Direct Brønsted Acid-Catalyzed Functionalization of Benzhydryl Alcohols and 2-Ethoxytetrahydrofuran using Potassium Trifluoroborate Salts

by

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♦ ABSTRACT

Metal-free transformations of organotrifluoroborates are advantageous since they avoid using frequently expensive and sensitive transition metals. Lewis acid-catalyzed reactions involving organotrifluoroborates have emerged as an alternative to metal-catalyzed protocols. However, these methods rely on generating unstable boron dihalide species thereby resulting in low functional group tolerance.

A Brønsted acid-catalyzed carbon-carbon bond forming methodology involving alkenyl- and alkynyltrifluoroborates and *in situ* generated carbocations has been developed. In the presence of HBF_4, we have shown that organotrifluoroborates react with benzhydryl alcohols to afford alkenes and alkynes in good to excellent yields. This protocol features excellent atom economy since alcohols and organotrifluoroborates react in a 1:1 ratio. Functional group tolerance superior to Lewis acid- and metal-catalyzed approaches was demonstrated.

Furthermore, we were able to extend this method to 2-ethoxytetrahydrofuran which underwent direct substitution to afford functionalized furans in moderate to excellent yields. A variety of alkenyl- and alkynyltrifluoroborates readily participated in this transformation.

♦ ACKNOWLEDGEMENTS

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And lastly, a special thanks goes out to my mother, Carolin. Absolutely none of this would have been possible without her love and support. I would like to thank her for being my role model and my number one supporter since day one. As well, I thank her for all of the opportunities she has given me in order to reach these successes. She has taught me to work hard for what I am passionate about and to always try my best. Thank you for always telling me how proud you are of me, especially when I needed it most. My work ethic and strength comes from her. ♥

"There's a drive in me that won't allow me to do certain things that are easy."

– JOHNNY DEPP –

♦ TABLE OF CONTENTS

♦ LIST OF TABLES

♦ LIST OF FIGURES

♦ LIST OF SCHEMES

LIST OF ABBREVIATIONS

DMSO	dimethyl sulfoxide
EtOAc	ethyl acetate
equiv	equivalents
TMS	trimethylsilyl
Et_2O	diethyl ether
CH_3CN	acetonitrile
DCM	dichloromethane
THF	tetrahydrofuran
THP	tetrahydropyran
HCl	hydrochloric acid
$KMnO_4$	potassium permanganate
PMA	phosphomolybdic acid
TLC	thin layer chromatography
HRMS	high resolution mass spectrometry
ESI	electrospray ionization
EI	electron impact
DART	direct analysis in real time
TOF	time-of-flight
aq	aqueous
h	hour(s)
Ph	phenyl
Boc	*tert*-butyloxycarbonyl
vs	versus
NMR	nuclear magnetic resonance
IR	infrared spectroscopy
HBF_4	tetrafluoroboric acid
FDA	Food and Drug Administration
MOM	methoxymethyl
HF	hydrogen fluoride
TfOH	trifluoromethanesulfonic acid
FDA	Food and Drug Administration
NDA	New Drug Application

♦ 1. INTRODUCTION

1.1 POTASSIUM TRIFLUOROBORATE SALTS

1.1.1 ORGANOBORON COMPOUNDS

In recent years, organoboron compounds have been increasingly used as reagents for carbon-carbon bond formation. Namely, this is due to the fact that these reagents have a low toxicity. In addition, these reagents are compatible with a wide range of functional groups[1]. The relative non-toxic nature of organoboron-containing compounds can be further supported by their presence in prescription pharmaceuticals (Figure 1). Bortezomib was initially approved by the FDA in 2003 for the treatment of multiple myeloma and mantle cell lymphoma. More recently, tavaborole was approved by the FDA in 2014 for the treatment of onychomycosis, a fungal infection of toenails. Additionally, earlier this year, the FDA accepted Anacor Pharmaceutical's New Drug Application (NDA) for the approval of crisaborole for the potential treatment of atopic dermatitis. Results from the FDA with regards to this review are anticipated early next year.

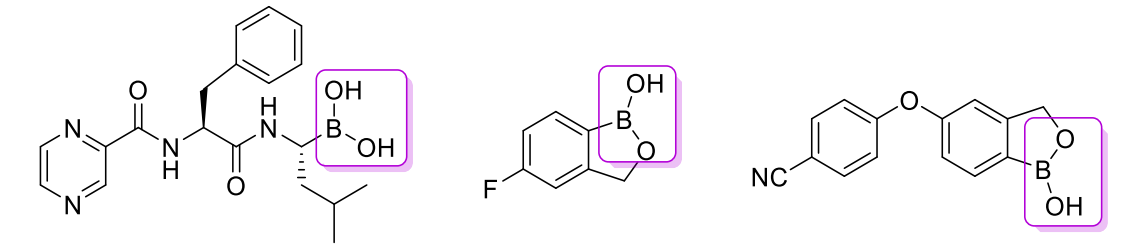


Figure 1: Organoboron-containing pharmaceuticals

Boronic acids and boronate esters are two popular subclasses of organoboron compounds (Figure 2). However, their prolonged storage is not without issues. Boronic acids usually contain boroxines, also known as boronic acid anhydrides, resulting in

difficulties in stoichiometry determination[2]. When the hydroxyl groups of boronic acids are replaced by alkoxy or aryloxy groups, this results in the formation of boronate esters. This is advantageous since with the hydroxyl groups removed, boronate esters lose the capability of acting as hydrogen bond donors and are, therefore, less polar and easier to handle[3]. However, although they display a higher stability as compared to free boronic acids, they are generally less reactive[2]. Furthermore, both boronic acids and boronate esters are sensitive to air and moisture due to the presence of an empty p-orbital on the boron atom[1].

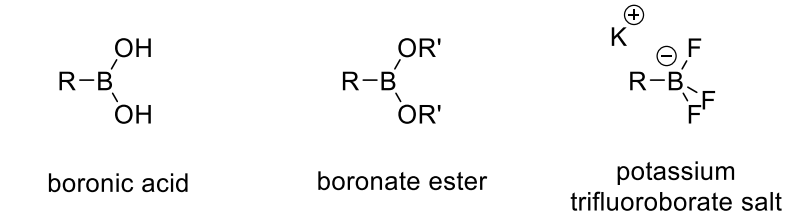
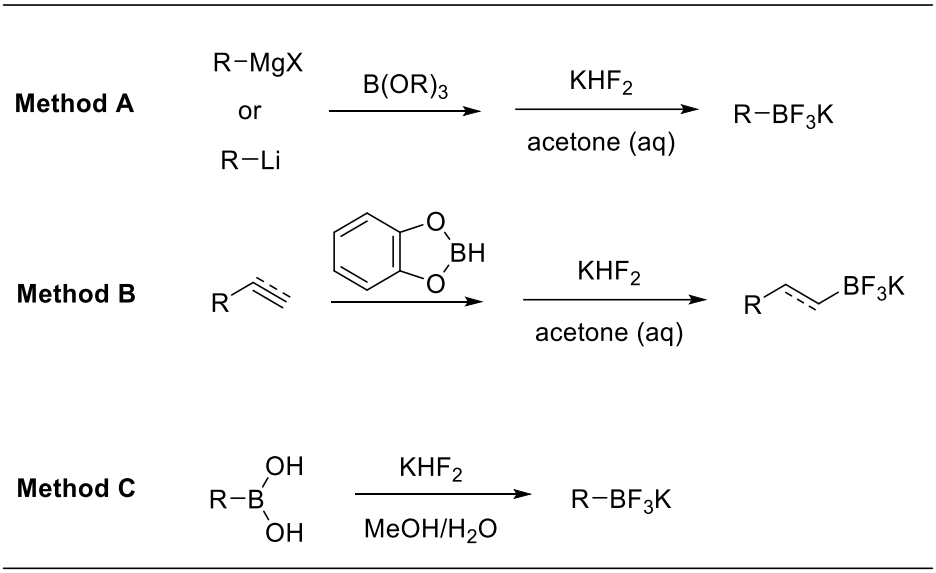


Figure 2: Organoboron compounds

In contrast, organotrifluoroborate salts have been gaining popularity as they have been shown to overcome the limitation of stability. Present as crystalline solids, they are both air and moisture stable, since they are not hygroscopic, which allows for indefinite storage at room temperature[2]. Organotrifluoroborates also exhibit greater intrinsic nucleophilicity than their boronic acid and boronate ester counterparts due to their tetracoordinated nature[4]. Furthermore, a wide variety are commercially available or can be easily prepared on a gram scale from inexpensive materials[1,2,5,6].

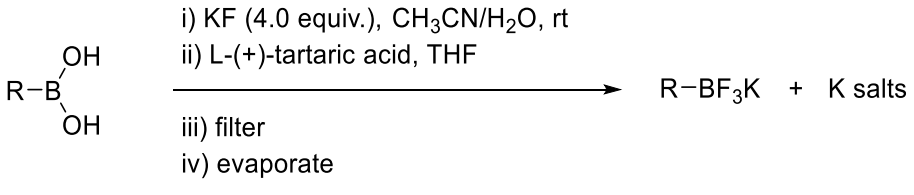
Potassium hydrogen difluoride, KHF_2, has been shown to serve as an appropriate fluorinating agent towards the synthesis of organotrifluoroborates and is compatible with many functional groups[2]. Over the years, several one-pot methods have been developed for the synthesis of trifluoroborate salts and several procedures are being continuously reported. Three general methods that use the inexpensive KHF_2 reagent are shown below and are widely used today[6] (Scheme 1). Firstly, organotrifluoroborates can be prepared from organolithium or Grignard reagents through reaction with trialkylborates and then subsequent reaction with KHF_2 (Scheme 1, Method A). Alternatively, hydroboration of alkenes or alkynes with catecholborane followed by reaction with KHF_2 would afford

alkanyl- or alkenyltrifluoroborates (Scheme 1, Method B). Lastly, treatment of boronic acids with aqueous KHF_2 is another popular method to furnish organotrifluoroborates (Scheme 1, Method C).



Scheme 1: General methods for the preparation of organotrifluoroborates

Although KHF_2 is safe to handle, the HF_2^- anion can cause extensive etching of glassware. As a result, Guy Lloyd-Jones and coworkers recently reported a new method for organotrifluoroborate preparation (Scheme 2). Through the use of KF and L-(+)-tartaric acid, a variety of aromatic, vinylic, allylic and alkyl boronic acids were converted to the corresponding organotrifluoroborate[7]. Filtration of the product mixture to remove residual KF and potassium bitartrate byproduct, followed by evaporation resulted in directly obtaining the organotrifluoroborate product. The methodology was also applied to pinacol boronates.



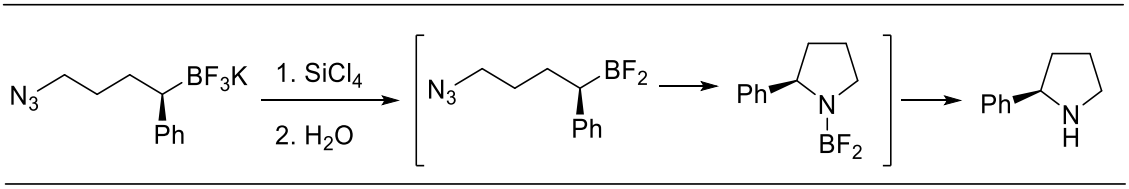
Scheme 2: Preparation of organotrifluoroborates salts under non-etching conditions

1.1.2 METAL-FREE REACTIONS OF TRIFLUOROBORATES

Organotrifluoroborates have been shown to act as boronic acid equivalents in palladium-catalyzed Suzuki-Miyaura couplings[8]. However, our research is focused on the development of metal-free reactions of organotrifluoroborates. Metal-free transformations of organotrifluoroborates are becoming increasingly prevalent due to the cost and toxicity associated with transition metals[9]. Namely, Lewis acid-catalyzed reactions have emerged as an alternative to metal-catalyzed protocols.

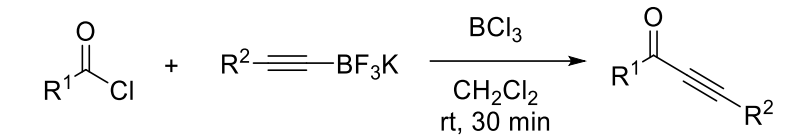
1.1.2.1 LEWIS ACID-CATALYZED REACTIONS OF TRIFLUOROBORATES

In 2002, Matteson and coworkers developed a mild and efficient route to the synthesis of asymmetric secondary amines via an intramolecular reaction between azides and alkyltrifluoroborates (Scheme 3). In this method, the Lewis acidic tetrachlorosilane defluorinates the alkyltrifluoroborate salt to yield the reactive alkyldifluoroborane intermediate[10].



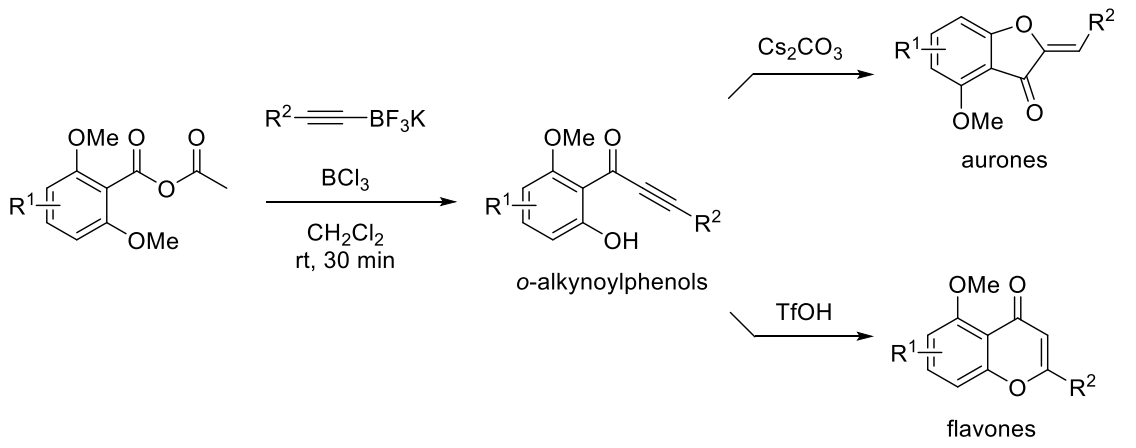
Scheme 3: Lewis acid-catalyzed reaction of azide and difluoroborane intermediate

More recently, our group has described a straightforward method for the preparation of ynones from acyl chlorides and alkynyltrifluoroborate salts in the presence of a Lewis acid (Scheme 4). Reactive organodichloroborane intermediate is formed upon exposure of alkynyltrifluoroborates with BCl_3[11].



Scheme 4: Lewis acid-catalyzed alkynylation of acyl chlorides

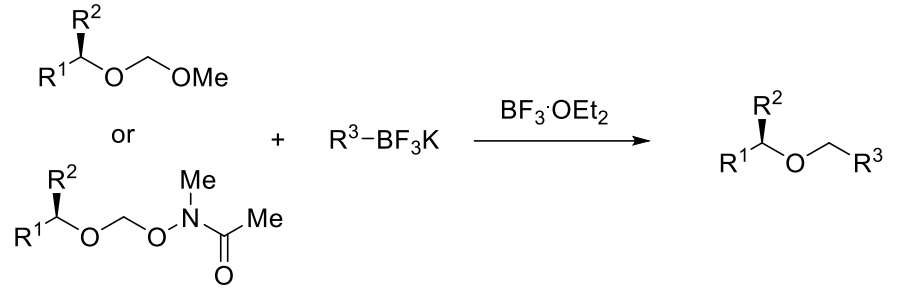
Our group was then able to employ a similar BCl_3 catalyzed protocol for the synthesis of sterically hindered *ortho*-demethylated ynones from mixed anhydrides and potassium alkynyltrifluoroborate salts (Scheme 5). The 2-hydroxy substituted ynone products were then converted to biologically active natural product scaffolds[12].



Scheme 5: Lewis acid-catalyzed preparation of sterically hindered ynones and their application to the synthesis of aurones and flavones

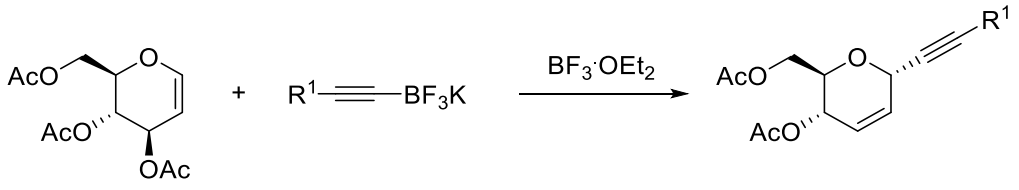
Additionally, organotrifluoroborates have also been shown to react with boron trifluoride ($BF_3{\cdot}OEt_2$). In 2009, Bode and coworkers developed a method for the synthesis of dialkyl ethers from *O*-methoxymethyl (MOM) acetals and aryl-, alkenyl- or alkynyltrifluoroborate salts (Scheme 6) [13]. In this method, interaction of trifluoroborate with $BF_3{\cdot}OEt_2$ resulted in the formation of Lewis acidic organodifluoroborane species. Although this reaction tolerated aryl-, alkenyl- and alkynyltrifluoroborates, electron-deficient substrates resulted in poor yields. Later in 2011, Bode and coworkers were able

to improve the reaction conditions through the use of a hydroxamate leaving group. This resulted in improved regioselectivity of challenging substrates, higher yields of the dialkyl ether products, reduction of the equivalents of Lewis acid and organotrifluoroborate as well as allowed for electron-withdrawing (hetero)-aryls to be present[14].



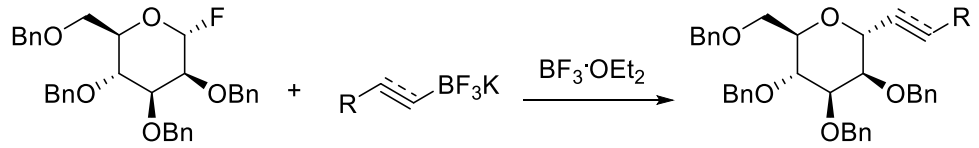
Scheme 6: Lewis acid-catalyzed synthesis of dialkyl ethers from organotrifluoroborates and acetals

Stefani and coworkers developed a highly stereoselective and mild method for the *C*-glycosidation of 3,4,6-tri-*O*-acetyl-D-glucal with alkynyltrifluoroborates (Scheme 7). This reaction was mediated by $BF_3{\cdot}OEt_2$ Lewis acid. They proposed that reaction of BF_3 and alkynyltrifluoroborate facilitates the generation of the organodifluoroborane Lewis acid. Activation of 3,4,6-tri-*O*-acetyl-D-glucal with organodifluoroborane results in the formation of an oxocarbenium ion and a nucleophilic tetracoordinated boron species. Attack at the C-1 position resulted in the formation of a variety of α-*C*-glycosides[15].



Scheme 7: Lewis acid-catalyzed synthesis of α-*C*-glycosides from potassium alkynyltrifluoroborates and D-glucals

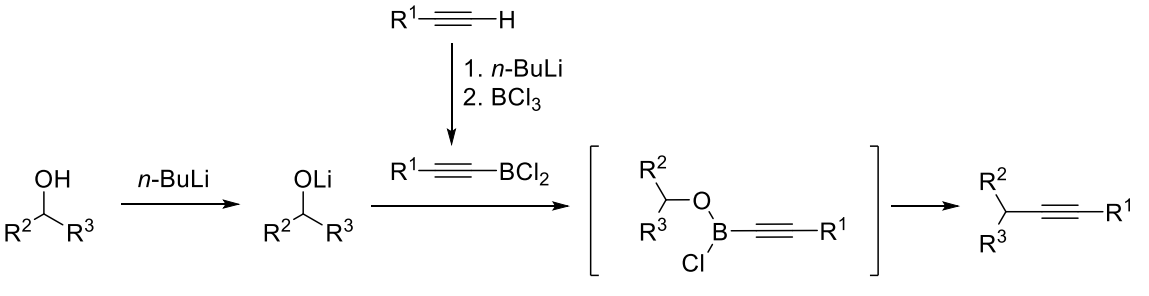
Liu and coworkers were also able to employ a $BF_3{\cdot}OEt_2$ mediated *C*-glycosylation approach through the coupling of organotrifluoroborates and glycosyl fluorides (Scheme 8). Alkenyl and alkynyl *C*-glycosides were obtained in good to excellent yields with high diastereoselectivity[16].



Scheme 8: Lewis acid-catalyzed direct *C*-glycosylation of glycosyl fluorides with organotrifluoroborates

1.1.2.1.1 REACTIONS OF ORGANODICHLOROBORANES WITH BENZHYDRYL ALCOHOLS

In 2006, Kabalka and coworkers have shown that the substitution of hydroxyl groups of benzhydryl alcohols can occur using alkynylboron dihalides[17] (Scheme 9). They reported a novel method for directly converting aryl and aliphatic alkynes to the corresponding alkynylboron dichlorides without the necessity to pre-form alkynyltrifluoroborates. Migration of the alkynyl group from boron to carbon occurs forming a variety of internal acetylenes in moderate to excellent yields.



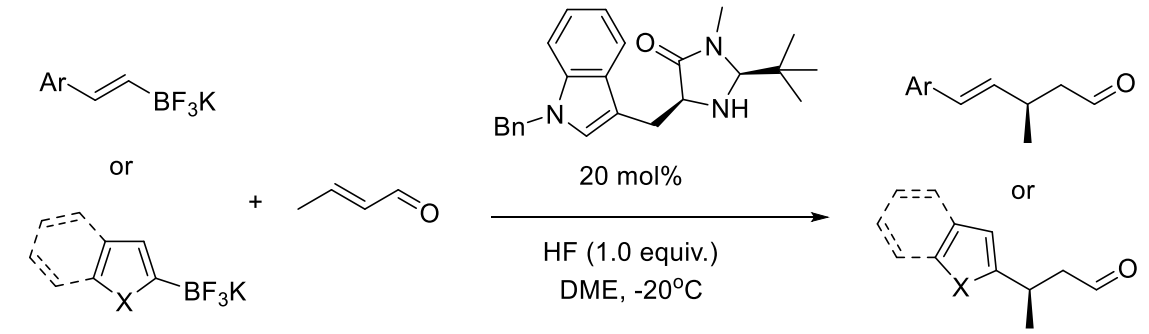
Scheme 9: Substitution of hydroxyl groups of benzhydryl alcohols with Lewis acidic alkynylboron dihalides

In summary, metal-free Lewis acid-catalyzed reactions of organotrifluoroborates have been extensively studied. However, the limitations of these protocols include the necessity to preform unstable boron dihalide intermediates thereby resulting in a narrow substrate scope.

1.1.2.2 REACTIONS OF TRIFLUOROBORATES WHICH OCCUR IN THE PRESENCE OF BRØNSTED ACIDS

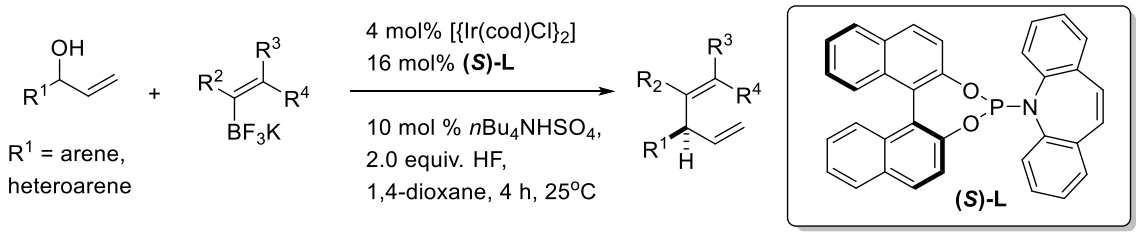
Contrary to the previously outlined methods for the Lewis acid-catalyzed reactions of organotrifluoroborates, Brønsted acid catalyzed reactions of organotrifluoroborates are uncommon. A literature survey only resulted in the findings that organotrifluoroborates have been shown to participate in reactions whereby Brønsted acids are present.

In the reaction shown by MacMillan and coworkers, vinyl and heteroaryl trifluoroborate salts were viable substrates for amine-catalyzed conjugate additions[18]. They found that exposing crotonaldehyde to organotrifluoroborates in the presence of an imidazolidinone catalyst and hydrofluoric acid resulted in the formation of the desired aldehyde products (Scheme 10). The authors suggest that the presence of HF is necessary for the sequestration of boron trifluoride by-product, by forming a BF_4K precipitate, which they confirmed by ^{19}F NMR. Notably, HF has been used for the preparation of trifluoroborate salts. Therefore, it may also act as a stabilizing agent for the trifluoroborates.



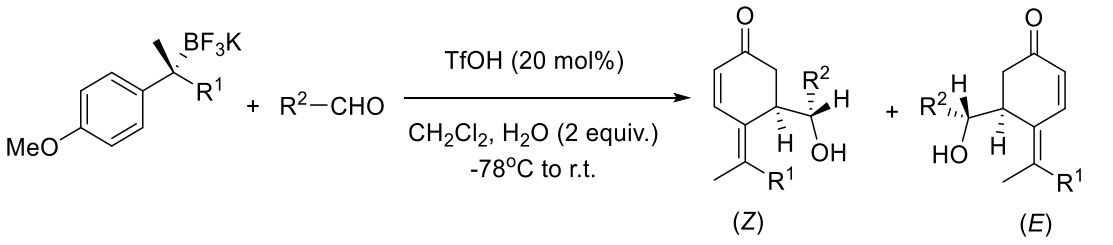
Scheme 10: Organocatalytic conjugate addition of trifluoro(organo)borates to α,β-unsaturated aldehydes in the presence of a Brønsted acid

In 2013, Carreira and coworkers showed an iridium-catalyzed asymmetric substitution reaction of allylic alcohols with vinyl trifluoroborates (Scheme 11). Although catalyzed by an Ir-(P,olefin) complex, the reaction took place in the presence of 2.0 equivalents a Brønsted acid, HF. Interestingly, in this case the authors suggested that HF was present as a trifluoroborate activator[19]. Later on, they showed that direct enantioselective substitution of allylic alcohols was possible with alkynyltrifluoroborates[20]. Notably, they were able to avoid the use of hazardous and corrosive HF in this protocol by using KHF_2 as an alternative fluoride source. Through the use of KHF_2 and CF_3COOH, they were able to generate HF *in situ*.



Scheme 11: Iridium-catalyzed enantioselective allylic vinylation using allylic alcohols and alkenyltrifluoroborates in the presence of a Brønsted acid

Aggarwal and coworkers reported the allylation-like addition of trifluoroborates to aldehydes in the presence of trifluoromethanesulfonic acid (Scheme 12). However, although a Brønsted acid was used, the procedure was mechanistically similar to Lewis acid-catalyzed transformations since a difluoroborane intermediate was formed[21].



Scheme 12: Addition of benzylic trifluoroborates to aldehydes in the presence of a Brønsted acid

1.2 RESEARCH OBJECTIVE

At the outset, we wanted to develop a set of metal-free Brønsted acid catalyzed reactions of organotrifluoroborates. By doing this, we would hopefully avoid issues associated with typical Lewis acid-catalyzed protocols, which involve the generation of unstable boron dihalide species. By avoiding the generation of Lewis acidic intermediates, there was promise to extend the substrate scope beyond ether, halide and alkyl substituents.

Inspired by the work described by Kabalka and coworkers (Section 1.1.2.1.1), we proposed that activation of benzhydryl alcohols could instead be accomplished via a Brønsted acid. Subsequently, in the presence of a nucleophilic organotrifluoroborate, reaction at the benzhydryl center could be possible. Unlike Lewis acidic boron dihalides, organotrifluoroborates do not need to be activated since they already have a tetracoordinated boron center and will readily react as nucleophiles.

1.3 BENZHYDRYL SCAFFOLDS

Development of methods for the synthesis of compounds which contain benzhydryl scaffolds are synthetically useful. Namely, the diphenylmethane scaffold is prevalent in natural products, bioactive compounds and several pharmaceuticals. The following Figure 3 illustrates three prescription pharmaceuticals present in the market which contain the benzhydryl scaffold.

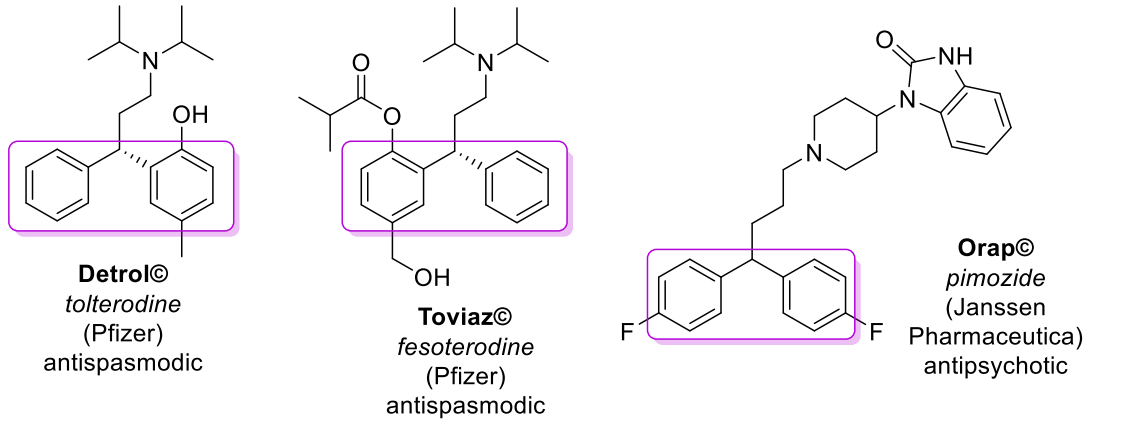


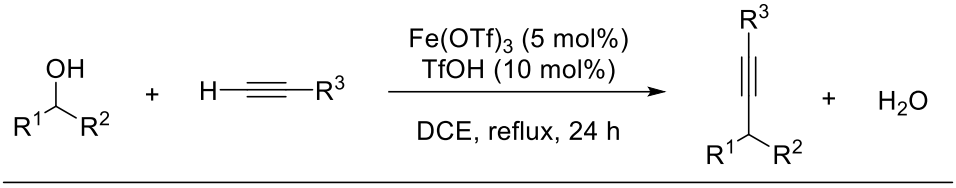
Figure 3: Benzhydryl scaffolds present in pharmaceuticals

1.3.1 SYNTHESIS OF BENZHYDRYL COMPOUNDS

1.3.1.1 METAL-CATALYZED REACTIONS OF BENZHYDRYL ALCOHOLS

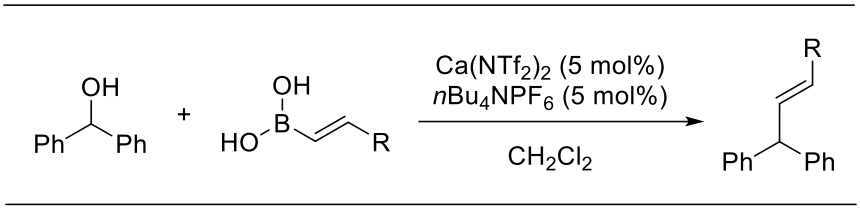
Several protocols have been described for the functionalization of benzhydryl centers[22]. However, direct metal-catalyzed dehydrative coupling reactions involving diarylmethanols have recently gained attention for several reasons. Firstly, a vast amount of diarylmethanol derivatives are commercially available or can be easily prepared. Secondly, the atom economy associated with these protocols is favourable as water is a major byproduct[23].

In 2009, Jiao and coworkers developed a sp-sp^3 carbon-carbon bond forming methodology between terminal alkynes and benzhydryl alcohols via a $Fe(OTf)_3$/TfOH co-catalyzed coupling reaction[24]. In this protocol, water was the sole byproduct (Scheme 13).



Scheme 13: Metal-catalyzed dehydrative coupling of benzhydryl alcohols with terminal alkynes

As well, metal-catalyzed alkenylation of benzhydryl alcohols are known[25]. Specifically, Gandon and coworkers have shown that the direct alkenylation of a variety of alcohols, including benzhydrols, occurs in the presence of 2.0 equivalents of vinylboronic acids through the use of a $Ca(NTf_2)_2$ catalyst[26] (Scheme 14).

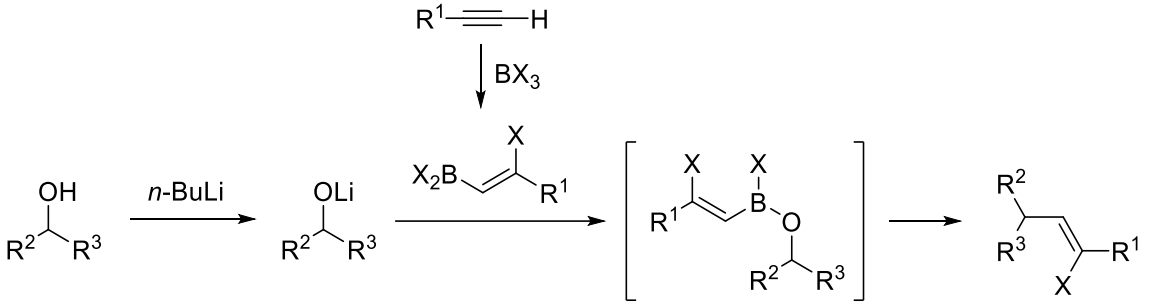


Scheme 14: Ca^{II}-catalyzed alkenylation of benzhydryl alcohols with vinylboronic acids

However, several disadvantages are present for these metal-catalyzed approaches. Specifically, these protocols oftentimes require the use of expensive, sensitive and toxic metal catalysts. As a result, low functional group tolerance is observed.

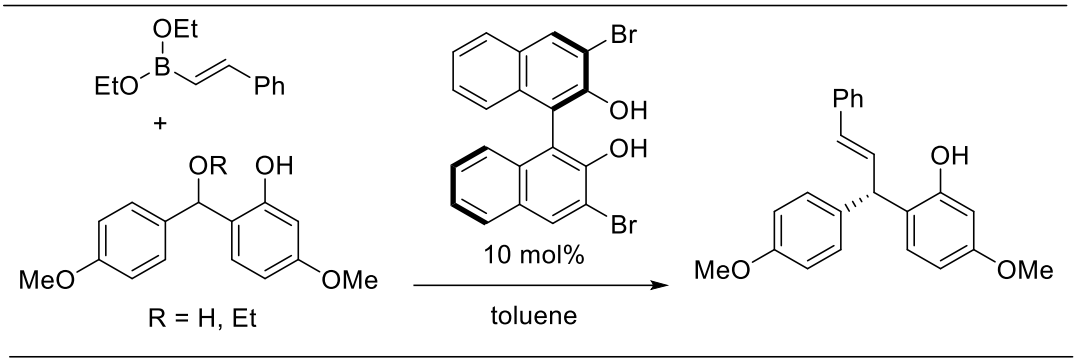
1.3.1.2 METAL-FREE REACTIONS OF BENZHYDRYL ALCOHOLS

To avoid these limitations, metal-free reactions of benzhydryl alcohols is of interest. Previously mentioned in Section 1.1.2.1.1, Kabalka and coworkers demonstrated that the substitution of hydroxyl groups of benzhydryl alcohols can occur using alkynylboron dihalides[17] (Scheme 9). They have also developed a similar metal-free methodology using benzhydryl alcohols and pre-formed alkenylboron dihalides[27] (Scheme 15). In both cases, the use of *n*-BuLi as well as the necessity to form unstable boron dihalide intermediates resulted in a narrow substrate scope.



Scheme 15: Metal-free substitution of benzylic hydroxyl groups with vinyl moieties using vinylboron dihalides

Other methods for the alkenylation of benzhydryl alcohols under metal-free conditions are known[28]. However, of interest, Schaus and coworkers illustrated that the enantioselective addition of alkenylboronates to benzhydryl alcohols and ethers occurs via a chiral biphenol catalyst[29] (Scheme 16). However, the necessity to use 2.0 equivalents of unstable alkenylboronates and the requirement of a 2-hydroxy substituted benzhydryl alcohol limits this methodology.

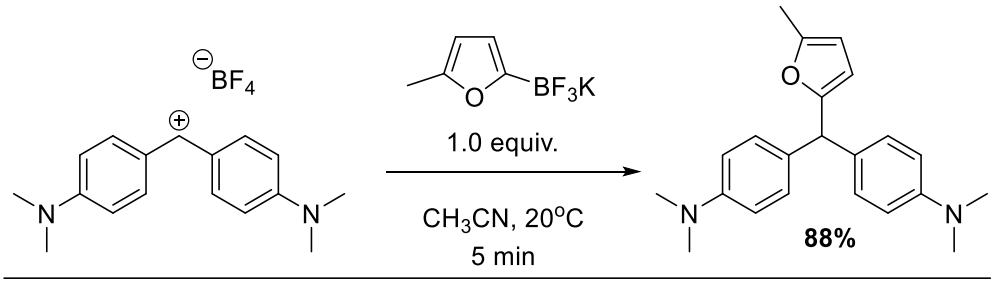


Scheme 16: Enantioselective addition of boronates to benzhydryl alcohols and ethers catalyzed by chiral biphenols

Although methods for the alkenyl- and alkynylation of benzhydryl alcohols under metal-free conditions are known, an operationally simple method, which avoids the use of *n*-BuLi, the necessity to pre-form unstable boron dihalide intermediates and avoid the use of unstable starting materials has not been developed. Furthermore, narrow substrate scopes for a number of these methods is observed.

1.3.1.3 METAL-FREE REACTION OF BENZHYDRYLIUM ION AND ORGANOTRIFLUOROBORATE

In 2012, Mayr and coworkers conducted a study which looked at determining the relative nucleophilicity of organoboron compounds in comparison with related nucleophiles[4a]. In this paper, they were able to show a single example of a pre-formed benzhydrylium carbocation reacting with a single potassium 5-methylfuran-2-yltrifluoroborate in the absence of a catalyst (Scheme 17).



Scheme 17: Transition metal-free C-C bond forming reaction of organo-trifluoroborate and benzhydrylium carbocation

1.4 α-FUNCTIONALIZED CYCLIC ETHER SCAFFOLDS

In addition to benzhydryl scaffolds, application of a Brønsted acid-catalyzed reaction of organotrifluoroborates towards the synthesis of ether scaffolds was also of interest. Ethers are an important functional group in organic chemistry as they are found among several bioactive compounds and pharmaceutical agents[30]. Tetrahydrofuran (THF) and tetrahydropyran (THP) rings are being increasingly observed in structures of new bioactive compounds and natural products[31]. Additionally, several bioactive molecules which contain α-functionalized cyclic ethers are known[32] (Figure 4).

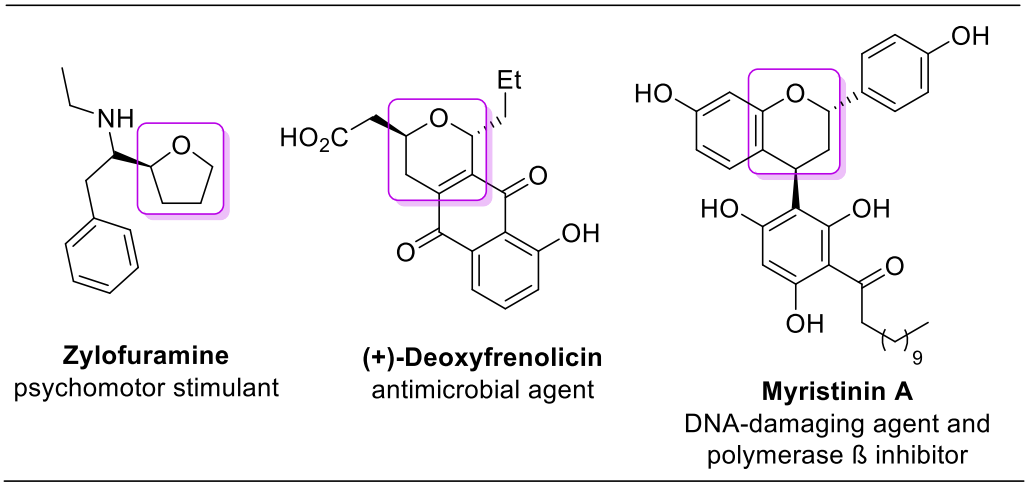


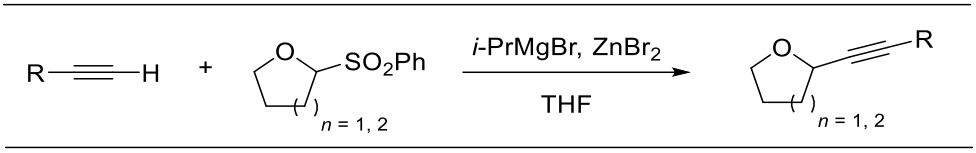
Figure 4: Bioactive molecules which contain α-functionalized cyclic ethers

1.4.1 METHODS FOR THE SYNTHESIS OF α-FUNCTIONALIZED TETRAHYDROFURANS AND TETRAHYDROPYRANS

C-glycosides are present in a number of natural products and enzymatically stable analogs of pharmaceutical importance. As a result, a number of protocols for their preparation has increased over the past several decades[33]. Namely, the carbon-carbon glycosidic bond shows an increased stability toward chemical and/or enzymatic hydrolysis. Thus, the development of new methodologies for the creation of anomeric carbon-carbon

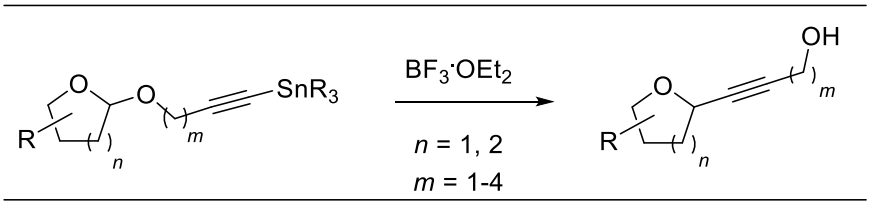
bonds is of interest. Specifically, the synthesis of 2-alkenyl and 2-alkynyl tetrahydrofurans and tetrahydropyrans haven been explored.

Ley and coworkers have shown that a direct substitution of 2-benzenesulfonyl cyclic ethers occurs by treatment with the corresponding organozinc reagents to afford alkynylated products (Scheme 18). Both 2-(phenylsulfonyl)tetrahydropyrans and 2-(phenylsulfonyl)tetrahydrofurans participated in the transformations[34].



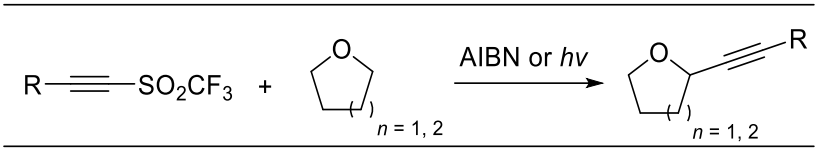
Scheme 18: Direct substitution of 2-benzenesulfonyl cyclic ethers using organozinc reagents

Later in 2004, Ley and coworkers demonstrated that anomeric oxygen to carbon rearrangements of alkynylstannane derivatives of furan and pyran rings occurs in the presence of a $BF_3{\cdot}OEt_2$ Lewis acid (Scheme 19). This rearrangement resulted in the formation of the corresponding carbon linked alkynol products[35].



Scheme 19: Rearrangements of alkynylstannane derivatives of furan and pyran rings catalyzed by $BF_3{\cdot}OEt_2$

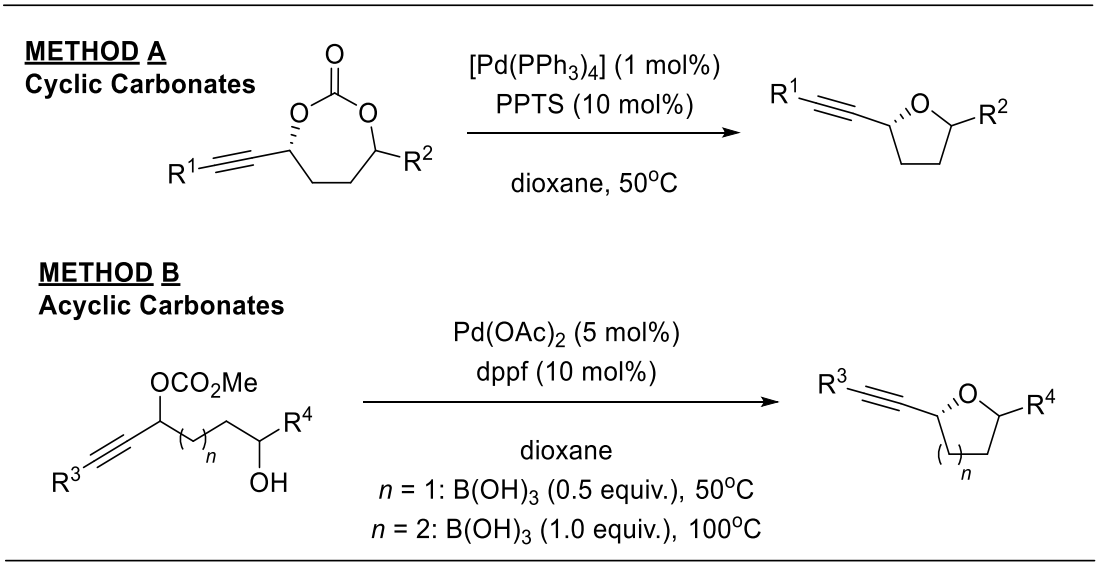
In 1996, Fuchs and coworkers showed that the alkynylation of C-H bonds occurs via reaction of THF or THP with acetylenic triflones[36]. Alkynylated furan and pyran derivatives were obtained in good to excellent yields (Scheme 20). The C-H functionalization protocol was later extended to the domain of olefins using THF and vinyl triflones[37].



Scheme 20: Alkynylation of C-H bonds via reaction with acetylenic triflones

Several additional methods for the synthesis of 2-alkenyl and 2-alkynyl tetrahydrofurans and tetrahydropyrans have been explored. However, all of these methods occur through tetrahydrofuranyl and tetrahydropyranyl α-oxy radical intermediates similar to the method described above[38].

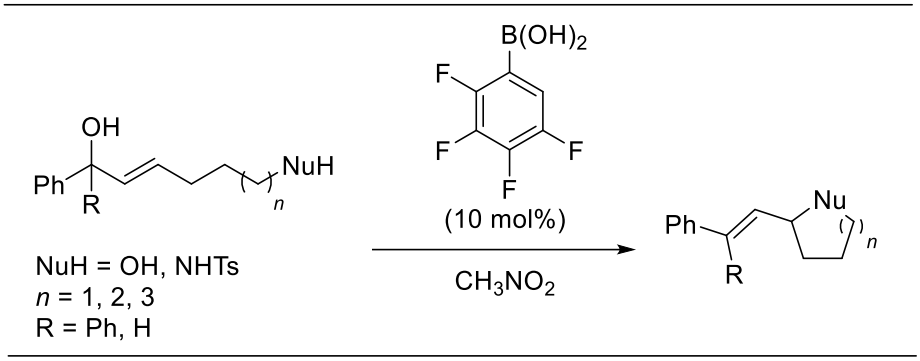
Also, Anderson and coworkers were able to prepare 2-alkynyl tetrahydrofurans and tetrahydropyrans from cyclic and acyclic carbonates (Scheme 21). These cyclizations were achieved through the use of palladium catalysts[39].



Scheme 21: Palladium-catalyzed cyclizations of cyclic and acyclic carbonates

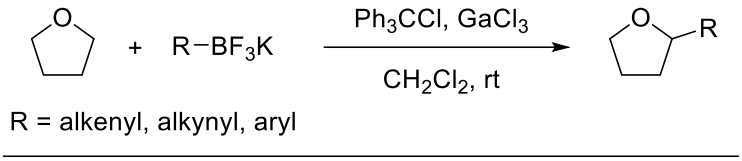
In addition, when looking at methods for the synthesis of 2-alkenyl and 2-alkynyl tetrahydrofurans and tetrahydropyrans, the use of boron-based compounds is limited. Namely, Hall and coworkers employed a boronic acid catalysis approach for the direct

cyclization of free allylic alcohols (Scheme 22). Mechanistic studies suggested that complete or near-complete ionization of allylic alcohols into allylic carbocation intermediates occurs when exposed to the boronic acid catalyst[40].



Scheme 22: Boronic acid catalyzed heterocyclizations of allylic alcohols

Additionally, Liu and coworkers illustrated that organotrifluoroborates and trityl ions can be used for the C-H functionalization of THF (Scheme 23). Trityl salts were generated by exposing trityl chlorides to $GaCl_3$ Lewis acid. This method was tolerant to alkenyl, alkynyl and aryltrifluoroborates. Mechanistic studies suggested that for THF and other saturated ethers, the trityl ion functioned as a hydride acceptor[41].

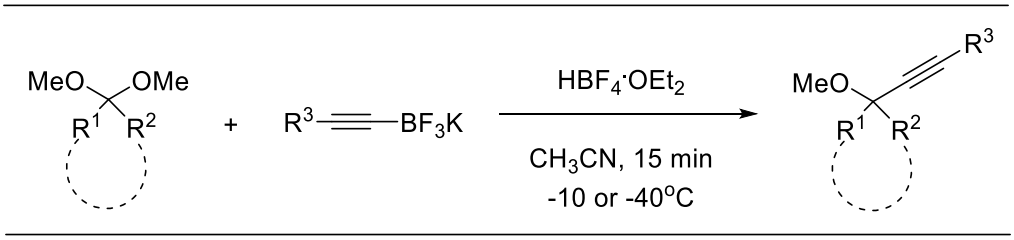


Scheme 23: C-H functionalization of THF using trifluoroborates and trityl ions

Although there are several protocols, which describe the preparation of these desired products, the necessity to use expensive metal catalysts, stoichiometric amounts of Lewis acid as well as sensitive reagents is what hinders the practicality of these methods. As a result, we wanted to develop an operationally simple protocol involving a metal-free transformation of organotrifluoroborates.

1.4.2 METAL-FREE REACTIONS OF TRIFLUOROBORATES (CONTINUED)

In addition to the methods described in Section 1.1.2 regarding metal-free reactions of trifluoroborates, our group recently developed a Brønsted-acid catalyzed methodology for the alkynylation of acetals and ketals with alkynyltrifluoroborates (Scheme 24). After the findings, which are described in the following Chapter 3 were obtained[42], this protocol for the preparation of propargylic ethers was developed as an extension of the substrates, which reacted under similar Brønsted acid-catalyzed conditions[43]. Similar to Lewis acid catalyzed methods shown by Bode[13,14] and Stefani[15], this Brønsted acid-catalyzed transformation was also proposed to occur through an oxocarbenium ion intermediate.



Scheme 24: Brønsted acid-catalyzed alkynylation of acetals and ketals with alkynyltrifluoroborates

In showing that the alkynylation of acetals and ketals occurs via a Brønsted acid catalyst, we wanted to probe at similar scaffolds, which could undergo an analogous transformation. Therefore, we envisioned that the synthesis of α-functionalized ethers could be possible if the described methodology could be extended to tetrahydrofuranyl and/or tetrahydropyranyl acetals.

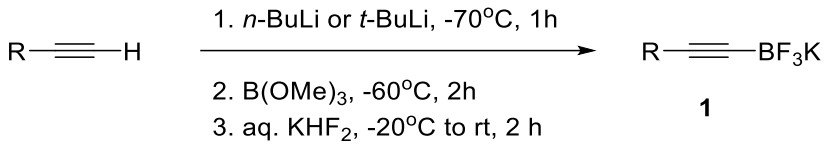
♦ 2. EXPERIMENTAL METHODS

2.1 GENERAL SYNTHETIC METHODS

All reactions were set up in 2 dram glass vials at room temperature under air. Unless otherwise noted, all other reagents and materials were obtained from commercial suppliers and used without further purification. Potassium trifluoroborate salts were synthesized according to published procedures[11,15,42,43,44]. Reaction progress was monitored *via* thin layer chromatography (TLC) on silica gel (60 Å) with visualization using ultraviolet light (254 nm) and by staining with potassium permanganate ($KMnO_4$) or phosphomolybdic acid (PMA). NMR characterization data was collected at 25°C on an Oxford AS400 NMR as solutions in deuterated solvents ($CDCl_3$, acetone-d_6 and DMSO-d_6 obtained from Cambridge Isotope Laboratories, Inc.). ^{1}H and ^{19}F NMR spectra were collected at 400 and 376 MHz, respectively, while ^{13}C $\{^{1}H\}$ and ^{11}B $\{^{1}H\}$ NMR spectra were collected at 100 and 128 MHz, respectively. Chemical shifts are expressed in ppm values. IR spectra were recorded on a Bruker ALPHA-P FTIR spectrometer using a platinum ATR with a diamond ATR crystal. Spectra are reported in terms of frequency of absorption (cm^{-1}) and only partial data is provided. Melting points were measured with a melting point apparatus and are uncorrected. High resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI), electron impact ionization (EI), direct analysis in real time (DART) ion source, and time-of-flight (TOF) mass analysis. Automated flash chromatography was conducted using a Biotage Isolera flash chromatography system using silica gel (60 Å, low acidity, obtained from SiliCycle) and reagent grade solvents.

2.2 SYNTHESIS OF POTASSIUM ALKYNYLTRIFLUOROBORATE SALTS

Potassium alkynyltrifluoroborate salts were prepared according to a known procedure[15].



General Procedure 1: To a solution of the indicated terminal alkyne (1.0 equiv.) in dry THF at −70 °C under argon atmosphere was added either *n*-BuLi or *t*-BuLi (1.0 equiv.) dropwise, and the solution was stirred for 1 h at this temperature. Trimethylborate (1.5 equiv.) was added dropwise at −60 °C. The solution was stirred at this temperature for 2 h. A saturated aqueous solution of KHF_2 (6.0 equiv.) was added at −20 °C. The mixture was allowed to stir for 1 h at −20 °C and for 1 h at room temperature. The solvent was removed under reduced pressure, and the resulting solid was placed under vacuum overnight to remove any remaining water. The solid was washed several times with hot acetone (4 × 10 mL), which was collected and concentrated to a volume of ∼10 mL. The product was precipitated with diethyl ether (30 mL) and cooled to 4 °C to complete precipitation. The crystalline solids were collected by gravity filtration and further dried under vacuum to afford alkynyltrifluoroborate salts **1a**-**k** (Figure 5).

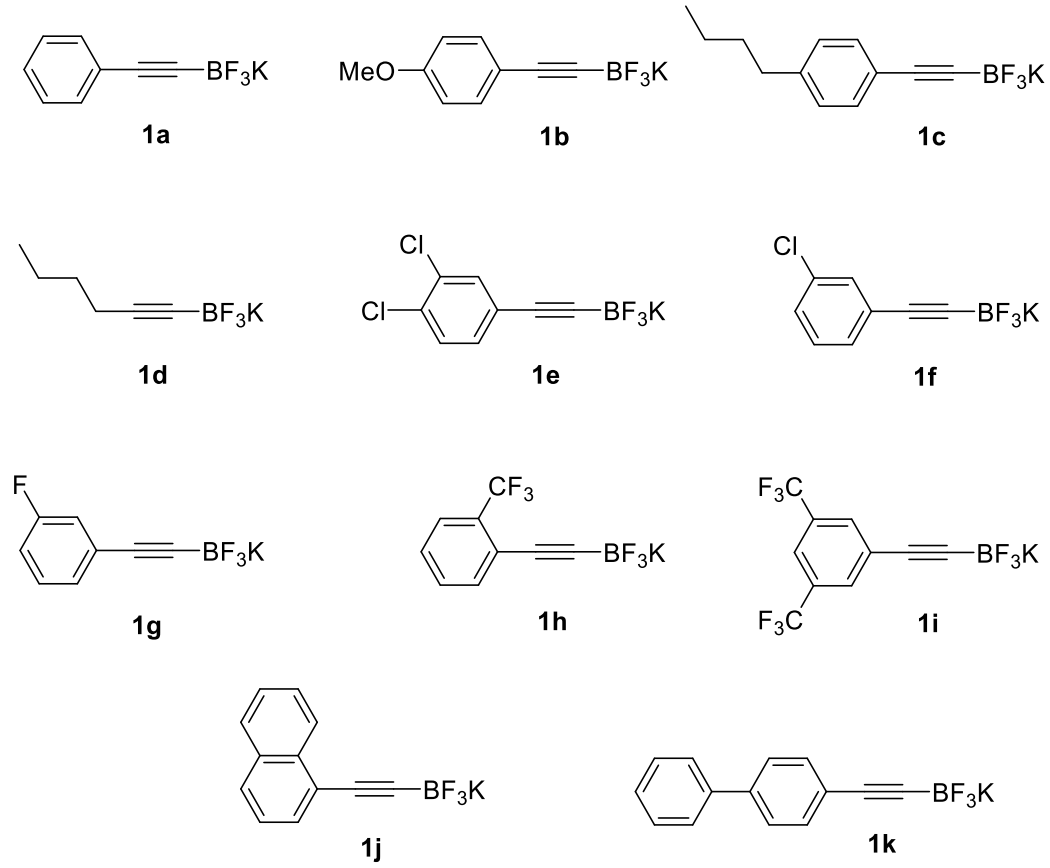
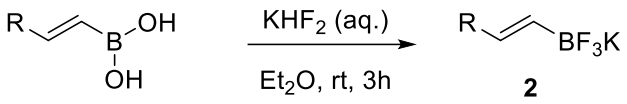


Figure 5: Potassium alkynyltrifluoroborate salts

2.3 SYNTHESIS OF POTASSIUM (*E*)-ALKENYLTRIFLUOROBORATE SALTS

Potassium (*E*)-alkenyltrifluoroborate salts were prepared according to a procedure modified from Molander and coworkers[44].



General Procedure 2: To a solution of the indicated boronic acid (1.0 equiv.) in Et_2O (6 mL) was added KHF_2 (2.8 equiv.), followed by H_2O (2.7 mL) over a period of 30 min. After stirring at rt for 3 h, the solvent was removed under reduced pressure, and the resulting solid was placed under vacuum overnight to remove any remaining water. The solid was washed several times with hot acetone (4 × 10 mL), which was collected and concentrated to a volume of ~10 mL. The product was precipitated with diethyl ether (30 mL) and cooled to 4 °C to complete precipitation. The crystalline solids were collected by gravity filtration and further dried under vacuum to afford (*E*)-alkenyltrifluoroborate salts **2a-d** (Figure 6).

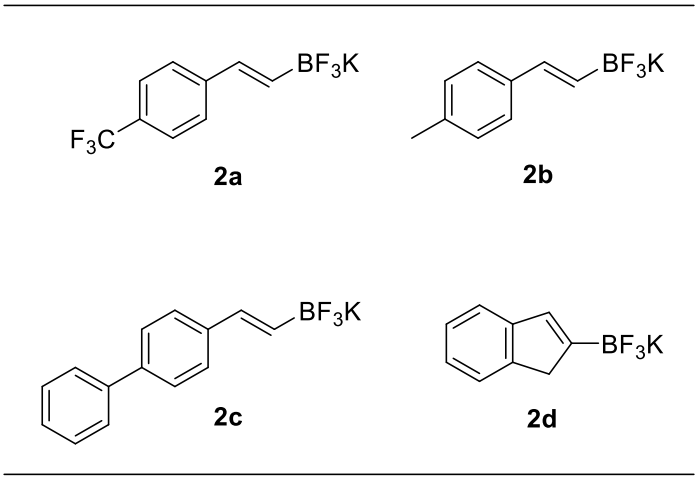
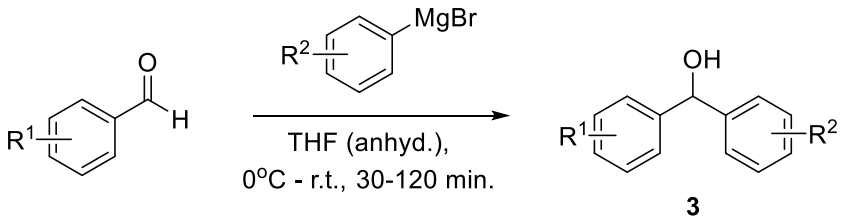


Figure 6: Potassium (*E*)-alkenyltrifluoroborate salts

2.4 SYNTHESIS OF BENZHYDRYL ALCOHOLS



General Procedure 3: A solution of the indicated benzaldehyde (1.0 equiv.) in dry THF was treated with the indicated phenylmagnesium bromide solution (1.1-4.0 equiv.) at 0 °C. After addition was complete, the mixture was allowed to stir at room temperature for 30−120 min. The reaction was quenched with aqueous 1 M HCl solution and extracted with 50 mL of EtOAc. The organic layer was washed with water (3 × 30 mL) followed by brine (1 × 25 mL). The organic layer was dried with $MgSO_4$ and concentrated. Purification by flash chromatography with hexanes/ethyl acetate afforded products **3a-i** (Figure 7).

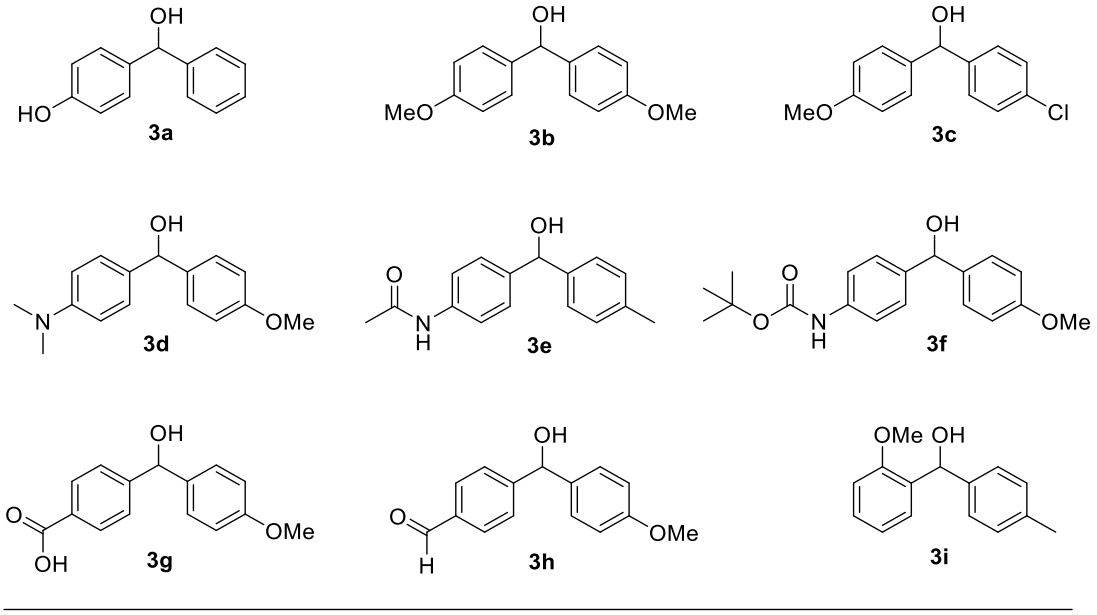
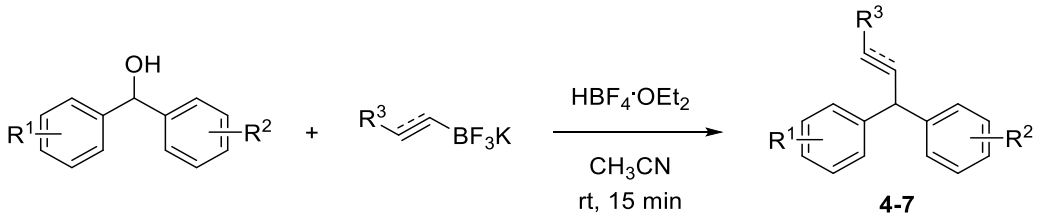


Figure 7: Benzhydryl alcohols

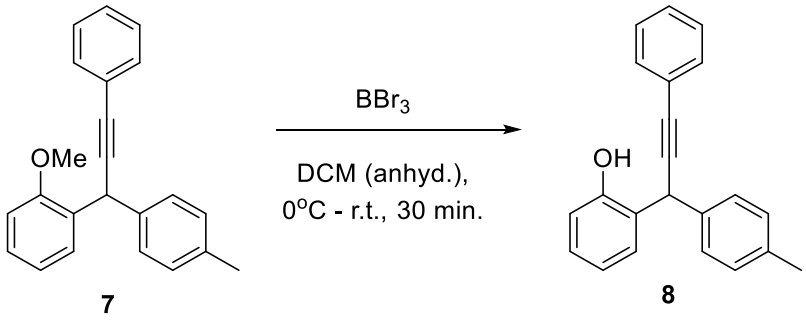
2.5 SYNTHESIS OF INTERNAL ALKENES AND ALKYNES



General Procedure 4: In a 2 mL vial containing a stir bar, the indicated benzhydrol alcohol (1.0 equiv.) and potassium trifluoroborate salt (1.0 equiv.) were added followed by addition of anhydrous acetonitrile (0.3 mL). $HBF_4 \cdot OEt_2$ (1.3-2.6 equiv.) was added dropwise, and the reaction was allowed to stir at room temperature for 15 min. The reaction was quenched with water and extracted in 20 mL of ethyl acetate. The organic layer was washed with water (3 × 15 mL) followed by brine (1 × 10 mL). The organic layer was dried with $MgSO_4$ and concentrated. The products were purified by flash chromatography with hexanes/ethyl acetate. In the cases where a CH_3CN/hexanes extraction was required, the product was solubilized in 5 mL of anhydrous acetonitrile in a 20 mL vial. Then, 1 mL of hexanes was added, forming a bilayer. The two layers were thoroughly mixed and then allowed to settle. The bottom acetonitrile layer was then removed and concentrated to afford the product. In the cases where a pentane wash was required, in a minimum of chloroform, the product was washed with 5 mL of pentane on a pipet column and eluted with diethyl ether to afford the product.

2.6 PROCEDURE FOR THE DEMETHYLATION OF **7**

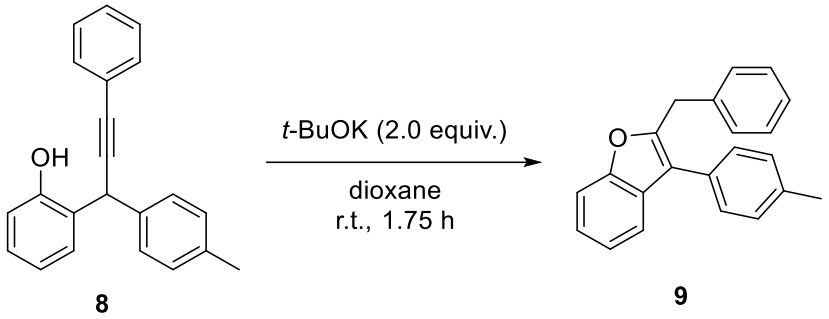
Phenol **8** was prepared according to a procedure modified from Hanson and coworkers[45].



General Procedure 5: A solution of the indicated *ortho*-methoxy-substituted product **7** (1.0 equiv.) in dry DCM (0.1 M) was treated with boron tribromide solution (3.0 equiv.) at 0 °C. After addition was complete, the mixture was allowed to stir at room temperature for 30 min. The reaction was quenched with water and extracted with 20 mL of EtOAc. The organic layer was washed with water (3 × 15 mL) followed by brine (1 × 10 mL). The organic layer was dried with $MgSO_4$ and concentrated. The product was purified by flash chromatography with hexanes/ethyl acetate and concentrated. Further purification *via* a CH_3CN/hexanes extraction afforded the desired demethylated product **8.**

2.7 CYCLIZATION OF INTERNAL ALKYNE **8**

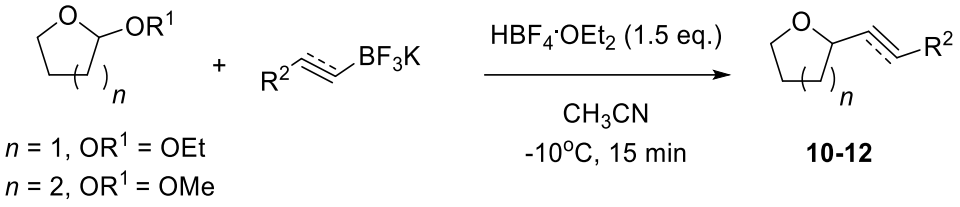
Benzofuran **9** was prepared according to a procedure by Luo and coworkers[46].



8 **9**

General Procedure 6: The indicated ortho-hydroxy-substituted product **8** (1.0 equiv.) was dissolved in anhydrous dioxane. Then, potassium *tert*-butoxide (2.0 equiv.) was added, and the reaction mixture was stirred at ambient temperature for 1.75 h. The reaction solution was then diluted with DCM (10 mL) and washed with brine (10 mL). The aqueous phase was extracted with DCM (2 × 10 mL). The combined organic phase was washed with water (3 × 15 mL) and brine (1 × 10 mL). The organic layer was dried with $MgSO_4$ and concentrated. The product was purified by flash chromatography with hexanes/diethyl ether and concentrated. Further purification via a CH_3CN/hexanes extraction afforded the desired demethylated product **9**.

2.8 SYNTHESIS OF 2-ALKENYL AND 2-ALKYNYL TETRAHYDROFURANS AND TETRAHYDROPYRANS



General Procedure 7: In a 2 dram vial containing a stir bar, the indicated potassium trifluoroborate salt (1.5 equiv.) was added at room temperature followed by the addition of anhydrous acetonitrile (C = 0.1 M). The indicated THF or THP (1.0 equiv.) was then added to the solution, and the solution was stirred at -10°C for 5 minutes. $HBF_4{\cdot}OEt_2$ (1.5 equiv.) was added to the stirring solution at -10°C. The solution was stirred at this temperature for 15 minutes. The reaction was quenched with water and extracted with 20 mL of ethyl acetate. The organic layer was washed with water (3 x 15 mL) followed by brine (1 x 10 mL). The organic layer was dried with $MgSO_4$ and concentrated. The crude product was purified by flash chromatography and concentrated. In the cases where a CH_3CN/hexanes extraction was required, the product was solubilized in 5 mL of acetonitrile and 1 mL of hexanes was added forming a bi-layer. The two layers were thoroughly mixed and cooled to 0°C in an ice bath to promote separation. The bottom acetonitrile layer was then removed and the extraction was performed again on the same hexanes layer. The acetonitrile extractions were then concentrated to afford products **10-12**.

♦ 3. METHODOLOGY DEVELOPMENT FOR THE ALKENYLATION AND ALKYNYLATION OF BENZHYDRYL ALCOHOLS WITH ORGANOTRIFLUOROBORATES

3.1 METHODOLOGY DEVELOPMENT

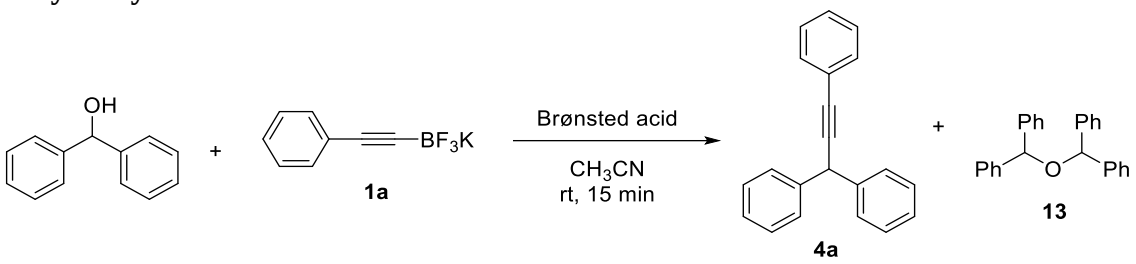
3.1.1 OPTIMIZATION OF REACTION CONDITIONS

Our initial efforts were focused on the preparation of secondary alkylacetylene **4a** from potassium phenylacetylenetrifluoroborate salt **1a** and commercially available diphenylmethanol (Table 1). After careful consideration, we chose to use tetrafluoroboric acid (HBF_4) as the catalyst. With a pK_a of 0.5 in water[47], this Brønsted acid has been shown to be strong enough to promote the formation of benzhydrylium carbocations from diarylmethanols[48]. Additionally, this Brønsted acid has a non-nucleophilic counter ion (BF_4^-) which will not react with the benzhydrylium carbocation once it is generated.

We initially began with a screen of solvents and found that the desired product **4a** was not formed in DCM (Table 1, entry 1) and DMSO (Table 1, entry 2). Alternatively, we found that when CH_3CN was used as the solvent, the reaction yielded alkyne **4a** solely in 35% yield (Table 1, entry 3).

We then focused our attention on determining the optimal equivalents of each starting material. We found that a slight excess of either diphenylmethanol (Table 1, entry 4) or potassium phenylacetylenetrifluoroborate salt (Table 1, entry 5) resulted in the formation of an inseparable mixture of product **4a** and the undesired dibenzhydryl ether byproduct **13.**

Table 1: Optimization of Conditions for the Preparation of Secondary Alkylacetylene 4a



Entry	Benzhydrol (equiv.)	BF_3K (equiv.)	Acid	Acid (equiv.)	Solvent	Yield (%)	Ratio 4a:13
1	1.0	1.0	$HBF_4{\cdot}OEt_2$	1.0	DCM	trace	
2	1.0	1.0	$HBF_4{\cdot}OEt_2$	1.6	DMSO	trace	
3	1.0	1.0	$HBF_4{\cdot}OEt_2$	1.0	CH_3CN	35	1:0
4[a]	1.2	1.0	$HBF_4{\cdot}OEt_2$	1.0	CH_3CN		4:3
5[a]	1.0	1.2	$HBF_4{\cdot}OEt_2$	1.0	CH_3CN		2:1
6[a]	1.0	1.0	$HBF_4{\cdot}OEt_2$	0.5	CH_3CN		1:1
7	1.0	1.0	$HBF_4{\cdot}OEt_2$	1.2	CH_3CN	37	25:1
8	1.0	1.0	$HBF_4{\cdot}OEt_2$	1.4	CH_3CN	37	1:0
9	1.0	1.0	$HBF_4{\cdot}OEt_2$	1.6	CH_3CN	41	1:0
10	1.0	1.0	$HBF_4{\cdot}OEt_2$	1.8	CH_3CN	36	1:0
11	1.0	1.0	$HBF_4{\cdot}OEt_2$	2.0	CH_3CN	34	1:0
12	1.0	1.0	4.0 M HCl	1.6	CH_3CN	trace	
13	1.0	1.0	$HSbF_6{\cdot}6H_2O$	1.5	CH_3CN	trace	
14[b]	1.0	1.0	$HBF_4{\cdot}OEt_2$	1.6	CH_3CN	36	1:0
15[c]	1.0	1.0	$HBF_4{\cdot}OEt_2$	1.6	CH_3CN		N/A
16[d]	1.0	1.0	$HBF_4{\cdot}OEt_2$	1.6	CH_3CN	34	1:0
17[e]	1.0	1.0	$HBF_4{\cdot}OEt_2$	1.6	CH_3CN	25	20:1

[a]The ratio has been determined by NMR analysis of crude reaction mixtures. [b]Reaction run at 0°C. [c]Reaction run at 40°C. Product and unidentified by-product synthesized. [d]Anhydrous conditions. [e]1.5 equiv. H_2O added.

Next, we looked at the effect of the acid catalyst loading on the reaction. Initially, we observed that using a substoichiometric amount of HBF_4 resulted in the formation of a 50/50 mixture of **4a** and **13** (Table 1 , entry 6). By gradually increasing the amount of HBF_4, we observed that the yield of the desired product **4a** was increasing, and that the formation of the undesired dibenzhydryl ether byproduct **13** was suppressed (Table 1, entries 7, 8). These observations were consistent with the findings that increasing the equivalents of HBF_4 results in inhibition of the formation of the dimer byproduct **13**[48]. In further increasing HBF_4 to 1.6 equivalents, we obtained a 41% yield of **4a** (Table 1, entry 9). Additional gradual increases in the amount of HBF_4 resulted in a decrease in product formation (Table 1, entries 10-11).

