Development of Visible Light Mediated Photocatalytic Alkynylation of Hydrogermanes

M.Sc. Thesis

By

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DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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A THESIS

Submitted in partial fulfillment

of the requirements for the award of the degree

of

Master of Science

by

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CANDIDATE'S DECLARATION

I hereby certify that the work which is been reported in this report entitled **"Development of Visible Light Mediated Photocatalytic Alkynylation of Hydrogermanes"** in the partial fulfillment of the requirements for the award of the Degree of Masters of Science and submitted to the Department of Chemistry, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the period from July 2022 to May 2023 under the supervision of Dr. Selvakumar Sermadurai, Assistant professor, Department of Chemistry, IIT Indore. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Tanu Chauhan 15/05/2023

(Signature of the student with the date)

(Tanu Chauhan)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

S. Selvakumar 15/05/2023

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Tanu Chauhan has successfully given her M.Sc. Oral Examination held on **16 May 2023.**

S. Selvakumar 18/05/2023

Signature of Supervisor of M.Sc. thesis

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Date: 18.05.2023

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Signature of Convener, DPGC

Dr. Umesh A. Kshirsagar

Date: 18.05.2023

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Signature of PSPC member

Dr. Dipak Kumar Roy

Date: 19.05.2023

S.S.B.

Signature of PSPC member

Dr. Satya S. Bulusu

Date: 18/5/23.

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[Tanu Chauhan]

DEDICATE TO MY FAMILY, FRIENDS

AND TEACHERS…….

ABSTRACT

Alkynylgermanes are a kind of essential synthetic block in organic chemistry. The established synthetic routes retain some drawbacks regarding harsh reaction conditions and expensive (or rare) metal catalysts. A mild and efficient photocatalytic method for the synthesis of value-added alkynylgermane is developed without using an excess of reagents. We employed ((phenylethynyl)sulfonyl) benzene and triphenylgermanium hydride as basic substrates, 4CzIPN as the organophotocatalyst, and *N*-cyclohexyl-4-methyl-benzenesulfonamide as hydrogen atom transfer (HAT) catalyst. Further, we extended our study to a number of substrates to check the scope of our reaction for the synthesis of alkynylsilane.

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ACRONYMS

δ	Chemical shift
ºC	degree celsius
equiv.	Equivalent
h	hour
HAT	Hydrogen Atom Transfer
mg	milligram
mmol	millimole
min	minutes
rt	room temperature
SET	Single Electron Transfer
TBHP	*Tert*-Butyl Hydroperoxide
THF	Tetrahydrofuran
4CzIPN	1,2,3,5-Tetrakis(carbazole-9-yl)-4,6-dicyanobenzene,2,4,5,6-Tetrakis(9*H*-carbazol-9-yl)isopthalonitrile

Chapter 1

INTRODUCTION

1.1. General Introduction

Organogermanium compounds are a class of chemical compounds that contain germanium (Ge) atoms bonded to organic (carbon-based) groups. Germanium is a chemical element that is similar to silicon in its properties and is found in Group 14 of the periodic table. Organogermanium compounds have been extensively studied for their diverse and interesting properties, making them important in various areas of chemistry and materials science.

Organogermanium compounds exhibit a wide range of structural diversity, including germanium atoms bonded to alkyl, aryl, or other organic groups. They can be synthesized through various methods, such as organometallic reactions, and can possess a wide range of physical, chemical, and biological properties. Some organogermanium compounds are known for their unique electrical, optical, and catalytic properties, which make them useful in applications such as semiconductors, sensors, and catalysts [1].

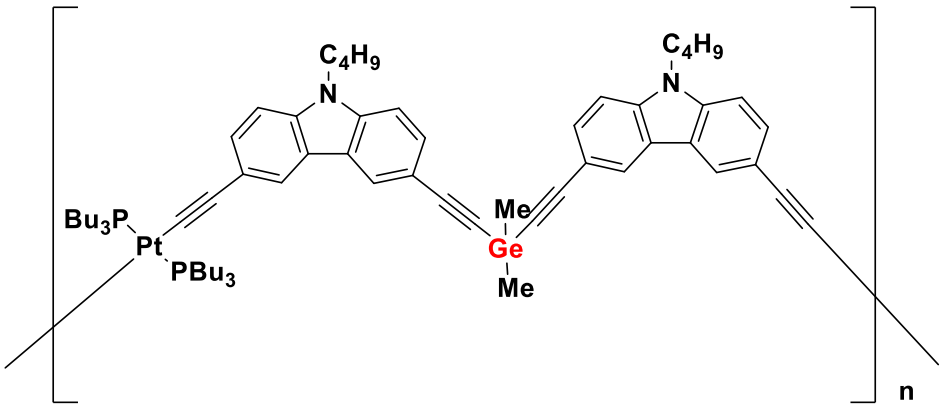


Figure 1: Photoluminescent organogermane polymer

Organogermanium compounds have also been studied for their potential biological activities, including anti-cancer, anti-viral, and immunomodulatory properties. Some organogermanium compounds have shown promising results in preclinical and clinical studies as potential drug candidates [2,3].

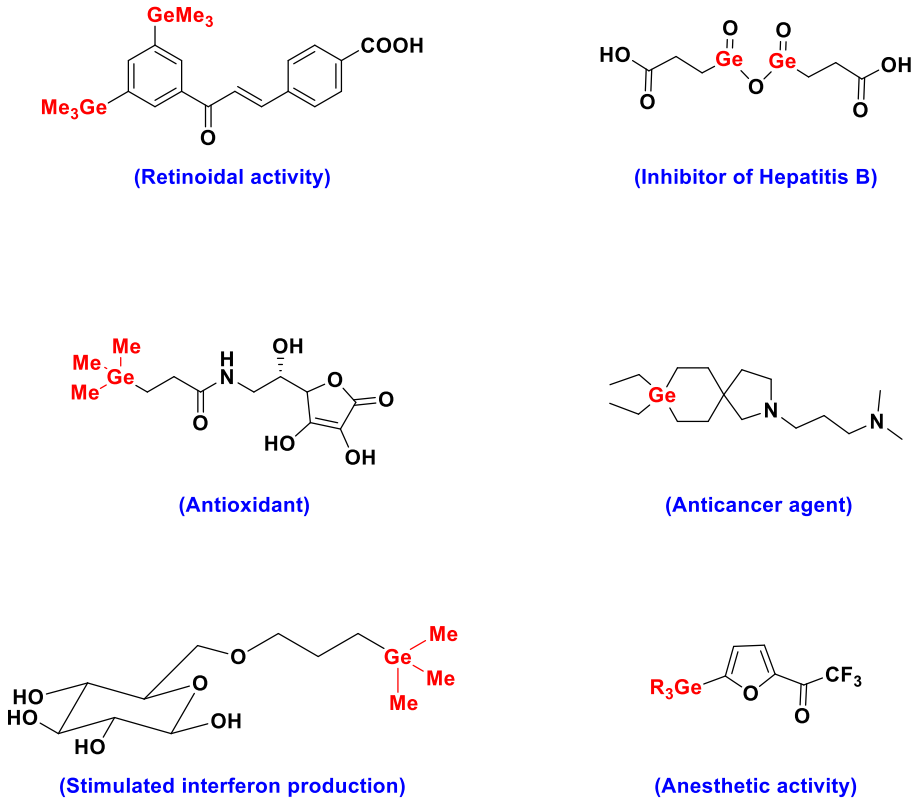
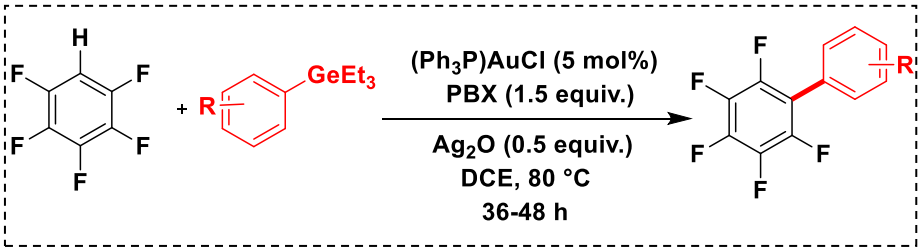


Figure 2: Biologically active organogermanium compounds

Overall, organogermanium compounds are a fascinating class of compounds with diverse properties and potential applications in various fields, including materials science, and medicinal chemistry. Continued research and exploration of their properties and applications are likely to reveal new insights and opportunities for their use in different areas of science and technology. Organogermanes are becoming more popular in organic synthesis and catalysis due to their stability and low toxicity. Germanium insertion into bioactive compounds has been acknowledged as a novel approach to drug development.

In the quest of exploring organogermanium compounds, we focused on alkynylgermanium compounds that can be used as versatile reagents in

organic synthesis for the construction of complex organic molecules. For example, they can be used as coupling partner in cross-coupling reactions, which are important transformations in organic synthesis for the formation of carbon-carbon/heteroatom bonds [4].



Scheme 1: Organogermane compound as coupling partner

They can be used in the synthesis of organogermanium polymers or as precursors for the preparation of germanium-containing thin films or nanoparticles. These materials can have interesting electronic, optical, and thermal properties, and can be used in areas such as optoelectronics, semiconductors, and sensors.

These are examples of the wide-ranging applications of alkynylgermanium compounds. Due to their unique properties and reactivity, alkynylgermanium compounds continue to be an active area of research in the various fields of chemistry.

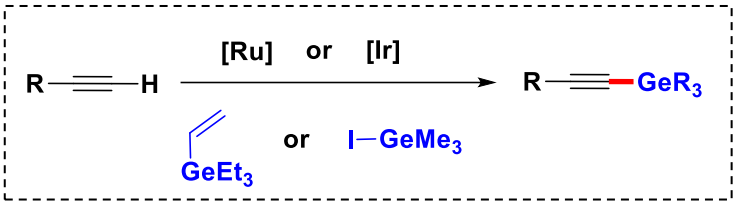
1.2. Previous work

Alkynylgermanes have previously been synthesized by Uhl **2010**, primarily by the treatment of organogermanium halides such as R_3Ge-Cl with metal acetylides [5].

Scheme 2: Synthesis of alkynylgermane using organometallic base

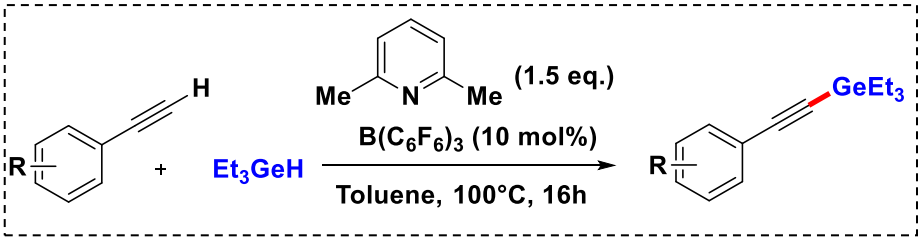
In order to avoid the use of organometallic reagent and basic conditions Marciniec in **2007**, and Rzonsowska in **2008** devised catalytic techniques using Ru or Ir-based catalysts respectively, which involve the

high-temperature germylative reaction of terminal alkynes with vinyl-substituted germanes or iodogermanes [6,7].



Scheme 3: Catalytic synthesis of alkynylgermane

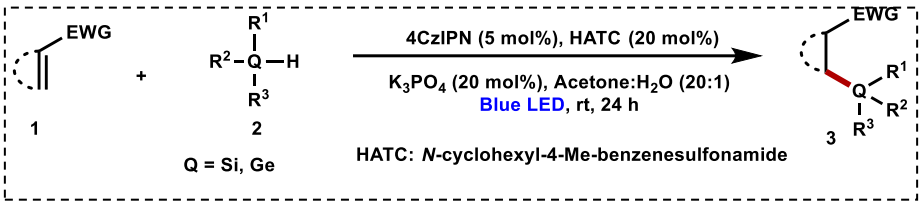
Recently, in **2022** Schoenebeck's group developed a direct C−H dehydrogenative germylation of terminal alkynes with hydrogermanes, with the motivation of avoiding both organometallic reagents and precious metal catalysts, but this method is also limited to triethyl germanium hydride as a germanium source and also this reaction condition requires 100 °C temperature [8,9].



Scheme 4: Synthesis of alkynylgermane using CDC method

1.3. Our hypothesis

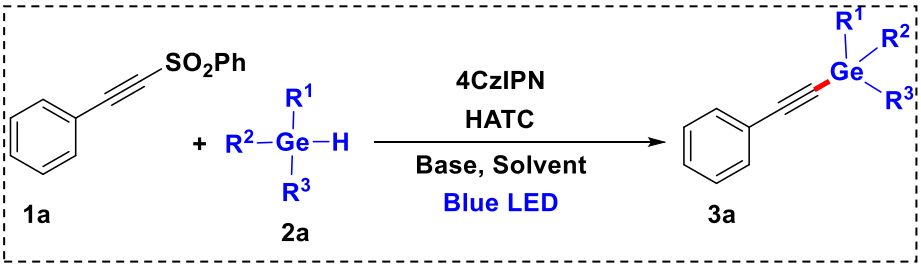
The generation of silyl radicals and germyl radicals from hydrosilanes and hydrogermanes in the process of synthesizing organosilanes and organogermanes respectively has garnered a lot of interest. C-H bonds are more typically functionalized using radical chemistry, which more frequently uses the production of radicals using hydrogen atom transfer (HAT).



Scheme 5: Photocatalytic hydrosilylation and hydrogermylation

For the site selectivity of the reaction electrophilic character of HAT is essential, because Si-H and Ge-H bonds are significantly more hydridic than the comparable C-H bonds. Our group recently established sulfonamides as a photoinduced hydrogen atom transfer catalyst for hydrosilylation and hydrogermylation under visible light irradiation to synthesize functionalized organosilanes and organogermanes [9]. (Scheme 5).

So, the main objective of our project is to synthesize value-added germanium compounds using alkyne sulfone as a substrate by generating germyl radical using sulfonamide as a HAT which can be easily synthesized in one step. The advantages of our approach are (a) metal-free (b) no harsh conditions (c) no excessive use of reagents.



Scheme 6: Proposed photo redox-catalyzed alkynylation of hydrogermane

Chapter 2

RESULTS & DISCUSSION

2.1. Optimization

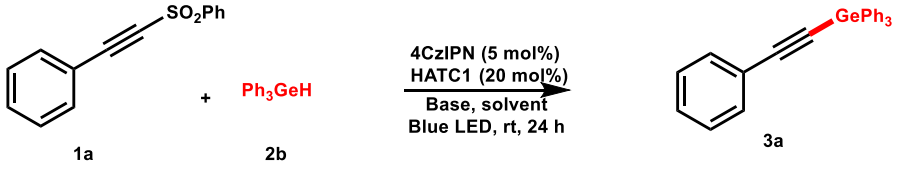
Solvent and base screening

To check the validity of our hypothesis we synthesized ((phenylethynyl)sulfonyl) benzene (**1a**) as a model substrate and reacted with triphenyl germanium hydride (**2b**) to optimize the reaction conditions (Table 1). First of all, we treated **1a** (1 equiv.) with **2b** (2 equiv.) in the presence of 5 mol% 4CzIPN along with K_3PO_4 (20 mol%) and HATC1 (20 mol%) in acetone-water (20:1). In this condition we found a 52% yield of **3a** (entry 1). In the next experiment, we did the same reaction using acetone instead of acetone-water and observed a significant decrease in the yield of **3a** (entry 2). This decrement probably corresponds to the base insolubility in acetone. Then we tried solvents of different combinations such as acetonitrile-water (20:1) and DMSO-water (20:1) while keeping the rest of the conditions same, we observed the desired product in 47% and 41% yields respectively (entries 3 & 4). Moving forward in this journey, after considering acetone-water as the best solvent system for the reaction, we screened different bases such as Cs_2CO_3 and K_2CO_3 (entries 5 & 6) where we observed 40% and 43% formation of the desired product. This compelled us to consider potassium phosphate as the best base for our reaction system. Also, a good amount (50%) of hydrogermylated product was detected when the reaction was performed in an Ir photocatalyst (entry 7).

Further, we also used potassium carbonate as the base while using acetonitrile-water as the solvent to give 52% of the desired product (entry 8). We also tried a condition similar to entry 8 but by taking 3 equiv of **2b** where we got a 43% yield (entry 9). We continued the exploration by tuning the equivalents as well as changing the concentration of the system, we tried a few more reactions (entries 10 - 13) and concluded that our reaction performs more efficiently in the

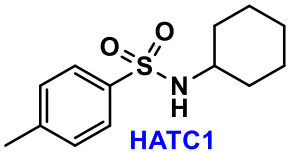
condition mentioned in entry 12. We also did another reaction (entry 14) in the end to get an enhanced yield of **3a** where we used trifluorotoluene as the solvent, *tetra*-n-butylammonium di-*tert*-butyl phosphate as the base (organic base), and the Ir catalyst but we observed only a 45% yield of **3a**. After getting a better reaction condition (entry 12) we moved towards the screening of different hydrogen atom transfer catalysts (HATCs).

Table 1: Optimization

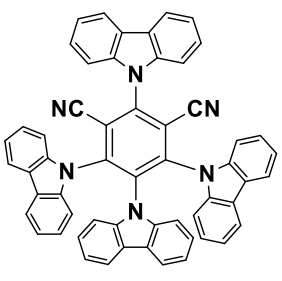


Entry	Solvent (20:1)	Base (20mol%)	Yield (%)[b]
1	Acetone : H_2O	K_3PO_4	52
2	Acetone	K_3PO_4	36
3	Acetonitrile : H_2O	K_3PO_4	47
4	DMSO : H_2O	K_3PO_4	41
5	Acetone : H_2O	Cs_2CO_3	40
6	Acetone : H_2O	K_2CO_3	43
7[c]	Acetone : H_2O	K_3PO_4	50
8	Acetonitrile : H_2O	K_2CO_3	52
9[d]	Acetonitrile : H_2O	K_2CO_3	43
10[e]	Acetone : H_2O	K_3PO_4	41
11[e,f]	Acetone : H_2O	K_3PO_4	54
12[f,g]	Acetone : H_2O	K_3PO_4	56
13[f,g,h]	Acetone : H_2O	K_3PO_4	48
14[c,f]	Triflurotoluene	Tetra-n-butylammonium di-*tert*-butyl phosphate	45

[a]Reaction conditions: **1a** (0.1 mmol), **2b** (0.2 mmol), solvent (1 ml), 450 nm blue LED, [b]Isolated yield, [c]$(Ir(dF(CF3)ppy]_2(dtbpy))PF_6$, [d]2b (0.3 mmol), [e]2b (0.12 mmol), [f]solvent (0.5 ml) , [g]2b (0.15 mmol),[h]base (50mol%)



HATC1

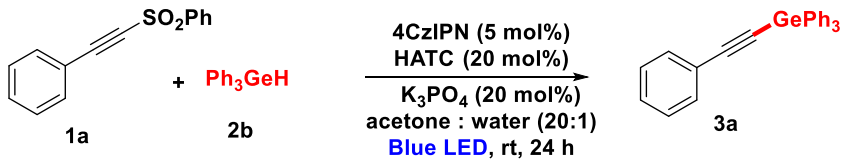


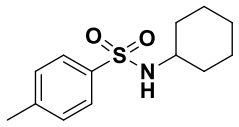
4CzIPN

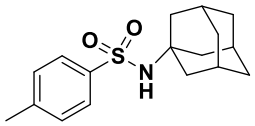
2.2. Screening of hydrogen atom transfer catalysts:

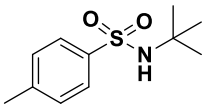
Considering acetone-water as the best solvent, 4CzIPN as the best photocatalyst, and K_3PO_4 as the best base for our hypothesized reaction, we started optimizing different HATCs. In this quest, we have found *N*-cyclohexyl-4-Me-benzenesulfonamide (HATC1) to be the best hydrogen atom transfer catalyst.

