

**General considerations and synthetic and spectroscopic data.**

**Table 1.** Crystal data and structure refinement for  $[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{FeCl}$

**Figure 1.** Solid-state structure of  $[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{FeCl}$ .

**Table 2.** Crystal data and structure refinement for  $\{[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (10).

**Figure 2.** Solid-state structure of  $\{[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (10).

**Table 3.** Crystal data and structure refinement for  $\{[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{Cp})\}$ .

**Figure 3.** Solid-state structure of  $[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{Cp})$ .

**Table 4.** Crystal data and structure refinement for  $\{[\text{SiP}^{i\text{Pr}}_2\text{S}]\text{Fe}\}_2$ .

**Figure 4.** Solid-state structure of  $\{[\text{SiP}^{i\text{Pr}}_2\text{S}]\text{Fe}\}_2$ .

**Table 5.** Crystal data and structure refinement for  $[\text{SiP}^{i\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}(\text{H})(\text{N}_2)$  (13).

**Figure 5.** Solid-state structure of  $[\text{SiP}^{i\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}(\text{H})(\text{N}_2)$  (13).

**Figure 6.** NMR spectra of 2-Ad( $\text{C}_6\text{H}_4\text{Br}$ ) (2).

**Figure 7.** NMR spectra of  $(2-i\text{Pr}_2\text{C}_6\text{H}_4)_2\text{Si}(\text{H})(\text{Cl})$  (3).

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**Figure 11.** NMR spectra of  $[\text{SiS}^{\text{Ad}}_3]\text{H}$  (7).

**Figure 12.**  $^1\text{H}$  NMR spectrum of  $[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{FeMe}$  (8).

**Figure 13.**  $^1\text{H}$  NMR spectrum of  $[\text{SiP}^{i\text{Pr}}\text{S}^{\text{Ad}}_2]\text{FeMe}$  (9).

**Figure 14.**  $^1\text{H}$  NMR spectrum of  $\{[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (10).

**Figure 15.**  $^1\text{H}$  NMR spectrum of  $\{[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{L})\}\text{BAr}^{\text{F}}_4$  (11).

**Figure 16.** NMR spectra of  $[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{H})(\text{N}_2)$  (12).

**Figure 17.** NMR spectra of  $[\text{SiP}^{i\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}(\text{H})(\text{N}_2)$  (13).

**Figure 18.**  $^1\text{H}$  NMR spectrum of  $\{[\text{SiP}^{i\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (14).

**Figure 19.**  $^1\text{H}$  NMR spectrum of  $\{[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (15).

**Figure 20.** EPR spectrum of  $\{[\text{SiP}^{i\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (14). (20K in 2-MeTHF).

**Figure 21.** EPR spectrum of  $\{[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (15). (20K in 2-MeTHF).

**Figure 22.** UV-VIS spectrum of  $[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{FeMe}$  (8). ( $\epsilon$  vs wavelength)

**Figure 23.** UV-VIS spectrum of  $[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{FeCl}$ . ( $\epsilon$  vs wavelength)

**Figure 24.** UV-VIS spectrum of  $[\text{SiP}^{i\text{Pr}}\text{S}^{\text{Ad}}_2]\text{FeMe}$  (9). ( $\epsilon$  vs wavelength)

**Figure 25.** UV-VIS spectrum of  $[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{FeMe}$ . ( $\epsilon$  vs wavelength)

**Figure 26.** UV-VIS spectrum of  $\{[\text{SiP}^{i\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (14). ( $\epsilon$  vs wavelength)

**Figure 27.** UV-VIS spectrum of  $\{[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (15). ( $\epsilon$  vs wavelength)

**Figure 28.** NIR spectrum of  $\{[\text{SiP}^{i\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (14). ( $\epsilon$  vs wavelength)

**Figure 29.** NIR spectrum of  $\{[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (15). ( $\epsilon$  vs wavelength)

**Figure 30.** Cyclic Voltammogram of 14.

**Figure 31. SQUID data of 14.**

**Table 5. Coordinates for optimized structure of  $[\text{SiP}^{i\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}(\text{H})(\text{N}_2)$  (13).**

**Table 6. Coordinates for optimized structure the isomer of  $[\text{SiP}^{i\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}(\text{H})(\text{N}_2)$  (13').**

**General Considerations.** All manipulations were carried out using standard Schlenk or glovebox techniques under an atmosphere of dinitrogen. Unless otherwise noted, solvents were degassed and dried by thoroughly sparging with N<sub>2</sub> gas followed by passage through an activated alumina column. Hexamethyldisiloxane was dried over CaH<sub>2</sub> and distilled. Pentane, hexamethyldisiloxane, benzene, methylcyclohexane, toluene, tetrahydrofuran, and diethylether were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran. Unless noted otherwise, all reagents were purchased from commercial vendors and used without further purification. Celite® 545) was dried at 150°C overnight before use. Compounds **1**<sup>1</sup> and HBAr<sup>F</sup><sub>4</sub>·2Et<sub>2</sub>O<sup>2</sup> were prepared according to literature procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and stored over 3-Å molecular sieves prior to use. Elemental analyses were performed by Midwest Microlabs.

**X-ray Crystallography Procedures.** X-ray diffraction studies were carried out at the Beckman Institute Crystallography Facility on a Brüker KAPPA APEX II diffractometer and solved using SHELX v. 6.14. The crystals were mounted on a glass fiber with Paratone-N oil. Data was collected at 100K using Mo Kα ( $\lambda = 0.710\,73\text{ \AA}$ ) radiation and solved using SHELXS<sup>3</sup> and refined against  $F^2$  on all data by full-matrix least squares with SHELXL.<sup>3</sup> X-ray quality crystals were grown as described in the experimental procedures.

**SQUID Measurements:** Measurements were recorded using a Quantum Designs SQUID magnetometer running MPMSR2 software (Magnetic Property Measurement System Revision 2). The samples were prepared under dinitrogen atmosphere in a polycarbonate capsule and suspended in the magnetometer in a plastic straw. recorded at 50000 G.

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<sup>1</sup> a) R. Talay, D. Rehder, *Zeit. f. Natur, B: Anorg. Chem.*, **1981**, 36, 451. b) M. Tamm, B. Dreßel, K. Baum, T. Lügger, T. Pape, *J. Organomet. Chem.*, **2003**, 677, 1.

<sup>2</sup> Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, 11, 3920.

<sup>3</sup> Sheldrick, G. M. *Acta. Cryst.* **2008**, A64, 112.

**Other Spectroscopic Measurements.** A Varian Mercury 300 MHz spectrometer equipped with an autoswitchable probe and a Varian Inova 500 MHz spectrometer equipped with an auto-x pfg broad band probe were used to collect  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ , and  $^{31}\text{P}$  spectra at room temperature.  $^1\text{H}$  and  $^{13}\text{C}$  spectra were referenced to residual solvent resonances.  $^{29}\text{Si}$  spectra were referenced to external tetramethylsilane ( $\delta = 0$  ppm), and  $^{31}\text{P}$  spectra were referenced to external 85% phosphoric acid ( $\delta = 0$  ppm). UV-VIS measurements were taken on a Cary 50 UV/Vis Spectrophotometer using quartz cuvettes with a teflon screw cap. IR measurements were obtained on samples prepared as KBr pellets or using a KBr disk solution cell using a Bio-Rad Excalibur FTS 3000 spectrometer. NIR measurements were obtained using a Nicolet FT-NIR spectrometer using quartz cuvettes capped with a Teflon screw cap. X-band EPR spectra were obtained on a Bruker EMX spectrometer.

### Electrochemistry

Electrochemical measurements were carried out in a glovebox under a dinitrogen atmosphere in a one-compartment cell using a CH Instruments 600B electrochemical analyzer. A glassy carbon electrode was used as the working electrode and platinum wire was used as the auxiliary electrode. The reference electrode was Ag/AgNO<sub>3</sub> in THF. The ferrocene couple Fc<sup>+</sup>/Fc was used as an external reference. Solutions (THF) of electrolyte (0.3 M tetra-*n*-butylammonium hexafluorophosphate) and analyte were also prepared under an inert atmosphere.

**DFT Calculations.** Geometry optimization for **13** was run on the Gaussian03<sup>4</sup> suite of programs starting from solid-state coordinates with the B3LYP<sup>5</sup> level of theory with the

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<sup>4</sup> Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu,

6-31G(d)<sup>6</sup> basis set for all atoms. An optimization of the isomer of **13**, in which the hydride ligand is *trans* to the phosphine ligand, was also conducted (Compound **13'**). Frequencies calculations on **13** and **13'** confirmed the optimized structures to be minima. The calculations were followed by additional energy calculations, which were run using the same functional but with the 6-311G(d,p)<sup>7</sup> basis set for all atoms.

### Synthesis of 2-Ad(C<sub>6</sub>H<sub>4</sub>Br) (**2**).

2-bromothiophenol (7.6 g, 40 mmol) was added to a stirring solution of 1-adamantol (7.6 g, 50 mmol) in a 3:2 mixture of approximately 300 ml of H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O. After stirring for 2 days, the solids were filtered and washed with water. The solids were extracted into ether, concentrated, and recrystallized from hot hexanes to yield the product, 2-Ad(C<sub>6</sub>H<sub>4</sub>Br) (8.2 g, 63 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.68 (dd, *J* = 7.8 Hz, 1.5 Hz, 1H), 7.62 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.29-7.16 (m, 2H), 2.02 (s, 3H), 1.91 (s, 6H), 1.63 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ): 139.9, 133.4, 132.8, 129.8, 126.7, 50.4, 43.6, 35.9, 29.9. HR-MS: Calc., 324.0370; Found, 324.0378.

**Synthesis of (2-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Si(H)(Cl) (**3**).** 2-*i*Pr<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>Br) (**1**) (63 mg, 0.23 mmol) was dissolved in 5 ml Et<sub>2</sub>O in a vial. The solution was cooled at -78 °C inside the glovebox

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G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

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and nBuLi (0.15 ml, 0.23 mmol, 1.6 M soln.) was added dropwise. The resulting solution was stirred for 1 hr at -78 °C upon which white solids were observed to precipitate out of solution. The mixture was stirred at RT for 1 hr. Volatiles were removed, and the pale powder was redissolved in 3 ml toluene. HSiCl<sub>3</sub> (15 mg, 0.11 mmol) was weighed out and diluted with 2 ml toluene. Both toluene solutions were cooled to -78 °C in the glovebox cold well and the HSiCl<sub>3</sub> solution was added dropwise to the lithiated thioether solution. The resulting mixture was allowed to warm up slowly overnight. The mixture was filtered through celite, and concentrated to yield (2-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Si(H)(Cl) (48 mg, 97 %). This material was used in subsequent reactions without any further purification. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ): 7.88 (dt, *J* = 10Hz, 2Hz, 2H), 7.30-7.26 (m, 2H), 7.14-7.07 (m, 5H), 1.93 (m, 2H), 1.85 (m, 2H), 1.06 (dd, *J* = 15Hz, 5Hz, 3H) 0.99 (dd, *J* = 15Hz, 5Hz, 3H) 0.86 (dd, *J* = 15Hz, 5Hz, 3H) 0.77 (dd, *J* = 15Hz, 5Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ): 144.1 (d, *J* = 46 Hz), 143.2 (d, *J* = 19Hz), 135.6 (d, *J* = 16 Hz), 131.7, 129.5, 128.4, 25.3 (d, *J* = 12 Hz), 24.6 (d, *J* = 12 Hz), 20.23 (d, *J* = 12 Hz), 20.15 (d, *J* = 18 Hz), 19.9 (d, *J* = 19 Hz), 19.4 (d, *J* = 9 Hz). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ): -21.3 (t, *J* = 32 Hz). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, δ): 0.39. IR (KBr pellet, cm<sup>-1</sup>): 2238, 2212 (ν[Si-H]). HR-MS: Calc., 450.1828; Found, 450.1841.

**Synthesis of (AdSC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Si(H)(Cl) (4).** 2-AdS(C<sub>6</sub>H<sub>4</sub>Br) (2) (75 mg, 0.23 mmol) was dissolved in 4 ml Et<sub>2</sub>O in a vial. The solution was cooled at -78 °C inside the glovebox and nBuLi (0.15 ml, 0.23 mmol, 1.6 M soln.) was added dropwise. The resulting solution was stirred for 1 hr at -78 °C upon which white solids were observed to precipitate out of solution. The mixture was stirred at RT for 1 hr. Volatiles were removed, and the white powder was redissolved in 3 ml toluene. HSiCl<sub>3</sub> (15 mg, 0.11 mmol) was weighed out and diluted with 2 ml toluene. Both toluene solutions were cooled to -78 °C in the glovebox cold well and the HSiCl<sub>3</sub> solution was added dropwise to the lithiated thioether solution. The resulting mixture was allowed to warm up slowly overnight. The mixture was filtered through celite, and concentrated to yield (AdSC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Si(H)(Cl) (59 mg, 96 %). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ): 7.84 (m, 2H), 7.52 (m, 2H), 7.07 (m, 4H), 6.84 (s, 1H), 1.95-1.82 (m, 18H), 1.44 (s, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ): 142.3, 138.0, 137.3, 126.8, 130.2, 128.0, 50.0, 43.8, 36.0 30.1. <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ): -20.4 IR (KBr pellet, cm<sup>-1</sup>): 2222, 2172(sh) (ν[Si-H]). HR-MS: Calc., 515.2263; Found, 515.2240.

### Synthesis of $[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{H}$ (**5**).

2-*i*Pr<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>Br) (2.0 g, 7.4 mmol) was dissolved in 50 ml Et<sub>2</sub>O. The flask was cooled to -78 °C and *n*BuLi (4.6 ml, 7.4 mmol) was added dropwise. The flask was stirred for 30 min., upon which a pale precipitate formed. The flask was stirred at RT for 1 hr, and volatiles were removed. The pale solid was redissolved in toluene and cooled to -78 °C. HSiCl<sub>3</sub> (480 mg, 3.5 mmol) was diluted with 6 ml toluene and also cooled to -78 °C. The silane was added dropwise to the cold solution of phosphine, and the resulting mixture was allowed to warm to RT slowly over several hours to form (2-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Si(H)(Cl) (**3**). This solution containing **3** was used directly in the subsequent reaction without any purification, *vide infra*.

In a separate flask, 2-AdS(C<sub>6</sub>H<sub>4</sub>Br) (1.15 g, 3.5 mmol) was dissolved in 20 ml ether. The flask was cooled to -78 °C, and *n*BuLi (2.2 ml, 3.5 mmol, 1.6 M soln.) was added dropwise. The resulting solution was stirred for 30 min., upon which a white precipitate formed. Volatiles were removed, and the white solid was redissolved in 10 ml toluene. This solution was cooled to -78 °C and added dropwise to a solution of **3** at -78 °C. The resulting mixture was allowed to warm to RT overnight. The pale yellow solution was filtered through celite, concentrated, and washed with a small amount of pentane (2 x 2 ml) to afford analytically pure  $[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{H}$  (1.8 g, 78 % overall yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ): 7.76 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 6.9 Hz, 2H), 7.29-6.92 (m, 10H), 2.11 (s, 6H), 2.03 (m, 2H), 1.95 (s, 3H), 1.55 (s, 6H), 1.13 (m, 12H), 0.94 (s, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ): 146.5 (d, *J* = 5 Hz), 146.1 (d, *J* = 5 Hz), 145.8 (d, *J* = 5 Hz), 144.5 (d, *J* = 21 Hz), 139.6, 139.4, 138.7, 138.6, 138.4, 132.3, 129.5, 128.8, 128.4, 127.8, 50.7, 44.9, 37.0, 30.9, 25.7, 20.9 (m). <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ): -32.9 (t, *J* = 26 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ): 2.0. IR (KBr pellet, cm<sup>-1</sup>): 2218 (ν[Si-H]). HR-MS: Calc., 659.3426; Found, 659.3404. Anal. Calcd for C<sub>40</sub>H<sub>56</sub>SiP<sub>2</sub>S: C, 72.91; H, 8.57; N, 0.00. Found: C, 73.02; H, 8.57; N, 0.00.

### Synthesis of $[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}_2]\text{H}$ (**6**).

2-AdS(C<sub>6</sub>H<sub>4</sub>Br) (2.4 g, 7.4 mmol) was dissolved in 50 ml Et<sub>2</sub>O. The flask was cooled to -78 °C and *n*BuLi (4.6 ml, 7.4 mmol, 1.6 M soln.) was added dropwise. The flask was stirred for 30 min., upon which a white precipitate formed. The flask was stirred at RT for 1 hr, and volatiles were removed. The white solid was redissolved in 50 ml toluene and cooled to -78 °C. HSiCl<sub>3</sub> (500 mg, 3.7 mmol) was diluted with 5 ml

toluene and also cooled to -78 °C. The silane was added dropwise to the cold solution of phosphine, and the resulting mixture was allowed to warm to RT slowly over several hours to form (AdSC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Si(H)(Cl) (**4**). This solution containing **4** was used directly in the subsequent reaction without any purification, *vide infra*.

In a separate flask, 2-*i*Pr<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>Br) (1.0 g, 3.7 mmol) was dissolved in 30 ml ether. The flask was cooled to -78 °C, and nBuLi (2.3 ml, 3.7 mmol, 1.6 M soln.) was added dropwise. The resulting solution was stirred for 30 min., upon which a pale precipitate formed. Volatiles were removed, and the pale solid was redissolved in 10 ml toluene. This solution was cooled to -78 °C and added dropwise to a solution of **4** at -78 °C. The resulting mixture was allowed to warm to RT overnight. The pale yellow solution was filtered through celite, concentrated, and washed with a small amount of pentane (2 x 2 ml) to afford analytically pure [SiP<sup>*i*Pr</sup>S<sup>Ad</sup><sub>2</sub>]H (2.0 g, 77 % overall yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ): 7.70 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 6.3 Hz, 1H), 7.25-7.10 (m, 7H), 6.95 (t, *J* = 7.5 Hz, 3H), 2.16 (s, 12H), 2.06 (m, 2H), 1.98 (s, 6H), 1.59 (s, 12H), 1.17 (dd, *J* = 14 Hz, 6.9 Hz, 6H), 1.00 (dd, *J* = 12 Hz, 7.2 Hz, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ): 145.5, 145.2, 144.9, 143.6 (d, *J* = 13 Hz), 138.6, 138.4, 138.1, 137.4 (d, *J* = 14 Hz), 131.7, 128.9, 128.5, 128.2, 127.9, 50.0, 44.2, 36.3, 30.3, 25.1, 20.3, 20.21, 20.20, 20.1. <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ): -30.3 (d, *J* = 26 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ): 1.9. IR (KBr pellet, cm<sup>-1</sup>): 2221 (ν[Si-H]). HR-MS: Calc., 709.3487; Found, 709.3488. Anal. Calcd for C<sub>44</sub>H<sub>57</sub>SiPS<sub>2</sub>: C, 74.53; H, 8.10; N, 0.00. Found: C, 74.24; H, 7.99; N, 0.00.

### Synthesis of [SiS<sup>Ad</sup><sub>3</sub>]H (**7**).

2-AdS(C<sub>6</sub>H<sub>4</sub>Br) (320 mg, 0.98 mmol) was dissolved in 10 ml Et<sub>2</sub>O. The solution was cooled to -78 °C and nBuLi (0.61 ml, 0.98 mmol, 1.6 M soln.) was added dropwise. The solution was stirred for 30 min., upon which a white precipitate was observed. The mixture was stirred for 1 hr at RT. Volatiles were removed, and the white solid was dissolved in 10 ml toluene. HSiCl<sub>3</sub> (40 mg, 0.30 mmol) was diluted with 2 ml of toluene and cooled to -78 °C. The HSiCl<sub>3</sub> was added dropwise to a solution of the lithiated thioether at -78 °C dropwise. The mixture was allowed to warm to RT overnight. The mixture was filtered through celite, and concentrated to yield a white powder. Washing with 3 ml of pentane afforded analytically pure [SiS<sup>Ad</sup><sub>3</sub>]H (0.22 g, 88%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ): 7.72 (d, *J* = 7.6 Hz, 3H), 7.21-7.11 (m, 6H), 7.00 (s, 1H), 6.93 (t, *J* = 7.6 Hz, 3H), 2.18 (s, 12H), 1.98 (s, 6H), 1.58 (s, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ): 144.6, 138.3, 138.0, 137.9, 129.0, 127.9, 49.8, 44.1, 36.2, 30.2. <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, δ): -31.0. IR (KBr pellet, cm<sup>-1</sup>): 2250 (ν[Si-H]). HR-MS: Calc., 758.3454;



Found, 758.3470. Anal. Calcd for  $C_{48}H_{58}SiS_3$ : C, 75.93; H, 7.70; N, 0.00. Found: C, 75.71; H, 7.80; N, 0.00.

