Self-regeneration of a silylium ion catalyst in carbonyl reduction

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Electronic Supplementary Information

Contents

1 General Information

All reactions were performed in flame-dried glassware using a glove box (O_2 < 0.5 ppm, H_2O < 0.5 ppm) or Schlenk techniques under a static pressure of argon. Reactions at low temperatures were performed using an ethanol cooling bath and a cryostat. Liquids or solutions were transferred either with syringes or canulas. Solvents were purified and dried following standard procedures: dichlormethane (CH_2Cl_2) was distilled from calcium hydride, hexane and tetrahydrofuran (THF) were distilled from potassium prior to use. Technical grade solvents for extraction and chromatography (cyclohexane and *tert*-butyl methyl ether) were distilled prior to use. All ketones were obtained from commercial suppliers and purified prior to use by distillation (for liquids) or dried under vacuum ($2 \cdot 10^{-1}$ mbar) (for solids). $[Ph_3C]^+[B(C_6F_5)_4]^-$[1] and *tert*-butylferrocenylmethylsilane[2] were prepared according to reported procedures.

Analytical thin layer chromatography (TLC) was performed on silica gel SIL G-25 glass plates from Macherey-Nagel. Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) by Merck using the indicated solvents. ^1H, ^{13}C, ^{19}F and ^{29}Si NMR spectra were recorded in C_6D_6 on Bruker AV 300, Bruker AV 400 and Varian Inova 500 instruments. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and referenced to the residual solvent resonance as the internal standard (C_6D_6: $\delta = 7.16$ and 128.1 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Infrared (IR) spectra were recorded on a Varian 3100 FT-IR spectrophotometer equipped with an ATR unit and are reported (w = weak, m = medium, s = strong) in wavenumbers (cm^{-1}). Gas liquid chromatography (GLC) was performed on a Shimadzu GC-17A gas chromatograph equipped with a SE-54 capillary column (30 m × 0.32 mm, 0.25 μm film thickness) by CS-Chromatographie Service using the following program: N_2 carrier gas, injection temperature 250 °C, detector temperature 300 °C; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 5 min. Mass spectral data as well as elemental analysis were obtained from the Analytical Facility at the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster.

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[1] a) C. Wang, G. Erker, G. Kehr and R. Fröhlich, *Organometallics*, 2005, **24**, 4760–4773; b) J. B. Lambert, L. J. Lin and S. Keinan, *Org. Biomol. Chem.*, 2003, **1**, 2559–2565.

[2] H. F. T. Klare and M. Oestreich, *Angew. Chem. Int. Ed.*, 2009, **48**, 9077–9079.

2 Experimental Details

2.1 General Procedure for the Silylium Ion-Catalysed Carbonyl Reduction

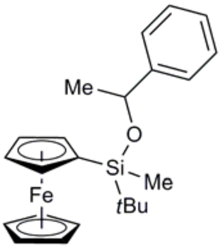
In a glove-box, a flame-dried 10-mL Schlenk tube equipped with a magnetic stir bar is charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (9.2 mg, 0.010 mmol, 5.0 mol%). The Schlenk tube is transferred to a fume cupboard and connected to an argon–vacuum manifold. Addition of dry CH_2Cl_2 (1.0 mL) results in a yellow solution, which is subsequently cooled to –60 °C using an ethanol cooling bath and a cryostat. After silane addition (**10**, 11 mg, 0.040 mmol, 0.20 equiv.), the now brown solution is stirred for 10 min, followed by successive addition of the carbonyl compound **2** (0.20 mmol, 1.0 equiv.) and the silane **10** (57 mg, 0.20 mmol, 1.0 equiv.) dissolved in dry CH_2Cl_2 (0.5 mL each). The reaction mixture is maintained at –60 °C for 2½ h, and the reaction is then terminated by the addition of dry hexane (10 mL), pre-cooled to –60 °C. Filtration over a small pad of Celite® and evaporation of the solvents under reduced pressure affords crude **13**, which is further purified by flash chromatography on silica gel using cyclohexane as eluent. The diastereomeric ratio is determined by GLC analysis prior to purification. All analytical data, unless stated otherwise, is reported for the mixture of diastereomers.

2.2 Control Experiments Concerning the Ipso-Substitution at Ferrocene

Treatment of acetophenone under standard conditions at –45 °C: According to the general procedure, the silylium ion catalyst was prepared at –45 °C. After the successive addition of acetophenone (**2a**, 24 mg, 0.20 mmol, 1.0 equiv.) and silane **10** (57 mg, 0.20 mmol, 1.0 equiv.), dissolved in dry CH_2Cl_2 (0.5 mL each), the reaction mixture was maintained at –45 °C for 1 h and the reaction was then terminated by the addition of dry hexane, pre-cooled to –45 °C, and filtered over a small pad of Celite®. The solvents were evaporated under reduced pressure and the residue was further purified by flash chromatography on silica gel using cyclohexane as eluent.

Treatment of the silicon ether derived from acetophenone under standard conditions at –45 °C: According to the general procedure, the silylium ion catalyst was prepared at –45 °C. A solution of silicon ether **13a** (81 mg, 0.20 mmol, 1.0 equiv.) in dry CH_2Cl_2 (1 mL) was added and the reaction mixture was maintained at –45 °C for 2½ h. The reaction was terminated as described above, the solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using cyclohexane as eluent.

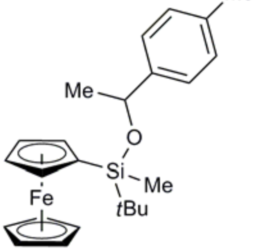
3 Characterisation Data for Compounds 13a, 13f–13p and 14a



13a

$C_{23}H_{30}FeOSi$
M = 406.41 g/mol

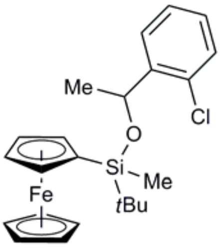
***tert*-Butylferrocenylmethyl(1-phenylethyloxy)silane (13a)**: Prepared from acetophenone (**2a**, 24.0 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product **13a** (66 mg, 82%) as an orange oil. $\boldsymbol{R_f}$ = 0.23 (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 51:49). **GLC** (SE-54): t_R = 23.8 min (major diastereomer), 24.0 min (minor diastereomer). **IR** (ATR): $\tilde{\nu}$ = 2956 (w), 2928 (w), 2890 (w), 2855 (w), 2361 (m), 2342 (m), 1252 (m), 1163 (m), 1092 (s), 1035 (s), 958 (m), 819 (s), 801 (s), 777 (s), 753 (s), 698 (s) cm^{-1}. **HRMS** (ESI) calculated for $C_{23}H_{30}FeOSi$ ($[M]^+$): 406.1410; Found: 406.1411. **Anal. Calcd** for $C_{23}H_{30}FeOSi$: C, 67.97; H, 7.44; Found: C, 68.06; H, 7.44. NMR data for diastereomeric mixture: **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.25 (s, 3H), 0.37 (s, 3H), 1.00 (s, 9H), 1.04 (s, 9H), 1.46 (d, *J* = 6.3 Hz, 3H), 1.50 (d, *J* = 6.3 Hz, 3H), 3.88 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 3.93 (m, 6H), 4.07 (s, 5H), 4.09 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 4.13–4.15 (m, 2H), 4.19 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 4.21 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 4.24 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 5.18 (q, *J* = 6.3 Hz, 1H), 5.22 (q, *J* = 6.3 Hz, 1H), 7.08–7.13 (m, 2H), 7.21–7.26 (m, 4H), 7.41–7.45 (m, 4H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –5.1, –4.7, 19.2, 19.3, 26.4, 26.5, 28.1, 28.1, 68.1, 68.2, 68.7, 68.8, 71.0, 71.0, 71.1, 71.2, 71.6, 71.7, 73.2, 73.5, 74.2, 74.3, 125.5, 125.6, 127.2, 127.3, 128.6, 128.6, 147.3, 147.4 ppm. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 11.0, 11.1 ppm.



13f

$C_{24}H_{32}FeOSi$
M = 420.44 g/mol

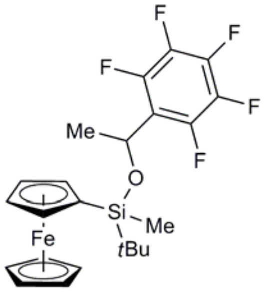
***tert*-Butylferrocenylmethyl[1-(4-methylphenyl)ethyloxy]silane (13f)**: Prepared from 4-methylacetophenone (**2f**, 26.8 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product **13f** (8 mg, 10%) as an orange oil. ***R*f** = 0.26 (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 52:48). **GLC** (SE-54): t_R = 23.8 min (minor diastereomer), 24.0 min (major diastereomer). **IR** (ATR): $\tilde{\nu}$ = 3096 (w), 2955 (w), 2927 (w), 2877 (w), 2855 (w), 2360 (w), 2343 (w), 1515 (w), 1472 (w), 1367 (w), 1251 (m), 1163 (m), 1093 (s), 1035 (s), 1003 (m), 958 (m), 816 (s), 793 (m), 776 (s), 756 (m), 719 (w), 700 (m), 597 (m) cm^{-1}. **HRMS** (ESI) calculated for $C_{24}H_{32}FeOSi$ ([M]$^+$): 420.1567; Found: 420.1557. **Anal. Calcd** for $C_{24}H_{32}FeOSi$: C, 68.56; H, 7.67; Found: C, 68.73; H, 7.68. NMR data for diastereomeric mixture: **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.28 (s, 3H), 0.39 (s, 3H), 1.02 (s, 9H), 1.06 (s, 9H), 1.49 (d, *J* = 6.3 Hz, 3H), 1.54 (d, *J* = 6.3 Hz, 3H), 2.13 (s, 3H), 2.15 (s, 3H), 3.90 (ddd, *J* = 2.3 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 3.94 (ddd, *J* = 2.3 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 3.96 (s, 5H), 4.09 (s, 5H), 4.10 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.1 Hz, 1H), 4.14 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.1 Hz, 1H), 4.17 (ddd, *J* = 2.3 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 4.20 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.1 Hz, 1H), 4.22 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.1 Hz, 1H), 4.27 (ddd, *J* = 2.3 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 5.20 (q, *J* = 6.3 Hz, 1H), 5.23 (q, *J* = 6.3 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 7.7, 2H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –5.1, –4.8, 19.2, 19.3, 21.1, 21.1, 26.4, 26.5, 28.1, 28.2, 68.2, 68.3, 68.7, 68.8, 70.9, 71.0, 71.1, 71.2, 71.5, 71.6, 73.2, 73.5, 74.2, 74.3, 125.5, 125.5, 129.3, 129.3, 136.5, 136.5, 144.4, 144.5 ppm. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 10.8, 10.9 ppm.



13g

$C_{23}H_{29}ClFeOSi$
M = 440.86 g/mol

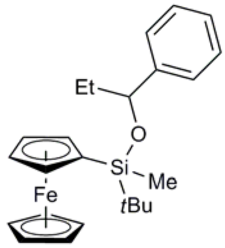
***tert*-Butylferrocenylmethyl[1-(2-chlorophenyl)ethyloxy]silane (13g)**: Prepared from 2-chloroacetophenone (**2g**, 30.9 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product **13g** (85.5 mg, 97%) as an orange oil. ***R*f** = 0.33 (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 78:22). **GLC** (SE-54): t_R = 24.4 min (minor diastereomer), 24.6 min (major diastereomer). **IR** (ATR): $\tilde{\nu}$ = 3097 (w), 2956 (w), 2928 (w), 2893 (w), 2855 (w), 2360 (w), 1472 (m), 1438 (w), 1421 (w), 1368 (w), 1253 (m), 1163 (m), 1133 (m), 1096 (s), 1035 (s), 956 (s), 820 (s), 805 (s), 778 (s), 752 (s), 703 (m) cm^{-1}. **HRMS** (ESI) calculated for $C_{23}H_{29}ClFeOSi$ ([M]$^+$): 440.1021; Found: 440.1020. **Anal. Calcd** for $C_{23}H_{29}ClFeOSi$: C, 62.66; H, 6.63; Found: C, 62.60; H, 6.68. NMR data for major diastereomer: **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.25 (s, 3H), 1.00 (s, 9H), 1.57 (d, *J* = 6.2 Hz, 3H), 3.91 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 4.11 (s, 5H), 4.19 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 4.21 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 4.28 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 5.78 (q, *J* = 6.2 Hz, 1H), 6.80 (ddd, *J* = 7.7 Hz, *J* = 7.7 Hz, *J* = 1.7 Hz, 1H), 7.03–7.10 (m, 1H), 7.13–7.16 (m, 1H), 7.86 (dd, *J* = 7.8 Hz, *J* = 1.7 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –5.0, 19.1, 25.9, 26.4, 67.6, 68.3, 68.8, 71.1, 71.3, 73.4, 74.0, 127.3, 127.5, 128.3, 129.4, 131.0, 144.8 ppm. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 12.2 ppm. NMR data for minor diastereomer: **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.40 (s, 3H), 1.03 (s, 9H), 1.52 (d, *J* = 6.2 Hz, 3H), 3.86 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 3.97 (s, 5H), 4.05–4.09 (m, 2H), 4.12 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 5.73 (q, *J* = 6.2 Hz, 1H), 6.80 (ddd, *J* = 7.7 Hz, *J* = 7.7 Hz, *J* = 1.7 Hz, 1H), 7.03–7.10 (m, 1H), 7.13–7.16 (m, 1H), 7.91 (dd, *J* = 7.8 Hz, *J* = 1.7 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –5.3, 19.1, 26.0, 26.3, 67.8, 68.4, 68.6, 70.9, 71.2, 73.1, 74.1, 127.4, 127.4, 128.4, 129.4, 131.0, 144.8 ppm. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 12.2 ppm.



13h

$C_{23}H_{25}F_5FeOSi$
M = 496.37 g/mol

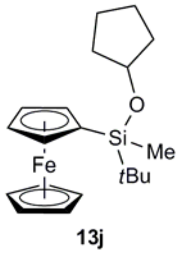
***tert*-Butylferrocenylmethyl(1-pentafluorophenylethyloxy)silane (13h)**: Prepared from pentafluoroacetophenone (**2h**, 42.0 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product **13h** (84.6 mg, 85%) as an orange oil. ***R*$_f$** = 0.33 (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 52:48). **GLC** (SE-54): t_R = 21.8 min (major diastereomer), 22.1 min (minor diastereomer). **IR** (ATR): $\tilde{\nu}$ = 3097 (w), 2932 (w), 2894 (w), 2858 (w), 2362 (w), 1653 (w), 1520 (m), 1500 (s), 1473 (w), 1420 (w), 1375 (w), 1302 (w), 1254 (w), 1151 (m), 1133 (m), 1105 (m), 1056 (m), 1036 (m), 987 (m), 964 (s), 891 (m), 821 (m), 804 (m), 775 (m), 746 (m), 698 (w) cm^{-1}. **HRMS** (ESI) calculated for $C_{23}H_{25}F_5FeOSi$ ([M]$^+$): 496.0939; Found: 496.0931. NMR data for diastereomeric mixture: **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.22 (s, 3H), 0.29 (s, 3H), 0.95 (s, 9H), 1.00 (s, 9H), 1.44 (d, *J* = 6.6 Hz, 3H), 1.46 (d, *J* = 6.6 Hz, 3H), 3.83, (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 3.92 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 3.95 (s, 5H), 4.06 (m, 6H), 4.08 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 4. 09 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 4.11 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 4.15 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 4.18 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 5.43 (q, *J* = 6.6 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –5.5, –5.3, 19.0, 19.1, 23.9, 24.0, 26.3, 26.3, 63.1, 63.2, 66.9, 67.0, 68.6, 68.7, 71.0, 71.1, 71.4, 71.5, 73.2, 73.3, 73.7, 73.8, 119.1 (m), 136.5 (m), 139.0 (m), 141.7 (m), 143.5 (m), 146.0 (m) ppm (two fluorine-substituted carbon atoms not detected). **^{19}F NMR** (282 MHz, C_6D_6): δ = –162.4 (2×), –156.3, –156.1, –143.6, –143.4. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 12.7, 13.1 ppm.



13i

$C_{24}H_{32}FeOSi$
M = 420.44 g/mol

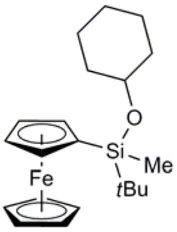
***tert*-Butylferrocenylmethyl(1-phenylpropyloxy)silane (13i)**: Prepared from propiophenone (**2i**, 26.8 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product **13i** (69.2 mg, 82%) as an orange oil. R_f = 0.30 (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 78:22). **GLC** (SE-54): t_R = 23.7 min (minor diastereomer), 23.8 min (major diastereomer). **IR** (ATR): $\tilde{\nu}$ = 3087 (w), 2958 (w), 2929 (w), 2883 (w), 2855 (w), 1472 (w), 1459 (w), 1420 (w), 1388 (w), 1361 (w), 1252 (m), 1162 (m), 1106 (m), 1084 (m), 1059 (m), 1035 (m), 1004 (m), 921 (w), 896 (w), 845 (m), 819 (s), 775 (s), 752 (m), 699 (s) cm^{-1}. **HRMS** (ESI) calculated for $C_{24}H_{32}FeOSi$ ($[M]^+$): 420.1567; Found: 420.1554. **Anal. Calcd** for $C_{24}H_{32}FeOSi$: C, 68.56; H, 7.67; Found: C, 68.64; H, 7.87. NMR data for major diastereomer: **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.19 (s, 3H), 0.92 (t, *J* = 7.5 Hz, 3H), 1.03 (s, 9H), 1.76–1.93 (m, 2H), 3.92 (ddd, *J* = 2.3 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 4.08 (s, 5H), 4.19 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.1 Hz, 1H), 4.22 (ddd, *J* = 2,3 Hz, *J* = 2.3 Hz, *J* = 1.1 Hz, 1H), 4.27 (ddd, *J* = 2.3 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 5.03 (t, *J* = 5.9 Hz, 1H), 7.08–7.13 (m, 1H), 7.20–7.25 (m, 2H), 7.38–7.42 (m, 2H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –4.5, 9.8, 19.2, 26.5, 34.3, 68.1, 68.8, 71.0, 71.3, 73.5, 74.2, 76.6, 126.4, 127.3, 128.4, 145.7 ppm. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 10.8 ppm. NMR data for minor diastereomer: **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.36 (s, 3H), 0.89 (t, *J* = 7.5 Hz, 3H), 1.05 (s, 9H), 1.76–1.93 (m, 2H), 3.87 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 3.93 (s, 5H), 4.06–4.08 (m, 2H), 4.12 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 5.00 (t, *J* = 5.8 Hz, 1H), 7.08–7.13 (m, 1H), 7.20–7.25 (m, 2H), 7.38–7.42 (m, 2H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –4.9, 9.4, 19.4, 26.5, 34.1, 68.2, 68.7, 70.9, 71.1, 73.3, 74.4, 76.5, 126.4, 127.3, 128.4, 145.4 ppm. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 11.1 ppm.



