

Supporting Information

Ferrocenyl-derived Electrophilic Phosponium Cations (EPCs) as Lewis Acid Catalysts

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1. Materials and Methods

General Remarks

All preparations and manipulations were carried out under an anhydrous N₂ atmosphere using standard Schlenk and glovebox techniques. All glassware was oven-dried and cooled under vacuum before use. Commercially available reagents such as dppf, XeF₂, Et₃SiH, 1-fluoropentane, 1,1'-diphenylethylene, and ketones were purchased from Sigma Aldrich, Strem or Apollo Scientific and used without further purification unless indicated otherwise. (C₅H₅)Fe(C₅H₄)PPh₂^[S1] and PhP(η⁵-C₅H₄)₂Fe^[S2] was prepared according to literature procedures. CH₂Cl₂, *n*-pentane, and toluene were dried using an Innovative Technologies solvent purification system. CD₂Cl₂ (Aldrich) was deoxygenated, distilled over CaH₂, then stored over 4 Å molecular sieves before use. Reactions were monitored using NMR spectroscopy. NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer and a Varian Agilent DD2 500 MHz spectrometer. Data for ¹H NMR spectroscopy is reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, dm = doublet of multiplets, b = broad), coupling constant (Hz), integration. Data for ¹³C NMR is reported in terms of chemical shift (δ / ppm). High-resolution mass spectra (HRMS) were obtained on a micro mass 70S-250 spectrometer (EI), an ABI/Sciex QStar Mass Spectrometer (DART), or on a JOEL AccuTOF-DART (DART). Mass spectrometry experiments were run for isolated products and reaction mixtures, however in some cases the high fragmentation of compounds or volatility did not allow for mass peak identification.

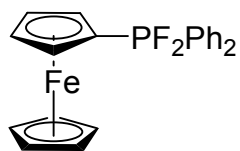
X-ray Diffraction Studies.

Single crystals were coated with Paratone-N oil, mounted using a glass fibre pin and frozen in a cold nitrogen stream on the goniometer. Data sets were collected on a Siemens Smart System CCD diffractometer which was equipped with a rotation anode using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Data reduction was performed using the SAINT software package and an absorption correction was applied using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least squares on F² using XL as implemented in the

SHELXTL suite of programs. All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors.

2. Synthesis of Catalysts and Precursors

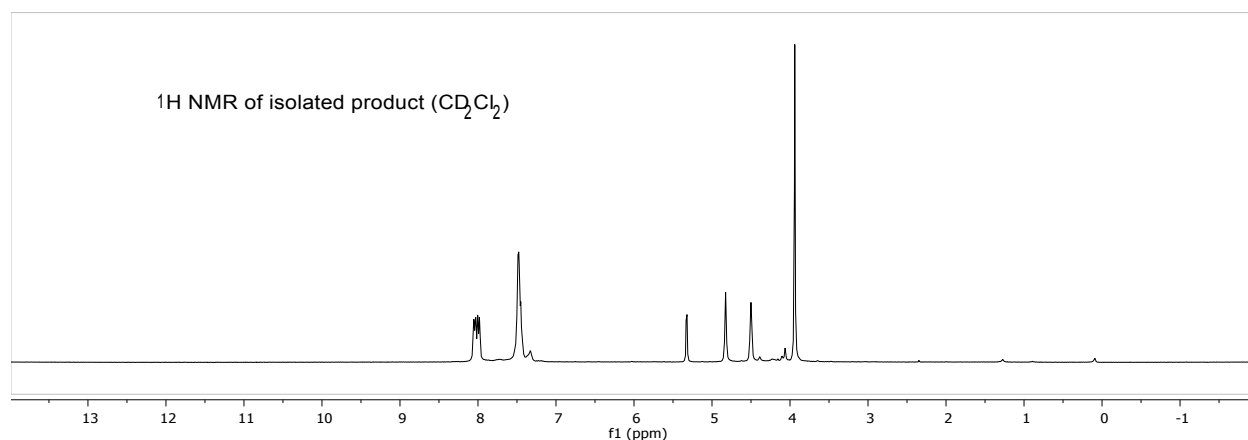
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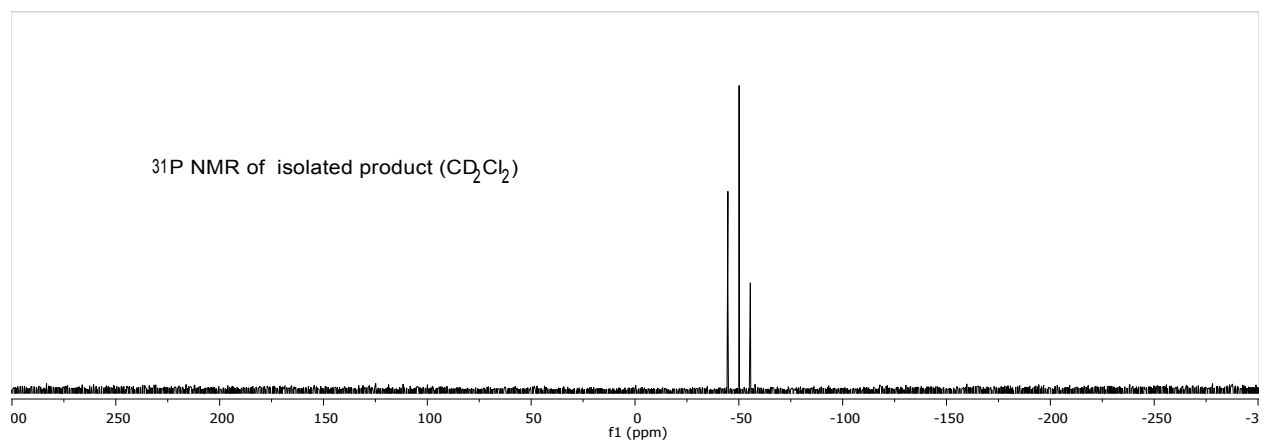
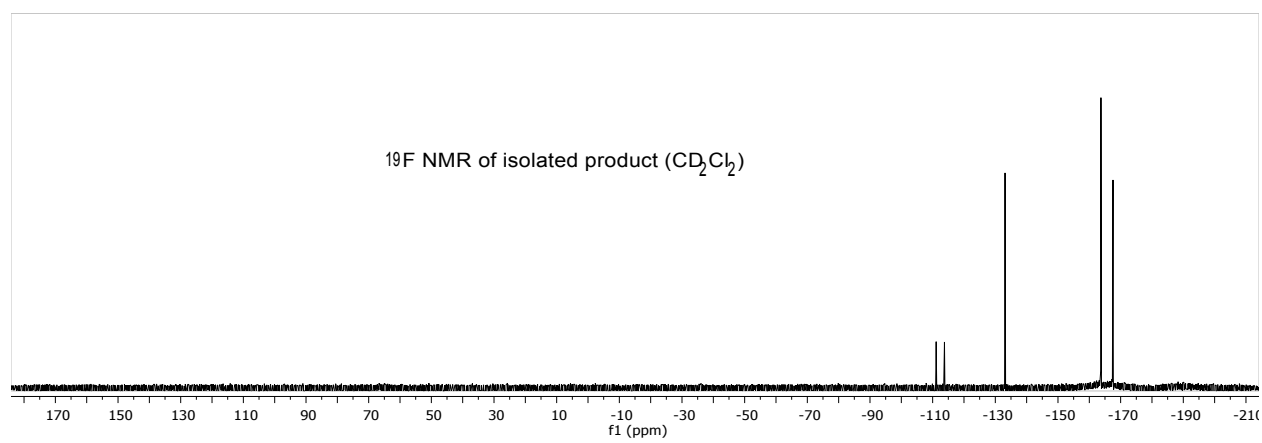
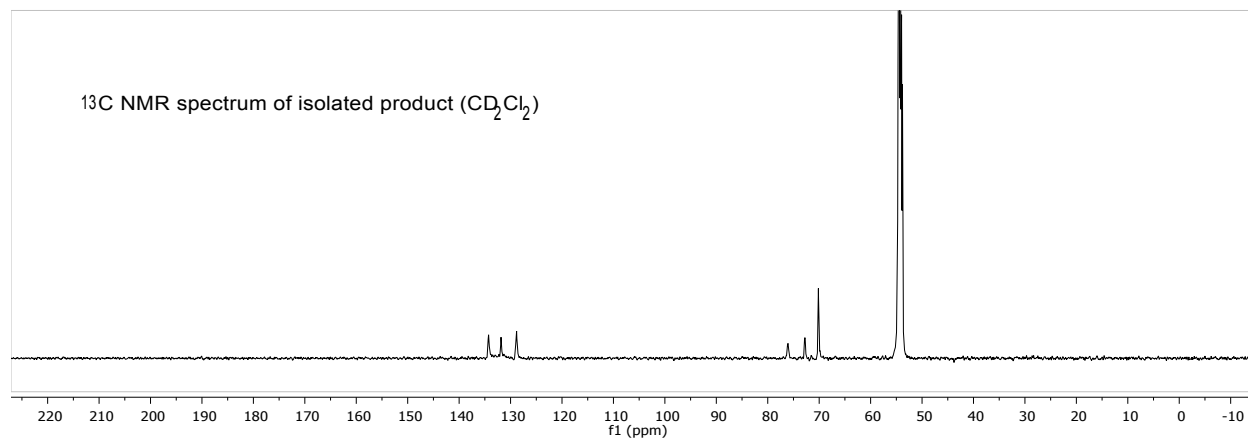


Synthesis of **CpFe(η⁵-C₅H₄PF₂Ph₂) 1**

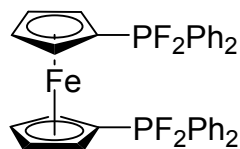
A solution of XeF₂ (34 mg, 0.20 mmol) in CH₂Cl₂ (1 mL) was added dropwise to a solution of phenylphosphinoferrocene (74 mg, 0.20 mmol) in CH₂Cl₂ (1 mL). Effervescence was immediately observed. After stirring 2 h volatiles were removed *in vacuo* resulting in a dull orange solid in quantitative yield (81 mg). X-ray quality crystals were obtained by cooling a saturated solution of the product in CH₂Cl₂ to -35 °C. ¹H NMR (CD₂Cl₂, [ppm]): 3.94 (s, 5H, Cp), 4.50 (s, 2H, Cp CH_β), 4.83 (2H, s, Cp CH_α), 7.44-7.50 (m, 6H, *p*-Ph, *m*-Ph), 7.96-8.08 (m, 4H, *o*-Ph) ¹³C {¹H} NMR (CD₂Cl₂, [ppm]): 70.2 (Cp C_β), 72.8 (d, Cp C_α, ²J_{PC} = 15 Hz), 76.0 (br m, Cp C_{ipso}), 128.9 (d, Ph, C_α, ²J_{PC} = 17 Hz), 131.8 (s, Ph, C_β) 134.2 (m). Resonances for *ipso*-carbon atoms on phenyl, Cp moieties were not observed. ¹⁹F {¹H} NMR (CD₂Cl₂, [ppm]): -42.7 (d, ¹J_{PF} = 656 Hz) ³¹P {¹H} NMR (CD₂Cl₂, [ppm]): -50.1 (t, ¹J_{PF} = 656 Hz); Elemental Analysis for C₂₂H₁₉F₂P: calcd.: C 64.7, H 4.7, found: C 63.1, H 4.9; HRMS (ESI-QTOF+): m/z 387.0596 ([CpFe(η⁵-C₅H₄POPPh₂)] (calc.: 387.0601)

Note: Repeated attempts to obtain satisfactory elemental analysis of **1** led consistently to low C values. This is attributed to incomplete combustion, presumably a result of the formation of metal-carbide.

