

Supporting Information for:

$\text{B}(\text{C}_6\text{F}_5)_3$ Catalyzed Synthesis of Benzofused-Siloles

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General Comments

Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques under argon, or in a MBraun UniLab glovebox, under an atmosphere of argon (< 0.1 ppm O_2/H_2O). Unless otherwise indicated, solvents were distilled from appropriate drying agents: Ether (NaK); *n*-hexane (NaK); and dichloromethane (CaH_2). Ether and dichloromethane were stored over activated 3Å molecular sieves while *n*-hexane was stored over a potassium mirror. All other compounds (excluding $B(C_6F_5)_3$) were purchased from commercial sources and used as received. Solvents for column chromatography were of technical grade and used without further purification. Column chromatography was performed on silica gel (230-400 mesh). NMR spectra were recorded on Bruker Avance III-400, Bruker Avance II-500 or Bruker Ascend-400 spectrometers. Chemical shifts are reported as dimensionless δ values and are frequency referenced relative to residual protio impurities in the NMR solvents for 1H and ^{13}C $\{^1H\}$ respectively, while ^{11}B $\{^1H\}$, ^{19}F $\{^1H\}$ and ^{29}Si shifts are referenced relative to external BF_3 -etherate, hexafluorobenzene and tetramethylsilane, respectively. Coupling constants J are given in Hertz (Hz) as positive values regardless of their real individual signs. The multiplicity of the signals are indicated as “s”, “d”, “t”, “q” “pent”, “sept” or “m” for singlet, doublet, triplet, quartet, pentet, septet or multiplet, respectively. High resolution mass spectra (HRMS) were recorded on a Waters QTOF mass spectrometer. GCMS analysis was performed on an Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD with triple axis detector. The column employed was an Agilent J&W HP-5ms ((5%-Phenyl)-methylpolysiloxane) of dimensions: length, 30 m; internal diameter, 0.250 mm; film, 0.25 μm . Microanalysis was performed by Mr Martin Jennings at the University of Manchester microanalytical service.

An INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) experiment was utilised to improve the sensitivity of ^{29}Si $\{^1H\}$ NMR experiments.

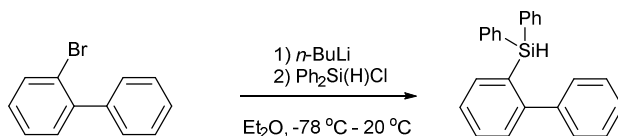
Procedure for drying $B(C_6F_5)_3$

$B(C_6F_5)_3$ was stirred with excess Et_3SiH (5 equiv.) in pentane for 72 h at ambient temperature. Solvent was removed and $B(C_6F_5)_3$ was dried *in vacuo* to give a dry white powder which was pure by ^{11}B and ^{19}F $\{^1H\}$ NMR spectroscopy.

General procedure 1: The synthesis of 2-(dialkyl/arylsilyl)biphenyls¹

To a solution of 2-bromobiphenyl (2 mL, 11.6 mmol) and TMEDA (1.9 mL, 12.76 mmol), in diethyl ether 20 mL, was added *n*-butyl-lithium (8 mL, 1.6 M in hexane) dropwise at -78 °C and stirred for 5 hours. To this solution was added diaryl/alkylchlorosilane (1.1 equiv.) dropwise at -78 °C and stirred for 1 hour. The reaction mixture was left to warm to ambient temperature and stirred for 24 hours. The product was extracted with ether and washed with sodium hydrogen carbonate (aq) and water. The organic layer was dried over magnesium sulfate. The solvent was removed under vacuum and purified by flash column chromatography.

4a 2-(Diphenylsilyl)biphenyl



Synthesized according to general procedure 1, starting with 2.3 mL of diphenylchlorosilane. The solvent was removed under vacuum and purified by flash column chromatography where the eluent was hexane : ethyl acetate (4 : 1) this gave the title compound, **4a** (2.2 g) as a white solid in 57 % yield.

¹H NMR (CDCl₃ 400 MHz) δ 7.54 (d, ³J_{HH} 7.3 Hz, 1H), 7.48 (dt, ³J_{HH} 1.3 Hz, ³J_{HH} 7.9 Hz, 1H), 7.45-7.43 (m, 4H), 7.40-7.29 (m, 8H), 7.25-7.18 (m, 5H), 5.16 (s, 1H)

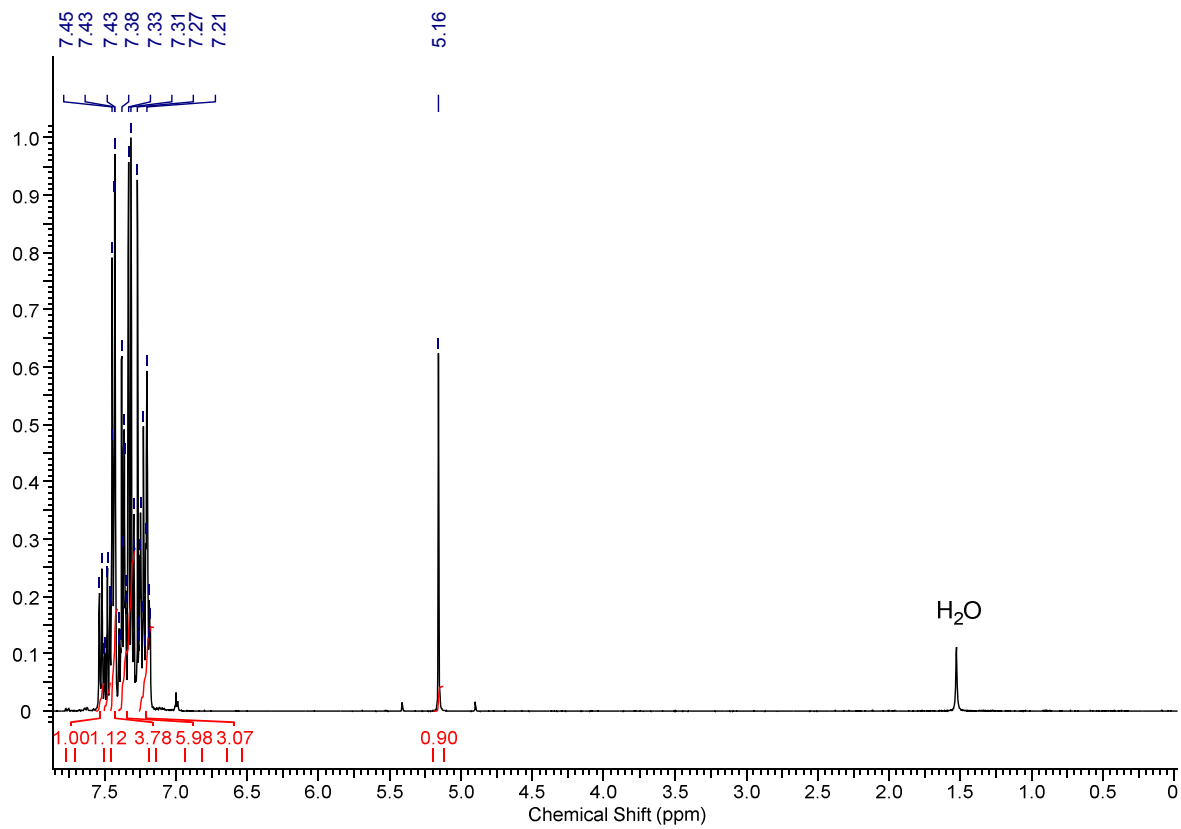
¹³C {¹H} NMR (CDCl₃ 100 MHz) δ 150.2, 143.1, 137.1, 135.7, 134.3, 132.3, 129.7, 129.5, 129.4, 129.3, 127.8, 127.7, 127.0, 126.4 ppm

²⁹Si {¹H} NMR (CDCl₃ 80 MHz) δ -21.2 ppm

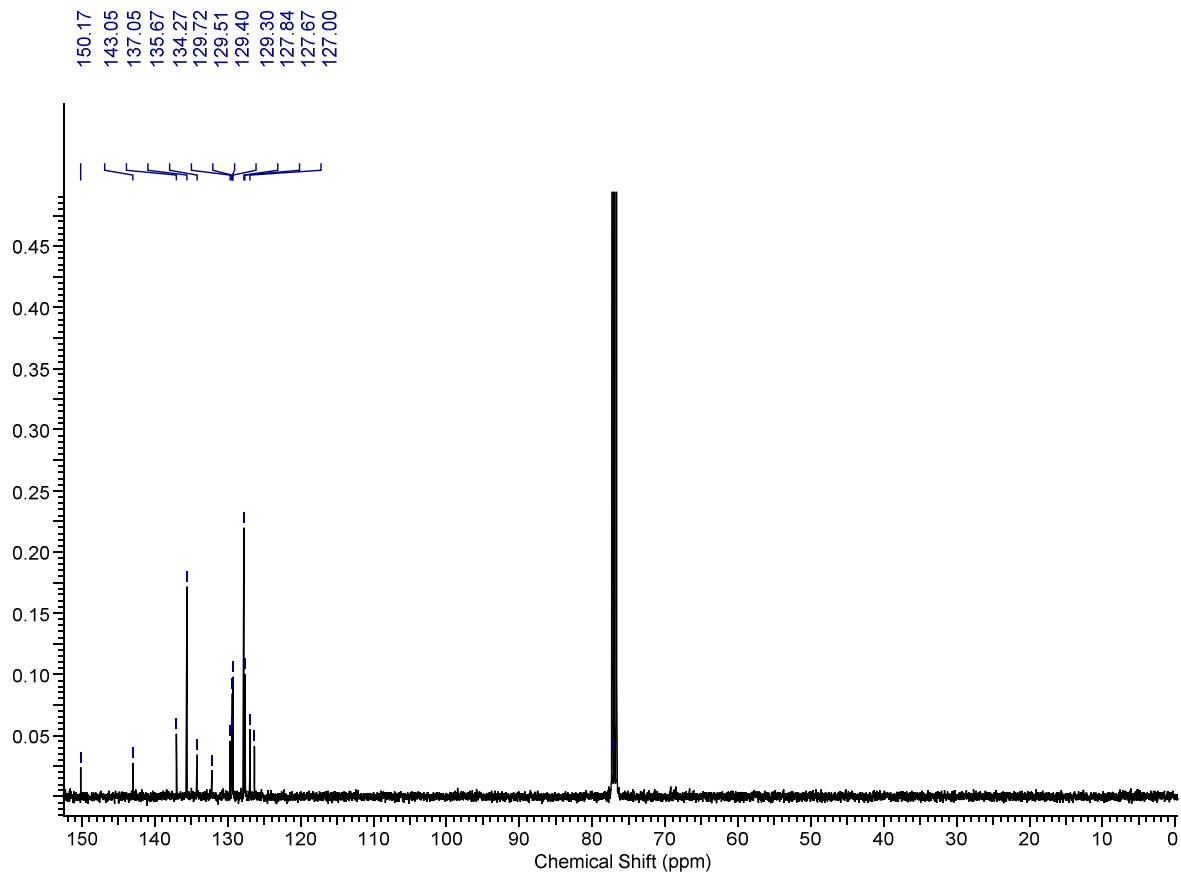
Mass Spec: Found 336.1329 *m/z*, Expected for M⁺ 336.1329 *m/z*

Elemental Analysis Expected C 85.70% H 5.95%, Found: C 85.62% H 6.39%

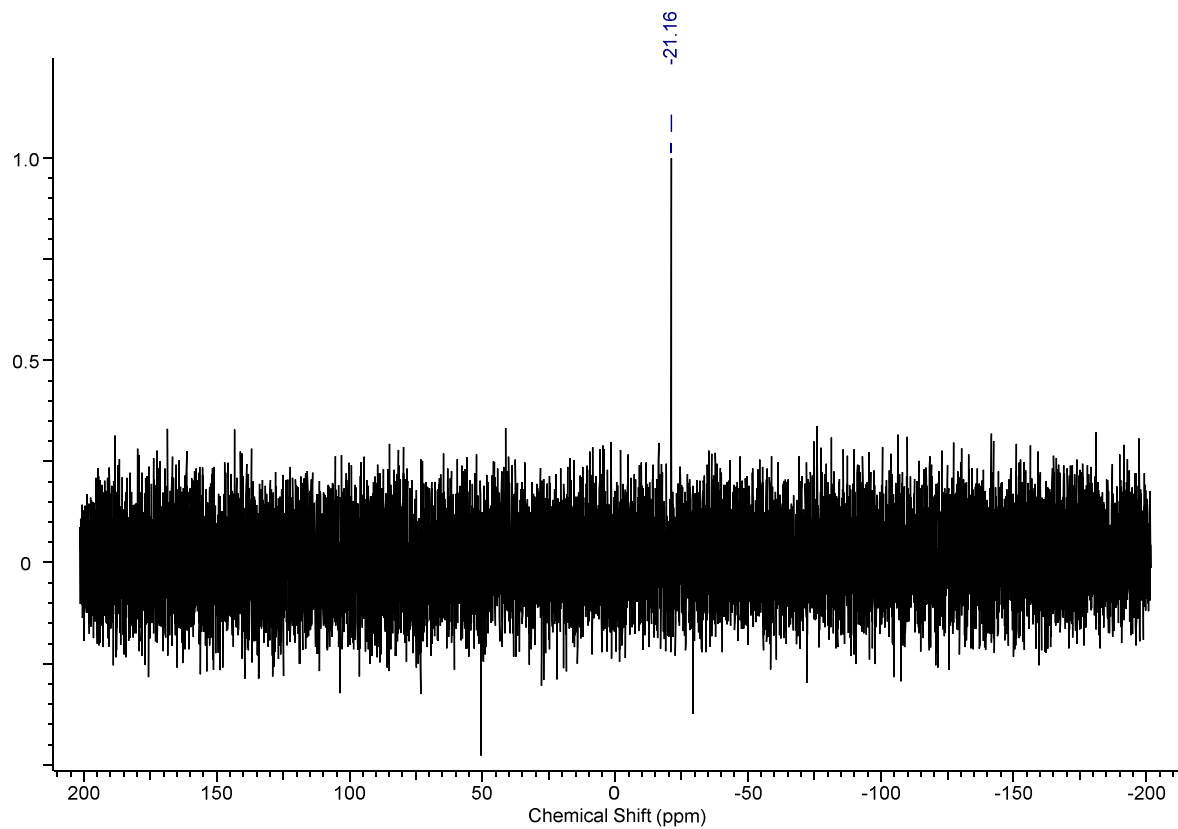
¹H NMR Spectrum: 4a 2-(Diphenylsilyl)biphenyl



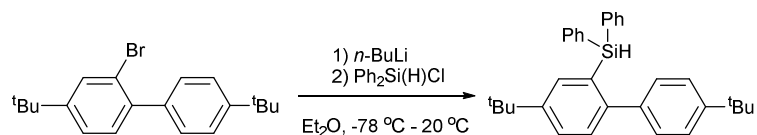
$^{13}\text{C} \{^1\text{H}\}$ NMR Spectrum : 4a 2-(Diphenylsilyl)biphenyl



^{29}Si $\{^1\text{H}\}$ NMR Spectrum: 4a 2-(Diphenylsilyl)biphenyl



4b bis(4,4'-di-*tert*butylbiphenyl-2-yl)silane

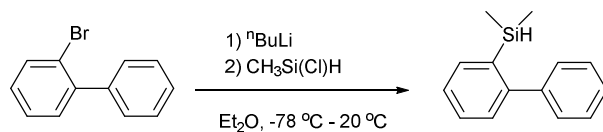


Synthesized according to general procedure 1, starting with 2.3 mL of diphenylchlorosilane. The solvent was removed under vacuum and purified by flash column chromatography where the eluent was pentane : DCM (10 : 1). This gave the title compound, **4b** (2.6 g) as a white crystalline solid in 75 % yield.

²⁹Si {¹H} NMR (CDCl₃ 80 MHz) δ -20.76 ppm

¹H and ¹³C {¹H} data in accordance with literature¹

4c 2-(Dimethylsilyl)biphenyl

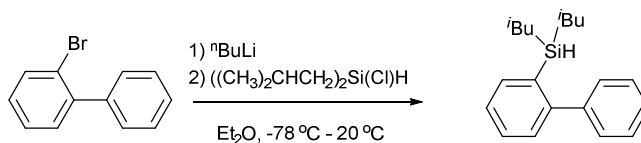


Synthesized according to general procedure 1, starting with 1.55 mL of dimethylchlorosilane. The solvent was removed under vacuum and purified by flash column chromatography where the eluent was hexane this gave the title compound, **4c** (1.8 g) as a colourless oil in 75 % yield.

^{29}Si { ^1H } NMR (CDCl_3 80 MHz) δ -17.9 ppm

^1H and ^{13}C { ^1H } NMR data was found to be in accordance with previously reported literature data literature²

4d 2-(Di-*isobutylsilyl*)biphenyl



Synthesized according to general procedure 1, starting with 2 mL of di-*isobutyl*chlorosilane. The solvent was removed under vacuum and purified by flash column chromatography where the eluent was pentane : DCM (10 : 1). This gave the title compound, **4d** (2.3 g) as a colourless oil in 69 % yield.

^1H NMR (CDCl_3 400 MHz) δ 7.71 (d, $^3J_{\text{HH}}$ 7.3 Hz, 1H), 7.47-7.32 (M, 8H), 4.31 (quintet, $^3J_{\text{HH}}$ 3.8 Hz, 1H, Si-*H*), 1.66 (septet, $^3J_{\text{HH}}$ 6.8 Hz, 2H), 0.89 (2 overlapped doublets, $^3J_{\text{HH}}$ 6.3 Hz, 12H), 0.65-0.52 (m, 4H)

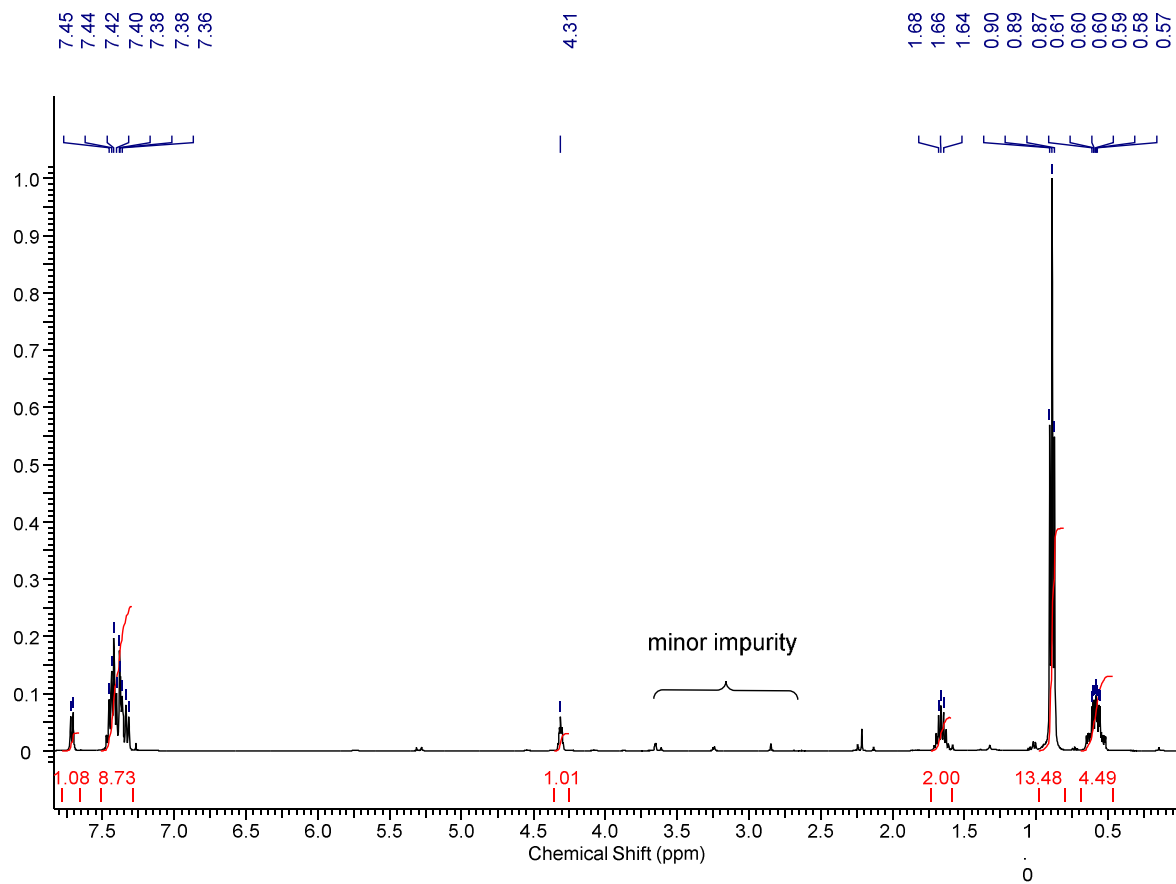
^{13}C $\{^1\text{H}\}$ NMR (CD_2Cl_2 100 MHz) δ 149.4, 143.8, 136.2, 134.9, 129.3, 129.2, 128.9, 127.7, 127.1, 126.3, 26.0, 25.4, 25.3, 23.8 ppm

^{29}Si $\{^1\text{H}\}$ NMR (CDCl_3 80 MHz) δ -13.07 ppm

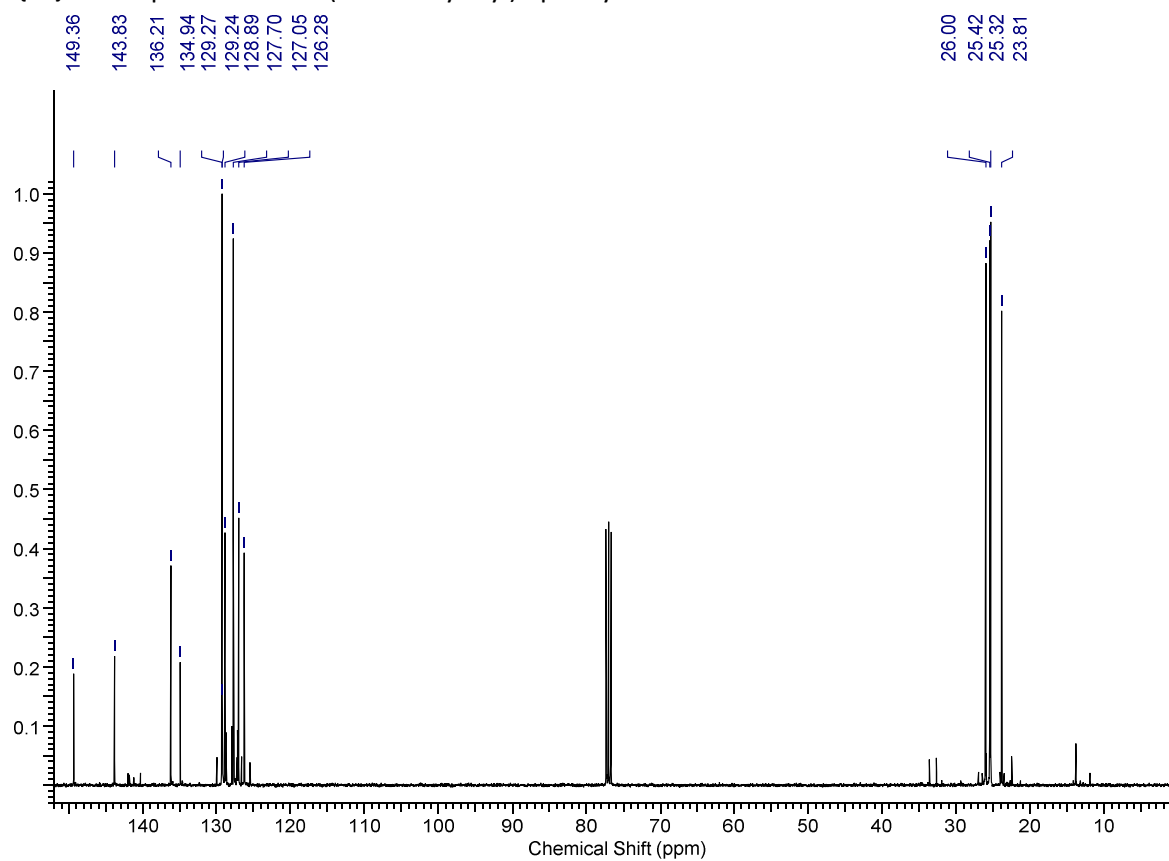
Mass Spec: Found 296.1945 m/z , Expected for M^+ 296.1955 m/z

Elemental Analysis Expected C 81.01% H 9.52%, Found: C 81.42% H 9.63%

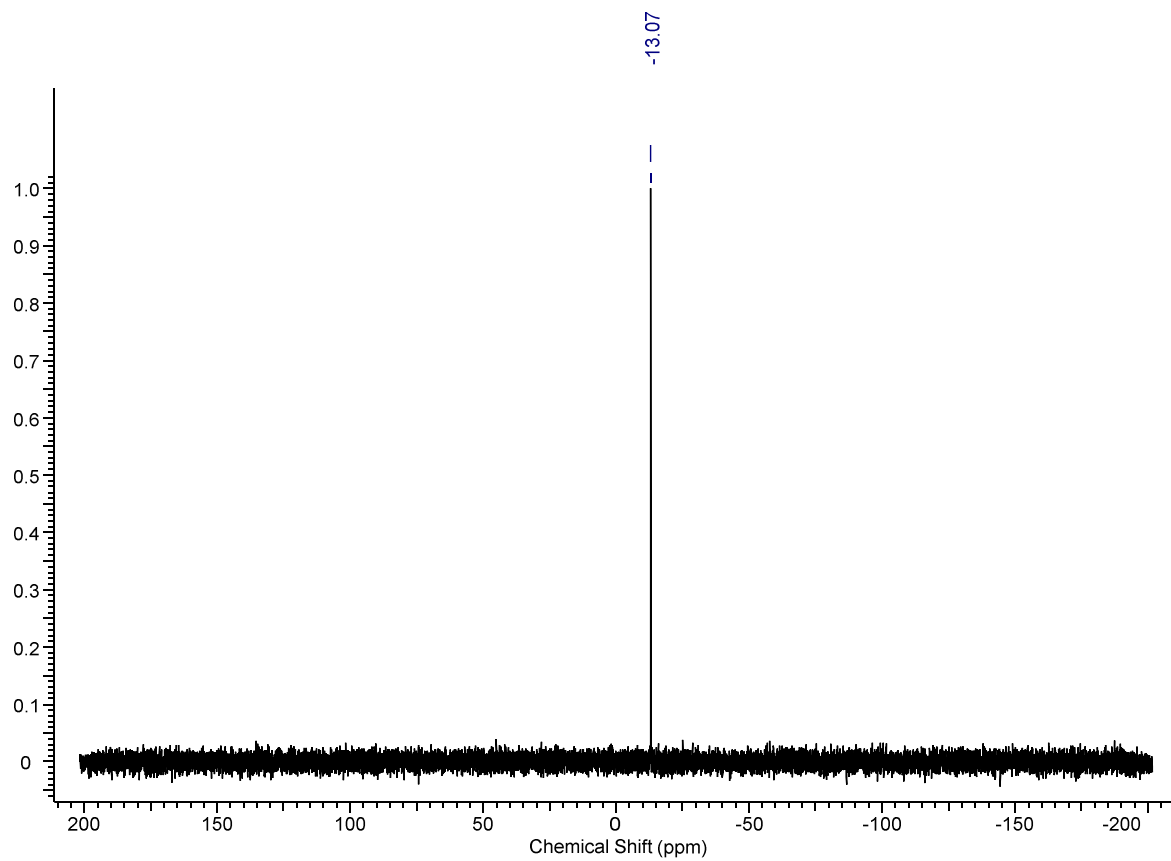
¹H NMR Spectrum: **4d** 2-(Di-*isobutylsilyl*)biphenyl



$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum: **4d** 2-(Di-*isobutylsilyl*)biphenyl



^{29}Si $\{^1\text{H}\}$ NMR Spectrum: **4d** 2-(Di-*isobutylsilyl*)biphenyl



General procedure 2: The synthesis of silafluorene derivatives.

In an oven dried J Youngs NMR tube charged with a d_6 -DMSO capillary, the appropriate 2-silylbiphenyl (**4a-d**, 1 equiv.) was added to a solution of BCF (x mol %) in anhydrous o - $C_6H_4Cl_2$. This solution was agitated for 5 minutes before the addition of Cl_2 -py (x mol %) and then heated. The solution was passed through a plug of silica and then dried under vacuum.

5a 9,9-Diphenyl-9-silafluorene



Synthesized according to general procedure 2, starting with 131 mg of 2-(Diphenylsilyl)biphenyl and 5 mol% BCF (10 mg) and Cl_2 -py (3 mg). Purified by flash column chromatography where the eluent was DCM this was then dried under high vacuum to give the title compound, **5a**, (117 mg) as a white solid in 90 % yield.