### Synthesis of $[SiP^{iPr}_2S^{Ad}]FeMe$ (**8**).

$[SiP^{iPr}_2S^{Ad}]H$  (490 mg, 0.75 mmol) and  $FeCl_2$  (95 mg, 0.75 mmol) were dissolved in approximately 50 ml of THF. The flask was cooled to  $-78\text{ }^{\circ}C$  and  $MeMgCl$  (0.50 ml, 1.5 mmol, 3M soln.) diluted with 10ml THF was added dropwise via cannula. A color change to dark red took place upon addition. The resulting mixture was allowed to warm up slowly overnight. Volatiles were removed. The solids were washed with a small amount of pentane and extracted into 25 ml of benzene, and filtered through celite. The red solution was concentrated, and the extraction with benzene was repeated. Removal of volatiles and washing with pentane yielded red **8** (0.34 g, 59 %). This material was used without any further purification in subsequent reactions.  $^1H$  NMR ( $C_6D_6$ ,  $\delta$ ): 8.8, 6.8, 5.8, 5.0, 3.2, 0.5, 0.2, -0.8, -1.8, -5.2, -8.5.  $\mu_{eff}$  (Evans' method,  $C_6D_6$ ,  $23\text{ }^{\circ}C$ ) =  $3.2\text{ }\mu_B$ . UV-VIS (in THF): (nm,  $\epsilon$  [ $mol^{-1}\text{ cm}^{-1}$ ]), 349 (4100, sh), 477 (2200, sh), 802 (140).

### Synthesis of $[SiP^{iPr}_2S^{Ad}]FeCl$ .

$[SiP^{iPr}_2S^{Ad}]FeMe$  (0.32 g, 0.44 mmol) was dissolved in 50 ml THF. The flask was cooled to  $-78\text{ }^{\circ}C$  and  $HCl$  (0.44 ml, 0.44 mmol, 1M soln.) was added dropwise. The resulting solution was stirred overnight and allowed to warm to room temperature. The volatiles were removed, and the residues were washed with pentane. The product was extracted into benzene, and the orange mixture was filtered through celite. Concentration of the dark orange solution yielded  $[SiP^{iPr}_2S^{Ad}]FeCl$  as an orange powder (0.28 g, 85%). Crystals suitable for X-ray diffraction were grown from layering pentane over a benzene solution of  $[SiP^{iPr}_2S^{Ad}]FeCl$ .  $^1H$  NMR ( $C_6D_6$ ,  $\delta$ ): 8.7, 6.6, 6.4, 6.1, 1.7, 0.6, 0.0, -2.6, -5.0, -8.1.  $\mu_{eff}$  (Evans' method,  $C_6D_6$ ,  $23\text{ }^{\circ}C$ ) =  $2.5\text{ }\mu_B$ . UV-VIS (in THF): (nm,  $\epsilon$  [ $mol^{-1}\text{ cm}^{-1}$ ]), 426 (2500), 475 (3200), 818 (80). Anal. Calcd for  $C_{40}H_{55}SiP_2SFeCl$ : C, 64.12; H, 7.40; N, 0.00. Found: C, 63.93.71; H, 7.14; N, 0.00.

### Synthesis of $[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}]_2\text{FeMe}$ (**9**).

$[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}]_2\text{H}$  (0.50 g, 0.71 mmol) and  $\text{FeCl}_2$  (110 mg, 0.85 mmol) was dissolved in 80 ml THF and the flask was cooled to  $-78\text{ }^\circ\text{C}$ .  $\text{MeMgCl}$  (0.56 ml, 1.7 mmol, 3M soln.) diluted with 10 ml THF was added dropwise to the solution via cannula. A color change to brown/dark red took place. The flask was allowed to warm to room temperature slowly overnight. Volatiles were removed, and the mixture was extracted into pentane and filtered through celite. This filtrate contains the product,  $[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}]_2\text{FeMe}$  (**9**), in addition to small amounts of free ligand, adamantane, and other products. Concentrating the filtrate to 20 ml and cooling at  $-35\text{ }^\circ\text{C}$  overnight precipitates out a red solid that contains most of the free ligand, as well as **9**. Concentration of the mother liquor to 15 ml and cooling at  $-35\text{ }^\circ\text{C}$  over several days yields analytically pure **9**. (0.25 g, 45 %).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 5.6, 5.5, 4.3, 1.1, 0.1, -1.8, -4.8.  $\mu_{\text{eff}}$  (Evans' method,  $\text{C}_6\text{D}_6$ ,  $23\text{ }^\circ\text{C}$ ) =  $2.9\text{ }\mu_{\text{B}}$ . UV-VIS (in THF): (nm,  $\epsilon$  [ $\text{mol}^{-1}\text{cm}^{-1}$ ]), 345 (5400, sh), 410 (3200, sh), 481 (1900, sh), 815 (70). Anal. Calcd for  $\text{C}_{45}\text{H}_{59}\text{SiP}_2\text{S}_2\text{Fe}$ : C, 69.38; H, 7.63; N, 0.00. Found: C, 69.76; H, 8.01; N, 0.00.

### Synthesis of $\{[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{N}_2)\}\text{BAr}^{\text{F}}_4$ (**10**).

$[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{FeMe}$  (100 mg, 0.14 mmol) was dissolved in a 2:1 mixture of  $\text{Et}_2\text{O}$  and benzene in a vial. The vial was cooled in the glovebox coldwell (dry ice/acetone bath).  $\text{HBar}^{\text{F}}_4 \cdot 2\text{Et}_2\text{O}$  (140 mg, 0.14 mmol) was dissolved in 2 ml  $\text{Et}_2\text{O}$  and also placed in the coldwell. The  $\text{HBar}^{\text{F}}_4 \cdot 2\text{Et}_2\text{O}$  solution was added dropwise to the solution of  $[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{FeMe}$ , resulting in a color change to green. The reaction mixture was stirred for 15 min. in the coldwell, after which it was stirred at room temperature for 15 min. The mixture was filtered through celite, concentrated, and recrystallized by layering a concentrated solution in  $\text{Et}_2\text{O}$  over a solution of 1:1 = hexamethyldisiloxane: pentane to yield green plates of  $\{[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (88 mg, 41 %) suitable for x-ray diffraction. The  $^1\text{H}$  NMR spectrum of this compound was taken in 10:1 =  $\text{C}_6\text{H}_6$ :d8-THF, due to the limited solubility of **10** in  $\text{C}_6\text{D}_6$ . Consequently, the reported NMR shifts are those of the solvento adduct,  $[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{THF})\text{BAr}^{\text{F}}_4$ . Room temperature magnetic moments were obtained by Evans method, in which the measurement was taken in  $\text{C}_6\text{D}_6/\text{C}_6\text{H}_6$  with a drop of  $\text{Et}_2\text{O}$  to dissolve **10** ( $\text{Et}_2\text{O}$  does not appear to displace  $\text{N}_2$  to a significant degree, if at all).  $^1\text{H}$  NMR ( $\text{d}_8$ -THF,  $\delta$ ): 11.5, 8.4, 7.7, 5.9, 4.4, 0.7, 0.0, -0.6, -2.6, -3.2, -4.5, -6.7, -8.4. (Evans' method,  $\text{C}_6\text{D}_6$ ,  $23\text{ }^\circ\text{C}$ )

= 3.2  $\mu_B$ . UV-VIS (in Et<sub>2</sub>O): (nm,  $\epsilon$  [mol<sup>-1</sup> cm<sup>-1</sup>]), 433 (1100, sh), 516 (630), 621 (310, sh), 855 (95, sh). IR (KBr liquid cell, Et<sub>2</sub>O, cm<sup>-1</sup>): 2156 ( $\nu$ [N<sub>2</sub>]).

### Synthesis of [SiP<sup>iPr</sup><sub>2</sub>S<sup>Ad</sup>]<sup>+</sup>Fe(Cp)

{[SiP<sup>iPr</sup><sub>2</sub>S<sup>Ad</sup>]<sup>+</sup>Fe(N<sub>2</sub>)}BAR<sup>F</sup><sub>4</sub> (17 mg, 0.011 mmol) was dissolved in 3 ml Et<sub>2</sub>O in a vial and placed inside the glovebox cold well (dry ice/acetone). CoCp<sub>2</sub> (2.0 mg, 0.011 mmol) was added. The color of the solution gradually changed from brown/green to red. The solution was stirred for 30 min. inside the cold well, after which it was stirred at room temperature for 30 min. Volatiles were removed, and the product was extracted into pentane and filtered through celite. Volatiles were removed, and the extraction was repeated once more. Concentration of the solution resulted in yellow [SiP<sup>iPr</sup><sub>2</sub>S<sup>Ad</sup>]<sup>+</sup>Fe(Cp) (4.6 mg, 56 %). Crystals suitable for X-ray diffraction were grown from slow evaporation of a concentration pentane solution, in a small vial inside a larger vial with hexamethyldisiloxane. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ): 7.94 (d,  $J$  = 6.9 Hz, 1H), 7.88 (d,  $J$  = 6.9 Hz, 1H), 7.78 (m, 1H), 7.54 (m, 1H), 7.26-6.95 (m, 8H), 4.58 (s, 5H), 2.87 (m, 1H), 2.50 (m, 1H), 2.13-0.74 (m, 38H), -0.35 (s, 3H). <sup>31</sup>P{<sup>1</sup>H}NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ ): 110.3 (d,  $J$  = 30 Hz, 1P), 92.3 (d,  $J$  = 30 Hz, 1P).

### Synthesis of {[SiP<sup>iPr</sup><sub>2</sub>S<sup>Ad</sup>]<sup>+</sup>Fe(L)}BAR<sup>F</sup><sub>4</sub> (11).

[SiP<sup>iPr</sup><sub>2</sub>S<sup>Ad</sup>]<sup>+</sup>FeMe (8.0 mg, 0.010 mmol) was dissolved in 6 ml of Et<sub>2</sub>O in a vial and placed in the glovebox cold well (dry ice/acetone). HBAR<sup>F</sup><sub>4</sub>·2Et<sub>2</sub>O (10 mg, 0.010 mmol) was dissolved in 2 ml Et<sub>2</sub>O and also cooled in the cold well. The HBAR<sup>F</sup><sub>4</sub>·2Et<sub>2</sub>O solution was added dropwise to the [SiP<sup>iPr</sup><sub>2</sub>S<sup>Ad</sup>]<sup>+</sup>FeMe solution, which resulted in a color change from red to orange. The solution was stirred in the well for 15 min., after which it was stirred at room temperature for an additional 15 min. Removals of volatiles yielded an orange film of {[SiP<sup>iPr</sup><sub>2</sub>S<sup>Ad</sup>]<sup>+</sup>Fe(Et<sub>2</sub>O)}BAR<sup>F</sup><sub>4</sub> (16 mg, 94 %). The <sup>1</sup>H NMR spectrum and magnetic moment by Evans method of this compound were measured in d<sub>8</sub>-THF, due to the limited solubility of **10** in C<sub>6</sub>D<sub>6</sub>. Consequently, the reported NMR shifts and magnetic moment are those of the solvento adduct, [SiP<sup>iPr</sup><sub>2</sub>S<sup>Ad</sup>]<sup>+</sup>Fe(THF)}BAR<sup>F</sup><sub>4</sub>. <sup>1</sup>H NMR (d<sub>8</sub>-THF,  $\delta$ ): 7.79, 7.57, 6.5, -0.1, -3.7, -6.2. (Evans' method, d<sub>8</sub>-THF, 23 °C) = 2.8  $\mu_B$ . UV-VIS (in THF): (nm,  $\epsilon$  [mol<sup>-1</sup> cm<sup>-1</sup>]), 431 (2200), 501 (2000), 870 (170).

### Synthesis of $[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{H})(\text{N}_2)$ (**12**).

$\{[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (80 mg, 0.050 mmol) was dissolved in 15 ml of 1:1 =  $\text{Et}_2\text{O}$ :toluene in a vial. The vial was placed inside the glovebox cold well (dry ice/acetone).  $\text{NaEt}_3\text{BH}$  (50  $\mu\text{L}$ , 0.050 mmol, 1M sln) was added via syringe, and the resulting mixture was stirred in the cold well for 1 hr. The vial was subsequently stirred at room temperature for 10 min., and volatiles were removed. The product was extracted into pentane and filtered through celite. The solution was concentrated, and the extraction was repeated once more. Removal of volatiles yielded  $[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{H})(\text{N}_2)$  (33 mg, 89 %).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 8.38 (d,  $J = 7.2$  Hz, 2H), 8.14 (dd,  $J = 7.0$  Hz, 1.5 Hz, 1H), 7.53 (d,  $J = 7.8$  Hz, 1H), 7.28-6.84 (m, 8H), 2.64 (m, 2H), 2.37 (s, 6H), 1.96 (s, 3H), 1.62-1.38 (m, 12H), 1.25-0.81 (m, 20H), -20.3 (t,  $J = 67$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 155.5 (m), 149.0, 148.6, 148.4, 147.6, 140.8, 132.6, 132.0, 126.4, 126.0, 124.7, 57.6, 44.3, 36.3, 32.1, 30.7, 29.2 (m), 19.6, 19.3, 18.6.  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 88.9 (m). IR (KBr liquid cell,  $\text{Et}_2\text{O}$ ,  $\text{cm}^{-1}$ ): 2055 ( $\nu[\text{N}_2]$ ), 1910 ( $\nu[\text{Fe-H}]$ ).

### Synthesis of $[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}_2]\text{Fe}(\text{H})(\text{N}_2)$ (**13**)

$[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}_2]\text{FeMe}$  (12 mg, 0.015 mmol) was dissolved in 4 ml  $\text{Et}_2\text{O}$  in a vial and cooled inside the glovebox cold well (dry ice/acetone).  $\text{HBAr}^{\text{F}}_4 \cdot 2\text{Et}_2\text{O}$  (15 mg, 0.015 mmol) was dissolved in 2 ml  $\text{Et}_2\text{O}$  and also cooled. The  $\text{HBAr}^{\text{F}}_4 \cdot 2\text{Et}_2\text{O}$  solution was added dropwise to the solution of  $[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}_2]\text{FeMe}$ , which resulted in a color change from red to orange. The solution was stirred inside the cold well for 20 min., and subsequently stirred at room temperature for 15 min. Volatiles were removed, and the orange oil was redissolved in 5 ml of 2:1 = toluene: $\text{Et}_2\text{O}$  and replaced inside the cold well.  $\text{NaEt}_3\text{BH}$  (15  $\mu\text{L}$ , 0.015 mmol, 1M soln.) was added via syringe, and the resulting mixture was stirred inside the well for 30 min. The mixture was stirred at room temperature for 20 min., which resulted in a color change from orange to brown/orange. Volatiles were removed, and the product was extracted into pentane, and filtered through celite. The orange solution was concentrated, and the extraction was repeated once more to yield  $[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}_2]\text{Fe}(\text{H})(\text{N}_2)$  (7.9 mg, 66 %). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a concentrated solution of **13** in a small vial into a larger vial with hexamethyldisiloxane.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 8.28 (d,  $J = 7.2$  Hz, 2H), 7.80 (d,  $J = 7.2$  Hz, 1H), 7.62 (d,  $J = 7.8$  Hz, 1H), 7.46 (d,  $J = 7.5$  Hz, 1H), 7.30-7.03 (m, 5H), 6.94 (t,  $J = 7.2$  Hz, 1H), 6.82 (t,  $J = 7.5$  Hz, 1H), 2.65 (m, 1H), 2.22-1.13 (m,

40H), 0.50 (dd,  $J = 14$  Hz, 7.2 Hz, 3H), -18.7 (d,  $J = 97$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 155.2, 154.8 (d,  $J = 38$  Hz), 151.8, 151.3 (d,  $J = 46$  Hz), 145.2, 144.3, 133.3 (d,  $J = 43$  Hz), 131.40, 131.9 (t,  $J = 8.8$  Hz), 127.2, 126.5, 125.5, 57.3, 56.5, 41.9, 41.6, 36.0, 30.3 (d,  $J = 20$  Hz), 20.9, 19.8, 19.6, 19.4.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 92.8 (d,  $J = 81$  Hz). IR (KBr pellet,  $\text{cm}^{-1}$ ): 2060 ( $\nu[\text{N}_2]$ ). Anal. Calcd for  $\text{C}_{44}\text{H}_{57}\text{SiP}_2\text{S}_2\text{FeN}_2$ : C, 66.65; H, 7.24; N, 3.53. Found: C, 66.31; H, 7.51; N, 3.36.

### Synthesis of $\{[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$ (14).

$[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}_2]\text{FeMe}$  (0.10 g, 0.13 mmol) was dissolved in 13 ml  $\text{Et}_2\text{O}$  in a vial and placed inside the glovebox cold well (dry ice/acetone).  $\text{HBAr}^{\text{F}}_4 \cdot 2\text{Et}_2\text{O}$  (0.13 g, 0.13 mmol) was dissolved in 3 ml  $\text{Et}_2\text{O}$  and also cooled. The  $\text{HBAr}^{\text{F}}_4 \cdot 2\text{Et}_2\text{O}$  solution was added dropwise to the solution of  $[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}_2]\text{FeMe}$ , which resulted in a color change from red to orange. The solution was stirred for 30 min. inside the cold well, and then stirred at room temperature for 10 min. Benzene (3 ml) was added and the solution was replaced inside the well.  $\text{Cr}(\text{C}_6\text{H}_6)_2$  (13 mg, 0.64 mmol) was added in one portion, and the mixture was stirred inside the cold well for 1.5 hr. The dark orange/red solution was subsequently stirred at room temperature for 40 min., and the volatiles were removed. The product was extracted into benzene, and separated from the yellow solids by filtration through celite. The solution was concentrated, and the extraction procedure was repeated once more. Layering a 1:1 mixture of methylcyclohexane:pentane over a concentrated  $\text{Et}_2\text{O}$  solution of the product at  $-35^\circ\text{C}$  resulted in formation of small microcrystals that analyzed for  $\{[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4 \cdot \text{MeCy}$  (0.11 g, 65 %).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 11.6, 7.9, 6.2, 2.7, -0.5, -4.0, -4.7, -9.3, -11.8, -15.5. (Evans' method,  $\text{C}_6\text{D}_6$ ,  $23^\circ\text{C}$ ) =  $4.3 \mu_{\text{B}}$ . IR (KBr pellet,  $\text{cm}^{-1}$ ): 1881 ( $\nu[\text{N}_2]$ ). UV-VIS (in  $\text{Et}_2\text{O}$ ): (nm,  $\epsilon$  [ $\text{mol}^{-1} \text{cm}^{-1}$ ]), 500 (3200, sh), 608 (1200, sh), 899 (1100). NIR (in  $\text{Et}_2\text{O}$ ): (nm,  $\epsilon$  [ $\text{mol}^{-1} \text{cm}^{-1}$ ]), 1360 (2780). Anal. Calcd for  $\text{C}_{127}\text{H}_{138}\text{N}_2\text{BF}_{24}\text{Si}_2\text{P}_2\text{S}_4\text{Fe}_2$ : C, 60.60; H, 5.52; N, 1.11. Found: C, 60.78; H, 5.74; N, 0.86.

