Supporting information for

Catalyst Design for Iron-Promoted Reductions: An Iron Disilyl-dicarbonyl Complex Bearing Weakly Coordinating η^2-(H-Si) Moieties

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General. Manipulation of air and moisture sensitive compounds was carried out under a dry nitrogen atmosphere using standard Schlenk tube techniques associated with a high-vacuum line or in the glove box which was filled with dry nitrogen. All solvents were distilled over appropriate drying reagents prior to use (benzene, toluene, pentane; Ph_2CO/Na). ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on a JEOL Lambda 600 or a Lambda 400 spectrometer at ambient temperature. ^{1}H, ^{13}C and ^{29}Si NMR chemical shifts (δ values) were given in ppm relative to the solvent signal (^{1}H, ^{13}C) or standard resonances (^{29}Si; external tetramethylsilane). Elemental analyses were performed by a Perkin Elmer 2400II/CHN analyzer. IR spectra were recorded on a JASCO FT/IR-550 spectrometer. Photo-irradiation was carried out by an Ushio high-pressure mercury lamp UM-453B-A (450 W). Starting materials, 1,2-bis(dimethylsily)benzene[1] and (η^4-C_6H_8)Fe(CO)$_3$[2] were synthesized by the method reported in the literature.

Preparation of Fe($Me_2SiC_6H_4SiMe_2$){$Me_2Si(H)C_6H_4Si(H)Me_2$}$_2$(CO)$_2$ (1). In a 100 mL Schlenk tube, (η^4-C_6H_8)Fe(CO)$_3$ (1.0 g, 4.50 mmol) was dissolved in pentane (50 mL), and 1,2-bis(dimethylsilyl)benzene (1.92 g, 9.88 mmol) was added to this solution at room temperature. After mixing this solution for 24 hrs at room temperature under irradiation by a high-pressure mercury lamp, the solvent was evaporated *in vacuo*. This crude product was dissolved in pentane (40 mL), and centrifuged to remove the small amount of insoluble materials. The supernatant was collected, concentrated to ca. 10 mL, and cooled at -35 °C to give **1** as coorless crystals (1.05 g, 2.11 mmol, 47 %). ^{1}H NMR (600 MHz, r.t., C_6D_6): δ = -10.2 (s, 2H, H-Si, with a satellite signal due to the coupling with ^{29}Si, $J_{Si\text{-}H}$ = 13.2 Hz), 0.74 (s, 24H, $SiMe_2$), 7.23-7.29 (m, 4H, C_6H_4) 7.51-7.56 (m, 4H, C_6H_4). ^{13}C NMR (150 MHz, r.t., C_6D_6): δ = 9.5 (s, $SiMe_2$), 128.9, 131.7, 153.5 (s, C_6H_4), 2108. (CO). ^{29}Si NMR (119 MHz, r.t., C_6D_6); δ = 35.5 (s, *Si*Me$_2$). IR (KBr, pellet): $\nu_{Si\text{-}H}$ = 1981 cm^{-1}, ν_{CO} = 1929 cm^{-1}. Anal calcd for $C_{22}H_{34}O_2FeSi_4$; C 52.99, H 6.87; found: C 52.84, H 6.77.

Preparation of Fe($Me_2SiC_6H_4SiMe_2$)($MeSCH_2CH_2CH_2SMe$)(CO)$_2$ (6). In a 20 mL schlenk tube, complex **1** (200 mg, 0.40 mmol) was dissolved in toluene (20 mL), and 2,6-dithiaheptane (55 mg, 0.40 mmol) was added. After stirring this solution for 12 hrs at room temperature, the solvent was removed in vacuo. The resulting solid was dissolved in ether (10 mL), concentrated to ca. 5 mL, and cooled at -35 °C to give **6** as yellow crystals (163 mg, 0.37 mmol, 93 %). ^{1}H NMR (600 MHz, r.t., C_6D_6): δ = 0.88 (s, 12H, $SiMe_2$), 1.13-1.19 (m, 2H, -CH_2-), 1.76-1.81 (m, 4H, SCH_2-), 1.80 (s, 6H, SMe), 7.28-7.32 (m, 2H, C_6H_4) 7.73-7.73 (m, 2H, C_6H_4). ^{13}C NMR (150 MHz, r.t., C_6D_6): δ = 5.15 (s, $SiMe_2$), 19.49 (s, -CH_2-), 23.78 (s, SMe), 35.11 (s, SCH_2-), 127.4, 131.4, 155.8 (s, C_6H_4), 209.4 (s, CO). ^{29}Si NMR (119 MHz, r.t., C_6D_6): δ = 40.8 (s, $SiMe_2$). IR (KBr): $\nu_{C\equiv O}$ = 1892, 1874 cm^{-1}; Anal calcd for $C_{17}H_{28}O_2FeSi_2$; C 46.35, H 6.41; found: C 46.21, H 6.38.

X-ray data collection and reduction

X-ray crystallography was performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα radiation ($\lambda = 0.71070$A). The data were collected at 123(2) K using☐ ω scan in the θ range of $3.2 \le \theta \le 27.5$ deg (**1**) and $3.3 \le \theta \le 27.5$ deg (**6**). The data obtained were processed using Crystal-Clear (Rigaku) on a Pentium computer, and were corrected for Lorentz and polarization effects. The structures were solved by direct methods[3], and expanded using Fourier techniques.[4] Hydrogen atoms were refined using the riding model**.** The final cycle of full-matrix least-squares refinement on F^2 was based on 5,780 observed reflections and 262 variable parameters for **1**, 4,220 observed reflections and 217 variable parameters for **6**. Neutral atom scattering factors were taken from Cromer and Waber.[5] All calculations were performed using the CrystalStructure[6] crystallographic software package except for refinement, which was performed using SHELXL-97[7]. Details of final refinement as well as the bond lengths and angles are summarized in **Table S1** and **S2**, and the numbering scheme employed is also shown in **Figure S-1** and **S-2**, which were drawn with ORTEP at 50% probability ellipsoid.

Deposited crystallographic data

CCDC 947204 (**1**) and 947205 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the hydrogenation of alkenes:

In a 50 mL Schlenk tube, **1** [1.2 mg (0.0025 mmol) (for 1-octene), 5 mg (0.01 mmol) (for methyl 10-undecenoate) or 25 mg (0.05 mmol) (for other alkenes)] and alkene (1 mmol) was dissolved in toluene (0.5 mL), and the atmosphere was replaced by 1 atm of hydrogen. The resulting mixture was stirred at room temperature, then anisole (108 μL, 1.0 mmol, internal standard) was added at room temperature. The yield of the product was determined by GC analysis.

Spectral Data of the products

n-Octane

^{1}H NMR (400 MHz, r.t., $CDCl_3$): $\delta = 0.88$ (t, $J_{\text{H-H}} = 7.2$ Hz, 6H, CH_3), 1.16-1.36 (m, 12H, -$(CH_2)_6$-). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): $\delta = 14.27, 22.86, 29.48, 32.10$.

methyl 10-undecanoate

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 0.88 (t, 3H, J_{H-H} = 7.4 Hz, $-CH_3$), 1.17-1.35 (m, 14H, $-CH_2-$), 1.53-1.67 (m, 2H, $-CH_2-$), 2.30 (t, 2H, J_{H-H} = 7.7 Hz, $-CH_2C(=O)-$), 3.66 (s, 3H, OMe). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ = 14.25, 22.83, 25.12, 29.31, 29.40, 29.45, 29.60, 29.70, 32.04, 34.28, 51.57, 174.50

Ethylbenzene

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 1.26 (t, 2H, J_{H-H} = 7.7 Hz, CH_3), 2.67 (q, 2H, J_{H-H} = 7.7 Hz, CH_2), 7.16-7.24 (m, 3H, C_6H_5), 7.27-7.33 (m, 2H, C_6H_5). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ = 15.75, 29.03, 125.73, 128.00, 128.45, 144.40.

Bibenzyl

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 2.93 (s, 4H, CH_2), 7.12-7.23 (m, 6H, C_6H_5), 7.24-7.32 (m, 4H, C_6H_5). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ = 37.9, 125.9, 128.3, 128.5, 141.8.

Norbornane

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 1.12-1.20 (m, 6H, CH_2), 1.43-1.51 (m, 4H, CH_2), 2.16-2.22 (m, 2H, CH). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ = 29.9, 36.5, 38.5.

Cyclopentane

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 1.52 (s, 10H, CH_2). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ = 25.9.

Cyclohexane

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 1.43 (s, 12H, CH_2). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ = 27.0.

Methylcyclohexane

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 0.86 (d, J_{H-H} = 5.8 Hz, 3H, CH_3), 1.04-1.28 (m, 4H, CH_2), 1.28-1.39 (m, 1H, CH), 1.54-1.72 (m, 6H, CH_2). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ = 22.9, 26.3, 26.4, 32.7, 35.4.

2,3-Dimethyl-2-butane

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 0.84 (d, J_{H-H} = 6.7 Hz, 12H, CH_3), 1.40 (septet, J_{H-H} = 6.7 Hz, 12H, CH). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ = 19.4, 33.7.

Hydrosilylation of alkenes:

Hydrosilylation of ethylene with dimethylphenylsilane catalyzed by 1

In a 50 mL Schlenk tube, **1** (5 mg, 0.01 mmol) was dissolved in dimethylphenylsilane (136 mg, 1.0 mmol) in toluene (0.5 mL), and the atmosphere was replaced by 1 atm of ethylene. The resulting mixture was stirred at room temperature for 5 hrs. After removal of the solvent, the product **3a** was isolated by distillation (5 Pa, r.t). Isolated yield: 95 % (156 mg, 0.95 mmol)

^{1}H NMR (400 MHz, r.t., CDCl$_3$): $\delta = 0.25$ (s, 6H, Si(CH$_3$)$_2$), 0.73 (q, 2H, $J_{\mathrm{H\text{-}H}} = 8.2$ Hz, SiCH$_2$), 0.96 (t, 2H, $J_{\mathrm{H\text{-}H}} = 8.2$ Hz, CH$_2$CH_3), 7.31-7.38 (m, 3H, C$_6$H$_5$), 7.48-7.54 (m, 2H, C$_6$H$_5$). ^{13}C NMR (100 MHz, r.t., CDCl$_3$): $\delta = -3.0$, 7.9, 30.2, 128.2, 129.2, 134.1, 140.0.

Hydrosilylation of ethylene with triethylsilane catalyzed by 1

In a 50 mL Schlenk tube, **1** (25 mg, 0.05 mmol) was dissolved in triethylsilane (116 mg, 1.0 mmol) in toluene (0.5 mL), and the atmosphere was replaced by 1 atm of ethylene. The resulting mixture was stirred at room temperature for 5 hrs. After the reaction was completed, the product **3b** was isolated by distillation (5 Pa, r.t). Isolated yield: 92 % (133 mg, 0.92 mmol)

^{1}H NMR (400 MHz, r.t., CDCl$_3$): $\delta = 0.50$ (q, 8H, $J_{\mathrm{H\text{-}H}} = 8.2$ Hz, CH_2CH$_3$), 0.93 (t, 12H, $J_{\mathrm{H\text{-}H}} = 8.2$ Hz, CH$_2$CH_3). ^{13}C NMR (100 MHz, r.t., CDCl$_3$): $\delta = 3.11$, 7.58.

Hydrosilylation of ethylene with triethoxysilane catalyzed by 1

In a 50 mL Schlenk tube, **1** (50 mg, 0.1 mmol) was dissolved in triethoxysilane (164 mg, 1.0 mmol) in toluene (0.5 mL), and the atmosphere was replaced by 1 atm of ethylene. The resulting mixture was stirred at room temperature for 5 hrs. After the reaction was completed, the product **3c** was isolated by distillation (5 Pa, r.t). Isolated yield: 96 % (184 mg, 0.95 mmol)

^{1}H NMR (400 MHz, r.t., CDCl$_3$): $\delta = 0.63$ (q, 2H, $J_{\mathrm{H\text{-}H}} = 7.7$ Hz, CH_2CH$_3$), 1.00 (t, 3H, $J_{\mathrm{H\text{-}H}} = 7.7$ Hz, CH$_2$CH_3), 1.23 (t, 9H, $J_{\mathrm{H\text{-}H}} = 6.8$ Hz, OCH$_2$CH_3), 3.82 (q, 6H, $J_{\mathrm{H\text{-}H}} = 6.8$ Hz, OCH_2CH$_3$). ^{13}C NMR (100 MHz, r.t., CDCl$_3$): $\delta = 2.40$, 6.62, 18.45, 58.47.

Hydrosilylation of ethylene with 1,1,1,3,3-pentamethyldisiloxane catalyzed by 1

In a 50 mL Schlenk tube, **1** (5 mg, 0.01 mmol) was dissolved in 1,1,1,3,3-pentamethyldisiloxane (195 μL, 1.0 mmol) in toluene (0.5 mL), and the atmosphere was replaced by 1 atm of ethylene. The resulting mixture was stirred at room temperature for 5 hrs. After the reaction was completed, the product **3d** was isolated by distillation (5 Pa, r.t). Isolated yield: 91 % (160 mg, 0.91 mmol)

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 0.03 (s, 6H, $Si(CH_3)_2$), 0.06 (s, 9H, $Si(CH_3)_3$), 0.49 (q, 2H, J_{H-H} = 8.2 Hz, $SiCH_2$), 0.92 (t, 3H, J_{H-H} = 8.2 Hz, CH_2CH_3). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ = -0.28, 1.93, 6.72, 10.03. ^{29}Si NMR (119 MHz, r.t., $CDCl_3$): δ = 7.05, 8.60. HRMS (EI) calcd for [$C_7H_{20}OSi_2$]: 176.1053, found 176.1058.

Hydrosilylation of ethylene with 1,1,1,3,5,5,5-heptamethyltrisiloxane catalyzed by 1

In a 50 mL Schlenk tube, **1** (5 mg, 0.01 mmol) was dissolved in 1,1,1,3,5,5,5-heptamethyltrisiloxane (271 μL, 1.0 mmol) in toluene (0.5 mL), and the atmosphere was replaced by 1 atm of ethylene. The resulting mixture was stirred at room temperature for 5 hrs. After the reaction was completed, the product **3e** was isolated by distillation (5 Pa, r.t). Isolated yield: 93 % (234 mg, 0.93 mmol)

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 0.00 (s, 3H, $SiCH_3$), 0.09 (s, 18H, $Si(CH_3)_3$), 0.43 (q, 2H, J_{H-H} = 7.7 Hz, $SiCH_2$), 0.91 (t, 3H, J_{H-H} = 7.7 Hz, CH_2CH_3). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ = -0.96, 1.82, 6.59, 9.31. ^{29}Si NMR (119 MHz, r.t., $CDCl_3$): δ = -20.55, 6.98. HRMS (EI) calcd for [$C_9H_{26}O_2Si_3$]-Me: 235.1006, found 235.1004.

Hydrosilylation of 1-octene with 1,1,1,3,3-pentamethyldisiloxane catalyzed by 1

In a 20 mL Schlenk tube, **1** (15 mg, 0.03 mmol) was dissolved in the mixture of 1-octene (156 μL, 1.0 mmol) and 1,1,1,3,3-pentamethyldisiloxane (195 μL, 1.0 mmol). The resulting mixture was stirred at 80 °C for 3 hrs. After the reaction, the product **3f** was isolated by distillation (8Pa, 70 °C). Isolated yield: 75 % (195 mg, 0.75 mmol). The reaction of 2-octene with 1,1,1,3,3-pentamethyldisiloxane was performed in the same manner to produce **3f** in 80 % yield.

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 0.03 (s, 6H, $Si(CH_3)_2$), 0.06 (s, 9H, $Si(CH_3)_3$), 0.45-0.55 (m, 2H, $SiCH_2$-), 0.88 (t, J_{H-H} = 7.2 Hz, 3H, -$(CH_2)_6CH_3$), 1.20-1.34 (m, 12H, -$(CH_2)_6$-). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ□= 0.34, 1.98, 14.09, 18.42, 22.65, 23.23, 29.29, 29.36, 31.94, 33.37. ^{29}Si NMR (119 MHz, r.t., $CDCl_3$): δ = 6.98, 7.63. HRMS (EI) calcd for [$C_{13}H_{32}OSi_2$]-Me: 245.1757, found 245.1759.

Hydrosilylation of 1-octene with 1,1,1,3,5,5,5-heptamethyltrisiloxane catalyzed by 1

In a 20 mL Schlenk tube, **1** (15 mg, 0.03 mmol) was dissolved in the mixture of 1-octene (156 μL, 1.0 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (271 μL, 1.0 mmol). The resulting mixture was stirred at 80 °C for 3 hrs. After the reaction, the product **3g** was isolated by distillation (5 Pa, 70 °C). Isolated yield: 73 % (244 mg, 0.73 mmol). The reaction of 2-octene with 1,1,1,3,5,5,5-heptamethyltrisiloxane was performed in the same manner to produce **3g** in 82 % yield.

^{1}H NMR (400 MHz, r.t., CDCl$_3$): δ = -0.01 (s, 3H, SiCH$_3$), 0.09 (s, 18H, Si(CH$_3$)$_3$), 0.42-0.47 (m, 2H, SiCH$_2$-), 0.88 (t, $J_{\text{H-H}}$ = 6.8 Hz, 3H, -(CH$_2$)$_6$-CH_3), 1.23-1.33 (m, 12H, -(CH$_2$)$_6$-). ^{13}C NMR (100 MHz, r.t., CDCl$_3$): δ = -0.26, 1.86, 14.11, 17.64, 22.67, 23.06, 29.25, 29.34, 31.93, 33.25. ^{29}Si NMR (119 MHz, r.t., CDCl$_3$): δ = -21.12, 6.78. HRMS (EI) calcd for [$C_{16}H_{38}O_2Si_3$]-Me: 319.1945, found 319.1941.

Hydrosilylation of cyclopentene with 1,1,1,3,3-pentamethyldisiloxane catalyzed by 1

In a 20 mL Schlenk tube, **1** (50 mg, 0.10 mmol) was dissolved in the mixture of cyclopentene (88 µL, 1.0 mmol) and 1,1,1,3,3-pentamethyldisiloxane (196 µL, 1.0 mmol). The resulting mixture was stirred at 80 °C for 3 hrs. After the reaction, the product **3h** was isolated by distillation (5 Pa, r.t). Isolated yield: 73 % (158 mg, 0.73 mmol)

^{1}H NMR (400 MHz, r.t., CDCl$_3$): δ = 0.02 (s, 6H, Si(CH$_3$)$_2$), 0.06 (s, 9H, Si(CH$_3$)$_3$), 0.86 (tt, $J_{\text{H-H}}$ = 8.2, 10.6 Hz, 1H, SiCH-), 1.20-1.36 (m, 2H, -CH$_2$-), 1.44-1.62 (m, 4H, -CH$_2$-), 1.65-1.78 (m, 2H, -CH$_2$-). ^{13}C NMR (100 MHz, r.t., CDCl$_3$): δ = -0.91, 2.12, 27.31, 27.55, 27.63. ^{29}Si NMR (119 MHz, r.t., CDCl$_3$): δ = 6.67, 7.52.

Hydrosilylation of cyclopentene with 1,1,1,3,5,5,5-heptamethyltrisiloxane catalyzed by 1

In a 20 mL Schlenk tube, **1** (50 mg, 0.1 mmol) was dissolved in the mixture of cyclopentene (88 µL, 1.0 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (271 µL, 1.0 mmol). The resulting mixture was stirred at 80 °C for 3 hrs. After the reaction, the product **3i** was isolated by distillation (5 Pa, r.t). Isolated yield: 78 % (226 mg, 0.78 mmol)

^{1}H NMR (400 MHz, r.t., CDCl$_3$): δ = 0.23 (s, 3H, SiCH$_3$), 0.28 (s, 18H, Si(CH$_3$)$_3$), 0.96-1.05 (m, 1H, SiCH), 1.54-1.65 (m, 4H, -CH$_2$-), 1.69-1.75 (m, 2H, -CH$_2$-), 1.86-1.92 (m, 2H, -CH$_2$-). ^{13}C NMR (100 MHz, r.t., CDCl$_3$): δ = -1.39, 2.19, 27.46, 27.66, 27.92. ^{29}Si NMR (119 MHz, r.t., CDCl$_3$): δ = -21.70, 6.59. HRMS (EI) calcd for [$C_{12}H_{30}O_2Si_3$]-Me: 275.1319, found 275.1319.

Hydrosilylation of styrene with 1,1,1,3,3-pentamethyldisiloxane catalyzed by 1

In a 20 mL Schlenk tube, **1** (50 mg, 0.1 mmol) was dissolved in the mixture of styrene (104 mg, 1 mmol) and 1,1,1,3,3-pentamethyldisiloxane (195 µL, 1.0 mmol). The resulting mixture was stirred at 80 °C for 3 hrs. After the reaction, the product (*E*)-[1-(phenyl)-2-(1,1,3,3,3-pentamethyldisiloxane)]ethene was isolated by silica-gel column chromatography with hexane as the eluent. Isolated yield: 42 % (104 mg, 0.42 mmol)

^{1}H NMR (400 MHz, r.t., CDCl$_3$): δ = 0.11 (s, 6H, Si(CH$_3$)$_2$), 0.22 (s, 9H, Si(CH$_3$)$_3$), 6.42 (d, J_{H-H} = 19.3 Hz, 1H, -CH=CH-), 6.93 (d, J_{H-H} = 19.3 Hz, 1H, -CH=CH-), 7.24-7.29 (m, 1H, C$_6$H$_5$), 7.31-7.39 (m, 2H, C$_6$H$_5$), 7.43-7.47 (m, 2H, C$_6$H$_5$). ^{13}C NMR (100 MHz, r.t., CDCl$_3$): δ = 0.95, 2.18, 126.66, 128.27, 128.67, 128.91, 138.40, 144.27. ^{29}Si NMR (119 MHz, r.t., CDCl$_3$): δ = -3.05, 8.48. HRMS (EI) calcd for [C$_{13}$H$_{22}$OSi$_2$]: 250.1209, found 250.1207.