1H NMR ($CDCl_3$ 400 MHz) δ 7.94 (d, $^3J_{HH}$ 7.9 Hz, 2H), 7.84 (d, $^3J_{HH}$ 6.6 Hz, 2H), 7.72-7.70 (m, 4H), 7.52 (td, $^3J_{HH}$ 7.6 Hz, 1.3 Hz, 2H), 7.45 (tt, $^3J_{HH}$ 6.3 Hz, 1.3 Hz, 2H) 7.40-7.34 (m, 6H)

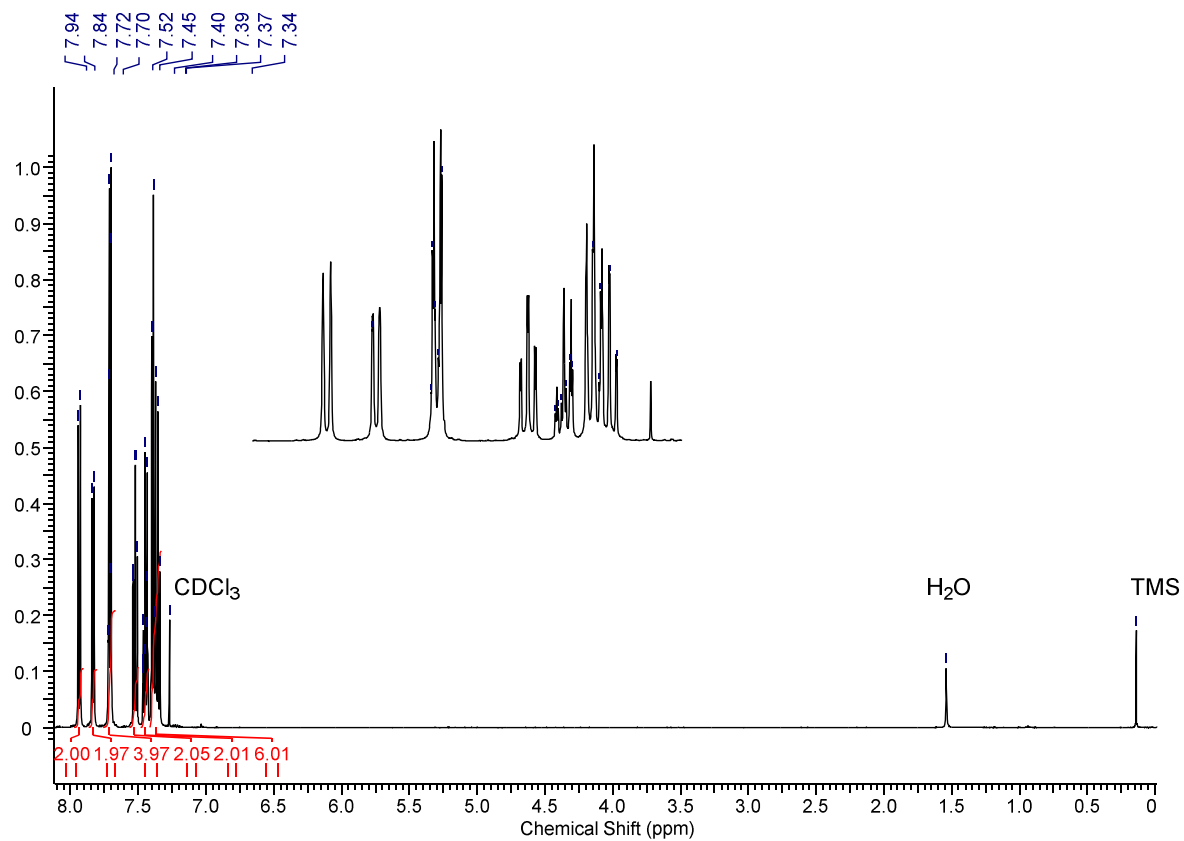
^{13}C NMR ($CDCl_3$ 100 MHz) δ 148.8, 135.9, 135.5, 134.0, 132.7, 130.7, 130.1, 128.1, 127.8, 121.2 ppm

^{29}Si { 1H } NMR ($CDCl_3$ 80 MHz) δ -12.7 ppm

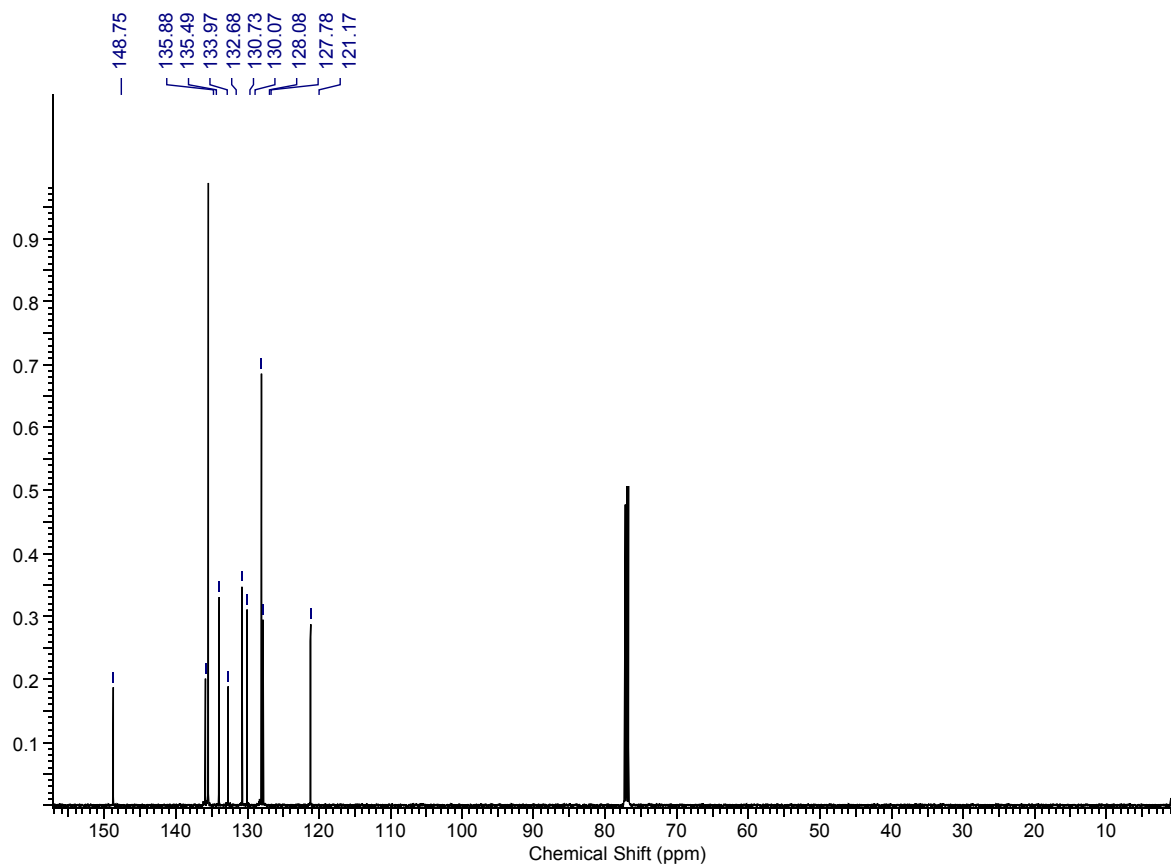
Mass Spec: 335.1245 m/z , Expected for M^+ 335.1251 m/z

Elemental Analysis Expected C 85.85% H 5.78%, Found: C 85.19% H 5.42%

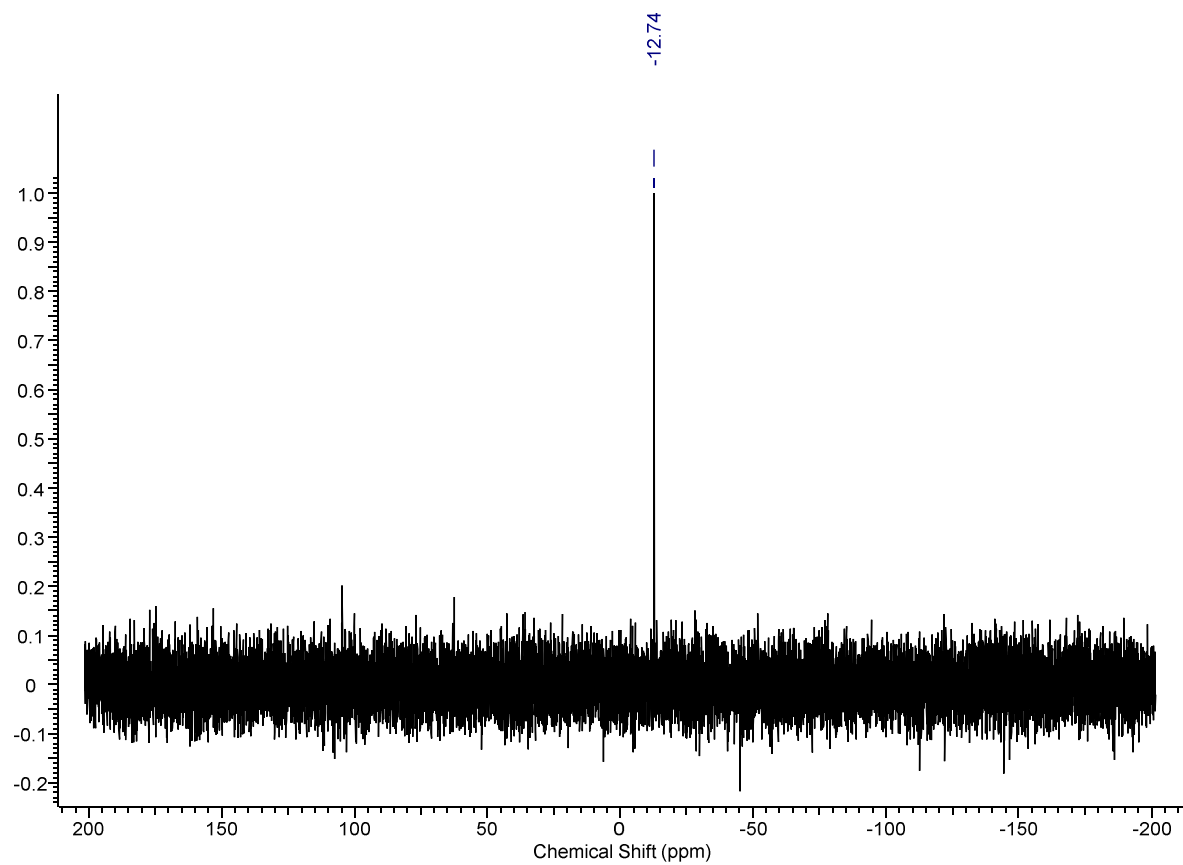
¹H NMR Spectrum: 5a 9,9-Diphenyl-9-silafluorene



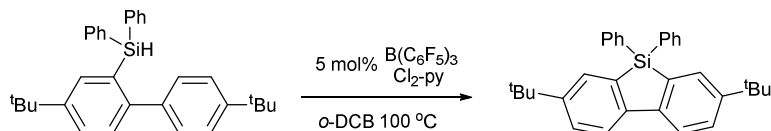
$^{13}\text{C} \{^1\text{H}\}$ NMR Spectrum: 5a 9,9-Diphenyl-9-silafluorene



^{29}Si $\{^1\text{H}\}$ NMR Spectrum: 5a 9,9-Diphenyl-9-silafluorene



5b 2,7-di-*tert*butyl-9,9-di-phenyl-9-silafluorene



Synthesized according to general procedure 2, starting with 86 mg of bis(4,4'-di-*tert*butylbiphenyl-2-yl)silane and 5 mol% BCF (10 mg) and $\text{Cl}_2\text{-py}$ (3 mg). Purified by flash column chromatography where the eluent was pentane, this was then dried under high vacuum to give the title compound **5b** (74 mg) as a white powder in 87 % yield.

Data for **5b** in accordance with literature¹

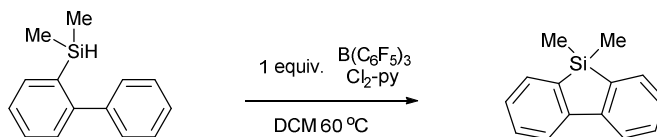
^1H NMR (CDCl_3 400 MHz) δ 7.79-7.77 (m, 4H), 7.68-7.66 (m, 4H), 7.49 (d, $^3J_{\text{HH}}$ 8.3 Hz, 4H), 7.44-7.35 (m, 6H), 1.36 (s, 18H).

^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 100 MHz) δ 150.1, 146.2, 135.6, 135.5, 133.4, 130.6, 129.9, 128.1, 127.9, 120.6, 34.8, 31.5 ppm

^{29}Si $\{^1\text{H}\}$ NMR (CDCl_3 80 MHz) δ -11.5 ppm.

LRMS Found: 446.24 m/z

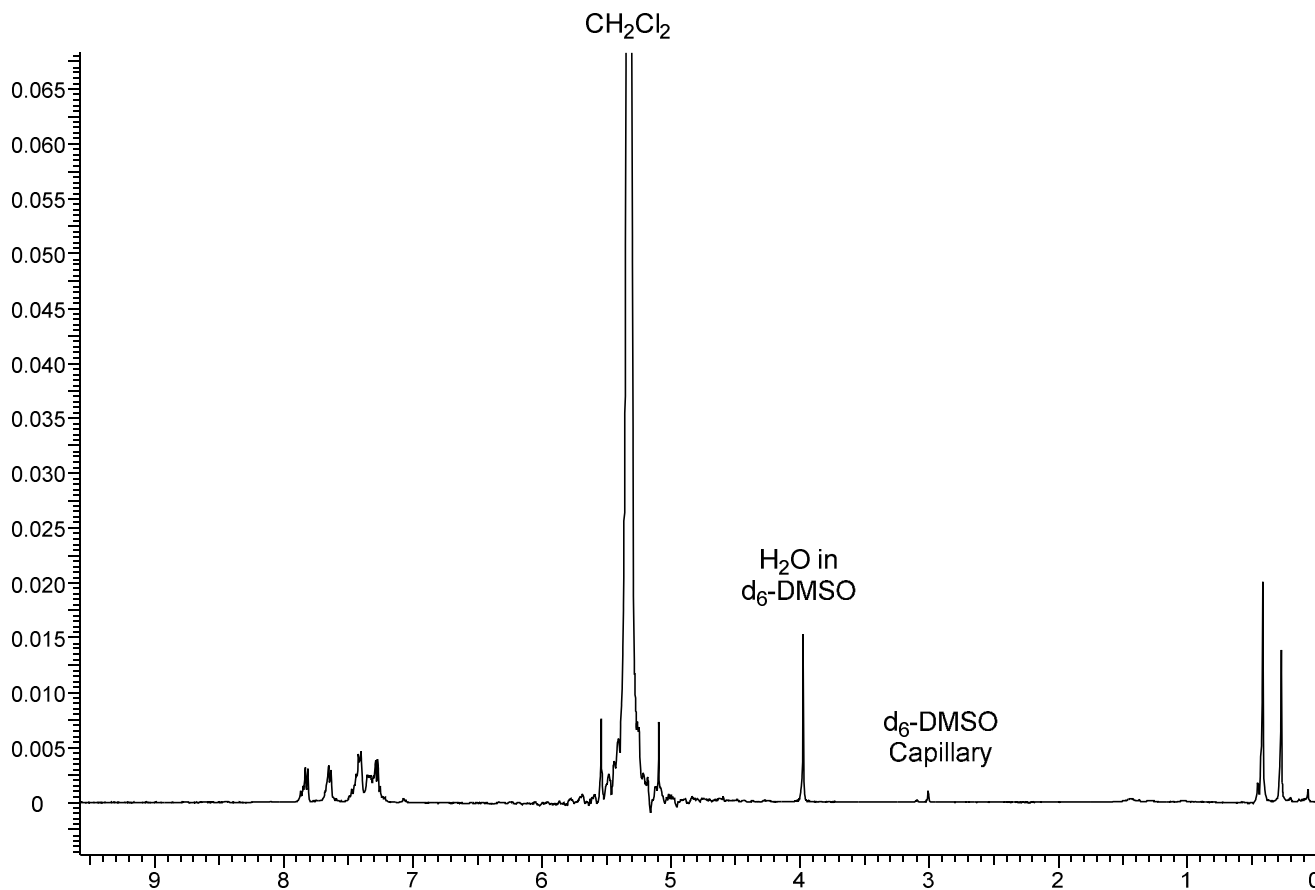
5c 9,9-Dimethyl-9-silafluorene



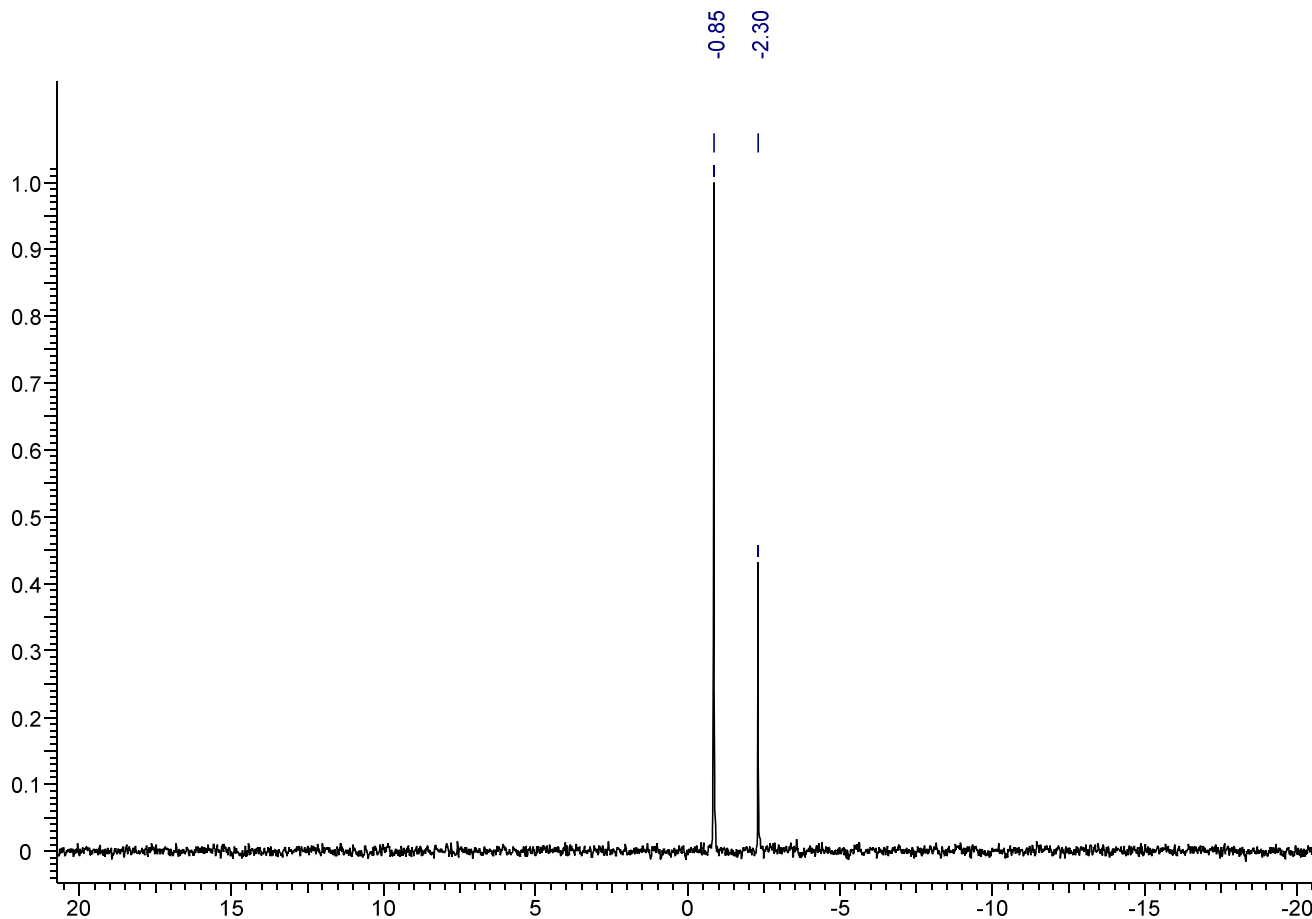
Synthesized according to general procedure 2, starting with 21 mg of 2-(Dimethylsilyl)biphenyl and 1 equivalent BCF (51 mg, 0.1 mmol) and Cl_2 -py (15 mg, 0.1 mmol). A 50 % conversion as observed in the 1H NMR spectrum with substituent scrambling as witnessed previously in the literature with small silicon substituents.³

Data for **5c** in accordance with literature²

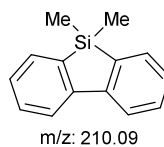
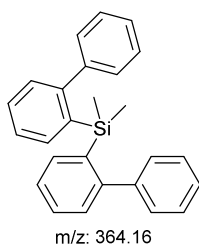
1H NMR Spectrum: *In-situ* 1H NMR spectrum with two Si-methyl resonances



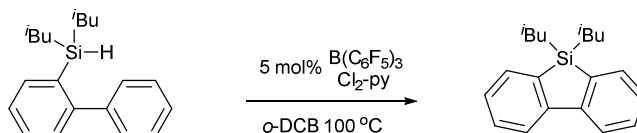
$^{29}\text{Si} \{^1\text{H}\}$ NMR Spectrum: *In-situ* $^{29}\text{Si} \{^1\text{H}\}$ NMR spectrum with two resonances



In the GC-MS there were peaks observed at 210.40 m/z and 364.56 m/z consistent with structures below, indicating substituents scrambling.



5d 9,9-Di-*isobutyl*-9-silafluorene



Synthesized according to general procedure 2, starting with 1 mL of 2-(Di-*isobutylsilyl*)biphenyl and 5 mol% BCF (86 mg, 0.17 mmol) and Cl₂-py (25 mg, 0.17 mmol). Purified by flash column chromatography where the eluent was pentane, this was then dried under high vacuum to give the title compound, **5d** (78 mg) as a colourless oil in 79 % yield.

¹H NMR (CD₂Cl₂ 400 MHz) δ 7.84 (d, ³J_{HH} 7.8 Hz, 2H), 7.66 (d, ³J_{HH} 7.0 Hz, 2H), 7.42 (t, ³J_{HH} 7.8 Hz, 2H), 7.26 (t, ³J_{HH} 7.3 Hz, 2H), 1.71 (septet, ³J_{HH} 6.5 Hz, 2H), 0.98 (d, ³J_{HH} 7.0 Hz, 4H) 0.81 (d, ³J_{HH} 6.5 Hz, 12H)

¹³C {¹H} NMR (CD₂Cl₂ 100 MHz) δ 148.7, 139.1, 134.0, 130.5, 127.8, 121.4, 26.5, 25.8, 24.3 ppm

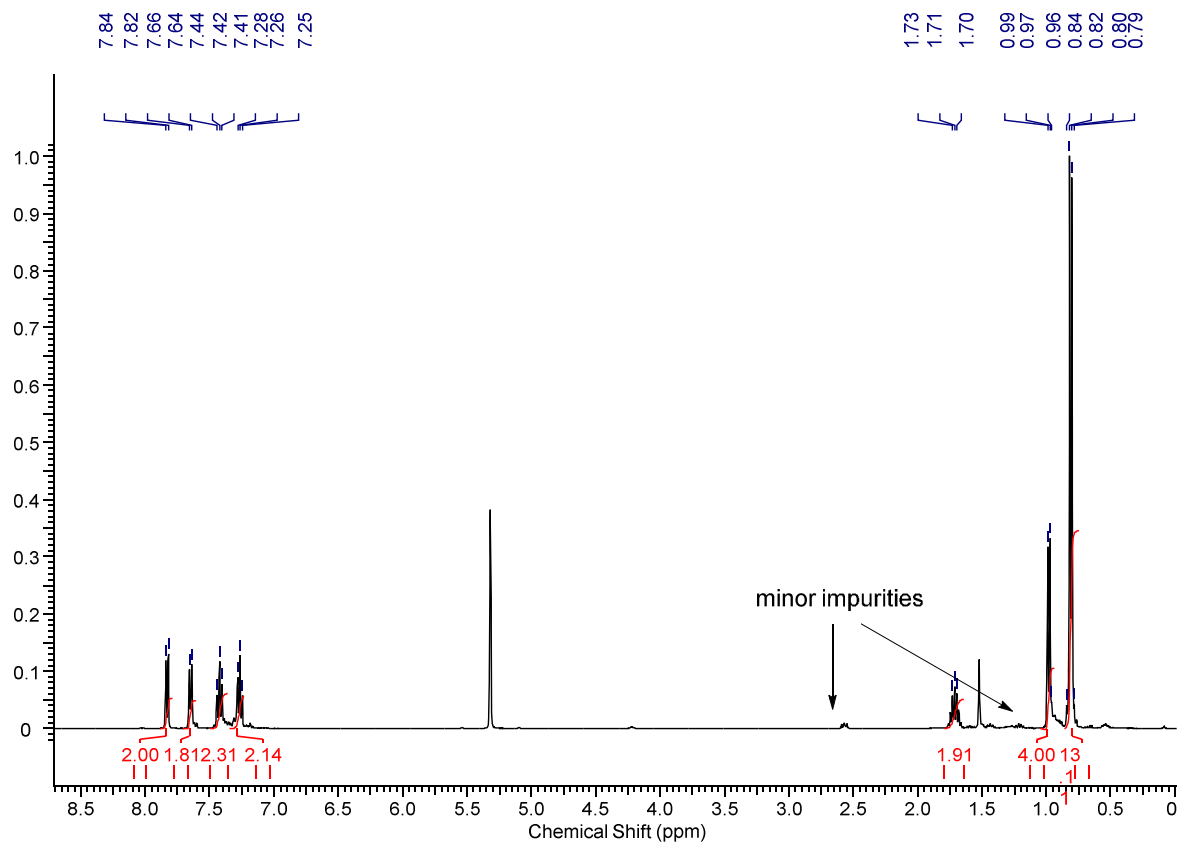
²⁹Si {¹H} NMR (CD₂Cl₂ 80 MHz) δ 1.36 ppm

Mass Spec: 294.1800 *m/z*, Expected for M⁺ 294.1798 *m/z*

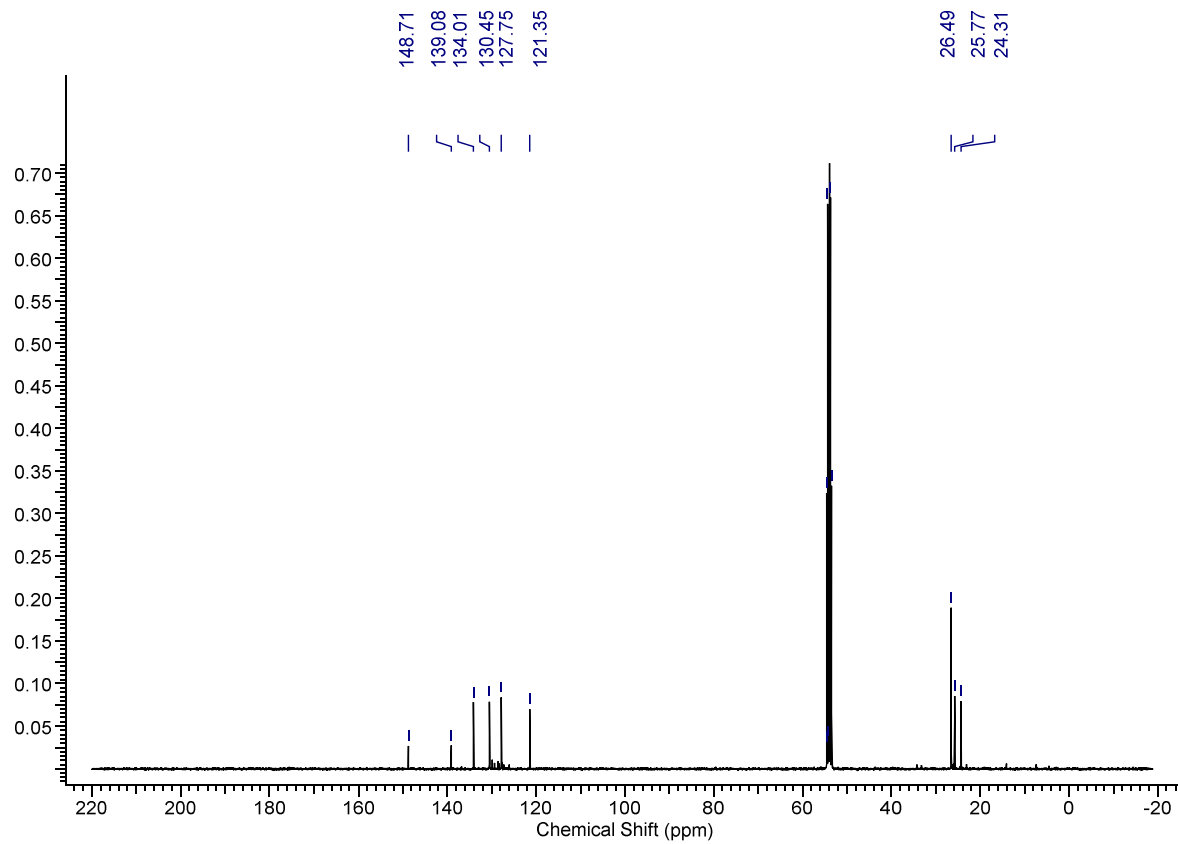
Elemental Analysis Expected C 81.57% H 8.90%, Found: C 79.52% H 9.56%

Inaccuracy in reported E.A. attributed to minor impurity carried through from initial synthesis of 4d. See ¹H NMR spectrum for 4d (S11) and 5d (S22).

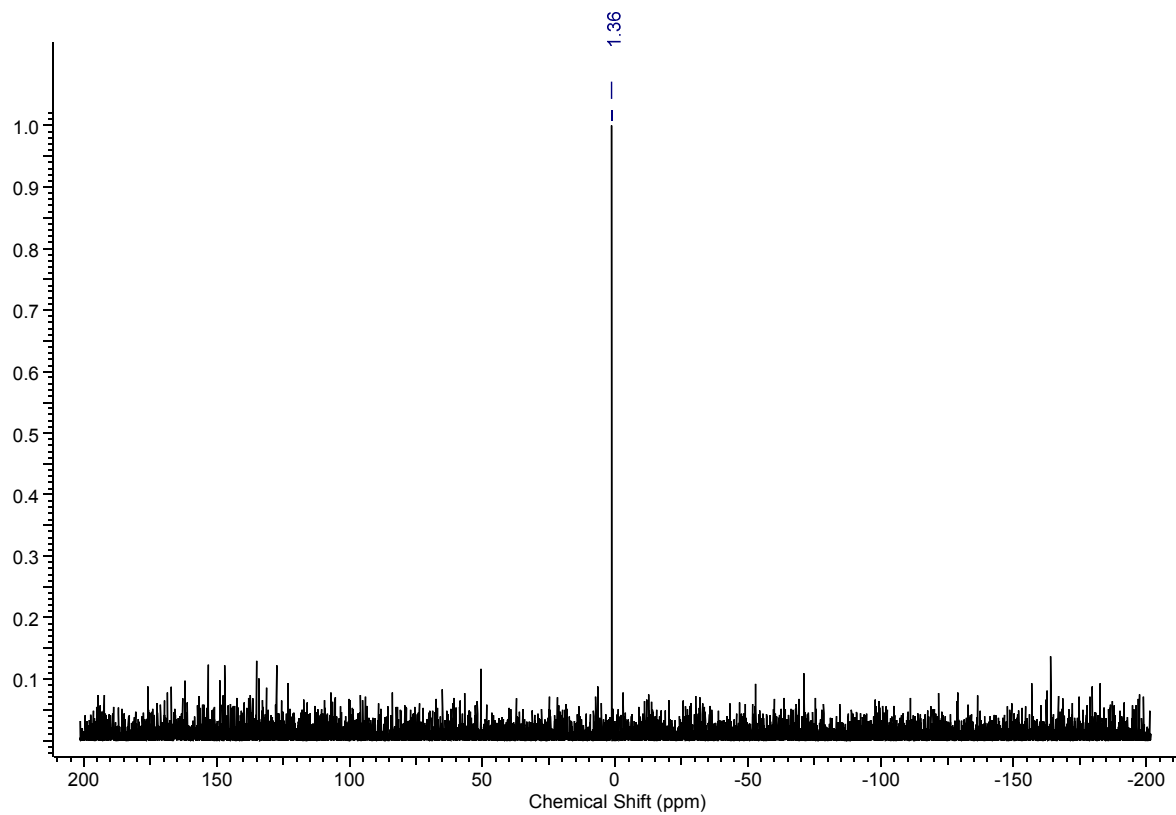
¹H NMR Spectrum: **5d** 9,9-Di-*isobutyl*-9-silafluorene



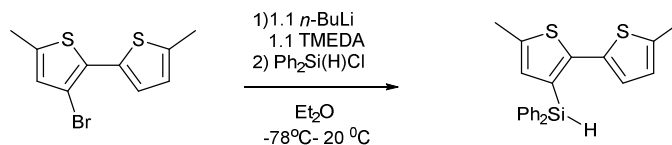
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum: 5d 9,9-Di-*isobutyl*-9-silafluorene



$^{29}\text{Si} \{^1\text{H}\}$ NMR Spectrum: 5d 9,9-Di-*isobutyl*-9-silafluorene



Synthesis of 6: 3-(Diphenylsilyl)-2,2'-dimethyl-bithiophene



To a solution of 3-bromo-5,5'-dimethyl-2,2'-biphenylene (2 g, 7.6 mmol) and TMEDA (1.1 equiv.), in diethyl ether 20 mL, was added *n*-butyl-lithium (1.1 equiv., 1.6 M in hexane) dropwise at -78 °C and stirred for 5 hours. To this solution was added diphenylchlorosilane (1.54 mL, 7.6 × 10⁻³ mol) dropwise at -78 °C and stirred for 1 hour. The reaction mixture was left to warm to room temperature and stirred for 64 hours. The product was extracted with ether and washed with sodium hydrogen carbonate (aq) and water. The organic layer was dried over magnesium sulfate. The solvent was removed under vacuum and purified by flash column chromatography (Eluent Hexane) and then by sublimation to give a yellow crystalline solid in 68 % yield. Minor impurity of 3,3'-dibromo-5,5'-dimethyl-2,2'-bithiophene present from synthesis 3-bromo-5,5'-dimethyl-2,2'-bithiophene that could not be readily separated in our hands.

