – mass spectrometry
h – hour
Hal – halogen
Halex – halogen exchange
Het – hetero
i-Bu – *iso*-butyl
i-Pr – *iso*-propyl
L – ligand
MTBE – methyl *tert*-butyl ether
n-Bu – *neo*-butyl
NFOBS – *N*-fluoro-*ortho*-benzenedisulfonimide
NFSI – *N*-fluorobenzenesulfonimide
NHC – *N*-heterocyclic carbenes
NIS – *N*-iodosuccinimide
NMR – nuclear magnetic resonance
o-Tol – *ortho*-tolyl
PET – positron emission tomography
PhH – benzene
PhMe – toluene
p-Ns – *para*-nitrobenzenesulfonyl
PTC – phase transfer catalyst
rt – room temperature
SCF – self consistent field
SET – single electron transfer
TBAF_{anh} – tetra-*n*-butylammonium fluoride anhydrous
TBDMS – *tert*-butyldimethylsilyl
t-Bu – *tert*-butyl
TfO – trifluoromethansulfonyl
THF – tetrahydrofuran
TMS – trimethylsilyl
UV – ultraviolet

INTRODUCTION

Organofluorine chemistry has attracted the attention of the scientific community since the first reported synthesis of fluoromethane in 1835.[1] During the last few decades fluorinated organic compounds have been widely applied in pharmaceutical sciences.[2] Introduction of fluorine atom(s) in the biologically active compounds often improves their properties and applicability. Currently approximately 20% of all commercial pharmaceuticals are based on the structures containing fluorine atom(s). Pharmaceuticals labeled with radioactive fluorine isotope F^{18} also play an important role in medicine for non-invasive imaging.[3]

Multiple approaches have been established for the fluorination, however to this day industrial procedures often use dangerous, corrosive, and toxic reagents. Transition metal catalyzed reactions can be an efficient alternative. Palladium catalysis has been well established for C-C, C-N, C-O, C-S, C-P cross-coupling reactions, while C-F – remains elusive. For fluorination reactions of arenes there are two predominant research areas: electrophilic Pd(IV) and nucleophilic Pd(II) catalysis. Fluorine sources differentiate both methods and their compatibility with substrate's functional groups.

This work will focus on design and synthesis of phosphine ligands suitable for Pd(II) catalyzed fluorination. First, a computational investigation will be conducted to develop new potential catalyst structures in order to explore the influence of phosphine ligand's sterics and electronics on problematic reductive elimination step. Second, a general approach for ligand terphenyl backbone synthesis and modification will be investigated. Third, synthesis of phosphines and a new strategy for coupling excessively bulky arenes with di(1-adamantyl) and cyclic phosphines will be studied. Last, new ligands will be screened to assess their activity for fluorination of (hetero)arenes.

1. LITERATURE REVIEW

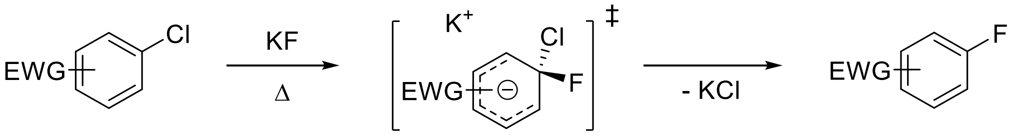
In this part of the thesis, various aspects of classical and modern methods for C-F bond formation will be discussed. It will include Halex reaction, Balz-Schiemann reaction, electrophilic fluorine sources, electrophilic Pd(IV) mediated fluorination and nucleophilic Pd(II) catalyzed fluorinations. Furthermore, various synthetic methods for phosphine ligands will be discussed. The objective of this section is to familiarize the reader with historical achievements related to fluorination reaction of aryl and heteroaryl systems, palladium catalysis and organophosphorus chemistry.

1.1 Classical C-F bond forming methods

Dumas and Peligot published the first synthesis of fluoromethane from dimethyl sulphate and potassium fluoride in 1835.[1] It was the first reported fluorinated compound and set the foundations for the organofluorine chemistry. Next, in 1892, Swarts reported a halogen exchange process using antimony (III) fluoride.[4] Later, this method progressed to a now well-known Halex process. This branch of organic chemistry underwent a renaissance in 1950s and 1960s.[5] Since then, new methodologies have been developed and will be discussed in the following subsections.

1.1.1 Halex process

Halex (halogen exchange) process is a versatile industrial method for introduction of fluorine atoms into arenes containing electron withdrawing groups and is classified as an aromatic nucleophilic substitution reaction (Scheme 1). This reaction proceeds through the formation of Meisenheimer complex in which heavier halogen atoms act as leaving groups. Rate of this reaction is determined by the nucleophile addition kinetics, in this case fluoride, to form the Meisenheimer complex. Because of the stronger electronegativity of chlorine atom, aryl chlorides are more suitable substrates than the corresponding aryl bromides and iodides.

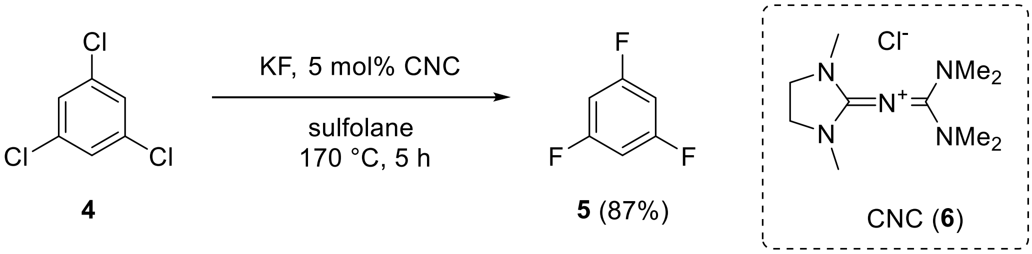


1 Meisenheimer complex 2 3

Scheme 1. Halex reaction mechanism

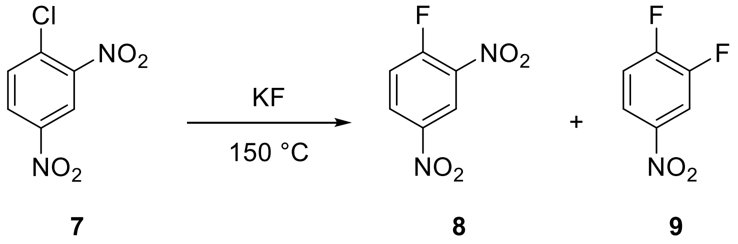
In classical Halex reactions high temperatures together with high boiling point solvents, such as sulfolane, aid in overcoming the energetic barrier of formation of the Meisenheimer complex **2**. Some studies and rational reasoning suggest that the sluggish nature of this reaction may be subdued by addition of “solvating agents” to aid in solvating the fluoride-anion and increasing its nucleophilicity. Phase transfer catalysts (PTC’s) are good candidates for this role due to their ability to undergo double displacement reactions with the fluoride nucleophile source. Additionally, PTC’s serve as a source of organic soluble counterions for the fluoride anion. Substrate’s electronic properties also play a major role in the rate determining step. More electron-withdrawing substrates tend to facilitate the formation of Meisenheimer complex and increase its stability.[6]

In 2004 Pleschke *et. al.* have developed a more specific catalyst for fluorodechlorination reaction, (*N*,*N*-dimethylimidazolidino)-tetramethylguanidinium chloride (CNC, **6**), and investigated its application for the large scale production of fluorinated organics.[7] For example, they were able to scale-up the Halex reaction to 3 mol scale with 5 mol% catalyst loading and produce trifluorobenzene in excellent 87% yield (Scheme 2).



Scheme 2. Large scale (3 mol) application of Halex process

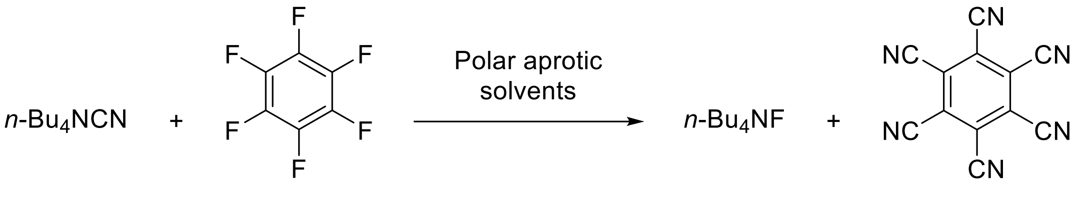
Another variation of Halex reaction is Ar-NO_2 exchange to Ar-F (fluorodenitration). It was first reported by Finger and Kruse in 1956.[8] They attempted to prepare 2,4-dinitrofluorobenzene (**8**) *via* the fluorodechlorination route at 150 °C using potassium fluoride as a nucleophile. However, their initial attempt was unsuccessful, and the formation of brown fumes was observed, presumably liberated nitrogen dioxide. Analysis of the resulting reaction mixture revealed the presence of 1,2-difluoro-4-nitrobenzene (**9**), indicating that displacement of chloro atom and one nitro group has occurred (Scheme 3).



Scheme 3. First observed fluorodenitration by Finger and Kruse[8]

Fluorodenitration could serve as a useful alternative route to prepare *meta*-fluorinated aromatics. However, it is restricted by the additional requirements limiting the substrate scope. Activation by other functional groups through mesomeric and inductive effects is necessary for the substitution to occur. Bulky *ortho*-groups are thought to assist fluorodenitration through electronic or steric factors.[9]

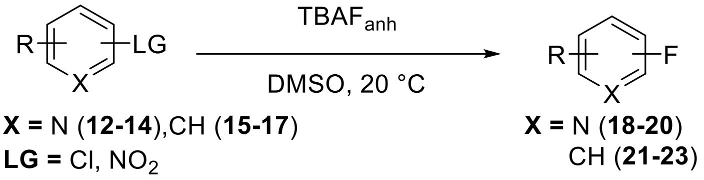
During the last few decades milder reaction conditions for the Halex process have been reported by DiMagno.[10] In 2005, a new preparative method for a soluble and highly nucleophilic fluoride-ion source was reported. The reaction between hexafluorobenzene (**10**) and tetrabutylammonium cyanide leads to the formation of anhydrous tetrabutylammonium fluoride (TBAF$_{anh}$) (Scheme 4).

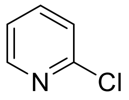
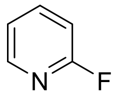
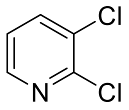
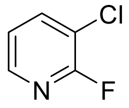
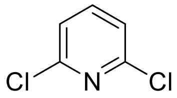
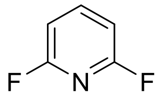
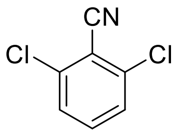
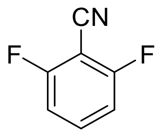
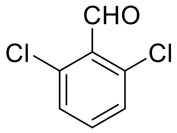
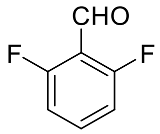
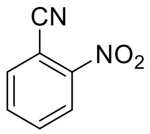
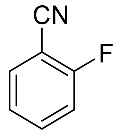


Scheme 4. Preparation of anhydrous tetrabutylammonium fluoride (TBAF$_{anh}$)

Following this discovery, DiMagno has investigated the use of TBAF$_{anh}$ as a fluorinating agent for primary alkyl halides and tosylates.[10] Surprisingly, rapid fluorination was observed even at low temperatures (-35 °C, 5 min, THF). These results prompted the investigation for the potential TBAF$_{anh}$ application for aromatic fluorodechlorination and fluorodenitration reactions. In 2006, Sun and DiMagno reported extensive work on fluorinations of various chloropyridines and activated chlorobenzenes (Table 1).[11] They were able to synthesize fluorinated aromatics at room temperature in excellent 80-95% yields by performing the Halex reaction in anhydrous aprotic solvents with TBAF$_{anh}$.

Table 1. Fluorination examples by DiMagno

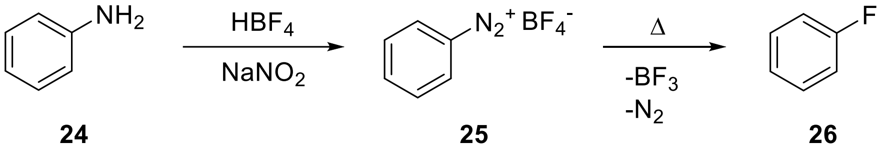


Entry	Substrate	Time	Product	Conversion, %
1	 **12**	14 days	 **18**	80
2	 **13**	1 h	 **19**	> 95
3	 **14**	1.5 h	 **20**	> 95
4	 **15**	1 h	 **21**	> 90
5	 **16**	1.5 h	 **22**	> 90
6	 **17**	10 min	 **23**	> 90

Despite good results in the mentioned cases, the Halex process has its drawbacks. One of the main limitations is the requirement of specific conditions and/or activated substrates. However, the Halex process has the major advantages with broad range of readily commercially available or easily accessible starting material and the elimination of the use of hydrogen fluoride. For these reasons, Halex is the only real rival to the diazonium-based industrial processes for the selective fluorination of aromatic compounds.

1.1.2 Balz-Schiemann reaction

In 1927, Balz and Schiemann introduced a method for selective fluorination of aromatic compounds.[12] Their method involves comparably mild reaction conditions in comparison to the previously described Halex process. This method consists of a formation of aryldiazonium tetrafluoroborate salt **25**, followed by its thermal (pyrolysis) or photochemical decomposition (Scheme 5).[13] Subsequently, years later, the industry adapted and improved this method to be more scalable. The industrial variation to the Balz-Schiemann method consisted of substituting the tetrafluoroborate anion with simple fluoride ion. Although this industrial approach involves the use of anhydrous, liquefied hydrogen fluoride, it still remains as the main cost-effective method for the large-scale production of selectively fluorinated aromatics today.



Scheme 5. Balz-Schiemann reaction

Successful fluorination by the Balz-Schiemann method greatly depends upon the isolation of the intermediate diazonium salt. The less soluble diazonium salts allow the easy removal of the impurities by filtration and trituration. This limits the possible side reactions in the following pyrolysis step and thus increases the product yields. The solubility of the diazonium tetrafluoroborate salt is also highly dependent on the substitution of arylamines. For example, diazonium fluoroborate salts formed from aminophenols are far more water soluble than simple anilines and, therefore, its isolation and purification are problematic.[14]

In 1961, Rigamonti *et. al.* investigated the possibility of replacing the tetrafluoroboric acid with hexafluorophosphoric acid.[15] They discovered that not only aryldiazonium hexafluorophosphates are far less water soluble than the tetrafluoroborate counterpart, but also pyrolysis of these diazonium salts leads to increased aryl fluoride yields. Authors attributed these results to the fact that phosphorous pentafluoride, produced during reaction, is a much weaker Lewis acid than boron trifluoride thus limits possible side reactions.

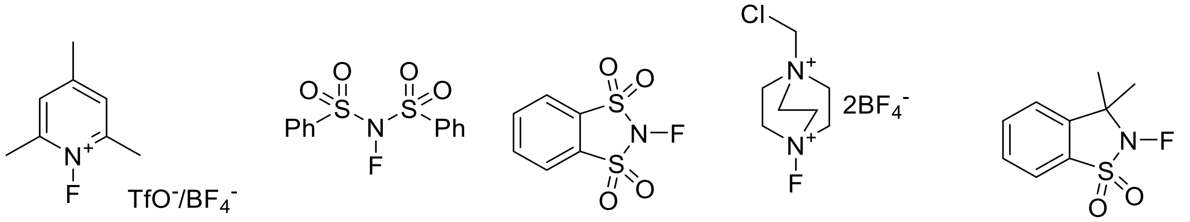
Suschitzky decided to expand on Rigamonti's ideas and in 1968 published his work including other possible counterions, hexafluoro- arsenates and antimonates, along with the previously investigated hexafluorophosphates.[16] Researchers conducted experiments comparing these counterions with tetrafluoroborates. They found that in general, diazonium hexafluoroantimonates are as practical to prepare as hexafluorophosphates. Also, hexafluoroantimonates were less soluble than their phosphorus analogs and even more stable to light and air exposure. Interestingly, according to their results, electron-withdrawing substituents did not reduce overall product yields. Consequently, Suschitzky *et. al.* were able to prepare fluorobenzoic acids and *o*-fluoronitrobenzene in generous 40% yield, compared to less than 10% with tetrafluoroborates.

1.2 Electrophilic fluorination

Early electrophilic fluorinating agents were based on those bearing O-F bond, such as trifluoromethyl hypofluorite (CF_3OF), trifluoroacetyl hypofluorite (CF_3COOF) or elemental fluorine (F_2).[17,18] However, these fluorinating agents are unselective, notoriously difficult to prepare and work with. For example, elemental fluorine requires special fluorine passivated nickel or copper equipment, is highly toxic and reactive. Despite these drawbacks, F_2 has been successfully used for the fluorination of some substrates.[19] Electrophilic fluorinating agents based on O-F or Xe-F bonds in general are more selective than elemental fluorine, but they have their disadvantages as well. For example, perchloryl fluoride (ClO_3F) is a powerful oxidizing agent and can cause unwanted runaway oxidation reactions or even explosions when mixed with organic substances. On the other hand, xenon difluoride (XeF_2) is stable fluoride, but it is made from the expensive xenon gas and for this reason it is a fairly impractical fluorinating agent for preparative chemistry.[20] Recently, the introduction of fluorinating agents based on N-F bond have played a major role in making this chemistry more widespread.[21]

1.2.1 N-F fluorinating agents

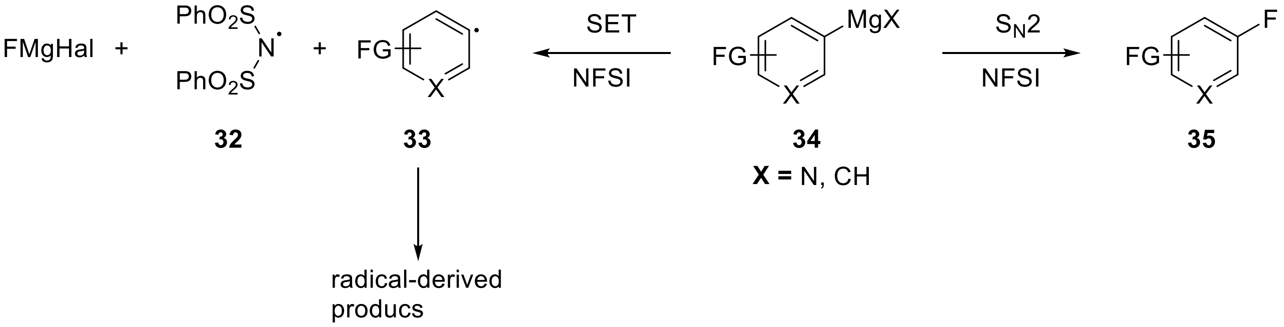
N-F reagents show a range of fluorinating abilities towards nucleophiles, most commonly, activated aromatic compounds and organomagnesium derivatives (Figure 1). N-F fluorine sources may not be as active as previously mentioned XeF_2 or F_2, but their inherent stability and ease of use greatly overcomes this minor disadvantage. These reagents provide organic chemists with a valuable and safer way to selectively fluorinate organic compounds.



Me$_3$NFPy (**27**) NFSI (**28**) NFOBS (**29**) Selectfluor (**30**) *N*-Fluorosultam (**31**)

Figure 1. Common N-F fluorination reagents

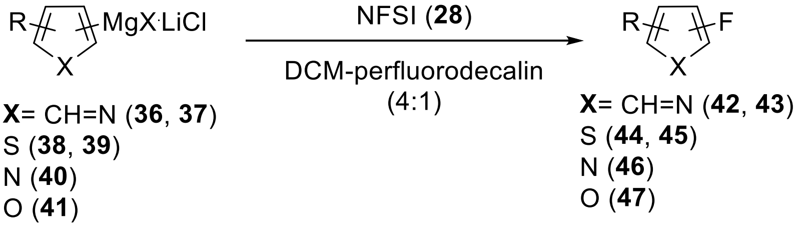
Knochel *et. al.* in 2010 has developed a general fluorination approach using arylmagnesium halogenides along with lithium chloride and *N*-fluorobenzenesulfonimide (NFSI, **28**) as a fluorine source.[21] Their investigation led to the discovery that fluorinated solvents have a major impact on the outcome of the reaction. For instance, reactions performed solely in THF led to very low yields, rarely exceeding 20%. On the other hand, reactions performed in DCM:perfluorodecalin (4:1) led to a significant yield improvement. They reasoned that this reaction proceeds through two competing pathways, i.e., S_N2 type substitution and aryl radical pathway (single electron transfer, SET, Scheme 6). This explanation is concordant with their findings that fluorinated cosolvents help to increase yields by acting as fluorine atom donors.

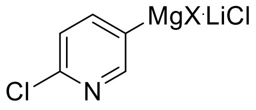
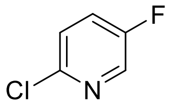


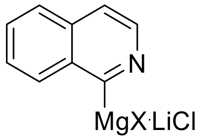
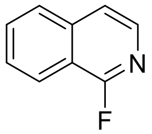
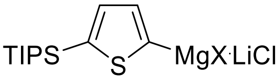
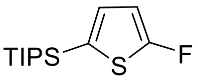
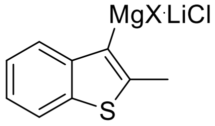
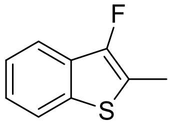
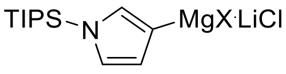
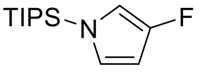
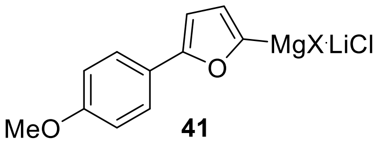
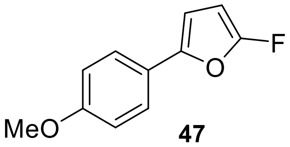
Scheme 6. Competing reaction pathways proposed by Knochel

This method is impressively versatile for fluorination of a variety of arenes and heteroarenes, including pyridines, pyrroles, thiophenes and furans (Table 2). For instance, arylmagnesium halides can be readily formed from electron rich heteroarenes by either direct magnesium insertion, or by halogen-RMgX exchange, and followed by fluorination with NFSI (**28**) *via* Knochel's protocol in satisfactory yields.

Table 2. Heteroaryl fluorination using Knochel's protocol



Entry	Substrate	Product	Yield, %
1	 **36**	 **42**	75

2	 **37**	 **43**	63
3	 **38**	 **44**	56
4	 **39**	 **45**	60
5	 **40**	 **46**	43
6	 **41**	 **47**	57

1.3 Palladium catalyzed fluorination

Palladium metal is probably the most versatile and exploited metal in catalysis due to its ability to promote multitude of organic reactions.[22] Lately, palladium prices have been soaring, forcing researchers to once again explore limits of these reactions and expand on their efficiency. Palladium catalysis has been well developed for C-C, C-N, C-O, C-S, C-P cross-coupling reactions, but C-F – methodology is lacking. For fluorination reactions of arenes there are two predominant research areas: Pd(IV) catalyzed electrophilic and Pd(II) nucleophilic approaches.[23] Fluorine sources differentiate both methods and their compatibility with substrate's functional groups. Electrophilic Pd(IV) is more compatible with hydrogen donors as opposed to Pd(II) nucleophilic approach. The details for both approaches will be discussed in the following subsections as well as criteria necessary for designing effective (hetero)arene fluorination catalysts (catalysis by design, rather than catalysis by scouting).

1.3.1 Palladium(IV) catalyzed electrophilic fluorination

Although there are several fluorination methods developed, transition metal facilitated fluorinations by either catalysis, or mediation remained elusive until quite recently. Sanford *et. al.* developed the first Pd(IV) mediated fluorination method.[24] They utilized N-F reagent's oxidative abilities to oxidatively fluorinate $[L_n]Pd^{II}$-R complexes which in-turn undergo C-F reductive elimination from Pd(IV) (Figure 2). Even though this method is an excellent example of direct C-H functionalization, it requires ortho directing groups to be present in order to achieve efficient and regioselective fluorination. Consequently, this greatly limits the substrate scope to only those bearing benzylic nitrogen or oxygen moieties.

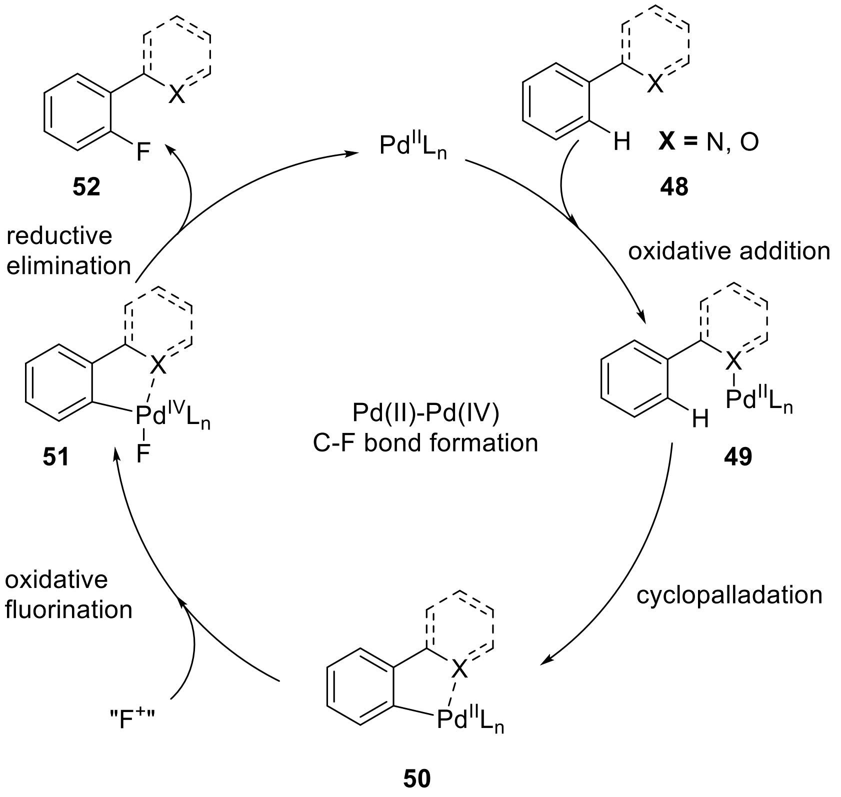
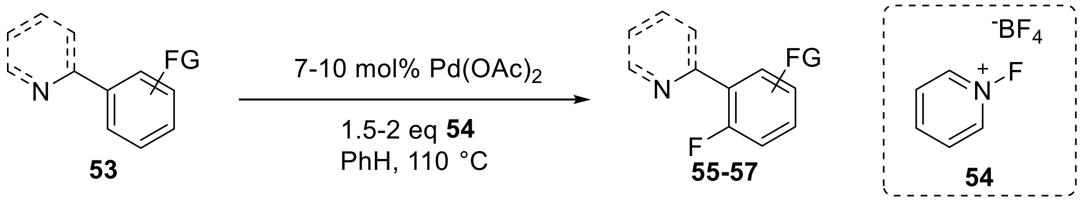


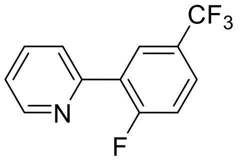
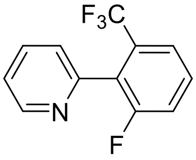
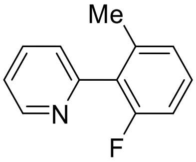
Figure 2. Pd(IV) catalytic cycle

In the initial screening for N-F fluorinating agents Sanford *et. al.* found that *N*-fluoropyridinium tetrafluoroborate (**54**, Table 3) was the most effective fluorine sources in their study.[24] This may be explained by increased fluorine electrophilicity and thermal stability of the reagent. Reaction rate was greatly accelerated by substituting standard thermal conditions with microwave irradiation. Despite the relatively harsh reaction conditions, this was the first breakthrough in Pd(IV) catalyzed fluorination methodology.

Table 3. Direct C-H fluorination examples

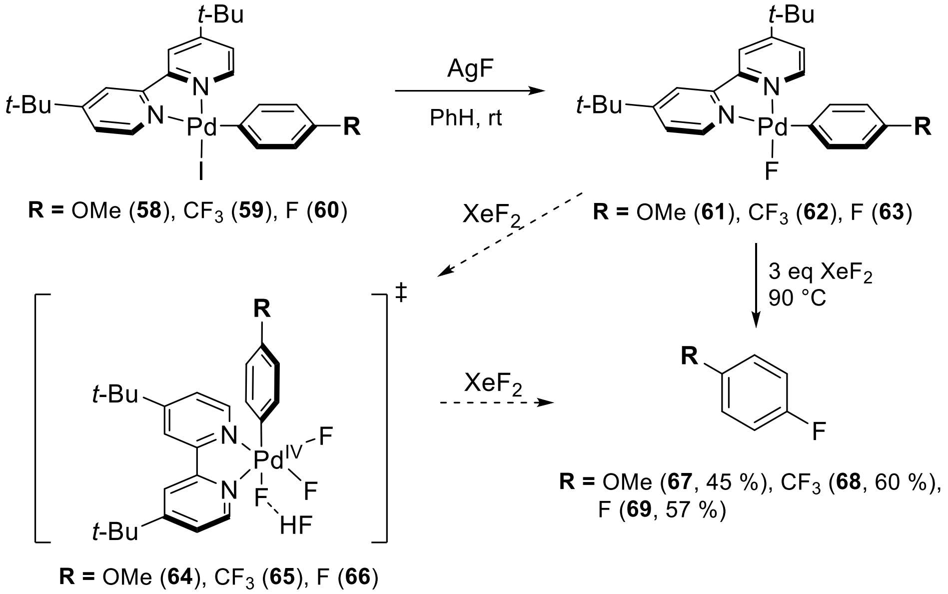


Entry	Product	Yield

1	 **55**	75%
2	 **56**	59%
3	 **57**	52%

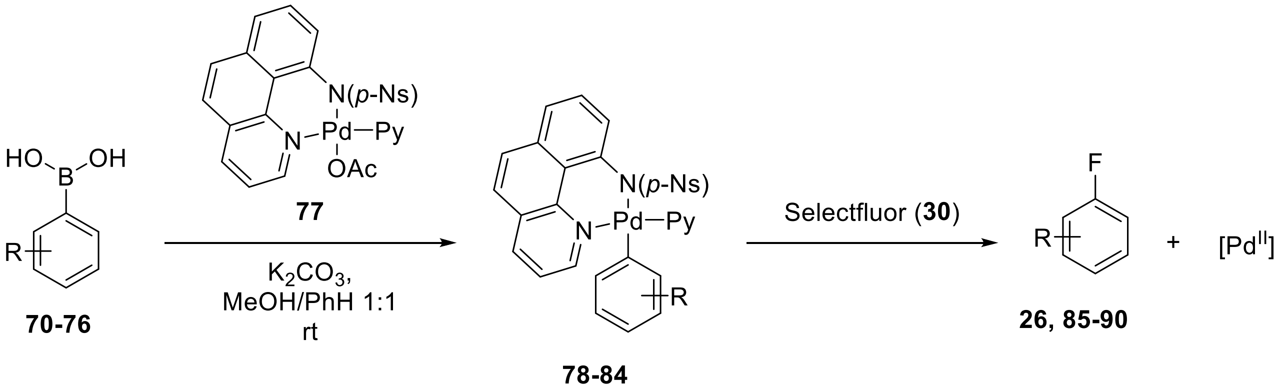
Sanford *et. al.* discovered that under these reaction conditions substrates underwent direct C-H activation furnishing fluorides in decent yields (Table 3).[24] The optimized reaction conditions showed good results for direct aromatic C-H fluorination of 2-phenylpyridine derivatives. Furthermore, it was noticed that under these reaction conditions, it was possible to achieve direct benzylic C-H activation furnishing benzylic fluorides. For example, 8-methylquinoline derivatives were successfully fluorinated.[24]

Sanford and Ball has conducted a study on the formation of C-F bonds when arylpalladium(II) complexes were treated with oxidizing fluorine sources (XeF_2, Scheme 7).[25] They hypothesize that this transformation occurs *via* Pd(IV) species formed by Pd oxidation with XeF_2. To gain mechanistic insight to this reaction, they designed a stable $Pd^{II}Ar(F)$ complexes **61-63** for NMR and crystallographic analyses. They based these complexes on rigid bidentate sp^2 *N*-donor ligands of 2,2-bipyridine backbone. Firstly, they treated the oxidative addition Pd(II) complexes **58-60** with silver fluoride (AgF) to substitute iodine with fluorine. Later, they treated these complexes with oxidizing fluorine source XeF_2, giving rise to Pd(IV) species **64-66**. Interestingly, these Pd(IV) complexes could be isolated in modest yields, which aided in their analysis. The formation of arylfluorides **67-69** was observed only when excess fluorinating agent was added (Scheme 7).



Scheme 7. Pd(IV) mediated fluorination

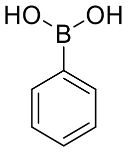
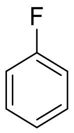
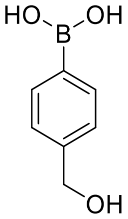
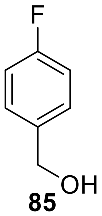
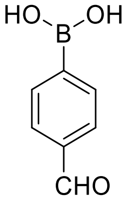
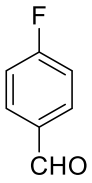
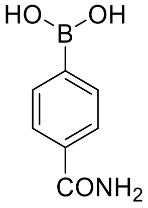
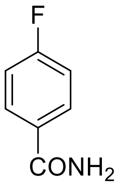
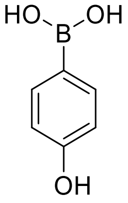
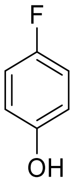
Radioactive fluorine (F^{18}) labeled pharmaceuticals have received ever-growing interest in medicinal applications for non-invasive imaging, usually as tracers for positron emission tomography (PET).[26] Most commonly, radiolabeled fluorine is introduced *via* the Halex process or other reactions that require harsh conditions. The biggest issue with the synthesis of F^{18} labeled pharmaceuticals is that fluorine has to be introduced in late-stage due to its rather short half-life (109 min). In 2008, Ritter *et. al.* has reported a new method for preparation of arylfluorides **26**, **85-90** from arylboronic acids **70-76** (Scheme 8).[27] This new method uses stoichiometric amounts of palladium, formed from the arylboronic acids, that in turn undergo the C-F bond formation. Although stoichiometric palladium quantities are a major disadvantage for such type of fluorinations, this method is versatile and mild enough to be used as a late-stage functionalization tool for introduction of radiolabeled fluorine to the molecules of interest.

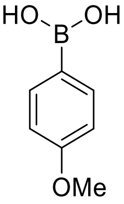
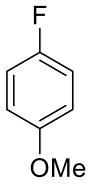
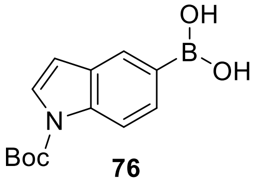
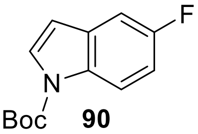


Scheme 8. Fluorination of arylboronic acids

During their research, the palladium complex **77** was designed based on nitrogen donor atom containing bidentate ligands that can resist oxidation by electrophilic fluorine sources.[27] It is noteworthy to mention, that arylpalladium complexes **78-84** derived from benzoquinoline palladacycle **77** are moisture and air-stable and are easily purified by column chromatography. Furthermore, they are compatible with a variety of functional groups that are too sensitive to most other fluorination conditions (Scheme 8, Table 4).

Table 4. Examples of fluorination of arylboronic acids

Entry	Arylboronic acid	Pd complex (yield, %)	Arylfluoride	Yield, %
1	 **70**	**78** (76)	 **26**	81
2	 **71**	**79** (80)	 **85**	70
3	 **72**	**80** (71)	 **86**	61
4	 **73**	**81** (73)	 **87**	74
5	 **74**	**82** (70)	 **88**	31

6	 **75**	**83** (79)	 **89**	46
7	 **76**	**84** (76)	 **90**	60

1.3.2 Pd (II) fluorinations

In 1997, Grushin's group was first to synthesize, and characterize Pd(II) fluoride complexes.[28] They conducted extensive studies to determine whether C-F reductive elimination was possible. Reductive elimination was envisioned as theoretically possible, but practically a very challenging step. It was postulated that since the oxidative addition to Pd(0) was definitive and proven by multiple studies, either the transmetalation or reductive elimination step must be inhibiting the successful transformation (Figure 3).[29] In 2010, results from thermolysis study of Wilkinson's type fluoride complexes were published.[30] They revealed that sterically undemanding phosphine ligands are unsuitable for palladium catalyzed fluorinations, owing to their inherent electronic properties and a wide range of possible rearrangement reactions.[30] Simultaneously, Buchwald's group demonstrated the feasibility of C-F reductive elimination from Pd(II) and subsequently developed the first example of catalytic fluorination of aryl halides and triflates under the more commonly encountered Pd(0)/Pd(II) catalytic cycle (*vide infra*, 1.3.2.2).[31]

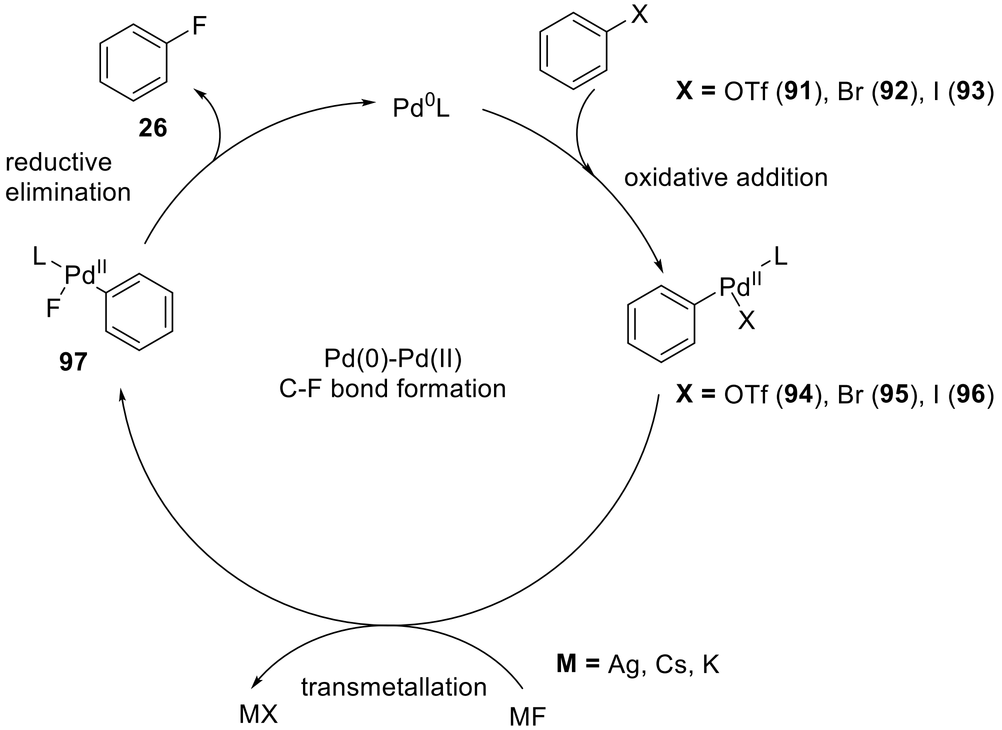
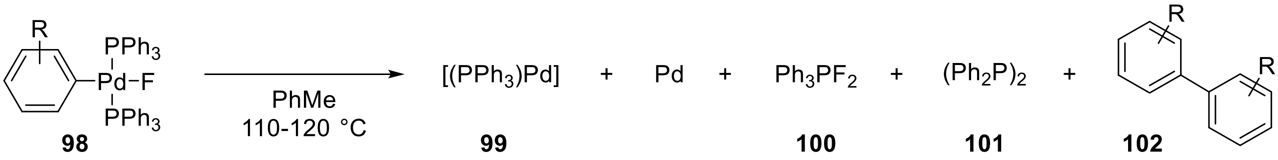


Figure 3. Pd(0)/Pd(II) catalytic cycle

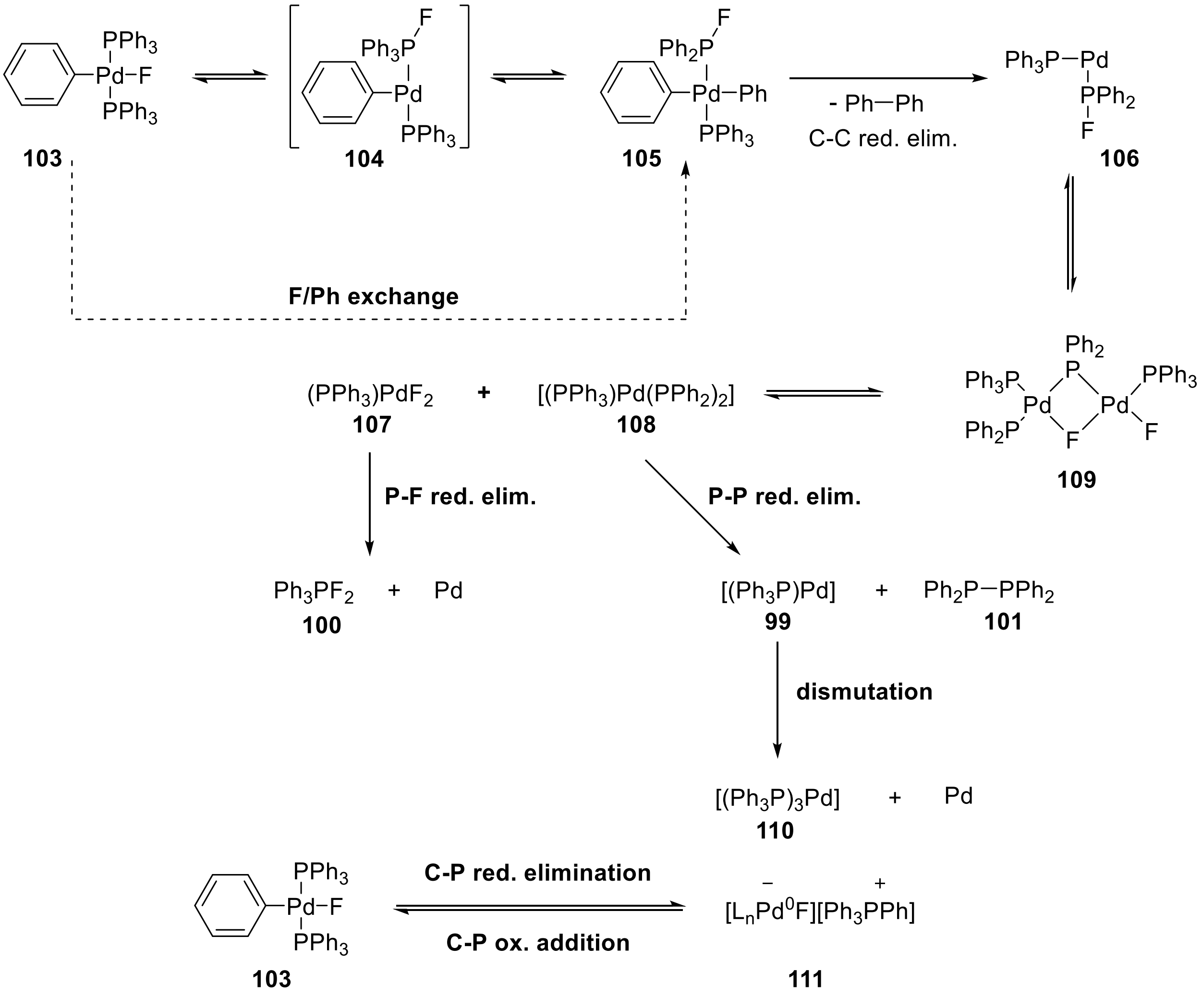
1.3.2.1 Bidentate ligands

Reductive elimination rates are usually represented in this order C-P > C-S > C-N > C-O and suggests that heteroatom electronic properties have a great impact on the reaction rate.[32] In the arylpalladium fluoride complex thermolysis study Grushin has observed a competing reaction pathway, where P-F reductive elimination was more favorable than C-F reductive elimination (Scheme 9).[30] Until then this type of reductive elimination was not attributable to Pd(II) species and has only been observed in Rh(I) organometallic chemistry. Interestingly, Grushin's extensive study has proved that P-F reductive elimination was, in fact, attributable to all platinum group metals. Elusive then, these findings were very important in understanding the reasons for P-F bond formation and the means of its control. Thermolysis of Pd fluoro-analogue of Wilkinson's catalyst **98** revealed that only P-F reductive elimination route took place, while no C-F reductive elimination products were observed. Yandulov was first to observe C-F reductive elimination in his study on (4-NO_2-Ph)-Pd-F complex thermolysis, evidentially ca. 10% of (4-NO_2-Ph)-F was formed.[33]



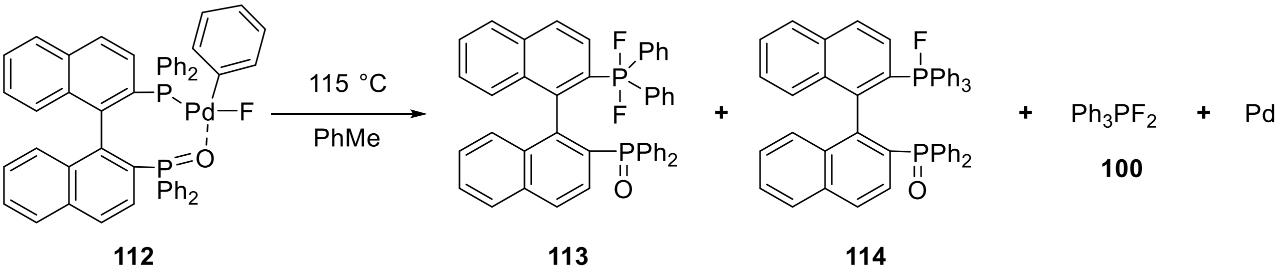
Scheme 9. Thermolysis of Wilkinson-type fluoride complexes

Analysis of various thermolysis results has led to another discovery concerning scrambling of aryl groups in the complex itself. Firstly, it was noticed that in some cases asymmetric biaryls were produced during the thermolysis reaction.[30] This observation has inspired researchers to conduct a mechanistic study on the P-P, P-F, C-C bond forming processes (Scheme 10). It was found that F/Ph exchange happens rather early in the mechanism, followed by C-C reductive elimination forming biphenyl biproduct. This is supported by earlier studies of similar Rh complexes demonstrating that Ph transfer (Ph/F exchange) in unimolecular.[34,35] Following the Ph/F exchange multiple complex rearrangements take place enabling P-F and P-P reductive eliminations. Interestingly, C-P reductive elimination appears to be reversible. This, in part, can be explained by the zwitterionic nature of $[L_nPd^0F]^-[Ph_3PPh]^+$ (**111**) and is accountable for the observed aryl group scrambling. Moreover, Grushin's group showed that additional phosphines do not have a significant impact on the outcome of the reaction. On the other hand, excess phosphine in the reaction mixture inhibits the competing Ar-P exchange reaction in Pd case.[36]



Scheme 10. Mechanistic investigation of Wilkinson-type fluoride complex **103** thermolysis

The palladium complex in which F and Ph ligands are *cis* to each other, should be a theoretically fitting candidate for C-F reductive elimination. Pd complex **112** was specially designed based on BINAP(O) ligand to see if reductive elimination would be promoted in constrained setting (Scheme 11).[37] However, thermolysis of this complex did not lead to formation of C-F bonds. Instead, a change of phosphorus oxidation state was observed along with P-F reductive elimination. These findings are consistent with Macgregor's in-depth computational study concluding that redox reaction occurs, *viz.* P(III)/Pd(II)→P(V)/Pd(0).[35]



Scheme 11. Thermolysis of [BINAP(O)Pd(Ph)F] complex

It is noteworthy, that P-F bond formation has been observed even with excessively bulky ligands (*t*-Bu$_3$P, *o*-Tol$_3$P, *t*-BuXantPhos).[38] These findings are not that surprising considering the size and electronic properties of the fluorine atom. This brings out a crucial, albeit disappointing, conclusion that vacant coordination site is not necessary at the Pd center, therefore P-F bond formation cannot be controlled by additional phosphine ligands in the system.[30]

1.3.2.2 Three-coordinate T shaped complexes

Reductive elimination of different alkyl groups, forming C-C bonds are quite common, in fact, many d^8 transition metal complexes (Ni(II)[39], Pd(II)[40], Pt(II)[41] and Au(III)[42]) have been studied for this exact reason. Reductive elimination seems to be symmetry driven reaction – most effective geometry is when phosphine ligand and alkyl groups are *trans* to each other. For Ni(II), preferred geometry is when Ni(II) is four-coordinate, in a sense, ligated by bis-phosphine ligands (BINAP, DPPF, dppe, dppp, etc.). Palladium, on the other hand, prefers three-coordinate state, the so-called T-shape complex geometry (Figure 4). Explanation for this observation ultimately lies within Pd 4d vs. Ni 3d orbital energy differences. This hypothesis was examined in-depth in 2015 Sakaki's computational and theoretical study on transition metal complexes.[43]

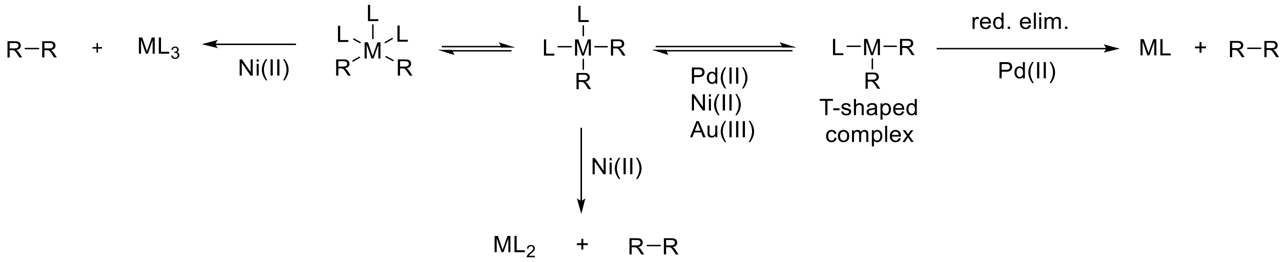


Figure 4. Optimal geometries of d^8 transition metal complexes for reductive elimination

Oxidative addition to Pd(0) species has been well documented as it is the first step in many established C-C bond forming reactions (Suzuki, Heck, Stille, etc.).[29] In general, greater electron-donating properties of phosphine ligands tend to increase the overall electron-richness of metal centers and subsequent oxidative addition rates. On the contrary, reductive C-Hal elimination has been rarely observed and is not well-described. In 2001, Hartwig published a study demonstrating that some [ArPd(Hal)(P*t*-Bu_3)] can produce Ar-Hal bonds in the presence of excess P*t*-Bu_3.[44] This observation ultimately revealed a few core principles on the electronic and steric influences of ligands to the reductive elimination of aryl halides from Pd(II) complexes. Even though electron-accepting properties of phosphine ligands are attributable to faster reductive elimination, for C-Hal bonds, strongly electron-donating ligands are more favorable. This, in-turn, demonstrates that additional steric bulk of the phosphine ligands can alter the thermodynamic properties of the system, making C-Hal reductive elimination more thermodynamically favorable. Moreover, this shows that oxidative addition to more sterically congested Pd(0) species is favorable despite its weak driving force. Finally, this demonstrates the possibility of palladium catalyzed aromatic Finkelstein reaction.

Since P-F reductive elimination is more favored than C-F (*vide supra*, 1.3.2.1) and is the major contributor for many unsuccessful fluorination attempts, the idea to omit phosphine moieties from the ligands gained more practical interest. Replacing phosphines with phosphorus-free *N*-heterocyclic carbene (NHC) or *N*-based ligands, in theory, provides a more favorable system for C-F reductive elimination. Following on this idea Yandulov has conducted an extensive computational study based on NHC ligated arylpalladium fluoride complexes (Figure 5).[33]

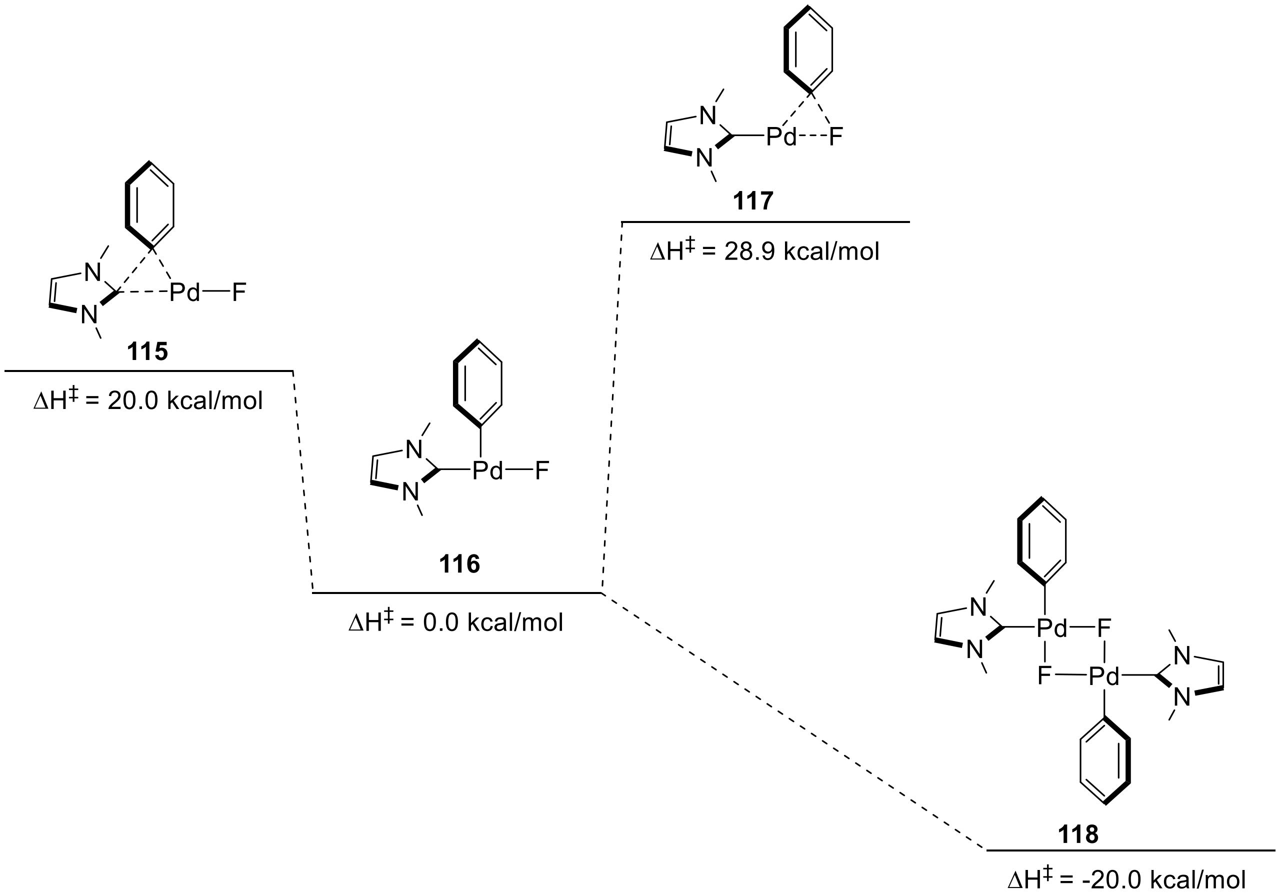
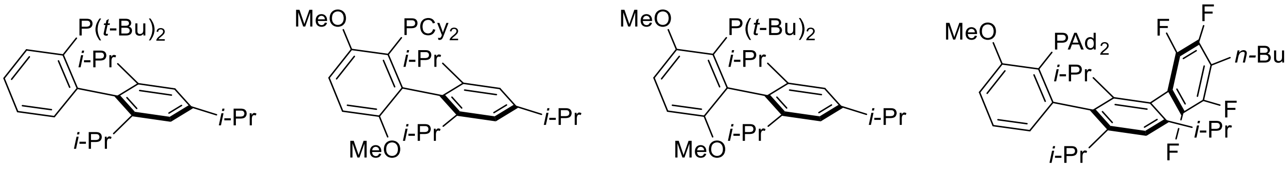


Figure 5. Pd(Ph)F(Me$_2$NHC) computed reactivity profile

Reductive C-F elimination from T-shaped Pd(Ph)F(Me$_2$NHC) (**117**) requires $\Delta H^{\ddagger}$ = 28.9 kcal/mol and $\Delta G^{\ddagger}$ = 29.8 kcal/mol, putting this reaction on the verge of being practical (long reaction times at 100 °C, Figure 5). However, further computational analysis showed that NHC bonding to the σ-aryl is even more thermodynamically favorable ($\Delta H^{\ddagger}$ = 20.0 kcal/mol). Moreover, computationally, the dissociation of dimer **118** to the monomeric three-coordinate Pd complex **116** requires additional energy input, making this reaction experimentally impractical at total $\Delta G^{\ddagger}$ = 43.3 kcal/mol.[33]

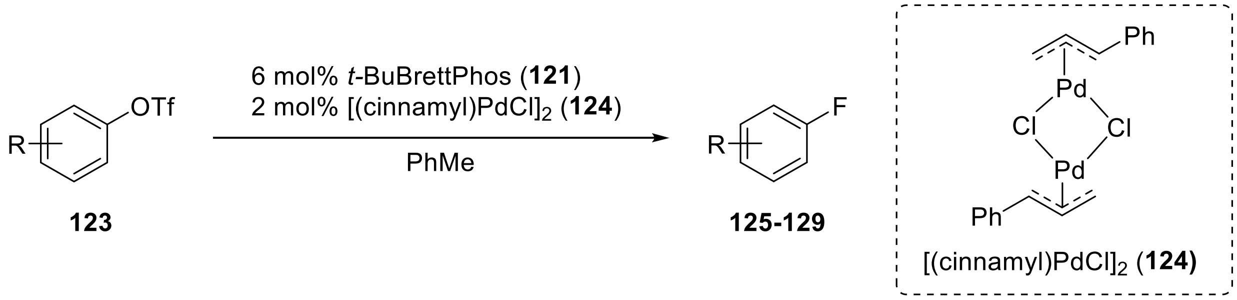
In 2009, Buchwald *et. al.* was first to demonstrate the feasibility of C-F reductive elimination from three-coordinate LPdAr(F) complexes and that this reaction can be conducted catalytically.[31] However, at the time, this reaction was limited to only electron-deficient aryl triflates (Table 5). This work was based on *t*-BuXPhos (**119**) and *t*-BuBrettPhos (**121**) ligands, previously developed for Buchwald-Hartwig C-N coupling reactions (Figure 6).[45] Even less sterically demanding BrettPhos (**120**) was able to prevent LPdAr(F) complex dimerization.[31] Nevertheless, this evolution set new foundations for future developments of catalytic Pd(0)/Pd(II) fluorinations.



*t*BuXPhos **(119)** BrettPhos **(120)** *t*BuBrettPhos **(121)** AlPhos **(122)**

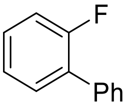
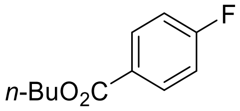
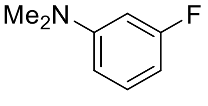
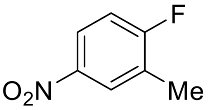
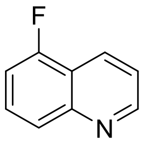
Figure 6. Ligands developed by Buchwald's group

Table 5. Selected aryl triflate fluorination examples

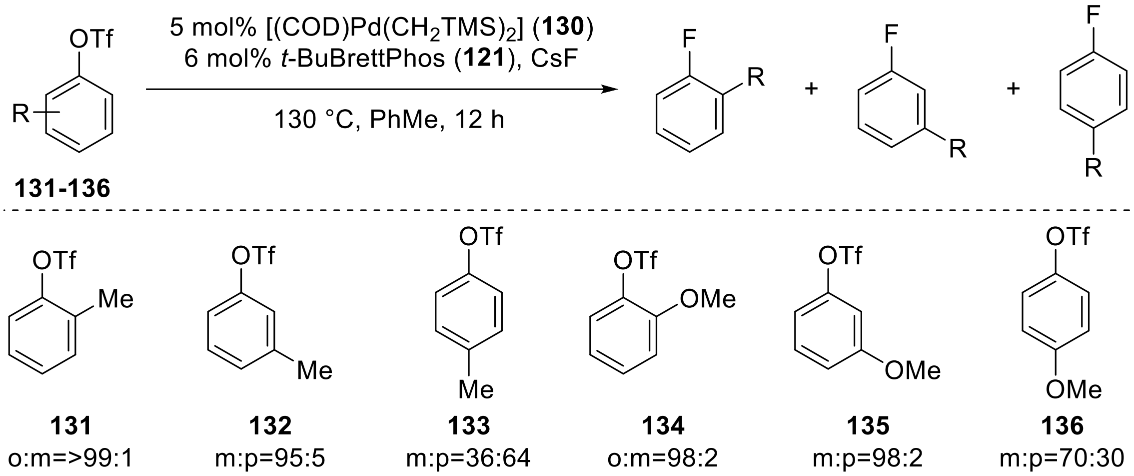


123 **125-129**

[(cinnamyl)PdCl]$_2$ (**124**)

Entry	Ar-F	Conversion, %
1	 **125**	82
2	 **126**	85
3	 **127**	84
4	 **128**	80
5	 **129**	75

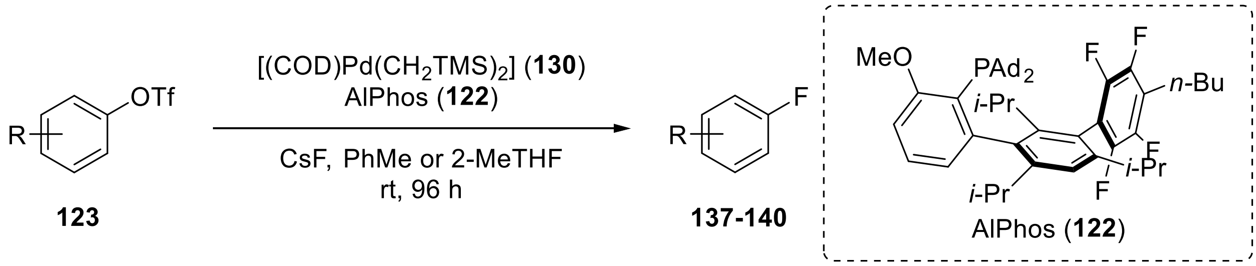
Interesting observation was made by the authors when they attempted to fluorinate more electron-rich substrates (Scheme 12).[46] GC and ^{19}F NMR analyzes revealed the formation of regioisomeric products. In contrast to control experiments with no catalyst, they hypothesized that regioisomer formation is, in fact, palladium-catalyzed process, and presumably involves Pd-benzyne intermediate.

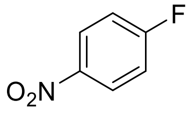


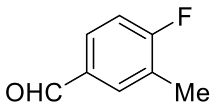
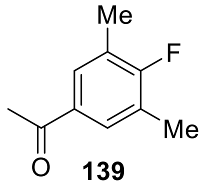
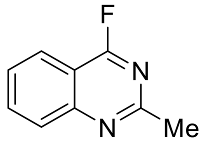
Scheme 12. Regioisomeric product formation from electron rich substrates

In 2015, Buchwald's group developed a new phosphine ligand AlPhos (**122**) for Pd(0)/Pd(II) catalyzed fluorination reactions (Figure 6).[47] This ligand was based on the common motif to Buchwald type ligands – biaryl backbone with additional perfluorophenyl moiety. The perfluorophenyl moiety was not only necessary to stabilize LPdAr(F) complex, but also to serve as an electron-withdrawing group to diminish electron donation to Pd(II) metal center, hence, reduce the energetic barrier for C-F reductive elimination. Intriguingly, this new ligand enabled aryl triflate fluorinations to be conducted at room temperature (Table 6). It is worth to mention, that this new catalytic system almost fully eliminated the regioselectivity issues.[47]

Table 6. Room temperature fluorination examples

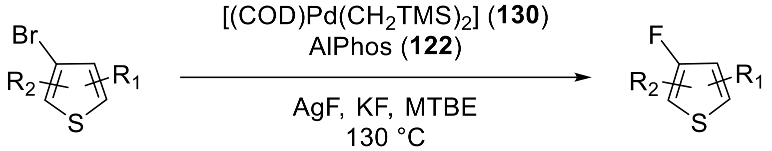


Entry	Product	Solvent	Pd, mol%	Yield, %
1	 **137**	PhMe	2	83

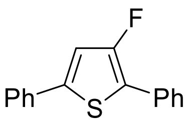
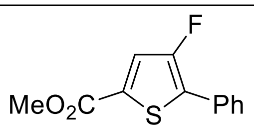
2	 **138**	2-MeTHF	2	82
3	 **139**	2-MeTHF	5	89
4	 **140**	2-MeTHF	5	83

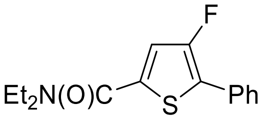
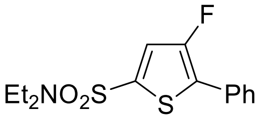
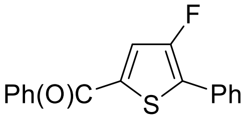
A more intriguing, yet more challenging set of substrates investigated by Buchwald's group was 5-membered heterocycles (Table 7). Previous studies on cross-coupling reactions of various 5-membered heteroaryl halides suggested, that the smaller size and increased electron richness of the substrate increases the already high kinetic barrier for C-F reductive elimination.[48] Studies of different substituents and substitution patterns determined, that electron withdrawing and/or sterically bulky substituents can, in fact, make this reaction synthetically useful for a limited scope of thiophenes.[49] Ultimate conclusion was that different ligand architecture or different transition metal catalysis is required to access a broader scope of fluorinated 5-membered heterocycles.

Table 7. Selected examples of thiophene fluorination



141 **142-146**

Entry	Product	Yield, %
1	 **142**	80
2	 **143**	93

3	 **144**	94
4	 **145**	93
5	 **146**	91

1.4 Synthesis of phosphine ligands

Phosphines are an inseparable part of organometallic chemistry and catalysis. Their everlasting influence on transition metal-catalyzed reactions provides access to new, simplified industrial processes.[50] Their electronic and steric properties can be fine-tuned for specific reactions. On the other hand, cyclic or “caged” phosphines are a relatively new field with an ever-increasing interest. There are several synthetic strategies to access various phosphines. Most commonly, phosphines are prepared through organometallic chemistry, such as organomagnesium or organolithium reactions with halophosphines. Additionally, this method involves highly reactive and corrosive reagents. Phosphines are also known to be profoundly malodorous and pyrophoric. Despite these inconveniences, it is one of the most established synthetic routes for the lab scale synthesis. Recently research has been migrating towards catalytic approach for synthesis of phosphines (*vide infra*, 1.4.3).[51]

1.4.1 Organometallic approach

Synthesis of phosphines through organomagnesium or organolithium intermediates is a practical and versatile way to synthesize mono-, di- and trisubstituted chlorophosphines, even on a larger scale.[52] Mono- and disubstituted chlorophosphines can then be reduced with $LiAlH_4$ to furnish corresponding phosphines (Figure 7). However, this approach involves working with highly reactive, toxic and corrosive chemicals. Since phosphines are highly prone to oxidation, reactions and work-up procedures must be carried out strictly under inert atmosphere.

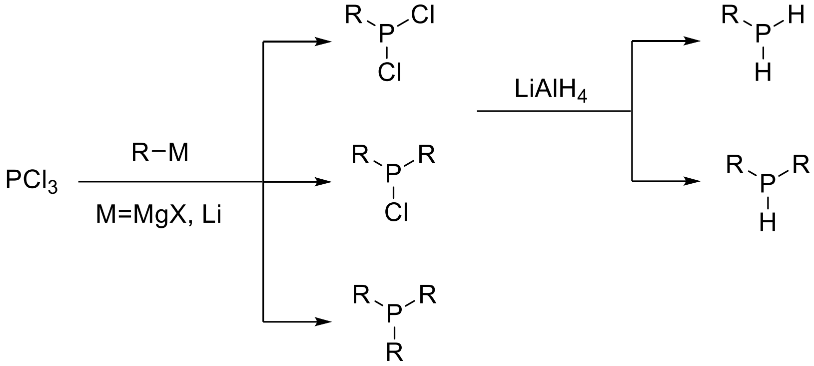


Figure 7. Synthesis of mono-, di- and trisubstituted phosphines

Third substitution at phosphorus gets increasingly difficult with the increasing steric bulkiness of the alkyl groups, rendering this method cumbersome for the synthesis of sterically congested trisubstituted phosphines (*t*-Bu_3P, Ad_3P, etc.).[53] On the other hand, preparation of less sterically bulky heteroleptic phosphines ($RPCl_2$, R_2PCl) proves to be a non-trivial task, since extreme P-Cl bond electrophilicity makes nucleophile addition difficult to control. Nevertheless, common way to synthesize heteroleptic phosphines is to use dialkylamines as protecting groups (Figure 8).[54] Typically this approach is higher yielding but requires larger scale synthesis to allow simpler purification *via* distillation.

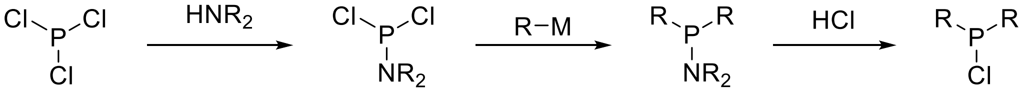


Figure 8. Heteroleptic phosphine synthesis

1.4.2 Nucleophilic approach

Phosphines are known as good electrophiles, but they also show remarkable nucleophilic properties. Phosphine nucleophiles are commonly prepared *via* deprotonation of phosphines with organometallic reagents generating transient phosphide anions. It is necessary to carefully control reaction stoichiometry due to phosphine's prolific affinity for overalkylation to produce stable phosphonium ions (Figure 9).[55]

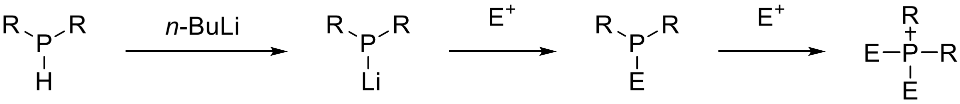
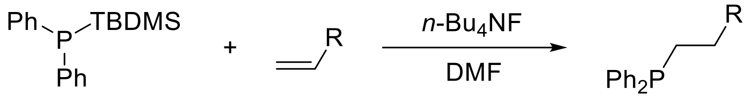


Figure 9. Alkylation of phosphine nucleophiles

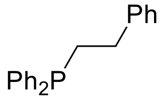
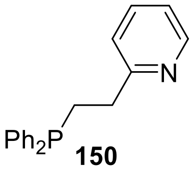
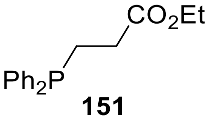
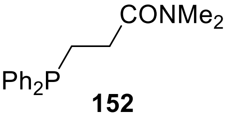
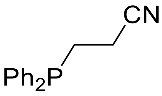
Notably, these reactions are usually conducted under harsh conditions. More sensitive functional groups must be protected in order to prevent side reactions. Moreover, there are no practical ways to control the reactivities of dialkylphosphides. Hayashi introduced a milder, more general way to prepare organophosphines in 2009.[56] His method involves the use of silyl groups on the phosphine as means to control reactivities *via* steric and electronic properties of the silyl group. Not only does this allow for selective activation of silylphosphines, but also electron-positive silyl moieties increase the nucleophilicity of the phosphorus atom. In turn, nucleophilic properties can be controlled by steric factors of the silyl substituents.