General Procedure for the Reduction of Carboxamides:[8,9]

In a 20 mL Schlenk tube, **1** (1.0 mg, 2.0 x 10^{-3} mmol) was dissolved in the mixture of toluene (0.5 mL) and carboxamide **4a-f** (1 mmol), and 1,2-bis(dimethylsilyl)benzene (BDSB: 475 μL, 2.2 mmo) was added to this solution. The solution was stirred at 80 °C for 30 min. After complete consumption of **4** was confirmed by TLC analysis, the reaction mixture was passed through a Florisil® column with Celite putting on the head. After removal of the solvent, purification of the residue by alumina column chromatography gave the amine **5a-f**.

Spectral Data of Amines

N,*N*-Dimethyl-(*p*-methoxybenzyl)amine (5a)

^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.22 (s, 6H), 3.34 (s, 2H), 3.80 (s, 3H), 6.86 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 45.0, 55.1, 63.6, 113.5, 130.1, 130.7, 158.6. IR (neat): ν = 2941, 2813, 2768, 1613, 1511, 1456, 1300, 1177, 1038, 854, 810 cm^{-1}.

N,*N*-Dimethyl-(*p*-bromobenzyl)amine (5b)

^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.22 (s, 6H), 3.36 (s, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 45.4, 63.7, 120.9, 130.7, 131.4, 138.1. IR (neat): ν = 2941, 2815, 1487, 1361, 1259, 1173, 1070, 1011, 856, 796 cm^{-1}.

N,*N*-Dimethyl-(*p*-methoxycarbonyl)amine (5c)

^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.21 (s, 6H), 3.46 (s, 2H), 3.91 (s, 3H), 7.38 (d, J = 8.2 Hz, 2H), 8.00 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 45.4, 51.9, 63.9, 128.8, 128.9, 129.5, 144.3, 166.9. IR (neat): ν = 2948, 2816, 2769, 1726, 1611, 1435, 1414, 1361, 1280, 1173, 1146, 1110, 1019, 968, 865, 757, 700 cm^{-1}.

N-Methylbenzylamine (5d)

^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.40 (s, 3H), 3.70 (s, 2H), 7.16-7.34 (m, 5H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 36.5, 61.0, 127.4, 128.7, 128.9, 140.5. IR (neat): ν = 3321, 3284, 3084, 3062, 2968, 2932, 2843, 2788, 1603, 1494, 1473, 1453, 1356, 1128, 1104, 1073, 1028, 824, 735, 698 cm^{-1}.

***N*,*N*-Dimethyl-3-phenylpropylamine (5e)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.80 (tt, *J* = 8.2, 7.7 Hz, 2H), 2.23 (s, 6H), 2.30 (t, *J* = 7.7 Hz, 2H), 2.63 (t, *J* = 8.2 Hz, 2H), 7.15–7.23 (m, 3H), 7.25–7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.5, 33.6, 45.5, 59.3, 125.7, 128.3, 128.4, 142.3. IR (neat): ν = 3062, 3026, 2942, 2764, 1603, 1496, 1454, 1265, 1030 cm^{-1}.

1-Benzylazepane (5f)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53–1.73 (m, 8H), 2.51–2.68 (m, 4H), 3.64 (s, 2H), 7.19–7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.1, 28.3, 55.7, 62.8, 126.7, 128.1, 128.88, 140.2. IR (neat): ν = 2925, 2852, 1453, 1354, 1153, 1071, 961, 745, 697 cm^{-1}.

Reduction of various carbonyl compounds

Reduction of 3-phenylpropanal catalyzed by 1

In a 20 mL Schlenk tube, 3-phenylpropanal (**4g**) (135 mg, 1.0 mmol) and 1,1,3,3-tetramethyldisiloxane (202 mg, 1.5 mmol) were added, then **1** (5 mg, 0.01 mmol) was added to the reaction mixture. The mixture was stirred at room temperature for 3 hrs. After complete conversion of the starting material, the reaction mixture was cooled to 0 °C, and quenched by addition of TBAF (2.0 mL, 1 M in THF) and stirred at room temperature for 1 hr. The residue was purified by silica-gel column chromatography to give the desired alcohol **5g**. Isolated yield: 92 % (125 mg, 0.92 mmol)

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 1.27 (br, 1H, OH), 1.87-1.94 (m, 2H, $-CH_2-$), 2.72 (t, $J_{H\text{-}H}$ = 7.3 Hz, 2H, $-CH_2C_6H_5$), 3.66-3.71 (m, 2H, $-CH_2OH$), 7.17-7.21 (m, 3H, C_6H_5), 7.27-7.31 (m, 2H, C_6H_5). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ = 32.1, 34.2, 62.3, 125.9, 128.40, 128.42, 141.8.

Reduction of 4-methoxybenzaldehyde catalyzed by 1

In a 20 mL Schlenk tube, 4-methoxybenzaldehyde (**4h**) (138 mg, 1.0 mmol) and 1,1,3,3-tetramethyldisiloxane (202 mg, 1.5 mmol) were added, then **1** (5 mg, 0.01 mmol) was added to the reaction mixture. The mixture was stirred at room temperature for 3 hrs. After complete conversion of the starting material, the reaction mixture was cooled to 0 °C, and quenched by addition of TBAF (2.0

mL, 1 M in THF) and stirred at room temperature for 1 hr. The residue was purified by silica-gel column chromatography to give the desired alcohol **5h**. Isolated yield: 97 % (134 mg, 0.97 mmol)

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 1.74 (br, 1H, OH), 3.81 (s, 3H, CH_3O), 4.62 (s, 2H, CH_2), 6.89-6.91 (m, 2H, C_6H_4), 7.26-7.31 (m, 2H, C_6H_4). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ = 55.2, 64.8, 113.9, 128.5, 133.1, 159.1.

Reduction of 1-(4-methoxyphenyl)ethanone catalyzed by 1

In a 20 mL Schlenk tube, 1-(4-methoxyphenyl)ethanone (**4i**) (151 mg, 1.0 mmol) and 1,1,3,3-tetramethyldisiloxane (202 mg, 1.5 mmol) were added, then **1** (5 mg, 0.01 mmol) was added to the reaction mixture. The mixture was stirred at room temperature for 6 hrs. After complete conversion of the starting material, the reaction mixture was cooled to 0 °C, and quenched by addition of TBAF (2.0 mL, 1 M in THF) and stirred at room temperature for 1 hr. The residue was purified by silica-gel column chromatography to give the desired alcohol **5i**. Isolated yield: 96 % (146 mg, 0.96 mmol)

^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ = 1.49 (d, $J_{H\text{-}H}$ = 6.8 Hz, 3H, $-CH_3$), 1.70 (br, 1H, OH), 3.81 (s, 3H, CH_3O), 4.87 (q, $J_{H\text{-}H}$ = 6.3 Hz, 1H, -CH-), 6.87-6.90 (m, 2H, C_6H_4), 7.29-7.32 (m, 2H, C_6H_4). ^{13}C NMR (100 MHz, r.t., $CDCl_3$): δ = 25.0, 55.3, 70.0, 113.9, 126.6, 138.0, 159.0.

Reduction of ethyl 3-phenylpropanoate catalyzed by 1

In a 20 mL Schlenk tube, ethyl 3-phenylpropanoate (**4j**) (178 mg, 1.0 mmol) and 1,1,3,3-tetramethyldisiloxane (336 mg, 2.5 mmol) were added, then **1** (15 mg, 0.03 mmol) was added to the reaction mixture. The mixture was stirred at room temperature for 3 hrs. After complete conversion of the starting material, the reaction mixture was cooled to 0 °C, and quenched by addition of TBAF (2.0 mL, 1 M in THF) and stirred at room temperature for 1 hr. The residue was purified by silica-gel column chromatography to give the desired alcohol **5g**. Isolated yield: 96 % (131 mg, 0.96 mmol)

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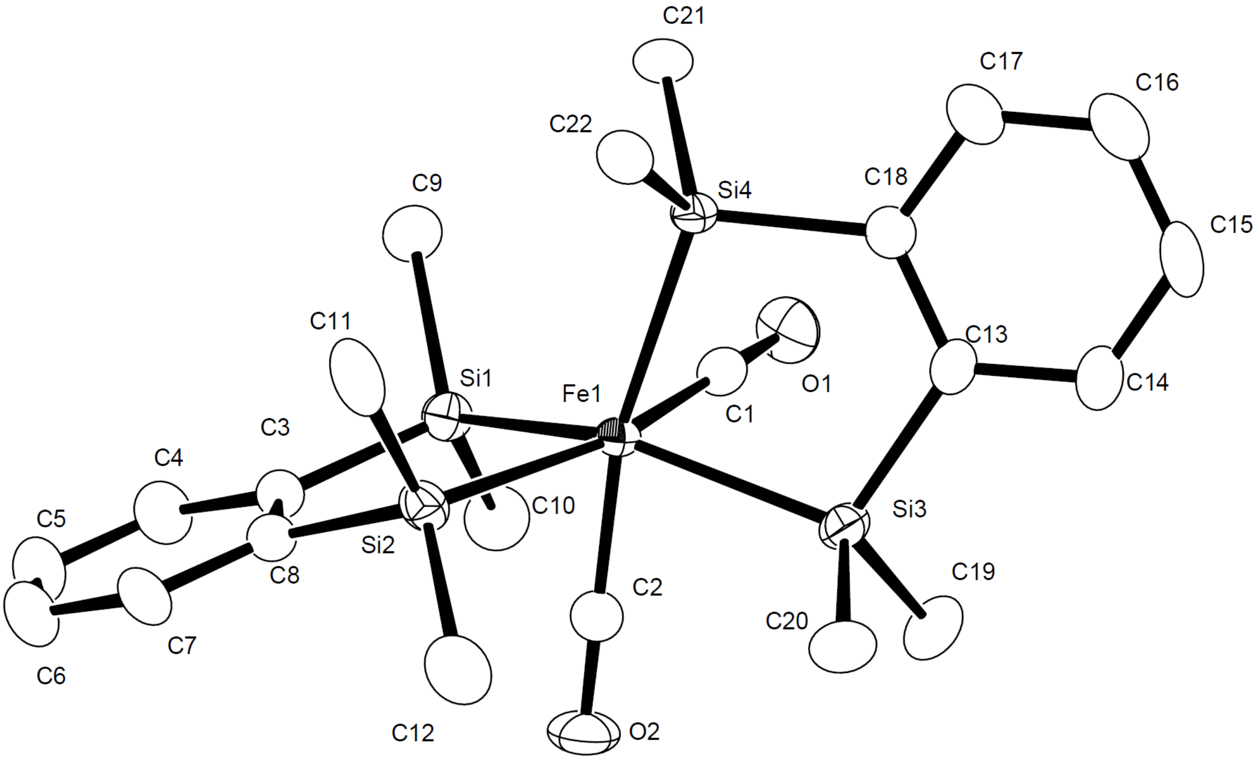


Figure S-1. ORTEP drawing of **1** (50% probability of the thermal ellipsoids).

Table S1-1. Crystal data and structure refinement for **1**

Empirical Formula	$C_{22}H_{32}FeO_2Si_4$
Formula Weight	496.68
Crystal Color, Habit	colorless, plate
Crystal Dimensions	0.120 X 0.100 X 0.030 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 17.122(3) Å b = 16.141(2) Å c = 9.4508(12) Å V = 2611.9(6) $Å^3$
Space Group	$Pna2_1$ (#33)
Z value	4
D_{calc}	1.263 g/cm^3
F_{000}	1048.00
μ(MoKα)	7.753 cm^{-1}
Temperature	-150.0^oC
Detector Aperture	70 x 70 mm
Data Images	720 exposures
ω oscillation Range	$-110.0 - 70.0^o$
Exposure Rate	$48.0 sec./^o$
Detector Swing Angle	-19.93^o
Detector Position	42.96 mm
Pixel Size	0.137 mm
$2\theta_{max}$	55.0^o
No. of Reflections Measured	Total: 20986 Unique: 5780 (R_{int} = 0.1369) Friedel pairs: 2613
Corrections	Lorentz-polarization Absorption (trans. factors: 0.849 - 0.977)
No. Observations (All reflections)	5780
No. Variables	262
Reflection/Parameter Ratio	22.06
Residuals: R1 (I>2.00σ(I))	0.0558
Residuals: R (All reflections)	0.0600
Residuals: wR2 (All reflections)	0.1434
Goodness of Fit Indicator	1.067
Flack Parameter (Friedel pairs = 2613)	-0.03(3)
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.78 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.69 $e^-/Å^3$

Table S1-2. Atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}
Fe1	0.75557(3)	0.96929(3)	0.38970(7)	1.393(11)
Si1	0.81740(6)	0.87067(6)	0.54196(11)	1.80(2)
Si2	0.88121(6)	0.98314(7)	0.27388(11)	1.92(2)
Si3	0.64484(6)	1.00156(7)	0.24194(12)	1.90(2)
Si4	0.73414(6)	1.10301(6)	0.49963(11)	1.60(2)
O1	0.6302(2)	0.9301(2)	0.5877(4)	2.79(6)
O2	0.7564(2)	0.8249(3)	0.2045(4)	3.26(7)
C1	0.6794(2)	0.9468(3)	0.5090(5)	1.94(6)
C2	0.7569(2)	0.8833(3)	0.2753(5)	2.12(7)
C3	0.9161(3)	0.8501(3)	0.4624(5)	1.99(6)
C4	0.9638(3)	0.7873(3)	0.5187(5)	2.83(8)
C5	1.0366(3)	0.7708(3)	0.4613(6)	3.14(9)
C6	1.0619(3)	0.8152(3)	0.3449(6)	3.20(9)
C7	1.0165(3)	0.8778(3)	0.2879(5)	2.65(8)
C8	0.9422(2)	0.8955(3)	0.3450(5)	2.00(6)
C9	0.8291(3)	0.9034(3)	0.7307(5)	2.61(7)
C10	0.7632(3)	0.7694(3)	0.5512(6)	2.68(8)
C11	0.9403(3)	1.0788(3)	0.3062(6)	3.10(9)
C12	0.8765(3)	0.9743(4)	0.0771(5)	3.67(11)
C13	0.5959(2)	1.0917(3)	0.3293(5)	1.89(6)
C14	0.5206(3)	1.1157(3)	0.2889(5)	2.61(7)
C15	0.4830(3)	1.1811(3)	0.3562(5)	2.93(9)
C16	0.5200(3)	1.2233(3)	0.4661(6)	2.85(8)
C17	0.5941(3)	1.2006(3)	0.5066(5)	2.53(7)
C18	0.6331(2)	1.1344(3)	0.4409(4)	1.82(6)
C19	0.5731(3)	0.9149(3)	0.2328(6)	3.01(8)
C20	0.6683(3)	1.0268(3)	0.0530(5)	2.81(8)
C21	0.7343(3)	1.0998(3)	0.6973(5)	2.35(7)
C22	0.7999(3)	1.1908(3)	0.4490(5)	2.39(7)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S1-3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe1	0.0208(3)	0.0156(3)	0.0165(3)	0.0001(2)	-0.0001(2)	-0.0018(2)
Si1	0.0260(5)	0.0215(5)	0.0209(5)	0.0018(4)	-0.0011(4)	0.0019(4)
Si2	0.0236(5)	0.0269(5)	0.0226(6)	0.0021(4)	0.0043(4)	0.0001(4)
Si3	0.0256(5)	0.0230(5)	0.0238(5)	-0.0010(4)	-0.0058(4)	-0.0029(4)
Si4	0.0207(5)	0.0191(5)	0.0209(5)	-0.0012(4)	-0.0002(4)	-0.0046(4)
O1	0.031(2)	0.036(2)	0.039(2)	-0.0082(13)	0.0102(13)	0.004(2)
O2	0.057(2)	0.029(2)	0.038(2)	0.007(2)	-0.007(2)	-0.017(2)
C1	0.025(2)	0.019(2)	0.030(2)	-0.001(2)	-0.005(2)	-0.003(2)
C2	0.027(2)	0.027(3)	0.026(2)	0.002(2)	-0.001(2)	-0.002(2)
C3	0.025(2)	0.022(2)	0.029(2)	0.003(2)	-0.004(2)	-0.004(2)
C4	0.038(3)	0.029(2)	0.040(3)	0.009(2)	-0.004(2)	0.001(2)
C5	0.032(2)	0.032(3)	0.056(3)	0.009(2)	-0.005(2)	-0.004(2)
C6	0.030(2)	0.032(3)	0.060(3)	0.007(2)	0.002(2)	-0.010(2)
C7	0.026(2)	0.031(2)	0.043(3)	0.004(2)	0.007(2)	-0.008(2)
C8	0.024(2)	0.025(2)	0.027(2)	0.001(2)	-0.002(2)	-0.005(2)
C9	0.036(2)	0.044(3)	0.019(2)	0.005(2)	-0.002(2)	0.002(2)
C10	0.041(3)	0.023(2)	0.039(3)	-0.004(2)	-0.000(2)	0.008(2)
C11	0.024(2)	0.029(3)	0.065(4)	0.001(2)	0.014(2)	0.006(2)
C12	0.044(3)	0.072(4)	0.024(3)	0.011(3)	0.011(2)	0.003(3)
C13	0.021(2)	0.024(2)	0.026(2)	-0.001(2)	-0.004(2)	0.004(2)
C14	0.024(2)	0.036(3)	0.039(3)	0.004(2)	-0.006(2)	0.002(2)
C15	0.024(2)	0.044(3)	0.044(3)	0.015(2)	0.001(2)	0.010(2)
C16	0.036(3)	0.029(2)	0.043(3)	0.009(2)	0.010(2)	0.004(2)
C17	0.033(2)	0.025(2)	0.039(3)	0.004(2)	0.005(2)	0.000(2)
C18	0.023(2)	0.020(2)	0.026(2)	-0.002(2)	0.002(2)	0.002(2)
C19	0.033(2)	0.034(3)	0.048(3)	-0.008(2)	-0.013(2)	-0.003(2)
C20	0.048(3)	0.038(3)	0.021(2)	0.004(2)	-0.005(2)	-0.001(2)
C21	0.035(2)	0.032(3)	0.022(2)	0.001(2)	-0.001(2)	-0.008(2)
C22	0.026(2)	0.025(2)	0.040(3)	-0.005(2)	0.005(2)	-0.007(2)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S1-4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Fe1	Si1	2.3928(12)	Fe1	Si2	2.4240(12)
Fe1	Si3	2.4116(13)	Fe1	Si4	2.4233(12)
Fe1	C1	1.762(4)	Fe1	C2	1.760(5)
Si1	C3	1.879(4)	Si1	C9	1.871(5)
Si1	C10	1.882(5)	Si2	C8	1.882(4)
Si2	C11	1.870(5)	Si2	C12	1.867(5)
Si3	C13	1.871(4)	Si3	C19	1.864(5)
Si3	C20	1.875(5)	Si4	C18	1.887(4)
Si4	C21	1.868(5)	Si4	C22	1.872(4)
O1	C1	1.155(5)	O2	C2	1.156(6)
C3	C4	1.406(6)	C3	C8	1.403(6)
C4	C5	1.385(7)	C5	C6	1.383(8)
C6	C7	1.384(7)	C7	C8	1.411(6)
C13	C14	1.400(6)	C13	C18	1.412(6)
C14	C15	1.391(7)	C15	C16	1.393(7)
C16	C17	1.376(6)	C17	C18	1.404(6)

Table S1-5. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
Si1	Fe1	Si2	86.58(4)	Si1	Fe1	Si3	147.11(5)
Si1	Fe1	Si4	113.68(5)	Si1	Fe1	C1	78.80(13)
Si1	Fe1	C2	80.75(15)	Si2	Fe1	Si3	114.60(5)
Si2	Fe1	Si4	104.23(4)	Si2	Fe1	C1	164.79(13)
Si2	Fe1	C2	77.54(13)	Si3	Fe1	Si4	86.38(4)
Si3	Fe1	C1	80.38(13)	Si3	Fe1	C2	79.88(14)
Si4	Fe1	C1	78.30(13)	Si4	Fe1	C2	165.45(15)
C1	Fe1	C2	103.87(18)	Fe1	Si1	C3	105.95(13)
Fe1	Si1	C9	115.65(15)	Fe1	Si1	C10	112.81(16)
C3	Si1	C9	109.56(19)	C3	Si1	C10	107.98(19)
C9	Si1	C10	104.7(3)	Fe1	Si2	C8	105.17(13)
Fe1	Si2	C11	118.83(16)	Fe1	Si2	C12	113.84(17)
C8	Si2	C11	105.16(19)	C8	Si2	C12	108.8(3)
C11	Si2	C12	104.4(3)	Fe1	Si3	C13	105.35(13)
Fe1	Si3	C19	112.50(16)	Fe1	Si3	C20	115.48(16)
C13	Si3	C19	108.01(19)	C13	Si3	C20	110.3(2)
C19	Si3	C20	105.1(3)	Fe1	Si4	C18	104.60(13)
Fe1	Si4	C21	113.82(15)	Fe1	Si4	C22	118.25(14)
C18	Si4	C21	107.63(18)	C18	Si4	C22	105.86(18)
C21	Si4	C22	106.0(2)	Fe1	C1	O1	178.3(4)
Fe1	C2	O2	177.2(4)	Si1	C3	C4	119.9(3)
Si1	C3	C8	120.7(3)	C4	C3	C8	119.4(4)
C3	C4	C5	120.9(5)	C4	C5	C6	119.6(5)
C5	C6	C7	120.8(5)	C6	C7	C8	120.4(5)
Si2	C8	C3	119.9(3)	Si2	C8	C7	121.1(3)
C3	C8	C7	118.9(4)	Si3	C13	C14	120.5(3)
Si3	C13	C18	120.5(3)	C14	C13	C18	118.9(4)
C13	C14	C15	120.8(4)	C14	C15	C16	120.1(4)
C15	C16	C17	119.8(5)	C16	C17	C18	121.2(4)
Si4	C18	C13	120.1(3)	Si4	C18	C17	120.7(3)
C13	C18	C17	119.2(4)				