¹H NMR (CDCl₃ 400 MHz) δ 7.57-7.54 (m, 4H), 7.44-7.35 (m, 6H), 6.79 (d, ³J_{HH} 3.5 Hz, 1H), 6.60 (d, ⁴J_{HH} 1.0 Hz, 1H), 6.58 (dd, ³J_{HH} = 3.5 Hz, ⁴J_{HH} 1.0 Hz, 1H), 5.51 (s, 1H), 2.44 (br-s, 6H)

¹³C {¹H} NMR (CDCl₃ 100 MHz) δ 144.0, 140.4, 139.4, 135.7, 135.0, 133.9, 133.1, 130.6, 129.6, 128.0, 126.6, 125.6, 15.3, 14.9 ppm

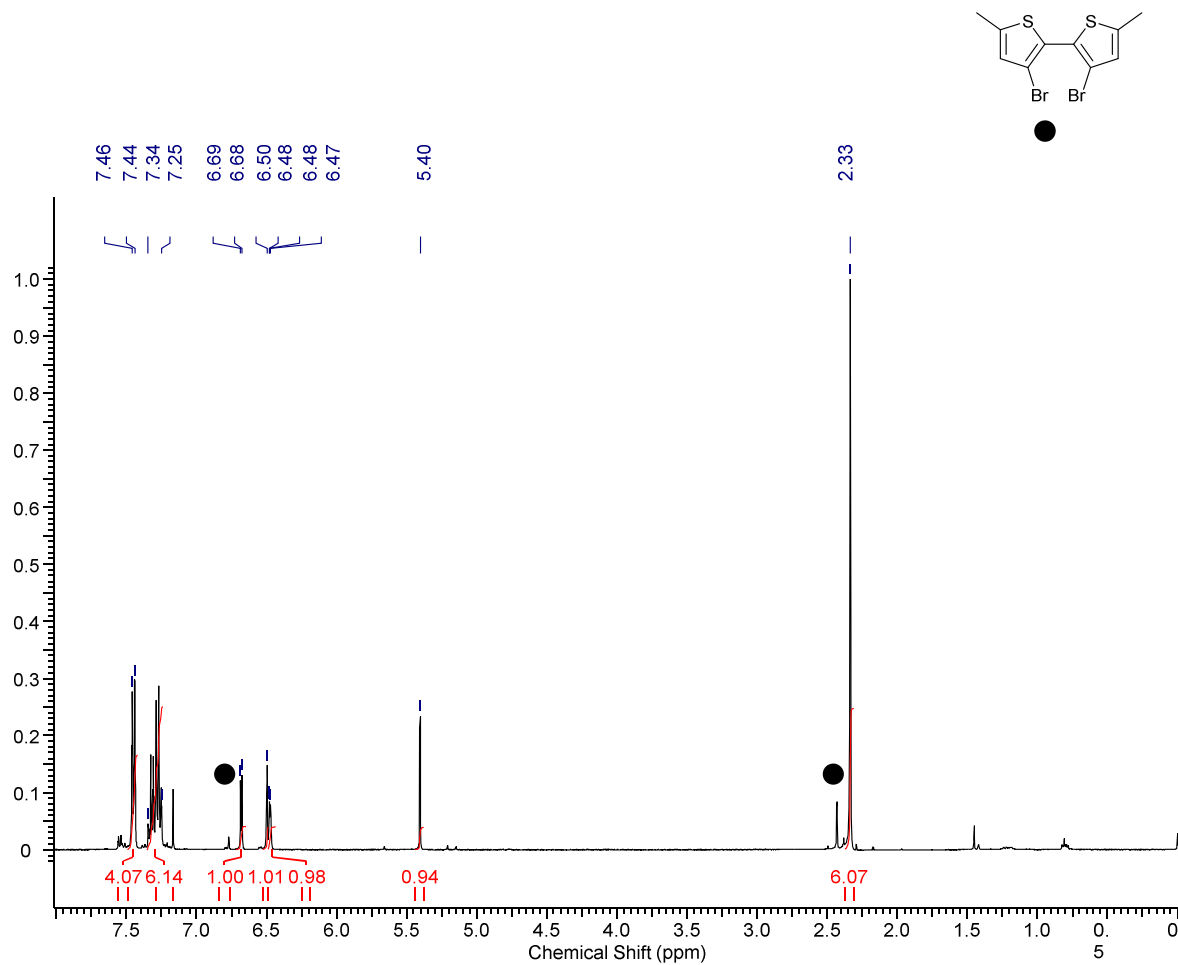
²⁹Si {¹H} NMR (CDCl₃ 80 MHz) δ -27.86 ppm

Mass Spec: 376.0758 *m/z*, Expected for M⁺ 376.0776 *m/z*

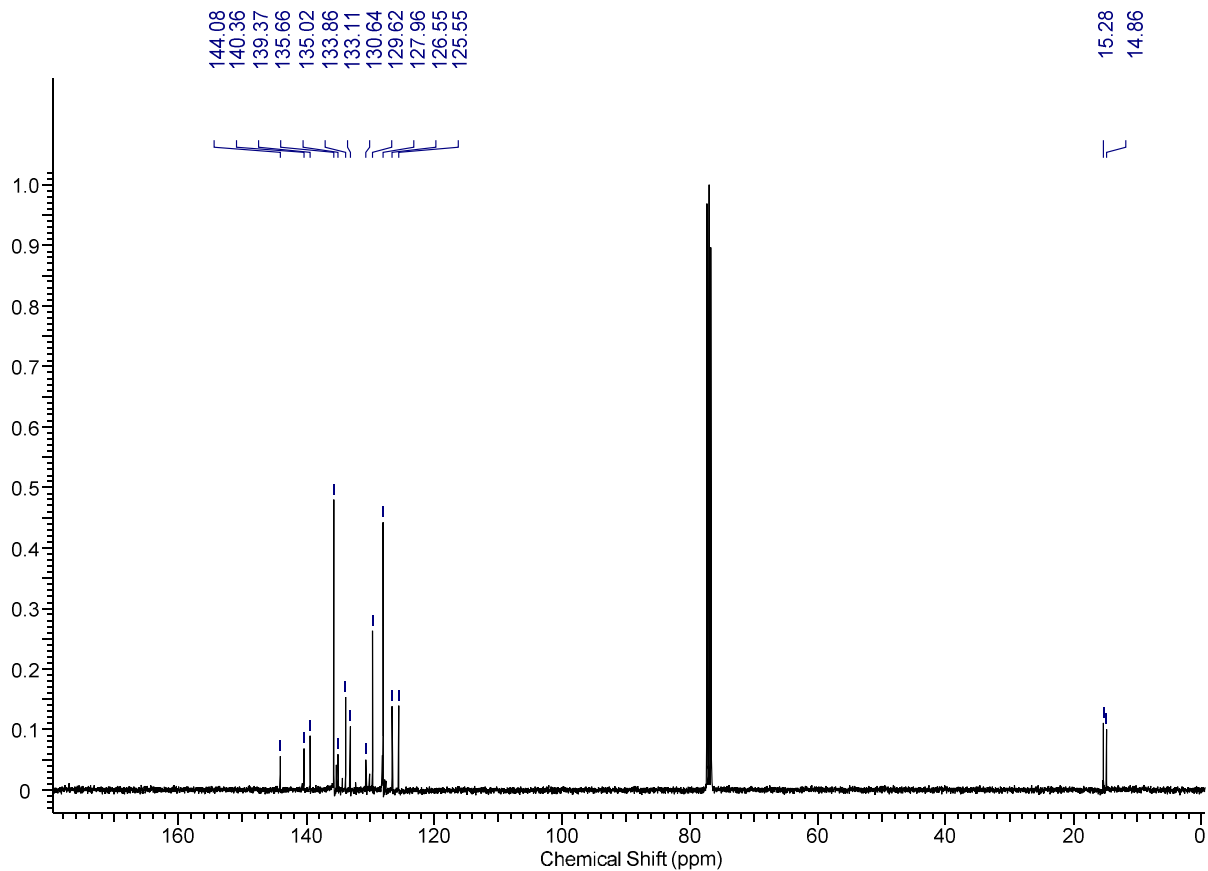
Elemental Analysis Expected C 70.16% H 5.35%, Found: C 69.85% H 5.45%

¹H NMR Spectrum: 3-(Diphenylsilyl)- 5,5'-dimethyl-2,2'-bithiophene

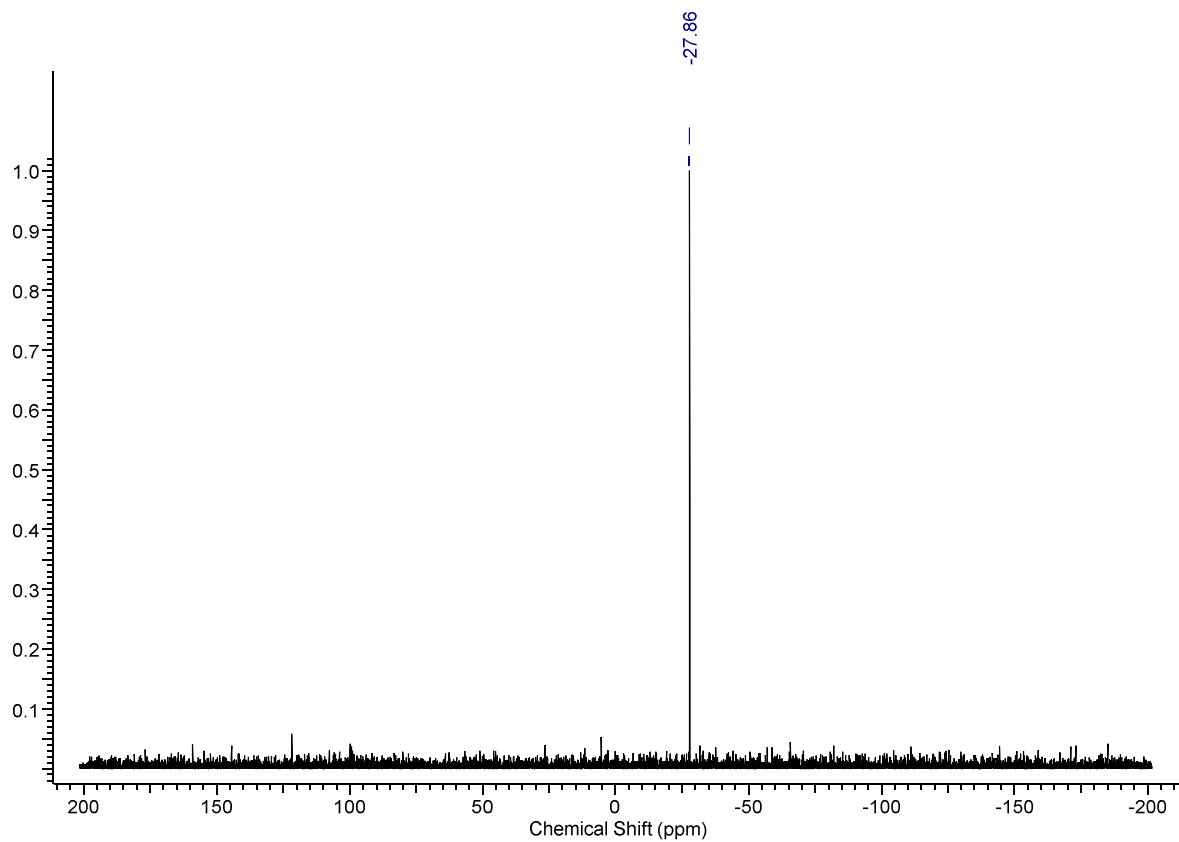
Minor impurity of 3,3'-dibromo-5,5'-dimethyl-2,2'-bithiophene present from synthesis 3-bromo-5,5'-dimethyl-2,2'-bithiophene



$^{13}\text{C} \{^1\text{H}\}$ NMR Spectrum: 3-(Diphenylsilyl)-2,2'-dimethyl-bithiophene



^{29}Si $\{^1\text{H}\}$ NMR Spectrum: 3-(Diphenylsilyl)-2,2'-dimethyl-bithiophene

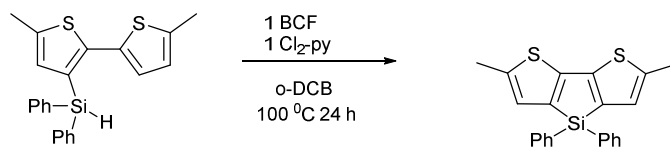


General procedure 3: Attempted synthesis of dithienosiloles

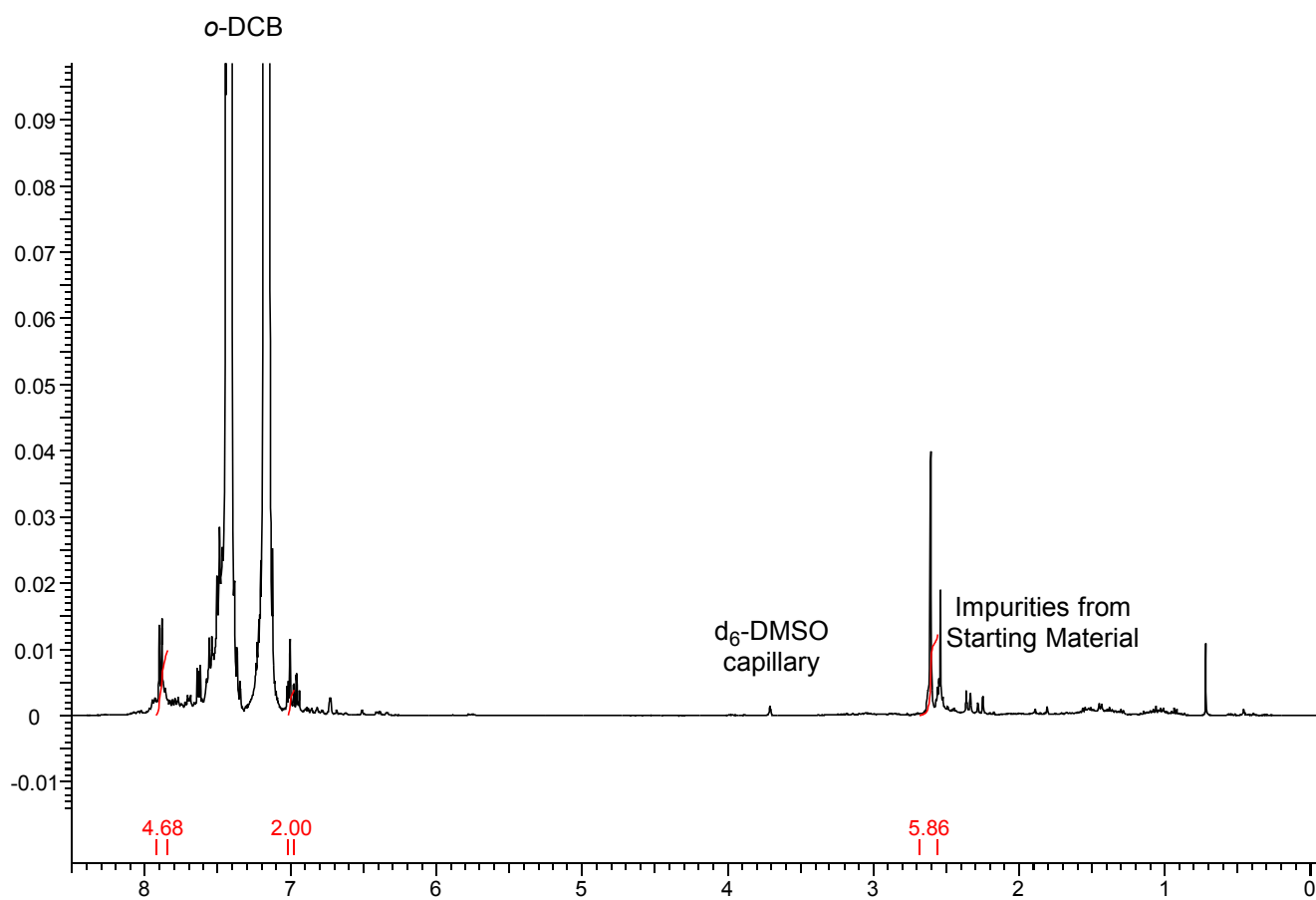
In an oven dried J Youngs NMR tube charged with a d_6 -DMSO capillary, **6** (1 equiv.) was added to a solution of BCF (x mol %) in CH_2Cl_2 . This solution was agitated for 5 minutes before the addition of base (x mol %) and then heated to 60/100 °C.

Initial stoichiometric test reactions:

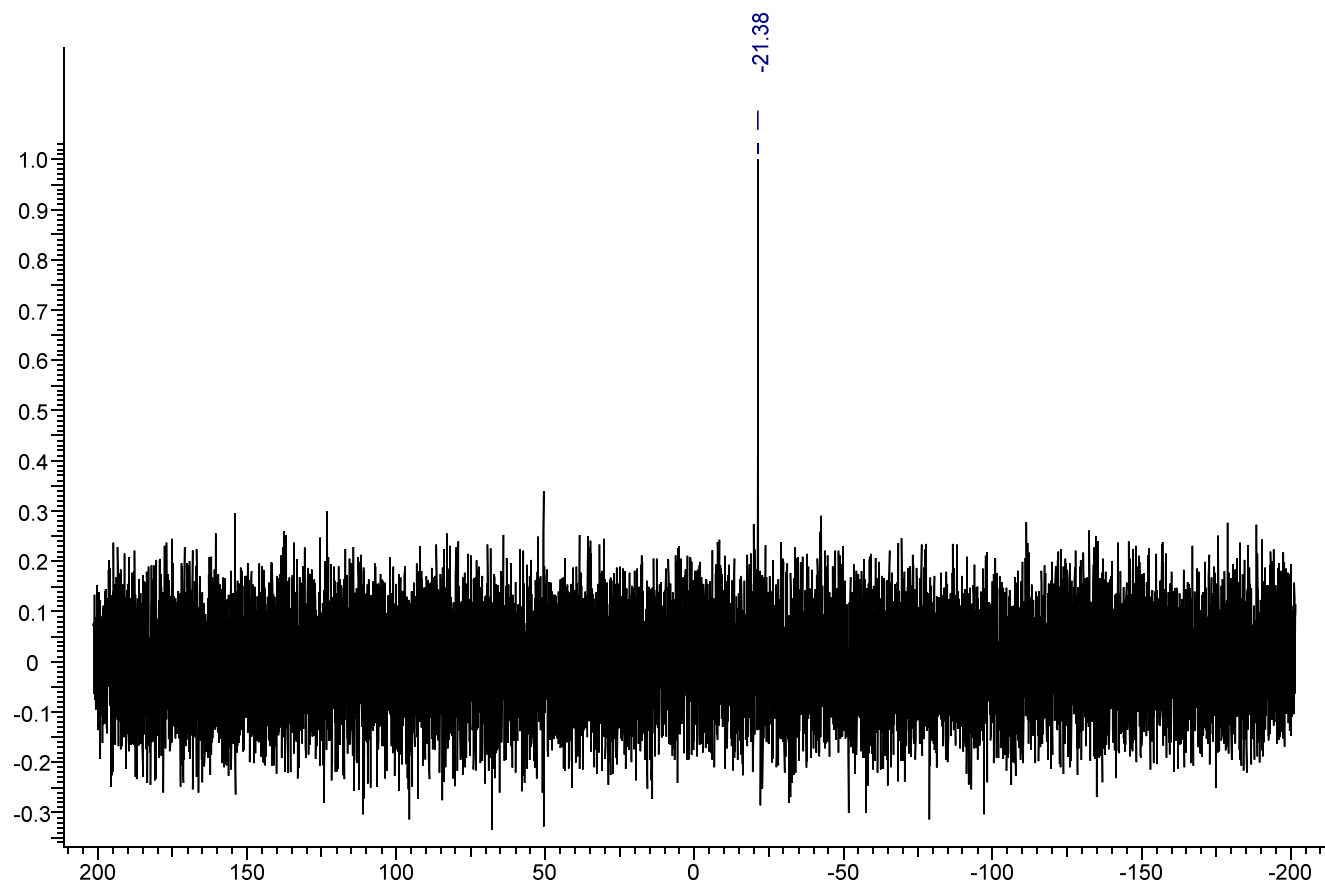
According to general procedure 3, starting with 38 mg of 3-(Diphenylsilyl)-5,5'-dimethyl-2,2'-bithiophene and one equivalent of BCF (51 mg) and Cl_2 -py (15 mg) in o-DCB or C_6D_5Br at 100 °C for 24 h. *In-situ* 1H / ^{29}Si NMR spectroscopy indicated full consumption of starting thiophene material. Attempts to purify by column chromatography on base treated silica were unsuccessful with the product of protodesilylation (5,5'-dimethyl-2,2'-bithiophene) repeatedly isolated



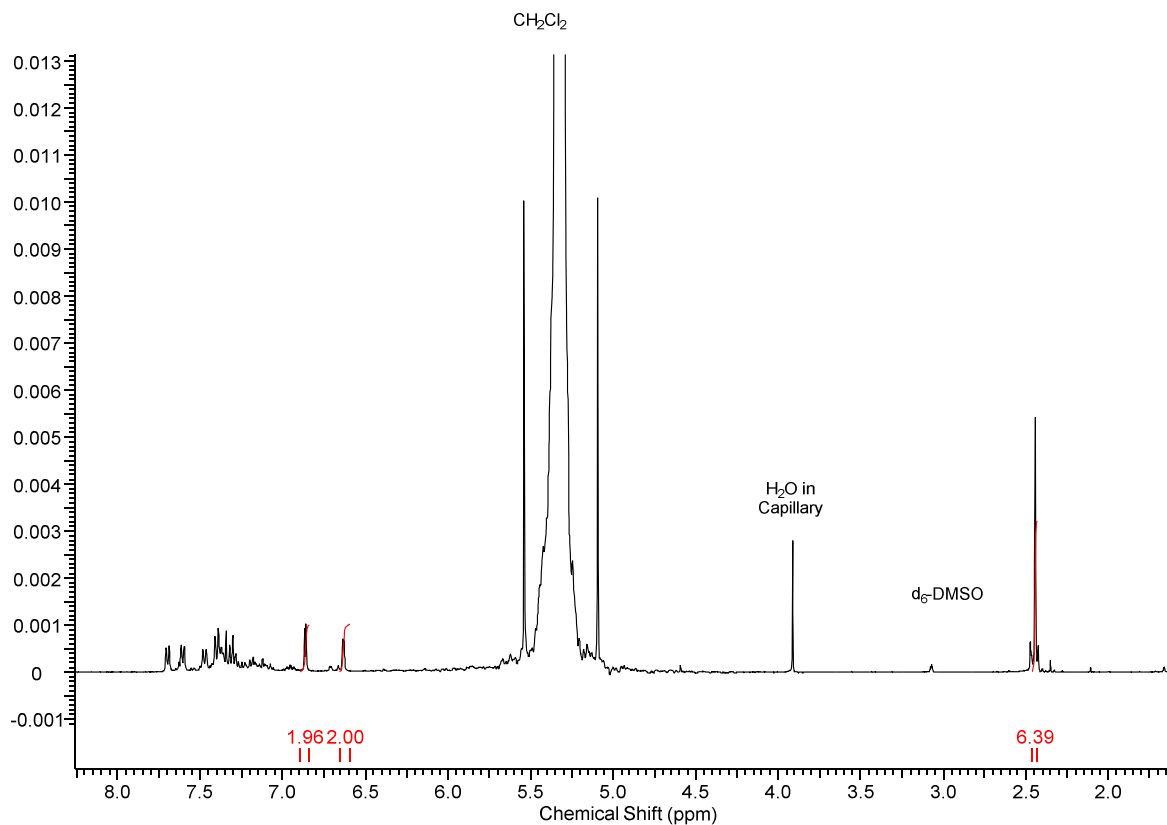
^1H NMR Spectrum: Reaction of **6** with 1 equiv. of BCF and $\text{Cl}_2\text{-py}$ at 100 °C for 24 h



^{29}Si $\{^1\text{H}\}$ NMR Spectrum: Reaction of **6** with 1 equiv. of BCF and $\text{Cl}_2\text{-py}$ at 100 °C for 24 h

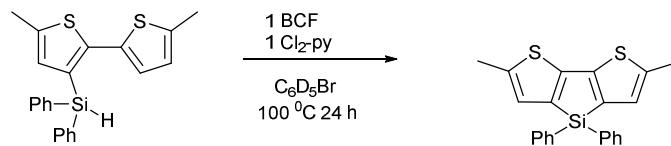


^1H NMR Spectrum: On removal of BCF through plug of silica

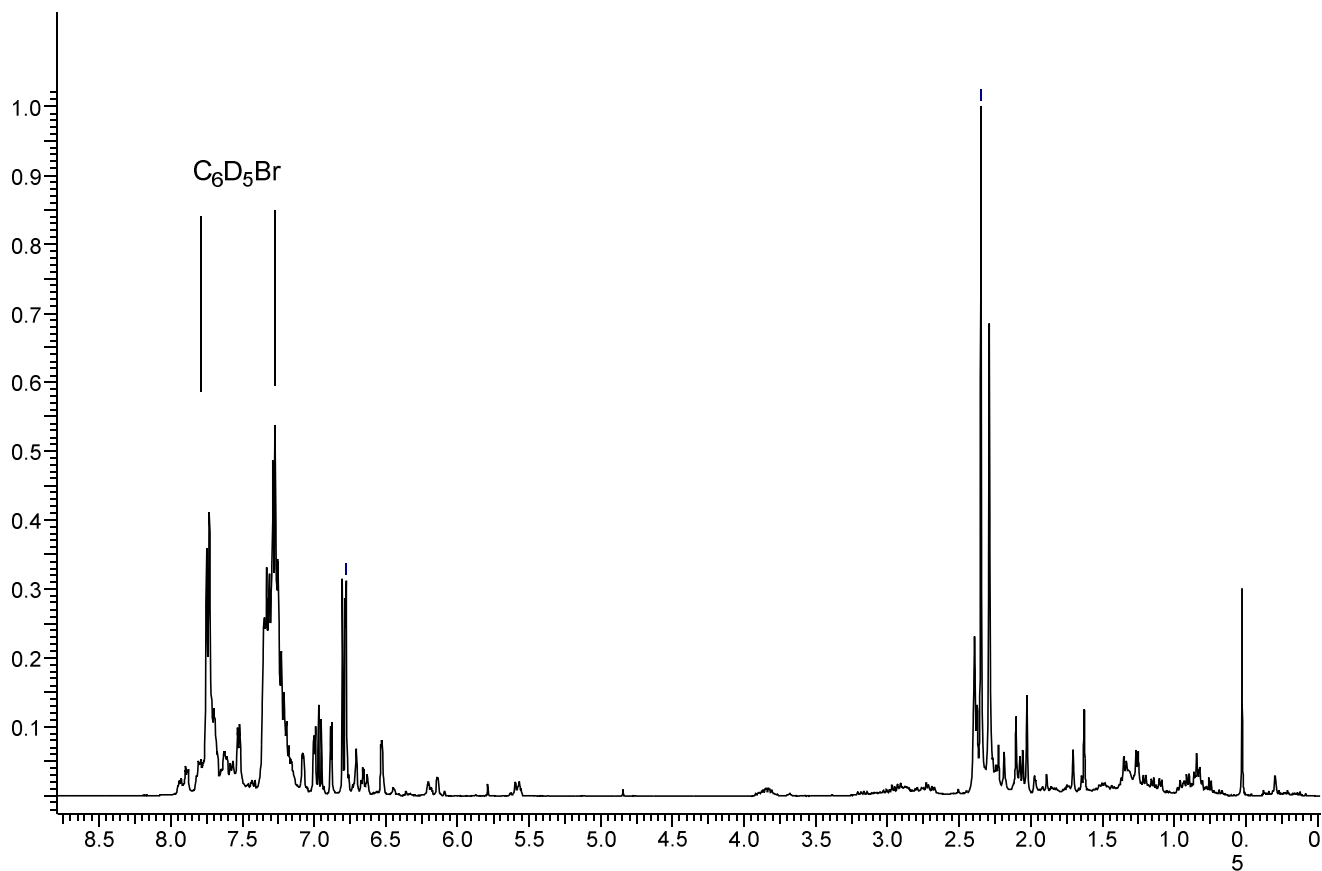


The observation of 5,5'-dimethyl-2,2'-bithiophene was attributed to protodesilylation on the column.

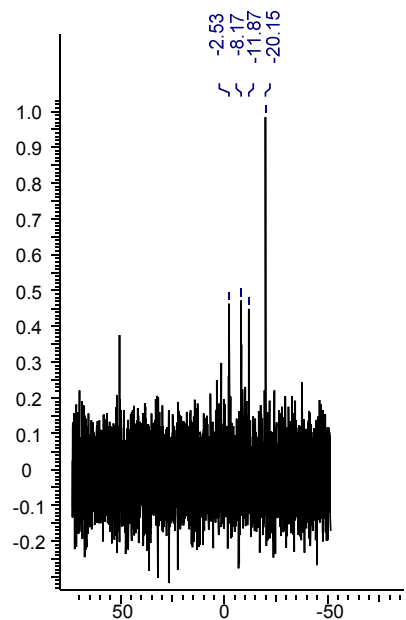
The stoichiometric reaction was repeated but in $\text{C}_6\text{D}_5\text{Br}$. The NMR spectra showed the growth of the symmetrical compound once more, but this time along with an array of other compounds.



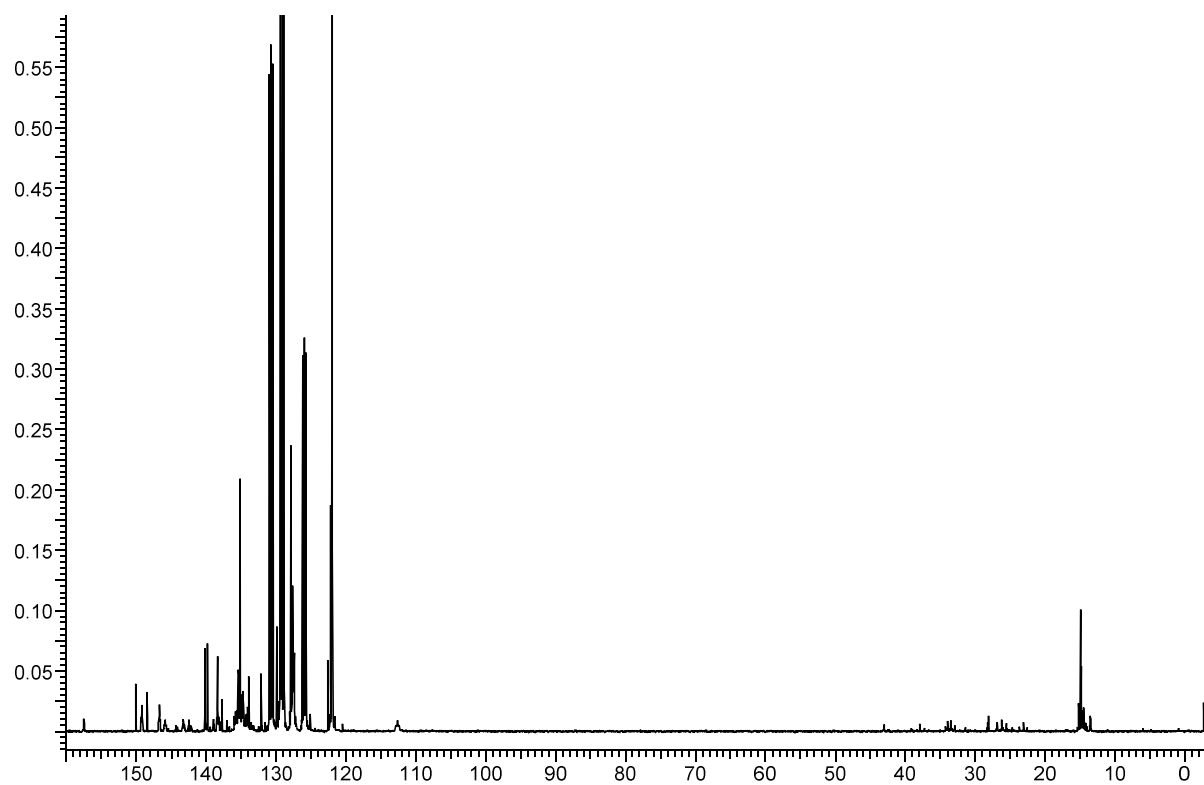
¹H NMR Spectrum: Reaction of **6** with 1 equiv. of BCF and Cl₂-py at 100 °C for 24 h in C₆D₅Br



$^{29}\text{Si} \{^1\text{H}\}$ NMR Spectrum: Reaction of **6** with 1 equiv. of BCF and Cl_2 -py at 100 °C for 24 h in $\text{C}_6\text{D}_5\text{Br}$



$^{13}\text{C} \{^1\text{H}\}$ NMR Spectrum: Reaction of **6** with 1 equiv. of BCF and Cl_2 -py at 100 °C for 24 h in $\text{C}_6\text{D}_5\text{Br}$

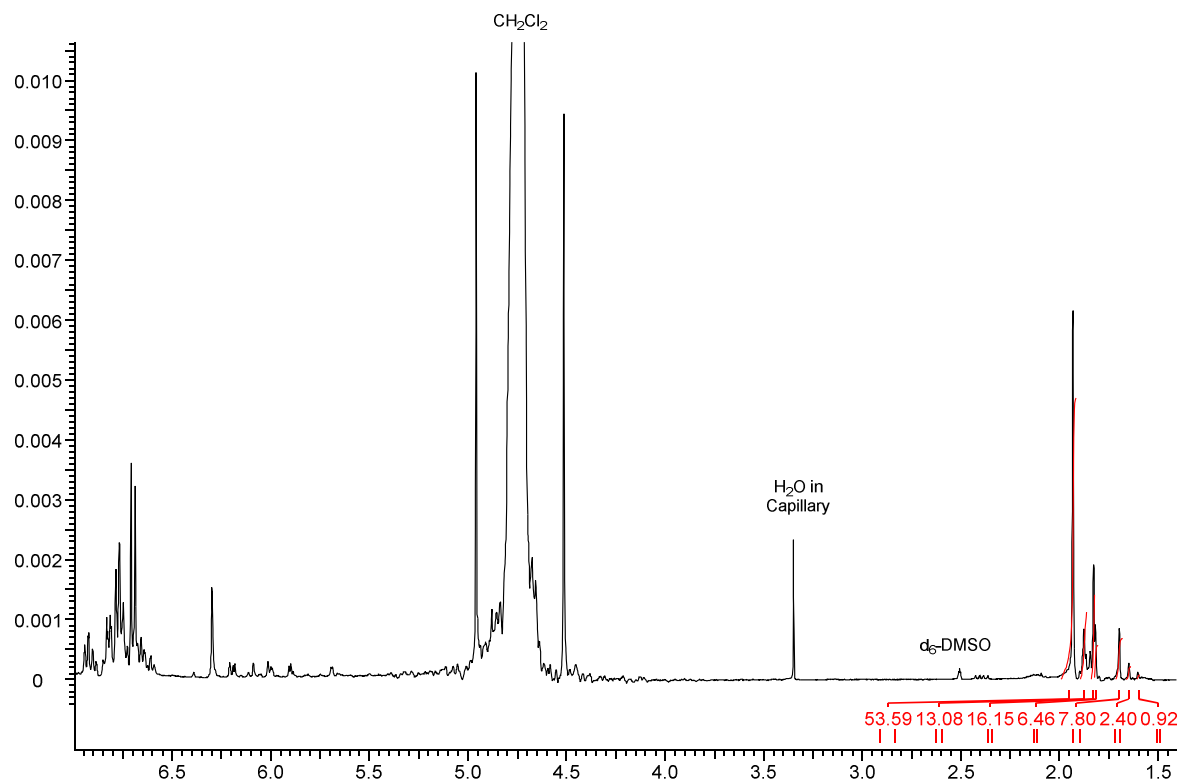


The reaction was repeated but with catalytic BCF (5 mol%) and Cl₂-py (5 mol%) and several methods were undertaken in an attempt to determine the major compound and any observation of the synthesis of the diethienosilole.