### Synthesis of $[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{H}$

2-AdS( $\text{C}_6\text{H}_4\text{Br}$ ) (1.5 g, 4.4 mmol) was dissolved in 100 ml  $\text{Et}_2\text{O}$ . The flask was cooled to  $-78^\circ\text{C}$  and  $n\text{BuLi}$  (2.8 ml, 4.4 mmol, 1.6 M soln.) was added dropwise. The flask was stirred for 30 min., upon which a white precipitate formed. The flask was stirred at RT for 1 hr, and volatiles were removed. The white solid was redissolved in 80 ml

toluene and cooled to -78 °C.  $\text{HSiCl}_3$  (300 mg, 2.2 mmol) was diluted with 4 ml toluene and also cooled to -78 °C. The silane was added dropwise to the cold solution of phosphine, and the resulting mixture was allowed to warm to RT slowly over several hours to form  $(\text{AdSC}_6\text{H}_4)_2\text{Si}(\text{H})(\text{Cl})$  (**4**). This solution containing **4** was used directly in the subsequent reaction without any purification, *vide infra*.

In a separate flask, 2- $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{Br})$  (0.75 g, 2.2 mmol) was dissolved in 60 ml ether. The flask was cooled to -78 °C, and  $\text{nBuLi}$  (1.4 ml, 2.2 mmol, 1.6 M soln.) was added dropwise. The resulting solution was stirred for 30 min., upon which a pale precipitate formed. The mixture was stirred at room temperature for 1 hr. Volatiles were removed, and the pale solid was redissolved in 15 ml toluene. This solution was cooled to -78 °C and added dropwise to a solution of **4** at -78 °C. The resulting mixture was allowed to warm to RT overnight. The pale orange solution was filtered through celite, concentrated, and washed with a small amount of pentane (5 x 2 ml) to afford analytically pure  $[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{H}$  (1.4 g, 81 % overall yield).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 7.68 (d,  $J = 7.5$  Hz, 2H), 7.40 (m, 6H), 7.30 (br, 2H), 7.10-6.99 (m, 10H), 6.93 (t,  $J = 8.0$  Hz, 1H), 6.84 (dd,  $J = 7.5$  Hz, 2.5 Hz, 1H), 1.97 (s, 12H), 1.90 (s, 6H), 1.51 (s, 12H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 142.0 (d,  $J = 3.3$  Hz), 141.6, 141.24, 141.16, 141.08, 136.4, 135.5 (d,  $J = 12.9$  Hz), 135.0 (d,  $J = 14.1$  Hz), 131.4, 131.3 (d,  $J = 19.2$  Hz), 127.0, 126.7, 125.9, 125.7 (d,  $J = 6.5$  Hz), 125.5, 125.3, 47.4, 41.4, 33.7, 27.8.  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): -20.5 (d,  $J = 27$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): -9.6. IR (KBr pellet,  $\text{cm}^{-1}$ ): 2220 ( $\nu[\text{Si-H}]$ ). Anal. Calcd for  $\text{C}_{50}\text{H}_{53}\text{SiPS}_2$ : C, 77.28; H, 6.87; N, 0.00. Found: C, 76.95; H, 6.72; N, 0.00.

### Synthesis of $[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{FeMe}$

$[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{H}$  (0.50 g, 0.64 mmol) and  $\text{FeCl}_2$  (98 mg, 0.77 mmol) was dissolved in 80 ml THF and the flask was cooled to -78 °C.  $\text{MeMgCl}$  (0.52 ml, 1.5 mmol, 3M soln.) diluted with 10 ml THF was added dropwise to the solution via cannula. A color change to dark red took place. The flask was allowed to warm to room temperature slowly overnight. Volatiles were removed, and the mixture was washed with 40 ml pentane, 15 ml  $\text{Et}_2\text{O}$ . The product was extracted into benzene and filtered through celite. The red solution was concentrated. The washing/extraction procedure was repeated once more and the red solution concentrated to yield analytically pure  $[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{FeMe}$  (0.30 g, 57 %).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 8.5, 5.5, 4.6, 4.3, -0.4, -0.6. (Evans' method,  $\text{C}_6\text{D}_6$ , 23 °C) = 3.2  $\mu_{\text{B}}$ . UV-VIS (in THF): (nm,  $\epsilon$  [ $\text{mol}^{-1} \text{cm}^{-1}$ ]), 405

(5400, sh), 485 (2700, sh), 820 (40). Anal. Calcd for  $C_{51}H_{55}SiPS_2Fe$ : C, 72.32; H, 6.54; N, 0.00. Found: C, 73.01; H, 6.65; N, 0.00.

### Synthesis of $\{[SiP^{Ph}S^{Ad}_2]Fe\}_2(N_2)\}BAr^F_4$ (15).

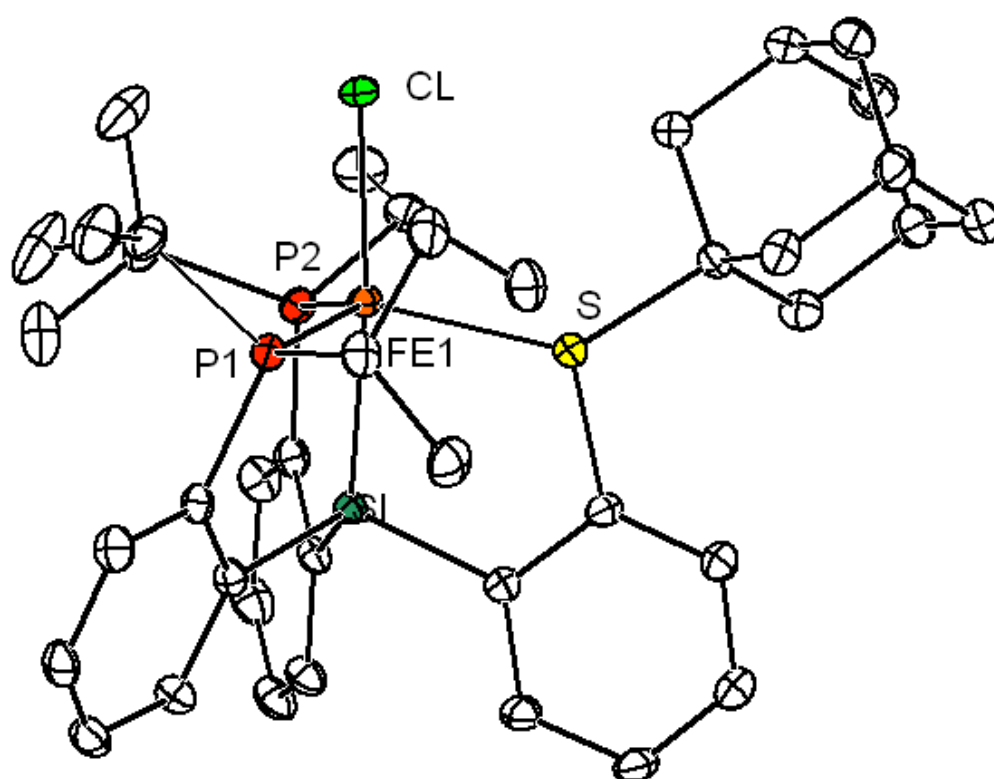
$[SiP^{Ph}S^{Ad}_2]FeMe$  (41 mg, 0.048 mmol) was dissolved in a 1:1 mixture of  $C_6H_6$ :  $Et_2O$  in a vial and placed inside the glovebox cold well (dry ice/acetone).  $HBar^F_4 \cdot 2Et_2O$  (49 mg, 0.048 mmol) was dissolved in 1.5 ml  $Et_2O$  and also cooled. The  $HBar^F_4 \cdot 2Et_2O$  solution was added dropwise to the solution of  $[SiP^{Ph}S^{Ad}_2]FeMe$ . The solution was stirred for 30 min. inside the cold well, and then stirred at room temperature for 10 min.  $Et_2O$  (5 ml) was added and the solution was replaced inside the well.  $Cr(C_6H_6)_2$  (5.0 mg, 0.024 mmol) was added in one portion, and the mixture was stirred inside the cold well for 1.5 hr. The red solution was subsequently stirred at room temperature for 3 hr., and the volatiles were removed. The product was extracted into a mixture of 1:1 pentane : benzene, and separated from the yellow solids by filtration through celite. The solution was concentrated, and the extraction procedure was repeated once more. Slow evaporation of a solution of 4:1  $Et_2O$  : at  $-35\text{ }^\circ\text{C}$  resulted in formation of small microcrystals that analyzed for  $\{[SiP^{Ph}S^{Ad}_2]Fe\}_2(N_2)\}BAr^F_4 \cdot MeCy$  (41 mg, 64 %).  $^1H$  NMR ( $C_6D_6$ ,  $\delta$ ): 15.5, 10.2, 9.7, 8.5, 8.1, 6.2, 5.4, 5.2, 4.5, 3.1, 2.7, 2.0, 0.5, -0.1, -0.6, -0.9, -2.9, -3.2, -3.4, -4.1, -4.6, -11.1. (Evans' method,  $C_6D_6$ ,  $23\text{ }^\circ\text{C}$ ) =  $4.5\text{ }\mu_B$ . IR (KBr pellet,  $cm^{-1}$ ): 1898 ( $\nu[N_2]$ ). UV-VIS (in  $Et_2O$ ): (nm,  $\epsilon$  [ $mol^{-1}\text{ cm}^{-1}$ ]), 500 (5100, sh), 601 (1790, sh), 921 (1650). NIR (in  $Et_2O$ ): (nm,  $\epsilon$  [ $mol^{-1}\text{ cm}^{-1}$ ]), 1310 (2330). Anal. Calcd for  $C_{139}H_{120}N_2BF_{24}Si_2P_2S_4Fe_2$ : C, 62.92; H, 4.93; N, 1.06. Found: C, 63.32; H, 5.38; N, 0.88.

**Table 1.** Crystal data and structure refinement for  $[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{FeCl}$ 

Identification code	ayt03	
Empirical formula	C <sub>40</sub> H <sub>55</sub> Cl Fe P <sub>2</sub> S Si	
Formula weight	749.23	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pca2(1)	
Unit cell dimensions	a = 15.5224(6) Å	a = 90°.
	b = 14.0036(5) Å	b = 90°.
	c = 17.1234(6) Å	g = 90°.
Volume	3722.1(2) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.337 Mg/m <sup>3</sup>	
Absorption coefficient	0.680 mm <sup>-1</sup>	
F(000)	1592	
Crystal size	2.33 x 1.55 x 1.48 mm <sup>3</sup>	
Theta range for data collection	2.29 to 33.13°.	
Index ranges	-22 ≤ h ≤ 23, -20 ≤ k ≤ 16, -24 ≤ l ≤ 25	
Reflections collected	57143	
Independent reflections	9936 [R(int) = 0.0400]	
Completeness to theta = 33.13°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4328 and 0.3004	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	12714 / 1 / 423	
Goodness-of-fit on F <sup>2</sup>	1.021	
Final R indices [I > 2σ(I)]	R1 = 0.0351, wR2 = 0.0853	
R indices (all data)	R1 = 0.0406, wR2 = 0.0887	
Largest diff. peak and hole	1.489 and -0.539 e.Å <sup>-3</sup>	



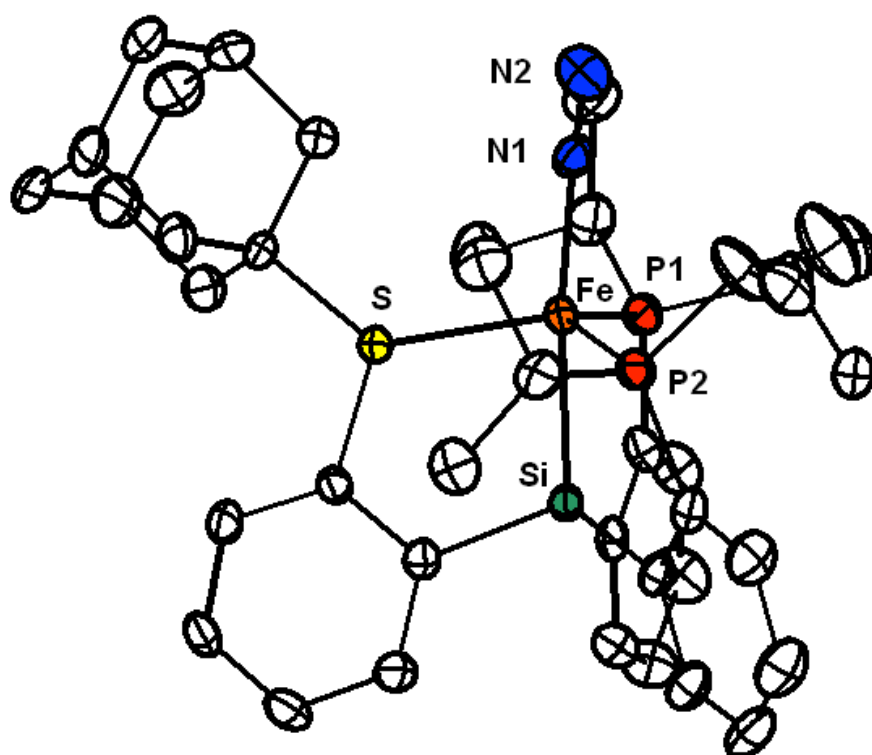
Figure 1. Solid-state structure of  $[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{FeCl}$ .



**Table 2.** Crystal data and structure refinement for  $\{[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (**10**).

Identification code	ayt05	
Empirical formula	C72 H67 B Cl F24 Fe N2 P2 S Si	
Formula weight	1640.48	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 16.5522(7) Å	a = 90°.
	b = 15.7697(6) Å	b = 102.447(2)°.
	c = 28.0672(11) Å	g = 90°.
Volume	7154.0(5) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.523 Mg/m <sup>3</sup>	
Absorption coefficient	0.446 mm <sup>-1</sup>	
F(000)	3348	
Crystal size	1.86 x 1.55 x 0.74 mm <sup>3</sup>	
Theta range for data collection	2.50 to 24.69°.	
Index ranges	-20 ≤ h ≤ 20, -19 ≤ k ≤ 19, -35 ≤ l ≤ 35	
Reflections collected	78211	
Independent reflections	14505 [R(int) = 0.0573]	
Completeness to theta = 24.69°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7336 and 0.4907	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	14505 / 120 / 1039	
Goodness-of-fit on F <sup>2</sup>	1.022	
Final R indices [I > 2σ(I)]	R1 = 0.0547, wR2 = 0.1339	
R indices (all data)	R1 = 0.0835, wR2 = 0.1503	
Largest diff. peak and hole	1.249 and -0.746 e.Å <sup>-3</sup>	

Figure 2. Solid-state structure of  $\{[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (10).

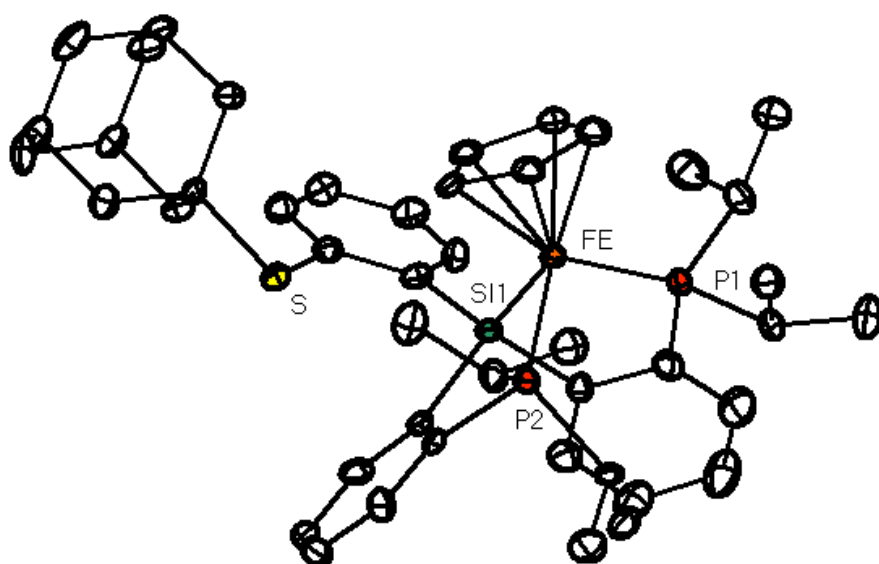


$\text{BAr}^{\text{F}}_4^-$  anion excluded from figure.

**Table 3.** Crystal data and structure refinement for  $\{[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{Cp})\}$ 

Identification code	ayt06	
Empirical formula	C <sub>96</sub> H <sub>120</sub> Fe <sub>2</sub> O P <sub>4</sub> S <sub>2</sub> Si <sub>4</sub>	
Formula weight	1701.98	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I-4	
Unit cell dimensions	a = 27.2245(6) Å	a = 90°.
	b = 27.2245(6) Å	b = 90°.
	c = 13.8202(4) Å	g = 90°.
Volume	10243.2(4) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.104 Mg/m <sup>3</sup>	
Absorption coefficient	0.474 mm <sup>-1</sup>	
F(000)	3616	
Crystal size	1.78 x 1.41 x 1.11 mm <sup>3</sup>	
Theta range for data collection	2.37 to 26.85°.	
Index ranges	-38 ≤ h ≤ 38, -38 ≤ k ≤ 38, -19 ≤ l ≤ 19	
Reflections collected	78637	
Independent reflections	14977 [R(int) = 0.0639]	
Completeness to theta = 26.85°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6213 and 0.4859	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	14977 / 99 / 533	
Goodness-of-fit on F <sup>2</sup>	1.077	
Final R indices [I > 2σ(I)]	R1 = 0.0498, wR2 = 0.1376	
R indices (all data)	R1 = 0.0612, wR2 = 0.1455	
Largest diff. peak and hole	1.316 and -0.475 e.Å <sup>-3</sup>	

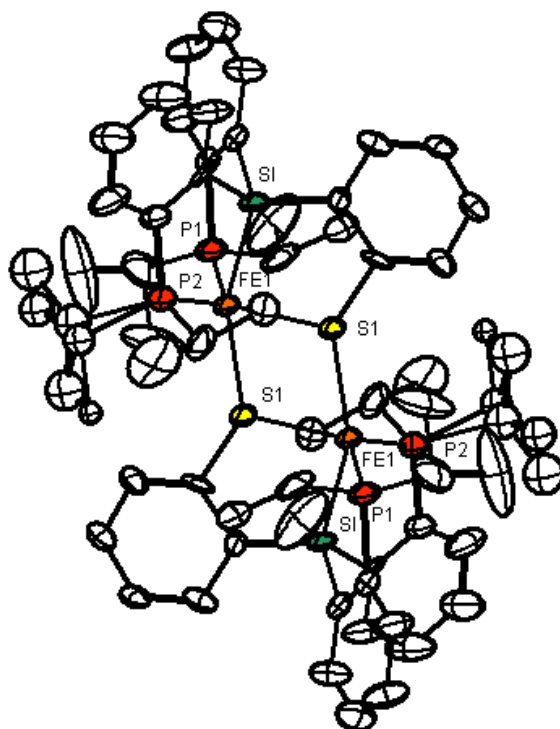
**Figure 3.** Solid-state structure of  $[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{Cp})$ .