Table S1-6. Torsion Angles(°) (Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Si1	Fe1	Si2	C8	11.35(5)	Si1	Fe1	Si2	C11	-105.95(6)
Si1	Fe1	Si2	C12	130.39(6)	Si2	Fe1	Si1	C3	-9.69(5)
Si2	Fe1	Si1	C9	111.88(6)	Si2	Fe1	Si1	C10	-127.63(6)
Si1	Fe1	Si3	C13	115.81(8)	Si1	Fe1	Si3	C19	-1.62(12)
Si1	Fe1	Si3	C20	-122.23(8)	Si3	Fe1	Si1	C3	122.80(8)
Si3	Fe1	Si1	C9	-115.63(8)	Si3	Fe1	Si1	C10	4.87(11)
Si1	Fe1	Si4	C18	-138.14(5)	Si1	Fe1	Si4	C21	-20.94(7)
Si1	Fe1	Si4	C22	104.43(6)	Si4	Fe1	Si1	C3	-113.74(5)
Si4	Fe1	Si1	C9	7.83(7)	Si4	Fe1	Si1	C10	128.33(5)
C1	Fe1	Si1	C3	174.48(14)	C1	Fe1	Si1	C9	-63.95(14)
C1	Fe1	Si1	C10	56.55(14)	C2	Fe1	Si1	C3	68.23(14)
C2	Fe1	Si1	C9	-170.20(14)	C2	Fe1	Si1	C10	-49.71(14)
Si2	Fe1	Si3	C13	-118.24(6)	Si2	Fe1	Si3	C19	124.33(6)
Si2	Fe1	Si3	C20	3.72(8)	Si3	Fe1	Si2	C8	-142.52(5)
Si3	Fe1	Si2	C11	100.18(7)	Si3	Fe1	Si2	C12	-23.48(8)
Si2	Fe1	Si4	C18	129.34(5)	Si2	Fe1	Si4	C21	-113.46(6)
Si2	Fe1	Si4	C22	11.91(7)	Si4	Fe1	Si2	C8	124.93(5)
Si4	Fe1	Si2	C11	7.63(7)	Si4	Fe1	Si2	C12	-116.03(6)
C2	Fe1	Si2	C8	-69.92(15)	C2	Fe1	Si2	C11	172.78(16)
C2	Fe1	Si2	C12	49.12(16)	Si3	Fe1	Si4	C18	14.86(5)
Si3	Fe1	Si4	C21	132.07(6)	Si3	Fe1	Si4	C22	-102.56(6)
Si4	Fe1	Si3	C13	-14.24(5)	Si4	Fe1	Si3	C19	-131.67(6)
Si4	Fe1	Si3	C20	107.72(6)	C1	Fe1	Si3	C13	64.50(13)
C1	Fe1	Si3	C19	-52.93(14)	C1	Fe1	Si3	C20	-173.55(14)
C2	Fe1	Si3	C13	170.59(15)	C2	Fe1	Si3	C19	53.16(15)
C2	Fe1	Si3	C20	-67.45(15)	C1	Fe1	Si4	C18	-66.05(14)
C1	Fe1	Si4	C21	51.15(14)	C1	Fe1	Si4	C22	176.52(14)
Fe1	Si1	C3	C4	-172.8(3)	Fe1	Si1	C3	C8	5.7(3)
C9	Si1	C3	C4	61.8(4)	C9	Si1	C3	C8	-119.7(3)
C10	Si1	C3	C4	-51.7(4)	C10	Si1	C3	C8	126.8(3)
Fe1	Si2	C8	C3	-12.0(3)	Fe1	Si2	C8	C7	172.1(3)
C11	Si2	C8	C3	114.3(3)	C11	Si2	C8	C7	-61.7(4)
C12	Si2	C8	C3	-134.3(3)	C12	Si2	C8	C7	49.7(4)
Fe1	Si3	C13	C14	-166.5(3)	Fe1	Si3	C13	C18	10.9(3)
C19	Si3	C13	C14	-46.0(4)	C19	Si3	C13	C18	131.3(3)
C20	Si3	C13	C14	68.3(4)	C20	Si3	C13	C18	-114.4(3)
Fe1	Si4	C18	C13	-13.6(3)	Fe1	Si4	C18	C17	166.9(3)
C21	Si4	C18	C13	-135.0(3)	C21	Si4	C18	C17	45.5(4)
C22	Si4	C18	C13	112.0(3)	C22	Si4	C18	C17	-67.5(3)
Si1	C3	C4	C5	179.7(3)	Si1	C3	C8	Si2	4.4(5)
Si1	C3	C8	C7	-179.6(3)	C4	C3	C8	Si2	-177.1(3)
C4	C3	C8	C7	-1.1(6)	C8	C3	C4	C5	1.2(6)
C3	C4	C5	C6	-1.7(7)	C4	C5	C6	C7	2.2(7)
C5	C6	C7	C8	-2.1(7)	C6	C7	C8	Si2	177.5(4)
C6	C7	C8	C3	1.5(6)	Si3	C13	C14	C15	178.1(3)
Si3	C13	C18	Si4	1.9(5)	Si3	C13	C18	C17	-178.5(3)
C14	C13	C18	Si4	179.3(3)	C14	C13	C18	C17	-1.1(6)
C18	C13	C14	C15	0.7(6)	C13	C14	C15	C16	-0.5(7)
C14	C15	C16	C17	0.7(7)	C15	C16	C17	C18	-1.2(7)
C16	C17	C18	Si4	-179.1(4)	C16	C17	C18	C13	1.4(6)

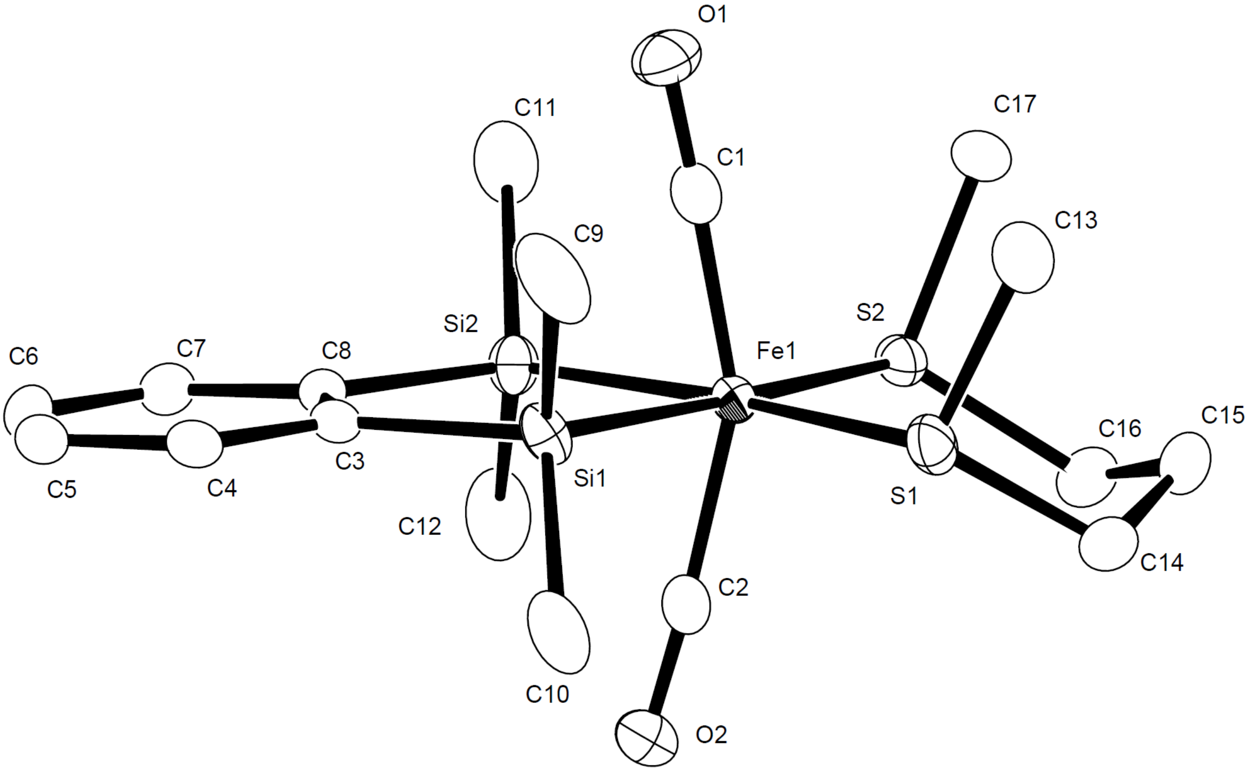


Figure S-2. ORTEP drawing of **6** (50% probability of the thermal ellipsoids).

Table S2-1. Crystal data and structure refinement for **6**

Empirical Formula	$C_{17}H_{28}FeO_2S_2Si_2$
Formula Weight	440.54
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.130 X 0.120 X 0.090 mm
Crystal System	monoclinic
Lattice Type	C-centered
Lattice Parameters	a = 16.522(4) Å
	b = 9.045(2) Å
	c = 15.932(4) Å
	β = 116.341(3) °
	V = 2133.7(8) Å^3
Space Group	Cc (#9)
Z value	4
D_{calc}	1.371 g/cm^3
F_{000}	928.00
μ(MoKα)	10.212 cm^{-1}
Temperature	-150.0°C
Detector Aperture	70 x 70 mm
Data Images	720 exposures
ω oscillation Range	-110.0 - 70.0°
Exposure Rate	32.0 sec./°
Detector Swing Angle	-19.91°
Detector Position	43.03 mm
Pixel Size	0.137 mm
$2\theta_{max}$	54.9°
No. of Reflections Measured	Total: 8514
	Unique: 4220 (R_{int} = 0.0287)
	Friedel pairs: 1777
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.799 - 0.912)
No. Observations (All reflections)	4220
No. Variables	217
Reflection/Parameter Ratio	19.45
Residuals: R1 (I>2.00σ(I))	0.0272
Residuals: R (All reflections)	0.0290
Residuals: wR2 (All reflections)	0.0652
Goodness of Fit Indicator	1.080
Flack Parameter (Friedel pairs = 1777)	-0.006(12)
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.41 e^-/Å^3
Minimum peak in Final Diff. Map	-0.22 e^-/Å^3

Table S2-2. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Fe1	0.06046(2)	1.03949(4)	0.14362(2)	1.386(7)
S1	0.18103(4)	1.19654(7)	0.20856(4)	2.045(11)
S2	-0.03816(4)	1.17740(6)	0.17634(4)	1.699(11)
Si1	0.15255(4)	0.88442(8)	0.10564(4)	1.715(11)
Si2	-0.05648(4)	0.86872(7)	0.06884(5)	1.632(11)
O1	0.1120(2)	0.8274(2)	0.29773(13)	2.51(4)
O2	-0.0014(2)	1.1274(3)	-0.05207(13)	2.93(4)
C1	0.0918(2)	0.9139(3)	0.2373(2)	1.71(4)
C2	0.0240(2)	1.0968(3)	0.0267(2)	1.96(5)
C3	0.0804(2)	0.7227(3)	0.0365(2)	1.52(4)
C4	0.1152(2)	0.6114(3)	-0.0004(2)	1.84(4)
C5	0.0608(2)	0.4962(3)	-0.0533(2)	2.22(5)
C6	-0.0293(2)	0.4912(3)	-0.0704(2)	2.15(5)
C7	-0.0640(2)	0.5999(3)	-0.0338(2)	1.88(4)
C8	-0.0100(2)	0.7165(3)	0.0206(2)	1.58(4)
C9	0.2544(2)	0.8036(4)	0.2080(2)	3.18(6)
C10	0.2037(3)	0.9709(4)	0.0326(3)	3.15(6)
C11	-0.1032(2)	0.7841(4)	0.1465(3)	2.98(6)
C12	-0.1614(2)	0.9411(4)	-0.0337(3)	3.07(6)
C13	0.2378(2)	1.1784(4)	0.3343(2)	2.57(5)
C14	0.1467(2)	1.3892(3)	0.1988(2)	2.73(6)
C15	0.0789(3)	1.4290(3)	0.2359(2)	2.82(6)
C16	-0.0179(2)	1.3746(3)	0.1766(2)	2.73(6)
C17	-0.0166(2)	1.1496(3)	0.2970(2)	1.90(4)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S2-3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe1	0.0215(2)	0.0166(2)	0.0162(2)	-0.00175(12)	0.00981(13)	-0.00189(12)
S1	0.0313(4)	0.0266(4)	0.0243(3)	-0.0119(3)	0.0164(3)	-0.0085(3)
S2	0.0269(4)	0.0196(3)	0.0177(3)	0.0052(3)	0.0096(3)	0.0006(3)
Si1	0.0185(4)	0.0284(4)	0.0198(4)	-0.0028(3)	0.0100(3)	-0.0076(3)
Si2	0.0176(4)	0.0199(4)	0.0234(4)	-0.0010(3)	0.0081(3)	-0.0036(3)
O1	0.0398(12)	0.0262(10)	0.0303(11)	0.0074(9)	0.0163(10)	0.0089(8)
O2	0.060(2)	0.0297(11)	0.0226(10)	0.0027(9)	0.0193(10)	0.0007(8)
C1	0.0195(12)	0.0231(13)	0.0227(12)	0.0012(10)	0.0096(11)	-0.0048(10)
C2	0.033(2)	0.0203(12)	0.025(2)	-0.0032(11)	0.0159(13)	-0.0051(11)
C3	0.0249(13)	0.0186(11)	0.0135(11)	0.0015(10)	0.0080(10)	0.0017(9)
C4	0.031(2)	0.0226(13)	0.0186(12)	0.0028(10)	0.0134(11)	0.0025(10)
C5	0.048(2)	0.0191(12)	0.0203(13)	0.0069(12)	0.0175(13)	0.0023(10)
C6	0.041(2)	0.0165(11)	0.0235(13)	-0.0036(11)	0.0131(12)	-0.0011(10)
C7	0.027(2)	0.0212(12)	0.0204(12)	-0.0044(10)	0.0083(11)	0.0011(10)
C8	0.0266(13)	0.0162(11)	0.0145(11)	-0.0003(10)	0.0068(11)	0.0013(9)
C9	0.023(2)	0.061(2)	0.030(2)	0.011(2)	0.0062(13)	-0.014(2)
C10	0.043(2)	0.049(2)	0.041(2)	-0.023(2)	0.030(2)	-0.023(2)
C11	0.035(2)	0.040(2)	0.047(2)	-0.0157(13)	0.026(2)	-0.015(2)
C12	0.023(2)	0.038(2)	0.043(2)	0.0061(12)	0.003(2)	-0.010(2)
C13	0.029(2)	0.033(2)	0.027(2)	-0.0043(12)	0.0043(12)	-0.0051(11)
C14	0.054(2)	0.025(2)	0.027(2)	-0.0136(13)	0.020(2)	-0.0010(11)
C15	0.059(2)	0.0178(13)	0.032(2)	-0.0019(13)	0.023(2)	-0.0020(11)
C16	0.053(2)	0.0198(13)	0.033(2)	0.0100(12)	0.021(2)	0.0057(11)
C17	0.030(2)	0.0255(13)	0.0197(12)	0.0057(11)	0.0133(11)	0.0027(10)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S2-4. Bond lengths (Å)

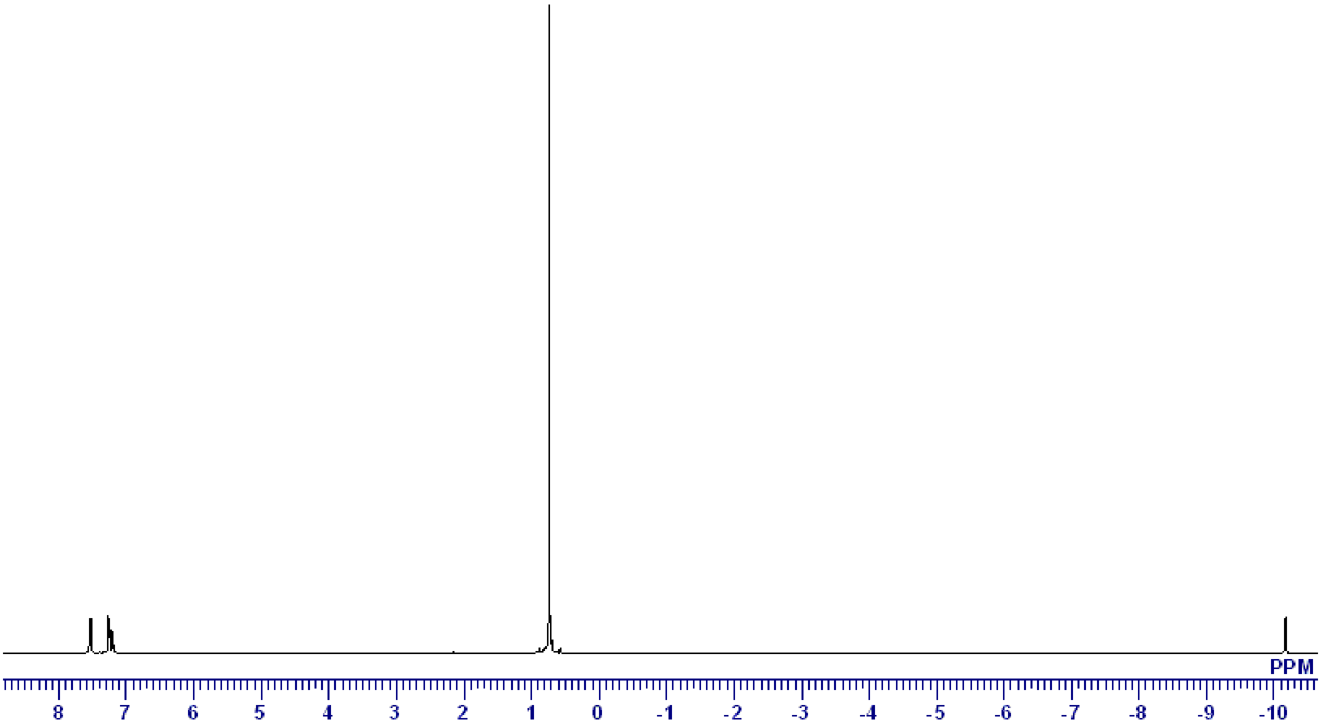
atom	atom	distance	atom	atom	distance
Fe1	S1	2.2864(8)	Fe1	S2	2.2883(9)
Fe1	Si1	2.3378(9)	Fe1	Si2	2.3442(8)
Fe1	C1	1.761(3)	Fe1	C2	1.763(3)
S1	C13	1.803(3)	S1	C14	1.818(3)
S2	C16	1.814(3)	S2	C17	1.811(3)
Si1	C3	1.900(3)	Si1	C9	1.895(3)
Si1	C10	1.885(5)	Si2	C8	1.897(3)
Si2	C11	1.887(4)	Si2	C12	1.895(3)
O1	C1	1.169(4)	O2	C2	1.165(4)
C3	C4	1.411(4)	C3	C8	1.402(4)
C4	C5	1.390(4)	C5	C6	1.390(5)
C6	C7	1.390(5)	C7	C8	1.406(4)
C14	C15	1.524(6)	C15	C16	1.533(5)

Table S2-5. Bond angles (º)

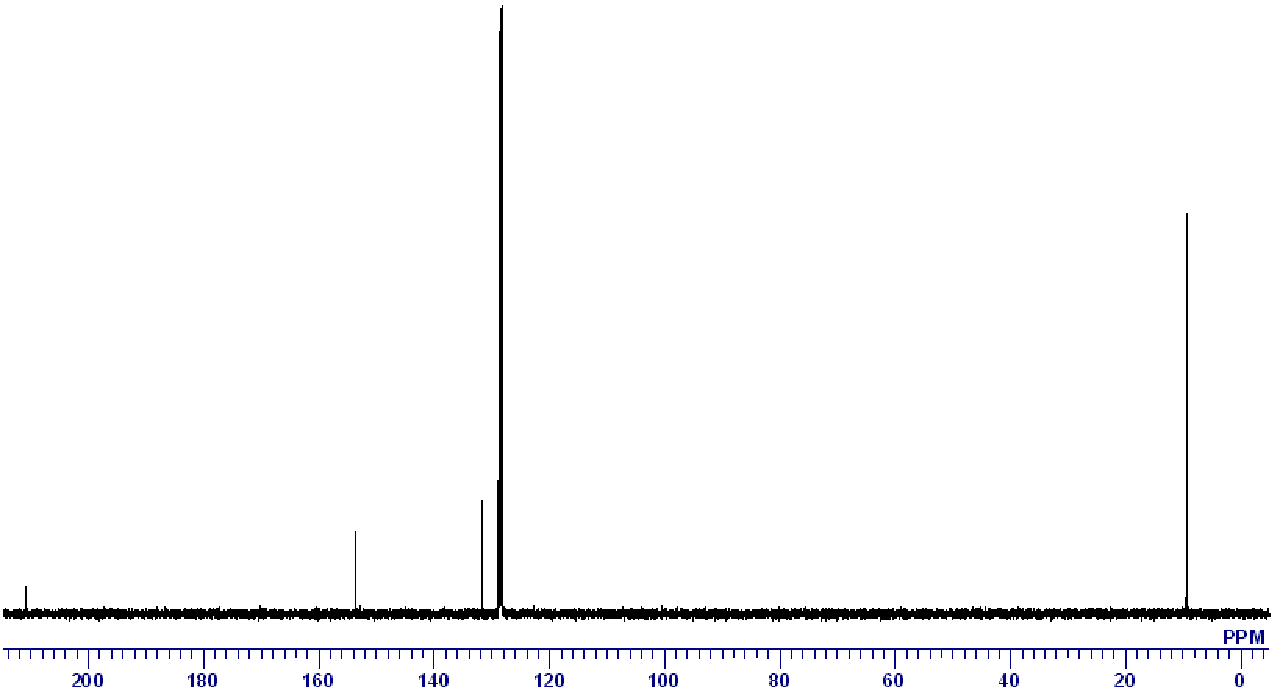
atom	atom	atom	angle	atom	atom	atom	angle
S1	Fe1	S2	97.11(3)	S1	Fe1	Si1	87.33(4)
S1	Fe1	Si2	174.54(4)	S1	Fe1	C1	98.49(8)
S1	Fe1	C2	96.67(9)	S2	Fe1	Si1	175.55(3)
S2	Fe1	Si2	88.02(3)	S2	Fe1	C1	97.46(11)
S2	Fe1	C2	97.86(10)	Si1	Fe1	Si2	87.56(4)
Si1	Fe1	C1	81.49(10)	Si1	Fe1	C2	81.90(10)
Si2	Fe1	C1	82.64(8)	Si2	Fe1	C2	80.71(9)
C1	Fe1	C2	156.89(12)	Fe1	S1	C13	111.44(11)
Fe1	S1	C14	112.36(10)	C13	S1	C14	99.84(14)
Fe1	S2	C16	112.78(13)	Fe1	S2	C17	109.99(10)
C16	S2	C17	100.66(14)	Fe1	Si1	C3	107.41(10)
Fe1	Si1	C9	116.12(12)	Fe1	Si1	C10	115.62(11)
C3	Si1	C9	106.90(12)	C3	Si1	C10	107.44(13)
C9	Si1	C10	102.77(15)	Fe1	Si2	C8	107.08(9)
Fe1	Si2	C11	114.77(10)	Fe1	Si2	C12	116.31(10)
C8	Si2	C11	109.13(14)	C8	Si2	C12	106.33(13)
C11	Si2	C12	102.80(15)	Fe1	C1	O1	178.1(3)
Fe1	C2	O2	176.6(3)	Si1	C3	C4	121.6(2)
Si1	C3	C8	118.66(19)	C4	C3	C8	119.7(2)
C3	C4	C5	120.9(3)	C4	C5	C6	119.4(3)
C5	C6	C7	120.1(3)	C6	C7	C8	121.5(3)
Si2	C8	C3	119.26(17)	Si2	C8	C7	122.3(3)
C3	C8	C7	118.4(3)	S1	C14	C15	116.7(3)
C14	C15	C16	115.5(3)	S2	C16	C15	117.26(19)

Table S2-6. Torsion Angles(°) (Those having bond angles > 160 or < 20 degrees are excluded.)