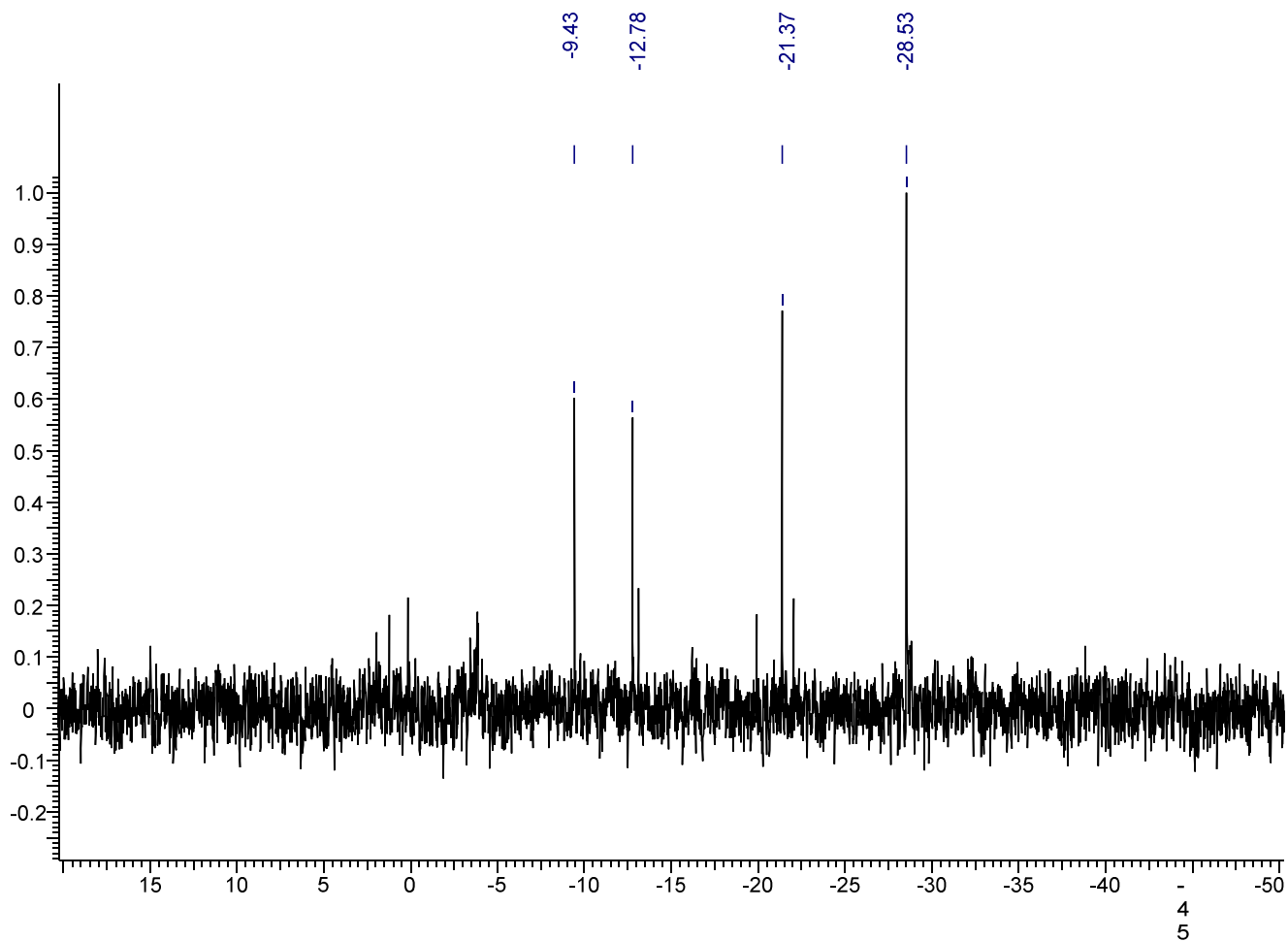
Catalytic test reaction

Synthesized according to general procedure 3, starting with 147 mg of 3-(Diphenylsilyl)- 5,5'-dimethyl-2,2'-bithiophene and 5 mol% of BCF (10 mg) and Cl₂-py (3 mg) in DCM at 60 °C for 148 h. *In-situ* ¹H / ²⁹Si {¹H} NMR spectroscopy indicated full consumption of **6** but the formation of a range of substituted bithiophene compounds.

¹H NMR Spectrum: **6** reaction with 5 mol% BCF Cl₂-py

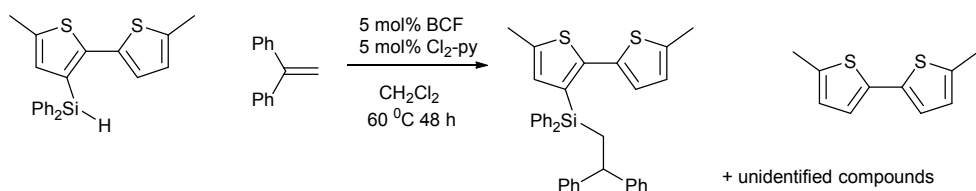


$^{29}\text{Si} \{^1\text{H}\}$ NMR Spectrum:

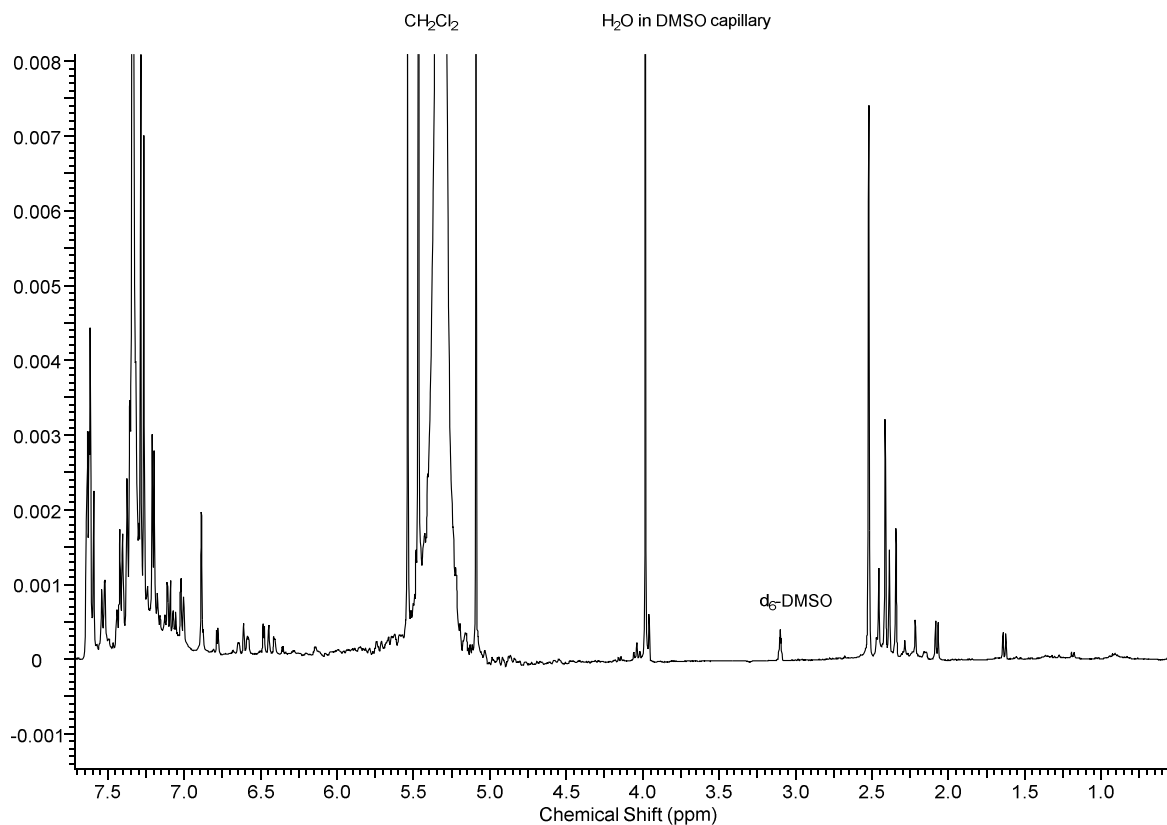


Stronger bases were tested to disfavour competing protodesilylation. When the base was changed to $\text{P}(\text{C}_6\text{F}_5)_2$ or 2-Fluoro-6-Methylpyridine the results were similar to that of $\text{Cl}_2\text{-py}$ by $^1\text{H} / ^{29}\text{Si} \{^1\text{H}\}$ NMR spectroscopy

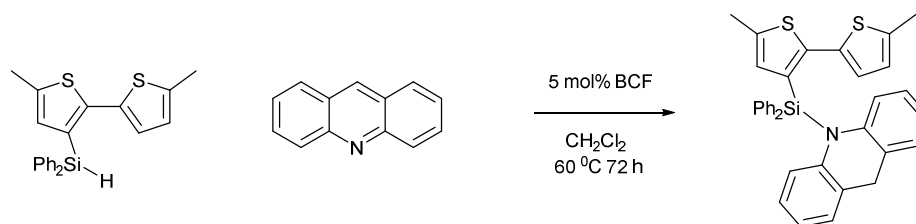
A range of H₂ scavengers were added to the reaction mixture in an attempt to drive the reaction forward by accepting the proton from [H-Cl₂-py]⁺ and hydride from [BCF-H]⁻. Methallyltrimethylsilane and 1,1-diphenylethylene (DPE) were used as each is rapidly hydrogenated using FLPs. However, methallyltrimethylsilane and DPE both underwent preferential hydrosilylation when combined with 6 and catalytic Cl₂-py / BCF. In the ¹H NMR spectra it was observed that the bithiophene reduction compounds still formed along with the suspected hydrosilylated product of the “H₂ scavenger”



¹H NMR Spectrum: Methallyltrimethylsilane as a “H₂ scavenger”



Attempts were made with other bases that would act as a hydride acceptor once protonated. The first of these, acridine, led to the hydrosilylated compound.

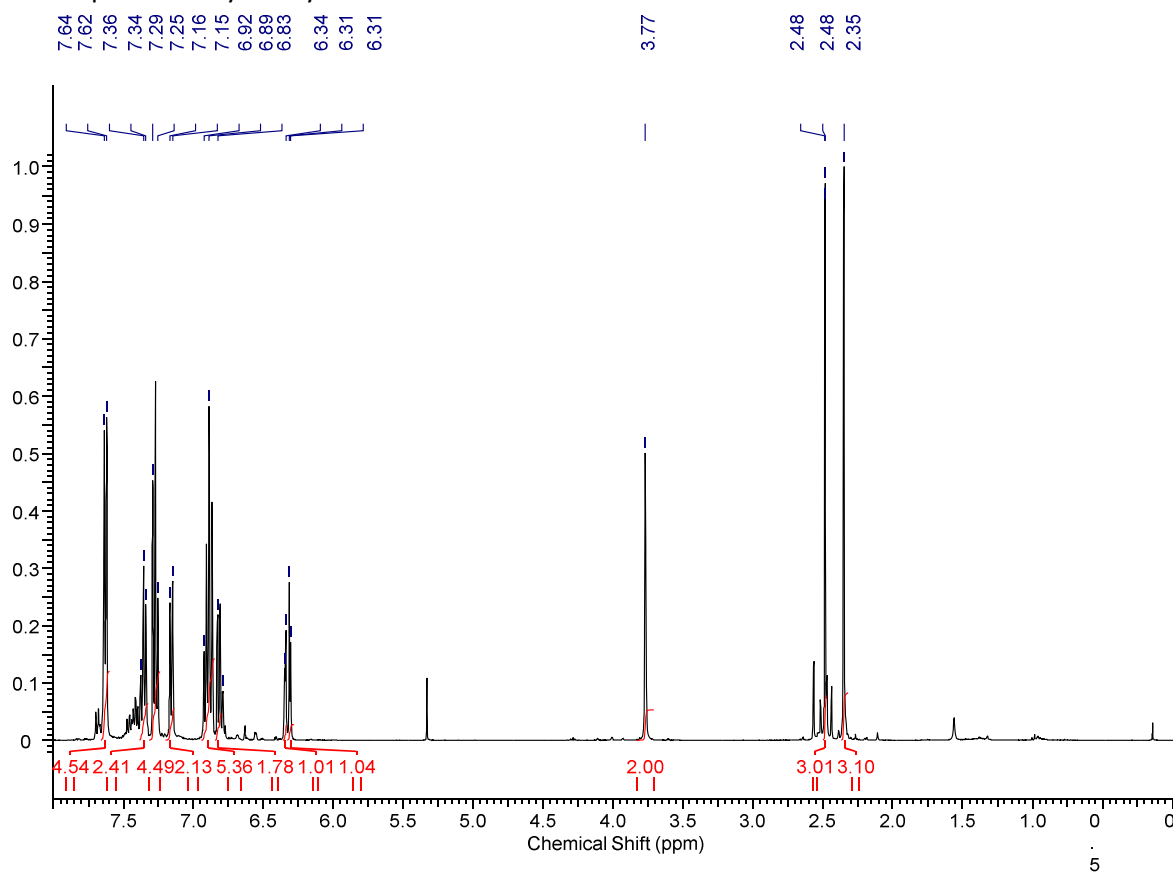


^1H NMR (CDCl_3 400 MHz) δ 7.64-7.62 (m, 4H), 7.37-7.34 (m, 2H), 7.29-7.25 (m, 4H), 7.17 (d, $^3J_{\text{HH}}$ 7.0 Hz, 2H), 6.92-6.87 (m, 5H), 6.83-6.79 (m, 3H), 6.35-6.34 (m, 1H), 6.32-6.31 (m, 1H), 3.77 (s, br, 2H), 2.48 (s, br, 3H), 2.35 (s, br, 3H)

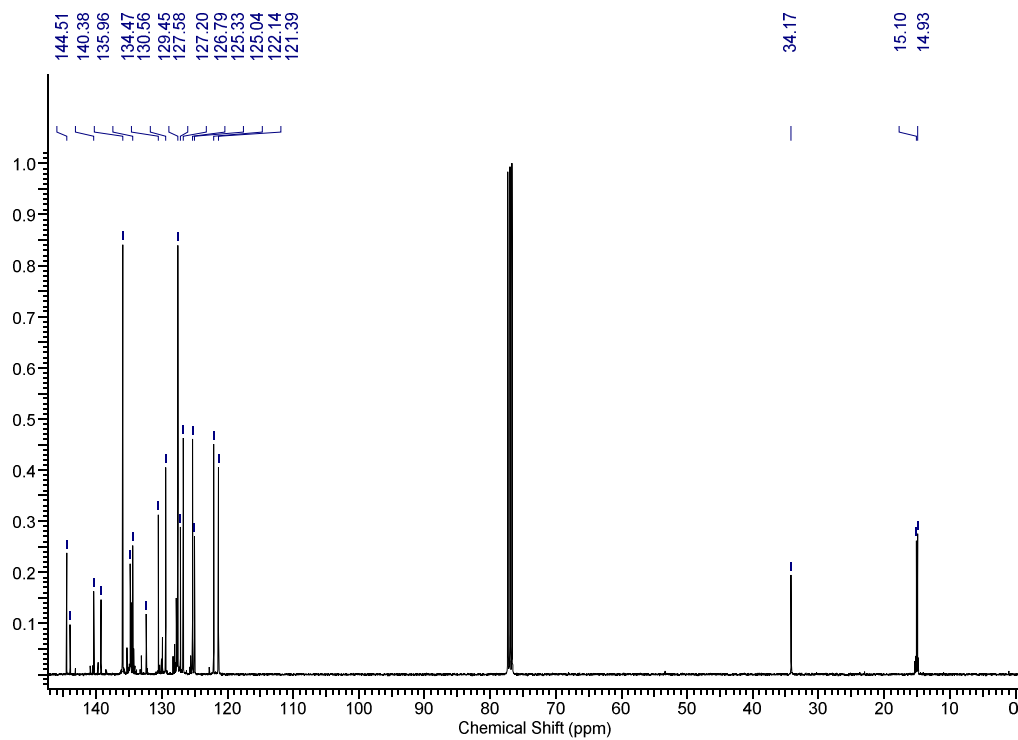
^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 100 MHz) δ 144.5, 140.4, 135.9, 134.4, 130.6, 129.5, 127.6, 127.2, 126.8, 125.3, 125.0, 122.1, 121.4, 34.2, 15.1, 14.9 ppm

^{29}Si $\{^1\text{H}\}$ NMR (CDCl_3 80 MHz) δ -19.48 ppm

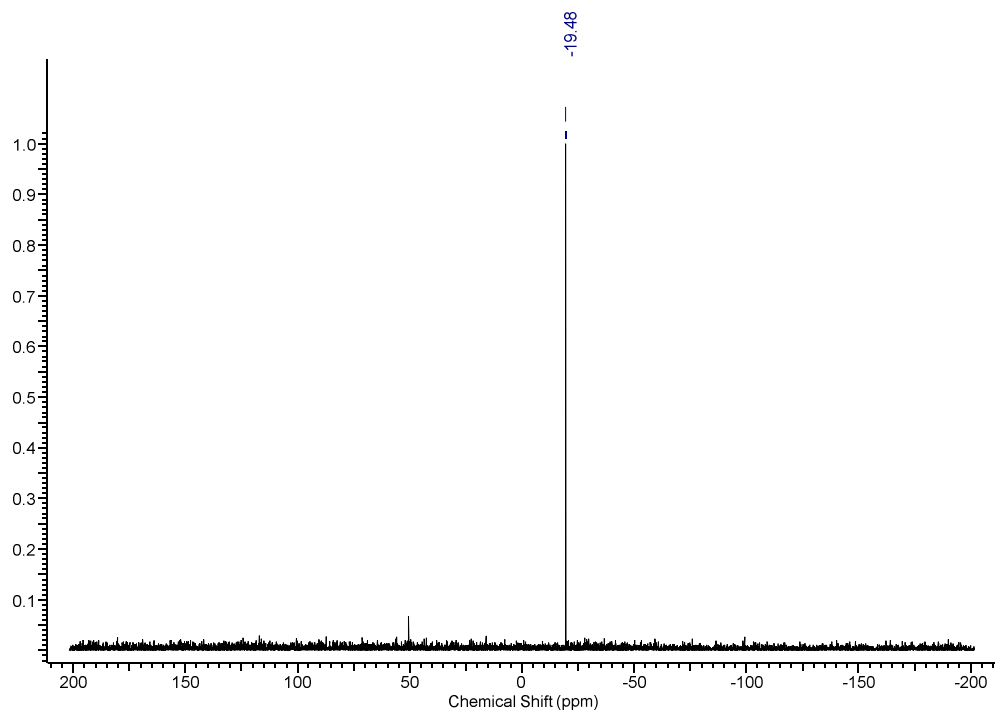
^1H NMR Spectrum: Hydrosilylated acridine



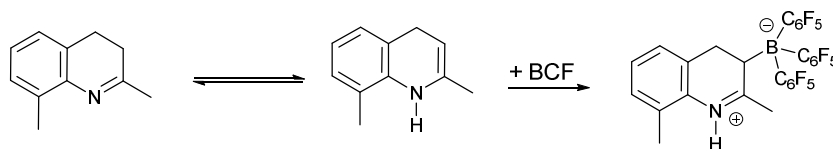
$^{13}\text{C} \{^1\text{H}\}$ NMR Spectrum: Hydrosilylated acridine



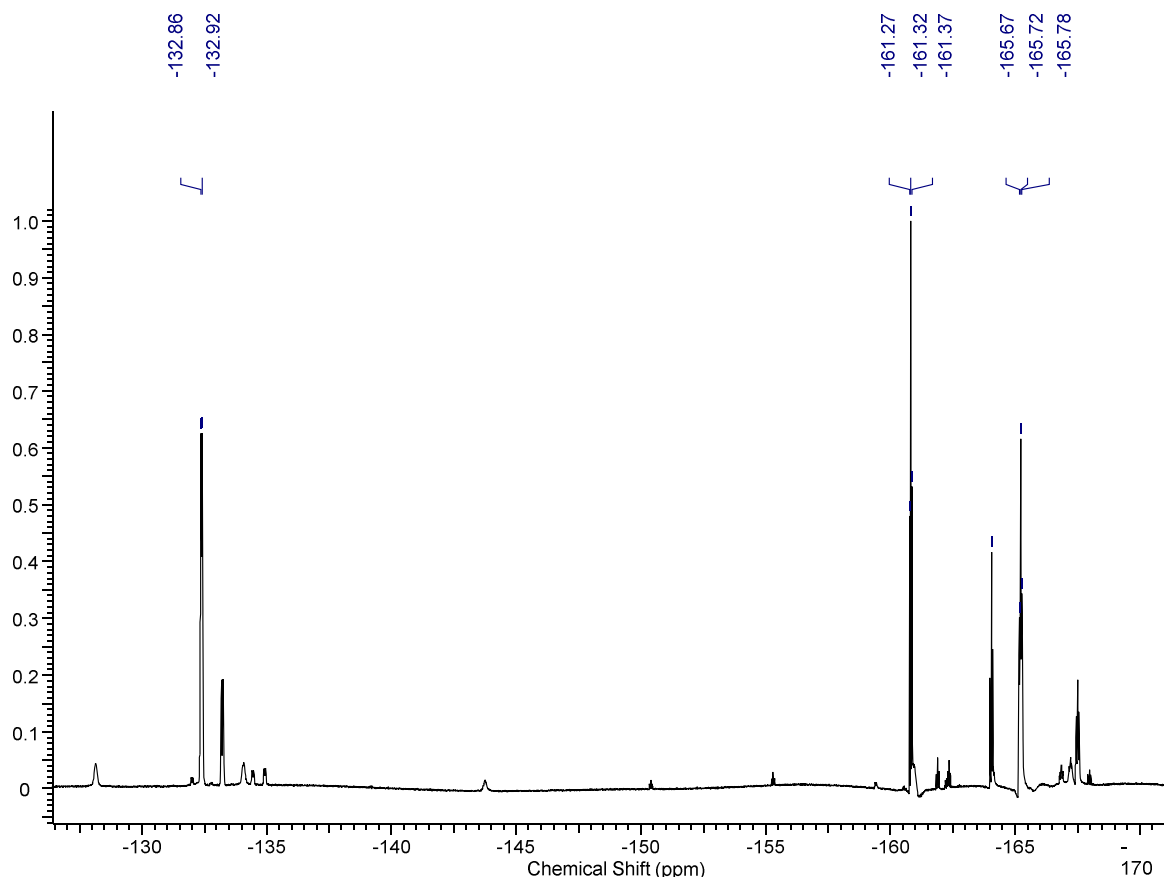
$^{29}\text{Si} \{^1\text{H}\}$ NMR Spectrum: Hydrosilylated acridine



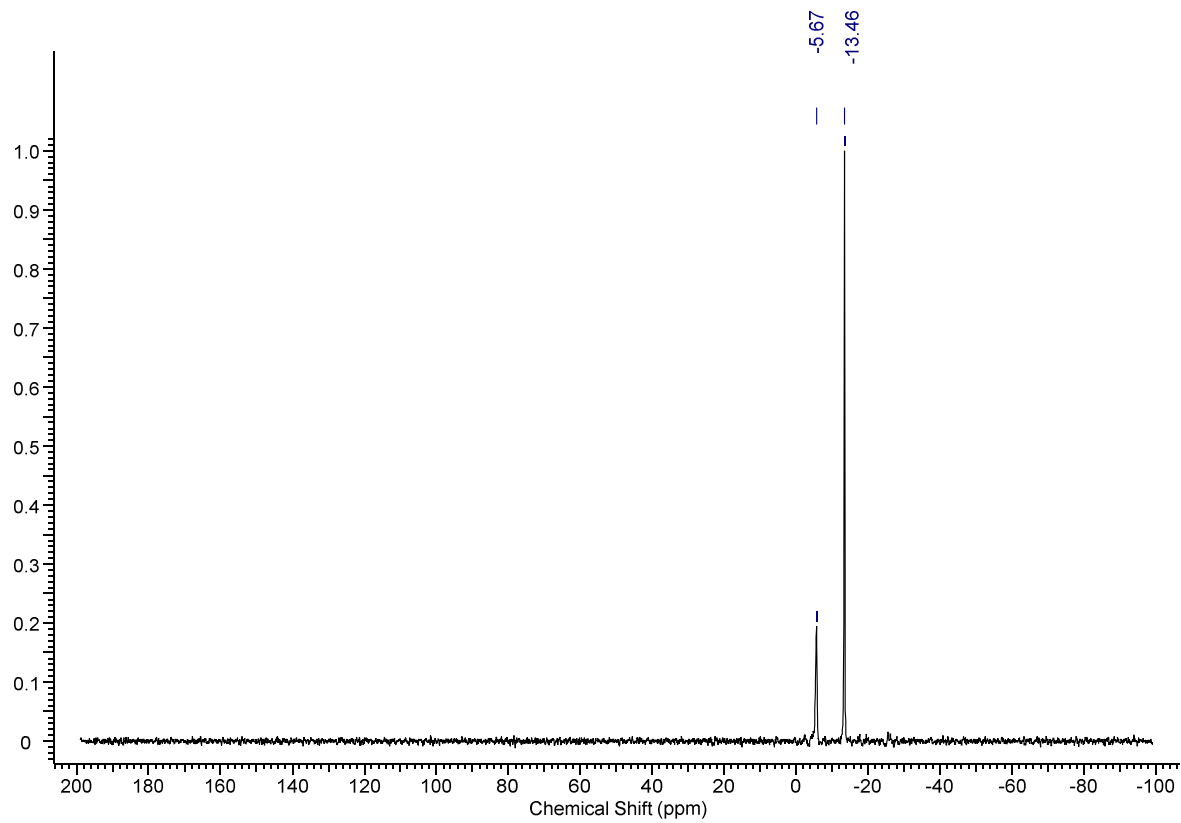
The bases tested for the second approach were acridine, benzo[*h*]quinoline, 8-methylquinoline and 2,8-dimethylquinoline which all form FLPs with BCF. In control reactions using Ph_3SiH / BCF three quinolines (benzo[*h*]quinoline, 8-methylquinoline and 2,8-dimethylquinoline) did not undergo 1,4-hydrosilylation due to the increased steric crowding around N. However, the addition of stoichiometric quantities of each of these three bases to catalytic BCF and **6** resulted in no significant dithienosilole formation instead a new BCF containing species is rapidly formed. In-situ NMR spectroscopy was consistent with the formation using 2,8-dimethylquinoline of a four coordinate BCF derived species containing an additional C-B bond. This is attributed to the quinoline reduction products reacting with BCF to form iminium zwitterions thus consuming BCF and preventing catalytic SEAr. Related C-B bond formation on combining an imine with BCF has been previously observed for $^t\text{Bu}(\text{CH}_3)\text{C}=\text{NBn}$, with steric bulk around N key for preventing $\text{N} \rightarrow \text{BCF}$ dative bond formation.⁴



^{19}F $\{^1\text{H}\}$ NMR Spectrum: In-situ NMR spectrum of the formation of zwitterion of BCF and 2,8-dimethylquinoline



^{11}B $\{^1\text{H}\}$ NMR Spectrum: In-situ NMR spectrum of the formation of zwitterion of BCF and 2,8-dimethylquinoline

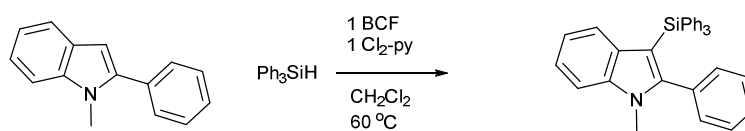


Open System Test

Attempts to cyclize **6** in an open system to minimize the amount of dissolved H₂ did not produce the protodesilylated product **7**, however, starting material **6** was the major species even after long reaction times.

In an oven dried J Youngs NMR tube charged with a d₆-DMSO capillary, **6** (147 mg) was added a solution of BCF (10mg, 5 mol %) in *o*-DCB. This solution was agitated for 5 minutes before the addition of base (3 mg, 5 mol %) and then taken into a glovebox and placed into an aluminium block and heated to 60 °C. The J Youngs cap was removed to allow the reaction to take place in an open system, the cap was replaced for monitoring by NMR spectroscopy. From ¹H / ²⁹Si NMR spectroscopy multiple products were observed along with a drop in reaction rate, 72 % of starting material was still present after 72 h.

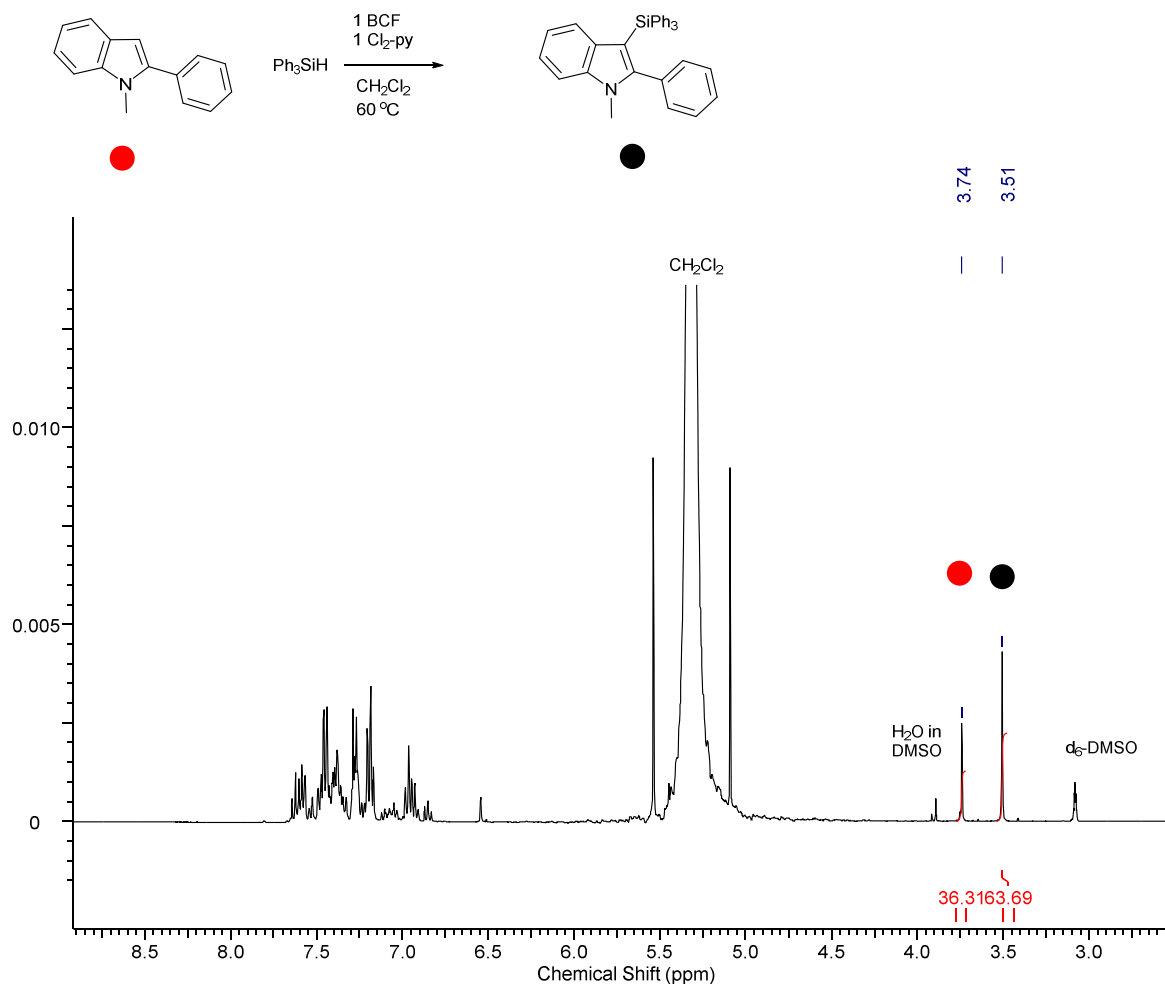
Electrophilic silylation 2-Phenylindole



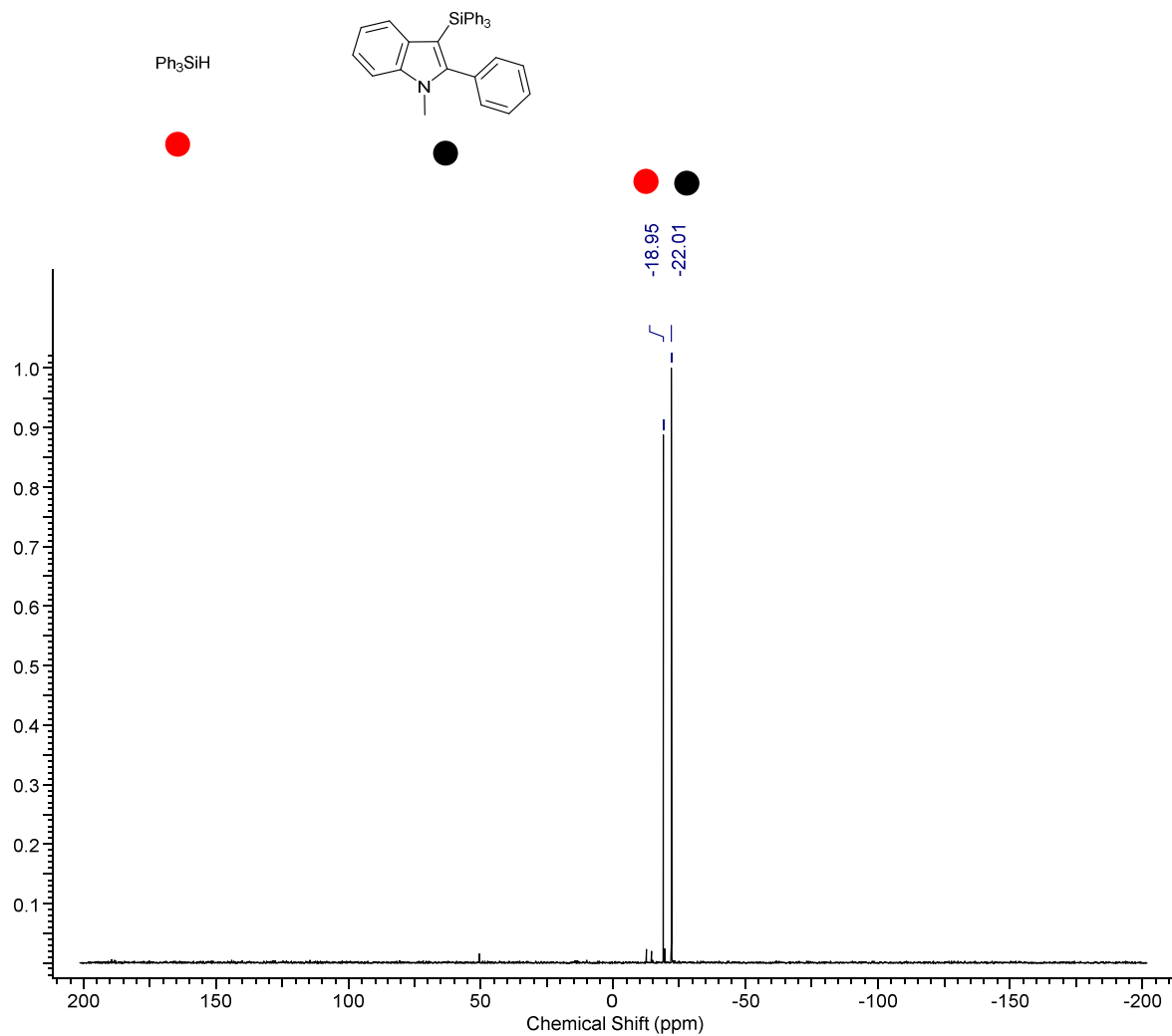
To an oven dried J Youngs NMR tube equipped with a $\text{d}_6\text{-dmsO}$ capillary, triphenylsilane (1 equiv.) was added to a solution of BCF (20 mg) in CH_2Cl_2 . This solution was agitated for 5 minutes before the addition of $\text{Cl}_2\text{-py}$ (1 equiv.) and 2-phenyl-N-methylindole (1 equiv.). The reaction was heated to 60°C and monitored by ^1H / ^{29}Si NMR spectroscopy.

