Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

E-H (E = R_3Si or H) bond activation by $B(C_6F_5)_3$ and heteroarenes; competitive dehydrosilylation, hydrosilylation and hydrogenation.

Liam D. Curless, Ewan R. Clark, Jay J. Dunsford and Michael J. Ingleson*

General Procedures:

General Considerations: All manipulations were performed using standard Schlenk techniques or in an argon-filled MBraun glovebox (O_2 levels below 0.5 ppm). Solvents used were purified by Innovative Technology PS-MD-5 solvent purification system or distilled from appropriate drying agents, degassed and stored over molecular sieves. Deuterated solvents were distilled from appropriate drying agents and degassed. All materials were prepared via standard procedures or purchased from commercial vendors and used as received apart from $B(C_6F_5)_3$ which was purchased and dried by treating with excess Et_3SiH at room temperature whilst monitoring periodically by ^{19}F NMR spectroscopy and then put under dynamic vacuum for 5 hours.

Synthesis of 2-Me-5-(Ph_3Si)-thiophene, 2

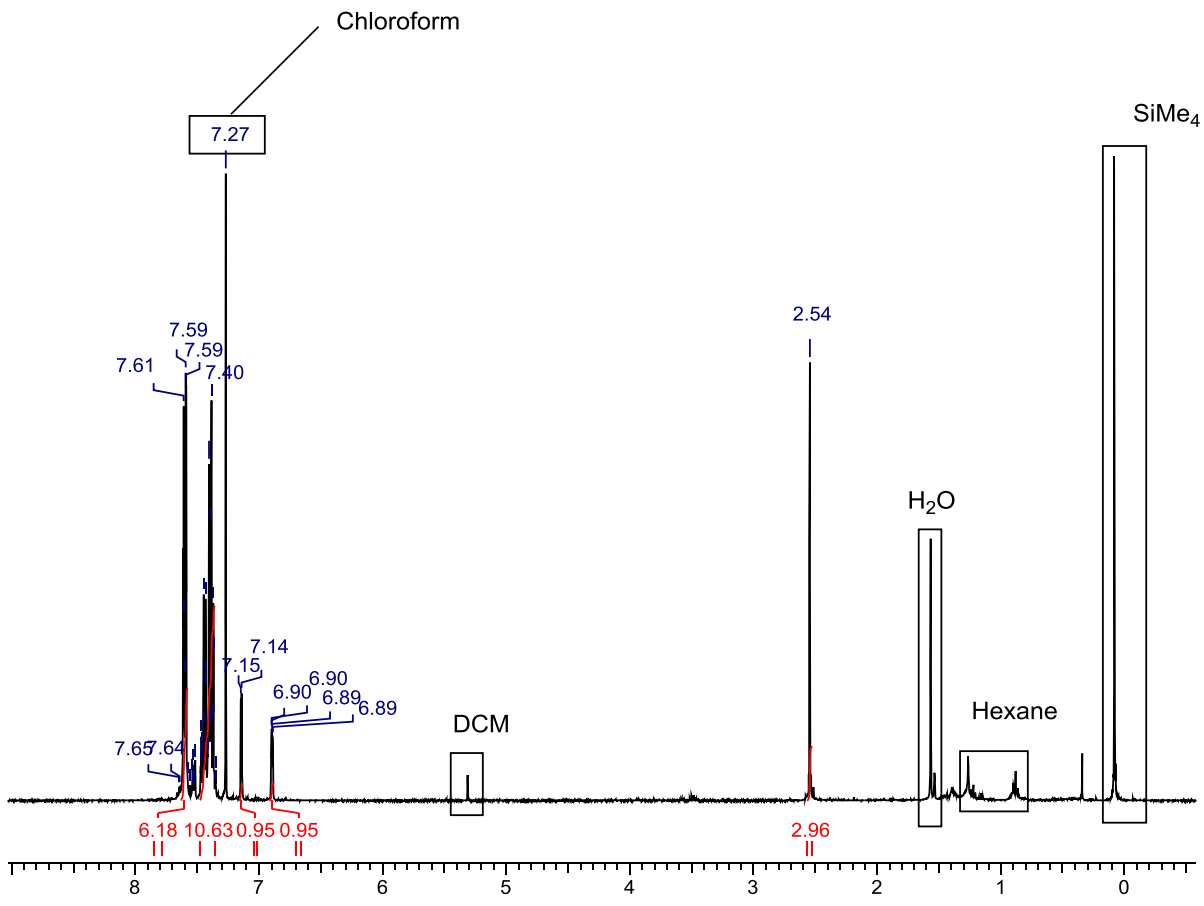
An oven-dried Schlenk flask containing a stirring bar was heated under reduced pressure and charged under an argon atmosphere. To a solution of 2-methylthiophene (0.50 mL, 5.16 mmol) in anhydrous Et_2O (10 mL) was added ^{n}BuLi (3.10 mL, 5.16 mmol,1.60 M in hexane) at -20 ^{o}C. The reaction was stirred at -20 ^{o}C for 1 hour. After 1 hour a solution of Ph_3SiCl (1.5 g, 5.16 mmol) in anhydrous Et_2O (10 mL) was added dropwise to the reaction vessel at – 20 ^{o}C. The solution was left to warm to 20 ^{o}C overnight. The solution was filtered and solvent removed. The crude product was purified by column chromatography on silica gel using hexane as the eluent to give pure product as a yellow crystalline material, 1.30 g in 71 % yield.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.66-7.63 (m, 3H), 7.48-7.40 (m, 12H), 7.18 (d, $^{3}J_{HH}$ = 3.3 Hz, 1H), 6.92 (dd, $^{3}J_{HH}$ = 3.3 Hz, $^{4}J_{HH}$ = 1.0 Hz 1H), 2.57 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 138.4 (s), 135.8 (s), 134.0 (s), 129.4 (s), 127.4 (s) 14.85 (s)

^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 298 K): δ -19.4 (s).

MS (EI) m/z [M]$^{+}$: Calculated for $C_{23}H_{20}SSi$: 356.1 Observed : 356.1



^{1}H NMR spectrum

Synthesis of *tert*-butylthiophene

An oven-dried Schlenk flask containing a stirring bar was heated under reduced pressure and charged under an argon atmosphere. In the dark to a yellow suspension of $AlCl_3$ (0.011 g, 84.13 mmol, 1.5 equiv.) in anhydrous CH_2Cl_2 (25 mL) was added a solution of 2-chloro-2-methylpropane (0.90 ml, 53.48 mmol, 0.9 equiv.) and thiophene (1.00 mL, 59.42 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (25 mL) at -78 ^oC. The reaction was stirred at -78 ^oC for 1 hour and then allowed to warm to room temperature and left to stir for 36 hours. The solution was slowly poured into water. The mixture was extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by column chromatography on silica gel using hexane as the eluent to give pure product as colourless oil, 0.53 mL in 70 % yield. NMR spectra are in accordance to literature values.[i]

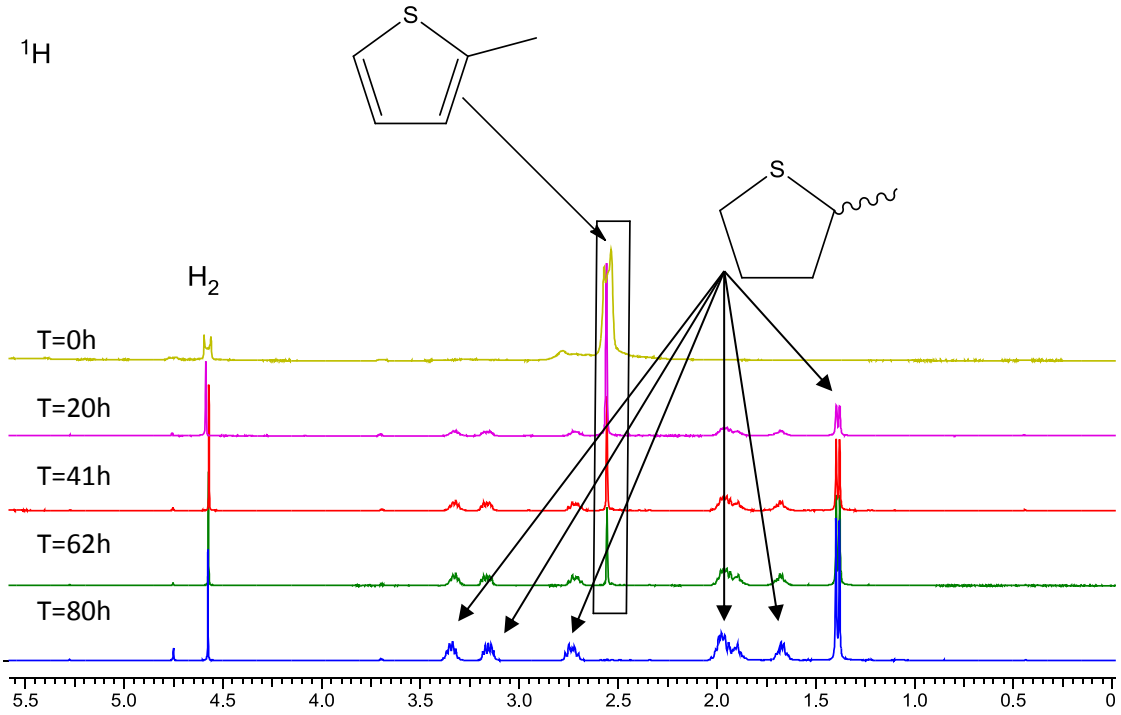
To simplify the analysis of spectra from silylation the results / spectra from hydrogenation reactions are included first.

General procedure for hydrogenation.

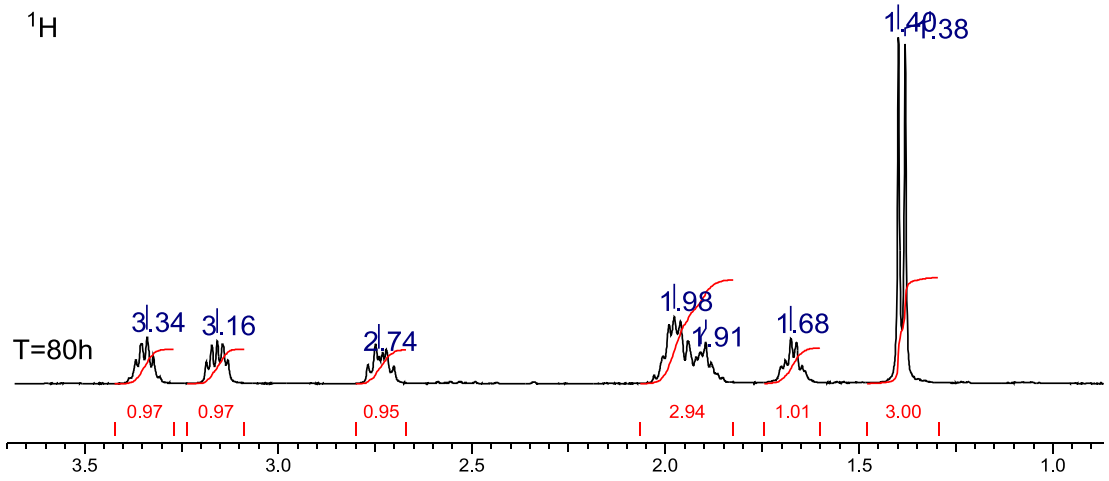
The reaction vessel (either a J. Young's NMR tube or a Schlenk fitted with a right angle J. Young's tap) containing the reagents and solvent (as specified in individual entries) was attached to a Schlenk line operating under H_2/D_2 as appropriate in the usual manner. The reaction mixture was freeze-pump-thaw degassed in liquid nitrogen for three cycles before once more being frozen and an atmosphere of H_2/D_2 admitted – the bulk of the vessel was maintained under dynamic gas pressure until liquid nitrogen temperatures were achieved whereupon the vessel was sealed and warmed to room temperature, giving an internal pressure of ca. four atmospheres.

Hydrogenation of 2-MT without base.

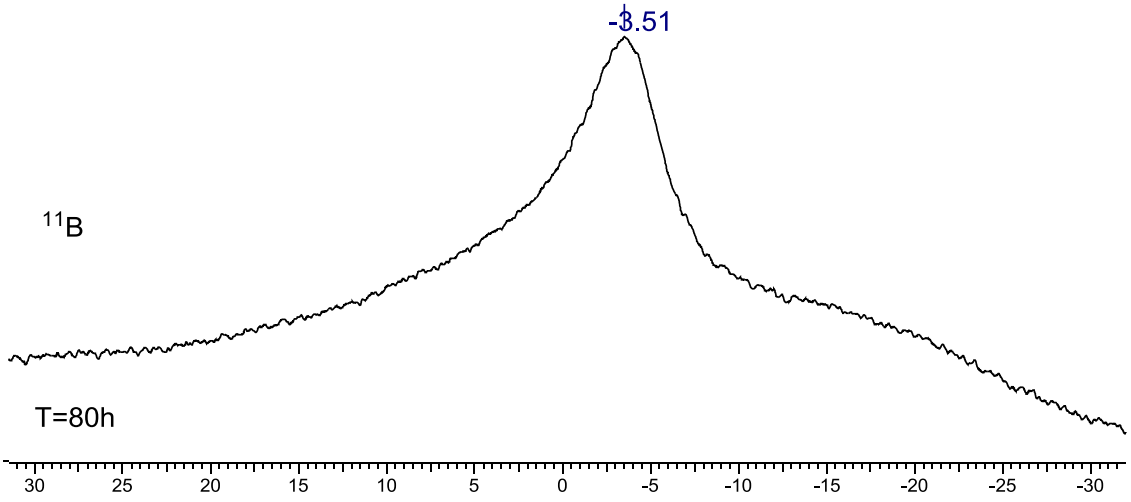
1,2-dichlorobenzene (o-DCB, 1 cm^3) was added to $B(C_6F_5)_3$ (51 mg, 0.10 mmol) in a J. Young's NMR tube fitted with a d_6-DMSO capillary. 2-methylthiophene (10 µl, 0.10 mmol) was added and the vessel sealed and inverted to ensure mixing. The whole was freeze-pump-thaw degassed and charged with 4 atmospheres of H_2. The vessel was heated to 100 ^oC in an oil bath for 80 hours with NMR spectra periodically recorded. After 62 hours, the vessel was recharged with additional H_2 and returned to heat for a further 18 hours after which reduction was judged complete by NMR.



Reaction progress can be observed clearly in the ^{1}H NMR aliphatic region, with loss of the Me singlet of 2-methylthiophene (δ 2.56) and the growth of a new broadened Me doublet (δ 1.39) and complex broad multiplets associated with the ring protons, with final integrals consistent with full reduction. At no point are vinylic peaks corresponding to partially reduced products observed.



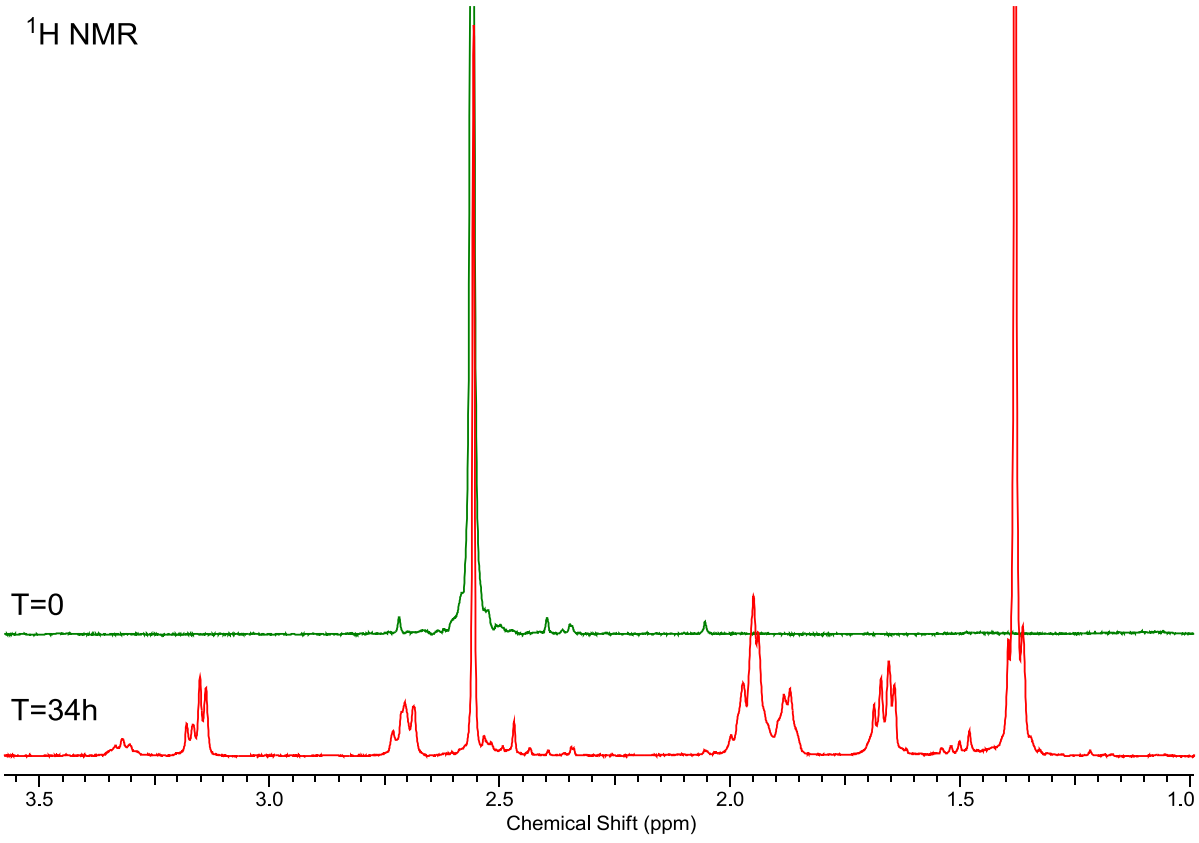
The broadening of the peaks is attributed to the existence of an equilibrium involving thio-ether-borane adducts, supported by the growth of a broadened signal at δ -3.51 in the ^{11}B NMR spectrum, consistent with a 4-coordinate boron centre, the only species observed after t = 80 h, and the upfield shifts observed in the ^{19}F NMR (at T = 80 h, δ -129.5, -155.3 and -163.1 ppm).



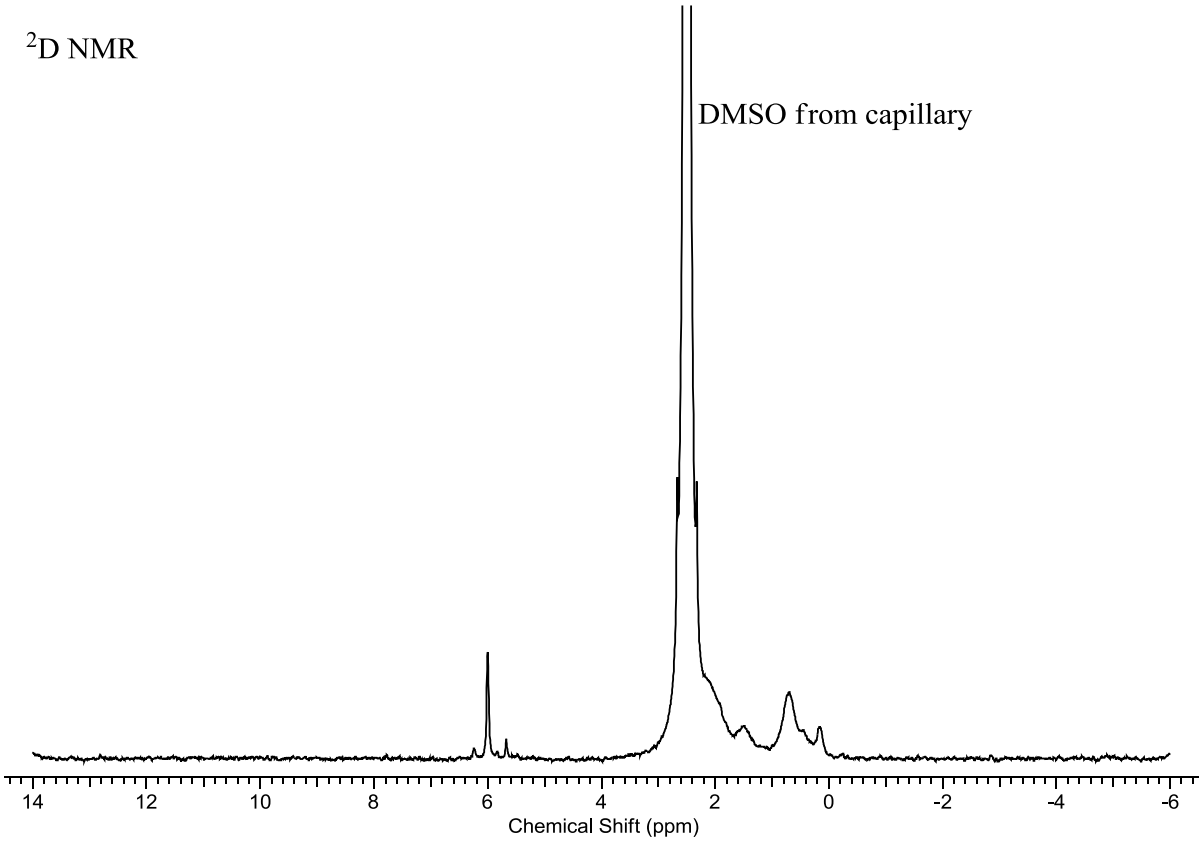
Reduction with D_2

To confirm the origin of incorporation of hydrogen into the molecule, the reduction was performed under D_2. $B(C_6F_5)_3$ (51 mg, 0.10 mmol) and 2-methylthiophene (10 μl, 0.10 mmol) were combined in a J. Young's NMR tube fitted with a d_6-DMSO capillary and dissolved in oDCB (0.80 cm^3). The vessel was freeze-thaw degassed and charged with D_2 (4 atm). At 20 ^oC no new aliphatic resonances were observed. The reaction was then heated at 100C for 34 hours.

The ^1H NMR spectrum shows clear growth of aliphatic peaks analogous to those seen for the reaction with H_2. The coupling patterns are complicated however, which may be understood as arising from the superimposition of the possible isotopomers. Importantly, the major signal at δ 1.39 corresponding to the 2-methyltetrahydrothiophene methyl group is a singlet, due to unobserved coupling to the ipso quadrupolar ^2D nucleus.