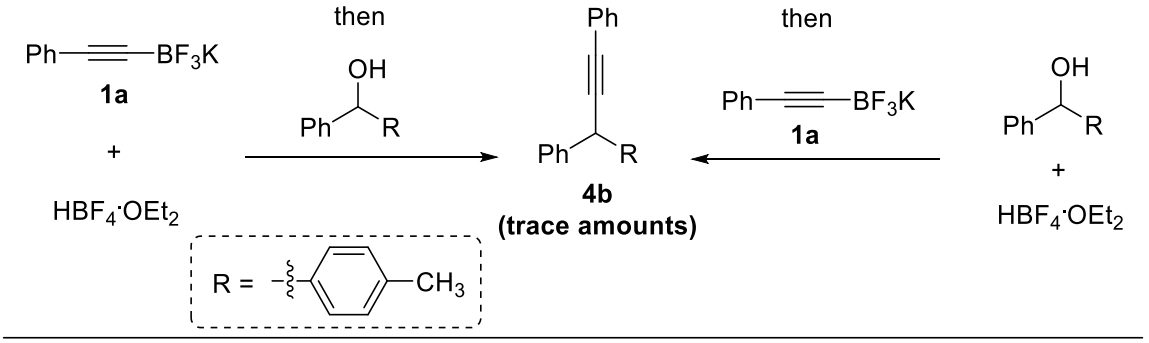
Efforts were then focused on seeing if alternative Brønsted acids could catalyze the reaction. HCl was initially tried since it could be purchased as an anhydrous solution in dioxane. This was important since the HBF_4 acid was purchased as an anhydrous complex with diethyl ether. However, only trace amounts of product was formed when HCl was used (Table 1, entry 12). Work-up NMR indicated that chlorodiphenylmethane emerged as a byproduct due to the competing reaction of the nucleophilic Cl^- anion with the benzhydrylium carbocation. Consequently, we realized that having an acid with a non-nucleophilic counter ion was important. As a result, we then wanted to see if $HSbF_6 \cdot 6H_2O$ could catalyze the reaction. This acid, like HBF_4, also contains a non-nucleophilic counter ion (SbF_6^-) which should not react with the benzhydrylium carbocation. However, this acid also only allowed for the formation of trace amounts of product **4a** to form (Table 1, entry 13). In this case, however, the starting material was not consumed. Neither the product nor the byproduct were observed.

With the tentatively optimized conditions at hand (Table 1, entry 9), we then focused our attention on manipulation of other reaction variables (Table 1, entries 14-17). With the reaction occurring within fifteen minutes at room temperature, we wanted to see the effect of reduced temperature. We observed that running the reaction at 0^oC (Table 1, entry 14) resulted in the disappearance of diphenylmethanol within thirty minutes, however, the yield decreased by 5%. We then wanted to see the effect of running the reaction at increased temperature. When the reaction was conducted at 40^oC (Table 1, entry

15), diphenylmethanol starting material disappeared within fifteen minutes, however, this resulted in the formation of an inseparable mixture of product **4a** and a new unidentified byproduct. Interestingly, the yield decreased from 41% to 34% when the reaction flask was dried and the reaction was conducted under argon (Table 1, entry 16). We then looked to see what the effect was of adding a controlled quantity of water. The yield decreased dramatically to 25% of product **4a** and trace amounts of the dibenzhydryl ether byproduct **13** was formed when 1.5 equivalents of water was introduced (Table 1, entry 17).

3.1.2 INVESTIGATION INTO THE ORDER OF ADDITION OF REAGENTS

The order of addition of reagents in this method was deemed to be very important. Initially, 4-methylbenzhydrol and potassium phenylacetylenetrifluoroborate salt **1a** were pre-stirred in acetonitrile for one minute at room temperature. No evidence of a reaction between the two starting materials was observed on TLC in the absence of the acid catalyst. Once HBF_4 was added, the reaction solution turned from a colourless transparent solution to bright yellow solution, which was translucent. Product formation was clearly evident on TLC. When the order of addition was changed, the reaction did not result in significant product formation (Scheme 25).



Scheme 25: Analyzing the order of addition of reagents

When potassium phenylacetylenetrifluoroborate salt and HBF_4 were pre-mixed, which was followed by the addition of 4-methylbenzhydrol, the reaction resulted in trace amounts of product **4b**. Several byproducts were observed on TLC. It turned out that potassium phenylacetylenetrifluoroborate salt **1a** decomposed in the presence of HBF_4. This was confirmed by a set of NMR studies (Figure 8 and Appendix III). Firstly, in deuterated acetonitrile solvent (CD_3CN), potassium phenylacetylenetrifluoroborate salt **1a** shows a signal at -134.90 ppm in a ^{19}F NMR (Figure 8, NMR A). HBF_4 shows a signal at -150.49 ppm (Figure 8, NMR B). Then, potassium phenylacetylenetrifluoroborate salt **1a** and HBF_4 were mixed in CD_3CN in an NMR tube and a ^{19}F NMR of the mixture was taken immediately. We observed that the fluorine peak of the potassium phenylacetylene-trifluoroborate salt **1a** had disappeared but that the fluorine peak for HBF_4 was still observed (Figure 8, NMR C). From looking at the proton and carbon NMRs of this reaction mixture, characteristic peaks from phenylacetylene were observed (see Appendix III for additional spectra). Therefore, we propose that when potassium phenylacetylene-trifluoroborate salt is exposed to HBF_4 in the absence of 4-methylbenzhydrol, protodeboronation occurs. As a result of the decomposition, the reaction does not take place once 4-methylbenzhydrol is added to the reaction mixture since only trace amounts of **4b** were observed.

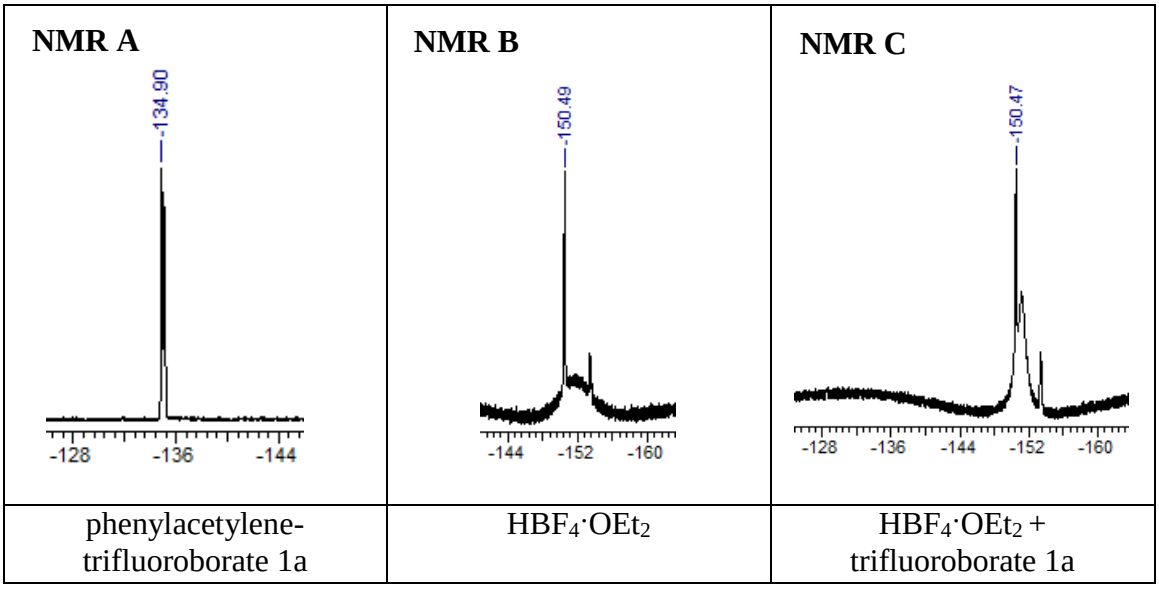


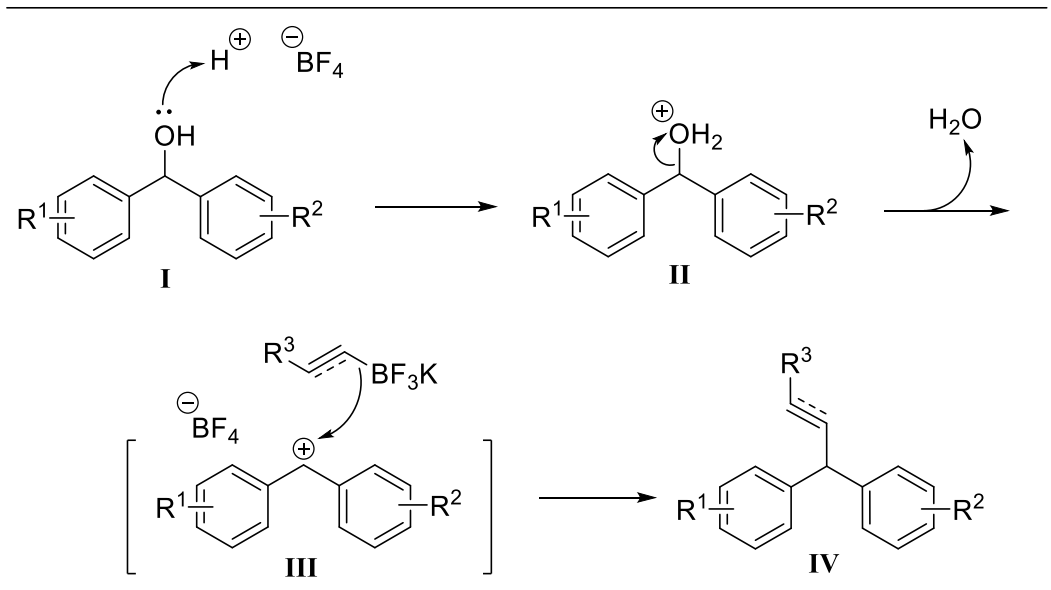
Figure 8: ^{19}F NMR study of potassium phenylacetylenetrifluoroborate 1a and $HBF_4 \cdot OEt_2$ in CD_3CN

Similarly, when potassium phenylacetylenetrifluoroborate **1a** was added to a mixture of 4-methylbenzhydrol and HBF_4, only trace amounts of desired product **4b** were observed on TLC (Scheme 25). After leaving the reaction for several hours, a significant amount of 4-methylbenzhydrol was still observed on TLC and only a faint product spot had appeared. After no change in the TLC after several hours, this illustrated that pre-mixing 4-methylbenzhydrol and HBF_4 was not advantageous.

Therefore, we found that it was imperative to add the HBF_4 catalyst as the last reagent in order for significant formation of the desired product.

3.2 PROPOSED MECHANISTIC PATHWAY

Illustrated in the following Scheme 26 is our proposed mechanistic pathway for the formation of internal alkenes and alkynes. We suggest that a Brønsted acid would protonate the hydroxyl group of the benzhydryl alcohol (**I**). Subsequently, the protonated alcohol, will dissociate in the form of a water molecule from the diphenylmethane compound (**II**) thus generating the benzhydrilum ion (**III**). The nucleophilic trifluoroborate present in the solution will then react with the electrophilic center, thus forming the final product (**IV**).



Scheme 26: Proposed mechanistic pathway for the preparation of internal alkenes and alkynes

3.3 RESULTS AND DISCUSSION

With the developed reaction conditions at hand, our next step was to look at the scope of benzhydryl alcohols and organotrifluoroborate salts that are capable of participating in the reaction.

3.3.1 REACTIONS OF PHENYLACETYLENETRIFLUOROBORATE SALT WITH BENZHYDRYL ALCOHOLS

Initial investigation into the substitution effects revealed that benzhydryl alcohols containing electron-donating substituents resulted in higher yields of the desired products as compared to when electron-withdrawing substituents were present (Figure 9). As previously discovered, when unsubstituted benzhydrol was used, product **4a** was obtained in 41% yield. Furthermore, the yield of **4b** was 67% when an electron-donating 4-methyl substituent was present. The reaction exhibited mild sensitivity to the steric hindrance. Electron-donating methyl group in the 2-position resulted in modest 51% yield of product **4c**.

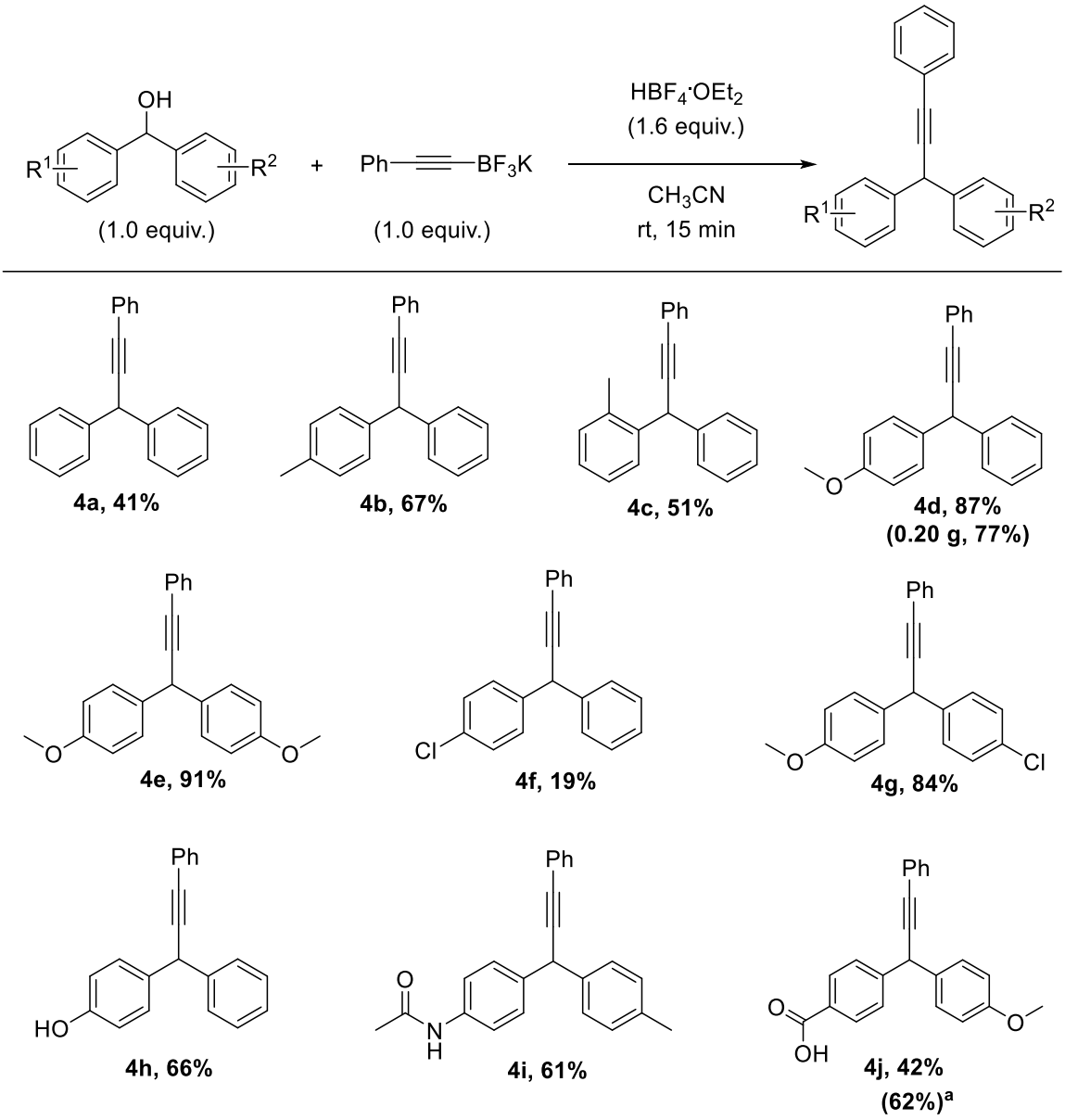


Figure 9: Reactions of phenylacetylenetrifluoroborate salt with benzhydryl alcohols. [a]Using 1.3 equiv of HBF_4

The yield further increased when stronger electron-donating 4-methoxy group was present. Product **4d** was obtained in excellent 87% yield. Notably, a scale-up reaction afforded 0.20 g of **4d** with a yield erosion of only 10%. Product **4e** was obtained in an even higher 91% yield when two methoxy groups were present in the *para*-positions. Conversely, a low 19% yield of product **4f** was obtained when an electron-withdrawing 4-

chloro group was present. We propose that destabilization of the carbocation intermediate occurs in the presence of electron-withdrawing groups. As a result, several unidentified byproducts were observed.

Next, we then wanted to explore into whether the destabilizing electron-withdrawing effect of one substituent in the 4-position could be off-set if an electron-donating group was present in the 4'-position. When (4-chlorophenyl)(4-methoxyphenyl)methanol was used, product **4g** was obtained in excellent 84% yield. Seemingly, the negative effect of an electron-withdrawing group can be overcome by applying this method.

Furthermore, we were pleased see that we were able to expand the scope to unprotected protic functional groups. Free phenol- and amide-containing substrates afforded products **4h** and **4i** in 66 and 61% yields, respectively. When a carboxylic acid functional group was present, modest 42% yield of **4j** was observed. However, we proposed that the carboxylic acid moiety could act as a source of protons during the reaction. As a result, we thought that in combination with the HBF_4 acid catalyst, excessive amounts of acid present could have been responsible for the poor yield of **4j**. Consequently, we found that the yield increased to 62% when the amount of HBF_4 was reduced to 1.3 equivalents.

3.3.2 REACTIONS OF VARIOUS ALKYNYLTRIFLUOROBORATES WITH BENZHYDRYL ALCOHOLS

Next, we looked to investigate into the scope of potassium alkynyltrifluoroborate salts that were tolerant to this method (Figure 10). A wide range of phenylacetylenetrifluoroborate salts that contained trifluoromethyl, chloro and fluoro functional groups acted as sufficient coupling partners to afford the desired products **5a-5e** in excellent yields. Notably, product **5e** was obtained in 82% yield when an unprotected aldehyde group was present on the benzhydryl alcohol. Furthermore, unsubstituted biphenyl- and naphthylacetylenetrifluoroborates afforded the desired products (**5f-5h**) in good yield.

We then looked to examine other substituents which were tolerant to the methodology. More specifically, we were able to expand the substrate scope to benzhydryl alcohols, which contained an amine functional group. The presence of a dimethylamine functional group resulted in a modest 53% yield of **5i**. In the presence of acid, the basic amine functional group could undergo protonation. As a result, we decided to increase the acid-to-substrate ratio with the expectation of obtaining an increased product yield. With the addition of 2.6 equivalents of HBF_4 (one equivalent more than the usual acid loading), we were able to improve the yield of **5i** to 61%. We then applied the same conditions to a benzhydryl alcohol, which contained a Boc-protected amine. We obtained a 51% yield of the deprotected product **5j**. This was to be expected since the Boc group is stable towards most bases and nucleophiles, however, it is acid-labile.

Hexynyltrifluoroborate salt was a good coupling partner in addition to the previously observed phenylacetylenetrifluoroborate derivatives. Desired product **5k** was formed in 73% yield.

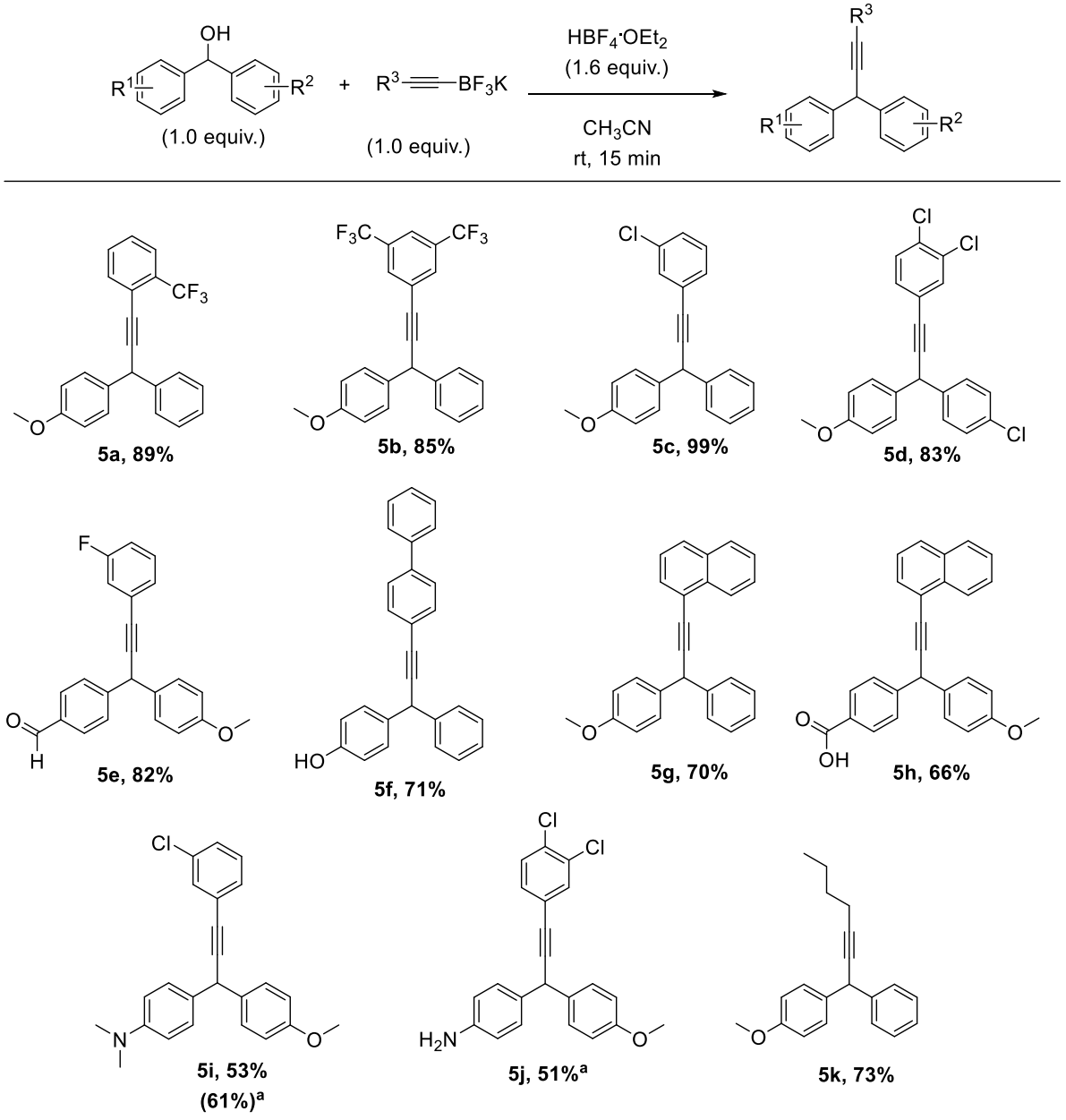


Figure 10: Reactions of various alkynyltrifluoroborates with benzhydryl alcohols. [a]Using 2.6 equivalents of HBF_4. For 5j, Boc-protected amine was used as the starting material.

3.3.3 REACTIONS OF *TRANS*-STYRYLTRIFLUOROBORATES WITH BENZHYDRYL ALCOHOLS

To our delight, we observed that potassium alkenyl trifluoroborate salts readily participated in the developed methodology (Figure 11). More specifically, alkenyl trifluoroborates such as potassium *trans*-styryl and 2-(3-fluorophenyl)vinyltrifluoroborate salts afford the desired products in good to excellent yields (**6a-6e**). Consistent with our previous findings, increasing the amount of HBF_4 from 1.6 to 2.6 equivalents in the presence of a dimethylamine substituent translated to a yield increase of **6d** from 67% to 84%. As well, decreasing the amount of HBF_4 from 1.6 to 1.3 equivalents in the presence of a carboxylic acid containing benzhydryl alcohol resulted in a modest yield increase of **6e** from 71% to 77%.

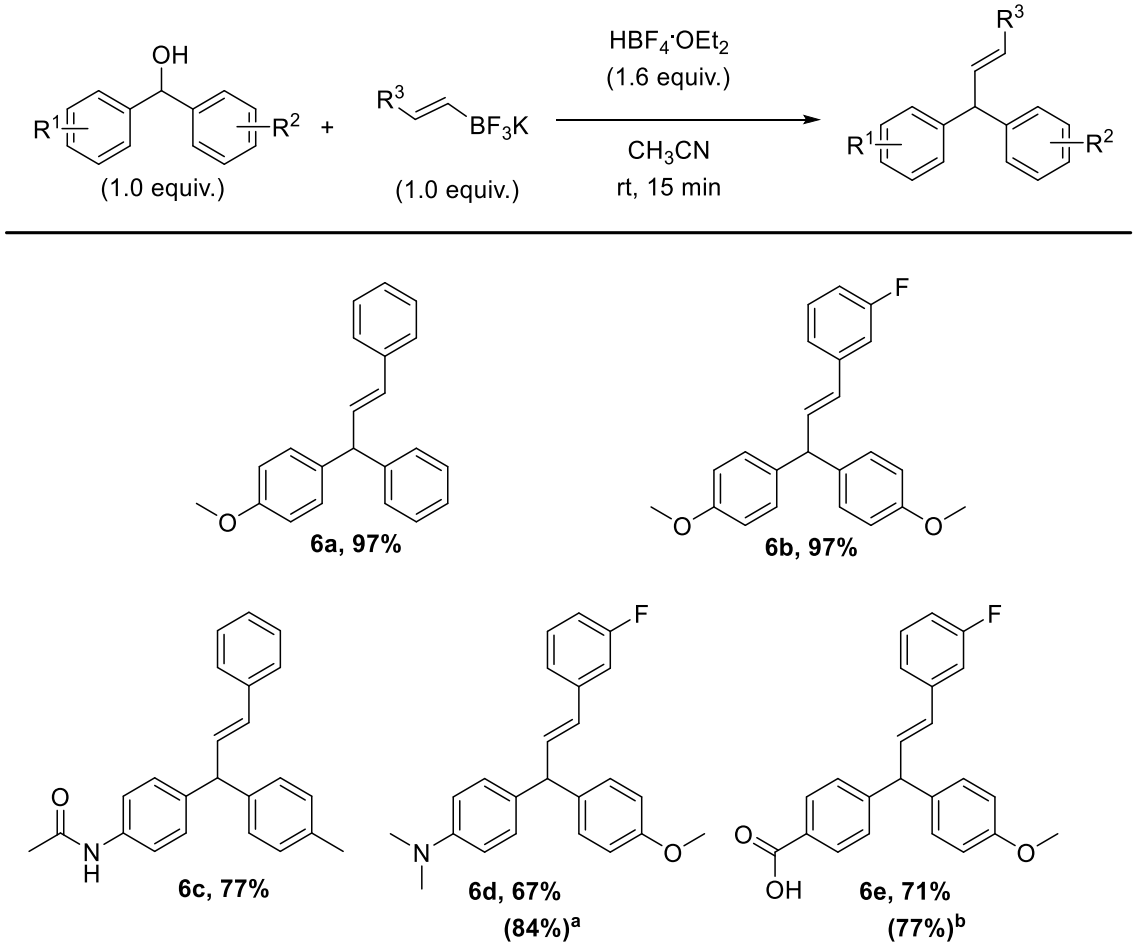


Figure 11: Reactions of *trans*-styryltrifluoroborates with benzhydryl alcohols. Using [a]2.6 or [b]1.3 equiv of HBF_4.

3.3.4 UNSUCCESSFUL TRIFLUOROBORATE SALT COUPLING PARTNERS

When looking into the substrate scope of organotrifluoroborates, a few did not prove to be successful coupling partners (Figure 12). More specifically, potassium phenylacetylenetrifluoroborate salts that contained *para*-methoxy (**1b**) or *para*-butyl (**1c**) groups did not react to form the desired products. Instead, the reactions resulted in the consumption of the benzhydrol starting material and subsequent formation of multiple unidentified byproducts. This illustrates that the method is not tolerant to phenylacetylenetrifluoroborates containing electron donating groups. This is contrary to what was observed in the above substrate scope, whereby, electron withdrawing halide groups on the phenylacetylenetrifluoroborates proved to be successful coupling partners. As a result, electron-rich trifluoroborates were poor coupling partners.

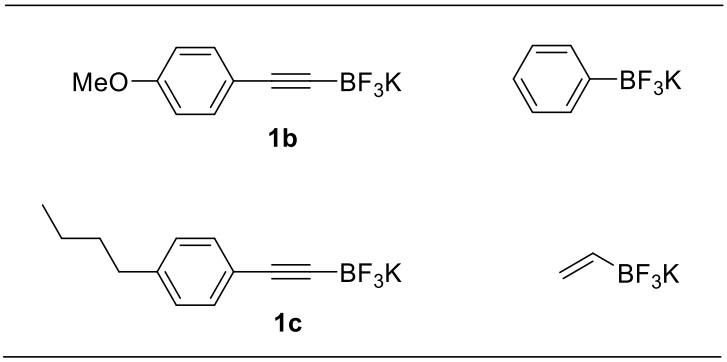


Figure 12: Organotrifluoroborates that did not participate in the developed methodology

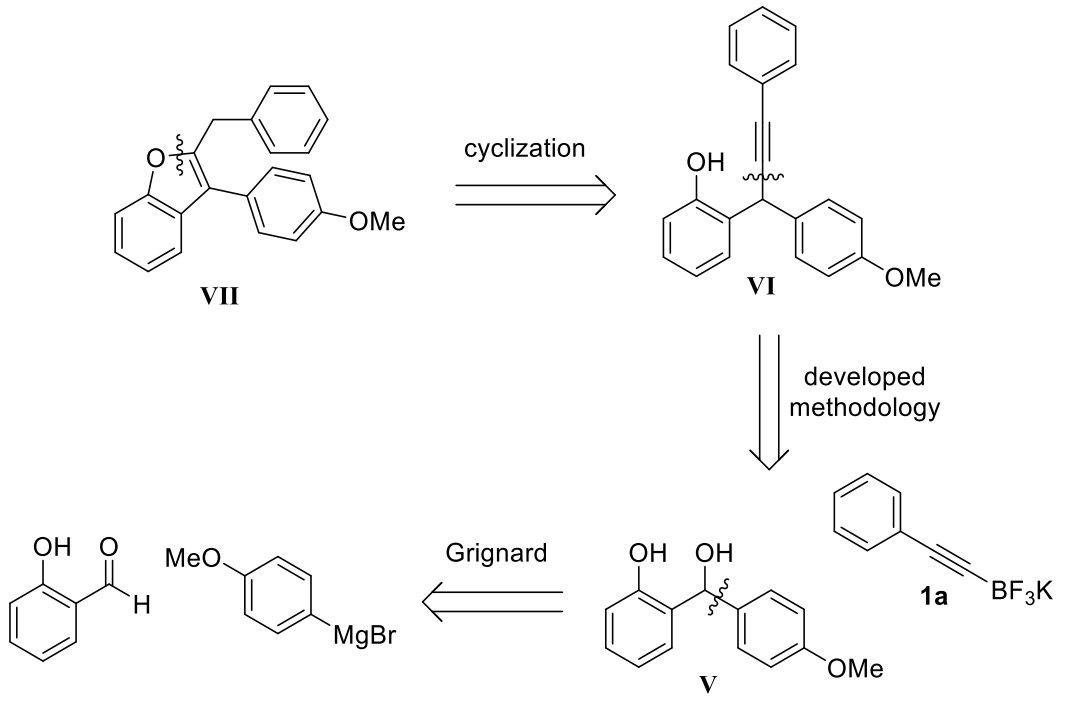
With hopes to expand the substrate scope to aryltrifluoroborates, we attempted the coupling reaction with potassium phenyltrifluoroborate salt. However, these efforts were unproductive as multiple byproduct spots were observed on a TLC plate. Moreover, benzhydrol starting material was still present after leaving the reaction for several hours. Due to no change in the concentration of starting material estimated by TLC, potassium phenyltrifluoroborate salt was likely decomposed by HBF_4.

Lastly, we observed that alkenyl trifluoroborate salts proved to be successful coupling partners in the developed methodology (Figure 11). Therefore, we wanted to see

if potassium vinyltrifluoroborate salt would react to afford the desired product. However, similar results were observed as in the case of potassium phenyltrifluoroborate, whereby, multiple byproducts were formed and benzhydrol starting material was still present after several hours.

3.3.5 APPLICATION OF THE DEVELOPED METHODOLOGY TO THE SYNTHESIS OF BENZOFURAN **9**

To illustrate the utility of the established method, we developed a preparation of synthetically useful benzofurans. Annulations of o*rtho*-propargyl phenols have been shown to occur in the presence of bases to form 2,3-disubstituted benzofurans[46]. We decided to apply this cyclization procedure to a product synthesized via our methodology. Our retrosynthetic analysis gave rise to a three-step approach illustrated in the following Scheme 27.

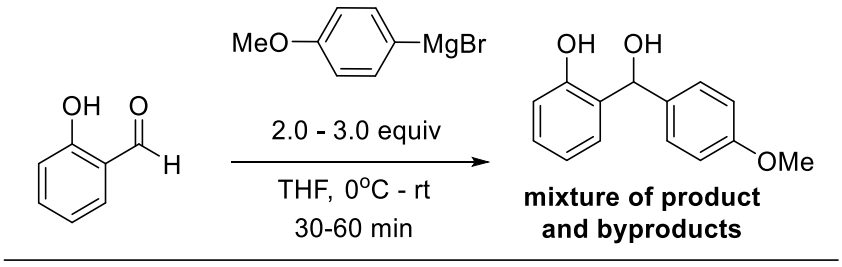


Scheme 27: Retrosynthetic analysis towards the synthesis of benzofuran

Initially, we proposed that the reaction of 2-hydroxybenzaldehyde with 4-methoxyphenylmagnesium bromide would result in the synthesis of 2-(hydroxy(4-

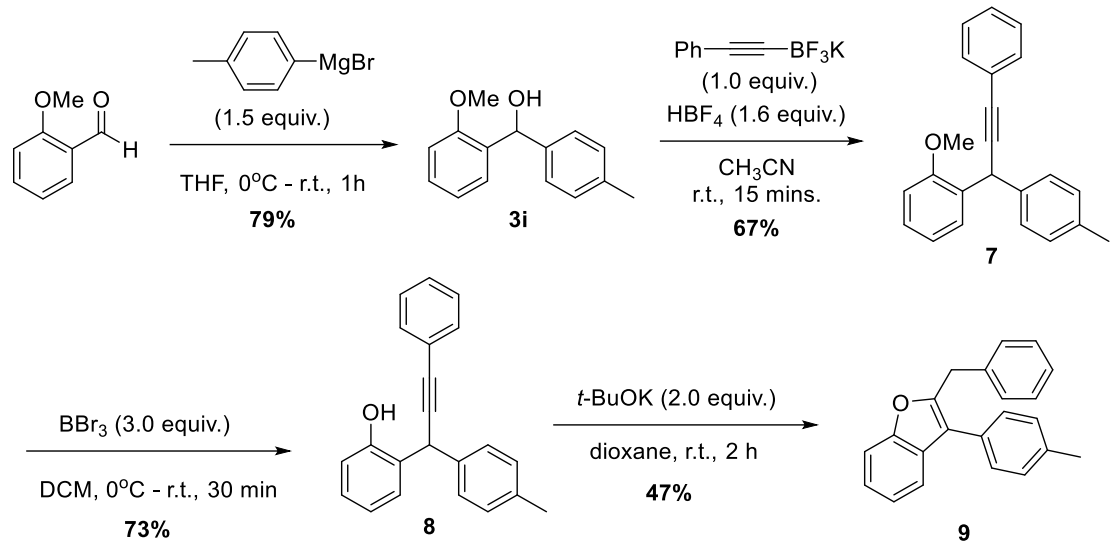
methoxyphenyl)methyl)phenol (**V**). This benzhydryl alcohol could then react with phenylacetylenetrifluoroborate salt **1a** under the developed methodology to afford o*rtho*-propargyl phenol (**VI**). After application of the known cyclization procedure[46], benzofuran (**VII**) should be obtained.

However, issues arose when trying to conduct the first step of the synthesis (Scheme 28). More specifically, when the reaction was initially run with 2.0 equivalents of 4-methoxyphenylmagnesium bromide, the 2-hydroxybenzaldehyde starting material was not completely consumed over the course of the reaction. However, a product spot had developed and was isolated after observing that the reaction was no longer progressing. NMR analysis showed that product had formed, however, inseparable byproducts co-eluted with the benzhydryl alcohol. A final attempt at the reaction resulted in the use of 3.0 equivalents of 4-methoxyphenylmagnesium bromide with the intentions of it reacting completely with 2-hydroxybenzaldehyde. Although complete consumption of 2-hydroxybenzaldehyde was observed, inseparable byproducts still contaminated the benzhydryl alcohol. As a result, we hypothesized that the hydroxyl group from 2-hydroxybenzaldehyde interfered during the reaction with the Grignard reagent, thus resulting in the formation of byproducts.



Scheme 28: Unsuccessful synthesis of 2-(hydroxy(4-methoxyphenyl)methyl)phenol

We then had to devise a new route towards the synthesis of 2,3-benzofurans. The 2-hydroxyl group is imperative for the cyclization to occur in the final step, however, we envisioned that demethylation of a 2-methoxy group could be a viable alternative. As a result, we looked to apply a Grignard reaction to 2-methoxybenzaldehyde as an alternative (Scheme 29).



Scheme 29: Application of the developed methodology to the synthesis of benzofuran 9

Successful reaction between 2-methoxybenzaldehyde and *p*-tolylmagnesium bromide resulting in benzhydryl alcohol **3i** in 79% yield. Applying the developed methodology to benzhydryl alcohol **3i** using phenylacetylenetrifluoroborate salt **1a** and HBF_4 catalyst afforded compound **7** in 67% yield. The additional step involved the demethylation[45] of **7** using boron tribromide to afford o*rtho*-propargyl phenol **8** in 73% yield. Applying the potassium *tert*-butoxide cyclization procedure by Luo and coworkers[46] to compound **8** resulted in 2,3-disubstituted benzofuran **9** in 47% yield.

♦ 4. METHODOLOGY DEVELOPMENT FOR THE PREPARATION OF 2-ALKENYL AND 2-ALKYNYL TETRAHYDROFURANS

4.1 SUBSTRATE SCOPE FOR THE SYNTHESIS OF 2-ALKENYL AND 2-ALKYNYL TETRAHYDROPYRANS

Recently, our group has also shown that acetals and ketals act as suitable starting materials under similar Brønsted acid-catalyzed conditions[43]. This methodology has also been optimized for 2-methoxytetrahydropyran, a cyclic acetal substrate[49]. Previously, compounds **10a** and **10b** were successful synthesized using this method[49] (Figure 13). Phenylacetylenetrifluoroborate was a good coupling partner which resulted in the synthesis of **10a** in excellent 82% yield. However, when *trans*-styryltrifluoroborate salt was used, product **10b** was synthesized in poor 36% yield.

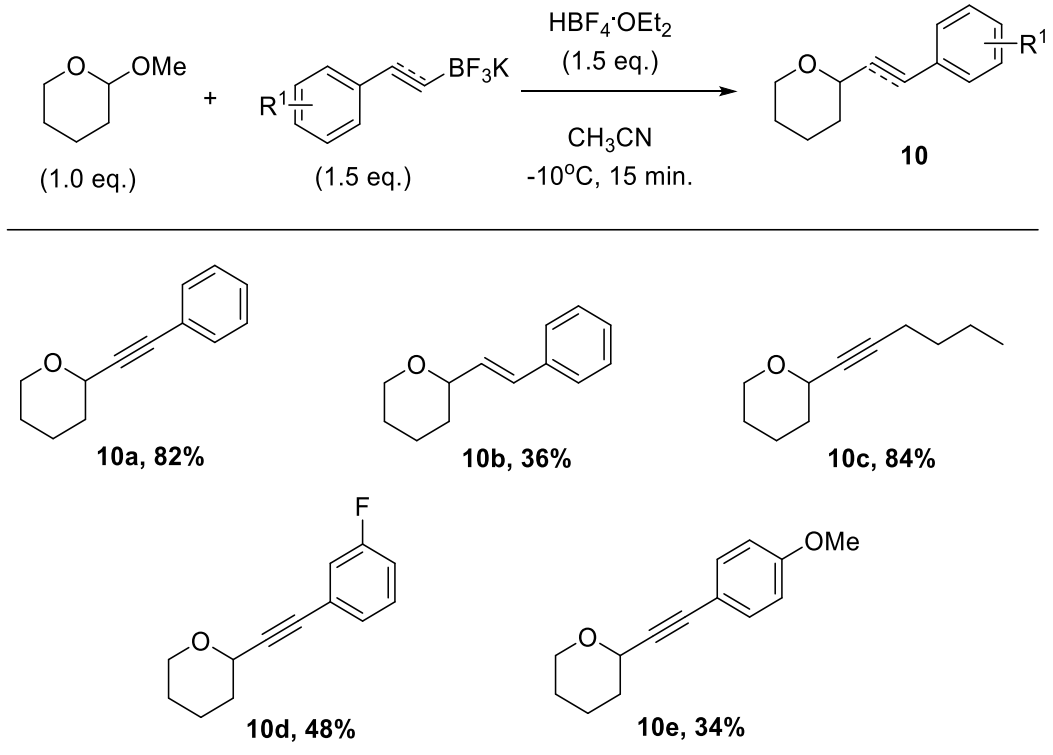


Figure 13: Reactions of organotrifluoroborates with 2-methoxytetrahydropyran

We then wanted to look into exploring other organotrifluoroborate salts, which were tolerant to this method. With poor results obtained from the use of an alkenyltrifluoroborate salt, we decided to focus on alkynyltrifluoroborates. We found that hexynyltrifluoroborate salt (**1d**) afforded **10c** in excellent 84% yield which was comparable to when phenylacetylenetrifluoroborate was used. We then looked to pursue reactions with other phenylacetylenetrifluoroborate derivatives. However, these efforts only provided products **10d** and **10e** in meager 48% and 34% yields, respectively. Evidently, both electron-poor and electron-rich alkynyltrifluoroborates proved to be problematic towards the developed methodology, whereas, sterically unhindered neutral organotrifluoroborates (such as phenylacetylenetrifluoroborate and hexynyltrifluoroborate) were successful.

4.2 TETRAHYDROFURAN VS TETRAHYDROPYRAN

With the substrate scope of organotrifluoroborates and 2-methoxytetrahydropyran looking discouraging due to only two products being synthesized in excellent yield, we looked to determine the rationale behind this observation. In 1992, Woods and coworkers proposed the six-membered oxocarbenium ring transition state model[50]. Later, in 1999, Woerpel and coworkers developed a general model, which explains the stereoselective reactions involving five-membered-ring oxocarbenium ions[51].

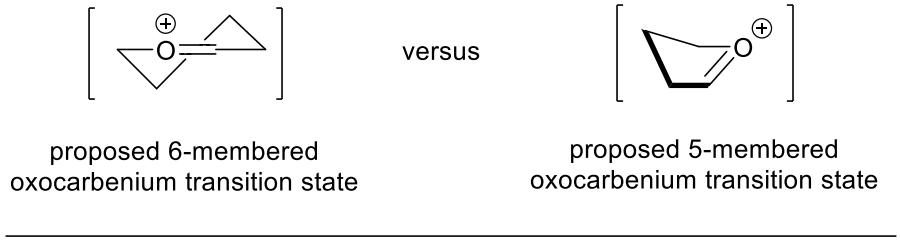


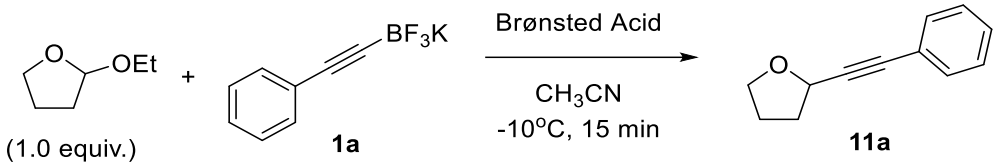
Figure 14: Transition state models for five- and six-membered oxocarbenium rings

In looking at the two transition states, it is evident that the 5-membered oxocarbenium ring transition state allows for easier approach of nucleophiles in terms of steric accessibility, as compared to the 6-membered oxocarbenium ion (Figure 14). Due to this revelation, we looked at applying the above methodology towards tetrahydrofuran cyclic acetals.

4.3 OPTIMIZATION REACTIONS FOR THE PREPARATION OF 2-ALKYNYLTETRAHYDROFURAN **11a**

Initially, we looked to investigate into the efficiency of the HBF_4 Brønsted acid-catalyst towards the substitution of 2-ethoxytetrahydrofuran by using unsubstituted potassium phenylacetylenetrifluoroborate salt **1a** as a model substrate (Table 2).

Table 2: Optimization of Conditions for the Synthesis of Tetrahydrofuran 11a

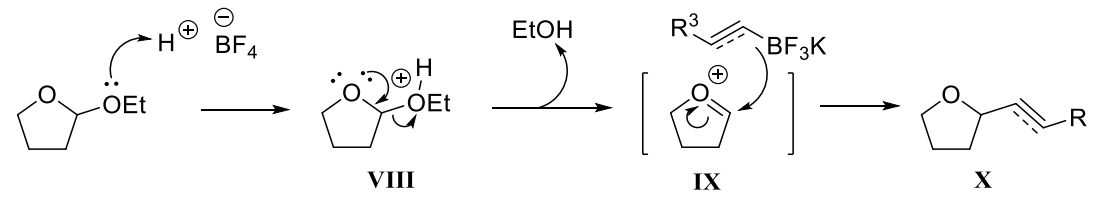


Entry	BF_3K (equiv.)	Brønsted Acid	Brønsted Acid (equiv.)	Yield (%)
1	1.1	$HBF_4{\cdot}OEt_2$	1.1	75
2	1.1	CF_3COOH	1.1	trace
3	1.5	$HBF_4{\cdot}OEt_2$	1.5	92

Previously, it has been found that when using acyclic acetals, a slight excess of 1.1 equivalents of both the organotrifluoroborate and HBF_4 acid catalyst afforded the desired products in good to excellent yields[43]. Therefore, we began our optimization with identical stoichiometry (Table 2, entry 1). We found that the substitution was achieved with 75% of the desired product **11a**. Attempts to use trifluoroacetic acid, a Brønsted acid with a similar pK_a to that of HBF_4, only resulted in trace amounts of product formation (Table 2, entry 2). However, increasing the amount of the organotrifluoroborate and HBF_4 catalyst to 1.5 equivalents resulted in higher yields when using the six-membered ring substrate, 2-methoxytetrahydropyran[49]. In applying these reaction conditions to 2-ethoxytetrahydrofuran, we were able to obtain product **11a** in an excellent 92% yield (Table 2, entry 3). Since other reaction conditions, such as reaction temperature and solvent were already extensively studied in our previous methodologies[42,43,49], we decided to explore the organotrifluoroborate substrate scope.

4.4 PROPOSED MECHANISTIC PATHWAY

Illustrated in the following Scheme 30 is our proposed mechanistic pathway for the formation of 2-alkenyl and 2-alkynyl tetrahydrofurans. We propose that initial protonation of 2-ethoxytetrahydrofuran occurs in the presence of the Brønsted acid catalyst. Subsequent elimination of ethanol from compound **VII** results in the formation of the 5-membered-ring oxocarbenium ion intermediate (**IX**). Reaction at the 2-position by nucleophilic organotrifluoroborate results in the generation of the desired product (**X**). With boron trifluoride being a byproduct, we propose that the *in situ* generation of ethanol is advantageous since it can act as a sequestering agent. Previously, McMillian and co-workers had to externally add hydrofluoric acid in order to sequester the boron trifluoride byproduct[18].



Scheme 30: Proposed mechanistic pathway for the preparation of 2-alkenyl and 2-alkynyl tetrahydrofurans

4.5 RESULTS AND DISCUSSION

With the developed reaction conditions at hand, our next step was to look at the scope of organotrifluoroborate salts that are capable of participating in the reaction.

4.5.1 REACTIONS OF ALKYNYLTRIFLUOROBORATE SALTS WITH 2-ETHOXYTETRAHYDROFURAN

Neutral naphthylacetylenetrifluoroborate salt proved to be a good coupling partner as product **11b** was obtained in a nearly quantitative yield (Figure 15). Both electron-rich *p*-butyl and *p*-methoxy substituted derivatives of phenylacetylenetrifluoroborate salt afforded products **11c** and **11d** in 93% and 78% yields, respectively. Remarkably, a scale-up reaction afforded 0.18 g of **11c** in essentially identical yield to the small-scale synthesis. The developed methodology was also tolerant to phenylacetylenetrifluoroborate derivatives, which contained electron-withdrawing substituents such as dichloro, fluoro and trifluoromethyl. Products **11e-11g** were obtained in good to excellent yields. Lastly, hexynyltrifluoroborate salt effectively participated in the reaction to afford 64% of product **11h**.

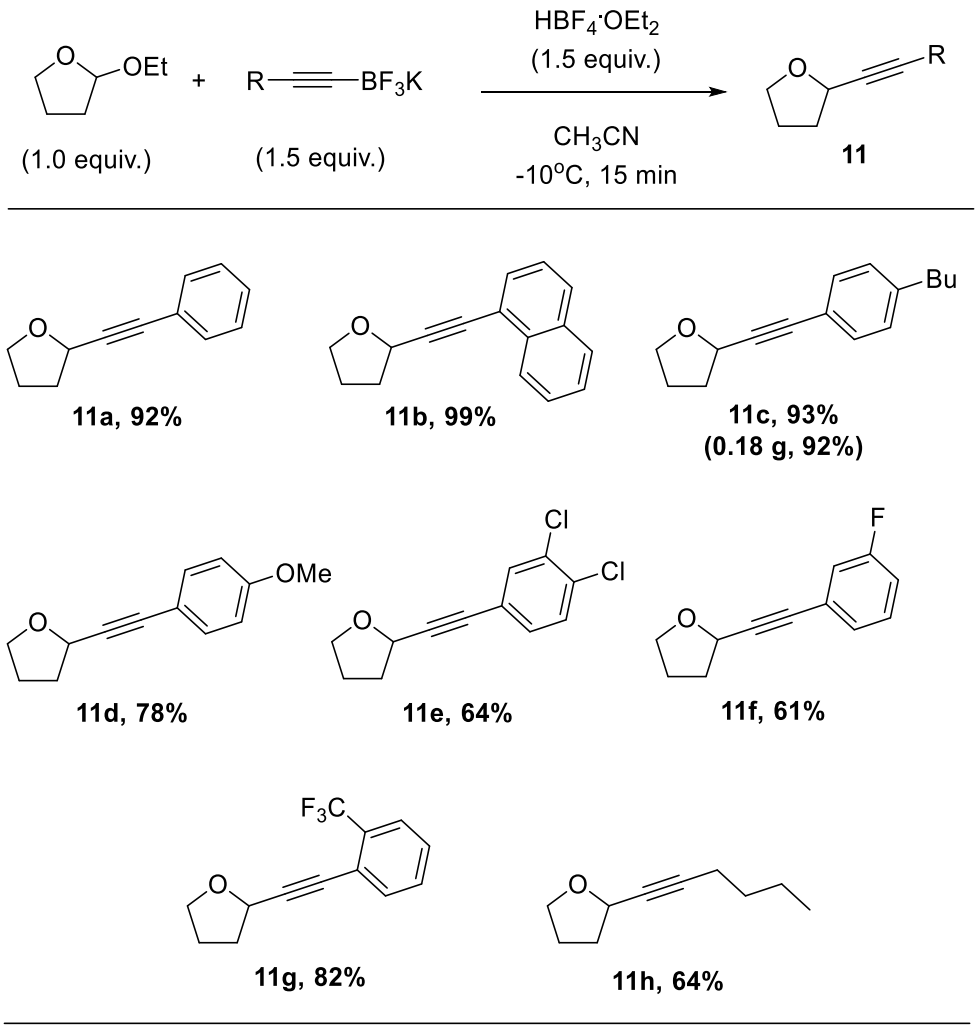


Figure 15: Reactions of potassium alkynyltrifluoroborate salts with 2-ethoxytetrahydrofuran

4.5.2 REACTIONS OF STYRYLTRIFLUOROBORATE SALTS WITH 2-ETHOXYTETRAHYDROFURAN

To our delight, we discovered that potassium alkenyltrifluoroborate salts also participated in the reaction. Namely, potassium *trans*-styryltrifluoroborate salts afforded the desired products in moderate to excellent yields (Figure 16).

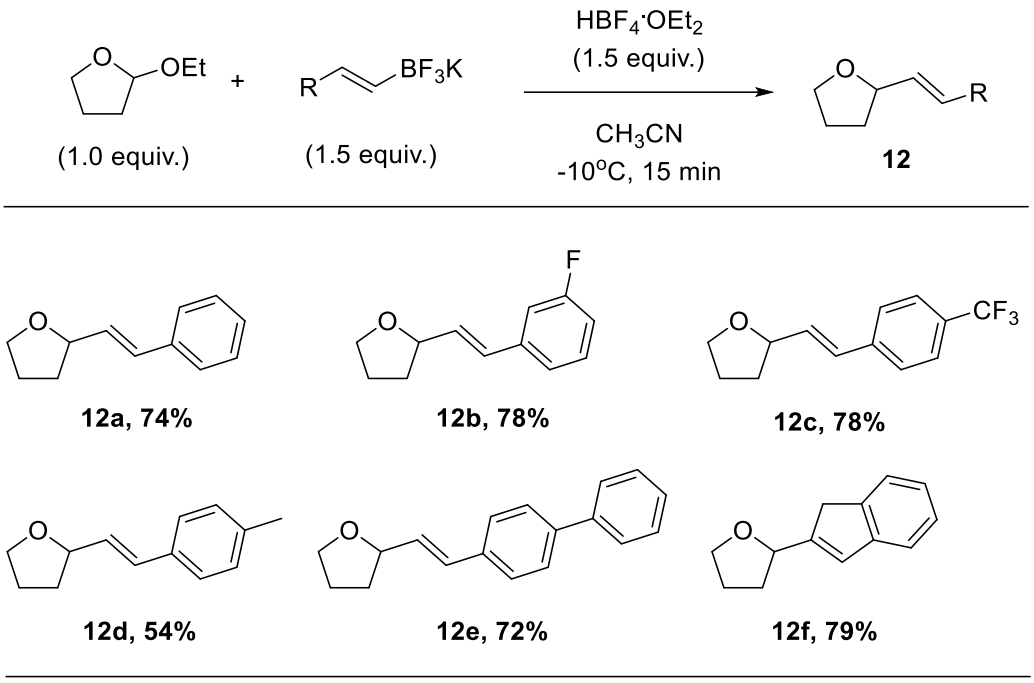


Figure 16: Reactions of potassium *trans*-styryltrifluoroborate salts with 2-ethoxytetrahydrofuran

When unsubstituted potassium trans-styryltrifluoroborate salt was used, product **12a** was obtained in 74% yield. We then looked at the effect of aromatic substituents on the styryltrifluoroborates. We found that potassium 2-(3-fluorophenyl)vinyltrifluoroborate and potassium (*E*)-trifluoro(4-(trifluoromethyl)styryl)borate (**2a**) reacted similarly to the unsubstituted *trans*-styryltrifluoroborate salt. Desired products **12b** and **12c** were formed in 78% yield. Conversely, electron-rich trans-styryltrifluoroborate salt derivative containing a methyl group in the *para*-position only resulted in a modest 54% yield of product **12d**. Additionally, product **12e** was obtained in 72% yield from reaction of 2-ethoxytetrahydrofuran with potassium (*E*)-4-phenylstyryltrifluoroborate salt (**2c**). Lastly, when potassium trifluoro(1*H*-inden-2-yl)borate (**2d**) was used, product **12f** was obtained in 79% yield.

♦ 5. CONCLUSIONS AND FUTURE WORK

A novel set of Brønsted acid-catalyzed reactions has been developed. At the outset, the preparation of internal alkenes and alkynes from benzhydryl alcohols and organotrifluoroborates has been shown[42]. This transformation was shown to proceed rapidly in the presence of a HBF_4 Brønsted acid without the necessity to exclude air or moisture. Excellent atom economy was illustrated as organotrifluoroborates and benzhydryl alcohols were shown to react in a 1:1 ratio. Additionally, functional group tolerance superior to that of Lewis acid- and metal-catalyzed approaches was demonstrated. Namely, this method was tolerant to a variety of unprotected functional groups such as free hydroxyl, amide, aldehyde and carboxylic acid.

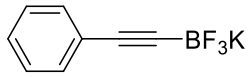
Additionally, Brønsted acid-catalyzed direct substitution of 2-ethoxytetrahydrofuran has been demonstrated[52]. Specifically, alkenyl- and alkynylation of 2-ethoxytetrahydrofuran readily occurred in the presence of alkenyl- and alkynyltrifluoroborates and HBF_4. Functionalized furans were obtained in moderate to excellent yields.

In future, further investigation into the scope of this reaction is of interest. We plan to look at other *in situ* generated carbocations that could participate in this reaction, as well as additional nucleophiles tolerant to this method. Furthermore, application of this method towards *C*-glycosylation of sugars is of interest. Currently, direct *C*-glycosylation of organotrifluoroborates with glycosyl fluorides is known[16]. However, this method requires the use of $BF_3{\cdot}OEt_2$ Lewis acid. Furthermore, *C*-glycosylation of 5-membered ring sugars using alkenyltrifluoroborates was not shown. Therefore, development of a Brønsted acid-catalyzed method involving organotrifluoroborates for *C*-glycosylation is of interest.

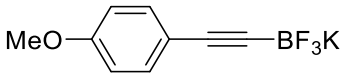
♦ 6. APPENDICES

APPENDIX I: COMPOUND CHARACTERIZATION DATA

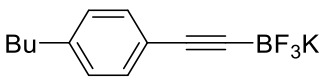
POTASSIUM TRIFLUOROBORATE SALTS



Potassium trifluoro(phenylethynyl)borate (1a)
The title compound was derived from phenylacetylene (2.45 g, 24.0 mmol, 1.0 equiv), *n*-BuLi (1.54 g, 24.0 mmol, 1.0 equiv), $B(OMe)_3$ (3.75 g, 36.1 mmol, 1.5 equiv), and aqueous KHF_2 (11.26 g, 144.2 mmol, 6.0 equiv) in 50 mL of THF. **1a** was obtained as a white crystalline solid (1.190 g, 24% yield). ^{1}H NMR (DMSO) δ 7.27-7.29 (m, 4H), 7.21-7.26 (m, 1H); ^{13}C {^{1}H} NMR (DMSO) δ 130.9, 128.2, 126.7, 125.5; ^{19}F NMR (DMSO) δ -131.71 (br. s, 3F); ^{11}B {^{1}H} NMR (DMSO) δ -1.55 (s, 1B); HRMS (ESI/M-) calcd. for $C_8H_5BF_3$ 169.0442, found 169.0438.



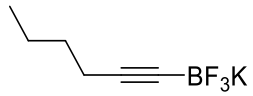
Potassium trifluoro((4-methoxyphenyl)ethynyl)borate (1b)
The title compound was derived from 4-ethynylanisole (1.00 g, 7.34 mmol, 1.0 equiv.), *n*-BuLi (0.470 g, 7.34 mmol, 1.0 equiv.), $B(OMe)_3$ (1.14 g, 11.0 mmol, 1.5 equiv.), and aqueous KHF_2 (3.462 g, 44.3 mmol, 6.0 equiv.) in 25 mL THF. **1b** was obtained as a white crystalline solid (2.609 g, 55% yield). ^{1}H NMR (DMSO) δ 7.20-7.22 (m, 2H), 6.83-6.85 (m, 2H), 3.73 (s, 3H); ^{13}C {^{1}H} NMR (DMSO) δ 158.0, 132.2, 117.8, 113.8, 55.0; ^{19}F NMR (DMSO) δ -131.50 (br. s, 3F); ^{11}B {^{1}H} NMR (DMSO) δ -1.67 (s, 1B); HRMS (ESI/M-) calcd. for $C_9H_7OBF_3$ 199.0548, found 199.0543.



Potassium ((4-butylphenyl)ethynyl)trifluoroborate (1c)
The title compound was derived from 1-butyl-4-ethynylbenzene (3.00 g, 18.0 mmol, 1.0 equiv.), *n*-BuLi (1.15 g, 18.0 mmol, 1.0 equiv.), $B(OMe)_3$ (2.81 g, 27.0 mmol, 1.5 equiv.), and aqueous KHF_2 (8.463 g, 108 mmol, 6.0 equiv.) in 50 mL THF. **1c** was obtained as a white crystalline solid (2.609 g, 55% yield). ^{1}H NMR (DMSO) δ 7.17-7.20 (m 2H), 7.08-7.10 (m, 2H), 2.54 (t, *J* = 7.4 Hz

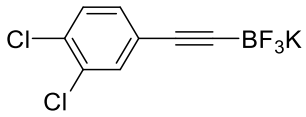
2H), 1.49-1.56 (m, 2H), 1.24-1.33 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (DMSO) δ 140.9, 130.8, 128.2, 122.8, 34.6, 32.9, 21.7, 13.8; ^{19}F NMR (DMSO) δ -131.60 (br. s, 3F); ^{11}B {^{1}H} NMR (DMSO) δ -1.67 (s, 1B); HRMS (ESI/M-) calcd. for $C_{12}H_{13}BF_3$ 225.1068, found 225.1065.

Potassium trifluoro(hex-1-yn-1-yl)borate (1d)



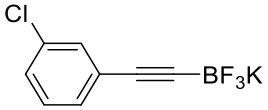
The title compound was derived from 1-hexyne (2.0 g, 23.6 mmol, 1.0 equiv), *n*-BuLi (1.51 g, 23.6 mmol, 1.0 equiv), $B(OMe)_3$ (3.68 g, 35.4 mmol, 1.5 equiv), and aqueous KHF_2 (11.06 g, 142 mmol, 6.0 equiv) in 25 mL of THF. **1d** was obtained as a white crystalline solid (1.659 g, 36% yield). ^{1}H NMR (DMSO) δ 1.98 (m, 2H) 1.33 (m, 4H), 0.85 (m, 3H); ^{13}C {^{1}H} NMR (DMSO) δ 31.1, 21.4, 18.5, 13.5; ^{19}F NMR (DMSO) δ -131.01 (br. s, 3F); ^{11}B {^{1}H} NMR (DMSO) δ -1.30 (s, 1B); HRMS (ESI/M-) calcd. for $C_6H_9BF_3$ 149.0755, found 149.0749.

Potassium trifluoro((3,4-dichlorophenyl)ethynyl)borate (1e)



The title compound was derived from 3,4-dichloro-1-ethynylbenzene (0.894 g, 5.22 mmol, 1.0 equiv), *n*-BuLi (0.335 g, 5.22 mmol, 1.0 equiv), $B(OMe)_3$ (0.81 g, 7.84 mmol, 1.5 equiv), and aqueous KHF_2 (2.45 g, 31.3 mmol, 6.0 equiv) in 17.5 mL of THF. **1e** was obtained as an off-white crystalline solid (0.618 g, 43% yield). ^{1}H NMR (DMSO) δ 7.51-7.54 (m, 2H), 7.26 (dd, J = 2.0, 8.2 Hz, 1H); ^{13}C {^{1}H} NMR (DMSO) δ 132.8, 131.7, 131.4, 130.9, 130.0, 126.4, 109.9; ^{19}F NMR (DMSO) δ -132.12 (br. s, 3F); ^{11}B {^{1}H} NMR (DMSO) δ -1.70 (s, 1B); HRMS (ESI/M-) calcd. for $C_8H_3BCl_2F_3$: calculated: 236.9662, found 236.9664.

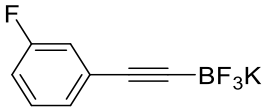
Potassium trifluoro((3-chlorophenyl)ethynyl)borate (1f)



The title compound was derived from 3-chloro-1 ethynylbenzene (0.44 g, 3.25 mmol, 1.0 equiv), *t*-BuLi (0.21 g, 3.25 mmol, 1.0 equiv), $B(OMe)_3$ (0.51 g, 4.87 mmol, 1.5 equiv), and aqueous KHF_2 (1.52 g, 19.5 mmol, 6.0 equiv) in 10.0 mL of THF. **1f** was obtained as a white crystalline solid (0.460 g, 59% yield). ^{1}H NMR (DMSO) δ 7.30-7.32 (m, 3H), 7.24-7.28 (m, 1H); ^{13}C {^{1}H} NMR (DMSO) δ 132.8, 130.3, 130.1, 129.7, 127.4, 126.9; ^{19}F NMR (DMSO) δ -131.98 (br. s, 3F); ^{11}B {^{1}H} NMR (DMSO) δ -1.51 (s, 1B);

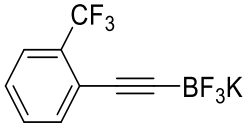
HRMS (ESI/M-) calcd. for $C_8H_4BClF_3$ 203.0052, found 203.0054.

Potassium trifluoro((3-fluorophenyl)ethynyl)borate (1g)



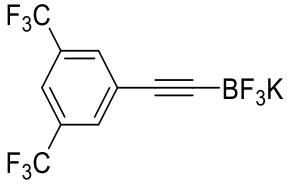
The title compound was derived from 1-ethynyl-3-fluorobenzene (0.67 g, 5.44 mmol, 1.0 equiv), *n*-BuLi (0.349 g, 5.44 mmol, 1.0 equiv), $B(OMe)_3$ (0.85 g, 8.16 mmol, 1.5 equiv), and aqueous KHF_2 (2.55 g, 32.7 mmol, 6.0 equiv) in 17.0 mL of THF. **1g** was obtained as a white crystalline solid (1.038 g, 84% yield). ^{1}H NMR (DMSO) δ 7.30-7.35 (m, 1H), 7.07-7.14 (m, 3H); ^{13}C {^{1}H} NMR (DMSO) δ 161.8 (d, J = 243.1 Hz), 130.3 (d, J = 9.2 Hz), 127.5 (d, J = 9.2 Hz), 127.3 (d, J = 3.1 Hz), 117.3 (d, J = 22.2 Hz), 114.0 (d, J = 21.5 Hz); ^{19}F NMR (DMSO) δ -113.49 (q, J = 6.6 Hz, 1F), -131.97 (br. s, 3F); ^{11}B {^{1}H} NMR (DMSO) δ -1.56 (s, 1B); HRMS (ESI/M-) calcd. for $C_8H_4BF_4$ 187.0348, found 187.0348.

Potassium trifluoro((2-(trifluoromethyl)phenyl)ethynyl) borate (1h)



The title compound was derived from 1-ethynyl-2-trifluoromethylbenzene (1.00 g, 5.70 mmol, 1.0 equiv), *n*-BuLi (0.365 g, 5.70 mmol, 1.0 equiv), $B(OMe)_3$ (0.89 g, 8.55 mmol, 1.5 equiv), and aqueous KHF_2 (2.67 g, 34.2 mmol, 6.0 equiv) in 17.0 mL of THF. **1h** was obtained as a white crystalline solid (0.879 g, 56% yield). ^{1}H NMR (DMSO) δ 7.65 (d, J = 7.4 Hz, 1H), 7.51-7.58 (m, 2H), 7.39-7.44 (m, 1H); ^{13}C {^{1}H} NMR (DMSO) δ 134.1, 132.0, 129.4 (q, J = 29.1 Hz), 126.9, 125.5 (q, J = 5.4 Hz), 123.7 (q, J = 273.0 Hz), 123.6; ^{19}F NMR (DMSO) δ -60.85 (s, 3F), -132.09 (br. s, 3F); ^{11}B {^{1}H} NMR (DMSO) δ -1.61 (s, 1B); HRMS (ESI/M-) calcd. for $C_9H_4BF_6$ 237.0316, found 237.0318.

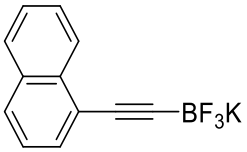
Potassium trifluoro((3,5-bis(trifluoromethyl)phenyl)-ethynyl)borate (1i)



The title compound was derived from 1-ethynyl-3,5-bis-(trifluoromethyl)benzene (1.00 g, 4.07 mmol, 1.0 equiv), *n*-BuLi (0.261 g, 4.07 mmol, 1.0 equiv), $B(OMe)_3$ (0.63 g, 6.11 mmol, 1.5 equiv), and aqueous KHF_2 (1.90 g, 24.4 mmol, 6.0 equiv) in 12.2 mL of THF. **1i** was obtained as a white crystalline solid (0.444 g, 32% yield). ^{1}H NMR (DMSO) δ 7.92-7.93 (m, 3H); ^{13}C {^{1}H} NMR (DMSO) δ

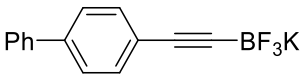
131.3, 130.6 (q, J = 33.0 Hz), 127.9, 123.0 (q, J = 273.0 Hz), 120.1; ^{19}F NMR (DMSO) δ -61.73 (s, 6F), -132.41 (br. s, 3F); ^{11}B {^{1}H} NMR (DMSO) δ -1.65 (s, 1B); HRMS (ESI/M-) calcd. for $C_{10}H_3BF_9$ 305.0190, found 305.0193.

Potassium trifluoro(naphthalen-1-ylethynyl)borate (1j)



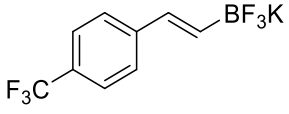
The title compound was derived from 1-ethynylnaphthalene (0.854 g, 5.44 mmol, 1.0 equiv), *n*-BuLi (0.349 g, 5.44 mmol, 1.0 equiv), $B(OMe)_3$ (0.85 g, 8.16 mmol, 1.5 equiv), and aqueous KHF_2 (2.55 g, 32.7 mmol, 6.0 equiv) in 17.0 mL of THF. **1j** was obtained as a slightly pink crystalline solid (0.876 g, 62% yield). ^{1}H NMR (DMSO) δ 8.33 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.51-7.61 (m, 3H), 7.42-7.45 (m, 1H); ^{13}C {^{1}H} NMR (DMSO) δ 132.9, 132.8, 128.9, 128.1, 126.9, 126.3, 126.2, 126.1, 125.5, 123.1; ^{19}F NMR (DMSO) δ -131.46 (br. s, 3F); ^{11}B {^{1}H} NMR (DMSO) δ -1.61 (s, 1B); HRMS (ESI/M-) calcd. for $C_{12}H_7BF_3$ 219.0598, found 219.0601.

Potassium trifluoro([1,1'-biphenyl]-4-ylethynyl)borate (1k)



The title compound was derived from 4-ethynylbiphenyl (1.00 g, 5.44 mmol, 1.0 equiv), *n*-BuLi (0.349 g, 5.44 mmol, 1.0 equiv), $B(OMe)_3$ (0.85 g, 8.16 mmol, 1.5 equiv), and aqueous KHF_2 (2.55 g, 32.7 mmol, 6.0 equiv) in 17.0 mL of THF. **1k** was obtained as an off-white crystalline solid (0.201 g, 13% yield). ^{1}H NMR (DMSO) δ 7.65-7.67 (d, J = 7.03 Hz, 2H), 7.58-7.61 (d, J = 8.6 Hz, 2H), 7.44-7.47 (m, 2H), 7.33-7.39 (m, 3H); ^{13}C {^{1}H} NMR (DMSO) δ 139.5, 138.3, 131.5, 128.9, 127.5, 126.48, 126.45, 124.7; ^{19}F NMR (DMSO) δ -131.70 (br. s, 3F); ^{11}B {^{1}H} NMR (DMSO) δ -1.22 (s, 1B); HRMS (ESI/M-) calcd. for $C_{14}H_9BF_3$ 245.0755, found 245.0757.

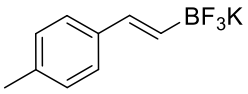
Potassium (*E*)-trifluoro(4-(trifluoromethyl)styryl)-borate (2a)



The title compound was derived from *trans*-2-[4-(trifluoromethyl) phenyl]vinylboronic acid (0.65 g, 3 mmol, 1.0 equiv.) and aqueous KHF_2 (0.66 g, 8.4 mmol, 2.8 equiv.) in 6 mL Et_2O. **2a** was obtained as a white crystalline solid (0.694 g, 83% yield). ^{1}H-NMR (DMSO) δ 7.58–7.60 (m, 2H), 7.51–7.53 (m, 2H), 6.56 (d, J = 18.0 Hz, 1H), 6.39 (dq,

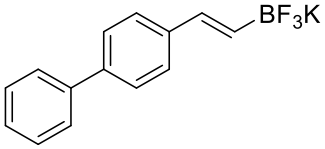
J = 3.5, 18.0 Hz, 1H); ^{13}C {^{1}H} NMR (DMSO) δ 144.3, 131.8 (q, *J* = 4.6 Hz), 125.9, 125.2 (q, *J* = 3.8 Hz), 124.7 (q, *J* = 300.6 Hz); ^{19}F NMR (DMSO) δ −60.60 (s, 3F), −138.31 (br. s, 3F).

Potassium (E)-trifluoro(4-methylstyryl)borate (2b)



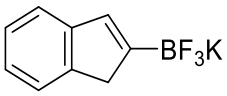
The title compound was derived from *trans*-2-(4-methylphenyl) vinylboronic acid (0.49 g, 3 mmol, 1.0 equiv.) and aqueous KHF_2 (0.66 g, 8.4 mmol, 2.8 equiv.) in 6 mL Et_2O. **2b** was obtained as a white crystalline solid (0.562 g, 84% yield). ^{1}H-NMR (DMSO) δ 7.19 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.42 (d, *J* = 18.0 Hz, 1H), 6.10 (dq, *J* = 3.5, 18.0 Hz, 1H), 2.25 (s, 3H); ^{13}C {^{1}H} NMR (DMSO) δ 137.6, 134.7, 132.8, 128.8, 125.3, 20.7; ^{19}F NMR (DMSO) δ −137.73 (br. s, 3F).

Potassium (*E*)-(2-([1,1′-biphenyl]-4-yl)vinyl)trifluoroborate (2c)



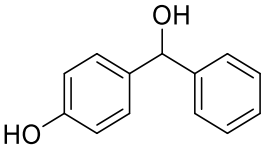
The title compound was derived from *trans*-2-(4-biphenyl) vinylboronic acid (0.67 g, 3 mmol, 1.0 equiv.) and aqueous KHF_2 (0.66 g, 8.4 mmol, 2.8 equiv.) in 6 mL Et_2O. **2c** was obtained as a white crystalline solid (0.108 g, 13% yield). ^{1}H-NMR (DMSO) δ 7.63–7.66 (m, 2H), 7.55–7.58 (m, 2H), 7.39–7.46 (m, 4H), 7.30–7.35 (m, 1H), 6.52 (d, *J*, = 18.0 Hz, 1H), 6.25 (dq, *J* = 3.5, 18.0 Hz, 1H); ^{13}C {^{1}H} NMR (DMSO) δ 140.1, 139.5, 137.5, 132.5, 128.9, 127.0, 126.6, 126.3, 125.9; ^{19}F NMR (DMSO) δ −137.85 (br. s, 3F).

Potassium trifluoro(1*H*-inden-2-yl)borate (2d)

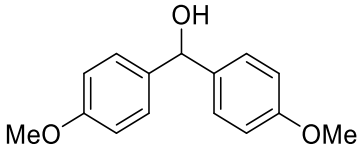


The title compound was derived from 1*H*-indene-2-boronic acid (0.48 g, 3 mmol, 1.0 equiv.) and aqueous KHF_2 (0.66 g, 8.4 mmol, 2.8 equiv.) in 6 mL Et_2O. **2d** was obtained as an off-white crystalline solid (0.537 g, 81% yield). ^{1}H-NMR (DMSO) δ 7.33–7.35 (m, 1H), 7.19–7.20 (m, 1H), 7.08–7.12 (m, 1H), 6.94–6.98 (m, 1H), 6.55 (s, 1H), 3.16 (s, 1H); ^{13}C {^{1}H} NMR (DMSO) δ 147.5, 145.7, 129.8, 125.4, 123.1, 122.2, 119.0, 41.7; ^{19}F NMR (DMSO) δ −137.30 (br. s, 3F); HRMS (ESI/M-) calcd. for $C_9H_7BF_3$ 183.0598, found 183.0609.

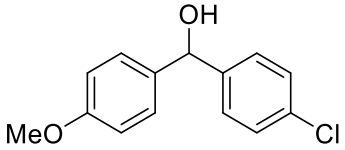
BENZHYDRYL ALCOHOLS



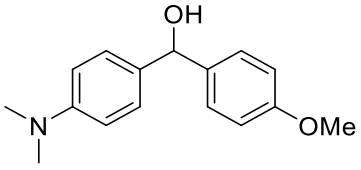
4-(hydroxy(phenyl)methyl)phenol (3a)
The title compound was derived from 4-hydroxybenzaldehyde (0.153 g, 1.25 mmol, 1.0 equiv) and phenylmagnesium bromide (0.453 g, 2.50 mmol, 2.0 equiv) in 5.0 mL of anhydrous THF. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (3:1) afforded product **3a** (0.196 g, 79% yield) as a white solid. IR (Diamond-ATR) *v* 3393, 3154, 1595, 1447, 1171, 1000, 815, 695, 556 cm^{-1}; ^{1}H NMR (DMSO) δ 9.22 (s, 1H), 7.26-7.34 (m, 4H), 7.12-7.19 (m, 3H), 6.67 (d, *J* = 8.6 Hz, 2H), 5.67 (d, *J* = 3.9 Hz, 1H), 5.59 (d, *J* = 3.9 Hz, 1H); ^{13}C {^{1}H} NMR (DMSO) δ 156.1, 146.1, 136.1, 127.9, 127.5, 126.4, 126.1, 114.7, 73.9.



