Development of Novel Transition Metal-Catalyzed Cross-Coupling Reactions and Applications Thereof

By

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B.S. Chemistry
B.S. Philosophy
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at the
Massachusetts Institute of Technology

June 2013

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Development of Novel Transition Metal-Catalyzed Cross-Coupling Reactions and Applications Thereof

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Submitted to the Department of Chemistry on May 23, 2013
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ABSTRACT

Chapter 1

The first example of Pd(0)/(II) catalyzed fluorination of aryl bromides is reported herein. Based on these data, an analogous method was developed for the fluorination of aryl triflates. The reaction proceeds under mild conditions and represents the first report of reductive elimination from a Pd(II) center of a C–F bond.

Chapter 2

Herein we report the first example of a Pd-catalyzed synthesis of aryl trifluoromethyl sulfides. A wide range of aryl bromides are converted to their corresponding trifluoromethyl sulfides in good to excellent yields. Furthermore, we were successful in synthesizing an intermediate in the synthesis of Toltrazuril in two steps from commercially available starting materials.

Chapter 3

The development of a novel precatalyst for Ni-catalyzed C–N bond formation is described herein. Furthermore, the substrate scope of the reaction has been expanded to include a wide range of nucleophiles and electrophiles. Finally, we report the first use of weak base in the Ni-catalyzed arylation of anilines.

Chapter 4

The development of a novel triptycene-based hole-transport material is reported. Computational as well as preliminary photophysical and voltammetric data suggests that this class of compounds could serve as an excellent host material for blue triplet emitters.

Thesis Supervisor: Stephen L. Buchwald
Title: Camille Dreyfus Professor of Chemistry

Acknowledgements

There are many people that I would like to acknowledge for helping me get to where I am today. First and foremost, I would liked to dedicate this thesis to my great grandmother, someone whom I wish could have been there for the major events of my life. To my grandfather who died shortly after I was born. To my great uncle Fima who passed only a few short weeks before my defense and only a few short months before my wedding. To my mother and grandmother for all of their support – there never has, nor ever will be, such an amazing pair of women. To my sister for always being there to kick me when I need it most. Usually, it hurt. To my dearest Stellochka, for all of her love and patience. She actually managed to (by some miracle) stay with me throughout my entire PhD, all the while studying in NYC toward her PharmD. I am sure that if it were not for her, I would not have been able to accomplish even a fraction of what I did. Not only did she put up with the long-distance, she actually agreed to marry me!

I would also like to thank to Prof. Steve Buchwald, for being a fantastic advisor. He pushed me when I needed it and gave me the freedom to explore some very strange and interesting chemistry in my 5 years. A special thank you also goes to Prof. Tim Swager for all of his insight into hole transport materials and just generally amazing things. I do not think I will ever understand even a fraction of what he does.

Dr. David Surry, a former post-doc in the group, deserves a tremendous amount of credit for helping out when I first started. It was an honor to work with him. I doubt I will ever meet anyone quite as creative or intelligent again. Dr. Gavin Jones was a brilliant computational chemistry mentor and a dear friend. I was pretty sad to see him go – who would I have lunch with?! I guess that is where Dr. Marcel Düfert, came in. Of course, he had the incredible honor and privilege to share a hood with me. And even after that we were still very good friends!

Amazing! I was sure he would kill me after a few months. But nope, he was just that good of a person. I very much miss our conversions. Some of the most interesting, and insane, ideas I have ever had were the result of a late night coffee break with him. Dr. Ruben Martin also deserves a special thank you. He was my first mentor, someone that got me interested in chemistry and ultimately the reason I joined the Buchwald Group. And of course there is Dr. Alexander Spokoyny - a lone organometallic chemist in the lab that actually understands the chemistry from a fundamental inorganic chemistry perspective. Even though we overlapped for only a year, I learned quite a bit from Alex. Some things chemistry related some things not. New Orleans will always be a special place thanks to Alex.

I would also like to individually thank Dr. John Robbins Debergh for helping me out with this thesis. I very much appreciate all of the proof reading that he put up with. Especially the first drafts.

And of course, I would like to thank Dr. Derk Frantz from the Swager Group. He did a great job doing the physical measurements of my TTC compounds. Hopefully something great will come of it!

As far as the graduate students go I would like to thank Nick Bruno for being an awesome gym buddy. Not just that, but also great friend. He is one of the brightest graduate students that I have seen come through the lab. An incredibly talented chemist, he is credited with developing our awesome new precatalysts that made my life EXCEEDINGLY easy. Thanks Nick! Nathan Park deserves a special shout out as well. I liked him the moment I found out he worked for the late David Gin. This is mostly because he spent time in NYC and I REALLY miss NYC. Of course, Nathan is also a brilliant chemist. He not only helped me with the Ni chemistry, he elevated it to a whole new level. I expect great things from you Nathan! James

Colombe, you actually volunteered to be an EHS Rep. What is wrong with you?? Ah well. I will miss our safety inspections and the various grumblings (mostly on my part) about how people refuse to follow the rules.

Now, while I would love to write a whole paragraph for each and every person I ever met and liked throughout my time here, but I can't. Because I need to hand this thing in at some point. So, Phil Milner, Katya Vinogradova, Nootaree Niljianskul, Mingjuan Su and all of the members of the Buchwald group past and present with whom I had the pleasure of working with – THANK YOU.

Finally, in accord with all prior agreements: Robert and Shelley ::nod:: - that's all you get despite the fact that you two have been my closest friends for over 10 years.

Preface

This thesis has been adapted from the following published articles co-written by the author:

Donald Watson, Mingjuan Su, **Georgiy Teverovskiy**, Jorge Garcia-Fortanet, Tom Kinzel, Stephen L. Buchwald "Formation of ArF from LPdAr(F): Catalytic Conversion of Aryl Triflates to Aryl Fluorides" *Science* **2009**, *325*, 1661

Georgiy Teverovskiy, David S. Surry, Stephen L. Buchwald "Pd-Catalyzed Synthesis of ArSCF3 Compounds under Mild Conditions" *Angew. Chem., Int. Ed.*, **2011**, *50*, 7312

Respective Contributions

The work described in this thesis is the result of collaboration between the author and various members of the Massachusetts Institute of Technology community. Described below are the respective contributions of these individuals to this body of work.

Chapter 1 describes the Pd-catalyzed formation of aryl fluorides from the corresponding aryl bromides and triflates. Dr. Donald Watson, Mingjuan Su and Dr. Tom Kinzel performed the work described in Scheme 4. Dr. Jorge Garcia-Fortanet and Dr. Yong Zhang did the work described in Table 3. All computational results were performed by the author with the aid of Dr. Gavin O. Jones.

Chapter 2 describes the Pd-catalyzed formation of aryltrifluormethylsulfides. The author conducted all of the experiments and Dr. Michael Takase solved the crystal structure depicted in Scheme 2. It is included for continuity and clarity.

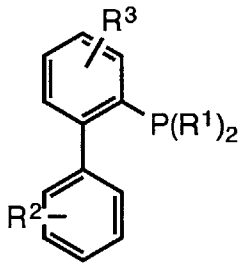
Chapter 3 describes the development of a novel Ni(0) precatalyst. Dr. Peter Mueller solved the crystal structure depicted in Figure 1. Compounds in Table 4 were synthesized using conditions developed by Nathan Park.

Chapter 4 describes the synthesis of a novel trypticene derived, carbazole based hole-transport material. The synthesis was carried out by the author while the physical measurements were performed by Dr. Derik K. Frantz of the Swager Group.

Table of Contents

Introduction

Transition metal-catalyzed cross-coupling reactions have become a staple of synthetic organic chemists. It is currently possible to cross-couple a wide range of aromatic electrophiles with a diverse array of nucleophiles. Advances in C–C and C–X bond forming reactions have provided facile access to a bevy of complex structures. These processes have been applied toward the synthesis of biologically active molecules and a range of novel electronic materials. Much of these advances have come from the development of the dialkylbiarylphopshine class of ligands and the use of N-heterocyclic carbene (NHC) ligands (Figure 1).



dialkylbiarylphosphine

R^1 = adamantyl, *t*Bu or Cy

R^2 = OMe, O*i*Pr, *i*Pr

R^3 = OMe, Me, H

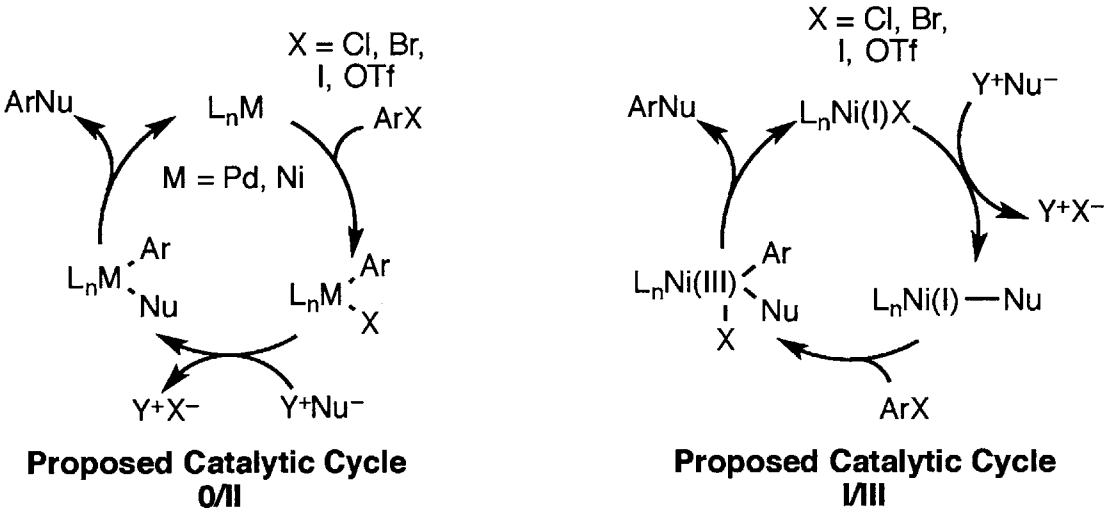
NHC

R^4 = adamantyl, arene

Figure 1. Dialkylbiarylphosphine and NHC-type ligand backbones

Transition metal-catalyzed cross-coupling reactions involve three elementary steps: oxidative addition, transmetallation and reductive elimination (Scheme 1). The main focus of this thesis is on transmetallation and reductive elimination of new types of nucleophiles. Oxidative addition of a d^{10} metal center onto an aryl halide or pseudohalide has three possible mechanistic pathways – S_NAr, 3-center 2-electron and a radical pathway. Pd(0)/(II) catalytic cycles generally involve a 3-center 2-electron transition state for oxidative addition. In a Ni-catalyzed process either a 3-

center 2-electron oxidative addition can occur or a radical type mechanism may be operating. Transmetallation onto a Pd(II) or a Ni(II) center depends on the nature of the nucleophile. In the case of arylation of amines, transmetallation involves amine binding and deprotonation. Transmetallation of nucleophiles such as fluoride or trifluoromethyl sulfide are presumed to proceed through an associative σ-bond metathesis process. Finally, reductive elimination occurs from a Pd(II) or Ni(II) center to generate the product and recover the Pd(0) or Ni(0) species. Ni-based systems may also proceed through a Ni(I)/(III) cycle. The fundamental steps are reversed in that transmetallation occurs first onto a Ni(I) species followed by oxidative addition and reductive elimination (Scheme 1).



Scheme 1. Typical Pd and Ni catalytic cycles

The key to the success of Pd-catalyzed cross-coupling reactions has been the development of novel classes of ligands. In our group, the focus has been on bulky, electron-rich, mono-dentate phosphine ligands. There are several factors that influence the development of this family of ligands. An electron-rich phosphine ligand facilitates oxidative addition by donating electron density into the Pd(0) center. Transmetallation is facilitated in dialkylbiarylphopshine-type

ligands by rotation around the C–P bond providing a much less sterically congested local environment for transmetallation to take place. Rotation once more around the C–P bond provides a crowded steric environment around the metal center, which facilitates reductive elimination by raising the ground state energy of the transmetallated Pd(II) complex relative to the transition state of reductive elimination. Furthermore, reductive elimination is accelerated in 3-coordinate Pd(II) complexes. Utilizing this class of ligands we have been successful in the employing phenols, primary and secondary aliphatic alcohols, amides, 5- and 6-membered heterocyclic amines, nitrites, cyantes, bromides and chlorides as viable cross-coupling partners with aryl halides and pseudohalides.

The body of work presented herein will fall into four distinct parts. The first is the development of a Pd-catalyzed cross-coupling reaction toward the synthesis of aryl fluorides. The second is the synthesis of aryl trifluoromethyl sulfides via cross-coupling. The third is synthesis, characterization and application of an air-stable Ni(0) precatalyst for C–N bond forming reactions. And finally, the fourth part will focus on applying Pd-catalyzed C–N bond forming processes toward the development of a novel structural class of hole-transport materials.

Chapter 1: Pd-Catalyzed Synthesis of Aryl Fluorides

1.1: Introduction

Due to the favorable properties of fluorine-containing organic molecules, specifically higher metabolic stability, as well as increased lipophilicity, a large percentage of the world's top grossing drugs, such as Lipitor, Risperdal and Zyvox, contain an aromatic carbon–fluorine bond (Figure 1).[1] In addition, the growing importance of Positron Emission Tomography (PET) in medicine has spurred development of new ways of introducing ^{18}F atoms onto aromatic rings.[2]

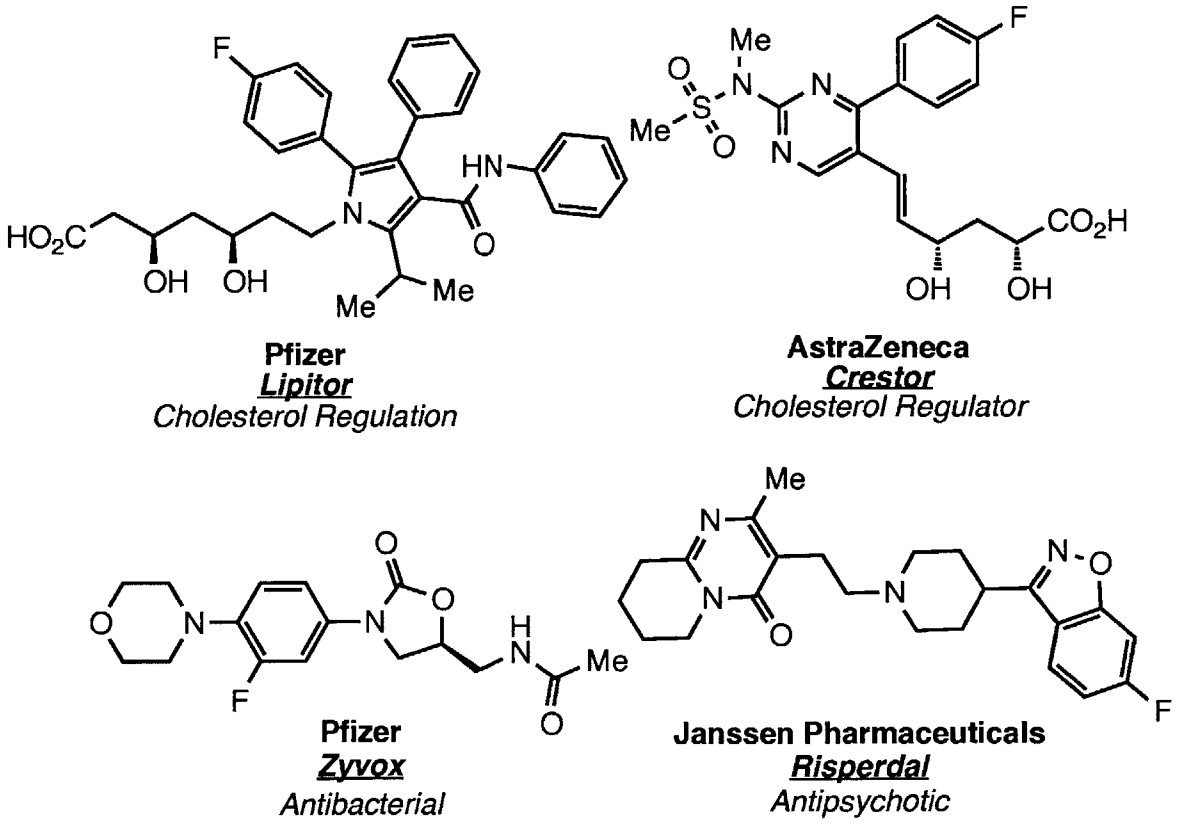
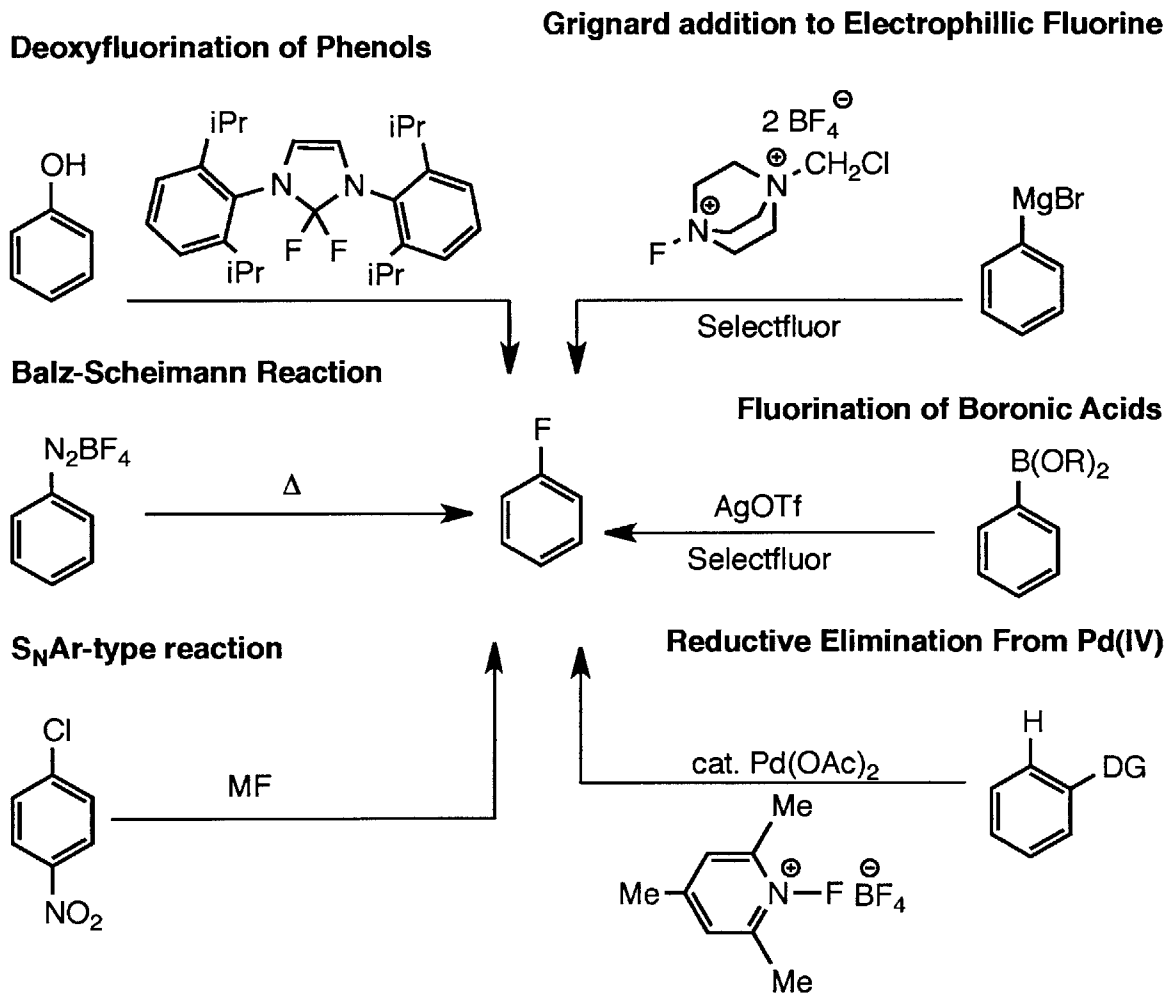


Figure 1. Various fluorine containing drugs currently on the market.

Early methods for the introduction of fluorine onto aromatic rings involved S_NAr reactions using a nucleophilic fluorine source[3] or a modification of the Sandmeyer reaction known as the

Balz-Schiemann reaction (Scheme 1).[4] More recently, electrophilic fluorine sources, such as Selectfluor, have been used in the presence of a silver salt to convert aromatic boronic acids[5] and stannanes[6] to their respective aryl fluorides. Selectfluor has also been used by Beller[7] and Knochel[8] in the fluorination of aromatic nucleophiles such as Grignard reagents. Nucleophilic attack on benzyne intermediates by the fluoride anion has also been explored.[9] In addition, Pd-catalyzed reactions involving reductive elimination of ArF products from Pd(IV) centers have



Scheme 1. Various methods for the synthesis of aryl fluorides.

been designed by Sanford[10] and Yu.[11] Mechanistic insights into reductive elimination from a Pd(IV) center were reported by Sanford[12] and Ritter.[13] While academically interesting, each of these Pd-catalyzed methods requires an *ortho*-directing group and as such are of limited synthetic utility. In 2011, Tobias Ritter published a method for deoxyfluorination of phenols using a nucleophillic fluorine source (Scheme 1).[14] The proposed mechanism involves *in situ* activation of the phenol followed by nucleophillic displacement by fluoride.[15]

Pd(0/II)-catalyzed cross-coupling has undergone tremendous evolution over the past 30 years and has allowed for the formation of aromatic or vinylic C–C, C–N, C–O and C–S bonds.[16]

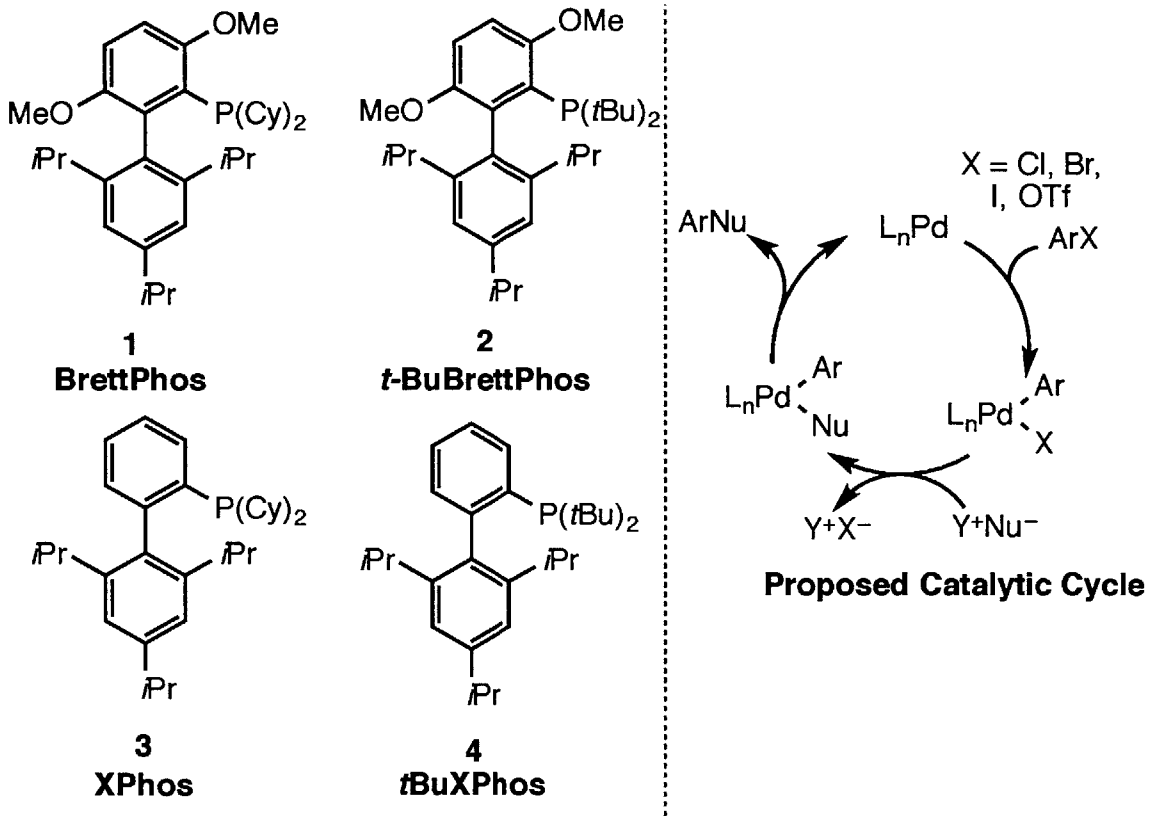
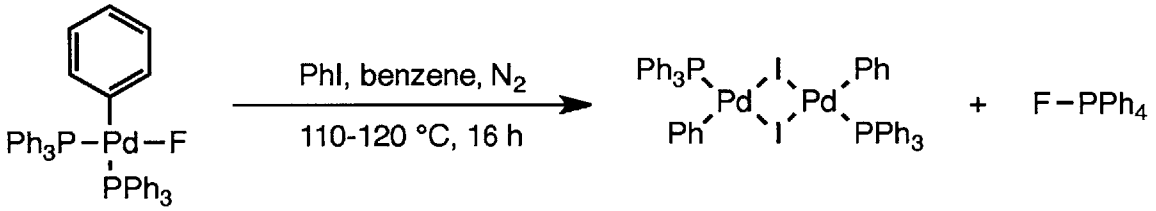


Figure 2. Ligands commonly employed in Pd-catalyzed cross-coupling reactions and the proposed catalytic cycle.

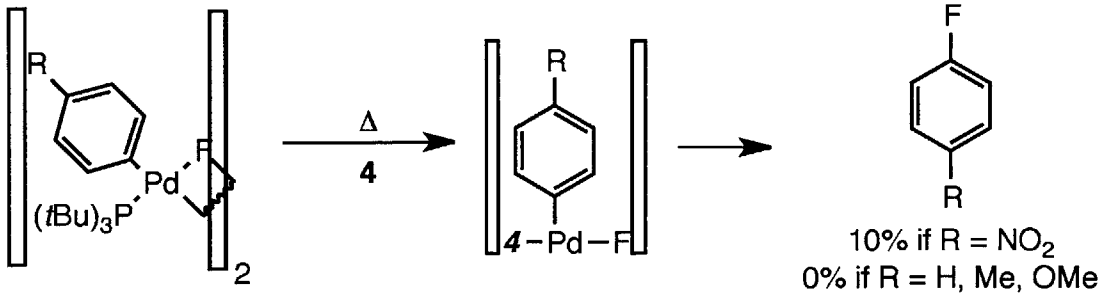
Our group has developed a set of dialkylbiarylphosphine ligands for use in Pd-catalyzed cross-coupling processes such as (Figure 2). The proposed catalytic cycle for Pd-catalyzed cross-coupling reactions is depicted in Figure 2 as well.

Due to the importance of ArF compounds, much attention has been devoted to the advancement of fluorination reactions of aryl halides and pseudohalides using palladium catalysis. Complexes of the type LPd(Ar)F, where L = $P(Ph)_3$ have been prepared and their ability to reductively eliminate C-F bonds has been studied extensively. In each case, however, extensive decomposition of the complex was observed with fluorination of the ligand being the major process of the reaction (Scheme 2).[17]



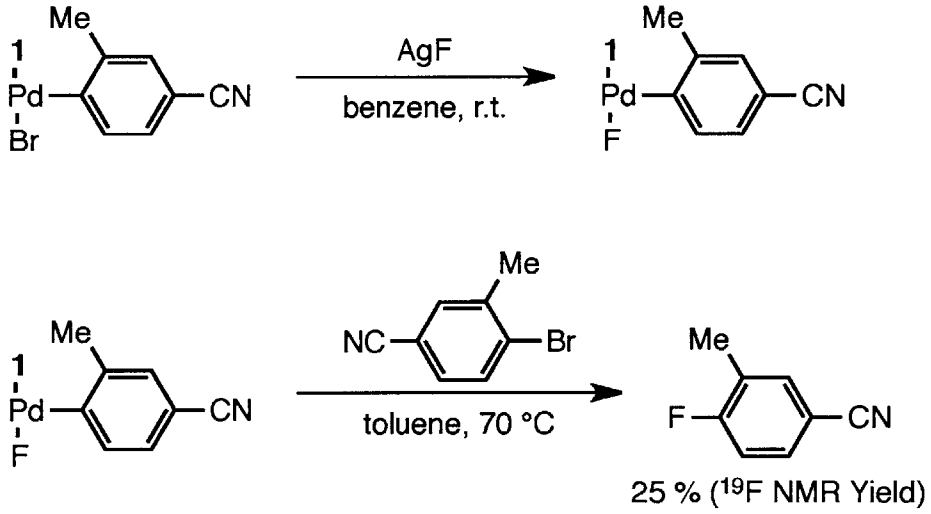
Scheme 2. Early work on the reductive elimination of aryl-F bonds from a Pd(II) center.

Early work by Yandulov has suggested that heating $(t\text{Bu})_3\text{PPd(Ar)F}$ dimer complexes, when in the presence of *t*BuXPhos (**4**) can effect reductive elimination to form aryl fluorides (Scheme 3).[18] However, it has been suggested in later publications that the observed ArF product could have arisen via an S_NAr reaction.[19]



Scheme 3. Demonstration of potential reductive elimination of aryl-F bonds from a Pd(II) center.

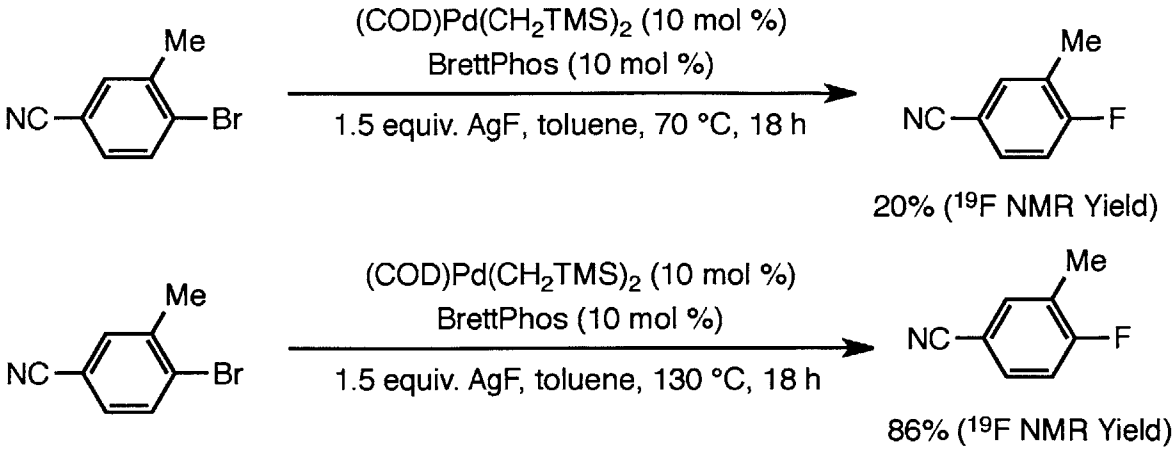
Based on this work, Dr. Donald Watson, a post-doctoral fellow in the Buchwald Group, and visiting student Mingjuan Su demonstrated unambiguously that reductive elimination of ArF from Pd(II) centers using BrettPhos (**1**) is feasible in stoichiometric reactions. Thus, when a (**1**)Pd(Ar)F complex was heated to 70 °C in the presence of an excess of aryl bromide, signals in the ^{19}F NMR spectrum were observed corresponding to the aryl fluoride compound which is reductively eliminated from the Pd complex.



Scheme 4. First example of reductive elimination of an aryl-F bond from a Pd(II) center.

1.2: Results and Discussion

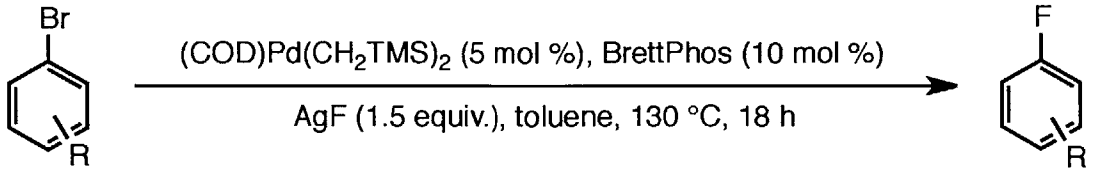
After demonstrating the viability of reductive elimination of ArF from (**1**)Pd(Ar)F, a catalytic version of the stoichiometric reaction was devised. Using 10 mol % of (COD)Pd($CH_2TMS)_2$ and 10 mol % of **1** in the presence of an aryl bromide at 70 °C, 20% of the desired aryl fluoride product was obtained. Encouraged by this result, the reaction was repeated at 130 °C, which resulted in full conversion of the aryl bromide and an 86% yield of product, as judged by ^{19}F NMR (Scheme 5).

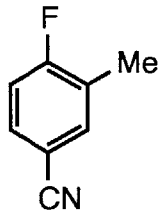
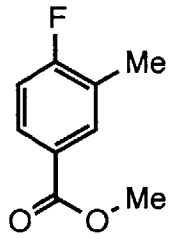
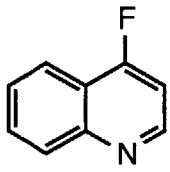
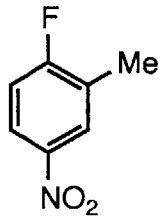


Scheme 5. First example of the Pd(0/II) catalyzed cross-coupling reaction toward the synthesis of aryl fluorides.

Currently, the Pd-catalyzed conversion of ArBr to ArF is only effective for the reaction of electron-deficient aryl bromides containing *ortho*-substituents (Table 1). Electron-neutral, electron-rich and electron-deficient aryl bromides without *ortho*-substitution do not afford ArF products. Control experiments have been performed for the reactions below to rule out the possibility that the reaction proceeds through an S_NAr pathway.

Table 1. Pd-catalyzed synthesis of aryl fluorides from aryl bromides.[a]

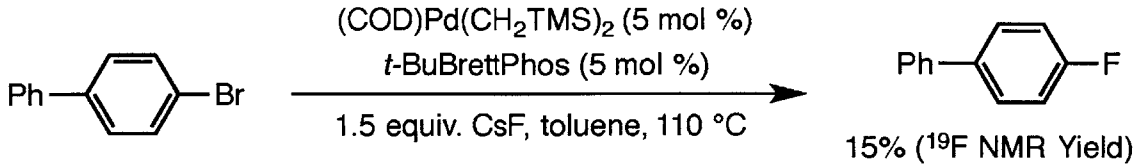


Entry	Product	Yield
1		85% Based on ^{19}F NMR
2		88% Based on ^{19}F NMR
3		74%
4		81%

a) ArBr (1 mmol); isolated yields are reported on a 1 mmol scale. ^{19}F NMR yields are reported relative to 4-fluorotoluene as standard.

An attempt was made to replace AgF with CsF as the fluoride source in order to reduce the amount of noble metal present in the reaction. The much bulkier ***t*BuBrettPhos (2)** was employed in order to facilitate the reductive elimination of ArF from the Pd(II) center. Reaction of 4-bromobiphenyl with CsF in the presence of catalytic amounts of $(COD)Pd(CH_2TMS)_2$ and **2** resulted in a poor yield (15%) of the desired product (Scheme 6). Although this system proved to

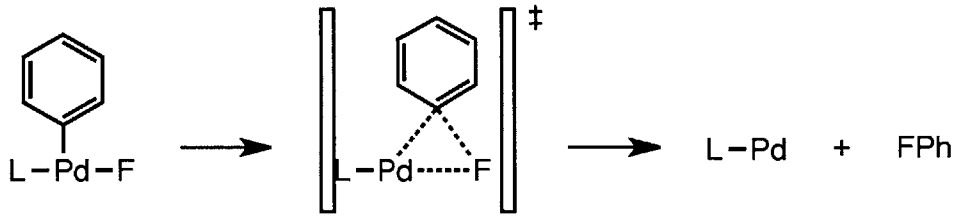
be inefficient for the formation of ArF products from aryl bromides, it found later use in the conversion of aryl triflates to their corresponding aryl fluorides.

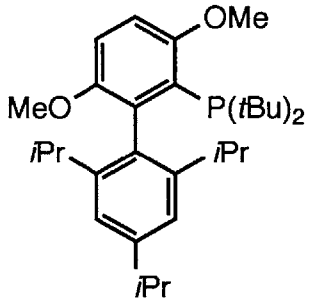
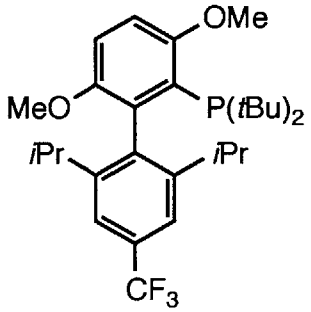
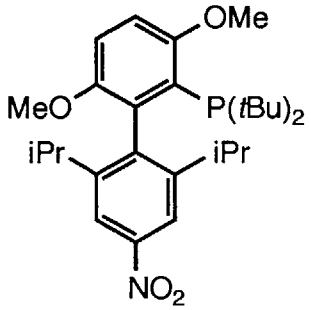


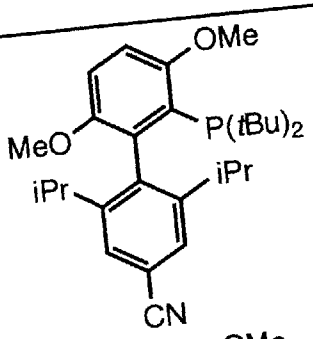
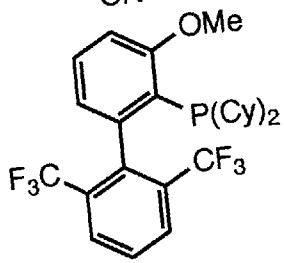
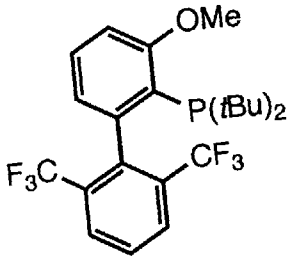
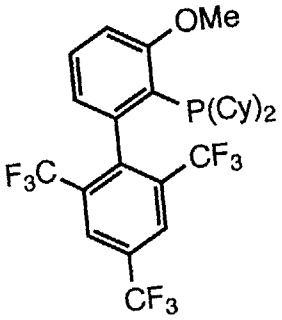
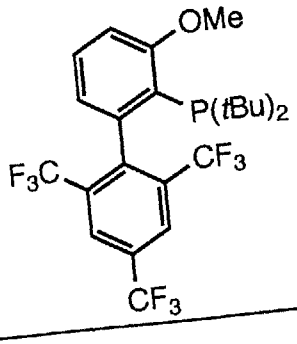
Scheme 6. First example of using CsF in the Pd(0/II)-catalyzed synthesis of aryl fluorides from aryl bromides.

Several strategies were pursued to improve the scope and yield of the conversion of aryl bromides to their corresponding fluorides. Computational analysis of the reactive intermediates indicated that modification of the ligand backbone could provide an appropriate avenue of exploration. A series of complexes were modeled using density functional theory (DFT) with the B3LYP functional at the 6-31G(d) level of theory for C, H, O and P atoms, 6-311++g(d,p) for F atoms and LANL2DZ with effective core potential for Pd in order to determine which ligand backbone could have the correct electronic and steric properties in order to facilitate reductive elimination of an aryl–F bond. Complexes with **2** as the ligand were taken to be the reference point (Table 2).

Table 2. Computational structure-reactivity analysis of the reductive elimination of aryl-F bonds from a Pd(II) center.



Entry	Ligand	$\Delta\Delta G^{\ddagger}$ (Kcal/mol)
1		0
2		+0.3
3		-1.4

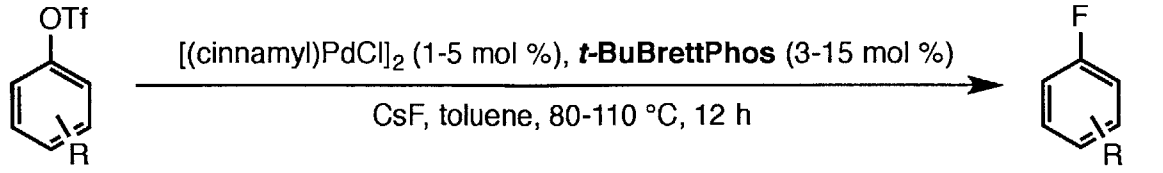
4		-0.2
5		+1.7
6		-1.0
7		+1.7
8		-0.3

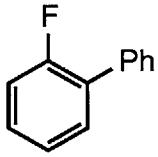
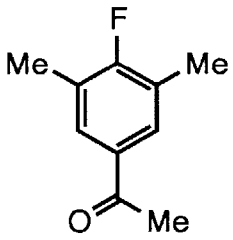
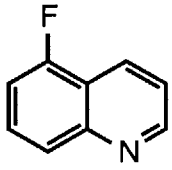
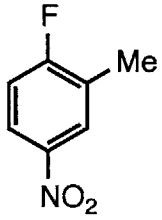
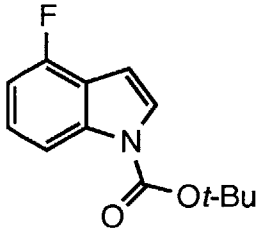
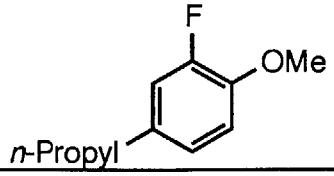
Based on these data, we attempted to synthesize a range of ligands in order to determine their efficacy in the reaction and to validate our computational model. Despite our best efforts, however, all attempts to synthesize these ligands failed at the C-P bond-forming event (Table 2, Entries 3, 4, 5 and 6). Under all attempted reaction conditions, the ligand backbone was consumed resulting in an inseparable mixture of various phosphine-containing species in all cases. Due to the extreme difficulty in the synthesis of ligands with electron-deficient bottom rings, this approach was put on hold.

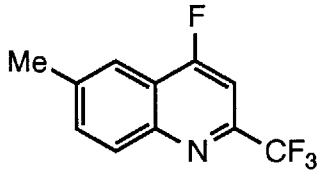
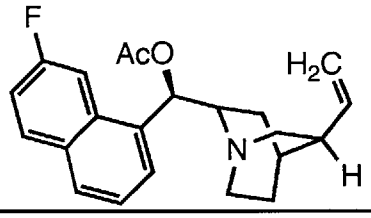
Concurrent with these efforts, Dr. Gracia-Fortanet and Dr. Yong Zhang developed an analogous system for the conversion of aryl triflates to their corresponding aryl fluorides.[20] Although this work was performed entirely by these postdoctoral associates, the results are presented in this context for completeness.

Aryl triflates provided a mechanistic pathway by which transmetallation occurs more readily; oxidative addition of an aryl triflate to a Pd(0) intermediate generates an cationic Pd(II) center. As such, it was believed that aryl triflates could provide ready access to the requisite LPd(Ar)F intermediate.[21] By utilizing **2** as the ligand, a wide range of aryl triflates were converted to their corresponding fluorides in good to excellent yields. In this way, both electron–deficient and –neural aryl trifluoromethansulfonates were transformed to the aryl fluoride products. Heteroaryl trifluoromethansulfonates, such as quinolones, pyridines and indoles, were also readily converted to the heteroaryl florides. Finally, Dr. Fortanet and Dr. Zhang were able to utilize the triflate derived from quinine as a viable substrate in the reaction, demonstrating the direct applicability of this chemistry in a more synthetically challenging context (Table 3).

Table 3. Pd-catalyzed synthesis of aryl fluorides from aryl trifluoromethansulfones.[a]



Entry	Product	Yield
1		82%
2		83%
3		75%
4		80%
5		73%
6		63%

7		83%
8		70%

a) ArOTf (1 mmol). Isolated yields are reported as an average of two runs.

1.3: Conclusion

Currently, the transformation of aryl bromides to the corresponding aryl fluorides is limited to electron-deficient substrates with *ortho*-substituents. An efficient method with much greater substrate scope has been developed for the conversion of aryl triflates to aryl fluorides using catalytic amounts of palladium and ligand **2**. Efforts to adapt the latter system to utilize aryl bromides are currently underway by other members of the Buchwald Group.

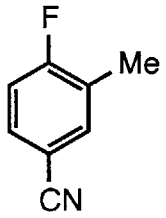
1.4: Experimental

$[Pd(cinnamyl)Cl]_2$[22] and $(COD)Pd(CH_2TMS)_2$[23] were prepared according to literature procedure and stored at –20 °C. *t*-BuBrettPhos[24] and BrettPhos[23] were prepared according to literature procedure. CsF was purchased from Aldrich Co. and was dried at 200°C for 12h under high vacuum (< 1 torr) prior to use and was stored and weighed inside a glovebox. AgF was purchased from Aldrich Co. and used as received. Anhydrous toluene was purchased from *J.* T. Baker in CYCLE-TAINER$^{(R)}$ solvent-delivery kegs and vigorously purged with argon for 2h. The solvent was further purified by passing it under argon pressure through two packed columns

of neutral alumina and copper (II) oxide. All other reagents from commercial sources were used as received. All reactions were performed in oven-dried, screw-cap test tubes with teflon seals under an atmosphere of argon. Flash chromatography was performed with silica gel from American International Chemical, Inc. (40-63 Micron).

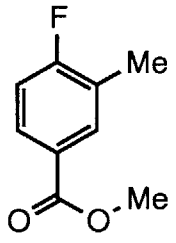
All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, IR spectroscopy, melting point (if necessary) and in most instances, elemental analysis. The ratio between reduction product and fluorination product was determined by GC analysis. ^{1}H, ^{13}C NMR, and ^{19}F spectra were recorded on a Varian XL 300 MHz or a Bruker DRX 400 MHz instrument. Infrared spectra were recorded on a Perkin-Elmer Model 2000 FT-IR using NaCl plates (thin film). All GC analyses were performed on an Agilent 6890 gas chromatograph with an FID detector using a J&W DB-200 column (30 m, 0.25 mm I.D.) or a DB-1 column (10 m, 0.1 mm I. D.). ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to residual $CHCl_3$ (7.27 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77 ppm) and were obtained with 1H decoupling. All coupling constants were reported in Hz. Melting points were obtained on a Mel-Temp capillary melting point apparatus. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA.

Synthesis of Fluoroarenes from Bromoarenes



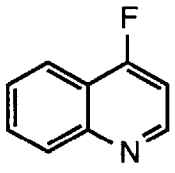
4-Fluoro-3-methylbenzonitrile. 4-Bromo-3-methylbenzonitrile (23.3 mg, 0.12 mmol), BrettPhos (6.4 mg, 0.012 mmol, 10 mol%), (COD)Pd($CH_2TMS)_2$ (2.3 mg, 0.006 mmol,

5 mol%) and AgF (22.8 mg, 0.18 mmol, 1.5 equivalents) and toluene (2 mL) were added to an oven dried resealable tube equipped with a stir bar. The tube was then sealed with a cap and taken out of the glove box, wrapped in aluminum foil and placed into a preheated 130°C oil bath with adequate stirring. After 18 h the tube was removed from the oil bath and allowed to cool to room temperature. *p*-Fluorotoluene (6.5 μL, 0.06 mmol, 0.5 equivalent) and dodecane (27.3 μL, 0.12 mmol, 1 equivalent) were added as standards. The reaction mixture was filtered through a glass filter and a plug of celite to remove all solids. The clear pale yellow solution was then analyzed by ^{19}F NMR (282 MHz) for yield and GC for conversion as well as reduction product. The yield is determined by comparing integration of the ^{19}F NMR resonance of *p*-Fluorotoluene (-118 ppm) and that of 4-fluoro-3-methylbenzonitrile (-108 ppm, 0.103 mmol, 85% yield). The ^{19}F-NMR chemical shift of the product corresponds to that of the authentic sample purchased from Alfa Aesar.



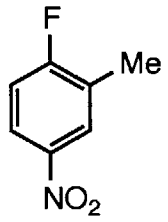
Methyl 4-fluoro-3-methylbenzoate. Methyl 4-bromo-3-methylbenzoate (27.5 mg, 0.12 mmol), BrettPhos (6.4 mg, 0.012 mmol, 10 mol%), (COD)Pd($CH_2TMS)_2$ (2.3 mg, 0.006 mmol, 5 mol%), AgF (22.8 mg, 0.18 mmol, 1.5 equivalents) and toluene (2 mL) were added to an oven dried resealable screw top test tube equipped with a stir bar. The tube was then sealed with a cap and taken out of the glove box, wrapped in aluminum foil and placed into a preheated 130°C oil bath with adequate stirring. After 18 h the tube was removed from the oil bath and allowed to cool to room temperature. *p*-Fluorotoluene (6.5 μL, 0.06 mmol, 0.5 equivalent) and dodecane (27.3 μL, 0.12 mmol, 1 equivalent) were added as standard. The reaction mixture was

filtered through a glass filter and a plug of celite to remove all solids. The clear yellow solution was then analyzed by ^{19}F NMR (282 MHz) for yield and GC for conversion as well as reduction product. The yield is determined by comparing integration of the ^{19}F NMR resonance of *p*-Fluorotoluene (-118 ppm) and that of methyl 4-fluoro-3-methylbenzoate (-110 ppm, 0.100 mmol, 88% yield). GC/MS analysis of the sample confirmed that the only compound in solution is methyl 4-fluoro-3-methylbenzoate.



4-Fluoroquinoline.[25] 4-Bromoquinoline (250 mg, 1.2 mmol), BrettPhos (64 mg, 0.12 mmol, 10 mol%), (COD)Pd($CH_2TMS)_2$ (23 mg, 0.06 mmol, 5 mol%), AgF (228 mg, 1.8 mmol, 1.5 equivalents) and toluene (20 mL) were added to a flame dried 50 mL schlenk flask equipped with a stir bar. The schlenk flask was sealed with a glass stopper and removed from the glove box, wrapped in aluminum foil and placed into a preheated 130°C oil bath. After 18 h the flask was removed from the oil bath and allowed to cool to room temperature. The solution was filtered through celite to afford a clear yellow liquid. The solvent was removed and the product was purified by column chromatography (Et_2O:Hexanes) to afford a clear yellow oil (131 mg, 0.89 mmol, 74%). The spectroscopic data correspond to those reported in the literature. ^1H NMR (300 MHz, CH_2Cl_2) δ 8.85 (dd, J = 8.5, 5.0 Hz, 1H), 8.11 (dddd, J = 9.0, 8.3, 1.7, 0.8 Hz, 2H), 7.78 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.61 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.11 (dd, J = 9.9, 5.0 Hz, 1H). ^{13}C NMR (75 MHz, CH_2Cl_2) δ 165.35 (d, J = 267.7 Hz), 151.67 (d, J = 7.8 Hz), 150.71 (d, J = 4.5 Hz), 130.62 (d, J = 1.0 Hz), 129.35 (d, J = 3.9 Hz), 127.04 (d, J = 1.6 Hz), 120.52 (d, J = 5.2 Hz), 119.64 (d, J = 13.1 Hz), 105.80 (d, J = 14.5 Hz). ^{19}F NMR (282 MHz, CH_2Cl_2) δ -116.43 (t, J = 9.2 Hz). IR (neat) ν_{max} 3065.75, 2927.95, 1910.32, 1630.93, 1605.94, 1564.88,

1508, 1499.66, 1467.94, 1418.78, 1394.03, 1303.44, 1261.31, 1252.29, 1216.13, 1184.18, 1157.05, 1085.59, 1054.67, 1030.7, 1010.67, 960.2, 875.58, 830.21, 809.46, 760.32, 714.69 cm^{-1}.

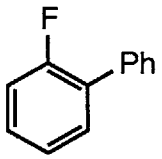


1-fluoro-2-methyl-4-nitrobenzene.[26] 1-bromo-2-methyl-4-nitrobenzene (216 mg, 1.0 mmol), BrettPhos (58.7 mg, 0.11 mmol, 10 mol%), (COD)Pd($CH_2TMS)_2$ (20 mg, 0.05 mmol, 5 mol%), AgF (200 mg, 1.5 mmol, 1.5 equivalents) and toluene (20 mL) were added to a flame dried 50 mL schlenk flask equipped with a stir bar. The schlenk flask was sealed with a glass stopper and removed from the glove box, wrapped in aluminum foil and placed into a preheated 130°C oil bath. After 18 h the flask was removed from the oil bath and allowed to cool to room temperature. The solution was filtered through silica to afford a clear yellow liquid. The solvent was removed and the product was purified by column chromatography (CH_2Cl_2:Hexanes) to afford a pale yellow solid (m.p., 36-38 °C, 128 mg, 0.83 mmol, 83%). The spectroscopic data correspond to those reported in the literature. ^1H NMR (300 MHz, CH_2Cl_2) δ 8.44 – 7.76 (m, 2H), 7.16 (t, J = 8.8 Hz, 1H), 2.38 – 2.35 (m, 3H). ^{13}C NMR (75 MHz, CH_2Cl_2) δ 165.07 (d, J = 255.6 Hz), 137.22 (d, J = 1056.9 Hz), 127.28 (d, J = 7.2 Hz), 127.00 (d, J = 19.6 Hz), 115.95 (d, J = 25.0 Hz), 14.53 (d, J = 3.4 Hz). ^{19}F NMR (282 MHz, CH_2Cl_2) δ -105.19 (q, J = 6.3 Hz). IR (neat) ν_{max} 3086.08, 1583.89, 1515.99, 1492.04, 1382.3, 1341.92, 1316.43, 1278.01, 1260.29, 1241.92, 1184.62, 1120.23, 1089.35, 924.7, 905.32, 827.59, 811.59, 759.52, 745.23, 697.27 cm^{-1}.

Synthesis of Fluoroarenes from Trifluoromethanesulfonates (Jorge Garcia-Fortanet/Yong Zhang)

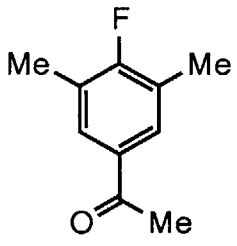
Representative procedure for the fluorination reaction of aryl triflates

To an over-dried screw-cap test tube equipped with a magnetic stir bar was added 1 mmol of substrate, 2 mmol of cesium fluoride 2 mol% $[Pd(cinnamyl)Cl]_2$ and 6 mol % *t*BuBrettPhos inside a glovebox. The test tube was then sealed off with a screw-cap and taken out of the glovebox. Toluene (5 mL) was promptly added via syringe in such a manner that any reagent on the side of the test tube was washed down to the bottom of the tube. The test tube was then placed in a pre-heated oil bath at 110 °C and stirred for 12 h. After cooling to room temperature, the reaction was diluted with EtOAc (~5 mL) and the resulting mixture was filtered through a plug of Celite. An aliquot of the filtrate was taken out for GC analysis. The rest of the filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel using hexane to give the title compound.

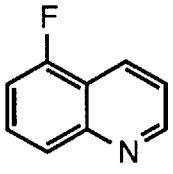


2-fluorobiphenyl.[27] The title compound was prepared according to the representative procedure with 2-biphenyl trifluoromethanesulfonate (302 mg, 1 mmol, 1.0 eq), cesium fluoride (304 mg, 2 mmol, 2.0 eq), [Pd(cinnamyl)Cl]2 (10.4 mg, 0.02 mmol) and *t*BuBrettPhos (29.4 mg, 0.06 mmol) in toluene (5 mL) at 110 °C for 12 h. Concentration and purification via flash column chromatography gave the desired product as a white solid; m.p. 72-74 °C; yield: 137 mg (81% yield). The spectroscopic data correspond to those reported in the literature. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, J= 8.0, 2H), 7.47-7.40 (m, 3H), 7.39-7.27 (m, 2H), 7.24-7.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.8 (d, J = 247.7), 135.8 (d, J = 1.0), 130.8 (d, J = 3.5), 129.1 (d, J = 2.9), 129.0 (d, J = 8.3), 128.4, 127.6, 124.4 (d, J = 3.7), 116.1 (d,

J = 22.8). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −118.4. IR (neat) ν_{max} 3023, 1614, 1567, 1506, 1389, 1258, 1187,1282, 1061, 925, 861, 834.

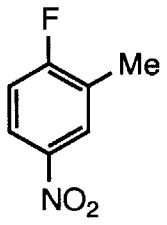


1-(4-fluoro-3,5-dimethylphenyl)ethanone. The title compound was prepared according to the representative procedure with 4-acetyl-2,6-dimethylphenyl trifluoromethanesulfonate (296 mg, 1 mmol, 1.0 eq), cesium fluoride (304 mg, 2 mmol, 2.0 eq), [Pd(cinnamyl)Cl]2 (10.4 mg, 0.02 mmol) and *t*BuBrettPhos (29.4 mg, 0.06 mmol) in toluene (5 mL) at 110 °C for 12h. Concentration and purification via flash column chromatography (10% EtOAc in hexane) gave the desired product as yellow oil. Yield: 141 mg, 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.58 (d, J = 7.0, 2H), 2.50 (s, 3H), 2.24 (d, J = 2.2, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 196.9, 162. 8 (d, J = 252.2), 132.5 (d, J = 3.7), 129.4 (d, J = 6.4), 124.6 (d, J = 18.8), 26.3, 14.5 (d, J = 4.1). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −113.9. IR (neat) ν_{max} 2959, 2926, 1685, 1597, 1487, 1418, 1358, 1319, 1181, 1094, 726 cm^{-1}.

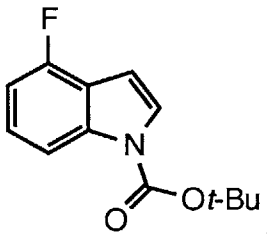


5-Fluoroquinoline.[25] The title compound was prepared according to the representative procedure with 5-quinolinyl trifluoromethanesulfonate (277 mg, 1 mmol, 1.0 eq), cesium fluoride (304 mg, 2 mmol, 2.0 eq), [Pd(cinnamyl)Cl]2 (10.4 mg, 0.02 mmol) and *t*BuBrettPhos (29.4 mg, 0.06 mmol) in toluene (5 mL) at 110 °C for 12h.

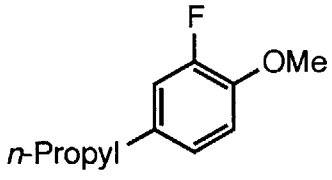
Concentration and purification via flash column chromatography (dichloromethane) gave 5-fluoroquinoline as yellow oil. yield: 108 mg (73% yield). The spectroscopic data correspond to those reported in the literature. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.91 (d, J = 4.2, 1H), 8.52-8.24 (m, 1H), 7.86 (t, J = 7.2, 1H), 7.58 (dt, J = 8.5, 4.2, 1H), 7.40 (dd, J = 8.4, 4.2, 1H), 7.16 (dd, J = 9.1, 8.3, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.7 (d, J = 255), 151.2, 148.9 (d, J = 3.0), 129.2 (d, J = 4.7), 128.9 (d, J = 9.1), 125.3 (d, J = 4.2), 121.1 (d, J = 2.7), 119.0 (d, J = 16.4), 110.1 (d, J = 19.3). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −123.3. IR (neat) ν_{max} 3070, 1636, 1598, 1567, 1470, 1400, 1251, 1069, 796 cm^{-1}.



1-fluoro-2-methyl-4-nitrobenzene.[26] The title compound was prepared according to the representative procedure with 2-methyl-4-nitrophenyl trifluoromethanesulfonate (285 mg, 1 mmol, 1.0 eq), cesium fluoride (304 mg, 2 mmol, 2.0 eq), [Pd(cinnamyl)Cl]2 (5.2 mg, 0.01 mmol) and *t*BuBrettPhos (14.7 mg, 0.03 mmol) in toluene (5 mL) at 110 °C for 12h. Concentration and purification via flash column chromatography (5% EtOAc in hexane) gave the desired product as colorless crystals. m.p. 39-41 °C. Yield: 128 mg, 82%. The spectroscopic data correspond to those reported in the literature. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.18-8.03 (m, 2H), 7.12 (t, J = 8.7, 1H), 2.35 (d, J = 2.0, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.8 (d, J = 256.2), 143.9, 127.1 (d, J = 7.1), 126.6 (d, J = 19.5), 123.4 (d, J = 10.0), 115.7 (d, J = 25.0), 14.6 (d, J = 5.0). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −106.4. IR (neat) ν_{max}: 3086, 1584, 1522, 1493, 1346, 1244, 1090, 905, 828, 746 cm^{-1}. Anal. calcd for $C_7H_6FNO_2$ C 54.20; H 3.90 found C 54.37; H 3.77.

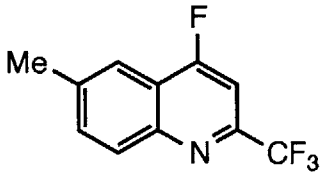


***tert*-butyl 4-fluoro-1*H*-indole-1-carboxylate.**[28] The title compound was prepared according to the representative procedure with 4-(N-Boc)indolyl trifluoromethanesulfonate (350 mg, 1 mmol, 1.0 eq), cesium fluoride (304 mg, 2 mmol, 2.0 eq), [Pd(cinnamyl)Cl]2 (10.4 mg, 0.02 mmol) and *t*BuBrettPhos (29.4 mg, 0.06 mmol) in toluene (5 mL) at 110 °C for 12h. Concentration and purification via flash column chromatography (2% EtOAc in hexane) gave the desired product as colorless oil that solidifies upon standing. m.p. 49-51 °C; Yield: 163 mg, 69%. The spectroscopic data correspond to those reported in the literature. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.96 (d, J = 8.3, 1H), 7.58 (d, J = 3.7, 1H), 7.25 (td, J = 8.2, 5.5, 1H), 6.93 (dd, J = 9.7, 8.1, 1H), 6.69 (d, J = 3.8, 1H), 1.70 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 155.7 (d, J = 247.3), 149.5, 137.3 (d, J = 9.3), 125.8, 124.8 (d, J = 7.5), 119.3 (d, J = 22.1), 111.2 (d, J = 3.8), 107.8 (d, J = 18.2), 102.7 (d, J = 4.2), 84.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ: −122.6 IR (neat) ν_{max}: 2980, 1737, 1588, 1491, 1437, 1348, 1286, 1220, 1133, 963, 749 cm^{-1}. Anal. calcd for $C_{13}H_{14}FNO_2$ C 66.37; H 6.00 found C 66.18; H 5.97.



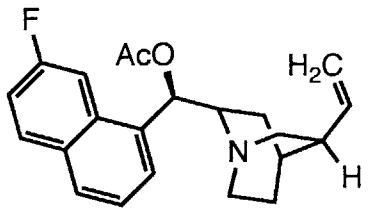
1-fluoro-2-methoxy-4-propylbenzene. The title compound was prepared according to the representative procedure with 2-methoxy-4-propylphenyl trifluoromethanesulfonate (332 mg, 1 9mol, 1.0 eq), cesium fluoride (304 mg, 2 mmol, 2.0 eq),

[Pd(cinnamyl)Cl]2 (10.4 mg, 0.02 mmol) and *t*BuBrettPhos (29.4 mg, 0.06 mmol) in cyclohexane (5 mL) at 130 °C for 12h. Concentration and purification via flash column chromatography (5% EtOAc in hexanes) gave the desired product as colorless oil. Yield: 106 mg, 63%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.97 (ddd, J = 11.4, 8.2, 1.1, 1H), 6.78 (d, J = 8.3, 1H), 6.73-6.65 (m, 1H), 3.88 (s, 3H), 2.55 (t, J = 7.5, 2H), 1.63 (dt, J = 7.5, 7.3, 2H), 0.95 (t, J = 7.3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.7 (d, J = 242.5), 147.1 (d, J = 10.8), 138.9 (d, J = 3.9), 120.4 (d, J = 6.5), 115.4 (d, J = 18.0), 113.5 (d, J = 1.7), 56.0, 37.7, 24.7 (d, J = 1.1), 13.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ: −140.6. IR (neat) ν_{max} 2961, 2934, 2872, 1609, 1518, 1465, 1417, 1269, 2826, 1153, 1282, 1035, 813, 773 cm^{-1}. Anal. calcd for $C_{13}H_{11}FO$ C 71.40; H 7.79 found C 71.18; H 8.00.



4-fluoro-6-methyl-2-(trifluoromethyl)quinoline. The title compound was prepared according to the representative procedure with 4-(6-methyl-2-trimethyl)-quinolinyl trifluoromethanesulfonate (229 mg, 1 mmol, 1.0 eq), cesium fluoride (304 mg, 2 mmol, 2.0 eq), [Pd(cinnamyl)Cl]2 (10.4 mg, 0.02 mmol) and *t*BuBrettPhos (29.4 mg, 0.06 mmol) in toluene (5 mL) at 80 °C for 12h. Concentration and purification via flash column chromatography (5% EtOAc in hexane) gave the desired product as a white solid. m.p. 107-110 °C. Yield: 192 mg, 84%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.06 (dd, J = 8.7, 1.3, 1H), 7.83 (s, 1H), 7.64 (dd, J = 8.7, 1.8, 1H), 7.34 (d, J = 9.6, 1H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.7 (d, J = 269.7), 148.1 (dq, J = 35.5, 8.4), 148.1 (d, J = 5.7), 139.5 (d, J = 1.7), 129.5 (d, J = 3.5), 121.1 (dq, J = 275.0, 4.5), 119.9 (d, J = 13.0), 119.1 (d, J = 4.5), 102.3 (dq, J = 19.1, 2.2),

21.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ: −68.0, −109.4. IR (neat) ν_{max} 1625, 1504, 1321, 1221, 1110, 831 cm^{-1}.



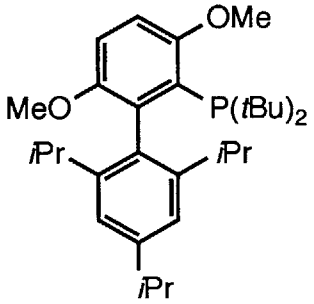
6-fluoro-O-acetyl-quinine. The title compound was prepared according to the representative procedure with O-acetyl-6-quininyl trifluoromethanesulfonate (242 mg, 0.5 mmol, 1.0 eq), cesium fluoride (152 mg, 1 mmol, 2.0 eq), [Pd(cinnamyl)Cl]2 (13 mg, 0.05 mmol) and *t*BuBrettPhos (36.8 mg, 0.15 mmol) in toluene (2.5 mL) at 110 °C for 12h. Concentration and purification via flash column chromatography (5% MeOH in EtOAc) gave the desired product as yellow foam. Yield: 132 mg, 74%. ^1H NMR (300 MHz, CD_3CN) δ: 8.84 (d, *J* = 4.5, 1H), 8.13 (dd, *J* = 9.3, 5.8, 1H), 8.00 (dd, *J* = 10.9, 2.7, 1H), 7.57 (ddd, *J* = 10.6, 9.0, 3.5, 2H), 6.23 (d, *J* = 9.1, 1H), 5.95 (ddd, *J* = 17.9, 10.3, 7.7, 1H), 5.15-4.90 (m, 2H), 3.38 (dd, *J* = 17.3, 8.8, 1H), 3.19-2.97 (m, 1H), 2.84 (dd, *J* = 13.6, 10.1, 1H), 2.59-2.34 (m, 2H), 2.26 (d, *J* = 9.6, 1H), 2.16-1.93 (m, 7H), 1.87-1.61 (m, 3H), 1.48 (ddd, *J* = 21.1, 9.7, 5.3, 3H). ^{13}C NMR (75 MHz, CD_3CN) δ: 169.8, 159.9 (d, *J* = 245.3), 149.2, 145.7 (d, *J* = 5.9), 145.2, 142, 132.5 (d, *J* = 9.6), 126.6 (d, *J* = 10.0), 119.7, 118.7 (d, *J* = 26.0), 116.9, 113.3 (d, *J* = 3.9), 107.1 (d, *J* = 23.4), 59.5, 55.5, 41.3, 39.4, 27.2, 26.9, 25.1, 19.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ: −114.2. IR (neat) ν_{max} 2943, 1745, 1625, 1514, 1468, 1230, 1026 cm^{-1}.

Computational Methods

All calculations were carried out with the Gaussian '03 suite.[29] All calculations were performed using the Becke[30-31] three-parameter hybrid functional combined with Lee–Yang–Parr[32] correlation functional. C, H, O, P, and S were computed at the 6-31G(d) level of theory, F was computed using 6-311++G(d,p) and for the Pd center, LANL2DZ+ECP was used.[33] Frequency calculations were undertaken to confirm the nature of the stationary points, yielding one imaginary frequency (NImag = 1) for transition states (TS) with largest contributions from internal coordinates involved in the reaction and none (NImag = 0) for minima. All optimizations were performed without any constraints (C1 symmetry). Geometry optimizations were carried out in the gas phase.