64 % conversion of the desired silylated compound as observed by ^1H NMR spectroscopy, however we were unable to separate it from 2-phenyl-N-methylindole by column chromatography. Mass spec showed a m/z^+ at 466 which is what is expected for the m/z^+ ion for the silylated indole compound. Importantly, no significant amount of reduced indoline species was observed by ^1H NMR spectroscopy.

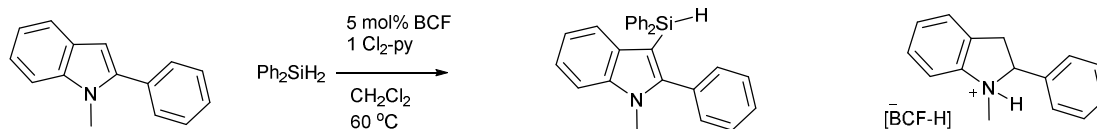
^1H NMR Spectrum: Reaction of triphenylsilane with 2-phenylindole



^{29}Si $\{^1\text{H}\}$ NMR Spectrum: Reaction of triphenylsilane with 2-phenylindole



Tandem intermolecular/intramolecular electrophilic silylation of 2-phenylindole

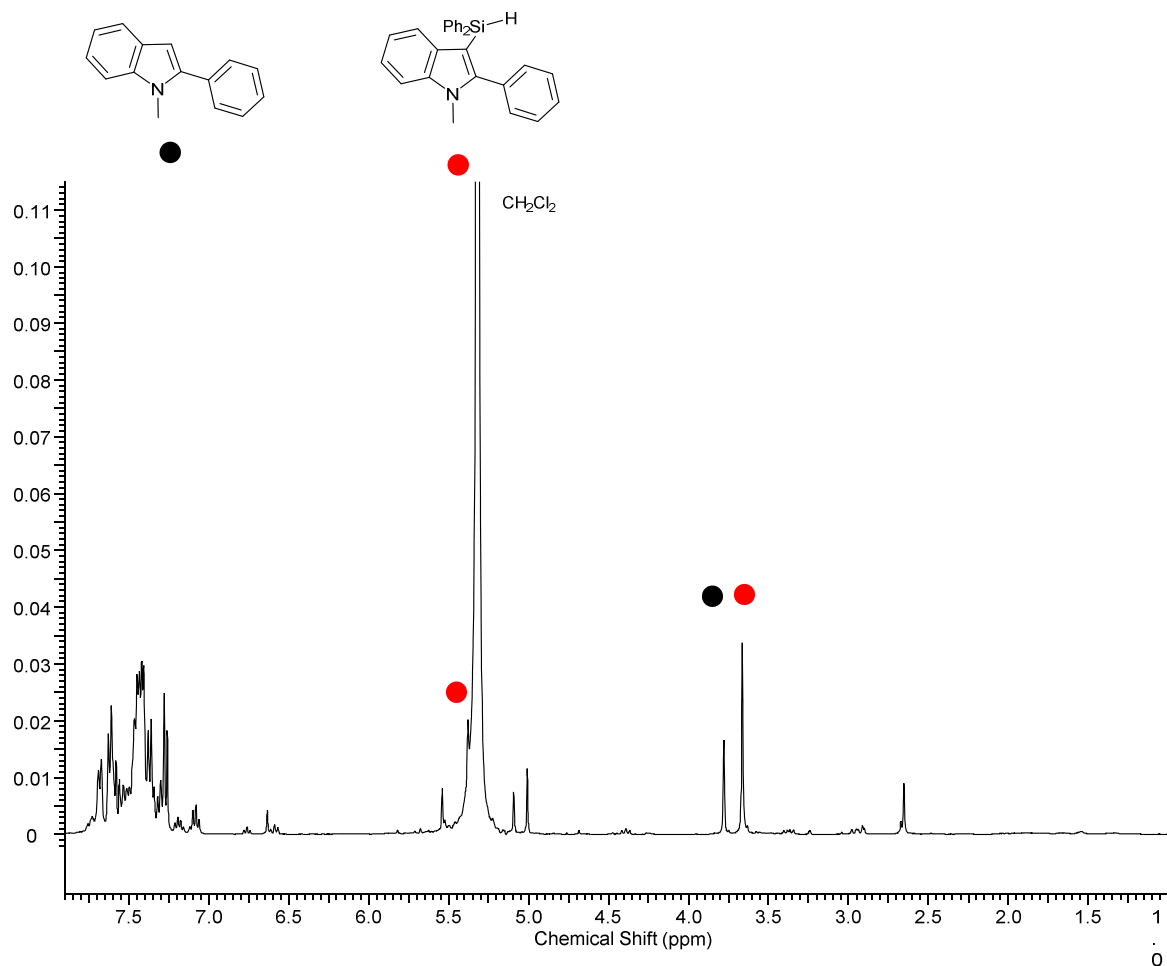


In an oven dried J Youngs NMR tube equipped with a $\text{d}_6\text{-dmsO}$ capillary, diphenylsilane (1 equiv.) was added to a solution of BCF (10 mg) in CH_2Cl_2 . This solution was agitated for 5 minutes before the addition of $\text{Cl}_2\text{-py}$ (1 equiv.) and 2-phenyl-N-methylindole (1 equiv.). The reaction was heated to 60°C and monitored by NMR spectroscopy. ^{19}F $\{^1\text{H}\}$ and ^{11}B $\{^1\text{H}\}$ NMR spectroscopy confirmed the formation of $[\text{BCF-H}]^+$ suppressing catalytic reactivity. We attribute the cation to the protonated indoline which has previously been reported to suppress catalytic reactivity with BCF.⁵

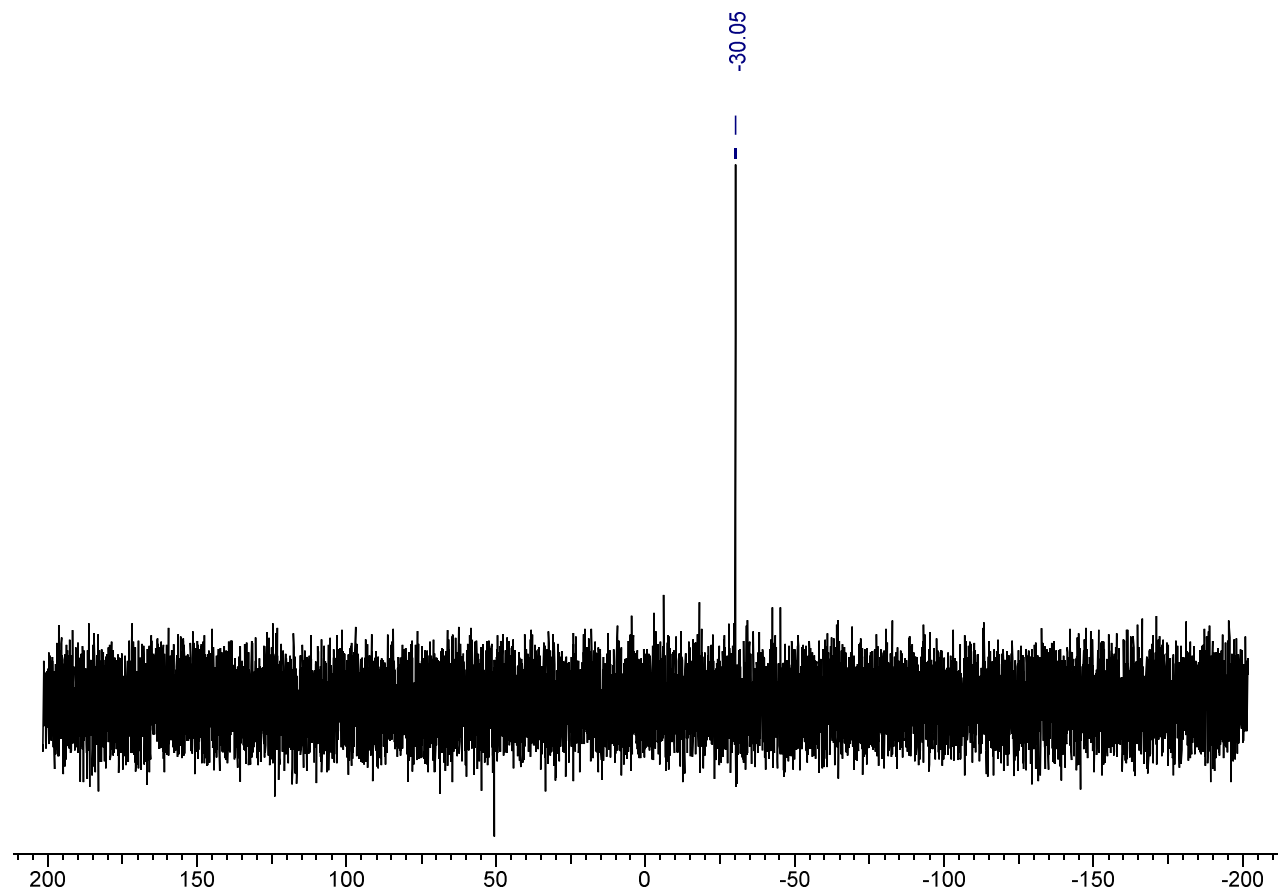
Mass Spectrometry:

$m/z^+ = 390.2$ of the C3 silylated indole compound, along with main fragment at 208.0 for the loss of the HSiPh_2^+ fragment indicate formation of the initial intermolecular electrophilic silylation product.

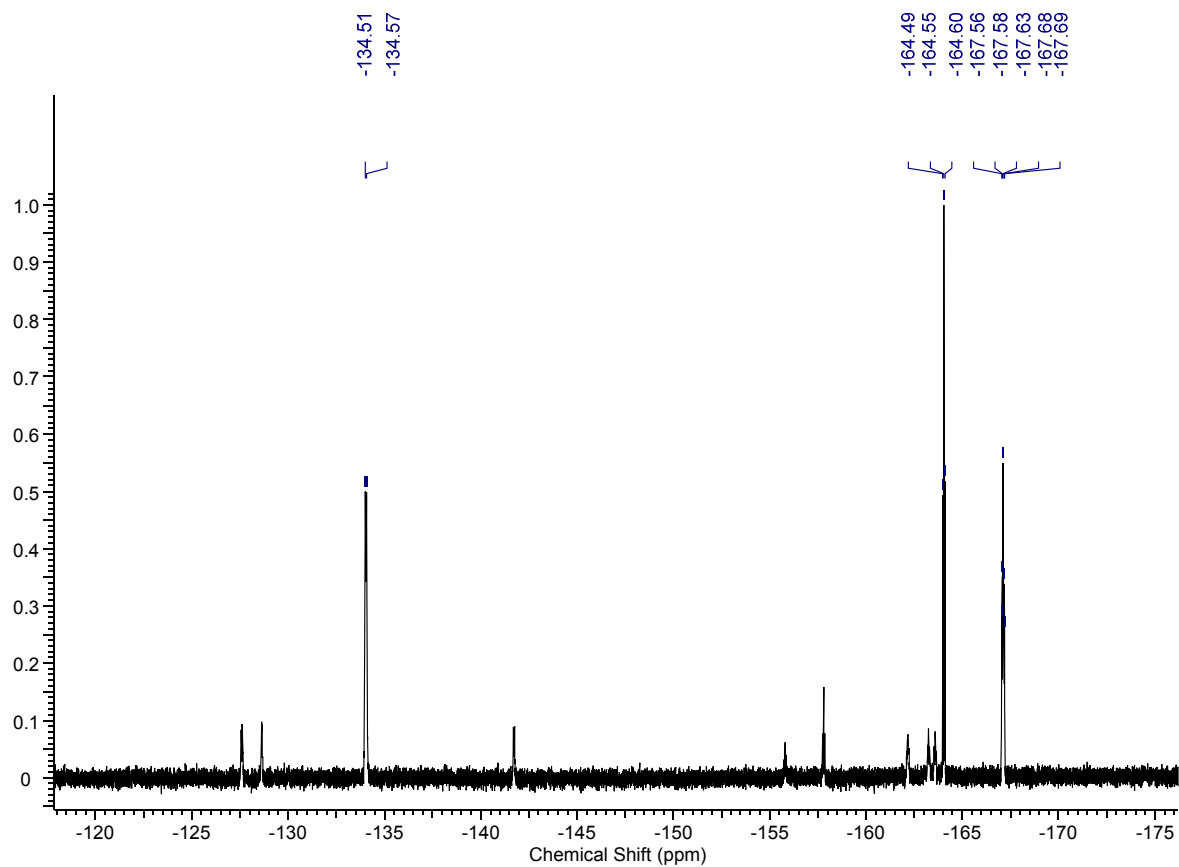
^1H NMR Spectrum: Reaction of diphenylsilane with 2-phenyl-N-methylindole



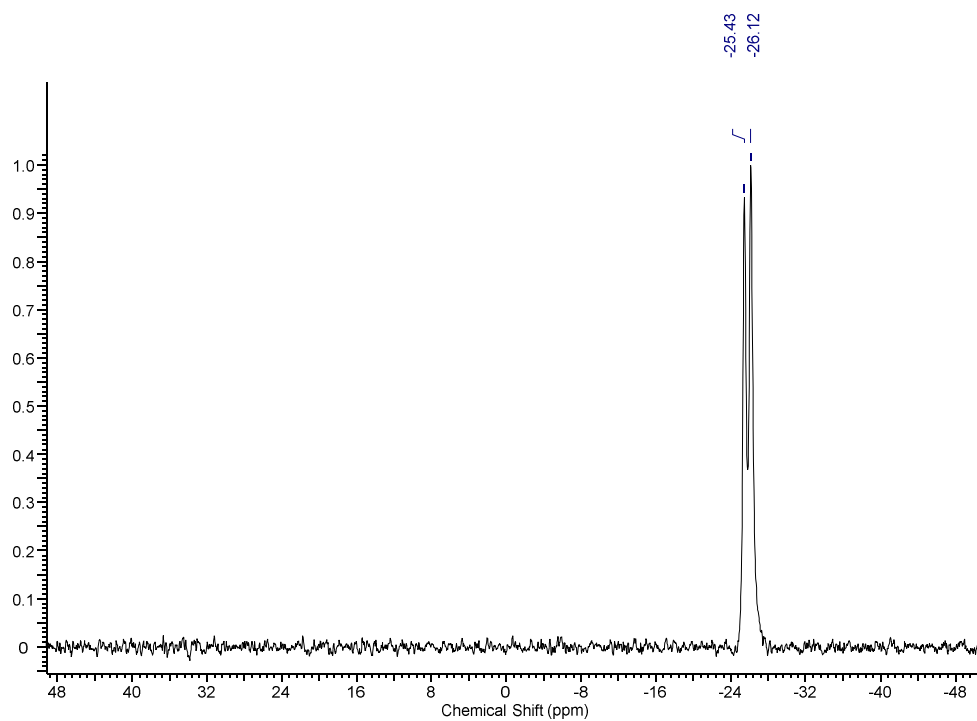
^{29}Si $\{^1\text{H}\}$ NMR Spectrum: Reaction of diphenylsilane with 2-phenyl-*N*-methylindole



^{19}F $\{^1\text{H}\}$ NMR Spectrum: Reaction of diphenylsilane with 2-phenyl-*N*-methylindole

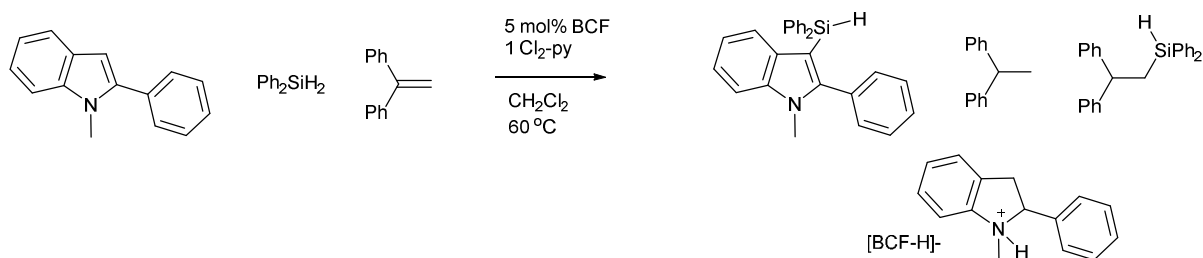


^{11}B $\{^1\text{H}\}$ NMR Spectrum: Reaction of diphenylsilane with 2-phenyl-*N*-methylindole

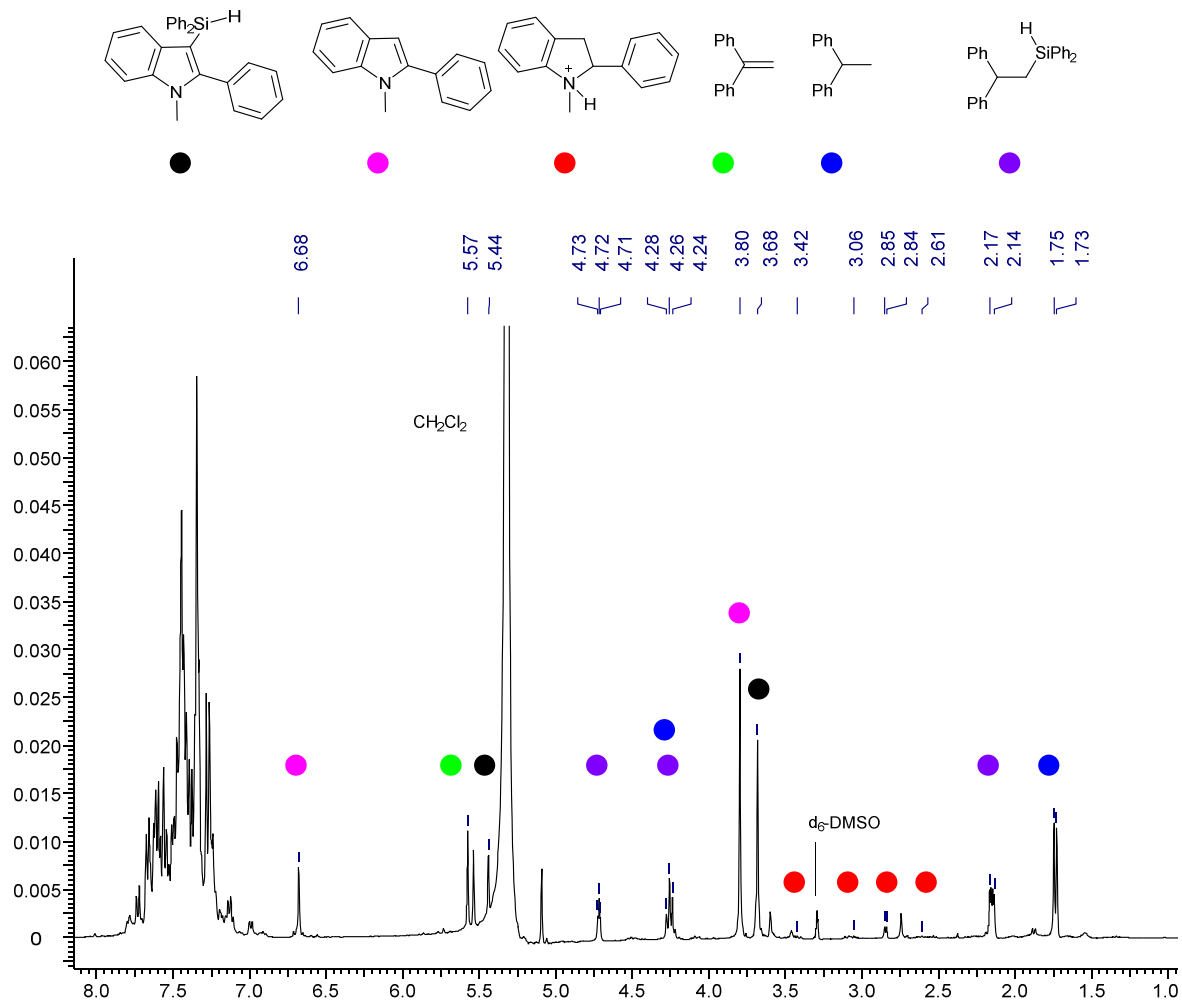


Tandem intermolecular/intramolecular electrophilic silylation of 2-phenyl-*N*-methylindole with DPE

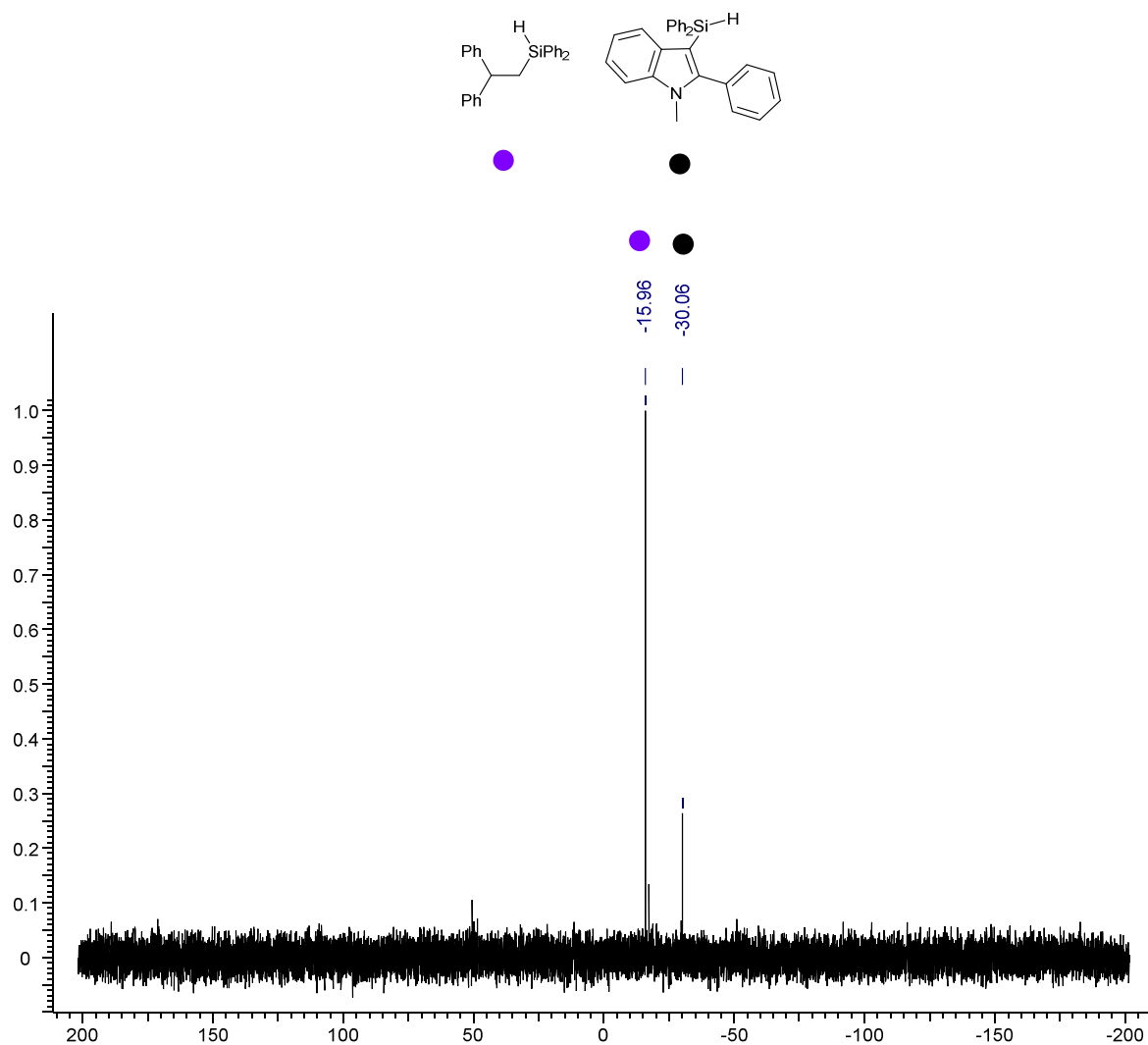
In an oven dried J Youngs NMR tube equipped with a d_6 -dmsO capillary, diphenylsilane (1 equiv.) was added to a solution of BCF (10 mg) in CH_2Cl_2 . This solution was agitated for 5 minutes before the addition of Cl_2 -py (1 equiv.), 2-phenyl-*N*-methylindole (1 equiv.) and DPE (1 equiv.). The reaction was heated to 60 °C and monitored by NMR spectroscopy. The initial electrophilic silylation occurred with no further reactivity to the silole observed. Competing hydrosilylation of DPE was observed along with the formation of $[BCF-H]^-$ suppressing any further reactivity along with minor aliphatic signals in the 1H NMR spectrum which are attributed to protonated indoline which has been previously reported to prevent further catalytic processes in the literature.⁵



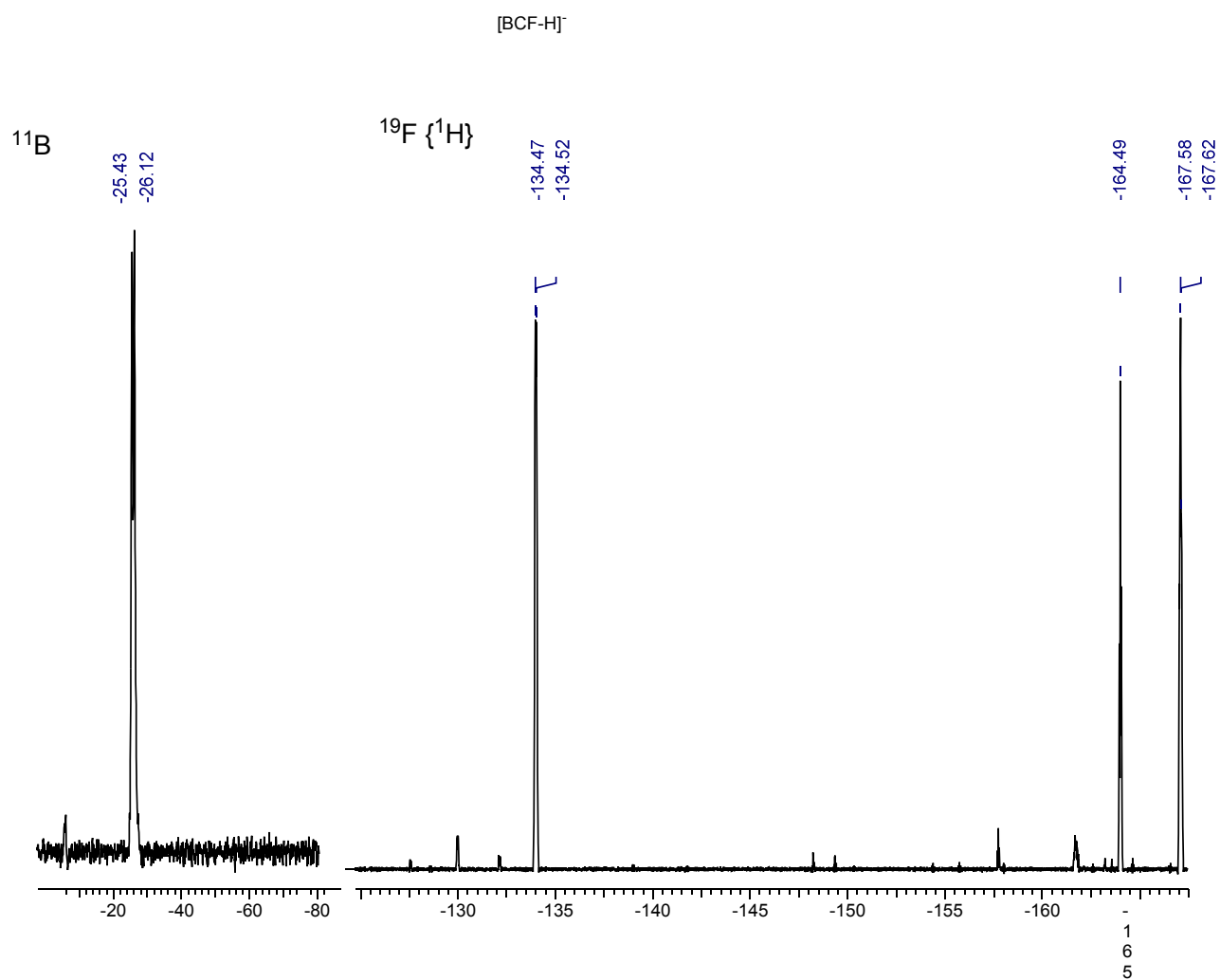
^1H NMR Spectrum: Reaction of diphenylsilane with 2-phenyl-*N*-methylindole in presence of DPE (resonances labelled with red are tentatively assigned as the N-Me-indolinium).