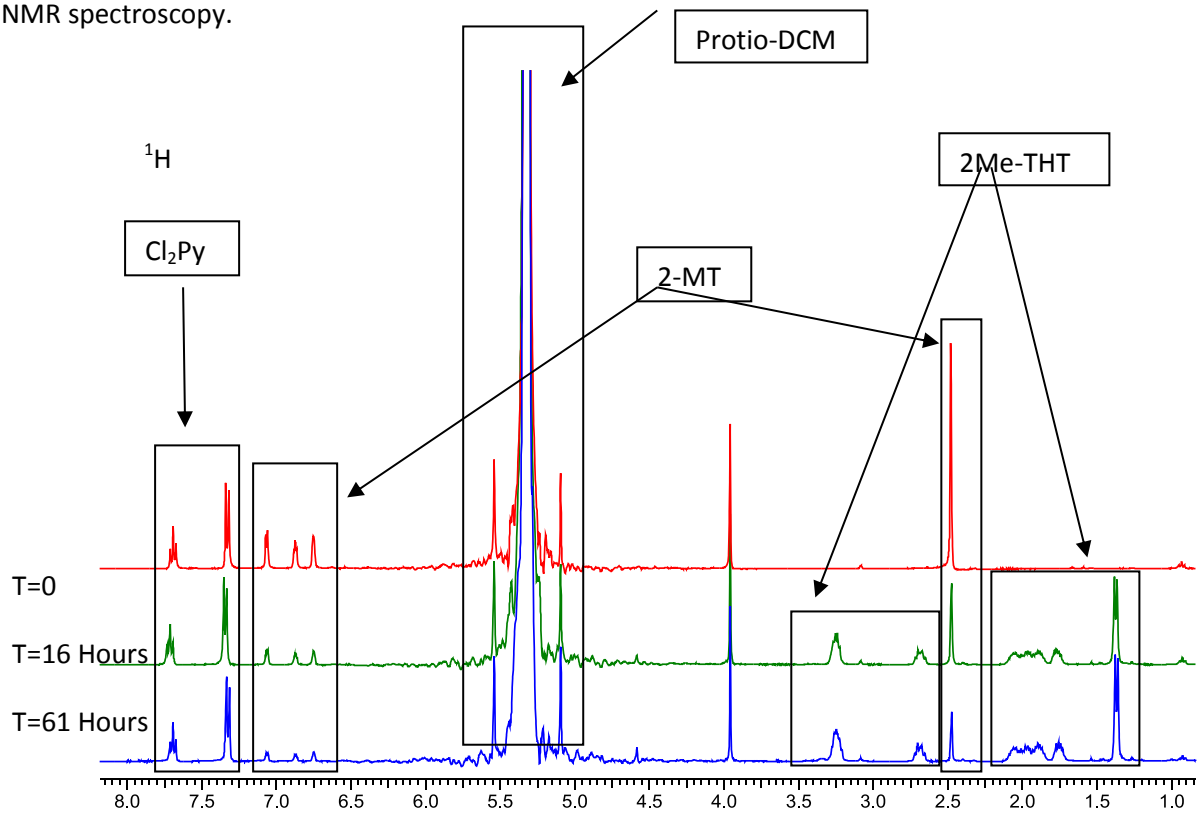


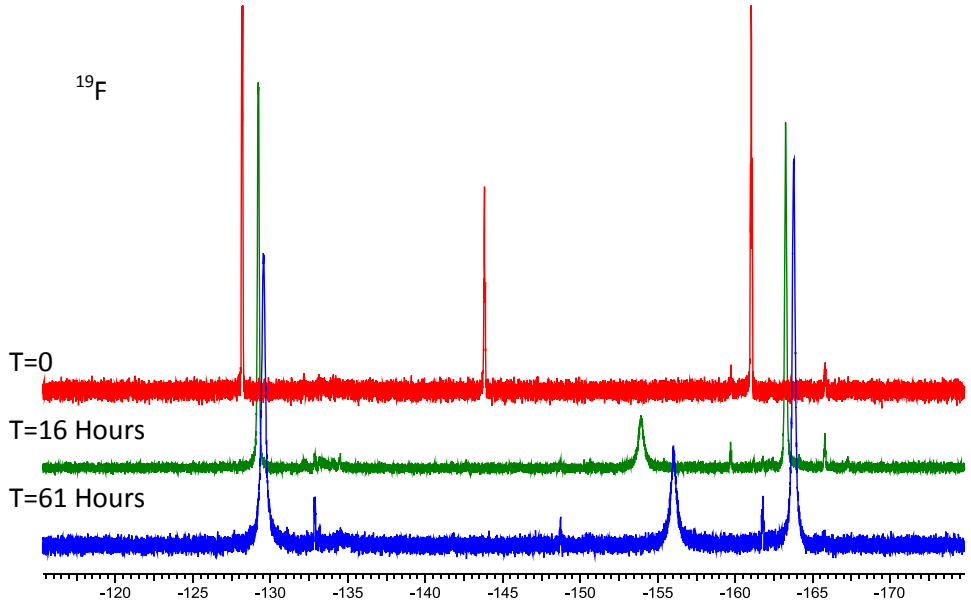
The ^2D NMR spectrum confirms the growth of aliphatic deuterium environments. The sharp singlet at δ 6.00 ppm corresponds to 2-methyl-5-deutero-thiophene, (confirmed by independent synthesis *via* lithiation of 2-methylthiophene and quench with D_2O) arising from the Lewis Acid catalysed H/D exchange.



Stoichiometric reduction of 2-Me-thiophene with base

2-Methylthiophene (10 µl, 0.10 mmol) and 2,6-dichloropyridine (15mg, 0.10 mmol) were combined in a J. Young's NMR tube fitted with a d6-DMSO capillary and DCM (1 cm^3) added. $B(C_6F_5)_3$ (51 mg, 0.10 mmol) was added and the tube inverted until dissolution was complete. The vessel was freeze-thaw degassed and charged with H_2 (4 atm) and stirred at room temperature for 16 hours, at which time conversion was 66% by NMR. The vessel was once more freeze-thaw degassed and recharged with H_2, and stirred at room temperature for a further 45 hours, giving a final conversion of 80% by NMR spectroscopy.





The ^{19}F resonances are broadened and shifted upfield, and the ^{11}B resonance is likewise broad and shifted into the four coordinate region of the spectrum (δ = 60ppm at T = 0, 7.4ppm at T = 16 h and -3.5 ppm at T = 61 h) , consistent with a dynamic equilibrium existing with a Lewis base, presumed to be 2-Me-THT. The minor peaks in the ^{19}F NMR spectrum are attributable to HC_6F_5. The sample was then analysed by GCMS.

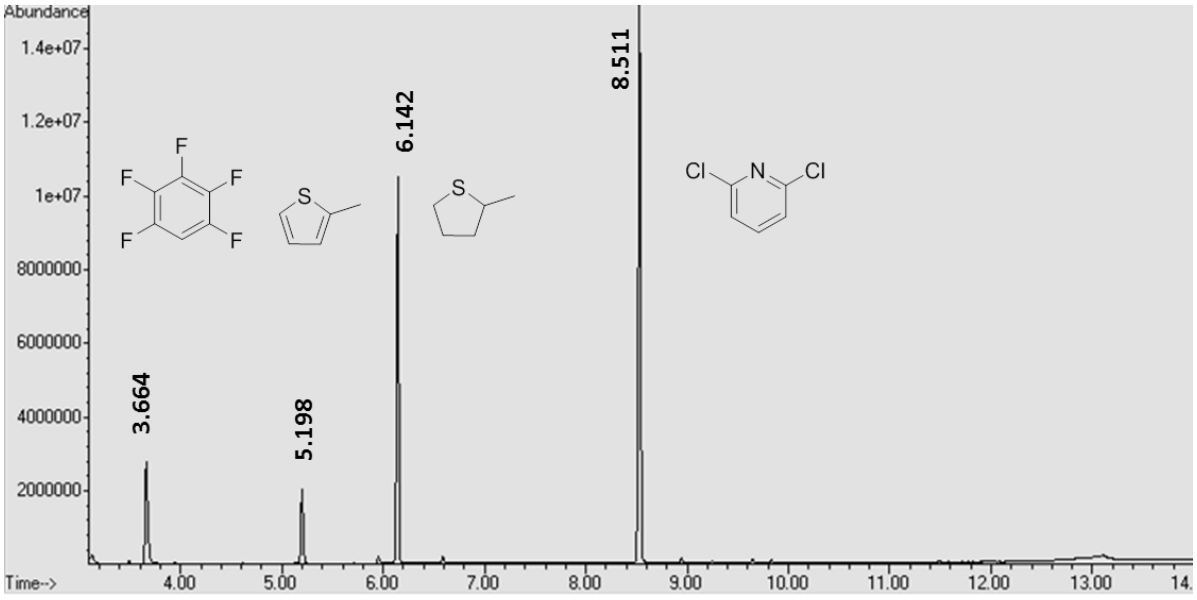
General Remarks for GCMS Analysis: GCMS analysis was performed on an Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD with triple axis detector. The column employed was an Agilent J&W HP-5ms ((5%-Phenyl)-methylpolysiloxane) of dimensions: length, 30 m; internal diameter, 0.250 mm; film, 0.25 µm.

GCMS Sample Preparation: Samples for GCMS analysis were taken directly from the reaction mixture, diluted with HPLC grade dichloromethane (1.5 mL, approx. concentration ~ 1mg/mL) and eluted through a small plug of silica prior to analysis.

GCMS Program of Analysis: Initial temperature of 50 ºC, held for 3 minutes, ramp 25 ºC/minute next 300 ºC, held for 5 minutes (total run time, 18 minutes). The temperature of the injector and detector were maintained at 300 ºC.

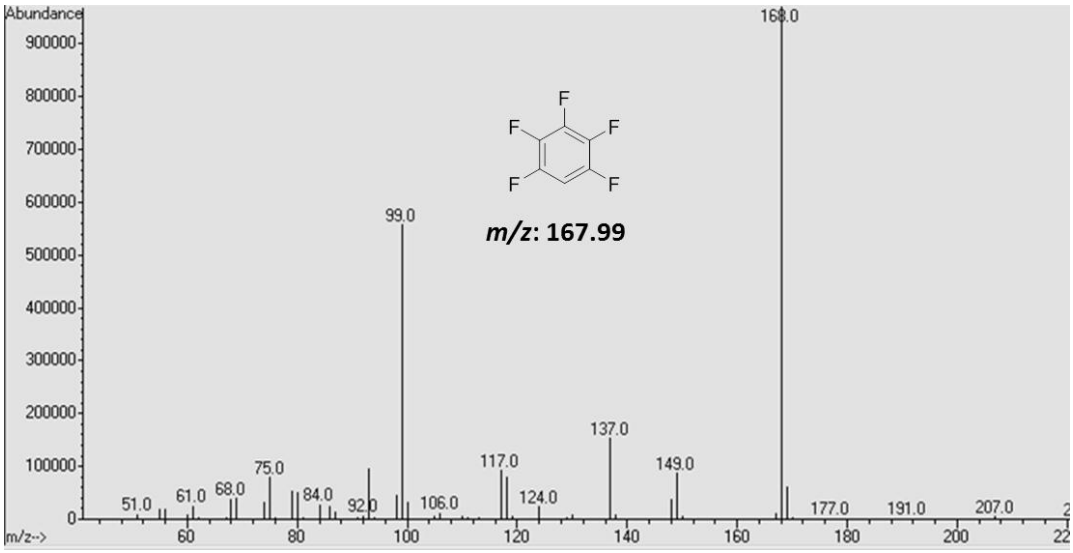
Retention Times of Analytes: Pentafluorobenzene, 3.664 minutes; 2-methylthiphene, 5.198 minutes; 2-methyltetrahydrothiophene, 6.142 minutes; 2,6-dichloropyridine, 8.511 minutes.

GCMS Trace:

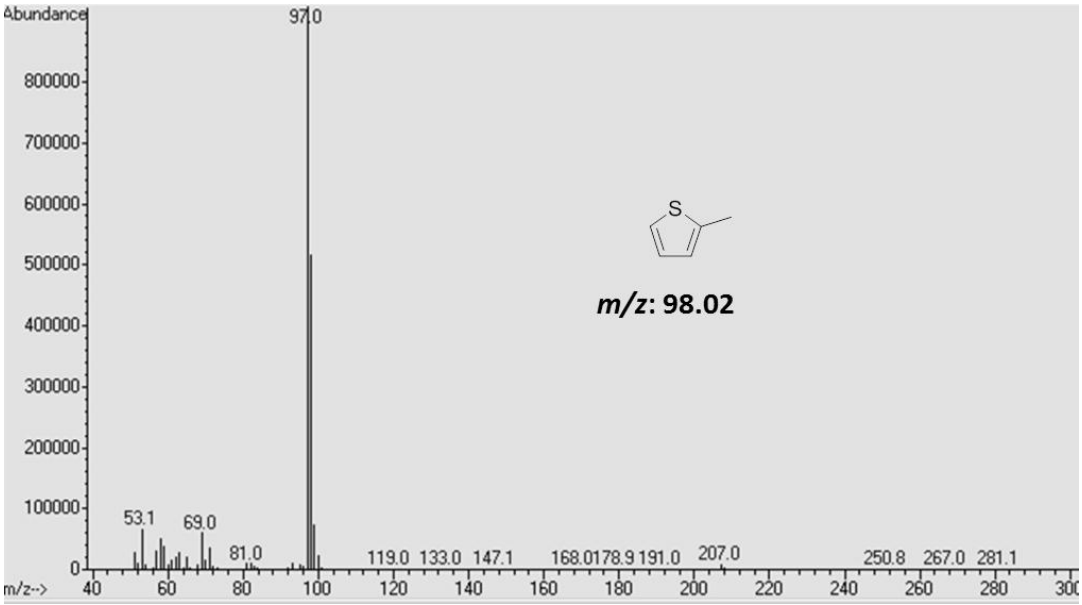


Mass Spectra of Analytes:

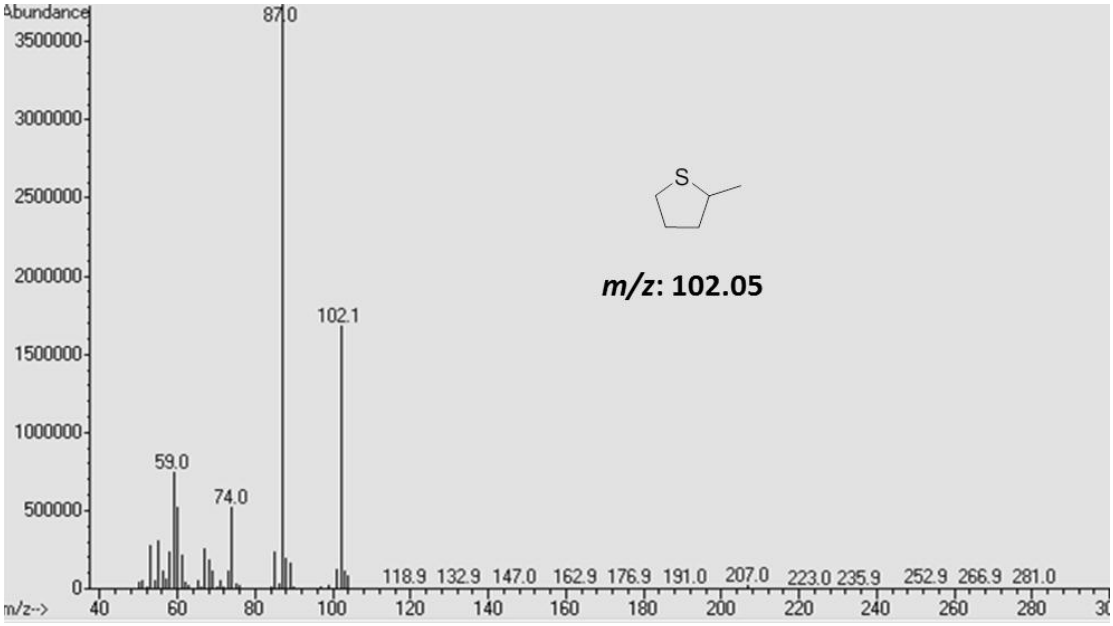
3.664 minutes – pentafluorobenzene:



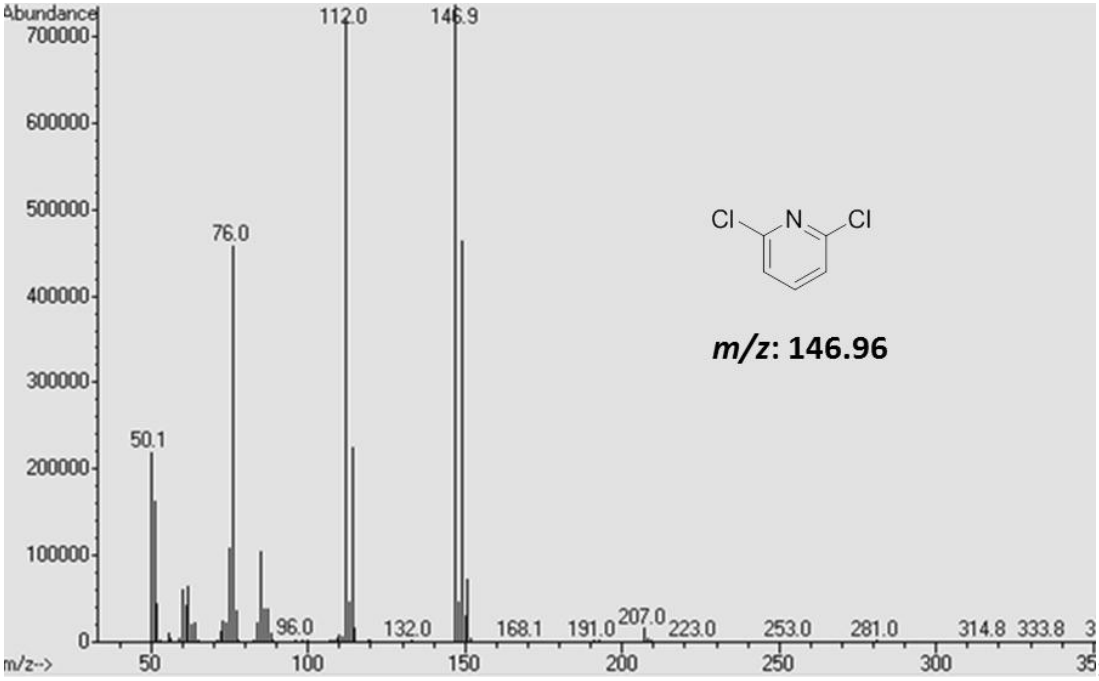
5.198 minutes – 2-methylthiophene:



6.142 minutes – 2-methyltetrahydrothiophene:

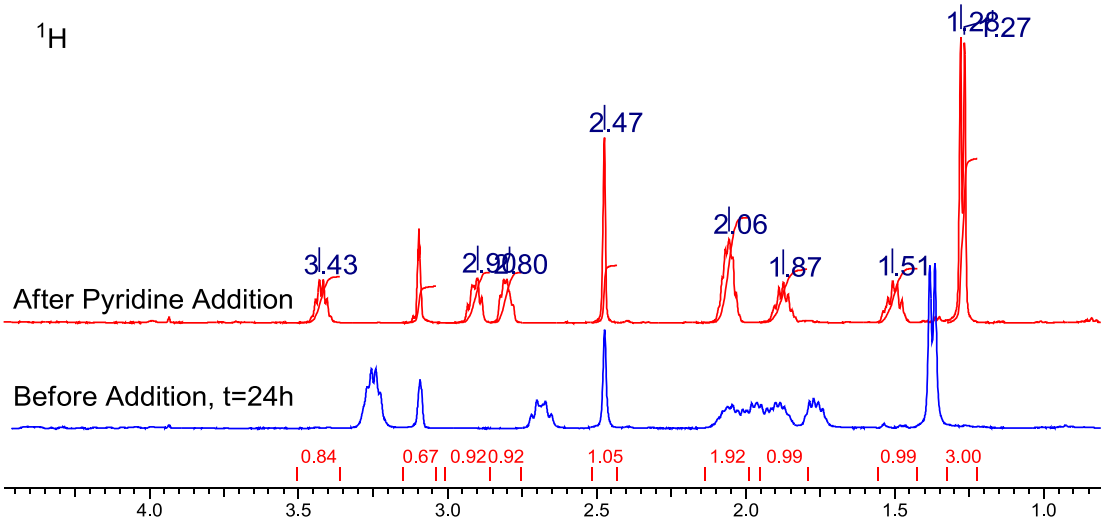


8.511 minutes – 2-methyltetrahydrothiophene

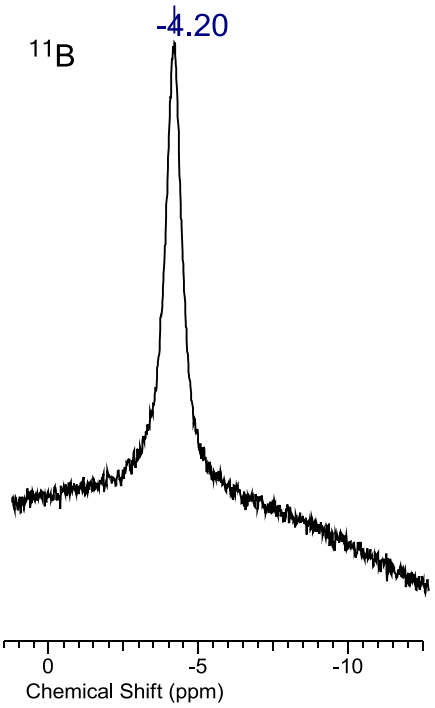


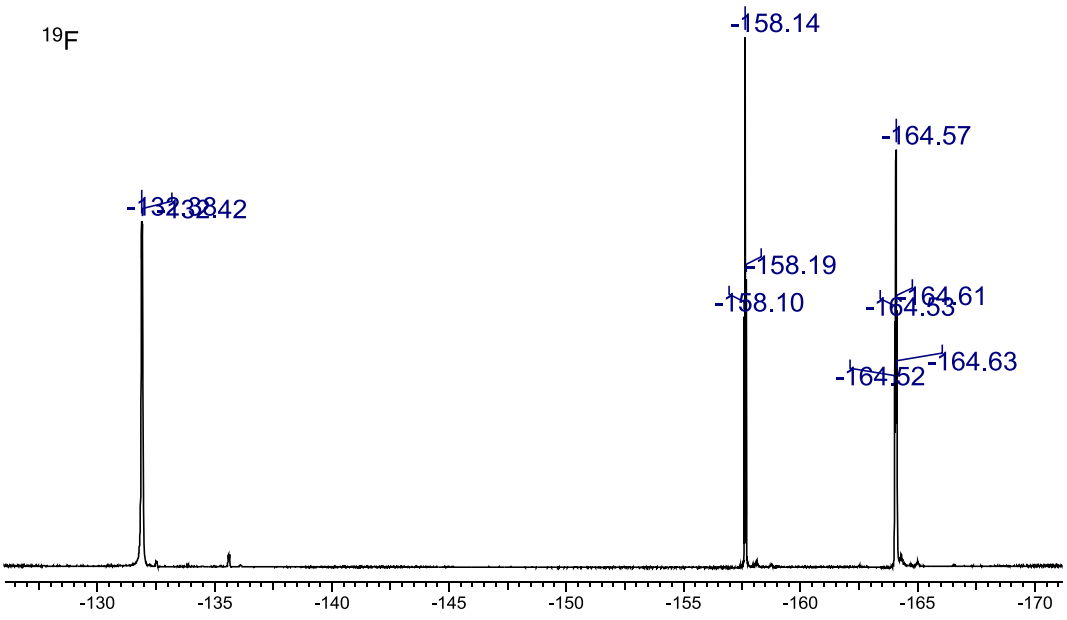
:

To obtain ^{1}H NMR shifts for 2-methyl-tetrahydrothiophene and confirm the existence of a product-$B(C_6F_5)_3$ equilibrium, the reaction was repeated. 2-Methylthiophene (10 μl, 0.10 mmol) and 2,6-dichloropyridine (15 mg, 0.10 mmol) were combined in a J. Young's NMR tube fitted with a d_6-DMSO capillary and DCM (1 cm^3) added. $B(C_6F_5)_3$ (51 mg, 0.10 mmol) was added and the tube inverted until dissolution was complete. The vessel was freeze-thaw degassed and charged with H_2 (4atm) and stirred at room temperature for 24 hours, at which time conversion was 76 % by NMR. Excess pyridine (20 μl, 0.25 mmol) was then added to cleave the S-B bond in the (2-Me-THT)$B(C_6F_5)_3$ adduct and the NMR recorded. Significant changes are observed in the ^{1}H signals, with better separation of peaks and an upfield shift in the methyl resonance of 2-methyl-tetrahydrothiophene, whilst tellingly the 2-methylthiophene resonance at δ 2.47 remains unchanged.