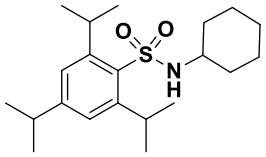
Significantly less amount of the desired product is formed when the N-cyclohexyl substituent is replaced with more sterically hindered 1-adamantyl and *tert*-butyl groups (HATC2 & HATC3) respectively. Only 34% product was detected on replacing p-tolylsulfonyl group in HATC1 with the 2,4,6- triisopropylarylsulfonyl group (HATC4). The required product was found to be produced in a 40% yield using the diaryl sulfonamide catalyst (HATC5), which was extremely effective for the abstraction of activated C(sp^3)-H bonds. It is important to mention here that replacing the *p*-tolylsulfonyl group with 3,5-bistrifluoromethylphenylsulfonyl was giving very good conversion of product 54% (HATC6).

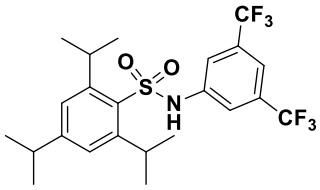


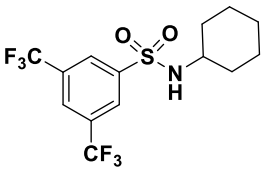

HATC1, 56%


HATC2, 41%


HATC3, 35%

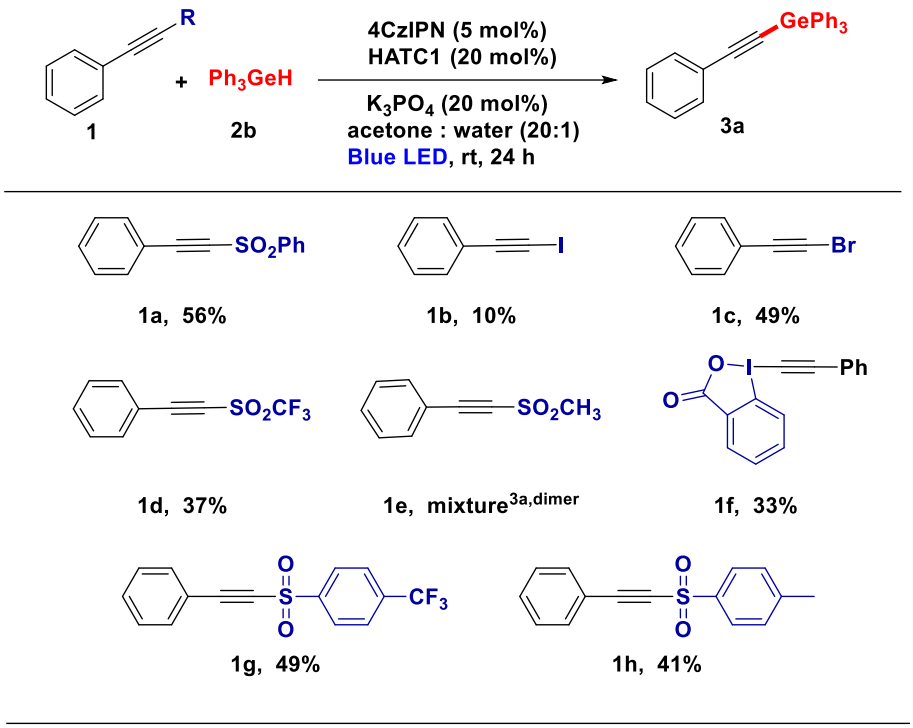

HATC4, 34%


HATC5, 40%

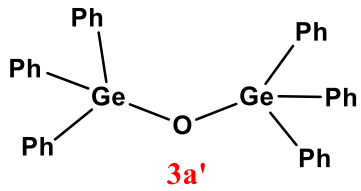

HATC6, 54%

2.3. Screening of substrates:

After getting the best reaction conditions, for enhancing the yield of **3a**, we tried to screen different substrates instead of **1a**. In this journey, we selected several substrates and employed them under our profound reaction conditions (in the previous section). Replacing R with Br (**1c**) gave a good yield (49%) of 3a but when we replaced R with I (**1b**), a poor yield of **3a** was obtained (10%).



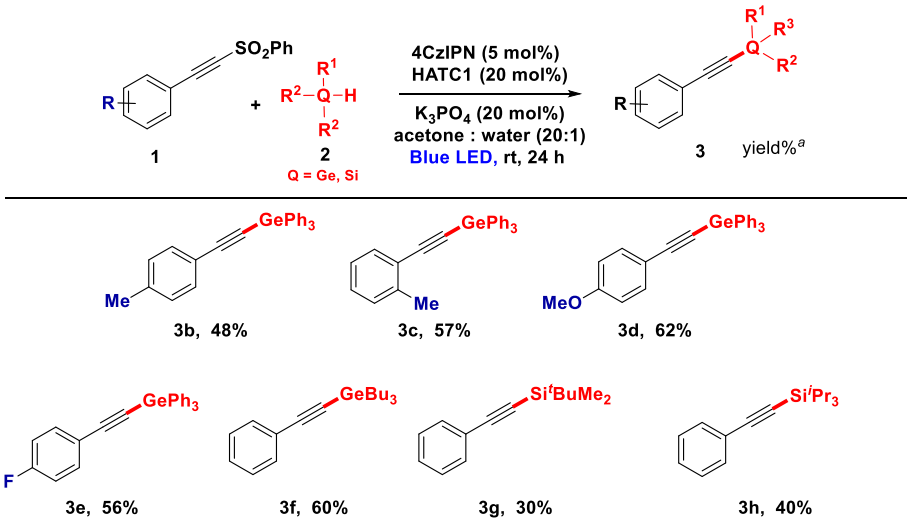
Substrate **1d** was also working in a good manner and giving a 37% yield of **3a** while substrate **1e**, where we substituted R with methyl sulfone, was working very poorly. With **1e**, a mixture of product **3a** and **3a'** was observed.



Moving forward, we tried a cyclic hypervalent iodine substrate (**1f**) which is also viable in our reaction conditions. With this substrate, we observed a good yield of **3a**. Further taking the electron-withdrawing group on the para position of the sulfone ring (**1g**) a good yield (49%) of the desired product was obtained while the electron donating group on the para position of the sulfone ring (**1h**) lead to a reduction in the yield (41%). After trying many substrates, we concluded that **1a** is the best substrate for our reaction.

2.4. Substrate scope:

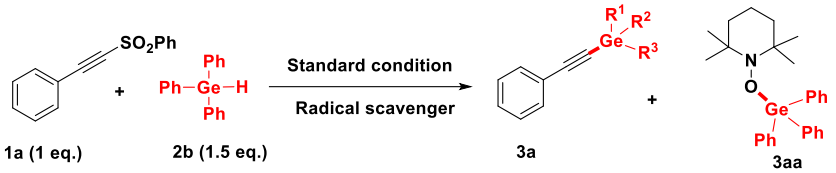
After obtaining the optimal reaction conditions, we studied the generality of this reaction with respect to the terminal alkynes. Phenyl rings are well tolerated with the electron-donating and electron-withdrawing functional groups. Electron donating groups such as 4-Me (**3b**), 2-Me (**3c**), and 4-OMe (**3d**) gave rise to the corresponding products in good yields. Additionally, in the presence of electron-withdrawing groups such as 4-F (**3e**), furnishing germylated product in 56% yield. We subsequently examined, the alkyl germanium hydride (**3f**) also gave rise to the corresponding product in good yield. We investigated the feasibility of silyl radical from the corresponding hydrosilane to extend the use of this method and we found that the corresponding silane (**3g**) and **(3h)** are well tolerated to give the corresponding product.



[a]*Isolated yield*

2.5. Control experiments:

Radical trapping experiment:



Entry	Radical scavenger	eq.	3a	3aa
1.	TEMPO	1.5	ND	-

ND = Not Detected

Stern-Volmer quenching experiment:

On the HORIBA SCIENTIFIC FLUOROMAX-4P modal, recordings of all fluorescence quenching studies were made. 1.47 mg of the photocatalyst 4CzIPN was combined with 15 mL of spectroscopic grade acetonitrile (make-Spectrochem), which was then utilized after the solvent had been degassed with argon to create a 1.25×10^{-4} M stock solution. Using a suitable volume of 4CzIPN from the stock solution and various quencher concentrations, the quenching experiment was carried out. 556 nm was used as the emission intensity, while the excitation wavelength was 360 nm.

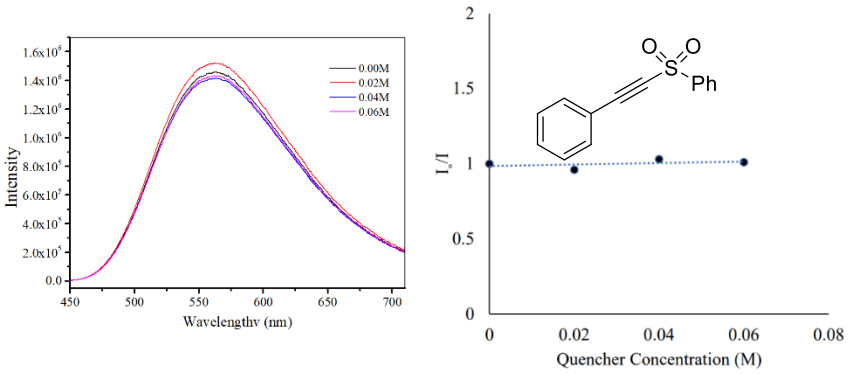


Figure 3: Fluorescence Quenching and stern-Volmer plot of 4CzIPN vs ((phenylethynyl)sulfonyl)benzene

As there is no significant decrease in fluorescence intensity of 4CzIPN, so we can exempt any kind of electron transfer process between 4CzIPN and ((phenylethynyl)sulfonyl)benzene.

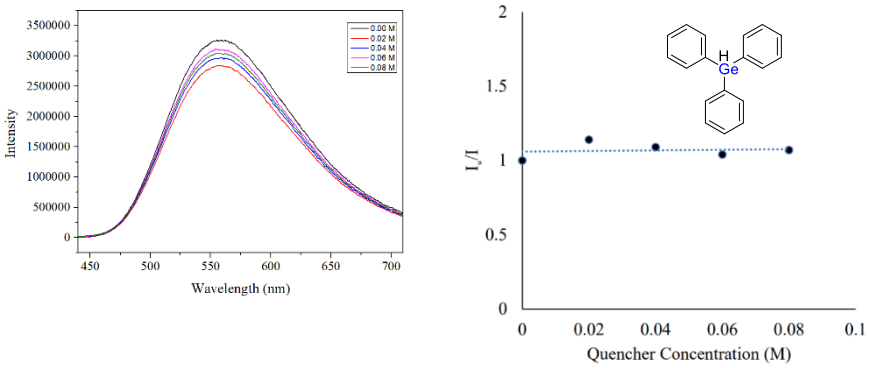


Figure 4: Fluorescence Quenching and Stern-Volmer plot of 4CzIPN vs Triphenylgermanium Hydride

As there is no significant decrease in the fluorescence intensity of 4CzIPN, so we can exempt any kind of electron transfer process between 4CzIPN and triphenylgermanium Hydride.

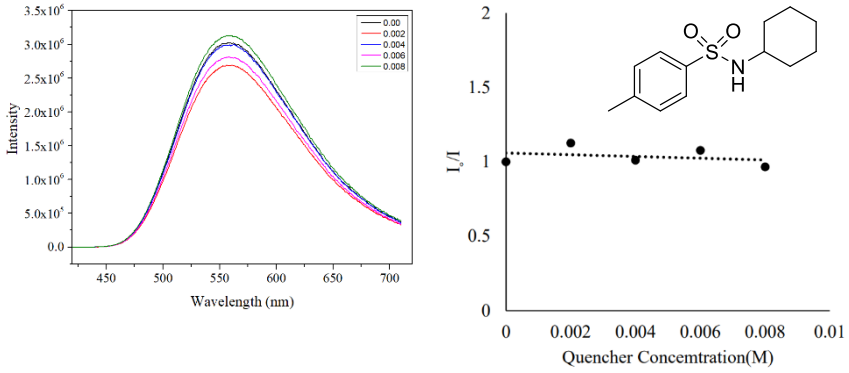


Figure 5: Fluorescence Quenching and Stern-Volmer plot of 4CzIPN vs N-cyclohexyl-4-methylbenzenesulfonamide

As there is no significant decrease in fluorescence intensity of 4CzIPN, so we can exempt any kind electron transfer process between 4CzIPN and N-cyclohexyl-4-methylbenzenesulfonamide.

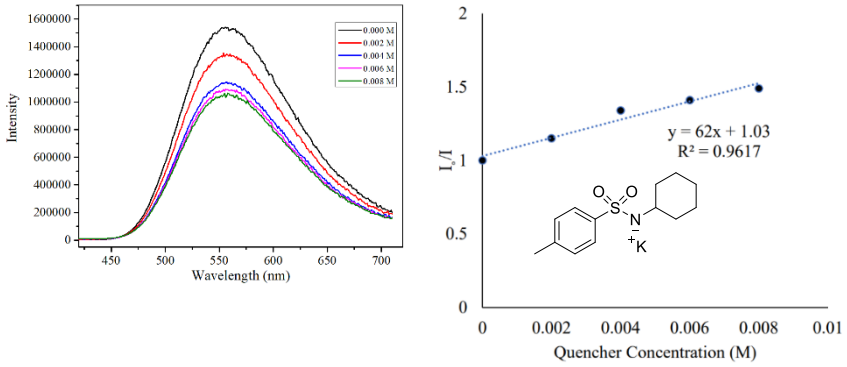


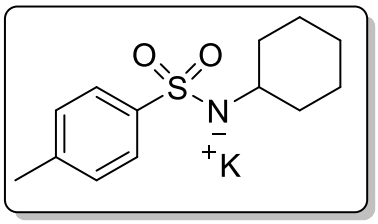
Figure 6: Fluorescence Quenching and Stern-Volmer plot of 4CzIPN vs potassium(I)cyclohexyl(tosyl)amide

As there is a significant decrease in the fluorescence intensity of 4CzIPN, we can conclude there might be an electron transfer process taking place between 4CzIPN and potassium(I)cyclohexyl(tosyl)amide.

Cyclic Voltammetry:

Using a three-electrode beaker-type cell and a C-H instrument model CHI1103C, cyclic voltammetry was measured at room temperature. Glassy carbon was used as the working electrode, a Pt-wire counter electrode, and Ag/AgCl (0.1M KCl aq. solution) as the working electrode in CH_3CN (15 mL, degassed and spectroscopic grade solvent) with $TBAPF_6$ (0.1M) electrode at a 0.1 V/s scan rate. No oxidation peak was observed for a sulfonamide HATC solution (0.005 M) in acetonitrile; this indicates that the excited 4CzIPN cannot oxidize HATC ($E_{1/2}^{red}$ [*4CzIPN / [4CzIPN] = +1.35 V versus saturated calomel electrode in MeCN).

Making *N*-cyclohexyl-4-methylbenzenesulfonamide Potassium Salt:



N-cyclohexyl-4-methylbenzenesulfonamide (HATC1) (98.8 mg, 0.39 mmol) was added to a solution of potassium tert-butoxide (43.76 mg, 0.39 mmol) in CH_3CN (4 mL). At room temperature, the mixture was agitated for three hours. The solvent was then extracted using a rotary evaporator. The salt was dried for three hours at a high vacuum (10 mbar pressure), producing a white solid that could be utilized right away for CV measurements. A beaker-type cell was filled with 15 mL of CH_3CN, 0.1M $TBAPF_6$ (582 mg), and the necessary potassium sulfonamide salt. The mixture was agitated for 10 minutes while N_2 gas was purged, and the CV was then recorded. The oxidation peak was noticed at + 0.83 V vs Ag/Ag^+ (0.1M KCl aq.) [+ 0.86 V vs. SCE]

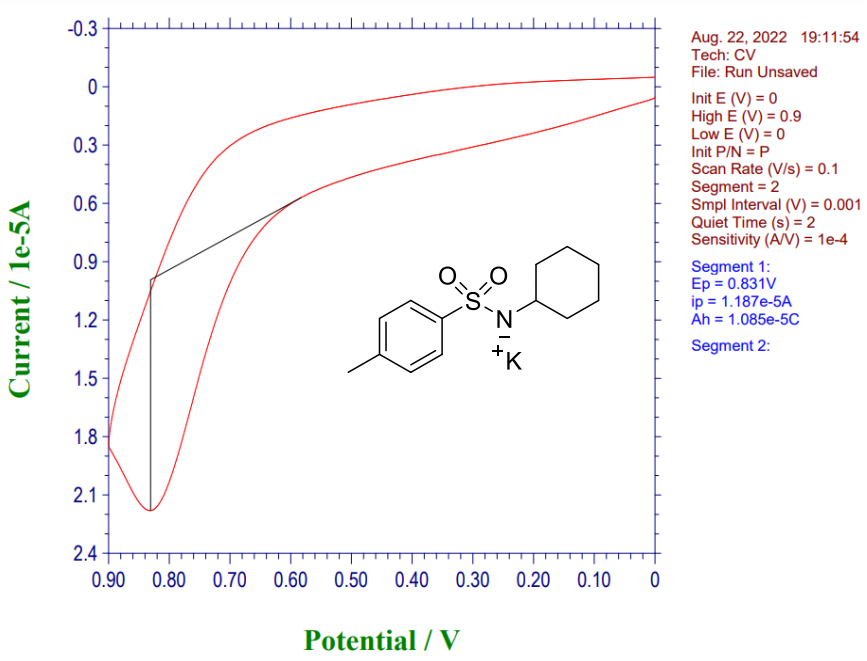


Figure 5: CV spectrum for Potassium Salt of N-cyclohexyl-4-methylbenzenesulfonamide

2.6. Plausible Mechanism: A plausible mechanism is suggested on the basis of previous reports [9] and control experiments, the reaction is following a radical pathway. At first, the photocatalyst 4CzIPN absorbs light from the blue LED and goes to an excited state to produce [4CzIPN]*. Then base abstract proton from sulfonamide to generate sulfamidyl anion. Now the excited photocatalyst takes up one electron from the sulfamidyl anion to generate sulfamidyl radical. This sulfamidyl radical then generates germyl radical through HAT. The generated germyl radical then attacks the substrate to generate species (II). After that species (II) rearranges to generate the final product (III) and the reduced photocatalyst gives a single electron to the phenyl sulfonyl radical to generate phenyl sulfonyl anion and regenerate the photocatalyst that will participate in the next photocatalytic cycle.