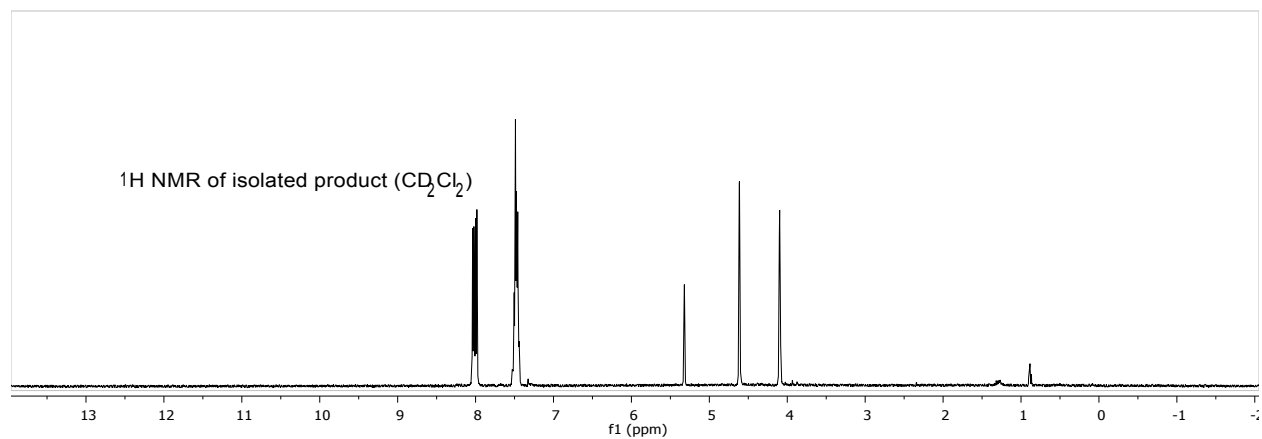


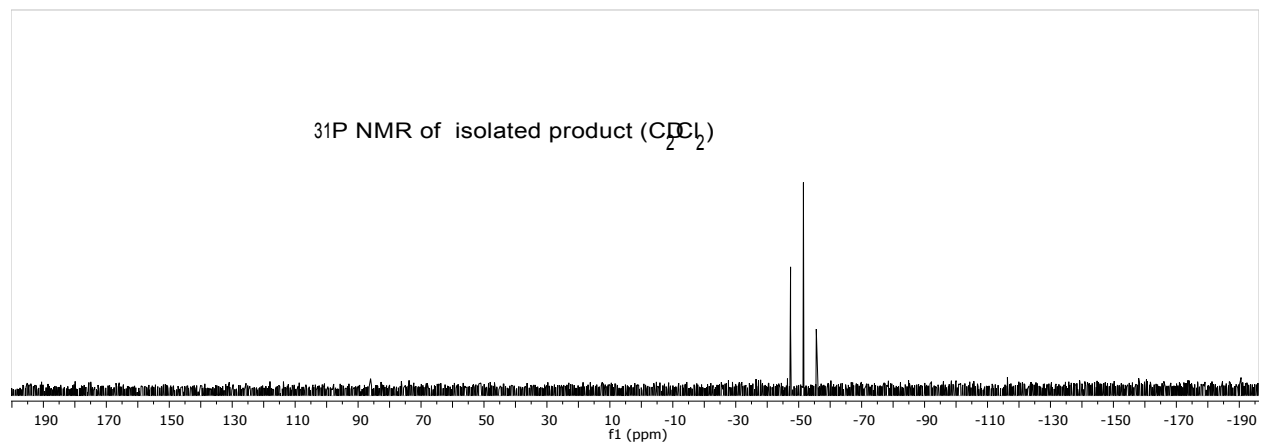
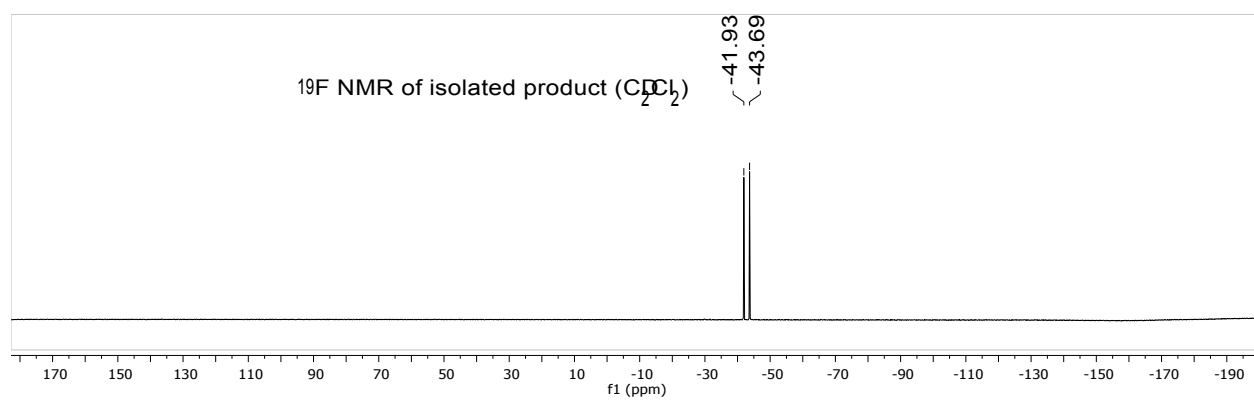
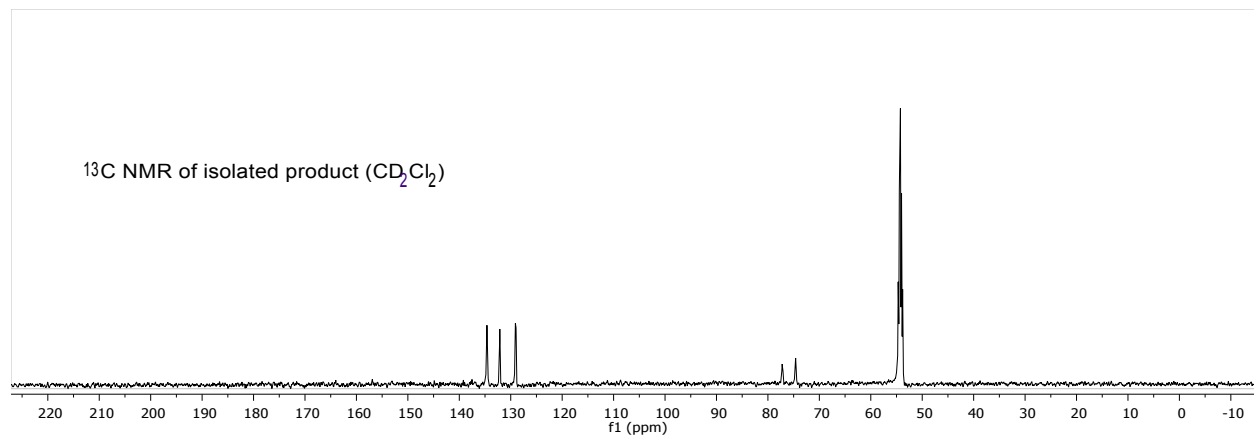


2.2

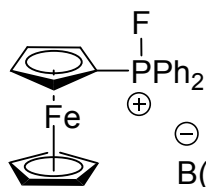


Fe(η^5 -C₅H₄PF₂Ph₂)₂ 2 A solution of XeF₂ (34 mg, 0.20 mmol) in CH₂Cl₂ (1 mL) was added dropwise to a solution of 1,1'-bis(diphenylphosphino)ferrocene (111 mg, 0.20 mmol) in CH₂Cl₂ (1 mL). Effervescence was immediately observed. After stirring for 1-2 min. a yellow solid precipitated from the solution. This was filtered and washed with pentane (2 x 1mL) and dried *in vacuo* to give 118 mg of product (94% yield). ¹H NMR (CD₂Cl₂, [ppm]): 4.10 (m, 4H, Cp, H_α), 4.62 (m, 4H, Cp CH_β), 7.47 (m, 12H, *p*-Ph, *m*-Ph), 8.00 (m, 8H, *o*-Ph) ¹³C{¹H} NMR (CD₂Cl₂, [ppm]): 74.6 (dt, Cp C_β, ³J_{PC} = 15 Hz, ⁴J_{FC} = 2 Hz), 77.2 (dt, Cp C_α, ²J_{PC} = 18 Hz, ³J_{FC} = 10 Hz), 129.0 (td, *i*-Ph, ²J_{PC} = 17 Hz, ⁴J_{FC} = 2 Hz), 132.1 (s, *i*-Ph) 134.6 (dt, *m*-Ph, ²J_{CP} = 13 Hz, ²J_{CF} = 10 Hz), 138.5 (td, *i*-Ph ¹J_{PC} = 182 Hz, ²J_{FC} = 28 Hz) Resonances for *ipso* carbon atoms on Cp moieties were not observed. ¹⁹F{¹H} NMR (CD₂Cl₂, [ppm]): -42.8 (d, ¹J_{PF} = 662 Hz) ³¹P{¹H} NMR (CD₂Cl₂, [ppm]): -51.5 (t, ¹J_{PF} = 662 Hz); Elemental Analysis for C₃₄H₂₈F₄P₂: calcd.: C 64.8, H 4.5, found: C: 64.9 H: 4.8. **HRMS** (ESI-QTOF+): m/z 587.0987 ([Fe(η^5 -C₅H₄P(OH)Ph₂) (η^5 -C₅H₄POPh₂))] (calc.: 587.0992)



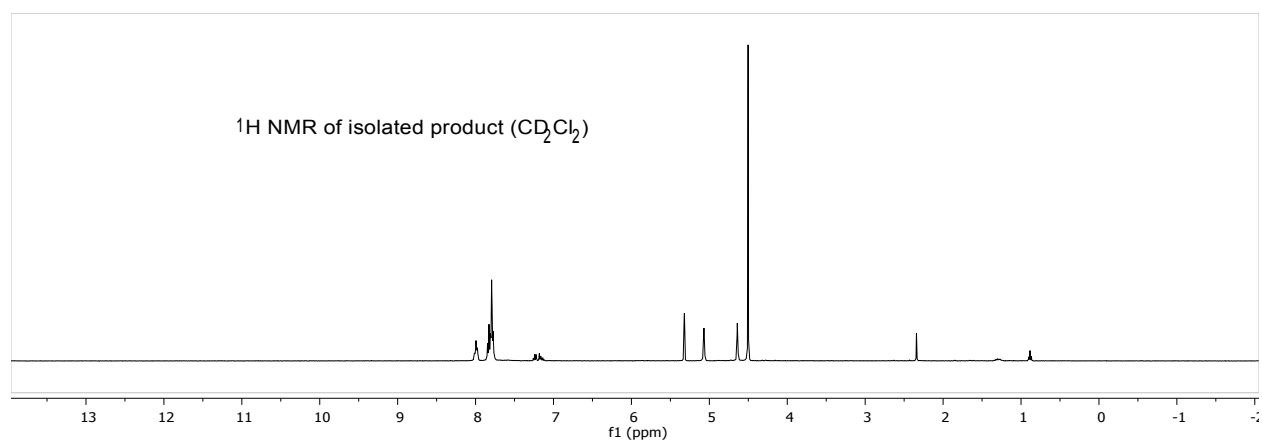


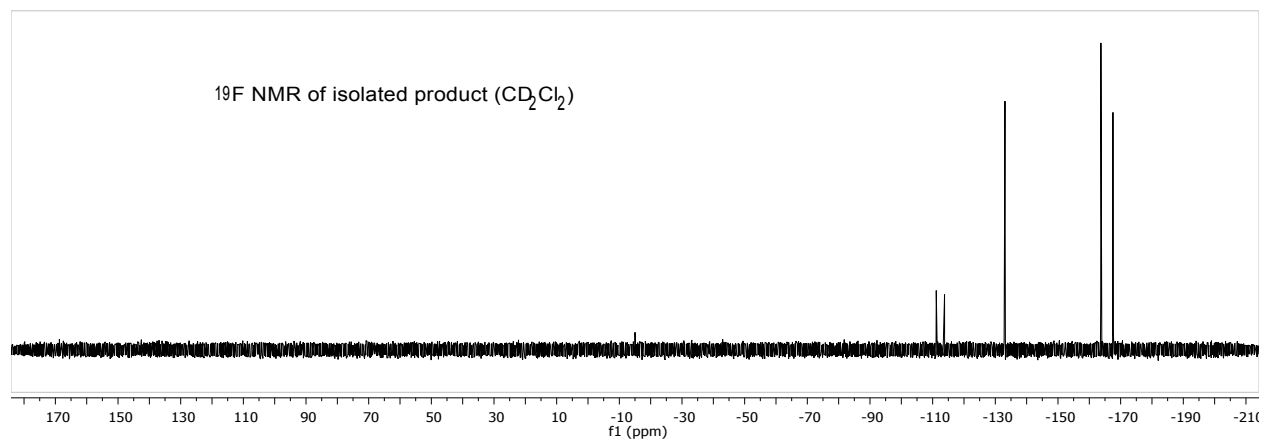
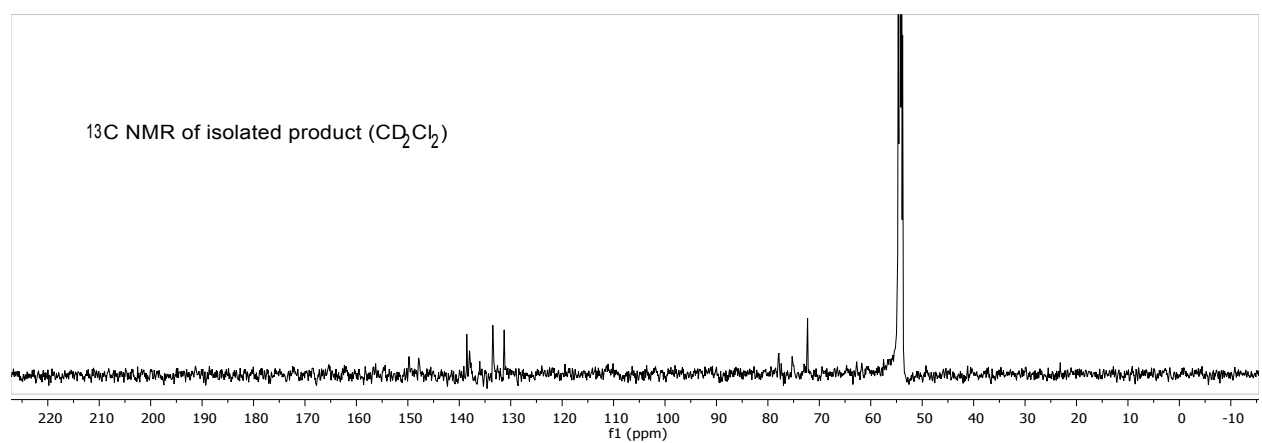
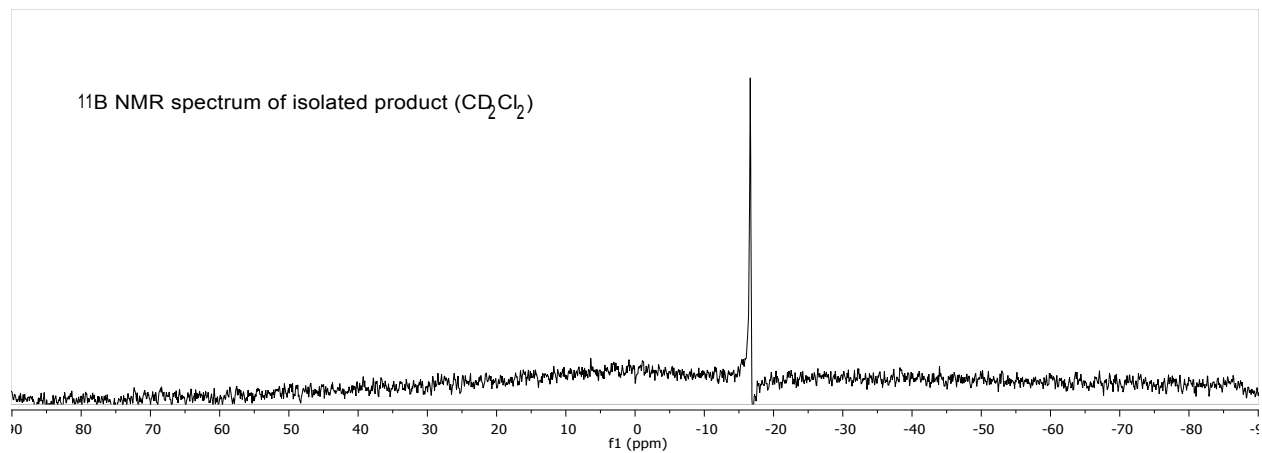
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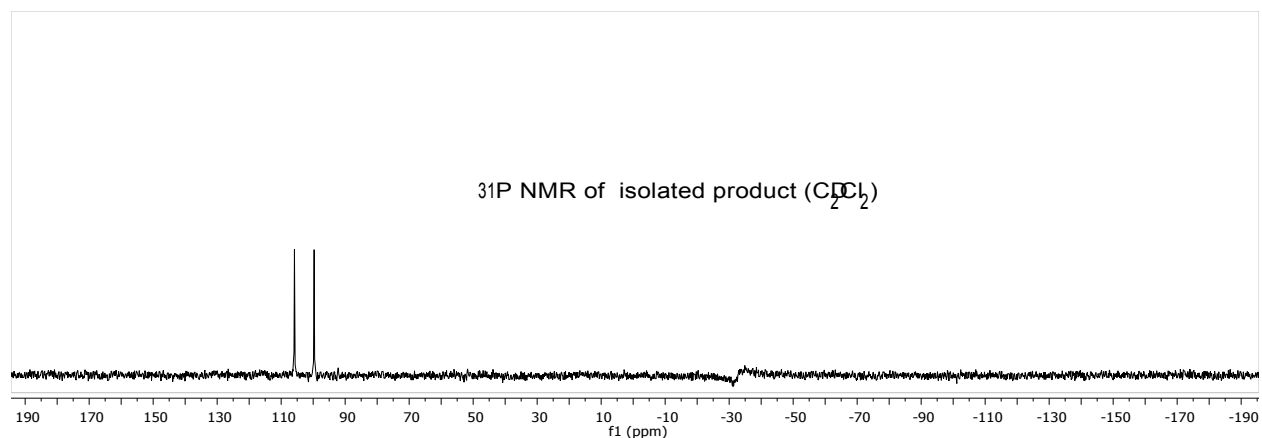