This method consists of two steps. First, silylphosphines are prepared from organophosphides and silylchlorides. Then these phosphines are conveniently purified *via* vacuum distillation and then used in the subsequent fluoride mediated phosphination step. Comparatively milder reaction conditions allow for more sensitive functional groups to be tolerated (Table 8).[56]

Table 8. Hayashi alkene phosphination

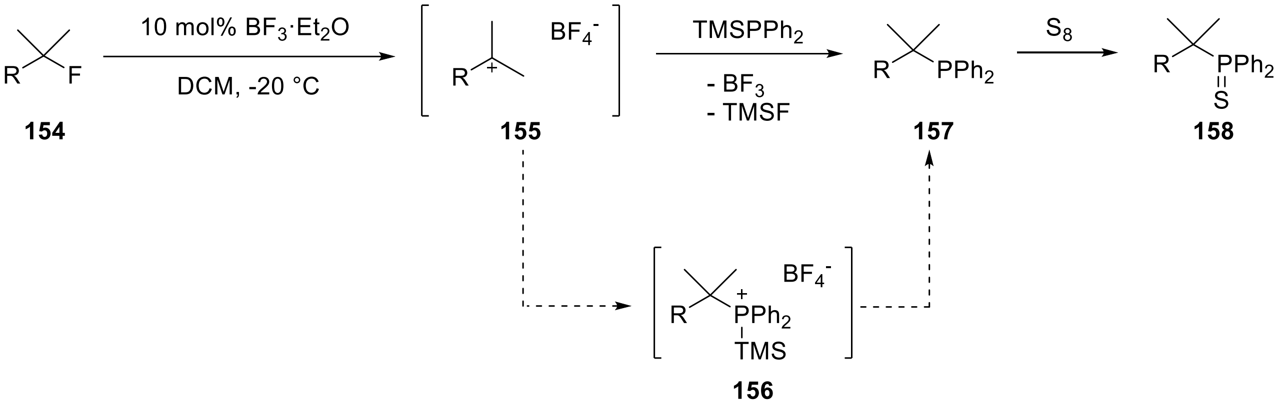


147 **148** **149-153**

Entry	Product	Yield, %
1	 **149**	89
2	 **150**	95
3	 **151**	82
4	 **152**	76
5	 **153**	81

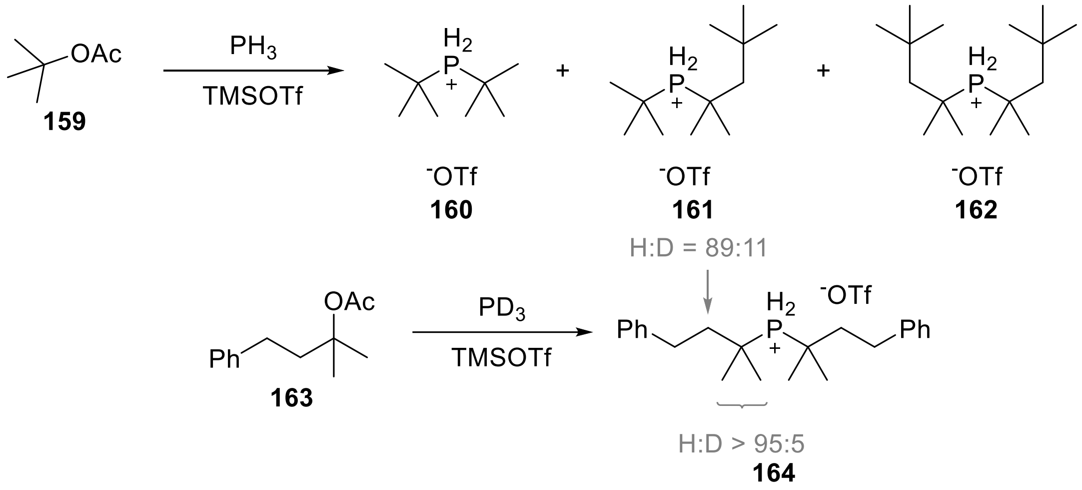
Oshima demonstrated a similar approach to the synthesis of *tert*-alkylated diphenylphosphines **157** from *tert*-alkyl fluorides **154** and diphenyl(trimethylsilyl)phosphane in 2004 (Scheme 13).[57] The unusually high $BF_3 \cdot Et_2O$ affinity with fluorine prompted them to investigate whereas it was possible to generate tertiary carbocations **155** *in situ*, thus providing a mild way to synthesize *tert*-

alkylphosphines **157**. After optimizing reaction conditions, Oshima was able to synthesize various *tert*-alkylphosphines. Additionally, this method was expanded to incorporate allyl fluorides, demonstrating the versatility of this approach. They opted to isolated phosphines as sulfides for easier analysis, although desulfurization step would be synthetically challenging, requiring harsh conditions and high temperatures.



Scheme 13. $BF_3{\cdot}Et_2O$ mediated phosphination of *tert*-alkyl fluorides

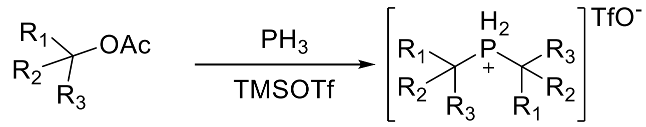
Phosphine gas (PH_3) can serve as an economical, albeit extremely pyrophoric and toxic source of phosphine nucleophile. PH_3 is deprotonated in strongly basic media (KOH in DMSO) to form PH_2^- transient species that can be further used for the addition to conjugated hydrocarbons.[58] In 2020, Ball's group reported a new elegant synthesis of di-*tert*-alkyl phosphines from tertiary alcohol acetates and *ex situ* generated PH_3 gas.[59] This method is intrinsically similar to Oshima's in a way that it uses *tert*-alkyl acetates instead of fluorides for carbocation generation (Scheme 14). In stark contrast to Oshima's work, telomerisation process was observed. While *t*-butyl acetate (**159**) easily undergoes ionization, inseparable mixture of products was formed, denoting that trapping of the carbocation is outcompeted by S_N1/E1 telomerisation process. Furthermore, when this reaction was conducted using deuterated phosphine (PD_3), H/D isotopic exchange was observed at the C_β position, showing that E1 is equally statistically likely.



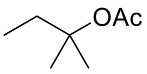
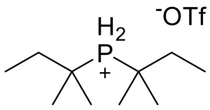
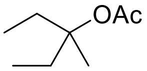
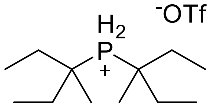
Scheme 14. S$_N$1/E1 telomerisation

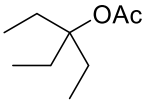
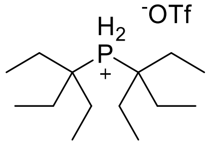
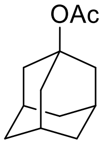
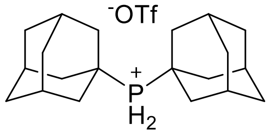
Ball’s umpolung (P$^-$/C$^+$) method for C-P bond formation provides a scalable and efficient approach to di-*tert*-alkyl phosphine triflates **169-172** synthesis from easy to access *tert*-alkyl acetates (**165-168**, Table 9). Basicity of the phosphine is increasing with each alkylation. After the second one, phosphine becomes sufficiently basic to be protonated by triflic acid present in the reaction mixture from carbocation generation step. Facile synthesis of these phosphine building blocks, that are essential for the synthesis of designed ligands, enables unique ways to modify catalyst’s properties, *vis-à-vis* catalyst performance.

Table 9. Versatility of Ball’s method



165-168 **169-172**

Entry	Acetate	Product	Yield, %
1	 **165**	 **169**	77
2	 **166**	 **170**	65

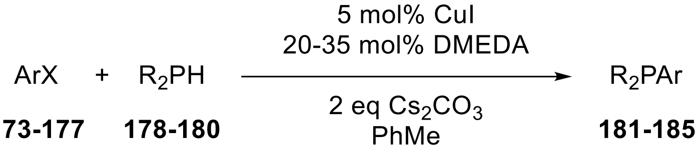
3	 **167**	 **171**	97
4	 **168**	 **172**	91

1.4.3 Transition metal catalyzed C-P bond formation

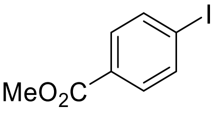
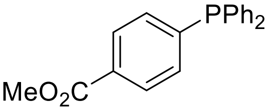
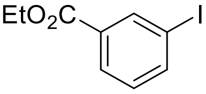
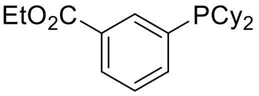
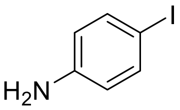
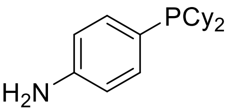
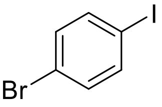
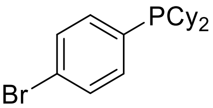
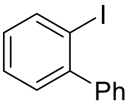
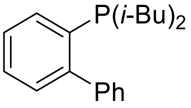
Although modern organophosphorus chemistry has a plethora of synthetic strategies for C-P bond formation, this field falls short in comparison to the advances reached in bond forming reactions for carbon with other first-row main-group elements. One of the pioneering strategies for the synthesis of organophosphorus compounds is the palladium catalyzed cross-coupling reactions of secondary phosphines and aryl (pseudo)halides.[60,61] Despite the need for more specific conditions, similar synthetic strategies involving Rh[56] and Cu[62,63] catalysis has also been established.

More recent investigations of copper catalyzed cross-coupling reactions by Buchwald's group has led to a new adaptation of Ulmann reaction for C-P bond formation.[63] This protocol allows for a wide range of functional groups to be tolerated, is experimentally non-tedious and inexpensive compared to other transition metal catalyzed syntheses (Table 10). However, this method cannot be used to couple sterically demanding phosphines with aryl or vinyl halides. Buchwald's work indicates that phosphine's electronic and steric properties are more important than aryl halide's for the success of the reaction. For example, less sterically demanding diarylphosphines show increased reactivity compared to their dialkyl analogues. Concurringly, highly sterically demanding *t*-Bu_2PH was inert under the same reaction conditions. Additionally, excess of dialkylphosphine must be used to achieve complete conversion, rendering purification steps laborious. Overall, this method is valuable for organophosphorus chemistry, given the wide functional group compatibility and inexpensive copper catalysts.

Table 10. Cu(I) catalyzed C-P cross-coupling

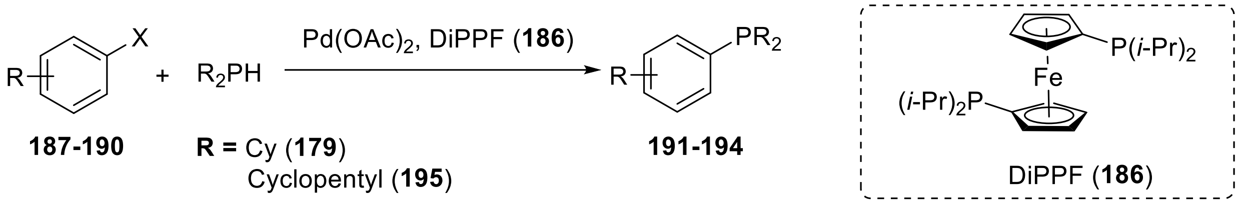


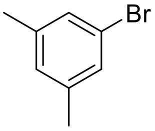
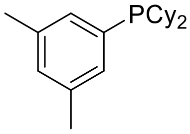
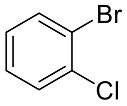
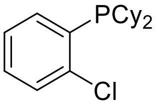
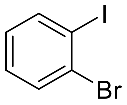
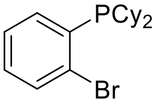
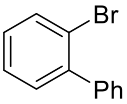
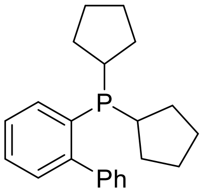
$$\underset{\textbf{173-177}}{ArX} + \underset{\textbf{178-180}}{R_2PH} \xrightarrow[\text{2 eq } Cs_2CO_3 \text{, PhMe}]{\text{5 mol\% CuI, 20-35 mol\% DMEDA}} \underset{\textbf{181-185}}{R_2PAr}$$

Entry	Ar-X	R_2PH	Product	Yield, %
1	 **173**	Ph_2PH (**178**)	 **181**	70
2	 **174**	Ph_2PH (**178**)	 **182**	85
3	 **175**	Cy_2PH (**179**)	 **183**	72
4	 **176**	Cy_2PH (**179**)	 **184**	72
5	 **177**	$(i\text{-}Bu)_2PH$ (**180**)	 **185**	73

In 2004, Buchwald's group reported a general method for cross-coupling of aryl halides with various thiols and secondary phosphines.[64] This method uses $Pd(OAc)_2$ as the precatalyst and bidentate ligand DiPPF (**186**, Table 11). Generally bidentate supporting ligands are superior for C-P and C-S cross-coupling reactions due to their strong coordination to palladium. This property hinders formed product binding to palladium, which would, in turn, deactivate the catalyst. After optimizing C-S cross-coupling reaction conditions they conducted a study whereas this method can be applied for C-P bond forming reactions. In this pioneering work they were able to shed light on a previously sparse area of dialkylphosphine and aryl halide coupling reactions. Interestingly, not only this method works well with electron-rich aryl halides, but in some cases mono-coupled products can be prepared from *o*-dihaloarenes (Entries 2 and 3, Table 11). Additionally, Stille *et. al.* demonstrated that silyl phosphines (*vide supra*, 1.4.2) can be used as coupling partners leading to easier purification of the product in comparison to the reactions with disubstituted phosphines.[65]

Table 11. Pd(OAc)$_2$/DiPPF mediated C-P cross-coupling



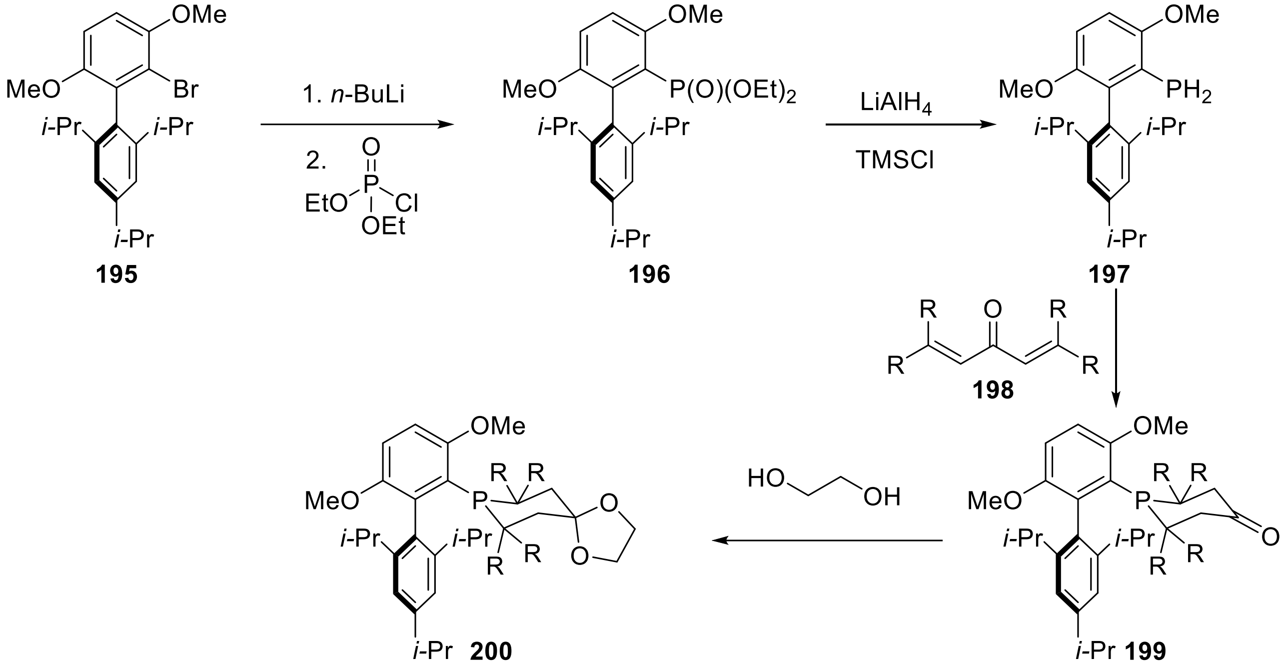
Entry	Substrate	Product	Yield, %
1	 **187**	 **191**	87
2	 **188**	 **192**	82
3	 **189**	 **193**	85
4	 **190**	 **194**	76

Catalyst activity can be controlled by the steric and electronic effects of the phosphine ligand. For example, Tolman's cone angle[66] describes steric effects of the phosphine ligand, while electronic effects can be assessed not only by IR analysis of phosphine-metal carbonyl complexes or phosphine Pt complexes, but also by $J_{\text{P-Se}}$ spin-spin coupling constants. NMR analysis of phosphine selenides is especially useful for determining electron-donating properties of mono- and multidentate phosphine ligands.[67] In general, $J_{\text{P-Se}}$ value increases with increasing electron-withdrawing effects of the substituents. Furthermore, since the Brønsted basicity of the heterophosphine compound cannot be observed directly, conveniently $J_{\text{P-Se}}$ values are directly related to the basicity of the phosphorus atom. Peter C. Kuntz conducted an extensive in-depth study concluding that for homologous series of phosphines $\text{PR}_n\text{R'}_{3\text{-}n}$ $J_{\text{P-Se}}$ constants and pK_B values correlate linearly to the degree of substitution (Table 12).

Table 12. Correlation between $J_{P\text{-}Se}$ and pK_B values

Phosphine	$^1J_{P\text{-}Se}$, Hz	pK_B
PMe_3	684	5.35
$PPhMe_2$	710	7.50
PPh_2Me	725	9.41
PPh_3	732	11.27
PCy_3	673	4.30
P(*t*-Bu)$_3$	692	2.60

Minor changes in phosphine or biaryl backbone are known to have great impact on the catalyst activity.[44,59,68] However, fine tuning of phosphine moiety is not a trivial task (*vide supra*). Shekhar developed a new class of phosphorinane based biaryl phosphine ligands to further explore their steric and electronic influence on catalytic activity.[69] Shekhar's synthesis of phosphine ligand consists of two key steps. Firstly, primary phosphine backbone **197** is formed and then cyclized with penta-1,4-diene-3-ones **198** to form phosphorinane ligands **199** (Scheme 15). In order to increase ligand stability keto-group was protected with ethylene glycol. Notably, *spiro*-cyclohexyl substituted phosphorinane ligands showed increased catalytic activity compared to both ordinary phosphine ligands (*t*-BuBrettPhos (**121**), AlPhos (**122**), etc.) and *gem*-dimethylphosphorinanes in challenging sulfoamidation and C-O cross-coupling reactions. Even though cyclic phosphine backbone affords slightly improved steric crowding, and forms less electrophilic Pd species than analogous dialkylphosphines (AlPhos (**122**), etc.), they are still effective at promoting sulfonamidation and C-N cross coupling reactions.[69]



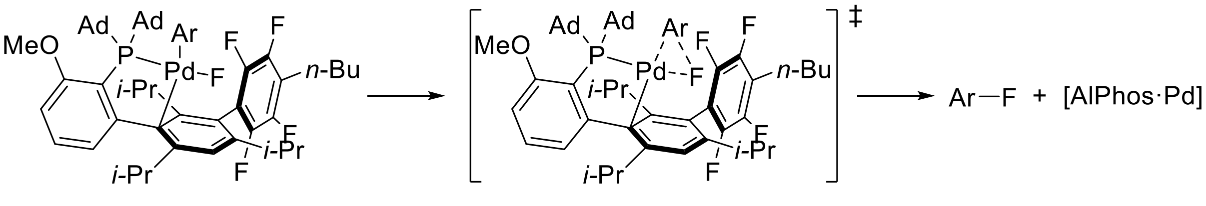
Scheme 15. General approach to biarylphosphorinane ligand synthesis

1.5 Computational evaluation of AlPhos (122) ligand

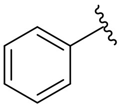
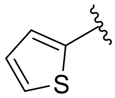
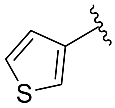
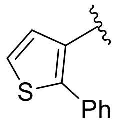
In previous works Buchwald's group has conducted a computational study on palladium-catalyzed amidation of five-membered heterocycles and one of the more significant parameters investigated was Ar-Pd-Br angles.[70] Computational analysis of these complexes indicate that Ar-Pd-Br angle is significantly wider for heteroaryl complexes. Unfortunately, Ar-Pd-F complexes bearing heteroaryl group are notoriously difficult to prepare, and to this day literature on synthesis of (Het)Ar-Pd-F complexes is scarce.[49] However, now density functional theory (DFT) calculations are a well-established field and a valuable tool for understanding and predicting the structure and reactivities of such complexes.[71]

DFT calculations revealed that heteroaryl complexes (Het)Ar-Pd-F (Entries 2-4, Table 13) show significantly wider ground-state Ar-Pd-F angles (θ) and energetically higher reductive elimination activation barriers ($\Delta G^{\ddagger}$) in comparison to phenyl group bearing complex (Entry 1, Table 13).[49] In case of 2-thienyl complex (Entry 2, Table 13) activation barrier lies 7 kcal/mol higher than phenyl substituted complex (Entry 1, Table 13) indicating that reductive elimination is ca. 5 orders of magnitude slower. Furthermore, Buchwald's DFT data presented in Table 13 show a distinct connection between reductive elimination energetic barriers $\Delta G^{\ddagger}$ and ground-state Ar-Pd-F angles, suggesting that decreased ground-state Ar-Pd-F angles correlate with energetically lower activation barriers. Furthermore, DFT analysis of *o*-phenyl-3-thienyl complex (Entry 4, Table 13) shows a significantly lower activation energy ($\Delta G^{\ddagger}$ = 22.8 kcal/mol) which corroborates with the known accelerating effect of ortho substituents on reductive elimination.[44]

Table 13. Computational analysis of Pd(Ar)F complexes



201-204

Entry	Ar	$\Delta G^{\ddagger}$, kcal/mol	Ar-Pd-F θ, deg[a]	Pd-C_{ipso}, Å	Pd-F, Å
1	 **201**	20.7	80.7	2.600	1.985
2	 **202**	27.7	82.3	2.536	1.977
3	 **203**	25.9	81.6	2.572	1.981
4	 **204**	22.8	81.7	2.578	1.990

[a] Ground-state geometry value

The results discussed in the last section illustrate that palladium catalyzed fluorination reaction for arenes and especially for heterocycles (i.e., thiophenes, pyridines, and fused ring systems) still remains a challenge to be solved. Buchwald's pioneering work in this field set the foundation for the research that is discussed in the next section.

2. RESULTS AND DISCUSSION

Functionalization of various arenes and heterocyclic compounds have been one of the main research objects in Labanauskas group at the Center of Physical and Technological Sciences (FTMC). Previous project related to synthesis and functionalization of cyclopropylthiophenes revealed a lack of methodology for installation of pharmaceutically important fluorine moiety in these small heterocycles.[72]

Literature overview suggests that currently C-F reductive elimination is still an obstruction for successful development of general Pd(II) catalyzed fluorination methodologies. As discussed previously (Subsection 1.3), correct catalyst geometry and steric properties enables the C-F reductive elimination and supporting ligand's electronics alter the overall energetic profile of the reaction.[47] Additionally, supporting ligand architecture is further complicated by the excessive electron richness of the small heterocycles.[49] Thus, two divergent approaches to solve the problems posed by small heterocycles, become apparent. Catalysis by design and catalysis by scouting. Both ways have their own challenges, but the former is more focused and offers a more fundamental evaluation of the problem which might lead to a more general solution.

The high energetic barrier for C-F reductive elimination may be altered by tuning the electronic and steric properties of the ligands and the substrates. Buchwald’s group demonstrated the feasibility of this approach with development of AlPhos ligand (**122**, Figure 10). However, it still has its drawbacks, mainly limited substrate scope. Two possible areas for modifications were envisioned to improve its applicability: a) modification to the ligand’s terphenyl backbone sterics (in blue, Figure 10) and b) modification of electronic profile and sterics in the phosphine moiety (in red). In order to compare the influence of sterics and electronics a set of ligands presented in Figure 10 was chosen. The most convenient strategy to increase the back-bone bulkiness is to modify the alkoxy group (methoxy to *tert*-butoxy). The usage of the cyclic phosphine framework would allow for a more “direct” steric hindrance at the Pd center. For example, 1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphaadamantane would act as a combination of both the sterics and the electronics (ligands **206** and **207**). 9-phosphabicyclo[3.3.1]nonane and its analogues would modify the sterics without much influence on the overall electronics (ligands **208-211**, *vide infra*).

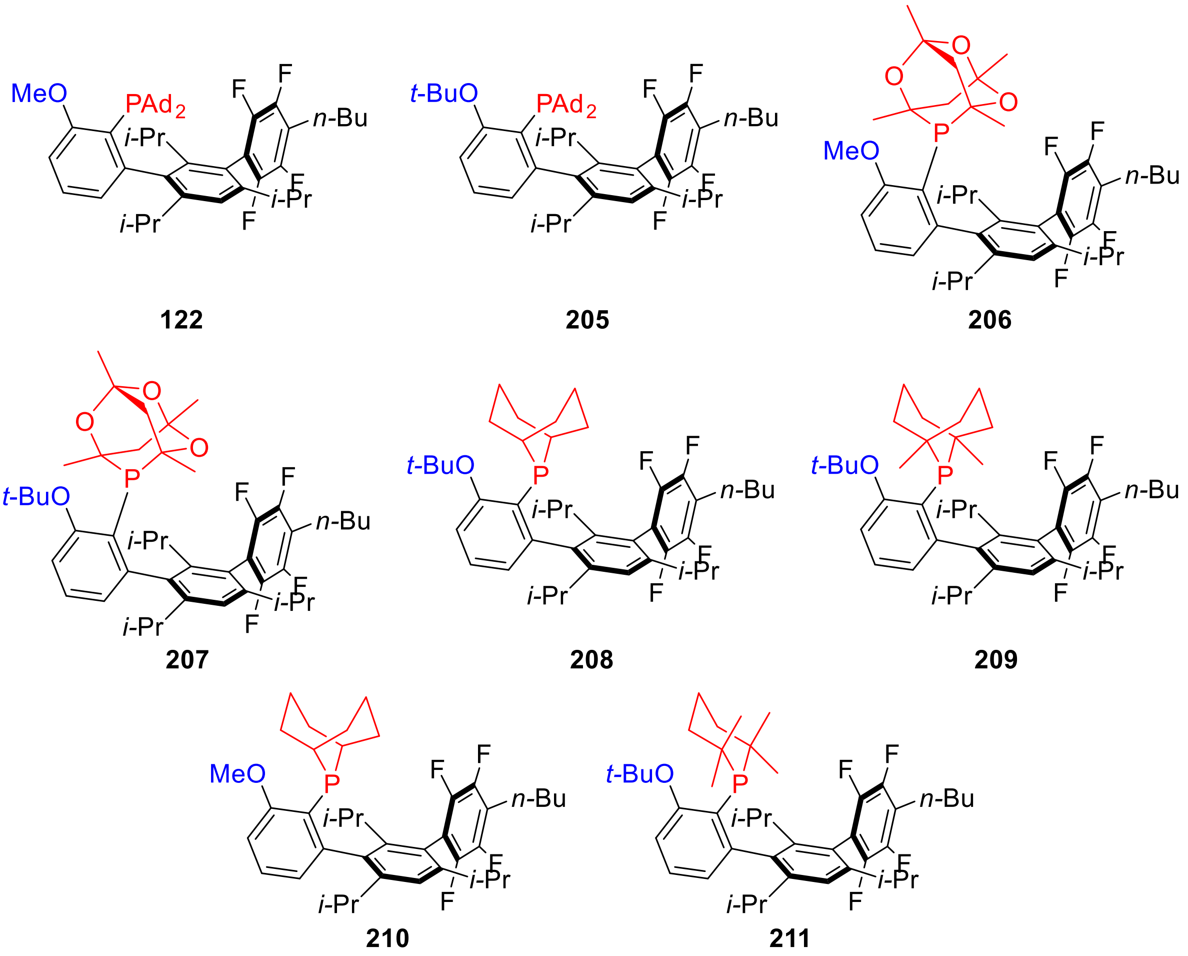


Figure 10. Ligand structures

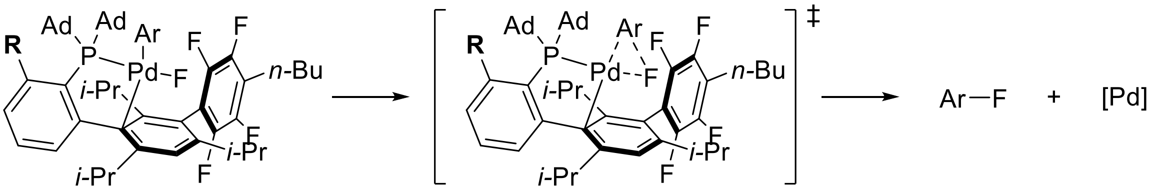
The overall goal of this research is to develop a new efficient catalytic system based on Pd(II) catalytic cycle for the fluorination of (hetero)arenes. The objectives of this project are a) the computational evaluation of modified ligands **205-211** based on AlPhos (**122**) backbone; b) the development of divergent synthesis for AlPhos and its analogues (**122**, **205-211**); c) the optimization of the methodologies for sterically demanding secondary (a)cyclic phosphines; d) the evaluation of the ligands for catalytic fluorination reactions of (hetero)arenes.

2.1 Computational evaluation

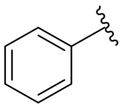
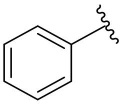
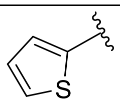
Previous studies by Buchwald *et. al.* suggests that increased steric bulk of the ligand may aid in overcoming the challenging C-F reductive elimination activation barrier $\Delta G^{\ddagger}$.[47,49] They hypothesized that diminished Ar-Pd-F angles correlate with lower activation energy barrier. In their computational study, ground state and transition state geometries were optimized at B3LYP/6-31G(d)-SDD(Pd) level theory. Then, single point (SCF) energies were calculated at hybrid M06/SDD-6-311+G(d,p)/SMD(THF) level theory. In this computational study the latter step was omitted to save expensive computational time. Ground-state and transition-state geometries were optimized, and frequency analysis was performed at B3LYP/6-31G(d)-SDD(Pd) level theory. All transition states had only one imaginary node and it corresponded to the C-F reductive elimination, Gibbs free activation energies were calculated from thermodynamic data received from frequency analysis.

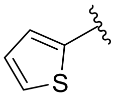
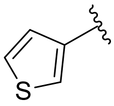
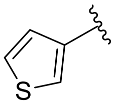
Following on this idea, DFT computational analysis was conducted to determine whereas modifications to the AlPhos ligand (**122**) could lower the activation energy barrier $\Delta G^{\ddagger}$ (Table 14). For more efficient evaluation two extremes of the ligand backbone were investigated (**122**, **205**). Optimized ground-state geometries showed promising results. In all cases, due to extreme steric influence of *tert*-butoxy group, decrease in Ar-Pd-F angle was observed. *Tert*-butoxy substituted 3-thienyl complex's **205c** Ar-Pd-F angle 78.5° (Entry 6, Table 14) was even smaller than methoxy substituted phenyl complex **122a** – 79.0° (Entry 1, Table 14). Unfortunately, transition-state geometry optimization of *tert*-butoxy group bearing complexes failed to converge. This may be caused by insufficient computational methods used, but different DFT methods would make computational results difficult to compare. Nevertheless, *tert*-butoxy AlPhos ligand **205** is a promising candidate for experimental investigation (*vide infra*).

Table 14. Computational comparison of **122** and **205** (hetero)aryl complexes



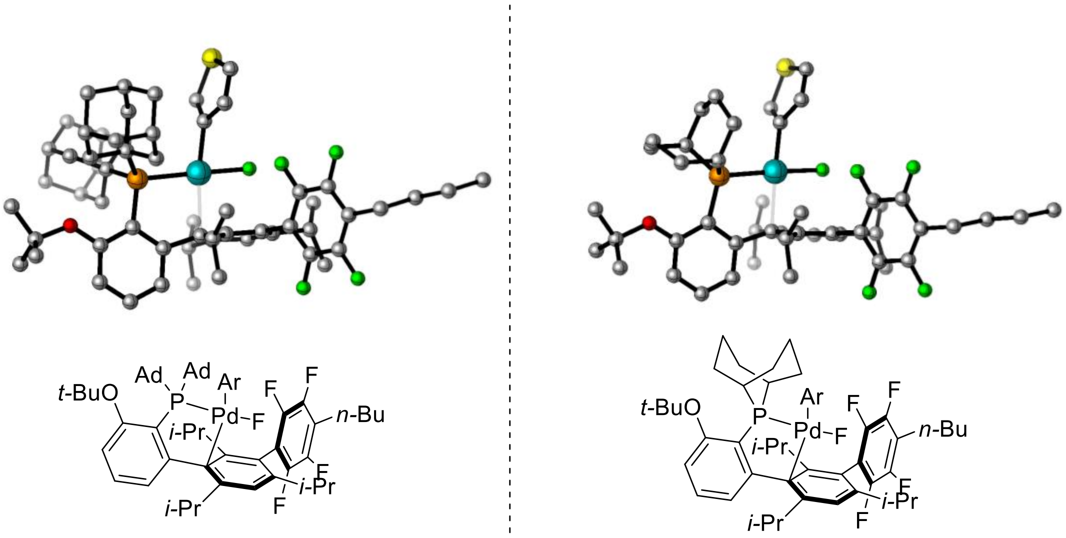
R = OMe (**122a-c**), *t*-BuO (**205a-c**)
a: Ar = Ph, **b:** Ar = 2-thienyl, **c:** Ar = 3-thienyl

Entry	Complex	Ar	θ(Ar-Pd-F), deg[a]	$\Delta G^{\ddagger}$, kcal/mol
1	**122a**		79.0	17.6
2	**205a**		78.6	-
3	**122b**		81.5	23.4

4	**205b**		81.1	-
5	**122c**		79.3	25.8
6	**205c**		78.5	-

[a] Ground-state geometry values

1-Adamanyl substituted phosphorus ligands are on the far-edge of the sterically demanding ligand spectrum.[68] Further increase in steric bulk of the ligand is largely limited by the availability of higher diamondoids. Henceforth, a new strategy to increase the steric hindrance at the catalytic center was developed. Close examination of the 3D structure of complex **205c** has aroused the idea that cyclic or “caged” phosphine structures, i.e., complex **208c**, should provide more “direct” steric hindrance at the catalytic center (Figure 11). Stimulated by Shekhar’s success[69] with phosphorinane-ligand based catalytic systems, new cyclic phosphine analogues **206**, **208**, **209** and **211** were computationally investigated.



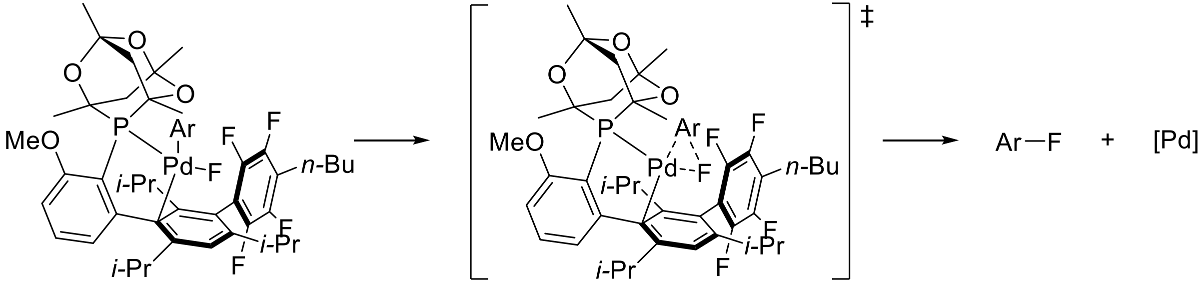
205c
Ar = 3-thienyl

208c
Ar = 3-thienyl

Figure 11. Optimized ground-state geometries of **205c** and **208c**

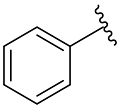
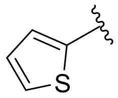
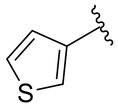
The new ligand **206** containing phosphatrioxa-adamantane moiety was submitted to the DFT calculations (Table 15). Comparison of phenyl complexes **206a** and **122a** showed that both the angle and the activation energy is augmented in the **206a** case (Δθ = +0.9°; $\Delta(\Delta G^{\ddagger})$ = +3 kcal/mol). Surprisingly, even though the decrease in Ar-Pd-F angle (Δθ = -0.7°) was noticed for the complex **206b,** increase in activation energy was seen ($\Delta(\Delta G^{\ddagger})$ = +1.7 kcal/mol). Favorable change (decrease) in activation energy (Δ(ΔG‡) = -0.2 kcal/mol) was observed for complex **206c** compared to analogous **122c**, however increase in its Ar-Pd-F angle was noted (Δθ = +0.6°).

Table 15. 1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphaadamantane based ligand **206** analysis



206a-c

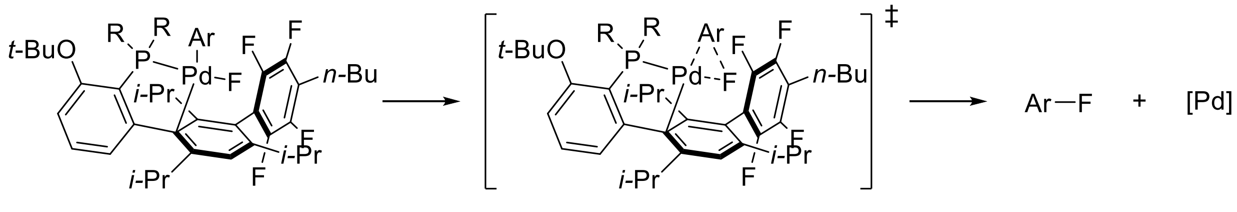
a: Ar = Ph, **b:** Ar = 2-thienyl, **c:** Ar = 3-thienyl

Entry	Complex	Ar	θ(Ar-Pd-F), deg^{a}	ΔG‡, kcal/mol
1	**206a**	 **a**	79.9	20.6
2	**206b**	 **b**	80.8	25.1
3	**206c**	 **c**	79.9	25.6

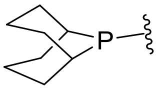
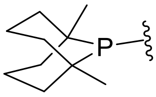
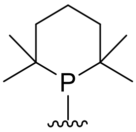
[a] Ground-state geometry values

Furthermore, complexes bearing phosphorinane motifs **208c**, **209c** and **211c** were compared to **122c**. In all cases, decrease in angles as well as activation energies was determined. The biggest decrease in Ar-Pd-F angle was observed for complex **209c** (Δθ = -2°, its Δ(ΔG‡) = -1.9 kcal/mol), while biggest decrease in activation energy was for the complex **211c** (Δ(ΔG‡) = -2.4 kcal/mol, its Δθ = -0.6°).

Table 16. Comparison of bicyclic and cyclic phosphine moieties



Ar = 3-thienyl (**c**)

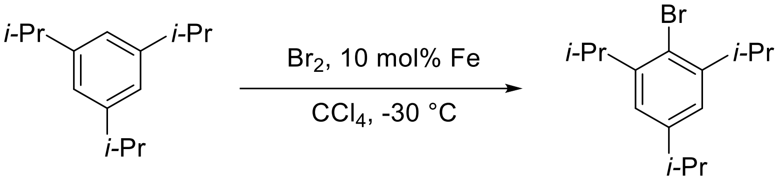
Entry	Complex	θ(Ar-Pd-F), deg[a]	ΔG‡, kcal/mol
1	 **208c**	78.6	24.3
2	 **209c**	77.3	23.9
3	 **211c**	78.7	23.4

[a] Ground-state geometry values

Favorable results from computational modeling of ligands based on cyclic "caged" phosphine structures, suggests that more "direct" steric hindrance at the palladium center has influence on the C-F reductive elimination energetics. Lowest activation energies were observed for complexes based on **206**, **208**, **209** and **211** ligands. Results presented in Table 15 and Table 16 suggest that not only steric, but also the electronic properties of the phosphine moiety alter the reaction's energetic profile. Although DFT analysis showed amenable results for the structures analyzed, synthesis of these ligands has not been resolved, yet.

2.2 Ligand backbone synthesis

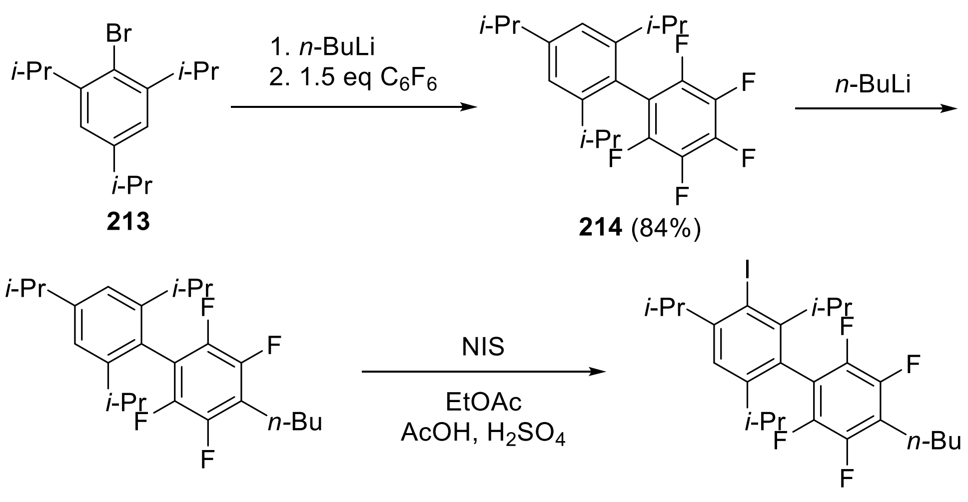
Procedure for the synthesis of AlPhos ligand (**122**) was adapted and optimized for 50 mmol scale from literature procedures.[47] Although it uses commercial 1-bromo-2,4,6-triisopropylbenzene (**213**) as a starting material, 1,3,5-triisopropylbenzene (**212**) was found to be a far better choice economically as a starting material for a larger scale synthesis. Unfortunately, bromination of 1,3,5-triisopropylbenzene (**212**) at 0 °C with elemental bromine (Br_2) produced a complex mixture of brominated products. However, lowering of the reaction temperature (-30 °C) and addition of Fe (10 mol%) gave far superior results (Scheme 16). Synthesis of 1-bromo-2,4,6-triisopropylbenzene (**213**) was carried out under these optimized conditions on a 0.34 mol scale of substrate and after vacuum distillation it yielded bromide **213** in 83%.



212 **213** (83%)

Scheme 16. Bromination of 1,3,5-triisopropylbenzene (**212**)

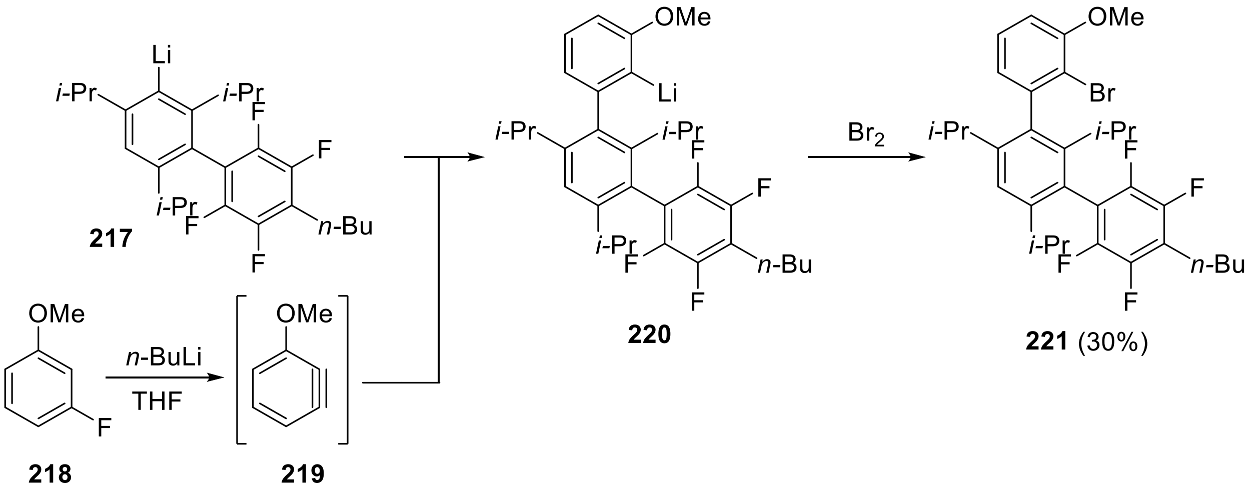
Literature procedure for coupling triisopropylphenyl moiety with perfluorobenzene uses 5 equivalents of the latter.[47] However, such protocol would be highly wasteful in terms of perfluorobenzene since afterwards it is hardly recoverable. Therefore, a slight optimization of the reaction conditions was required (Scheme 17). 1-Bromo-2,4,6-triisopropylbenzene (**213**) was lithiated with *n*-BuLi at -78 °C and then cannulated to a solution of perfluorobenzene in THF at -78 °C (Scheme 17). This modification to the original literature protocol gave a slightly lower 84% yield (lit. 87%)[47] but allowed to reduce the amount of perfluorobenzene to only 1.5 eq. Additionally, product **214** is hardly soluble even in boiling methanol, so crystallization solvent was changed from methanol to isopropanol, which allowed to greatly attenuate the amount of solvent required for purification, thus decreasing the overall waste and environmental impact. After crystallization, compound **214** was further subjected to *n*-butylation reaction with *n*-BuLi which yielded biaryl **215** in almost quantitative 95% yield. Notably, no significant by-product formation was observed (GC-MS), so additional purification procedures were successfully omitted. The iodination step was performed following literature procedure[47] and furnished aryliodide **216** in an excellent 91% yield. However, the purification method was slightly modified. The original protocol calls for multiple triturations with hexanes which can be tedious. Thus, purification was performed *via* crystallization from isopropanol which gave a considerably higher 91% yield (lit. 80%)[47].



213 **214** (84%) **215** (95%) **216** (91%)

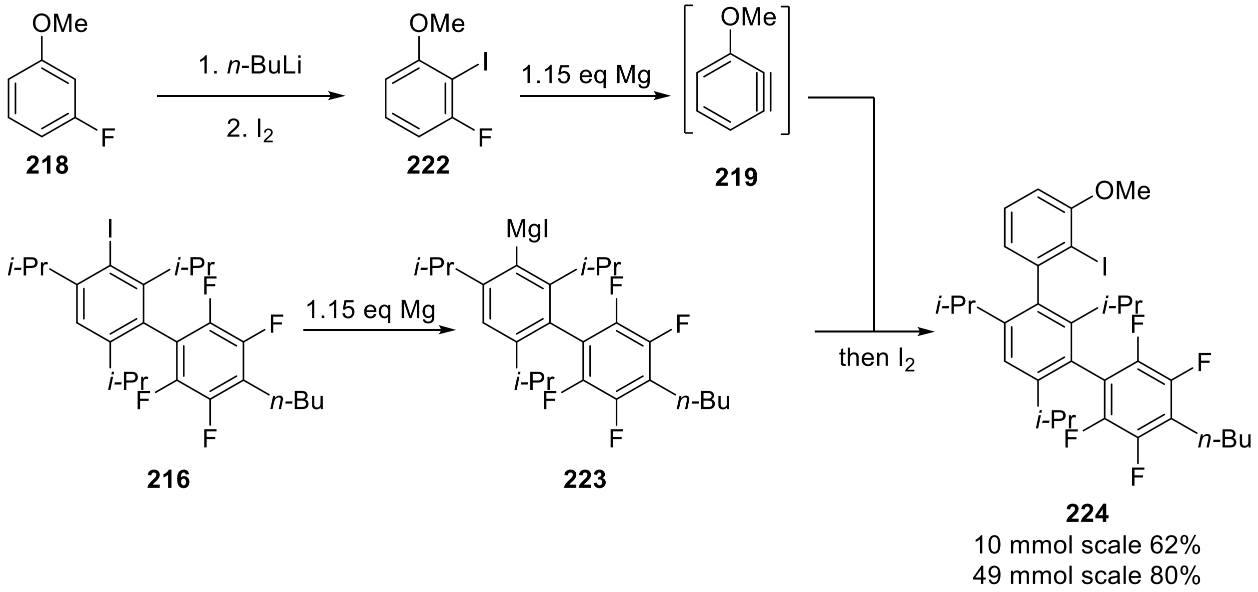
Scheme 17. Synthesis of biphenyl **216**

Far more troublesome was the final step in the backbone synthesis (Scheme 18). The literature procedure consists of multiple stages performed one after another without purification of the intermediates. Iodide **216** was lithiated with *t*-BuLi at -78 °C to give organolithium species **217**, which was then cannula-transferred to a solution of (2-fluoro-6-methoxyphenyl)lithium prepared from fluoroanisole **218** and *n*-BuLi at -78 °C. Then the temperature of the reaction mixture was increased to -40 °C, which allowed the coupling partner methoxybenzyne (**219**) to be generated *in situ*. Afterwards, the lithium species **220** was quenched with elemental bromine (Br_2), furnishing the ligand backbone in a very modest yield of 30% (Scheme 18). Not only does this protocol use highly pyrophoric and dangerous lithiation agent (*t*-BuLi), which is not usually associated with larger scale synthesis, but also requires multiple non-trivial manipulations to be performed.[47] Moreover, GC-MS analysis of the reaction mixture revealed a significant amount of 3'-bromo-4-butyl-2,3,5,6-tetrafluoro-2',4',6'-triisopropyl-1,1'-biphenyl (38%) which indicates that the addition to methoxybenzyne **219** was rather sluggish and benzyne degradation was a more favorable reaction. Furthermore, as judged from GC-MS analysis, this protocol yielded a mixture of iodinated and brominated products **224** (5%) and **221** (30%) respectively. This might have been caused by the oxidative nature of bromine toward iodide ions. Fortunately, this mixture was resolved by multiple crystallizations from hexanes. As a tangent, carbon tetrabromide (CBr_4) was investigated as a more convenient to handle and non-oxidizing source of bromine. Even though formation of iodide **224** was suppressed, no increase in reaction yield was observed. Hence, a better protocol was mandatory.



Scheme 18. Synthesis of bromide **221** following literature procedure[47]

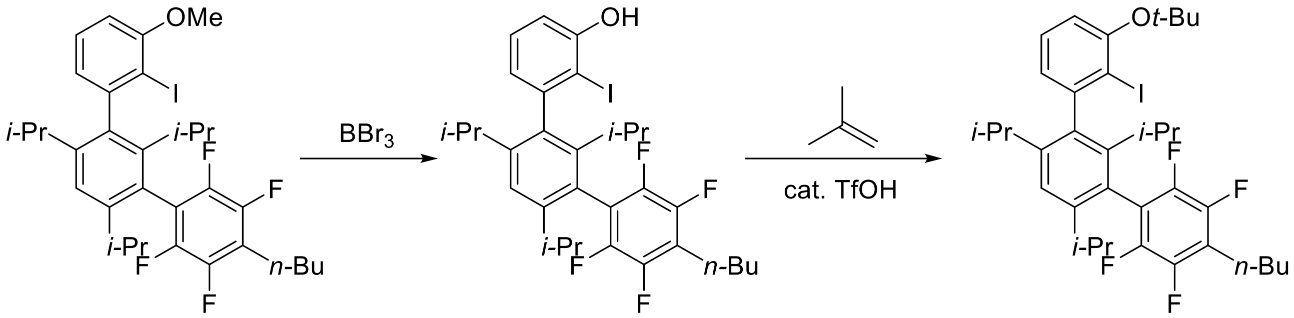
The new protocol used a similar strategy based on organometallic species coupling with methoxyaryne **219** (Scheme 18). Iodofluoroanisole **222** was prepared from 1-fluoro-3-methoxybenzene (**218**) by lithiation at low temperature (-90 °C) and subsequent quenching with iodine solution in THF (Scheme 19). Arylmagnesium species **223** was prepared from iodide **216** under standard conditions with excess of magnesium turnings (2.3 eq) present for successive aryne generation step. After complete iodide conversion to organomagnesium species (TLC analysis), iodoanisole **222** solution in THF was introduced dropwise for the *in situ* generation of methoxybenzyne **219**. A slow addition rate was necessary to ensure that aryne **219** was sufficiently trapped by the Grignard reagent **223**. Following complete consumption of the starting materials, reaction mixture was quenched with iodine (I_2) solution in THF (ca. 0.5 M). Ligand backbone **224** was obtained in a preeminent 80% yield after crystallization from isopropanol. Notably, iodine was preferred over bromine, not only because iodoarene **224** showed a greater propensity for crystallization, but also to ease the final step in ligand synthesis (*vide infra*, 2.5). Moreover, it is worth mentioning that larger scale reaction led to higher yields.



Scheme 19. Synthesis of iodide **224**

Reflecting on the results discussed in Subsection 2.1, a method for modification of the ligand backbone **224** was needed. Methoxy group was conveniently hydrolyzed with boron tribromide (BBr_3) under mild reaction conditions and after simple work-up yielded hydroxyterphenyl **225** quantitatively (Scheme 20). Even though *tert*-butylation with isobutene in the presence of a catalytic amount of triflic acid is a mild and very attractive route, isobutene commercial availability is somewhat limited. Nevertheless, this was solved by a more classic approach. Isobutene was prepared by dehydration of *tert*-butanol over alumina catalyst bed in a quartz tube reactor heated to ~370 °C. The tube reactor was made from 20×300 mm fused-quartz tube, filled with alumina beads. Nichrome wire coil was used for heating and asbestos for thermal insulation. Temperature was carefully controlled with a variable transformer and maintained at ~370 °C. This improvised set-up was capable of generating 100 grams of isobutene gas per hour from 146 g of *tert*-butanol. Prior to the *tert*-

butylation reaction, the required amount isobutene was condensed in a N_2 (liq.)/acetone cooled trap. Then the liquefied gas was transferred to the reaction mixture and the reaction was started by carefully adding a catalytic amount of triflic acid. Complete *tert*-butylation was found to occur within 40 minutes on 18 mmol scale. It was observed, that once all isobutene is consumed in polymerization side-reactions, product **226** was dealkylated under strongly acidic conditions back to hydroxyterphenyl **225**, therefore constant monitoring of the reaction was necessary. Under these careful considerations, the second backbone **226** was synthesized in excellent 76% yield.



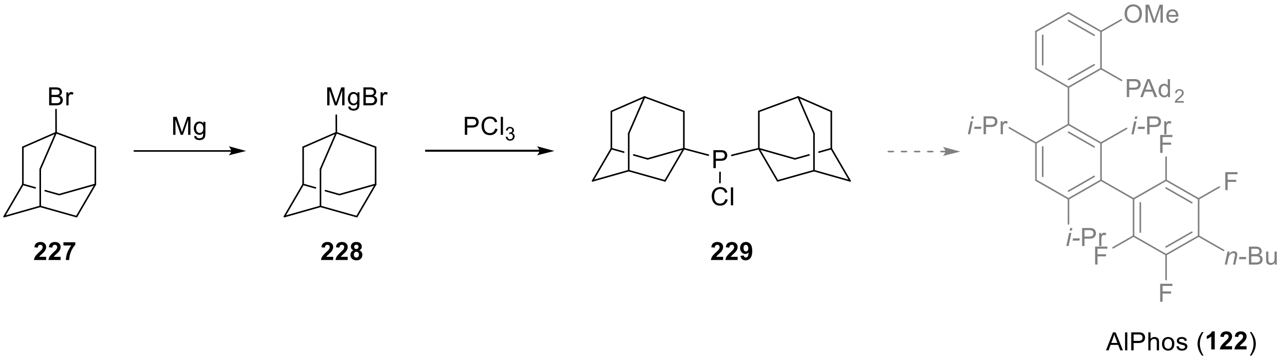
224 **225** (99 %) **226** (76 %)

Scheme 20. Synthesis of *tert*-butylterphenyl **226**

2.3 Phosphine synthesis

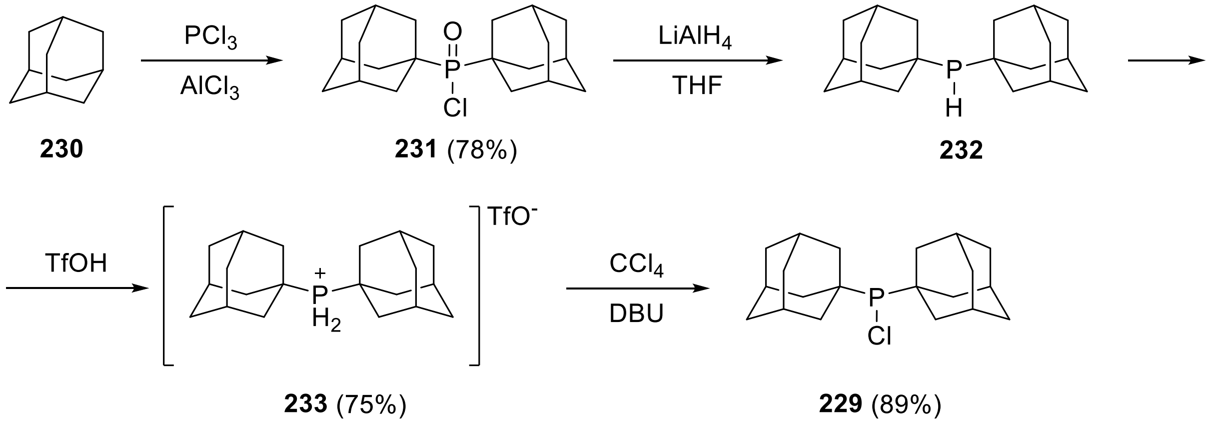
2.3.1 Synthesis of di(1-adamantyl)chloro- and di(1-adamantyl)phosphine

Final stage of the AlPhos ligand synthesis was the coupling of di(1-adamantyl)chlorophosphine (Ad_2PCl, **229**) with the AlPhos ligand backbone **224**.[47] Literature suggests an interesting approach for the synthesis of Ad_2PCl (**229**). (1-Adamantyl)magnesium bromide (**228**) is prepared from 1-bromoadamantane (**227**) and then reacted with phosphorus trichloride (PCl_3) (Scheme 21).[70] Conveniently, this method avoids working with reactive and toxic secondary phosphines. Unfortunately, this deceivingly attractive strategy manifested itself as a very non-trivial endeavor. Multiple reaction conditions and ethereal solvents were tested. Reaction with 15 equivalents of Mg in ether, same as literature procedure[70], did not yield an appreciable amount of Grignard's reagent **228**. Bizarrely, when a sample from an unstirred reaction mixture was quenched with *N,N*-dimethylformamide (DMF), 10% of the corresponding aldehyde was observed (GC-MS). Unfortunately, even the reaction of 1-bromoadamante (**227**) with a highly reactive Rieke magnesium or lithium sand were vague and did not yield any 1-adamantylmagnesium bromide or 1-adamantyllithium cleanly. Consequently, an unambiguous strategy was needed.



Scheme 21. Synthesis of di(1-adamantyl)chlorophosphine (**229**)

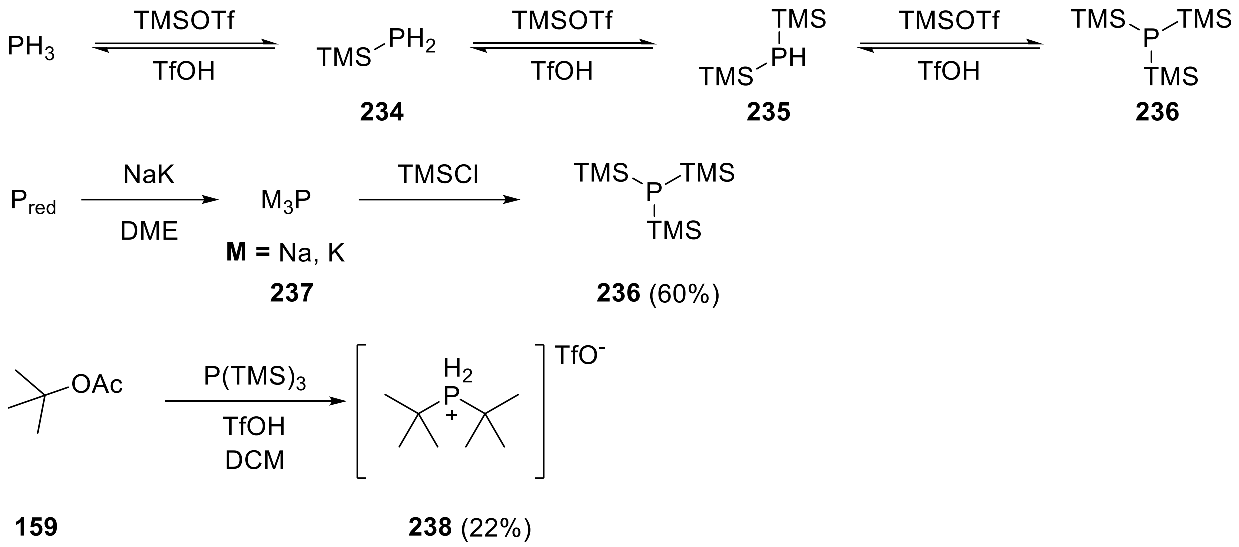
A different strategy for the synthesis of di(1-adamantyl)chlorophosphine (**229**) was developed (Scheme 22). Adamantane (**230**) reacted with PCl_3 in Kinnear–Perren reaction and after recrystallization from toluene gave di(1-adamantanyl)phosphinic chloride ($Ad_2P(O)Cl$, **231**) in 78% yield on 2.2 mol scale. It was then reduced with lithium aluminum hydride to di(1-adamantyl)phosphine (**232**). Given that secondary phosphines are profusely susceptible to oxidation, a new work-up procedure was developed. After quenching the reaction mixture with degassed water, sodium potassium tartrate solution was added until the thick emulsion dissipated. The product was extracted with of degassed dichloromethane (2-3 times the volume). Then the organic phase was cannula-transferred to a new reaction flask and treated with an equimolar amount of triflic acid. After trituration with ether, phosphine triflate **233** was obtained as an air-stable crystalline solid in good 75% yield. Notably, this method was scalable enough that the synthesis of di(1-adamantyl)phosphine triflate (**233**) was successfully performed on a 2.2 mol scale. Finally, it was chlorinated with CCl_4 in the presence of 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) furnishing compound **229** in an excellent 89% yield.



Scheme 22. Synthesis of di(1-adamantyl)chlorophosphine (**229**)

2.3.2 Tris(trimethylsilyl)phosphine

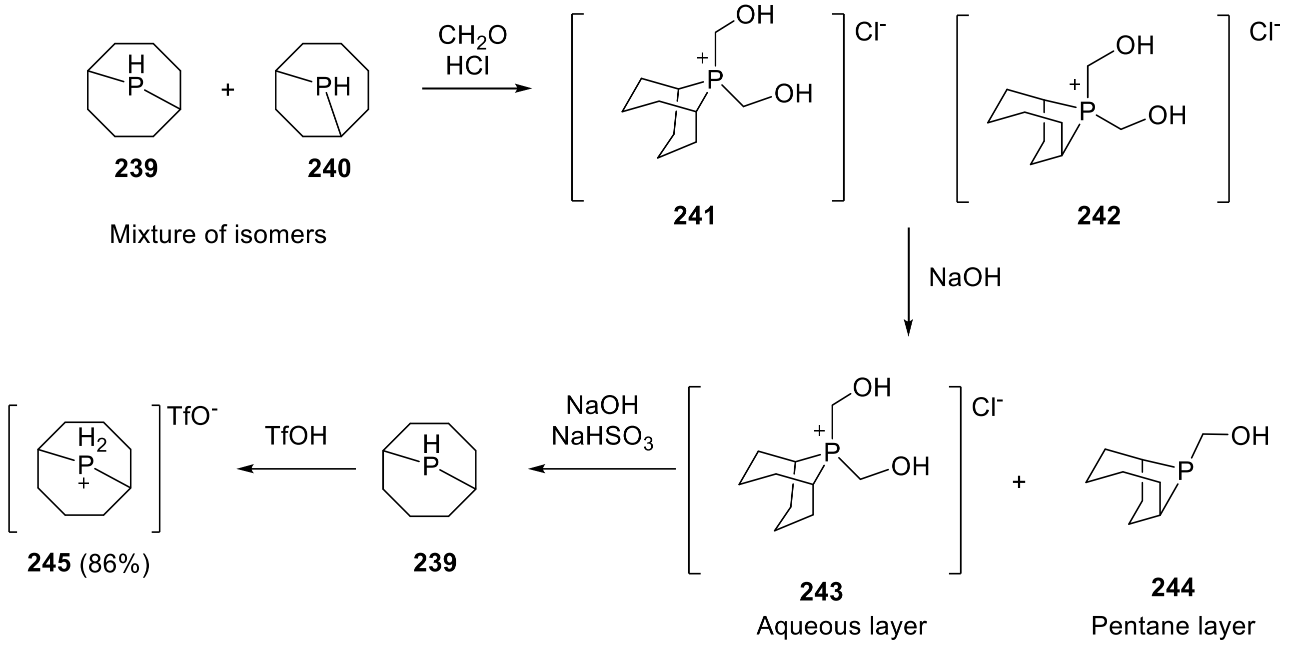
Ball's demonstrated that less substituted *tert*-butylacetate (**159**) undergoes telomerisation reaction in his umpolung (P^-/C^+) approach for the synthesis of di-*tert*-alkylphosphine (*vide supra*, 1.4.2).[59] Notably, phosphine addition to *tert*-butyl carbocation is outcompeted by the parasitic $S_N1/E1$ reaction pathway (Scheme 14). His method is in part based on an industrial scale tris(trimethylsilyl)phosphine (**236**) synthesis.[73] Phosphine gas is trimethylsilylated by trimethylsilyl triflate in solution. Under Ball's reaction conditions, absence of base allows for an equilibrium of various phosphine nucleophiles to be established (Scheme 23). This reasoning thus inspired a new approach to the umpolung (P^-/C^+) synthesis idea. Same equilibrium could be generated by the reaction of tris(trimethylsilyl)phosphine (**236**) with triflic acid in solution. Under these reaction conditions, the efficiency of carbocation trapping by phosphine nucleophiles would not be limited by the rate of phosphine gas introduction to the system. Therefore, to test this hypothesis, the synthesis of tris(trimethylsilyl)phosphine (**236**) was undertaken. Phosphine **236** was prepared by first reacting NaK alloy with red phosphorus in dimethoxyethane (DME). The formed phosphide **237** was then trimethylsilylated with trimehylsilyl chloride and after vacuum distillation afforded the tris(trimethylsilyl)phosphine (**236**) in 60% yield. It is worth mentioning that the synthesis of **236** took 5 days to complete, involved specialized equipment and exceptional planning along with strict use of Schlenk techniques. Noteworthily, tris(trimethylsilyl)phosphine (**236**) is pyrophoric and profusely malodorous. As proof of concept, an experiment with *tert*-butyl acetate (**237**) was conducted (Scheme 23). Results from this experiment were intriguing - no higher-chain phosphine products were observed (from NMR analysis) and di-(*tert*-butyl)phosphine triflate (**238**) was obtained in a modest 22% yield, indicating that extensive reaction optimization is still needed. Nevertheless, these results demonstrate that *in situ* presence of phosphine can solve the telomerisation issue (*vide supra*, 1.4.2).



Scheme 23. Synthesis and reactions of tris(trimethylsilyl)phosphine (**236**)

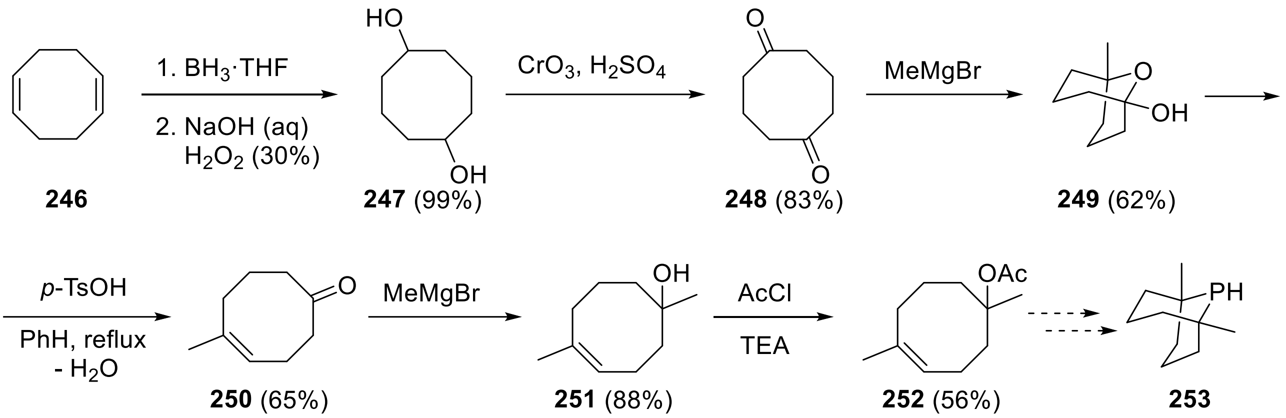
2.4 Toward the synthesis of 1,5-dimethyl-9-phosphabicyclo[3.3.1]nonane

9-Phosphabicyclo[3.3.1]nonane (**239**) was necessary for the synthesis of ligands **208** and **210**. Unfortunately, phosphabicyclononane (phobane) is commercially available only as a mixture of [3.3.1] and [4.2.1] isomers (**239** and **240**, respectively). Providentially, Pringle *et. al.* suggested a convenient method for the separation of these isomers.[74] The reported separation procedure was based on the different isomer reactivities. Following the literature protocol, the mixture of isomers was quaternized with formaldehyde and after crystallization from isopropanol yielded a mixture of phosphonium salts **241** and **242** in 60% yield. Afterwards, one hydroxymethyl group was cleaved from the more reactive [4.2.1] isomer **242** with NaOH (aq., 1 eq, ca. 1 M) and hydroxymethylphosphine **244** was removed by repeated liquid-liquid extractions with pentane. Phosphonium salt **243** was then conveniently dehydroxymethylated with a mixture of sodium hydroxide and sodium bisulfite in aqueous solution and isolated by repeated extractions with pentane. Phosphine **239** was treated with triflic acid furnishing the air-stable triflate salt **245** in 86% yield for more convenient handling and storage of the material.



Scheme 24. Phobane isomer separation

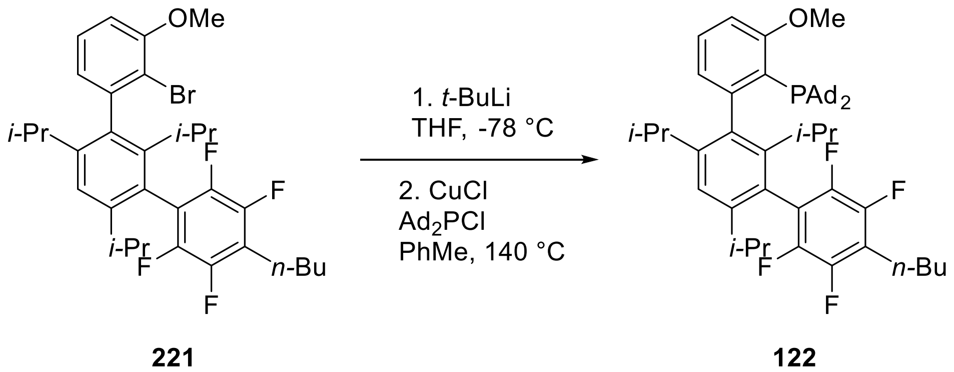
Disappointingly, at the time of this project, 1,5-dimethylcycloocta-1,5-diene was no longer commercially available as a starting material for the synthesis of 1,5-dimethyl-9-phosphabicyclo[3.3.1]nonane (**253**), which was needed for the synthesis of the ligand **209**, thus, a more total-synthesis-like strategy was developed (Scheme 25). Starting with cycloocta-1,5-diene (COD, **246**), hydroboration, and subsequent oxidation with hydrogen peroxide yielded cyclooctane-1,5-diol (**247**) in a good 69% yield. For this synthesis, borane·THF adduct was prepared by reacting sodium borohydride suspension in THF with neat $BF_3 \cdot Et_2O$. Following Jones oxidation, cyclooctane-1,5-dione (**248**) was obtained in 83% yield. Unfortunately, due to strong transannular interaction, double Grignard addition to diketone **248** was unfeasible.[75] Instead, 5-methyl-9-oxabicyclo[3.3.1]nonan-1-ol (**249**) was formed in 62% yield. Concisely, 5-methyl-9-oxabicyclo[3.3.1]nonan-1-ol (**249**) was refluxed with *p*-TsOH in benzene with a Dean-Stark apparatus and thus, after column chromatography, gave 5-methylcyclooct-4-en-1-one (**250**) in 65% yield. 1,5-Dimethylcyclooct-4-en-1-ol (**251**) was obtained in 88% yield after treating enone **250** with methylmagnesium bromide. Unfortunately, acetylation was the last step accomplished in the synthesis of 1,5-dimethyl-9-phosphabicyclo[3.3.1]nonane (**253**) due to impending submission deadlines. The second acetoxy group will be introduced by acetoxymercuration-demercuration[76] reaction and then the phosphination with $P(TMS)_3$ (**236**, *vide supra*, 2.3.2) should yield the elusive 1,5-dimethyl-9-phosphabicyclo[3.3.1]nonane (**253**).



