

Electronic Supporting Information:

Facile synthesis of five-membered cyclic RE₂P–H iron(0) complexes

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General working methods:

All reactions were performed, if not stated otherwise under dried and deoxygenated argon atmosphere using Schlenk or glovebox techniques. The used argon (>99.998%) was purified by a system of three columns (deoxygenation by a BTS copper catalyst (BASF PuriStarR R3-15S) at ca. 100 °C, removing moisture with silica gel, phosphorus pentoxide desiccant with indicator (Sicapent®) and calcium chloride). glassware, spatulae, cannulae as well as filter papers were dried in a compartment dryer at 110 °C for at least one hour. Additionally, the glassware was heated with a Teclu burner (up to 1600 °C) or if sensitive with heat gun (up to 550 °C) under active vacuum (<0.03 mbar) flushed with argon and the kept under vacuum for min. 5 to 10 minutes. Sterile syringes were purged with argon three times before use. The solvents were dried by standard procedures by refluxing over proper desiccants under an argon atmosphere (n-pentane, petroleum ether 40/65 and toluene over sodium wire (o = 2 mm); diethyl ether stabilized with 3,5-di-tertbutyl-4-hydroxytoluene (BHT) and tetrahydrofuran over benzophenone and sodium wire) for several days and distilled before use. Alternatively, diethyl ether and toluene were dried using a Mbraun SPS-800 solvent purification system. Transfer of solvents or solutions was achieved by the use of stainless steel cannulae (o = 2 mm and 4 mm) connecting two glass vessels, one of which was under argon overpressure and the other had a vent (commonly a cannula was used) to the atmosphere. For filtration Schlenk frits or stainless steel cannulae (o = 1 mm and 2 mm) with Whatman® Cytiva grade 595 cellulose filter paper or for finer residues Whatman® glass microfiber filters (grade gF/B) or were used. After use, cannulas made of stainless steel were cleaned with acetone, water and diluted hydrochloric acid and glassware by storage in a concentrated solution of potassium hydroxide in ¹PrOH for at least two days (in the case of glass frits only overnight) and in diluted hydrochloric acid for several hours. Afterwards, the glassware was washed with water, subsequently with demineralised water and acetone. glass joints were greased with OKS 1112 grease or with PTFE paste (Carl Roth).

The chloro phosphanes **1a,b,c**, **2a,b** and **3b,c** were synthesised according to literature procedures.¹⁻⁴ N,N'-dimethyl-ethylenediamine, N,N'-diisopropyl-ethylenediamine, N-methyl- and N-isopropyl ethanolamine, pinacol and catechol were purchased and used as received. 1,2-Dimethylaminobenzene was prepared fresh following a reported procedure.⁵ K[Fe(CO)₄H] was synthesised from Fe(CO)₅ following literature procedures and kept as a solid in the freezer (-40°C) until usage.⁶

Experimental protocols:

General procedure for the (attempted) reduction of chloro phosphanes **1a,2a,3b**:

Method 1) In a Schlenk tube the phosphane (0.6 mmol, 1 eq.) was dissolved in 2 mL Et₂O. In another Schlenk tube a suspension of Li[AlH₄] (0.9 mmol, 1.5 eq) in 3 mL Et₂O was prepared. The Li[AlH₄]

suspension was added slowly with a transfer canula to the phosphane solution under constant stirring. After complete addition the canula was rinsed with 1 mL Et₂O.

Method 2) In a Schlenk tube the phosphane (0.7 mmol, 1 eq.) was dissolved in 3 mL THF. While stirring 0.7 mL (0.7 mL, 1 eq.) of a Li-selectride solution in THF (c = 1 M) were added to the solution.

Synthesis of [tetracarbonyl(2-chloro-1,3-dimethyl-1,3,2-diazaphospholidine-κP)iron(0)] **1b**^{Fe}:

1b^{Fe}: In a 250 mL Schlenk flask 2.25 g (6 mmol, 1 eq.) Fe₂(CO)₉ were suspended in 85 mL THF at 0 °C. In a 50 mL Schlenk tube 1.01 g (7 mmol, 1.1 eq.) **1b** were dissolved in 10 mL THF at 0 °C and then added to the Fe₂(CO)₉ suspension with a syringe. After the addition the syringe was rinsed twice with 2.5 mL THF. Then the ice bath was removed and the dark red mixture was stirred for 2.5 hours at room temperature after which the solvent was removed. The product was then sublimed from the crude residue on a cold finger at 0 °C under a pressure of 8·10⁻² mbar. The yield could be increased if the Schlenk flask was heated to 40 °C and the pressure was reduced to 4·10⁻² mbar. The product was obtained as yellow needles in moderate yields.

Yield: 820 mg, 39%; **Melting point:** 69 °C; **Elemental analysis:** calculated (%) C 29.99 H 3.15 N 8.74 , found (%) C 30.00 H 3.33 N 8.55; **MS:** (EI, 70 eV, selected data): m/z = 558.0 [2M-Cl-CO+O]⁺, 530.0 [2M-Cl-2CO+O]⁺, 502.0 [2M-Cl-3CO+O]⁺, 474.0 [2M-Cl-4CO+O]⁺, 418.0 [2M-Cl-6CO+O]⁺, 362.1 [2M-Cl-8CO+O]⁺, 306.1 [2M-Cl-8CO-Fe+O]⁺, 318.9 [M-H]⁺, 285.0 [M-Cl]⁺, 257.0 [M-Cl-CO]⁺, 229.0 [M-Cl-2CO]⁺, 201.0 [M-Cl-3CO]⁺, 117.1 [M-Cl-Fe-4CO]⁺; **IR** (ATR diamond) in cm⁻¹: 2859 (w, ν (C-H)), 2058 (s, ν (C=O)), 1978 (w, ν (C=O)), 1928(vs, ν (C=O)); **¹H-NMR:** (400 MHz, 298 K, THF-d₈): 3.45 - 3.34 (m, 2H, C₂H₄), 3.28 - 3.22 (m, 2H, C₂H₄), 2.84 (d, ³J_{P,H} = 16.9 Hz, 6H, N-CH₃). **¹³C{¹H}-NMR:** (101 MHz, 298 K, THF-d₈): 213.4 (d, = 20 Hz, CO), 51.3 (d, = 6 Hz, N-CH₃), 33.0 (d, = 8 Hz, C₂H₄); **³¹P-NMR:** (203 MHz, 298 K, THF-d₈): 182.0 (s_{sat}, ¹J_{Fe,P} = 47 Hz).

Synthesis of [tetracarbonyl(2-chloro-4,5-dimethyl-1,3,2-dioxaphospholane-κP)iron(0)] **3b**^{Fe} and [tetracarbonyl(2-chloro-2H-benzo[4,5-c]-1,3,2-dioxaphospholane-κP)iron(0)] **3c**^{Fe} :

3b^{Fe}: In a 250 mL Schlenk flask 99 mg (0.3 mmol, 1 eq.) Fe₂(CO)₉ were suspended in 2.5 mL THF at 0 °C. In a 50 mL Schlenk tube 51 mg (0.3 mmol, 1 eq.) **3b** were dissolved in 2.5 mL THF at 0 °C and then added to the Fe₂(CO)₉ suspension with a transfer canula. After the addition the canula was rinsed twice with 1.5 mL THF. Then the ice bath was removed and the orange mixture was stirred for 1.5 hours at room temperature after which the solvent was removed. An almost quantitative conversion was observed by ³¹P{¹H}-NMR spectroscopy.

Conversion: >95% (estimated from ³¹P{¹H}-NMR); **¹H-NMR:** (400 MHz, 298 K, THF-d₈): 1.39 (s, 6H, 2xCH₃), 1.30 (s, 6H, 2xCH₃); **¹³C{¹H}-NMR:** (126 MHz, 298 K, THF-d₈): 211.3 (d, ²J_{P,C} = 22 Hz, CO), 92.5 (d, ²J_{P,C} = 7.1 Hz, Me₂C-O), 25.2 (d, ²J_{P,C} = 6 Hz, -CH₃), 24.5 (d, ²J_{P,C} = 3 Hz, -CH₃); **³¹P-NMR:** (162 MHz, 298 K, THF-d₈): 202.6 (s_{sat}, ¹J_{Fe,P} = 55 Hz).

3c^{Fe}: In a 250 mL Schlenk flask 2.54 g (7 mmol, 1 eq.) Fe₂(CO)₉ were suspended in 30 mL THF at 0 °C. In a 50 mL Schlenk tube 1.51 g (9 mmol, 1.2 mmol) **3c** were dissolved in 50 mL THF at 0 °C and then added to the Fe₂(CO)₉ suspension with a transfer canula. After the addition the canula was rinsed twice with 10 mL THF. Then the ice bath was removed and the dark red mixture was stirred for 1.5 hours at room temperature after which the solvent was removed. The product was obtained in 95% conversion estimated from ³¹P{¹H}-NMR spectroscopy. Attempts to purify the crude product via common-work-up was not possible. Inert column chromatography (h = 4 cm, o = 1 cm, Al₂O₃, PE, -20 °C) allowed the isolation of **3c**^{Fe}, however, in negligible amounts. Vacuum distillation (Oil bath: 140 °C, Thermometer:

N.A., Pressure: $5 \cdot 10^{-3}$ mbar) also allowed the isolation of **3c^{Fe}** as an orange oil, but also in this case only small amounts (less than a drop) were obtained as decomposition occurs at these temperatures.

Conversion: 94% (estimated from $^{31}\text{P}\{^1\text{H}\}$ -NMR); **Yield:** — ; **MS:** (EI, 70 eV, selected data): $m/z = 319.0$ $[\text{M}]^+$, 313.9 $[\text{M}-\text{CO}]^+$, 285.9 $[\text{M}-2\text{CO}]^+$, 257.9 $[\text{M}-3\text{CO}]^+$, 229.9 $[\text{M}-4\text{CO}]^+$, 139.0 $[\text{M}-\text{Fe}-4\text{CO}-\text{Cl}]^+$; **^1H -NMR:** (300 MHz, 298 K, C_6D_6): 6.66 (m, 2H, benzo), 6.53 (m, 2H, benzo); **$^{13}\text{C}\{^1\text{H}\}$ -NMR:** (76 MHz, 298 K, C_6D_6): 210.6 (d, = 16 Hz, CO), 145.4 (d, = 8 Hz, benzo ($\text{C}^{\text{ipso-O}}$)), 124.8 (s, benzo (C^{meta})), 113.5 (d, = 7 Hz, benzo (C^{ortho})); **^{31}P -NMR:** (122 MHz, 298 K, C_6D_6): 210.5 (s_{sat} , $^1J_{\text{Fe,P}} = 74$ Hz).

1,3,2-Diazaphospholidine $\text{Fe}(\text{CO})_4$ complexes:

Synthesis of [tetracarbonyl(1,3-di(1-methylethyl)-1,3,2-diazaphospholidine- κP)iron(0)] **4a^{Fe}**:

In a 100 mL Schlenk flask 1.35 g (6 mmol, 1 eq.) $\text{K}[\text{Fe}(\text{CO})_4\text{H}]$ were dissolved in 30 mL THF at 0 °C. In a 25 mL Schlenk tube 1.09 g (5 mmol, 0.8 eq.) **1a** were dissolved in 25 mL THF at 0 °C and then added to the $\text{K}[\text{Fe}(\text{CO})_4\text{H}]$ suspension with a transfer canula. After the addition the canula was rinsed with 10 mL THF. Then the ice bath was removed and the yellow-brown mixture was stirred for 1.5 hours at room temperature after which the solvent was removed. The crude product was extracted from the residue with 50 mL (30+10+10 mL) *n*-pentane and the filtrate was dried to become a red oil. After further purification via inert column chromatography ($h = 11$ cm, $\phi = 4.5$ cm, SiO_2 PE (2.5% NEt_3), -20 °C) from which the first fraction (PE, 2.5% NEt_3) contained product. After removal of solvent and drying under reduced pressure ($3 \cdot 10^{-2}$ mbar) the product was obtained as a red-orange oil in moderate yield.

Yield: 1.63 g, 67%; **Elemental analysis:** calculated (%) C 42.13 H 5.60 N 8.11, found (%) C 41.83 H 5.65 N 8.14; **MS:** (EI, 70 eV, selected data): $m/z = 342.0$ $[\text{M}]^{+*}$, 314.0 $[\text{M}-\text{CO}]^{+*}$, 286.0 $[\text{M}-2\text{CO}]^{+*}$, 258.0 $[\text{M}-3\text{CO}]^{+*}$, 230.0 $[\text{M}-4\text{CO}]^{+*}$, 173.1 $[\text{M}-\text{Fe}-4\text{CO}-\text{H}]^{+*}$; **IR** (ATR diamond) $\tilde{\nu}$ in cm^{-1} : (2970, 2934, 2872) (m, $\nu(\text{C}-\text{H})$), 2187 (w, $\nu(\text{P}-\text{H})$), 2048 (vs, $\nu(\text{C}=\text{O})$), 1971 (w, $\nu(\text{C}=\text{O})$), 1919 (vs, $\nu(\text{C}=\text{O})$); **^1H -NMR:** (500 MHz, 298 K, THF- d_8): 7.84 (d, $^1J_{\text{P,H}} = 344$ Hz, 1H), 3.92 (m, 2H, C_2H_4), 3.24 (m, 2H, C_2H_4), 1.23 (d, $^3J_{\text{H,H}} = 6.5$ Hz, 6H, $2x\text{CH}_3$), 1.15 (d, $^3J_{\text{H,H}} = 6.5$ Hz, 6H, $2x\text{CH}_3$); **$^{13}\text{C}\{^1\text{H}\}$ -NMR:** (125.78 MHz, 298 K, THF- d_8): 214.5 (d, $^2J_{\text{P,C}} = 21$ Hz, CO), 46.1 (d, $^2J_{\text{P,C}} = 9$ Hz, C_2H_4), 42.3 (s, $\text{CH}(\text{Me})_2$), 21.6 (d, $^3J_{\text{P,C}} = 7$ Hz, CH_3), 19.8 (d, $^3J_{\text{P,C}} = 3$ Hz, CH_3); **$^{31}\text{P}\{^1\text{H}\}$ -NMR:** (203 MHz, 298 K, THF- d_8): 124.4 (s_{sat} , $^1J_{\text{Fe,P}} = 30$ Hz); **^{31}P -NMR:** (203 MHz, 298 K, THF- d_8): 124.4 (dm, $^1J_{\text{P,H}} = 344$ Hz).

Synthesis of [tetracarbonyl(1,3-dimethyl-1,3,2-diazaphospholidine- κP)iron(0)] **4b^{Fe}**:

In a 500 mL Schlenk flask 4.06 g (20 mmol, 1 eq.) $\text{K}[\text{Fe}(\text{CO})_4\text{H}]$ were dissolved in 180 mL THF at 0 °C. In a 100 mL Schlenk tube 3.12 g (20 mmol, 1 eq.) **1b** were dissolved in 40 mL THF at 0 °C and then added to the $\text{K}[\text{Fe}(\text{CO})_4\text{H}]$ suspension with a transfer canula. After the addition the canula was rinsed twice with 10 mL THF. Then the ice bath was removed and the mixture was stirred for 1 hour at room temperature after which the solvent was removed. The crude product was extracted from the residue with 60 mL (30+15+15 mL) *n*-pentane and then the red filtrate was dried to become a red oil. After further purification via inert column chromatography ($h = 10$ cm, $\phi = 4.5$ cm, SiO_2 PE (5% NEt_3), -20 °C) from which the first fraction and also the second (PE:Et₂O, 1:1 + 5% NEt_3) contained product and were combined. After solvent removal under reduced pressure ($3 \cdot 10^{-2}$ mbar) the product was obtained as a red oil in good yield.

Yield: 4.23 g, 76%; **Elemental analysis:** calculated (%) C 33.60 H 3.88 N 9.79, found (%) C 33.41 H 3.99 N 9.78; **MS:** (EI, 70 eV, selected data): $m/z = 285.9$ $[\text{M}]^{+*}$, 257.9 $[\text{M}-\text{CO}]^{+*}$, 229.9 $[\text{M}-2\text{CO}]^{+*}$, 201.9 $[\text{M}-3\text{CO}]^{+*}$, 173.9 $[\text{M}-4\text{CO}]^{+*}$, 117.0 $[\text{M}-\text{Fe}-4\text{CO}-\text{H}]^{+*}$; **IR:** (toluene solution) in cm^{-1} 3027 (m, C-H), 2054 (s, P-H), 1980 (s(br) CO), 1944 (vs(br), CO); **^1H -NMR:** (500 MHz, 298 K, THF- d_8): 7.47 (d, $^1J_{\text{P,H}} = 357$ Hz, 1H), 3.28 – 3.20 (m, 2H, backbone- C_2H_4), 3.13 – 3.07 (m, 2H, C_2H_4), 2.75 (d, $^1J_{\text{P,H}} = 14.4$ Hz, 6H, $2x\text{N-Me}$)

$^{13}\text{C}\{^1\text{H}\}$ -NMR: (126 MHz, 298 K, THF- d_8): 214.02 (d, $^2J_{\text{P,C}} = 21$ Hz, CO), 53.62 (d, $=3$ Hz, C_2H_4), 34.58 (d, $=7$ Hz, N- CH_3); **$^{31}\text{P}\{^1\text{H}\}$ -NMR:** (162 MHz, 298 K, THF- d_8): 144.1 (s_{sat} , $^1J_{\text{Fe,P}} = 29$ Hz); **^{31}P -NMR:** (162 MHz, 298 K, THF- d_8): 144.0 (dm, $^1J_{\text{P,H}} = 358$ Hz).