^{29}Si $\{^1\text{H}\}$ NMR Spectrum: Reaction of diphenylsilane with 2-phenyl-*N*-methylindole in presence of DPE

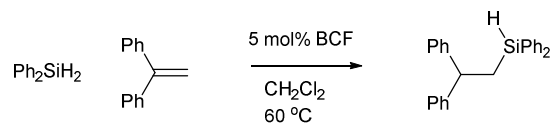


^{19}F $\{^1\text{H}\}$ and ^{11}B NMR Spectra: Reaction of diphenylsilane with 2-phenyl-*N*-methylindole in presence of DPE showing formation of $[\text{BCF-H}]^-$



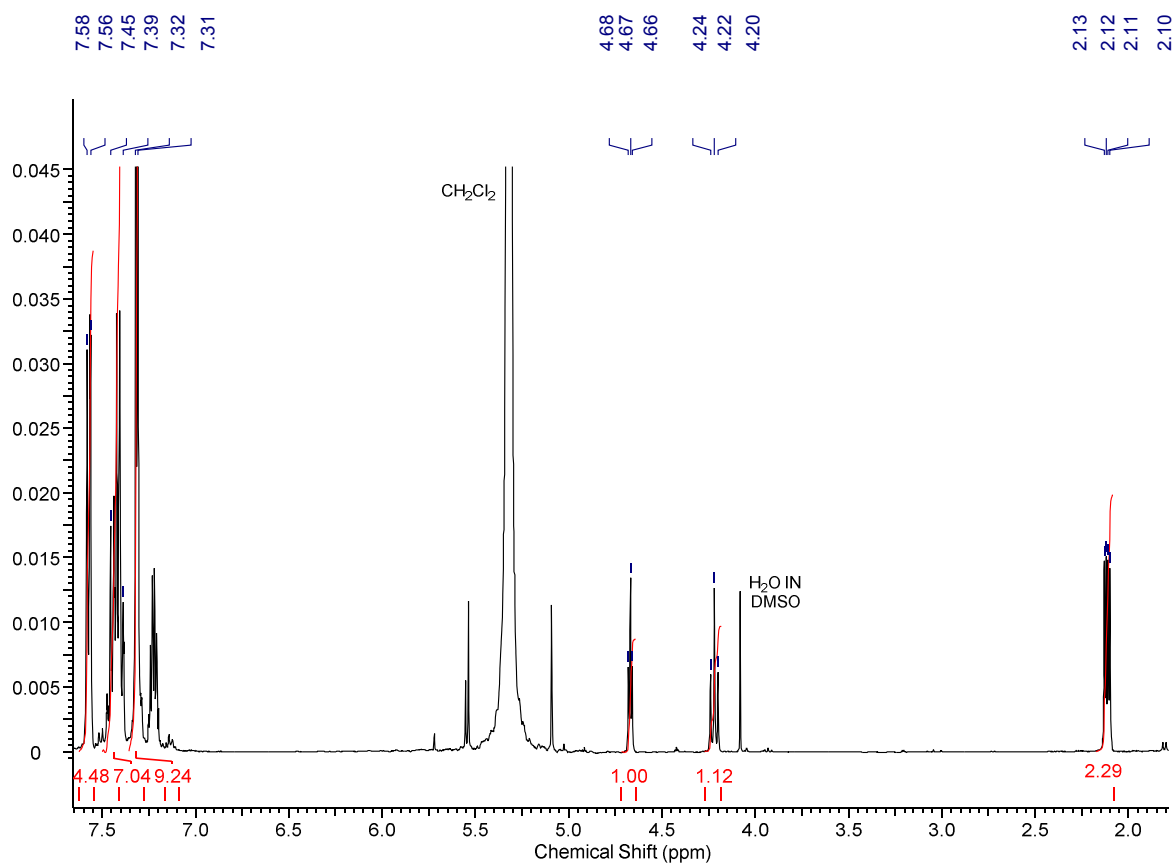
Hydrosilylation of DPE

To confirm the hydrosilylated product of DPE with diphenylsilane an independent synthesis was carried out.

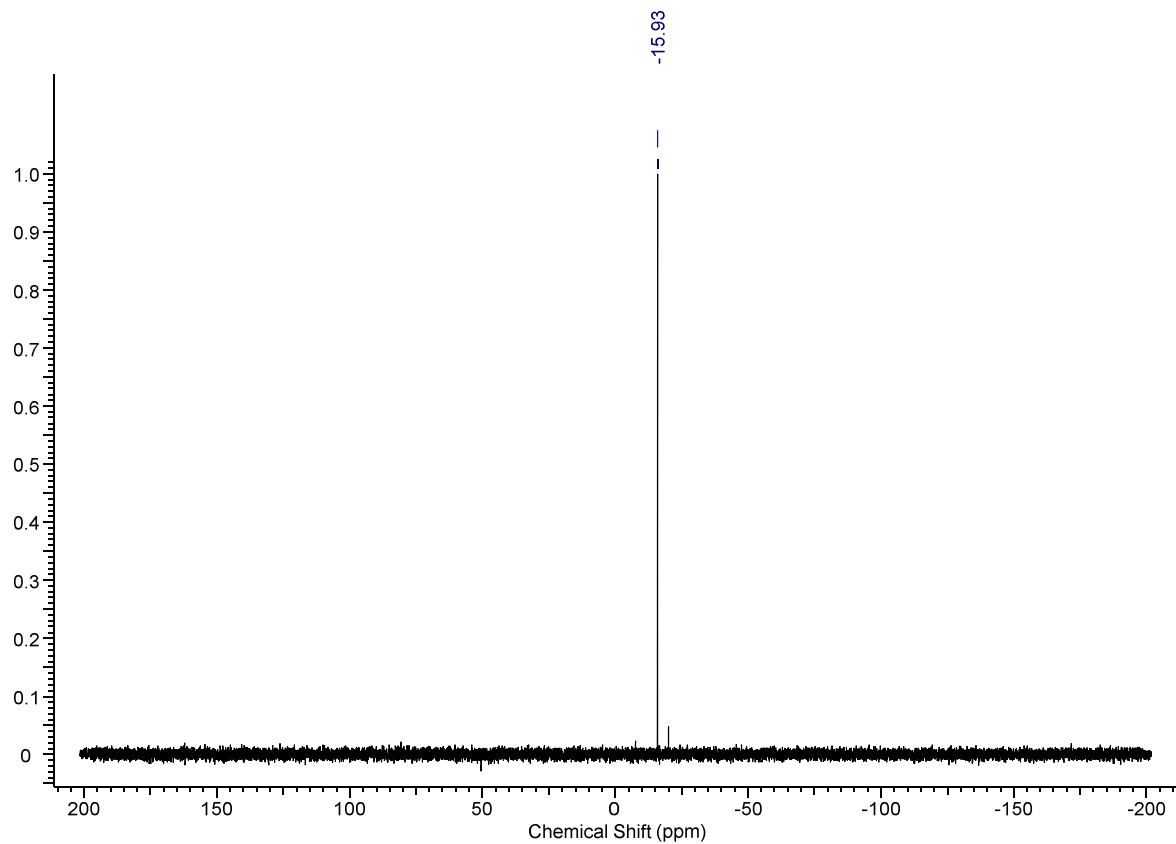


In an oven dried J Youngs NMR tube equipped with a d_6 -dmsO capillary, diphenylsilane (1 equiv.) was added to a solution of BCF (10 mg) in CH_2Cl_2 . This solution was agitated for 5 minutes before the addition DPE (1equiv.). The reaction was heated to 60°C and monitored by NMR spectroscopy.

^1H NMR spectrum: Hydrosilylation of DPE after 6 hours



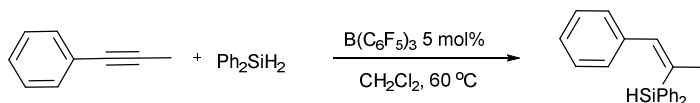
^{29}Si $\{^1\text{H}\}$ NMR spectrum: Hydrosilylation of DPE after 6 hours



General Procedure 4: Hydrosilylation of Alkynes

In an oven dried J Youngs NMR tube equipped with a d₆-dmsO capillary, diphenylsilane (1 equiv.) was added to a solution of BCF (X mol %) in CH₂Cl₂. This solution was agitated for 5 minutes before the addition of alkyne (1 equiv.). The reaction was heated to 60 °C and monitored by NMR spectroscopy.

12a 2-(diphenylsilyl)-3-phenyl-2-propene



Synthesized according to general procedure 4, starting with 73 μL of diphenyl silane and 5 mol% BCF (10 mg) with the addition of 49 μL of 1-phenyl-1-propyne. After 4 h at 60 °C there was a 85 % conversion to the *trans*-hydrosilylated product.

The *cis* hydrosilylation product was formed as the minor product as assigned by the presence of a new Si-H peak in the ^1H NMR spectrum and a minor resonance in the ^{29}Si $\{^1\text{H}\}$ NMR spectrum. On close inspection there is a shoulder on the methyl resonance attributed to the methyl of the *cis* hydrosilylation compound.

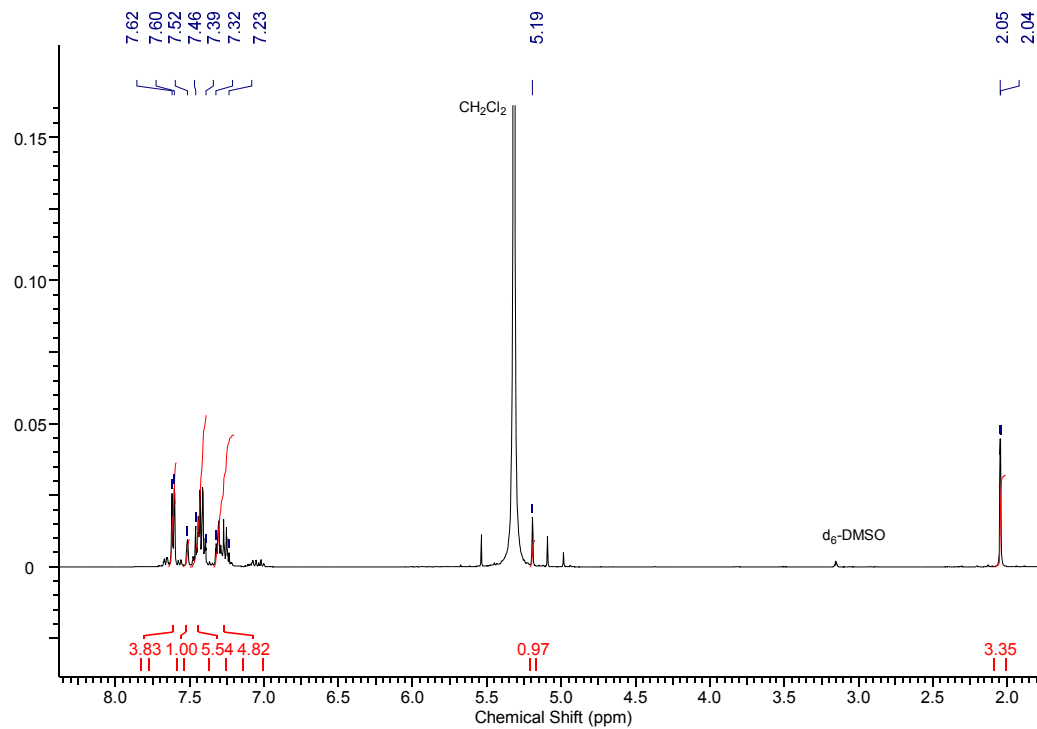
In-situ data

^1H NMR (CD_2Cl_2 400 MHz) δ 7.63-7.60 (m, 4H), 7.52 (s, br, 1H), 7.46-7.39 (m, 6H), 7.32-7.23 (m, 5H), 5.19 (s, 1H), 2.05 (d, $^4J_{\text{HH}}$ 1.5 Hz, 3H)

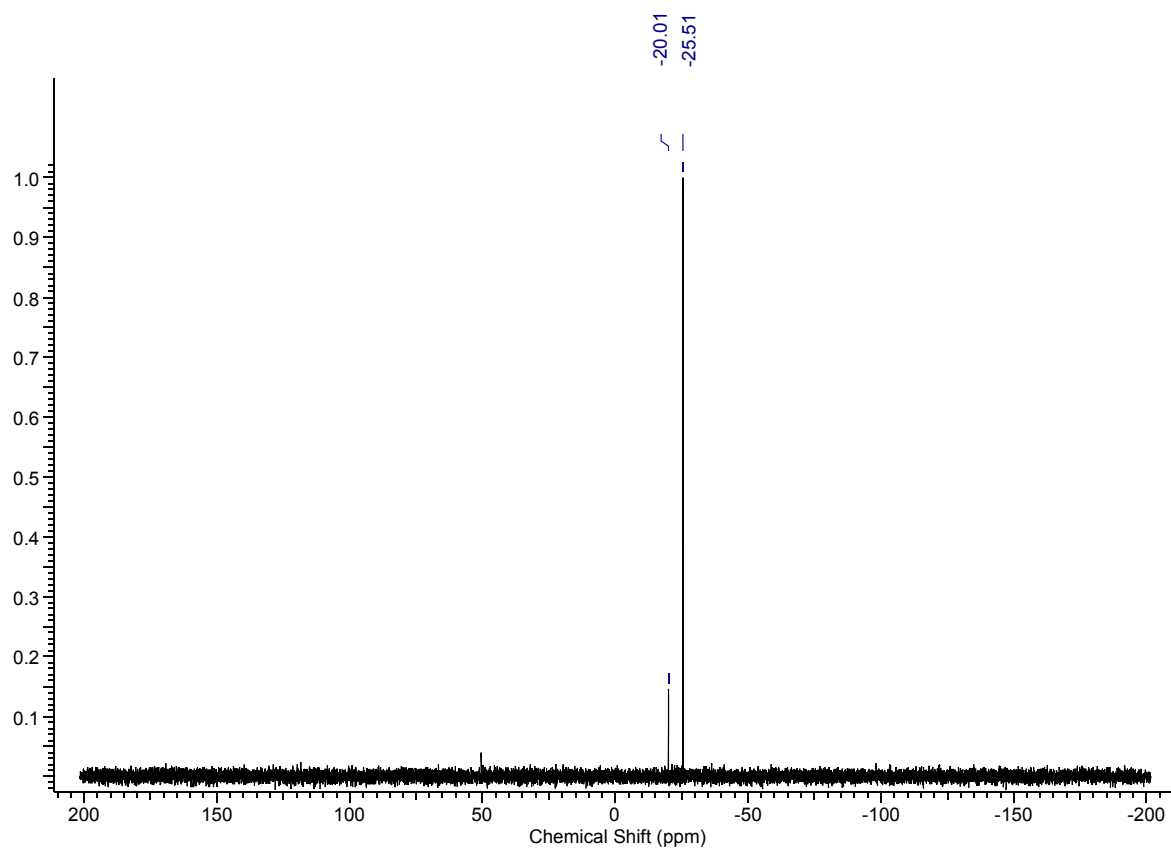
^{29}Si $\{^1\text{H}\}$ NMR (CD_2Cl_2 80 MHz) δ -25.51 ppm

Mass Spec: 300.1322 m/z , Expected for M^+ 300.1329 m/z

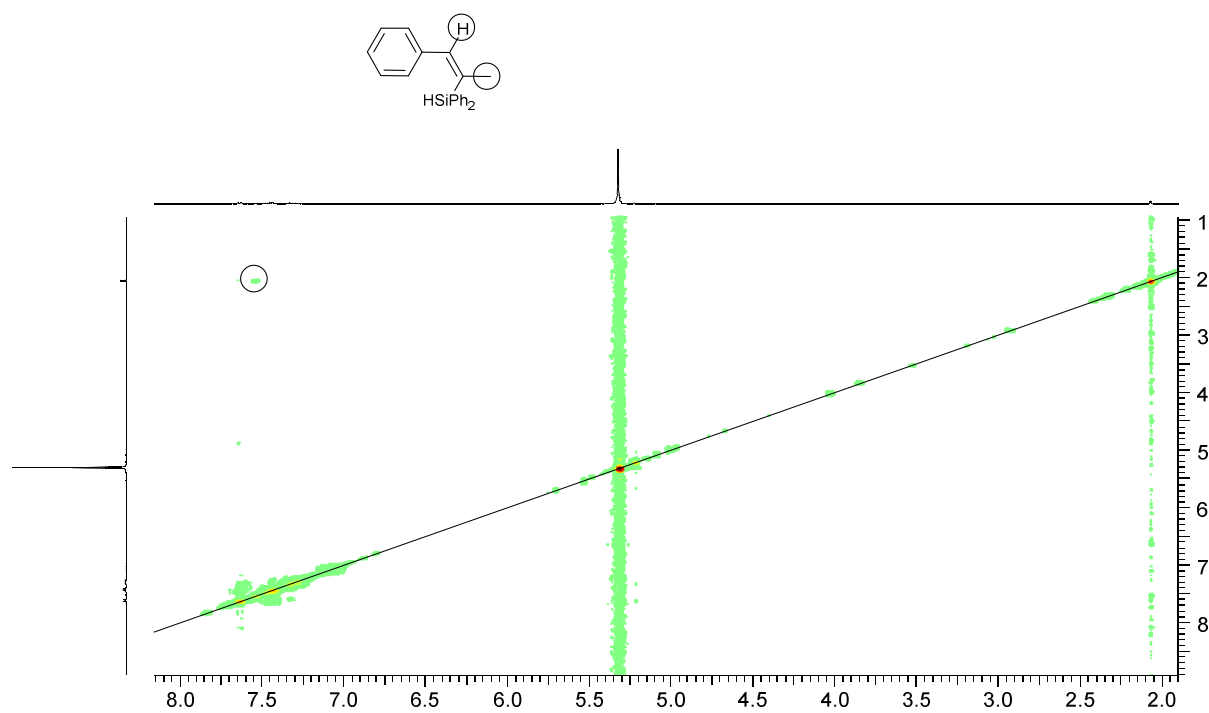
^1H NMR Spectrum: *In-situ* spectrum of hydrosilylation of 1-phenyl-1-propyne



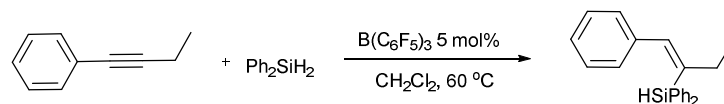
$^{29}\text{Si} \{^1\text{H}\}$ NMR Spectrum: *In-situ* spectrum of hydrosilylation of 1-phenyl-1-propyne



NOESY NMR Spectrum: *In-situ* spectrum of hydrosilylation of 1-phenyl-1-propyne showing a through space interaction between the methyl resonance and the *H*3 resonance indicating that they are cis to each other and that trans hydrosilylation is the dominant reaction.



12b 3-(diphenylsilyl)-4-phenyl-3-butene



Synthesized according to general procedure 4, starting with 73 μL of diphenyl silane and 5mol% BCF (10 mg) with the addition of 56 μL of 1-phenyl-1-butyne. After 2 h at 60°C there was a 75 % conversion to the *trans*-hydrosilylated product.

In-situ data

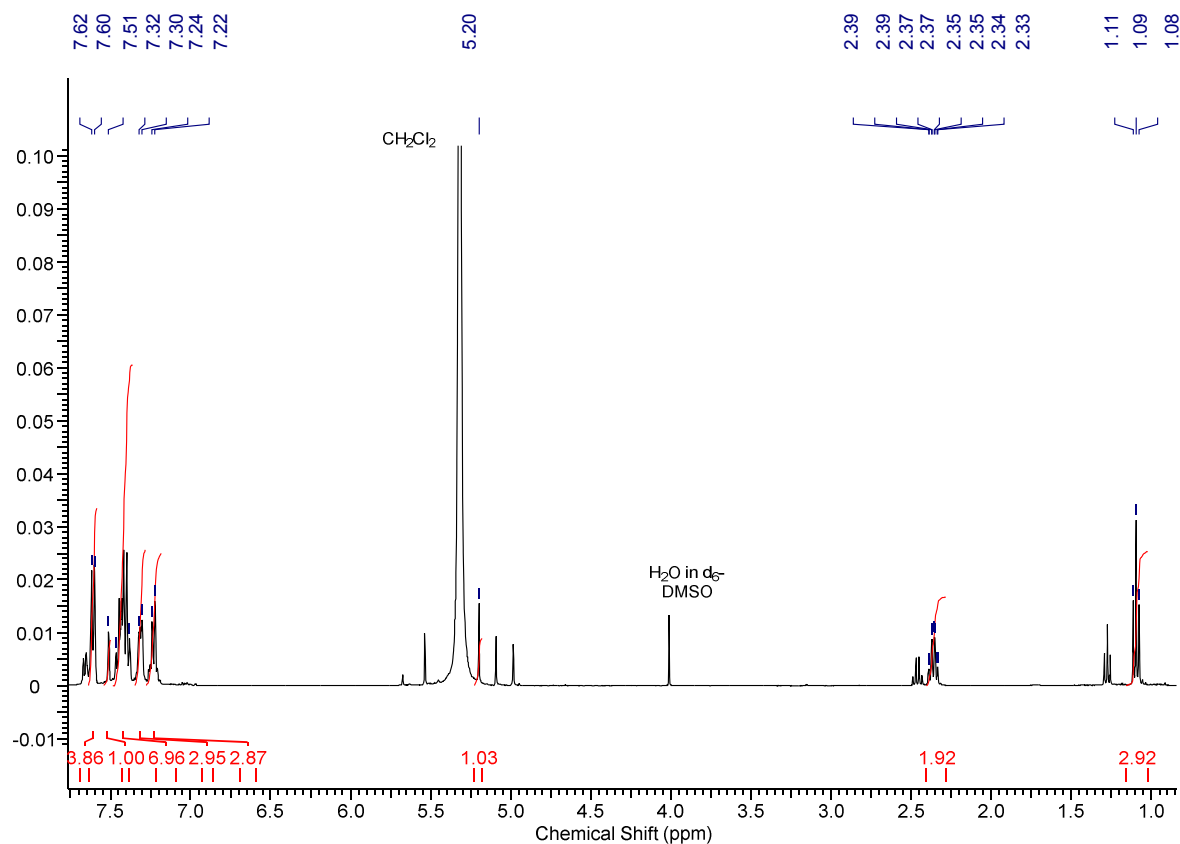
^1H NMR (CD_2Cl_2 400 MHz) 7.62-7.60 (m, 4H), 7.51 (s, br, 1H), 7.32-7.30 (m, 6H), 7.24 (m, 3H), 7.22 (m, 2H), 5.20 (s, 1H), 2.35 (dq, $^3J_{\text{HH}}$ 7.5 Hz, $^4J_{\text{HH}}$ 1.2 Hz, 2H), 0.81 (t, $^3J_{\text{HH}}$ 7.5 Hz, 3H)

The *cis* hydrosilylation product was formed at the minor product as observed by the new Si-H and Et peaks in ^1H NMR spectroscopy and a minor resonance in the ^{29}Si $\{^1\text{H}\}$ NMR spectrum.

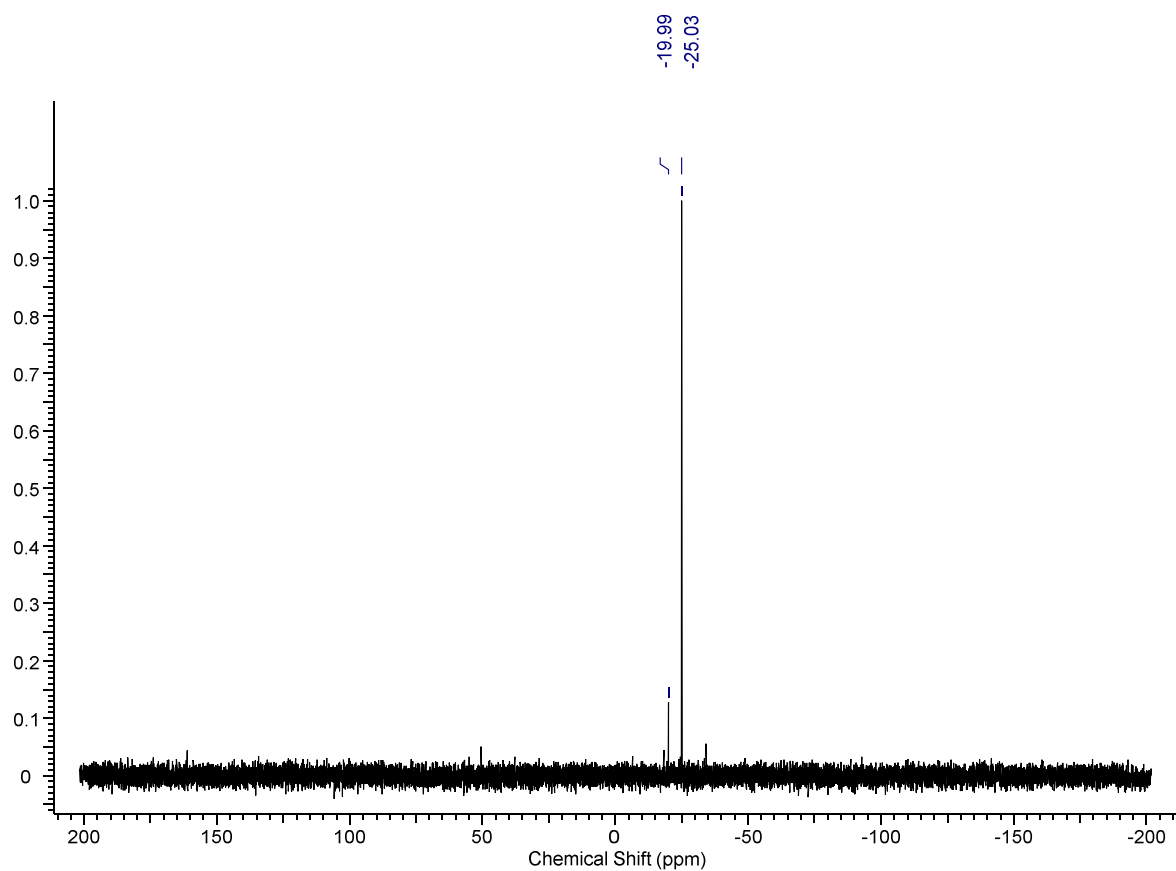
^{29}Si $\{^1\text{H}\}$ NMR (CD_2Cl_2 80 MHz) δ -25.03

Accurate Mass Spec. 314.1481 m/z , Expected for M^+ 314.1485 m/z

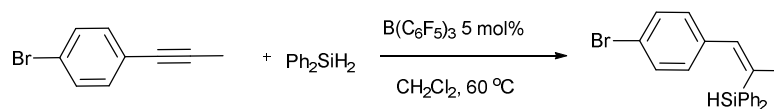
^1H NMR Spectrum: In-situ spectrum of hydrosilylation of 1-phenyl-1-butyne



$^{29}\text{Si} \{^1\text{H}\}$ NMR Spectrum: In-situ spectrum of hydrosilylation of 1-phenyl-1-butyne



12c 2-(diphenylsilyl)-3-(4-bromo)phenyl-2-propene



Synthesized according to general procedure 4, starting with 73 μL of diphenyl silane and 5mol% BCF (10 mg) with the addition of 55 μL of 1-phenyl-1-butyne. After 48 h at 60 $^\circ\text{C}$ there was an 89 % conversion to the *trans*-hydrosilylated product. The compound was isolated by preparative thin layer chromatography with the eluent 9:1 Pentane : DCM in 85 % yield.

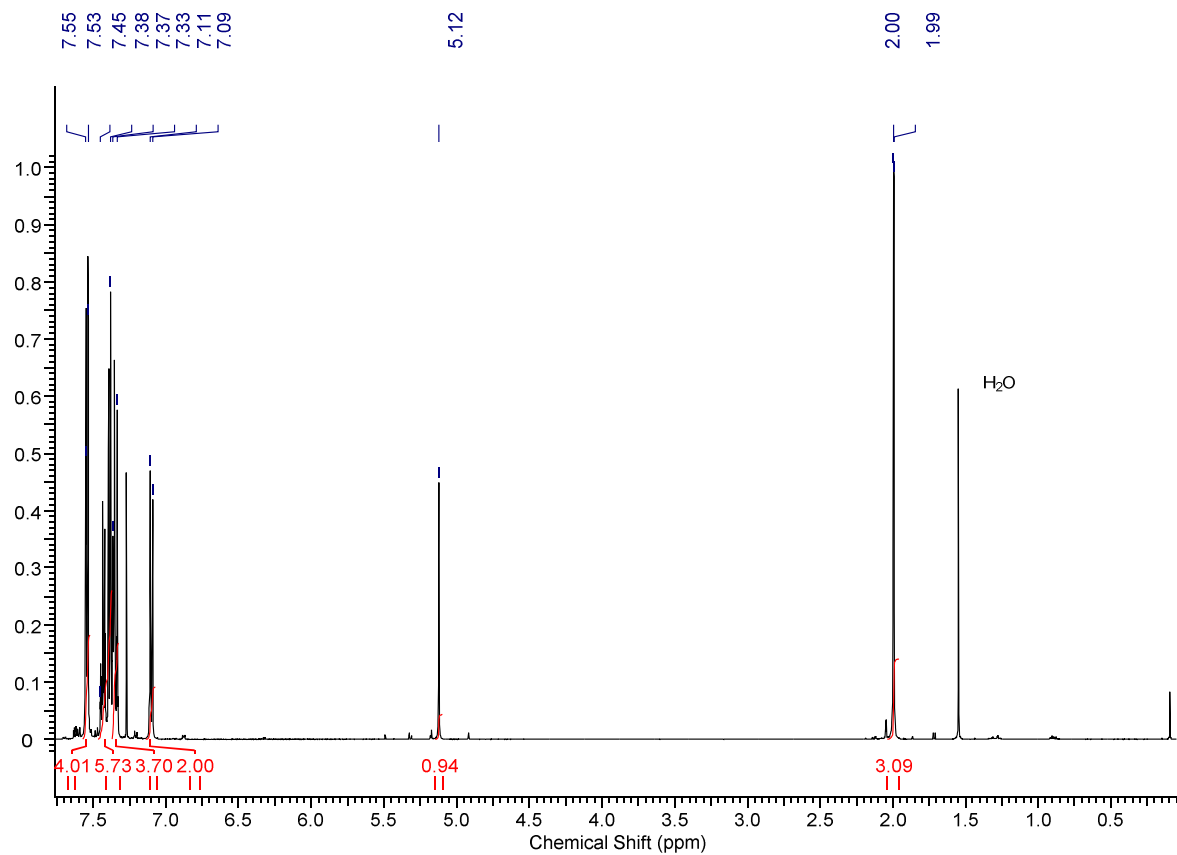
^1H NMR (CD_2Cl_2 400 MHz) 7.56-7.53 (m, 4H), 7.45-7.33 (m, 9H), 7.10(d, $^3J_{\text{HH}}$ 8.2 Hz, 2H), 5.12 (s, 1H), 7.22 (d, $^3J_{\text{HH}}$ 1.6 Hz 3H)

^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 100 MHz) δ 144.1, 137.7, 135.7, 135.0, 133.2, 130.9, 130.3, 129.7, 128.1, 121.1, 25.4 ppm

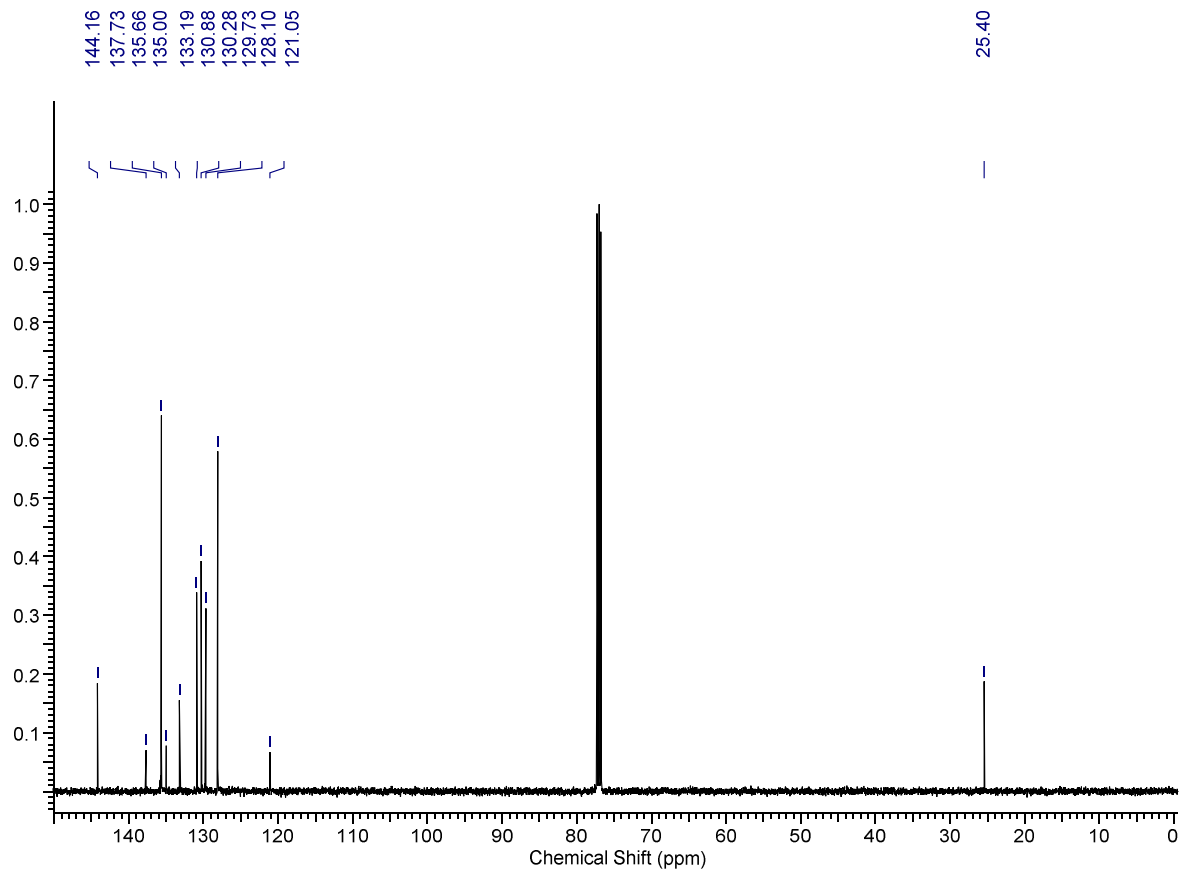
^{29}Si $\{^1\text{H}\}$ NMR (CDCl_3 80 MHz) δ -24.99 ppm