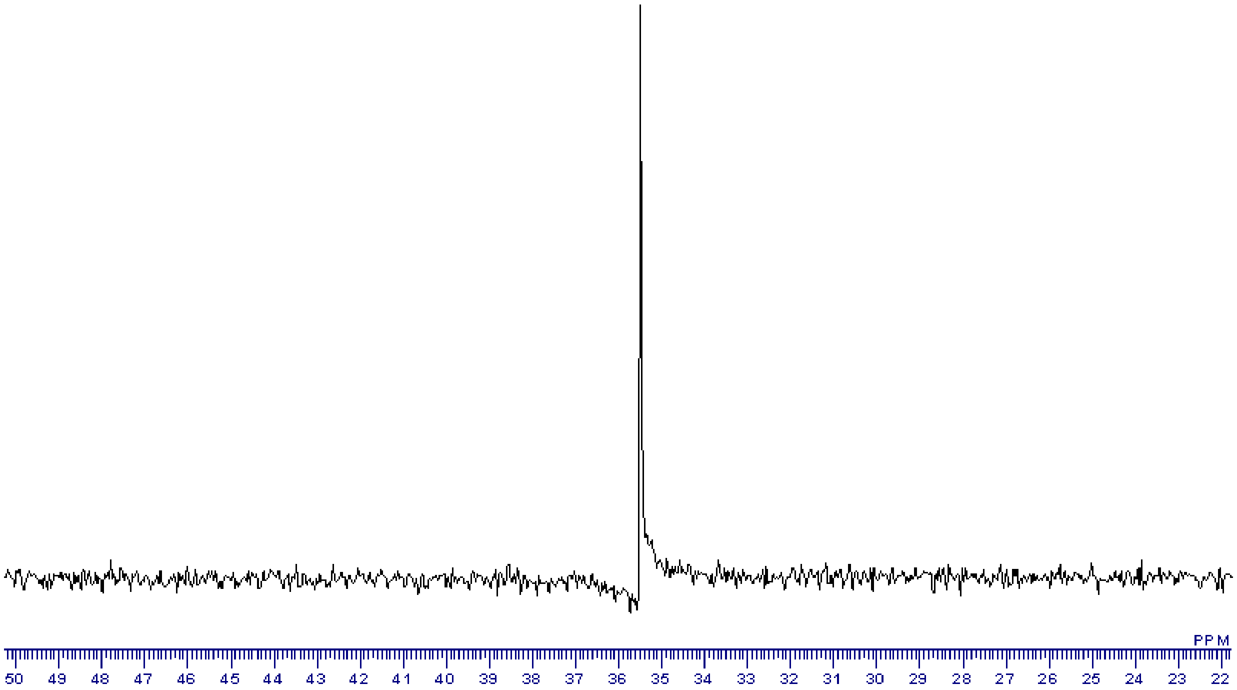
atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
S1	Fe1	S2	C16	31.21(4)	S1	Fe1	S2	C17	-80.27(4)
S2	Fe1	S1	C13	78.96(4)	S2	Fe1	S1	C14	-32.15(4)
S1	Fe1	Si1	C3	-176.38(3)	S1	Fe1	Si1	C9	64.08(4)
S1	Fe1	Si1	C10	-56.46(3)	Si1	Fe1	S1	C13	-100.70(4)
Si1	Fe1	S1	C14	148.19(4)	C1	Fe1	S1	C13	-19.72(11)
C1	Fe1	S1	C14	-130.82(11)	C2	Fe1	S1	C13	177.78(10)
C2	Fe1	S1	C14	66.67(11)	S2	Fe1	Si2	C8	178.69(4)
S2	Fe1	Si2	C11	-60.03(4)	S2	Fe1	Si2	C12	59.99(5)
Si2	Fe1	S2	C16	-146.90(3)	Si2	Fe1	S2	C17	101.62(4)
C1	Fe1	S2	C16	130.79(8)	C1	Fe1	S2	C17	19.31(8)
C2	Fe1	S2	C16	-66.57(9)	C2	Fe1	S2	C17	-178.05(9)
Si1	Fe1	Si2	C8	-1.80(4)	Si1	Fe1	Si2	C11	119.49(4)
Si1	Fe1	Si2	C12	-120.49(5)	Si2	Fe1	Si1	C3	1.70(4)
Si2	Fe1	Si1	C9	-117.84(4)	Si2	Fe1	Si1	C10	121.62(4)
C1	Fe1	Si1	C3	84.62(8)	C1	Fe1	Si1	C9	-34.92(8)
C1	Fe1	Si1	C10	-155.46(8)	C2	Fe1	Si1	C3	-79.25(9)
C2	Fe1	Si1	C9	161.21(10)	C2	Fe1	Si1	C10	40.67(9)
C1	Fe1	Si2	C8	-83.53(11)	C1	Fe1	Si2	C11	37.75(11)
C1	Fe1	Si2	C12	157.78(11)	C2	Fe1	Si2	C8	80.39(11)
C2	Fe1	Si2	C11	-158.33(11)	C2	Fe1	Si2	C12	-38.31(11)
Fe1	S1	C14	C15	53.54(17)	C13	S1	C14	C15	-64.66(19)
Fe1	S2	C16	C15	-51.0(3)	C17	S2	C16	C15	66.1(3)
Fe1	Si1	C3	C4	177.35(13)	Fe1	Si1	C3	C8	-1.26(17)
C9	Si1	C3	C4	-57.4(3)	C9	Si1	C3	C8	124.01(18)
C10	Si1	C3	C4	52.36(19)	C10	Si1	C3	C8	-126.25(18)
Fe1	Si2	C8	C3	1.63(18)	Fe1	Si2	C8	C7	-175.90(15)
C11	Si2	C8	C3	-123.15(18)	C11	Si2	C8	C7	59.3(2)
C12	Si2	C8	C3	126.60(18)	C12	Si2	C8	C7	-50.9(3)
Si1	C3	C4	C5	-177.95(15)	Si1	C3	C8	Si2	-0.3(3)
Si1	C3	C8	C7	177.38(14)	C4	C3	C8	Si2	-178.89(18)
C4	C3	C8	C7	-1.3(4)	C8	C3	C4	C5	0.6(4)
C3	C4	C5	C6	0.3(4)	C4	C5	C6	C7	-0.6(4)
C5	C6	C7	C8	0.0(4)	C6	C7	C8	Si2	178.5(2)
C6	C7	C8	C3	1.0(4)	S1	C14	C15	C16	-72.1(3)
C14	C15	C16	S2	70.8(4)					



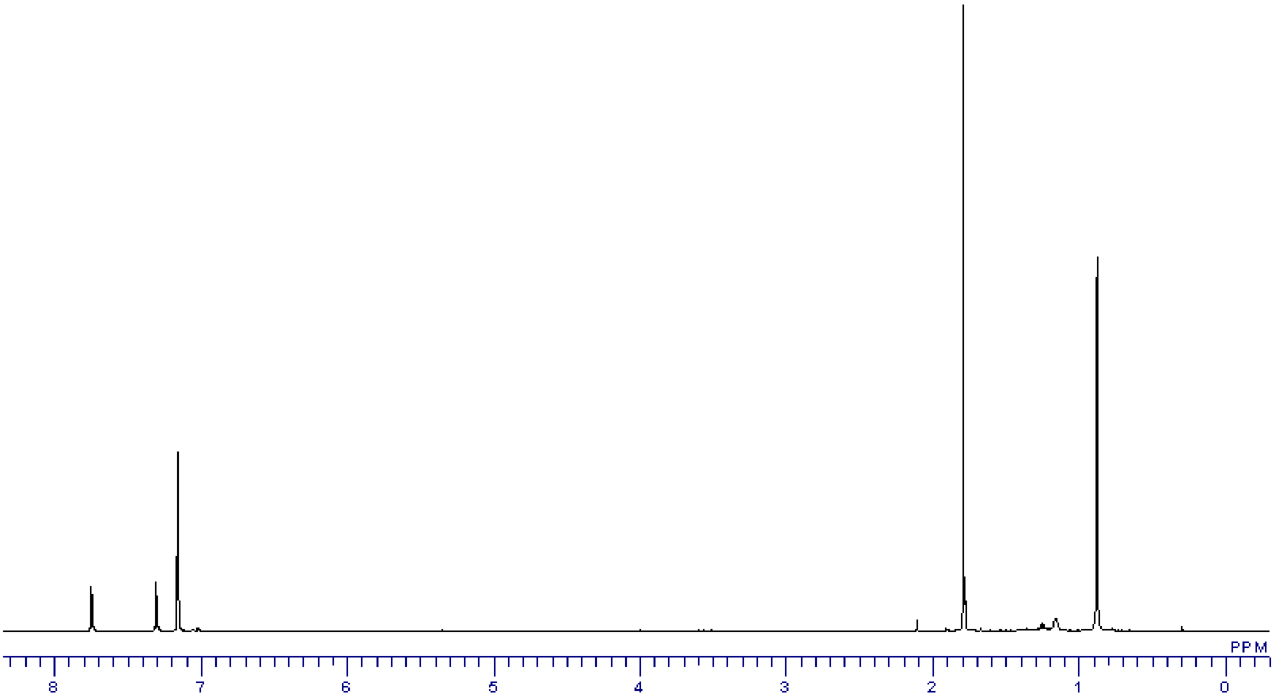
^{1}H NMR spectrum of **1** (C_6D_6, r.t.)



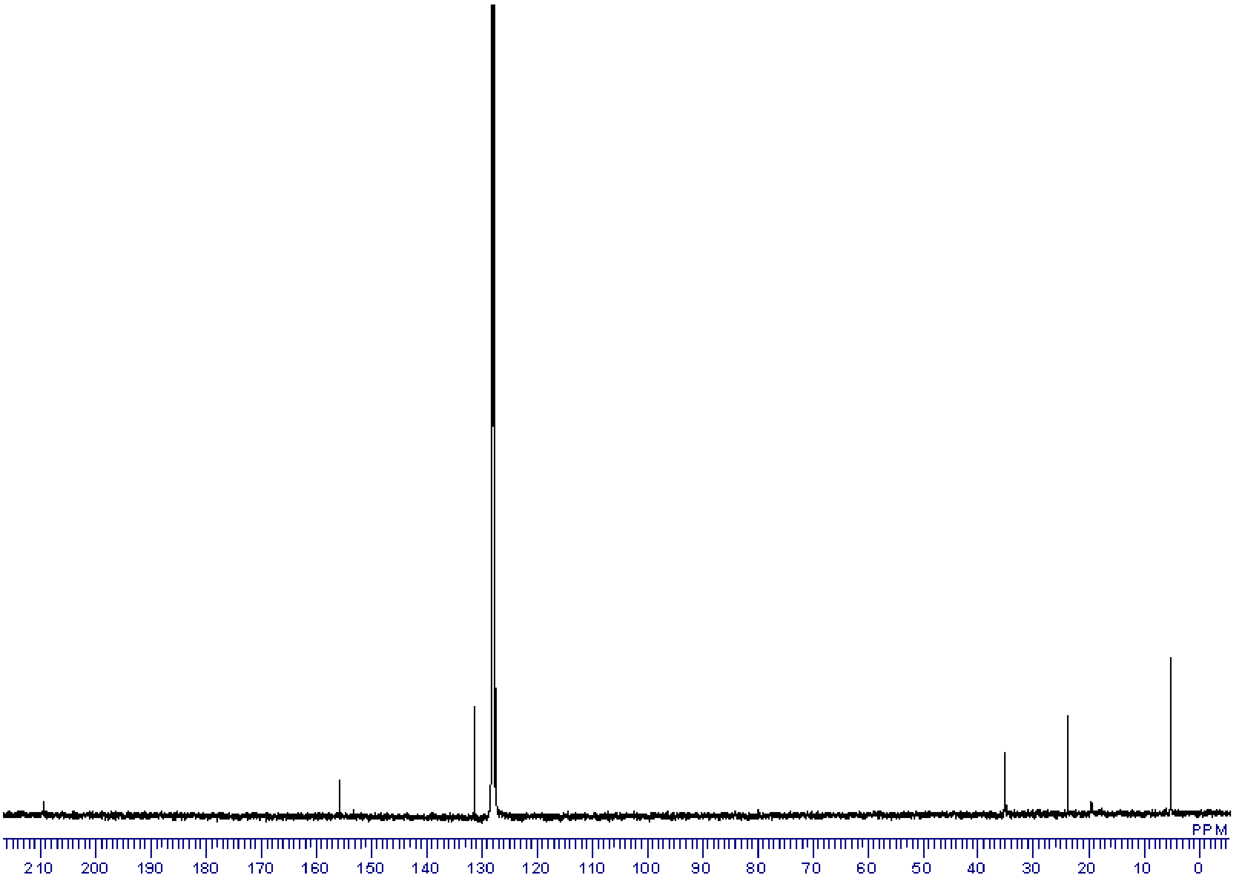
^{13}C NMR spectrum of **1** (C_6D_6, r.t.)



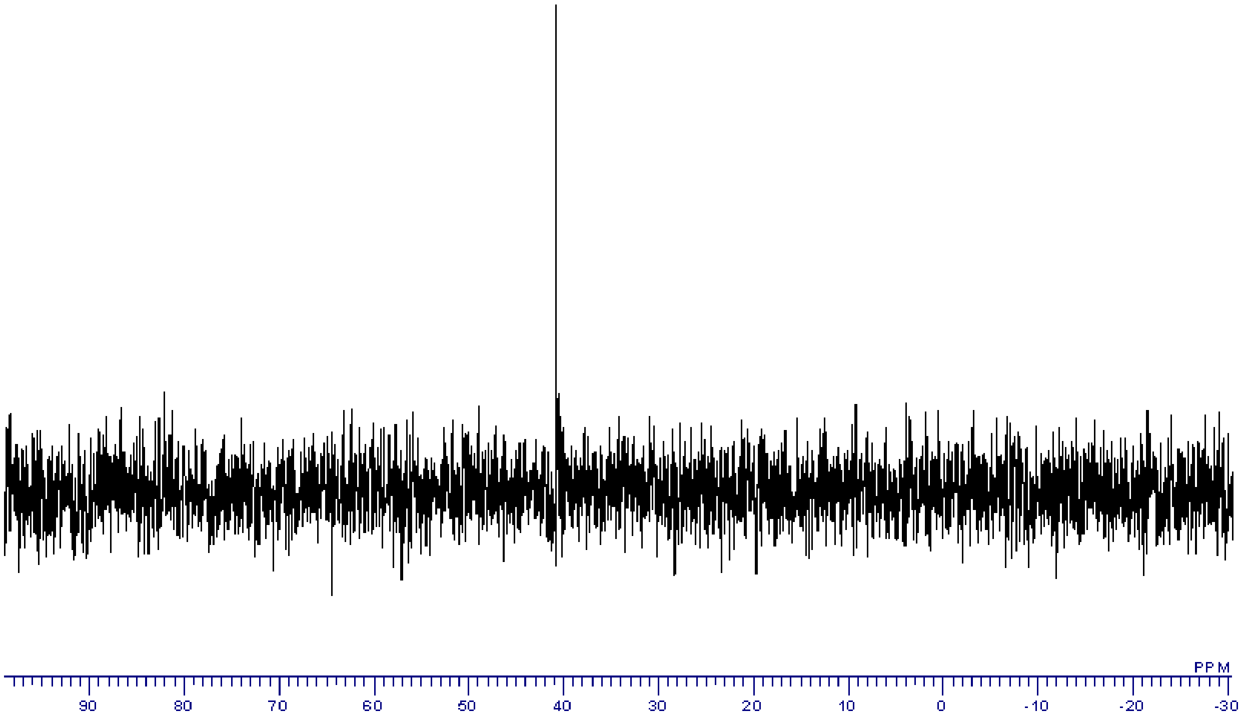
^{29}Si NMR spectrum of **1** (C_6D_6, r.t.)



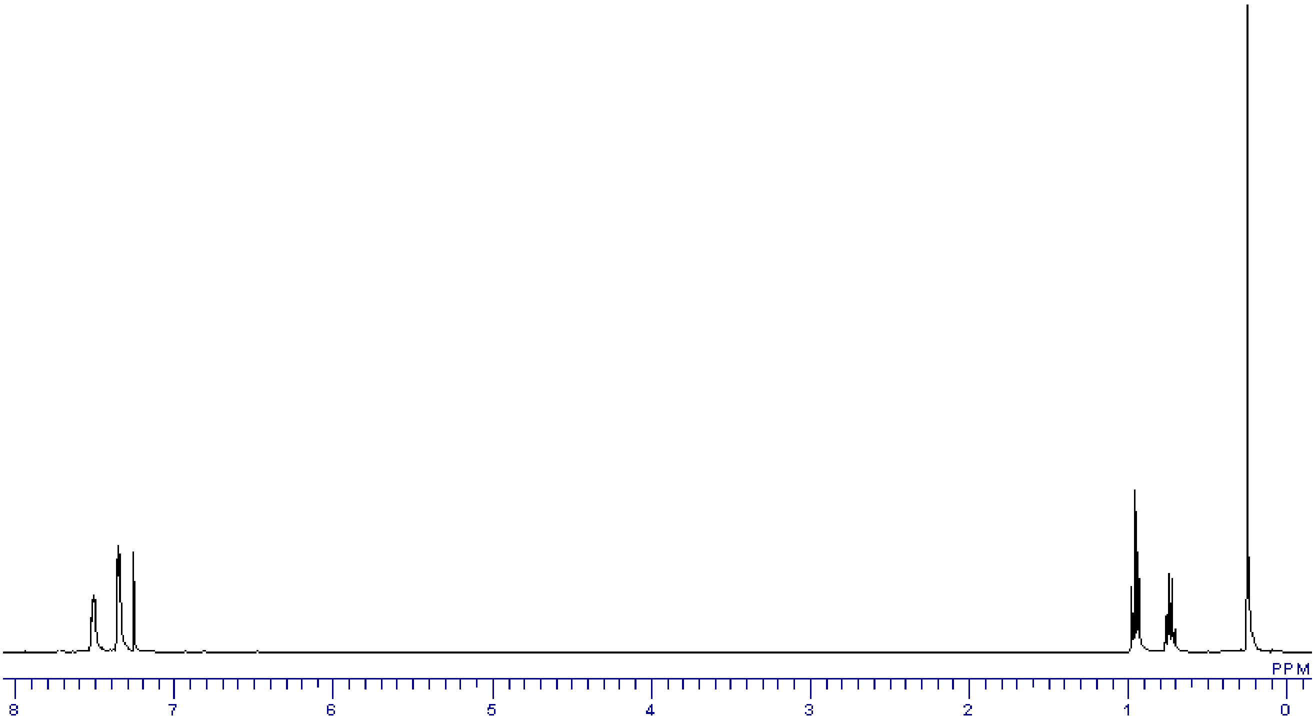
^{1}H NMR spectrum of **6** (C_6D_6, r.t.)



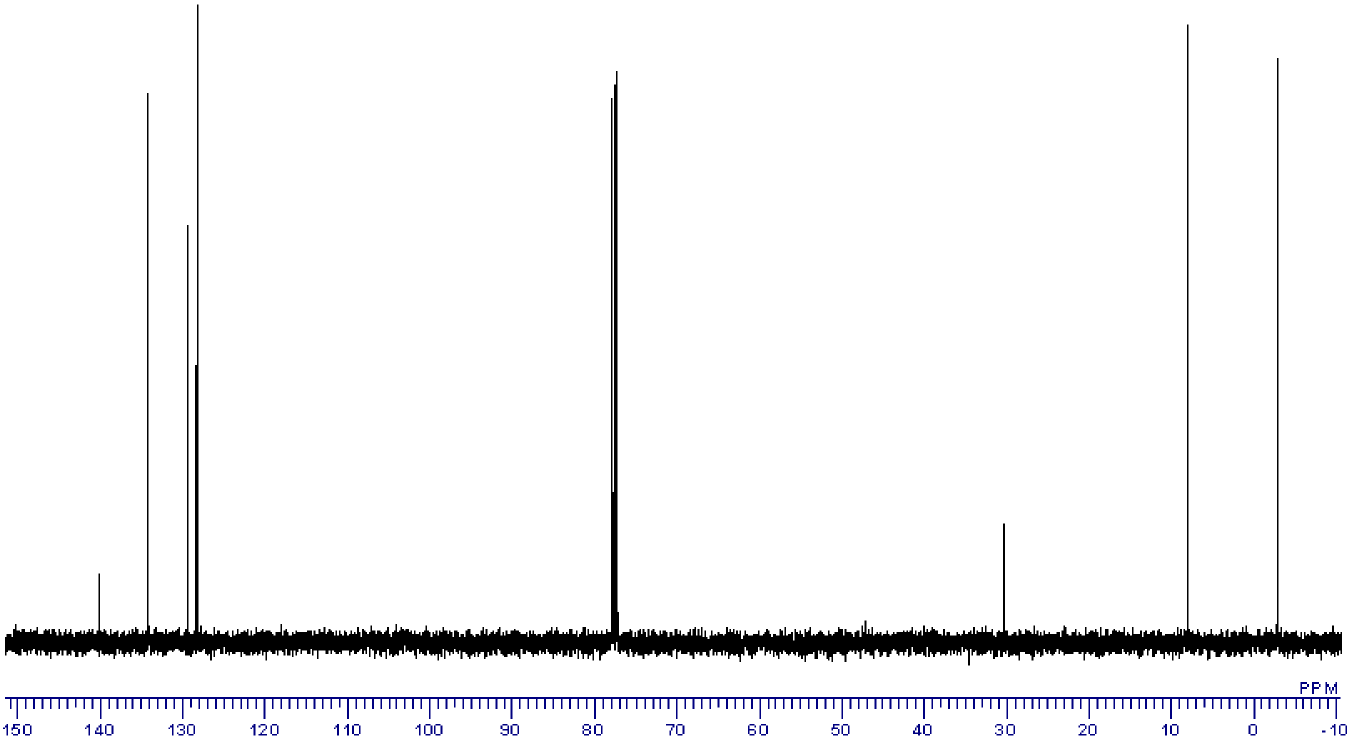
^{13}C NMR spectrum of **6** (C_6D_6, r.t.)