Synthesis of [tetracarbonyl(1,3-dimethyl-1H-benzo[4,5-c]-2,3-dihydro-1,3,2-diazaphosphole- κP)iron(0)] **4c^{Fe}**:

In a three necked 250 mL round bottom flask, equipped with a dropping funnel and a vacuum adapter, 1.03 g (8 mmol, 1 eq.) freshly prepared 1,2-dimethylaminobenzene was dissolved in 10 mL Et_2O and 2.5 mL (18 mmol, 2.4 eq.) NEt_3 were added. The dropping funnel was charged with 7.5 mL Et_2O and 0.7 mL (11 mmol, 1.4 mmol) PCl_3 . The round bottom flask was cooled to 0 °C in an ice bath and the PCl_3 solution was added dropwise to the diaminobenzene over the period of 20 minutes. After the addition was completed the dropping funnel was rinsed with 3 mL Et_2O . The mixture was stirred for 1.5 hours at 0 °C, after which the formed colourless suspension was filtered through a glass filter (P3) and the residue was washed four times (20+10+30+20 mL) with Et_2O . The solvent was removed from the filtrate under reduced pressure (100 mbar) at room temperature. And the residual colourless powder was suspended in 20 mL THF and added via a transfer canula to a cooled (0 °C) solution of 1.58 mg (8 mmol, 1 eq.) $\text{K}[\text{Fe}(\text{CO})_4\text{H}]$ in 30 mL THF in a 100 mL Schlenk tube. After addition the canula was rinsed with 20 mL THF. The reaction mixture was stirred at room temperature for 30 minutes after which the solvent was removed under reduced pressure ($3 \cdot 10^{-2}$ mbar). After thorough drying the product was extracted from the red residue with 100 mL *n*-pentane. Removal of the solvent under reduced pressure ($3 \cdot 10^{-2}$ mbar) gives a red-brown powder in moderate yield. Further purification via column chromatography (h = 10 cm, $\phi = 1$ cm, SiO_2 , PE: Et_2O (2.5% NEt_3), -20 °C) is possible however leads to a decrease of the yield below 10%.

Yield: 1.52 g, 59%; **Melting point:** 131 °C; **Elemental analysis:** calculated (%) C 43.15 H 3.32 N 8.39, found (%) C 42.58 H 3.33 N 8.27; **MS:** (EI, 70 eV, selected data): m/z (%) 333.9 [$\text{M}]^{+\bullet}$, 305.9 [$\text{M-CO}]^{+\bullet}$, 277.9 [$\text{M-2CO}]^{+\bullet}$, 249.9 [$\text{M-3CO}]^{+\bullet}$, 249.9 [$\text{M-3CO}]^{+\bullet}$, 222.0 [$\text{M-4CO}]^{+\bullet}$, 182.0 [$\text{M-4CO-Fe+O}]^{+\bullet}$ 165 [$\text{M-4CO-Fe-H}]^{+\bullet}$; **IR** (ATR diamond) $\tilde{\nu}$ in cm^{-1} : 2932(m, $\nu(\text{C-H})$), 2052 (m, $\nu(\text{P-H})$), 2029 (m, $\nu(\text{C=O})$), 1910 (vs, $\nu(\text{C=O})$); **^1H -NMR:** (300 MHz, 298 K, THF- d_8): 8.94 (d, $^1J_{\text{P,H}} = 358.4$ Hz, 1H, P-H), 6.58 – 6.68 (m, 4H, C_6H_4), 3.10 (d, $^3J_{\text{P,H}} = 11.9$ Hz, 6H, N- CH_3); **$^{13}\text{C}\{^1\text{H}\}$ -NMR:** (76 MHz, 298 K, THF- d_8): 212.1 (d, $^2J_{\text{P,C}} = 20$ Hz, CO), 138.8 (d, $^XJ_{\text{P,C}} = 2$ Hz, C_6H_4), 119.9 (s, C_6H_4), 107.9 (d, $^XJ_{\text{P,C}} = 5$ Hz, C_6H_4), 28.0 (d, $^2J_{\text{P,C}} = 9$ Hz, N- CH_3); **$^{31}\text{P}\{^1\text{H}\}$ -NMR:** (122 MHz, 298 K, THF- d_8): 151.8 (s_{sat} , $^1J_{\text{Fe,P}} = 33$ Hz) **^{31}P -NMR:** (122 MHz, 298 K, THF- d_8): 151.8 (dhept, $^1J_{\text{P,H}} = 356$ Hz, $^3J_{\text{P,H}} = 12$ Hz).

1,3,2-Oxazaphospholidine $\text{Fe}(\text{CO})_4$ complexes:

Synthesis of [tetracarbonyl(3-(1-methylethyl)-1,3,2-oxazaphospholidine- κP)iron(0)] **5a^{Fe}**:

In a 100 mL Schlenk flask 1.47 g (7 mmol, 1 eq.) $\text{K}[\text{Fe}(\text{CO})_4\text{H}]$ were dissolved in 20 mL THF at 0 °C. In a 25 mL Schlenk tube 1.03 g (6 mmol, 0.9 eq.) **2a** were dissolved in 10 mL THF at 0 °C and then added to the $\text{K}[\text{Fe}(\text{CO})_4\text{H}]$ suspension with a transfer canula. After the addition the canula was rinsed with 5 mL THF. Then the ice bath was removed and the yellow-brown mixture was stirred for 18 hours at room temperature after which the solvent was removed. The crude product was extracted from the residue with 40 mL (20+10+10 mL) *n*-pentane and the filtrate was dried to become a red oil. After further purification via inert column chromatography (h = 11 cm, $\phi = 4.5$ cm, SiO_2 PE (2.5% NEt_3), -20 °C) from which the first fraction (PE, 2.5% NEt_3) contained product. After removal of solvent and drying under reduced pressure ($3 \cdot 10^{-2}$ mbar) the product was obtained as an orange oil in moderate yield.

Yield: 1.00 g, 47%; **Elemental analysis:** calculated (%) C 35.91 H 4.02 N 4.65 , found (%) C 36.47 H 4.31 N 4.67; **¹H-NMR:** (500 MHz, 298 K, C₆D₆): 7.54 (d, ¹J_{P,H} = 375 Hz, 1H, P-H), 3.70 (dhept, ³J_{P,H} = 9.2 Hz, ³J_{H,H} = 6.7 Hz, 1H, CHMe₂), 3.44 (pent, ³J_{H,H} = 8.4 Hz 1H, O-CH₂), 3.38 – 3.29 (m, 1H, O-CH₂), 2.46 – 2.30 (m, 1H, N-CH₂), 2.04 (m, 1H, N-CH₂), 0.88 (d, ³J_{H,H} = 6.7 Hz, 3H, CH₃), 0.71 (d, ³J_{H,H} = 6.7 Hz, 3H, CH₃); **¹³C{¹H}-NMR:** (126 MHz, 298 K, C₆D₆): 212.3 (d, ²J_{P,C} = 22 Hz, CO), 67.5 (d, ²J_{P,C} = 10 Hz, O-CH₂), 44.5 (d, ²J_{P,C} = 9.1 Hz, N-CH₂), 40.1 (d, ²J_{P,C} = 2.1 Hz, N-CHMe₂), 20.9 (d, ²J_{P,C} = 7.7 Hz, CH₃), 19.0 (d, ²J_{P,C} = 7.7 Hz, CH₃); **³¹P{¹H}-NMR:** (203 MHz, 298 K, C₆D₆): 169.9 (s_{sat}, ¹J_{Fe,P} = 32 Hz); **³¹P-NMR:** (203 MHz, 298 K, C₆D₆): 169.9 (dm, ¹J_{P,H} = 375 Hz).

Synthesis of [tetracarbonyl(3-methyl-1,3,2-oxazaphospholidine-κP)iron(0)] **5b**^{Fe}:

In a 100 mL Schlenk flask 1.57 g (8 mmol, 1 eq.) K[Fe(CO)₄H] were dissolved in 20 mL THF at 0 °C. In a 25 mL Schlenk tube 1.10 g (8 mmol, 1 eq.) **2b** were dissolved in 10 mL THF at 0 °C and then added to the K[Fe(CO)₄H] suspension with a transfer canula. After the addition the canula was rinsed with 5 mL THF. Then the ice bath was removed and the yellow-brown mixture was stirred for 18 hours at room temperature after which the solvent was removed. The crude product was extracted from the residue with 40 mL (20+10+10 mL) *n*-pentane and the filtrate was dried to become a red oil. After further purification via inert column chromatography (h = 11 cm, ø= 4.5 cm, SiO₂ PE:Et₂O (2.5% NEt₃), -20 °C) from which the first (PE, 2.5% NEt₃) and second (PE:Et₂O, 2:1, 2.5% NEt₃) fraction contained product. After removal of solvent and drying under reduces pressure (3·10⁻² mbar) the product was obtained as an orange oil in bad yield.

Yield: 660 mg, 32%; **Elemental analysis:** calculated (%) C 30.80 H 2.95 N 5.13 , found (%) C 31.59 H 3.39 N 5.14; **IR** (ATR diamond) $\tilde{\nu}$ in cm⁻¹: 2906 (m, ν (C-H)), 2250 (w, ν (P-H)), 2057 (s, ν (C=O)), 1972 (vs, ν (C=O)); **¹H-NMR:** (400 MHz, 298 K, C₆D₆): 7.34 (d, ¹J_{P,H} = 382 Hz, 1H), 3.52 – 3.39 (m(br), 1H, O-CH₂), 3.29 – 3.21 (m(br), 1H, O-CH₂), 2.23 (d, ³J_{P,H} = 13.7 Hz, 3H, N-CH₃), 2.23 (m(br), 1H, N-CH₂), 2.03 – 1.94 (m(br), 1H, N-CH₂); **¹³C{¹H}-NMR:** (126 MHz, 298 K, C₆D₆): 212.5 (d, ²J_{P,C} = 22 Hz, CO), 68.0 (s, O-CH₂), 50.8 (s, N-CH₂), 32.0 (s, N-CH₃); **³¹P{¹H}-NMR:** (203 MHz, 298 K, C₆D₆): 179.4 (s); **³¹P-NMR:** (203 MHz, 298 K, C₆D₆): 179.4 (d, ¹J_{P,H} = 382 Hz).

Synthesis of [tetracarbonyl(4,4,5,5-tetramethyl-1,3,2-dioxaphospholane-κP)iron(0)] **6b**^{Fe}:

In a 100 mL Schlenk flask 1.05 g (5 mmol, 1 eq.) K[Fe(CO)₄H] were dissolved in 20 mL THF at 0 °C. In a 25 mL Schlenk tube 950 mg (5 mmol, 1 eq.) **3b** were dissolved in 5 mL THF at 0 °C and then added to the K[Fe(CO)₄H] suspension with a transfer canula. After the addition the canula was rinsed with 5 mL THF. Then the ice bath was removed and the yellow-brown mixture was stirred for 1 hour at room temperature after which the solvent was removed. The crude product was extracted from the residue with 30 mL (10+10+10 mL) *n*-pentane and the filtrate was dried to become a red oil. After further purification via inert column chromatography (h = 11 cm, ø= 4.5 cm, SiO₂ PE:Et₂O (2.5% NEt₃), -20 °C) from which the first fraction (PE, 2.5% NEt₃) contained product. After removal of solvent and drying under reduces pressure (3·10⁻² mbar) the product was obtained as an orange oil in low yield.

Yield: 445 mg, 28%; **Melting point:** 37 °C; **Elemental analysis:** calculated (%) C 38.01 H 4.15 , found (%) C 39.30 H 4.55; **MS:** (EI, 70 eV, selected data): m/z = 316.0 [M]⁺⁺, 288.0 [M-CO]⁺⁺, 260.0 [M-2CO]⁺⁺, 232.0 [M-3CO]⁺⁺, 204 [M-4CO]⁺⁺; **IR** (ATR diamond) $\tilde{\nu}$ in cm⁻¹: 2985 (m, ν (C-H)), 2321 (w, ν (P-H)), 2056 (s, ν (C=O)), 1988 (m, ν (C=O)), 1925 (vs, ν (C=O)); **¹H-NMR:** (500 MHz, 298 K, C₆D₆): 8.06 (d, ¹J_{P,H} = 409 Hz, 1H, P-H), 0.95 (s, 6H, C(CH₃)₂), 0.70 (s, C(CH₃)₂); **¹³C{¹H}-NMR:** (126 MHz, 298 K, C₆D₆): 212.43 (d, ²J_{P,C} = 23 Hz, CO), 88.1 (d, ²J_{P,C} = 6 Hz, C₂Me₄), 24.4 (d, ³J_{P,C} = 5 Hz, C₂(CH₃)₄), 21.7 (d, ³J_{P,C} = 4 Hz, C₂(CH₃)₄); **³¹P{¹H}-NMR:** (203 MHz, 298 K, C₆D₆): 196.4 (s_{sat}, ¹J_{Fe,P} = 36 Hz); **³¹P-NMR:** (203 MHz, 298 K, C₆D₆): 196.4 (d, ¹J_{P,H} = 409 Hz).

Synthesis of [tetracarbonyl(1H benzo[4,5-c]-2,3-dihydro-1,3,2-dioxaphosphole-κP)iron(0)] **6c^{Fe}**:

In a 100 mL Schlenk flask 425 mg (2 mmol, 1 eq.) K[Fe(CO)₄H] were dissolved in 10 mL THF at 0 °C. In a 25 mL Schlenk tube 400 mg (2 mmol, 1.1 eq.) **3c** were dissolved in 3 mL THF at 0 °C and then added to the K[Fe(CO)₄H] suspension with a transfer canula. After the addition the canula was rinsed twice with 3.5 mL THF. Then the ice bath was removed and the yellow-brown mixture was stirred for 2.5 hours at room temperature after which the solvent was removed. The crude product was extracted from the residue with 60 mL (15+10+10+10+10+5 mL) *n*-pentane and the red filtrate was dried to become a yellow beige solid. The product can be recrystallized from a saturated *n*-pentane solution, however an impurity (2 – 5%) with a δ(³¹P) chemical shift of 192 ppm was still observed. Further attempts to purify the crude product via inert column chromatography (h = 11 cm, φ = 4.5 cm, SiO₂ PE:Et₂O (2.5% NEt₃), –20 °C) lead to hydrolysis (**7** in only small yields. If under the same conditions NEt₃ is not used nothing is collected in several fractions for several PE:Et₂O ratios.

Yield: 505 mg, 82% (crude product, after solvent removal; 2% impurity); **MS:** (EI, 70 eV, selected data): m/z (%) 307.9 [M]⁺, 279.9 [M-CO]⁺, 251.9 [M-2CO]⁺, 223.9 [M-3CO]⁺, 196.0 [M-4CO]⁺; **IR** (ATR diamond) $\tilde{\nu}$ in cm⁻¹: 2985 (m, ν(C-H)), 2321 (w, ν(P-H)), 2056 (s, ν(C=O)), 1988 (m, ν(C=O)), 1925 (vs, ν(C=O)); **¹H-NMR:** (500 MHz, 298 K, C₆D₆): 8.67 (d, ¹J_{P,H} = 432 Hz, 1H, P-H), 7.26 – 7.21 (m, 2H, C₆H₄), 7.12 – 7.07 (m, 2H, C₆H₄); **¹³C{¹H}-NMR:** (126 MHz, 298 K, THF-d₈): 211.6 (d, ²J_{P,C} = 22 Hz, CO), 148.1 (d, ²J_{P,C} = 6 Hz, C₆H₄), 125.3 (s, C₆H₄), 114.1 (d, ²J_{P,C} = 7 Hz, C₆H₄); **³¹P{¹H}-NMR:** (203 MHz, 298 K, THF-d₈): 228.7 (s_{sat}, ¹J_{Fe,P} = 40 Hz), **³¹P-NMR:** (203 MHz, 298 K, THF-d₈): 228.7 (d, ¹J_{P,H} = 432 Hz).