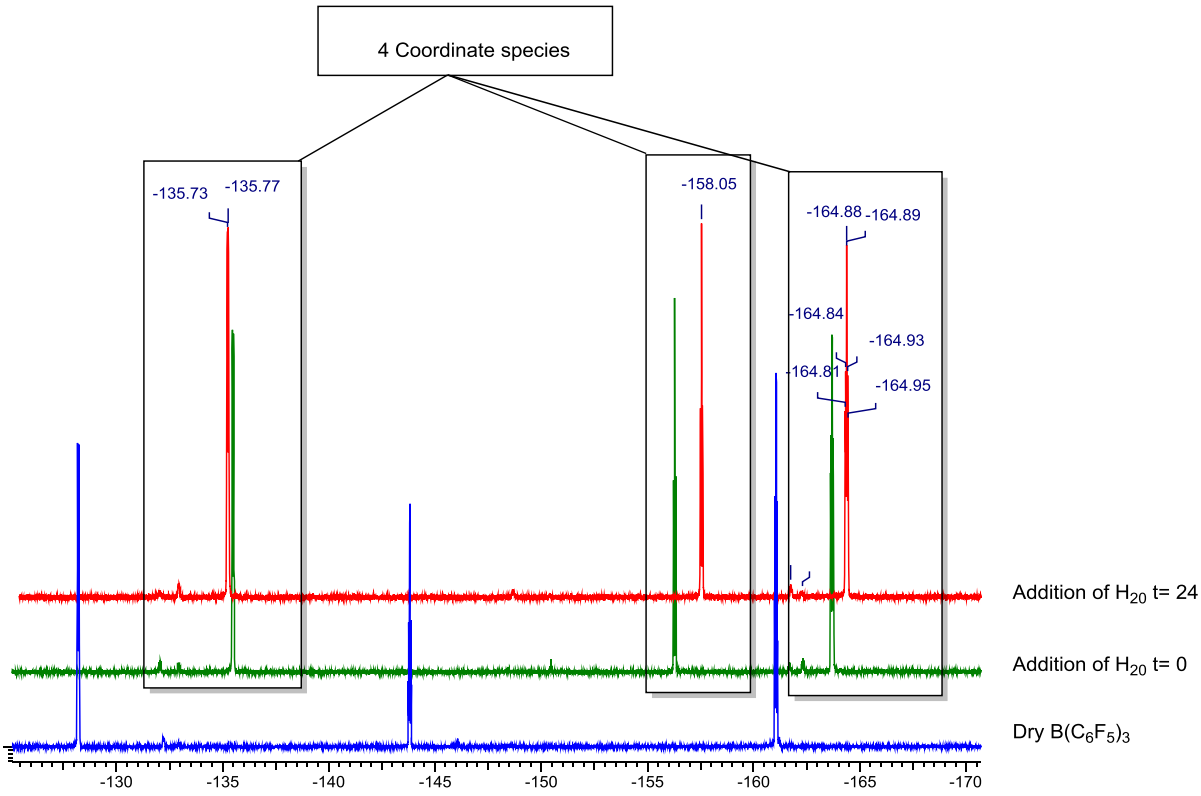
The ^{11}B and ^{19}F NMR spectra show sharp peaks, consistent with the formation of (Pyridine)-$B(C_6F_5)_3$.


11B
-4.20
0
-5
-10
Chemical Shift (ppm)


19F
-158.14
-164.57
-132.38
-132.42
-158.19
-158.10
-164.61
-164.53
-164.63
-164.52
-130
-135
-140
-145
-150
-155
-160
-165
-170

Hydrogenation in the presence of H_2O

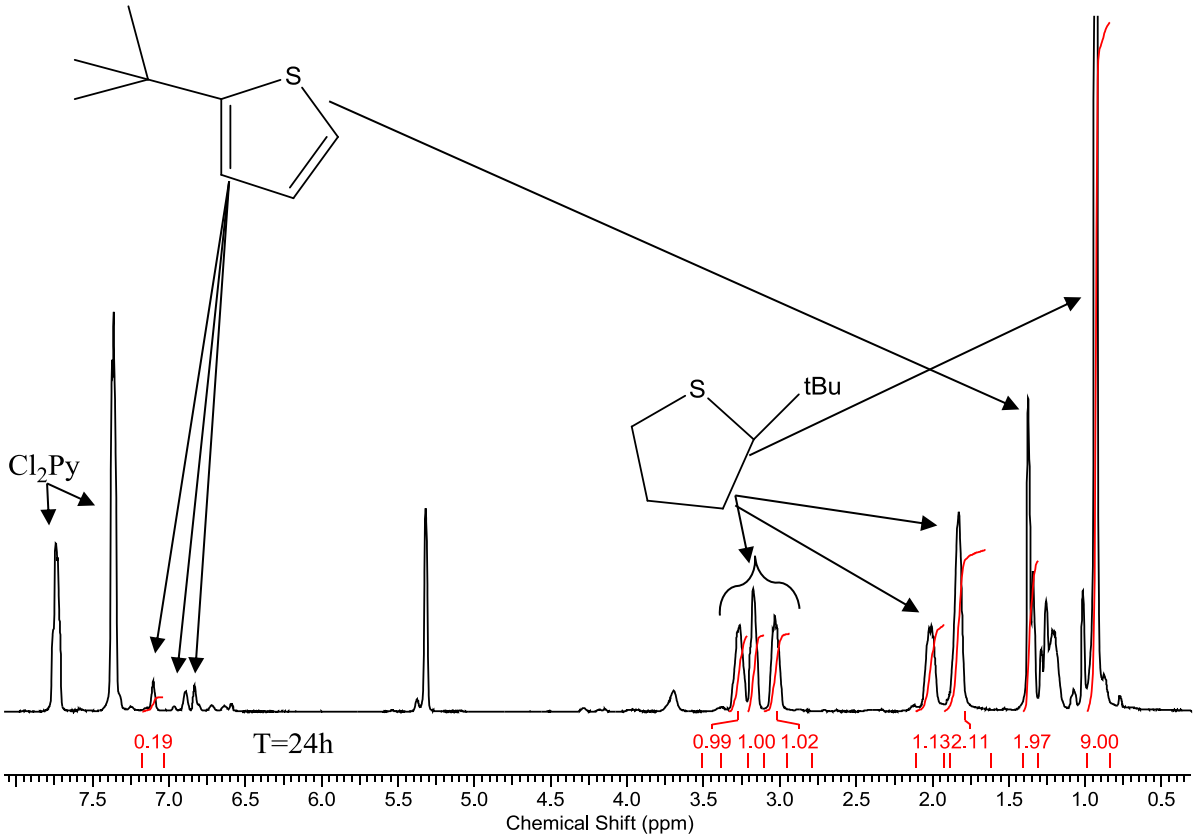
Repeating the hydrogenation of 2-MT in the presence of stoichiometric H_2O prevented reduction of 2-MT precluding a mechanism initiated by a strong Brønsted acid. On addition of H_2O it was observed that the 4 coordinate H_2O adduct of $B(C_6F_5)_3$ was formed.



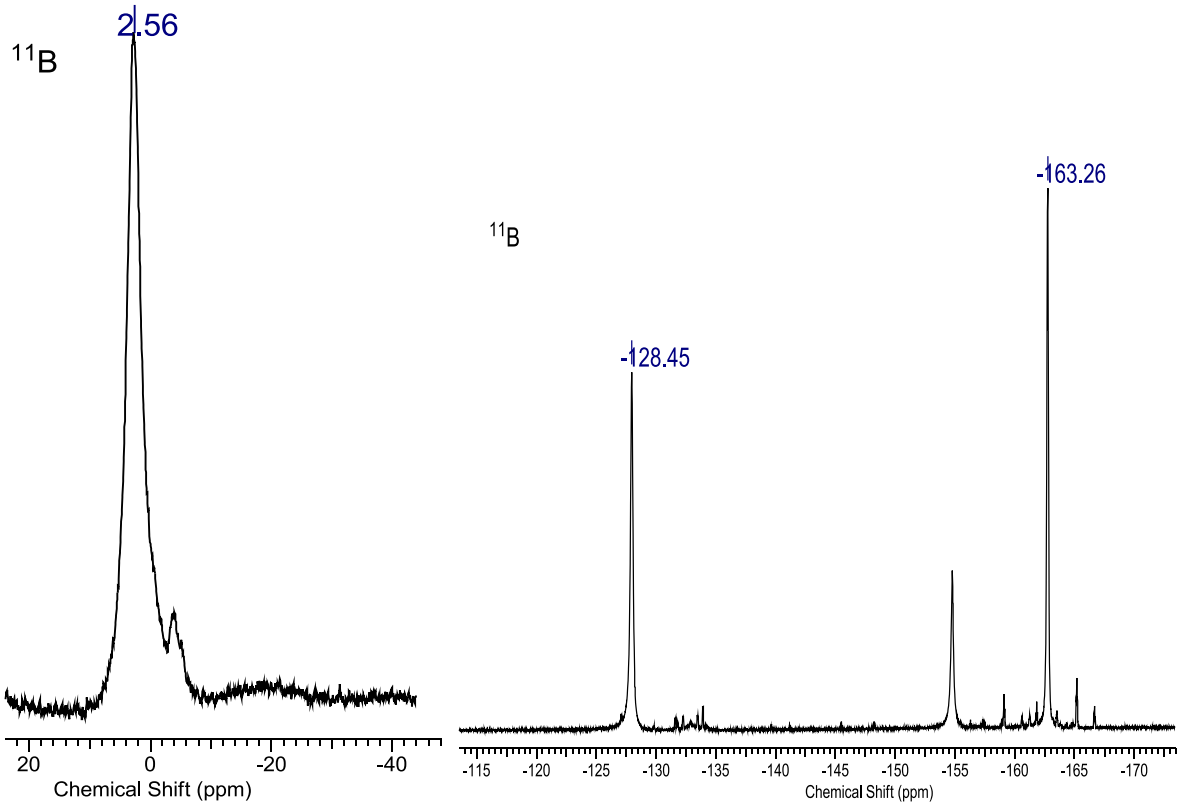
Hydrogenation of 2-tBu-thiophene

2-tert-butylthiophene (16 mg, 0.11 mmol) was dissolved in d_2-DCM (0.8 cm^3) in a 10 cm^3 volume J. Young's ampoule and $B(C_6F_5)_3$ (58 mg, 0.11 mmol) and 2,6-dichloropyridine (17 mg, 0.11 mmol) added. The vessel was freeze-pump-thaw degassed and placed under H_2(4 atm) and inverted for 24 hours. After 24 hours, the H_2 was released and the solution transferred to a J. Young's NMR tube and the NMR recorded, showing 80 % conversion to 2-tert-butyl-tetrahydrothiophene.

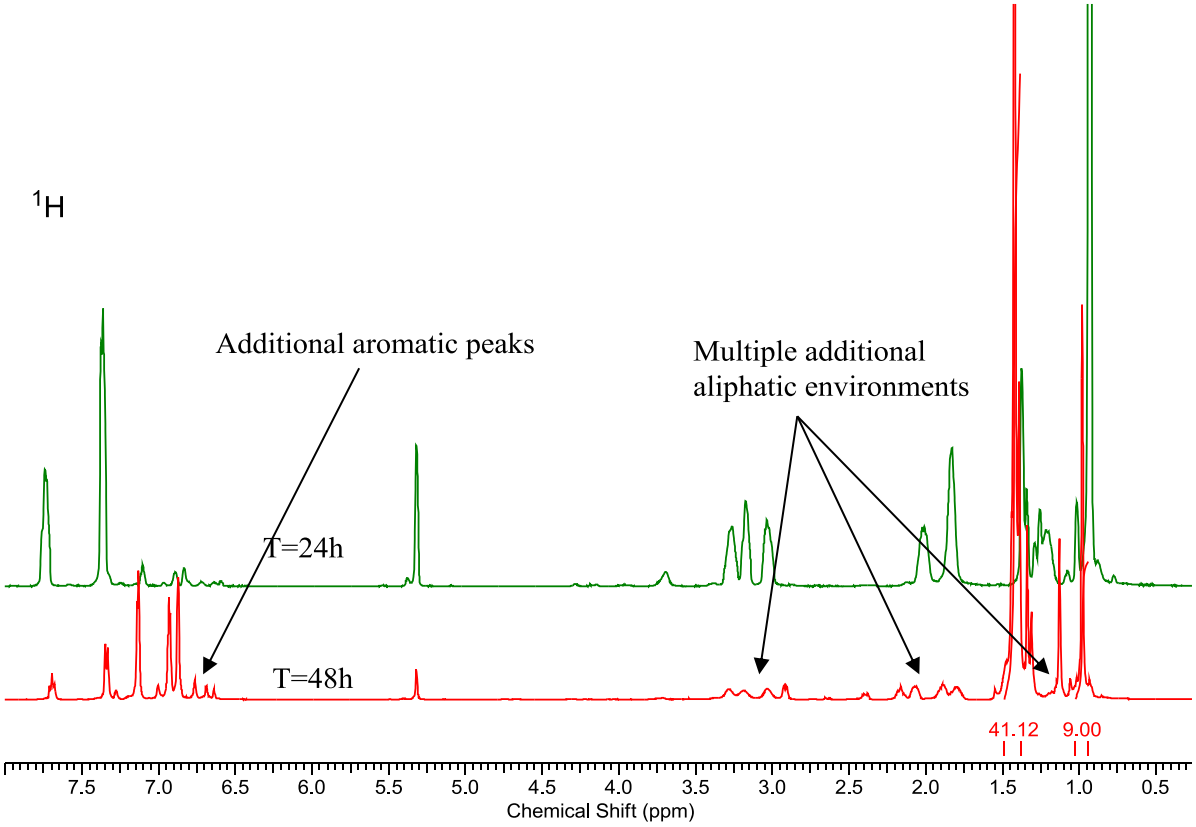
^{1}H NMR



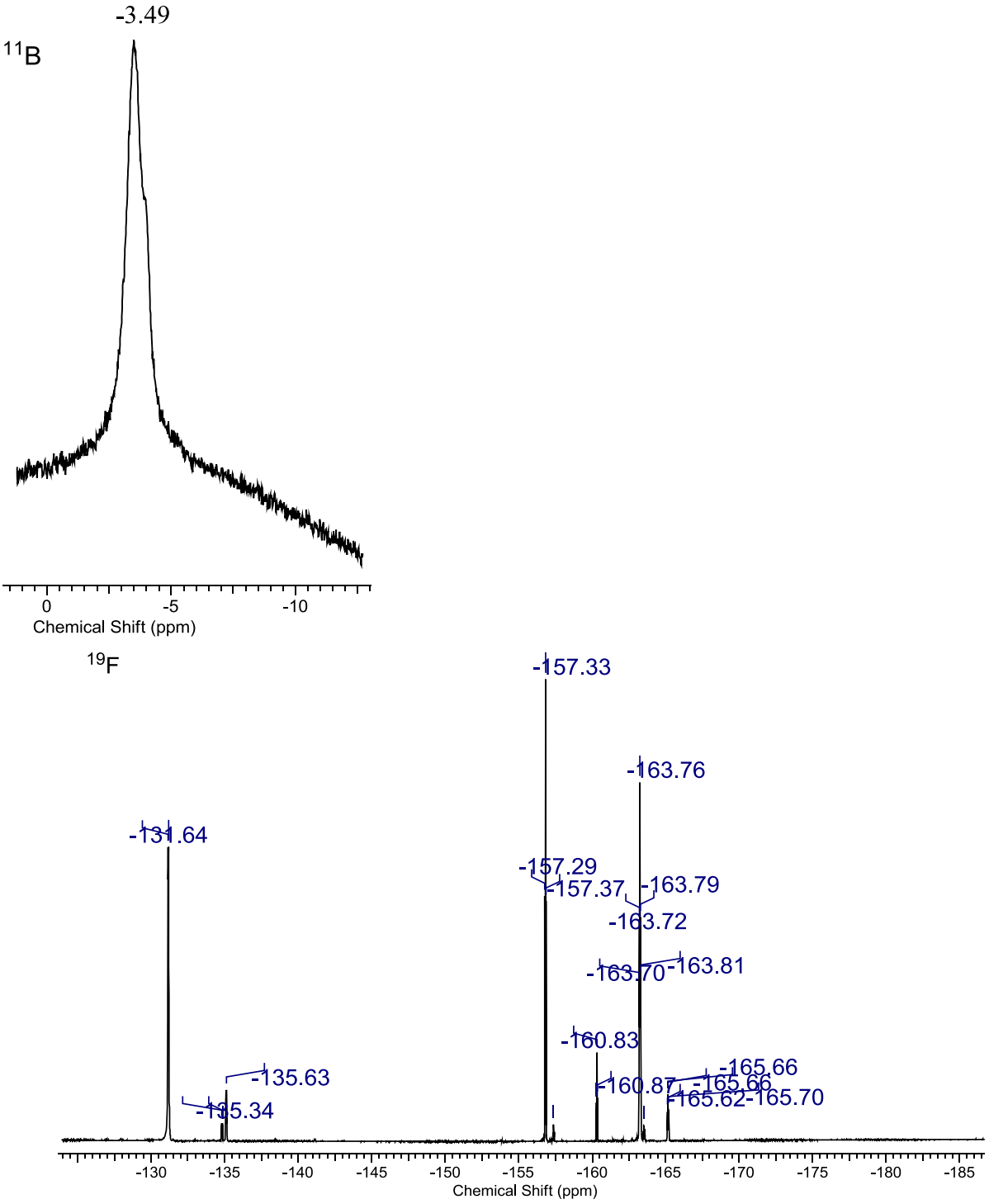
In addition to the major reduction product, several new ^{t}Bu containing minor products had formed, accompanied by small quantities of broad downfield aliphatic environments. Examination of the aromatic region also revealed the formation of new thiophene resonances – from this we may conclude that the Lewis acid / Brønsted acids present in solution enable the retro Friedel-Crafts reaction, allowing ^{t}Bu migration. Subsequent reduction then results in the range of ^{t}Bu peaks and minor products observed. As for the 2-methylthiophene reduction, the ^{11}B and ^{19}F NMR show upfield shifted resonances consistent with the formation of 4-coordinate borane/thio-ether adducts.



This solution was returned to a fresh 10cm^3 J. Young's NMR tube and additional 2-tert-buytlthiophene (88 mg, 0.63 mmol) added. The vessel was freeze-pump-thaw degassed, charged with H_2 (4 atm) and inverted for 24 hours after which the solution was again decanted *via* canula transfer into a J. Young's NMR tube and the spectra recorded. ^{1}H NMR showed a 9:41 ratio of 2-tBu-THT to 2-tBuT and additional resonances associated with retro-Friedel-Crafts type chemistry. Thus, whilst the TON of the catalyst is greater than 1, catalyst inhibition by product is still observed and the retro Friedel Crafts type reactivity outcompetes reduction under those conditions.



To confirm the presence of thioether/borane adduct equilibrium, excess pyridine (20 ml, 0.25 mmol) was added and the spectra rerecorded. This resulted in changes in aliphatic peak positions, indicative of a modification in binding and sharp, upfield shifts in the ^{11}B and ^{19}F NMR (shown).

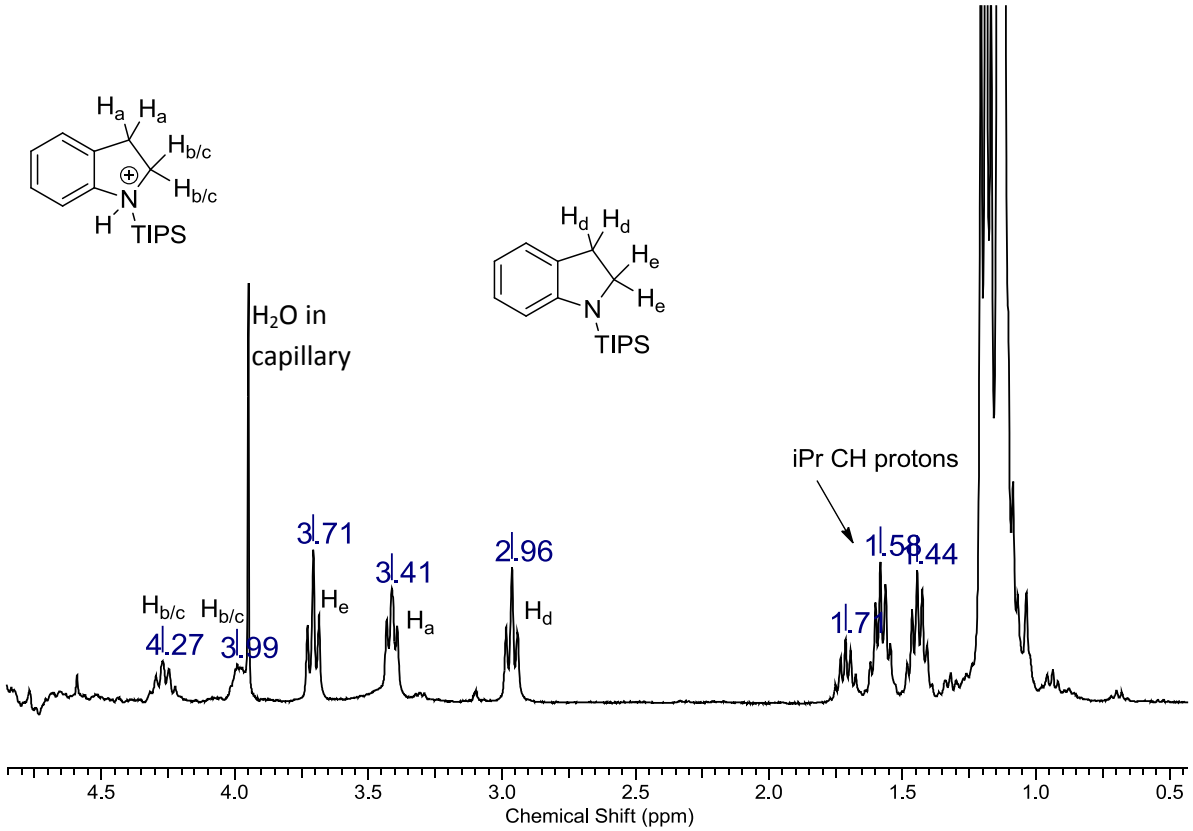


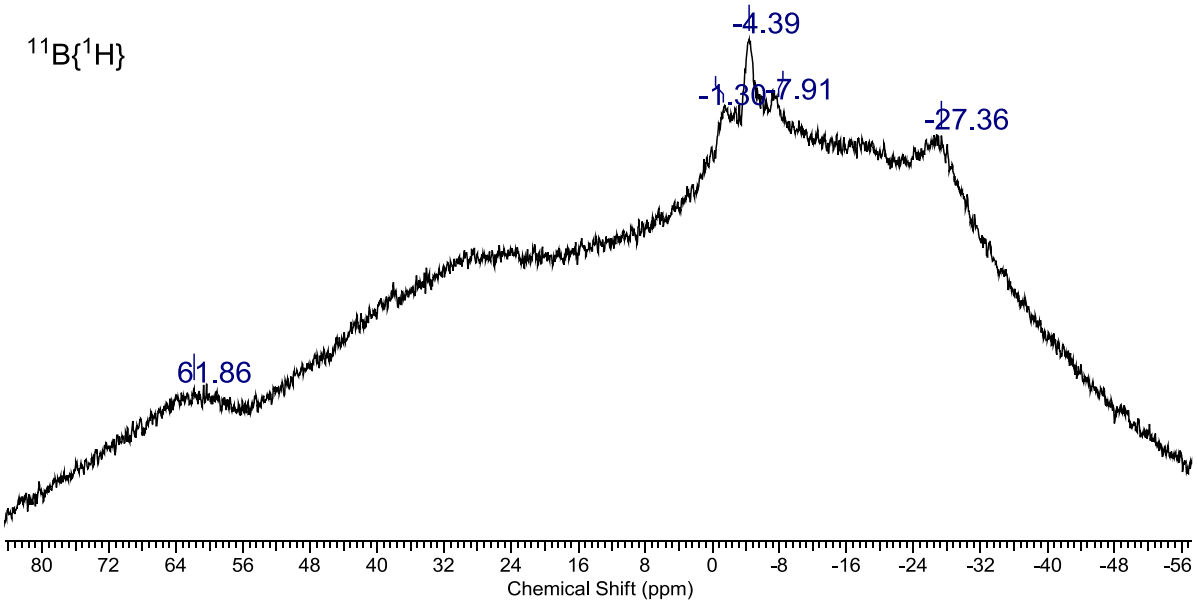
The ^{19}F NMR also shows an unknown, minor C_6F_5- containing product, presumed to arise from borane degradation caused by carbocations / Brønsted acids generated during retro Friedel Crafts reactivity.