**Table 4.** Crystal data and structure refinement for  $\{[\text{SiP}^{\text{Pr}}_2\text{S}]\text{Fe}\}_2$ .

Identification code	ayt072	
Empirical formula	C70 H104 Fe2 P4 S2 Si2	
Formula weight	1301.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.2792(14) Å	a = 90°.
	b = 18.8853(18) Å	b = 90.993°.
	c = 14.6011(19) Å	g = 90°.
Volume	3385.4(7) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.277 Mg/m <sup>3</sup>	
Absorption coefficient	0.660 mm <sup>-1</sup>	
F(000)	1392	
Crystal size	0.26 x 0.11 x 0.11 mm <sup>3</sup>	
Theta range for data collection	2.40 to 23.70°.	
Index ranges	-15 ≤ h ≤ 14, -23 ≤ k ≤ 23, -18 ≤ l ≤ 16	
Reflections collected	47126	
Independent reflections	6631 [R(int) = 0.2393]	
Completeness to theta = 23.70°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8471 and 0.9309	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	6631 / 47 / 348	
Goodness-of-fit on F <sup>2</sup>	1.613	
Final R indices [I > 2σ(I)]	R1 = 0.1426, wR2 = 0.3305	
R indices (all data)	R1 = 0.2502, wR2 = 0.3619	
Largest diff. peak and hole	1.881 and -1.043 e.Å <sup>-3</sup>	

**Figure 4.** Solid-state structure of  $\{[\text{SiP}^{i\text{Pr}}_2\text{S}]\text{Fe}\}_2$ .



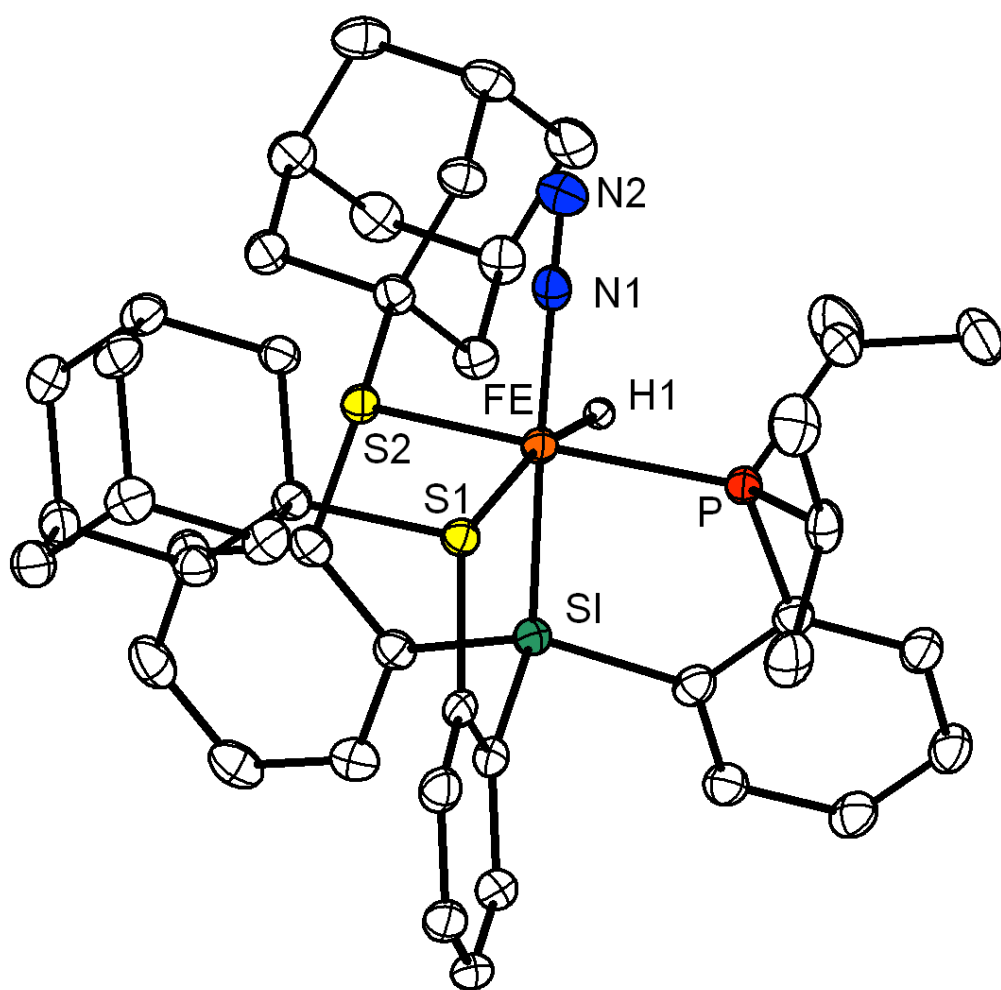
The crystal for this data set was obtained from a reaction of  $\{[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  with  $\text{KC}_8$ . The reaction gives multiple products but a crystal was grown from the reaction mixture and the data collected. The crystal was of poor quality, and only connectivity could be determined. We nevertheless include the data in the supporting information as we find it helpful in viewing the molecular structure.

**Table 5.** Crystal data and structure refinement for [SiP<sup>iPr</sup>S<sup>Ad</sup><sub>2</sub>]**Fe(H)(N<sub>2</sub>) (13).**

Identification code	ayt09
Empirical formula	C <sub>58</sub> H <sub>80</sub> Fe N <sub>2</sub> P S <sub>2</sub> Si
Formula weight	984.27
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 11.0806(5) Å      a = 93.7520(10)°. b = 13.0186(6) Å      b = 105.5990(10)°. c = 19.1039(10) Å      g = 91.5850(10)°.
Volume	2645.8(2) Å <sup>3</sup>
Z	2
Density (calculated)	1.235 Mg/m <sup>3</sup>
Absorption coefficient	0.456 mm <sup>-1</sup>
F(000)	1058
Crystal size	0.21 x 0.19 x 0.11 mm <sup>3</sup>
Theta range for data collection	2.22 to 31.45°.
Index ranges	-15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -27 ≤ l ≤ 26
Reflections collected	58590
Independent reflections	16055 [R(int) = 0.0660]
Completeness to theta = 31.45°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9104 and 0.9516
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	16055 / 81 / 654
Goodness-of-fit on F <sup>2</sup>	1.161
Final R indices [I > 2σ(I)]	R1 = 0.0579, wR2 = 0.1453
R indices (all data)	R1 = 0.0926, wR2 = 0.1598
Largest diff. peak and hole	0.931 and -0.418 e.Å <sup>-3</sup>

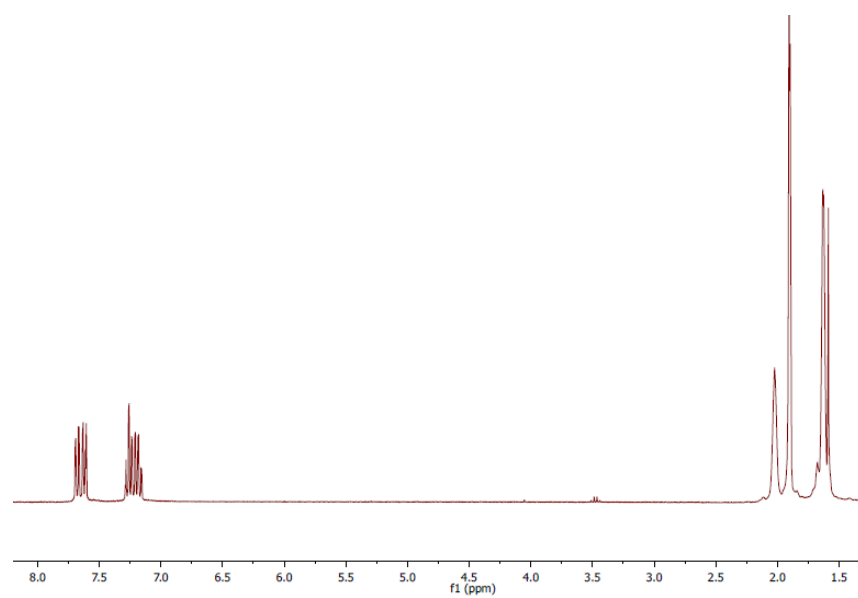


**Figure 5.** Solid-state structure of  $[\text{SiP}^{i\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}(\text{H})(\text{N}_2)$  (**13**).