Synthesis of triethylammonium[tetracarbonyl([2-hydroxy-phenoxy]-phosphinito-κP)ferrate(0)] **7**:

6c^{Fe} was synthesized from 900 mg (5 mmol, 1 eq.) of **3c** and 1.06 g (5 mmol, 1 eq.) K[Fe(CO)₄H]. The crude product was charged on an inert column for purification (h = 11 cm, φ = 4.5 cm, SiO₂ PE:Et₂O (2.5% NEt₃), –20 °C). An initial yellow band on the column stopped, after one third the height and could only be eluted with THF (2.5% NEt₃). After removing the solvent from this fraction, a colourless solid **7** was obtained in very low yield.

Yield: 80 mg, 4%; **Elemental analysis:** calculated (%) C 44.99 H 5.19 N 3.28, found (%) C 45.43 H 5.29 N 3.36; **¹H-NMR:** (500 MHz, 298 K, C₆D₆): 10.66 (s(br), 1H, O-H), 9.34 (s(br), 1H, N-H), 8.87 (d, ¹J_{P,H} = 414 Hz, 1H, P-H), 7.34 (dt, ³J_{H,H} = 8 Hz, ³J_{H,H} = 1.6 Hz, 1H, C₆H₄), 7.17 (dd, ²J_{H,H} = 8 Hz, ³J_{H,H} = 1.6 Hz, 1H, C₆H₄), 6.91 (m, ^XJ_{P,H} = 9.4 Hz, ³J_{H,H} = 1.6 Hz, 1H, C₆H₄), 6.73 – 6.69 (m, 1H, C₆H₄), 1.96 (q, ³J_{H,H} = 7.3 Hz, 6H, N-CH₂-Me), 0.51 (t, ³J_{H,H} = 7.3 Hz, 9H, N-CH₂-CH₃); **¹³C{¹H}-NMR:** (126 MHz, 298 K, THF-d₈): 215.7 (d, ²J_{P,C} = 23 Hz, CO), 149.3 (d, ³J_{P,C} = 4 Hz, HO-C₆H₄), 145.3 (d, ³J_{P,C} = 16 Hz, P-O-C₆H₄), 125.85 (d, ^XJ_{P,C} = 1.7 Hz, C₆H₄), 123.30 (d, ^XJ_{P,C} = 4.3 Hz, C₆H₄), 120.74 (d, ^XJ_{P,C} = 1.6 Hz, C₆H₄), 118.24 (d, ^XJ_{P,C} = 1.6 Hz, C₆H₄), 45.50 (s, N-CH₂-Me), 8.06 (s, N-CH₂-CH₃); **³¹P{¹H}-NMR:** (203 MHz, 298 K, THF-d₈): 159.3 (s_{sat}, ¹J_{Fe,P} = 28 Hz); **³¹P-NMR:** (203 MHz, 298 K, THF-d₈): 159.3 (d, ¹J_{P,H} = 414 Hz).

References

- (1) Jones, A. S.; McGuigan, C.; Walker, R. T. Synthesis of Some Nucleoside Cyclic Phosphoramidates and Related Compounds via Phosphoramidites. *J. Chem. Soc. Perkin Trans. 1* **1985**, No. 6, 199–202. <https://doi.org/10.1039/p19850000199>.
- (2) Breen, D.; Kennedy, A. R.; Suckling, C. J. A Divergent Synthesis of Minor Groove Binders with Tail Group Variation. *Org. Biomol. Chem.* **2009**, 7 (1), 178–186. <https://doi.org/10.1039/b814452d>.
- (3) Denmark, S. E.; Stadler, H.; Dorow, R. L.; Kim, J. H. Carbanion-Accelerated Claisen Rearrangements. 8. Phosphonamide Anion-Stabilizing Groups. *J. Org. Chem.* **1991**, 56 (17), 5063–5079. <https://doi.org/10.1021/jo00017a016>.
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Design and Synthesis. In *Focus on Catalysts*; 2012; pp 81–131. [https://doi.org/10.1016/S1351-4180\(13\)70046-1](https://doi.org/10.1016/S1351-4180(13)70046-1).

- (5) Wang, Y.-F.; Zhang, M.-T. Proton-Coupled Electron-Transfer Reduction of Dioxygen: The Importance of Precursor Complex Formation between Electron Donor and Proton Donor. *J. Am. Chem. Soc.* **2022**, *144* (27), 12459–12468. <https://doi.org/10.1021/jacs.2c04467>.
- (6) Brunet, J. J.; Commenges, G.; Kindela, F. B.; Neibecker, D. Ligand Substitution Processes on Carbonylmetal Derivatives. 1. Reaction of Tetracarbonylhydridoferrates with Phosphines. *Organometallics* **1992**, *11* (3), 1343–1350. <https://doi.org/10.1021/om00039a045>.

NMR Spectra of

1b^{Fe}

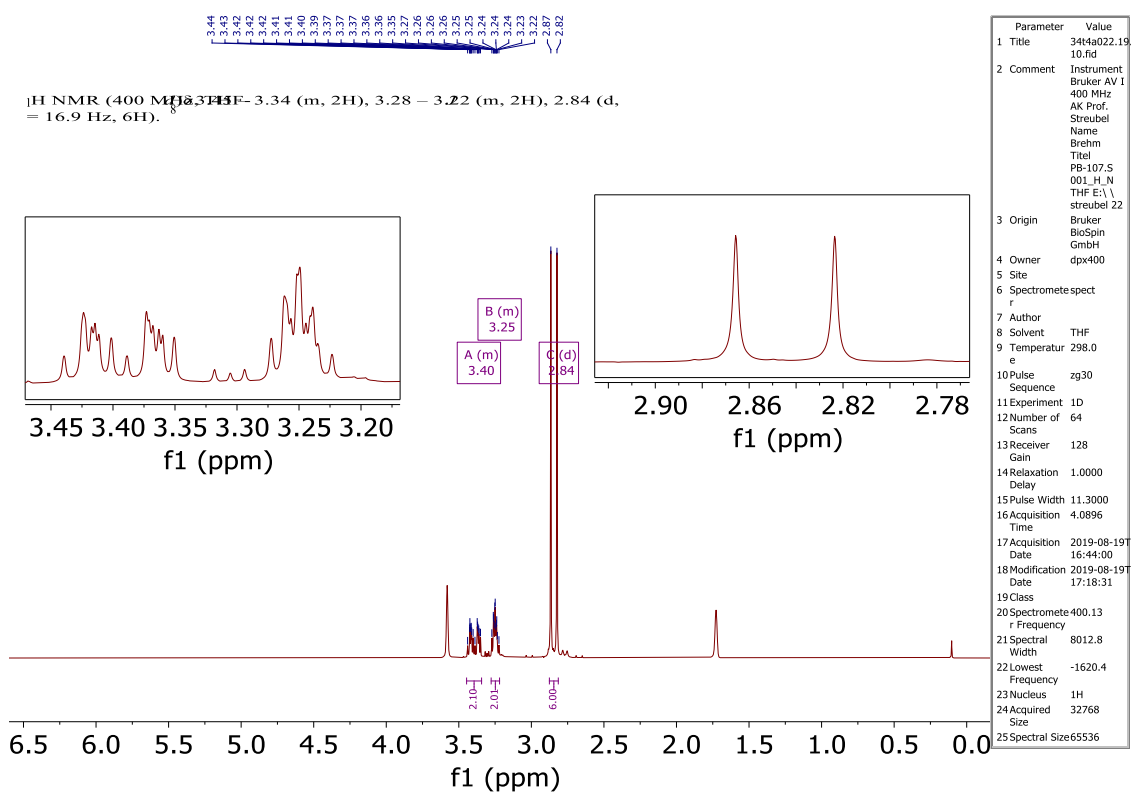


Figure 1 ¹H-NMR spectrum of 1b^{Fe} in THF-d₈.

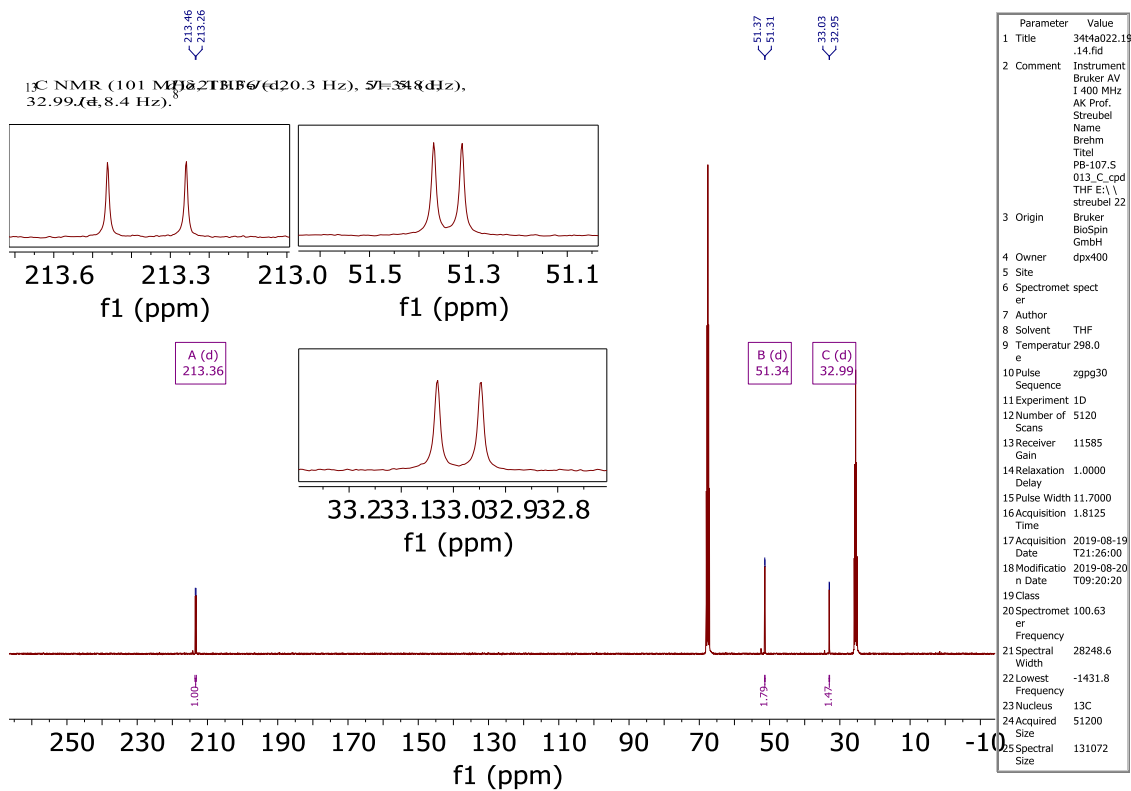


Figure 2 ¹³C{¹H}-NMR spectrum of **1b^{Fe}** in THF-d₈.

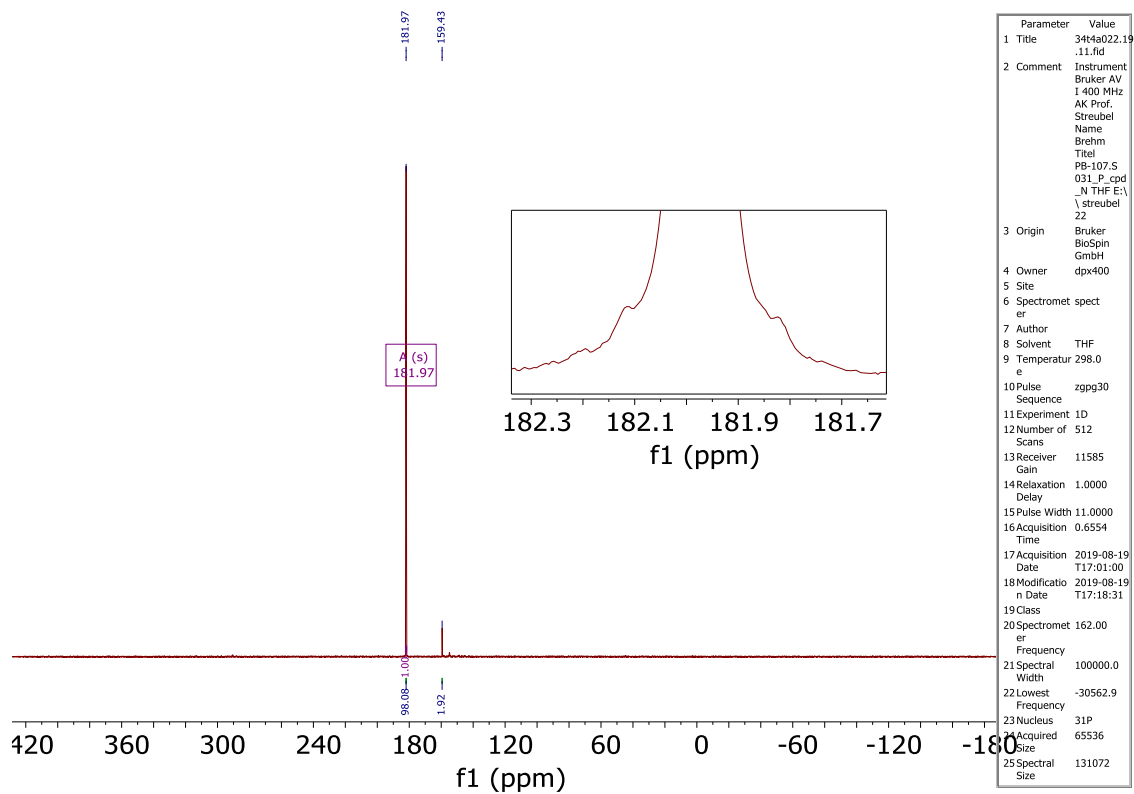


Figure 3 ³¹P{¹H}-NMR spectrum of **1b^{Fe}** in THF-d₈.

3b^{Fe}

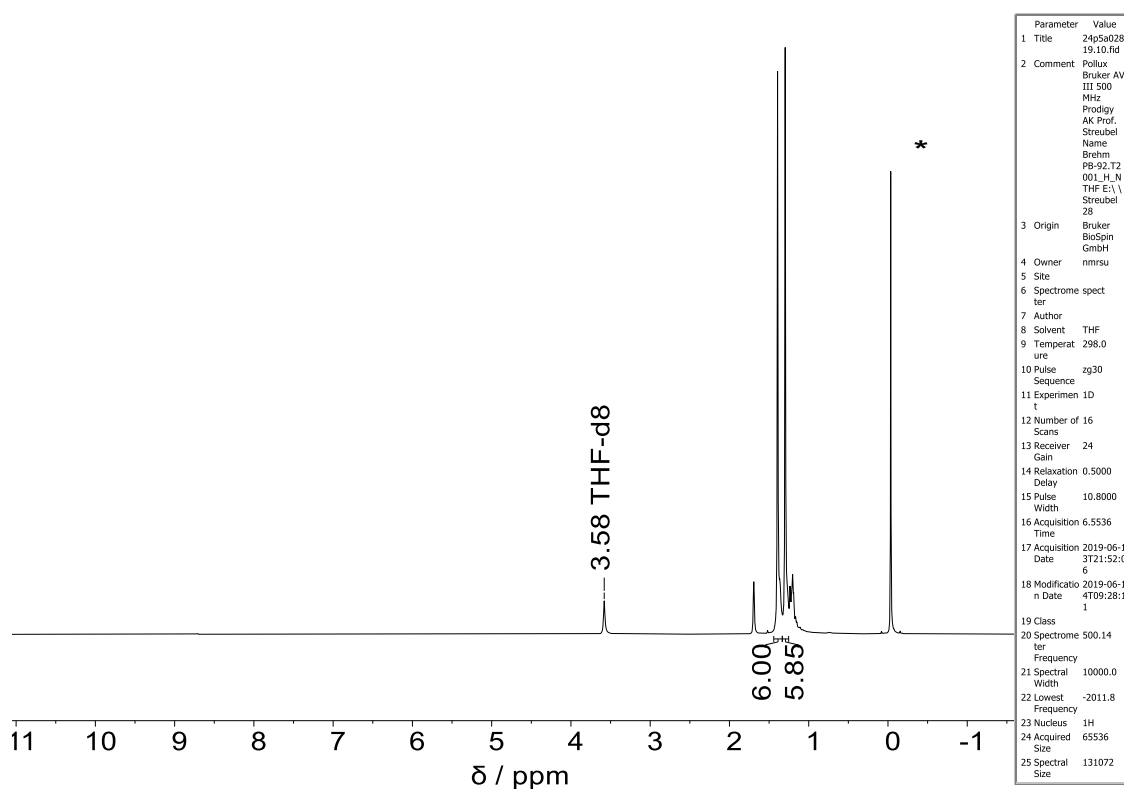


Figure 4 ¹H-NMR spectrum of 3b^{Fe} in THF-d₈.