N-TIPS-indole reduction with BCF/Cl_2-py.

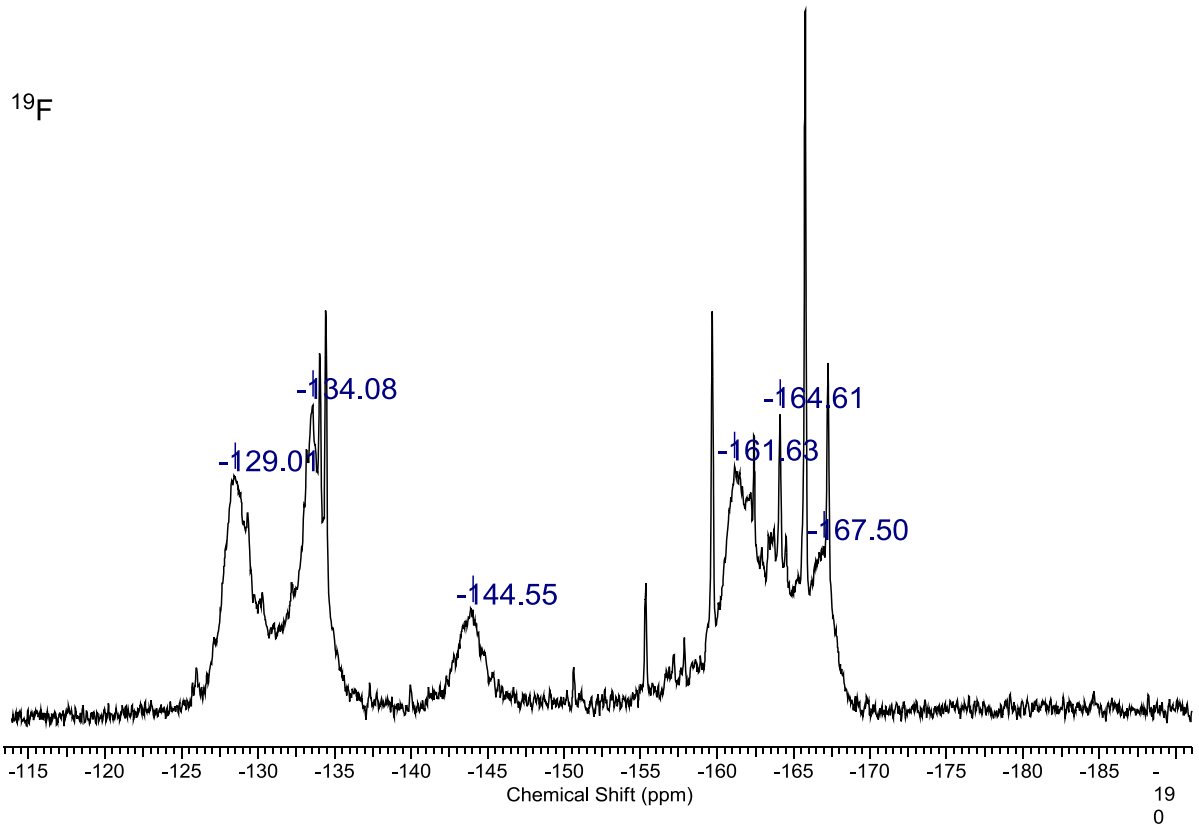
2,6-dichloropyridine (19 mg, 0.12 mmol), N-TIPS-indole (34 mg, 0.12 mmol) and $B(C_6F_5)_3$ (64 mg, 0.12 mmol) were combined in a J. Young's NMR tube fitted with a d_6-DMSO capillary and dissolved in DCM (1 cm^3). The vessel was freeze-pump-thaw degassed and placed under H_2 (4 atm). After inverting for 16 hours, reduction was found to have proceeded to 80 % completion (calculated by conversion of starting material i.e. 20 % residual N-TIPS indole). The reduction peaks are assigned to an approximately equal production of N-TIPS-indoline and protonated N-TIPS indoline.

^1H

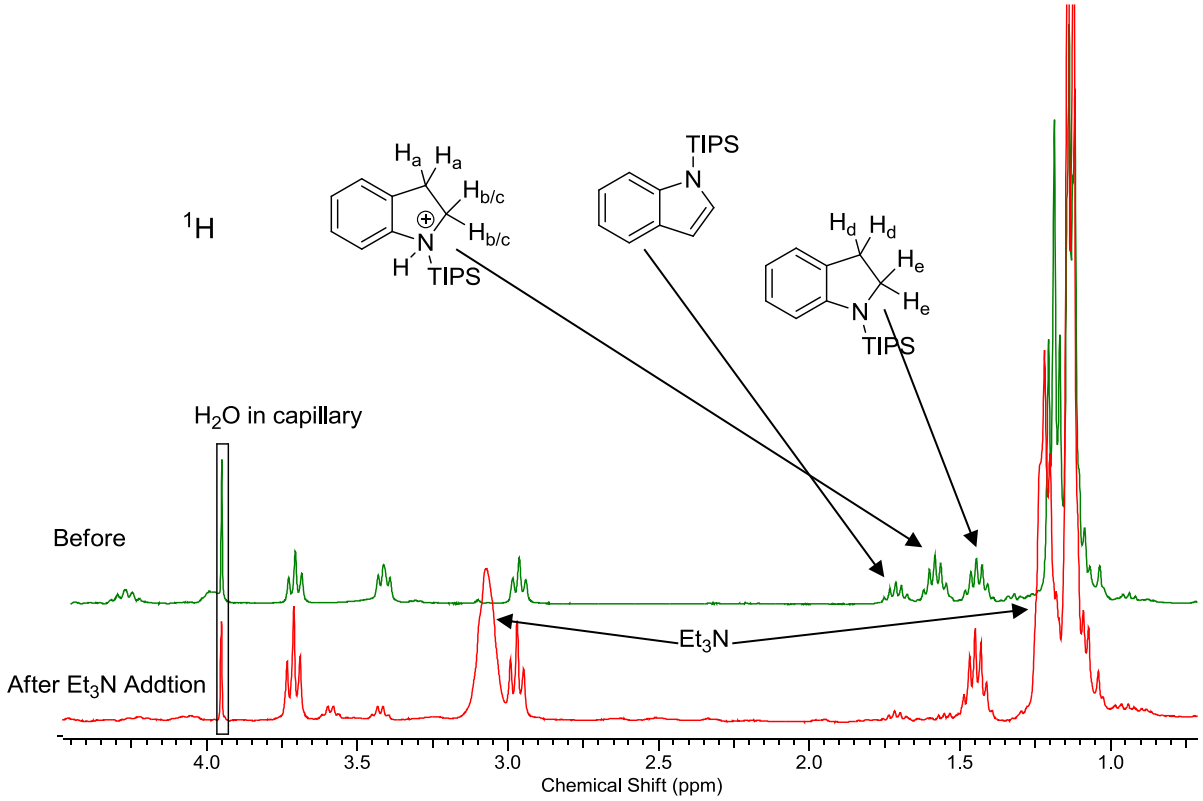




The ^{11}B NMR shows the growth of new, sharp peaks at δ -1.30, -4.39, -7.91 and a broad peak at approximately -27 ppm which increases in intensity upon broadband ^{1}H decoupling. The ^{19}F NMR shows the peaks for $B(C_6F_5)_3$ to be considerably broadened and up-field shifted, indicating the existence of a dynamic system. Additionally, there are broad peaks centred at d=-134, -162 and -168 which, coupled with the B-H fragment found by ^{11}B NMR, shows the formation of $[HB(C_6F_5)_3]^-$. This may be understood in terms of FLP chemistry, wherein the newly formed N-TIPS-indoline is a strong, hindered base and so may activate H_2 to form the ion pair of borohydride and protonated indoline.

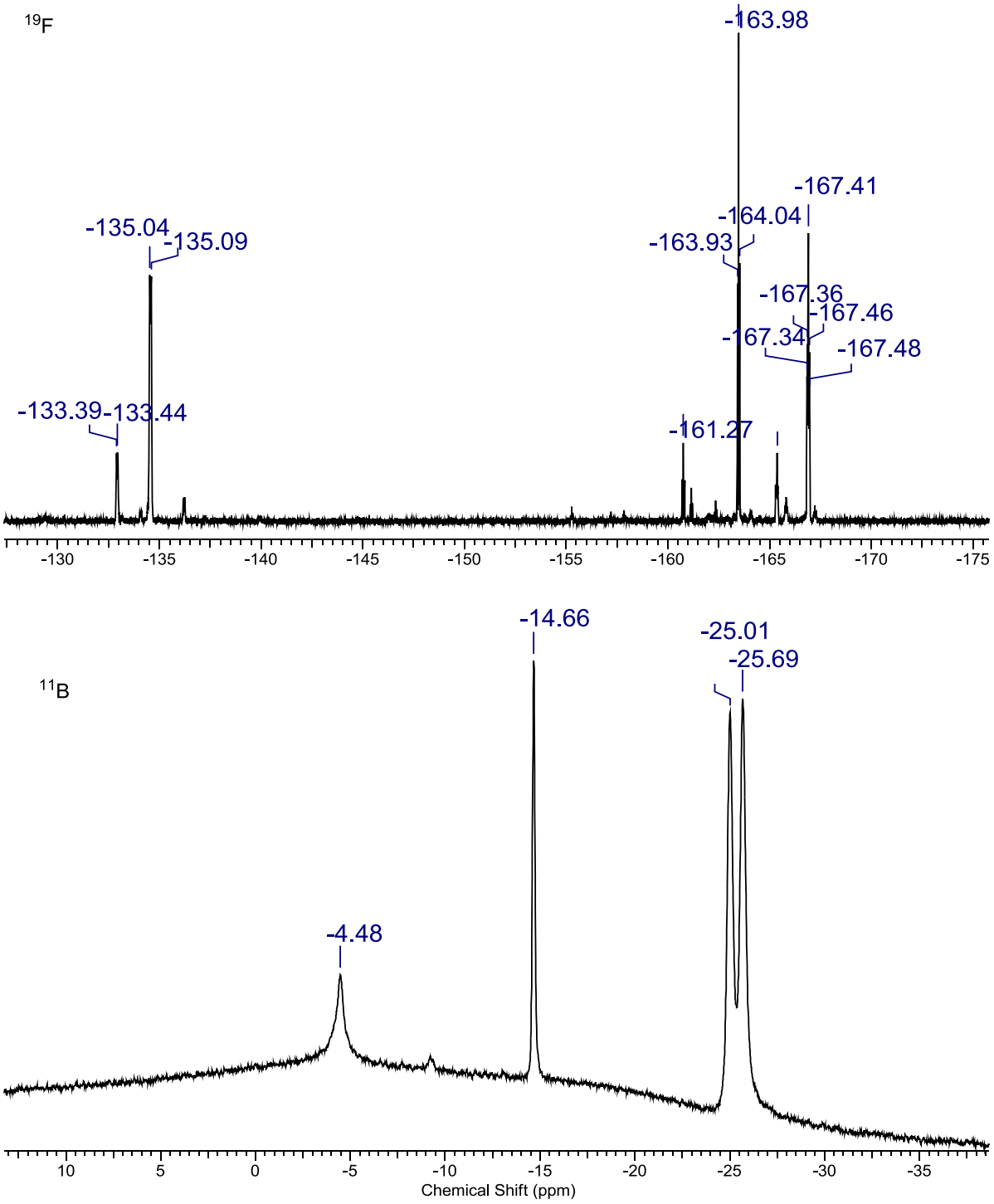


The vessel was recharged with H_2 and stirred for a further 48 hours after which time no further reduction was found to have occurred. To confirm the formation of protonated N-TIPS-indoline, Et_3N (17 μl, 0.12 mmol) was added. The ^1H NMR clearly shows the loss of intensity in the protonated-N-TIPS-indoline peaks and the gain in intensity of the N-TIPS Indoline resonances relative to those of residual N-TIPS-indole. The broadening in the Et_3N peaks arises from exchange processes.



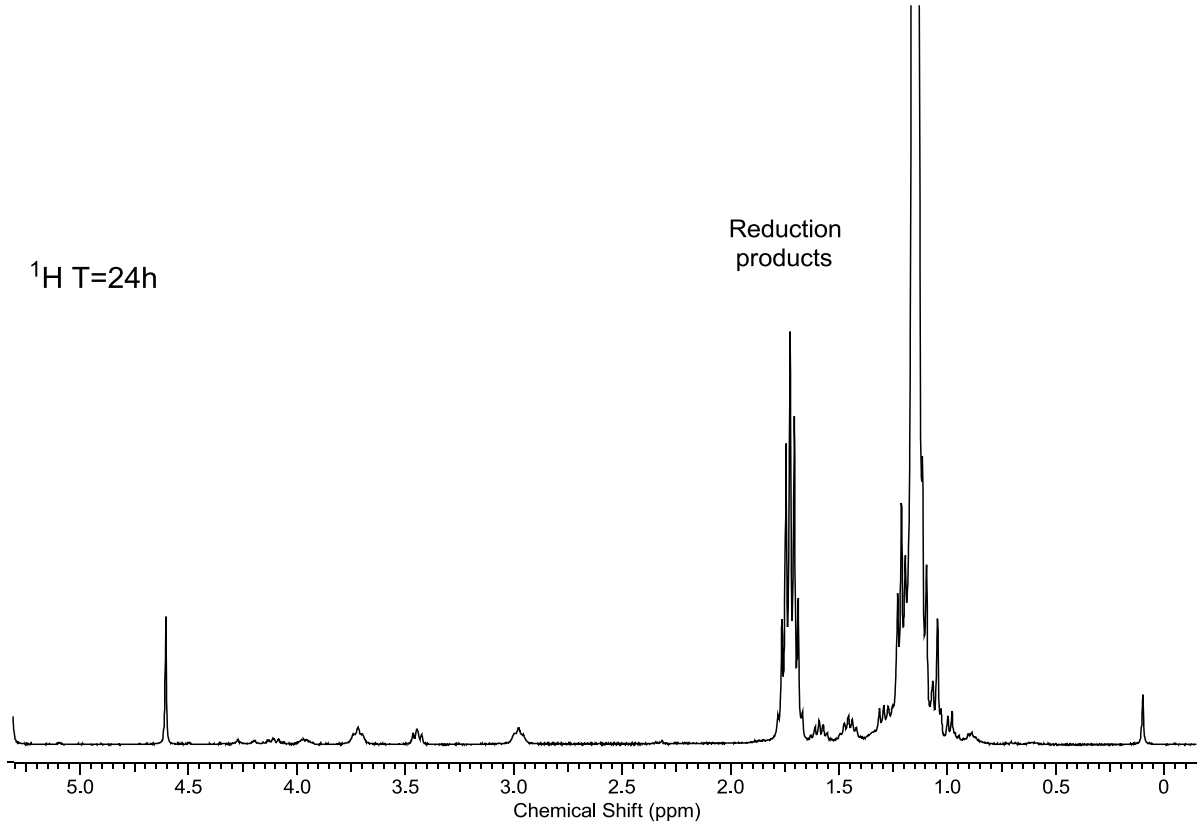
The ^{11}B NMR is dominated by a doublet at δ -25.35, consistent with the presence of $[HB(C_6F_5)_3]^-$, as are the major peaks (δ -135.0, -164.0, -167.5) in the ^{19}F NMR, with minor peaks corresponding to 4-coordinate borane species. This is consistent with the addition of a strong, coordinating base (a) [deprotonating N-TIPS-indolene-H] and (b) binding to remaining $B(C_6F_5)_3$, resulting in cessation of equilibrium and a stable ion pair of $[Et_3NH][HB(C_6F_5)_3]$. The absence of imine and enamine formation (as seen from the ^1H)

precludes the possibility that this may have formed from dehydrogenation of Et_3N.



N-TIPS-indole reduction with BCF without Cl_2-py.

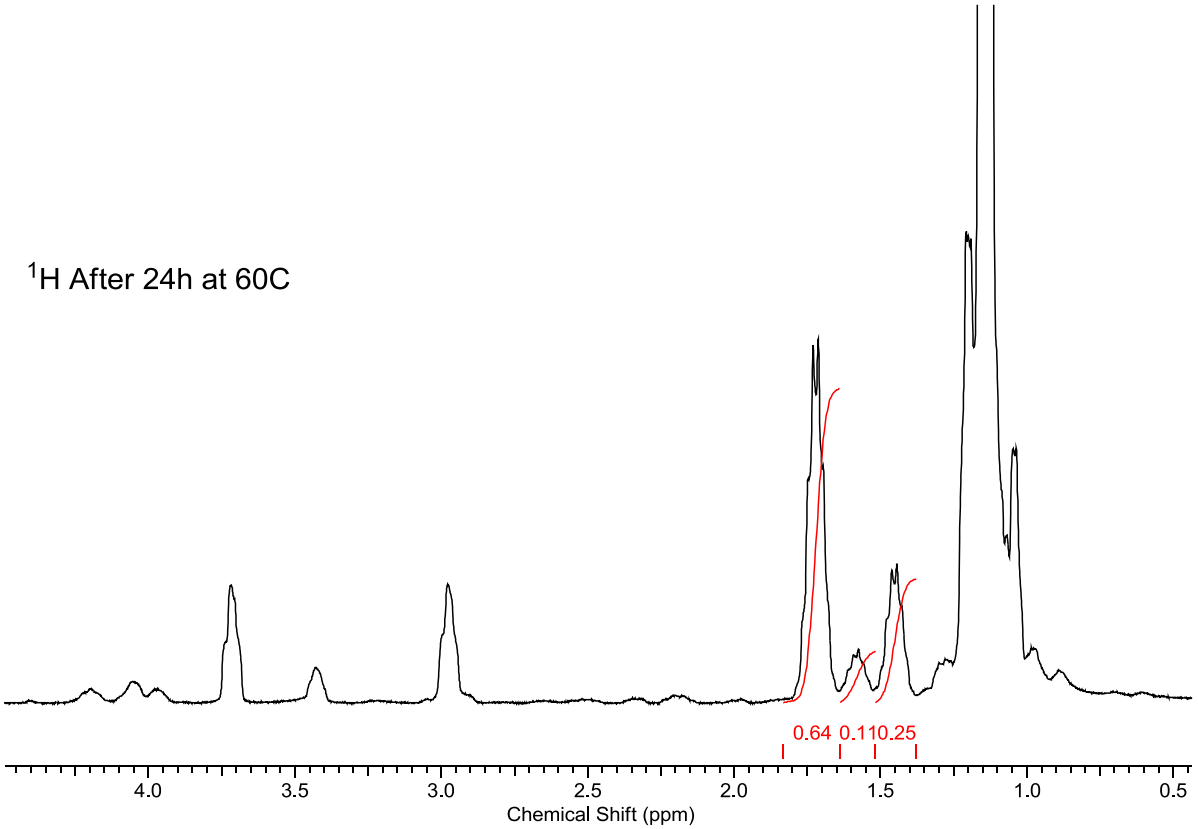
N-TIPS-indole (19 mg, 0.07 mmol) and $B(C_6F_5)_3$ (36 mg, 0.07 mmol) were combined in a J. Young's NMR tube and dissolved in d_2-DCM (0.8 cm^3). The vessel was freeze-pump-thaw degassed and charged with H_2 (4 atm), and then inverted for 24 hours. NMR spectroscopy showed that reduction had proceeded only by 16 %.



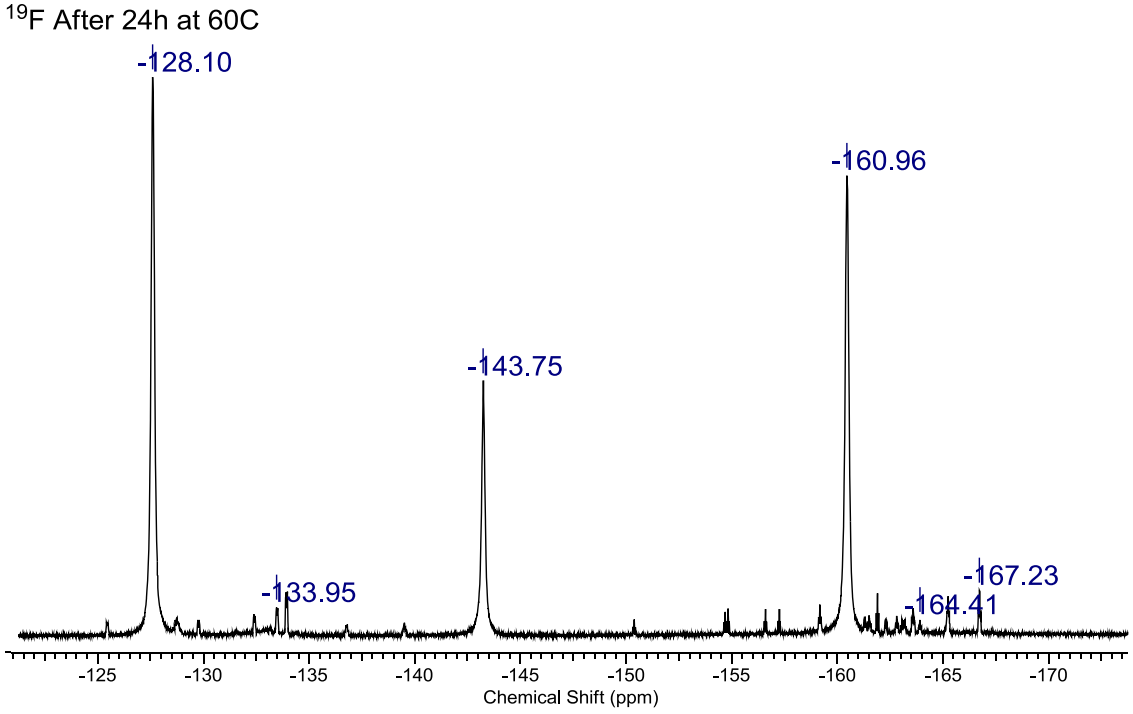
The reaction vessel was heated to 60 ^oC for 24 hours and the NMR spectra recorded. Reduction remained unfinished, with only ~35 % conversion of starting material.

Product ratios after 24h – 1 (Indoline-H) : 1.6 (Indoline) : 20.7 (TIPS-Indole)

Product ratios after 24h – 1 (Indoline-H) : 3.3 (Indoline) : 8.0 (TIPS-Indole)



The ^{19}F NMR spectrum shows that free borane with slightly broadened peaks remains the dominant fluorine containing species, with the line width suggesting that it exists in equilibrium with a small concentration of a Lewis base. Small quantities of $[HB(C_6F_5)_3]^-$ are also evident, further supporting the hypothesis of FLP-type H_2 sequestration.