Cartesian Coordinates for Ground State Structures:

Minimum energy structures for LPd(Ph)F where L is:



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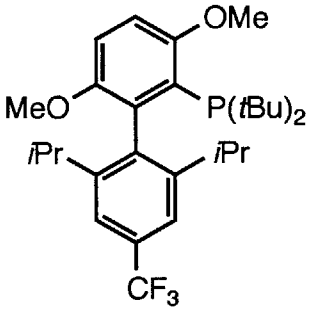

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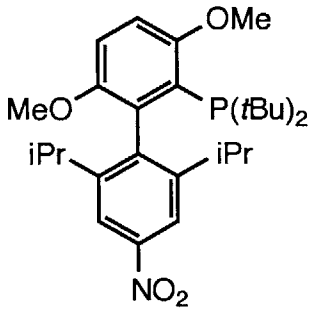

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C	-1.99101300	-0.35599400	-1.24726600
C	0.81390600	-1.99310400	0.08364200
C	-0.60214100	-1.95659200	0.14014100
C	-2.11285900	-0.20588600	1.21790300
C	1.44602900	-3.26727400	0.09595300
C	-3.58193100	1.09431000	-0.17621600
C	-3.15048700	0.71320800	1.08446700
C	0.71326200	-4.44164400	0.24073700
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C	-0.67546300	-4.39710900	0.31789300
C	1.45347700	3.57273500	1.27528600
C	1.55559700	3.73010500	-1.12613100
C	2.40297200	5.54843700	0.23835100
C	2.04596400	4.83659600	1.38358300
C	2.14770900	4.99293300	-1.01618100
H	-3.63145000	1.14809900	1.95045100
H	1.20862600	-5.40403000	0.27324000
H	-3.42425900	0.89302300	-2.28702100
H	-1.22856900	-5.32353300	0.41437400
H	1.16203200	3.05183500	2.18258600
H	1.33317900	3.33912100	-2.11332600
H	2.85969900	6.53124400	0.32193700
H	2.21620200	5.26401500	2.36937300
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C	-1.51435200	-0.99527500	-2.54937400
O	2.80123400	-3.28774200	-0.07676400
C	3.49163200	-4.52444200	0.01232300

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H	3.35165600	-4.99319000	0.99462700
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C	2.95645100	-0.50577200	-1.60955300
C	3.04973500	0.91940600	-2.18790900
C	4.39131100	-1.02017500	-1.38038000
C	2.28503600	-1.40487800	-2.66500700
H	2.06864500	1.28793800	-2.49403900
H	3.46510000	1.63869500	-1.47767800
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H	2.87784200	-1.35891900	-3.58811800
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H	1.27207500	-0.92453300	2.92057700
H	2.43134800	0.19274800	3.65210200
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H	4.26360200	-1.21748700	2.90674000
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H	4.50609200	-1.71277800	1.22934200
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H	-2.43994300	1.05837300	3.82382700
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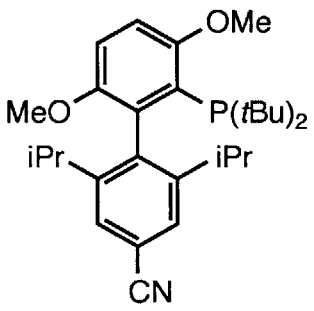

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C	1.90566400	0.67196600	0.12173000
C	1.56793000	-1.61433400	1.19695600
C	1.57639600	3.08231300	0.11250000
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C	-3.61350600	-1.37386000	1.25798500
C	-3.80307800	-1.40036200	-1.14256500
C	-5.73345800	-1.93803700	0.22549500
C	-4.95866500	-1.74608000	1.36929700
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H	1.57817600	-3.62883400	1.94724100
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H	1.63075500	-3.30926200	-2.31242400
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H	-3.36295300	-1.31532600	-2.13062600
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H	0.33744700	6.10872500	-0.01249700
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H	1.93079600	5.69263800	-0.69768400
C	-1.50713500	2.44344200	-1.59822100
C	-2.65695400	1.59504300	-2.17578100
C	-2.03866100	3.87251100	-1.36853300
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H	-2.30686200	0.60659800	-2.47979100
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C	3.03736600	-1.19866500	3.22675700
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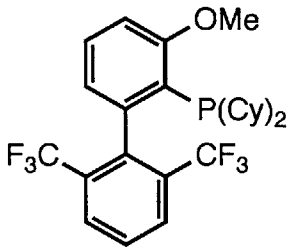

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C	4.42481800	0.25526900	2.22050600
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C	3.38387700	-2.66076700	-2.58575700
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H	2.18345600	1.79466000	1.69621500
H	2.97530100	2.73755800	-0.32903000
H	1.56398800	3.55009500	-0.98791300

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H	2.75115900	3.36706800	-4.60012700
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H	3.87205200	2.36212700	-2.62418900
H	-0.16344500	2.22104400	-2.39033100
H	0.10952200	0.51433600	-2.70961200
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H	2.70058300	1.26444700	4.20079200
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H	1.72946200	-1.31946800	-2.89443100
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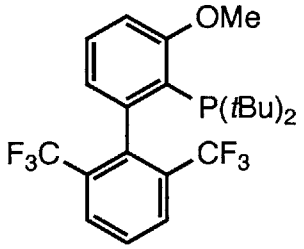

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C	-0.73668900	-2.28969900	1.35958300
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H	3.17821400	-0.19604600	-2.05922000
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C	1.20778400	2.53373200	2.15479800
C	-0.37855700	4.15333200	1.10445600
C	-1.24753500	2.26064100	2.47993500
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H	-0.40681200	3.72044900	-3.17651600
H	-1.75365900	2.84475300	-2.44325300
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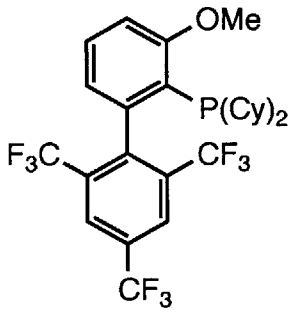
H	1.12658700	-5.03474500	0.59726700



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C	0.41512600	2.77549500	0.59086800
F	-2.19025300	2.03028000	0.39949600
C	-1.53878500	-1.33136800	-0.31718900
C	-0.76443500	-3.58601000	-0.85472400
C	-2.17619800	-0.67609900	-1.40966000
C	0.98910500	-1.92084000	-0.46371000
C	-0.37682100	-2.27412600	-0.53914100
C	-2.23442600	-1.30407300	0.92375400
C	1.93742500	-2.93944400	-0.74914700
C	-3.98710500	0.08179800	0.00178700
C	-3.42944500	-0.60195600	1.07329800
C	1.54186900	-4.24203300	-1.06871800
C	-3.37850400	0.01428200	-1.24158100
C	0.18762400	-4.56036800	-1.11468500
C	2.44480800	-0.11612300	1.57382800
C	2.71180800	0.35404800	-1.37678900
C	3.83079100	-0.78764000	1.65394800
C	3.66838800	-0.83597400	4.19042000
C	4.52333700	-0.42887700	2.98173200
C	1.57491200	-0.55206400	2.76989600
C	2.01778000	0.46473200	-2.74992400
C	3.43937000	1.67185500	-1.02788600
C	2.26372100	-0.22249900	4.10541300
C	3.01011100	0.87231200	-3.85222100
C	0.83270100	3.07065000	1.89091500
C	0.48131100	3.76209900	-0.39894700
C	4.43409800	2.06058700	-2.13647000
C	1.42907600	5.31902900	1.20262300
C	1.34225200	4.34018900	2.19260100
C	0.99225400	5.02775900	-0.09168100
C	3.74450400	2.17313700	-3.50253600
H	-3.91219400	-0.56983000	2.04323500
H	2.27908600	-5.00618800	-1.28165400
H	-3.82210800	0.52754900	-2.08598500
H	-0.11967800	-5.57275900	-1.36072500
H	2.59381700	0.96981800	1.66602300
H	3.45463000	-0.44785200	-1.42800500
H	4.46423200	-0.49293200	0.81016600
H	3.71374800	-1.87491500	1.59224300
H	3.58295900	-1.93250600	4.21771400
H	4.16028900	-0.53667700	5.12453600
H	5.50595200	-0.91646500	3.02724600
H	4.71058100	0.65457200	3.01423300
H	1.39065100	-1.63112000	2.71273800
H	0.59582000	-0.06322800	2.72655900
H	1.21390900	1.20918500	-2.68824500
H	1.54295000	-0.48441100	-3.01525100
H	3.97701200	1.58325200	-0.07740100
H	2.70809600	2.47673400	-0.90023400
H	2.33826100	0.86955000	4.21322300
H	1.63997300	-0.57621300	4.93592600
H	3.74669700	0.06716900	-3.99526300
H	2.47457500	0.97705600	-4.80431000
H	0.74488700	2.33127300	2.68125900
H	0.12925500	3.55558300	-1.40522400
H	4.91916900	3.00870600	-1.87223100
H	5.23252000	1.30511500	-2.19445500
H	1.82259600	6.30423500	1.43900400
H	1.66118000	4.56070500	3.20892800
H	1.03982400	5.78823700	-0.86793000
H	3.02199600	3.00170500	-3.47496200
H	4.47708600	2.42010400	-4.28154600
H	-1.82111300	-3.83057300	-0.90058000
C	-1.81289700	-2.04697900	2.17775700
C	-1.66596900	-0.65914500	-2.84006700
O	3.25101900	-2.57849700	-0.69871900
C	4.25422200	-3.54890000	-0.96805400
H	5.20554800	-3.02615700	-0.85820800
H	4.21098100	-4.37950400	-0.25288800
H	4.16889100	-3.94036000	-1.98918800
F	-2.77310700	-2.93541500	2.52899500
F	-1.67988700	-1.19209000	3.21820900
F	-0.66282500	-2.73518400	2.07787900
F	-2.66938100	-0.98291100	-3.68963900
F	-1.24860200	0.57794700	-3.19314200

F	-0.65525700	-1.51013700	-3.09226200
C	-5.28727800	0.82391200	0.17710100
F	-5.43522100	1.79997000	-0.73557300
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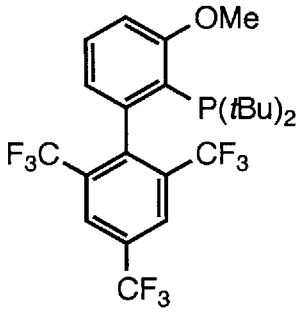

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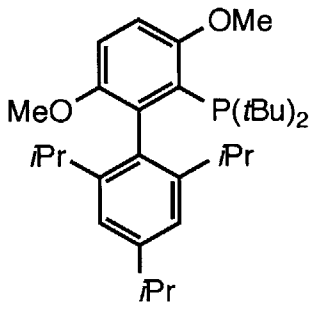
F	-2.37099400	1.40286500	-0.53255100
C	-0.74990100	-1.56664800	0.12828200
C	0.64069800	-3.52270300	0.48940500
C	-1.40711400	-1.54273100	-1.13667400
C	1.86190100	-1.41715300	0.16633900
C	0.64587800	-2.13434400	0.26891200
C	-1.58031700	-1.37531200	1.26944700
C	3.05696200	-2.18672800	0.24641700
C	-3.52427400	-0.98192300	-0.11366400
C	-2.93433500	-1.07679100	1.14014600
C	3.04030800	-3.56499900	0.47738500
C	-2.76890200	-1.24497600	-1.24299900
C	1.82532300	-4.23011800	0.60474900
C	-0.73610200	3.51789300	1.22091000
C	-0.27113000	3.91044900	-1.11534100
C	-0.70500900	5.78607700	0.36259300
C	-0.87587000	4.89525100	1.42338000
C	-0.41335500	5.28791300	-0.90716900
H	-3.52986800	-0.90072600	2.02874000
H	3.96591000	-4.12232900	0.54652900
H	-3.23169600	-1.19990000	-2.22022300
H	1.80994000	-5.30173900	0.78122800
H	-0.90590500	2.84153600	2.05259200
H	-0.07979100	3.54610300	-2.11792400
H	-0.81548200	6.85568900	0.52095500
H	-1.12994400	5.26552200	2.41404200
H	-0.30500900	5.96740200	-1.74965700
H	-0.31059800	-4.03967600	0.56623200
C	-1.13005800	-1.46766800	2.71602300
C	-0.73695800	-1.82499100	-2.46894500
O	4.22776300	-1.51540200	0.06034300
C	5.46148800	-2.21103400	0.18054100
H	6.23917700	-1.46422900	0.01273600
H	5.58260600	-2.64254900	1.18158500
H	5.55131500	-3.00213600	-0.57379300
F	-1.93522100	-2.31898700	3.39558200
F	-1.23934500	-0.26572300	3.32806300
F	0.13073900	-1.89814500	2.90159800
F	-1.58118500	-2.48593200	-3.29236500
F	-0.40799900	-0.67179200	-3.10646300
F	0.38173600	-2.56667000	-2.38647800
C	-4.99471800	-0.67212500	-0.22825300
F	-5.31460500	-0.18931300	-1.44157100
F	-5.38660100	0.21839000	0.70079800
F	-5.73402200	-1.79407500	-0.03620900
C	2.94096400	0.84067100	-1.65927600
C	2.26034500	2.03811800	-2.35186500
C	4.41968000	1.20203600	-1.41600700
C	2.88999100	-0.35675300	-2.62825400
H	1.23105500	1.79720900	-2.63249000
H	2.23770200	2.93033900	-1.72042500
H	2.81735900	2.28490500	-3.26555500
H	4.96940200	0.39269800	-0.93857500
H	4.88319300	1.39121200	-2.39342600
H	4.54550700	2.11209600	-0.82544100
H	3.38667000	-0.06030600	-3.56168700
H	3.41478200	-1.22994900	-2.23674000
H	1.87003500	-0.64196300	-2.88064300
C	2.65513400	1.22629000	1.52300700
C	2.78607400	2.75162800	1.32150400
C	1.64773000	0.96286200	2.65785600
C	4.01601600	0.66737200	1.97823700
H	3.54620900	3.01566700	0.58263900
H	1.84360000	3.21737400	1.03283100
H	3.09611400	3.19648800	2.27617900
H	1.57633100	-0.10027200	2.89414200
H	1.98927300	1.48364400	3.56194300
H	0.64930000	1.32946200	2.41488500
H	4.30683600	1.20534500	2.89048600
H	3.96004000	-0.39447600	2.22665200
H	4.80751200	0.81184600	1.24244000

Cartesian Coordinates for Transition State Structures:

Transition state structures for LPd(Ph)F where L is:



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C	0.92876000	3.24660200	0.05428300
F	-0.77875700	3.14493800	-0.11780600
C	-1.51347000	-0.79425800	0.12630800
C	-1.33595500	-3.24873000	0.29079400
C	-2.08164700	-0.38488600	-1.11675000
C	0.79494600	-2.05739400	0.06300100
C	-0.62264500	-2.02366600	0.17090800
C	-2.03043300	-0.23242200	1.33104000
C	1.43214000	-3.32804800	0.05650300
C	-3.51858500	1.22858300	0.03776800
C	-3.00159700	0.77073100	1.25074700
C	0.71270600	-4.50810900	0.21664200
C	-3.05678000	0.61840500	-1.12900300
C	-0.67346400	-4.46936600	0.33725000
C	1.25484300	3.69086800	1.34821100
C	1.52325700	3.85148200	-1.06639600
C	2.90845900	5.20567600	0.40688600
C	2.25788100	4.64748400	1.51159200
C	2.52431800	4.80407600	-0.87749000
H	-3.37228800	1.21626000	2.16998600
H	1.21340400	-5.46838000	0.22951400
H	-3.46658600	0.93120300	-2.08505400
H	-1.21844100	-5.39917500	0.44701900
H	0.73428400	3.28474000	2.20966600
H	1.21564700	3.56477400	-2.06628700
H	3.68298300	5.95492300	0.54246000
H	2.52331700	4.96412300	2.51815600
H	3.00176100	5.24391500	-1.75072400
C	-1.61384400	-0.71712600	2.71960400
C	-1.73137100	-1.05362700	-2.44544900
O	2.78491300	-3.33736800	-0.14869300
C	3.48443200	-4.56863700	-0.07947200
H	4.53656500	-4.32370800	-0.23604500
H	3.36632700	-5.04458800	0.90254800
H	3.15634200	-5.26461200	-0.86237100
C	-4.56454700	2.33310500	0.00292300
C	2.83968800	-0.57417700	-1.75158400
C	2.88627600	0.85654500	-2.33052900
C	4.28990100	-1.07987400	-1.62116700
C	2.10316600	-1.47624800	-2.75956900
H	1.88305400	1.23574500	-2.54185800
H	3.36522700	1.56882700	-1.65327500
H	3.45785300	0.84399100	-3.26899000
H	4.33787400	-2.09290400	-1.22590300
H	4.74045600	-1.08576200	-2.62330500
H	4.90944500	-0.42904700	-0.99980900
H	2.60633000	-1.40094400	-3.73292900
H	2.11535500	-2.52612800	-2.45742700
H	1.06654700	-1.16619800	-2.90458500
C	2.95394400	-0.29189500	1.42573300
C	3.77927000	1.00024400	1.23326800
C	2.02997200	-0.08872300	2.64004700
C	3.90697800	-1.45399800	1.76446100
H	4.52400400	0.91171500	0.43789400
H	3.14712600	1.86553500	1.02294900
H	4.32508200	1.20645100	2.16375700
H	1.42659000	-0.97946600	2.84162000
H	2.64219900	0.10693900	3.53059500
H	1.35908300	0.76003000	2.49246600
H	4.49727700	-1.15873700	2.64314300
H	3.36305900	-2.36484400	2.02453600
H	4.60666300	-1.68814400	0.96163100
H	-0.70444600	-1.31474900	2.60787000
H	-0.87821600	-1.71644100	-2.27595900
H	-4.68590200	2.69095600	1.03455900
C	-5.93343100	1.80223800	-0.46636100
H	-5.88022600	1.42702100	-1.49566600
H	-6.28280700	0.98153000	0.17054600
H	-6.68642400	2.59926500	-0.44094500
C	-4.10823200	3.53155500	-0.85091200
H	-3.11996700	3.87983900	-0.53741200
H	-4.04475400	3.26044700	-1.91201200
H	-4.82401400	4.35822700	-0.76355600
C	-1.30435100	0.43766800	3.69283400
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H	-0.63542300	1.17704300	3.24439700
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C	-2.69329100	-1.63117000	3.33898900
H	-2.36176600	-2.00680200	4.31518900
H	-3.62673900	-1.07632700	3.49256300
H	-2.91442100	-2.48379800	2.69328300
C	-1.32924900	-0.03980300	-3.53403200
H	-2.17706100	0.58442800	-3.83835800
H	-0.53691700	0.62912800	-3.18195700

H	-0.97231300	-0.56332600	-4.42944900
C	-2.89765400	-1.93459300	-2.94106200
H	-3.78362500	-1.32616100	-3.15856300
H	-2.61757600	-2.46044800	-3.86231900
H	-3.17867300	-2.67640800	-2.18801400
O	-2.70305200	-3.14720300	0.34578700
C	-3.46839300	-4.33820300	0.42762700
H	-3.25537700	-4.89583000	1.34963700
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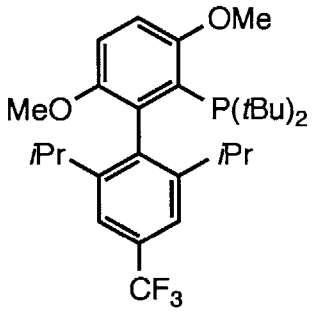

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F	-1.82359600	2.53425500	-0.35150000
C	-0.97464200	-1.32715000	0.07165300
C	0.12731800	-3.51865500	0.31306900
C	-1.59402400	-1.16947600	-1.20329500
C	1.64301900	-1.60024600	0.11353800
C	0.31944200	-2.11635100	0.17765900
C	-1.71095800	-0.99417900	1.24958100
C	2.72045400	-2.52534800	0.16562200
C	-3.55580900	-0.21899100	-0.13184700
C	-2.98277500	-0.43315200	1.11893000
C	2.50495900	-3.88919000	0.34012800
C	-2.87326500	-0.60569900	-1.27723700
C	1.20752100	-4.38703200	0.41734900
C	-0.30940700	3.83920000	1.28285900
C	0.09661300	4.13516900	-1.10039900
C	0.68180300	5.90347300	0.46559700
C	0.20907400	5.11367900	1.51802400
C	0.61129800	5.40574500	-0.83994100
H	-3.53634500	-0.14666800	2.00588500
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H	-3.33896900	-0.45694500	-2.24465700
H	1.05869300	-5.45311500	0.53899300
H	-0.70538600	3.24439700	2.09968500
H	0.02282400	3.76728000	-2.11795100
H	1.07647700	6.89725400	0.65599700
H	0.23089300	5.49296000	2.53745700
H	0.95192100	6.01533900	-1.67424400
C	-1.19363300	-1.26841100	2.66107300
C	-0.96050800	-1.66559800	-2.50139600
O	3.97782000	-2.01258400	0.00426900
C	5.09595200	-2.87620200	0.13141500
H	5.97691400	-2.24520900	0.00104500
H	5.13110600	-3.34603900	1.12268700
H	5.09364700	-3.65610400	-0.64087400
C	-4.94703700	0.34264900	-0.23144700
C	3.02426000	0.53453100	-1.68076400
C	2.53133100	1.86322400	-2.29300100
C	4.55028000	0.63501100	-1.49036600
C	2.73983300	-0.59495800	-2.68869700
H	1.46772100	1.81557300	-2.54111100
H	2.66923300	2.71348600	-1.61933100
H	3.09547300	2.06533200	-3.21402000
H	4.97601400	-0.28182900	-1.08595000
H	5.00545100	0.81299300	-2.47429500
H	4.84102400	1.47076800	-0.85032800
H	3.22775200	-0.34723700	-3.64093300
H	3.13497900	-1.55613100	-2.35129700
H	1.67283700	-0.70660200	-2.89109600
C	2.89392100	0.89150200	1.48737000
C	3.15031100	2.40155000	1.27932400
C	1.91749700	0.73466900	2.66668200
C	4.21309500	0.20402100	1.88739900
H	3.90746400	2.60102400	0.51634400
H	2.23913300	2.94156900	1.01333100
H	3.52331500	2.82405500	2.22169500
H	1.70351600	-0.31796100	2.87736900
H	2.36808100	1.16983200	3.56868400
H	0.97527700	1.25033000	2.47244000
H	4.61161200	0.72838100	2.76705700
H	4.05936700	-0.84010700	2.16951000
H	4.97451600	0.24161000	1.10788800
H	-0.12145300	-1.47309300	2.59018900
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C	-0.95370300	-0.59489500	-3.60912400
H	-1.96735800	-0.35876700	-3.95191900
H	-0.49707400	0.33704800	-3.25999300
H	-0.39167800	-0.95460500	-4.47940100
C	-1.66752900	-2.94483500	-2.99758100
H	-2.71172000	-2.73852600	-3.26149000
H	-1.16703700	-3.33654100	-3.89158600
H	-1.66418900	-3.72165200	-2.22785200

O	-1.17461300	-3.95011800	0.32326500
C	-1.42775600	-5.34264100	0.42529100
H	-1.05030800	-5.75462700	1.37067000
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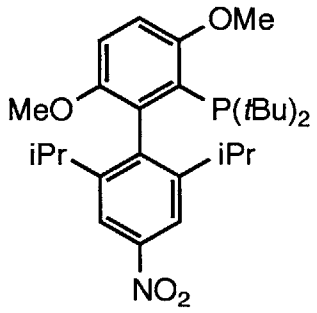

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C	-0.07706700	2.17273600	0.12371000
C	1.25596800	1.68296800	0.17110200
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C	-0.27080000	3.57906600	0.18540500
C	2.92726500	-2.26308000	-0.16046500
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C	2.09929500	3.96997100	0.40738500
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C	-2.64795700	-3.16636500	-1.13053200
C	-4.28786000	-4.12574200	0.38924300
C	-3.45059600	-3.82428600	1.46754400
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H	2.89312400	-2.35305800	1.96686400
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H	2.94400500	-1.96464300	-2.26830200
H	2.91876700	4.66939800	0.52029900
H	-1.56169400	-2.99091800	2.10495600
H	-2.31887900	-2.94199200	-2.13928600
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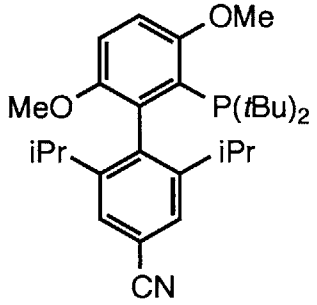

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C	1.30909400	-1.82323700	1.20206900
C	2.02801900	2.82311800	0.18873900
C	0.92090500	-3.77600200	-0.20193600
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C	3.41153200	2.84300800	0.34020900
C	1.15680500	-3.00848600	-1.34428500
C	4.12819700	1.65072100	0.38015300
C	-3.73598900	-1.23800400	1.25070000
C	-4.02970900	-0.98497300	-1.15335000
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H	1.11475200	-3.48921800	-2.31533000
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H	-3.14758700	1.89173100	-1.55984600
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C	3.19333100	-1.39338100	-3.07053900
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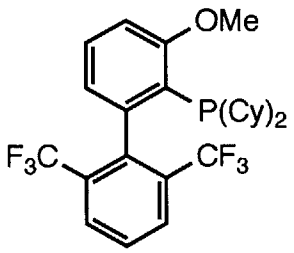

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C	-1.53492900	0.95056500	4.06842800
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H	-0.89816200	0.24936700	-3.00698700
H	-0.13595100	1.82547200	-2.85825900
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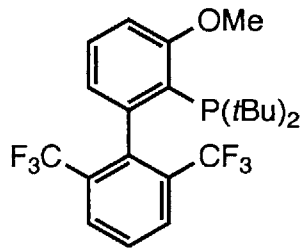

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C	0.87529500	-2.37308000	-1.22798200
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O	2.96298700	2.70947400	0.47267200
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F	-0.93594500	-1.83342600	3.01329500
F	1.17759400	-1.32191200	2.96048600
F	2.12994800	-2.89318400	-3.15497400
F	0.81628000	-1.17172900	-3.27005900
F	2.67735300	-1.05536200	-2.15146400
C	0.47727500	2.60171300	-1.58074100
C	-0.84443200	2.53173000	-2.37928500
C	0.76559900	4.08143300	-1.26220000
C	1.60779600	2.06859600	-2.48131800
H	-1.04499200	1.51345000	-2.72562000
H	-1.70716100	2.85759100	-1.79112900
H	-0.76529300	3.18810200	-3.25665600
H	1.70114000	4.21129600	-0.71961700
H	0.85063500	4.62496600	-2.21294700
H	-0.03894500	4.55635200	-0.69590400
H	1.64843600	2.68635000	-3.38859500
H	2.58531400	2.12659500	-1.99621100
H	1.43331800	1.03967600	-2.79607100
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C	-1.70047300	3.05380000	1.13588500
C	-0.61613900	1.34269000	2.59729000
C	0.59787500	3.44733900	2.08553900
H	-1.59185000	3.86427400	0.40971400
H	-2.42473600	2.33405800	0.74839000
H	-2.12529300	3.49274400	2.04822600
H	0.30216300	0.83967600	2.90698000
H	-1.02904500	1.85356400	3.47749600
H	-1.33683400	0.58745600	2.27906700
H	0.09471800	3.91237500	2.94442100
H	1.52583400	3.00124600	2.45038700
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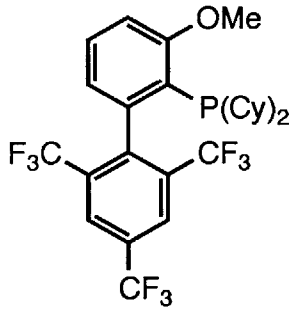

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C	-1.54406700	-1.25339900	0.73119600
C	-0.65023700	-3.13427300	2.00752800
C	-2.20916100	-1.62284700	-0.46712500
C	1.01858200	-1.69901300	0.93465500
C	-0.32972300	-2.01424500	1.22225500
C	-2.22110400	-0.32650900	1.56469100
C	2.01106000	-2.57426800	1.44662000
C	-4.03109300	-0.08858400	-0.02656700
C	-3.43289600	0.25000700	1.18092000
C	1.68395200	-3.68772700	2.22607900
C	-3.42329700	-1.03657500	-0.83801000
C	0.34742700	-3.95843900	2.50705600
C	2.53380000	0.98508300	0.88009900
C	2.58804800	-0.83897600	-1.48888000
C	4.06124400	0.77332600	0.90636800
C	4.22680600	2.15944000	3.03106000
C	4.76002100	1.95326400	1.60689700
C	1.98717400	1.18390900	2.30714400
C	2.07358700	-2.10437700	-2.20070700
C	2.80858100	0.29302600	-2.51638700
C	2.70317300	2.34166800	3.02396400
C	3.04755500	-2.54458100	-3.30854000

C	-0.09123600	3.67918600	0.12747000
C	0.53774000	3.37454200	-2.21138500
C	3.78161600	-0.14221400	-3.62515600
C	1.40742200	5.26419200	-0.95014800
C	0.69572100	4.83282000	0.17352800
C	1.31715200	4.53058100	-2.13755500
C	3.30055600	-1.42154600	-4.32428900
H	-3.90721100	0.97685800	1.83031000
H	2.45659500	-4.34146300	2.61189700
H	-3.89138200	-1.32622700	-1.77175900
H	0.08868000	-4.82151200	3.11383200
H	2.34093400	1.91880600	0.33308600
H	3.54645700	-1.08614100	-1.02069100
H	4.46067700	0.67161500	-0.10867000
H	4.29518500	-0.15550800	1.43574600
H	4.48653500	1.28380500	3.64508900
H	4.71264500	3.02513200	3.49930400
H	5.84418100	1.78031100	1.62394000
H	4.59789400	2.87033000	1.02194300
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H	1.09075700	-1.90392600	-2.64279200
H	1.93521100	-2.92020900	-1.48352500
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H	1.83963000	0.55843800	-2.95975500
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H	2.32261200	2.42863800	4.04985800
H	4.00353200	-2.84433200	-2.85290100
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H	0.44973200	2.81970600	-3.13915000
H	3.89866300	0.67085300	-4.35300100
H	4.77685300	-0.31685600	-3.18924500
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H	0.73677300	5.40401700	1.09833000
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H	4.03131100	-1.74454300	-5.07679400
H	-1.69220600	-3.35468800	2.21810800
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C	-1.70842800	-2.64420900	-1.47102000
O	3.30065100	-2.26904500	1.12336900
C	4.34771200	-3.12695400	1.55693300
H	5.26761100	-2.69068900	1.16457400
H	4.40535300	-3.17047200	2.65165500
H	4.22483000	-4.14084000	1.15658300
F	-2.68022900	0.02593600	3.84739100
F	-1.45665700	1.50788100	2.84023900
F	-0.61457200	-0.42459100	3.36764000
F	-2.69589200	-3.51994600	-1.77518700
F	-1.36553100	-2.03736500	-2.63498400
F	-0.65255700	-3.36898400	-1.07150100
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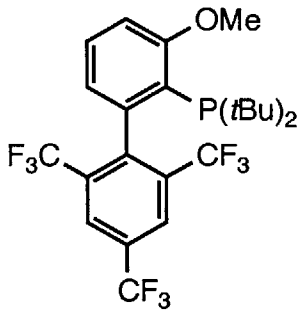
F	-5.49047300	0.59928000	-1.75122300
F	-5.52888400	1.73259900	0.11351300
F	-6.38452300	-0.26296400	0.03119300



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F	-2.30184500	1.79037300	-0.68275400
C	-0.67446900	-1.59625600	0.25464200
C	0.79839700	-3.43577000	0.86009000
C	-1.32809100	-1.77643200	-1.00026500
C	1.93674800	-1.33907300	0.28610200
C	0.74575900	-2.08613000	0.47053700
C	-1.52208000	-1.28087300	1.35489500
C	3.16023100	-2.04090600	0.46028700
C	-3.46183100	-1.08876400	-0.08365200
C	-2.87765800	-1.00847200	1.17520800
C	3.20109500	-3.38072600	0.85629100
C	-2.69107500	-1.50993500	-1.15772100
C	2.01196500	-4.07297000	1.06269600
C	-1.25180600	3.37405000	1.09171900
C	-0.75734400	3.85549300	-1.24920500
C	-0.73161100	5.64529800	0.39859500
C	-1.07305200	4.72515600	1.39469700
C	-0.58321000	5.20174500	-0.91922300
H	-3.48192800	-0.72595800	2.02984200
H	4.14798000	-3.88756000	0.99469000
H	-3.14684100	-1.62517200	-2.13360900
H	2.03854900	-5.11469500	1.36935500
H	-1.54344700	2.66373600	1.85812300
H	-0.66150700	3.51785000	-2.27525000
H	-0.60287200	6.69586300	0.64202500
H	-1.21432400	5.05787000	2.42044700
H	-0.33707100	5.90858800	-1.70840600
H	-0.12974300	-3.98122800	0.99908600
C	-1.08842400	-1.17543800	2.80391800
C	-0.64888600	-2.22761600	-2.27940600
O	4.29946500	-1.33976100	0.19778800
C	5.56228800	-1.95696100	0.40701100

H	6.30687400	-1.19966300	0.15653400
H	5.69146500	-2.26093300	1.45301100
H	5.69728000	-2.82725600	-0.24691500
F	-1.88057100	-1.95500600	3.57957900
F	-1.24212200	0.09236400	3.26043000
F	0.17933400	-1.54106000	3.05539200
F	-1.44898100	-3.08202100	-2.95929700
F	-0.42613900	-1.17554700	-3.10961800
F	0.52695300	-2.85232700	-2.10523800
C	-4.93503700	-0.82983900	-0.25606000
F	-5.38139500	0.09538700	0.61559900
F	-5.65672400	-1.95679200	-0.04072900
F	-5.22385500	-0.40868400	-1.50250200
C	2.89582500	0.78163500	-1.79519000
C	2.15689600	1.90042300	-2.56483500
C	4.36562400	1.20864200	-1.61645700
C	2.86444500	-0.49597000	-2.65551900
H	1.13268000	1.60401600	-2.81034900
H	2.10390900	2.83447300	-1.99772100
H	2.69336800	2.10378900	-3.50165200
H	4.95133400	0.45226000	-1.09551400
H	4.80450100	1.34615900	-2.61392800
H	4.47021000	2.15967700	-1.08900200
H	3.34574000	-0.27737300	-3.61801500
H	3.41091900	-1.31926000	-2.18941300
H	1.84795500	-0.82621400	-2.86787100
C	2.59767800	1.50665600	1.30256800
C	2.54363700	2.99660400	0.89736800
C	1.64420400	1.29617300	2.49320600
C	4.01889800	1.15633100	1.78135500
H	3.25981300	3.24636200	0.11003100
H	1.54701600	3.29811100	0.56804900
H	2.80142600	3.60459400	1.77421800
H	1.65848500	0.26325000	2.84686500
H	1.96878300	1.93763900	3.32340200
H	0.61606700	1.56359700	2.24299600
H	4.27912100	1.84397300	2.59764300
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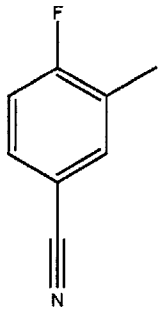
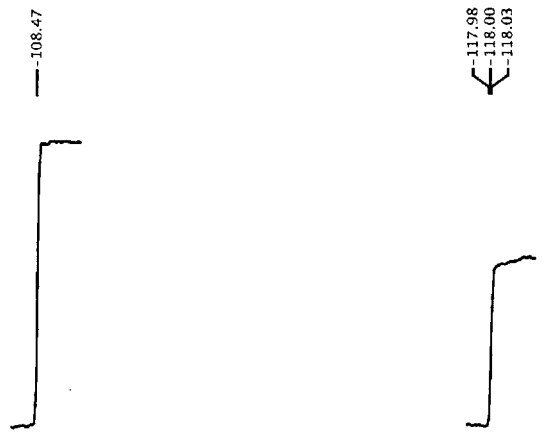

F
N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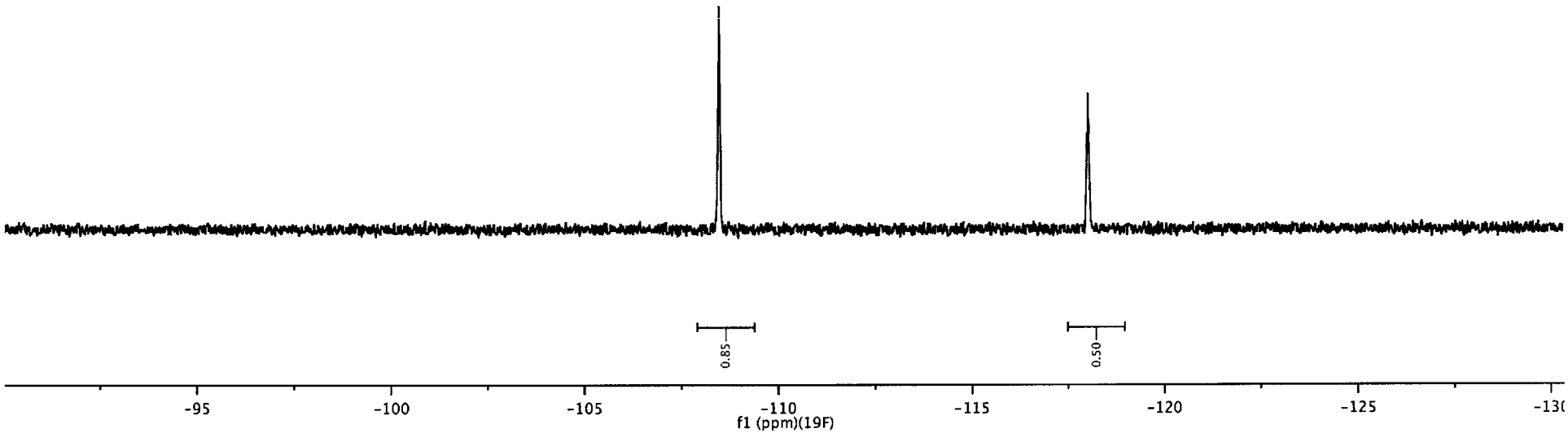
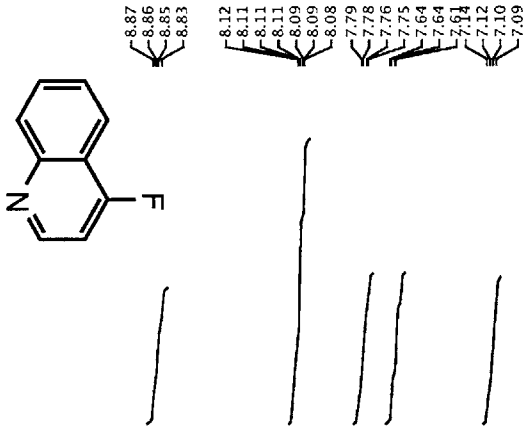
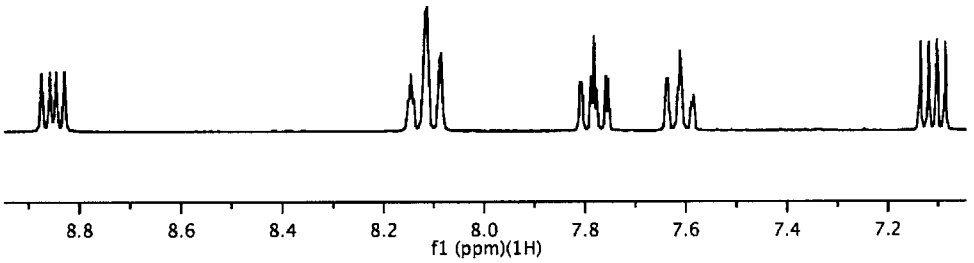
-118.03

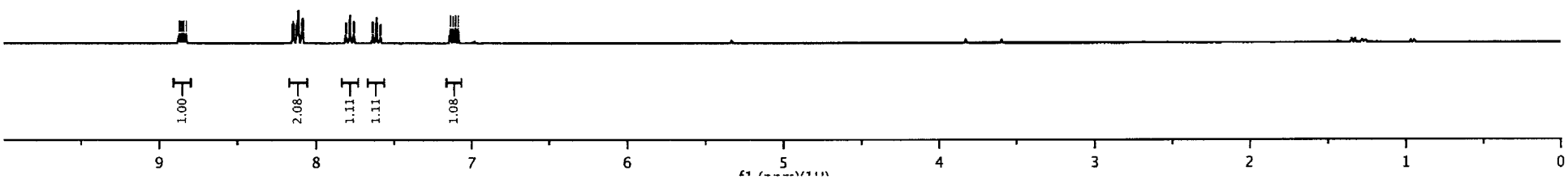

0.85
0.50
-95
-100
-105
-110
-115
-120
-125
f1 (ppm)(19F)

F
O
O

-110.47
-110.50
-117.99
-118.02
-118.05
0.88
0.50
95
100
105
110
115
120
125


8.87
8.86
8.85
8.83
8.12
8.11
8.11
8.11
8.09
8.09
8.08
7.79
7.78
7.76
7.75
7.64
7.64
7.61
7.14
7.12
7.10
7.09
N
F


8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
f1 (ppm)(1H)


1.00
2.08
1.11
1.11
1.08
9
8
7
6
5
4
3
2
1
0

167.12
163.58
151.73
151.62
150.74
150.68
130.63
130.62
129.37
129.32
127.05
127.03
120.56
120.49
119.72
119.55
105.90
105.70
N
F
260
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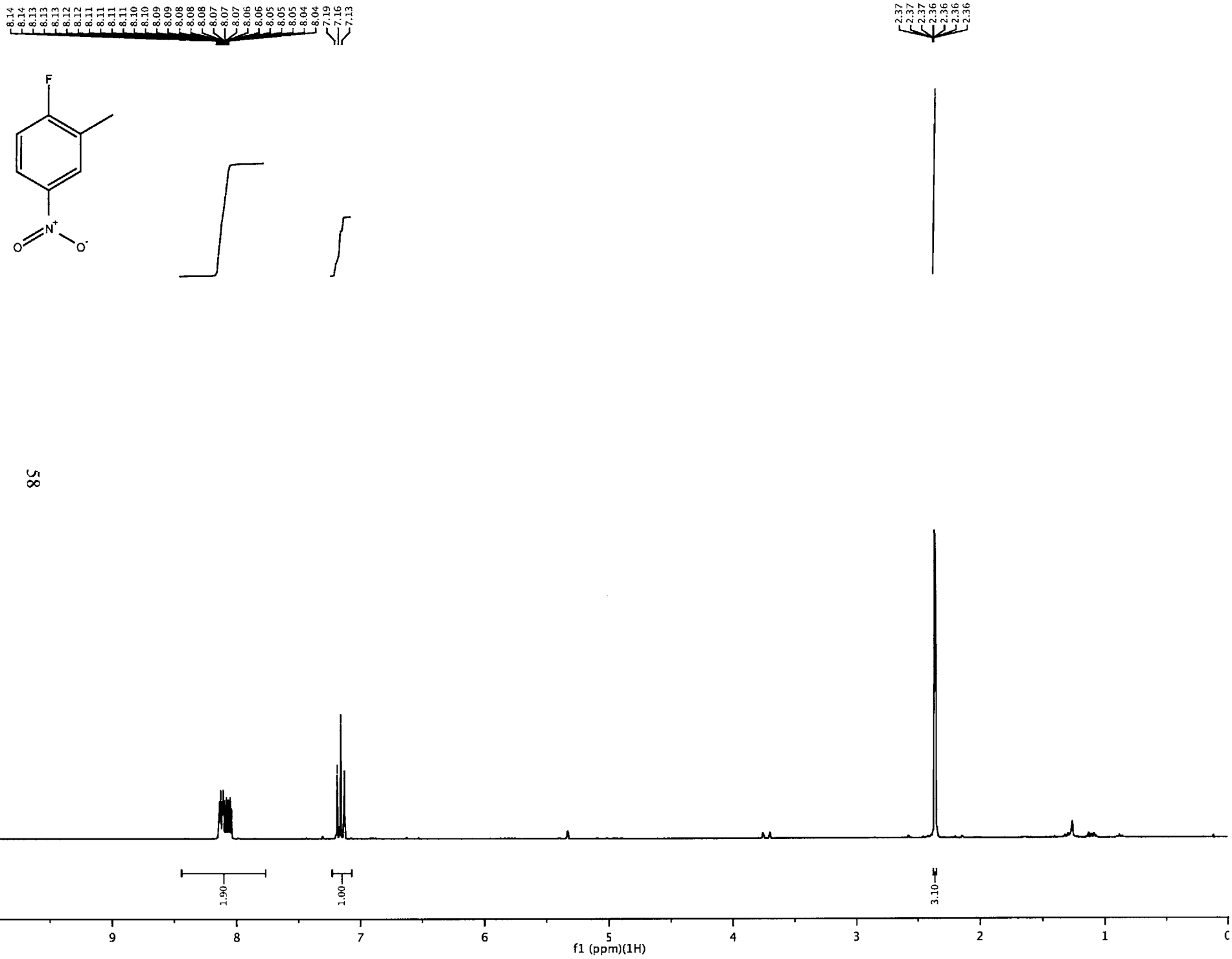
220
200
180
160
140
120
100
80
60
40
20
0

57


8.14
8.14
8.13
8.13
8.12
8.12
8.11
8.11
8.11
8.11
8.10
8.10
8.09
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8.04
8.04
7.19
7.16
7.13
2.37
2.37
2.37
2.36
2.36
2.36
2.36
F
N+
O
O-
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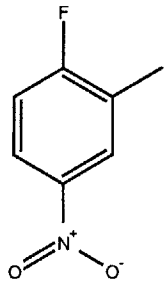
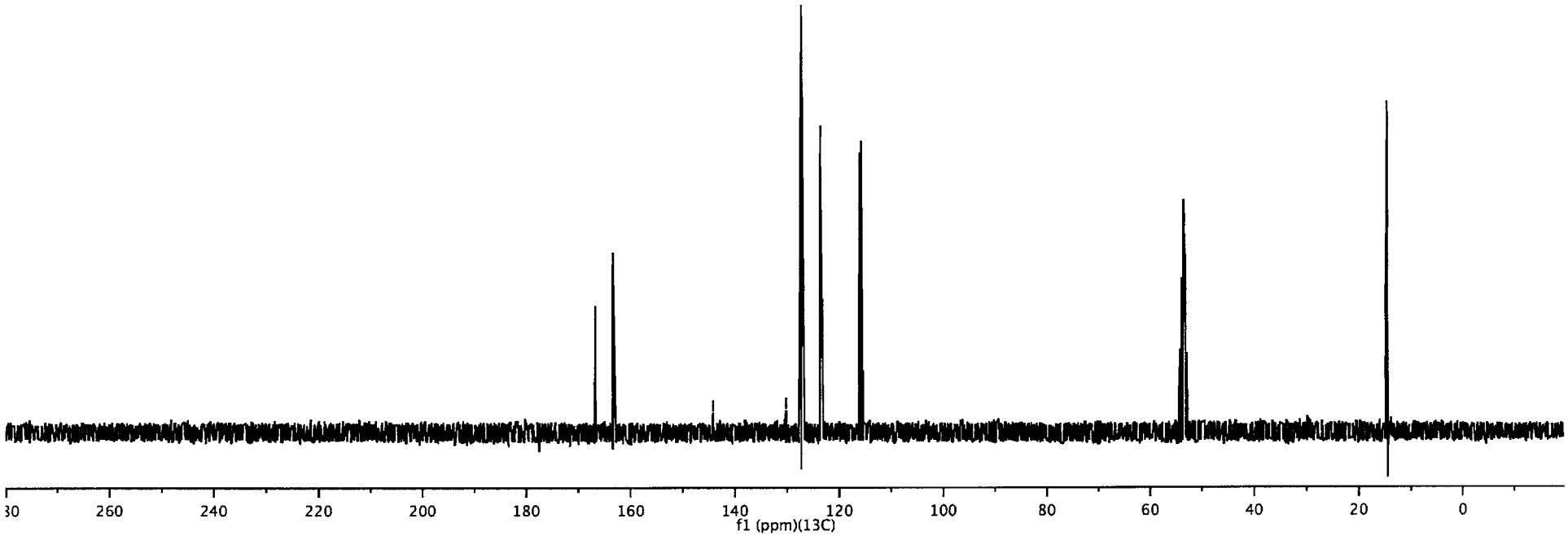
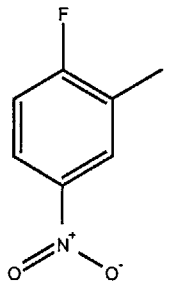
1.00
3.10
9
8
7
6
5
4
3
2
1
f1 (ppm)(1H)



166.77
163.38
144.22
130.22
127.33
127.24
127.13
126.87
123.69
123.55
116.11
115.78
14.55
14.50

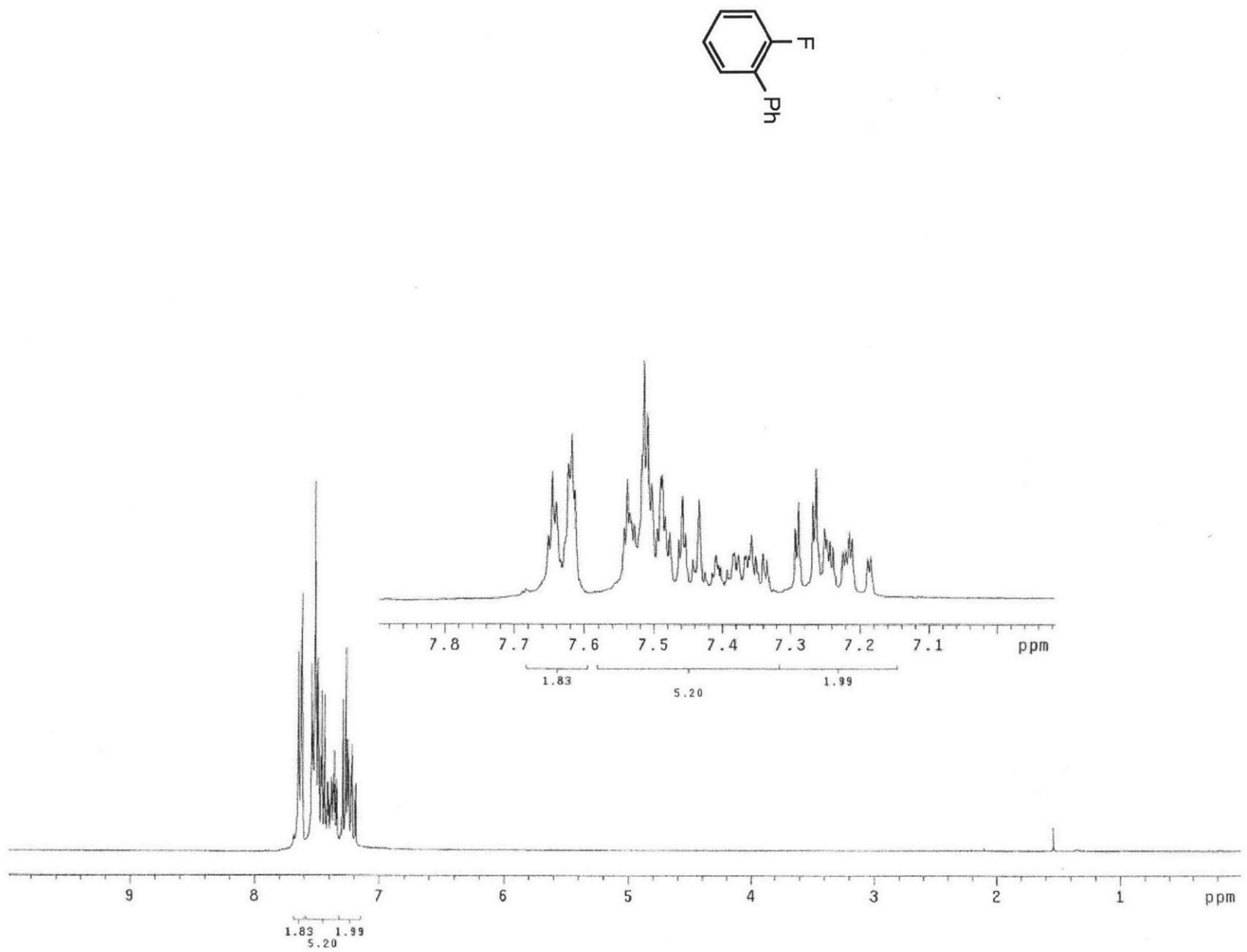




-105.16
-105.18
-105.20
-105.23

60

150
100
50
0
-50
-100
-150
f1 (ppm)(19F)


F
Ph
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
ppm
1.83
5.20
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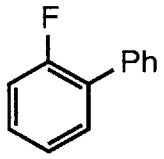
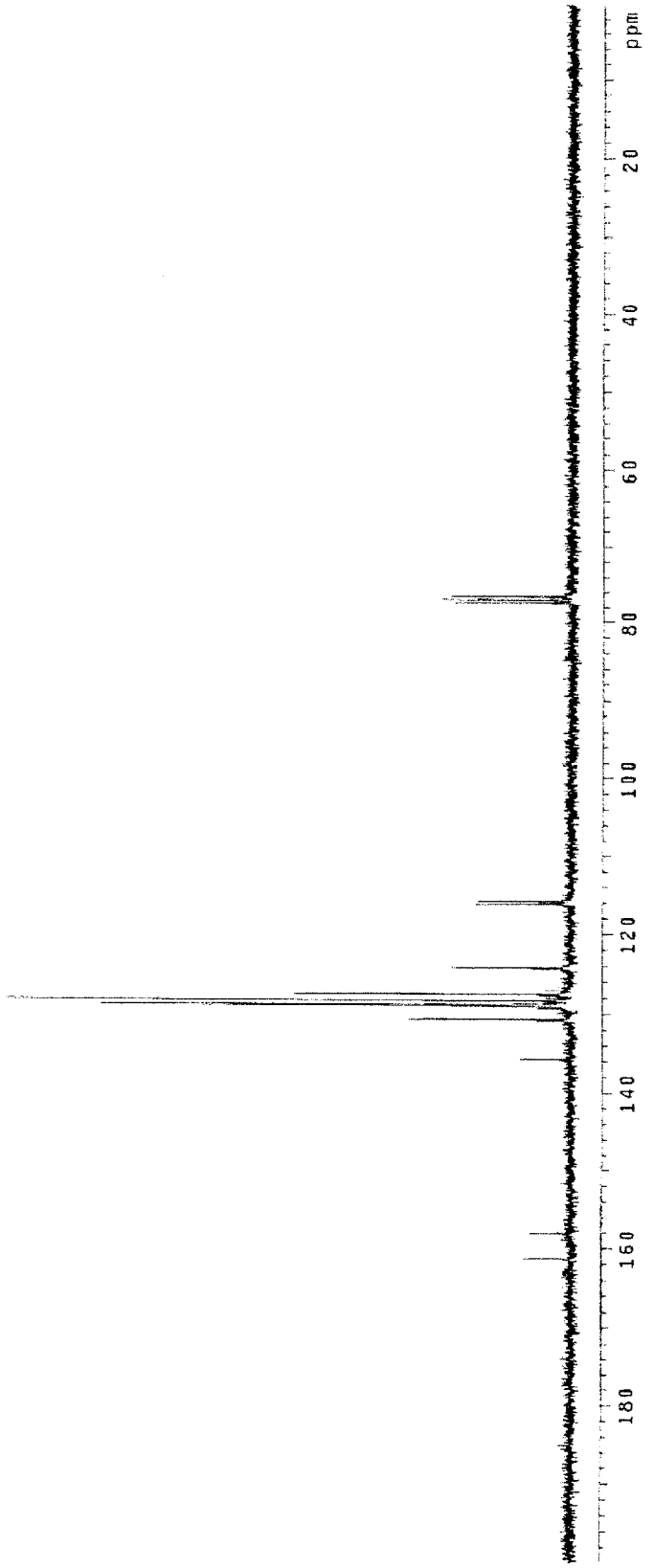
4
3
2
1
ppm
1.83
1.99
5.20


F
Ph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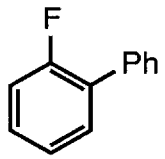
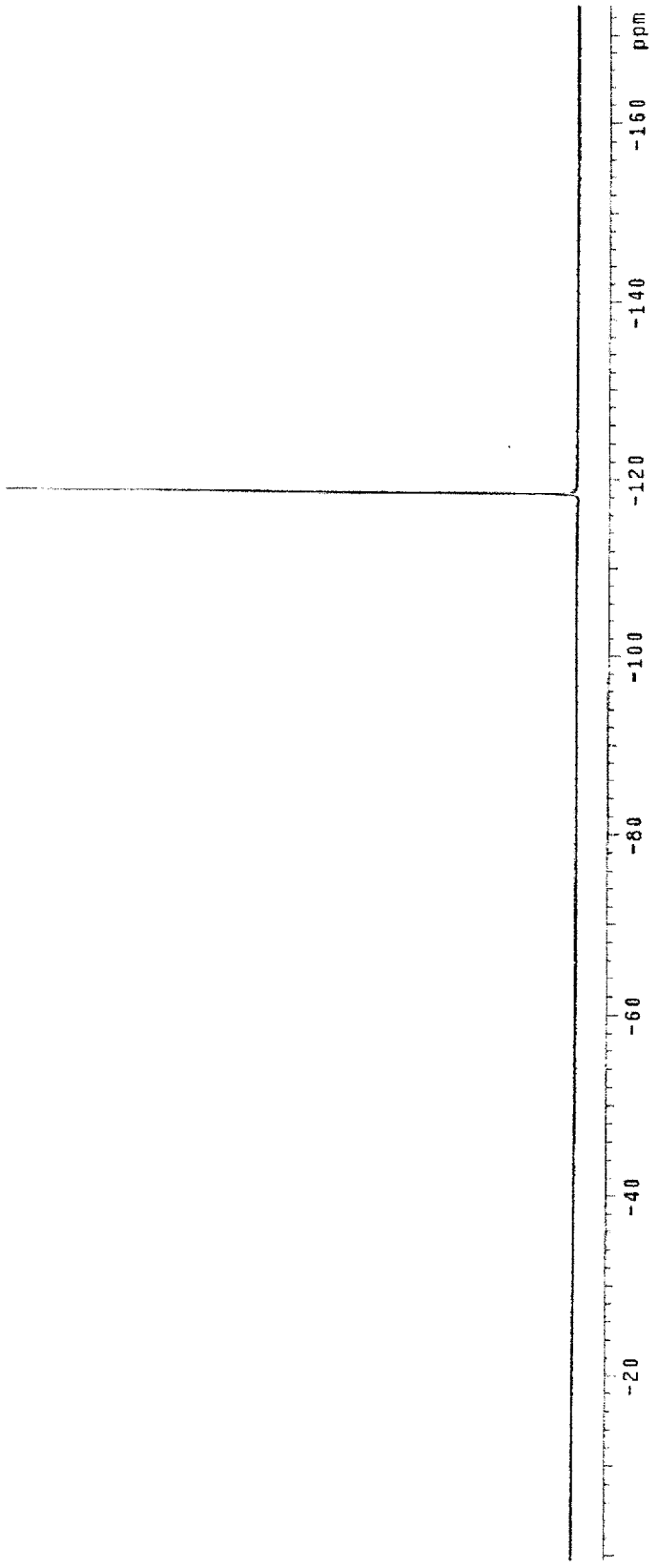
60
80
100
120
140
160
180


F
Ph


ppm
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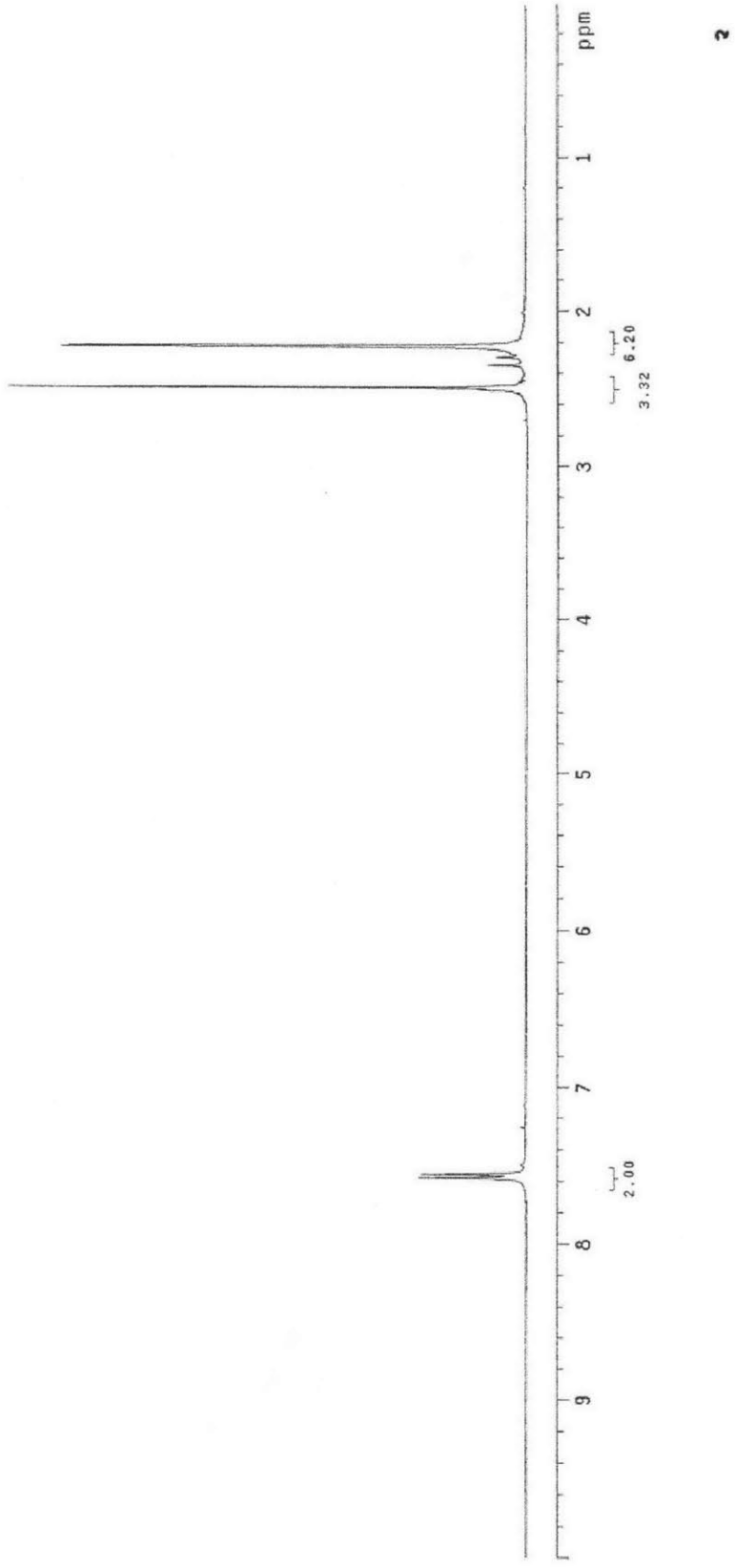
-120
-100
-80
-60
-40
-20


F
Me
Me
O
Me


ppm
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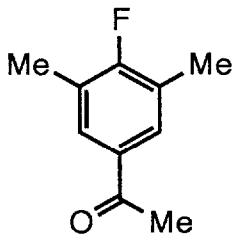
2
3
4
5
6
7
8
9
6.20
3.32
2.00


F
Me
Me
O
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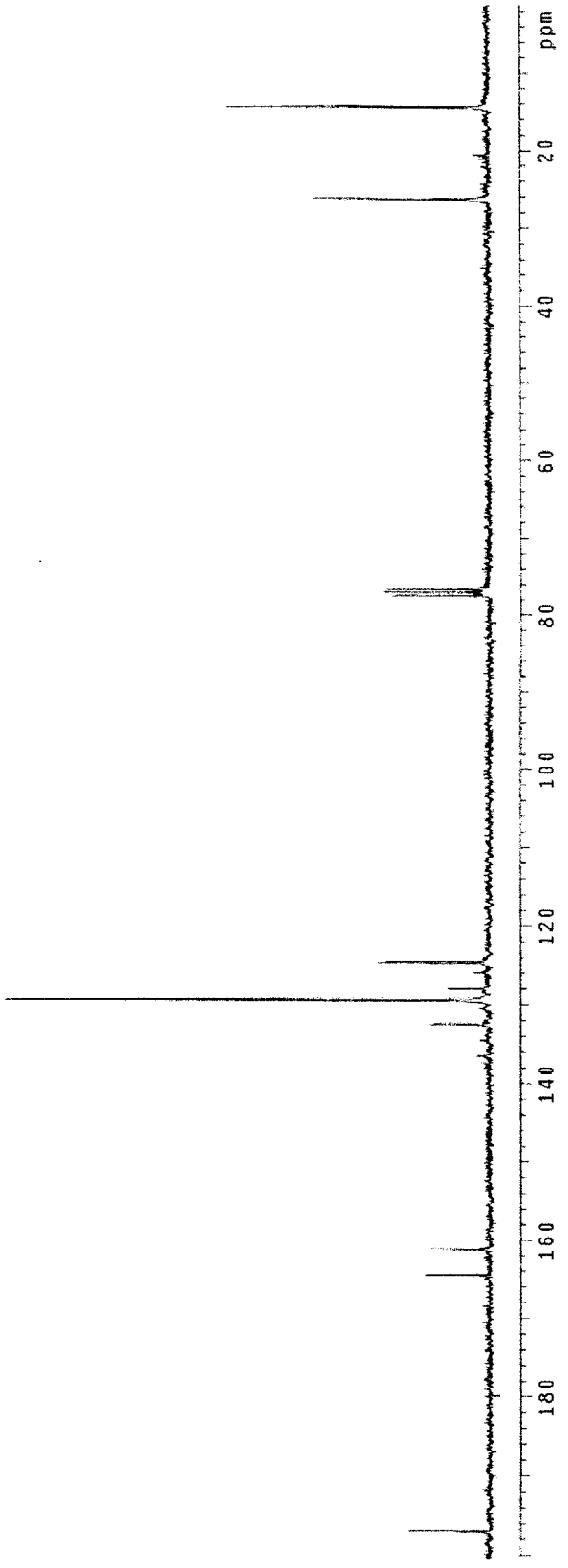
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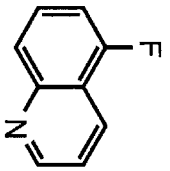

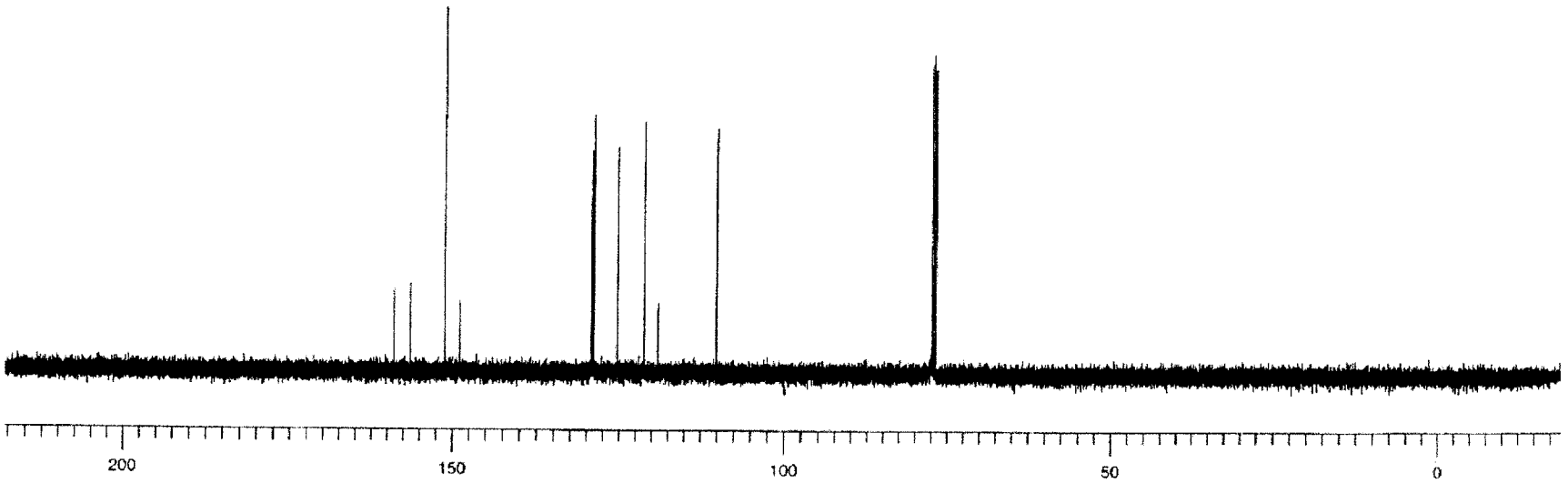

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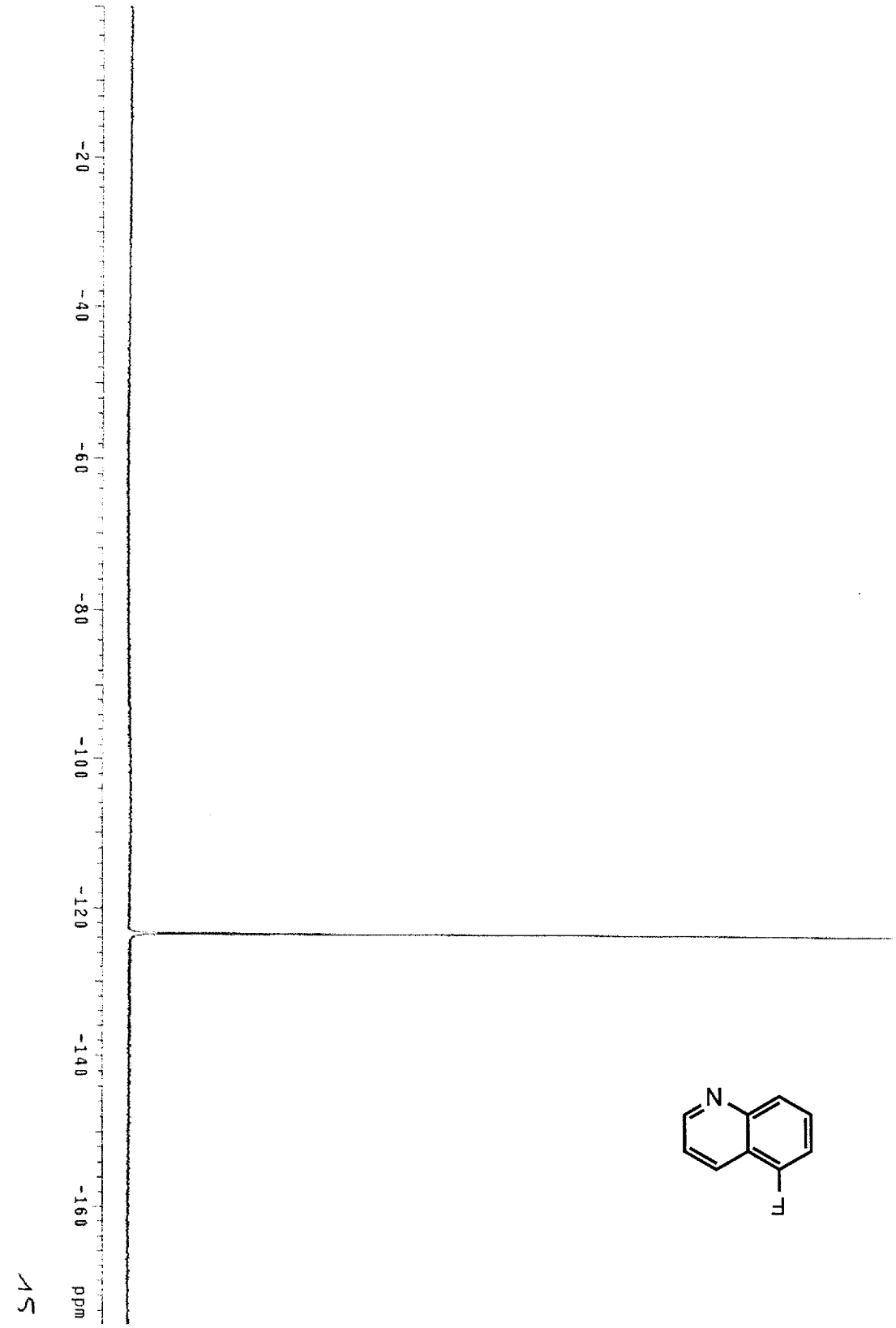

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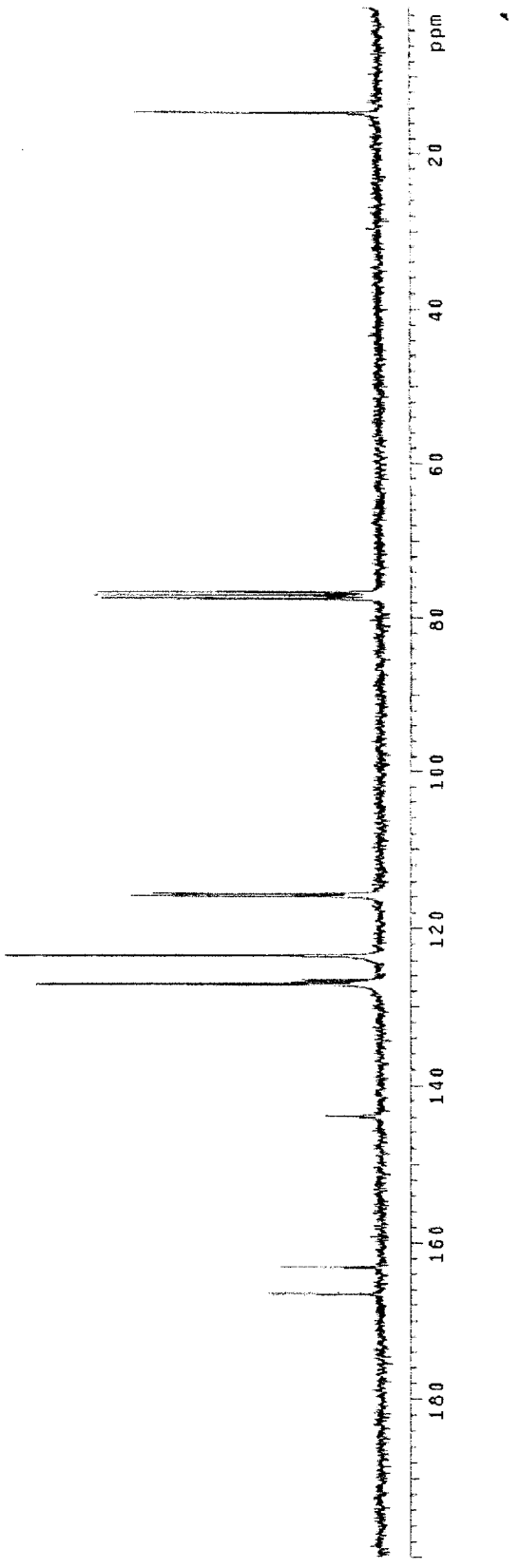
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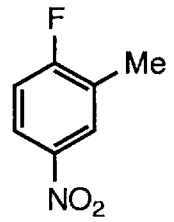
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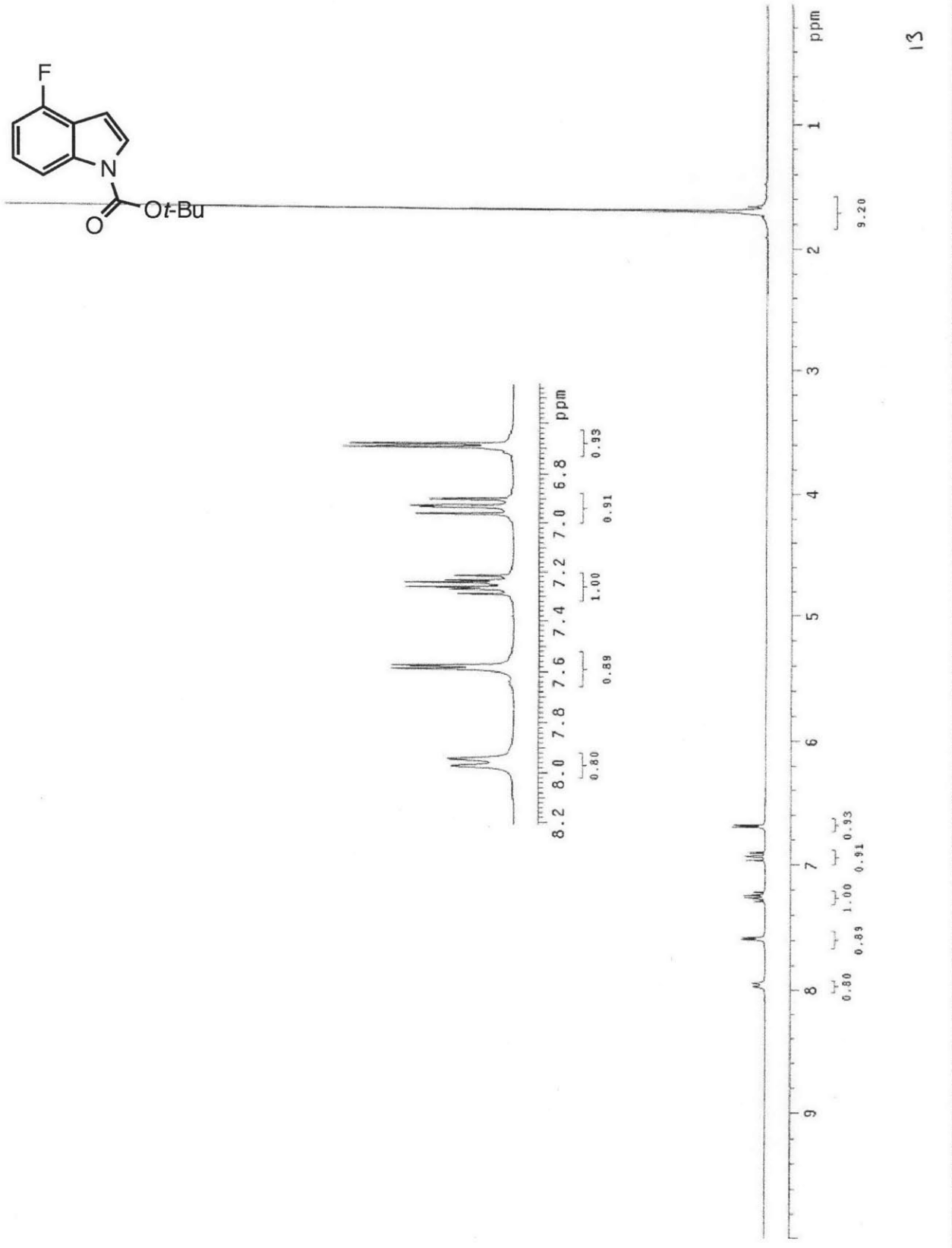
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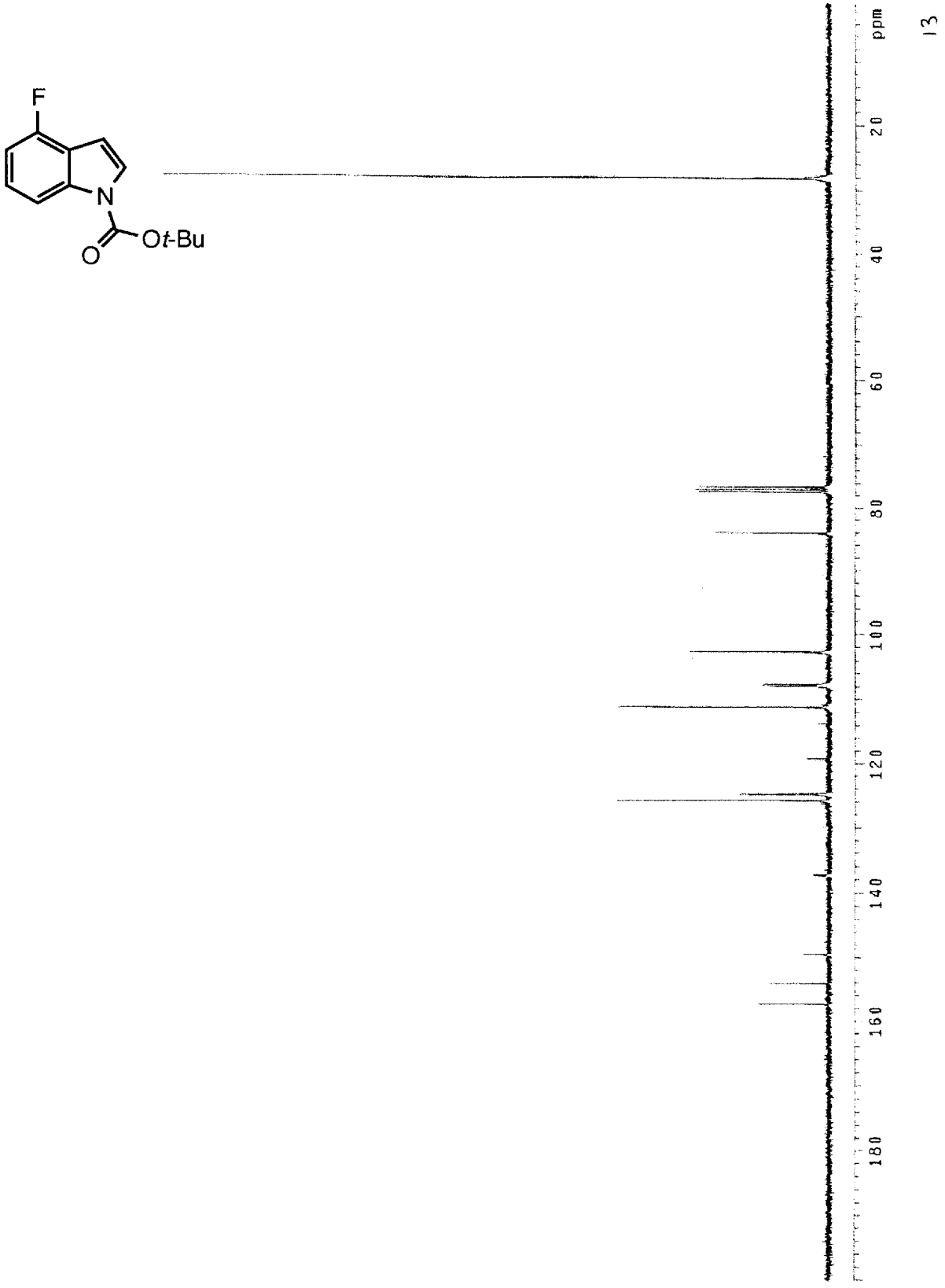