¹³C NMR (126 MHz, THF-d₈) (d_{11.7} Hz), 91.72 (d), 24.46 (d, = 6.0 Hz), 23.73 (d).

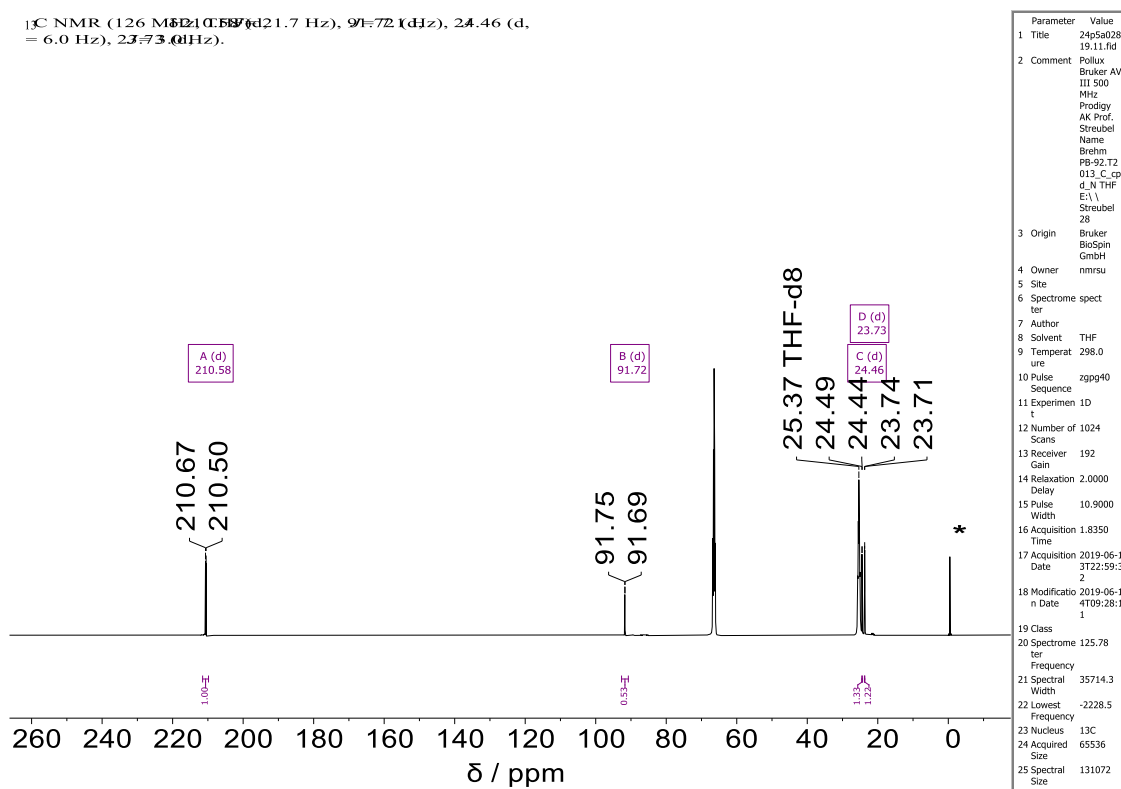


Figure 5 ¹³C{¹H}-NMR spectrum of 3b^{Fe} in THF-d₈.

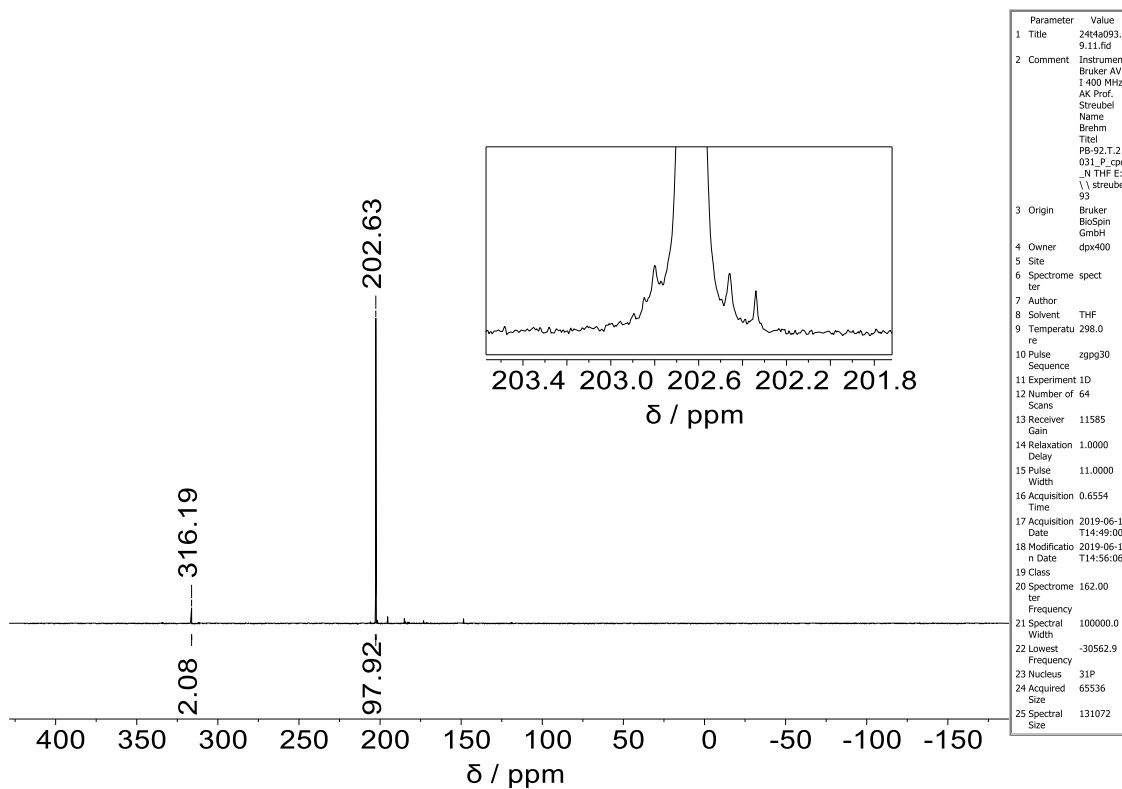


Figure 6 $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of $3b^{\text{Fe}}$ in THF-d₈.

$3c^{\text{Fe}}$

^1H NMR (500 MHz, THF-d₈) δ : 7.31 (d, 6.0, 3.4 Hz, 1H), 7.20 (d, 6.0, 3.4 Hz, 1H).

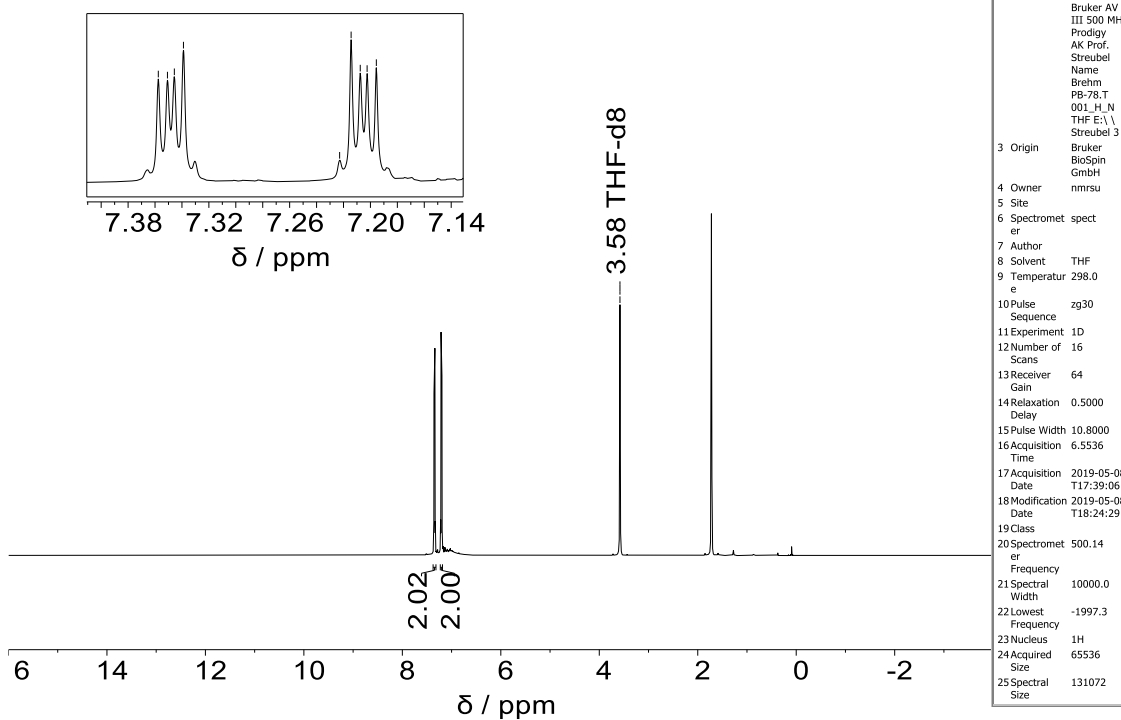
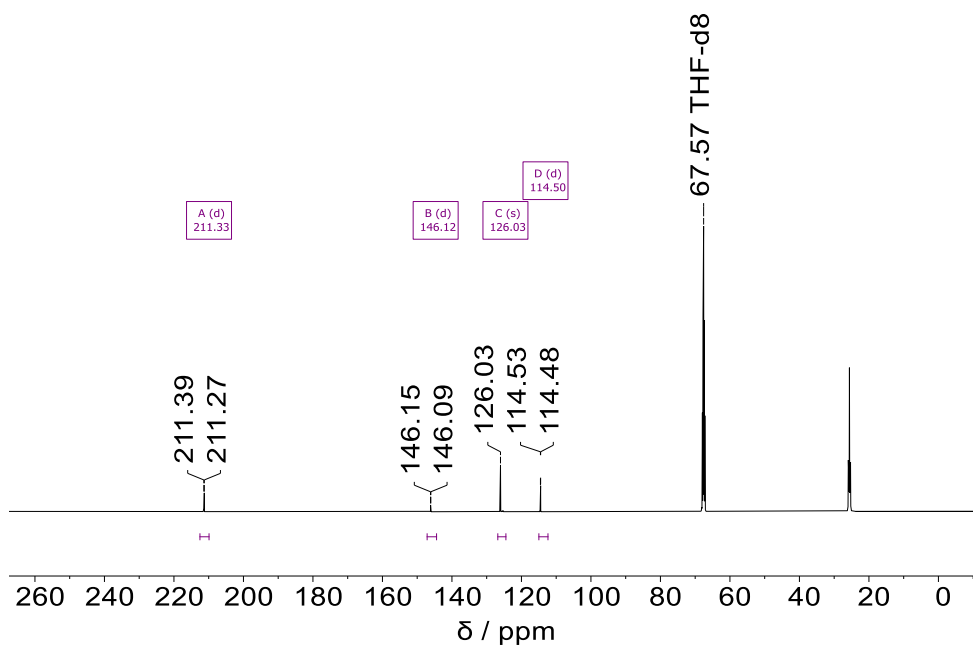


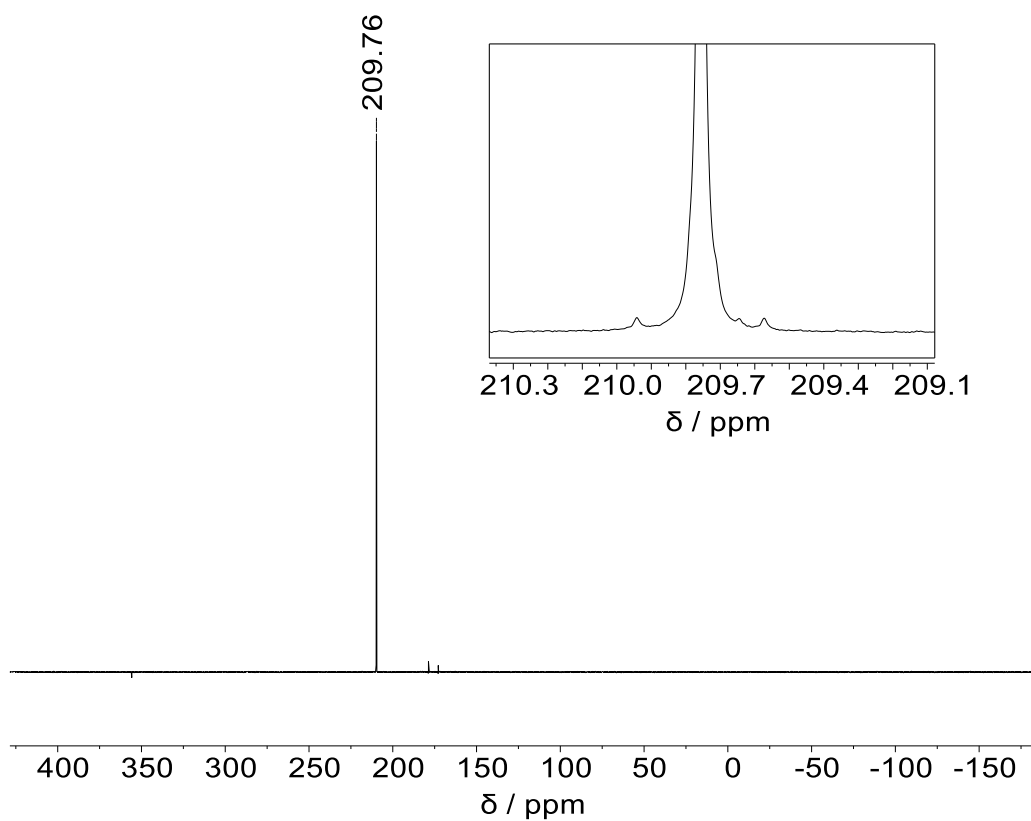
Figure 7 ^1H -NMR spectrum of $3c^{\text{Fe}}$ in THF-d₈.

^{13}C NMR (126 MHz, THF-d₈) δ : 211.39, 211.27, 146.15, 146.09, 126.03, 114.53, 114.48, 67.57 (THF-d₈), 126.03, 114.50 (cd, 6.7 Hz).



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3 Origin	Bruker BioSpin GmbH
4 Owner	nmsu
5 Site	
6 Spectrometer specter	
7 Author	
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15 Pulse Width	10.9000
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18 Modification Date	2019-05-09 T13:46:30
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20 Spectrometer specter	125.78
21 Frequency	35714.3
22 Lowest Frequency	-1996.5
23 Nucleus	^{13}C
24 Acquired Size	65536
25 Spectral Size	131072

Figure 8 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of 3c^{Fe} in THF-d₈.

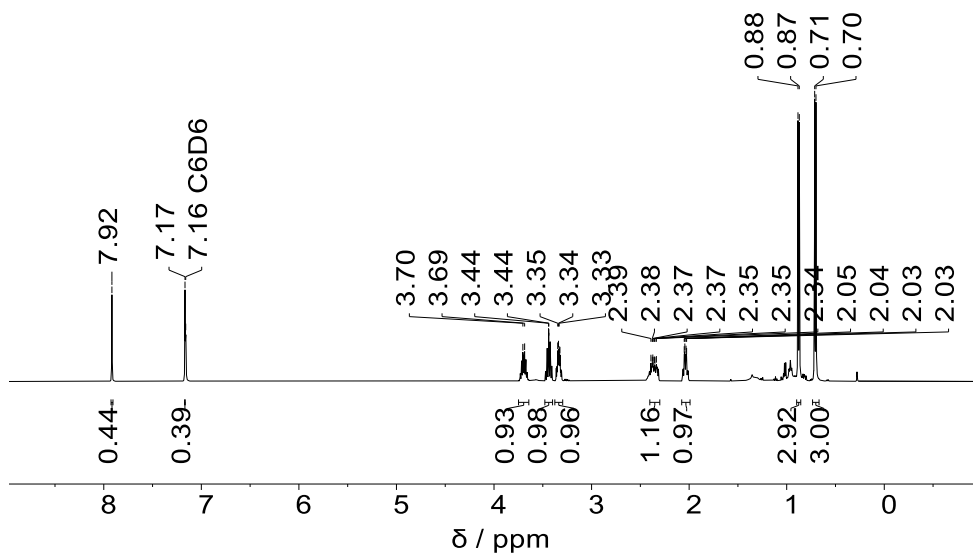


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7 Author	
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17 Acquisition Date	2019-05-08 T19:20:24
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20 Spectrometer specter	202.48
21 Frequency	125000.0
22 Lowest Frequency	-38204.8
23 Nucleus	^{31}P
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25 Spectral Size	262144

Figure 9 $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of 3c^{Fe} in THF-d₈.