Silylation Studies:
General Procedure A

An oven-dried J.Young's NMR tube or Schlenk containing a stirring bar was heated under reduced pressure and then charged under an argon atmosphere. To a solution of tris(pentafluorophenyl)borane (x mol %) in anhydrous CH_2Cl_2, the appropriate silane (y equiv) was added and stirred/agitated until homogenous. A respective arene (z equiv.) was added and finally a base (x equiv.) was added to the reaction mixture and stirred. In certain examples the reaction mixture was heated to 60 ^{o}C and the reaction was monitored by NMR spectroscopy. In the cases where reactions were carried out in a Schlenk flask aliquots of the reaction mixture were taken periodically to monitor the reaction's progress via NMR spectroscopy.

In examples that were monitored in J. Youngs NMR tubes the reactions were performed in protio solvent in the presence of a sealed capillary containing wet d_6-DMSO (hence impurities of residual protio DMSO and H_2O and generally observed)

Throughout the silylation does not proceed to completion with unreacted 2-MT (or other heteroarene) always observed.

The use of $(H_2O)B(C_6F_5)_3$ (a strong Brønsted acid) in place of $B(C_6F_5)_3$ resulted in no silylation indicating that Lewis acid activation of R_3Si-H via I is essential. This reaction was to confirm that the transfer of a proton from (H_2O)-$B(C_6F_5)_3$ to the heteroarene did not proceed more rapidly than the reaction of (H_2O)-$B(C_6F_5)_3$ with the silane. If it did it could lead to heteroarene reduction by a different mechanism, catalysed by a protic/Bronsted acid.

Silylation of 2-Me-thiophene, base free

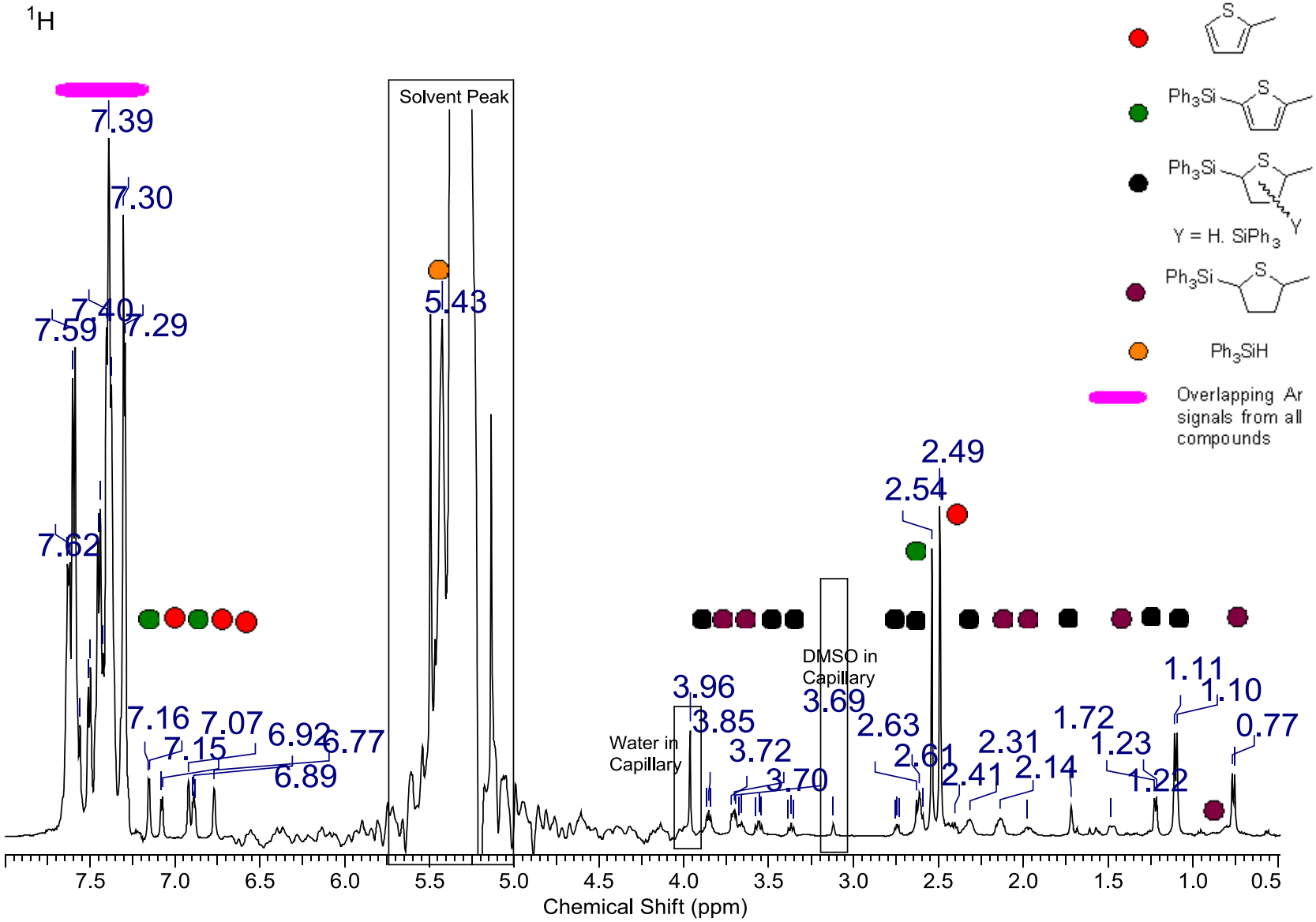
According to general procedure A, a solution of tris(pentafluorophenyl)borane (51 mg, 0.10 mmol) and triphenylsilane (26 mg, 0.10 mmol) in anhydrous CH_2Cl_2 (1 mL) was reacted with 2-methylthiophene (10 µL, 0.10 mmol) and left to stir for 24 h. This afforded a 34 % conversion, according to NMR spectroscopy, to sila-Friedel Crafts product, **2,** and a conversion of 31 %, combined yield of isomers, according to NMR spectroscopy, to hydrosilylation products, **3**.

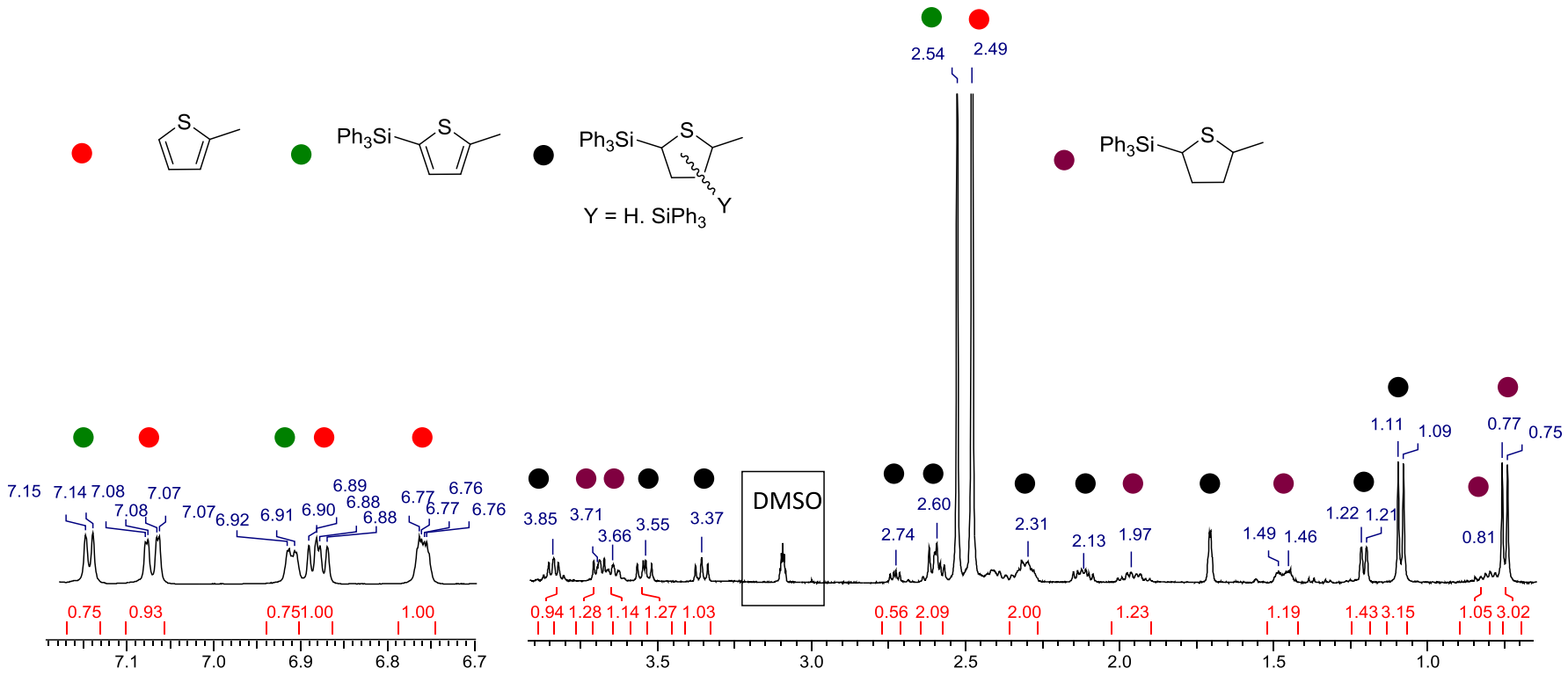
^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.63-7.29 (m, 15H), 7.15 (d, $^{3}J_{HH}$ = 3.3 Hz, 1H), 6.92 (d, $^{3}J_{HH}$ = 3.3 Hz, 1H), 2.54 (s, 3H).

^{29}Si{^{1}H} NMR (79 MHz, CD_2Cl_2, 298 K): δ -20.3 (s).

The next page shows a representative ^{1}H NMR spectrum after electrophilic silylation.

At no point are resonances for 2-Me-THT observed.





Expansion of the aromatic region (left) and the aliphatic region (right)

Silylation of 2-Me-thiophene with stoichiometric 2,6-dichlorpyridine / $B(C_6F_5)_3$

According to general procedure A, to a solution of tris(pentafluorophenyl)borane(51 mg, 0.10 mmol) and triphenylsilane (26 mg, 0.10 mmol) in anhydrous CH_2Cl_2 (1 mL) was added 2-methylthiophene (10 µL, 0.10 mmol) and 2,6- dichloropyridine (15 mg, 0.10 mmol) and the reaction was stirred for 24 hours with periodic monitoring by NMR spectroscopy. This afforded a 52 % conversion to sila-Friedel Crafts product, according to NMR spectroscopy, and a conversion of 22 % to 2-Me-5-(Ph_3Si)-tetrahydrothiophene, **3**, and 9 % to 2-Me-tetrahydrothiophene, 2-MT-THT, according to NMR spectroscopy.

Compound 2-Me-5-(Ph_3Si)-thiophene, 2

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): 7.15 (d, $^3J_{HH}$ = 3.3 Hz, 1H), 6.92 (d, $^3J_{HH}$ = 3.3 Hz, 1H), 2.54 (s, 3H).

^{29}Si{^{1}H} NMR (79 MHz, CD_2Cl_2, 298 K): δ -20.3 (s).

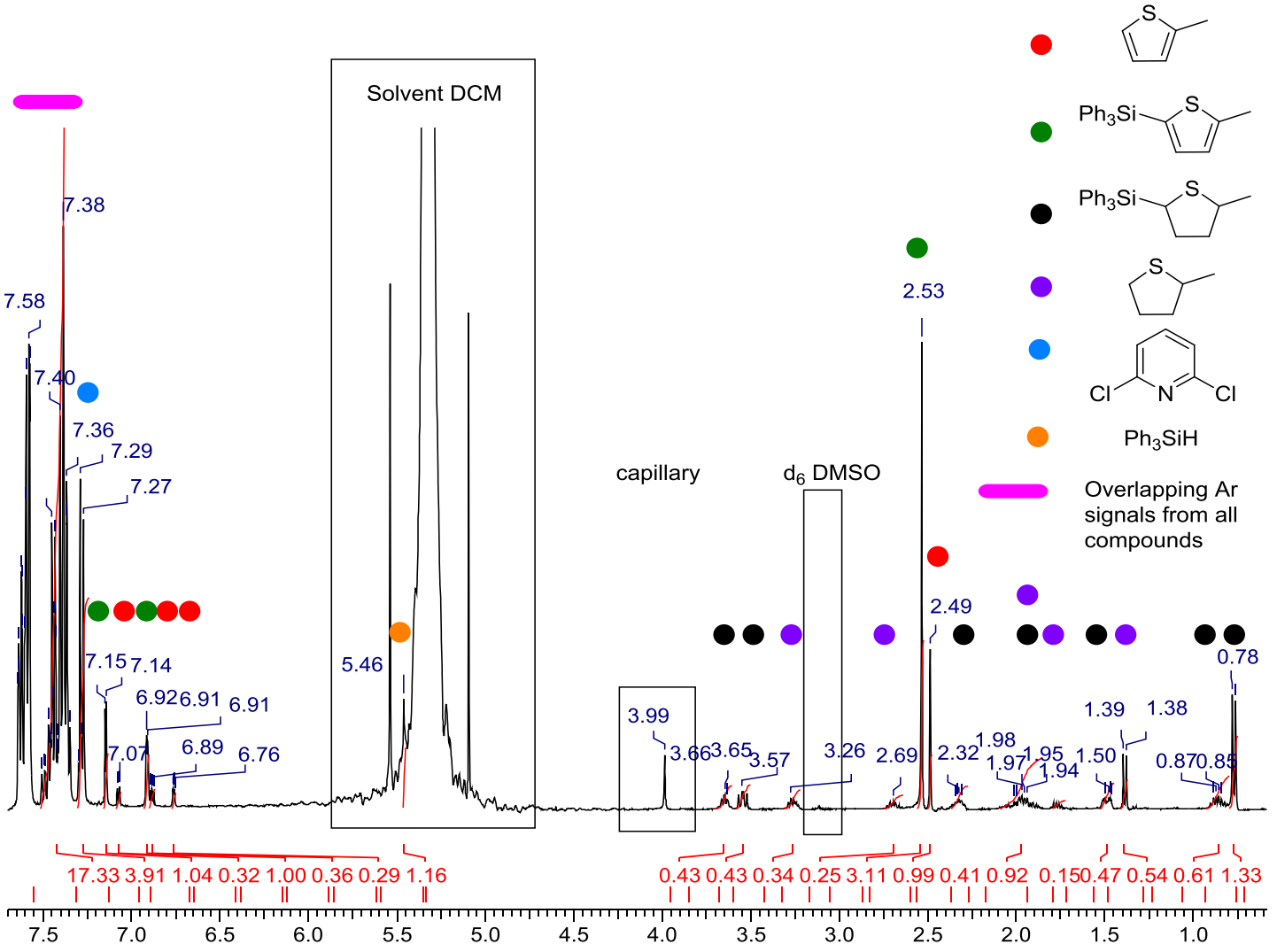
Compound 2-Me-5-(Ph_3Si)-tetrahydrothiophene, 3

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K):, 3.68.3.61 (m, 1H), 3.55 (dd, $^3J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 7.6 Hz), 2.37-2.29 (m, 1H), 2.09-1.86 (m, 1H), 1.51-1.46 (m, 1H), 0.90-0.84 (m, 1H) 0.77 (d, $^3J_{HH}$ = 7.1 Hz, 1H)

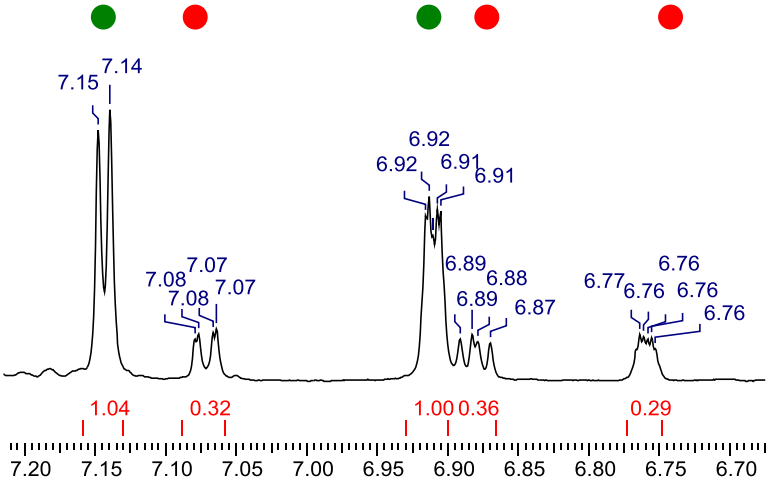
^{29}Si{^{1}H} NMR (79 MHz, CD_2Cl_2, 298 K): -13.6 (s)

The ^{1}H NMR resonances for the Ph_3Si moiety are overlapped for 2 and 3 thus are not reported above.

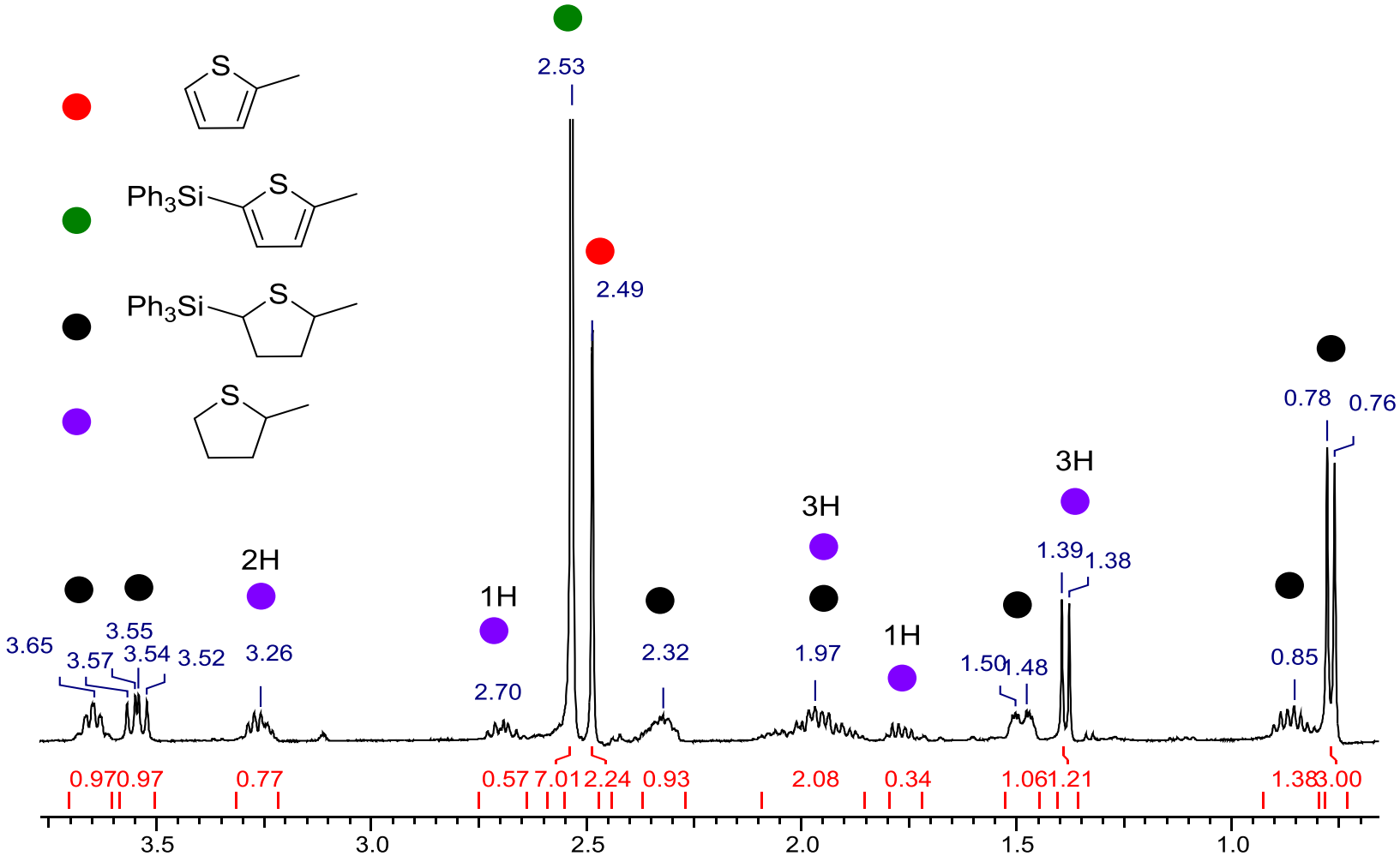
The next page shows a representative ^{1}H NMR spectrum for the reaction mixture



^{1}H NMR spectrum of reaction mixture after 24 h (Resonance at 3.99 = H_2O in capillary)



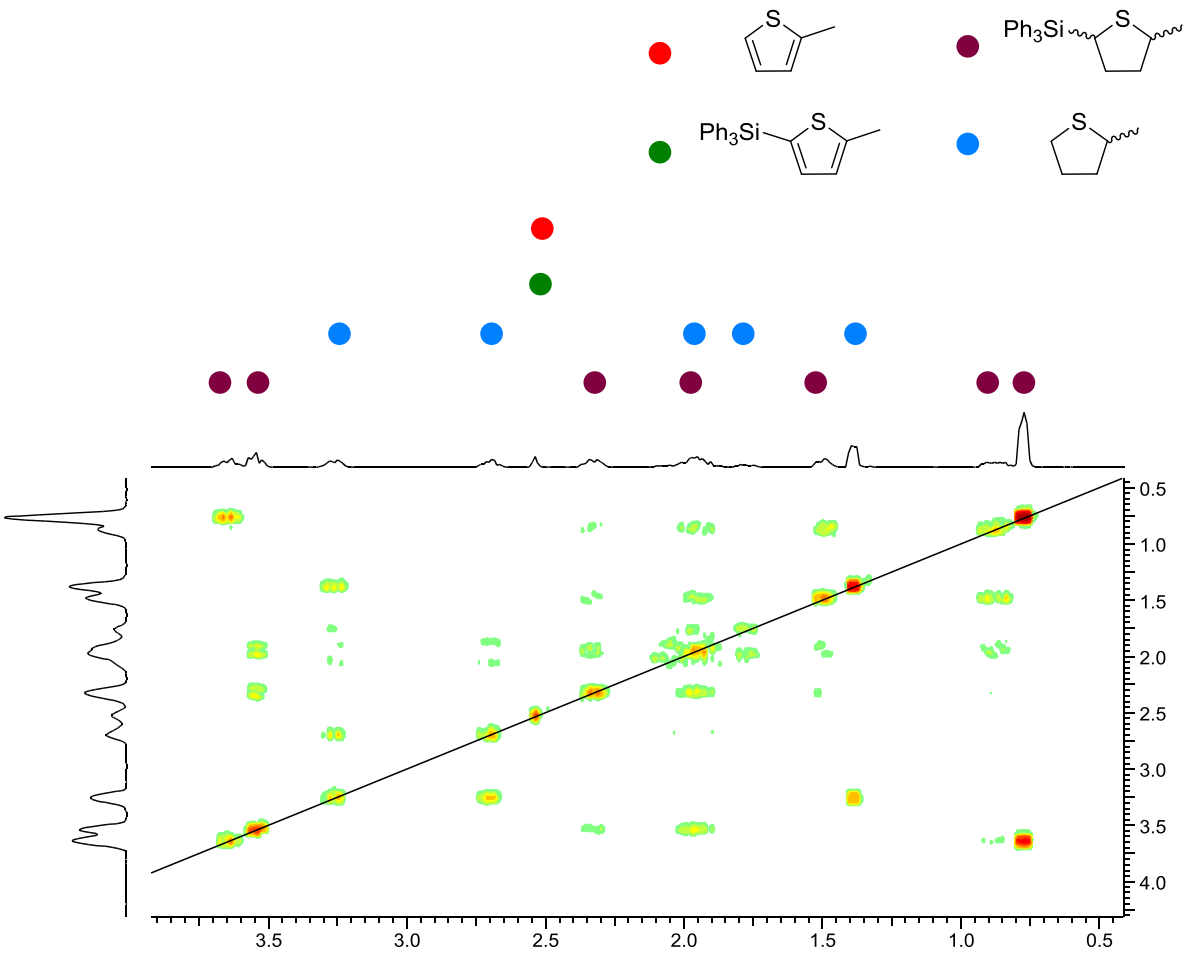
An expansion of the aromatic region.