Scheme 25. Synthesis plan of **253**

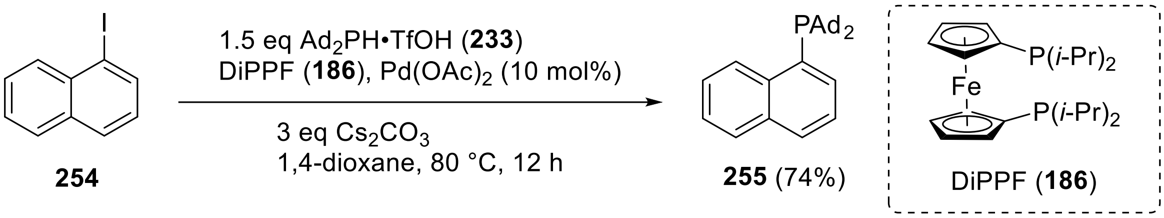
2.5 C-P cross coupling

Literature suggests an eccentric approach for coupling di-(1-adamantyl)chlorophosphine (**229**) with the ligand backbone (Scheme 26).[47] Bromoterphenyl **221** is lithiated with *t*-BuLi, then organocopper species is formed by the addition of copper (I) chloride. Then the reaction mixture is diluted with anhydrous toluene and lighter solvents are tediously removed under high vacuum, while maintaining the reaction mixture temperature at -78 °C. Afterwards Ad$_2$PCl (**229**) is added, and the reaction mixture is transferred to a glass pressure vessel and heated to 140 °C. Not only is this method hardly scalable, it poses an explosion hazard. Nevertheless, multiple vain attempts to replicate this literature procedure were made. Unfortunately, this endeavor was unfruitful, and the only product formed was the dehalogenated backbone. Thus, a more eloquent and scalable method was developed.



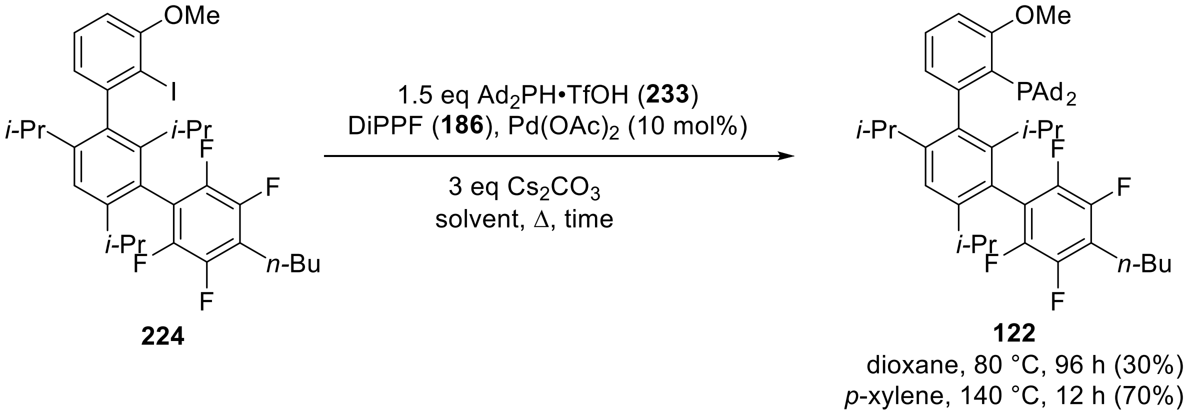
Scheme 26. CuCl mediated C-P cross coupling

The new strategy was based on palladium catalyzed C-P cross-coupling reaction (*vide supra*, 2.5, Scheme 27). First, to test whereas it was possible to couple excessively bulky di(1-adamantyl)phosphine triflate (**233**) with iodoarenes, 1-iodonaphthalene (**254**) was chosen as an alternate substrate. Coupling reaction with di(adamantly)phosphine salt **233**, DiPPF (**186**) as the ligand, 10 mol% of palladium acetate and cesium carbonate as the base, yielded phosphine **255** in good 74% yield.



Scheme 27. Synthesis of phosphine **255**

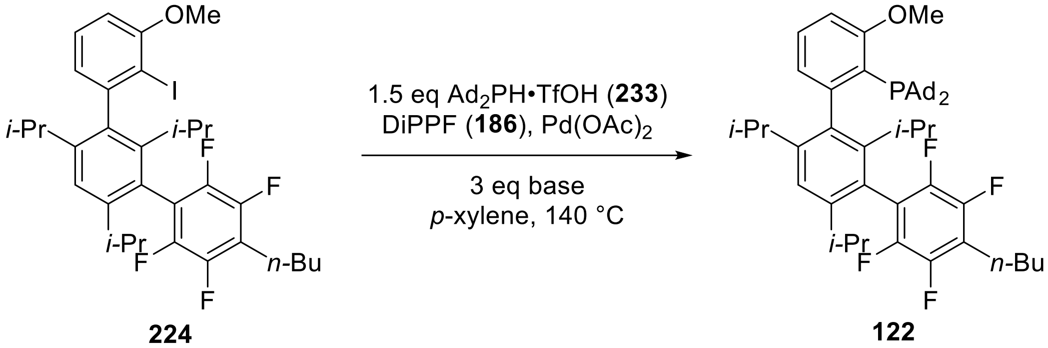
However, under the same reaction conditions, coupling of the ligand backbone **224** with di(adamantly)phosphine salt **233** was very sluggish and ultimately showed only 30% conversion after 96 h (Scheme 28). On the other hand, excessive steric hindrance of both the backbone and the phosphine suggests that higher temperatures may be necessary. Thus, the reaction solvent was changed from 1,4-dioxane to higher boiling *p*-xylene. Fortunately, the increase in reaction temperature allowed the ligand **122** to be formed in a respectable 70% yield.



Scheme 28. Terphenyl **224** C-P cross-coupling reaction with phosphine triflate **233**

Considering the overall economics of the synthesis, lower palladium loadings were investigated. Diminishing results were observed with lower palladium loadings and cesium carbonate as the base (Entries 1-3, Table 17). Cesium carbonate is hardly soluble under these reaction conditions, thus may be the culprit for slower and less yielding reactions. However, reactions with more economical and soluble sodium *tert*-butoxide showed promising results. Palladium loadings were successfully reduced from 10 mol% to 2.5-5 mol% without significant decrease in the yield (Entries 4-7, Table 17).

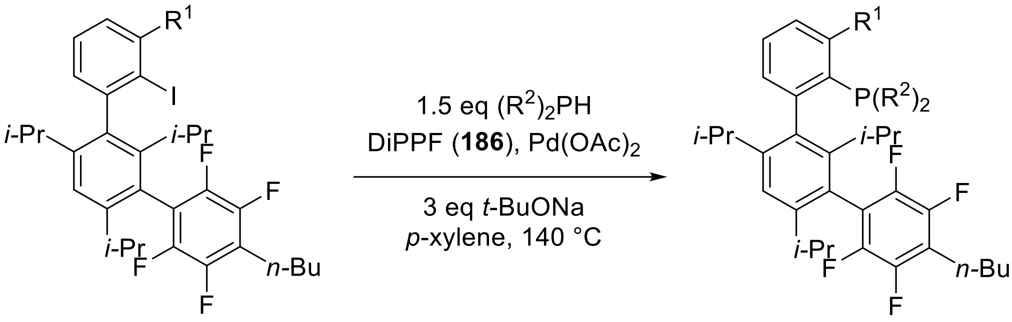
Table 17. C-P cross coupling reaction optimization



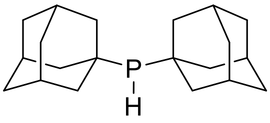
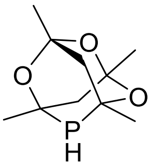
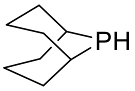
Entry	Pd, mol%	Base	Yield, %
1	10	Cs_2CO_3	70
2	5	Cs_2CO_3	40
3	1	Cs_2CO_3	n/a
4	10	NaO*t*-Bu	80
5	5	NaO*t*-Bu	70
6	2.5	NaO*t*-Bu	69
7	1	NaO*t*-Bu	30

After optimizing the C-P cross-coupling reaction conditions for sterically congested substrates, “caged” phosphines were investigated as the coupling partners (Table 18). Yields from coupling of the methoxy- and *tert*-butoxy ligand backbones **224** and **226** with di(1-adamantyl)phosphine (**232**) were similar (69% and 65%, respectively, Entry 1 and 2, Table 18), suggesting that additional steric hindrance from *tert*-butoxy group does not impede the coupling reaction. However, lesser results were observed with 1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphaadamantane (CgPH, **256**). Even though coupling of iodide **224** with phosphine **256** falls under statistically similar results to di(1-adamantyl)phosphine (**232**) and 9-phosphabicyclo[3.3.1]nonane (**239**), same could not be said for the *tert*-butoxy analogue **226**. Substantial reduction in yield was observed along with significant darkening of the reaction mixture. Presumably, CgPH (**256**) undergoes decomposition under high temperatures and highly basic reaction conditions.

Table 18. Synthesis of ligands (product yields, %)

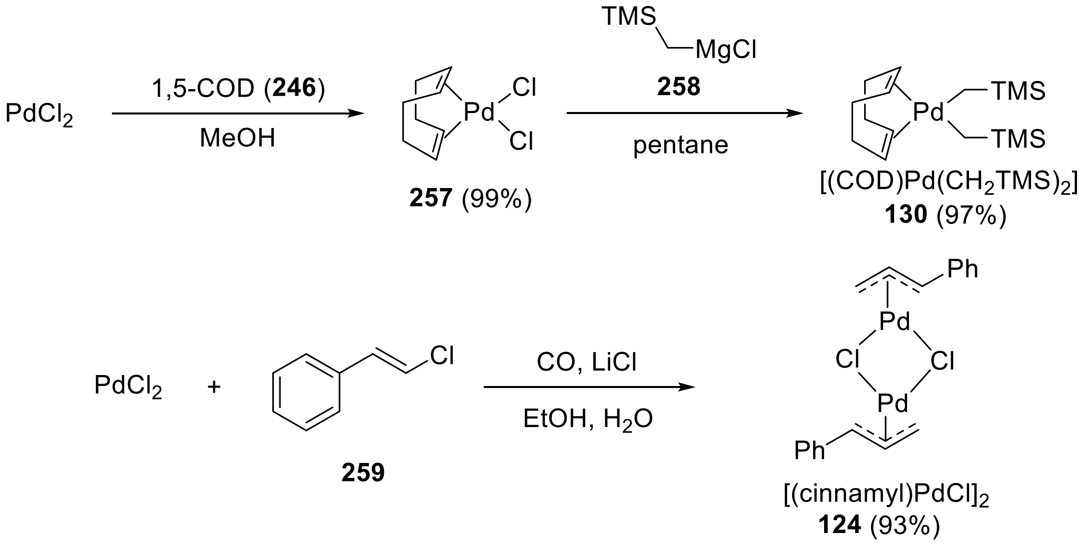


224, 226 → **122, 205-208, 210**

Entry	$(R^2)_2$PH R^1	 **232**	 **256**	 **239**
1	MeO **224**	**122** (69)	**206** (57)	**210** (62)
2	*t*-BuO **226**	**205** (65)	**207** (20)	**208** (-)

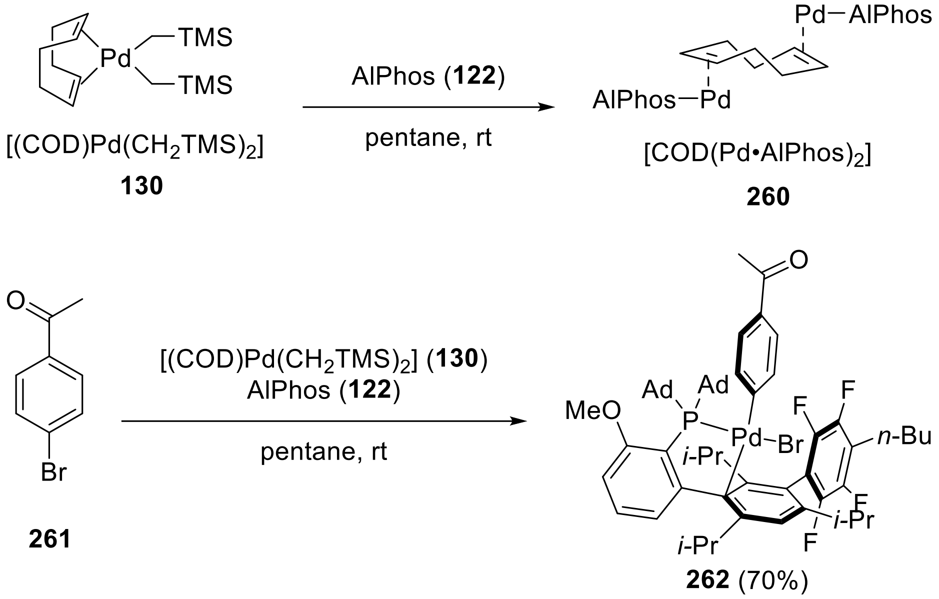
2.6 Palladium precatalyst synthesis

Literature suggest two optimal palladium precatalysts for fluorination reactions, bis[(trimethylsilyl)methyl](1,5-cyclooctadiene)palladium(II) ([(COD)Pd(CH_2TMS)$_2$], **130**) and [(cinnamyl)PdCl]$_2$ (**124**).[31,77] However, [(COD)Pd(CH_2TMS)$_2$] (**130**) is expensive and more importantly, vastly unstable above 0 °C. Therefore, synthesis of precatalyst **130** was investigated. Dichloro(1,5-cyclooctadiene)palladium(II) ((COD)PdCl$_2$, **257**) was quantitively prepared by sonicating a mixture of cycloocta-1,5-diene (COD, **246**) and palladium chloride in methanol under argon atmosphere (Scheme 29). (Trimethylsilyl)methylmagnesium chloride (**258**) was then prepared from (chloromethyl)trimethylsilane and added to a suspension of (COD)PdCl$_2$ (**257**) in pentane. After complete transmetallation, as judged by disappearance of characteristic yellow color of (COD)PdCl$_2$, reaction mixture was filtered and filtrate were repeatedly extracted with cold pentane. Solvents were then removed *in vacuo* while maintaining the mixture's temperature below 0 °C yielding [(COD)Pd(CH_2TMS)$_2$] (**130)** in excellent 97% yield. Additionally, as a less fastidious precatalyst alternative, [(cinnamyl)PdCl]$_2$ (**124**) was prepared in superb 93% yield by treating a mixture of palladium chloride, lithium chloride and cinnamyl chloride (**259**) with carbon monoxide.



Scheme 29. Synthesis of [(COD)Pd(CH$_2$TMS)$_2$] (**130**) and [(cinnamyl)PdCl]$_2$ (**124**)

According to the literature procedures, the formation of the catalyst **260** can be synthesized from [(COD)Pd(CH$_2$TMS)$_2$] (**130**) and AlPhos ligand (**122**) (Scheme 30). However, attempts to prepare complex **260** were unsuccessful. Literature suggests that the reaction should be conducted at room temperature. However, during the reaction excessive precipitation of the palladium black was observed, suggesting that the rate of complex formation is outcompeted by [(COD)Pd(CH$_2$TMS)$_2$] (**130**) decomposition. To find out whether [(COD)Pd(CH$_2$TMS)$_2$] (**130**) could be used for fluorination reactions *per se*, preparation of 1-(4-bromophenyl)ethan-1-one (**261**) oxidative addition complex under the same reactions conditions was attempted. Amusingly, complex **262** was formed in 70% yield and no formation of palladium black was observed, suggesting that oxidative addition outcompeted precatalyst decomposition reaction and thus complex **130** may be used as a precatalyst.

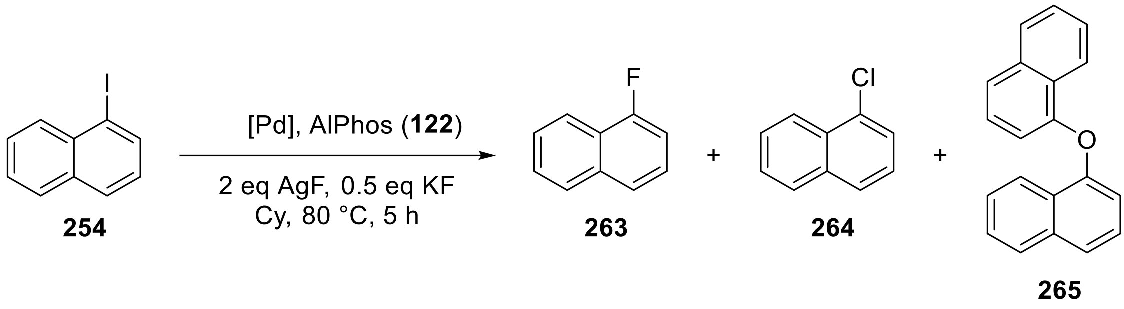


Scheme 30. Synthesis of palladium complexes **260** and **262**

2.7 Fluorination optimization

The fluorination reaction itself had to be optimized prior to screening of the new ligands. According to literature cyclohexane suppresses the formation of dehalogenated products, and thus it was the solvent of choice.[46] Unexpectedly, results from fluorination of 1-iodonaphtalene (**254**) using $[(COD)Pd(CH_2TMS)_2]$ (**130**) as a precatalyst were rather ambiguous. After 5 h only 5% (GC-MS) of 1-fluoronaphtalene (**263**) was observed (Entry 1, Table 19) along with precipitation of palladium black, suggesting that it may not be sufficiently stable under these fluorination reaction conditions. In order to avoid this fastidious precatalyst altogether, different precatalysts were investigated. Opposing to what literature[77] suggests, palladium acetate was an effective precatalyst and formed 33% of 1-fluoronaphtalene (**263**, Entry 2, Table 19). The best results were obtained when $[(cinnamyl)PdCl]_2$ (**124**, Entry 3, Table 19) was used in place of $[(COD)Pd(CH_2TMS)_2]$ (**130**). Full conversion of starting material occurred within 5 h. Additionally C-Cl reductive elimination was observed due to chloride presence in the reaction mixture, indicating that aryl chlorides are mostly inactive under this catalytic system. Notably, diaryl ether **265** formation is caused by residual moisture content in the reaction mixture.[38] Additionally, superior results were achieved when cyclohexane was dried on a potassium mirror and inorganic fluorides were heated in high vacuum.

Table 19. Palladium precatalyst screening



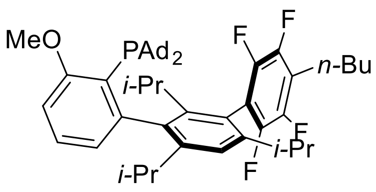
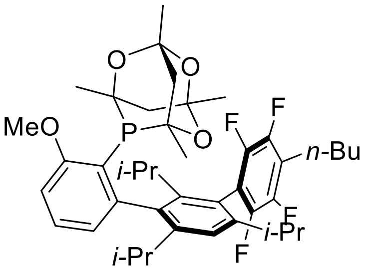
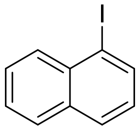
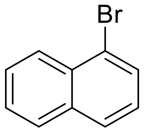
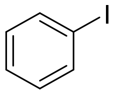
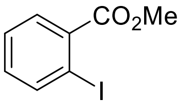
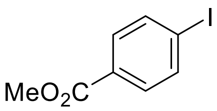
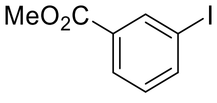
Entry	[Pd]	mol%	Ar-F, %	Ar-Cl, %	ArOAr, %
1	[(COD)Pd(CH_2TMS)$_2$]	5	5	5	4.3
2	Pd(OAc)$_2$	10	33	0.31	0
3	[(cinnamyl)PdCl]$_2$	2	92	4	3

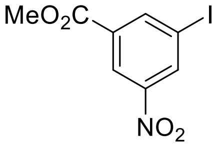
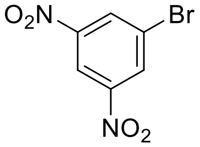
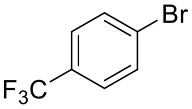
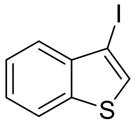
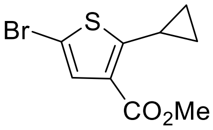
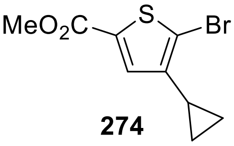
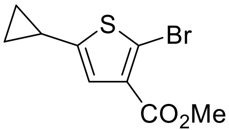
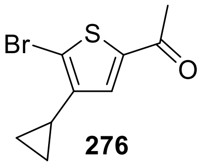
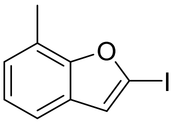
2.8 Ligand screening for fluorination reaction

After optimizing the fluorination reaction conditions, synthesized ligands **122**, **205**, **206** and **210** were submitted to extensive screening to assess their catalytic activity (Table 20, Appendix 2). Substrates **173**, **174**, **254**, **266-277** were chosen based on availability or their synthetic relevance. Care was taken to exclude moisture from the reaction by vacuum-drying the inorganic fluorides and storing cyclohexane on a potassium mirror under argon. Anhydrous reaction conditions gave superior results compared to the reaction optimization. Substrates **254**, **173**, **271** showed exceptional reactivities and were fully converted to corresponding fluorides with ligand **122** in only 2 h. Different reaction rates were observed comparing iodo- and bromonaphthalenes **254** and **266** (Entries 1 and 2, Table 20), suggesting that in this case oxidative addition was the rate limiting step. On the other hand, steric effects to the reaction rate were noticed comparing methyl *o*-, *m*- and *p*-iodobenzoates (**268**, **174**, **173**, Entries 4-6, Table 20). Fluorination of methyl 2-iodobenzoate (**268**) was sluggish and only 5% conversion to methyl 2-fluorobenzoate was seen after 24 h (GC-MS). In comparison, *para* isomer **173** was the most reactive and gave full conversion in 2 h and the *meta*-iodobenzoate **174**, falling slightly short, was fluorinated in 6 h. Similarly, electron deficient *meta* substituted arenes **269** and **270** were successfully fluorinated in 6 h (Entries 7, 8 Table 20). Curiously, slightly slower reaction rate was noticed for iodobenzene (**267**), full conversion attained in 24 h (Entry 3, Table 20), signifying that additional steric bulk may be necessary for efficient smaller substrate fluorinations. Following on this idea, bromothiophenes **273-276** (Entries 11-14, Table 20) were subjected to fluorination, as well. Methyl 5-bromo-4-cyclopropylthiophene-2-carboxylate (**274**, Entry 13, Table 20) showed unusually high reactivity towards fluorination and was successfully fluorinated preeminently in 24 h, potentially giving access to a novel class of fluorinated thiophenes. However, similarly to *o*-

iodobenzoate (**268**), methyl 2-bromo-5-cyclopropylthiophene-3-carboxylate (**275**, Entry 11, Table 20) was vastly unreactive and no fluorinated product were formed even after 24 h. Unfortunately, 3-iodobenzo[*b*]thiophene (**272**) and 2-iodo-7-methylbenzofuran (**277**) could not be fluorinated under the same reaction conditions, presumably owing to their increased electron richness and diminished steric bulk (Entries 10, 15, Table 20).

Table 20. Screening of ligands and substrates

		Ligands	
		 **122**	 **206**
Entry	Substrate	Conversion, %[a]	Conversion, %[a]
1	 **254**	91[b]	16[c]
2	 **266**	90[d]	3[c]
3	 **267**	71[d]	0[d]
4	 **268**	5[d]	5[c]
5	 **173**	83[b]	7[c]
6	 **174**	86[c]	0[d]

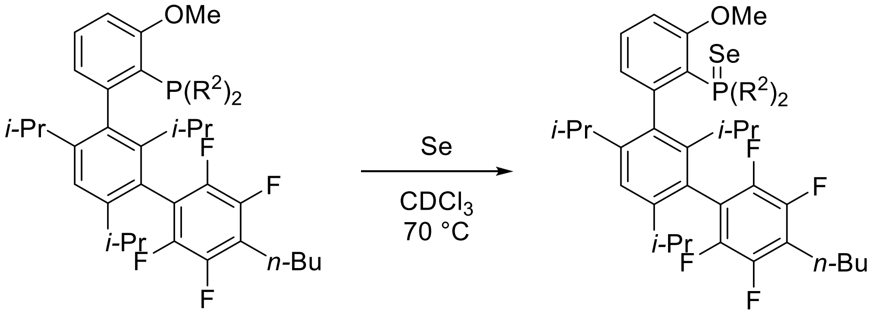
7	 **269**	100^c	0^d
8	 **270**	91^c	0^d
9	 **271**	94^b	2^d
10	 **272**	0^d	0^d
11	 **273**	0^d	0^d
12	 **274**	33^d	0^d
13	 **275**	0^d	0^d
14	 **276**	3^d	0^d
15	 **277**	0^d	0^d

^{a}estimated by GC, duration – ^{b}2 h, ^{c}6 h, ^{d}24 h

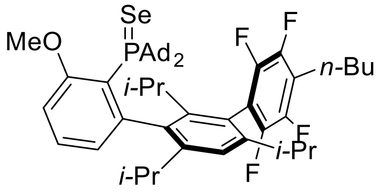
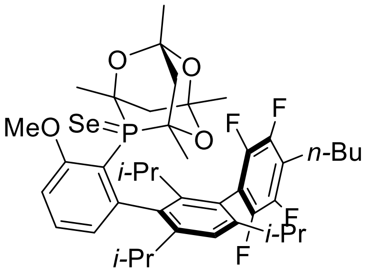
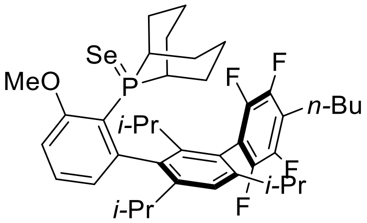
In contrast, screening results from ligands **205**, **206** and **210** were not as amenable as **122**. While **205** and **210** were inactive, **206** showed some equivocal activity. 1-Iodonaptalene (**254**) was sluggishly fluorinated achieving 16% (GC-MS) conversion after 6 h reaction time. Ostensibly, different reaction conditions may need to be investigated. At this point, it’s not entirely clear whether different steric and electronic properties of the ligand hinder the oxidative addition or reductive elimination step. Additional experimentation is needed to determine these effects. Thermolysis of corresponding Ar-Pd-F complexes may give insight on this issue too but is yet to be conducted. Nevertheless, GC-MS analysis of the resulting rection mixtures revealed interesting details. Even though fluorination activity was modest at best, formation of diaryl ethers and/or self-coupling products suggests that ligand (**206**) may be useful for other type cross-coupling reactions with heteroarenes (Appendix 2).

Furthermore, to gain some insight on the electronic properties of the ligands, phosphine selenides **278-280** were prepared by treating phosphine ligands **122**, **206**, **210** with elemental selenium in chloroform. NMR analysis of these selenides (Table 21) gave some insight into electronics of the corresponding phosphines. 1,3,5,7-Tetramethyl-2,4,6-trioxa-8-phosphaadamantane based ligand selenide **280** (Entry 3, Table 21) showed increased electron donating properties, thus it may be suitable for more electron donating substrates in cross-coupling reactions. This idea is corroborated with data presented in Appendix 2. The formation of self-coupling or biaryl ether products is more favorable than C-F reductive elimination. On the other hand, selenide **280** showed favorable decreased electron donating properties of ligand **210**, compared to AlPhos (**122**, Entry 1, Table 21), but in this case steric properties may be impeding the fluorination reaction.

Table 21. Phosphine selenide synthesis and evaluation of ${}^{1}J_{\text{P-Se}}$ coupling constants



122, 206, 210 → **278-280**

Entry	Selenide	${}^{1}J_{\text{P-Se}}$, Hz	δ(P), ppm
1	 **278**	719.7	85.6
2	 **279**	767.6	35.0
3	 **280**	683.1	36.8

3. CONCLUSIONS

Fluorinated (hetero)arenes continue to attract the attention of organic chemists due to their unique properties and their potential as building blocks for new biologically active compounds. As literature suggests, one of the most universal methods for synthesizing fluorinated (hetero)arenes is palladium catalysis. The research described in this thesis was conducted to investigate the steric and electronic influences of various phosphine ligands on C-F reductive elimination.

Computational evaluation of cyclic "caged" phosphine ligands revealed that complexes based on these structures may have favorable catalytic properties. Evaluation of tetramethyl-2,4,6-trioxa-8-phosphaadamantane based ligand **206** showed that both steric and electronic properties are equally important, thus a "golden ratio" between them must be found for an efficient fluorination catalyst design.

During this project a new high yielding and scalable one-pot procedure for the synthesis of AlPhos ligand backbone (**224**) was developed. Replacement of bromine with iodine in the final backbone synthesis step has not only solved the halogen impurity issues, but also allowed for more convenient purification techniques to be used.

A divergent approach for the synthesis of AlPho**s** ligand analogs was developed and optimized for multi-gram-scale synthesis, thus ligand diversity was increased. Methoxy group cleavage with BBr_3 and subsequent *tert*-butylation with isobutene was found to be the most useful route.

A new umpolung synthetic strategy for cyclic and bicyclic phosphines was conceptualized and is currently under development. The use of $P(TMS)_3$ for *in situ* generation of phosphine nucleophile solved the telomerisation issue presented in literature overview. Furthermore, a medium scale synthesis for di(1-adamanyl)phosphine triflate (**233**) was developed and tested on 2.2 mol.

A general protocol for cross coupling the highly sterically demanding aryl backbone with equally sterically demanding phosphines was developed, optimized, and applied for more convenient synthesis of multiple ligands. Higher reaction temperatures, sodium *tert*-butoxide as the base and *p*-xylene as solvent allowed for higher yielding and more efficient C-P cross coupling reactions to be carried out.

A convenient and mild fluorination protocol was optimized to work with less fastidious palladium sources and without the need of a glovebox. This protocol was successfully implemented for fluorination of cyclopropylthiophene **274**, potentially giving access to a novel class of thiophene derivatives.

Extensive screening of the ligands was conducted giving valuable insight into the ligand design. 1,3,5,7-Tetramethyl-2,4,6-trioxa-8-phosphaadamantane based ligand **206** showed some modest catalytic activity that corresponded with the computational data. Therefore, this is a valid approach for phosphine ligand design, and “caged” phosphine structures can be used in fluorination ligand architecture.

4. EXPERIMENTAL

4.1 General experimental details

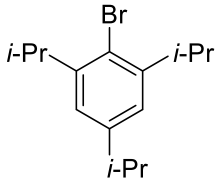
All reactions were performed under an argon atmosphere unless otherwise specified. Commercially available starting materials were bought from Apollo Scientific (UK), Sigma-Aldrich, Strem, Biosynth. THF, Et_2O, *p*-xylene, 1,4-dioxane and toluene were dried in a solvent still over Na/benzophenone, CCl_4 was dried over P_2O_5 and DBU over CaH_2, cyclohexane was dried over molecular sieves (4Å) and stored over potassium mirror under argon. KF and AgF were dried in high vacuum at 140 °C for 8 h prior to each ligand screening. Anhydrous AgF was prepared by dissolving Ag_2CO_3 in concentrated HF followed by precipitation with acetone.

NMR spectra were recorded on Bruker Avance III spectrometer (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, 162 MHz for ^{31}P NMR and 376 MHz for ^{19}F NMR). Chemical shifts δ are reported with respect to the residual solvent peak and are given in ppm. GC-MS analyzes were performed on Shimadzu GCMS-QP2010 ultra plus system using a Restek Rxi-5ms (30 m, 0.25 mmID) column. Reactions were monitored by TLC using Merk TLC silica gel 60 F_{254} plates and visualized using UV light (254 nm), cerium ammonium molybdate (CAM) or $KMnO_4$ stain. Column chromatography was performed on ZEOprep 60 silica gel (35-70 µm, Apollo Scientific).

Quantum chemical calculations were performed using Gaussian 09.[78] All geometry optimizations were performed using the B3LYP[79] functional and the 6-31+G(d) basis set. The optimized geometries were verified by frequency computations – transition-state (one imaginary frequency) or ground-state (zero imaginary frequencies). GaussView[80] was used to construct all structures for geometrical optimization. The 3D images of optimized geometries were generated in CYLview.[81]

4.2 Experimental procedures

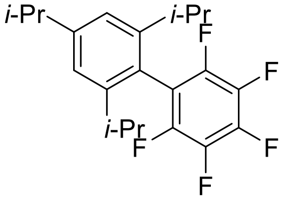
2-Bromo-1,3,5-triisopropylbenzene (**213**)



1,3,5-Triisopropylbenzene (**212**, 1 eq, 0.34 mol, 70 g) was dissolved in CCl_4 (172 mL) and Fe powder (10 mol%, 0.034 mol, 1.92 g) was added. Reaction mixture was cooled to -30 °C and a solution of bromine (1 eq, 0.34 mol, 55 g) in CCl_4 (172 mL) was added dropwise over a 60 min period while maintaining -30 °C. Then the reaction mixture was allowed to warm-up to room temperature, and it was filtered. Afterwards, the mixture was transferred to a separatory funnel and washed with water (2×700 mL) and a saturated aqueous solution of $NaHCO_3$ (2×500 mL). The organic phase was separated, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. After vacuum distillation, compound **213** (81 g, 83%) was obtained as a colorless oil.

(**213**): bp = 85 °C (0.8 mbar); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 1.9 Hz, 2H), 3.52 (hept, *J* = 6.9 Hz, 2H), 2.91 (hept, *J* = 7.0 Hz, 1H), 1.38 – 1.18 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 147.4, 123.6, 122.3, 34.0, 33.6, 24.0, 23.1; MS (EI) calcd for $C_{15}H_{23}Br$ [M+]: 282/284; found 282/284.

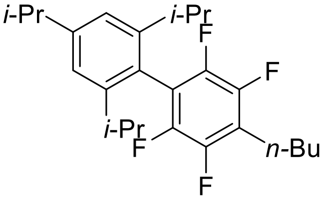
2,3,4,5,6-Pentafluoro-2',4',6'-triisopropyl-1,1'-biphenyl (**214**)



A solution of *n*-BuLi (2.5 M in hexanes, 1.1 eq, 0.17 mol, 66 mL) was added dropwise to a solution of bromide **213** in THF (375 mL) at -78 °C while maintaining the temperature. After complete addition, the reaction mixture was stirred for 1 h and then cannula-transferred to a cooled to -78 °C solution of hexafluorobenzene (1.5 eq, 0.23 mol, 42 g). After complete addition, the reaction mixture was allowed to warm-up to room temperature over night. Then all solvents were removed *in vacuo*, the material was suspended in hexanes (500 mL) and filtered through a layer of Celite®. Afterwards, filtrates were concentrated and recrystallized from *i*-PrOH (250 mL). After filtration biphenyl **214** (38 g) was collected as a white crystalline solid. Filtrates were concentrated and recrystalized from a minimal amount of *i*-PrOH to give additional 8.2 g (46 g combined, yield 84%).

(**214**):^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 2H), 2.88 (hept, *J* = 6.9 Hz, 1H), 2.34 (hept, *J* = 6.8 Hz, 2H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.05 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 147.6, 121.3, 119.9, 34.3, 31.5, 24.0, 23.9; MS (EI) calcd for $C_{21}H_{23}F_5$ [M+]: 370; found 370.

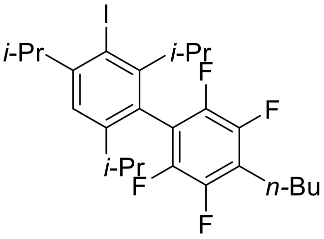
4-Butyl-2,3,5,6-tetrafluoro-2',4',6'-triisopropyl-1,1'-biphenyl (**215**)



A solution of *n*-BuLi (2.5 M in hexanes, 1.1 eq, 88 mmol, 36 mL) was added dropwise to a solution of biphenyl **214** (1 eq, 80 mmol, 30 g) in THF (240 mL) at -78 °C, while maintaining the temperature. After complete addition, the reaction mixture was allowed to slowly warm-up to room temperature overnight. Then, all solvents were removed *in vacuo*. The remaining material was suspended in hexanes (400 mL) and filtered through a layer of silica gel eluting with hexanes. Filtrates were then evaporated *in vacuo* to give product **215** (32 g, 97%) as a thick oil.

(**215**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 2H), 2.87 (hept, *J* = 7.0 Hz, 1H), 2.79 – 2.67 (m, 2H), 2.40 (hept, *J* = 7.0 Hz, 2H), 1.67 – 1.54 (m, 2H), 1.38 (hept, *J* = 7.3 Hz, 2H), 1.22 (d, *J* = 7.0 Hz, 6H), 1.04 (d, *J* = 6.9 Hz, 12H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 147.6, 121.4, 121.2, 120.1, 119.9, 116.8, 34.3, 31.5, 31.4, 24.1, 24.0, 22.8, 22.5, 13.8; MS (EI) calcd for $C_{25}H_{32}F_4$ [M+]: 408; found 408.

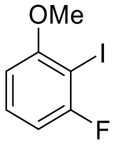
4-Butyl-2,3,5,6-tetrafluoro-3'-iodo-2',4',6'-triisopropyl-1,1'-biphenyl (**216**)



NIS (2.5 eq, 195 mmol, 43.83 g) was added in a single portion to a solution of compound **215** (1 eq, 78 mmol, 32 g) in a mixture of EtOAc (203 mL) and acetic acid (203 mL). It was followed by the dropwise addition of H_2SO_4 (conc., 21 mL) with vigorous stirring. The reaction was then heated at 50 °C for 17 h. The reaction mixture was allowed to cool to room temperature and diluted with hexanes (500 mL) and water (500 mL). Organic layer was separated, washed with NaOH (aq., 2 M, 2×300 mL), Na_2SO_3 (saturated aq., 1×300 mL) and brine (1×200 mL). The organic layer was then separated, dried with Mg_2SO_4, filtered and concentrated *in vacuo*. The crude product was then recrystallized from *i*-PrOH (200 mL) and after filtration iodide **216** (33.27 g, 80%) was obtained as an off-white crystalline solid.

(**216**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 3.88 (p, *J* = 7.3 Hz, 1H), 3.73 – 3.37 (m, 1H), 2.89 – 2.69 (m, 2H), 2.48 – 2.23 (m, 1H), 1.70 (p, *J* = 7.7 Hz, 2H), 1.60 – 1.38 (m, 4H), 1.31 (d, *J* = 6.8 Hz, 6H), 1.24 – 1.07 (m, 6H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.96 (d, *J* = 7.2 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 148.9, 147.7, 121.2, 110.2, 42.0, 40.5, 35.6, 31.5, 30.3, 25.4, 24.0, 23.4, 22.8, 22.4, 21.1, 20.1, 13.8; MS (EI) calcd for $C_{25}H_{31}F_4I$ [M+]: 534; found 534.

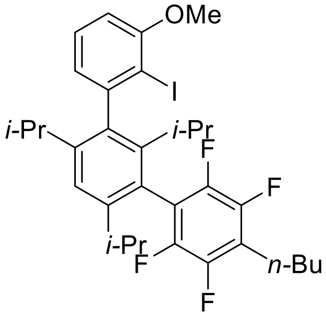
1-Fluoro-2-iodo-3-methoxybenzene (**222**)



A solution of *n*-BuLi (2.5 M in hexanes, 1.2 eq, 240 mmol, 96 mL) was added dropwise to solution of 1-fluoro-3-methoxybenzene (**218**) (1 eq, 0.20 mmol, 25 g) in THF (400 mL) while maintaining -90 °C. After complete addition, reaction was stirred at -90 °C for 30 min and then solution of iodine (I_2, 1.1 eq, 0.22 mol, 56 g) in THF (200 mL) was added dropwise to the reaction mixture while maintaining -90 °C. After complete iodine addition, the reaction mixture was warmed-up to room temperature and saturated aq. solution of Na_2SO_3 (300 mL) was added. Organic phase was separated and dried over $MgSO_4$, filtered and concentrated. Vacuum distillation was performed to provide compound **222** (46 g, 91%) as a colourless liquid.

(**222**): bp = 79-80 °C (2 mbar); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 1H), 6.72 (t, *J* = 7.9 Hz, 1H), 6.61 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 161.6, 159.9, 159.8, 130.3, 130.2, 108.4, 108.2, 106.4 (×2), 77.2, 74.3, 74.0, 56.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.4 (t, *J* = 7.0 Hz); MS (EI) calcd for C_7H_6FIO [M+]: 252; found 252.

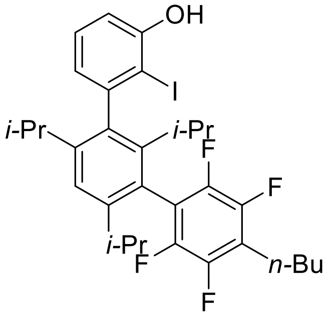
4-Butyl-2,3,5,6-tetrafluoro-2''-iodo-2',4',6'-triisopropyl-3''-methoxy-1,1':3',1''-terphenyl (**224**)



A flame-dried two neck round bottom flask, equipped with a Teflon coated stir bar, was charged with magnesium (2.3 eq, 110 mmol, 2.70 g). The flask was fitted with an oven-dried reflux condenser, and the second opening was fitted with an addition funnel. The system was connected to a Schlenk line, and flushed with argon. Anhydrous THF (190 mL**)** was added to the flask via cannula, and the flask was placed into a pre-heated oil bath to reflux. Once refluxing, a solution of iodide **216** (1 eq, 49 mmol, 26 g) in THF (50 mL) was added dropwise via the addition funnel. Consumption of starting material was monitored *via* TLC (hexanes) until the iodoarene was completely consumed. Then, a solution of compound **222** (1.04 eq, 50 mmol, 12.6 g) in THF (120 mL) was slowly added to the reaction mixture (1-2 drops per second). After complete addition of **222** the reaction was monitored via TLC (40:1 hexanes:EtOAc) until its full consumption. The reaction mixture was allowed to cool to rt and then a solution of iodine (I_2, 1.05 eq, 51 mmol, 12.8 g) in THF (100 mL) was added dropwise until the reaction mixture maintained a persistent purple color (the entire iodine solution was not always used). At this time, the flask was opened to the air and its content was transferred to a separatory funnel. The reaction mixture was quenched by subsequently adding an aq. solution of HCl (2 M, 200 mL) and saturated aq. solution of Na_2SO_3 (50 mL). The organic phase was separated, and the aqueous layer was extracted with EtOAc (2×200 mL). Combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Crude product was recrystallized from a minimal amount of *i*-PrOH to yield product **224** (32.74 g, 80%) as a white powder.

(**224**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 2H), 6.89 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.81 (dd, *J* = 8.2, 1.3 Hz, 1H), 3.97 (s, 3H), 2.83 (t, *J* = 7.7 Hz, 2H), 2.71 (hept, *J* = 7.0 Hz, 1H), 2.46-2.35 (m, 2H),, 1.70 (dq, *J* = 12.8, 7.5 Hz, 2H), 1.46 (hept, *J* = 7.8, 7.3 Hz, 2H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 3H), 1.05 (d, *J* = 6.8 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.84 (ddd, *J* = 11.0, 7.2, 1.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 148.3, 148.2, 147.6, 146.1, 143.3, 143.0, 141.1, 128.6, 123.2, 121.5, 120.5, 120.2, 120.0, 119.8, 118.4, 118.2, 118.0, 108.8, 56.4, 34.7, 32.1, 31.6, 31.5, 30.8, 30.7, 24.9, 24.2 (×2), 23.5, 22.7, 22.4, 21.9, 21.5, 14.1, 13.8.

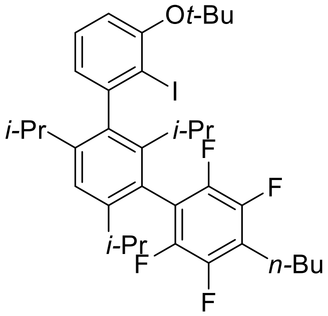
4''-Butyl-2'',3'',5'',6''-tetrafluoro-2-iodo-2',4',6'-triisopropyl-[1,1':3',1''-terphenyl]-3-ol (225)



A solution of BBr_3 (1 M in DCM, 2.8 eq, 28 mmol, 28 mL) was added to a solution of **224** (1 eq, 10 mmol, 6.4 g) in DCM (30 mL) at 0 °C. The reaction was then taken out of ice/salt water bath and stirred at room temperature for 16 h. Then, the reaction was quenched with MeOH (3.5 mL), transferred to a separatory funnel and washed with water (2×50 mL), saturated aq. solution of $NaHCO_3$ (2×50 mL) and brine (1×50 mL). The organic phase was separated, dried over $MgSO_4$, filtered, and evaporated to provide product **225** (6.26 g, 99%) as a very sticky colorless syrup.

(**225**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 2H), 6.98 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.82 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.54 (s, 1H), 2.81 (t, *J* = 7.7 Hz, 2H), 2.69 (p, *J* = 7.2 Hz, 1H), 2.39 (h, *J* = 7.0 Hz, 2H), 1.83 – 1.61 (m, 2H), 1.43 (h, *J* = 7.3 Hz, 2H), 1.22 (d, *J* = 6.9 Hz, 3H), 1.15 (dd, *J* = 12.0, 6.8 Hz, 6H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.81 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 148.6, 147.7, 147.0, 146.2, 143.7, 143.4, 140.8, 129.2, 122.9, 121.7, 120.6, 120.3, 120.1, 120.0, 118.2, 118.0, 117.8, 112.9, 32.1, 31.5, 30.9, 30.7, 25.0, 24.3, 24.2, 24.1, 24.0, 23.4, 22.7, 22.4, 21.9, 21.6, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.87, -145.66 (ddd, *J* = 84.4, 24.4, 13.0 Hz.

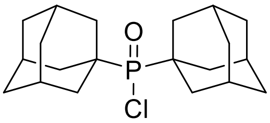
3''-(Tert-butoxy)-4-butyl-2,3,5,6-tetrafluoro-2''-iodo-2',4',6'-triisopropyl-1,1':3',1''-terphenyl (226)



Isobutene was prepared by dehydration of *tert*-butanol over alumina catalyst bed in a quartz tube reactor heated to 370 °C. The tube reactor was made from a 20×300 mm fused-quartz tube, filled with alumina beads. Nichrome wire coil was used for heating and asbestos for thermal insulation. Temperature was carefully controlled with a variable transformer and maintained at ~370 °C. Condensed isobutene (100 eq, 200 mL) was added to a solution of **225** (1 eq, 18 mmol, 11.3 g) in DCM (100 mL) at -78 °C. Then, triflic acid (1 mL) was cautiously added via glass pipette. After 40 minutes, TLC showed that all of the starting material **225** was consumed, so the reaction mixture was quenched with triethylamine (10 mL) and cooling was discontinued. After warming up to room temperature, the reaction mixture was washed with water (2×100 mL). The organic phase was separated, dried over $MgSO_4$, filtered and concentrated. The product was purified by column chromatography on silica gel eluting with (40:1 hexanes:EtOAc) to give compound **227** (9.36 g, 76%) as a white solid.

(**227**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 2H), 7.06 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.93 (d, *J* = 7.4 Hz, 1H), 2.80 (t, *J* = 7.7 Hz, 2H), 2.68 (h, *J* = 7.2 Hz, 1H), 2.38 (dq, *J* = 17.0, 6.9 Hz, 2H), 1.67 (t, *J* = 7.7 Hz, 2H), 1.51 (s, 9H), 1.47 – 1.33 (m, 2H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H), 1.13 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.81 (dd, *J* = 12.9, 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 148.2, 148.1, 147.6, 143.1, 141.5, 127.9, 125.2, 121.6, 120.4, 120.1, 120.0, 119.9, 119.8, 118.4, 118.2, 118.0, 81.7, 53.4, 32.2, 31.5, 30.8, 29.2, 24.9, 24.2 (×2), 23.4, 22.7, 22.4, 21.8, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.9 (broad), -145.8.

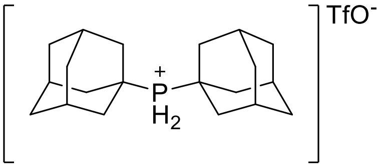
Di-(1-adamantantyl)phosphinic chloride (**231**)



Aluminum chloride (1.05 eq, 2.31 mol, 308 g) was added to a solution of adamantane (1 eq, 2.2 mol, 300 g) in PCl_3 (5 eq, 11 mol, 960 mL) and the mixture was refluxed with stirring for 18 h (condenser was vented to a HCl trap). Then excess PCl_3 was distilled off and the residue suspended in DCM (1.5 L). Very cautiously, while stirring, the suspension was poured on to 2 kg of crushed ice. Afterwards the mixture was filtered through a layer of Celite®, phases were separated, and the aqueous phase was additionally extracted with DCM (2×200 mL). Combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was recrystallized from toluene (1.5 L) to furnish product **231** (308 g, 78%) as a crystalline solid.

(**231**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (dd, *J* = 5.6, 3.0 Hz, 12H), 2.07 (q, *J* = 3.5 Hz, 6H), 1.78 (d, *J* = 2.9 Hz, 12H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 53.4, 46.0, 45.4, 36.9, 36.8, 36.4, 36.3, 27.9, 27.8.

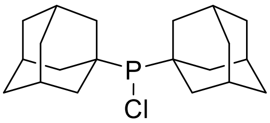
Di-(1-adamantyl)phosphonium trifluoromethanesulfonate (**233**)



Phosphinic chloride **231** (1 eq, 0.86 mol, 304 g) was suspended in THF (1.5 L) under argon atmosphere in a 6 L flask with mechanical stirring. Reaction mixture was cooled to 10 °C in an ice bath and $LiAlH_4$ (1.15 eq, 1 mol, 37 g) was carefully added in portions. After complete addition reaction was warmed to the room temperature and stirred for 16 h. Then the reaction was carefully quenched with EtOAc (150 mL) and diluted with DCM (3 L). To this mixture aq. solution of potassium sodium tartrate (ca. 20%, 500 mL) was added dropwise followed by water (500 mL). The organic phase was cannula-transferred to a new 6 L flask flushed with argon and then, very carefully, triflic acid was added dropwise (1.05 eq, 0.9 mol, 135 g). Then the mixture was concentrated *in vacuo* and the residue triturated with diethyl ether (1 L). The product was collected by filtration, washed with diethyl ether (2×200 mL) and dried in vacuum. Reaction yielded triflate salt **233** (293 g, 75%) as a colorless crystalline solid.

(**233**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (d, *J* = 469.2 Hz, 2H), 2.20 (dd, *J* = 6.6, 2.9 Hz, 12H), 2.13 (q, *J* = 3.3 Hz, 6H), 1.83 (d, *J* = 2.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.8 (×2), 35.4(×3), 35.1, 27.5, 27.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.33; ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.15.

Di-(1-adamantyl)chlorophosphine (**229**)

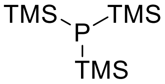


Schlenk tube was charged with triflate salt **233** (1 eq, 6 mmol, 2.72 g). The tube was connected to a Schlenk line and the flask was evacuated and backfilled with argon. This process was repeated a total of three times, followed by the addition of degassed CCl_4. Degassed DBU (1 eq, 6 mmol, 0.91

g) was added to this mixture and the reaction was heated at 60 °C for 3 days. Then the reaction mixture was cooled to room temperature and the lower CCl_4 layer was transferred to a new Schlenk flask. Solvents were removed under high vacuum to provide chlorophosphine **229** (1.8 g, 89%) as an off-white solid.

(**229**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14 – 1.96 (m, 6H), 1.96 – 1.80 (m, 12H), 1.76 – 1.57 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.7, 40.3, 39.9, 39.0, 38.9, 37.0, 36.9, 36.7, 36.4 (×2), 36.3 (×2), 36.1, 36.0, 35.6, 31.7, 28.5, 28.4, 27.9, 27.8, 27.2, 27.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 140.1; MS (EI) calcd for $C_{20}H_{30}ClP$ [M+]: 336; found 336.

Tris(trimethylsilyl)phosphine (**236**)

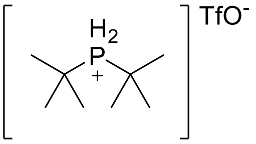


All glassware was dried in an oven at 200 °C overnight. For safety reasons, the synthesis was performed over a large metal tray filled with sand. High purity argon (5.0), dried *via* inline Drierite® filter, was used for the Schlenk line. Note, that all waste produced in this synthesis is highly pyrophoric and toxic and should be quenched with *i*-PrOH with adequate safety precautions!

Under argon atmosphere sodium (1.7 eq, 0.24 mol, 5.47 g) and potassium (1.3 eq, 0.18 mol, 7.1 g) were combined and melted in anhydrous DME (280 mL). After Na/K alloy forms, the mixture was refluxed for 3 h (until the mixture became slightly purple). Then, the mixture was cooled to room temperature and under argon counterflow red phosphorous (red P, 1 eq, 0.14 mol, 4.34 g) was added. The mixture was refluxed for 3 days and cooled to room temperature. Trimethylsilyl chloride (3.3 eq, 0.46 mol, 90 g) solution in DME (70 mL) was introduced dropwise to the black phosphide mixture freshly redistilled under argon and the mixture was refluxed for an additional 4 h. Then the thick mixture was cooled to room temperature and, strictly under argon atmosphere, filtered through a layer of dry celite in a Schlenk filter. The remaining solids were washed with anhydrous, 40-60 petroleum ether (3×60 mL). Filtrates were distilled under argon atmosphere to remove all solvents and the remaining liquid was transferred to a short path distillation apparatus and redistilled under vacuum to yield $P(TMS)_3$ (**236**, 20.8 g, 60 %) as a colorless, slightly viscous liquid.

(**236**): bp = 64-65 °C (4 mbar); ^{1}H NMR (400 MHz, C_6D_6) δ 0.08 (d, J = 4.7 Hz, 27H); ^{13}C NMR (100 MHz, C_6D_6) δ 2.55.

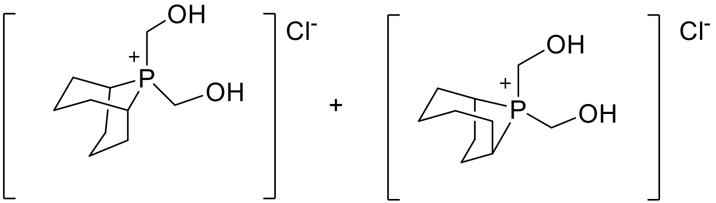
Di-tert-butylphosphonium trifluoromethanesulfonate (238)



Under argon atmosphere triflic acid (2 eq, 2 mmol, 0.300 g) was added to DCM (10 mL) and the solution was cooled to -30 °C. Neat $P(TMS)_3$ (**236**, 1 eq, 1 mmol, 0.250 g) was added dropwise to this solution while maintaining -30 °C. Then a solution of *tert*-butyl acetate (2 eq, 2 mmol, 0.232 g) in DCM (1 mL) was added dropwise while maintaining -30 °C. After complete addition, cooling was discontinued. The reaction mixture was stirred at room temperature for 16 h and then concentrated *in vacuo*. Trituration of the resulting material with diethyl ether (2 mL) and subsequent filtration yielded product **238** (64 mg, 22%) as a white crystalline solid.

(**238**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.41 (d, J = 473.5 Hz, 2H), 1.57 (d, J = 18.0 Hz, 18H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 122.1, 31.4, 31.1, 27.4 (×2); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.5.

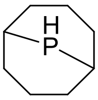
Mixture of 9,9-bis(hydroxymethyl)-9-phosphabicyclo[3.3.1]nonan-9-ium and 9,9-bis(hydroxymethyl)-9-phosphabicyclo[4.2.1]nonan-9-ium chlorides (241 and 242)



241 **242**

A commercial solution of phobane isomers ([3.3.1] and [4.2.1], ca. 60% in toluene, 80 mL) was added to a degassed aq. formaldehyde solution (ca. 35%, 105 mL) under argon atmosphere. A degassed aq. HCl (5 M, 126 mL) solution was added dropwise to this mixture and the reaction mixture was stirred for an additional 2 h. Then the reaction mixture was evaporated to dryness *in vacuo* and the resulting solids were triturated with *i*-PrOH, filtered and recrystallized from a mixture of MeOH (175 mL) and *i*-PrOH (175 mL) to yield a 3:1 mixture of **241** and **242** (57 g, ca. 70%)

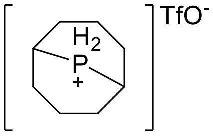
9-phosphabicyclo[3.3.1]nonane (239)



The mixture of **241** and **242** (1 eq, 36 mmol, 8.50 g) was dissolved in water (20 mL) and the solution was degassed by bubbling argon for 20 min through the solution. Degassed pentane (35 mL) was added to this solution, and it was followed by the dropwise addition of degassed aq. solution of NaOH (1 M, 16 mL). The reaction was stirred for 10 min at room temperature. Then the pentane layer was separated, and the aqueous layer was extracted with pentane (3×10 mL). Degassed aq. solution of NaOH (1 M, 1 mL) was added to the aqueous layer followed by repeated extractions with pentane (3×30 mL). The organic phase was separated, and pentane (50 mL) and then degassed aq. solution of NaOH (1 M, 38 mL) was added. The reaction mixture was stirred for 5 min before being transferred to an argon flushed flask charged with $Na_2S_2O_5$. It was stirred for an additional 2 h. Afterwards, the pentane layer was separated, and the aqueous layer was repeatedly extracted with pentane (2×20 mL). Combined organic phases were transferred to a Schlenk flask and evaporated to dryness under vacuum with in-line liquid nitrogen cooled trap yielding product **239** (2.87 g, 86%).

(**239**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 (dt, *J* = 192.0, 3.6 Hz, 1H), 2.33 – 1.48 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.0, 33.9, 30.1, 30.0, 29.4, 22.7, 22.6 (×3), 22.2, 22.1; ^{31}P NMR (162 MHz, C_6D_6) δ -54.03.

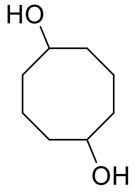
9-Phosphabicyclo[3.3.1]nonan-9-ium trifluoromethanesulfonate (245)



Phosphine **239** (1 eq, 20 mmol, 2.87 g) was dissolved in degassed DCM (20 mL) and triflic acid (1.1 eq) was carefully added in a dropwise fashion. After complete addition, the reaction mixture was stirred for 30 min and concentrated *in vacuo*. The resulting oil was triturated with diethyl ether (20 mL) and filtered to yield salt **245** (4.96 g, overall yield 86%) as a crystalline solid.

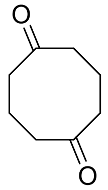
(**245**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (d, *J* = 516.0 Hz, 2H), 3.10 – 2.94 (m, 2H), 2.41 – 2.07 (m, 10H), 1.88 – 1.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.0, 118.8, 28.1, 28.0, 20.3, 20.2, 19.3, 18.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ -13.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.6.

Cyclooctane-1,5-diol (**247**)



Sodium borohydride (3 eq, 0.55 mmol, 21.0 g) was suspended in anhydrous THF (1 L) under argon atmosphere. Then the suspension was cooled to 0 °C and $BF_3 \cdot Et_2O$ (3.7 eq, 0.68 mol, 84 mL) was added dropwise while maintaining the reaction temperature below 5 °C. After complete addition the reaction mixture was stirred for 1 h at 0 °C and neat 1,5-cyclooctadiene (1 eq, 0.19 mol, 20.0 g) was added dropwise to the reaction mixture. After complete addition, the reaction was stirred for 1 h at room temperature and then refluxed for an additional 1 h. Then the mixture was carefully quenched with aq. NaOH (3 M, 369 mL) and then H_2O_2 (ca. 30%, 184 mL) was introduced at such rate that the reaction mixture refluxed gently. After the addition was complete, it was allowed to cool to room temperature. Brine was then added, and the mixture was transferred to a separatory funnel. The organic phase was separated, and the aqueous layer was extracted with DCM (2×200 mL). Combined organic phases were washed with a mixture of aq. KI (ca. 10%, 50 mL) and saturated Na_2SO_3 (100 mL). Organic phase was separated, dried with $MgSO_4$, filtered, and concentrated to yield diol **247** (26.4 g, 99%) as a thick syrup. The product was used in the next step without additional purification.

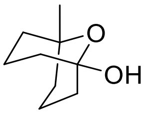
Cyclooctane-1,5-dione (**248**)



Jones reagent was prepared by dissolving CrO_3 (4 eq, 0.80 mol, 80 g) in conc. H_2SO_4 (69 mL) and then diluted with ice (200 g). The Jones reagent was added to a solution of diol **247** (1 eq, 207 mmol, 29.8 g) in acetone (310 mL) maintaining the reaction mixture temperature below 17 °C. After stirring for 2 h the reaction mixture was quenched by dropwise addition of *i*-PrOH while maintaining the reaction mixture temperature below 10 °C. Then the reaction mixture was filtered through a layer of Celite® and the solids were repeatedly extracted with acetone (3×300 mL). Combined extracts were concentrated and then redissolved in DCM (300 mL). The resulting solution was dried with Na_2SO_4, filtered through a layer of Celite® and concentrated to yield diketone **248** (19.7 g, 68%).

(**248**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 – 2.47 (m, 8H), 2.23 – 2.11 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.2, 42.3, 22.1; MS (EI) calcd for $C_8H_{12}O_2$ [M+]: 140; found 140.

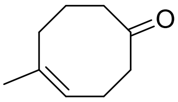
5-Methyl-9-oxabicyclo[3.3.1]nonan-1-ol (**249**)



A solution of methylmagnesium bromide (1 M in THF, 1.5 eq, 71 mL) was added to a solution of compound **248** (1 eq, 140 mmol, 19.7 g) in THF (300 mL) at -5 °C. After stirring for 1 h the reaction mixture was quenched with water (125 mL) and saturated aq. NH_4Cl solution (250 mL) was added. Organic phase was separated, and the aqueous layer was extracted with DCM (2×100 mL). Combined organic phases were dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography on silica gel eluting with (10:3 hexanes:EtOAc) to give **249** (13.1 g, 59%) as a white solid. (Caution, the product is volatile!)

(**249**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.37 (s, 1H), 2.25 – 2.03 (m, 2H), 1.98 – 1.88 (m, 2H), 1.75 – 1.49 (m, 8H), 1.24 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 95.5, 75.4, 35.5, 34.6, 31.7, 20.7; MS (EI) calcd for $C_9H_{16}O_2$ [M+]: 156; found 156.

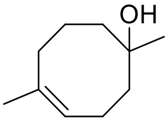
5-Methylcyclooct-4-en-1-one (**250**)



p-Toluenesulfonic acid monohydrate (10 mol%, 6.4 mmol, 1.12 g) was added to a solution of **249** (1 eq, 64 mmol, 10 g) in benzene (960 mL). Reaction flask was fitted with a Dean-Stark apparatus and the mixture was refluxed for 72 h. Then the reaction mixture was neutralized with triethylamine (1 mL) and concentrated. The product was purified by column chromatography on silica gel, eluting with (1:1 DCM:hexanes) to give ketone **250** (5.76 g, 65%) as a colorless oil.

(**250**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (t, *J* = 8.1, 1H), 2.54 – 2.41 (m, 4H), 2.41 – 2.29 (m, 2H), 2.23 – 2.08 (m, 2H), 1.69 (s, 3H), 1.67 – 1.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.9, 138.2, 123.8, 47.6, 40.5, 31.4, 24.1, 22.7, 22.6; MS (EI) calcd for $C_9H_{14}O$ [M+]: 138; found 138

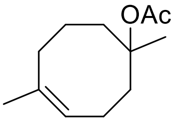
1,5-Dimethylcyclooct-4-en-1-ol (**251**)



A solution of methymagnesium bromide (3 M in THF, 1.3 eq, 42 mmol, 14 mL) was added to a solution of ketone **250** (1 eq, 33 mmol, 4.54 g) in THF (164 mL) at 0 °C. After stirring for 1 h the reaction was quenched with saturated aq. NH_4Cl (50 mL). Phases were separated and aqueous phase was extracted with DCM (2×50 mL). Combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Reaction yielded alcohol **251** (4.49 g, 89%) as a colorless oil.

(**251**): ^1H NMR (400 MHz, $CDCl_3$ δ 2.31 – 2.21 (m, 1H), 2.17 – 2.04 (m, 3H), 1.80 – 1.55 (m, 11H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 125.1, 73.6, 43.6, 37.8, 31.5, 30.7, 25.6, 24.3, 23.0; MS (EI) calcd for $C_{10}H_{18}O$ [M+]: 154; found 154.

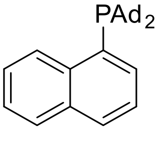
1,5-Dimethylcyclooct-4-en-1-yl acetate (**252**)



A solution of acetyl chloride (1.1 eq, 29 mmol, 2.24 g) in DCM (5 mL) was added to a solution of alcohol **251** (1 eq, 26 mmol, 4.0 g) in DCM (60 mL) at 0 °C. After complete addition cooling was discontinued and the mixture was stirred for 24 h. Then the reaction mixture was transferred to a separatory funnel and washed with water (2×50 mL). The organic layer was separated and dried over $MgSO_4$, filtered, and concentrated. The product was purified using column chromatography on silica gel, eluting with (1:1 DCM:hexanes) to give ester **252** (2.84 g, 56%) as a colorless liquid.

(**252**): ^1H NMR (400 MHz, $CDCl_3$) δ 5.59 – 5.37 (m, 1H), 3.40 (s, 2H), 2.39 – 1.89 (m, 9H), 1.85 – 1.73 (m, 1H), 1.72 – 1.54 (m, 4H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.18, 135.54, 124.63, 87.95, 51.50, 40.98, 34.47, 29.73, 27.12, 23.78, 23.26, 22.83.

Di(adamantant-1-yl)(naphthalen-1-yl)phosphine (**255**)



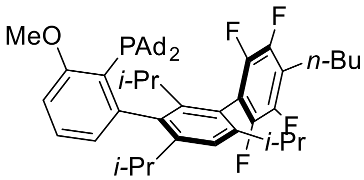
Under argon atmosphere DiPPF (**186**, 13 mol%, 54 mg) and $Pd(OAc)_2$ (10 mol%, 22 mg) were suspended in anhydrous and degassed 1,4-dioxane (1 mL) and stirred for 1 h. Schlenk flask is charged with di(1-adamantyl)phosphine triflate **233** (1 eq, 1 mmol, 0.45 g) and Cs_2CO_3 (2.2 eq, 2.2 mmol, 0.78 g) and cycled on the Schlenk line three times. Degassed anhydrous 1,4-dioxane (6.5 mL/mmol) is introduced *via* syringe. The catalyst suspension was transferred *via* syringe to this reaction mixture, and it was heated at 90 °C. After 12 h of heating, reaction mixture was cooled to room temperature, filtered through a layer of Celite® and concentrated. Product was purified using column chromatography on silica gel eluting with (30:1 hexanes:Et_2O). Reaction yielded **255** (0.32 g, 74%) as a white solid.

(**255**): ^{1}H NMR (400 MHz, C_6D_6) δ 9.66 (t, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 7.1 Hz, 1H), 7.69 (dd, *J* = 19.2, 8.2 Hz, 2H), 7.36 (dd, *J* = 28.6, 7.4 Hz, 3H), 2.19 – 1.97 (m, 12H), 1.89 – 1.70 (m, 6H), 1.62 – 1.55 (m, 12H); ^{13}C NMR (100 MHz, C_6D_6) δ 140.5, 134.5, 134.4, 134.1, 132.5, 132.2, 129.5, 128.5, 125.6 (×2), 125.5, 123.9, 42.0, 41.9, 36.9, 28.9, 28.8; ^{31}P NMR (162 MHz, C_6D_6) δ 13.4; MS (EI) calcd for $C_{10}H_{18}O$ [M+]: 428; found 428.

GP1. General procedure for C-P cross-coupling

Under argon atmosphere DiPPF (**186**, 2.5 – 10 mol%) and $Pd(OAc)_2$ (3.25 – 13 mol%) (Pd:L 1:1.3) were suspended in anhydrous and degassed 1,4-dioxane (4 mL/mmol ($Pd(OAc)_2$) and stirred for 1 h. Schlenk flask is charged with aryl iodide (1 eq), phosphine triflate (1.5 eq) and NaO*t*-Bu (3 eq) and cycled on the Schlenk line three times. Degassed anhydrous *p*-xylene (10 mL/mmol of substrate) was introduced *via* syringe. The catalyst suspension was transferred *via* syringe to this reaction mixture, and it was heated at 140 °C (in an oil bath) until iodide is completely consumed (TLC analysis). Note, freebase phosphines are introduced as stock solutions in *p*-xylene just before the heating step. After aryl iodide was completely consumed, reaction mixture was filtered through a layer of Celite® and concentrated. Products were purified using column chromatography on silica gel eluting with (30:1 hexanes:Et_2O)

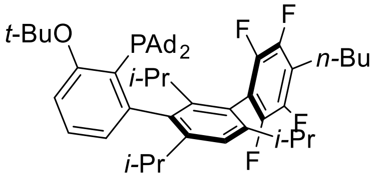
Di(adamantan-1-yl)(4''-butyl-2'',3'',5'',6''-tetrafluoro-2',4',6'-triisopropyl-3-methoxy-[1,1':3',1''-terphenyl]-2-yl)phosphane (**AlPhos, 122**)



GP1 was performed using iodide **224** (1 eq, 10 mmol, 6.41 g), Pd(OAc)$_2$ (2.5 mol%) and DiPPF (**186**, 3.25 mol%). After purification ligand **122** (5.6 g, 69%) was obtained as an off-white solid.

(**122**): ^{1}H NMR (400 MHz, C_6D_6) δ 7.49 (s, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 7.01 (dd, *J* = 7.2, 3.5 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 3.32 (s, 3H), 3.22 (p, *J* = 7.1 Hz, 1H), 2.96 (hept, *J* = 6.7 Hz, 1H), 2.69 (hept, *J* = 6.8 Hz, 1H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.16 – 2.08 (m, 12H), 1.95 – 1.91 (m, 6H), 1.77 – 1.63 (m, 12H), 1.54 (d, *J* = 6.8 Hz, 3H), 1.43 (p, *J* = 7.6 Hz, 2H), 1.24 (dd, *J* = 7.0, 2.2 Hz, 6H), 1.15 (t, *J* = 6.6 Hz, 7H), 1.06 (d, *J* = 7.1 Hz, 3H), 0.74 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 162.3, 152.6, 152.2, 148.8, 148.1, 144.7, 140.8, 126.3, 123.8, 123.3, 121.4, 120.6, 120.1, 119.9, 109.1, 53.6, 42.4, 39.4, 39.1, 37.5, 32.6, 31.9, 31.7, 31.2, 29.7, 26.7, 24.5, 24.4, 23.2, 22.8, 22.5, 22.1, 14.2, 13.8; ^{19}F NMR (376 MHz, C_6D_6) -136.9 (dd, *J* = 24.2, 12.7 Hz), -137.2 (dd, *J* = 24.3, 12.5 Hz), -145.3 (dd, *J* = 24.4, 12.7 Hz), -145.6 (dd, *J* = 24.2, 12.5 Hz); ^{31}P NMR (162 MHz, C_6D_6) δ 35.8.

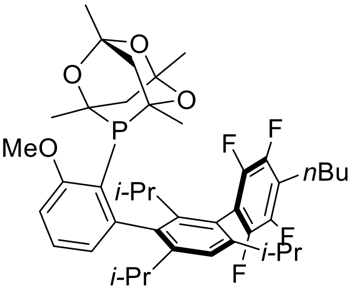
Di(adamantan-1-yl)(3-(tert-butoxy)-4''-butyl-2'',3'',5'',6''-tetrafluoro-2',4',6'-triisopropyl-[1,1':3',1''-terphenyl]-2-yl)phosphane (**205**)



GP1 was performed using iodide **226** (1 eq, 0.5 mmol, 0.341 g), Pd(OAc)$_2$ (10 mol%) and DiPPF (**186**, 13 mol%). After purification ligand **205** (0.276 g, 65%) was obtained as an off-white solid. Compound appears to be unstable, multiple purifications did not yield satisfactory results.

(**205**): ^{1}H NMR (400 MHz, C_6D_6) δ 7.50 (s, 1H), 7.10-6.98 (m, 1H), 6.95 – 6.87 (m, 1H), 2.97 (pd, *J* = 7.0, 2.7 Hz, 1H), 2.83 (p, *J* = 6.8 Hz, 1H), 2.59 – 2.43 (m, 3H), 2.07 – 1.89 (m, 8H), 1.84 (s, 4H), 1.70 – 1.59 (m, 12H), 1.38 (p, *J* = 7.7 Hz, 3H), 1.27 – 0.99 (m, 34H), 0.71 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 155.4, 155.1, 148.4, 147.3, 144.7, 144.4, 143.6, 140.8, 140.7, 137.1 (×2) , 125.6, 124.4, 122.7, 122.5, 121.7, 121.0 (×2), 120.4, 120.2, 118.1, 116.6, 116.4, 77.9, 77.8, 43.6, 43.4, 36.7, 36.5, 34.6, 34.2, 34.0, 31.7, 31.3, 31.2, 30.2, 28.9, 28.8, 28.6 (×2), 27.6, 25.3, 24.1, 24.0 (×3), 23.9, 23.8 (×2), 22.7, 22.5, 22.2, 14.0, 13.4; ^{19}F NMR (376 MHz, C_6D_6) δ -137.5, -138.3 (ddd, *J* = 28.4, 24.2, 12.6 Hz), -140.9 (ddd, *J* = 24.0, 12.5, 5.9 Hz), -145.6 (td, *J* = 23.8, 23.4, 12.6 Hz); ^{31}P NMR (162 MHz, C_6D_6) δ 18.0.