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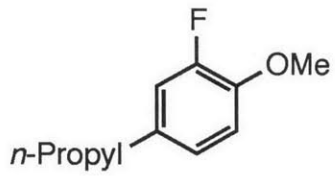

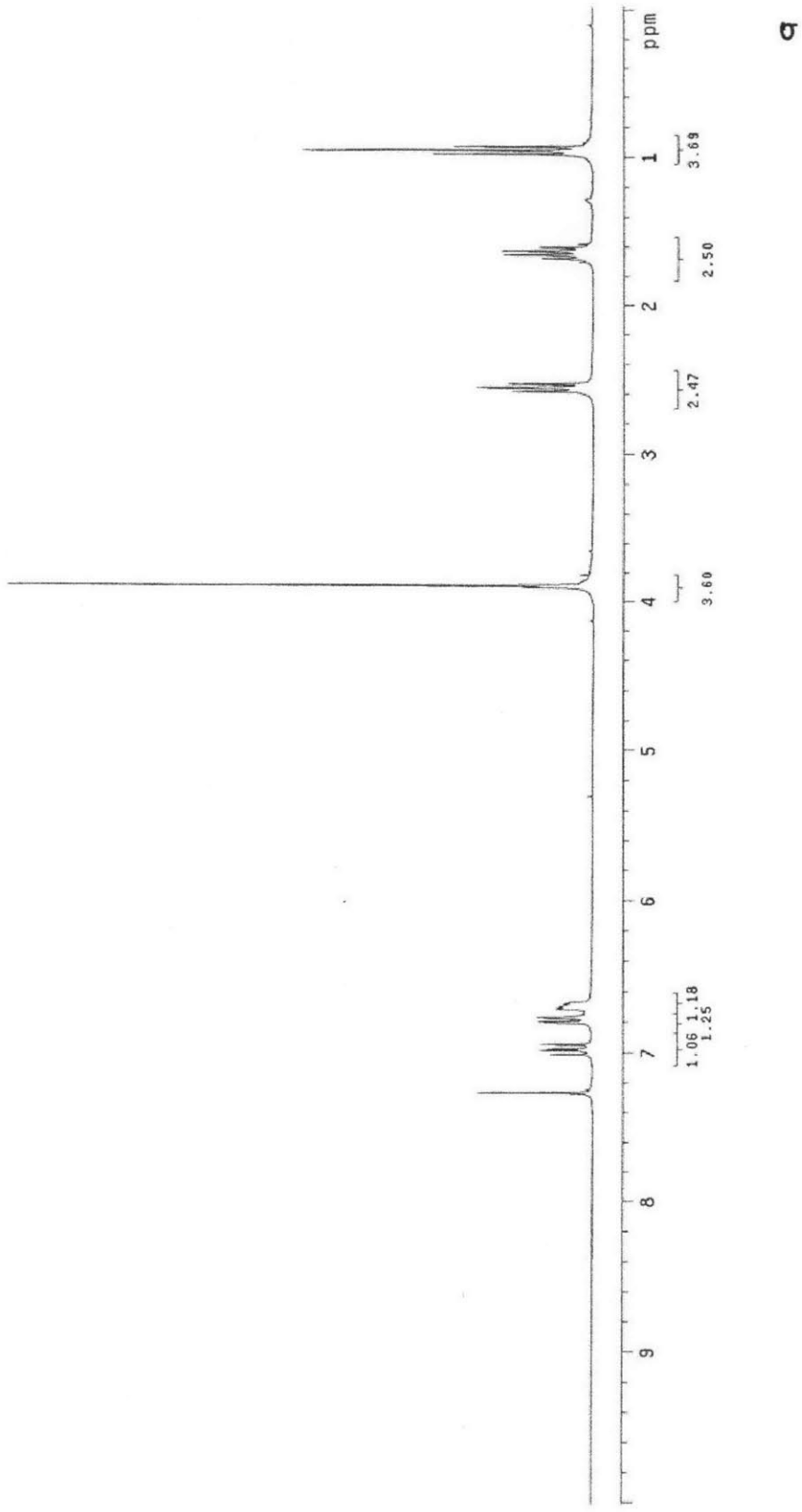

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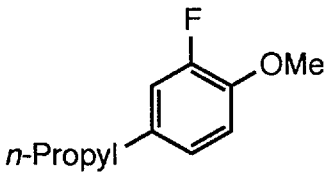

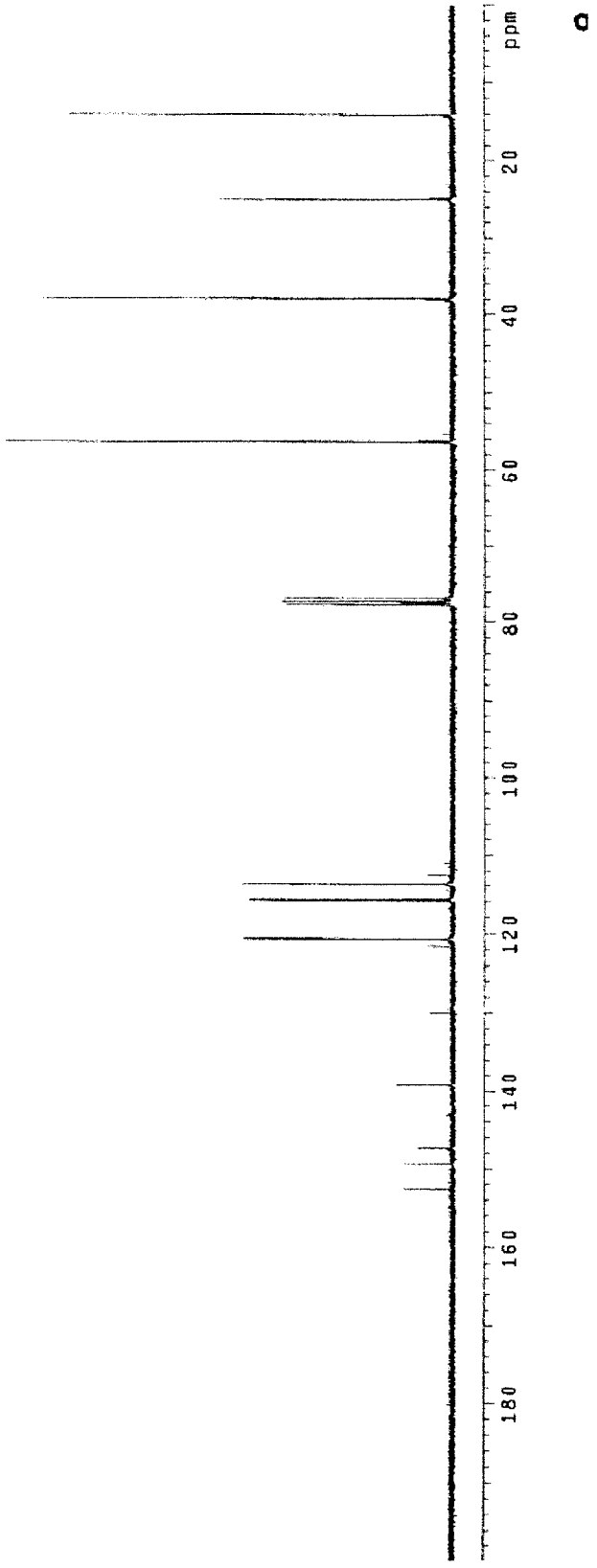

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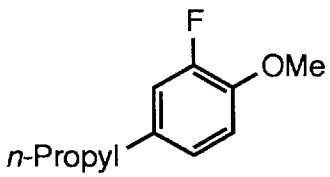

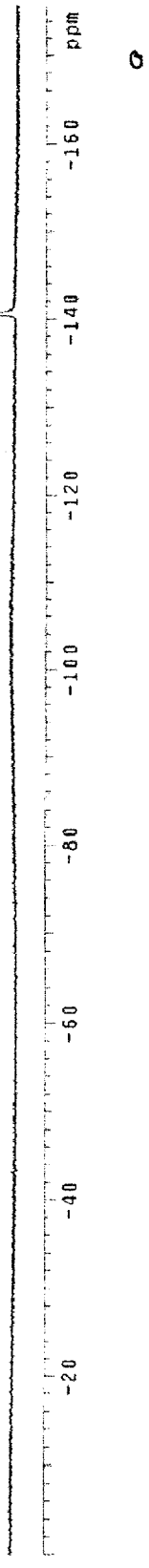

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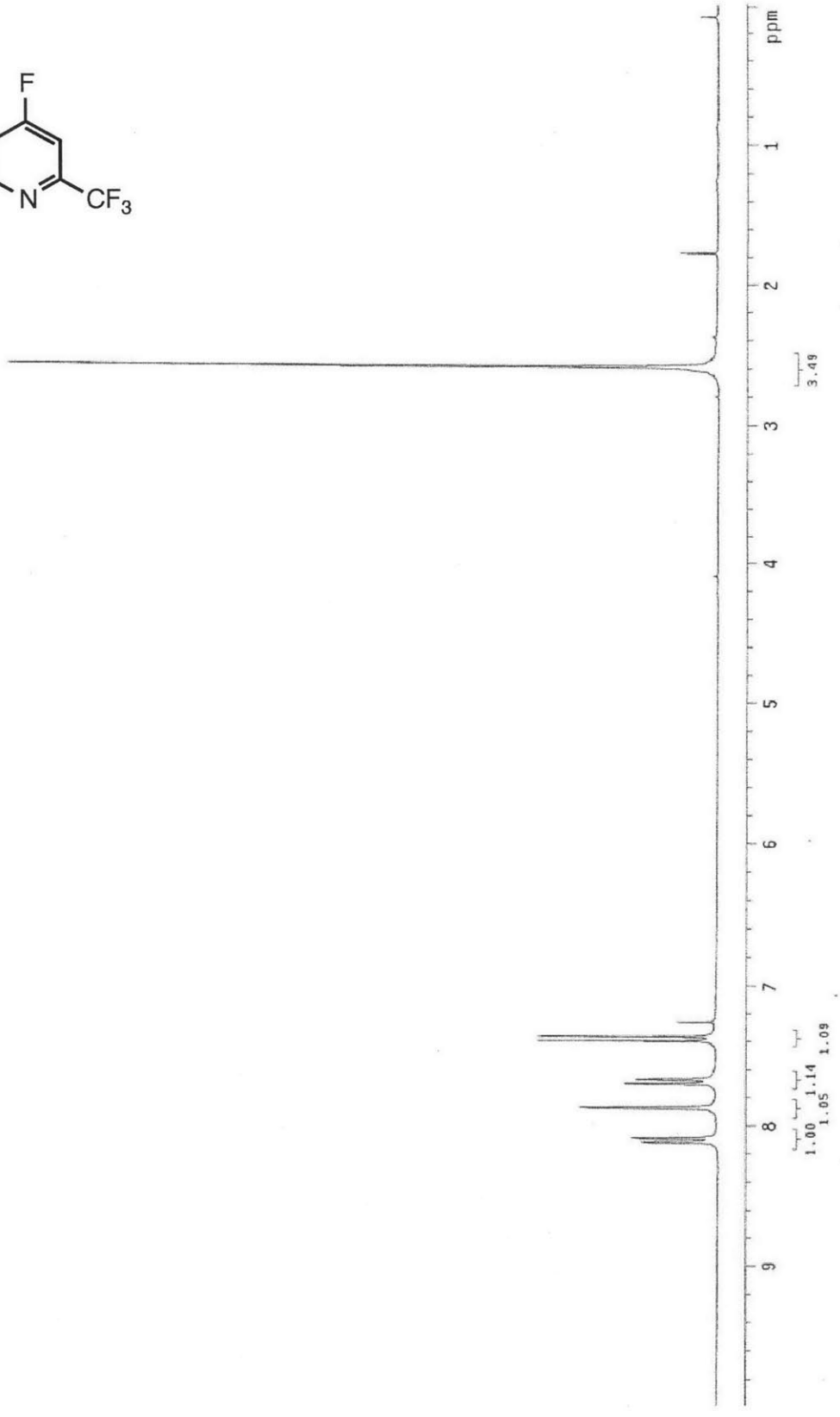

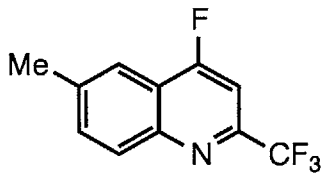
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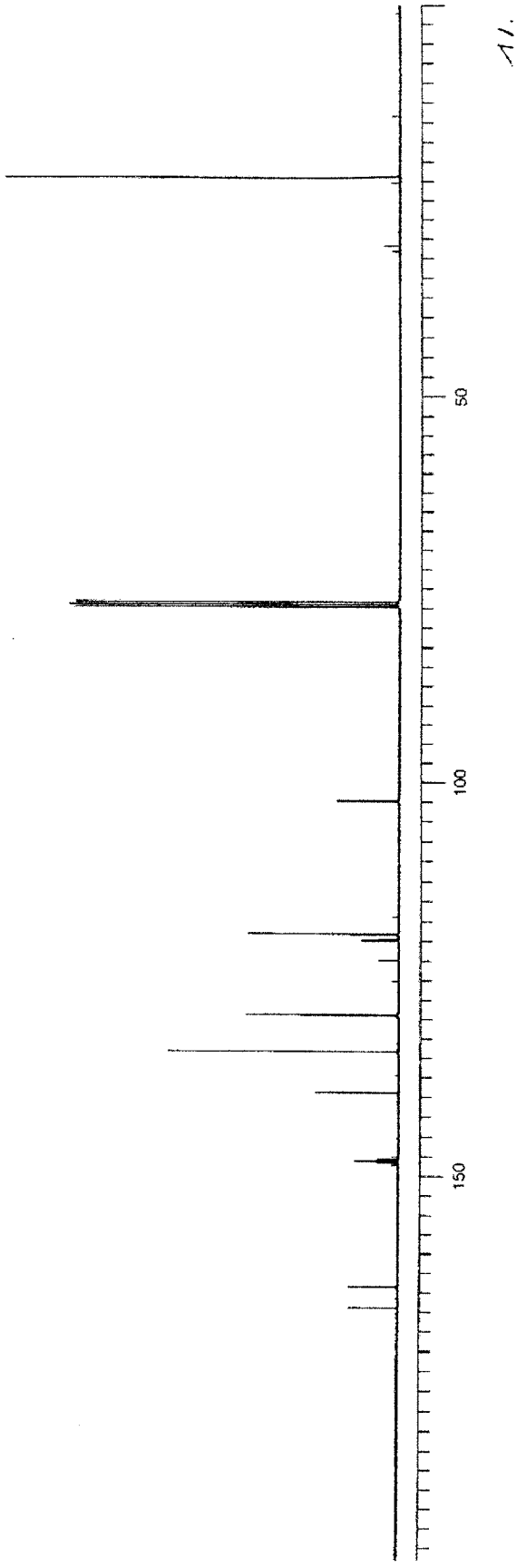
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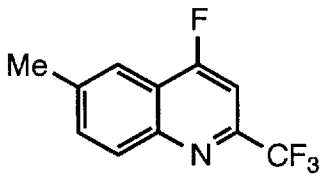

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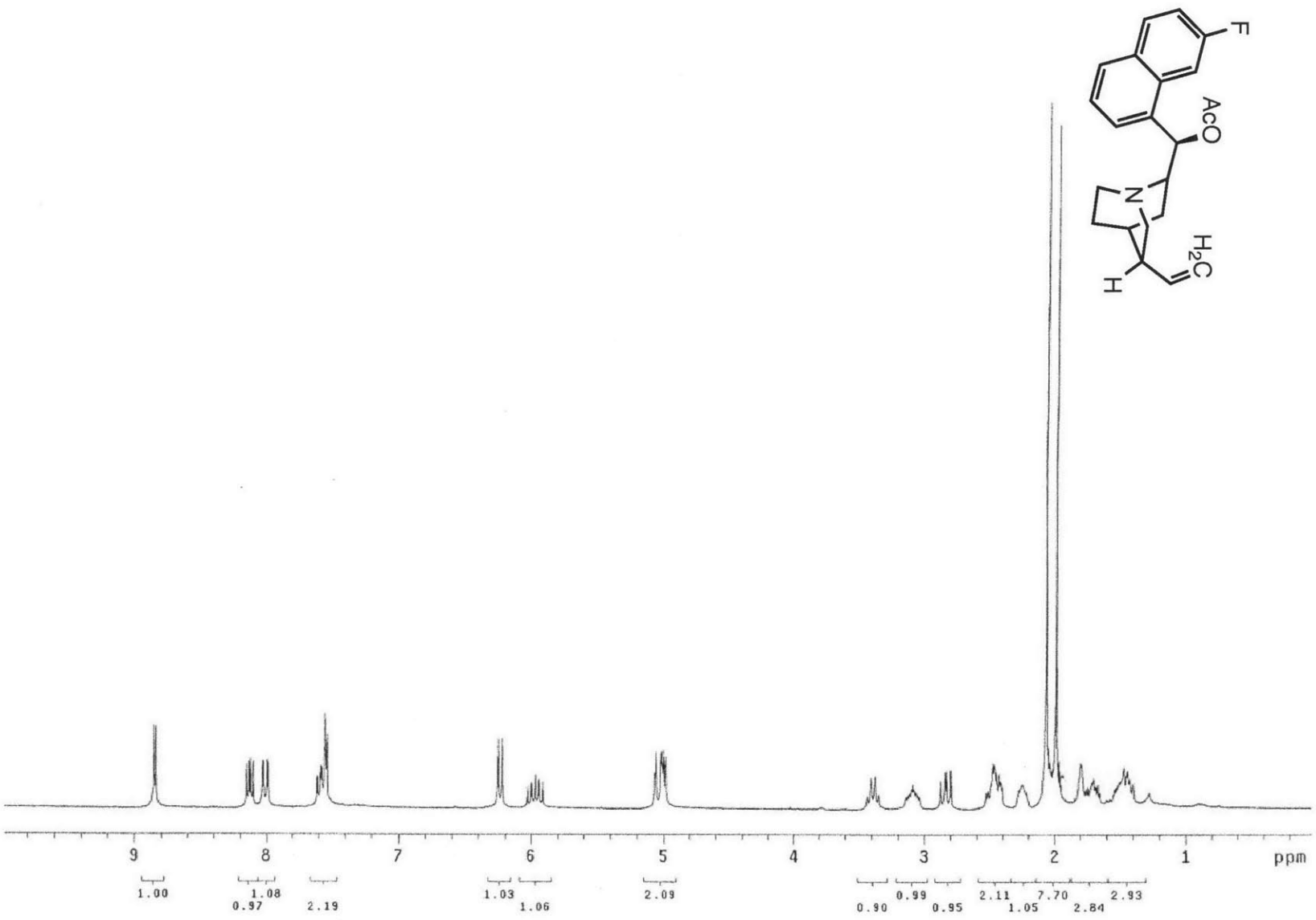
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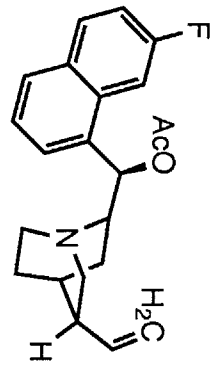

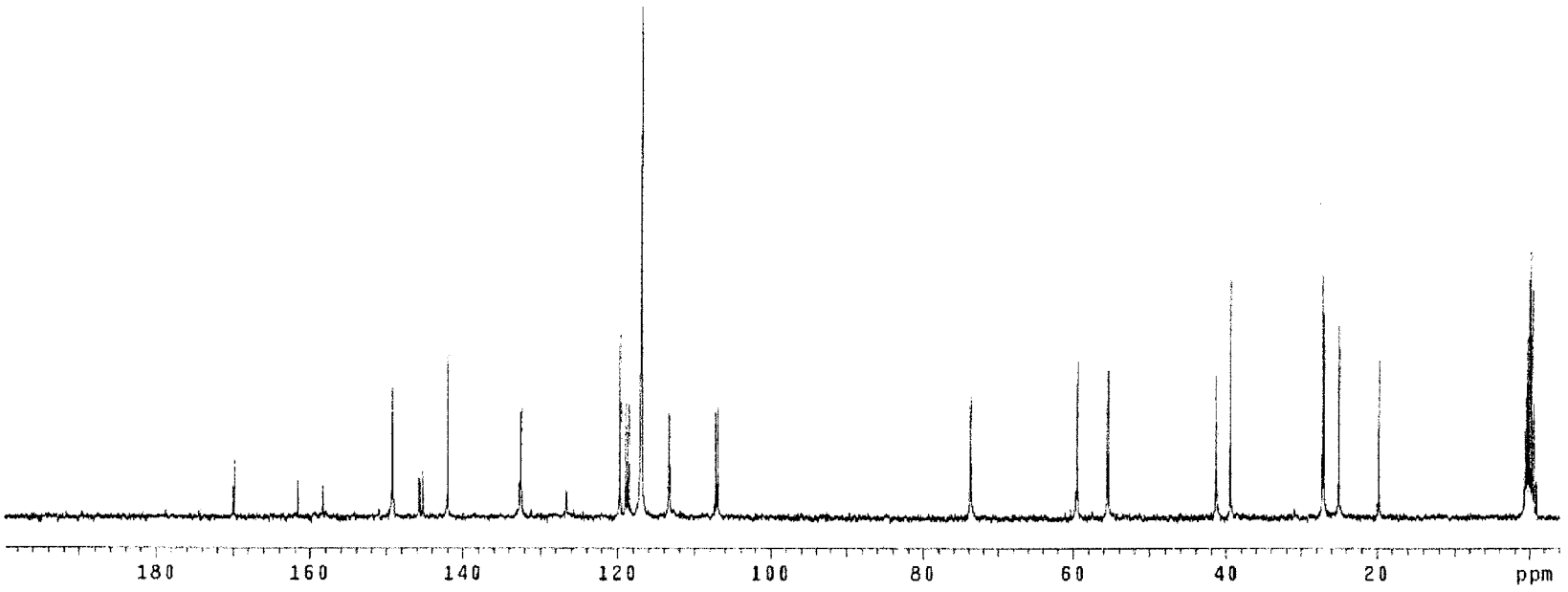

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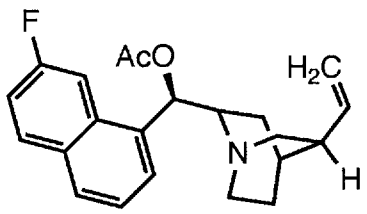
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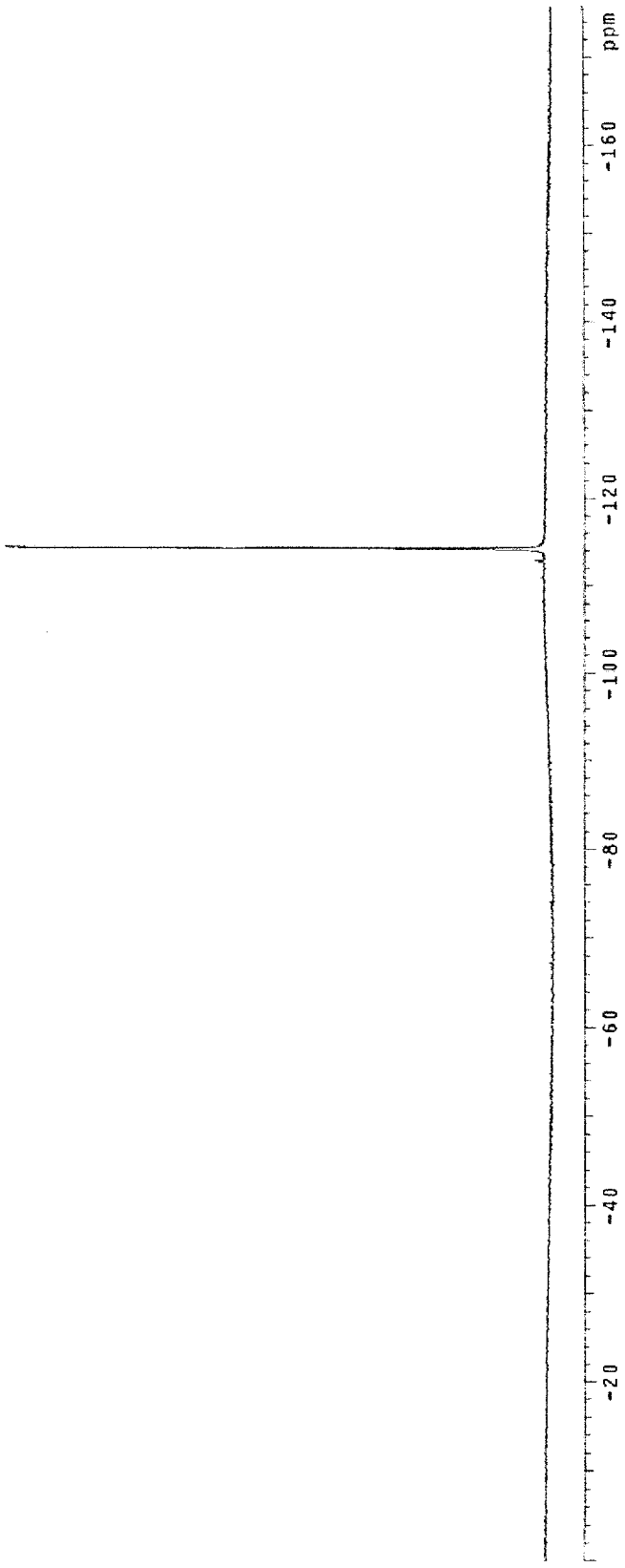
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1.5: References

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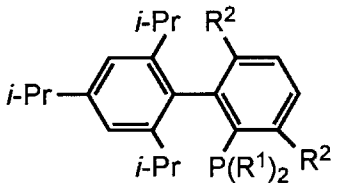
Chapter 2: Pd-Catalyzed Synthesis of Ar–SCF3 Compounds Under Mild Conditions

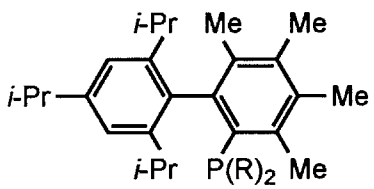
2.1: Introduction

The unique chemical properties of aryl trifluoromethyl sulfides ($ArSCF_3$) have been known for over 60 years.[1-2] The capacity of SCF_3 to act as a lipophilic electron-withdrawing group has resulted in the incorporation of $ArSCF_3$ components into a number of pharmaceutical and agrochemical agents.[3-5] Unfortunately, direct access to this important class of compounds is complicated by a lack of efficient, safe and general methods.[1,6-14]

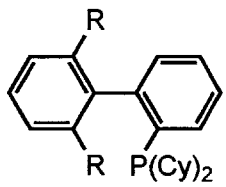
Significant advances in Pd-catalyzed cross-coupling processes have allowed for efficient access to a diverse array of functionalized aromatic products, including aryl sulfides.[15-17] While the coupling of many aromatic or aliphatic thiols with aryl halides has been achieved with very high efficiency,[18] the analogous transformation to form aryl trifluoromethyl sulfides has not been reported. As gaseous CF_3SH (b.p. = -36 °C)[19] can be difficult to handle in a laboratory setting, several SCF_3 salts have been developed, however, most of these decompose under standard cross-coupling conditions.[8]



1: R^1= Cy, R^2= OMe (BrettPhos)
2: R^1 = *t*-Bu, R^2 = OMe (*t*-BuBrettPhos)
3: R^1 = Cy, R^2 = H (XPhos)



4: R = *t*-Bu
5: $P(t\text{-Bu})_3$
6: $P(Cy)_3$



7: R = O*i*-Pr (RuPhos)
8: R = OMe (SPhos)
9: BINAP

Figure 1. Various ligands commonly employed in Pd-catalyzed cross-coupling reactions

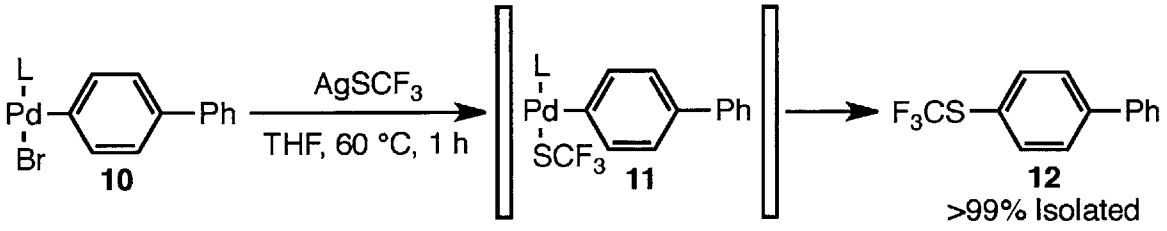
It has been postulated that reductive elimination of Ar–SR from a palladium center is initiated via a nucleophilic attack on the electrophilic hydrocarbyl group by the metal-bound thiolate.[20]

Thus, metal-catalyzed Ar–SCF_3 coupling might be complicated by the reduced nucleophilicity of the SCF_3 anion[4] as compared to a standard thiolate.

Recent reports from our group regarding novel ligands including BrettPhos (**1**), *t*-BuBrettPhos (**2**), XPhos (**3**) and 3,4,5,6-tetramethyl(*t*-Bu)XPhos (**4**) (Figure 1), have allowed for the successful coupling of weak nucleophiles traditionally thought to be reluctant participants in the transmetalation or reductive elimination steps of a typical Pd(0)/Pd(II) catalytic cycle. Specifically, using these catalyst systems has allowed for the direct formation of diaryl ether,[21] aryl fluoride,[22] aryl trifluoromethyl,[23] and aryl nitro compounds[24] from their corresponding aryl halides or pseudo halides. In light of these results, we hypothesized that a similar Pd-based system might allow for the formation of an aromatic C–SCF_3 bond.

2.2: Results and Discussion

As we suspected that reductive elimination from putative intermediate **11** would be rate limiting in any catalytic process, we began our investigation by attempting its preparation from oxidative addition complex **10** via treatment with $AgSCF_3$ (Scheme 2). We were surprised when this procedure did not provide the expected transmetalation complex but instead led directly to the Ar–SCF_3 product **12** (presumably via **11**).



Scheme 1. Formation of $ArSCF_3$ via transmetalation and reductive elimination from an isolated LPdAr(Br) complex.

Computational analysis employing the B3LYP functional with C, H, O, P and S atoms at the 6-31G(d) level of theory, the F atom at the 6-311++G(d,p) level of theory and the Pd center at the LANL2DZ level with effective core potential confirmed that reductive elimination from the postulated Pd(II) intermediate **11** is facile. These findings further indicated that the barrier to reductive elimination of Ar–SCF_3 (13 kcal/mol) is twice as high as that of Ar–SCH_3 (6.4 kcal/mol). As such, while we were correct in asserting that reductive elimination of SCF_3 would be more difficult compared with the SCH_3 analog, the transformation should nonetheless occur readily.

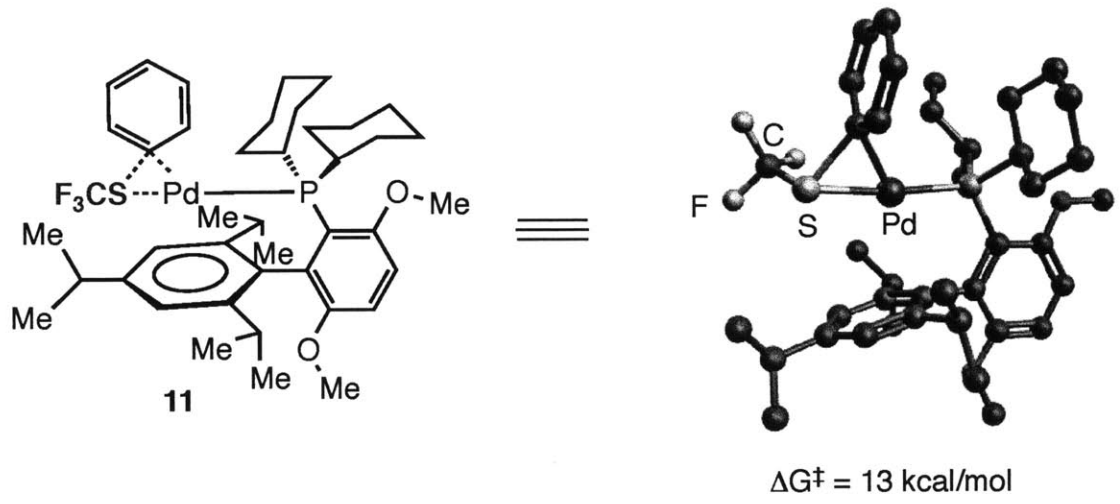


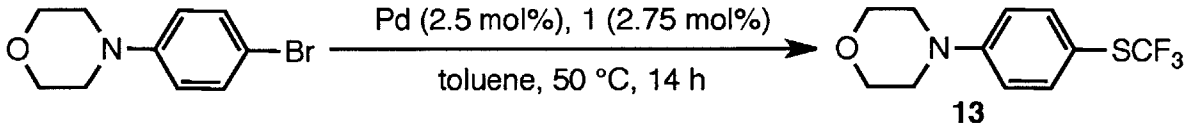
Figure 2. Proposed transition state for the reductive elimination of Ar–SCF_3 from a Pd(II) center.

Given these findings, we attempted to convert 4-(4-bromophenyl)morpholine to the corresponding trifluoromethyl sulfide using $AgSCF_3$ and a catalytic quantity of **1** and (COD)Pd(CH_2TMS)$_2$ (Table 1). However, under these conditions, formation of product **13** was not observed. We surmised that failure to observe the coupled product might be due to the inefficient transfer of the SCF_3 anion to **10** under catalytic conditions. Thus, we elected to

examine the use of a number of alternative, but previously reported, sources of anionic SCF_3 (Table 1).[8,10]

Clark's[9] work on the use of $(Bu)_4NI$ and $AgSCF_3$ for S_NAr reactions with aryl halides indicated to us that the addition of a quaternary ammonium salt might be beneficial. Consistent with this hypothesis, the addition of 1 equivalent of $(Bu)_4NI$ to the reaction mixture increased the yield of **13** from 0 % to 55 % (Table 1). Further examination of different ammonium salts revealed that $Ph(Me)_3NI$ was more effective than $(Bu)_4NI$ and that switching to a more soluble ammonium salt, $Ph(Et)_3NI$, provided a nearly quantitative yield of the desired product (Table 1). Based on the work reported by Clark, it is presumed that the iodide anion binds to $AgSCF_3$ in order generate an anionic "ate" complex. We hypothesize that a large diffuse cation further aids in the solubility of this complex. It is worth noting that while the use of quaternary ammonium iodides and bromides allowed for catalytic turnover, the corresponding chloride analogs were ineffective.

Table 1. Examination of different SCF3 sources.[a]



13

Entry	$MSCF_3$	Additive	Yield
1	$CsSCF_3$	None	10%
2	$(Me)_4NSCF_3$	None	20%
3	$AgSCF_3$	None	0%
4	$AgSCF_3$	$(Bu)_4NI$	55%

5	$AgSCF_3$	$(Bu)_4NBr$	56%
6	$AgSCF_3$	$(Bu)_4NCl$	7%
7	$AgSCF_3$	$(Hexyl)_4NI$	11%
8	$AgSCF_3$	$Bn(Me)_3NI$	0%
9	$AgSCF_3$	$Bn(Bu)_3NI$	72%
10	$AgSCF_3$	$Ph(Me)_3NI$	80%
11	$AgSCF_3$	$Ph(Et)_3NI$	>99%

a) $(COD)Pd(CH_2TMS)_2$ (2.5 mol %), PhMe (4 mL); all reactions are run on 0.2 mmol scale and all reported yields are based on GC data.

Attempts to synthesize and characterize the proposed transmetallating species by subjecting $AgSCF_3$ to one equivalent $(Me)_3PhNI$ in acetonitrile yielded an unexpected silver "ate" complex (**14**), which was characterized via single crystal X-Ray diffraction (Figure 3). Compound **14** is chemically competent and is able to transfer two SCF_3 groups onto a Pd(II) center. Whether this species is present in solution is difficult to ascertain as the SCF_3 groups interconvert on the NMR time scale impeding solution-based analysis.

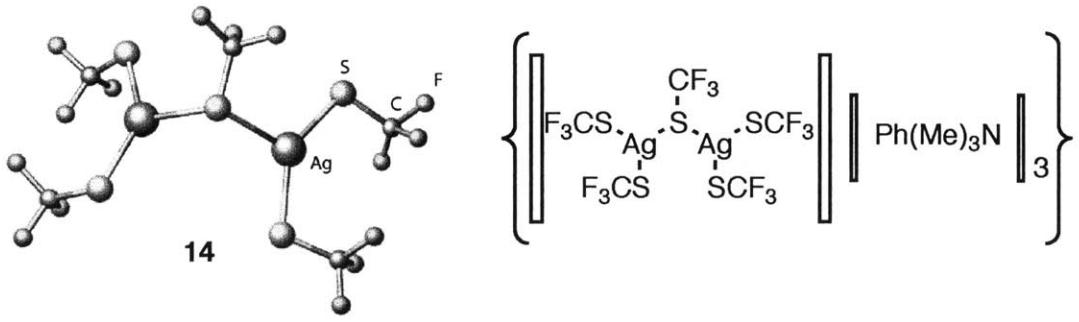
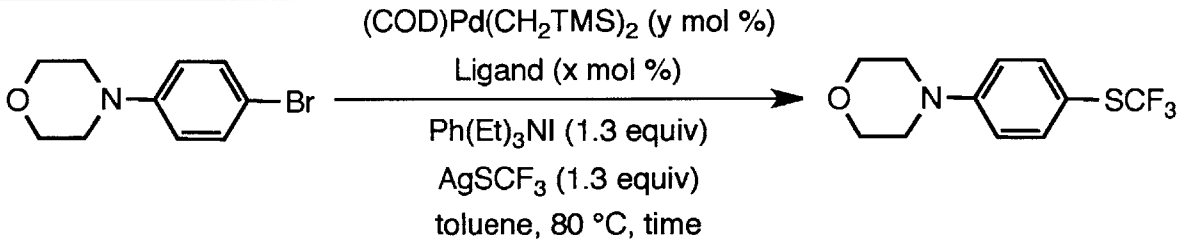


Figure 3. Crystal structure of possible transmetalating species.

With the optimal combination of $Ph(Et)_3NI$ and $AgSCF_3$ realized, we re-examined other ligands, which have proved to be effective supporting ligands for various Pd-catalyzed cross-coupling reactions.[25-29] Our survey revealed that only dialkylbiarylphosphine based ligands were successful in carrying out this transformation; other ligands, such as **5** or **6**, did not perform well even with higher catalyst loadings.

Table 2. Examination of various ligands commonly employed in Pd-catalyzed reactions.[a]

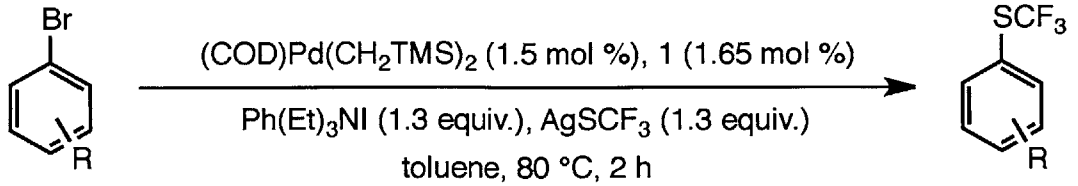


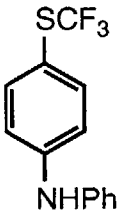
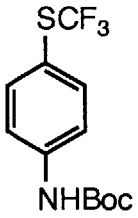
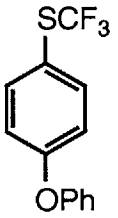
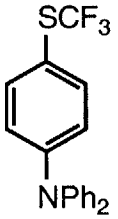
Entry	Ligand	Time (h)	Yield
1	1	1	>99%[b]
2	2	1.5	60%[b]
3	3	1	84%[c]
4	4	2	<1%[c]
5	5	2	36%[d]
6	6	2	3%[d]
7	7	2	0%[d]
8	8	2	29%[d]
9	9	2	0%[d]

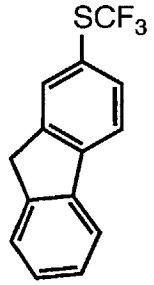
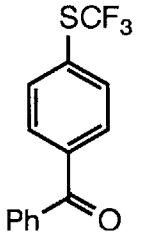
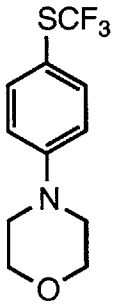
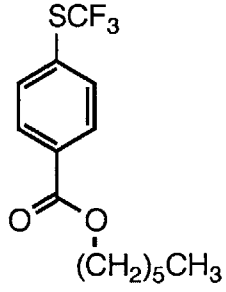
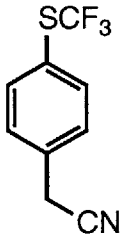
a) PhMe (4 mL); all reactions are run on 0.2 mmol scale and all reported yields are based on GC data. b) 1.15 mol % Pd, 1.27 mol % L. c) 1.5 mol % Pd, 1.65 mol % L. d) 2.5 mol % Pd, 2.75 mol % L.

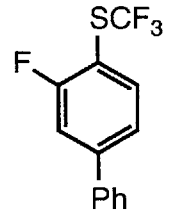
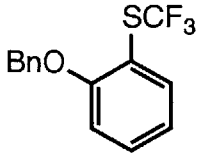
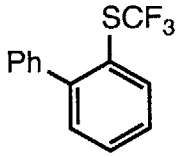
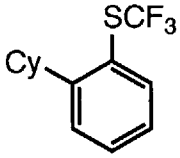
Accordingly, we were successful in converting electron-rich, -neutral and -deficient aryl bromides to their respective aryl trifluoromethyl sulfides in 2 hours at 80 °C using 1.5 - 3.5 mol % of Pd and 1.65 – 3.85 mol % of **1**. Electron-neutral and electron-rich substrates were coupled more efficiently than the corresponding electron-poor aryl bromides. Similarly, this effect has been noted previously in the coupling of aryl halides with $NaNO_2$.[24] Substrates containing acid-sensitive functional groups, such as BOC-protected anilines and nitriles, were tolerated and coupled in high yield along with substrates containing ketones, esters, and free NH groups of anilines (Table 3). Aryl bromides containing bulky *ortho*-groups, e.g., *o*-cyclohexyl and *o*-phenyl groups, could also be coupled successfully, although they required the use of the smaller ligand XPhos (**3**) (Table 3).

Table 3. Pd-catalyzed coupling of aryl bromides.[a]



Entry	Product	Yield
1		97%[b]
2		95%
3		99%
4		98%[c]

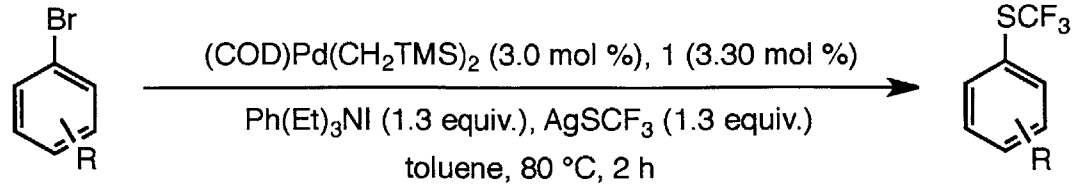
5		96%
6		85%[c]
7		>99%
8		97%[c]
9		97%[c]

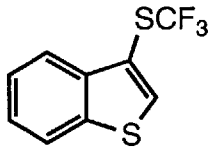
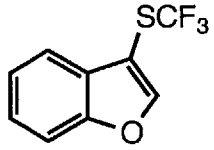
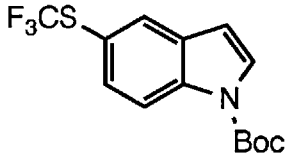
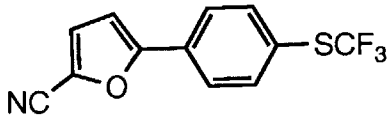
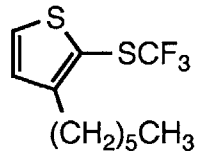
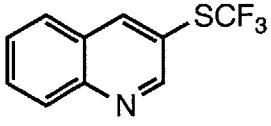
10		96%
11		96%
12		96%[d]
13		93%[d]

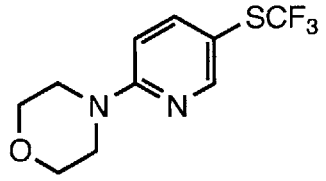
a) ArBr (1 mmol), PhMe (5 mL); isolated yields, average of two runs. b) 3.0 mol % Pd, 3.3 mol % **1**. c) 2.0 mol % Pd, 2.2 mol % **1**. d) 3.0 mol % Pd, 3.3 mol % **3**.

Heteroaryl bromides, such as those containing indoles, pyridines, quinolines, thiophenes and furans, also represent viable substrates (Table 4). Unfortunately, attempts to extend this methodology to the coupling of aryl chlorides or aryl triflates were unsuccessful. We are currently working to understand and overcome these limitations.

Table 4. Pd-catalyzed formation of heteroaryl–SCF_3 compounds.[a]

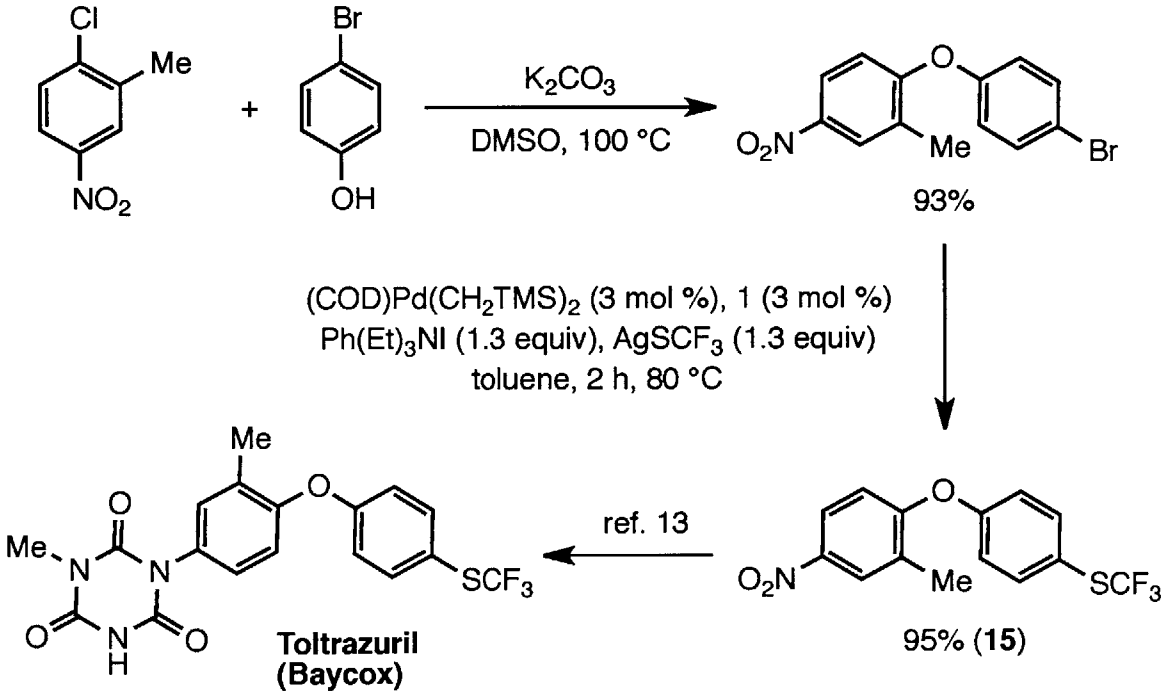


Entry	Product	Yield
1		94%
2		81%
3		93%
4		99%
5		96%
6		96%

7		98%

a) ArBr (1 mmol), PhMe (5 mL); isolated yields, average of two runs. b) 1.5 mol % Pd, 1.65 mol % **1**. c) 3.5 mol % Pd, 3.85 mol % **1**.

Finally, to demonstrate the utility of this method, we prepared an intermediate in the reported synthesis of Toltrazuril,[30] an antiprotozoal agent. To that end, intermediate **15** can be assembled from readily available starting materials in an overall yield of 88%, while the key C–SCF_3 bond-forming process proceeded in 95% yield (Scheme 2).



Scheme 2. Synthesis of Toltrazuril intermediate.

2.3: Conclusion

In summary, we have developed a general method for the Pd-catalyzed Ar–SCF_3 bond-forming reaction. Using this method, a wide range of aryl bromides were converted into their corresponding aryl trifluoromethyl sulfides. Additionally, we have been successful in generating a variety of heterocyclic aryl trifluoromethyl sulfides from heteroaryl bromide precursors. Considering the utility of Ar–SCF_3 compounds as biologically active agents, and the mild reaction conditions employed, we expect this method to be implemented in the discovery of novel biologically active compounds.

2.4: Experimental

General Information. Reactions were set up on a benchtop (not in a glove box) and were stirred with Teflon-coated magnetic stir bars. All reactions were performed in oven-dried, screw-cap test-tubes with Teflon seals under an atmosphere of argon. Toluene was purchased from J.T. Baker in CYCLE-TAINER® solvent-delivery kegs and vigorously purged with argon for 2 h. The solvent was further purified by passing it under argon pressure through two packed columns of neutral alumina and copper (II) oxide. Flash chromatography was performed on a Biotage Isolera 4 using SNAP 25g prepacked silica cartriges and a solvent gradient of dichloromethane:hexane (0 → 80%) unless otherwise noted. The preparation of (COD)Pd($CH_2TMS)_2$ has been previously described and it is commercially available from Aldrich.[22] The preparation of BrettPhos has also been previously described and it is available from Strem and Aldrich.[31] All quaternary ammonium salts were purchased from either Alfa or Aldrich and the bulk stored in a glovebox. Small quantities (~2 g) were periodically removed in glass vials and used immediately (within 3 h). AgF was purchased from Aldrich and stored as is

in the glovebox. Anhydrous MeCN and anhydrous CS_2 were purchased from Aldrich in Sure-Seal® bottles and used as received. All aryl bromides were purchased from Matrix Scientific, Aldrich or Alfa unless otherwise noted and used as received. Yields refer to isolated yields of compounds greater than 95% purity as determined by gas chromatography and ^1H NMR. Quoted yields are representative and so may differ slightly from the average values given in Tables 2 and 3, as well Scheme 3.

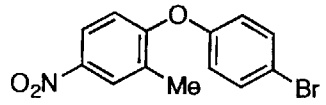
^1H NMR spectra were recorded on a Varian Inova-500 NMR spectrometer in deuterochloroform operating at 500 MHz. ^{13}C NMR spectra were recorded on a Varian Inova-500 NMR spectrometer in deuterochloroform operating at 126 MHz. ^{19}F NMR spectra were recorded on a Varian Inova-500 NMR spectrometer in deuterochloroform operating at 471 MHz. Chemical shifts are quoted relative to residual solvent in the case of ^1H and ^{13}C NMR spectra and relative to $CFCl_3$ as zero in the case of ^{19}F NMR spectra. The following abbreviations are used singularly or in combination to indicate the multiplicity of signals: s singlet, d doublet, t triplet, q quartet, m multiplet. NMR spectra were acquired at 298 K. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer as thin films on KBr plates. Selected absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}). GC analyses were performed on an Agilent 6970 equipped with an FID detector and a Hewlett Packard 10 m × 0.2 mm HP-1 capillary column using dodecane as an internal standard. Melting points were determined on a Mel-Temp II capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Inc., Nocross, GA.

Procedure for the Synthesis of $AgSCF_3$:[10]

To an oven dried 200 mL Schlenk flask equipped with a stir bar was added AgF (15 g, 118 mmol). The flask was fitted with a glass stopper and evacuated and refilled with Ar (this

procedure was repeated a total of three times). Under Ar pressure, the stopper was removed and replaced with a reflux condenser. The system was once again evacuated and refilled with Ar (this procedure was also repeated a total of three times). Dry MeCN (100 mL) was injected into the flask in two 50 mL portions via the side arm followed by CS_2 (15 mL). The flask was then placed into a preheated 80°C oil bath with efficient stirring. After several minutes the reaction mixture became brown in color. After 14 h the reaction mixture was black, at which time the flask was removed from the oil bath and the contents were allowed to cool to room temperature. The reflux condenser was replaced with a distillation head and excess CS_2 was removed by distillation. The remaining solvent was removed under reduced pressure with the aid of a rotary evaporator to produce a black residue, which was then redissolved in EtOAc and filtered through a pad of celite. The flask was then wrapped in aluminum foil and the solvent was once again removed under reduced pressure with the aid of a rotary evaporator. The resulting yellow solid was dissolved in a minimum amount of MeCN to produce a clear yellow solution, which was transferred to a 500 mL round bottom flask wrapped in aluminum foil. Et_2O (~300 mL) was carefully layered on top of the yellow solution. The flask was stoppered and left at room temperature overnight after which it was placed in a freezer set to -20°C for 24 h to produce an off-white crystalline solid. The flask was removed from the freezer and the solution was filtered while cold to collect the white material, which was then dried under vacuum over night to yield 7.5g (90%). The white solid was stored in a refrigerator (5 °C) with the exclusion of light.

Procedure for the Synthesis of 1-(4-Bromophenoxy)-2-methyl-4-nitrobenzene:



4-bromophenol (858 mg, 5 mmol, 1 equiv) and K_2CO_3 (1.8 g, 12.5 mmol, 2.5 equiv) were added to a 100 mL round bottom flask equipped with a stir bar. The flask was stoppered with a rubber septum and evacuated and refilled three times with Ar. Subsequently, DMSO (10 mL) was added to the mixture and the flask was placed into a preheated 70 °C oil bath for 30 min. The solution was then removed form the oil bath and allowed to cool to room temperature. 2-chloro-4-nitrotoluene was added as a solid to the reaction mixture. The flask was then placed into an oil bath and heated to 110 °C for 12 hours. The flask was removed from the oil bath and allowed to cool to room temperature. The solution was diluted with Et_2O and poured into a separatory funnel. The organic layer was washed three times with water followed by brine, dried over Mg_2SO_4 and filtered. The filtrate was then concentrated under reduced pressure with the aid of a rotary evaporator and the residue was purified via silica gel column chromatography (1% EtOAc in hexanes) to afford the pure compound as a pale yellow solid (1.44g, 93% yield), m.p. 57.2-58.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 2.3 Hz, 1H), 7.99 (dd, J = 9.0, 2.7 Hz, 1H), 7.51 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 9.0 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.29 (s), 155.27 (s), 143.66 (s), 133.92 (s), 130.48 (s), 127.58 (s), 123.89 (s), 122.09 (s), 118.17 (s), 116.97 (s), 17.07 (s). IR (film) ν_{max} 3091.03, 295.21, 2851.65, 2019.97, 1892.11, 1616.37, 1594.71, 1578.89, 1518.20, 1480.85, 1343.51, 1245.75, 1209.41, 1092.78, 1068.76, 1010.62, 931.81, 898.87, 844.90, 824.27, 802.71, 746.29, 650.07 cm^{-1}. Anal. Calcd. For $C_{14}H_{10}BrNO_3$: C, 50.67; H, 3.27. Found: C, 50.77; H, 3.31

Procedure for the Examination of Various Trifluoromethylthiolate Salts:

(COD)Pd($CH_2TMS)_2$ (1.9 mg, 0.005 mmol, 2.5 mol %), BrettPhos (3.0 mg, 0.0055 mmol, 2.75 mol %) and 0.2 mmol of 4-(4-bromophenyl)morpholino were added to a flame dried 8 mL test tube with Teflon screw cap equipped with magnetic stir bar. The tube was sealed and evacuated and refilled with Ar (this procedure was repeated a total of three times). After which toluene (2 mL) was added to the tube. The solution was placed into a preheated 80°C oil bath with stirring for 60 s. The tube was removed from the oil bath generating solution **A**.

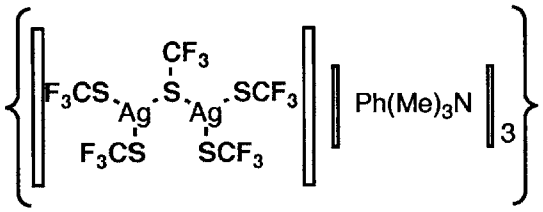
In an N_2 glovebox the SCF_3 salt (0.26 mmol, 1.3 equiv) was added to a flame dried 16 mL re-sealable screw cap tube equipped with two magnetic stir bars. The tube was evacuated and refilled with Ar (this procedure was repeated a total of three times). Solution **A** was added via cannula. The tube containing solution **A** was then washed with toluene (3 mL), which was then cannulated over once more. The tube was placed into a preheated 80°C oil bath with stirring for 14 h at which point the tube was removed and allowed to cool. Dodecane (45 μL, 0.20 mmol) was added to the cooled reaction tube. The reaction tube was then opened and the reaction mixture diluted with EtOAc. The resulting solution was analyzed using GC and GC/MS methods.

Procedure for the Examination of Various Quaternary Ammonium Salt Additives:

(COD)Pd($CH_2TMS)_2$ (1.9 mg, 0.005 mmol, 2.5 mol %), BrettPhos (3.0 mg, 0.0055 mmol, 2.75 mol %) and 0.2 mmol of 4-(4-bromophenyl)morpholino were added to a flame dried 8 mL test tube with Teflon screw cap equipped with magnetic stir bar. The tube was sealed and evacuated and refilled with Ar (this procedure was repeated a total of three times). After which toluene (2 mL) was added to the tube. The solution was placed into a preheated 80°C oil bath with stirring for 60 s. The tube was removed from the oil bath generating solution **A**.

$AgSCF_3$ (54.0 mg, 0.26 mmol, 1.3 equiv) and a quaternary ammonium salt additive (0.26 mmol, 1.3 equiv) were added to a flame dried 16 mL re-sealable screw cap tube equipped with two magnetic stir bars. The tube was evacuated and refilled with Ar (this procedure was repeated a total of three times). Solution **A** was added via cannula. The tube containing solution A was then washed with 3 mL of dry toluene, which was then cannulated over once more. The tube was placed into a preheated 80°C oil bath with stirring for 14 h after which point the tube was removed and allowed to cool. Dodecane (45 μL, 0.20 mmol) was added to the cooled reaction tube. The reaction tube was opened and the reaction mixture diluted with EtOAc. The resulting solution was analyzed using GC and GC/MS methods.

Synthesis and characterization of 14:



In a nitrogen filled glovebox, to a 20 mL vial equipped with a magnetic stir bar was added an $AgSCF_3$ (208 mg, 1 mmol) and $(Me)_3NI$ (305 mg, 1 mmol). To this mixture was added MeCN (1 mL). The clear solution was allowed to stir at room temperature for 1 h at which point a white precipitate formed. The solids were removed by filtration and the resulting solution was concentrated under vacuum to yield a clear, colorless glassy solid. A sample of this compound was then transferred to a small vial and dissolved in a minimum amount of THF. Clear, colorless crystals suitable for X-ray diffraction were grown via vapor diffusion of Et_2O. Note that this

compound is extremely air and moisture sensitive and can only be handled under an inter atmosphere.

Evaluation of the Chemical Competence of Compound 14:

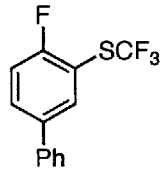
In a nitrogen filled glove box, **10** (87.5 mg, 0.1 mmol) and **14** (32.75 mg, 0.02 mmol) were added to an oven dried 8 mL screw top test tube equipped with a stir bar and a Teflon screw cap. Toluene (2 mL) was then added to the test tube at which point it was removed from the glovebox and placed into a preheated 80° C oil bath. The reaction was allowed to cool and dodecane (22.5 μ L, 0.1 mmol) was added as standard. The contents of the tube were then diluted with ethyl acetate and filtered through a pad of silica. The solution as analyzed using GC methods to determine a yield of 40 % based on palladium.

General Procedure A. (COD)Pd($CH_2TMS)_2$ (5.8 mg, 0.015 mmol, 1.5 mol %), BrettPhos (8.9 mg, 0.0165 mmol, 1.65 mol %) and 1 mmol of starting aryl bromide, if solid, were added to a flame dried 8 mL test tube with Teflon screw cap equipped with magnetic stir bar. The tube was sealed and evacuated and refilled with Ar (this procedure was repeated a total of three times). After which toluene (2 mL) was added to the tube as well as aryl bromide if liquid. The solution was placed into a preheated 80°C oil bath for 60 s. The tube was removed from the oil bath generating solution **A**.

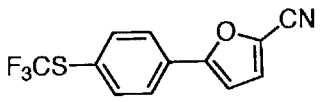
$AgSCF_3$ (280 mg, 1.3 mmol, 1.3 equiv) and $(Ph)(Et)_3NI$ (400 mg, 1.3 mmol, 1.3 equiv) were added to a flame dried 16 mL re-sealable screw cap tube equipped with two magnetic stir bars. The tube was evacuated and refilled with Ar (this procedure was repeated a total of three times). Solution **A** was added via cannula. The tube containing solution A was then washed with toluene which (3 mL) was then cannulated over once more. The tube was placed into a preheated 80 °C oil bath with stirring for 2 h at which point the tube was removed and allowed to cool. The

reaction mixture was then filtered through Si_2O eluting with EtOAc. The solvent was removed under reduced pressure and the residue was purified via silica gel column chromotagraphy.

General Procedure B. As General Procedure A but with XPhos as ligand.

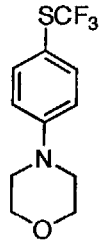


4-Fluoro-3-((trifluoromethyl)thio)-1,1'-biphenyl. Following general procedure A, 4-fluoro-3-bromo-1,1'-biphenyl (251 mg, 1 mmol) was used. Purification via column chromatography provided the compound as a clear colorless oil (259.8 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.67 (dd, J = 7.8, 1.8 Hz, 2H), 7.60 δ 7.53 (m, 2H), 7.51 (t, J = 7.8 Hz, 1H), 7.18 (t, J = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.58 (s), 162.61 (s), 142.47 (s), 136.41 (d, J = 3.2 Hz), 135.53 (d, J = 18.1 Hz), 130.60 (s), 130.41 (q, J = 308.1 Hz), 130.12 (s), 129.52 (d, J = 8.2 Hz), 125.78 (s), 116.63 (d, J = 21.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.71 (s), -114.47 δ -114.59 (m). IR (film) ν_{max}1609.44, 1514.40, 1471.51, 1237.92, 1160.72, 1117.48, 1098.31, 1082.37, 837.39, 791.78, 694.48 cm $^{-1}$. Anal. Calcd. For $C_{13}H_8F_4S$: C, 57.35; H, 2.96. Found: C, 57.24; H, 2.95.

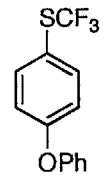


5-(4-((Trifluoromethyl)thio)phenyl)furan-2-carbonitrile. Following general procedure A, 5-(4-bromophenyl)furan-2-carbonitrile (248 mg, 1 mmol) was used. Purification via column chromatography provided the compound as an orange solid (258.5 mg, 96%), m.p. 77.3-81.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 δ 7.65 (m, 4H), 7.17 (d, J = 3.7 Hz, 1H), 6.81 (d, J = 3.7 Hz,

1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.59 (s), 137.37 (d, J = 0.8 Hz), 131.44 (s), 128.56 (q, J = 308.5 Hz), 126.60 (s), 126.24 (s), 126.14 (dd, J = 4.3, 2.2 Hz), 124.70 (s), 112.22 (s), 108.50 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.48 (s). IR (film) ν_{max} 2231.21, 1478.49, 1123.61, 1087.13, 1024.82, 838.42, 796.26 cm^{-1}. Anal. Calcd. For $C_{12}H_6F_3NOS$: C, 53.53; H, 2.25. Found: C, 53.43; H, 2.12.

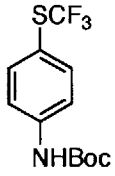


4-(4-((Trifluoromethyl)thio)phenyl)morpholine. Following general procedure A, 4-(4-bromophenyl)morpholine (242 mg, 1 mmol) was used. Purification via column chromatography provided the compound as a pale yellow oil (262 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 8.8 Hz, 1H), 6.88 (d, J = 9.0 Hz, 1H), 3.88 δ 3.82 (m, 2H), 3.25 δ 3.19 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.59 (s), 138.61 (d, J = 0.5 Hz), 130.45 (q, J = 308.3 Hz), 115.92 (s), 113.03 (q, J = 2.0 Hz), 67.31 (s), 48.60 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -44.17 (s). IR (film) ν_{max} 2966.02, 2857.40, 1594.34, 1502.18, 1451.02, 1381.75, 1352.25, 1305.79, 1263.12, 1240.05, 1122.89, 1051.78, 928.78, 819.87, 754.13, 670.94, 579.60, 557.18, 528.69, 472.80 cm^{-1} Anal. Calcd. For $C_{11}H_{12}F_3NOS$: C, 50.18; H, 4.59. Found: C, 50.47; H, 4.68.

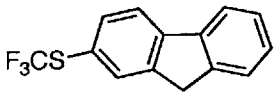


4-Phenoxy-((trifluoromethyl)thio)benzene. Following general procedure A, 4-Phenoxy-bromobenzene (249 mg, 1 mmol) was used. Purification via column chromatography

provided the compound as a colorless oil (263 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 δ 7.61 (m, 2H), 7.47 δ 7.40 (m, 2H), 7.28 δ 7.21 (m, 1H), 7.16 δ 7.09 (m, 2H), 7.07 δ 7.03 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.18 (s), 156.34 (s), 139.10 (d, J = 0.7 Hz), 130.81 (s), 130.36 (q, J = 308.1 Hz), 125.32 (s), 120.84 (s), 119.34 (s), 117.96 (q, J = 2.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.66 (s). IR (film) ν_{max} 1582.89, 1488.04, 1280.75, 1246.21, 1118.86, 1084.24, 869.61, 835.22, 755.96, 692.86 cm^{-1}. Anal. Calcd. For $C_{13}H_9F_3OS$: C, 57.77; H, 3.36. Found: C, 58.01; H, 3.46.

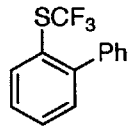


***tert*-Butyl (4-((trifluoromethyl)thio)phenyl)carbamate** Following general procedure A, tert-Butyl (4-bromophenyl)carbamate (272 mg, 1 mmol) was used. Purification via column chromatography provided the compound as a white solid (263 mg, 91%), m.p. 93.4-94.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 6.98 (s, 1H), 1.51 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.23 (s), 141.95 (s), 138.20 (s), 130.30 (q, J = 308.1 Hz), 119.59 (s), 117.75 (q, J = 2.1 Hz), 81.95 (s), 28.89 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.65 (s). IR (film) ν_{max} 3329.19, 2988.12, 1699.19, 1587.43, 1525.85, 1402.61, 1371.69, 1312.17, 1127.98, 836.17, 773.97, 672.85, 522.71 cm^{-1}. Anal. Calcd. For $C_{12}H_{14}F_3NO_2S$: C, 49.14; H, 4.81. Found: C, 49.24; H, 4.75.

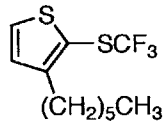


2-((Trifluoromethyl)thio)fluorene Following general procedure A, 2-bromofluorene (245 mg, 1 mmol) was used. Purification via column chromatography provided the compound as a pale yellow solid (259 mg, 97%), m.p. 44.5-47.8 °C. Note: the starting material was contaminated with 5% of 2,7-dibromofluorene, as a result the ^{19}F NMR spectrum

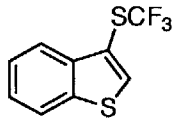
exhibits a second, minor fluorine signal corresponding to 5% of 2,7-bis((trifluoromethyl)thio)fluorene. These two compounds are inseparable by column chromatography. The yield has been corrected for this impurity. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.79 δ 7.64 (m, 3H), 7.58 δ 7.52 (m, 1H), 7.47 δ 7.38 (m, 1H), 3.80 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.14 (s), 145.05 (s), 144.39 (s), 140.93 (s), 135.93 (d, J = 0.7 Hz), 133.73 (d, J = 0.7 Hz), 130.66 (q, J = 308.2 Hz), 128.63 (s), 127.75 (s), 125.86 (s), 122.37 (q, J = 2.1 Hz), 121.26 (s), 121.21 (s), 37.35 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.15 (s). IR (film) ν_{max} 3066.87, 2898.42, 1603.59, 1466.72, 1450.07, 1410.34, 1111.22, 1073.50, 829.35, 767.41, 732.25, 592.42, 461.39, 416.97 cm^{-1}. Anal. Calcd. For $C_{14}H_9F_3S$: C, 63.15; H, 3.41. Found: C, 62.89; H, 3.41.



4-((Trifluoromethyl)thio)-1,1'-biphenyl[32] Following general procedure B, 4-bromo-1,1'-biphenyl (233 mg, 1 mmol) was used along with 3 mol % (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol % XPhos (15.7 mg). Purification via column chromatography provided the compound as a colorless oil (244 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.8 Hz, 1H), 7.58 (td, J = 7.5, 1.3 Hz, 1H), 7.55 δ 7.46 (m, 5H), 7.45 δ 7.40 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.68 (s), 141.03 (s), 137.94 (d, J = 0.9 Hz), 132.07 (s), 131.46 (s), 130.47 (s), 130.38 (q, J = 308.5 Hz), 129.04 (s), 128.74 (s), 128.46 (s), 124.07 (dd, J = 3.7, 1.8 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.11 (s). IR (film) ν_{max} 3060.97, 3030.76, 2927.66, 1948.39, 1587.68, 1466.00, 1447.50, 1430.45, 1107.02, 1074.22, 1037.25, 1008.09, 758.02, 700.00, 614.29 cm^{-1}. Anal. Calcd. For $C_{13}H_9F_3S$: C, 61.41; H, 3.57. Found: C, 61.30; H, 3.64.

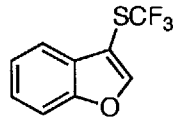


3-Hexyl-2-((trifluoromethyl)thio)thiophene Following general procedure A, 3-hexyl-2-bromothiophene (247 mg, 1 mmol) was used along with 3.5 mol % (COD)Pd(CH_2TMS_2) (13.6 mg) and 3.85 mol % BrettPhos (20.7 mg). Purification via column chromatography provided the compound as a colorless oil (249 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 5.4 Hz, 1H), 7.07 (d, J = 5.5 Hz, 1H), 3.09 – 2.66 (m, 2H), 1.64 (dt, J = 15.5, 7.6 Hz, 2H), 1.37 (tdd, J = 10.5, 7.9, 5.1 Hz, 6H), 0.94 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.95 (d, J = 0.8 Hz), 132.91 (s), 129.79 (s), 129.29 (q, J = 311.0 Hz), 115.75 (dd, J = 4.7, 2.4 Hz), 32.35 (s), 31.13 (s), 29.78 (s), 29.65 (s), 23.31 (s), 14.73 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -44.95 (s). IR (film) ν_{max} 2929.43, 2859.56, 1523.88, 1466.92, 1395.96, 1117.80, 839.88, 754.91, 736.45, 659.91, 497.80 cm^{-1}. Anal. Calcd. For $C_{11}H_{15}F_3S_2$: C, 49.23; H, 5.63. Found: C, 49.49; H, 5.83.

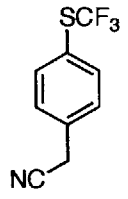


3-((Trifluoromethyl)thio)benzo[b]thiophene. Following general procedure A, 3-bromobenzothiophene (213 mg, 1 mmol) was used along with 3 mol % (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol % BrettPhos (17.7 mg). Purification via column chromatography provided the compound as a colorless oil (217.5 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (dd, J = 8.1, 0.4 Hz, 1H), 7.99 (s, 1H), 7.95 δ 7.89 (m, 1H), 7.56 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 7.52 δ 7.45 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.20 (s), 140.15 (s), 138.66 (d, J = 1.0 Hz), 130.04 (q, J = 309.9 Hz), 126.12 (d, J = 2.5 Hz), 126.09 (s), 123.62 (s), 123.58 (s), 115.97 (q, J = 2.1 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.75 (s). IR (film) ν_{max} 3102.09, 3059.97, 2927.53, 2274.12, 1913.00, 1792.20, 1651.05, 1584.28, 1480.22, 1454.92, 1421.76, 1317.46, 1255.44,

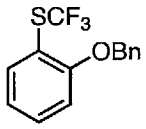
1107.70, 1063.23, 962.79, 838.40, 754.96, 730.99, 703.99, 606.21 cm^{-1} . Anal. Calcd. For $C_9H_5F_3S_2$: C, 46.14; H, 2.15. Found: C, 46.40; H, 2.26.