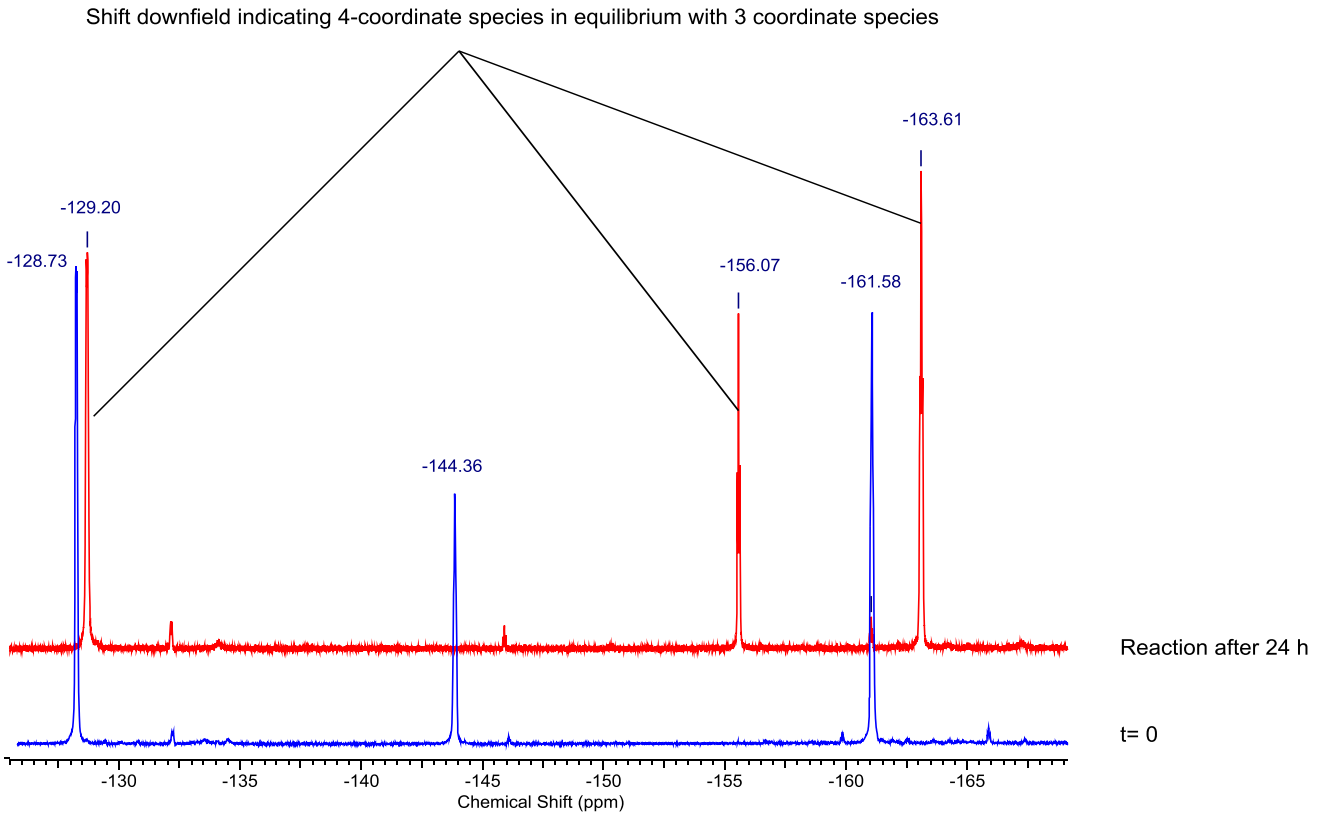
^{1}H NMR spectrum of reaction mixture after 24 h highlighting formation of, **2**, and complex nature of aliphatic region.

No resonances corresponding to double hydrosilylation are observed. The assignment as mono-hydrosilylated / mono hydrogenated product is based on relative integrals and subsequent GC-MS.

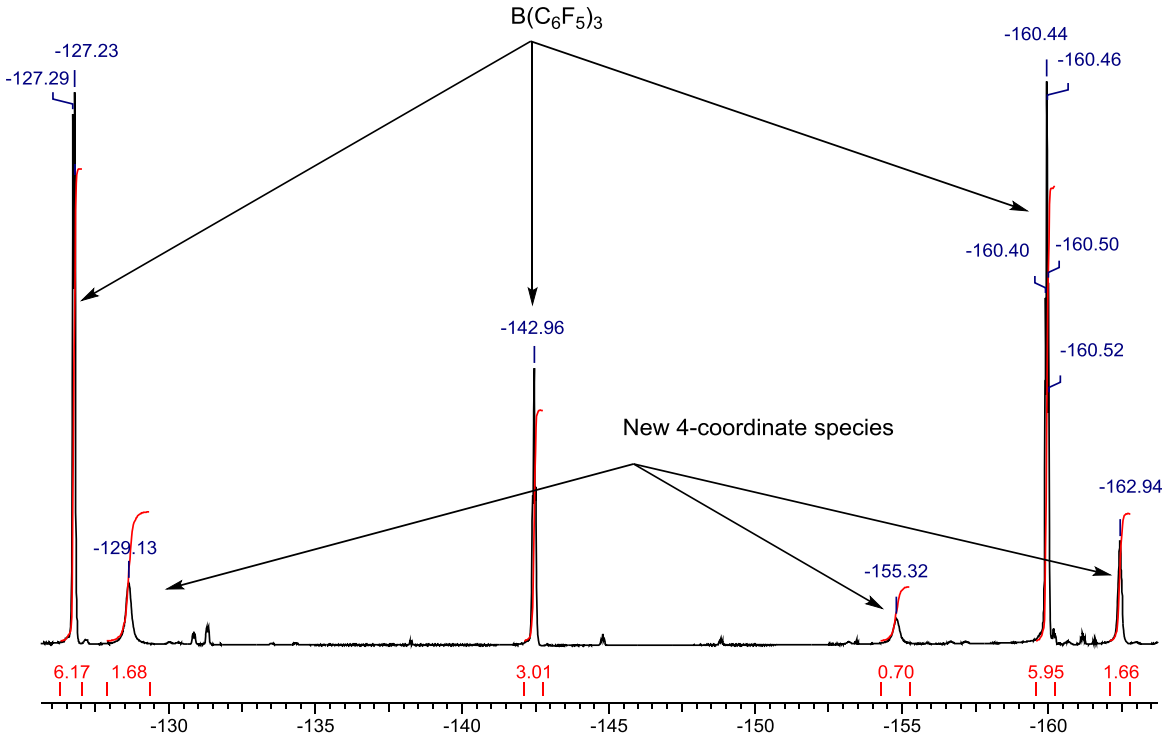
COSY NMR spectrum of aliphatic region after 24 h.



It was observed via ^{11}B and ^{19}F NMR spectroscopy that a 4 coordinate boron species was being formed during electrophilic silylation / hydrogenation.



A ^{19}F NMR spectrum of the reaction after 24 h was recorded at – 80 ^{o}C and compared to a spectrum of equimolar tetrahydrothiophene and $B(C_6F_5)_3$ at – 80 ^{o}C.



Above $^{19}F\{^{1}H\}$ NMR spectrum at -80C after 24h catalytic silylation.

The new compound is closely comparable to (THT)-$B(C_6F_5)_3$ at this temperature (see below), thus is assigned as 2-Me-THT coordinated to $B(C_6F_5)_3$.

Compound Tetrahydrothiophene- $B(C_6F_5)_3$

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): 2.81 (br, 4H), 1.93 (br, 4H)

^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): -2.9 (br)

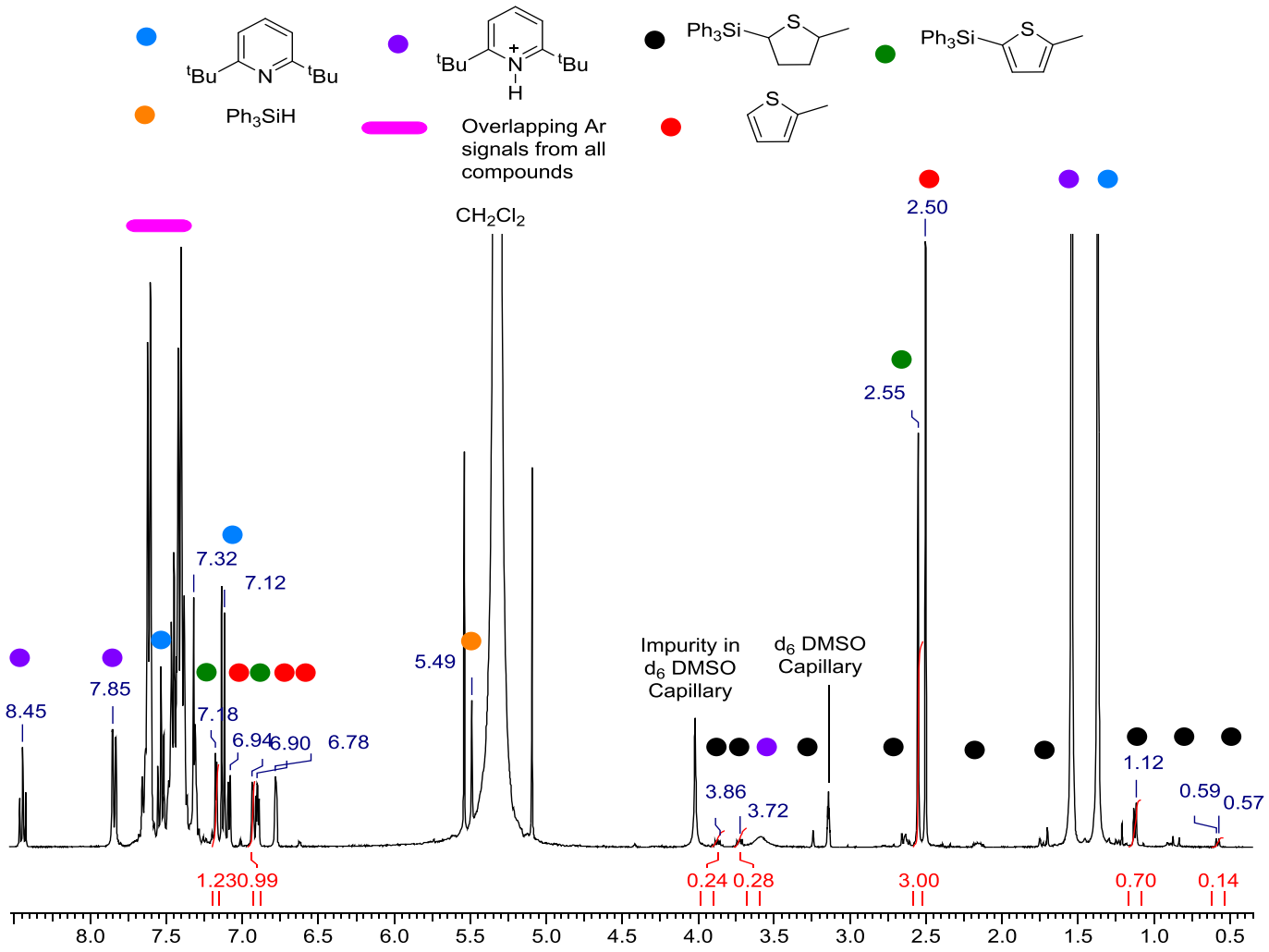
^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): 130.7 (br), -156.6 (br), -164.7 (br)

^{11}B NMR (128 MHz, CD_2Cl_2, 193 K): -3.4 (br)

$^{19}F\{^{1}H\}$ NMR (377 MHz, CD_2Cl_2, 193 K): -129.5 (br, 6F), -155.1 (br, 6F), -162.9 (br, 6F)

Silylation of 2-Me-thiophene with 2,6-tert-butylpyridine as base

According to general procedure A, to solution of tris(pentafluorophenyl)borane(51 mg, 0.1 mmol) and triphenylsilane (26 mg, 0.10 mmol) in anhydrous CH_2Cl_2 (1 mL) was added 2-methylthiophene (10 µL, 0.10 mmol) and 2,6,-ditertbutylpyridine (19 mg, 0.10 mmol) were left to stir for 72 hours. The reaction was periodically monitored by NMR spectroscopy. This afforded a 39 % conversion to sila-Friedel Crafts product, according to NMR spectroscopy and a conversion of 10 %, % combined yield of reduction products, according to NMR spectroscopy.

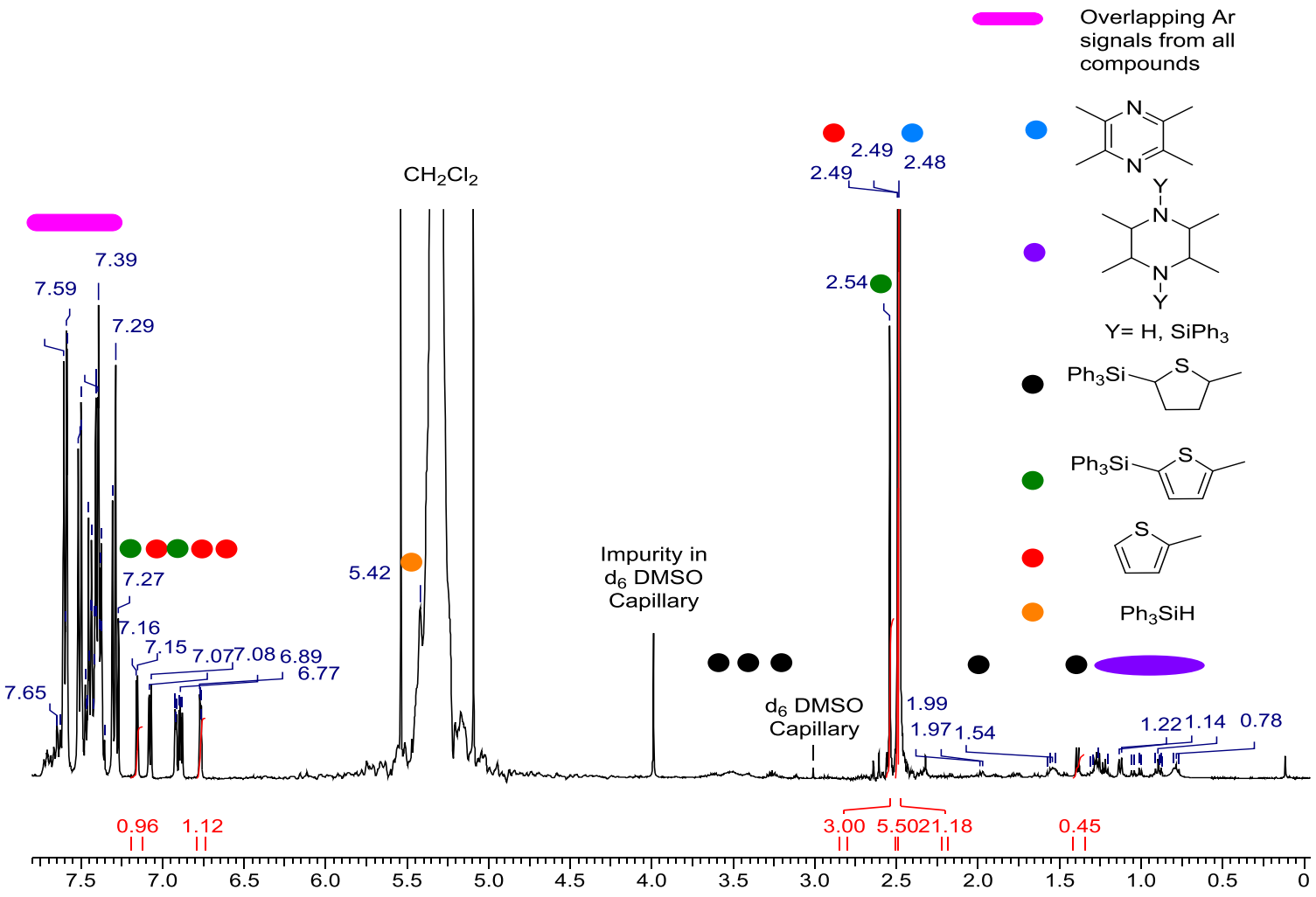


^{1}H NMR spectrum of reaction mixture after 24 h. (Impurity at 3.99 in capillary is H_2O)

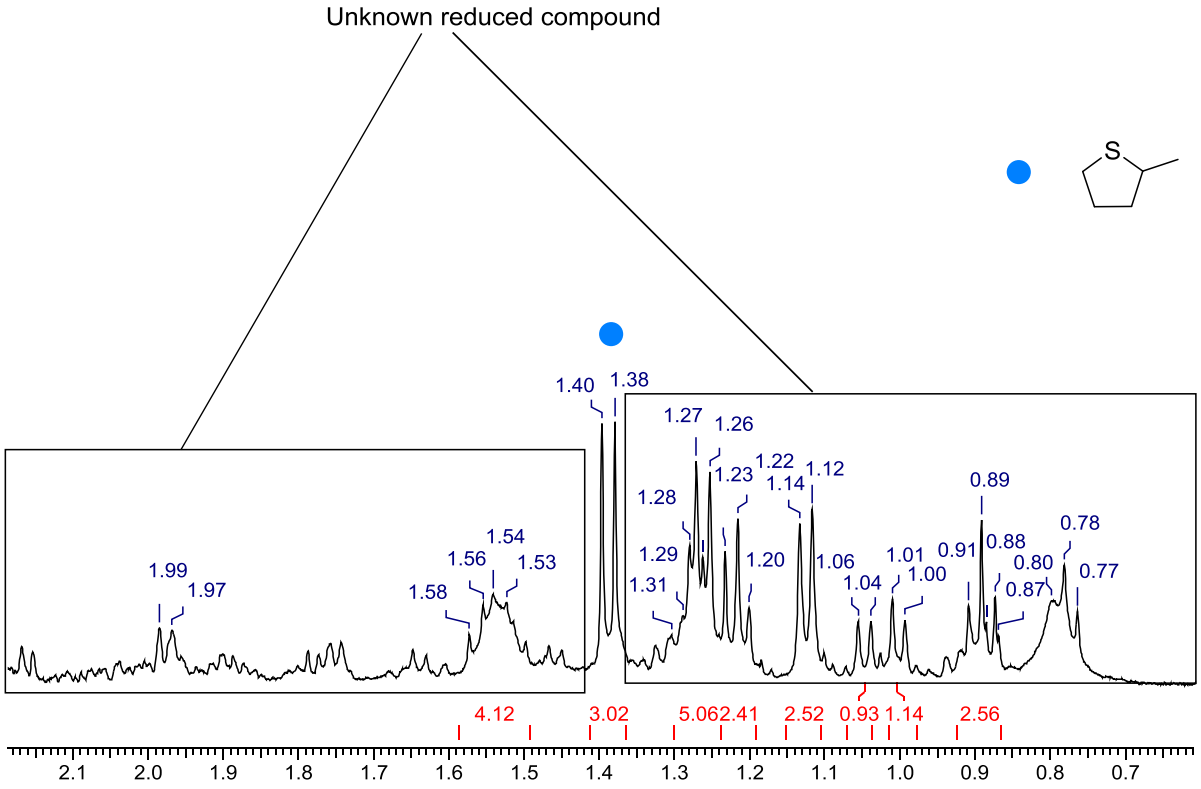
Silylation of 2-Me-thiophene with 2, 3, 5, 6-tetramethylpyrazine as base

Tetramethylpyrazine is a less nucleophilic analogue of 2,6-lutidine, however this produced a significantly more complex aliphatic region attributable to pyrazine hydrogenation (or hydrosilylation) as observed with tetramethylpyrazine / $B(C_6F_5)_3$ under H_2.[21] Therefore it was not pursued as a base to catalyse silylation.

According to general procedure A, to solution of tris(pentafluorophenyl)borane(51 mg, 0.10 mmol) and triphenylsilane (26 mg, 0.10 mmol) in anhydrous CH_2Cl_2 (1 mL) was added 2-methylthiophene (10 μL, 0.10 mmol) and 2,3,5,6-tetramethylpyrazine (13.6 mg, 0.10 mmol) were left to stir for 72 hours. The reaction was periodically monitored by NMR spectroscopy.



^{1}H NMR spectrum of reaction mixture after 24 h (impurity at 3.99 in capillary is H_2O)

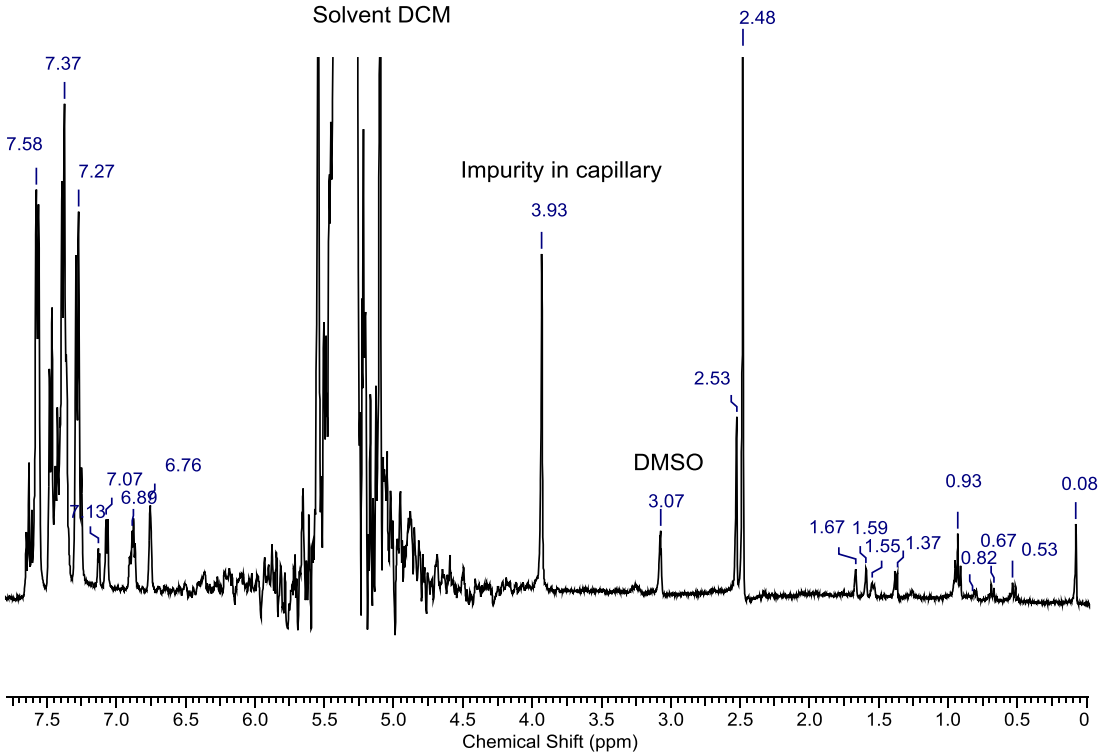


^{1}H NMR spectrum of reaction mixture after 24 h highlighting formation of, **2**, and complex nature of aliphatic region.