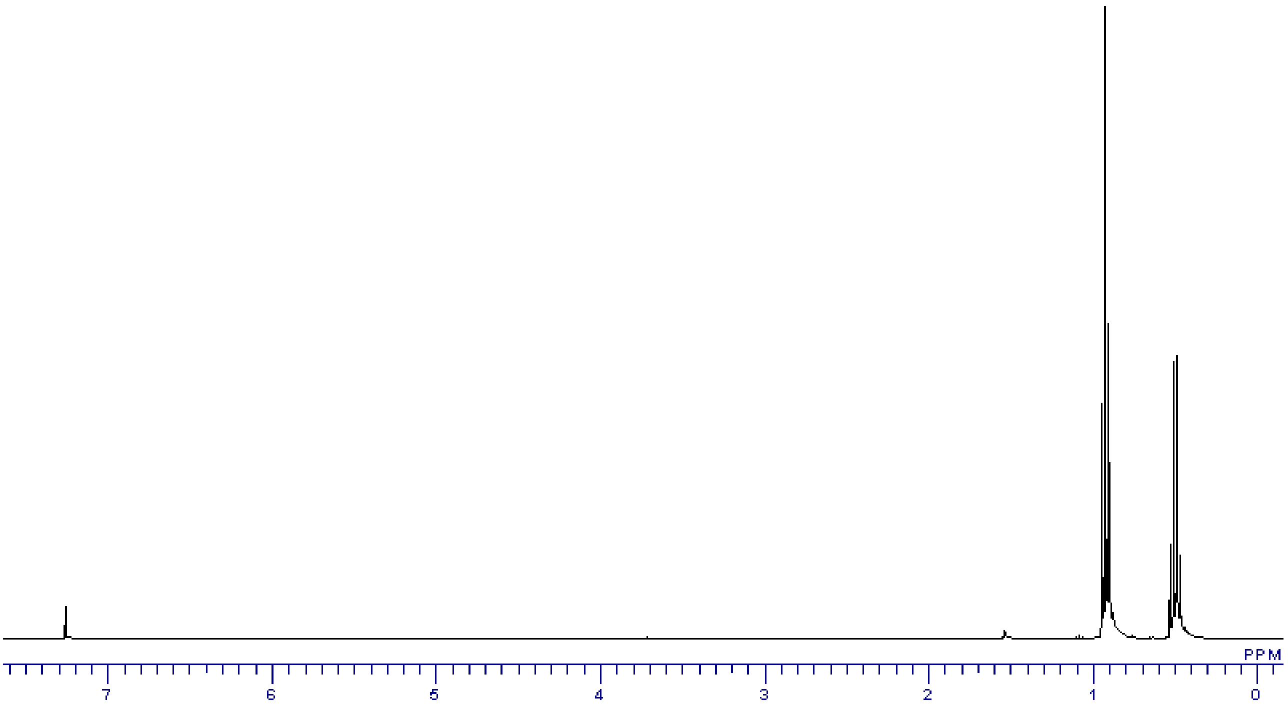
^{29}Si NMR spectrum of **6** (C_6D_6, r.t.)



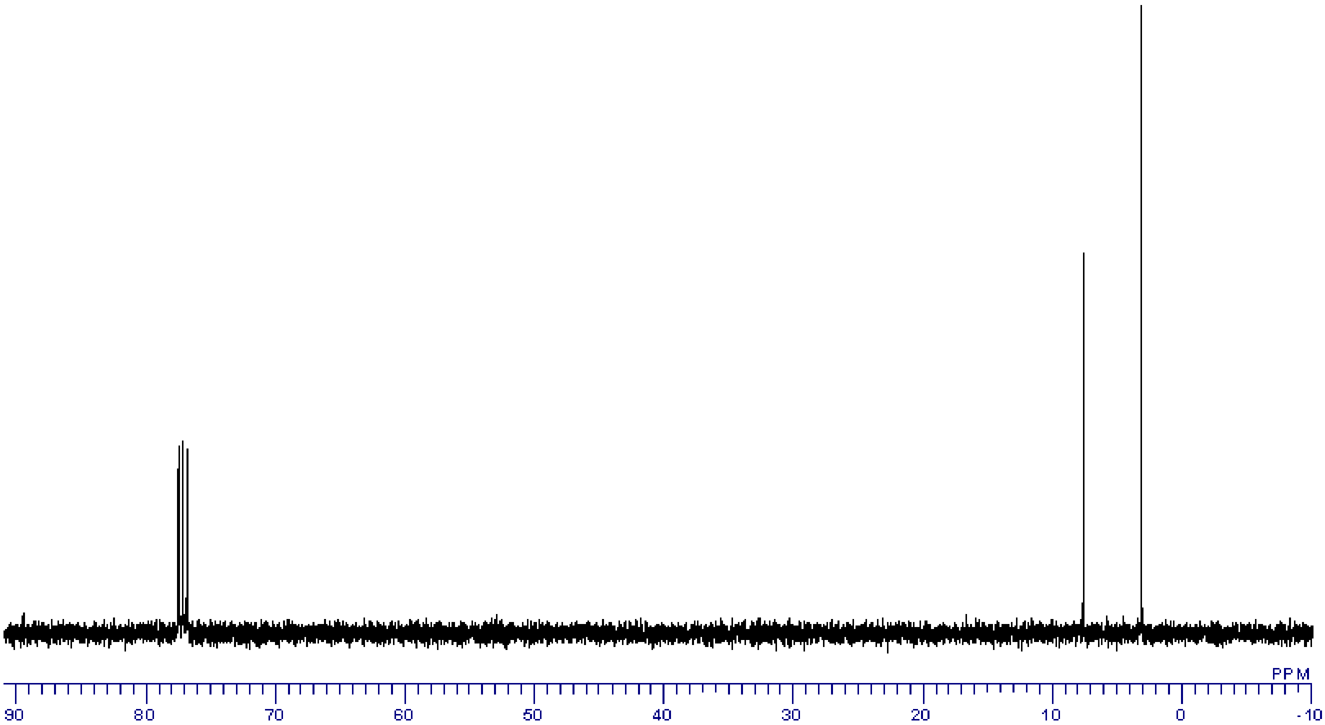
^{1}H NMR spectrum of **3a** ($CDCl_3$, r.t.)



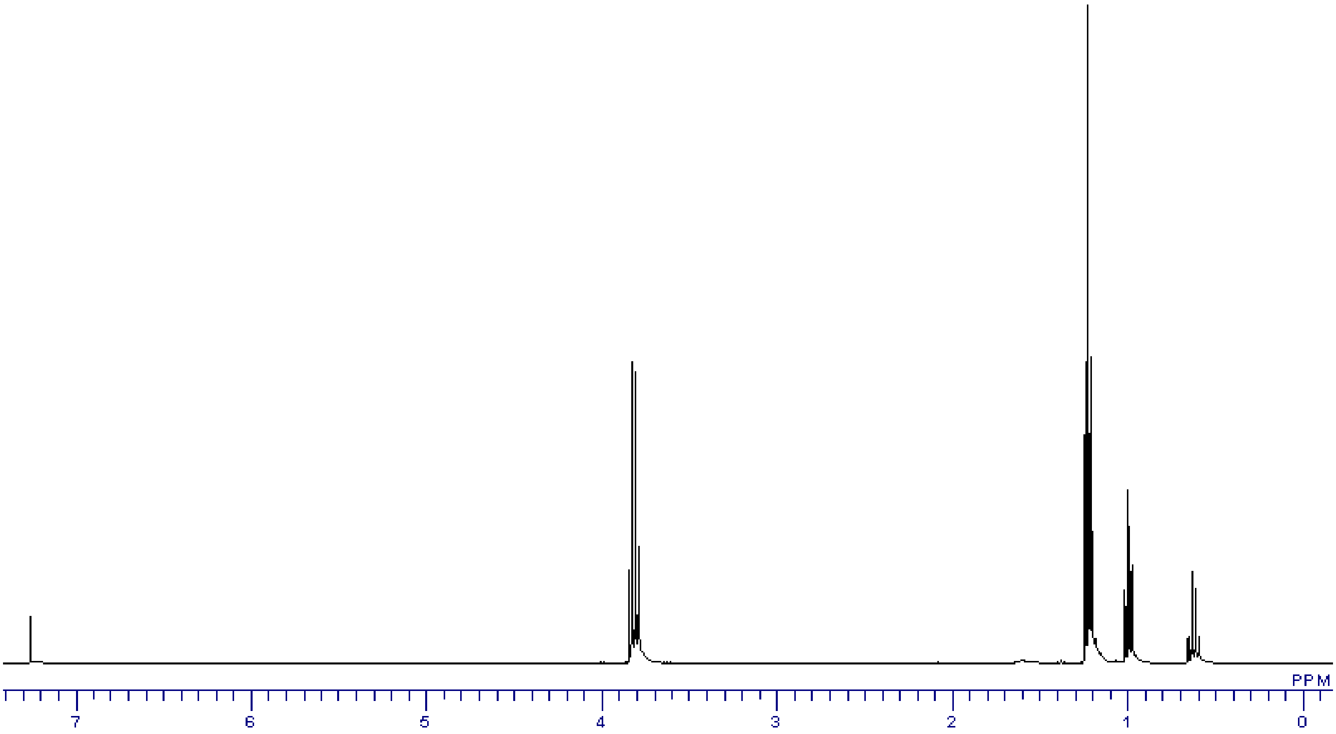
^{13}C NMR spectrum of **3a** ($CDCl_3$, r.t.)



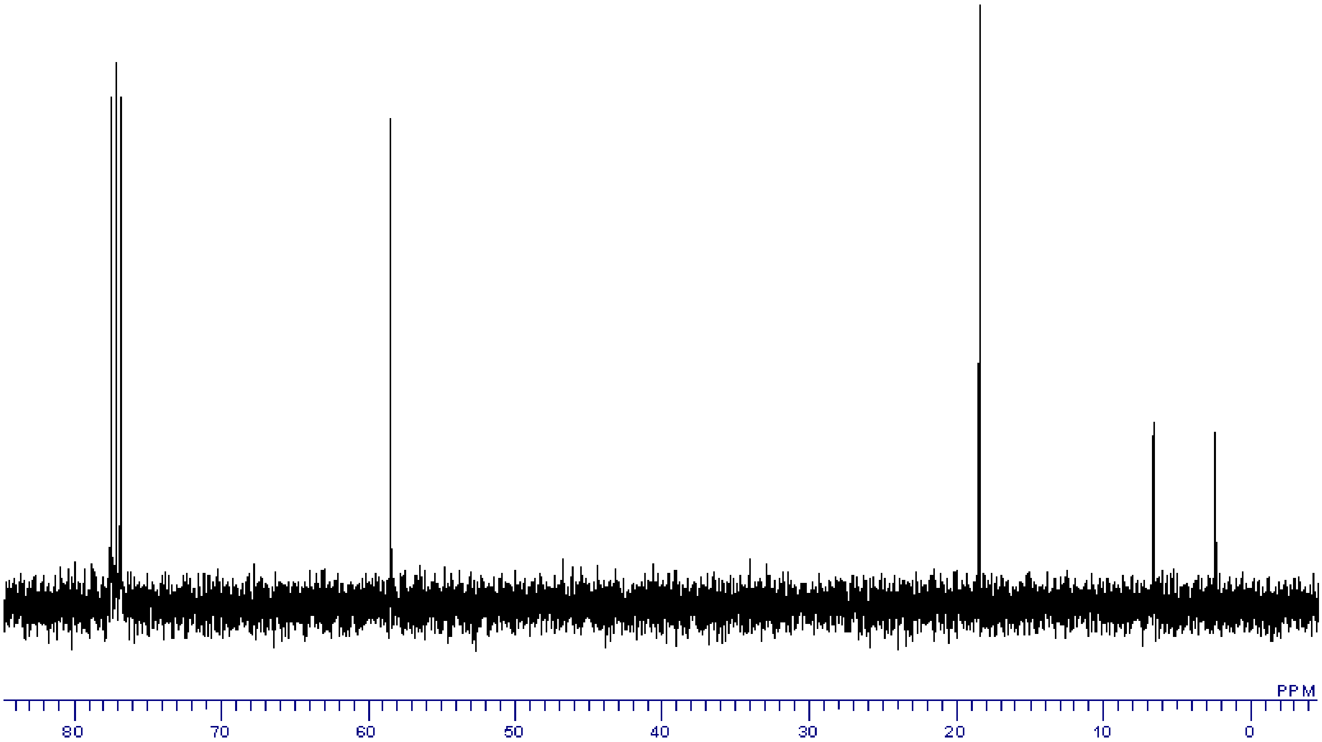
^{1}H NMR spectrum of **3b** ($CDCl_3$, r.t.)



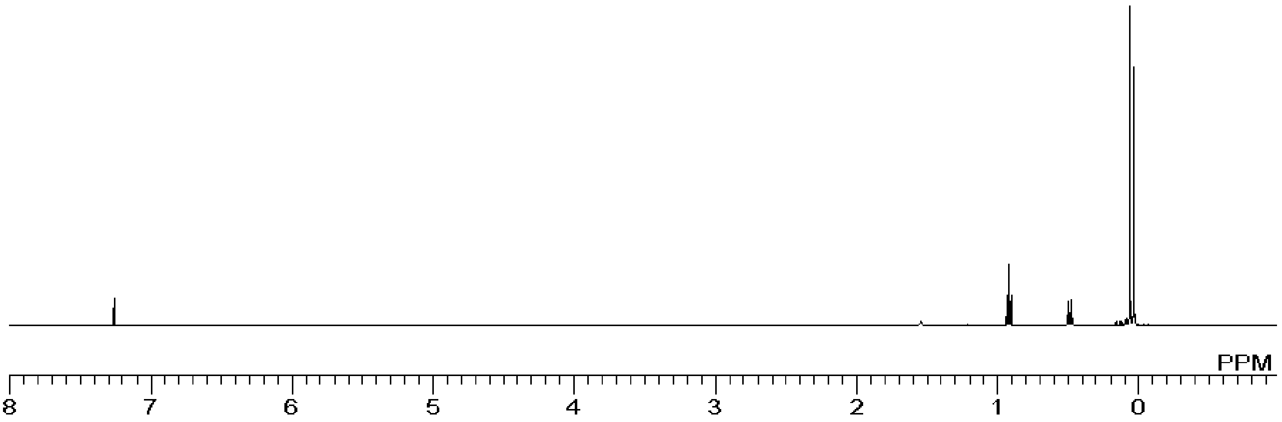
^{13}C NMR spectrum of **3b** ($CDCl_3$, r.t.)



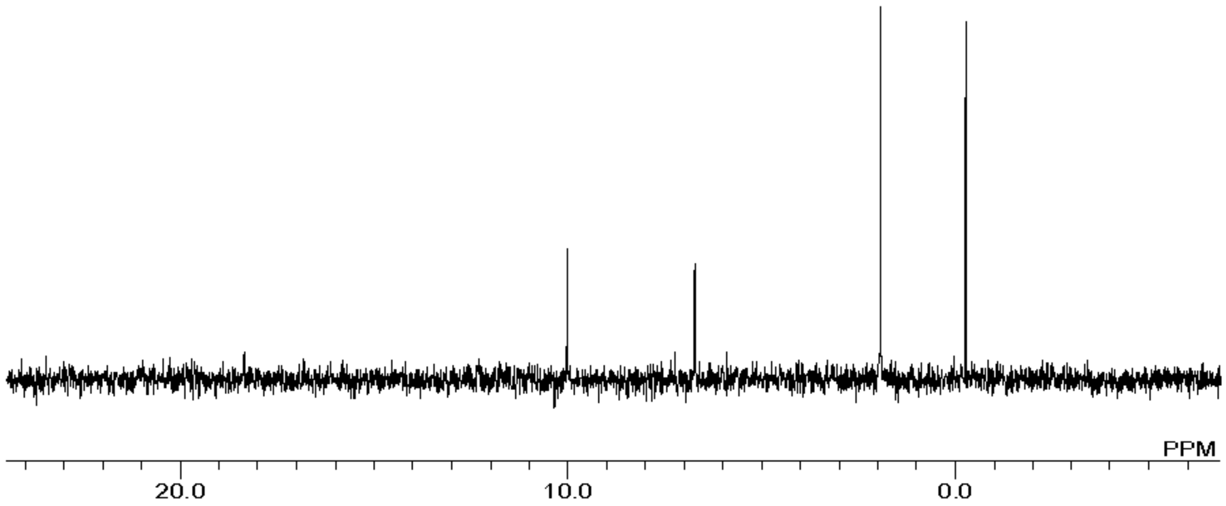
^{1}H NMR spectrum of **3c** ($CDCl_3$, r.t.)



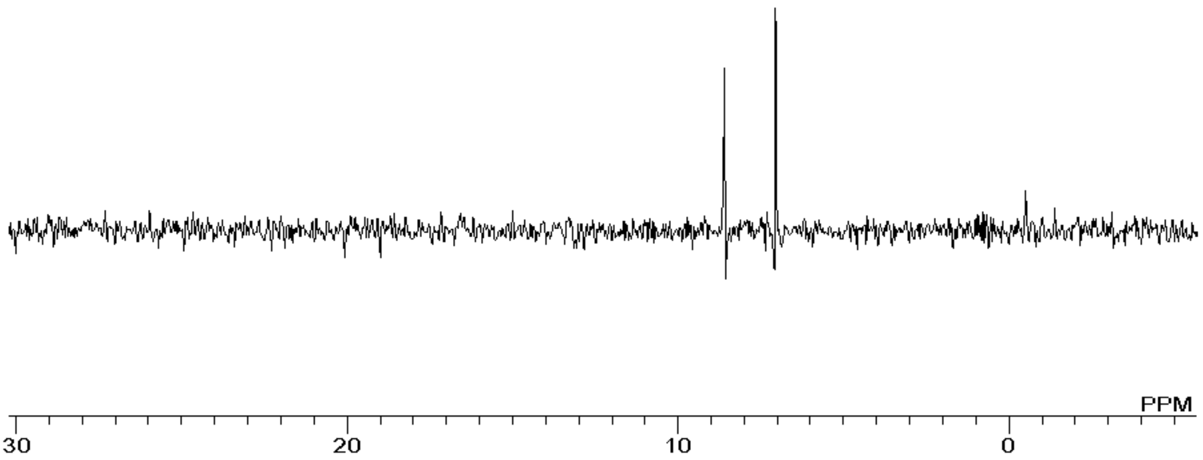
^{13}C NMR spectrum of **3c** ($CDCl_3$, r.t.)



^{1}H NMR spectrum of **3d** ($CDCl_3$, r.t.)

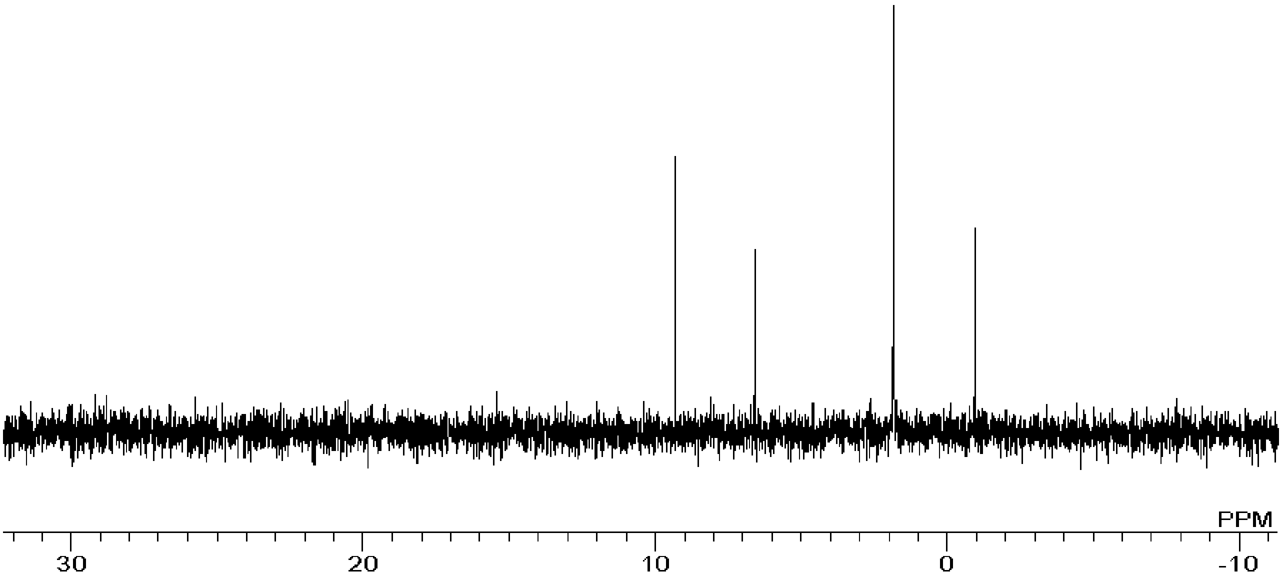


^{13}C NMR spectrum of **3d** ($CDCl_3$, r.t.)