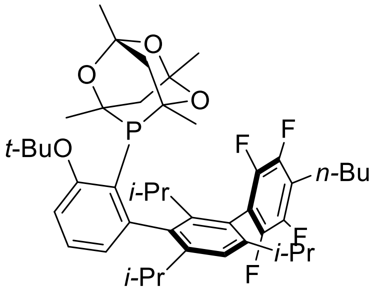
8-(4''-Butyl-2'',3'',5'',6''-tetrafluoro-2',4',6'-triisopropyl-3-methoxy-[1,1':3',1''-terphenyl]-2-yl)-1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphaadamantane (206)



GP1 was performed using iodide **224** (1 eq, 0.5 mmol, 0.32 g), $Pd(OAc)_2$ (2.5 mol%) and DiPPF (**186**, 3.25 mol%). After purification ligand **206** (208 mg, 57%) was obtained as an off-white solid.

(**206**): ^{1}H NMR (400 MHz, C_6D_6) δ 7.46 (s, 1H), 7.08 – 6.95 (m, 1H), 6.94 – 6.82 (m, 1H), 6.40 (d, *J* = 8.2 Hz, 1H), 3.32 (s, 3H), 3.22 – 3.09 (m, 1H), 2.83 (p, *J* = 6.8 Hz, 1H), 2.66 (qt, *J* = 15.1, 6.9 Hz, 1H), 2.57 – 2.52 (m, 3H), 2.39 (dd, *J* = 12.5, 5.7 Hz, 1H), 2.15 – 1.97 (m, 1H), 1.93 – 1.62 (m, 3H), 1.58 – 1.06 (m, 30H), 0.99 (dd, *J* = 28.5, 7.0 Hz, 2H), 0.74 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 162.1, 148.1 (×2), 144.0, 139.7, 130.3, 125.5, 125.4, 120.4, 120.0, 119.9, 110.0, 97.2, 97.1, 95.7, 95.6, 75.8, 75.6, 74.2, 73.9, 54.4, 47.9, 47.6, 40.0, 34.6, 32.4, 31.9, 31.6, 31.3, 31.1, 30.9, 30.8, 30.2, 29.8, 29.6, 28.4 (×2), 27.6, 27.3, 26.9, 26.3 (×2), 26.2, 25.4, 24.5, 24.2, 23.9, 23.7, 22.7 (×2), 22.5 (×2), 22.2, 21.5, 21.3, 13.4; ^{19}F NMR (376 MHz, C_6D_6) δ -134.5 (dd, *J* = 24.0, 12.9 Hz), -135.7 (dd, *J* = 24.8, 12.5 Hz), -136.2 (dd, *J* = 24.3, 13.0 Hz), -136.6 (dd, *J* = 24.8, 12.9 Hz), -137.3 – -137.8 (m), -145.3 – -145.9 (m), -146.1 (dd, *J* = 24.4, 12.7 Hz); ^{31}P NMR (162 MHz, C_6D_6) δ -20.6, -21.2.

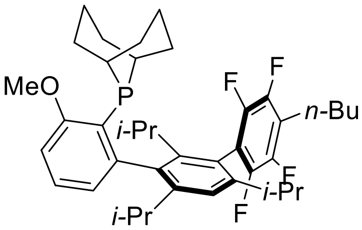
8-(3-(Tert-butoxy)-4''-butyl-2'',3'',5'',6''-tetrafluoro-2',4',6'-triisopropyl-[1,1':3',1''-terphenyl]-2-yl)-1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphaadamantane (207)



GP1 was performed using iodide **227** (1 eq, 0.5 mmol, 0.341 g), $Pd(OAc)_2$ (10 mol%) and DiPPF (13 mol%). After purification ligand **207** (77 mg, 20%) was obtained as an off-white solid.

(**207**): ^{1}H NMR (400 MHz, C_6D_6) δ 7.40 – 7.19 (m, 1H), 6.87 – 6.66 (m, 2H), 2.84 (dtd, *J* = 36.9, 16.0, 14.9, 7.4 Hz, 1H), 2.57 – 2.26 (m, 1H), 2.16 (dd, *J* = 21.7, 12.4 Hz, 0H), 1.93 – 1.77 (m, 1H), 1.70 – 1.45 (m, 1H), 1.42 – 1.30 (m, 5H), 1.26 (s, 3H), 1.23 – 1.06 (m, 22H), 1.02 – 0.90 (m, 9H), 0.84 – 0.68 (m, 8H), 0.65 (d, *J* = 7.0 Hz, 2H), 0.53 (t, *J* = 7.3 Hz, 3H).; ^{13}C NMR (100 MHz, C_6D_6) δ 159.0, 151.7, 151.3, 147.5, 147.4, 147.2, 146.1, 143.1, 139.7, 137.8, 137.7, 124.4, 123.5, 123.4, 122.6, 122.0, 120.9, 119.7, 119.1, 118.8, 115.1, 95.8 (×2), 94.8, 78.6, 78.5, 74.8, 74.7, 73.5, 73.1, 47.0, 46.8, 39.1, 34.0, 33.4, 31.3, 31.2, 30.8, 30.7, 30.6, 30.5, 30.3, 30.1, 30.0, 29.3 (×2), 29.0 (×3), 28.9, 28.8, 28.6, 27.9, 27.8, 26.5, 26.1, 26.0, 24.3, 23.8, 23.4, 23.3, 23.1, 22.9, 22.2, 21.9, 21.6 (×2), 21.3, 21.0, 13.2, 12.6; ^{19}F NMR (376 MHz, C_6D_6) δ -136.1 (dd, *J* = 24.1, 12.5 Hz), -136.7 (dd, *J* = 24.1, 12.6 Hz), -137.3 (dd, *J* = 24.7, 12.5 Hz), -137.5 (dd, *J* = 24.4, 12.6 Hz), -145.5 (dtd, *J* = 36.8, 24.4, 12.7 Hz), -145.8 (dd, *J* = 24.3, 12.7 Hz); ^{31}P NMR (162 MHz, C_6D_6) δ -16.8.

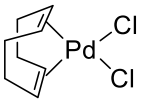
9-(4''-Butyl-2'',3'',5'',6''-tetrafluoro-2',4',6'-triisopropyl-3-methoxy-[1,1':3',1''-terphenyl]-2-yl)-9-phosphabicyclo[3.3.1]nonane (**210**)



GP1 was performed using iodide **224** (1 eq, 1.5 mmol, 0.960 g), $Pd(OAc)_2$ (10 mol%) and DiPPF (**186**, 13 mol%). After purification ligand **210** (0.609 g, 62%) was obtained as an off-white solid.

(**210**): ^{1}H NMR (400 MHz, C_6D_6) δ 7.44 (s, 1H), 7.12 – 7.04 (m, 1H), 7.00 – 6.90 (m, 1H), 6.47 (d, *J* = 8.2 Hz, 1H), 3.44 – 3.30 (m, 1H), 3.21 (s, 3H), 3.05 – 2.87 (m, 1H), 2.77 (dt, *J* = 13.5, 6.3 Hz, 1H), 2.64 (p, *J* = 6.7 Hz, 1H), 2.56 (t, *J* = 7.7 Hz, 2H), 2.36 – 2.03 (m, 4H), 2.00 – 1.62 (m, 7H), 1.50 – 1.39 (m, 6H), 1.27 – 1.10 (m, 12H), 1.09 – 0.99 (m, 4H), 0.98 – 0.91 (m, 3H), 0.91 – 0.80 (m, 1H), 0.74 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 162.0 (×3), 149.3, 148.3, 148.1, 147.7, 144.3, 144.1, 143.8, 143.5, 143.4, 137.8, 129.6, 126.2, 125.0, 124.9, 124.0, 120.4, 120.2, 119.6, 119.3, 118.0, 110.1 (×2), 108.6, 54.2, 53.2, 32.8, 32.3, 32.2, 31.9, 31.8, 31.7 (×2), 31.6, 31.4, 31.3, 30.6, 30.5, 30.1, 30.0, 29.1, 28.9, 28.2 (×2), 28.1, 26.8, 26.7, 26.5, 26.4, 26.3, 25.6, 25.5, 23.5 (×2), 23.3 (×2), 23.2, 23.1, 22.9, 22.8, 22.1 (×2), 21.7, 21.6, 21.5, 21.4, 21.3, 20.6, 20.5 (×2), 20.3, 12.6; ^{19}F NMR (376 MHz, C_6D_6) δ -137.3 – -138.2 (m), -145.3 (ddd, *J* = 43.6, 24.2, 12.7 Hz), -145.8 (ddd, *J* = 56.1, 24.4, 12.6 Hz); ^{31}P NMR (162 MHz, C_6D_6) δ 38.6, -9.9.

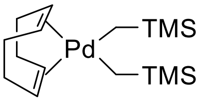
Dichloro(1,5-cyclooctadiene)palladium(II) (257)



Under argon atmosphere cycloocta-1,5-diene (COD, **246**, 3 eq, 17 mmol, 1.85 g) was added to a $PdCl_2$ (1 eq, 5.6 mmol, 1.00 g) in MeOH (50 mL). After stirring for 48 h, the suspension was filtered, washed with MeOH (2×5 mL) and dried in high vacuum. Reaction yielded complex **257** (1.54 g, 96%) as a yellow powder.

(**257**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (s, 4H), 3.11 – 2.69 (m, 4H), 2.64 – 2.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.7, 31.0.

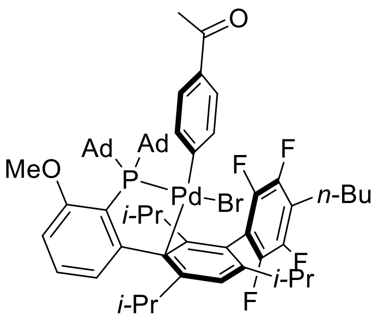
Bis[(trimethylsilyl)methyl](1,5-cyclooctadiene)palladium(II) (130)



A solution of (trimethylsilyl)methylmagnesium chloride (1 M in Et_2O, 2.5 eq, 2.5 mL) was added to a suspension of complex **257** (1 eq, 1 mmol, 0.258 g) in Et_2O (9 mL) at -15 °C. After stirring for 30 min, the reaction was quenched with acetone (0.6 mL). Then solvents were removed under vacuum, while maintaining the temperature below -10 °C. Product was extracted with pentanes (4×20 mL). Combined extracts were concentrated *in vacuo* to yield complex **130** (0.377 g, 97 %).

(**130**): ^{1}H NMR (400 MHz, C_6D_6) δ 5.06 (q, *J* = 2.2 Hz, 4H), 2.21 – 1.61 (m, 8H), 0.69 (s, 4H), 0.26 (s, 18H); ^{13}C NMR (100 MHz, C_6D_6) δ 111.8, 28.9, 11.4, 3.6.

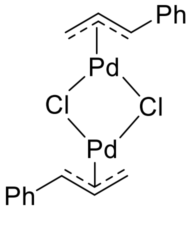
Synthesis of complex 262



A Schlenk flask was charged with AlPhos (**122**, 1.1 eq, 0.13 mmol, 100 mg) and bis[(trimethylsilyl)methyl](1,5-cyclooctadiene)palladium(II) (**130**, 1 eq, 0.11 mmol, 43 mg). The flask was connected to a Schlenk line and cycled three times. 1-(4-Bromophenyl)ethan-1-one (3 eq, 0.38 mmol, 75 mg) in anhydrous degassed pentane (5 mL) was added and the mixture was sonicated for 5 minutes. Then, after stirring for 24 h, the mixture was filtered under argon and washed with pentane (3×10 ml). Complex **262** (100 mg, 70%) was isolated as a yellow-green solid.

(**262**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 6H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.28 (dd, *J* = 7.6, 2.7 Hz, 1H), 3.84 (s, 3H), 3.15 (hept, *J* = 7.1 Hz, 1H), 2.74 (t, *J* = 7.7 Hz, 2H), 2.49 – 2.17 (m, 11H), 2.12 – 1.92 (m, 6H), 1.81 – 1.42 (m, 23H), 1.35 (h, *J* = 7.4 Hz, 2H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.20 (d, *J* = 7.1 Hz, 3H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H), 0.83 – 0.67 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 160.8, 156.8, 152.3, 150.5, 150.1, 140.8, 131.9, 131.6, 129.9, 129.8, 128.9, 126.6, 125.2, 124.6, 123.2, 109.3, 54.0, 47.5, 47.4, 46.4, 42.5, 40.2, 36.4, 36.1, 33.2, 31.5, 31.1, 29.6, 29.5, 29.3, 29.2, 26.6, 26.4, 26.3, 25.4, 24.9, 24.3, 23.7, 22.8, 22.4, 22.2 (×2), 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.7 (dd, *J* = 23.8, 12.8 Hz), -137.0 – -137.5 (m), -144.6 (dd, *J* = 23.6, 12.3 Hz), -146.1 – -146.5 (m); ^{31}P NMR (162 MHz, $CDCl_3$) δ 67.1.

Palladium(π-cinnamyl) chloride dimer (124)



Cinnamyl chloride (4 eq, 23 mmol, 3.50 g) in EtOH (11 mL) was added to a solution of $PdCl_2$ (1 eq, 5.6 mmol, 1 g) and LiCl (4 eq, 23.5 mmol, 1 g) in water (1.5 mL). CO gas was bubbled through the reaction mixture for 3 h. Then, the reaction mixture was filtered, and the solids were washed with

MeOH (10 mL) and Et_2O (15 mL) and dried under vacuum. Reaction yielded complex **124** (1.35 g, 93%) as a yellow powder.

(**124**): ^{1}H NMR (400 MHz, DMSO) δ 7.66 – 7.56 (m, 2H), 7.44 – 7.29 (m, 3H), 6.44 (dt, *J* = 12.3, 9.7 Hz, 1H), 5.17 (d, *J* = 12.2 Hz, 1H), 3.88 (s, 2H); ^{13}C NMR (100 MHz, DMSO-*d₆*) δ 137.5, 129.2, 128.7, 128.6, 113.6, 87.5, 65.0.

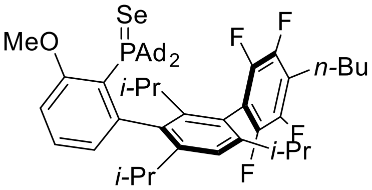
GP2. General procedure for fluorination reaction for ligand screening

Under argon atmosphere ligand (6 mol%) and [(cinnamyl)PdCl]$_2$ (2 mol%) were suspended in cyclohexane (5 mL/mmol) and sonicated for 10 minutes. Then, a solution of (hetero)aryl halide (1 eq) in cyclohexane (5 mL/mmol) was added. After stirring for 15 minutes mixture was transferred to a flask charged with AgF (2 eq) and KF (1 eq) and refluxed under argon. Periodically samples were taken and analyzed by GC-MS. Analysis data provided in Appendix 2.

GP3. General procedure for preparation of phosphine selenides

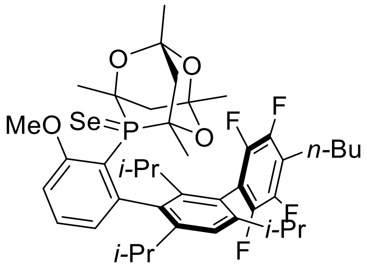
Selenium powder (20 eq, 50 mg) was added to a solution of ligand (1 eq, 20 mg) in $CDCl_3$ (0.7 mL). The reaction vial was flushed with argon and heated at 70 °C. After stirring for 48 h at 70 °C reaction mixture was filtered through a syringe filter into an NMR tube and NMR spectrum were recorded.

Di-(adamantan-1-yl)-(4''-butyl-2'',3'',5'',6''-tetrafluoro-2',4',6'-triisopropyl-3-methoxy-[1,1':3',1''-terphenyl]-2-yl)phosphine selenide (278)



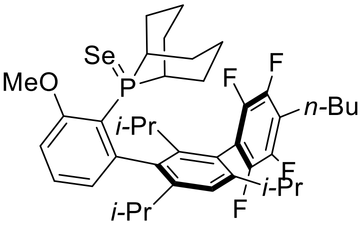
(**278**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (td, *J* = 7.9, 1.4 Hz, 1H), 7.07 (s, 1H), 6.97 (dd, *J* = 8.0, 3.6 Hz, 1H), 6.87 – 6.71 (m, 1H), 3.93 (s, 3H), 2.44 – 2.30 (m, 1H), 2.30 – 2.06 (m, 12H), 2.01 – 1.90 (m, 7H), 1.74 – 1.56 (m, 16H), 1.48 – 1.34 (m, 3H), 1.30 – 1.23 (m, 3H), 1.16 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.81 – 0.75 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (×2), 152.7, 152.6, 146.8, 146.4, 146.0, 143.6, 142.3, 140.4, 130.3 (×2), 129.8 (×2), 120.2, 119.4, 119.3, 116.4, 115.9, 108.9 (×2), 53.9, 47.1, 47.0, 46.8, 46.7, 39.7, 39.6, 36.7 (×3), 36.6, 32.2, 31.6, 30.9, 30.4, 29.7 (×2), 29.6 (×2), 26.9, 25.4, 24.7, 24.2, 23.2, 22.7, 22.4, 22.3 (×2), 21.5, 13.8; ^{19}F NMR (376 MHz, CDCl$_3$) δ -134.9 (dd, *J* = 24.3, 12.8 Hz), -138.2 (dd, *J* = 24.3, 12.5 Hz), -146.3 (dd, *J* = 24.2, 12.4 Hz), -146.7 (dd, *J* = 24.3, 12.6 Hz); ^{31}P NMR (162 MHz, CDCl$_3$) δ 85.6 (t, *J* = 718.5 Hz).

8-(4''-Butyl-2'',3'',5'',6''-tetrafluoro-2',4',6'-triisopropyl-3-methoxy-[1,1':3',1''-terphenyl]-2-yl)-1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphaadamantane 8-selenide (**279**)



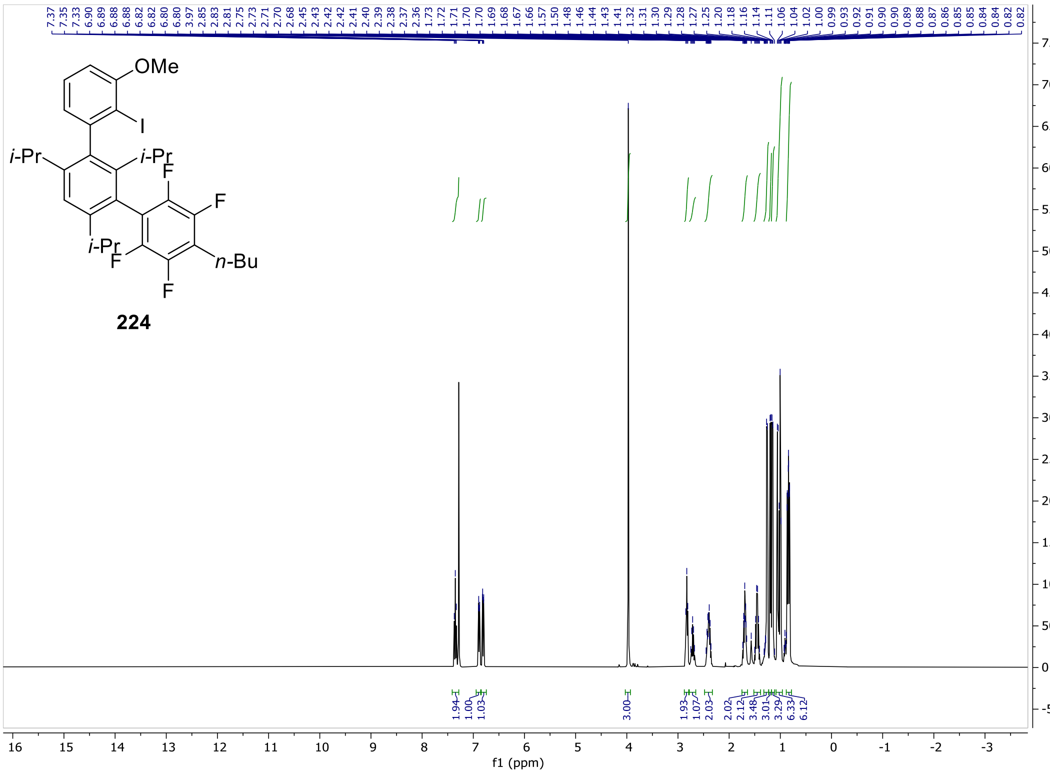
(**279**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 – 7.29 (m, 1H), 7.21 – 7.05 (m, 1H), 7.04 – 6.92 (m, 1H), 6.92 – 6.66 (m, 1H), 4.04 – 3.76 (m, 3H), 2.97 (dd, *J* = 16.7, 9.8 Hz, 1H), 2.88 – 2.40 (m, 5H), 2.41 – 2.21 (m, 1H), 2.20 – 2.04 (m, 1H), 2.03 – 1.74 (m, 2H), 1.71 – 1.59 (m, 4H), 1.52 – 1.15 (m, 20H), 1.15 – 1.06 (m, 3H), 1.07 – 1.01 (m, 2H), 1.00 – 0.94 (m, 3H), 0.93 – 0.87 (m, 1H), 0.83 (dd, *J* = 12.2, 7.1 Hz, 1H), 0.80 – 0.70 (m, 2H), 0.69 – 0.59 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.9 (×2), 160.8, 148.0, 147.8 (×2), 147.7, 147.4, 146.1, 145.6, 143.8, 143.4, 143.2, 141.0, 139.5, 139.0, 138.9, 132.5, 131.9, 131.8, 130.4, 129.5, 125.9, 125.8, 125.7, 121.3, 120.9, 120.0, 119.8 (×2), 119.6, 118.6, 110.7 (×2), 109.8 (×2), 97.3, 97.2, 96.9, 96.7, 96.5, 95.8 (×2), 95.7, 95.4, 76.0, 75.9, 75.7, 75.6, 74.3, 74.0, 73.9, 55.4 (×2), 55.0, 47.8, 47.6, 42.8, 42.6, 41.3, 40.0, 39.9, 33.0, 32.1 (×2), 31.9, 31.8, 31.7, 31.6, 31.5, 31.4, 31.1, 31.0, 30.9, 30.5 (×2), 30.4, 30.3, 29.7, 29.5, 28.5, 27.9, 27.4, 27.3, 26.9 (×2), 26.2, 26.1, 25.7, 25.3, 25.2, 24.8, 24.7, 24.6, 24.4, 24.2, 24.1 (×2), 24.0, 23.9, 23.8, 23.5, 23.2, 23.0, 22.9, 22.8, 22.7, 22.5 (×2), 22.4 (×2), 22.2 (×2), 22.0, 21.5, 21.3, 21.2, 21.0 (×2), 13.8; ^{19}F NMR (376 MHz, CDCl$_3$) δ -134.6 (dd, *J* = 24.3, 12.4 Hz), -135.1 – -135.3 (m), -135.3, -136.1 (dd, *J* = 24.4, 12.7 Hz), -136.4 (dd, *J* = 24.1, 12.6 Hz), -137.7 (ddd, *J* = 47.0, 24.1, 12.1 Hz), -138.4 (dd, *J* = 24.0, 12.4 Hz), -145.7 – -146.7 (m); ^{31}P NMR (162 MHz, CDCl$_3$) δ 35.0 (t, *J* = 767.5 Hz).

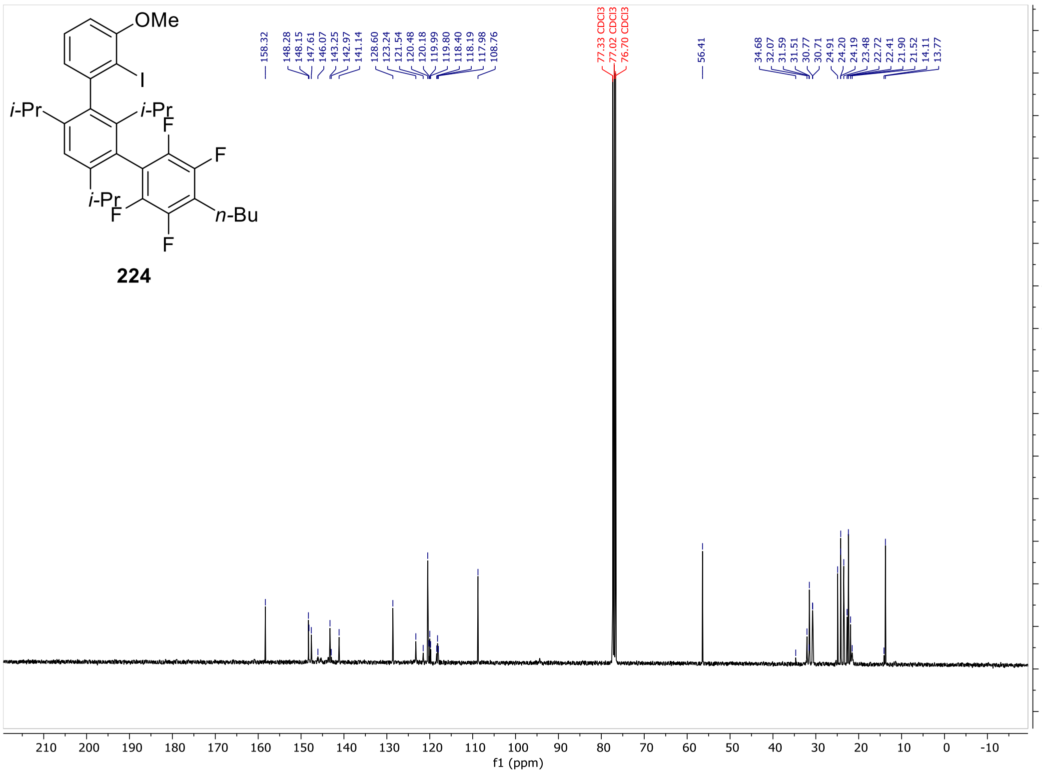
9-(4''-Butyl-2'',3'',5'',6''-tetrafluoro-2',4',6'-triisopropyl-3-methoxy-[1,1':3',1''-terphenyl]-2-yl)-9-phosphabicyclo[3.3.1]nonane 9-selenide (**280**)



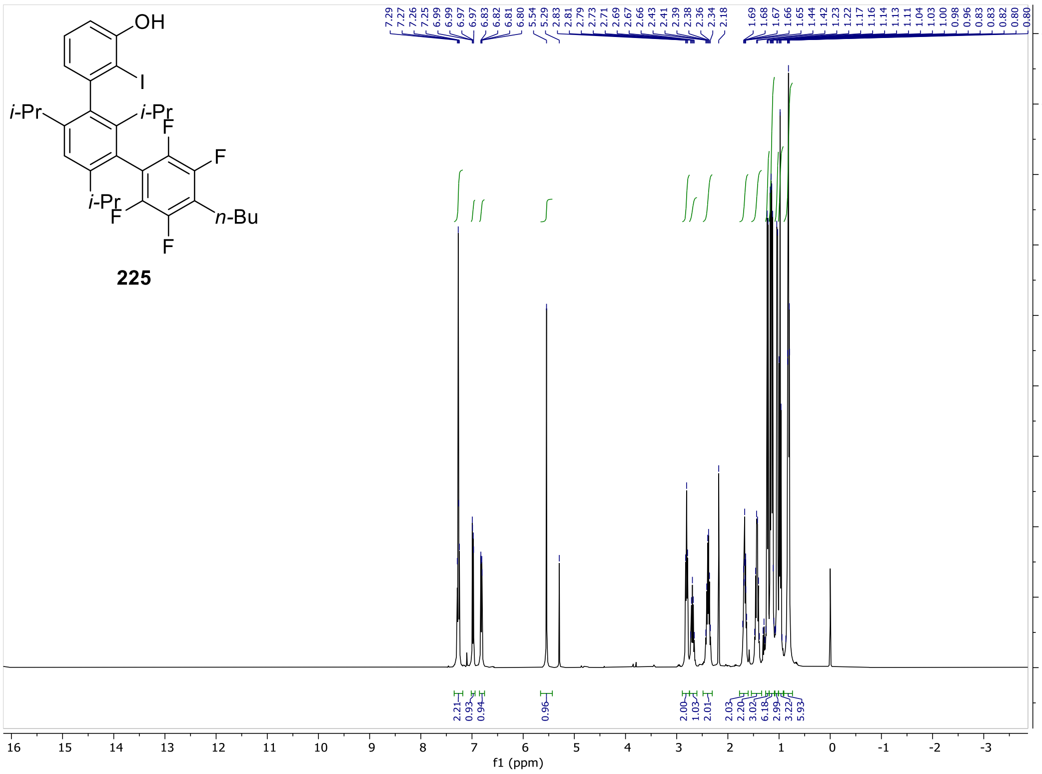
(**280**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.47 – 7.36 (m, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.17 (m, 1H), 7.03 – 6.74 (m, 1H), 4.08 – 3.78 (m, 4H), 3.57 – 3.44 (m, 1H), 3.38 (p, *J* = 6.6 Hz, 1H), 3.15 – 2.91 (m, 1H), 2.92 – 2.75 (m, 3H), 2.74 – 2.65 (m, 1H), 2.56 (p, *J* = 6.6 Hz, 1H), 2.46 – 2.24 (m, 1H), 2.17 – 1.72 (m, 1H), 1.74 – 1.51 (m, 3H), 1.51 – 1.24 (m, 6H), 1.23 – 1.02 (m, 11H), 1.01 – 0.93 (m, 5H), 0.93 – 0.74 (m, 6H), 0.68 (dd, *J* = 12.0, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 163.1, 149.4, 149.3, 148.6, 145.6, 130.5, 130.4, 129.5, 126.7, 126.6, 120.4, 120.1 (×2), 112.3, 111.9, 77.3, 77.0, 76.7, 56.3, 56.2, 55.3, 55.2, 36.2, 35.8, 35.4, 32.4, 32.2, 31.5, 31.3, 31.2, 30.9, 30.5 (×2), 29.8, 29.1, 29.0, 28.8, 27.7, 27.4 (×2), 26.9 (×2), 26.4, 25.6, 24.6, 24.5 (×2), 24.2, 24.1, 23.8, 23.7, 23.6, 23.5, 23.1, 22.7, 22.5, 22.4 (×2), 22.3 (×3), 21.4, 21.1, 20.7, 13.8; ^{19}F NMR (376 MHz, CDCl$_3$) δ -129.0 (dd, *J* = 18.4, 4.0 Hz), -136.3 (t, *J* = 19.5 Hz), -137.7 (d, *J* = 68.9 Hz), -138.0 – -138.6 (m), -139.1 (ddd, *J* = 24.4, 12.8, 4.3 Hz), -141.9 (dd, *J* = 20.6, 3.9 Hz), -145.6, -144.9 – -146.1 (m); ^{31}P NMR (162 MHz, CDCl$_3$) δ 38.9 (t, *J* = 683.1 Hz), 34.7.

4.3 Select NMR spectra

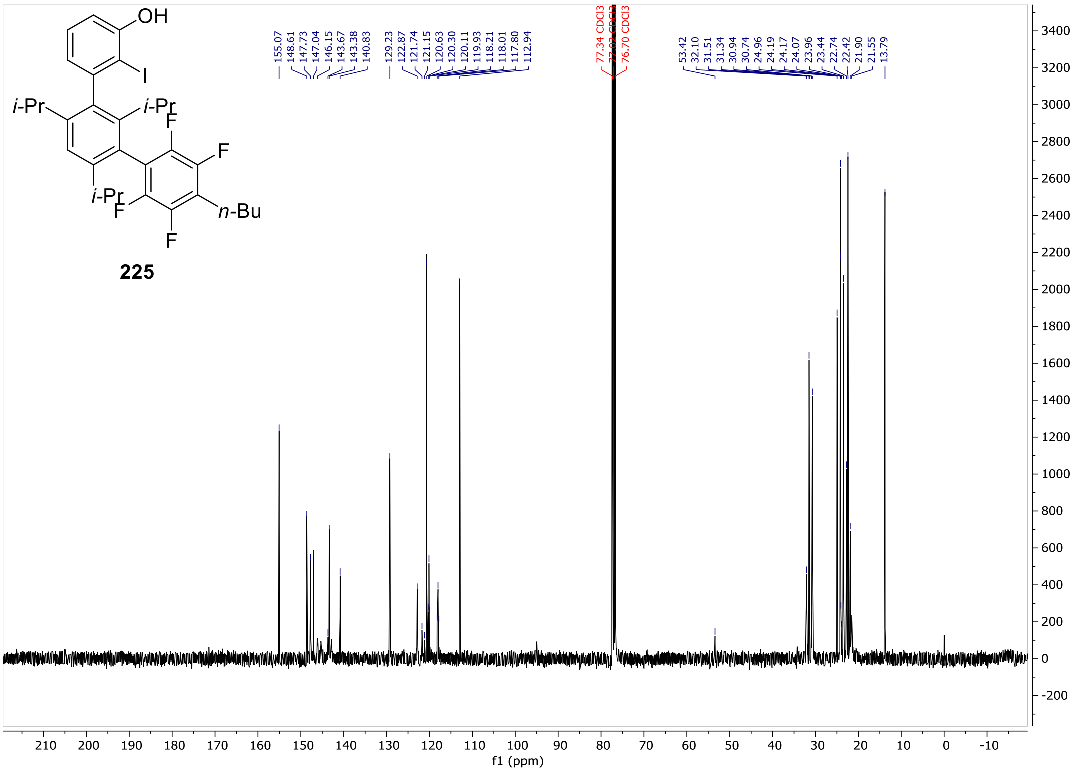

224

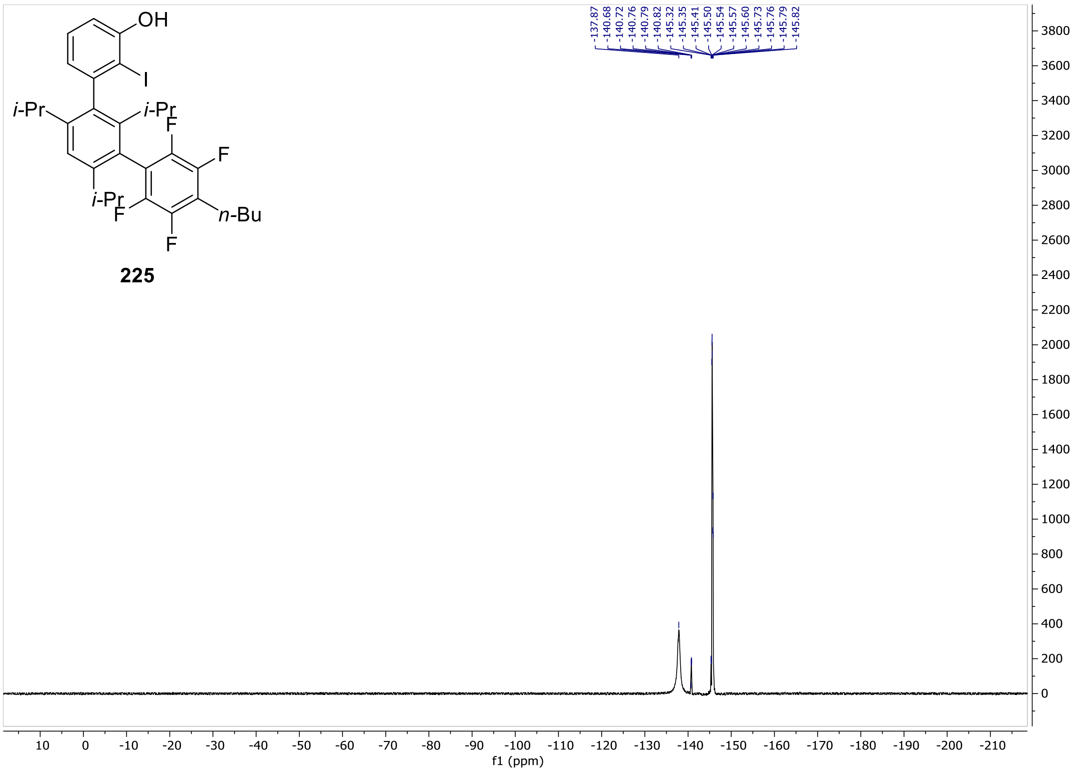

224

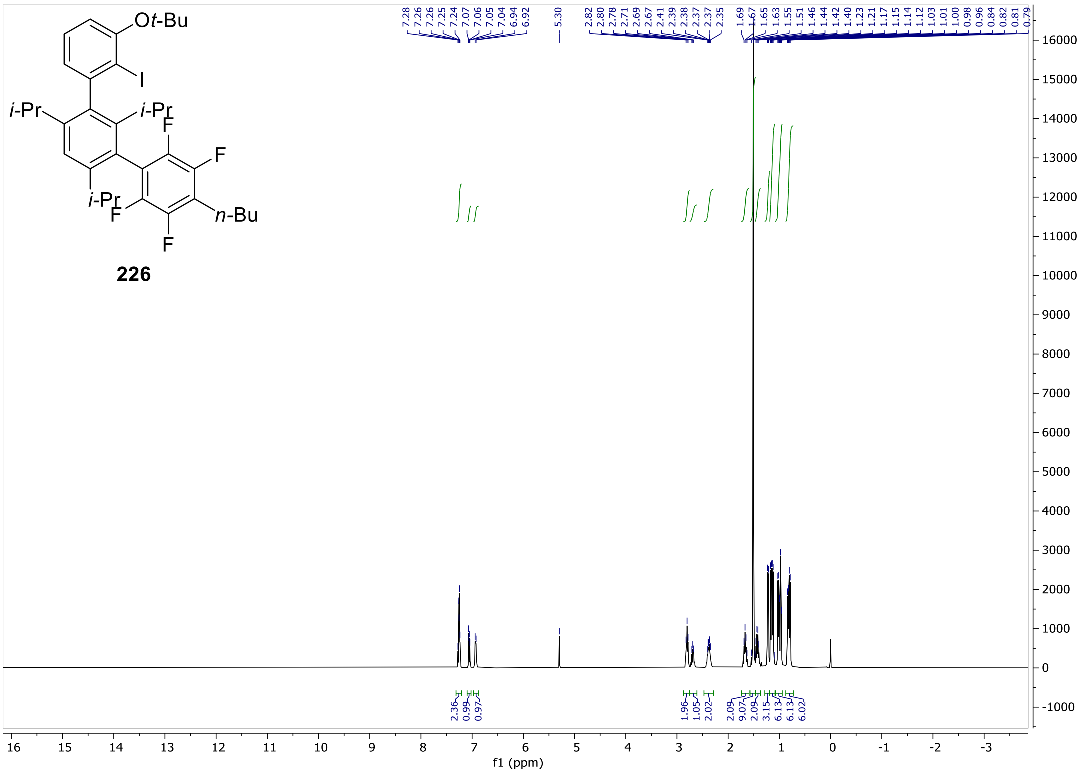
OMe
I
i-Pr
i-Pr
F
F
i-Pr
F
n-Bu
F
158.32
148.28
148.15
147.61
146.07
143.25
142.97
141.14
128.60
123.24
121.54
120.48
120.18
119.99
119.80
118.40
118.19
117.98
108.76
77.33 CDCl3
77.02 CDCl3
76.70 CDCl3
56.41
34.68
32.07
31.59
31.51
30.77
30.71
24.91
24.20
24.19
23.48
22.72
22.41
21.90
21.52
14.11
13.77
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


225

OH
I
i-Pr
i-Pr
F
F
i-Pr
F
n-Bu
F
7.29
7.27
7.26
7.25
6.99
6.99
6.97
6.97
6.83
6.82
6.81
6.80
5.54
5.29
2.83
2.81
2.79
2.73
2.71
2.69
2.67
2.66
2.43
2.41
2.39
2.38
2.36
2.34
2.18
1.69
1.68
1.67
1.66
1.65
1.44
1.42
1.23
1.22
1.17
1.16
1.14
1.13
1.11
1.04
1.03
1.00
0.98
0.96
0.83
0.83
0.82
0.80
0.80
2.21
0.93
0.94
0.96
2.00
1.03
2.01
2.03
2.20
3.02
6.18
2.99
3.22
5.93
4500
4000
3500
3000
2500
2000
1500
1000
500
0
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

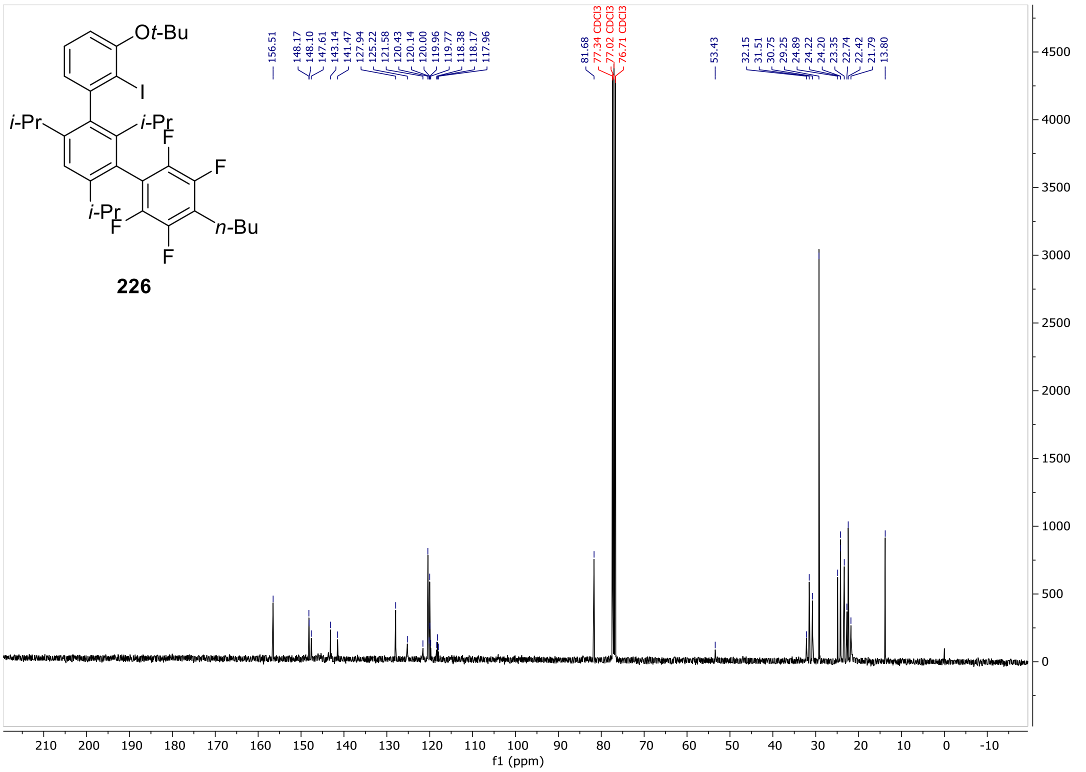

OH
I
i-Pr
i-Pr
F
F
i-Pr
F
n-Bu
F
225
155.07
148.61
147.73
147.04
146.15
143.67
143.38
140.83
129.23
122.87
121.74
121.15
120.63
120.30
120.11
119.93
118.21
118.01
117.80
112.94
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
53.42
32.10
31.51
31.34
30.94
30.74
24.96
24.19
24.17
24.07
23.96
23.44
22.74
22.42
21.90
21.55
13.79
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OH
I
i-Pr
i-Pr
F
F
i-Pr
F
n-Bu
F
225
-137.87
-140.68
-140.72
-140.76
-140.79
-140.82
-145.32
-145.35
-145.41
-145.50
-145.54
-145.57
-145.60
-145.73
-145.76
-145.79
-145.82
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



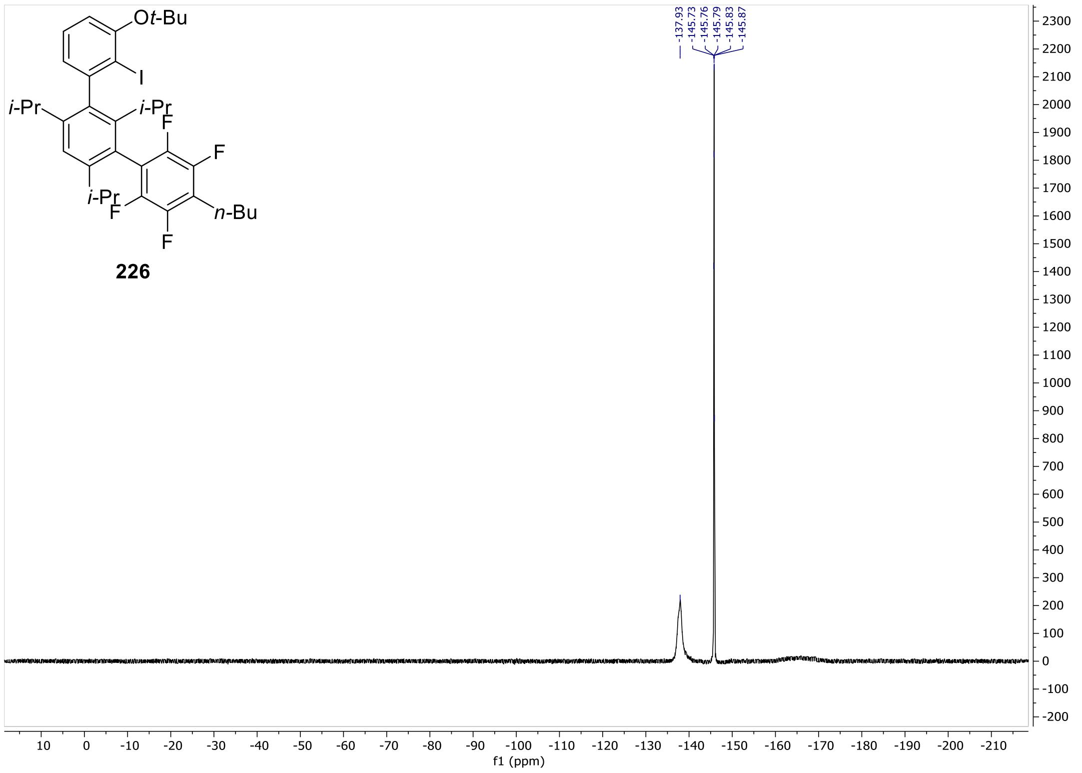
Ot-Bu
I
i-Pr
i-Pr
F
F
i-Pr
F
n-Bu
F
7.28 7.26 7.26 7.25 7.24 7.07 7.06 7.05 7.04 6.94 6.92
5.30
2.82 2.80 2.78 2.71 2.69 2.67 2.41 2.39 2.38 2.37 2.37 2.35
1.69 1.67 1.65 1.63 1.55 1.51 1.46 1.44 1.42 1.40 1.23 1.21 1.17 1.15 1.14 1.12 1.03 1.01 1.00 0.98 0.96 0.84 0.82 0.81 0.79
2.36 0.99 0.97
1.96 1.05 2.02
2.09 9.07 2.09 3.15 6.13 6.13 6.02
f1 (ppm)

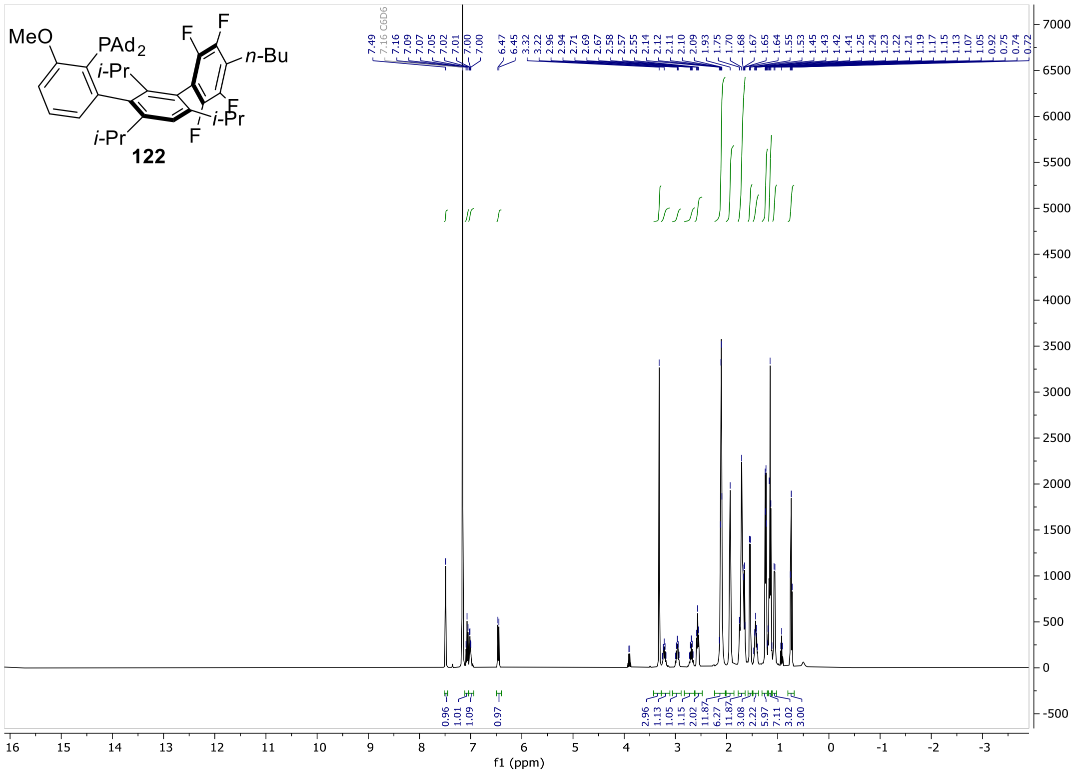
226

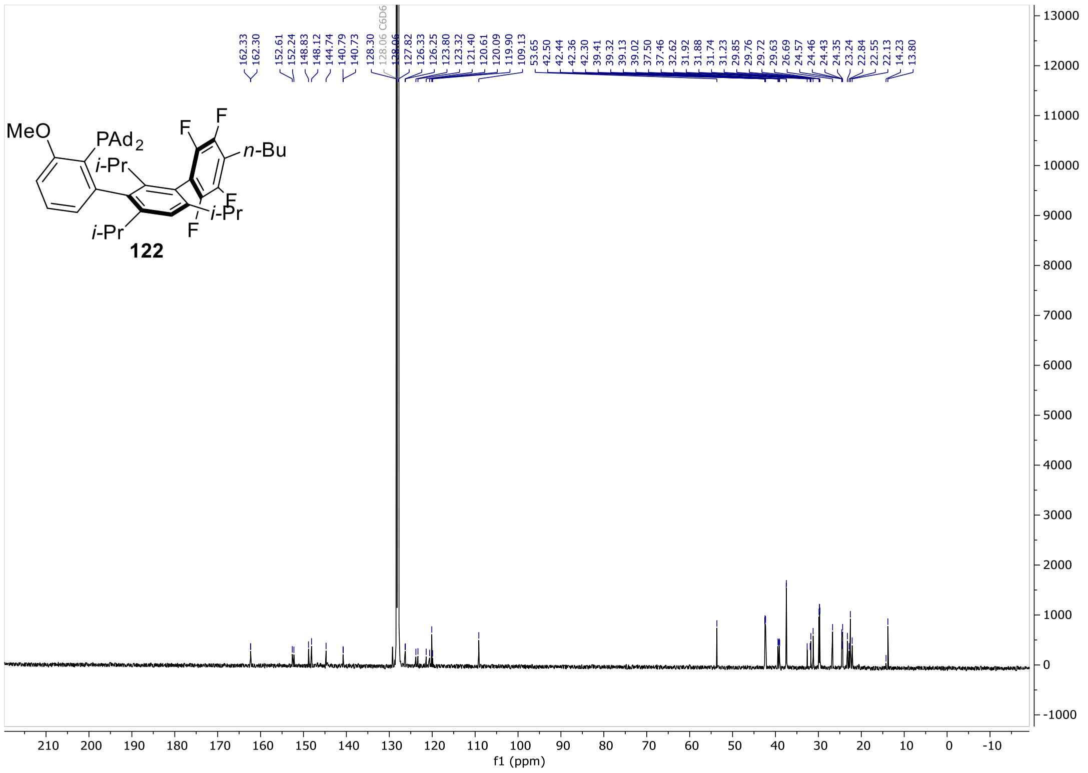


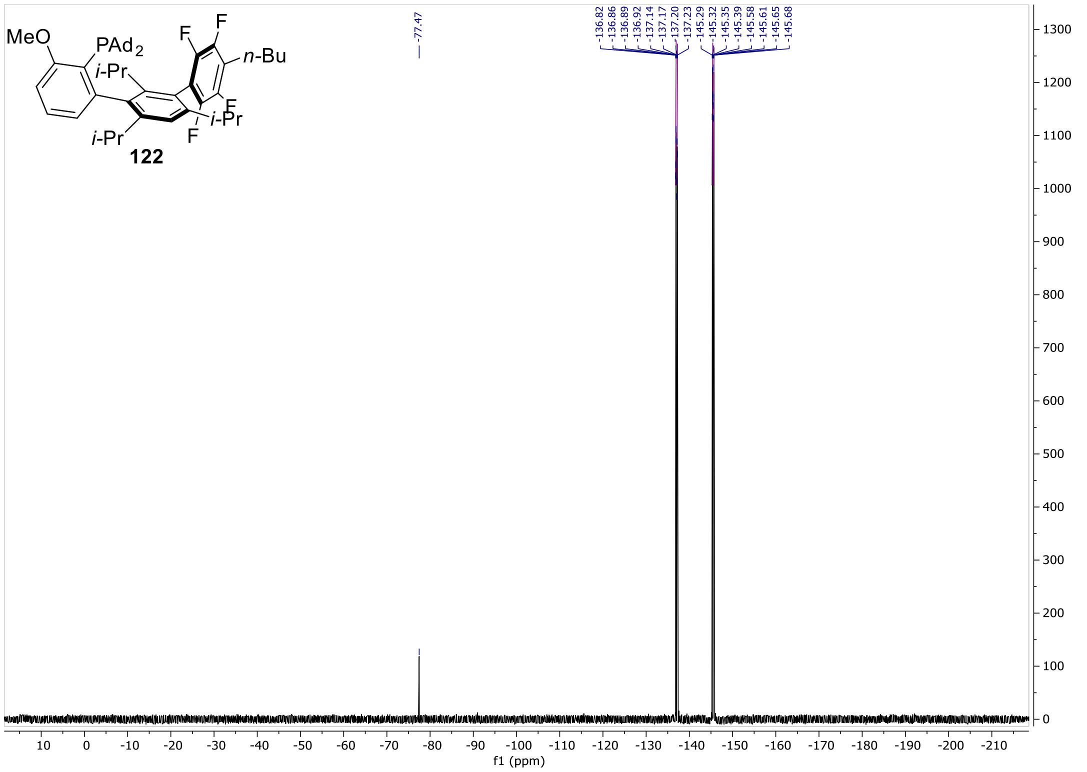
Ot-Bu
I
i-Pr
i-Pr
F
F
i-Pr
F
n-Bu
F
156.51
148.17 148.10 147.61 143.14 141.47 127.94 125.22 121.58 120.43 120.14 120.00 119.96 119.77 118.38 118.17 117.96
81.68
77.34 CDCl3 77.02 CDCl3 76.71 CDCl3
53.43
32.15 31.51 30.75 29.25 24.89 24.22 24.20 23.35 22.74 22.42 21.79
13.80
f1 (ppm)

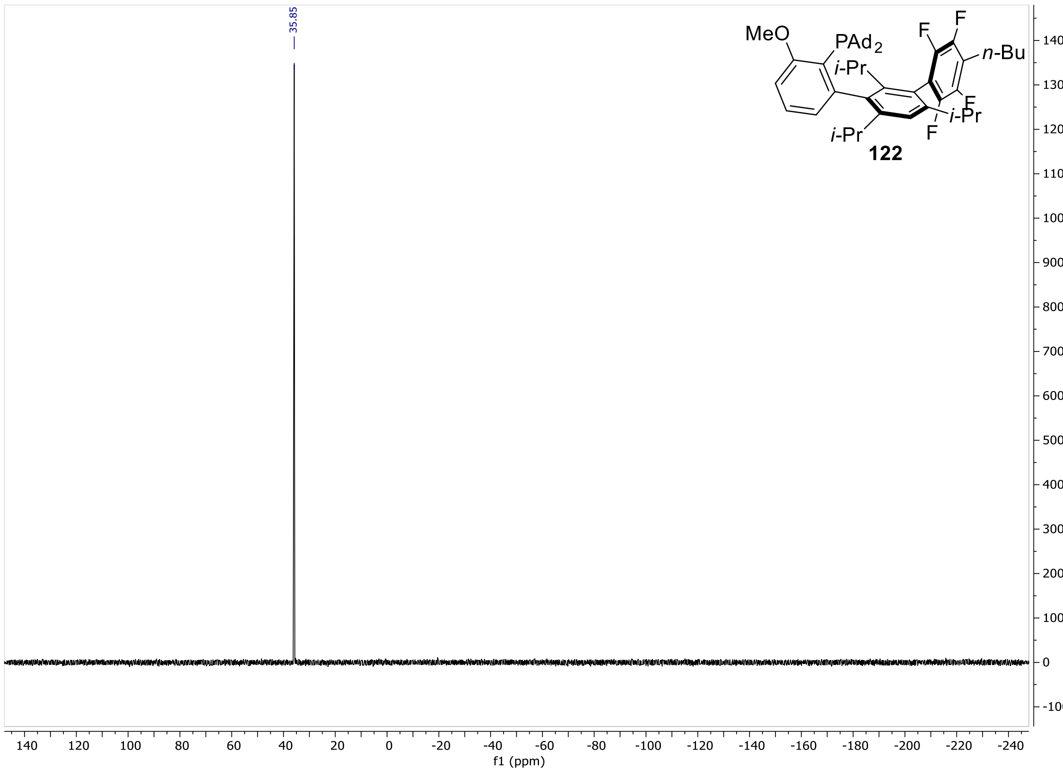
226


226
Ot-Bu
I
i-Pr
i-Pr
F
F
i-Pr
F
n-Bu
F
-137.93
-145.73
-145.76
-145.79
-145.83
-145.87
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

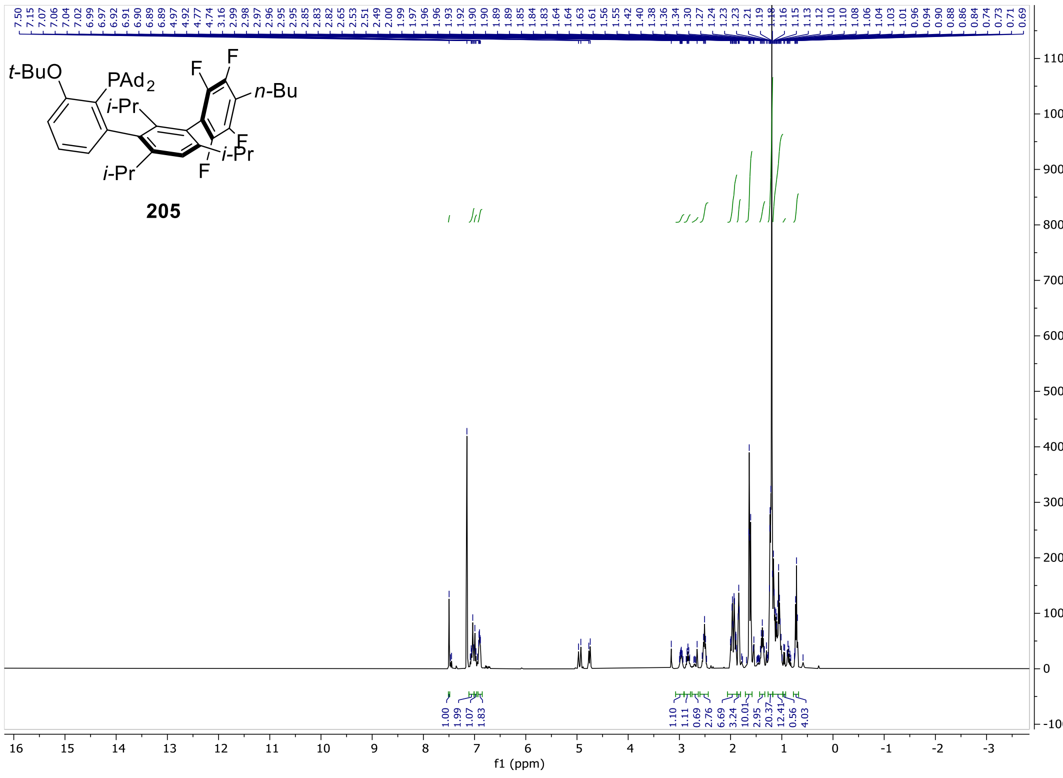

122
MeO
PAd$_2$
i-Pr
F
F
n-Bu
F
i-Pr
i-Pr
F
7.49
7.16 C6D6
7.16
7.09
7.07
7.05
7.02
7.01
7.00
7.00
6.47
6.45
3.22
2.96
2.94
2.71
2.69
2.67
2.58
2.57
2.55
2.14
2.12
2.11
2.10
2.09
1.93
1.75
1.70
1.68
1.67
1.65
1.64
1.55
1.53
1.45
1.43
1.42
1.41
1.25
1.24
1.23
1.22
1.21
1.19
1.17
1.15
1.13
1.07
1.05
0.92
0.75
0.74
0.72
0.96
1.01
1.09
0.97
2.96
1.13
1.05
1.15
2.02
11.87
6.27
11.87
3.08
2.22
5.97
7.11
3.02
3.00
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


162.33
162.30
152.61
152.24
148.83
148.12
144.74
140.79
140.73
128.30
128.06 C6D6
128.06
127.82
126.33
126.25
123.80
123.32
121.40
120.61
120.09
119.90
109.13
53.65
42.50
42.44
42.36
42.30
39.41
39.32
39.13
39.02
37.50
37.46
32.62
31.92
31.88
31.74
31.23
29.85
29.76
29.72
29.63
26.69
24.57
24.46
24.43
24.35
23.24
22.84
22.55
22.13
14.23
13.80
MeO
PAd2
i-Pr
F
F
n-Bu
F
i-Pr
i-Pr
F
122
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

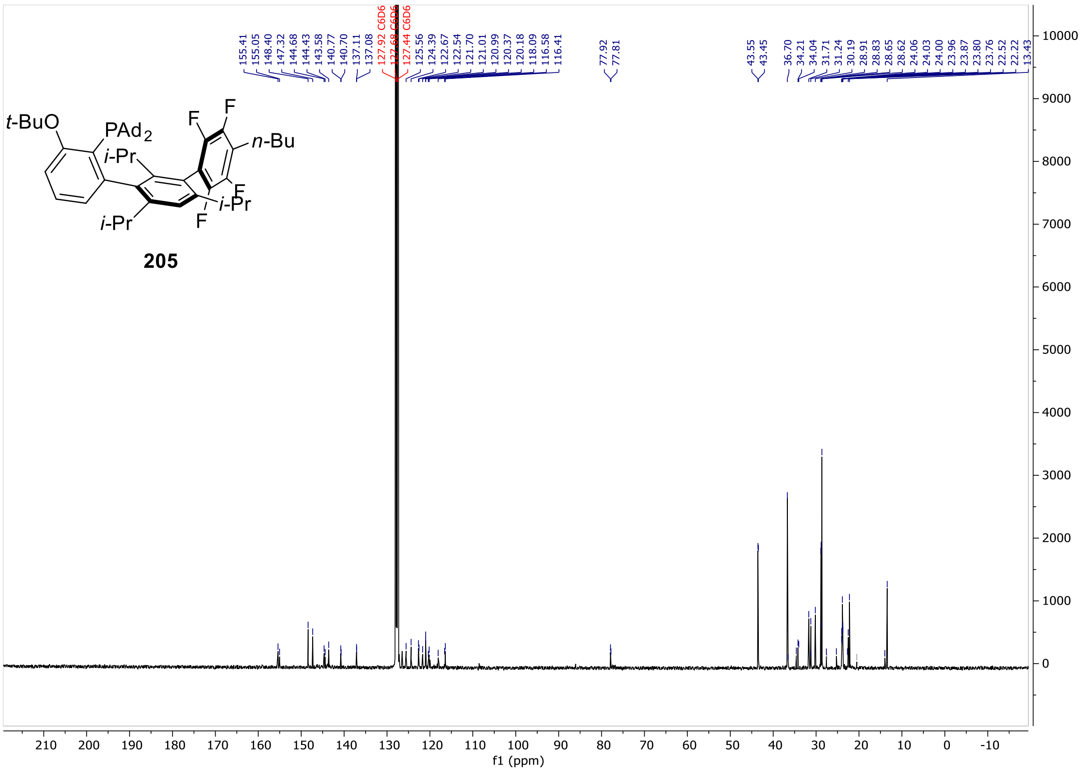

-77.47
-136.82
-136.86
-136.89
-136.92
-137.14
-137.17
-137.20
-137.23
-145.29
-145.32
-145.35
-145.39
-145.58
-145.61
-145.65
-145.68
MeO
PAd2
i-Pr
F
F
n-Bu
F
i-Pr
i-Pr
F
122
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

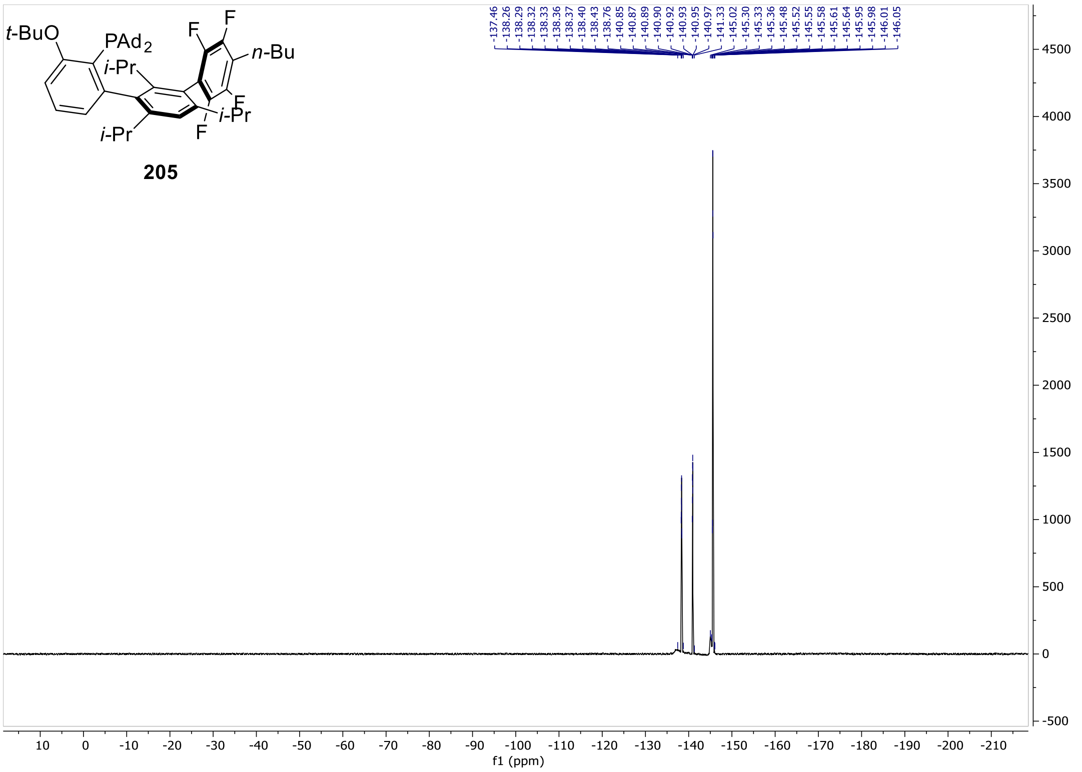

35.85
MeO
PAd2
i-Pr
F
F
n-Bu
F
i-Pr
F
i-Pr
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

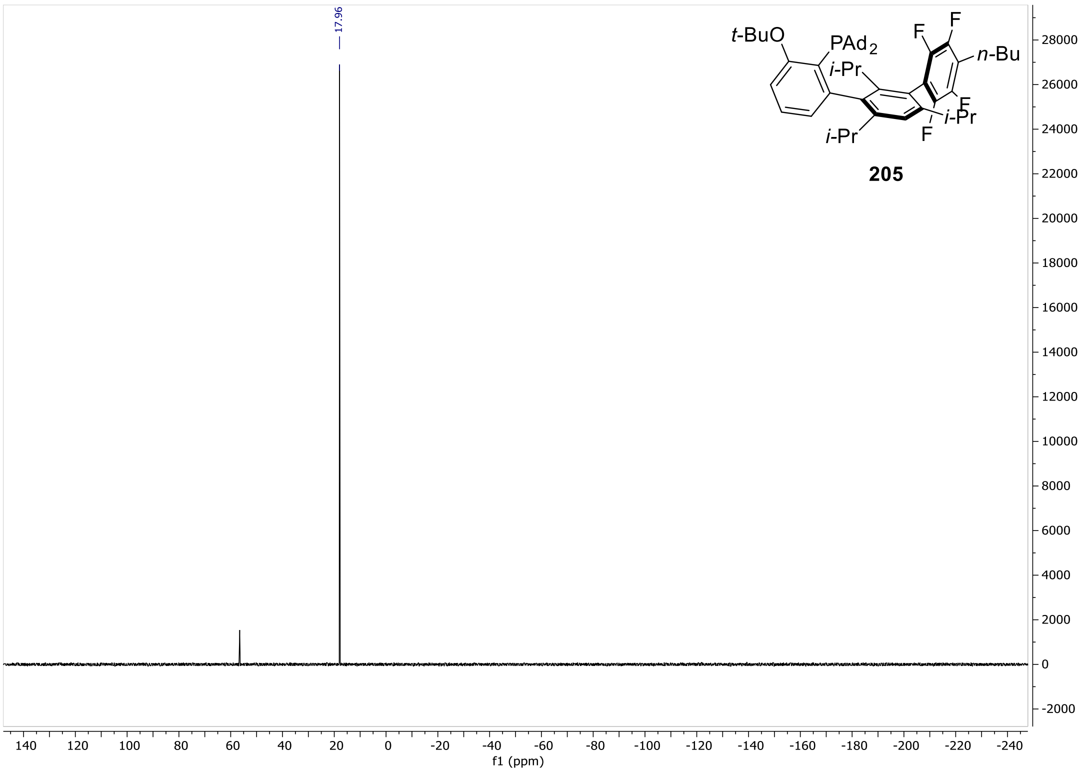
122

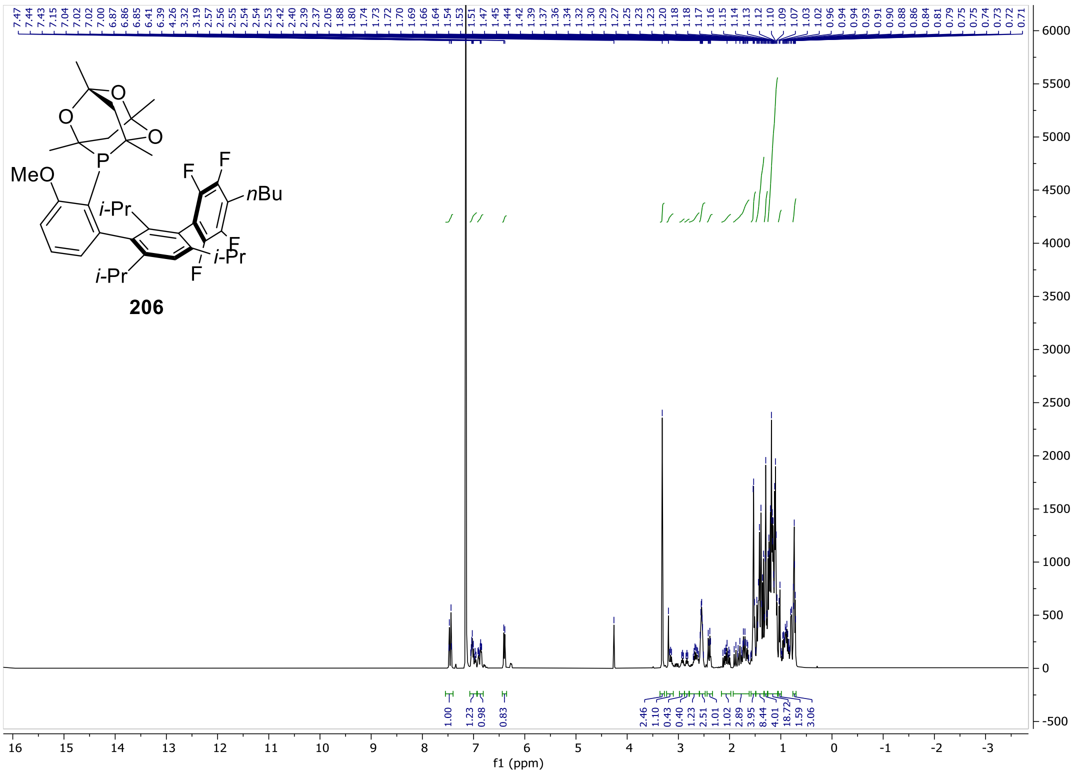

7.50
7.15
7.07
7.06
7.04
7.02
6.99
6.97
6.92
6.91
6.90
6.89
6.89
4.97
4.92
4.77
4.74
3.16
2.99
2.98
2.97
2.96
2.95
2.95
2.85
2.83
2.82
2.65
2.53
2.51
2.49
2.00
1.99
1.97
1.96
1.96
1.93
1.92
1.90
1.90
1.89
1.89
1.85
1.84
1.83
1.64
1.64
1.63
1.61
1.56
1.55
1.42
1.40
1.38
1.36
1.34
1.30
1.27
1.24
1.23
1.23
1.21
1.19
1.18
1.16
1.15
1.13
1.12
1.10
1.10
1.08
1.06
1.04
1.03
1.01
0.96
0.94
0.90
0.88
0.86
0.84
0.74
0.73
0.71
0.69
t-BuO
PAd2
i-Pr
F
F
n-Bu
F
i-Pr
F
i-Pr
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.00
1.99
1.07
1.83
1.10
1.11
0.69
2.76
6.69
3.24
10.01
2.95
20.37
12.41
0.56
4.03
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