4a^{Fe}

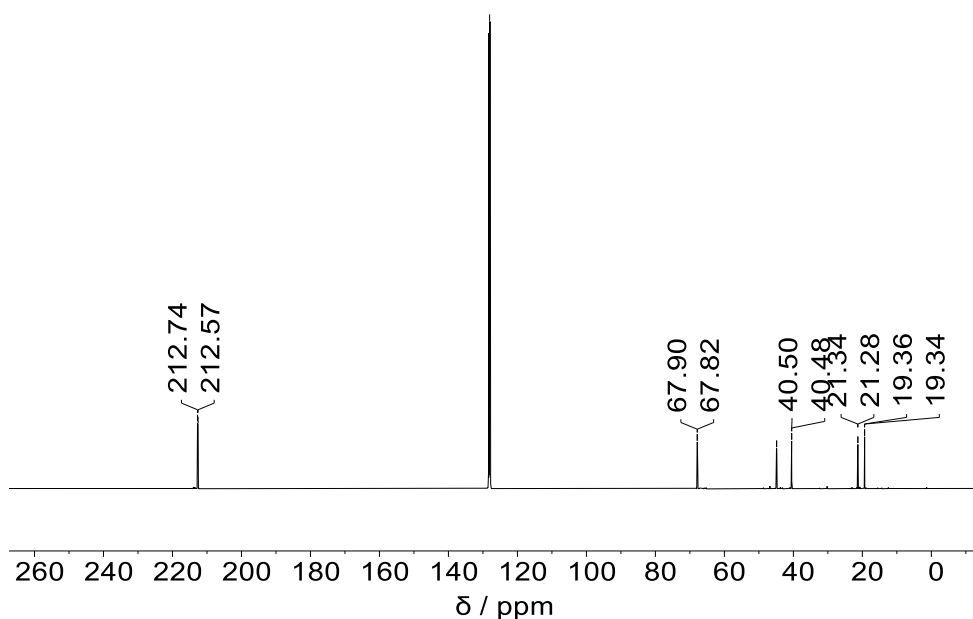
¹H NMR (500 MHz, C₆D₆) δ: 7.92 (d, 3H, 3.74 Hz, 1H) / 7.16 (d, 3H, 3.74 Hz, 1H), 3.38 (m, 1H), 2.46 (m, 1H) / 2.03 (d, 3H, 2.03 Hz, 3H), 0.88 (t, 3H) / 0.70 (t, 3H).



Parameter	Value
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4 Owner	nmsu
5 Site	
6 Spectrometer spect	
7 Author	
8 Solvent	C6D6
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23 Nucleus	¹ H
24 Acquired Size	65536
25 Spectral Size	131072

Figure 10 ¹H-NMR spectrum of 3c^{Fe} in C₆D₆.

¹³C NMR (126 MHz, C₆D₆) δ: 212.74 (d, 2.1 Hz), 212.57 (d, 2.1 Hz), 67.90 (d, 1.1 Hz), 67.82 (d, 1.1 Hz), 40.49 (d, 2.1 Hz), 40.34 (d, 2.1 Hz), 21.28 (t, 5.0 Hz), 19.36 (t, 5.0 Hz), 19.34 (t, 5.0 Hz).



Parameter	Value
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5 Site	
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7 Author	
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Sequence	
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22 Lowest Frequency	-2092.5
23 Nucleus	¹³ C
24 Acquired Size	65536
25 Spectral Size	131072

Figure 11 ¹³C[¹H]-NMR spectrum of 4a^{Fe} in C₆D₆.

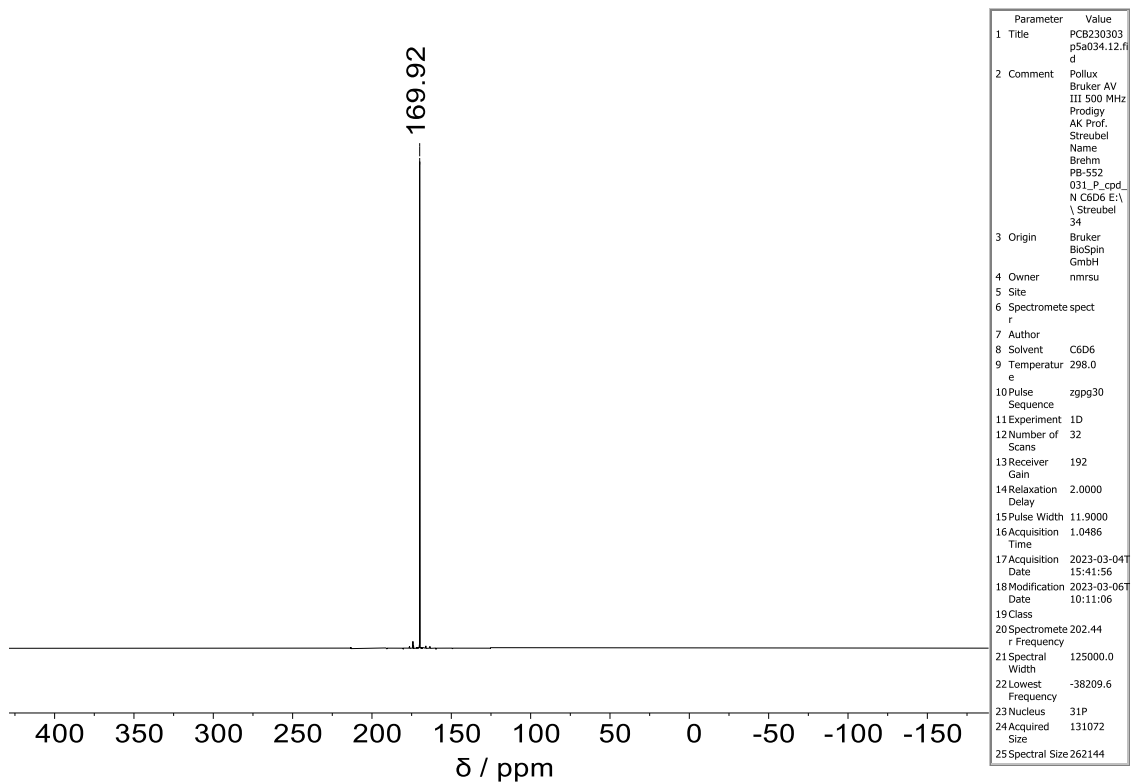


Figure 12 $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of $4a^{\text{Fe}}$ in C_6D_6 .

$4b^{\text{Fe}}$

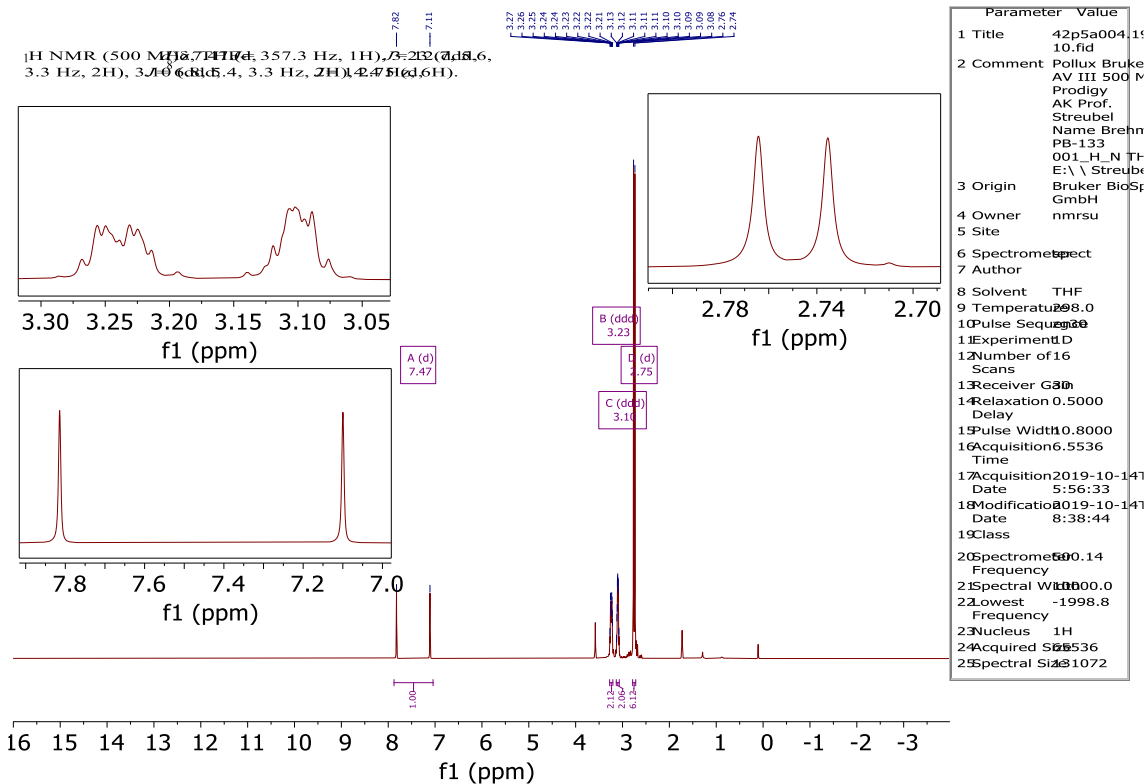


Figure 13 ^1H -NMR spectrum of $4b^{\text{Fe}}$ in THF-d_8 .

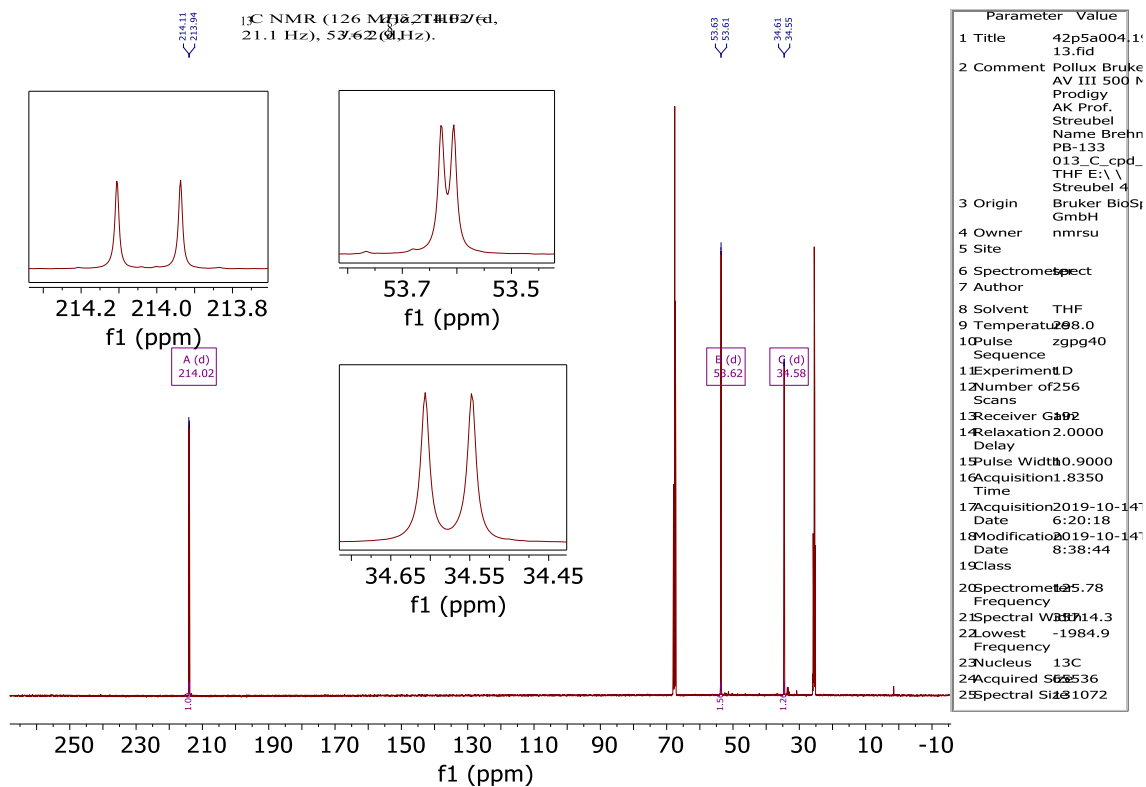


Figure 14 ¹³C{¹H}-NMR spectrum of **4b^{Fe}** in THF-d₈.

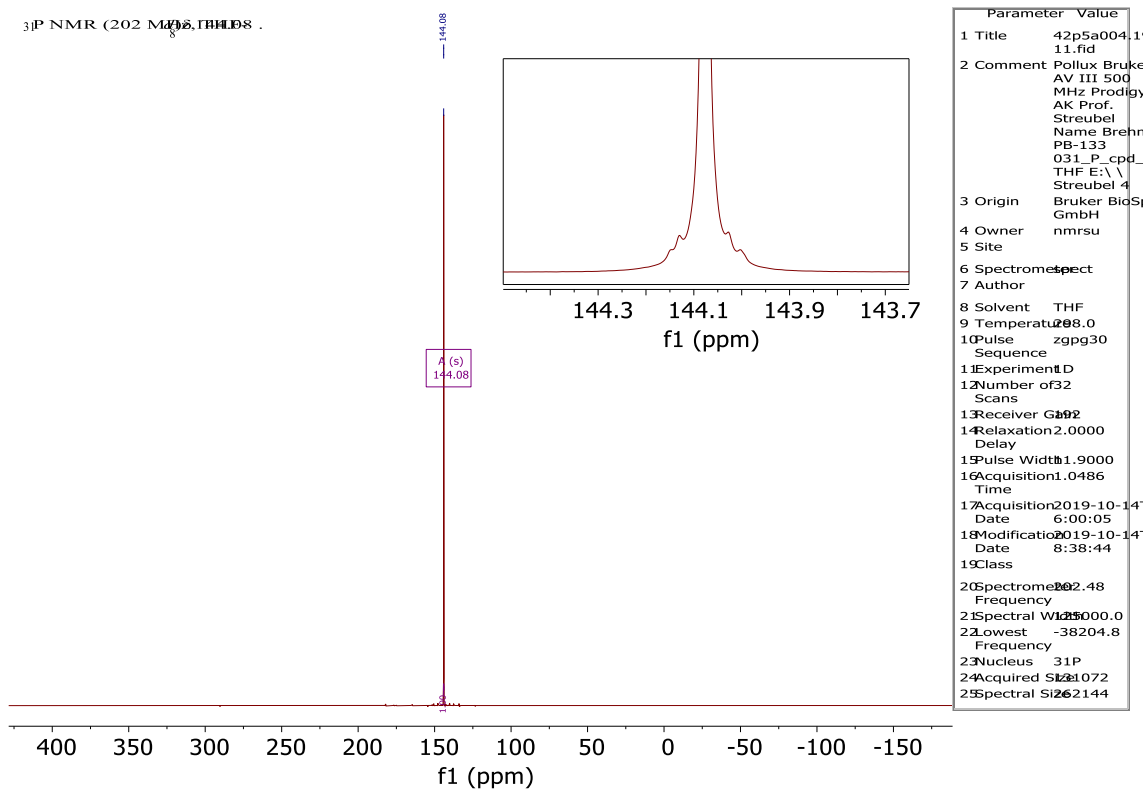
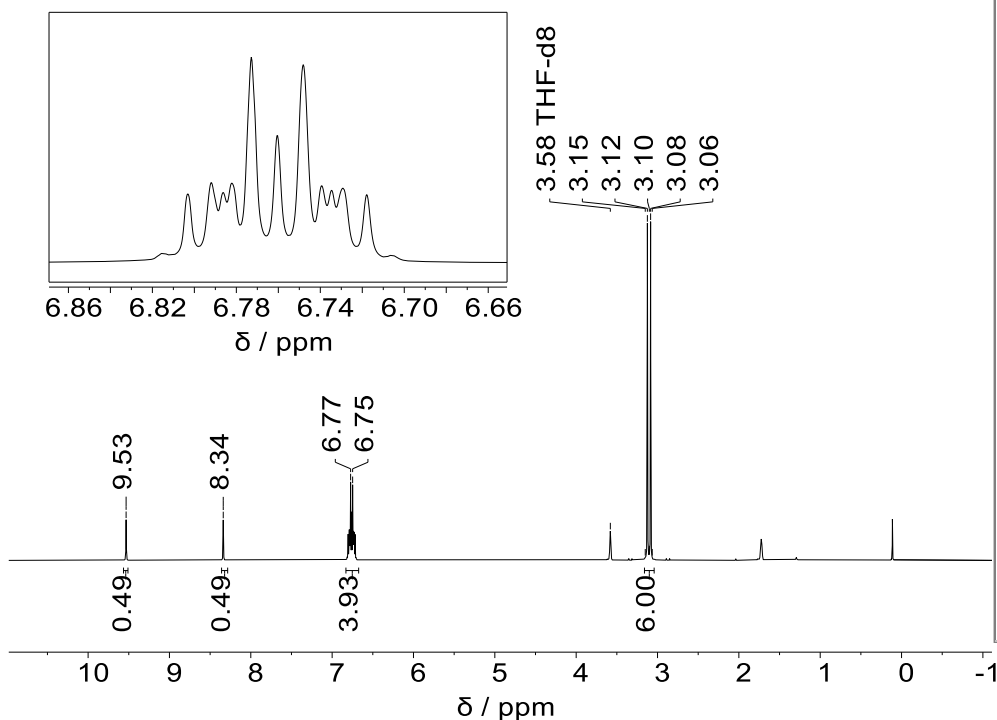


Figure 15 ³¹P{¹H}-NMR spectrum of **4b^{Fe}** in THF-d₈.