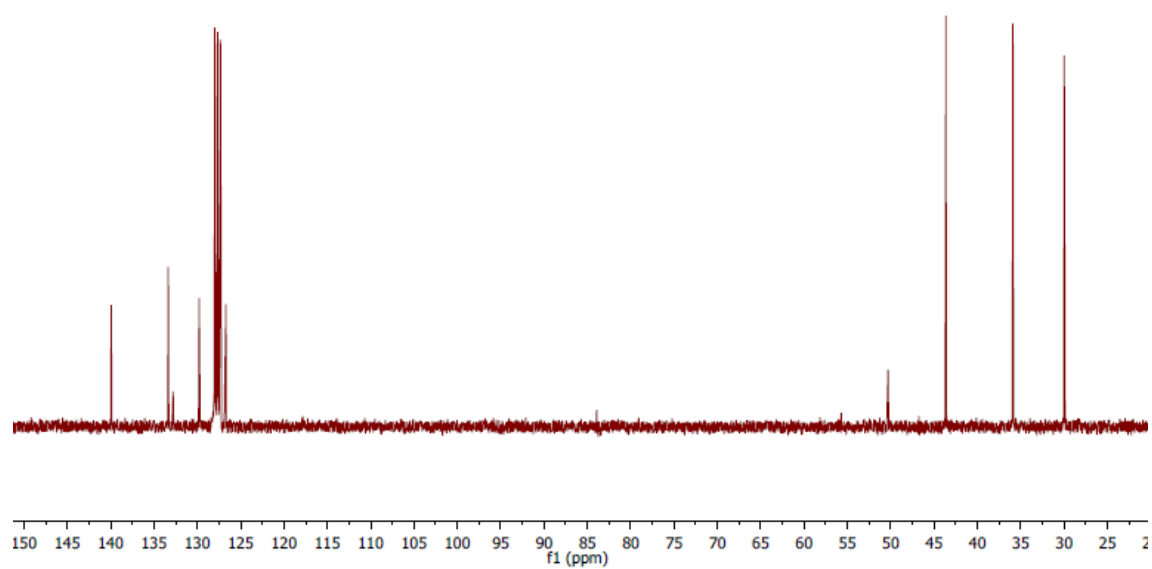


**Figure 6. NMR spectra of 2-Ad(C<sub>6</sub>H<sub>4</sub>Br) (2).**

**<sup>1</sup>H**

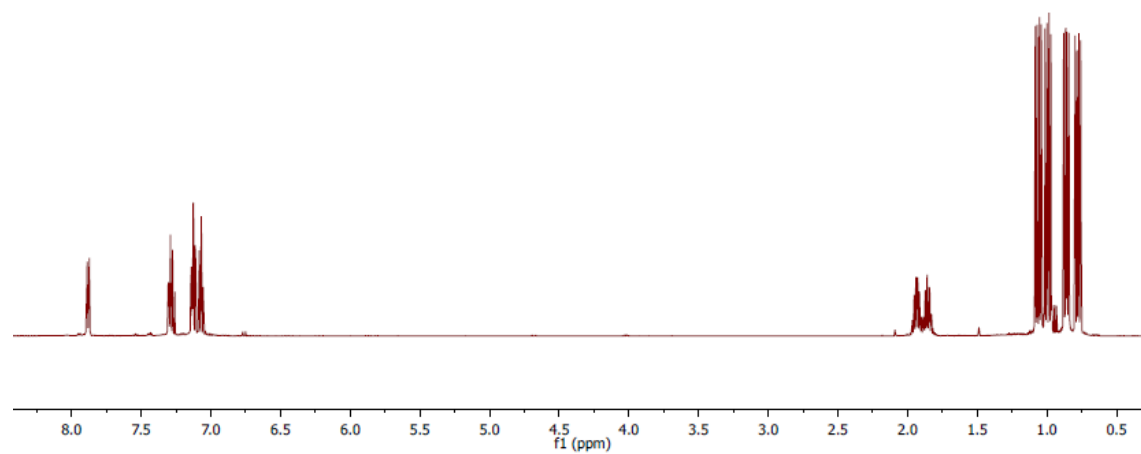


**<sup>13</sup>C{<sup>1</sup>H}**

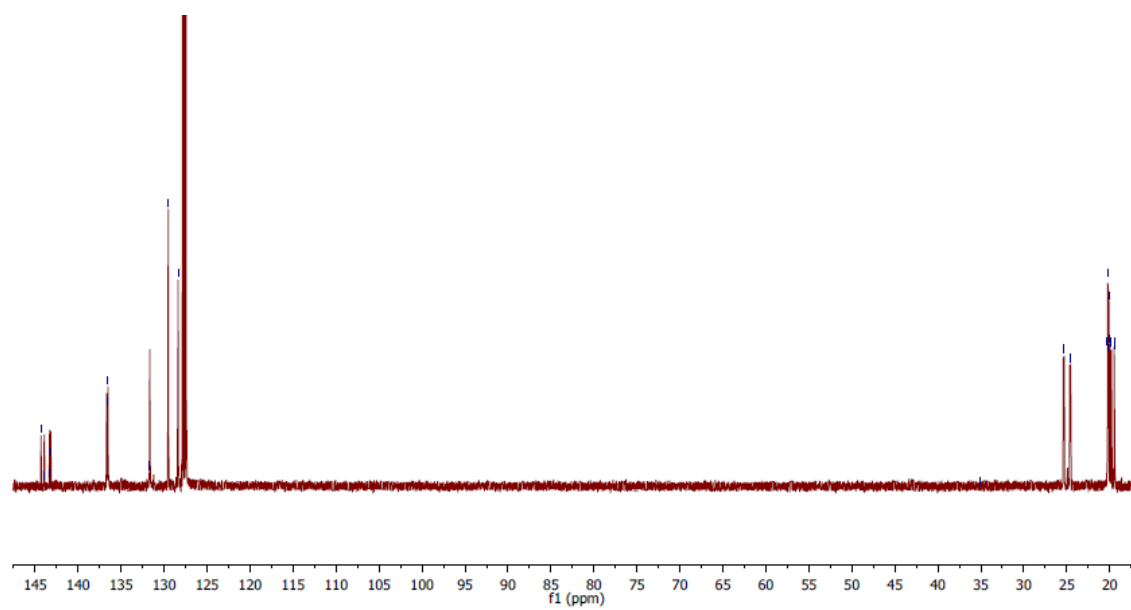


**Figure 7. NMR spectra of (2-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Si(H)(Cl) (3).**

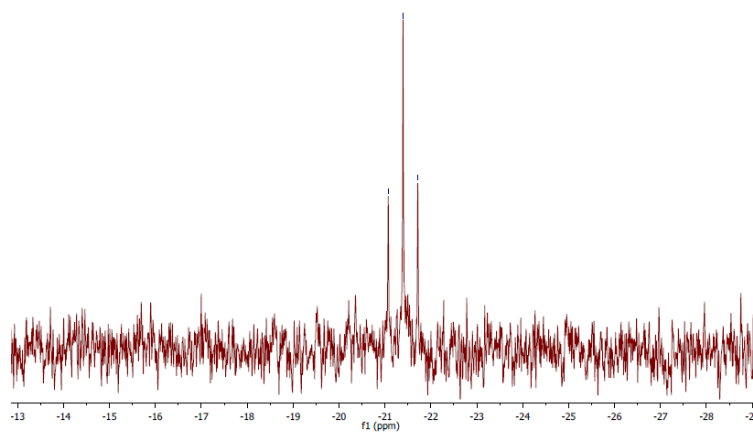
<sup>1</sup>H



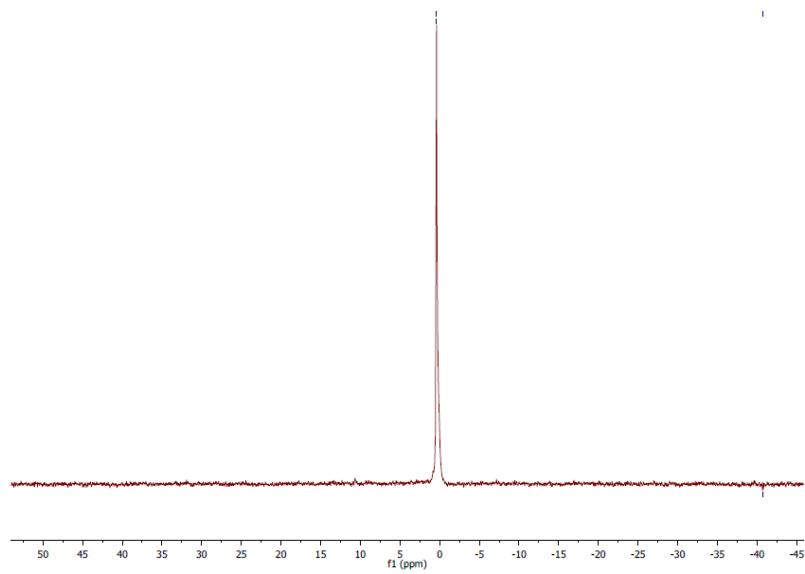
<sup>13</sup>C{<sup>1</sup>H}



$^{29}\text{Si}\{^1\text{H}\}$

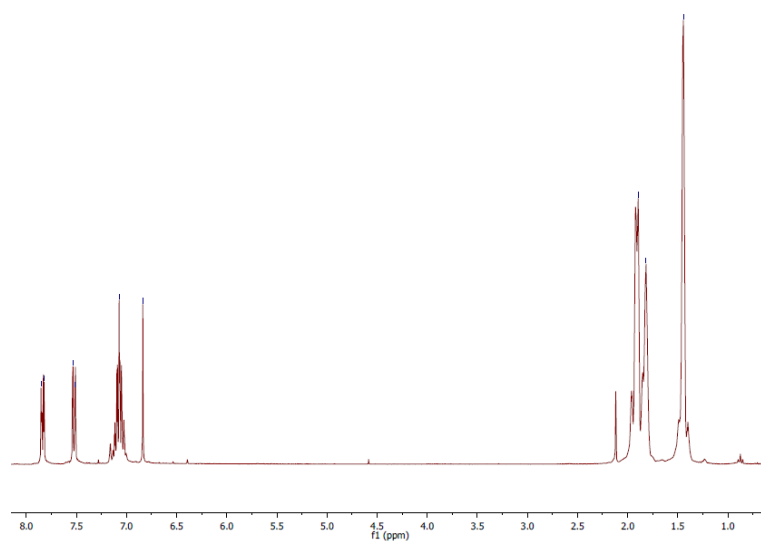


$^{31}\text{P}\{^1\text{H}\}$

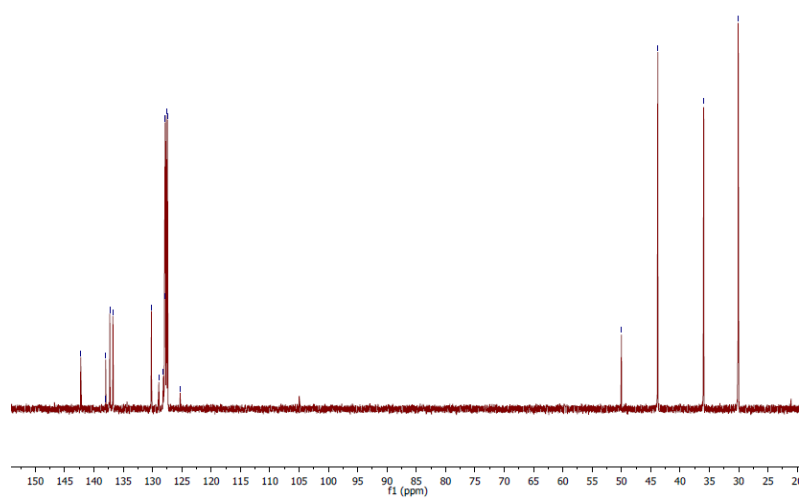


**Figure 8. NMR spectra of (AdSC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Si(H)(Cl) (4).**

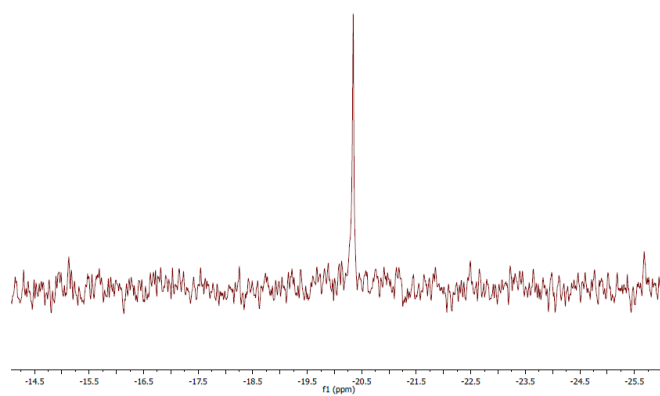
**<sup>1</sup>H**



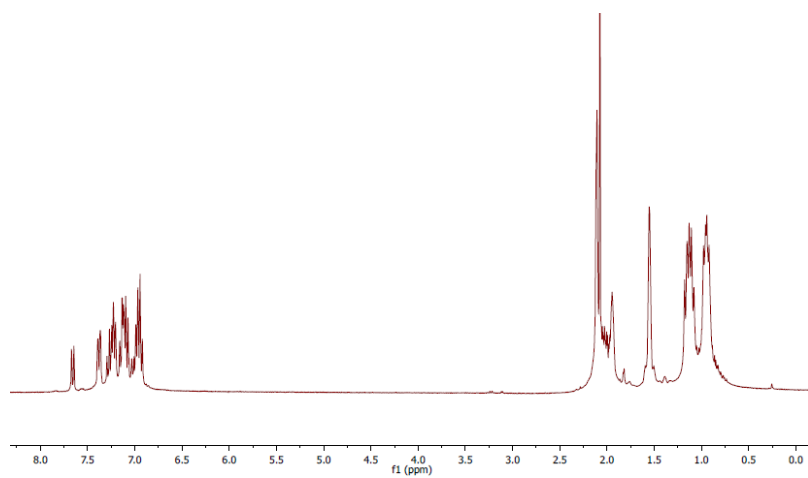
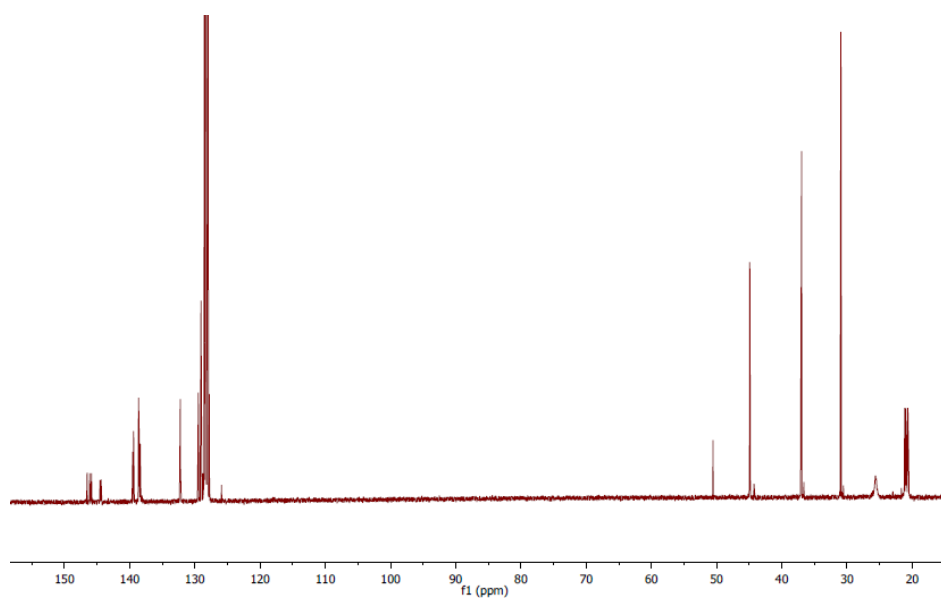
**<sup>13</sup>C{<sup>1</sup>H}**



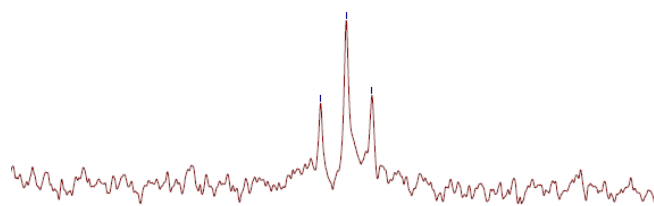
**<sup>29</sup>Si{<sup>1</sup>H}**



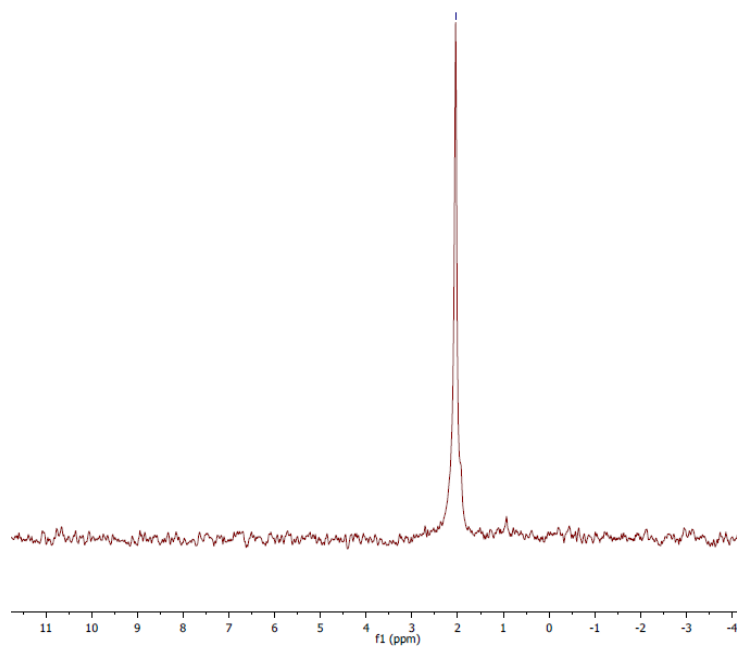
**Figure 9. NMR spectra of [SiP<sup>i</sup>Pr<sub>2</sub>S<sup>Ad</sup>]H (5).**

 $^1\text{H}$  $^{13}\text{C}\{^1\text{H}\}$ 

$^{29}\text{Si}\{\text{}^1\text{H}\}$

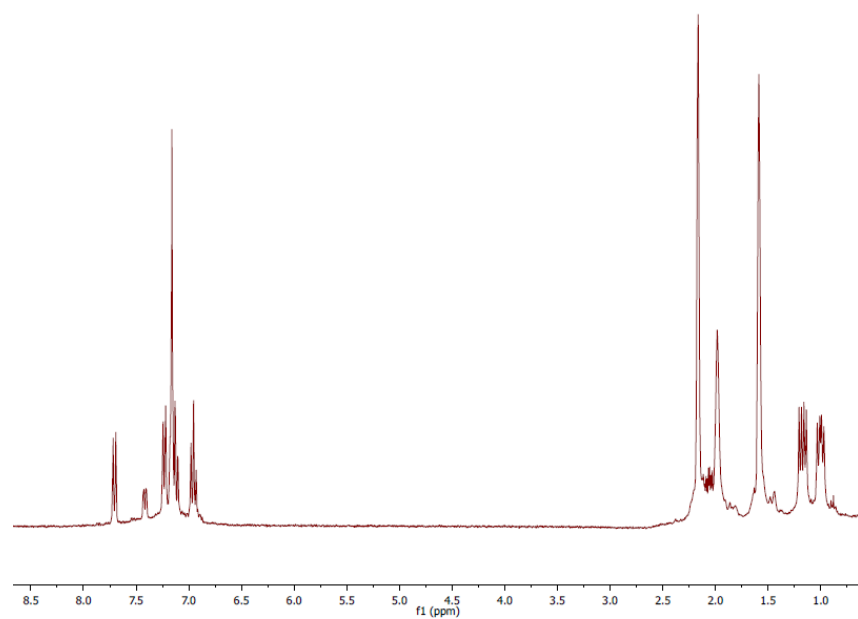


$^{31}\text{P}\{\text{}^1\text{H}\}$

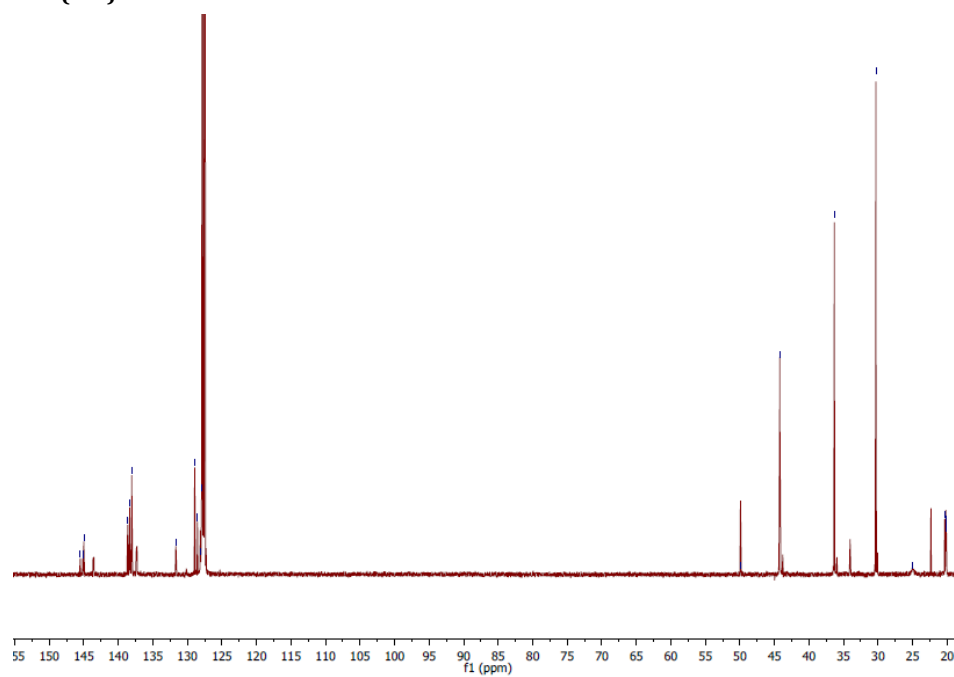


**Figure 10. NMR spectra of  $[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}_2]\text{H}$  (6).**

$^1\text{H}$

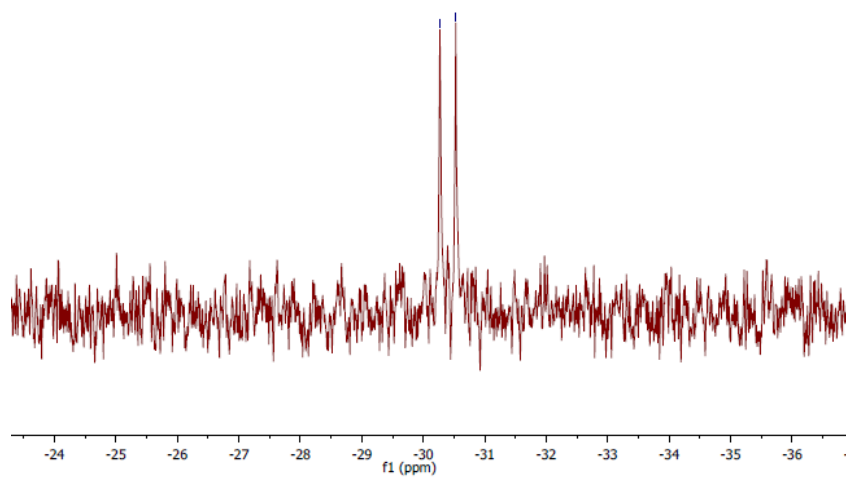


$^{13}\text{C}\{^1\text{H}\}$

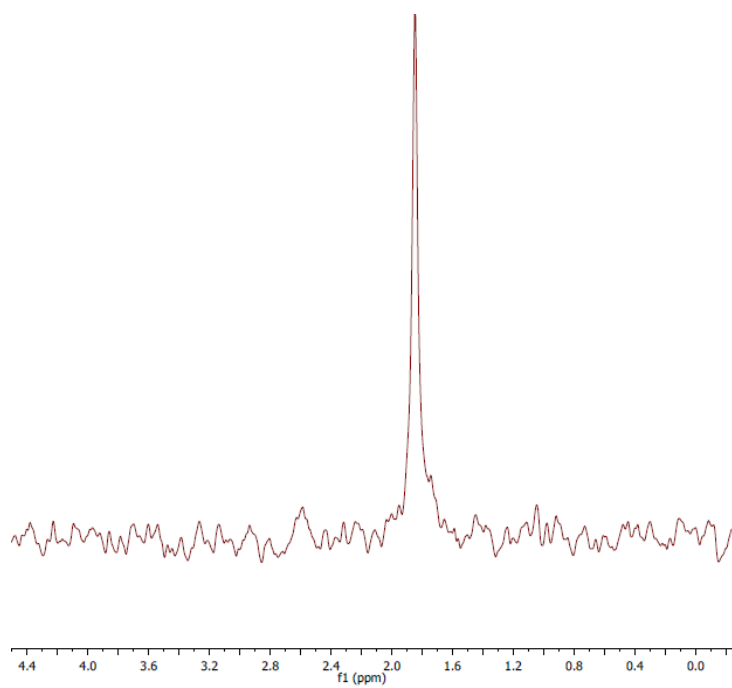




$^{29}\text{Si}\{^1\text{H}\}$

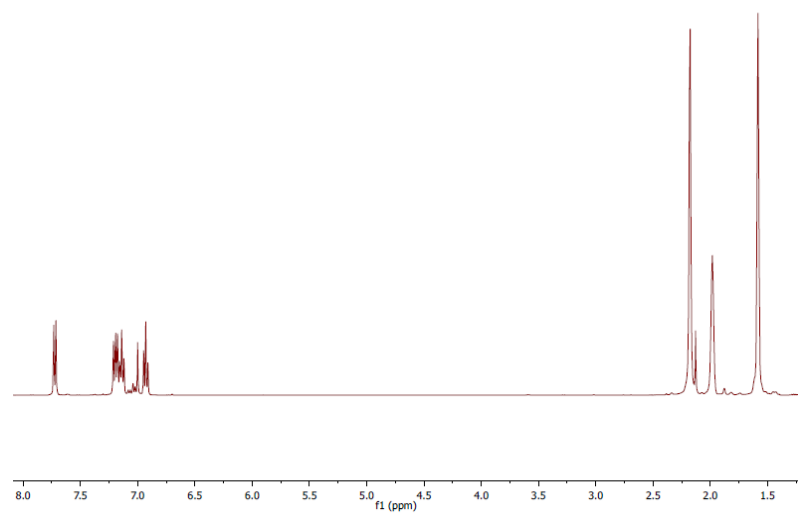


$^{31}\text{P}\{^1\text{H}\}$

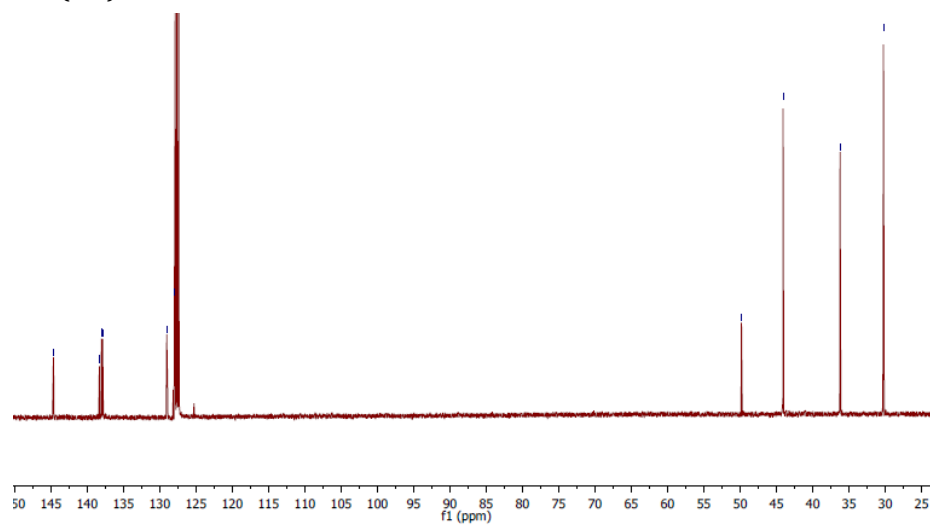


**Figure 11. NMR spectra of [SiS<sup>Ad</sup><sub>3</sub>]H (7).**

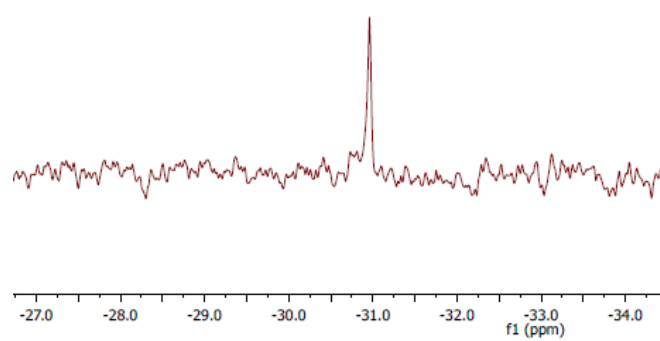
**<sup>1</sup>H**



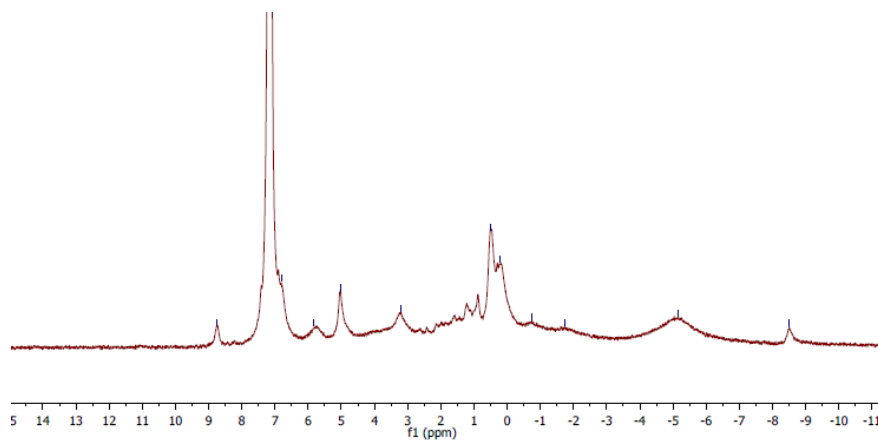
**<sup>13</sup>C{<sup>1</sup>H}**



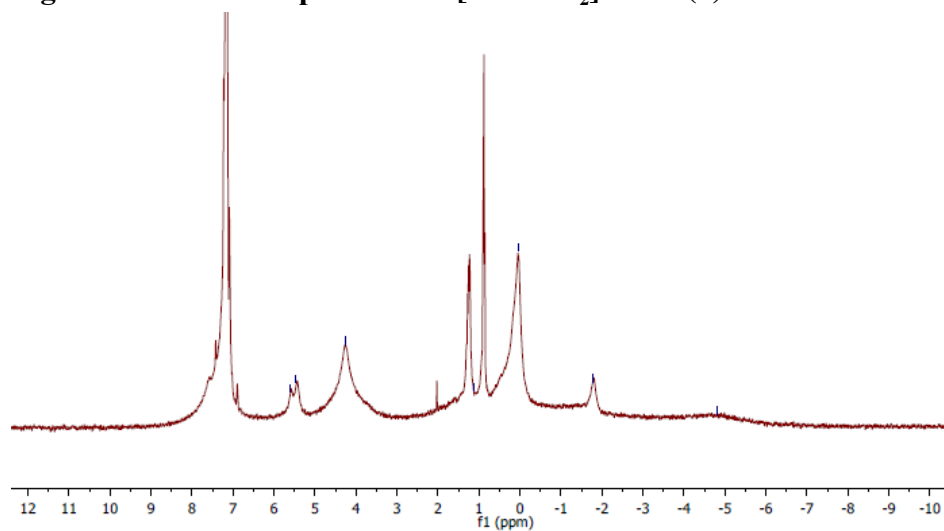
**<sup>29</sup>Si{<sup>1</sup>H}**



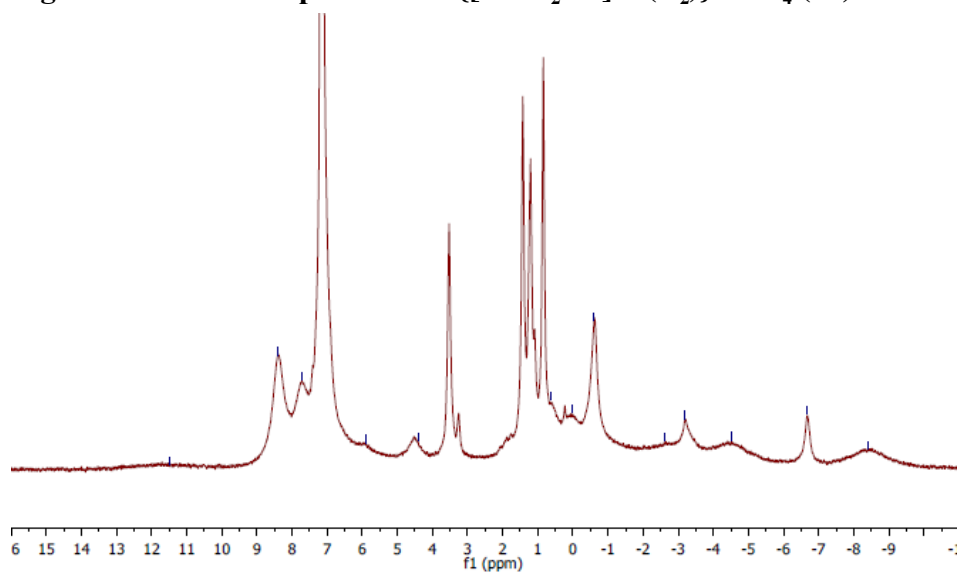
**Figure 12.**  $^1\text{H}$  NMR spectrum of  $[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{FeMe}$  (**8**).



