

# Supporting Information:

## Synthesis of Iron P-N-P' and P-NH-P' Asymmetric Hydrogenation Catalysts

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### Experimental

#### General Considerations

All procedures and manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk-line and glove box techniques unless stated otherwise. All solvents were degassed and dried using standard procedures prior to all manipulations and reactions unless stated otherwise.

Deuterated solvents were purchased from Cambridge Isotope Laboratories or Sigma Aldrich, degassed, and dried over activated molecular sieves prior to use. All other reagents were purchased from commercial sources and utilized without further purification. NMR spectra were recorded at ambient temperature and pressure using a Varian Gemini 400 MHz spectrometer (400 MHz for  $^1\text{H}$ , 100 MHz for  $^{13}\text{C}$ , 376 MHz for  $^{19}\text{F}$ , and 161 MHz for  $^{31}\text{P}$ ), or an Agilent DD2-600 MHz spectrometer (600 MHz for  $^1\text{H}$ , 151 MHz for  $^{13}\text{C}$ , 564 MHz for  $^{19}\text{F}$ , and 243 MHz for  $^{31}\text{P}$ ) unless stated otherwise. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane (TMS). All  $^{31}\text{P}$  chemical shifts were measured relative to 85% phosphoric acid as an external reference. Gas Chromatography was done on a Perkin Elmer Clarus 400 Chromatograph equipped with a chiral column (CP chirasil-Dex CB 25 m x 2.5 mm) to determine substrate conversion and enantiopurity. Hydrogen gas was used as the mobile phase, and the oven temperature was set at 130°C. Retention times for phenylethanol are 7.58 and 8.03 minutes, and for acetophenone is 4.56 minutes. All of the hydrogenation reactions were performed in a 50 mL stainless steel Parr Hydrogenation reactor at constant temperatures and pressures. The temperature was maintained at 50°C using a constant temperature water bath and was purged of oxygen by flushing the reactor several times with 5 atm of  $\text{H}_2$  (g). The elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Some complexes gave unsatisfactory carbon analyses but acceptable hydrogen and nitrogen content because of a combustion problem due to the tetrafluoroborate, hexafluorophosphate and tetraphenylborate anions, as previously reported in the literature.<sup>59</sup> These complexes are denoted with \*\* following the EA results.

### Synthesis of PN Precursors 2defg

For **2d-f**, illustrated with **2d**:

*BOC-Protection*: Following a  $\text{LiAlH}_4$  reduction of commercially available amino acids,<sup>1</sup> the corresponding amino alcohols were purified using a short silica plug to remove alumina impurities. Phenylglycinol (2.7 g, 20 mmol) was dissolved in 60 mL DCM and  $\text{NEt}_3$  (2.8 mL, 21 mmol), then cooled to 0°C. To the cooled solution,  $(\text{Boc})_2\text{O}$  (4.6 g, 21 mmol) in 10 mL DCM was added and stirred for 18 h, being allowed to slowly warm to RT. 80 mL  $\text{H}_2\text{O}$  was added and allowed to stir for a further 0.5 h and then the organics were collected, and the aqueous phase was washed with DCM (2 x 50 mL). The organics were combined, washed with brine (2 x 70 mL) and  $\text{H}_2\text{O}$  (70 mL), then dried with  $\text{Na}_2\text{SO}_4$ , filtered and dried under reduced pressure to yield a white solid.

*Tosylation:* The white solid (BOC-protected) (5.0 g, 21.5 mmol) was dissolved in 120 mL DCM and NEt<sub>3</sub> (7 mL, 54 mmol), then cooled to 0°C. To the cooled solution, TsCl (5.0 g, 26 mmol) was added and stirred for 18 h, being allowed to slowly warm to RT. 100 mL H<sub>2</sub>O was added and allowed to stir for a further 1 h and then the organics were collected, and the aqueous phase was washed with DCM (2 x 70 mL). The organics were combined, washed with brine (2 x 70 mL), aqueous NH<sub>4</sub>Cl (2 x 70 mL) and H<sub>2</sub>O (2 x 70 mL), then dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and dried under reduced pressure to yield a white solid.

*Phosphide Reaction:* All steps of this synthesis were conducted using an inert argon atmosphere. In a flask KPPH<sub>2</sub> (from 2 g HPPH<sub>2</sub> and 450 mg KH – 10 mmol) was dissolved in 70 mL THF and transferred to a Schlenk line. The solution was cooled to -40°C and the white solid (tosylated product) (2 g, 5 mmol) in 25 mL dry THF was added dropwise to the cooled solution. The solution was stirred at -40°C for 6 h, then warmed to RT and stirred for 10 h, then dried under reduced pressure to yield a bright orange residue. In a nitrogen filled glovebox, the residue was quickly dissolved in 70 mL pentane, and the excess phosphide was quenched dropwise with ~3 mL MeOH. The white KOMe by-product was filtered off and the solution was concentrated to half volume. The solution was then placed in a freezer for 0.5 h, and a white powder was collected and dried.

*BOC Deprotection:* (\*inert atmosphere) The white solid (from phosphide reaction) (0.68 g, 1.7 mmol) was dissolved in 30 mL distilled DCM and cooled to 0°C. To the cooled solution, CF<sub>3</sub>CO<sub>2</sub>H (5.5 mL) was added dropwise and the solution was stirred at 0°C for 1 h then RT for 14 h, before being quenched with 40 mL degassed H<sub>2</sub>O. Then, the organics were collected and the aqueous phase was extracted with DCM (2 x 20 mL). The organics were combined and washed with NaHCO<sub>3</sub> (30 mL) and water (50 mL). The solution was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and dried under reduced pressure, to yield an off-white solid. Overall Yield from phenylglycinol = 27%. Characteristic <sup>31</sup>P {<sup>1</sup>H} NMR peak at -22.0 for **2d**, -22.5 for **2e** and -21.7 ppm for **2f**.

For **2g**:

*BOC-Protection:* To a flask containing commercially available (1R,2S)-(-)-2-amino-1,2-diphenylethanol (3 g, 14 mmol) and sodium carbonate (3.5 g, 33 mmol), 60 mL THF and 30 mL H<sub>2</sub>O were added and the solution was cooled to 0°C under air. To the cooled solution, (Boc)<sub>2</sub>O (3.5 g, 16 mmol) in 15 mL THF was added. The solution was stirred at 0°C for 1 h, then RT for 3 h, before 60 mL H<sub>2</sub>O was added and stirred for an additional 0.5 h. The organics were collected, and the aqueous phase was washed with ethyl acetate (2 x 50 mL). The organics were combined, washed with brine (2 x 70 mL) and H<sub>2</sub>O (70 mL), then

dried with  $\text{MgSO}_4$ , filtered and dried under reduced pressure. To the residue, 18 mL of DCM was added to partially dissolve the residue, followed by 150 mL of hexanes. The slurry was stirred for 18 h and the white solid was collected by filtration and dried under reduced pressure to yield a pure, white solid.

*Cyclisation:* The resultant white powder (3.9 g, 12 mmol) was dissolved in 110 mL of DCM and  $\text{NEt}_3$  (5.2 mL, 51 mmol), and the solution was cooled to  $-40^\circ\text{C}$ . To the cooled solution,  $\text{SOCl}_2$  (1.5 mL, 13 mmol) in 9 mL DCM was added and the cooled solution was stirred for 1.5 h. It was then quenched with 8 mL  $\text{H}_2\text{O}$ , warmed to RT, and the organics were extracted. The aqueous phase was washed with DCM (2 x 30 mL), then the organics were combined and washed with brine (2 x 70 mL) and water (70 mL). The solution was then dried with  $\text{MgSO}_4$ , filtered and dried under reduced pressure to yield the crude residue.

*Oxidation:* The crude residue from cyclisation (4.4 g, 12 mmol) was dissolved in 25 mL DCM, 40 mL MeCN and 50 mL  $\text{H}_2\text{O}$  then cooled to  $0^\circ\text{C}$  before  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  (26 mg) was added.  $\text{NaIO}_4$  (4 g, 19 mmol) was added in portions and the solution was stirred at  $0^\circ\text{C}$  for 1 h, then RT for 1.5 h. The organics were collected, and the aqueous phase was washed with ether (2 x 40 mL). The combined organics were washed with brine (2 x 70 mL) and water (30 mL), then the solution was then dried with  $\text{MgSO}_4$ , filtered and dried under reduced pressure. The residue was dissolved in 8 mL of DCM and stirred with 100 mL of hexanes for 5 hours, to yield a white solid that was collected by filtration and dried under reduced pressure to yield a pure, white solid.

*Phosphide Reaction:* All steps of this synthesis were conducted using an inert argon atmosphere. The white solid (from oxidation) (3 g, 8 mmol) was dissolved in 40 mL dry THF and cooled to  $-78^\circ\text{C}$ . To the cooled solution,  $\text{KPPH}_2$  (from 1.7 g  $\text{HPPH}_2$  and 400 mg  $\text{KH}$  – 8.5 mmol) in 20 mL THF was added dropwise, and the solution was stirred at  $-78^\circ\text{C}$  for 1.5 h, then RT for 18 h. To quench the excess phosphide, 25 mL degassed brine and 2.5 mL 2N  $\text{H}_2\text{SO}_4$  (degassed) were added and the solution was stirred for 1 h. Degassed aqueous  $\text{Na}_2\text{CO}_3$  (~10 mL) was added to make the solution slightly basic, and then the organics were collected. The aqueous phase was extracted with 15 mL DCM, and then the organics were combined and washed with brine (2 x 30 mL) and water (20 mL). The solution was dried with  $\text{MgSO}_4$ , filtered, and dried under reduced pressure. To the residue, 10 mL MeOH and 10 mL MeCN were added and stirred for 4 h. The slurry was cooled in the freezer for 1 h, then the white solid was collected and dried under reduced pressure.

*BOC Deprotection:* (\*inert atmosphere) The white solid (from phosphide reaction) (3 g, 6.2 mmol) was dissolved in 25 mL distilled DCM and cooled to  $0^\circ\text{C}$ . To the cooled solution,  $\text{CF}_3\text{CO}_2\text{H}$  (7 mL) was added

dropwise and the solution was stirred at 0°C for 1 h then RT for 4 h, before being dried under reduced pressure. The residue was dissolved in 25 mL DCM, neutralized with degassed aqueous Na<sub>2</sub>CO<sub>3</sub> (~25 mL), and the organics were collected. The aqueous phase was extracted with 15 mL DCM, and then the organics were combined and washed with brine (2 x 25 mL) and water (25 mL). The solution was dried with MgSO<sub>4</sub>, filtered, and dried under reduced pressure, to yield an oily solution that solidified to a white solid upon standing. Yield = 2 g = 37% overall (from (1R,2S)-(-)-2-amino-1,2-diphenylethanol). Characteristic <sup>31</sup>P {<sup>1</sup>H} NMR peak at -8.3 ppm.

### Synthesis of P-N-P' Ligands **4a,c-g**

R<sup>1</sup> = R<sup>2</sup> = H **4a**: In a nitrogen filled glovebox, **2a** (0.6 g, 2.6 mmol) was added to a solution of *o*-(diphenylphosphino)benzaldehyde (0.76 g, 2.6 mmol) and Na<sub>2</sub>SO<sub>4</sub> (5 g, 35 mmol) in 30 mL of DCM. The mixture was stirred for 24 hours, then filtered through a frit and concentrated to 2 mL. With rigorous stirring, 8 mL of cold ethanol was added and the flask was sealed and stored at -30 °C for 48 hours to yield a white powder. The powder was filtered and washed with cold ethanol, then dried under reduced pressure to yield pure P-N-P' ligand. Yield = 980 mg = 75%.

<sup>1</sup>H NMR (400MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ: 8.77 (d, 1H, HC=N, <sup>4</sup>J<sub>HH</sub> = 4.7 Hz), 7.8 (dd, 1H, Ar-CH, J = 3.9, 7.5 Hz), 7.1-7.4 (m, 22H, Ar-CH, P-Ar-CH), 6.8 (dd, 1H, Ar-CH, J = 7.4, 4.6 Hz), 3.5 (t, 2H, N-CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz), and 2.1 (t, 2H, P-CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz) ppm. <sup>31</sup>P {<sup>1</sup>H} (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ: -13.2 (s), -19.5 (s) ppm. <sup>13</sup>C {<sup>1</sup>H} (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ: 159.5 (d, HC=N, J = 20 Hz), 137-139 (Ar-C, P-Ar-C), 127-134 (Ar-C, P-Ar-C), 57.8 (d, N-CH<sub>2</sub>, J = 21.1 Hz) and 29.5 (d, P-CH<sub>2</sub>, J = 12.8 Hz) ppm. Anal. Calcd. For [C<sub>33</sub>H<sub>29</sub>P<sub>2</sub>N]: C 79.0, H 5.82, N 2.79, Found: C 77.83, H 5.59, N 2.81. MS (TOF-DART, m/z<sup>+</sup>): 502.185 [C<sub>33</sub>H<sub>30</sub>P<sub>2</sub>N]<sup>+</sup>. <sup>5</sup>Complex was made multiple times in an attempt to synthesize pure compound (acceptable EA) however silica grease impurities (observed in <sup>1</sup>H NMR) caused the carbon analyses to be low. The compound could therefore not be isolated as 100% pure.

R<sup>1</sup> = Me, R<sup>2</sup> = Ph **4c**: In a nitrogen filled glovebox, **2c** (0.1 g, 0.31 mmol) was added to a solution of *o*-(diphenylphosphino)benzaldehyde (0.091 g, 0.31 mmol) and Na<sub>2</sub>SO<sub>4</sub> (1 g, 7 mmol) in 5 mL of DCM. The mixture was stirred for 24 hours, then filtered through a frit and concentrated to 1 mL. With rigorous stirring, 8 mL of cold pentane was added and the flask was sealed and stored at -30 °C for 24 hours to yield a white powder. The powder was filtered and washed with cold pentane, then dried under reduced pressure to yield pure P-N-P' ligand. Yield = 120 mg = 65%.

$^1\text{H}$  NMR (400MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 8.80 (d, 1H,  $\text{HC}=\text{N}$ ,  $^4J_{\text{HH}} = 4.90$  Hz), 7.6 (m, 2H, Ar-CH), 7.0-7.4 (m, 26H, Ar-CH, P-Ar-CH), 6.8 (m, 1H, Ar-CH), 3.72 (d, 1H,  $\text{CH}(\text{Ph})$ ,  $^3J_{\text{HH}} = 5.6$  Hz), 3.63 (dq, 1H,  $\text{CH}(\text{CH}_3)$   $^3J_{\text{HH}} = 5.6$  and 6.1Hz), and 0.95 (d, 3H,  $\text{CH}_3$ ,  $^3J_{\text{HH}} = 6.1$  Hz) ppm.  $^{31}\text{P}$   $\{^1\text{H}\}$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : -8.1 (s), -14.5 (s) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  (100 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 157.7 (C=N), 132-134 (Ar-C, P-Ar-C), 126-130 (Ar-C, P-Ar-C), 68.6 ( $\text{CH-Me}$ ), 51.3 ( $\text{CH-Ph}$ ) and 19.8 ( $\text{CH}_3$ ) ppm. Anal. Calcd. For  $[\text{C}_{40}\text{H}_{35}\text{P}_2\text{N}]$ : C 81.19, H 5.96, N 2.37, Found: C 80.75, H 5.10, N 1.93. MS (TOF-DART,  $m/z^+$ ): 592.232  $[\text{C}_{40}\text{H}_{36}\text{P}_2\text{N}]^+$ .

$\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{H}$  **4d**: In a nitrogen filled glovebox, **2d** (0.15 g, 0.49 mmol) was added to a solution of *o*-(diphenylphosphino)benzaldehyde (0.14 g, 0.48 mmol) and  $\text{Na}_2\text{SO}_4$  (2 g, 14 mmol) in 8 mL of DCM. The mixture was stirred for 24 hours, then filtered through a frit and concentrated to 1 mL. With rigorous stirring, 8 mL of cold ethanol was added and the flask was sealed and stored at  $-30^\circ\text{C}$  for 48 hours to yield a white solid. The solid was filtered and washed with cold ethanol, then dried under reduced pressure to yield pure P-N-P' ligand. Yield = 150 mg = 55%.

$^1\text{H}$  NMR (400MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 8.68 (d, 1H,  $\text{N}=\text{CH}$ ,  $^4J_{\text{HH}} = 4.6$  Hz), 7.76 (ddd, 1H, Ar-CH,  $J = 1.5, 3.9$  and 7.8 Hz), 7.05-7.32 (m, 27H, Ar-CH), 6.78 (ddd, 1H, Ar-CH,  $J = 1.3, 4.6$  and 7.7 Hz), 4.16 (quart., 1H,  $\text{C}(\text{Ph})\text{H}$ ,  $^3J_{\text{HH}} = 7.8$  Hz) and 2.41 (qd, 2H,  $\text{CH}_2$ ,  $^2J_{\text{HH}}$  and  $^3J_{\text{HH}} = 13.6$  and 7.1 Hz) ppm.  $^{31}\text{P}$   $\{^1\text{H}\}$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : -12.8 (s), -22.9 (s) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  (100 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 158.8 (d, C=N,  $J = 19.8$  Hz), 126-135 (Ar-C and P-Ar-C), 72.5 (d, CH,  $J = 16.4$  Hz) and 53.4 (quint,  $\text{CH}_2$ ,  $J = 27.2$  Hz) ppm. Anal. Calcd. For  $[\text{C}_{39}\text{H}_{33}\text{P}_2\text{N}]$ : C 81.1, H 5.76, N 2.43, Found: C 79.07, H 5.79, N 2.36. MS (ESI,  $m/z^+$ ): 578.2  $[\text{C}_{39}\text{H}_{34}\text{P}_2\text{N}]^+$ . Complex was made multiple times in an attempt to synthesize pure compound (acceptable EA) however silica grease impurities (observed in  $^1\text{H}$  NMR) caused the carbon analyses to be low. The compound could therefore not be isolated as 100% pure.

$\text{R}^1 = \text{CH}_2\text{Ph}$ ,  $\text{R}^2 = \text{H}$  **4e**: In a nitrogen filled glovebox, **2e** (0.27 g, 0.85 mmol) was added to a solution of *o*-(diphenylphosphino)benzaldehyde (0.25 g, 0.85 mmol) and  $\text{Na}_2\text{SO}_4$  (2 g, 14 mmol) in 10 mL of DCM. The mixture was stirred for 24 hours, then filtered through a frit and concentrated to 2 mL, sealed and stored at  $-30^\circ\text{C}$  for 48 hours to yield a pale yellow solid. The solution was decanted off and the solid was dried under reduced pressure to yield pure P-N-P' ligand. Yield = 230 mg = 46%.

$^1\text{H}$  NMR (400MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 8.37 (d, 1H,  $\text{N}=\text{CH}$ ,  $^4J_{\text{HH}} = 4.7$  Hz), 7.71 (ddd, 1H, Ar-CH,  $J = 1.6, 3.9$  and 7.6 Hz), 7.15-7.45 (m, 25H, Ar-CH), 7.01 (dd, 2H, Ar-CH,  $J = 1.7$  and 7.9 Hz), 6.86 (ddd, 1H, Ar-CH,  $J = 1.5, 4.5$  and 7.6 Hz) 3.28 (m, 1H, CH) 2.99 (dd, 1H, CH-P,  $^3J_{\text{HH}}$  and  $^2J_{\text{HH}} = 4.9$  and 13.3 Hz), 2.74 (dd, 1H, CH-P,  $^3J_{\text{HH}}$  and  $^2J_{\text{HH}} = 8.1$  and 13.3 Hz), 2.33 (dd, 1H, CH-Ph,  $^3J_{\text{HH}} = 5.1$  and 13.6 Hz) and 2.13 (dd, 1H, CH-Ph,  $^3J_{\text{HH}} = 8.1$  and 13.6 Hz) ppm.  $^{31}\text{P}$   $\{^1\text{H}\}$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : -14.1 (s), -23.1 (s) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  (100 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ :

158.1 (d, C=N,  $J = 19.3$  Hz), 125-140 (Ar-C and P-Ar-C), 70.3 (d, CH,  $J = 14.1$  Hz) 43.5 (d, CH<sub>2</sub>-P,  $J = 9.0$  Hz) and 34.5 (d, CH<sub>2</sub>-Ph,  $J = 12.8$  Hz) ppm. Anal. Calcd. For [C<sub>40</sub>H<sub>35</sub>P<sub>2</sub>N]: C 80.2, H 5.96, N 2.37, Found: C 79.29, H 6.18, N 2.27. MS (ESI,  $m/z^+$ ): 592.2 [C<sub>40</sub>H<sub>36</sub>P<sub>2</sub>N]<sup>+</sup>.

$R^1 = iPr$ ,  $R^2 = H$  **4f**: In a nitrogen filled glovebox, **2f** (0.1 g, 0.37 mmol) was added to a solution of *o*-(diphenylphosphino)benzaldehyde (0.11 g, 0.37 mmol) and Na<sub>2</sub>SO<sub>4</sub> (2 g, 14 mmol) in 8 mL of DCM. The mixture was stirred for 24 hours, then filtered through a frit and concentrated to 1 mL. With rigorous stirring, 8 mL of cold pentane was added and the flask was sealed and stored at -30 °C for 24 hours to yield a pale yellow solution and a pale grey residue. The residue was discarded and the solution was dried under reduced pressure to yield pure P-N-P' ligand as a pale yellow oily solid. Yield = 100 mg = 50%.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 8.65 (d, 1H, HC=N,  $^4J_{HH} = 4.77$  Hz), 7.75 (ddd, 1H, Ar-CH,  $J = 1.4, 3.9$  and  $7.7$  Hz), 7.70 (dd, 1H, Ar-CH,  $J = 3.3$  and  $5.7$  Hz), 7.55 (dd, 1H, Ar-CH,  $J = 3.3$  and  $5.7$  Hz), 7.2-7.4 (m, 20H, P-Ar-CH), 6.85 (ddd, 1H, Ar-CH,  $J = 1.4, 4.6$  and  $7.7$  Hz), 2.88 (m, 1H, N-C-H), 2.31 (dd, 1H, CH<sub>2</sub>,  $^3J_{HH}$  and  $^2J_{HH} = 4.3$  and  $13.8$  Hz), 2.15 (dd, 1H, CH<sub>2</sub>,  $^3J_{HH}$  and  $^2J_{HH} = 8.9$  and  $13.8$  Hz), 1.82 (m, 1H, *iPr*-CH), and 0.73 (dd, 6H, *iPr*-CH<sub>3</sub>,  $^3J_{HH} = 5.0, 6.7$  Hz) ppm. <sup>31</sup>P {<sup>1</sup>H} (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : -13.3 (s), -22.0 (s) ppm. <sup>13</sup>C {<sup>1</sup>H} (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 158.5 (d, C=N,  $J = 19.8$  Hz), 128-140 (Ar-C and P-Ar-C), 74.3 (d, N-C,  $J = 13$  Hz), 33.6 (d, *iPr*-CH,  $J = 8.6$  Hz), 32.7 (d, CH<sub>2</sub>,  $J = 13$  Hz), 19.3 (s, *iPr*-CH<sub>3</sub>) and 17.6 (s, *iPr*-CH<sub>3</sub>) ppm. Anal. Calcd. For [C<sub>36</sub>H<sub>35</sub>P<sub>2</sub>N]: C 79.5, H 6.49, N 2.58, Found: C 78.6, H 7.04, N 2.19. MS (ESI,  $m/z^+$ ): 544.23 [C<sub>36</sub>H<sub>36</sub>P<sub>2</sub>N]<sup>+</sup>.

$R^1 = R^2 = Ph$  **4g**: In a nitrogen filled glovebox, **2g** (0.15 g, 0.41 mmol) was added to a solution of *o*-(diphenylphosphino)benzaldehyde (0.12 g, 0.41 mmol) and Na<sub>2</sub>SO<sub>4</sub> (2 g, 14 mmol) in 10 mL of dichloromethane. The mixture was stirred for 24 hours, then filtered through a frit and concentrated to 1 mL. With rigorous stirring, 8 mL of cold ethanol was added, the solution was concentrated to half volume, and the vial was sealed and stored at -30 °C for 2 hours to yield a pale yellow solid. The solid was filtered and washed with cold ethanol, then dried under reduced pressure to yield pure P-N-P' ligand. Yield = 151 mg = 58%.

<sup>1</sup>H NMR (400MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 8.99 (d, 1H, N=CH,  $^4J_{HH} = 5.6$  Hz), 7.68 (td, 2H, Ar-CH,  $J = 1.7$  and  $7.7$  Hz), 6.85-7.45 (m, 31H, Ar-CH), 6.81 (ddd, 1H, Ar-CH,  $J = 1.4, 4.8$  and  $7.6$  Hz), 4.83 (dd, 1H, N-CHPh,  $^3J_{HH} = 5.8$  and  $8.2$  Hz) and 4.22 (dd, 1H, P-CHPh,  $^3J_{HH}$  and  $^3J_{HP} = 5.5$  and  $8.2$  Hz) ppm. <sup>31</sup>P {<sup>1</sup>H} (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : -7.17 (s), -15.36 (s) ppm. <sup>13</sup>C {<sup>1</sup>H} (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 158.4 (C=N), 133-135 (Ar-C and P-Ar-C), 126-131 (Ar-C and P-Ar-C), 78.9 (d, N-CHPh,  $J = 21.0$  Hz) and 52.0 (d, P-CHPh,  $J = 16.1$  Hz) ppm. Anal. Calcd. For [C<sub>45</sub>H<sub>37</sub>P<sub>2</sub>N]: C 82.68, H 5.70, N 2.14, Found: C 82.50, H 6.16, N 2.14. MS (ESI,  $m/z^+$ ): 654.2 [C<sub>45</sub>H<sub>38</sub>P<sub>2</sub>N]<sup>+</sup>.