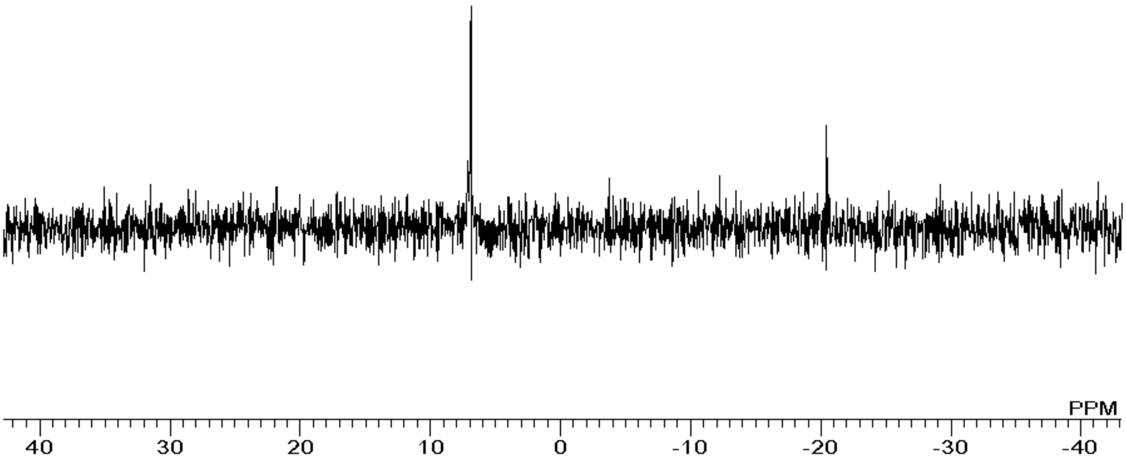


^{29}Si NMR spectrum of **3d** ($CDCl_3$, r.t.)

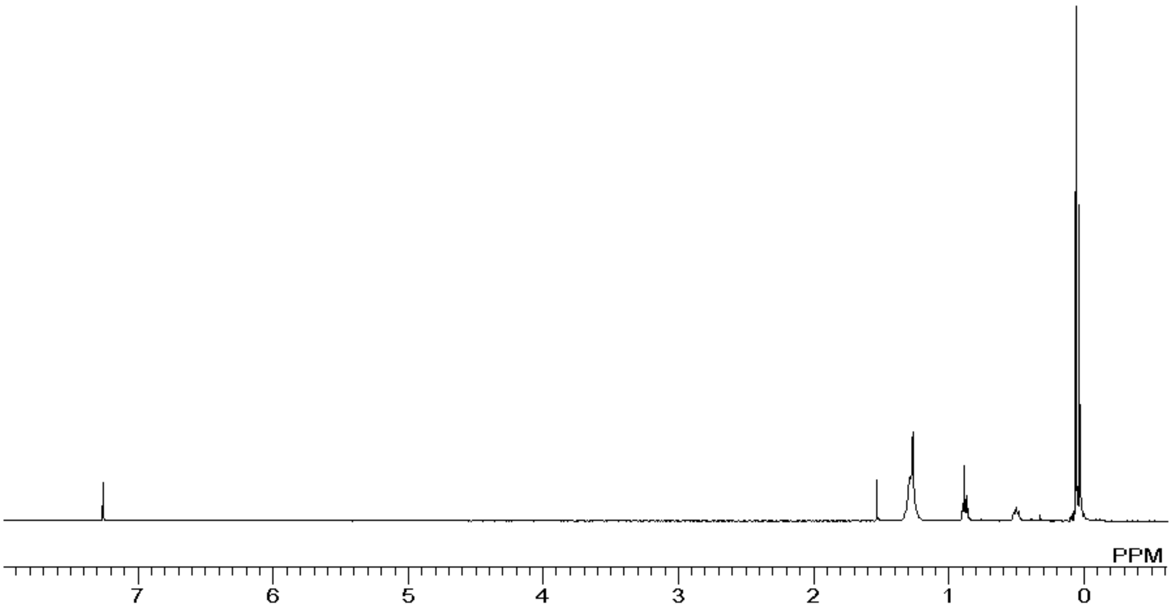
^{1}H NMR spectrum of **3e** (CDCl$_3$, r.t.)



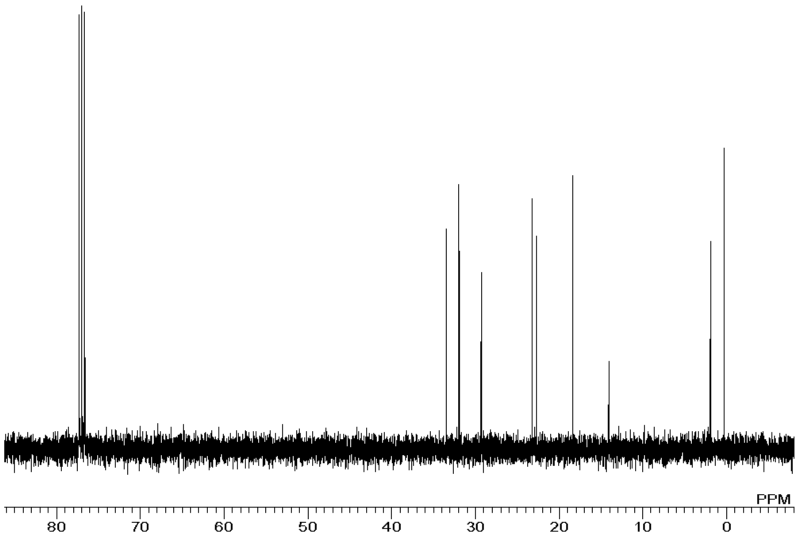
^{13}C NMR spectrum of **3e** (CDCl$_3$, r.t.)



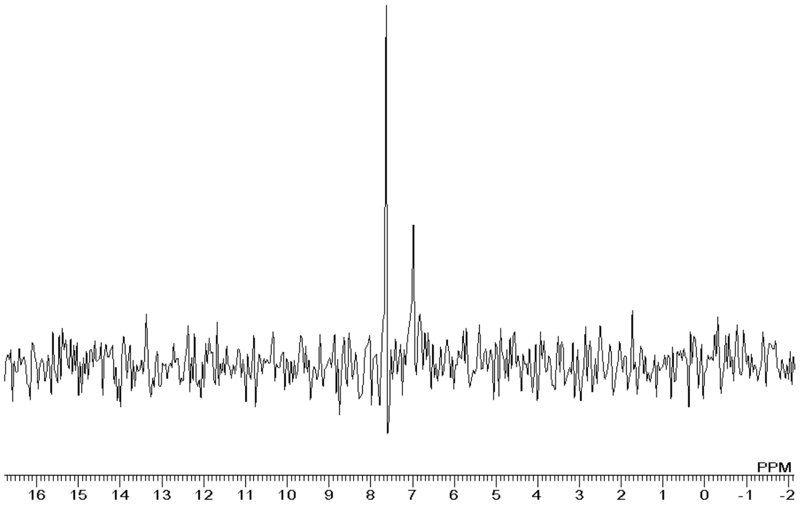
^{29}Si NMR spectrum of **3e** (CDCl$_3$, r.t.)



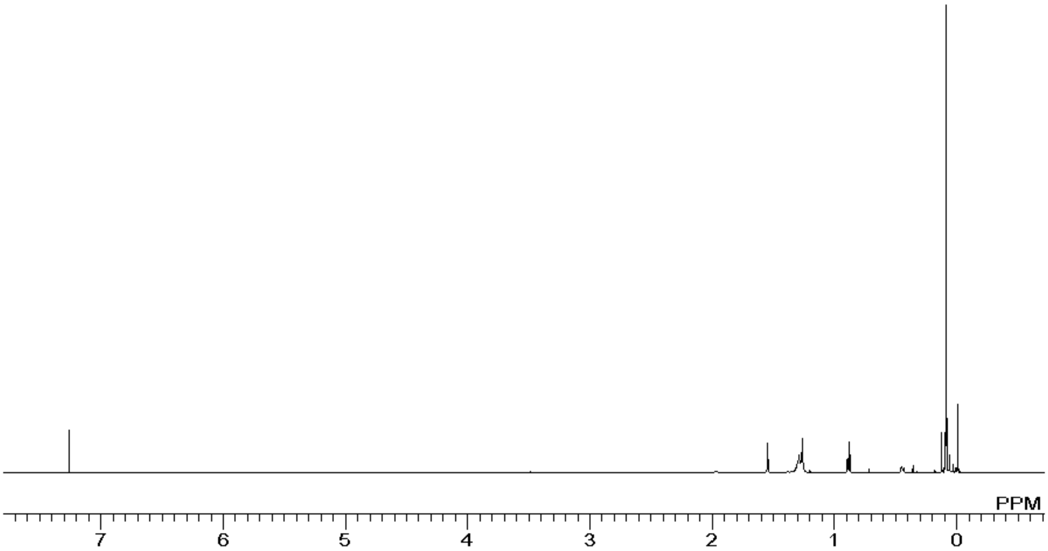
^{1}H NMR spectrum of **3f** ($CDCl_3$, r.t.)



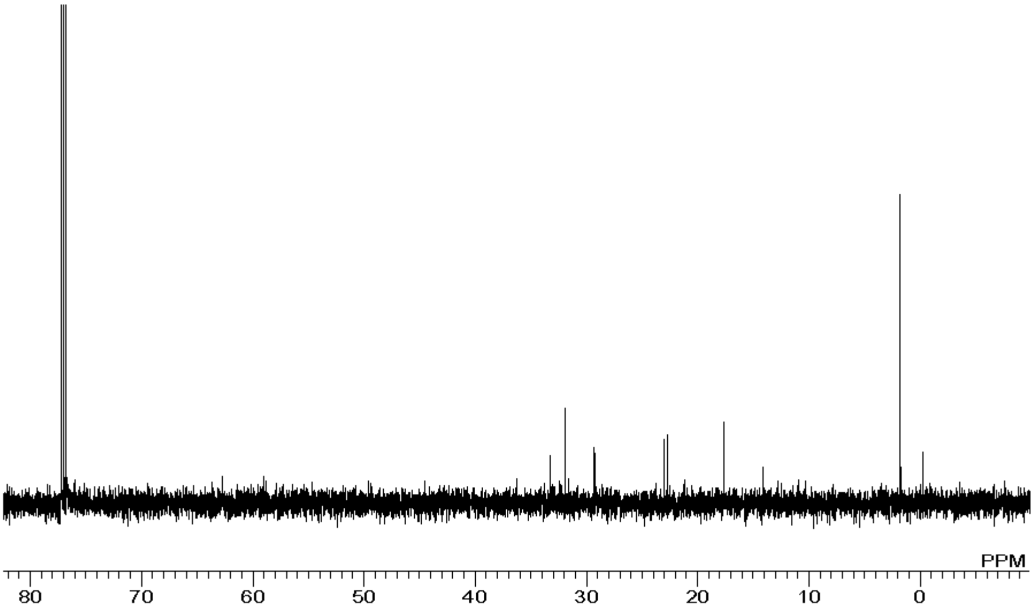
^{13}C NMR spectrum of **3f** ($CDCl_3$, r.t.)



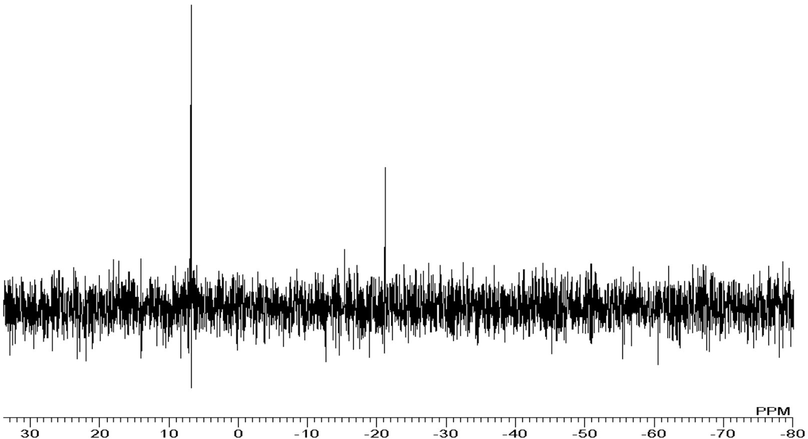
^{29}Si NMR spectrum of **3f** ($CDCl_3$, r.t.)



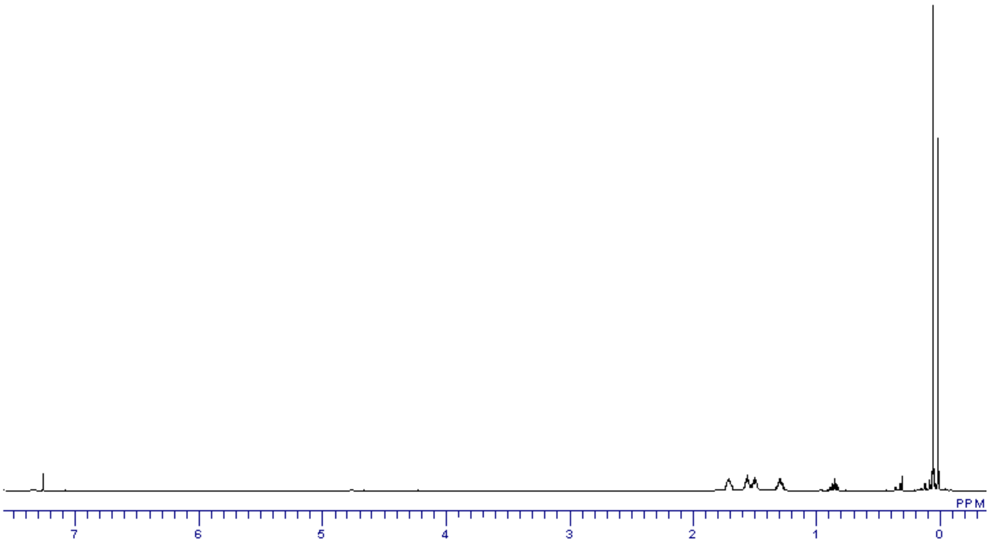
^{1}H NMR spectrum of **3g** ($CDCl_3$, r.t.)



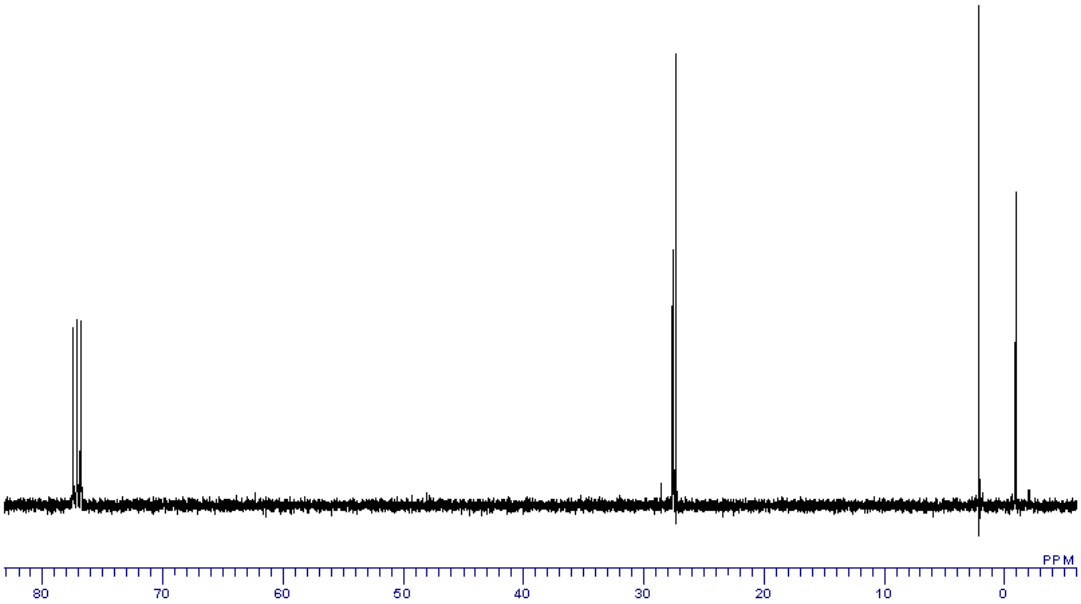
^{13}C NMR spectrum of **3g** ($CDCl_3$, r.t.)



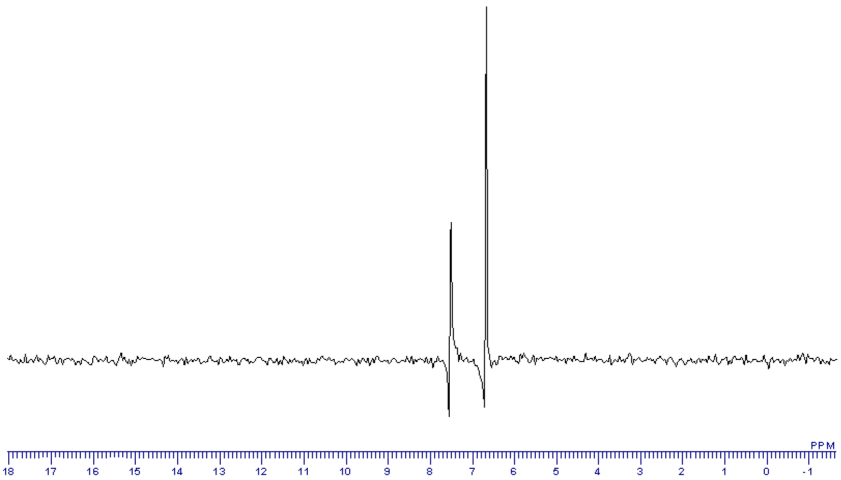
^{29}Si NMR spectrum of **3g** ($CDCl_3$, r.t.)



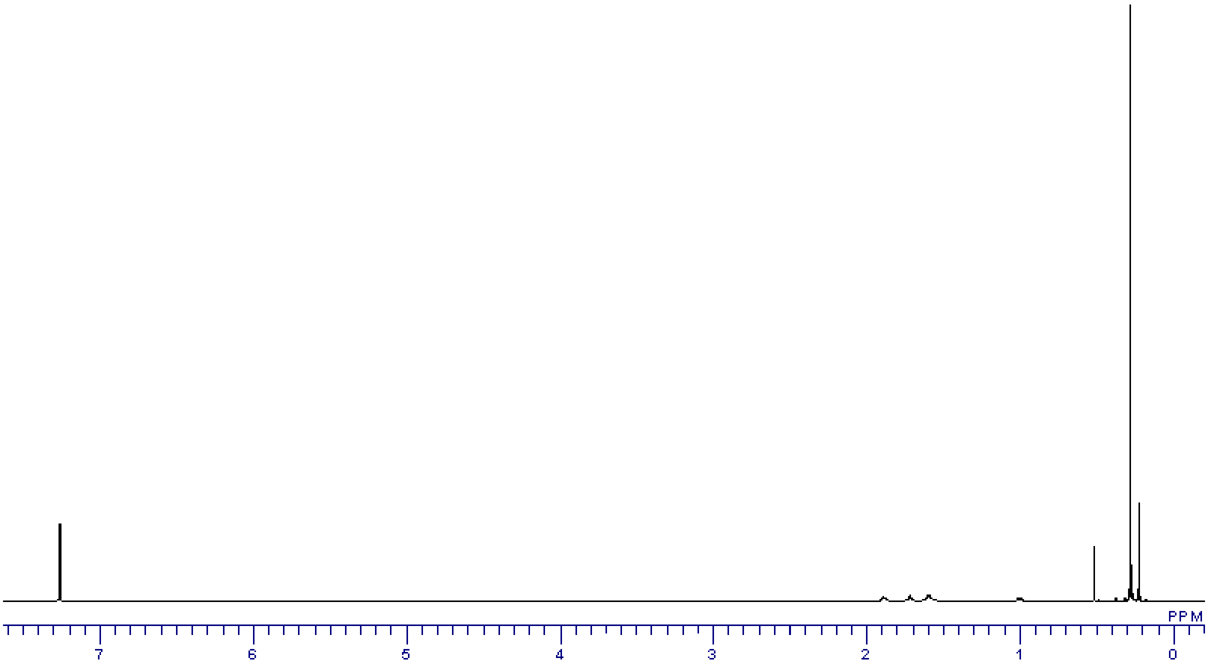
^{1}H NMR spectrum of **3h** ($CDCl_3$, r.t.)



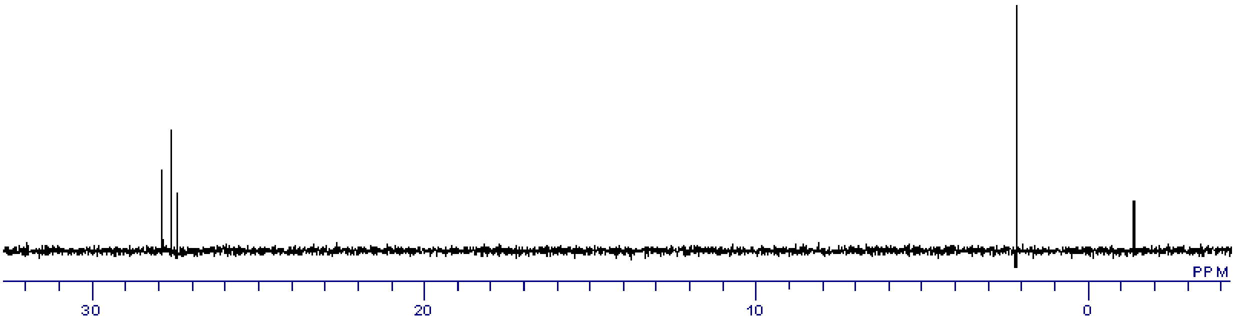
^{13}C NMR spectrum of **3h** ($CDCl_3$, r.t.)