$\text{B}(\text{C}_6\text{F}_5)_4^-$ **3** To a solution of 41 mg (0.10 mmol)

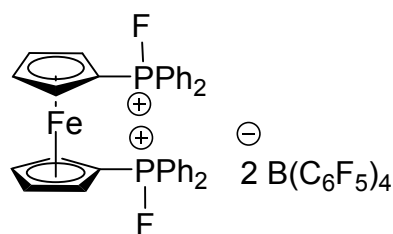
1 in toluene was added 186 mg freshly prepared $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4] \cdot 2(\text{C}_7\text{H}_8)$ (0.19 mmol, 1.9 equivalents). Stirring for 3 h resulted in precipitation of a dark yellow oil. Washing with toluene (1 x 0.5 mL) and pentane (3 x 0.5 mL) and drying *in vacuo* resulted in 90 mg of **3** as a dull orange solid (84% yield). X-ray quality crystals were obtained by slow diffusion of n-pentane into a saturated solution of **4** in dichloromethane at -35°C , ^1H NMR (CD_2Cl_2 , [ppm]): 4.50 (s, 5H, Cp), 4.64 (m, 2H, Cp, H_α), 5.07 (m, 2H, Cp, H_β), 7.79-7.85 (m, 8H, *o*-Ph, *m*-Ph), 7.99 (t, 2H, *p*-Ph, , $^3J_{\text{HH}} = 7$ Hz) ^{11}B NMR (CD_2Cl_2 , [ppm]): - 16.7 $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): 72.3 (s, Cp), 75.2 (d, Cp C_α , $^2J_{\text{PC}} = 17$ Hz), 77.9 (d, Cp C_β , $^3J_{\text{PC}} = 13$ Hz), 131.3 (d, Ph, $J_{\text{PC}} = 14$ Hz), 133.5 (d, Ph, $J_{\text{PC}} = 13$ Hz), 138.5 (s, Ph) signals for ipso carbon atom not observed. $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): - 112.5 (d, $^1J_{\text{PF}} = 998$ Hz) $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): 102.9 (d, $^1J_{\text{PF}} = 998$ Hz) Elemental Analysis for $\text{C}_{46}\text{H}_{19}\text{BF}_{21}\text{PF}$: calcd.: C 51.8, H 1.8, found: C: 51.0, H: 1.5; **HRMS** (ESI-QTOF+): m/z 387.0596 ($[\text{CpFe}(\eta^5\text{-C}_5\text{H}_4\text{POPh}_2)]$) (calc.: 387.0601)







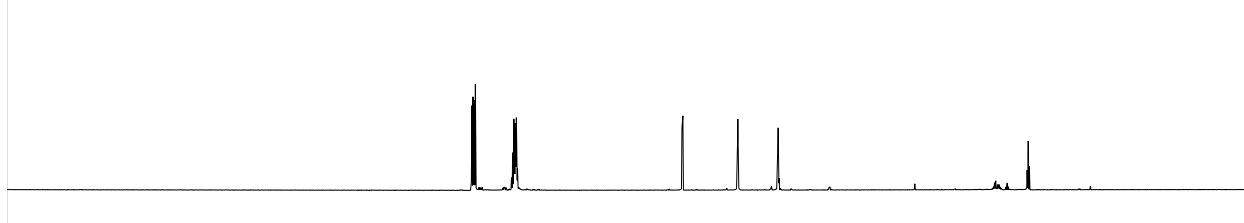
2.4



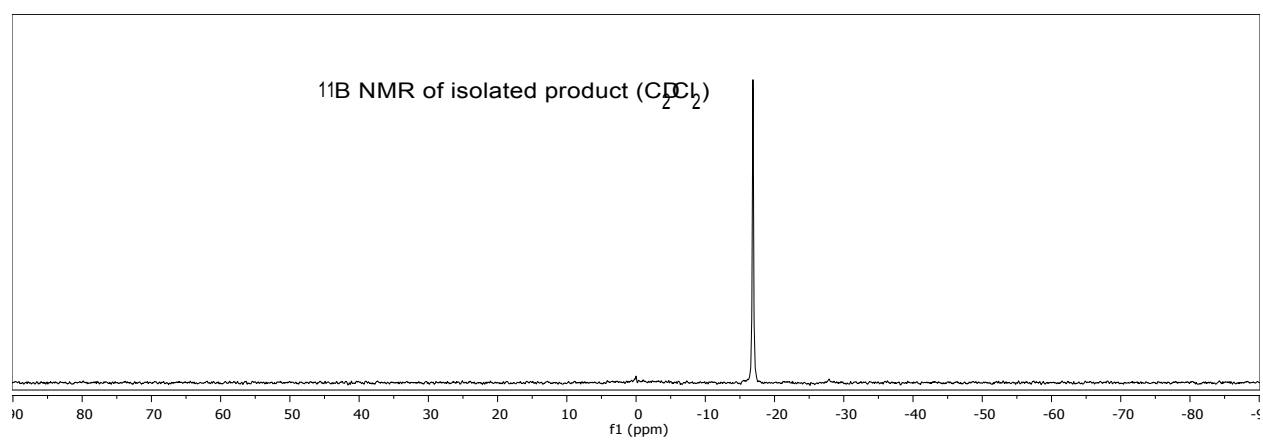
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PFPh}_2)_2] 2[\text{B}(\text{C}_6\text{F}_5)_4]$ **4**

To a solution of 63 mg (0.10 mmol) **2** in toluene was added 186 mg freshly prepared $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4] \cdot 2(\text{C}_7\text{H}_8)$ (0.19 mmol, 1.9 equivalents). Stirring for 3 hours resulted in precipitation of a dark yellow oil. Washing with toluene (1 x 0.5 mL) and pentane (3 x 0.5 mL) and drying *in vacuo* resulted in 156 mg of **4** as a dull orange solid (80% yield). X-ray quality crystals were obtained by slow diffusion of *n*-pentane into a saturated solution of **4** in dichloromethane at -35°C , ^1H NMR (CD_2Cl_2 , [ppm]): 4.51 (m, Cp CH_α), 5.19 (m, 4H, Cp CH_β), 7.47 (m, 12H, *p*-Ph, *m*-Ph), 7.72 (m, 4H, Ph), 7.79 (m, 4H, Ph), 8.04 (m, 2H, *p*-Ph) ^{11}B NMR (CD_2Cl_2 , [ppm]): -16.7 $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): 74.6 (d, Cp C_β , $^3J_{\text{PC}} = 15$ Hz), 77.2 (m, Cp C_α), 129.0 (d, *i*-Ph, $^2J_{\text{PC}} = 17$ Hz), 132.1 (s, *m*-Ph), 134.5 (d, *o*-Ph, $^2J_{\text{CP}} = 11$ Hz). Signals for *ipso* carbon atoms on Cp, phenyl rings not observed. $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): -42.8 (d, $^1J_{\text{PF}} = 662$ Hz) $^1\text{ }^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): -51.5 (t, $^1J_{\text{PF}} = 662$ Hz); Elemental Analysis for $\text{C}_{82}\text{H}_{28}\text{B}_2\text{F}_{42}\text{P}_2\text{Fe}$: calcd.: C 50.5, H 1.5, found: C 51.0, H 1.5; **HRMS** (ESI-QTOF+): m/z 587.0987 ($[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OH})\text{Ph}_2)(\eta^5\text{-C}_5\text{H}_4\text{POPPh}_2)]$) (calc.: 587.0992)

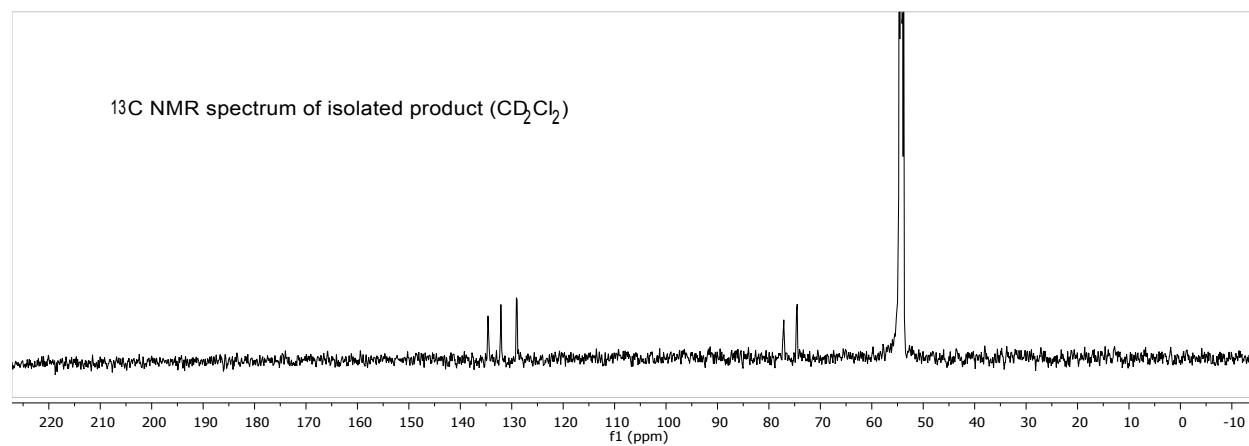
^1H NMR spectrum of isolated product (CD_2Cl_2)

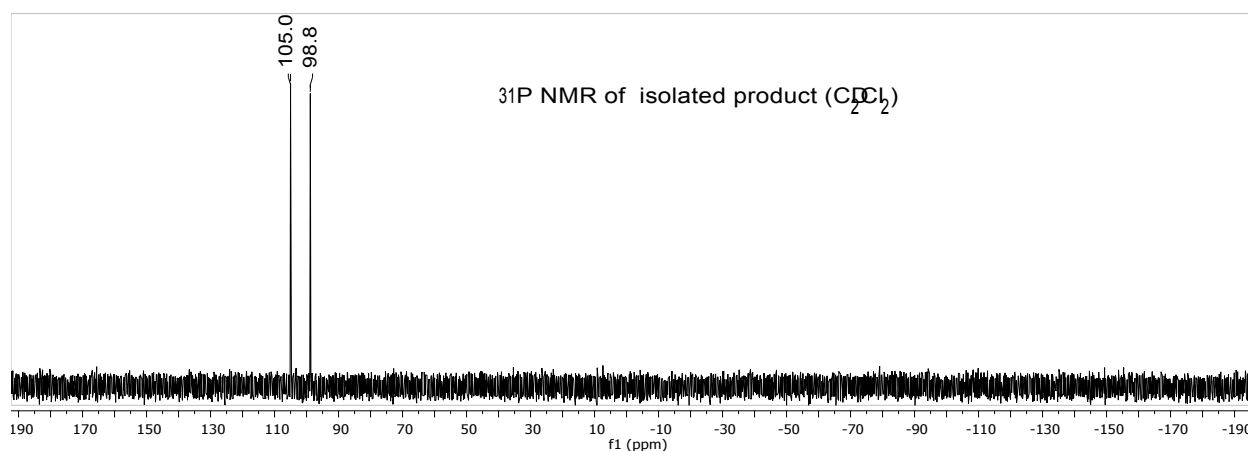
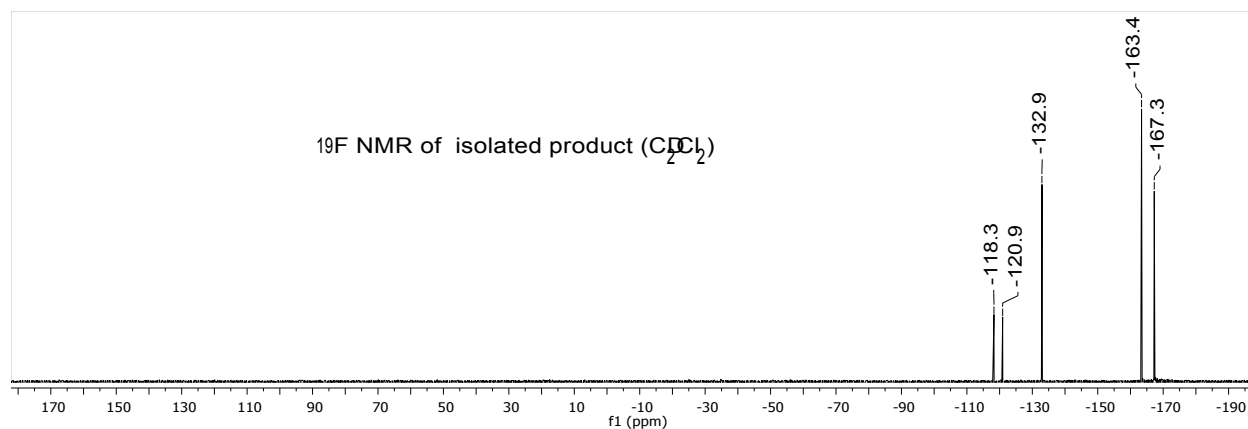


^{11}B NMR of isolated product (CD_2Cl_2)

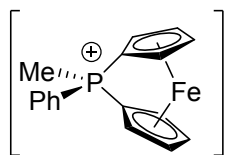


^{13}C NMR spectrum of isolated product (CD_2Cl_2)