### Synthesis of P-NH-P' Ligands 5a,c-f

$R^1 = R^2 = H$  **5a**: In a nitrogen filled glovebox, **4a** (0.055 g, 0.11 mmol) and  $NaBH_4$  (0.012 g, 0.31 mmol) were dissolved in 5 mL ethanol, sealed, and transferred to a Schlenk line. The solution was refluxed under argon for 24 hours, then 8 mL of distilled water was added to neutralize the excess  $NaBH_4$ . The flask was then opened to air, and the product was extracted with 20 mL DCM. The aqueous phase was further extracted with DCM (2x15 mL), and the combined organics were washed with saturated  $NH_4Cl$  solution (3x15 mL) and water (3x15 mL), dried with  $Na_2SO_4$ , and dried under reduced pressure to yield a clean, white powder. Yield = 54 mg = 97%.

$^1H$  NMR (400MHz,  $CD_2Cl_2$ )  $\delta$ : 7.2-7.4 (m, 22H, Ar-CH), 7.15 (td, 1H, Ar-CH,  $J = 1.4$  and 7.4 Hz), 6.78 (ddd, 1H, Ar-CH,  $J = 1.4, 4.5$  and 7.7 Hz), 3.8 (d, 2H, N-CH<sub>2</sub>-Ph,  $^3J_{HH} = 1.8$  Hz), 2.51 (quart., 2H, N-CH<sub>2</sub>,  $^3J_{HH} = 8.1$  Hz), 1.94 (t, 2H, P-CH<sub>2</sub>,  $^3J_{HH} = 8.1$  Hz), 1.28 (br-s, 1H, NH) ppm.  $^{31}P$  { $^1H$ } (161 MHz,  $CD_2Cl_2$ )  $\delta$ : -16.1 (s), -20.6 (s) ppm.  $^{13}C$  { $^1H$ } (100 MHz,  $CD_2Cl_2$ )  $\delta$ : 128-135 (Ar-C and P-Ar-C), 52.0 (N-CH<sub>2</sub>-Ph), 45.8 (N-CH<sub>2</sub>-CH<sub>2</sub>) and 28.7 (P-CH<sub>2</sub>) ppm. Anal. Calcd. For  $[C_{33}H_{31}P_2N]$ : C 78.71, H 6.21, N 2.78, Found: C 78.82, H 6.66, N 2.40. MS (ESI,  $m/z^+$ ): 504.2  $[C_{33}H_{32}P_2N]^+$ .

$R^1 = Me$ ,  $R^2 = Ph$  **5c**: In a nitrogen filled glovebox, **4c** (0.052 g, 0.088 mmol) and  $NaBH_4$  (0.010 g, 0.26 mmol) were dissolved in 4 mL of ethanol, sealed, and transferred to a Schlenk line. The solution was refluxed under argon for 24 hours, then 6 mL of distilled water was added to neutralize the excess  $NaBH_4$ . The flask was then opened to air, and the product was extracted with 15 mL of DCM. The aqueous phase was further extracted with DCM (2x10 mL), and the combined organics were washed with saturated  $NH_4Cl$  solution (10 mL), brine (10 mL) and water (10 mL), dried with  $MgSO_4$ , and dried under reduced pressure to yield a clean, white powder. Yield = 37 mg = 71%.

$^1H$  NMR (600MHz,  $CD_2Cl_2$ )  $\delta$ : 7.57 (m, 2H, Ph-CH), 7.10-7.42 (m, 26H, Ph-CH), 6.85 (ddd, 1H, Ph-CH,  $J = 1.4, 4.5$  and 7.7 Hz), 3.96 (dd, 1H, N-CH<sub>2</sub>,  $^3J_{HH}$  and  $^2J_{HH} = 2.2$  and 13.7 Hz), 3.87 (dd, 1H, N-CH<sub>2</sub>,  $^3J_{HH}$  and  $^2J_{HH} = 2.4$  and 13.7 Hz), 3.83 (m, 1H, P-C(Ph)H), 2.77 (m, 1H, N-C(Me)H), 1.29 (br-s, 1H, NH) and 1.00 (d, 3H, CH<sub>3</sub>,  $^3J_{HH} = 6.7$  Hz) ppm.  $^{31}P$  { $^1H$ } (161 MHz,  $CD_2Cl_2$ )  $\delta$ : -11.15 (s), -16.15 (s) ppm.  $^{13}C$  { $^1H$ } (150 MHz,  $CD_2Cl_2$ )  $\delta$ : 126-135 (Ph-C), 53.39 (N-C(Me)H), 49.22 (N-CH<sub>2</sub>), 48.36 (P-C(Ph)H) and 17.16 (-CH<sub>3</sub>) ppm. Anal. Calcd. For  $[C_{33}H_{31}P_2N]$ : C 80.92, H 6.28, N 2.36 Found: C 80.62, H 6.31, N 2.34. MS (ESI,  $m/z^+$ ): 594.2  $[C_{40}H_{38}P_2N]^+$ .

$R^1 = Ph$ ,  $R^2 = H$  **5d**: In a nitrogen filled glovebox, **4d** (0.13 g, 0.23 mmol) was dissolved in 3 mL of THF and brought up in a syringe and stoppered. In a separate flask in the nitrogen filled glovebox,  $LiAlH_4$  (0.018 g,

0.47 mmol) was dissolved in 5 mL of THF, sealed, and transferred to a Schlenk line. The solution was cooled using an ice bath to 0°C, and the solution of P-N-P' ligand was slowly added. The solution was stirred at 0°C for 30 minutes, room temperature for 1 hour and then refluxed under argon for 18 hours. The solution was cooled in an ice bath and 0.5 mL of water was added to quench any excess LiAlH<sub>4</sub>, then the solution was filtered under air through a frit to remove any lithium salts, and washed with 3 mL of THF. 10 mL of water was added to wash the solution, and the aqueous phase was further washed with 10 mL of DCM. The combined organics were washed with saturated NH<sub>4</sub>Cl solution (10 mL), brine (10 mL) and water (10 mL), dried with MgSO<sub>4</sub>, filtered, and dried under reduced pressure to yield a clear oil that solidified on standing. Yield = 120 mg = 92%.

<sup>1</sup>H NMR (400MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ: 7.15-7.45 (m, 28H, Ar-CH), 6.89 (m, 1H, Ar-CH), 3.71 (s, 2H, N-CH<sub>2</sub>-Ph), 3.62 (m, 1H, N-CH), 2.33 (d, 2H, CH<sub>2</sub>-PPh<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz) and 1.29 (br-s, 1H, NH) ppm. <sup>31</sup>P {<sup>1</sup>H} (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ: -16.4 (s), -23.5 (s) ppm. <sup>13</sup>C {<sup>1</sup>H} (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ: 132-134 (Ar-C and P-Ar-C), 127-129 (Ar-C and P-Ar-C), 60.0 (d, N-CH J = 15.9 Hz), 50.1 (d, N-CH<sub>2</sub>-Ph, J = 20.7 Hz) and 38.2 (d, CH<sub>2</sub>-PPh<sub>2</sub>, J = 14.3 Hz) ppm. Anal. Calcd. For [C<sub>39</sub>H<sub>35</sub>P<sub>2</sub>N]: C 80.81, H 6.09, N 2.42, Found: C 79.19<sup>5</sup>, H 6.80, N 2.26. MS (ESI, m/z<sup>+</sup>): 580.2 [C<sub>39</sub>H<sub>36</sub>P<sub>2</sub>N]<sup>+</sup><sup>5</sup>. Complex was made multiple times in an attempt to synthesize pure compound (acceptable EA) however silica grease impurities (observed in <sup>1</sup>H NMR) caused the carbon analyses to be low. The compound could therefore not be isolated as 100% pure.

R<sup>1</sup> = CH<sub>2</sub>Ph, R<sup>2</sup> = H **5e**: In a nitrogen filled glovebox, **4e** (0.075 g, 0.13 mmol) was dissolved in 2 mL of THF and brought up in a syringe and stoppered. In a separate flask in the nitrogen filled glovebox, LiAlH<sub>4</sub> (0.010 g, 0.26 mmol) was dissolved in 4 mL of THF, sealed, and transferred to a Schlenk line. The solution was cooled using an ice bath to 0°C, and the solution of P-N-P' ligand was slowly added. The solution was stirred at 0°C for 30 minutes, room temperature for 1 hour and then refluxed under argon for 18 hours. The solution was cooled in an ice bath and 0.5 mL of water was added to quench any excess LiAlH<sub>4</sub>, then the solution was filtered under air through a frit to remove any lithium salts, and washed with 3 mL of THF. 10 mL of water was added to wash the solution, and the aqueous phase was further washed with 10 mL of DCM. The combined organics were washed with saturated NH<sub>4</sub>Cl solution (10 mL), brine (10 mL) and water (10 mL), dried with MgSO<sub>4</sub>, filtered, and dried under reduced pressure to yield a clear oil that solidified on standing. Yield = 66 mg = 89%.

<sup>1</sup>H NMR (400MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ: 7.0-7.3 (m, 26H, Ar-CH), 6.97 (m, 2H, Ar-CH), 6.74 (m, 1H, Ar-CH), 3.80 (d, 2H, N-CH<sub>2</sub>-Ph, <sup>3</sup>J<sub>HH</sub> = 2.0 Hz), 2.76 (m, 1H, N-CH), 2.70 (m, 2H, CH<sub>2</sub>-P), 2.03 (d, 2H, CH<sub>2</sub>-Ph, <sup>3</sup>J<sub>HH</sub> = 6.1 Hz) and 1.20 (br-s, 1H, NH) ppm. <sup>31</sup>P {<sup>1</sup>H} (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ: -16.0 (s), -23.4 (s) ppm. <sup>13</sup>C {<sup>1</sup>H} (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ: 132-134 (Ar-C and P-Ar-C), 126-129 (Ar-C and P-Ar-C), 56.2 (N-CH), 49.0 (N-CH<sub>2</sub>-Ph) 41.2 (CH<sub>2</sub>-

P) and 33.3 (CH<sub>2</sub>-Ph) ppm. Anal. Calcd. For [C<sub>40</sub>H<sub>37</sub>P<sub>2</sub>N]: C 80.92, H 6.28, N 2.36, Found: Due to glassy nature of compound, sample could not be extracted for EA. NMR shows small signal for silica grease impurity, therefore compound could not be made 100% pure. MS (ESI, m/z<sup>+</sup>): 594.2 [C<sub>40</sub>H<sub>38</sub>P<sub>2</sub>N]<sup>+</sup>.

R<sup>1</sup> = *i*Pr, R<sup>2</sup> = H **5f**: In a nitrogen filled glovebox, **4f** (0.133 g, 0.24 mmol) was dissolved in 2 mL of THF and brought up in a syringe and stoppered. In a separate flask in the nitrogen filled glovebox, LiAlH<sub>4</sub> (0.020 g, 0.52 mmol) was dissolved in 6 mL of THF, sealed, and transferred to a Schlenk line. The solution was cooled using an ice bath to 0°C, and the solution of P-N-P' ligand was slowly added. The solution was stirred at 0°C for 30 minutes, room temperature for 1 hour and then refluxed under argon for 18 hours. The solution was cooled in an ice bath and 0.5 mL of water was added to quench any excess LiAlH<sub>4</sub>, then the solution was filtered under air through a frit to remove any lithium salts, and washed with 4 mL of THF. 15 mL of water was added to wash the solution, and the aqueous phase was further washed with 3x10 mL of DCM. The combined organics were washed with saturated NH<sub>4</sub>Cl solution (15 mL), brine (15 mL) and water (15 mL), dried with MgSO<sub>4</sub>, filtered, and dried under reduced pressure to yield a clear oil. Yield = 120 mg = 90%.

<sup>1</sup>H NMR (400MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ: 7.21-7.45 (m, 22H, Ph-CH), 7.15 (td, 1H, Ph-CH, J = 1.4 and 7.5 Hz), 6.86 (ddd, 1H, Ph-CH, J = 1.3, 4.5 and 7.7 Hz), 4.28 (m, 1H, N-CH<sub>2</sub>), 4.17 (m, 1H, N-CH<sub>2</sub>), 3.88 (m, 2H, CH<sub>2</sub>-P), 2.40 (m, 1H, N-CH), 1.95 (m, 1H, *i*Pr-CH), 1.62 (br-m, 1H, NH) and 0.79 (dd, 6H, *i*Pr-CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.8 and 3.7 Hz) ppm. <sup>31</sup>P {<sup>1</sup>H} (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ: -16.09 (s), -22.15 (s) ppm. <sup>13</sup>C {<sup>1</sup>H} (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ: 127-134 (Ph-C), 62.07 (N-CH<sub>2</sub>), 59.80 (N-CH), 49.89 (CH<sub>2</sub>-P) 20.31 (*i*Pr-CH) and 17.10 (*i*Pr-CH<sub>3</sub>) ppm. Anal. Calcd. For [C<sub>36</sub>H<sub>37</sub>P<sub>2</sub>N]: C 79.24, H 6.84, N 2.57, Anal. Calcd. For [C<sub>36</sub>H<sub>37</sub>P<sub>2</sub>N]-2H<sub>2</sub>O (observed in <sup>1</sup>H NMR, from aqueous workup steps): C 74.30, H 7.10, N 2.40, Found: C 74.69, H 7.81, N 1.58. MS (ESI, m/z<sup>+</sup>): 546.2 [C<sub>36</sub>H<sub>38</sub>P<sub>2</sub>N]<sup>+</sup>.

### Synthesis of [Fe(P-N-P')(NCMe)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub> **6a,c-g**

R<sup>1</sup> = R<sup>2</sup> = H **6a**: In a nitrogen filled glovebox, **4a** (0.097 g, 0.19 mmol) and [Fe(H<sub>2</sub>O)<sub>6</sub>][BF<sub>4</sub>]<sub>2</sub> (0.065 g, 0.19 mmol) were stirred in 12 mL of acetonitrile for 16 hours. The solution was then concentrated to 1.5 mL and washed with pentane (2 x 6 mL). The acetonitrile layer was then dried to yield pure product as a deep red solid. Yield = 160 mg = 98%.

<sup>1</sup>H NMR (400MHz, CD<sub>3</sub>CN) δ: 8.75 (s, 1H, N=CH), 7.45-7.93 (m, 23H, Ph-CH), 7.40 (m, 1H, Ph-CH), 3.84 (dt, 2H, N-CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 14.0 and 6.8 Hz), 3.02 (dt, 2H, CH<sub>2</sub>-PPh<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 6.4 and 2.9 Hz) and 1.99 (s, NC-CH<sub>3</sub>/NC-CD<sub>3</sub>) ppm. <sup>31</sup>P {<sup>1</sup>H} (161 MHz, CD<sub>3</sub>CN) δ: Extreme second order doublets centered at 54.94 ppm,

apparent coupling  $^2J_{PP} = 151.7$  Hz).  $^{13}\text{C}$   $\{^1\text{H}\}$  (100 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 176.9 (N=CH), 129-137 (Ar-C and P-Ar-C), 117.3 (NCMe), 67.8 (N-CH<sub>2</sub>), 22.7 (CH<sub>2</sub>-PPh<sub>2</sub>) and 0.77 (NC-CH<sub>3</sub>) ppm. Anal. Calcd. For  $[\text{FeC}_{39}\text{H}_{38}\text{P}_2\text{N}_4][\text{BF}_4]_2$ : C 54.8, H 4.5, N 6.6, Found: C 54.22, H 4.48, N 6.59. MS (ESI,  $m/z^+$ ): 278.6  $[\text{FeC}_{33}\text{H}_{29}\text{P}_2\text{N}]^{+2}$  (loss of three MeCN).

$\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{Ph}$  **6c**: In a nitrogen filled glovebox, **4c** (0.038 g, 0.063 mmol) and  $[\text{Fe}(\text{H}_2\text{O})_6][\text{BF}_4]_2$  (0.021 g, 0.063 mmol) were stirred in 4 mL of acetonitrile for 16 hours. The solution was then concentrated to 0.5 mL and washed with pentane (2 x 6 mL). The acetonitrile layer was then dried to yield pure product as a deep red solid. Yield = 58 mg = 97%.

$^1\text{H}$  NMR (400MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 8.67 (s, 1H, N=CH), 7.16-7.92 (m, 27H, Ar-CH and P-Ar-CH), 7.00 (d, 2H, Ar-CH and P-Ar-CH,  $J = 7.45$  Hz), 4.14 (1H, C(Me)H, overlapping – determined indirectly using  $^1\text{H}$ - $^{13}\text{C}$  HSQC), 4.10 (1H, C(Ph)H, overlapping – determined indirectly using  $^1\text{H}$ - $^{13}\text{C}$  HSQC), 1.29 (d, 3H, -CH<sub>3</sub>,  $^3J_{\text{HH}} = 4.71$  Hz), 1.99 (s, 9H, CH<sub>3</sub>CN) ppm.  $^{31}\text{P}$   $\{^1\text{H}\}$  (161 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 72.31 (d,  $^2J_{\text{PP}} = 149.4$  Hz) and 54.31 (d,  $^2J_{\text{PP}} = 149.4$  Hz) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  (100 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 175.5 (N=CH), 127-137 (Ar-C and P-Ar-C), 119.8 (NCMe), 73.38 (C(Me)H), 49.07 (C(Ph)H), 19.22 (-CH<sub>3</sub>) and 0.49 (NCCH<sub>3</sub>) ppm. Anal. Calcd. For  $[\text{FeC}_{46}\text{H}_{44}\text{P}_2\text{N}_4][\text{BF}_4]_2$ : C 58.51, H 4.70, N 5.93, Found: C 55.19, H 4.53, N 4.93.\*\* MS (DART,  $m/z^+$ ): 388.3  $[\text{FeC}_{46}\text{H}_{44}\text{P}_2\text{N}_4]^{2+}$ .

$\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{H}$  **6d**: In a nitrogen filled glovebox, **4d** (0.238 g, 0.41 mmol) and  $[\text{Fe}(\text{H}_2\text{O})_6][\text{BF}_4]_2$  (0.139 g, 0.41 mmol) were stirred in 18 mL of acetonitrile for 16 hours. The solution was then concentrated to 3 mL and washed with pentane (2 x 6 mL). The acetonitrile layer was then dried to yield pure product as a deep red solid. Yield = 365 mg = 97%.

$^1\text{H}$  NMR (400MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 7.92 (N=CH, determined indirectly via  $^1\text{H}$ - $^{13}\text{C}$  HSQC), 7.96 (m, 3H, Ar-CH and P-Ar-CH), 7.84 (m, 2H, Ar-CH and P-Ar-CH), 7.23-7.77 (m, 22H, Ar-CH and P-Ar-CH), 7.16 (m, 2H, Ar-CH and P-Ar-CH), 4.72 (td, 1H, C(Ph)H,  $^3J_{\text{HH}} = 3.4$  and 11.5 Hz), 3.66 (ddd, 1H, CH<sub>2</sub>,  $^3J_{\text{HH}}$  and  $^2J_{\text{HH}} = 4.0$ , 13.0 and 14.7 Hz), 3.26 (ddd, 1H, CH<sub>2</sub>,  $^3J_{\text{HH}}$  and  $^2J_{\text{HH}} = 7.0$ , 12.5 and 14.6 Hz), 1.99 (s, 9H, CH<sub>3</sub>CN) ppm.  $^{31}\text{P}$   $\{^1\text{H}\}$  (161 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 54.8 (d,  $^2J_{\text{PP}} = 151$  Hz) and 50.5 (d,  $^2J_{\text{PP}} = 151$  Hz) ppm (roofing doublets).  $^{13}\text{C}$   $\{^1\text{H}\}$  (100 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 176.8 (N=CH), 129-137 (Ar-C and P-Ar-C), 120.8 (NCMe), 77.4 (N-C(Ph)H), 27.4 (CH<sub>2</sub>) and 1.0 (NCCH<sub>3</sub>) ppm. Anal. Calcd. For  $[\text{FeC}_{45}\text{H}_{42}\text{P}_2\text{N}_4][\text{BF}_4]_2$ : C 58.1, H 4.6, N 6.0, Found: C 55.01, H 4.26, N 5.35.\*\* MS (ESI,  $m/z^+$ ): 337  $[\text{C}_{41}\text{H}_{36}\text{P}_2\text{N}_2]^{2+}$  (loss of two MeCN) and 316.6  $[\text{C}_{39}\text{H}_{33}\text{P}_2\text{N}]^{2+}$  (loss of three MeCN).

$\text{R}^1 = \text{CH}_2\text{Ph}$ ,  $\text{R}^2 = \text{H}$  **6e**: In a nitrogen filled glovebox, **4e** (0.086 g, 0.15 mmol) and  $[\text{Fe}(\text{H}_2\text{O})_6][\text{BF}_4]_2$  (0.049 g, 0.15 mmol) were stirred in 8 mL of acetonitrile for 16 hours. The solution was then concentrated to 1.5

mL and washed with pentane (2 x 6 mL). The acetonitrile layer was then dried to yield pure product as a deep red solid. Yield = 136 mg = 96%.

$^1\text{H}$  NMR (400MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 8.33 (d, 1H, N=CH,  $^4J_{\text{HH}} = 5.4$  Hz), 7.92 (t, 2H, Ph-CH,  $J = 8.0$  Hz), 7.2-7.8 (m, 25H, Ph-CH), 6.95 (d, 2H, Ph-CH,  $J = 4.8$  Hz), 4.00 (m, 1H, N-CH), 3.27 ( $\text{CH}_2$ -Ph, 1H, overlapping with 3.20 - determined indirectly from  $^1\text{H}$ - $^1\text{H}$  COSY), 3.20 ( $\text{CH}_2$ -PPh $_2$ , 1H, overlapping with 3.27 - determined indirectly from  $^1\text{H}$ - $^1\text{H}$  COSY), 3.08 (dd, 1H,  $\text{CH}_2$ -PPh $_2$ ,  $^3J_{\text{HH}}$  and  $^2J_{\text{HH}} = 7.7$  and 14.0 Hz), 2.80 (m, 1H,  $\text{CH}_2$ -Ph) and 2.00 (s, NC-CH $_3$ /NC-CD $_3$ ) ppm.  $^{31}\text{P}$  { $^1\text{H}$ } (161 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 54.7 (d,  $^2J_{\text{PP}} = 151$  Hz) and 51.7 (d,  $^2J_{\text{PP}} = 151$  Hz) ppm (roofing doublets).  $^{13}\text{C}$  { $^1\text{H}$ } (100 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 176.1 (d, N=CH,  $J = 5.4$  Hz), 127-137 (Ar-C and P-Ar-C), 118.6 (NCMe), 76.1 (N-CH), 39.3 ( $\text{CH}_2$ -PPh $_2$ ), 27.8 ( $\text{CH}_2$ -Ph) and 0.5 (NC-CH $_3$ ) ppm. Anal. Calcd. For  $[\text{FeC}_{46}\text{H}_{44}\text{P}_2\text{N}_4][\text{BF}_4]_2$ : C 58.5, H 4.7, N 5.9, Found: C 56.39, H 5.0, N 5.49.\*\* MS (ESI,  $m/z^+$ ): 606.2  $[\text{FeC}_{36}\text{H}_{35}\text{P}_2\text{N}] \text{Li}^+$  (loss of three MeCN).

$\text{R}^1 = i\text{Pr}$ ,  $\text{R}^2 = \text{H}$  **6f**: In a nitrogen filled glovebox, **4f** (0.099 g, 0.18 mmol) and  $[\text{Fe}(\text{H}_2\text{O})_6][\text{BF}_4]_2$  (0.061 g, 0.18 mmol) were stirred in 10 mL of acetonitrile for 16 hours. The solution was then concentrated to 1.5 mL and washed with pentane (2 x 6 mL). The acetonitrile layer was then dried to yield pure product as a deep red solid. Yield = 152 mg = 94%.

$^1\text{H}$  NMR (400MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 8.58 (s, 1H, N=CH), 7.96 (m, 2H, Ph-CH), 7.4-7.8 (m, 18H, Ph-CH), 7.30 (m, 4H, Ph-CH), 3.74 (dm, 1H, N-CH), 3.32 (m, 1H,  $\text{CH}_2$ -PPh $_2$ ), 2.84 (dd, 1H,  $\text{CH}_2$ -PPh $_2$ ,  $^3J_{\text{HH}}$  and  $^2J_{\text{HH}} = 7.8$  and 14.7 Hz), 1.94 (s, NC-CH $_3$ /NC-CD $_3$ ), 1.25 (m, 1H,  $i\text{Pr}$ -CH), 0.87 (d, 3H,  $i\text{Pr}$ -CH $_3$ ,  $^3J_{\text{HH}} = 6.2$  Hz) and 0.00 (d, 3H,  $i\text{Pr}$ -CH $_3$ ,  $^3J_{\text{HH}} = 6.5$  Hz) ppm.  $^{31}\text{P}$  { $^1\text{H}$ } (161 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 53.8 (d,  $^2J_{\text{PP}} = 151.6$  Hz) and 57.3 (d,  $^2J_{\text{PP}} = 151.6$  Hz) ppm.  $^{13}\text{C}$  { $^1\text{H}$ } (100 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 177.9 (N=CH), 129-138 (Ar-C and P-Ar-C), 121.0 (NCMe), 87.5 (N-CH), 30.0 ( $i\text{Pr}$ -CH), 24.4 ( $\text{CH}_2$ -PPh $_2$ ), 19.2 ( $i\text{Pr}$ -CH $_3$ ), 18.1 ( $i\text{Pr}$ -CH $_3$ ) and 1.2 (NC-CH $_3$ ) ppm. Anal. Calcd. For  $[\text{FeC}_{42}\text{H}_{44}\text{P}_2\text{N}_4][\text{BF}_4]_2$ : C 58.9, H 4.7, N 5.9, Found: C 47.08, H 4.44, N 4.87.\*\* MS (ESI,  $m/z^+$ ): 606.2  $[\text{FeC}_{36}\text{H}_{35}\text{P}_2\text{N}] \text{Li}^+$  (loss of three MeCN).