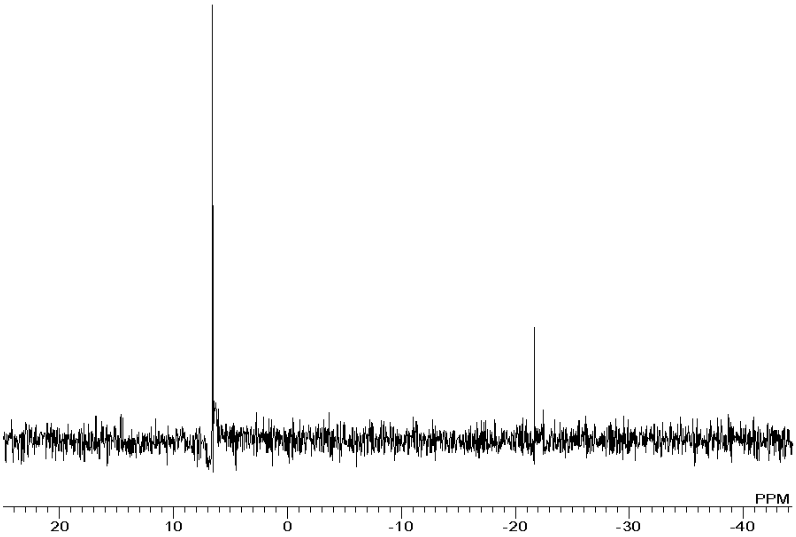
^{29}Si NMR spectrum of **3h** ($CDCl_3$, r.t.)



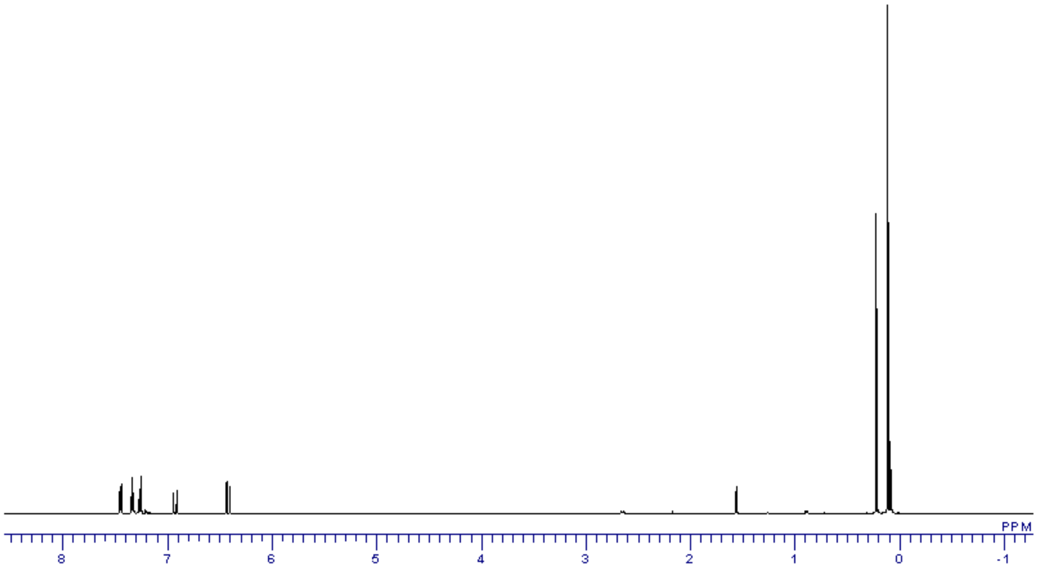
^{1}H NMR spectrum of **3i** (CDCl$_3$, r.t.)



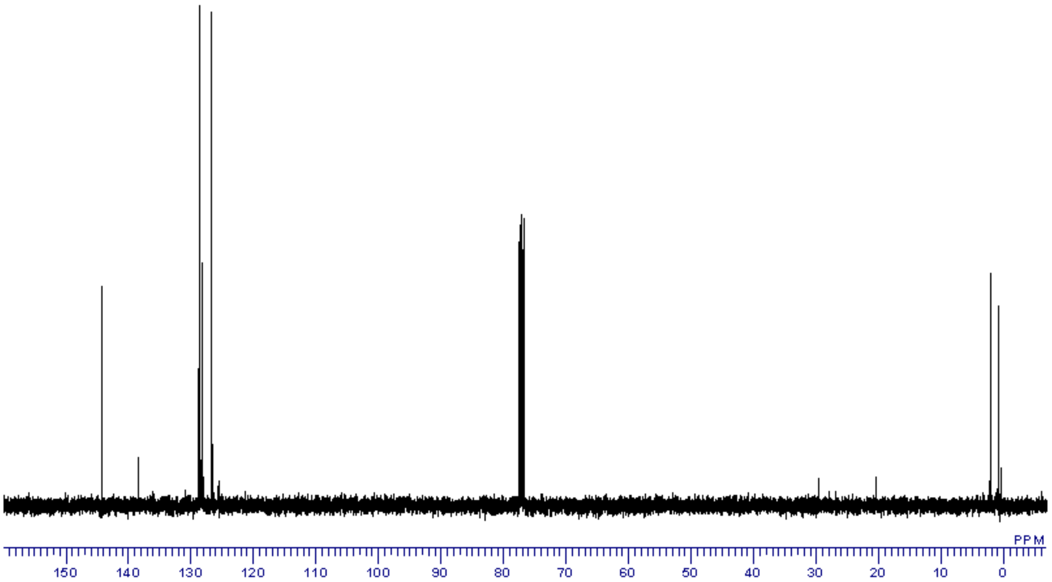
^{13}C NMR spectrum of **3i** (CDCl$_3$, r.t.)



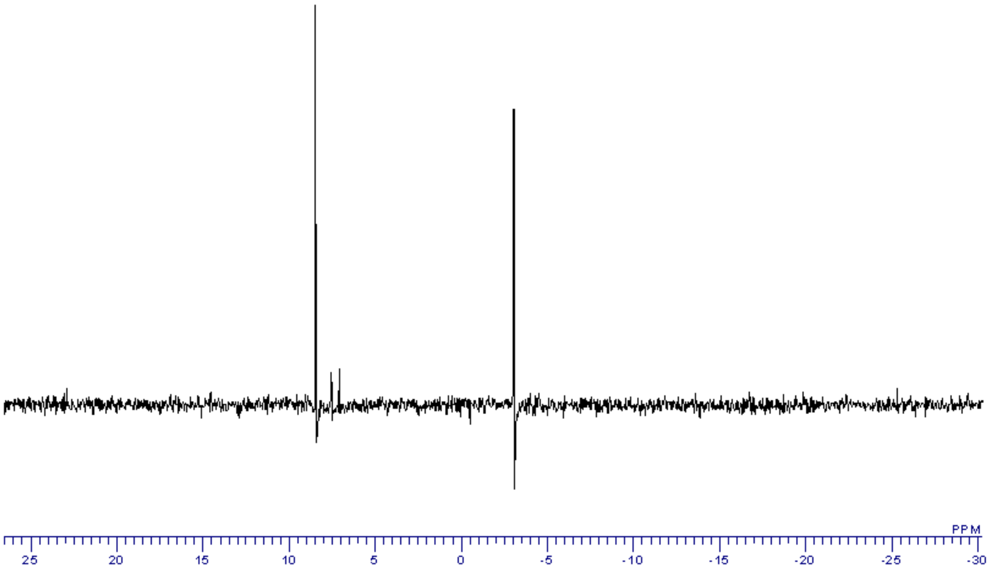
^{29}Si NMR spectrum of **3i** (CDCl$_3$, r.t.)



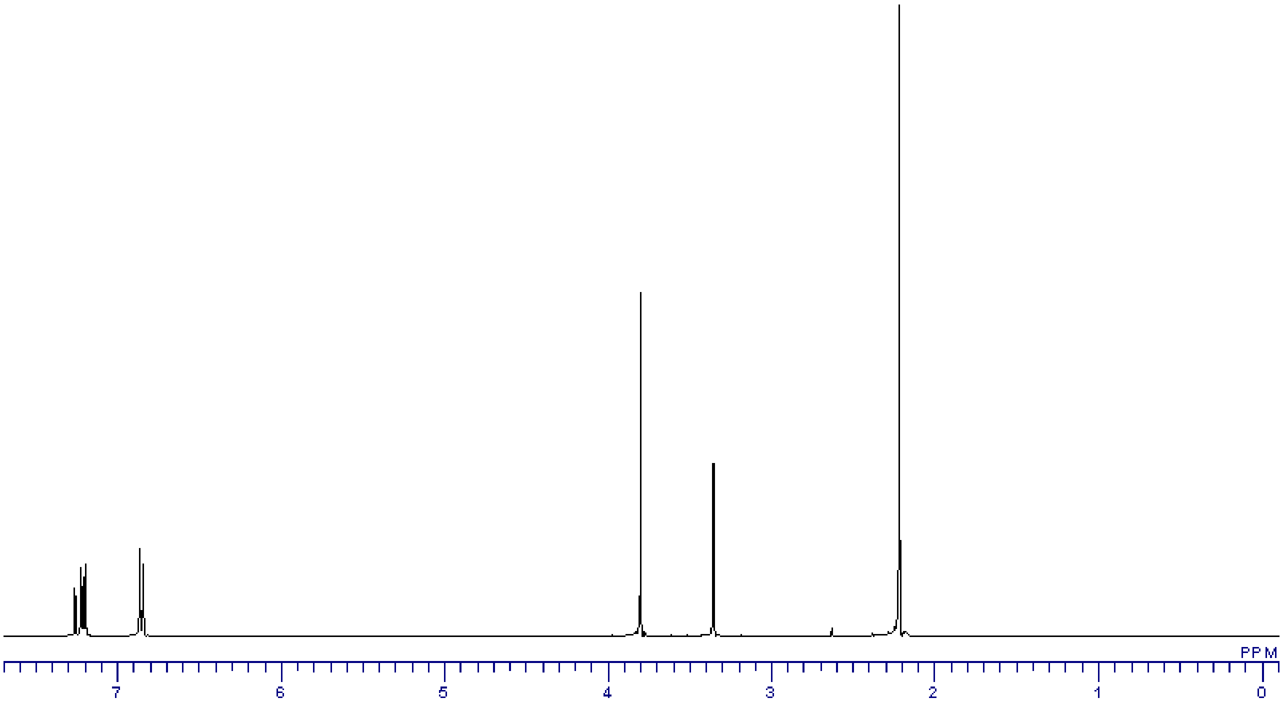
^{1}H NMR spectrum of (*E*)-[1-(phenyl)-2-(1,1,3,3,3-pentamethyldisiloxane)]ethene ($CDCl_3$, r.t.)



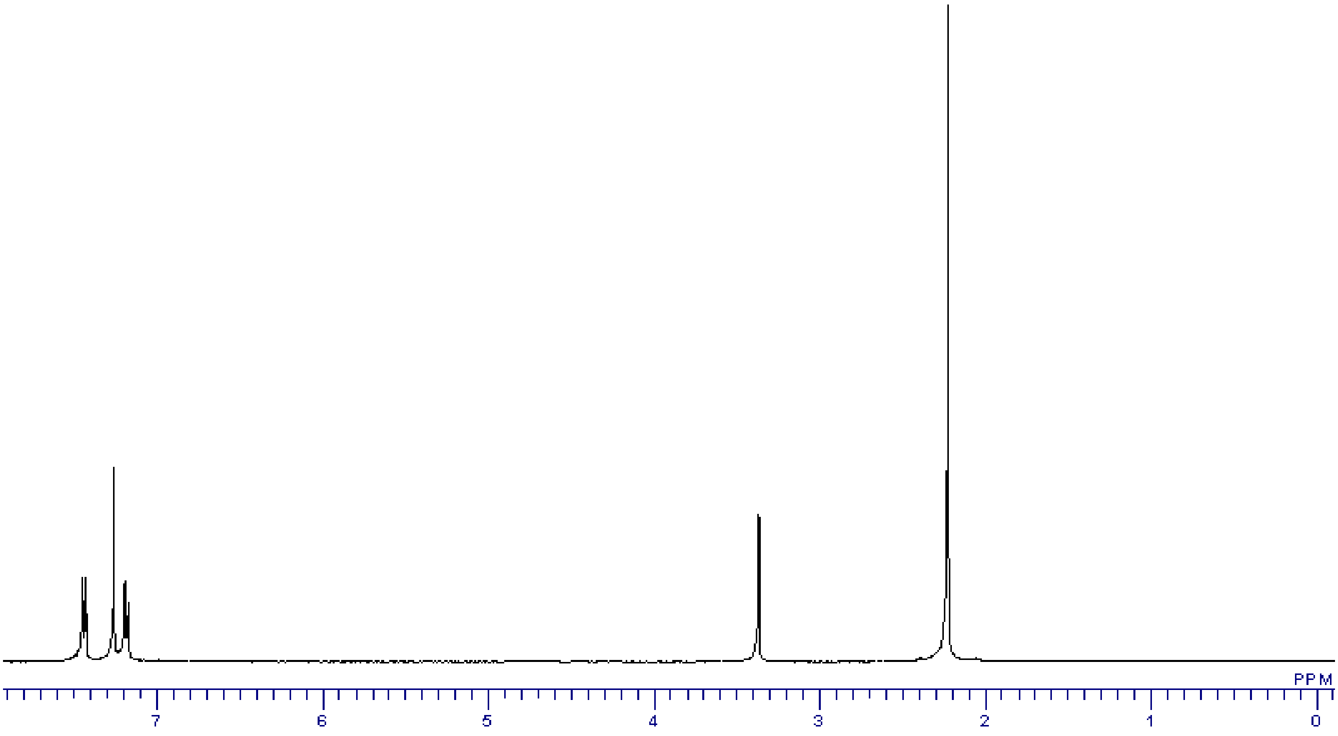
^{13}C NMR spectrum of (*E*)-[1-(phenyl)-2-(1,1,3,3,3-pentamethyldisiloxane)]ethene ($CDCl_3$, r.t.)



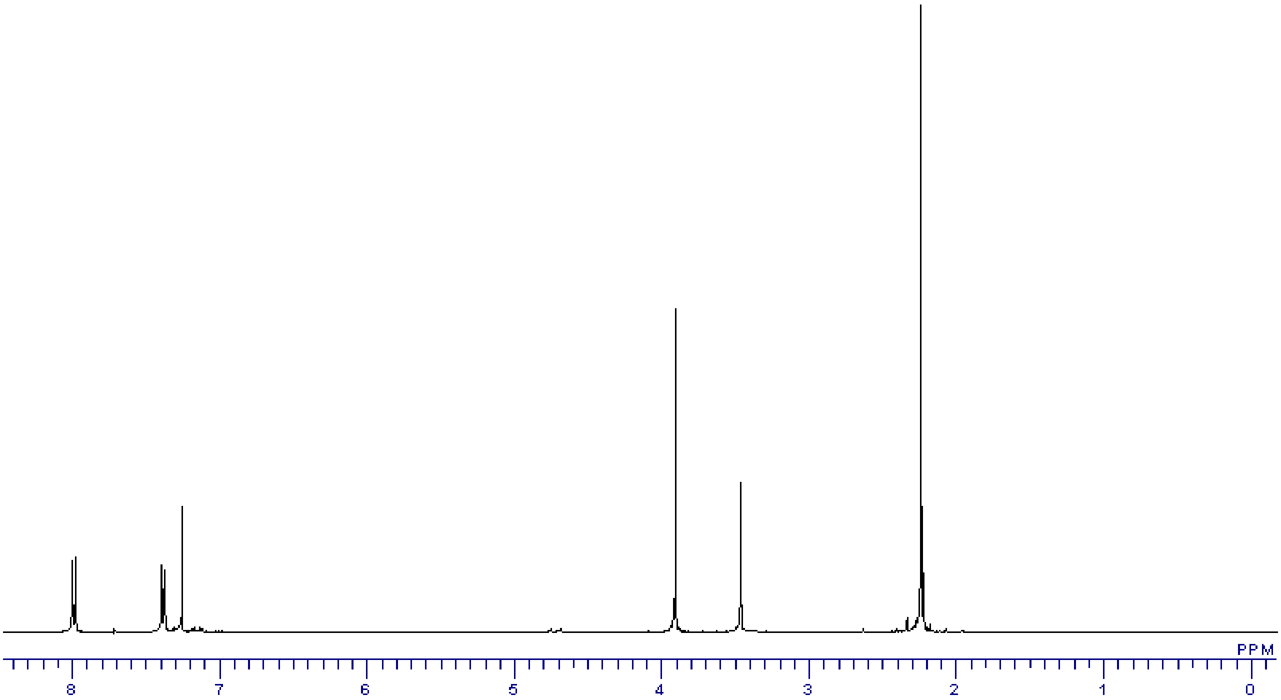
^{29}Si NMR spectrum of (*E*)-[1-(phenyl)-2-(1,1,3,3,3-pentamethyldisiloxane)]ethene ($CDCl_3$, r.t.)



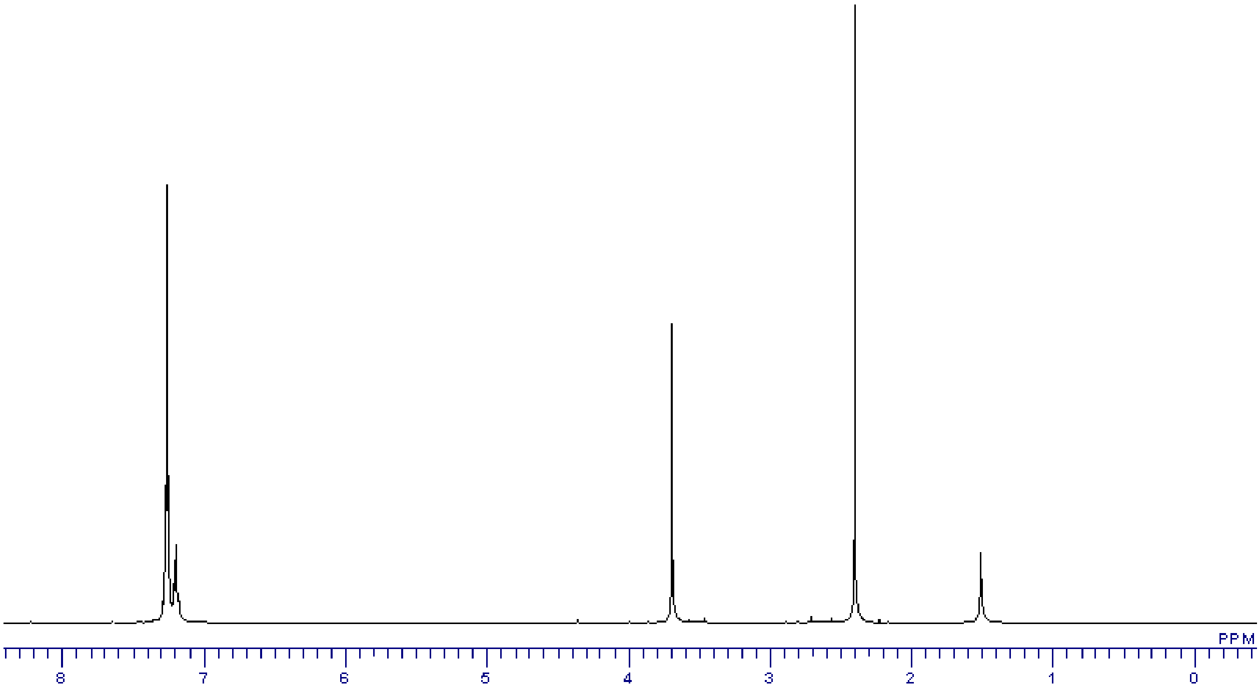
^{1}H NMR spectrum of **5a** ($CDCl_3$, r.t.)



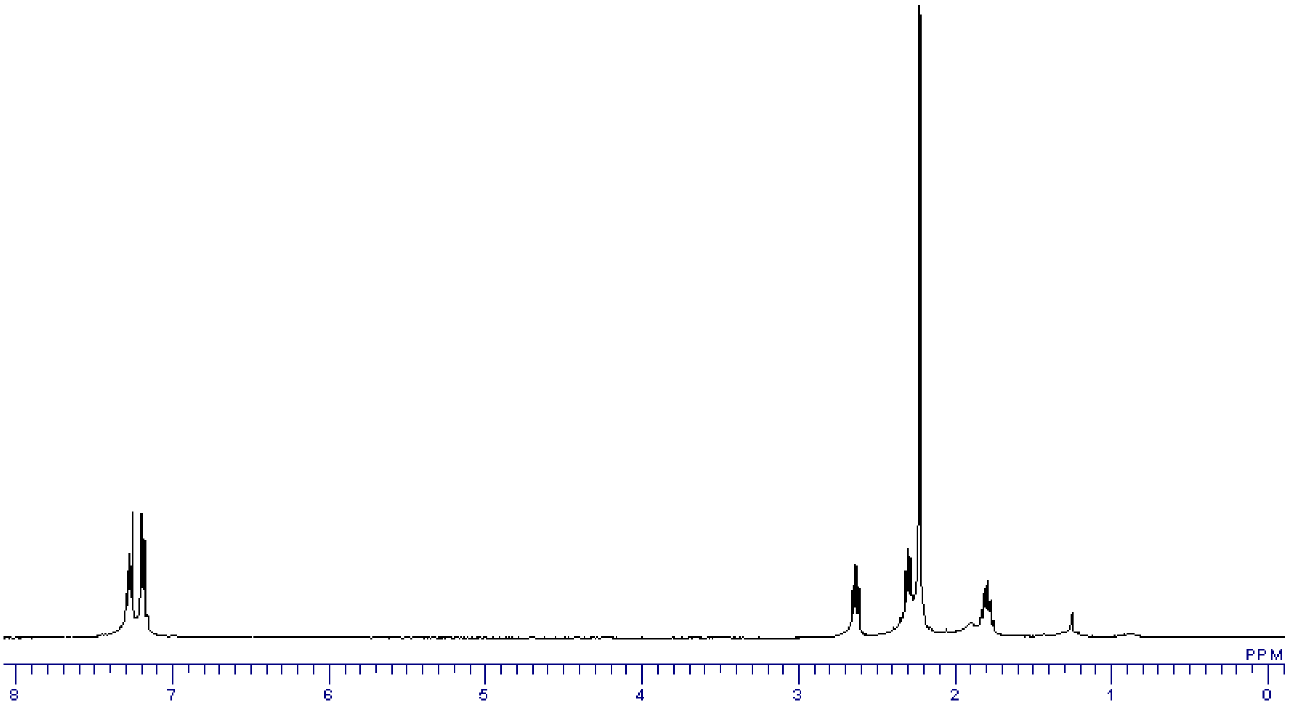
^{1}H NMR spectrum of **5b** ($CDCl_3$, r.t.)