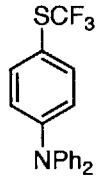
3-((Trifluoromethyl)thio)benzofuran. Following general procedure A, 3-bromobenzofuran (197 mg, 1 mmol) was used along with 3.5 mol % (COD)Pd(CH_2TMS_2) (13.6 mg) and 3.85 mol % BrettPhos (20.7 mg). Purification via column chromatography provided the compound as a colorless oil (218 mg, 81%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.79 (dd, J = 6.1, 2.8 Hz, 1H), 7.66 – 7.54 (m, 1H), 7.49 – 7.36 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.19 (s), 152.29 (d, J = 1.2 Hz), 129.67 (q, J = 309.8 Hz), 128.75 (s), 126.37 (s), 124.84 (s), 120.74 (d, J = 0.6 Hz), 112.70 (s), 103.95 (dd, J = 5.3, 2.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.40 (s). IR (film) ν_{max} 1531.97, 1449.90, 1253.30, 1112.40, 1014.83, 853.98, 745.36, 610.17 cm^{-1}.



2-(4-((trifluoromethyl)thio)phenyl)acetonitrile.[33] Following general procedure A, 2-(4-bromophenyl)acetonitrile (196 mg, 1 mmol) was used along with 2 mol % (COD)Pd(CH_2TMS_2) (7.78 mg) and 2.2 mol % BrettPhos (11.8 mg). Purification via column chromatography provided the compound as a yellow oil (211.5 mg, 97%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 3.79 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.65 (d, J = 0.8 Hz), 133.89 (s), 130.15 (q, J = 308.1 Hz), 129.80 (s), 125.10 (q, J = 2.2 Hz), 117.86 (s), 24.08 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.85 (s). IR (film) ν_{max} 3066.62, 2926.19, 2253.47, 1923.91, 1599.82, 1495.68, 1412.15, 1115.88, 1086.84, 1018.86, 838.60, 799.92, 755.92, 570.38, 532.31, 501.04 cm^{-1}.

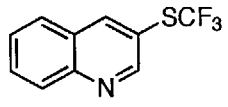


2-(Benzyloxy)-((trifluoromethyl)thio)benzene. Following general procedure A, 2-(benzyloxy)-bromobenzene (263 mg, 1 mmol) was used along with 2 mol % (COD)Pd(CH_2TMS_2) (7.78 mg) and 2.2 mol % BrettPhos (11.8 mg). Purification via column chromatography provided the compound as a colorless oil (273 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.9, 1.1 Hz, 1H), 7.56 (d, J = 7.5 Hz, 2H), 7.53 δ 7.46 (m, 3H), 7.42 (t, J = 7.3 Hz, 1H), 7.07 (ddd, J = 6.7, 3.4, 2.4 Hz, 2H), 5.24 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.40 (s), 139.32 (s), 137.16 (s), 133.61 (s), 130.58 (q, J = 308.9 Hz), 129.42 (s), 128.77 (s), 127.72 (s), 122.25 (s), 114.02 (s), 113.78 (d, J = 1.2 Hz), 71.33 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.37 (s). IR (film) ν_{max} 3068.01, 2928.67, 1583.50, 1477.33, 1443.18, 1380.53, 1281.14, 1250.72, 1111.30, 1062.45, 755.77, 696.24 cm^{-1}. Anal. Calcd. For $C_{14}H_{11}F_3OS$: C, 59.15; H, 3.90. Found: C, 59.23; H, 3.98.

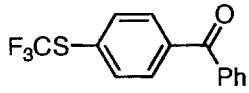


N,N-Diphenyl-4-((trifluoromethyl)thio)aniline. Following general procedure A, N,N-diphenyl-4-bromoaniline (324 mg, 1 mmol) was used along with 2 mol % (COD)Pd(CH_2TMS_2) (7.78 mg) and 2.2 mol % BrettPhos (11.8 mg). Purification via column chromatography provided the compound as a colorless oil (338 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.7 Hz, 2H), 7.39 (dd, J = 8.3, 7.5 Hz, 4H), 7.29 δ 7.23 (m, 4H), 7.23 δ 7.18 (m, 2H), 7.12 (d, J = 8.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.25 (s), 147.54 (s), 138.39 (s), 130.52 (q, J = 308.5 Hz), 130.43 (s), 126.48 (s), 125.18 (s), 122.40 (s), 115.33 (d, J = 1.8 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.96 (s). IR (film) ν_{max} 3036.97, 1582.95, 1491.51,

1331.58, 1316.23, 1284.84, 1116.86, 1088.70, 826.15, 754.96, 696.26, 522.71 cm^{-1}. Anal. Calcd. For $C_{19}H_{14}F_3NS$: C, 66.07; H, 4.09. Found: C, 66.16; H, 4.14.

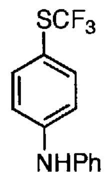


3-((Trifluoromethyl)thio)quinoline Following general procedure A, 3-bromoquinoline (208 mg, 1 mmol) was used along with 3 mol % (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol % BrettPhos (17.7 mg). Purification via column chromatography provided the compound as a colorless solid (220.5 mg, 96%), m.p. 42.8-44.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (d, J = 2.1 Hz, 1H), 8.49 (d, J = 1.8 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.94 δ 7.68 (m, 2H), 7.68 δ 7.47 (m, 1H). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (d, J = 2.1 Hz, 1H), 8.49 (d, J = 1.8 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.94 δ 7.68 (m, 2H), 7.68 δ 7.47 (m, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.62 (s). IR (film) ν_{max} 3038.86, 1616.58, 1565.41, 1358.42, 1143.05, 1131.95, 1113.51, 1081.70, 956.02, 913.81, 785.79, 755.83, 648.17 cm^{-1}. Anal. Calcd. For $C_{10}H_6F_3NS$: C, 52.40; H, 2.64. Found: C, 52.21; H, 2.52

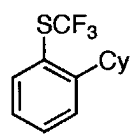


4-((Trifluoromethyl)thio)benzaphenone Following general procedure A, 4-bromobenzophenone (261 mg, 1 mmol) was used along with 2 mol % (COD)Pd(CH_2TMS_2) (7.78 mg) and 2.2 mol % BrettPhos (11.8 mg). Purification via column chromatography provided the compound as a pale yellow solid (234 mg, 83%), m.p. 67.8-70.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (ddd, J = 9.6, 7.5, 1.6 Hz, 4H), 7.75 (d, J = 8.2 Hz, 2H), 7.64 δ 7.57 (m, 1H), 7.48 (t, J = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.14 (s), 140.14 (s), 137.47 (s), 136.22 (d, J = 0.6 Hz), 133.68 (s), 131.38 (s), 130.74 (s), 130.07 (q, J = 308.4 Hz), 129.77 (dd, J = 4.2, 2.1 Hz), 129.19 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.06 (s). IR (film) ν_{max} 1654.00, 1578.58,

1396.12, 1285.17, 1114.11, 1081.89, 847.44, 731.07, 696.46, 665.30 cm^{-1}. Anal. Calcd. For $C_{14}H_9F_3OS$: C, 59.57; H, 3.21. Found: C, 59.85; H, 3.19

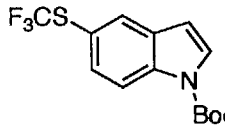


N-Phenyl-4-((trifluoromethyl)thio)aniline Following general procedure A, N-phenyl-4-bromoaniline (248 mg, 1 mmol) was used along with 3 mol % (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol % BrettPhos (17.7 mg). Purification via column chromatography provided the compound as a colorless oil (264.5 mg, 98%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.5 Hz, 2H), 7.42 (t, J = 7.9 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 8.7 Hz, 2H), 5.91 (s, 1H). ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.5 Hz, 2H), 7.42 (t, J = 7.9 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 8.7 Hz, 2H), 5.91 (s, 1H). ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.5 Hz, 2H), 7.42 (t, J = 7.9 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 8.7 Hz, 2H), 5.91 (s, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -44.29 (s). IR (film) ν_{max} 3401.73, 1587.40, 1507.52, 1319.13, 1116.19, 1088.41, 822.33, 752.58, 697.30 cm^{-1}. Anal. Calcd. For $C_{13}H_{10}F_3NS$: C, 57.98; H, 3.74. Found: C, 57.89; H, 3.65.

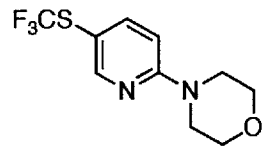


2-Cyclohexyl-((trifluoromethyl)thio)benzene Following general procedure B, 2-cyclohexyl-bromobenzene (239 mg, 1 mmol) was used along with 3 mol % (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol % XPhos (15.7 mg). Purification via column chromatography provided the compound as a colorless oil (264.5 mg, 93%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 7.8 Hz, 1H), 7.49 (td, J = 7.8, 1.2 Hz, 1H), 7.44 (dd, J = 7.9, 1.5 Hz,

1H), 7.25 (td, J = 7.7, 1.6 Hz, 1H), 3.63 δ 3.27 (m, 1H), 2.07 δ 1.67 (m, 5H), 1.63 δ 1.40 (m, 4H), 1.37 δ 1.19 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.73 (s), 138.99 (d, J = 0.4 Hz), 132.20 (s), 130.40 (q, J = 308.3 Hz), 128.20 (s), 127.22 (s), 123.57 (dd, J = 3.6, 1.7 Hz), 42.07 (s), 34.86 (s), 27.50 (s), 26.86 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.95 (s). IR (film) ν_{max} 2929.78, 2854.56, 1471.68, 1449.71, 1119.09, 1101.59, 1036.40, 758.59, 497.98 cm^{-1} Anal. Calcd. For $C_{13}H_{15}F_3S$: C, 59.98; H, 5.81. Found: C, 59.96; H, 5.93

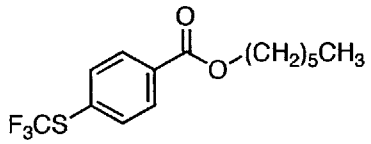


***tert*-Butyl 5-((trifluoromethyl)thio)-1H-indole-1-** Following general procedure A, *tert*-Butyl 5-bromo-1H-indole-1- (296 mg, 1 mmol) was used. Purification via column chromatography provided the compound as a colorless solid (311 mg, 98%), m.p. 43.7-44.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 1.5 Hz, 1H), 7.68 (d, J = 3.6 Hz, 1H), 7.60 (dd, J = 8.6, 1.6 Hz, 1H), 6.59 (d, J = 3.7 Hz, 1H), 1.71 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.98 (s), 137.14 (s), 132.67 (s), 132.16 (s), 130.59 (q, J = 307.9 Hz), 130.47 (s), 128.04 (s), 118.13 (dd, J = 4.0, 1.9 Hz), 116.74 (s), 107.60 (s), 85.11 (s), 28.74 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.73 (s). IR (film) ν_{max} 2982.41, 1741.32, 1453.10, 1371.67, 1342.33, 1156.49, 1135.85, 1115.89, 1084.84, 1023.84, 765.79, 726.28 cm^{-1}. Anal. Calcd. For $C_{14}H_{14}F_3NO_2S$: C, 52.99; H, 4.45. Found: C, 53.15; H, 4.49

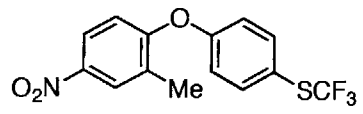


4-(5-((Trifluoromethyl)thio)pyridin-2-yl)morpholine Following general procedure A, 4-(5-bromopyridin-2-yl)morpholine (243 mg, 1 mmol) was used along with 3 mol % (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol % BrettPhos (17.7 mg). Purification via column chromatography provided the compound as a pale yellow solid (258.5 mg, 98%), m.p.

79.2-82.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, J = 2.2 Hz, 1H), 7.64 (dd, J = 8.9, 2.3 Hz, 1H), 6.57 (d, J = 8.9 Hz, 1H), 3.79 δ 3.67 (m, 4H), 3.59 δ 3.45 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.51 (s), 156.21 (s), 145.68 (s), 130.01 (q, J = 308.8 Hz), 108.31 (dd, J = 3.9, 1.9 Hz), 107.32 (s), 67.19 (s), 45.56 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -44.70 (s). IR (film) ν_{max} 2972.62, 2906.71, 2854.08, 1587.30, 1494.11, 1251.56, 1145.38, 1108.98, 942.35, 805.01 cm^{-1}.



Hexyl 4-((trifluoromethyl)thio)benzoate Following general procedure A, Hexyl 4-bromobenzoate (285 mg, 1 mmol) was used along with 2 mol % (COD)Pd(CH_2TMS_2) (7.78 mg) and 2.2 mol % BrettPhos (11.8 mg). Purification via column chromatography provided the compound as a colorless oil (298.5 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 4.32 (t, J = 6.7 Hz, 2H), 1.82 δ 1.63 (m, 2H), 1.52 δ 1.37 (m, 2H), 1.36 δ 1.24 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.15 (s), 136.20 (d, J = 0.8 Hz), 136.20 (d, J = 0.8 Hz), 131.03 (s), 130.32 (dd, J = 4.2, 2.1 Hz), 130.00 (q, J = 308.3 Hz), 66.25 (s), 32.12 (s), 29.30 (s), 26.35 (s), 23.21 (s), 14.59 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.20 (s). IR (film) ν_{max} 2959.03, 2933.12, 2860.72, 1726.32, 1597.35, 1468.47, 1399.69, 1305.74, 1273.46, 1017.39, 856.38, 764.98, 692.89, 502.89 cm^{-1}. Anal. Calcd. For $C_{13}H_{15}F_3O_2S$: C, 54.89; H, 5.59. Found: C, 55.09; H, 5.71



1-(4-((Trifluoromethyl)thio)phenoxy)-2-methyl-4-nitrobenzene[30] Following general procedure A, 1-(4-bromophenoxy)-2-methyl-4-nitrobenzene (308 mg, 1 mmol) was used along with 3 mol % (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol % BrettPhos (17.7 mg). Purification via column chromatography provided the compound as a colorless oil (314 mg, 95%), m.p. 62-63 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 2.7 Hz,

1H), 8.03 (dd, J = 8.9, 2.8 Hz, 1H), 7.67 (d, J = 8.7 Hz, 2H), 7.21 δ 7.00 (m, 2H), 6.93 (d, J = 8.9 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.19 (s), 159.02 (s), 144.34 (s), 139.34 (s), 131.42 (s), 130.16 (q, J = 308.2 Hz), 127.68 (s), 123.89 (s), 120.33 (s), 119.99 (dd, J = 4.4, 2.2 Hz), 118.73 (s), 16.97 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.48 (s). IR (film) ν_{max} 3092.96, 2928.72, 2856.16, 2270.72, 2023.09, 1903.95, 1617.82, 1581.03, 1522.70, 1485.23, 1345.34, 1247.74, 1213.91, 1117.85, 1087.46, 1013.59, 931.93, 900.25, 856.71, 830.53, 803.93, 747.36, 519.60 cm^{-1}. Anal. Calcd. For $C_{14}H_{10}F_3NO_3S$: C, 51.06; H, 3.06. Found: C, 51.30; H, 3.06

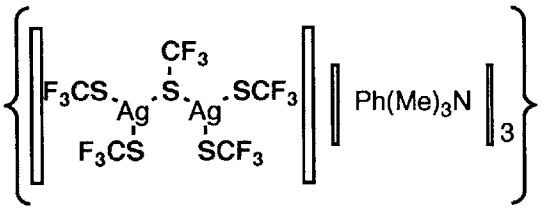


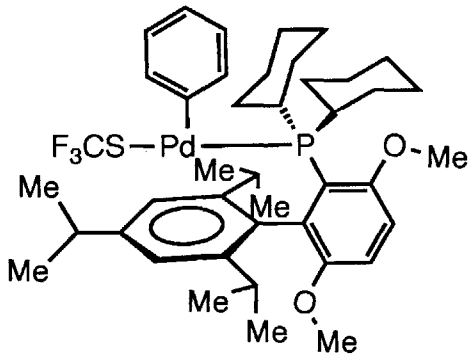
Table 5. Crystal data for structure refinement of **14**.

Identification code	x10014	
Empirical formula	C31.97 H42 Ag2 F14.90 I0.04 N3 S4.96	
Formula weight	1130.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.5476(12) Å	a= 94.448(3)°.
	b = 9.7862(12) Å	b= 91.096(3)°.
	c = 25.535(4) Å	g = 116.480(2)°.
Volume	2125.3(5) $Å^3$	
Z	2	
Density (calculated)	1.767 Mg/m^3	
Absorption coefficient	1.285 mm^{-1}	
F(000)	1128	
Crystal size	0.15 x 0.15 x 0.05 mm^3	
Theta range for data collection	1.60 to 29.57°.	
Index ranges	-13<=h<=13, -13<=k<=13, -35<=l<=35	
Reflections collected	94863	
Independent reflections	11848 [R(int) = 0.0351]	
Completeness to theta = 29.57°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9385 and 0.8306	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11848 / 895 / 655	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0228, wR2 = 0.0458	
R indices (all data)	R1 = 0.0303, wR2 = 0.0485	
Largest diff. peak and hole	0.474 and -0.559 $e.Å^{-3}$	

Computational Methods

All calculations were carried out with the Gaussian '03 suite.[34] All calculations were performed using the Becke[35-37] three-parameter hybrid functional combined with Lee–Yang–Parr correlation functional. C, H, O, P, and S were computed at the 6-31G(d) level of theory, F was computed using 6-311++G(d,p) and for the Pd center, LANL2DZ+ECP was used.[38] Frequency calculations were undertaken to confirm the nature of the stationary points, yielding one imaginary frequency (NImag = 1) for transition states (TS) with largest contributions from internal coordinates involved in the reaction and none (NImag = 0) for minima. All optimizations were performed without any constraints (C1 symmetry). Geometry optimizations were carried out in the gas phase.

Cartesian Coordinates for Ground State Structures:



Pd	-0.24716900	-1.15161400	-0.15961800
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C	0.90723400	-2.63704000	-0.89803600
C	-1.54933700	1.39144000	-0.05540700
C	-0.85506000	3.74827900	0.18812000
C	-2.30079800	0.98151400	1.08369200
C	0.95928000	2.11647600	0.19917400
C	-0.42317100	2.39336500	0.11309500
C	-2.10086500	1.18100000	-1.35529500
C	1.86802900	3.19373800	0.37657700
C	-1.84331700	1.25564200	2.51587100
C	-1.41458800	1.68636400	-2.62371800
C	-4.10386100	0.17487600	-0.36840800
C	-5.50494300	-0.40498300	-0.51180500
C	-6.52789000	0.71836900	-0.78175700
C	-5.60618000	-1.50726800	-1.58027500
C	-3.35137400	0.57235900	-1.47736200
C	1.42042700	4.50761400	0.45032900
C	-3.54967400	0.38118300	0.89368000
C	0.05723000	4.78411600	0.35310700
C	2.85600000	0.20396800	-1.26210100
C	2.57239400	0.15107500	1.73675800
C	4.35703100	0.31830700	-0.92322200
C	4.86678400	0.84986300	-3.35915300
C	5.21406700	-0.03448200	-2.15378600
C	2.49830200	1.10023000	-2.46555900
C	1.88578200	0.74815700	2.98030800
C	2.91636400	-1.32937200	1.99658300

C	3.37031300	0.76470900	-3.68822000
C	2.78479900	0.60806200	4.22244000
C	-2.68071900	2.38044600	3.16034300
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C	-1.24441800	0.58144600	-3.68314500
C	1.94894900	-3.66069300	-2.84090200
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C	3.18219100	-0.85281000	4.47715500
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C	4.13879700	3.89786500	0.70852500
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H	3.93524300	4.42478100	1.64951200
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H	-5.76148200	-0.86019300	0.45410000
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H	6.27746000	0.06546000	-1.89956400
H	5.05265000	-1.08950600	-2.41766800
H	2.64021500	2.15444800	-2.19383400
H	1.44255000	0.97976700	-2.72928800
H	0.93905000	0.22443300	3.16279800
H	1.64286100	1.80393600	2.82029100
H	3.39308600	-1.78922300	1.12433200
H	1.98519700	-1.88440200	2.16280300
H	3.13182100	-0.25254200	-4.02997800
H	3.12006800	1.44105000	-4.51592200
H	3.69265900	1.21330000	4.07943900
H	2.26853200	1.02196100	5.09822900
H	-2.65684300	3.29082500	2.55471000
H	-2.29918200	2.61664800	4.16137900
H	-3.72902100	2.07633200	3.26514100
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H	-2.90499300	-0.34394900	3.58013500
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H	0.67670300	-1.93284800	-2.93354200
H	1.25496300	-3.66526100	0.96940900
H	4.04055500	-2.53824200	3.40251400
H	4.79044100	-0.98816900	3.03249000
H	3.16361200	-5.40608800	-2.46574000
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C	-1.81670600	-3.76574100	1.07621800
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F	-2.99515400	-4.08818000	1.66259000
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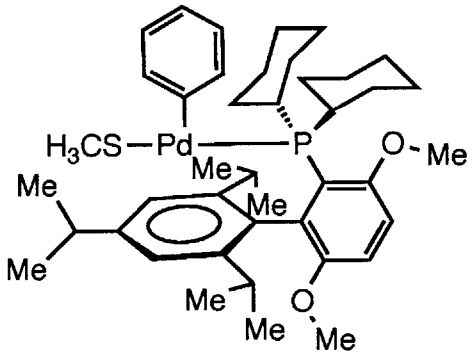
S	-2.08221200	-2.65720500	-0.31230800



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C	-2.45231200	0.61699700	1.15285100
C	0.52890400	2.01514400	-0.19875600
C	-0.88204100	2.04849900	-0.24229200

C	-2.38583500	0.28836100	-1.27666800
C	1.25092100	3.22997500	-0.34309700
C	-1.97763100	1.26334800	2.45257200
C	-1.84627700	0.58999400	-2.67421800
C	-4.13683700	-0.78440400	0.05590200
C	-5.41311900	-1.60891700	0.16489700
C	-6.65047500	-0.71080500	-0.04716700
C	-5.45110600	-2.82371400	-0.77591700
C	-3.51351300	-0.52866100	-1.16729600
C	0.59379600	4.43922400	-0.53801100
C	-3.58182100	-0.20373600	1.19596800
C	-0.79973800	4.47293300	-0.58688800
C	2.65461300	0.12580400	-1.32179700
C	2.51202900	0.76813700	1.61954900
C	4.13741000	0.49166900	-1.10514700
C	4.48649900	0.57348800	-3.62563100
C	4.99150000	0.00644200	-2.29182600
C	2.14000500	0.70693800	-2.65452800
C	1.81148700	1.59246800	2.71719500
C	3.07134400	-0.53209700	2.23083000
C	3.00419200	0.23758600	-3.83824700
C	2.78317900	1.90833400	3.86917100
C	-2.99085900	2.30817300	2.96338200
C	-1.68025400	0.21691400	3.54410200
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O	-2.90107300	3.26933000	-0.46751500
C	1.44596000	-3.22874900	-1.50208000
C	1.99381500	-3.50506600	0.82749600
C	4.05266700	-0.22692800	3.37612700
C	3.19486700	-4.78071900	-0.85232600
C	-1.47985800	-0.69057800	-3.44800100
C	2.42324200	-4.17069800	-1.84344300
C	2.97135900	-4.44752800	0.48396800
C	3.39614200	0.63331200	4.46515100
C	-2.84144400	1.44500300	-3.48602700
C	-3.60373800	4.48686900	-0.65150000
C	3.38379700	4.33082800	-0.35843900
H	4.42603600	4.02300900	-0.25680800
H	3.13102700	5.03126900	0.44800100
H	3.24718000	4.82896900	-1.32705700
H	-1.04415400	1.79369000	2.24401000
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H	-6.66349800	0.12617000	0.66024900
H	-7.57543200	-1.28550300	0.08561400
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H	1.14527400	5.36468800	-0.65111200
H	-4.05037000	-0.40160600	2.15693600
H	-1.29525000	5.42425100	-0.73899800
H	2.61215700	-0.96601300	-1.41388600
H	3.34673200	1.36845800	1.24417300
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H	6.04001400	0.28875600	-2.12871600
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H	0.95905300	1.02685700	3.11237000
H	1.41325400	2.52679600	2.30861000
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H	1.82881100	-3.27748400	1.87584700
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H	2.56760200	-4.43597200	-2.88869500
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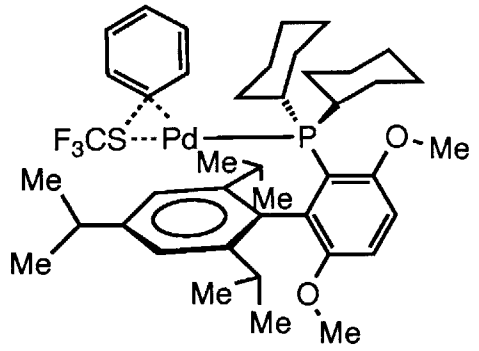
Cartesian Coordinates for Transition State Structures:



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C	-1.14143300	2.35592000	-0.12549300
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C	-2.13777000	1.18765400	2.44293000
C	-1.92438900	1.03058100	-2.71690700
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C	-5.03837100	-2.01570100	-0.14623100
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C	-4.56966200	-3.38193400	-0.68055800
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C	2.39655100	1.16961900	1.68647000
C	1.95428100	1.24952900	-2.65257900
C	4.12706000	0.50897200	-3.73430000
C	2.96450500	1.50936300	-3.78267800
C	3.80051600	0.27376000	-1.21835500
C	1.66977000	1.88584100	2.84204500
C	2.90187800	-0.20446600	2.18258800
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C	2.58976200	2.04338700	4.06659700
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C	3.14221500	0.69382600	4.54613000
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H	-4.21797700	-3.30521700	-1.71637900
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H	3.36020000	2.53218000	-3.69078000
H	3.41883000	-0.75135800	-1.29230700
H	4.32766600	0.34998300	-0.26095000
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H	3.41275000	-0.75143100	1.38491300
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H	3.03945000	-3.41801600	-3.59856900
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H	-4.01202000	5.14637500	0.45345800
C	-0.57774600	-4.01150500	1.40546000
F	0.16982900	-5.13040000	1.44616400
F	-1.82662900	-4.35153800	1.78706000
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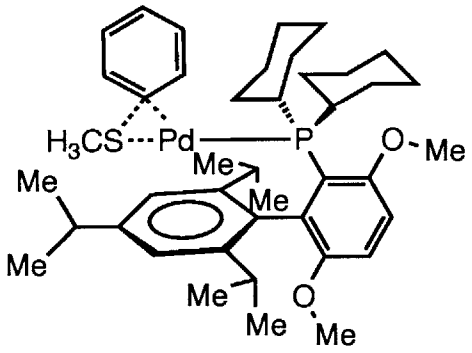

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C	-2.49180000	-0.24230000	-1.22714800
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C	-2.25375300	1.15859100	2.37059500
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C	-0.52968100	4.54518600	-0.91341700
C	-3.36264800	-0.85496800	1.35222300
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C	1.72678000	0.57313900	-2.75025600
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C	2.67585700	0.69334900	-3.95441900
C	3.70918600	0.21262400	-1.21432600
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O	-3.67502100	2.63680600	-0.71452700
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H	4.90163200	-3.54177700	1.10632500
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S	-0.25271700	-3.55810300	0.81245800
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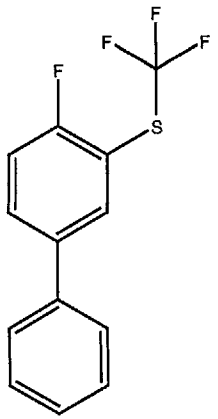
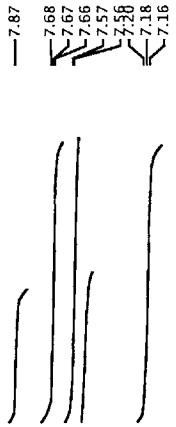
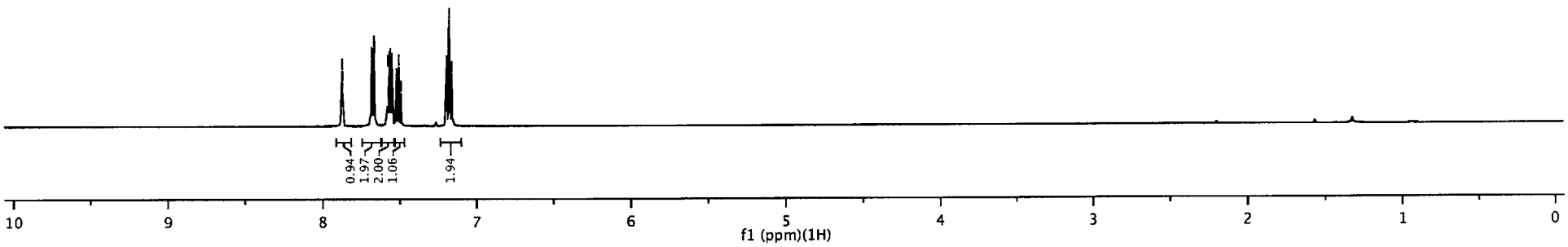
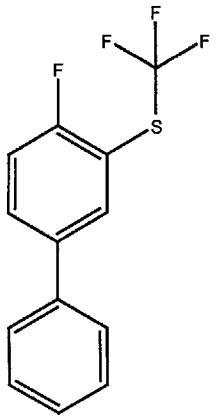
H	1.20656500	-4.48250800	2.53349800
H	5.18420300	-4.16136400	-1.29172900


F
F
F
F
S

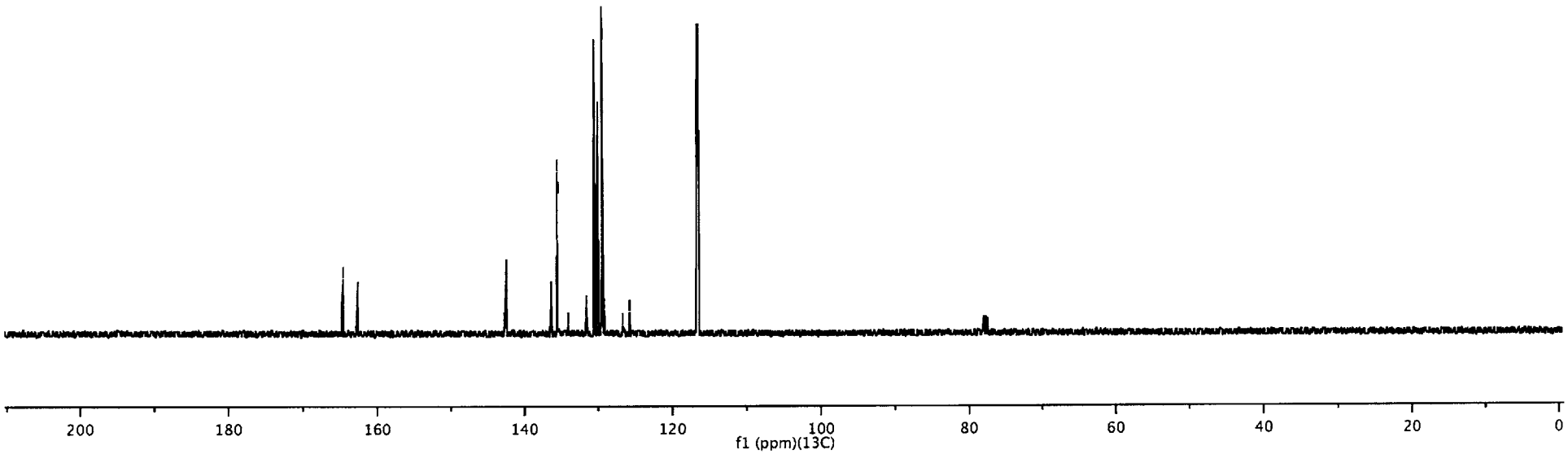

7.87
7.68
7.67
7.66
7.57
7.18
7.16

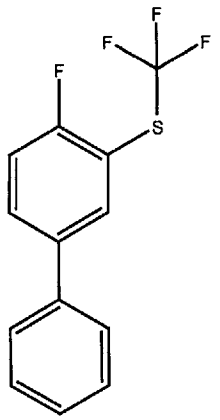

0.94
1.97
2.00
1.06
1.94
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)



164.58
162.61
142.47
136.43
136.40
135.60
135.46
131.63
130.60
130.12
129.55
129.49
129.18
125.78
116.72
116.55

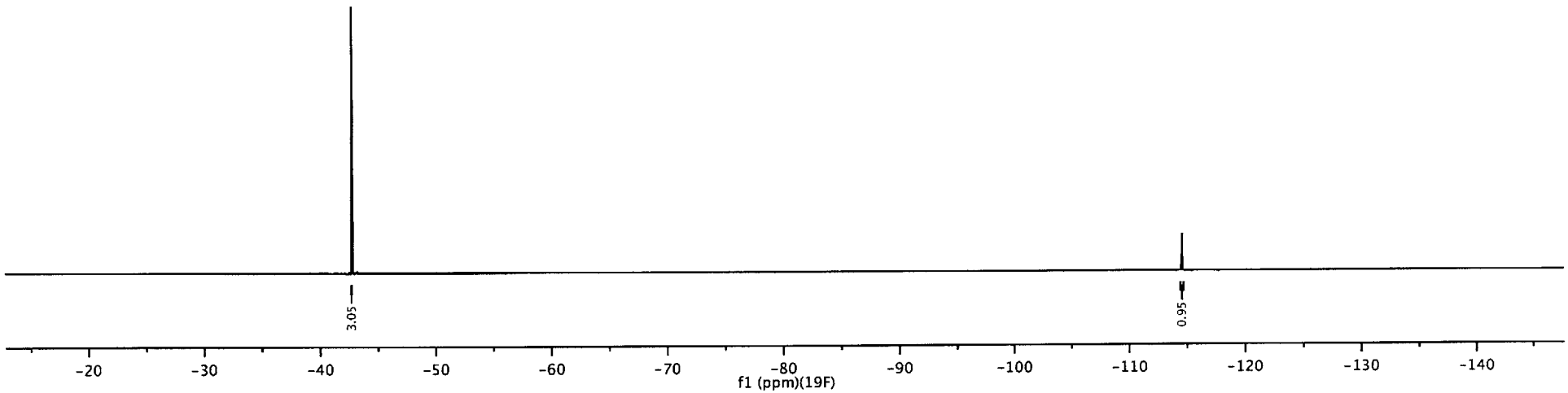
127

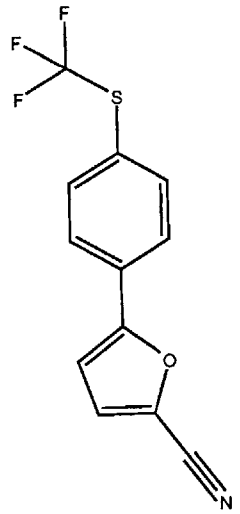


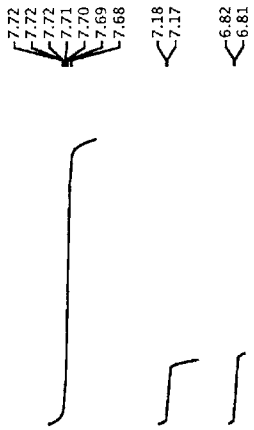

F
F
F
F
S

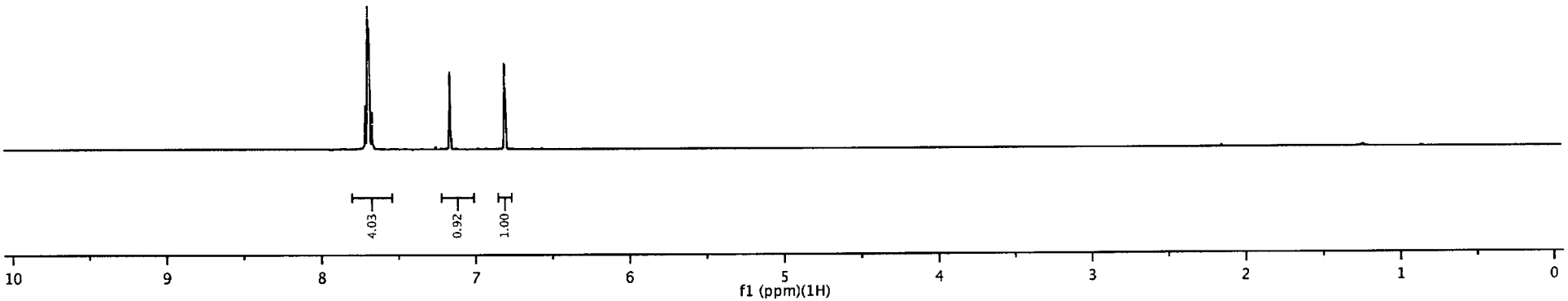
-42.71

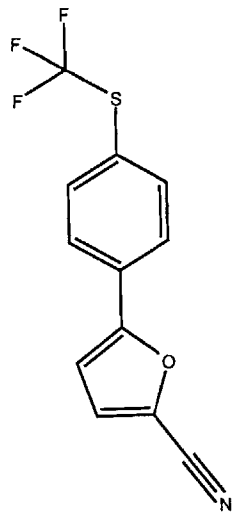

-114.50
-114.52
-114.53
-114.54
-114.56


3.05
0.95
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)(19F)


F
F
F
S
O
N

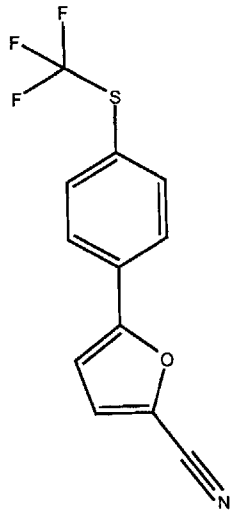

7.72
7.72
7.72
7.71
7.70
7.69
7.68
7.18
7.17
6.82
6.81


4.03
0.92
1.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)



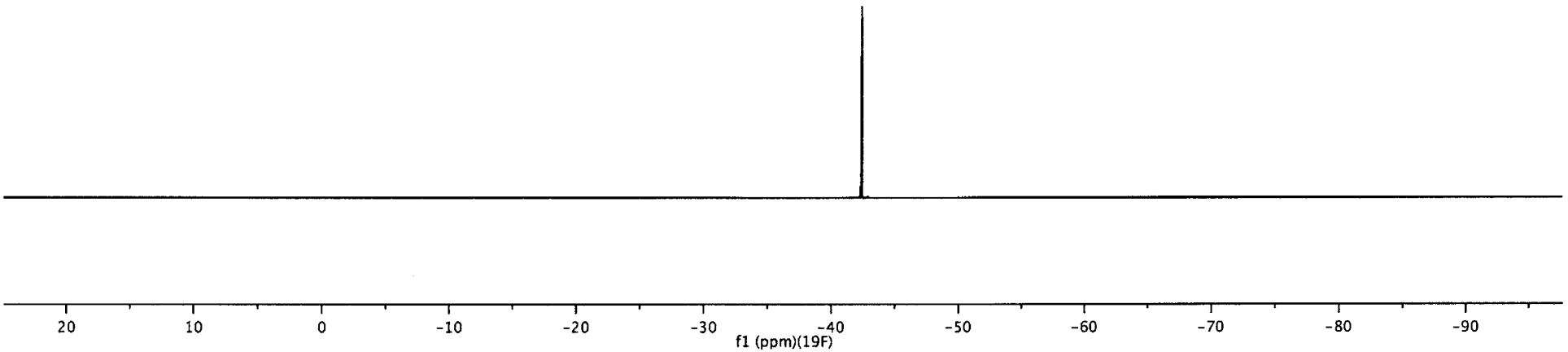
157.59
137.37
137.37
133.81
131.44
131.35
128.90
126.60
126.45
126.24
126.16
126.14
126.13
126.11
124.70
112.22
108.50

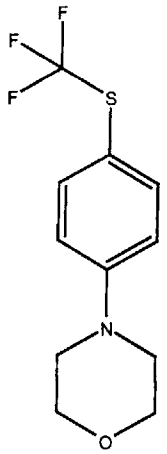
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)(13C)



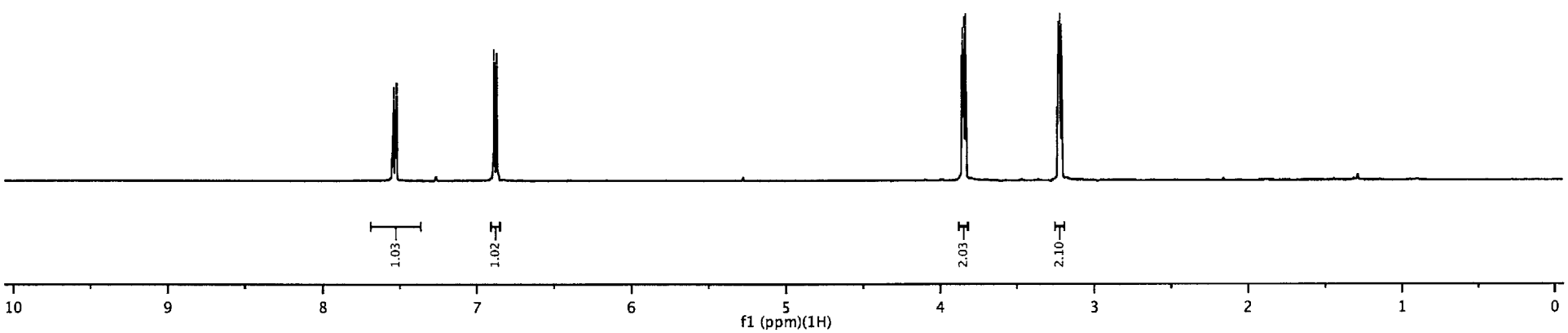
131

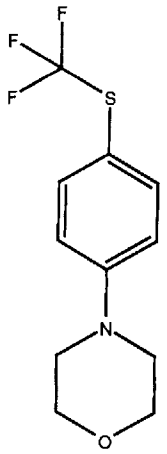
-42.48




F
F
F
S
N
O

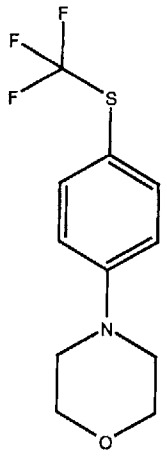

7.54
7.52
6.89
6.87
3.86
3.85
3.84
3.23
3.22
3.21


1.03
1.02
2.03
2.10
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

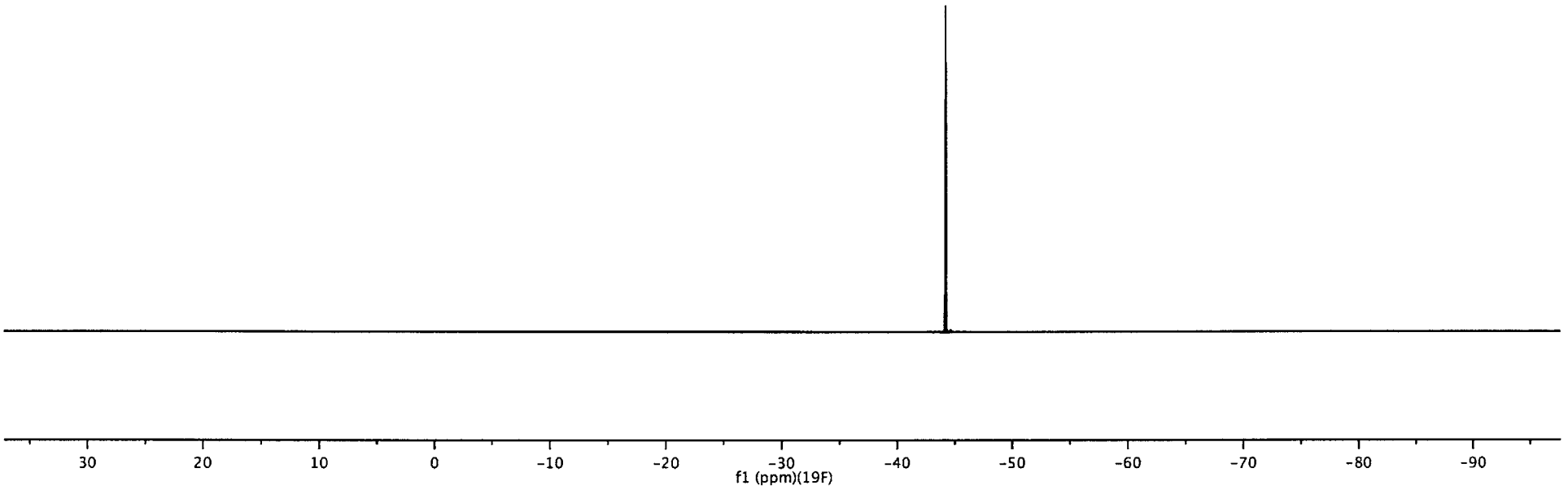


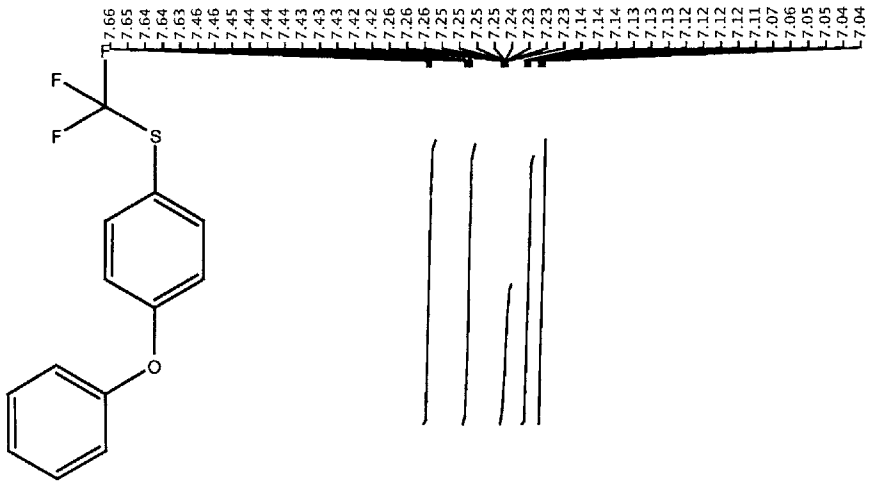
153.59
138.61
138.61
134.13
131.68
129.23
126.78
115.92
113.06
113.04
113.03
113.01
67.31
48.60

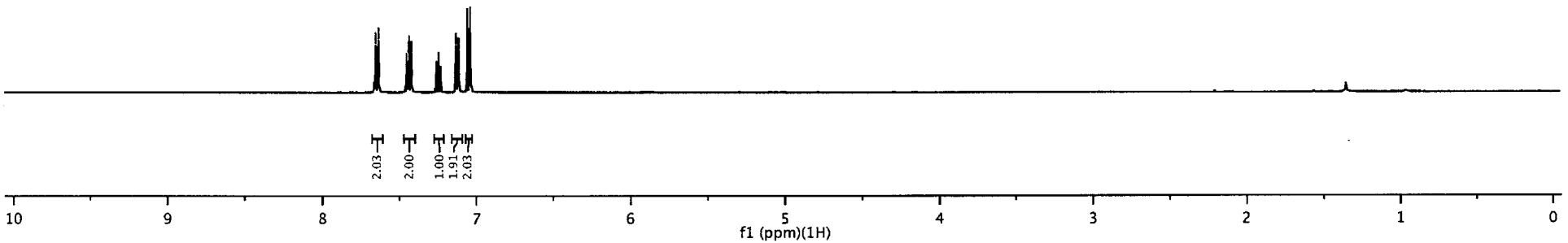
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)(13C)

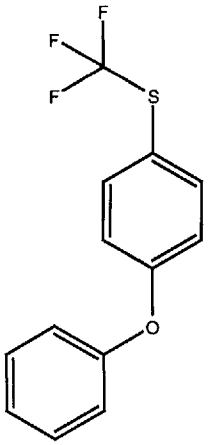


-44.17

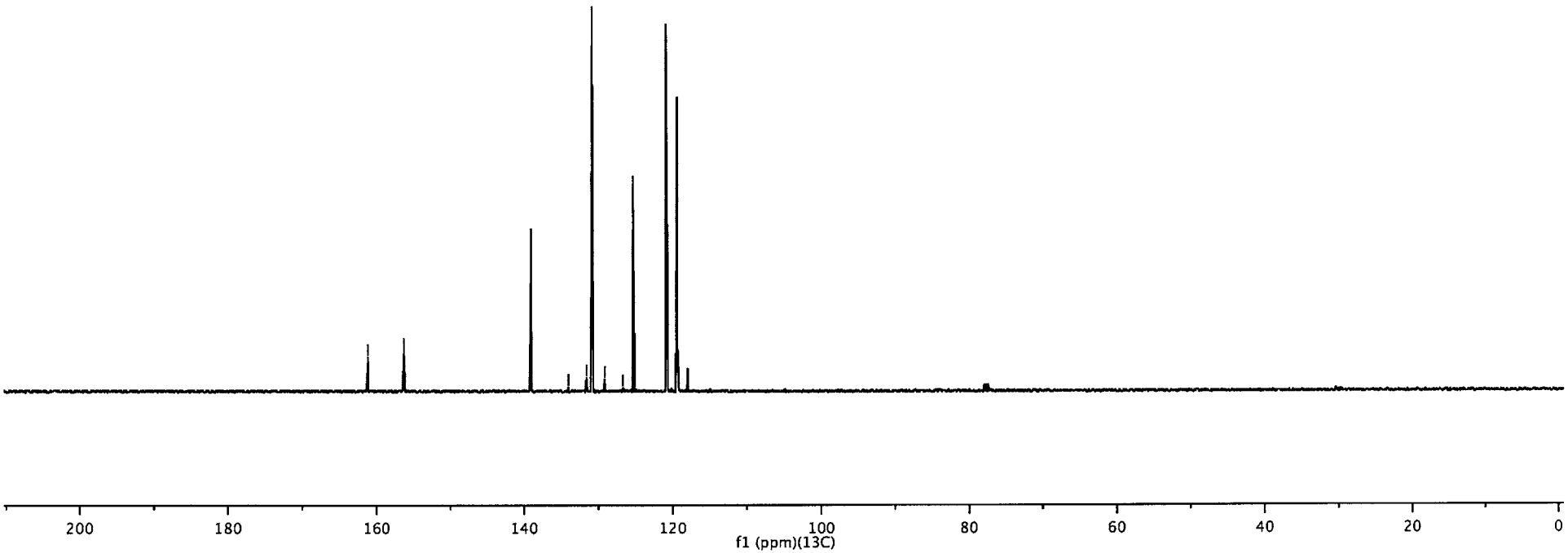


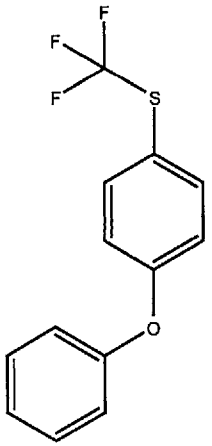

7.66
7.65
7.64
7.64
7.63
7.46
7.46
7.45
7.44
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.26
7.26
7.25
7.25
7.25
7.25
7.24
7.23
7.23
7.23
7.14
7.14
7.14
7.13
7.13
7.12
7.12
7.12
7.12
7.11
7.07
7.06
7.05
7.05
7.04
7.04
F
F
S
O


2.03
2.00
1.00
1.91
2.03
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

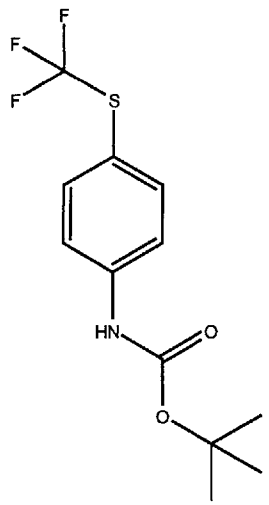


161.18
156.34
139.10
139.10
134.03
131.58
130.81
129.13
126.68
125.32
120.84
119.34
117.98
117.97
117.95
117.93

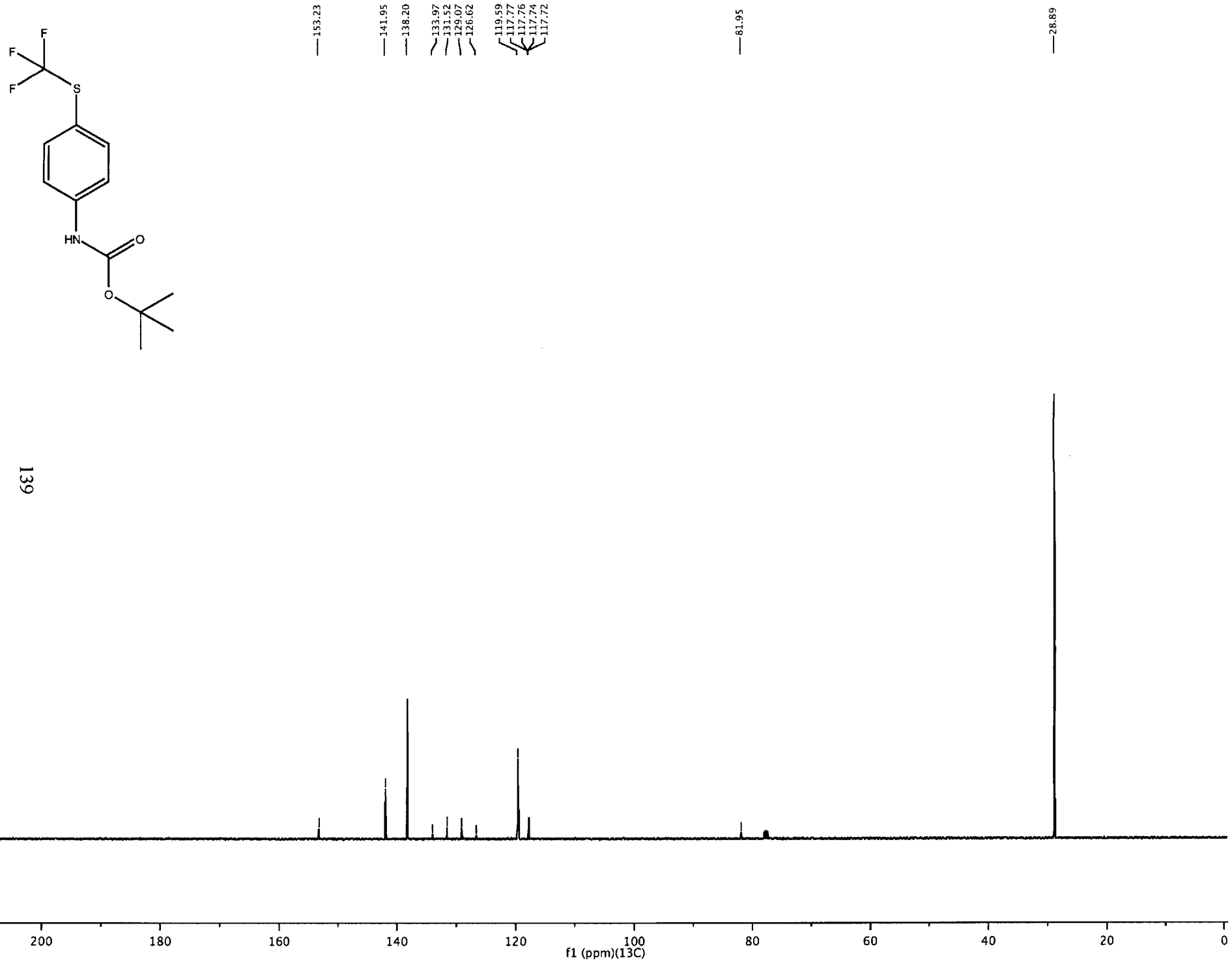


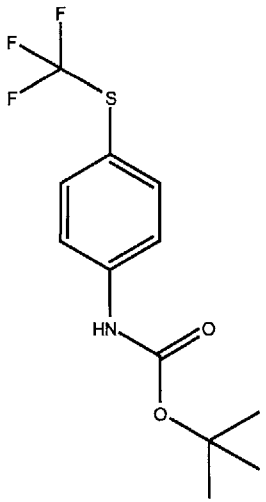


137


F
F
F
S
HN
O
O

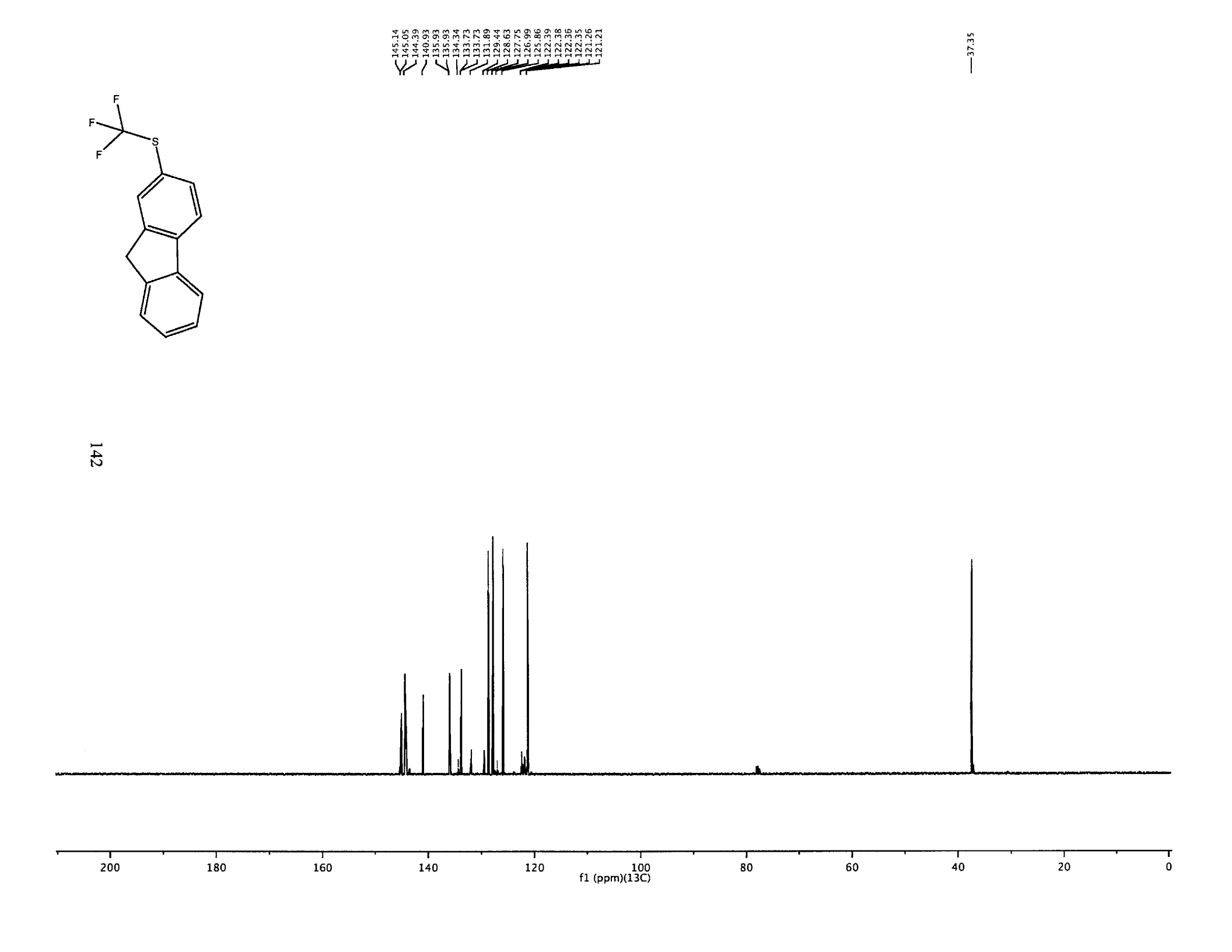
7.55
7.53
7.45
7.44
6.98
1.51
2.00
2.06
1.03
9.08
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

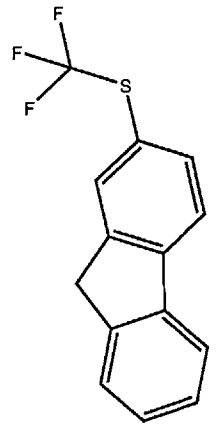

153.23
141.95
138.20
133.97
131.52
129.07
126.62
119.59
117.77
117.76
117.74
117.72
81.95
28.89
F
F
F
S
HN
O
O
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)(13C)


F
F
F
S
HN
O
O

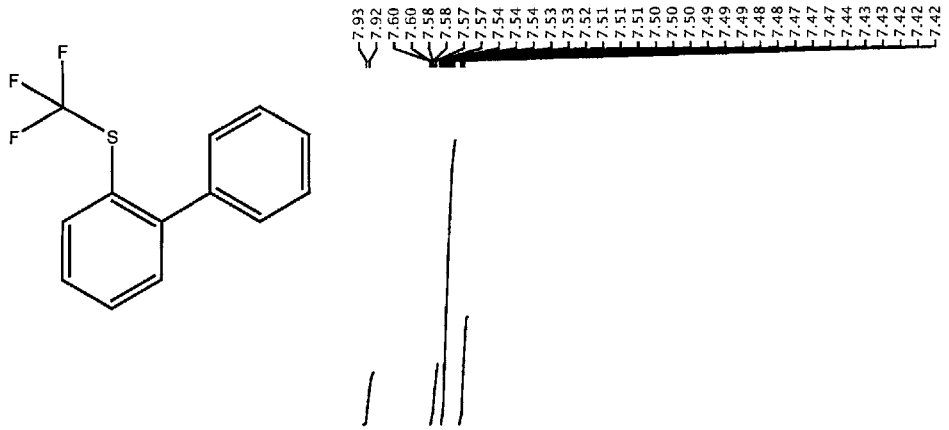
-43.65
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)

7.81
7.79
7.78
7.77
7.77
7.77
7.76
7.75
7.73
7.73
7.72
7.71
7.70
7.70
7.69
7.69
7.69
7.67
7.65
7.57
7.56
7.56
7.56
7.55
7.54
7.54
7.54
7.52
7.47
7.46
7.46
7.46
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.39
3.80
F
F
F
S
4.05
0.97
1.90
2.14
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)


145.14
145.05
144.39
140.93
135.93
135.93
134.34
133.73
133.73
131.89
129.44
128.63
127.75
126.99
125.86
122.39
122.38
122.36
122.35
121.26
121.21
37.35
F
F
F
S
142
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)(13C)



143


F
F
F
S
7.93
7.92
7.60
7.58
7.58
7.57
7.57
7.54
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.51
7.50
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.47
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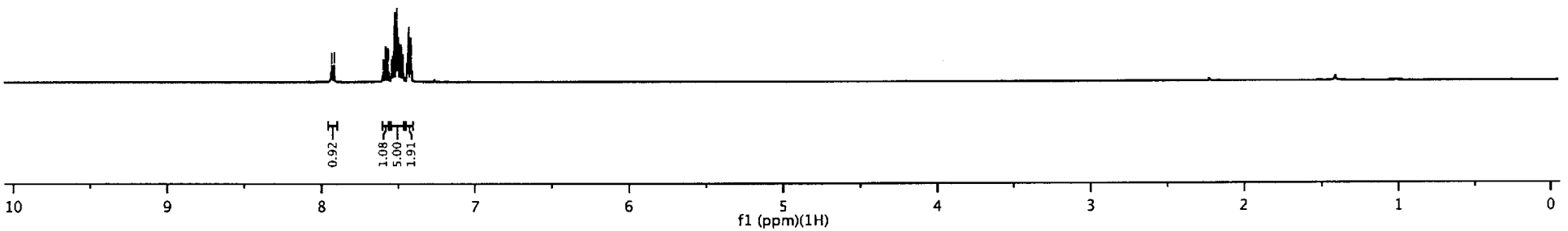
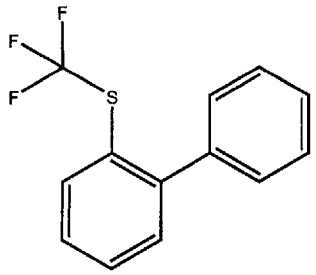
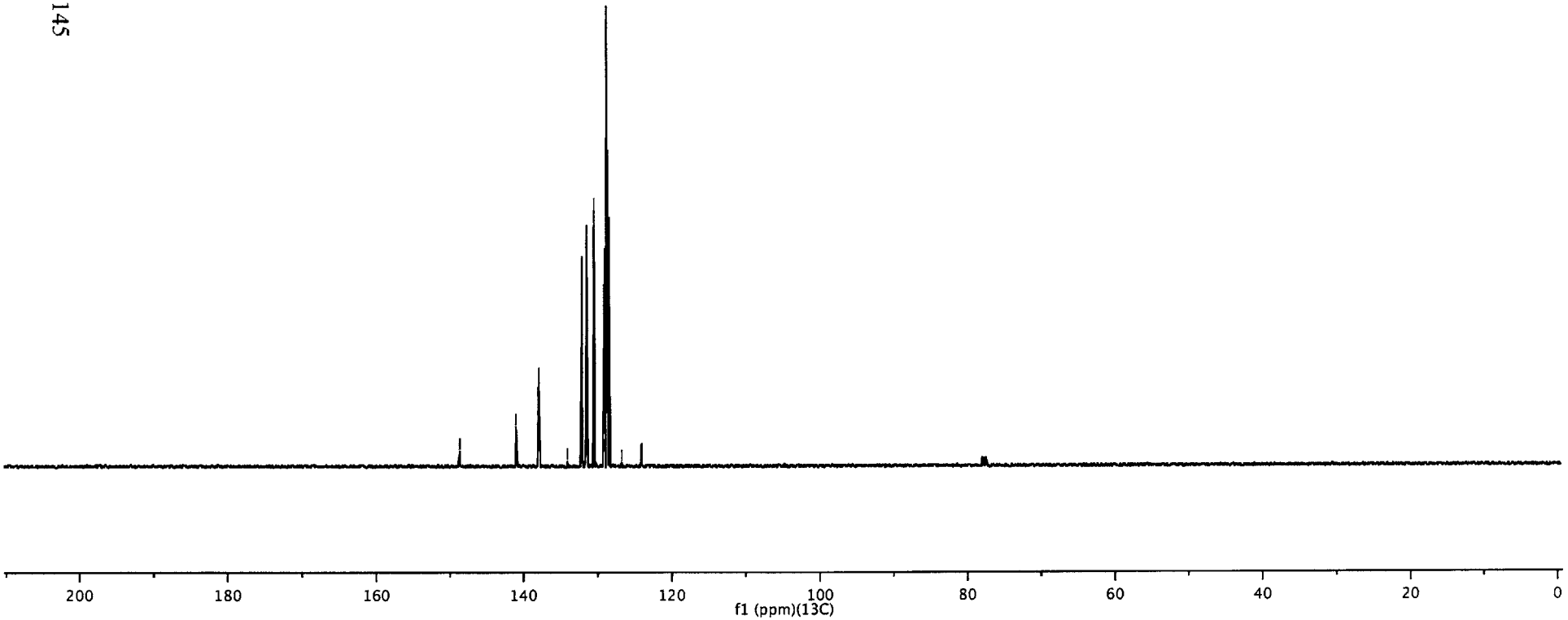
7.44
7.43
7.43
7.42
7.42
7.42

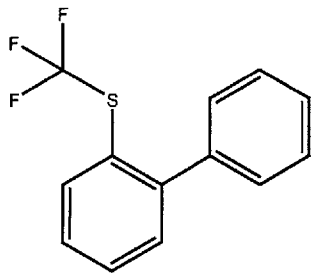

0.92
1.08
5.00
1.91
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)



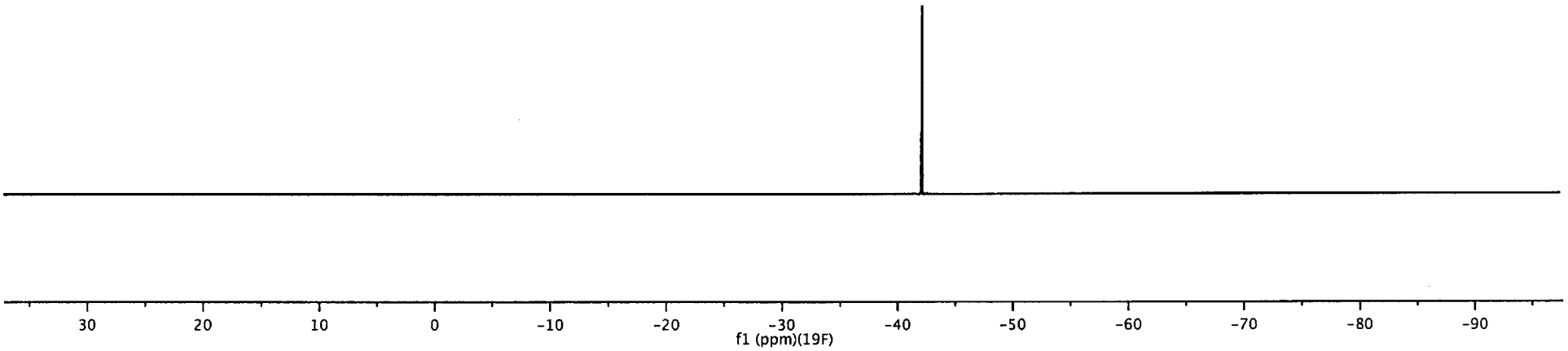
148.68
141.03
137.95
137.94
134.06
132.07
131.61
131.46
130.47
129.16
129.04
128.74
128.46
126.71
124.09
124.08
124.06
124.05

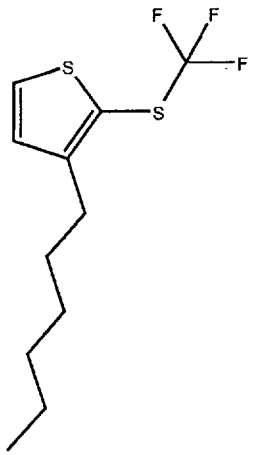
145



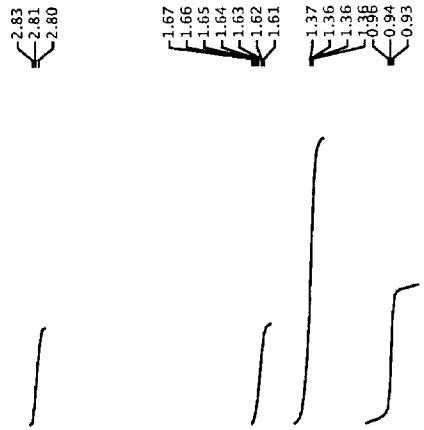


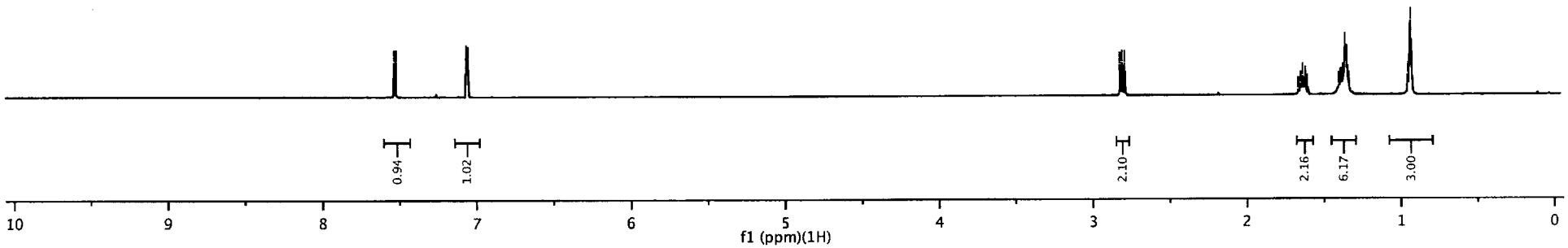
-42.11

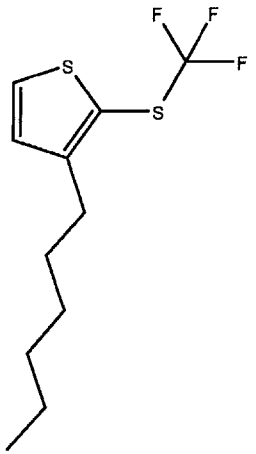



F
F
F
S
S

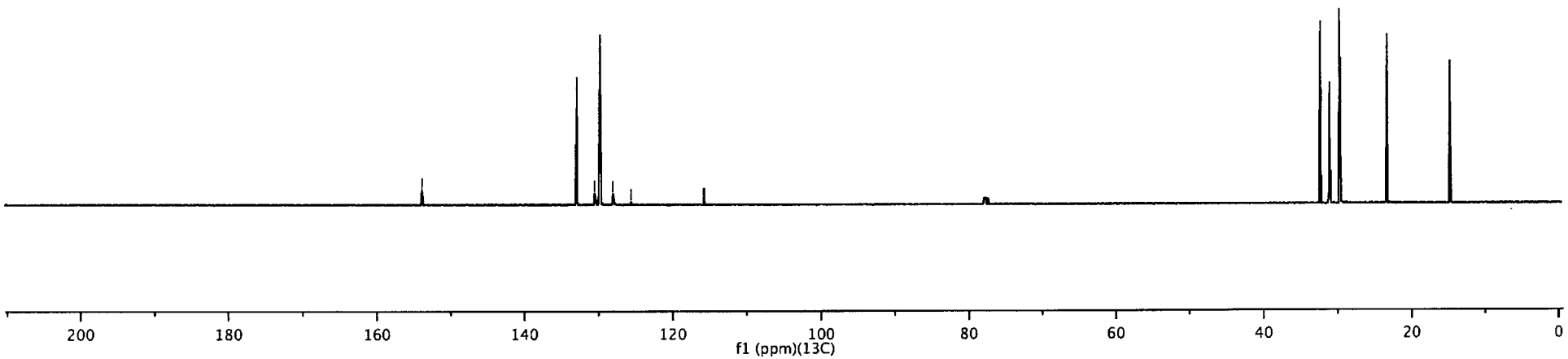

7.54
7.53
7.07
7.06

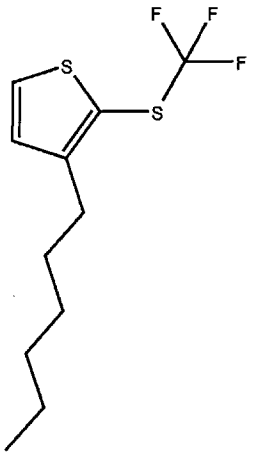

2.83
2.81
2.80
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.37
1.36
1.36
0.94
0.93