$\text{R}^1 = \text{R}^2 = \text{Ph}$  **6g**: In a nitrogen filled glovebox, **4g** (0.038 g, 0.058 mmol) and  $[\text{Fe}(\text{H}_2\text{O})_6][\text{BF}_4]_2$  (0.019 g, 0.057 mmol) were stirred in 5 mL of acetonitrile for 16 hours. The solution was then concentrated to 1 mL and washed with pentane (2 x 6 mL). The acetonitrile layer was then dried to yield pure product as a deep red solid. Yield = 55 mg = 96%.

$^1\text{H}$  NMR (400MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 8.15 (s, 1H, N=CH), 6.95-7.80 (m, 34H, Ph-CH), 5.17 (dd, 1H, N-CH(Ph),  $^3J_{\text{HH}} = 13.0$  and 7.3 Hz), 4.88 (dd, 1H, CH(Ph)-PPh $_2$ ,  $^3J_{\text{HH}} = 7.7$  and 13.0 Hz) and 2.00 (s, 9H, NC-CH $_3$ ) ppm.  $^{31}\text{P}$  { $^1\text{H}$ } (161 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 69.79 (d,  $^2J_{\text{PP}} = 148.5$  Hz) and 53.34 (d,  $^2J_{\text{PP}} = 148.5$  Hz).  $^{13}\text{C}$  { $^1\text{H}$ } (100 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 177.9 (N=CH), 127-137 (Ar-C and P-Ar-C), 117.6 (NCMe), 81.7 (N-CH(Ph)), 46.6 (CH(Ph)-PPh $_2$ ) and 0.34

(NC-CH<sub>3</sub>) ppm. Anal. Calcd. For [FeC<sub>51</sub>H<sub>46</sub>P<sub>2</sub>N<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub>: C 60.87, H 4.61, N 5.57, Found: C 59.57, H 4.67, N 5.07. MS (ESI, m/z<sup>+</sup>): 415.2 [FeC<sub>51</sub>H<sub>46</sub>P<sub>2</sub>N<sub>4</sub>]<sup>+2</sup>.

### Synthesis of [Fe(P-NH-P')(NCMe)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub> **7a,c-f**

R<sup>1</sup> = R<sup>2</sup> = H **7a**: In a nitrogen filled glovebox, **5a** (0.103 g, 0.20 mmol) and [Fe(H<sub>2</sub>O)<sub>6</sub>][BF<sub>4</sub>]<sub>2</sub> (0.069 g, 0.20 mmol) were stirred in 14 mL of acetonitrile for 16 hours. The solution was then concentrated to 1.5 mL and washed with pentane (2 x 6 mL). The acetonitrile layer was then dried to yield pure product as a deep red solid. Yield = 167 mg = 98%.

<sup>1</sup>H NMR (400MHz, CD<sub>3</sub>CN) δ: 7.90 (m, 2H, Ph-CH), 7.80 (m, 2H, Ph-CH), 7.45-7.75 (m, 17H, Ph-CH), 7.37 (t, 1H, Ph-CH, J = 8.3 Hz), 7.28 (m, 2H, Ph-CH), 3.54 (dd, 1H, Ph-CH<sub>2</sub>-NH, <sup>3</sup>J<sub>HH</sub> and <sup>4</sup>J<sub>HH</sub> = 13.0 and 3.8 Hz), 3.44 (t, 1H, CH<sub>2</sub>-PPh<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 14.6 Hz), 3.19 (m, 1H, Ph-CH<sub>2</sub>-NH), 3.10 (m, 1H, NH-CH<sub>2</sub>-CH<sub>2</sub>), 2.49 (m, 1H, CH<sub>2</sub>-PPh<sub>2</sub>), 2.38 (m, 1H, NH), 2.32 (m, 1H, NH-CH<sub>2</sub>-CH<sub>2</sub>) and 1.99 (s, NC-CH<sub>3</sub>/NC-CD<sub>3</sub>) ppm. <sup>31</sup>P {<sup>1</sup>H} (161 MHz, CD<sub>3</sub>CN) δ: 58.69 (d, <sup>2</sup>J<sub>PP</sub> = 141.9 Hz) and 43.74 (d, <sup>2</sup>J<sub>PP</sub> = 141.9 Hz) ppm. <sup>13</sup>C {<sup>1</sup>H} (100 MHz, CD<sub>3</sub>CN) δ: 127-141 (Ar-C and P-Ar-C), 119.1 (NCMe), 57.3 (Ph-CH<sub>2</sub>-NH), 53.8 (HN-CH<sub>2</sub>-CH<sub>2</sub>), 24.2 (CH<sub>2</sub>-PPh<sub>2</sub>) and 0.49 (NC-CH<sub>3</sub>) ppm. Anal. Calcd. For [FeC<sub>39</sub>H<sub>40</sub>P<sub>2</sub>N<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub>: C 54.7, H 4.7, N 6.5, Found: C 53.22, H 4.96, N 6.27. \*\* MS (ESI, m/z<sup>+</sup>): 339.3 [FeC<sub>39</sub>H<sub>40</sub>P<sub>2</sub>N<sub>4</sub>]<sup>2+</sup>, 318.1 (loss of MeCN), 300.1 (loss of two MeCN) and 279.6 (loss of three MeCN).

R<sup>1</sup> = Me, R<sup>2</sup> = Ph **7c**: In a nitrogen filled glovebox, **5c** (0.030 g, 0.050 mmol) and [Fe(H<sub>2</sub>O)<sub>6</sub>][BF<sub>4</sub>]<sub>2</sub> (0.017 g, 0.50 mmol) were stirred in 5 mL of acetonitrile for 16 hours. The solution was then concentrated to 1 mL and washed with pentane (2 x 4 mL). The acetonitrile layer was then dried to yield pure product as a bright pink solid. Yield = 47 mg = 99%.

<sup>1</sup>H NMR (500MHz, CD<sub>3</sub>CN) δ: 7.00-7.68 (m, 29H, Ph-CH), 3.99 (dd, 1H, P-C(Ph)H, J = 7.7 and 12.2 Hz), 3.82 (dd, 1H, N-CH<sub>2</sub>, <sup>4</sup>J<sub>HH</sub> and <sup>3</sup>J<sub>HH</sub> = 5.1 and 13.1 Hz), 3.04 (m, 1H, N-CH<sub>2</sub>), 2.88 (m, 1H, N-C(Me)H), 1.99 (s, NC-CH<sub>3</sub>/NC-CD<sub>3</sub>), 1.92 (NH, determined indirectly using <sup>1</sup>H-<sup>1</sup>H-COSY) and 1.17 (d, 3H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 5.8 Hz) ppm. <sup>31</sup>P {<sup>1</sup>H} (202 MHz, CD<sub>3</sub>CN) δ: 74.30 (d, <sup>2</sup>J<sub>PP</sub> = 138.4 Hz) and 43.31 (d, <sup>2</sup>J<sub>PP</sub> = 138.4 Hz) ppm. <sup>13</sup>C {<sup>1</sup>H} (125 MHz, CD<sub>3</sub>CN) δ: 126-137 (Ph-C), 122.0 (NCMe), 62.50 (N-C(Me)H), 52.78 (N-CH<sub>2</sub>), 50.50 (P-C(Ph)H), 17.11 (-CH<sub>3</sub>) and 1.31 (NC-CH<sub>3</sub>) ppm. Anal. Calcd. For [FeC<sub>46</sub>H<sub>46</sub>P<sub>2</sub>N<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub>(extra MeCN in solution, verified by NMR): C 58.39, H 5.00, N 7.09, Found: C 48.80, H 4.58, N 7.85. \*\* MS (ESI, m/z<sup>+</sup>): 656.2 [FeC<sub>40</sub>H<sub>37</sub>P<sub>2</sub>N<sub>4</sub>][Li]<sup>+</sup> (loss of three MeCN).

R<sup>1</sup> = Ph, R<sup>2</sup> = H **7d**: In a nitrogen filled glovebox, **5d** (0.075 g, 0.13 mmol) and [Fe(H<sub>2</sub>O)<sub>6</sub>][BF<sub>4</sub>]<sub>2</sub> (0.044 g, 0.13 mmol) were stirred in 10 mL of acetonitrile for 16 hours. The solution was then concentrated to 1.5

mL and washed with pentane (2 x 6 mL). The acetonitrile layer was then dried to yield pure product as a bright purple solid. Yield = 114 mg = 99%.

$^1\text{H}$  NMR (600MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 7.25-7.88 (m, 28H, Ph-CH), 6.76 (s, 1H, Ph-CH), 3.63 (t, 1H, P-CH<sub>2</sub>,  $^3J_{\text{HH}} = 13.8$  Hz), 3.46 (m, 1H, N-C(Ph)H), 3.15 (m, 1H, N-CH<sub>2</sub>), 2.94 (t, 1H, N-CH<sub>2</sub>), 2.77 (m, 1H, P-CH<sub>2</sub>), 2.00 (NH, determined indirectly using  $^1\text{H}$ - $^1\text{H}$ -COSY) and 1.98 (s, NC-CH<sub>3</sub>/NC-CD<sub>3</sub>) ppm.  $^{31}\text{P}$   $\{^1\text{H}\}$  (242 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 49.07 (d,  $^2J_{\text{PP}} = 139.1$  Hz) and 41.22 (d,  $^2J_{\text{PP}} = 139.1$  Hz) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  (150 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 126-133 (Ph-C), 120.4 (NCMe), 67.24 (N-C(Ph)H), 53.84 (N-CH<sub>2</sub>), 32.92 (P-CH<sub>2</sub>) and 0.68 (NC-CH<sub>3</sub>) ppm. Anal. Calcd. For  $[\text{FeC}_{45}\text{H}_{44}\text{P}_2\text{N}_4][\text{BF}_4]_2$ : C 57.98, H 4.76, N 6.01, Found: C 54.66, H 4.92, N 6.04. \*\* MS (DART,  $m/z^+$ ): 380.2  $[\text{FeC}_{45}\text{H}_{44}\text{P}_2\text{N}_4]^{2+}$ .

$\text{R}^1 = \text{CH}_2\text{Ph}$ ,  $\text{R}^2 = \text{H}$  **7e**: In a nitrogen filled glovebox, **5e** (0.025 g, 0.042 mmol) and  $[\text{Fe}(\text{H}_2\text{O})_6][\text{BF}_4]_2$  (0.014 g, 0.42 mmol) were stirred in 5 mL of acetonitrile for 16 hours. The solution was then concentrated to 1 mL and washed with pentane (2 x 4 mL). The acetonitrile layer was then dried to yield pure product as a bright pink solid. Yield = 38 mg = 95%.

$^1\text{H}$  NMR (600MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 7.06-7.83 (m, 29H, Ph-CH), 3.90 (m, 1H, N-CH<sub>2</sub>), 3.73 (m, 1H, P-CH<sub>2</sub>), 3.13 (m, 1H, CH<sub>2</sub>-Ph), 3.02 (m, 1H, N-CH<sub>2</sub>), 2.71 (m, 1H, N-C(Bn)H), 2.60 (m, 1H, P-CH<sub>2</sub>), 2.23 (m, 1H, Ph-CH<sub>2</sub>), 1.98 (s, NC-CH<sub>3</sub>/NC-CD<sub>3</sub>), 1.97 (NH, determined indirectly using  $^1\text{H}$ - $^1\text{H}$ -COSY) ppm.  $^{31}\text{P}$   $\{^1\text{H}\}$  (242 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 48.82 (d,  $^2J_{\text{PP}} = 139.9$  Hz) and 41.38 (d,  $^2J_{\text{PP}} = 139.9$  Hz) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  (150 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 126-133 (Ph-C), 123.0 (NCMe), 63.78 (N-C(Bn)H), 52.72 (N-CH<sub>2</sub>), 37.87 (P-CH<sub>2</sub>), 30.1 (Ph-CH<sub>2</sub>) and 1.06 (NC-CH<sub>3</sub>) ppm. Anal. Calcd. For  $[\text{FeC}_{46}\text{H}_{46}\text{P}_2\text{N}_4][\text{BF}_4]_2$ : C 58.39, H 4.90, N 5.92, Found: C 49.34, H 4.78, N 5.56. \*\* MS (ESI,  $m/z^+$ ): 656.2  $[\text{FeC}_{40}\text{H}_{37}\text{P}_2\text{N}][\text{Li}]^+$  (loss of three MeCN).

$\text{R}^1 = i\text{Pr}$ ,  $\text{R}^2 = \text{H}$  **7f**: In a nitrogen filled glovebox, **5f** (0.063 g, 0.12 mmol) and  $[\text{Fe}(\text{H}_2\text{O})_6][\text{BF}_4]_2$  (0.039 g, 0.12 mmol) were stirred in 12 mL of acetonitrile for 16 hours. The solution was then concentrated to 2 mL and washed with pentane (2 x 5 mL). The acetonitrile layer was then dried to yield pure product as a bright pink solid. Yield = 88 mg = 83%.

$^1\text{H}$  NMR (400MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 7.22-7.86 (m, 24H, Ph-CH), 4.12 (m, 1H, N-CH(*i*Pr)), 3.66 (m, 1H, N-CH<sub>2</sub>), 3.44 (m, 1H, P-CH<sub>2</sub>), 2.84 (m, 1H, N-CH<sub>2</sub>), 2.13 (P-CH<sub>2</sub>, determined indirectly from  $^{13}\text{C}$ - $^1\text{H}$  HSQC), 1.99 (s, NC-CH<sub>3</sub>/NC-CD<sub>3</sub>), 1.43 (br s, 1H, NH), 1.19 (m, 1H, *i*Pr-CH) and 0.77 (br m, 6H, *i*Pr-CH<sub>3</sub>) ppm.  $^{31}\text{P}$   $\{^1\text{H}\}$  (161 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 49.55 (d,  $^2J_{\text{PP}} = 139.8$  Hz) and 41.25 (d,  $^2J_{\text{PP}} = 139.8$  Hz) ppm.  $^{13}\text{C}$   $\{^1\text{H}\}$  (100 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 128-135 (Ar-C and P-Ar-C), 121.90 (NCMe), 62.01 (N-CH(*i*Pr)) 51.69 (N-CH<sub>2</sub>), 23.95 (P-CH<sub>2</sub>), 20.64 (*i*Pr-CH), 12.55 (*i*Pr-CH<sub>3</sub>) and 0.83 (NC-CH<sub>3</sub>) ppm. Anal. Calcd. For  $[\text{FeC}_{42}\text{H}_{46}\text{P}_2\text{N}_4][\text{BF}_4]_2$ : C 56.16, H 5.16, N 6.23, Found: C 47.42, H 4.38, N 6.23. \*\* MS (ESI,  $m/z^+$ ): 362.2  $[\text{FeC}_{42}\text{H}_{46}\text{P}_2\text{N}_4]^{2+}$  and 608.2  $[\text{FeC}_{36}\text{H}_{37}\text{P}_2\text{N}]\text{Li}^+$ .

## NMR of Complexes

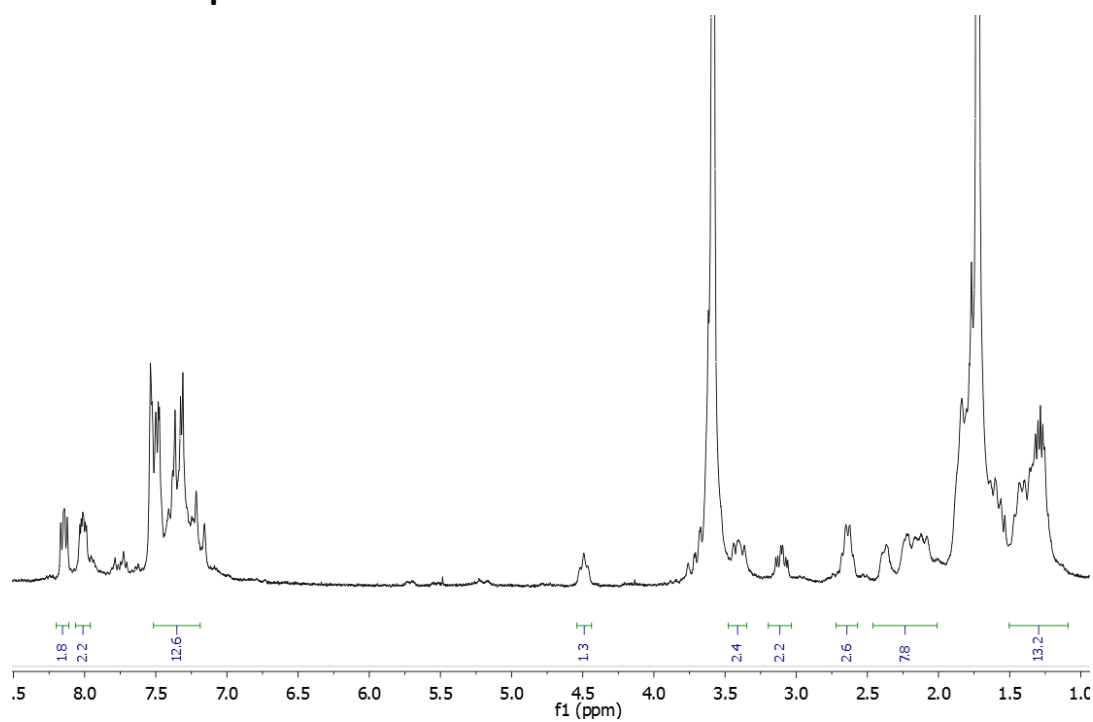


Figure 1:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{THF-d}_8$ ) of **1d**.

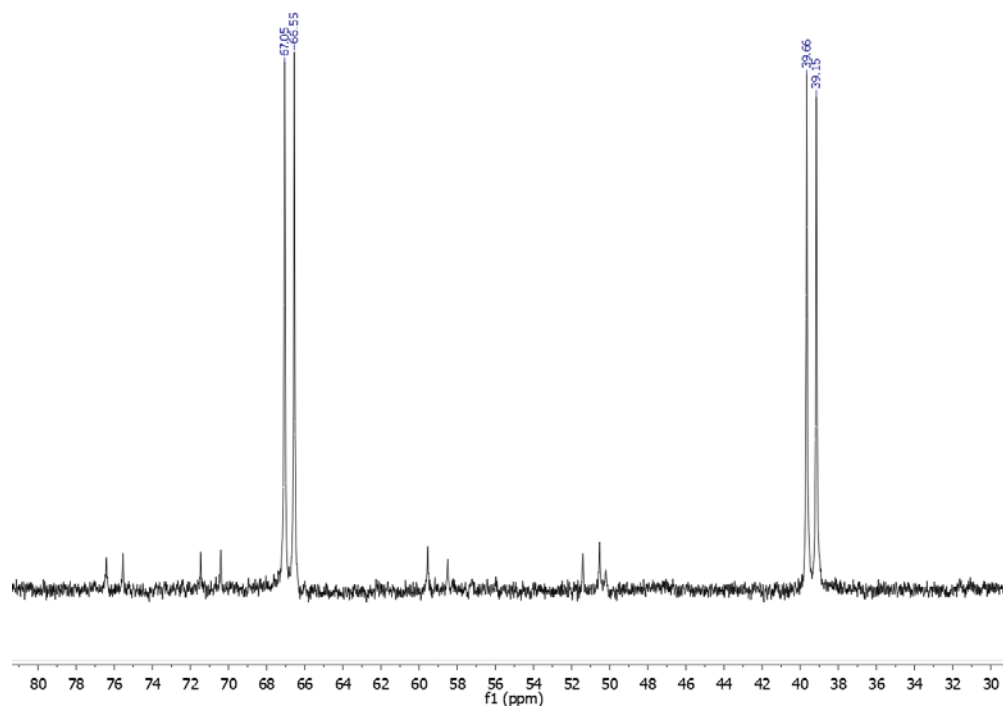


Figure 2:  $^{31}\text{P} \{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{THF-d}_8$ ) of **1d**.

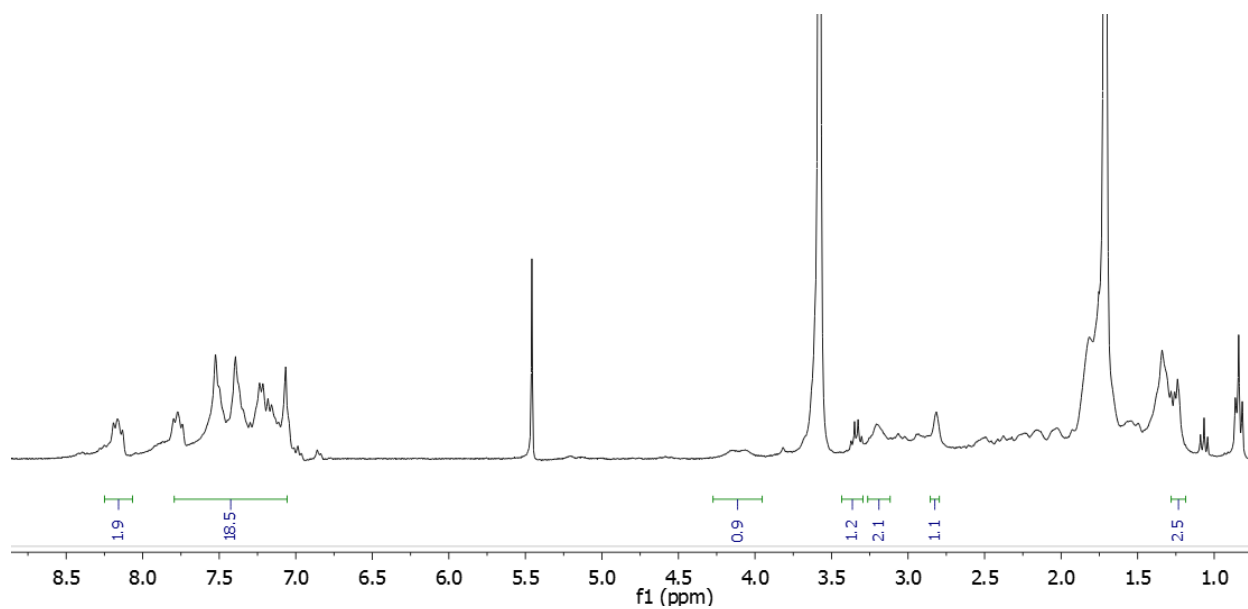


Figure 3:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{THF-d}_8$ ) of 1e. See solvent signal from residual DCM and pentane.

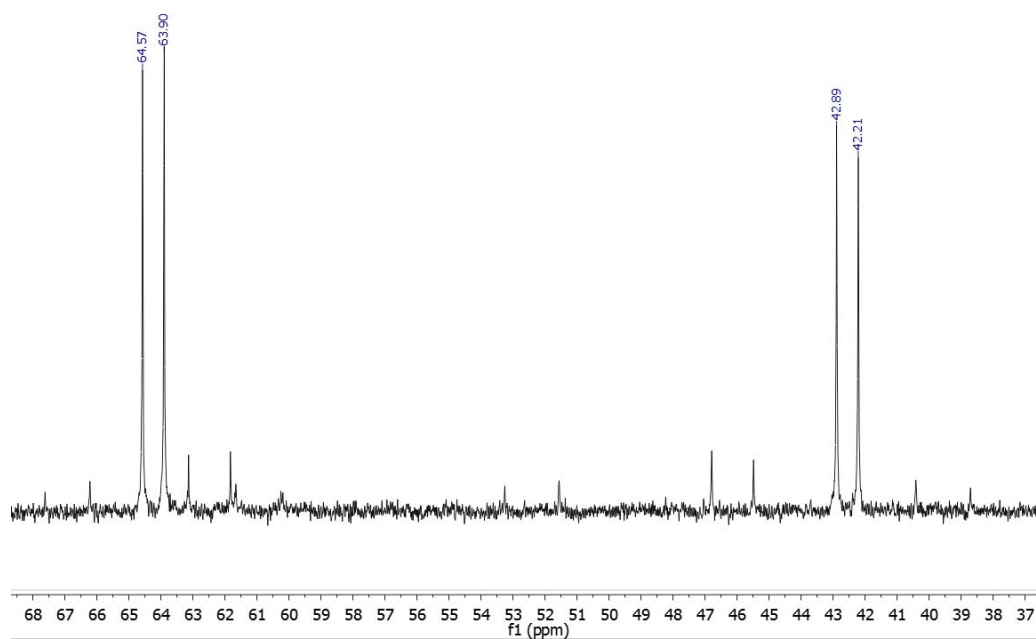


Figure 4:  $^{31}\text{P} \{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{THF-d}_8$ ) of 1e.