2.5

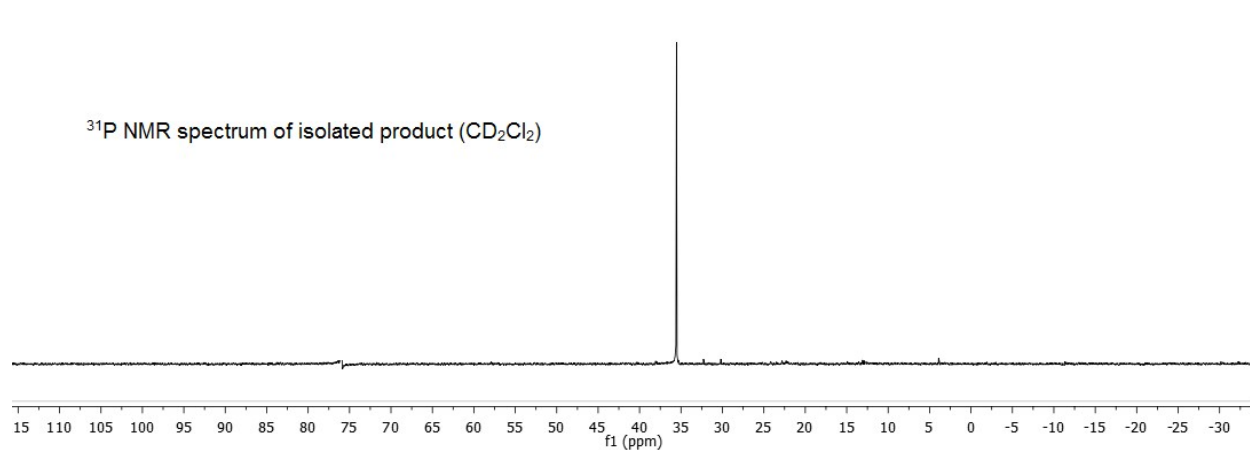
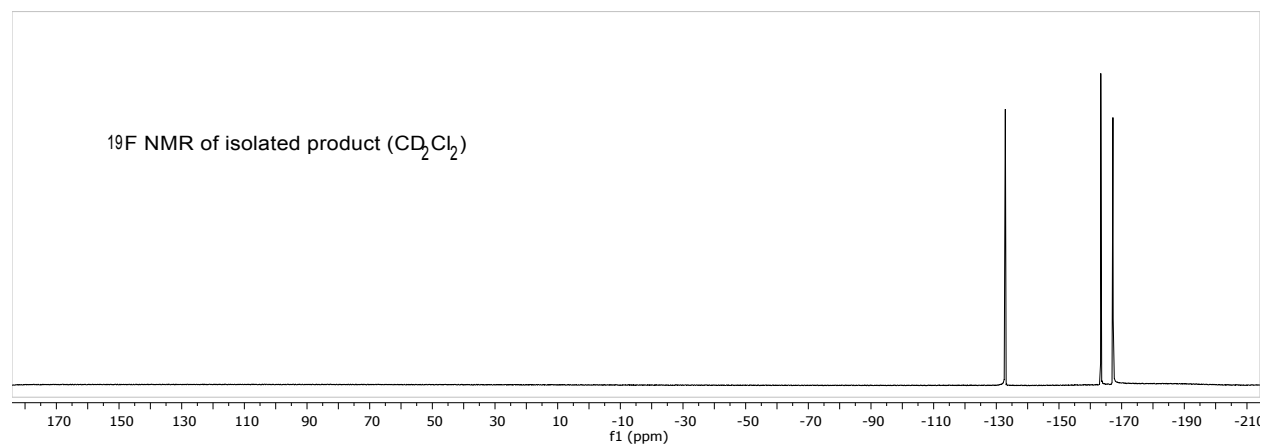
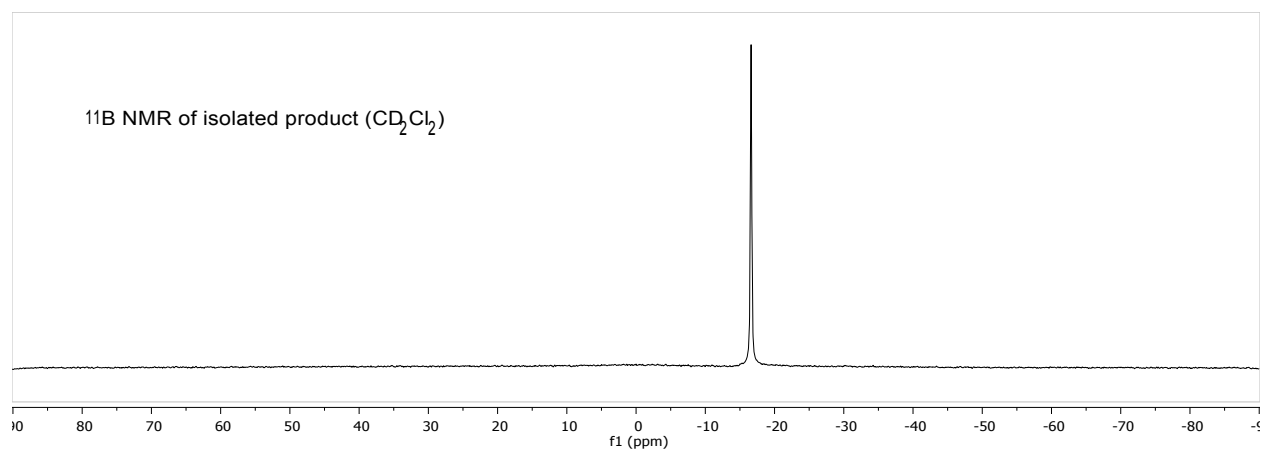


[B(C₆F₅)₄]

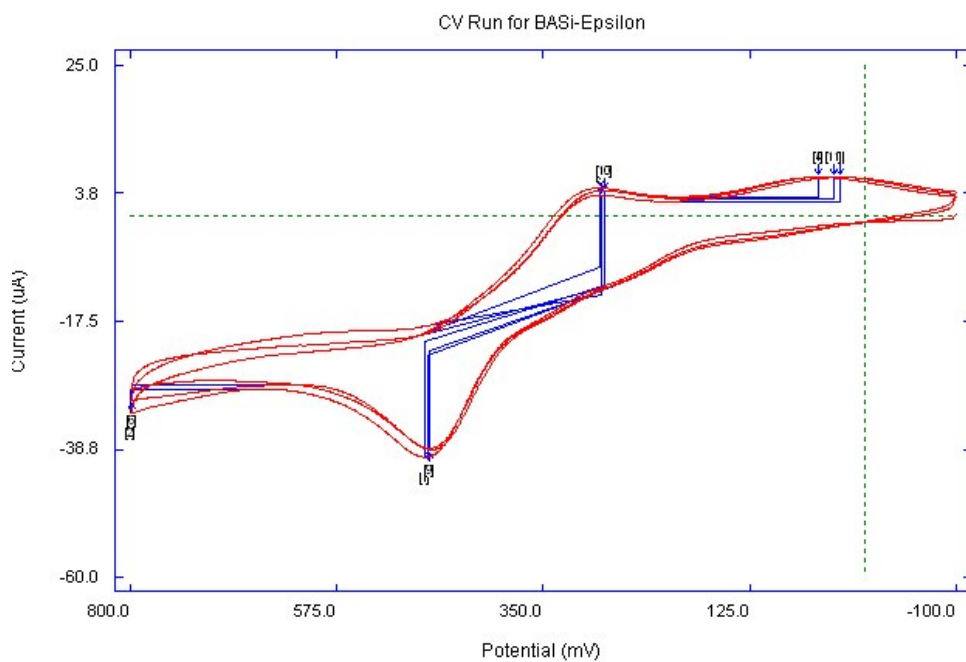
[PhMeP(η⁵-C₅H₄)₂Fe][B(C₆F₅)₄] 7 To a solution of Fe(η-C₅H₄)₂PPh in toluene

was added a solution of MeOTf in toluene. Successive precipitations yielded .050 g of the product (80% yield). ¹H NMR (CD₂Cl₂, [ppm]): 2.39 (d, 3H, CH₃, ²J_{PH} = 14 Hz), 4.50 (m, 2H, Cp), 4.80 (m, 2H, Cp), 5.06 (m, 2H, Cp), 5.11 (m, 2H, Cp), 7.79-7.85 (m, 4H, *o*-Ph, *m*-Ph), 7.99 (t, 1H, *p*-Ph, ³J_{HH} = 7 Hz) ¹¹B{¹H}: - 16.7 ¹³C {¹H} NMR (CD₂Cl₂, [ppm]): 12.1 (d, Me, ¹J_{CP} = 221 Hz), 72.3 (s, Cp), 75.2 (d, Cp, ²J_{PC} = 17 Hz), 77.9 (d, Cp ³J_{PC} = 13 Hz), 131.3 (d, Ph, ²J_{PC} = 14 Hz),

133.5 (d, Ph, $^3J_{PC} = 13$ Hz), 138.5 (s, Ph) signals for ipso carbon atom not observed. ^{31}P { ^1H } NMR (CD_2Cl_2 , [ppm]): 35.6. Elemental Analysis for $\text{C}_{41}\text{H}_{16}\text{BF}_{20}\text{P}$: calcd.: C 49.9 H 1.6 found: C 50.2, H 1.9 **HRMS** (ESI-QTOF+): m/z 307.0343 (**(Ph(O)P($\eta^5\text{-C}_5\text{H}_4$) $_2$ Fe)**) (calc.: 307.0339)



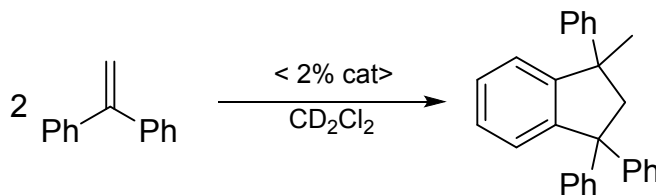
2.6 Cyclic Voltammogram of 3



Cyclic voltammogram obtained in CH_2Cl_2 with 0.1M $[\text{nBu}_4\text{N}][\text{PF}_6]$ as electrolyte and referenced against ferrocene (glassy carbon working electrode, step = 5mV, sc = 200 mV/s).

2 Lewis Acid Catalysis

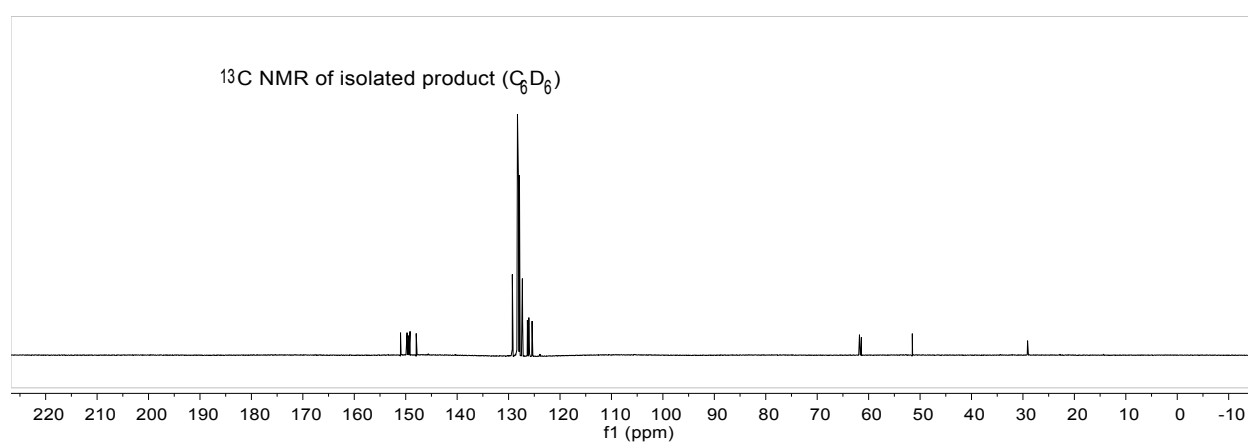
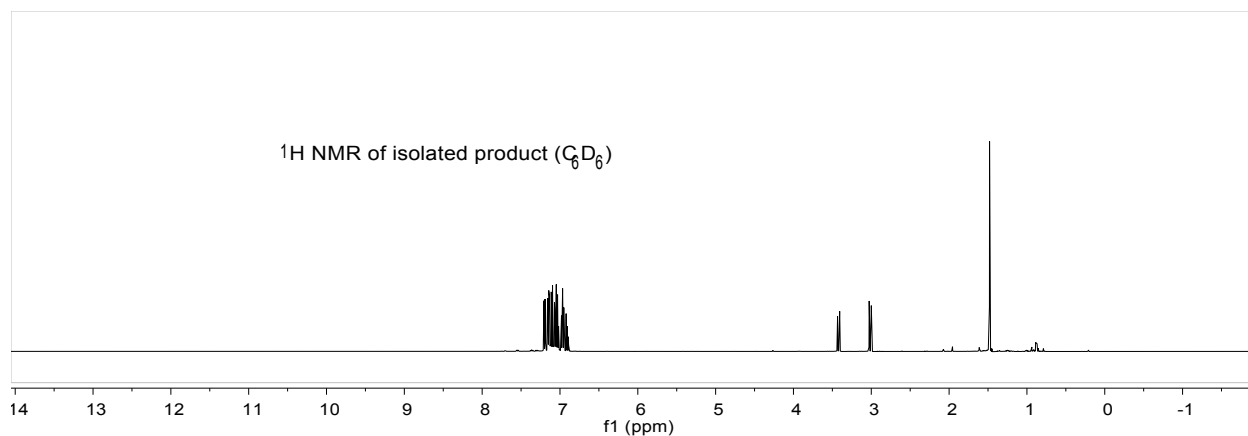
2.1 Friedel-Crafts dimerization of 1,1-diphenylethylene with **3**, **4** and **7** as catalysts



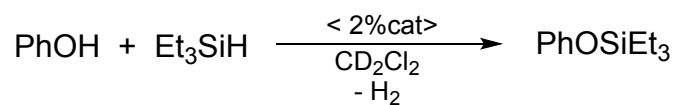
- 3** (2 mol%, 50°C, 4 d): 10% conversion
4 (2 mol%, rt, 2 d): > 99% conversion
7 (2 mol%, 50 °C, 3 d): 0% conversion

Catalyst **3** (2.1 mg, 2 mol%), **4** (3.9 mg, 2 mol%) or **7** (2.2 mg, 2 mol%) were added to a solution of 1,1-diphenylethylene (18 mg, 0.1 mmol) in CD_2Cl_2 (0.7 mL). The reaction mixtures were either left at ambient temperature (**4**) or heated to 50 °C for 2-4 days (**3,7**) and monitored by NMR spectroscopy. After the reaction catalyzed by **4** had been observed to go to completion by NMR, all volatiles were removed from the reaction mixture *in vacuo* and the remaining residue was suspended in n-pentane. The mixture was filtered through a Celite plug and the solvent was removed *in vacuo* resulting in isolated 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene as a colorless solid (15.9 mg, 88% yield). The isolated product was re-dissolved in C_6D_6 ; NMR data is reported in this solvent.^[S3]

^1H NMR (C_6D_6 , [ppm]): δ = 1.48 (3H, s, CH_3), 3.02 (1H, d, CH_2 , $^3J_{\text{HH}} = 14$ Hz), 3.42 (1H, d, CH_2 , $^3J_{\text{HH}} = 14$ Hz), 6.90 - 7.23 (19H, m); **$^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , [ppm]):** δ = 29.1 (1C, s, CH_3), 51.5 (1C, s, CH_2), 61.4 (1C, s, CPh), 61.8 (1C, s, CPh), 125.4 (1C, s, Ph), 125.9 (1C, s, Ph), 126.0 (1C, s, Ph), 126.3 (1C, s, Ph), 127.3 (1C, s, Ph), 127.3 (2C, s, Ph), 127.9 (2C, s, Ph), 128.0 (2C, s, Ph), 128.3 (2C, s, Ph), 128.3 (2C, s, Ph), 129.1 (2C, s, Ph), 129.3 (2C, s, Ph), 147.9 (1C, s, Ph), 149.1 (1C, s, Ph), 149.4 (1C, s, Ph), 149.7 (1C, s, Ph), 151.0 (1C, s, Ph).