0.94
1.02
2.10
2.16
6.17
3.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

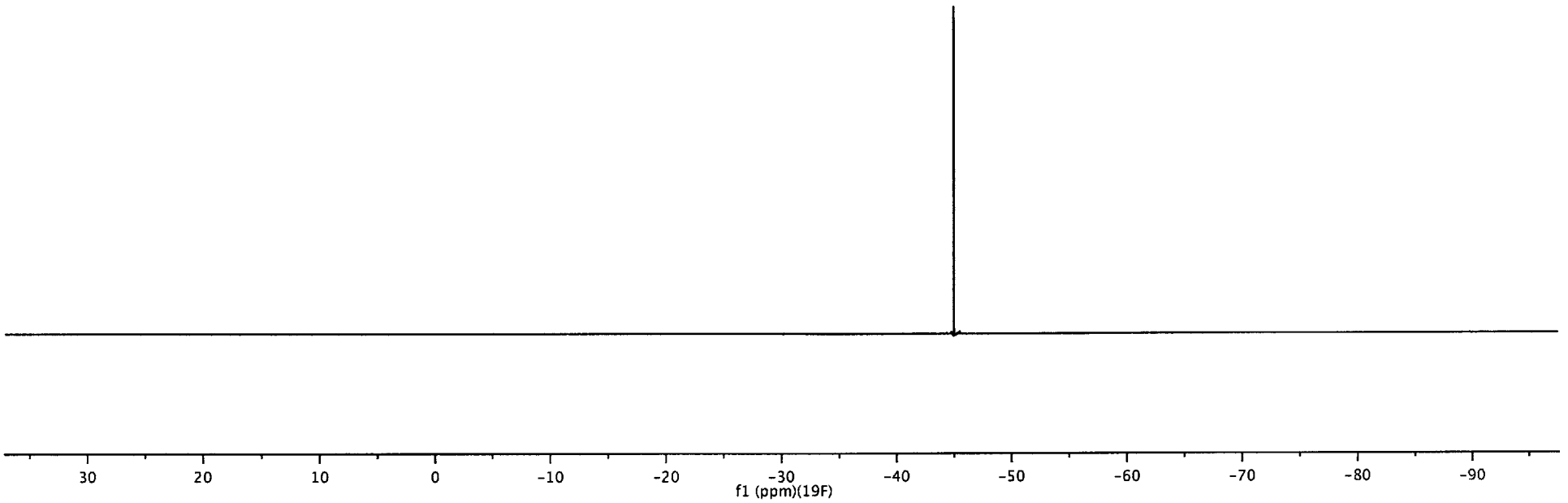


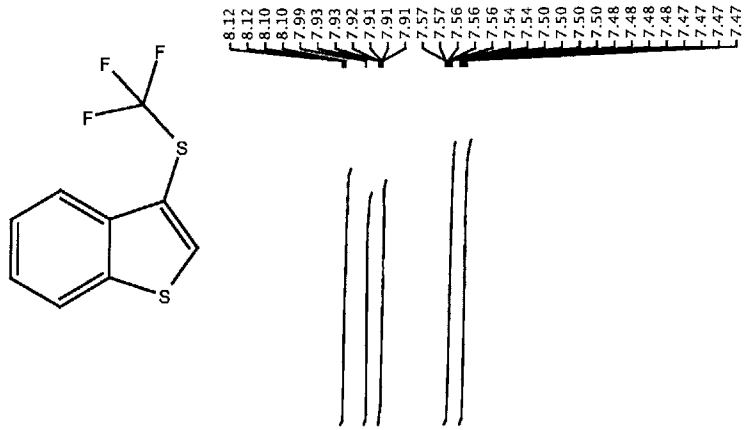
153.95
153.94
133.00
132.91
130.52
129.79
128.05
125.58
115.78
115.76
115.74
115.72
32.35
31.13
29.78
29.65
23.31
14.73

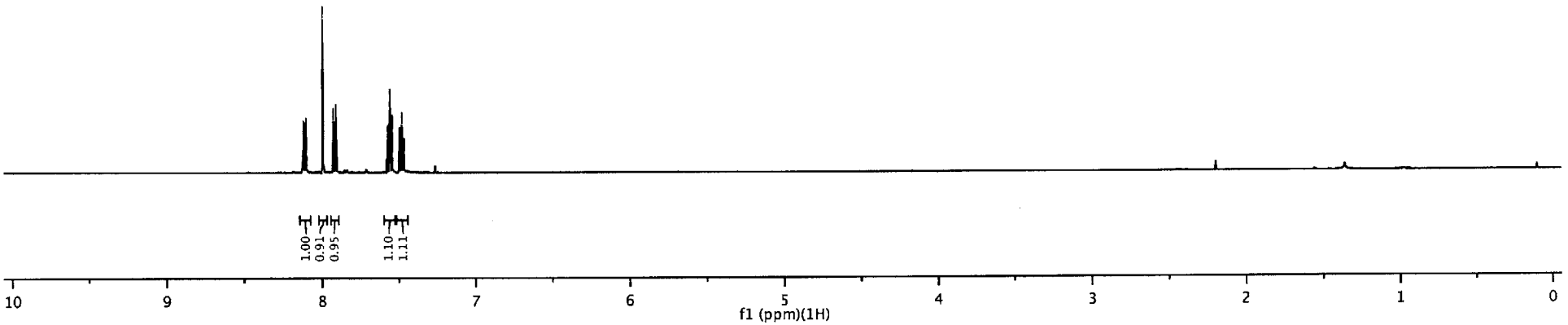


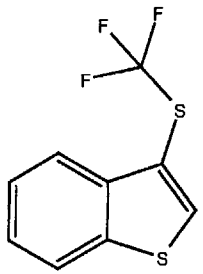


149



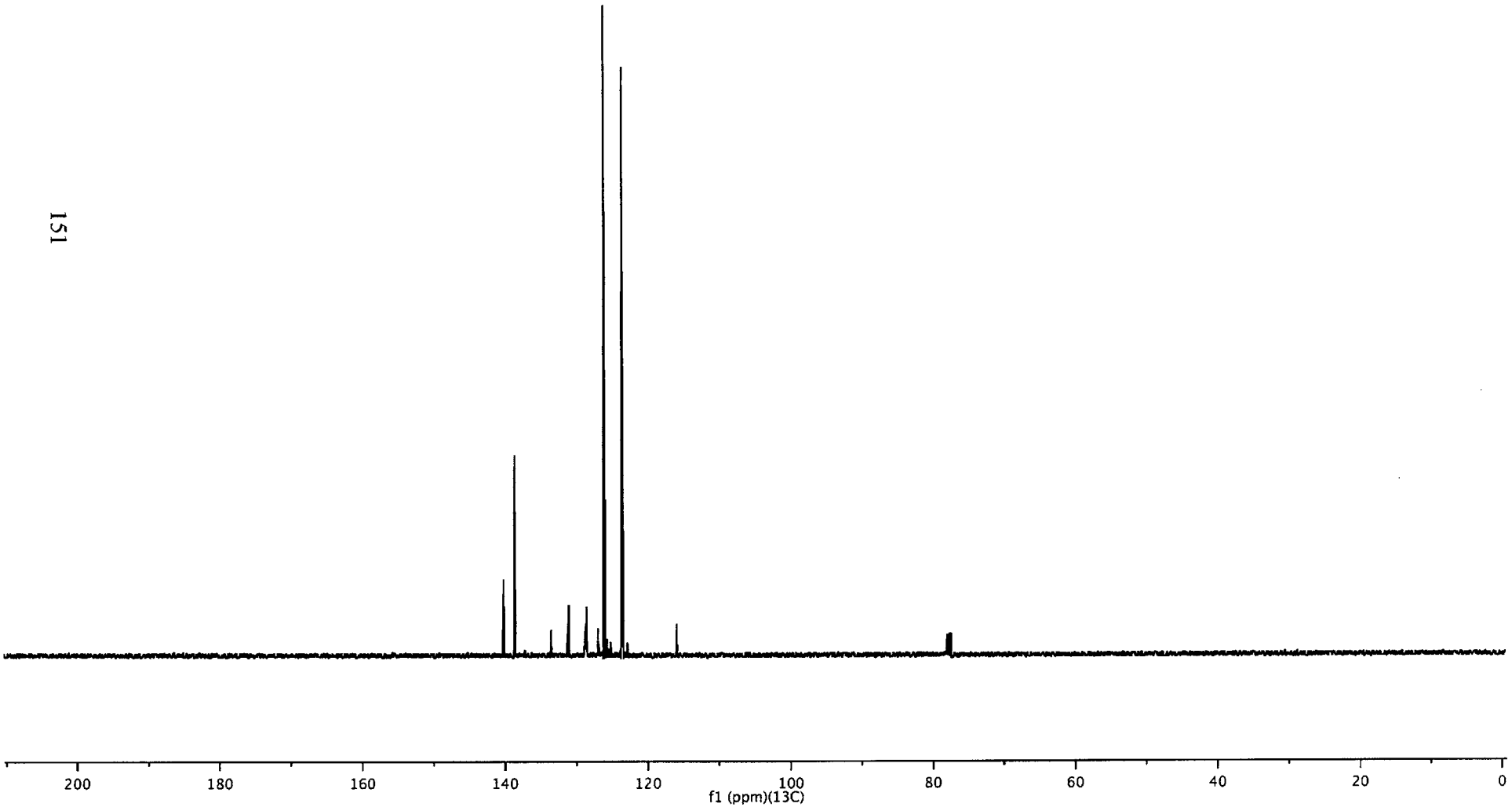

F
F
F
S
S
8.12
8.12
8.10
8.10
7.99
7.93
7.93
7.92
7.91
7.91
7.91
7.57
7.57
7.56
7.56
7.56
7.54
7.54
7.50
7.50
7.50
7.48
7.48
7.48
7.47
7.47
7.47

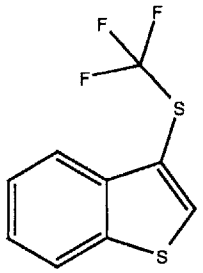

1.00
0.91
0.95
1.10
1.11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)



140.20
140.15
138.66
138.66
131.06
128.60
126.96
126.13
126.11
126.09
123.62
115.97
115.96
115.94

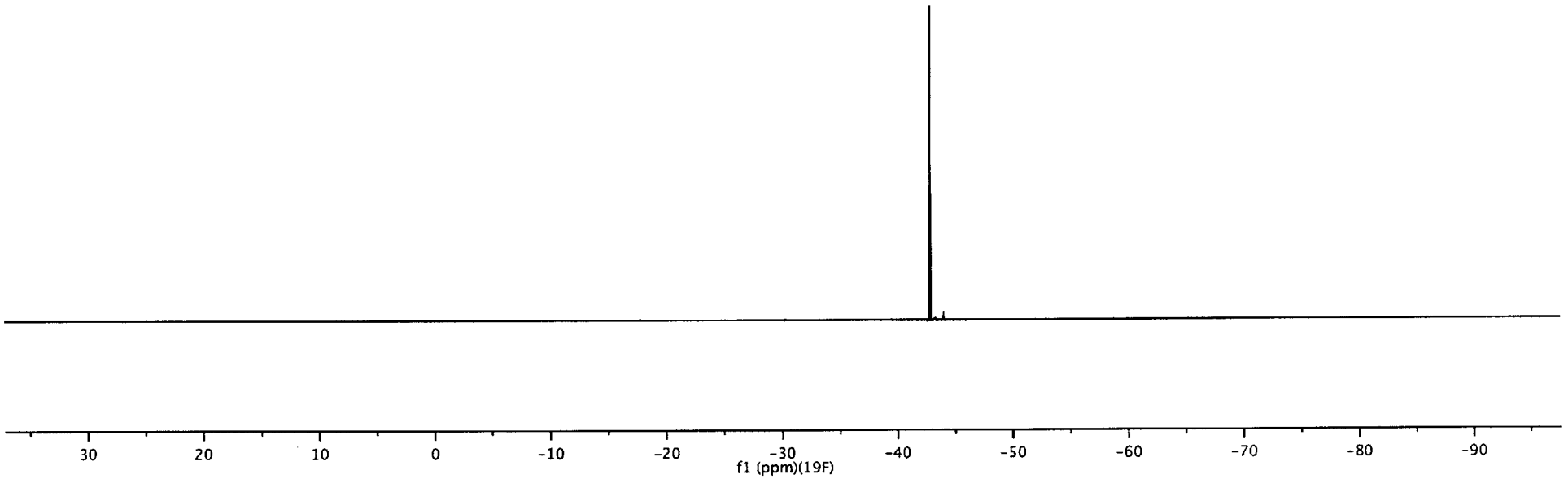
151

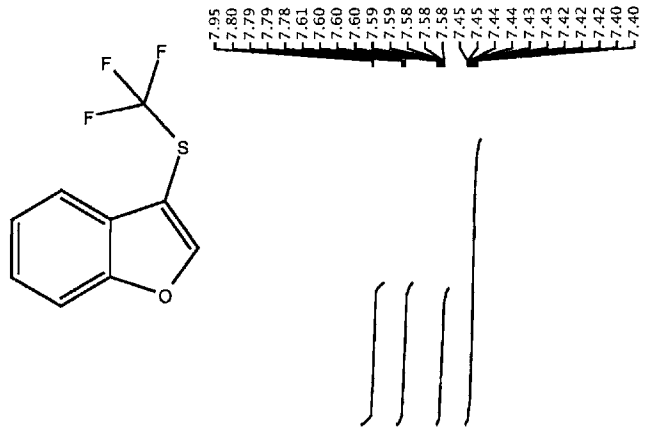




-42.75

152




F
F
F
S
O

7.95
7.80
7.79
7.79
7.78
7.61
7.60
7.60
7.60
7.59
7.59
7.58
7.58
7.58
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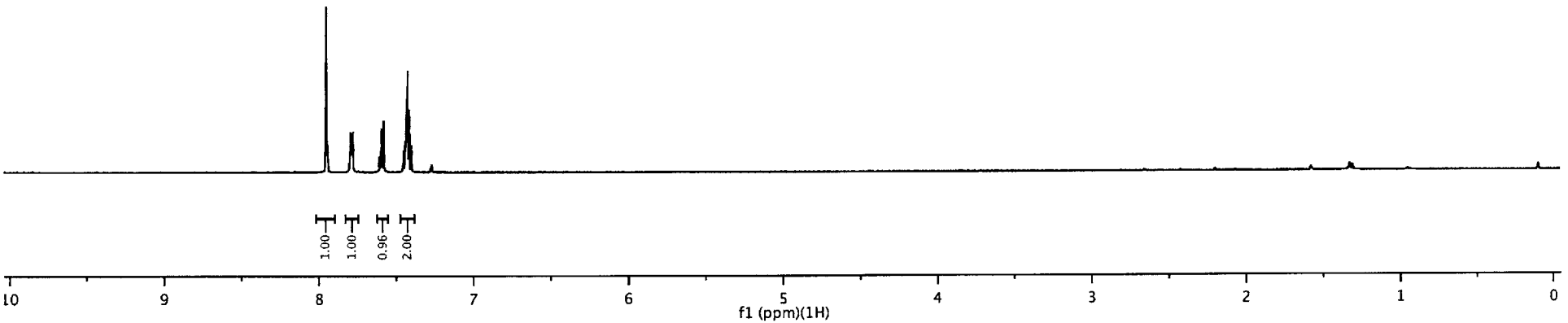
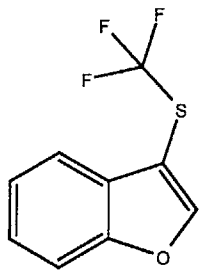
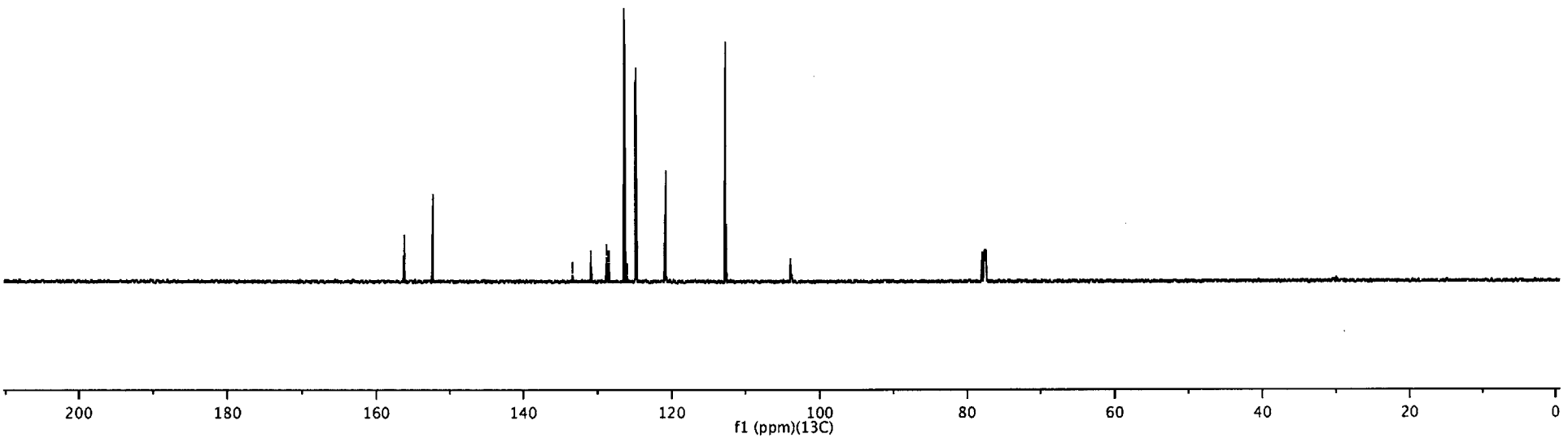
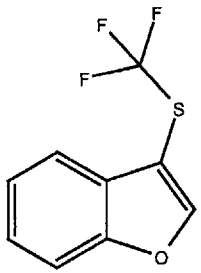
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.40
7.40


1.00
1.00
0.96
2.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

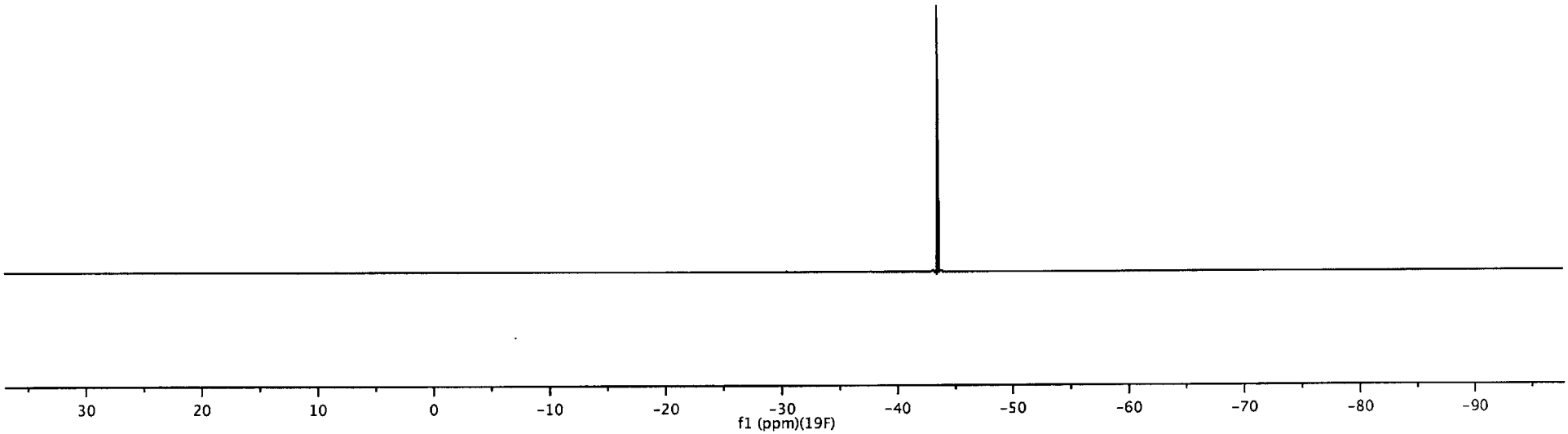


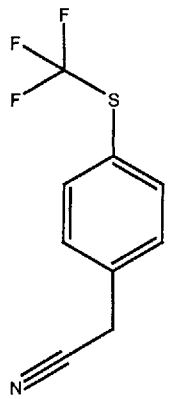
156.19
152.30
152.29
133.37
130.90
128.75
128.44
126.37
125.98
124.84
120.75
120.74
112.70
103.98
103.96
103.94
103.91

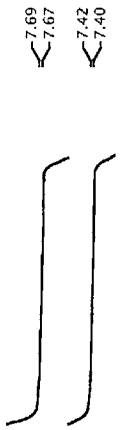




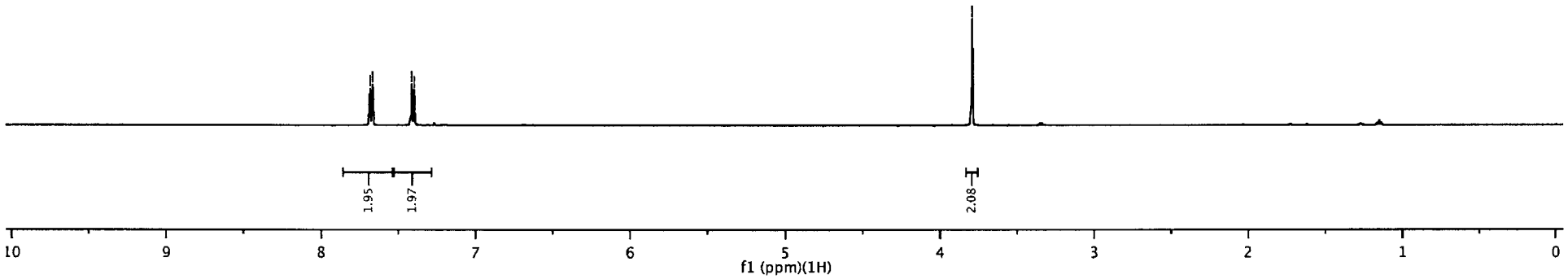
-43.40

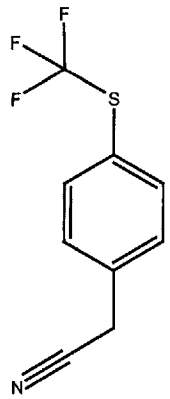



F
F
F
S
N


7.69
7.67
7.42
7.40


3.79

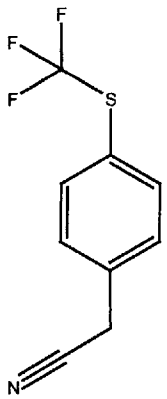

1.95
1.97
2.08
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)



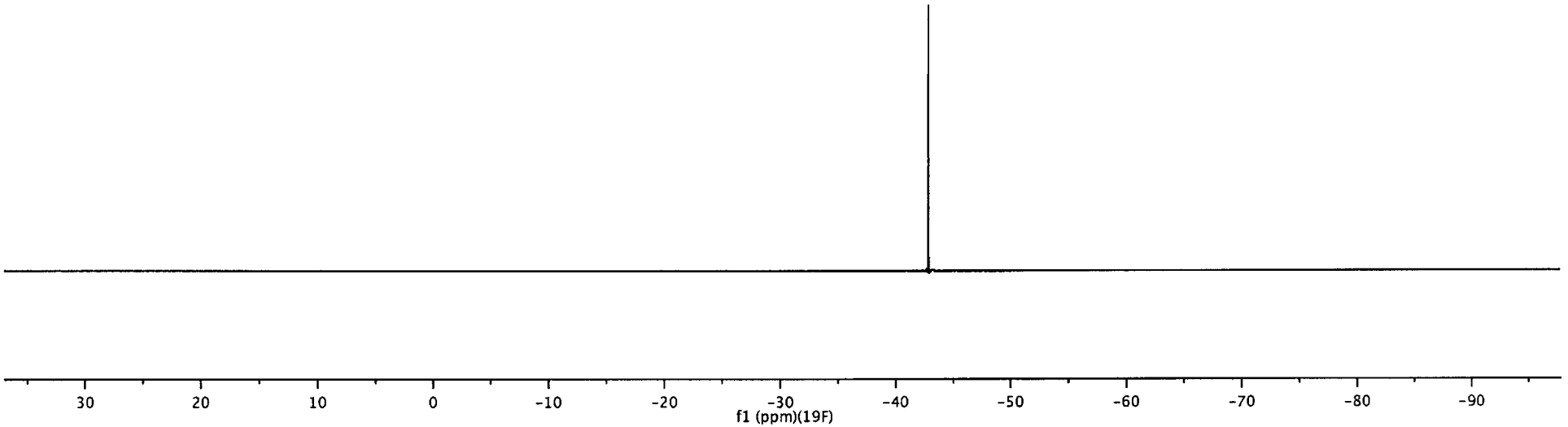
137.65
137.64
133.89
133.82
131.37
129.80
128.92
126.47
125.12
125.11
125.09
125.07
117.86
24.08

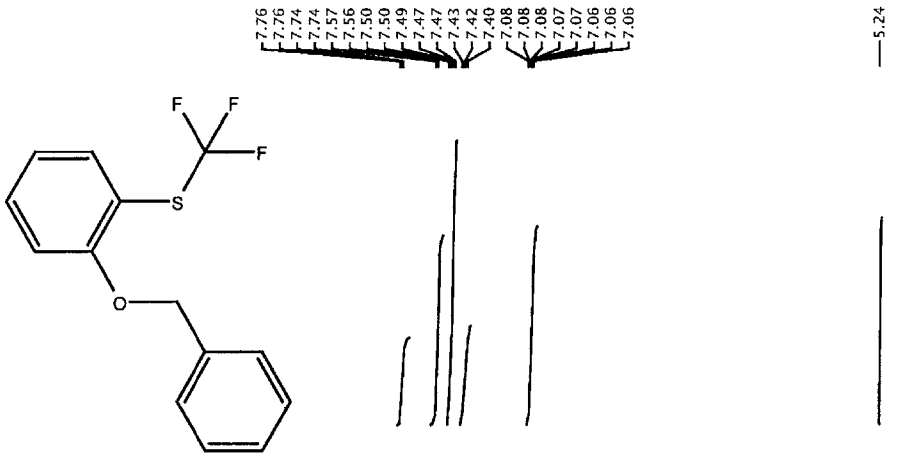
157

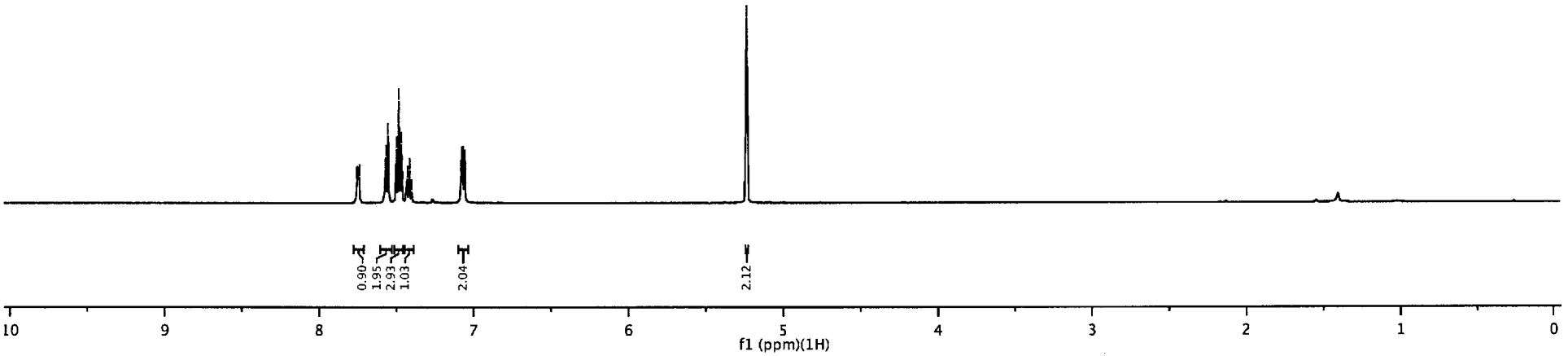
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)(13C)

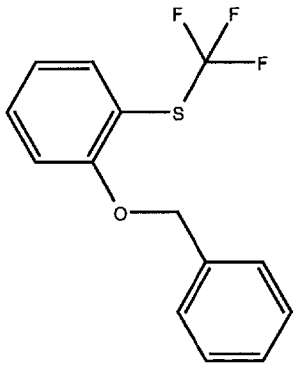


158




7.76
7.76
7.74
7.74
7.57
7.56
7.50
7.50
7.49
7.47
7.47
7.43
7.42
7.40
7.08
7.08
7.08
7.07
7.07
7.06
7.06
7.06
5.24
F
F
F
S
O


0.90
1.95
2.93
1.03
2.04
2.12
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)



160.40
139.32
137.16
134.26
133.61
131.81
129.42
129.35
128.77
127.72
126.90
122.25
114.02
113.78
113.77
71.33

160

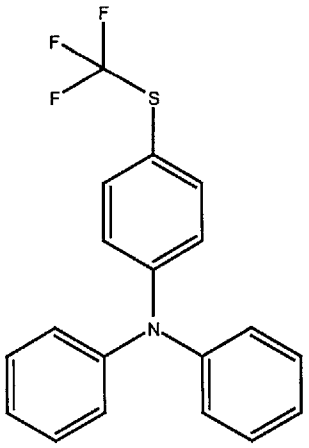
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)(13C)

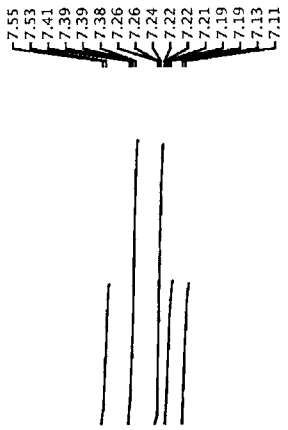
-42.37

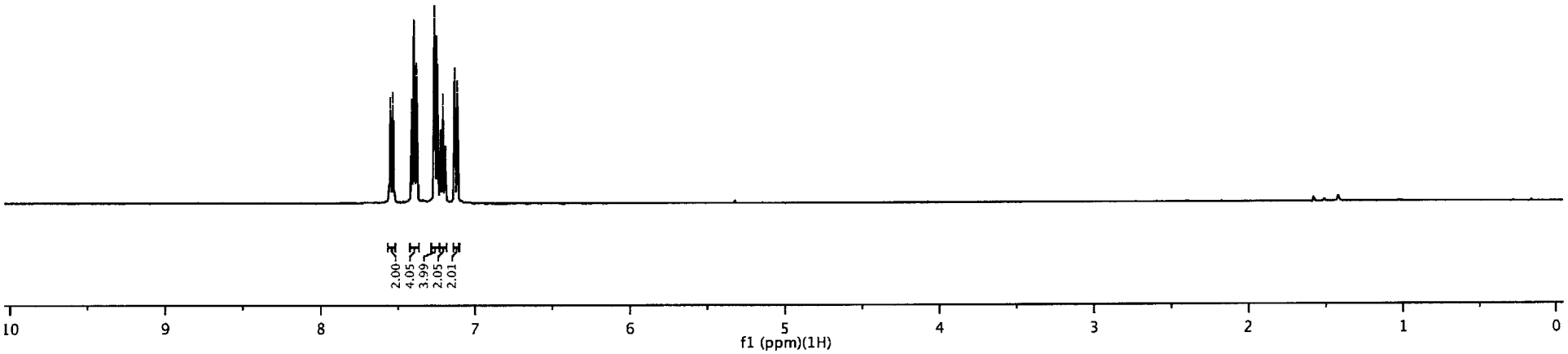
161

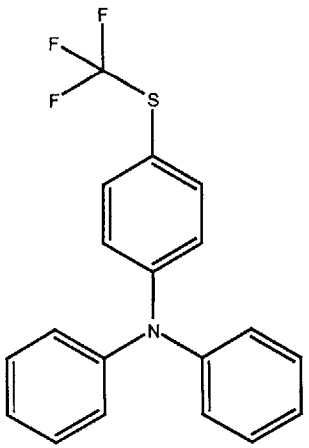
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

f1 (ppm)(19F)


F
F
F
S
N

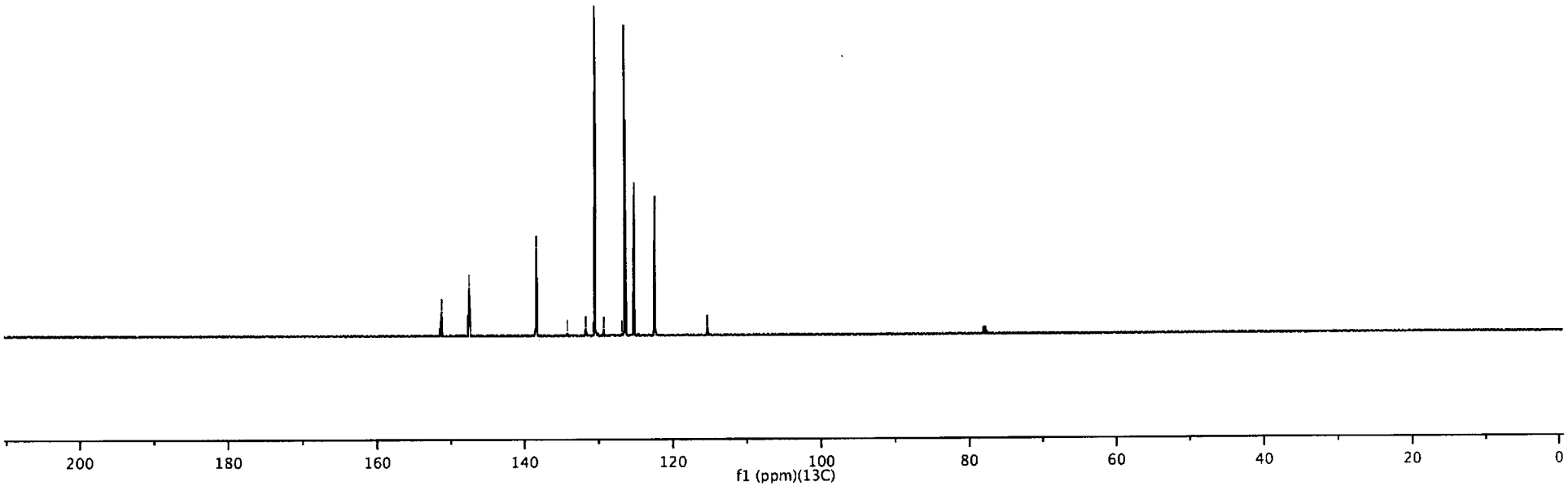

7.55
7.53
7.41
7.39
7.39
7.38
7.26
7.26
7.24
7.22
7.22
7.21
7.19
7.19
7.13
7.11

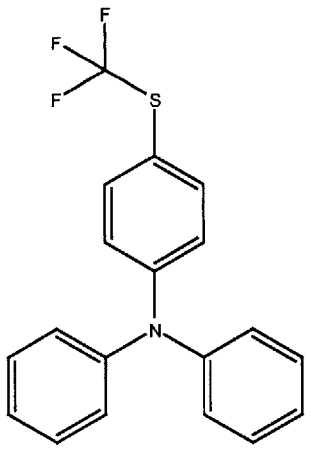

2.00
4.05
3.99
2.05
2.01
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)



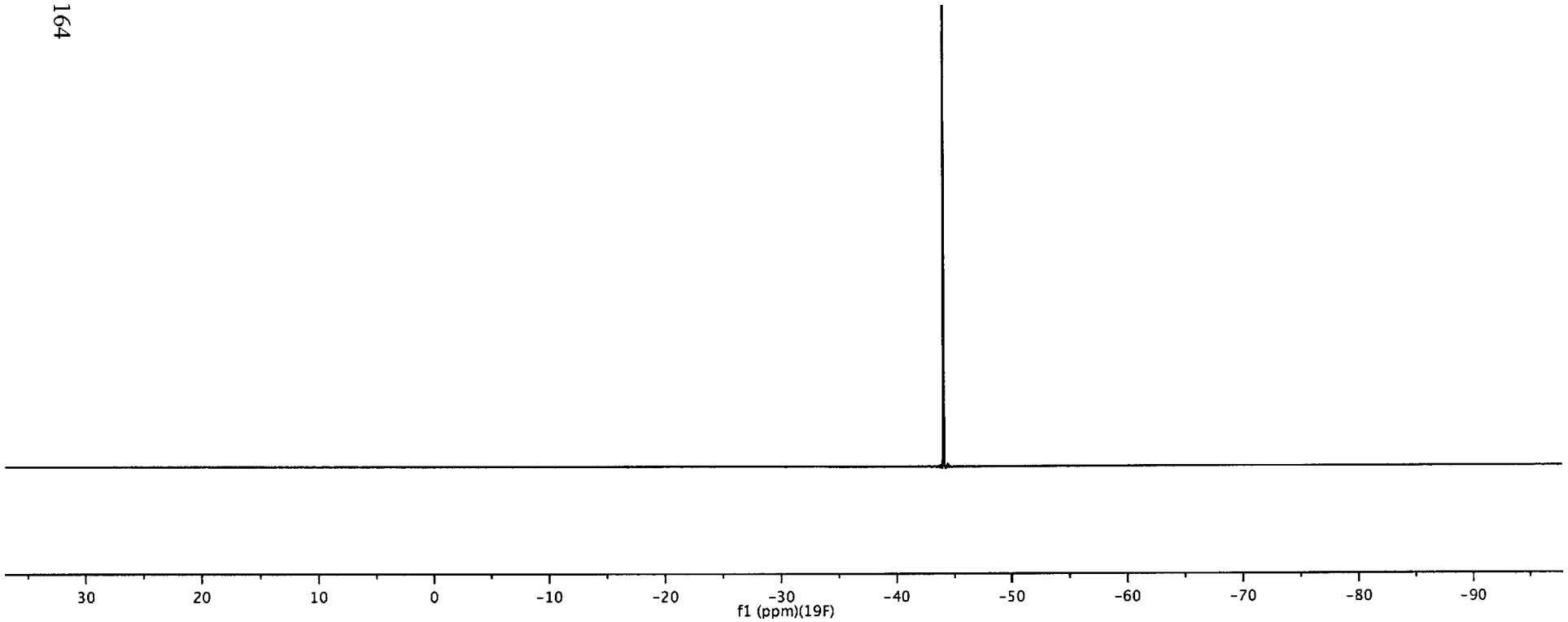
151.25
147.54
138.39
134.20
131.75
130.43
129.29
126.84
126.48
125.18
122.40
115.34
115.32

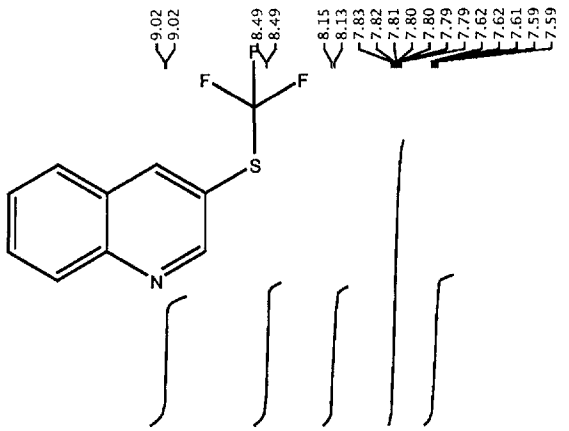
163

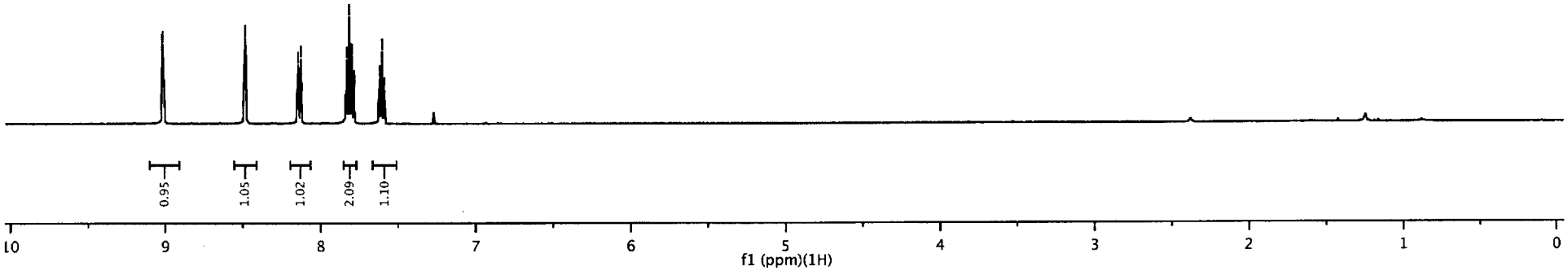


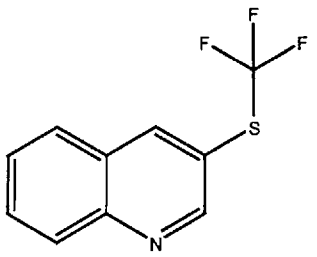


164



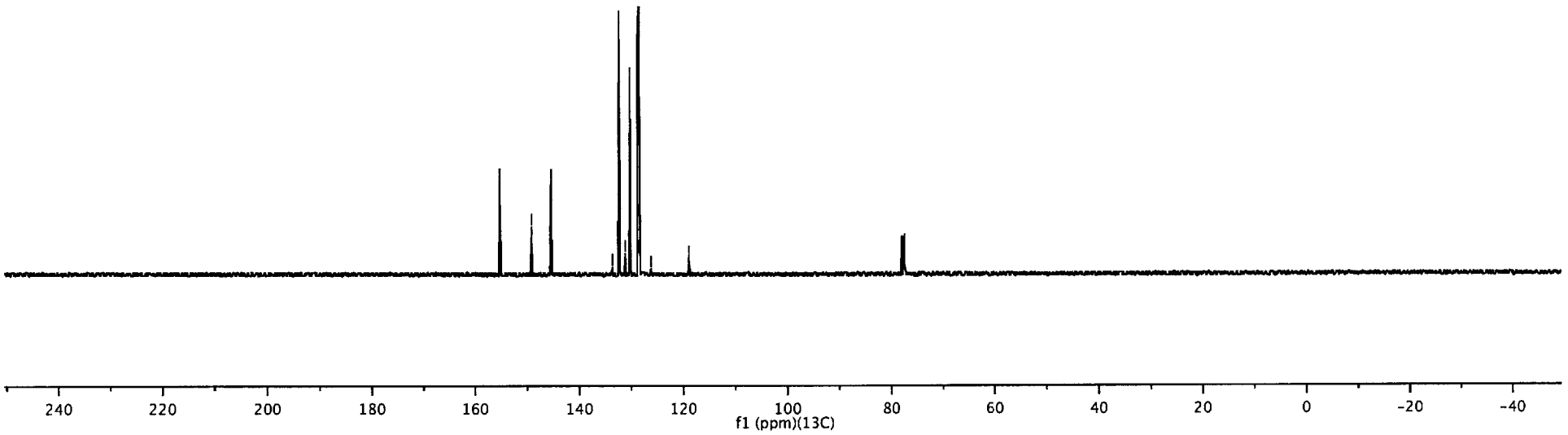

9.02
9.02
8.49
8.49
8.15
8.13
7.83
7.82
7.81
7.80
7.80
7.79
7.79
7.62
7.62
7.61
7.59
7.59
F
F
F
S
N

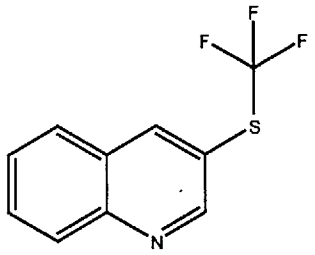

0.95
1.05
1.02
2.09
1.10
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)



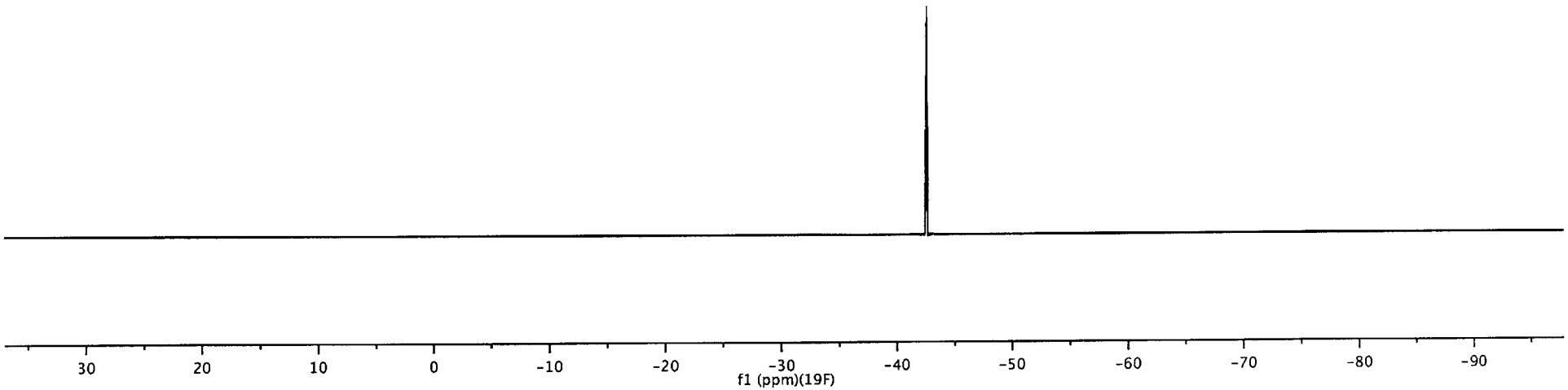
155.24
149.05
145.39
133.58
132.32
131.12
130.20
128.76
128.67
128.47
118.92
118.91
118.89

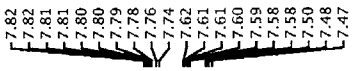
166

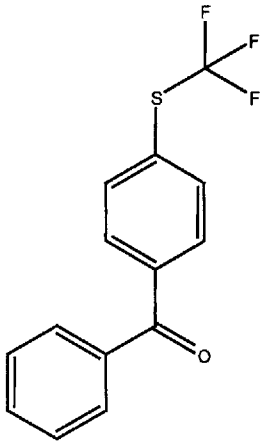


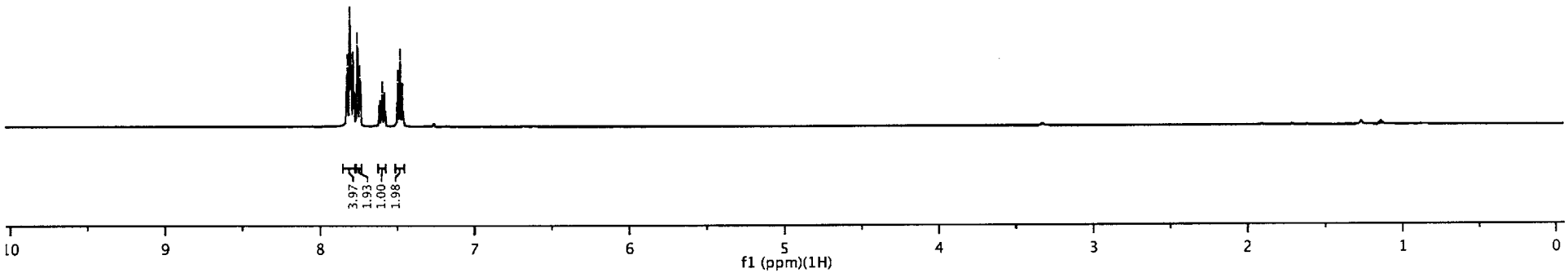


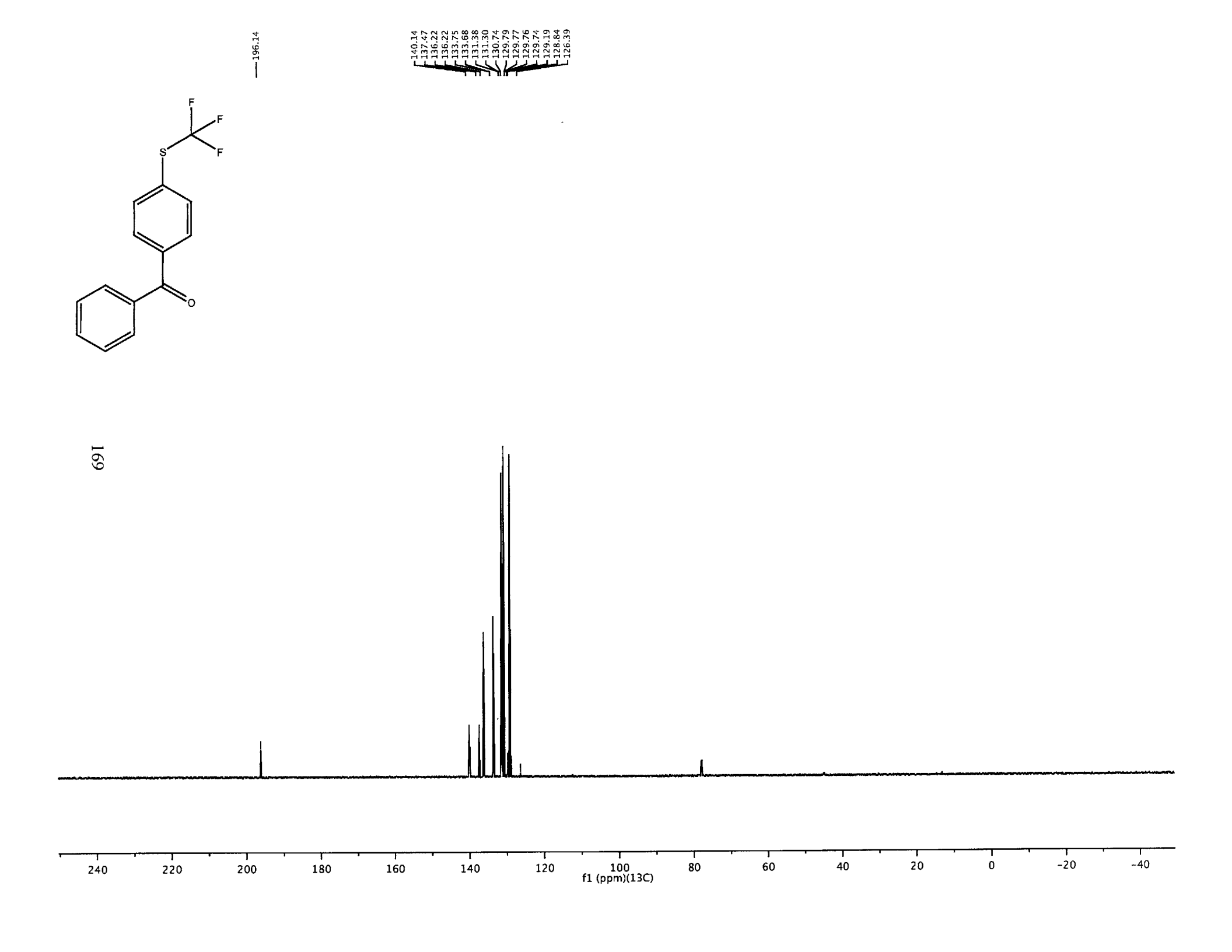
-42.62

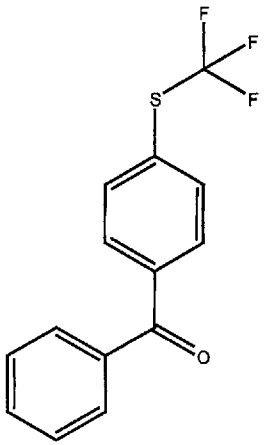



7.82
7.82
7.81
7.81
7.80
7.80
7.79
7.78
7.76
7.74
7.62
7.61
7.61
7.60
7.59
7.58
7.58
7.50
7.48
7.47


F
F
F
S
O

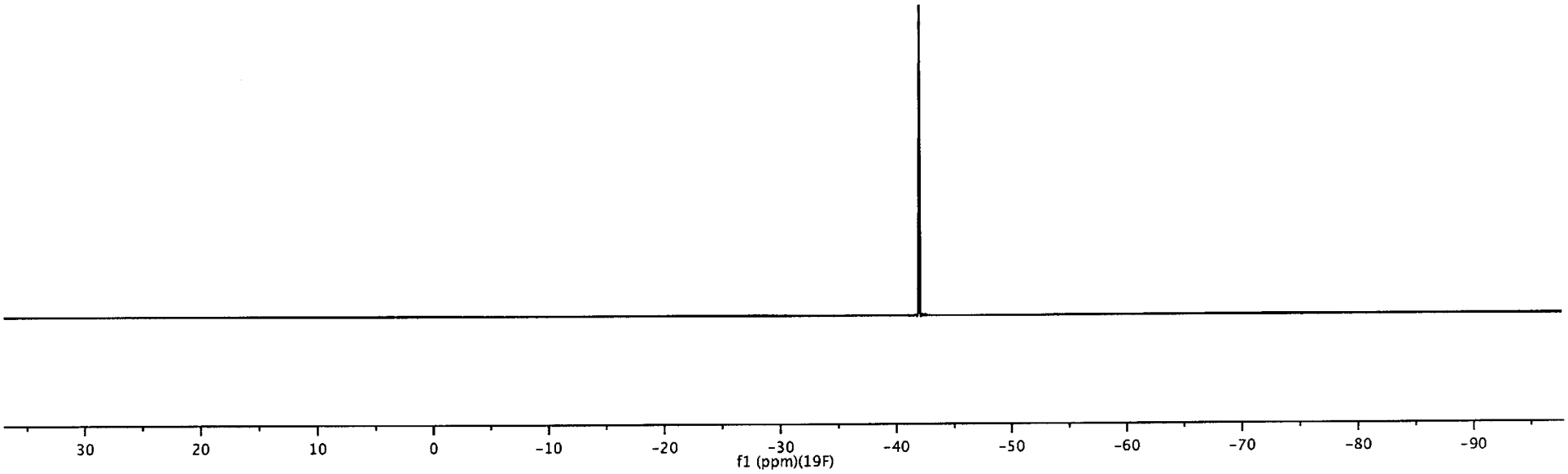

3.97
1.93
1.00
1.98
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)


196.14
140.14
137.47
136.22
136.22
133.75
133.68
131.38
131.30
130.74
129.79
129.77
129.76
129.74
129.19
128.84
126.39
F
F
F
S
O
169
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)(13C)



170

-42.06

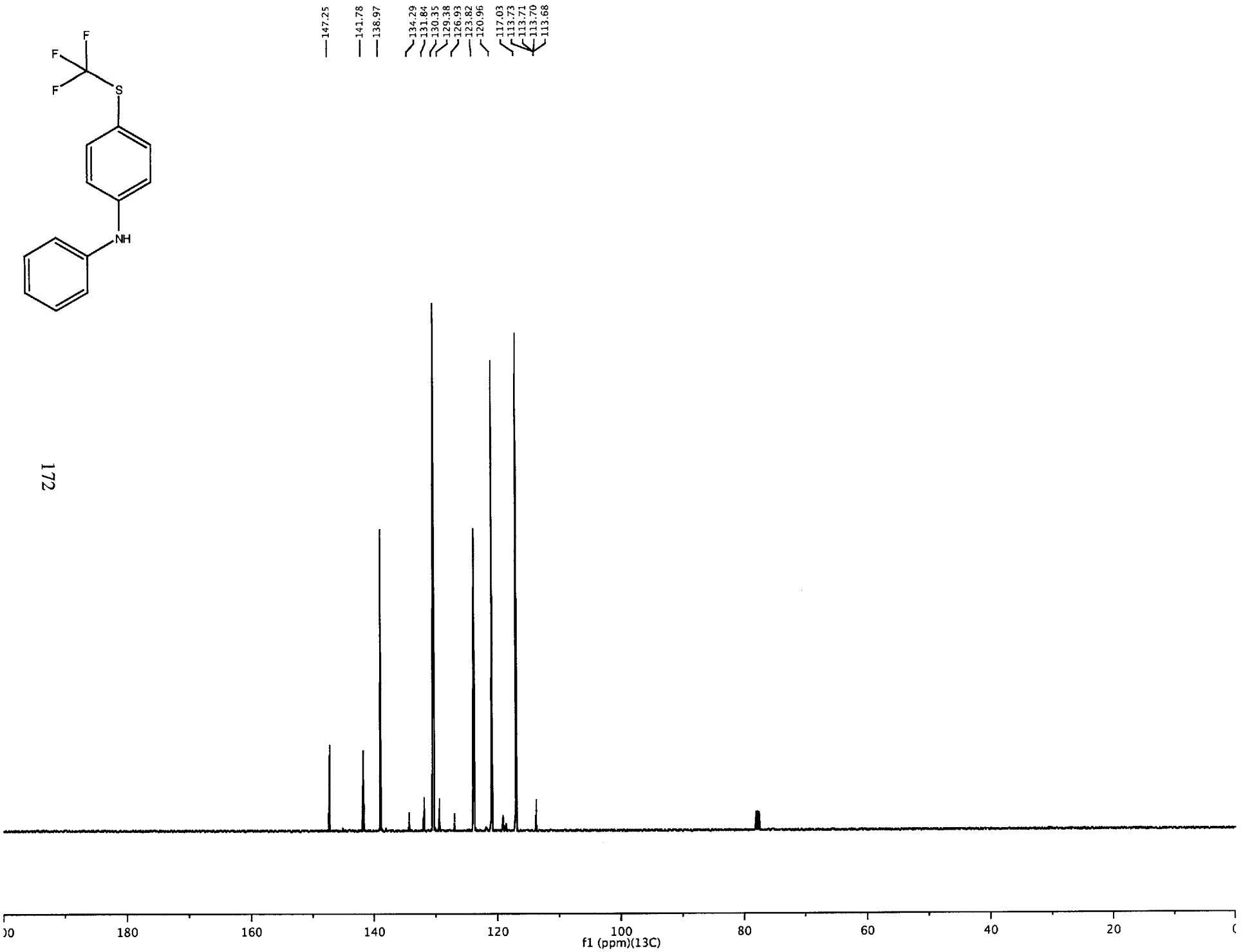


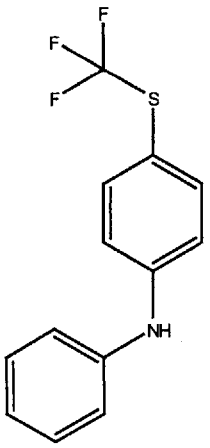
F
F
F
S
NH

7.59
7.58
7.44
7.42
7.41
7.22
7.21
7.18
7.16
7.15
7.06
7.05
5.91

171

1.95
1.94
1.93
1.08
2.11
1.07
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)


147.25
141.78
138.97
134.29
131.84
130.35
129.38
126.93
123.82
120.96
117.03
113.73
113.71
113.70
113.68
F
F
F
S
NH
172
180
160
140
120
100
80
60
40
20
f1 (ppm)(13C)

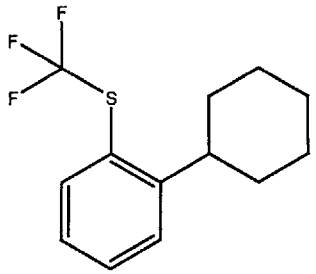


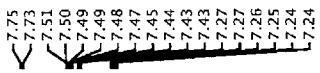
-44.29

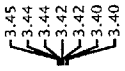
173

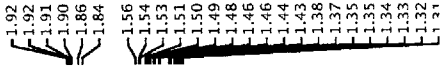
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

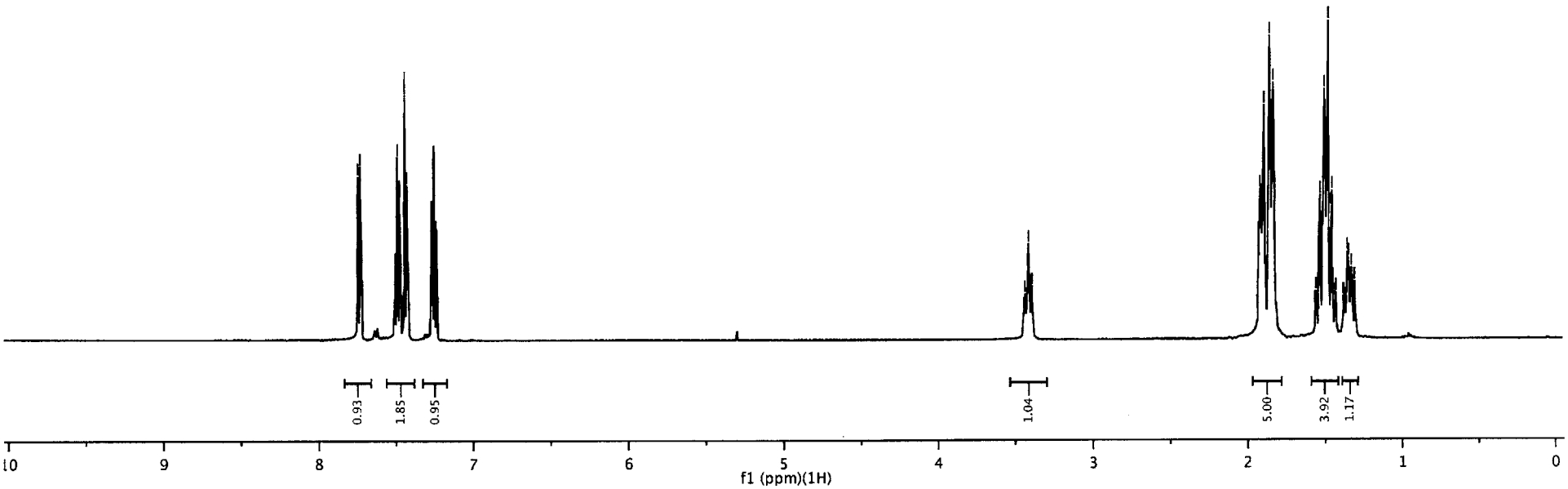
f1 (ppm)(19F)

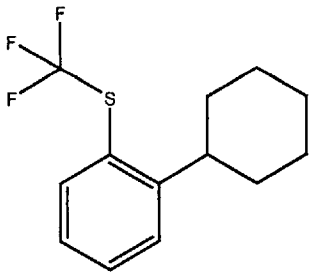

F
F
F
S


7.75
7.73
7.51
7.50
7.49
7.49
7.48
7.47
7.45
7.44
7.43
7.43
7.27
7.27
7.26
7.25
7.24
7.24


3.45
3.44
3.44
3.42
3.42
3.40
3.40


1.92
1.92
1.91
1.90
1.86
1.84
1.56
1.54
1.53
1.51
1.50
1.49
1.48
1.46
1.46
1.44
1.43
1.38
1.37
1.35
1.35
1.34
1.33
1.32

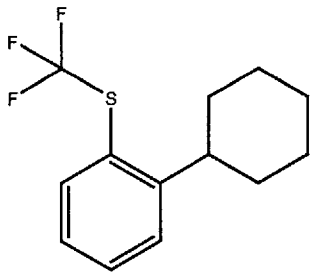

0.93
1.85
0.95
1.04
5.00
3.92
1.17
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)



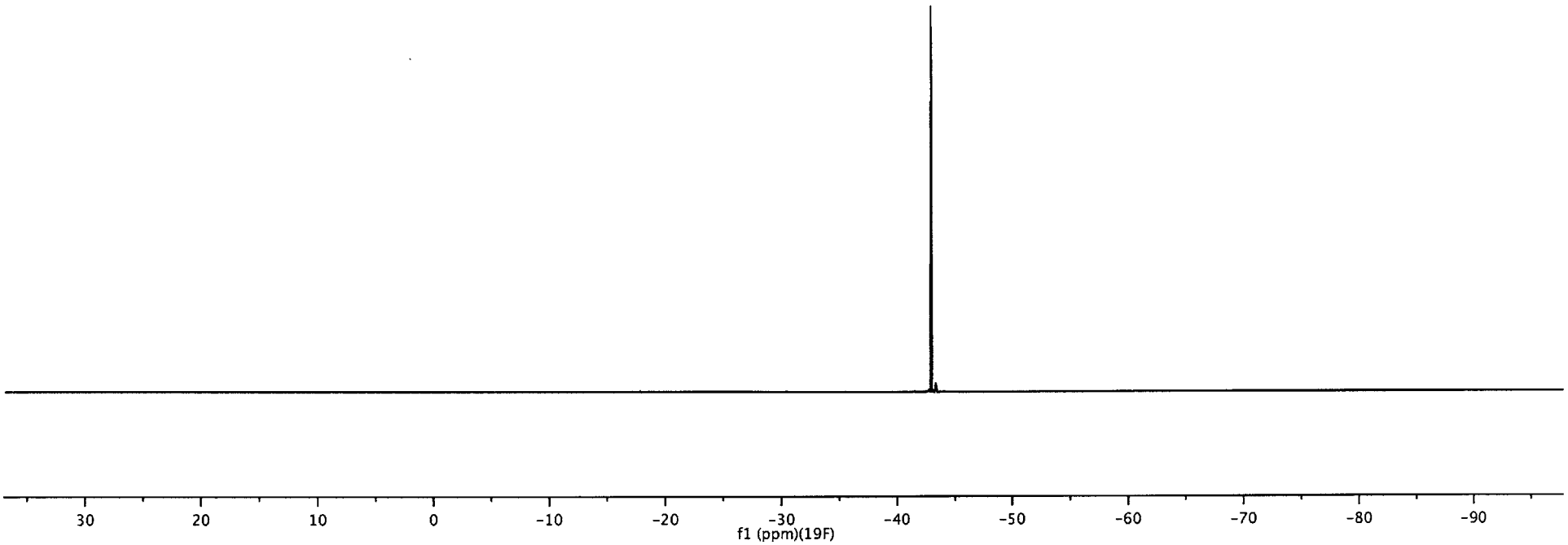
153.73
138.99
138.99
134.67
132.20
131.62
129.17
128.20
127.22
126.72
123.59
123.58
123.56
123.55

42.07
34.86
27.50
26.86

240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40
f1 (ppm)(13C)


F
F
F
S

-42.95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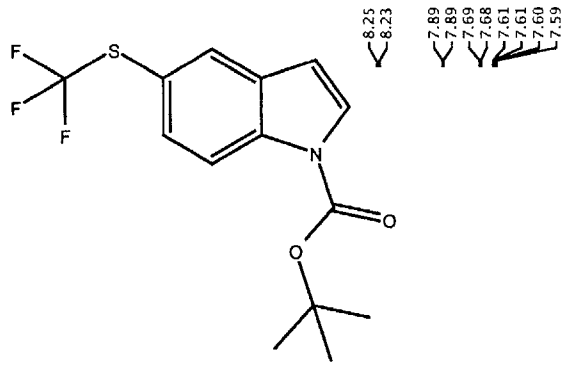
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)



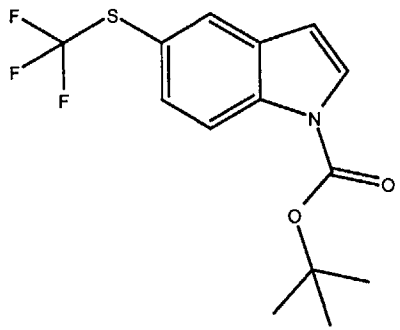
8.25
8.23
7.89
7.89
7.69
7.68
7.61
7.61
7.60
7.59
6.59
6.58
1.71

177

1.00
0.96
0.95
0.90
0.97
9.10

10 9 8 7 6 5 4 3 2 1 0

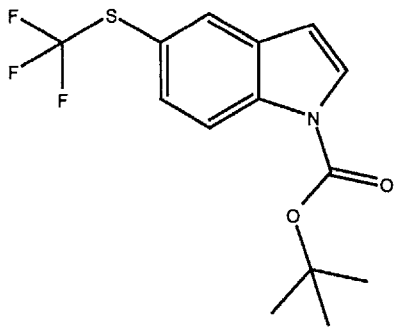
f1 (ppm)(1H)



149.98
137.14
134.27
132.67
132.16
131.82
130.47
129.37
128.04
126.92
118.16
118.14
118.13
118.11
116.74
107.60
85.11
28.74

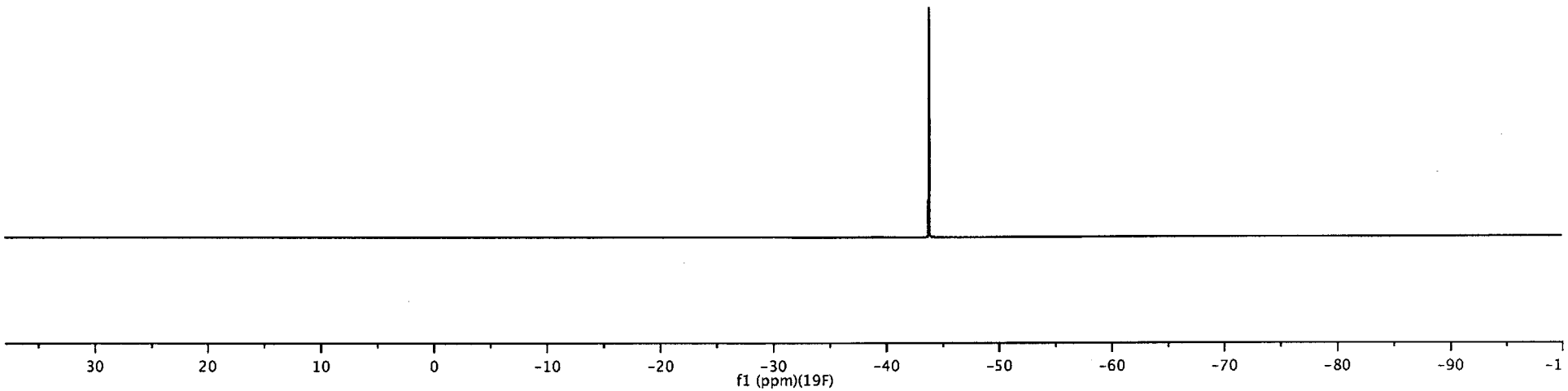
200 180 160 140 120 100 80 60 40 20

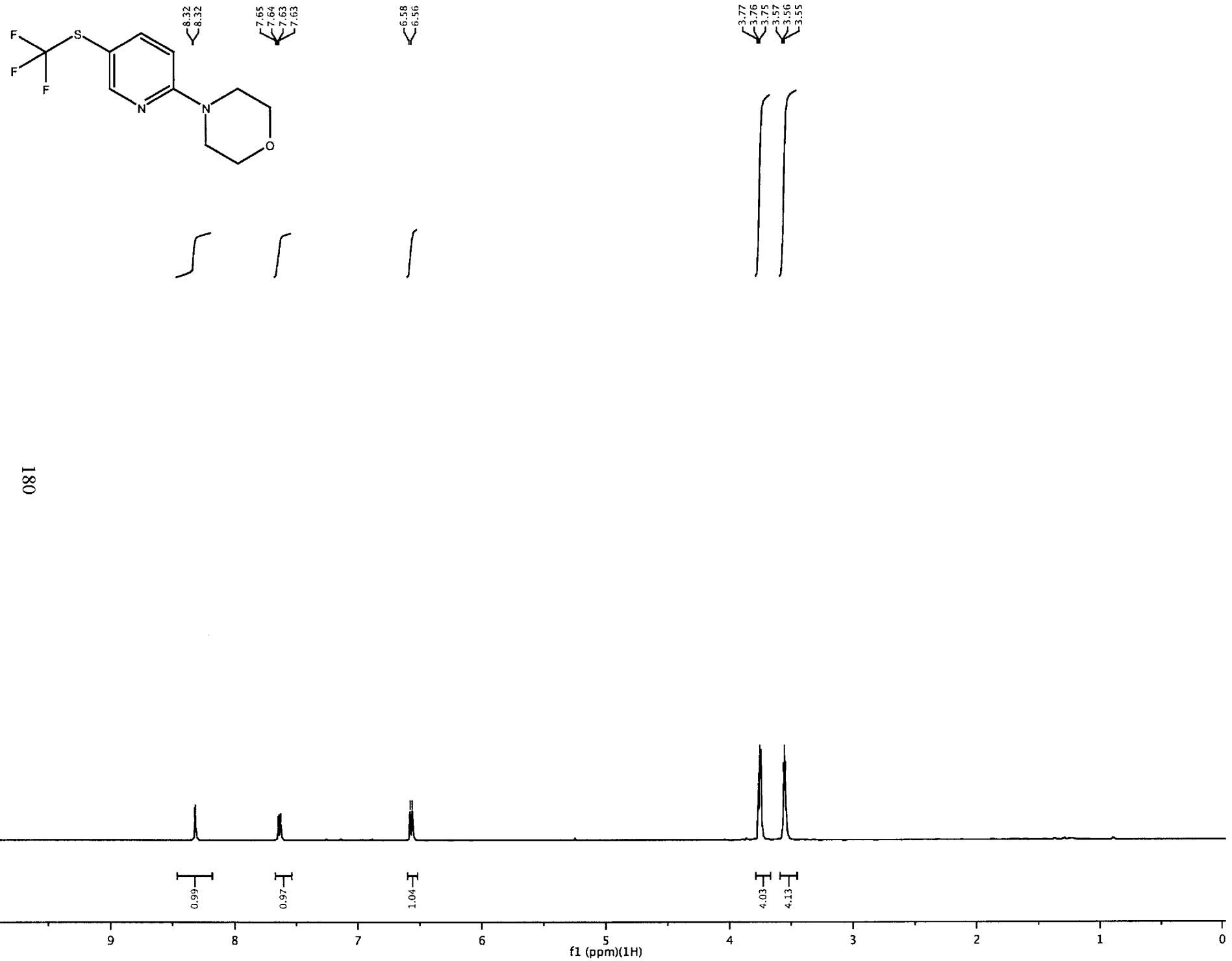
f1 (ppm)(13C)