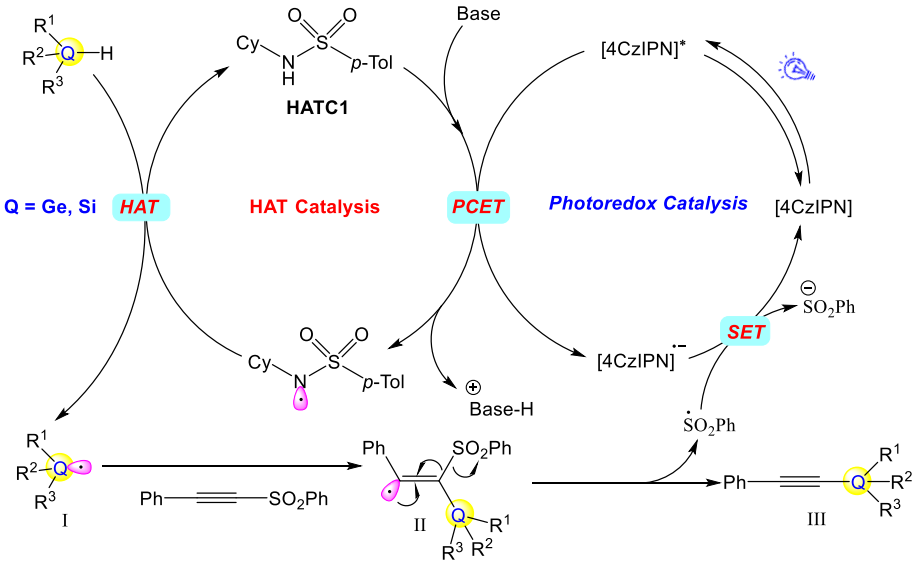
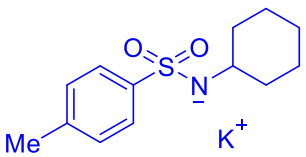


Figure 6: Plausible mechanism



4CzIPN*/4CzIPN$^{\bullet-}$

HATC1 [N$^{\bullet}$/N^{-}] = +0.86V vs SCE in CH_3CN

PC*/PC$^{\bullet-}$ = +1.35V vs SCE in CH_3CN

Chapter 3

EXPERIMENTAL SECTION

3.1. General Information

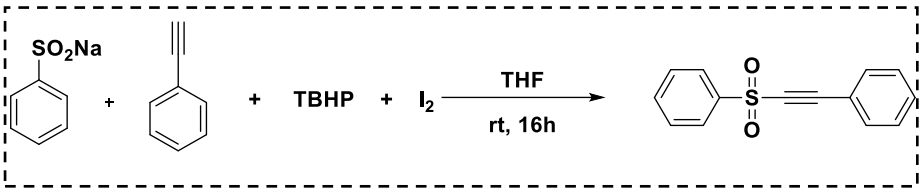
All of the chemicals and solvents were purchased from commercial sources. There was no purification done before using the chemicals and the solvent only hexane was distilled before use. All of the reactions were performed in an inert medium under the supervision of Merck 60 F254 precoated silica gel plates for TLC, and UV detection was used to monitor the results. Column Chromatography using silica gel (100-200 mesh and 230- 400 mesh) was used to get the pure products.

3.2. Instrumentation

Through NMR Spectra captured on a Bruker Advance 500 Spectrometer at 500 MHz (^{1}H) in $CDCl_3$, the purified products were verified. All chemical shift values are mentioned in the δ scale in ppm. The residual solvent peaks of $CDCl_3$ were recorded at 7.26. The multiplicities of desired peaks were denoted as given:

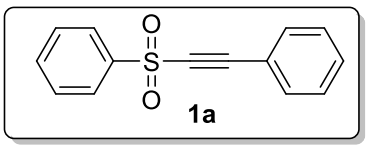
s = singlet
d = doublet
dd = doublet of doublet
t = triplet
q = quartet
m = multiplet

3.3.1. General synthesis of alkynylsulfones:

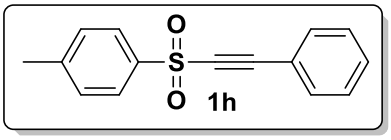


Scheme 7: Synthesis of Alkynylsulfones

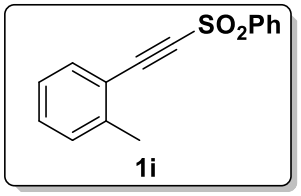
Appropriate phenylacetylene (3.0 mmol, 1.0 equiv.), iodine (1.5 mmol, 0.5 equiv.), and TBHP (9 mmol, 3.0 equiv.) were dissolved to a suspension of corresponding benzenesulfinic acid sodium salt (6 mmol, 2.0 equiv.) in (16 mL) of THF. The mixture was stirred for 16 h at 25 ℃ before the excess iodine was quenched with 10% aq. Sodium thiosulfate. The product was extracted into ethyl acetate (3 × 20 mL). The combined organic phases were washed with H_2O, and brine and dried over Na_2SO_4, and then filtered and concentrated in a vacuum. Then the residue was purified by column chromatography on silica gel using ethyl acetate and hexane mixtures as eluent to obtain pure samples of **1a, 1h, 1i, 1j, 1k, and 1l** as a yellowish solid [10].



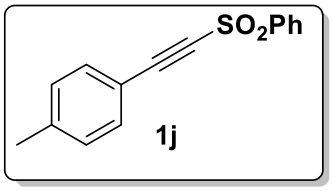
((Phenylethynyl)sulfonyl)benzene(1a): Yellow solid; 40% (290 mg);**^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.10 - 8.07 (m, 2 H), 7.71 - 7.68 (m, 1 H), 7.62 - 7.60 (m, 2H), 7.59 - 7.52 (m, 2 H), 7.49 - 7.46 (m, 1 H), 7.38 (m, 2 H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ ppm 141.9, 134.3, 132.9, 131.7, 129.5, 128.8, 127.5, 118.0, 93.6, 85.5; **IR** (neat): 3697, 2926, 2339, 2177, 1572, 1485, 1443, 1317, 1151, 1078, 847, 758, 722, 684, 648, 568, 532 cm^{-1}.



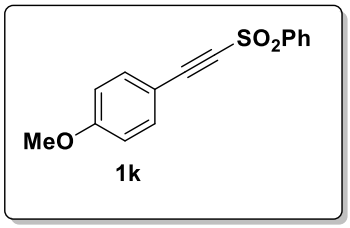
1-Methyl-4-((phenylethynyl)sulfonyl)benzene (1h): Yellow solid; 34% (260 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.56 - 7.50 (m, 2H), 7.49 - 7.44 (m, 1H), 7.42 - 7.33 (m, 4H), 2.47 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.5, 139.1, 132.9, 131.6, 130.1, 128.8, 127.7, 118.18, 9.11, 85.7, 21.9; **IR** (neat): 3681, 2923, 2339, 2174, 1587, 1483, 1321, 1148, 1075, 843, 808, 755, 674, 527 cm^{-1}.



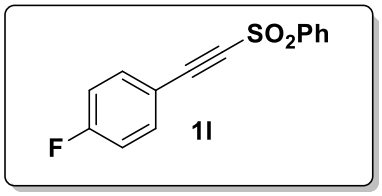
1-Methyl-2-((Phenylsulfonyl)ethynyl)benzene (1i): Yellow solid; 52% (404 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.11 - 8.05 (m, 2H), 7.71 - 7.57 (m, 1H), 7.63 - 7.57 (m, 2H),7.51 - 7.43 (m, 1H), 7.40 - 7.33 (m, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.10 - 7.15 (m, 1H), 2.38 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ ppm 142.6, 142.3, 134.2, 133.2, 131.7, 130.0, 129.5, 127.4, 126.0, 117.8, 93.3, 89.1, 20.5; **IR** (neat): 3693, 2923, 2340, 2167, 1481, 1445, 1316, 1151, 1077, 861, 756, 718, 684, 647, 542 cm^{-1}.



1-Methyl-4-((Phenylsulfonyl)ethynyl)benzene (1j): Yellow solid; 30% (234 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.10 - 8.06 (m, 2H), 7.71 - 7.65 (m, 1H), 7.62 - 7.56 (m, 2H),7.42 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ ppm 142.6, 142.1, 134.2, 132.8, 129.6, 129.5, 127.5, 114.8, 94.3, 85.0, 21.9; **IR** (neat): 3686, 2923, 2339, 2171, 1442, 1324, 1153, 1014, 850, 810 682, 608, 560, 505 cm^{-1}.

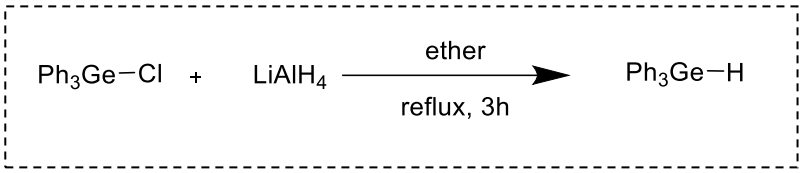


1-Methoxy-4-((Phenylsulfonyl)ethynyl)benzene (1k): Yellow solid; 48% (400 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 9.5 Hz, 2H), 7.73 - 7.63 (m, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ ppm 162.3,142.2, 134.8, 134.1, 129.5, 127.4, 114.6, 109.6, 94.8, 84.7, 55.6.



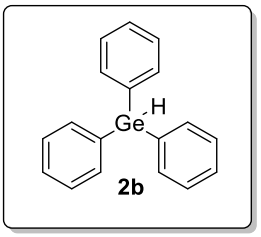
1-Fluoro-4-((phenylsulfonyl)ethynyl)benzene (1l): Yellow solid; 12% (90 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.4 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.53 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.5 (d, *J* = 255.1 Hz), 141.7, 135.2 (d, *J* = 8.9 Hz), 134.3, 129.5, 127.5, 116.4 (d, *J* = 22.5 Hz), 114.1 (d, *J* = 3.7 Hz), 92.5, 85.4 (d, *J* = 1.8 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.67 – -107.06 (m, 1H).

3.3.2. Synthesis of triphenylgermanium hydride (2b):



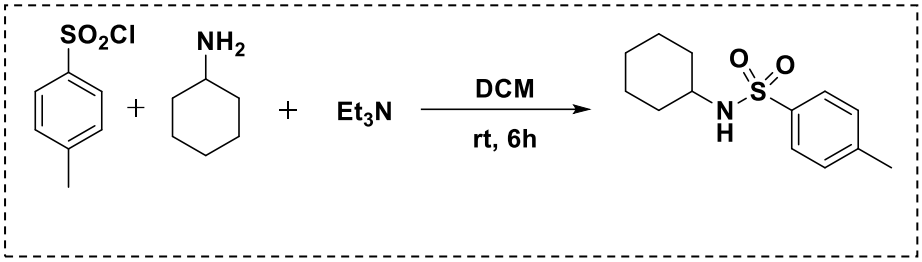
Scheme 8: Synthesis of triphenylgermanium hydride

$LiAlH_4$ (1.93 mmol, 1.28 equiv.) was added to an oven-dried RB in 4 ml of ether in an inert atmosphere at 0°C. Additionally, in another flame-dried flask, Ph_3GeCl (1.5 mmol, 1 equiv.) was added in 4mL ether. After that Ph_3GeCl solution was added dropwise to the solution of $LiAlH_4$. Reflux the resulting mixture for 3h. After 3h reaction mixture was quenched with 2M H_2SO_4 solution. Diethyl ether was used to extract the product (3×20 mL). The mixed organic phases were concentrated and dried over Na_2SO_4 after being filtered. Purification was done by silica gel column chromatography using hexane as the eluent to afford the desired germanium hydride in 88% yield. Hexane was used as the eluent during the silica gel column chromatography purification process, which produced the required germanium hydride in an 88% yield [11].



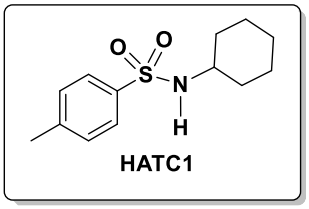
Triphenylgermanium hydride (2b): Colourless liquid; 88% (402 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 - 7.53 (m, 6H), 7.43 - 7.36 (m, 9H), 5.72 (s, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.6, 135.2, 129.3, 128.4.

3.3.3. Procedure for the Synthesis of Hydrogen Transfer Atom Catalyst.



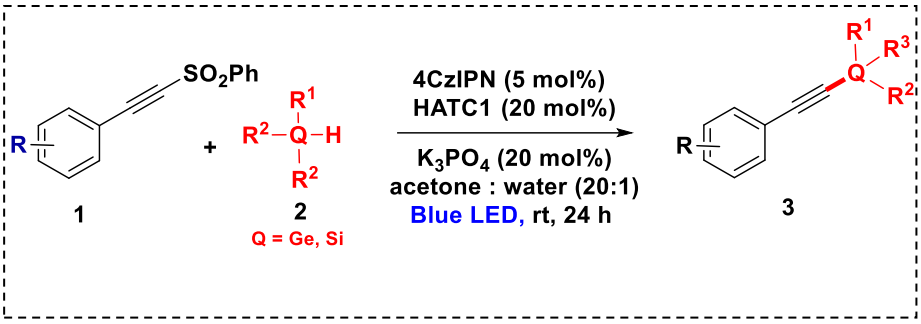
Scheme 9: Synthesis of HATC1

To a solution of (40 mL) DCM, cyclohexylamine (0.5g, 5 mmol Et_3N (0.5g, 5 mmol, 1 equiv.) and *p*-toluenesulfonyl chloride (0.95 g, 5 mmol, 1 equiv.) were added. The mixture was then swirled for 6 hours at 25 ℃. After that, (40 mL) of $NaHCO_3$ was used to quench the reaction mixture. DCM was used to extract the product (3 × 20 mL). The combined organic phase was concentrated in a vacuum and dried on Na_2SO_4. The pure product was obtained after purification by column using 8% of EtOAc and hexane solution in 80% yield [12].



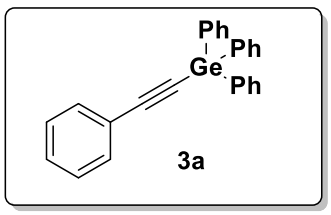
N-Cyclohexyl-4-methylbenzenesulfonamide: White solid 50% (612 mg)**;** ^{1}**H NMR** (500 MHz, $CDCl_3$) δ ppm 7.75 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.29 (d, *J* = 7.6 Hz, 1H), 3.25 - 3.03 (m, 1H), 2.43 (s, 3H), 1.67 - 1.54 (m, 10H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ ppm 143.2, 138.6, 129.7, 127.0, 52.7, 34.0, 25.3, 24.7, 21.6; **IR** (neat): 3686, 3304, 2931, 2855, 2339, 1766, 1595, 1426, 1321, 1150, 1069, 995, 880, 812, 658, 555 cm^{-1}.

3.3.4. General synthesis of alkynylgermane 3(a-f) & alkynylsilane 3g:



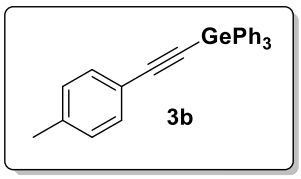
Scheme 10: Synthesis of alkynylgermane and alkynylsilane

To an oven-dried reaction tube **1** (0.1mmol, 1equiv), Ph_3Ge-H **2** (0.2 mmol, 2 equiv), 5 mol% 4CzIPN, 20 mol% K_3PO_4, and 20 mol % **HATC** were taken with acetone and water (20:1) as a solvent and sealed the reaction tube. After that, the reaction mixture was degassed via freeze pump thaw (×3 times) and provided an argon atmosphere to the reaction mixture. The sealed reaction tube was then placed under the blue LED lamp and irradiated for 24h. After completion of the reaction, the reaction mixture was filtered, and dried over Na_2SO_4, and the solvent was removed on a rotatory evaporator under reduced pressure. The crude product was purified by flash column chromatography using silica gel (mesh 100-200) using hexane to give the desired product **3(a-f)** & **(3g-h).**

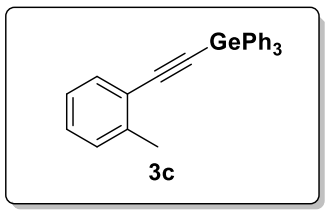


Triphenyl(phenylethynyl)germane (3a): Colourless liquid; 56% (22.68 mg)**;** ^{1}**H NMR** (500 MHz, $CDCl_3$) δ ppm 7.71 - 7.65 (m, 6H), 7.60 - 7.57 (m, 2H), 7.44 - 7.38 (m, 9H), 7.37 - 7.31 (m, 3H); ^{13}**C NMR**

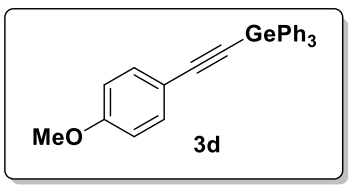
(126 MHz, $CDCl_3$) δ ppm 135.2, 134.6, 132.2, 129.5, 128.7, 128.42 128.3, 128.01, 108.1, 88.7; **HRMS** (ESI, *m/z*) - $[M+Na]^+$ Calcd $C_{26}H_{20}Ge$ 429.0674, found 429.0683.



Triphenyl(p-tolylethynyl)germane (3b): Colourless liquid; 48% (20.1 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 - 7.66 (m, 6H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.42 (dd, *J* = 5.5, 1.7 Hz, 9H), 7.15 (d, *J* = 7.9 Hz, 2H), 2.37 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.0, 135.5, 134.7, 132.2, 129.6, 129.1, 128.5, 120.2, 108.5, 87.9, 21.7.

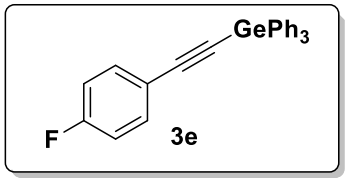


Triphenyl(o-tolylethynyl)germane (3c): Colourless liquid; 57% (24.2 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 - 7.66 (m, 6H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 9H), 7.24 (s, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 2.53 (s, 3H); **^{13}C NMR** (126 MHz $CDCl_3$) δ 141.0, 135.5, 134.7, 132.6, 129.6, 129.6, 128.8, 128.5, 125.6, 123.0, 107.2, 92.7, 21.1.



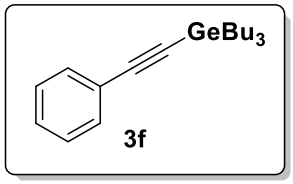
((4-Methoxyphenyl)ethynyl)triphenylgermane (3d): Colourless liquid; 62% (27.4 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.4

Hz, 6H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 5.2 Hz, 9H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.0, 135.6, 134.7, 133.8, 129.6, 128.5, 115.4, 114.0, 108.4, 87.0, 55.5; **IR** (neat): 3697, 2932, 2329, 2171, 1599, 1502, 1312, 1251, 1147, 1077, 1020, 859, 823, 770, 720, 683, 616, 565, 530 cm^{-1}.



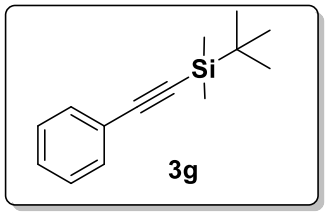
3e

((4-Fluorophenyl)ethynyl)triphenylgermane (3e): Colourless liquid; 56% (24 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 - 7.65 (m, 6H), 7.59 - 7.54 (m, 2H), 7.45 - 7.41 (m, 9H), 7.03 (t, *J* = 8.7 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.9 (d, *J* = 250.1 Hz), 137.6, 135.2, 134.7, 134.5, 134.3 (d, *J* = 8.4 Hz), 129.7, 129.5, 128.6, 128.1, 119.3 (d, *J* = 3.6 Hz), 115.7 (d, *J* = 22.1 Hz), 107.0, 88.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -110.0.