2.2 Dehydrocoupling of Et₃SiH and Phenol with **3**, **4** and **7** as catalysts.



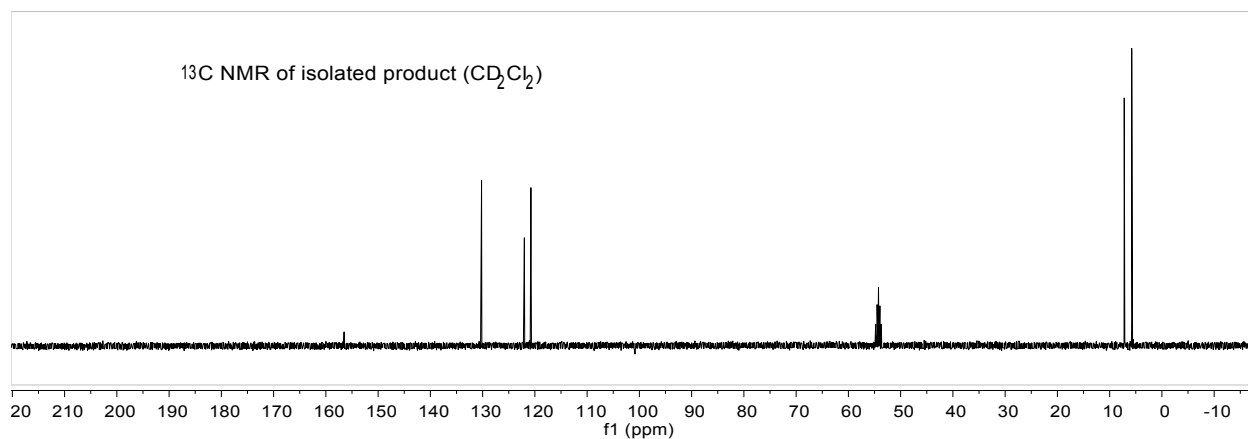
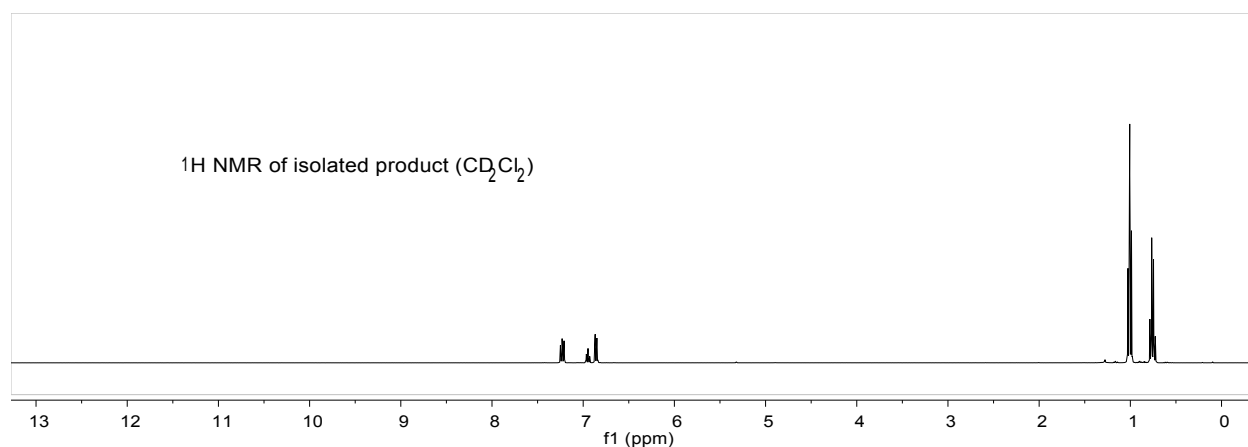
3 (7 d, 50 °C): 97% conversion

4 (1 d, rt): >99% conversion

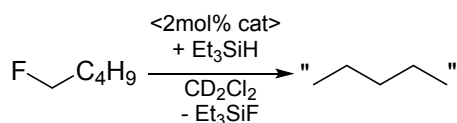
7 (3 d, 50 °C): 0% conversion

Catalyst **3** (2.1 mg, 2 mol%), **4** (3.9 mg, 2 mol%) or **7** (2.2 mg, 2 mol%) were added to a solution of Et₃SiH (17 μL, 0.10 mmol) and PhOH (9.4 mg, 0.10 mmol) in CD₂Cl₂ (0.7 mL) at ambient temperature. The reaction mixtures were either left at ambient temperature (**4**) or heated to 50 °C for 2-4 days (**3,7**) and monitored by NMR spectroscopy. After the reaction catalyzed by **4** had been observed to go to completion by NMR, all volatiles were removed *in vacuo* and the remaining residue was suspended in *n*-pentane. The mixture was filtered through a Celite plug and the solvent was removed *in vacuo* giving triethyl(phenoxy)silane as a colourless oil (16.2 mg, 78% yield).^[S3]

¹H NMR (CD₂Cl₂, [ppm]): δ = 0.75 (6H, quart. of d., CH₂, ³J_{HH} = 8 Hz), 0.96 (9H, t, CH₃, ³J_{HH} = 8 Hz), 6.85 (1H, t, *p*-Ph, ³J_{HH} = 7 Hz), 6.89 - 6.94 (2H, m, *o*/*m*-Ph), 7.07 - 7.15 (2H, m, *o*/*m*-Ph); **¹³C{¹H} (C₆D₆, [ppm]):** δ = 5.4 (3C, s, CH₂), 6.9 (3C, s, CH₃), 120.3 (2C, s, *o*/*m*-Ph), 121.7 (1C, s, *p*-Ph), 129.8 (2C, s, *o*/*m*-Ph), 156.2 (1C, s, *i*-Ph).



2.3 Hydrodefluorination of fluoropentane in the presence of Et₃SiH using **3**, **4** and **7** as catalysts.

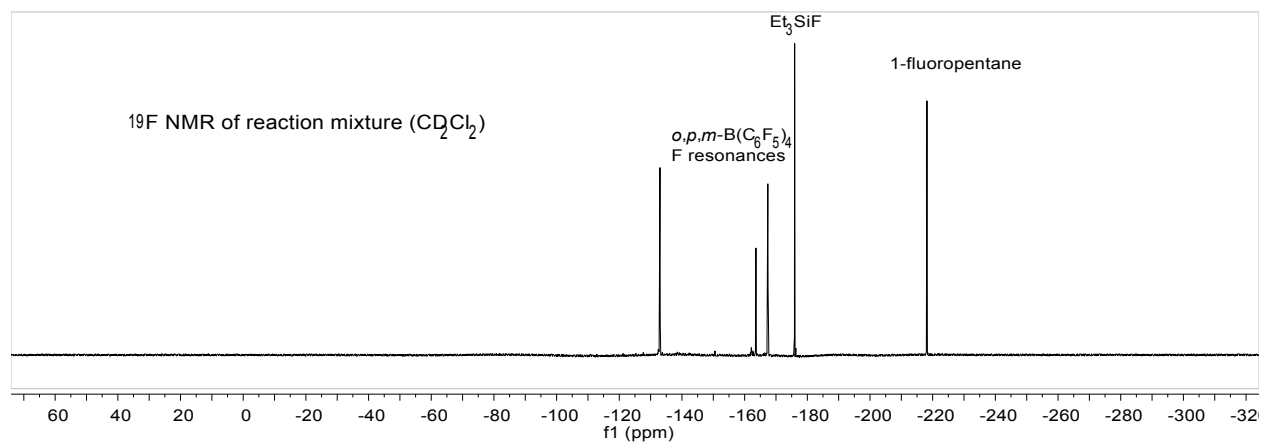


3 : <1% (4 d, 50 °C)

4 : 55% (7 d, rt)

7 : 0% (3 d, 50 °C)

Catalyst **2** (2.1 mg, 2 mol%), **4** (3.9 mg, 2 mol%), or **7** (2.0 mg, 2 mol%) were added to a solution of Et₃SiH (17 μL, 0.10 mmol) and fluoropentane (9 mg, 0.10 mmol) in CD₂Cl₂ (0.7 mL). The reaction mixture containing catalyst **2** was left at ambient temperature and monitored at intervals by ¹H, ¹³C and ¹⁹F NMR spectroscopy over seven days, while the reaction mixtures of **4** and **7** were heated to 50 °C for 4 days. Conversion was determined by means of ¹⁹F NMR spectroscopy (consumption of fluoropentane and formation of Et₃SiF).^[S3]



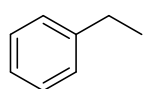
¹⁹F NMR spectrum of reaction with catalyst **4** after 7 d at ambient temperature showing 1-fluoropentane product, unreacted Et₃SiF, and resonances for B(C₆F₅)₄ anion (P-F doublet of dication too small to be seen in this view).

2.4 Hydrodeoxygenation of Ketones

2.4.1 General Procedure for Ketone Hydrodeoxygenation

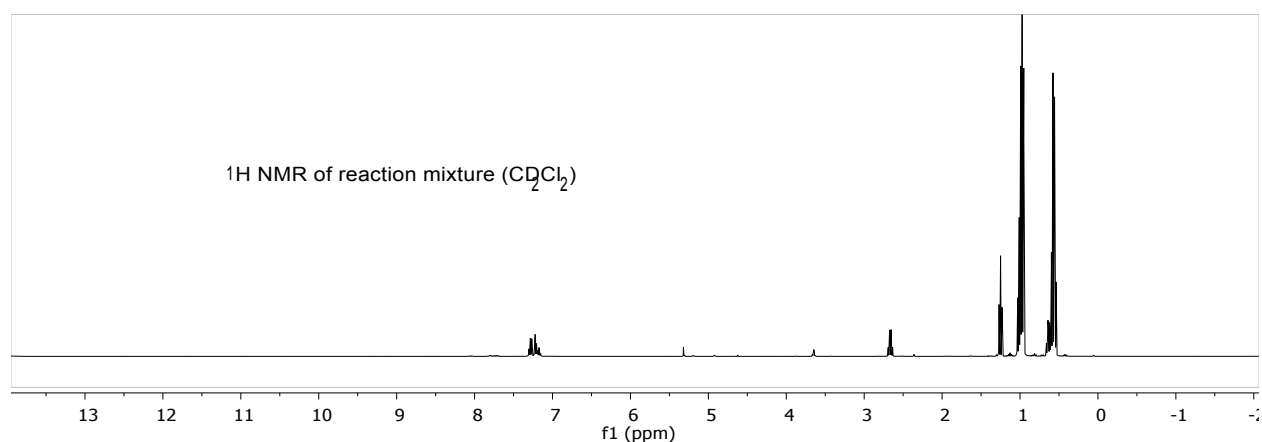
All reactions were carried out under identical conditions on a 0.1 mmol scale. In a glove box the respective catalysts (2 mol%, **3**: 2.1 mg, **4**: 3.9 mg) were added to a solution of Et₃SiH (0.21 mmol – 2.1 Eq) in CD₂Cl₂ (0.7 mL). 0.10 mmol (one equivalent) of the respective substrate was then added. The reaction mixture was transferred to a NMR tube, sealed and monitored by ¹H NMR ¹³C NMR spectroscopy in all cases as well as ¹⁹F NMR spectroscopy in the case of 4-fluorobenzophenone. When catalyst **4** was used >90% deoxygenation was obtained for most substrates. 1-benzyl-4-methoxybenzene was isolated by filtering the reaction mixture through Celite and removing bis(triethylsilyl) *in vacuo*. For other samples toluene was added as an internal standard to determine degree of conversion after the times reported herein. The bis(triethylsilyl) ether by-product can be observed in the spectra of the reaction mixtures.

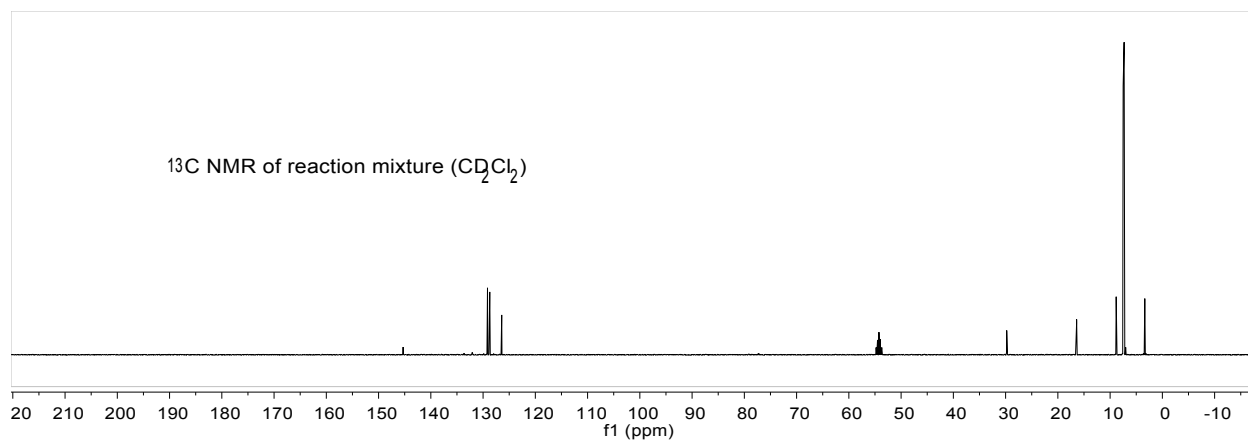
2.4.2 Ethylbenzene [S4]



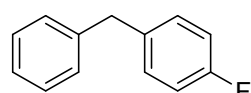
¹H NMR (400 MHz, CD₂Cl₂): δ = 7.26 (m, 5H); 2.70 (q, ³J_{HH} = 8 Hz, 2H); 1.29 (t, ³J_{HH} = 8 Hz, 3H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 145.3; 129.2; 128.7; 126.4;

29.8; 16.4 ppm.