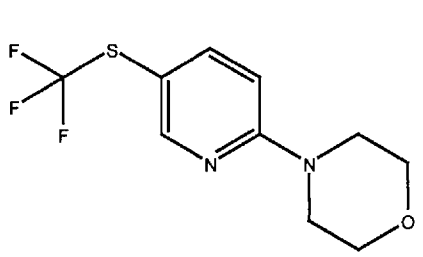


-43.73

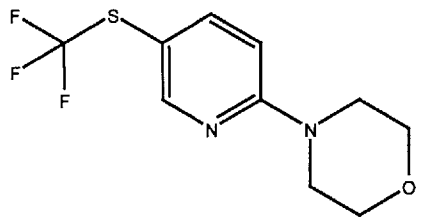
179



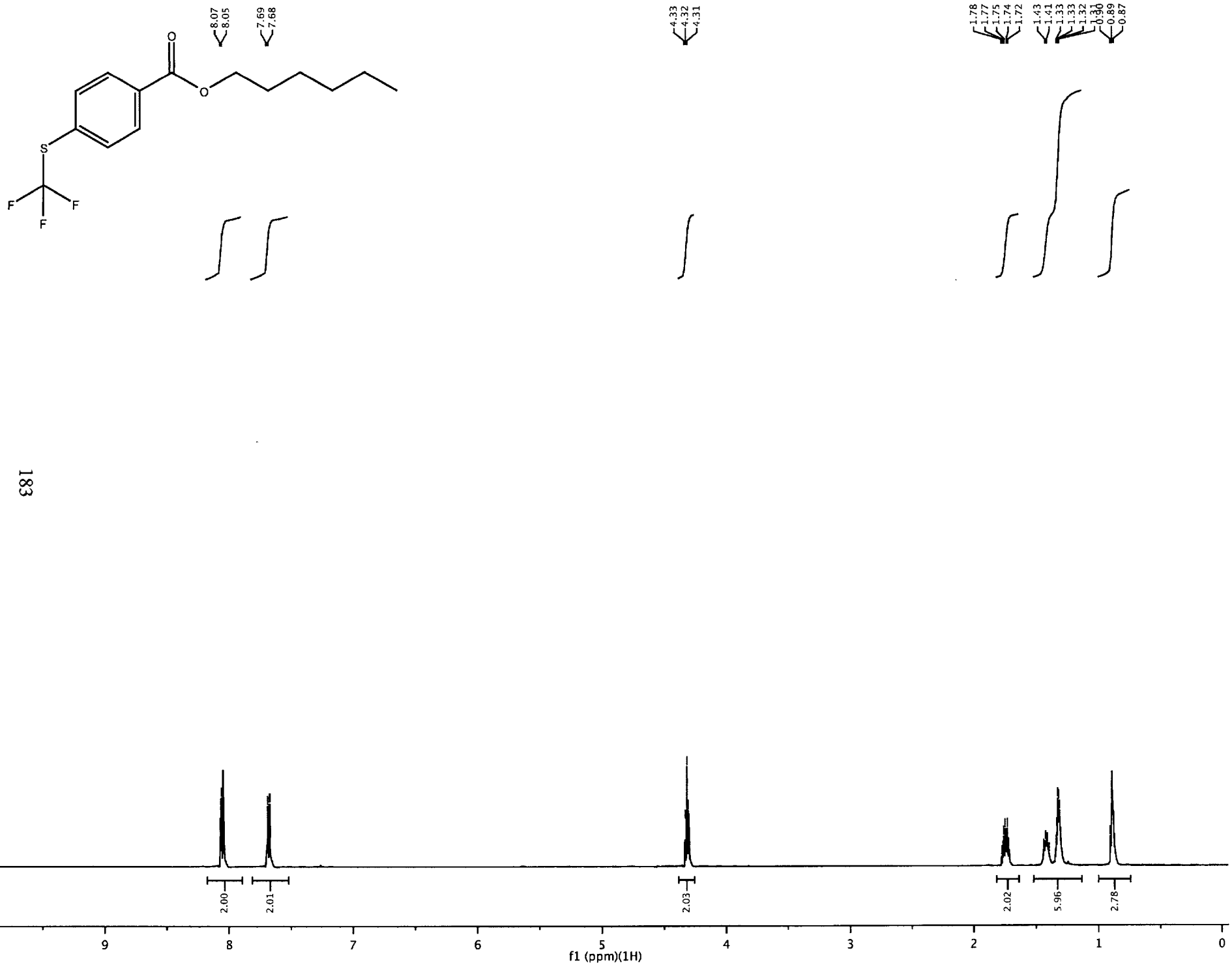

F
F
F
S
N
N
O
8.32
8.32
7.65
7.64
7.63
7.63
6.58
6.56
3.77
3.76
3.75
3.57
3.56
3.55
0.99
0.97
1.04
4.03
4.13
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

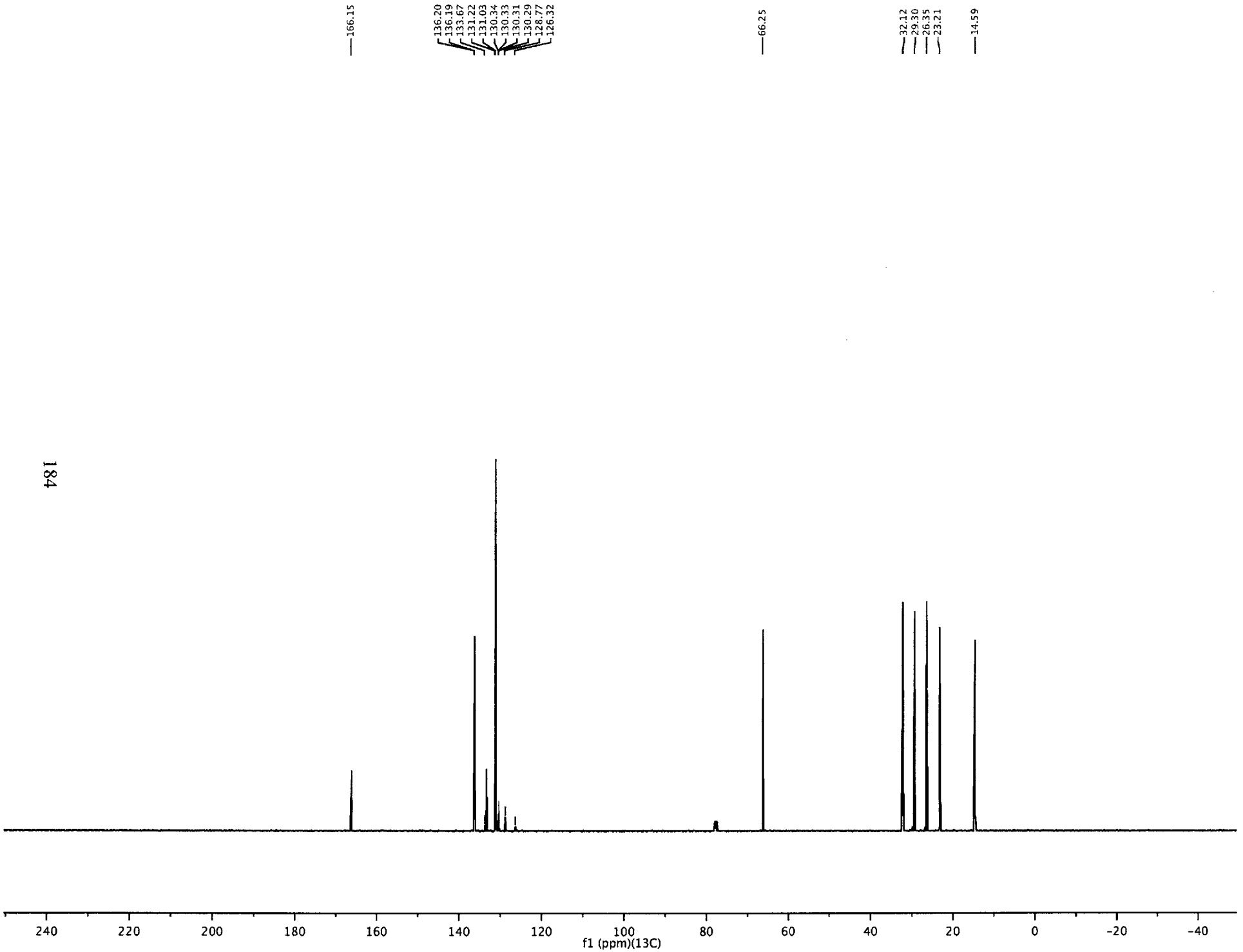

F
F
F
S
N
N
O

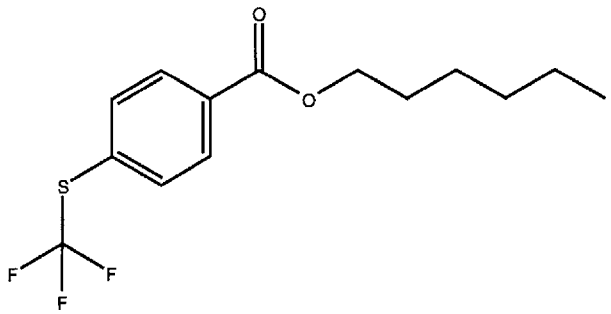
160.51
156.21
145.68
133.69
131.24
128.79
126.33
108.33
108.32
108.30
108.28
107.32
67.19
45.56
200
180
160
140
120
100
80
60
40
20
f1 (ppm)(13C)


F
F
F
S
N
N
O

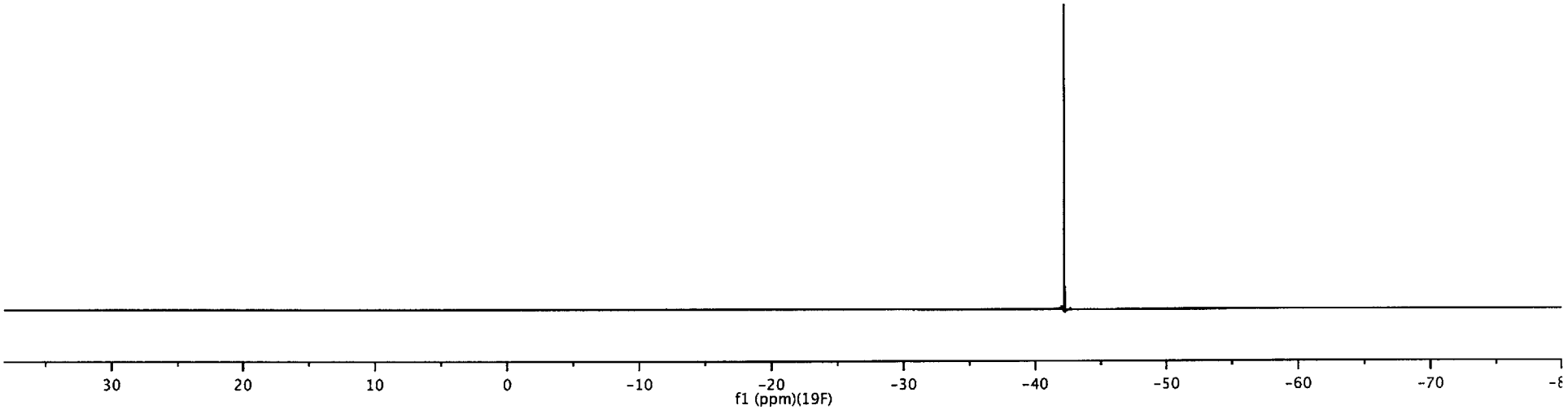
-44.70
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)(19F)


8.07
8.05
7.69
7.68
4.33
4.32
4.31
1.78
1.77
1.75
1.74
1.72
1.43
1.41
1.33
1.33
1.32
1.31
0.90
0.89
0.87
O
O
S
F
F
F
2.00
2.01
2.03
2.02
5.96
2.78
0
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

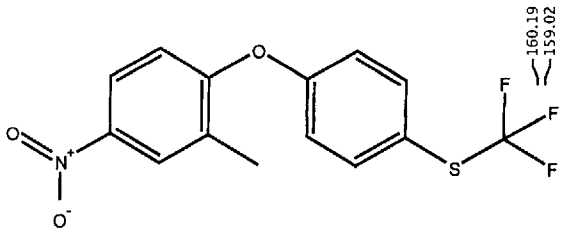

166.15
136.20
136.19
133.67
131.22
131.03
130.34
130.33
130.31
130.29
128.77
126.32
66.25
32.12
29.30
26.35
23.21
14.59
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)(13C)


O
O
S
F
F
F

-42.20


30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)(19F)

8.16
8.16
8.04
8.04
8.02
8.02
7.68
7.67
7.07
7.06
7.06
7.05
7.05
7.04
6.94
6.93
2.37
O
F
F
F
S
O
N+
O-
0.95
0.99
1.96
2.01
1.04
3.18
10
9
8
7
6
5
4
3
2
1
f1 (ppm)(1H)



160.19
159.02
144.34
133.34
133.03
131.42
131.38
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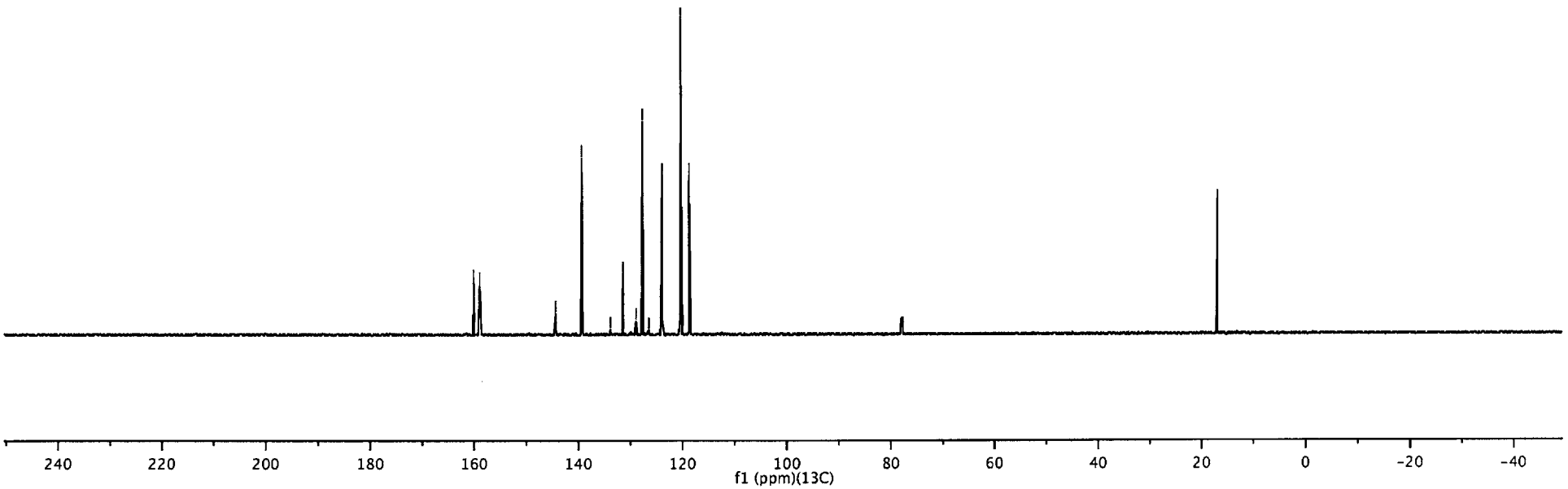
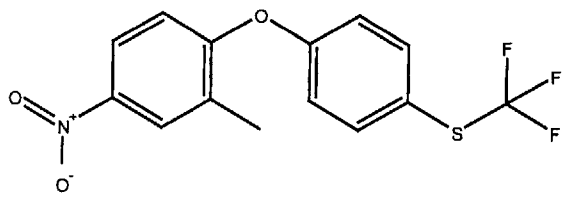
127.68
126.48
123.89
120.33
120.02
120.00
119.98
119.96
118.73
16.97





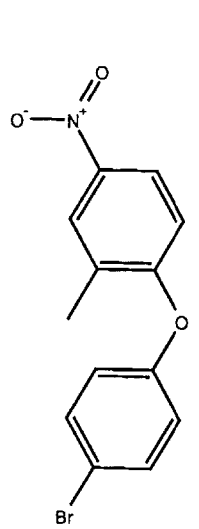
-43.48

188

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -8

f1 (ppm)(19F)

8.14
8.14
8.00
8.00
7.98
7.98
7.52
7.50
6.92
6.91
6.80
6.78
2.38
O
N
O
O
Br
0.80
0.88
1.71
1.76
0.92
3.00
f1 (ppm)(1H)


O
N+
O-
O
Br

161.29
155.27
143.66
133.92
130.48
127.58
123.89
122.09
118.17
116.97
17.07
190
200
180
160
140
120
100
80
60
40
20
f1 (ppm)(13C)

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Chapter 3: The Development of a Precatalyst for Ni-Catalyzed C–N Bond Formation

3.1: Introduction

Aromatic carbon-nitrogen bonds are ubiquitous in pharmaceuticals, agrochemicals and electronic materials.[1-3] Over the past twenty years, the continued development of methods for Pd-catalyzed carbon-nitrogen formation has rendered it as one of the most important and versatile tools available to organic chemists.[4-7] Contributing significantly to this success has been the operational simplicity of the method and the development of readily activated precatalysts.[8-9] This success is in sharp contrast to the analogous Ni-catalyzed methodology, which has seen little adoption by mainstream synthetic chemists.[10-11] While Ni-based systems offer a 1,000-fold price advantage relative to Pd-based ones, most of the existing methods either require an expensive and air- and moisture-sensitive Ni(0) precursor[12-15] or the combination of a Ni(II) precursor with a reducing agent.[11-12,16-17] The development of an air-stable, highly active Ni(0) precatalyst would be of great interest to the community of synthetic chemists.[18]

First reported by our group in 1997,[12] nickel-catalyzed carbon-nitrogen bond forming reactions have been expanded by Fort,[16,19] Chatani,[14,20] Garg,[13,21] and others[17,22-24] to include phenol-derived electrophiles such as sulfamates, carbamates, carbonates and pivalates, which are traditionally considered to be inert under palladium-catalyzed reaction conditions.[25] This orthogonal-electrophile approach could allow for multiple transition metal-catalyzed processes to be carried out on a single precursor for rapid derivatization.[13] Despite these advances, the substrate scope of Ni-catalyzed C–N bond formation has remained narrow. With the exception of pyridinyl and quinolinyl substrates, there exist no reports for the use of heterocyclic aryl halides or pseudo halides as substrates nor are there examples of the arylation of heteroaromatic amines. Finally, the use of substrates containing base sensitive functional groups is usually not possible as the chemistry, to date, has required a strong base.[26]

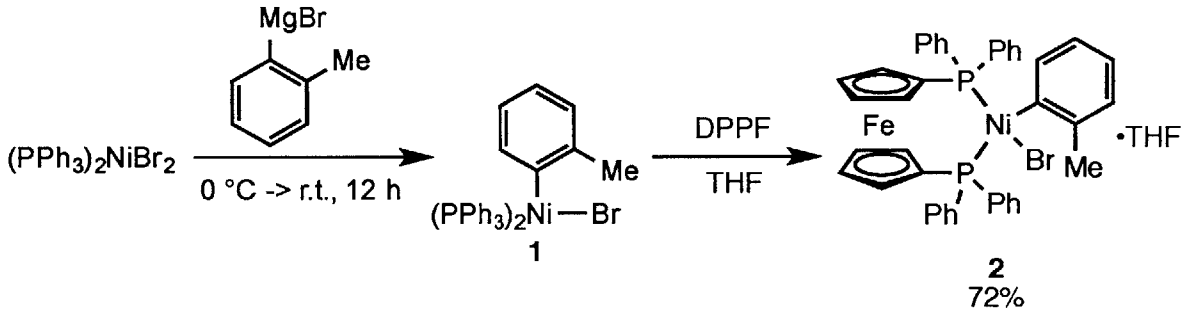
Several attempts have been made toward the development of an air-stable, readily activated Ni(0) precatalyst. First reported in 1960 by Chat and Shaw, Ni(II) oxidative addition complexes have been demonstrated to be air- and moisture-stable compounds.[27] In 2007, Yang reported the first use of a (bis)triphenylphosphine Ni(II) oxidative addition complex as a precatalyst in C-N bond-forming processes.[22,28-29] While significant, the preparation of these complexes required the use of air- and moisture-sensitive $Ni(COD)_2$, thus limiting their general applicability. In 2012, Garg reported the use of $(DME)NiCl_2$ as a precatalyst when combined with phenyl boronic acid as an activator.[11] This approach has also been explored by our group[12] as well as others, such as Knochel[17] and Fort.[16] The use of an activator complicates synthetic procedures and is often incompatible with a wide range of functional groups. Recently, Hartwig reported a 1,1'-bis(diphenylphosphino)ferrocene (DPPF) ligated Ni-cinnamyl complex for use in Suzuki-Miyaura reactions.[30] While the authors claim that this complex is air- and moisture-stable, they nevertheless recommend storage under inert atmosphere, suggesting decomposition of the complex does occur in ambient atmosphere.

In 2009, McNeil reported the use of 1,2-bis(diphenylphosphino)ethane (DPPE) and 1,3-bis(diphenylphosphino)propane (DPPP) ligated Ni(II) oxidative addition complexes in polymerization reactions.[31] While the synthesis of the starting (bis)triphenylphosphine complexes still required the use of $Ni(COD)_2$, McNeil demonstrated the feasibility of ligand exchange on such complexes with chelating phosphine ligands to generate isolable, air-stable nickel (II) oxidative addition complexes. Furthermore, Beckmann reported an operationally simple procedure toward the synthesis of these complexes starting from $NiBr_2$, triphenylphosphine and *o*-tolylmagnesiumbromide.[32] Based on the demonstrated air- and

moisture-stability of Ni(II) oxidative addition complexes, we elected to employ the analogous DPPF complexes for use in nickel-catalyzed C-N bond forming reactions.

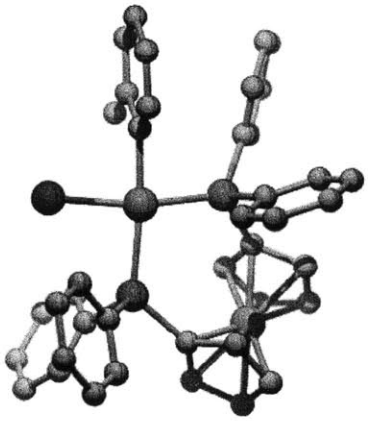
3.2: Results and Discussion

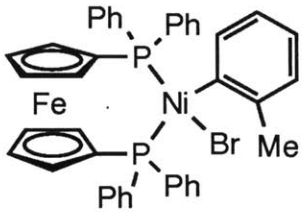
We began our investigation by synthesizing [(bis)triphenylphosphine](*o*-tolyl)bromonickel (**1**) based on the method of Beckmann. Due to our previous experience with nickel-based catalytic systems we chose to utilize DPPF as the supporting ligand. Following the procedure of McNeil, we obtained **2** as the THF complex in good yield (Scheme 1).



Scheme 1. Synthesis of **2**.

This complex was characterized with the aid of single-crystal X-ray crystallography (Figure 1). To our knowledge, this represents the first reported example of a nickel oxidative addition complex utilizing DPPF as the ancillary ligand. Consistent with structural data reported by McNeil, **2** is a diamagnetic species with a square planar Ni(II) center and exhibits a characteristic doublet splitting pattern in the ^{31}P NMR spectrum.

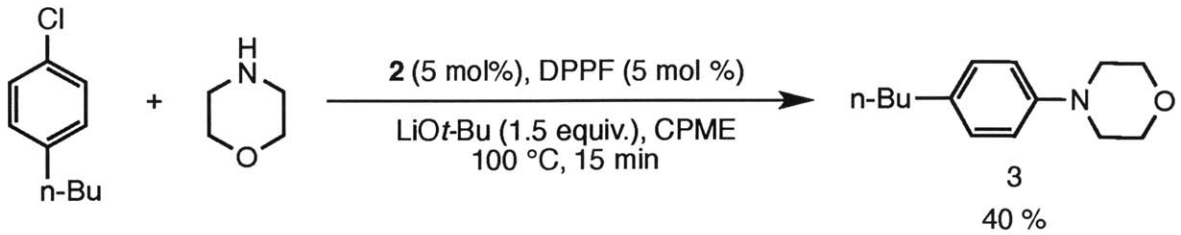




2

Figure 1. X-Ray Crystal Structure of **2**.

Utilizing conditions previously developed in our group based on the use of DPPF/Ni by Dr. Eun Jin Cho, we attempted to couple *p*-chloro-*n*-butylbeznene with morpholine in the presence of a catalytic quantity of **2** (Scheme 2); initial attempts resulted in a modest yield of **3** (40 %). We surmised that the incomplete conversion of the aryl chloride could be attributed to either catalyst decomposition or problems with activation. In 2011, Hartwig reported the use of benzonitrile as an additive in facilitating the α-arylation of ketones in the presence of catalytic



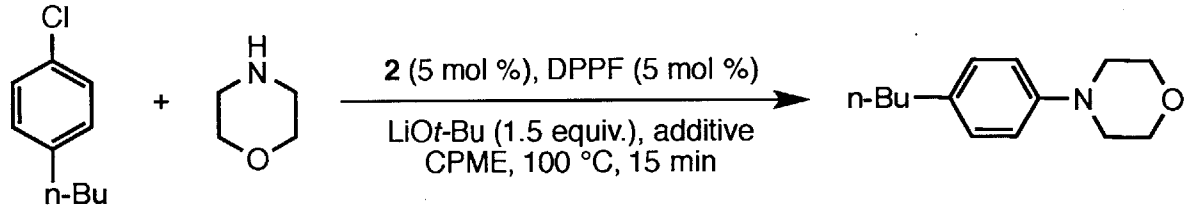
3

40 %

Scheme 2. Initial attempt to use **2** as a precatalyst in C–N bond forming reactions.

amounts of 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) and $Ni(COD)_2$.[33] He postulated that the benzonitrile stabilized the active Ni(0) species and inhibited possible catalyst deactivation. Stoichiometric studies revealed that the presence of benzonitrile facilitates the oxidative addition of aryl chlorides to Ni(0).[34] As such, we added 10 mol % benzonitrile to our previous reaction conditions which resulted in 81% yield of product. Complete consumption of the aryl chloride was seen using one equivalent of benzonitrile. Further optimization revealed that acetonitrile worked equally well in facilitating the process (Table 1). Due to its lower boiling point relative to benzonitrile, we elected to use acetonitrile as an additive in our subsequent work.

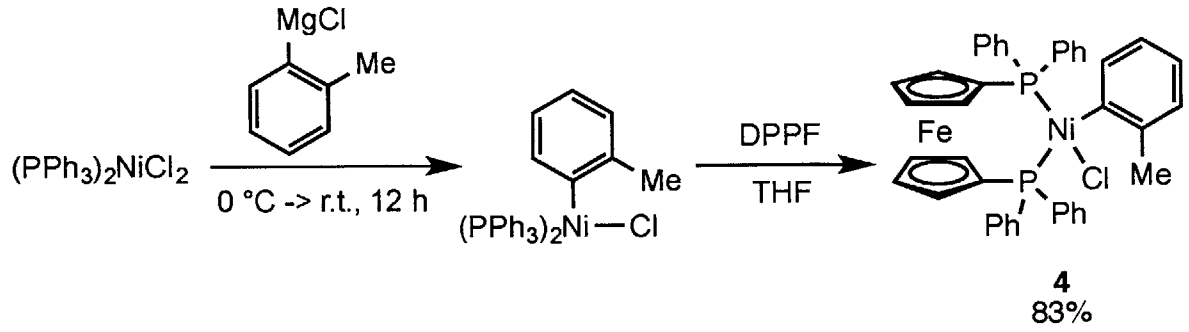
Table 1. Examination of cyano containing additives in facilitating Ni-Catalyzed C–N bond formation.[a]



Entry	Additive	Amount	Yield (GC)
1	None	0	40%
2	PhCN	10 mol %	80%
3	PhCN	20 mol %	81%
4	PhCN	1 equiv	89%
5	MeCN	1 equiv	85%

a) amine (1.5 equiv.), CPME (1 mL); all reactions are run on 0.4 mmol scale and all reported yields are based on GC data.

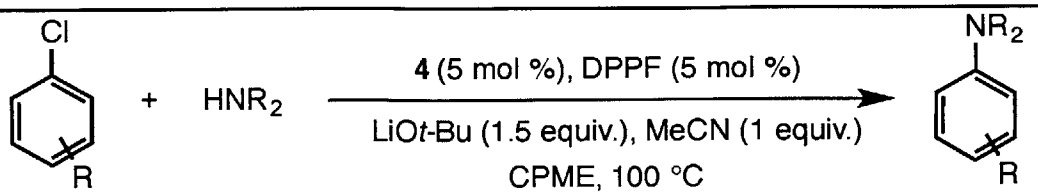
While **1** proved to be an effective catalyst, we chose to employ the chloride analog, **4**, due to its ease of preparation and cost considerations. Complexes **2** and **4** are nearly identical in effecting the desired C-N bond formation reaction (Scheme 3).

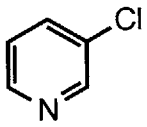
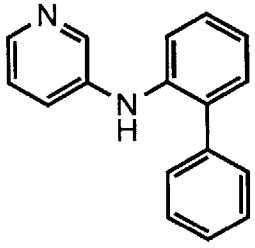
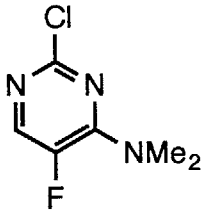
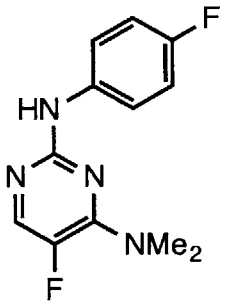
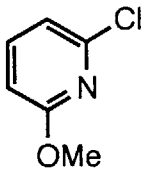
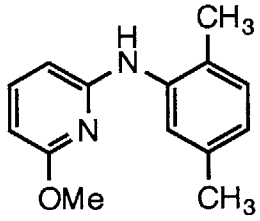
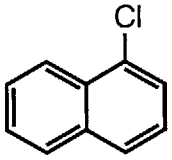
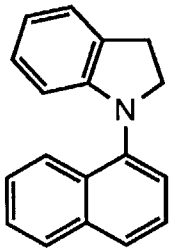
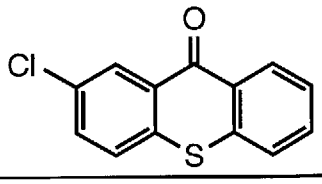
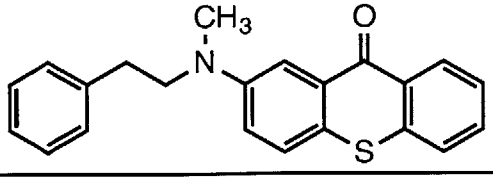


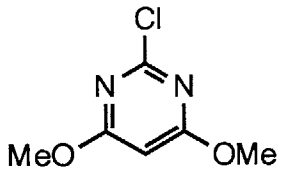
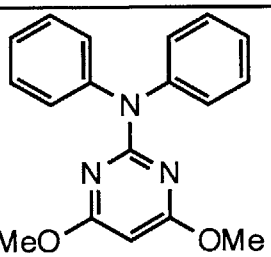
Scheme 3. Synthesis of **4**.

With suitable conditions in hand, we examined the substrate scope of the Ni- catalyzed C–N bond-forming reaction. With 1 equiv. of acetonitrile, 1.5 equiv. of Li*O*t*Bu* and catalytic quantities of **4** and DPPF, a range of primary and secondary amines could be coupled with a wide array of aryl chlorides. Electron-rich, -neutral, and -deficient anilines were successfully arylated with electron-rich, -neutral, and -deficient aryl chlorides. Further, we were successful in the arylation of anilines bearing *ortho*-methyl or *ortho*-phenyl groups. In contrast to prior reports which have deemed the arlyation of diphenyl amine with aryl chlorides to be exceedingly difficult, our system allowed the arylation of diphenyl amine proceeded in 78% yield (Table 2).[29,35] Although anilines reacted in good to excellent yields, the use of primary alkyl amines resulted nearly quantitative reduction of the aryl halide through a β-hydride elimination pathway.[12] Finally, the use of 5-membered heteroaromatic amines failed to provide the desired product; instead, the starting aryl chloride was recovered in quantitative yield.

Table 2. Ni-catalyzed arylation of primary and secondary amines with aryl chlorides.[a]



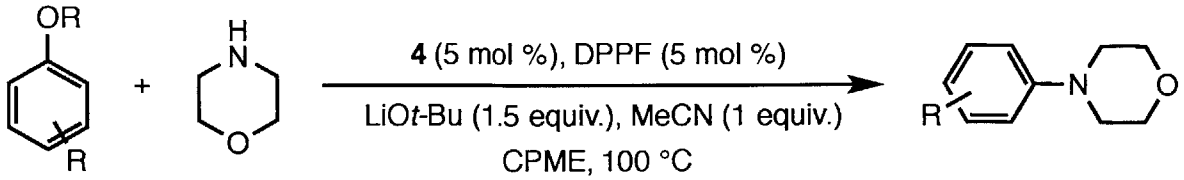
Entry	Aryl Chloride	Product	Time (h)	Yield
1			1	94%
2			16	77%[b]
3			1	80%
4			1	60%
5			1	83%

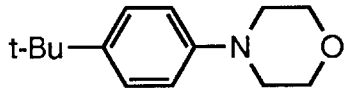
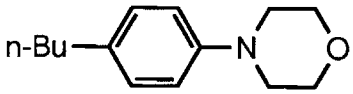
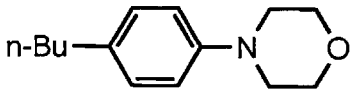
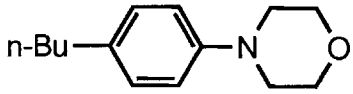
6			16	78%[c]

a) ArCl (1 mmol), amine (1.5 mmol), CPME (2 mL); isolated yields. b) 7.5 mol % **4**, 7.5 mol % DPPF, 130 °C. c) 10.0 mol % **4**, 10 mol % DPPF, 130 °C.

Further evaluation of substrates indicated that phenol derivatives could be employed as electrophiles. Previous reports regarding the use of aryl tosylates suggested that electron-rich electrophiles were poor substrates providing little, if any, of the desired product. Our catalyst, however, provides nearly quantitative yields for the arylation of morpholine with an aryl benzenesulfonate. Further, while aryl triflates represent some of the most commonly employed phenol-derived electrophiles in Pd-catalyzed cross-coupling reactions, there exist no reports of their use in C-N bond-forming reactions employing Ni-based catalysts which provide product in yields greater than 4%.[11] Under our reaction conditions, were successful in the arylation of morpholine with 4-*n*-butylphenyl trifluoromethanesulfonate in quantitative yield. Finally, aryl sulfamates were also successfully coupled with morpholine to provide the desired product providing the desired product 65% yield (Table 3).

Table 3. Arylation of morpholine with various phenol derived electrophiles.[a]

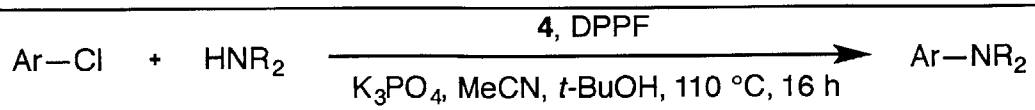


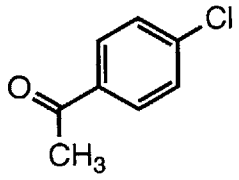
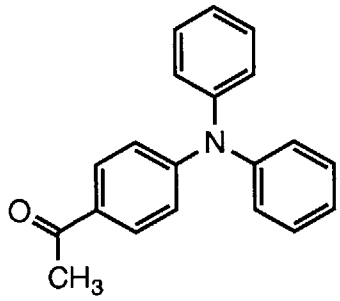
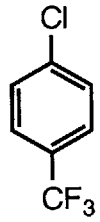
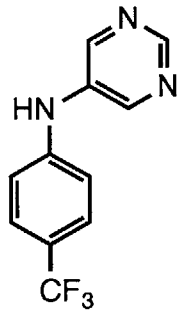
Entry	R	Product	Time (h)	Yield (GC)
1	SO_2Ph		16	87%
2	SO_2CF_3		1	91%
3	SO_2NEt_2		1	65%
4	CO*t*Bu	N/A	1	0%[b]
5	SO_2Me		14	5%

a) amine (1.5 equiv.), CPME (1 mL); all reactions are run on 0.4 mmol scale and all reported yields are based on GC data.

In order to further improve the scope of the reaction, we explored the possibility of utilizing weak bases in effecting C-N bond formation. While the use of carbonate and phosphate bases in Pd-catalyzed cross-coupling reactions is well known, there are no reports of analogous reactions employing Ni-based systems. Employing conditions developed by Nathan Park, a graduate student in the group, for the use of K_3PO_4 in the reaction, we were successful in the coupling of aryl chlorides and anilines bearing base-sensitive functional groups (Table 4). Aryl halides bearing sensitive functional groups, such as methyl ketones, provided the desired product in 62% yield. Furthermore, base-sensitive anilines, such as 5-aminopyrimidine, were successfully arylated in 75% yield.

Table 4. Ni-catalyzed arylation of primary and secondary amines with aryl chlorides under weakly basic conditions.[a]



Entry	R	Product	Yield (GC)
3			62%[b]
4			75%

a) ArCl (1 mmol), amine (1.5 mmol), K_3PO_4 (3 mmol), MeCN (1 mmol), **4** (5 mol %), DPPF (5 mol %), CPME (2 mL); isolated yields. b) 10.0 mol % **4**, 10 mol % DPPF.

3.3: Conclusion

We have developed an air- and moisture-stable, versatile precatalyst for Ni-catalyzed C-N bond forming reactions. Successful characterization of this complex provided conclusive evidence for a DPPF ligated Ni(II) oxidative addition complex bearing a square planar Ni(II) center. Furthermore, we were able to expand the scope of traditional Ni-based cross-coupling reactions to include a wide range of electrophiles and nucleophiles previously deemed difficult. Finally, for the first time we were able to demonstrate the feasibility of employing a weak base for the coupling of substrates that bear base-sensitive functional groups. Work is currently

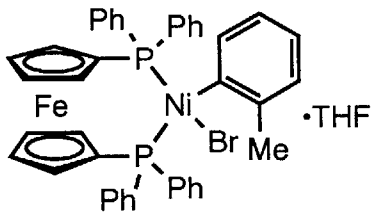
ongoing in the group to determine the precise mechanism by which the catalyst operates, the mechanism of catalyst activation and expansion of the substrate scope to include 5-membered heterocyclic aryl halides and amines.

3.4: Experimental

General Information. Reactions were set-up on a bench top (not in a glove box) and were stirred with Teflon-coated magnetic stir bars. All reactions were performed in oven-dried, screw-cap test tubes with Teflon seals under an atmosphere of nitrogen. THF was purchased from J.T. Baker in CYCLE-TAINER® solvent-delivery kegs and vigorously purged with argon for 2 h. The solvent was further purified by passing it under argon pressure through two packed columns of neutral alumina and copper (II) oxide. Anhydrous MeCN, anhydrous CPME, anhydrous *tert*-butanol and anhydrous bezonitrile were purchased from Aldrich in Sure-Seal® bottles and used as received. Pentane was also purchased from Aldrich and used as received. Flash column chromatography was performed using 40-63 micron silica purchased from Silicycle. $NiBr_2$, $NiCl_2$, $(PPh_3)_2NiBr_2$ and $(PPh_3)_2NiCl_2$ were purchased from Strem and used as recieved. PPh_3 was purchased from Aldrich and used as received. The preparation of [(bis)triphenylphosphine](*o*-tolyl)bromonickel and [(bis)triphenylphosphine](*o*-tolyl)chloronickel has been previously described.[32] Li*Ot*-Bu was purchased from Strem and stored in a nitrogen filled glovebox. Small quantities (~2 g) were periodically removed in glass vials and stored in a dessicator for up to one week. K_3PO_4 was purchased from Aldrich and stored in a nitrogen filled glovebox. Small quantities (~5 g) were periodically removed from the bulk, finely ground inside the glovebox with a mortar and pestle and stored in a dessicator for up to one week. All aryl chlorides and amines were purchased from Matrix Scientific, Aldrich, Alfa,

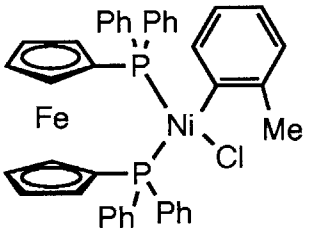
Oakwood Chemicals or Combi-Block unless otherwise noted and used as received. Yields refer to isolated yields of compounds greater than 95% purity as determined by gas chromatography and ^{1}H NMR. Quoted yields are representative and so may differ slightly from the average values given in Tables 2 and 5, as well Schemes 1 and 3.

All ^{1}H NMR spectra were recorded on a Varian Inova-500 NMR spectrometer in deuterochloroform operating at 500 MHz. All ^{13}C NMR spectra were recorded on a Varian Inova-500 NMR spectrometer in deuterochloroform or deuteromethylenechloride operating at 126 MHz. All ^{19}F NMR spectra were recorded on a Varian Inova-500 NMR spectrometer in deuterochloroform operating at 471 MHz. All ^{31}P NMR spectra were recorded on a Varian Inova-500 NMR spectrometer in deuterochloroform operating at 220 MHz. Chemical shifts are quoted relative to residual solvent in the case of ^{1}H and ^{13}C NMR spectra and relative to $CFCl_3$ as zero in the case of ^{19}F NMR spectra. The following abbreviations are used singularly or in combination to indicate the multiplicity of signals: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. NMR spectra were acquired at 298 K. All IR spectra were taken on a Thermo Scientific – Nicolet iS5 spectrometer (iD5 ATR – diamond). Selected absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}). GC analyses were performed on an Agilent 6970 equipped with an FID detector and a Hewlett Packard 10 m × 0.2 mm HP-1 capillary column using dodecane as an internal standard. Melting points were determined on a Mel-Temp II capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Inc., Nocross, GA.



[1,1'-Bis(diphenylphosphino)ferrocene](*o*-tolyl)bromonickel•THF (2).

[Bistriphenylphosphine](*o*-tolyl)bromonickel (753 mg, 1 mmol) and 1,1'-Bis(diphenylphosphino)ferrocene (560 mg, 1.02 mmol, 1.02 equiv) were added to an oven-dried 25 mL resealable test tube with Teflon screw cap equipped with a magnetic stir bar. The sealed tube was evacuated and refilled with N_2 (this sequence was repeated a total of three times) and THF (20 mL) was added via syringe. The resulting orange mixture was allowed to stir at room temperature for 30 min to provide a cloudy red solution. The tube was then opened to air and the mixture was filtered through a glass fiber filter pad to remove all insoluble material. The clear red solution was poured into a 250 mL beaker containing pentane (100 mL) causing the precipitation of a yellow solid. The mixture was stirred for 5 min and the solid was isolated by filtration and dried under vacuum to provide the title compound as a yellow solid (615 mg, 72% yield). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.55 – 8.20 (m, 4H), 8.07 (dt, J = 9.9, 4.1 Hz, 2H), 7.55 (q, J = 3.1 Hz, 7H), 7.48 – 7.33 (m, 2H), 7.31 (t, J = 6.5 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.95 – 6.80 (m, 2H), 6.68 (dd, J = 10.8, 7.8 Hz, 2H), 6.54 (t, J = 7.4 Hz, 1H), 6.45 – 6.29 (m, 1H), 6.18 (d, J = 7.4 Hz, 1H), 5.24 (s, 1H), 4.65 (s, 1H), 4.31 (d, J = 16.5 Hz, 2H), 4.11 (d, J = 8.6 Hz, 2H), 3.62 (s, 1H), 3.44 (s, 1H), 2.49 (s, 3H). ^{31}P NMR (121 MHz, CD_2Cl_2) δ 30.13 (d, J = 26.0 Hz), 10.59 (d, J = 26.0 Hz). Anal Calc'd for $C_{45}H_{43}BrFeNiOP_2$: C, 63.14, H, 5.06. Found: C, 63.34; H, 4.98.



[1,1'-Bis(diphenylphosphino)ferrocene](*o*-tolyl)chloronickel (4)

[Bistriphenylphosphine](*o*-tolyl)chloronickel (2.95 mg, 4.5 mmol) and 1,1'-Bis(diphenylphosphino)ferrocene (2.66 mg, 4.8 mmol, 1.07 equiv) were added to an oven-dried 500 mL round bottom flask equipped with a magnetic stir bar and stoppered with a rubber septum. The sealed flask was evacuated and refilled with N_2 (this sequence was repeated a total of three times) and THF (64 mL) was added via syringe. The orange mixture was allowed to stir at room temperature for 2 h. Pentane (144 mL) was then added via syringe and the resulting mixture was allowed to stir for 2 h to produce a yellow suspension. Additional pentane (100 mL) was added and the product was isolated by filtration to produce a yellow solid. The solid was dissolved in dichloromethane (10 mL) and the resulting red suspension was filtered through a glass fiber filter to collect a clear red solution in a 100 mL round bottom flask and concentrated. The resulting residue was the triturated in pentane with the aid of sonication to produce a pale yellow suspension. The solid was isolated by filtration to collect the title compound as a yellow solid (2.7 g, 83% yield). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.28 (s, 4H), 8.08 (s, 2H), 7.55 (d, J = 11.6 Hz, 7H), 7.33 (d, J = 38.9 Hz, 3H), 7.09 (s, 1H), 6.86 (s, 2H), 6.70 (s, 2H), 6.53 (s, 1H), 6.41 (s, 1H), 6.21 (s, 1H), 5.25 (s, 1H), 4.65 (s, 1H), 4.32 (d, J = 27.7 Hz, 2H), 4.12 (d, J = 8.6 Hz, 2H), 3.63 (s, 1H), 3.42 (s, 1H), 2.55 (s, 3H). ^{31}P NMR (121 MHz, CD_2Cl_2) δ 28.55 (d, J = 26.0 Hz), 11.15 (d, J = 25.9 Hz). Anal Calc'd for $C_{41}H_{35}ClFeNiP_2$: C, 66.58, H, 4.77. Found: C, 66.34, H, 4.85.

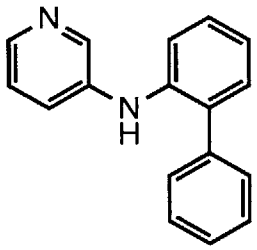
Procedure for the Examination of Various Additives:

2 (15.7 mg, 0.02 mmol, 5 mol %), DPPF (11.08 mg, 0.02 mmol, 5 mol %) and LiO*t*-Bu (48 mg, 0.6 mmol, 1.5 equiv.) were added to an oven-dried 8 mL test tube with Teflon screw cap equipped with a magnetic stir bar. The sealed tube was evacuated and refilled with N_2 (this sequence was repeated a total of three times). After which, 4-*n*-butylchlorobenzene (67.4 μL, 0.4 mmol, 1 equiv.), morpholine (52 μL, 0.6 mmol, 1.5 equiv.), benzonitrile or acetonitrile (10, 20, or 100 mol % relative to 4-*n*-butylchlorobenzene) and CPME (1 mL) were added via syringe. The tube was placed into a preheated oil bath at 100 °C with stirring for 15 min. The tube was then removed from the oil bath and its contents were allowed to cool. Dodecane (90 μL, 0.4 mmol) was added syringe and the reaction tube was opened to ambient atmosphere, diluted with EtOAc and filtered through a pad of silica gel. The filtrate was analyzed using GC and GC/MS methods.

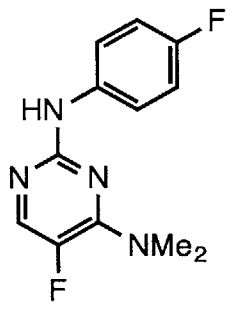
General Procedure for the Arylation of Primary and Secondary Amines Using Strong Base:

4 (37.15 mg, 0.05 mmol, 5 mol %), DPPF (27.7 mg, 0.05 mmol, 5 mol %), LiO*t*-Bu (120 mg, 1.5 mmol, 1.5 equiv.) and aryl chloride (1 mmol, 1 equiv.) and amine (1.5 mmol, 1.5 equiv.), if solid, were added to an oven-dried 16 mL test tube with Teflon screw cap equipped with a magnetic stir bar. The sealed tube was evacuated and refilled with N_2 (this sequence was repeated a total of three times). After which aryl chloride and amine, if liquid, acetonitrile (52 μL, 1 mmol, 1 equiv.) and CPME (2 mL) were added via syringe. Tube was placed into a preheated oil bath at 100 °C with stirring for 1-16 h. The tube was then removed from the oil bath and its contents were allowed to cool. The reaction mixture was diluted with EtOAc and methanol and filtered through a glass fiber filter. The homogenous filtrate was collected and the

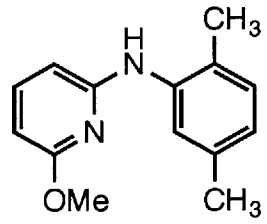
solvent removed under reduced pressure with the aid of a rotary evaporator. The residue was purified via silica gel column chromatography.



***N*-([1,1'-biphenyl]-2-yl)pyridin-3-amine.** Following the general procedure, 3-chloropyridine (113.5 mg, 1 mmol) was used along with 2-aminobiphenyl (253.8 mg, 1.5 mmol, 1.5 equiv.). Purification via column chromatography provided the title compound as an off-white solid (231.5 mg, 94% yield, 132-134 °C m.p.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.15 (d, J = 3.6 Hz, 1H), 7.48 δ 7.40 (m, 4H), 7.37 (dd, J = 15.2, 6.9 Hz, 3H), 7.30 (t, J = 7.5 Hz, 2H), 7.16 (dd, J = 7.8, 4.6 Hz, 1H), 7.09 (t, J = 7.3 Hz, 1H), 5.71 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.63, 141.10, 140.85, 139.68, 139.40, 133.24, 131.87, 129.95, 129.69, 129.12, 128.39, 124.43, 124.38, 123.00, 118.81. IR (neat) ν_{max}: 3233.66, 2922, 1575.26, 1516.02, 1469.64, 1432.68, 1407.25, 1345.86, 1302.82, 1161.49, 1103.72, 1046.64, 1020.88, 1008.39, 884.83, 789.27, 778.47, 756.51, 742.69 cm^{-1}. Anal Calc'd for $C_{17}H_{14}N_2$: C, 82.90, H, 5.73. Found: C, 82.46, H, 5.91.

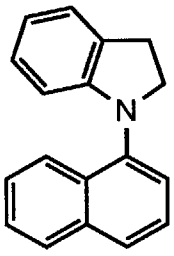


5-fluoro-N^2-(4-fluorophenyl)-N^4,N^4-dimethylpyrimidine-2,4-diamine. Following the general procedure, 2-chloro-5-fluoro-N,N-dimethylpyrimidin-4-amine (175 mg, 1 mmol) was used along with 4-fluoroaniline (253.8 mg, 1.5 mmol, 1.5 equiv.), **4** (55.7 mg, 0.075 mmol, 7.5 mol %), DPPF (41.55 mg, 0.075 mmol, 7.5 mol %). The reaction was stirred at 130 °C for 16 h. Purification via column chromatography provided the title compound as a tan colored solid (193 mg, 77% yield, 160-161 °C m.p.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 6.7 Hz, 1H), 7.56 δ 7.42 (m, 2H), 7.10 (s, 1H), 6.99 (t, J = 8.7 Hz, 2H), 3.20 (d, J = 2.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.74 (d, J = 240.3 Hz), 156.02 (d, J = 1.7 Hz), 153.15 (d, J = 6.3 Hz), 142.80 (d, J = 26.2 Hz), 142.67 (d, J = 245.3 Hz), 137.09 (d, J = 2.5 Hz), 121.13 (d, J = 7.6 Hz), 115.95 (d, J = 22.3 Hz), 39.74, 39.68. ^{19}F NMR (471 MHz, $CDCl_3$) δ -119.42 ? -127.77 (m), -159.73. IR (neat) ν_{max}: 3216.09, 3046.55, 1626.86, 1603.04, 1590.66, 1544.36, 1506.34, 1435.91, 1415, 1396.93, 1278.67, 1207.47, 1154.77, 1097.23, 1019.55, 932.3, 924.87, 871.8, 837.4, 816.03, 791.44, 767.23 cm^{-1}.



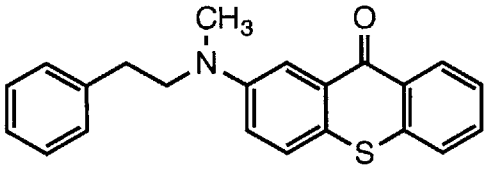
***N*-(2,5-dimethylphenyl)-6-methoxypyridin-2-amine**. Following the general procedure, 2-chloro-6-methoxypyridine (143 mg, 1 mmol) was used along with 2,5-dimethylaniline (181.5 mg, 1.5 mmol, 1.5 equiv.). Purification via column chromatography

provided the title compound as a dark yellow liquid (182 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 δ 7.31 (m, 2H), 7.14 (d, J = 7.6 Hz, 1H), 6.89 (d, J = 7.5 Hz, 1H), 6.20 (dd, J = 10.1, 8.1 Hz, 2H), 6.12 (s, 1H), 3.93 (s, 3H), 2.35 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.41, 156.07, 140.91, 139.12, 137.08, 131.40, 128.24, 125.43, 124.05, 100.18, 99.70, 54.07, 21.87, 18.30. IR (neat) ν_{max}: 3386, 2943.38, 1599.46, 1575.27, 1524.2, 1489.28, 1452.84, 1418.37, 1338.87, 1258.98, 1144.61, 1118.72, 1080.29, 1038.26, 1001.85, 779.47, 726.83 cm^{-1}. Anal Calc'd for $C_{14}H_{16}N_2O$: C, 73.66, H, 7.06. Found: C, 73.70, H, 7.14.



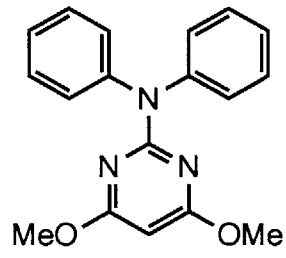
1-(naphthalen-1-yl)indoline. Following the general procedure, 1-chloronaphthalene (162.62 mg, 1 mmol) was used along with indoline (178.5 mg, 1.5 mmol, 1.5 equiv.). Purification via column chromatography provided the title compound as white solid (147.7 mg, 60% yield, 86-88 °C m.p.). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.22 (d, J = 8.3 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.74 δ 7.41 (m, 4H), 7.32 (d, J = 7.2 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.82 (t, J = 7.4 Hz, 1H), 6.32 (d, J = 7.9 Hz, 1H), 4.05 (d, J = 53.2 Hz, 2H), 3.31 (d, J = 30.2 Hz, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 151.94, 143.10, 135.60, 131.44, 131.19, 129.10, 127.67, 126.98, 126.94, 126.44, 126.23, 125.42, 124.90, 120.52, 119.10, 109.54, 56.33, 29.75. IR (neat) ν_{max}: 3050.19, 2947.51, 2842.23, 1604.6, 1574.11, 1506.22, 1482.39, 1456.11, 1438.38, 1398.4, 1329.25, 1297.2, 1262.34, 1222.44, 1162.83, 1117.23, 1072.6,

1050.18, 1026.46, 1019.83, 973.59, 947.47, 925.22, 871.79, 842.22, 799.24, 787.92, 782.55, 765.11, 748.97, 735.93 cm^{-1}.



2-(methyl(phenethyl)amino)-9*H*-thioxanthen-9-one.

Following the general procedure, 2-chlorothioxanthone (246 mg, 1 mmol) was used along with N-methylphenethylamine (202.5 mg, 1.5 mmol, 1.5 equiv.). Purification via column chromatography provided the title compound as an orange solid (285 mg, 83% yield, 102-103 °C m.p.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 2.5 Hz, 1H), 7.56 (d, J = 3.5 Hz, 2H), 7.44 (d, J = 8.9 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.24 (d, J = 7.6 Hz, 3H), 7.09 (d, J = 7.0 Hz, 1H), 3.67 (t, J = 7.6 Hz, 2H), 2.98 (s, 3H), 2.90 (t, J = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.75, 148.17, 140.06, 138.58, 132.34, 130.74, 130.57, 129.59, 129.45, 129.33, 127.64, 127.07, 126.73, 126.30, 119.18, 111.03, 55.37, 39.46, 33.62. IR (neat) ν_{max}: 2934.14, 1626.82, 1592.04, 1493.5, 1450.64, 1433.21, 1413.04, 1383.19, 1351.28, 1332.64, 1219.48, 1193.04, 1135.51, 1116.9, 1073.79, 1033.12, 942.57, 859.05, 800.32, 737.92, 697.78 cm^{-1}.

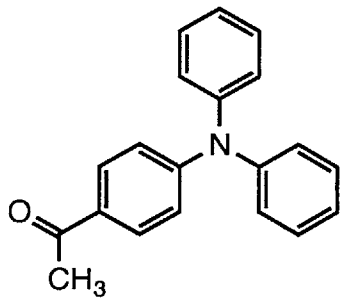


4,6-dimethoxy-*N*,*N*-diphenylpyrimidin-2-amine. Following the general procedure, 2-chloro-4,6-dimethoxypyrimidine (172 mg, 1 mmol) was used along with diphenylamine (253 mg, 1.5 mmol, 1.5 equiv.), **4** (74.3 mg, 0.1 mmol, 10 mol %), and DPPF (55.4, 0.1 mmol, 10 mol %). The reaction was stirred at 130 °C for 16 h. Purification via column chromatography provided the title compound as a brown colored solid (242 mg, 78% yield, 154-155 °C m.p.). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.41 (d, J = 6.4 Hz, 8H), 7.25 (t, J = 6.2 Hz, 2H), 5.64 (s, 1H), 3.72 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 172.43, 161.44, 145.49, 129.30, 128.54, 125.91, 81.64, 54.22. IR (neat) ν_{max}: 2948.28, 1566.38, 1491.72, 1462.15, 1423.02, 1398.31, 1362.05, 1286.48, 1271.02, 1241.36, 1191.31, 1156.54, 1059.79, 1000.54, 952.44, 798.79, 758.13 cm^{-1}. Anal Calc'd for $C_{18}H_{17}N_3O_2$: C, 70.34 H, 5.58. Found: C, 70.24, H, 5.63.

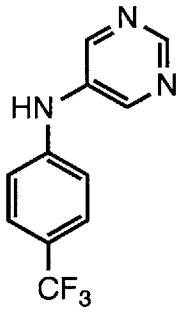
General Procedure for the Arylation of Primary and Secondary Amines Using Weak Base:

4 (37.15 mg, 0.05 mmol, 5 mol %), DPPF (27.7 mg, 0.05 mmol, 5 mol %), K_3PO_4 (636 mg, 3 mmol, 3 equiv.) and aryl chloride (1 mmol, 1 equiv.) and amine (1.5 mmol, 1.5 equiv.), if solid, were added to an oven-dried 16 mL test tube with Teflon screw cap equipped with a magnetic stir bar. The sealed tube was evacuated and refilled with N_2 (this sequence was repeated a total of three times). After which, aryl chloride and amine, if liquid, acetonitrile (52 μL, 1 mmol, 1 equiv.) and *t*BuOH (2 mL) were added via syringe. Tube was placed into a preheated oil bath at 110 °C with stirring for 16 h. The vessel was then removed from the oil bath and its contents were allowed to cool. The reaction was mixture was then diluted with EtOAc and methanol and

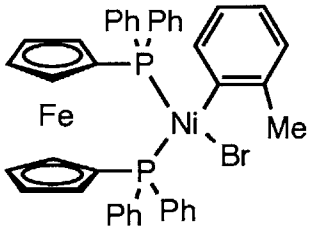
filtered through a glass fiber filter. The clear filtrate was then collected and the solvent removed under reduced pressure with the aid of a rotary evaporator. The residue was then purified via silica gel column chromatography.



1-(4-(diphenylamino)phenyl)ethan-1-one.[36] Following the general procedure, 4-chloroacetophenone (130 mg, 1 mmol) was used along with diphenylamine (253.8 mg, 1.5 mmol, 1.5 equiv.), **4** (74.3 mg, 0.1 mmol, 10 mol %), DPPF (55.4 mg, 0.1 mmol, 10 mol %). Purification via column chromatography provided the title compound as a yellow colored solid (177 mg, 62% yield, 143-145 °C m.p.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.7 Hz, 2H), 7.33 (t, J = 7.8 Hz, 4H), 7.15 (dd, J = 12.0, 7.6 Hz, 6H), 7.00 (d, J = 8.7 Hz, 2H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.20, 152.87, 147.20, 130.62, 130.47, 130.34, 126.67, 125.36, 120.39, 27.01. IR (neat) ν_{max}: 3036.99, 1668.47, 1581.74, 1486.34, 1416.81, 1356.04, 1331.44, 1264.29, 1186.3, 1171.29, 1149.29, 1115.91, 1074.41, 953.4, 903.67, 845.05, 820.82, 768.59, 754.91, 728.65 cm^{-1}.



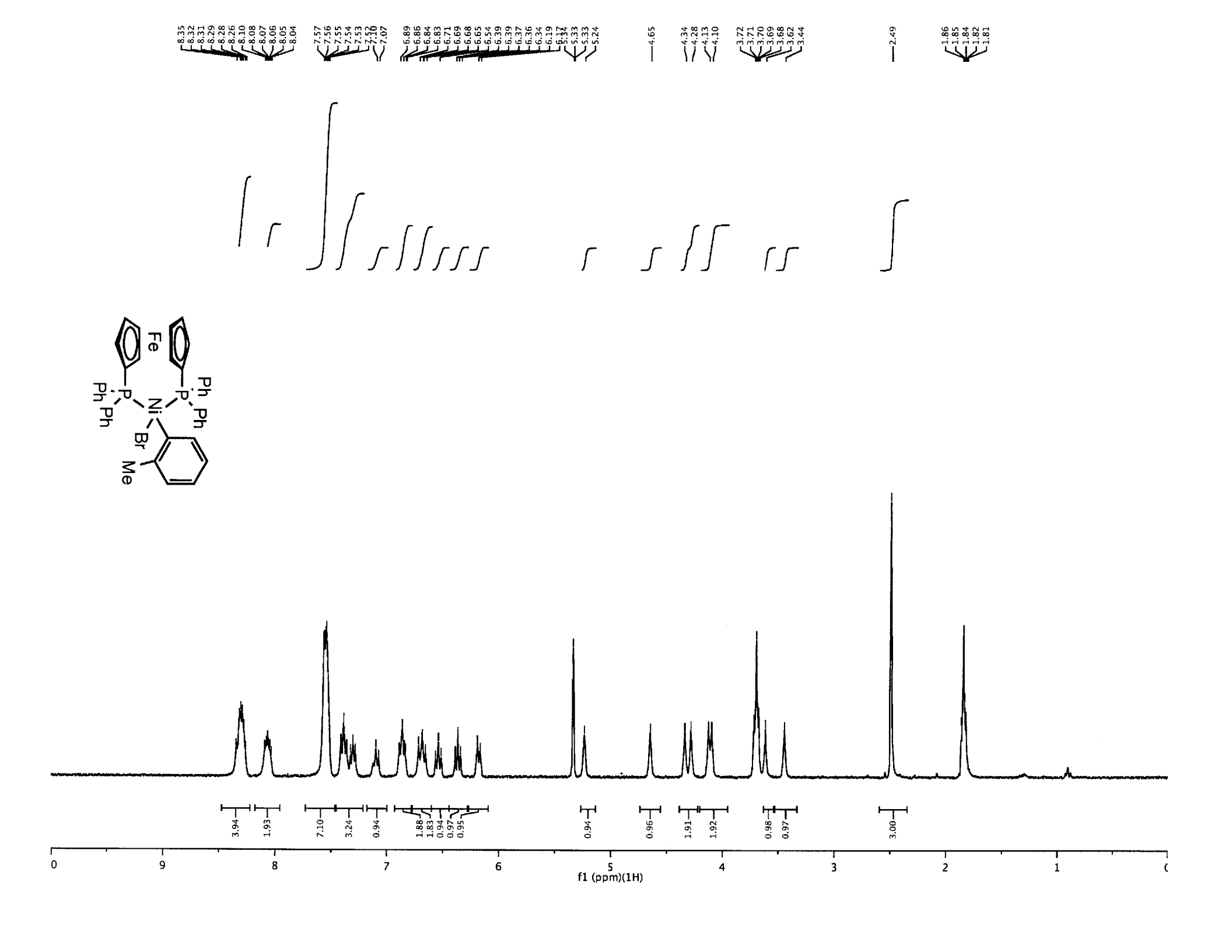
***N*-(4-(trifluoromethyl)phenyl)pyrimidin-5-amine**.[37] Following the general procedure, 1-chloro-4-(trifluoromethyl)benzene (180 mg, 1 mmol) was used along with 5-aminopyrimidine (140 mg, 1.5 mmol, 1.5 equiv.). Purification via column chromatography provided the title compound as a white solid (179.4 mg, 75% yield, 177-179 °C m.p.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.63 (s, 2H), 7.56 (d, J = 7.9 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 6.23 (s, 1H). ^{13}C NMR (126 MHz, CDCl3) δ 152.97, 147.57, 144.98, 137.60, 127.85 (q, J = 3.7 Hz), 124.85 (q, J = 271.6 Hz), 124.82 (q, J = 32.9 Hz), 117.36. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.08 .



Crystal Sructure Coordinates

Table 1. Crystal data and structure refinement for 12029.