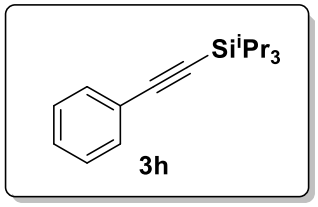


3f

Tributyl(phenylethynyl)germane (3f): Colourless liquid; 60% (20.7 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 - 7.43 (m, 2H), 7.32 - 7.27 (m, 3H), 1.52 - 1.44 (m, 7H), 1.41 - 1.36 (m, 6H), 0.92 (td, *J* = 7.8, 7.2, 3.9 Hz, 15H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 132.1, 128.3, 128.0, 124.1, 105.9, 93.1, 27.6, 26.6, 14.3, 13.9.

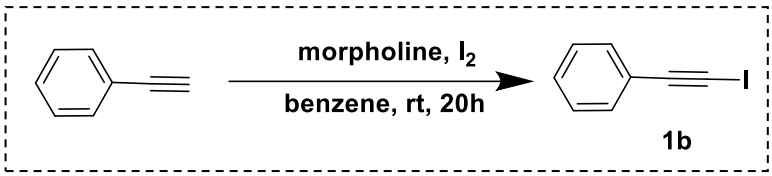


Tert-butyldimethy(phenylethynyl)silane (3g); Colourless liquid; 30% (6.4 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (s, 2H), 7.30 (s, 3H), 1.00 (s, 9H), 0.18 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 132.1, 128.6, 128.3, 123.4, 105.9, 92.6, 26.3, 16.9, -4.4.



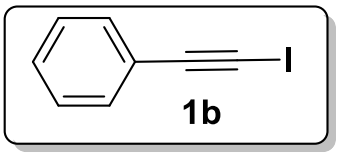
Triisopropyl(phenylethynyl)silane(3h); Colourless liquid; 40% (10.3 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.30 (dd, *J* = 5.1, 1.9 Hz, 3H), 1.14 (s, 21H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 132.2, 128.4, 128.3, 123.7, 107.5, 90.6, 18.8, 11.5.

3.3.5. Procedure for the synthesis of (iodoethynyl)benzene (1b).



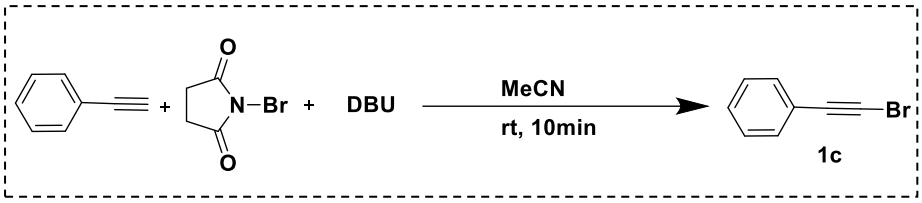
Scheme 11: Synthesis of 1b

To an oven-dried RB, iodine (3.3 mmol, 1.1 equiv.) was dissolved in 30mL benzene under an argon atmosphere and then treated with morpholine (9 mmol, 3 equiv.). After stirring for 30 min at room temperature, phenylacetylene (3 mmol, 1 equiv.) was added. And then the reaction was continued for 20h. The resulting suspension was filtrated and diluted with ether. The organic layer was washed with sat. NH_4Cl, $NaHCO_3$, and water dried over $MgSO_4$. The solvent was evaporated and purified by column chromatography using hexane as the eluent to afford the desired iodoalkyne product [13].



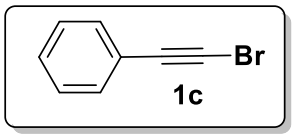
(Iodoethynyl)benzene (1b): Yellow liquid; 84% (589 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 - 7.43 (m, 2H), 7.35 - 7.29 (m, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 132.4, 128.9, 128.4, 123.5, 94.3, 6.4; **IR** (neat): 3688, 3056, 2923, 1589, 1484, 1440, 1063, 1023, 914, 816, 750, 684, 517 cm^{-1}.

3.3.6. Procedure for the synthesis of (Bromoethynyl)benzene (1c).



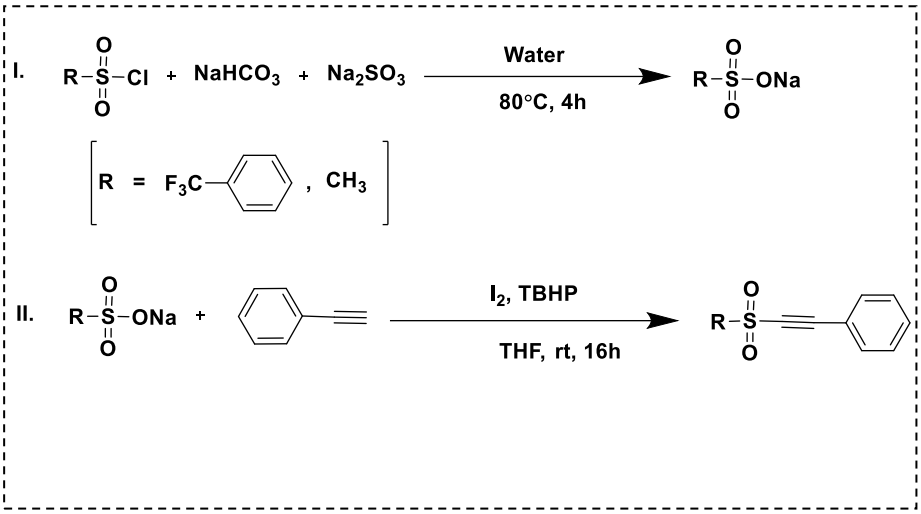
Scheme 12: Synthesis of 1c

To an oven, dried round bottom flask phenylacetylene (6 mmol, 1.0 equiv), NBS (6.6 mmol, 1.1 equiv), and DBU (6.6 mmol, 1.1 equiv) in MeCN (12 mL) were added. For 10 minutes, the mixture was mixed at room temperature and then the solution was poured into water and then extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was concentrated under reduced pressure, filtered, and with water. Purification was done using flash column chromatography using hexane as the eluent to afford the desired bromoalkyne product [14].



(Bromoethynyl)benzene (1c): Yellow liquid; 71% (775 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 - 7.45 (m, 2H), 7.34 (tdd, J = 8.8, 6.9, 4.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 132.1, 128.8, 128.5, 122.8, 80.2, 49.9; **IR** (neat): 3701, 3060, 2924, 2197, 1750, 1593, 1485, 1442, 1166, 1063, 1024, 751, 686, 610, 515 cm^{-1}.

3.3.7. General Synthesis of (methylsulfonyl)ethynyl)benzene (1e) & 1-((phenylethynyl)sulfonyl)-4-(trifluoromethyl)benzene (1g).

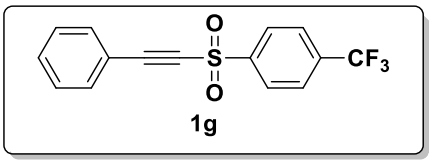


Scheme 13: Synthesis of 1e &1g

I. To 25 mL RB sodium sulfite (4 mmol, 2 equiv.), sodium bicarbonate (4 mmol, 2 equiv.) and the sulfonyl chloride (2 mmol, 1 equiv.) was taken and dissolved in 2mL of distilled water and then the reaction mixture was stirred for 4h at 80 ℃. After that reaction mixture was cooled to room temperature and water was removed at reduced pressure. To that white residue 5 mL ethanol was added and concentrated the filtrate under reduced pressure to obtain the 4-(trifluoromethyl)benzenesulfonic acid, sodium salt.

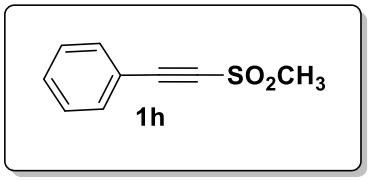
II. Phenylacetylene (0.835 mmol, 1.0 equiv.), iodine (0.417 mmol, 0.5 equiv.), and TBHP (2.5 mmol, 3.0 equiv.) were added to a suspension of benzenesulfinic acid sodium salt (1.67 mmol, 2.0 equiv.) in (5 mL) of THF. The excess iodine was quenched with 10% $Na_2S_2O_3$ solution after the mixture had been agitated for 16 hours at room temperature. The product was extracted into ethyl acetate (3 × 20 mL). The combined organic phases were washed with H_2O, brine dried over Na_2SO_4, and then filtered and concentrated in a vacuum. Flash column chromatography was used to clean up the impurified product using 2%

EtOAc and hexane mixture as eluent to obtain a pure sample of **1g and 1e** in good yield [15].



1g

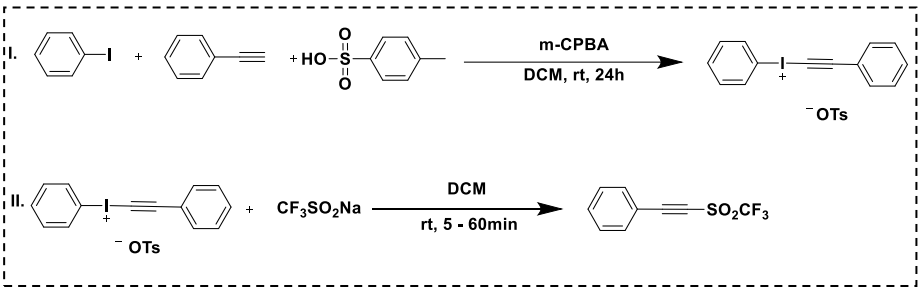
1-((Phenylethynyl)sulfonyl)-4-(trifluoromethyl)benzene(1g): Yellow solid; 40% (108 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.2 Hz, 2H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.57 - 7.53 (m, 2H), 7.53 - 7.49 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.3, 135.9 (d, *J* = 33.2 Hz), 133.0, 132.1, 128.6 (d, *J* = 96.4 Hz), 126.7 (q, *J* = 3.7 Hz), 124.3, 122.1, 117.5, 95.1, 84.8.; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -63.23; **IR** (neat): 3687, 2925, 2172, 1747, 1322, 1149, 1057, 834, 710, 659, 586, 526 cm^{-1}.



1h

(Methylsulfonyl)ethnyl benzene(1g): Yellow solid; 27% (169 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 3.30 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.0, 131.9, 129.0, 117.6, 91.7, 84.6, 46.9.

3.3.8. Procedure for the synthesis of (((trifluoromethyl)sulfonyl)ethynyl)benzene (1d).

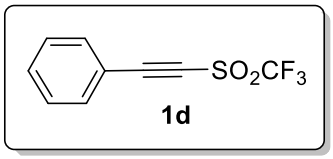


Scheme 14: Synthesis of 1d

I. Addition of m-CPBA (3 mmol, 1 equiv.) to a solution of iodobenzene (3 mmol, 1 equiv.), para-toluene sulphonic acid monohydrate (3 mmol, 1 equiv.) and phenylacetylene (6 mmol, 2 equiv.) in 25 mL of DCM over a period of 1h at 0°C in 100 mL RB. After that reaction mixture was stirred for 24h at room temperature. After 24h reaction mixture was reduced to half volume in reduced pressure at ambient temperature. Addition of diethyl ether (10 mL) to the reaction mixture in a dropwise manner, with gentle stirring. Reduce the resulting homogeneous solution again to half volume in reduced pressure. Addition of diethyl ether (50 mL) again with gentle stirring over a period of 1h. Allow the resulting suspension to stand for 1h, after that filtered the precipitate and washed with ether. Dried the precipitate under a vacuum to obtain the product. Recrystallization was done in DCM and ether to obtain the pure phenyl(phenylethynyl)iodonium 4-methyl benzenesulfonate [16].

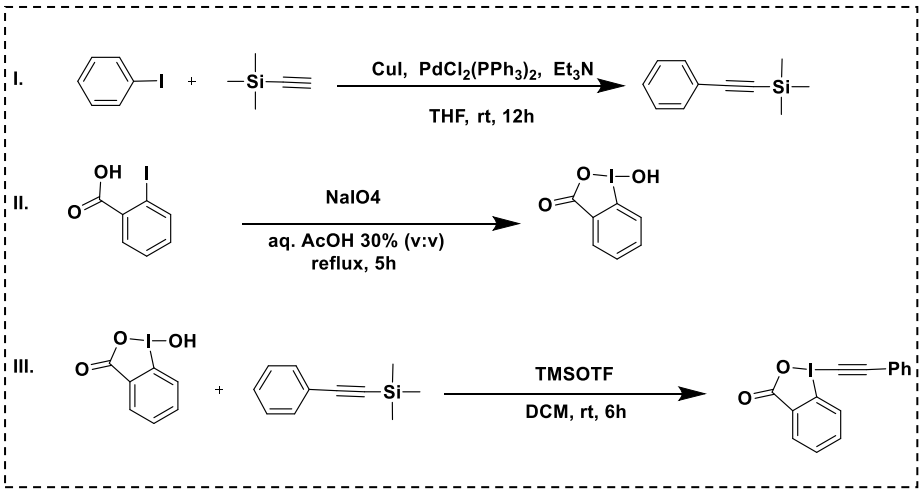
II. To an oven-dried 100 mL RB charged with phenyl(phenylethynyl)iodonium 4-methyl benzenesulfonate (0.83 mmol, 1 equiv.) and sodium trifluoromethanesulfinate (1.66 mmol, 2 equiv.), the flask was evacuated and backfilled with argon three times. To the mixture, 10 mL DCM was added and stirred vigorously at room temperature for 5 – 60 min. After that, the reaction mixture was concentrated in a vacuum and purified by column chromatography on

silica gel using mixture of hexane and ethyl acetate as eluents to afford the desired (((trifluoromethyl)sulfonyl)ethynyl)benzene [17].



(((Trifluoromethyl)sulfonyl)ethynyl)benzene (1d): Yellow liquid; 18% (37 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 - 7.67 (m, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H):); **^{13}C NMR** (126 MHz, CDCl3)δ 133.7 (d, *J* = 1.9 Hz), 133.4 (d, *J* = 1.5 Hz), 129.1 (d, *J* = 5.6 Hz), 119.0 (dq, *J* = 322.4, 4.1Hz,), 115.8 (d, *J* = 86.3 Hz), 100.8, 77.3 (dd, *J* = 178.9, 2.2 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -79.56.

3.3.9. Procedure for the synthesis of 1-[Phenylethynyl]-1,2-benziodoxol-3-(1*H*)-one (1f).



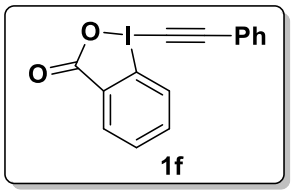
Scheme 15: Synthesis of 1f

I. Iodobenzene (4 mmol, 1 equiv.), $PdCl_2(PPh_3)_2$ (0.04 mmol, 1 mol%) and CuI (0.08 mmol, 2 mol%) was dissolved in (16 mL) tetrahydofuran. Addition of Et_3N (10 mmol, 2.5 equiv.) was done under O_2 free atmosphere and the resulting mixture was stirred for 1h at room

temperature. And then trimethylsilylacetylene (6 mmol, 1.5 equiv.) was added to the reaction mixture and stirred the suspension at room temperature for 12h. After completion of the reaction the reaction mixture was reduced under reduced pressure. Cosolvent dichloromethane and ethyl acetate are used to dissolve the residue. Filtered the resulting mixture through celite and reduced the cosolvent under reduced pressure. Purification was done by silica gel column chromatography using hexane as the eluent to afford the desired 2-(Trimethylsilyl)ethynyl) benzene [18].

II. To the aqueous solution of acetic acid 7.5 mL, $NaIO_4$ (4.23 mmol, 1.05 equiv.) and 2- iodobenzoic acid (4.03 mmol, 1 equiv.) were added. The mixture was agitated stirred and refluxed for 4h. After that, the reaction mixture was diluted with cold water and allowed to cool to room temperature while being kept out of the light. After an hour, the crude product was recovered via filtering to get the pure product EBX, the unclean crystals were washed with cold water, then acetone, then dried by air in the dark [19].

III. To the suspension of 1-[Hydroxy]-1,2-benziodoxol-3-(1*H*)-one (0.7 mmol, 1 equiv.), trimethylsilyl triflate (0.77 mmol, 1.1 equiv.) was added dropwise in DCM (2mL) at 0℃. (Trimethylsilyl)ethynyl)benzene was added dropwise and stirred the mixture for one hour. A white solid formed after the following suspension was agitated for 6 hours at room temperature. The mixture was then saturated using the solution of $NaHCO_3$, and vigorous stirring was done for 30 minutes. The organic layer of the mother liquors was washed with sat. $NaHCO_3$, dried on $MgSO_4$ and the solvent was evaporated under low pressure. The resulting solid was recrystallized in ethyl acetate and methanol (7:3). To obtain the pure product the solution was allowed to cool to room temperature, then keep in the freezer overnight, filtered, and dried under high vacuum to afford the 1-[Phenylethynyl]-1,2-benziodoxol-3-(1*H*)-one [20].



1-[Phenylethynyl]-1,2-benziodoxol-3-(1*H*)-one(1f): Brown solid; 42% (105 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.47 - 8.39 (m, 1H), 8.29 - 8.20 (m, 1H), 7.83 - 7.72 (m, 2H), 7.66 - 7.57 (m, 2H), 7.53 - 7.47 (m, 1H), 7.47 - 7.40 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.7, 135.0, 133.0, 132.6, 131.7, 131.5, 130.9, 128.9, 126.4, 120.7, 116.3, 106.7, 50.3; **IR** (neat): 3688, 3054, 2923, 2339, 2133, 1607, 1432, 1329, 1294, 1003, 799, 683, 557, 527 cm^{-1}.

Chapter 4
CONCLUSION

In conclusion, we have demonstrated a mild and efficient photocatalytic method for the synthesis of alkynylgermane without using an excess of base or catalysts. This method is operationally simple, and metal-free using 4CzIPN as an organophotocatalyst. Also, extended our approach to the synthesis of alkynylsilane. Our tests have shown the formation of products that are mostly new compounds that could play a very important role in organogermanium chemistry and organic synthesis as well as being precursors for optoelectronic materials.