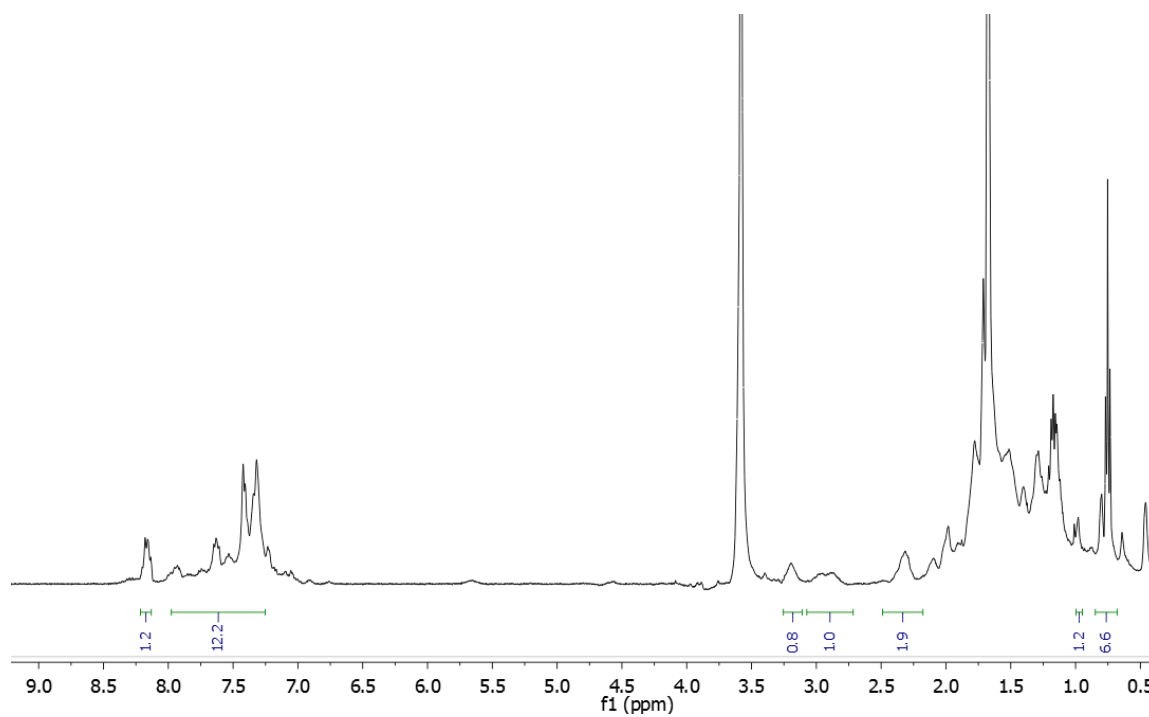


Figure 5:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{THF-d}_8$ ) of **1f**.

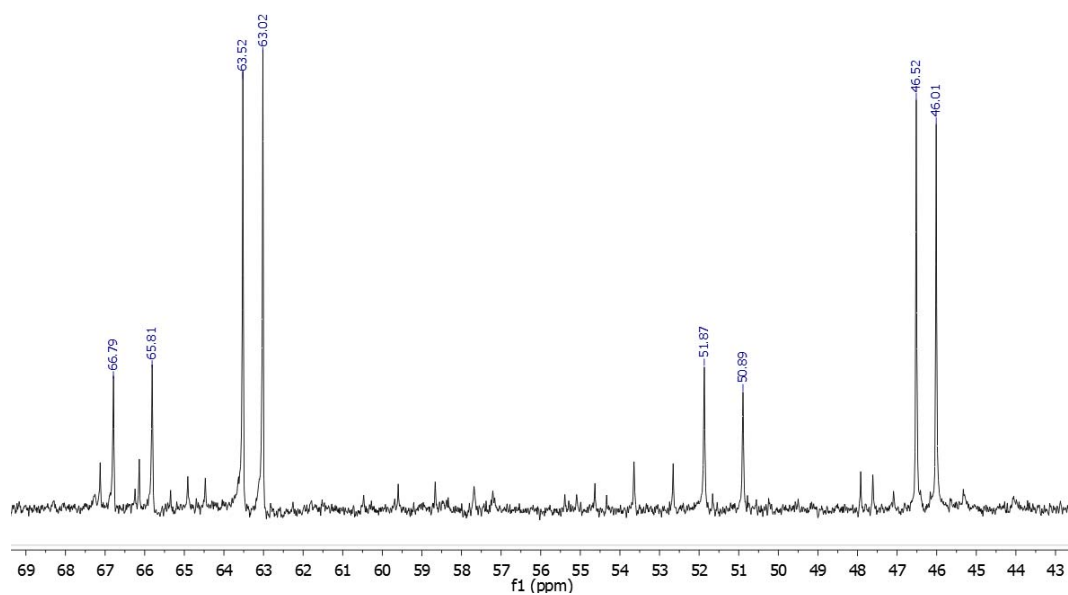


Figure 6:  $^{31}\text{P} \{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{THF-d}_8$ ) of **1f**. See signals for major (trans-CO) and minor (cis-CO).

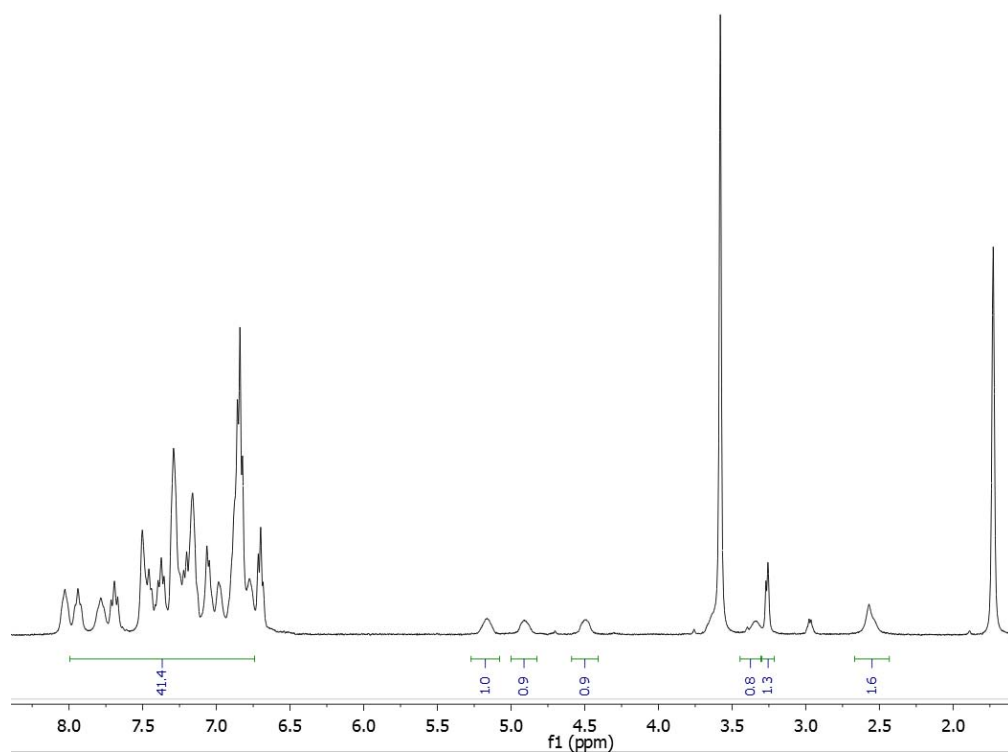


Figure 7:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{THF-d}_8$ ) of 3.

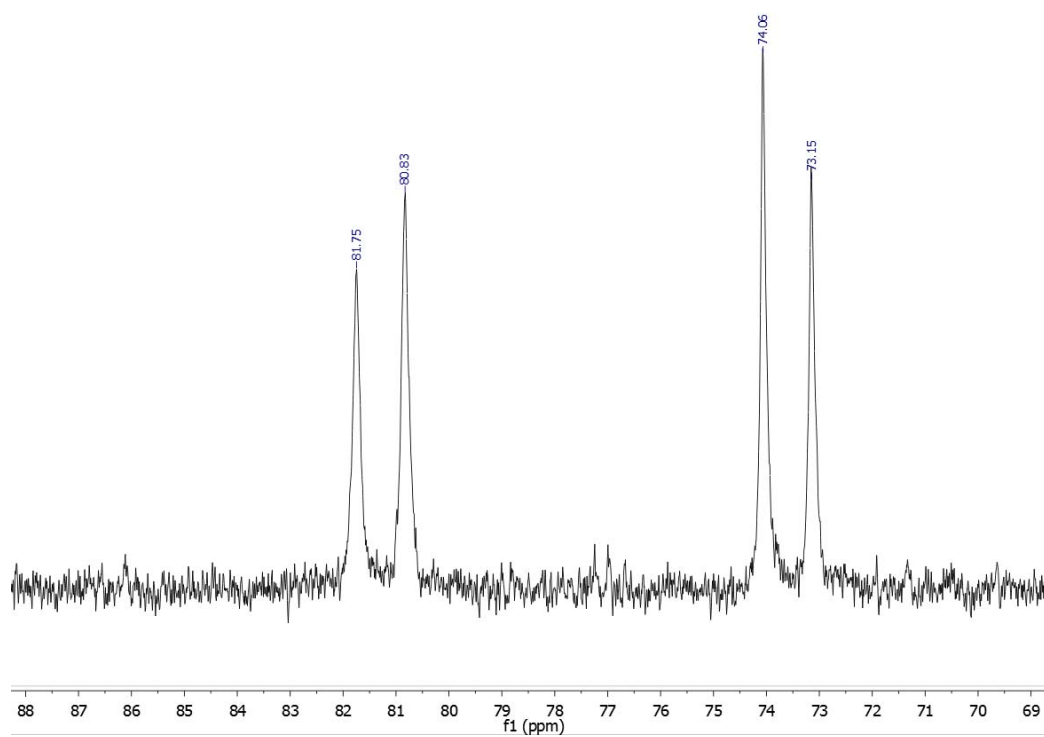


Figure 8:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{THF-d}_8$ ) of 3.

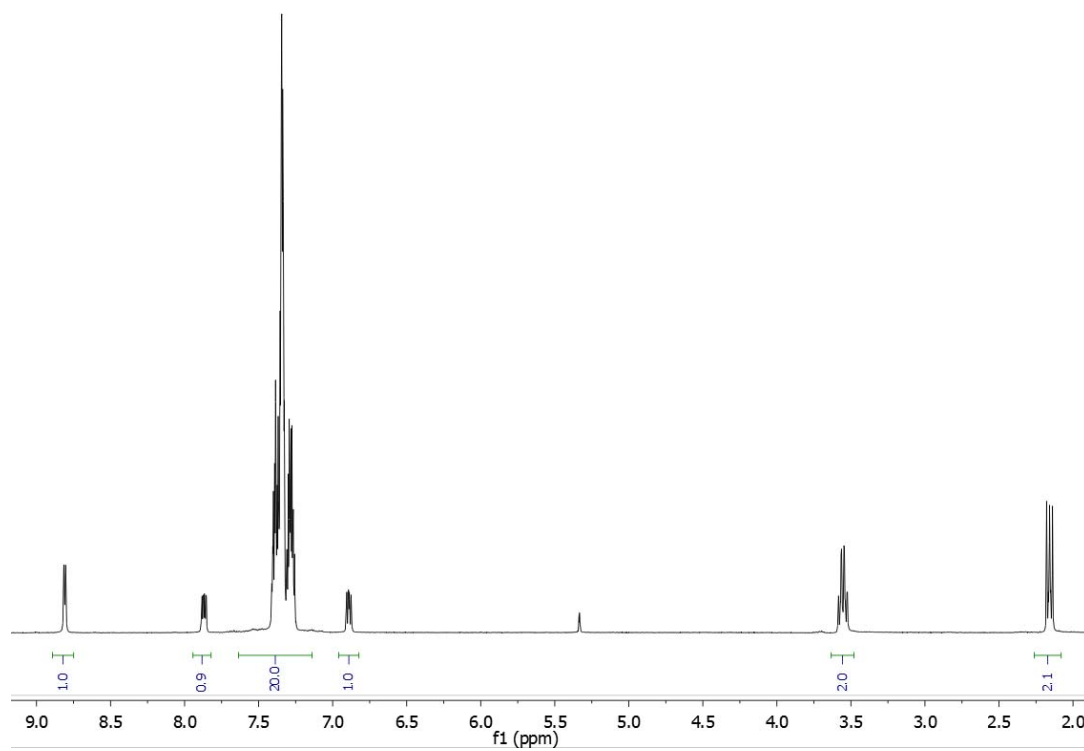


Figure 9: <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of 4a.

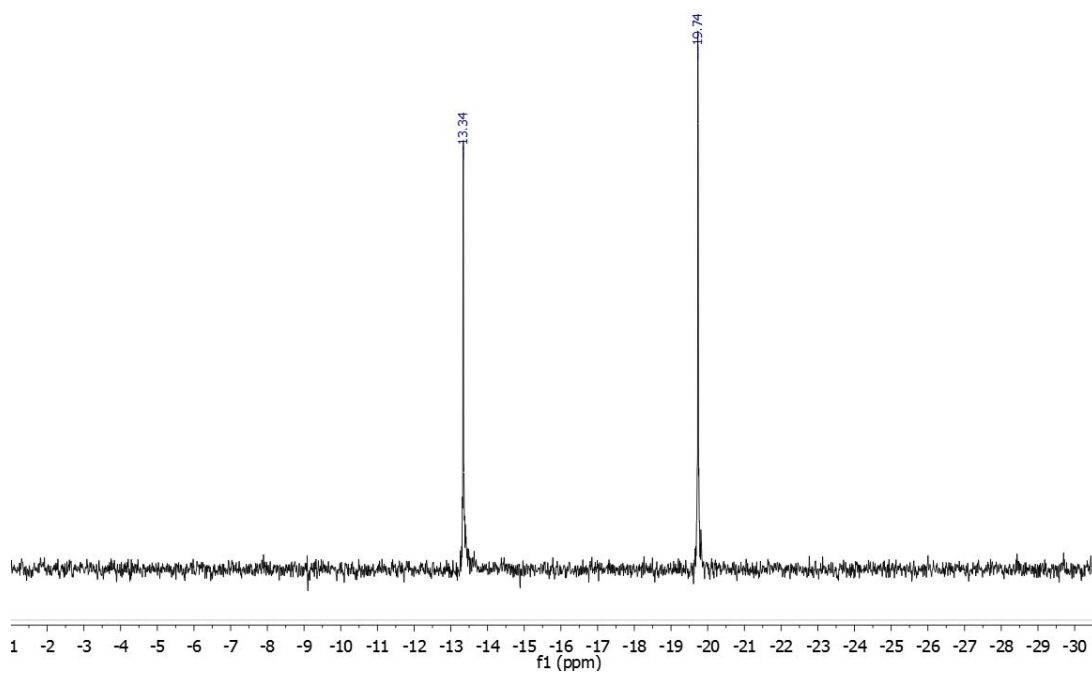


Figure 10: <sup>31</sup>P {<sup>1</sup>H} NMR spectrum (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of 4a.

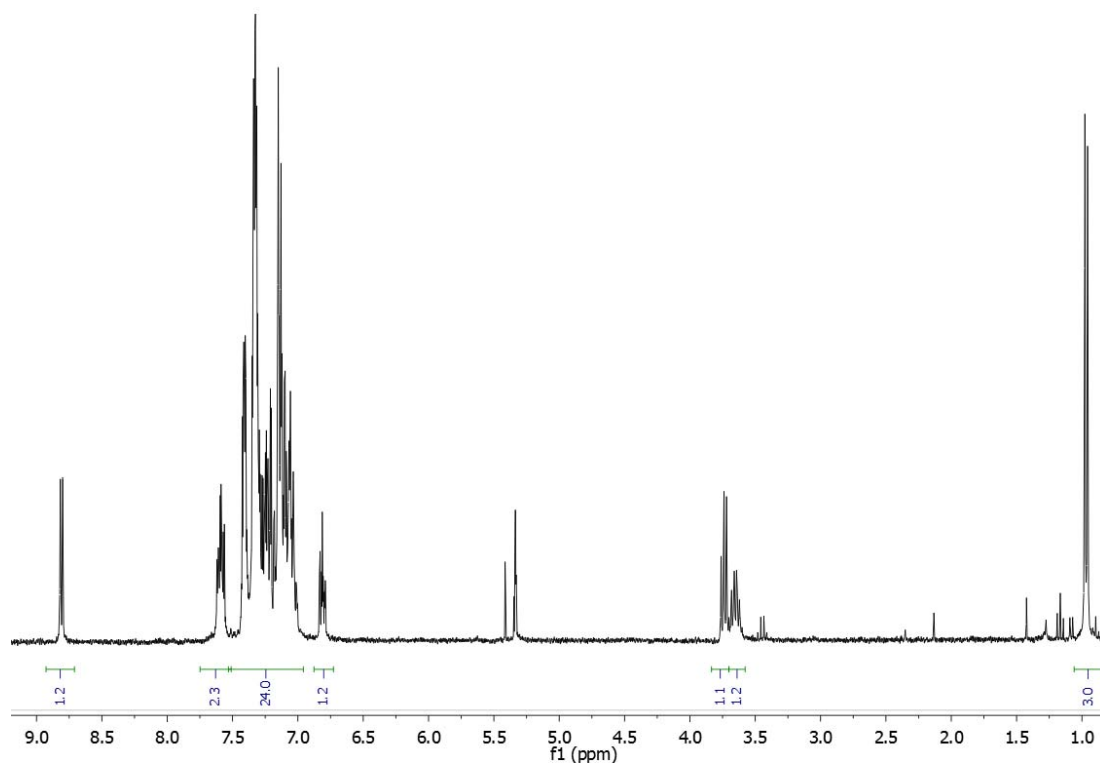


Figure 11: <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of 4c.

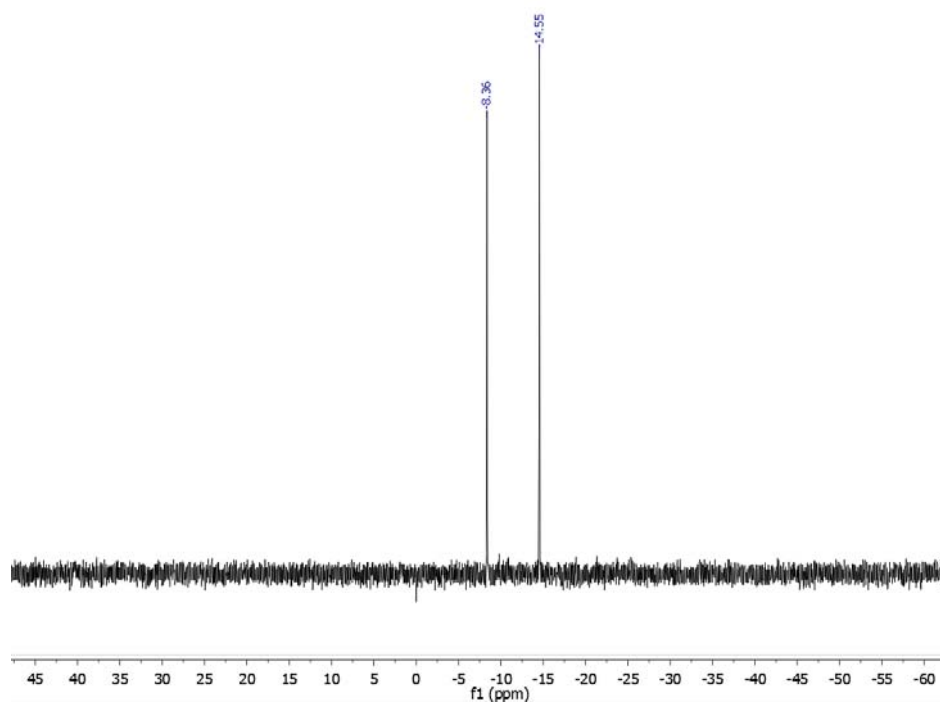


Figure 12: <sup>31</sup>P {<sup>1</sup>H} NMR spectrum (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of 4c.

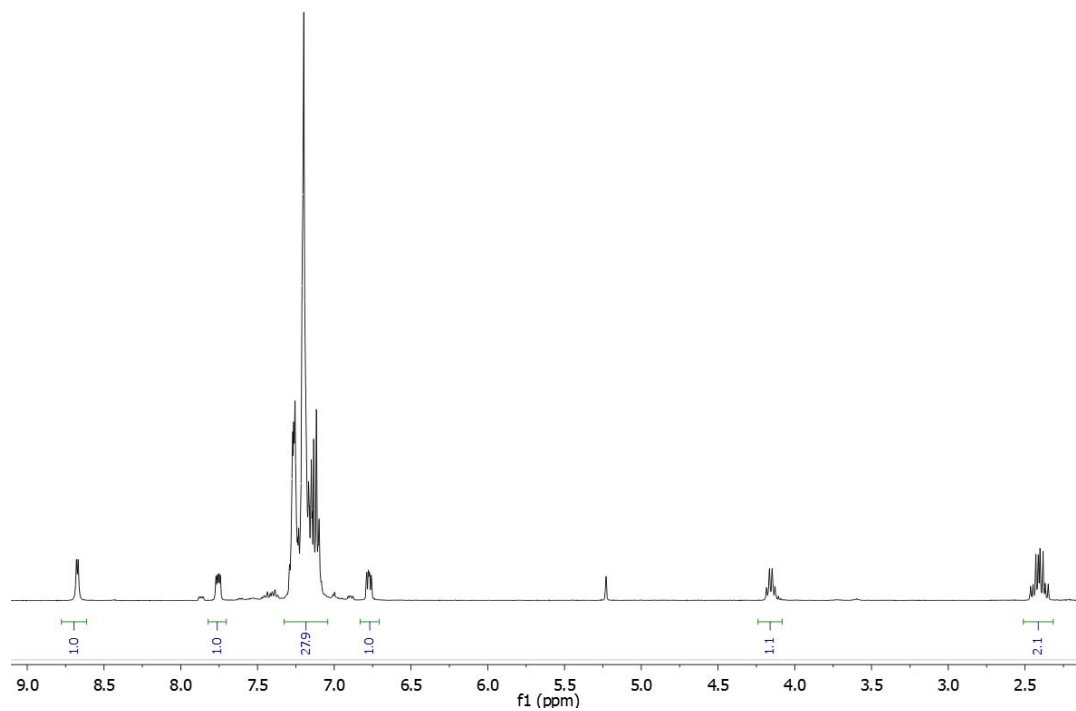


Figure 13:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 4d.

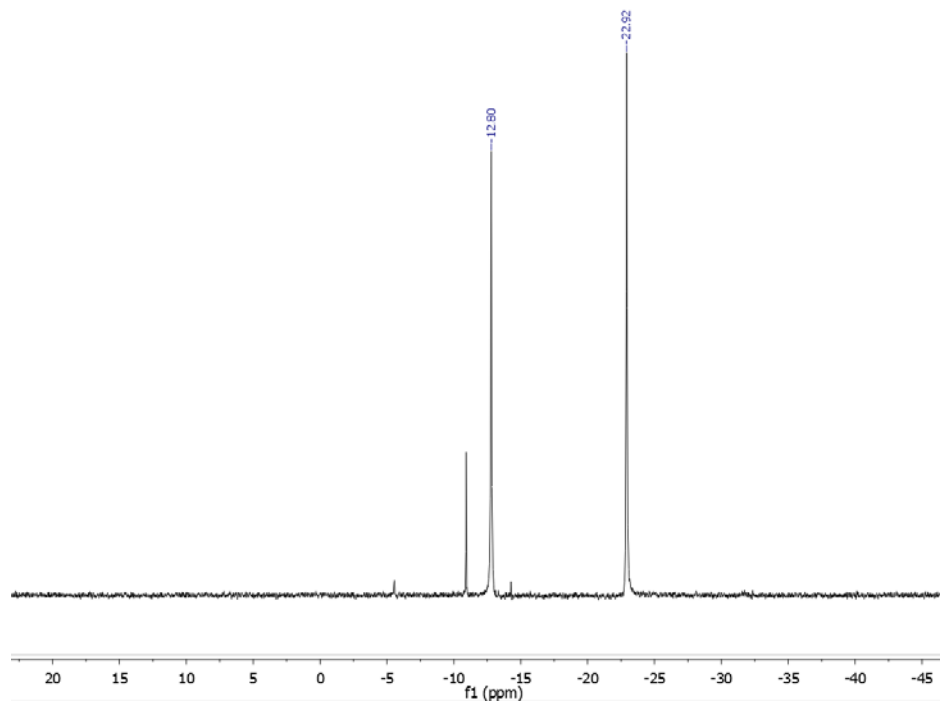


Figure 14:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 4d.

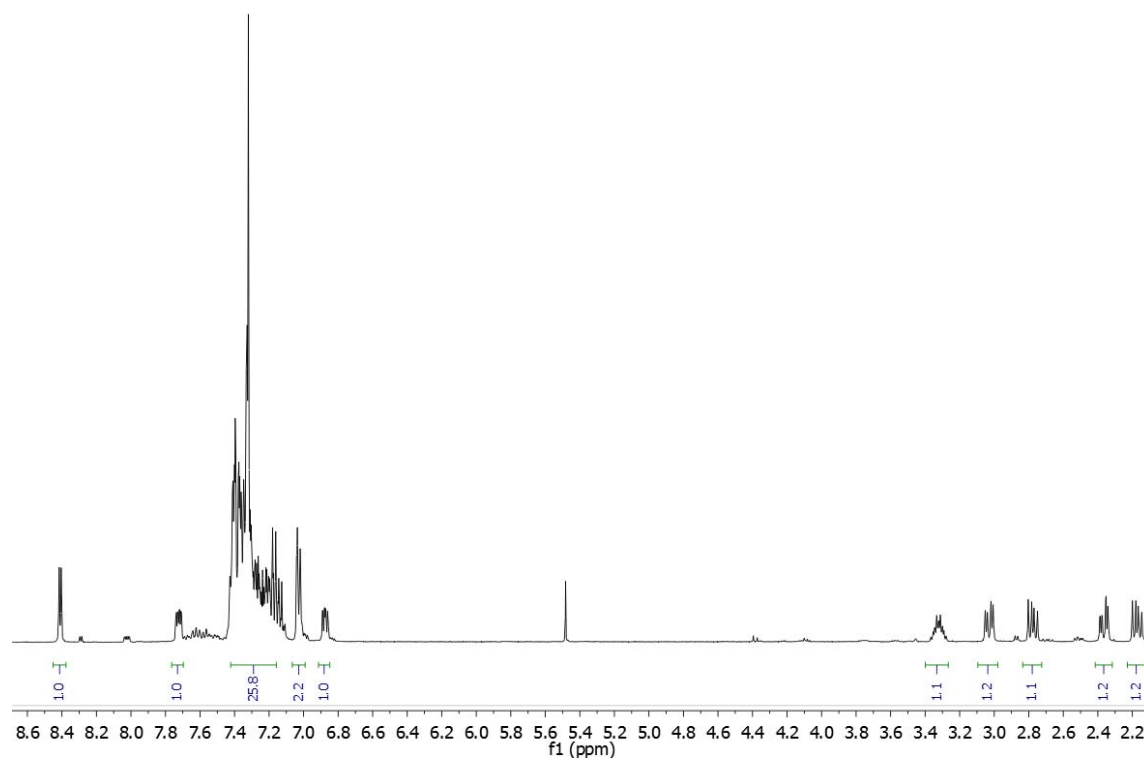


Figure 15: <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of 4e.