Bis(4-methoxyphenyl)methanol (3b)
The title compound was derived from 4-methoxybenzaldehyde (0.139 g, 1.02 mmol, 1.0 equiv) and 4-methoxyphenylmagnesium bromide (0.649 g, 3.07 mmol, 3.0 equiv) in 3.0 mL of anhydrous THF. Purification by silica gel column chromatography using hexanes/EtOAc (5:1) afforded product **3b** (0.248 g, 99% yield) as a yellow solid. IR (Diamond-ATR) *v* 3287, 1608, 1507, 1239, 1167, 1028, 809, 549 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.26 (d, *J* = 8.2 Hz, 4H), 6.86 (d, *J* = 9.0 Hz, 4H), 5.75 (s, 1H), 3.78 (s, 6H), 2.18 (s, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 158.9, 136.4, 127.7, 113.8, 75.4, 55.3.

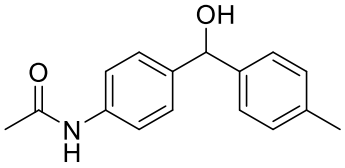


(4-chlorophenyl)(4-methoxyphenyl)methanol (3c)
The title compound was derived from 4-chlorobenzaldehyde (0.1413 g, 1.01 mmol, 1.0 equiv) and 4-methoxyphenylmagnesium bromide (0.850 g, 4.02 mmol, 4.0 equiv) in 3.0 mL of anhydrous THF. Purification by silica gel chromatography using hexanes/EtOAc (5:1) afforded product **3c** (0.203 g, 81% yield) as an off-white solid. IR (Diamond-ATR) *v* 3300, 1509, 1247, 1170, 1031, 1004, 802, 551, 516 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.30 (s, 4H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.77 (d, *J* = 3.1 Hz, 1H), 3.79 (s, 3H), 2.20 (d, *J* = 3.5 Hz, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 159.2, 142.4, 135.8, 133.1, 128.5, 127.9, 127.7, 114.0, 75.2, 55.3.



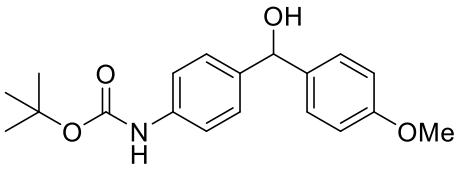
(4-(dimethylamino)phenyl)(4-methoxyphenyl)-methanol (3d)

The title compound was derived from 4-(dimethylamino)benzaldehyde (0.174 g, 1.17 mmol, 1.0 equiv) and 4-methoxyphenylmagnesium bromide (0.271 g, 1.28 mmol, 1.1 equiv) in 3.0 mL of anhydrous THF. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (5:1) afforded product **3d** (0.174, 58% yield) as an off white solid. IR (Diamond-ATR) *v* 3299, 1612, 1510, 1244, 1169, 1031, 804, 550 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 6.69 (d, *J* = 9.0 Hz, 2H), 5.73 (d, *J* = 3.5 Hz, 1H), 3.78 (s, 3H), 2.92 (s, 6H), 2.07 (d, *J* = 3.9 Hz, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 158.7, 150.1, 136.6, 132.2, 127.64, 127.56, 113.7, 112.5, 75.5, 55.3, 40.6.



***N*-(4-(hydroxy(*p*-tolyl)methyl)phenyl)acetamide (3e)**

The title compound was derived from 4-acetamidobenzaldehyde (0.192 g, 1.18 mmol, 1.0 equiv) and 4-methylphenylmagnesium bromide (0.459 g, 2.35 mmol, 2.0 equiv) in 3.0 mL of anhydrous THF. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (1:1) afforded product **3e** (0.199 g, 66% yield) as a yellow solid. Mp 139−142 °C; IR (Diamond-ATR) *v* 3309, 1657, 1601, 1535, 1412, 1318, 1268, 1012, 819, 758, 552, 477 cm^{-1}; ^{1}H NMR (DMSO) δ 9.85 (s, 1H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.21-7.25 (m, 4H), 7.09 (d, *J* = 7.8 Hz, 2H), 5.72 (d, *J* = 4.3 Hz, 1H), 5.60 (d, *J* = 3.9 Hz, 1H), 2.25 (s, 3H), 2.01 (s, 1H); ^{13}C {^{1}H} NMR (DMSO) δ 168.0, 142.8, 140.5, 137.8, 135.5, 128.5, 126.5, 126.1, 118.7, 73.7, 23.9, 20.6; HRMS (ESI-TOF) *m/z* [M+H]+ calcd for $C_{16}H_{18}NO_2$ 256.1332, found 256.1329.

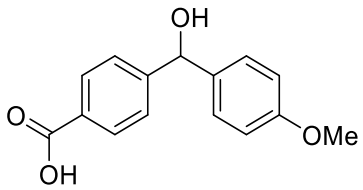


***tert*-butyl (4-(hydroxy(*p*-tolyl)methyl)phenyl)-carbamate (3f)**

The title compound was derived from 4-(Boc-amino)benzaldehyde (0.100 g, 0.45 mmol, 1.0 equiv) and 4-methoxyphenylmagnesium bromide (0.239 g, 1.13 mmol, 2.5 equiv) in 3.0 mL of anhydrous THF. Purification by silica gel chromatography using hexanes/EtOAc (3:1)

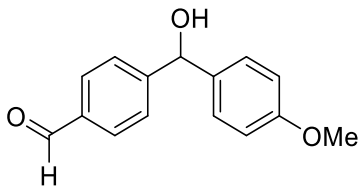
afforded product **3f** (0.111 g, 74% yield) as a yellow solid. Mp 106−109 °C; IR (Diamond-ATR) *v* 3367, 1696, 1507, 1235, 1157, 1035, 824, 574 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.24-7.32 (m, 6H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.47 (s, 1H), 5.75 (s, 1H), 3.78 (s, 3H), 2.16 (s, 1H), 1.50 (s, 9H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 159.0, 152.7, 138.7, 137.6, 136.2, 127.8, 127.1, 118.5, 113.8, 80.5, 75.4, 55.3, 28.3; HRMS (ESI-TOF) *m/z* [M+Na]+ calcd for $C_{19}H_{23}NO_4Na$ 352.1519, found 352.1520.

4-(hydroxy(4-methoxyphenyl)methyl)benzoic acid (3g)



The title compound was derived from 4-formylbenzoic acid (0.174 g, 1.16 mmol, 1.0 equiv) and 4-methoxyphenylmagnesium bromide (0.737 g, 3.48 mmol, 3.0 equiv) in 5.0 mL of anhydrous THF. Purification by silica gel chromatography using hexanes/EtOAc/AcOH (1.5:1:0.01% v/v) afforded product **3g** (0.208 g, 69% yield) as a white solid. Mp 158-160 °C; IR (Diamond-ATR) *v* 3468, 2920, 1675, 1607, 1508, 1423, 1293, 1228, 1169, 1025, 742, 551 cm^{-1}; ^{1}H NMR (DMSO) δ 12.80 (s, 1H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.92 (s, 1H), 5.71 (s, 1H), 3.71 (s, 3H); ^{13}C {^{1}H} NMR (DMSO) δ 167.2, 158.2, 150.9, 137.2, 129.2, 129.1, 127.5, 126.1, 113.5, 73.4, 55.0; HRMS (ESI-TOF) *m/z* [M-H]- calcd for $C_{15}H_{13}O_4$ 257.0819, found 257.0817.

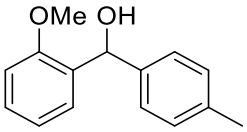
4-(hydroxy(4-methoxyphenyl)methyl)benzaldehyde (3h)



The title compound was derived from 4-(diethoxymethyl) benzaldehyde (0.258 g, 1.24 mmol, 1.0 equiv) and 4-methoxyphenylmagnesium bromide (0.419 g, 1.98 mmol, 1.6 equiv) in 3.0 mL of anhydrous THF. Purification by silica gel chromatography using hexanes/EtOAc (3:1) afforded product **3h** (66.0 mg, 22% yield) as a yellow oil. IR (Diamond-ATR) *v* 3421, 1690, 1605, 1509, 1244, 1169, 1027, 818, 785, 554 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.98 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.86 (s, 1H), 3.79 (s, 3H), 2.34 (s, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 191.9, 159.4, 150.6, 135.5, 135.4, 129.9, 128.1, 126.8, 114.2, 75.5, 55.3;

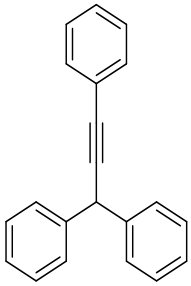
HRMS (EI) *m/z* [M+] calcd for $C_{15}H_{14}O_3$ 242.0943, found 242.0944.

(2-methoxyphenyl)(*p*-tolyl)methanol (3i)



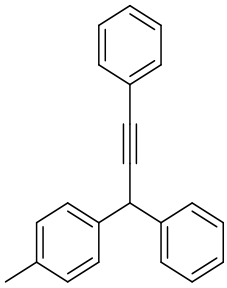
The title compound was derived from 2-methoxybenzaldehyde (0.298 g, 2.19 mmol, 1.0 equiv) and *p*-tolylmagnesium bromide (0.642 g, 3.29 mmol, 1.5 equiv) in 5.0 mL of anhydrous THF. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (gradient: 49:1 → 12:1) afforded product **3i** (0.396 g, 79% yield) as a white solid. IR (Diamond-ATR) *v* 3298, 1598, 1486, 1280, 1240, 1186, 1029, 806, 749, 556 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26-7.20 (m, 4H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.92 (t of d, *J* = 0.8, 7.4 Hz, 1H), 6.85 (d of d, *J* = 0.8, 8.6 Hz, 1H), 6.00 (s, 1H), 3.76 (s, 3H), 3.05 (s, 1H), 2.31 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 156.6, 140.3, 136.6, 132.1, 128.8, 128.5, 127.7, 126.4, 120.7, 110.6, 71.9, 55.3, 21.0.

INTERNAL ALKENES AND ALKYNES



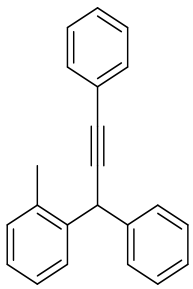
prop-2-yne-1,1,3-triyltribenzene (4a)

The title compound was derived from diphenylmethanol (13.3 mg, 0.072 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (**1a**) (15.0 mg, 0.072 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (18.7 mg, 0.12 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by automated flash column chromatography on silica gel using hexanes and subsequent CH_3CN/ hexanes extraction afforded product **4a** (7.8 mg, 41% yield) as a yellow oil. IR (Diamond-ATR) *v* 2922, 1595, 1488, 1451, 755, 689, 558 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.43-7.49 (m, 6H), 7.29-7.34 (m, 7H), 7.21-7.25 (m, 2H), 5.21 (s, 1H); ^{13}C {^1H} NMR ($CDCl_3$) δ 141.7, 131.7, 128.6, 128.2, 128.0, 127.9, 126.9, 123.5, 90.2, 84.9, 43.8.



(3-(*p*-tolyl)prop-1-yne-1,3-diyl)dibenzene (4b)

The title compound was derived from phenyl(*p*-tolyl)methanol (21.1 mg, 0.11 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (**1a**) (22.1 mg, 0.11 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (27.5 mg, 0.17 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes afforded product **4b** (20.2 mg, 67% yield) as a yellow oil. IR (Diamond-ATR) *v* 2921, 1654, 1602, 1490, 1448, 1275, 1176, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42-7.48 (m, 4H), 7.28-7.33 (m, 7H), 7.20-7.24 (m, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 5.17 (s, 1H), 2.31 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 141.9, 138.8, 136.5, 131.7, 129.3, 128.6, 128.2, 127.9, 127.83, 127.75, 126.8, 123.6, 90.4, 84.7, 43.4, 21.0.

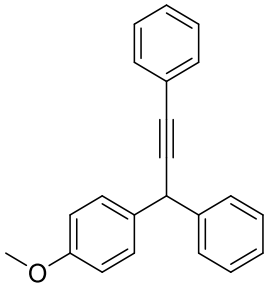


(3-(*o*-tolyl)prop-1-yne-1,3-diyl)dibenzene (4c)

The title compound was derived from phenyl(*o*-tolyl)methanol (21.1 mg, 0.11 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (**1a**) (22.1 mg, 0.11 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (27.5 mg, 0.17 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes afforded product **4c** (15.2 mg, 51% yield) as a yellow oil. IR (Diamond-ATR) ν 2923, 1597, 1489, 1449, 1266, 1027, 754, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50 (dd, J = 1.6, 7.03 Hz, 1H), 7.44-7.46 (m, 2H), 7.37-7.39 (m, 2H), 7.27-7.32 (m, 5H), 7.14-7.25 (m, 4H), 5.38 (s, 1H), 2.33 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ

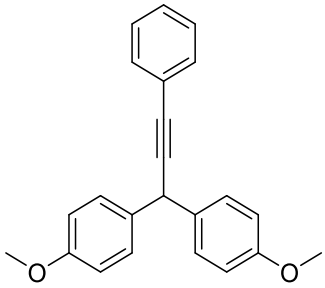
140.7, 139.4, 135.9, 131.6, 130.7, 128.8, 128.5, 128.2, 128.0, 127.9, 127.1, 126.7, 126.3, 123.6, 90.2, 84.5, 40.8, 19.7.

(3-(4-methoxyphenyl)prop-1-yne-1,3-diyl)dibenzene (4d)



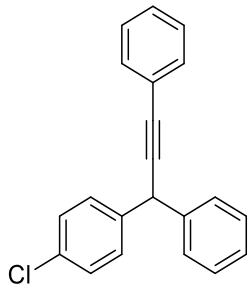
The title compound was derived from (4-methoxyphenyl) (phenyl)methanol (21.5 mg, 0.10 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (**1a**) (20.9 mg, 0.10 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (26.0 mg, 0.16 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes/diethyl ether (40:1) afforded product **4d** (26.2 mg, 87% yield) as a yellow oil. IR (Diamond-ATR) *v* 2930, 1598, 1507, 1247, 1173, 1029, 755, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41-7.48 (m, 4H), 7.28-7.36 (m, 7H), 7.20-7.24 (m, 1H), 6.85 (d, *J* = 9.0 Hz, 2H), 5.16 (s, 1H), 3.77 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 158.5, 142.0, 133.9, 131.7, 128.9, 128.6, 128.2, 127.9, 127.8, 126.8, 123.5, 114.0, 90.5, 84.7, 55.3, 42.9.

4,4'-(3-phenylprop-2-yne-1,1-diyl)bis(methoxybenzene) (4e)



The title compound was derived from bis(4-methoxyphenyl)methanol (**3b**) (22.3 mg, 0.091 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (**1a**) (19.0 mg, 0.091 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (23.7 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Aqueous workup afforded product **4e** (27.2 mg, 91% yield) as a yellow/orange oil. IR (Diamond-ATR) *v* 2930, 1601, 1506, 1244, 1170, 1027, 756, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.48-7.51 (m, 2H), 7.36 (d, *J* = 8.2 Hz, 4H), 7.31-7.33 (m, 3H), 6.88 (d, *J* = 8.6 Hz, 4H), 5.15 (s, 1H), 3.81 (s, 6H); ^{13}C {^1H} NMR ($CDCl_3$) δ 158.4, 134.3, 131.6, 128.8, 128.2, 127.9, 123.6, 113.9, 90.8, 84.5, 55.3, 42.1.

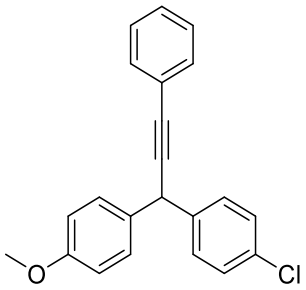
(3-(4-chlorophenyl)prop-1-yne-1,3-diyl)dibenzene (4f)



The title compound was derived from (4-chlorophenyl)(phenyl)methanol (21.7 mg, 0.10 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)- borate (**1a**) (20.6 mg, 0.10 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (25.7 mg, 0.16 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by automated flash column chromatography on silica gel using hexanes and subsequent CH_3CN/hexanes extraction afforded product **4f** (5.7 mg, 19% yield) as a yellow oil. IR

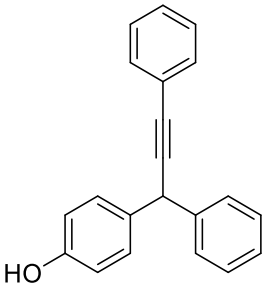
(Diamond-ATR) *v* 2924, 1487, 1089, 1014, 753, 690, 555 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.46-7.48 (m, 2H), 7.35-7.42 (m, 5H), 7.29-7.33 (m, 6H), 7.24-7.27 (m, 1H), 5.18 (s, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 141.2, 140.3, 132.7, 131.7, 129.3, 128.7, 128.3, 128.1, 127.8, 127.1, 123.2, 89.6, 85.2, 43.2.

1-chloro-4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)benzene (4g)

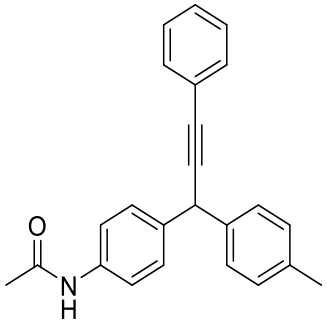


The title compound was derived from (4-chlorophenyl)(4-methoxyphenyl)methanol (**3c**) (22.4 mg, 0.090 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (**1a**) (18.7 mg, 0.090 mmol, 1.0 equiv), and $HBF_4{\cdot}OEt_2$ (23.4 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes/EtOAc (10:1) afforded product **4g** (25.3 mg, 84% yield) as a yellow oil. IR (Diamond-ATR) *v* 2928, 1599, 1508, 1487, 1248, 1172, 1089, 1014, 755, 690, 555 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.45-7.47 (m, 2H), 7.27-7.36 (m, 9H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.13 (s, 1H), 3.78 (s, 3H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 158.6, 140.6, 133.4, 132.6, 131.7, 129.2, 128.8, 128.7, 128.2, 128.1, 123.3, 114.1, 89.9, 85.0, 55.3, 42.3.

4-(1,3-diphenylprop-2-yn-1-yl)phenol (4h)

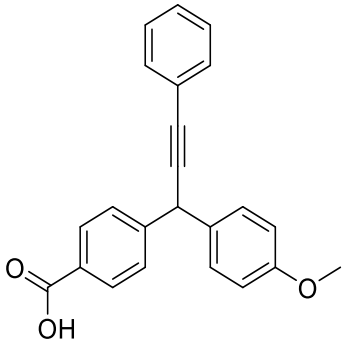


The title compound was derived from 4-(hydroxy(phenyl)methyl)phenol (**3a**) (21.1 mg, 0.11 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (**1a**) (21.9 mg, 0.11 mmol, 1.0 equiv), and $HBF_4{\cdot}OEt_2$ (27.3 mg, 0.17 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification was conducted by automated flash column chromatography on silica gel using hexanes/EtOAc (5:1) and subsequent CH_3CN/hexanes extraction afforded product **4h** (19.9 mg, 66% yield) as a burgundy/brown oil. IR (Diamond-ATR) *v* 3317, 3025, 1596, 1509, 1489, 1441, 1169, 754, 690, 552 cm^{-1}; ^{1}H NMR (CDCl3) 7.41-7.48 (m, 4H), 7.28-7.33 (m, 7H), 7.22-7.24 (m, 1H), 6.77-6.79 (m, 2H), 5.14 (s, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 154.4, 142.0, 134.1, 131.7, 129.1, 128.6, 128.2, 127.9, 127.8, 126.8, 123.5, 115.4, 90.4, 84.7, 42.9.



_N_-(4-(3-phenyl-1-(_p_-tolyl)prop-2-yn-1-yl)phenyl)-acetamide (4i)

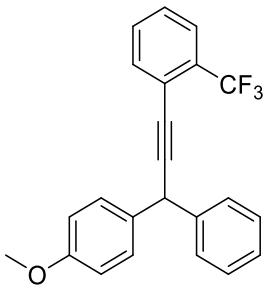
The title compound was derived from _N_-(4-hydroxy(_p_-tolyl)methyl)phenyl)acetamide (**3e**) (22.6 mg, 0.088 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (**1a**) (18.4 mg, 0.088 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (22.9 mg, 0.141 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification was conducted by silica gel column chromatography using hexanes/EtOAc (1:2) and subsequent CH_3CN/hexanes extraction afforded product **4i** (18.3 mg, 61% yield) as a yellow oil. IR (Diamond-ATR) *v* 3301, 2922, 1662, 1599, 1508, 1407, 1314, 754, 689 cm^{-1}; ^1H NMR ($CDCl_3$) 7.45-7.49 (m, 4H), 7.38-7.40 (m, 3H), 7.30-7.33 (m, 4H), 7.14 (d, J = 7.8 Hz, 2H), 5.15 (s, 1H), 2.34 (s, 3H), 2.15 (s, 3H); $^{13}C\{^1H\}$ NMR (CDCl3) δ 168.3, 138.7, 137.9, 136.6, 136.5, 131.6, 129.3, 128.4, 128.2, 127.9, 127.7, 123.5, 120.1, 90.3, 84.7, 42.8, 24.5, 21.0; HRMS (ESI-TOF) *m/z* [M+H]+ calcd for $C_{24}H_{22}NO$ 340.1696, found 340.1693.



4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)-benzoic acid (4j)

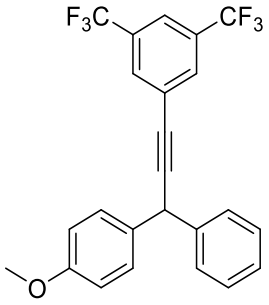
The title compound was derived from 4-(hydroxy(4-methoxyphenyl)methyl)benzoic acid (**3g**) (13.8 mg, 0.053 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)-borate (**1a**) (11.1 mg, 0.053 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (11.2 mg, 0.069 mmol, 1.3 equiv) in 0.3 mL of CH_3CN. Purification was conducted by silica gel column chromatography using hexanes/ EtOAc/AcOH (2:1:0.01% v/v) and subsequent CH_3CN/hexanes extraction afforded product **4j** (11.3 mg, 62% yield) as a yellow oil. IR (Diamond-ATR) *v* 2919, 1691, 1607, 1508, 1297, 1246, 1173, 758, 740, 691, 554 cm^{-1}; ^1H NMR (acetone-d_6) 8.02 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.50 7.53 (m, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.37-7.38 (m, 3H), 6.92 (d, *J* = 8.6 Hz, 2H), 5.41 (s, 1H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 159.9, 148.3, 134.5, 132.5, 131.0, 129.8, 129.4, 129.2, 128.7, 124.3, 115.0, 91.0, 85.8, 55.6, 43.3 (the carbonyl carbon and one aromatic carbon were not resolved in this spectrum); HRMS (ESI-TOF) *m/z* [M-H]- calcd for $C_{23}H_{17}O_3$ 341.1183, found 341.1186.

1-(3-(4-methoxyphenyl)-3-phenylprop-1-yn-1-yl)-2-(trifluoromethyl)benzene (5a)

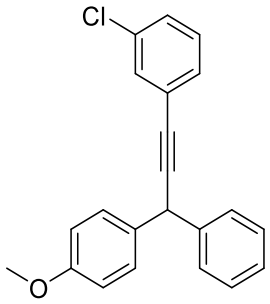


The title compound was derived from (4-methoxyphenyl)(phenyl)methanol (17.6 mg, 0.082 mmol, 1.0 equiv), potassium trifluoro((2-(trifluoromethyl)phenyl)ethynyl)-borate (**1h**) (22.6 mg, 0.082 mmol, 1.0 equiv), and $HBF_4{\cdot}OEt_2$ (21.2 mg, 0.13 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes/EtOAc (15:1) afforded product **5a** (26.8 mg, 89% yield) as a yellow/orange oil. IR (Diamond-ATR) *v* 2929, 1601, 1508, 1314, 1249, 1167, 1127, 1031, 764, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.64 (d, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.42-7.47 (m, 3H), 7.30−7.38 (m, 5H), 7.21-7.24 (m, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.20 (s, 1H), 3.77 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 158.5, 141.6, 134.1, 133.5, 131.6, 131.3, 128.9, 128.6, 127.8, 127.6, 126.9, 125.7 (q, *J* = 5.4 Hz), 123.6 (q, *J* = 273.7 Hz), 121.8, 114.0, 96.4, 80.7, 55.2, 43.2; ^{19}F NMR ($CDCl_3$) δ −62.17 (s, 3F); HRMS (EI) *m/z* [M+] calcd for $C_{23}H_{17}F_3O$ 366.1232, found 366.1231.

1-(3-(4-methoxyphenyl)-3-phenylprop-1-yn-1-yl)-3,5-bis(trifluoromethyl)benzene (5b)

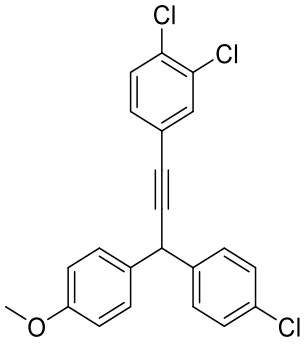


The title compound was derived from (4-methoxyphenyl)(phenyl)methanol (14.8 mg, 0.069 mmol, 1.0 equiv), potassium trifluoro((3,5-bis(trifluoromethyl)phenyl)-ethynyl)borate (**1i**) (23.8 mg, 0.069 mmol, 1.0 equiv), and $HBF_4{\cdot}OEt_2$ (17.9 mg, 0.11 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes/EtOAc (14:1) afforded product **5b** (25.6 mg, 85% yield) as a yellow/orange oil. IR (Diamond-ATR) *v* 2928, 1600, 1509, 1381, 1275, 1171, 1129, 697, 681 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88 (s, 2H), 7.78 (s, 1H), 7.25-7.41 (m, 7H), 6.88 (d, *J* = 9.0, 2H), 5.20 (s, 1H), 3.79 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 158.8, 141.1, 132.9, 131.8 (q, *J* = 33.7 Hz), 131.6 (q, *J* = 4.6 Hz), 128.9, 128.8, 127.8, 127.2, 125.8, 123.0 (q, *J* = 273.0 Hz), 121.3 (q, *J* = 3.8 Hz), 114.2, 94.5, 81.8, 55.3, 42.9; ^{19}F NMR ($CDCl_3$) δ -63.13 (s, 6F); HRMS (EI) *m/z* [M+] calcd for $C_{24}H_{16}F_6O$ 434.1105, found 434.1100.



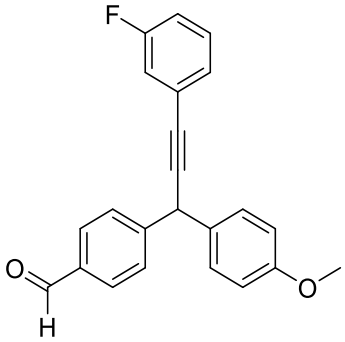
1-chloro-3-(3-(4-methoxyphenyl)-3-phenylprop-1-yn-1-yl)benzene (5c)

The title compound was derived from (4-methoxyphenyl)(phenyl)methanol (19.3 mg, 0.090 mmol, 1.0 equiv), potassium trifluoro((3-chlorophenyl)ethynyl)borate (**1f**) (21.9 mg, 0.090 mmol, 1.0 equiv), and $HBF_4{\cdot}OEt_2$ (23.4 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes/EtOAc (14:1) afforded product **5c** (29.7 mg, 99% yield) as a yellow/orange oil. IR (Diamond-ATR) *v* 2930, 1592, 1507, 1247, 1173, 1030, 780, 696, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45-7.46 (m, 1H), 7.39-7.41 (m, 2H), 7.30-7.35 (m, 5H), 7.19-7.28 (m, 3H), 6.86 (d, J = 9.0 Hz, 2H), 5.16 (s, 1H), 3.77 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 158.6, 141.7, 134.0, 133.5, 131.6, 129.8, 129.4, 128.9, 128.6, 128.2, 127.8, 126.9, 125.2, 114.0, 91.9, 83.3, 55.3, 42.9; HRMS (EI) *m/z* [M+] calcd for $C_{22}H_{17}ClO$ 332.0968, found 332.0962.



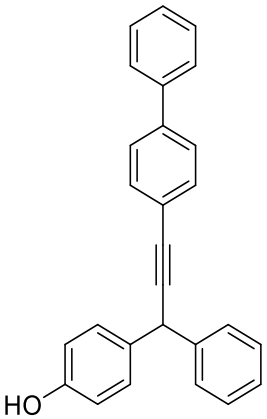
1,2-dichloro-4-(3-(4-chlorophenyl)-3-(4-methoxyphenyl)prop-1-yn-1-yl)benzene (5d)

The title compound was derived from (4-chlorophenyl)(4-methoxyphenyl)methanol (**3c**) (18.6 mg, 0.075 mmol, 1.0 equiv), potassium trifluoro((3,4-dichlorophenyl)ethynyl)-borate (**1e**) (20.7 mg, 0.075 mmol, 1.0 equiv), and $HBF_4{\cdot}OEt_2$ (19.3 mg, 0.12 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes/EtOAc (20:1) afforded product **5d** (25.0 mg, 83% yield) as a yellow oil. IR (Diamond-ATR) *v* 2926, 1508, 1487, 1461, 1173, 1089, 1031, 817 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.54 (d, *J* = 2.0 Hz, 1H), 7.35-7.37 (m, 1H), 7.25−7.33 (m, 7H), 6.87 (d, *J* = 9.0 Hz, 2H), 5.12 (s, 1H), 3.79 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 158.8, 140.0, 133.3, 132.9, 132.8, 132.48, 132.45, 130.8, 130.3, 129.1, 128.80, 128.79, 123.2, 114.2, 92.1, 82.8, 55.3, 42.3; HRMS (EI) *m/z* [M+] calcd for $C_{22}H_{15}Cl_3O$ 400.0188, found 400.0186.



4-(3-(3-fluorophenyl)-1-(4-methoxyphenyl)prop-2-yn-1-yl)benzaldehyde (5e)

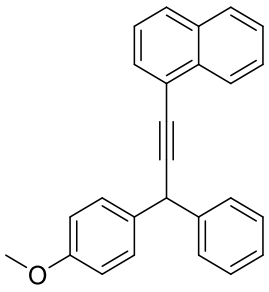
The title compound was derived from 4-(hydroxy(4-methoxyphenyl)methyl)benzaldehyde (**3h**) (21.1 mg, 0.087 mmol, 1.0 equiv), potassium trifluoro((3-fluorophenyl)-ethynyl)borate (**1g**) (19.7 mg, 0.087 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (22.6 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes/EtOAc (6:1) afforded product **5e** (24.6 mg, 82% yield) as a yellow oil. IR (Diamond-ATR) *v* 2926, 1697, 1603, 1578, 1508, 1246, 1148, 1032, 783, 681 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.99 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.25-7.28 (m, 2H), 7.15-7.18 (m, 1H), 7.00−7.05 (m, 1H), 6.88 (d, *J* = 9.0 Hz, 2H), 5.23 (s, 1H), 3.79 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 191.7, 162.3 (d, *J* = 246.14 Hz), 158.9, 148.5, 135.2, 132.4, 130.1, 129.8 (d, *J* = 6.2 Hz), 128.9, 128.4, 127.5 (d, *J* = 3.1 Hz), 124.9, 118.5 (d, *J* = 23.0 Hz), 115.6 (d, *J* = 21.5 Hz), 114.3, 90.3, 84.3, 55.3, 43.0; ^{19}F NMR ($CDCl_3$) δ -112.97 (s, 1F); HRMS (EI) *m/z* [M+] calcd for $C_{23}H_{17}FO_2$ 344.1213, found 344.1217.



4-(3-([1,1′-biphenyl]-4-yl)-1-phenylprop-2-yn-1-yl)-phenol (5f)

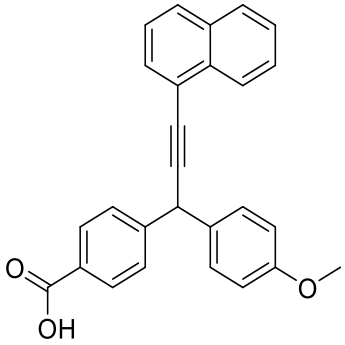
The title compound was derived from 4-(hydroxy(phenyl)methyl)phenol (**3a**) (16.7 mg, 0.083 mmol, 1.0 equiv), potassium trifluoro([1,1'-biphenyl]-4-ylethynyl)borate (**1k**) (23.6 mg, 0.083 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (21.6 mg, 0.13 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (5:1) afforded product **5f** (21.3 mg, 71% yield) as an orange/pink oil. IR (Diamond-ATR) *v* 3331, 2922, 1597, 1508, 1485, 1447, 1170, 840, 761, 692, 560 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.57-7.59 (m, 2H), 7.53 (s, 4H), 7.41-7.45 (m, 4H), 7.29-7.36 (m, 5H), 7.21-7.25 (m, 1H), 6.78 (d, *J* = 8.6 Hz, 2H), 5.17 (s, 1H), 4.84 (s, 1H); ^{13}C {^1H} NMR ($CDCl_3$) δ 154.4, 142.0, 140.7, 140.4, 134.1, 132.1, 129.1, 128.8, 128.6, 127.8, 127.5, 127.0, 126.9, 126.8, 122.4, 115.4, 91.1, 84.6, 43.0; HRMS (EI) *m/z* [M+] calcd for $C_{27}H_{20}O$ 360.1514, found 360.1509.

1-(3-(4-methoxyphenyl)-3-phenylprop-1-yn-1-yl)-naphthalene (5g)

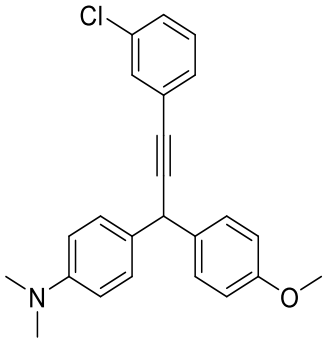


The title compound was derived from (4-methoxyphenyl) (phenyl)methanol (18.5 mg, 0.086 mmol, 1.0 equiv), potassium trifluoro(naphthalen-1-ylethynyl)borate (**1j**) (22.2 mg, 0.086 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (22.3 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (20:1) afforded product **5g** (21.0 mg, 70% yield) as a yellow oil. IR (Diamond-ATR) *v* 2926, 1603, 1507, 1246, 1174, 1030, 797, 772, 696, 564 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.33 (d, *J* = 7.42, Hz, 1H), 7.78-7.84 (m, 2H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.47-7.54 (m, 4H), 7.33-7.44 (m, 5H), 7.23-7.27 (m, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.33 (s, 1H), 3.78 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 158.6, 142.1, 134.0, 133.5, 133.2, 130.4, 129.0, 128.7, 128.4, 128.2, 127.9, 126.9, 126.7, 126.3, 125.2, 121.2, 114.1, 95.5, 82.9, 55.3, 43.3 (one aromatic carbon was not resolved in this spectrum); HRMS (EI) *m/z* [M+] calcd for $C_{26}H_{20}O$ 348.1514, found 348.1508.

4-(1-(4-methoxyphenyl)-3-(naphthalen-1-yl)prop-2-yn-1-yl)-benzoic acid (5h)

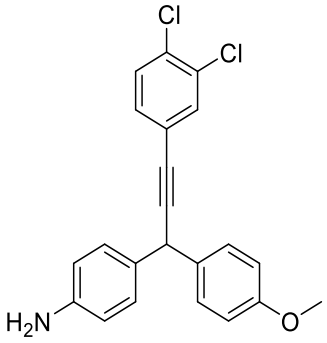


The title compound was derived from 4-(hydroxy(4-methoxyphenyl)methyl)benzoic acid (**3g**) (19.7 mg, 0.076 mmol, 1.0 equiv), potassium trifluoro(naphthalen-1-ylethynyl)borate (**1j**) (19.7 mg, 0.076 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (19.8 mg, 0.12 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes/EtOAc/AcOH (1.5:1:0.01% v/v) afforded product **5h** (19.8 mg, 66% yield) as a yellow oil. IR (Diamond-ATR) *v* 2922, 1689, 1606, 1507, 1245, 1174, 1032, 771 cm^{-1}; ^1H NMR (acetone-d_6) δ 8.33-8.36 (m, 1H), 8.06 (d, *J* = 8.2 Hz, 2H), 7.93-7.97 (m, 2H), 7.72-7.78 (m, 3H), 7.49-7.62 (m, 5H), 6.96 (d, *J* = 8.6 Hz, 2H), 5.61 (s, 1H), 3.79 (s, 3H); ^{13}C {^1H} NMR (acetone-d_6) δ 159.9, 148.3, 134.5, 134.4, 134.3, 131.4, 131.1, 129.9, 129.6, 129.4, 128.8, 127.9, 127.5, 126.8, 126.4, 121.8, 115.1, 96.2, 83.8, 55.6, 43.7 (the carbonyl carbon and one aromatic carbon were not resolved in this spectrum); HRMS (EI) *m/z* [M+] for $C_{27}H_{20}O_3$ 392.1412, found 392.1417.



4-(3-(3-chlorophenyl)-1-(4-methoxyphenyl)prop-2-yn-1-yl)-*N*,*N*dimethylaniline (5i)

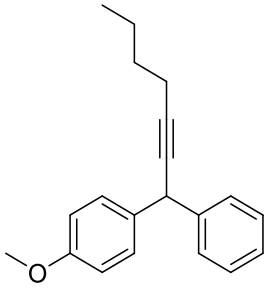
The title compound was derived from (4-(dimethylamino)phenyl)(4-methoxyphenyl)methanol (**3d**) (20.5 mg, 0.080 mmol, 1.0 equiv), potassium trifluoro((3-chlorophenyl)ethynyl)borate (**1f**) (19.4 mg, 0.080 mmol, 1.0 equiv), and $HBF_4{\cdot}OEt_2$ (33.6 mg, 0.21 mmol, 2.6 equiv) in 0.3 mL of CH_3CN. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (3:1) afforded product **5i** (18.4 mg, 61% yield) as a brown oil. IR (Diamond-ATR) *v* 2926, 1607, 1507, 1246, 1172, 1033, 782, 680, 555 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44−7.45 (m, 1H), 7.31−7.33 (m, 3H), 7.18-7.26 (m, 4H), 6.85 (d, *J* = 8.6 Hz, 2h), 6.69 (d, *J* = 9.0 Hz, 2H), 5.08 (s, 1H), 3.78 (s, 3H), 2.91 (s, 6H); ^{13}C {^1H} NMR ($CDCl_3$) δ 158.4, 149.6, 134.3, 134.0, 131.5, 129.8, 129.6, 129.4, 128.8, 128.4, 128.0, 125.5, 113.9, 112.7, 92.7, 82.8, 55.3, 41.9, 40.6; HRMS (ESI-TOF) *m/z* [M+H]+ calcd for $C_{24}H_{23}ClNO$ 376.1463, found 376.1458.



4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)aniline (5j)

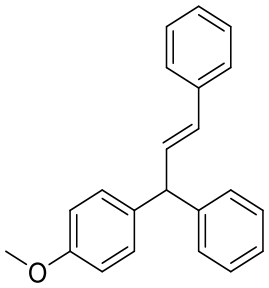
The title compound was derived from tert-butyl (4-(hydroxy(*p*-tolyl)methyl)phenyl)carbamate (**3f**) (20.5 mg, 0.062 mmol, 1.0 equiv), potassium trifluoro((3,4-dichlorophenyl)ethynyl)borate (**1e**) (17.3 mg, 0.062 mmol, 1.0 equiv), and $HBF_4{\cdot}OEt_2$ (26.2 mg, 0.16 mmol, 2.6 equiv) in 0.3 mL of CH_3CN. Purification was conducted by silica gel column chromatography using hexanes/EtOAc (1.3:1) followed by a pentane wash and subsequent CH_3CN/hexanes extraction to afford product **5j** (15.3 mg, 51% yield) as a burgundy oil. IR (Diamond-ATR) *v* 3372, 2928, 1607, 1506, 1461, 1244, 1173, 1127, 1030, 817, 729, 569 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53 (m, 1H), 7.34−7.36 (m, 1H), 7.24−7.30 (m, 3H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 5.05 (s, 1H), 3.78 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 158.5, 145.3, 133.9, 133.3, 132.3, 132.1, 131.5, 130.8, 130.2, 128.7, 128.6, 123.7, 115.3, 114.0, 93.3, 82.0, 55.3, 42.0; HRMS (ESI-TOF) *m/z* [M+H]+ calcd for $C_{22}H_{18}Cl_2NO$ 382.0760, found 382.0758.

1-methoxy-4-(1-phenylhept-2-yn-1-yl)benzene (5k)



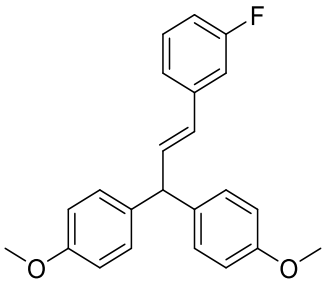
The title compound was derived from (4-methoxyphenyl)(phenyl)methanol (23.1 mg, 0.11 mmol, 1.0 equiv), potassium trifluoro(hex-1-yn-1-yl)borate (**1d**) (20.3 mg, 0.11 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (27.9 mg, 0.17 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes/EtOAc (15:1) afforded product **5k** (21.9 mg, 73% yield) as a yellow oil. IR (Diamond-ATR) *v* 2929, 1653, 1598, 1508, 1248, 1172, 1029, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34-7.36 (m, 2H), 7.26-7.30 (m, 4H), 7.17-7.21 (m, 1H), 6.82 (d, *J* = 9.0 Hz, 2H), 4.92 (s, 1H), 3.76 (s, 3H), 2.28 (td, *J* = 2.4, 7.0 Hz, 2H), 1.51-1.56 (m, 2H), 1.41−1.46 (m, 2H), 0.92 (t, *J* = 7.0 Hz, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 158.3, 142.8, 134.7, 128.8, 128.4, 127.7, 126.5, 113.8, 84.9, 80.8, 55.2, 42.4, 31.1, 22.0, 18.6, 13.6.

(*E*)-(3-(4-methoxyphenyl)prop-1-ene-1,3-diyl)dibenzene (6a)



The title compound was derived from (4-methoxyphenyl)(phenyl)methanol (21.4 mg, 0.100 mmol, 1.0 equiv), potassium trifluoro(*E*)-2-phenylethenylborate (21.0 mg, 0.100 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (25.9 mg, 0.16 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes/EtOAc (15:1) afforded product **6a** (29.0 mg, 97% yield) as a pale yellow oil. IR (Diamond-ATR) *v* 2927, 1607, 1508, 1244, 1175, 1031, 966, 829, 744, 693, 549 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35−7.37 (m, 2H), 7.19−7.32 (m, 8H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.65 (dd, *J* = 7.4, 15.6 Hz, 1H), 6.32 (d, *J* = 15.6 Hz, 1H), 4.84 (d, *J* = 7.4 Hz, 1H), 3.77 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 158.1, 143.8, 137.3, 135.6, 132.9, 131.1, 129.6, 128.6, 128.5, 128.4, 127.2, 126.34, 126.26, 113.8, 55.2, 53.3.

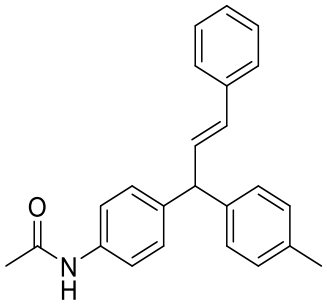
(*E*)-4,4′- (3-(3-fluorophenyl)prop-2-ene-1,1-diyl)bis-(methoxybenzene) (6b)



The title compound was derived from bis(4-methoxyphenyl)methanol (**3b**) (21.0 mg, 0.086 mmol, 1.0 equiv), potassium trifluoro(2-(3-fluorophenyl)vinyl)borate (19.6 mg, 0.086 mmol, 1.0 equiv), and $HBF_4 \cdot OEt_2$ (22.3 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes/EtOAc (9:1) afforded product **6b** (29.1 mg, 97% yield) as a pink oil. IR (Diamond-ATR) *v* 2929, 1608, 1581, 1506, 1242, 1173,

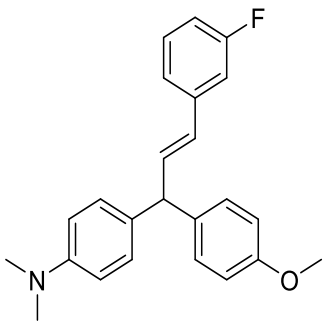
1033, 964, 825, 553 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.20−7.25 (m, 1H), 7.05−7.13 (m, 6H), 6.84−6.91 (m, 5H), 6.61−6.66 (m, 1H), 6.26 (d, *J* = 15.6 Hz, 1H), 4.79 (d, *J* = 7.4 Hz, 1H), 3.78 (s, 6H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 163.1 (d, *J* = 245.4 Hz), 158.2, 139.7 (d, *J* = 7.7 Hz), 135.6, 134.7, 129.9 (d, *J* = 3.1 Hz), 129.8 (d, *J* = 2.3 Hz), 129.5, 122.1 (d, *J* = 2.3 Hz), 113.94 (d, *J* = 21.5 Hz), 113.87, 112.7 (d, *J* = 22.2 Hz), 55.2, 52.4; ^{19}F NMR ($CDCl_3$) δ −113.70 (q, *J* = 9.3 Hz, 1F); HRMS (EI) *m/z* [M+] calcd for $C_{23}H_{21}FO_2$ 348.1526, found 348.1523.

(*E*)-*N*-(4-(3-phenyl-1-(*p*-tolyl)allyl)phenyl)acetamide (6c)



The title compound was derived from *N*-(4-hydroxy(*p*-tolyl)methyl)phenyl)acetamide (**3e**) (22.4 mg, 0.088 mmol, 1.0 equiv), potassium trifluoro(*E*)-2-phenylethenylborate (18.5 mg, 0.088 mmol, 1.0 equiv), and $HBF_4{\cdot}OEt_2$ (22.8 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH_3CN. Purification was conducted by silica gel column chromatography using hexanes/EtOAc (1:2) and subsequent CH_3CN/hexanes extraction afforded product **6c** (23.2 mg, 77% yield) as a pale white/yellow oil. IR (Diamond-ATR) *v* 3294, 2922, 1662, 1599, 1509, 1407, 1369, 1315, 1262, 966, 816, 741, 691, 522 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.41−7.43 (m, 2H), 7.34−7.37 (m, 2H), 7.15−7.29 (m, 5H), 7.10 (s, 4H), 6.61 (dd, *J* = 7.4, 16.0 Hz, 1H), 6.31 (d, *J* = 15.6 Hz, 1H), 4.81 (d, *J* = 7.4 Hz, 1H), 2.32 (s, 3H), 2.13 (s, 3H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 168.3, 140.4, 139.7, 137.2, 136.2, 136.0, 132.6, 131.2, 129.2, 129.1, 128.5, 128.4, 127.2, 126.3, 120.0, 53.2, 24.5, 21.0; HRMS (ESI-TOF) *m/z* [M+H]+ calcd for $C_{24}H_{24}NO$ 342.1852, found 342.1849.

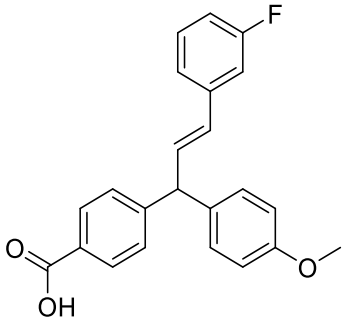
(*E*)-4-(3-(3-fluorophenyl)-1-(4-methoxyphenyl)allyl)-*N*,*N*-dimethylaniline (6d)



The title compound was derived from (4-(dimethylamino)phenyl)(4-methoxyphenyl)methanol (**3d**) (21.4 mg, 0.083 mmol, 1.0 equiv), potassium trifluoro(2-(3-fluorophenyl)vinyl) borate (18.9 mg, 0.083 mmol, 1.0 equiv), and $HBF_4{\cdot}OEt_2$ (34.9 mg, 0.2 mmol, 2.6 equiv) in 0.3 mL of CH_3CN. Purification by silica gel column chromatography using hexanes/EtOAc (6:1) afforded product **6d** (25.1 mg, 84% yield) as a pale white/yellow oil. IR (Diamond-ATR) *v* 2926, 1609, 1507, 1244, 1174, 1140, 1034, 813, 774, 552 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.19−7.25 (m,

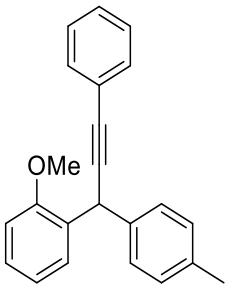
1H), 7.04−7.15 (m, 6H), 6.83−6.90 (m, 3H), 6.62−6.71 (m, 3H), 6.27 (d, *J* = 16.0 Hz, 1H), 4.75 (d, *J* = 7.4 Hz, 1H), 3.78 (s, 3H), 2.91 (s, 6H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 163.1 (d, *J* = 244.6 Hz), 158.1, 149.3, 140.0 (d, *J* = 7.7 Hz), 136.0, 135.1, 131.4, 129.9, 129.8, 129.5, 129.1, 122.1 (d, *J* = 3.1 Hz), 113.79, 113.78 (d, *J* = 21.5 Hz), 112.74, 112.65 (d, *J* = 22.2 Hz), 55.2, 52.3, 40.7; ^{19}F NMR ($CDCl_3$) δ −113.82 (q, *J* = 9.3 Hz, 1F); HRMS (ESI-TOF) *m/z* [M+H]+ calcd for $C_{24}H_{25}FNO$ 362.1915, found 362.1912.

(*E*)-4-(3-(3-fluorophenyl)-1-(4-methoxyphenyl)allyl)-benzoic acid (6e)



The title compound was derived from 4-(hydroxy(4-methoxyphenyl)methyl)benzoic acid (**3g**) (21.4 mg, 0.083 mmol, 1.0 equiv), potassium trifluoro(2-(3-fluorophenyl)vinyl) borate (18.9 mg, 0.083 mmol, 1.0 equiv), and $HBF_4{\cdot}OEt_2$ (17.4 mg, 0.12 mmol, 1.3 equiv) in 0.3 mL of CH_3CN. Purification was conducted by silica gel column chromatography using hexanes/EtOAc/AcOH (2:1:0.01% v/v) and subsequent CH_3CN/hexanes extraction afforded product **6e** (23.0 mg, 77% yield) as a pale yellow oil. IR (Diamond-ATR) *v* 2922, 1685, 1607, 1508, 1245, 1176, 1033, 963, 778, 683, 548 cm^{-1}; ^{1}H NMR (acetone-*d*$_6$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.22−7.37 (m, 5H), 6.89−7.01 (m, 4H), 6.49 (d, *J* = 16.0 Hz, 1H), 5.01 (d, *J* = 8.2 Hz, 1H), 3.77 (s, 3H); ^{13}C {^{1}H} NMR (acetone-*d*$_6$) δ 164.1 (d, J = 243.1 Hz), 159.5, 150.4, 141.0 (d, *J* = 7.7 Hz), 136.0, 134.9, 131.3, 131.2, 131.1 (d, *J* = 3.1 Hz), 130.8, 130.4, 129.4, 123.52, 123.50, 114.8 (d, *J* = 20.7 Hz), 113.4 (d, *J* = 22.2 Hz), 55.6, 54.2; ^{19}F NMR (acetone-*d*$_6$) δ -115.09 (q, *J* = 9.3 Hz, 1F); HRMS (ESI-TOF) *m/z* [M+H]+ calcd for $C_{23}H_{20}FO_3$ 363.1391, found 363.1388.

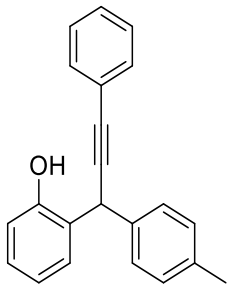
1-methoxy-2-(3-phenyl-1-(*p*-tolyl)prop-2-yn-1-yl)-benzene (7)



The title compound was derived from (2-methoxyphenyl)(p-tolyl)methanol (**3i**) (65.8 mg, 0.288 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (**1a**) (60.0 mg, 0.288 mmol, 1.0 equiv), and $HBF_4{\cdot}OEt_2$ (74.6 mg, 0.461 mmol, 1.6 equiv) in 1.0 mL of CH_3CN. Purification by automated flash column chromatography on silica gel using hexanes/diethyl ether (99:1) afforded product **7** (60.1 mg, 67% yield) as a yellow oil. IR (Diamond-ATR) *v* 1597, 1488, 1460, 1243, 1103, 1026, 803, 749, 690, 560, 524 cm^{-}

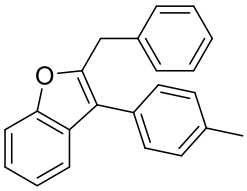
[1]; ^{1}H NMR ($CDCl_3$) δ 7.60−7.62 (m, 1H), 7.44−7.47 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.25−7.29 (m, 3H), 7.19−7.23 (m, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.95 (t of d, *J* = 1.1, 7.4 Hz, 1H), 6.84−6.86 (m, 1H), 5.65 (s, 1H), 3.82 (s, 3H), 2.29 (s, 3H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 156.1, 138.8, 136.0, 131.7, 130.5, 129.0, 128.9, 128.13, 128.05, 127.71, 127.68, 123.8, 120.9, 110.7, 91.2, 83.3, 55.5, 36.2, 21.0; HRMS (DART-TOF+) *m/z* [M+H] calcd for $C_{23}H_{21}O$ 313.1592, found 313.1600.

2-(3-phenyl-1-(*p*-tolyl)prop-2-yn-1-yl)phenol (8)



The title compound was derived from 1-methoxy-2-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)benzene (**7**) (60.1 mg, 0.192 mmol, 1.0 equiv) and boron tribromide solution [1.0 M in methylene chloride] (0.145 g, 0.577 mmol, 3.0 equiv) in 2.0 mL of anhydrous DCM. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (gradient: 24:1 → 9:1) and subsequent CH_3CN/hexanes extraction afforded product **8** (42.0 mg, 73% yield) as a yellow oil. IR (Diamond-ATR) *v* 3527, 1595, 1488, 1454, 1185, 1087, 822, 749, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.48−7.52 (m, 2H), 7.41−7.44 (m, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.31−7.35 (m, 3H), 7.19−7.22 (m, 1H), 7.17 (m, 2H), 6.96 (t of d, *J* = 1.2, 7.4 Hz, 1H), 6.85 (d of d, *J* = 1.2, 8.2 Hz, 1H), 5.50 (s, 1H), 5.44 (s, 1H), 2.35 (s, 3H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 153.3, 137.2, 136.7, 131.7, 129.5, 129.4, 128.5, 128.23, 128.19, 127.6, 127.5, 123.0, 121.0, 116.6, 89.1, 85.3, 38.2, 21.0; HRMS (DART-TOF+) *m/z* [M+H] calcd for $C_{22}H_{19}O$ 299.1436, found 299.1437.

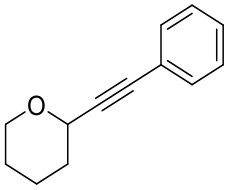
BENZOFURAN



2-benzyl-3-(*p*-tolyl)benzofuran (9)

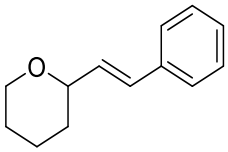
The title compound was derived from 2-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)phenol (**8**) (42.0 mg, 0.141 mmol, 1.0 equiv) and *t*-BuOK (31.6 mg, 0.282 mmol, 2.0 equiv) in 1.13 mL of anhydrous dioxane. Purification by automated flash column chromatography on silica gel using hexanes/diethyl ether (gradient: 99:1 → 49:1) and subsequent CH_3CN/hexanes extraction afforded product **9** (19.7 mg, 47% yield) as a yellow solid. Mp 65−68 °C; IR (Diamond-ATR) *v* 1512, 1492, 1453, 1159, 977, 820, 740, 719, 694, 492, 454 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.57−7.59 (m, 1H), 7.40−7.45 (m, 3H), 7.20−7.31 (m, 9H), 4.20 (s, 2H), 2.42 (s, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 154.3, 152.3, 138.0, 137.0, 129.5, 129.4, 128.9, 128.8, 128.6, 128.5, 126.5, 123.9, 122.6, 119.8, 118.1, 111.1, 32.9, 21.3; HRMS (DART-TOF+) *m/z* [M+H] calcd for $C_{22}H_{19}O$ 299.1436, found 299.1440.

2-ALKENYL AND 2-ALKYNYL TETRAHYDROPYRANS



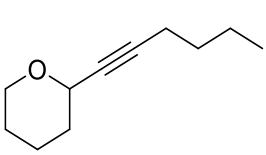
2-(phenylethynyl)tetrahydro-2*H*-pyran (10a)

The title compound was derived from 2-methoxytetrahydropyran (18.7 mg, 0.161 mmol, 1.0 equiv.), potassium trifluoro(phenylethynyl)borate (**1a)** (50.3 mg, 0.242 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (32.9 μL, 0.242 mmol, 1.5 equiv.) in 1.61 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (49:1) and subsequent CH_3CN/hexanes extraction afforded product **10a** (24.6 mg, 82% yield) as a yellow oil. ^1H NMR ($CDCl_3$) δ 7.44-7.46 (m, 2H), 7.28-7.31 (m, 3H), 4.49-4.52 (m, 1H), 4.02-4.07 (m, 1H), 3.56-3.62 (m, 1H), 1.89-1.94 (m, 2H), 1.75-1.82 (m, 1H), 1.55-1.65 (m, 3H) ; ^{13}C {^1H} NMR ($CDCl_3$) δ 131.7, 128.23, 128.16, 122.7, 88.1, 85.15, 67.41, 66.59, 32.15, 25.64, 21.79.



(*E*)-2-styryltetrahydro-2*H*-pyran (10b)

The title compound was derived from 2-methoxytetrahydropyran (11.6 mg, 0.100 mmol, 1.0 equiv.), potassium trifluoro(*E*)-2-phenylethenylborate (31.5 mg, 0.150 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (20.4 μL, 0.150 mmol, 1.5 equiv.) in 1.0 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 49:1) and subsequent CH_3CN/hexanes extraction afforded product **10b** (6.7 mg, 36% yield) as a yellow oil. ^1H NMR ($CDCl_3$) δ 7.37-7.39 (m, 2H), 7.19-7.32 (m, 3H), 6.57-6.61 (m, 1H), 6.18-6.24 (m, 1H), 4.06-4.09 (m, 1H), 3.95-4.00 (m, 1H), 3.51-3.58 (m, 1H), 1.88-1.91 (m, 1H), 1.72-1.76 (m, 1H), 1.43-1.65 (m, 4H); ^{13}C {^1H} NMR ($CDCl_3$) δ 137.0, 130.8, 129.7, 128.5, 127.4, 126.4, 78.0, 68.4, 32.2, 25.9, 23.4.

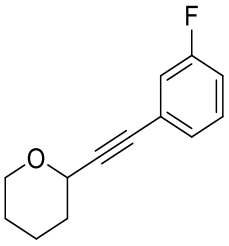


2-(hex-1-tn-1-yl)tetrahydro-2*H*-pyran (10c)

The title compound was derived from 2-methoxytetrahydropyran (31.4 mg, 0.271 mmol, 1.0 equiv.), potassium trifluoro(hex-1-yn-1-yl)borate (**1d**) (76.3 mg, 0.406 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (55.2 μL, 0.406 mmol, 1.5 equiv.) in 2.71 mL of CH_3CN (C = 0.1 M). Aqueous work-up afforded product **10c** (37.8 mg, 84% yield) as a yellow oil. ^1H NMR ($CDCl_3$) δ 4.21-4.24 (m, 1H), 3.95-

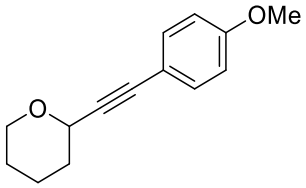
3.99 (m, 1H), 3.47-3.52 (m, 1H), 2.20-2.24 (m, 2H), 1.80-1.85 (m, 2H), 1.38-1.57 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 85.7, 79.1, 67.3, 66.6, 32.5, 30.7, 25.7, 21.94, 21.90, 18.4, 13.5.

2-((3-fluorophenyl)ethynyl)tetrahydro-2*H*-pyran (10d)



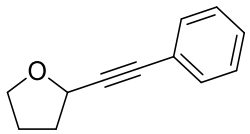
The title compound was derived from 2-methoxytetrahydropyran (17.1 mg, 0.147 mmol, 1.0 equiv.), potassium trifluoro((3-fluorophenyl)ethynyl)borate (**1g**) (49.8 mg, 0.220 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (30.0 μL, 0.220 mmol, 1.5 equiv.) in 1.5 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (49:1) and subsequent CH_3CN/hexanes extraction afforded product **10d** (14.3 mg, 48% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.21-7.29 (m, 2H), 7.12-7.16 (m, 1H), 6.99-7.04 (m, 1H), 4.48-4.51 (m, 1H), 4.01-4.06 (m, 1H), 3.56-3.62 (m, 1H), 1.87-1.96 (m, 2H), 1.73-1.82 (m, 1H), 1.55-1.66 (m, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 162.3 (d, *J* = 246.1 Hz), 129.8 (d, *J* = 9.2 Hz), 127.6 (d, *J* = 3.1 Hz), 124.6 (d, *J* = 9.2 Hz), 118.5 (d, *J* = 23.0 Hz), 115.6 (d, *J* = 21.5 Hz), 89.1, 83.9, 67.3, 66.7, 32.1, 25.6, 21.8. ^{19}F NMR ($CDCl_3$) δ −113.12 (m, 1F);

2-((4-methoxyphenyl)ethynyl)tetrahydro-2*H*-pyran (10e)



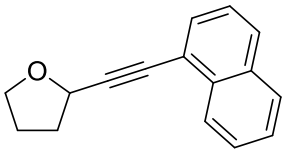
The title compound was derived from 2-methoxytetrahydropyran (16.1 mg, 0.139 mmol, 1.0 equiv.), potassium trifluoro((4-methoxyphenyl)ethynyl)-borate (**1b**) (49.5 mg, 0.208 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (28.3 μL, 0.208 mmol, 1.5 equiv.) in 1.39 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 97:3) and subsequent CH_3CN/hexanes extraction afforded product **10e** (10.2 mg, 34% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.37-7.40 (m, 2H), 6.81-6.83 (m, 2H), 4.47-4.49 (m, 1H), 4.02-4.07 (m, 1H), 3.80 (s, 3H), 3.55-3.60 (m, 1H), 1.90 (m, 2H), 1.74-1.81 (m, 1H), 1.55-1.63 (m, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 133.2, 114.9, 113.8, 86.7, 85.0, 67.6, 66.7, 55.2, 32.3, 25.7, 21.9.

2-ALKENYL AND 2-ALKYNYL TETRAHYDROFURANS



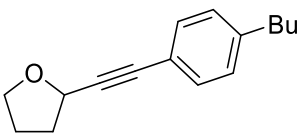
2-(phenylethynyl)tetrahydrofuran (11a)

The title compound was derived from 2-ethoxytetrahydrofuran (20.2 mg, 0.174 mmol, 1.0 equiv.), potassium trifluoro(phenylethynyl)borate (**1a)** (54.4 mg, 0.261 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (35.6 µL, 0.261 mmol, 1.5 equiv.) in 1.74 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 50:1 → 17:1) and subsequent CH_3CN/hexanes extraction afforded product **11a** (27.5 mg, 92% yield) as a yellow oil. ^1H NMR ($CDCl_3$) δ 7.42-7.44 (m, 2H), 7.28-7.30 (m, 3H), 4.79-4.83 (m, 1H), 3.98-4.04 (m, 1H), 3.83-3.88 (m, 1H), 2.20-2.26 (m, 1H), 2.04-2.12 (m, 2H), 1.90-1.98 (m, 1H); ^{13}C {^1H} NMR ($CDCl_3$) δ 131.7, 128.19, 128.16, 122.78, 89.0, 84.4, 68.6, 67.9, 33.4, 25.5; IR (Diamond-ATR) *v* 2979, 2950, 2870, 1489, 1333, 1047, 914, 754, 689 cm^{-1}.



2-(naphthalene-1-ylethynyl)tetrahydrofuran (11b)

The title compound was derived from 2-ethoxytetrahydrofuran (15.7 mg, 0.135 mmol, 1.0 equiv.), potassium trifluoro(naphthalene-1-ylethynyl)borate (**1j**) (52.2 mg, 0.202 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (27.5 µL, 0.202 mmol, 1.5 equiv.) in 1.35 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (99:1) and subsequent CH_3CN/hexanes extraction afforded product **11b** (29.7 mg, 99% yield) as a yellow oil. ^1H NMR ($CDCl_3$) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.81 (t, *J* = 9.0 Hz, 2H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.48-7.57 (m, 2H), 7.40 (t, *J*, = 7.4 Hz, 1H), 4.95-4.98 (m, 1H), 4.05-4.11 (m, 1H), 3.89-3.94 (m, 1H), 2.25-2.35 (m, 1H), 2.11-2.23 (m, 2H), 1.93-2.04 (m, 1H); ^{13}C {^1H} NMR ($CDCl_3$) δ 133.3, 133.1, 130.5, 128.7, 128.2, 126.7, 126.3, 126.1, 125.1, 120.4, 94.1, 82.5, 68.8, 67.9, 33.6, 25.5; IR (Diamond-ATR) *v* 2978, 2948, 2868, 1394, 1331, 1045, 912, 798, 770, 567 cm^{-1}.

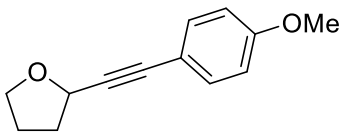


2-((4-butylphenyl)ethynyl)tetrahydrofuran (11c)

The title compound was derived from 2-ethoxytetrahydrofuran (15.3 mg, 0.131 mmol, 1.0 equiv.), potassium ((4-butylphenyl)ethynyl)trifluoroborate (**1c**) (52.1 mg, 0.197 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (26.8 µL, 0.197 mmol, 1.5 equiv.) in 1.31 mL of CH_3CN (C = 0.1 M).

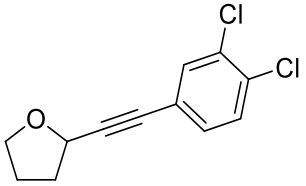
Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 16:1) afforded product **11c** (28.0 mg, 93% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.32-7.35 (m, 2H), 7.09-7.11 (m, 2H), 4.79-4.82 (m, 1H), 3.98-4.03 (m, 1H), 3.82-3.87 (m, 1H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.18-2.27 (m, 1H), 2.02-2.14 (m, 2H), 1.88-1.98 (m, 1H), 1.53-1.61 (m, 2H), 1.28-1.38 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 143.3, 131.6, 128.3, 119.9, 88.3, 84.6, 68.6, 67.8, 35.5, 33.4, 33.3, 25.5, 22.3, 13.9; IR (Diamond-ATR) *v* 2955, 2928, 2858, 1508, 1458, 1333, 1049, 914, 831, 561 cm^{-1}.

2-((4-methoxyphenyl)ethynyl)tetrahydrofuran (11d)



The title compound was derived from 2-ethoxytetrahydrofuran (17.2 mg, 0.148 mmol, 1.0 equiv.), potassium trifluoro((4-methoxyphenyl)ethynyl)-borate (**1b**) (53.0 mg, 0.223 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (30.3 μL, 0.223 mmol, 1.5 equiv.) in 1.48 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 12:1) afforded product **11d** (23.3 mg, 78% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.35-7.38 (m, 2H), 6.80-6.83 (m, 2H), 4.78-4.81 (m, 1H), 3.98-4.03 (m, 1H), 3.82-3.87 (m, 1H), 3.79 (s, 3H), 2.18-2.25 (m, 1H), 2.02-2.14 (m, 2H), 1.89-1.98 (m, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 159.5, 133.1, 114.9, 113.8, 87.6, 84.3, 68.7, 67.8, 55.2, 33.4, 25.5; IR (Diamond-ATR) *v* 2952, 2870, 2837, 1605, 1507, 1288, 1244, 1171, 1046, 1028, 830 cm^{-1}.

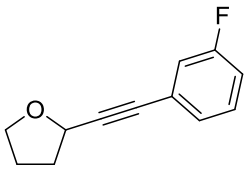
2-((3,4-dichlorophenyl)ethynyl)tetrahydrofuran (11e)



The title compound was derived from 2-ethoxytetrahydrofuran (14.5 mg, 0.124 mmol, 1.0 equiv.), potassium trifluoro((3,4-dichlorophenyl)ethynyl)borate (**1e**) (51.7 mg, 0.187 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (25.4 μL, 0.187 mmol, 1.5 equiv.) in 1.24 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (99:1) and subsequent CH_3CN/hexanes extraction afforded product **11e** (19.3 mg, 64% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.51-7.52 (m, 1H), 7.35-7.37 (m, 1H), 7.23-7.26 (m, 1H), 4.77-4.80 (m, 1H), 3.96-4.02 (m, 1H), 3.83-3.88 (m, 1H), 2.19-2.28 (m, 1H), 2.02-2.14 (m, 2H), 1.90-1.99 (m, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 133.3, 132.7, 132.4, 130.8, 130.3, 122.8, 91.2, 82.2, 68.4, 68.1, 33.3, 25.5; IR

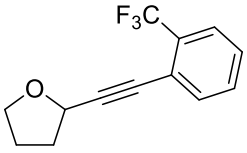
(Diamond-ATR) *v* 2979, 2951, 2870, 1462, 1130, 1048, 1029, 878, 818, 682 cm^{-1}.

2-((3-fluorophenyl)ethynyl)tetrahydrofuran (11f)



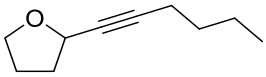
The title compound was derived from 2-ethoxytetrahydrofuran (18.3 mg, 0.158 mmol, 1.0 equiv.), potassium trifluoro((3-fluorophenyl)ethynyl)borate (**1g**) (53.5 mg, 0.237 mmol, 1.5 equiv.) and $HBF_4 \cdot OEt_2$ (32.2 µL, 0.237 mmol, 1.5 equiv.) in 1.58 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (50:1) and subsequent CH_3CN/hexanes extraction afforded product **11f** (18.4 mg, 61% yield) as a yellow oil. ^1H NMR ($CDCl_3$) δ 7.19-7.28 (m, 2H), 7.11-7.14 (m, 1H), 6.98-7.03 (m, 1H), 4.79-4.82 (m, 1H), 3.98-4.03 (m, 1H), 3.84-3.89 (m, 1H), 2.20-2.29 (m, 1H), 2.03-2.13 (m, 2H), 1.90-1.99 (m, 1H); ^{13}C {^1H} NMR ($CDCl_3$) δ 162.3 (d, *J* = 246.1 Hz), 129.8 (d, *J* = 9.2 Hz), 127.5 (d, *J* = 3.8 Hz), 124.6 (d, *J* = 9.2 Hz), 118.5 (d, *J* = 22.2 Hz), 115.6 (d, *J* = 21.5 Hz), 90.1, 83.2 (d, *J* = 3.8 Hz), 68.5, 68.0, 33.3, 25.5; ^{19}F NMR ($CDCl_3$) δ -113.14 (q, *J* = 5.9 Hz, 1F); IR (Diamond-ATR) *v* 2980, 2952, 2872, 1579, 1485, 1173, 1149, 1048, 869, 782, 681 cm^{-1}.

2-((2-(trifluoromethyl)phenyl)ethynyl)tetrahydrofuran (11g)



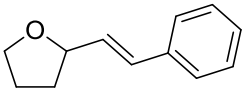
The title compound was derived from 2-ethoxytetrahydrofuran (14.5 mg, 0.123 mmol, 1.0 equiv.), potassium trifluoro((2-(trifluoromethyl)phenyl)ethynyl)-borate (**1h**) (51.7 mg, 0.187 mmol, 1.5 equiv.) and $HBF_4 \cdot OEt_2$ (25.5 µL, 0.187 mmol, 1.5 equiv.) in 1.25 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 16:1) and subsequent CH_3CN/hexanes extraction afforded product **11g** (24.7 mg, 82% yield) as a yellow oil. ^1H NMR ($CDCl_3$) δ 7.62-7.64 (m, 1H), 7.56-7.58 (m, 1H), 7.45-7.48 (m, 1H), 7.37-7.40 (m, 1H), 4.85-4.87 (m, 1H), 3.98-4.04 (m, 1H), 3.85-3.91 (m, 1H), 2.18-2.26 (m, 1H), 2.06-2.17 (m, 2H), 1.90-1.99 (m, 1H); ^{13}C {^1H} NMR ($CDCl_3$) δ = 133.9, 131.8, 131.3, 128.0, 125.7 (q, *J* = 5.4 Hz), 123.5 (q, *J* = 273.8 Hz), 121.1 (q, *J* = 2.3 Hz), 95.0, 80.3, 68.5, 67.9, 33.1, 25.1; ^{19}F NMR ($CDCl_3$) δ -62.48 (s, 3F); IR (Diamond-ATR) *v* 2981, 2874, 1315, 1166, 1128, 1109, 1049, 1032, 764 cm^{-1}.

2-(hex-1-yn-1-yl)tetrahydrofuran (11h)



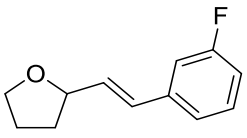
The title compound was derived from 2-ethoxytetrahydrofuran (22.9 mg, 0.197 mmol, 1.0 equiv.), potassium trifluoro(hex-1-yn-1-yl)borate (**1d**) (55.6 mg, 0.296 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (40.2 μL, 0.296 mmol, 1.5 equiv.) in 1.97 mL of CH_3CN (C = 0.1 M). Aqueous workup afforded product **11h** (19.3 mg, 64% yield) as a yellow oil. A pure sample was obtained after the work-up. Attempts to run the crude product through a pad of silica gel resulted in the decomposition of **11h**. ^1H NMR ($CDCl_3$) δ 4.53-4.57 (m, 1H), 3.91-3.97 (m, 1H), 3.75-3.80 (m, 1H), 2.20 (td, *J* = 2.0, 7.0 Hz, 2H), 2.08-2.16 (m, 1H), 1.97-2.07 (m, 1H), 1.82-1.95 (m, 2H), 1.44-1.52 (m, 2H), 1.35-1.42 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C {^1H} NMR ($CDCl_3$) δ 85.2, 79.9, 68.4, 67.6, 33.5, 30.7, 25.4, 21.9, 18.4, 13.6; IR (Diamond-ATR) *ν* 2956, 2931, 2871, 1458, 1355, 1332, 1051, 907 cm^{-1}.

(*E*)-2-styryltetrahydrofuran (12a)



The title compound was derived from 2-ethoxytetrahydrofuran (20.0 mg, 0.172 mmol, 1.0 equiv.), potassium *trans*-styryltrifluoroborate (54.2 mg, 0.258 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (35.1 μL, 0.258 mmol, 1.5 equiv.) in 1.72 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 19:1) and subsequent CH_3CN/hexanes extraction afforded product **12a** (22.3 mg, 74% yield) as a yellow oil. ^1H NMR ($CDCl_3$) δ 7.37-7.39 (m, 2H), 7.28-7.32 (m, 2H), 7.20-7.25 (m, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.20 (dd, *J* = 6.3, 15.6 Hz, 1H), 4.44-4.50 (m, 1H), 3.94-4.00 (m, 1H), 3.81-3.86 (m, 1H), 2.08-2.16 (m, 1H), 1.88-2.04 (m, 2H), 1.67-1.75 (m, 1H); ^{13}C {^1H} NMR ($CDCl_3$) δ 136.8, 130.5, 130.4, 128.5, 127.4, 126.4, 79.6, 68.1, 32.4, 25.9; IR (Diamond-ATR) *ν* 2971, 2867, 1493, 1448, 1049, 963, 745, 691 cm^{-1}.

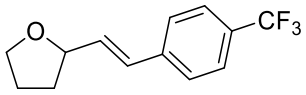
(*E*)-2-(3-fluorostyryl)tetrahydrofuran (12b)



The title compound was derived from 2-ethoxytetrahydrofuran (18.1 mg, 0.156 mmol, 1.0 equiv.), potassium 2-(3-fluorophenyl)vinyltrifluoroborate (53.4 mg, 0.234 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (31.9 μL, 0.234 mmol, 1.5 equiv.) in 1.56 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 19:1) and subsequent CH_3CN/hexanes extraction afforded product

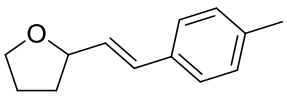
12b (23.4 mg, 78% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.23-7.28 (m, 1H), 7.06-7.14 (m, 2H), 6.89-6.94 (m, 1H), 6.55 (d, *J* = 15.6 Hz, 1H), 6.22 (dd, *J* = 6.3, 16.0 Hz, 1H), 4.45-4.50 (m, 1H), 3.94-4.00 (m, 1H), 3.82-3.87 (m, 1H), 2.09-2.17 (m, 1H), 1.89-2.04 (m, 2H), 1.65-1.75 (m, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 163.0 (d, *J* = 245.4 Hz), 139.2 (d, *J* = 7.7 Hz), 132.0, 129.9 (d, *J* = 8.4 Hz), 129.1 (d, *J* = 3.1 Hz), 122.3 (d, *J* = 3.1 Hz), 114.2 (d, *J* = 21.5 Hz), 112.8 (d, *J* = 21.5 Hz), 79.3, 68.2, 32.3, 25.9; ^{19}F NMR ($CDCl_3$) δ -113.71 (q, *J* = 6.3 Hz, 1F); IR (Diamond-ATR) *ν* 2972, 2869, 1582, 1487, 1445, 1264, 1142, 1050, 962, 870, 776, 682 cm^{-1}.