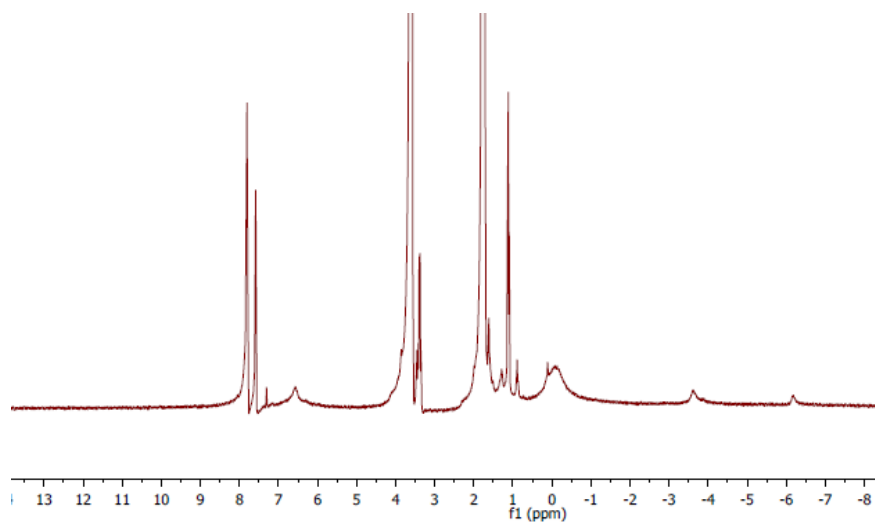
**Figure 13.**  $^1\text{H}$  NMR spectrum of  $[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}_2]\text{FeMe}$  (**9**).



**Figure 14.**  $^1\text{H}$  NMR spectrum of  $\{[\text{SiP}^{\text{iPr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (**10**).

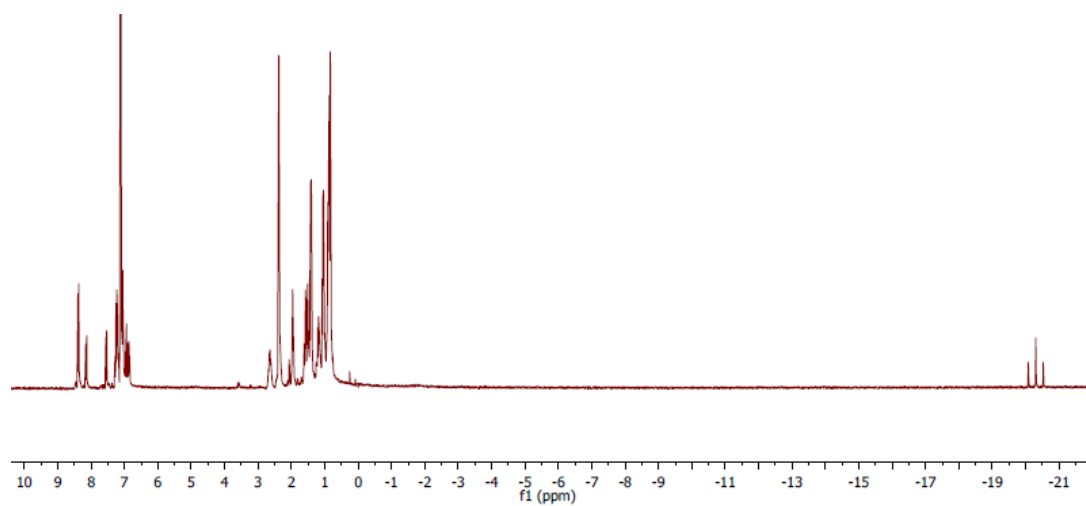


**Figure 15.  $^1\text{H}$  NMR spectrum of  $\{[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{L})\}\text{BAr}^{\text{F}}_4$  (11).**

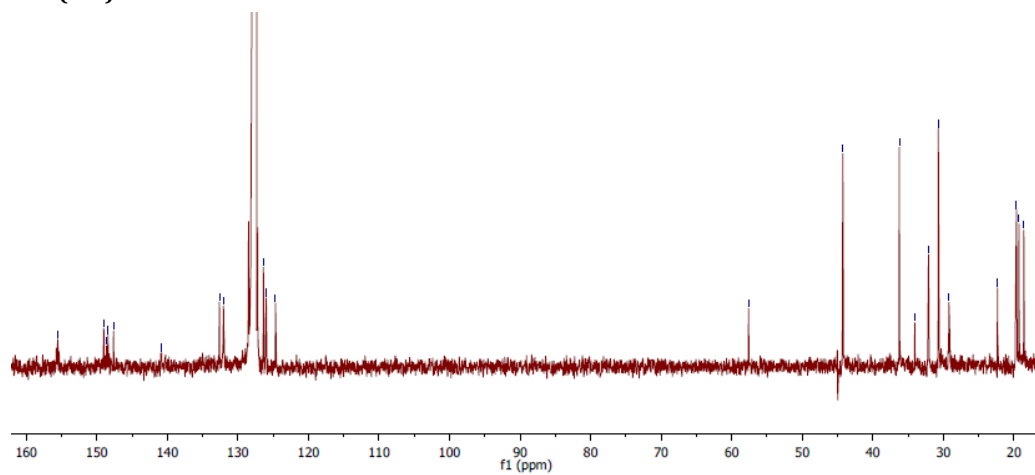


**Figure 16. NMR spectra of  $[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{Fe}(\text{H})(\text{N}_2)$  (12).**

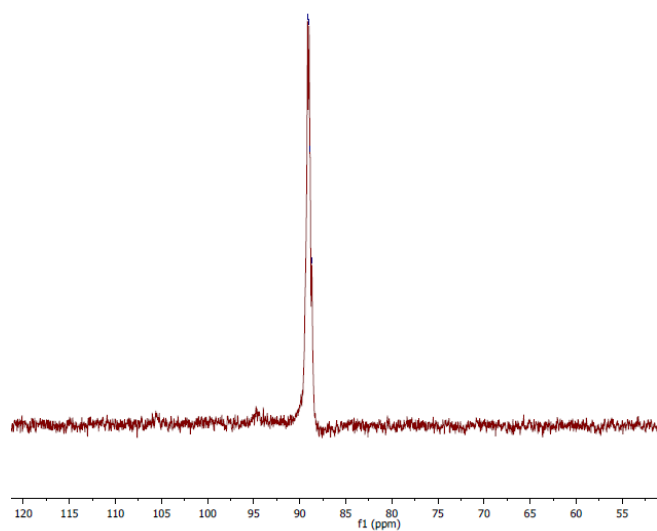
$^1\text{H}$



$^{13}\text{C}\{^1\text{H}\}$

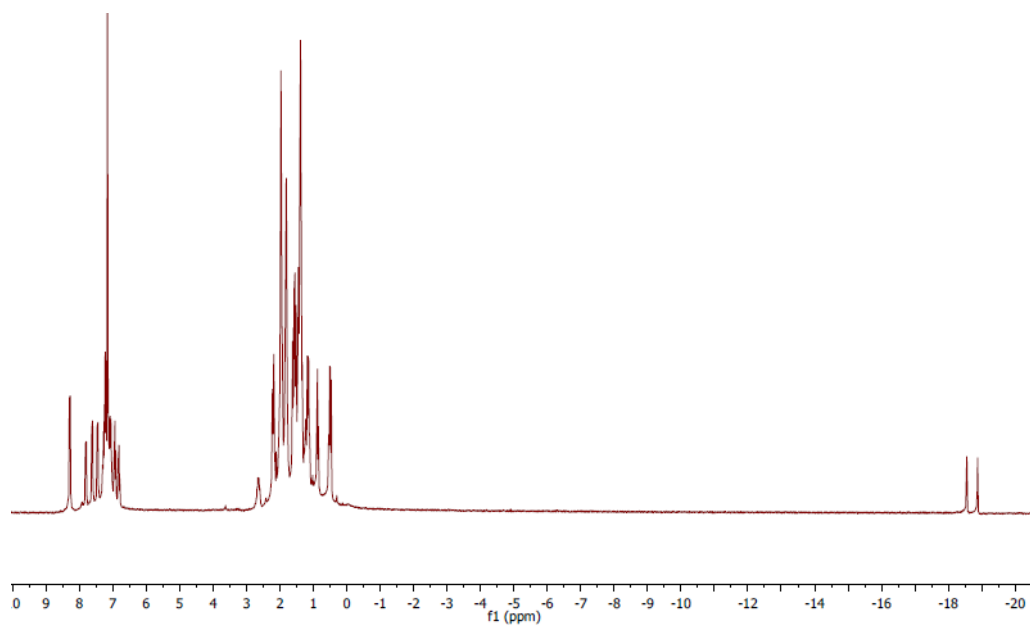


$^{31}\text{P}\{^1\text{H}\}$

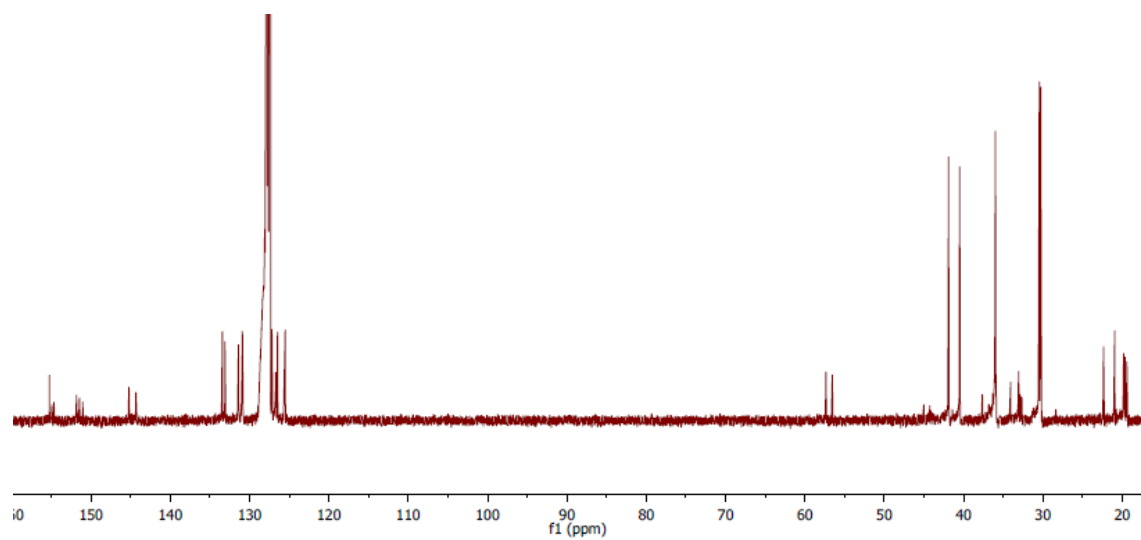


**Figure 17. NMR spectra of  $[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}_2]\text{Fe}(\text{H})(\text{N}_2)$  (13).**

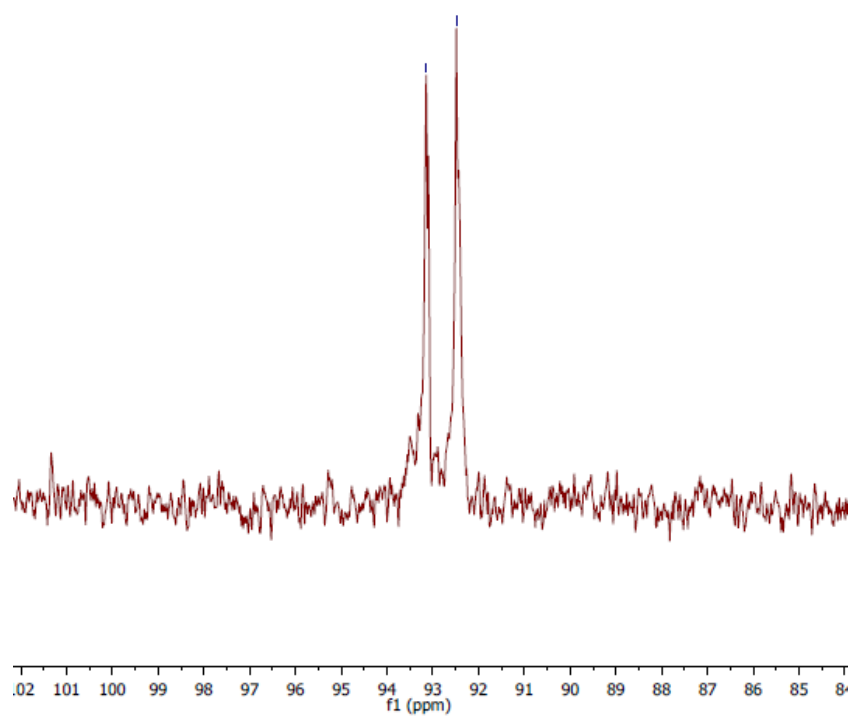
$^1\text{H}$



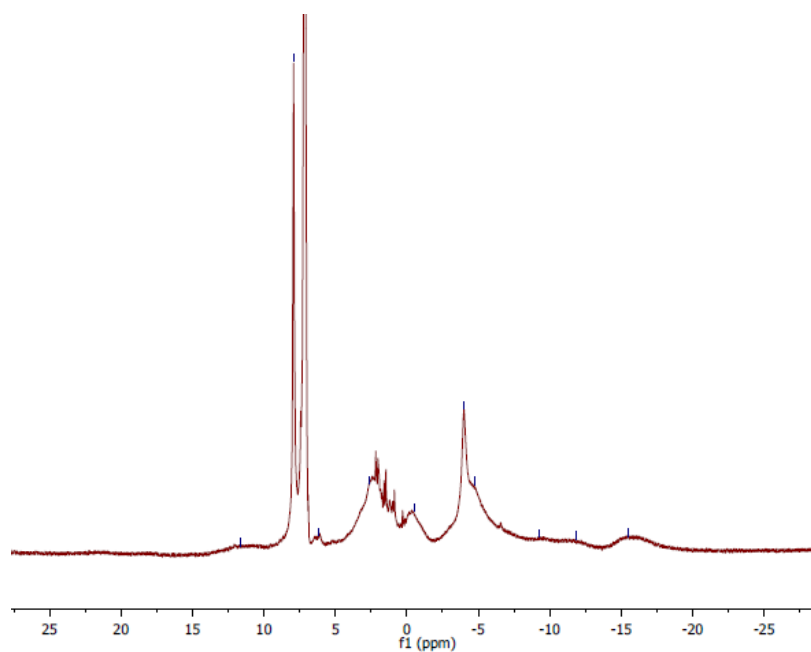
$^{13}\text{C}\{^1\text{H}\}$



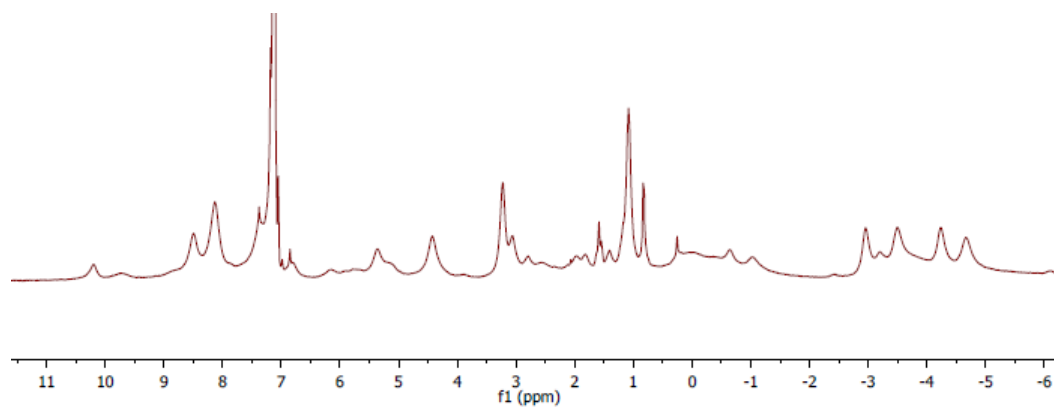
$^{31}\text{P}\{^1\text{H}\}$



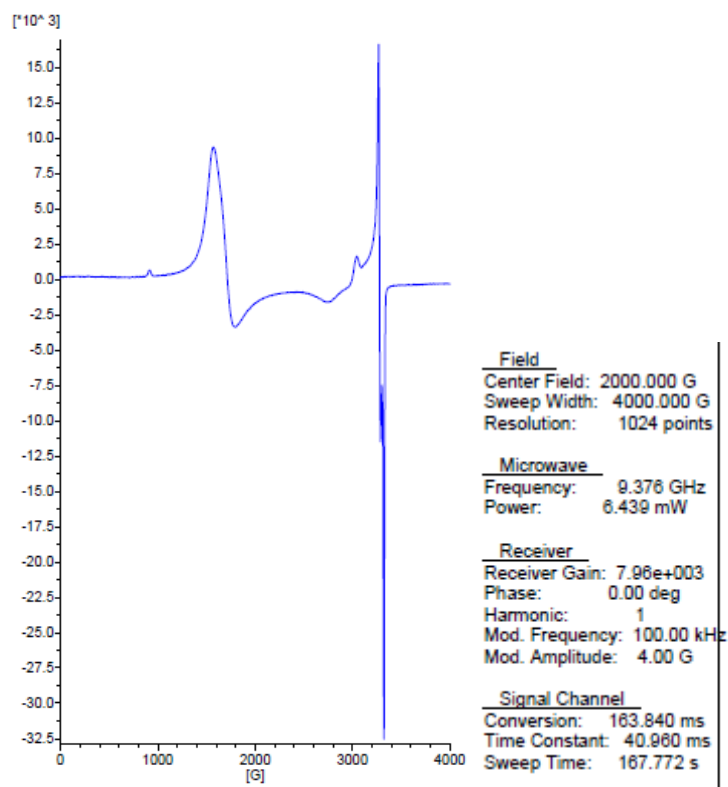
**Figure 18.**  $^1\text{H}$  NMR spectrum of  $\{[\text{SiP}^{\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (**14**).