Identification code	12029	
Empirical formula	C45 H43 Br Fe Ni O P2	
Formula weight	856.20	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.9477(17) Å	a= 90°.
	b = 20.815(3) Å	b= 117.886(2)°.
	c = 14.756(3) Å	g = 90°.
Volume	3786.7(9) $Å^3$	
Z	4	
Density (calculated)	1.502 Mg/m^3	
Absorption coefficient	2.055 mm^{-1}	
F(000)	1760	
Crystal size	0.20 x 0.15 x 0.10 mm^3	
Theta range for data collection	1.66 to 29.57°.	
Index ranges	-19<=h<=19, -28<=k<=28, -20<=l<=20	
Reflections collected	100890	
Independent reflections	10621 [R(int) = 0.0456]	
Completeness to theta = 29.57°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8209 and 0.6840	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10621 / 319 / 484	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0229, wR2 = 0.0535	
R indices (all data)	R1 = 0.0301, wR2 = 0.0566	
Largest diff. peak and hole	0.436 and -0.264 $e.Å^{-3}$	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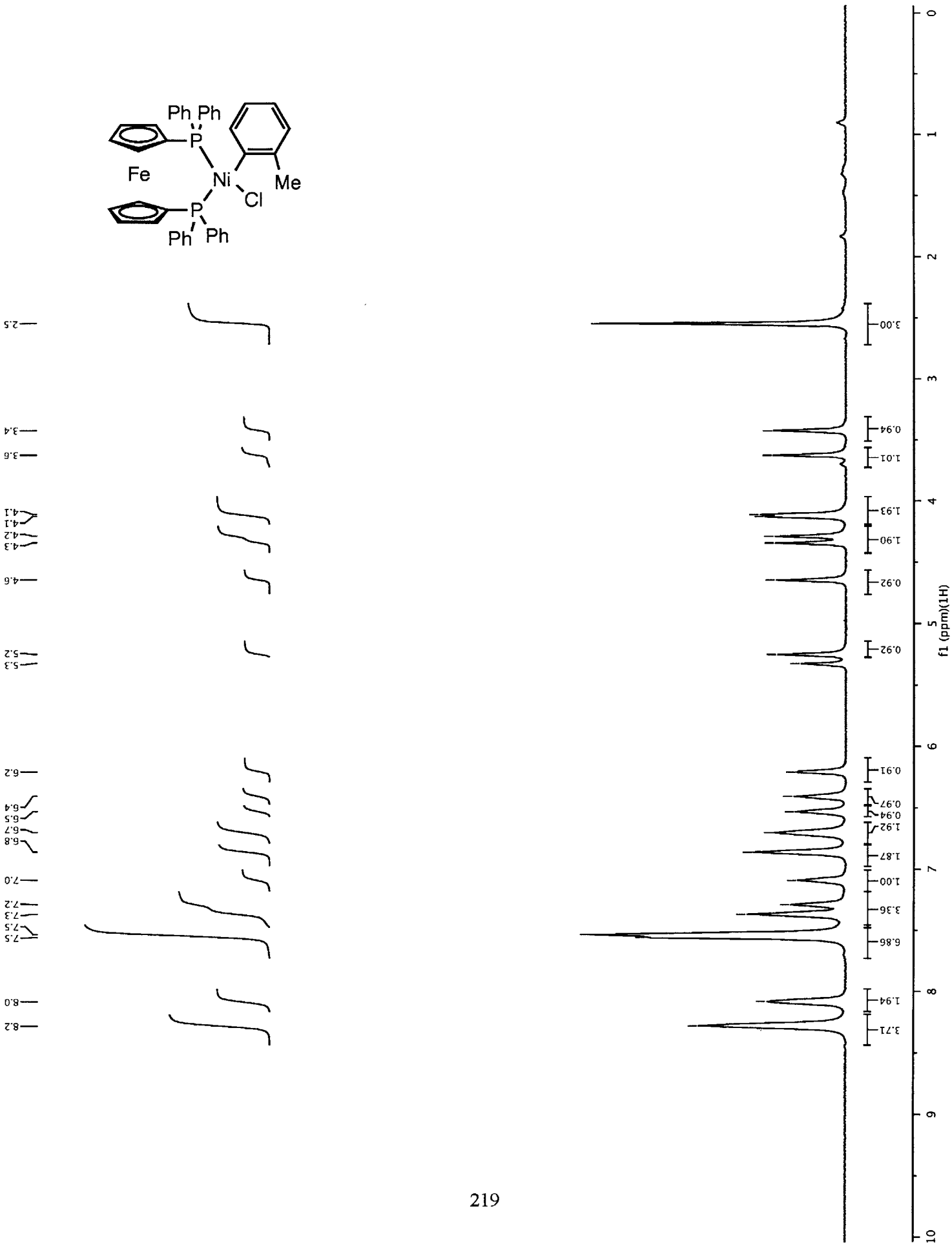
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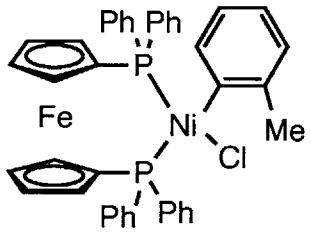
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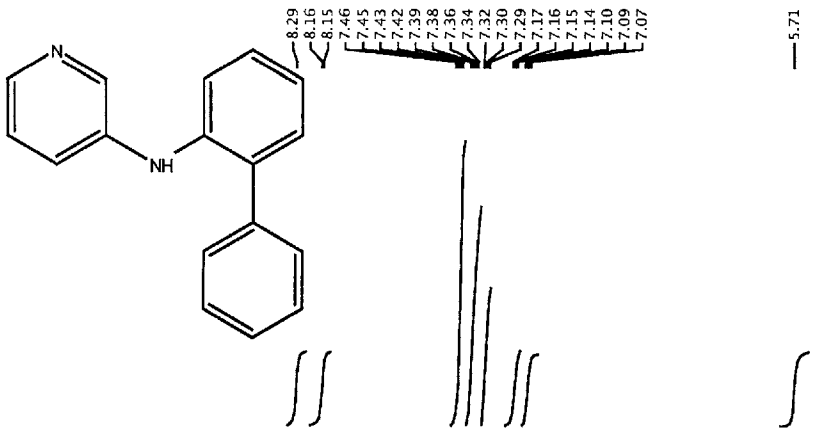
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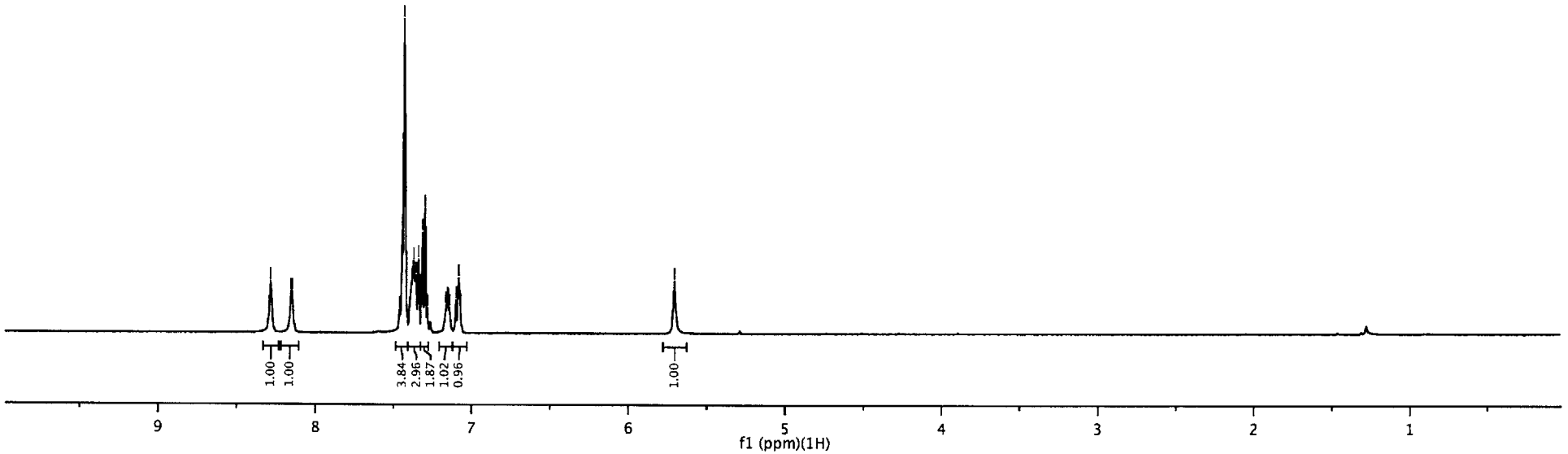
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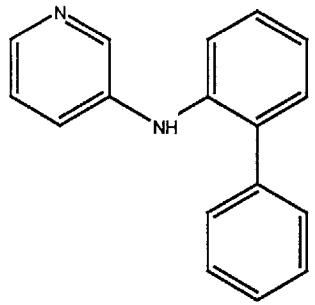

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222

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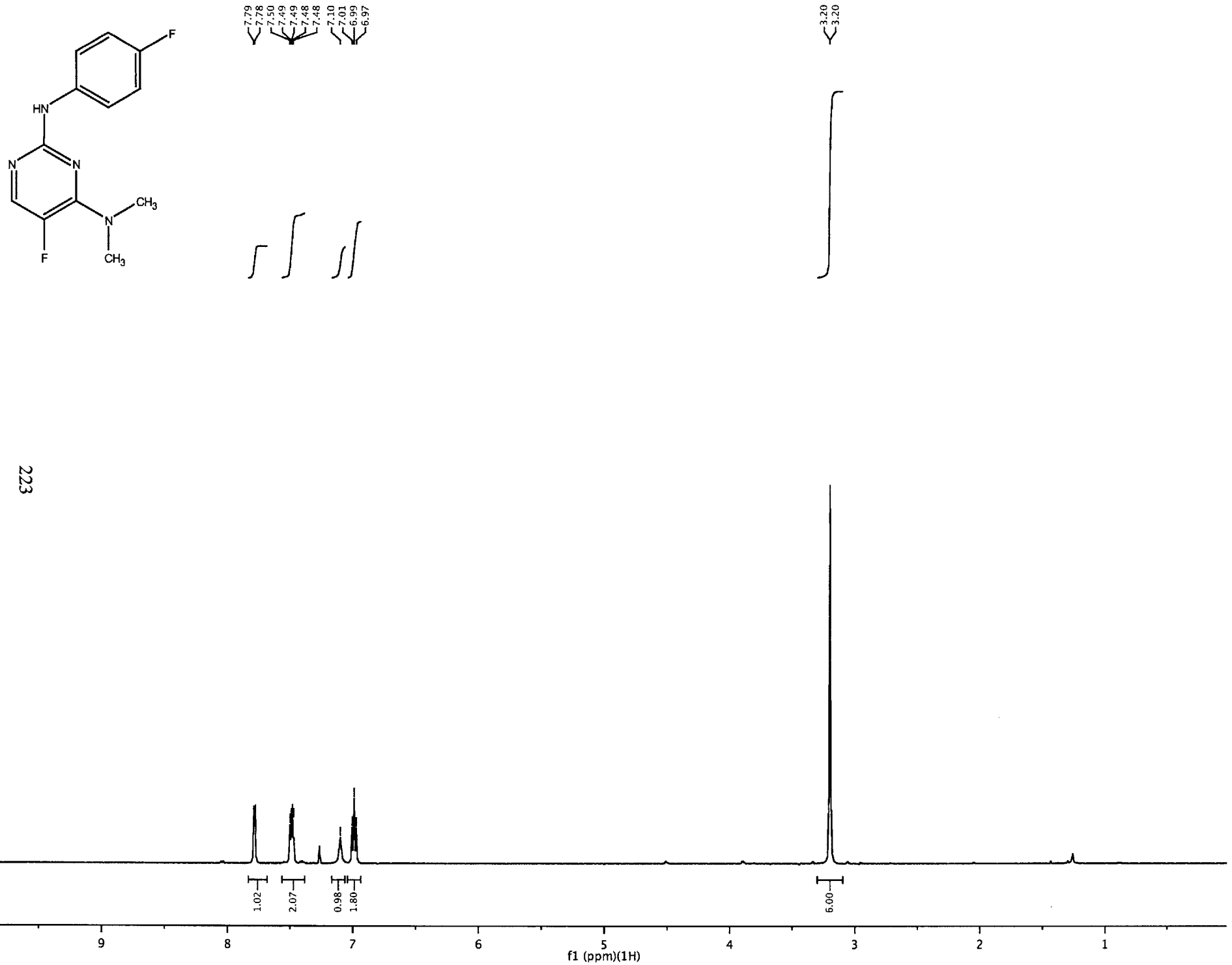
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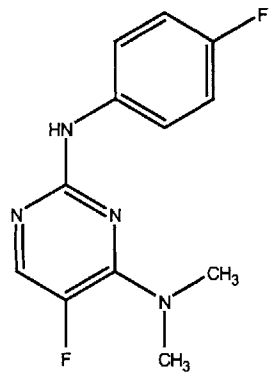
HN
N
N
CH3
N
F
CH3
7.79
7.78
7.50
7.49
7.49
7.48
7.48
7.10
7.01
6.99
6.97
3.20
3.20
1.02
2.07
0.98
1.80
6.00
9
8
7
6
5
4
3
2
1
f1 (ppm)(1H)



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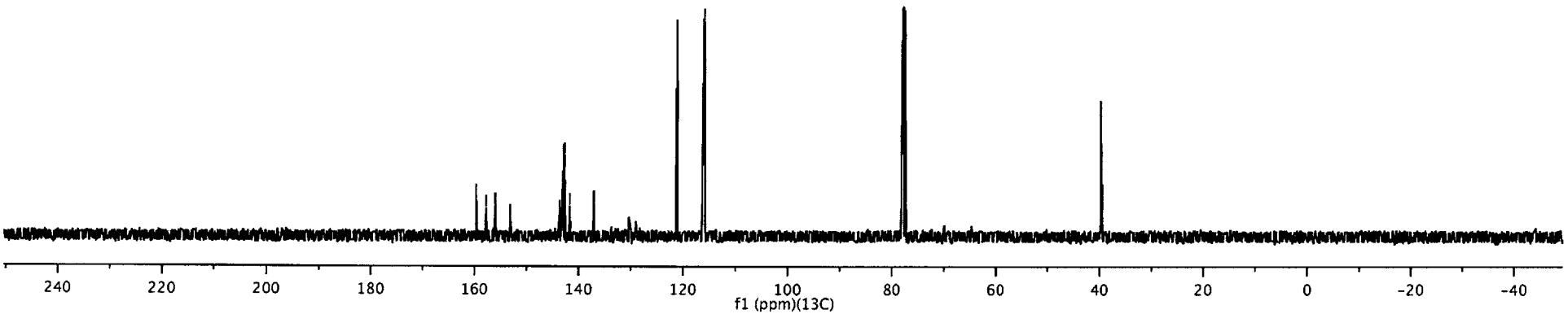
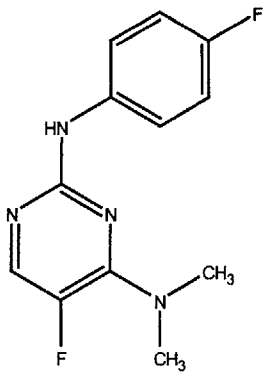
157.78
156.03
156.02
153.17
153.12
143.64
142.91
142.70
141.69
137.10
137.08
121.16
121.10
116.04
115.86
39.74
39.68




F
HN
N
N
CH3
N
F
CH3

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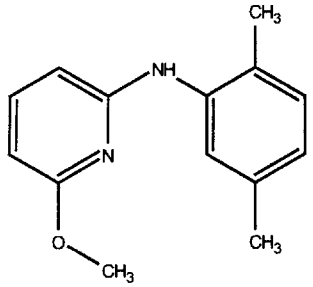
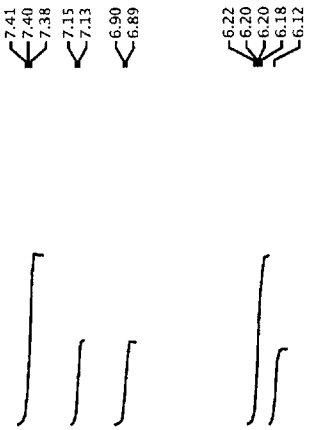
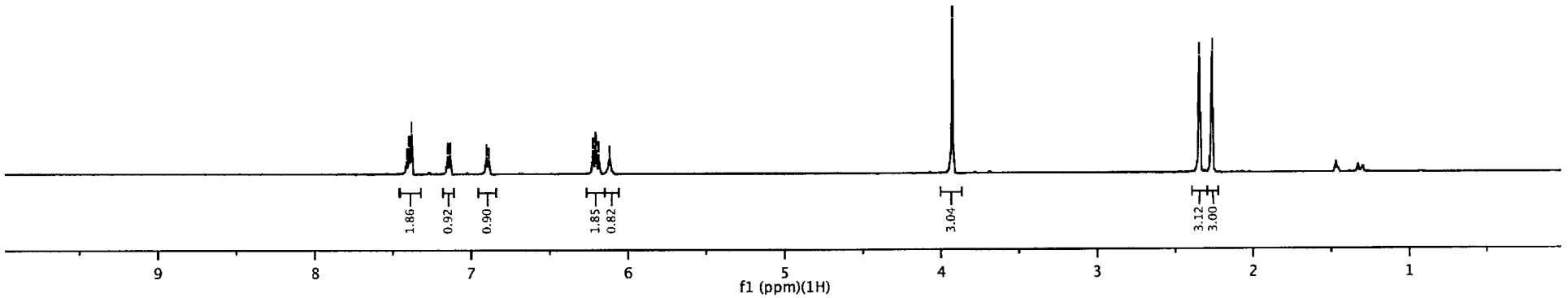
-122.00
-159.73
1.00
1.04
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)(19F)


CH3
NH
N
O
CH3
CH3


7.41
7.40
7.38
7.15
7.13
6.90
6.89
6.22
6.20
6.20
6.18
6.12
3.93
2.35
2.26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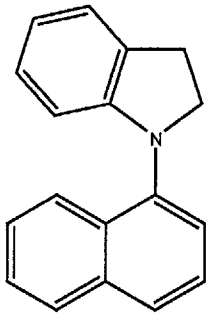
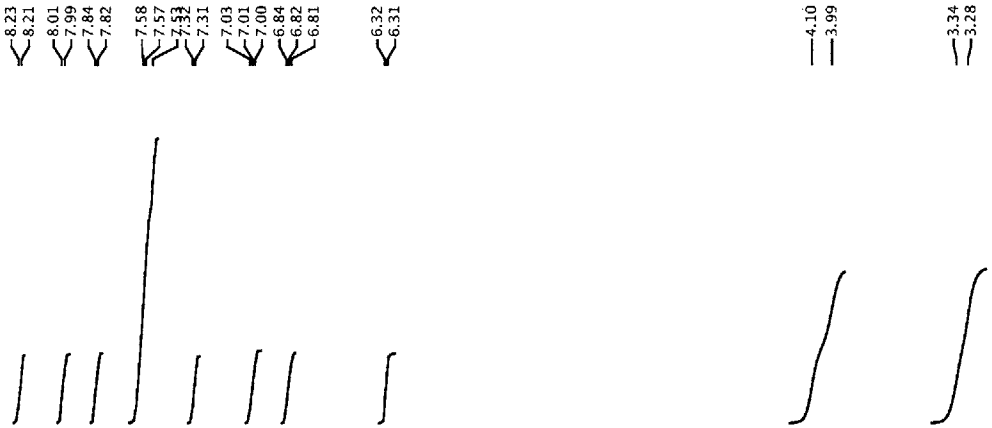
0.92
0.90
1.85
0.82
3.04
3.12
3.00
9
8
7
6
5
4
3
2
1
f1 (ppm)(1H)

164.41
156.07
140.91
139.12
137.08
131.40
128.24
125.43
124.05
100.18
99.70
54.07
21.87
18.30

227

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8.21
8.01
7.99
7.84
7.82
7.58
7.57
7.53
7.31
7.03
7.01
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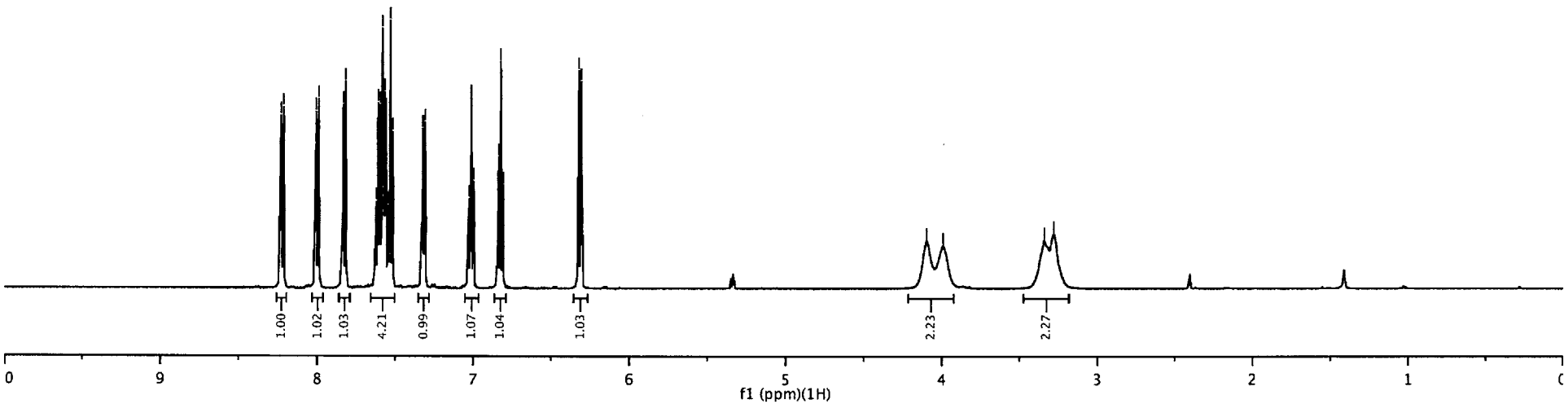
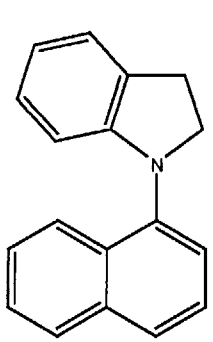
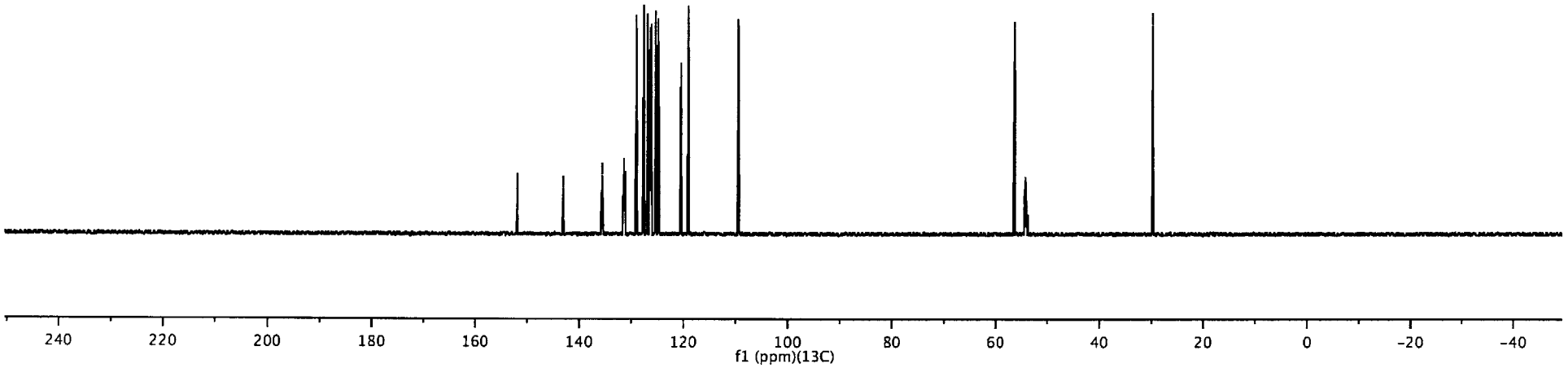
6.32
6.31
4.10
3.99
3.34
3.28


1.00
1.02
1.03
4.21
0.99
1.07
1.04
1.03
2.23
2.27
0
9
8
7
6
5
4
3
2
1
f1 (ppm)(1H)




151.94
143.10
131.44
129.10
127.67
126.98
126.94
126.44
126.23
125.42
124.90
120.52
56.33
29.75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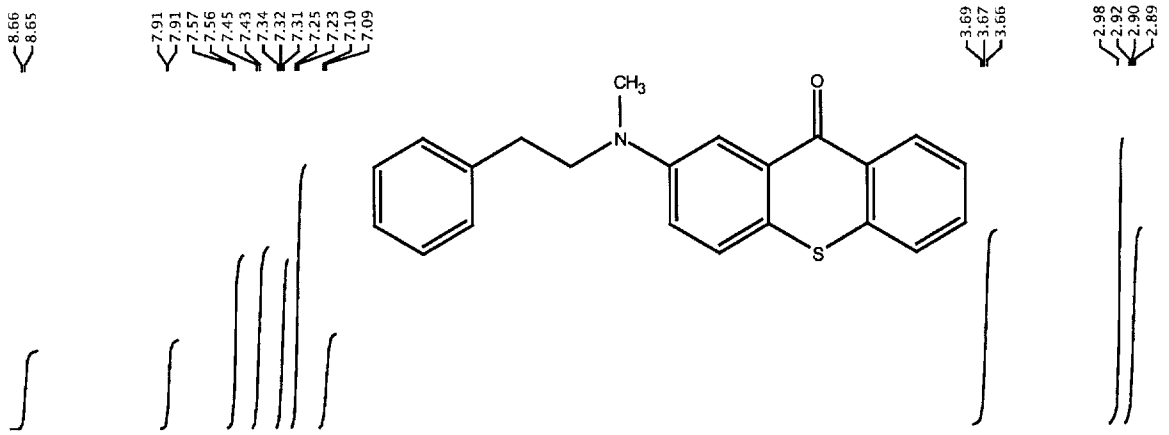
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)(13C)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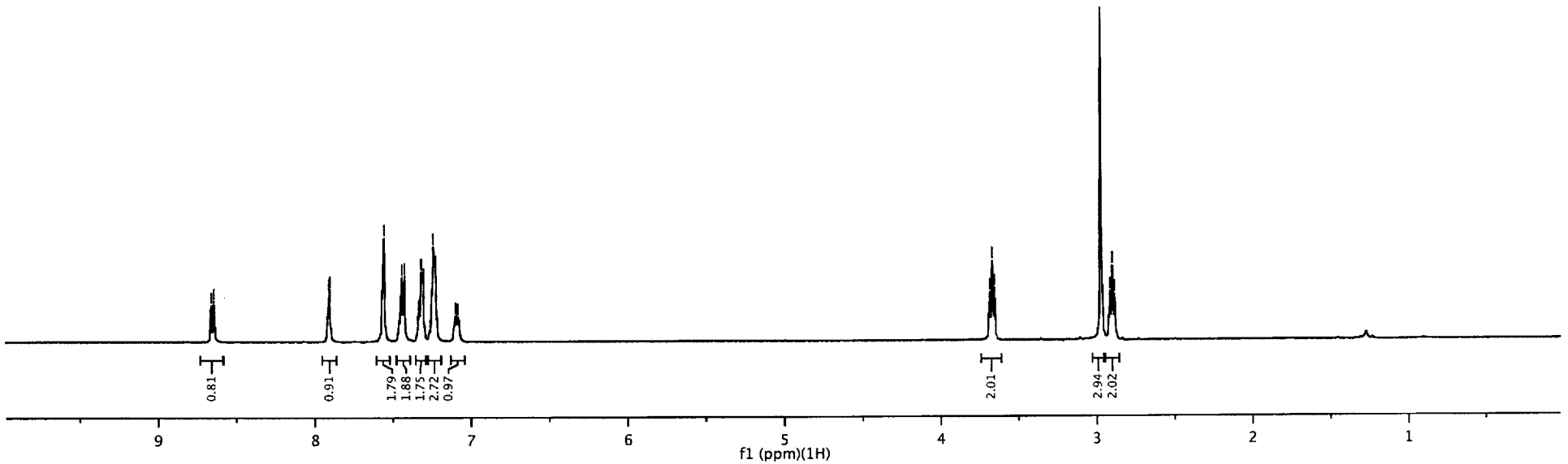
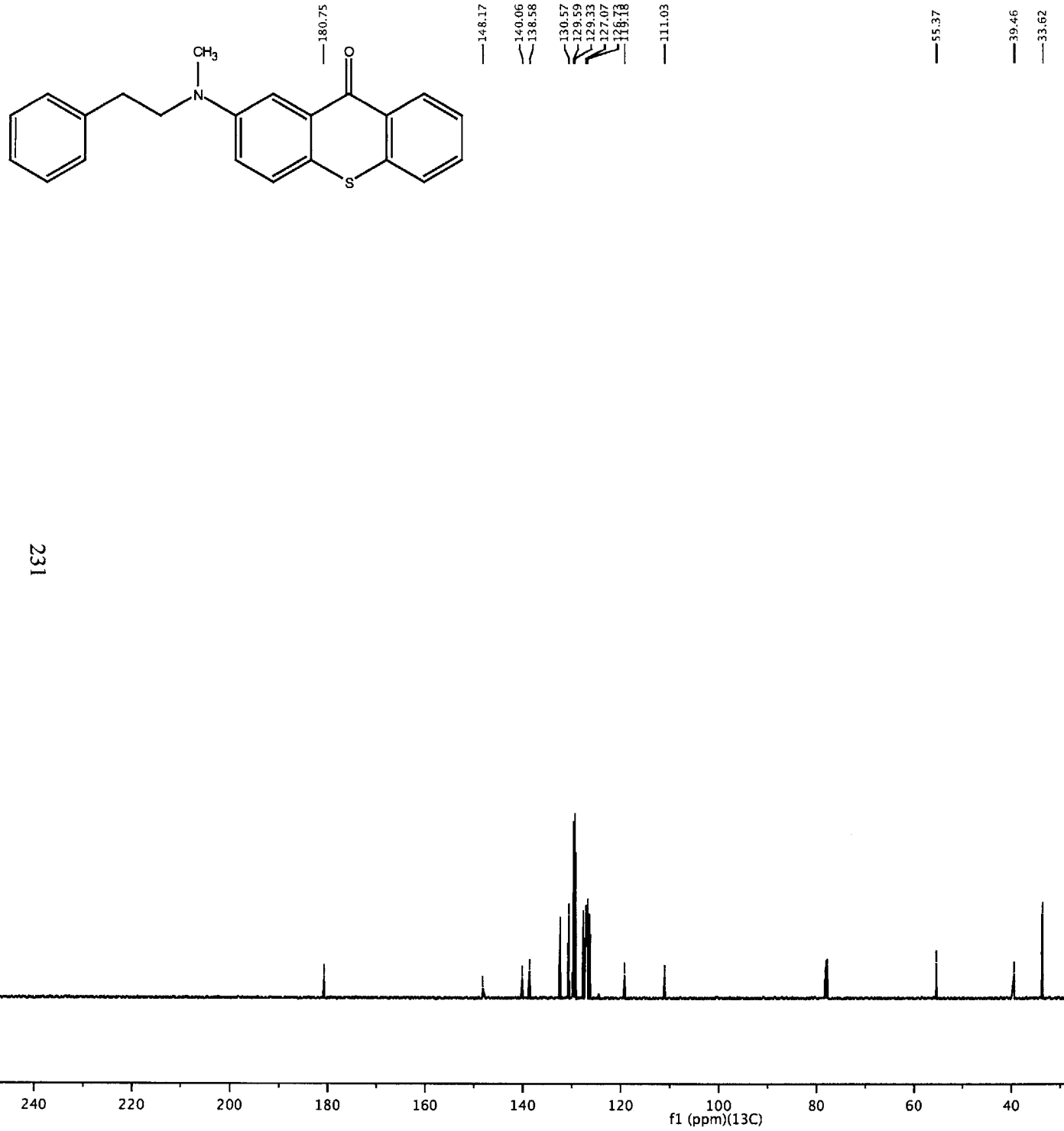
8.65
7.91
7.91
7.57
7.56
7.45
7.43
7.34
7.32
7.31
7.25
7.23
7.10
7.09
3.69
3.67
3.66
2.98
2.92
2.90
2.89
CH3
N
O
S


0.81
0.91
1.79
1.88
1.75
2.72
0.97
2.01
2.94
2.02
9
8
7
6
5
4
3
2
1
f1 (ppm)(1H)


CH3
N
O
S
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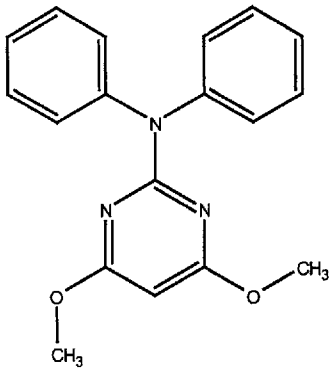
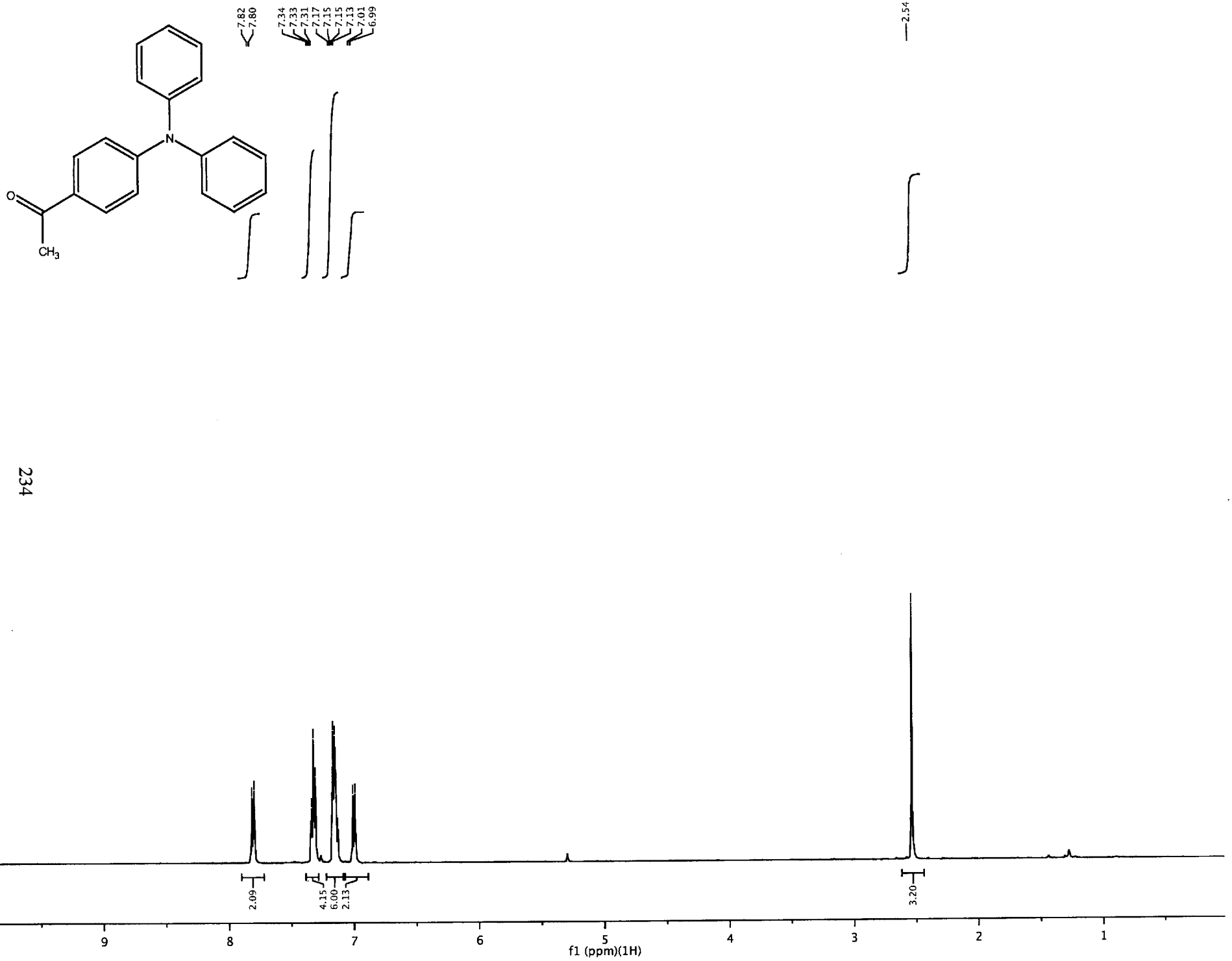
148.17
140.06
138.58
130.57
129.59
129.33
127.07
126.73
119.18
111.03
55.37
39.46
33.62
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)(13C)

7.43
7.42
7.40
7.39
7.27
7.25
7.24
5.64
3.72
N
N
N
O
CH3
O
CH3
7.71
1.97
0.87
6.00


N
N
N
O
CH3
O
CH3

172.43
161.44
145.49
129.30
128.54
125.91
81.64
54.22
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)(13C)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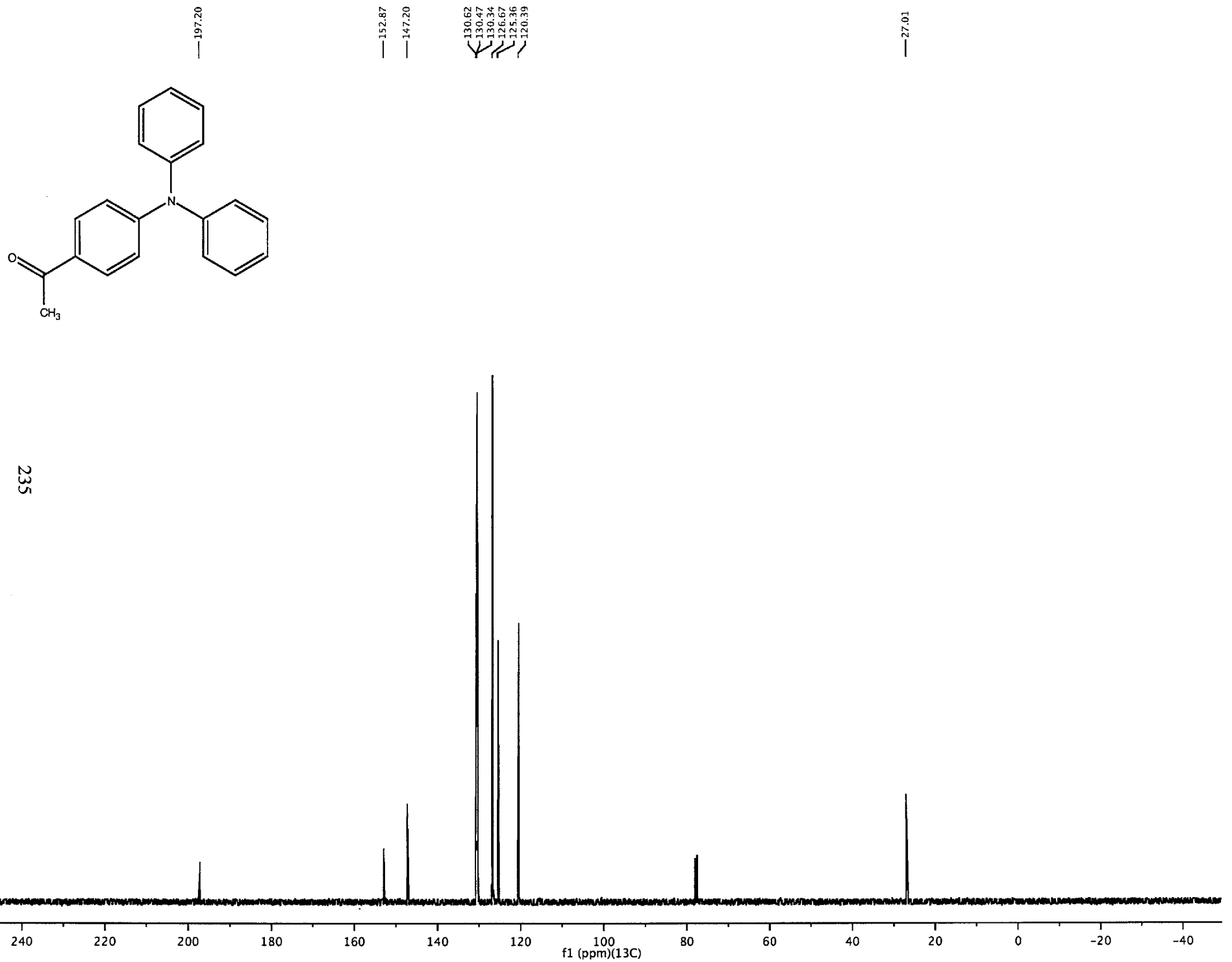
7.33
7.31
7.17
7.15
7.15
7.13
7.01
6.99
2.54
O
N
CH3
2.09
4.15
6.00
2.13
3.20
9
8
7
6
5
4
3
2
1
f1 (ppm)(1H)


197.20
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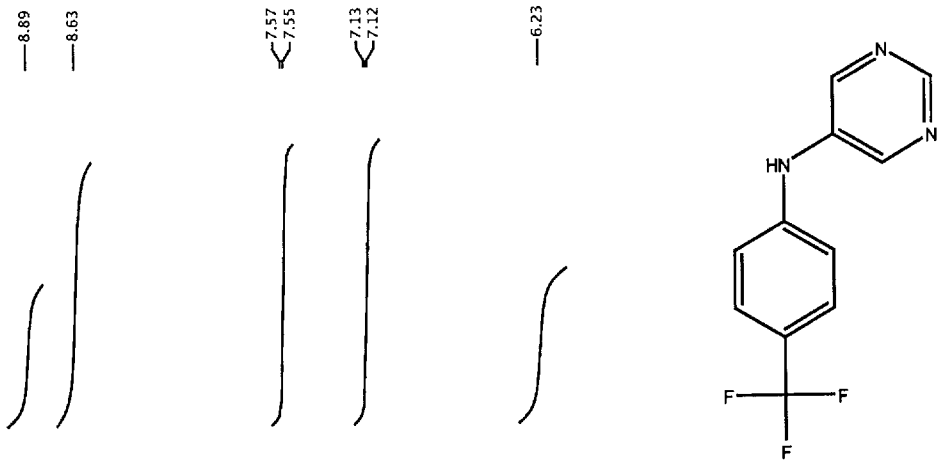
147.20
130.62
130.47
130.34
126.67
125.36
120.39
27.01
O
N
CH3
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)(13C)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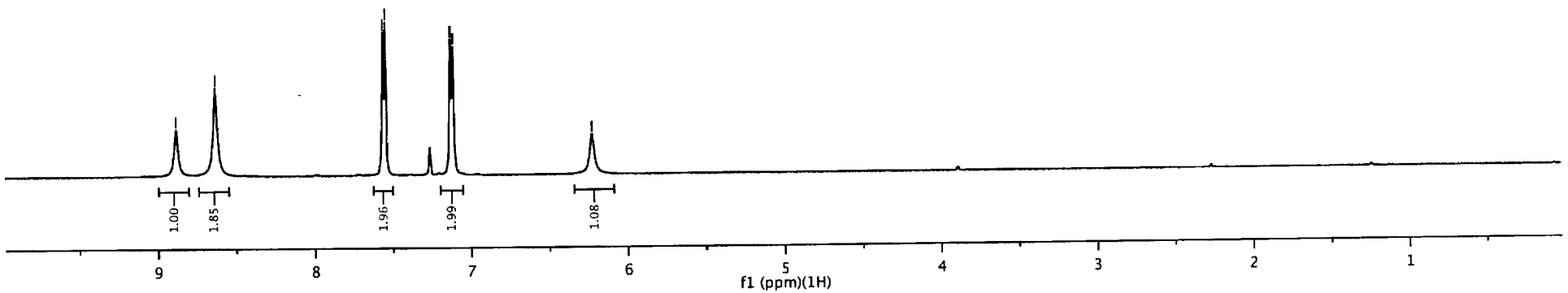
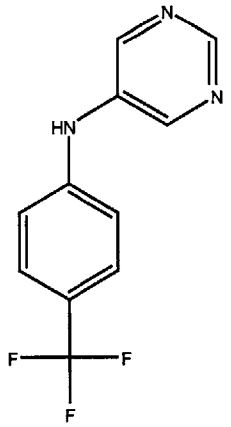
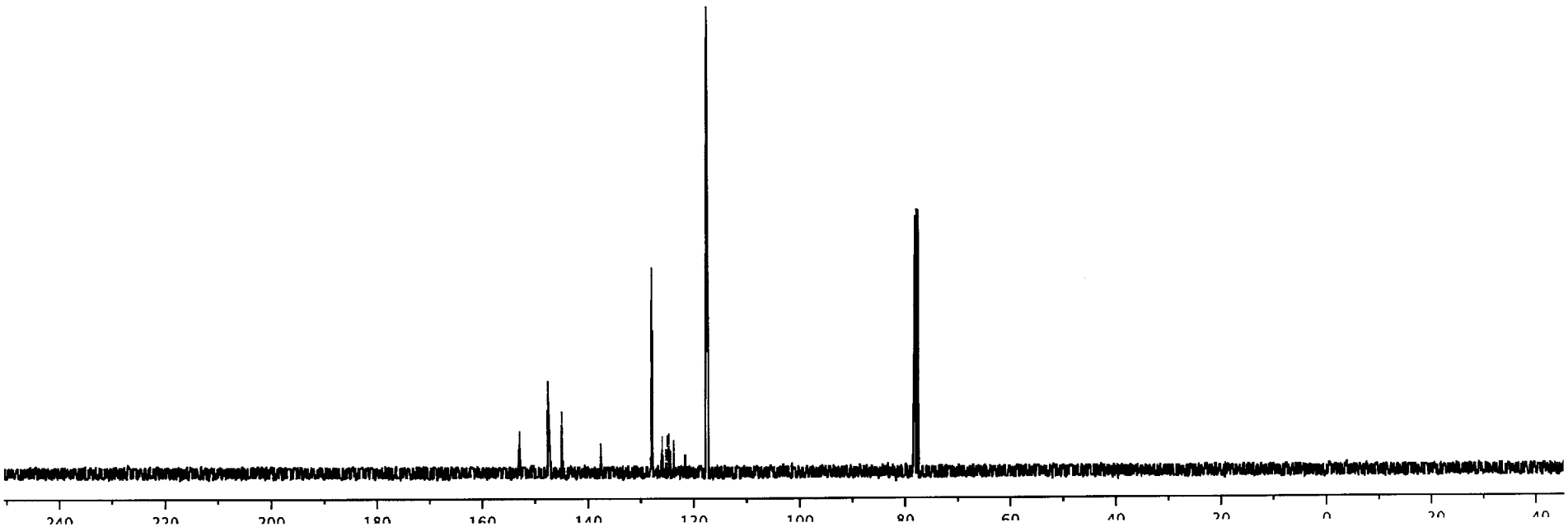
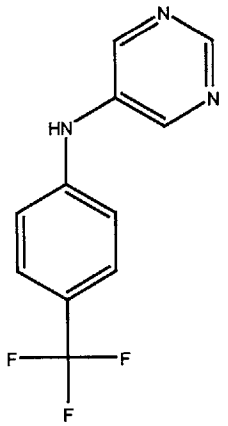
7.55
7.13
7.12
6.23
N
N
HN
F
F
F


1.00
1.85
1.96
1.99
1.08
9
8
7
6
5
4
3
2
1
f1 (ppm)(1H)



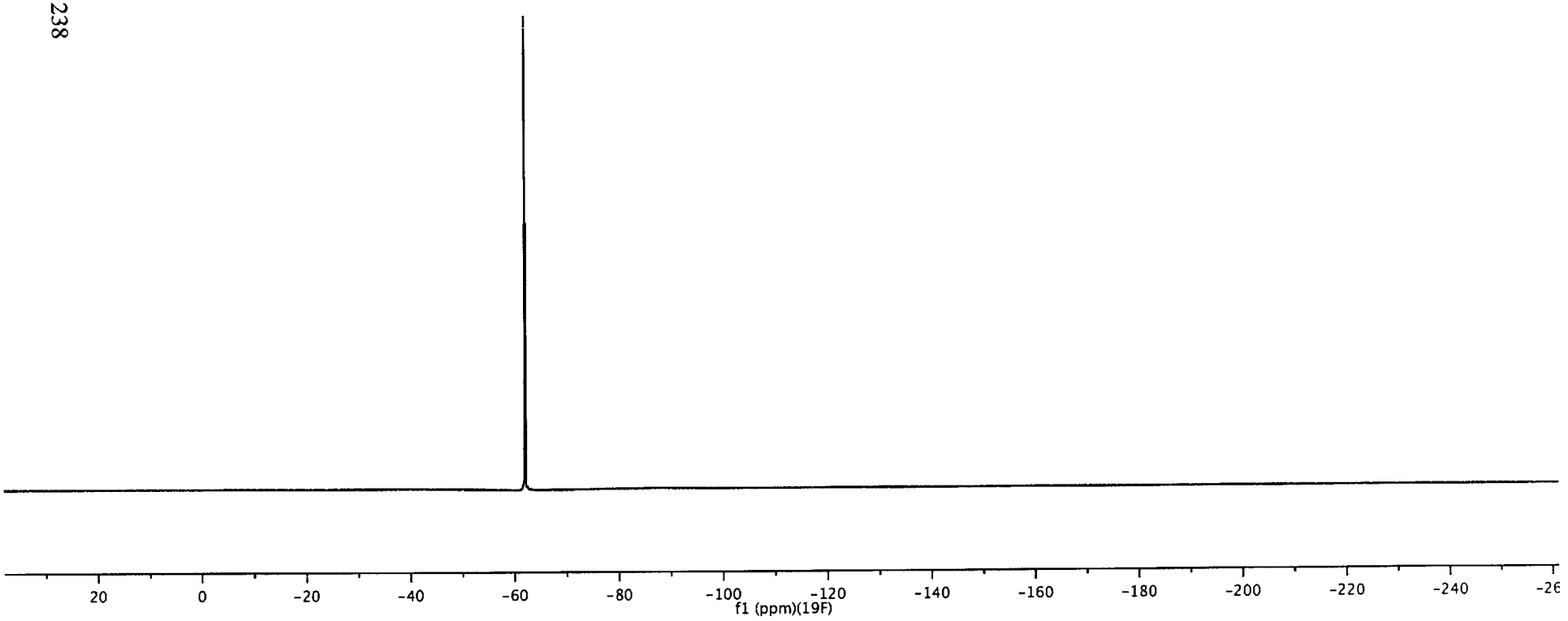
152.97
147.57
144.98
137.60
128.09
127.90
127.87
127.84
127.81
125.93
125.21
124.95
124.68
124.42
123.78
121.62
117.36




N
N
HN
F
F
F

-62.08

238


20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)(19F)

3.5: References

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Chapter 4: Development of a Novel Triptycene-Based Hole-Transport Material for Use in Triplet Emitters

4.1: Introduction

First developed in 1987 by Tang and Van Slyke[1] and later elaborated on by Forrest[2-6] and others,[7-13] thin film organic light emitting diodes (OLEDs) have gained prominence in both academic and applied settings.[14-15] OLEDs have become a ubiquitous feature of modern smart phones and are currently making inroads into television displays in the form of the LG Curved Display. OLEDs do not require a backlit surface and as such are capable of displaying perfect contrast ratios. Furthermore, they may be printed onto a diverse set of surface materials allowing for the production of flexible displays.

A typical OLED device is based on a stacked architecture (Figure 1).[16] In its simplest incarnation, an OLED stack consists of an indium tin oxide (ITO) coated glass surface, a hole-transport layer, an emission layer, an electron-transport layer and a cathode.[2] Variations on this stack have been developed by many groups to include hole blocking and electron blocking layers, as well as other layers to assist with charge injection and recombination.[14] Upon charge injection into the stack, holes and electrons recombine within the emissive layer to produce an excited state with a singlet (S_1) to triplet (T_1) ratio of 1:3. Radiative decay from a singlet state is called fluorescence and it is the most common type of radiative decay in organic molecules. Radiative decay from a triplet state is called phosphorescence and it is typically difficult to achieve in simple organic compounds at temperatures above 100 K. Furthermore, long-lived triplet states either self-annihilate to form a singlet or decay through other non-radiative pathways. As a result, early OLED designs utilizing fluorescent materials could only employ 25% of the resulting excited states.[17]

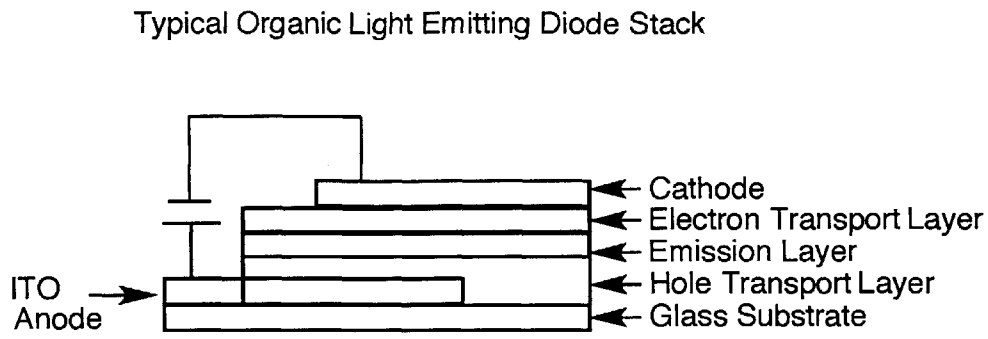


Figure 1. Graphical representation of a stacked OLED structure.

In 1998, the Forrest and Thompson groups reported the first use of an electrophosphorescent material in an OLED device (PHOLED).[2] In 1999, the same researchers reported the use of $Ir(ppy)_3$ in the emissive layer to achieve internal quantum efficiencies for green OLED devices of nearly 100% (Figure 2).[5] In transition metal complexes there is a strong spin-orbit coupling such that the triplet state attains singlet character at the metal center allowing for facile triplet emission.[18] As a result, efficient phosphorescence may be achieved from the triplet state of these complexes.[6]

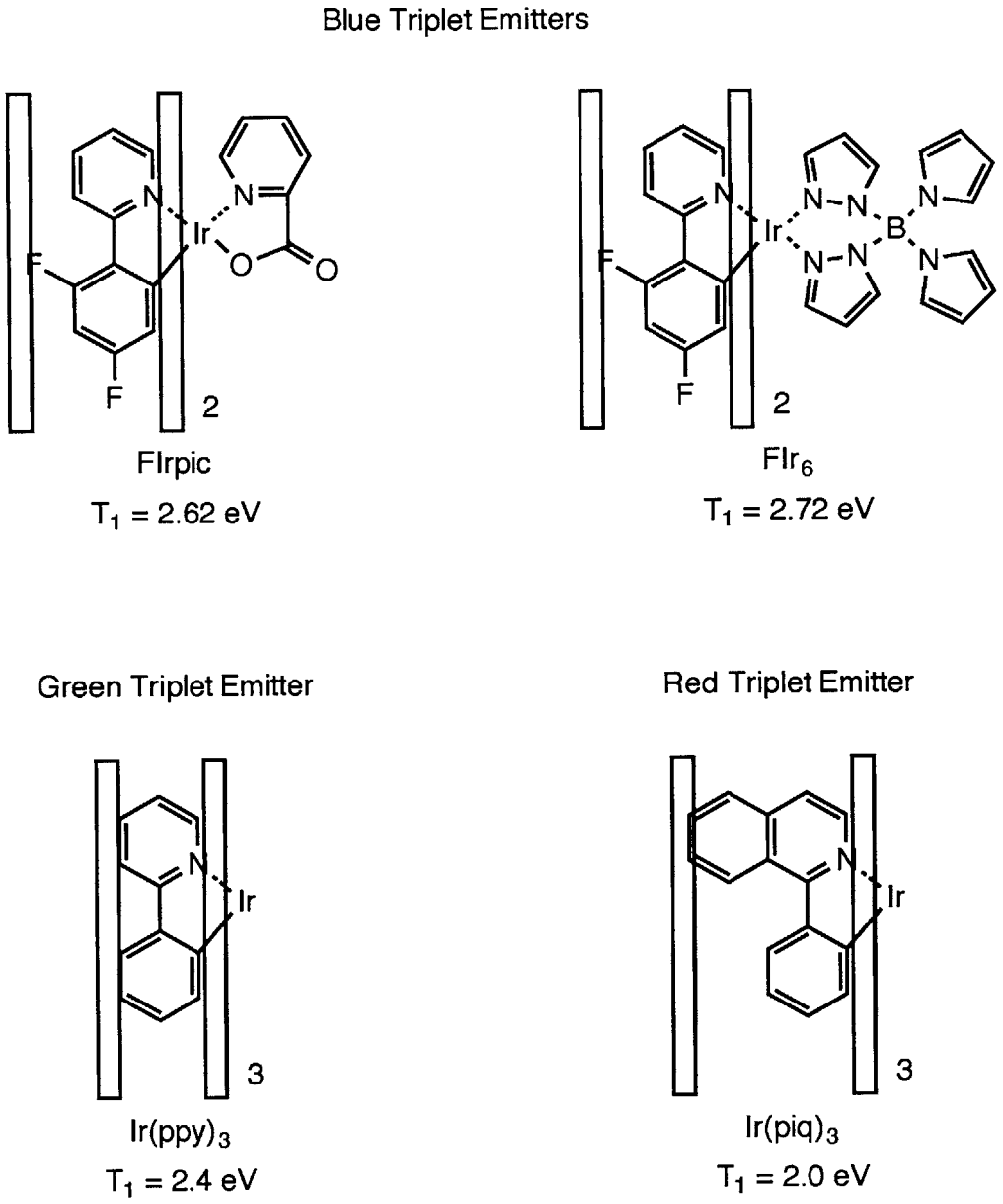
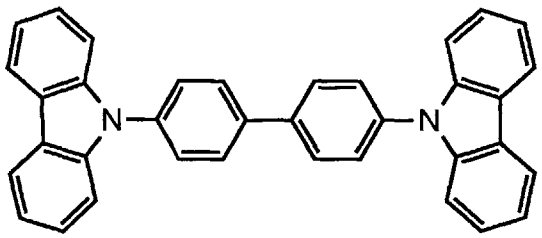


Figure 2. Commonly employed blue, green and red triplet emitters.

The advent of triplet emitters has necessitated the development of myriad hole-transport materials that may act as suitable hosts for the emitter.[14,19-20] Due to emission from the triplet state of the guest molecule, a high lying triplet state has become a prerequisite for the host layer.[21] This is typically achieved by employing compounds containing either carbazole[22] or

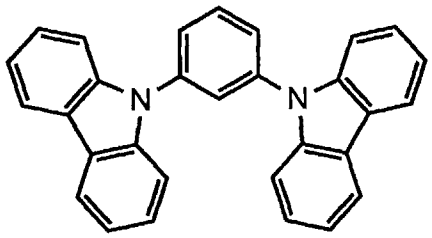
silane[23] moieties (Figure 2). Some of the earliest such compounds are CBP, mCP and UGH2 which exhibit high lying triplet states of 2.6 eV,[5] 2.9 eV[21] and 3.5 eV[23] respectively.



CBP

T_1 = 2.6 eV

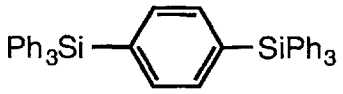
T_g = 62 °C



mCP

T_1 = 2.9 eV

T_g = 60 °C



UGH2

T_1 = 3.5 eV

T_g = none

Figure 3. Early hole-transport host materials for triplet emitters.

While CBP has proven to be an effective host material for red and green triplet emitters, it is inefficient for blue emitters. Since the triplet state of CBP is lower than that of a typical blue triplet emitter, such as FIr_6 (2.6 eV vs. 2.72 eV), CBP acts as a thermodynamic sink, preventing localization of the excited triplet states onto the Ir complex.[21] In such cases, mCP and UGH2

may be employed as they exhibit higher energy triplet states relative to the emitter. Attempts have been made to increase the T_1 energy level of CBP and other carbazole derivatives.[22,24] While CBP and mCP are effective host materials, they exhibit low glass transition temperatures (T_g) and high degrees of crystallinity.[14,25] Furthermore, the UGH family of compounds displays poor charge transport properties limiting the efficiency of charge recombination within the emitter.[26] As a possible solution, Cheng proposed the use of triptycene as the backbone for a series of non-crystalline host materials with high lying triplet states and good charge transfer properties (Figure 3).[27]

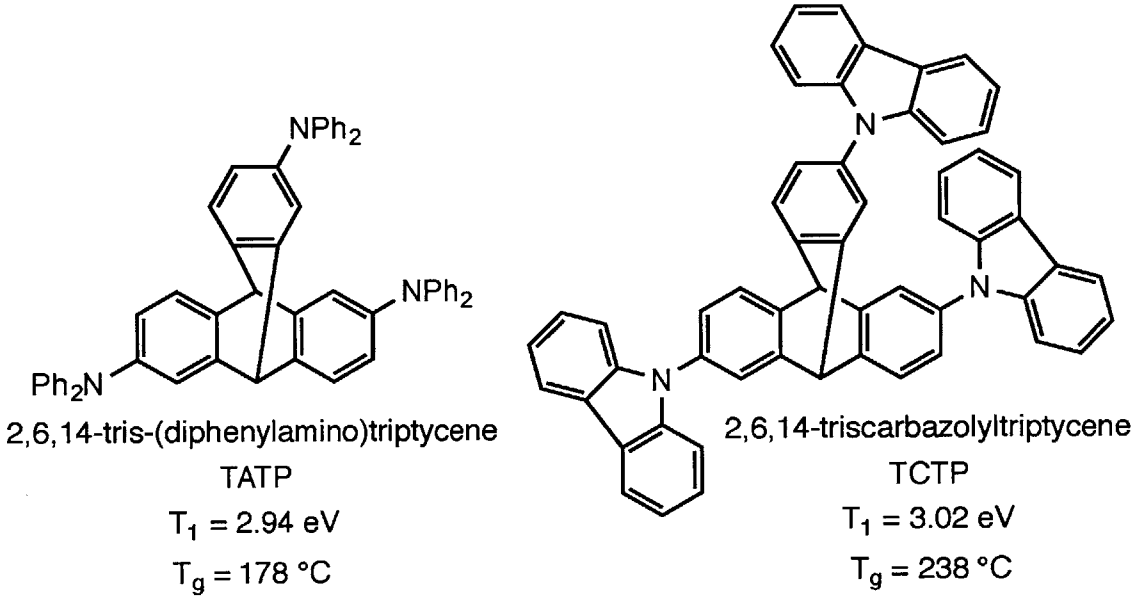
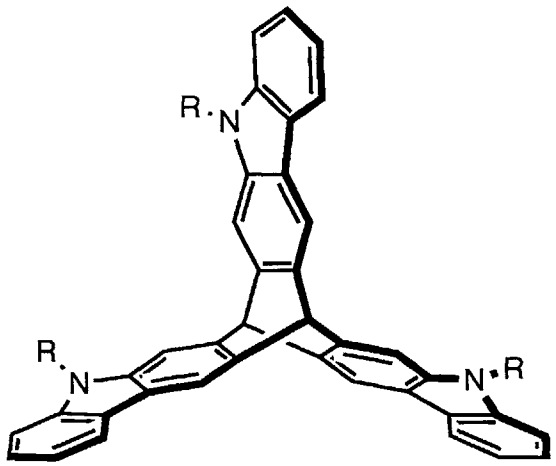


Figure 4. First use of triptycene-based hole-transport host materials.

4.2: Results and Discussion

Intrigued by the idea of utilizing a three-dimensional core in the synthesis of a host material, we proposed the development of a novel core structure incorporating both the unique structural

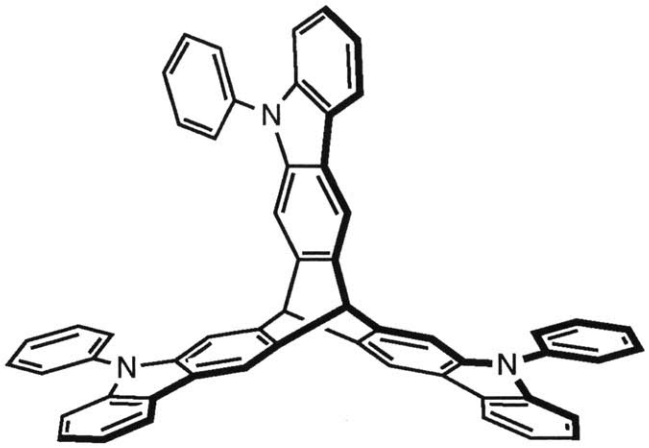
properties of triptycene and the electronic properties of carbazole. This core, (7s,15r)-5,7,13,15-tetrahydro-7,15-[2,3]epicarbazolobenzo[1,2-b:4,5-b']dicarbazole (TTC), may be rapidly elaborated upon in order to obtain the desired electronic and physical properties of the bulk material (Figure 5).



TTC

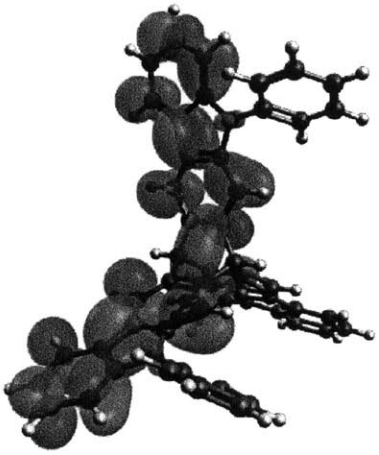
Figure 5. Proposed TTC core structure.

DFT calculations utilizing the B3LYP functional at the 6-31g(d) level of theory for all atoms indicate that the HOMO level of these compounds remains localized on all three wings of the central core, while the LUMO may be delocalized throughout the molecule or localized on the R groups depending on the electron –withdrawing or –donating nature of R (Figure 6, where R=Ph). As a result, the overall electronic properties of the material may be systematically tuned by modification of the R substituents.



TTC-Ph

HOMO

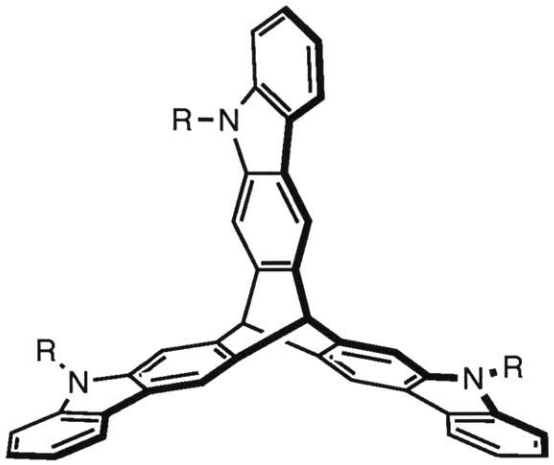


LUMO

Figure 6. Kohn-Sham graphical respresentation of the HOMO and LUMO levels in TTC-Ph.[28]

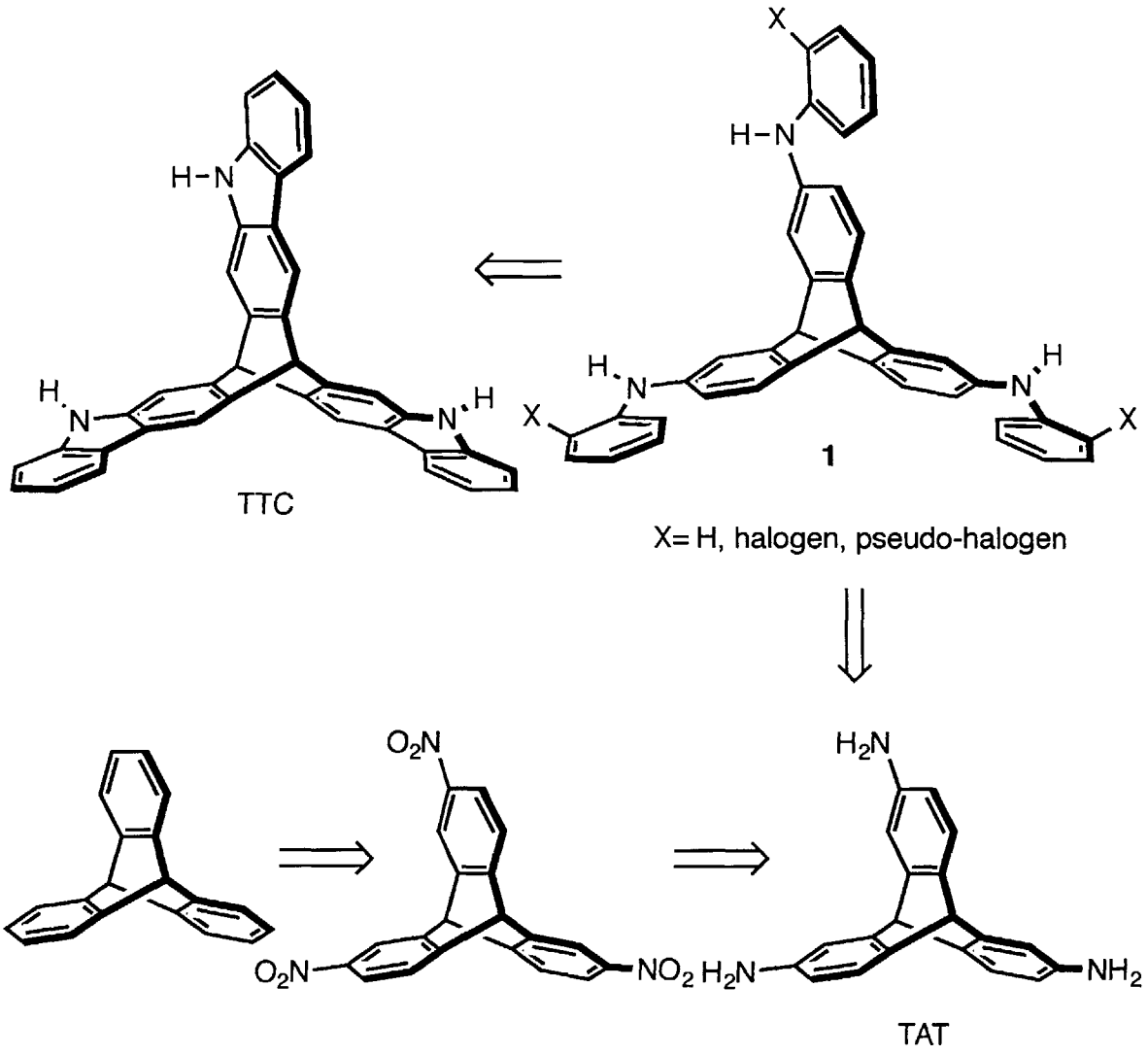
Computational evidence further suggests that HOMO/LUMO transition energies of 1.91-3.37 eV may be attained through careful selection of the R group substituents. Furthermore, the singlet and triplet energies may also be tuned to the desired values such that the triplet state would be sufficiently high to accommodate blue triplet emitters (Table 1). Finally, due to the three-dimensional structure inherent to all TTC derived materials, we anticipate very few, if any, derivatives to be crystalline solids.

Table 1. Computational analysis of the electronic properties of several proposed TTC derived structures.



Entry	R=	HOMO (eV)	LUMO (eV)	ΔE	S_1 (eV)	T_1 (eV)
1	Ph	-5.47	-2.15	3.27	3.32	3.05
2	*p*-Tol	-5.45	-2.15	3.30	3.30	3.05
3	4-PhNMe$_2$	-5.36	-1.99	3.37	3.27	3.05
4	4-PhOCF$_3$	-5.58	-2.45	3.13	3.33	3.05
5	4-PhSCF$_3$	-5.61	-2.78	2.83	3.19	3.04
6	4-PhSF$_5$	-5.69	-3.78	1.91	3.18	3.04
7	4-PhSO$_3$CF$_3$	-5.70	-3.26	2.45	3.05	2.96
8	C$_6$F$_5$	-5.66	-2.85	2.80	3.30	3.04
9	CBP	-5.50	-2.59	2.91	3.44	2.94
10	mCP	-5.52	-2.31	3.21	3.33	3.05
11	4-Ph-NPh$_2$	-5.42	-2.15	3.27	3.32	3.02
12	4-pyr	-5.58	-2.45	3.13	3.38	3.05

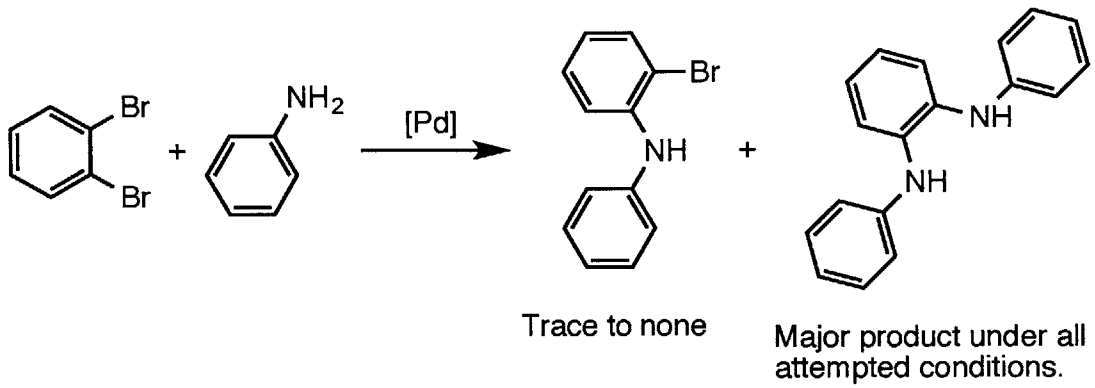
A retrosynthetic analysis of the core structure indicated a clear avenue toward the synthesis of the TTC core. The central core may be constructed via tandem triple C–H activation from intermediate **1**, wherein **1** contains either a halide or pseudo halide positioned *ortho* to the nitrogen. Intermediate **1** may be constructed via arylation of triaminotriptycene (TAT), which in turn may be readily synthesized via nitration and reduction of triptycene (Scheme 1).[29]



Scheme 1. Retrosynthetic analysis of TTC.

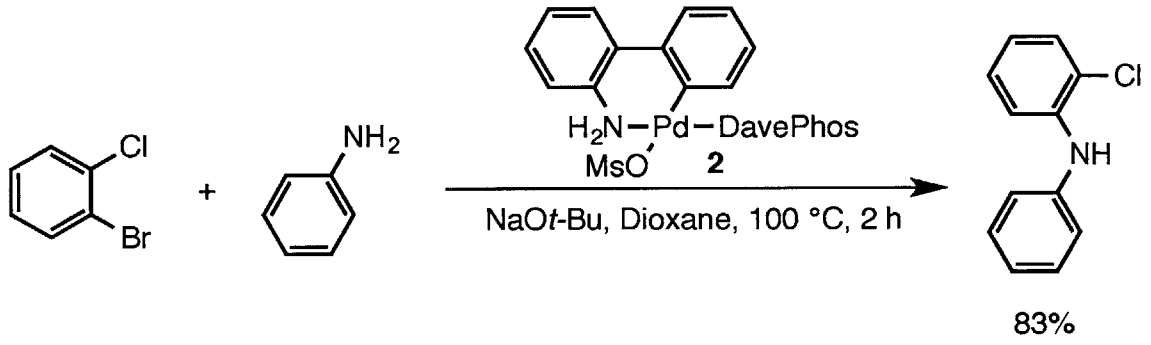
We began by examining the feasibility of synthesizing **1** utilizing a model system. Previous reports from Bedford[30-31] and Fagnou[32-33] suggested that ring-closing C–H activation to form carbazoles is greatly accelerated when the *ortho* halide is bromide rather than chloride; as such, we attempted to prepare a model compound for **1** utilizing an *ortho* bromide substrate (Scheme

2). However, despite examination of multiple reaction conditions and catalytic systems,[34] the major product observed in all cases was diamination of 1,2-dibromobenzene.



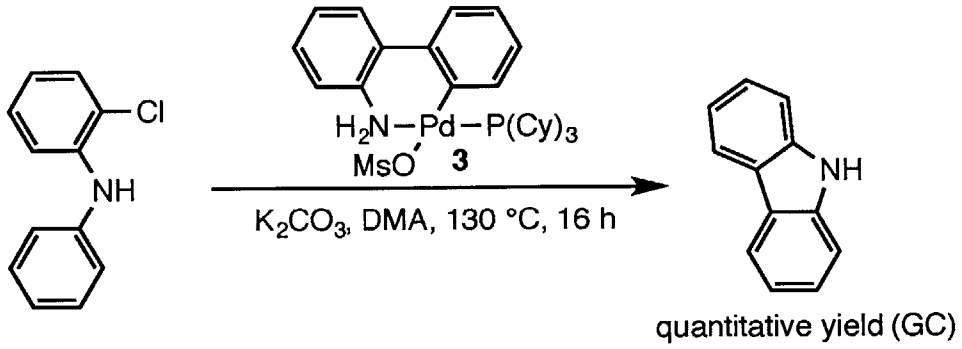
Scheme 2. The attempted use of 1,2-dibromobenzene in a model system toward the synthesis of **1**.

In light of these results, we elected to employ 1-bromo-2-chlorobenzene in order to prevent the formation of the diamine product (Scheme 3). Evaluation of a range of reaction conditions lead us to employ catalytic quantities of **2** in the presence of aniline and 1-bromo-2-chlorobenzene to produce 83% of the desired product and only trace amounts of diamination.



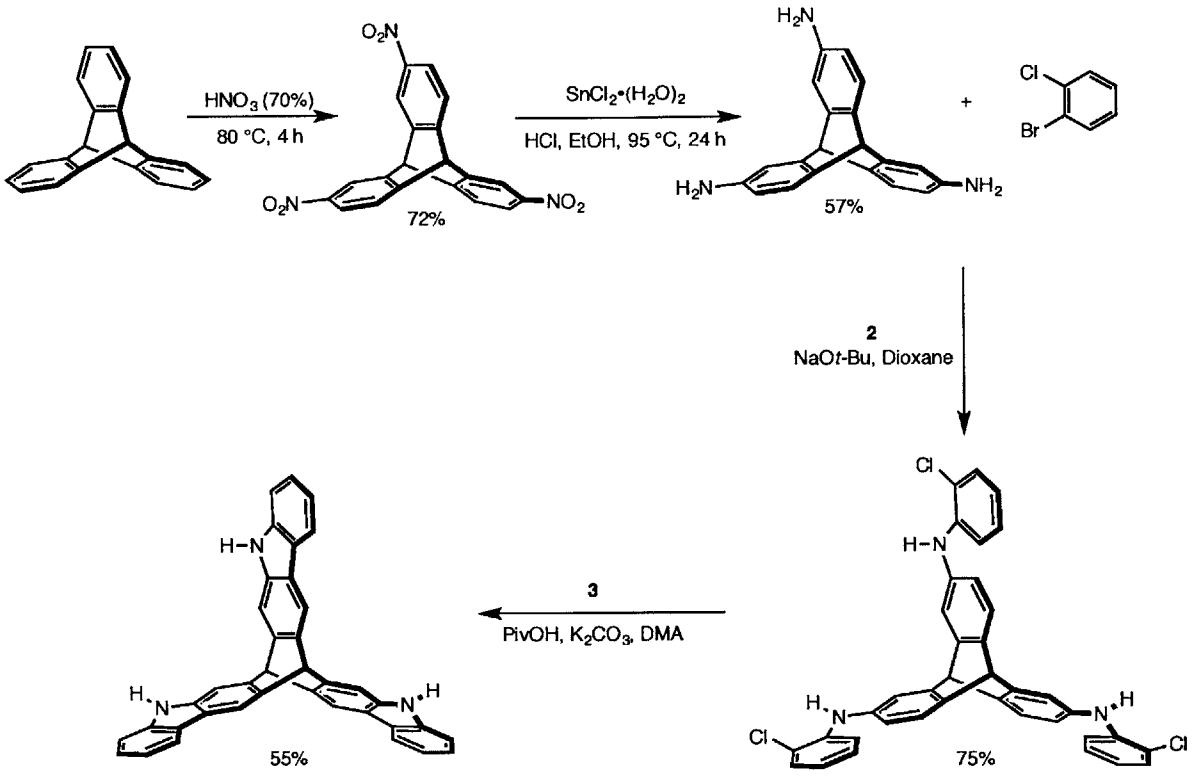
Scheme 3. The use of 1-bromo-2-chlorobenzene in a model system toward the synthesis of **1**.

With the optimized conditions for the synthesis of **1** realized, we explored the synthesis of the final carbazole product. Employing a modified version of the conditions developed by Fagnou toward the synthesis of carbazoles, we were successful in obtaining quantitative yields of the desired product (Scheme 4).[33]



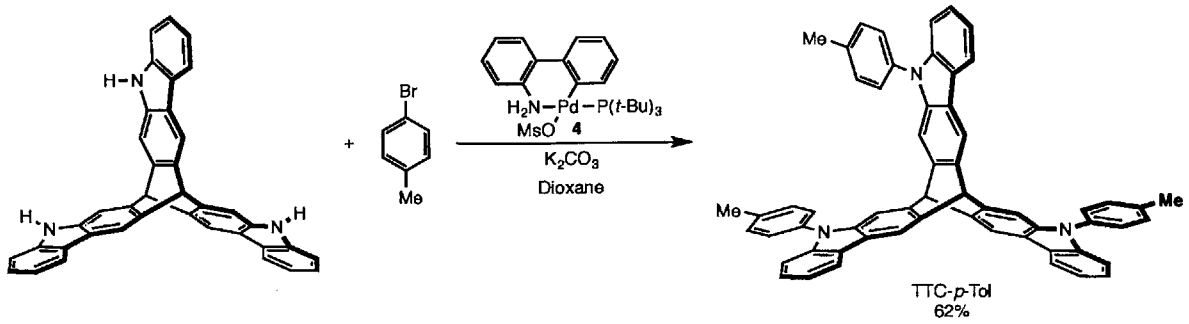
Scheme 4. Cyclization of model substrate toward the synthesis of the TTC core.

Having demonstrated the feasibility of the synthetic route in our model system, we endeavored to apply these conditions toward the synthesis of TTC and its derivatives. Utilizing previously reported reaction conditions, we were able to obtain 2,6,14-trinitrotrypticene in 76% yield starting from triptycene.[29] Reduction with $SnCl_2$ under acidic conditions resulted in clean formation of 2,6,14-triaminotriptycene in 57% yield with no chromatographic purification required.[35] Arylation of TAT under our previously optimized conditions in the presence of 1-bromo-2-chlorobenzene provided **1** in 75% yield on multigram scale. Finally, in the presence of catalytic quantities of **3**, PivOH and finely ground K_2CO_3, we were successful in obtaining TTC in 55% yield.



Scheme 5. Synthesis of TTC core.

Having synthesized the TTC core, we next attempted to perform N-arylation to generate the desired class of TTC derivatives. In the presence of 4-bromotoluene, finely ground K_2CO_3 and catalytic amounts of **4** we successfully obtained TTC-*p*-Tol in 62% yield and >99% purity. The final compound did not exhibit a melting point up to 400 °C and appeared to be an amorphous solid.



Scheme 6. Arylation of TTC toward the 1st generation of TTC derived hole-transport host material: TTC-*p*-Tol.

Having obtained the desired compound, we began to explore its physical properties in order to determine whether a) they conform to predicted values and b) whether they would indicate that the compound could be a good hole-transport material. We began by evaluating the photophysical properties of TTC-*p*-Tol. Dr. Derik K. Frantz, of the Swager Group, was able to obtain all of the relevant measurements such as molar absorptivity, fluorescence and phosphorescence spectra as well as the cyclic voltammetry data for determination of the HOMO/LUMO energy levels and band gaps.

One of the most important aspects of developing novel hole-transport materials to serve as hosts for blue triplet emitters is ensuring a triplet energy level of greater than 2.9 eV. Theoretical predictions (*vide supra*) indicate that the TTC family of compounds has the potential for high lying triplet states. In solution, TTC-*p*-Tol displays a maximum absorbance peak at 313 nm and fluorescence maxima at 357 nm and 374 nm. This corresponds to an $S_1 \rightarrow S_0$ transition of 3.47 eV (Figure 7).[27] The quantum yield (Φ_F) was determined to be 0.29. A low quantum yield may be explained by the very small Stoke's shift observed for TTC-*p*-Tol and reabsorption of fluorescence emission.

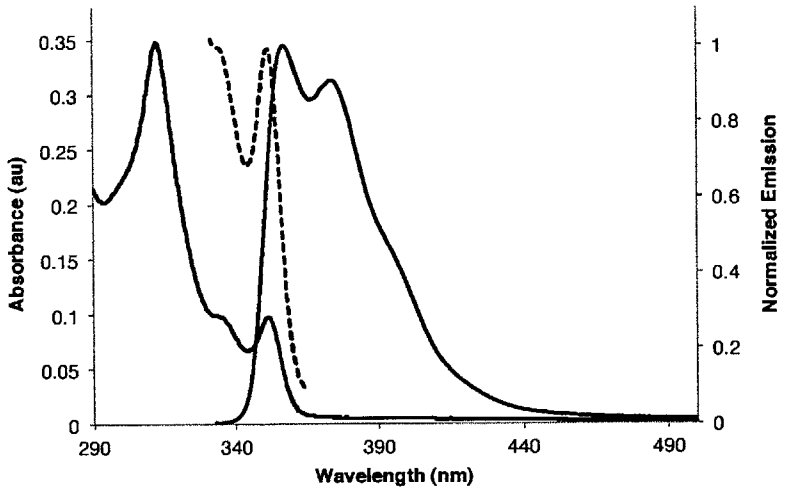


Figure 7. Absorbance (4.85×10^{-6} mol/L solution) and emission spectra ($\lambda_{ex} = 313$ nm) of TTC-*p*-Tol in CH_2Cl_2. Dashed line represents absorbance in the range 365–330 nm multiplied by 3.5 to emphasize correspondence with fluorescence transition.