(*E*)-2-(4-(trifluoromethyl)styryl)tetrahydrofuran (12c)



The title compound was derived from 2-ethoxytetrahydrofuran (14.4 mg, 0.124 mmol, 1.0 equiv.), potassium (*E*)-trifluoro(4-(trifluoromethyl)-styryl)borate (51.7 mg, 0.186 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (25.3 μL, 0.186 mmol, 1.5 equiv.) in 1.24 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 16:1) and subsequent CH_3CN/hexanes extraction afforded product **12c** (23.5 mg, 78% yield) as a yellow oil. ^{1}H-NMR ($CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.31 (dd, *J* = 6.6, 16.0 Hz, 1H), 4.50 (q, *J* = 6.6 Hz, 1H), 3.96–4.01 (m, 1H), 3.83–3.89 (m, 1H), 2.11–2.19 (m, 1H), 1.92–2.04 (m, 2H), 1.68–1.77 (m, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 140.3 (q, *J* = 1.5 Hz), 133.3, 129.4, 129.1, 128.8, 126.5, 125.4 (q, *J* = 3.8 Hz), 79.2, 68.3, 32.3, 25.9; ^{19}F NMR ($CDCl_3$) δ −62.50 (s, 1F); IR (Diamond-ATR) *ν* 2977, 2869, 1612, 1322, 1162, 1103, 1066, 1047, 860, 813 cm^{-1}.

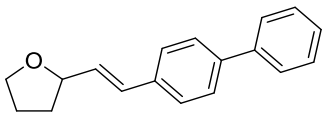
(*E*)-2-(4-methylstyryl)tetrahydrofuran (12d)



The title compound was derived from 2-ethoxytetrahydrofuran (18.5 mg, 0.159 mmol, 1.0 equiv.), potassium (*E*)-trifluoro(4-methylstyryl)borate (**2**) (53.6 mg, 0.239 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (32.5 μL, 0.239 mmol, 1.5 equiv.) in 1.59 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 16:1) afforded product **12d** (16.1 mg, 54% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.26-7.28 (m, 2H), 7.10-7.11 (m, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.15 (dd, *J* = 6.6, 15.6 Hz, 1H),

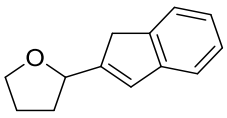
4.45 (q, J = 6.7 Hz, 1H), 3.94-3.99 (m, 1H), 3.80-3.86 (m, 1H), 2.32 (s, 3H), 2.07-2.15 (m, 1H), 1.88-2.01 (m, 2H), 1.66-1.75 (m, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 137.3, 134.1, 130.4, 129.4, 129.2, 126.3, 79.77, 68.1, 32.4, 25.9, 21.2; IR (Diamond-ATR) ν 2970, 2922, 2864, 1513, 1050, 964, 795, 513 cm^{-1}.

(*E*)-2-(2-([1,1′-biphenyl]-4-yl)vinyl)tetrahydrofuran (12e)



The title compound was derived from 2-ethoxytetrahydrofuran (13.9 mg, 0.120 mmol, 1.0 equiv.), potassium (*E*)-(2-([1,1′-biphenyl]-4-yl)vinyl)trifluoroborate (51.4 mg, 0.180 mmol, 1.5 equiv.), and $HBF_4{\cdot}OEt_2$ (24.5 μL, 0.180 mmol, 1.5 equiv.) in 1.20 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 13:1) and subsequent CH_3CN/hexanes extraction afforded product **12e** (21.6 mg, 72% yield) as a white solid. ^{1}H-NMR ($CDCl_3$) δ 7.53–7.60 (m, 4H), 7.40–7.46 (m, 4H), 7.31–7.35 (m, 1H), 6.62 (d, J = 15.6 Hz, 1H), 6.25 (dd, J = 6.6, 15.6 Hz, 1H), 4.49 (q, J = 6.6 Hz, 1H), 3.95–4.01 (m, 1H), 3.82–3.86 (m, 1H), 2.10–2.18 (m, 1H), 1.89–2.02 (m, 2H), 1.68–1.77 (m, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 140.7, 140.2, 135.9, 130.6, 129.9, 128.7, 127.2, 127.1, 126.9, 126.8, 79.7, 68.2, 32.4, 25.9; IR (Diamond-ATR) ν 2928, 2852, 1486, 1048, 971, 854, 758, 687, 489 cm^{-1}; HRMS (DART-TOF+) m/z [M + H] calcd for $C_{18}H_{19}O$ 251.1436, found 251.1437.

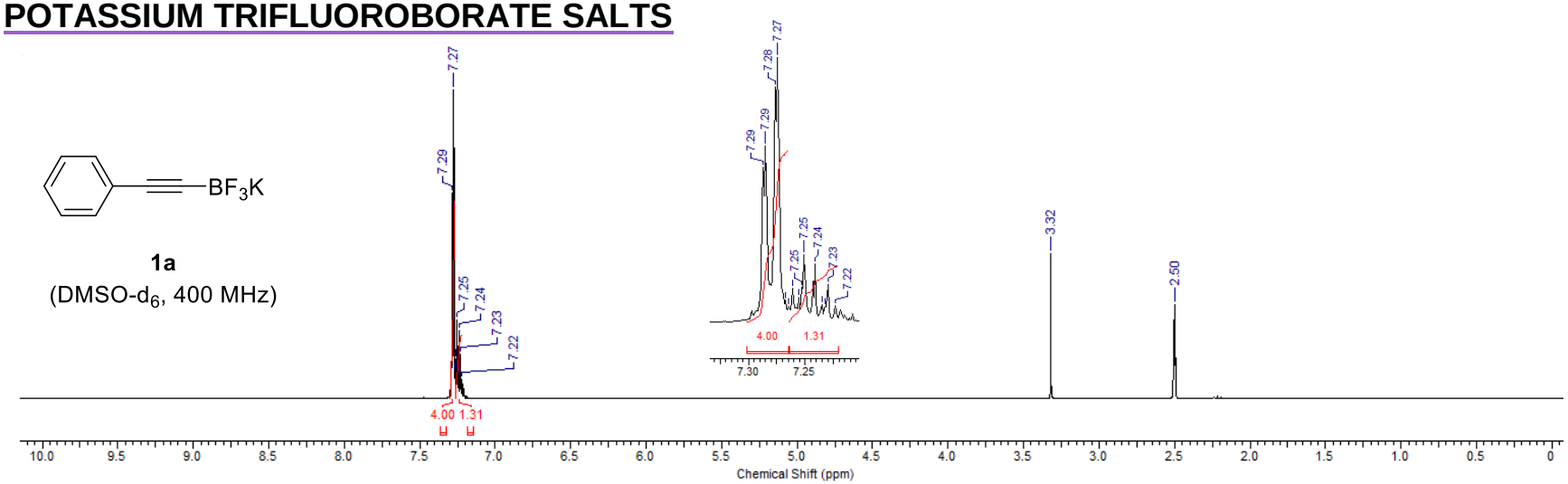
2-(1*H*-inden-2-yl)tetrahydrofuran (12f)

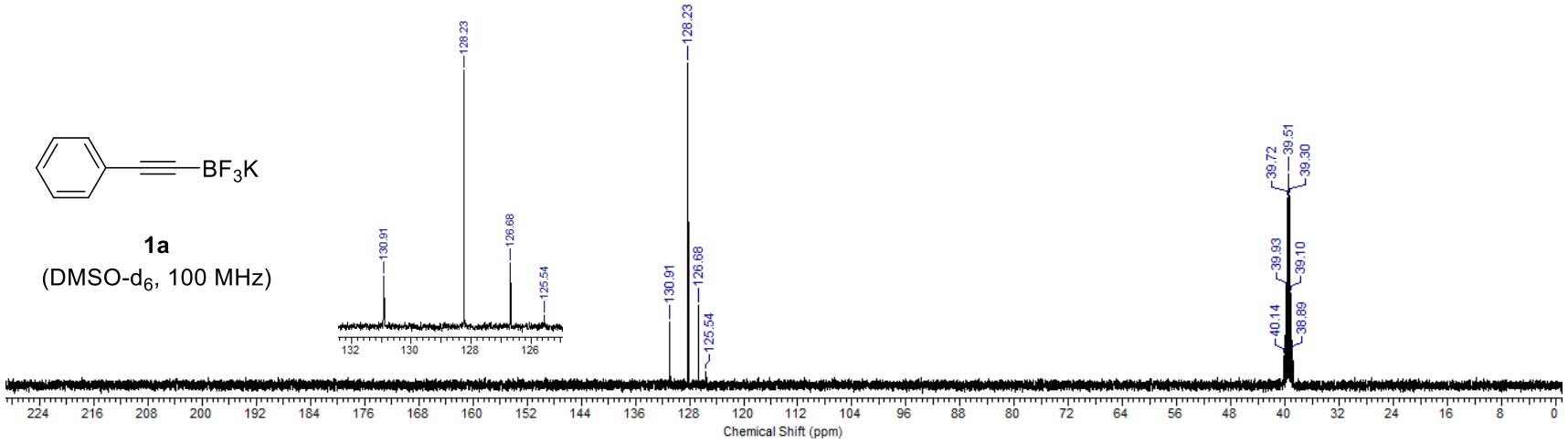


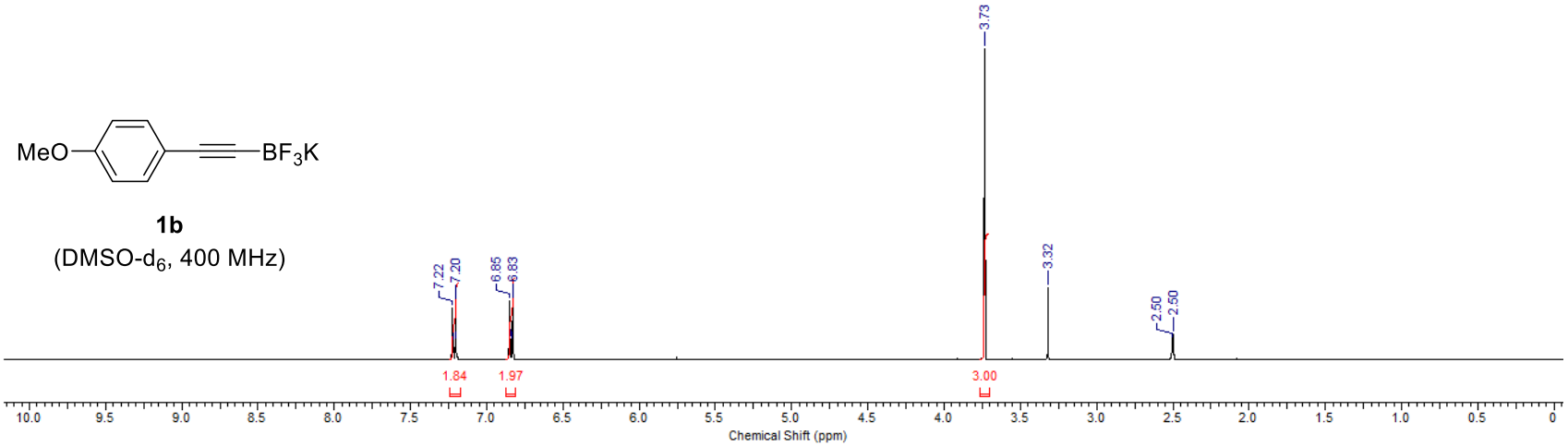
The title compound was derived from 2-ethoxytetrahydrofuran (18.7 mg, 0.161 mmol, 1.0 equiv.), potassium trifluoro(1*H*-inden-2-yl)borate (53.6 mg, 0.242 mmol, 1.5 equiv.) and $HBF_4{\cdot}OEt_2$ (32.9 μL, 0.242 mmol, 1.5 equiv.) in 1.61 mL of CH_3CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 13:1) and subsequent CH_3CN/hexanes extraction afforded product **12f** (23.6 mg, 79% yield) as a yellow oil. ^{1}H-NMR ($CDCl_3$) δ 7.40–7.42 (m, 1H), 7.30–7.32 (m, 1H), 7.21–7.25 (m, 1H), 7.11–7.15 (m, 1H), 6.71 (s, 1H), 4.82 (t, J = 7.0 Hz, 1H), 3.97–4.02 (m, 1H), 3.84–3.90 (m, 1H), 3.39 (s, 2H), 2.15–2.23 (m, 1H), 1.95–2.03 (m, 2H), 1.81–1.89 (m, 1H); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 150.4, 144.7, 143.2, 126.6, 126.3, 124.2, 123.6, 120.6, 77.7, 68.2, 38.1, 32.1, 26.0; IR (Diamond-ATR) ν 2971, 2868, 1459, 1390, 1050, 916, 850, 751, 716, 555 cm^{-1}.

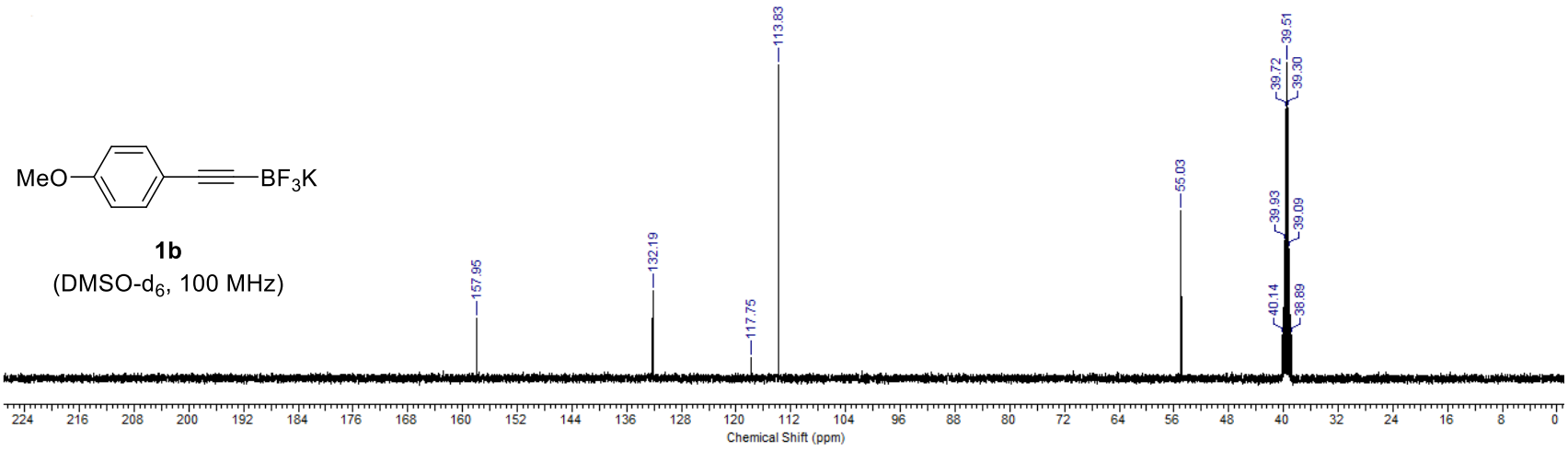
APPENDIX II: NMR SPECTRA

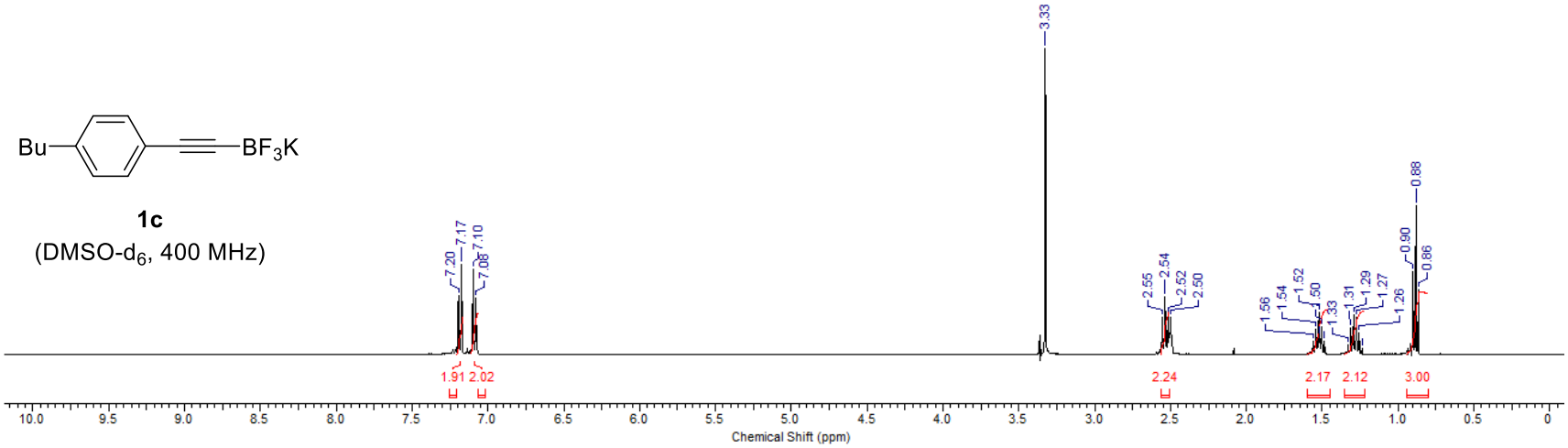
POTASSIUM TRIFLUOROBORATE SALTS

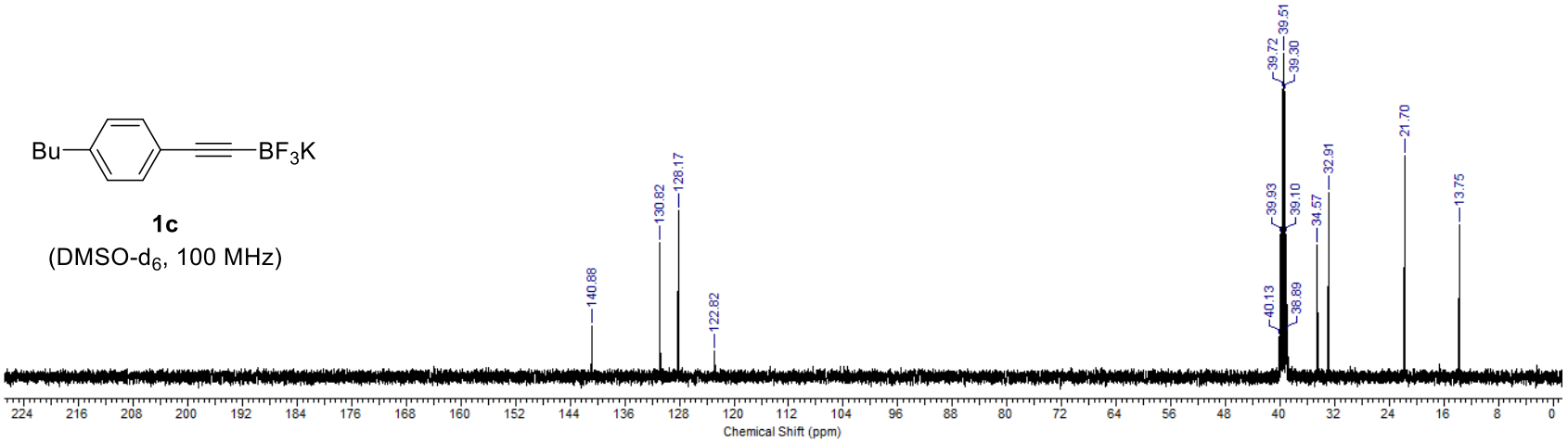


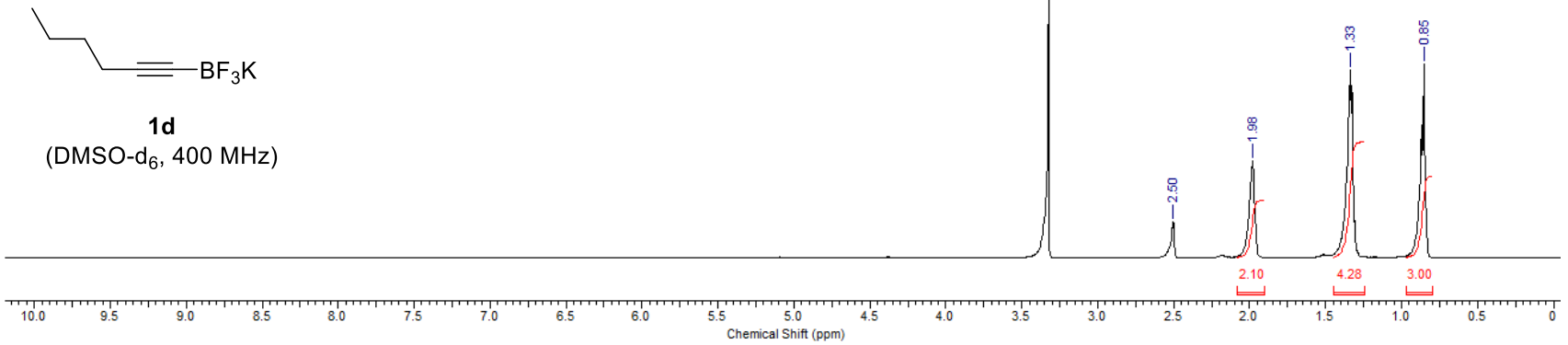



MeO
BF3K
1b
(DMSO-d6, 400 MHz)
7.22
7.20
6.85
6.83
3.73
3.32
2.50
2.50
1.84
1.97
3.00
Chemical Shift (ppm)

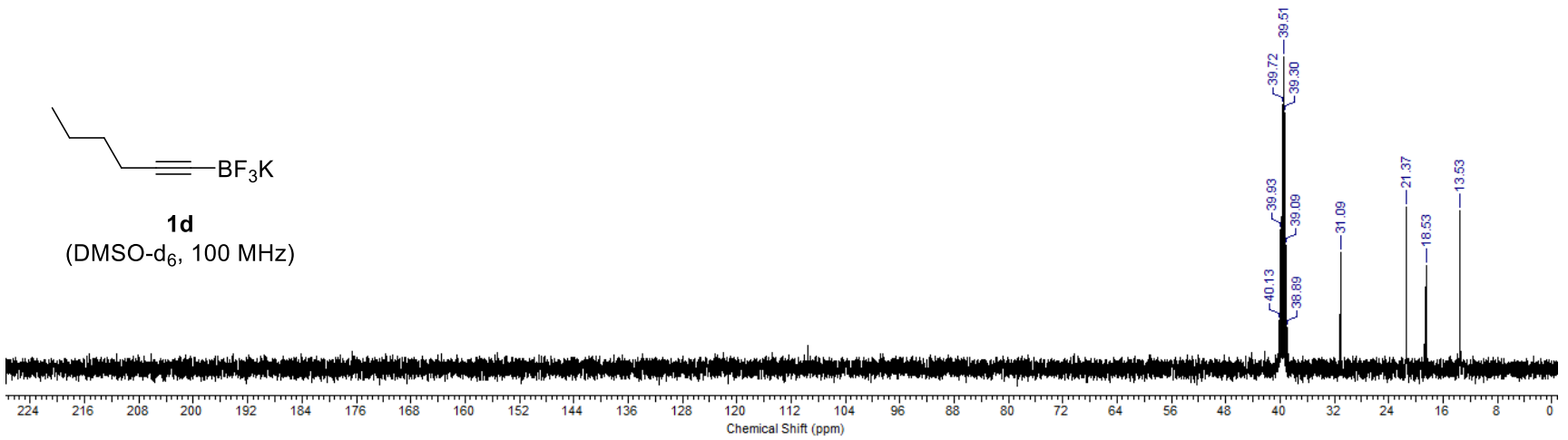

MeO
BF3K
1b
(DMSO-d6, 100 MHz)
157.95
132.19
117.75
113.83
55.03
39.93
39.72
39.51
39.30
39.09
40.14
38.89
Chemical Shift (ppm)


Bu
BF3K
1c
(DMSO-d6, 400 MHz)
3.33
7.20
7.17
7.10
7.08
2.55
2.54
2.52
2.50
1.56
1.54
1.52
1.50
1.33
1.31
1.29
1.27
1.26
0.90
0.88
0.86
1.91
2.02
2.24
2.17
2.12
3.00
Chemical Shift (ppm)

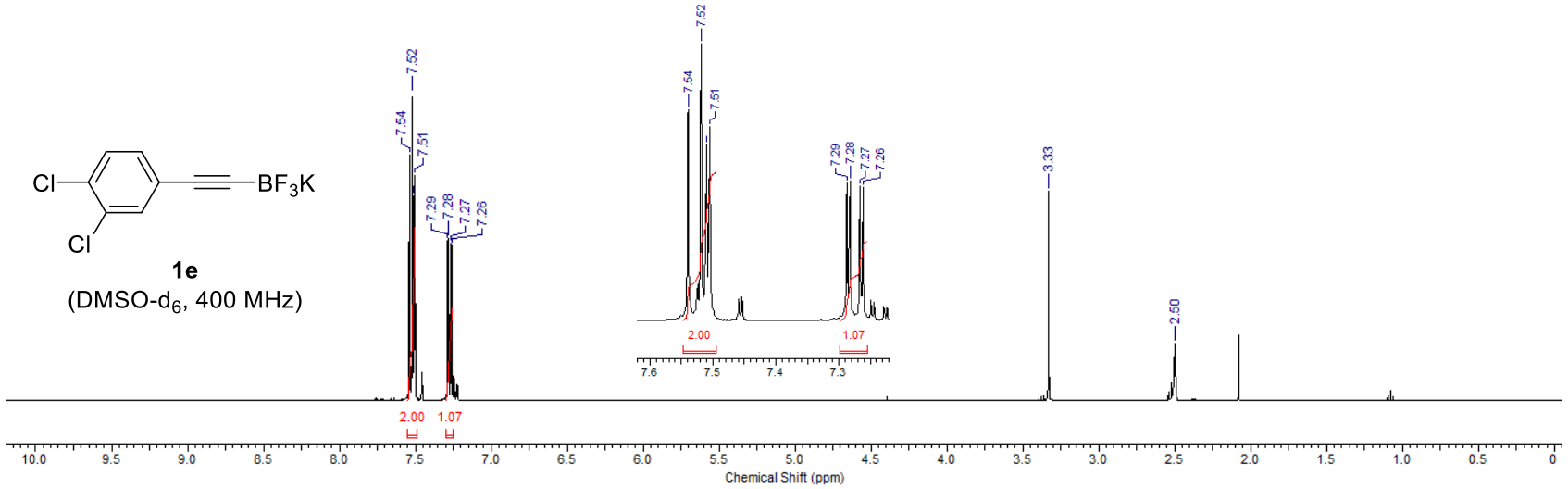

Bu
BF3K
1c
(DMSO-d6, 100 MHz)
140.88
130.82
128.17
122.82
39.72
39.51
39.30
39.93
39.10
34.57
32.91
21.70
13.75
40.13
38.89
Chemical Shift (ppm)

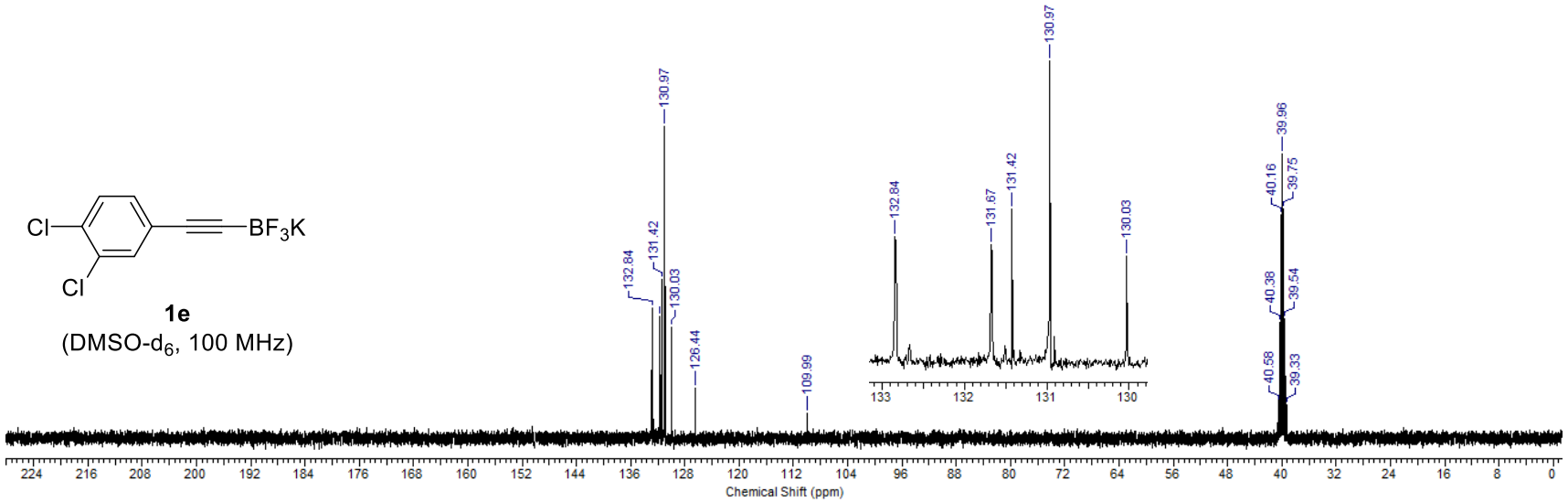


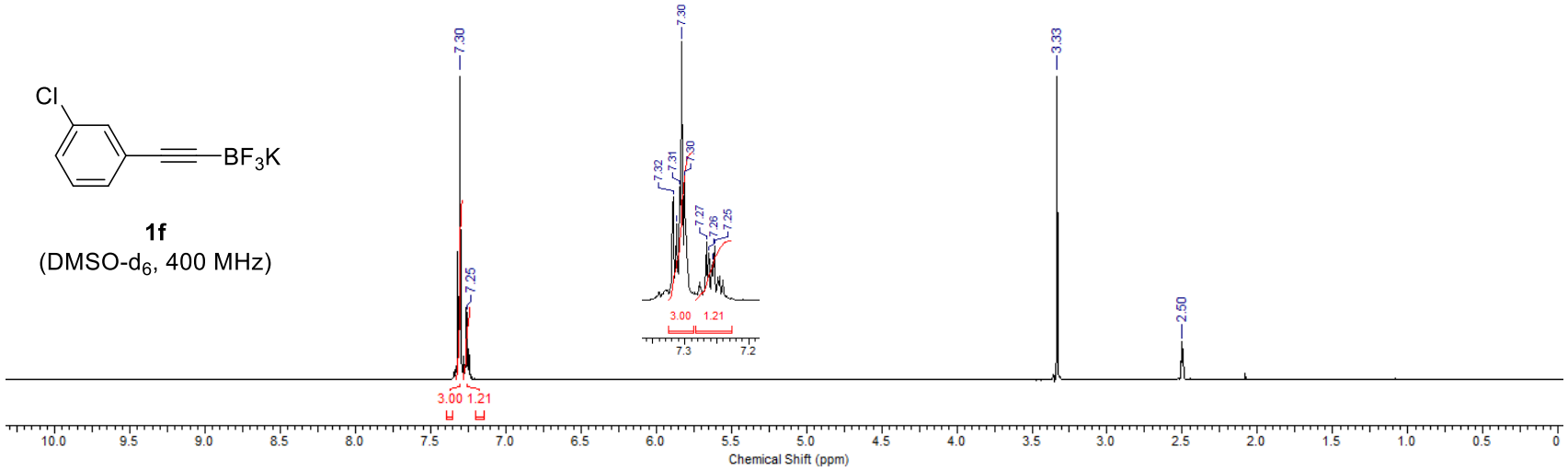
1d
(DMSO-d_6, 400 MHz)

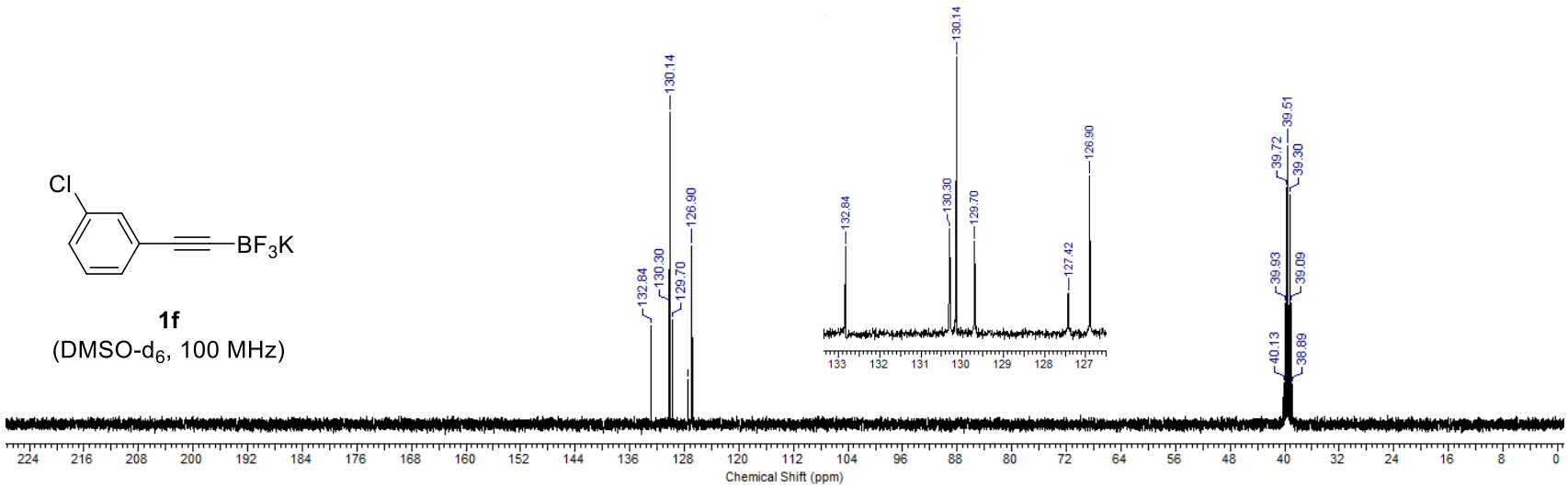


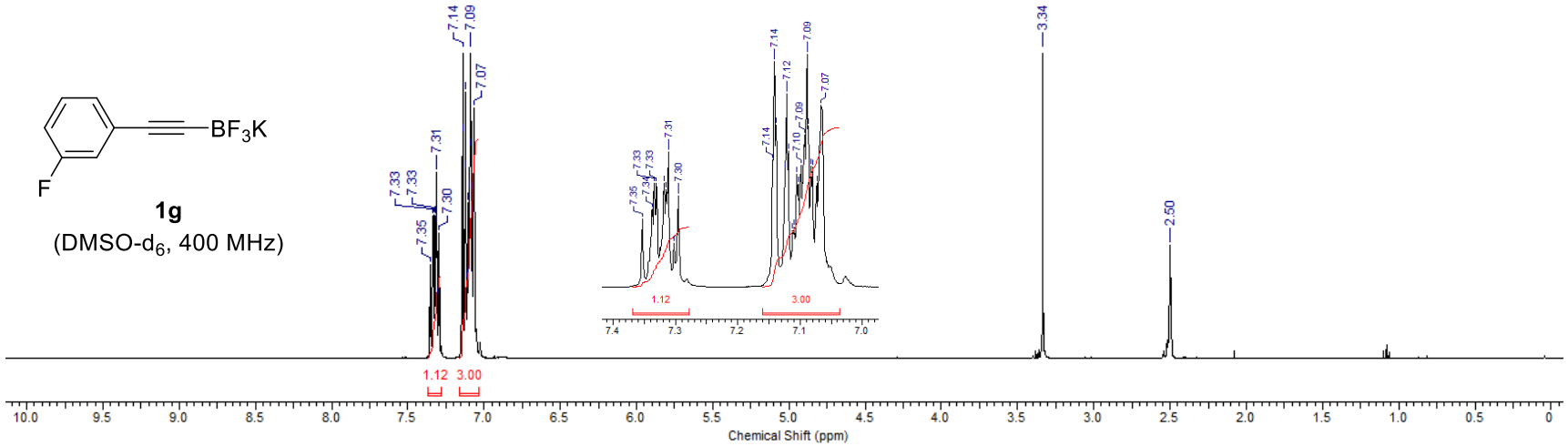
1d
(DMSO-d_6, 100 MHz)

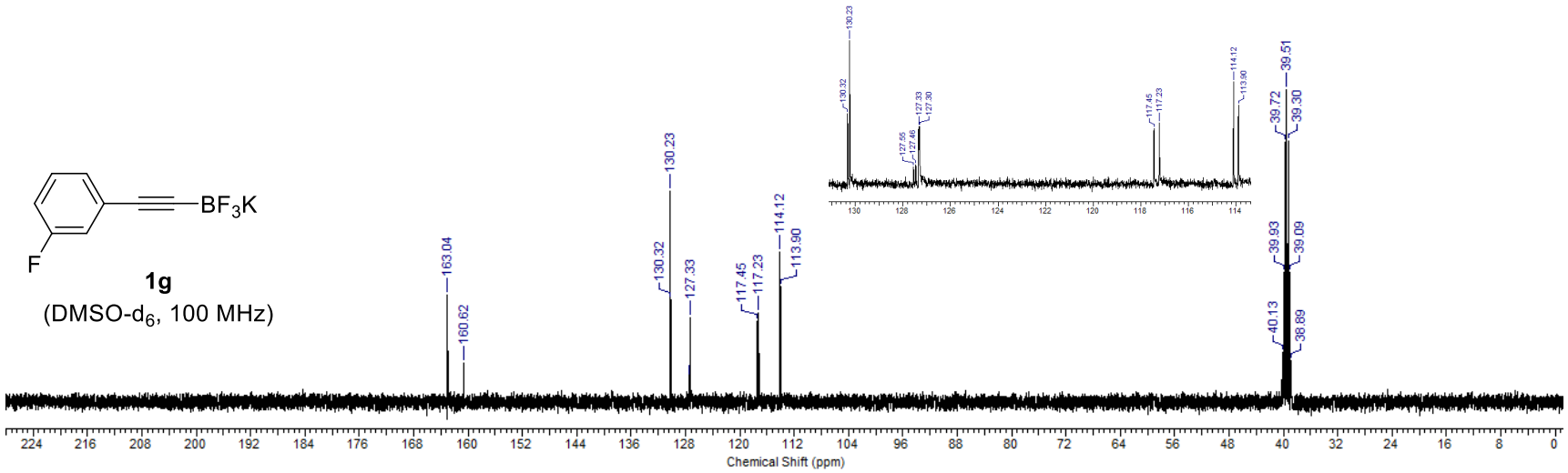

Cl
Cl
BF3K
1e
(DMSO-d6, 400 MHz)
7.52
7.54
7.51
7.29
7.28
7.27
7.26
2.00
1.07
3.33
2.50
Chemical Shift (ppm)

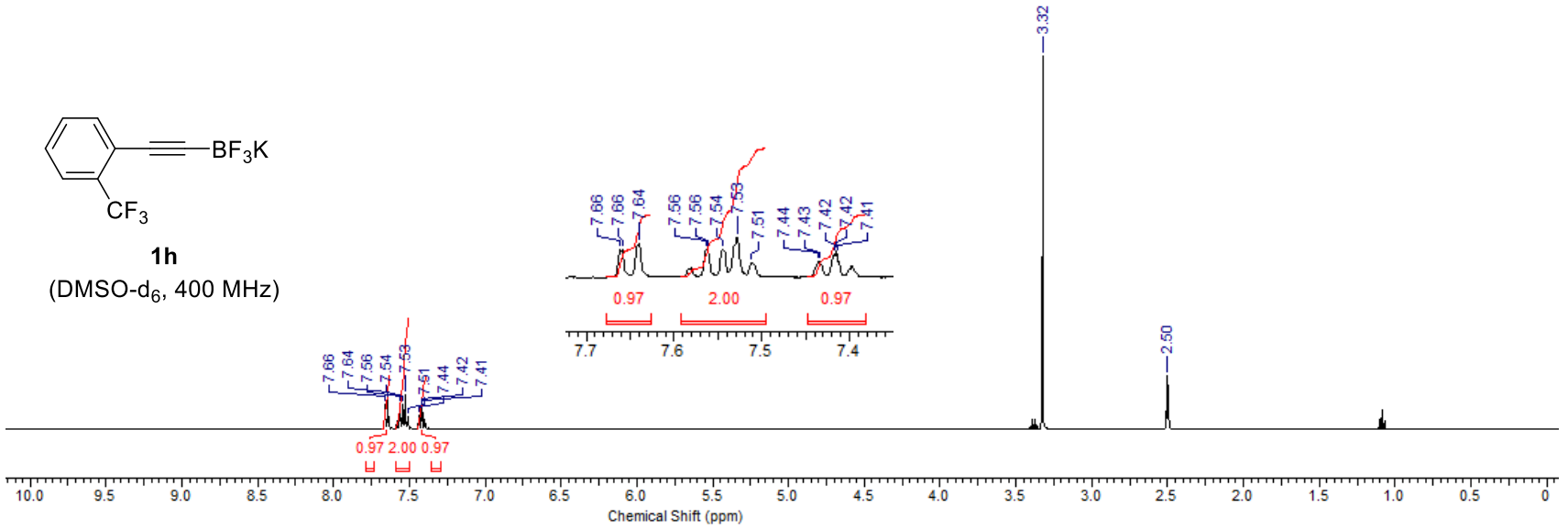

Cl
Cl
BF3K
1e
(DMSO-d6, 100 MHz)
130.97
131.42
132.84
130.03
126.44
109.99
131.67
40.16
39.96
39.75
40.38
39.54
40.58
39.33
Chemical Shift (ppm)

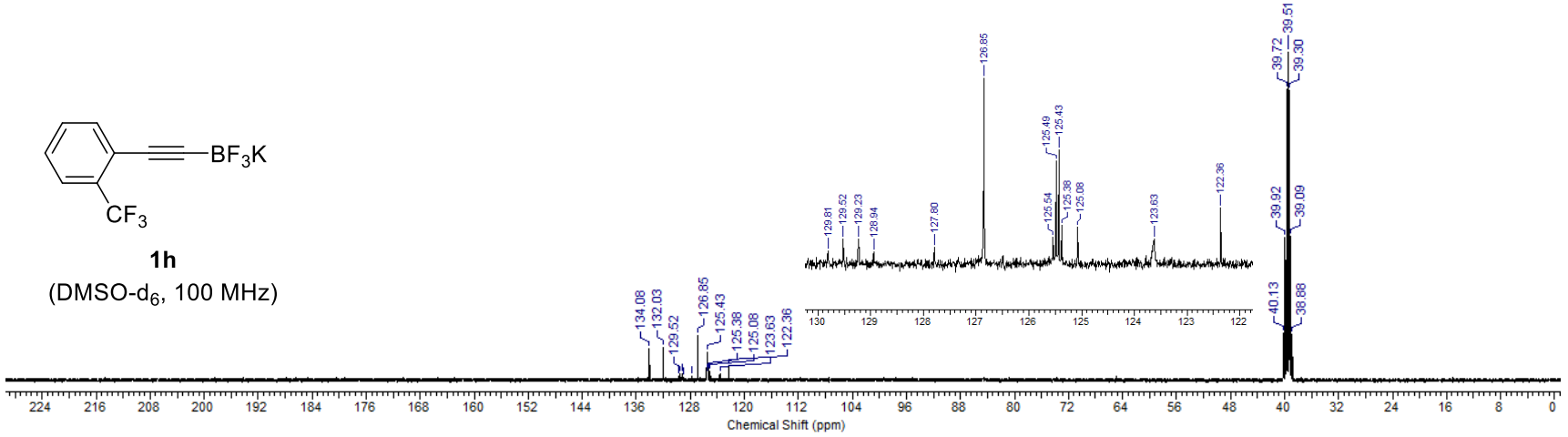

Cl
BF3K
1f
(DMSO-d6, 400 MHz)
7.30
7.25
3.33
2.50
3.00 1.21
Chemical Shift (ppm)

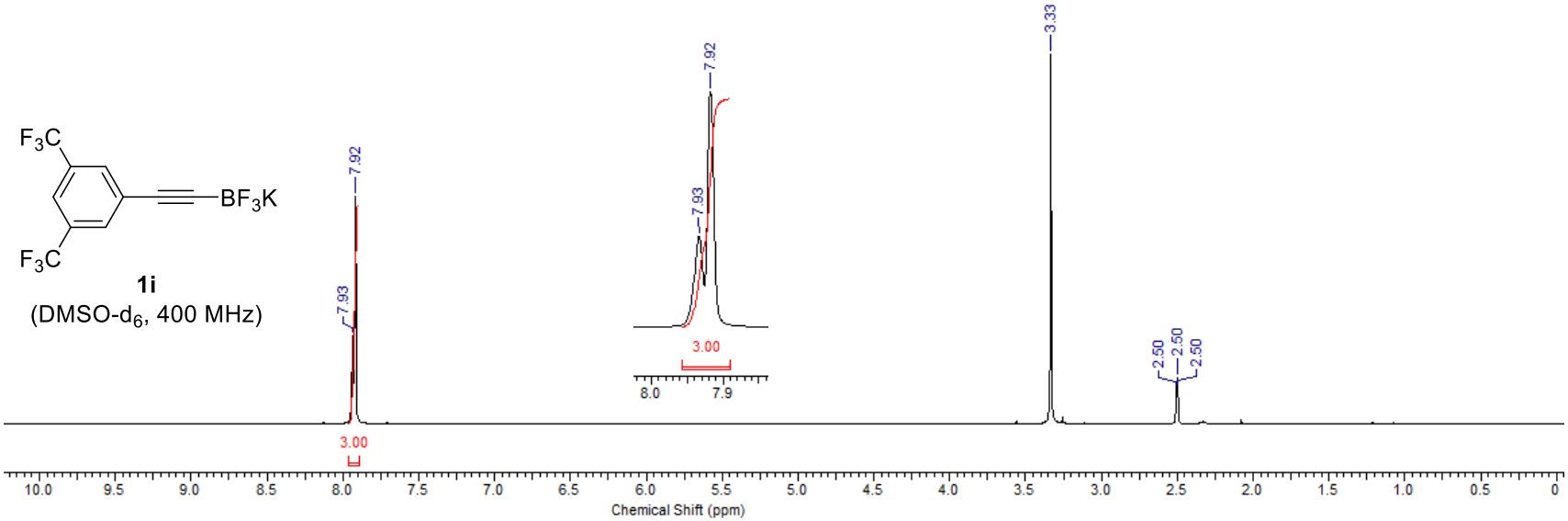

Cl
BF3K
1f
(DMSO-d6, 100 MHz)
132.84
130.30
129.70
130.14
126.90
127.42
39.72
39.51
39.30
39.93
39.09
40.13
38.89
Chemical Shift (ppm)

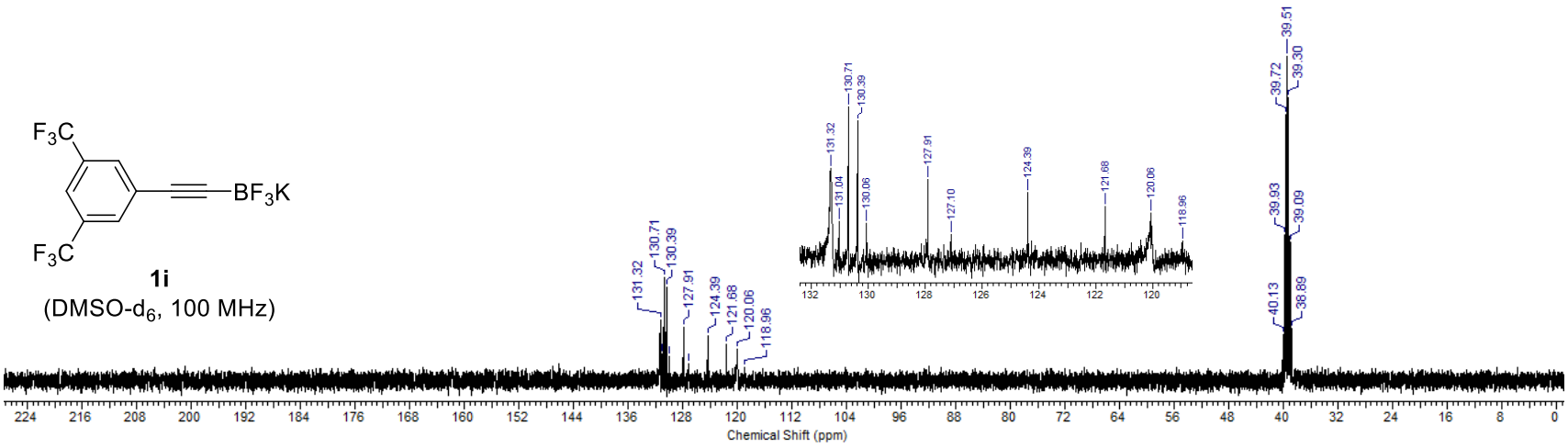

BF3K
F
1g
(DMSO-d6, 400 MHz)
7.33
7.33
7.35
7.31
7.30
7.14
7.09
7.07
3.34
2.50
1.12
3.00
Chemical Shift (ppm)

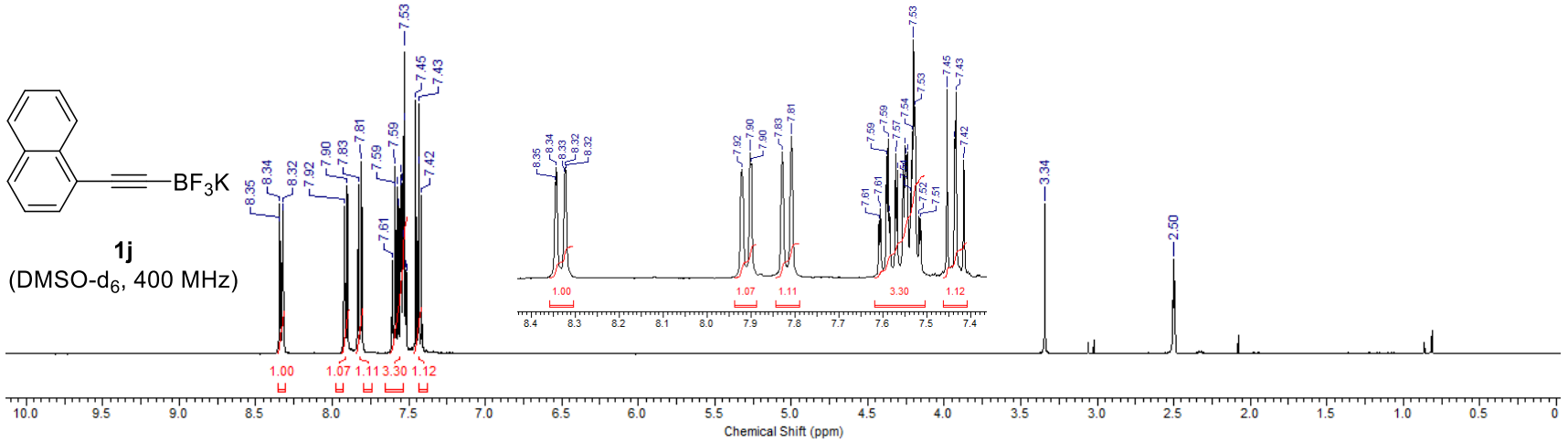

BF3K
F
1g
(DMSO-d6, 100 MHz)
163.04
160.62
130.32
130.23
127.33
117.45
117.23
114.12
113.90
39.93
39.72
39.51
39.30
39.09
40.13
38.89
Chemical Shift (ppm)

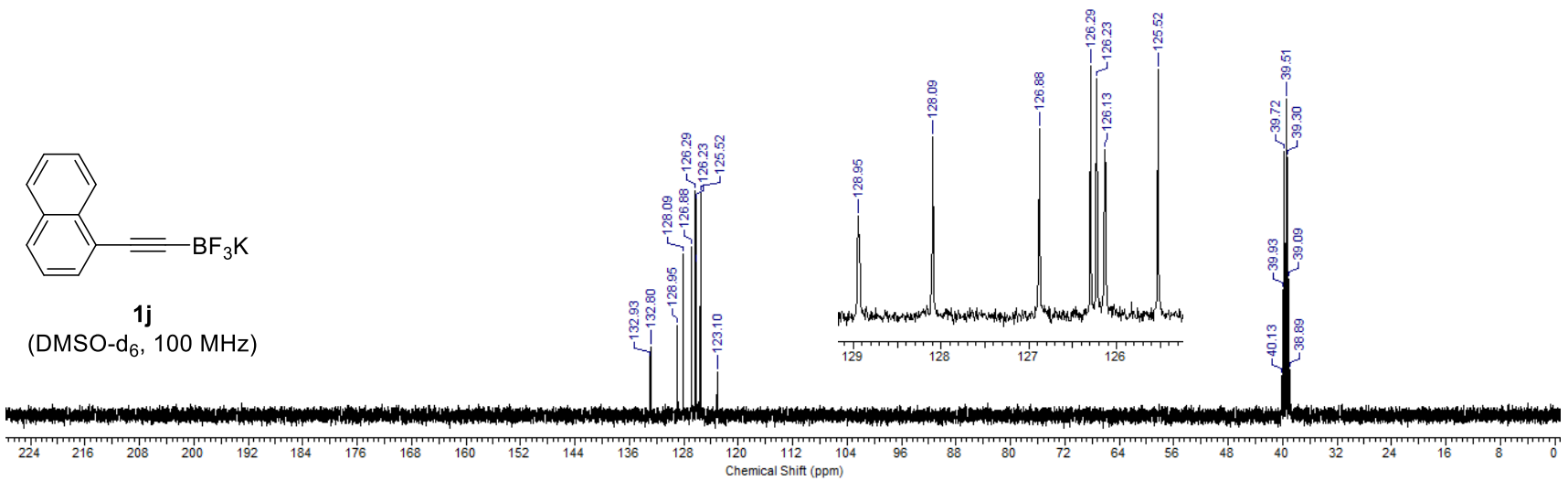

BF3K
CF3
1h
(DMSO-d6, 400 MHz)
7.66
7.64
7.56
7.54
7.53
7.51
7.44
7.43
7.42
7.41
0.97
2.00
0.97
3.32
2.50
Chemical Shift (ppm)

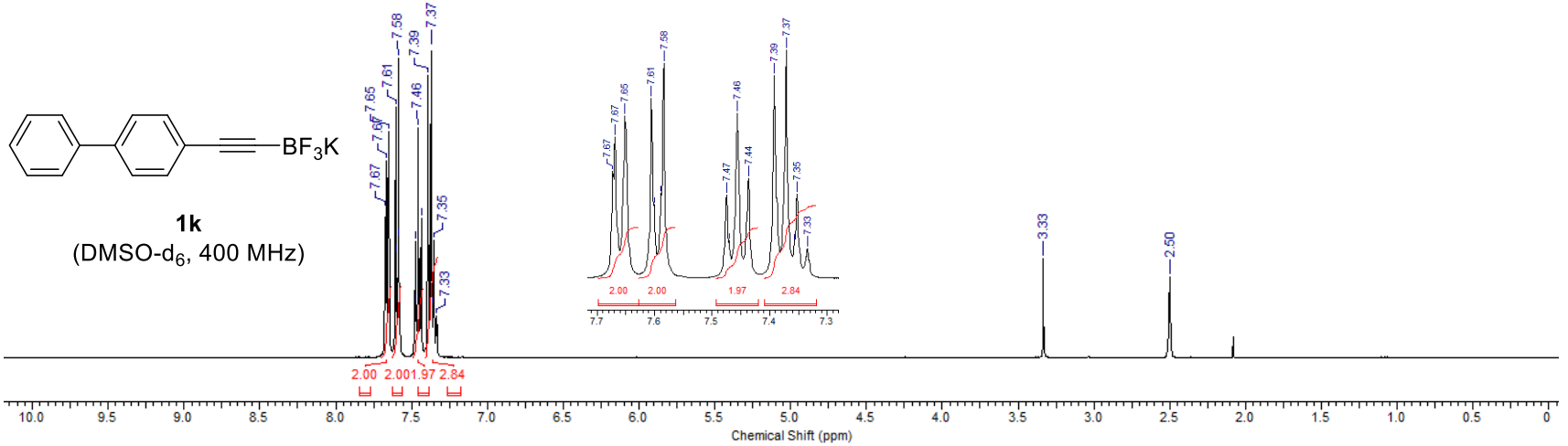

BF3K
CF3
1h
(DMSO-d6, 100 MHz)
134.08
132.03
129.52
126.85
125.43
125.38
125.08
123.63
122.36
129.81
129.52
129.23
128.94
127.80
125.54
125.49
125.43
125.38
125.08
123.63
122.36
39.72
39.51
39.30
39.92
39.09
40.13
38.88
Chemical Shift (ppm)

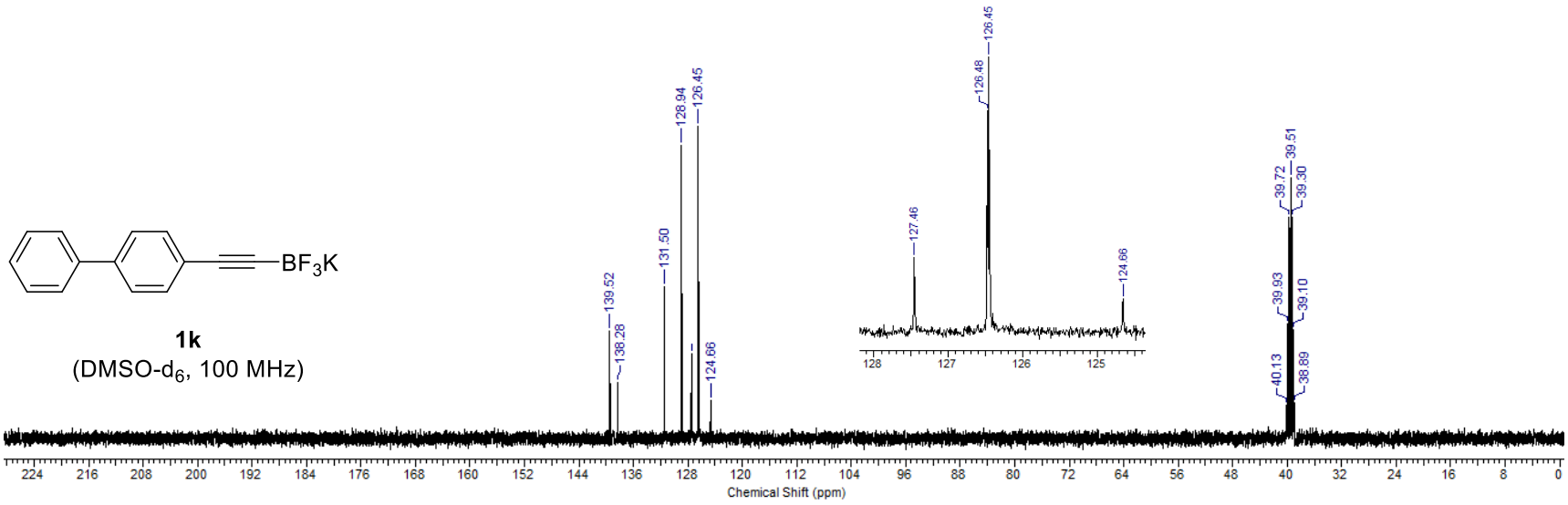

F3C
BF3K
F3C
1i
(DMSO-d6, 400 MHz)
7.93
7.92
3.00
7.93
7.92
3.00
8.0
7.9
3.33
2.50
2.50
2.50
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

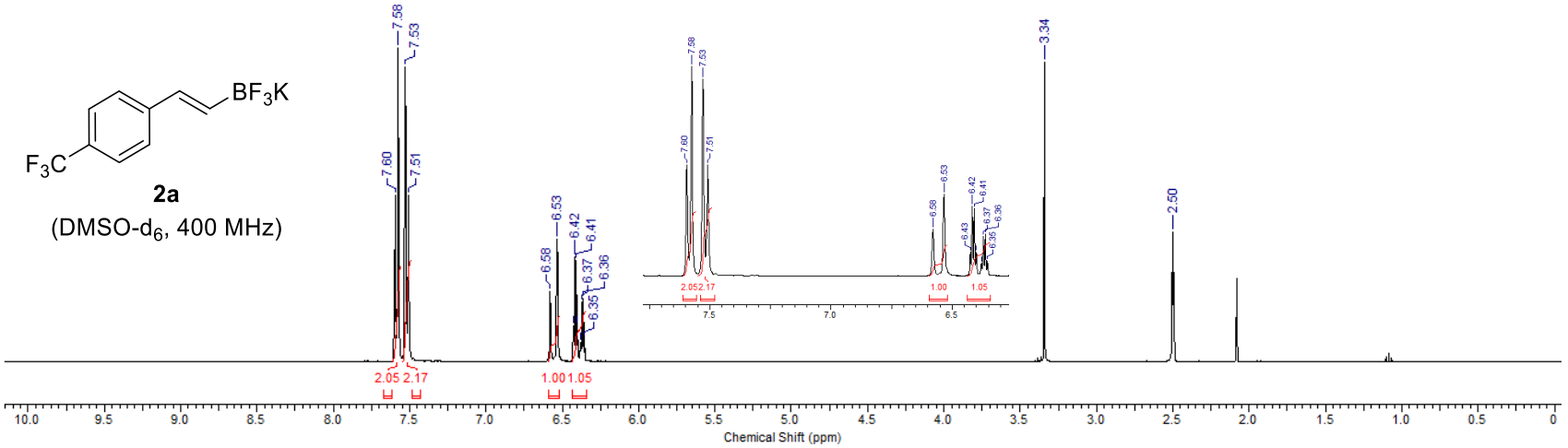

F3C
BF3K
F3C
1i
(DMSO-d6, 100 MHz)
131.32
130.71
130.39
127.91
124.39
121.88
120.06
118.96
131.32
131.04
130.71
130.39
130.06
127.91
127.10
124.39
121.88
120.06
118.96
132
130
128
126
124
122
120
39.51
39.72
39.30
39.93
39.09
40.13
38.89
224
216
208
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

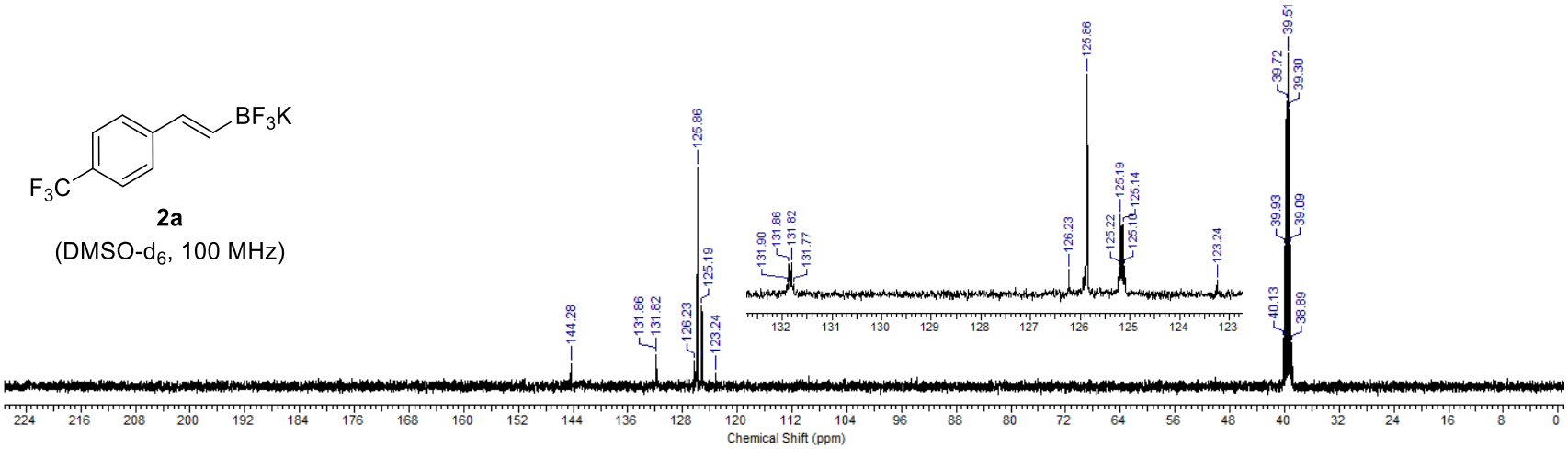

BF3K
1j
(DMSO-d6, 400 MHz)
8.35
8.34
8.32
7.92
7.90
7.83
7.81
7.61
7.59
7.53
7.45
7.43
7.42
3.34
2.50
1.00
1.07
1.11
3.30
1.12
Chemical Shift (ppm)

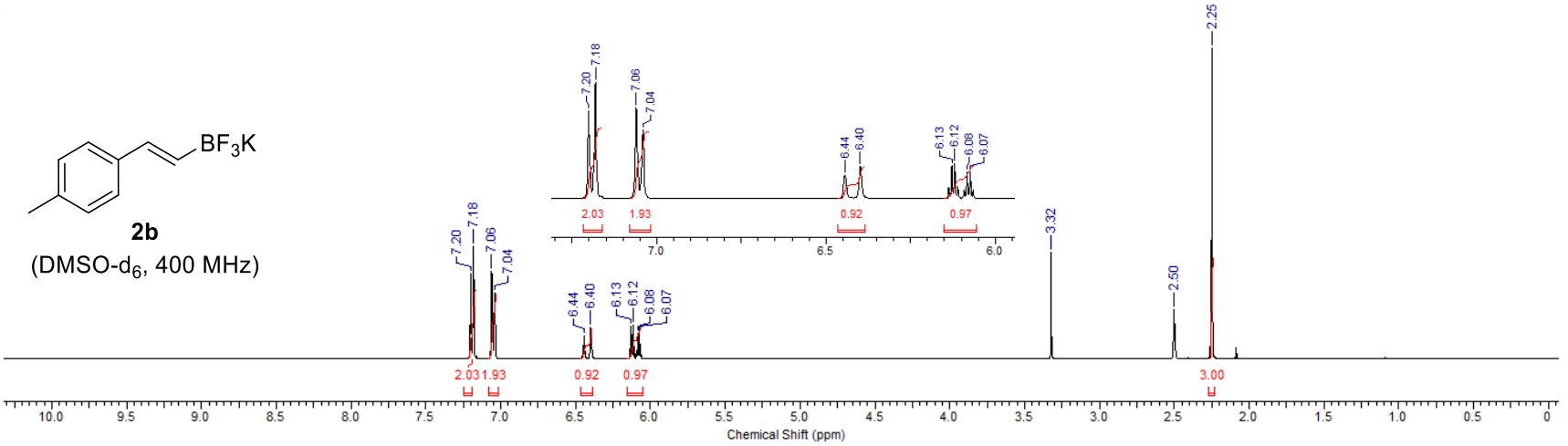

BF3K
1j
(DMSO-d6, 100 MHz)
132.93
132.80
128.95
128.09
126.88
126.29
126.23
125.52
123.10
39.93
39.72
39.51
39.30
39.09
40.13
38.89
Chemical Shift (ppm)

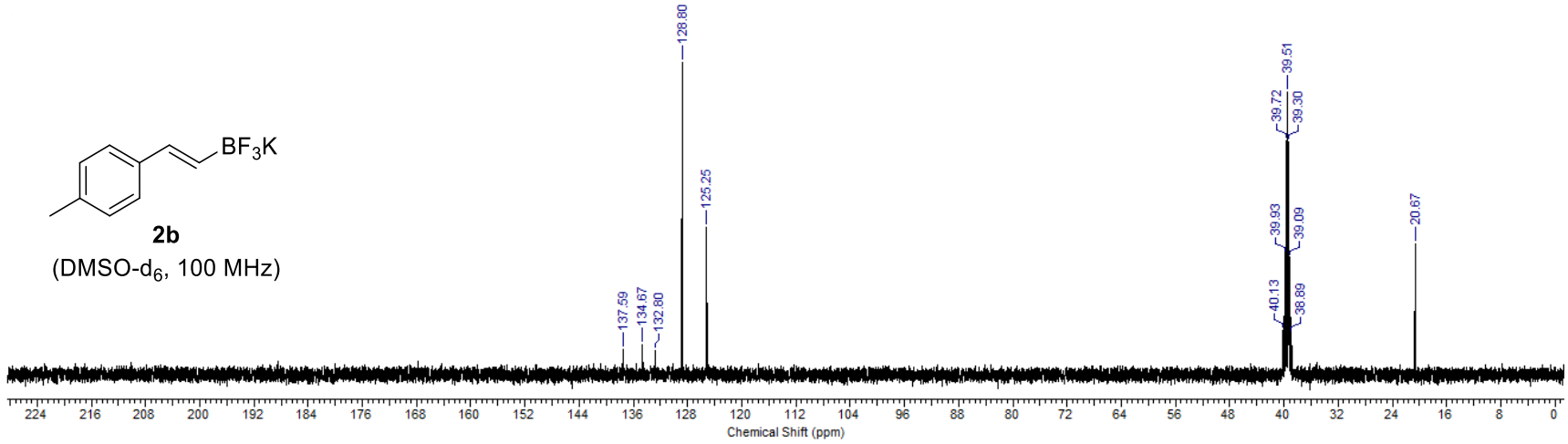

BF3K
1k
(DMSO-d6, 400 MHz)
7.67
7.65
7.61
7.58
7.46
7.39
7.37
7.35
7.33
2.00 2.00 1.97 2.84
3.33
2.50
Chemical Shift (ppm)

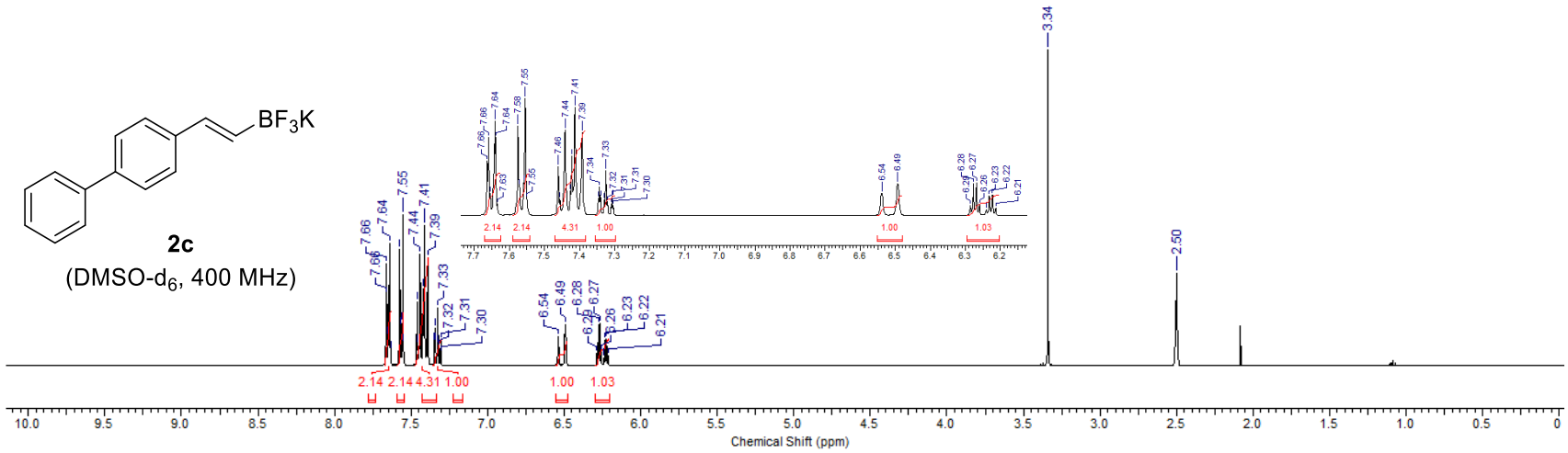

BF3K
1k
(DMSO-d6, 100 MHz)
139.52
138.28
131.50
128.94
126.45
126.48
124.66
127.46
39.72
39.51
39.30
39.93
39.10
40.13
38.89
Chemical Shift (ppm)

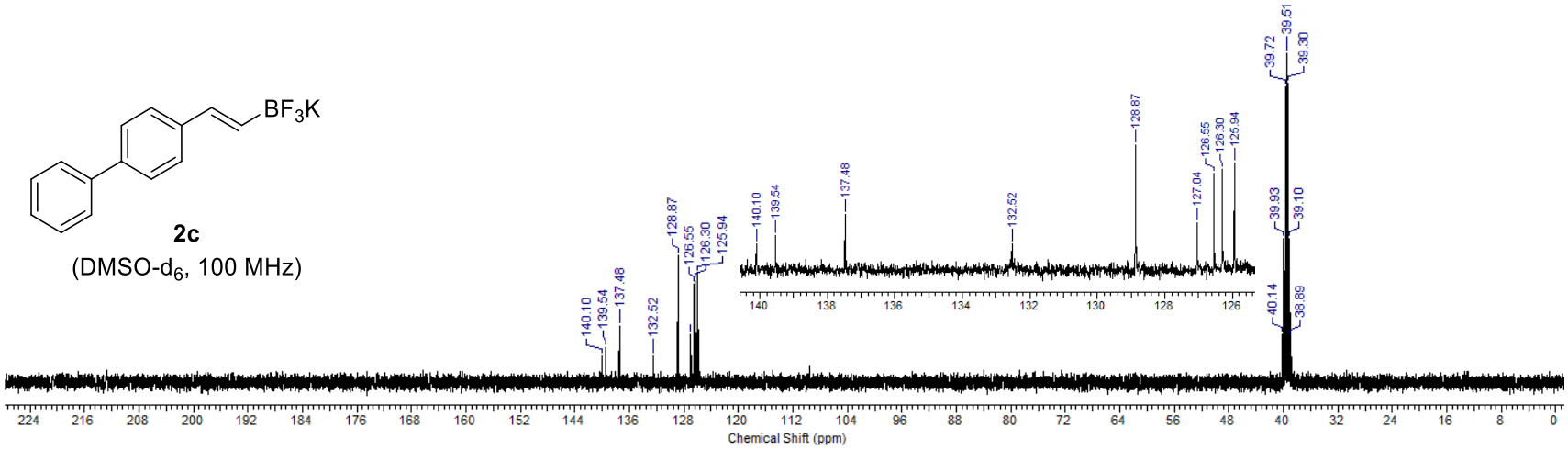

BF3K
F3C
2a
(DMSO-d6, 400 MHz)
7.60
7.58
7.53
7.51
6.58
6.53
6.42
6.41
6.37
6.36
6.35
3.34
2.50
2.05
2.17
1.00
1.05
Chemical Shift (ppm)

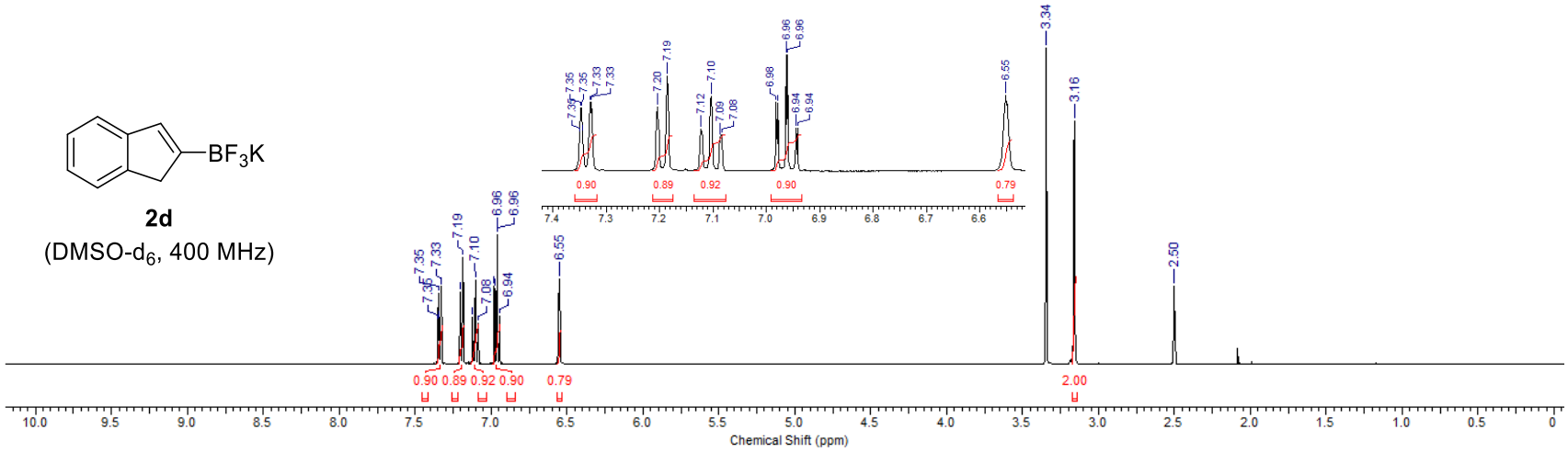

BF3K
F3C
2a
(DMSO-d6, 100 MHz)
144.28
131.86
131.82
126.23
125.86
125.19
123.24
131.90
131.77
126.22
125.14
39.72
39.51
39.30
39.93
39.09
40.13
38.89
Chemical Shift (ppm)