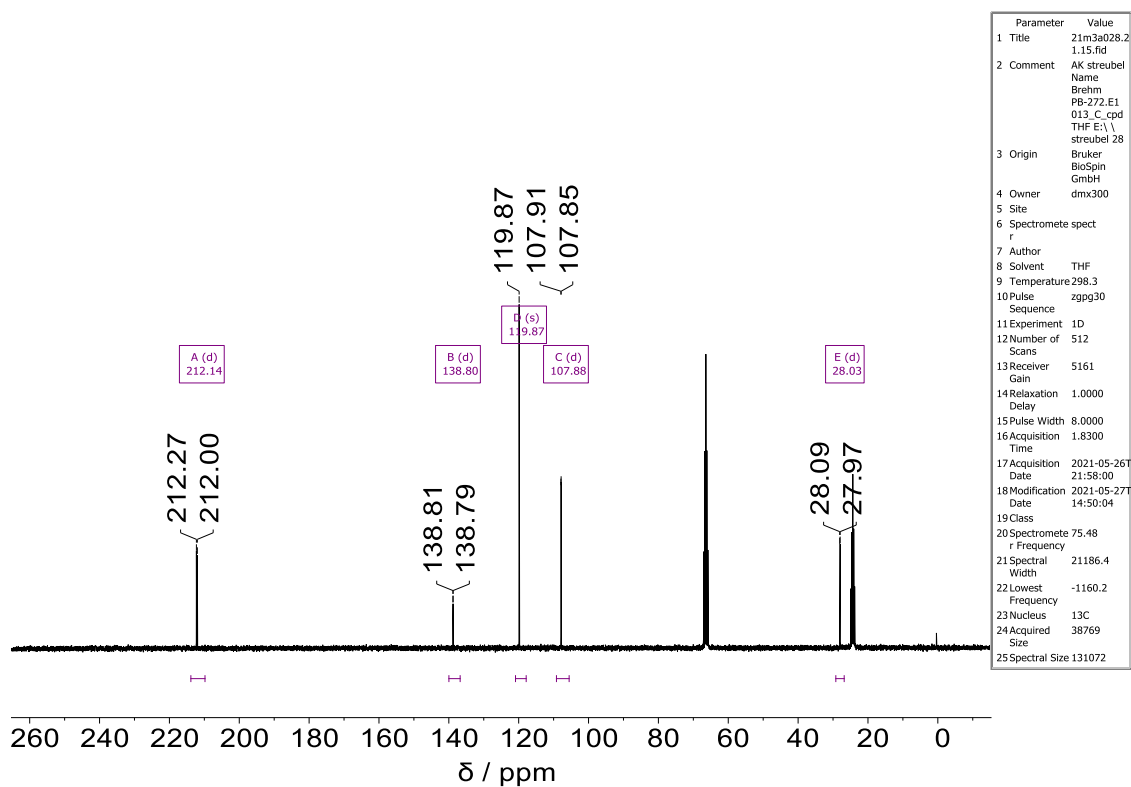
$4c^{Fe}$

1H NMR (300 MHz, THF-d₈) δ : 6.85 – 6.68 (m, 4H), 3.61 (d, 2H), 3.58 (s, 1H), 3.15 (s, 1H), 3.12 (s, 1H), 3.10 (s, 1H), 3.08 (s, 1H), 3.06 (s, 1H), 6.77 (d, 1H), 6.75 (d, 1H), 8.34 (s, 1H), 9.53 (s, 1H)



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7 Author	
8 Solvent	THF
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Scans	
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Frequency	
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Size	
25 Spectral	65536
Size	

Figure 16 1H -NMR spectrum of $4c^{Fe}$ in THF-d₈.



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6 Spectromete	spect
er	
7 Author	
8 Solvent	THF
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13 Receiver	5161
Gain	
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Width	
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Frequency	
23 Nucleus	^{13}C
24 Acquired	38769
Size	
25 Spectral	131072
Size	

Figure 17 $^{13}C\{^1H\}$ -NMR spectrum of $4c^{Fe}$ in THF-d₈.

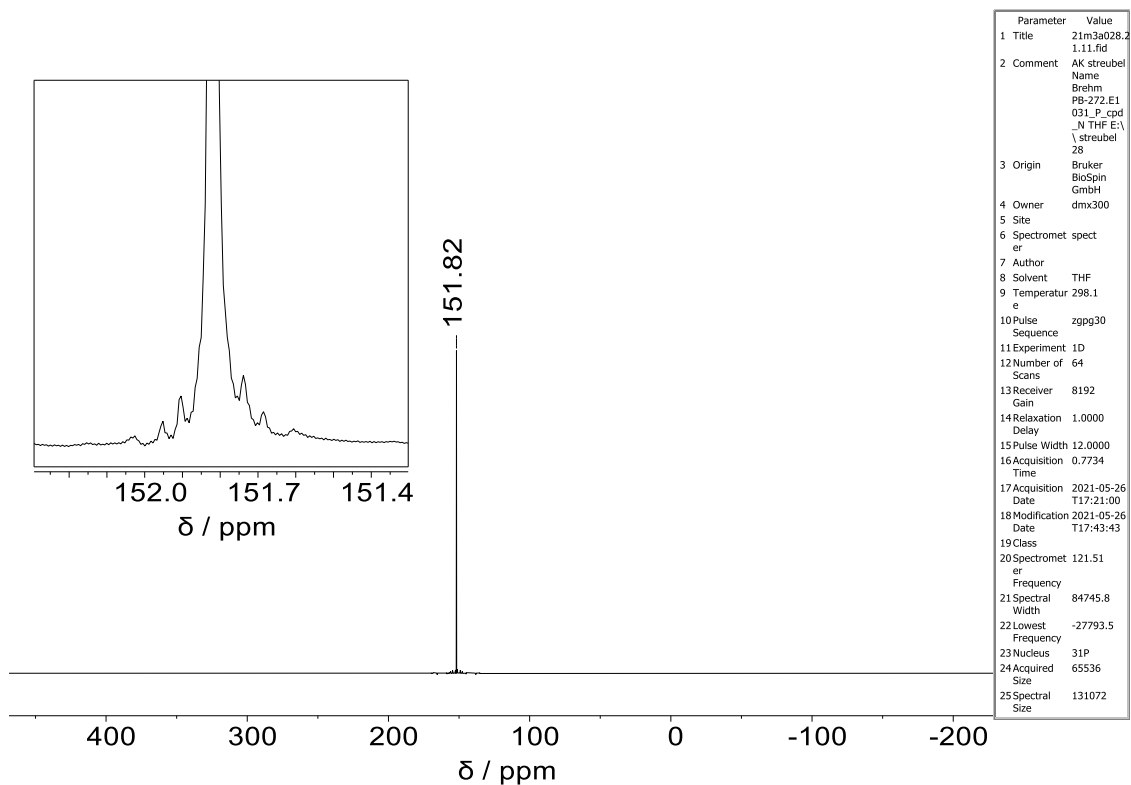


Figure 18 $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of $4c^{\text{Fe}}$ in THF- d_8 .

5a^{Fe}

^1H NMR (500 MHz, C_6D_6 , δ , 374.5 Hz, 1H) δ 7.92 (d, 1H), 7.17 (d, 1H), 7.16 (d, 1H), 3.38 (m, 1H), 2.46 – 2.30 (m, 7H), 2.04 (d, 1H), 0.88 (d, 3H), 0.87 (d, 3H), 0.71 (d, 3H), 0.70 (d, 3H).

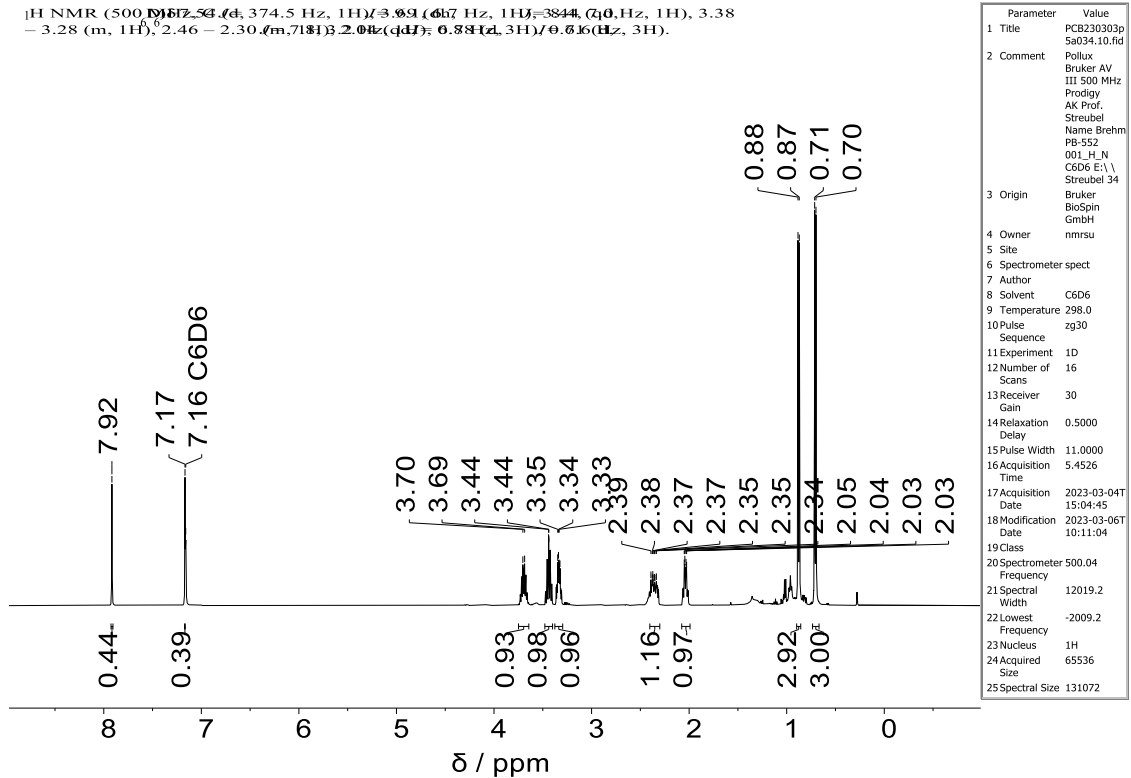


Figure 19 ^1H -NMR spectrum of $5a^{\text{Fe}}$ in C_6D_6 .

^{13}C NMR (126 MHz, C_6D_6) δ : 212.74 (d, 2.1 Hz), 212.57 (d, 2.1 Hz), 131.86 (d, 1.2 Hz), 67.90 (d, 1.2 Hz), 67.82 (d, 1.2 Hz), 40.49 (d, 2.1 Hz), 40.48 (d, 2.1 Hz), 21.34 (d, 1.2 Hz), 19.36 (d, 1.2 Hz), 19.34 (d, 1.2 Hz).

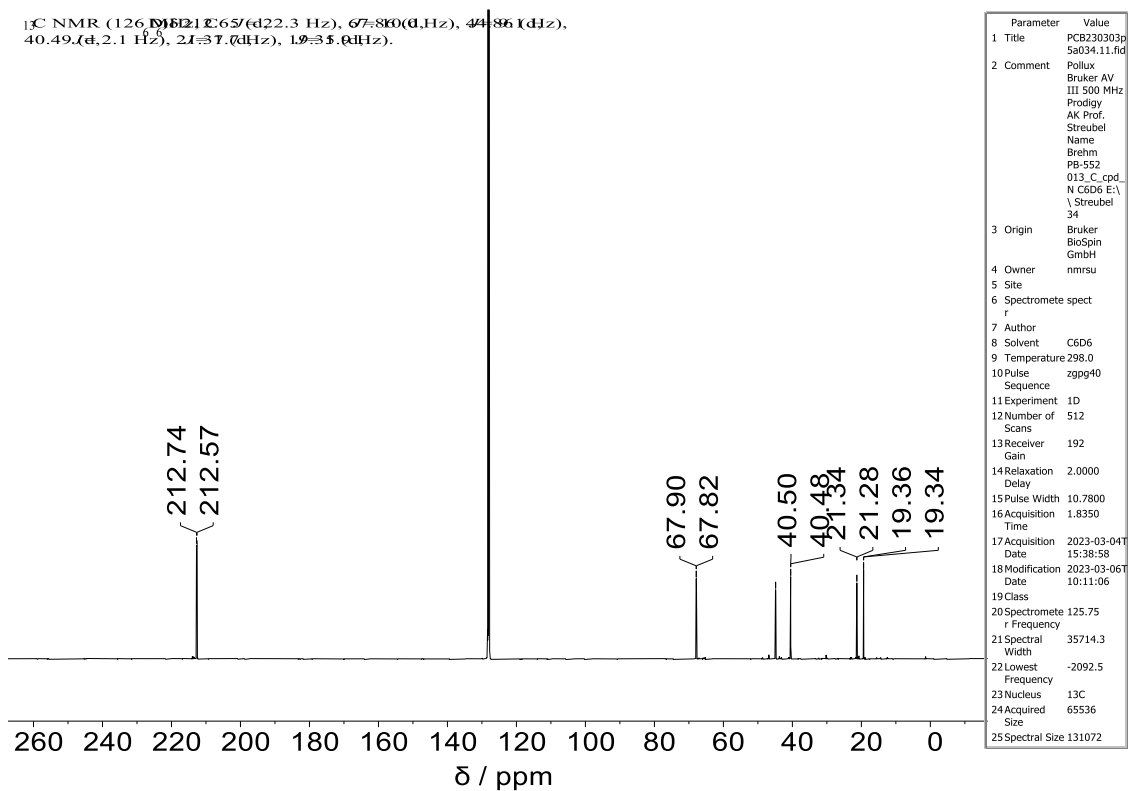


Figure 20 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of $5a^{\text{Fe}}$ in C_6D_6 .

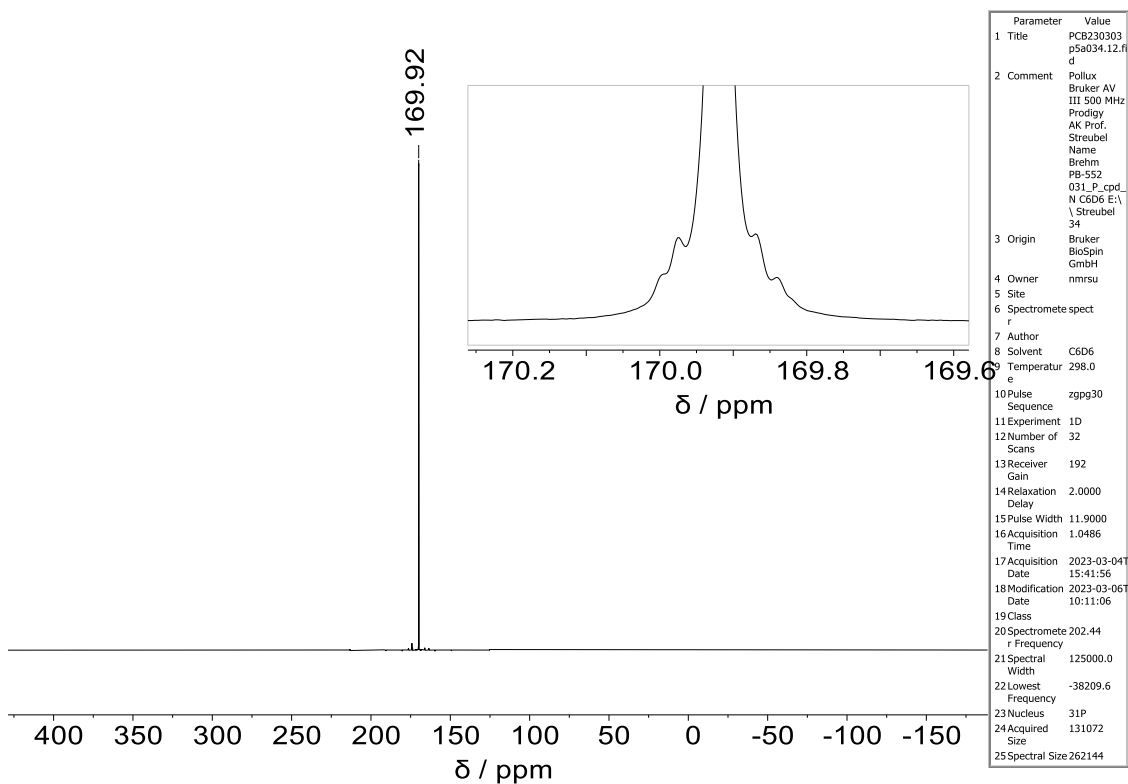


Figure 21 $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of $5a^{\text{Fe}}$ in C_6D_6 .