CHARACTERIZATION DATA

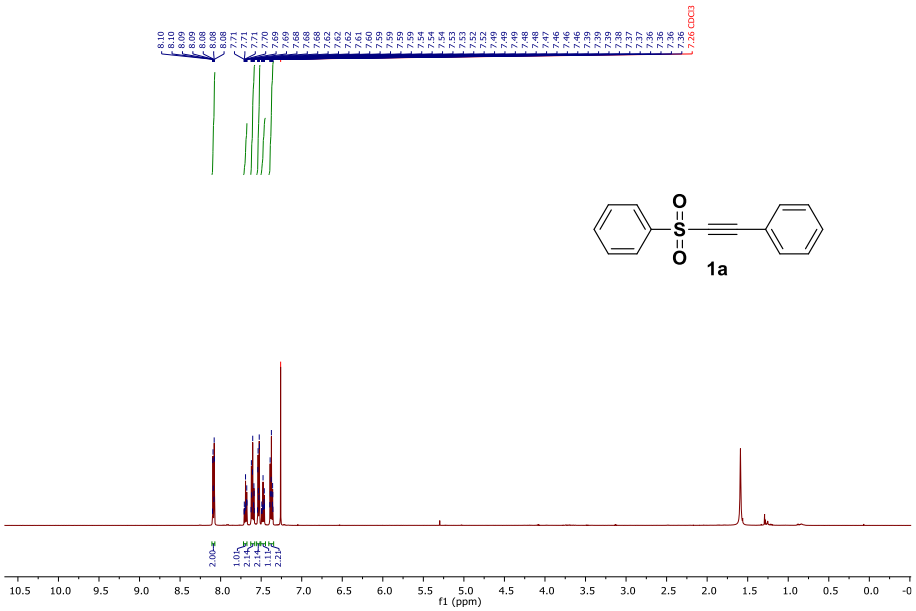


Figure 7: ^{1}H NMR Spectrum of 1a

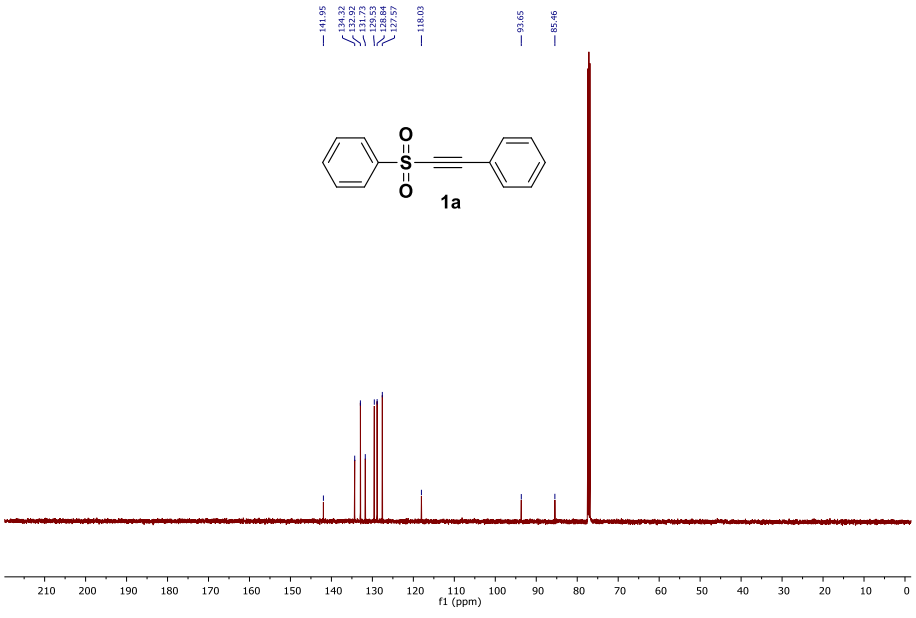


Figure 8: ^{13}C NMR Spectrum of 1a

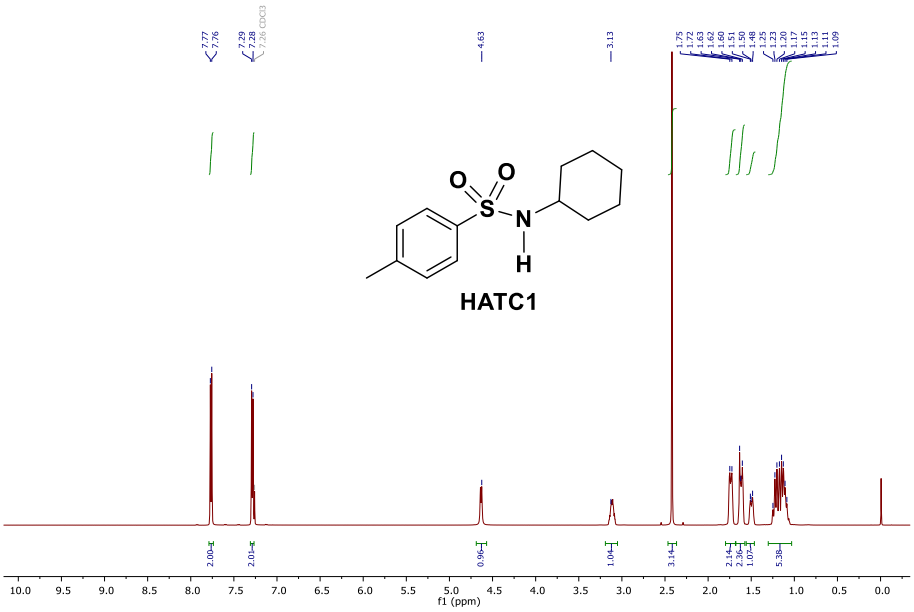


Figure 9: ^{1}H NMR Spectrum of HATC1

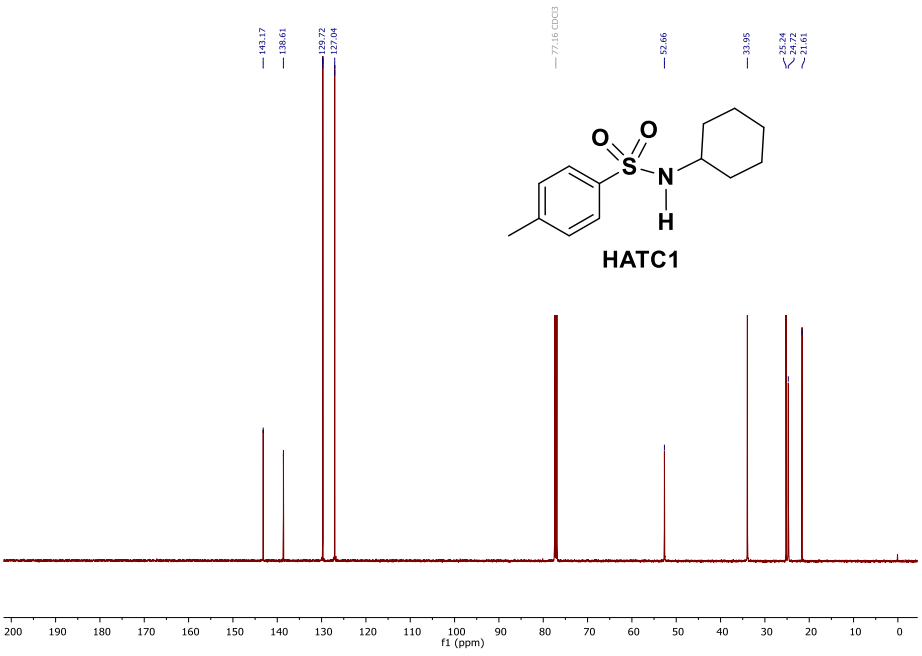


Figure 10: ^{13}C NMR Spectrum of HATC1

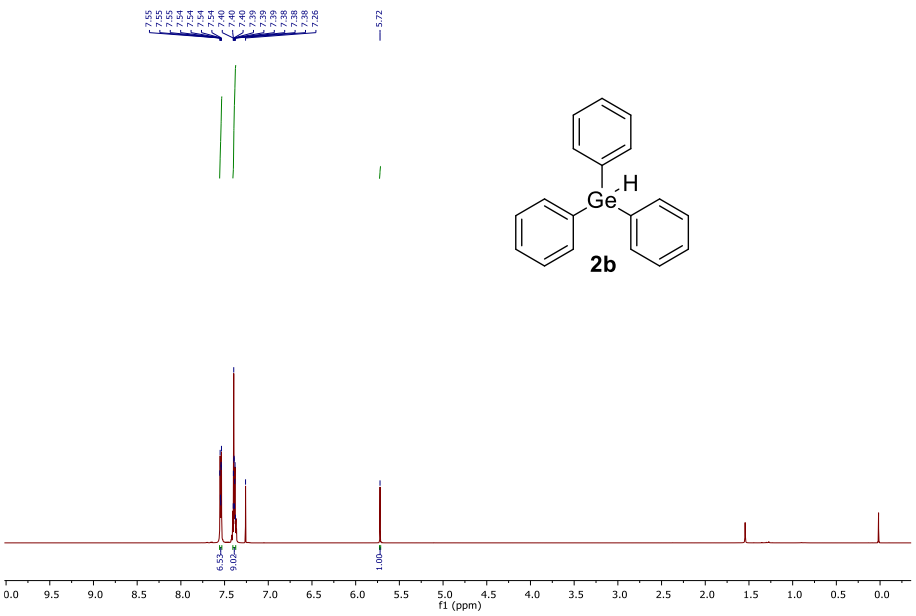


Figure 11: ^{1}H NMR Spectrum of 2b

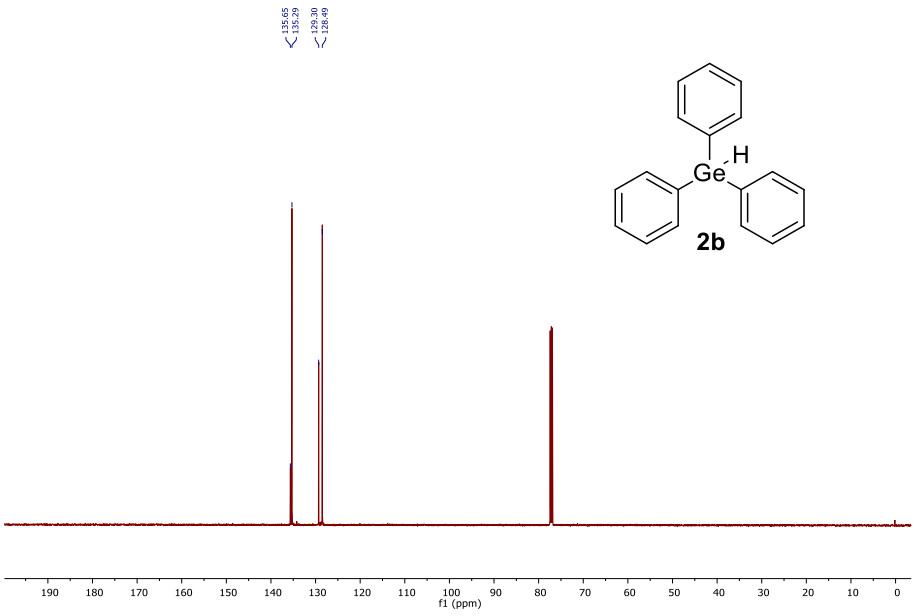


Figure 12: ^{13}C NMR Spectrum of 2b

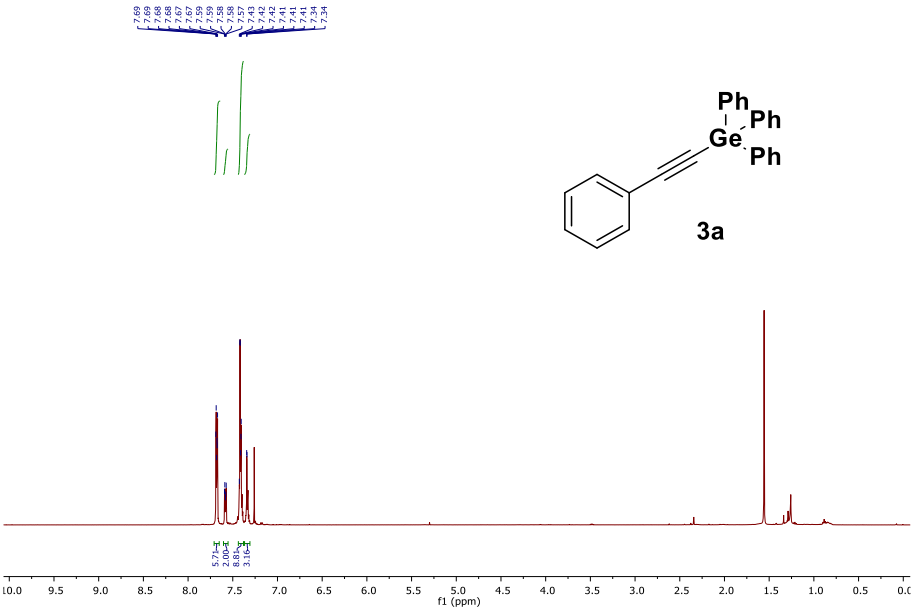


Figure 13: ^{1}H NMR Spectrum of 3a

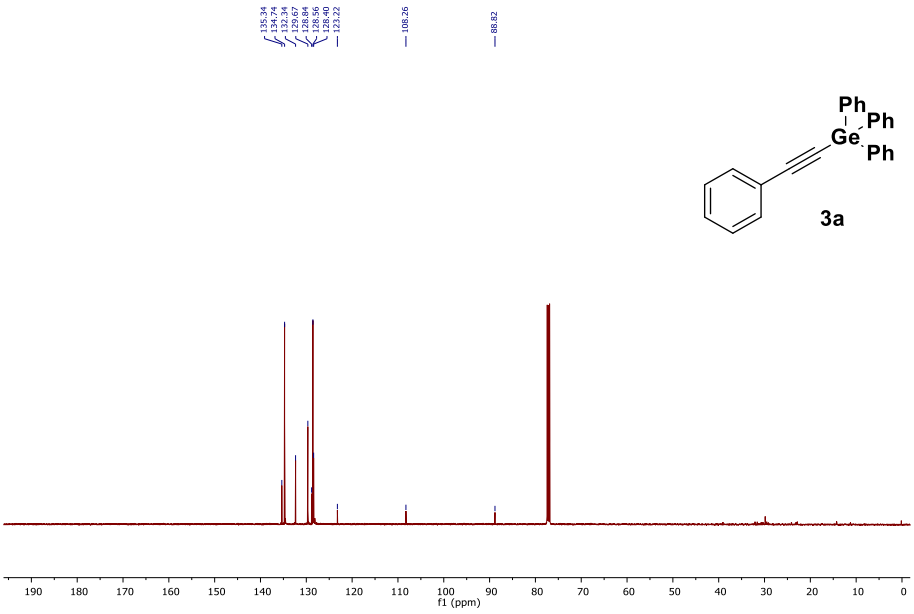


Figure 14: ^{13}C NMR Spectrum of 3a

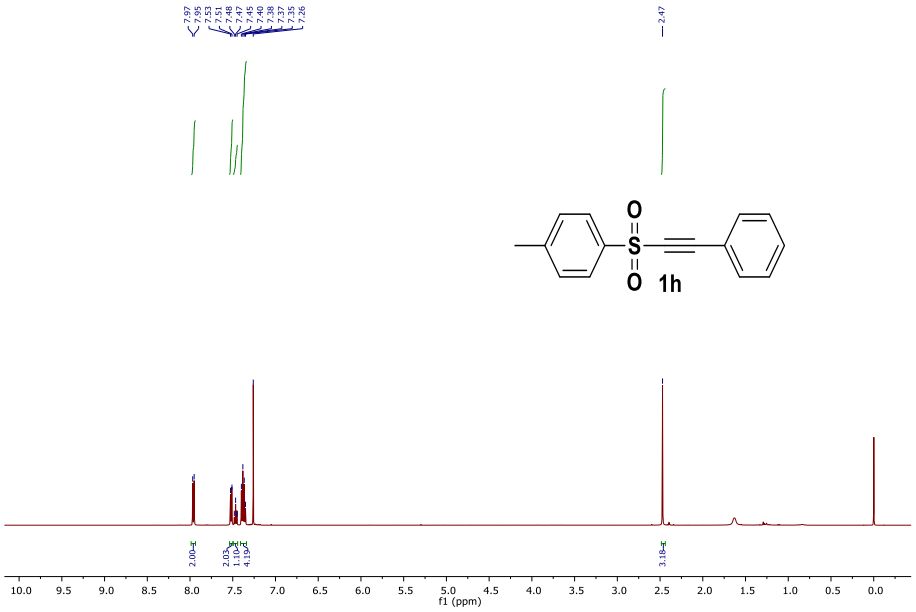


Figure 15: ^{1}H NMR Spectrum of 1h

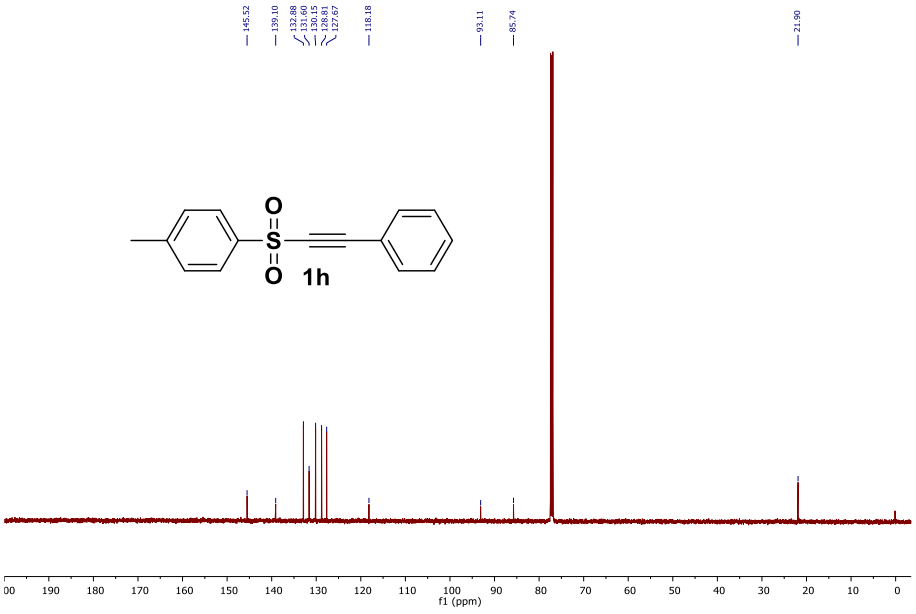


Figure 16: ^{13}C NMR Spectrum of 1h

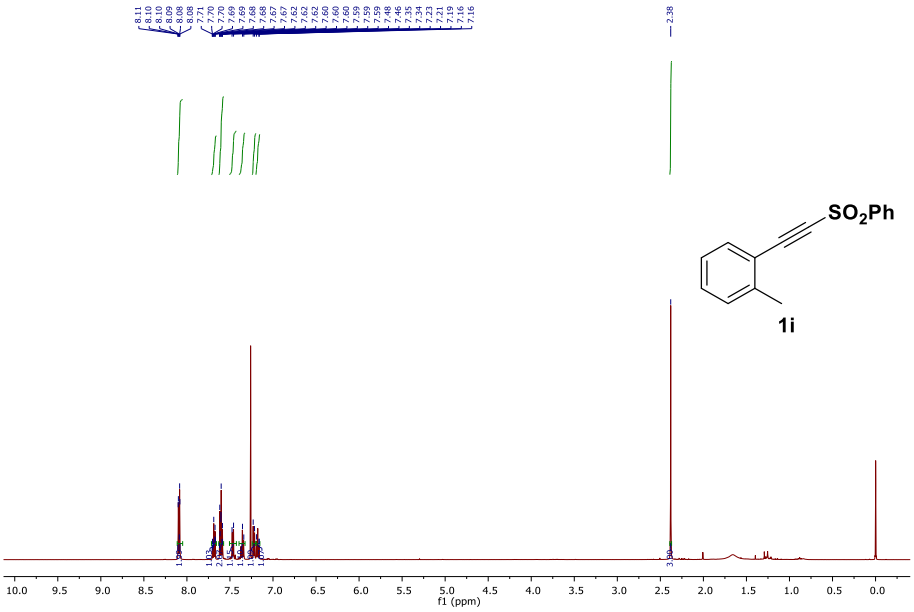


Figure 17: ^{1}H NMR Spectrum of 1i