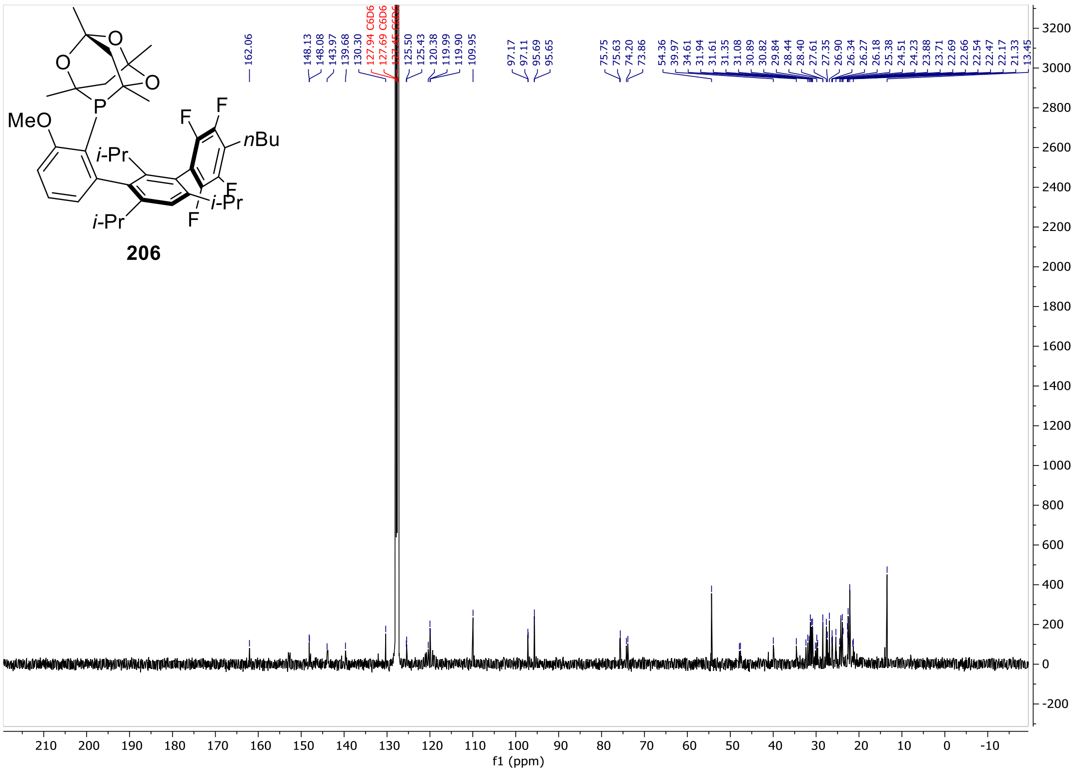
205

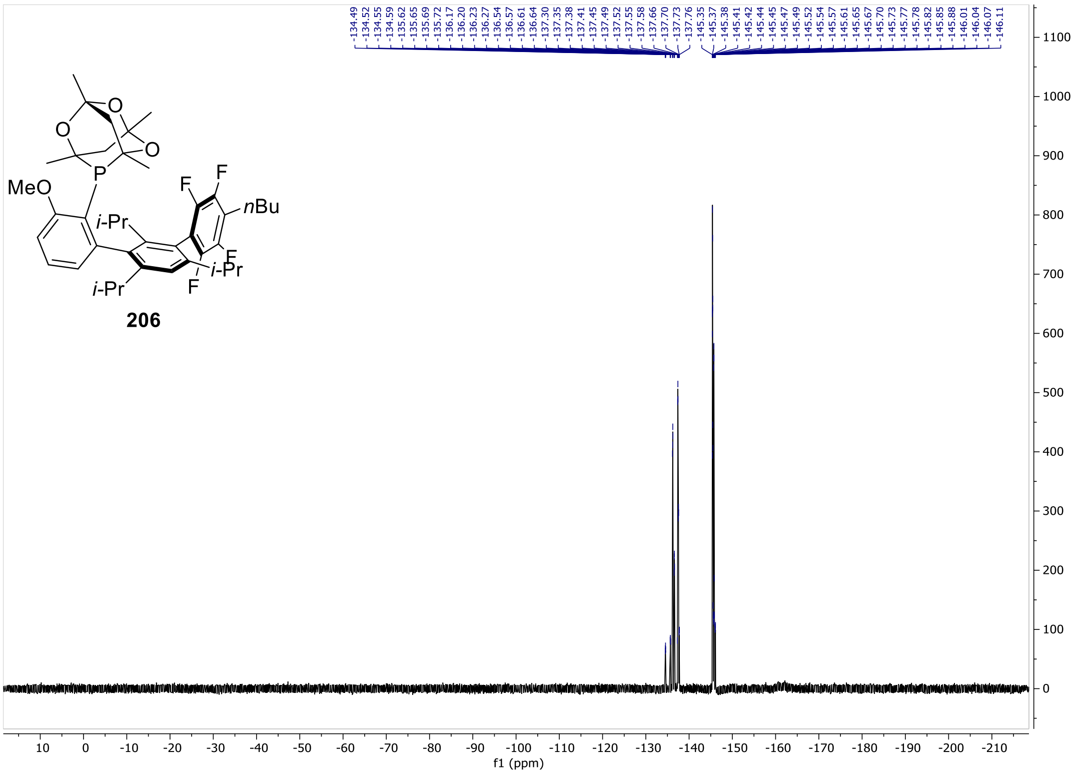

155.41
155.05
148.40
147.32
144.68
144.43
143.58
140.77
140.70
137.11
137.08
127.92 C6D6
127.68 C6D6
127.44 C6D6
125.56
124.39
122.67
122.54
121.70
121.01
120.99
120.37
120.18
118.09
116.58
116.41
77.92
77.81
43.55
43.45
36.70
34.21
34.04
31.71
31.24
30.19
28.91
28.83
28.65
28.62
24.06
24.03
24.00
23.96
23.87
23.80
23.76
22.52
22.22
13.43
t-BuO
PAd2
i-Pr
F
F
n-Bu
F
i-Pr
i-Pr
F
205
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

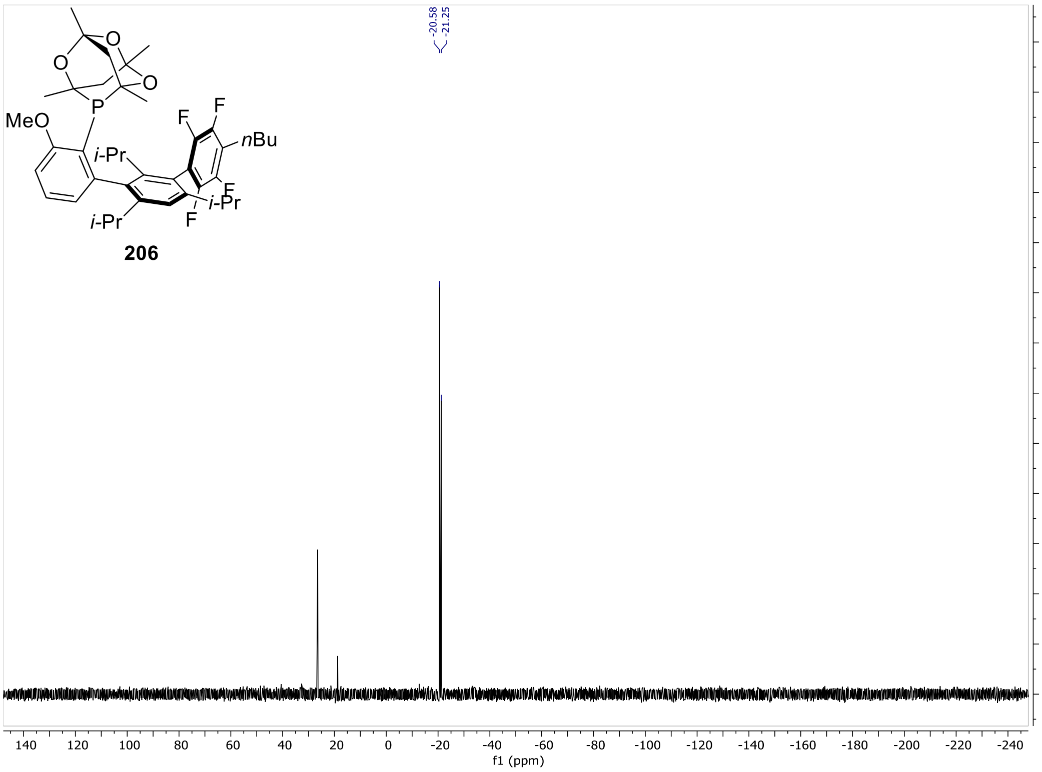

-137.46
-138.26
-138.29
-138.32
-138.33
-138.36
-138.37
-138.40
-138.43
-138.76
-140.85
-140.87
-140.89
-140.90
-140.92
-140.93
-140.95
-140.97
-141.33
-145.02
-145.30
-145.33
-145.36
-145.48
-145.52
-145.55
-145.58
-145.61
-145.64
-145.95
-145.98
-146.01
-146.05
t-BuO
PAd2
i-Pr
F
F
n-Bu
F
i-Pr
i-Pr
F
205
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


17.96
t-BuO
PAd2
i-Pr
F
F
n-Bu
F
i-Pr
F
i-Pr
205
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

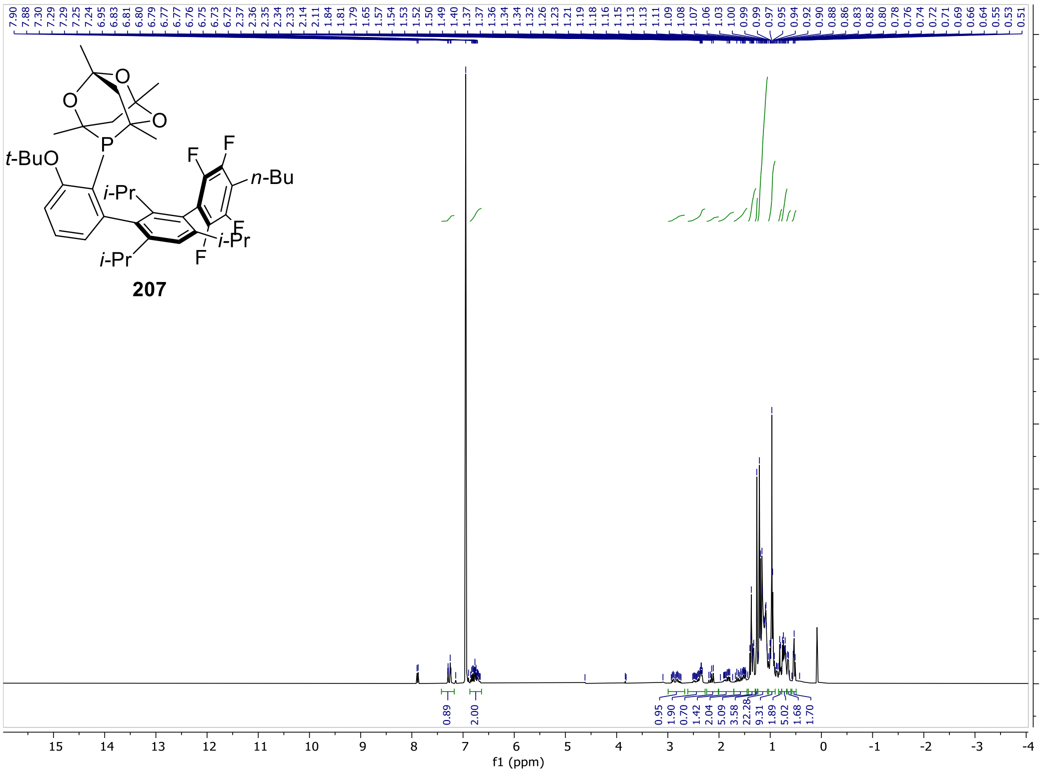

7.47 7.44 7.43 7.15 7.04 7.02 7.02 7.00 6.87 6.86 6.85 6.41 6.39 4.26 3.32 3.19 2.57 2.56 2.55 2.54 2.54 2.53 2.42 2.40 2.39 2.37 2.05 1.88 1.80 1.74 1.73 1.72 1.70 1.69 1.66 1.64 1.54 1.53 1.51 1.47 1.45 1.44 1.42 1.39 1.37 1.36 1.34 1.32 1.30 1.29 1.27 1.25 1.23 1.23 1.20 1.18 1.18 1.17 1.16 1.15 1.14 1.13 1.12 1.10 1.09 1.07 1.03 1.02 0.96 0.94 0.94 0.93 0.91 0.90 0.88 0.86 0.84 0.81 0.79 0.75 0.75 0.74 0.73 0.72 0.71
O
O
O
P
MeO
i-Pr
F
F
nBu
F
i-Pr
F
i-Pr
206
1.00
1.23
0.98
0.83
2.46
1.10
0.43
0.40
1.23
2.51
1.01
1.02
2.89
3.95
8.44
4.01
18.72
1.59
3.06
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


MeO
P
O
O
O
F
F
nBu
i-Pr
F
i-Pr
i-Pr
F
206
162.06
148.13
148.08
143.97
139.68
130.30
127.94 C6D6
127.69 C6D6
127.45 C6D6
125.50
125.43
120.38
119.99
119.90
109.95
97.17
97.11
95.69
95.65
75.75
75.63
74.20
73.86
54.36
39.97
34.61
31.94
31.61
31.35
31.08
30.89
30.82
29.84
28.44
28.40
27.61
27.35
26.90
26.34
26.27
26.18
25.38
24.51
24.23
23.88
23.71
22.69
22.66
22.54
22.47
22.17
21.33
13.45
f1 (ppm)

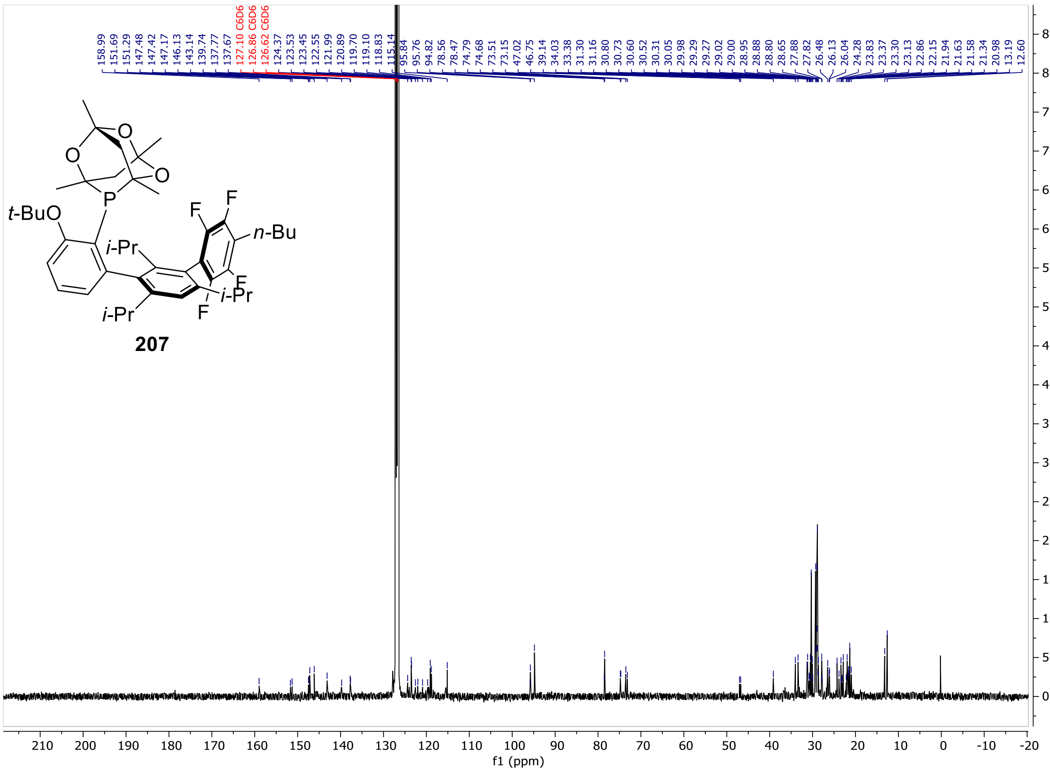

MeO
P
O
O
O
F
F
nBu
i-Pr
F
i-Pr
i-Pr
F
206
-134.49
-134.52
-134.55
-134.59
-135.62
-135.65
-135.69
-135.72
-136.17
-136.20
-136.23
-136.27
-136.54
-136.57
-136.61
-136.64
-137.30
-137.35
-137.38
-137.41
-137.45
-137.49
-137.52
-137.55
-137.58
-137.66
-137.70
-137.73
-137.76
-145.35
-145.37
-145.38
-145.41
-145.42
-145.44
-145.45
-145.47
-145.49
-145.52
-145.54
-145.57
-145.61
-145.65
-145.67
-145.70
-145.73
-145.77
-145.78
-145.82
-145.85
-145.88
-146.01
-146.04
-146.07
-146.11
f1 (ppm)

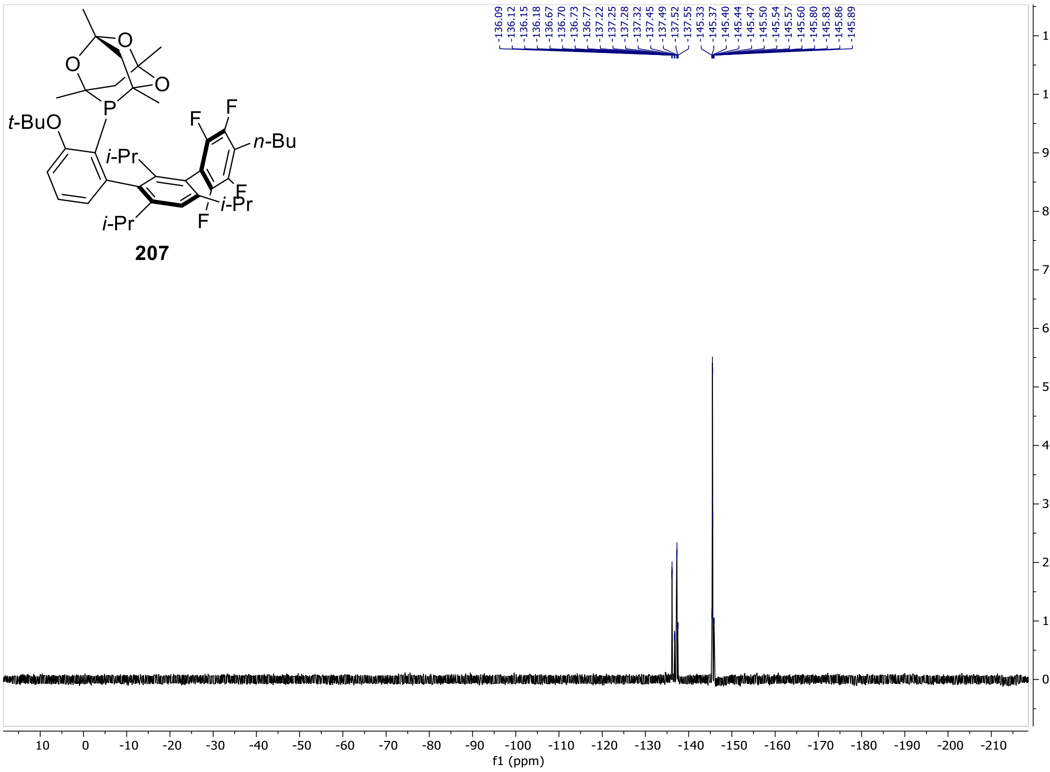

-20.58
-21.25
MeO
P
O
O
O
F
F
nBu
i-Pr
i-Pr
F
F
i-Pr
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

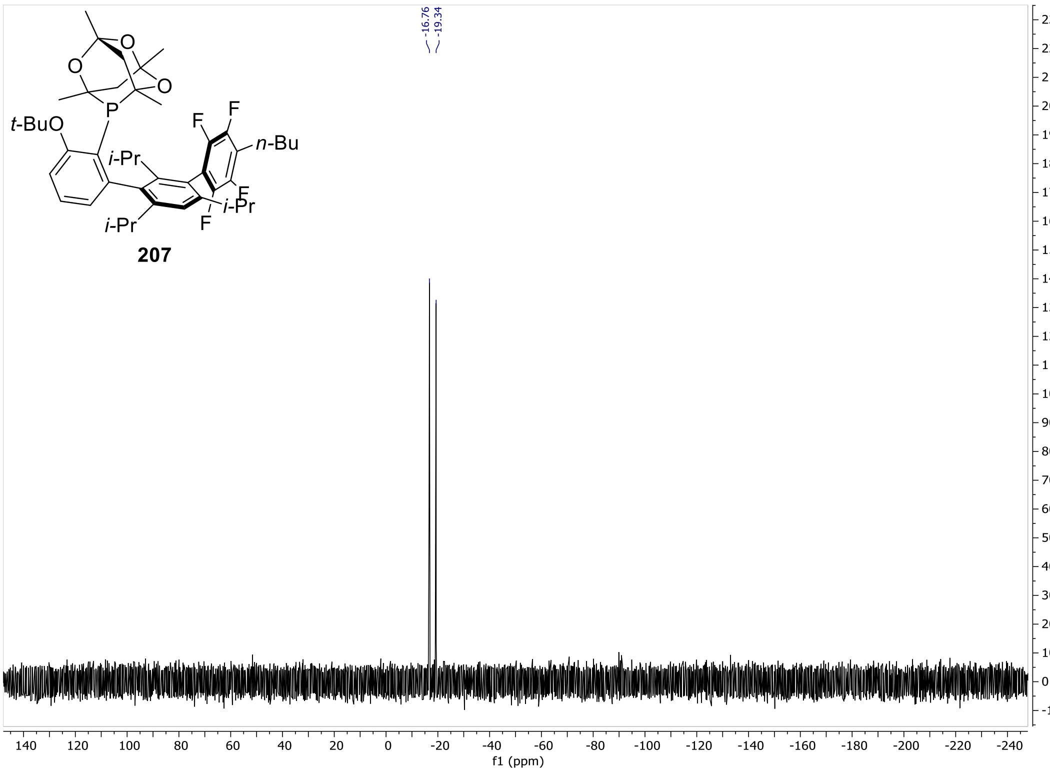
206

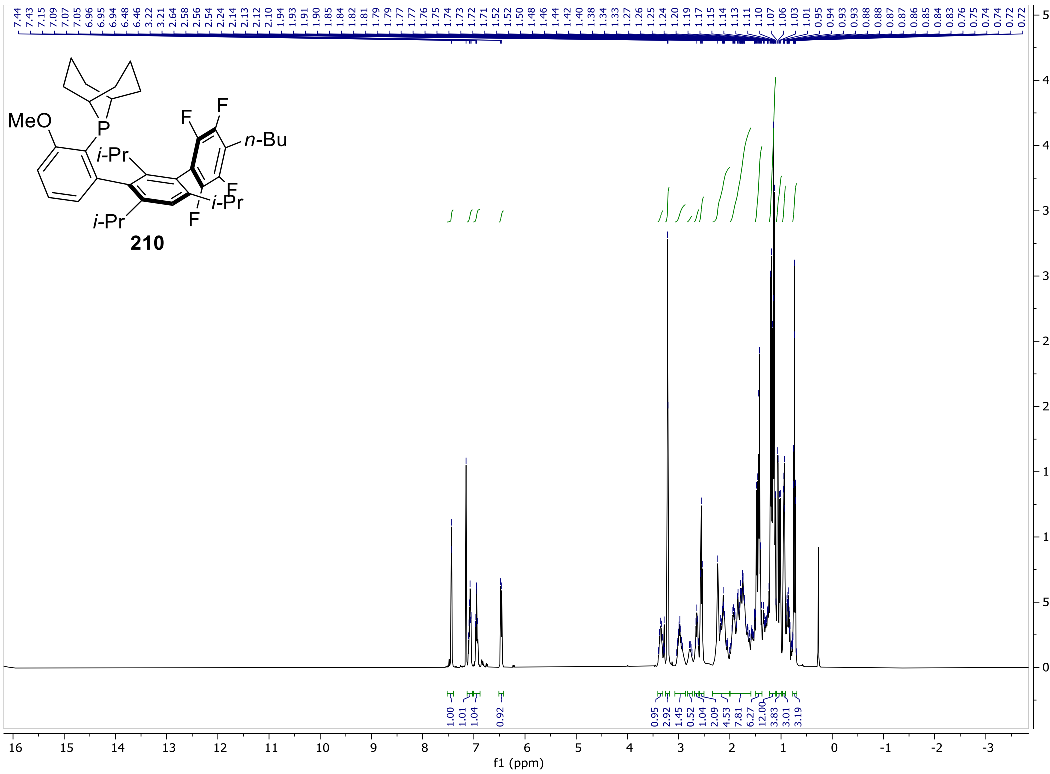

7.90
7.88
7.30
7.29
7.29
7.25
7.24
6.95
6.83
6.81
6.80
6.79
6.77
6.77
6.76
6.75
6.73
6.72
2.37
2.36
2.35
2.34
2.33
2.14
2.11
1.84
1.81
1.79
1.65
1.57
1.54
1.53
1.52
1.50
1.49
1.40
1.37
1.37
1.36
1.34
1.34
1.32
1.26
1.23
1.21
1.19
1.18
1.16
1.15
1.13
1.13
1.11
1.09
1.08
1.07
1.06
1.03
1.00
0.99
0.99
0.97
0.95
0.94
0.92
0.90
0.88
0.86
0.83
0.82
0.80
0.78
0.76
0.74
0.72
0.71
0.69
0.66
0.64
0.55
0.53
0.51
t-BuO
P
O
O
O
F
F
n-Bu
i-Pr
i-Pr
F
F
i-Pr
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0.89
2.00
0.95
1.90
0.70
1.42
2.04
5.09
3.58
22.28
9.31
1.89
5.02
1.68
1.70
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

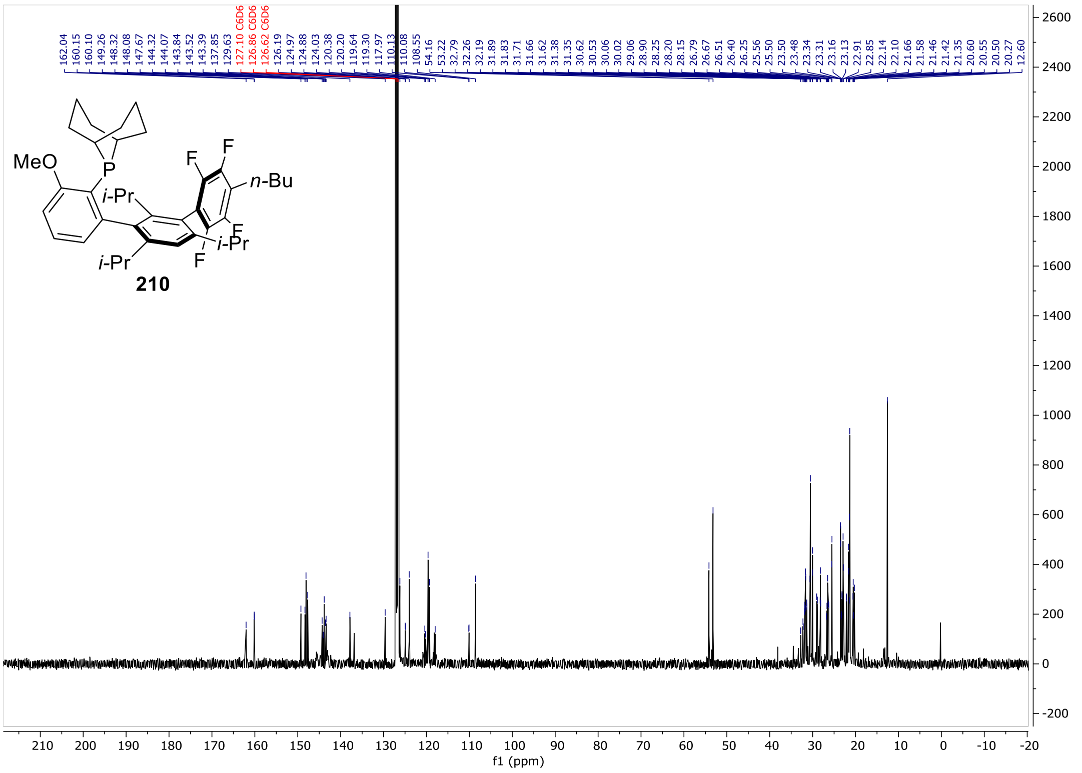
207

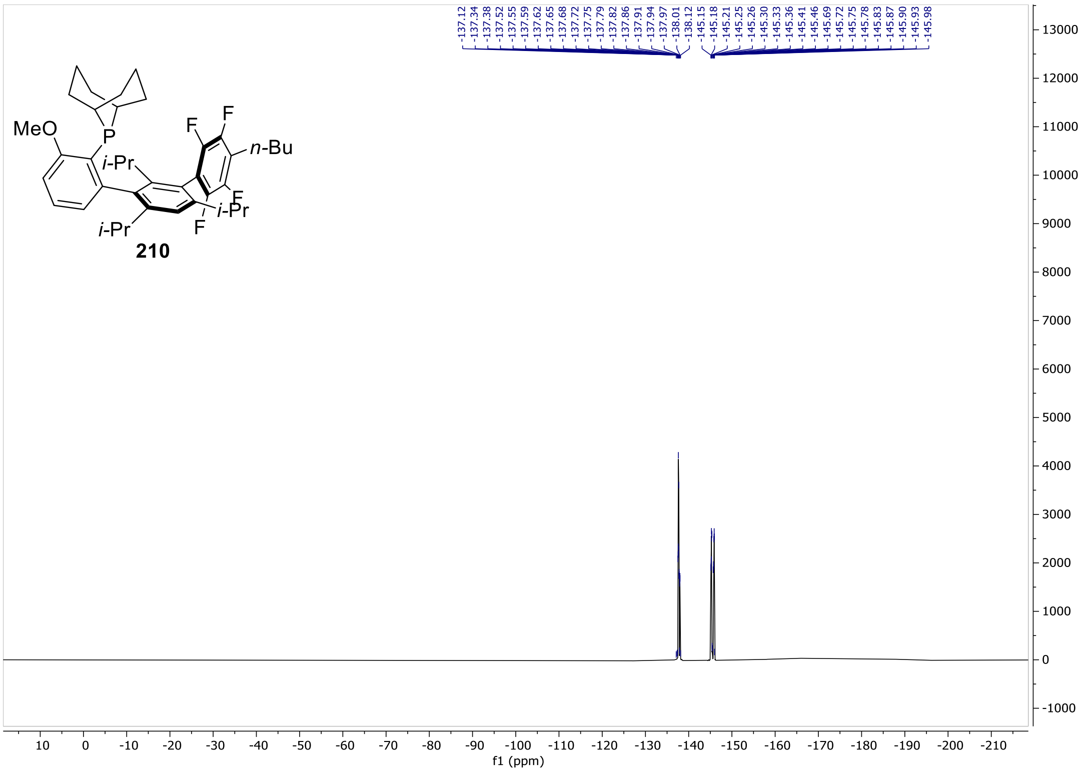

158.99
151.69
151.29
147.48
147.42
147.17
146.13
143.14
139.74
137.77
137.67
127.10 C6D6
126.86 C6D6
126.62 C6D6
124.37
123.53
123.45
122.55
121.99
120.89
119.70
119.10
118.83
115.14
95.84
95.76
94.82
78.56
78.47
74.79
74.68
73.51
73.15
47.02
46.75
39.14
34.03
33.38
31.30
31.16
30.80
30.73
30.60
30.52
30.31
30.05
29.98
29.29
29.27
29.02
29.00
28.95
28.88
28.80
28.65
27.88
27.82
26.48
26.13
26.04
24.28
23.83
23.37
23.30
23.13
22.86
22.15
21.94
21.63
21.58
21.34
20.98
13.19
12.60
O
O
O
O
P
t-BuO
i-Pr
i-Pr
F
F
n-Bu
F
F
i-Pr
207
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)
8500 8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0

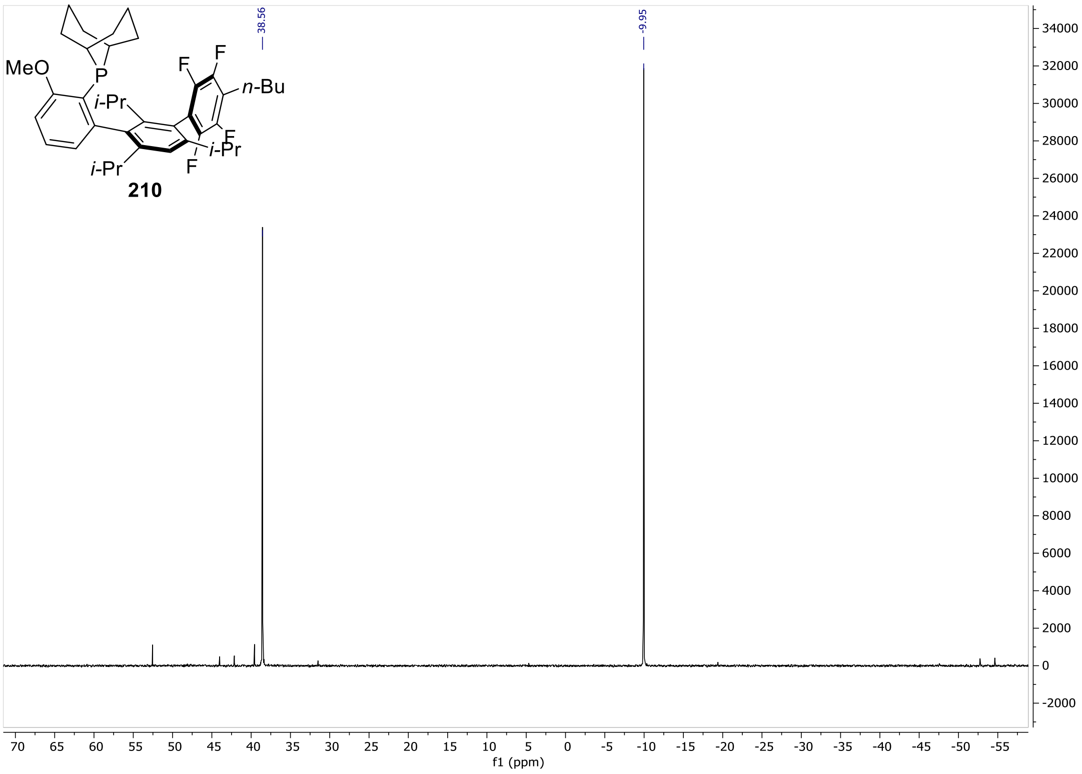

-136.09
-136.12
-136.15
-136.18
-136.67
-136.70
-136.73
-136.77
-137.22
-137.25
-137.28
-137.32
-137.45
-137.49
-137.52
-137.55
-145.33
-145.37
-145.40
-145.44
-145.47
-145.50
-145.54
-145.57
-145.60
-145.80
-145.83
-145.86
-145.89
O
O
O
O
P
t-BuO
i-Pr
i-Pr
F
F
n-Bu
F
F
i-Pr
207
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
1100 1000 900 800 700 600 500 400 300 200 100 0

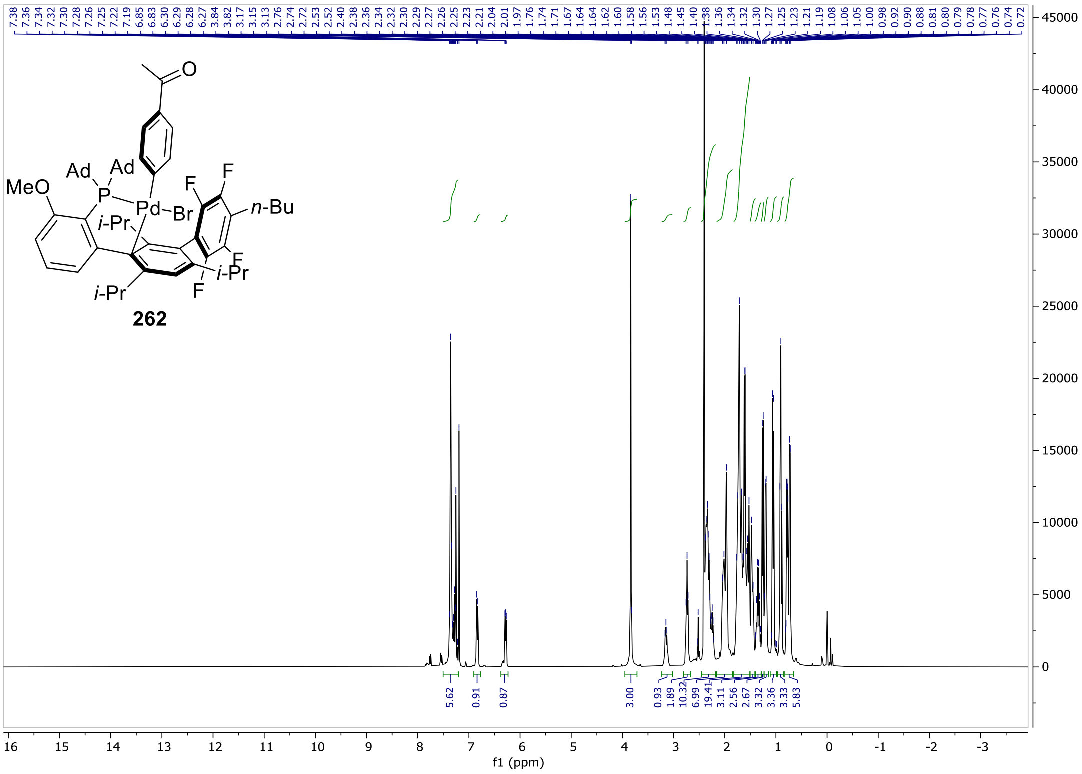

207
-16.76
-19.34
t-BuO
O
O
O
P
F
F
n-Bu
i-Pr
F
i-Pr
F
i-Pr
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

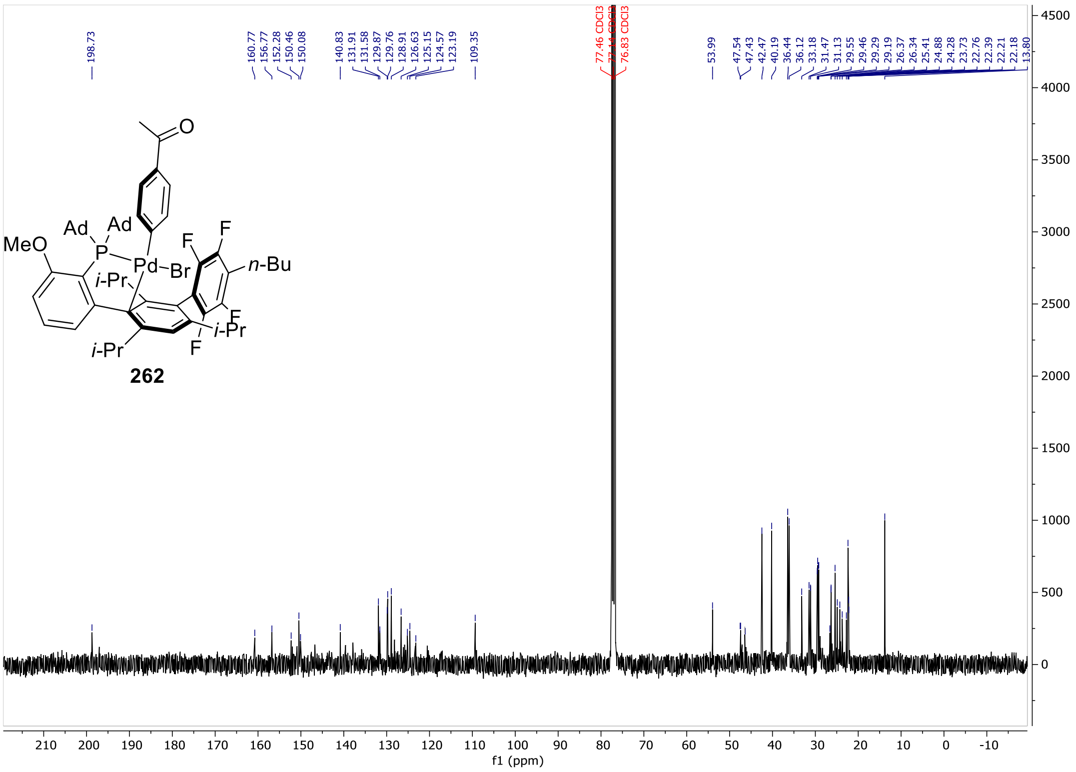

210
7.44
7.43
7.15
7.09
7.07
7.05
6.96
6.95
6.94
6.48
6.46
3.22
3.21
2.64
2.58
2.56
2.54
2.24
2.14
2.13
2.12
2.10
1.94
1.93
1.91
1.90
1.85
1.84
1.82
1.81
1.79
1.79
1.77
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.52
1.52
1.50
1.48
1.46
1.44
1.42
1.40
1.38
1.34
1.33
1.27
1.26
1.25
1.24
1.20
1.19
1.17
1.15
1.14
1.13
1.11
1.10
1.07
1.06
1.03
1.01
0.95
0.94
0.93
0.93
0.88
0.88
0.87
0.86
0.85
0.84
0.83
0.76
0.75
0.74
0.72
0.72
MeO
P
F
F
n-Bu
i-Pr
F
i-Pr
F
i-Pr
1.00
1.01
1.04
0.92
0.95
2.92
1.45
0.52
1.04
2.09
4.53
7.81
6.27
12.00
3.83
3.01
3.19
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


162.04
160.15
160.10
149.26
148.32
148.08
147.67
144.32
144.07
143.84
143.52
143.39
137.85
129.63
127.10 C6D6
126.86 C6D6
126.62 C6D6
126.19
124.97
124.88
124.03
120.38
120.20
119.64
119.30
117.97
110.13
110.08
108.55
54.16
53.22
32.79
32.26
32.19
31.89
31.83
31.71
31.66
31.62
31.38
31.35
30.62
30.53
30.06
30.02
29.06
28.90
28.25
28.20
28.15
26.79
26.67
26.51
26.40
26.25
25.56
25.50
23.50
23.48
23.34
23.31
23.16
23.13
22.91
22.85
22.14
22.10
21.66
21.58
21.46
21.42
21.35
20.60
20.55
20.50
20.27
12.60
MeO
P
i-Pr
F
F
n-Bu
F
i-Pr
i-Pr
F
210
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

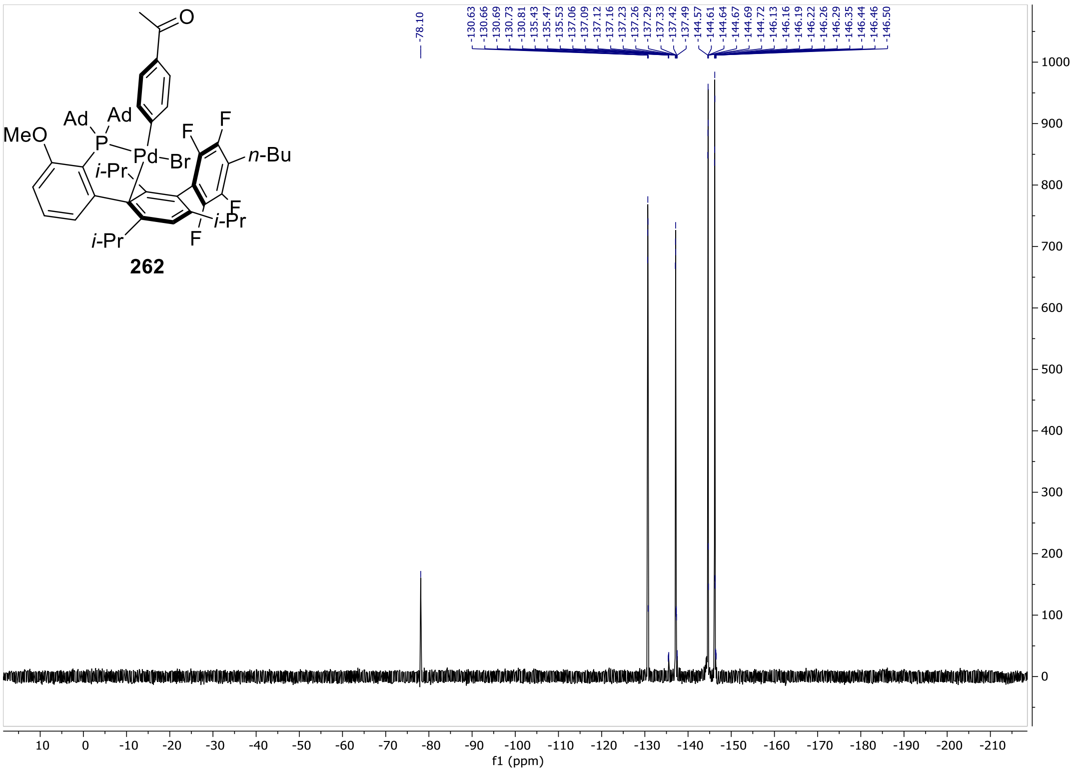

-137.12
-137.34
-137.38
-137.52
-137.55
-137.59
-137.62
-137.65
-137.68
-137.72
-137.75
-137.79
-137.82
-137.86
-137.91
-137.94
-137.97
-138.01
-138.12
-145.15
-145.18
-145.21
-145.25
-145.26
-145.30
-145.33
-145.36
-145.41
-145.46
-145.69
-145.72
-145.75
-145.78
-145.83
-145.87
-145.90
-145.93
-145.98
MeO
P
i-Pr
F
F
n-Bu
F
i-Pr
i-Pr
F
210
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


MeO
P
i-Pr
F
F
n-Bu
F
i-Pr
i-Pr
F
210
38.56
-9.95
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55
f1 (ppm)

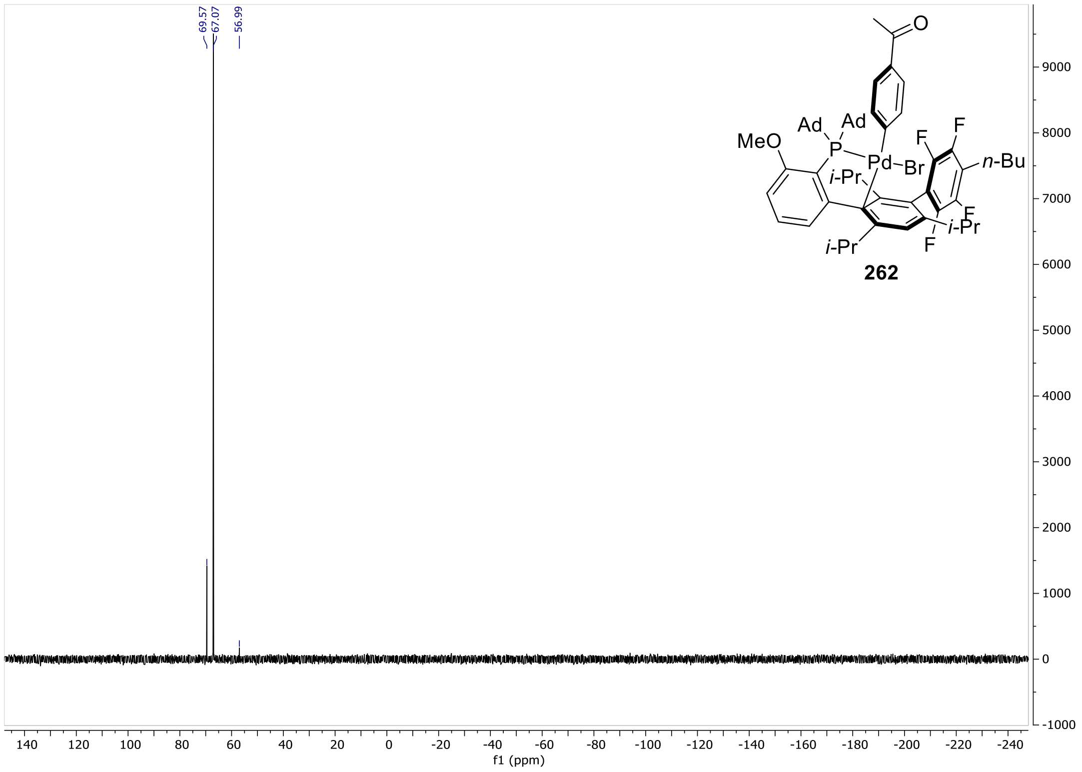

O
Ad
Ad
MeO
P
Pd
Br
i-Pr
F
F
n-Bu
F
i-Pr
i-Pr
F
262
7.38 7.36 7.34 7.32 7.30 7.28 7.26 7.25 7.22 7.19 6.85 6.83 6.30 6.29 6.28 6.27 3.84 3.82 3.17 3.15 3.13 2.76 2.74 2.72 2.53 2.52 2.40 2.38 2.36 2.34 2.32 2.30 2.29 2.27 2.26 2.25 2.23 2.21 2.04 2.01 1.97 1.76 1.74 1.71 1.67 1.64 1.64 1.62 1.60 1.58 1.56 1.53 1.48 1.45 1.40 1.38 1.36 1.34 1.32 1.30 1.27 1.25 1.23 1.21 1.19 1.08 1.06 1.05 1.00 0.98 0.92 0.90 0.88 0.81 0.80 0.79 0.78 0.77 0.76 0.74 0.72
5.62
0.91
0.87
3.00
0.93
1.89
10.32
6.99
19.41
3.11
2.56
2.67
3.32
3.36
3.33
5.83
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


198.73
160.77
156.77
152.28
150.46
150.08
140.83
131.91
131.58
129.87
129.76
128.91
126.63
125.15
124.57
123.19
109.35
77.46 CDCl3
77.14 CDCl3
76.83 CDCl3
53.99
47.54
47.43
42.47
40.19
36.44
36.12
33.18
31.47
31.13
29.55
29.46
29.29
29.19
26.37
26.34
25.41
24.88
24.28
23.73
22.76
22.39
22.21
22.18
13.80
O
Ad
Ad
MeO
P
Pd
Br
F
F
n-Bu
i-Pr
F
i-Pr
i-Pr
F
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

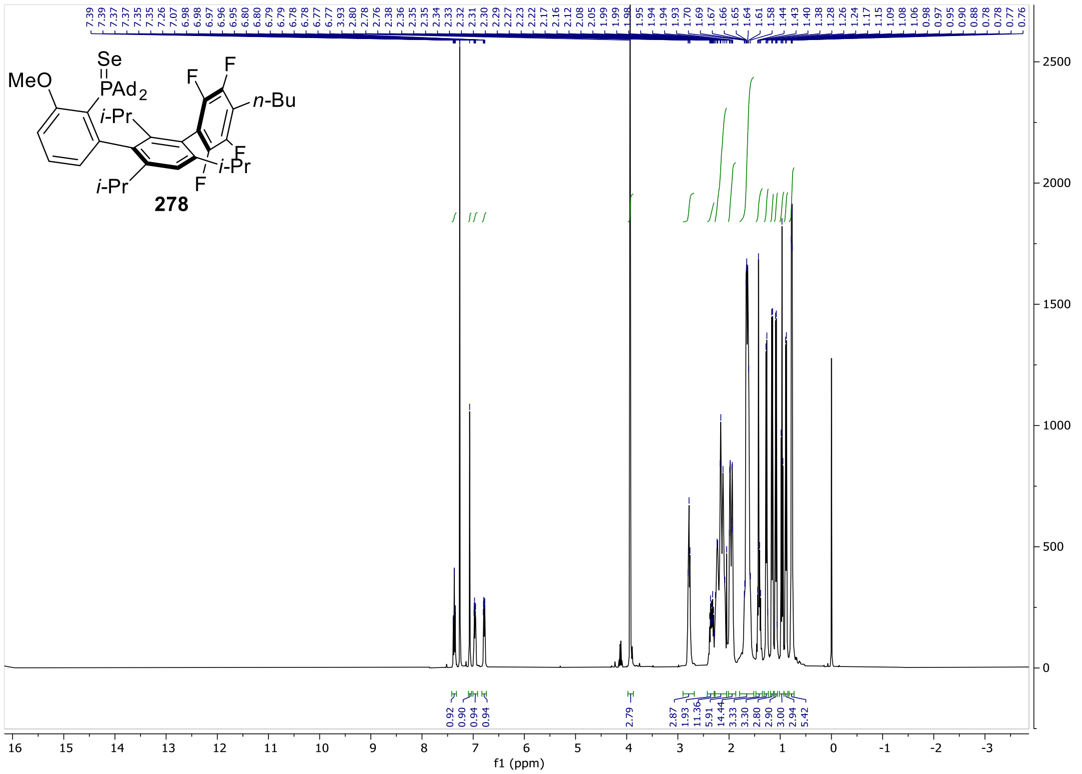
262


-78.10
-130.63
-130.66
-130.69
-130.73
-130.81
-135.43
-135.47
-135.53
-137.06
-137.09
-137.12
-137.16
-137.23
-137.26
-137.29
-137.33
-137.42
-137.49
-144.57
-144.61
-144.64
-144.67
-144.69
-144.72
-146.13
-146.16
-146.19
-146.22
-146.26
-146.29
-146.35
-146.44
-146.46
-146.50
O
Ad
Ad
MeO
P
Pd
Br
F
F
n-Bu
i-Pr
F
i-Pr
i-Pr
F
1000
900
800
700
600
500
400
300
200
100
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

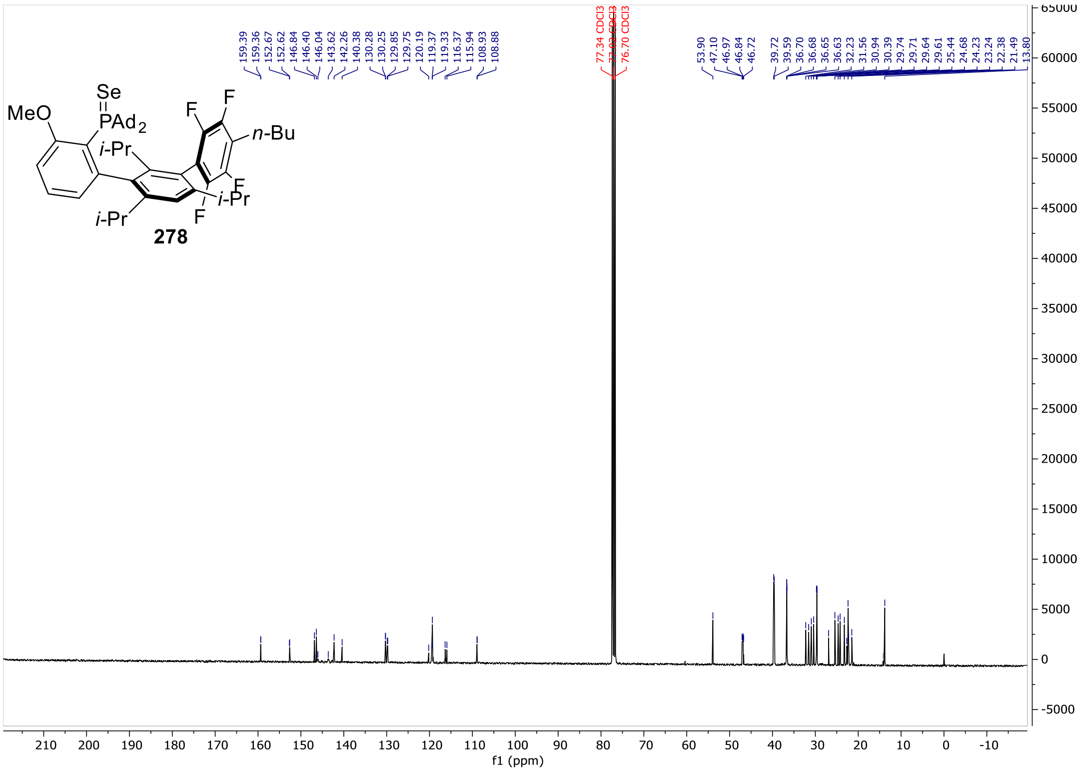
262


69.57
67.07
56.99
MeO
Ad
Ad
P
Pd
Br
i-Pr
i-Pr
i-Pr
F
F
F
F
n-Bu
O
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

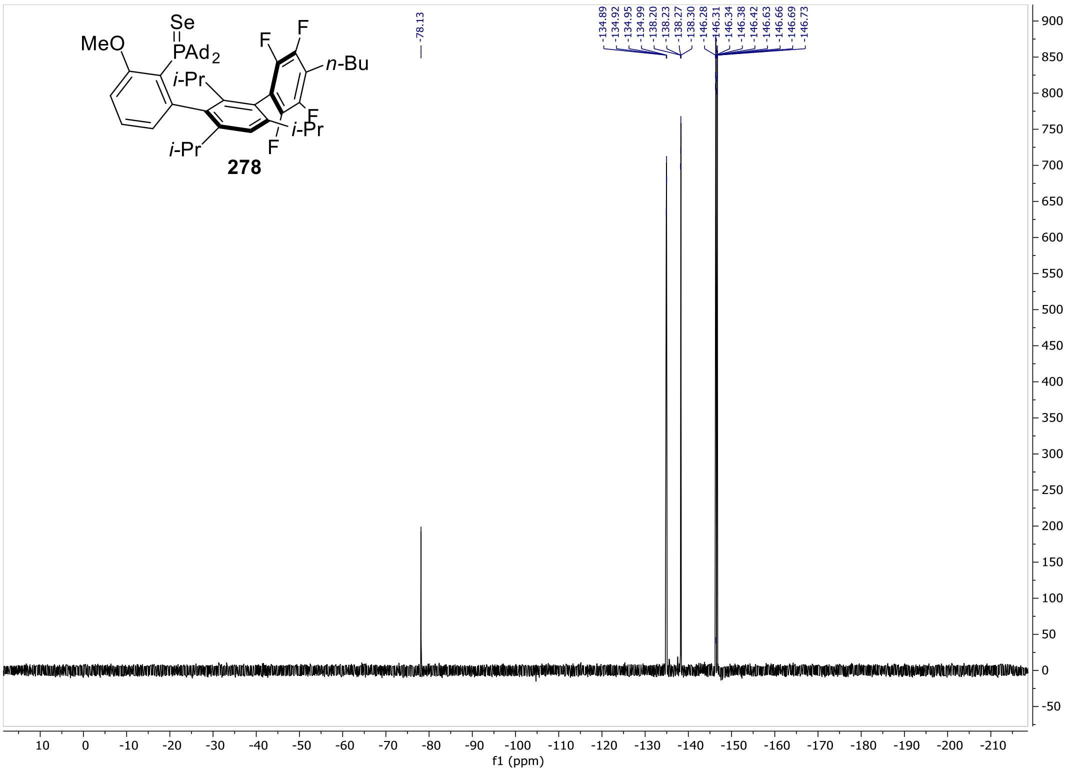
262


7.39
7.39
7.37
7.37
7.35
7.35
7.26
7.07
6.98
6.98
6.97
6.96
6.95
6.80
6.80
6.79
6.79
6.78
6.78
6.77
6.77
3.93
2.80
2.78
2.76
2.38
2.36
2.35
2.35
2.34
2.33
2.32
2.31
2.30
2.29
2.27
2.23
2.22
2.17
2.16
2.12
2.08
2.05
1.99
1.99
1.98
1.95
1.94
1.94
1.93
1.70
1.69
1.67
1.66
1.65
1.64
1.61
1.58
1.44
1.43
1.40
1.38
1.28
1.26
1.24
1.17
1.15
1.09
1.08
1.06
0.98
0.97
0.95
0.90
0.88
0.78
0.78
0.77
0.76
MeO
Se
PAd$_2$
i-Pr
i-Pr
i-Pr
F
F
F
F
n-Bu
2500
2000
1500
1000
500
0
0.92
0.90
0.94
0.94
2.79
2.87
1.93
11.36
5.91
14.44
3.33
3.30
2.80
2.90
3.00
2.94
5.42
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

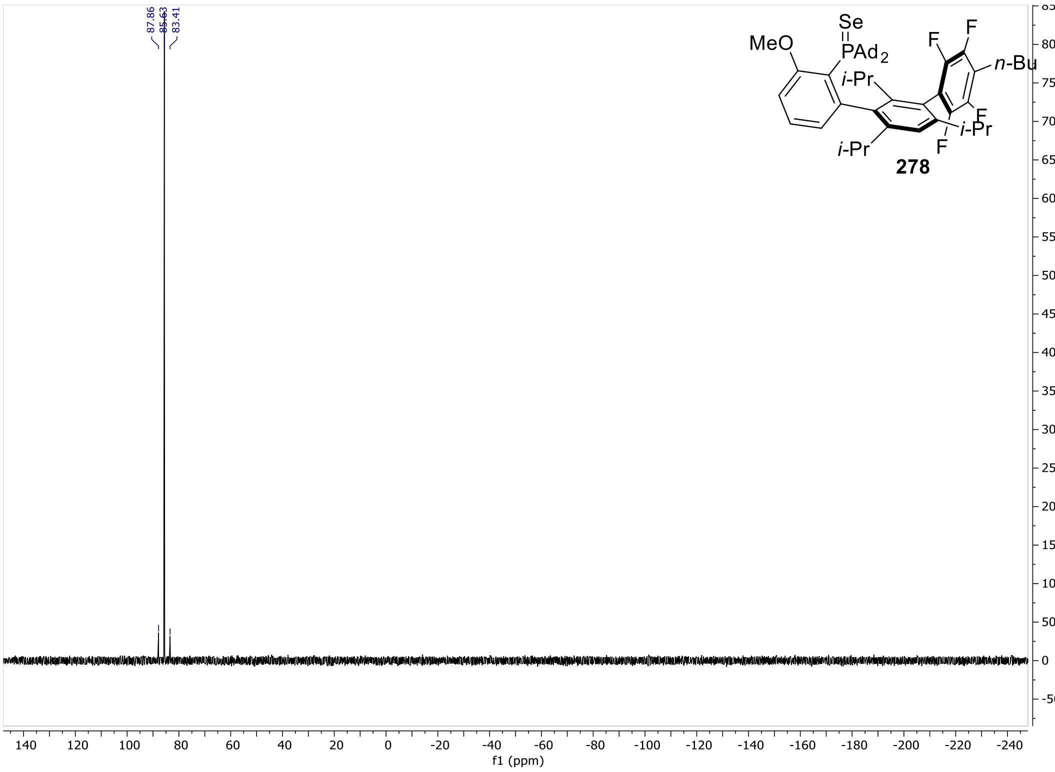
278



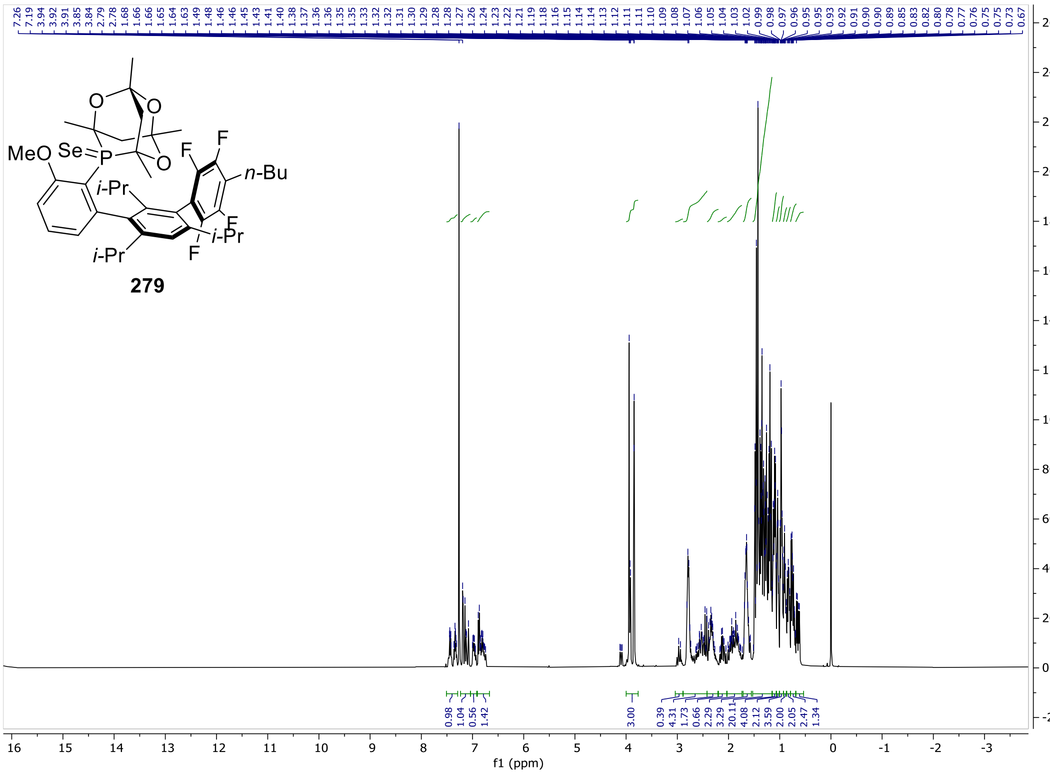
159.39
159.36
152.67
152.62
146.84
146.40
146.04
143.62
142.26
140.38
130.28
130.25
129.85
129.75
120.19
119.37
119.33
116.37
115.94
108.93
108.88
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
53.90
47.10
46.97
46.84
46.72
39.72
39.59
36.70
36.68
36.65
36.63
32.23
31.56
30.94
30.39
29.74
29.71
29.64
29.61
25.44
24.68
24.23
23.24
22.38
21.49
13.80
Se
MeO
PAd2
i-Pr
F
F
n-Bu
F
i-Pr
i-Pr
F
278
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



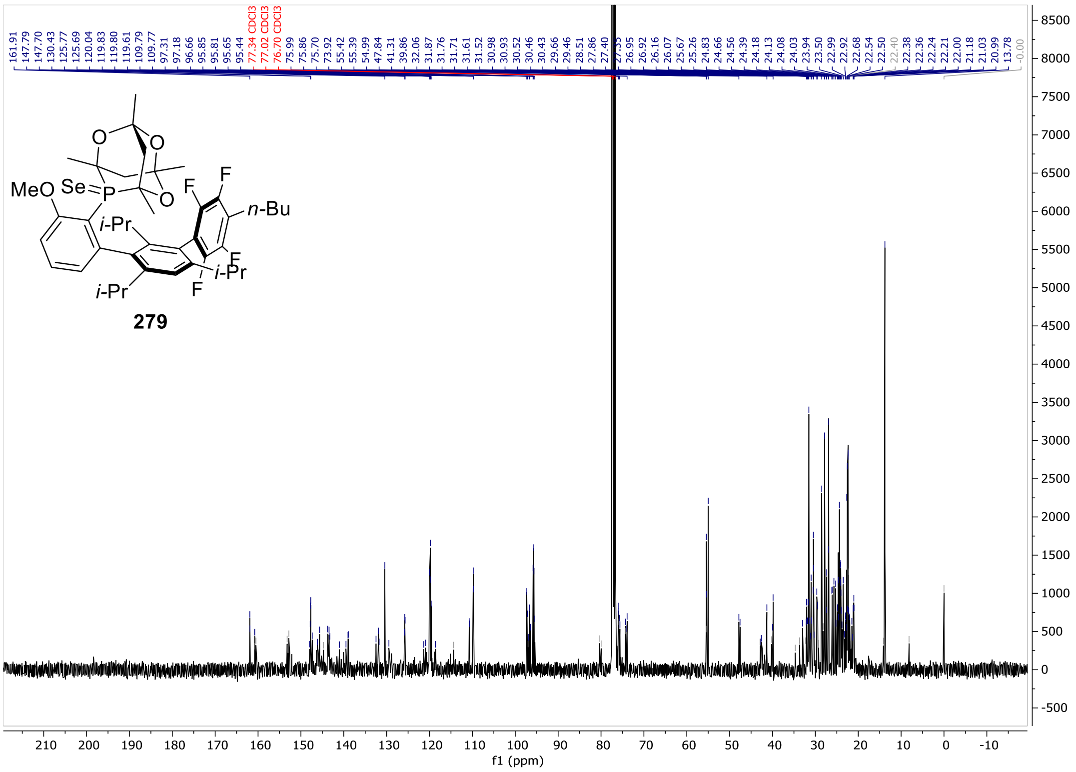
Se
MeO
PAd2
i-Pr
F
F
n-Bu
F
i-Pr
i-Pr
F
278
-78.13
-134.89
-134.92
-134.95
-134.99
-138.20
-138.23
-138.27
-138.30
-146.28
-146.31
-146.34
-146.38
-146.42
-146.63
-146.66
-146.69
-146.73
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

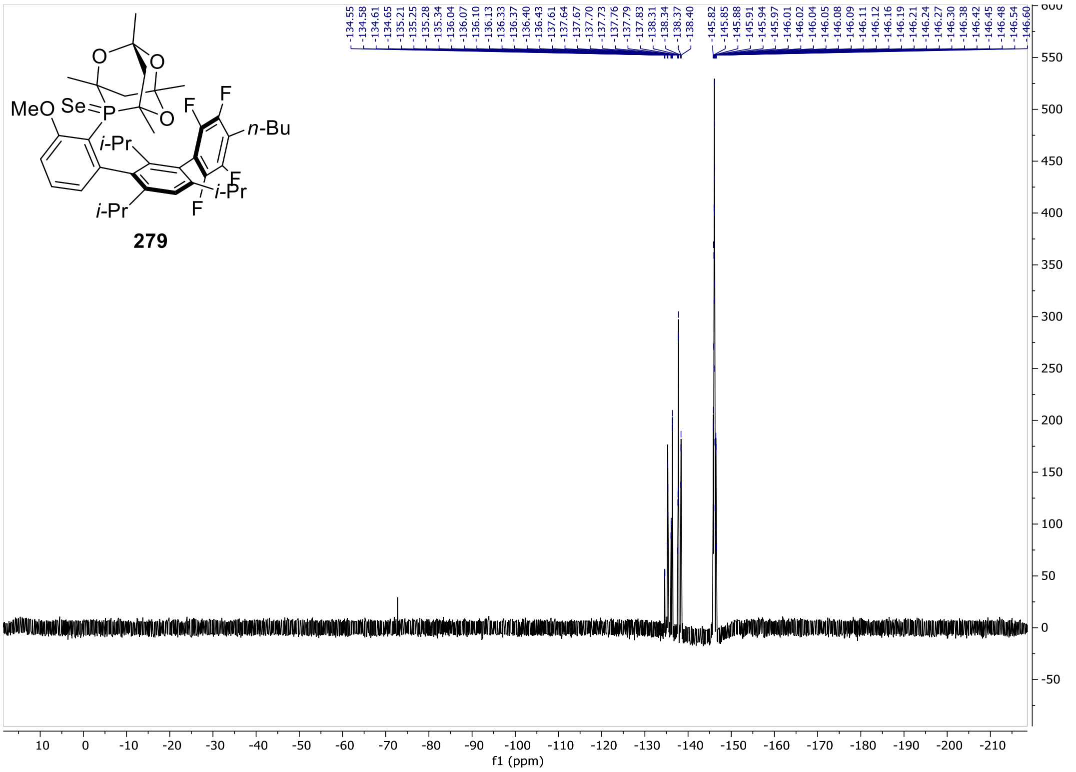

87.86
85.63
83.41
MeO
Se
PAd2
i-Pr
F
F
n-Bu
F
i-Pr
F
i-Pr
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