5b^{Fe}

¹H NMR (400 MHz, C₆D₆) δ: 7.82 (d, 3H, J = 8.1 Hz), 7.16 (d, 3H, J = 8.1 Hz), 6.86 (s, 1H), 3.45 (s, 3H), 2.25 (d, 2H), 2.22 (d, 2H), 2.00 (s, 1H), 1.99 (s, 1H).

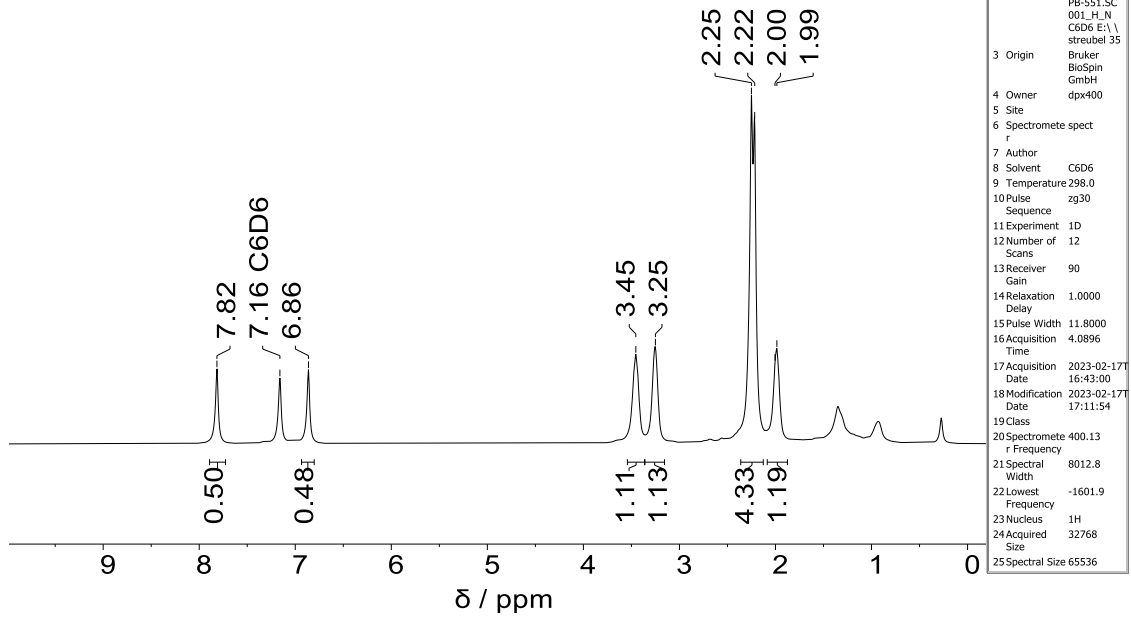


Figure 22 ¹H-NMR spectrum of 5b^{Fe} in C₆D₆.

¹³C NMR (126 MHz, C₆D₆) δ: 212.56, 212.38, 69.29 – 67.70 (m), 50.77, 31.97.

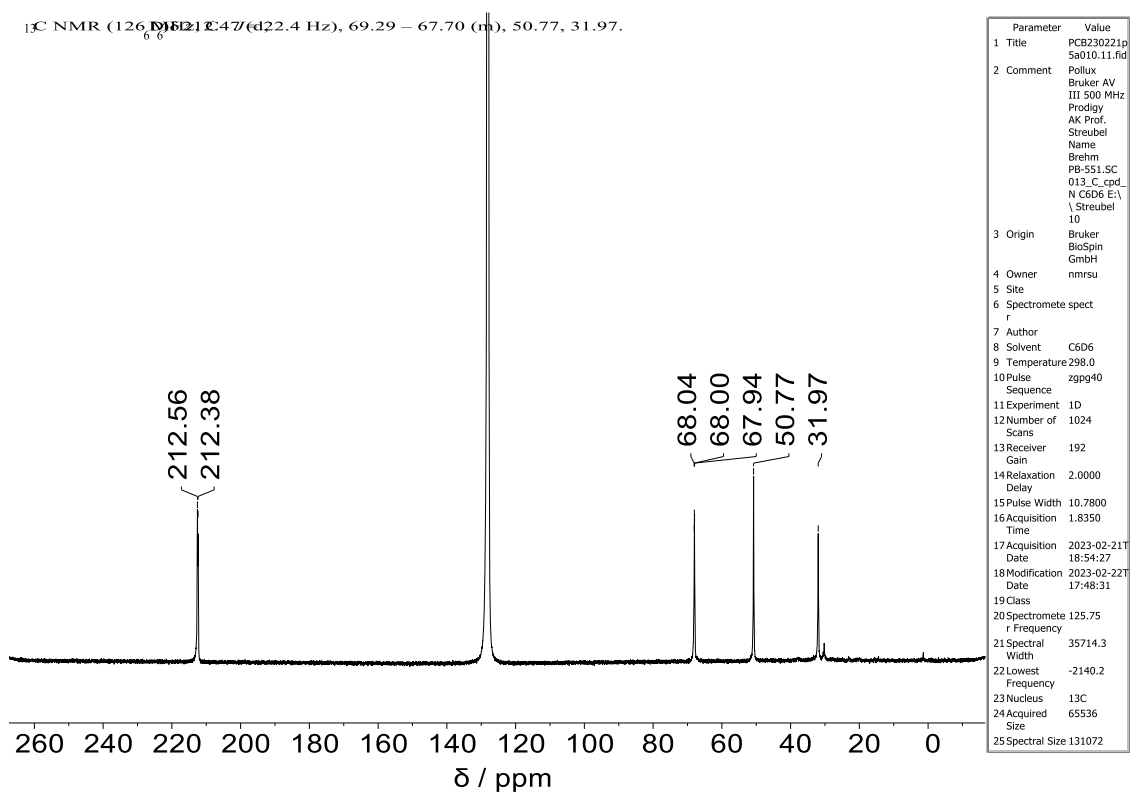


Figure 23 ¹³C[¹H]-NMR spectrum of 5b^{Fe} in C₆D₆.

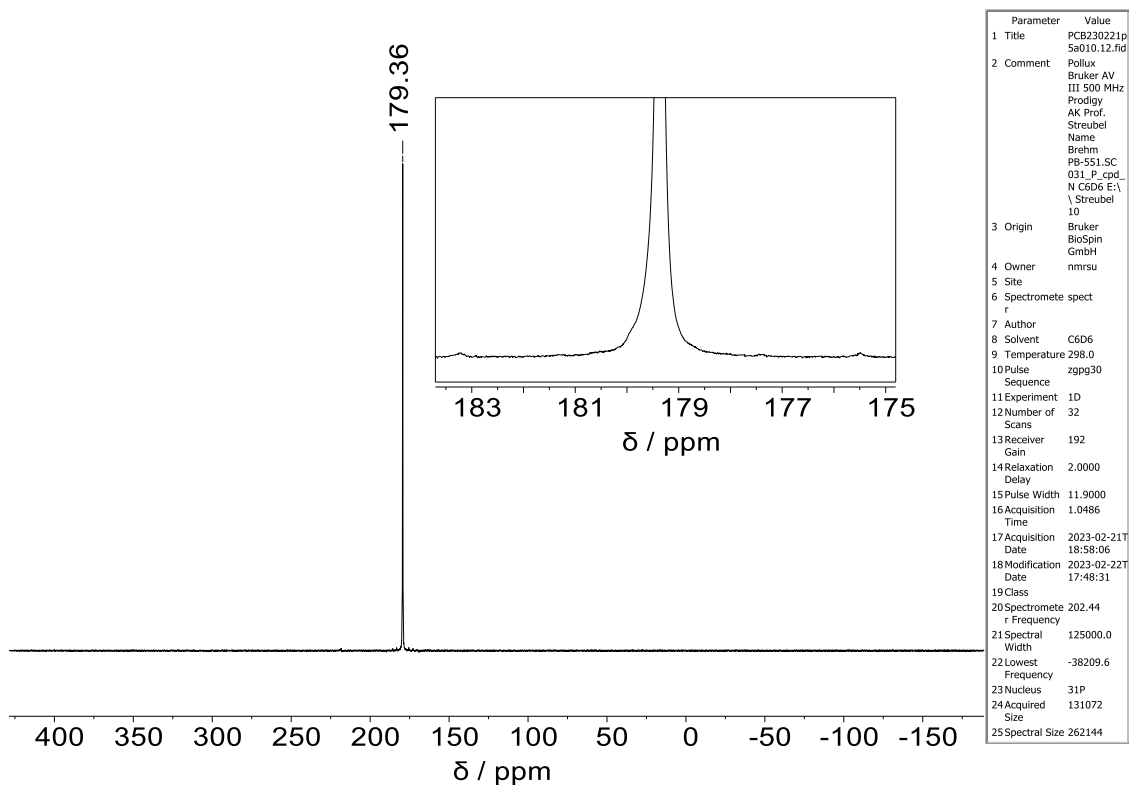


Figure 24 $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of $5b^{\text{Fe}}$ in C_6D_6 .

$6b^{\text{Fe}}$

^1H NMR (500 MHz, C_6D_6 , 409.3 Hz, 1H), 0.95 (s, 6H), 0.70 (s, 6H).

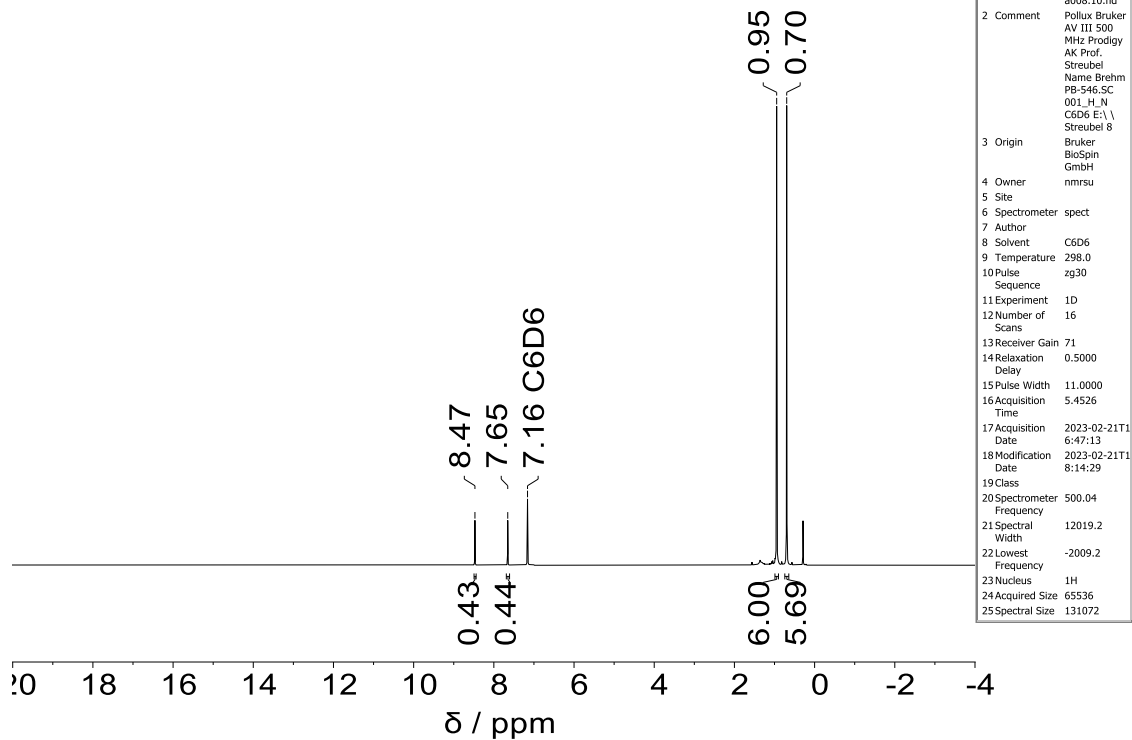


Figure 25 ^1H -NMR spectrum of $6b^{\text{Fe}}$ in C_6D_6 .

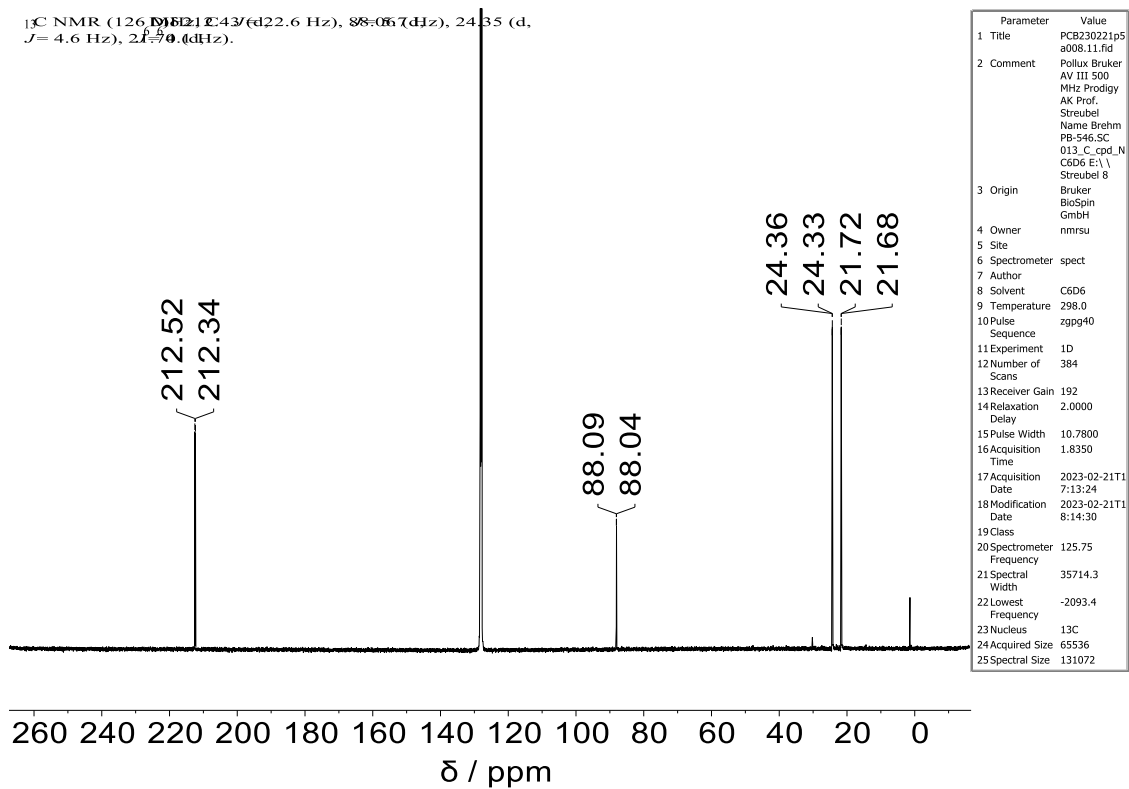


Figure 26 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of $6b^{\text{Fe}}$ in C_6D_6 .