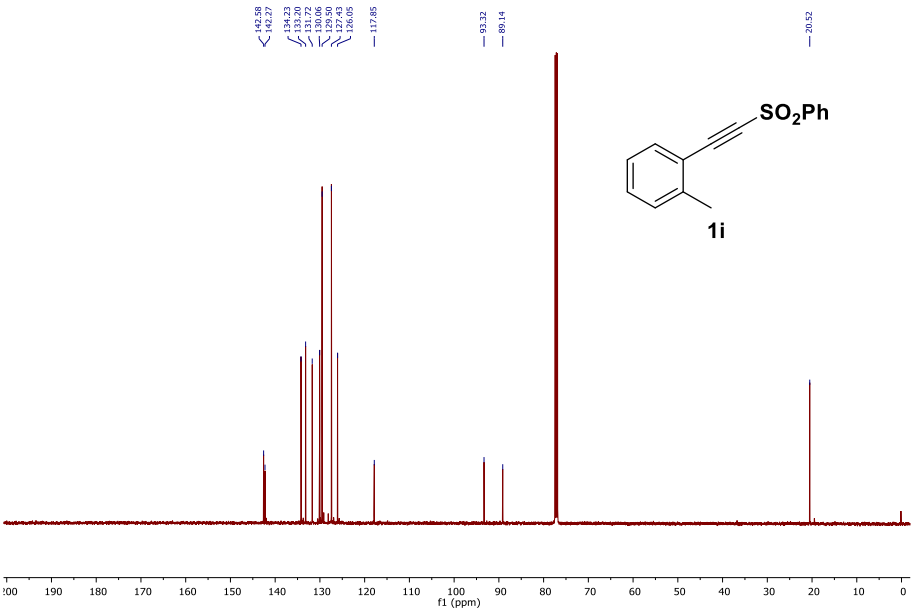


Figure 18: ^{13}C NMR Spectrum of 1i

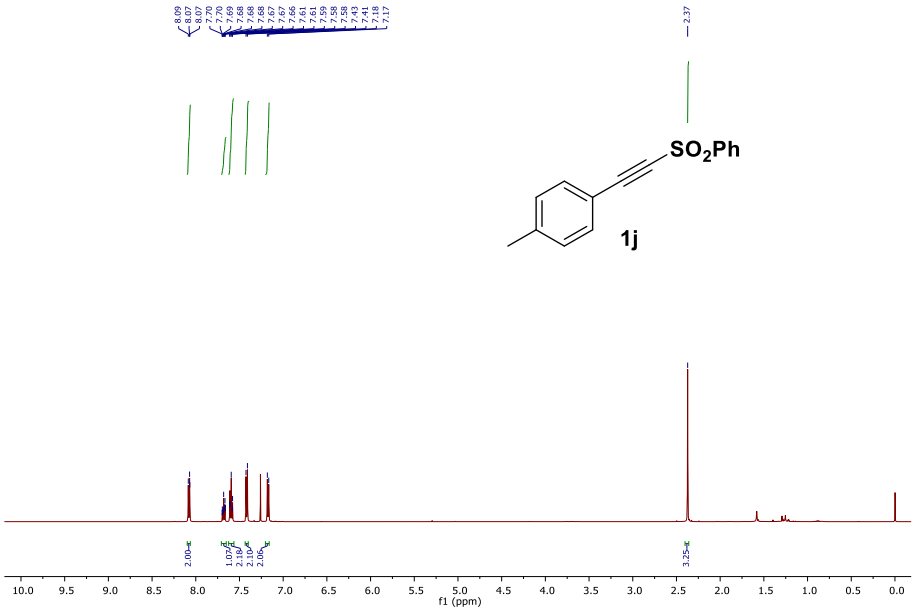


Figure 19: ^{1}H NMR Spectrum of 1j

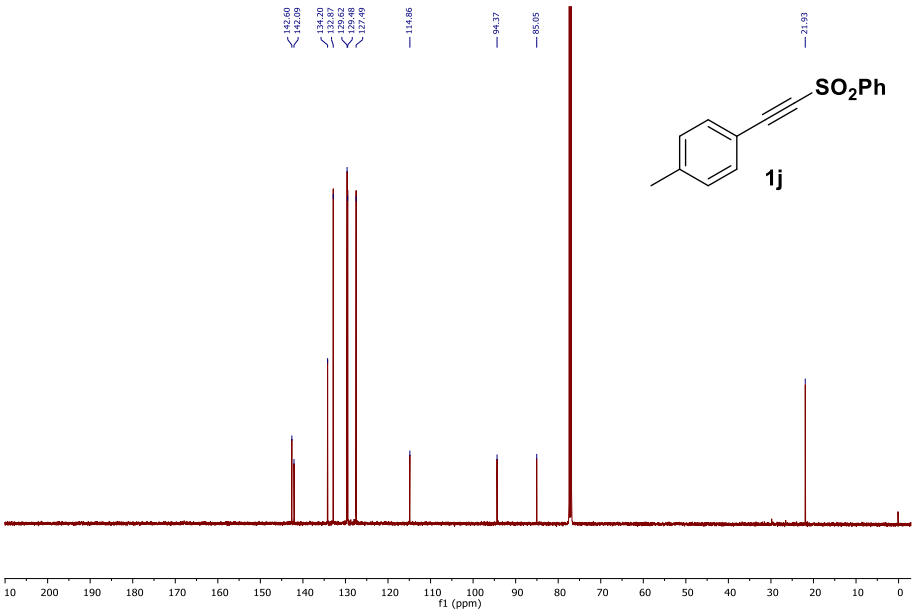


Figure 20: ^{13}C NMR Spectrum of 1j

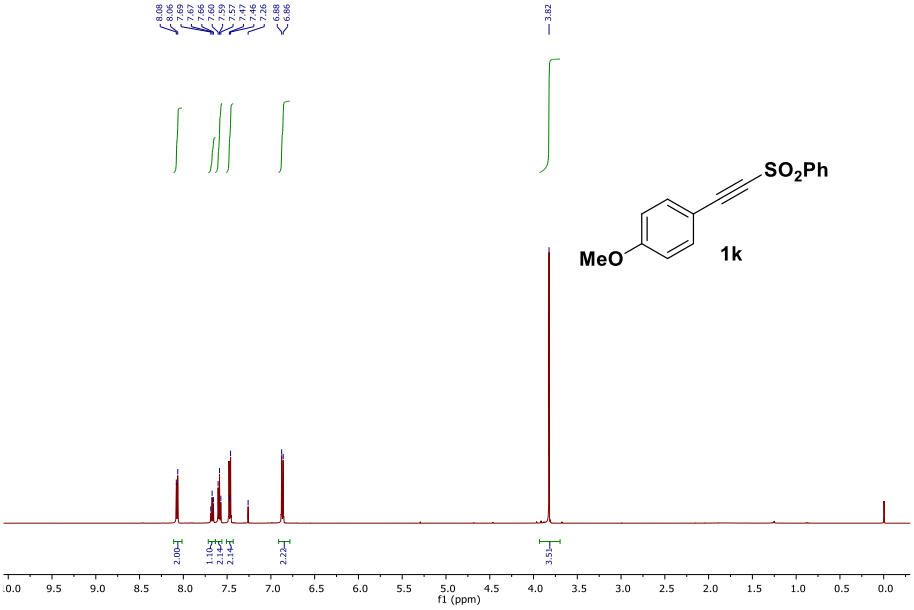


Figure 21: [1]H NMR Spectrum of 1k

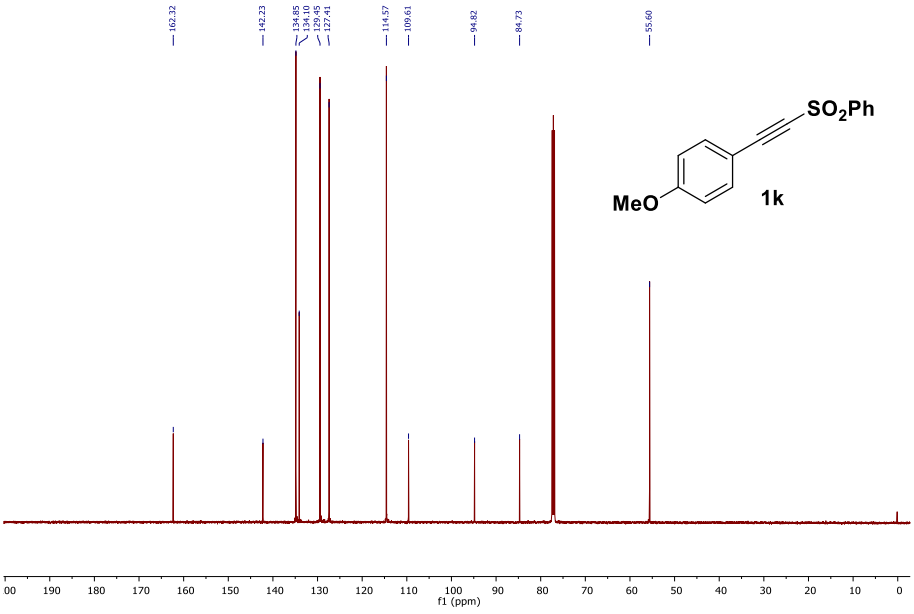


Figure 22: [13]C NMR Spectrum of 1k

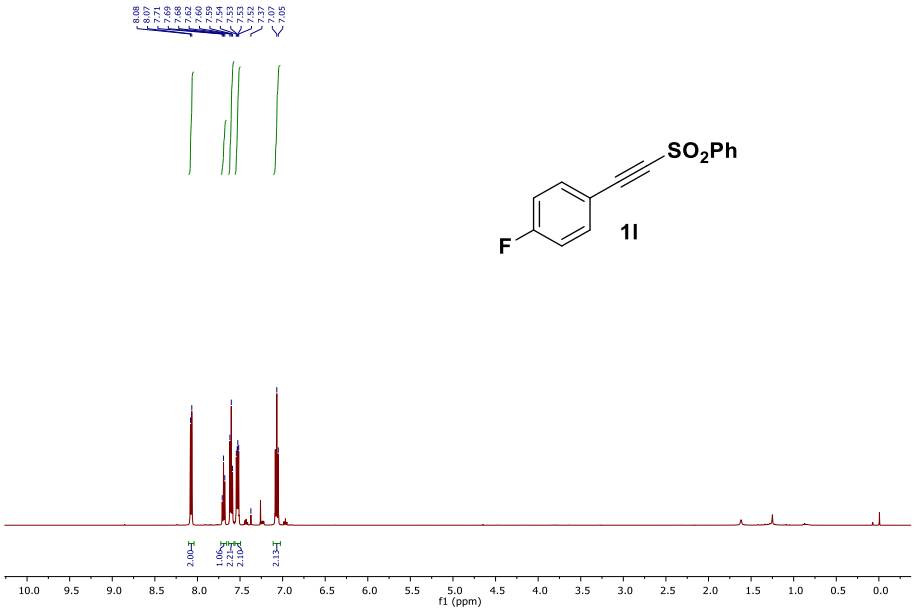


Figure 23: ^{1}H NMR Spectrum of 1l

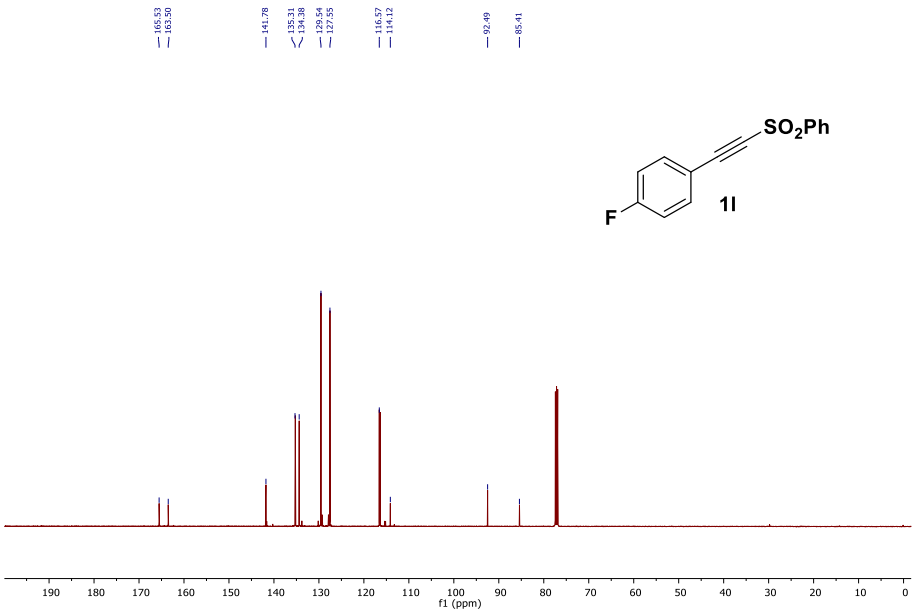


Figure 24: ^{13}C NMR Spectrum of 1l

Figure 25: ^{19}F NMR Spectrum of 1l

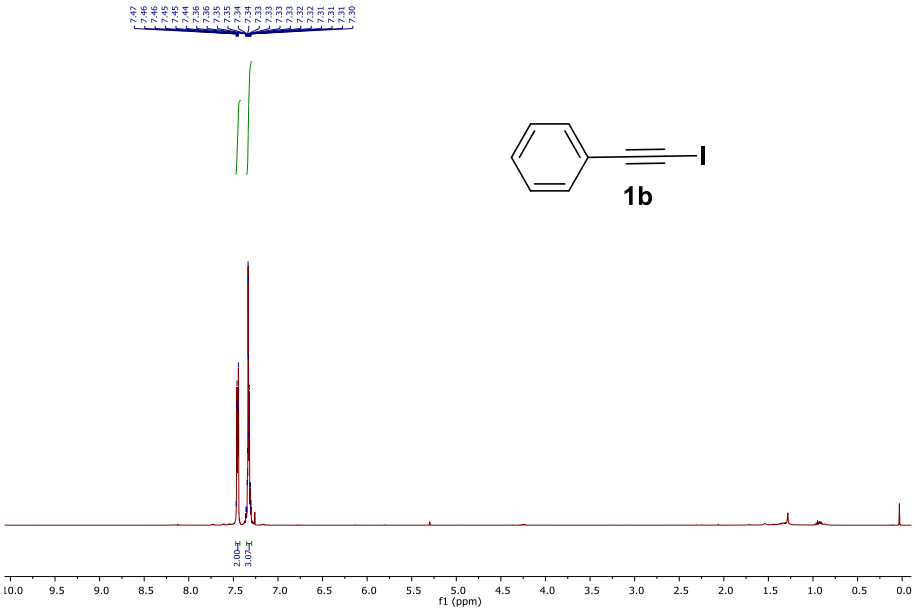


Figure 26: ^{1}H NMR Spectrum of 1b

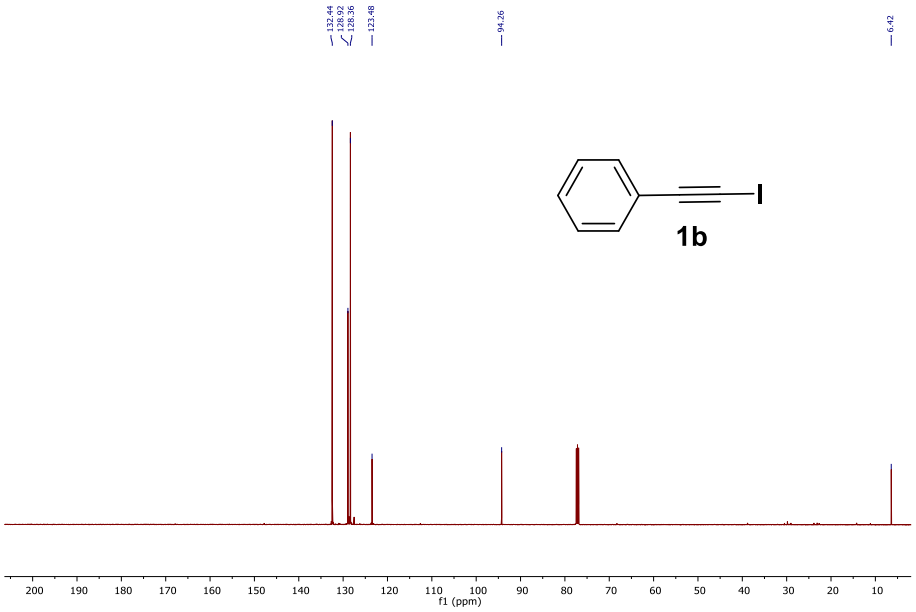


Figure 27: ^{13}C NMR Spectrum of 1b

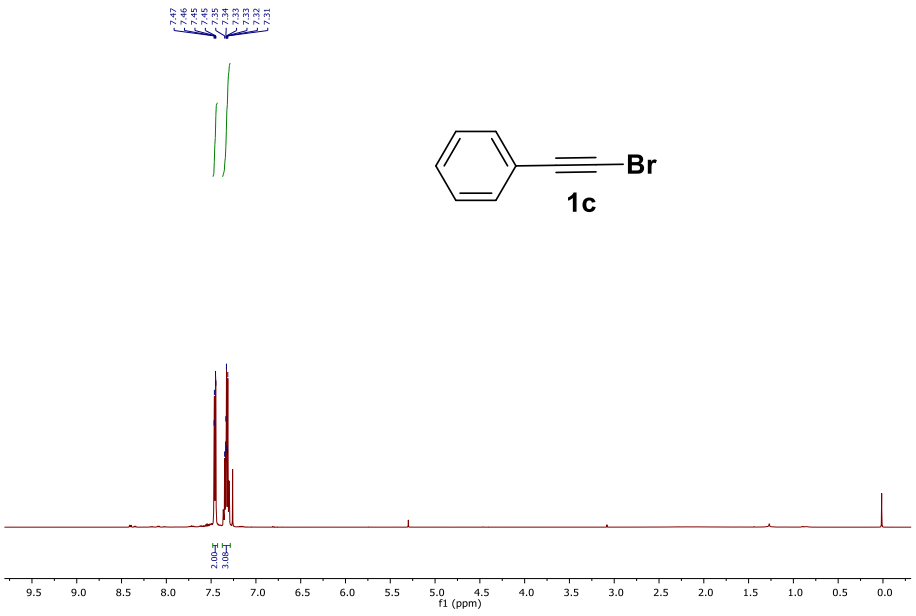


Figure 28: ^{1}H NMR Spectrum of 1c

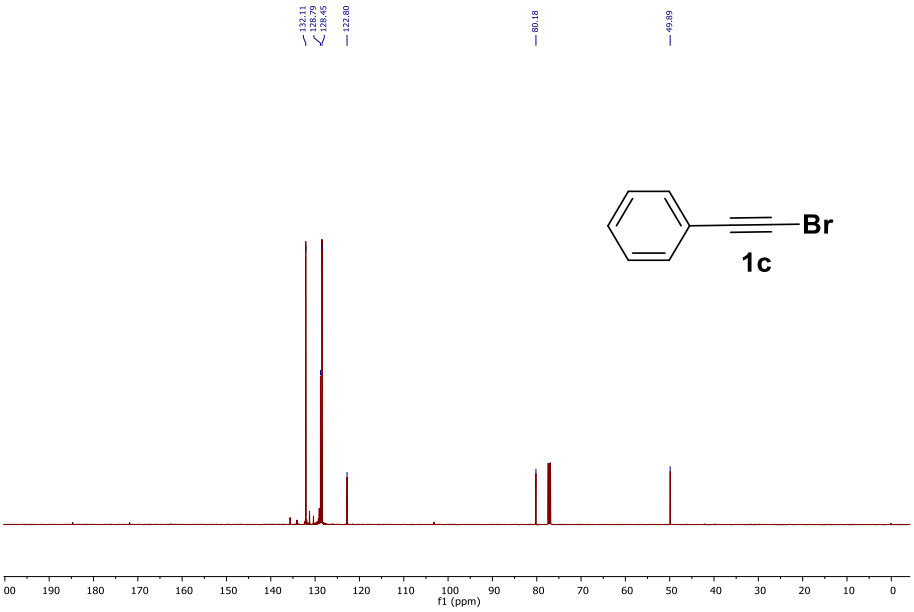