Mass Spec: 378.0446 m/z , Expected for M^+ 378.0439 m/z

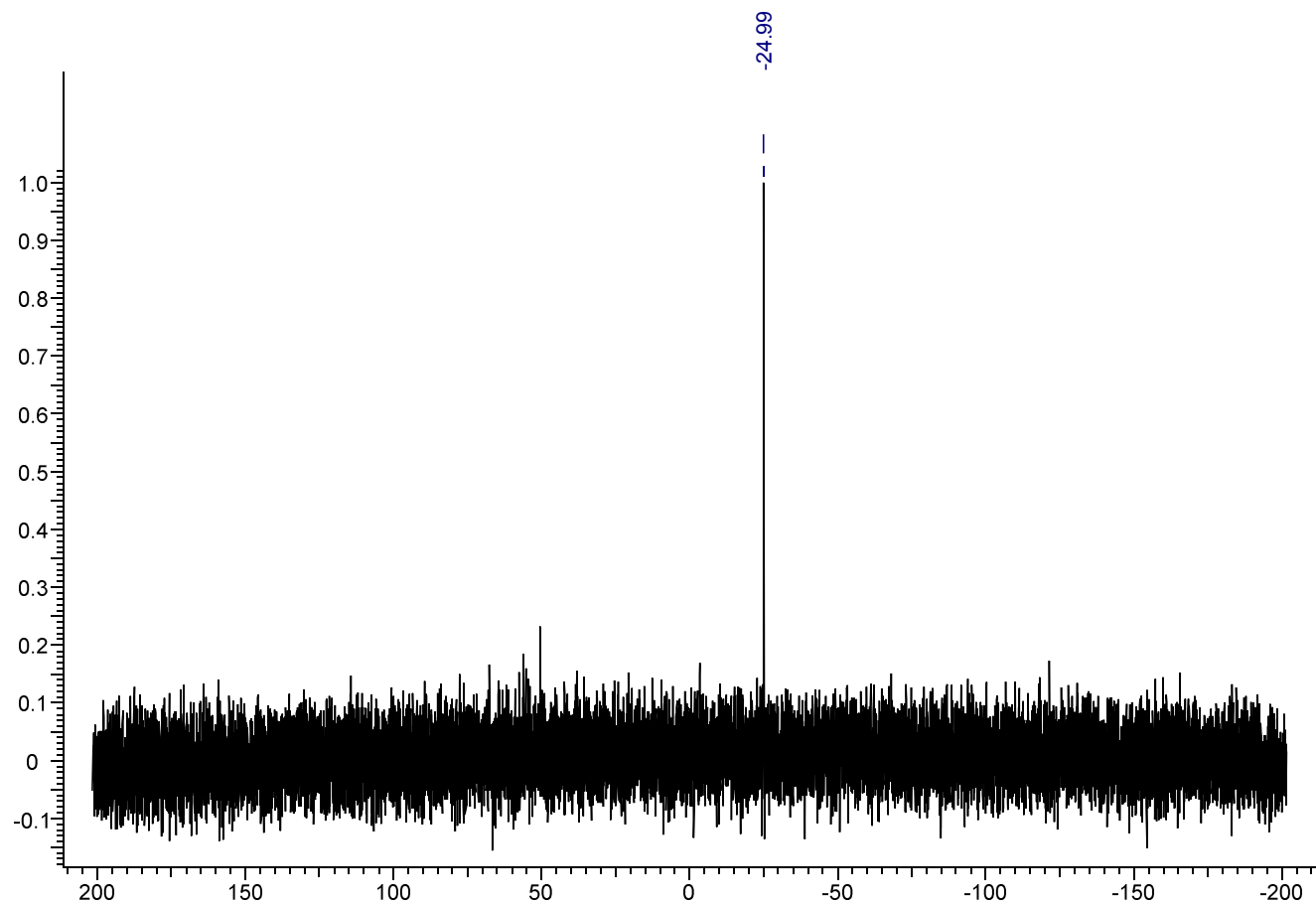
¹H NMR Spectrum: ¹H NMR spectrum of hydrosilylation of 1-(4-bromophenyl)-1-propyne



$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum: Hydrosilylation of 1-(4-bromophenyl)-1-propyne

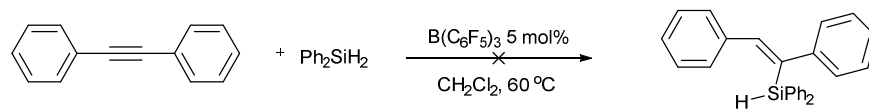


^{29}Si $\{^1\text{H}\}$ NMR Spectrum: Hydrosilylation of 1-(4-bromophenyl)-1-propyne

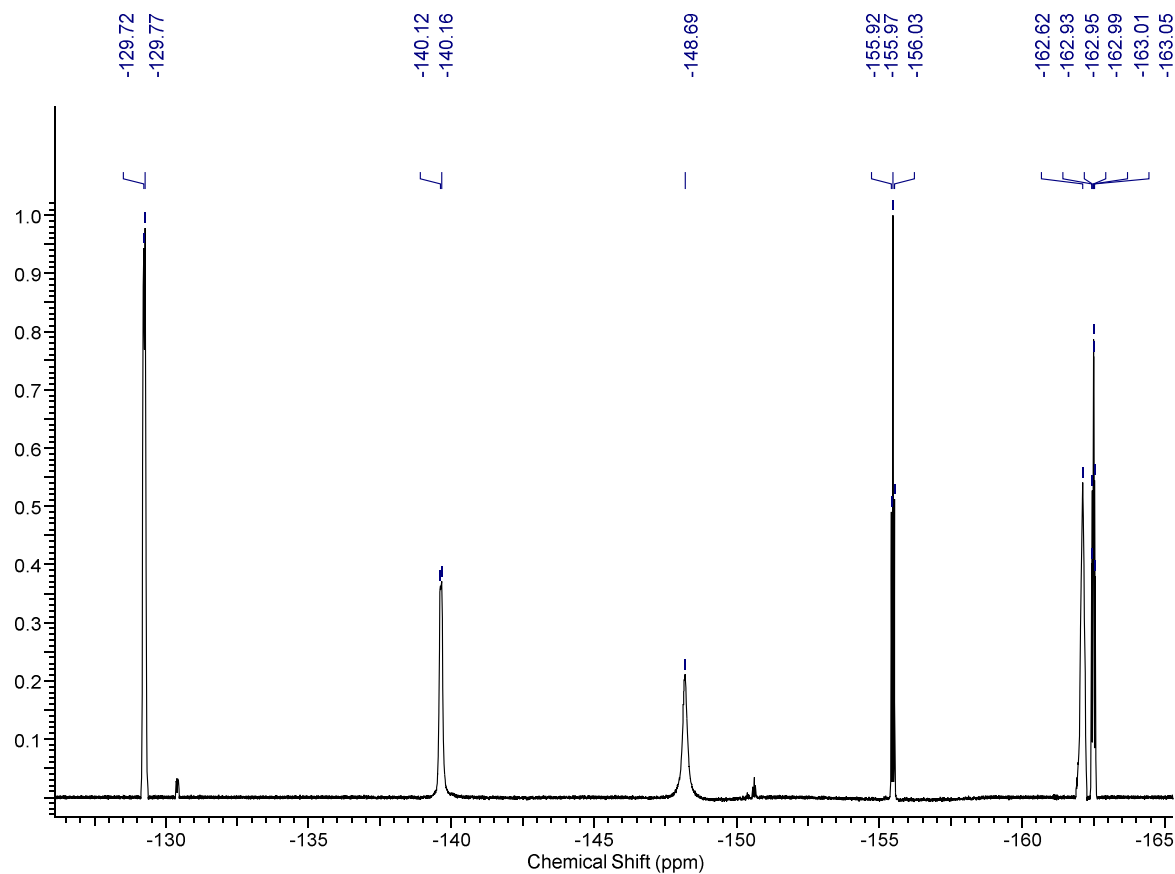


Attempted Hydrosilylation of diphenylacetylene

Hydrosilylation did not proceed. Unidentified 3- and 4- coordinate boron species were observed in the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum.

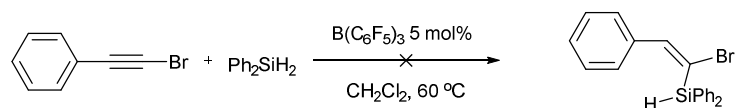


$^{19}\text{F}\{^1\text{H}\}$ NMR Spectrum: In-situ spectrum of attempted catalytic hydrosilylation of diphenylacetylene

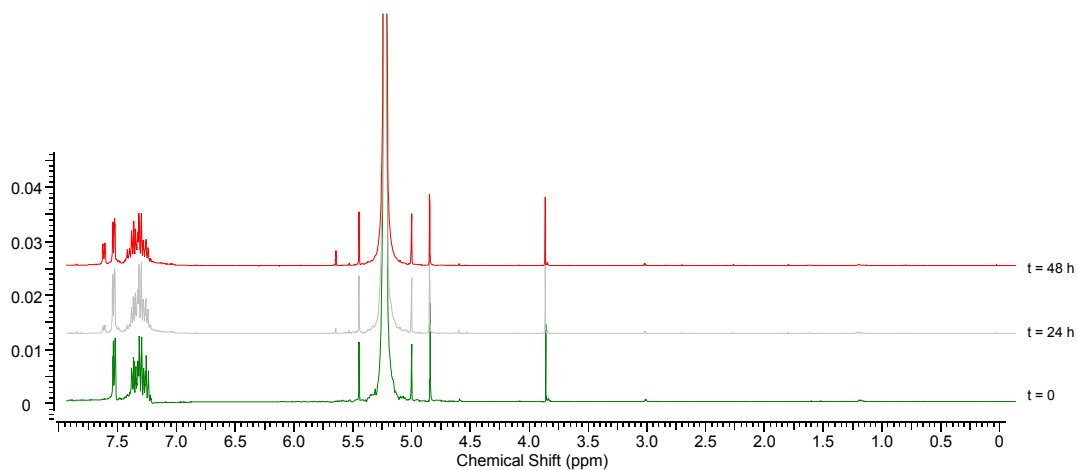


Attempted Hydrosilylation of 1-bromophenylacetylene

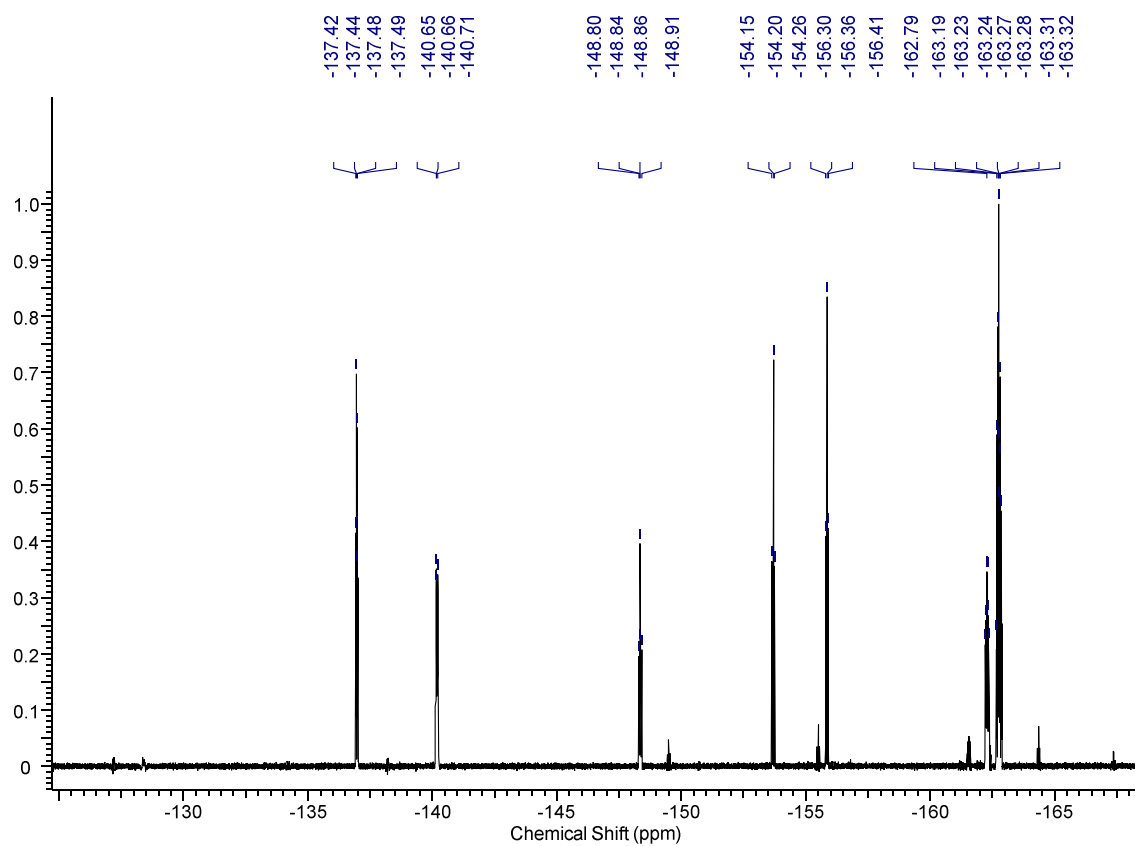
Hydrosilylation did not proceed to any significant extent even after prolonged reaction time. Unidentified 3- and 4- coordinate boron species were observed in ^{19}F $\{^1\text{H}\}$ NMR spectrum. ^1H and ^{29}Si $\{^1\text{H}\}$ NMR indicate minor amounts of new Si-H compound after 48 h.



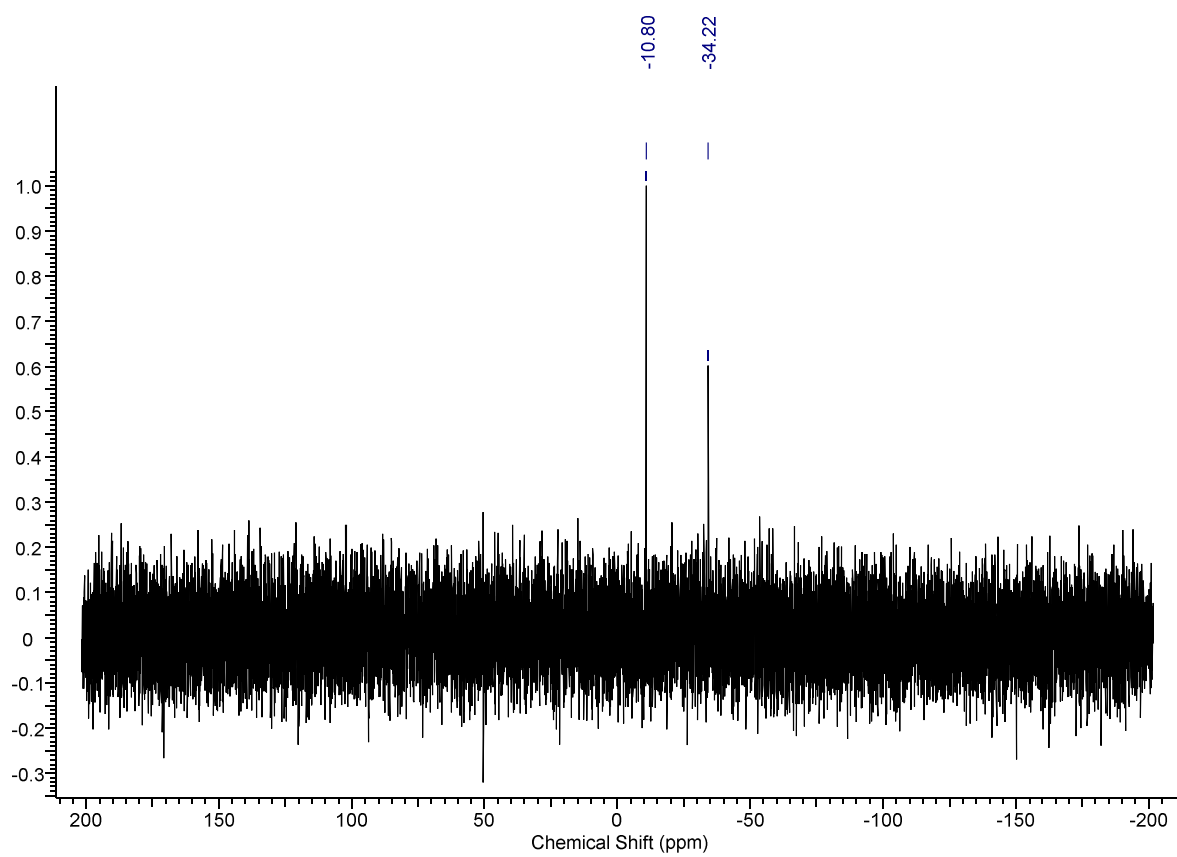
^1H NMR Spectrum: In-situ spectrum of hydrosilylation of 1-bromophenylacetylene



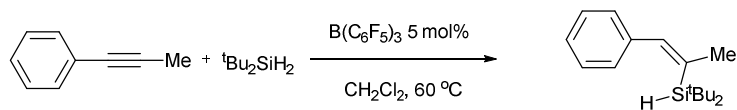
^{19}F $\{^1\text{H}\}$ NMR Spectrum: In-situ spectrum of hydrosilylation of 1-bromophenylacetylene



$^{29}\text{Si} \{^1\text{H}\}$ NMR Spectrum: In-situ spectrum of hydrosilylation of 1-bromophenylacetylene

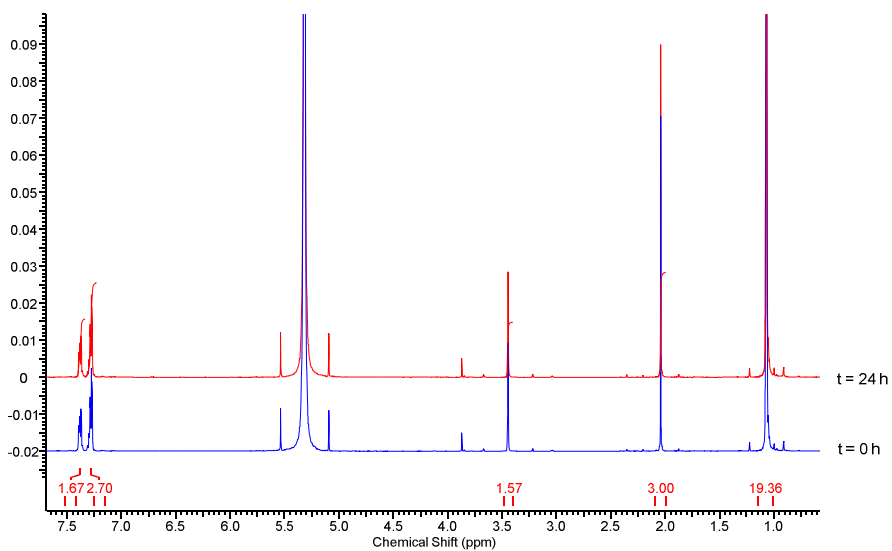


Hydrosilylation: di-*tert*butylsilane

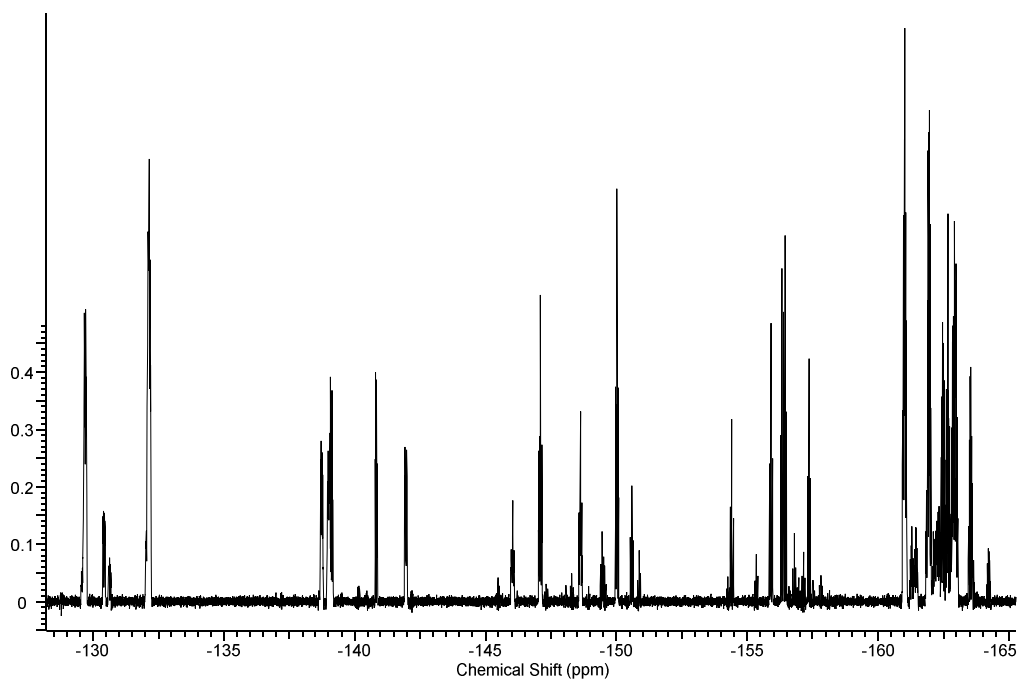


No reaction occurred. Attributed to *tert*butyl groups providing too much steric bulk for $\text{S}_{\text{N}}2$ attack by alkyne to silicon centre (in the Si-H-B species). Multiple unidentified compounds observed in ^{19}F $\{^1\text{H}\}$ NMR spectrum.

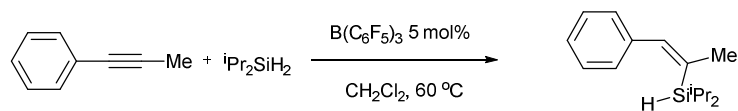
^1H NMR Spectrum: Hydrosilylation with di-*tert*butylsilane



^{19}F $\{^1\text{H}\}$ NMR Spectrum: Hydrosilylation with di-*tert*butylsilane

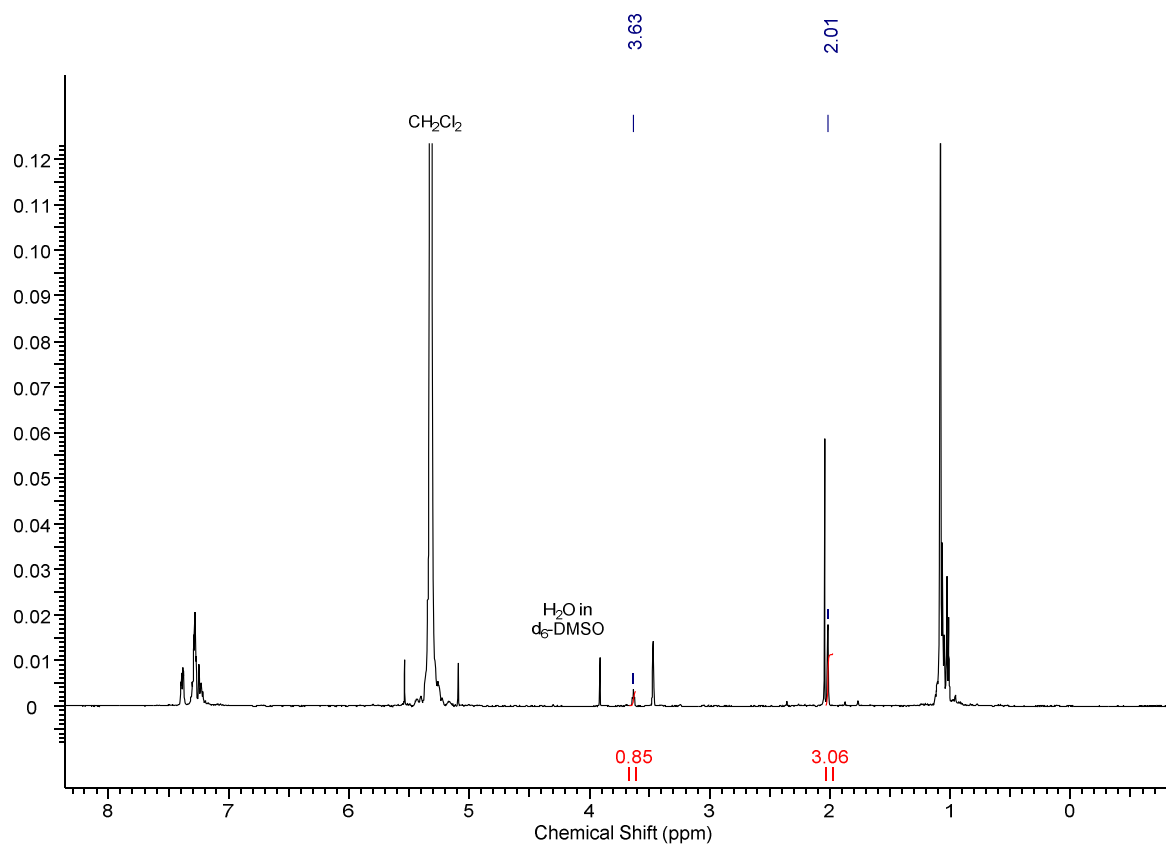


Attempted Hydrosilylation with di-*isopropylsilane*

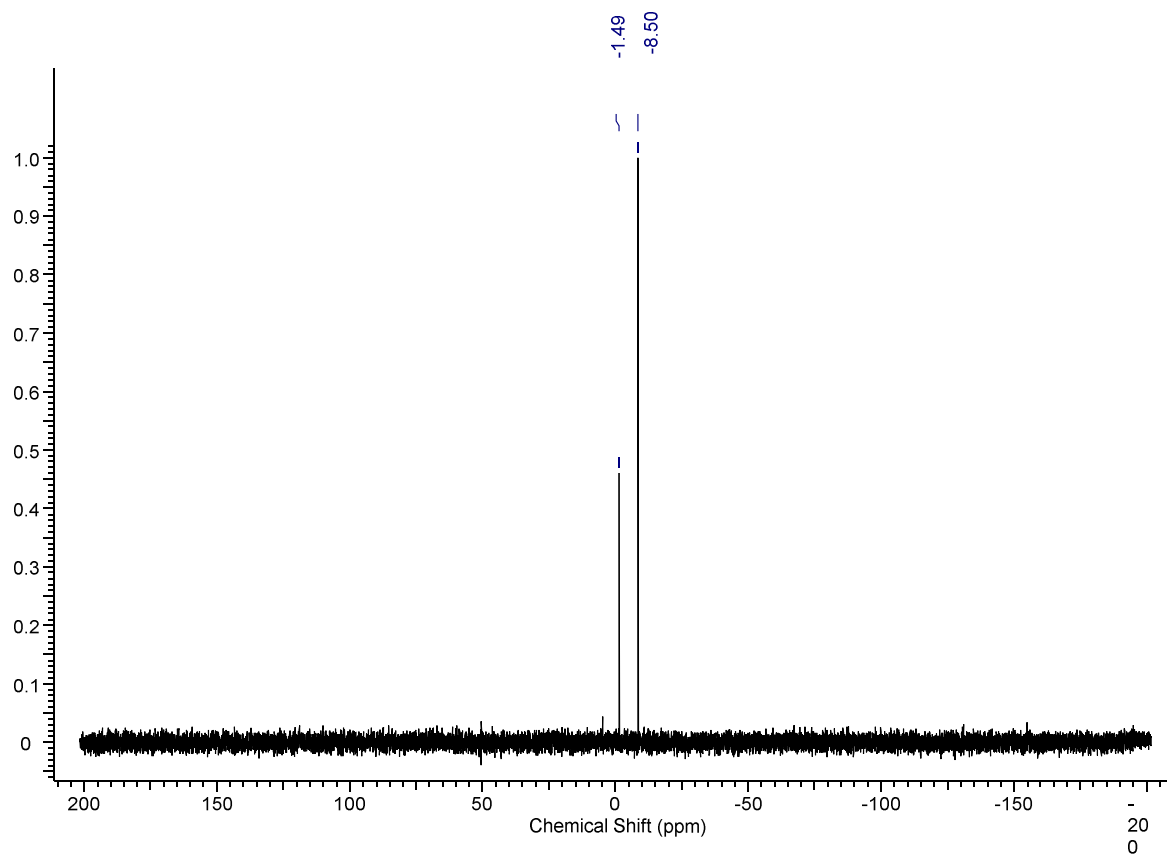


Reaction proceeds slowly. The ^{19}F $\{^1\text{H}\}$ NMR spectrum showed the decomposition of BCF to unidentified compounds.

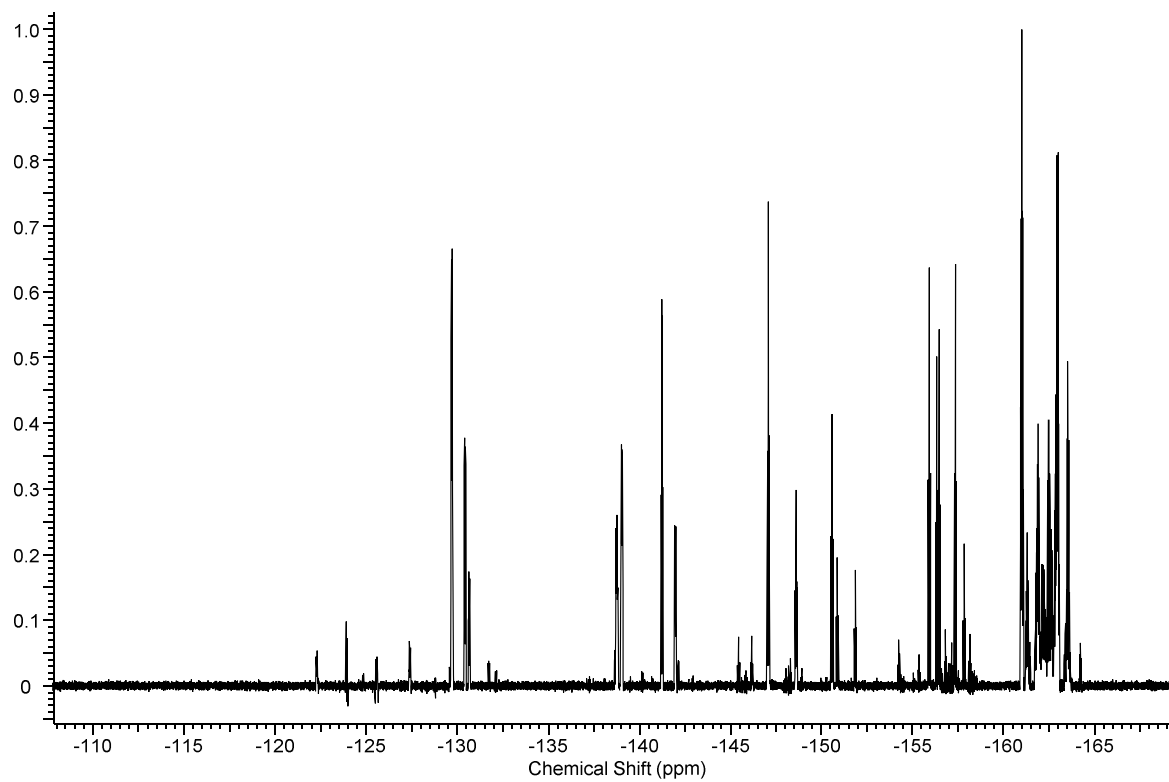
^1H NMR Spectrum: Hydrosilylation using di-*isopropylsilane*



^{29}Si $\{^1\text{H}\}$ NMR Spectrum: Hydrosilylation with di-*isopropylsilane*



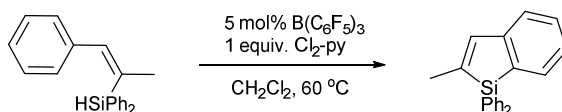
^{19}F $\{^1\text{H}\}$ NMR Spectrum: Hydrosilylation di-*isopropylsilane*



General Procedure 5: Intramolecular dehydrosilylation: Synthesis of Silaindenes

In an oven dried J Youngs NMR tube equipped with a d₆-dmsO capillary, Cl₂-py (1 equiv.) was added to a solution of a vinyl silane (1 equiv.) and BCF (5 mol %) in CH₂Cl₂. The reaction was heated to 60 °C and monitored by NMR spectroscopy.

13a 2-methyl-1,1-diphenyl-1-silaindene



Synthesized according to general procedure 5, starting with 73 μ L of diphenyl silane and 5 mol% BCF (10 mg) with the addition of 43 μ L of 1-phenyl-1-propyne and subsequent addition of 1 equivalent of Cl₂-py (58 mg). After 72 h at 60 °C there was a 70 % conversion to the silaindene product by ¹H NMR spectroscopy. The separation of silaindene and vinyl silane was not possible in our hands using column chromatography due to their similar *r_f* values in a number of common eluents. Preparative TLC with an eluent of hexane : DCM (9 : 1) lead to several bands. Taking the top two thirds of the top band gave ca. 82 % of the silaindene and 18 % of the *cis* and *trans* vinylsilane mixture (**12a**).