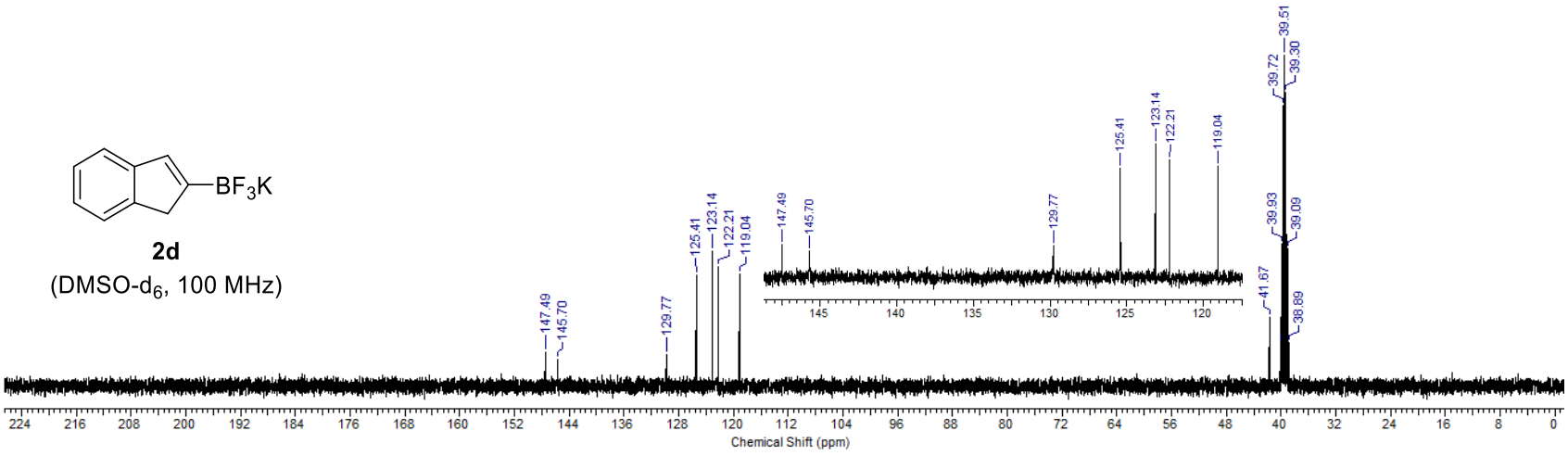

BF3K
2b
(DMSO-d6, 400 MHz)
7.20
7.18
7.06
7.04
6.44
6.40
6.13
6.12
6.08
6.07
3.32
2.50
2.25
2.03
1.93
0.92
0.97
3.00
Chemical Shift (ppm)


BF3K
2b
(DMSO-d6, 100 MHz)
128.80
125.25
137.59
134.67
132.80
39.72
39.51
39.30
39.93
39.09
40.13
38.89
20.67
Chemical Shift (ppm)

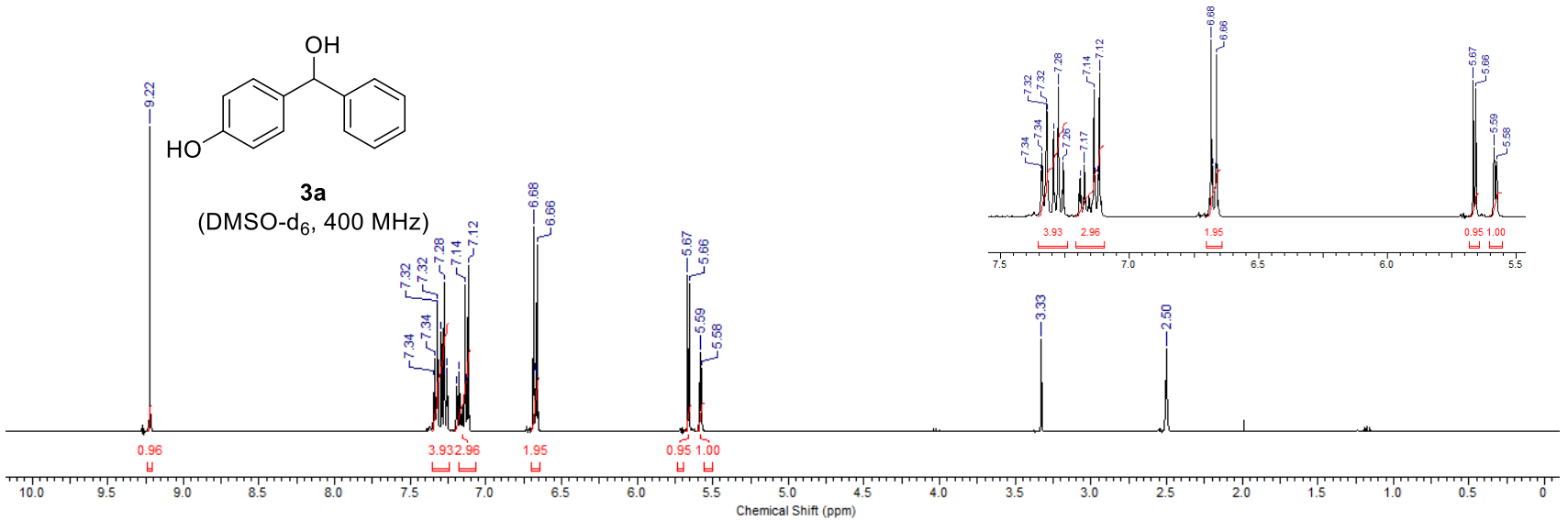

BF3K
2c
(DMSO-d6, 400 MHz)
Chemical Shift (ppm)

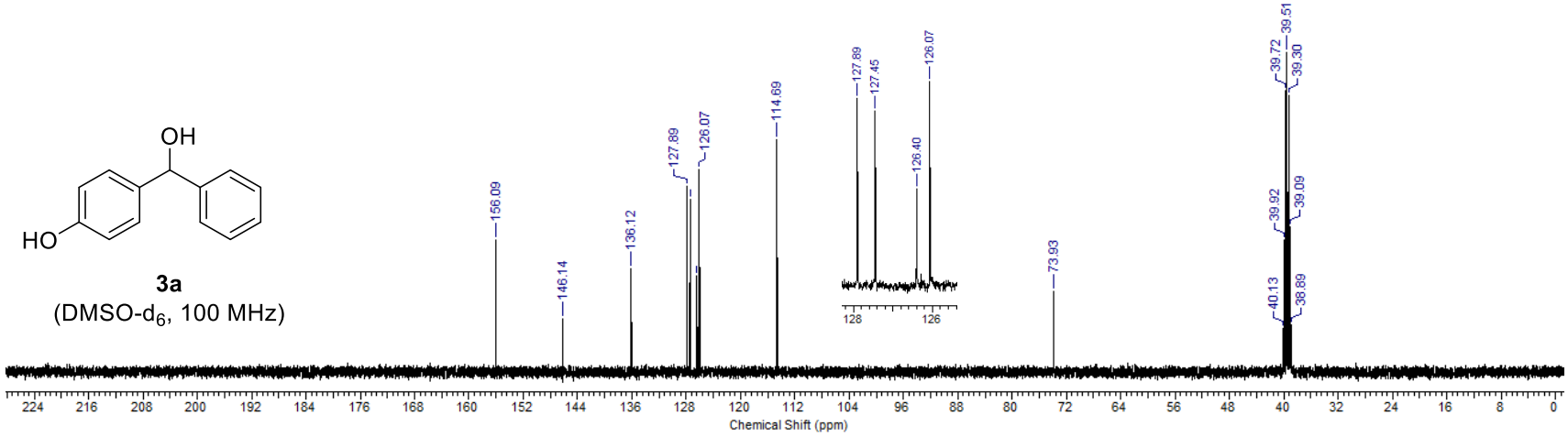

BF3K
2c
(DMSO-d6, 100 MHz)
Chemical Shift (ppm)

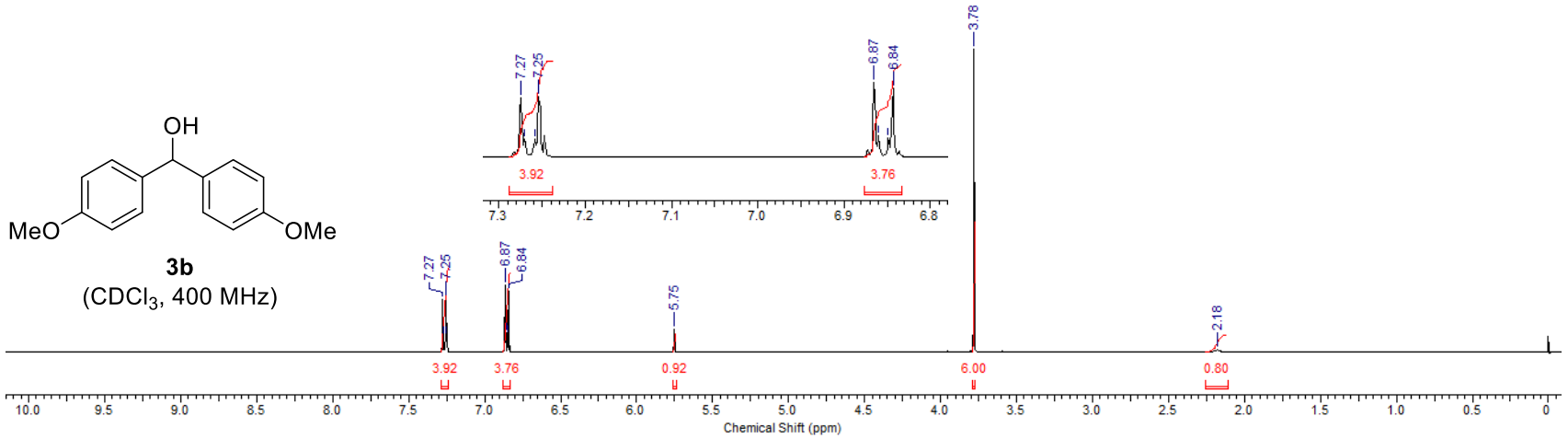

BF3K
2d
(DMSO-d6, 400 MHz)
7.35
7.33
7.19
7.10
7.08
6.96
6.94
6.55
3.34
3.16
2.50
0.90
0.89
0.92
0.90
0.79
2.00
Chemical Shift (ppm)

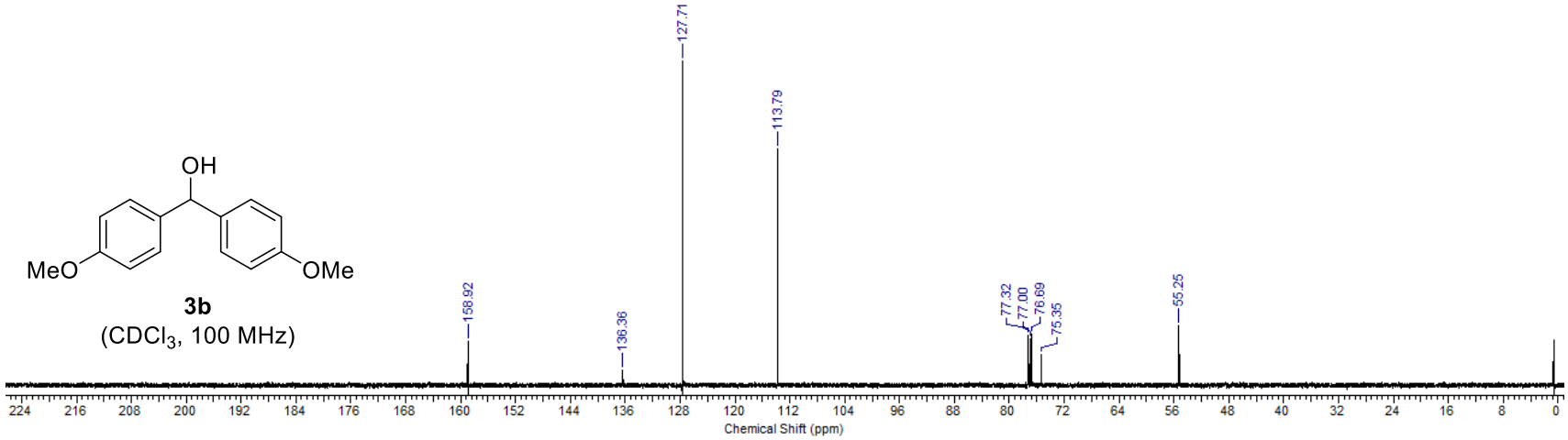

BF3K
2d
(DMSO-d6, 100 MHz)
147.49
145.70
129.77
125.41
123.14
122.21
119.04
41.67
39.93
39.72
39.51
39.30
39.09
38.89
Chemical Shift (ppm)

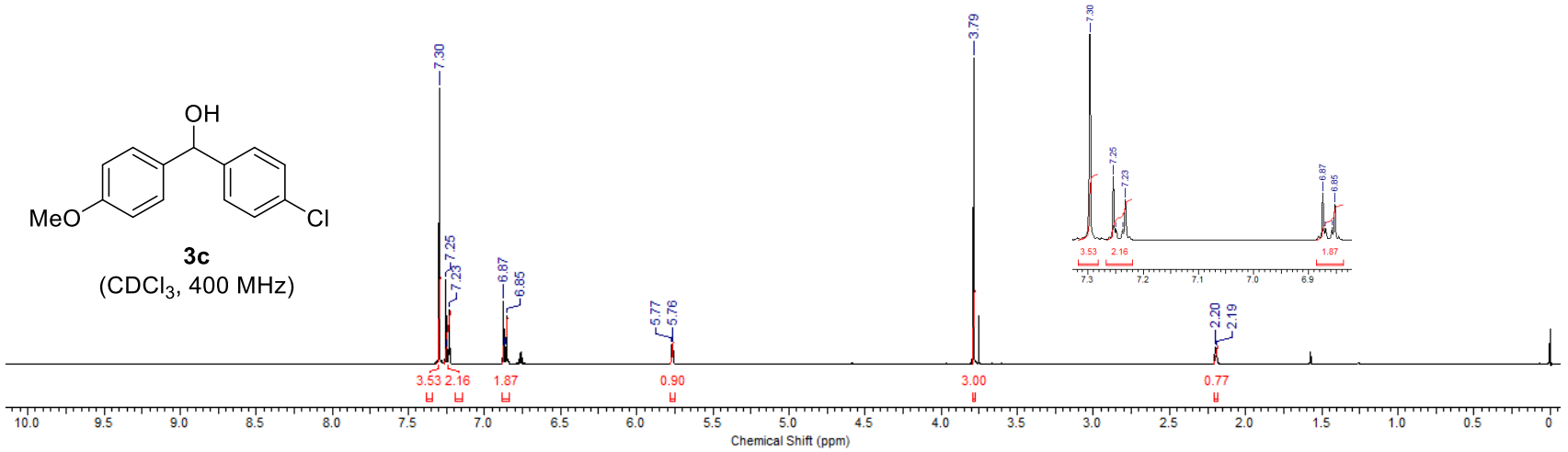
BENZHYDRYL ALCOHOLS

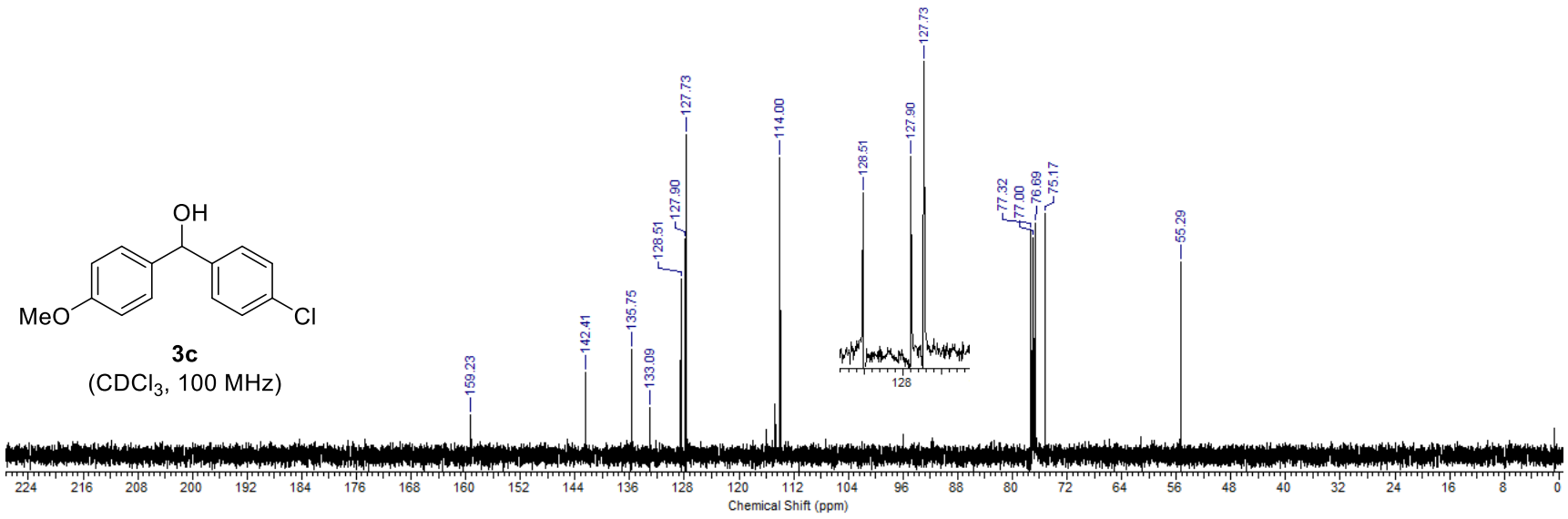


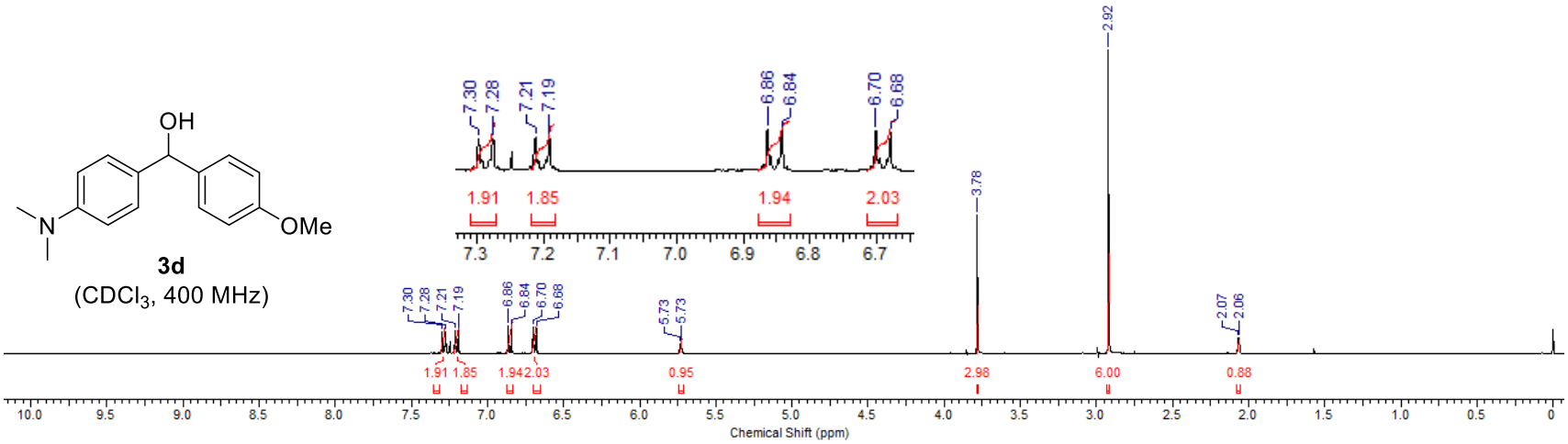


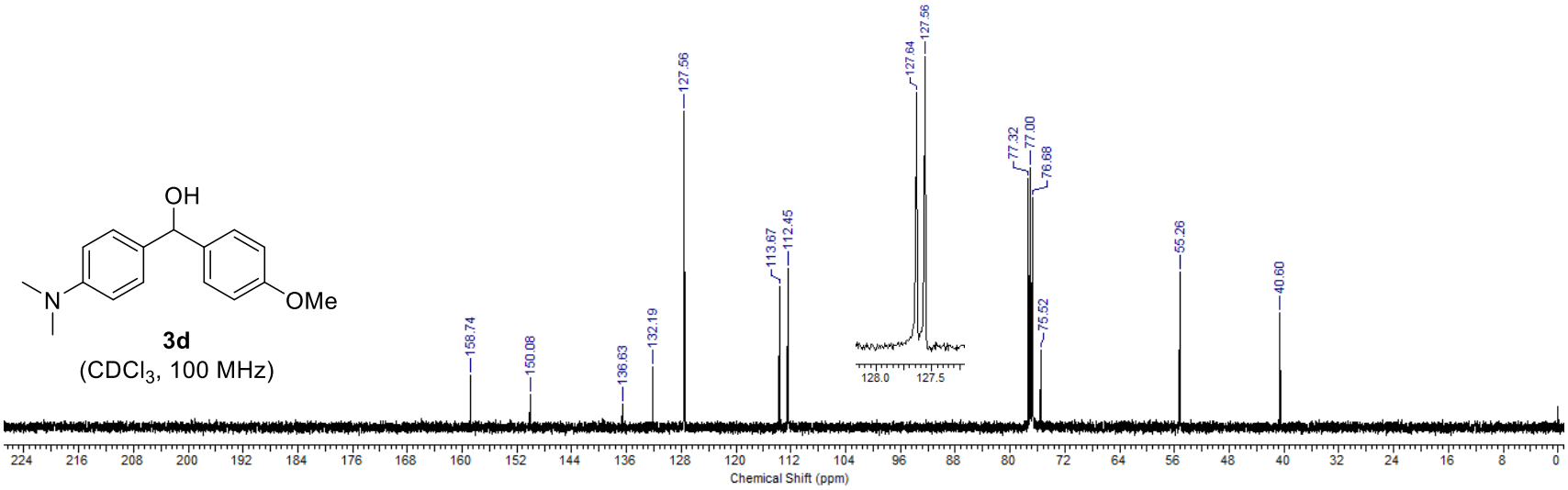

OH
MeO
OMe
3b
(CDCl3, 400 MHz)
7.27
7.25
6.87
6.84
3.78
5.75
2.18
3.92
3.76
0.92
6.00
0.80
Chemical Shift (ppm)

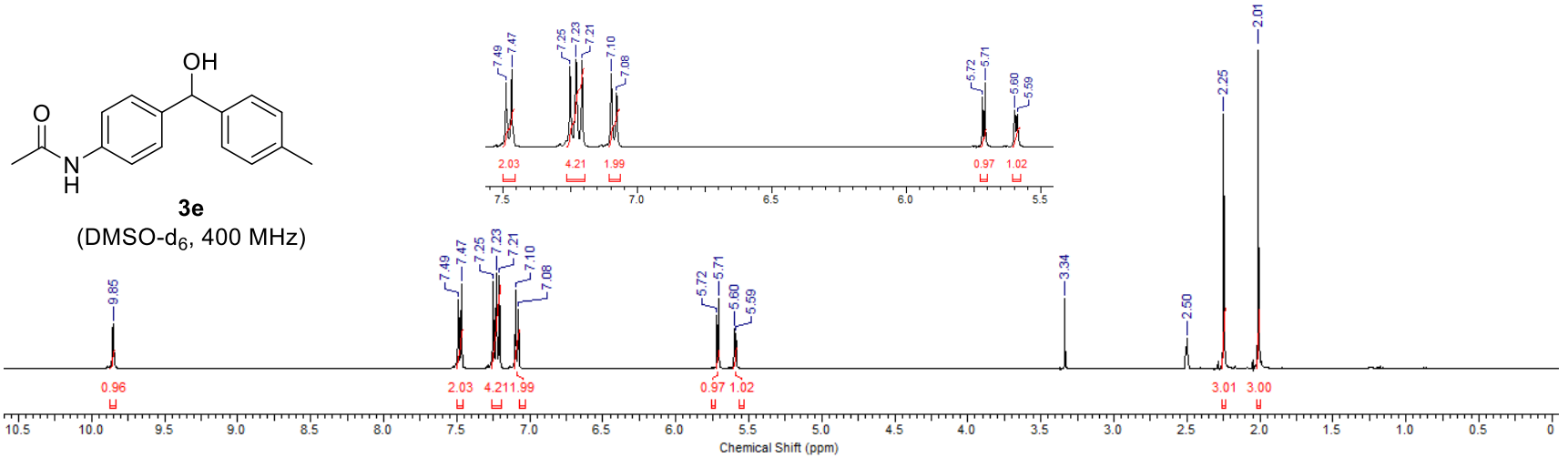

OH
MeO
OMe
3b
(CDCl3, 100 MHz)
158.92
136.36
127.71
113.79
77.32
77.00
76.69
75.35
55.25
Chemical Shift (ppm)

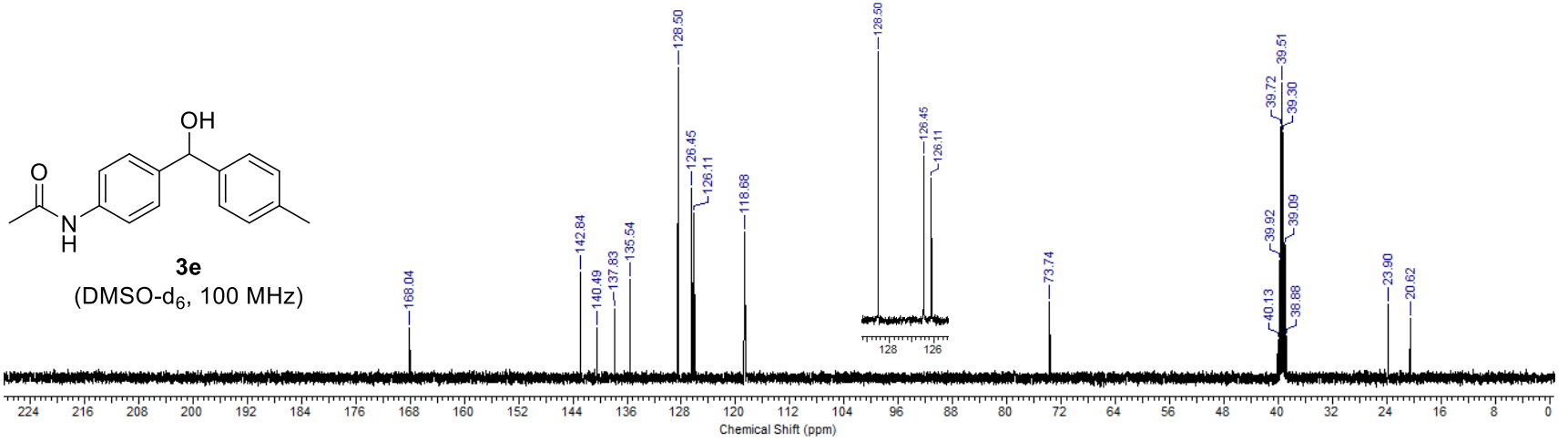

OH
MeO
Cl
3c
(CDCl3, 400 MHz)
7.30
7.25
7.23
6.87
6.85
5.77
5.76
3.79
2.20
2.19
3.53
2.16
1.87
0.90
3.00
0.77
Chemical Shift (ppm)

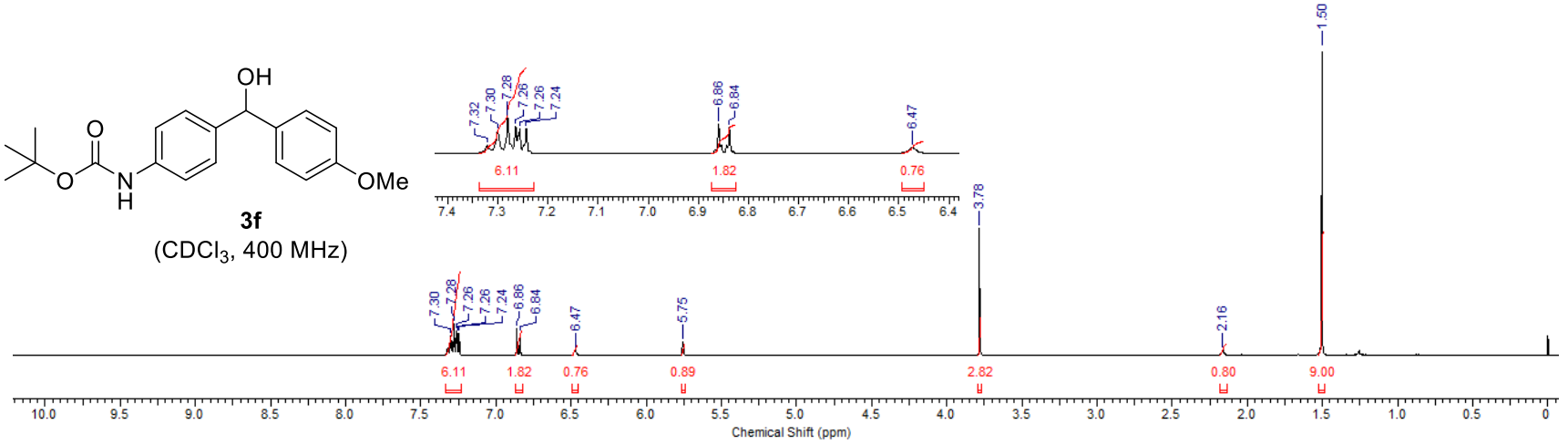

OH
MeO
Cl
3c
(CDCl3, 100 MHz)
159.23
142.41
135.75
133.09
128.51
127.90
127.73
114.00
77.32
77.00
76.69
75.17
55.29
Chemical Shift (ppm)

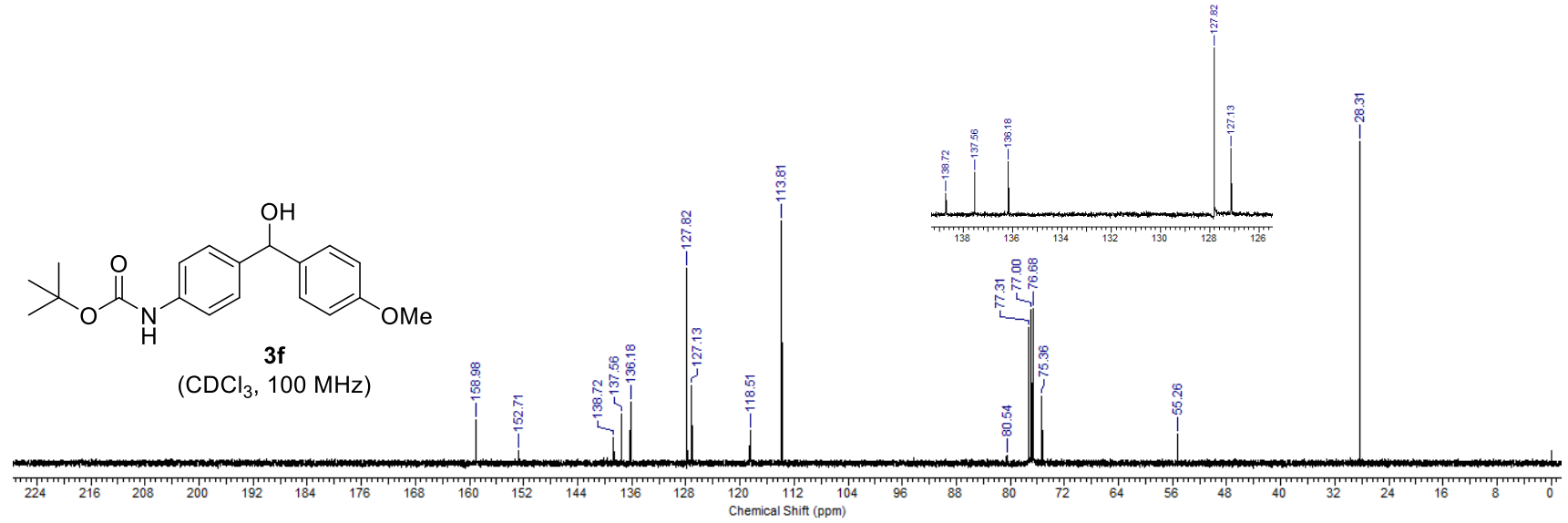

OH
N
OMe
3d
(CDCl3, 400 MHz)
7.30
7.28
7.21
7.19
6.86
6.84
6.70
6.68
1.91
1.85
1.94
2.03
3.78
2.92
5.73
5.73
2.07
2.06
0.95
2.98
6.00
0.88
Chemical Shift (ppm)

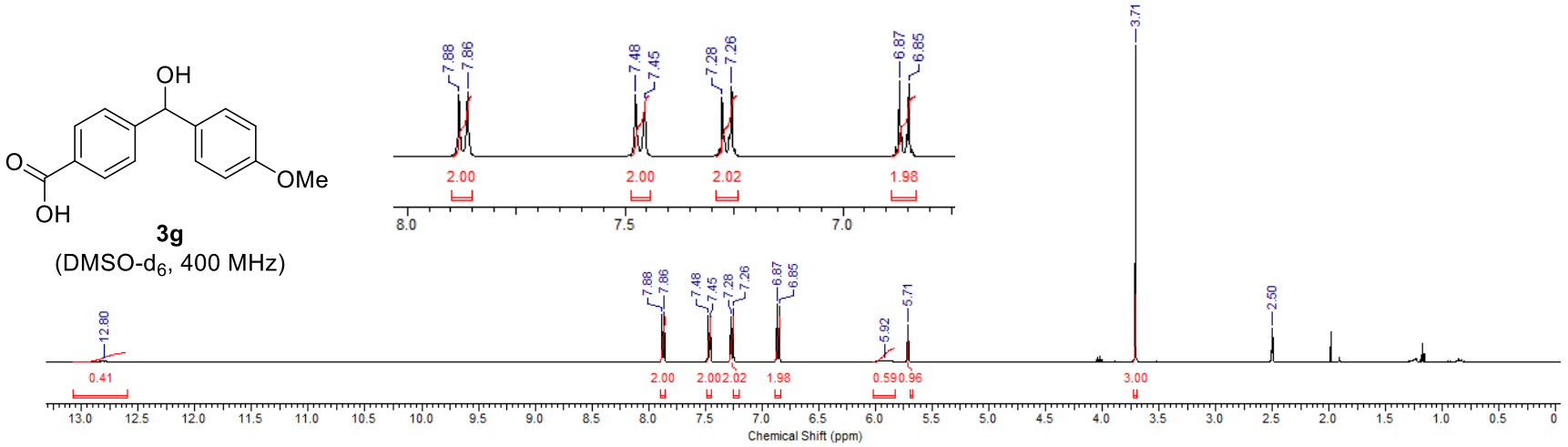

OH
N
OMe
3d
(CDCl3, 100 MHz)
158.74
150.08
136.63
132.19
127.56
113.67
112.45
127.64
127.56
77.32
77.00
76.68
75.52
55.26
40.60
Chemical Shift (ppm)

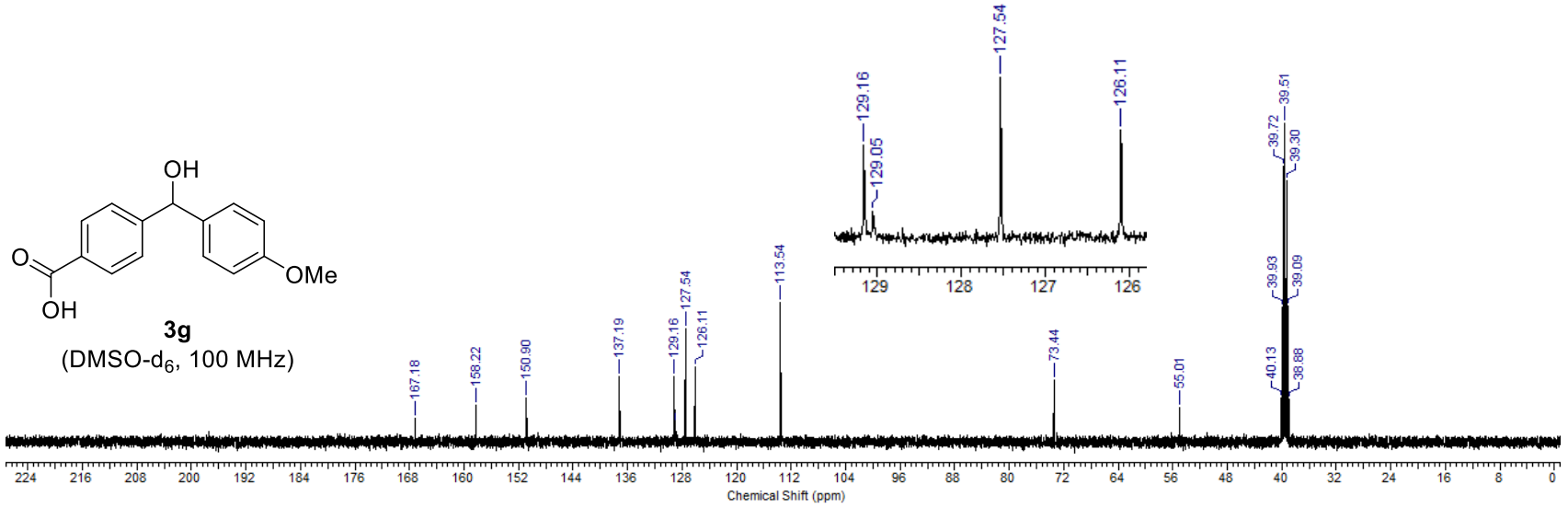

OH
O
N
H
3e
(DMSO-d6, 400 MHz)
9.85
7.49
7.47
7.25
7.23
7.21
7.10
7.08
5.72
5.71
5.60
5.59
3.34
2.50
2.25
2.01
0.96
2.03
4.21
1.99
0.97
1.02
3.01
3.00
Chemical Shift (ppm)

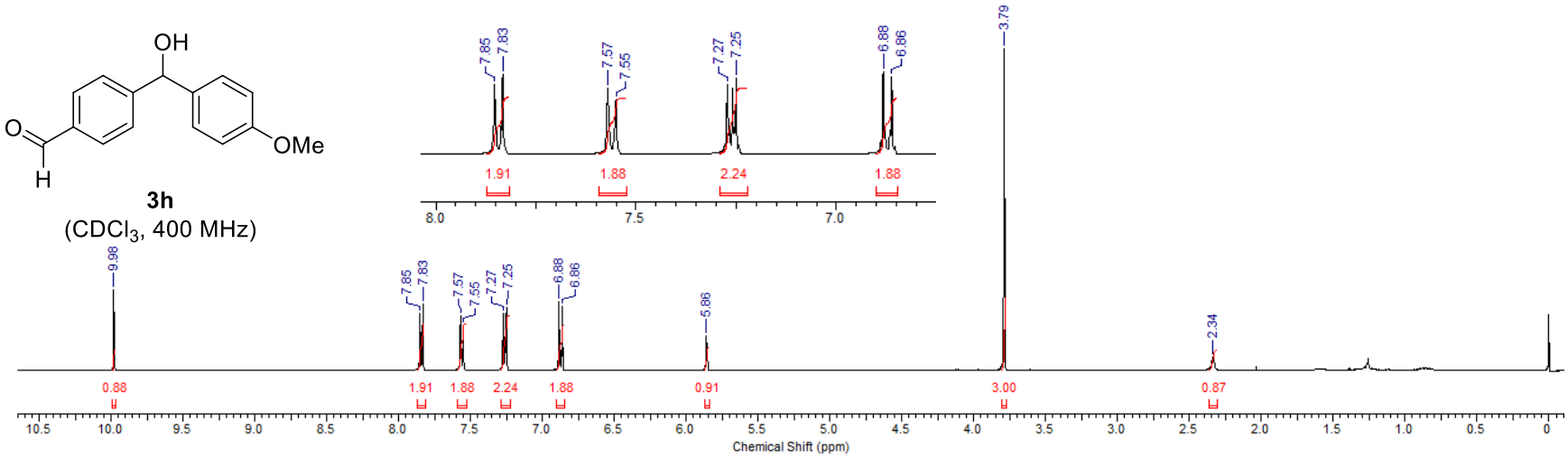

OH
O
N
H
3e
(DMSO-d6, 100 MHz)
168.04
142.84
140.49
137.83
135.54
128.50
126.45
126.11
118.68
73.74
39.72
39.51
39.30
39.09
39.92
40.13
38.88
23.90
20.62
Chemical Shift (ppm)

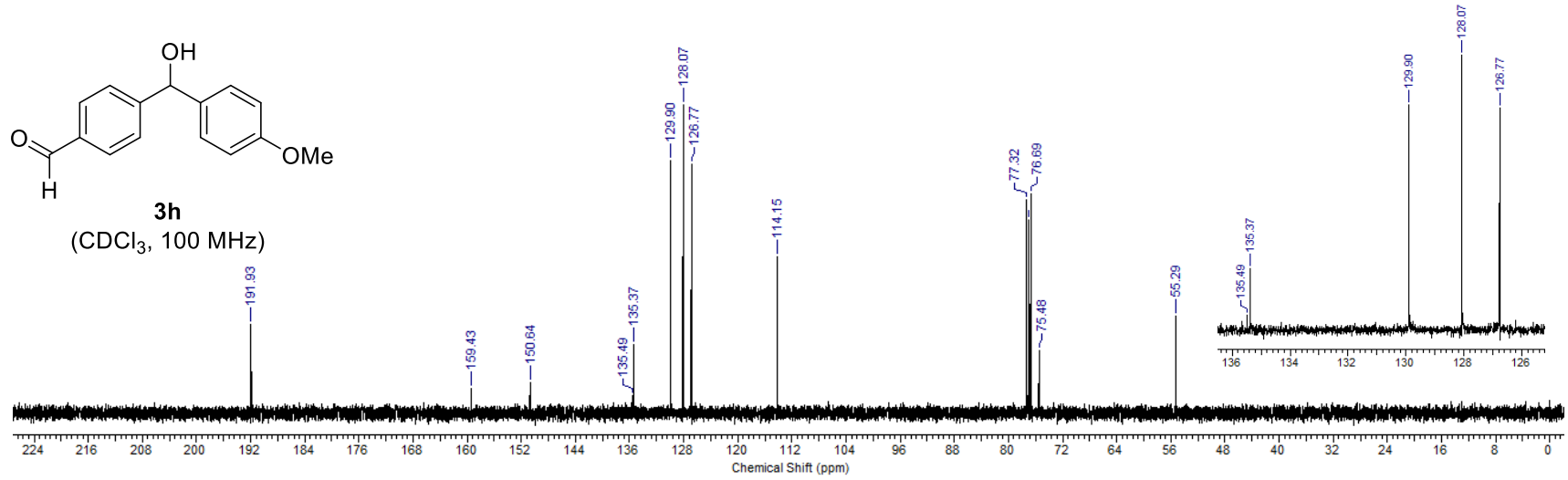

OH
O
O
N
H
OMe
3f
(CDCl3, 400 MHz)
7.32
7.30
7.28
7.26
7.26
7.24
6.86
6.84
6.47
6.11
1.82
0.76
3.78
1.50
5.75
2.16
0.89
2.82
0.80
9.00
Chemical Shift (ppm)

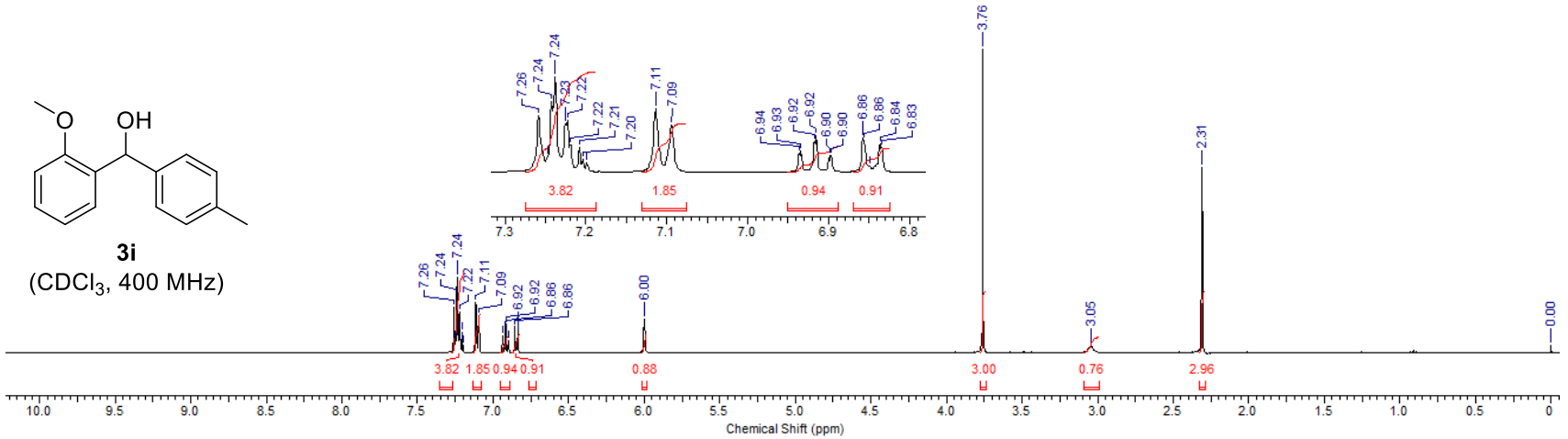

OH
O
O
N
H
OMe
3f
(CDCl3, 100 MHz)
158.98
152.71
138.72
137.56
136.18
127.82
127.13
118.51
113.81
77.31
77.00
76.68
75.36
80.54
55.26
28.31
Chemical Shift (ppm)

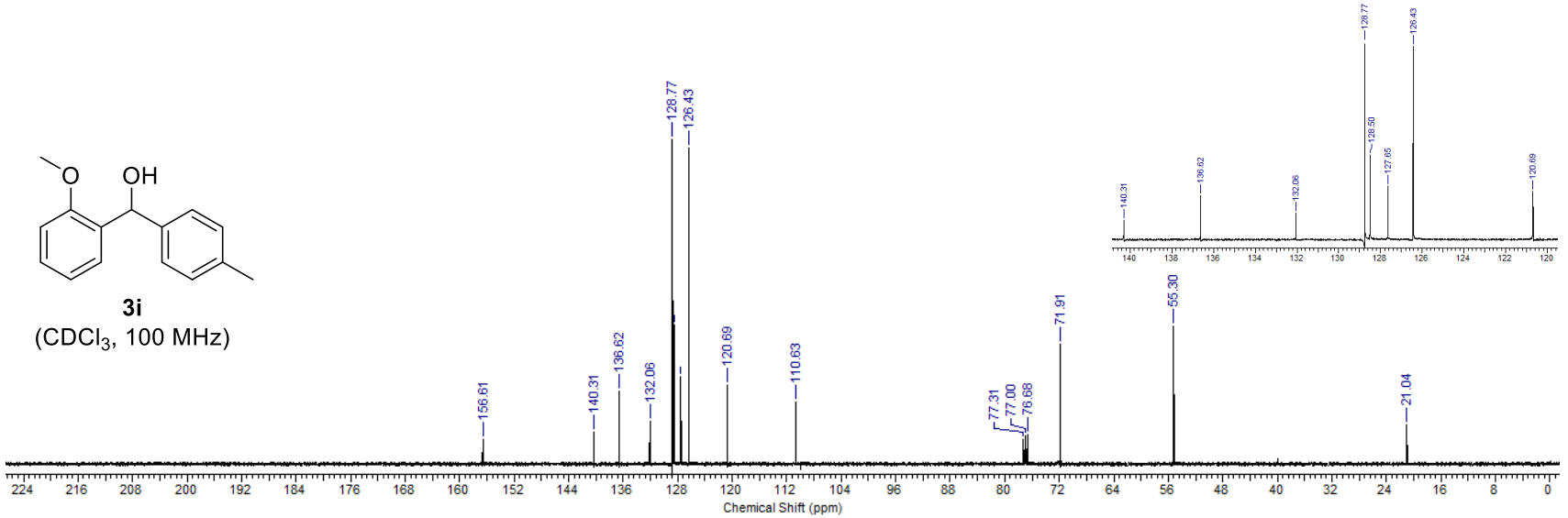

OH
O
OMe
OH
3g
(DMSO-d6, 400 MHz)
7.88
7.86
7.48
7.45
7.28
7.26
6.87
6.85
3.71
2.00
2.00
2.02
1.98
12.80
5.92
5.71
2.50
0.41
2.00
2.00
2.02
1.98
0.59
0.96
3.00
Chemical Shift (ppm)


OH
O
OMe
OH
3g
(DMSO-d6, 100 MHz)
129.16
129.05
127.54
126.11
39.72
39.51
39.30
39.93
39.09
40.13
38.88
167.18
158.22
150.90
137.19
129.16
127.54
126.11
113.54
73.44
55.01
Chemical Shift (ppm)

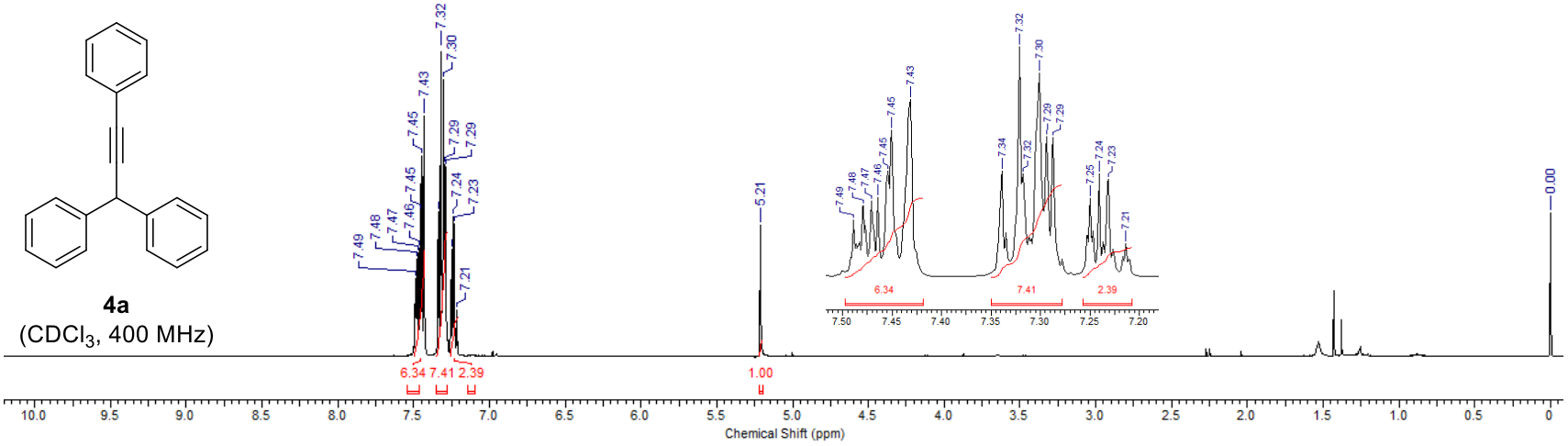

OH
O
OMe
H
3h
(CDCl3, 400 MHz)
Chemical Shift (ppm)

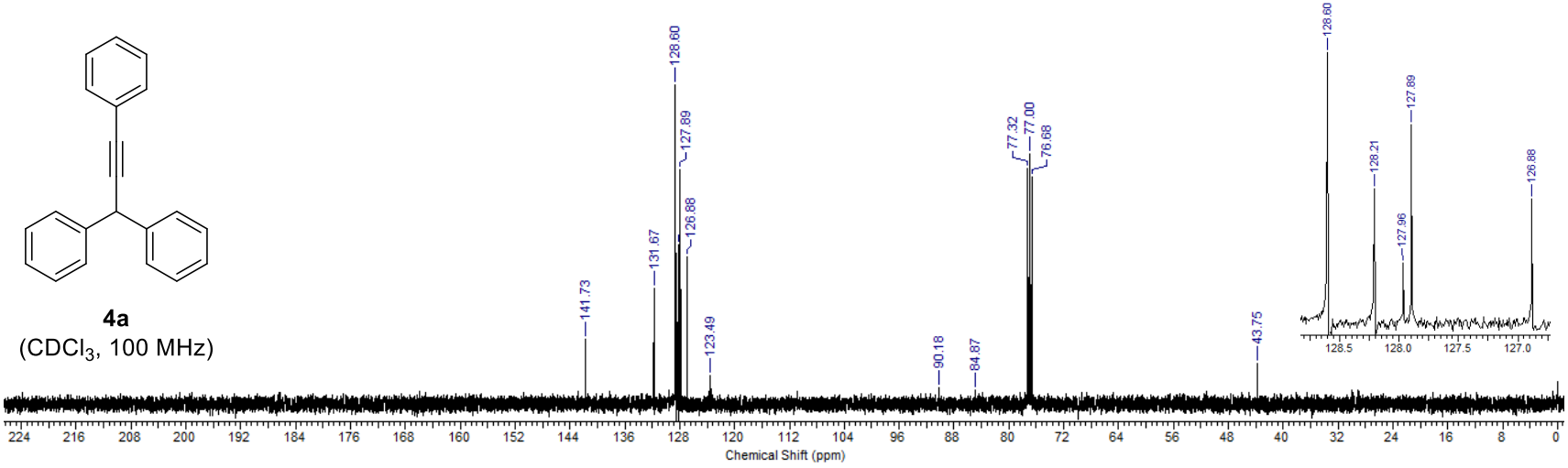

OH
O
OMe
H
3h
(CDCl3, 100 MHz)
Chemical Shift (ppm)

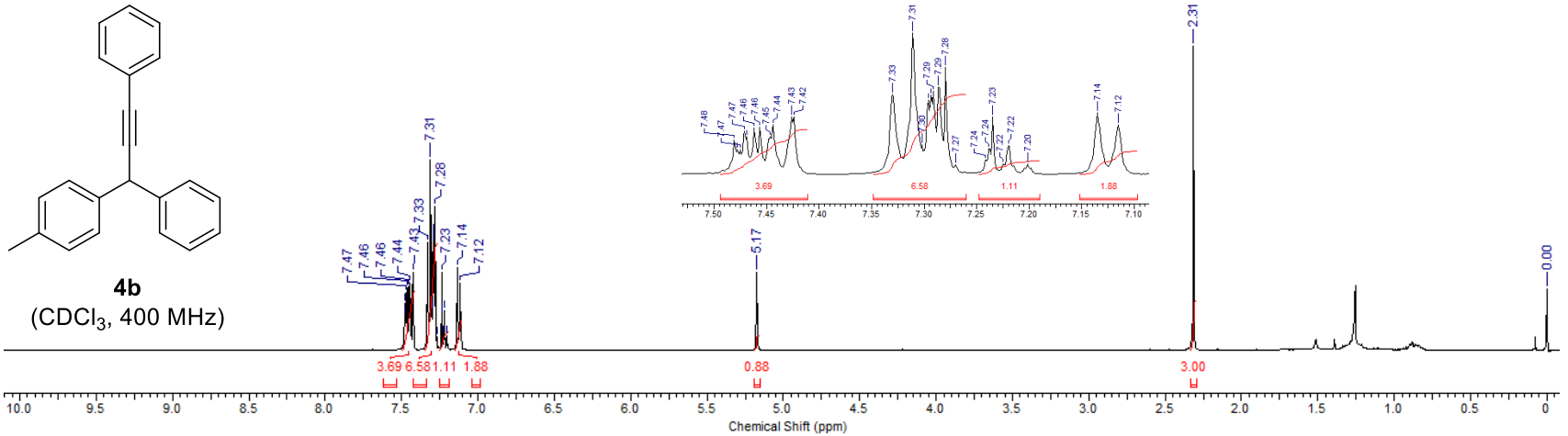

O
OH
3i
(CDCl3, 400 MHz)
Chemical Shift (ppm)

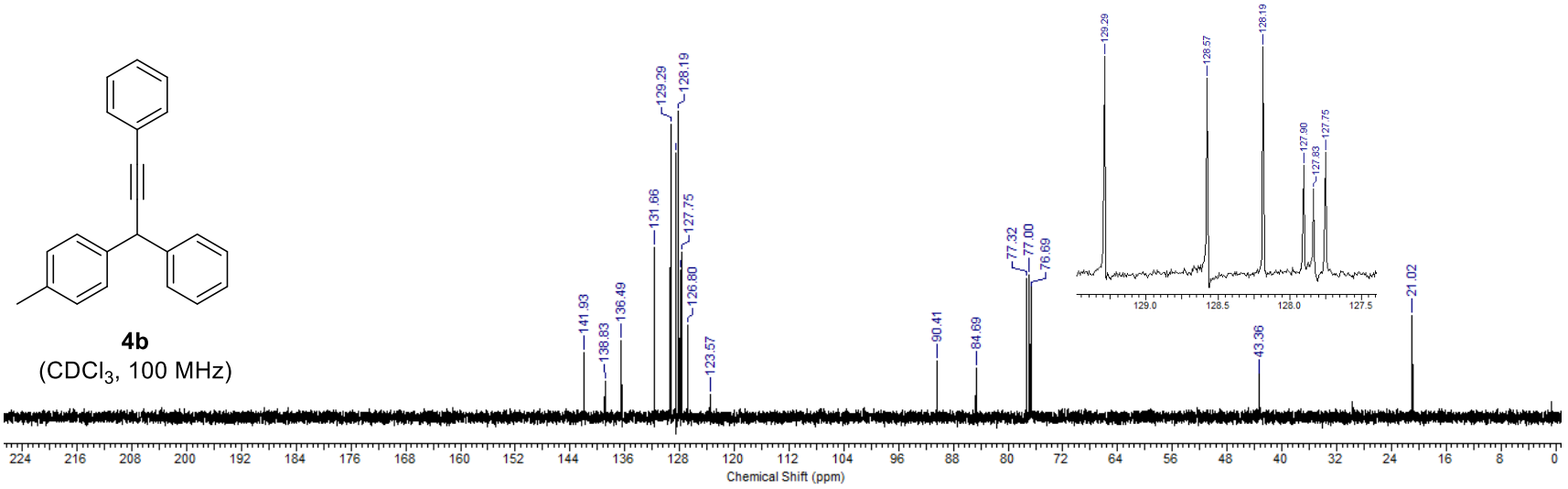

O
OH
3i
(CDCl3, 100 MHz)
Chemical Shift (ppm)

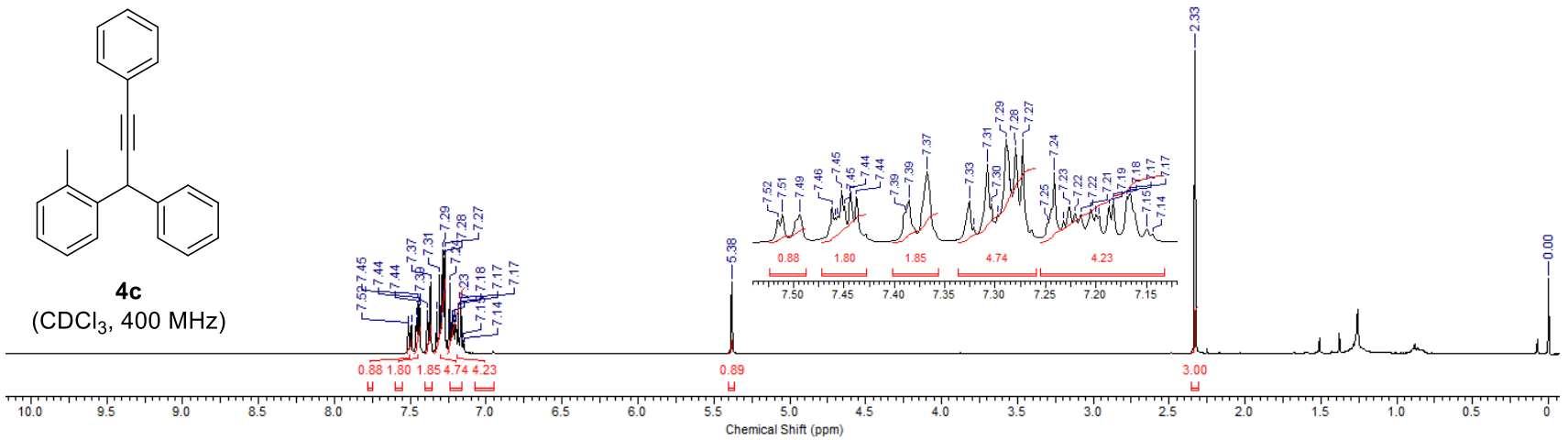
INTERNAL ALKENES AND ALKYNES

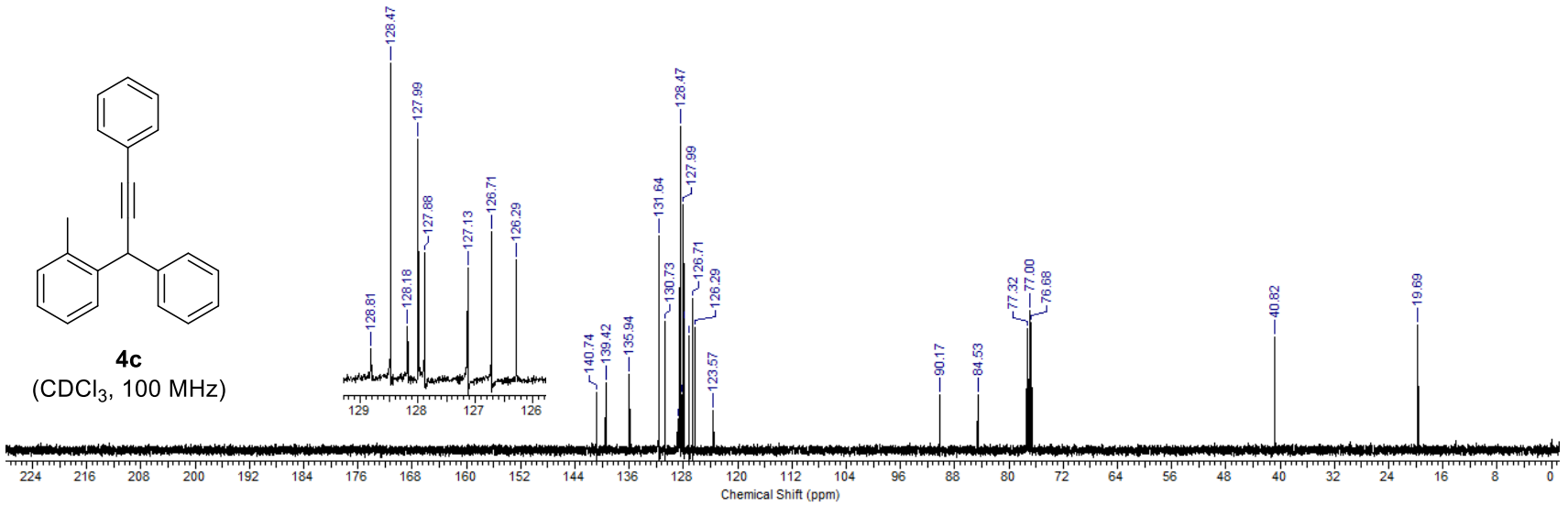


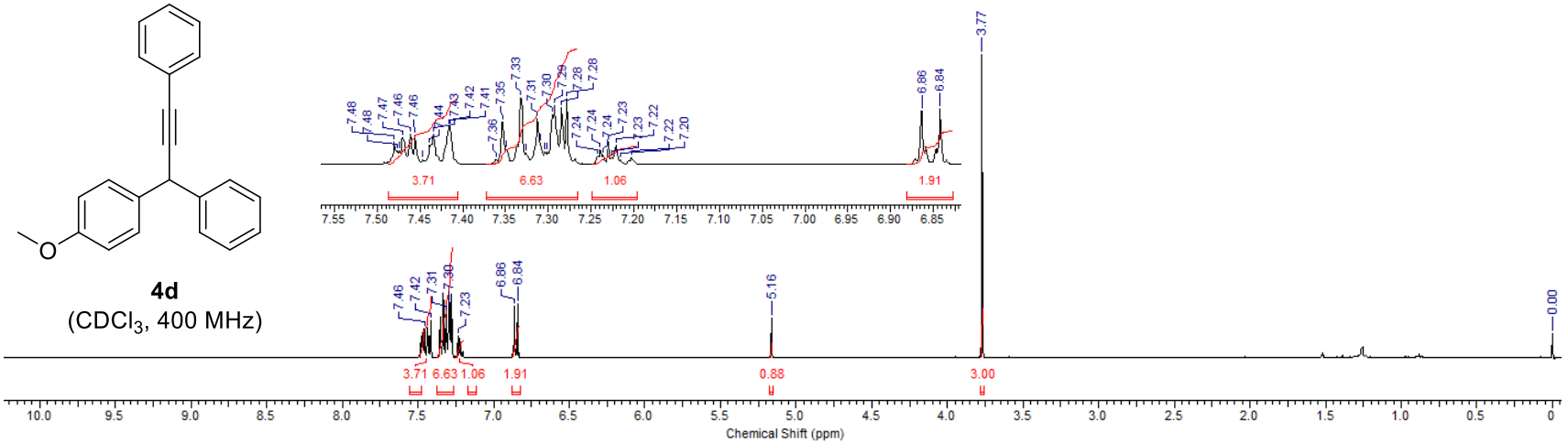



4b
(CDCl3, 400 MHz)
7.47
7.46
7.46
7.44
7.43
7.33
7.31
7.28
7.23
7.14
7.12
5.17
2.31
0.00
3.69
6.58
1.11
1.88
0.88
3.00
Chemical Shift (ppm)

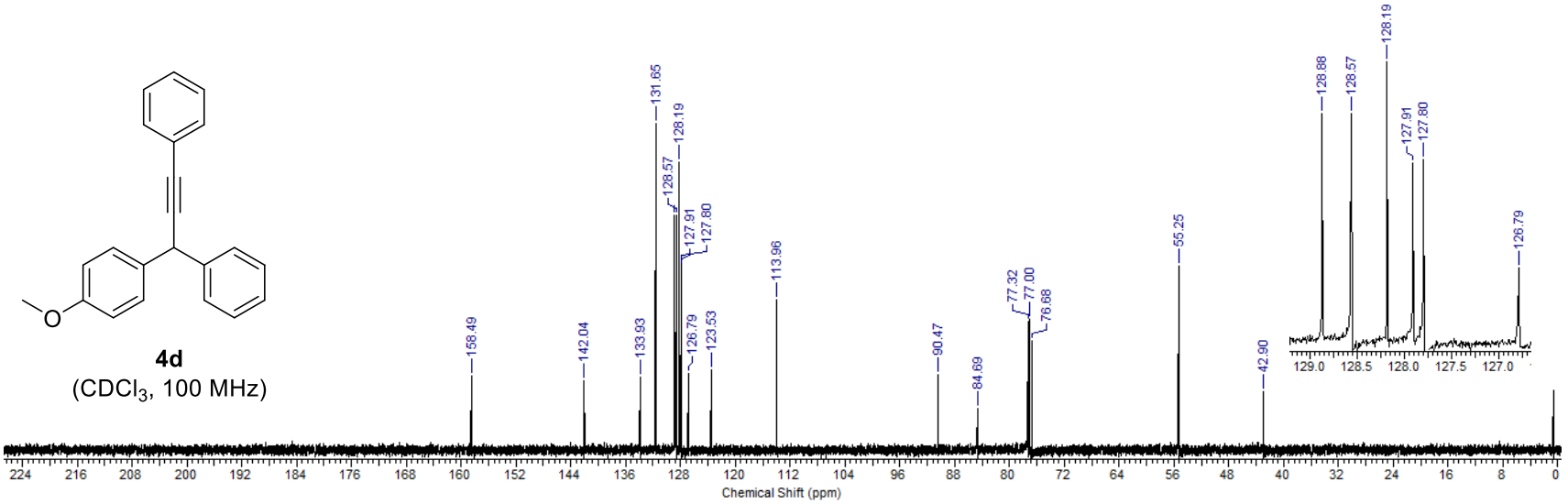

4b
(CDCl3, 100 MHz)
141.93
138.83
136.49
131.66
129.29
128.19
127.75
126.80
123.57
90.41
84.69
77.32
77.00
76.69
43.36
21.02
Chemical Shift (ppm)


4c
(CDCl3, 400 MHz)
0.88 1.80 1.85 4.74 4.23
0.89
3.00
Chemical Shift (ppm)

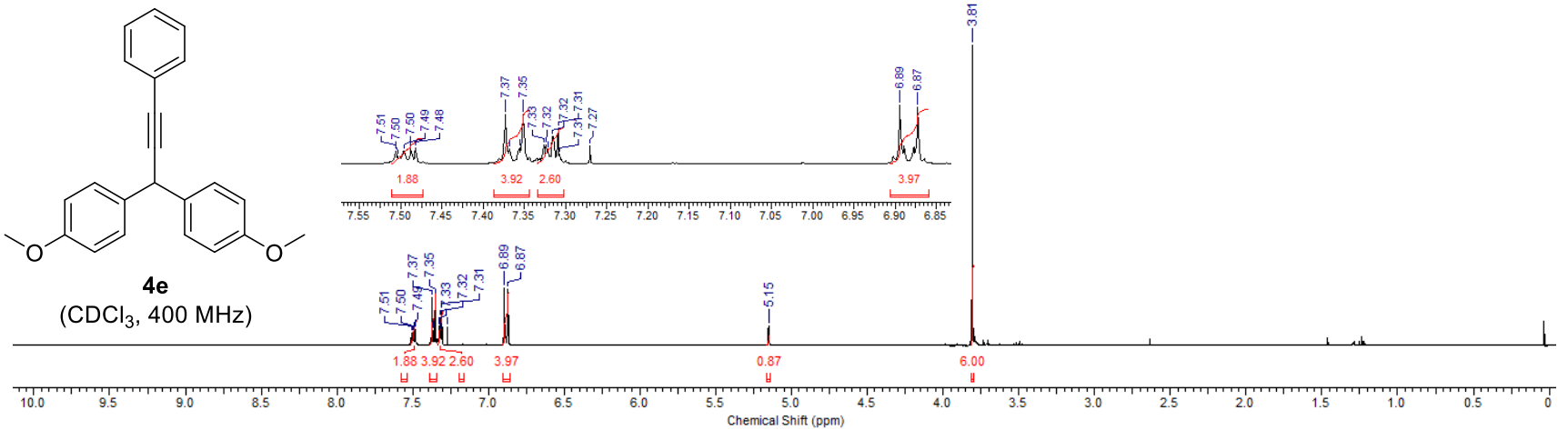

4c
(CDCl3, 100 MHz)
Chemical Shift (ppm)

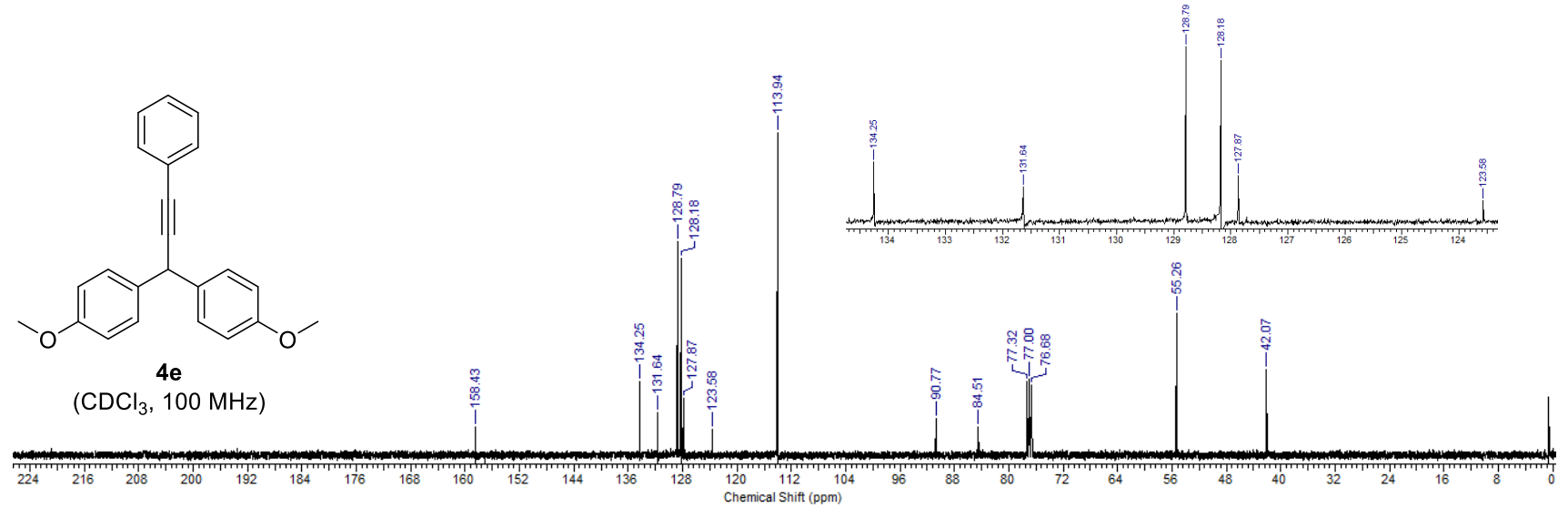


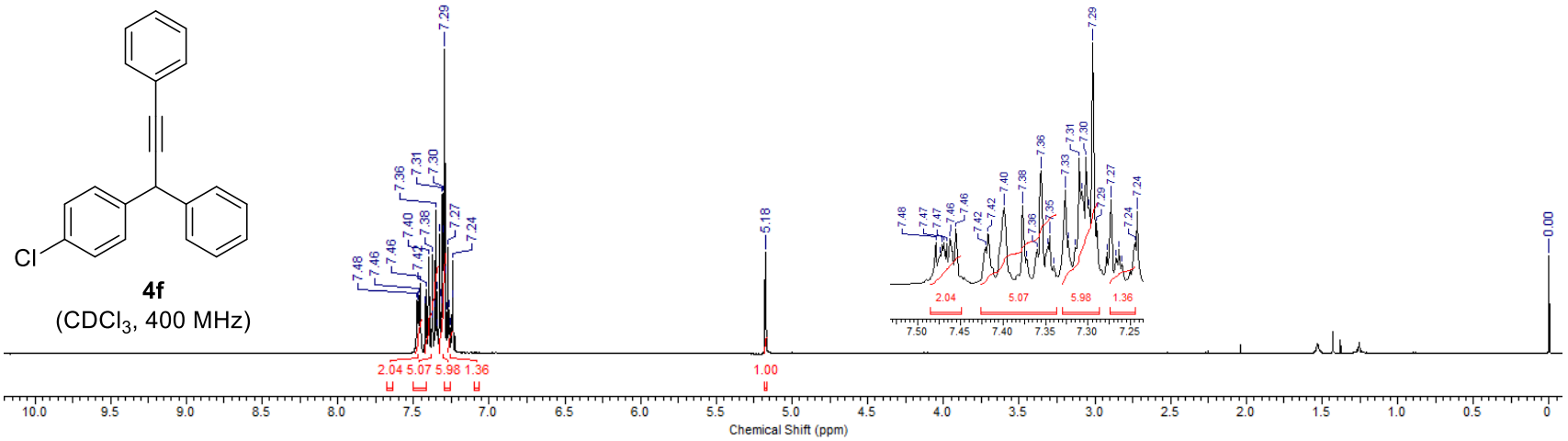
4d
($CDCl_3$, 400 MHz)