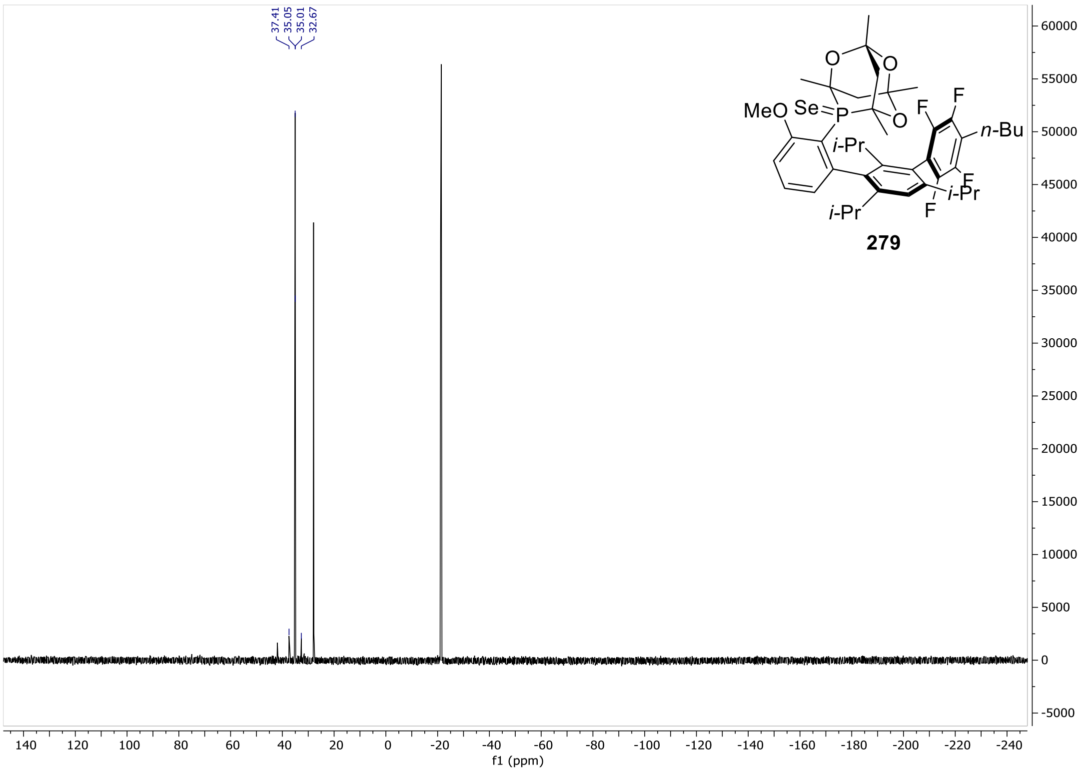
278


7.26
7.19
3.94
3.92
3.91
3.85
3.84
2.79
2.78
1.68
1.66
1.66
1.65
1.64
1.63
1.49
1.48
1.46
1.46
1.45
1.43
1.41
1.40
1.38
1.37
1.36
1.36
1.35
1.35
1.33
1.32
1.32
1.31
1.30
1.29
1.28
1.28
1.27
1.26
1.24
1.23
1.22
1.21
1.19
1.18
1.16
1.15
1.14
1.14
1.13
1.12
1.11
1.11
1.10
1.09
1.08
1.07
1.06
1.05
1.04
1.03
1.02
0.99
0.98
0.97
0.96
0.95
0.95
0.93
0.92
0.91
0.90
0.90
0.89
0.85
0.83
0.82
0.80
0.78
0.77
0.76
0.75
0.73
0.67
O
O
O
MeO
Se
P
F
F
n-Bu
i-Pr
F
i-Pr
F
i-Pr
0.98
1.04
0.56
1.42
3.00
0.39
4.31
1.73
0.66
2.29
3.29
20.11
4.08
2.12
3.59
2.00
2.05
2.47
1.34
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

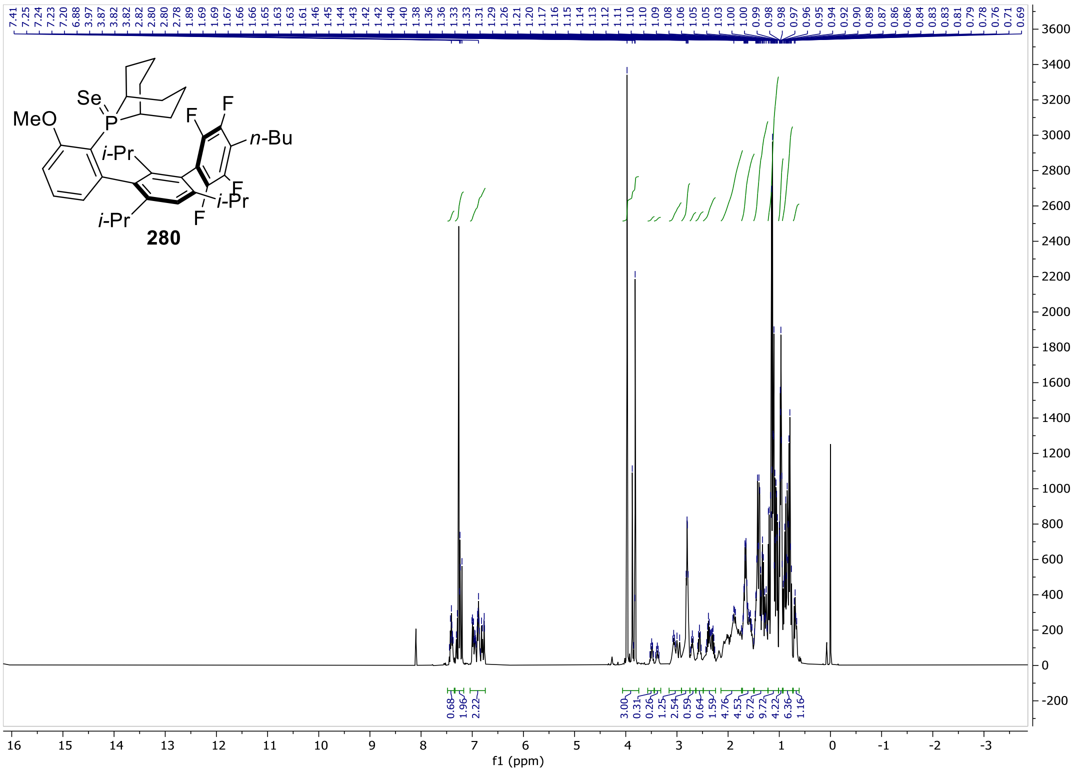
279


161.91
147.79
147.70
130.43
125.77
125.69
120.04
119.83
119.80
119.61
109.79
109.77
97.31
97.18
96.66
95.85
95.81
95.65
95.44
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
75.99
75.86
75.70
73.92
55.42
55.39
54.99
47.84
41.31
39.86
32.06
31.87
31.76
31.71
31.61
31.52
30.98
30.93
30.52
30.46
30.43
29.66
29.46
28.51
27.86
27.40
27.35
26.95
26.92
26.16
26.07
25.67
25.26
24.83
24.66
24.56
24.39
24.18
24.13
24.08
24.03
23.94
23.50
22.99
22.92
22.68
22.54
22.50
22.40
22.38
22.36
22.24
22.21
22.00
21.18
21.03
20.99
13.78
-0.00
MeO
Se
P
O
O
O
F
F
n-Bu
i-Pr
F
i-Pr
i-Pr
F
279
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

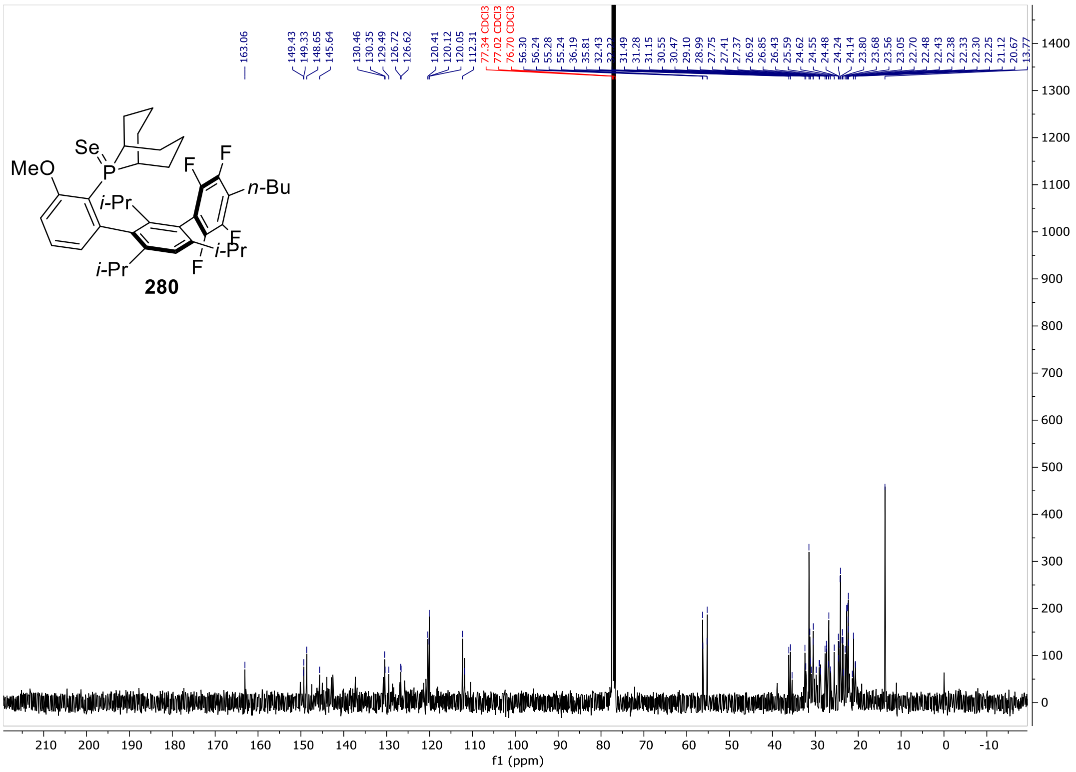

-134.55
-134.58
-134.61
-134.65
-135.21
-135.25
-135.28
-135.34
-136.04
-136.07
-136.10
-136.13
-136.33
-136.37
-136.40
-136.43
-137.61
-137.64
-137.67
-137.70
-137.73
-137.76
-137.79
-137.83
-138.31
-138.34
-138.37
-138.40
-145.82
-145.85
-145.88
-145.91
-145.94
-145.97
-146.01
-146.02
-146.04
-146.05
-146.08
-146.09
-146.11
-146.12
-146.16
-146.19
-146.21
-146.24
-146.27
-146.30
-146.38
-146.42
-146.45
-146.48
-146.54
-146.60
MeO
Se
P
O
O
O
F
F
n-Bu
i-Pr
F
i-Pr
i-Pr
F
279
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

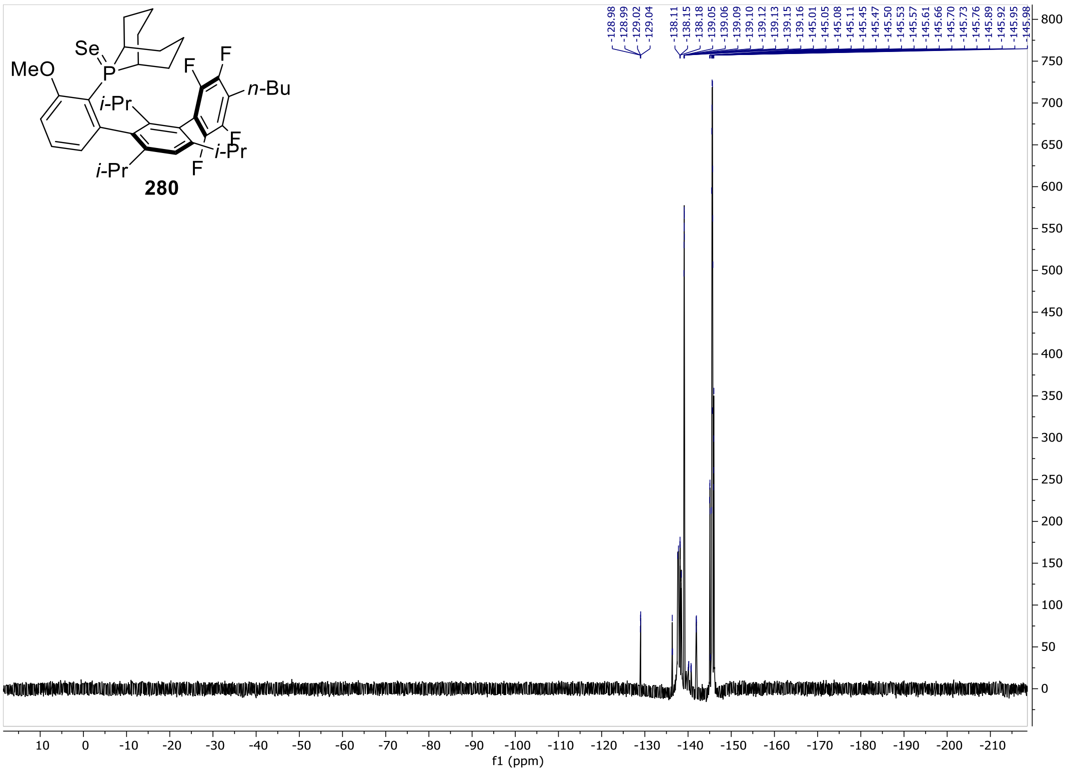

37.41
35.05
35.01
32.67
MeO
Se
P
O
F
n-Bu
i-Pr
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

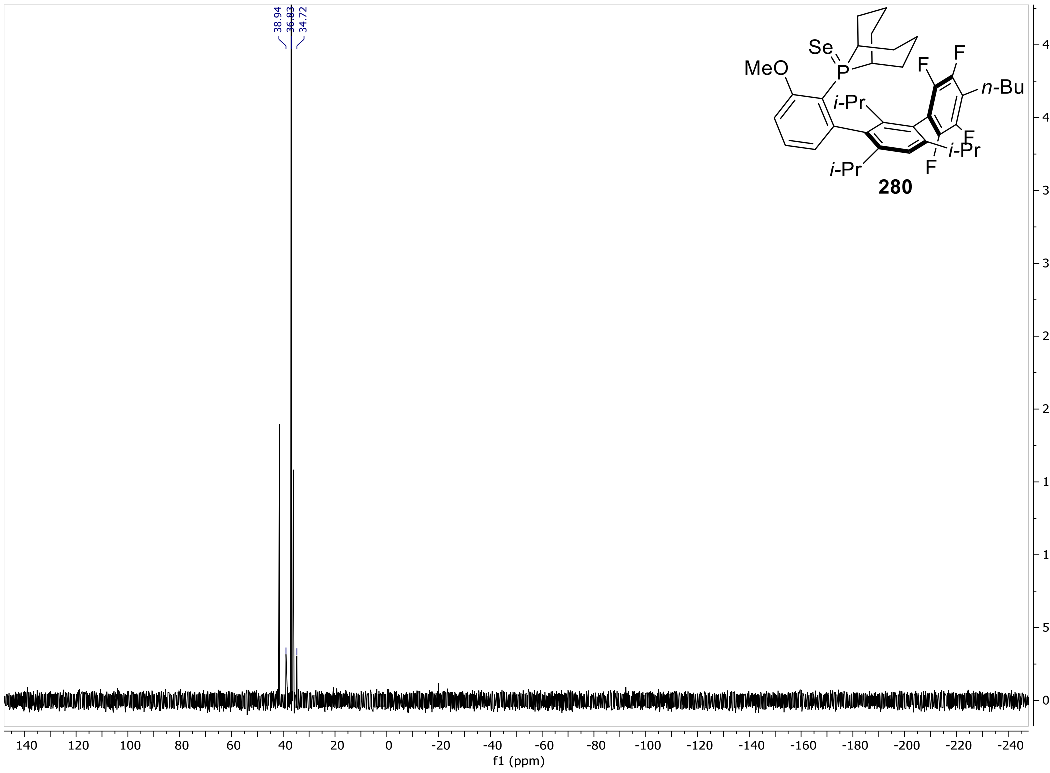
279


7.41
7.25
7.24
7.23
7.20
6.88
3.97
3.87
3.82
3.82
2.82
2.80
2.78
1.89
1.69
1.69
1.67
1.66
1.66
1.65
1.63
1.63
1.61
1.46
1.45
1.44
1.43
1.42
1.40
1.40
1.38
1.36
1.36
1.33
1.33
1.31
1.29
1.26
1.21
1.20
1.17
1.16
1.15
1.14
1.13
1.12
1.11
1.10
1.10
1.09
1.08
1.06
1.05
1.05
1.03
1.00
1.00
0.99
0.98
0.98
0.97
0.96
0.95
0.94
0.92
0.90
0.89
0.87
0.86
0.84
0.83
0.81
0.79
0.78
0.76
0.71
0.69
Se
MeO
P
F
n-Bu
i-Pr
0.68
1.96
2.22
3.00
0.31
0.26
1.25
2.54
0.59
0.64
1.59
4.76
4.53
6.72
9.72
4.22
6.36
1.16
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

280


163.06
149.43
149.33
148.65
145.64
130.46
130.35
129.49
126.72
126.62
120.41
120.12
120.05
112.31
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
56.30
56.24
55.28
55.24
36.19
35.81
32.43
32.22
31.49
31.28
31.15
30.55
30.47
29.10
28.99
27.75
27.41
27.37
26.92
26.85
26.43
25.59
24.62
24.55
24.48
24.24
24.14
23.80
23.68
23.56
23.05
22.70
22.48
22.43
22.38
22.33
22.30
22.25
21.12
20.67
13.77
Se
P
MeO
i-Pr
F
F
n-Bu
F
i-Pr
i-Pr
F
280
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-128.98
-128.99
-129.02
-129.04
-138.11
-138.15
-138.18
-139.05
-139.06
-139.09
-139.10
-139.12
-139.13
-139.15
-139.16
-145.01
-145.05
-145.08
-145.11
-145.45
-145.47
-145.50
-145.53
-145.57
-145.61
-145.66
-145.70
-145.73
-145.76
-145.89
-145.92
-145.95
-145.98
Se
P
MeO
i-Pr
F
F
n-Bu
F
i-Pr
i-Pr
F
280
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


38.94
36.83
34.72
MeO
Se
P
F
F
n-Bu
i-Pr
F
i-Pr
F
i-Pr
280
4500
4000
3500
3000
2500
2000
1500
1000
500
0
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

5. REFERENCES

1. Dumas, J.; Peligot, E. Ueber den Holzgeist und die verschiedenen ätherartigen Verbindungen, welche er bildet [German]. *Ann. Pharm*. **1835**, *15*, 1–60.
2. Inoue, M.; Sumii, Y.; Shibata, N. Contribution of Organofluorine Compounds to Pharmaceuticals. *ACS Omega* **2020**, *5*, 10633– 10640.
3. Alauddin, M. M. Positron emission tomography (PET) imaging with ^{18}F-based radiotracers *Am. J. Nucl. Med. Mol. Imaging* **2012**, *2*, 55– 76.
4. Swart, E *Bull. Acad. Roy. Belg*. **1892**, 29874.
5. Hudlicky, M. Organic Fluorine Chemistry, Plenum Press: New York, 1971
6. Artamkina, G. A.; Egorov, M. P.; Beletskaya, I. P. *Chem. Rev.* **1982**, *82*, 427.
7. Pleschke, A.; Marhold, A.; Schneider, M.; Kolomeitsev, A.; Röschenthaler, G.V. Halex reactions of aromatic compounds catalysed by 2-azaallenium, carbophosphazenium, aminophosphonium and diphosphazenium salts: a comparative study. *J. Fluorine Chem*., **2004**, *125*, 1031-1038.
8. Finger, G. C.; Kruse, C. W. Aromatic Fluorine Compounds. VII. Replacement of Aromatic -Cl and -NO_2 Groups by -F^{1,2}. *J. Am. Chem. Soc*. **1956**, *78*, 6034.
9. Clark, J. H.; Smith, D. K. Nucleophilic routes to selectively fluorinated aromatics. *J. Fluorine Chem*., **1985**, *26*, 2233.
10. Sun, H.; DiMagno, S. G. Anhydrous Tetrabutylammonium Fluoride *J. Am. Chem. Soc.* **2005**, *127*, 2050 – 2051.
11. Sun, H.; DiMagno, S. G. Room-Temperature Nucleophilic Aromatic Fluorination: Experimental and Theoretical Studies. *Angew. Chem. Int. Ed***.** **2006**, *45*, 2720.
12. Balz, G.; Schiemann, G. "Über aromatische Fluorverbindungen, I.: Ein neues Verfahren zu ihrer Darstellung" [Aromatic fluorine compounds. I. A new method for their preparation.]. *Chem. Ber.,* **1927**, 60 (5), 1186–1190.
13. Swain, C. G.; Rogers R. J. Mechanism of formation of aryl fluorides from arenediazonium fluoborates *J. Am. Chem. Soc.* **1975**, *97*, 4, 799–800.
14. Roe, A. Preparation of Aromatic Fluorine Compounds from Diazonium Fluoborates. In Organic Reactions; *John Wiley & Sons, Inc.: Hoboken, NJ, USA*, **2011**; pp. 193–228.
15. Rutherford, K. G.; Redmond, W.; Rigamonti, J. The Use of Hexafluorophosphoric Acid in the Schiemann Reaction. *J. Org. Chem.* **1961**, *26*, 5149.
16. Sellers, C.; Suschitzky, H. The Use of Arenediazonium Hexafluoro-antimonates and -arsenates in the Preparation of Aryl Fluorides. *J. Chem. Soc. C* **1968**, 2317.
17. Middleton, W. J.; Bingham, E. M. *J. Am. Chem. Soc*., **1980**, *102*, 4845–4846.

18. Chambers, R. D.; Greenhall M. P.; Hutchinson J. *J. Chem. Soc*., *Chem. Commun*., **1995**, 21.
19. Rozen, S.; Lerman, O. *J. Org. Chem*. **1980**, 45, 672.
20. Lal, G. S.; Pez, G. P.; Syvret, R. G.; *Chem. Rev*., **1996**, 96, 1737–1756
21. Yamada, S.; Gavryushin, A.; Knochel, P. Convenient Electrophilic Fluorination of Functionalized Aryl and Heteroaryl Magnesium Reagents *Angew. Chem. Int. Ed.* **2010**, *49*, 2215.
22. Biffis, A.; Centomo, P.; Del Zotto, A.; Zecca, M. Pd Metal Catalysts for Cross-couplings and Related Reactions in the 21st Century: A Critical Review. *Chem. Rev.* **2018**, *118*, 2249– 2295.
23. Furuya, T.; Benitez, Di.; Tkatchouk, E.; Strom, A. E.; Tang, P.-P.; Goddard, W. A.; Ritter, T. Mechanism of C–F Reductive Elimination from Palladium(IV) Fluorides. *J. Am. Chem. Soc.* **2010**, *132*, 3793– 3807
24. Hull, K. L.; Anani, W. Q.; Sanford, M. S. Palladium-catalyzed fluorination of carbon-hydrogen bonds. *J. Am. Chem. Soc.* **2006**, *128*, 7134–7135.
25. Ball, N. D.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 3796.
26. Ametamey, S. M.; Honer, M.; Schubiger, P. A. *Chem. Rev.* **2008**, *108*, 1501.
27. Furuya, T.; Kaiser, H. M.; Ritter, T. Palladium-mediated fluorination of arylboronic acids. *Angew. Chem. Int. Ed.* **2008**, *47*, 5993–5996.
28. Fraser, S. L.; Antipin, M. Yu.; Khroustalyov, V. N.; Grushin, V. V. Molecular Fluoro Palladium Complexes. *J. Am. Chem. Soc.* **1997**, *119*, 4769–4770.
29. Lu, J.; Donnecke, S.; Paci, I.; Leitch, D. C. A reactivity model for oxidative addition to palladium enables quantitative predictions for catalytic cross-coupling reactions. *Chem. Sci.* **2022**, *13*, 3477– 3488.
30. Grushin, V. V. The Organometallic Fluorine Chemistry of Palladium and Rhodium: Studies toward Aromatic Fluorination. *Acc. Chem. Res.* **2010**, *43* (1), 160-171.
31. Watson, D. A.; Su, M.; Teverovskiy, G.; Zhang, Y.; García-Fortanet, J.; Kinzel, T.; Buchwald, S. L. Formation of ArF from LPdAr(F): Catalytic Conversion of Aryl Triflates to Aryl Fluorides *Science,* **2009**, *325*, 1661.
32. Kalek, M.; Stawinski, J. Palladium-Catalyzed C−P Bond Formation: Mechanistic Studies on the Ligand Substitution and the Reductive Elimination. An Intramolecular Catalysis by the Acetate Group in Pd(II) Complexes. *Organometallics,* **2008**, *27* (22), 5876-5888.
33. Yandulov, D. V.; Tran, N. T. Aryl-Fluoride Reductive Elimination from Pd(II): Feasibility Assessment from Theory and Experiment. *J. Am. Chem. Soc.* **2007**, *129*, 1342–1358.

34. Macgregor, S. A.; Roe, D. C.; Marshall, W. J.; Bloch, K. M.; Bakhmutov, V. I.; Grushin, V. V. The F/Ph Rearrangement Reaction of [$(Ph_3P)_3RhF$], the Fluoride Congener of Wilkinson's Catalyst. *J. Am. Chem. Soc.* **2005**, *127*, 15304–15321.
35. Macgregor, S. A.; Wondimagegn, T. Mechanism of the [$RhF(PPh_3)_3$] to *cis*-[$RhPh(PPh_3)_2(PFPh_2)$] Interconversion: P-C Activation and F/Ph Exchange *via* a Metallophosphorane Pathway. *Organometallics,* **2007**, *26*, 1143–1149.
36. Grushin, V. V. Thermal Stability, Decomposition Paths, and Ph/Ph Exchange Reactions of [$(Ph_3P)_2$ Pd(Ph)X] (X) I, Br, Cl, F, and HF_2). *Organometallics,* **2000**, *19,* 1888–1900.
37. Marshall, W. J.; Grushin, V. V. Palladium(II) and Palladium(0) Complexes of BINAP(O) (2-(Diphenylphosphino)-2′-(diphenyl-phosphinyl)1,1′-binaphthyl). *Organometallics,* **2003**, *22*, 555−562.
38. Grushin, V. V. The Organometallic Fluorine Chemistry of Palladium and Rhodium: Studies toward Aromatic Fluorination. *Acc. Chem. Res.* **2010**, *43* (1), 160-171.
39. Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. Reductive Elimination of d8-Organotransition Metal Complexes. *Bull. Chem. Soc. Jpn*. **1981**, *54*, 1857.
40. Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 17, 4992–4998.
41. Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. Mechanism of Thermal Decomposition of Di-*n*-butylbis(triphenylphosphine) platinum(II) *J. Am. Chem. Soc.* **1972**, *94*, 5258.
42. Tamaki, A.; Magennis, S. A.; Kochi, J. K. Catalysis by gold. Alkyl isomerization, *cis-trans* rearrangement, and reductive elimination of alkylgold(III) complexes. *J. Am. Chem. Soc.* **1974**, *96* (19), 6140–6148.
43. Sakaki, S. Theoretical and Computational Study of a Complex System Consisting of Transition Metal Element(s): How to Understand and Predict Its Geometry, Bonding Nature, Molecular Property, and Reaction Behavior. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 889– 938.
44. Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc*. **2001**, *123*, 1232-1233.
45. Fors, B. P.; Watson, D. A.; Biscoe, M. R.; Buchwald, S. L. A Highly Active Catalyst for Pd-Catalyzed Amination Reactions: Cross-Coupling Reactions Using Aryl Mesylates and the Highly Selective Monoarylation of Primary Amines Using Aryl Chlorides. *J. Am. Chem. Soc.* **2008**, *130*, 41, 13552–13554.
46. Milner, P. J.; Kinzel, T.; Zhang, Y.; Buchwald, S. L. J. Studying Regioisomer Formation in the Pd-Catalyzed Fluorination of Aryl Triflates by Deuterium Labeling. *J. Am. Chem. Soc.* **2014**, *136*, 15757–15766.

47. Sather, A. C.; Lee, H. G.; De La Rosa, V. Y.; Yang, Y.; Müller, P.; Buchwald, S. L. A Fluorinated Ligand Enables Room-Temperature and Regioselective Pd-Catalyzed Fluorination of Aryl Triflates and Bromides. *J. Am. Chem. Soc.* **2015**, *137* (41), 13433–13438.
48. Su, M.; Hoshiya, N.; Buchwald, S. L. Palladium-Catalyzed Amination of Unprotected Five-Membered Heterocyclic Bromides. *Org. Lett.* **2014**, *16*, 832−835.
49. Milner, P. J.; Yang, Y.; Buchwald, S. L. In-Depth Assessment of the Palladium-Catalyzed Fluorination of Five-Membered Heteroaryl Bromides. *Organometallics* **2015**, *34*, 4775–4780.
50. Clevenger, A. L.; Stolley, R. M.; Aderibigbe, J.; Louie, J. *Chem. Rev.* **2020**, 120, *13*, 6124–6196.
51. Tappe, F. M. J.; Trepohl, V. T.; Oestreich, M. Transition-Metal-Catalyzed C–P Cross-Coupling Reactions *Synthesis* **2010**, 3037–3062. Trends in the Usage of Bidentate Phosphines as Ligands in Nickel Catalysis.
52. Köster, M.; Kreher, A.; Hänisch, C. Synthesis of ternary group 13/15 chain compounds. *Dalton Trans*, **2018**, *47*, 7875– 7878.
53. Kendall, A. J.; Tyler, D. R. The Synthesis of Heteroleptic Phosphines. *Dalton Trans.* **2015**, *44*, 12473-12483.
54. Nöth, H.; Vetter, H. J. Darstellung und Reaktionen von Dimethylamino-halogen-phosphanen $(Me_2N)_3PX$. *Chem. Ber.* **1963**, *96*, 1109–1118.
55. Almlof, J.; Gropen, O. Relativistic Effects in Chemistry. *In Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, **1996**; Vol. 8, pp 206-210.
56. Hayashi, M. Organophosphine Syntheses via Activation of the Phosphorus-Silicon Bond of Silylphosphines. *Chem. Rev*., **2009**, *9*, 236–245.
57. Hirano, K.; Yorimitsu, H.; Oshima, K. Boron Trifluoride-Mediated Alkylation of Diphenylphosphine with tert-Alkyl Fluoride. *Org. Lett.* **2004**, *6*, 4873–4875.
58. Trofimov, B. A.; Brandsma, L.; Arbuzova, S. N.; Malysheva S. F.; Gusarova, N. K. Reactions of Elemental Phosphorus and Phosphine with Electrophiles in Superbasic Systems: XIV.1 Phosphorylation of 2-Vinylnaphthalene with Elemental Phosphorus and Phosphines in the KOH-DMSO System. *Tetrahedron Lett*., **1994**, *35*, 7647–7650.
59. Barber, T.; Argent, S. P.; Ball, L. T. Expanding Ligand Space: Preparation, Characterization, and Synthetic Applications of Air-Stable, Odorless Di-tert-alkylphosphine Surrogates. *ACS Catal.* **2020**, *10*, 5454– 5461.
60. Murata, M.; Buchwald, S.L. A general and efficient method for the palladium-catalyzed cross-coupling of thiols and secondary phosphines. *Tetrahedron,* **2004**, *60,* 7397-7403.

61. Uozumi Y.; Suzuki N.; Ogiwara A.; Hayashi T. Preparation of optically active binaphthylmonophosphines (MOP's) containing various functional groups. *Tetrahedron*, **1994**, *50* (15), 4293-4302.
62. Allen, D. V.; Venkataraman, D. Copper-Catalyzed Synthesis of Unsymmetrical Triarylphosphines. *J. Org. Chem.* **2003**, *68*, 4590– 4593.
63. Gelman, D.; Jiang, L.; Buchwald, S. L. Copper-Catalyzed C−P Bond Construction via Direct Coupling of Secondary Phosphines and Phosphites with Aryl and Vinyl Halides. *Org. Lett.* **2003**, *5*, 2315.
64. Murata, M.; Buchwald, S. L. A General and Efficient Method for the Palladium-Catalyzed Cross-Coupling of Thiols and Secondary Phosphines. *Tetrahedron,* **2004**, *60*, 7397– 7403.
65. Tunney, S. E.; Stille, J. K. Palladium-Catalyzed Coupling of Aryl Halides with (Trimethylstannyl) diphenylphosphine and (Trimethylsilyl) diphenylphosphine. *J. Org. Chem.* **1987**, *52*, 748– 753.
66. Tolman, C. A. Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis. *Chem. Rev.* **1977**, 77, *3*, 313–348.
67. Beckmann, U.; Süslüyan, D.; Kunz, P. C. Is the ^{1}J PSe Coupling Constant a Reliable Probe for the Basicity of Phosphines? A ^{31}P NMR Study. *Phosphorus, Sulfur, and Silicon and the Related Elements* **2011**, *186* (10), 2061-2070.
68. Chen, L.; Ren, P.; Carrow, B. P. Tri(1-adamantyl)phosphine: Expanding the Boundary of Electron-Releasing Character Available to Organophosphorus Compounds. *J. Am. Chem. Soc.* **2016**, *138* (20), 6392–6395.
69. Laffoon, S. D.; Chan, V. S.; Fickes, M. G.; Kotecki, B.; Ickes, A. R.; Henle, J.; Napolitano, J. G.; Franczyk, T. S.; Dunn, T. B.; Barnes, D. M.; Haight, A. R.; Henry, R. F.; Shekhar, S. Pd-Catalyzed Cross-Coupling Reactions Promoted by Biaryl Phosphorinane Ligands. *ACS Catal.* **2019**, *9*, 11691– 11708.
70. Su, M.; Buchwald, S. L. A Bulky Biaryl Phosphine Ligand Allows for Palladium-Catalyzed Amidation of Five-Membered Heterocycles as Electrophiles. *Angew. Chem. Int. Ed.* **2012**, *51*, 4710−4713.
71. Bonney, K. J.; Schoenebeck, F. Experiment and Computation: A Combined Approach to Study the Reactivity of Palladium Complexes in Oxidation States 0 to IV. *Chem. Soc. Rev.* **2014**, *43*, 6609.
72. Paškevičius, T.; Lapinskaitė, R.; Stončius, S.; Sadzevičienė, R.; Judžentienė, A.; Labanauskas, L. Palladium-Catalyzed Synthesis of Cyclopropylthiophenes and Their Derivatization. *Molecules* **2023**, *28*, 3770.

73. NIPPON CHEMICAL INDUSTRIAL CO LTD - US2019/263845, 2019, A1
74. Downing, J. H.; Gee, V.; Pringle, P. G. A simple procedure for the separation of the catalytically important phosphabicyclononane isomers. *Chem. Commun.* **1997**, 16, 1527-1528.
75. Kobayashi, K.; Sasaki, A.; Kanno, Y.; Suginome, H. A new route to γ-substituted γ-lactones and δ-substituted δ-lactones based on the regioselective β-scission of alkoxyl radicals generated from transannular hemiacetals. *Tetrahedron,* **1991**, *47*, 7245– 7258.
76. Larock, R. C. Solvomercuration/Demercuration Reactions in Organic Synthesis; Springer-Verlag: Berlin, **1986**; Chapter 3.
77. Sather, A. C.; Buchwald, S. L. The Evolution of Pd^0/Pd^{II}-Catalyzed Aromatic Fluorination. *Acc. Chem. Res.* **2016**, *49*, 10, 2146–2157.
78. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.
79. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
80. Dennington, R.; Keith, T.; Millam, J. GaussView, version 5; Semichem Inc.: Shawnee Mission, KS, 2009.
81. Legault, C. Y. CYLview, version 2.0; Université de Sherbrooke: Quebec, Canada, 2020; http://www.cylview.org.

SUMMARY

VILNIUS UNIVERSITY

FACULTY OF CHEMISTRY AND GEOSCIENCES

TOMAS PAŠKEVIČIUS

Development of new phosphine ligands for Pd(0)/Pd(II) catalyzed (hetero)aryl fluorinations

Pharmaceutical sciences have focused on the unique properties of fluorinated compounds, that tend to exhibit more favorable biological activities in comparison to their non-fluorinated counterparts. However, catalytic approaches for C-F bond formation are lacking. Palladium catalysis has been established and well-studied for the C-C, C-O, C-N, C-S, C-P cross-coupling reactions. On the other hand, palladium catalyzed fluorination reactions are a relatively new field in organic chemistry. The work described in this thesis focuses on the design and synthesis of phosphine ligands and their steric and electronic influences on fluorination reactions.

Divergent approach for the synthesis of AlPhos ligand and its new analogues with differing phosphine moieties was developed and adapted. It allowed for multi-gram-scale synthesis of phosphine ligands and therefore increased their diversity. A new synthetic strategy for cyclic and bicyclic phosphines based on umpolung (C^+/P^-) method was conceptualized and is currently under development. Telomerisation issue reported in literature was solved by generating phosphine nucleophile *in situ* using $P(TMS)_3$.

Cyclic "caged" phosphine ligand architecture was assessed by computational and empirical methods. The results showed that both sterics and electronics affect the catalytical cycle, however, their influences have to be tuned for the optimal catalytic activity. Potential lead ligand candidate, based on 1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphaadamantane framework, was identified for further study. Fluorination reaction was optimized to work with less fastidious palladium sources and without the need of a glovebox for more consistent screening of the ligands.

SANTRAUKA

VILNIAUS UNIVERSITETAS

CHEMIJOS IR GEOMOKSLŲ FAKULTETAS

TOMAS PAŠKEVIČIUS

Naujų fosfininių ligandų Pd(0)/Pd(II) katalizuojamam (hetero)aromatinių junginių fluorinimui kūrimas

Fluorinti organiniai junginiai pasižymi ne tik unikaliomis fizikinėmis bei cheminėmis savybėmis, bet ir išskirtiniu biologiniu aktyvumu. Dėl šių priežasčių, fluoro atomą(-us) turintys junginiai yra plačiai naudojami medicininėje chemijoje ir farmacijoje. Nors ir literatūroje aprašyta daugybė klasikinių metodų C-F ryšio formavimui, katalitinių atitikmenų nėra gausu. Paladžiu katalizuojamos kryžminio jungimo reakcijos yra vienas universaliausių metodų C-C, C-O, C-N, C-S, C-P ryšių formavimui. Tačiau efektyvių analogiškų metodikų C-F ryšio suformavimui trūksta. Šiame darbe aprašoma fosfininių ligandų erdvinių ir elektroninių savybių įtaka katalitinei sistemai.

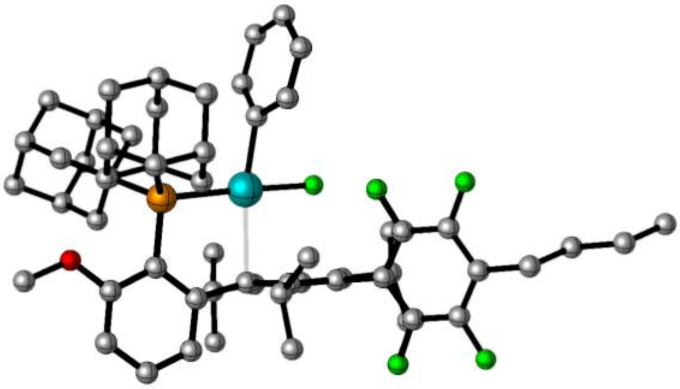
Remiantis kompiuterinio modeliavimo duomenimis, ciklinės fosfininų ligandų struktūros gali pasižymėti palankiomis erdvinėmis bei elektroninėmis savybėmis turinčiomis įtakos katalizatoriaus aktyvumui. Šių savybių suderinimas leistų sėkmingai atlikti (hetero)aromatinių junginių fluorinimo reakcijas. Iš kompiuterinės kvantinės chemijos ir eksperimentinių duomenų buvo atrinktas naujas potencialus fosfininis ligandas tolimesniems tyrimams.

Šiame darbe aprašomos naujos fosfininių darinių ir ligandų sintezės metodikos. Sėkmingai sukurta nauja ligando karkaso sintezė bei patogus būdas jo modifikacijai. Pradėta plėtoti ir nauja ciklinių fosforo atomą turinčių struktūrų sintezės metodika. Iš $P(TMS)_3$ *in situ* generuojant fosforo nukleofilus pavyko išspręsti literatūroje aprašytas telomerizacijos reakcijos keliamas problemas. Taip pat, optimizuotas ir pritaikytas naujas fluorinimo reakcijos protokolas fosfininių ligandų aktyvumo įvertinimui.

6. APPENDIX

6.1 Appendix 1. Computational data

122a GS



```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           1.187014 (Hartree/Particle)
 Thermal correction to Energy=                    1.251545
 Thermal correction to Enthalpy=                  1.252489
 Thermal correction to Gibbs Free Energy=         1.087814
 Sum of electronic and zero-point Energies=          -3296.075543
 Sum of electronic and thermal Energies=             -3296.011011
 Sum of electronic and thermal Enthalpies=           -3296.010067
 Sum of electronic and thermal Free Energies=        -3296.174743
```

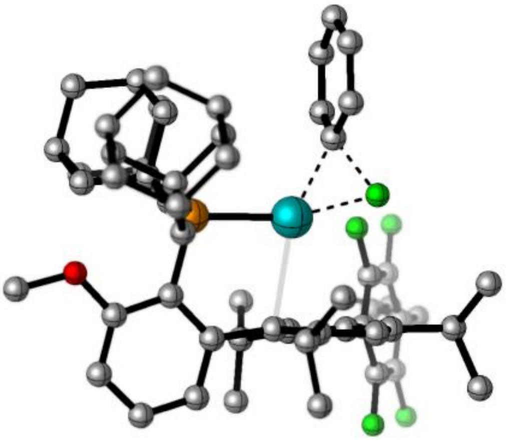
46	-0.527291000	-0.100234000	-1.086187000
15	-2.503022000	0.177953000	0.299097000
6	-4.204964000	-0.283061000	-0.549349000
6	-4.462386000	-1.807951000	-0.418367000
1	-3.597269000	-2.366815000	-0.787617000
1	-4.607331000	-2.083147000	0.630520000
6	-5.713422000	-2.226559000	-1.225928000
1	-5.858356000	-3.308641000	-1.104564000
6	-5.512446000	-1.891920000	-2.716167000
1	-6.391985000	-2.203864000	-3.296206000
1	-4.652123000	-2.444826000	-3.116834000
6	-5.283856000	-0.376322000	-2.862947000
1	-5.116424000	-0.125446000	-3.918725000
6	-4.031494000	0.031928000	-2.058011000
1	-3.159515000	-0.510030000	-2.436902000
1	-3.824655000	1.096268000	-2.209527000
6	-5.464671000	0.465871000	-0.040241000
1	-5.626780000	0.253084000	1.017137000
1	-5.338930000	1.547338000	-0.141146000

6	-6.715212000	0.041592000	-0.847246000
1	-7.581808000	0.590728000	-0.454292000
6	-6.945587000	-1.473240000	-0.691000000
1	-7.846517000	-1.779662000	-1.240242000
1	-7.114747000	-1.724357000	0.365732000
6	-6.514288000	0.384157000	-2.334900000
1	-6.372659000	1.466697000	-2.458726000
1	-7.407845000	0.110937000	-2.913051000
6	-2.565687000	1.958795000	1.064233000
6	-2.875577000	2.964055000	-0.081957000
1	-2.185065000	2.812282000	-0.914421000
1	-3.887348000	2.808972000	-0.471424000
6	-2.759940000	4.418265000	0.428046000
1	-2.988094000	5.094939000	-0.405587000
6	-1.326520000	4.678379000	0.928170000
1	-0.613795000	4.537913000	0.106408000
1	-1.226607000	5.718246000	1.269575000
6	-1.010993000	3.709716000	2.083765000
1	0.017026000	3.871955000	2.434318000
6	-1.135156000	2.251888000	1.587585000
1	-0.900429000	1.568533000	2.412632000
1	-0.403525000	2.066977000	0.796135000
6	-3.543549000	2.214124000	2.240173000
1	-4.577229000	2.014604000	1.947600000
1	-3.310319000	1.541475000	3.070880000
6	-3.430599000	3.678303000	2.730767000
1	-4.147782000	3.822524000	3.550757000
6	-3.758956000	4.645903000	1.577796000
1	-4.787245000	4.481936000	1.225289000
1	-3.704592000	5.685577000	1.929288000
6	-2.001726000	3.945507000	3.238586000
1	-1.915579000	4.976011000	3.609934000
1	-1.768674000	3.279919000	4.081803000
6	-2.211010000	-1.061245000	1.687808000
6	-3.162095000	-1.308260000	2.714737000
6	-2.943747000	-2.253135000	3.719802000
1	-3.680805000	-2.417361000	4.496064000
6	-1.777257000	-3.010432000	3.704773000
1	-1.609718000	-3.760175000	4.473208000
6	-0.841431000	-2.813930000	2.701910000
1	0.057650000	-3.419553000	2.676268000
6	-1.026692000	-1.842231000	1.699097000
8	-4.322705000	-0.595132000	2.651976000
6	-5.285858000	-0.734890000	3.686694000
1	-5.684210000	-1.756075000	3.731823000
1	-6.092637000	-0.044653000	3.434799000
1	-4.867326000	-0.462431000	4.663280000
6	0.108354000	-1.798888000	0.690535000
6	1.349749000	-1.158052000	1.043916000
6	2.484744000	-1.384712000	0.242063000
6	2.440992000	-2.290183000	-0.844782000

6	1.268884000	-3.003430000	-1.068613000
1	1.255428000	-3.737250000	-1.867067000
6	0.100744000	-2.781098000	-0.346748000
6	1.403586000	-0.333885000	2.342209000
1	0.363012000	-0.182070000	2.636843000
6	2.030811000	1.075164000	2.267821000
1	3.117876000	1.049885000	2.372782000
1	1.644221000	1.678475000	3.097735000
1	1.790722000	1.590077000	1.335437000
6	2.064082000	-1.127282000	3.492607000
1	1.522616000	-2.050524000	3.714309000
1	2.069792000	-0.517458000	4.404445000
1	3.097176000	-1.396867000	3.261002000
6	3.631035000	-2.538722000	-1.764119000
1	4.379355000	-1.767081000	-1.563605000
6	3.238865000	-2.403266000	-3.248663000
1	2.636607000	-3.255792000	-3.587217000
1	4.139851000	-2.373694000	-3.873290000
1	2.652734000	-1.493108000	-3.396549000
6	4.287348000	-3.901324000	-1.462833000
1	4.611135000	-3.967012000	-0.418652000
1	5.162753000	-4.053391000	-2.105270000
1	3.589045000	-4.726120000	-1.651210000
6	-1.100620000	-3.676460000	-0.640963000
1	-1.950018000	-3.307302000	-0.061706000
6	-1.499138000	-3.651531000	-2.128731000
1	-1.644854000	-2.626167000	-2.482175000
1	-2.429375000	-4.211776000	-2.282435000
1	-0.732262000	-4.110700000	-2.762568000
6	-0.833958000	-5.122319000	-0.177216000
1	0.017085000	-5.560100000	-0.711633000
1	-1.711014000	-5.751872000	-0.370295000
1	-0.615816000	-5.166761000	0.894834000
6	3.783783000	-0.674576000	0.481117000
6	4.827380000	-1.257611000	1.199477000
9	4.653555000	-2.470058000	1.769125000
6	6.060295000	-0.630937000	1.359547000
9	7.011879000	-1.259800000	2.079313000
6	6.328832000	0.614955000	0.794750000
6	7.667646000	1.297968000	0.940208000
1	8.184951000	0.882628000	1.810720000
1	7.502040000	2.363543000	1.138595000
6	8.559794000	1.152381000	-0.309661000
1	8.030523000	1.569689000	-1.176065000
1	8.714303000	0.085329000	-0.520174000
6	9.916841000	1.848207000	-0.150869000
1	9.754035000	2.912389000	0.071363000
1	10.439395000	1.430337000	0.721318000
6	10.804789000	1.715468000	-1.392287000
1	11.016945000	0.663246000	-1.617886000
1	11.764287000	2.226103000	-1.252606000

1	10.319863000	2.151568000	-2.274085000
6	5.290787000	1.191445000	0.060688000
9	5.486550000	2.395445000	-0.514610000
6	4.057800000	0.568110000	-0.100867000
9	3.112080000	1.200446000	-0.807291000
6	-0.650035000	1.447776000	-2.368608000
6	-1.378945000	1.445002000	-3.558597000
1	-1.999031000	0.596861000	-3.829410000
6	-1.313164000	2.525580000	-4.445819000
1	-1.900546000	2.498539000	-5.361875000
6	-0.502375000	3.623715000	-4.165213000
6	0.269246000	3.613548000	-3.001455000
1	0.938088000	4.443137000	-2.779895000
6	0.205977000	2.530299000	-2.123194000
1	-0.454737000	4.465165000	-4.852244000
9	1.139526000	-0.359456000	-2.160241000
1	0.853032000	2.527631000	-1.251167000

122a TS



```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           1.185019 (Hartree/Particle)
 Thermal correction to Energy=                    1.249273
 Thermal correction to Enthalpy=                  1.250218
 Thermal correction to Gibbs Free Energy=         1.085184
 Sum of electronic and zero-point Energies=          -3296.046941
 Sum of electronic and thermal Energies=             -3295.982686
 Sum of electronic and thermal Enthalpies=           -3295.981742
 Sum of electronic and thermal Free Energies=        -3296.146776
```

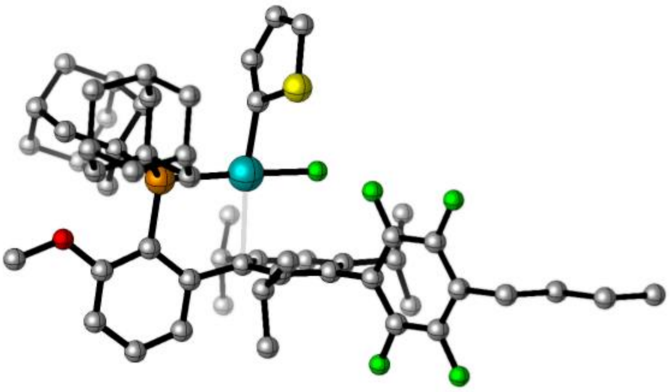
46	-0.670474000	-0.491943000	1.049081000
15	-2.352263000	0.369302000	-0.420524000
6	-2.009246000	-0.513148000	-2.057662000
6	-2.850940000	-0.360999000	-3.192128000
6	-2.624766000	-1.044017000	-4.389854000
1	-3.280679000	-0.904183000	-5.240130000

6	-1.558805000	-1.931779000	-4.478364000
1	-1.387145000	-2.481323000	-5.399903000
6	-0.724865000	-2.117118000	-3.386511000
6	-0.914132000	-1.413975000	-2.181300000
8	-3.920356000	0.473568000	-3.045729000
6	-4.758282000	0.738587000	-4.161201000
1	-4.193254000	1.179216000	-4.991814000
1	-5.500797000	1.456768000	-3.809460000
1	-5.269061000	-0.168400000	-4.507973000
6	0.111196000	-1.765309000	-1.115813000
6	-0.119672000	-2.921963000	-0.319427000
6	0.900106000	-3.374082000	0.517446000
6	2.135821000	-2.741634000	0.618719000
6	2.396212000	-1.645994000	-0.236296000
6	1.415936000	-1.172609000	-1.139670000
6	-1.400630000	-3.750273000	-0.402393000
1	-2.141116000	-3.175849000	-0.964552000
6	-2.001051000	-4.053294000	0.983405000
1	-1.373395000	-4.742940000	1.559383000
1	-2.985942000	-4.523359000	0.875846000
1	-2.113562000	-3.137106000	1.571999000
6	-1.154796000	-5.058322000	-1.180746000
1	-0.797858000	-4.860037000	-2.196709000
1	-2.082246000	-5.639234000	-1.255366000
1	-0.406808000	-5.682548000	-0.677686000
6	3.170438000	-3.296815000	1.594517000
1	3.964685000	-2.552766000	1.706427000
6	3.819713000	-4.577074000	1.028192000
1	3.075258000	-5.373487000	0.905944000
1	4.595968000	-4.946993000	1.708731000
1	4.277656000	-4.393605000	0.050998000
6	2.590515000	-3.537765000	3.000955000
1	2.076632000	-2.645589000	3.368347000
1	3.397387000	-3.797226000	3.696791000
1	1.875223000	-4.369437000	3.010846000
6	1.721824000	-0.115762000	-2.216315000
1	0.749513000	0.208751000	-2.594153000
6	2.453683000	1.171211000	-1.776060000
1	2.134048000	1.516611000	-0.790872000
1	2.235759000	1.966358000	-2.498963000
1	3.539033000	1.046326000	-1.759387000
6	2.465713000	-0.738912000	-3.419442000
1	3.430192000	-1.160300000	-3.125802000
1	2.648886000	0.030305000	-4.179925000
1	1.884166000	-1.537620000	-3.887209000
6	-0.487855000	0.365963000	2.986750000
6	0.163576000	1.607330000	3.086445000
1	0.973812000	1.847087000	2.406458000
6	-0.238730000	2.517675000	4.061567000
1	0.252064000	3.487909000	4.110641000
6	-1.241251000	2.191628000	4.981804000

6	-1.812295000	0.915324000	4.932570000
1	-2.565187000	0.626419000	5.663460000
6	-1.420010000	-0.009093000	3.966914000
1	-1.845064000	-1.007700000	3.957132000
1	-1.547802000	2.905161000	5.741387000
9	0.652336000	-0.867418000	2.703744000
1	0.716733000	-4.249677000	1.130262000
6	-4.177539000	-0.040400000	0.133191000
6	-4.556704000	-1.456058000	-0.373266000
6	-5.292554000	0.946910000	-0.300349000
6	-4.150942000	-0.082582000	1.687569000
1	-4.600123000	-1.468426000	-1.467361000
1	-3.793441000	-2.179294000	-0.069049000
6	-5.926007000	-1.894084000	0.195181000
6	-6.663009000	0.504288000	0.265784000
1	-5.077472000	1.956235000	0.062905000
1	-5.349783000	0.997191000	-1.388328000
1	-3.375177000	-0.777844000	2.021979000
1	-3.875200000	0.894889000	2.098322000
6	-5.521210000	-0.513574000	2.252559000
1	-6.157793000	-2.897911000	-0.186045000
6	-7.011975000	-0.900965000	-0.260312000
6	-5.868524000	-1.922146000	1.734837000
1	-7.424254000	1.223281000	-0.067092000
6	-6.607681000	0.481648000	1.804424000
1	-5.457001000	-0.525650000	3.348470000
1	-7.078340000	-0.889232000	-1.357532000
1	-7.995616000	-1.214798000	0.115502000
1	-5.114162000	-2.645558000	2.072841000
1	-6.833793000	-2.252128000	2.143496000
1	-7.584130000	0.191837000	2.216984000
1	-6.383554000	1.485742000	2.190393000
6	-2.112335000	2.271524000	-0.669204000
6	-2.444225000	2.962394000	0.684356000
6	-2.896282000	2.971806000	-1.807233000
6	-0.602019000	2.480422000	-0.948522000
1	-3.508433000	2.860184000	0.921739000
1	-1.885933000	2.489388000	1.497722000
6	-2.096856000	4.466923000	0.622800000
6	-2.555118000	4.481582000	-1.847643000
1	-2.634673000	2.520208000	-2.769231000
1	-3.974713000	2.848692000	-1.678433000
1	-0.014995000	1.983310000	-0.168598000
1	-0.335565000	2.010363000	-1.902868000
6	-0.247852000	3.982725000	-1.002870000
1	-2.349403000	4.920188000	1.590104000
6	-2.911065000	5.138133000	-0.499703000
6	-0.592032000	4.641469000	0.346148000
1	-3.140061000	4.948486000	-2.652251000
6	-1.051478000	4.662613000	-2.127233000
1	0.827704000	4.082111000	-1.201124000

1	-3.987169000	5.036366000	-0.299829000
1	-2.694614000	6.214993000	-0.534998000
1	-0.007360000	4.182960000	1.153474000
1	-0.330624000	5.708730000	0.324016000
1	-0.799249000	5.730707000	-2.181654000
1	-0.792074000	4.221956000	-3.100346000
6	3.750296000	-1.009610000	-0.131176000
6	3.988020000	0.049912000	0.750036000
6	4.862412000	-1.491221000	-0.820414000
6	5.252802000	0.606338000	0.903029000
6	6.128156000	-0.930685000	-0.669652000
6	6.363564000	0.129959000	0.204044000
6	7.730517000	0.748200000	0.373978000
1	8.488442000	0.020178000	0.067957000
1	7.893137000	0.958212000	1.437579000
6	7.913100000	2.051742000	-0.430146000
1	7.735447000	1.846971000	-1.494767000
1	7.147703000	2.774112000	-0.117330000
6	9.306160000	2.665819000	-0.248584000
1	10.067622000	1.935509000	-0.556985000
1	9.480723000	2.856420000	0.819734000
6	9.494601000	3.965444000	-1.037662000
1	10.497661000	4.380514000	-0.888015000
1	9.359733000	3.799591000	-2.113547000
1	8.768897000	4.726704000	-0.726465000
9	2.969180000	0.573303000	1.451707000
9	5.408369000	1.636428000	1.758707000
9	7.148666000	-1.450871000	-1.380763000
9	4.727242000	-2.532798000	-1.668957000
1	0.097254000	-2.821081000	-3.450456000

122b GS



```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           1.153842 (Hartree/Particle)
 Thermal correction to Energy=                    1.217844
```

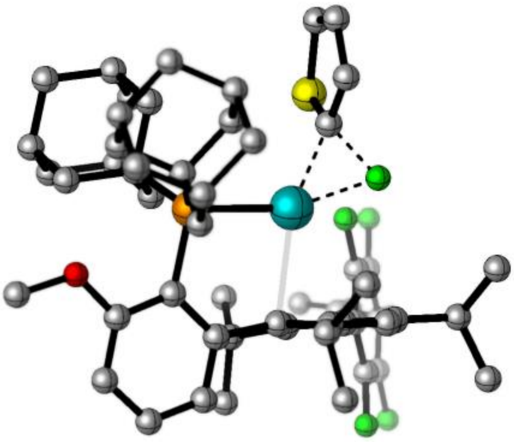
Thermal correction to Enthalpy= 1.218789
Thermal correction to Gibbs Free Energy= 1.055325
Sum of electronic and zero-point Energies= -3616.871999
Sum of electronic and thermal Energies= -3616.807996
Sum of electronic and thermal Enthalpies= -3616.807052
Sum of electronic and thermal Free Energies= -3616.970516

46	-0.599539000	-0.200564000	-1.069118000
15	-2.525857000	0.196192000	0.290902000
6	-4.219264000	-0.381859000	-0.485937000
6	-4.418243000	-1.898473000	-0.223020000
1	-3.544623000	-2.452944000	-0.576175000
1	-4.518863000	-2.091684000	0.849463000
6	-5.675131000	-2.424862000	-0.954510000
1	-5.776311000	-3.497323000	-0.739292000
6	-5.524492000	-2.208382000	-2.472245000
1	-6.407218000	-2.596346000	-2.999258000
1	-4.655375000	-2.763437000	-2.850266000
6	-5.354488000	-0.703139000	-2.749902000
1	-5.223167000	-0.536099000	-3.827280000
6	-4.097109000	-0.182617000	-2.019590000
1	-3.211755000	-0.716126000	-2.379972000
1	-3.939267000	0.873533000	-2.257961000
6	-5.493461000	0.363035000	-0.000696000
1	-5.620136000	0.230214000	1.074016000
1	-5.411607000	1.436266000	-0.191958000
6	-6.747391000	-0.168905000	-0.735438000
1	-7.621729000	0.382244000	-0.362799000
6	-6.919717000	-1.672003000	-0.448979000
1	-7.822077000	-2.052948000	-0.947009000
1	-7.054111000	-1.840080000	0.629006000
6	-6.597723000	0.056612000	-2.251376000
1	-6.498841000	1.129456000	-2.466455000
1	-7.495966000	-0.294649000	-2.777999000
6	-2.598644000	2.039570000	0.862676000
6	-3.015220000	2.926383000	-0.345474000
1	-2.373693000	2.715011000	-1.203198000
1	-4.043132000	2.705530000	-0.649731000
6	-2.924625000	4.423561000	0.028137000
1	-3.227100000	5.013242000	-0.847168000
6	-1.476788000	4.776901000	0.416277000
1	-0.805006000	4.583201000	-0.428388000
1	-1.400163000	5.846059000	0.659586000
6	-1.061643000	3.927205000	1.632064000
1	-0.022524000	4.152928000	1.906306000
6	-1.152811000	2.427539000	1.269352000
1	-0.843045000	1.826728000	2.132455000
1	-0.464090000	2.205009000	0.449868000
6	-3.519169000	2.364510000	2.069626000
1	-4.557521000	2.099834000	1.855070000
1	-3.209343000	1.780117000	2.941577000

6	-3.438015000	3.870371000	2.421528000
1	-4.114371000	4.060477000	3.266569000
6	-3.867720000	4.718506000	1.209419000
1	-4.906662000	4.487236000	0.934181000
1	-3.835503000	5.786575000	1.466075000
6	-1.994710000	4.230178000	2.818481000
1	-1.928979000	5.292182000	3.093024000
1	-1.689822000	3.651533000	3.702204000
6	-2.184316000	-0.907765000	1.773515000
6	-3.105033000	-1.083118000	2.843294000
6	-2.846377000	-1.943283000	3.913048000
1	-3.561221000	-2.054284000	4.718871000
6	-1.669527000	-2.684985000	3.925336000
1	-1.471176000	-3.369301000	4.745742000
6	-0.762397000	-2.556167000	2.885679000
6	-0.989468000	-1.670046000	1.814938000
8	-4.275872000	-0.391259000	2.755016000
6	-5.203583000	-0.445023000	3.830668000
1	-5.594611000	-1.459769000	3.974865000
1	-6.021453000	0.219695000	3.548047000
1	-4.752629000	-0.089667000	4.765132000
6	0.117954000	-1.685984000	0.775632000
6	1.355126000	-0.993303000	1.056379000
6	2.490097000	-1.284835000	0.278182000
6	2.452900000	-2.295741000	-0.712843000
6	1.292232000	-3.046900000	-0.858424000
1	1.288856000	-3.856112000	-1.580196000
6	0.124795000	-2.774333000	-0.154482000
6	1.399680000	-0.036097000	2.259067000
1	0.357684000	0.131989000	2.538816000
6	2.007599000	1.364119000	2.023592000
1	3.094321000	1.365119000	2.135042000
1	1.609028000	2.053862000	2.776694000
1	1.764172000	1.762956000	1.036609000
6	2.070623000	-0.690840000	3.488183000
1	1.536390000	-1.587404000	3.812981000
1	2.071597000	0.017610000	4.325557000
1	3.105591000	-0.975977000	3.286430000
6	3.641391000	-2.614984000	-1.610980000
1	4.384066000	-1.822818000	-1.483781000
6	3.237787000	-2.614753000	-3.098927000
1	2.646897000	-3.502465000	-3.356997000
1	4.133821000	-2.625428000	-3.730957000
1	2.635645000	-1.730497000	-3.321543000
6	4.311438000	-3.938810000	-1.191070000
1	4.637253000	-3.906871000	-0.145717000
1	5.187859000	-4.139042000	-1.818638000
1	3.622152000	-4.784796000	-1.302714000
6	-1.062044000	-3.712011000	-0.356555000
1	-1.908038000	-3.315581000	0.208669000
6	-1.479506000	-3.804434000	-1.836899000

1	-1.627534000	-2.809681000	-2.268598000
1	-2.411345000	-4.374249000	-1.934633000
1	-0.719476000	-4.313085000	-2.440654000
6	-0.763218000	-5.113709000	0.211565000
1	0.089815000	-5.577085000	-0.297286000
1	-1.630855000	-5.770537000	0.076402000
1	-0.534887000	-5.072970000	1.281676000
6	3.785213000	-0.547789000	0.447519000
6	4.824169000	-1.045464000	1.234824000
6	6.046206000	-0.390710000	1.345834000
6	6.312194000	0.793720000	0.659618000
6	7.646831000	1.491076000	0.766932000
1	8.017742000	1.391501000	1.793318000
1	7.505304000	2.559501000	0.574453000
6	8.700992000	0.929367000	-0.208823000
1	8.324659000	1.022520000	-1.236497000
1	8.828681000	-0.144559000	-0.017395000
6	10.055009000	1.638735000	-0.088468000
1	9.918520000	2.713977000	-0.271441000
1	10.420500000	1.548576000	0.944368000
6	11.107841000	1.084984000	-1.053775000
1	11.288259000	0.018126000	-0.873926000
1	12.064448000	1.607959000	-0.942974000
1	10.786577000	1.195184000	-2.096645000
6	5.284138000	1.277773000	-0.150489000
6	4.058016000	0.626786000	-0.260861000
9	1.049258000	-0.551810000	-2.144504000
6	-0.859287000	1.203042000	-2.475629000
6	-1.559392000	1.253657000	-3.656529000
16	0.308221000	2.506116000	-2.466392000
6	-1.211517000	2.347113000	-4.512431000
1	-2.310040000	0.524349000	-3.941722000
6	-0.217120000	3.129776000	-3.997715000
1	-1.691878000	2.539210000	-5.468330000
1	0.220242000	4.026301000	-4.419190000
9	6.999058000	-0.926918000	2.136619000
9	4.653049000	-2.194767000	1.923988000
9	5.473465000	2.413552000	-0.849997000
9	3.117813000	1.167883000	-1.042862000
1	0.146854000	-3.147368000	2.884713000

122b TS



```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           1.153842 (Hartree/Particle)
 Thermal correction to Energy=                    1.217844
 Thermal correction to Enthalpy=                  1.218789
 Thermal correction to Gibbs Free Energy=         1.055325
 Sum of electronic and zero-point Energies=          -3616.871999
 Sum of electronic and thermal Energies=             -3616.807996
 Sum of electronic and thermal Enthalpies=           -3616.807052
 Sum of electronic and thermal Free Energies=        -3616.970516
```

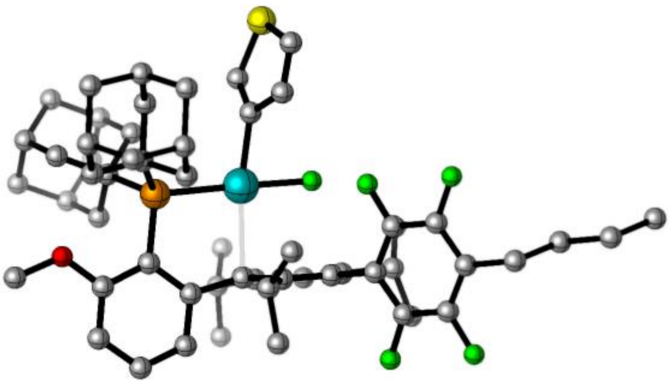
46	-0.599539000	-0.200564000	-1.069118000
15	-2.525857000	0.196192000	0.290902000
6	-4.219264000	-0.381859000	-0.485937000
6	-4.418243000	-1.898473000	-0.223020000
1	-3.544623000	-2.452944000	-0.576175000
1	-4.518863000	-2.091684000	0.849463000
6	-5.675131000	-2.424862000	-0.954510000
1	-5.776311000	-3.497323000	-0.739292000
6	-5.524492000	-2.208382000	-2.472245000
1	-6.407218000	-2.596346000	-2.999258000
1	-4.655375000	-2.763437000	-2.850266000
6	-5.354488000	-0.703139000	-2.749902000
1	-5.223167000	-0.536099000	-3.827280000
6	-4.097109000	-0.182617000	-2.019590000
1	-3.211755000	-0.716126000	-2.379972000
1	-3.939267000	0.873533000	-2.257961000
6	-5.493461000	0.363035000	-0.000696000
1	-5.620136000	0.230214000	1.074016000
1	-5.411607000	1.436266000	-0.191958000
6	-6.747391000	-0.168905000	-0.735438000
1	-7.621729000	0.382244000	-0.362799000
6	-6.919717000	-1.672003000	-0.448979000
1	-7.822077000	-2.052948000	-0.947009000
1	-7.054111000	-1.840080000	0.629006000

6	-6.597723000	0.056612000	-2.251376000
1	-6.498841000	1.129456000	-2.466455000
1	-7.495966000	-0.294649000	-2.777999000
6	-2.598644000	2.039570000	0.862676000
6	-3.015220000	2.926383000	-0.345474000
1	-2.373693000	2.715011000	-1.203198000
1	-4.043132000	2.705530000	-0.649731000
6	-2.924625000	4.423561000	0.028137000
1	-3.227100000	5.013242000	-0.847168000
6	-1.476788000	4.776901000	0.416277000
1	-0.805006000	4.583201000	-0.428388000
1	-1.400163000	5.846059000	0.659586000
6	-1.061643000	3.927205000	1.632064000
1	-0.022524000	4.152928000	1.906306000
6	-1.152811000	2.427539000	1.269352000
1	-0.843045000	1.826728000	2.132455000
1	-0.464090000	2.205009000	0.449868000
6	-3.519169000	2.364510000	2.069626000
1	-4.557521000	2.099834000	1.855070000
1	-3.209343000	1.780117000	2.941577000
6	-3.438015000	3.870371000	2.421528000
1	-4.114371000	4.060477000	3.266569000
6	-3.867720000	4.718506000	1.209419000
1	-4.906662000	4.487236000	0.934181000
1	-3.835503000	5.786575000	1.466075000
6	-1.994710000	4.230178000	2.818481000
1	-1.928979000	5.292182000	3.093024000
1	-1.689822000	3.651533000	3.702204000
6	-2.184316000	-0.907765000	1.773515000
6	-3.105033000	-1.083118000	2.843294000
6	-2.846377000	-1.943283000	3.913048000
1	-3.561221000	-2.054284000	4.718871000
6	-1.669527000	-2.684985000	3.925336000
1	-1.471176000	-3.369301000	4.745742000
6	-0.762397000	-2.556167000	2.885679000
6	-0.989468000	-1.670046000	1.814938000
8	-4.275872000	-0.391259000	2.755016000
6	-5.203583000	-0.445023000	3.830668000
1	-5.594611000	-1.459769000	3.974865000
1	-6.021453000	0.219695000	3.548047000
1	-4.752629000	-0.089667000	4.765132000
6	0.117954000	-1.685984000	0.775632000
6	1.355126000	-0.993303000	1.056379000
6	2.490097000	-1.284835000	0.278182000
6	2.452900000	-2.295741000	-0.712843000
6	1.292232000	-3.046900000	-0.858424000
1	1.288856000	-3.856112000	-1.580196000
6	0.124795000	-2.774333000	-0.154482000
6	1.399680000	-0.036097000	2.259067000
1	0.357684000	0.131989000	2.538816000
6	2.007599000	1.364119000	2.023592000

1	3.094321000	1.365119000	2.135042000
1	1.609028000	2.053862000	2.776694000
1	1.764172000	1.762956000	1.036609000
6	2.070623000	-0.690840000	3.488183000
1	1.536390000	-1.587404000	3.812981000
1	2.071597000	0.017610000	4.325557000
1	3.105591000	-0.975977000	3.286430000
6	3.641391000	-2.614984000	-1.610980000
1	4.384066000	-1.822818000	-1.483781000
6	3.237787000	-2.614753000	-3.098927000
1	2.646897000	-3.502465000	-3.356997000
1	4.133821000	-2.625428000	-3.730957000
1	2.635645000	-1.730497000	-3.321543000
6	4.311438000	-3.938810000	-1.191070000
1	4.637253000	-3.906871000	-0.145717000
1	5.187859000	-4.139042000	-1.818638000
1	3.622152000	-4.784796000	-1.302714000
6	-1.062044000	-3.712011000	-0.356555000
1	-1.908038000	-3.315581000	0.208669000
6	-1.479506000	-3.804434000	-1.836899000
1	-1.627534000	-2.809681000	-2.268598000
1	-2.411345000	-4.374249000	-1.934633000
1	-0.719476000	-4.313085000	-2.440654000
6	-0.763218000	-5.113709000	0.211565000
1	0.089815000	-5.577085000	-0.297286000
1	-1.630855000	-5.770537000	0.076402000
1	-0.534887000	-5.072970000	1.281676000
6	3.785213000	-0.547789000	0.447519000
6	4.824169000	-1.045464000	1.234824000
6	6.046206000	-0.390710000	1.345834000
6	6.312194000	0.793720000	0.659618000
6	7.646831000	1.491076000	0.766932000
1	8.017742000	1.391501000	1.793318000
1	7.505304000	2.559501000	0.574453000
6	8.700992000	0.929367000	-0.208823000
1	8.324659000	1.022520000	-1.236497000
1	8.828681000	-0.144559000	-0.017395000
6	10.055009000	1.638735000	-0.088468000
1	9.918520000	2.713977000	-0.271441000
1	10.420500000	1.548576000	0.944368000
6	11.107841000	1.084984000	-1.053775000
1	11.288259000	0.018126000	-0.873926000
1	12.064448000	1.607959000	-0.942974000
1	10.786577000	1.195184000	-2.096645000
6	5.284138000	1.277773000	-0.150489000
6	4.058016000	0.626786000	-0.260861000
9	1.049258000	-0.551810000	-2.144504000
6	-0.859287000	1.203042000	-2.475629000
6	-1.559392000	1.253657000	-3.656529000
16	0.308221000	2.506116000	-2.466392000
6	-1.211517000	2.347113000	-4.512431000