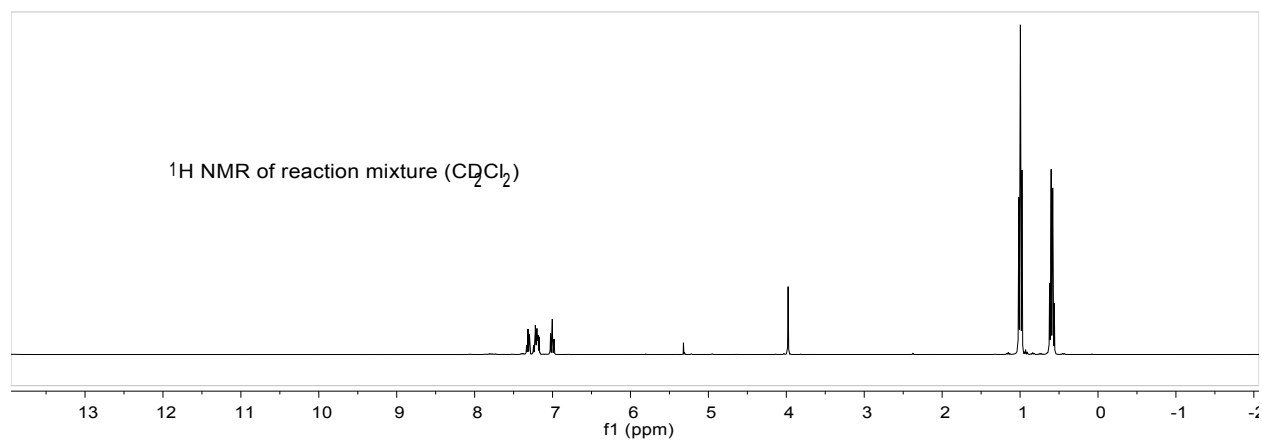


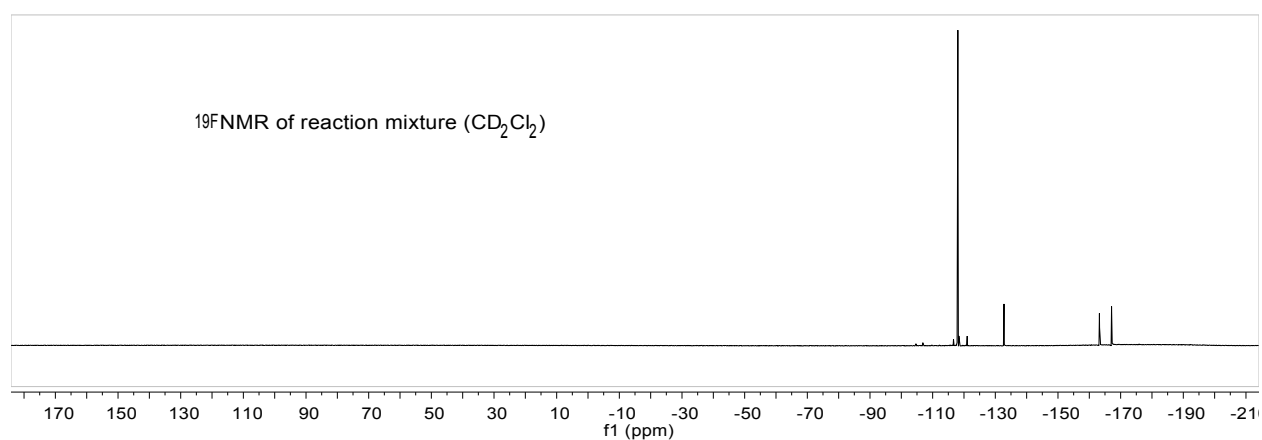
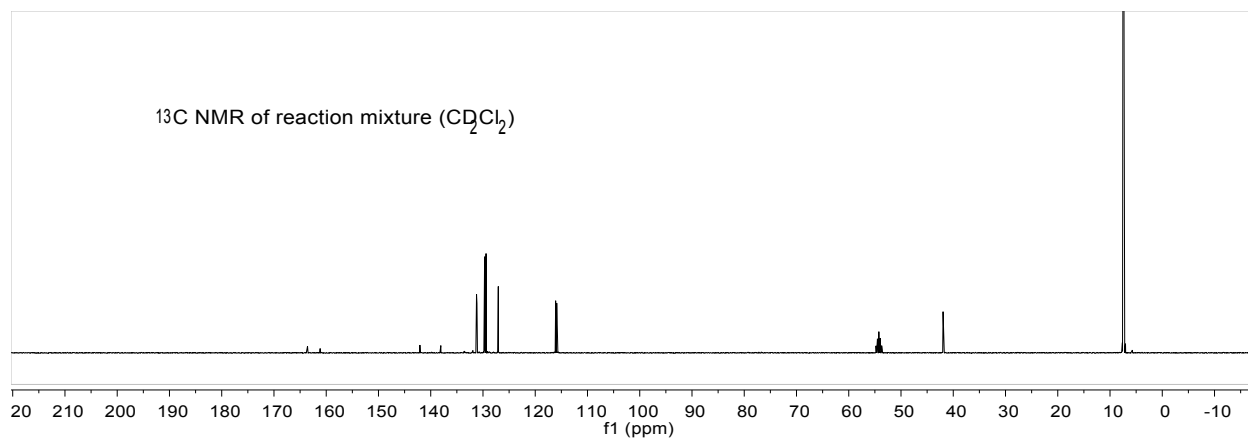


2.4.3 1-Benzyl-4-fluorobenzene^[S4]

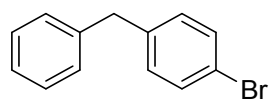


¹H NMR (500 MHz, CD₂Cl₂): δ = 7.30 (m, 2H); 7.20 (m, 5H); 7.00 (m, 2H); 3.97 (s, 2H); ¹³C NMR (126 MHz, CD₂Cl₂): δ = 162.0 (d, ¹J_{CF} = 243 Hz); 141.8; 137.8; 130.9; 129.3 (d, ²J_{CF} = 34 Hz); 126.8; 115.7 (d, ³J_{CF} = 21 Hz); 41.6; ¹⁹F NMR (376 MHz, CD₂Cl₂): δ = -118.1 (s) ppm.

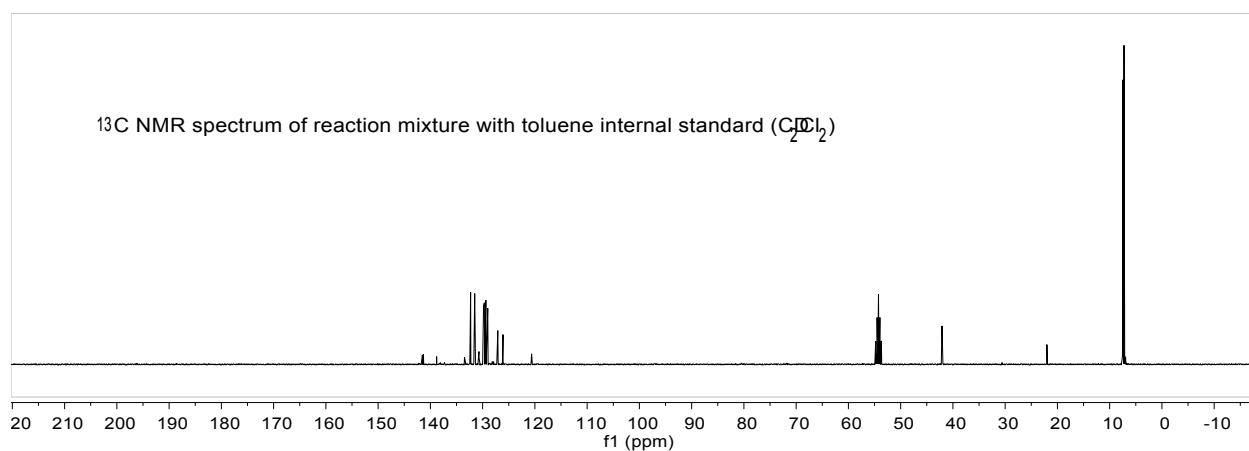
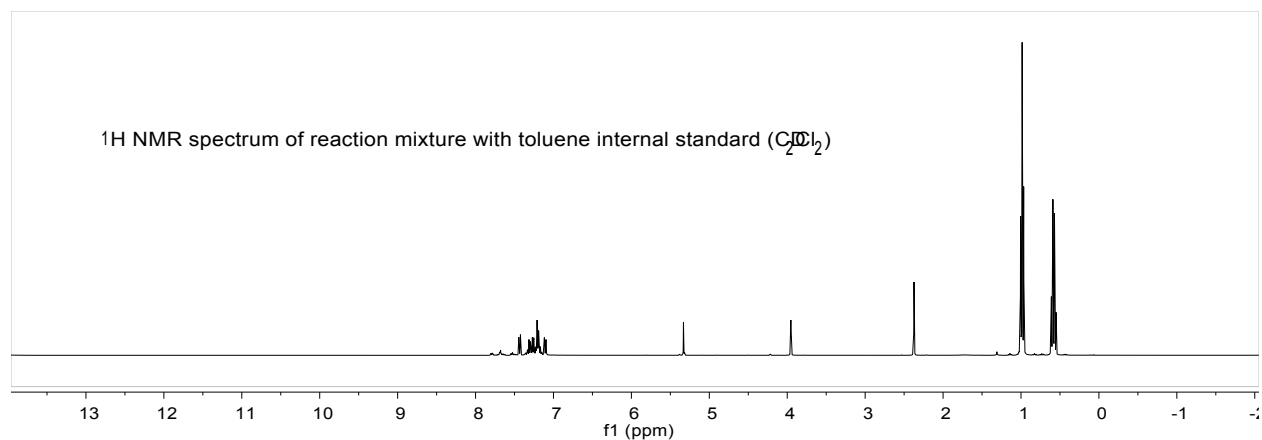




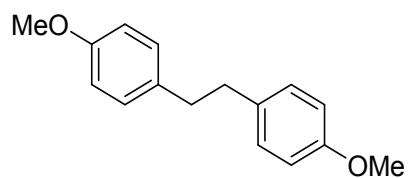
2.4.4 1-Benzyl-4-bromobenzene^[S4]



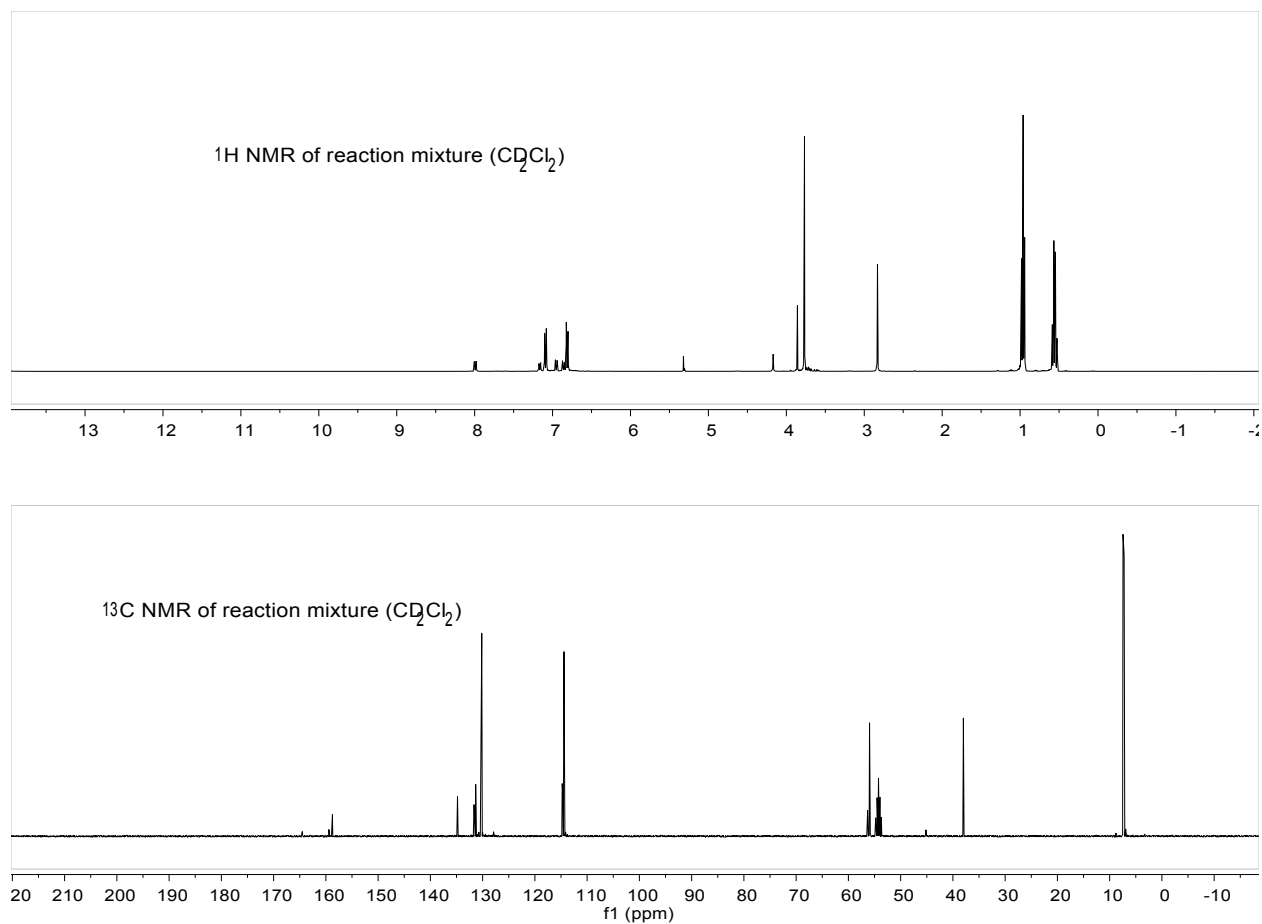
¹H NMR (500 MHz, CD₂Cl₂): δ = 7.43 (m, 2H); 7.30 (m, 2H); 7.22 (m, 1H); 7.20 (m, 2H); 7.11 (m, 2H); 3.94 (s, 2H); ¹³C NMR (126 MHz, CD₂Cl₂): δ = 141.5; 141.3; 132.3; 131.4; 129.7; 129.4; 127.1; 120.6; 42.0 ppm.



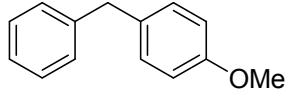
2.4.5 1,2-Bis(4-methoxyphenyl)ethane^[S4]

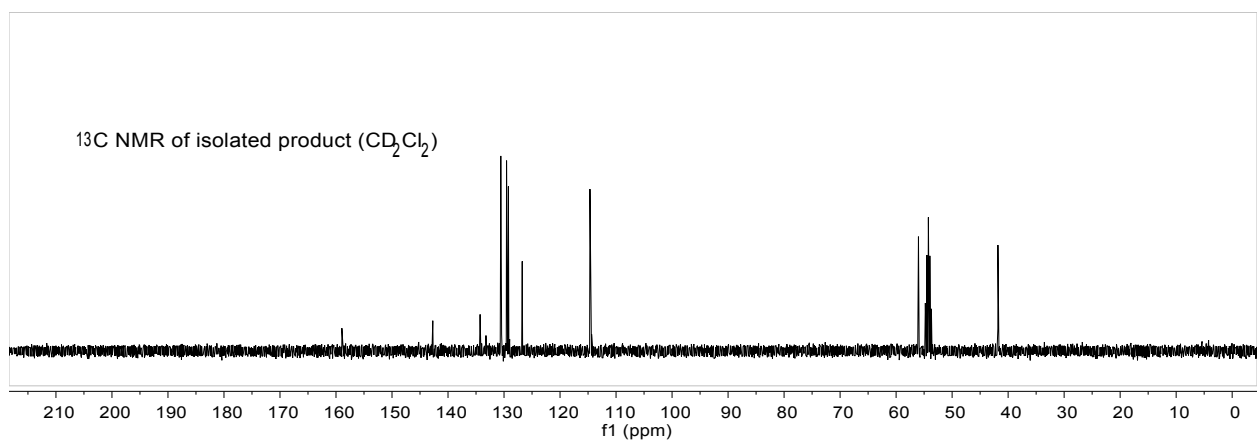
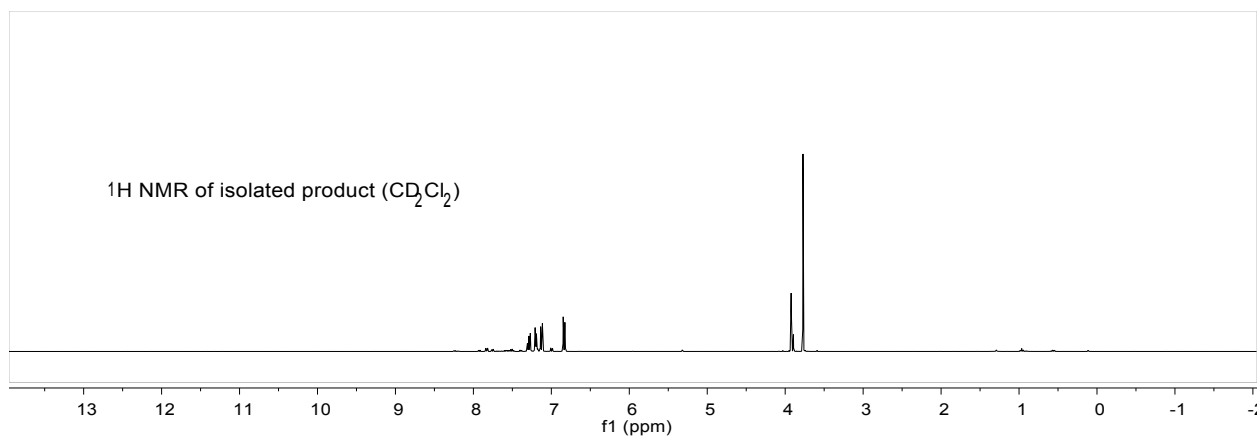


¹H NMR (500 MHz, CD₂Cl₂): δ = 7.09 (m, 4H); 6.81 (m, 4H); 3.76 (s, 6H); 2.83 (s, 4H); **¹³C NMR (126 MHz, CD₂Cl₂):** δ = 158.8; 134.7; 130.2; 114.4; 55.4; 38.0 ppm. **DART MS:** m/z: 260.16538 (calcd. for M+NH₄⁺: 260.16505).