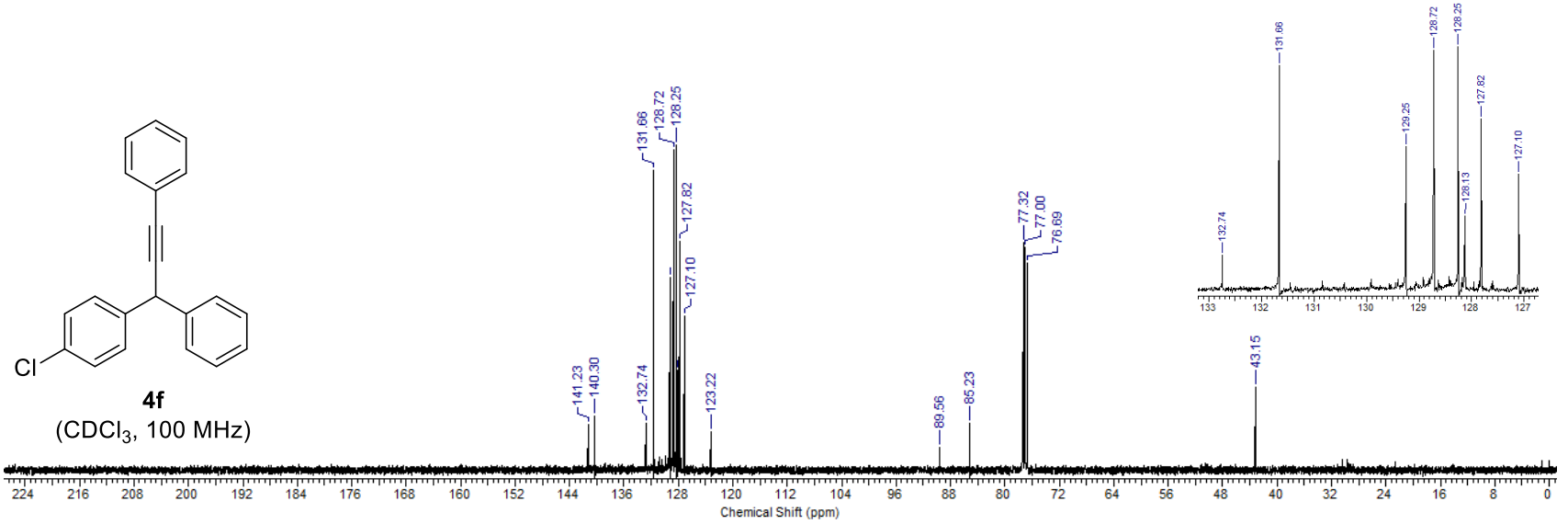


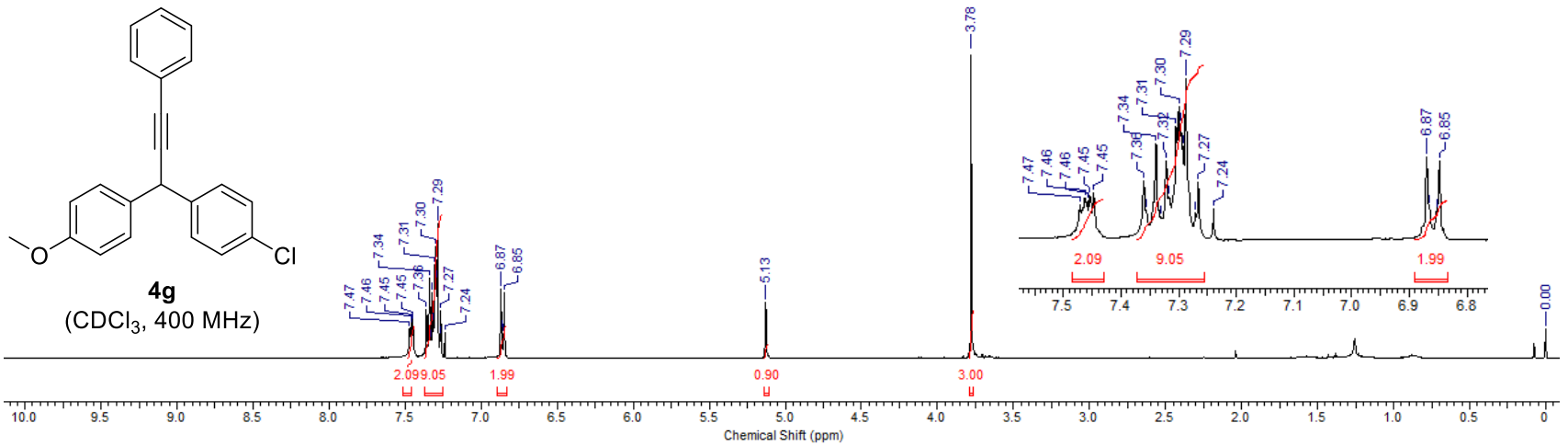
4d
($CDCl_3$, 100 MHz)

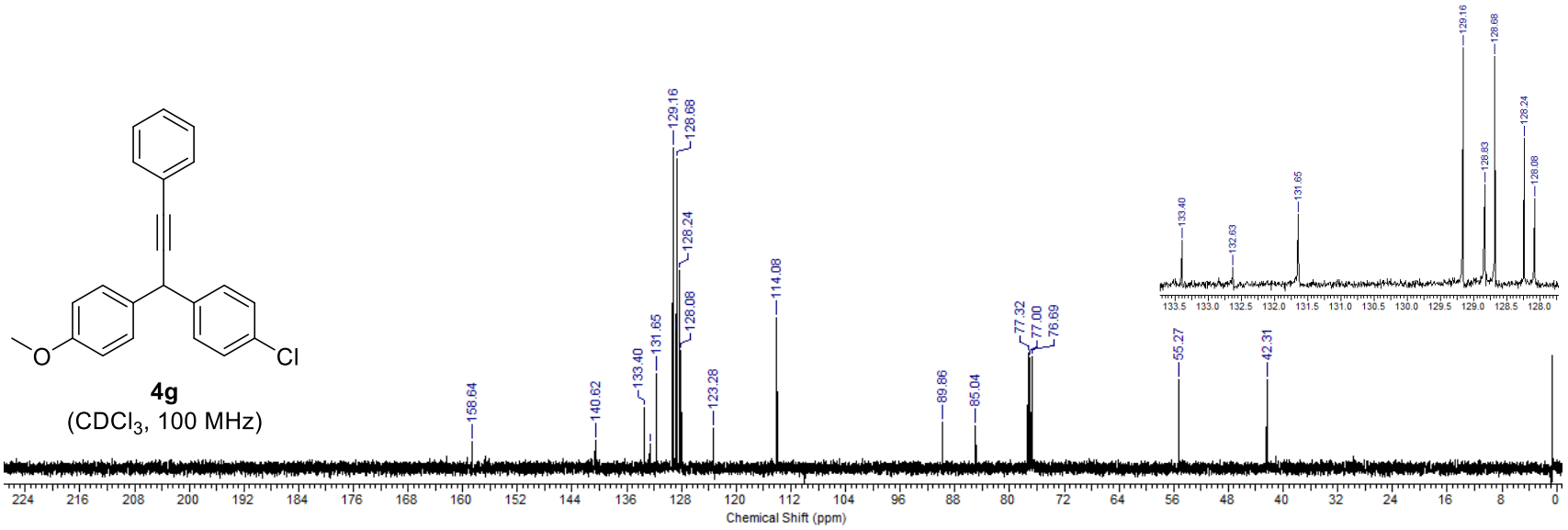

4e
(CDCl3, 400 MHz)
Chemical Shift (ppm)

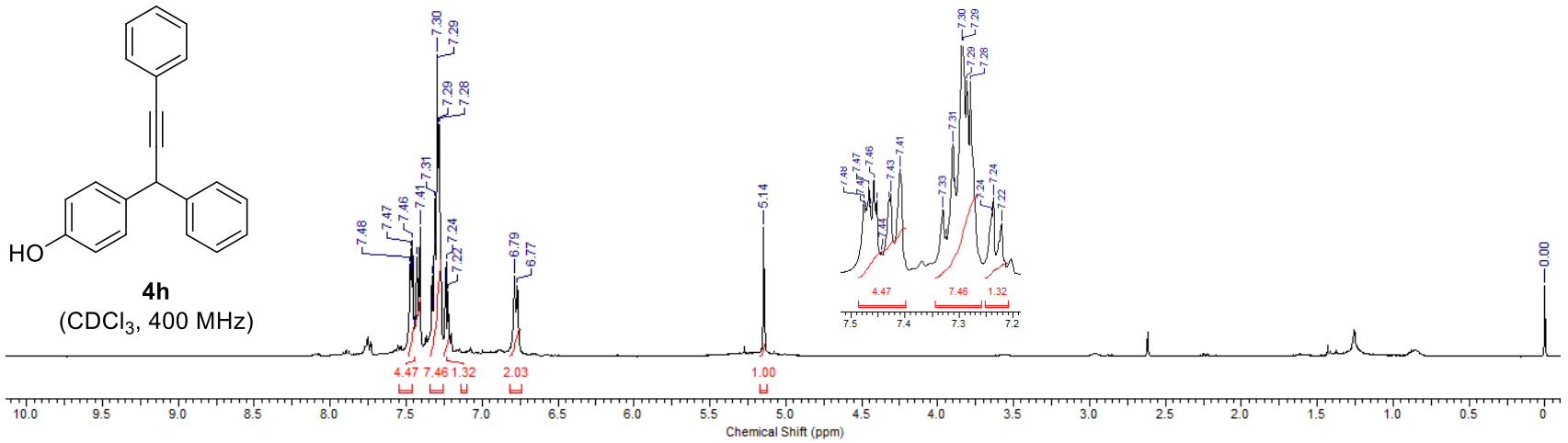

4e
(CDCl3, 100 MHz)
Chemical Shift (ppm)

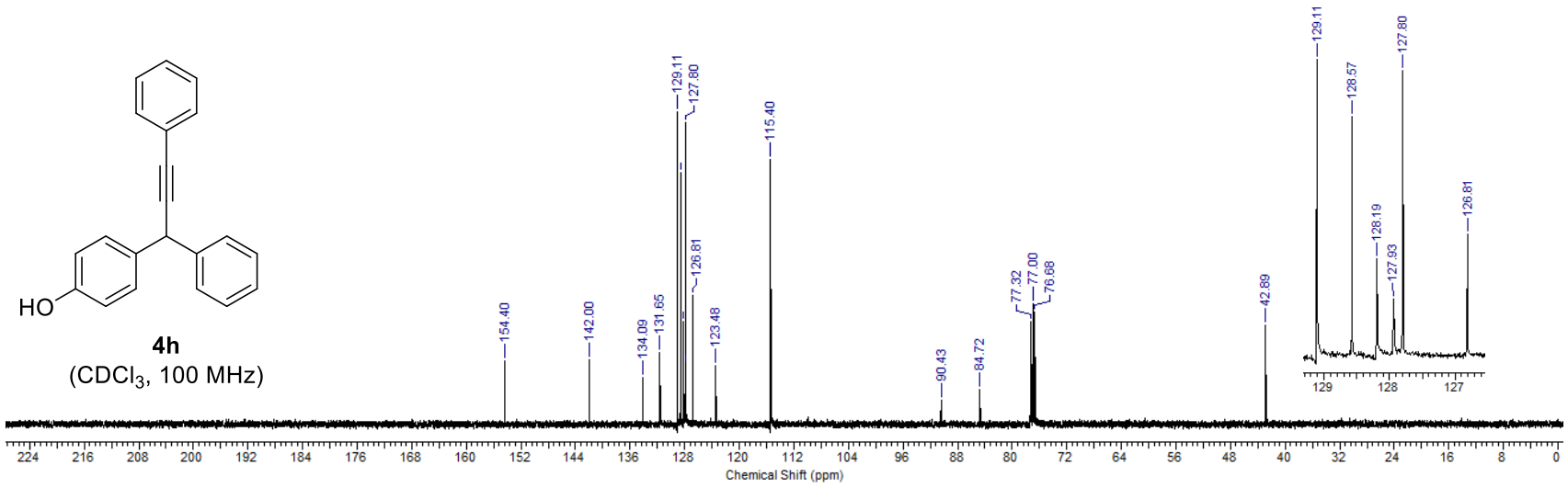

Cl
4f
(CDCl3, 400 MHz)
7.48
7.46
7.46
7.42
7.40
7.38
7.36
7.31
7.30
7.27
7.24
5.18
0.00
2.04 5.07 5.98 1.36
1.00
Chemical Shift (ppm)

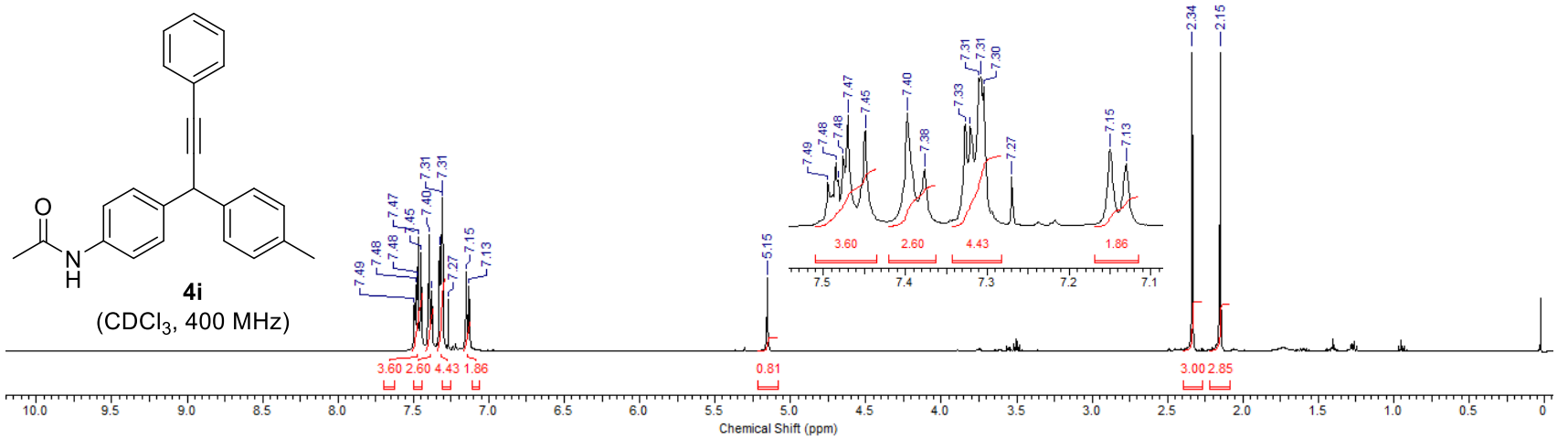

Cl
4f
(CDCl3, 100 MHz)
141.23
140.30
132.74
131.66
128.72
128.25
127.82
127.10
123.22
89.56
85.23
77.32
77.00
76.69
43.15
Chemical Shift (ppm)

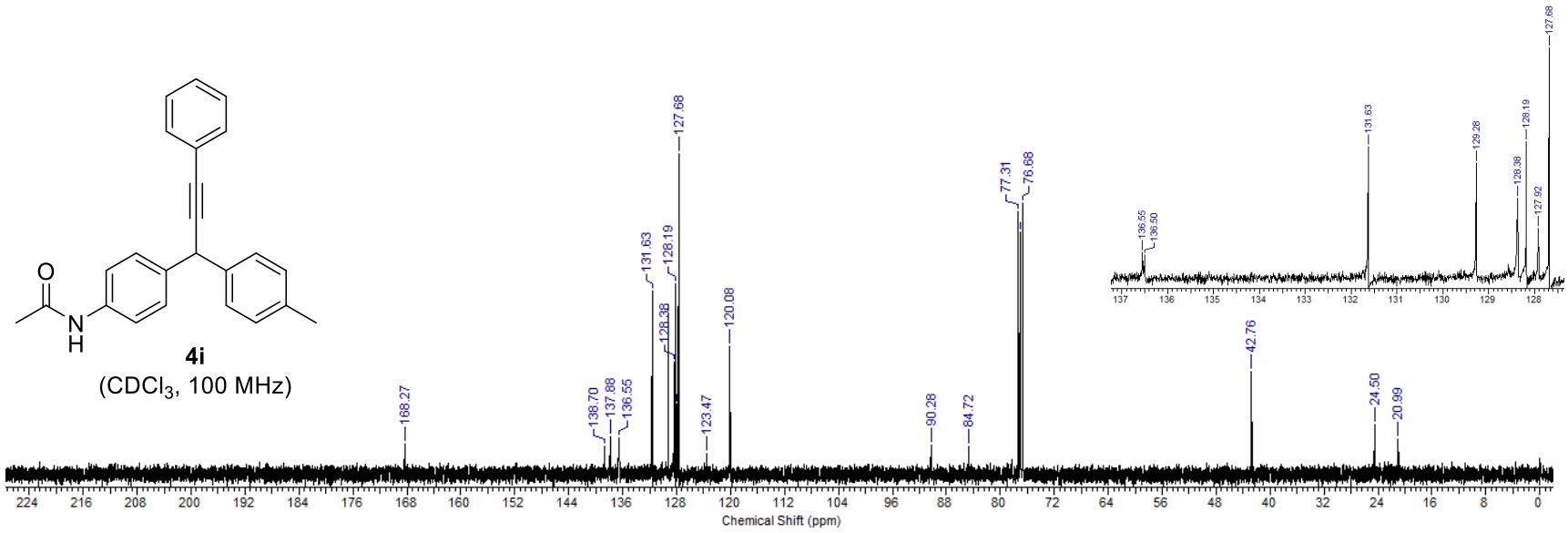

4g
(CDCl3, 400 MHz)
Chemical Shift (ppm)

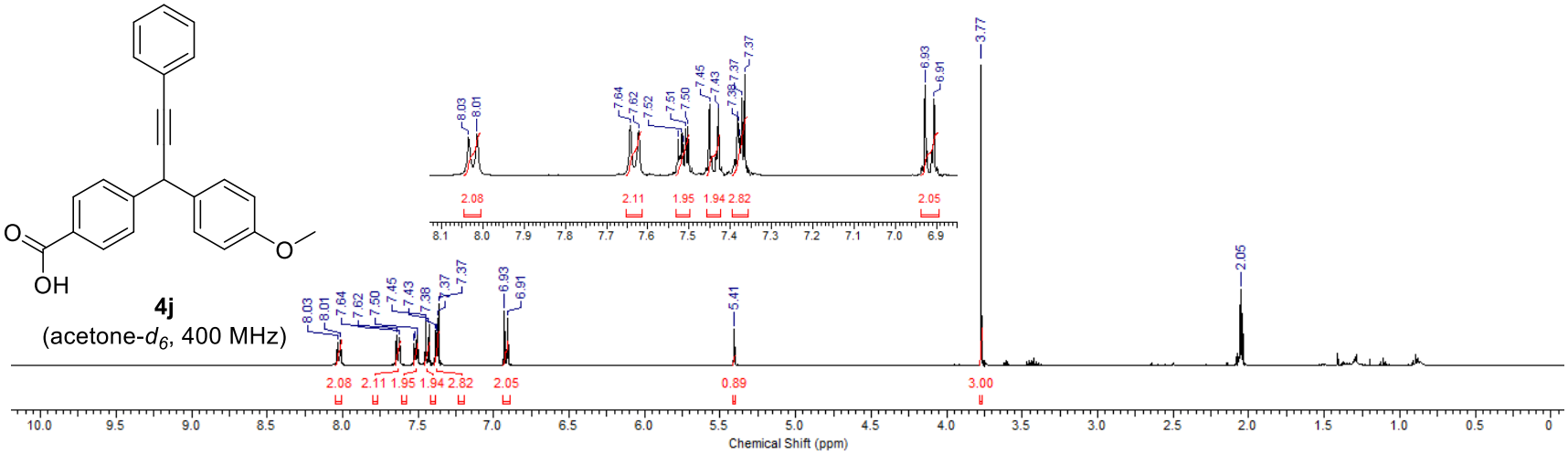

4g
(CDCl3, 100 MHz)
Chemical Shift (ppm)

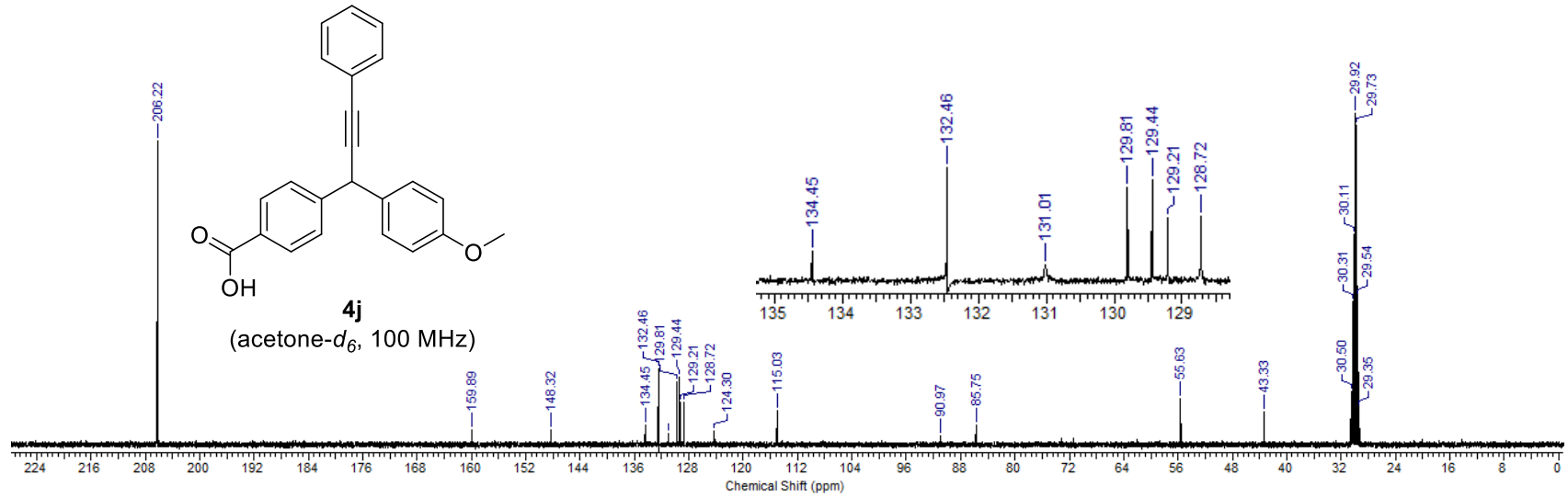

HO
4h
(CDCl3, 400 MHz)
7.48
7.47
7.46
7.41
7.31
7.30
7.29
7.29
7.28
7.24
7.22
6.79
6.77
5.14
0.00
4.47
7.46
1.32
2.03
1.00
Chemical Shift (ppm)

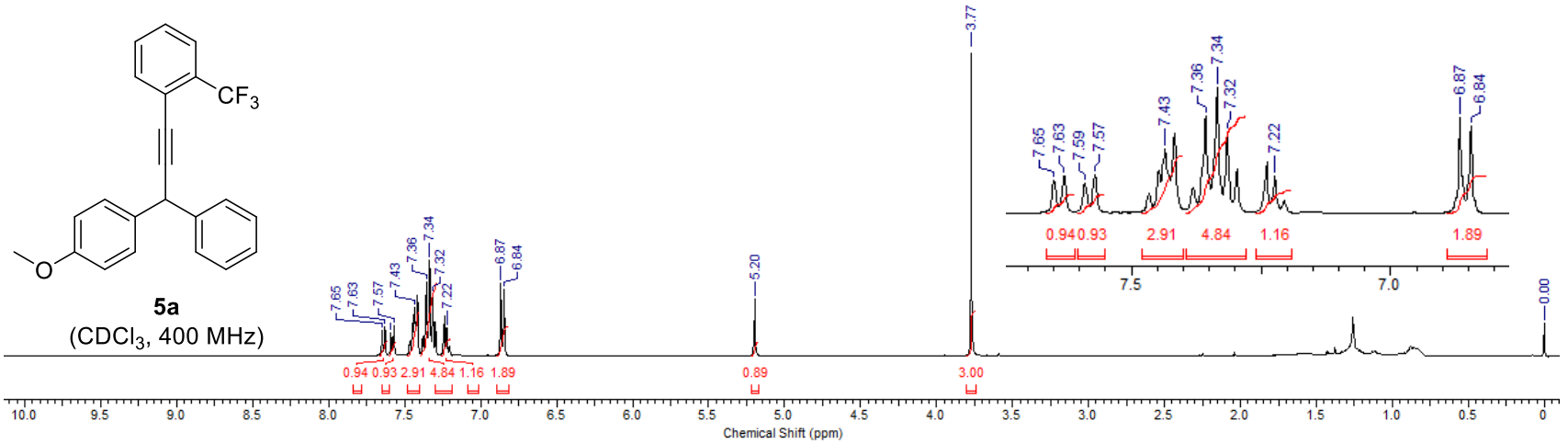

HO
4h
(CDCl3, 100 MHz)
154.40
142.00
134.09
131.65
129.11
127.80
126.81
123.48
115.40
90.43
84.72
77.32
77.00
76.68
42.89
129.11
128.57
128.19
127.93
127.80
126.81
Chemical Shift (ppm)

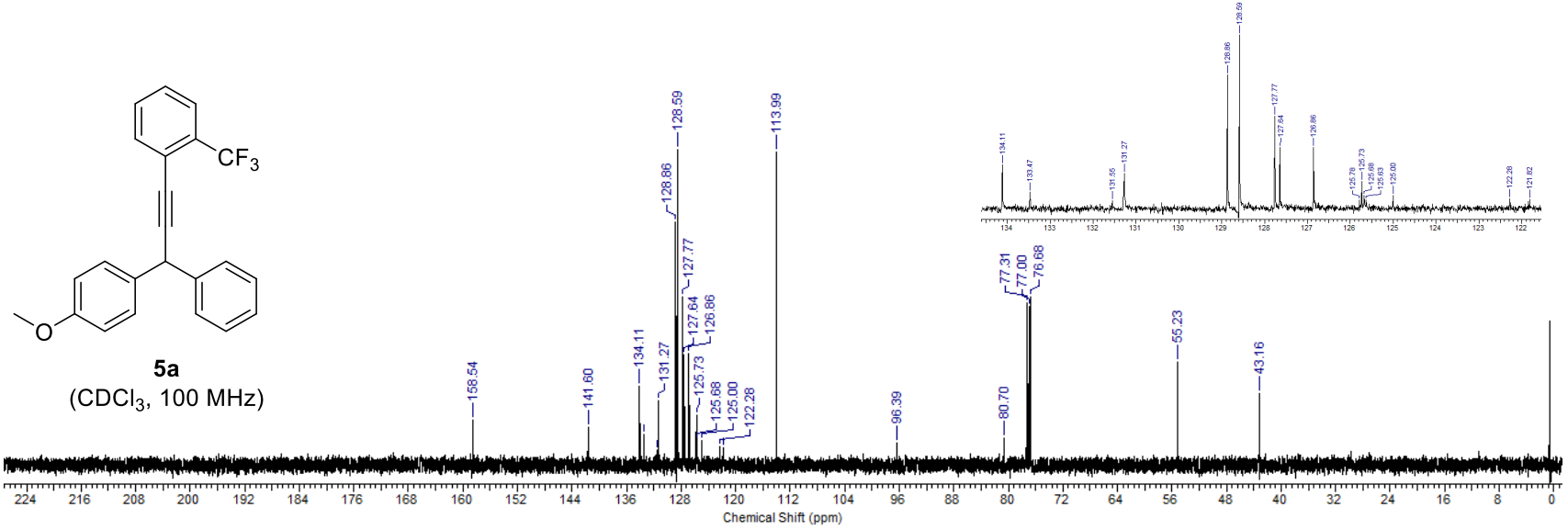

4i
(CDCl3, 400 MHz)
Chemical Shift (ppm)

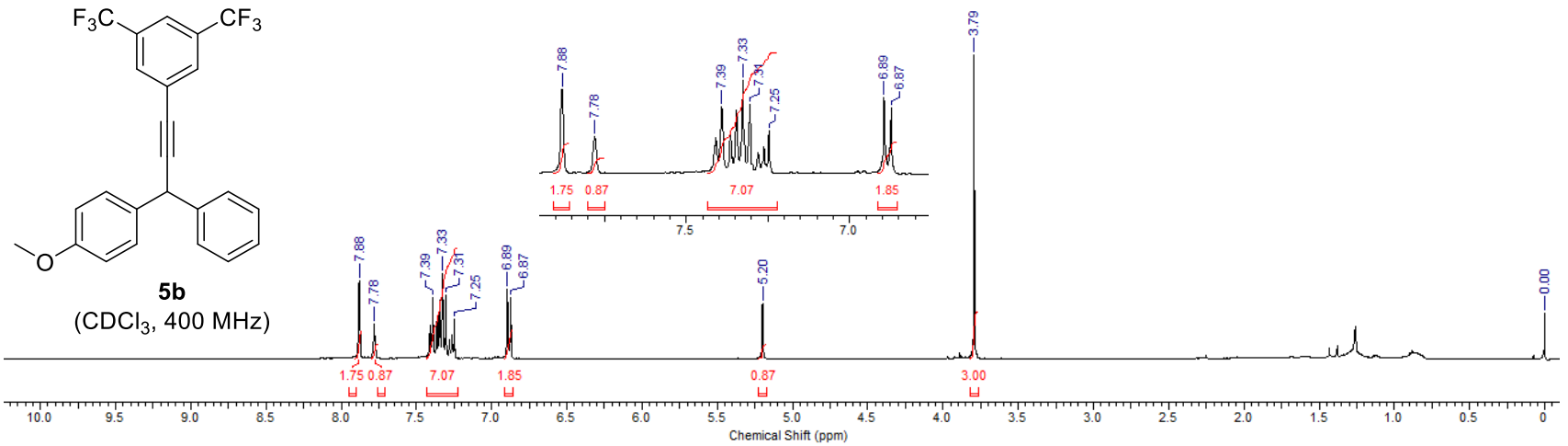

4i
(CDCl3, 100 MHz)
Chemical Shift (ppm)

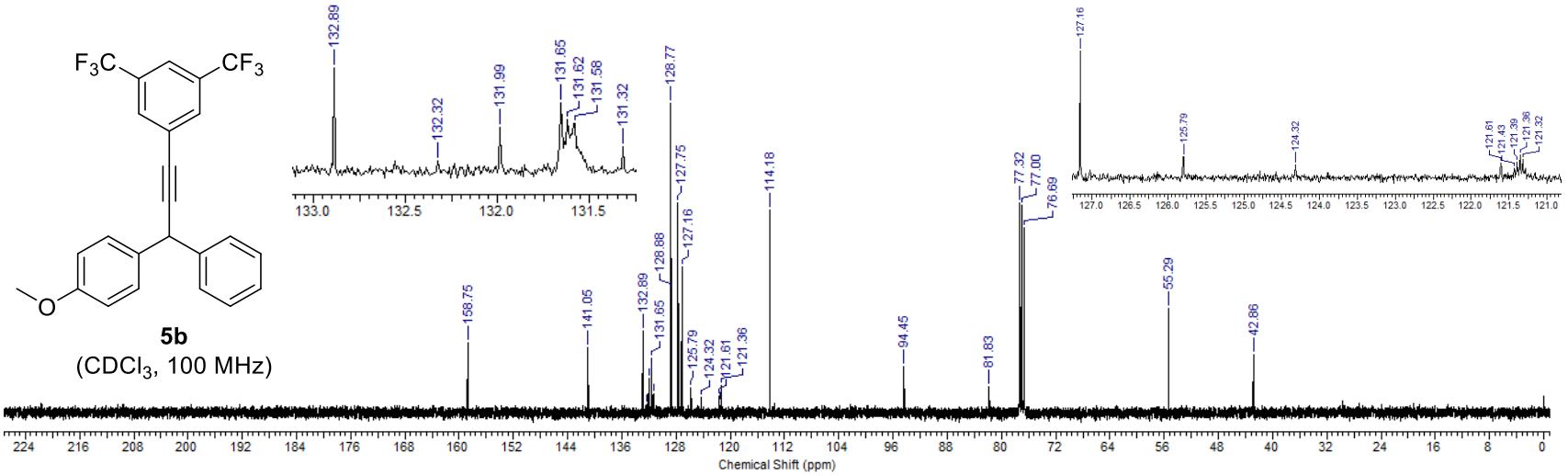

4j
(acetone-d_6, 400 MHz)
Chemical Shift (ppm)

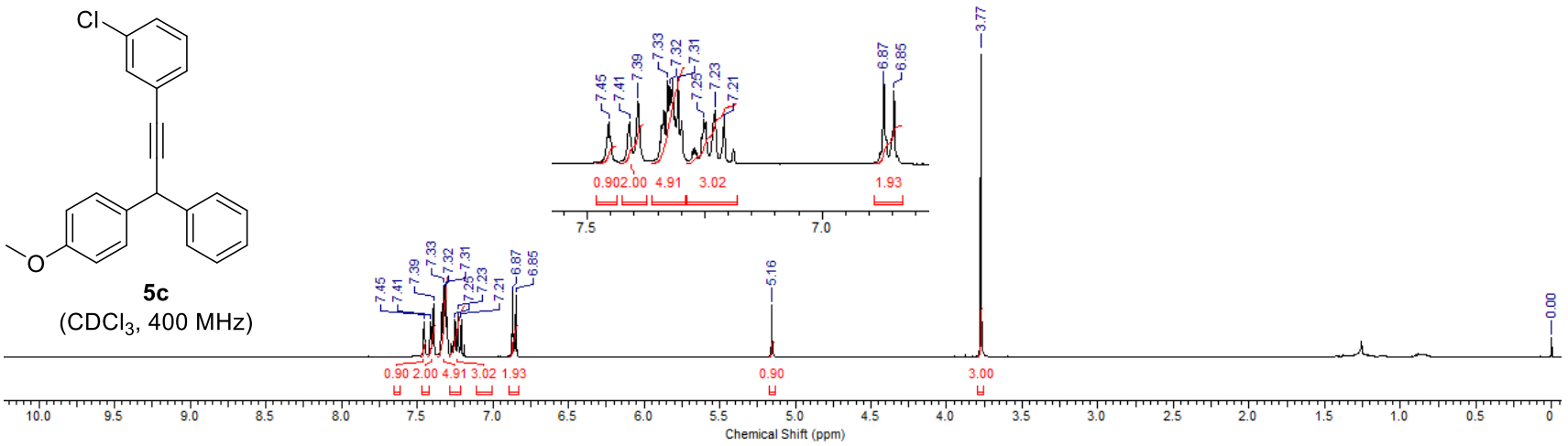

4j
(acetone-d_6, 100 MHz)
Chemical Shift (ppm)

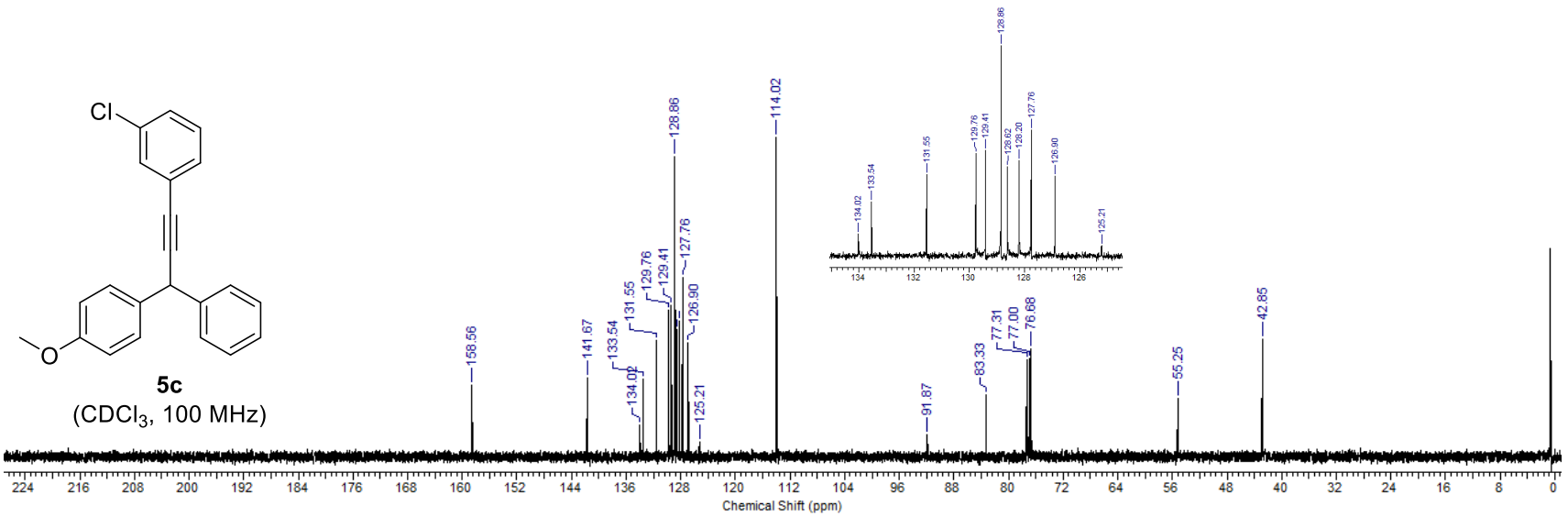

CF3
O
5a
(CDCl3, 400 MHz)
7.65
7.63
7.57
7.43
7.36
7.34
7.32
7.22
6.87
6.84
5.20
3.77
0.00
0.94 0.93 2.91 4.84 1.16 1.89
0.89
3.00
Chemical Shift (ppm)

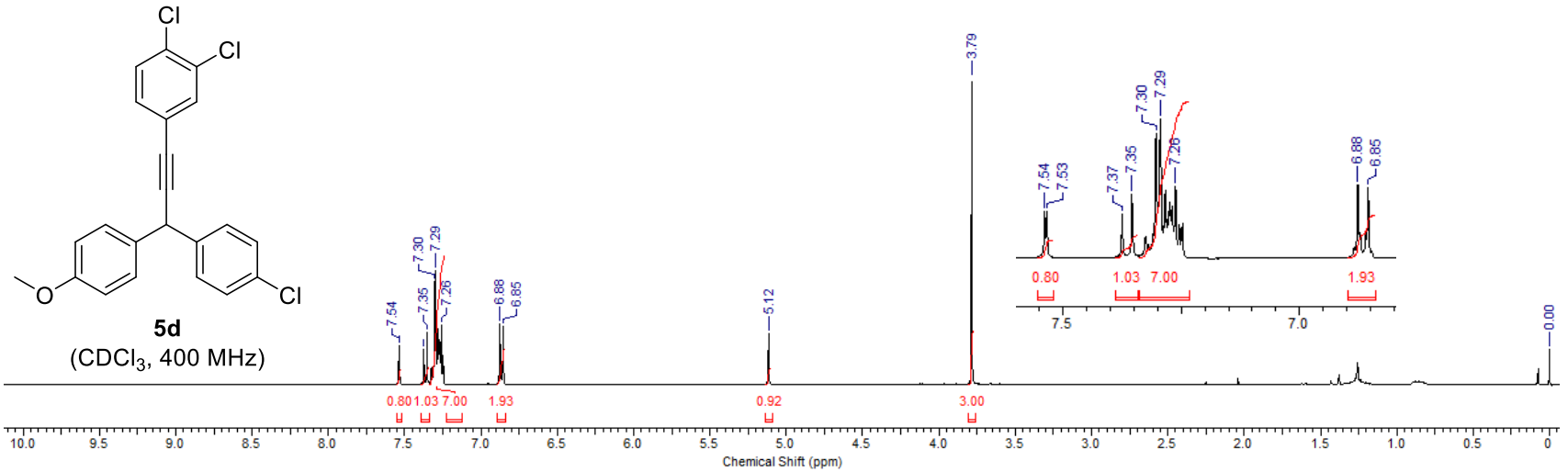

CF3
O
5a
(CDCl3, 100 MHz)
158.54
141.60
134.11
131.27
128.86
128.59
127.77
127.64
126.86
125.73
125.68
125.00
122.28
113.99
96.39
80.70
77.31
77.00
76.68
55.23
43.16
Chemical Shift (ppm)

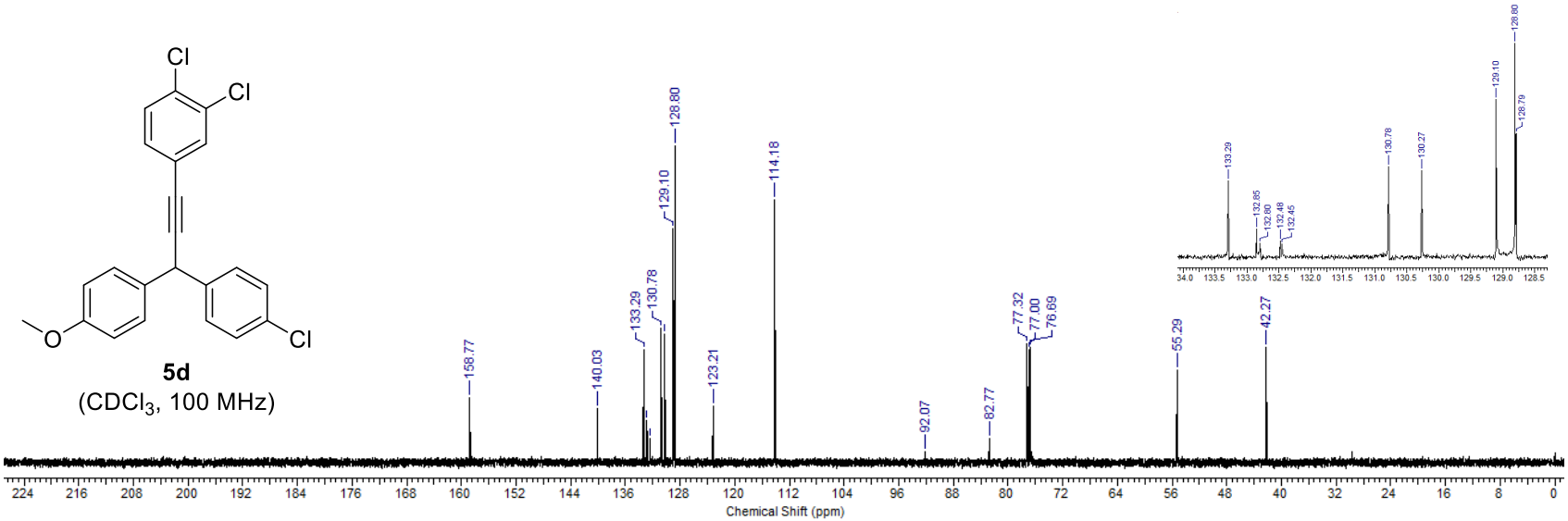

F3C
CF3
O
5b
(CDCl3, 400 MHz)
7.88
7.78
7.39
7.33
7.31
7.25
6.89
6.87
5.20
3.79
0.00
1.75
0.87
7.07
1.85
0.87
3.00
Chemical Shift (ppm)

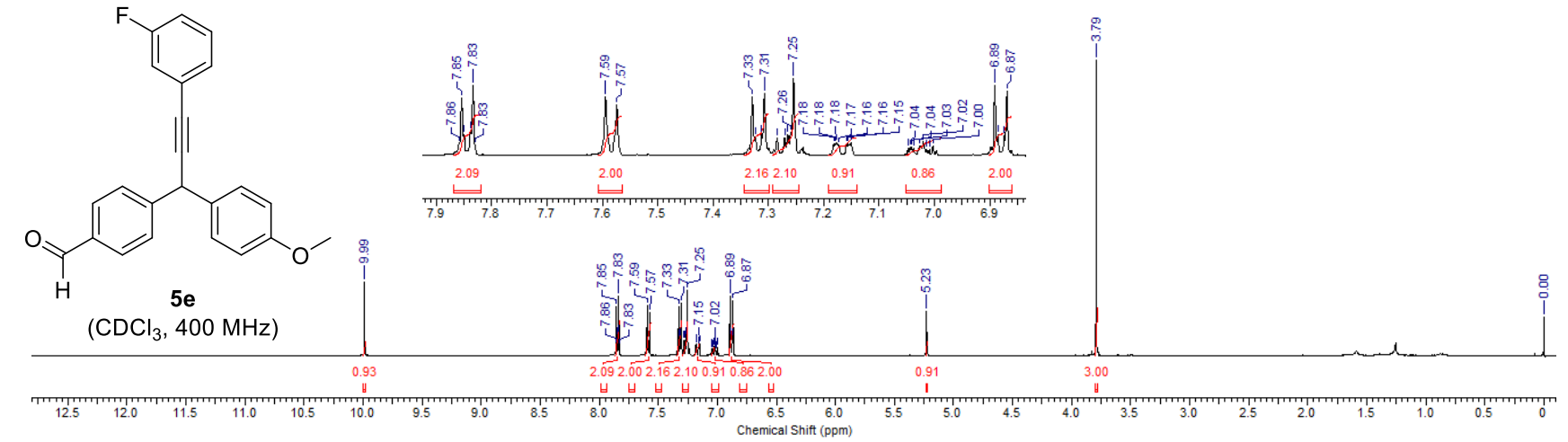

F3C
CF3
O
5b
(CDCl3, 100 MHz)
132.89
132.32
131.99
131.65
131.62
131.58
131.32
128.77
128.88
127.75
127.16
114.18
77.32
77.00
76.69
158.75
141.05
132.89
131.65
125.79
124.32
121.61
121.36
94.45
81.83
55.29
42.86
Chemical Shift (ppm)

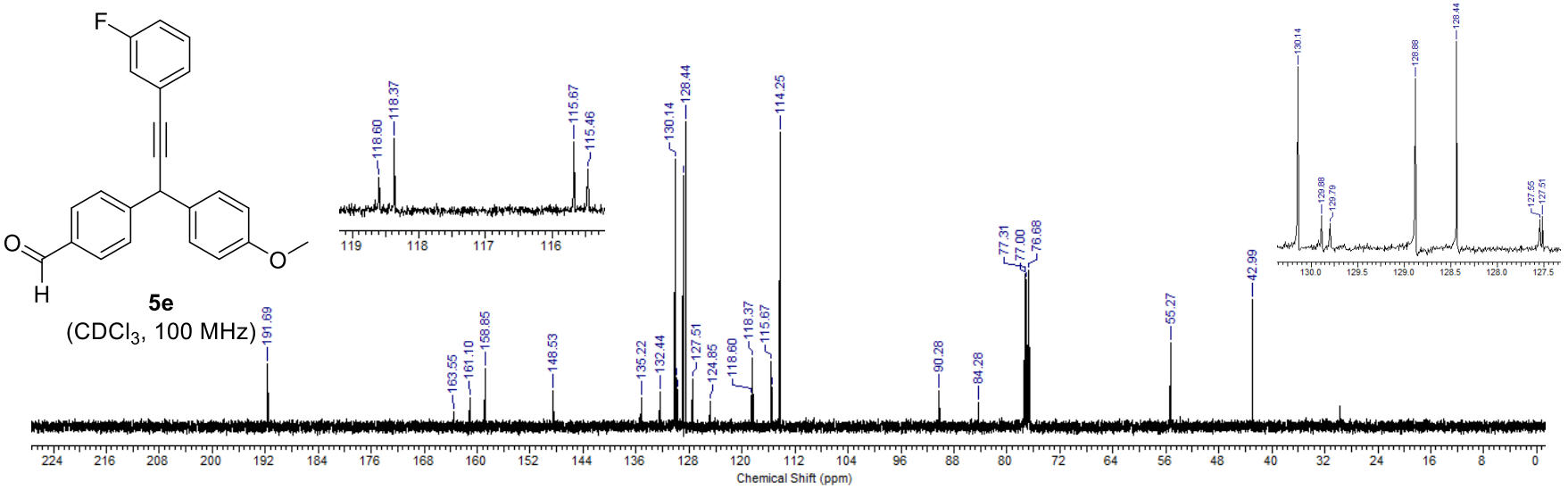

Cl
O
5c
(CDCl3, 400 MHz)
7.45
7.41
7.39
7.33
7.32
7.31
7.25
7.23
7.21
6.87
6.85
5.16
3.77
0.00
0.90 2.00 4.91 3.02 1.93
0.90
3.00
Chemical Shift (ppm)

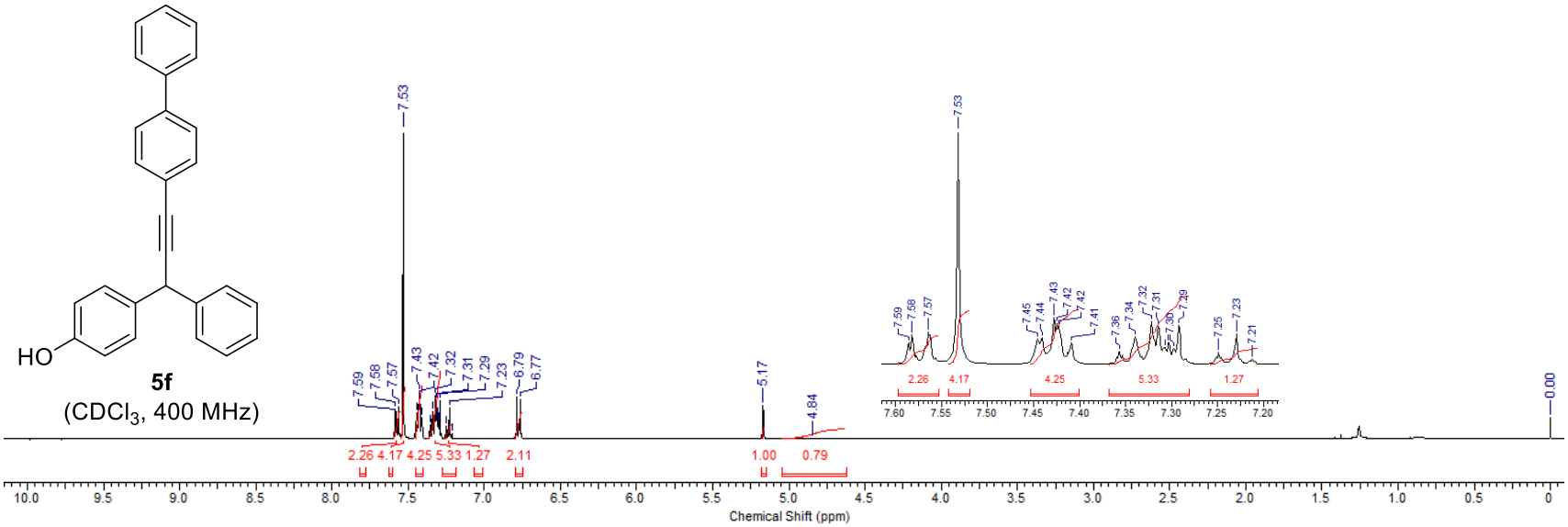

Cl
O
5c
(CDCl3, 100 MHz)
158.56
141.67
133.54
134.02
131.55
129.76
129.41
128.86
127.76
126.90
125.21
114.02
91.87
83.33
77.31
77.00
76.68
55.25
42.85
Chemical Shift (ppm)

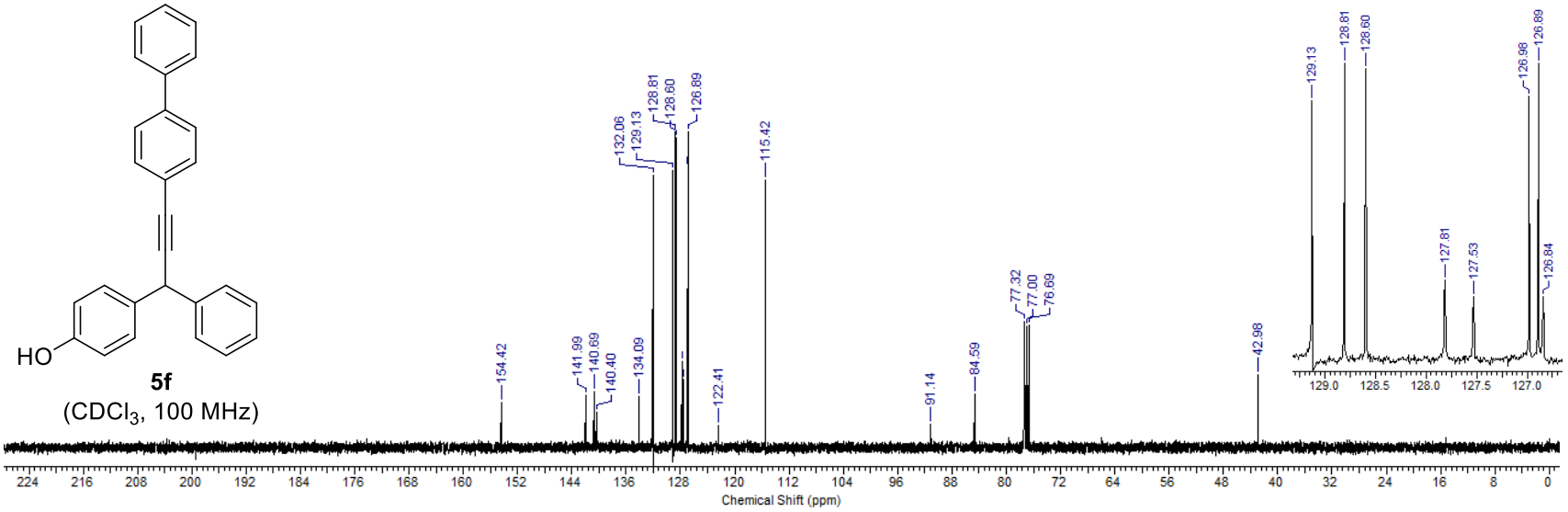

Cl
Cl
O
Cl
5d
(CDCl3, 400 MHz)
7.54
7.53
7.37
7.35
7.30
7.29
7.26
6.88
6.85
5.12
3.79
0.00
0.80
1.03
7.00
1.93
0.92
3.00
Chemical Shift (ppm)

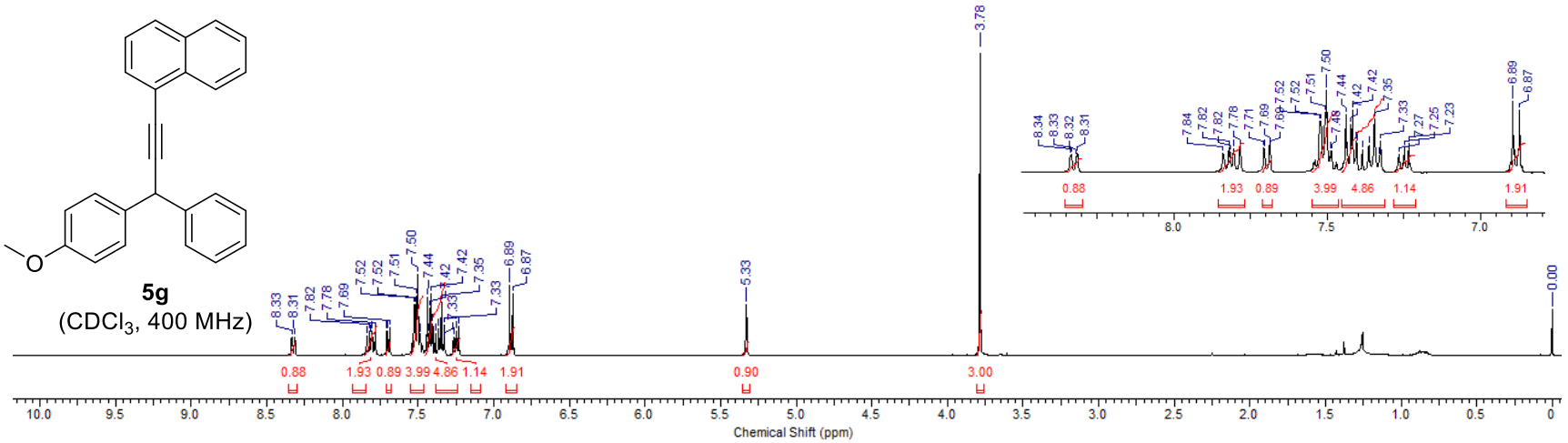

Cl
Cl
O
Cl
5d
(CDCl3, 100 MHz)
158.77
140.03
133.29
130.78
129.10
128.80
123.21
114.18
92.07
82.77
77.32
77.00
76.69
55.29
42.27
Chemical Shift (ppm)

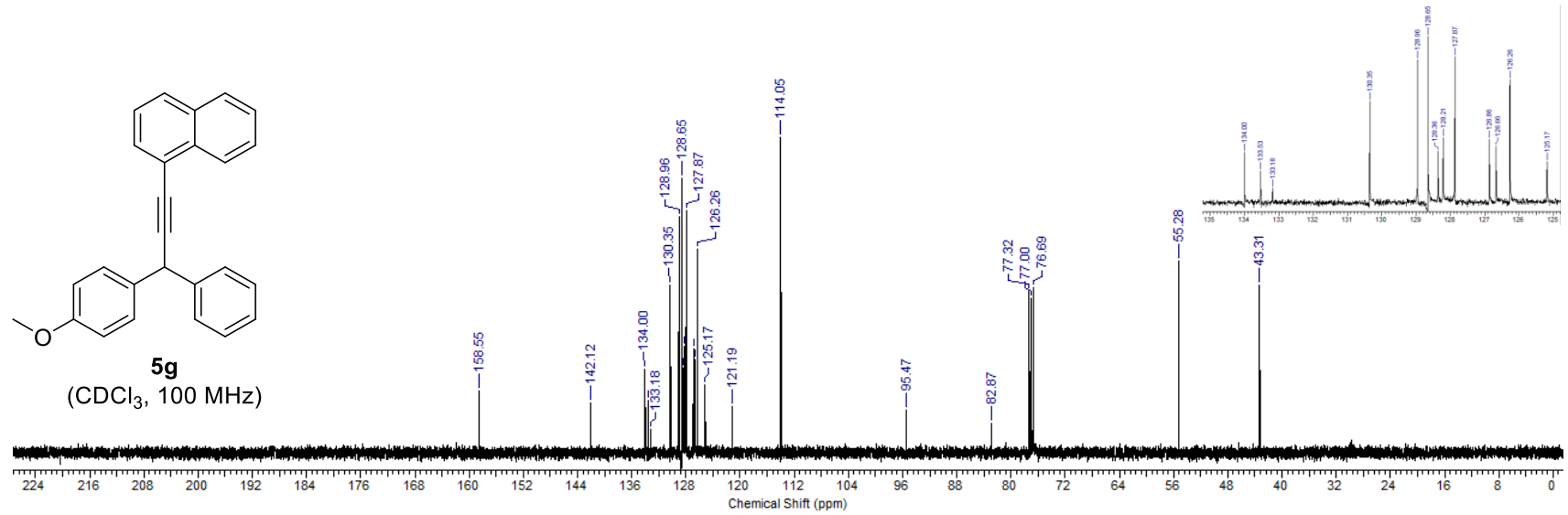

F
O
O
H
5e
(CDCl3, 400 MHz)
Chemical Shift (ppm)

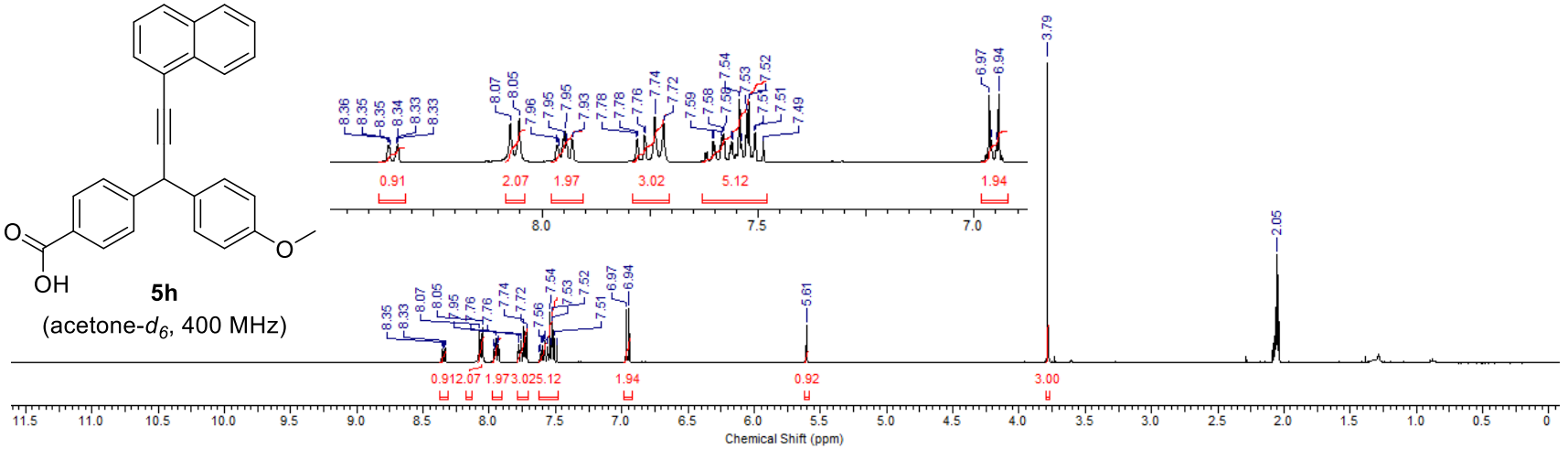

F
O
O
H
5e
(CDCl3, 100 MHz)
Chemical Shift (ppm)

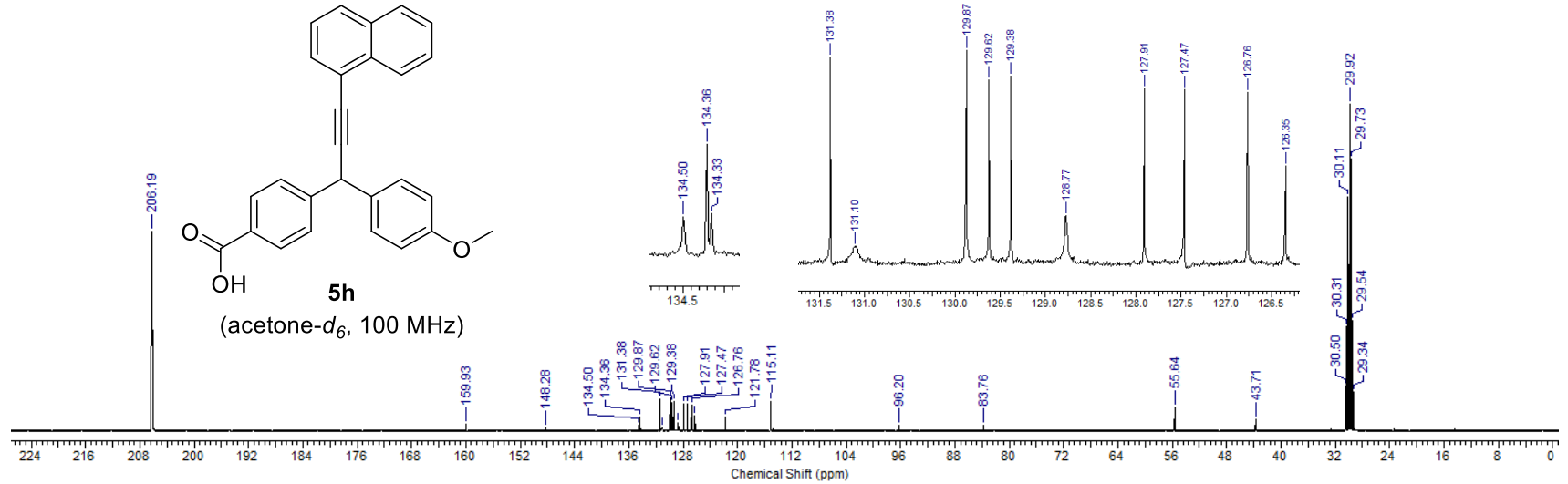

HO
5f
(CDCl3, 400 MHz)
7.59
7.58
7.57
7.53
7.43
7.42
7.32
7.31
7.29
7.23
6.79
6.77
5.17
4.84
0.00
2.26 4.17 4.25 5.33 1.27 2.11
1.00 0.79
Chemical Shift (ppm)

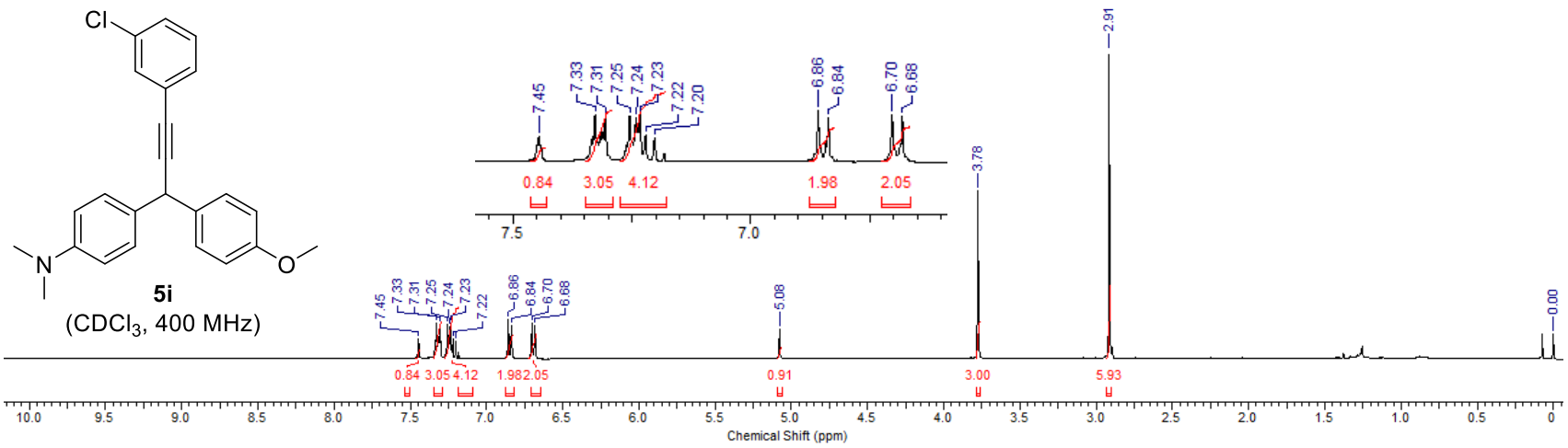

HO
5f
(CDCl3, 100 MHz)
154.42
141.99
140.69
140.40
134.09
132.06
129.13
128.81
128.60
126.89
122.41
115.42
91.14
84.59
77.32
77.00
76.69
42.98
127.81
127.53
126.84
Chemical Shift (ppm)

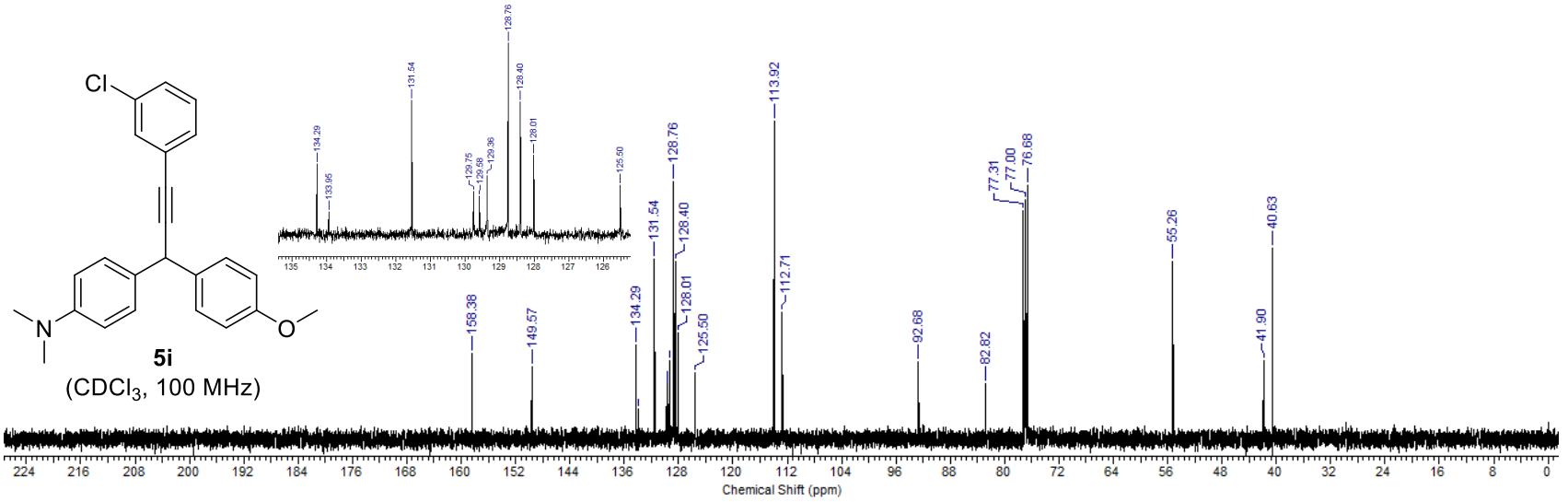

5g
(CDCl3, 400 MHz)
Chemical Shift (ppm)

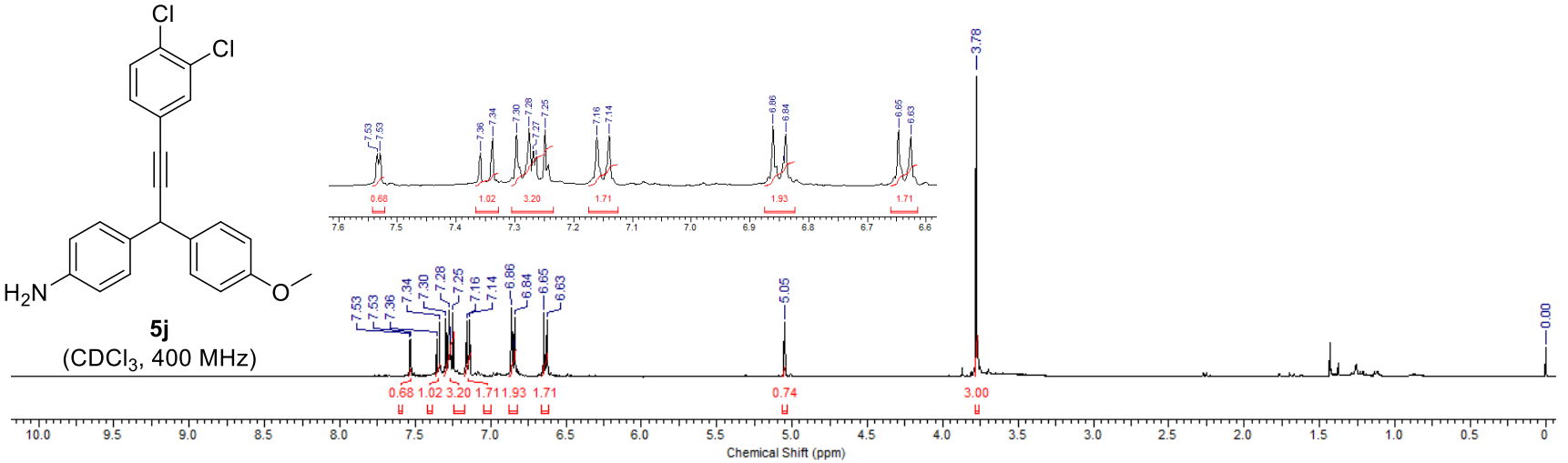

5g
(CDCl3, 100 MHz)
Chemical Shift (ppm)

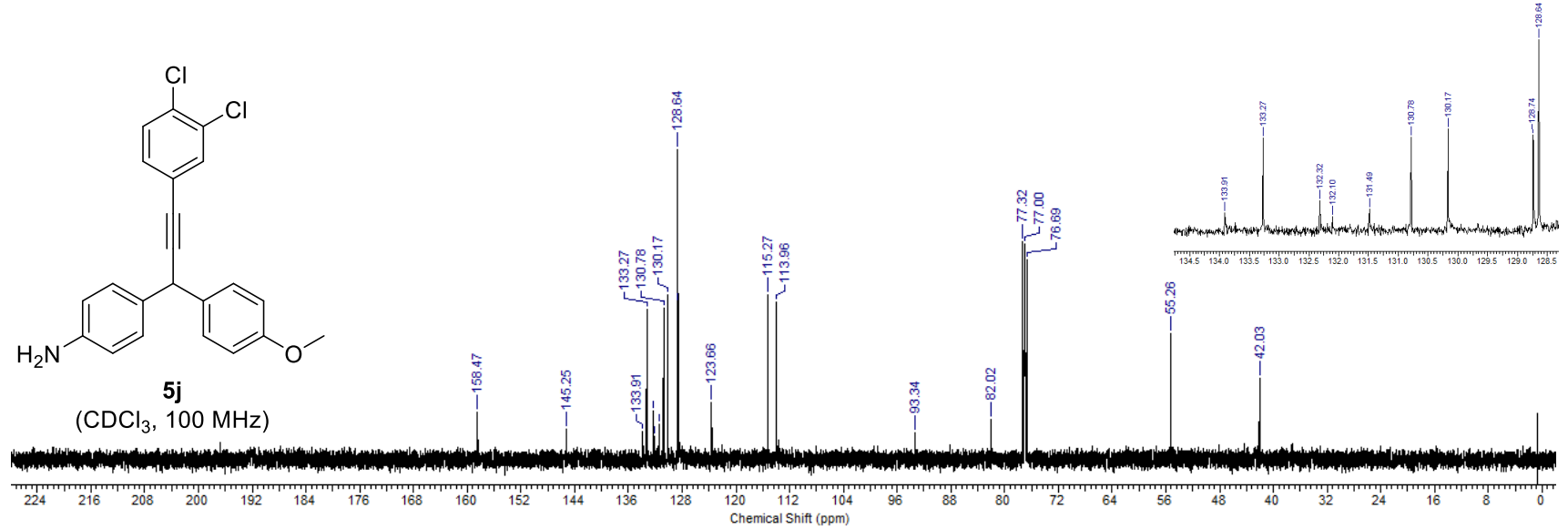

5h
(acetone-d_6, 400 MHz)
Chemical Shift (ppm)

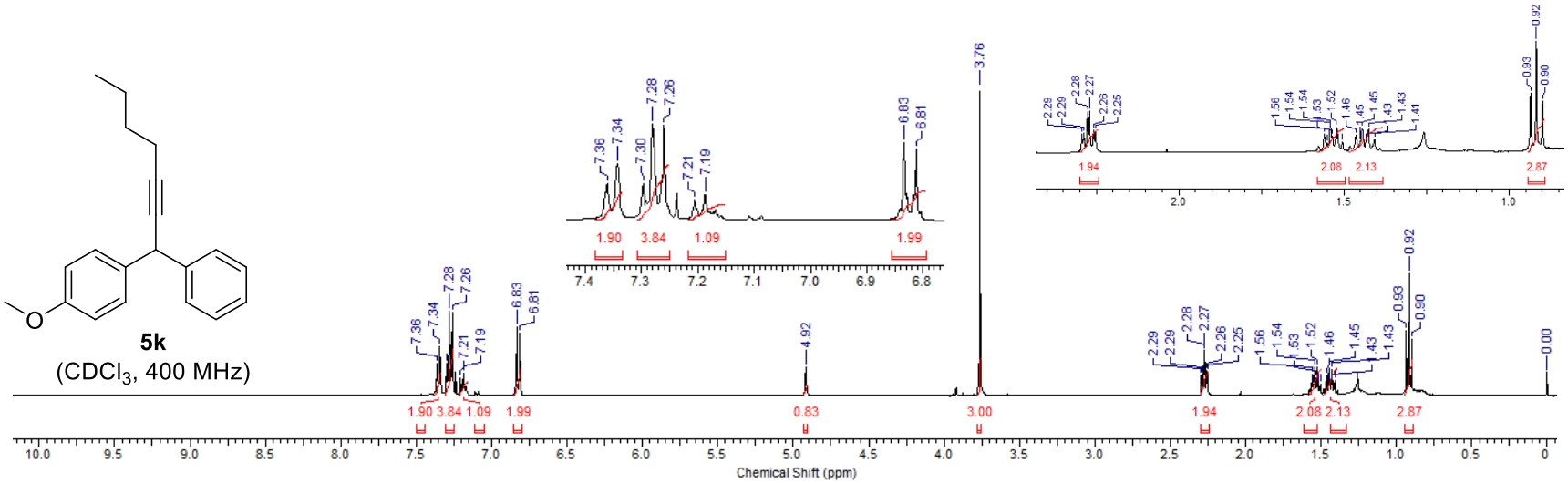

5h
(acetone-d_6, 100 MHz)
Chemical Shift (ppm)