13j

$C_{20}H_{30}FeOSi$
M = 370.38 g/mol

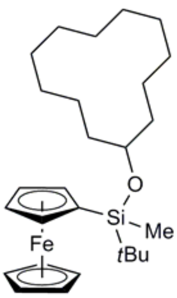
***tert*-Butylferrocenylmethyl(cyclopentyloxy)silane (13j)**: Prepared from cyclopentanone (**2j**, 16.8 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product **13j** (62.6 mg, 85%) as an orange oil. ***R*$_f$** = 0.26 (cyclohexane). **GLC** (SE-54): t_R = 21.1 min. **IR** (ATR): $\tilde{\nu}$ = 3098 (w), 2955 (m), 2928 (m), 2855 (m), 1472 (m), 1422 (w), 1388 (w), 1360 (w), 1251 (m), 1163 (s), 1107 (s), 1051 (s), 1035 (s), 1003 (m), 940 (w), 900 (w), 818 (s), 775 (s), 729 (w), 701 (w) cm^{-1}. **HRMS** (ESI) calculated for $C_{20}H_{30}FeOSi$ ($[M]^+$): 370.1410; Found: 370.1404. **Anal. Calcd** for $C_{20}H_{30}FeOSi$: C, 64.86; H, 8.16; Found: C, 65.14; H, 8.24. **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.36 (s, 3H), 1.01 (s, 9H), 1.44–1.53 (m, 2H), 1.60–1.72 (m, 3H), 1.73–1.78 (m, 1H), 1.79–1.85 (m, 2H), 3.94 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 4.10 (s, 5H), 4.20 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 4.21 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 4.23 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 4.53 (m, 1H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –5.0, 19.1, 23.6, 23.6, 26.5, 36.4, 36.4, 68.7, 68.7, 71.0, 71.1, 73.5, 74.2, 75.1 ppm. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 9.1 ppm.



13k

$C_{21}H_{32}FeOSi$
M = 384.41 g/mol

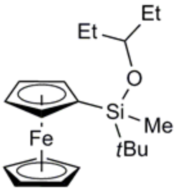
***tert*-Butylferrocenylmethyl(cyclohexyloxy)silane (13k)**: Prepared from cyclohexanone (**2k**, 19.6 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product **13k** (75.4 mg, 95%) as an orange oil. ***R*$_f$** = 0.28 (cyclohexane). **GLC** (SE-54): t_R = 22.2 min. **IR** (ATR): $\tilde{\nu}$ = 2929 (s), 2854 (m), 2360 (m), 2342 (m), 1472 (w), 1449 (w), 1370 (w), 1250 (m), 1163 (m), 1094 (s), 1051 (m), 1034 (m), 1001 (m), 862 (m), 817 (s), 775 (s), 703 (m) cm^{-1}. **HRMS** (ESI) calculated for $C_{21}H_{32}FeOSi$ ($[M]^+$): 384.1567 ; Found: 384.1564. **Anal. Calcd** for $C_{21}H_{32}FeOSi$: C, 65.61; H, 8.39; Found: C, 65.52; H, 8.53. **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.36 (s, 3H), 1.03 (s, 9H), 1.19–1.31 (m, 3H), 1.36–1.41 (m, 1H), 1.45–1.57 (m, 2H), 1.70–1.76 (m, 2H), 1.81–1.90 (m, 2H), 3.94 (ddd, *J* = 2.1 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 4.00 (m, 1H), 4.09 (s, 5H), 4.20 (m, 2H), 4.25 (ddd, *J* = 2.1 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –4.9, 19.2, 24.1, 24.2, 26.1, 26.5, 36.3, 36.3, 68.7, 68.8, 70.9, 71.0, 71.1, 73.5, 74.2 ppm. **^{29}Si NMR:** (60 MHz, C_6D_6): δ = 8.7 ppm.



13l

$C_{27}H_{44}FeOSi$
M = 468.59 g/mol

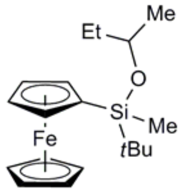
tert*-Butylferrocenylmethyl(cyclododecyloxy)silane (13l)**: Prepared from cyclododecanone (**2l**, 36.5 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product **13l** (81.1 mg, 86%) as an orange solid. **m.p.** = 73 °C. ***R R_f = 0.33 (cyclohexane). **GLC** (SE-54): t_R = 29.1 min. **IR** (ATR): $\tilde{\nu}$ = 3092 (w), 2930 (s), 2855 (s), 2361 (w), 1472 (s), 1419 (w), 1298 (w), 1249 (s), 1097 (s), 1064 (s), 1032 (s), 1003 (m), 970 (w), 935 (w), 866 (w), 815 (w), 771 (s), 737 (m), 702 (w) cm^{-1}. **HRMS** (ESI) calculated for $C_{27}H_{44}FeOSi$ ($[M]^+$): 468.2506; Found: 468.2499. **Anal. Calcd** for $C_{27}H_{44}FeOSi$: C, 69.21; H, 9.46; Found: C, 69.40; H, 9.65. **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.40 (s, 3H), 1.07 (s, 9H), 1.34–1.51 (m, 18H), 1.56–1.67 (m, 2H), 1.73–1.85 (m, 2H), 3.97 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 4.11 (s, 5H), 4.15–4.19 (m, 1H), 4.20 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 4.22 (ddd, *J* = 2.3 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz, 1H), 4.27 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –4.6, 19.3, 20.6, 20.8, 23.2, 23.2, 23.3, 23.4, 25.4, 25.8, 25.8, 26.6, 32.4, 32.6, 68.8, 68.8, 70.9, 71.2, 71.2, 73.5, 74.3 ppm. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 8.3 ppm.



13m

$C_{20}H_{32}FeOSi$
M = 372.40 g/mol

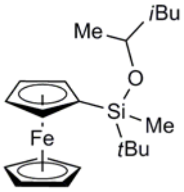
***tert*-Butylferrocenylmethyl(pent-3-yloxy)silane (13m)**: Prepared from 3-pentanone (**2m**, 17.2 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product **13m** (58.7 mg, 79%) as an orange oil. R_f = 0.38 (cyclohexane). **GLC** (SE-54): t_R = 20.9 min. **IR** (ATR): $\tilde{\nu}$ = 2959 (w), 2929 (w), 2878 (w), 2855 (w), 1461 (w), 1251 (m), 1161 (m), 1128 (w), 1107 (m), 1065 (s), 1035 (s), 1003 (s), 818 (s), 775 (s), 731 (m), 695 (w) cm^{-1}. **HRMS** (ESI) calculated for $C_{20}H_{32}FeOSi$ ($[M]^+$): 372.1567; Found: 372.1565. **Anal. Calcd** for $C_{20}H_{32}FeOSi$: C, 64.50; H, 8.66; Found: C, 64.64; H, 8.71. **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.36 (s, 3H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.94 (t, *J* = 7.5 Hz, 3H), 1.05 (s, 9H), 1.51–1.63 (m, 4H), 3.87 (tt, *J* = 5.6 Hz, *J* = 5.7 Hz, 1H), 3.95 (ddd, *J* = 2.3 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 4.08 (s, 5H), 4.19 (ddd, J = 2.3 Hz, J = 2.3 Hz, J = 1.1 Hz, 1H), 4.20 (ddd, J = 2.3 Hz, J = 2.3 Hz, J = 1.1 Hz, 1H), 4.22 (ddd, J = 2.3 Hz, J = 1.1 Hz, J = 1.1 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ =–4.5, 9.5, 9.5, 19.3, 26.7, 28.9, 29.2, 68.7, 68.8, 71.0, 71.1, 73.6, 74.3, 74.7 ppm. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 8.1 ppm.



13n

$C_{19}H_{30}FeOSi$
M = 358.37 g/mol

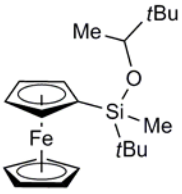
***tert*-Butylferrocenylmethyl(but-2-yloxy)silane (13n)**: Prepared from 2-butanone (**2n**, 14.5 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product **13n** (31.5 mg, 44%) as an orange oil. R_f = 0.28 (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 50:50). **GLC** (SE-54): t_R = 19.2, 19.3 min. **IR** (ATR): $\tilde{\nu}$ = 3097 (w), 2959 (m), 2929 (m), 2880 (w), 2855 (m), 1472 (m), 1422 (w), 1373 (m), 1251 (m), 1163 (m), 1134 (w), 1107 (s), 1049 (s), 1035 (s), 1004 (s), 947 (m), 895 (w), 818 (s), 775 (s), 730 (m), 695 (w) cm^{-1}. **HRMS** (ESI) calculated for $C_{19}H_{30}FeOSi$ ([M]$^+$): 358.1410; Found: 358.1408. NMR data for mixture of diastereomers: **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.24 (s, 3H), 0.24 (s, 3H), 0.81 (t, J = 7.5 Hz, 3H), 0.82 (t, J = 7.5 Hz, 3H), 0.91 (s, 9H), 0.92 (s, 9H), 1.05 (d, J = 6.0 Hz, 3H), 1.08 (d, J = 6.0 Hz, 3H), 1.29–1.55 (m, 4H), 3.8–23.84 (m, 2H), 3.85–3.94 (m, 2H), 3.96 (s, 5H), 3.96 (s, 5H), 4.07–4.09 (m, 4H), 4.11 (ddd, J = 2.3 Hz, J = 1.1 Hz, J = 1.1 Hz, 1H), 4.12 (ddd, J = 2.3 Hz, J = 1.1 Hz, J = 1.1 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –4.8, –4.7, 9.9, 9.9, 19.1, 19.3, 23.2, 23.3, 26.5, 26.6, 32.8, 32.8, 68.7, 68.7, 68.8, 68.8, 70.1, 70.3, 70.9, 71.0, 71.1, 71.1, 73.5, 73.6, 74.2, 74.3 ppm. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 8.4, 8.4 ppm.



13o

$C_{21}H_{34}FeOSi$
M = 386.42 g/mol

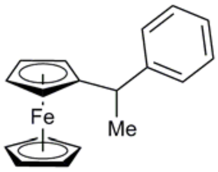
***tert*-Butylferrocenylmethyl[(4-methyl)pent-2-yloxy]silane (13o)**: Prepared from 4-methyl-2-pentanone (**2o**, 20.0 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product **13o** (62.5 mg, 79%) as an orange oil. R_f = 0.31 (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 60:40). **GLC** (SE-54): t_R = 20.4 min (major diastereomer), 20.5 min (minor diastereomer). **IR** (ATR): $\tilde{\nu}$ = 3099 (w), 2956 (m), 2928 (m), 2855 (m), 1427 (m), 1421 (w), 1368 (m), 1251 (m), 1160 (s), 1125 (m), 1073 (s), 1035 (s), 1001 (m), 961 (w), 892 (w), 818 (s), 775 (s), 736 (m), 693 (w) cm^{-1}. **HRMS** (ESI) calculated for $C_{21}H_{34}FeOSi$ ([M]$^+$): 386.1723; Found: 386.1722. **Anal. Calcd** for $C_{21}H_{34}FeOSi$: C, 65.27; H, 8.87; Found: C, 65.62; H, 8.50. NMR data for major diastereomer: **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.38 (s, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 1.06 (s, 9H), 1.20 (d, *J* = 6.1 Hz, 3H), 1.33 (ddd, *J* = 13.3 Hz, *J* = 6.6 Hz, *J* = 6.6 Hz, 2H), 1.67–1.82 (m, 1H), 3.96–3.98 (m, 1H), 4.10 (s, 5H), 4.12–4.18 (m, 1H), 4.19–4.22 (m, 2H), 4.24–4.26 (m, 1H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –4.6, 19.2, 23.2, 23.5, 24.2, 25.1, 26.7, 49.8, 67.5, 68.7, 68.7, 70.9, 71.2, 73.6, 74.2 ppm. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 8.1 ppm. NMR data for minor diastereomer: **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.39 (s, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H), 1.06 (s, 9H), 1.22 (d, *J* = 6.1 Hz, 3H), 1.52–1.63 (m, 2H), 1.67–1.82 (m, 1H), 3.96–3.98 (m, 1H), 4.10 (s, 5H), 4.12–4.18 (m, 1H), 4.19–4.22 (m, 2H), 4.24–4.26 (m, 1H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –4.2, 19.3, 23.2, 23.3, 24.3, 25.0, 26.7, 49.8, 67.5, 68.7, 68.8, 71.0, 71.1, 73.6, 74.4 ppm. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 8.3 ppm.



13p

$C_{21}H_{34}FeOSi$
M = 386.42 g/mol

***tert*-Butylferrocenylmethyl[(3,3-dimethyl)but-2-yloxy]silane (13p):** Prepared from 3,3-dimethyl-2-butanone (**2p**, 20.0 mg, 0.200 mmol, 1.00 equiv.) according to the general procedure; purification by flash chromatography on silica gel using cyclohexane as eluent and subsequent Kugelrohr distillation to remove residual silane **10** afforded the analytically pure product **13p** (59.3 mg, 77%) as an orange oil. ***R*$_f$** = 0.50 (cyclohexane). Diastereomeric ratio was determined by GLC analysis prior to purification (dr = 58:42). **GLC** (SE-54): t_R = 20.7 min (major diastereomer), 20.8 min (minor diastereomer). **IR** (ATR): $\tilde{\nu}$ = 2956 (m), 2930 (m), 2891 (w), 2856 (m), 2360 (w), 2336 (w), 1473 (w), 1391 (w), 1372 (w), 1251 (m), 1161 (m), 1116 (s), 1095 (s), 1058 (w), 1025 (s), 1003 (m), 964 (m), 818 (s), 793 (s), 776 (s), 755 (m), 696 (m) cm^{-1}. **HRMS** (ESI) calculated for $C_{21}H_{34}FeOSi$ ([M]$^+$): 386.1723; Found: 386.1720. **Anal. Calcd** for $C_{21}H_{34}FeOSi$: C, 65.27; H, 8.87; Found: C, 65.06; H, 8.96. NMR data for major diastereomer: **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.37 (s, 3H), 0.95 (s, 9H), 1.05 (s, 9H), 1.13 (d, *J* = 6.2 Hz, 3H), 3.82 (q, *J* = 6.2 Hz, 1H), 3.94 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 4.07 (s, 5H), 4.18–4.20 (m, 2H), 4.23 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –3.6, 18.9, 19.3, 26.2, 26.8, 36.0, 68.7, 68.9, 71.0, 71.1, 73.7, 74.3, 76.5 ppm. **^{29}Si NMR** (60 MHz, C_6D_6): δ = 7.2 ppm. NMR data for minor diastereomer: **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.36 (s, 3H), 0.97 (s, 9H), 1.06 (s, 9H), 1.14 (d, *J* = 6.2 Hz, 3H), 3.70 (q, *J* = 6.2 Hz, 1H), 3.96 (ddd, *J* = 2.3 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 4.08 (s, 5H), 4.18–4.20 (m, 3H) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ = –4.3, 18.8, 19.6, 26.2, 26.9, 35.9, 68.8, 68.9, 71.0, 71.1, 73.8, 74.5, 76.9 ppm. ^{29}**Si NMR** (60 MHz, C_6D_6): δ = 7.8 ppm.



14a

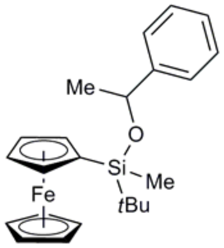
$C_{18}H_{18}FeOSi$
M = 290.18 g/mol

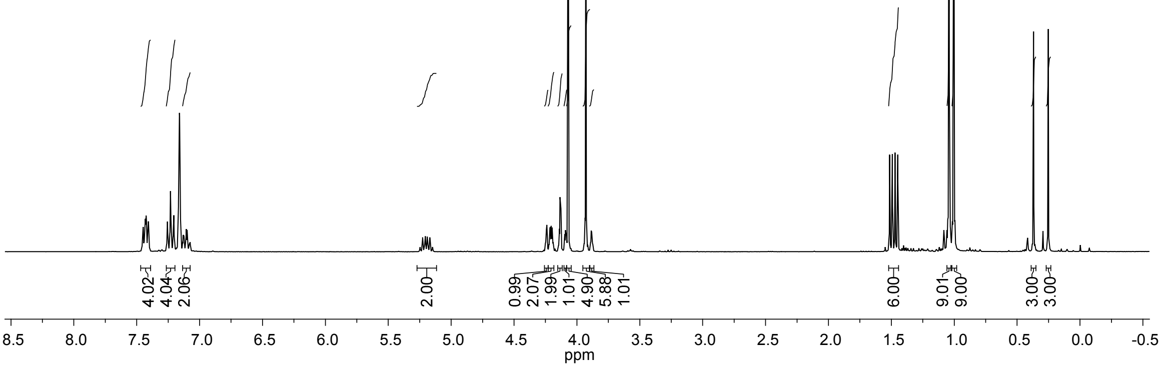
1-Ferrocenyl-1-phenylethane (14a): Prepared from acetophenone (**2a**, 24 mg, 0.20 mmol, 1.0 equiv.) and silane **10** (57.3 mg, 0.200, 1.00 equiv.); purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product **14a** (31.8 mg, 55%) as an orange oil. – Prepared from silicon ether **13a** (81 mg, 0.20 mmol, 1.0 equiv.); purification by flash chromatography on silica gel using cyclohexane as eluent afforded the analytically pure product **14a** (22.0 mg, 38%) as an orange oil. $\boldsymbol{R_f}$ = 0.32 (cyclohexane). **GLC** (SE-54): t_R = 19.9 min. **IR** (ATR): $\tilde{\nu}$ = 3085 (w), 3026 (w), 2967 (w), 2930 (w), 1600 (w), 1439 (m), 1450 (m), 1369 (w), 1296 (w), 1259 (w), 1181 (w), 1105 (m), 1023 (m), 1000 (m), 908 (m), 817 (s), 770 (m), 755 (m), 730 8m), 698 (s) cm^{-1}. **HRMS** (ESI) calculated for $C_{18}H_{18}Fe$ ([M]$^+$): 290.0753; Found: 290.0760. ^{1}**H NMR** (300 MHz, C_6D_6): δ = 1.50 (d, *J* = 7.1 Hz, 3H), 3.75 (q, *J* = 7.1 Hz, 1H), 3.91–3.92 (m, 1H), 3.92–3.926 (m, 1H), 3.99–4.01 (m, 1H), 4.02 (s, 5H), 4.07–4.08 (m, 1H), 7.17–7.19 (m, 5H) ppm. ^{13}**C NMR** (75 MHz, C_6D_6): δ = 23.0, 40.2, 57.3, 66.7, 67.3, 68.0, 68.3, 68.9, 126.3, 127.6, 128.5, 147.9 ppm.