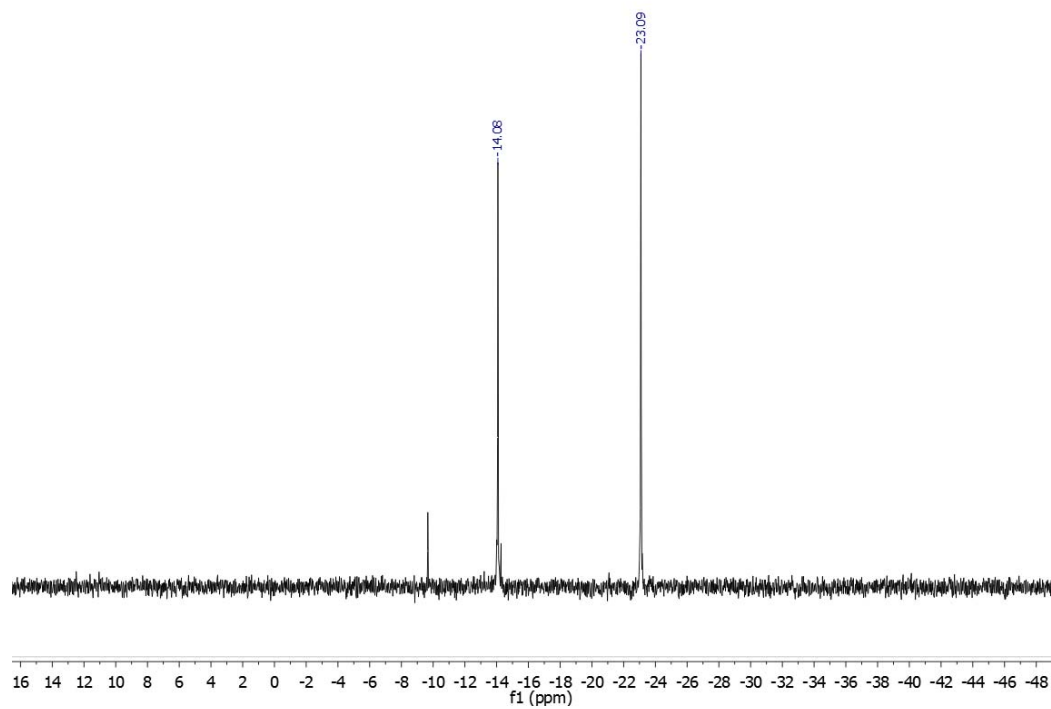


Figure 16: <sup>31</sup>P {<sup>1</sup>H} NMR spectrum (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of 4e.

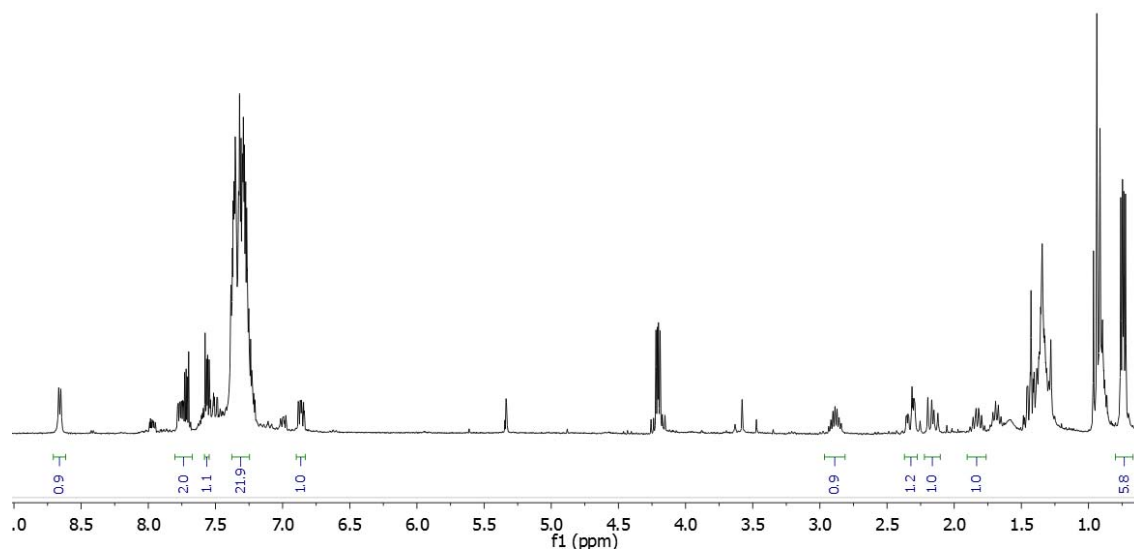


Figure 17:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 4f. Also see water, pentane, and ethyl acetate solvent peaks.

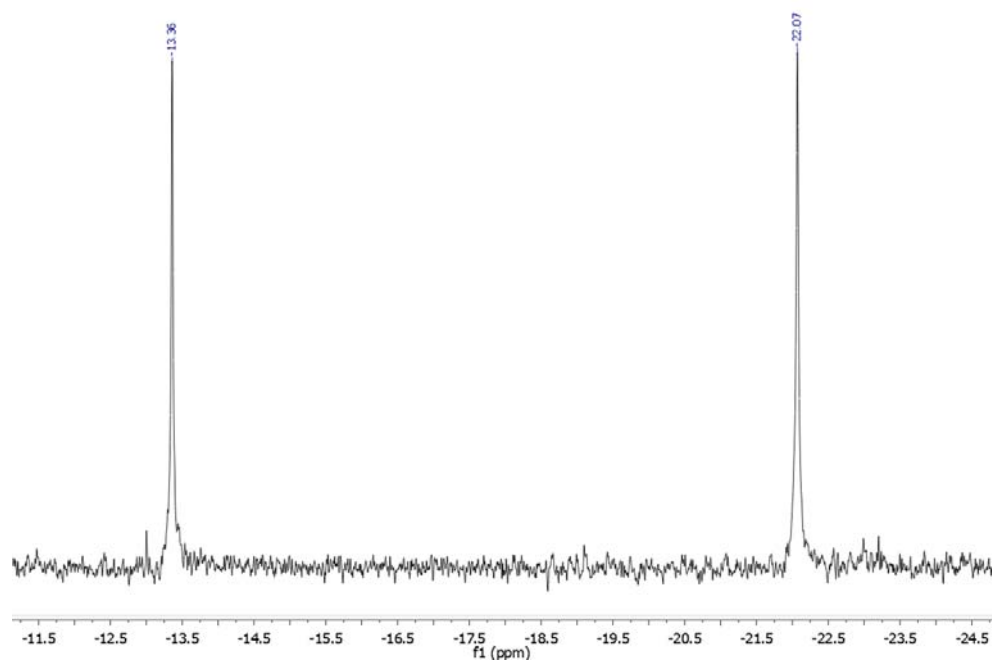


Figure 18:  $^{31}\text{P} \{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 4f.

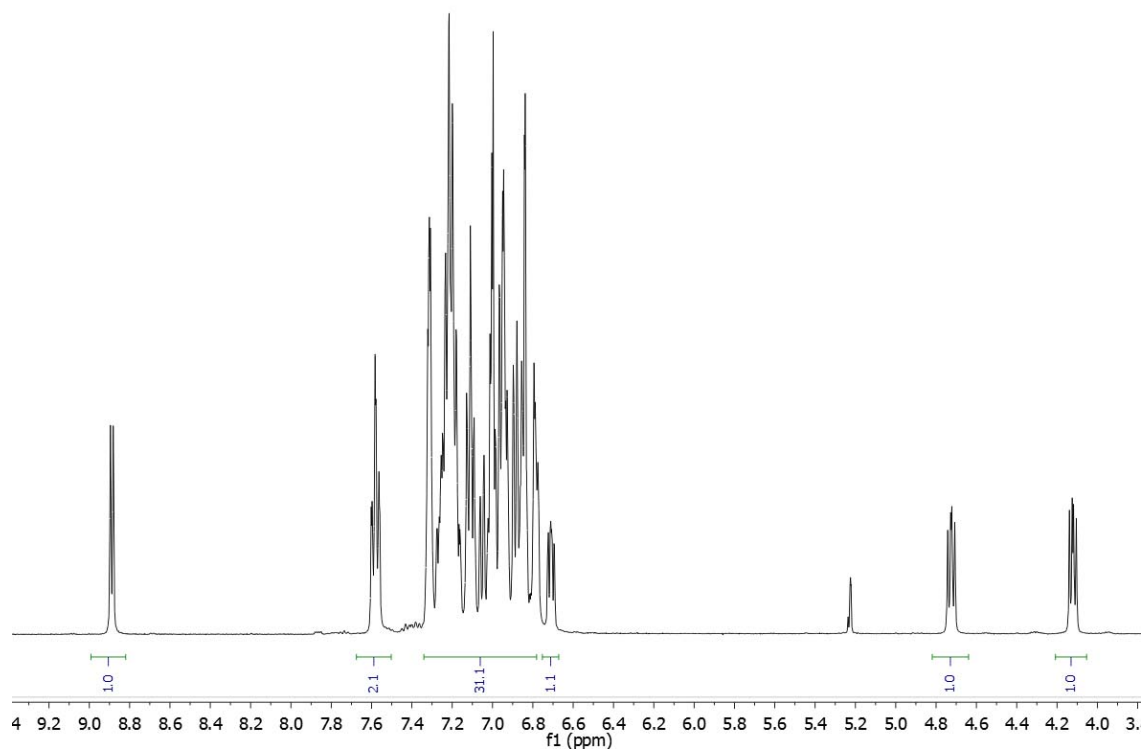


Figure 19:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 4g.

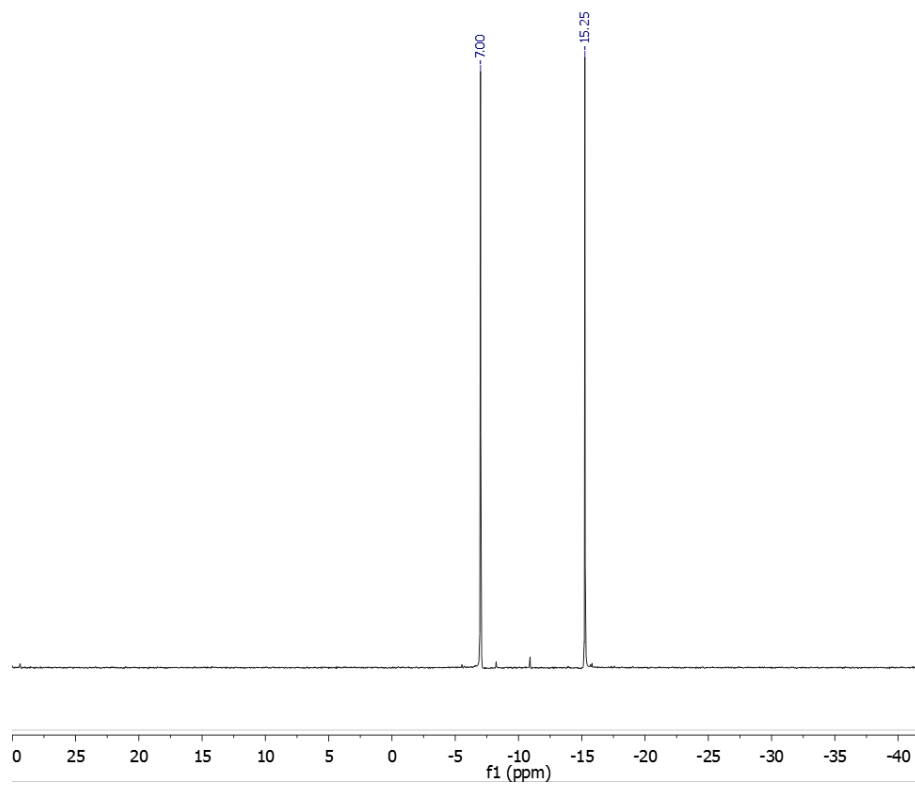


Figure 20:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 4g.

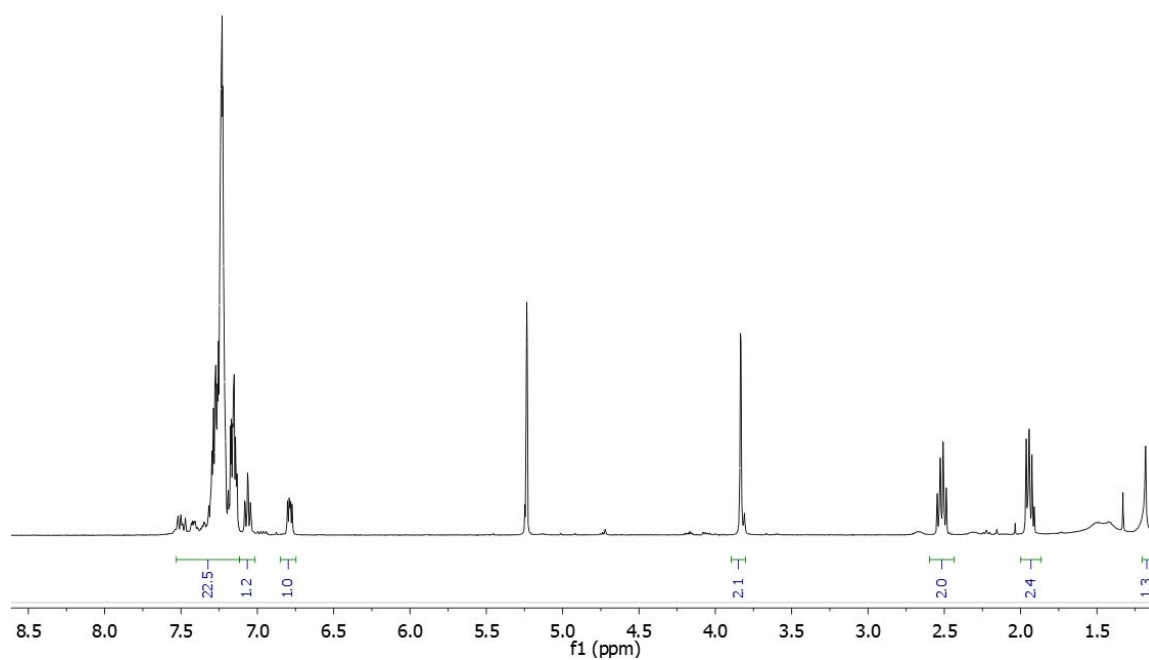


Figure 21:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 5a.

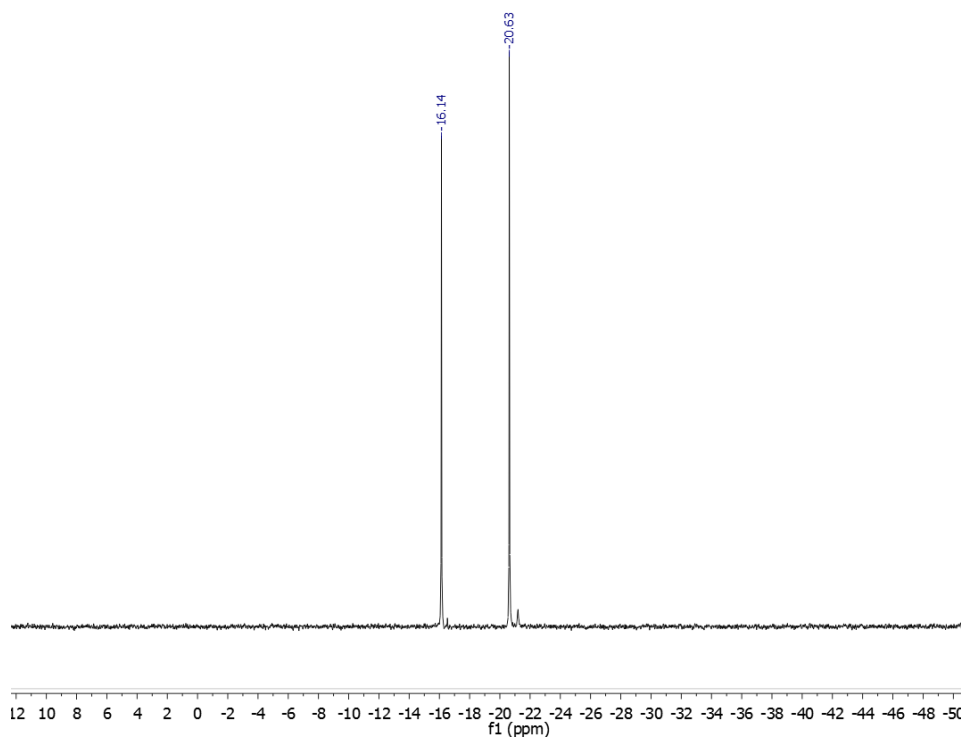


Figure 22:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 5a.

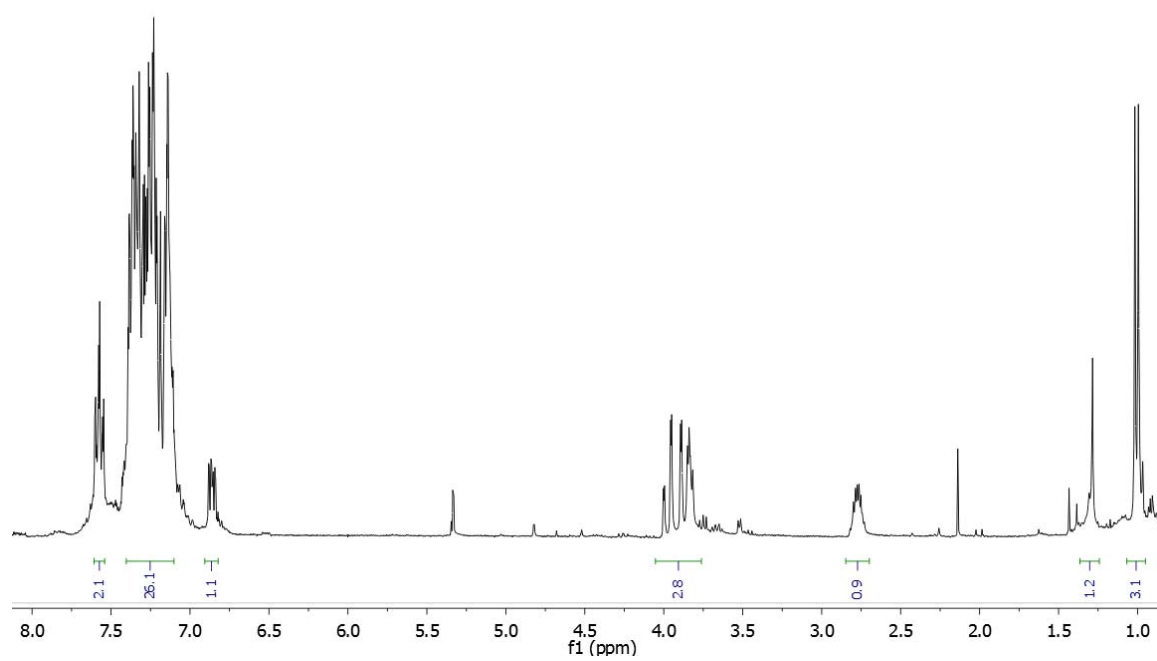


Figure 23:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 5c.

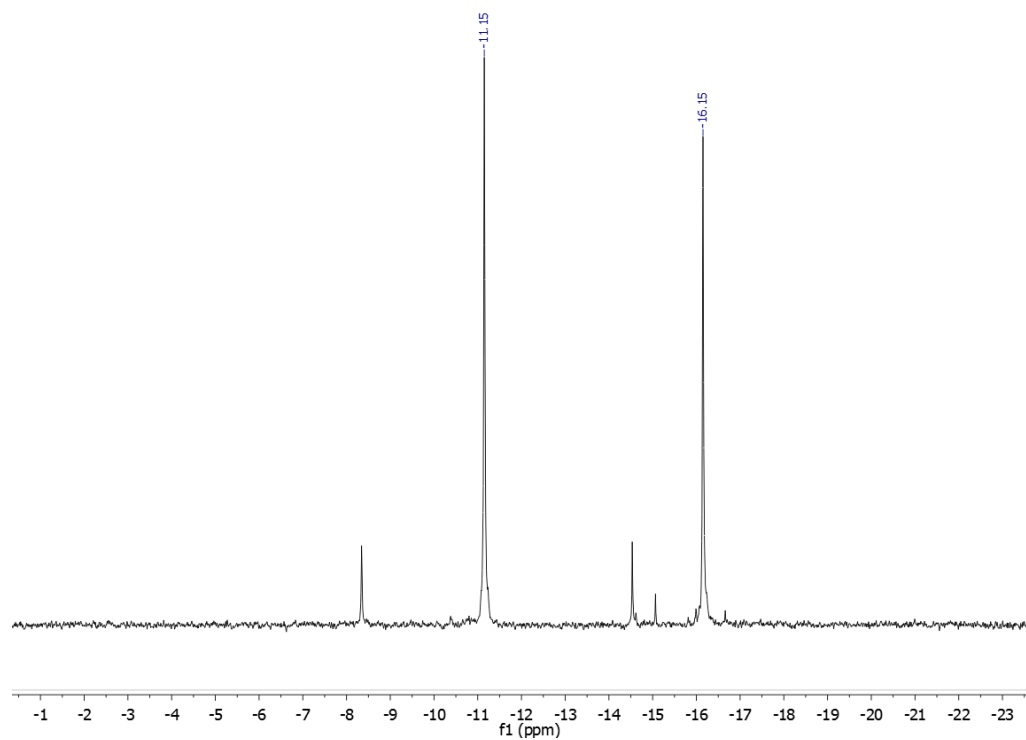


Figure 24:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 5c.

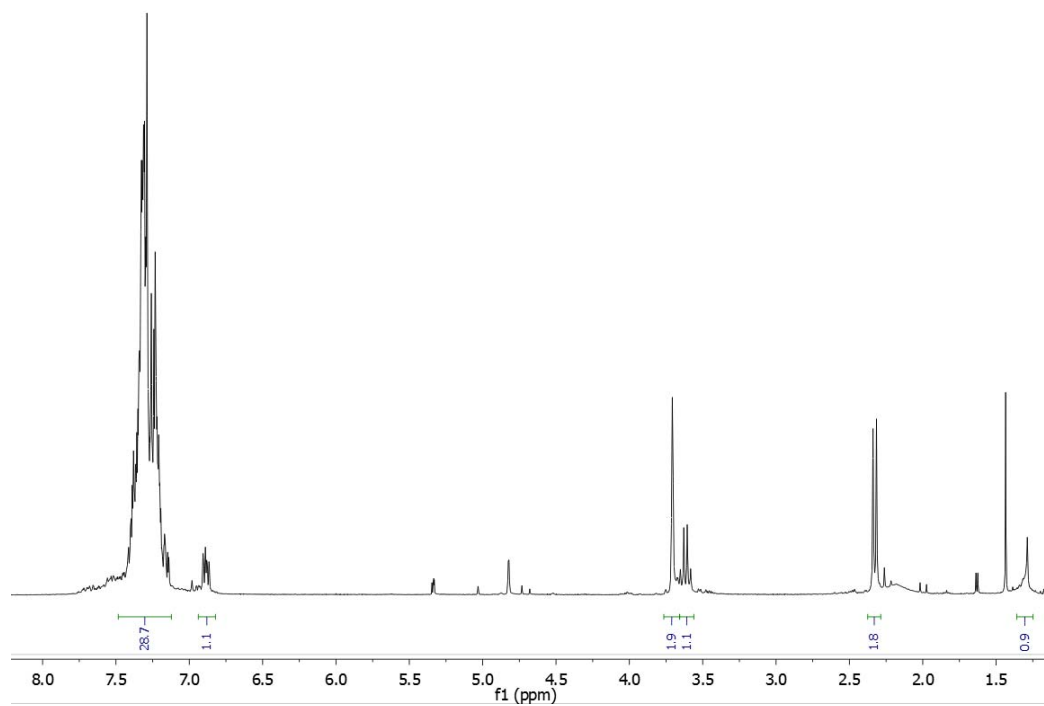


Figure 25:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 5d.