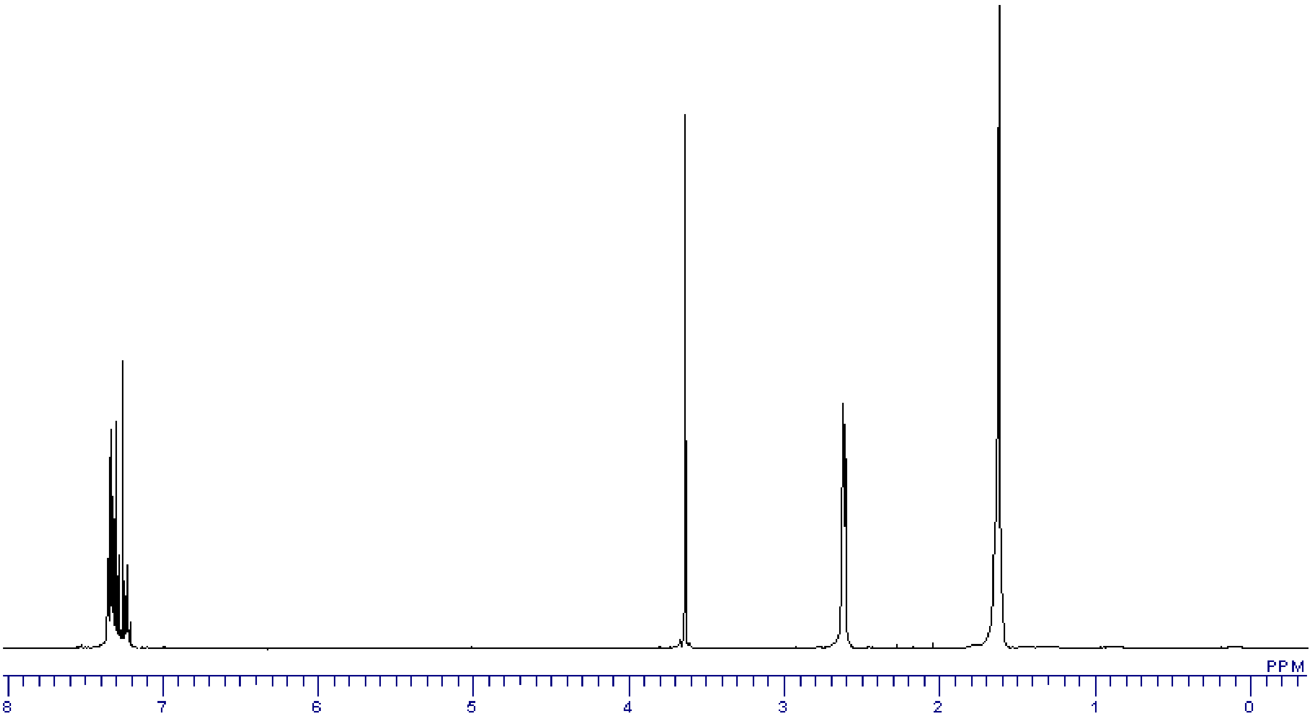
^{1}H NMR spectrum of **5c** ($CDCl_3$, r.t.)



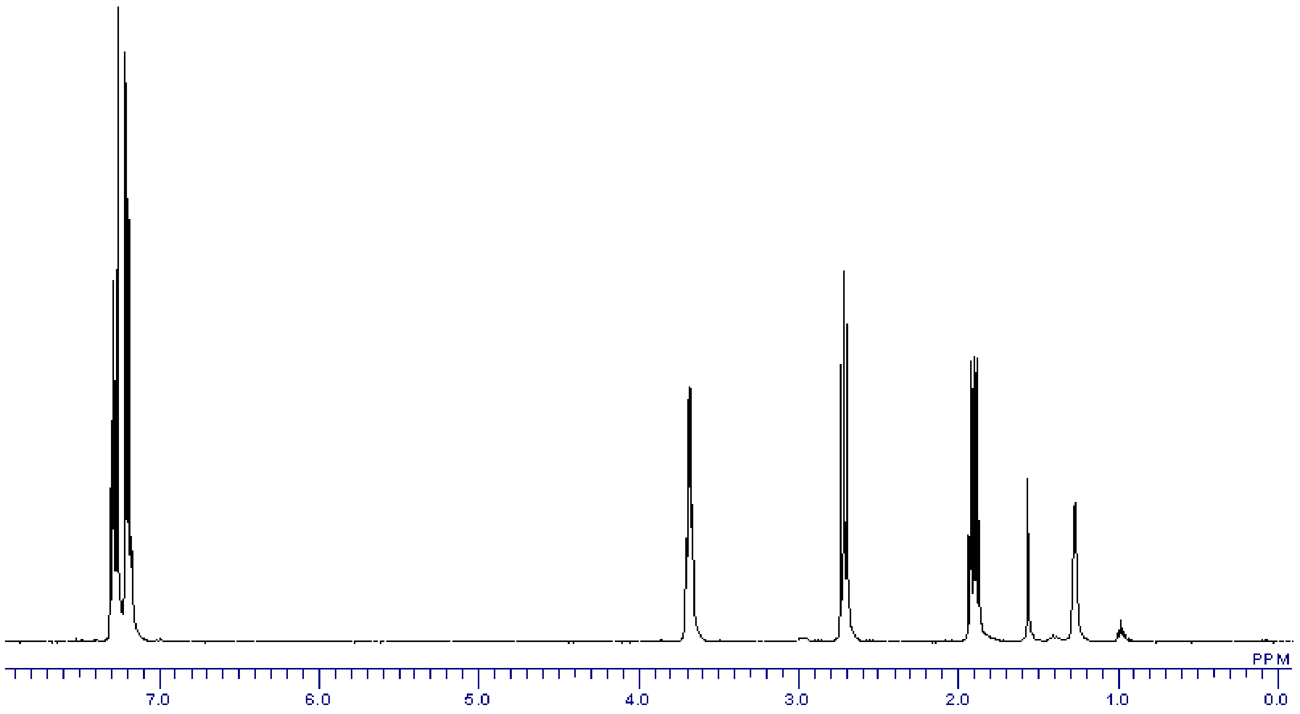
^{1}H NMR spectrum of **5d** ($CDCl_3$, r.t.)



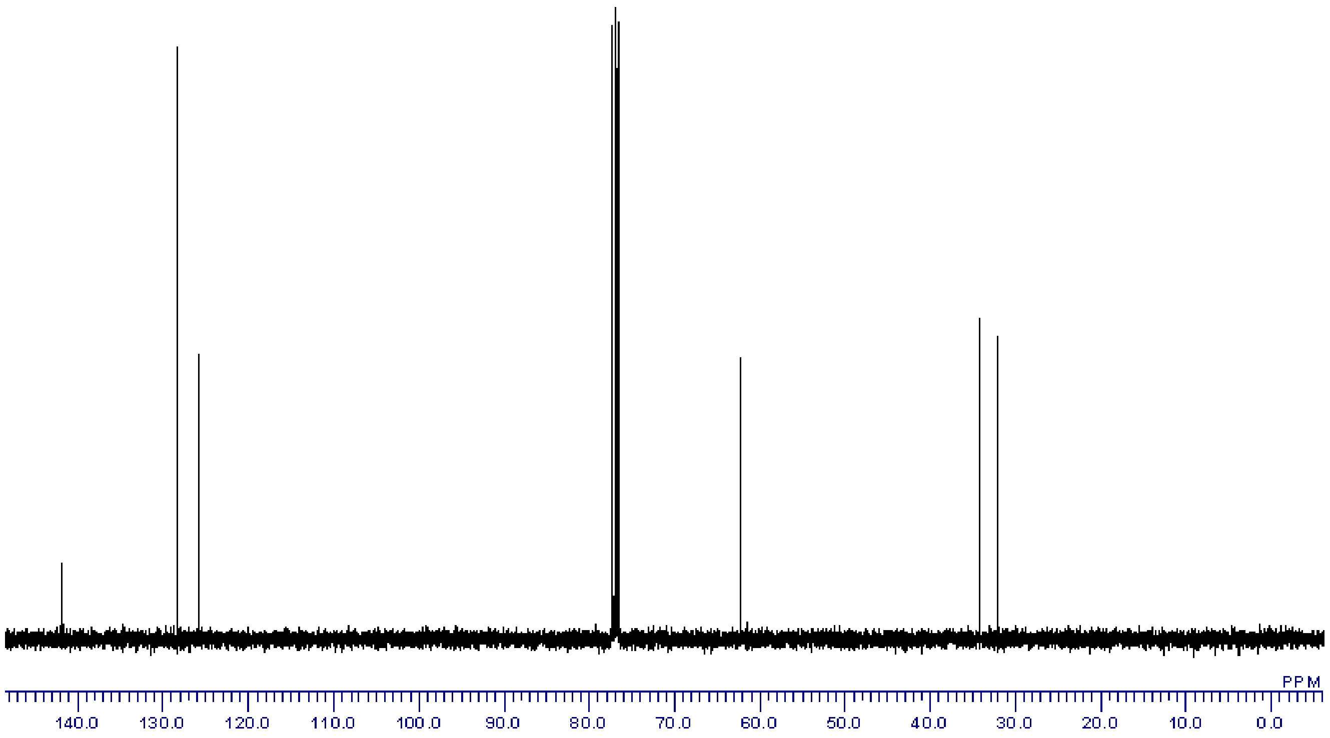
^{1}H NMR spectrum of **5e** ($CDCl_3$, r.t.)



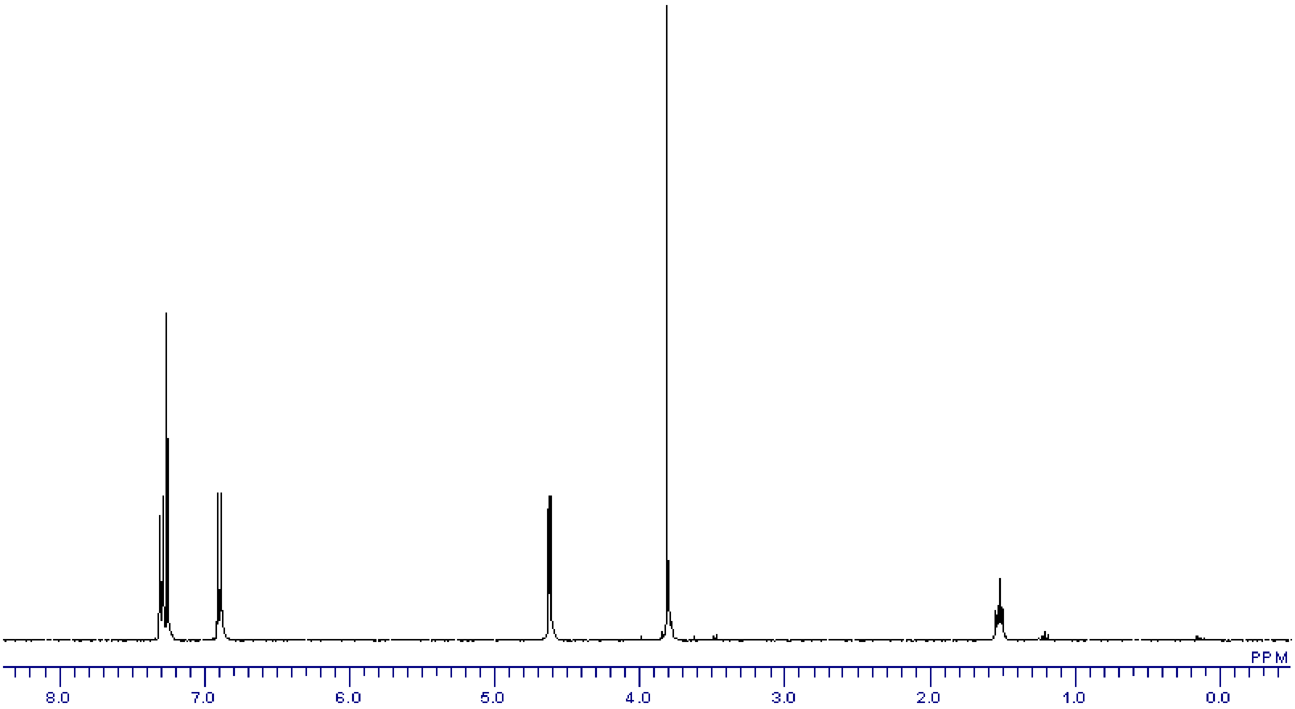
^{1}H NMR spectrum of **5f** ($CDCl_3$, r.t.)



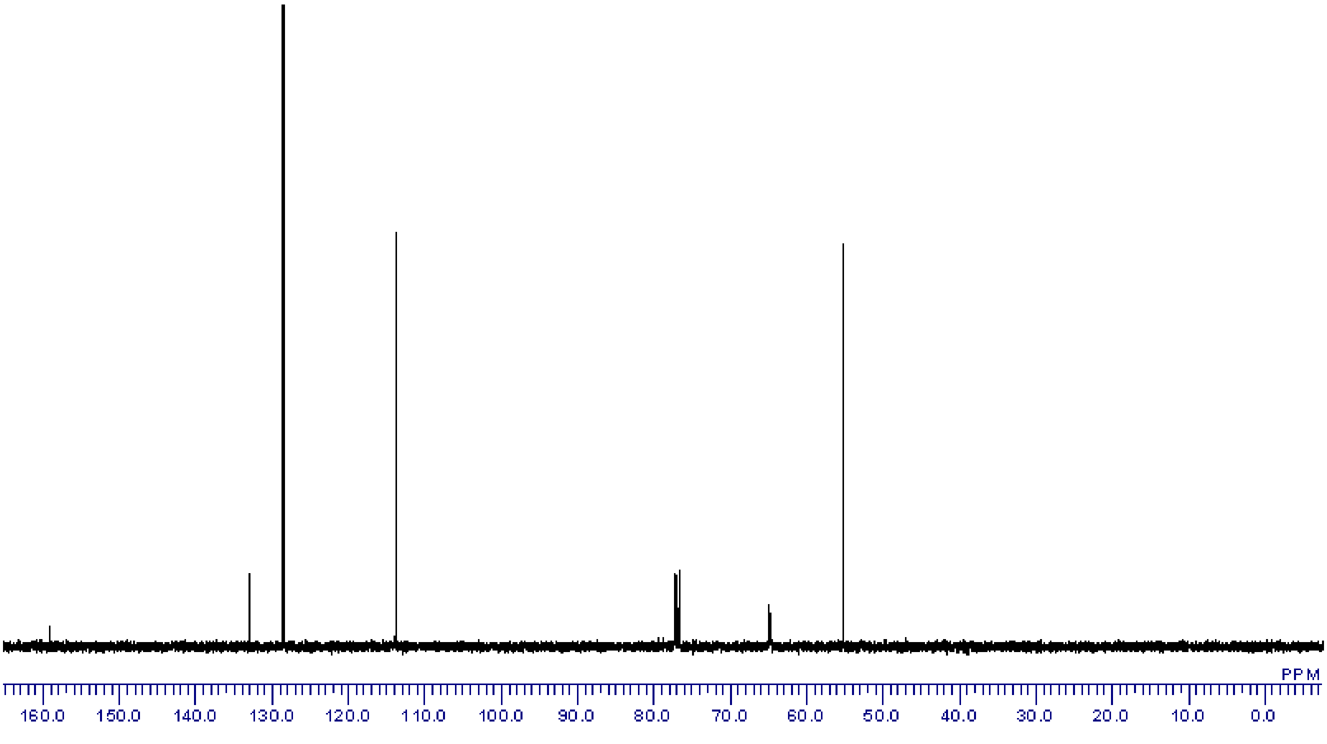
^{1}H NMR spectrum of **5g** ($CDCl_3$, r.t.)



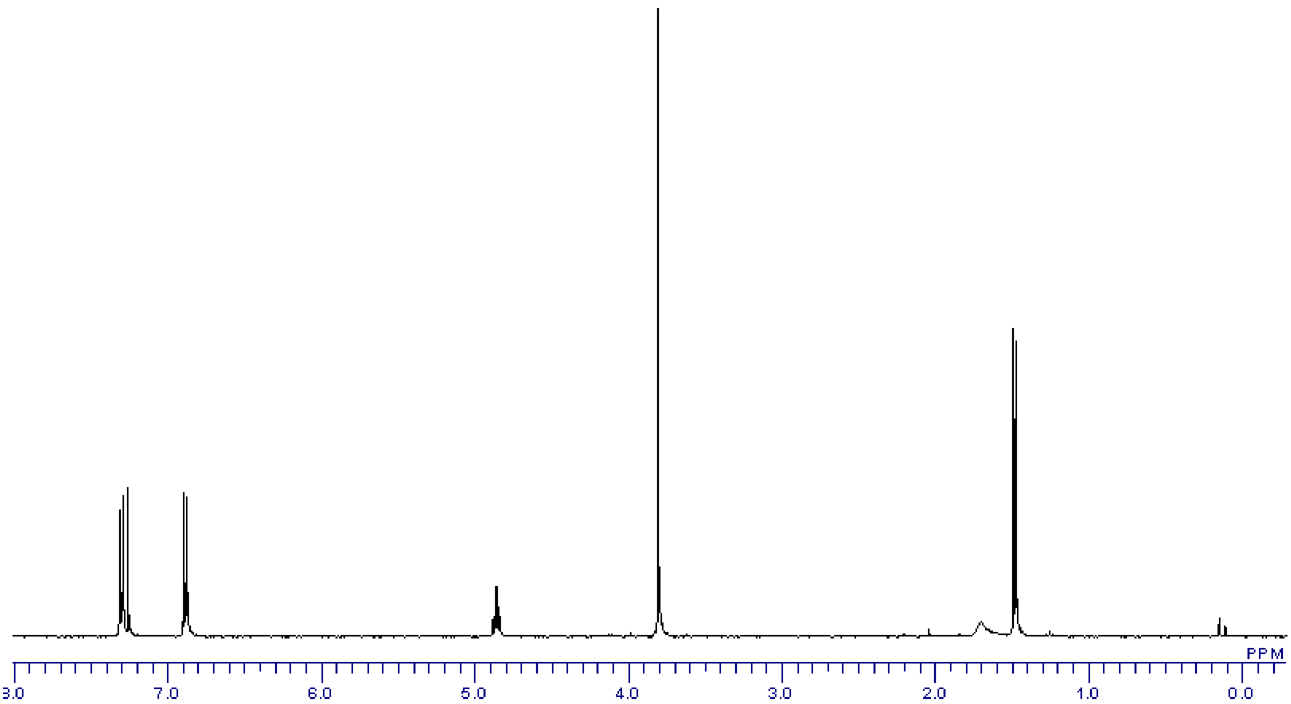
^{13}C NMR spectrum of **5g** ($CDCl_3$, r.t.)



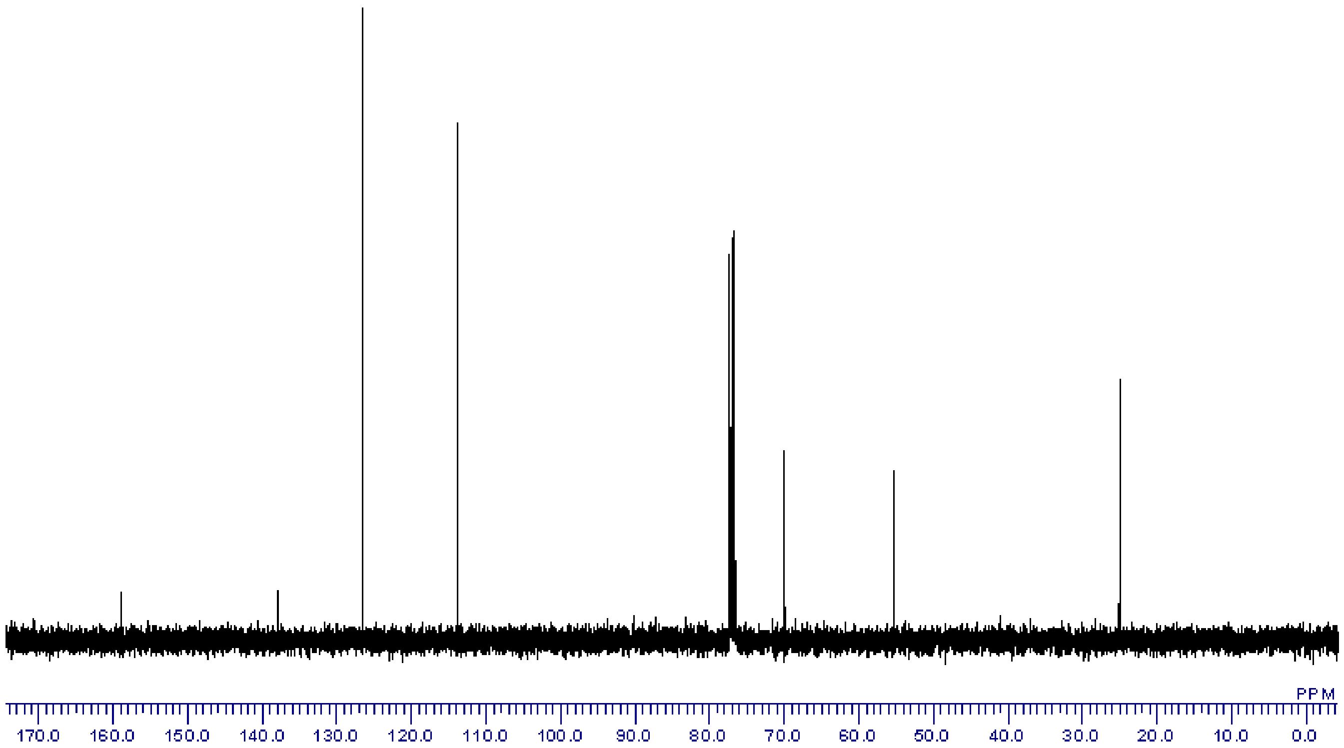
^{1}H NMR spectrum of **5h** (CDCl$_3$, r.t.)



^{13}C NMR spectrum of **5h** (CDCl$_3$, r.t.)



^{1}H NMR spectrum of **5i** (CDCl$_3$, r.t.)



^{13}C NMR spectrum of **5i** (CDCl$_3$, r.t.)