4 ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR Spectra for Compounds 13a, 13f–13p and 14

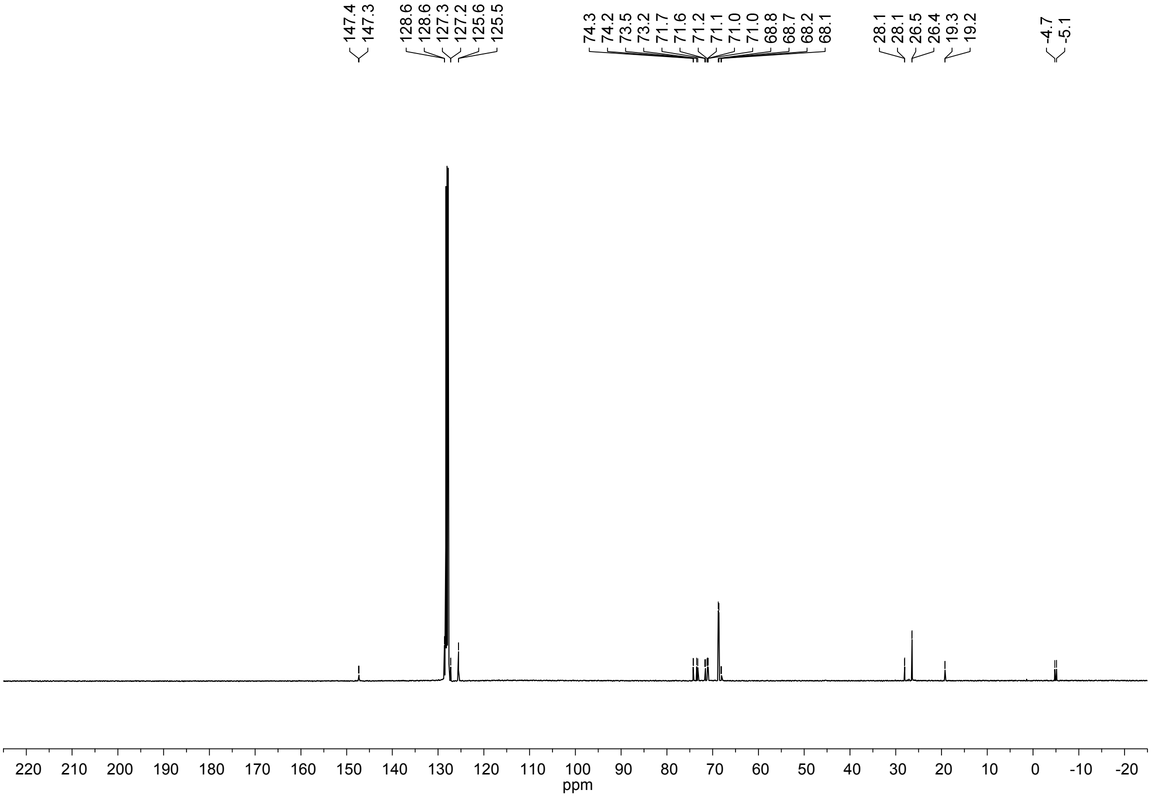
***tert*-Butylferrocenylmethyl(1-phenylethoxy)silane (13a):**

^{1}H NMR:

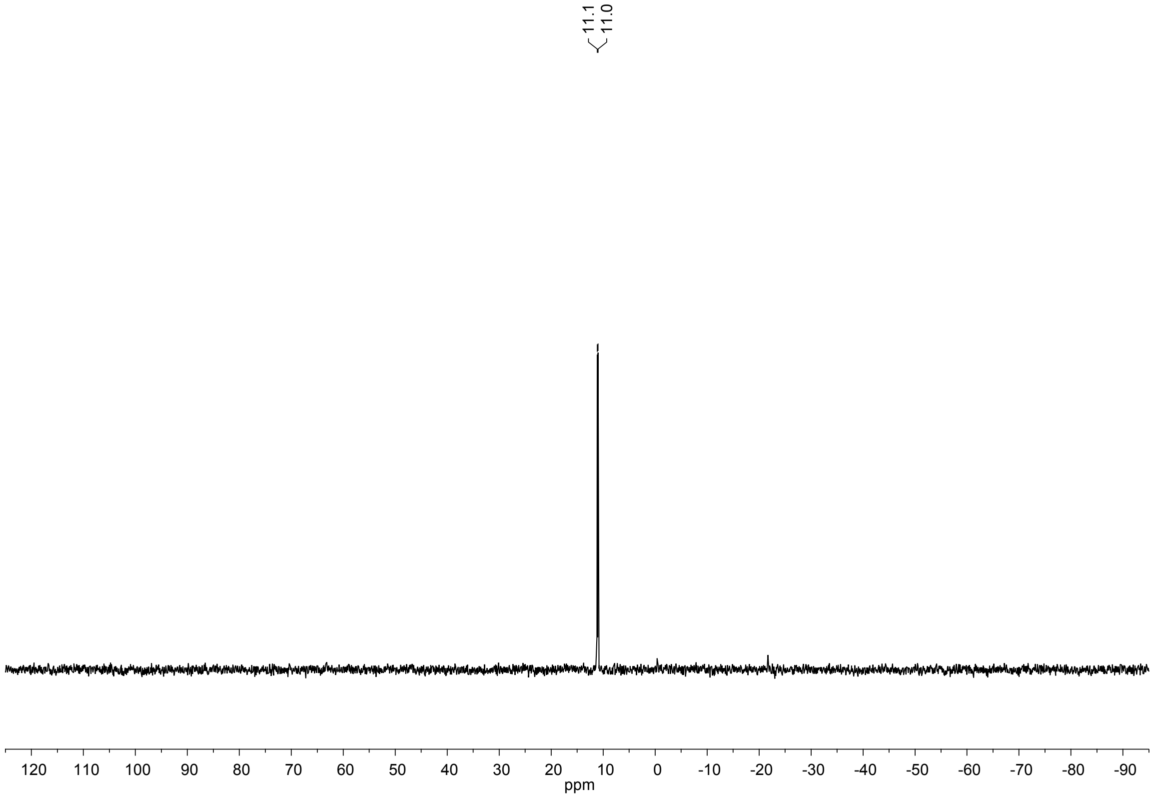




^{13}C NMR:

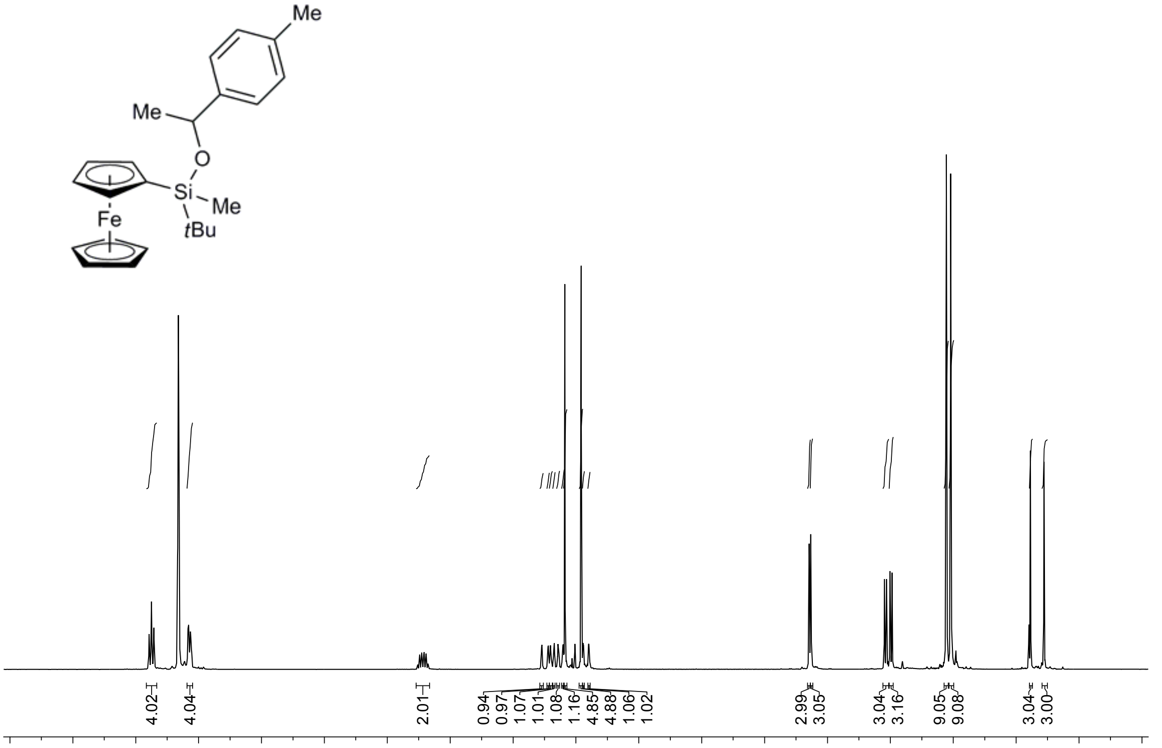


^{29}Si NMR:

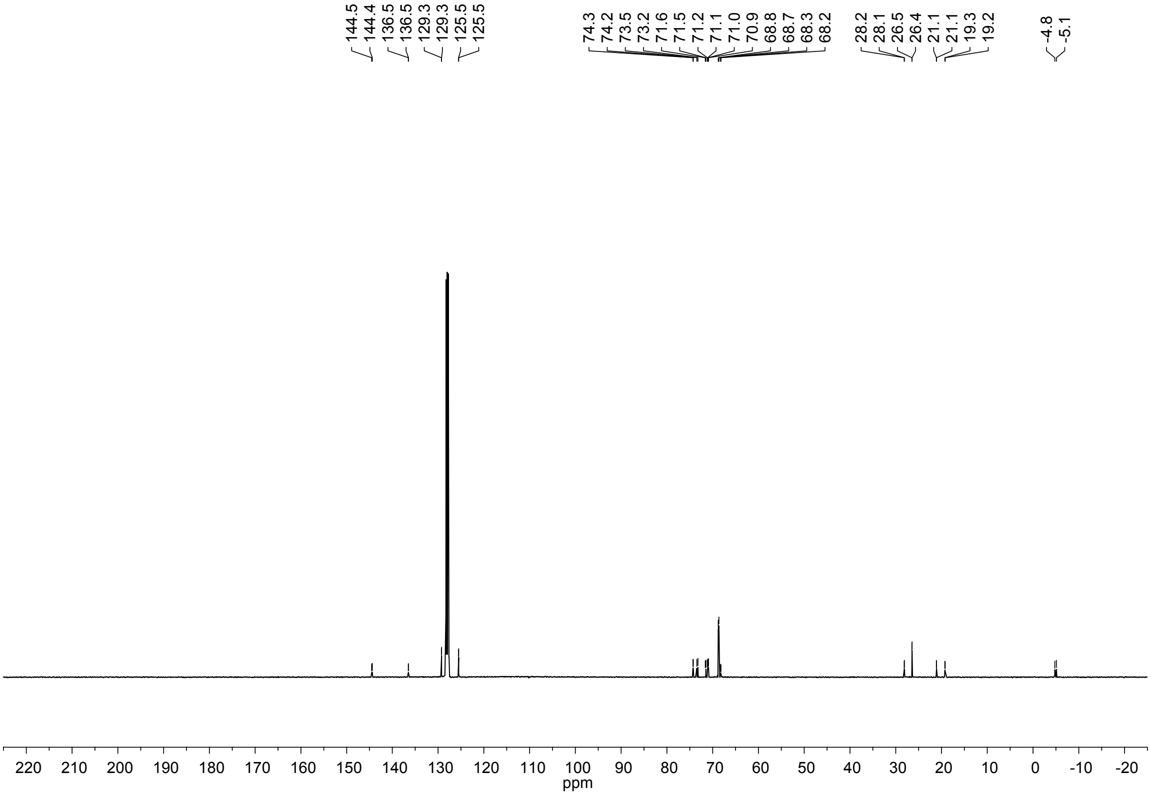


tert-Butylferrocenylmethyl[1-(4-methylphenyl)ethoxy]silane (13f):

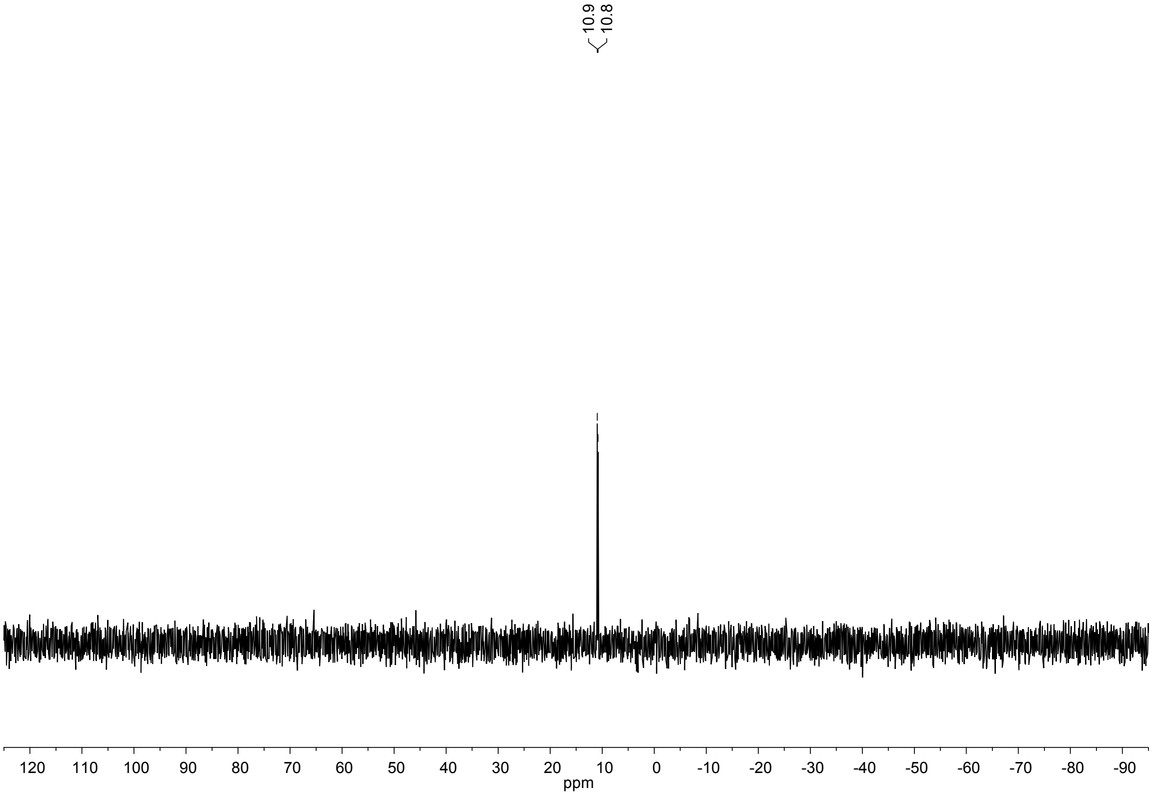
^{1}H NMR:



^{13}C NMR:

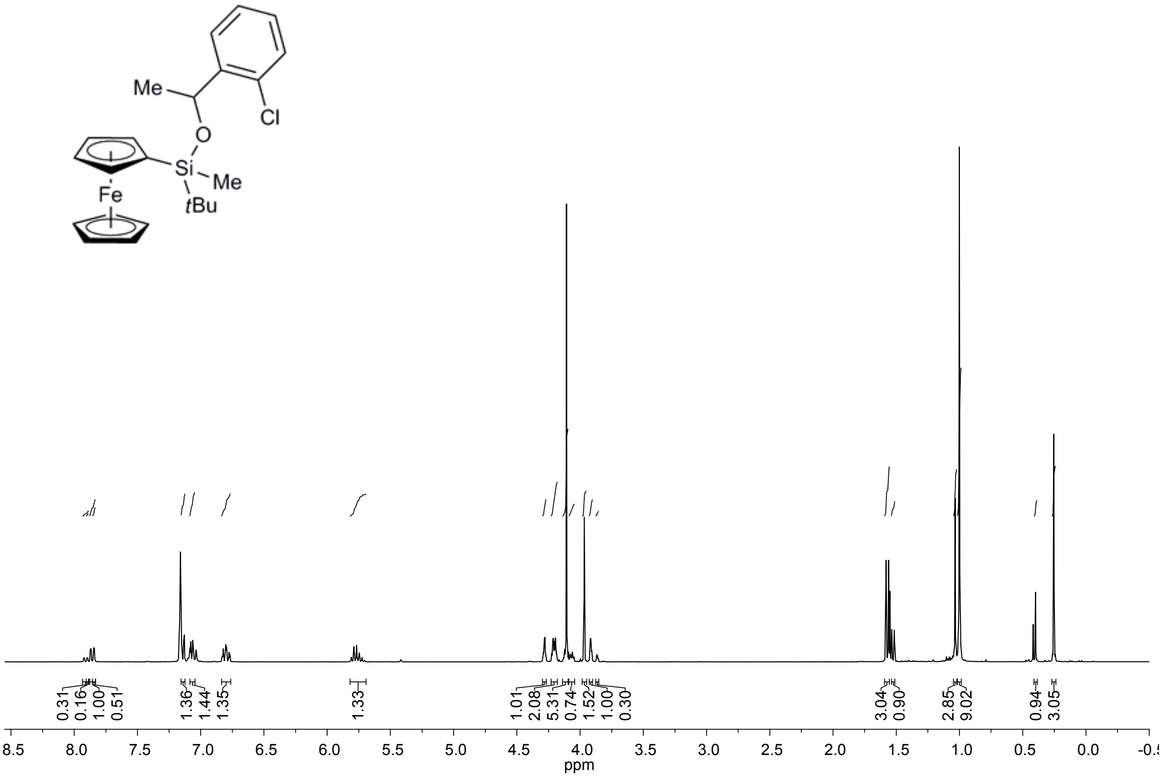


^{29}Si NMR:

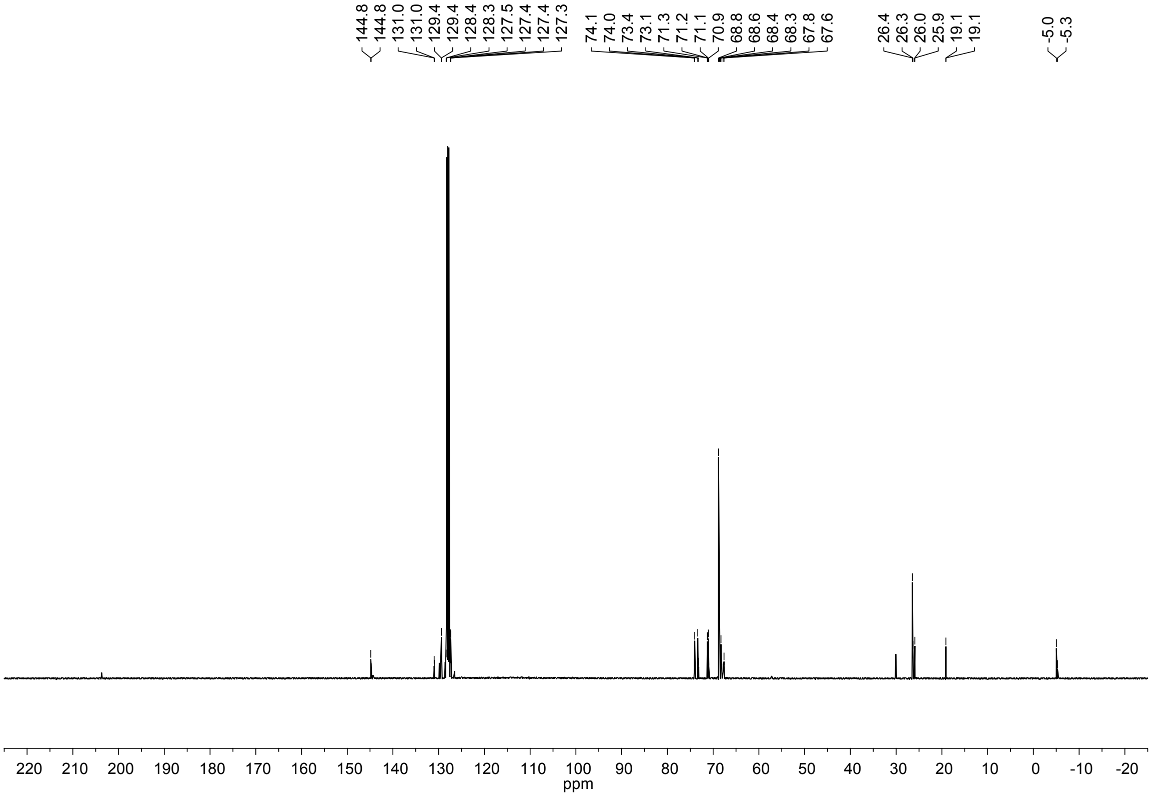


***tert*-Butylferrocenylmethyl[1-(2'-chlorophenyl)ethoxy]silane (13g):**

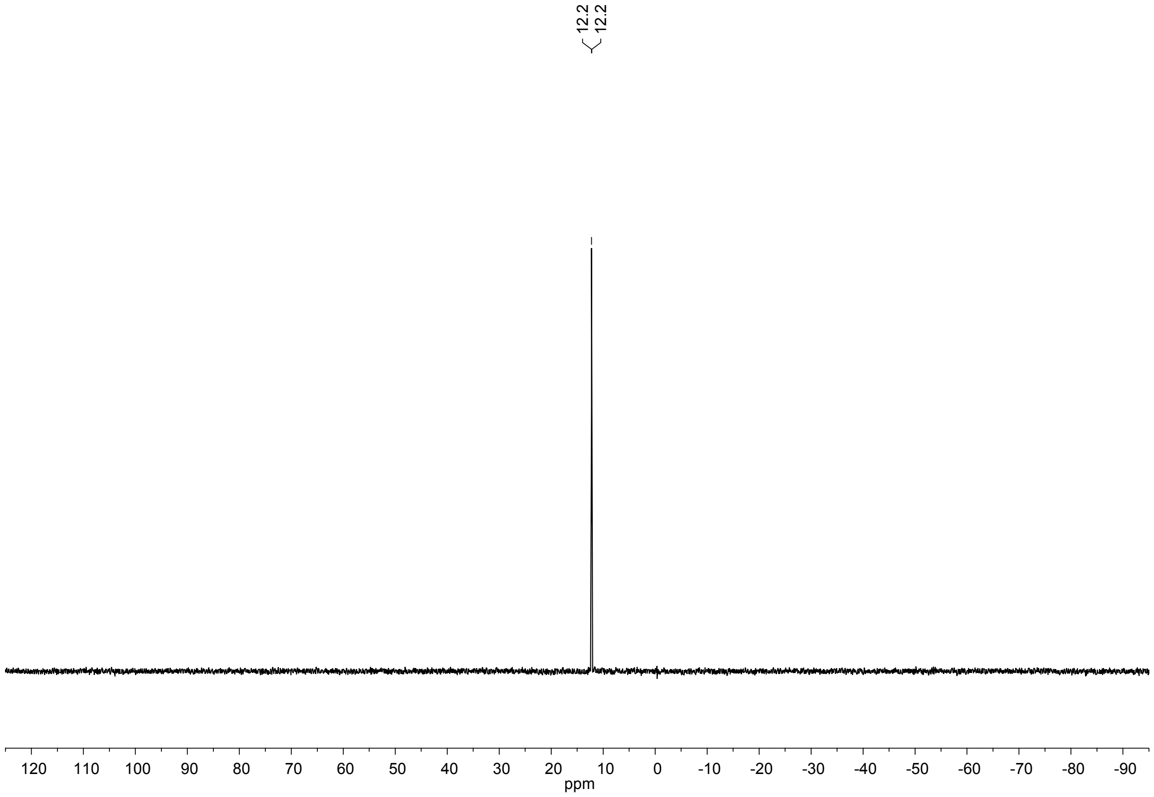
^{1}H NMR:



^{13}C NMR:

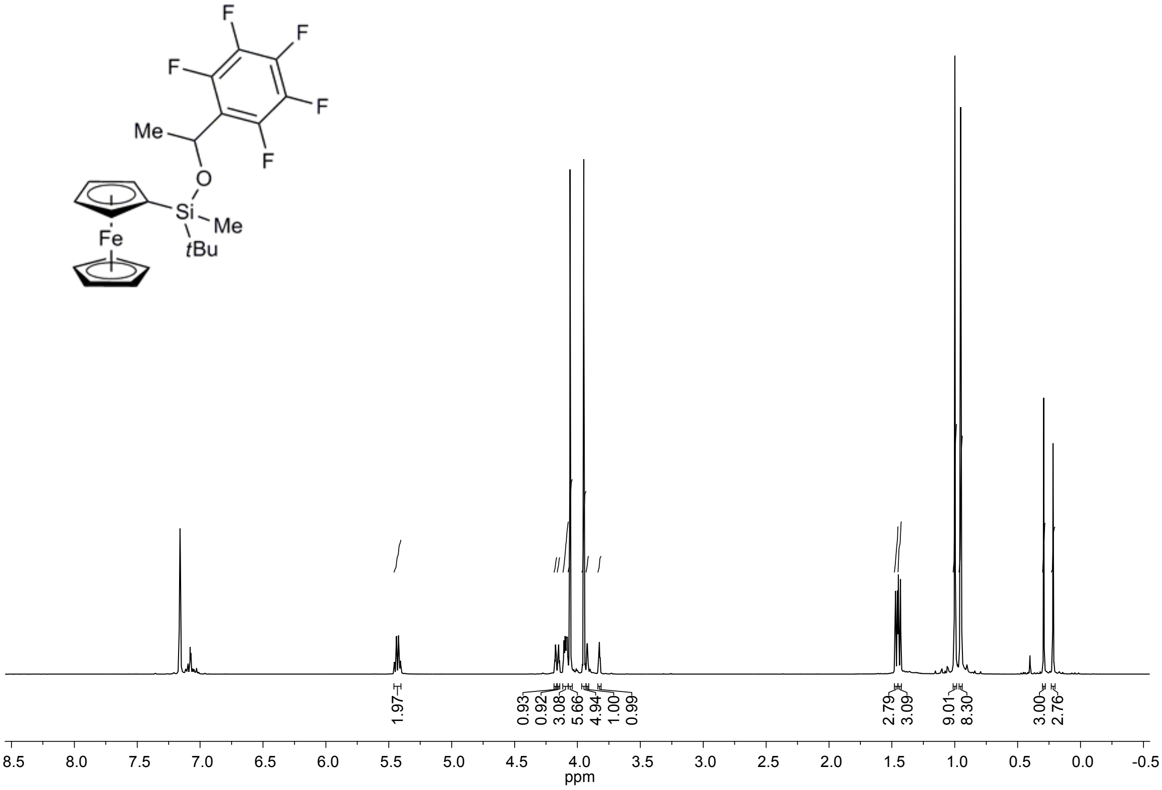


^{29}Si NMR:

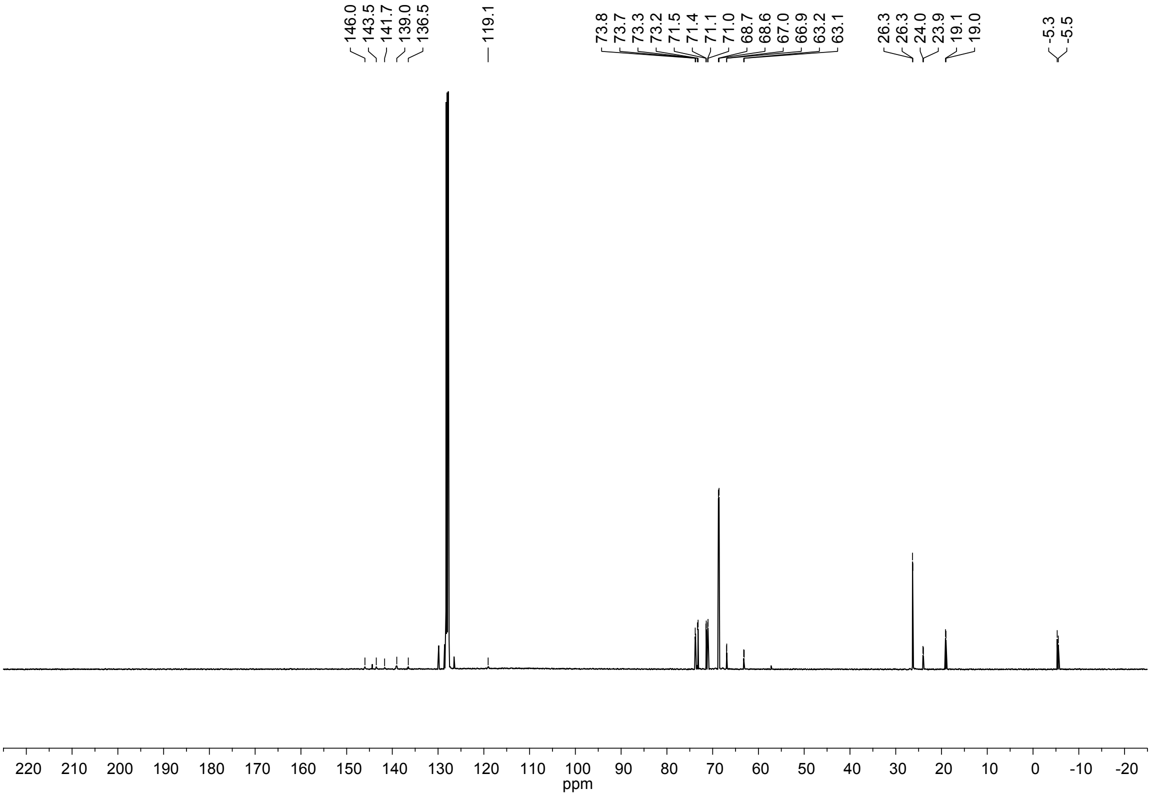


tert-Butylferrocenylmethyl[1-(2',3',4',5',6'-pentafluorophenyl)ethoxy]silane (13h):

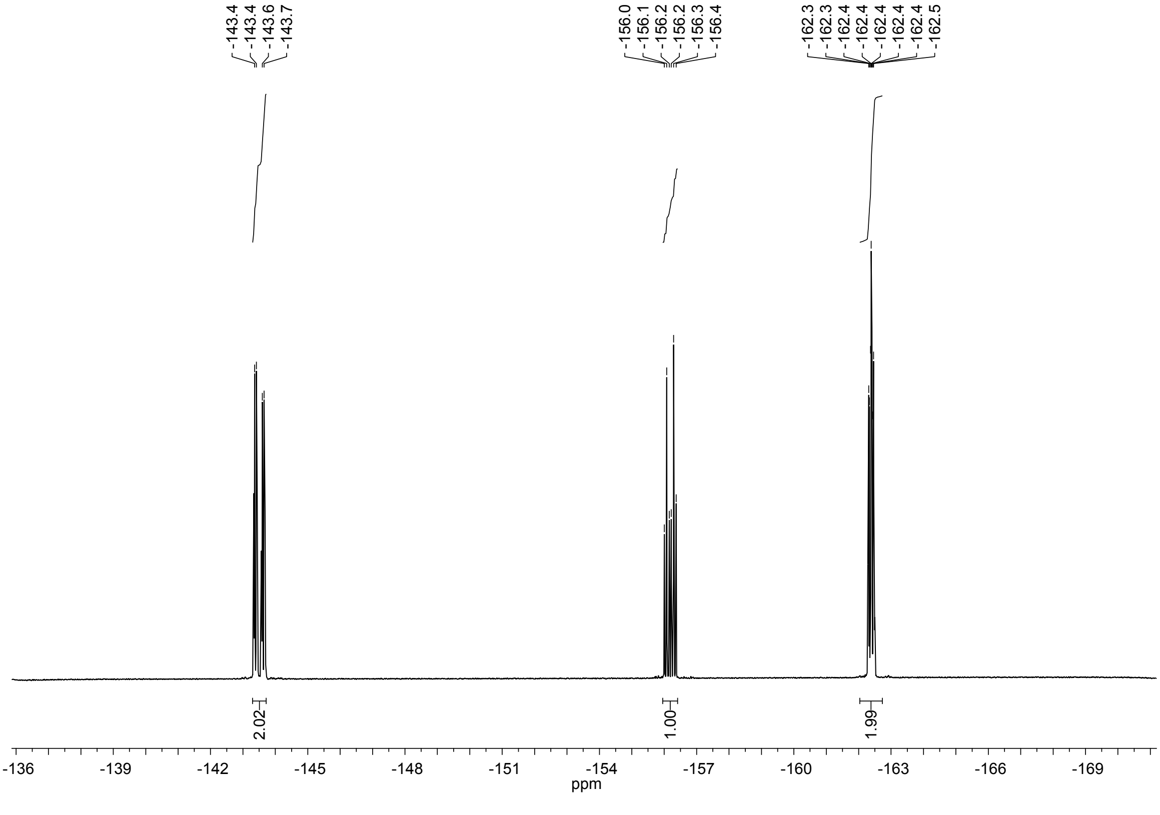
^{1}H NMR:



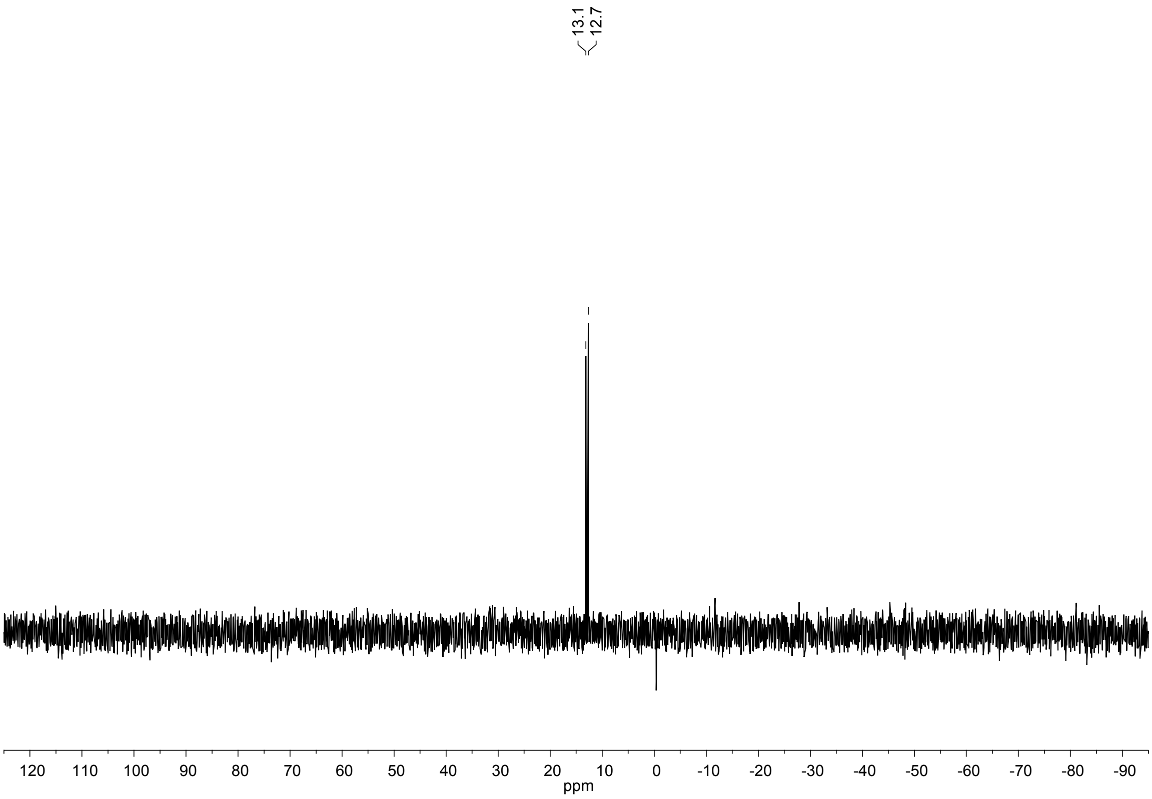
^{13}C NMR:



^{19}F NMR:

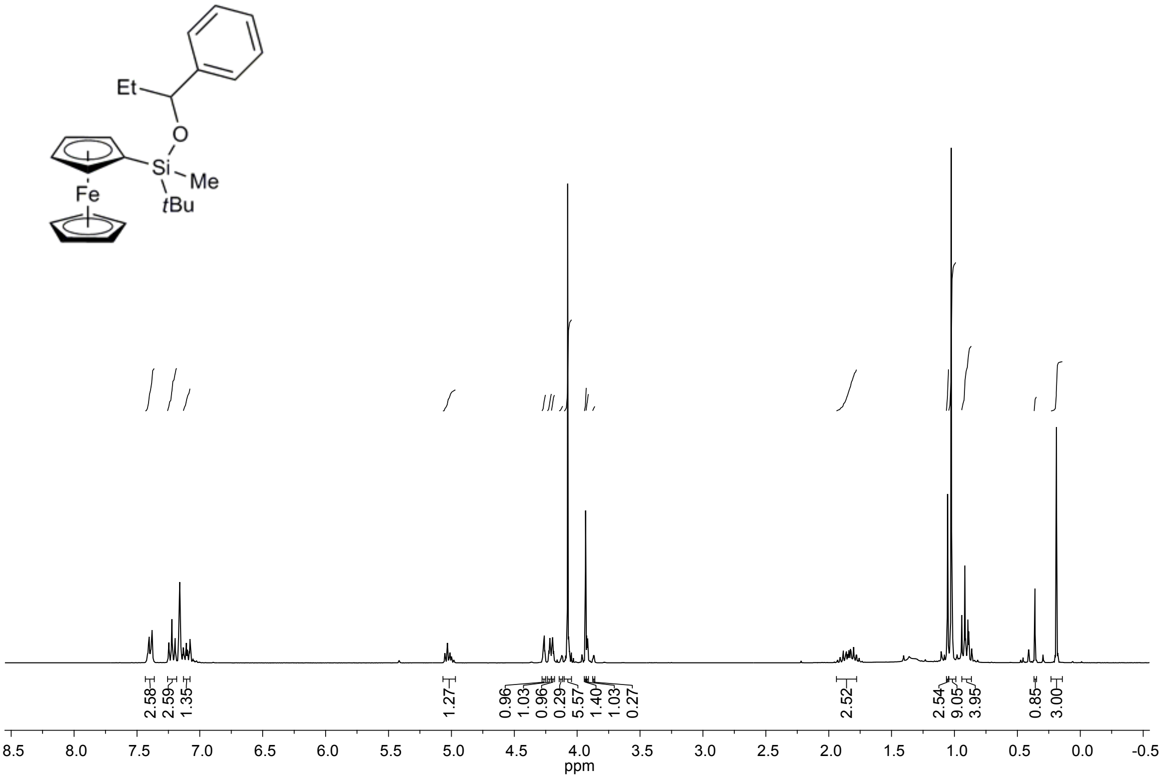


^{29}Si NMR:

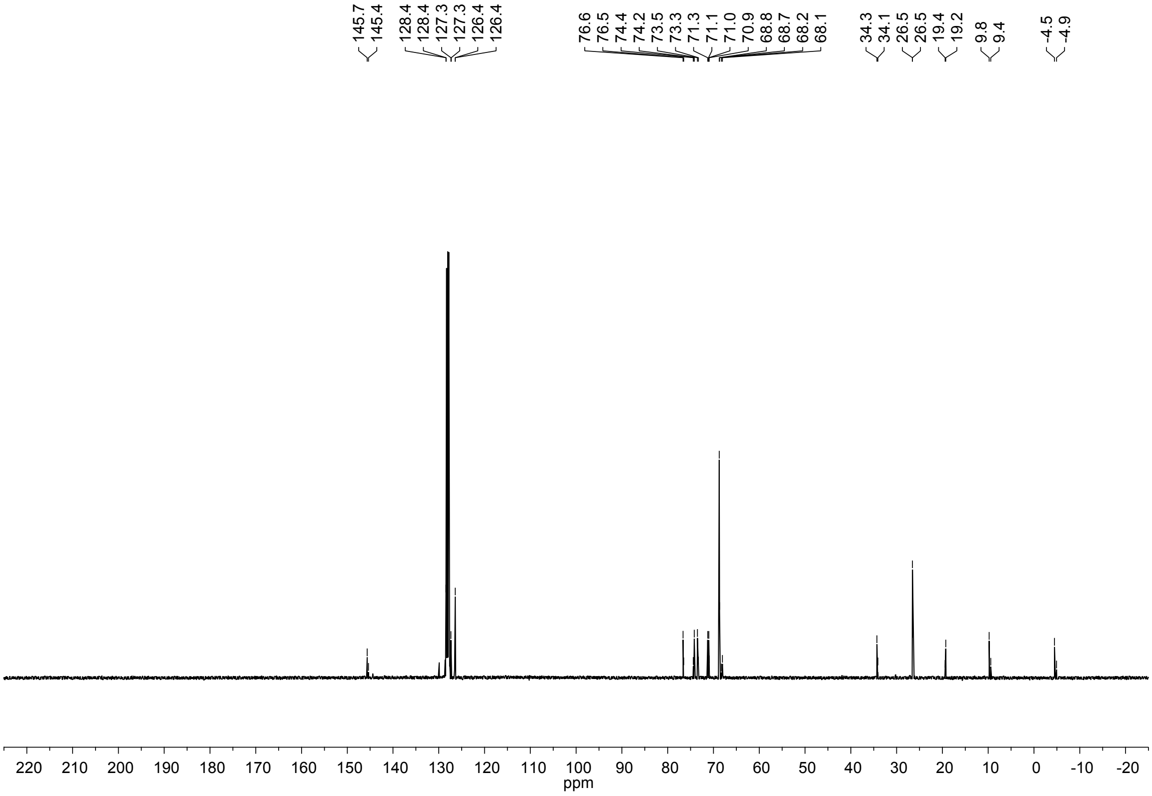


***tert*-Butylferrocenylmethyl(1-phenylpropoxy)silane (13i):**

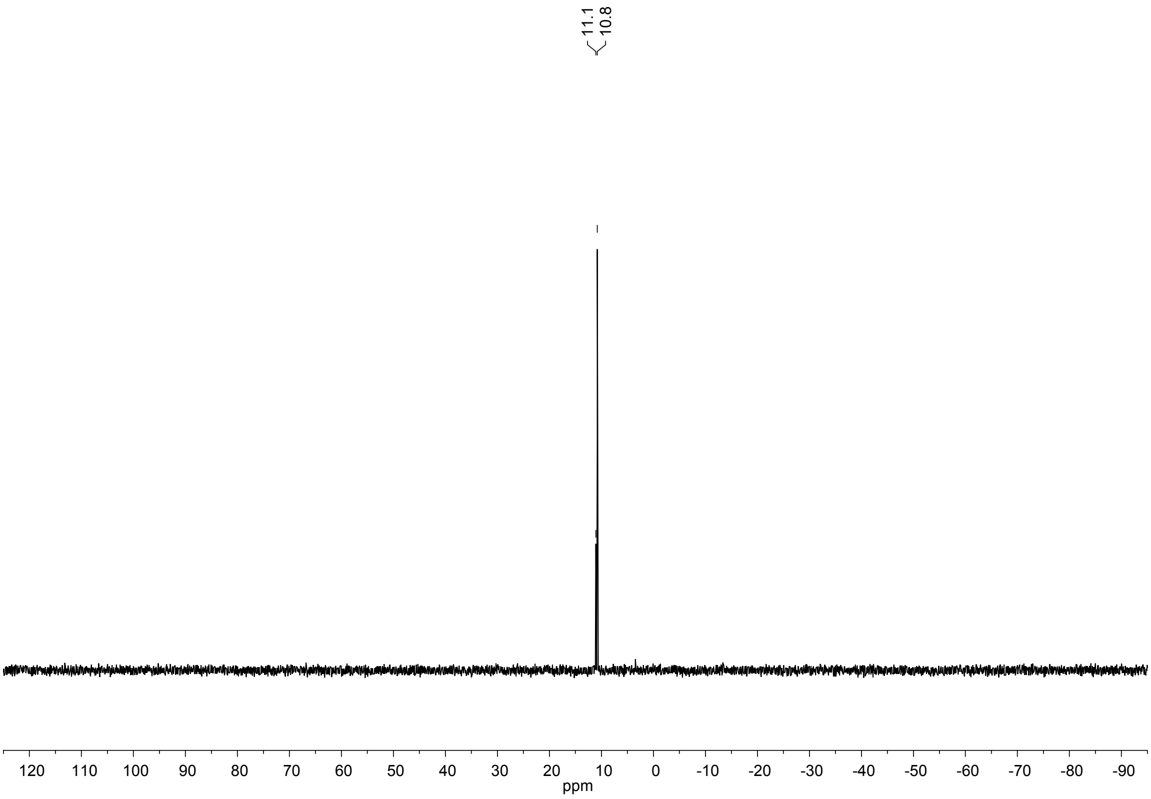
^{1}H NMR:



^{13}C NMR:

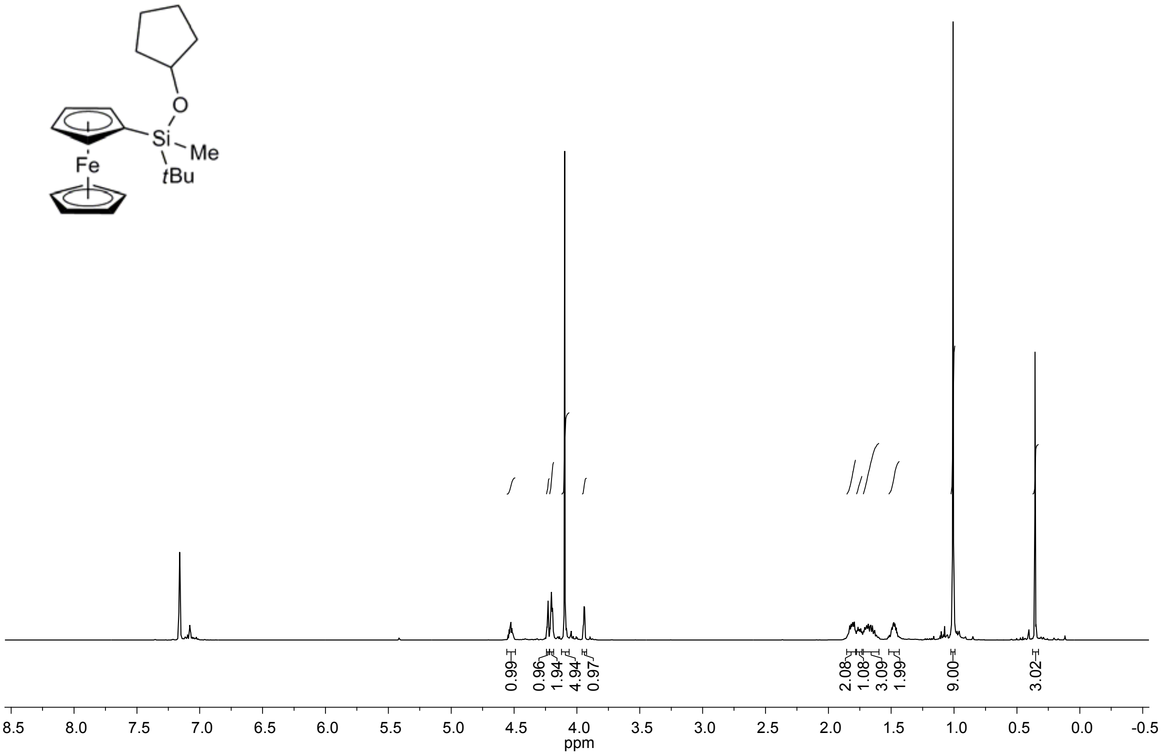


^{29}Si NMR:

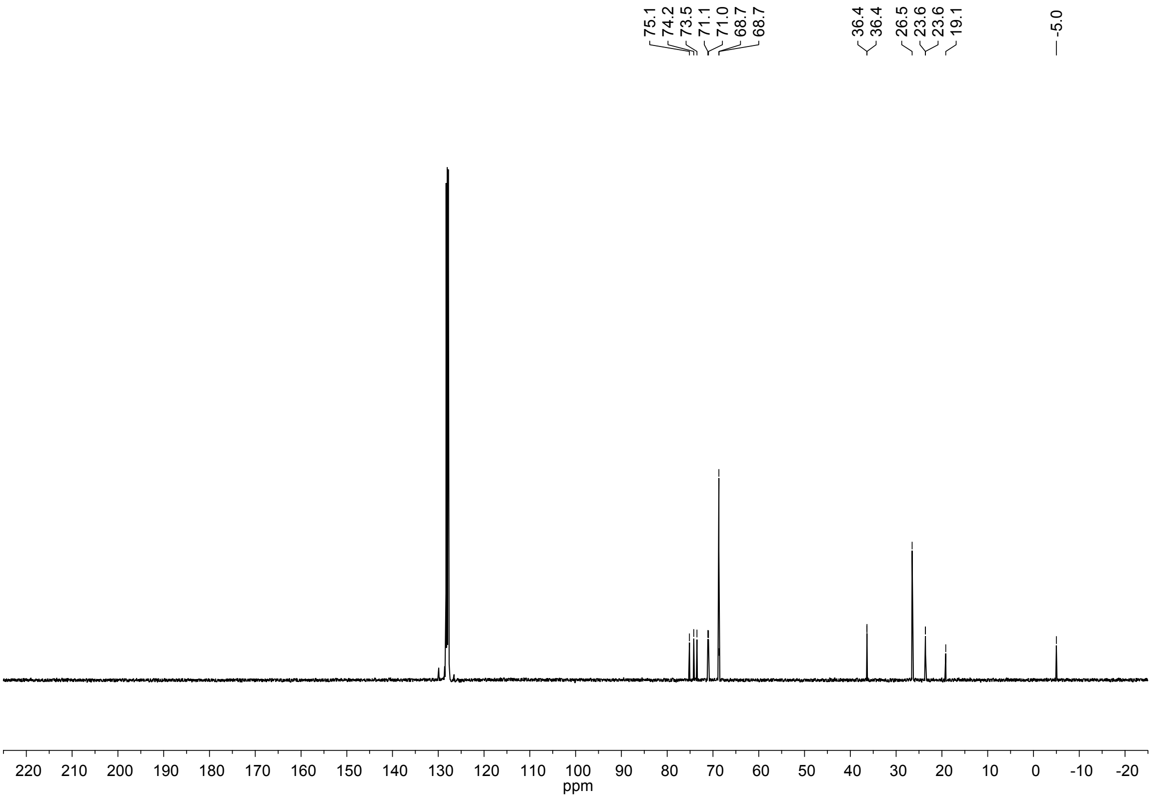


***tert*-Butylferrocenylmethyl(cyclopentyloxy)silane (13j):**

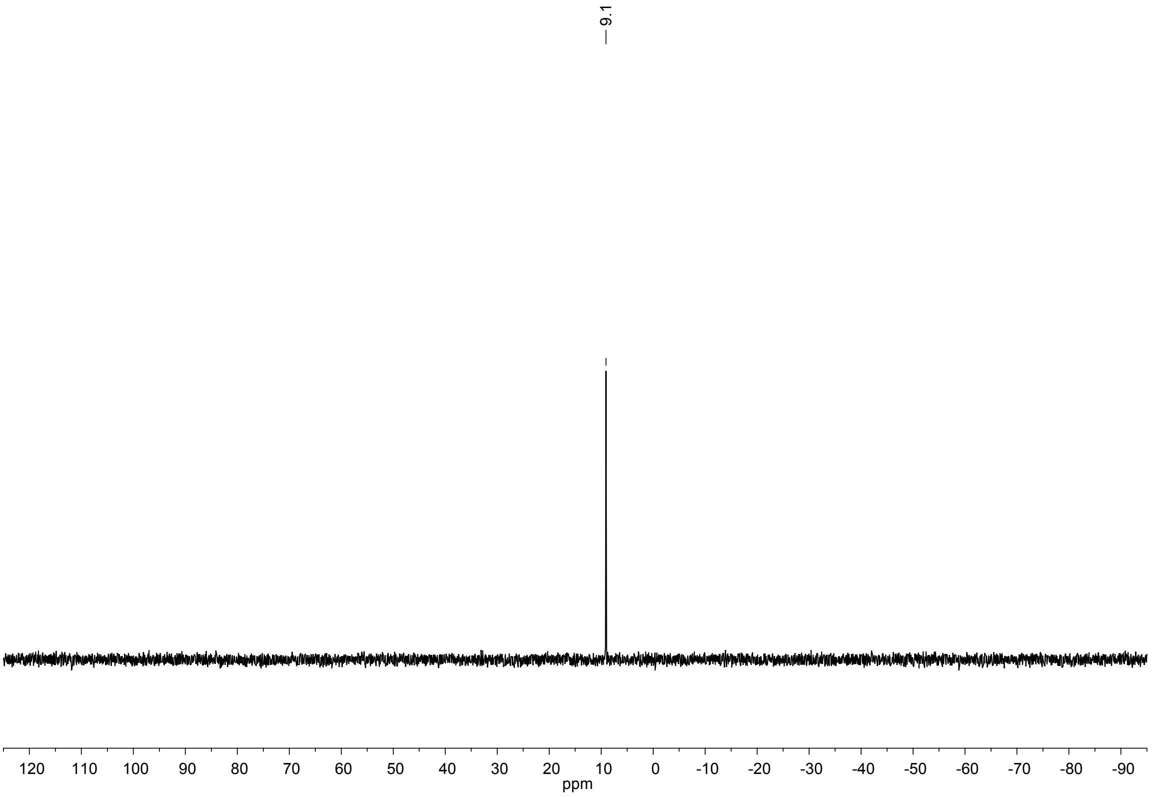
^{1}H NMR:



^{13}C NMR:

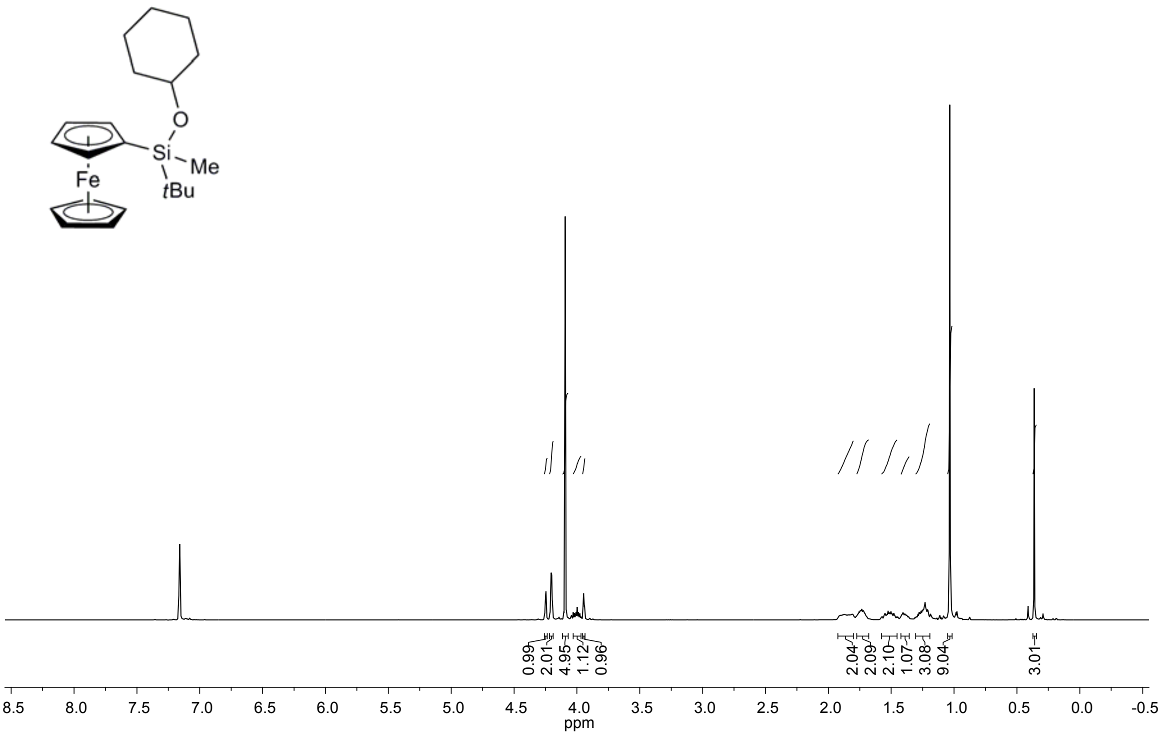


^{29}Si NMR:

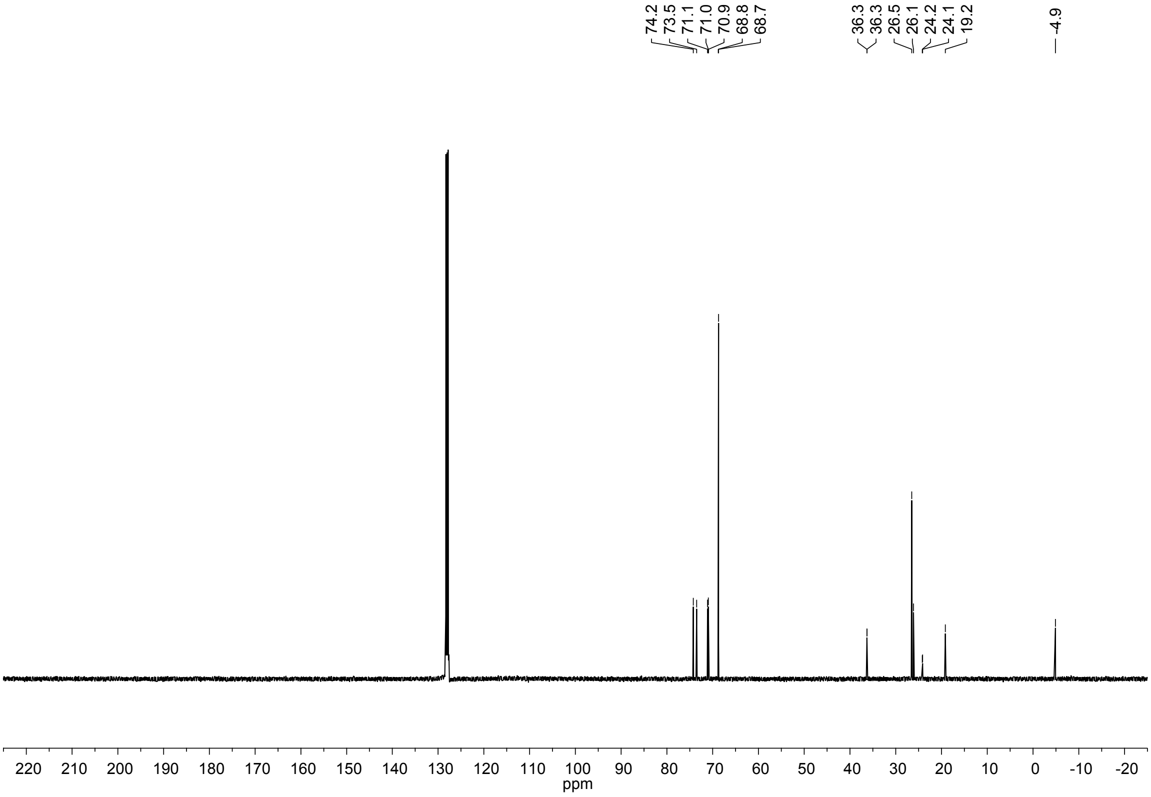


***tert*-Butylferrocenylmethyl(cyclohexyloxy)silane (13k):**

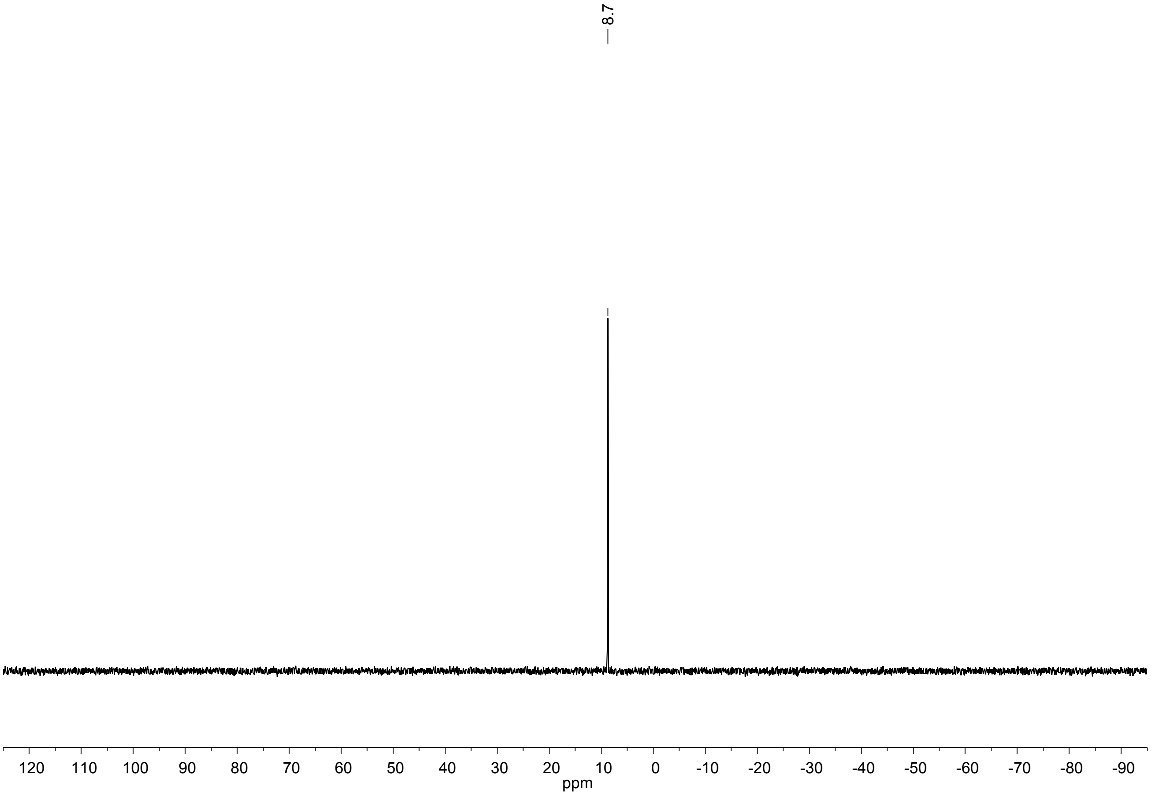
^{1}H NMR:



^{13}C NMR:

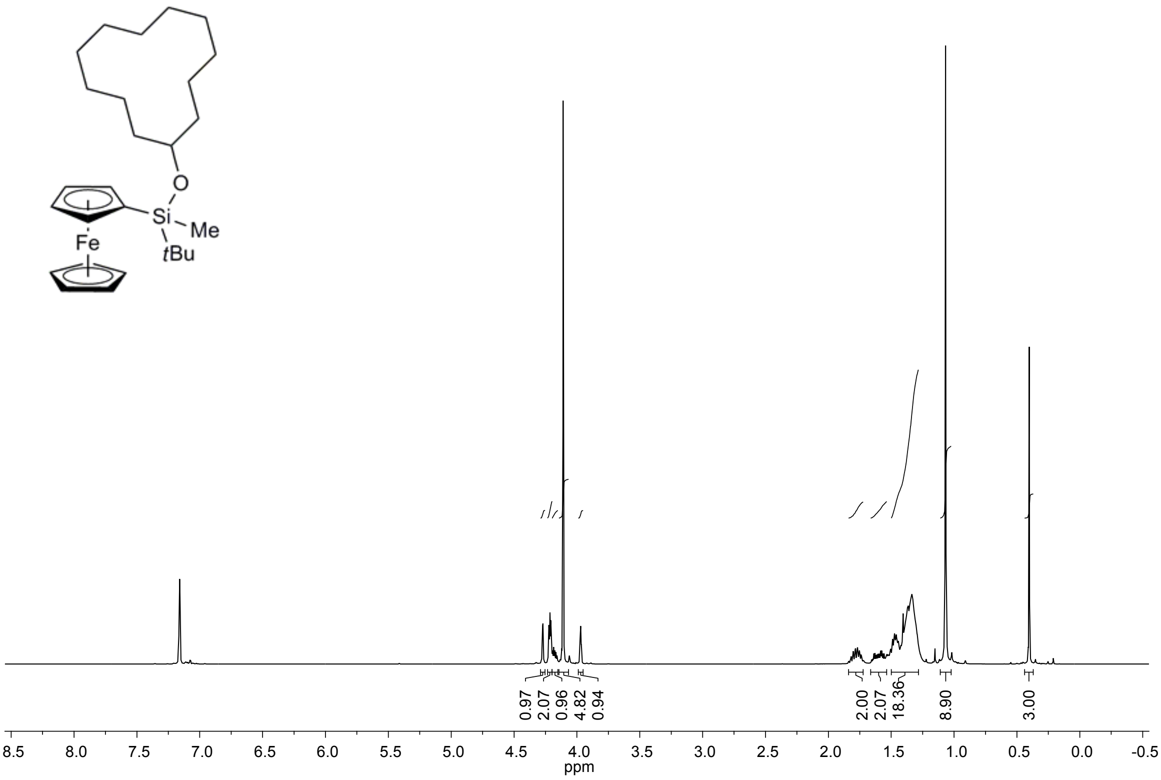


^{29}Si NMR:

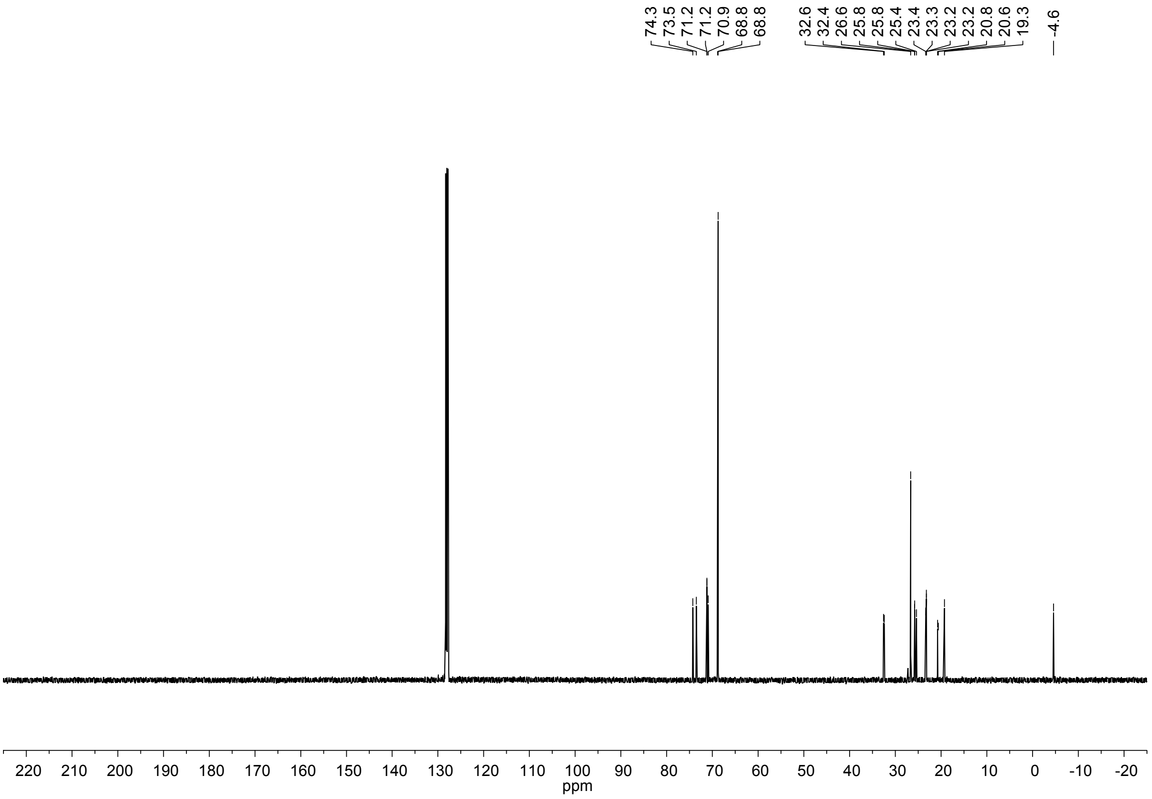


***tert*-Butylferrocenylmethyl(cyclododecyloxy)silane (13l):**

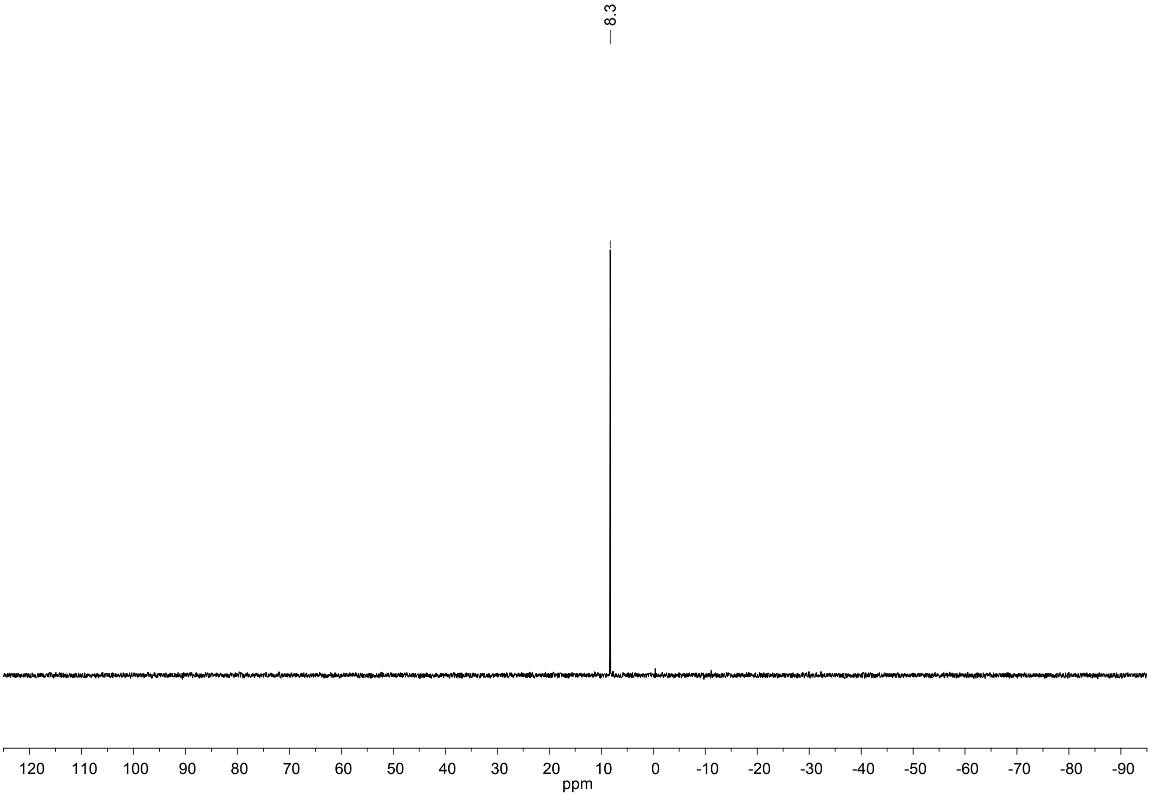
^{1}H NMR:



^{13}C NMR:

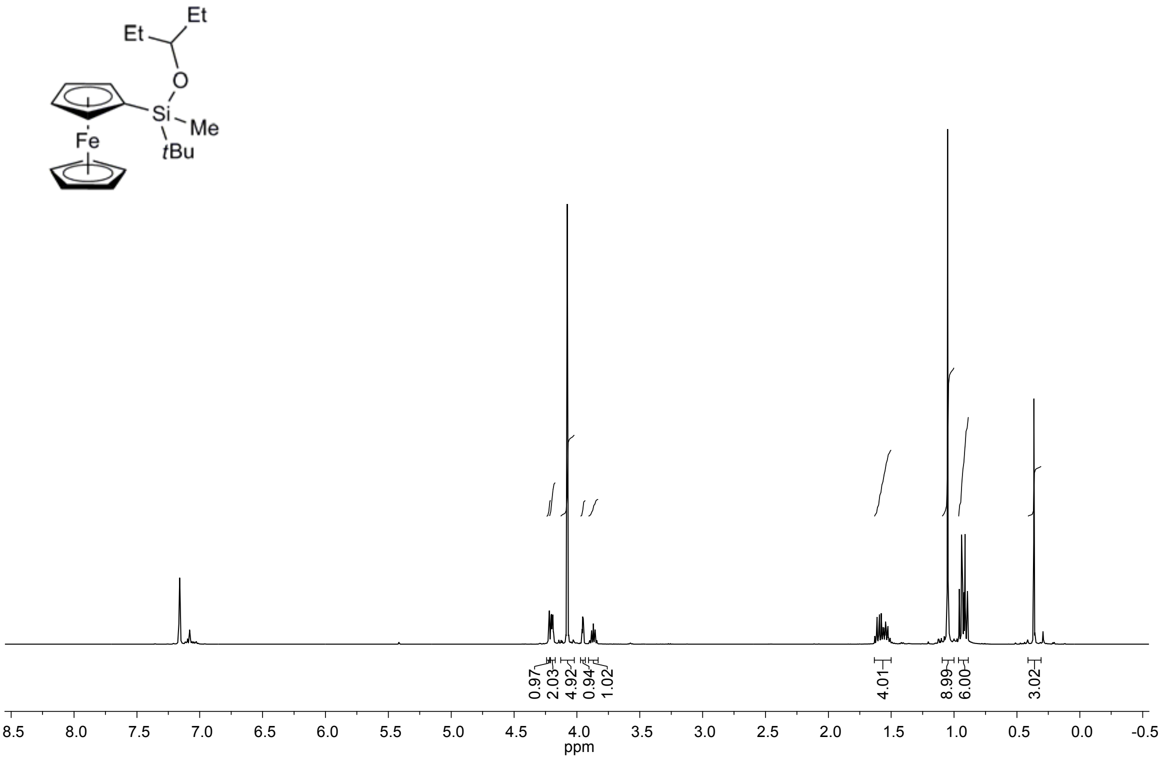


^{29}Si NMR:

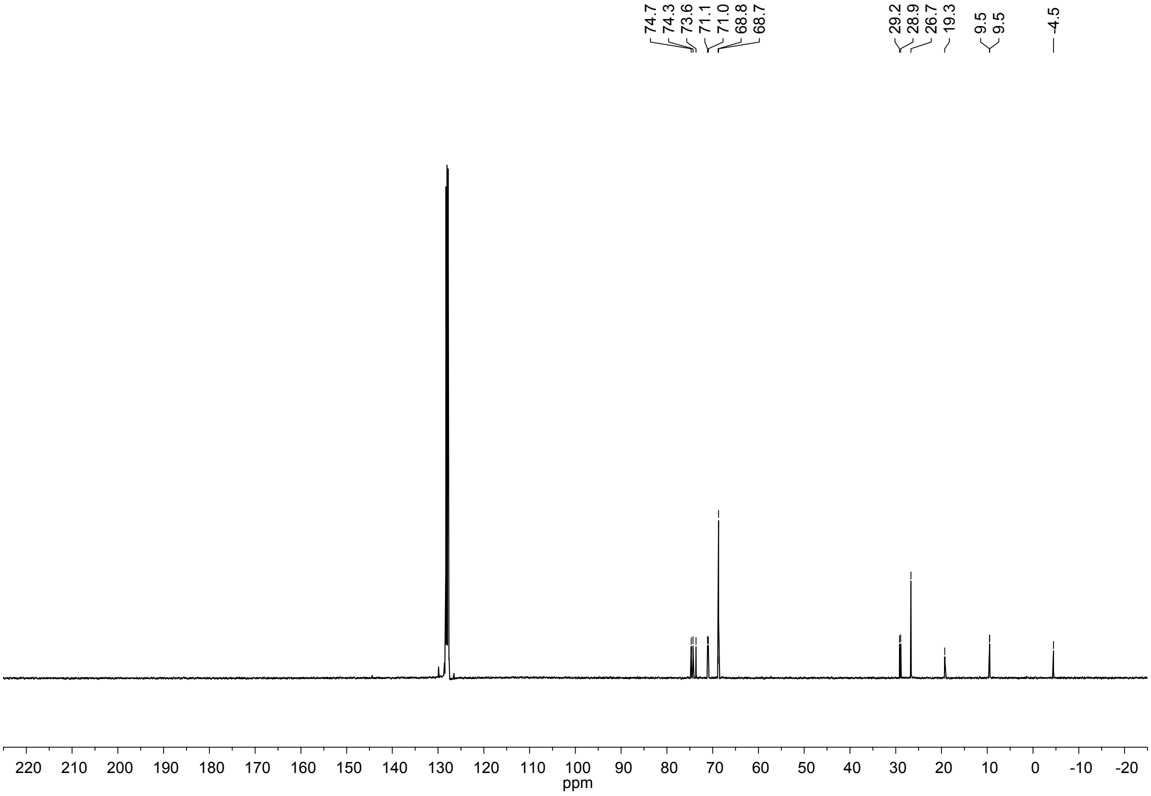


tert-Butylferrocenylmethyl(pent-3-yloxy)silane (13m):

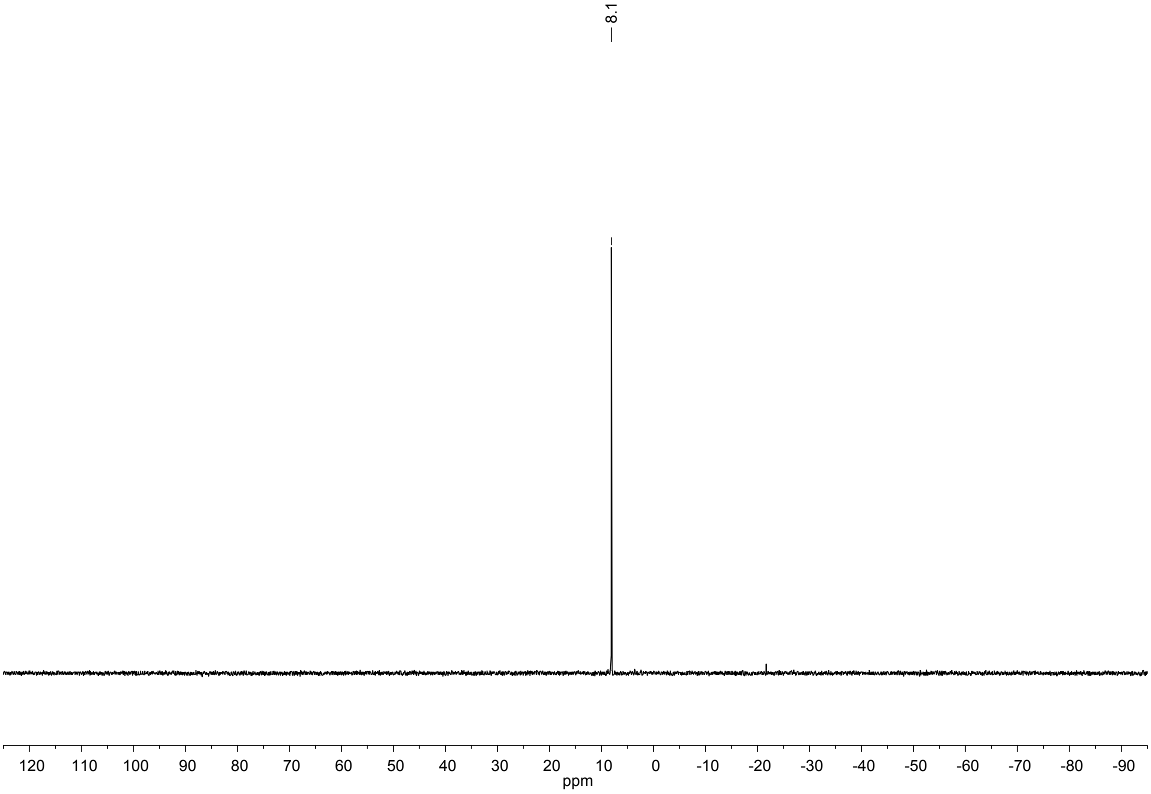
^{1}H NMR:



^{13}C NMR:

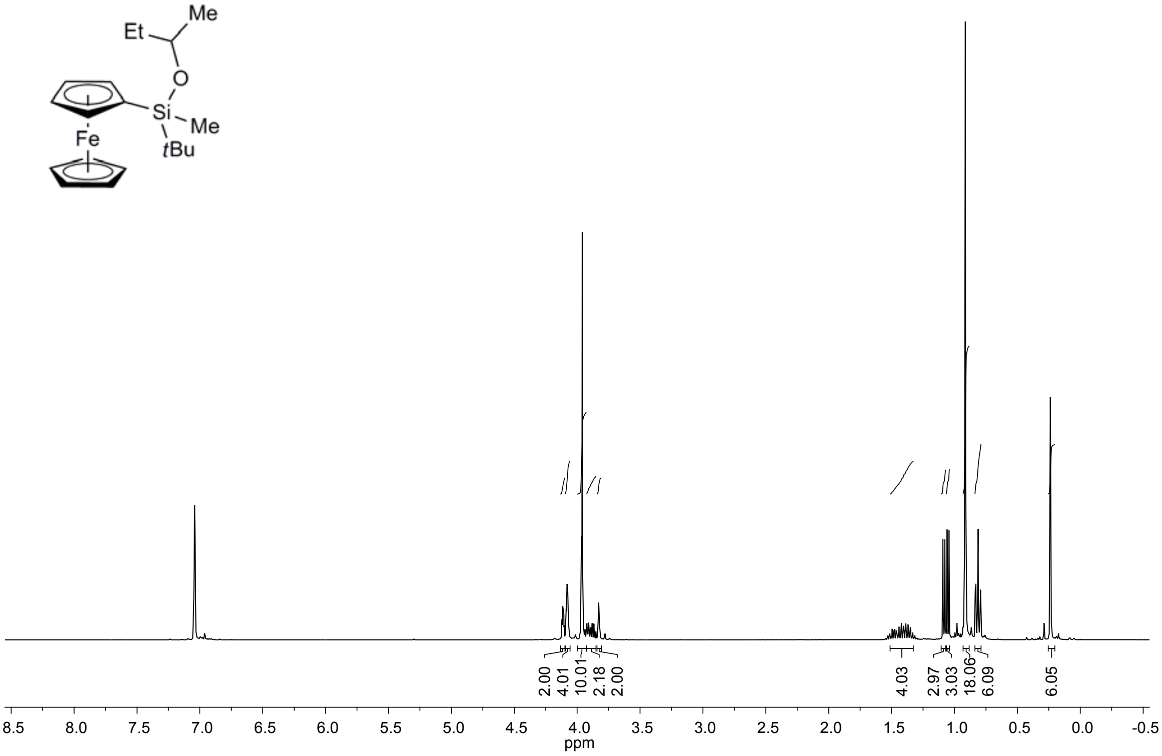


^{29}Si NMR:

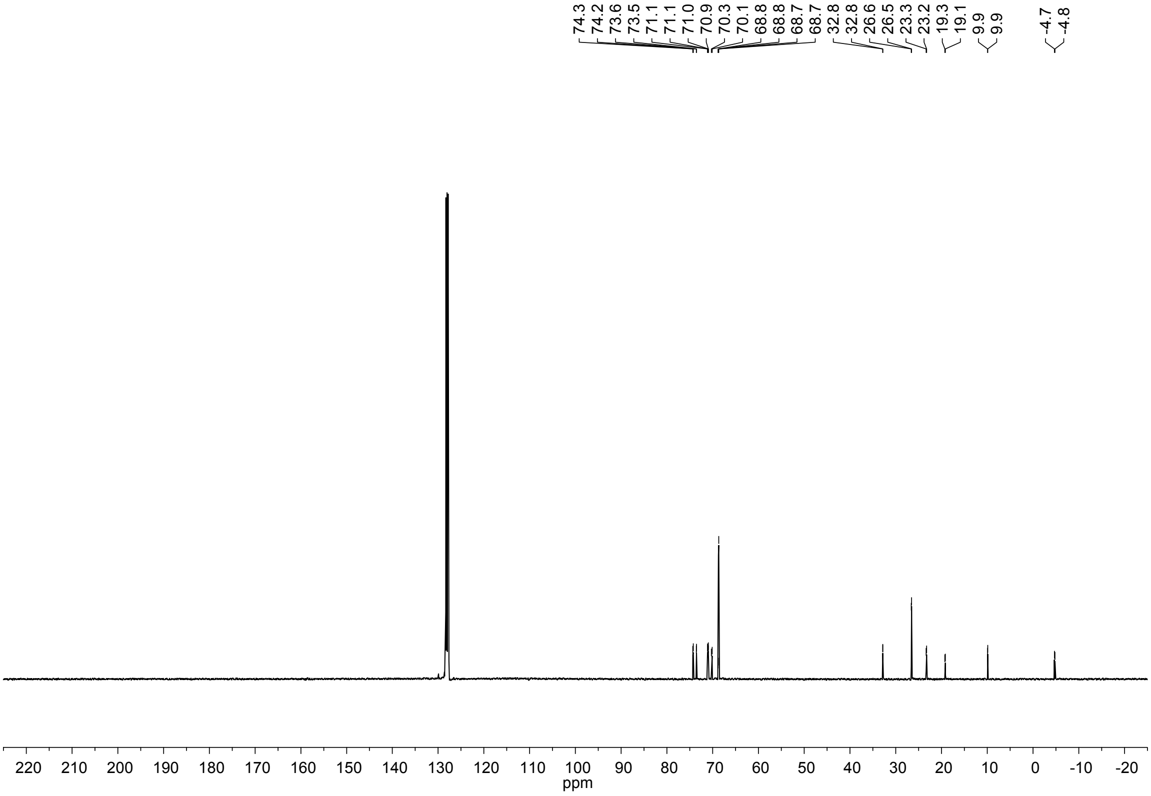


tert-Butylferrocenylmethyl(but-2-yloxy)silane (13n):

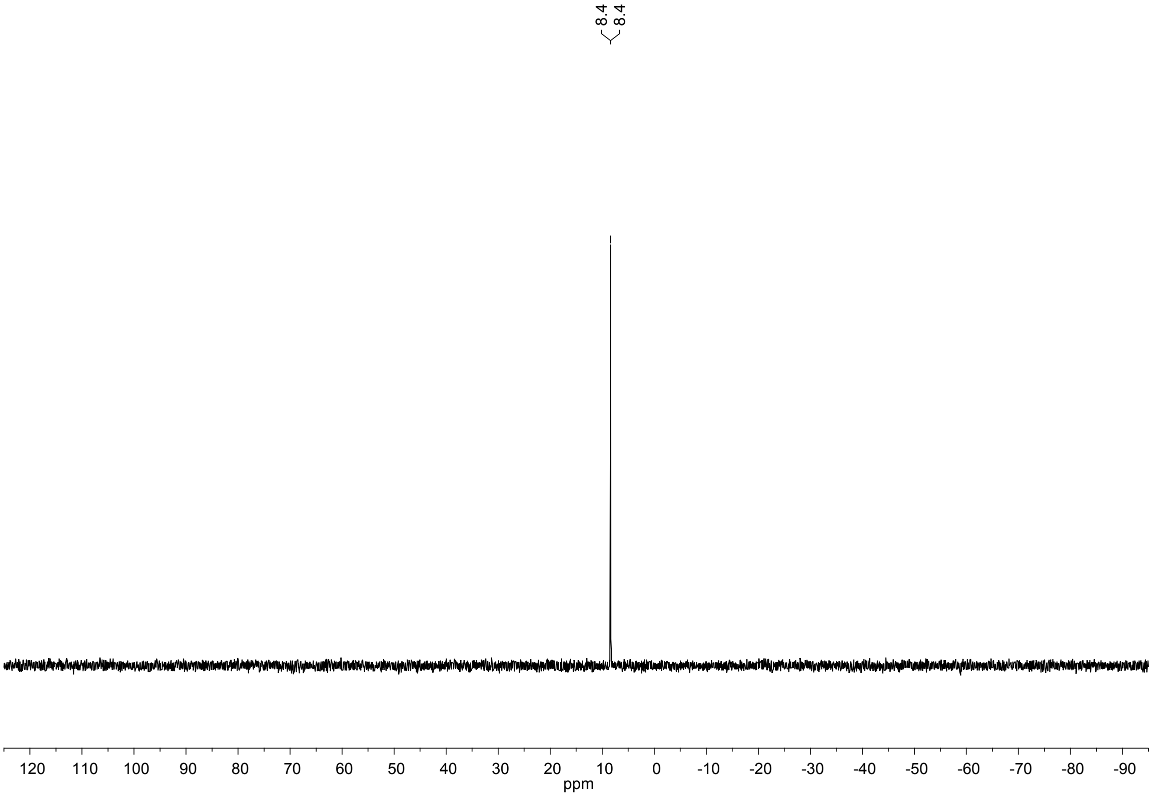
^{1}H NMR:



^{13}C NMR:

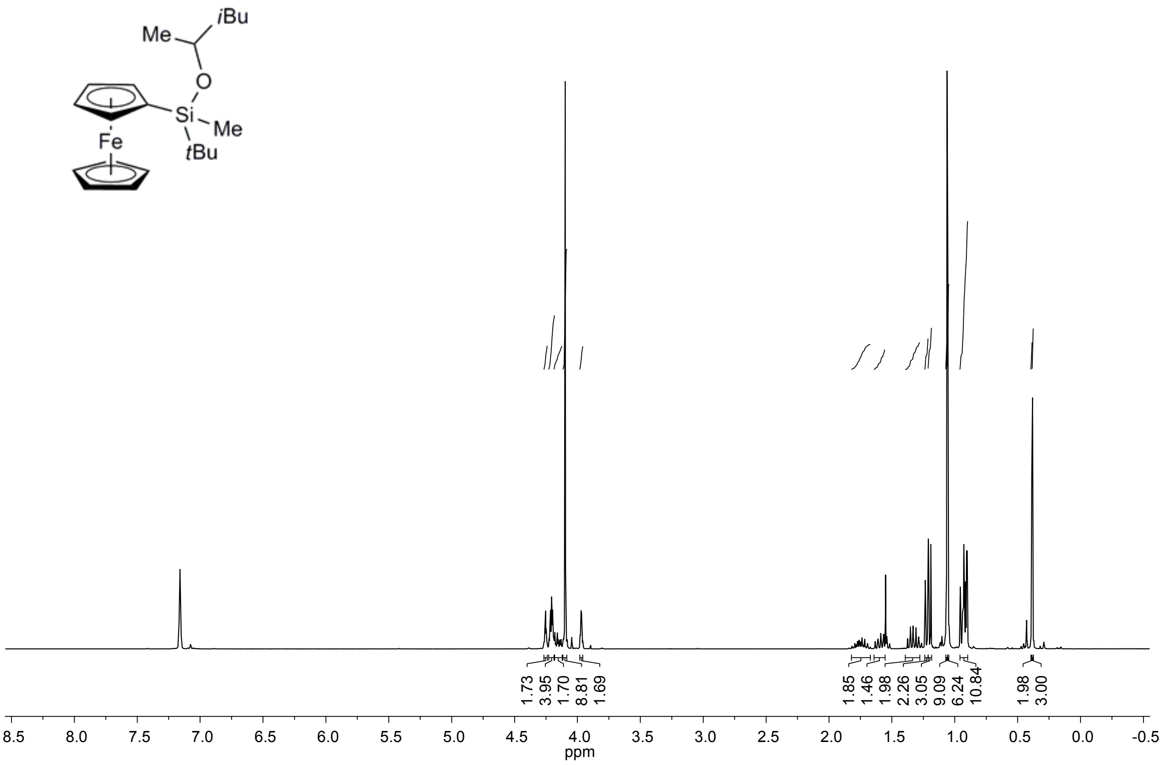


^{29}Si NMR:

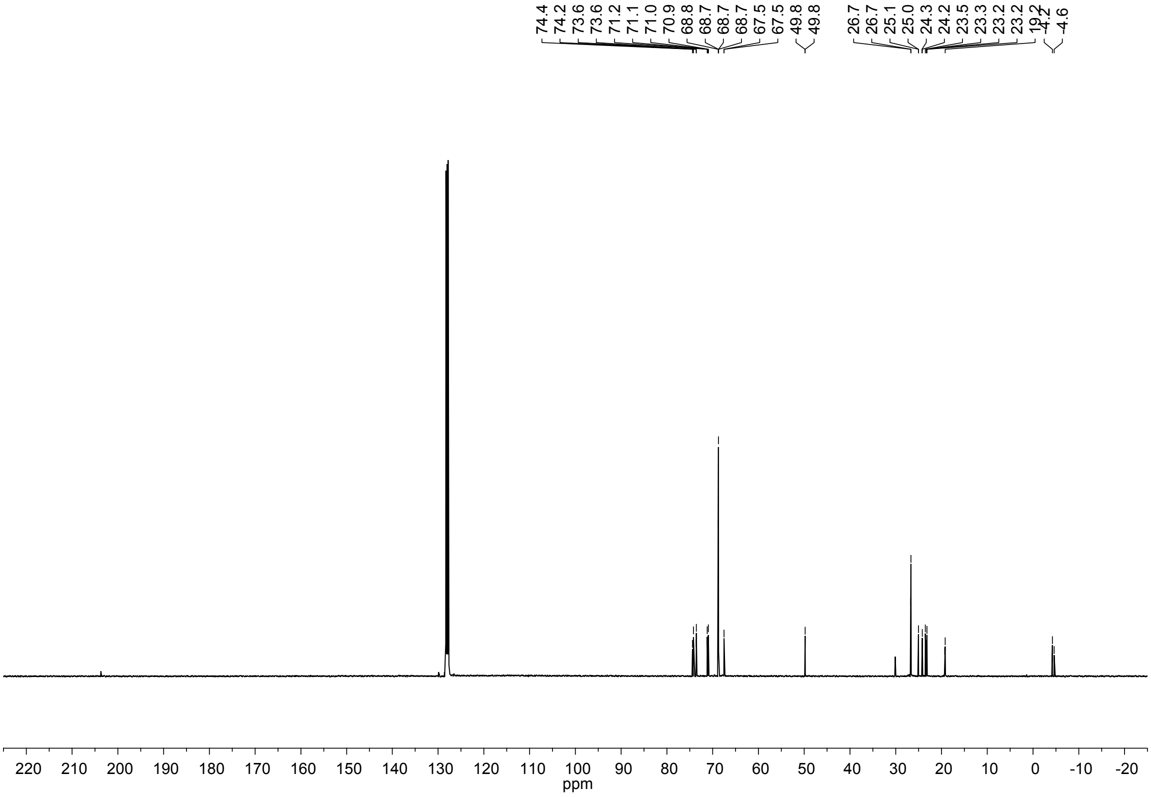


***tert*-Butylferrocenylmethyl[(4-methyl)pent-2-yloxy]silane (13o):**

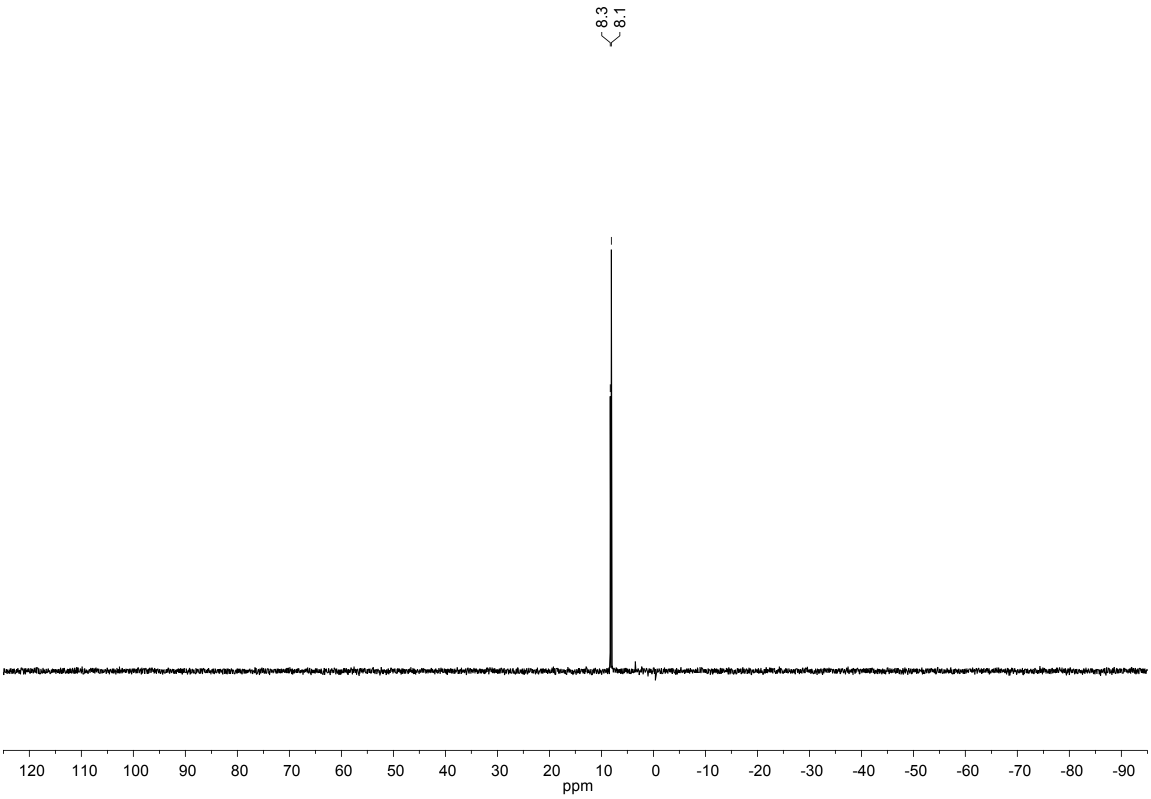
^{1}H NMR:



^{13}C NMR:

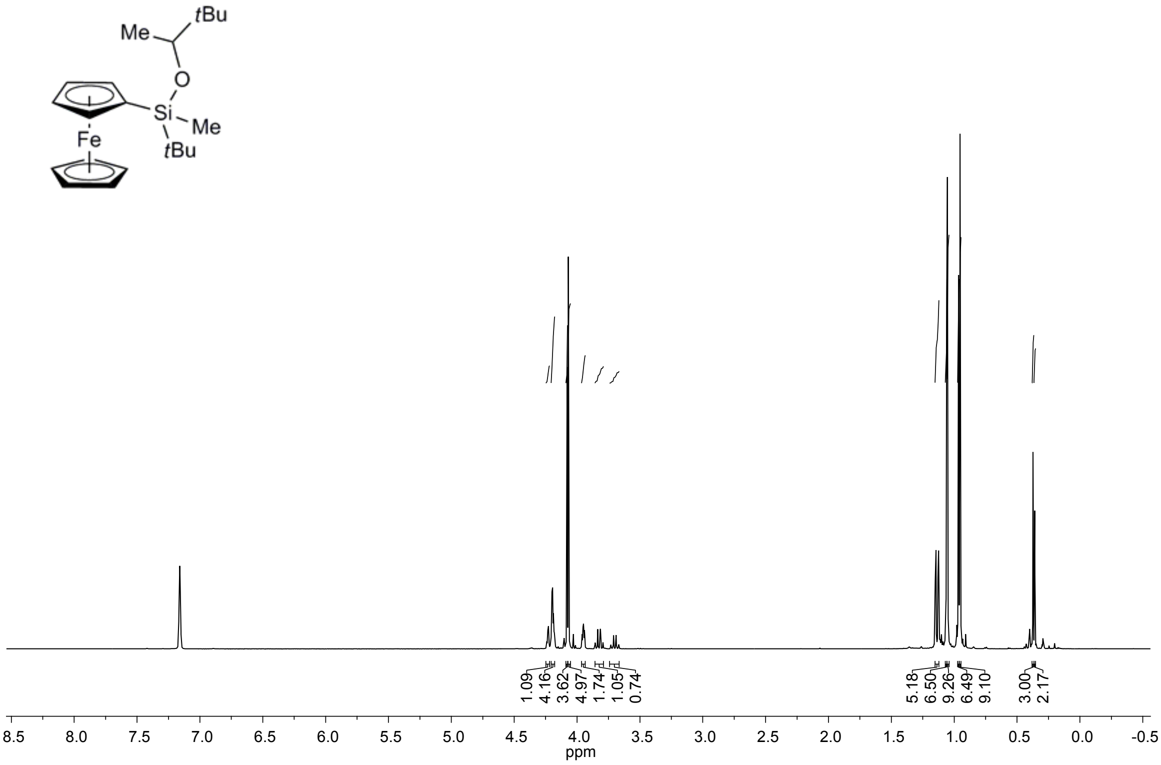


^{29}Si NMR:

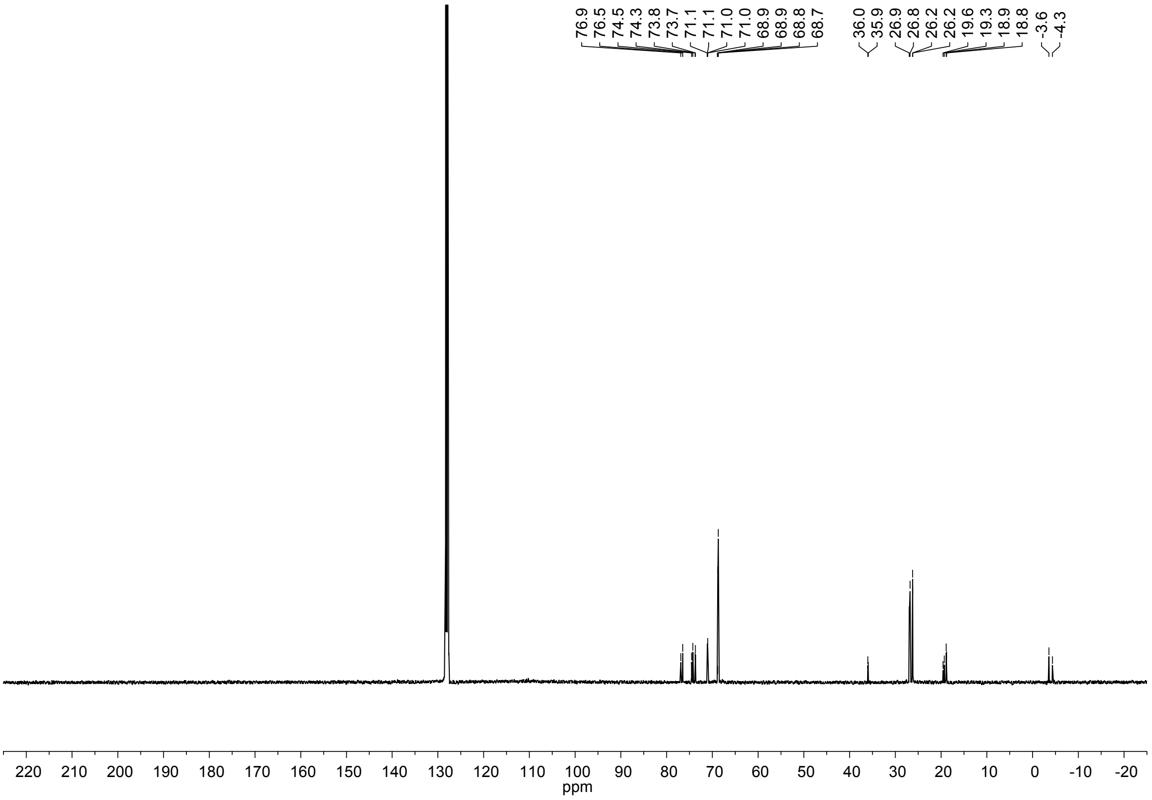


tert-Butylferrocenylmethyl[(3,3-dimethyl)but-2-yloxy]silane (13p):

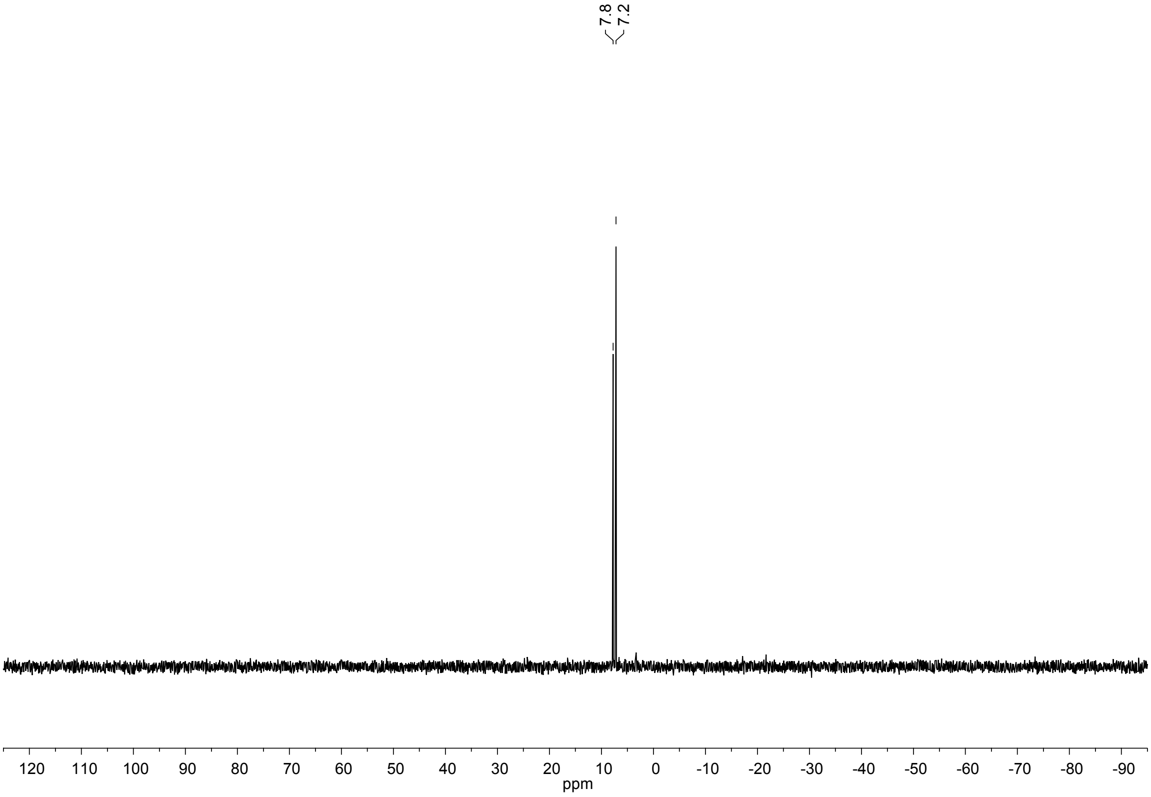
^{1}H NMR:



^{13}C NMR:

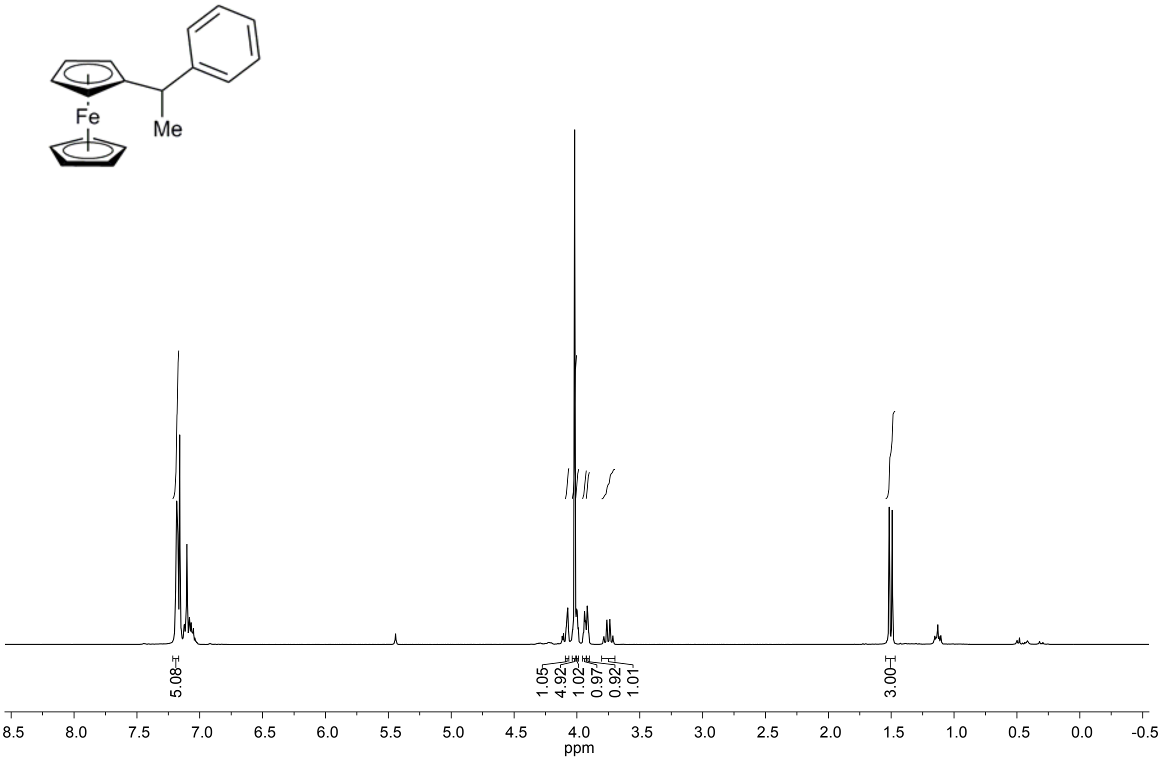


^{29}Si NMR:

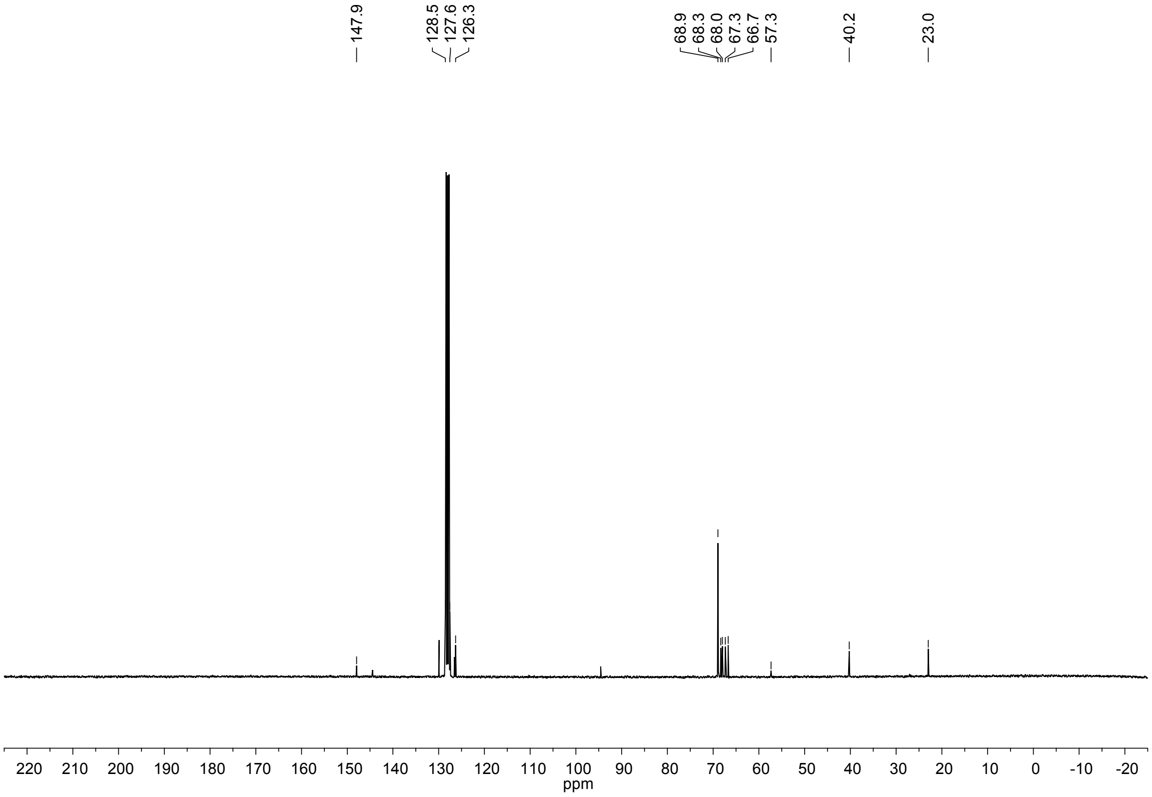


1-Ferrocenyl-1-phenylethane (14a):

^{1}H NMR:



^{13}C NMR:


147.9
128.5
127.6
126.3
68.9
68.3
68.0
67.3
66.7
57.3
40.2
23.0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
ppm