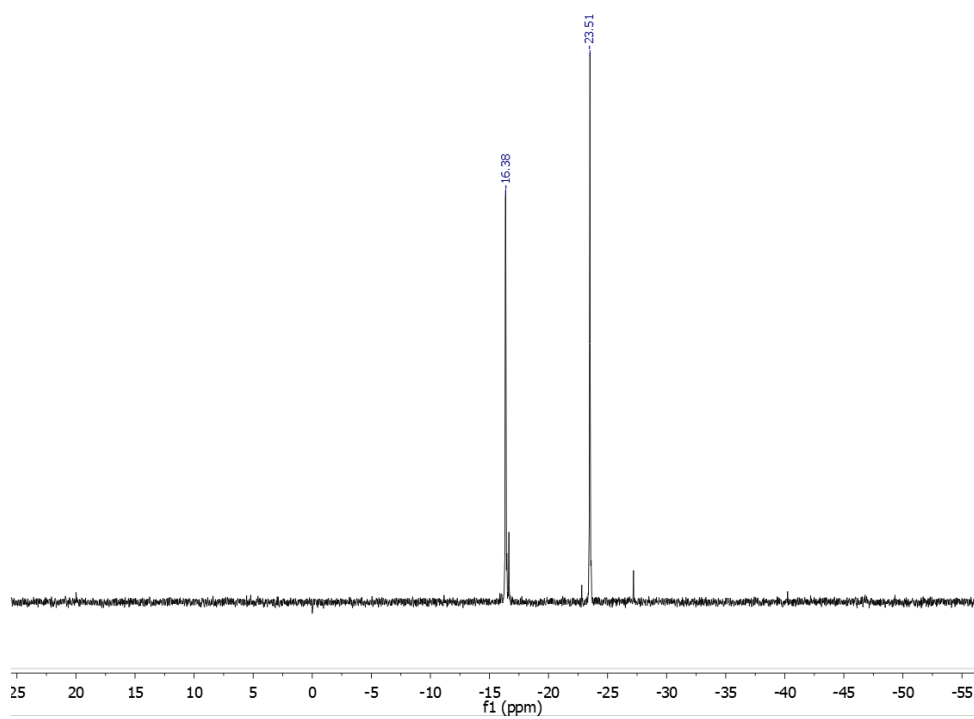


Figure 26:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 5d.

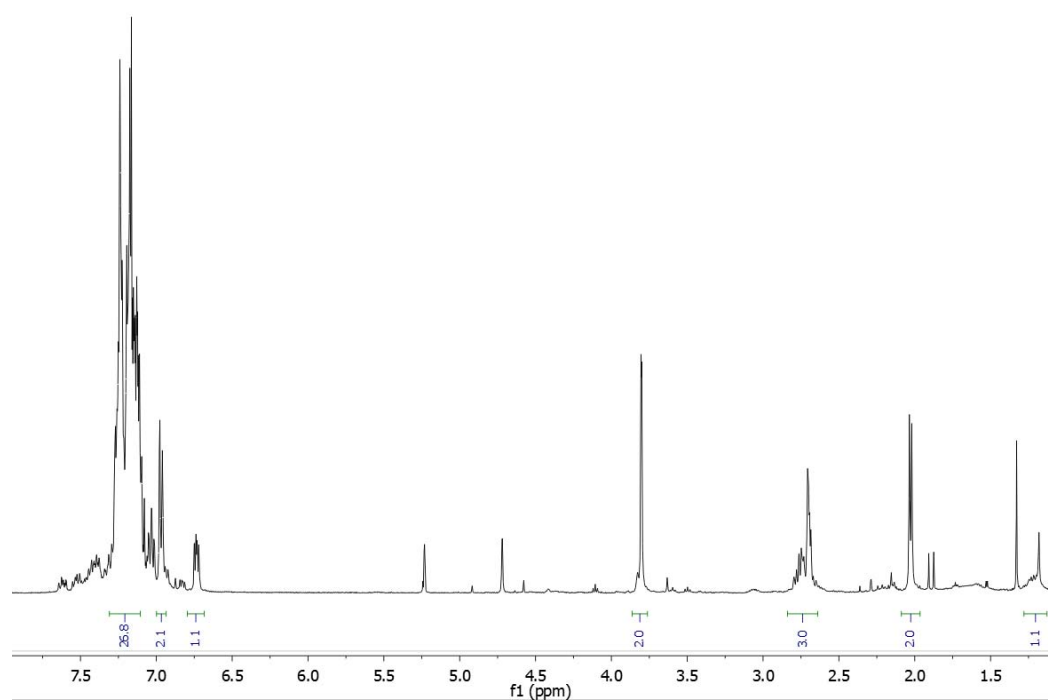


Figure 27:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 5e.

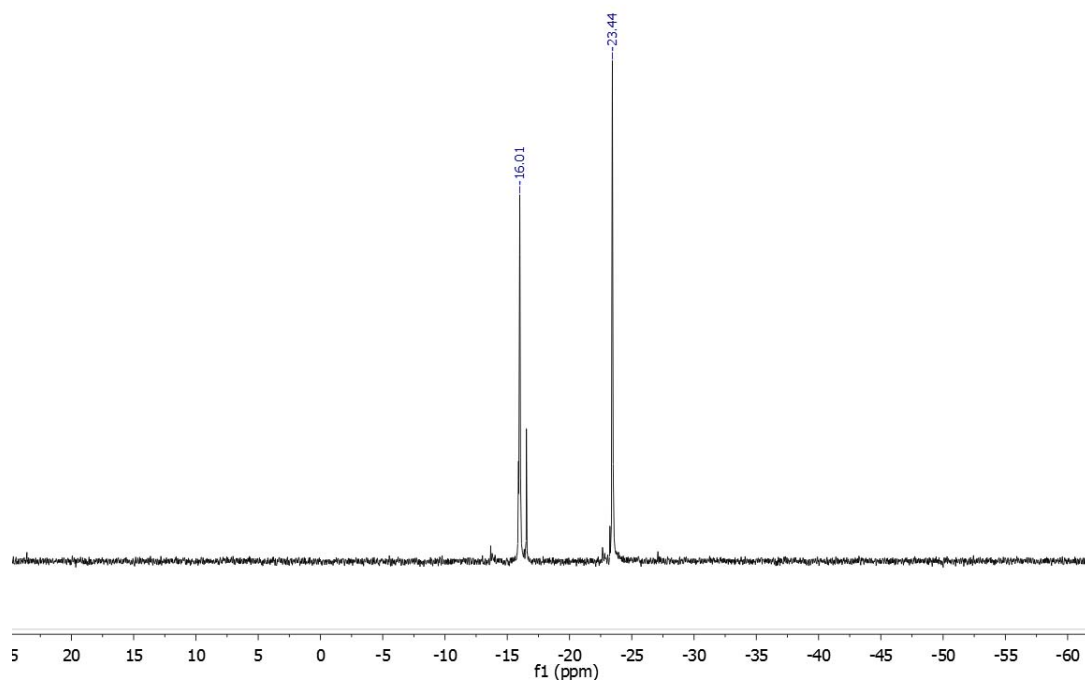


Figure 28:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 5e.

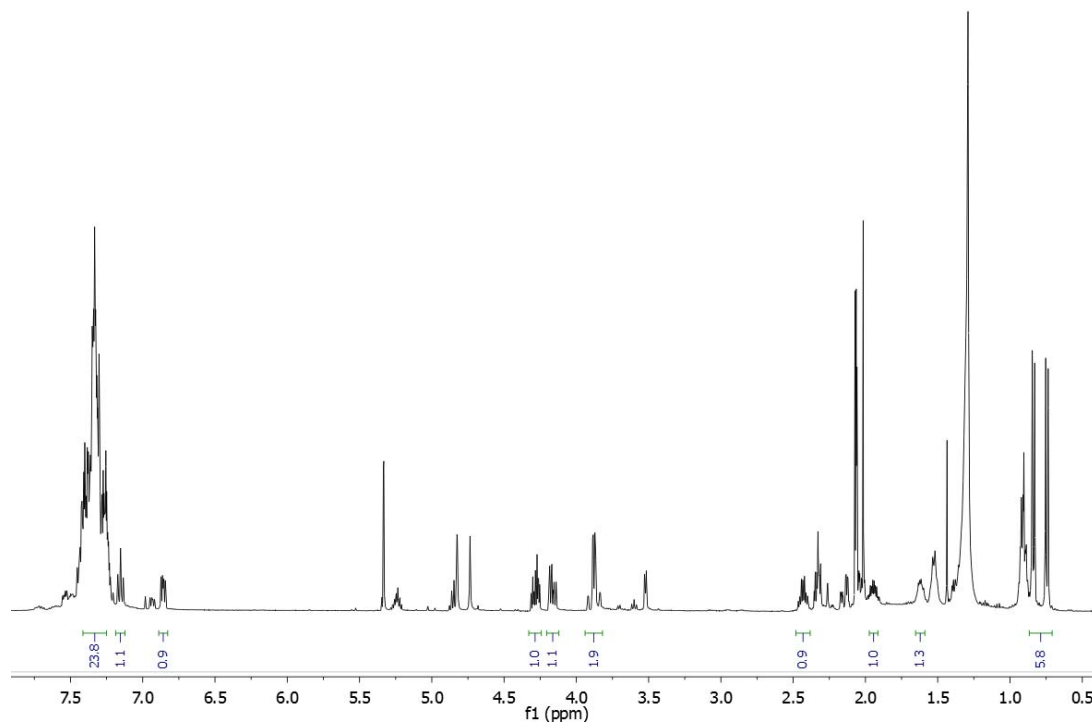


Figure 29:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 5f. Also see water, pentane, and ethyl acetate solvent peaks.

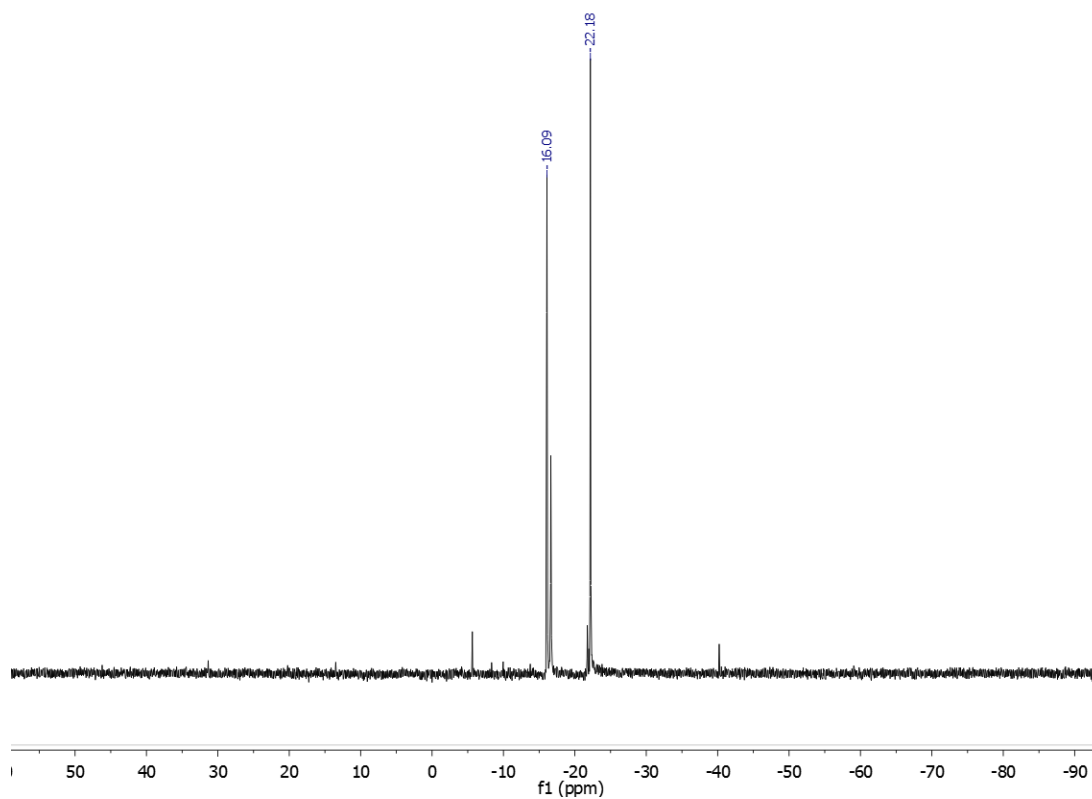


Figure 30:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 5f.

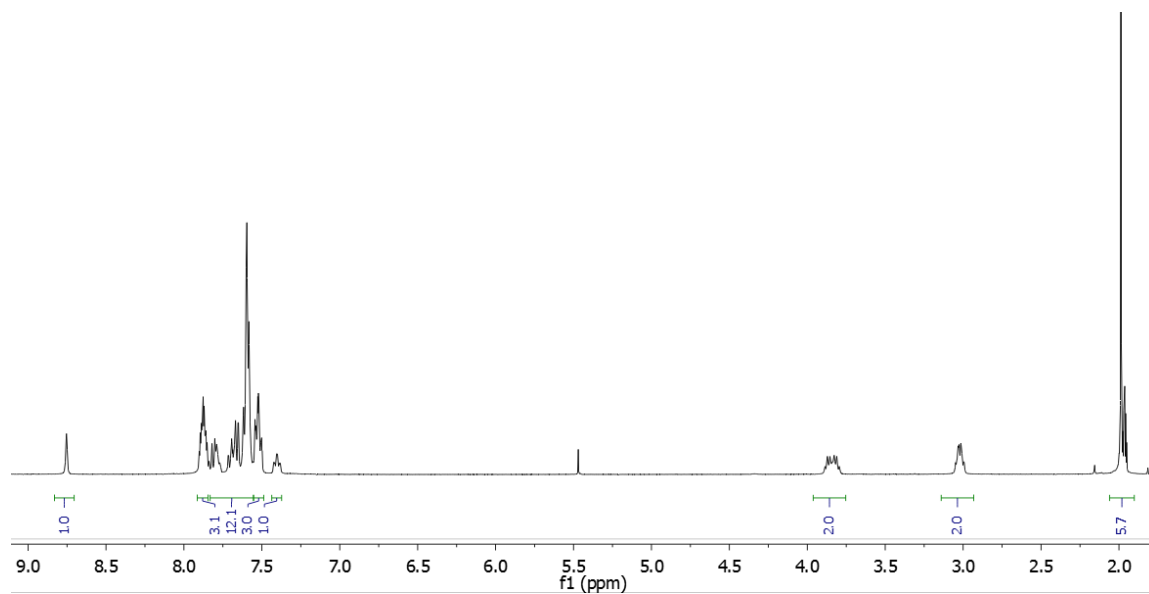


Figure 31:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_3\text{CN}$ ) of 6a.

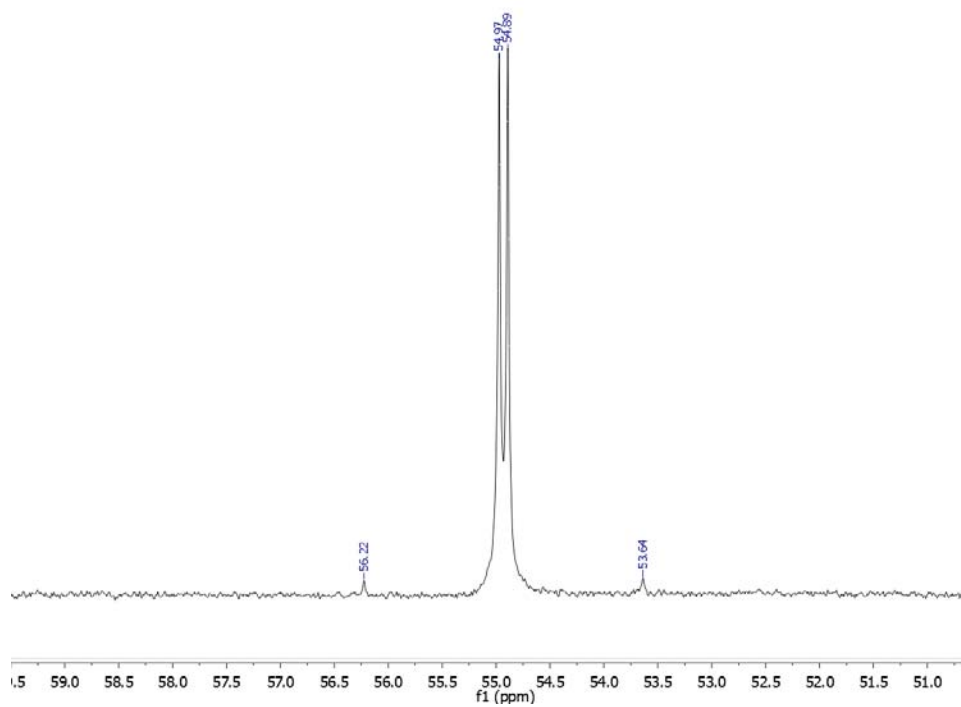


Figure 32:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_3\text{CN}$ ) of 6a.

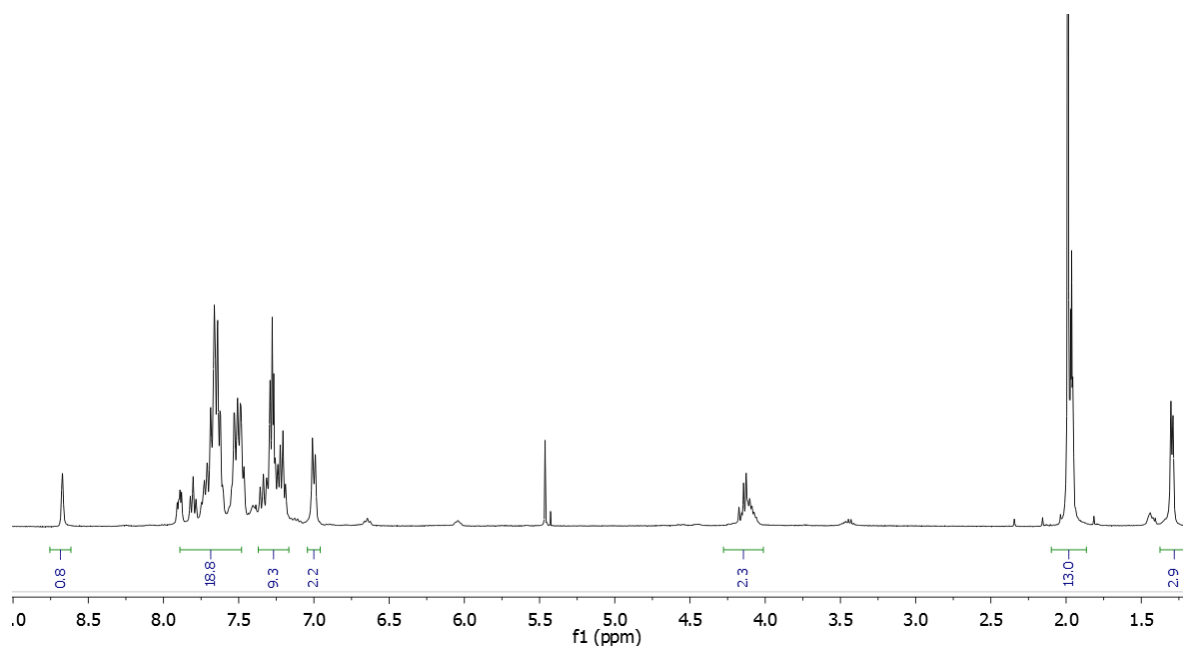


Figure 33:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_3\text{CN}$ ) of 6c.

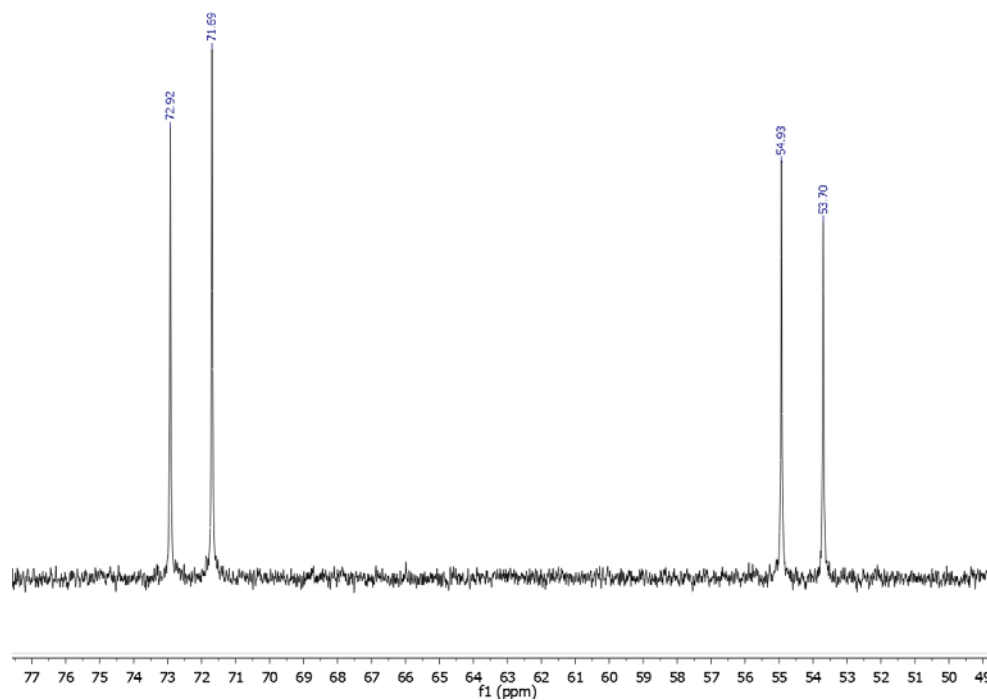


Figure 34:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_3\text{CN}$ ) of 6c.

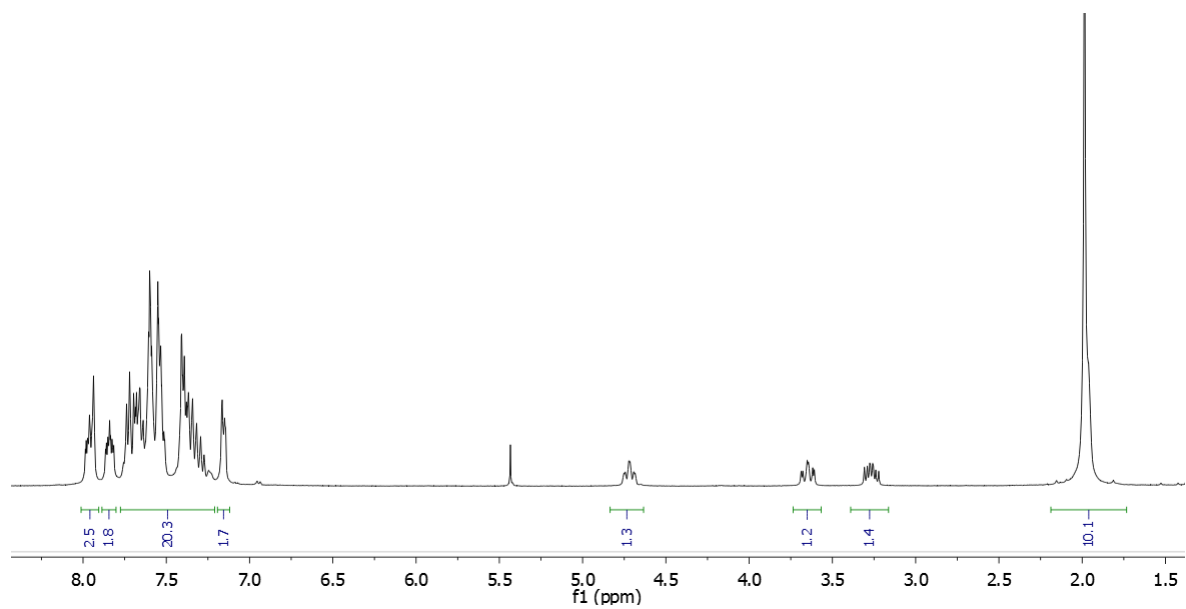


Figure 35:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_3\text{CN}$ ) of **6d**.

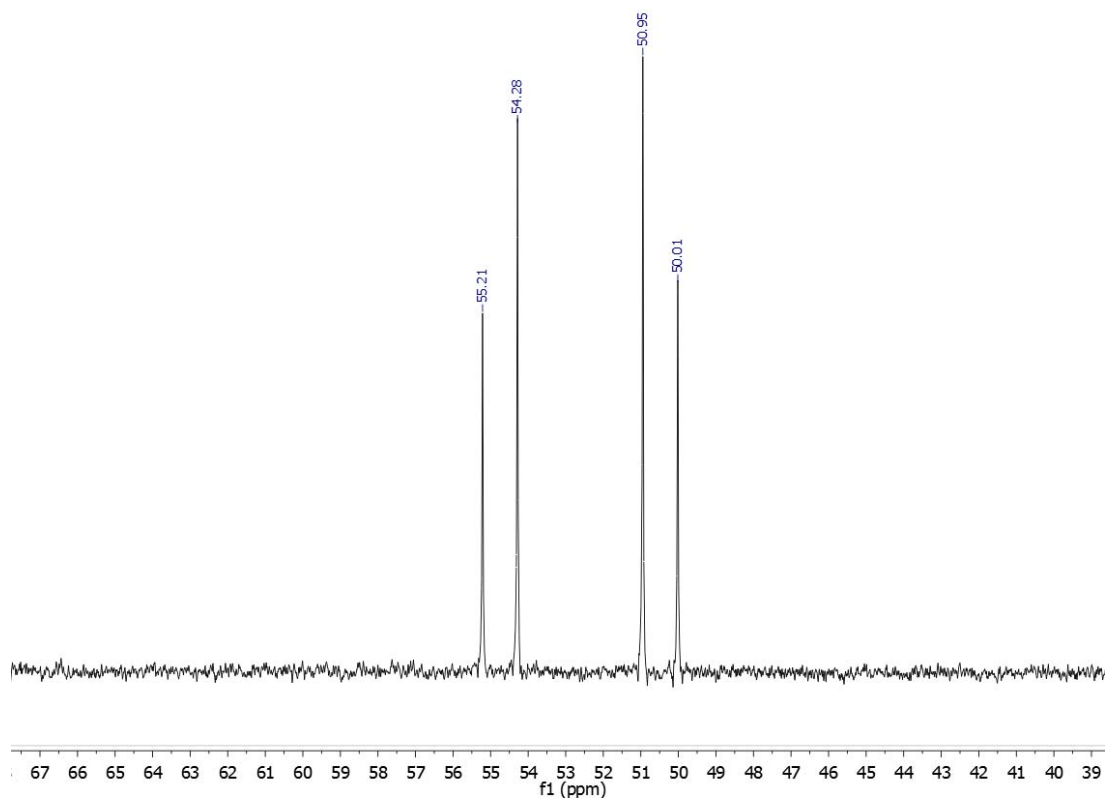


Figure 36:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_3\text{CN}$ ) of **6d**.