1	-2.310040000	0.524349000	-3.941722000
6	-0.217120000	3.129776000	-3.997715000
1	-1.691878000	2.539210000	-5.468330000
1	0.220242000	4.026301000	-4.419190000
9	6.999058000	-0.926918000	2.136619000
9	4.653049000	-2.194767000	1.923988000
9	5.473465000	2.413552000	-0.849997000
9	3.117813000	1.167883000	-1.042862000
1	0.146854000	-3.147368000	2.884713000

122c GS



```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           1.153616 (Hartree/Particle)
 Thermal correction to Energy=                    1.217771
 Thermal correction to Enthalpy=                  1.218716
 Thermal correction to Gibbs Free Energy=         1.054833
 Sum of electronic and zero-point Energies=          -3616.873770
 Sum of electronic and thermal Energies=             -3616.809615
 Sum of electronic and thermal Enthalpies=           -3616.808671
 Sum of electronic and thermal Free Energies=        -3616.972554
```

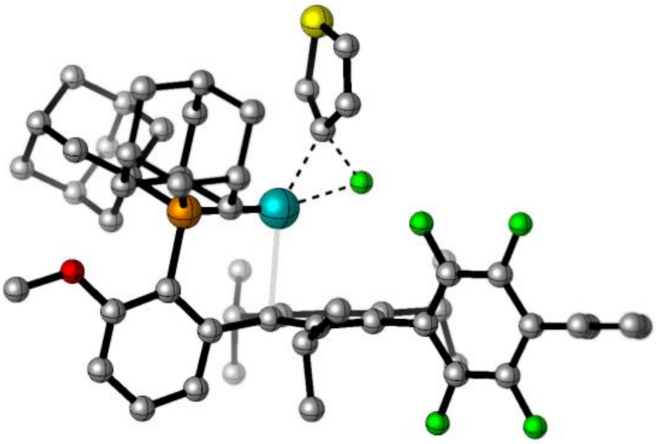
46	-0.531281000	-0.062466000	-1.056932000
15	-2.505663000	0.135892000	0.327970000
6	-4.208336000	-0.291085000	-0.533626000
6	-4.455291000	-1.822027000	-0.481600000
1	-3.592405000	-2.356066000	-0.889957000
1	-4.585171000	-2.153376000	0.553069000
6	-5.711960000	-2.205778000	-1.297169000
1	-5.849025000	-3.293648000	-1.231401000
6	-5.525655000	-1.791943000	-2.769386000
1	-6.407655000	-2.079439000	-3.358127000
1	-4.664593000	-2.316506000	-3.205116000
6	-5.309374000	-0.269008000	-2.838055000
1	-5.154441000	0.037736000	-3.881078000
6	-4.053065000	0.109920000	-2.024163000

1	-3.175458000	-0.392567000	-2.444235000
1	-3.867578000	1.184905000	-2.111255000
6	-5.467974000	0.422235000	0.025798000
1	-5.618120000	0.154286000	1.072258000
1	-5.348725000	1.508248000	-0.019819000
6	-6.723775000	0.032819000	-0.790750000
1	-7.589721000	0.554690000	-0.360981000
6	-6.943358000	-1.489509000	-0.712601000
1	-7.847649000	-1.772685000	-1.268715000
1	-7.100854000	-1.796959000	0.330954000
6	-6.539924000	0.454072000	-2.260266000
1	-6.406898000	1.542506000	-2.329179000
1	-7.437152000	0.204831000	-2.843530000
6	-2.564895000	1.880871000	1.171561000
6	-2.892800000	2.940681000	0.080851000
1	-2.211228000	2.834320000	-0.765966000
1	-3.908176000	2.800445000	-0.305267000
6	-2.778377000	4.367696000	0.662112000
1	-3.020353000	5.083919000	-0.133664000
6	-1.340107000	4.609713000	1.157028000
1	-0.636818000	4.512388000	0.320596000
1	-1.240147000	5.631804000	1.548295000
6	-1.007160000	3.586784000	2.259823000
1	0.023913000	3.736640000	2.606835000
6	-1.129593000	2.155138000	1.692320000
1	-0.882018000	1.432115000	2.478724000
1	-0.406170000	2.014743000	0.883861000
6	-3.530290000	2.069928000	2.370011000
1	-4.565598000	1.877992000	2.078094000
1	-3.283192000	1.357076000	3.162408000
6	-3.419358000	3.508258000	2.932070000
1	-4.127509000	3.607236000	3.766471000
6	-3.765530000	4.530812000	1.833137000
1	-4.796786000	4.378957000	1.483891000
1	-3.712807000	5.551607000	2.236338000
6	-1.986038000	3.758654000	3.435938000
1	-1.901864000	4.770227000	3.856534000
1	-1.739218000	3.054344000	4.243054000
6	-2.197213000	-1.163785000	1.654818000
6	-3.139265000	-1.471689000	2.673498000
6	-2.905982000	-2.465875000	3.626260000
1	-3.636311000	-2.675984000	4.397794000
6	-1.733256000	-3.211236000	3.563812000
1	-1.554465000	-3.999357000	4.290131000
6	-0.805046000	-2.953423000	2.567507000
6	-1.004970000	-1.931460000	1.619016000
8	-4.305252000	-0.764854000	2.656607000
6	-5.259086000	-0.964654000	3.690470000
1	-5.650371000	-1.989514000	3.685794000
1	-6.072322000	-0.267892000	3.480945000
1	-4.834044000	-0.740046000	4.676350000

6	0.125266000	-1.818352000	0.610384000
6	1.367753000	-1.199350000	1.003247000
6	2.503163000	-1.377707000	0.190941000
6	2.461625000	-2.219070000	-0.947268000
6	1.291595000	-2.919926000	-1.213373000
1	1.279385000	-3.605759000	-2.053182000
6	0.120973000	-2.737911000	-0.484428000
6	1.419942000	-0.446978000	2.344324000
1	0.379235000	-0.318010000	2.649271000
6	2.037881000	0.968275000	2.339593000
1	3.125509000	0.944292000	2.440131000
1	1.649992000	1.526821000	3.199614000
1	1.792228000	1.527472000	1.434488000
6	2.089142000	-1.294953000	3.449758000
1	1.552843000	-2.230952000	3.626143000
1	2.095788000	-0.732198000	4.391314000
1	3.122592000	-1.547302000	3.200893000
6	3.651398000	-2.411069000	-1.880693000
1	4.397088000	-1.648651000	-1.639569000
6	3.254689000	-2.194554000	-3.354437000
1	2.654774000	-3.029177000	-3.738626000
1	4.153796000	-2.126167000	-3.978638000
1	2.664688000	-1.279877000	-3.449934000
6	4.313401000	-3.785624000	-1.656831000
1	4.639696000	-3.907379000	-0.618567000
1	5.187913000	-3.898429000	-2.308527000
1	3.617595000	-4.601218000	-1.889298000
6	-1.081085000	-3.609232000	-0.837922000
1	-1.932332000	-3.265731000	-0.246260000
6	-1.464899000	-3.496812000	-2.325735000
1	-1.588122000	-2.450964000	-2.624478000
1	-2.403145000	-4.031108000	-2.518150000
1	-0.700259000	-3.935225000	-2.976733000
6	-0.826421000	-5.079923000	-0.453002000
1	0.029190000	-5.490980000	-1.001229000
1	-1.703730000	-5.693510000	-0.691093000
1	-0.621575000	-5.185738000	0.617405000
6	3.802916000	-0.682906000	0.469196000
6	4.849043000	-1.311156000	1.144691000
6	6.086383000	-0.700536000	1.330698000
6	6.356960000	0.574755000	0.836961000
6	7.701842000	1.240006000	1.006249000
1	8.224357000	0.775664000	1.848423000
1	7.546127000	2.294728000	1.261963000
6	8.579729000	1.153358000	-0.259145000
1	8.043823000	1.617911000	-1.096993000
1	8.724216000	0.097491000	-0.525685000
6	9.943519000	1.831152000	-0.081028000
1	9.791151000	2.883944000	0.196033000
1	10.472716000	1.366407000	0.762983000
6	10.816081000	1.754479000	-1.337986000

1	11.017052000	0.713372000	-1.618626000
1	11.781193000	2.250211000	-1.184173000
1	10.324614000	2.238049000	-2.190927000
6	5.315971000	1.197823000	0.146428000
6	4.078790000	0.590320000	-0.041196000
9	1.149093000	-0.220945000	-2.125525000
9	7.040783000	-1.375202000	2.003488000
9	4.674355000	-2.555458000	1.640581000
9	5.513230000	2.431522000	-0.361227000
9	3.131832000	1.266597000	-0.704650000
1	0.099063000	-3.548885000	2.504430000
6	-0.695635000	1.543172000	-2.250327000
6	-1.453551000	1.728958000	-3.366417000
6	0.248910000	2.612692000	-2.068113000
16	-1.072286000	3.231145000	-4.182214000
1	-2.204978000	1.091308000	-3.806888000
6	0.152379000	3.596269000	-3.009155000
1	0.990020000	2.628368000	-1.277516000
1	0.736766000	4.503343000	-3.097183000

122c TS



```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           1.153616 (Hartree/Particle)
 Thermal correction to Energy=                    1.217771
 Thermal correction to Enthalpy=                  1.218716
 Thermal correction to Gibbs Free Energy=         1.054833
 Sum of electronic and zero-point Energies=          -3616.873770
 Sum of electronic and thermal Energies=             -3616.809615
 Sum of electronic and thermal Enthalpies=           -3616.808671
 Sum of electronic and thermal Free Energies=        -3616.972554
```

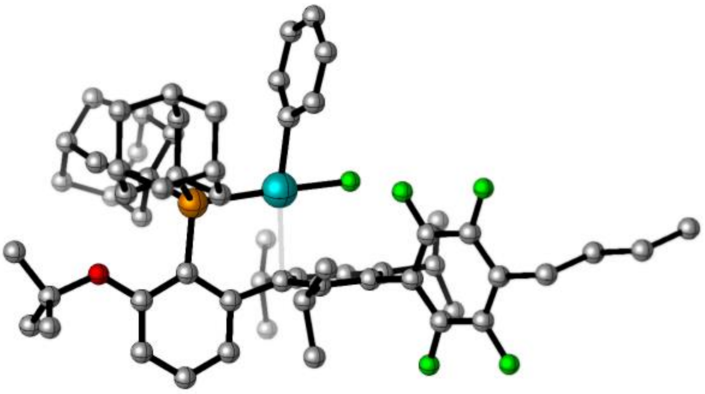
46	-0.531281000	-0.062466000	-1.056932000
15	-2.505663000	0.135892000	0.327970000
6	-4.208336000	-0.291085000	-0.533626000
6	-4.455291000	-1.822027000	-0.481600000

1	-3.592405000	-2.356066000	-0.889957000
1	-4.585171000	-2.153376000	0.553069000
6	-5.711960000	-2.205778000	-1.297169000
1	-5.849025000	-3.293648000	-1.231401000
6	-5.525655000	-1.791943000	-2.769386000
1	-6.407655000	-2.079439000	-3.358127000
1	-4.664593000	-2.316506000	-3.205116000
6	-5.309374000	-0.269008000	-2.838055000
1	-5.154441000	0.037736000	-3.881078000
6	-4.053065000	0.109920000	-2.024163000
1	-3.175458000	-0.392567000	-2.444235000
1	-3.867578000	1.184905000	-2.111255000
6	-5.467974000	0.422235000	0.025798000
1	-5.618120000	0.154286000	1.072258000
1	-5.348725000	1.508248000	-0.019819000
6	-6.723775000	0.032819000	-0.790750000
1	-7.589721000	0.554690000	-0.360981000
6	-6.943358000	-1.489509000	-0.712601000
1	-7.847649000	-1.772685000	-1.268715000
1	-7.100854000	-1.796959000	0.330954000
6	-6.539924000	0.454072000	-2.260266000
1	-6.406898000	1.542506000	-2.329179000
1	-7.437152000	0.204831000	-2.843530000
6	-2.564895000	1.880871000	1.171561000
6	-2.892800000	2.940681000	0.080851000
1	-2.211228000	2.834320000	-0.765966000
1	-3.908176000	2.800445000	-0.305267000
6	-2.778377000	4.367696000	0.662112000
1	-3.020353000	5.083919000	-0.133664000
6	-1.340107000	4.609713000	1.157028000
1	-0.636818000	4.512388000	0.320596000
1	-1.240147000	5.631804000	1.548295000
6	-1.007160000	3.586784000	2.259823000
1	0.023913000	3.736640000	2.606835000
6	-1.129593000	2.155138000	1.692320000
1	-0.882018000	1.432115000	2.478724000
1	-0.406170000	2.014743000	0.883861000
6	-3.530290000	2.069928000	2.370011000
1	-4.565598000	1.877992000	2.078094000
1	-3.283192000	1.357076000	3.162408000
6	-3.419358000	3.508258000	2.932070000
1	-4.127509000	3.607236000	3.766471000
6	-3.765530000	4.530812000	1.833137000
1	-4.796786000	4.378957000	1.483891000
1	-3.712807000	5.551607000	2.236338000
6	-1.986038000	3.758654000	3.435938000
1	-1.901864000	4.770227000	3.856534000
1	-1.739218000	3.054344000	4.243054000
6	-2.197213000	-1.163785000	1.654818000
6	-3.139265000	-1.471689000	2.673498000
6	-2.905982000	-2.465875000	3.626260000

1	-3.636311000	-2.675984000	4.397794000
6	-1.733256000	-3.211236000	3.563812000
1	-1.554465000	-3.999357000	4.290131000
6	-0.805046000	-2.953423000	2.567507000
6	-1.004970000	-1.931460000	1.619016000
8	-4.305252000	-0.764854000	2.656607000
6	-5.259086000	-0.964654000	3.690470000
1	-5.650371000	-1.989514000	3.685794000
1	-6.072322000	-0.267892000	3.480945000
1	-4.834044000	-0.740046000	4.676350000
6	0.125266000	-1.818352000	0.610384000
6	1.367753000	-1.199350000	1.003247000
6	2.503163000	-1.377707000	0.190941000
6	2.461625000	-2.219070000	-0.947268000
6	1.291595000	-2.919926000	-1.213373000
1	1.279385000	-3.605759000	-2.053182000
6	0.120973000	-2.737911000	-0.484428000
6	1.419942000	-0.446978000	2.344324000
1	0.379235000	-0.318010000	2.649271000
6	2.037881000	0.968275000	2.339593000
1	3.125509000	0.944292000	2.440131000
1	1.649992000	1.526821000	3.199614000
1	1.792228000	1.527472000	1.434488000
6	2.089142000	-1.294953000	3.449758000
1	1.552843000	-2.230952000	3.626143000
1	2.095788000	-0.732198000	4.391314000
1	3.122592000	-1.547302000	3.200893000
6	3.651398000	-2.411069000	-1.880693000
1	4.397088000	-1.648651000	-1.639569000
6	3.254689000	-2.194554000	-3.354437000
1	2.654774000	-3.029177000	-3.738626000
1	4.153796000	-2.126167000	-3.978638000
1	2.664688000	-1.279877000	-3.449934000
6	4.313401000	-3.785624000	-1.656831000
1	4.639696000	-3.907379000	-0.618567000
1	5.187913000	-3.898429000	-2.308527000
1	3.617595000	-4.601218000	-1.889298000
6	-1.081085000	-3.609232000	-0.837922000
1	-1.932332000	-3.265731000	-0.246260000
6	-1.464899000	-3.496812000	-2.325735000
1	-1.588122000	-2.450964000	-2.624478000
1	-2.403145000	-4.031108000	-2.518150000
1	-0.700259000	-3.935225000	-2.976733000
6	-0.826421000	-5.079923000	-0.453002000
1	0.029190000	-5.490980000	-1.001229000
1	-1.703730000	-5.693510000	-0.691093000
1	-0.621575000	-5.185738000	0.617405000
6	3.802916000	-0.682906000	0.469196000
6	4.849043000	-1.311156000	1.144691000
6	6.086383000	-0.700536000	1.330698000
6	6.356960000	0.574755000	0.836961000

6	7.701842000	1.240006000	1.006249000
1	8.224357000	0.775664000	1.848423000
1	7.546127000	2.294728000	1.261963000
6	8.579729000	1.153358000	-0.259145000
1	8.043823000	1.617911000	-1.096993000
1	8.724216000	0.097491000	-0.525685000
6	9.943519000	1.831152000	-0.081028000
1	9.791151000	2.883944000	0.196033000
1	10.472716000	1.366407000	0.762983000
6	10.816081000	1.754479000	-1.337986000
1	11.017052000	0.713372000	-1.618626000
1	11.781193000	2.250211000	-1.184173000
1	10.324614000	2.238049000	-2.190927000
6	5.315971000	1.197823000	0.146428000
6	4.078790000	0.590320000	-0.041196000
9	1.149093000	-0.220945000	-2.125525000
9	7.040783000	-1.375202000	2.003488000
9	4.674355000	-2.555458000	1.640581000
9	5.513230000	2.431522000	-0.361227000
9	3.131832000	1.266597000	-0.704650000
1	0.099063000	-3.548885000	2.504430000
6	-0.695635000	1.543172000	-2.250327000
6	-1.453551000	1.728958000	-3.366417000
6	0.248910000	2.612692000	-2.068113000
16	-1.072286000	3.231145000	-4.182214000
1	-2.204978000	1.091308000	-3.806888000
6	0.152379000	3.596269000	-3.009155000
1	0.990020000	2.628368000	-1.277516000
1	0.736766000	4.503343000	-3.097183000

205a GS



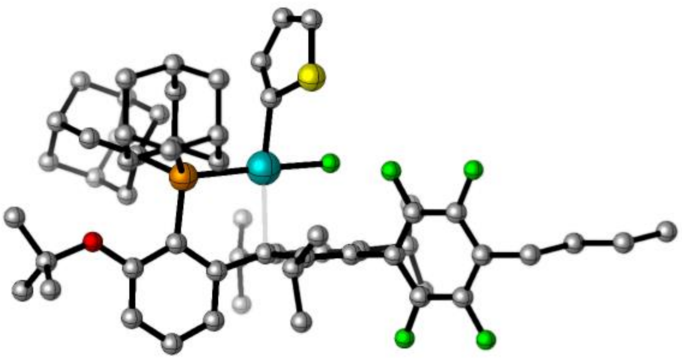
46	0.185364000	0.161615000	1.268943000
15	2.254467000	0.243534000	-0.013307000
6	3.866976000	0.021103000	1.061494000
6	4.165920000	-1.489453000	1.251438000
1	3.283163000	-1.996952000	1.649735000
1	4.407148000	-1.955735000	0.291067000
6	5.348336000	-1.699135000	2.226302000

1	5.524284000	-2.778262000	2.332137000
6	5.010572000	-1.088737000	3.600151000
1	5.841991000	-1.249348000	4.300457000
1	4.129632000	-1.583811000	4.030400000
6	4.740037000	0.417169000	3.426384000
1	4.476592000	0.861654000	4.395247000
6	3.553797000	0.616088000	2.458506000
1	2.662749000	0.128797000	2.865556000
1	3.314588000	1.681478000	2.379755000
6	5.148420000	0.700169000	0.521324000
1	5.393178000	0.288506000	-0.455555000
1	4.996710000	1.775681000	0.395606000
6	6.334069000	0.487409000	1.492623000
1	7.220656000	0.981098000	1.071102000
6	6.608113000	-1.018973000	1.660095000
1	7.461894000	-1.177966000	2.333211000
1	6.877827000	-1.466379000	0.692599000
6	5.996365000	1.105935000	2.862414000
1	5.822068000	2.185711000	2.758070000
1	6.840891000	0.983833000	3.554724000
6	2.330942000	1.865201000	-1.072858000
6	2.539403000	3.079433000	-0.123852000
1	1.792333000	3.073785000	0.671944000
1	3.522016000	3.031230000	0.356023000
6	2.442057000	4.404600000	-0.914956000
1	2.598851000	5.235340000	-0.214847000
6	1.045623000	4.521916000	-1.553695000
1	0.276713000	4.520461000	-0.771572000
1	0.954513000	5.473201000	-2.096497000
6	0.831459000	3.339806000	-2.517774000
1	-0.169611000	3.401717000	-2.964953000
6	0.940097000	2.008574000	-1.741395000
1	0.779374000	1.173541000	-2.433741000
1	0.155541000	1.954921000	-0.981857000
6	3.391358000	1.920124000	-2.196281000
1	4.395833000	1.823344000	-1.780344000
1	3.245710000	1.084197000	-2.886089000
6	3.293051000	3.253284000	-2.976614000
1	4.067173000	3.256815000	-3.757015000
6	3.519903000	4.435039000	-2.015180000
1	4.521564000	4.371894000	-1.566630000
1	3.476385000	5.385552000	-2.564797000
6	1.901611000	3.374855000	-3.624541000
1	1.828138000	4.310414000	-4.196108000
1	1.740788000	2.551801000	-4.335350000
6	2.121264000	-1.253238000	-1.165451000
6	3.136373000	-1.706743000	-2.071542000
6	2.940826000	-2.871351000	-2.826200000
1	3.700243000	-3.216440000	-3.506106000
6	1.781224000	-3.622142000	-2.701261000
1	1.662284000	-4.529813000	-3.286795000

6	0.794773000	-3.214849000	-1.822760000
1	-0.105991000	-3.805572000	-1.700823000
6	0.938512000	-2.041243000	-1.062750000
8	4.303706000	-0.991533000	-2.142019000
6	5.385273000	-1.240973000	-3.116034000
6	-0.261710000	-1.813513000	-0.155799000
6	-1.485614000	-1.296466000	-0.721523000
6	-2.679491000	-1.411343000	0.015957000
6	-2.711310000	-2.106523000	1.248814000
6	-1.549173000	-2.726896000	1.691792000
1	-1.590165000	-3.305069000	2.608371000
6	-0.327819000	-2.595680000	1.039849000
6	-1.450875000	-0.736170000	-2.153225000
1	-0.393233000	-0.604998000	-2.390986000
6	-2.115962000	0.636220000	-2.394783000
1	-3.189211000	0.548274000	-2.578492000
1	-1.675336000	1.091675000	-3.289429000
1	-1.968350000	1.322228000	-1.558463000
6	-1.996812000	-1.755841000	-3.178983000
1	-1.409052000	-2.677096000	-3.188942000
1	-1.953434000	-1.322554000	-4.185851000
1	-3.034827000	-2.026588000	-2.972735000
6	-3.972035000	-2.233143000	2.095930000
1	-4.720187000	-1.544002000	1.694697000
6	-3.718060000	-1.813206000	3.557250000
1	-3.124305000	-2.562706000	4.095450000
1	-4.671639000	-1.710600000	4.089152000
1	-3.172691000	-0.866839000	3.583978000
6	-4.562128000	-3.654725000	1.998977000
1	-4.789698000	-3.923331000	0.961850000
1	-5.487101000	-3.724277000	2.583638000
1	-3.861859000	-4.400897000	2.394087000
6	0.860103000	-3.374809000	1.597942000
1	1.745253000	-3.102907000	1.019049000
6	1.133866000	-3.032850000	3.075111000
1	1.211255000	-1.951180000	3.221554000
1	2.066733000	-3.503025000	3.409076000
1	0.332531000	-3.394160000	3.729390000
6	0.659378000	-4.893120000	1.423306000
1	-0.225308000	-5.242943000	1.967741000
1	1.528400000	-5.438042000	1.811542000
1	0.534873000	-5.163680000	0.369794000
6	-3.966982000	-0.798082000	-0.448625000
6	-4.938406000	-1.532816000	-1.127923000
9	-4.700087000	-2.822185000	-1.452201000
6	-6.162478000	-0.982622000	-1.498183000
9	-7.040423000	-1.759855000	-2.164719000
6	-6.496449000	0.336265000	-1.194494000
6	-7.826353000	0.942661000	-1.573140000
1	-8.254528000	0.369494000	-2.401552000
1	-7.658952000	1.963376000	-1.936967000

6	-8.828848000	0.985704000	-0.401717000
1	-8.385918000	1.554946000	0.425921000
1	-8.992234000	-0.034598000	-0.028950000
6	-10.171093000	1.612113000	-0.797708000
1	-9.996805000	2.627727000	-1.180333000
1	-10.606225000	1.042260000	-1.631041000
6	-11.170921000	1.667385000	0.361774000
1	-11.391167000	0.663051000	0.743833000
1	-12.118758000	2.120291000	0.049692000
1	-10.776983000	2.259850000	1.196435000
6	-5.533236000	1.066519000	-0.496232000
9	-5.794706000	2.348161000	-0.168189000
6	-4.309190000	0.519696000	-0.124979000
9	-3.437032000	1.297530000	0.529439000
6	0.166600000	1.937773000	2.228295000
6	0.783455000	2.195469000	3.454000000
1	1.395686000	1.441373000	3.937625000
6	0.613192000	3.422705000	4.104764000
1	1.115304000	3.595420000	5.055079000
6	-0.193478000	4.413588000	3.548223000
6	-0.854973000	4.148731000	2.347446000
1	-1.519508000	4.892695000	1.911860000
6	-0.686903000	2.920066000	1.706310000
1	-0.322424000	5.368871000	4.051393000
9	-1.531150000	0.041375000	2.290668000
1	-1.252222000	2.726511000	0.799542000
6	4.886527000	-1.082589000	-4.562643000
1	5.732227000	-1.206994000	-5.247543000
1	4.118648000	-1.801076000	-4.850042000
1	4.479155000	-0.077374000	-4.710171000
6	6.096975000	-2.580532000	-2.845141000
1	5.536932000	-3.466550000	-3.145612000
1	7.045455000	-2.593769000	-3.392896000
1	6.324315000	-2.668264000	-1.777775000
6	6.403232000	-0.122388000	-2.845711000
1	5.940002000	0.862887000	-2.925613000
1	6.854177000	-0.221765000	-1.854958000
1	7.206851000	-0.183301000	-3.586694000

205b GS



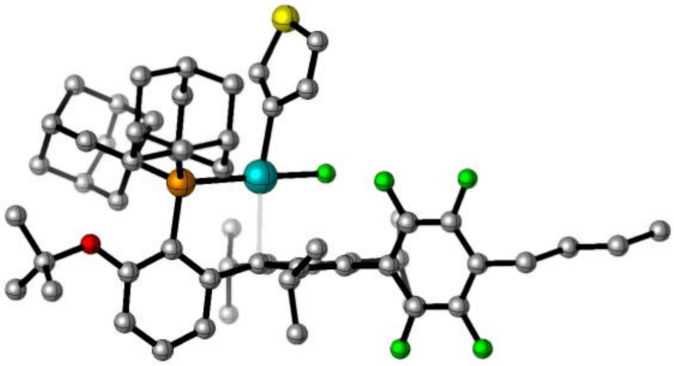
46	-0.252392000	0.054701000	-1.280357000
15	-2.283390000	0.232431000	-0.027095000
6	-3.899244000	-0.156464000	-1.040462000
6	-4.159744000	-1.686120000	-1.038881000
1	-3.278468000	-2.215014000	-1.410246000
1	-4.348461000	-2.037430000	-0.019934000
6	-5.367024000	-2.041974000	-1.936937000
1	-5.511523000	-3.130554000	-1.906814000
6	-5.090176000	-1.591578000	-3.383764000
1	-5.937574000	-1.856388000	-4.031350000
1	-4.208440000	-2.112102000	-3.781219000
6	-4.859904000	-0.068708000	-3.399635000
1	-4.642347000	0.263594000	-4.423413000
6	-3.649078000	0.281447000	-2.506168000
1	-2.751338000	-0.216870000	-2.885386000
1	-3.450246000	1.356066000	-2.555030000
6	-5.184411000	0.546816000	-0.536587000
1	-5.381743000	0.247708000	0.490470000
1	-5.060404000	1.632770000	-0.545283000
6	-6.393655000	0.187919000	-1.432004000
1	-7.279363000	0.706396000	-1.039258000
6	-6.628170000	-1.333780000	-1.410012000
1	-7.497904000	-1.593916000	-2.029062000
1	-6.852530000	-1.670092000	-0.387396000
6	-6.118997000	0.647912000	-2.876041000
1	-5.975281000	1.736700000	-2.905190000
1	-6.981362000	0.421349000	-3.518349000
6	-2.369669000	1.964199000	0.824028000
6	-2.662835000	3.060747000	-0.239879000
1	-1.949329000	2.985596000	-1.062571000
1	-3.662074000	2.929165000	-0.667706000
6	-2.584489000	4.465203000	0.403285000
1	-2.799998000	5.209673000	-0.374258000
6	-1.172379000	4.701864000	0.970660000
1	-0.430063000	4.644241000	0.166241000
1	-1.104753000	5.707518000	1.409257000
6	-0.876599000	3.637656000	2.044124000

1	0.137907000	3.779737000	2.439593000
6	-0.959508000	2.229529000	1.412878000
1	-0.737452000	1.476568000	2.177769000
1	-0.206347000	2.131878000	0.626469000
6	-3.389293000	2.102602000	1.980617000
1	-4.403954000	1.927289000	1.618954000
1	-3.185456000	1.350624000	2.748397000
6	-3.313253000	3.514420000	2.608683000
1	-4.058332000	3.573665000	3.415005000
6	-3.622079000	4.576409000	1.536693000
1	-4.636976000	4.430086000	1.140076000
1	-3.594884000	5.581233000	1.980763000
6	-1.905064000	3.751647000	3.183895000
1	-1.847755000	4.744719000	3.650828000
1	-1.688049000	3.014687000	3.970451000
6	-2.098209000	-1.123713000	1.278575000
6	-3.087673000	-1.502515000	2.247088000
6	-2.861378000	-2.592537000	3.098241000
1	-3.604898000	-2.884173000	3.819457000
6	-1.692240000	-3.335184000	3.019396000
1	-1.549208000	-4.184924000	3.681481000
6	-0.725824000	-2.993222000	2.091859000
6	-0.903001000	-1.897142000	1.230093000
8	-4.260265000	-0.795169000	2.279438000
6	-5.313242000	-0.951591000	3.304749000
6	0.280363000	-1.724626000	0.289660000
6	1.501517000	-1.141981000	0.804217000
6	2.697208000	-1.320362000	0.085315000
6	2.734365000	-2.125143000	-1.079952000
6	1.581057000	-2.799685000	-1.462361000
1	1.629314000	-3.460250000	-2.320852000
6	0.358815000	-2.622376000	-0.825166000
6	1.457205000	-0.428747000	2.165825000
1	0.397974000	-0.285749000	2.389263000
6	2.102767000	0.972382000	2.244819000
1	3.176552000	0.921029000	2.439776000
1	1.653161000	1.522560000	3.079616000
1	1.948580000	1.553971000	1.333583000
6	2.013839000	-1.318642000	3.300783000
1	1.436021000	-2.239373000	3.414939000
1	1.962535000	-0.773462000	4.251187000
1	3.055312000	-1.599229000	3.128884000
6	3.992943000	-2.309647000	-1.918963000
1	4.733268000	-1.576897000	-1.587058000
6	3.721067000	-2.026234000	-3.409947000
1	3.140495000	-2.833078000	-3.874611000
1	4.668795000	-1.950570000	-3.956190000
1	3.155001000	-1.097633000	-3.515961000
6	4.604076000	-3.707993000	-1.696928000
1	4.842258000	-3.876280000	-0.641182000
1	5.525965000	-3.818434000	-2.279887000

1	3.912050000	-4.497186000	-2.015583000
6	-0.819187000	-3.462956000	-1.306586000
1	-1.704424000	-3.146470000	-0.752275000
6	-1.098011000	-3.258021000	-2.808145000
1	-1.179272000	-2.194386000	-3.052811000
1	-2.030328000	-3.759424000	-3.094533000
1	-0.297555000	-3.676260000	-3.428834000
6	-0.601934000	-4.956575000	-0.993782000
1	0.287931000	-5.345227000	-1.502284000
1	-1.464061000	-5.543853000	-1.331958000
1	-0.477997000	-5.128004000	0.080341000
6	3.986998000	-0.678395000	0.502459000
6	4.941102000	-1.360109000	1.257944000
6	6.169590000	-0.794632000	1.585470000
6	6.526529000	0.483787000	1.159023000
6	7.868399000	1.094565000	1.483533000
1	8.234192000	0.671388000	2.424917000
1	7.739652000	2.171503000	1.638747000
6	8.916007000	0.863662000	0.375222000
1	8.536479000	1.281077000	-0.566970000
1	9.035562000	-0.216388000	0.213953000
6	10.276276000	1.489193000	0.705261000
1	10.148341000	2.568425000	0.870124000
1	10.644750000	1.076661000	1.655335000
6	11.321034000	1.259591000	-0.391456000
1	11.495177000	0.189110000	-0.555326000
1	12.281643000	1.716840000	-0.128688000
1	10.995905000	1.691936000	-1.345538000
6	5.582785000	1.157340000	0.381751000
6	4.351718000	0.595880000	0.055065000
9	1.478378000	-0.120322000	-2.267858000
6	-0.393638000	1.684049000	-2.444346000
6	-0.992257000	1.951881000	-3.651757000
16	0.788455000	2.934823000	-2.125184000
6	-0.560440000	3.163155000	-4.280827000
1	-1.726414000	1.302081000	-4.115544000
6	0.399041000	3.821228000	-3.564683000
1	-0.958569000	3.525554000	-5.225084000
1	0.881739000	4.763317000	-3.793138000
9	7.033437000	-1.515642000	2.329612000
9	4.680829000	-2.611769000	1.695438000
9	5.869532000	2.393199000	-0.072904000
9	3.498011000	1.314434000	-0.682280000
1	0.185162000	-3.576046000	2.012497000
6	-4.771208000	-0.668075000	4.715900000
1	-5.602876000	-0.690327000	5.428357000
1	-4.022473000	-1.382617000	5.058585000
1	-4.325051000	0.330848000	4.750290000
6	-6.031603000	-2.307579000	3.172742000
1	-5.455310000	-3.165781000	3.520063000
1	-6.957118000	-2.277559000	3.757950000

1	-6.301759000	-2.481370000	2.126095000
6	-6.335323000	0.143837000	2.964821000
1	-5.871713000	1.132176000	2.963797000
1	-6.798969000	-0.029186000	1.990227000
1	-7.129070000	0.139441000	3.718811000

205c GS



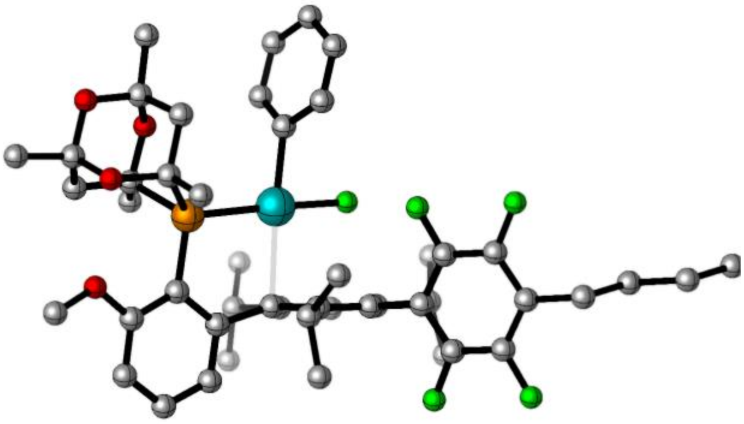
46	-0.213610000	0.333127000	-1.242026000
15	-2.246163000	0.209388000	0.070785000
6	-3.901041000	0.138923000	-0.962005000
6	-4.207678000	-1.332545000	-1.345758000
1	-3.347950000	-1.768856000	-1.862039000
1	-4.389836000	-1.932695000	-0.449328000
6	-5.443460000	-1.415421000	-2.270525000
1	-5.623889000	-2.470827000	-2.515874000
6	-5.183868000	-0.617282000	-3.561922000
1	-6.052176000	-0.685431000	-4.231800000
1	-4.327522000	-1.041430000	-4.103451000
6	-4.904577000	0.852447000	-3.195636000
1	-4.697330000	1.429505000	-4.106668000
6	-3.665119000	0.927513000	-2.275917000
1	-2.794278000	0.514552000	-2.796333000
1	-3.429848000	1.973262000	-2.057002000
6	-5.150721000	0.726818000	-0.263547000
1	-5.341522000	0.185349000	0.661004000
1	-4.989039000	1.776739000	-0.003157000
6	-6.389062000	0.638715000	-1.186144000
1	-7.250929000	1.061705000	-0.651667000
6	-6.669749000	-0.832713000	-1.543816000
1	-7.561231000	-0.906776000	-2.181877000
1	-6.882132000	-1.411820000	-0.633431000
6	-6.130116000	1.443612000	-2.472705000
1	-5.953252000	2.500171000	-2.229043000
1	-7.010889000	1.409747000	-3.128822000
6	-2.262544000	1.669678000	1.342920000
6	-2.478267000	2.998605000	0.565037000
1	-1.765337000	3.075672000	-0.257257000
1	-3.480925000	3.030976000	0.125123000

6	-2.313669000	4.210250000	1.509626000
1	-2.473010000	5.125534000	0.925221000
6	-0.891593000	4.215319000	2.101265000
1	-0.153589000	4.291519000	1.293145000
1	-0.753499000	5.090583000	2.751388000
6	-0.675508000	2.918729000	2.904730000
1	0.341865000	2.901727000	3.317662000
6	-0.845842000	1.699790000	1.972216000
1	-0.682907000	0.780267000	2.546931000
1	-0.088620000	1.727864000	1.183046000
6	-3.280173000	1.602825000	2.505650000
1	-4.302096000	1.578340000	2.123215000
1	-3.129644000	0.684700000	3.081336000
6	-3.120890000	2.827033000	3.440856000
1	-3.866965000	2.747508000	4.244243000
6	-3.349817000	4.126772000	2.645492000
1	-4.368294000	4.144637000	2.232113000
1	-3.260413000	4.997522000	3.309889000
6	-1.705374000	2.838500000	4.046409000
1	-1.589206000	3.693662000	4.726486000
1	-1.540419000	1.929942000	4.643029000
6	-2.092513000	-1.442363000	0.977427000
6	-3.081818000	-2.025359000	1.836017000
6	-2.902247000	-3.319125000	2.344216000
1	-3.649109000	-3.766890000	2.976643000
6	-1.775921000	-4.065087000	2.029510000
1	-1.670008000	-5.072117000	2.423897000
6	-0.802049000	-3.521267000	1.212788000
6	-0.933544000	-2.221728000	0.694493000
8	-4.210960000	-1.297477000	2.104983000
6	-5.246694000	-1.678764000	3.086142000
6	0.263263000	-1.835009000	-0.162680000
6	1.486886000	-1.426718000	0.486795000
6	2.679125000	-1.398937000	-0.261167000
6	2.712639000	-1.861690000	-1.598688000
6	1.553669000	-2.402536000	-2.143792000
1	1.596246000	-2.806243000	-3.149234000
6	0.331136000	-2.389611000	-1.481088000
6	1.456010000	-1.151831000	2.000553000
1	0.399767000	-1.063848000	2.262669000
6	2.130981000	0.141102000	2.508649000
1	3.202452000	0.008394000	2.675791000
1	1.688892000	0.414931000	3.473804000
1	1.994135000	0.980259000	1.823969000
6	1.999418000	-2.357163000	2.802205000
1	1.411620000	-3.261465000	2.626080000
1	1.955332000	-2.134683000	3.875491000
1	3.037996000	-2.580235000	2.546228000
6	3.970604000	-1.819734000	-2.457922000
1	4.710780000	-1.200142000	-1.943921000
6	3.701628000	-1.155407000	-3.822633000

1	3.118526000	-1.810700000	-4.481988000
1	4.650408000	-0.943676000	-4.330316000
1	3.138366000	-0.230127000	-3.680749000
6	4.581330000	-3.227424000	-2.612570000
1	4.820494000	-3.668333000	-1.639061000
1	5.502967000	-3.180680000	-3.204814000
1	3.888390000	-3.903677000	-3.128227000
6	-0.859597000	-3.045669000	-2.175506000
1	-1.743130000	-2.886059000	-1.553841000
6	-1.132357000	-2.423636000	-3.558570000
1	-1.190402000	-1.332524000	-3.494345000
1	-2.074355000	-2.805688000	-3.970567000
1	-0.338962000	-2.666721000	-4.274480000
6	-0.665523000	-4.569950000	-2.294891000
1	0.218533000	-4.813464000	-2.895288000
1	-1.536044000	-5.026164000	-2.781534000
1	-0.544527000	-5.038571000	-1.312797000
6	3.960957000	-0.866935000	0.306610000
6	4.945598000	-1.702178000	0.834172000
6	6.159479000	-1.212021000	1.307309000
6	6.469432000	0.146619000	1.265274000
6	7.789300000	0.689143000	1.758322000
1	8.204227000	-0.003951000	2.497193000
1	7.611727000	1.641923000	2.270235000
6	8.812746000	0.908633000	0.625683000
1	8.384757000	1.598868000	-0.113161000
1	8.982543000	-0.043289000	0.104413000
6	10.148291000	1.462979000	1.136085000
1	9.969027000	2.411682000	1.661654000
1	10.565133000	0.773427000	1.883887000
6	11.170388000	1.683234000	0.016436000
1	11.397353000	0.744517000	-0.503394000
1	12.112164000	2.082616000	0.409412000
1	10.793093000	2.392315000	-0.730389000
6	5.494819000	0.980681000	0.714962000
6	4.280253000	0.493592000	0.243152000
9	1.513881000	0.419531000	-2.244735000
9	7.052916000	-2.086356000	1.813364000
9	4.730003000	-3.034054000	0.899916000
9	5.733512000	2.305490000	0.637831000
9	3.390513000	1.368608000	-0.245964000
1	0.079950000	-4.097474000	0.956557000
6	-0.263342000	2.212061000	-1.962879000
6	-0.947296000	2.719529000	-3.025770000
6	0.702019000	3.152932000	-1.459606000
16	-0.473599000	4.364913000	-3.395370000
1	-1.689795000	2.254653000	-3.656679000
6	0.691131000	4.352662000	-2.109720000
1	1.394172000	2.928515000	-0.656267000
1	1.306101000	5.224206000	-1.924500000
6	-6.206531000	-0.479332000	3.103985000

1	-6.696254000	-0.344123000	2.136338000
1	-6.986407000	-0.654954000	3.851986000
1	-5.684233000	0.442589000	3.366159000
6	-4.657227000	-1.828818000	4.498924000
1	-5.473415000	-2.001319000	5.208717000
1	-3.948722000	-2.650710000	4.603038000
1	-4.147403000	-0.904985000	4.790310000
6	-6.050217000	-2.904444000	2.612224000
1	-5.517483000	-3.853432000	2.679737000
1	-6.954838000	-2.993907000	3.223267000
1	-6.359807000	-2.762788000	1.571723000

206a GS



```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           0.969596 (Hartree/Particle)
 Thermal correction to Energy=                    1.031023
 Thermal correction to Enthalpy=                  1.031968
 Thermal correction to Gibbs Free Energy=         0.873918
 Sum of electronic and zero-point Energies=          -3132.443425
 Sum of electronic and thermal Energies=             -3132.381997
 Sum of electronic and thermal Enthalpies=           -3132.381053
 Sum of electronic and thermal Free Energies=        -3132.539102
```

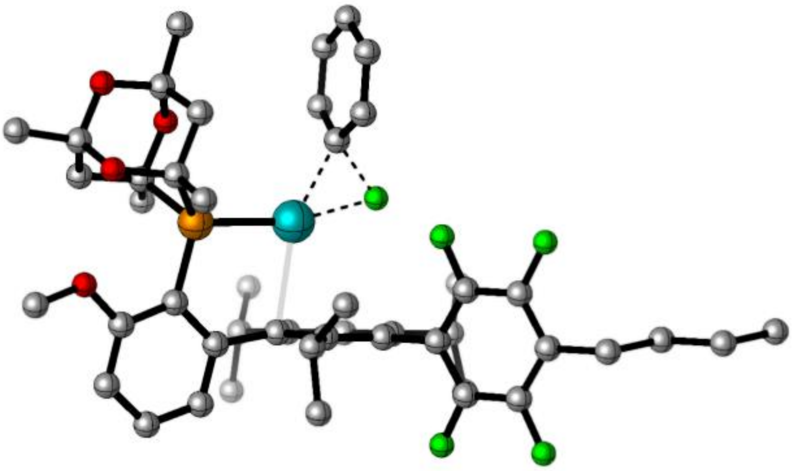
46	0.762978000	0.663548000	0.789850000
15	2.735411000	-0.096461000	-0.324935000
6	4.383017000	0.307177000	0.584016000
6	5.615072000	-0.163423000	-0.194973000
1	5.591398000	-1.238275000	-0.371322000
6	3.335074000	0.780422000	-1.932289000
6	2.491605000	-1.944746000	-0.513334000
6	3.341886000	-2.842122000	-1.217067000
6	3.148105000	-4.226618000	-1.172499000
1	3.831917000	-4.889739000	-1.688228000
6	2.071523000	-4.752263000	-0.467901000
1	1.921806000	-5.827796000	-0.430624000
6	1.174151000	-3.896470000	0.153426000

6	1.354507000	-2.502030000	0.126599000
8	4.342942000	-2.295088000	-1.951503000
6	5.031610000	-3.094509000	-2.902968000
6	0.202440000	-1.737315000	0.745649000
6	-0.940883000	-1.436872000	-0.077221000
6	-2.156940000	-1.086998000	0.548489000
6	-2.274115000	-1.096496000	1.954919000
6	-1.178309000	-1.497124000	2.720761000
1	-1.286152000	-1.520542000	3.799784000
6	0.056462000	-1.793315000	2.165993000
6	-0.810546000	-1.619666000	-1.599303000
1	0.257774000	-1.723820000	-1.795589000
6	-1.272770000	-0.448513000	-2.490725000
1	-2.352571000	-0.445421000	-2.654909000
1	-0.799262000	-0.544806000	-3.474967000
1	-0.988852000	0.519688000	-2.068919000
6	-1.457752000	-2.943096000	-2.060306000
1	-1.007912000	-3.802302000	-1.553542000
1	-1.309190000	-3.073270000	-3.139308000
1	-2.532316000	-2.966594000	-1.862951000
6	-3.545761000	-0.679310000	2.683490000
1	-4.230621000	-0.244589000	1.950744000
6	-3.256059000	0.416638000	3.729146000
1	-2.732848000	0.011491000	4.604240000
1	-4.196580000	0.854015000	4.085161000
1	-2.626776000	1.194728000	3.289931000
6	-4.256146000	-1.899903000	3.302068000
1	-4.511442000	-2.640512000	2.536302000
1	-5.181071000	-1.589835000	3.802453000
1	-3.622043000	-2.391762000	4.049784000
6	1.213281000	-2.144593000	3.098135000
1	2.124952000	-2.203072000	2.495522000
6	1.423642000	-1.047009000	4.161549000
1	1.436493000	-0.052646000	3.704722000
1	2.368113000	-1.207932000	4.694641000
1	0.621019000	-1.052398000	4.907745000
6	1.018166000	-3.517343000	3.769569000
1	0.097516000	-3.539563000	4.364283000
1	1.855723000	-3.733665000	4.443545000
1	0.962162000	-4.324939000	3.032439000
6	-3.367555000	-0.673768000	-0.233594000
6	-4.400894000	-1.568153000	-0.514016000
6	-5.568379000	-1.174152000	-1.161089000
6	-5.778649000	0.146140000	-1.556224000
6	-7.053930000	0.592600000	-2.229576000
1	-7.502962000	-0.262790000	-2.744585000
1	-6.810294000	1.341152000	-2.991934000
6	-8.074697000	1.192386000	-1.240538000
1	-7.612963000	2.045172000	-0.725526000
1	-8.306474000	0.447195000	-0.467523000
6	-9.369739000	1.643465000	-1.926297000

1	-9.129685000	2.383586000	-2.702691000
1	-9.820761000	0.787738000	-2.448576000
6	-10.386349000	2.239772000	-0.947318000
1	-10.669553000	1.511424000	-0.177700000
1	-11.301198000	2.551992000	-1.463460000
1	-9.975175000	3.118637000	-0.436098000
6	-4.752446000	1.045280000	-1.261671000
6	-3.583292000	0.655088000	-0.615588000
9	-0.882606000	1.216137000	1.778387000
9	-6.516527000	-2.102918000	-1.401027000
9	-4.282307000	-2.862438000	-0.147453000
9	-4.895011000	2.339741000	-1.610968000
9	-2.644568000	1.581023000	-0.385073000
1	0.297816000	-4.295592000	0.652965000
1	6.499962000	0.077023000	0.407403000
6	5.733749000	0.603600000	-1.520645000
6	3.458571000	2.265076000	-1.541357000
1	2.537900000	2.652348000	-1.103538000
6	4.632392000	2.456675000	-0.568018000
1	3.681576000	2.832186000	-2.453214000
8	5.816858000	1.989958000	-1.209423000
8	4.411187000	1.740973000	0.658987000
8	4.624267000	0.341124000	-2.380447000
6	4.878853000	3.902468000	-0.185937000
1	4.001673000	4.317995000	0.313298000
1	5.737596000	3.953032000	0.489524000
1	5.099627000	4.486443000	-1.084135000
6	2.385205000	0.551372000	-3.097661000
1	2.340730000	-0.510568000	-3.358635000
1	1.379243000	0.902264000	-2.852798000
1	2.747994000	1.104762000	-3.971178000
6	4.381258000	-0.193443000	2.018741000
1	3.510066000	0.183650000	2.558743000
1	4.371566000	-1.288154000	2.045915000
1	5.285769000	0.161227000	2.526130000
6	6.985096000	0.263711000	-2.309650000
1	7.021019000	-0.805077000	-2.535886000
1	6.986865000	0.830471000	-3.244579000
1	7.871331000	0.534749000	-1.729473000
1	5.699239000	-3.819303000	-2.419437000
1	4.329446000	-3.626767000	-3.555826000
1	5.620415000	-2.394808000	-3.496721000
6	1.090672000	2.636101000	0.941812000
6	1.897023000	3.195724000	1.933829000
6	1.944395000	4.581417000	2.115497000
6	1.198207000	5.428798000	1.294887000
6	0.384099000	4.873794000	0.305922000
6	0.318643000	3.487985000	0.143563000
1	2.504301000	2.564314000	2.574804000
1	2.575909000	4.995830000	2.899294000
1	1.241536000	6.506624000	1.432167000

1	-0.220915000	5.516774000	-0.330371000
1	-0.364820000	3.075457000	-0.593837000

206a TS



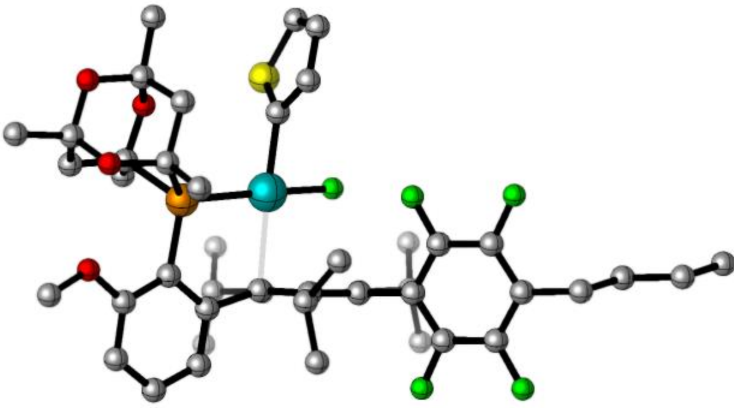
```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           0.967711 (Hartree/Particle)
 Thermal correction to Energy=                    1.028907
 Thermal correction to Enthalpy=                  1.029852
 Thermal correction to Gibbs Free Energy=         0.872100
 Sum of electronic and zero-point Energies=          -3132.410597
 Sum of electronic and thermal Energies=             -3132.349400
 Sum of electronic and thermal Enthalpies=           -3132.348456
 Sum of electronic and thermal Free Energies=        -3132.506208
```

46	0.758011000	0.641156000	0.715436000
15	2.751786000	-0.114378000	-0.312101000
6	4.368367000	0.327352000	0.636138000
6	5.639622000	-0.060076000	-0.124082000
1	5.671317000	-1.130373000	-0.326542000
6	3.358236000	0.801955000	-1.891260000
6	3.388024000	2.282951000	-1.458454000
1	3.593496000	2.889915000	-2.348548000
6	2.537274000	-1.968491000	-0.530165000
6	3.423920000	-2.821019000	-1.241756000
6	3.254988000	-4.209302000	-1.272004000
1	3.965420000	-4.836049000	-1.797457000
6	2.167413000	-4.784108000	-0.625701000
1	2.033423000	-5.862240000	-0.644556000
6	1.241462000	-3.973443000	0.015077000
6	1.394982000	-2.576133000	0.061723000
8	4.440835000	-2.219048000	-1.909651000
6	5.187501000	-2.957458000	-2.865477000
6	0.221419000	-1.866784000	0.710738000

6	-0.919450000	-1.530873000	-0.091599000
6	-2.105825000	-1.104104000	0.552984000
6	-2.185112000	-1.046069000	1.962200000
6	-1.081884000	-1.462252000	2.707655000
1	-1.157251000	-1.448834000	3.789551000
6	0.115225000	-1.873341000	2.128558000
6	-0.819690000	-1.732087000	-1.614309000
1	0.243468000	-1.862617000	-1.823707000
6	-1.262485000	-0.553023000	-2.504757000
1	-2.344271000	-0.518576000	-2.653131000
1	-0.806436000	-0.665362000	-3.495575000
1	-0.941978000	0.407035000	-2.089980000
6	-1.503633000	-3.041159000	-2.061392000
1	-1.066467000	-3.908650000	-1.557532000
1	-1.373029000	-3.178922000	-3.141861000
1	-2.575557000	-3.040329000	-1.849512000
6	-3.437240000	-0.586924000	2.704024000
1	-4.115477000	-0.131894000	1.976826000
6	-3.127415000	0.494451000	3.756933000
1	-2.551631000	0.091199000	4.598833000
1	-4.061933000	0.897048000	4.165782000
1	-2.551543000	1.312152000	3.314775000
6	-4.176939000	-1.789625000	3.325321000
1	-4.442764000	-2.528338000	2.561771000
1	-5.097608000	-1.459698000	3.821067000
1	-3.554124000	-2.291081000	4.076135000
6	1.254026000	-2.328156000	3.039474000
1	2.165861000	-2.380820000	2.436218000
6	1.516622000	-1.338916000	4.191783000
1	1.602123000	-0.311724000	3.825201000
1	2.445839000	-1.601019000	4.710927000
1	0.712649000	-1.359284000	4.936462000
6	0.993002000	-3.739119000	3.604400000
1	0.070151000	-3.759952000	4.196136000
1	1.817866000	-4.047416000	4.258212000
1	0.898411000	-4.483249000	2.807669000
6	-3.332040000	-0.707165000	-0.215445000
6	-4.367325000	-1.608294000	-0.465937000
6	-5.542386000	-1.228160000	-1.108620000
6	-5.760368000	0.083315000	-1.527899000
6	-7.042985000	0.513524000	-2.197979000
1	-7.495985000	-0.353774000	-2.688962000
1	-6.807626000	1.244461000	-2.979815000
6	-8.054726000	1.135187000	-1.213247000
1	-7.589185000	2.000158000	-0.722491000
1	-8.278504000	0.407904000	-0.421037000
6	-9.356415000	1.569289000	-1.897398000
1	-9.123952000	2.290760000	-2.693416000
1	-9.811582000	0.701146000	-2.394979000
6	-10.364293000	2.188474000	-0.923698000
1	-10.640635000	1.478567000	-0.134599000

1	-11.283686000	2.488444000	-1.438990000
1	-9.948808000	3.079220000	-0.437082000
6	-4.734040000	0.990669000	-1.259975000
6	-3.559101000	0.612472000	-0.619003000
9	-0.765411000	1.770375000	1.711519000
9	-6.490852000	-2.163080000	-1.319482000
9	-4.245035000	-2.894249000	-0.074815000
9	-4.882661000	2.278486000	-1.629681000
9	-2.620741000	1.547148000	-0.404487000
1	0.363096000	-4.413137000	0.475160000
6	4.529570000	2.512897000	-0.454349000
1	6.499585000	0.207659000	0.502733000
6	5.749928000	0.744977000	-1.428161000
1	2.436083000	2.603274000	-1.030200000
6	2.446375000	0.554203000	-3.082889000
1	2.471376000	-0.499746000	-3.377056000
1	1.416763000	0.833855000	-2.844127000
1	2.787700000	1.156357000	-3.932717000
6	4.359200000	-0.203662000	2.058911000
1	5.246270000	0.160861000	2.589966000
1	3.470592000	0.148334000	2.587089000
1	4.371981000	-1.298754000	2.066215000
8	5.751009000	2.126561000	-1.081487000
6	4.689071000	3.959404000	-0.031563000
1	5.534350000	4.039492000	0.657968000
1	4.886880000	4.581384000	-0.909421000
1	3.781860000	4.309906000	0.463957000
6	7.038028000	0.492382000	-2.190736000
1	7.893911000	0.791530000	-1.579588000
1	7.135384000	-0.566562000	-2.444632000
1	7.034857000	1.084048000	-3.110138000
8	4.680291000	0.447819000	-2.323936000
8	4.320970000	1.760445000	0.749672000
1	5.846534000	-3.693817000	-2.387460000
1	4.527344000	-3.469162000	-3.576396000
1	5.788384000	-2.218635000	-3.396212000
6	0.503216000	2.722779000	1.118359000
6	1.237542000	3.294399000	2.168374000
6	1.611674000	4.632959000	2.091188000
6	1.235023000	5.425899000	0.999873000
6	0.456862000	4.856934000	-0.013575000
6	0.062198000	3.521541000	0.050449000
1	1.511954000	2.695044000	3.030382000
1	2.199761000	5.062224000	2.899827000
1	1.525395000	6.471591000	0.951986000
1	0.130219000	5.463049000	-0.856303000
1	-0.592612000	3.101929000	-0.706011000

206b GS



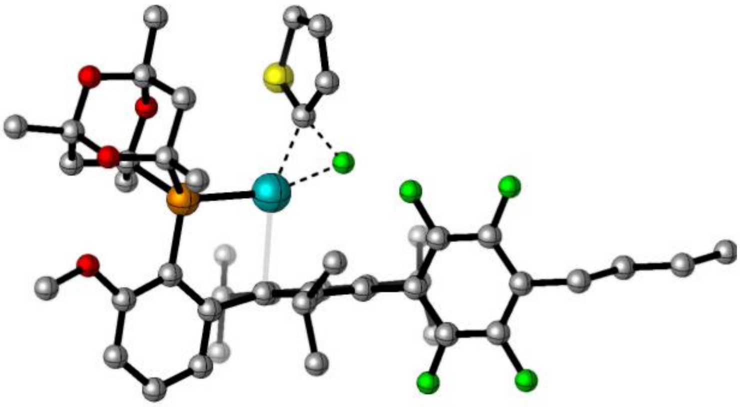
```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           0.936512 (Hartree/Particle)
 Thermal correction to Energy=                    0.997419
 Thermal correction to Enthalpy=                  0.998363
 Thermal correction to Gibbs Free Energy=         0.841627
 Sum of electronic and zero-point Energies=          -3453.238343
 Sum of electronic and thermal Energies=             -3453.177436
 Sum of electronic and thermal Enthalpies=           -3453.176492
 Sum of electronic and thermal Free Energies=        -3453.333228
```

46	0.726973000	0.658590000	0.704264000
15	2.729075000	-0.093406000	-0.372311000
6	4.309600000	0.417371000	0.597351000
6	5.598158000	-0.043942000	-0.091322000
1	5.619002000	-1.126550000	-0.217315000
6	3.386112000	0.715829000	-1.996839000
6	2.519511000	-1.947136000	-0.506166000
6	3.403020000	-2.848918000	-1.160711000
6	3.189899000	-4.230893000	-1.141849000
1	3.893246000	-4.898143000	-1.624994000
6	2.069949000	-4.748649000	-0.501556000
1	1.903251000	-5.822219000	-0.486410000
6	1.158288000	-3.888923000	0.093226000
6	1.357458000	-2.496782000	0.091261000
8	4.457561000	-2.305993000	-1.817794000
6	5.200817000	-3.101042000	-2.731176000
6	0.210609000	-1.724493000	0.712397000
6	-0.933323000	-1.412422000	-0.107581000
6	-2.154374000	-1.082303000	0.521009000
6	-2.271466000	-1.112680000	1.926402000
6	-1.174260000	-1.519189000	2.688907000
1	-1.285457000	-1.559607000	3.767066000
6	0.060552000	-1.808670000	2.133500000
6	-0.795386000	-1.561909000	-1.632484000

1	0.273346000	-1.674611000	-1.823503000
6	-1.236371000	-0.358427000	-2.490728000
1	-2.315403000	-0.333859000	-2.657345000
1	-0.761639000	-0.432586000	-3.476354000
1	-0.939509000	0.591176000	-2.035979000
6	-1.452652000	-2.865468000	-2.132671000
1	-1.015465000	-3.742131000	-1.644810000
1	-1.295237000	-2.968685000	-3.213269000
1	-2.529084000	-2.883858000	-1.946259000
6	-3.545524000	-0.712390000	2.659914000
1	-4.235816000	-0.279284000	1.931472000
6	-3.263047000	0.379069000	3.712152000
1	-2.728037000	-0.025678000	4.580114000
1	-4.206964000	0.800927000	4.077683000
1	-2.647662000	1.169822000	3.275930000
6	-4.243556000	-1.943603000	3.271412000
1	-4.492952000	-2.681171000	2.500721000
1	-5.170851000	-1.645089000	3.774353000
1	-3.604685000	-2.434767000	4.015457000
6	1.210166000	-2.195621000	3.061141000
1	2.127487000	-2.229931000	2.465015000
6	1.412465000	-1.148908000	4.175585000
1	1.429697000	-0.133333000	3.770345000
1	2.354153000	-1.334728000	4.705172000
1	0.606512000	-1.190696000	4.917062000
6	1.008193000	-3.596069000	3.672161000
1	0.080063000	-3.642566000	4.253651000
1	1.837592000	-3.838798000	4.347179000
1	0.962626000	-4.372548000	2.902054000
6	-3.367757000	-0.667953000	-0.256150000
6	-4.393507000	-1.567535000	-0.547632000
6	-5.565109000	-1.174559000	-1.187628000
6	-5.786920000	0.149402000	-1.563799000
6	-7.065710000	0.593877000	-2.231859000
1	-7.509252000	-0.259538000	-2.754800000
1	-6.827346000	1.351260000	-2.987185000
6	-8.090145000	1.177478000	-1.236985000
1	-7.634421000	2.029117000	-0.714850000
1	-8.316073000	0.423900000	-0.470398000
6	-9.388851000	1.624754000	-1.918327000
1	-9.154709000	2.373421000	-2.688285000
1	-9.833551000	0.770211000	-2.447911000
6	-10.409611000	2.204666000	-0.933818000
1	-10.686699000	1.467455000	-0.170436000
1	-11.327123000	2.514147000	-1.446874000
1	-10.005039000	3.082258000	-0.415221000
6	-4.768509000	1.053436000	-1.257272000
6	-3.594735000	0.664901000	-0.617920000
9	-0.867704000	1.190072000	1.771668000
9	-6.505102000	-2.108294000	-1.440344000
9	-4.262506000	-2.865785000	-0.199724000

9	-4.923003000	2.351082000	-1.588359000
9	-2.663679000	1.593299000	-0.374930000
1	0.259814000	-4.283257000	0.555815000
6	1.038670000	2.623918000	0.785653000
6	0.587673000	3.593400000	-0.076752000
6	0.720693000	4.925381000	0.427118000
1	0.158769000	3.373376000	-1.050912000
1	0.455517000	5.813614000	-0.139945000
1	6.440225000	0.254723000	0.545344000
6	5.762561000	0.664119000	-1.444180000
6	3.434158000	2.221521000	-1.690676000
1	2.477894000	2.602526000	-1.333774000
6	4.532745000	2.512314000	-0.656078000
1	3.700913000	2.741882000	-2.618788000
8	5.772804000	2.066935000	-1.201881000
8	4.269946000	1.850723000	0.590181000
8	4.713895000	0.306089000	-2.346794000
6	4.679995000	3.984972000	-0.329250000
1	3.750113000	4.368809000	0.096753000
1	5.489622000	4.113731000	0.394384000
1	4.922548000	4.543190000	-1.238321000
6	2.510930000	0.379055000	-3.194315000
1	2.516864000	-0.697777000	-3.389405000
1	1.481143000	0.706404000	-3.026142000
1	2.902385000	0.890961000	-4.080601000
6	4.248381000	0.003759000	2.057651000
1	3.347875000	0.403569000	2.528183000
1	4.255127000	-1.086864000	2.154904000
1	5.120911000	0.408486000	2.583046000
6	7.068499000	0.339755000	-2.146548000
1	7.159963000	-0.736282000	-2.316327000
1	7.099741000	0.860480000	-3.107367000
1	7.909389000	0.675960000	-1.533912000
1	5.826032000	-3.839427000	-2.212903000
1	4.539271000	-3.616697000	-3.437676000
1	5.835546000	-2.400458000	-3.274119000
16	1.548948000	3.357990000	2.275818000
6	1.228864000	4.963193000	1.697308000
1	1.467638000	5.830310000	2.300366000

206b TS



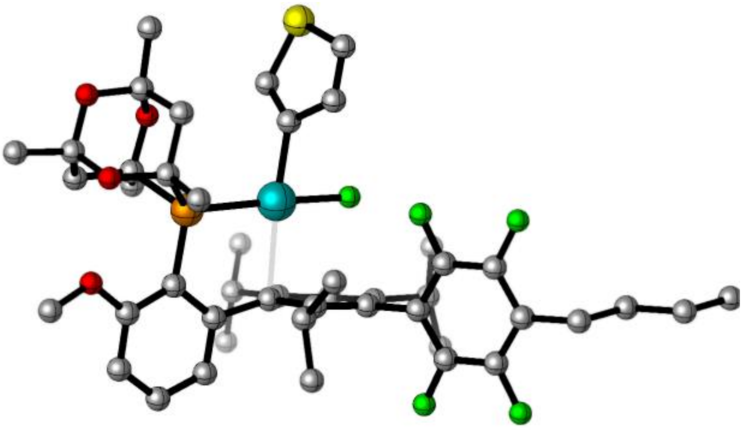
```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           0.933859 (Hartree/Particle)
 Thermal correction to Energy=                    0.994793
 Thermal correction to Enthalpy=                  0.995737
 Thermal correction to Gibbs Free Energy=         0.838160
 Sum of electronic and zero-point Energies=          -3453.197568
 Sum of electronic and thermal Energies=             -3453.136633
 Sum of electronic and thermal Enthalpies=           -3453.135689
 Sum of electronic and thermal Free Energies=        -3453.293266
```

46	0.720577000	0.622085000	0.653297000
15	2.745830000	-0.117194000	-0.340035000
6	4.346420000	0.417097000	0.584775000
6	5.628432000	0.017531000	-0.151125000
1	5.686274000	-1.061553000	-0.292914000
6	3.329315000	0.722563000	-1.967884000
6	3.319983000	2.225680000	-1.621949000
1	3.511894000	2.786144000	-2.545088000
6	2.555954000	-1.980522000	-0.470261000
6	3.456003000	-2.857329000	-1.133289000
6	3.289984000	-4.246054000	-1.109203000
1	4.008781000	-4.892077000	-1.598728000
6	2.194805000	-4.796870000	-0.454500000
1	2.063565000	-5.875251000	-0.431806000
6	1.259374000	-3.964161000	0.143200000
6	1.409984000	-2.566065000	0.134766000
8	4.481735000	-2.279140000	-1.808499000
6	5.243636000	-3.052983000	-2.723846000
6	0.235215000	-1.829206000	0.750407000
6	-0.905750000	-1.523669000	-0.068371000
6	-2.098021000	-1.083399000	0.557844000
6	-2.187144000	-0.990303000	1.964906000
6	-1.085629000	-1.381476000	2.728725000
1	-1.168973000	-1.340144000	3.809305000

6	0.117421000	-1.800598000	2.169913000
6	-0.800855000	-1.779574000	-1.582240000
1	0.264140000	-1.908314000	-1.784067000
6	-1.254994000	-0.641830000	-2.519900000
1	-2.336371000	-0.629712000	-2.674440000
1	-0.792966000	-0.787956000	-3.503436000
1	-0.951394000	0.339589000	-2.143935000
6	-1.474855000	-3.110405000	-1.978179000
1	-1.030359000	-3.955661000	-1.444062000
1	-1.346339000	-3.287039000	-3.053164000
1	-2.546230000	-3.108624000	-1.763071000
6	-3.447240000	-0.523217000	2.687841000
1	-4.127588000	-0.097409000	1.945177000
6	-3.155200000	0.590880000	3.711467000
1	-2.568187000	0.221377000	4.560910000
1	-4.096335000	0.984907000	4.113283000
1	-2.598276000	1.409658000	3.247699000
6	-4.174956000	-1.716223000	3.341822000
1	-4.428602000	-2.480465000	2.599727000
1	-5.101551000	-1.382362000	3.823546000
1	-3.549665000	-2.186812000	4.110254000
6	1.254860000	-2.217184000	3.100908000
1	2.168451000	-2.293185000	2.502799000
6	1.511841000	-1.180750000	4.212434000
1	1.601499000	-0.169367000	3.805339000
1	2.437428000	-1.422380000	4.747694000
1	0.703228000	-1.169670000	4.952167000
6	0.994984000	-3.604769000	3.721666000
1	0.071816000	-3.603383000	4.313222000
1	1.819654000	-3.884441000	4.388334000
1	0.902608000	-4.381277000	2.956032000
6	-3.318491000	-0.705285000	-0.228636000
6	-4.359089000	-1.607756000	-0.450842000
6	-5.531873000	-1.240598000	-1.104456000
6	-5.741446000	0.058261000	-1.565424000
6	-7.024394000	0.473817000	-2.243845000
1	-7.468188000	-0.400108000	-2.731745000
1	-6.792170000	1.202537000	-3.028361000
6	-8.045496000	1.090661000	-1.265672000
1	-7.590390000	1.963161000	-0.778293000
1	-8.263814000	0.365432000	-0.470068000
6	-9.349880000	1.507053000	-1.955651000
1	-9.123268000	2.227225000	-2.754506000
1	-9.793901000	0.631440000	-2.450190000
6	-10.367280000	2.119521000	-0.987616000
1	-10.637917000	1.410211000	-0.196005000
1	-11.288488000	2.406871000	-1.506826000
1	-9.963095000	3.017074000	-0.504024000
6	-4.708184000	0.966627000	-1.329682000
6	-3.534821000	0.601415000	-0.677906000
9	-0.803447000	1.836891000	1.622144000

9	-6.487578000	-2.174587000	-1.284180000
9	-4.243912000	-2.881697000	-0.019852000
9	-4.847545000	2.242117000	-1.742286000
9	-2.586450000	1.533955000	-0.501916000
1	0.378085000	-4.387650000	0.612844000
6	0.455538000	2.684602000	0.974091000
6	0.097130000	3.592863000	-0.015352000
6	0.633480000	4.890676000	0.210991000
1	-0.561194000	3.332593000	-0.836473000
1	0.513949000	5.713694000	-0.488782000
6	4.453869000	2.540262000	-0.632039000
1	6.480324000	0.341250000	0.460089000
6	5.720731000	0.749901000	-1.499317000
1	2.358704000	2.546064000	-1.211929000
6	2.426581000	0.380123000	-3.142574000
1	2.474812000	-0.689841000	-3.368309000
1	1.390734000	0.652630000	-2.923930000
1	2.758104000	0.933766000	-4.028381000
6	4.340671000	-0.025925000	2.037543000
1	5.219859000	0.384821000	2.547283000
1	3.445659000	0.348527000	2.539314000
1	4.369326000	-1.118170000	2.114249000
8	5.686114000	2.148774000	-1.234890000
6	4.575257000	4.012141000	-0.291734000
1	5.406449000	4.151710000	0.405263000
1	4.774026000	4.586198000	-1.201555000
1	3.652004000	4.370262000	0.168445000
6	7.015692000	0.485348000	-2.245983000
1	7.863072000	0.840987000	-1.653567000
1	7.139585000	-0.583942000	-2.437406000
1	6.999012000	1.021948000	-3.198402000
8	4.659970000	0.372996000	-2.376137000
8	4.262747000	1.851997000	0.612192000
16	1.337609000	3.490308000	2.262532000
6	1.317094000	5.011133000	1.393291000
1	1.868269000	5.861065000	1.773764000
1	5.897744000	-3.767583000	-2.207674000
1	4.594386000	-3.594373000	-3.422624000
1	5.850034000	-2.334477000	-3.275768000