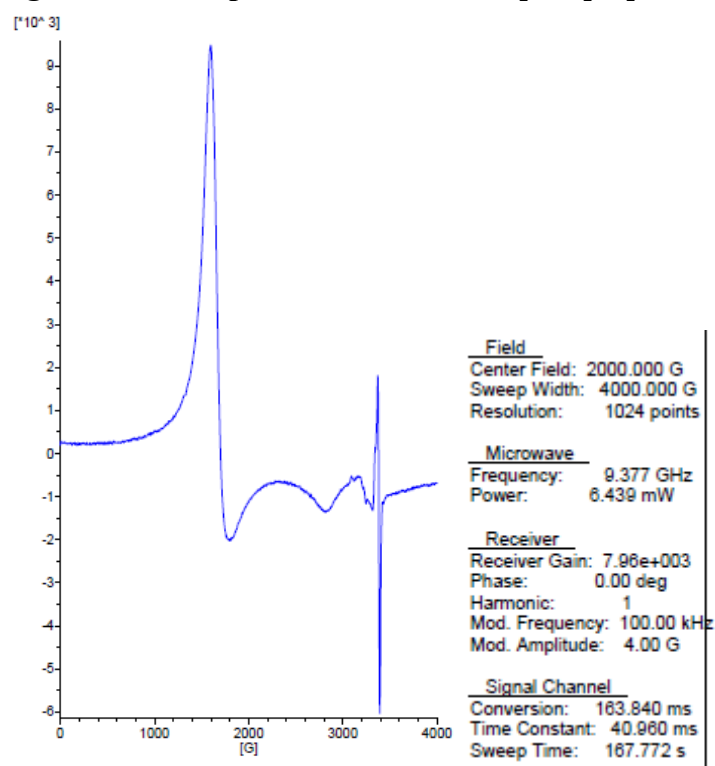
**Figure 19.**  $^1\text{H}$  NMR spectrum of  $\{[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (**15**).



**Figure 20. EPR spectrum of  $\{[\text{SiP}^{\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (14). (20K in 2-MeTHF)**

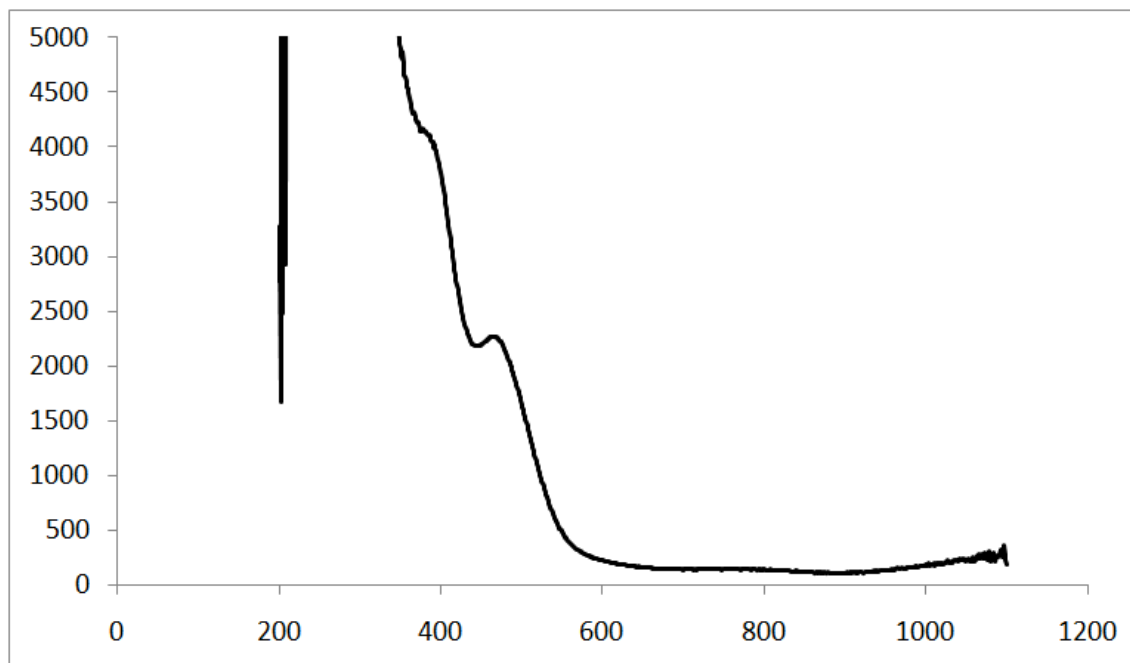


**Figure 21. EPR spectrum of  $\{[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{Fe}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (15). (20K in 2-MeTHF)**

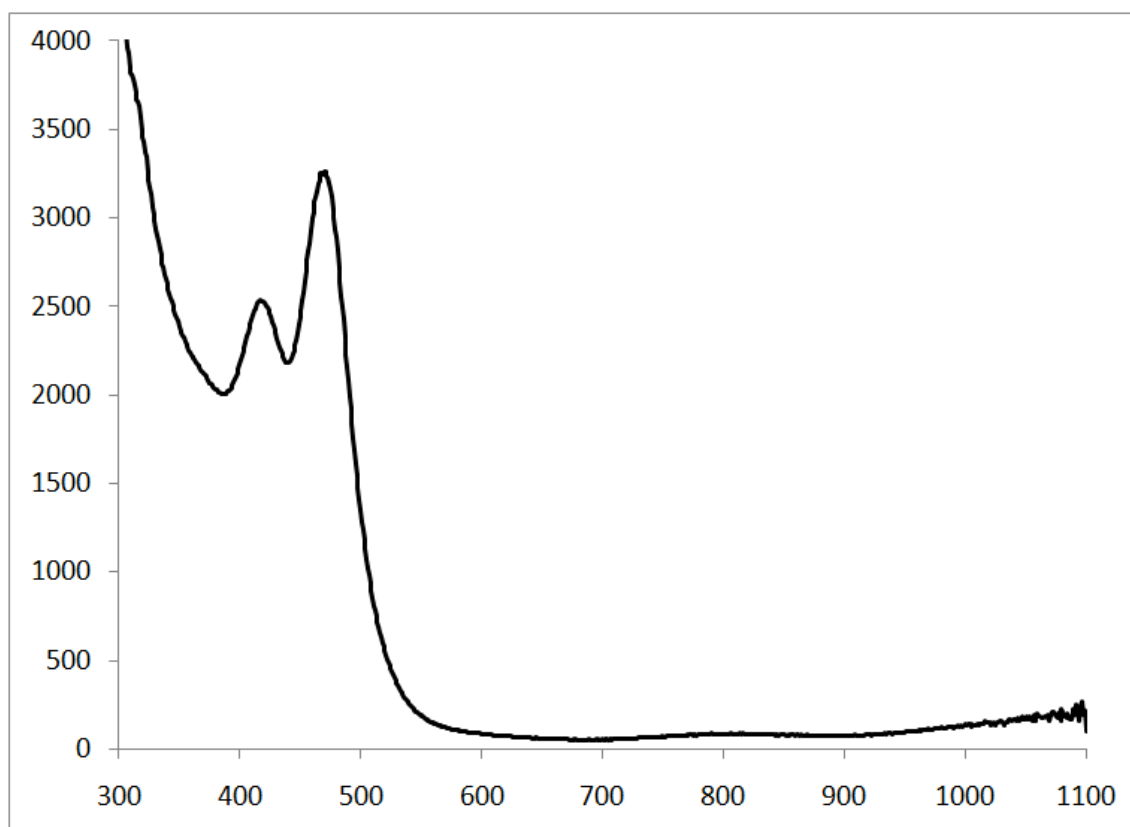




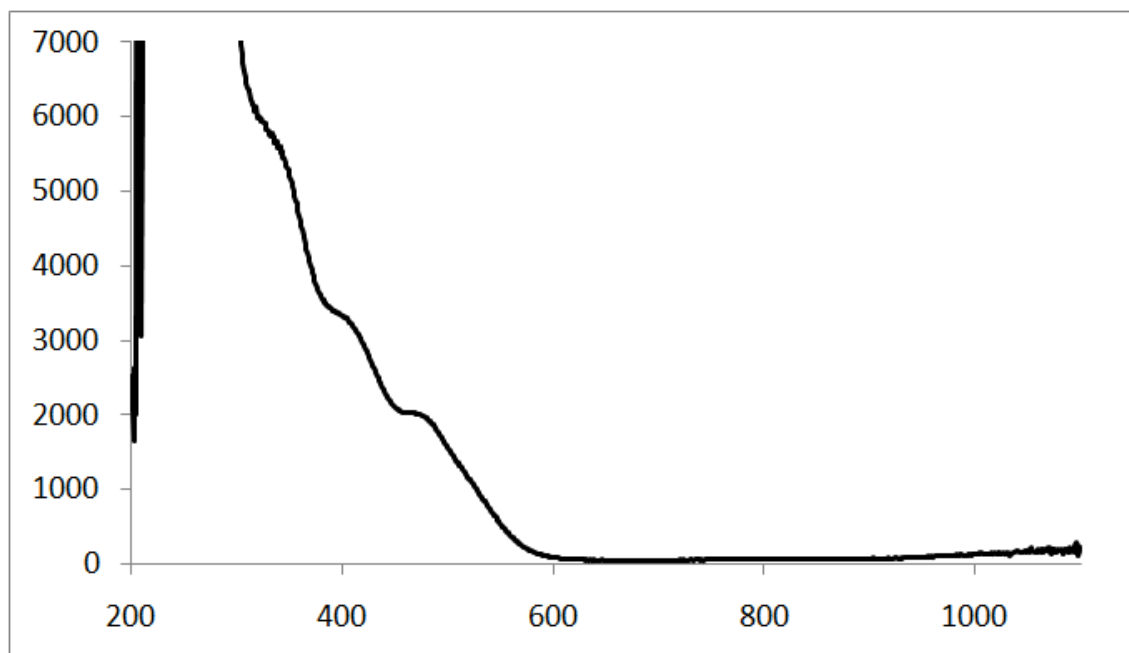
**Figure 22. UV-VIS spectrum of  $[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{FeMe}$  (8). ( $\epsilon$  vs wavelength)**



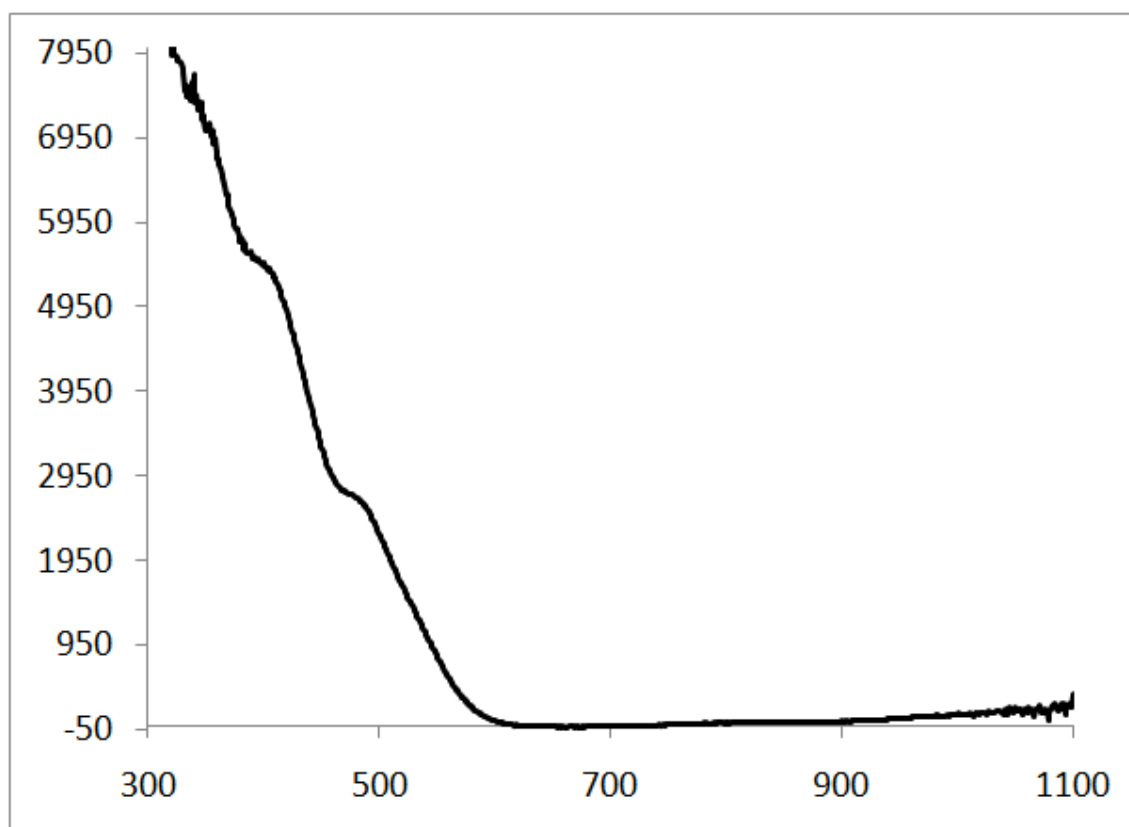
**Figure 23. UV-VIS spectrum of  $[\text{SiP}^{i\text{Pr}}_2\text{S}^{\text{Ad}}]\text{FeCl}$ . ( $\epsilon$  vs wavelength)**



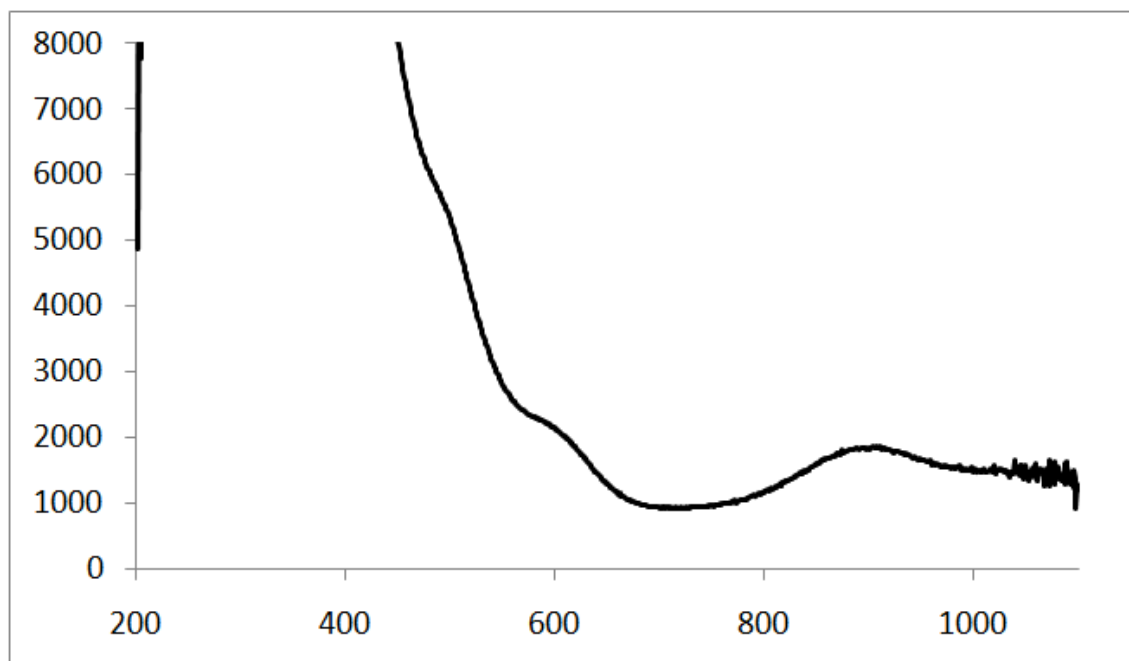
**Figure 24. UV-VIS spectrum of  $[\text{SiP}^{\text{iPr}}\text{S}^{\text{Ad}}_2]\text{FeMe}$  (9). ( $\epsilon$  vs wavelength)**



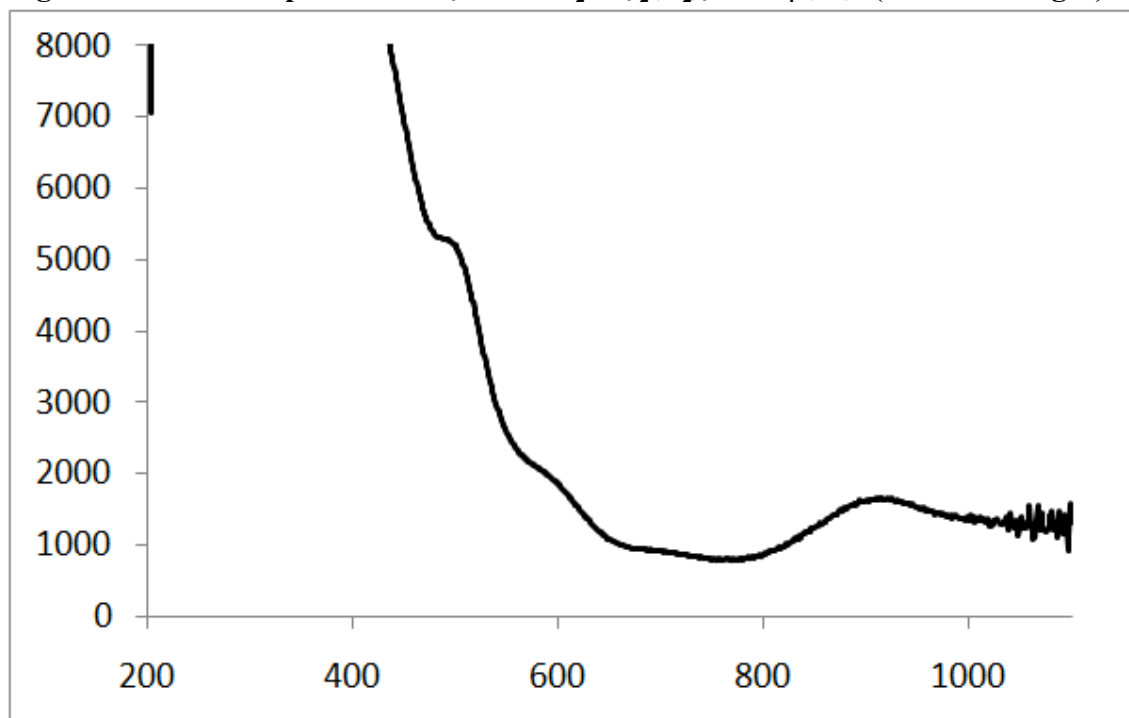
**Figure 25. UV-VIS spectrum of  $[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{FeMe}$ . ( $\epsilon$  vs wavelength)**



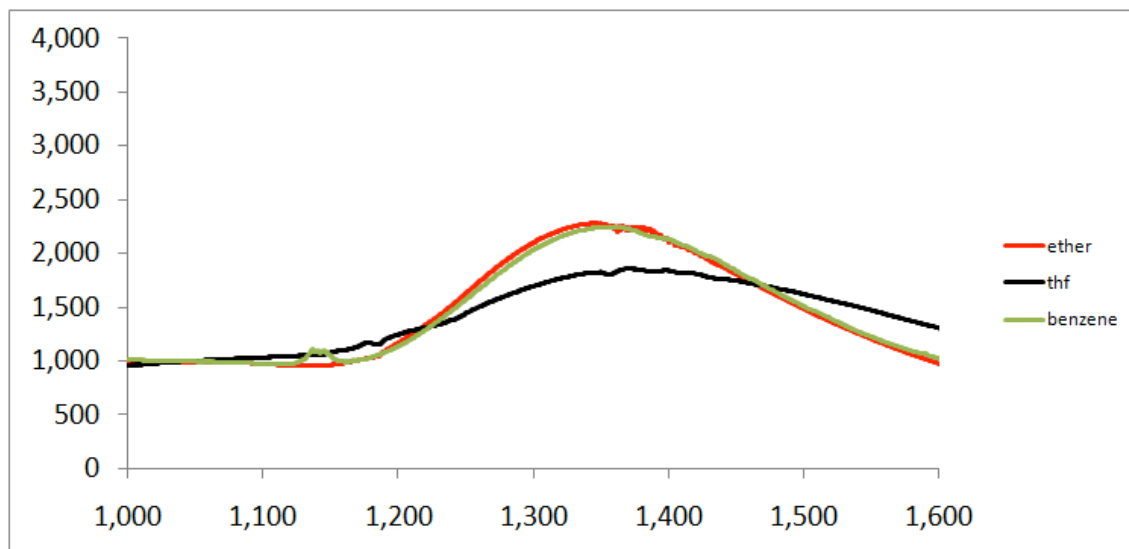
**Figure 26. UV-VIS spectrum of  $\{[\text{SiP}^{i\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (14). ( $\epsilon$  vs wavelength)**