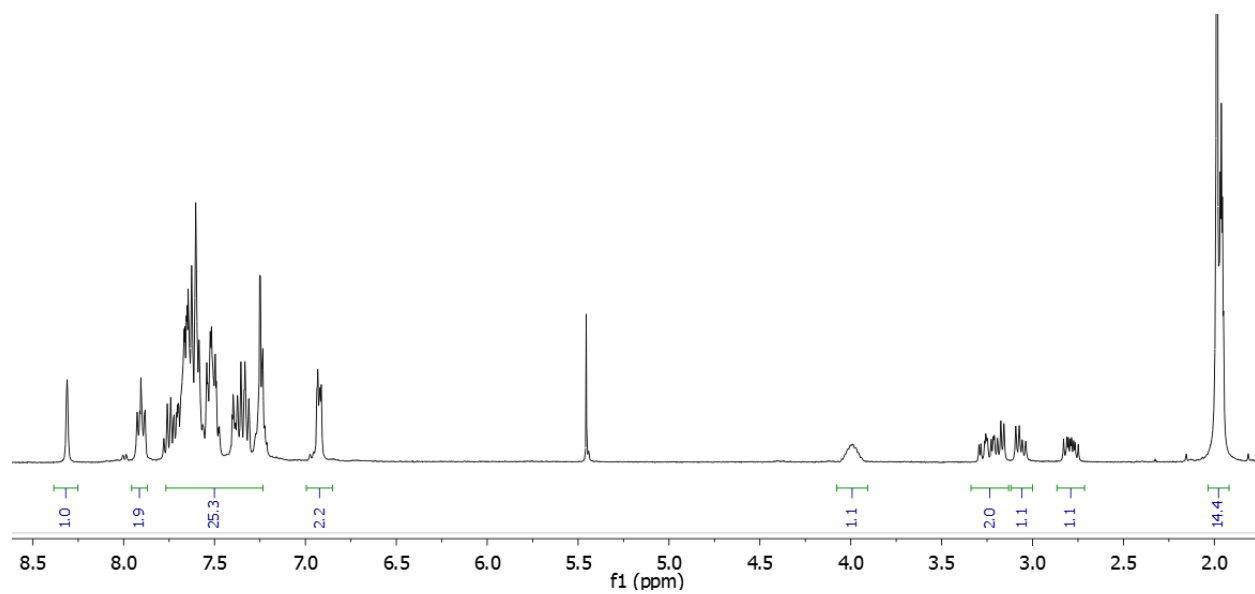


Figure 37:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_3\text{CN}$ ) of 6e.

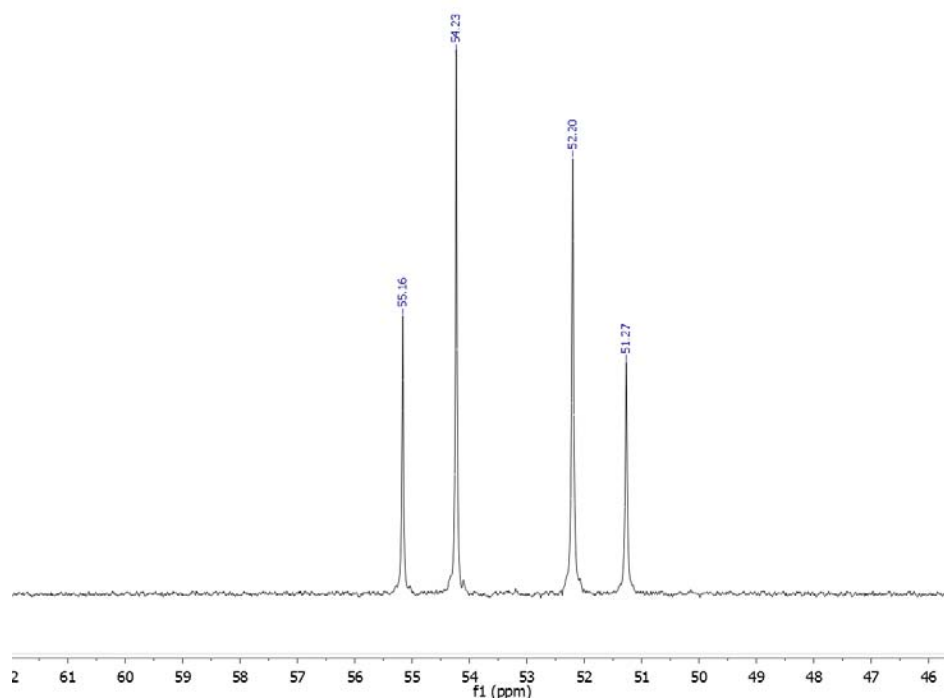


Figure 38:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_3\text{CN}$ ) of 6e.

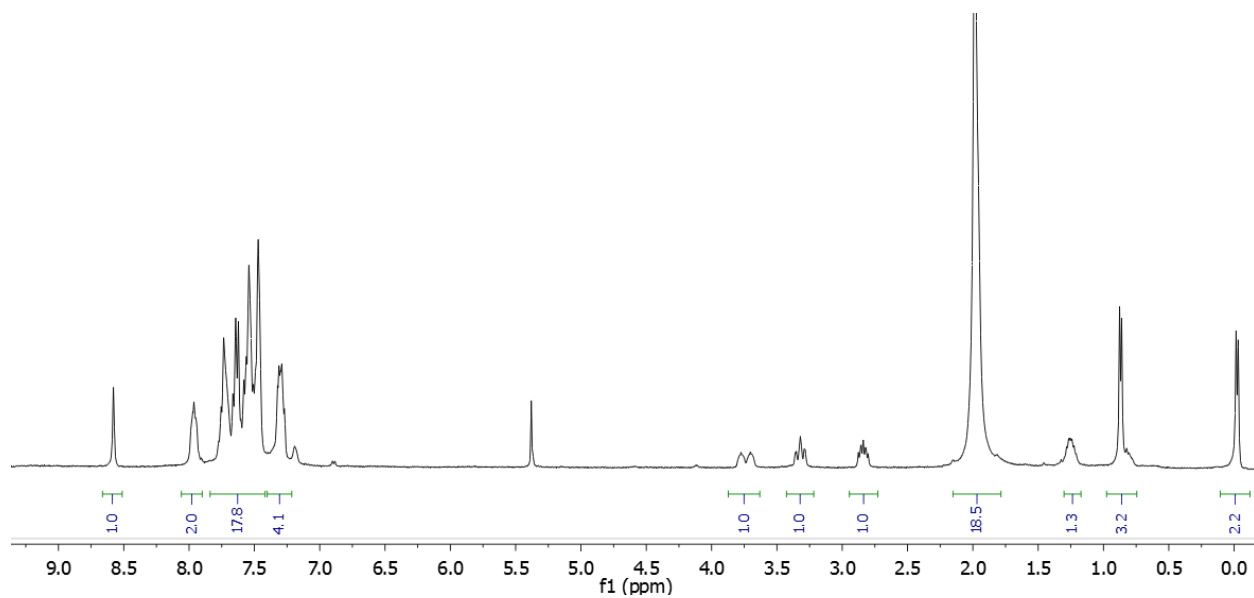


Figure 39:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_3\text{CN}$ ) of 6f.

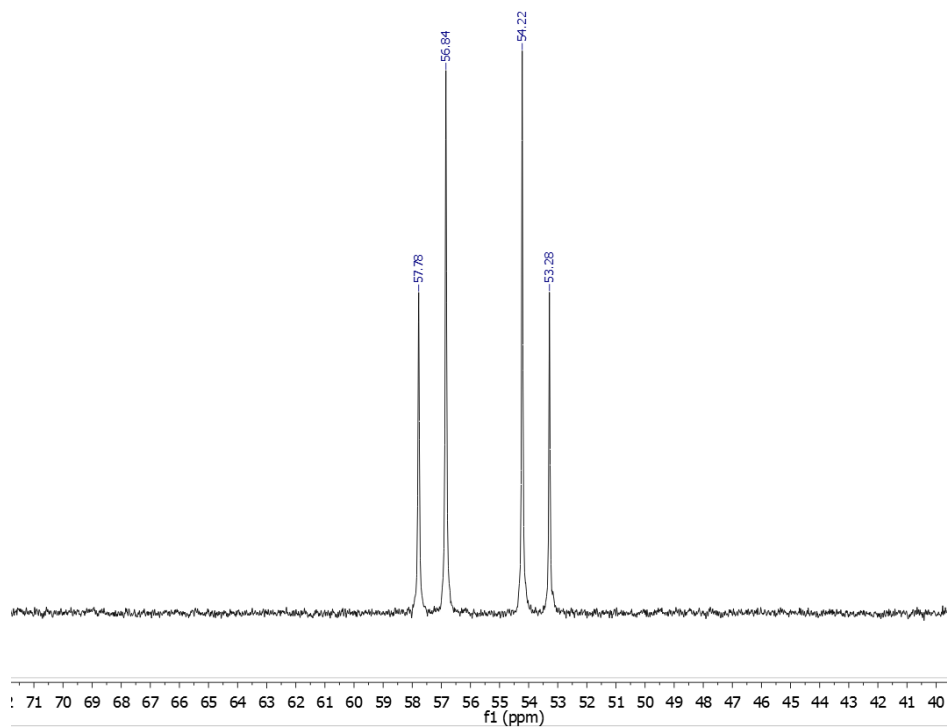


Figure 40:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_3\text{CN}$ ) of 6f.

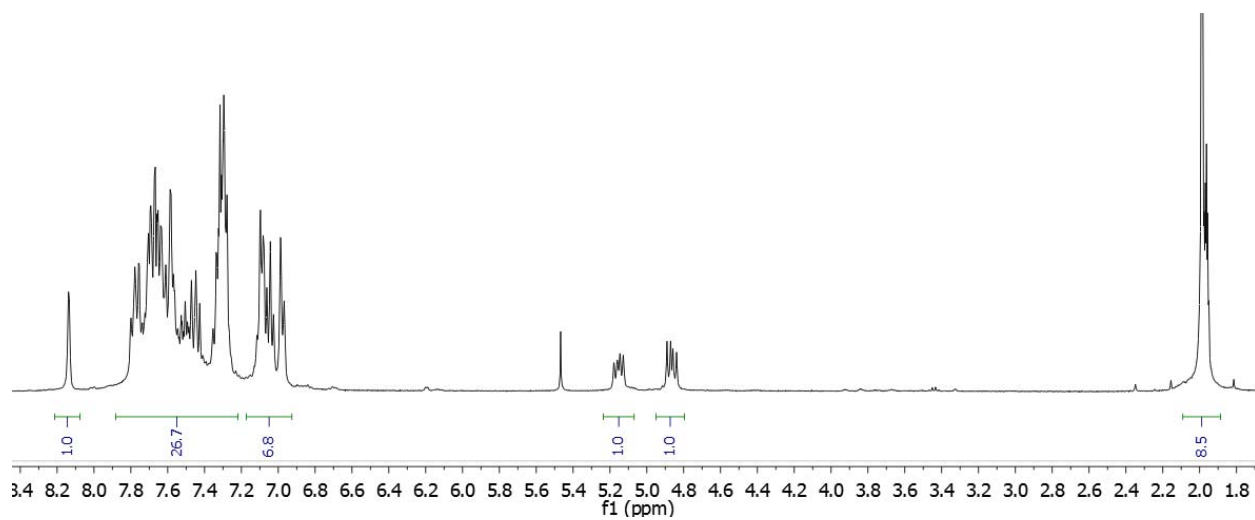


Figure 41:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_3\text{CN}$ ) of 6g.

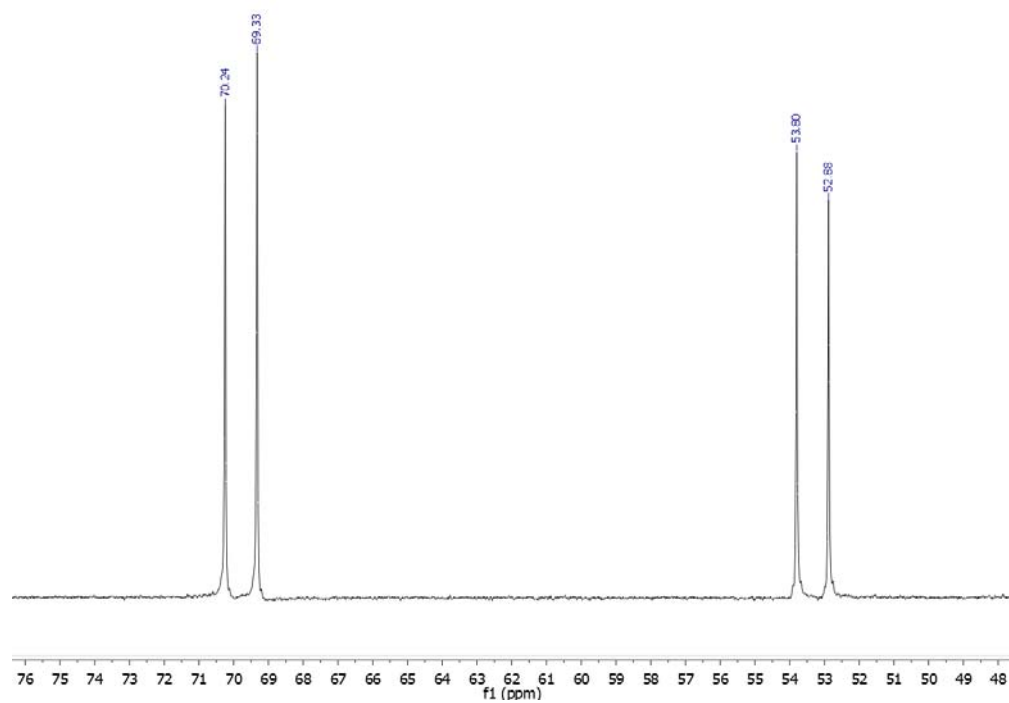


Figure 42:  $^{31}\text{P} \{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_3\text{CN}$ ) of 6g.

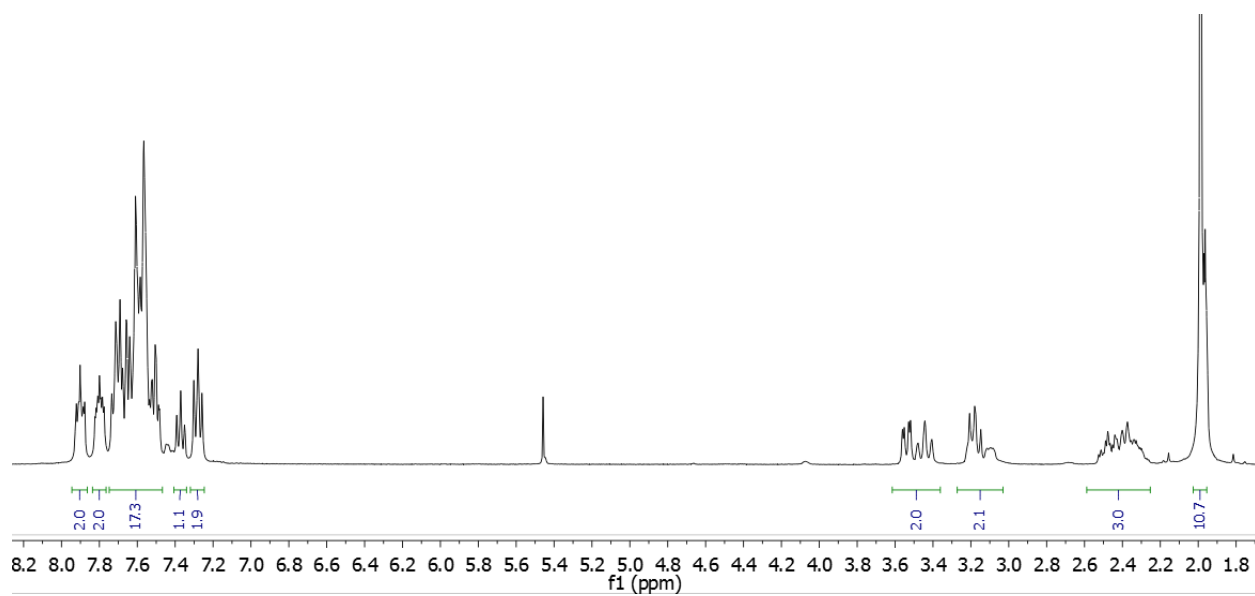


Figure 43:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_3\text{CN}$ ) of 7a.

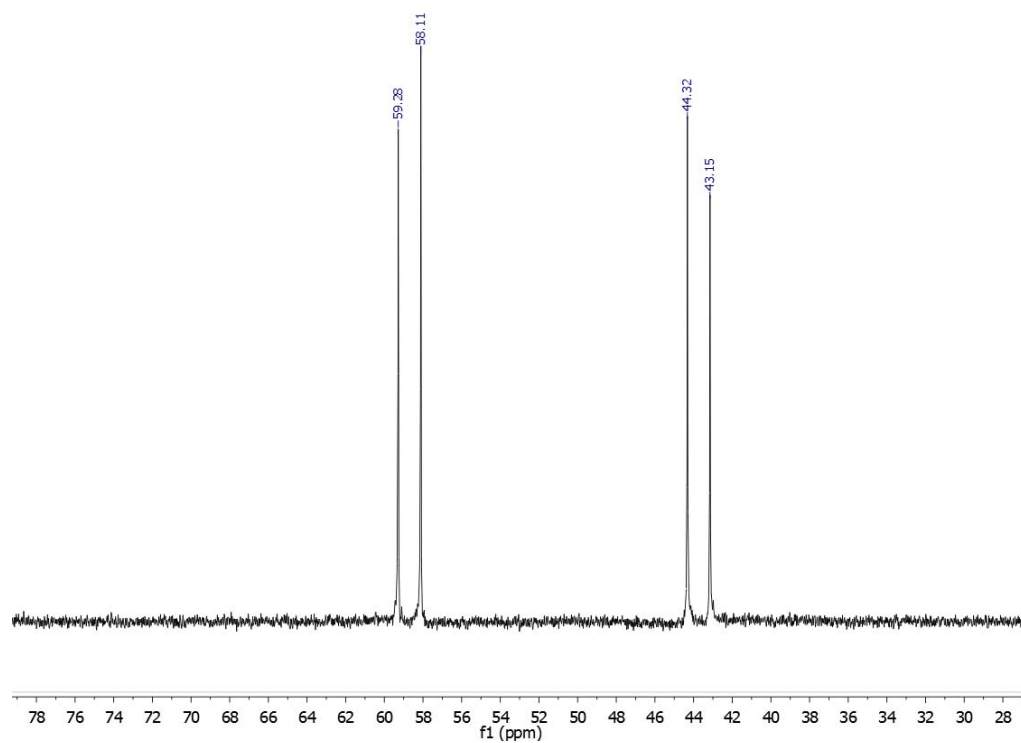


Figure 44:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_3\text{CN}$ ) of 7a.

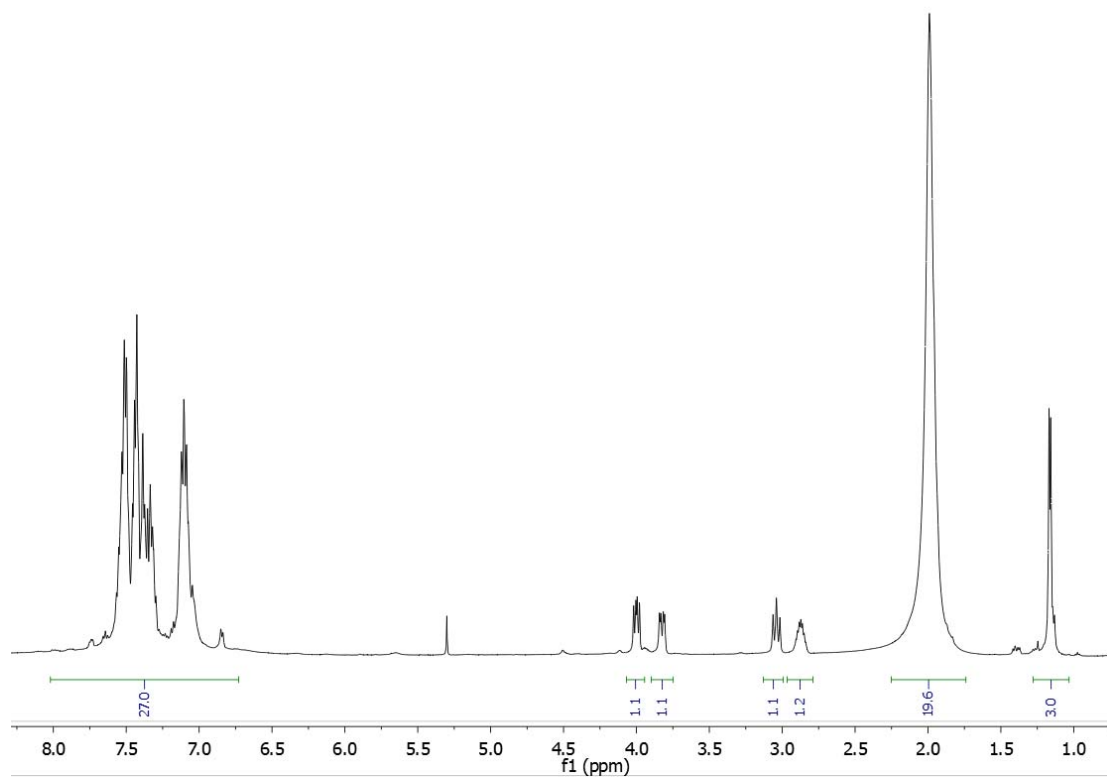


Figure 45:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_3\text{CN}$ ) of **7c**.

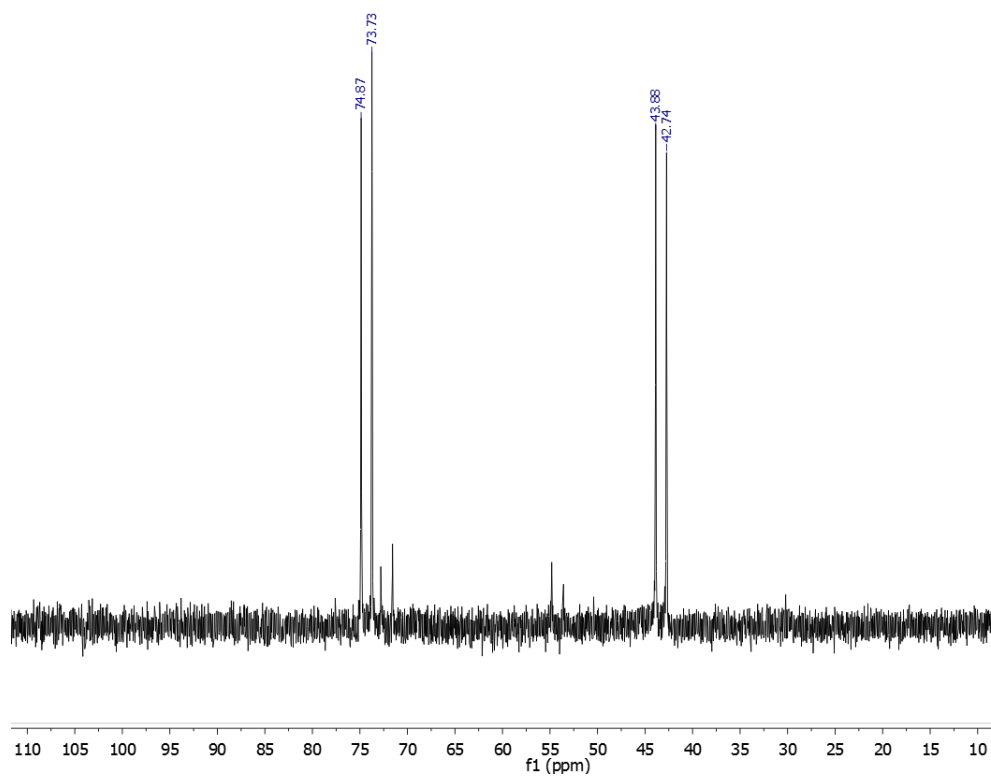


Figure 46:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_3\text{CN}$ ) of **7c**.

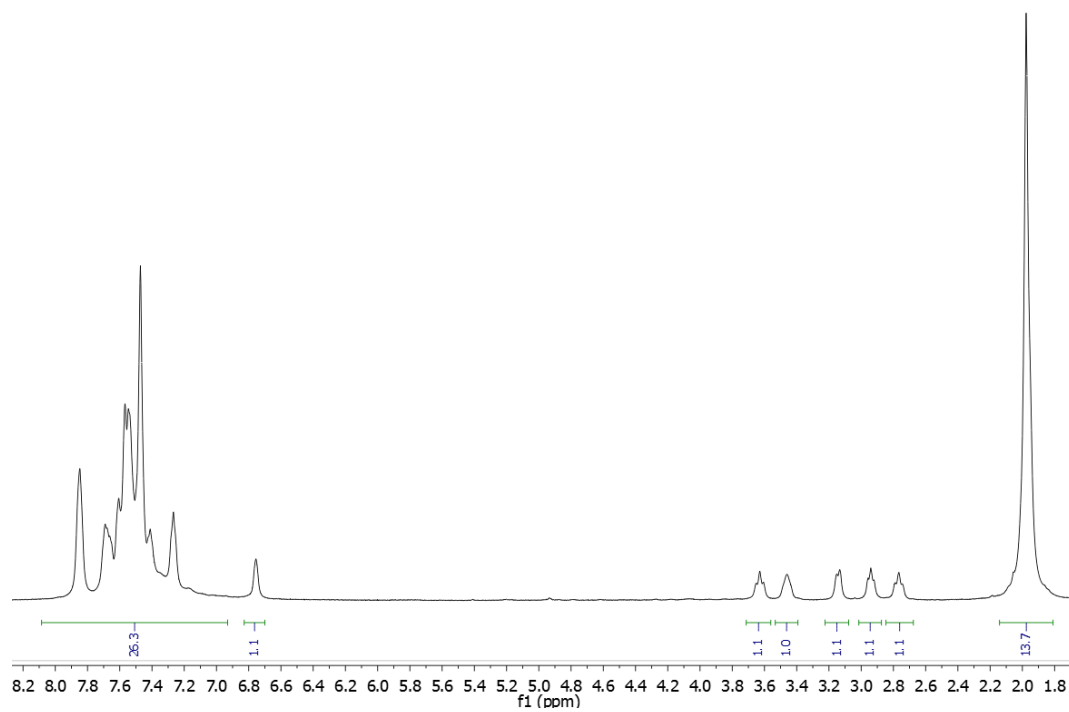


Figure 47:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_3\text{CN}$ ) of 7d.