The unknown product(s) are tentatively attributed to pyrazine hydrogenation / hydrosilylation as previously observed. [ii]

Silylation of 2-Me-thiophene sealed under vacuum

According to general procedure A, to a solution of tris(pentafluorophenyl)borane (51 mg, 0.10 mmol) and triphenylsilane (26 mg, 0.10 mmol) in anhydrous CH_2Cl_2 (1 mL) was added 2-methylthiophene (10 µL, 0.10 mmol) and 2,6,-dichloropyridine (15 mg, 0.10 mmol). The reaction mixture was then freeze pumped thawed for three cycles. The ampoule was sealed and the reaction mixture was left to stir for 24 hours. The reaction was periodically monitored by NMR spectroscopy. This afforded a 33 % conversion to sila-Friedel Crafts product, according to NMR spectroscopy. Reductions products in the aliphatic region were also observed although the complexity was greatly reduced. The reduction of 2-methylthiophene to 2-methyl-tetrahydrothiophene was not observed.



(impurity in capillary is H2O in DMSO)

Variation in Silane

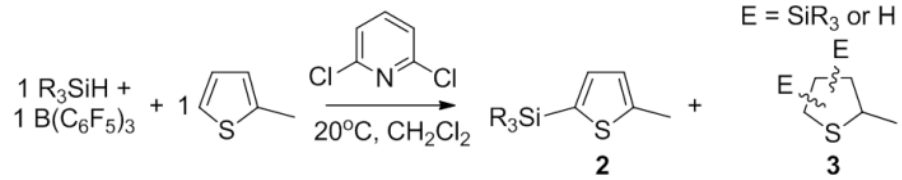


Table: Stoichiometric silylation of 2-MT with various silanes.

Entry	R_3SiH	Time (h)	2 (%)[a,b]	3 (%)[a,b]
1	Ph_3SiH	24	51	33
2	Ph_2MeSiH	72	19	26
3	$PhMe_2SiH$	72	9	31
4[d]	Et_3SiH	4	18	20

[a] = yields based on conversion of 2-MT. [b] = yields by ^{1}H NMR spectroscopy.

Whilst multiple attempts to observe all products from Ph_3SiH silylation of 2-MT by GC-MS and MS were unsuccessful due to the high M_w of silylated products the analogous reactions using other lighter silanes allowed unambiguous identification of all products by GC-MS which were in complete support of the conclusions made by NMR spectroscopy.

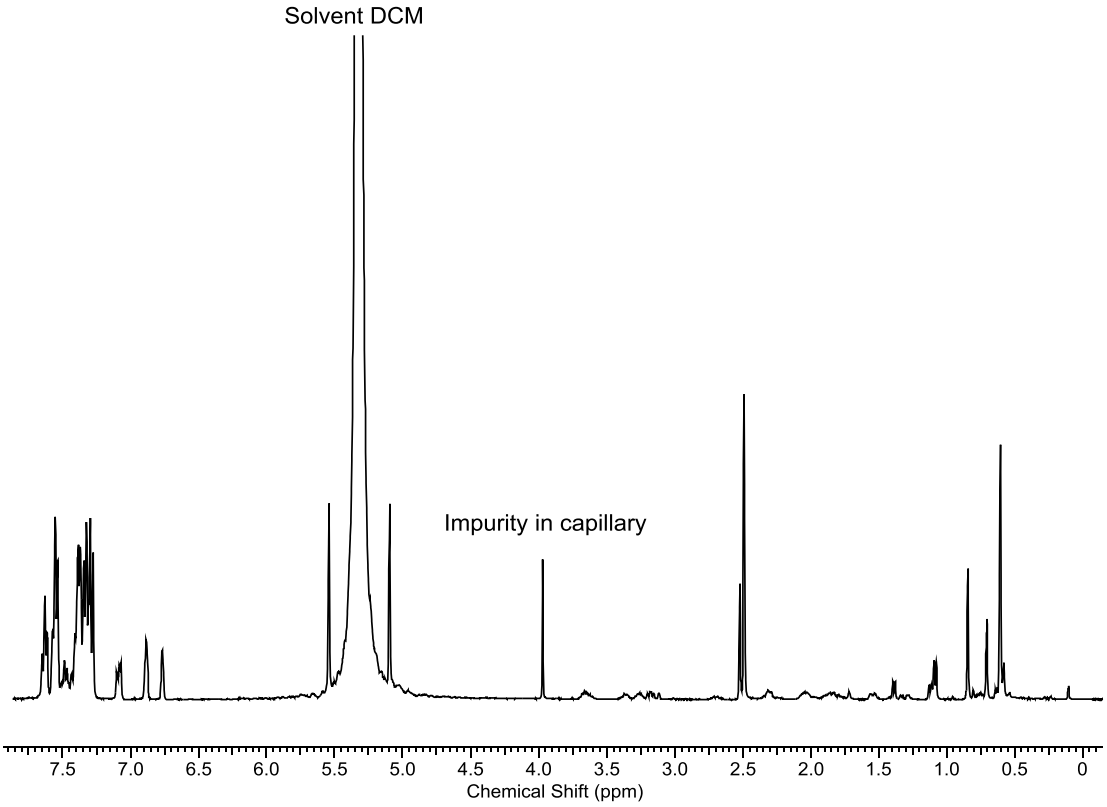
For example GC-MS traces from silylation with Et_3SiH / BCF / Cl_2-py are provided later in the SI.

Silylation of 2-MT with Ph_2MeSiH

According to general procedure A, a solution of tris(pentafluorophenyl)borane (51 mg, 0.10 mmol) and diphenylmethylsilane (19.8 µL, 0.10 mmol) in anhydrous CH_2Cl_2 (1 mL) was reacted with 2-methylthiophene (10 µL, 0.10 mmol) and 2,6- dichloropyridine (15 mg, 0.10 mmol) left to stir for 24 hours. This afforded a 19 % conversion to sila-Friedel Crafts product, according to NMR spectroscopy and a conversion of 26 % combined yield of reduction products, according to NMR spectroscopy.

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.57-7.27 (m, 10H), 7.10 (d, $^{3}J_{HH}$ = 3.3 Hz, 1H), 6.92 (m, 1H), 2.52 (s, 3H) 0.84 (s,3H).

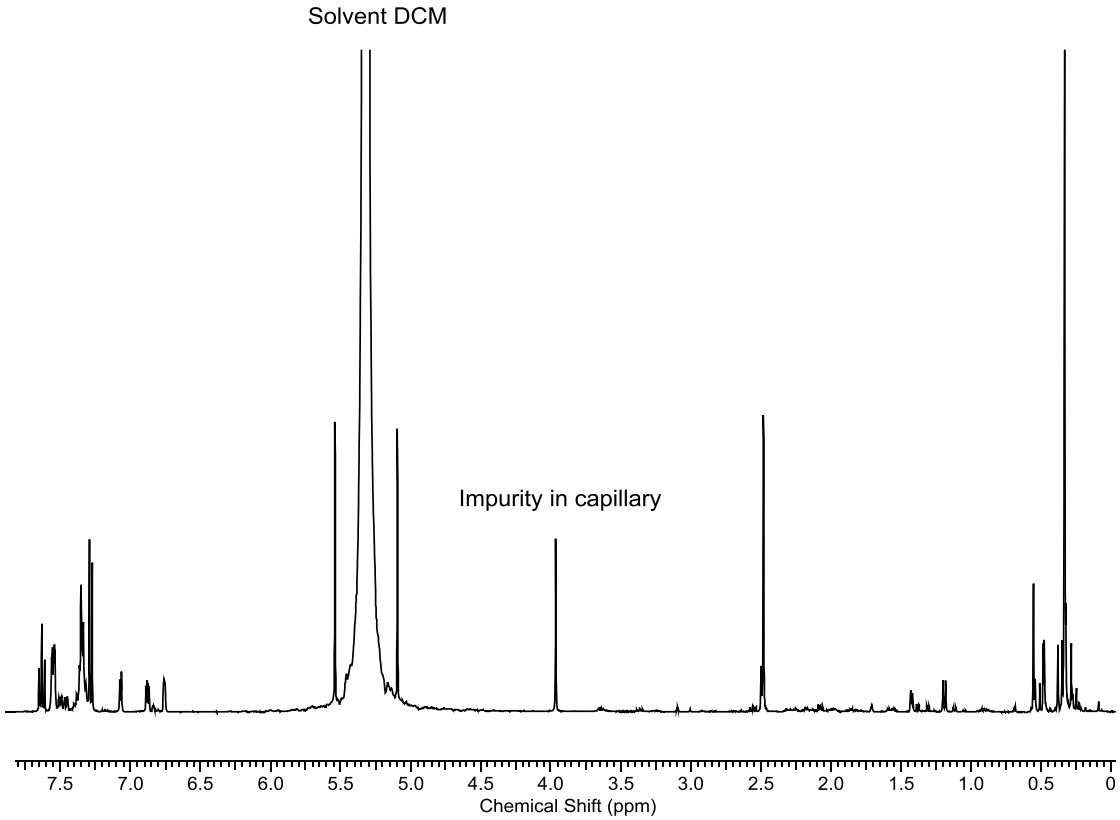
^{29}Si{^{1}H} NMR (79 MHz, CD_2Cl_2, 298 K): δ -16.3 (s).



Silylation of 2-MT with $PhMe_2SiH$

According to general procedure A, a solution of tris(pentafluorophenyl)borane (51 mg, 0.10 mmol) and phenyldimethylsilane (13.6 µL, 0.10 mmol) in anhydrous CH_2Cl_2 (1 mL) was reacted with 2-methylthiophene (10 µL, 0.10 mmol) and 2,6- dichloropyridine (15 mg, 0.10 mmol) left to stir for 24 hours. This afforded a 9 % conversion to sila-Friedel Crafts product, according to NMR spectroscopy and a conversion of 31 % combined yield of reduction products, according to NMR spectroscopy.

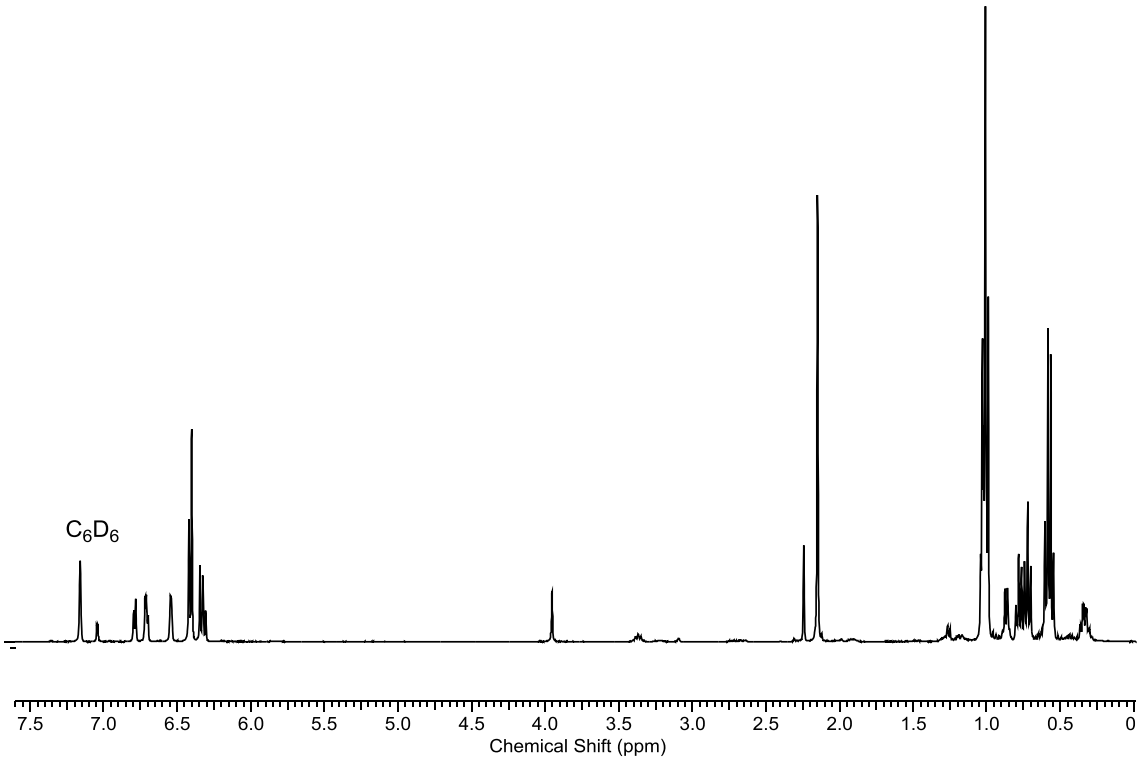
^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.56-7.34 (m, 10H), 7.10 (s, br , 1H), 6.84 (m, 1H), 2.50 (s, 3H) 0.55 (s, 6H).



Silylation of 2-MT with Et_3SiH

According to general procedure A, a solution of tris(pentafluorophenyl)borane (51 mg, 0.1 mmol) and triethylsilane (12 µL, 0.10 mmol) in anhydrous CH_2Cl_2 (1 mL) was reacted with 2-methylthiophene (10 µL, 0.10 mmol) and 2,6- dichloropyridine (15 mg, 0.10 mmol) left to stir for 4 hours. This afforded an 18 % conversion to sila-Friedel Crafts product, according to NMR spectroscopy and a conversion of 20 %, combined yield of reduction products, according to NMR spectroscopy.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 6.94 (d, $^3J_{HH}$ = 3.0 Hz, 1H), 6.60 (d, $^3J_{HH}$ = 3.5 Hz, 1H), 2.13 (s, 3H), 0.67 (q, $^3J_{HH}$ = 7.8 Hz, 6H) 0.61 (t, $^3J_{HH}$ = 7.8 Hz, 9H).



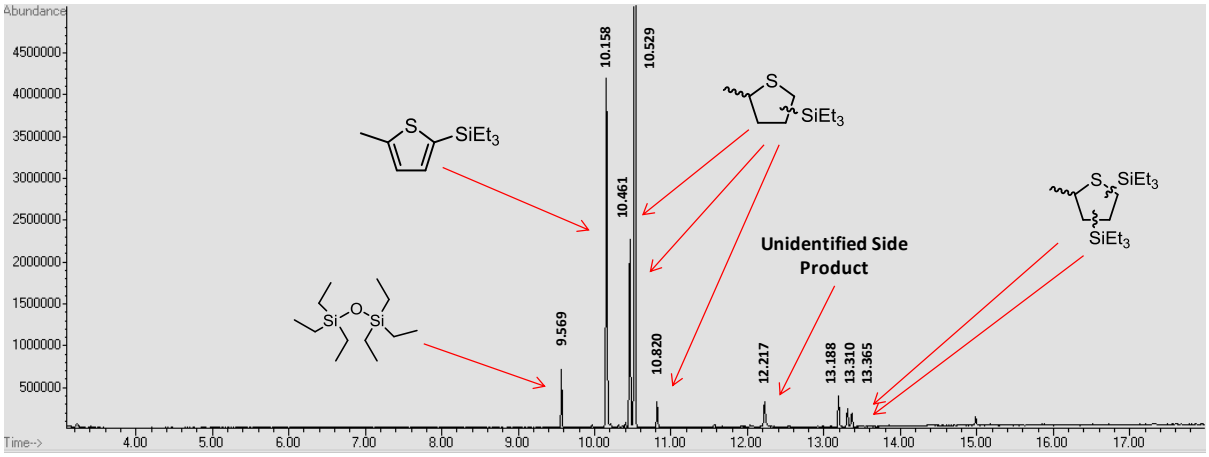
General Remarks for GCMS Analysis: GCMS analysis was performed on an Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD with triple axis detector. The column employed was an Agilent J&W HP-5ms ((5%-Phenyl)-methylpolysiloxane) of dimensions: length, 30 m; internal diameter, 0.250 mm; film, 0.25 µm.

GCMS Sample Preparation: Samples for GCMS analysis were taken directly from the reaction mixture, diluted with dichloromethane and eluted through a small plug of silica. The samples were put under vacuum to remove excess dichloromethane before dissolving in HPLC grade dichloromethane (1.5 mL, approx. concentration ~ 1mg/mL) prior to analysis. The absence of 2-Me-THT is due to its high volatility.

GCMS Program of Analysis: Initial temperature of 50 ºC, held for 3 minutes, ramp 25 ºC/minute next 300 ºC, held for 5 minutes (total run time, 18 minutes). The temperature of the injector and detector were maintained at 300 ºC.

Retention Times of Analytes: Hexamethyldisiloxane, 9.569 minutes; triethyl(5-methylthiophen-2-yl)silane, 10.158 minutes; triethyl(5-methyltetrahydrothiophen-2-yl)silane, 10.461 minutes; triethyl(5-methyltetrahydrothiophen-2-yl)silane, 10.529 minutes; triethyl(5-methyltetrahydrothiophen-2-yl)silane, 10.820 minutes; unidentified side product, 12.217 minutes; double hydrosilylation product, 13.310 minutes; double hydrosilylation product, 13.365 minutes.

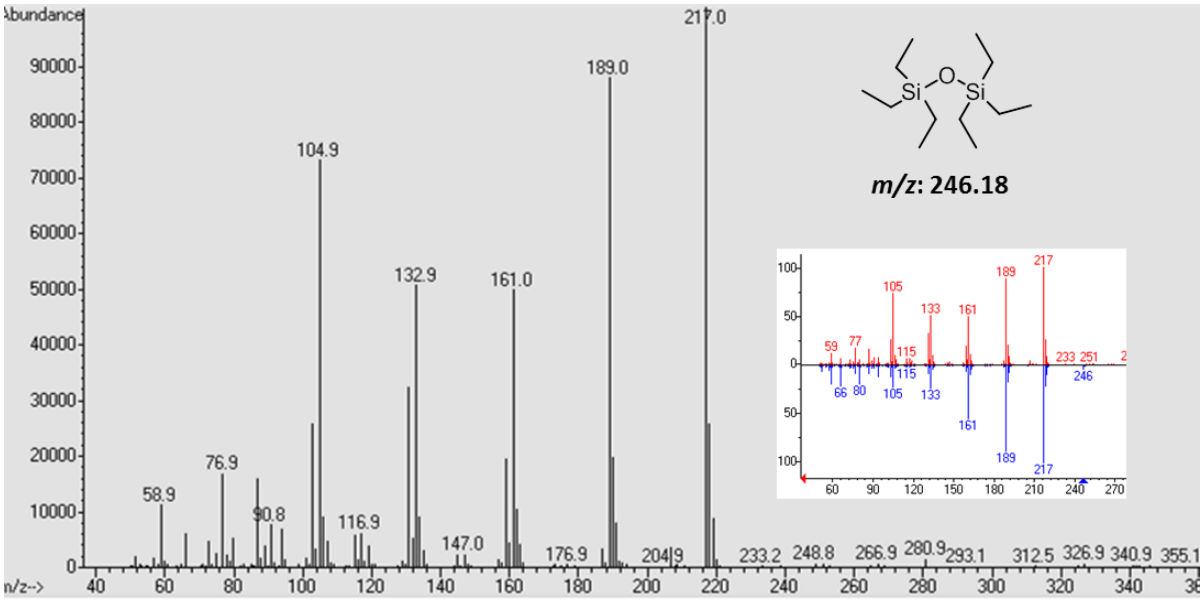
GCMS Trace:



Approximate Ratios of Hydrogenated Sila-Friedel Crafts Products Based upon Corrected Peak Areas (Assuming Response Factors are Similar Between Regioisomers): 19 : 78 : 3.

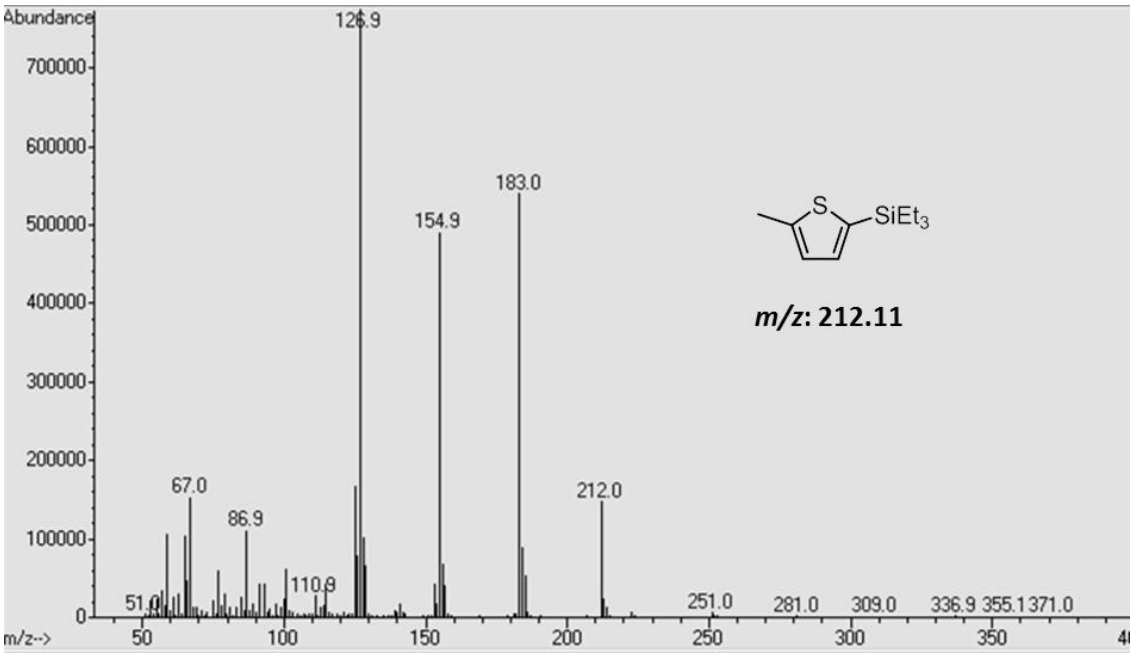
Mass Spectra of Analytes:

9.569 minutes - hexamethyldisiloxane:

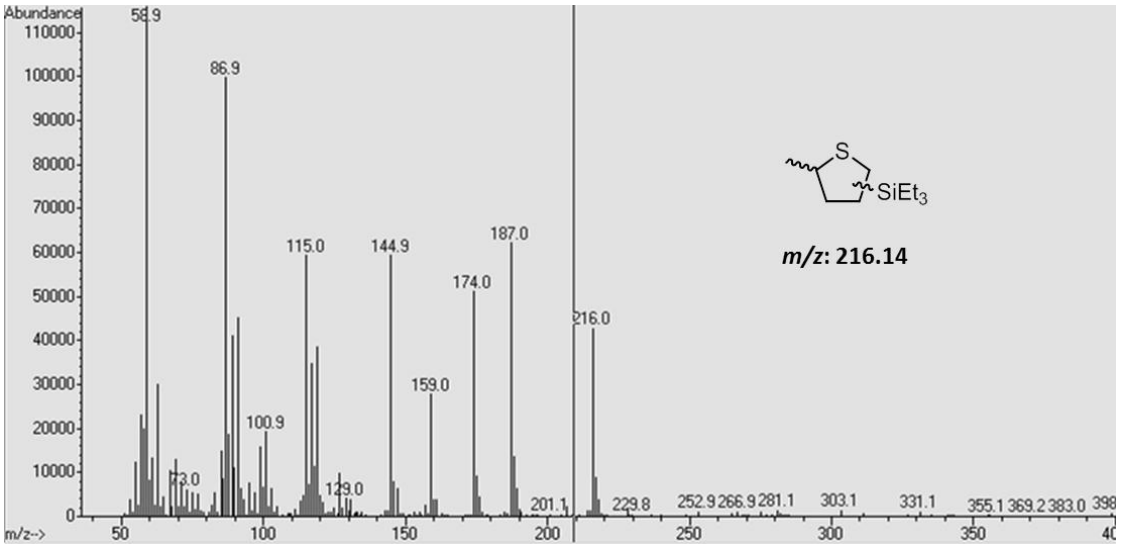


Head-to-tail comparison of measured (red) and library sample (blue) inset.