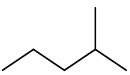


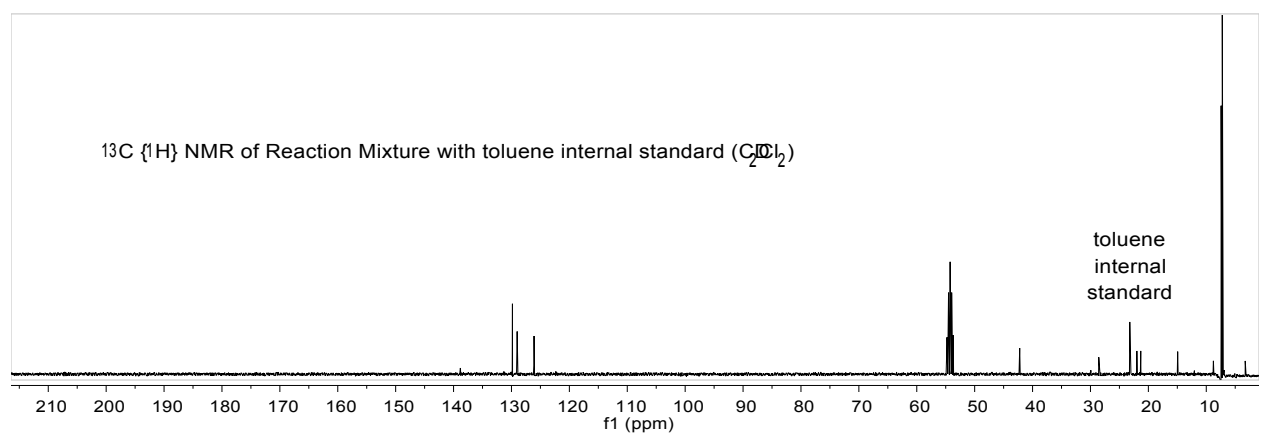
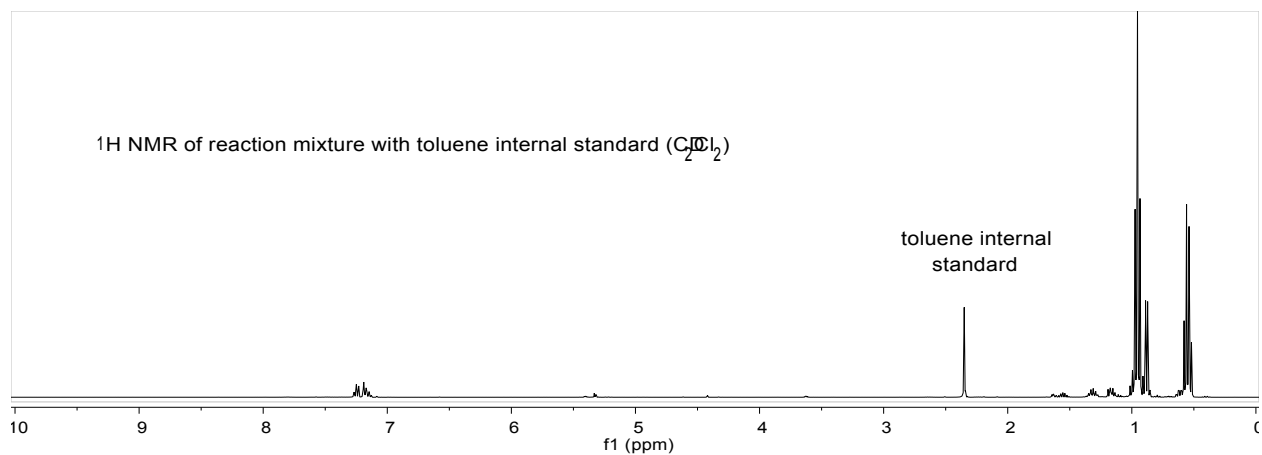
2.4.6 1-Benzyl-4-methoxybenzene^[S4]


Isolated Yield = 81%. ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.28 (m, 2H); 7.19 (m, 3H); 7.12 (m, 2H); 6.84 (m, 2H); 3.92 (s, 2H); 3.77 (s, 3H); **¹³C NMR (126 MHz, CD₂Cl₂):** δ = 158.9; 142.7; 134.3; 130.6; 129.5; 129.2; 126.7; 114.6; 56.0; 41.8 ppm. **DART MS:** m/z: 216.13914 (calcd. for M+NH₄⁺: 216.13884).

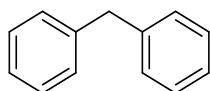


2.4.7 Isopentane^[S4]


¹H NMR (400 MHz, CD₂Cl₂): δ = 1.55 (m, 1H); 1.30 (m, 2H); 1.17 (m, 2H), 0.88 (d, $^3J_{\text{HH}}$ = 6.8 Hz 6H); 0.87 (m, 3H overlapping d); ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ = 42.0; 28.3; 23.0; 21.8; 14.7.



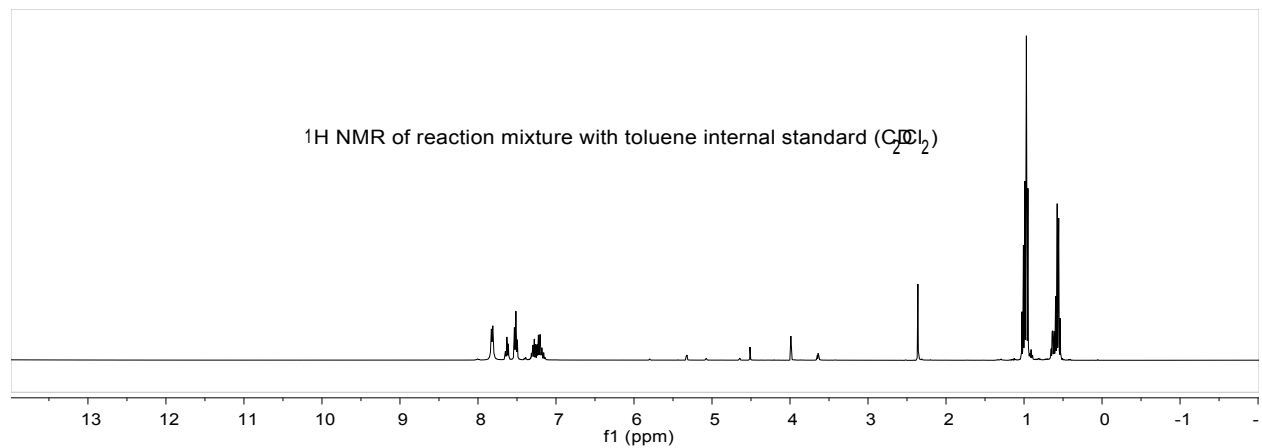
2.4.8 Diphenylmethane ^[S4]

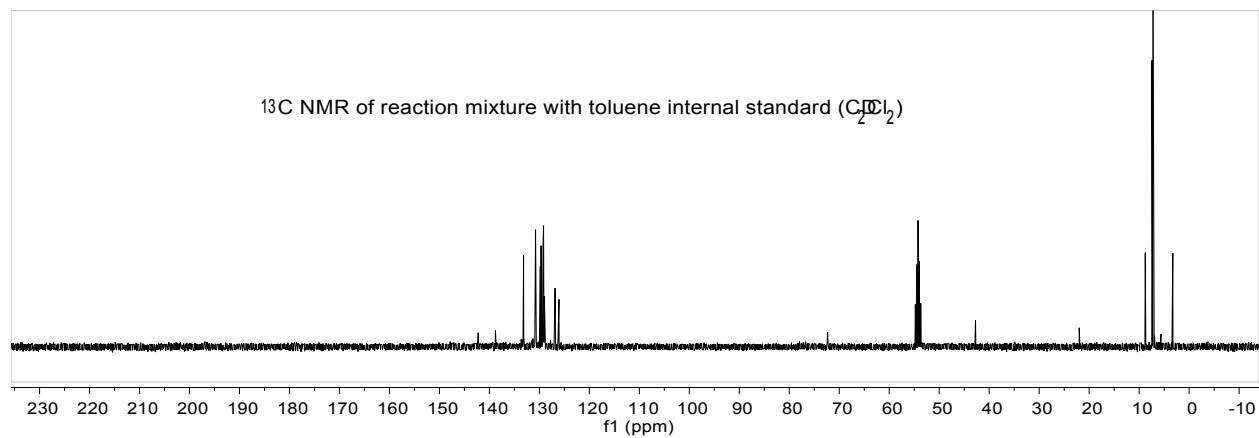


^1H NMR (500 MHz, CD_2Cl_2): $\delta = 7.29$ (m, 4H); 7.20 (m, 6H); 3.98 (s, 2H);

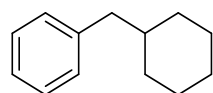
$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): $\delta = 141.4$; 128.8; 128.4; 126.0; 41.9 ppm.

DART MS: m/z: (calcd. for $\text{M}+\text{NH}_4^+$: 186.12827).





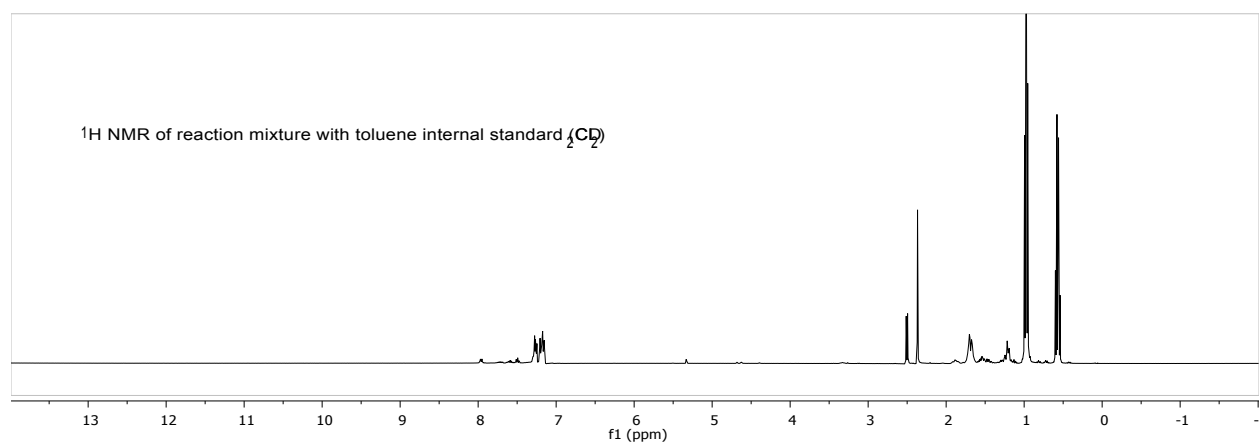
2.4.9 Phenylcyclohexylmethane^[S4]

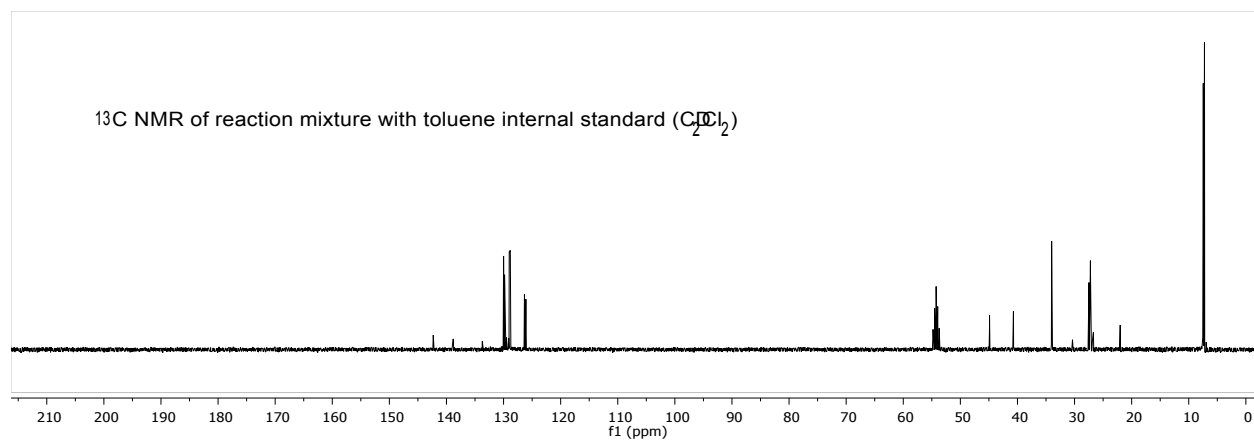


¹H NMR (500 MHz, CD₂Cl₂): δ = 7.27 (m, 2H); 7.18 (m, 3H); 2.50 (d, 2H, ¹J_{HH} = 7.1Hz); 1.89 (m, H); 1.69 (m, 6H); 1.51 (m, 2H); 1.21 (m, 2H) ¹³C{¹H}

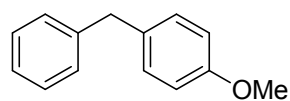
NMR (126 MHz, CD₂Cl₂): δ = 141.4; 128.8; 128.4; 126.0; 41.9 ppm. EI MS:

m/z: 174.1405 (calcd. for M⁺: 174.1409).