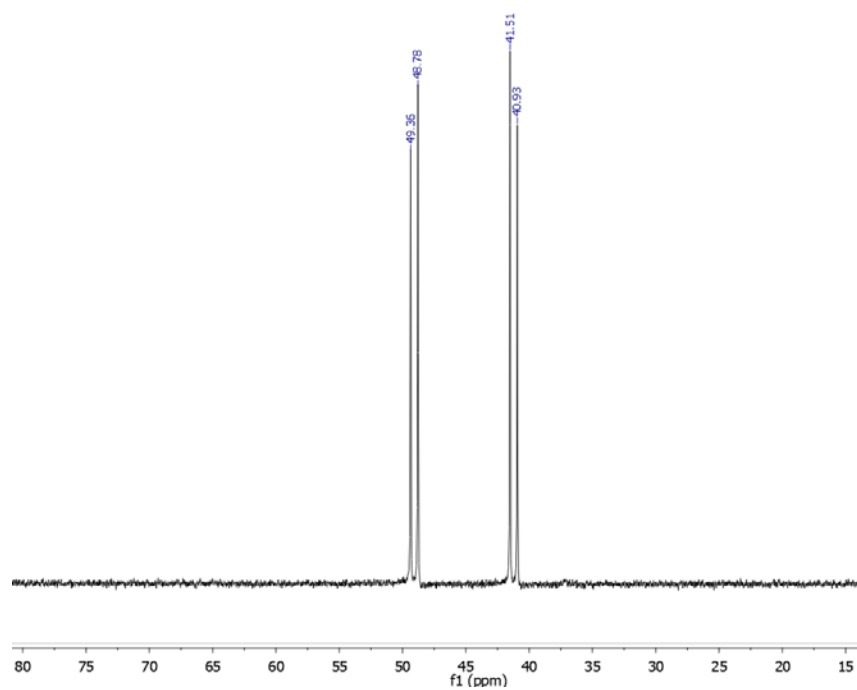


Figure 48:  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_3\text{CN}$ ) of 7d.

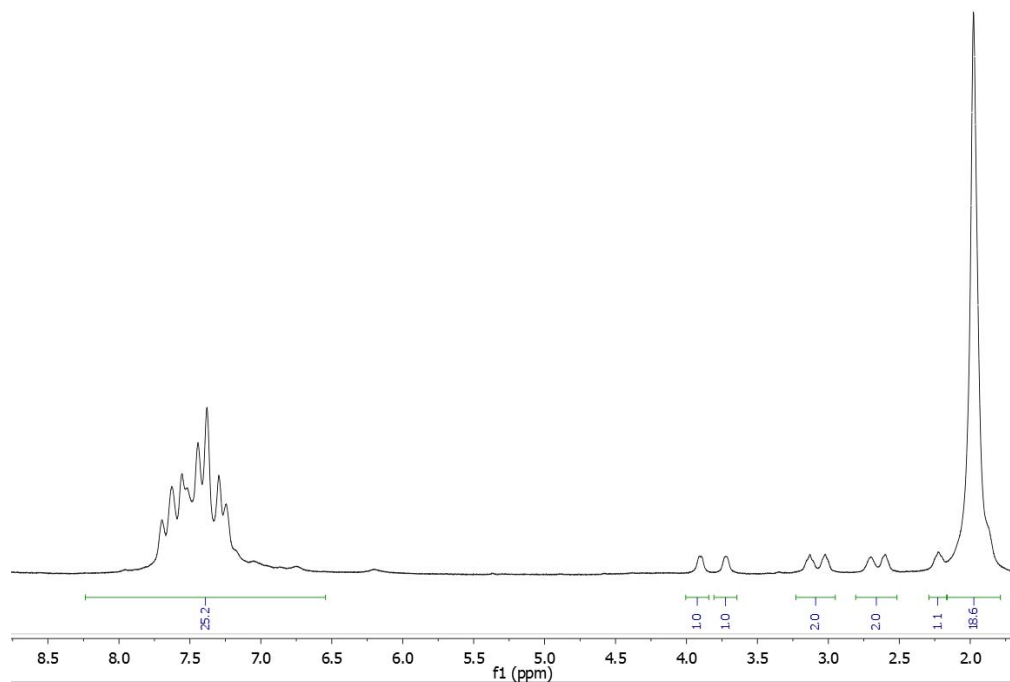


Figure 49: <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>3</sub>CN) of 7e.

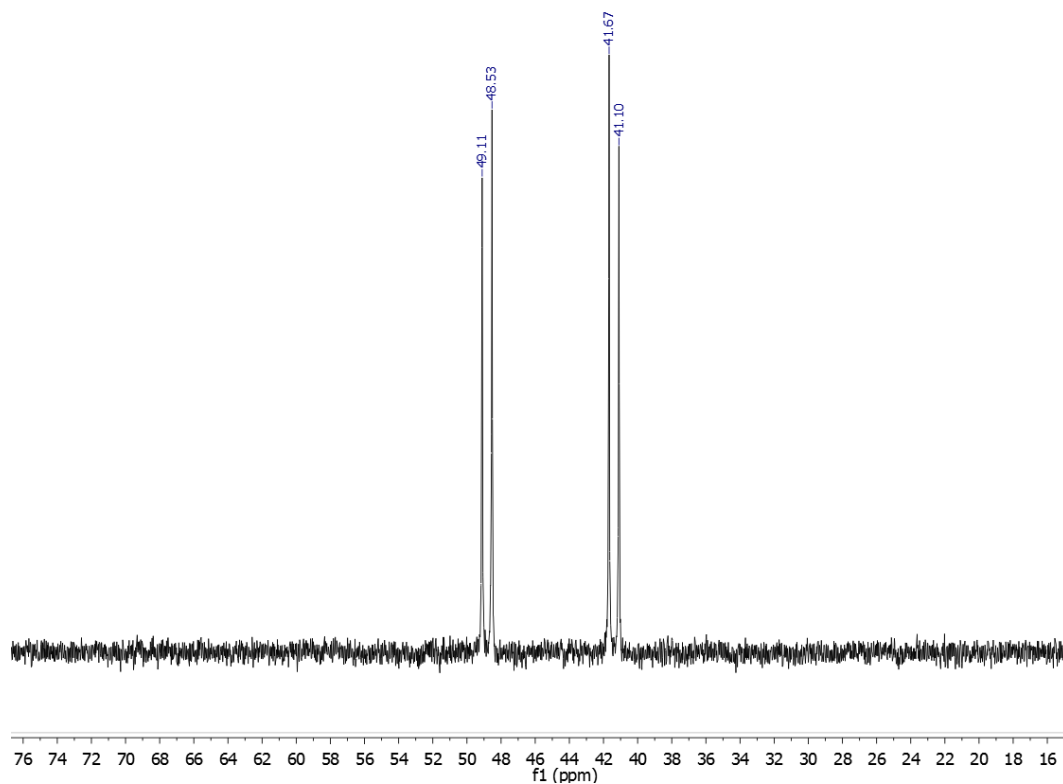


Figure 50: <sup>31</sup>P {<sup>1</sup>H} NMR spectrum (161 MHz, CD<sub>3</sub>CN) of 7e.

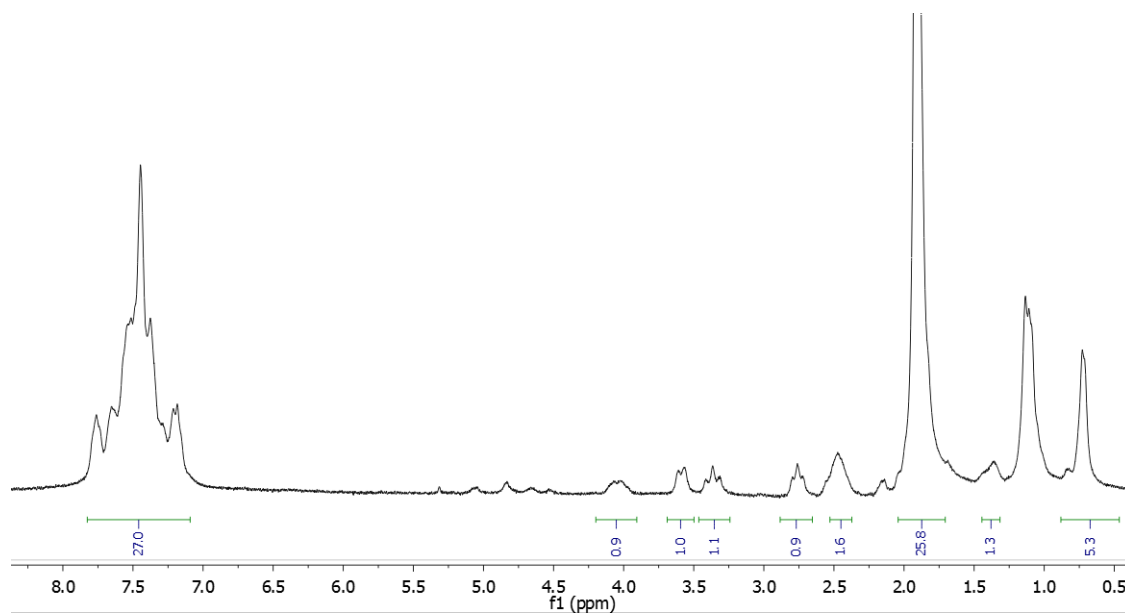


Figure 51:  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_3\text{CN}$ ) of **7f**.

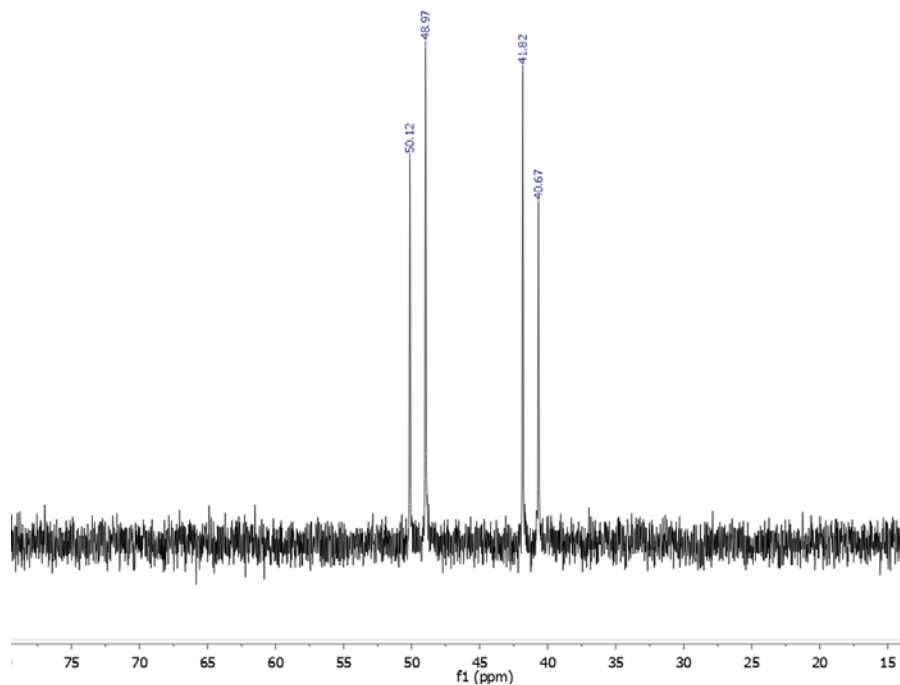


Figure 52:  $^{31}\text{P} \{^1\text{H}\}$  NMR spectrum (161 MHz,  $\text{CD}_3\text{CN}$ ) of **7f**.

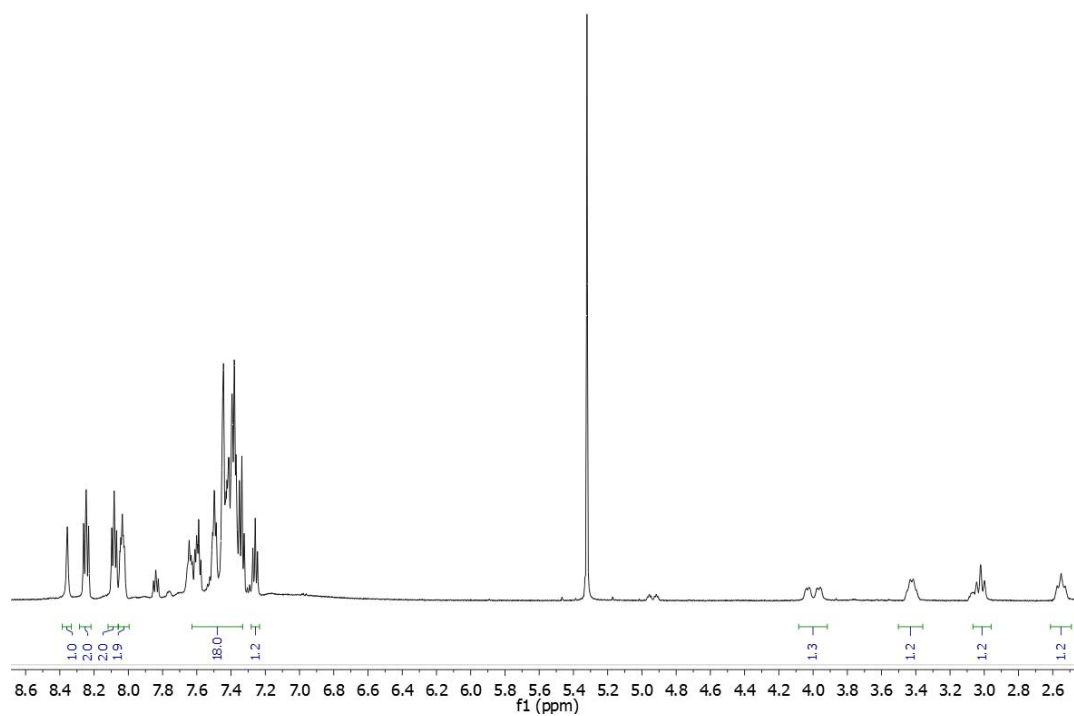


Figure 53: <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of 8a. Small signals also detected for minor (trans) species.

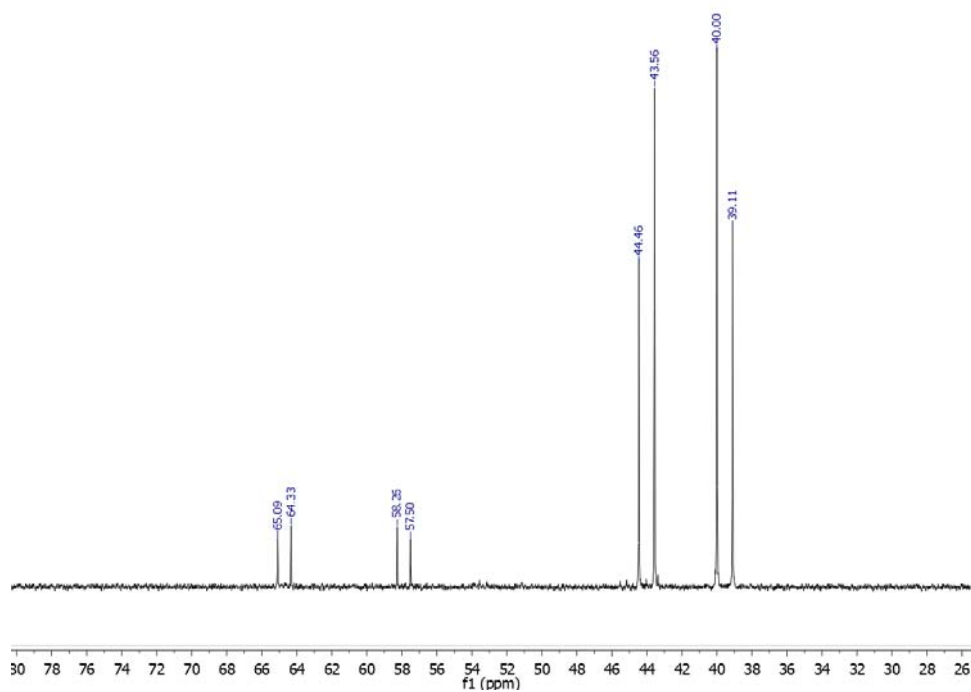


Figure 54: <sup>31</sup>P {<sup>1</sup>H} NMR spectrum (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of 8a. Spectrum shows major (cis) and minor (trans) species.

## Crystallographic Data

**Table 1:** Selected crystal data, data collection and refinement parameters for 1d.

Empirical formula	C44 H59 B Br F4 Fe N O4 P2	
Formula weight	950.43	
Temperature	147(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	a = 12.668(4) Å	$\alpha = 91.596(8)^\circ$ .
	b = 13.157(4) Å	$\beta = 108.974(7)^\circ$ .
	c = 14.033(5) Å	$\gamma = 95.657(7)^\circ$ .
Volume	2196.6(12) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.437 Mg/m <sup>3</sup>	
Absorption coefficient	1.385 mm <sup>-1</sup>	
F(000)	988	
Crystal size	0.180 x 0.150 x 0.140 mm <sup>3</sup>	
Theta range for data collection	1.538 to 27.589°.	
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18	
Reflections collected	36754	
Independent reflections	18201 [R(int) = 0.0232]	
Completeness to theta = 25.242°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6627	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	18201 / 398 / 1027	
Goodness-of-fit on F <sup>2</sup>	1.060	
Final R indices [I > 2sigma(I)]	R1 = 0.0441, wR2 = 0.1152	
R indices (all data)	R1 = 0.0586, wR2 = 0.1227	
Absolute structure parameter	0.034(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.734 and -0.485 e.Å <sup>-3</sup>	

**Table 2: Selected crystal data, data collection and refinement parameters for 3.**

Empirical formula	C <sub>57</sub> H <sub>58</sub> Br F <sub>4</sub> Fe N <sub>2</sub> O <sub>2</sub> P <sub>2</sub>	
Formula weight	1087.56	
Temperature	147(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	C 2 2 21	
Unit cell dimensions	a = 20.4589(7) Å	α = 90°.
	b = 17.3014(6) Å	β = 90°.
	c = 14.5749(6) Å	γ = 90°.
Volume	5159.0(3) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.400 Mg/m <sup>3</sup>	
Absorption coefficient	1.188 mm <sup>-1</sup>	
F(000)	2248	
Crystal size	0.260 x 0.200 x 0.110 mm <sup>3</sup>	
Theta range for data collection	1.541 to 27.514°.	
Index ranges	-26 ≤ h ≤ 26, -22 ≤ k ≤ 22, -18 ≤ l ≤ 18	
Reflections collected	45277	
Independent reflections	5943 [R(int) = 0.0548]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6911	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	5943 / 12 / 353	
Goodness-of-fit on F <sup>2</sup>	1.145	
Final R indices [I > 2σ(I)]	R1 = 0.0420, wR2 = 0.1017	
R indices (all data)	R1 = 0.0460, wR2 = 0.1034	
Absolute structure parameter	0.021(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.630 and -0.637 e.Å <sup>-3</sup>	

**Table 3: Selected crystal data, data collection and refinement parameters for 6a.**

Empirical formula	C <sub>39</sub> H <sub>38</sub> B <sub>2</sub> F <sub>8</sub> Fe N <sub>4</sub> P <sub>2</sub>	
Formula weight	854.14	
Temperature	147(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.6495(17) Å	α = 110.891(3)°.
	b = 18.491(3) Å	β = 92.273(4)°.
	c = 21.832(3) Å	γ = 90.535(3)°.
Volume	4012.2(10) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.414 Mg/m <sup>3</sup>	
Absorption coefficient	0.527 mm <sup>-1</sup>	
F(000)	1752	
Crystal size	0.20 x 0.07 x 0.05 mm <sup>3</sup>	
Theta range for data collection	1.00 to 27.65°.	
Index ranges	-13 ≤ h ≤ 13, -19 ≤ k ≤ 24, -28 ≤ l ≤ 28	
Reflections collected	57026	
Independent reflections	18498 [R(int) = 0.0544]	
Completeness to theta = 27.65°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.7188	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	18498 / 20 / 1049	
Goodness-of-fit on F <sup>2</sup>	1.009	
Final R indices [I > 2σ(I)]	R1 = 0.0470, wR2 = 0.0984	
R indices (all data)	R1 = 0.0800, wR2 = 0.1115	
Largest diff. peak and hole	0.822 and -0.658 e.Å <sup>-3</sup>	

**Table 4: Selected crystal data, data collection and refinement parameters for 6e.**

Empirical formula	C <sub>46</sub> H <sub>45</sub> B <sub>2</sub> F <sub>8</sub> Fe N <sub>4</sub> O <sub>0.50</sub> P <sub>2</sub>	
Formula weight	953.27	
Temperature	147(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 11.8424(3) Å	α = 90°.
	b = 10.3752(2) Å	β = 103.524(1)°.
	c = 19.0248(4) Å	γ = 90°.
Volume	2272.71(9) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.393 Mg/m <sup>3</sup>	
Absorption coefficient	3.946 mm <sup>-1</sup>	
F(000)	982	
Crystal size	0.100 x 0.050 x 0.020 mm <sup>3</sup>	
Theta range for data collection	3.839 to 66.554°.	
Index ranges	-13 ≤ h ≤ 13, -12 ≤ k ≤ 12, - 21 ≤ l ≤ 22	
Reflections collected	28140	
Independent reflections	7510 [R(int) = 0.0368]	
Completeness to theta = 67.679°	95.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6667	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	7510 / 1 / 580	
Goodness-of-fit on F <sup>2</sup>	1.001	
Final R indices [I > 2σ(I)]	R1 = 0.0355, wR2 = 0.0878	
R indices (all data)	R1 = 0.0394, wR2 = 0.0894	
Absolute structure parameter	0.034(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.764 and -0.303 e.Å <sup>-3</sup>	

**Table 5: Selected crystal data, data collection and refinement parameters for 8a.**

Empirical formula	C <sub>34</sub> H <sub>29</sub> Br <sub>2</sub> Fe N O P <sub>2</sub>	
Formula weight	745.19	
Temperature	147(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 <sub>1</sub> /n	
Unit cell dimensions	a = 10.2441(9) Å	α = 90°.
	b = 12.5920(12) Å	β = 92.532(2)°.
	c = 28.518(3) Å	γ = 90°.
Volume	3675.1(6) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.347 Mg/m <sup>3</sup>	
Absorption coefficient	2.696 mm <sup>-1</sup>	
F(000)	1496	
Crystal size	0.28 x 0.21 x 0.15 mm <sup>3</sup>	
Theta range for data collection	1.43 to 27.47°.	
Index ranges	-8 ≤ h ≤ 13, -16 ≤ k ≤ 16, - 36 ≤ l ≤ 36	
Reflections collected	34118	
Independent reflections	8413 [R(int) = 0.0604]	
Completeness to theta = 27.47°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6858	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	8413 / 5 / 381	
Goodness-of-fit on F <sup>2</sup>	1.028	
Final R indices [I > 2σ(I)]	R1 = 0.0367, wR2 = 0.0790	
R indices (all data)	R1 = 0.0577, wR2 = 0.0839	
Largest diff. peak and hole	0.720 and -0.371 e.Å <sup>-3</sup>	

**Table 6: Selected crystal data, data collection and refinement parameters for Fe(PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CHNCH*i*PrCH<sub>2</sub>PPh<sub>2</sub>)Br<sub>2</sub>.**

Empirical formula	C73 H70 Br4 Fe2 N P4	
Formula weight	1516.52	
Temperature	147(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.2404(4) Å	α = 90°.
	b = 14.3315(4) Å	β = 94.945(2)°.
	c = 23.1281(8) Å	γ = 90°.
Volume	3381.7(2) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.489 Mg/m <sup>3</sup>	
Absorption coefficient	7.422 mm <sup>-1</sup>	
F(000)	1534	
Crystal size	0.080 x 0.040 x 0.030 mm <sup>3</sup>	
Theta range for data collection	1.917 to 66.665°.	
Index ranges	-11 ≤ h ≤ 12, -17 ≤ k ≤ 17, -26 ≤ l ≤ 27	
Reflections collected	10940	
Independent reflections	10751 [R(int) = 0.0316]	
Completeness to theta = 67.679°	95.6 %	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	10751 / 1 / 761	
Goodness-of-fit on F <sup>2</sup>	1.492	
Final R indices [I > 2σ(I)]	R1 = 0.0708, wR2 = 0.1918	
R indices (all data)	R1 = 0.0765, wR2 = 0.1947	
Absolute structure parameter	0.475(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.199 and -0.849 e.Å <sup>-3</sup>	

## References

- (1) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, 7, 702.