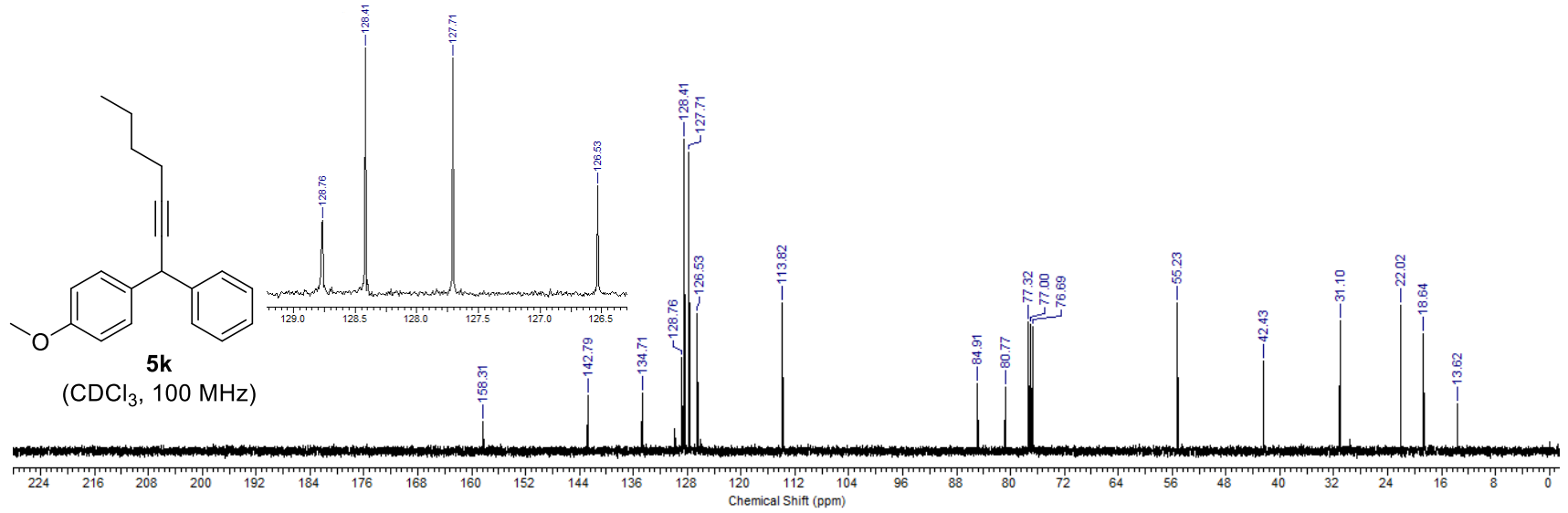

Cl
N
O
5i
(CDCl3, 400 MHz)
Chemical Shift (ppm)

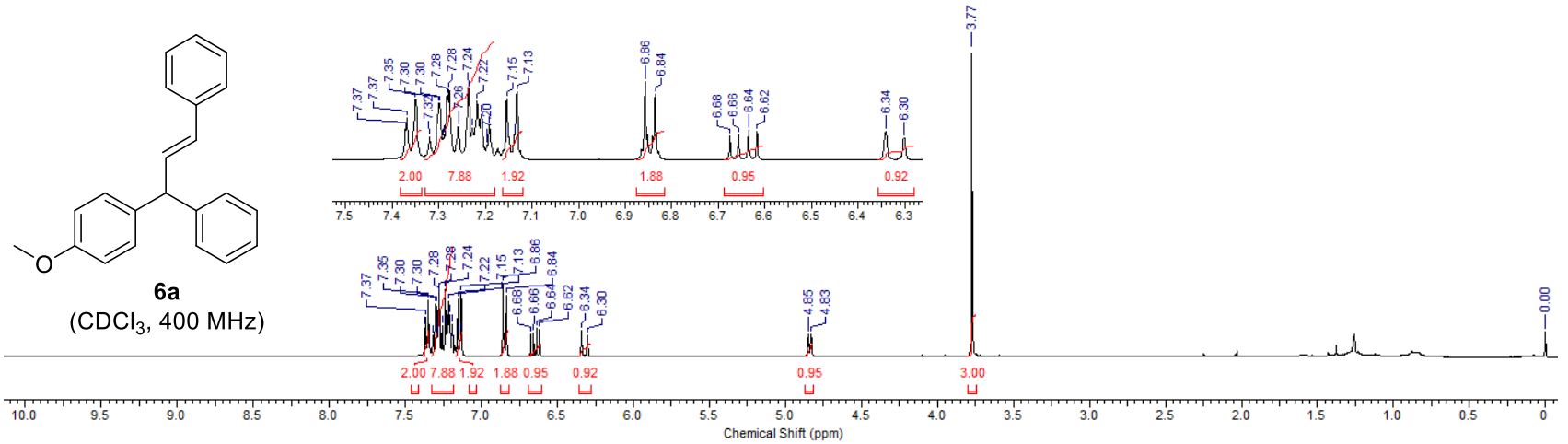

Cl
N
O
5i
(CDCl3, 100 MHz)
Chemical Shift (ppm)

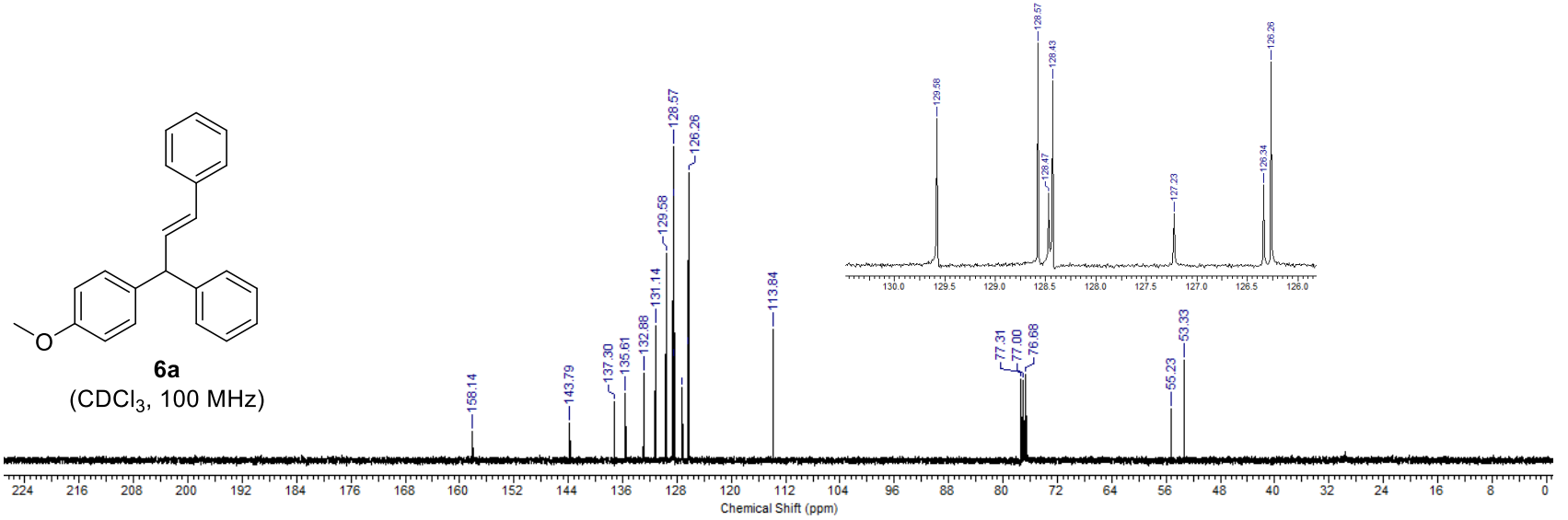

Cl
Cl
H2N
O
5j
(CDCl3, 400 MHz)
Chemical Shift (ppm)

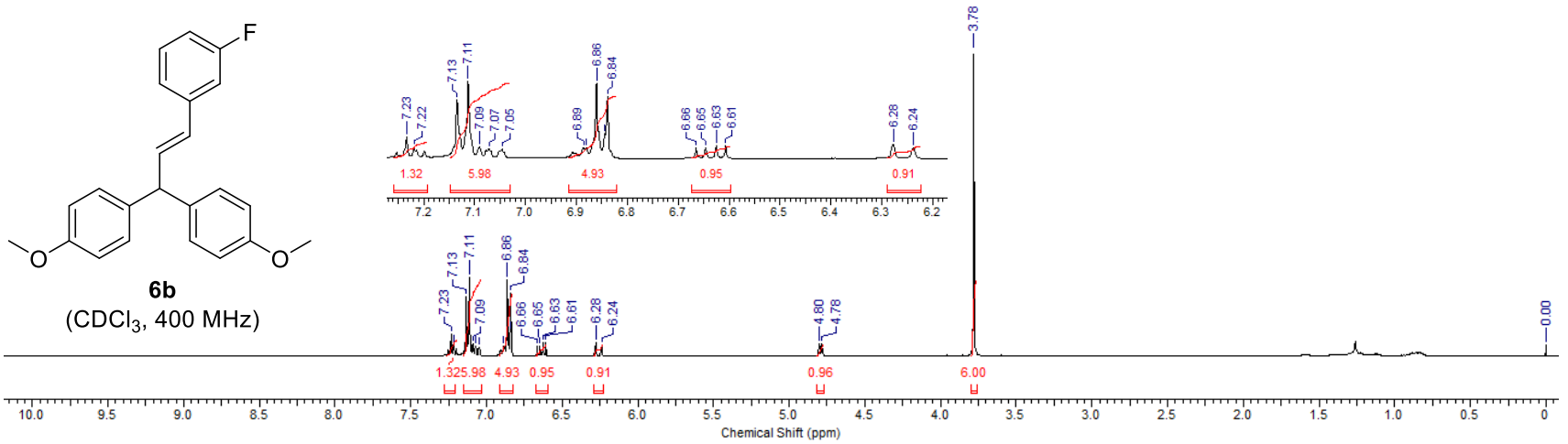

Cl
Cl
H2N
O
5j
(CDCl3, 100 MHz)
Chemical Shift (ppm)

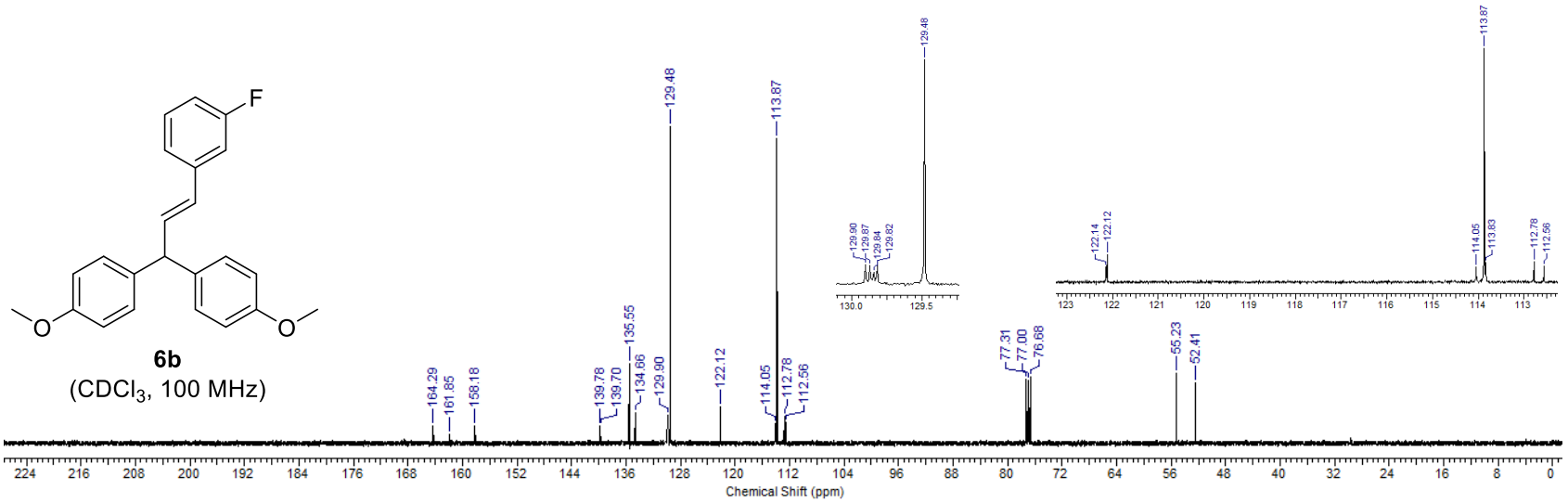

5k
(CDCl3, 400 MHz)
Chemical Shift (ppm)

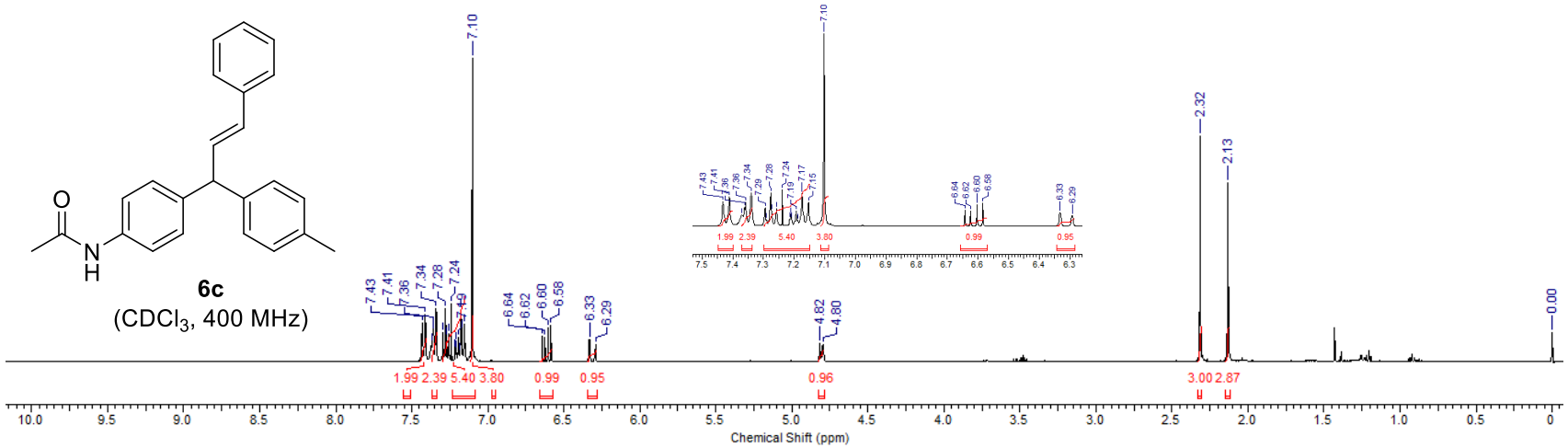

5k
(CDCl3, 100 MHz)
Chemical Shift (ppm)

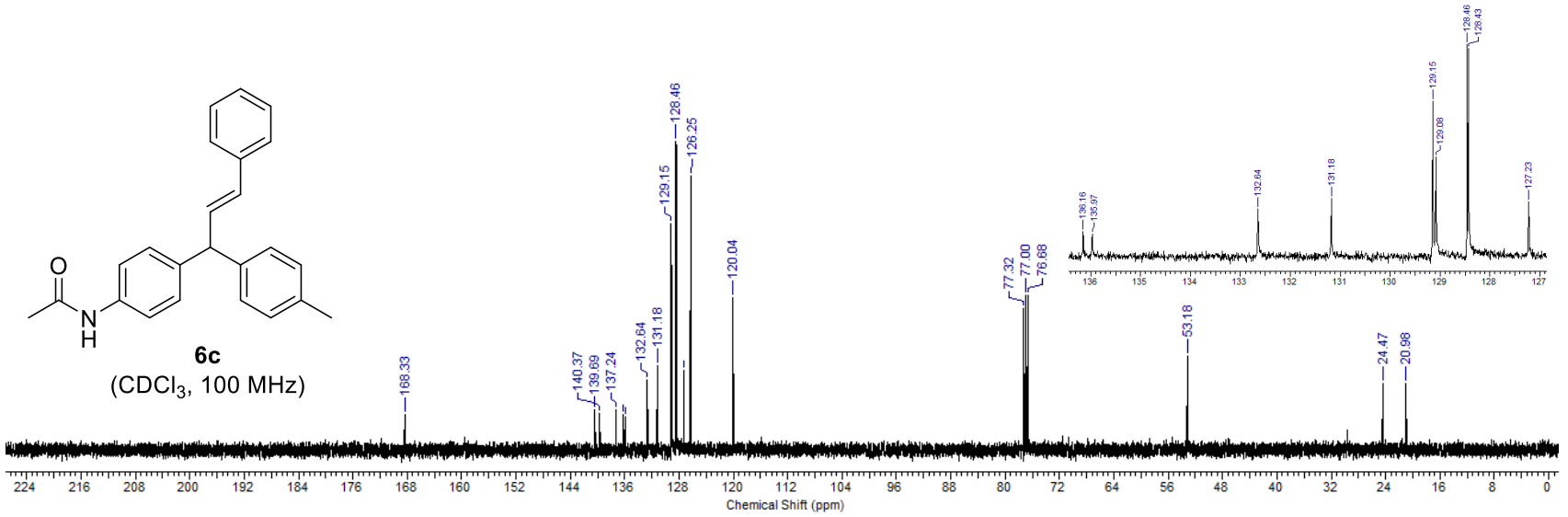

6a
(CDCl3, 400 MHz)
Chemical Shift (ppm)

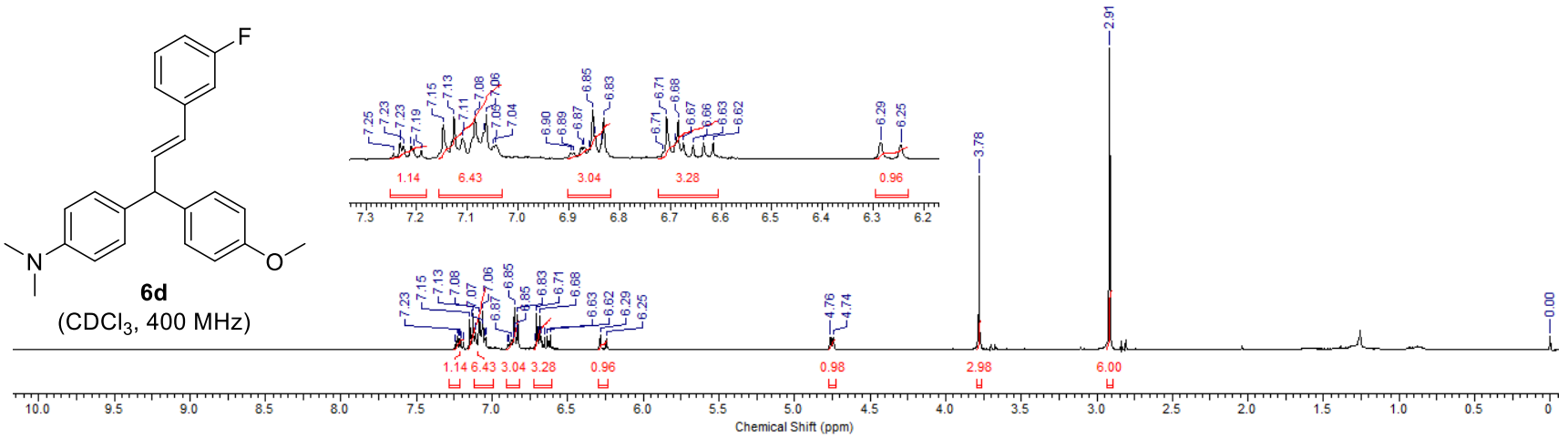

6a
(CDCl3, 100 MHz)
Chemical Shift (ppm)

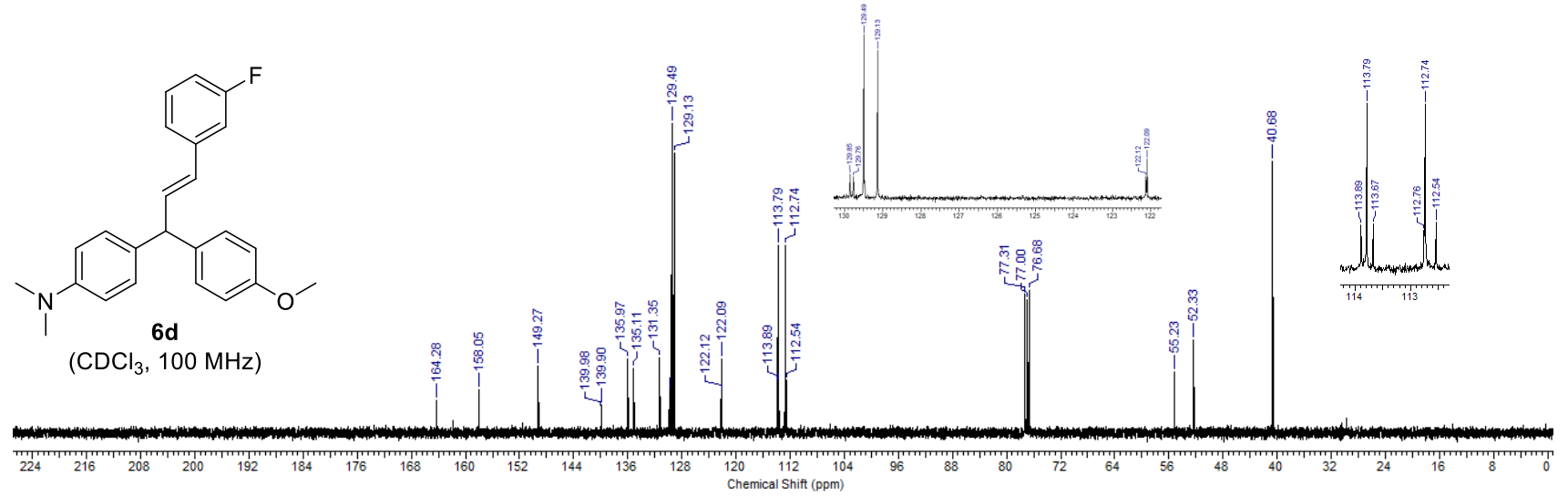

F
O
O
6b
(CDCl3, 400 MHz)
7.23
7.22
7.13
7.11
7.09
7.07
7.05
6.89
6.86
6.84
6.66
6.65
6.63
6.61
6.28
6.24
3.78
4.80
4.78
0.00
1.32
5.98
4.93
0.95
0.91
0.96
6.00
Chemical Shift (ppm)

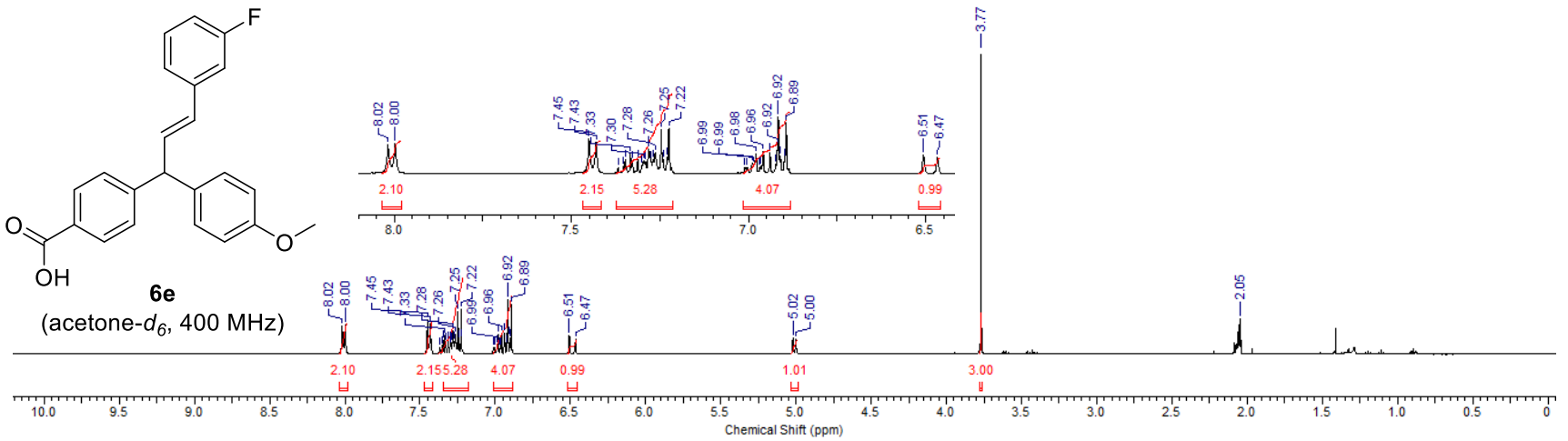

F
O
O
6b
(CDCl3, 100 MHz)
164.29
161.85
158.18
139.78
139.70
135.55
134.66
129.90
129.48
122.12
114.05
113.87
112.78
112.56
77.31
77.00
76.68
55.23
52.41
Chemical Shift (ppm)

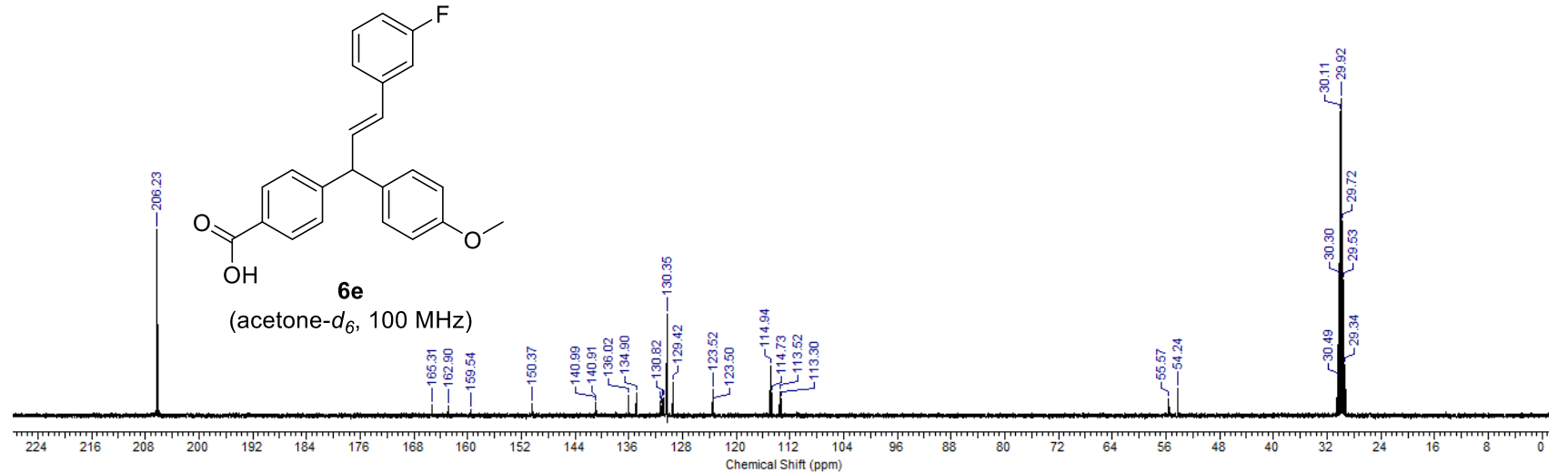

6c
(CDCl3, 400 MHz)
Chemical Shift (ppm)

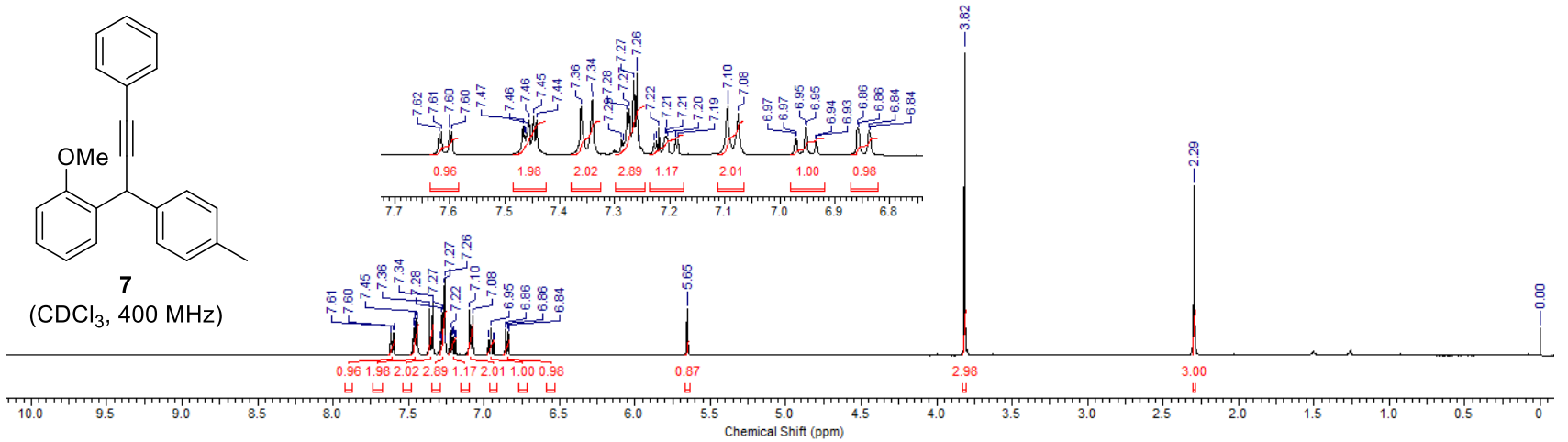

6c
(CDCl3, 100 MHz)
Chemical Shift (ppm)

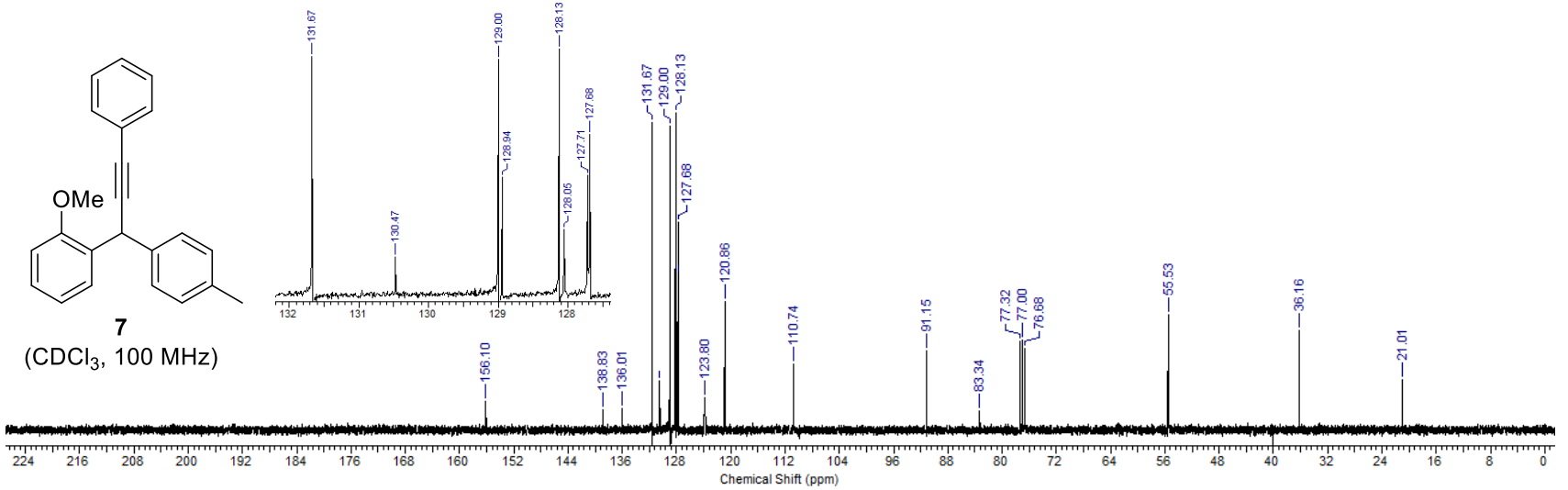

F
N
O
6d
(CDCl3, 400 MHz)
Chemical Shift (ppm)

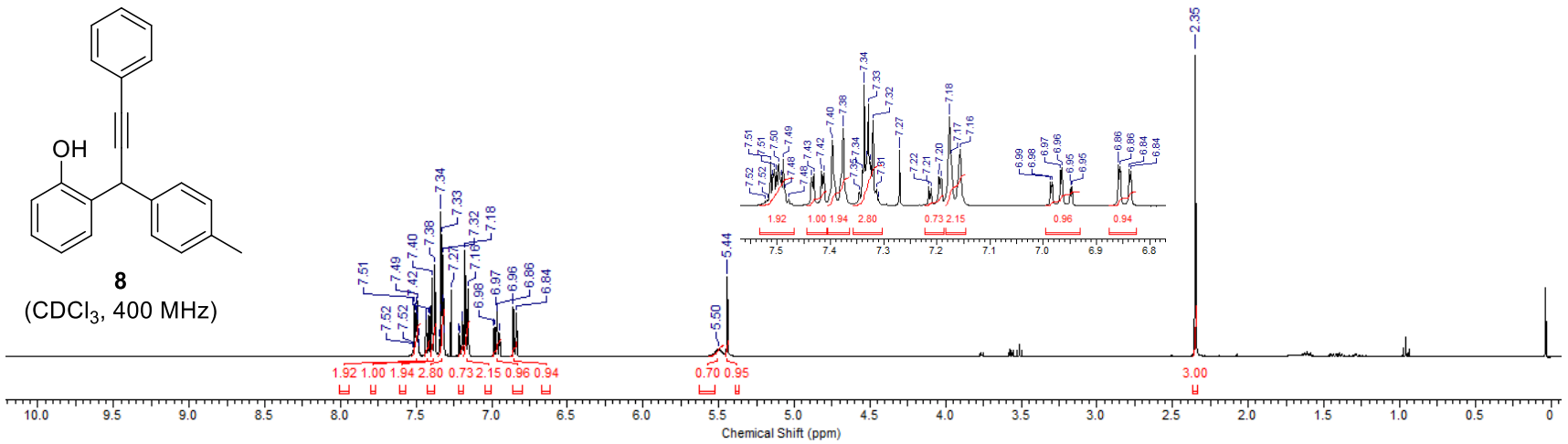

F
N
O
6d
(CDCl3, 100 MHz)
Chemical Shift (ppm)

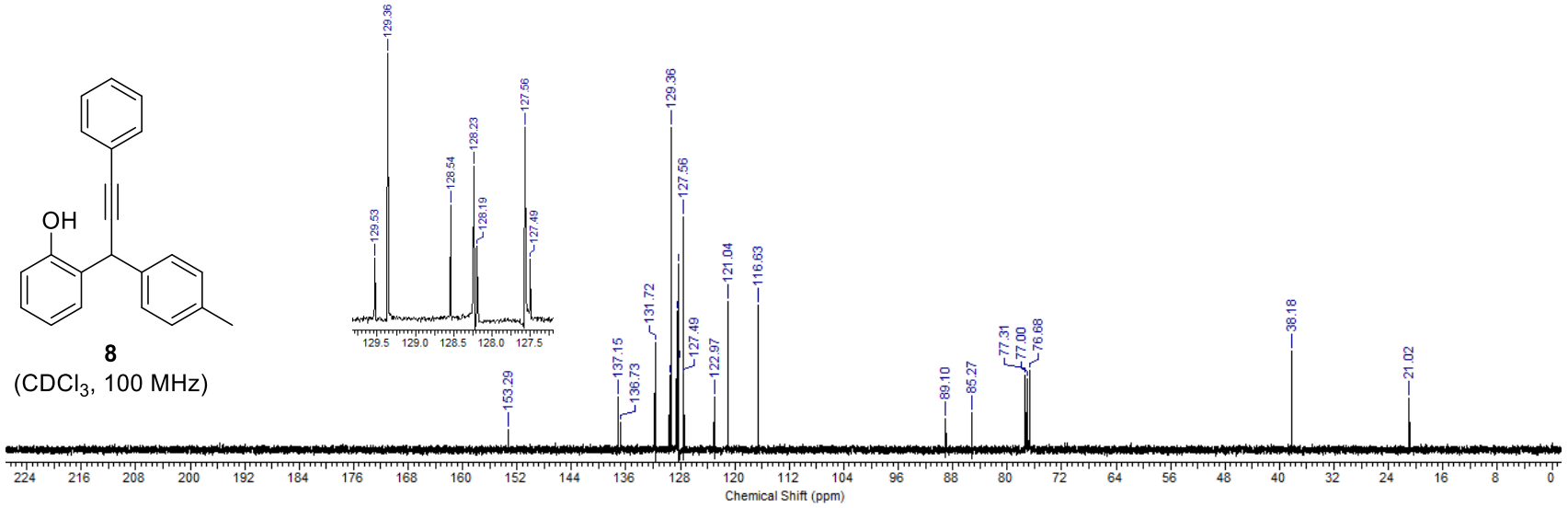

F
O
OH
O
6e
(acetone-d_6, 400 MHz)
Chemical Shift (ppm)


F
O
OH
O
6e
(acetone-d_6, 100 MHz)
Chemical Shift (ppm)

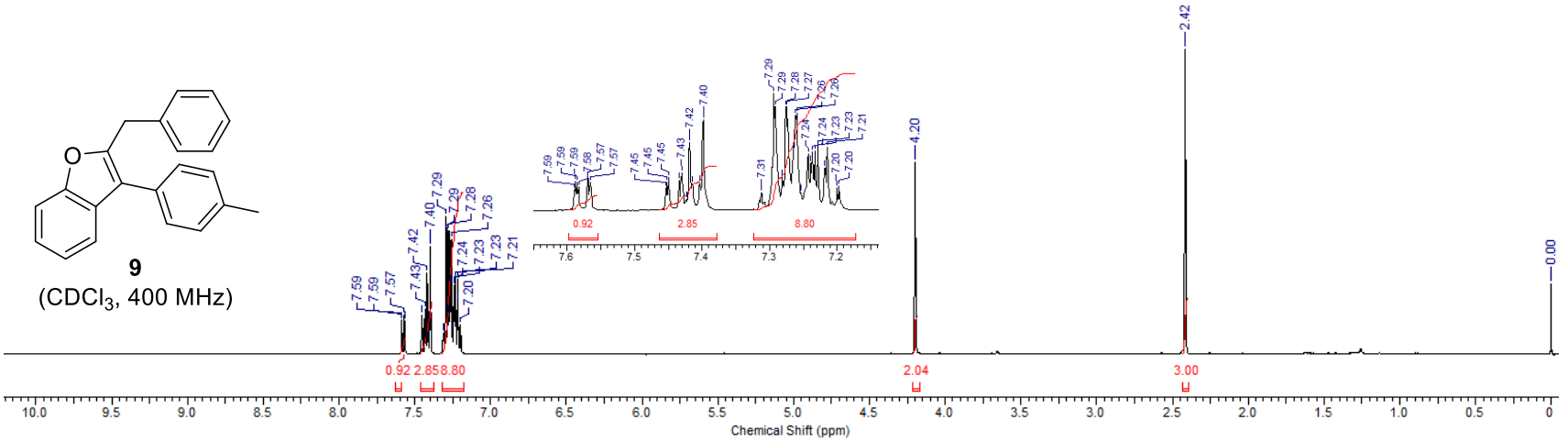

OMe
7
(CDCl3, 400 MHz)
Chemical Shift (ppm)

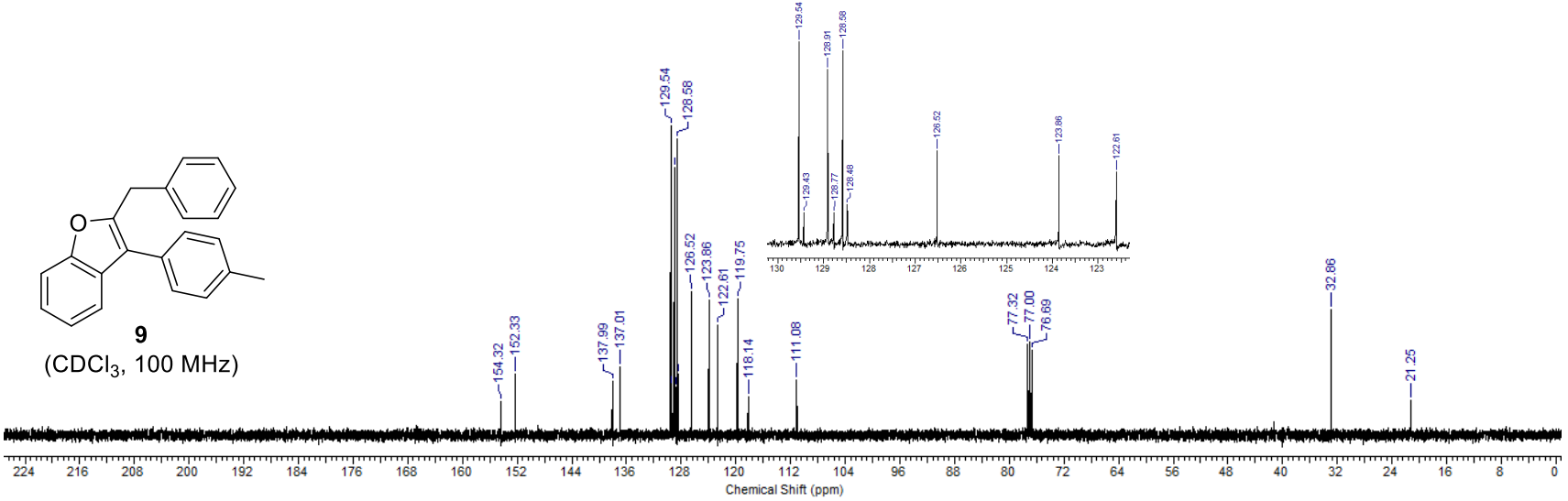

OMe
7
(CDCl3, 100 MHz)
Chemical Shift (ppm)


OH
8
(CDCl3, 400 MHz)
Chemical Shift (ppm)

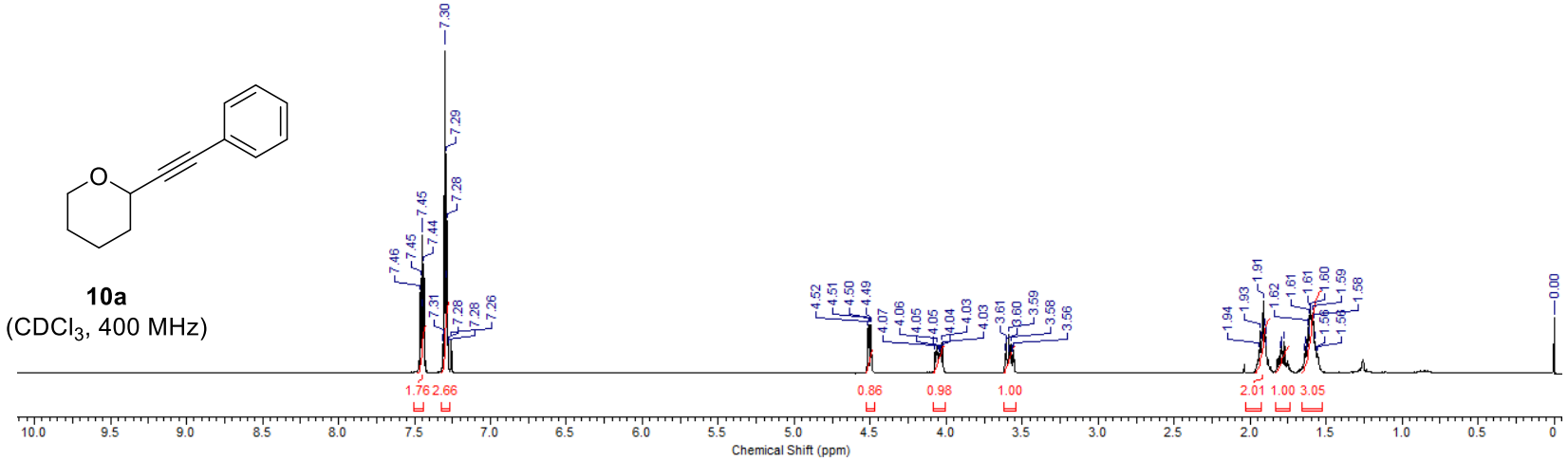

OH
8
(CDCl3, 100 MHz)
Chemical Shift (ppm)

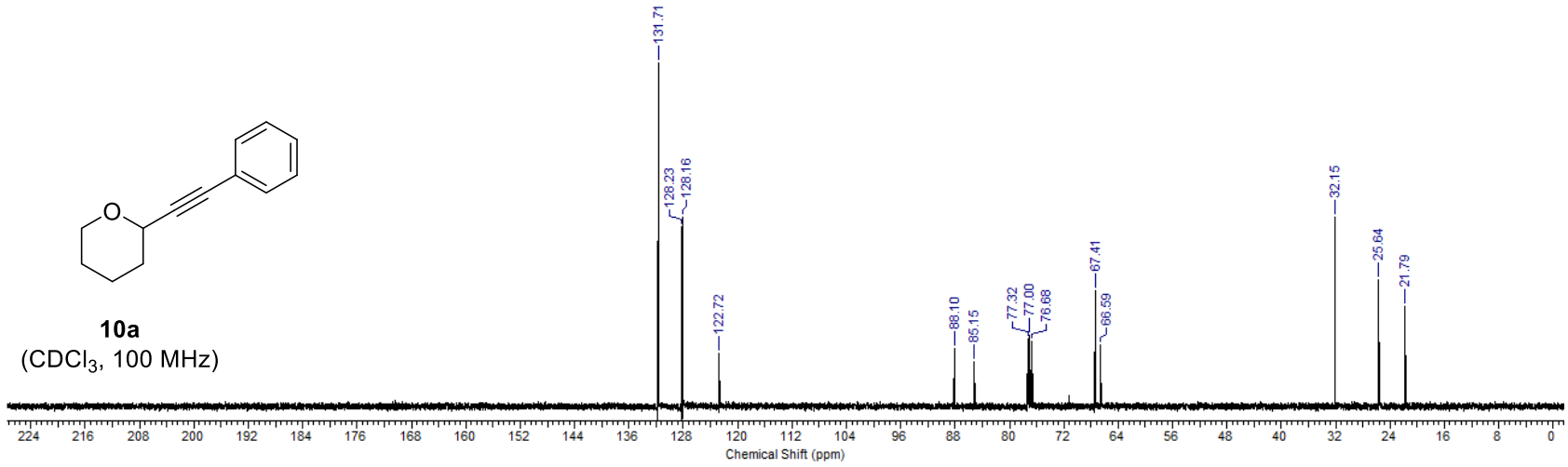
BENZOFURAN

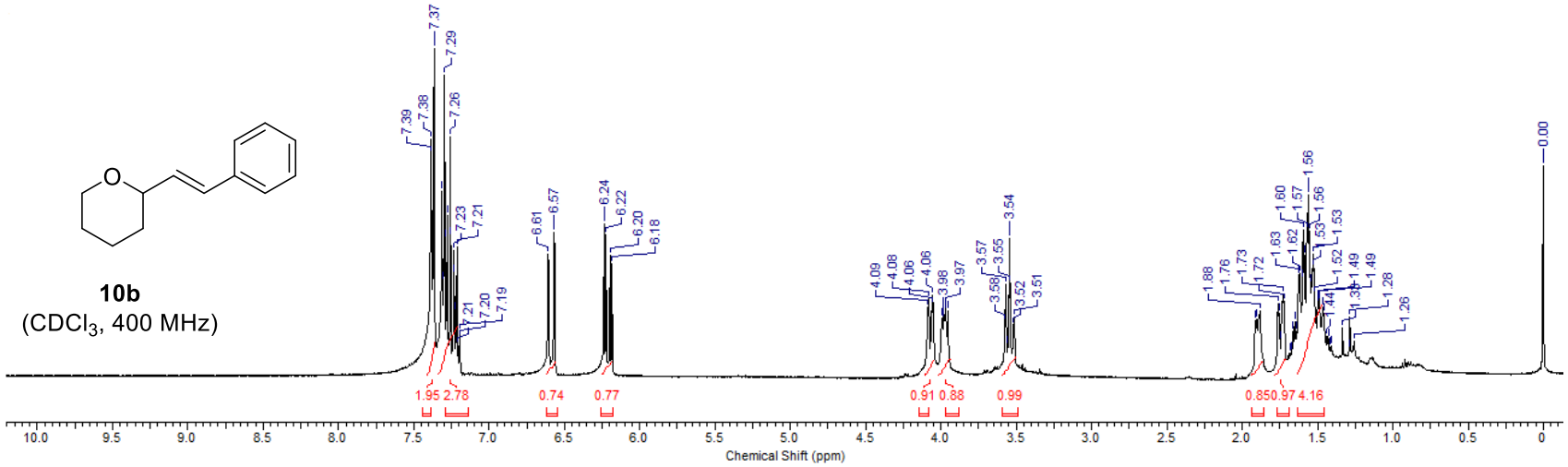

9
(CDCl3, 400 MHz)
Chemical Shift (ppm)

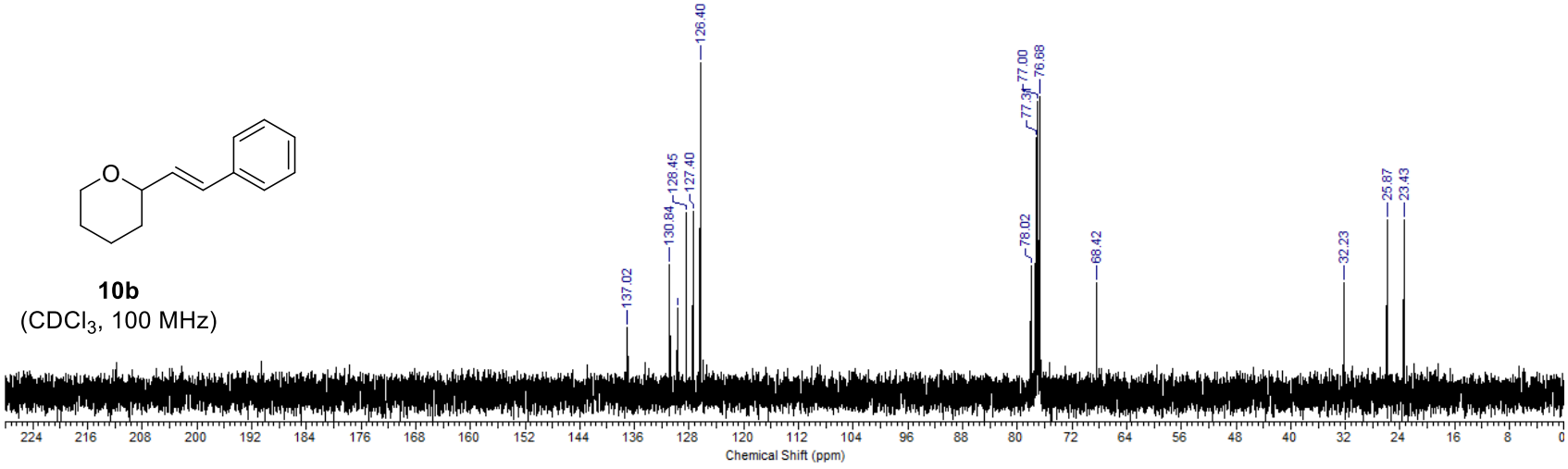

9
(CDCl3, 100 MHz)
Chemical Shift (ppm)

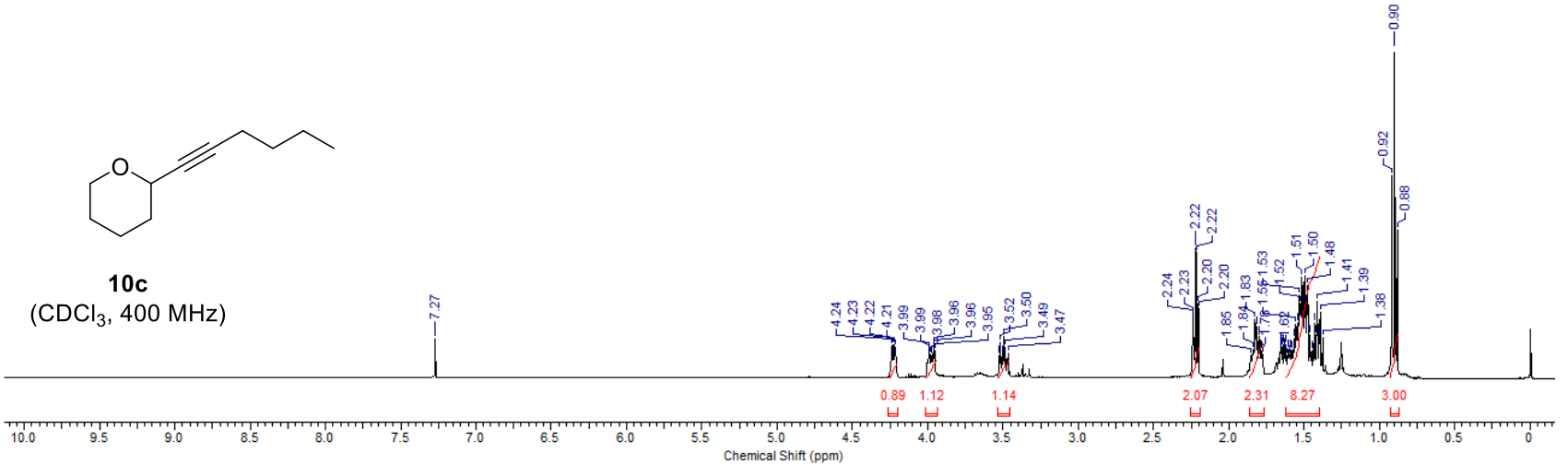
2-ALKENYL AND 2-ALKYNYL TETRAHYDROPYRANS

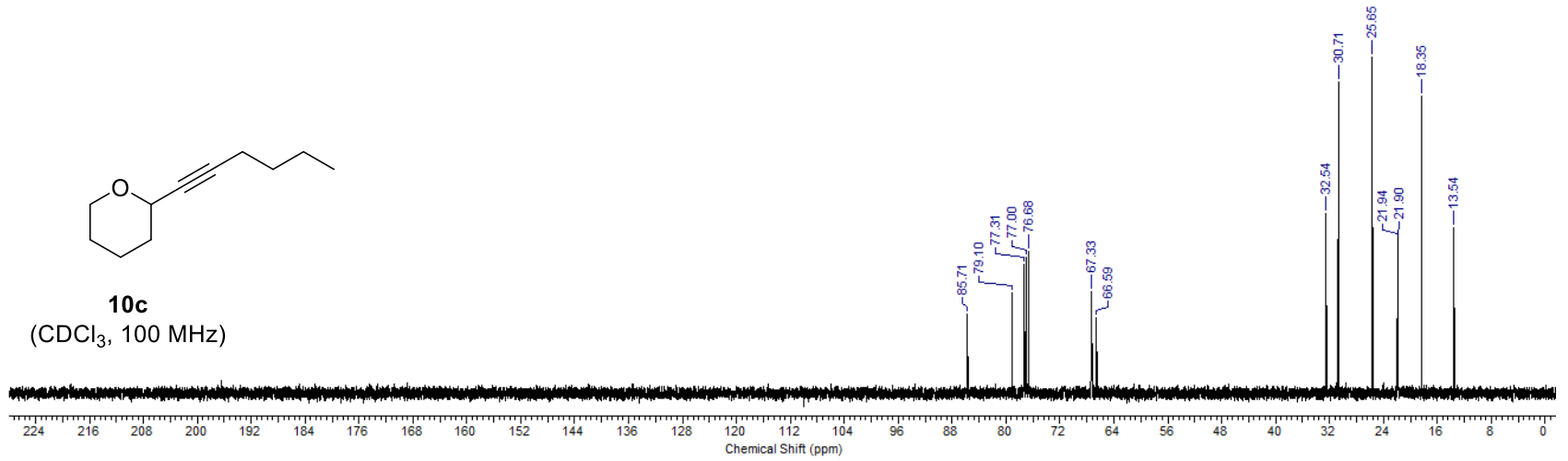


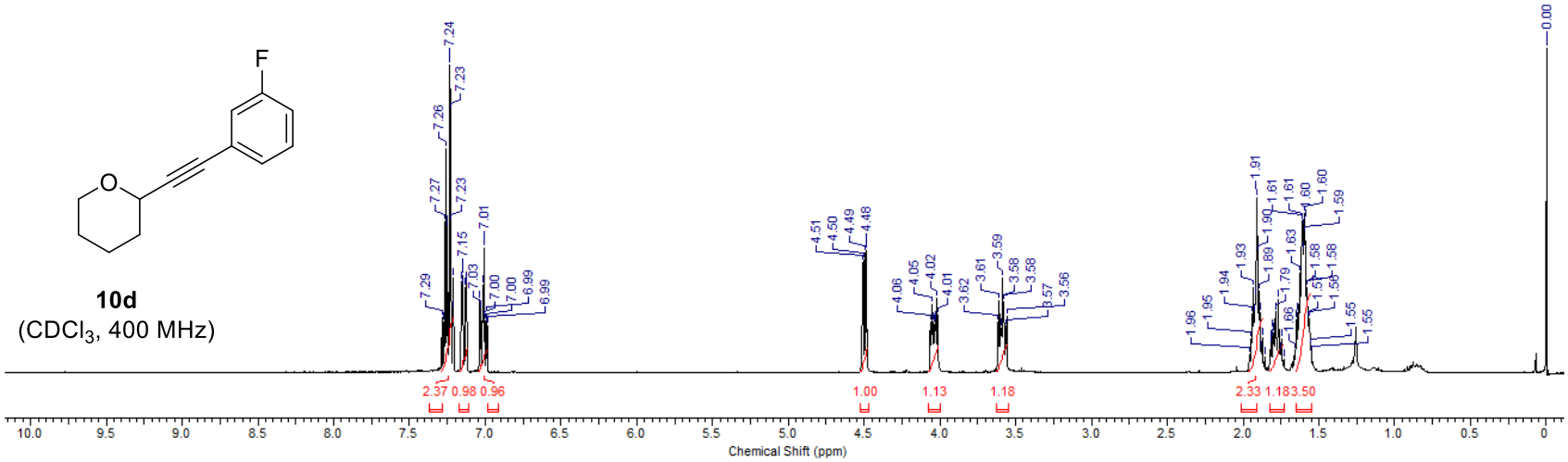


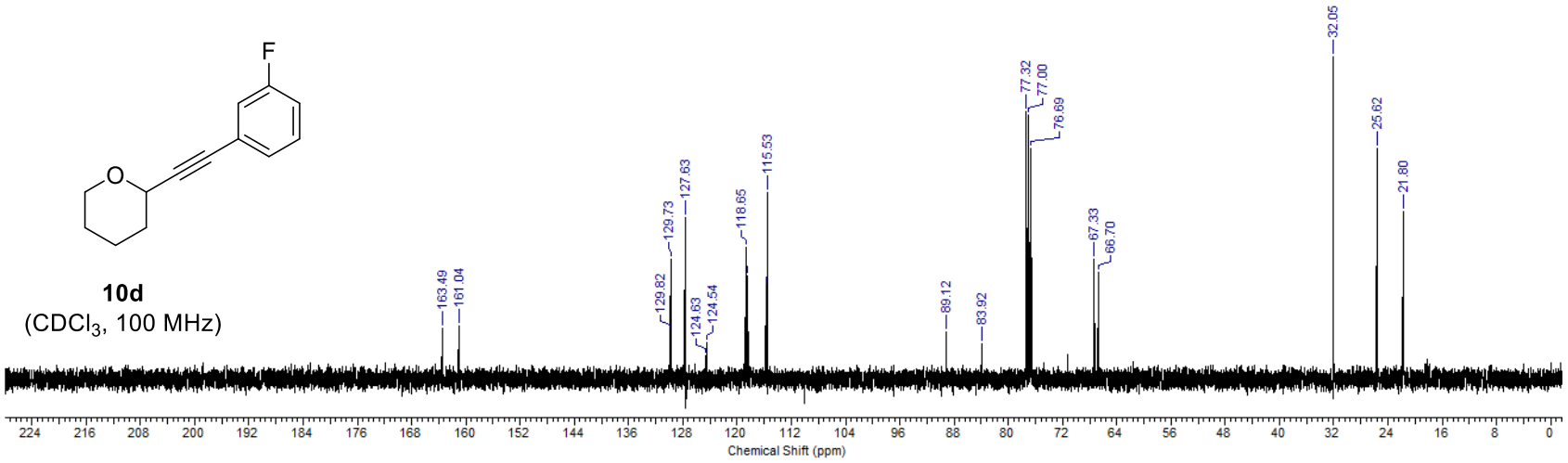

10b
(CDCl3, 400 MHz)
Chemical Shift (ppm)

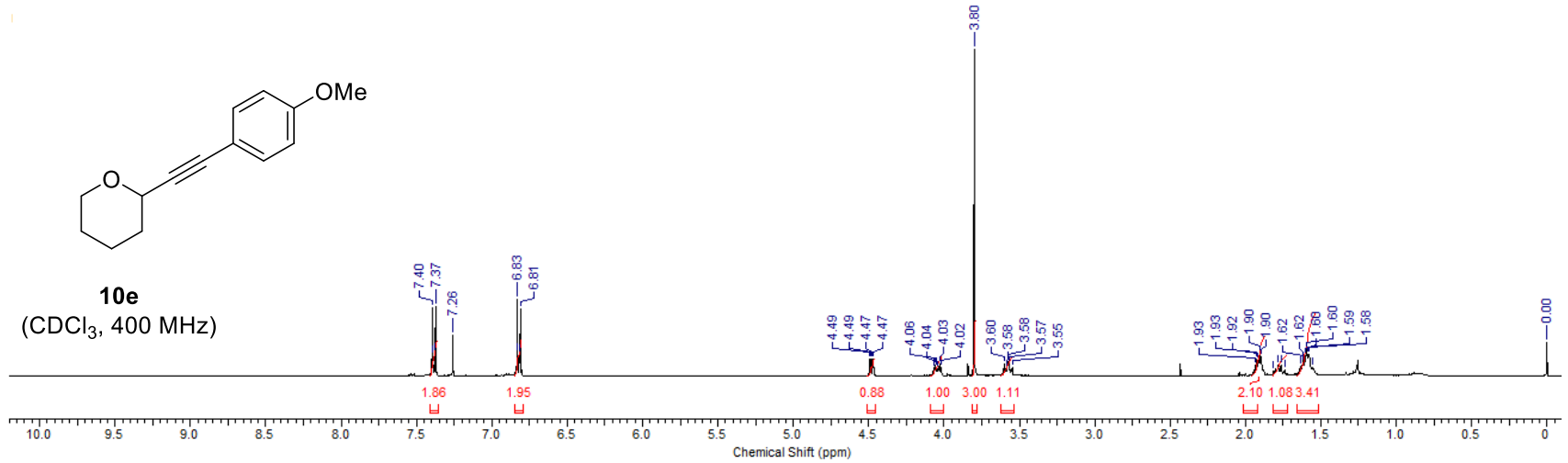

10b
(CDCl3, 100 MHz)
Chemical Shift (ppm)

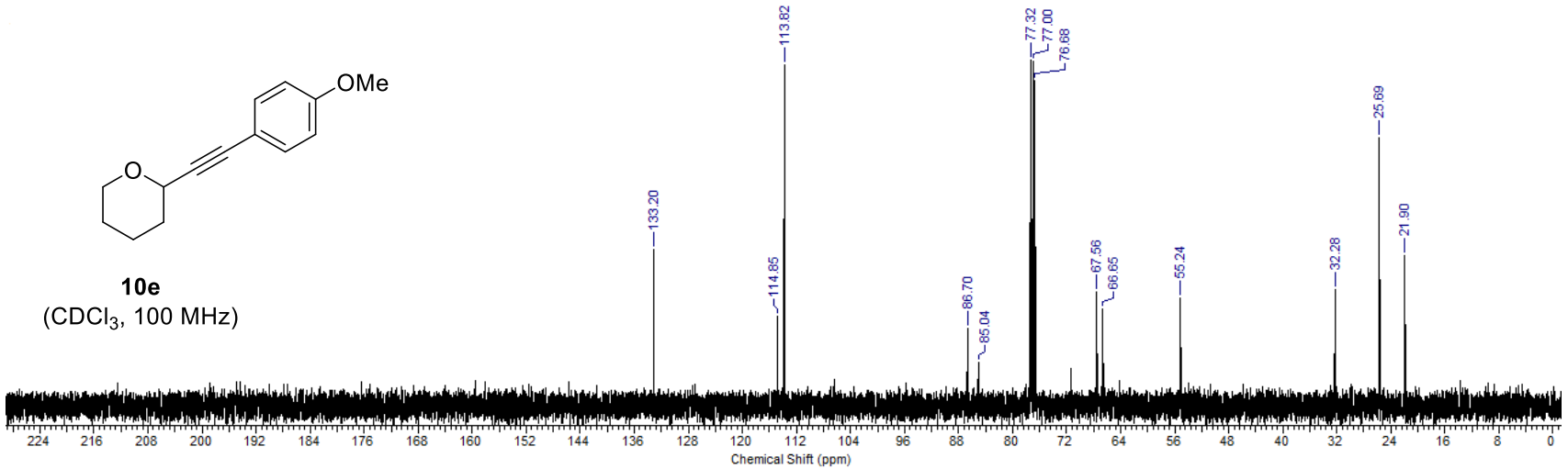

O
10c
(CDCl3, 400 MHz)
7.27
4.24
4.23
4.22
4.21
3.99
3.99
3.98
3.96
3.96
3.95
3.52
3.50
3.49
3.47
2.24
2.23
2.22
2.22
2.20
2.20
1.85
1.84
1.83
1.59
1.53
1.52
1.51
1.50
1.48
1.41
1.39
1.38
0.92
0.90
0.88
0.89
1.12
1.14
2.07
2.31
8.27
3.00
Chemical Shift (ppm)


O
10c
(CDCl3, 100 MHz)
85.71
79.10
77.31
77.00
76.68
67.33
66.59
32.54
30.71
25.65
21.94
21.90
18.35
13.54
Chemical Shift (ppm)

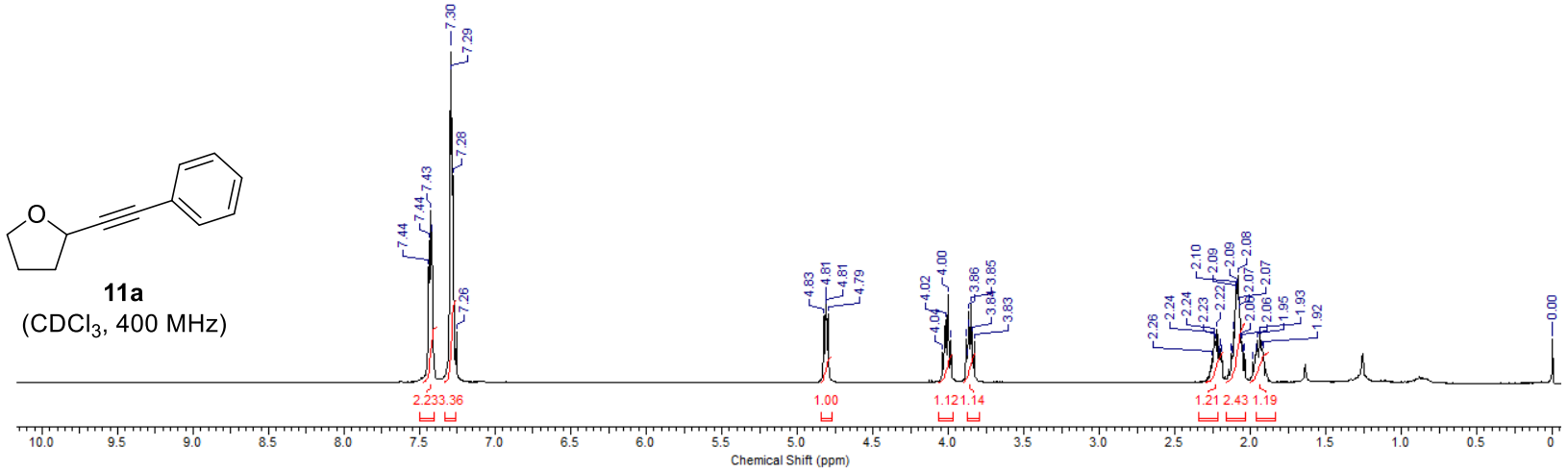

F
O
10d
(CDCl3, 400 MHz)
Chemical Shift (ppm)

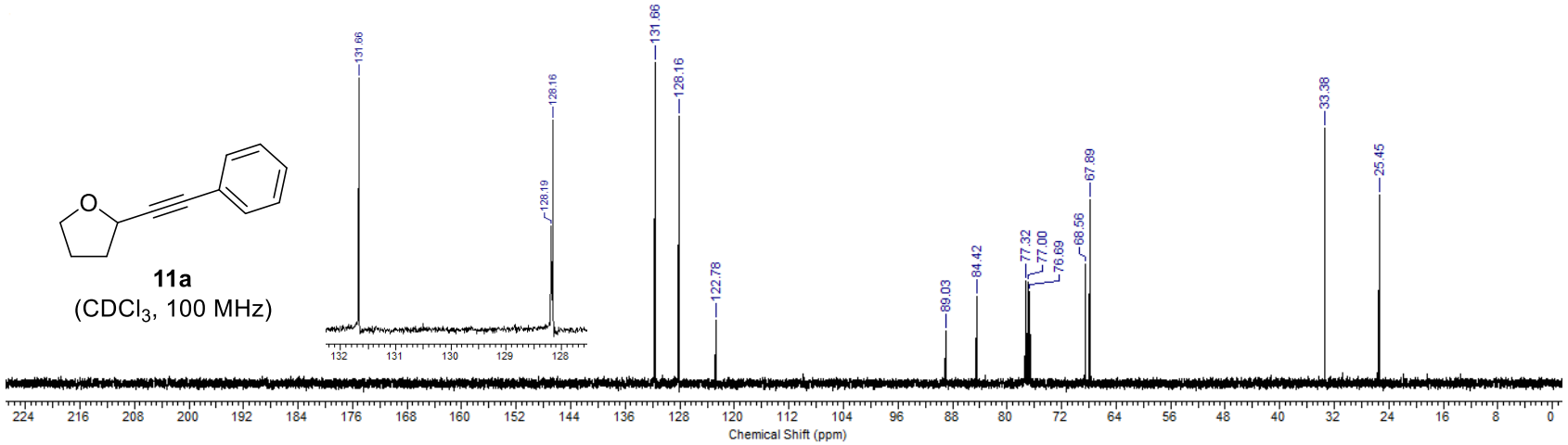

F
O
10d
(CDCl3, 100 MHz)
Chemical Shift (ppm)

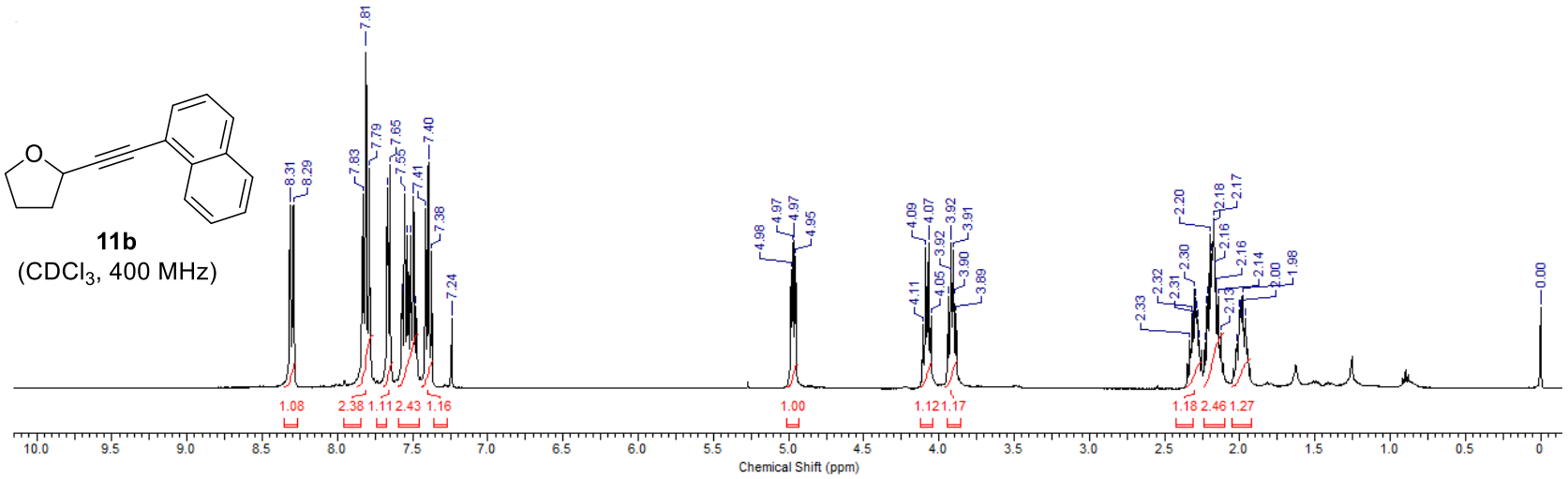

OMe
O
10e
(CDCl3, 400 MHz)
7.40
7.37
7.26
6.83
6.81
4.49
4.49
4.47
4.47
4.06
4.04
4.03
4.02
3.80
3.60
3.58
3.58
3.57
3.55
1.93
1.93
1.92
1.90
1.90
1.62
1.62
1.60
1.60
1.59
1.58
0.00
1.86
1.95
0.88
1.00
3.00
1.11
2.10
1.08
3.41
Chemical Shift (ppm)

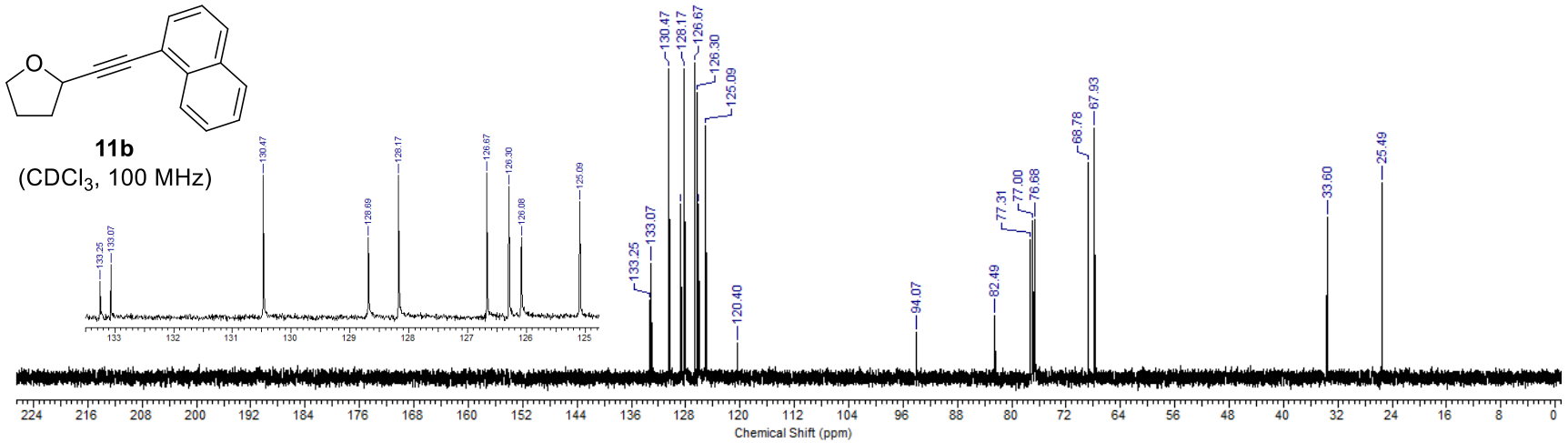

OMe
O
10e
(CDCl3, 100 MHz)
133.20
114.85
113.82
86.70
85.04
77.32
77.00
76.68
67.56
66.65
55.24
32.28
25.69
21.90
Chemical Shift (ppm)

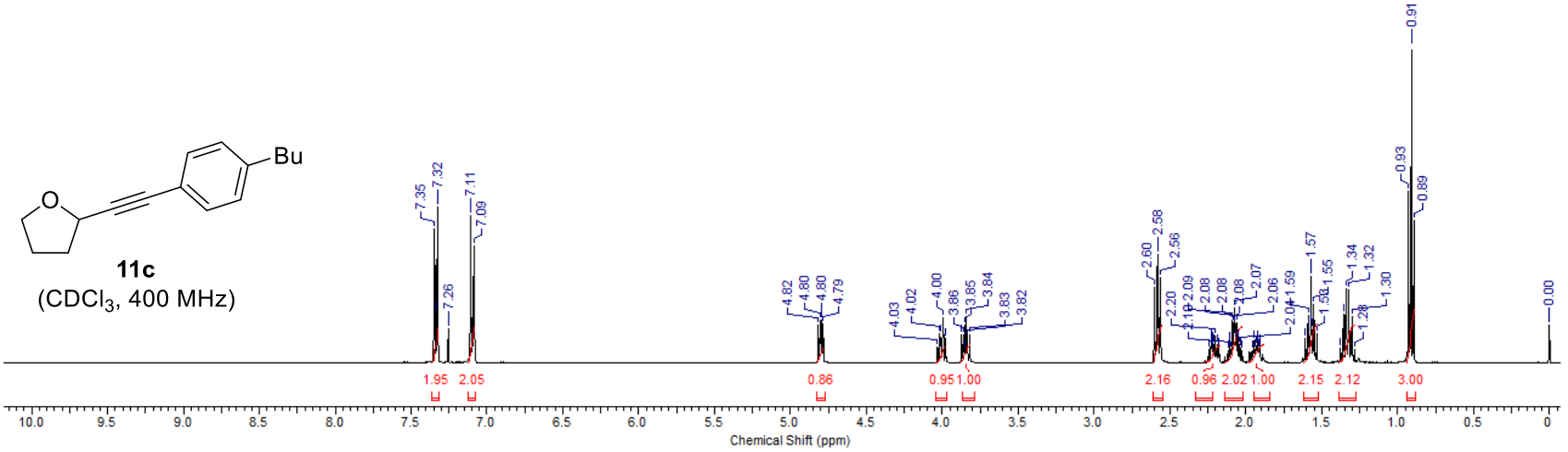
2-ALKENYL AND 2-ALKYNYL TETRAHYDROFURANS