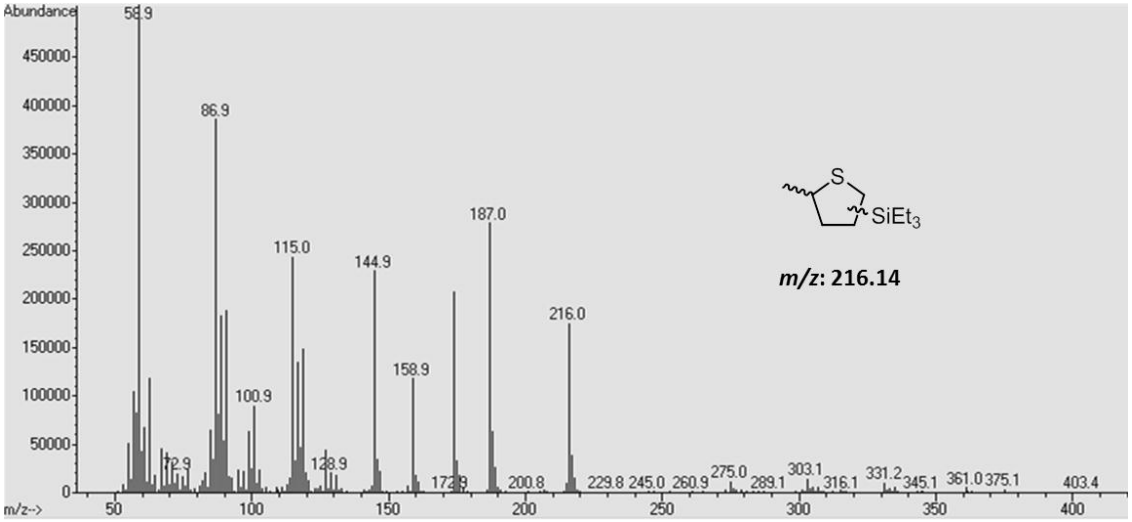
10.158 minutes - triethyl(5-methylthiophen-2-yl)silane:



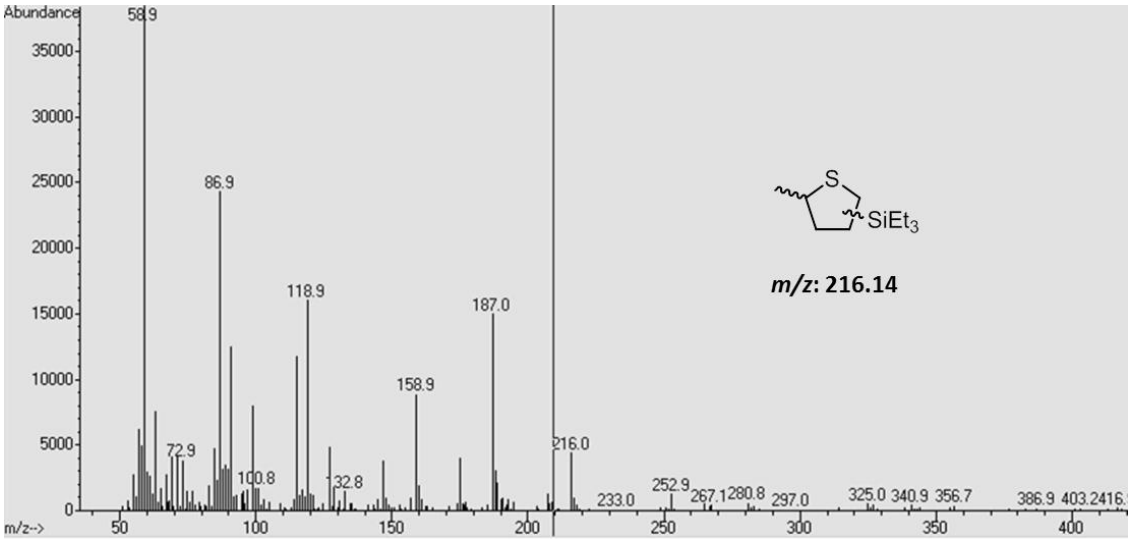
10.461 minutes - triethyl(5-methyltetrahydrothiophen-2-yl)silane:



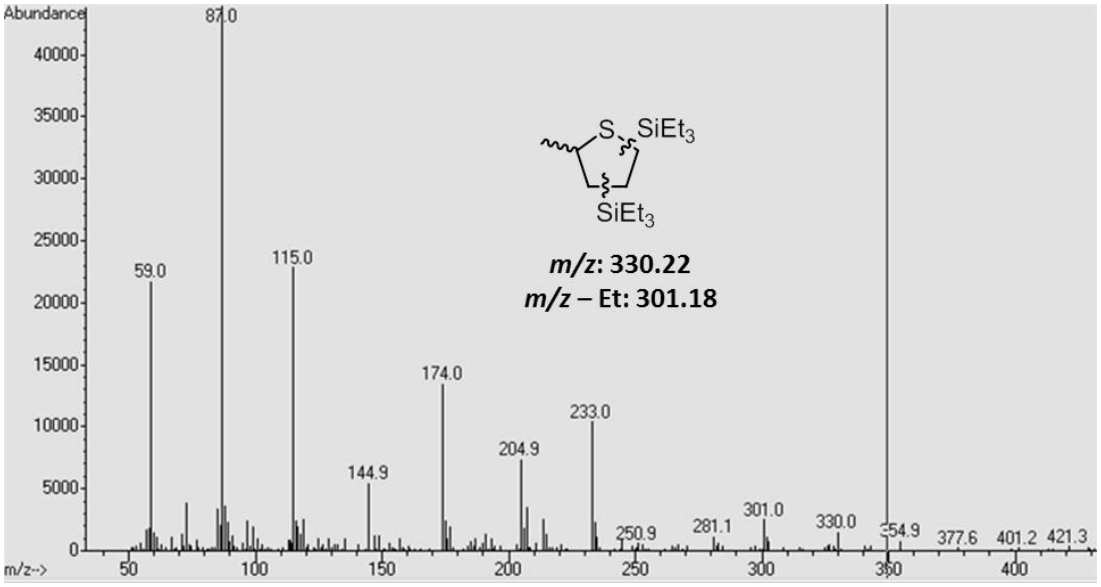
10.529 minutes - triethyl(5-methyltetrahydrothiophen-2-yl)silane:



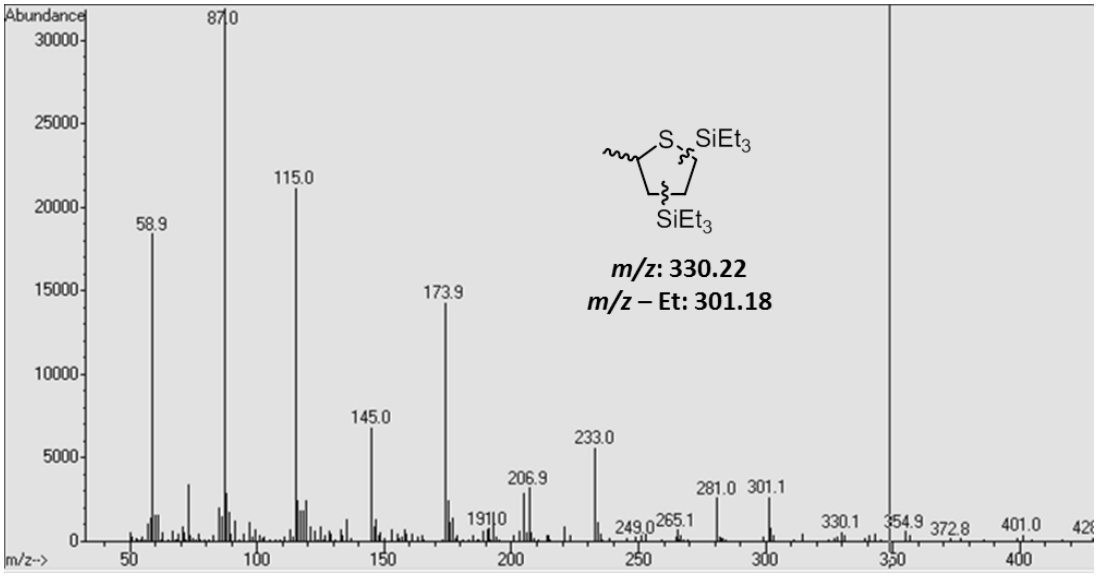
10.820 minutes - triethyl(5-methyltetrahydrothiophen-2-yl)silane:



13.310 minutes - double hydrosilylation product:



13.365 minutes - double hydrosilylation product:



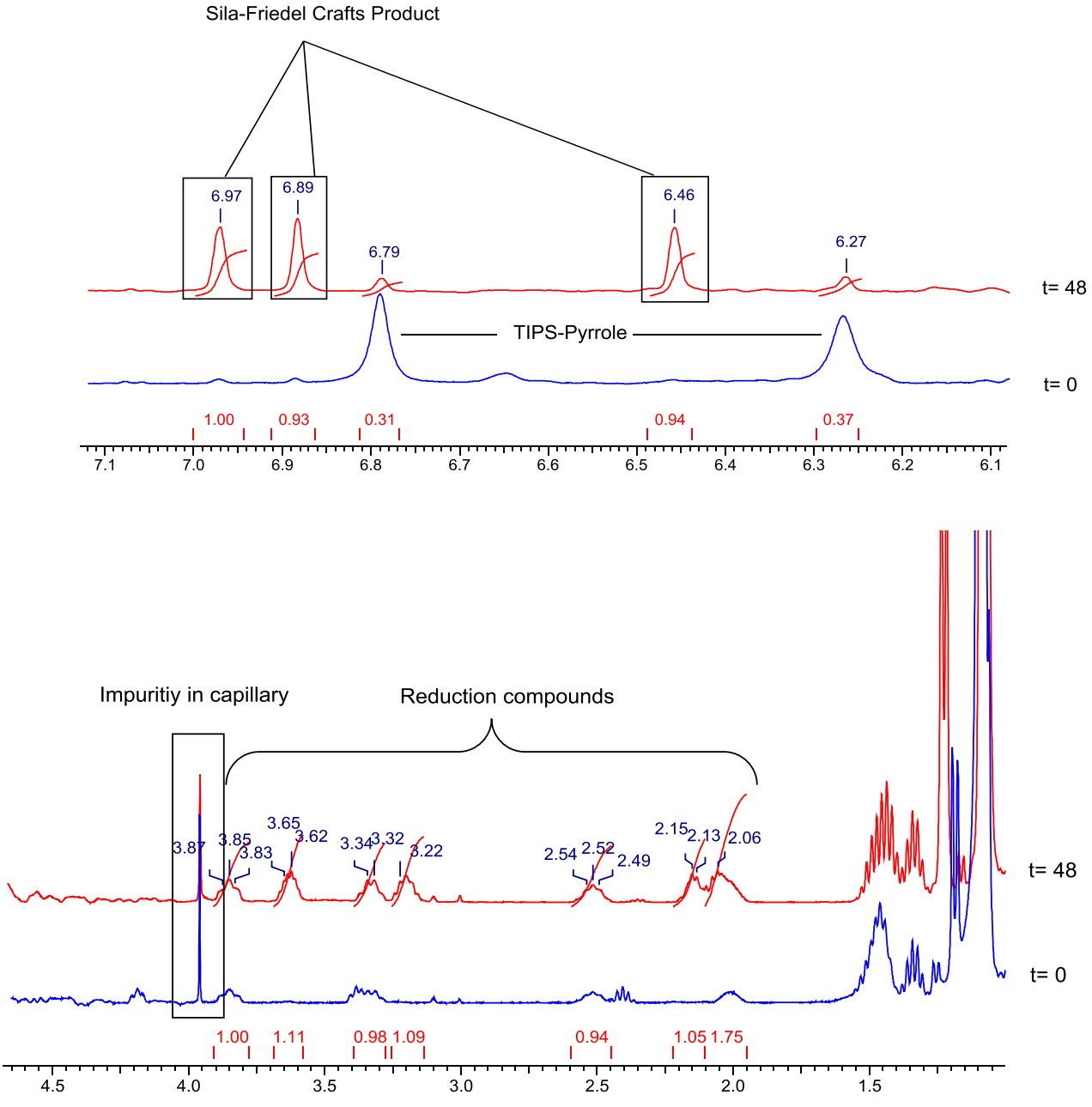
As the samples were put under vacuum, volatile materials such as 2-methylthiophene and 2-methyl-tetrahydrothiophene were not observed by GC-MS.

Silylation of N-TIPS-pyrrole with Ph_3SiH / $B(C_6F_5)_3$ and 2,6-Cl_2-py

According to general procedure A, a solution of tris(pentafluorophenyl)borane (51 mg, 0.10 mmol) and triphenylsilane (26mg, 0.10 mmol) in anhydrous CH_2Cl_2 (1 mL) was reacted with 1-(triisopropylsilyl)pyrrole (25 µL, 0.10 mmol) and 2,6-dichloropyridine (15 mg, 0.10 mmol) left to stir for 48 hours. This afforded a 42 % conversion to sila-Friedel Crafts product, according to NMR spectroscopy and a conversion of 45 to reduction products, combined yield of reduction products, according to NMR spectroscopy.

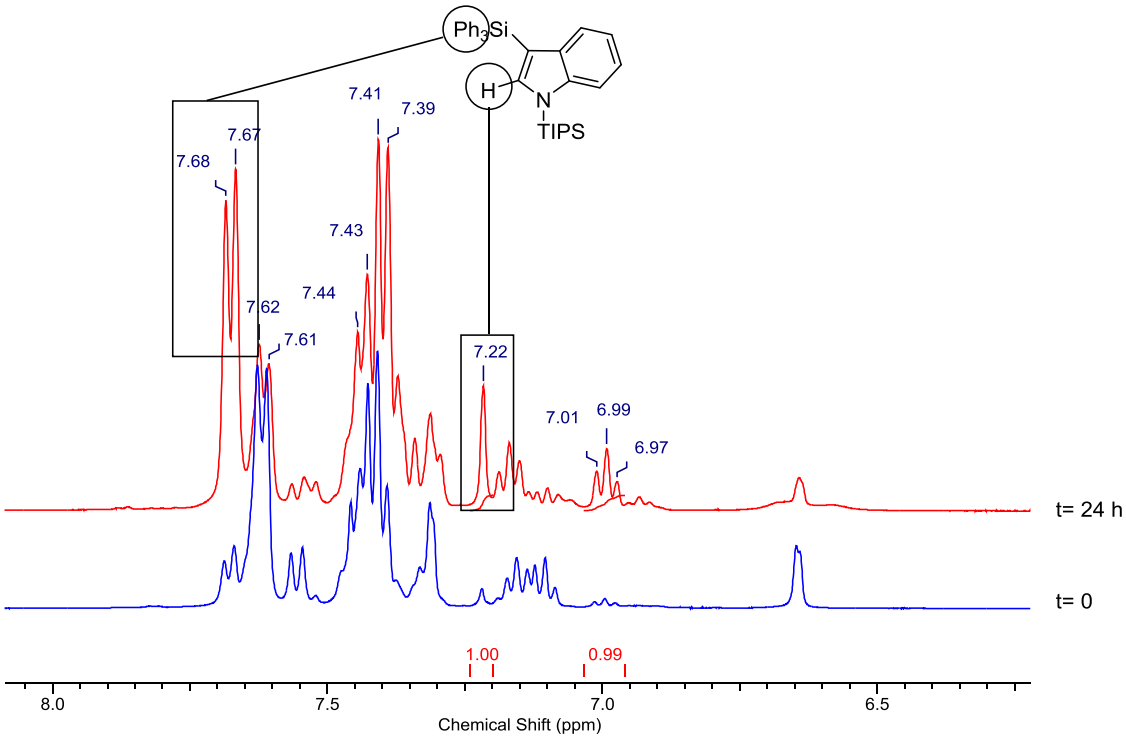
N-TIPS-3-(Ph_3Si)-pyrrole

^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ 7.61-7.35 (m, 10H), 6.97 (s, br, 1H), 6.89 (s, br, 1H), 6.46 (s, br, 1H), 1.53-1.37 (m, 3H) 1.09 (d, $^3J_{HH}$ = 6.56 Hz, 18H).

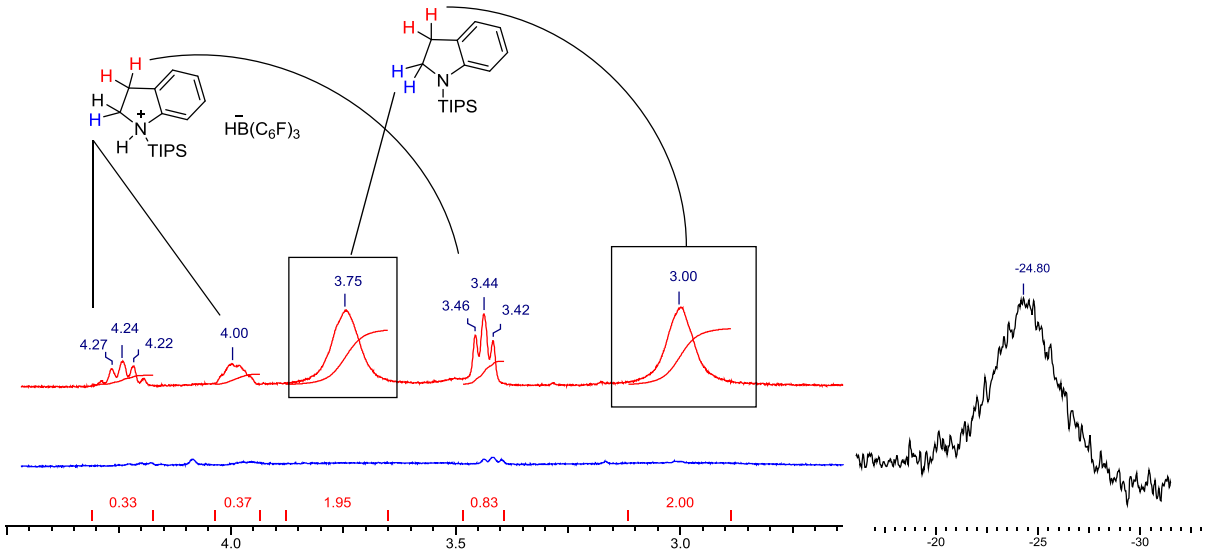


Silylation of N-TIPS-indole with Ph_3SiH / $B(C_6F_5)_3$ and 2,6-Cl_2-py

According to general procedure A, a solution of tris(pentafluorophenyl)borane (51 mg, 0.10 mmol) and triphenylsilane (26mg, 0.10 mmol) in anhydrous CH_2Cl_2 (1 mL) was reacted with 1-(Triisopropylsilyl)indole (27 µL, 0.10 mmol) and 2,6- dichloropyridine (15 mg, 0.10 mmol) left to stir for 24 hours. This afforded a 59 % conversion to sila-Friedel Crafts product, according to NMR spectroscopy and a conversion of 19 % to TIPS-Indoline according to NMR spectroscopy.



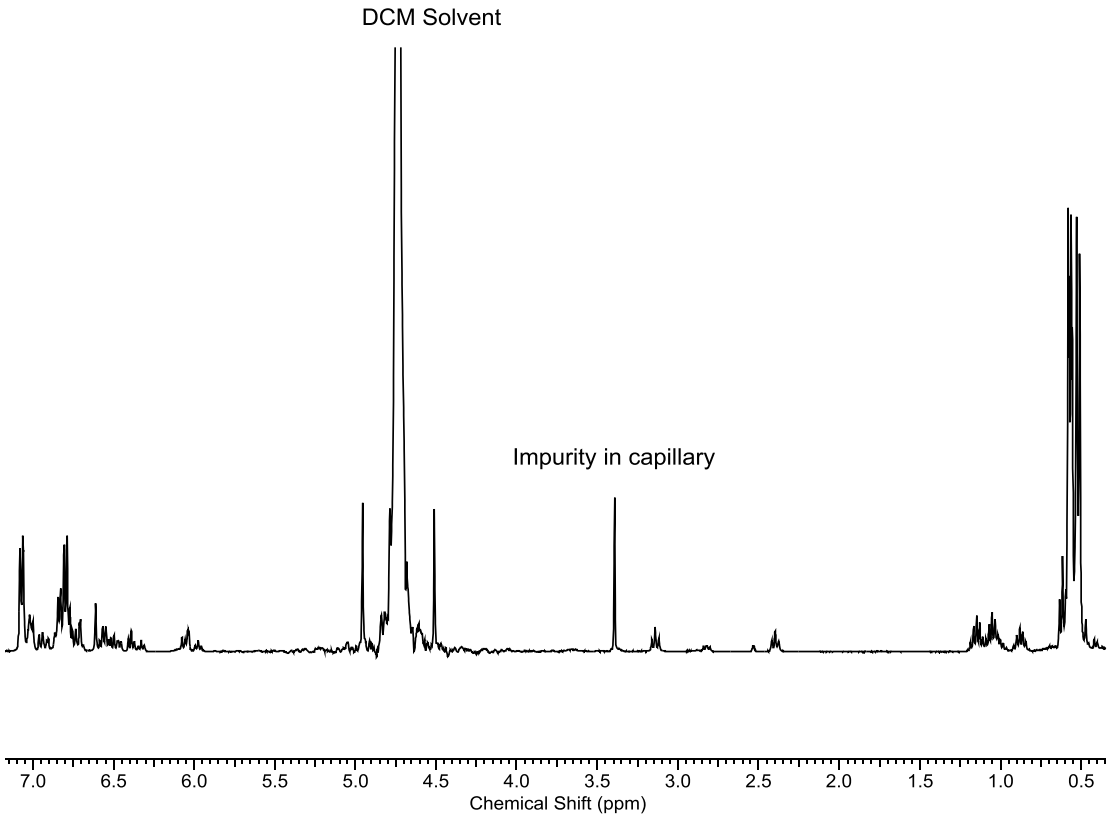
^{1}H NMR spectrum showed the growth of singlet overtime indicating formation of N-TIPS-3-(Ph_3Si)-indole.



^{1}H NMR spectrum of aliphatic region indicated reduction to N-TIPS-indoline and [*N*-H-*N*-TIPS-indolinium][HB(C_6F_5)$_3$]. The signal at -25 ppm in the ^{11}B NMR spectrum (right) supports this. Addition of base (Et_3N) resulted in conversion of all N-TIPS-indolinium to N-TIPS-indoline and a sharpening of the resonance at -25 ppm in the ^{11}B NMR spectrum to become a clear doublet consistent with [HB(C_6F_5)$_3$]$^{-}$.

Silylation of N-TIPS-indole with Ph_3SiH / $B(C_6F_5)_3$ without 2,6-Cl_2-py

According to general procedure A, a solution of tris(pentafluorophenyl)borane (51 mg, 0.10 mmol) and triphenylsilane (26mg, 0.10 mmol) in anhydrous CH_2Cl_2 (1 mL) was reacted with 1-(Triisopropylsilyl)indole (27 µL, 0.10 mmol) left to stir for 24 hours. This afforded a 30 % conversion to sila-Friedel Crafts product, according to NMR spectroscopy and a conversion of 21 % to TIPS-Indoline according to NMR spectroscopy.



References:

[i] F. Mohanazadeh H. Amini Bull .*Korean Chem.Soc*. 2010, **31**, 3038

[ii] Transition Metal Complexes and Main Group Frustrated Lewis Pairs for Stoichiometric and Catalytic P-P and H-H Bond Activation by Stephen Joseph Geier, PhD. Thesis, 2010.
Department of Chemistry University of Toronto