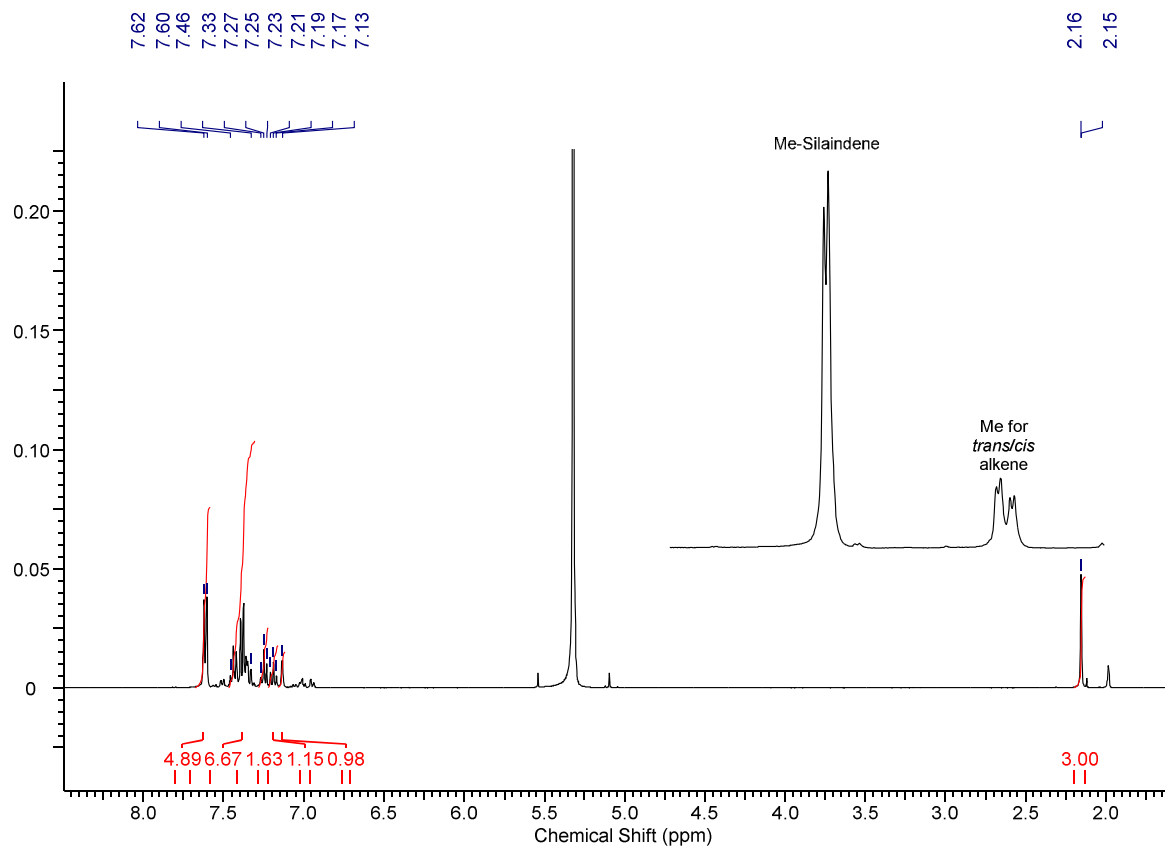
¹H NMR (CD₂Cl₂ 400 MHz) δ 7.62-7.60 (m, 5H), 7.46-7.33 (m, 7H), 7.27-7.23 (m, 1H), 7.19 (t, ³J_{HH} 7.3 Hz, 1H), 7.13 (s, br, 1H), 2.16 (d, ⁴J_{HH} 1.3 Hz, 3H)

¹³C {¹H} NMR (CDCl₃ 100 MHz) δ 145.6, 135.7, 135.4, 134.3, 133.1, 132.3, 130.0, 128.2, 127.8, 126.3, 18.0 ppm

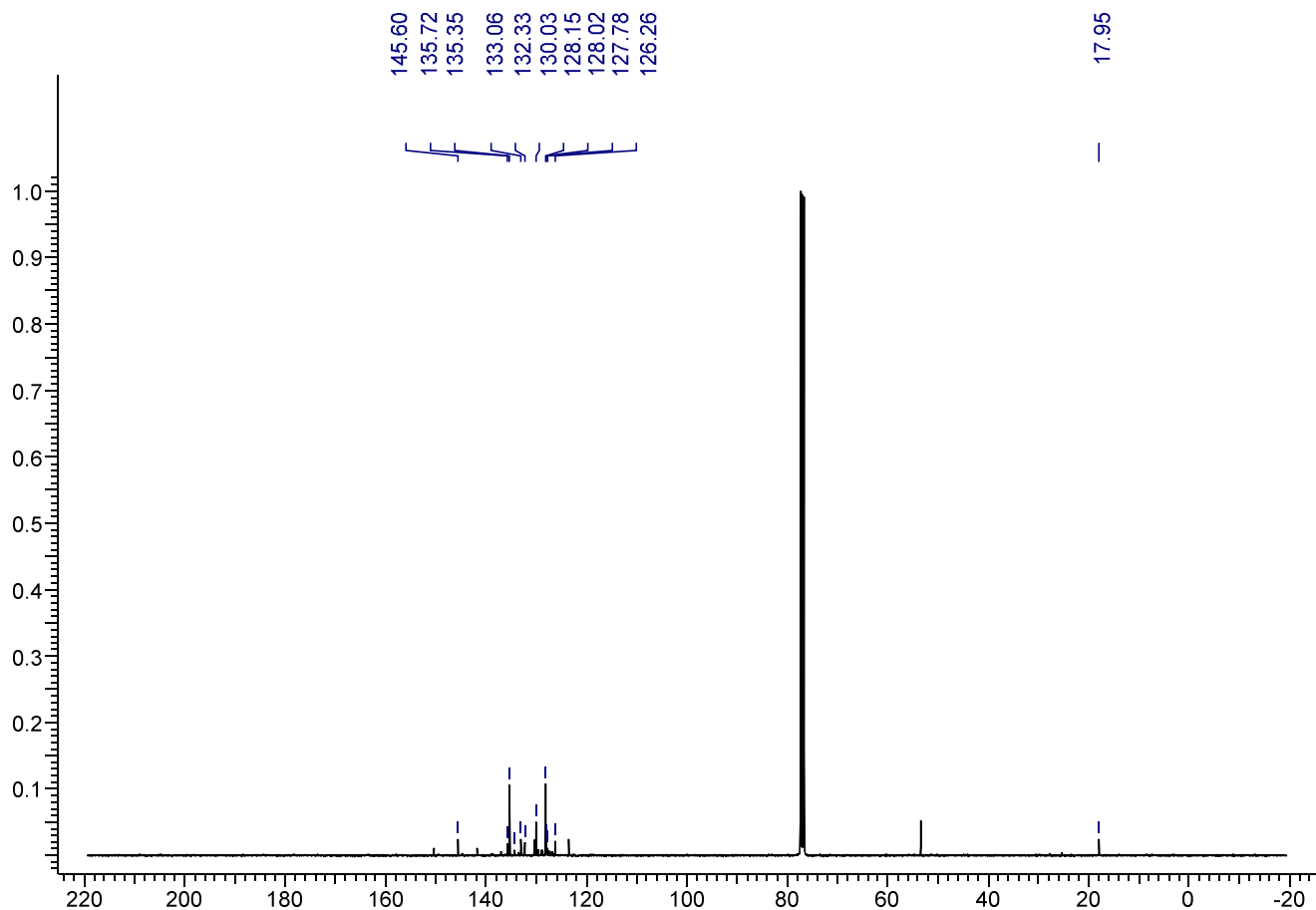
²⁹Si {¹H} NMR (CD₂Cl₂ 80 MHz) δ -9.16 ppm

Mass Spec: 298.1165 *m/z*, Expected for M⁺ 298.1172 *m/z*

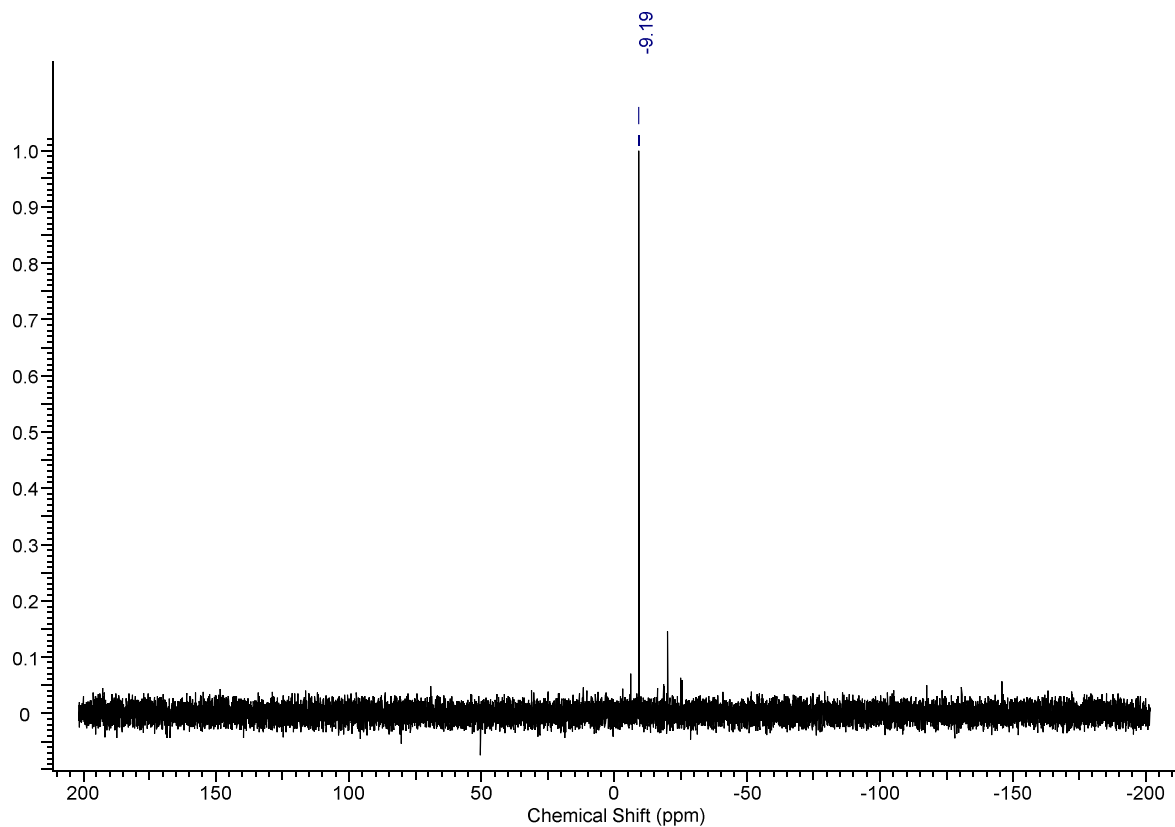
¹H NMR Spectrum: 2-methyl-1, 1-diphenyl-1-silaindene after preparative TLC



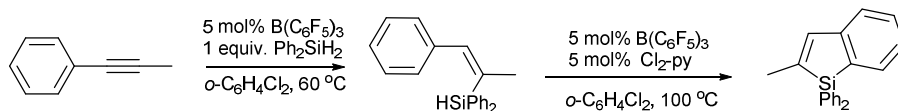
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum: 2-methyl-1, 1-diphenyl-1-silaindene after preparative TLC



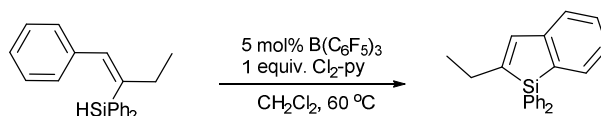
^{29}Si $\{^1\text{H}\}$ NMR Spectrum: 2-methyl-1, 1-diphenyl-1-silaindene after preparative TLC



The reaction was repeated in *o*-DCB with the first step, hydrosilylation, at 60 °C and the following ring closure step, dehydrosilylation, at 100 °C however this resulted in decomposition of BCF to a multitude of species (by ^{19}F $\{^1\text{H}\}$ NMR spectroscopy) and a drop in conversion to ca. 17 %



13b 2-ethyl-1, 1-diphenyl-1-silaindene



Synthesized according to general procedure 5, starting with 73 μL of diphenyl silane and 5mol% BCF (10 mg) with the addition of 56 μL of 1-phenyl-1-propyne and subsequent addition of 1 equivalent of $\text{Cl}_2\text{-py}$ (58 mg). After 24 h at 60 $^\circ\text{C}$ there was a 78 % conversion to the silaindene product. The separation of silaindene and vinyl silane was not possible in our hands due to their similar *rf* values in a number of common eluents. Preparative TLC with an eluent of hexane : DCM (9 : 1) lead to several bands. Taking the top two thirds of the top band gave 89 % of the silaindene and 11 % of the *cis* and *trans* vinylsilane.

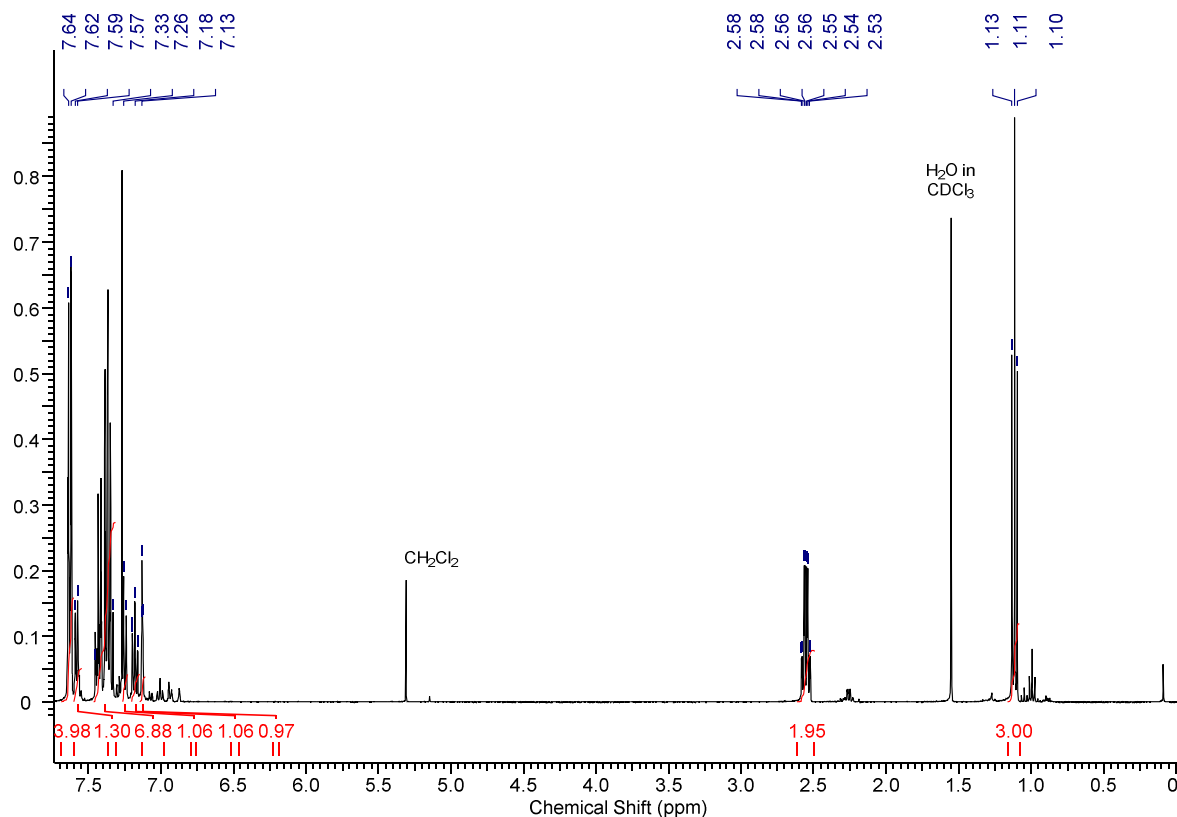
^1H NMR (CDCl_3 400 MHz) δ 7.64-7.62 (m, 4H), 7.59 (d, $^3J_{\text{HH}}$ 7.6 Hz, 1H), 7.45-7.33 (m, 7H), 7.26 (d, $^3J_{\text{HH}}$ 7.6 Hz, 1H), 7.18 (dt, $^4J_{\text{HH}}$ 1.0 Hz, $^3J_{\text{HH}}$ 7.6 Hz, 1H), 7.13 (t, $^4J_{\text{HH}}$ 1.0 Hz, 1H), 2.56 (dq, $^4J_{\text{HH}}$ 1.8 Hz, $^3J_{\text{HH}}$ 7.3 Hz, 2H), 1.11 (t, $^3J_{\text{HH}}$ 7.6 Hz, 3H)

^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 100 MHz) δ 150.3, 148.2, 143.2, 135.4, 135.2, 133.0, 132.5, 130.3, 130.0, 128.1, 126.3, 124.6, 25.5, 13.8 ppm

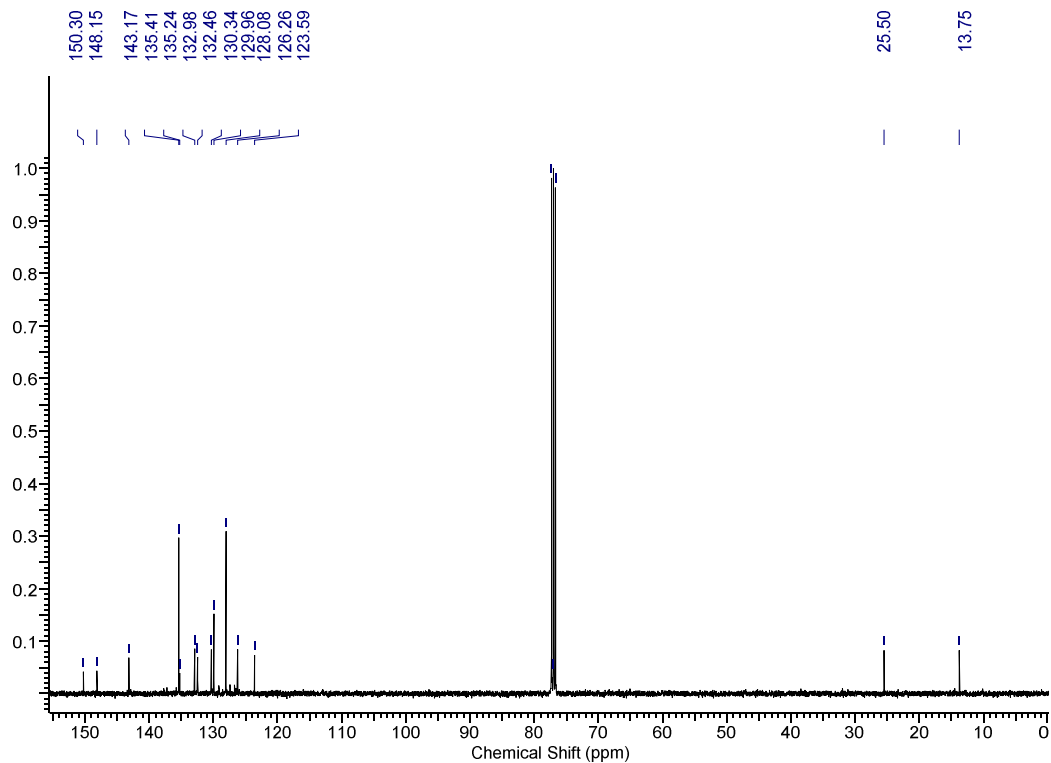
^{29}Si $\{^1\text{H}\}$ NMR (CDCl_3 0 MHz) δ -9.11 ppm

Mass Spec. 312.1329 *m/z*, Expected for M^+ 312.1338 *m/z*

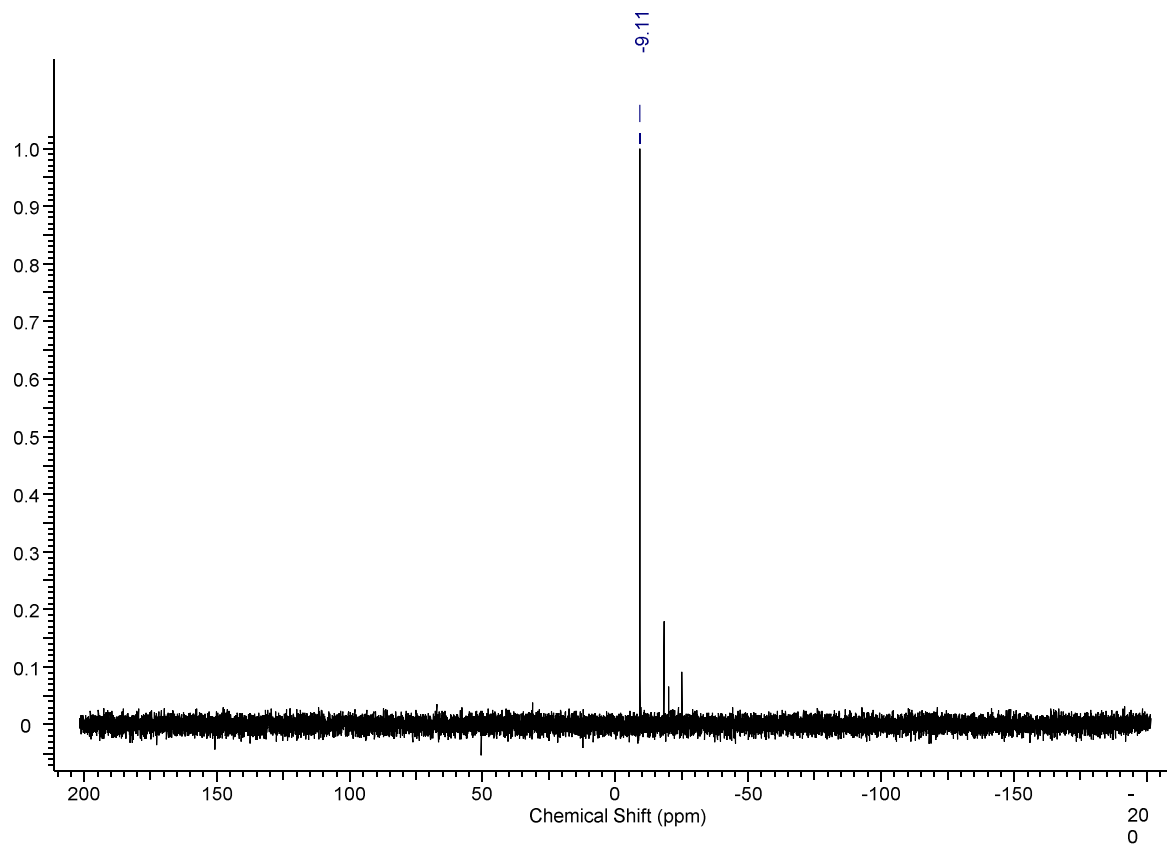
^1H NMR Spectrum: 2-ethyl-1,1-diphenyl-1-silaindene after preparative TLC



$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum: 2-ethyl-1,1-diphenyl-1-silaindene after preparative TLC

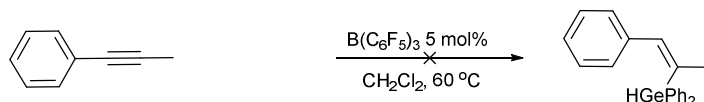


^{29}Si $\{^1\text{H}\}$ NMR Spectrum: 2-ethyl-1,1-diphenyl-1-silaindene after preparative TLC



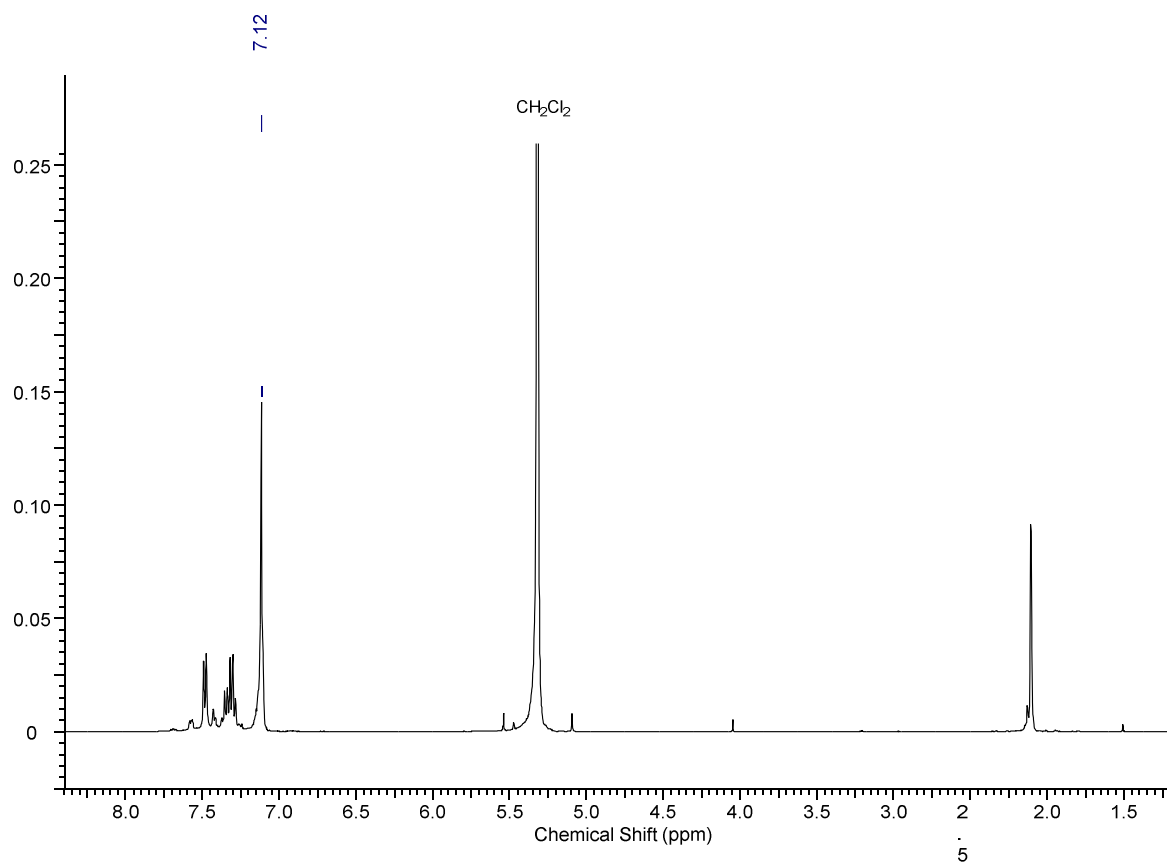
General Procedure 6: Attempted Hydrogermylation of Alkynes

In an oven dried J Youngs NMR tube equipped with a d₆-dmsO capillary, diphenylgermane (1 equiv.) was added to a solution of BCF (X mol %) in 1 ml of solvent. This solution was agitated for 5 minutes before the addition of 1-phenyl-1-propyne (1 equiv.). The reaction was monitored by NMR spectroscopy.



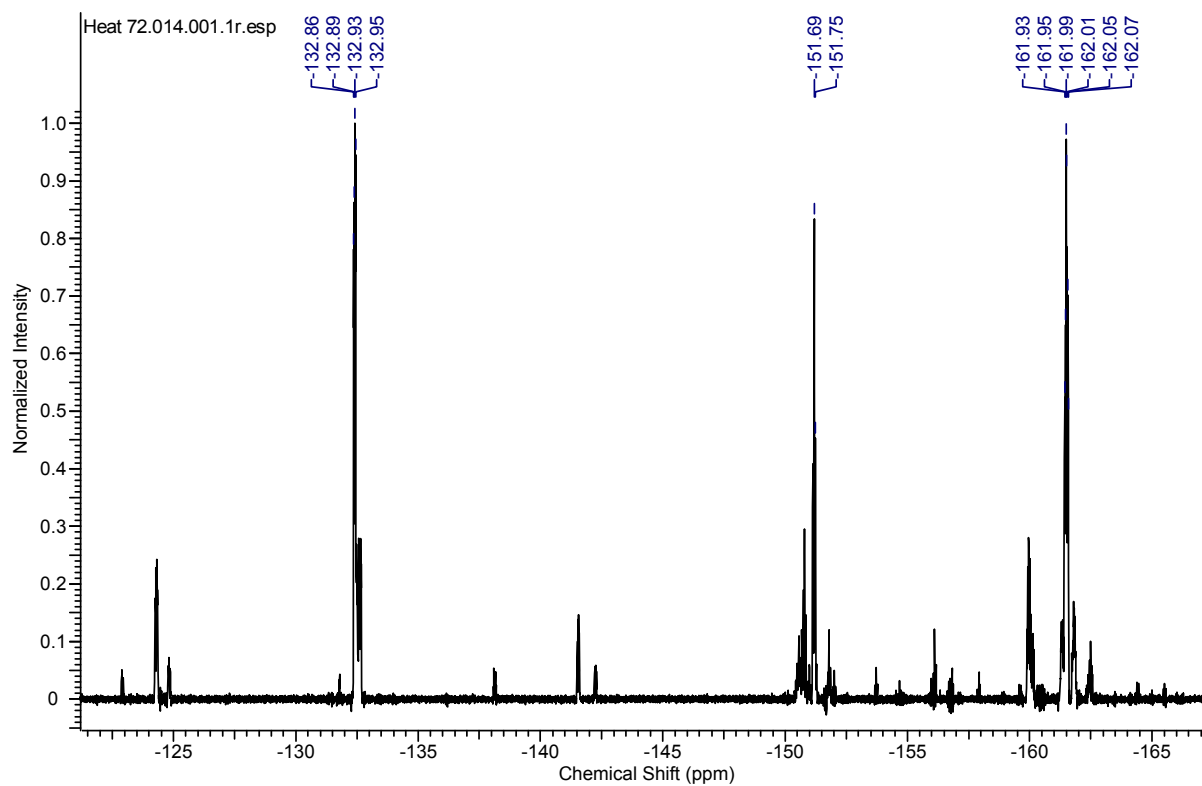
It was observed that the reaction in CH₂Cl₂ lead to solvent activation and the appearance of benzene in the ¹H NMR spectrum.

Representative ¹H NMR spectrum: Hydrogermylation in CH₂Cl₂



The reaction was repeated in *o*-DCB. It was observed in the ^{19}F $\{^1\text{H}\}$ NMR spectrum that BCF was not stable to these conditions.

^{19}F $\{^1\text{H}\}$ NMR spectrum: Hydrogermylation in *o*-DCB

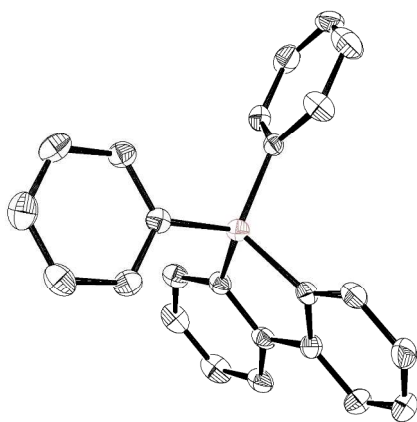


X-ray data

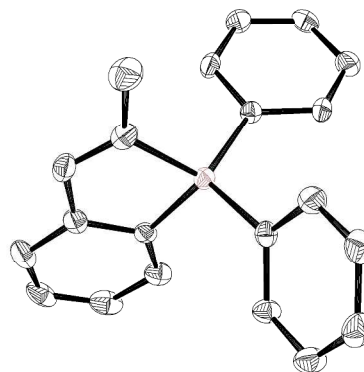
Data for compounds **5a** and **13a** were recorded on an Agilent Supernova diffractometer, with Mo K α radiation (mirror monochromator, $\lambda=0.7107$). The CrysAlisPro⁶ software package was used for data collection, cell refinement and data reduction. For all data sets the CrysAlisPro software package was used for empirical absorption corrections, which were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Structure **5a** was solved using direct methods⁷ and refined against F^2 using the Crystals⁸ software package. Structure **13a** was solved, a large Max Peak is reported due to a Si atom from unresolved disorder resulting from a minor 5 % conformation, using direct methods and refined against F^2 using the OLEX2⁹ software package. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all located in a difference map and repositioned geometrically. Experimental details are given below in Table 1.

Crystallographic data for **5a** and **13a** have been deposited with the Cambridge Crystallographic Data Center under the references: 1026176; and 1026175. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) *via* www.ccdc.cam.ac.uk/data_request/cif.



5a



13a

Table 1: Crystallographic data for 5a and 14a

	5a	13a
Formula	C ₂₄ H ₁₈ Si ₁	C ₂₁ H ₁₈ Si
MW (g/mL)	334.47	298.21
Crystal size (mm)	0.10 x 0.12 x 0.15	0.3 x 0.3 x 0.2
Crystal system	orthorhombic	Monoclinic
Space group	P 21 21 21	P2 ₁ /c
a (Å)	8.9263(18)	18.6476(10)
b (Å)	17.961(4)	9.6898(4)
c (Å)	22.275(5)	19.1479(11)
α(°)	90	90
β(°)	90	108.925(6)
γ(°)	90	90
V (Å ³)	3571.3(12)	3272.8(3)
Z	8	8
ρ _{calculated} (g/cm ³)	1.244	1.2093
Temperature (K)	99.99(10)	150
Wavelength (Å)	0.71073	0.71073
Θ(°)	4.099 – 26.368	3.02-26.00
no. of unique reflections	4071	6374
max. and min. transmission	1.000 – 0.725	1.000-0.663
Final R indices [I>2σ(I)]	0.0393	0.2075
R indices (all data)	0.0617	0.1024
Goodness-of-fit on F ²	0.9984	1.053
Peak/hole (e.Å ⁻³)	0.45, -0.51	1.95, -0.38

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