Figure 29: ^{13}C NMR Spectrum of 1c

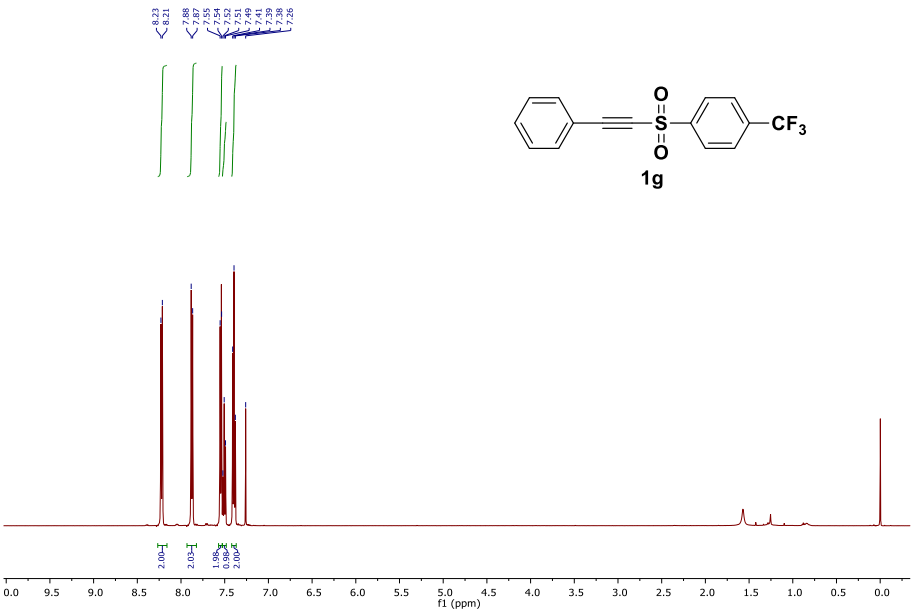


Figure 30: ^{1}H NMR Spectrum of 1g

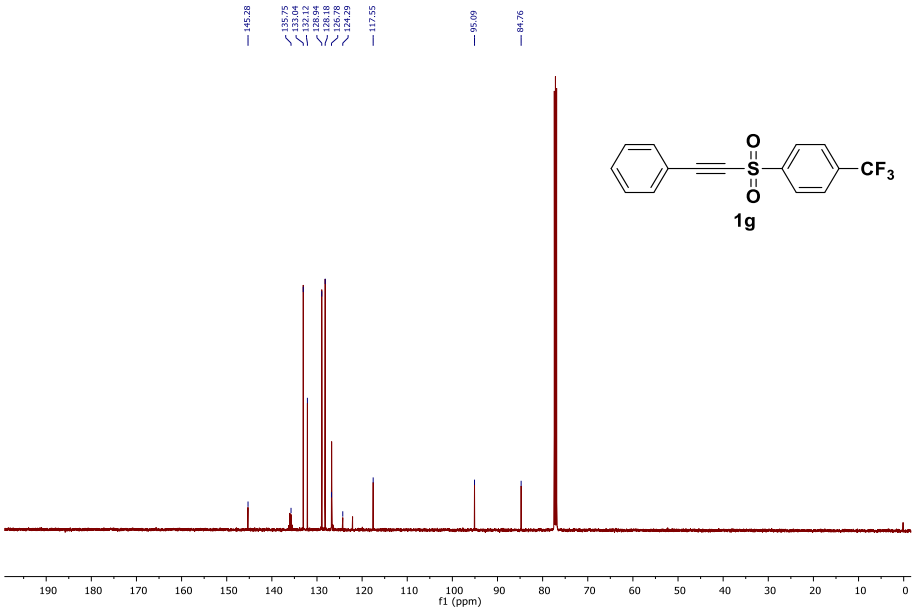


Figure 31: ^{13}C NMR Spectrum of 1g

Figure 32: ^{19}F NMR Spectrum of 1g

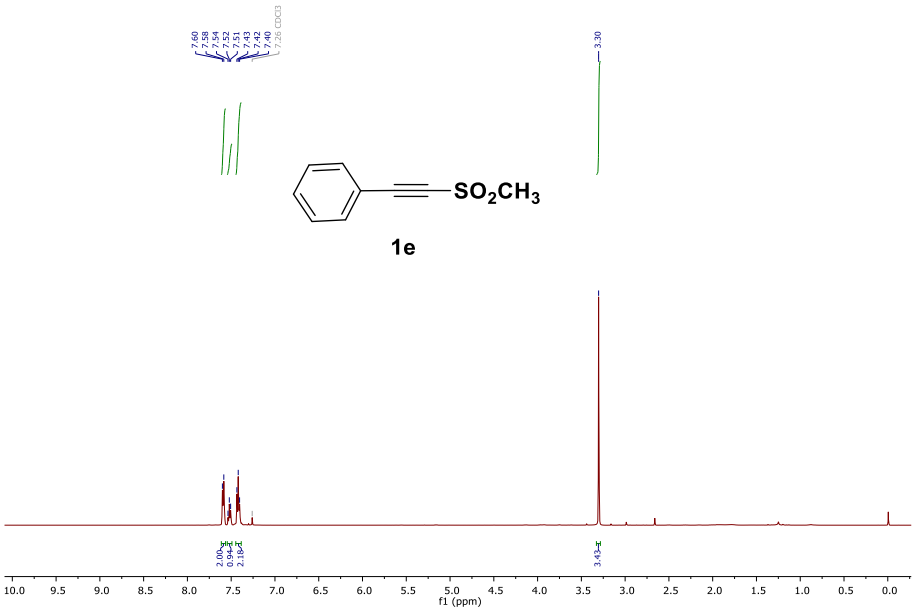


Figure 33: [1]H NMR Spectrum of 1e

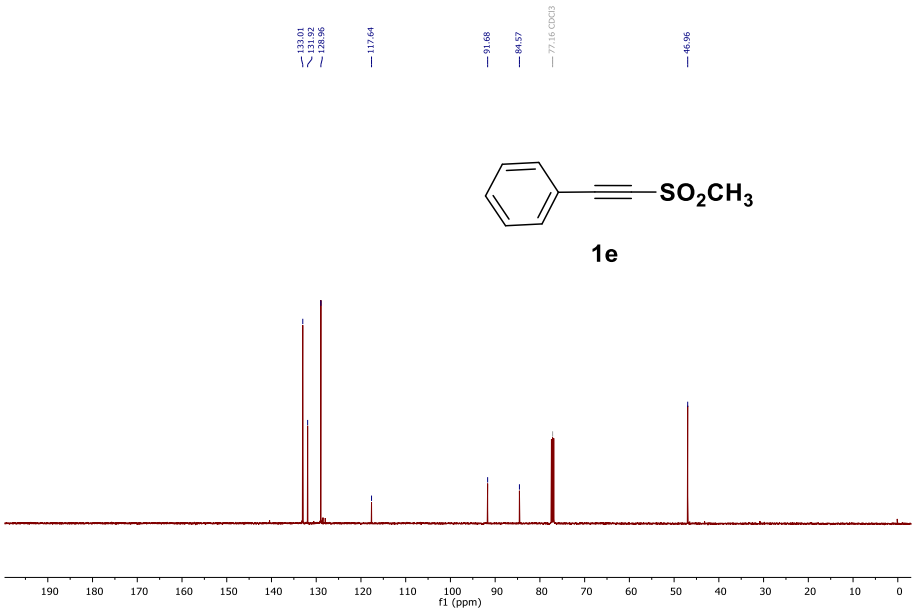


Figure 34: [13]C NMR Spectrum of 1e

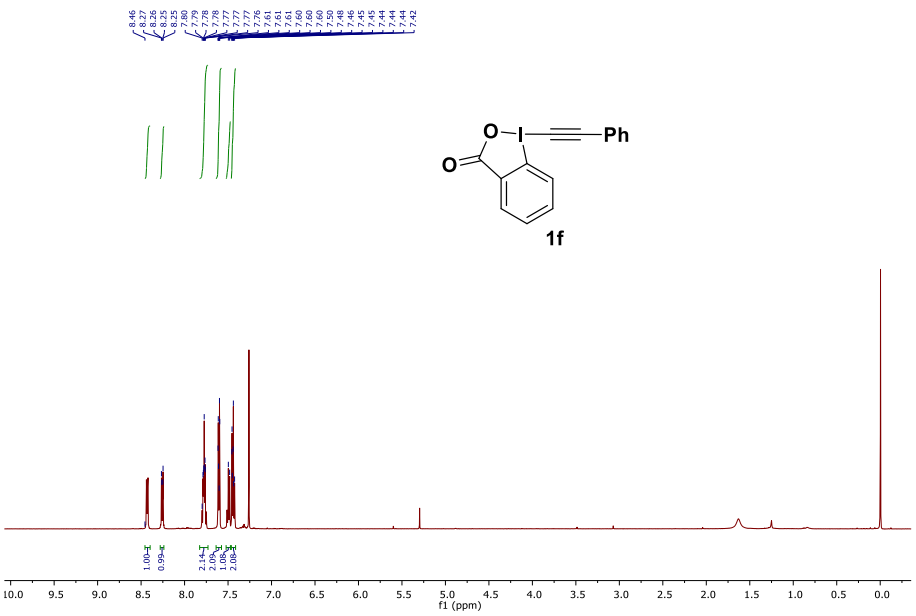


Figure 35: [1]H NMR Spectrum of 1f

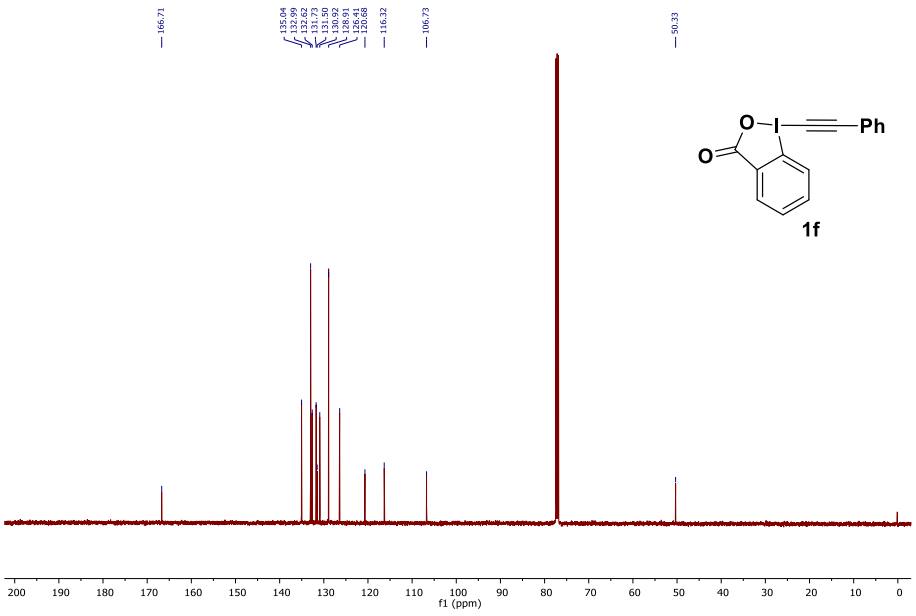


Figure 36: [13]C NMR S Spectrum of 1f

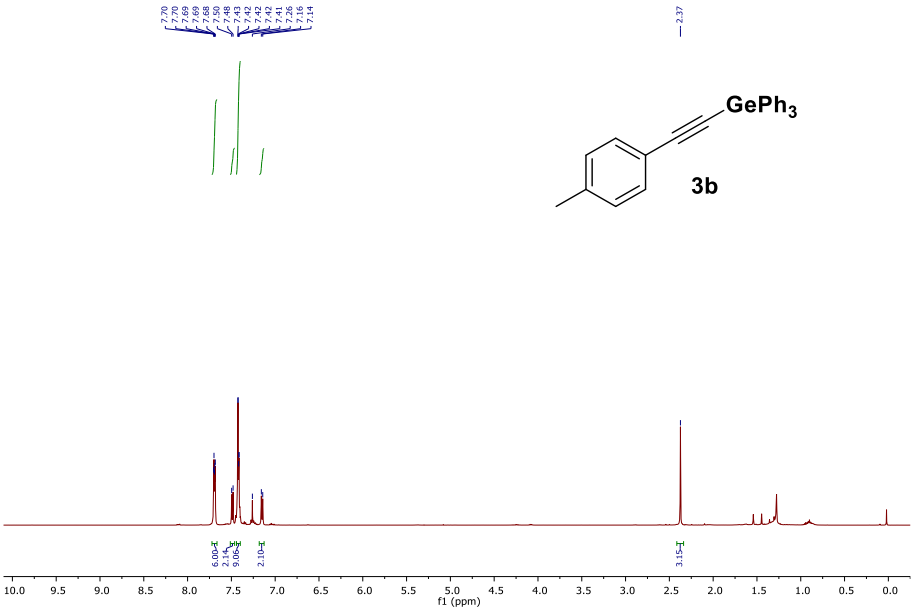


Figure 37: ^{1}H NMR Spectrum of 3b

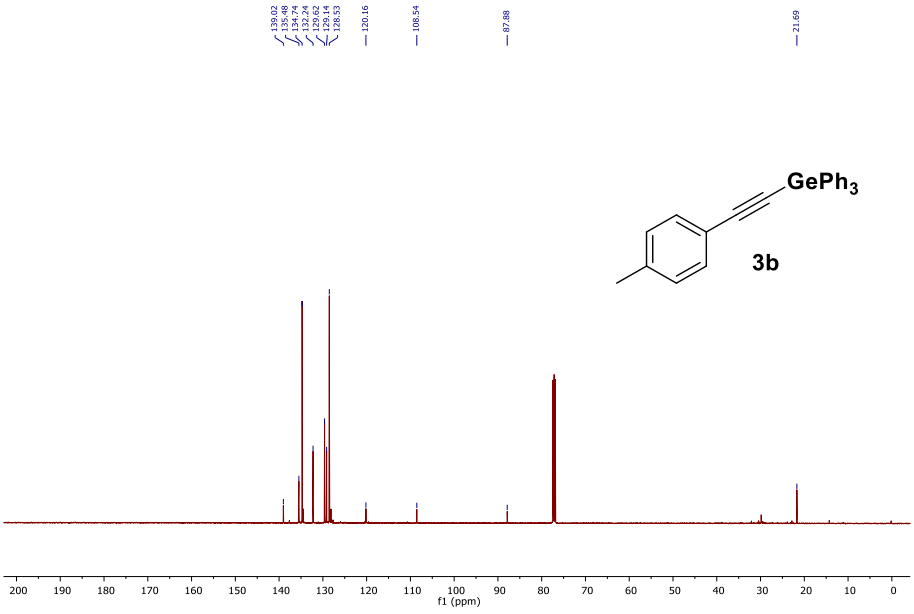


Figure 38: ^{13}C NMR Spectrum of 3b

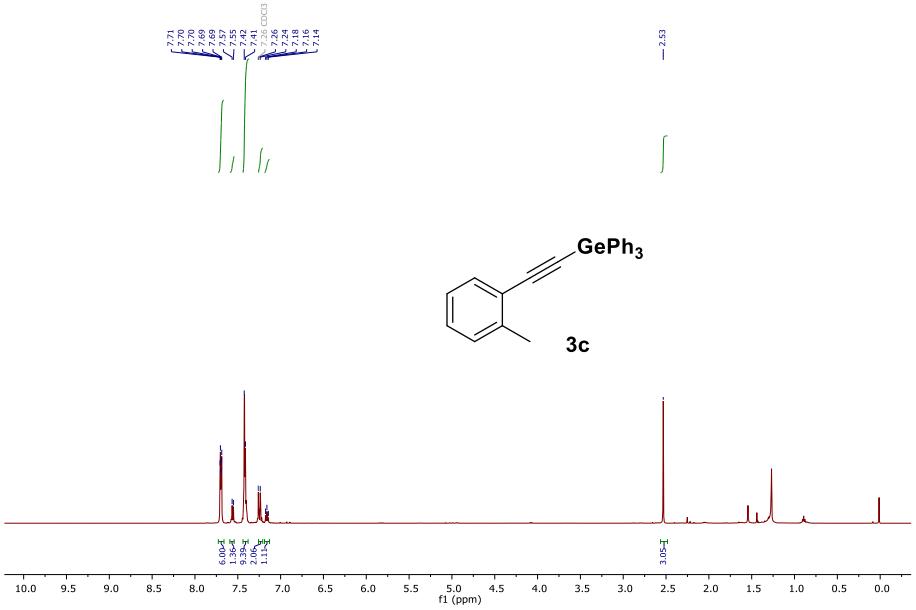


Figure 39: ^{1}H NMR Spectrum of 3c

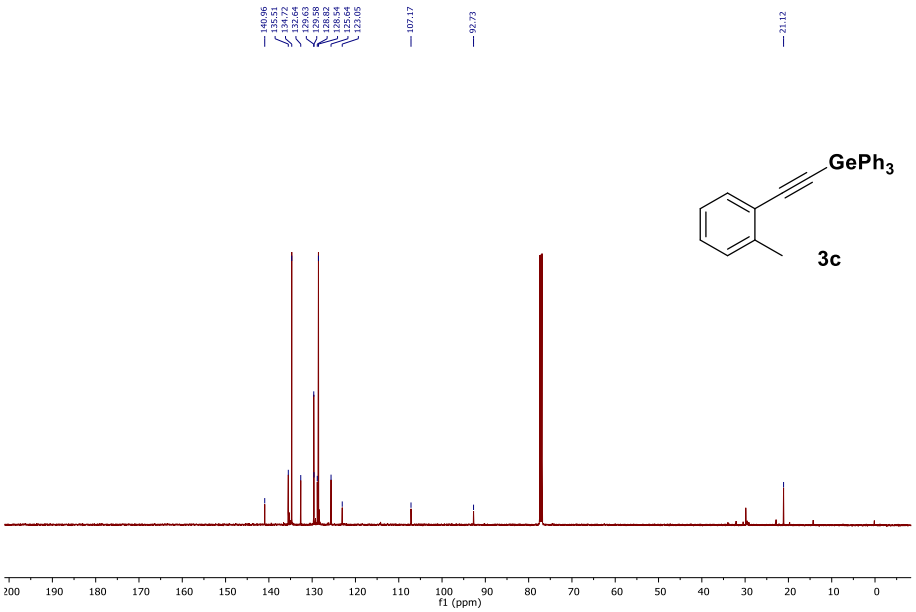


Figure 40: ^{13}C NMR Spectrum of 3c

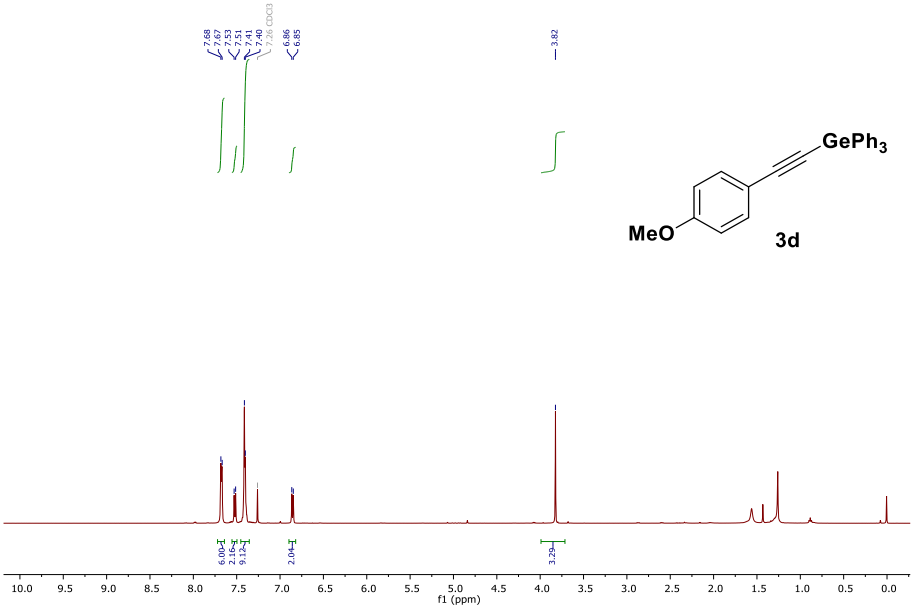