A high lying singlet state in organic molecules is often an indication of a similarly high lying triplet state. Phosphorescence measurements of TTC-*p*-Tol in solution at 77 K indicated a maximum at 420 nm corresponding to a $T_1 \rightarrow S_0$ transition of 2.95 eV.[27] This value is in excellent agreement with the predicted values. Furthermore, the transition is higher in energy than blue triplet emitters, which have triplet energies ranging from 2.6-2.8 eV. As such, we believe that TTC-*p*-Tol could be a potentially promising class of hole-transport host materials for use in blue PHOLEDs.

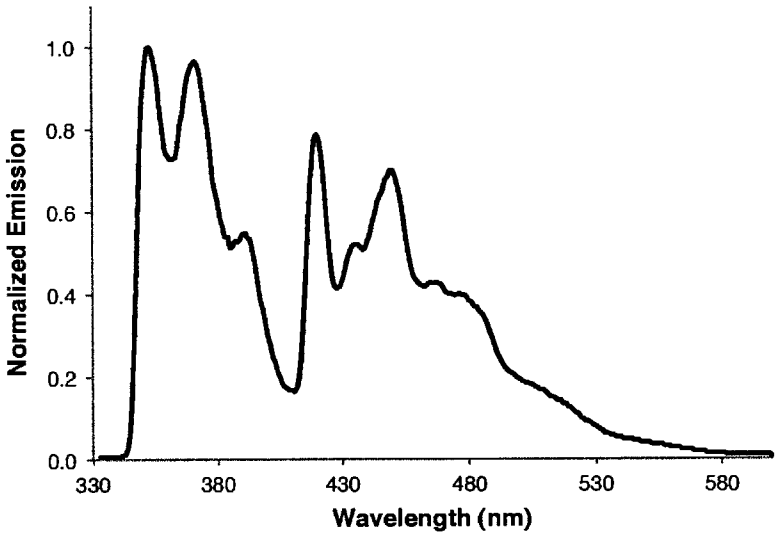


Figure 8. Emission spectrum (λ_{ex} = 313 nm) of TTC-*p*-Tol in frozen glass solution (1×10^{-5} mol/L in 2-methyltetrahydrofuran), showing fluorescence (340–410 nm) and phosphorescence (415–540 nm) transitions.

Finally, we examined the HOMO/LUMO band gap of the material in order to determine whether TTC-*p*-Tol could be compatible for hole-transfer processes. Furthermore, a deep HOMO level could suggest greater stability under oxidative conditions. The band gap energy was obtained from the λ_{onset} of the absorption spectrum and was measured to be 3.39 eV. Cyclic voltammetric measurements indicate a HOMO of -5.32 eV. Estimation of the LUMO energy level was obtained by addition of the HOMO energy level to the band gap and is approximated to be -1.84 eV. This is largely consistent with the predicted values. Collectively these data suggest that TTC-*p*-Tol could be an excellent candidate for a new generation of hole-transport host materials for use in PHOLED devices.

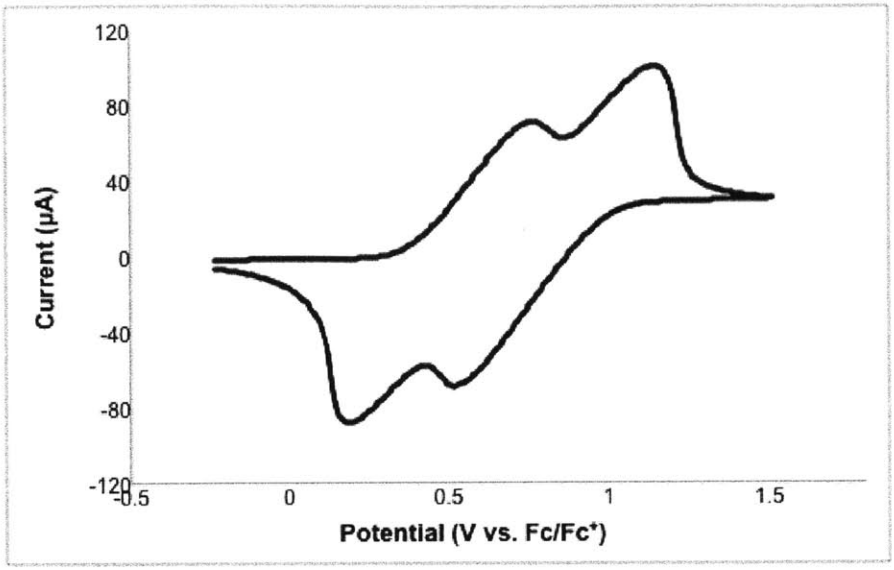


Figure 9. Cyclic voltammogram of TTC-*p*-Tol (performed under N_2, 0.1 M NBu_4PF_6 in CH_2Cl_2, Pt (WE), Pt wire (CE), $Ag/AgNO_3$ (RE), scan rate 0.005 V/s, plotted vs. Fc/Fc^+ couple (0.237 vs. $Ag/AgNO_3$).

4.3: Conclusion

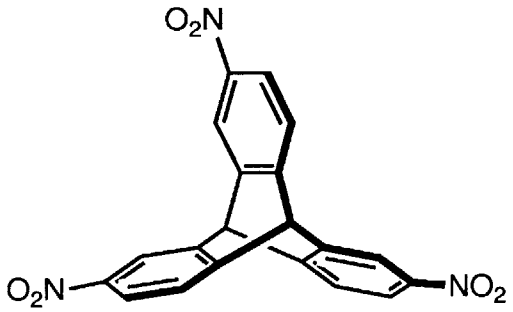
Based on computational predictions, we have successfully synthesized a new class of three-dimensional carbazole-based hole-transport host materials for use in PHOLED devices. We were successful in synthesizing the central TTC core on a gram scale as well as a derivative, TTC-*p*-Tol on >500 mg scale. Both the photophysical analysis of TTC-*p*-Tol as well as cyclic voltammetry data suggest that this derivative could be a suitable hole-transport material. Furthermore, due to the modular nature of the synthesis, rapid derivatization is predicted to be facile, limited only by the solubility of the final compound and accessibility of the starting aryl halide or pseudo halide.

4.4: Experimental

General Information. Reactions were set up on a bench top (not in a glove box) and were stirred with Teflon-coated magnetic stir bars. Anhydrous 1,4-dioxane and anhydrous dimethylacetamide (DMA) were purchased from Aldrich in Sure-Seal® bottles and used as received. The preparations of **2**, **3** and **4** were previously reported and all three are commercially available from Strem and Aldrich.[36] 1-Bromo-2-chlorobenzene was purchased from Alfa Aesar and used as received. Anhydrous NaO*t*-Bu was purchased from Aldrich and stored in a nitrogen-filled glovebox. Small quantities were periodically removed (~2g) and stored in a desiccator for up to one week. Anhydrous K_2CO_3 was purchased from Aldrich, ground into a fine powder and stored in a glass vial in a 140 °C oven. Pivalic acid and LiCl were purchased from Aldrich and used as received. Nitric acid (70%) was purchased from Aldrich and used as received. Concentrated HCl (37%) was purchased from Macron and used as received. Absolute ethanol was purchased from Pharmco and used as received. Glass fiber filters (GF/F, 0.7 μm pore size) were purchased from Whatman. Unless otherwise stated, flash column chromatography was performed using 40-63 micron silica purchased from Silicycle. Yields refer to isolated yields of compounds of an indicated purity as determined by high performance liquid chromatography (HPLC). Quoted yields are for representative runs and so may differ slightly from the average values indicated.

All ^{1}H NMR spectra were recorded on a Varian Inova-500 NMR spectrometer in a deuterated solvent operating at 500 MHz. All ^{13}C NMR spectra were recorded on a Varian Inova-500 NMR spectrometer in a deuterated solvent operating at 126 MHz. Chemical shifts are quoted relative to residual solvent. The following abbreviations are used singularly or in combination to indicate the multiplicity of signals: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All

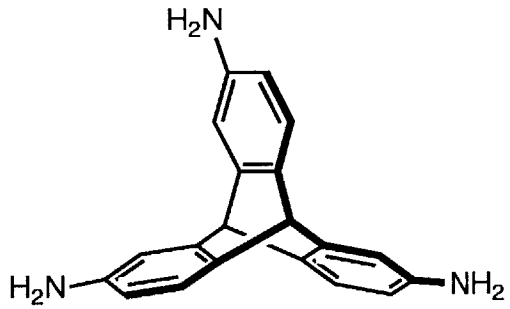
NMR spectra were acquired at 298 K. All IR spectra were taken on a Thermo Scientific – Nicolet iS5 spectrometer (iD5 ATR – diamond). Selected absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}). HPLC analyses were performed on an Agilent 1100 series system equipped with an 5 μm Econosphere® silica column. Melting points were determined using a Mel-Temp II capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Inc., Nocross, GA. High resolution mass spectrometry was performed using a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR-MS).



2,6,14 – Trinitrotriptycene[29]:

70% HNO_3 (200 mL) was added to a 500 mL round bottom flask equipped with a magnetic stir bar. The flask was placed in a 0 °C ice bath, and solid triptycene (10 g, 40 mmol) was added slowly to the stirred solution of HNO_3 at 0 °C. The mixture was stirred for 1 h, after which time the flask was equipped with a reflux condenser and placed into an 80 °C bath, and stirred at this temperature for 4 h. The reaction mixture became a homogenous, pale yellow solution after 30 min. The flask was then removed from the oil bath and the resulting brown solution was poured onto ice water (500 mL) yielding a white suspension. The mixture was stirred for approximately

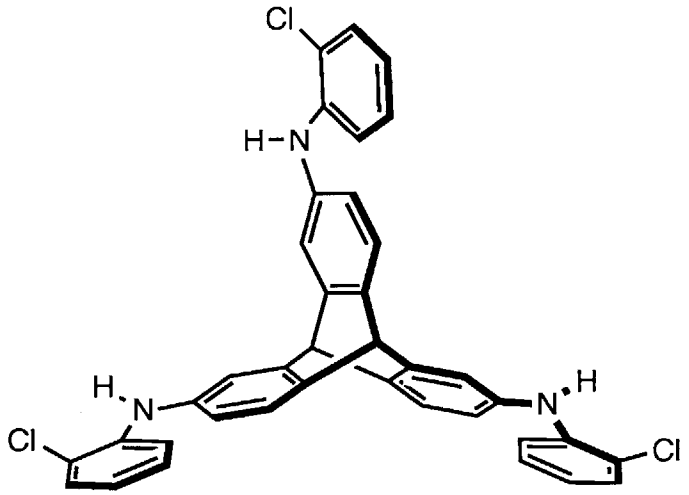
30 minutes and the white solid was collected by filtration and washed with water (500 mL) to remove trace amounts of nitric acid. The resulting solid was transferred to a 200 mL round bottom flask and dissolved in ethyl acetate. The resulting biphasic solution was transferred to a separatory funnel and the organic phase was washed twice with brine (50 mL), dried over $MgSO_4$, filtered and concentrated The resulting foam was dissolved in EtOAc and treated with silica gel (45 g) in a 200 mL round bottom flask. The solvent was removed under reduced pressure with the aid of a rotatory evaporator and the resulting pale yellow solid was further dried under vacuum (100 mTorr) with heating (50 °C) for 12 h (NOTE: omission of this step complicates purification via column chromatography). The dried solid was purified by flash column chromatography (EtOAc:hexanes 15% → 30%, in 5% increments of 1 L fractions, 25% is repeated twice) to provide the title compound as a pale yellow solid (11 g, 72 % yield, ~ 90 % purity, major contaminant is 2,7-dinitrotriptycene, m.p. = 173-176 °C). (NOTE: it is possible to collect 2,7,14 - trinitrotriptycene as well in the later fractions). ^{1}H NMR conforms to literature. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.34 (m, 3H), 8.04 (m, 3H), 7.68 (m, 1H), 7.68 (m, 2H), 5.90 (s, 1H), 5.90 (s, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 150.58, 150.18, 146.82, 145.13, 144.76, 125.79, 125.73, 123.02, 122.99, 120.27, 120.19, 53.91, 53.75. IR (neat) ν_{max} : 1511.54, 1337.98, 1197.84, 1167.52, 913.98, 902.1, 871.91, 859.18, 844.22, 829.6, 775.84, 734.14, 647.85, 608.79 cm^{-1}.



2,6,14 – Triaminotriptycene[29]:

2,6,14 – trinitrotriptycene (2 g, 90% purity as above, 6.6 mmol, 6 mmol effective) and $SnCl_2 \bullet (H_2O)_2$ (26 g, 115 mmol, 20 mmol per $-NO_2$) were added to a 500 mL round bottom flask equipped with a magnetic stir bar. Absolute EtOH (200 mL) and concentrated HCl (50 mL) were then added to the solid mixture. The flask was equipped with a reflux condenser and placed into a preheated oil bath at 100 °C with stirring. The reaction mixture quickly became homogenous and after 1 h a white precipitate began to form. After 24 h, the flask was removed from the oil bath and its contents were allowed to cool to room temperature. The white solid was then filtered, washed with absolute EtOH (300 mL) and allowed to air dry. The solid was then collected, dissolved in water (50 mL) and poured into a separatory funnel containing saturated aqueous $NaHCO_3$ solution (200 mL) and EtOAc (300 mL). The aqueous phase was tested to ensure a basic pH and then extracted twice with EtOAc (50 mL). The combined organic layers were washed twice with brine (50 mL), dried over $MgSO_4$ and filtered. Solvent was removed under reduced pressure with the aid of a rotary evaporator to produce a yellow residue, which was then dissolved in EtOAc (20 mL) and filtered through a glass fiber filter. Solvent was once again removed under reduced pressure and further dried under vacuum (100 mTorr) with heating (80 °C) for 12 h to provide the title compound as a white solid (875 mg, 57%, >97% purity). ^1H

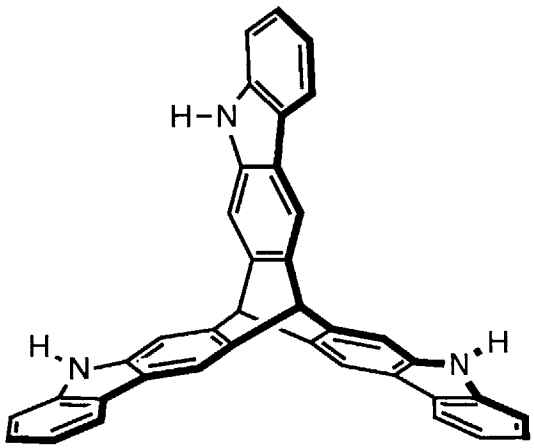
NMR (500 MHz, CD_3OD) δ 7.05 – 6.96 (m, 3H), 6.79 – 6.72 (m, 3H), 6.34 – 6.26 (m, 3H), 5.00 (s, 1H), 4.99 (s, 1H). ^{13}C NMR (126 MHz, CD_3OD) δ 149.32, 148.63, 145.32, 145.13, 138.26, 137.50, 124.45, 124.19, 112.99, 112.71, 112.23, 112.00, 54.86, 53.86. IR (neat) ν_{max} : 3339.23, 1615.81, 1475.48, 1328.23, 1295.77, 1259.64, 1186.56, 1139.23, 1115.44, 832.84, 770.98, 637.33, 572.82 cm^{-1}.



N^2,N^6,N^{14}-tris(2-chlorophenyl)- 2,6,14-triaminotriptycene (1):

2,6,14-triaminotriptycene (1.495 g, 5 mmol), **2** (342 mg, 0.45 mmol, 9 mol%, 3 mol% per C-N bond), and NaO*t*-Bu (2.13g, 22.5 mmol, 4.5 equiv., 1.25 equiv. per NH_2) were added to an oven dried 25 mL round bottom flask equipped with a magnetic stir bar and stoppered with a rubber septum. The sealed vessel was evacuated and backfilled with N_2 (this procedure was repeated a total of three times) and then 1-bromo-2-chlorobenzene (2.2 mL, 18.75 mmol, 1.25 equiv. per NH_2) and 1,4-dioxane (10 mL) were add via syringe under pressure of N_2. The flask was placed into a preheated 100 °C oil bath with efficient stirring. The reaction mixture quickly became green and then red in color. After 2 h the flask was removed from the oil bath and allowed to cool to room temperature. The flask was opened and its contents were diluted with

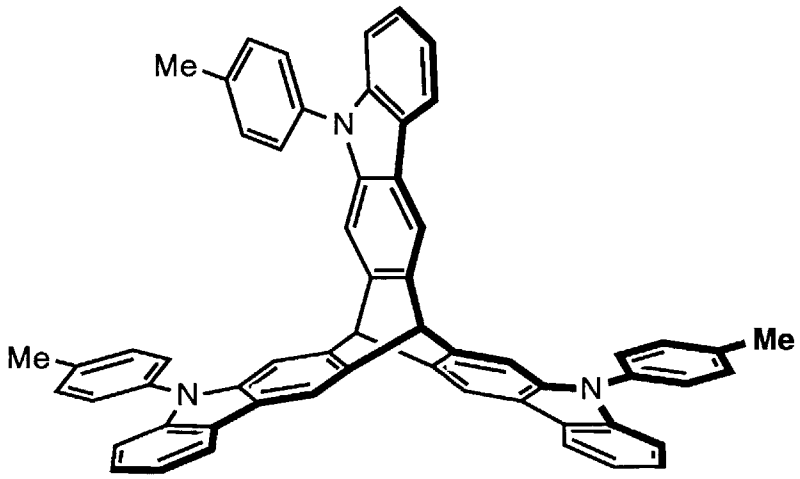
dichloromethane, filtered through a pad of SiO_2 into a 200 mL round bottom flask, concentrated and further dried under vacuum (100 mTorr) with heating (80 °C) for 12 h. The resulting dark-colored solid was redissolved in dichloromethane and treated with silica gel. Solvent was once again removed under reduced pressure with the aid of a rotary evaporator and further dried under vacuum (100 mTorr). The resulting dark solid was purified by silica gel column chromatography (DCM:hexanes 0% → 45%, in 5% increment 500 mL fractions) to afford the title compound as a white solid (2.33 g, 74% yield, >99% purity, m.p. 135 °C). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.34 (ddd, J = 7.4, 5.7, 1.6 Hz, 6H), 7.24 (d, J = 2.1 Hz, 3H), 7.19 (ddd, J = 8.2, 4.9, 1.5 Hz, 3H), 7.11 (dddd, J = 8.3, 7.2, 2.7, 1.6 Hz, 3H), 6.84 – 6.77 (m, 6H), 6.07 (s, 3H), 5.34 (s, 1H), 5.31 (s, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 147.49, 147.05, 140.89, 140.85, 140.15, 139.64, 139.39, 139.23, 129.97, 127.84, 124.68, 124.49, 121.63, 121.58, 120.62, 120.59, 116.97, 116.74, 116.68, 116.43, 116.06, 115.99, 53.76, 53.06. IR (neat) ν_{max} : 3400.68, 1589.3, 1495.52, 1475.24, 1447.13, 1405.92, 1307.9, 1183.03, 1114.93, 1047.88, 1032.9, 950.83, 821.8, 739.15, 709.63 cm^{-1}. Anal. Calcd. For $C_{38}H_{26}Cl_3N_3$: C, 72.33; H, 4.15. Found: C, 72.26; H, 4.23.



7,13,15,21-tetrahydro-5H-7,15-[3,4]epicarbazolobenzo[1,2-b:4,5-b']dicarbazole (TTC):

Compound **1** (1.89g mg, 3 mmol), **3** (585 mg, 30 mol%, 10 mol% per C-C bond), K_2CO_3 (3.72 g, 27 mmol, 9 equiv.) and PivOH (275 mg, 2.7 mmol, 0.9 equiv., 30 mol% per C-C bond) were added to an oven-dried 25 mL Schlenk flask equipped with a magnetic stir bar and stoppered with a rubber septum. The sealed vessel was evacuated and backfilled with N_2 (this procedure was repeated a total of three times). DMA (15 mL) was added via syringe. And the septum was removed and replaced with a glass stopper under pressure of N_2. The flask was then placed into a preheated 110 °C oil bath with efficient stirring. The reaction mixture slowly became yellow and eventually black in color. After 16 h, the flask was removed from the oil bath and its contents were allowed to cool to room temperature. The resulting black liquid was poured onto a saturated solution of LiCl (150 mL) and extracted three times with EtOAc (200 mL). The combined organic layers were then washed once with saturated LiCl solution (50 mL), twice with brine (100 mL), dried over Na_2SO_4, decanted into a 1 L round bottom flask and concentrated. The resulting solid was redissolved in EtOAc (20 mL) and filtered through a glass fiber filter (0.7 μm pore size) to remove all insoluble material. Solvent was once again removed under reduced pressure with the aid of a rotary evaporator and the resulting red-colored solid was further dried under vacuum (100 mTorr) for 12 h with heating (130 °C). The contents of the flask were

allowed to cool to room temperature. The resulting solid was triturated in Et_2O (30 mL) with the aid of sonication to produce a homogenous white solid suspended in a red solution. The flask was then cooled to -78 °C and its contents were collected by filtration. The material was washed three times with cold Et_2O (10 mL) and dried under vacuum to provide the title compound as a tan colored solid (1.075 g, ~80% purity, 55% effective yield). The material may be carried on to the next step or purified further via recrystallization (1 mL toluene/10 mg of compound, 130 °C, efficiency of ~90%) until >99.9% purity is attained. Decomp onset at 330 °C, full decomp >350 °C, m.p. not found. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.19 (s, 1H), 8.15 (s, 2H), 8.13 – 8.06 (m, 1H), 8.03 (d, J = 7.9 Hz, 3H), 7.78 (s, 2H), 7.55 (s, 1H), 7.38 (s, 2H), 7.37 – 7.11 (m, 9H), 5.80 (s, 1H), 5.66 (s, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 145.54, 144.85, 140.53, 140.49, 138.18, 138.16, 137.99, 137.68, 125.66, 125.63, 123.90, 123.84, 120.42, 120.35, 120.33, 119.91, 119.83, 115.72, 115.55, 111.36, 107.11, 107.02, 55.61, 55.07. IR (neat) ν_{max} : 2953.45, 1605.84, 1512.07, 1472.77, 1444.79, 1369.51, 1331, 1253.34, 1226.31, 1181.45, 1112.47, 1016.17, 930.97 cm^{-1}. Anal. Calcd. For $C_{38}H_{23}N_3$: C, 87.50; H, 4.44. Found: C, 87.49; H, 4.37.



5,13,21-tri-p-tolyl-7,13,15,21-tetrahydro-5H-7,15-[3,4]epicarbazolobenzo[1,2-b:4,5-b']dicarbazole (TTC-*p*-Tol):

TTC (521 mg, 1 mmol), K_2CO_3 (1.24 g, 9 mmol, 9 equiv., 3 equiv. per C-N bond), and **4** (171 mg, 30 mol%, 10 mol% per C-N bond) were added to an oven dried 16 mL test tube with Teflon screw cap equipped with two stir bars. The sealed vessel was evacuated and backfilled with Ar (this procedure was repeated a total of three times). After which, *p*-bromotoluene (684 mg, 4 mmol, 4 equiv.) and 1,4-dioxane (10 mL) were added via syringe under pressure of Ar. The tube was then placed into a preheated 110 °C oil bath with stirring. After 18 h, the tube was removed from the oil bath and allowed to cool to room temperature. An aliquot (10 μL) was removed under pressure of Ar and analyzed for the presence of starting material with the aid of HPLC. The silver-colored mixture was filtered through a pad of SiO_2, which was further washed with dichloromethane (300 mL), concentrated and further dried under vacuum (100 mTorr) with heating (80 °C) for 12 h. The contents of the flask were allowed to cool to room temperature and the resulting solid was dissolved in dichloromethane and treated with silica gel. Solvent was removed under reduced pressure with the aid of a rotary evaporator and further dried under vacuum (<200 mTorr) and with heating (80 °C). The compound was then purified via flash column chromatography on a Biotage Isolera 4 using SNAP 100g prepacked silica cartridges (dichloromethane:hexanes 15 → 35%, 40 CV). The resulting solid was analyzed for purity via HPLC (12% EtOAc:Hexanes, 5 μm SiO_2, 15 min). If the purity was less than 99.9%, the solid may be loaded onto silica once again and repurified using a SNAP ULTRA 340g prepacked cartridge EtOAc:Hexanes (0 → 20%, 20 CV) . Each fraction was subsequently analyzed via HPLC to determine purity. The resulting compound was then dried under vacuum at 130 °C for

12 h to produce a white solid (487 mg, 62%, >99.9% purity, m.p. not found, solid darkens above 350 °C in air). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.19 (s, 2H), 8.11 (d, J = 9.7 Hz, 1H), 8.09 (ddd, J = 8.6, 7.3, 1.0 Hz, 2H), 7.54 (s, 1H), 7.51 – 7.38 (m, 15H), 7.38 – 7.28 (m, 6H), 7.24 (dtd, J = 7.6, 6.2, 1.7 Hz, 3H), 5.81 (s, 1H), 5.67 (s, 1H), 2.56 (s, 3H), 2.54 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 144.95, 144.35, 141.57, 141.55, 139.35, 139.33, 139.20, 137.96, 137.94, 137.89, 137.83, 137.79, 135.15, 130.69, 130.65, 127.26, 127.21, 125.25, 125.24, 123.44, 123.40, 120.04, 119.91, 119.86, 119.77, 119.75, 115.22, 115.12, 109.91, 105.84, 105.75, 96.31, 55.26, 54.61, 21.25, 21.23. IR (neat) ν_{max} : 2953.45, 1605.84, 1512.07, 1472.77, 1444.79, 1369.51, 1331, 1253.34, 1226.31, 1181.45, 1112.47, 1016.17, 930.97, 875.71, 843.22, 811.77, 762.69, 735.58, 723.11, 712.25, 705.65 cm^{-1}. HRMS calc'd for $C_{59}H_{42}N_3$ $[M+H]^+$: 792.3373, found 792.3360.

Photophysics Experimental Section

Absorption spectra were measured on a Cary 50 UV-Vis spectrophotometer. Emission spectra were measured on a **TTC-*p*-Tol**. Room temperature measurements were conducted using 10 mm quartz cuvettes and CH_2Cl_2 as solvent. Molar extinction coefficients were measured in triplicate, using three separately prepared solutions, and calculated according to the Beer–Lambert law ($\varepsilon = Acl$).

Quantum yield measurements[37] were calculated compared to a quinine sulfate standard in an aqueous H_2SO_4 (0.5 mol/L) solution. Standard curves of fluorescence intensity over absorbance were recorded for the sample and the standard at concentrations at which absorbance at 315 nm roughly equaled 0.00 (blank), 0.02, 0.04, 0.06, 0.08, and 0.10 (Figure S1).

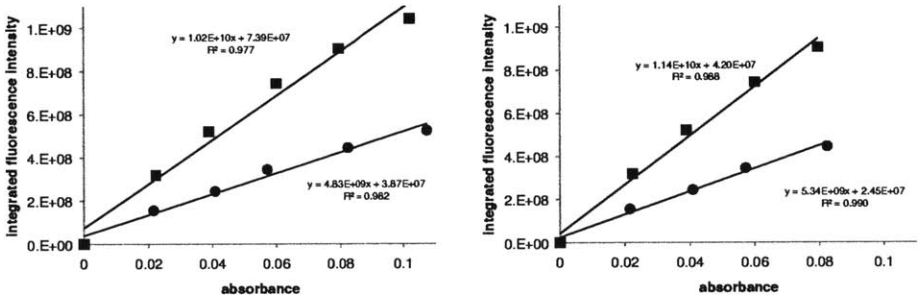


Figure S1. Plots of integrated fluorescence intensity over absorbance for compound **TTC-*p*-Tol** in CH_2Cl_2 (circles) and quinine sulfate in an aqueous H_2SO_2 (0.5 mol/L) solution (squares). Left: all six points data points for each measurement are shown; right: the highest absorbance measurement is omitted.

The slopes of integrated fluorescence intensity over absorbance (*dFI/dA)* were then used to calculate the quantum yield of **TTC-*p*-Tol** by Eq. 1:

$$\Phi_X = \Phi_{ST}\left[\frac{\left(\frac{dFI}{dA}\right)_X}{\left(\frac{dFI}{dA}\right)_{ST}}\right]\left(\frac{\eta_X^2}{\eta_{ST}^2}\right) \quad \text{(Eq. 1)}$$

where Φ is fluorescence quantum yield, η is the refractive index of the solvent (1.4242 for CH_2Cl_2 and 1.34 for 0.5 mol/L H_2SO_4 solution), and X and ST refer to sample and standard, respectively. Using the well-established value of 0.55 for Φ_{ST},[38-39] Φ_X was calculated to be 0.294 using all six points (Figure S1, left) and 0.292 using only the first five points (Figure S1, right).

Low-temperature emission spectra were recorded by submerging a glass NMR tube containing a degassed solution of **TTC-*p*-Tol** (1×10^{-5} mol/L) in 2-methyltetrahydrofuran into a liquid nitrogen Dewar assembly, forming a solid glass. Excitation spectra (λ_{ex} = 290–380 nm, integration time = 1.0 s) at λ_{em} = 420 nm, 450 nm, and 480 nm, were very similar to the absorbance spectrum of **TTC-*p*-Tol** at wavelengths above ~325 nm. At wavelengths below 325 nm, a noticeable portion of the incoming light was absorbed by the glass NMR tube, distorting the excitation spectra.

Photophysics Measurements:

Absorbance peaks: λ = 313 nm (ε = 70,800 ± 900 L mol^{-1} cm^{-1}); λ = 351 nm (ε = 19,800 ± 400 L mol^{-1} cm^{-1}).

Fluorescence peaks: λ = 357 nm (rel. intensity = 1); λ = 374 nm (rel. intensity = 0.91).

Fluorescence quantum yield (Φ_F) = 0.29, calculated by comparison to quinine sulfate in 0.5 mol/L H_2SO_4 (aq).

Phosphorescence: λ_{phos}(max) = 420 nm.

Electrochemsitry Experimental Section

Cyclic voltammetry (CV) measurements were performed under N_2 in a glove box on an Eco Chemie Autolab potentiostat (Model PGSTAT20) using a $Ag/AgNO_3$ reference electrode (containing a solution of 0.01 M $AgNO_3$, 0.1 Bu_4NPF_6 in CH_3CN), a Pt button working electrode, and a Pt wire counter electrode. Measurements were performed at a sweep rate of 5 mV/s in dry, degassed CH_2Cl_2 with Bu_4NPF_6 (0.1 M) as electrolyte. The ferrocene/ferrocenium (Fc/Fc^+) couple was used as an external standard, measured immediately after measurement of **TTC-*p*-Tol**, as the Fc/Fc^+ oxidation peak overlaps with that of **TTC-*p*-Tol**. The HOMO energy level was calculated by the equation E_{HOMO} (eV) = – [E_{onset} – $E_{onset}(Fc/Fc^+)$] – 4.80 eV, where E_{onset} is the onset oxidation potential for the first oxidation of **TTC-*p*-Tol** and $E_{onset}(Fc/Fc^+)$ is the onset oxidation potential for the Fc/Fc^+ couple. The value –4.80 is the HOMO energy of ferrocene compared to the vacuum level. The LUMO energy was calculated by the equation E_{LUMO} (eV) = $E_{HOMO} + E_{gap}$, where E_{gap} is the optical band gap as determined by the onset wavelength (366 nm = 3.39 eV) of the lowest energy absorption peak.

Electrochemical Measurements:

Observation: Two reversible oxidations that are only observable with slow scan rate (5 mV/s).

Half-wave potentials = $E_{1/2} = 0.5 \times (E_{pa} + E_{ca})$. Values given in V vs. Fc/Fc^+ [$E_{1/2}(Fc/Fc^+)$ set to 0; measured value of Fc/Fc^+ couple was 0.24 V vs. $Ag/AgNO_3$ in original measurement].

$E_{1/2}1 = 0.49$
$E_{1/2}2 = 0.83$

Estimation of HOMO and LUMO levels:

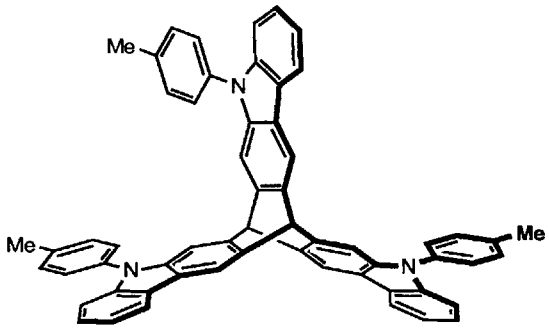
First oxidation onset potential (E_{onset}) = 0.28 V (vs. Fc/Fc^+)
E_{HOMO} (eV) = $-(E1_{onset} - E(Fc/Fc^+)_{onset}) -4.80 = -5.23$ eV
(The E_{HOMO} of Fc lies at –4.80 eV)
l_{onset} (from absorption spectrum) = 366 nm

Band gap = $E_{gap} = hc/l_{onset}$ = 3.39 eV (h = Planck's constant; c = speed of light)
E_{LUMO} (eV) = $E_{HOMO} + E_{gap}$ = 1.84 eV

Computational Methods

All calculations were carried out with the Gaussian '03 suite.[40] All calculations were performed using the Becke[41-42] three-parameter hybrid functional combined with Lee–Yang–Parr correlation functional.[43] C, H, and N were computed at the 6-31G(d) level of theory, F was computed using 6-311++G(d,p). Frequency calculations were undertaken to confirm the nature of the stationary points, yielding one imaginary frequency (NImag = 1) for transition states (TS) with largest contributions from internal coordinates involved in the reaction and none (NImag = 0) for minima. All optimizations were performed without any constraints (C1 symmetry). Geometry optimizations were carried out in the gas phase. All HOMO and LUMO energy levels were calculated using Natural Bond Orbital version 3.1 (NBO 3.1) population analysis developed by Weinhold and co-workers and as implemented in Gaussian '03.[44]

Cartesian Coordinates for Optimized Structures



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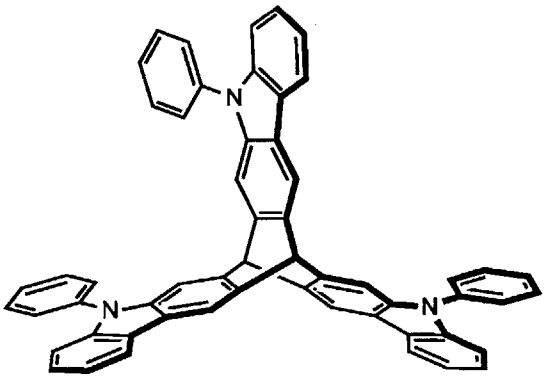

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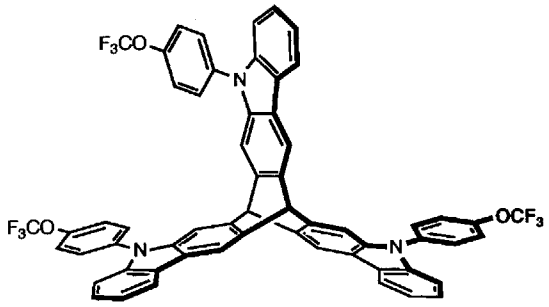

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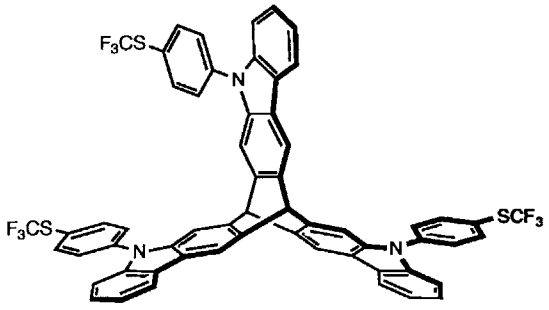

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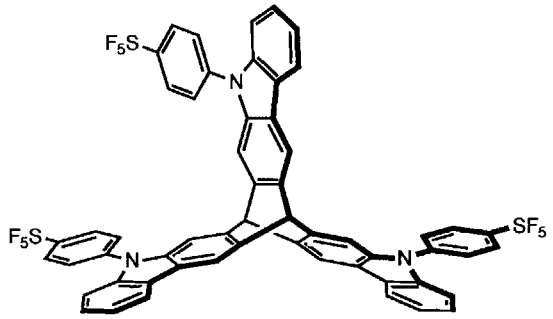

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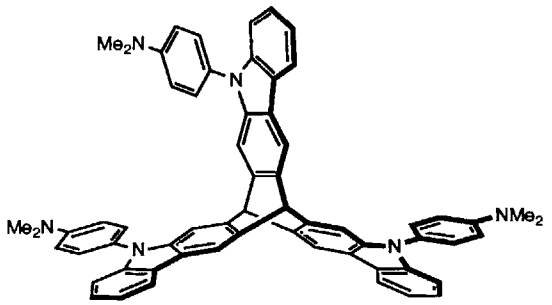

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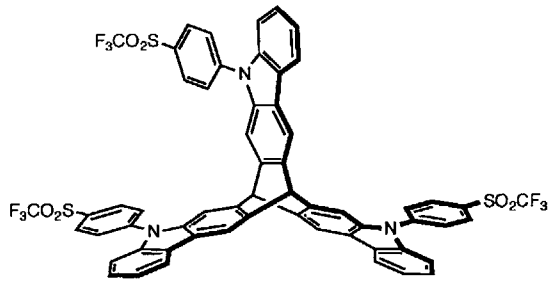

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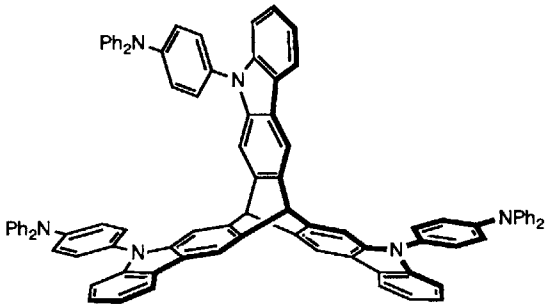

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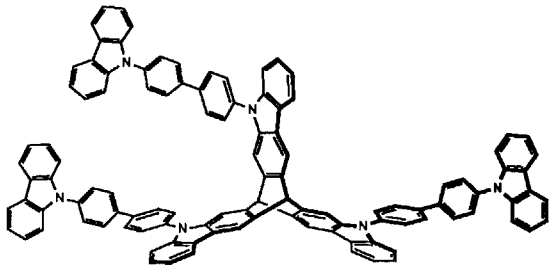

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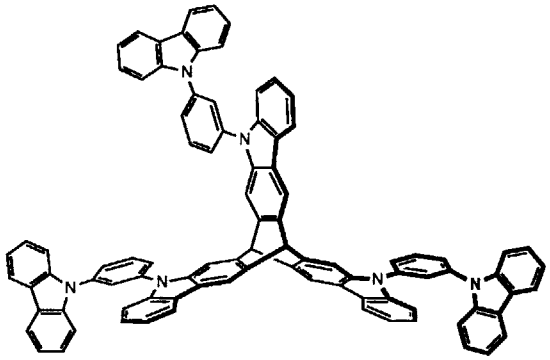

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H	-11.28644300	-4.50752600	-1.09004500
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H	-0.04153600	9.88646300	-2.33040100
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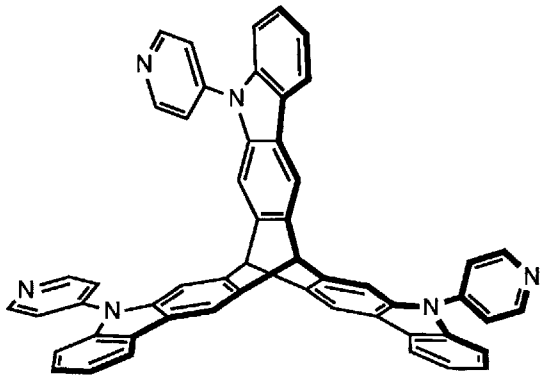

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C	3.03502300	-0.19104700	-0.76078200
C	1.67996500	-0.10959900	-0.47645700
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H	3.39131100	-0.20577000	-1.78575100
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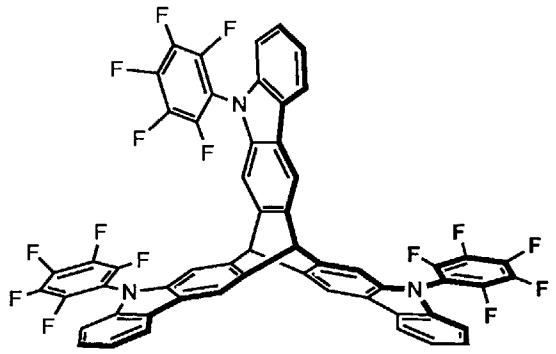

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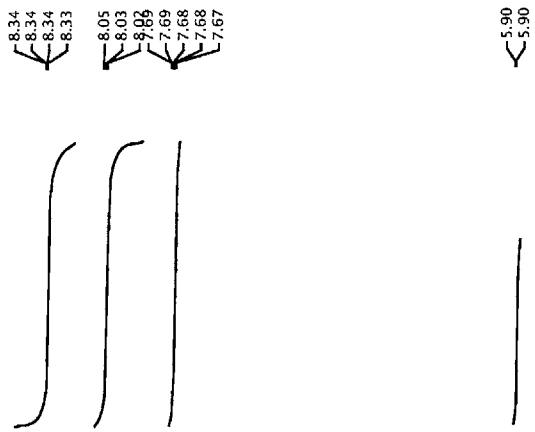
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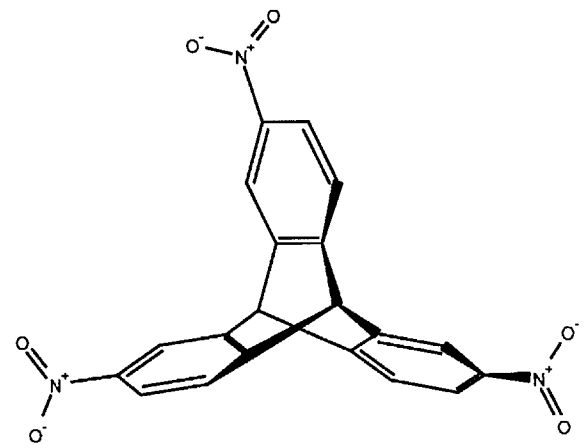

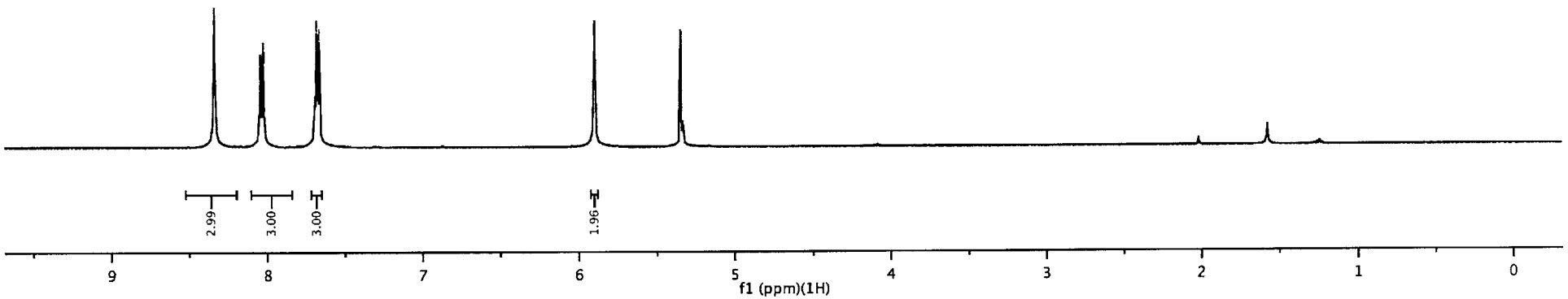
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8
7
6
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4
3
2
1
0
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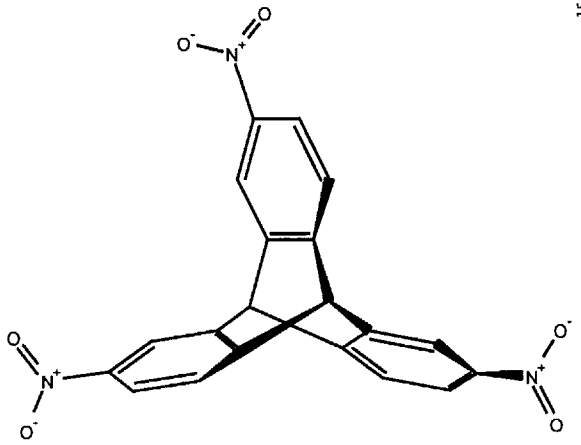

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144.76

125.79
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122.99
120.27
120.19

288

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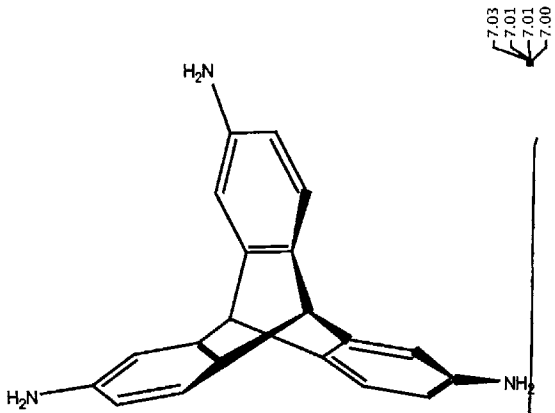
f1 (ppm)(13C)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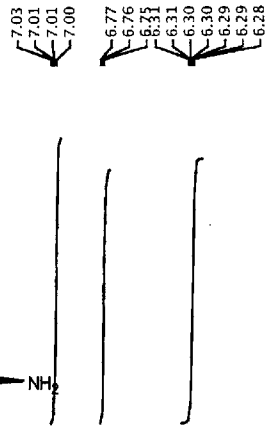
NH2
H2N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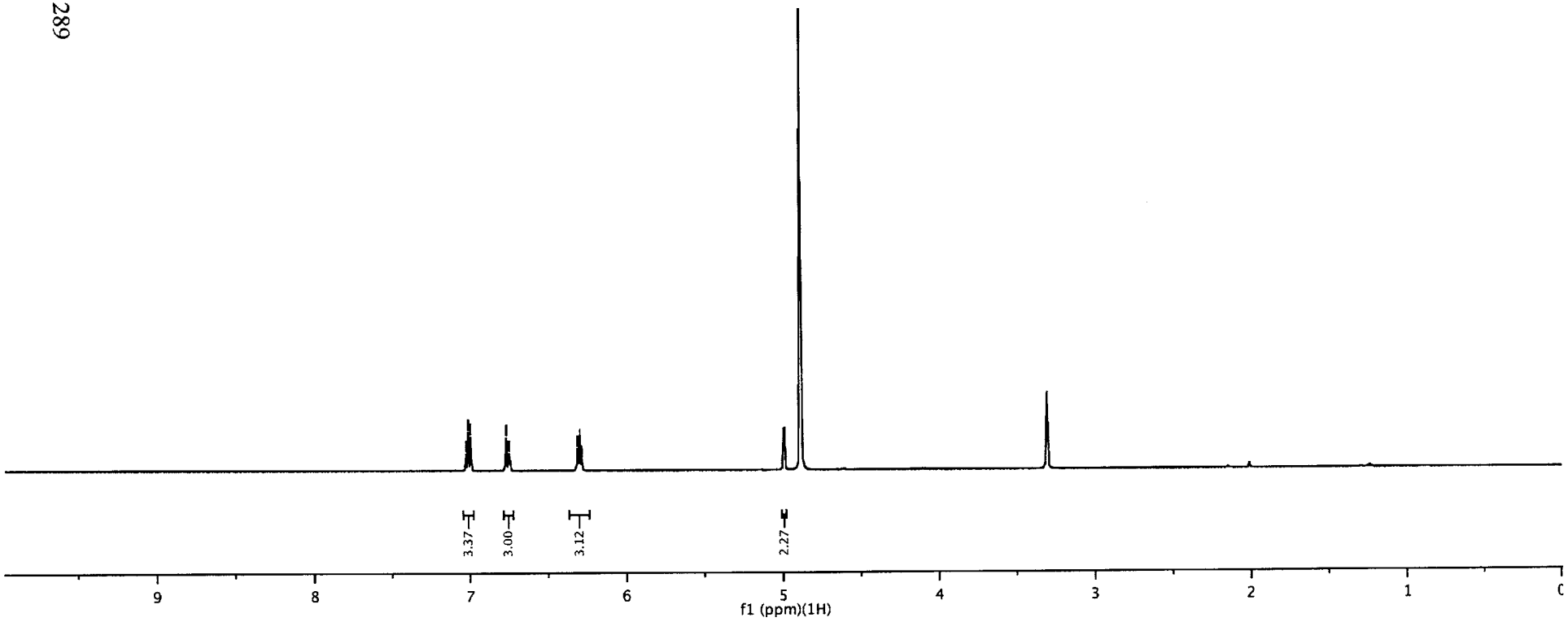
289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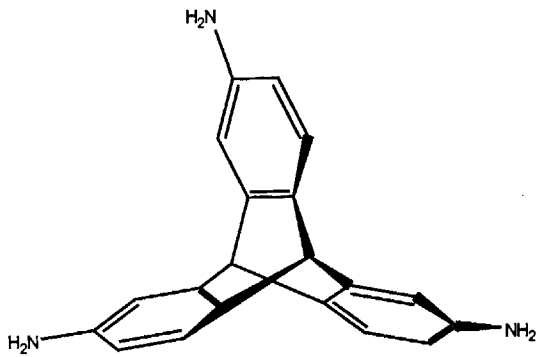

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55.18

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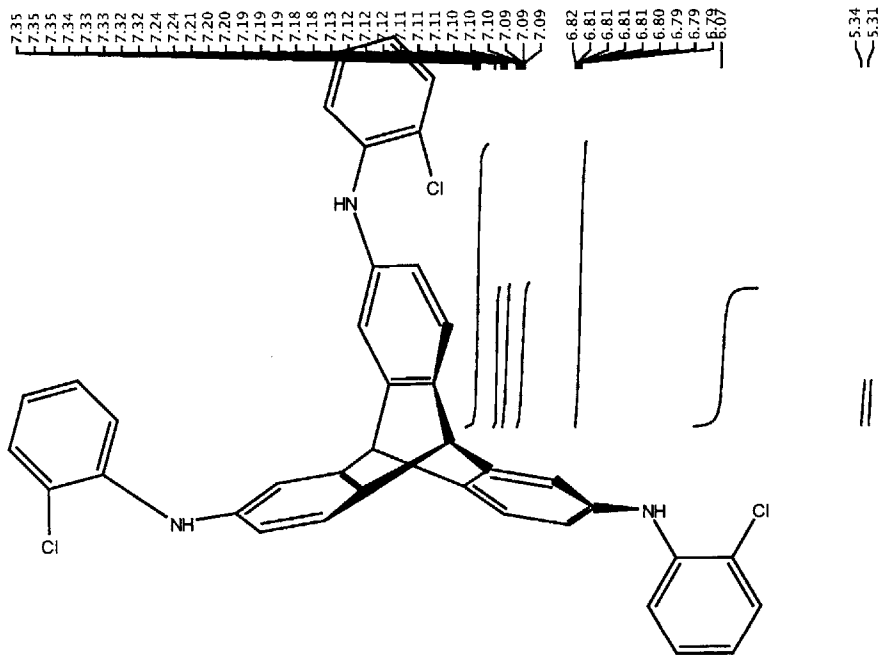
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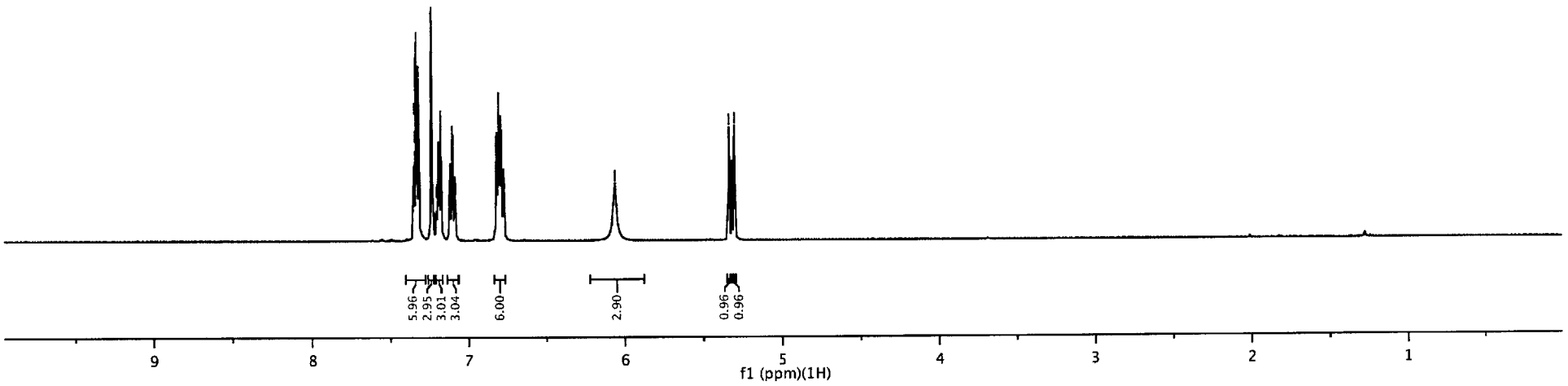
Cl
NH
Cl
NH
Cl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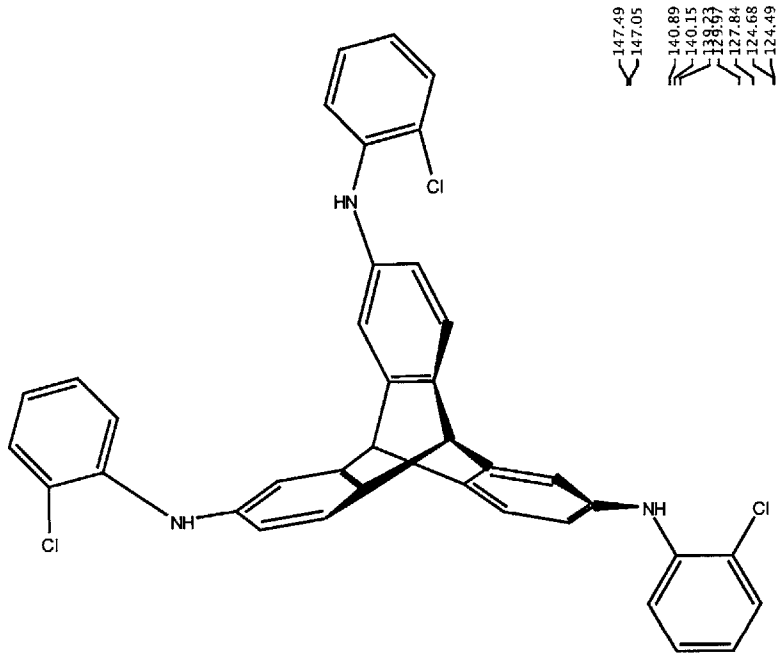
f1 (ppm)(1H)



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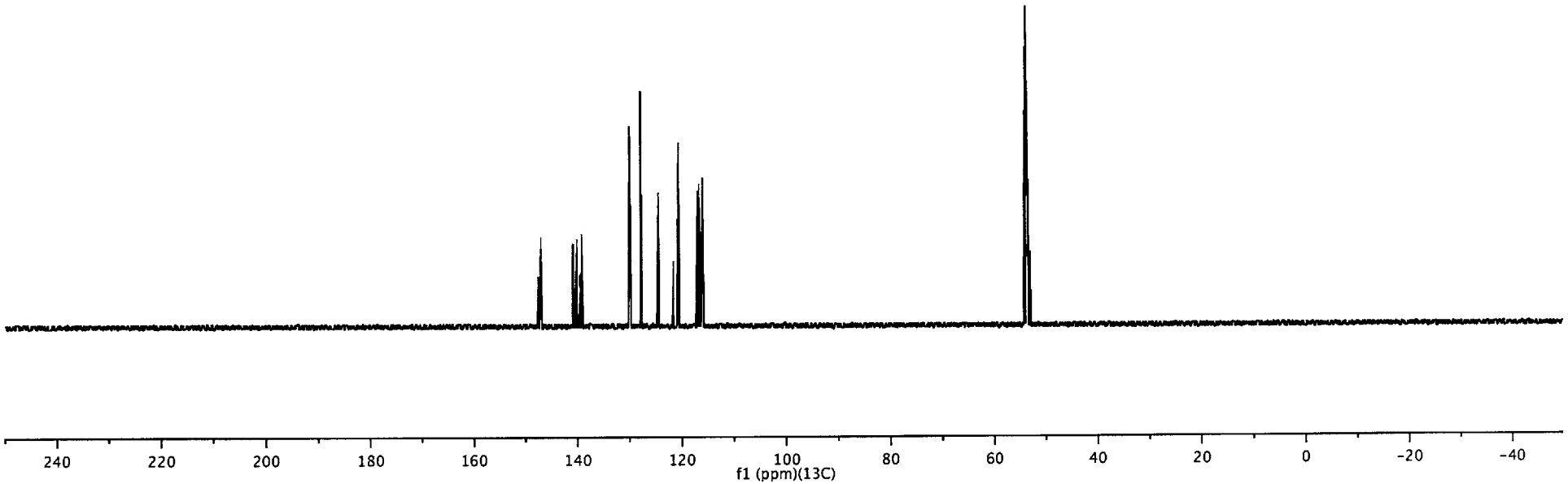
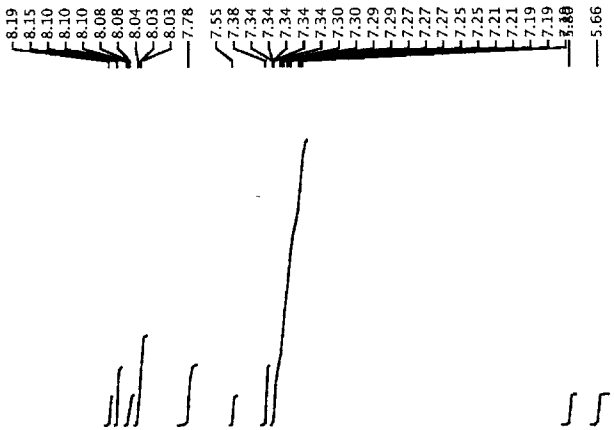
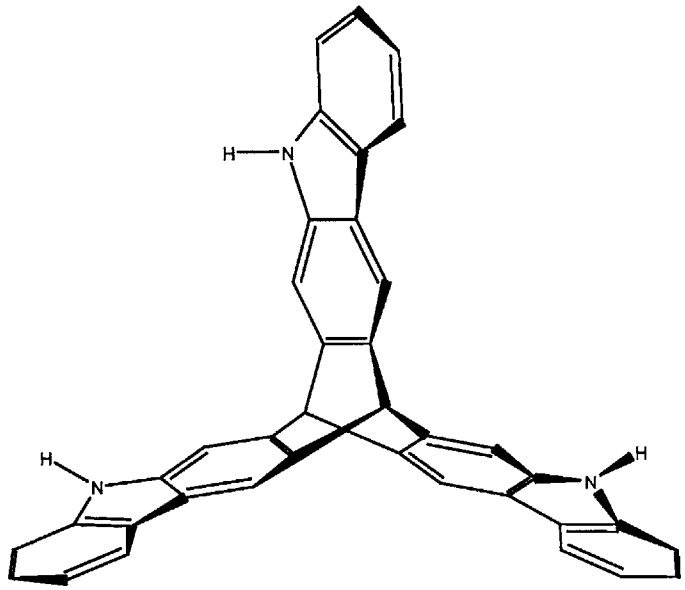
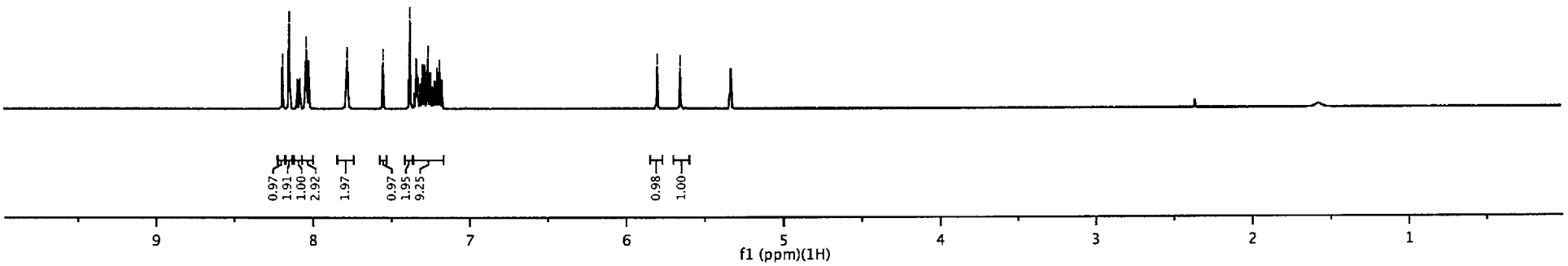
53.06

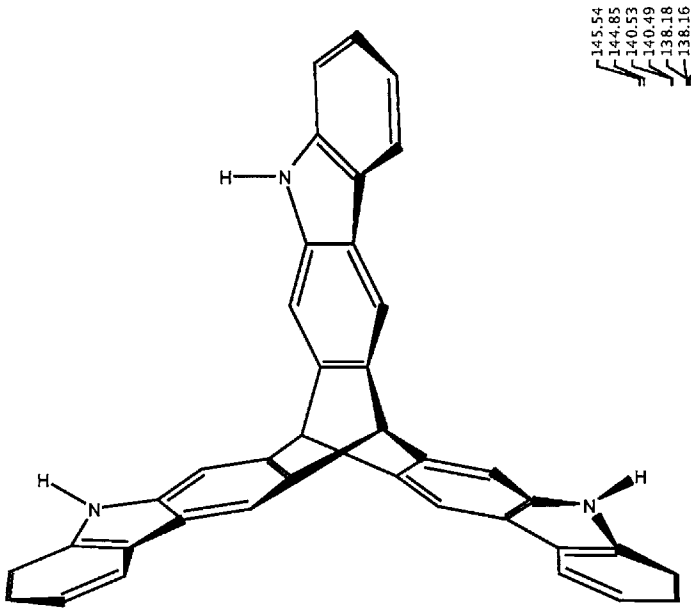
292




8.19
8.15
8.10
8.10
8.10
8.08
8.08
8.04
8.03
8.03
7.78
7.55
7.38
7.34
7.34
7.34
7.34
7.30
7.29
7.29
7.27
7.27
7.27
7.25
7.25
7.21
7.21
7.19
7.19
5.66


H
N
H
N
N
H

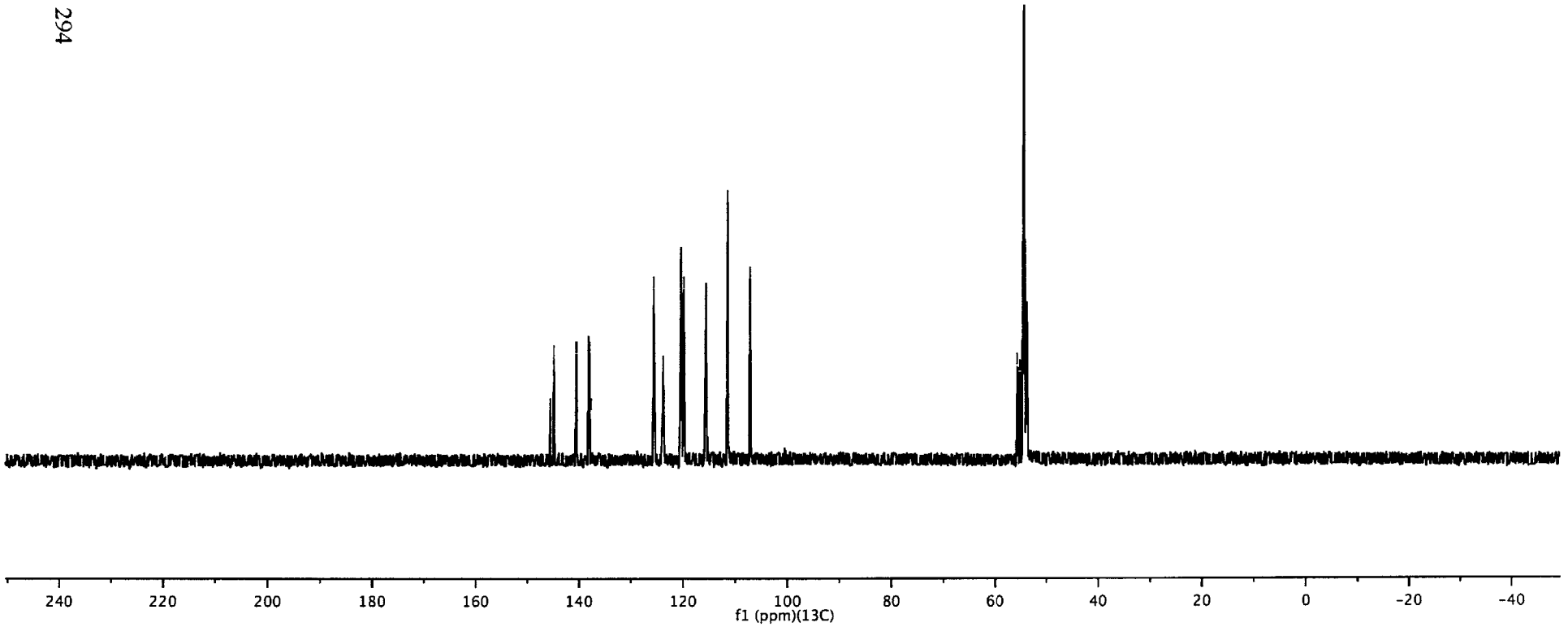

0.97
1.91
1.00
2.92
1.97
0.97
1.95
9.25
0.98
1.00
9
8
7
6
5
4
3
2
1
f1 (ppm)(1H)

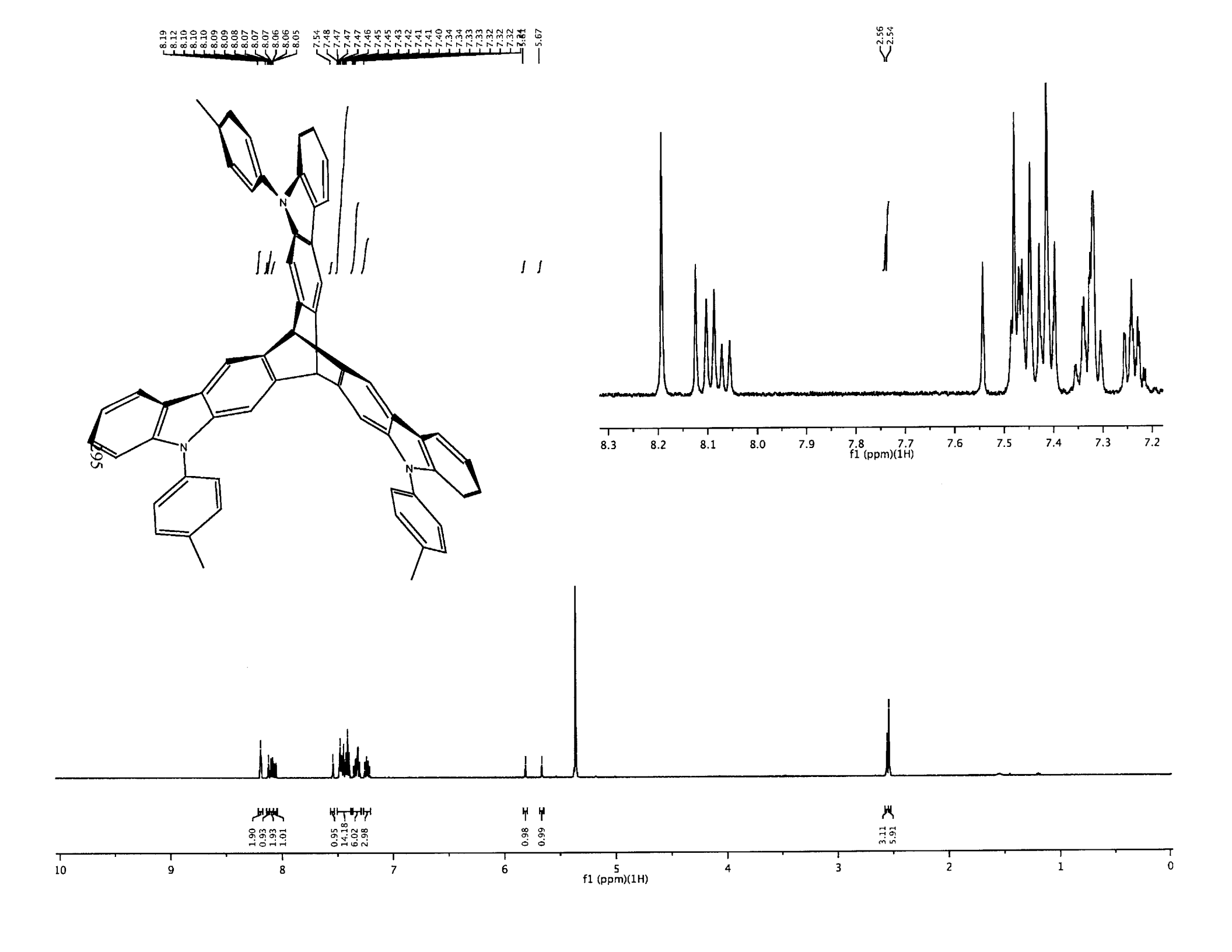


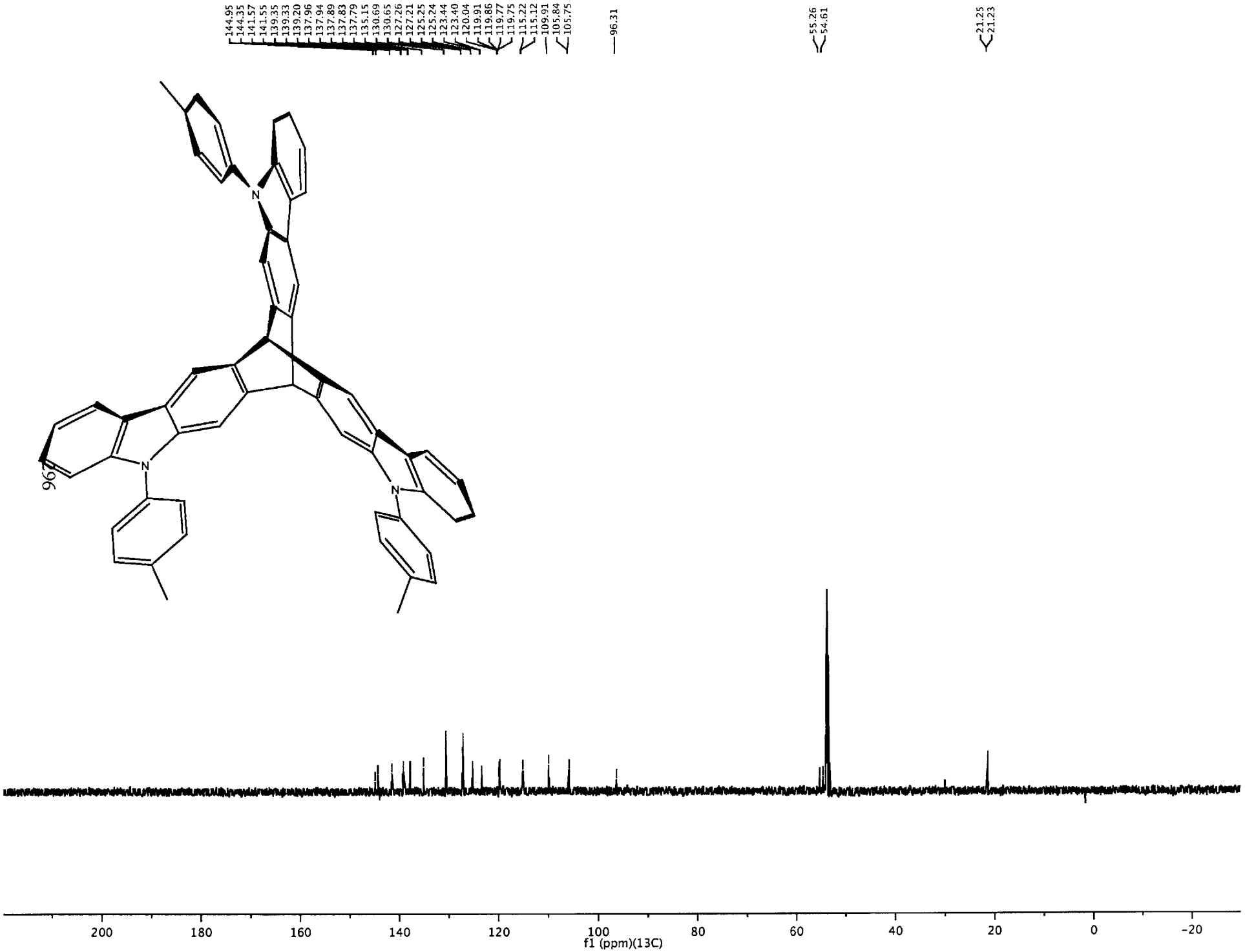
145.54
144.85
140.53
140.49
138.18
138.16
137.99
137.68
125.66
125.63
123.90
123.84
120.42
120.35
120.33
119.91
119.83
115.72
115.55
111.36
107.11
107.02

55.61
55.07

294




8.19 8.12 8.10 8.10 8.10 8.09 8.09 8.08 8.07 8.07 8.07 8.06 8.06 8.05
7.54 7.48 7.47 7.47 7.47 7.46 7.45 7.45 7.43 7.42 7.41 7.41 7.40 7.34 7.33 7.33 7.32 7.32 7.31 7.31
5.67
2.56 2.54
N
N
N
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)(1H)
1.90 0.93 1.93 1.01
0.95 14.18 6.02 2.98
0.98 0.99
3.11 5.91
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)(1H)


144.95
144.35
141.57
141.55
139.35
139.33
139.20
137.96
137.94
137.89
137.83
137.79
135.15
130.69
130.65
127.26
127.21
125.25
125.24
123.44
123.40
120.04
119.91
119.86
119.77
119.75
115.22
115.12
109.91
105.84
105.75
96.31
55.26
54.61
21.25
21.23
N
N
N
96
200
180
160
140
120
100
80
60
40
20
0
-20
f1 (ppm)(13C)

4.5: References

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