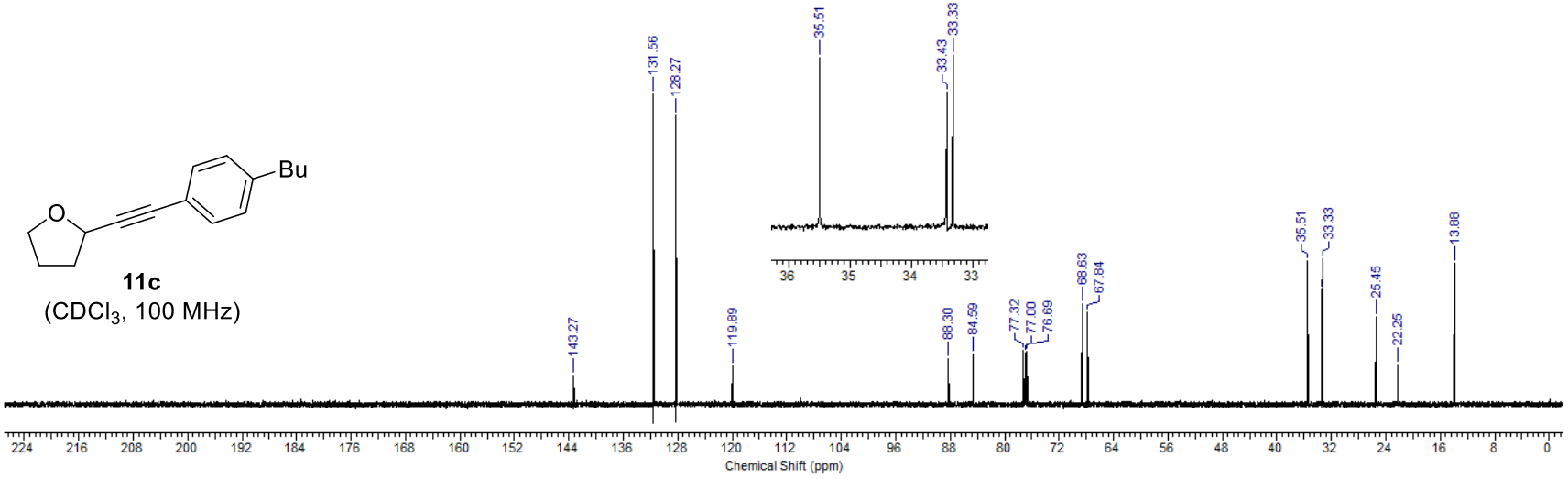


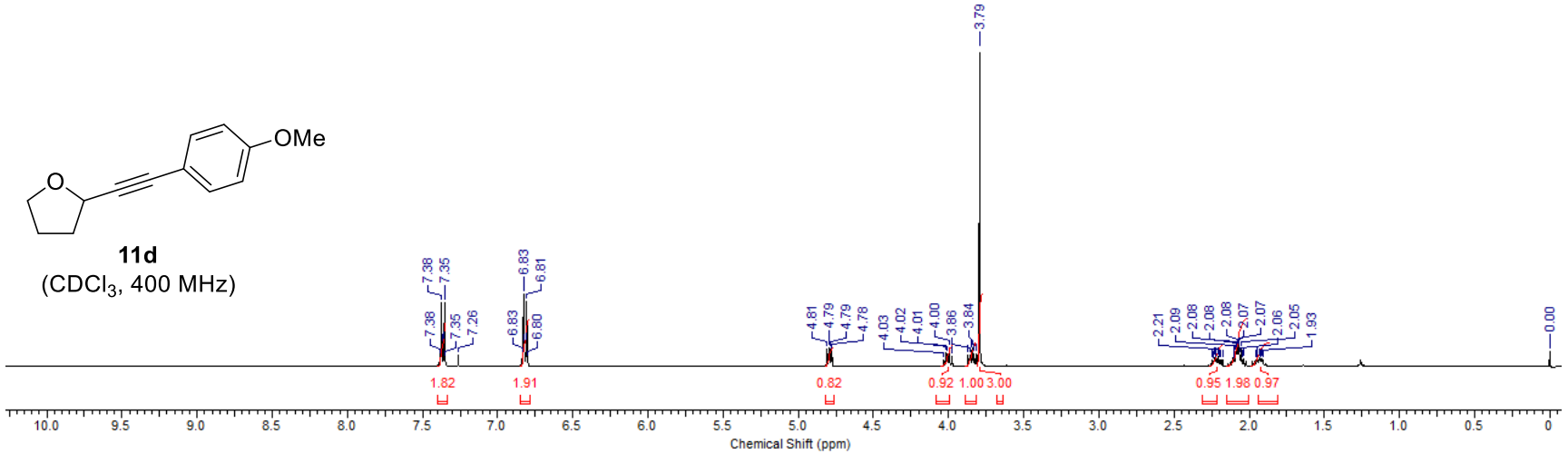


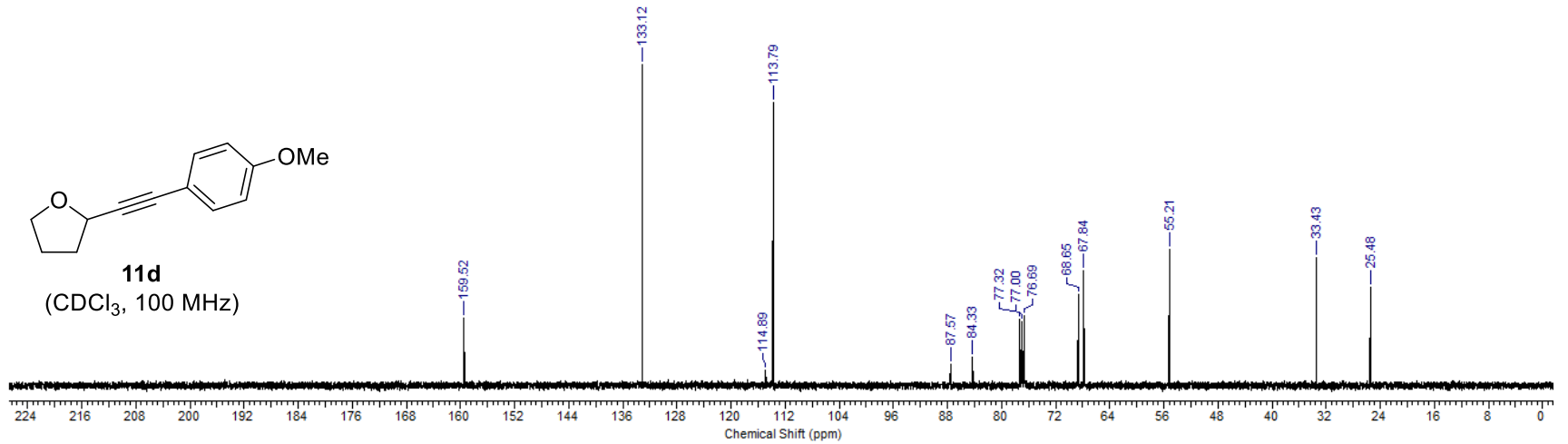

11b
(CDCl3, 400 MHz)
Chemical Shift (ppm)

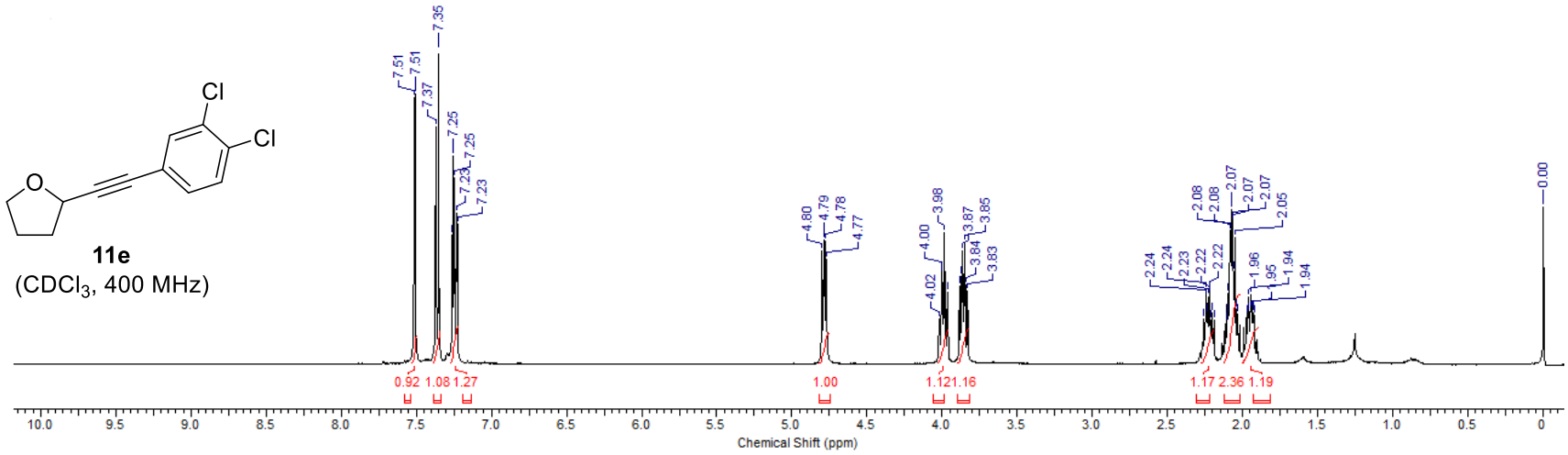

11b
(CDCl3, 100 MHz)
Chemical Shift (ppm)

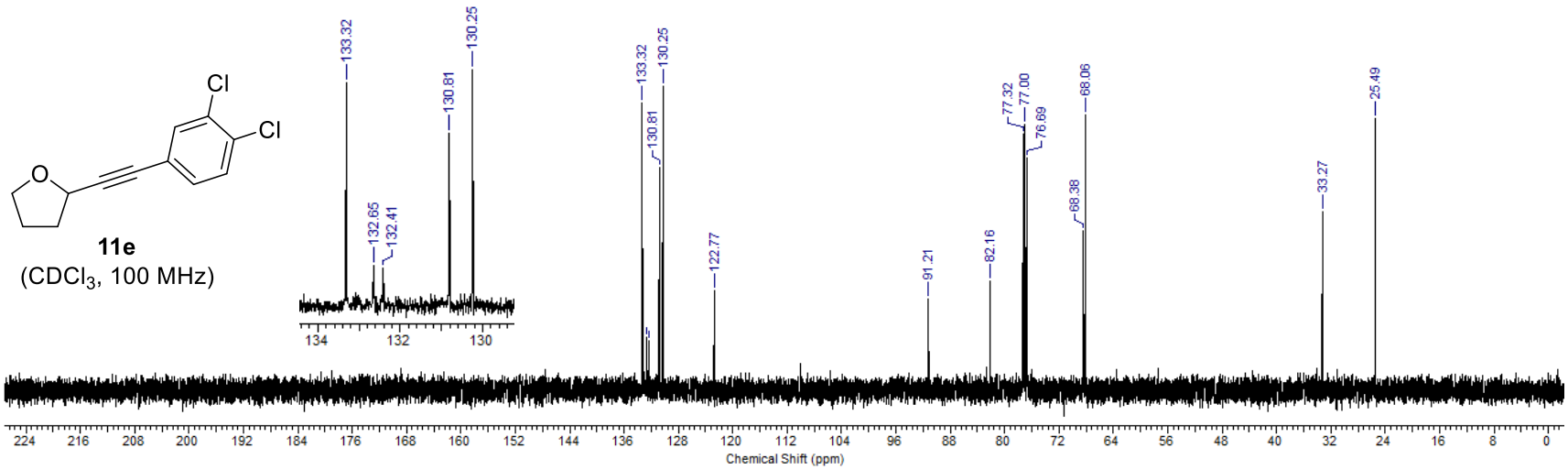

Bu
O
11c
(CDCl3, 400 MHz)
Chemical Shift (ppm)

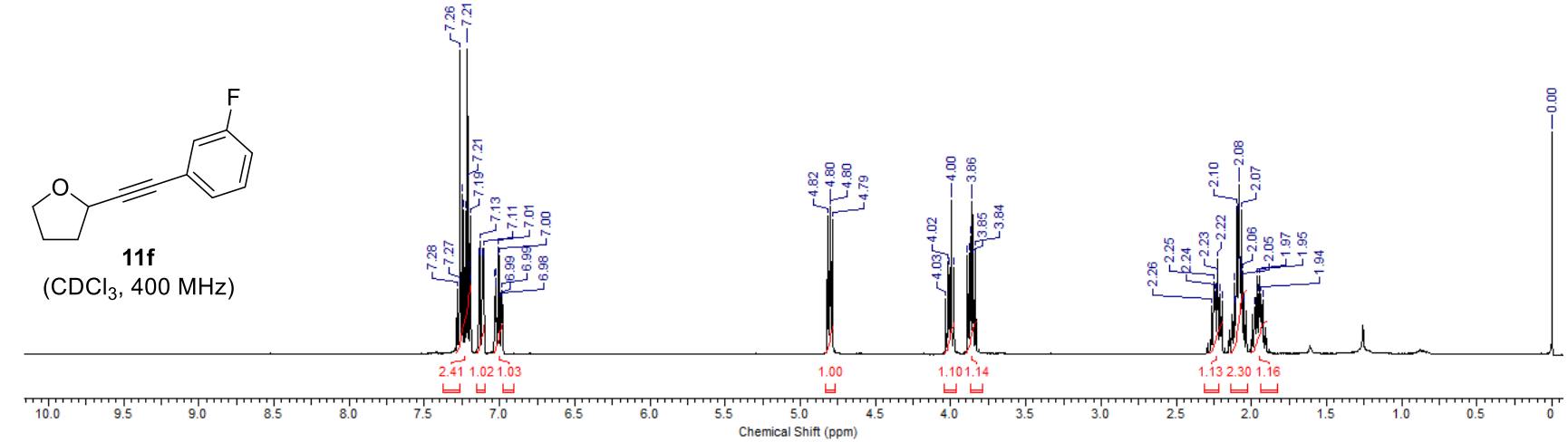

Bu
O
11c
(CDCl3, 100 MHz)
Chemical Shift (ppm)

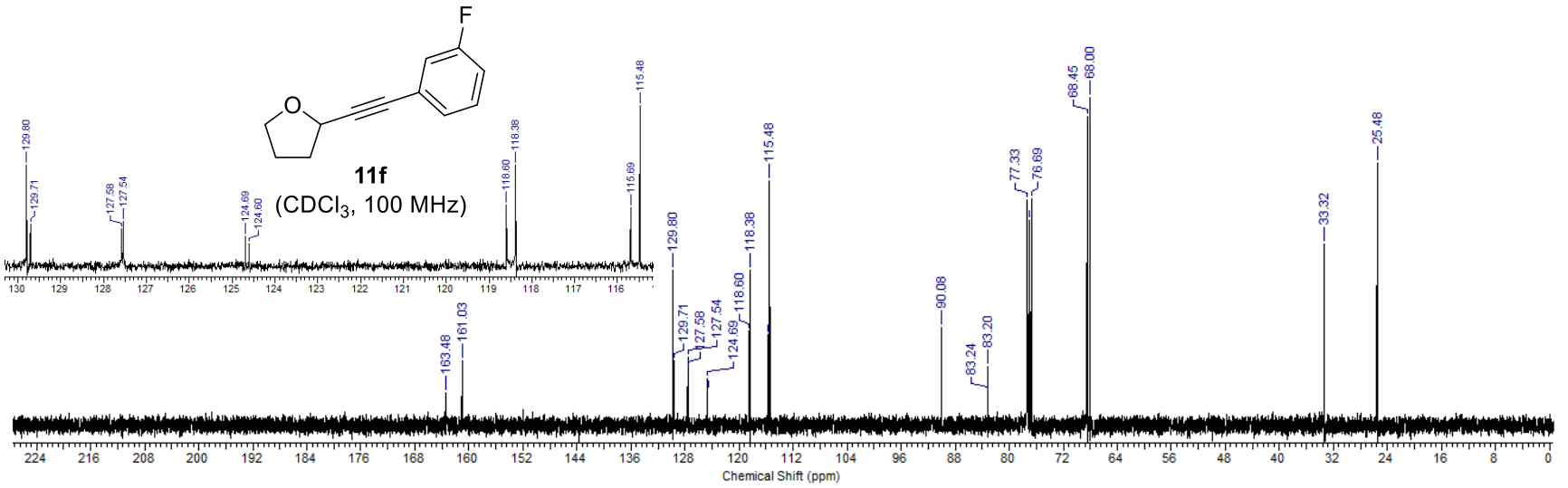

OMe
O
11d
(CDCl3, 400 MHz)
7.38
7.35
7.36
7.35
7.26
6.83
6.81
6.83
6.80
4.81
4.79
4.79
4.78
4.03
4.02
4.01
4.00
3.86
3.84
3.79
2.21
2.09
2.08
2.08
2.08
2.07
2.07
2.06
2.05
1.93
0.00
1.82
1.91
0.82
0.92
1.00
3.00
0.95
1.98
0.97
Chemical Shift (ppm)

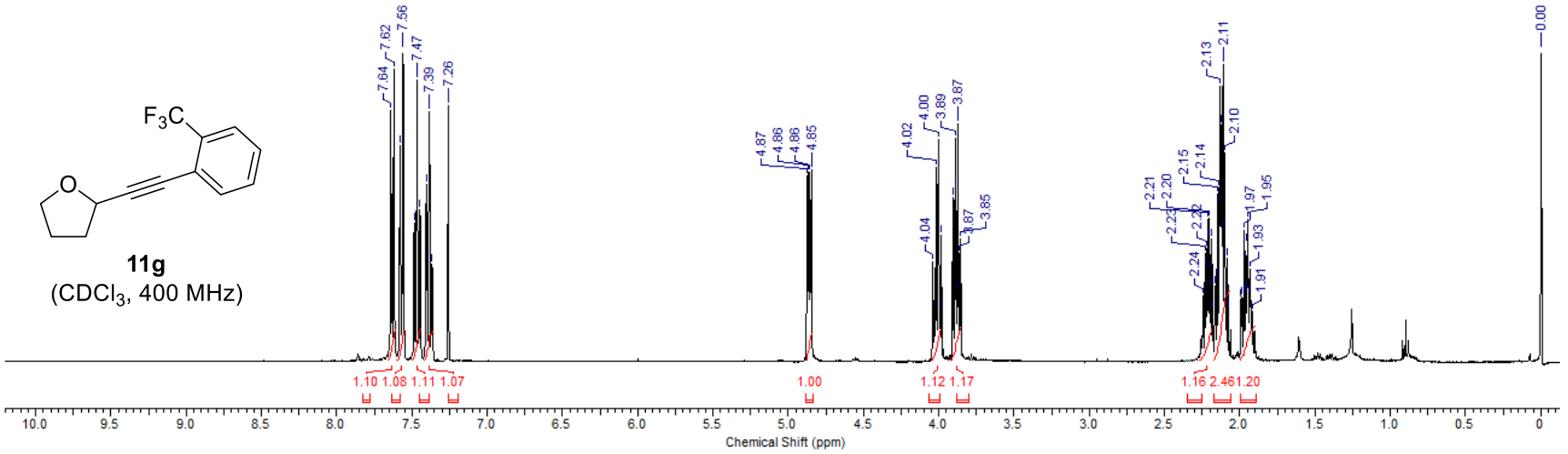

OMe
O
11d
(CDCl3, 100 MHz)
159.52
133.12
114.89
113.79
87.57
84.33
77.32
77.00
76.69
68.65
67.84
55.21
33.43
25.48
Chemical Shift (ppm)

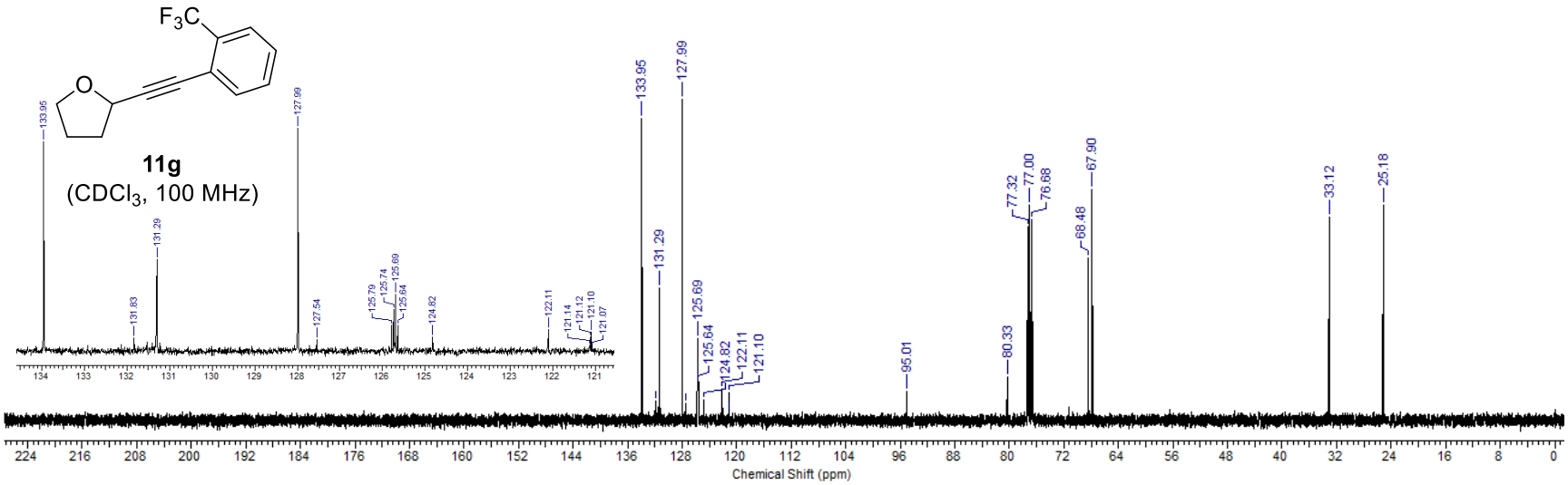

Cl
Cl
O
11e
(CDCl3, 400 MHz)
7.51
7.51
7.37
7.35
7.25
7.25
7.23
7.23
4.80
4.79
4.78
4.77
4.00
3.98
3.87
3.85
3.84
3.83
4.02
2.24
2.24
2.23
2.22
2.22
2.08
2.08
2.07
2.07
2.07
2.05
1.96
1.95
1.94
1.94
0.00
0.92
1.08
1.27
1.00
1.12
1.16
1.17
2.36
1.19
Chemical Shift (ppm)

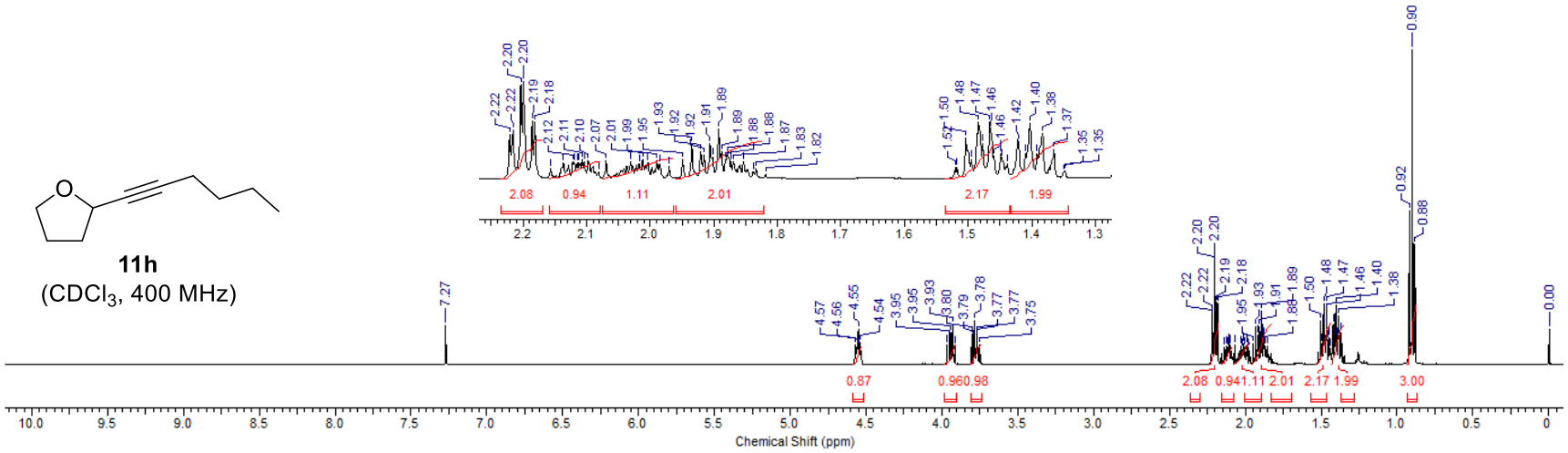

Cl
Cl
O
11e
(CDCl3, 100 MHz)
133.32
132.65
132.41
130.81
130.25
133.32
130.81
130.25
122.77
91.21
82.16
77.32
77.00
76.69
68.38
68.06
33.27
25.49
Chemical Shift (ppm)


F
O
11f
(CDCl3, 400 MHz)
Chemical Shift (ppm)

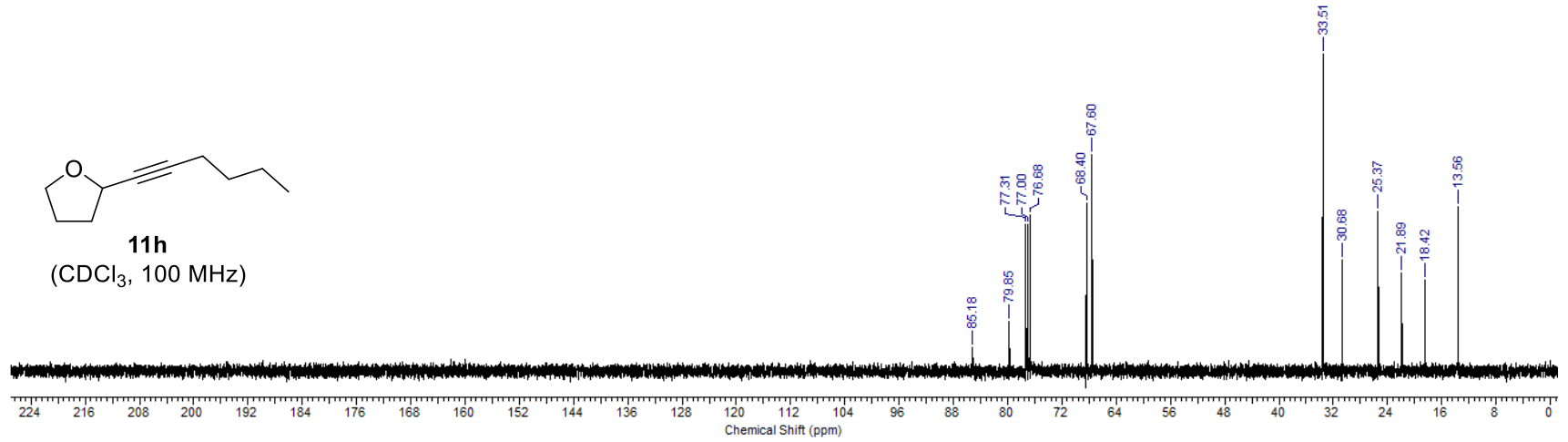

F
O
11f
(CDCl3, 100 MHz)
Chemical Shift (ppm)


F3C
O
11g
(CDCl3, 400 MHz)
7.64
7.62
7.56
7.47
7.39
7.26
4.87
4.86
4.86
4.85
4.02
4.00
3.89
3.87
4.04
3.87
3.85
2.21
2.20
2.15
2.14
2.13
2.11
2.10
1.97
1.95
1.93
1.91
0.00
1.10 1.08 1.11 1.07
1.00
1.12 1.17
1.16 2.46 1.20
Chemical Shift (ppm)

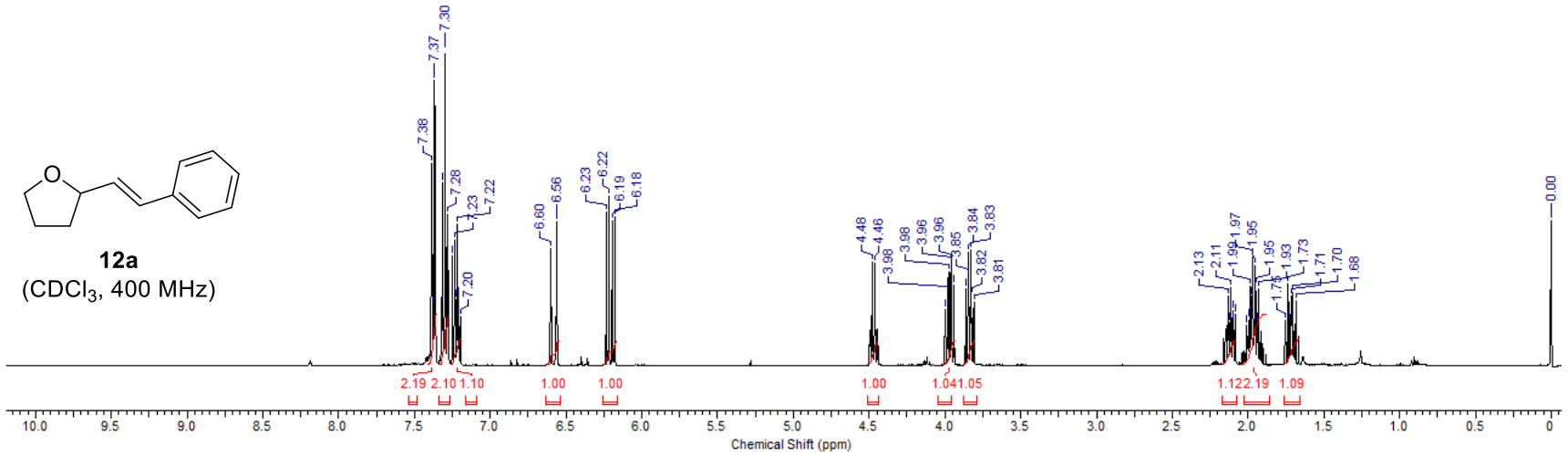

F3C
O
11g
(CDCl3, 100 MHz)
133.95
131.29
127.99
131.83
127.54
125.79
125.74
125.69
125.64
124.82
122.11
121.14
121.12
121.10
121.07
133.95
131.29
127.99
125.69
125.64
124.82
122.11
121.10
95.01
80.33
77.32
77.00
76.68
68.48
67.90
33.12
25.18
Chemical Shift (ppm)

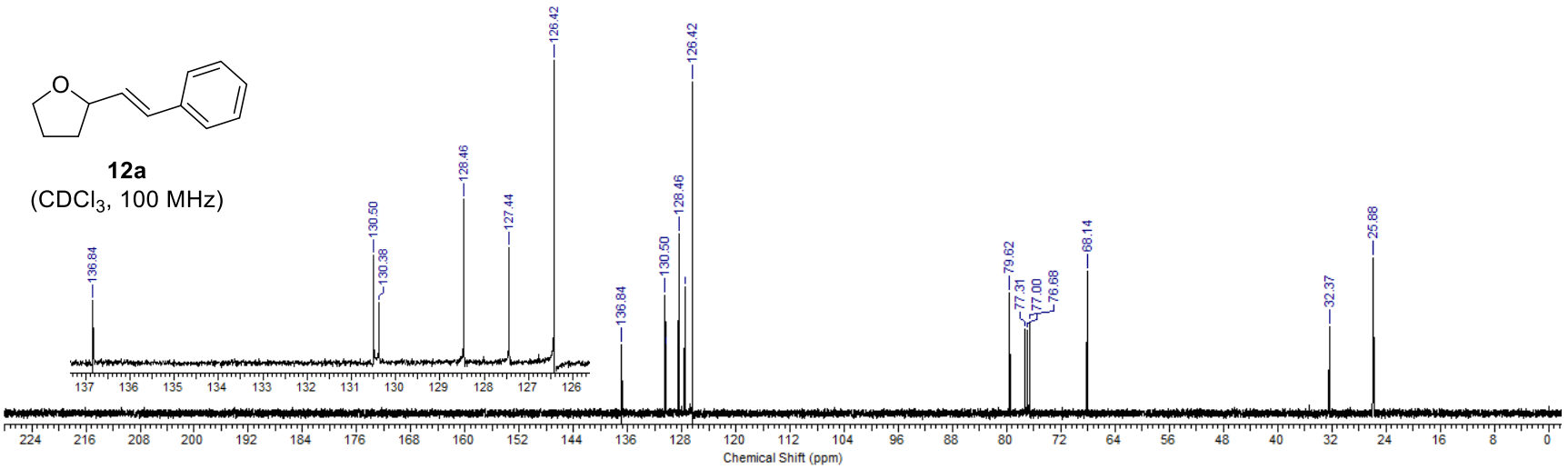


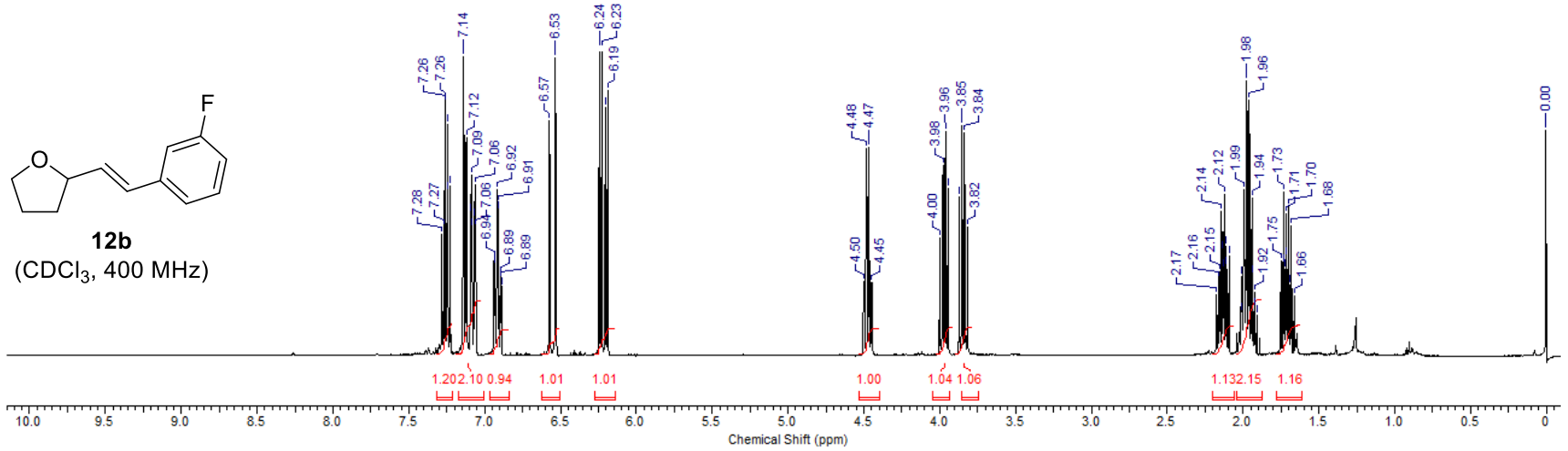
11h
($CDCl_3$, 400 MHz)

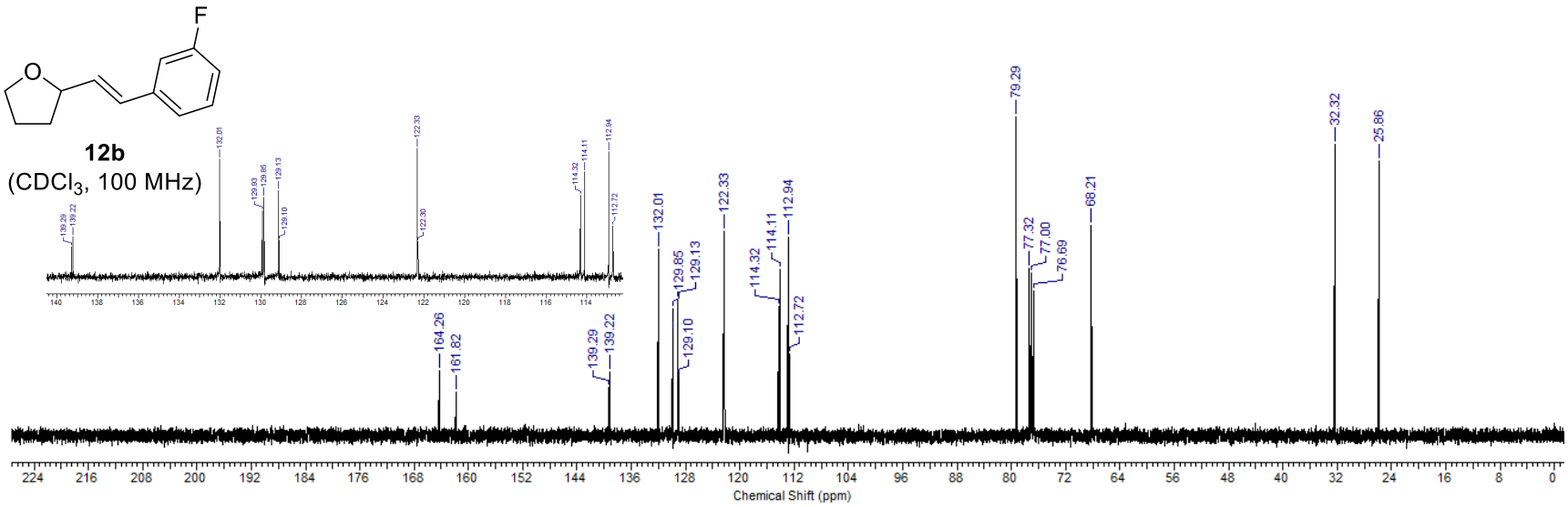


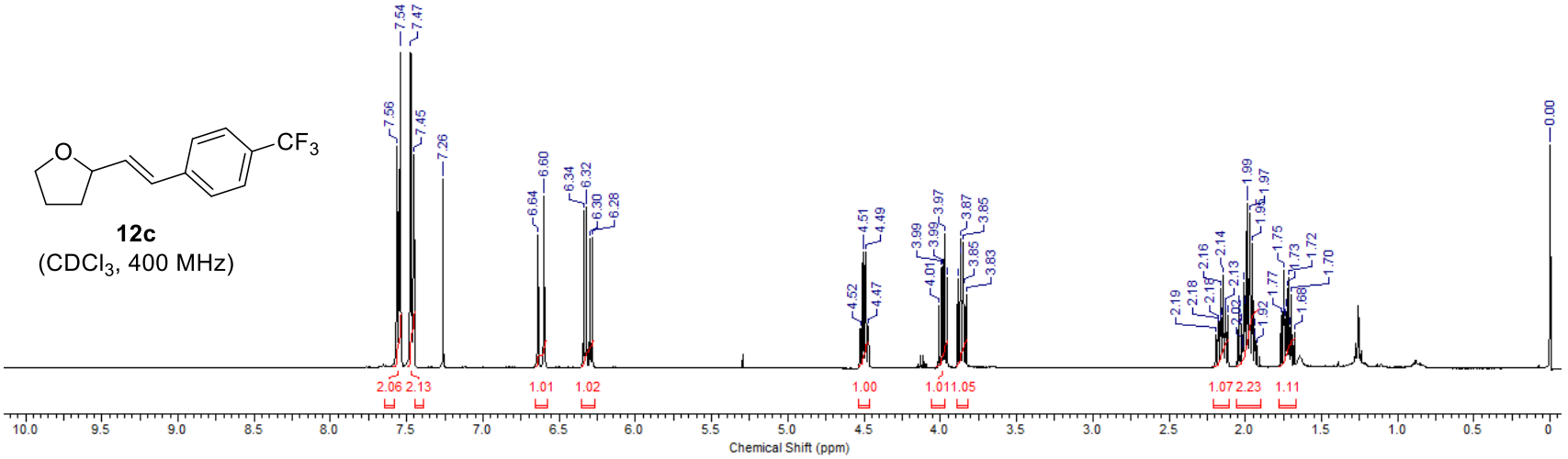
11h
($CDCl_3$, 100 MHz)

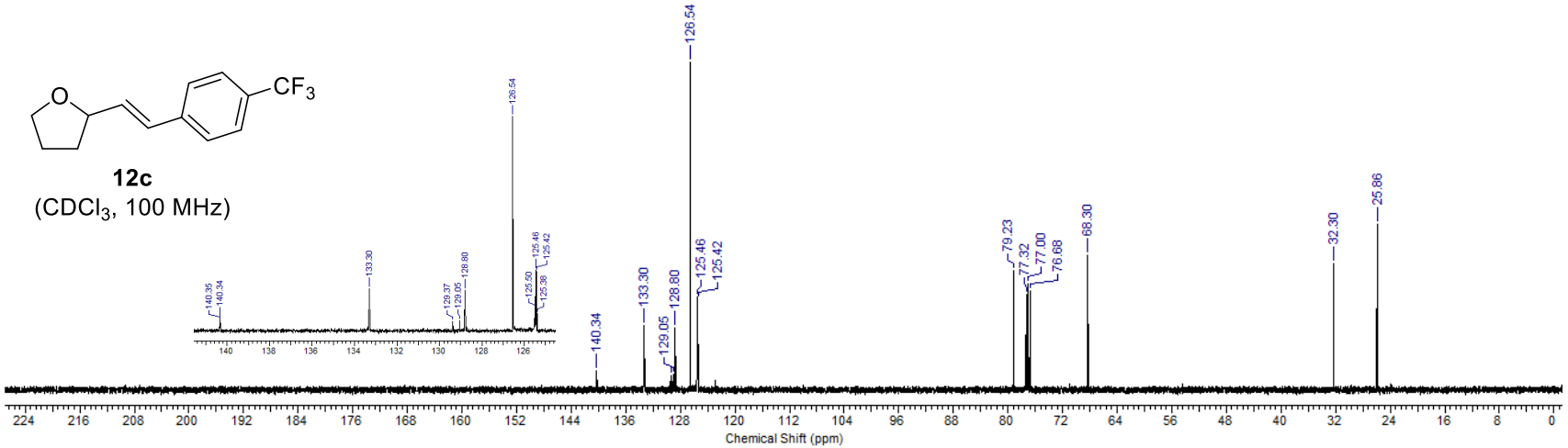

12a
(CDCl3, 400 MHz)
7.38
7.37
7.30
7.28
7.23
7.22
7.20
6.60
6.56
6.23
6.22
6.19
6.18
4.48
4.46
3.98
3.98
3.96
3.96
3.85
3.84
3.83
3.82
3.81
2.13
2.11
1.99
1.97
1.95
1.95
1.93
1.76
1.73
1.71
1.70
1.68
0.00
2.19 2.10 1.10
1.00
1.00
1.00
1.04 1.05
1.12 2.19
1.09
Chemical Shift (ppm)

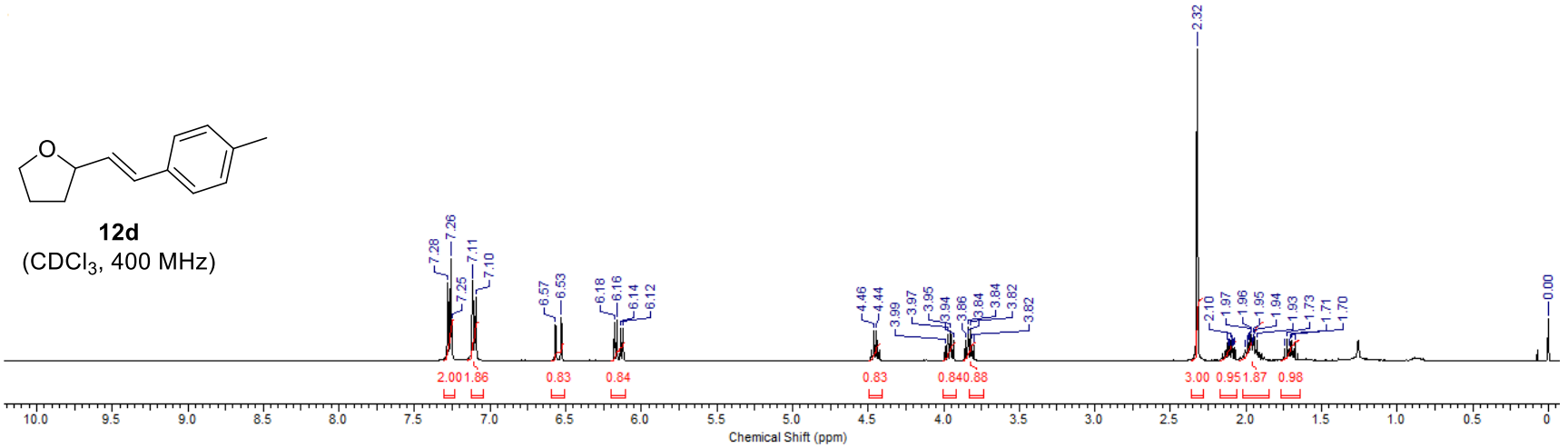

12a
(CDCl3, 100 MHz)
136.84
130.50
130.38
128.46
127.44
126.42
136.84
130.50
128.46
126.42
79.62
77.31
77.00
76.68
68.14
32.37
25.88
Chemical Shift (ppm)

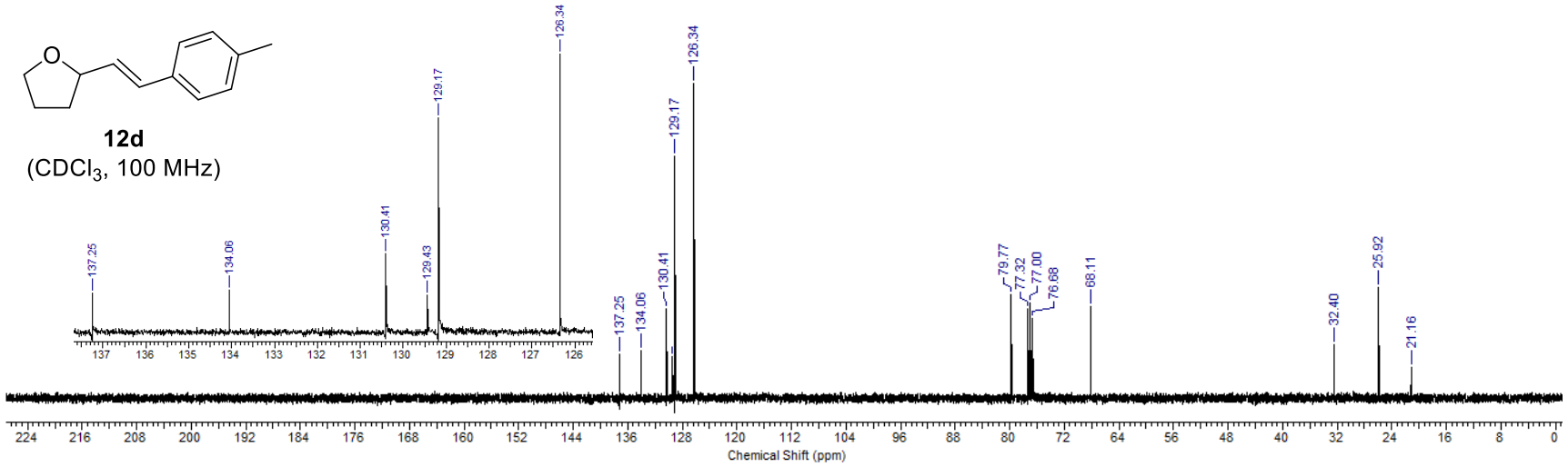

F
O
12b
(CDCl3, 400 MHz)
7.28
7.27
7.26
7.26
7.14
7.12
7.09
7.06
6.94
7.06
6.92
6.91
6.89
6.89
6.57
6.53
6.24
6.23
6.19
4.48
4.47
4.50
4.45
3.98
3.96
3.85
3.84
4.00
3.82
2.17
2.16
2.15
2.14
2.12
1.99
1.98
1.96
1.94
1.92
1.75
1.73
1.71
1.70
1.68
1.66
0.00
1.20
2.10
0.94
1.01
1.01
1.00
1.04
1.06
1.13
2.15
1.16
Chemical Shift (ppm)

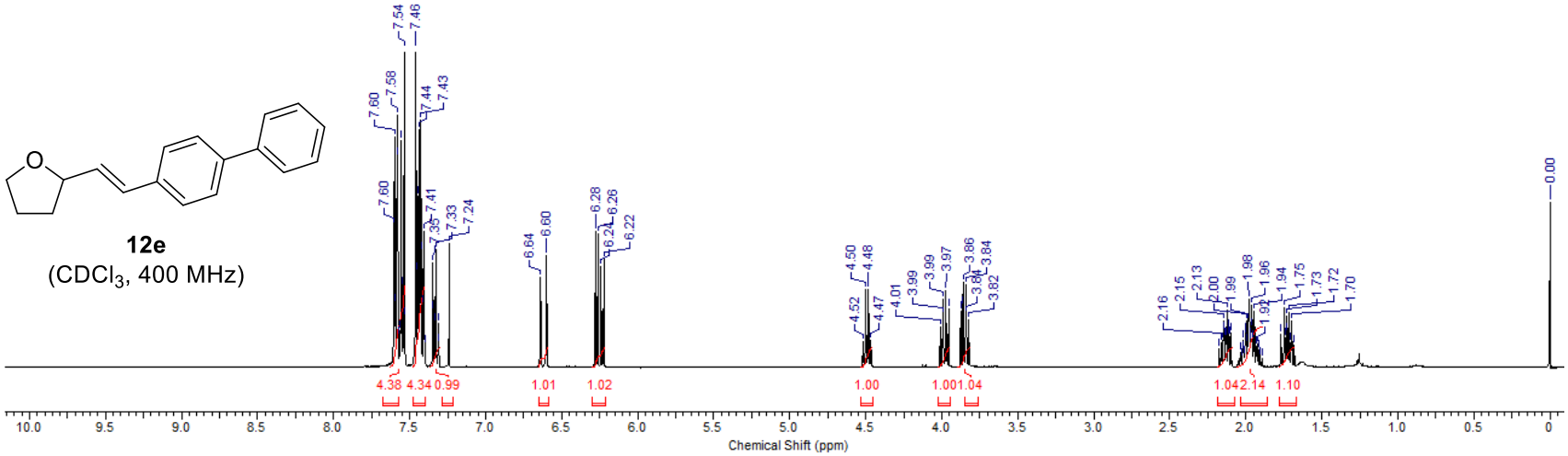

F
O
12b
(CDCl3, 100 MHz)
164.26
161.82
139.29
139.22
132.01
129.85
129.13
129.10
122.33
114.32
114.11
112.94
112.72
79.29
77.32
77.00
76.69
68.21
32.32
25.86
Chemical Shift (ppm)

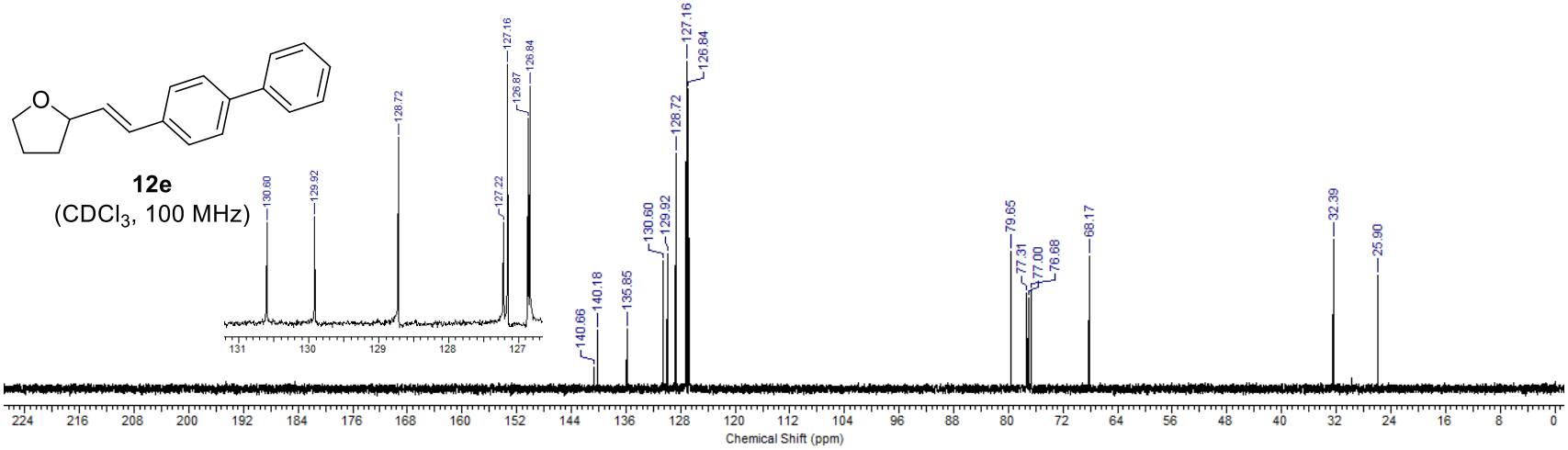

O
CF3
12c
(CDCl3, 400 MHz)
7.54
7.47
7.56
7.45
7.26
6.64
6.60
6.34
6.32
6.30
6.28
4.51
4.49
4.52
4.47
3.99
3.97
4.01
3.87
3.85
3.85
3.83
2.19
2.18
2.16
2.14
2.13
2.02
1.99
1.97
1.92
1.77
1.75
1.73
1.72
1.70
1.68
0.00
2.06
2.13
1.01
1.02
1.00
1.01
1.05
1.07
2.23
1.11
Chemical Shift (ppm)

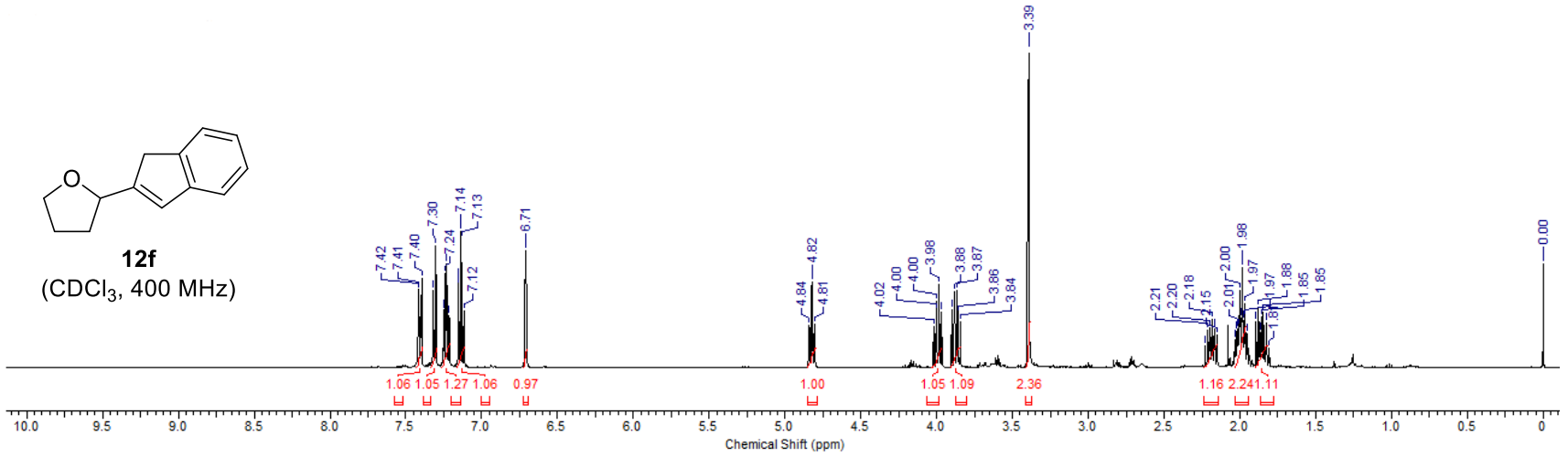

O
CF3
12c
(CDCl3, 100 MHz)
126.54
140.34
133.30
129.05
128.80
125.46
125.42
79.23
77.32
77.00
76.68
68.30
32.30
25.86
Chemical Shift (ppm)

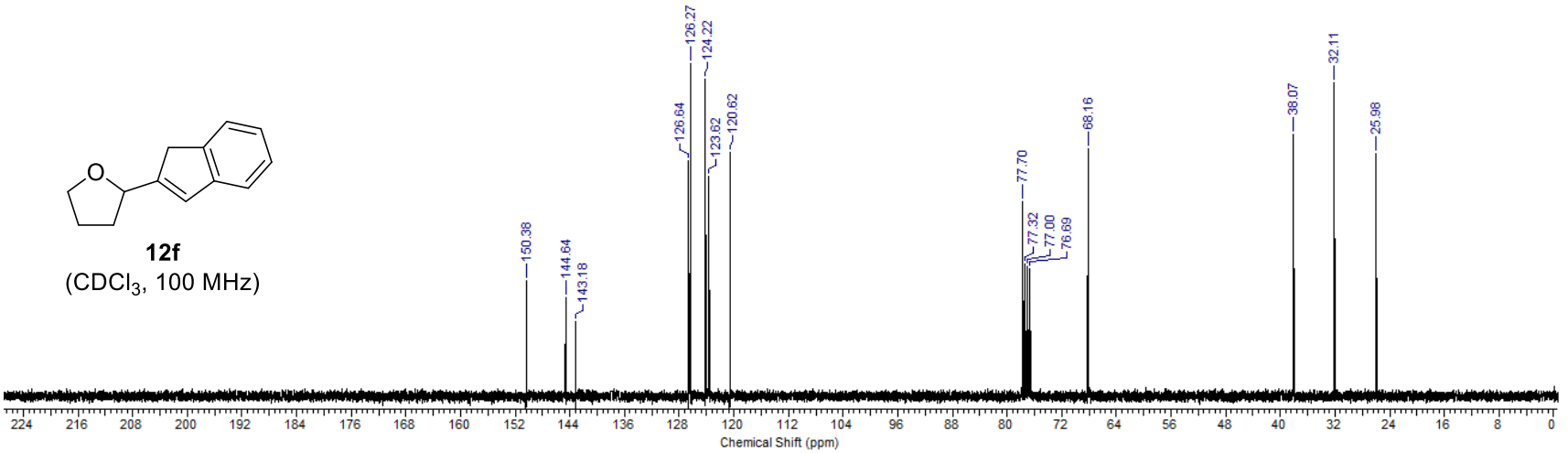

12d
(CDCl3, 400 MHz)
7.28
7.26
7.25
7.11
7.10
6.57
6.53
6.18
6.16
6.14
6.12
4.46
4.44
3.99
3.97
3.95
3.94
3.86
3.84
3.84
3.82
3.82
2.32
2.10
1.97
1.96
1.95
1.94
1.93
1.73
1.71
1.70
0.00
2.00 1.86 0.83 0.84 0.83 0.84 0.88 3.00 0.95 1.87 0.98
Chemical Shift (ppm)


12d
(CDCl3, 100 MHz)
137.25
134.06
130.41
129.43
129.17
126.34
137.25
134.06
130.41
129.17
126.34
79.77
77.32
77.00
76.68
68.11
32.40
25.92
21.16
Chemical Shift (ppm)


12e
(CDCl3, 400 MHz)
Chemical Shift (ppm)


12e
(CDCl3, 100 MHz)
Chemical Shift (ppm)


12f
(CDCl3, 400 MHz)
7.42
7.41
7.40
7.30
7.24
7.14
7.13
7.12
6.71
4.84
4.82
4.81
4.02
4.00
4.00
3.98
3.88
3.87
3.86
3.84
3.39
2.21
2.20
2.18
2.15
2.01
2.00
1.98
1.97
1.97
1.88
1.85
1.85
0.00
1.06 1.05 1.27 1.06 0.97
1.00
1.05 1.09
2.36
1.16 2.24 1.11
Chemical Shift (ppm)

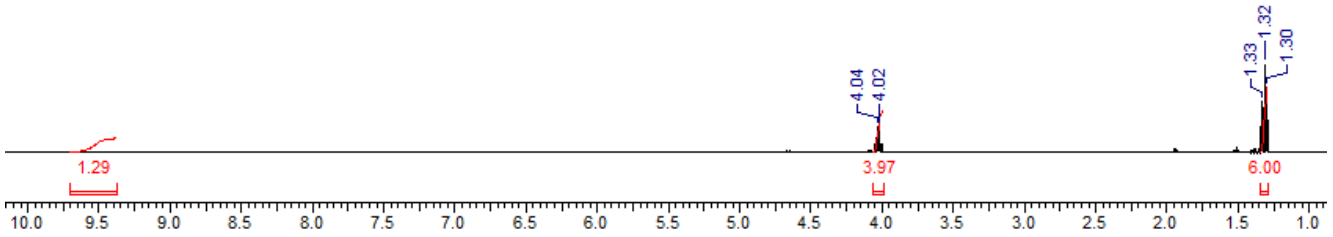

12f
(CDCl3, 100 MHz)
150.38
144.64
143.18
126.64
126.27
124.22
123.62
120.62
77.70
77.32
77.00
76.69
68.16
38.07
32.11
25.98
Chemical Shift (ppm)

APPENDIX III: NMR STUDIES

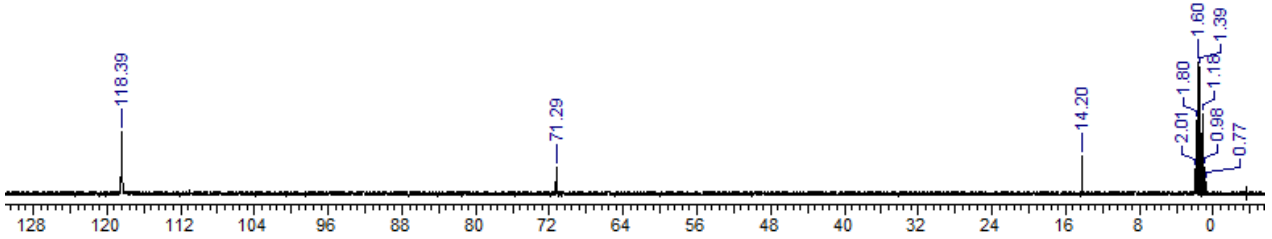
NMR 1:

16 µL of $HBF_4 \cdot OEt_2$ in 0.6 mL of CD_3CN was transferred to a NMR tube and the following spectra were acquired immediately.

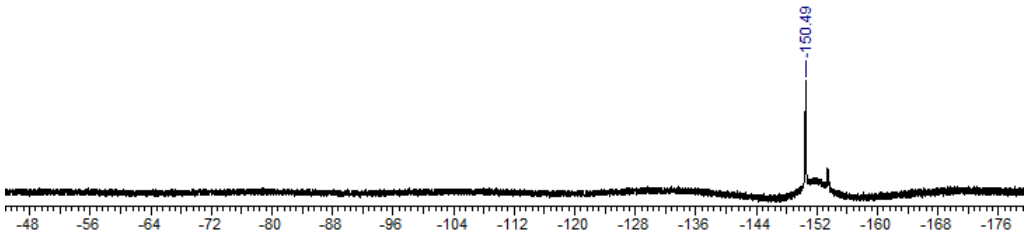
^{1}H NMR



^{13}C NMR



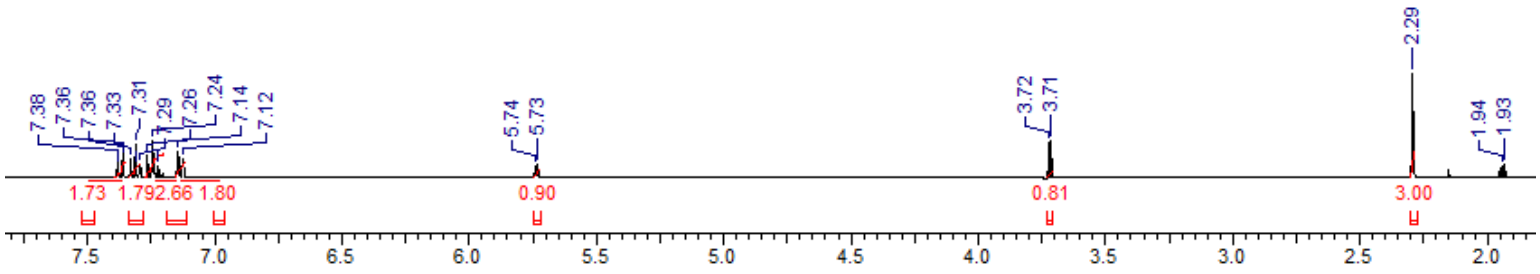
^{19}F NMR



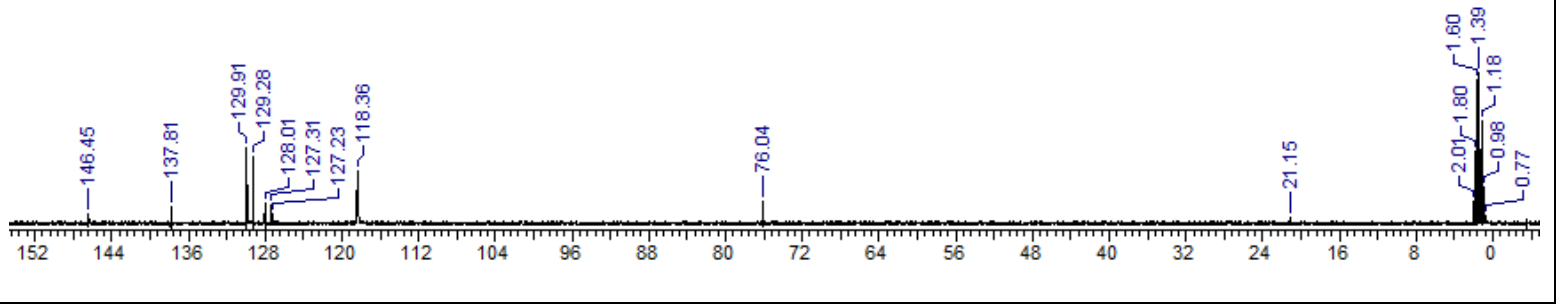
NMR 2:

14.0 mg of 4-methylbenzhydryl alcohol in 0.6 mL of CD_3CN was transferred to a NMR tube and the following spectra were acquired immediately.

^{1}H NMR



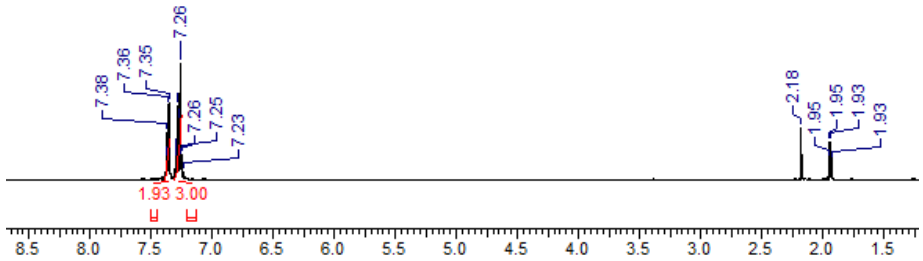
^{13}C NMR



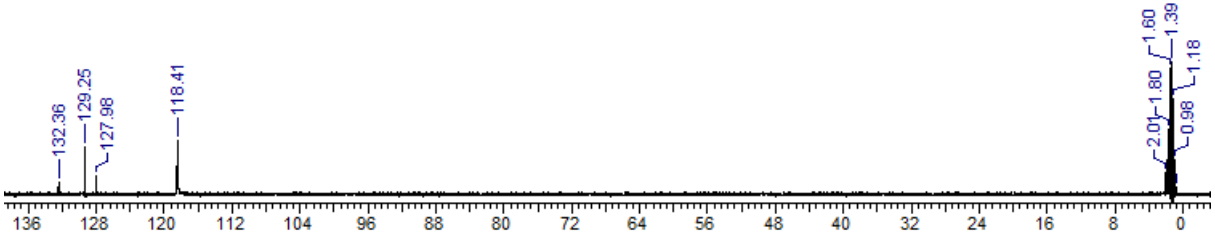
NMR 3:

14.7 mg of potassium phenylacetylenetrifluoroborate **1a** in 0.6 mL of CD_3CN was transferred to a NMR tube and the following spectra were acquired immediately.

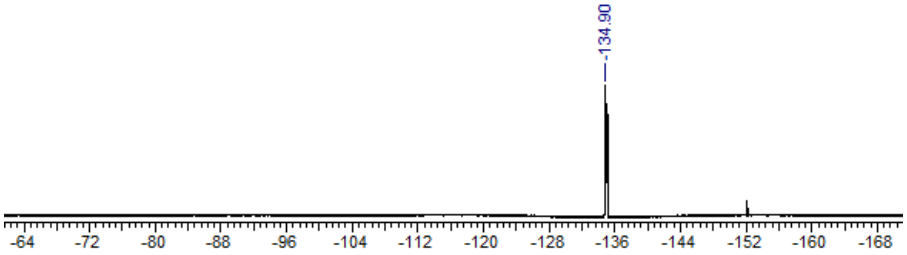
^{1}H NMR



^{13}C NMR



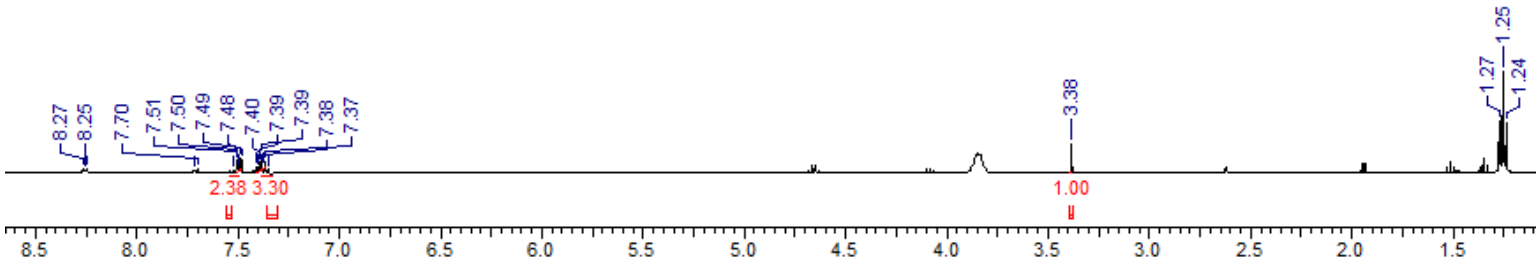
^{19}F NMR



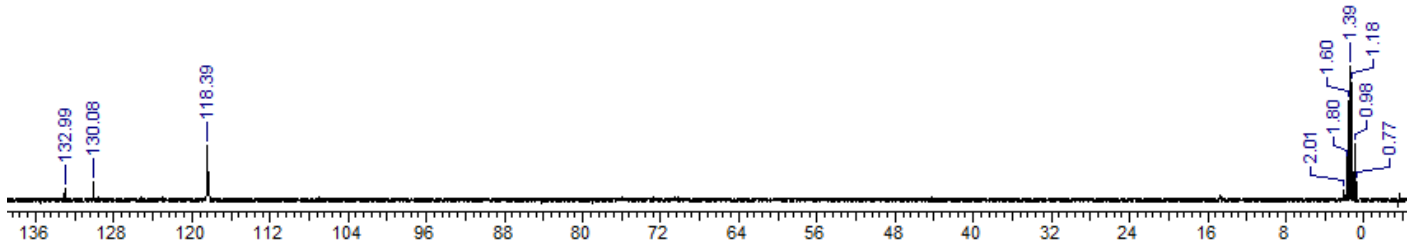
NMR 4:

In a NMR tube containing 14.7 mg of potassium phenylacetylenetrifluoroborate **1a** (1.0 equiv.) and 0.6 mL of CD_3CN, 16 μL of $HBF_4 \cdot OEt_2$ (1.6 equiv.) was added. The NMR tube was gently mixed and the following spectra were acquired immediately.

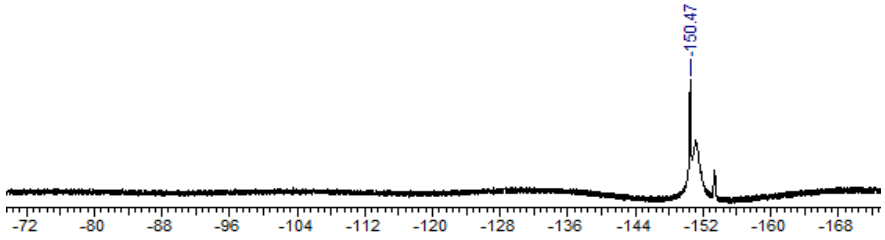
^{1}H NMR



^{13}C NMR



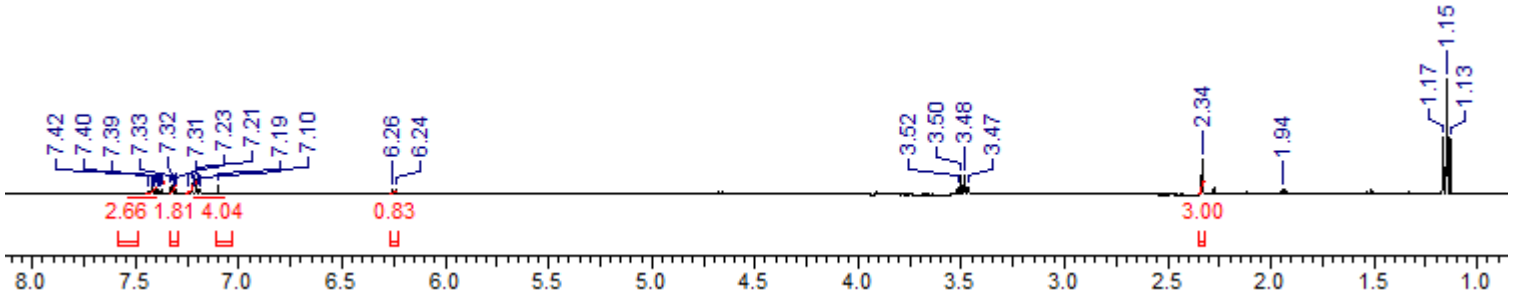
^{19}F NMR



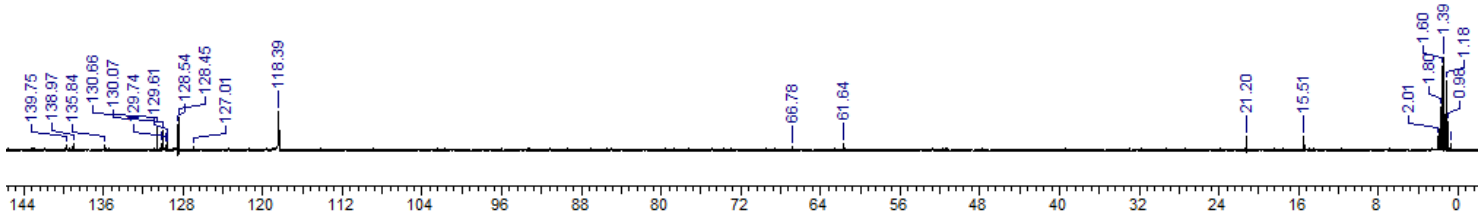
NMR 5:

In a NMR tube containing 14.0 mg of 4-methylbenzhydryl alcohol (1.0 equiv.) and 0.6 mL of CD_3CN, 16 μL of $HBF_4 \cdot OEt_2$ (1.6 equiv.) was added. The NMR tube was gently mixed and the following spectra were acquired immediately.

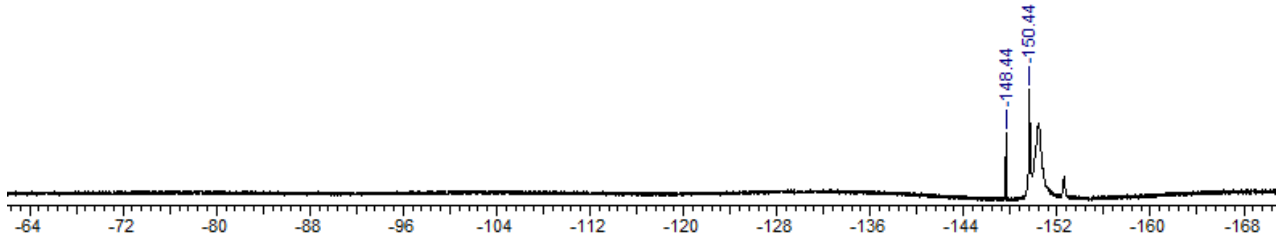
^{1}H NMR



^{13}C NMR



^{19}F NMR



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