Figure 41: ^{1}H NMR Spectrum of 3d

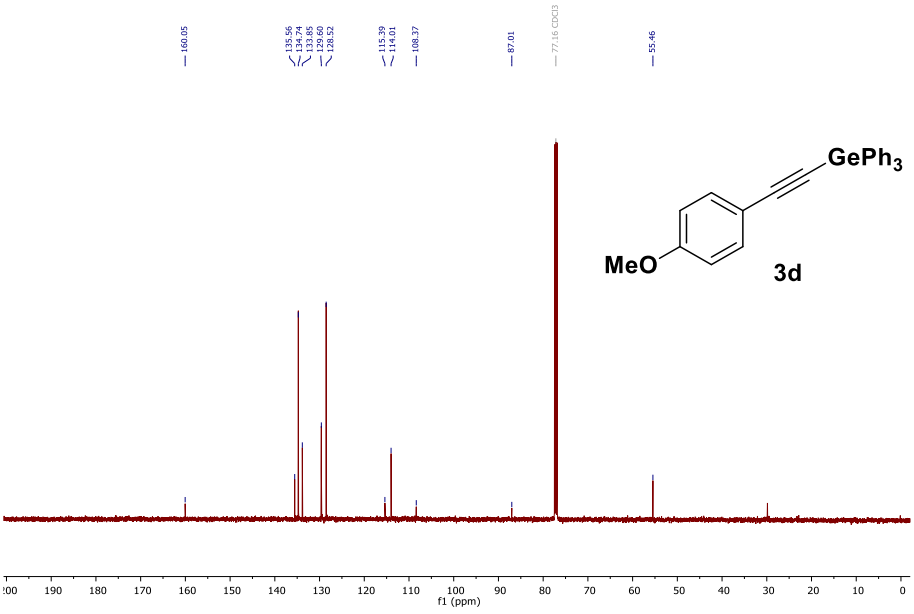


Figure 42: ^{13}C NMR Spectrum of 3d

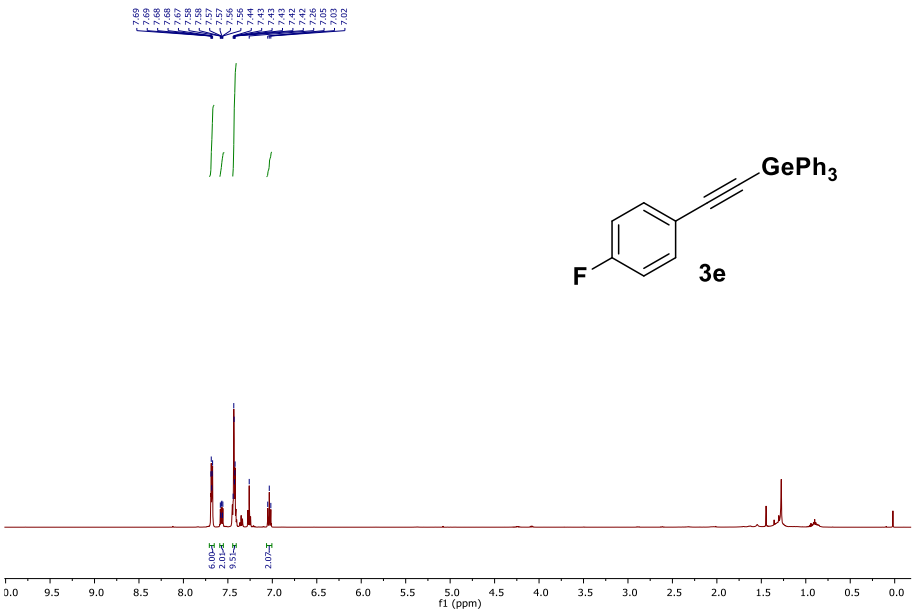


Figure 43: ^{1}H NMR Spectrum of 3e

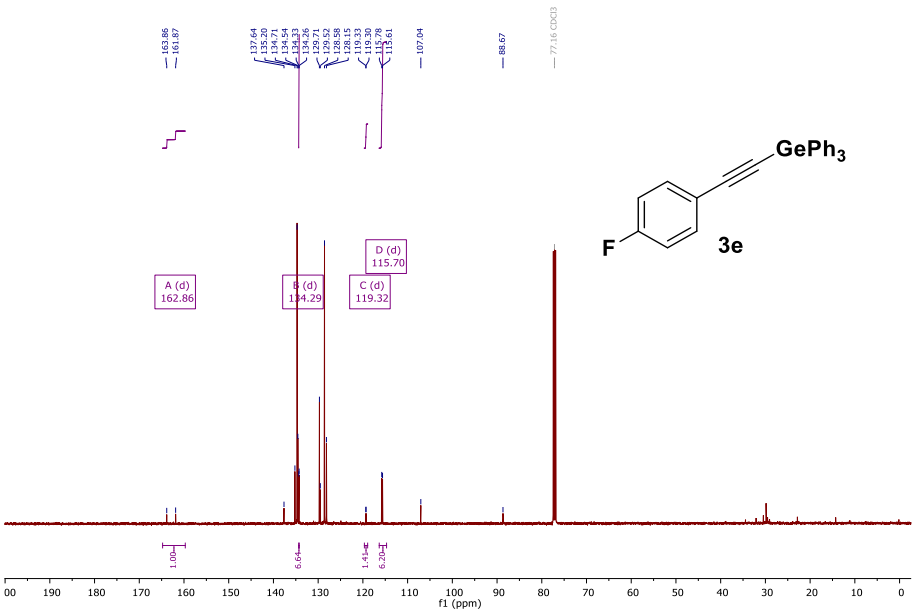


Figure 44: ^{13}C NMR Spectrum of 3e

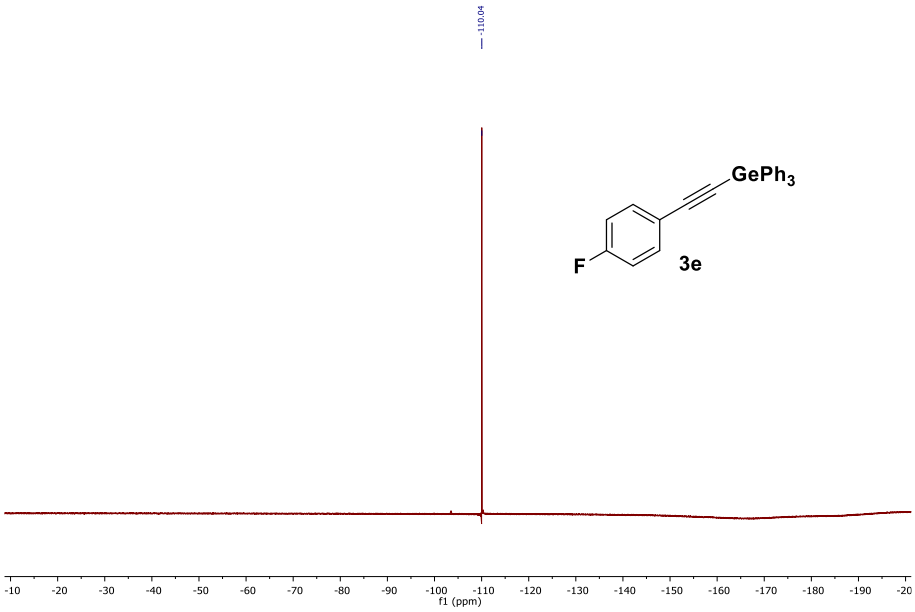


Figure 45: ^{19}F NMR Spectrum of 3e

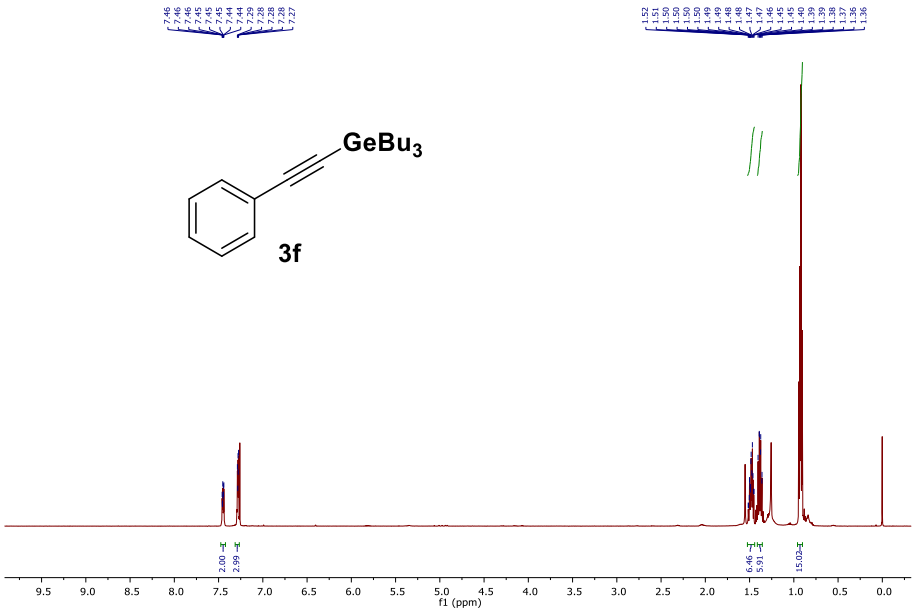


Figure 46: ^{1}H NMR Spectrum of 3f

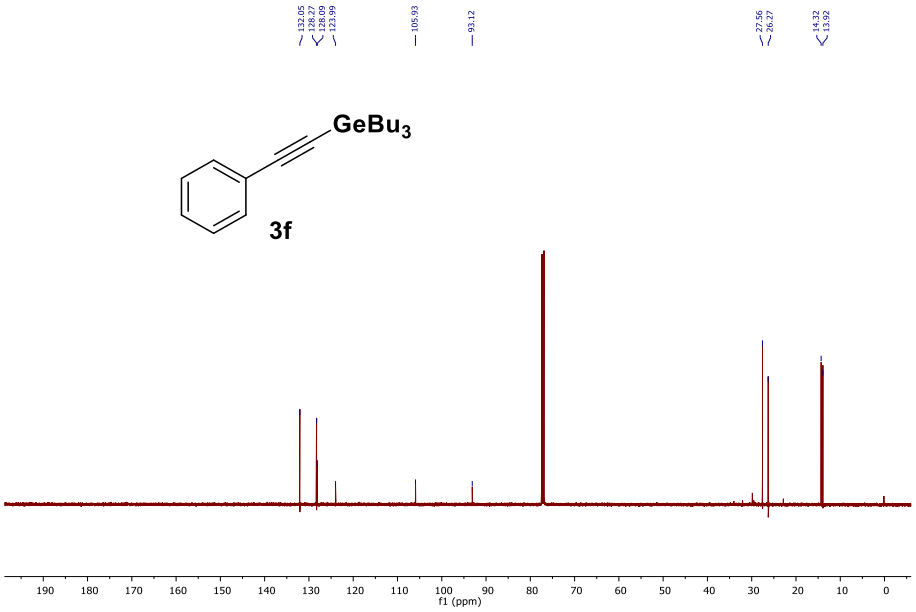


Figure 47: ^{13}C NMR Spectrum of 3f

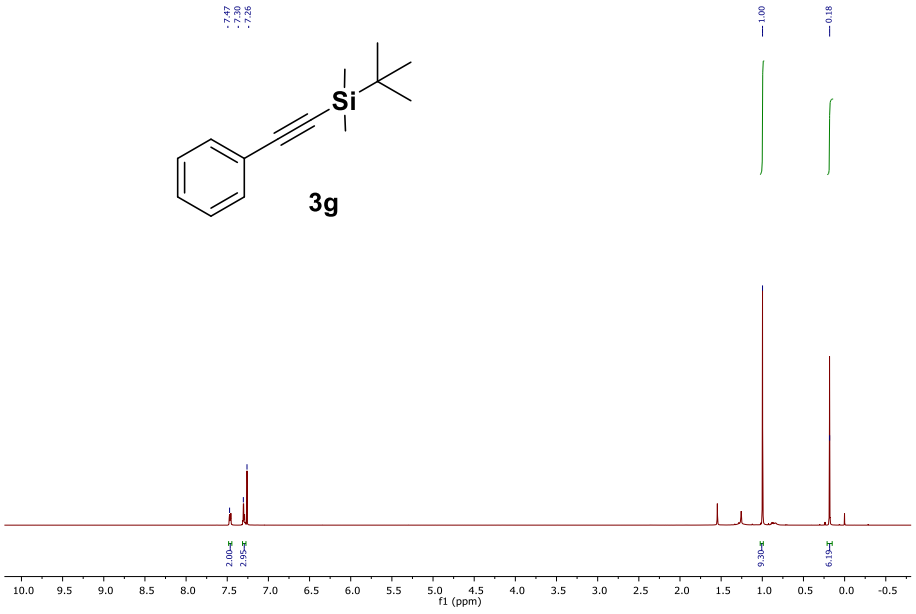


Figure 48: ^{1}H NMR Spectrum of 3g

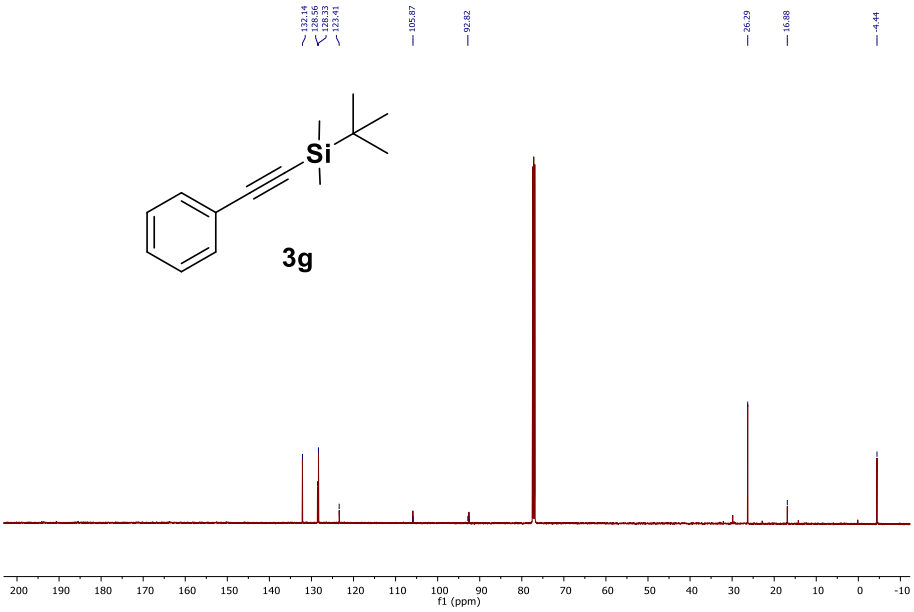


Figure 49: ^{13}C NMR Spectrum of 3g

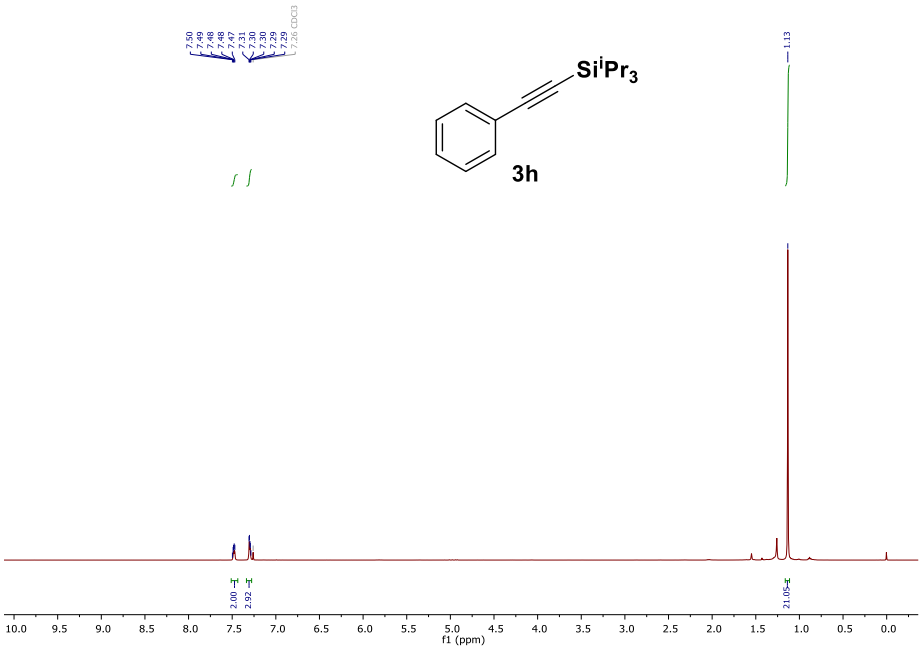


Figure 50: ^{1}H NMR Spectrum of 3h

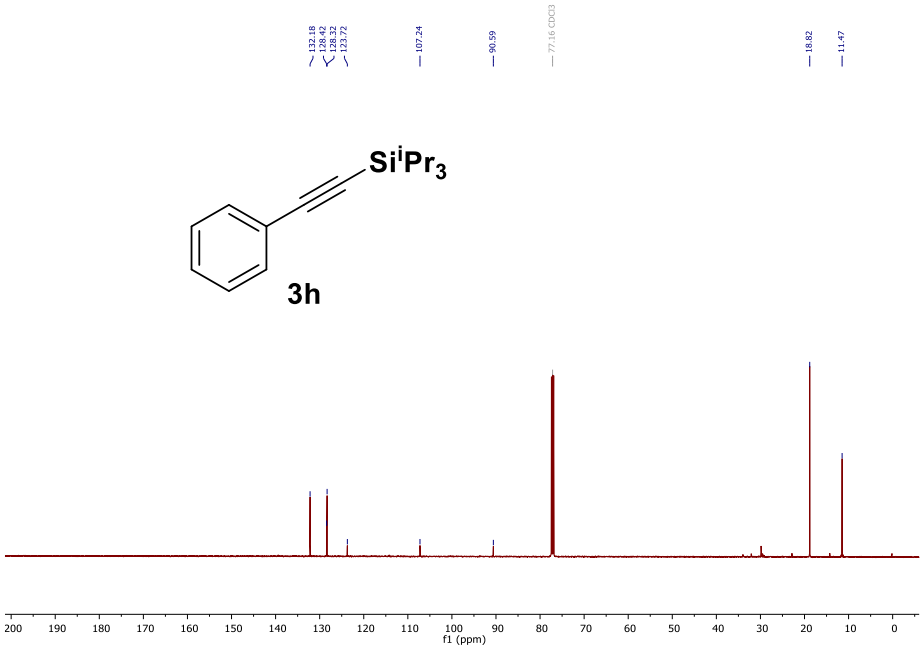


Figure 51: ^{13}C NMR Spectrum of 3h

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