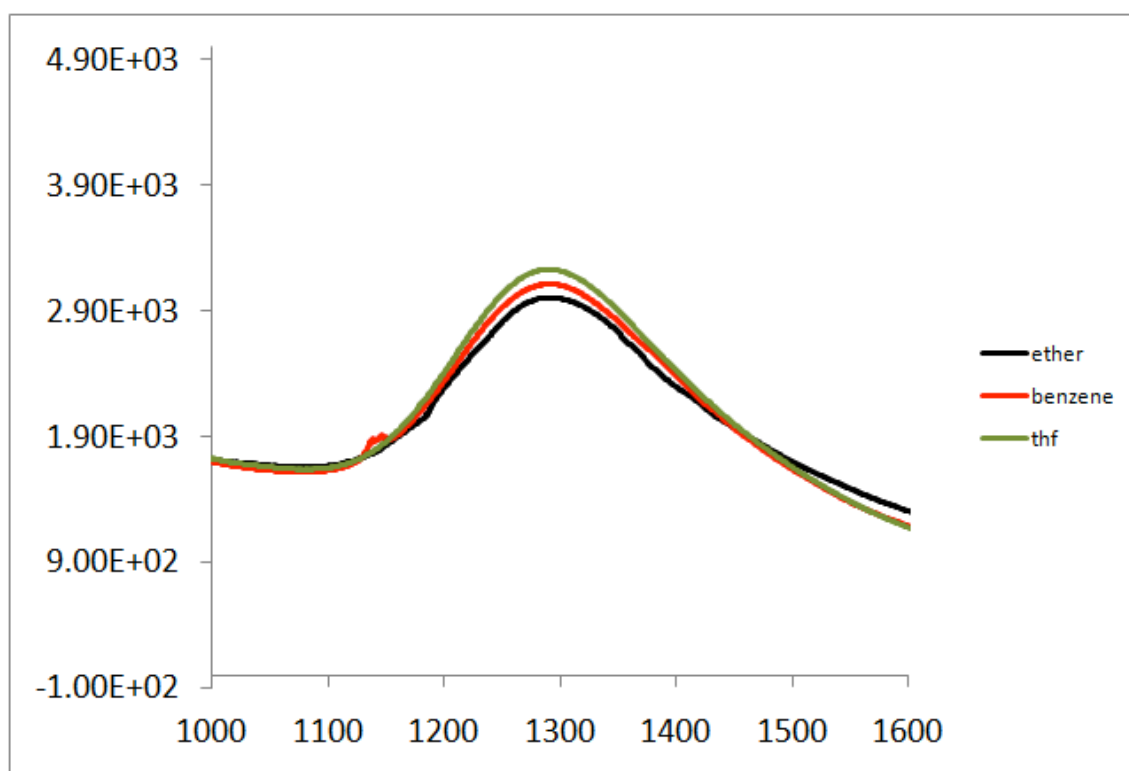
**Figure 27. UV-VIS spectrum of  $\{[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (15). ( $\epsilon$  vs wavelength)**



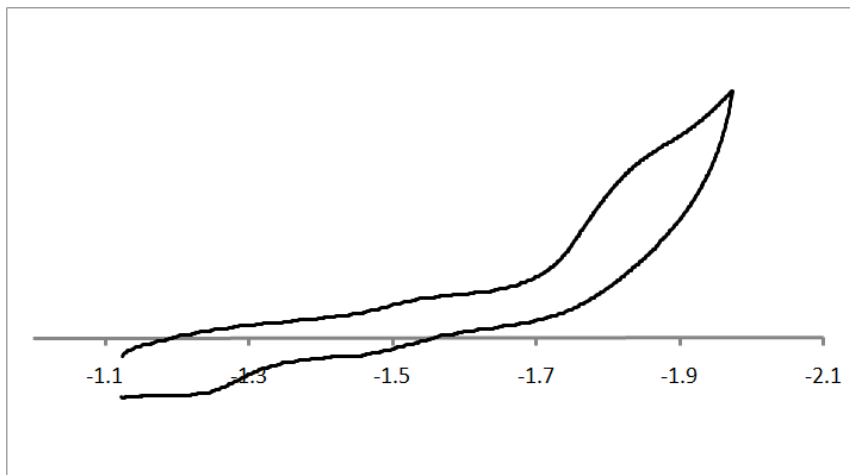
**Figure 28. NIR spectrum of  $\{[\text{SiP}^{\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (14). ( $\epsilon$  vs wavelength)**



**Figure 29. NIR spectrum of  $\{[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)\}\text{BAr}^{\text{F}}_4$  (15). ( $\epsilon$  vs wavelength)**

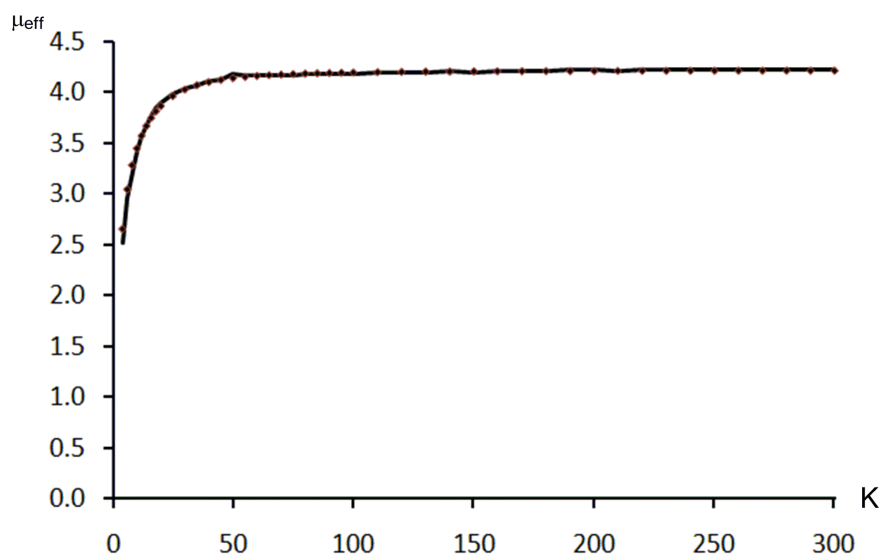


**Figure 30.** Cyclic Voltammogram of **14**.



Reference against  $\text{Fc}/\text{Fc}^+$ . In THF solution with 0.3 M  $\text{TBAPF}_6$ .

**Figure 31.** SQUID data for **14**.



Fitting parameters

Spin = 1.5;  $g = 2.178$ ;  $D = |17.3| \text{ cm}^{-1}$ ;  $E/D = 0.05$

Field; 5T.

In considering the spin-state of each metal center for this system we could consider scenarios in which;

- $S = 2$  Fe(II) center antiferromagnetically coupled to an  $S = \frac{1}{2}$  Fe(I) center
- $S = 1$  Fe(II) center ferromagnetically coupled to an  $S = \frac{1}{2}$  Fe(I) center

- c)  $S = 0$  Fe(II) and  $S = 3/2$  Fe(I) uncoupled
- d) a) or b), with an  $S = 3/2$  state which is largely separated from other spin states

The geometry about both metal centers is presumably trigonal bipyramidal. Due to the strong donation from the phosphines and the silyl anchor in the ligand scaffold, the  $d_{z^2}$  orbital along the Si-Fe-N axis is raised in energy significantly, precluding population of this orbital. Indeed, we have yet to observe an iron complex chelated by these silyl anchor containing scaffolds that can be described as high-spin. All five-coordinate Fe(II) complexes have  $S = 1$  states, and all Fe(I) complexes have  $S = 1/2$  states. Thus, scenario a), or any other description in which  $S > 1$  in any individual metal center is unlikely.

Upon examining the SQUID data, however, we find that there is hardly any temperature dependence. This is consistent with a ground state ( $S = 3/2$ ) that is largely separated from other spin states. Therefore, we cannot extract any meaningful coupling parameters within the temperature range; we instead model the magnetic data of the species as a well isolated  $S = 3/2$  paramagnet (characterized by one  $g$ -value, and one set of  $zfs$  parameters). We do, however, favor scenario b), with large separation of the  $S = 3/2$  manifold. In fact, judging from the HWHM of the IVCT peak, which shows a  $\nu_{1/2}$  much smaller ( $2010\text{ cm}^{-1}$ ) than that predicted from a Class II mixed valent system ( $4120\text{ cm}^{-1}$ ), the system could be better described as two Fe(1.5) centers that are ferromagnetically coupled.

This behavior is consistent with double exchange, where a high-spin configuration for the molecule is favored in a mixed-valent system.<sup>8</sup>

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<sup>8</sup> Bechlars, B.; D'Alessandro, D. M.; Jenkins, D. M.; Iavarone, A. T.; Glover, S. T.; Kubiak, C. P.; Long, J. R. *Nat. Chem.* **2010**, 2, 362.

**Table 5. Coordinates for optimized structure of [SiP<sup>iPr</sup>S<sup>Ad</sup>]<sub>2</sub>Fe(H)(N<sub>2</sub>) (13).**

Fe	0.24088	0.38125	-0.76996
H	1.73042	0.45081	-0.53885
S	0.49755	-1.69692	0.36221
S	-2.15014	0.57911	-0.74489
P	0.84995	2.44328	-1.3745
Si	0.19756	1.26235	1.28535
N	0.31102	-0.27838	-2.44365
C	-2.58456	-1.94748	-1.76468
H	-1.55209	-2.18795	-1.49784
H	-2.56257	-1.45086	-2.74334
C	-3.20327	-1.00675	-0.70671
C	-3.19945	-1.69675	0.66921
H	-3.62963	-1.03104	1.42697
H	-2.17245	-1.91901	0.97468
C	1.4683	3.41242	0.09014
C	0.55027	-0.05737	2.62007
C	-1.60185	1.81482	1.68834
C	-3.40593	-3.25451	-1.84482
H	-2.94392	-3.91111	-2.59348
C	-5.47895	-1.997	-1.20159
H	-6.50922	-1.74709	-1.48804
C	2.22853	-2.46597	0.08761
C	3.34253	-1.67407	0.7943
H	3.172	-1.66308	1.87685
H	3.33105	-0.634	0.45112
C	0.50338	-1.38578	2.15511
N	0.35218	-0.66672	-3.50304
C	1.2519	2.84446	1.36751
C	-2.60902	1.49848	0.75757
C	4.96275	-2.33388	-1.03097
H	4.98516	-1.30435	-1.41255
H	5.94325	-2.77861	-1.25093
C	2.22856	-3.92271	0.59783
H	2.05159	-3.94617	1.67683

H	1.42103	-4.48955	0.11675
C	2.48355	-2.47023	-1.43301
H	2.49136	-1.44501	-1.80918
H	1.67799	-3.00575	-1.9525
C	-3.27573	3.04338	2.98599
H	-3.52919	3.6421	3.85737
C	-0.29245	3.67624	-2.23538
H	0.34462	4.50431	-2.56927
C	2.3457	2.36918	-2.5649
H	2.10918	1.49518	-3.18384
C	-4.24804	2.75067	2.02837
H	-5.26137	3.12767	2.13996
C	-3.91235	1.99635	0.90481
H	-4.65531	1.82952	0.13387
C	3.5973	-4.58078	0.30196
H	3.57915	-5.61127	0.68116
C	-4.02112	-3.00625	0.58502
H	-4.01016	-3.49135	1.56994
C	1.74766	3.52109	2.49321
H	1.61018	3.0958	3.48518
C	2.42188	4.73656	2.36992
H	2.80337	5.24167	3.25414
C	0.41206	-2.46534	3.04512
H	0.27913	-3.47438	2.67048
C	0.60465	0.13751	4.01104
H	0.63773	1.14903	4.40942
C	3.84717	-3.13469	-1.73225
H	4.00745	-3.1236	-2.81814
C	2.11725	4.65104	-0.02562
C	-5.47345	-2.6844	0.17919
H	-6.0694	-3.60674	0.14412
H	-5.94007	-2.03047	0.92894
C	4.7107	-2.33178	0.49001
H	5.49664	-1.75606	0.99621
C	-4.85671	-2.93585	-2.25168
H	-5.44304	-3.86198	-2.32735
H	-4.87716	-2.46222	-3.24287



C	3.84928	-4.58615	-1.21714
H	3.07247	-5.17147	-1.72837
H	4.81145	-5.06746	-1.44018
C	0.4711	-2.23742	4.41988
H	0.40972	-3.07588	5.10875
C	-1.96938	2.59366	2.79897
H	-1.21138	2.86785	3.52979
C	4.71108	-3.78348	1.0103
H	4.55228	-3.79589	2.09746
H	5.68681	-4.25305	0.82429
C	-3.39269	-3.94498	-0.46539
H	-2.36239	-4.19539	-0.17986
H	-3.95353	-4.88894	-0.51025
C	0.59195	-0.93368	4.90435
H	0.64026	-0.75215	5.97516
C	2.59518	5.30912	1.10839
H	3.10577	6.26345	1.0061
C	-1.35706	4.25994	-1.29712
H	-1.96178	4.99702	-1.84155
H	-0.91239	4.76283	-0.43329
H	-2.03591	3.48825	-0.92656
C	-0.94457	3.02407	-3.46636
H	-1.65084	2.24511	-3.16166
H	-0.21405	2.56221	-4.1389
H	-1.50042	3.77535	-4.0419
C	2.55997	3.55861	-3.51799
H	2.79868	4.48407	-2.98239
H	1.70116	3.75225	-4.16583
H	3.41518	3.33967	-4.17026
C	3.65677	2.06782	-1.81992
H	4.44144	1.82046	-2.54646
H	3.55057	1.22541	-1.13246
H	3.99771	2.93405	-1.24333
C	-4.65716	-0.68964	-1.12145
H	-5.12482	-0.02654	-0.3882
H	-4.66484	-0.17153	-2.0887
H	2.25997	5.11117	-0.99932

**Table 6. Coordinates for optimized structure the isomer of [SiP<sup>iPr</sup>S<sup>Ad</sup><sub>2</sub>]Fe(H)(N<sub>2</sub>) (13').**

Fe	-0.27363	0.06291	-0.76444
S	1.39792	-1.65021	0.01567
S	-2.5607	0.56701	-0.67361
P	0.50384	2.18073	-1.27552
Si	-0.1374	0.76369	1.35238
N	-0.24284	-0.60382	-2.44737
C	-3.13514	-1.8811	-1.86314
H	-2.09602	-2.16586	-1.68599
H	-3.16823	-1.3068	-2.79866
C	-3.6381	-1.01819	-0.68966
C	-3.54428	-1.82031	0.61952
H	-3.8987	-1.21436	1.46163
H	-2.49937	-2.08255	0.81771
C	1.07565	3.06219	0.25789
C	0.54812	-0.61546	2.47982
C	-1.8813	1.29945	1.94067
C	-4.00477	-3.15256	-1.98707
H	-3.62647	-3.75251	-2.82484
C	-5.97551	-1.89897	-1.07007
H	-7.01675	-1.59827	-1.24752
C	3.29308	-1.78224	-0.12627
C	4.05658	-0.80978	0.7889
H	3.8378	-1.03925	1.83867
H	3.72872	0.22131	0.6188
C	1.10785	-1.72601	1.81338
N	-0.13158	-1.01198	-3.49223
C	0.88924	2.38041	1.48207
C	-2.90228	1.26898	0.97164
C	5.88526	-0.62761	-0.95158
H	5.60317	0.40584	-1.1861
H	6.96562	-0.7112	-1.13424
C	3.75199	-3.22583	0.18456
H	3.55433	-3.46752	1.23236
H	3.18903	-3.93772	-0.43258
C	3.60195	-1.49085	-1.61055

H	3.25235	-0.49095	-1.88301
H	3.05893	-2.20218	-2.2473
C	-3.4538	2.40837	3.45628
H	-3.66249	2.84864	4.42818
C	-0.67167	3.432	-2.07342
H	-0.02974	4.25643	-2.40357
C	2.00656	2.26897	-2.46821
H	1.89632	1.34172	-3.04567
C	-4.43468	2.40443	2.46314
H	-5.40855	2.84935	2.65006
C	-4.15439	1.85242	1.21389
H	-4.8972	1.90043	0.42534
C	5.2702	-3.36688	-0.07354
H	5.57181	-4.39726	0.1577
C	-4.41101	-3.09798	0.49511
H	-4.33522	-3.66425	1.43265
C	1.37259	2.98013	2.65766
H	1.26323	2.46307	3.60931
C	1.99362	4.2287	2.6345
H	2.362	4.67325	3.55613
C	1.36973	-2.91854	2.49918
H	1.68969	-3.80107	1.9581
C	0.35823	-0.72175	3.86715
H	-0.08281	0.10975	4.41165
C	5.12341	-1.61336	-1.86251
H	5.327	-1.37923	-2.91572
C	1.67448	4.33246	0.24237
C	-5.88036	-2.70446	0.24162
H	-6.50721	-3.60456	0.17633
H	-6.26328	-2.10804	1.08128
C	5.57754	-0.94332	0.52681
H	6.11229	-0.23696	1.17536
C	-5.47144	-2.75947	-2.24371
H	-6.09468	-3.65835	-2.34826
H	-5.55498	-2.20104	-3.18643
C	5.57794	-3.05208	-1.54922
H	5.05966	-3.76527	-2.20475

H	6.65379	-3.16052	-1.7441
C	1.17606	-2.98931	3.8802
H	1.38631	-3.91722	4.40584
C	-2.19176	1.88282	3.1816
H	-1.42156	1.95103	3.94654
C	6.02985	-2.38376	0.83986
H	5.83594	-2.62158	1.89487
H	7.11291	-2.48184	0.6832
C	-3.90316	-3.96037	-0.67749
H	-2.86224	-4.26248	-0.50142
H	-4.49738	-4.88166	-0.7533
C	0.68912	-1.88105	4.57121
H	0.53212	-1.93104	5.64583
C	2.13195	4.914	1.42436
H	2.60103	5.89455	1.40133
C	-1.70519	4.02689	-1.10783
H	-2.29175	4.79308	-1.63169
H	-1.2337	4.49867	-0.24114
H	-2.40414	3.27165	-0.74502
C	-1.35455	2.82186	-3.3099
H	-2.10075	2.07917	-3.01377
H	-0.6472	2.3268	-3.98358
H	-1.86853	3.60585	-3.88079
C	2.08	3.42971	-3.47533
H	2.17985	4.40187	-2.97838
H	1.21822	3.47709	-4.14525
H	2.97192	3.29869	-4.10208
C	3.32964	2.19727	-1.69362
H	4.14762	1.92406	-2.37176
H	3.29505	1.46438	-0.88659
H	3.57776	3.16266	-1.24242
C	-5.10729	-0.6233	-0.95064
H	-5.48863	-0.0116	-0.12735
H	-5.17868	-0.02581	-1.86849
H	1.79343	4.87225	-0.6941
H	-0.83557	-1.16812	-0.07157