206c GS



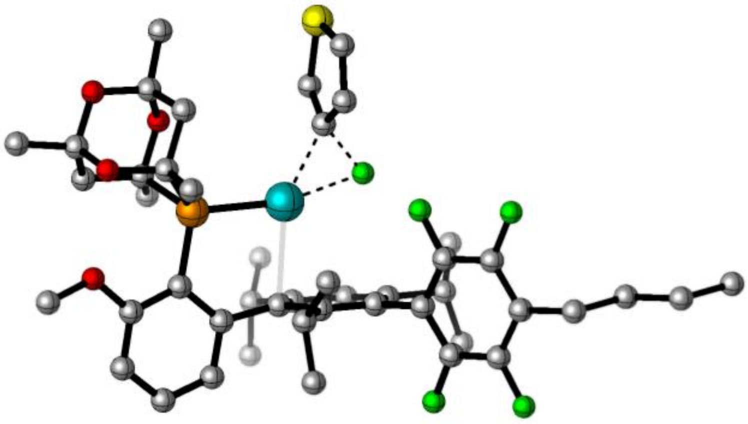
```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           0.936225 (Hartree/Particle)
 Thermal correction to Energy=                    0.997250
 Thermal correction to Enthalpy=                  0.998194
 Thermal correction to Gibbs Free Energy=         0.841013
 Sum of electronic and zero-point Energies=          -3453.236467
 Sum of electronic and thermal Energies=             -3453.175442
 Sum of electronic and thermal Enthalpies=           -3453.174498
 Sum of electronic and thermal Free Energies=        -3453.331679
```

46	0.773825000	0.701283000	0.717424000
15	2.755510000	-0.153869000	-0.307204000
6	4.405159000	0.267589000	0.591200000
6	5.626807000	-0.287441000	-0.148387000
1	5.572450000	-1.370129000	-0.255978000
6	3.385062000	0.613785000	-1.958574000
6	2.473073000	-2.004382000	-0.398271000
6	3.304719000	-2.960153000	-1.046273000
6	3.072196000	-4.334691000	-0.931048000
1	3.742583000	-5.042040000	-1.403930000
6	1.974594000	-4.793801000	-0.212797000
1	1.794988000	-5.861507000	-0.121552000
6	1.094856000	-3.882826000	0.352786000
6	1.315023000	-2.497350000	0.256174000
8	4.326297000	-2.482097000	-1.799809000
6	4.986726000	-3.346590000	-2.714020000
6	0.179643000	-1.670087000	0.823408000
6	-0.962553000	-1.413525000	-0.018157000
6	-2.177139000	-1.021857000	0.583456000
6	-2.291644000	-0.934528000	1.988245000
6	-1.197927000	-1.288412000	2.778888000
1	-1.305233000	-1.238810000	3.856985000
6	0.033113000	-1.634137000	2.244974000
6	-0.825108000	-1.671467000	-1.528434000

1	0.243028000	-1.802170000	-1.710336000
6	-1.257390000	-0.529105000	-2.470694000
1	-2.336970000	-0.504344000	-2.634065000
1	-0.788418000	-0.681648000	-3.449963000
1	-0.946007000	0.448257000	-2.091238000
6	-1.491451000	-3.001257000	-1.940123000
1	-1.065868000	-3.845964000	-1.389998000
1	-1.330114000	-3.181025000	-3.010089000
1	-2.569032000	-2.996300000	-1.759263000
6	-3.558824000	-0.459188000	2.688495000
1	-4.244391000	-0.076075000	1.928240000
6	-3.258257000	0.710385000	3.647954000
1	-2.732270000	0.369369000	4.548341000
1	-4.194456000	1.178789000	3.974497000
1	-2.627411000	1.449766000	3.148324000
6	-4.272294000	-1.626674000	3.398786000
1	-4.528130000	-2.423812000	2.692275000
1	-5.196798000	-1.276655000	3.872847000
1	-3.639831000	-2.060320000	4.182924000
6	1.181332000	-1.956274000	3.197777000
1	2.092161000	-2.065469000	2.600917000
6	1.413444000	-0.811935000	4.205312000
1	1.461601000	0.157426000	3.700294000
1	2.347871000	-0.973152000	4.755654000
1	0.604562000	-0.756016000	4.942561000
6	0.955711000	-3.288011000	3.939295000
1	0.037734000	-3.256617000	4.537767000
1	1.791017000	-3.490107000	4.620417000
1	0.876060000	-4.130435000	3.244809000
6	-3.393871000	-0.668408000	-0.218965000
6	-4.420270000	-1.589462000	-0.432095000
6	-5.599557000	-1.248525000	-1.087577000
6	-5.829740000	0.042299000	-1.561052000
6	-7.120283000	0.432023000	-2.240467000
1	-7.557333000	-0.455088000	-2.710275000
1	-6.899998000	1.149000000	-3.039230000
6	-8.142693000	1.055801000	-1.268056000
1	-7.694406000	1.942001000	-0.799500000
1	-8.348541000	0.343164000	-0.457865000
6	-9.455542000	1.445256000	-1.957685000
1	-9.241534000	2.152742000	-2.771249000
1	-9.893106000	0.555905000	-2.433117000
6	-10.473678000	2.064894000	-0.994998000
1	-10.732672000	1.367360000	-0.189145000
1	-11.400698000	2.333619000	-1.513873000
1	-10.075849000	2.974999000	-0.529921000
6	-4.810158000	0.968436000	-1.335979000
6	-3.629268000	0.631162000	-0.681113000
9	-0.891246000	1.336328000	1.611454000
9	-6.540218000	-2.200003000	-1.257104000
9	-4.283929000	-2.856589000	0.013580000

9	-4.971023000	2.237668000	-1.761183000
9	-2.701556000	1.581887000	-0.515217000
1	0.202437000	-4.231661000	0.861544000
6	1.104902000	2.675316000	0.718226000
6	1.951087000	3.375896000	1.521541000
6	0.200607000	3.533805000	0.003947000
16	1.685398000	5.103032000	1.396953000
1	2.739265000	3.017008000	2.166517000
6	0.404423000	4.860263000	0.250667000
1	-0.587171000	3.166952000	-0.644556000
1	-0.132726000	5.710341000	-0.150321000
1	6.515812000	-0.035185000	0.443048000
6	5.774592000	0.389666000	-1.519312000
6	3.551669000	2.116199000	-1.661677000
1	2.641342000	2.559048000	-1.256013000
6	4.726262000	2.332457000	-0.694629000
1	3.797752000	2.615109000	-2.606886000
8	5.898816000	1.788965000	-1.294790000
8	4.474037000	1.702581000	0.574078000
8	4.662040000	0.108487000	-2.369282000
6	5.021588000	3.790036000	-0.403864000
1	4.153446000	4.272130000	0.048653000
1	5.871654000	3.853695000	0.281381000
1	5.278271000	4.303841000	-1.334750000
6	2.430437000	0.339533000	-3.110064000
1	2.357702000	-0.734956000	-3.305434000
1	1.434268000	0.731015000	-2.886615000
1	2.806944000	0.828645000	-4.015473000
6	4.380651000	-0.134589000	2.055873000
1	3.522563000	0.312866000	2.562316000
1	4.329093000	-1.223427000	2.158855000
1	5.296488000	0.219803000	2.542759000
6	7.019045000	-0.037060000	-2.276612000
1	7.026751000	-1.119282000	-2.429614000
1	7.039592000	0.464864000	-3.247662000
1	7.910177000	0.248683000	-1.711212000
1	5.635429000	-4.066602000	-2.198648000
1	4.265854000	-3.888559000	-3.337691000
1	5.592887000	-2.694036000	-3.343016000

206c TS



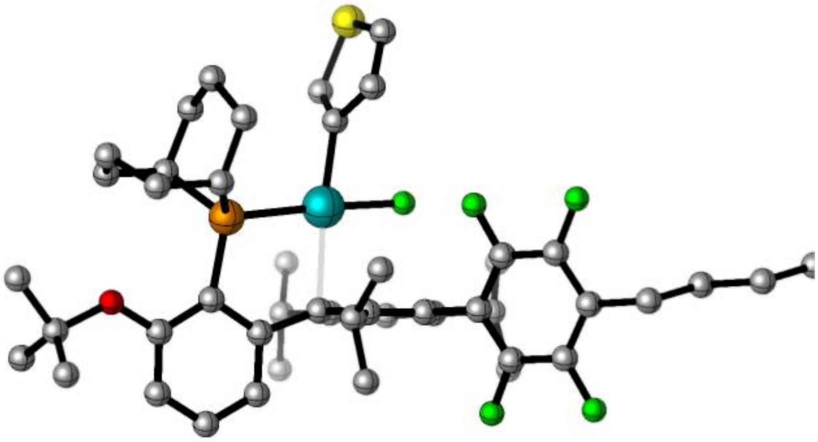
```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           0.933814 (Hartree/Particle)
 Thermal correction to Energy=                    0.994924
 Thermal correction to Enthalpy=                  0.995868
 Thermal correction to Gibbs Free Energy=         0.837119
 Sum of electronic and zero-point Energies=          -3453.194224
 Sum of electronic and thermal Energies=             -3453.133114
 Sum of electronic and thermal Enthalpies=           -3453.132170
 Sum of electronic and thermal Free Energies=        -3453.290918
```

46	0.792914000	0.653351000	0.709996000
15	2.773615000	-0.155900000	-0.293163000
6	4.413397000	0.222433000	0.644832000
6	5.661821000	-0.204955000	-0.133546000
1	5.653169000	-1.274013000	-0.344567000
6	3.398483000	0.752904000	-1.868989000
6	3.484957000	2.228283000	-1.419074000
1	3.697734000	2.838438000	-2.305243000
6	2.513448000	-2.005493000	-0.494801000
6	3.371147000	-2.883861000	-1.209699000
6	3.187928000	-4.270579000	-1.200004000
1	3.877846000	-4.918204000	-1.727551000
6	2.111084000	-4.816688000	-0.511710000
1	1.966786000	-5.893570000	-0.497842000
6	1.205646000	-3.979751000	0.125021000
6	1.372953000	-2.583263000	0.129797000
8	4.372351000	-2.306857000	-1.922659000
6	5.090482000	-3.077717000	-2.874600000
6	0.207918000	-1.842182000	0.759552000
6	-0.938359000	-1.542996000	-0.051195000
6	-2.119886000	-1.087273000	0.579576000
6	-2.192588000	-0.965499000	1.986341000
6	-1.086928000	-1.350828000	2.743208000
1	-1.157065000	-1.291699000	3.823947000

6	0.107102000	-1.789902000	2.176448000
6	-0.842059000	-1.796763000	-1.566141000
1	0.218257000	-1.953766000	-1.770752000
6	-1.259497000	-0.635423000	-2.491501000
1	-2.340967000	-0.575860000	-2.634070000
1	-0.813277000	-0.791331000	-3.480951000
1	-0.909233000	0.327703000	-2.108966000
6	-1.548542000	-3.105885000	-1.976051000
1	-1.133073000	-3.964603000	-1.439718000
1	-1.411187000	-3.281777000	-3.050152000
1	-2.622055000	-3.077858000	-1.775133000
6	-3.442016000	-0.475555000	2.713366000
1	-4.123673000	-0.051937000	1.970506000
6	-3.129268000	0.649135000	3.719081000
1	-2.545231000	0.282785000	4.571969000
1	-4.062290000	1.064568000	4.118383000
1	-2.560452000	1.451249000	3.240576000
6	-4.177890000	-1.651148000	3.388999000
1	-4.442523000	-2.424279000	2.659943000
1	-5.098653000	-1.301864000	3.871220000
1	-3.552097000	-2.116275000	4.160342000
6	1.245417000	-2.214174000	3.101938000
1	2.154681000	-2.296341000	2.498712000
6	1.516044000	-1.180078000	4.212181000
1	1.607120000	-0.169434000	3.802477000
1	2.444013000	-1.426454000	4.741195000
1	0.712729000	-1.164793000	4.957647000
6	0.977898000	-3.599962000	3.723162000
1	0.057436000	-3.591457000	4.318923000
1	1.803542000	-3.887565000	4.385426000
1	0.875103000	-4.374547000	2.956847000
6	-3.351081000	-0.723752000	-0.197753000
6	-4.387302000	-1.634755000	-0.405441000
6	-5.567491000	-1.280391000	-1.053315000
6	-5.790376000	0.013460000	-1.521847000
6	-7.079706000	0.414149000	-2.197249000
1	-7.522781000	-0.468607000	-2.669576000
1	-6.855685000	1.132153000	-2.994066000
6	-8.097457000	1.041274000	-1.222272000
1	-7.643492000	1.923234000	-0.751113000
1	-8.307640000	0.327400000	-0.414307000
6	-9.407769000	1.441068000	-1.910871000
1	-9.188979000	2.149144000	-2.722653000
1	-9.850886000	0.555736000	-2.388626000
6	-10.422134000	2.064865000	-0.946952000
1	-10.685654000	1.367174000	-0.142718000
1	-11.347318000	2.340443000	-1.465484000
1	-10.018794000	2.971508000	-0.479851000
6	-4.763254000	0.931449000	-1.297092000
6	-3.583341000	0.578471000	-0.650806000
9	-0.762389000	1.842428000	1.618660000

9	-6.516857000	-2.223096000	-1.220633000
9	-4.260965000	-2.904361000	0.033462000
9	-4.915469000	2.204308000	-1.714390000
9	-2.644742000	1.522475000	-0.477006000
1	0.331106000	-4.397843000	0.611882000
6	0.439538000	2.766835000	0.968343000
6	-0.054380000	3.512783000	-0.160223000
6	0.385015000	4.801567000	-0.166992000
1	-0.712687000	3.090857000	-0.909866000
1	0.189779000	5.569336000	-0.904527000
6	4.646269000	2.408342000	-0.427353000
1	6.537330000	0.026145000	0.486238000
6	5.789305000	0.605678000	-1.432147000
1	2.548834000	2.571502000	-0.974401000
6	2.464162000	0.553942000	-3.052433000
1	2.443813000	-0.496864000	-3.357964000
1	1.449570000	0.871828000	-2.797468000
1	2.819279000	1.151635000	-3.899822000
6	4.406609000	-0.323370000	2.062124000
1	5.315722000	0.001623000	2.581454000
1	3.541746000	0.054381000	2.611272000
1	4.379712000	-1.418134000	2.056788000
8	5.844801000	1.983239000	-1.073146000
6	4.868779000	3.842863000	0.007827000
1	5.738363000	3.884281000	0.669906000
1	5.057453000	4.472478000	-0.866469000
1	3.991107000	4.216149000	0.538357000
6	7.059778000	0.311922000	-2.209370000
1	7.932447000	0.568819000	-1.602760000
1	7.111784000	-0.746795000	-2.477283000
1	7.072078000	0.914668000	-3.121476000
8	4.701557000	0.356684000	-2.320115000
8	4.422805000	1.655019000	0.773052000
1	5.754640000	-3.806497000	-2.391951000
1	4.409573000	-3.603164000	-3.555306000
1	5.684975000	-2.358869000	-3.439164000
16	1.361408000	5.165286000	1.226352000
6	1.183655000	3.531744000	1.833006000
1	1.633755000	3.252935000	2.773618000

208c GS



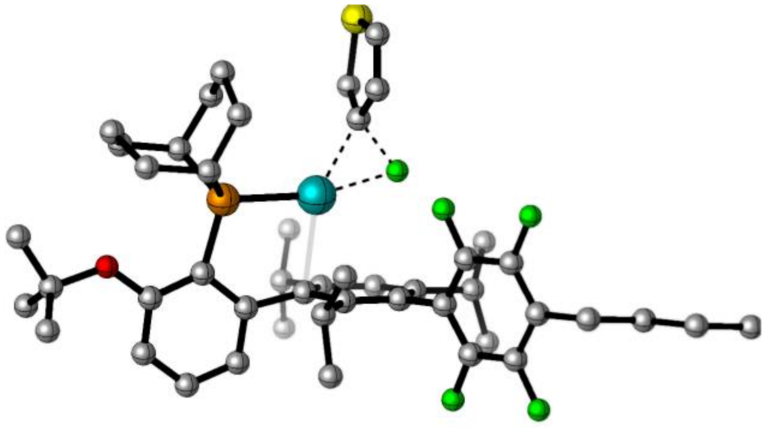
```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           0.977053 (Hartree/Particle)
 Thermal correction to Energy=                    1.037057
 Thermal correction to Enthalpy=                  1.038001
 Thermal correction to Gibbs Free Energy=         0.879421
 Sum of electronic and zero-point Energies=          -3268.032054
 Sum of electronic and thermal Energies=             -3267.972050
 Sum of electronic and thermal Enthalpies=           -3267.971105
 Sum of electronic and thermal Free Energies=        -3268.129686
```

46	0.672388000	1.269036000	0.589318000
15	2.777456000	0.537815000	-0.393583000
6	4.310552000	1.579659000	-0.056690000
6	3.888453000	3.042374000	-0.354413000
1	3.139802000	3.341545000	0.374712000
6	5.573107000	1.175871000	-0.841483000
1	5.915611000	0.204236000	-0.487378000
6	2.840100000	0.804433000	-2.252769000
6	2.467596000	2.293908000	-2.474169000
1	2.489723000	2.482222000	-3.557242000
6	2.948740000	-1.295578000	0.074058000
6	4.020514000	-2.225230000	-0.156541000
6	3.944794000	-3.526266000	0.363038000
1	4.762345000	-4.210835000	0.225613000
6	2.829058000	-3.975972000	1.050838000
1	2.802179000	-4.994129000	1.429485000
6	1.762013000	-3.119877000	1.239017000
6	1.815274000	-1.796498000	0.772178000
8	5.107365000	-1.826415000	-0.884477000
6	6.235203000	-2.702208000	-1.265043000
6	0.545749000	-1.049868000	1.121570000
6	-0.602481000	-1.205062000	0.268466000

6	-1.883659000	-0.942332000	0.796188000
6	-2.044323000	-0.593864000	2.156316000
6	-0.918977000	-0.540794000	2.983158000
1	-1.058862000	-0.284432000	4.028012000
6	0.367884000	-0.730839000	2.507456000
6	-0.367927000	-1.737735000	-1.154882000
1	0.715862000	-1.740627000	-1.289895000
6	-0.916052000	-0.877815000	-2.312746000
1	-1.980146000	-1.045726000	-2.494017000
1	-0.387770000	-1.146886000	-3.235751000
1	-0.764684000	0.189423000	-2.128974000
6	-0.809984000	-3.208574000	-1.298361000
1	-0.285352000	-3.851268000	-0.584429000
1	-0.577955000	-3.568557000	-2.308192000
1	-1.882665000	-3.336545000	-1.135066000
6	-3.399520000	-0.259559000	2.767470000
1	-4.129365000	-0.188628000	1.956600000
6	-3.376724000	1.114651000	3.466911000
1	-2.815950000	1.079992000	4.409376000
1	-4.399001000	1.430524000	3.707238000
1	-2.901141000	1.855204000	2.819326000
6	-3.873919000	-1.382805000	3.711108000
1	-3.945530000	-2.340306000	3.183990000
1	-4.861043000	-1.142566000	4.123451000
1	-3.183605000	-1.511358000	4.553643000
6	1.548402000	-0.596409000	3.468807000
1	2.469148000	-0.734845000	2.892759000
6	1.607792000	0.810214000	4.097012000
1	1.599591000	1.583756000	3.323031000
1	2.520060000	0.919337000	4.695992000
1	0.751554000	0.995748000	4.755526000
6	1.522494000	-1.680775000	4.561955000
1	0.616506000	-1.607750000	5.174971000
1	2.385130000	-1.568669000	5.229590000
1	1.557502000	-2.687135000	4.132084000
6	-3.118031000	-0.986519000	-0.053447000
6	-3.965145000	-2.095322000	-0.060242000
6	-5.157933000	-2.113936000	-0.776720000
6	-5.581645000	-1.016458000	-1.524741000
6	-6.884515000	-1.015485000	-2.287531000
1	-7.163210000	-2.049368000	-2.515130000
1	-6.735321000	-0.500687000	-3.243662000
6	-8.033013000	-0.329867000	-1.519458000
1	-7.742404000	0.703754000	-1.289966000
1	-8.174751000	-0.837201000	-0.555445000
6	-9.351246000	-0.333181000	-2.302671000
1	-9.198773000	0.167512000	-3.269312000
1	-9.631501000	-1.370117000	-2.536554000
6	-10.496570000	0.349334000	-1.548202000
1	-10.695775000	-0.150840000	-0.592543000
1	-11.423819000	0.333394000	-2.132010000

1	-10.257931000	1.397287000	-1.329760000
6	-4.742418000	0.098533000	-1.507337000
6	-3.548826000	0.122301000	-0.791224000
9	-1.117181000	1.748226000	1.334707000
9	-5.916258000	-3.228799000	-0.736191000
9	-3.631394000	-3.194594000	0.648805000
9	-5.096635000	1.195693000	-2.206719000
9	-2.798812000	1.229249000	-0.841837000
1	0.870828000	-3.453358000	1.759623000
6	0.598505000	3.263072000	0.303972000
6	1.061363000	4.208357000	1.170371000
6	-0.224201000	3.843049000	-0.719290000
16	0.559807000	5.824022000	0.718592000
1	1.660633000	4.086857000	2.063417000
6	-0.323257000	5.202847000	-0.639449000
1	-0.741121000	3.262751000	-1.476703000
1	-0.866198000	5.877732000	-1.288953000
6	7.113977000	-1.807089000	-2.149062000
1	7.459834000	-0.926359000	-1.603556000
1	7.993112000	-2.372754000	-2.473536000
1	6.571478000	-1.482154000	-3.039760000
6	5.773908000	-3.887393000	-2.133319000
1	6.657121000	-4.377115000	-2.557079000
1	5.199829000	-4.647407000	-1.604250000
1	5.162918000	-3.519576000	-2.964077000
6	7.070121000	-3.102380000	-0.035109000
1	6.568762000	-3.783684000	0.652564000
1	7.990404000	-3.592062000	-0.371615000
1	7.351791000	-2.205451000	0.525971000
6	3.347389000	3.364333000	-1.774241000
1	2.742663000	4.273899000	-1.689243000
1	4.181994000	3.629364000	-2.429433000
1	4.769271000	3.674521000	-0.172183000
1	6.358254000	1.901868000	-0.582644000
6	4.179718000	0.402200000	-2.901430000
1	4.320206000	-0.674576000	-2.778641000
1	4.092163000	0.587784000	-3.982330000
6	5.419687000	1.152098000	-2.376179000
1	6.315873000	0.698746000	-2.811892000
1	5.409787000	2.175508000	-2.757174000
1	1.431975000	2.432086000	-2.160569000
1	2.044026000	0.196033000	-2.698298000
1	4.528770000	1.508724000	1.016002000

208c TS



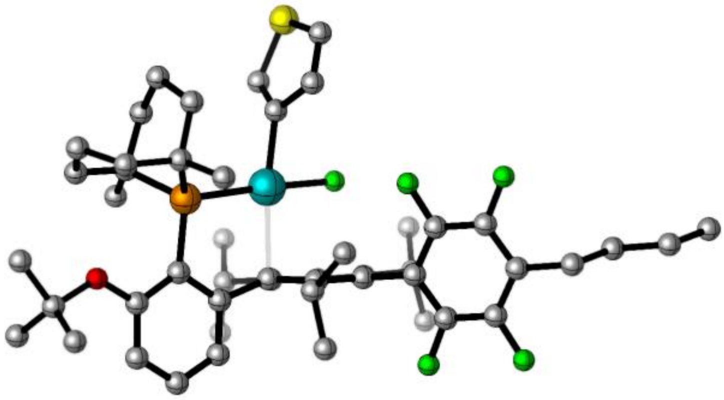
```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           0.975248 (Hartree/Particle)
 Thermal correction to Energy=                    1.034911
 Thermal correction to Enthalpy=                  1.035855
 Thermal correction to Gibbs Free Energy=         0.879830
 Sum of electronic and zero-point Energies=          -3267.995631
 Sum of electronic and thermal Energies=             -3267.935968
 Sum of electronic and thermal Enthalpies=           -3267.935024
 Sum of electronic and thermal Free Energies=        -3268.091049
```

46	0.689628000	1.185310000	0.505157000
15	2.772672000	0.451938000	-0.415325000
6	4.244319000	1.544518000	0.015660000
6	3.722158000	2.984991000	-0.242836000
1	2.889537000	3.175441000	0.436220000
6	5.556701000	1.232062000	-0.727395000
1	5.929402000	0.267710000	-0.379042000
6	2.910647000	0.761071000	-2.265820000
6	2.464389000	2.237528000	-2.448885000
1	2.498692000	2.468967000	-3.523527000
6	2.942651000	-1.377747000	0.064200000
6	4.031209000	-2.283693000	-0.161397000
6	3.969996000	-3.596588000	0.330081000
1	4.794380000	-4.271353000	0.182907000
6	2.858065000	-4.066890000	1.010711000
1	2.842224000	-5.090698000	1.374671000
6	1.781359000	-3.225364000	1.216550000
6	1.810546000	-1.897910000	0.759910000
8	5.122553000	-1.839729000	-0.858393000
6	6.286305000	-2.673961000	-1.215858000
6	0.535991000	-1.164509000	1.128439000
6	-0.623210000	-1.296527000	0.294867000
6	-1.879022000	-0.888722000	0.803997000
6	-2.007994000	-0.417658000	2.131509000

6	-0.869222000	-0.382990000	2.939374000
1	-0.973712000	-0.046300000	3.965581000
6	0.396427000	-0.738353000	2.482341000
6	-0.435584000	-1.923897000	-1.096801000
1	0.644934000	-2.001828000	-1.236301000
6	-0.936739000	-1.095018000	-2.297735000
1	-2.012056000	-1.197195000	-2.461822000
1	-0.438404000	-1.449286000	-3.208601000
1	-0.708356000	-0.032439000	-2.173716000
6	-0.963412000	-3.371948000	-1.162297000
1	-0.476149000	-4.004638000	-0.413449000
1	-0.752534000	-3.798954000	-2.150625000
1	-2.041444000	-3.432276000	-0.995415000
6	-3.345411000	0.007364000	2.731552000
1	-4.063090000	0.121475000	1.913885000
6	-3.270219000	1.370644000	3.445090000
1	-2.672215000	1.320309000	4.363174000
1	-4.276757000	1.697779000	3.732179000
1	-2.823242000	2.125633000	2.793030000
6	-3.891176000	-1.089919000	3.669217000
1	-3.998228000	-2.043543000	3.142199000
1	-4.872051000	-0.803405000	4.067173000
1	-3.217738000	-1.248872000	4.520351000
6	1.580747000	-0.667161000	3.447043000
1	2.485444000	-0.933109000	2.891954000
6	1.791696000	0.755983000	3.999033000
1	1.919009000	1.473340000	3.181504000
1	2.685354000	0.788395000	4.634289000
1	0.940639000	1.088701000	4.604770000
6	1.433300000	-1.684459000	4.594183000
1	0.543093000	-1.477800000	5.199745000
1	2.304944000	-1.641581000	5.258430000
1	1.348652000	-2.707773000	4.213194000
6	-3.119855000	-0.918577000	-0.038102000
6	-4.018057000	-1.986440000	-0.002110000
6	-5.202825000	-1.979811000	-0.730773000
6	-5.571924000	-0.899311000	-1.531217000
6	-6.870678000	-0.891512000	-2.301318000
1	-7.035408000	-1.887267000	-2.729156000
1	-6.782801000	-0.189718000	-3.136633000
6	-8.085817000	-0.508905000	-1.431904000
1	-7.915018000	0.482549000	-0.991008000
1	-8.162676000	-1.215421000	-0.594841000
6	-9.399709000	-0.502751000	-2.222484000
1	-9.314277000	0.201510000	-3.062052000
1	-9.557547000	-1.494300000	-2.670092000
6	-10.611990000	-0.130633000	-1.362902000
1	-10.740722000	-0.836488000	-0.533294000
1	-11.535769000	-0.136905000	-1.952321000
1	-10.498972000	0.871038000	-0.930707000
6	-4.684763000	0.177565000	-1.554102000

6	-3.497068000	0.172096000	-0.827651000
9	-1.047821000	2.304283000	1.143987000
9	-6.017649000	-3.052235000	-0.652247000
9	-3.743972000	-3.067016000	0.758303000
9	-4.974642000	1.261072000	-2.301719000
9	-2.692438000	1.243038000	-0.916033000
1	0.900061000	-3.577004000	1.741962000
6	0.094059000	3.281023000	0.469809000
6	0.672637000	4.212895000	1.301083000
6	-0.399310000	3.860274000	-0.753283000
16	0.731024000	5.790252000	0.538020000
1	1.050363000	4.085017000	2.304741000
6	-0.103935000	5.184617000	-0.865490000
1	-0.950398000	3.294750000	-1.495639000
1	-0.325457000	5.849950000	-1.690199000
6	7.176593000	-1.734687000	-2.040945000
1	7.483291000	-0.863574000	-1.457789000
1	8.079306000	-2.272046000	-2.348505000
1	6.660992000	-1.394409000	-2.941737000
6	5.888440000	-3.846324000	-2.131385000
1	6.798277000	-4.314316000	-2.522351000
1	5.300579000	-4.625847000	-1.647407000
1	5.312172000	-3.468880000	-2.982404000
6	7.084593000	-3.086265000	0.034516000
1	6.578241000	-3.802016000	0.682223000
1	8.031938000	-3.538207000	-0.278928000
1	7.316166000	-2.198057000	0.631311000
6	3.271783000	3.321316000	-1.688569000
1	2.645885000	4.218385000	-1.634544000
1	4.142493000	3.611461000	-2.283449000
1	4.522383000	3.684276000	0.039195000
1	6.297436000	1.985574000	-0.419905000
6	4.292695000	0.449214000	-2.871038000
1	4.475724000	-0.624050000	-2.778624000
1	4.244764000	0.669564000	-3.948212000
6	5.476344000	1.232030000	-2.268152000
1	6.409137000	0.817917000	-2.665964000
1	5.450529000	2.261641000	-2.631457000
1	1.416082000	2.309195000	-2.148666000
1	2.163811000	0.128864000	-2.761266000
1	4.423623000	1.448356000	1.093492000

209c GS



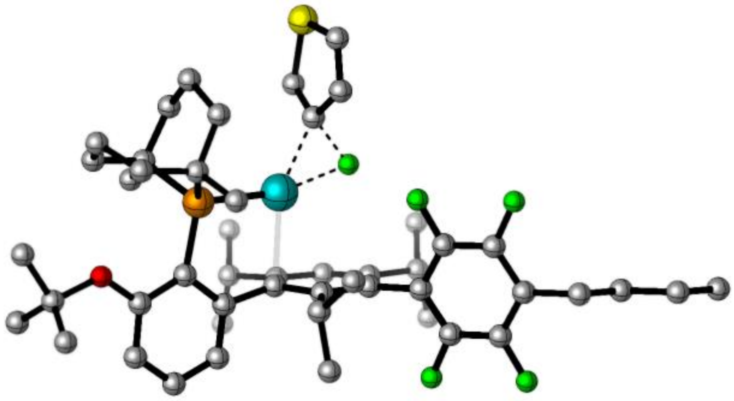
```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           1.033339 (Hartree/Particle)
 Thermal correction to Energy=                    1.096024
 Thermal correction to Enthalpy=                  1.096968
 Thermal correction to Gibbs Free Energy=         0.934319
 Sum of electronic and zero-point Energies=          -3346.600801
 Sum of electronic and thermal Energies=             -3346.538115
 Sum of electronic and thermal Enthalpies=           -3346.537171
 Sum of electronic and thermal Free Energies=        -3346.699820
```

46	0.622131000	1.270905000	0.519009000
15	2.755912000	0.482109000	-0.354440000
6	4.326897000	1.352314000	0.270922000
6	4.040599000	2.862272000	0.050635000
1	3.219245000	3.144724000	0.708608000
6	5.614990000	0.911398000	-0.463297000
1	5.832624000	-0.122962000	-0.190339000
6	3.020483000	0.895604000	-2.188237000
6	2.831553000	2.439129000	-2.268574000
1	2.995643000	2.717972000	-3.320306000
6	2.783611000	-1.374545000	0.074023000
6	3.799965000	-2.361924000	-0.174137000
6	3.685837000	-3.645257000	0.380199000
1	4.460502000	-4.372969000	0.219525000
6	2.588992000	-4.019029000	1.139011000
1	2.535080000	-5.021493000	1.554806000
6	1.570033000	-3.109902000	1.342520000
6	1.648614000	-1.808594000	0.819260000
8	4.879575000	-2.034434000	-0.949784000
6	5.921717000	-2.987486000	-1.386806000
6	0.395962000	-1.020631000	1.154341000
6	-0.778226000	-1.225629000	0.340863000
6	-2.038590000	-0.872501000	0.862111000
6	-2.168710000	-0.409067000	2.191740000

6	-1.032813000	-0.346862000	2.998286000
1	-1.147575000	-0.021111000	4.026304000
6	0.241741000	-0.611005000	2.520010000
6	-0.605924000	-1.920062000	-1.021124000
1	0.466898000	-1.910409000	-1.224597000
6	-1.267376000	-1.250819000	-2.245075000
1	-2.315278000	-1.537351000	-2.359700000
1	-0.745524000	-1.576553000	-3.152322000
1	-1.216426000	-0.160582000	-2.196337000
6	-1.014861000	-3.408261000	-0.950691000
1	-0.418142000	-3.955752000	-0.215738000
1	-0.858414000	-3.880817000	-1.928289000
1	-2.067283000	-3.530711000	-0.682374000
6	-3.502193000	0.022554000	2.789398000
1	-4.234985000	0.077449000	1.979753000
6	-3.412709000	1.433491000	3.404594000
1	-2.844036000	1.430729000	4.342987000
1	-4.417870000	1.807326000	3.633736000
1	-2.913389000	2.112062000	2.708706000
6	-4.017007000	-1.020331000	3.801450000
1	-4.130563000	-2.004126000	3.333879000
1	-4.990736000	-0.714653000	4.202092000
1	-3.326955000	-1.125850000	4.647451000
6	1.422390000	-0.479005000	3.480588000
1	2.342637000	-0.621628000	2.906755000
6	1.483477000	0.923204000	4.118671000
1	1.441680000	1.706742000	3.355735000
1	2.410156000	1.038158000	4.693516000
1	0.646719000	1.091856000	4.806009000
6	1.388814000	-1.564248000	4.574151000
1	0.476028000	-1.491966000	5.177126000
1	2.244766000	-1.449193000	5.250005000
1	1.430963000	-2.570802000	4.146366000
6	-3.288447000	-0.943507000	0.037378000
6	-4.168190000	-2.023015000	0.122108000
6	-5.364064000	-2.063714000	-0.588467000
6	-5.759295000	-1.017077000	-1.420376000
6	-7.063528000	-1.040903000	-2.180393000
1	-7.359074000	-2.082032000	-2.345579000
1	-6.907867000	-0.586467000	-3.165525000
6	-8.199743000	-0.293319000	-1.453042000
1	-7.891875000	0.746868000	-1.283088000
1	-8.348643000	-0.742346000	-0.461598000
6	-9.518683000	-0.319537000	-2.234638000
1	-9.360283000	0.127317000	-3.226356000
1	-9.813620000	-1.363334000	-2.413451000
6	-10.653759000	0.417460000	-1.516765000
1	-10.860821000	-0.031066000	-0.537461000
1	-11.580898000	0.386200000	-2.100132000
1	-10.399317000	1.471336000	-1.351037000
6	-4.888715000	0.071506000	-1.491954000

6	-3.692183000	0.116443000	-0.782643000
9	-1.176888000	1.814865000	1.197501000
9	-6.154829000	-3.148538000	-0.457462000
9	-3.863839000	-3.073304000	0.915081000
9	-5.213279000	1.119303000	-2.276060000
9	-2.906010000	1.190062000	-0.930894000
1	0.689104000	-3.389401000	1.909658000
6	0.544850000	3.229553000	0.048187000
6	0.998196000	4.268656000	0.803950000
6	-0.291928000	3.685651000	-1.027345000
16	0.467061000	5.819941000	0.187177000
1	1.587406000	4.254372000	1.711166000
6	-0.411257000	5.043685000	-1.092315000
1	-0.797744000	3.020532000	-1.719772000
1	-0.962921000	5.637540000	-1.810063000
6	6.840812000	-2.145386000	-2.281919000
1	7.320941000	-1.346682000	-1.711773000
1	7.626099000	-2.787047000	-2.693793000
1	6.290380000	-1.705016000	-3.116003000
6	5.325234000	-4.110428000	-2.252350000
1	6.140300000	-4.724512000	-2.650289000
1	4.640324000	-4.771526000	-1.721332000
1	4.785075000	-3.676714000	-3.100312000
6	6.777897000	-3.485034000	-0.204879000
1	6.302007000	-4.234000000	0.428338000
1	7.696864000	-3.931915000	-0.599020000
1	7.061403000	-2.637400000	0.427330000
6	3.713350000	3.353905000	-1.380377000
1	3.181595000	4.306201000	-1.277282000
1	4.641166000	3.595714000	-1.905216000
1	4.924442000	3.409954000	0.411093000
1	6.434089000	1.521469000	-0.052367000
6	4.404574000	0.465673000	-2.716157000
1	4.451586000	-0.624281000	-2.695915000
1	4.449422000	0.763670000	-3.775108000
6	5.630216000	1.050393000	-1.995612000
1	6.527891000	0.555123000	-2.380304000
1	5.751817000	2.098915000	-2.272169000
1	1.785792000	2.660913000	-2.056699000
6	1.933105000	0.229846000	-3.042303000
1	2.010553000	-0.863472000	-3.016403000
1	0.932986000	0.512628000	-2.703582000
1	2.035223000	0.546462000	-4.088921000
6	4.507362000	1.106169000	1.776450000
1	5.370284000	1.676590000	2.145347000
1	3.628410000	1.429825000	2.341427000
1	4.691024000	0.048188000	1.996754000

209c TS



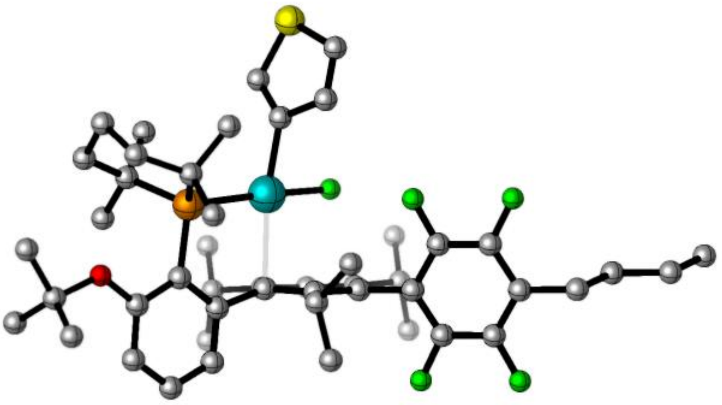
```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           1.031085 (Hartree/Particle)
 Thermal correction to Energy=                    1.093638
 Thermal correction to Enthalpy=                  1.094582
 Thermal correction to Gibbs Free Energy=         0.934118
 Sum of electronic and zero-point Energies=           -3346.564708
 Sum of electronic and thermal Energies=              -3346.502156
 Sum of electronic and thermal Enthalpies=            -3346.501211
 Sum of electronic and thermal Free Energies=         -3346.661675
```

46	0.638491000	1.168911000	0.486199000
15	2.741408000	0.422648000	-0.380661000
6	4.249812000	1.407138000	0.232898000
6	3.807458000	2.883328000	0.012426000
1	2.944593000	3.076334000	0.654160000
6	5.568650000	1.081195000	-0.504762000
1	5.872795000	0.071380000	-0.220527000
6	2.979902000	0.826295000	-2.221889000
6	2.636227000	2.344078000	-2.293960000
1	2.732326000	2.646152000	-3.347906000
6	2.803402000	-1.429628000	0.057212000
6	3.858379000	-2.370962000	-0.186609000
6	3.760599000	-3.685705000	0.292863000
1	4.557028000	-4.388049000	0.122978000
6	2.648773000	-4.119574000	0.996167000
1	2.605056000	-5.142915000	1.359131000
6	1.604782000	-3.243023000	1.222431000
6	1.658509000	-1.917624000	0.760938000
8	4.958468000	-1.956406000	-0.889795000
6	6.091771000	-2.825811000	-1.261726000
6	0.391220000	-1.163653000	1.131145000
6	-0.787571000	-1.323071000	0.324879000
6	-2.027792000	-0.867993000	0.831526000
6	-2.135487000	-0.349153000	2.142344000

6	-0.990608000	-0.321903000	2.938909000
1	-1.080985000	0.035055000	3.959036000
6	0.265541000	-0.705449000	2.478398000
6	-0.653840000	-2.052412000	-1.023629000
1	0.417723000	-2.088040000	-1.234371000
6	-1.297705000	-1.381566000	-2.256255000
1	-2.357809000	-1.626240000	-2.357398000
1	-0.797533000	-1.745150000	-3.161419000
1	-1.200530000	-0.293322000	-2.229352000
6	-1.120925000	-3.521451000	-0.923448000
1	-0.540728000	-4.079528000	-0.183176000
1	-0.992942000	-4.018659000	-1.893121000
1	-2.174528000	-3.596021000	-0.642821000
6	-3.456550000	0.125987000	2.741119000
1	-4.180479000	0.231197000	1.927797000
6	-3.340463000	1.509179000	3.409546000
1	-2.733216000	1.473269000	4.322188000
1	-4.335432000	1.870208000	3.696427000
1	-2.882198000	2.231333000	2.728759000
6	-4.017976000	-0.927053000	3.719277000
1	-4.152709000	-1.894479000	3.224900000
1	-4.987643000	-0.604457000	4.117045000
1	-3.339864000	-1.074402000	4.568785000
6	1.446416000	-0.650035000	3.447593000
1	2.363721000	-0.789049000	2.867871000
6	1.555450000	0.711617000	4.160462000
1	1.533597000	1.536132000	3.441009000
1	2.492130000	0.767732000	4.727583000
1	0.735335000	0.869037000	4.870514000
6	1.374777000	-1.788384000	4.484688000
1	0.457775000	-1.718644000	5.082023000
1	2.227651000	-1.733459000	5.172291000
1	1.390553000	-2.772429000	4.006161000
6	-3.279367000	-0.896837000	0.005364000
6	-4.203634000	-1.939595000	0.082177000
6	-5.392516000	-1.927174000	-0.639886000
6	-5.741639000	-0.862946000	-1.470707000
6	-7.047545000	-0.845183000	-2.228612000
1	-7.237066000	-1.846171000	-2.633496000
1	-6.953934000	-0.163234000	-3.079488000
6	-8.245512000	-0.419403000	-1.355277000
1	-8.049373000	0.576827000	-0.936184000
1	-8.328458000	-1.107256000	-0.503468000
6	-9.567155000	-0.401008000	-2.132605000
1	-9.476804000	0.286623000	-2.985314000
1	-9.749220000	-1.396937000	-2.560901000
6	-10.762692000	0.010003000	-1.267227000
1	-10.896682000	-0.679115000	-0.424516000
1	-11.692564000	0.012528000	-1.847012000
1	-10.625081000	1.016312000	-0.853300000
6	-4.827532000	0.189573000	-1.534772000

6	-3.635777000	0.176835000	-0.816042000
9	-1.106494000	2.306376000	1.075359000
9	-6.233357000	-2.975371000	-0.520868000
9	-3.951991000	-3.003011000	0.874910000
9	-5.094668000	1.254935000	-2.316007000
9	-2.799863000	1.219487000	-0.952774000
1	0.723636000	-3.569393000	1.763278000
6	0.029260000	3.253943000	0.344809000
6	0.600878000	4.236992000	1.119292000
6	-0.472133000	3.758053000	-0.908427000
16	0.640160000	5.769845000	0.268043000
1	0.981754000	4.171564000	2.127692000
6	-0.189884000	5.076295000	-1.096818000
1	-1.017836000	3.145637000	-1.616767000
1	-0.418161000	5.690709000	-1.958353000
6	7.019498000	-1.904465000	-2.065851000
1	7.364447000	-1.064382000	-1.459385000
1	7.897561000	-2.472112000	-2.389939000
1	6.519075000	-1.516871000	-2.956062000
6	5.648671000	-3.963754000	-2.198765000
1	6.538696000	-4.468949000	-2.588912000
1	5.019564000	-4.720687000	-1.730628000
1	5.098306000	-3.547050000	-3.048622000
6	6.876979000	-3.293044000	-0.021476000
1	6.358065000	-4.021374000	0.601685000
1	7.817340000	-3.750673000	-0.347224000
1	7.122690000	-2.429089000	0.604598000
6	3.455959000	3.331619000	-1.427020000
1	2.869890000	4.253383000	-1.344817000
1	4.367737000	3.619532000	-1.956335000
1	4.621250000	3.523977000	0.384543000
1	6.335517000	1.761765000	-0.103149000
6	4.395610000	0.520995000	-2.754322000
1	4.534536000	-0.562380000	-2.738982000
1	4.414762000	0.822643000	-3.813291000
6	5.573139000	1.202813000	-2.038451000
1	6.505791000	0.769846000	-2.417153000
1	5.619072000	2.254454000	-2.326829000
1	1.580245000	2.455288000	-2.037366000
6	1.957208000	0.058932000	-3.069752000
1	2.126009000	-1.023719000	-3.027131000
1	0.936405000	0.262567000	-2.736270000
1	2.035184000	0.367123000	-4.121191000
6	4.464299000	1.179615000	1.736396000
1	5.270943000	1.830298000	2.100391000
1	3.563768000	1.414245000	2.310144000
1	4.751408000	0.143724000	1.952598000

211c GS



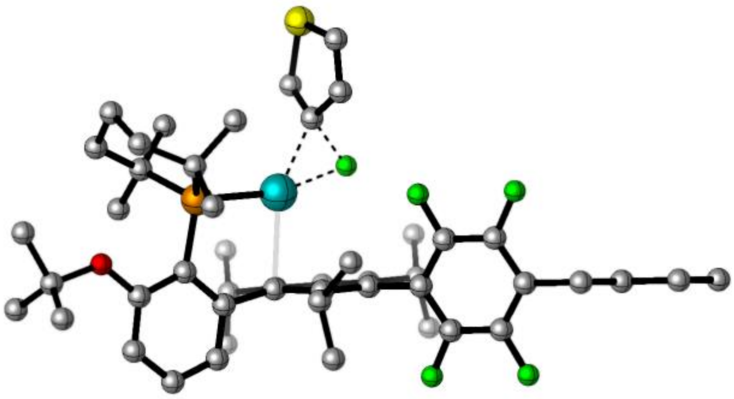
```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           1.024598 (Hartree/Particle)
 Thermal correction to Energy=                    1.087915
 Thermal correction to Enthalpy=                  1.088859
 Thermal correction to Gibbs Free Energy=         0.927010
 Sum of electronic and zero-point Energies=          -3308.513350
 Sum of electronic and thermal Energies=             -3308.450032
 Sum of electronic and thermal Enthalpies=           -3308.449088
 Sum of electronic and thermal Free Energies=        -3308.610937
```

46	0.662685000	1.264503000	0.596673000
15	2.805736000	0.583157000	-0.306359000
6	4.345907000	1.296941000	0.633234000
6	3.936328000	2.659297000	1.219227000
1	3.089265000	2.556997000	1.901309000
6	5.585017000	1.491562000	-0.268276000
1	6.051676000	0.518339000	-0.436871000
6	3.059837000	1.005846000	-2.177720000
6	2.236357000	2.269625000	-2.493727000
6	2.843076000	-1.285555000	-0.075637000
6	3.913680000	-2.166238000	-0.436223000
6	3.844926000	-3.525078000	-0.101143000
1	4.652698000	-4.192682000	-0.345507000
6	2.739374000	-4.049105000	0.555280000
1	2.715243000	-5.106598000	0.804132000
6	1.678486000	-3.224148000	0.879865000
6	1.712719000	-1.853534000	0.571605000
8	4.988465000	-1.632150000	-1.102872000
6	6.148753000	-2.414614000	-1.577622000
6	0.447868000	-1.138208000	1.015854000
6	-0.730132000	-1.235897000	0.189036000
6	-1.987775000	-0.944443000	0.752427000
6	-2.108582000	-0.617007000	2.123186000

6	-0.969170000	-0.646945000	2.923361000
1	-1.076419000	-0.432743000	3.981258000
6	0.300669000	-0.888538000	2.416958000
6	-0.559608000	-1.742383000	-1.252059000
1	0.516682000	-1.746126000	-1.434701000
6	-1.166335000	-0.868145000	-2.368600000
1	-2.240412000	-1.025215000	-2.486720000
1	-0.699232000	-1.135196000	-3.324104000
1	-0.993492000	0.196776000	-2.189352000
6	-1.015338000	-3.209298000	-1.403506000
1	-0.458004000	-3.869979000	-0.732941000
1	-0.836710000	-3.547277000	-2.431661000
1	-2.078409000	-3.337369000	-1.187487000
6	-3.435382000	-0.241596000	2.771740000
1	-4.174840000	-0.105327000	1.978260000
6	-3.332067000	1.102106000	3.521011000
1	-2.756440000	1.003411000	4.449707000
1	-4.332863000	1.457886000	3.793914000
1	-2.832653000	1.842174000	2.890996000
6	-3.947223000	-1.375704000	3.682607000
1	-4.069396000	-2.310451000	3.124575000
1	-4.916191000	-1.106447000	4.119361000
1	-3.250716000	-1.564767000	4.508478000
6	1.471546000	-0.924116000	3.395772000
1	2.389652000	-1.062617000	2.819675000
6	1.602522000	0.395857000	4.180524000
1	1.622177000	1.256593000	3.505071000
1	2.522221000	0.394737000	4.778051000
1	0.762746000	0.541741000	4.869316000
6	1.361023000	-2.120408000	4.360888000
1	0.451146000	-2.059741000	4.969050000
1	2.218743000	-2.137124000	5.043935000
1	1.340972000	-3.072503000	3.820632000
6	-3.251184000	-0.945137000	-0.055967000
6	-4.112629000	-2.042251000	-0.074948000
6	-5.331899000	-2.017559000	-0.746173000
6	-5.770809000	-0.884690000	-1.429566000
6	-7.104157000	-0.833984000	-2.135903000
1	-7.414512000	-1.854273000	-2.382676000
1	-6.985117000	-0.292495000	-3.081524000
6	-8.202805000	-0.148926000	-1.297410000
1	-7.879469000	0.870906000	-1.050995000
1	-8.312141000	-0.682391000	-0.343321000
6	-9.554539000	-0.101117000	-2.019544000
1	-9.434733000	0.424528000	-2.977519000
1	-9.868713000	-1.124438000	-2.269678000
6	-10.648549000	0.583587000	-1.194123000
1	-10.814552000	0.060875000	-0.244203000
1	-11.601806000	0.603738000	-1.734273000
1	-10.376724000	1.619659000	-0.958468000
6	-4.917921000	0.219837000	-1.396815000

6	-3.698348000	0.198542000	-0.727188000
9	-1.118935000	1.741373000	1.359161000
9	-6.102267000	-3.124478000	-0.721386000
9	-3.769785000	-3.173718000	0.577049000
9	-5.286171000	1.350799000	-2.031929000
9	-2.938781000	1.300356000	-0.751525000
1	0.804585000	-3.625945000	1.381110000
6	0.546578000	3.223896000	0.132897000
6	1.116738000	4.300824000	0.740871000
6	-0.442526000	3.626403000	-0.830870000
16	0.509716000	5.818503000	0.109341000
1	1.831903000	4.343847000	1.547988000
6	-0.557879000	4.977746000	-0.969572000
1	-1.057163000	2.928127000	-1.387517000
1	-1.210660000	5.533028000	-1.631107000
6	7.020528000	-1.395257000	-2.326577000
1	7.291283000	-0.550765000	-1.688952000
1	7.945064000	-1.885689000	-2.647700000
1	6.515096000	-1.016360000	-3.218309000
6	5.733562000	-3.489816000	-2.599137000
1	6.631765000	-3.865215000	-3.101102000
1	5.213395000	-4.348833000	-2.175976000
1	5.086449000	-3.043186000	-3.361063000
6	6.970739000	-2.952694000	-0.393700000
1	6.441624000	-3.676861000	0.226305000
1	7.874780000	-3.439628000	-0.774842000
1	7.280639000	-2.122810000	0.249782000
1	4.783794000	3.074041000	1.781947000
1	6.304009000	2.089384000	0.311196000
6	4.534525000	1.255243000	-2.560462000
1	5.042087000	0.293966000	-2.632860000
1	4.528113000	1.687763000	-3.571520000
6	5.340372000	2.158059000	-1.624150000
1	6.310941000	2.370685000	-2.090931000
1	4.849124000	3.131529000	-1.499492000
1	1.169162000	2.100485000	-2.350112000
6	2.520630000	-0.142329000	-3.048427000
1	3.067914000	-1.075322000	-2.889256000
1	1.458116000	-0.323765000	-2.871599000
1	2.631301000	0.136008000	-4.105214000
6	4.742048000	0.383155000	1.805769000
1	5.593465000	0.838641000	2.328945000
1	3.933993000	0.278065000	2.533367000
1	5.047856000	-0.612883000	1.476477000
1	2.401899000	2.540553000	-3.545302000
1	3.653618000	3.383553000	0.452989000
1	2.503184000	3.129843000	-1.875732000

211c TS



```
- Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.

 Zero-point correction=                           1.022125 (Hartree/Particle)
 Thermal correction to Energy=                    1.085375
 Thermal correction to Enthalpy=                  1.086320
 Thermal correction to Gibbs Free Energy=         0.924186
 Sum of electronic and zero-point Energies=          -3308.475704
 Sum of electronic and thermal Energies=             -3308.412453
 Sum of electronic and thermal Enthalpies=           -3308.411509
 Sum of electronic and thermal Free Energies=        -3308.573642
```

46	0.670770000	1.221151000	0.500811000
15	2.786739000	0.515272000	-0.354863000
6	4.294148000	1.350894000	0.524807000
6	3.810696000	2.735429000	1.000900000
1	2.987581000	2.643925000	1.712256000
6	5.530358000	1.522877000	-0.382542000
1	6.020828000	0.552734000	-0.486993000
6	3.017151000	0.863953000	-2.240960000
6	2.157215000	2.103461000	-2.562636000
1	2.258986000	2.343197000	-3.630197000
6	2.851198000	-1.344617000	-0.027163000
6	3.939883000	-2.216478000	-0.346770000
6	3.889758000	-3.569618000	0.015846000
1	4.710385000	-4.229992000	-0.204458000
6	2.784729000	-4.095942000	0.669805000
1	2.772791000	-5.148166000	0.941112000
6	1.708938000	-3.279347000	0.968034000
6	1.720948000	-1.915912000	0.628888000
8	5.017518000	-1.677409000	-1.007022000
6	6.198682000	-2.448719000	-1.441676000
6	0.444970000	-1.211803000	1.065556000
6	-0.732814000	-1.299900000	0.249639000
6	-1.971721000	-0.876791000	0.786867000
6	-2.071631000	-0.430269000	2.124605000

6	-0.926865000	-0.464670000	2.919164000
1	-1.012596000	-0.170808000	3.959934000
6	0.322351000	-0.847763000	2.437941000
6	-0.596251000	-1.914331000	-1.153024000
1	0.477951000	-1.973932000	-1.341097000
6	-1.175768000	-1.098261000	-2.326883000
1	-2.254668000	-1.227308000	-2.436153000
1	-0.718456000	-1.442660000	-3.262234000
1	-0.967099000	-0.029944000	-2.218193000
6	-1.108837000	-3.369751000	-1.200969000
1	-0.571001000	-4.004653000	-0.490468000
1	-0.953194000	-3.784377000	-2.204704000
1	-2.173924000	-3.443060000	-0.968926000
6	-3.385511000	0.028402000	2.751315000
1	-4.111862000	0.178201000	1.947394000
6	-3.249544000	1.378568000	3.480712000
1	-2.632781000	1.294774000	4.383628000
1	-4.237896000	1.735199000	3.794737000
1	-2.792017000	2.127277000	2.828409000
6	-3.953711000	-1.062806000	3.682456000
1	-4.097741000	-2.005826000	3.145024000
1	-4.919628000	-0.750470000	4.097146000
1	-3.275102000	-1.254816000	4.522552000
6	1.490142000	-0.900490000	3.421014000
1	2.404544000	-1.082179000	2.850138000
6	1.674507000	0.424898000	4.184562000
1	1.737028000	1.272395000	3.494959000
1	2.592384000	0.393768000	4.783933000
1	0.842875000	0.618652000	4.871682000
6	1.330751000	-2.072848000	4.409434000
1	0.419162000	-1.963799000	5.008758000
1	2.183139000	-2.109987000	5.098649000
1	1.275811000	-3.033622000	3.887392000
6	-3.234724000	-0.879330000	-0.022945000
6	-4.139594000	-1.941300000	0.015050000
6	-5.344838000	-1.910127000	-0.679098000
6	-5.729593000	-0.808412000	-1.442202000
6	-7.050772000	-0.771948000	-2.172084000
1	-7.246945000	-1.761568000	-2.600570000
1	-6.975652000	-0.066126000	-3.005400000
6	-8.230654000	-0.372154000	-1.262739000
1	-8.027760000	0.613739000	-0.823002000
1	-8.293490000	-1.081475000	-0.426753000
6	-9.568776000	-0.338219000	-2.010723000
1	-9.497065000	0.367937000	-2.849987000
1	-9.759279000	-1.324750000	-2.456721000
6	-10.745835000	0.052911000	-1.111589000
1	-10.861838000	-0.653903000	-0.280892000
1	-11.687751000	0.066697000	-1.671430000
1	-10.600176000	1.050402000	-0.679485000
6	-4.836555000	0.263809000	-1.464053000

6	-3.628956000	0.232665000	-0.772788000
9	-1.058726000	2.358142000	1.138139000
9	-6.165127000	-2.978197000	-0.600217000
9	-3.854148000	-3.040234000	0.744750000
9	-5.141753000	1.367399000	-2.175018000
9	-2.820683000	1.301432000	-0.854057000
1	0.839363000	-3.684591000	1.473750000
6	0.041299000	3.285761000	0.313931000
6	0.656525000	4.302757000	1.003148000
6	-0.525236000	3.726207000	-0.934942000
16	0.679657000	5.779630000	0.059297000
1	1.101826000	4.287052000	1.986301000
6	-0.232310000	5.024785000	-1.216967000
1	-1.116740000	3.084598000	-1.576555000
1	-0.499470000	5.593160000	-2.098607000
6	7.075320000	-1.429631000	-2.185572000
1	7.331573000	-0.579008000	-1.550332000
1	8.007483000	-1.916665000	-2.489409000
1	6.581637000	-1.059808000	-3.087402000
6	5.821706000	-3.544801000	-2.455535000
1	6.737296000	-3.932608000	-2.914965000
1	5.282660000	-4.392962000	-2.034178000
1	5.204701000	-3.113002000	-3.250345000
6	7.003224000	-2.956168000	-0.231714000
1	6.479948000	-3.691435000	0.379901000
1	7.931356000	-3.418588000	-0.584569000
1	7.271009000	-2.112870000	0.413311000
1	4.642433000	3.256294000	1.495411000
1	6.233906000	2.174854000	0.156651000
6	4.477694000	1.132486000	-2.660724000
1	5.007997000	0.180524000	-2.700638000
1	4.448204000	1.519678000	-3.690221000
6	5.276771000	2.096253000	-1.779257000
1	6.245033000	2.287359000	-2.260255000
1	4.779249000	3.072507000	-1.715515000
1	1.102495000	1.924329000	-2.347426000
6	2.482047000	-0.322161000	-3.059091000
1	3.059907000	-1.234494000	-2.884886000
1	1.431968000	-0.527152000	-2.837925000
1	2.549460000	-0.079938000	-4.128530000
6	4.711459000	0.537798000	1.761218000
1	5.517993000	1.071017000	2.282724000
1	3.888540000	0.420674000	2.470184000
1	5.085316000	-0.455077000	1.495767000
1	2.449015000	2.989002000	-1.991509000
1	3.451227000	3.371904000	0.188418000

6.2 Appendix 2. Ligand screening data

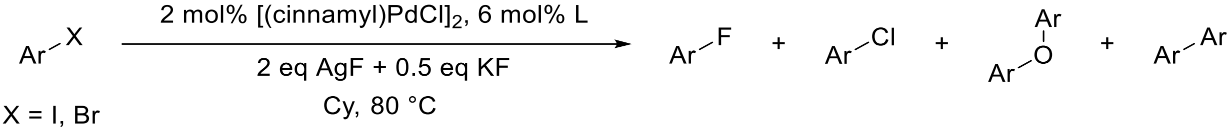
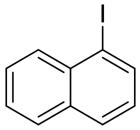
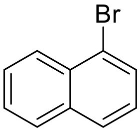
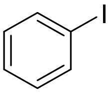
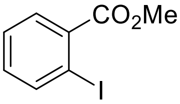
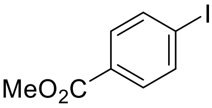
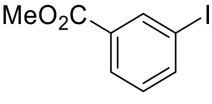
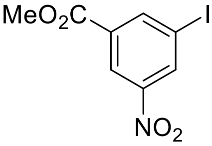


Table 22. AlPhos (**122**) and *t*-BuAlPhos (**205**) ligand screening

			Ligands and reaction time, h					
			122			**205**		
Entry	Substrate		2	6	24	2	6	24
1	 **254**	SM	0	n/a	n/a	97	97	95
		Ar-F	90	n/a	n/a	1	1	3
		Ar-Cl	3	n/a	n/a	0	0	0
		ArOAr	2	n/a	n/a	1	1	2
		Ar-Ar	4	n/a	n/a	0	0	0
2	 **266**	SM	24	18	7	100	100	100
		Ar-F	76	78	90	0	0	0
		Ar-Cl	2	2	2	0	0	0
		ArOAr	0	0	1	0	0	0
		Ar-Ar	0	0	1	0	0	0
3	 **267**	SM	55	8	1	100	97	95
		Ar-F	29	70	71	0	0	0
		Ar-Cl	3	4	4	0	0	0
		ArOAr	7	12	18	0	0	0
		Ar-Ar	6	6	7	0	3	5
4	 **268**	SM	92	n/a	91	95	93	93
		Ar-F	5	n/a	4	0	0	0
		Ar-Cl	0	n/a	0	0	0	0
		ArOAr	2	n/a	1	2	3	4
		Ar-Ar	1	n/a	5	2	2	2
5	 **173**	SM	0	n/a	n/a	92	91	87
		Ar-F	83	n/a	n/a	0	0	0
		Ar-Cl	1	n/a	n/a	1	1	1
		ArOAr	13	n/a	n/a	8	8	11
		Ar-Ar	0	n/a	n/a	0	0	1
6	 **174**	SM	5	0	n/a	98	97	94
		Ar-F	79	86	n/a	0	0	0
		Ar-Cl	4	0	n/a	0	0	0
		ArOAr	10	11	n/a	0	0	0
		Ar-Ar	2	2	n/a	2	3	6
7	 **269**	SM	19	0	n/a	100	100	100
		Ar-F	79	100	n/a	0	0	0
		Ar-Cl	2	0	n/a	0	0	0
		ArOAr	0	0	n/a	0	0	0
		Ar-Ar	0	0	n/a	0	0	0

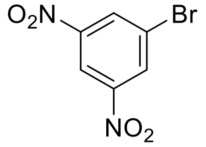
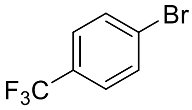
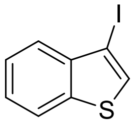
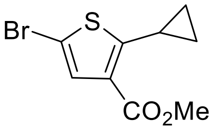
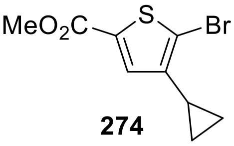
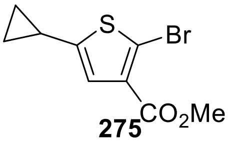
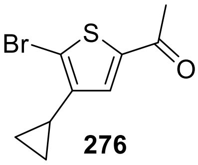
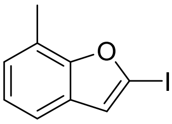
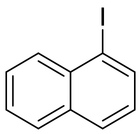
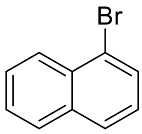
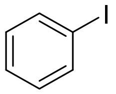
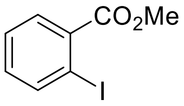
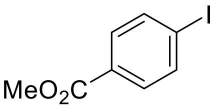
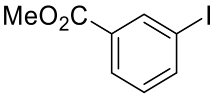
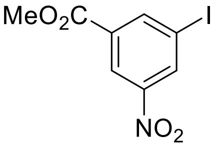
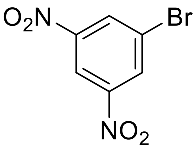
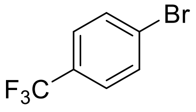
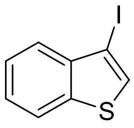
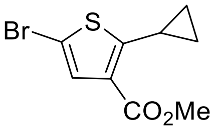
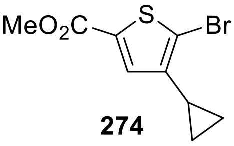
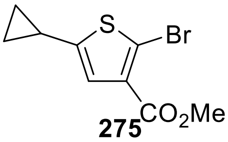
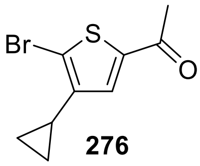
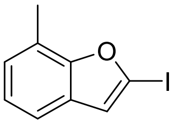
			Ligands and reaction time, h					
			122			**205**		
Entry	Substrate		2	6	24	2	6	24
8	 **270**	SM	19	0	n/a	100	100	100
		Ar-F	80	100	n/a	0	0	0
		Ar-Cl	1	0	n/a	0	0	0
		ArOAr	0	0	n/a	0	0	0
		Ar-Ar	0	0	n/a	0	0	0
9	 **271**	SM	0	n/a	n/a	100	100	99
		Ar-F	94	n/a	n/a	0	0	0
		Ar-Cl	1	n/a	n/a	0	0	0
		ArOAr	4	n/a	n/a	0	0	0
		Ar-Ar	0	n/a	n/a	0	0	1
10	 **272**	SM	100	96	92	97	50	14
		Ar-F	0	0	0	0	0	0
		Ar-Cl	0	4	8	1	0	0
		ArOAr	0	0	0	0	0	0
		Ar-Ar	0	0	0	0	0	0
11	 **273**	SM	89	86	81	n/a	n/a	n/a
		Ar-F	0	0	0	n/a	n/a	n/a
		Ar-Cl	0	0	0	n/a	n/a	n/a
		ArOAr	0	0	0	n/a	n/a	n/a
		Ar-Ar	10	13	19	n/a	n/a	n/a
12	 **274**	SM	87	81	58	n/a	n/a	n/a
		Ar-F	5	11	33	n/a	n/a	n/a
		Ar-Cl	7	6	5	n/a	n/a	n/a
		ArOAr	0	0	0	n/a	n/a	n/a
		Ar-Ar	2	2	3	n/a	n/a	n/a
13	 **275**	SM	87	84	78	n/a	n/a	n/a
		Ar-F	0	0	0	n/a	n/a	n/a
		Ar-Cl	0	0	0	n/a	n/a	n/a
		ArOAr	0	0	0	n/a	n/a	n/a
		Ar-Ar	13	16	22	n/a	n/a	n/a
14	 **276**	SM	92	90	88	n/a	n/a	n/a
		Ar-F	2	2	3	n/a	n/a	n/a
		Ar-Cl	5	6	6	n/a	n/a	n/a
		ArOAr	0	0	0	n/a	n/a	n/a
		Ar-Ar	1	2	3	n/a	n/a	n/a
15	 **277**	SM	65	53	30	n/a	n/a	n/a
		Ar-F	0	0	0	n/a	n/a	n/a
		Ar-Cl	0	0	0	n/a	n/a	n/a
		ArOAr	1	2	3	n/a	n/a	n/a
		Ar-Ar	34	45	68	n/a	n/a	n/a

Table 23. Screening of ligands **206** and **210**

			Ligands and reaction time, h					
			206			**210**		
Entry	Substrate		2	6	24	2	6	24
1	 **254**	SM	78	65	n/a	100	100	n/a
		Ar-F	6	16	n/a	0	0	n/a
		Ar-Cl	1	3	n/a	0	0	n/a
		ArOAr	0	0	n/a	0	0	n/a
		Ar-Ar	13	16	n/a	0	0	n/a
2	 **266**	SM	96	94	n/a	100	100	n/a
		Ar-F	2	3	n/a	0	0	n/a
		Ar-Cl	1	3	n/a	0	0	n/a
		ArOAr	0	0	n/a	0	0	n/a
		Ar-Ar	0	0	n/a	0	0	n/a
3	 **267**	SM	84	83	76	100	100	n/a
		Ar-F	0	0	0	0	0	n/a
		Ar-Cl	1	0	0	0	0	n/a
		ArOAr	0	0	0	0	0	n/a
		Ar-Ar	15	17	24	0	0	n/a
4	 **268**	SM	89	75	68	100	100	n/a
		Ar-F	4	5	5	0	0	n/a
		Ar-Cl	1	5	2	0	0	n/a
		ArOAr	0	0	0	0	0	n/a
		Ar-Ar	6	10	24	0	0	n/a
5	 **173**	SM	60	24	0	100	n/a	n/a
		Ar-F	4	7	4	0	n/a	n/a
		Ar-Cl	1	1	1	0	n/a	n/a
		ArOAr	30	67	95	0	n/a	n/a
		Ar-Ar	0	0	0	0	n/a	n/a
6	 **174**	SM	80	76	70	100	100	n/a
		Ar-F	0	0	0	0	0	n/a
		Ar-Cl	0	0	0	0	0	n/a
		ArOAr	0	0	0	0	0	n/a
		Ar-Ar	20	23	30	0	0	n/a
7	 **269**	SM	100	100	100	100	100	n/a
		Ar-F	0	0	0	0	0	n/a
		Ar-Cl	0	0	0	0	0	n/a
		ArOAr	0	0	0	0	0	n/a
		Ar-Ar	0	0	0	0	0	n/a
8	 **270**	SM	100	100	100	100	100	n/a
		Ar-F	0	0	0	0	0	n/a
		Ar-Cl	0	0	0	0	0	n/a
		ArOAr	0	0	0	0	0	n/a
		Ar-Ar	0	0	0	0	0	n/a
9		SM	100	94	85	100	100	n/a
		Ar-F	0	1	2	0	0	n/a

			Ligands and reaction time, h					
			206			**210**		
Entry	Substrate		2	6	24	2	6	24
	 **271**	Ar-Cl	0	1	2	0	0	n/a
		ArOAr	0	0	4	0	0	n/a
		Ar-Ar	0	2	5	0	0	n/a
10	 **272**	SM	91	90	84	100	100	n/a
		Ar-F	0	0	0	0	0	n/a
		Ar-Cl	0	0	0	0	0	n/a
		ArOAr	0	0	0	0	0	n/a
		Ar-Ar	9	10	16	0	0	n/a
11	 **273**	SM	96	94	88	n/a	n/a	n/a
		Ar-F	0	0	0	n/a	n/a	n/a
		Ar-Cl	0	0	0	n/a	n/a	n/a
		ArOAr	0	0	0	n/a	n/a	n/a
		Ar-Ar	4	6	12	n/a	n/a	n/a
12	 **274**	SM	93	90	87	n/a	n/a	n/a
		Ar-F	0	0	0	n/a	n/a	n/a
		Ar-Cl	0	0	0	n/a	n/a	n/a
		ArOAr	0	0	0	n/a	n/a	n/a
		Ar-Ar	7	10	13	n/a	n/a	n/a
13	 **275**	SM	85	85	80	n/a	n/a	n/a
		Ar-F	0	0	0	n/a	n/a	n/a
		Ar-Cl	0	0	0	n/a	n/a	n/a
		ArOAr	0	0	0	n/a	n/a	n/a
		Ar-Ar	15	15	20	n/a	n/a	n/a
14	 **276**	SM	100	100	100	n/a	n/a	n/a
		Ar-F	0	0	0	n/a	n/a	n/a
		Ar-Cl	0	0	0	n/a	n/a	n/a
		ArOAr	0	0	0	n/a	n/a	n/a
		Ar-Ar	0	0	0	n/a	n/a	n/a
15	 **277**	SM	72	66	63	100	100	n/a
		Ar-F	0	0	0	0	0	n/a
		Ar-Cl	0	0	0	0	0	n/a
		ArOAr	0	0	0	0	0	n/a
		Ar-Ar	28	34	36	0	0	n/a