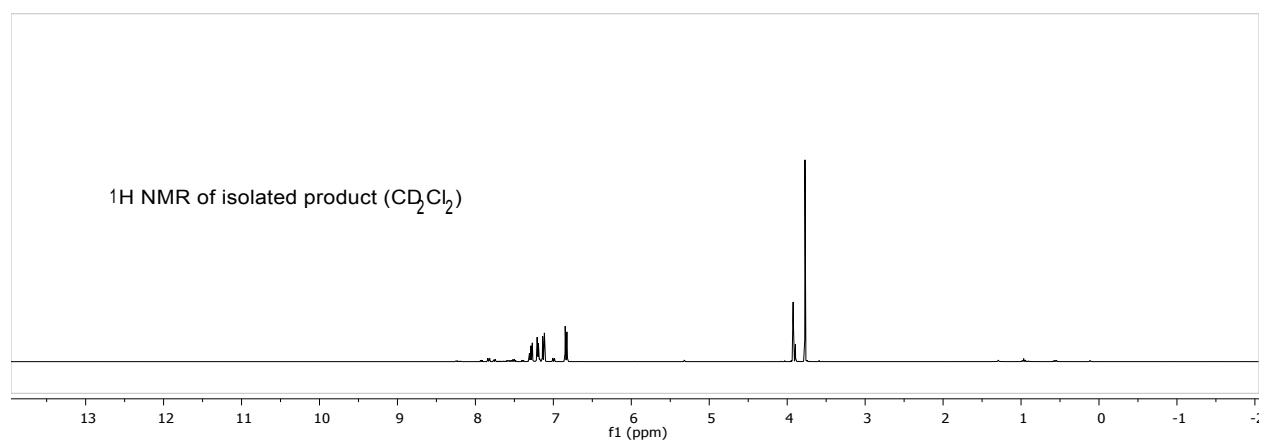


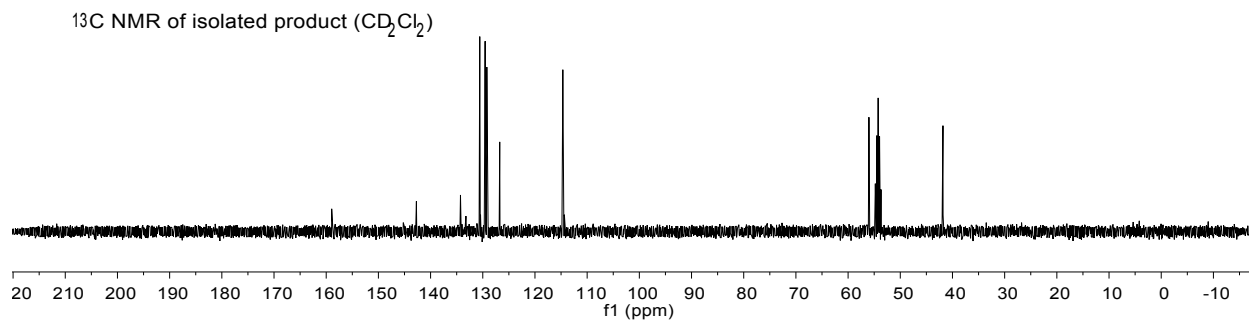


2.4.10 1-Benzyl-4-methoxybenzene^[S4]

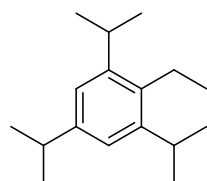


Isolated Yield = 80%. ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.28 (m, 2H); 7.19 (m, 3H); 7.12 (m, 2H); 6.84 (m, 2H); 3.92 (s, 2H); 3.77 (s, 3H); **¹³C NMR (126 MHz, CD₂Cl₂):** δ = 158.9; 142.7; 134.2; 130.5; 129.5; 129.2; 126.7; 114.6; 55.7; 41.5 ppm. **DART MS: m/z: 216.13914 (calcd. for M+NH₄⁺: 216.13884).**

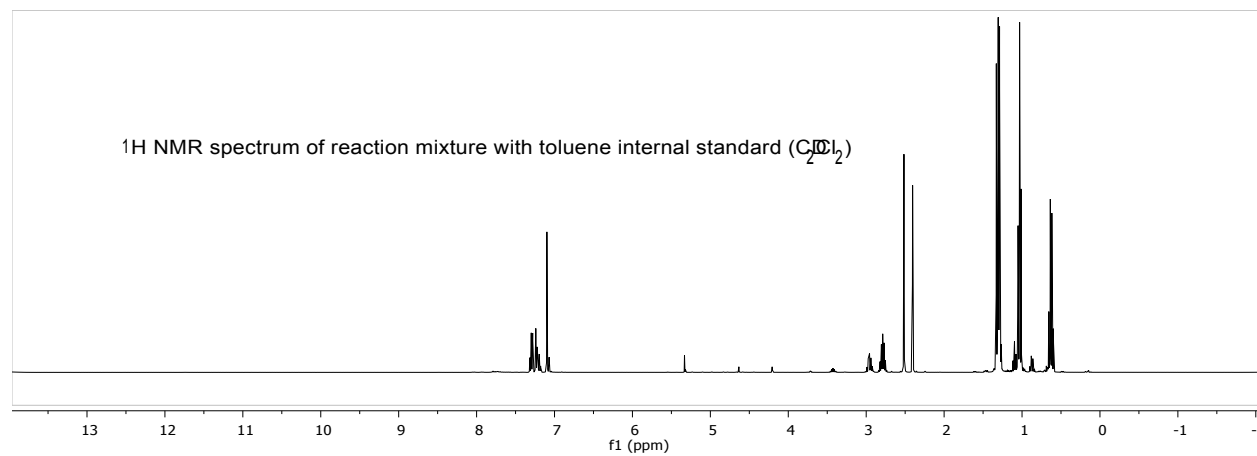


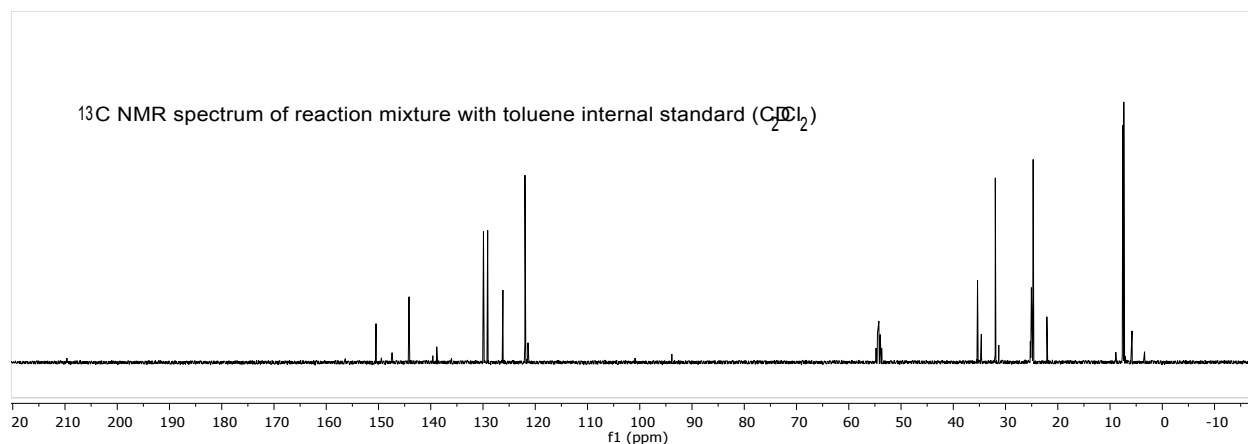


2.4.11 1-Ethyl-2,4,6-triisopropylbenzene^[S5]



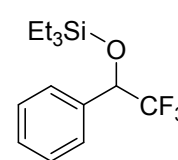
¹H NMR (400 MHz, CD₂Cl₂): δ = 7.10 (s, 2H); 2.95 (sept, ³J_{HH} = 7 Hz, 1H); 2.79 (sept, ³J_{HH} = 7 Hz, 2H); 7.12 (m, 2H); 1.32 (d, ³J_{HH} = 7 Hz, 6H); 1.30 (d, ³J_{HH} = 7 Hz, 6H); ¹³C NMR (126 MHz, CD₂Cl₂): δ = 150.5; 144.1; 122.0; 35.4; 32.0; 25.0 (br); 24.7

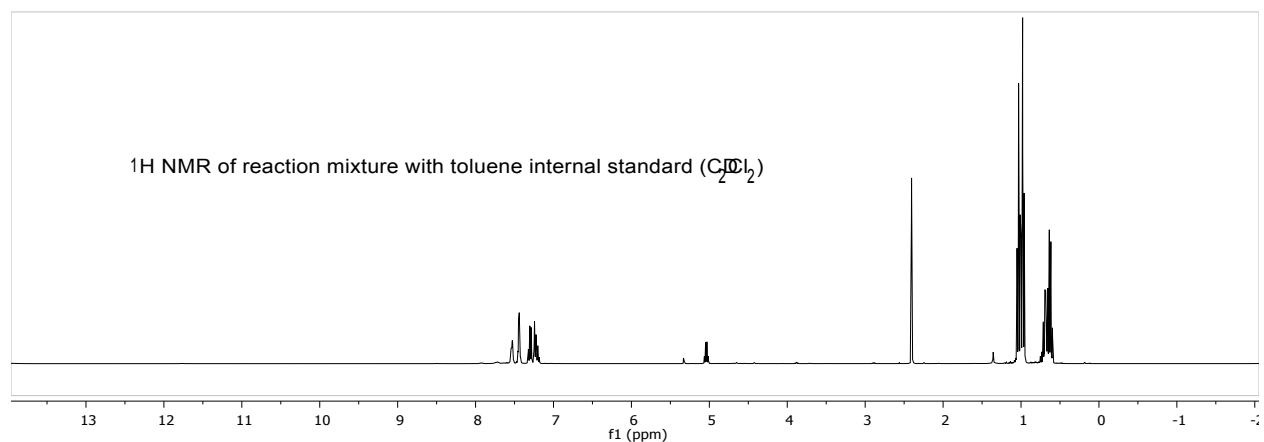


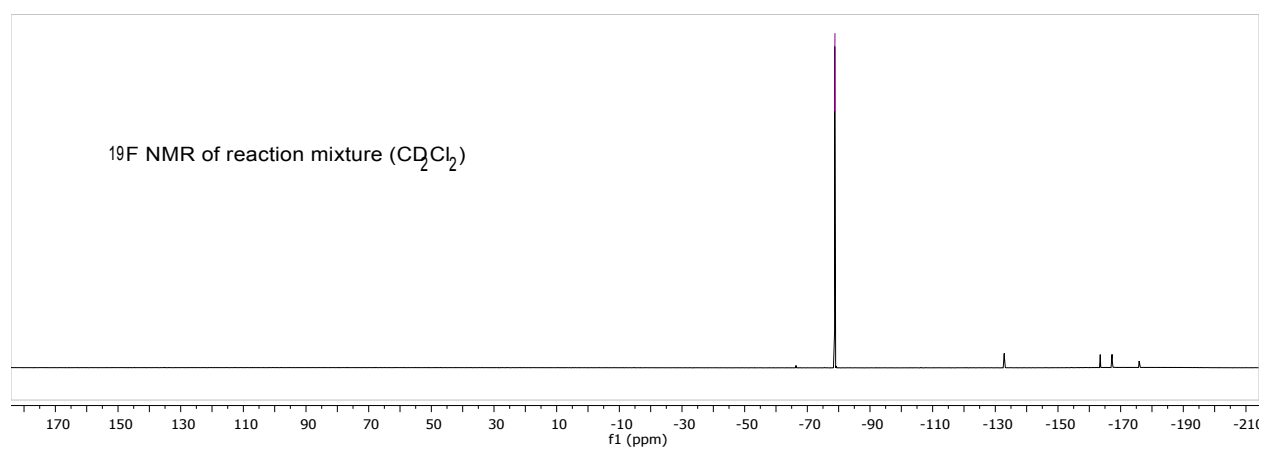
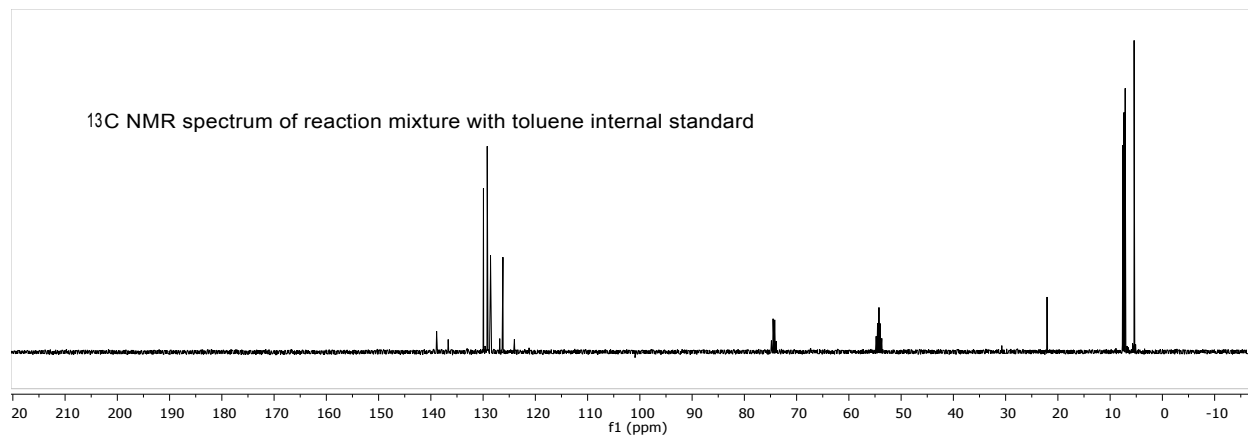


2.5 Hydrosilylation of 2,2,2-trifluoroacetophenone

Triethyl(2,2,2-trifluoro-1-phenylethoxy)silane^[S4]


¹H NMR (400 MHz, CD₂Cl₂): δ = 7.53 (m, 2H); 7.44 (m, 3H); 5.04 (q, ³J_{HF} = 7 Hz, 1H); 0.98 (t, ³J_{HH} = 8 Hz, 9H); 0.63 (q, ³J_{HH} = 8 Hz, 6H); ¹³C NMR (126 MHz, CD₂Cl₂): δ = 136.7; 129.6; 128.8; 128.1; 124.9 (q, ¹J_{CF} = 282 Hz); 73.9 (q, ²J_{CF} = 32 Hz); 6.7, 4.9; ¹⁹F NMR (564 MHz, CD₂Cl₂): δ = -78.8 (d, ³J_{HF} = 7 Hz);. **DART MS:** m/z: 308.16629 (calcd. for M+NH₄⁺: 308.165751).





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- [S1] G. P. Sollott, H. E. Mertwoy, S. Portnoy and J. L. Snead, *Journal of Organic Chemistry*, 1963, **28**, 1090-1092. G. Marr and T. Hunt, *Journal of the Chemical Society C: Organic*, 1969, 1070-1072.
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- [S3] M.H. Holthausen, R.R. Hiranandani and D.W. Stephan *Chem. Sci.*, 2015, **6**, 2016-2021.
- [S4] M. Mehta, M.H. Holthausen, I. Mallov, M. Perez, Z.-W. Qu, S. Grimme and D.W. Stephan *Angew. Chem.*, 2015, **84**, 8250-8254.
- [S5] F.A. Bottino, P. Finochiaro, E. Libertini, A. Reale, and A. Recca *J. Chem. Soc Perkins Transaction. II: Physical. Organic Chemistry*, 1982, **1**, 77-81.