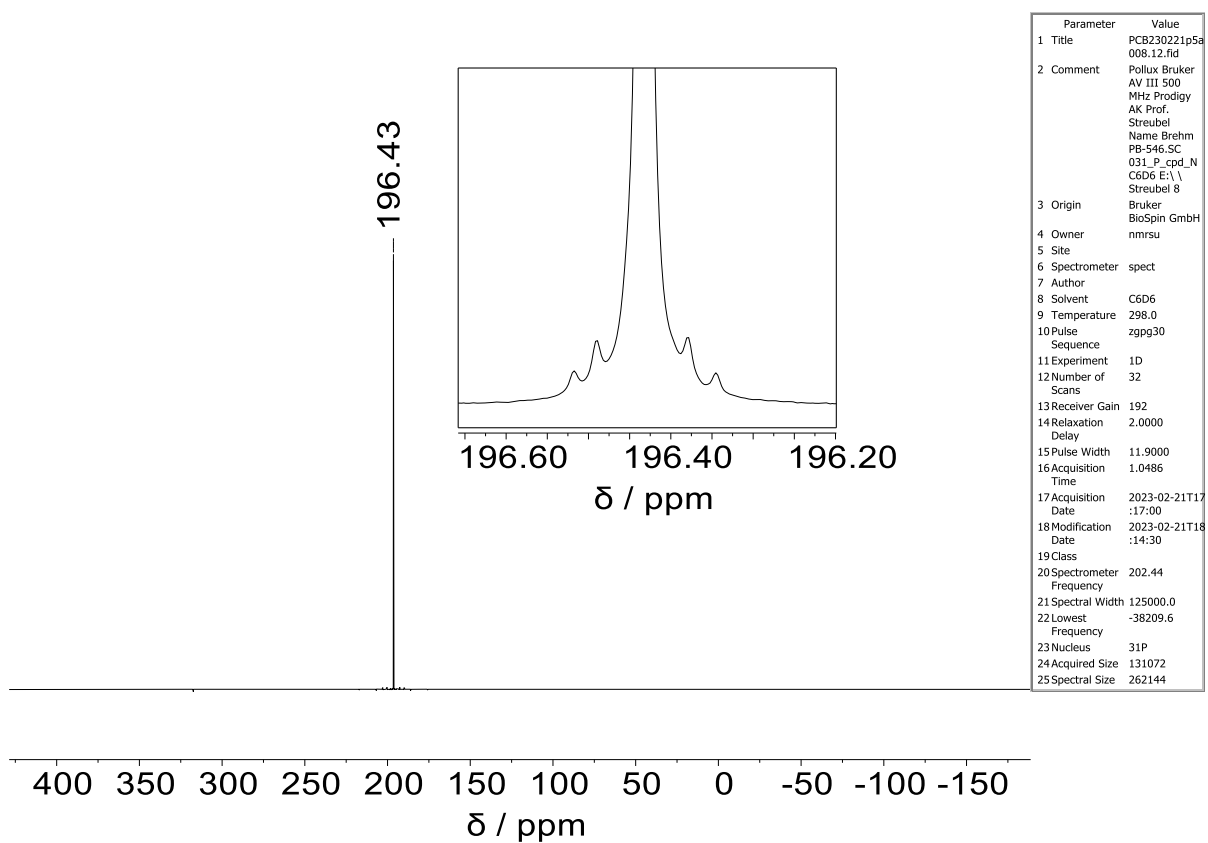


Figure 27 $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of $6b^{\text{Fe}}$ in C_6D_6 .

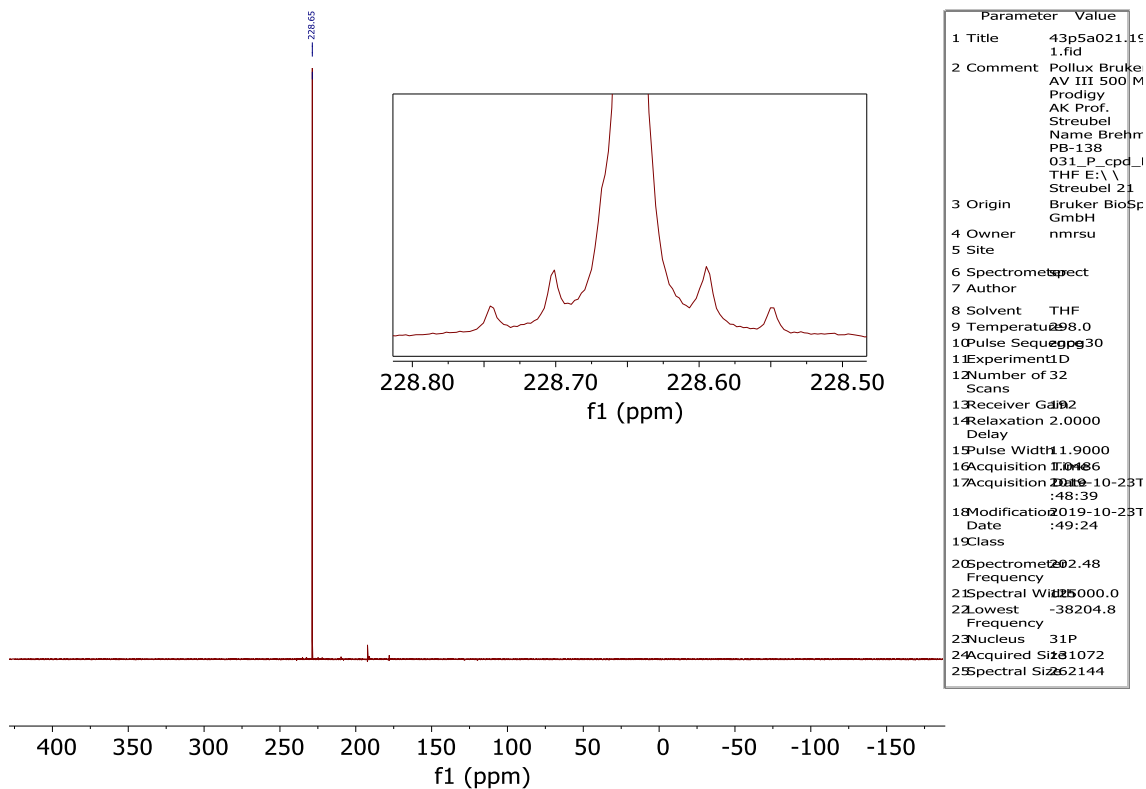


Figure 30 $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of $6c^{\text{Fe}}$ in C_6D_6 .

7

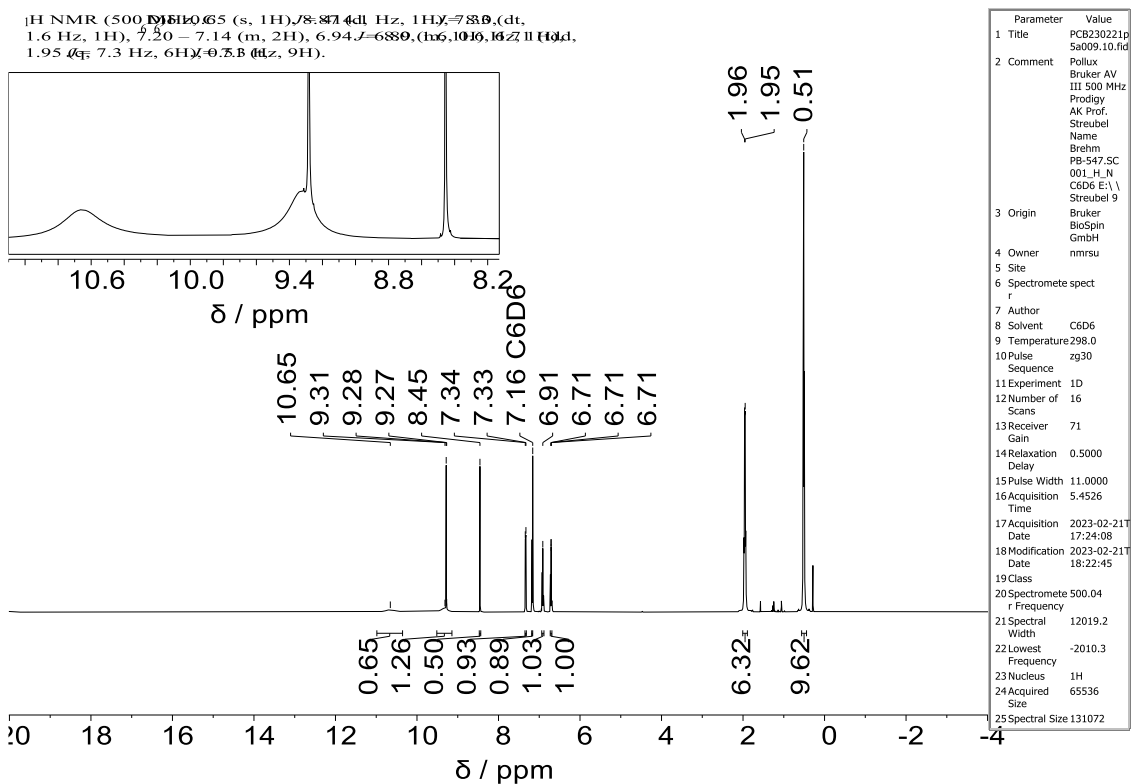


Figure 31 ^1H -NMR spectrum of 7 in C_6D_6 .

^{13}C NMR (126 MHz, C_6D_6) δ : 215.74 (d), 215.56 (d), 149.32 (d), 149.29 (d), 145.20 (d), 125.85 (d), 125.84 (d), 123.32 (d), 123.28 (d), 120.75 (d), 120.74 (d), 118.25 (d), 118.24 (d), 45.50 (d), 8.06 (d).

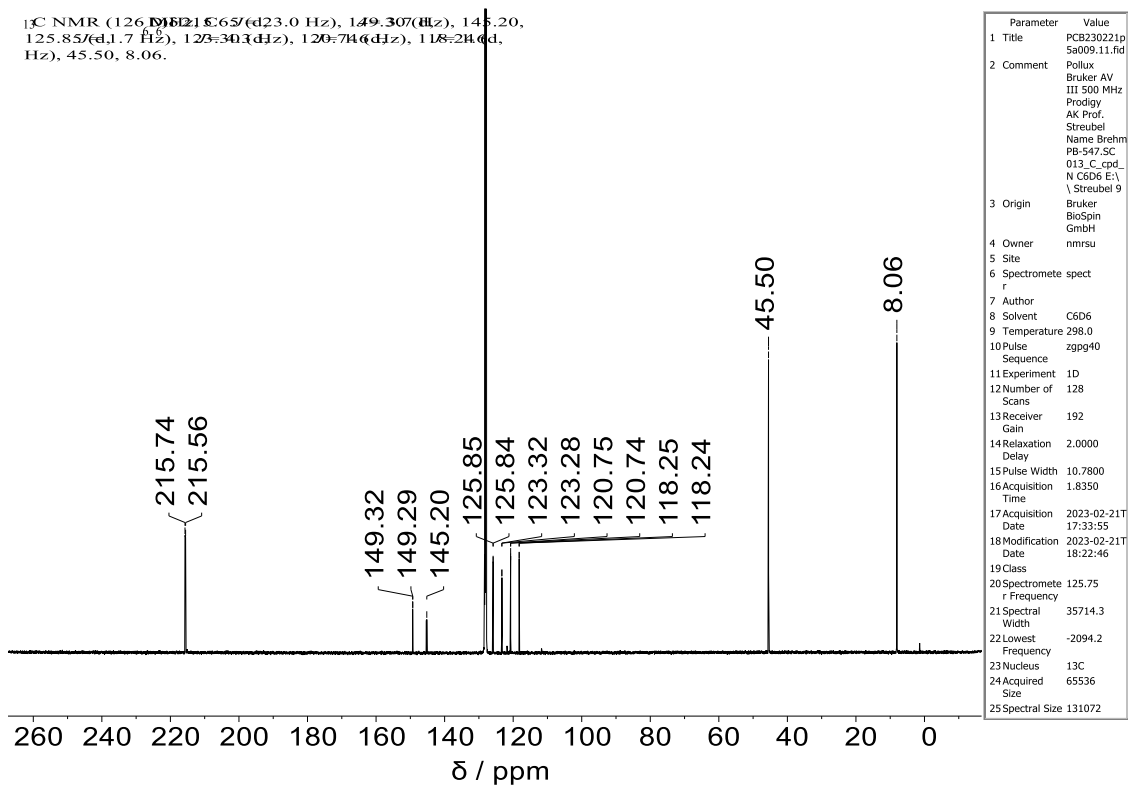


Figure 32 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **7** in C_6D_6 .

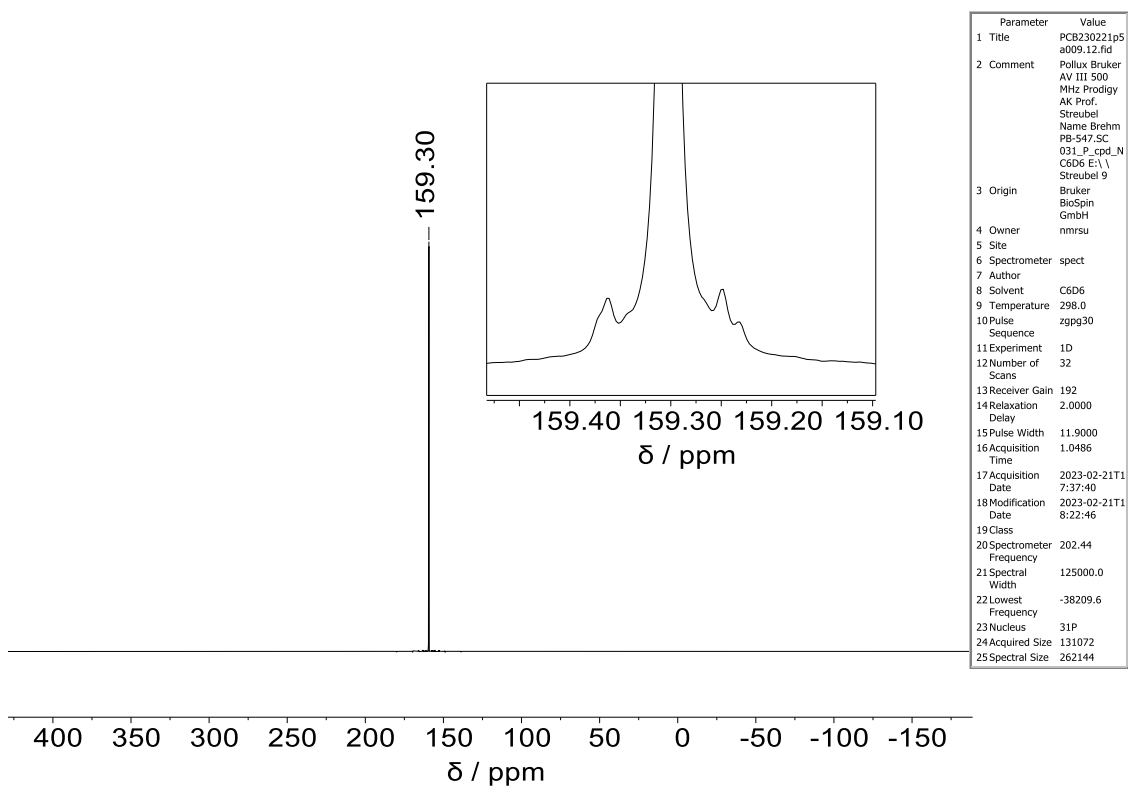
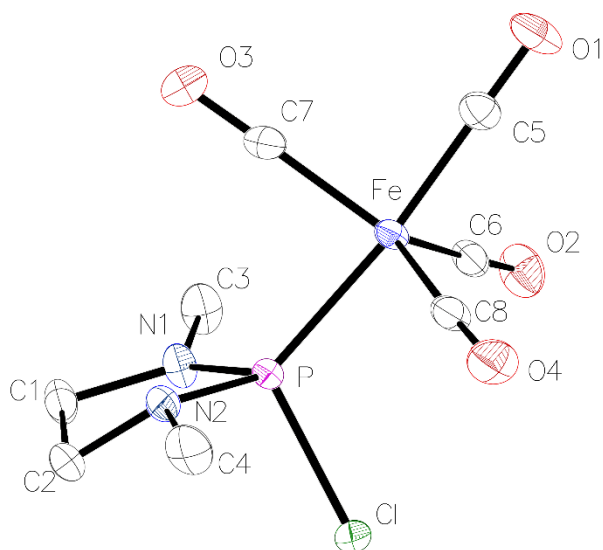
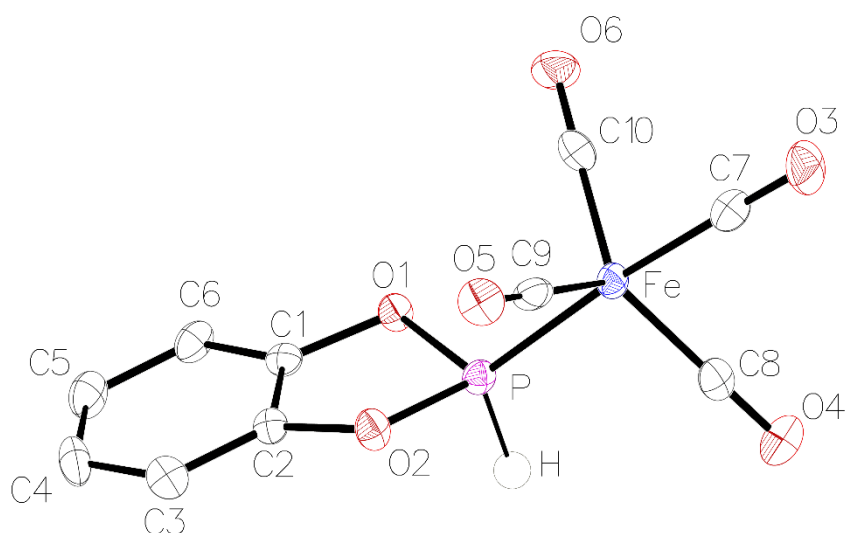


Figure 33 $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **7** in C_6D_6 .

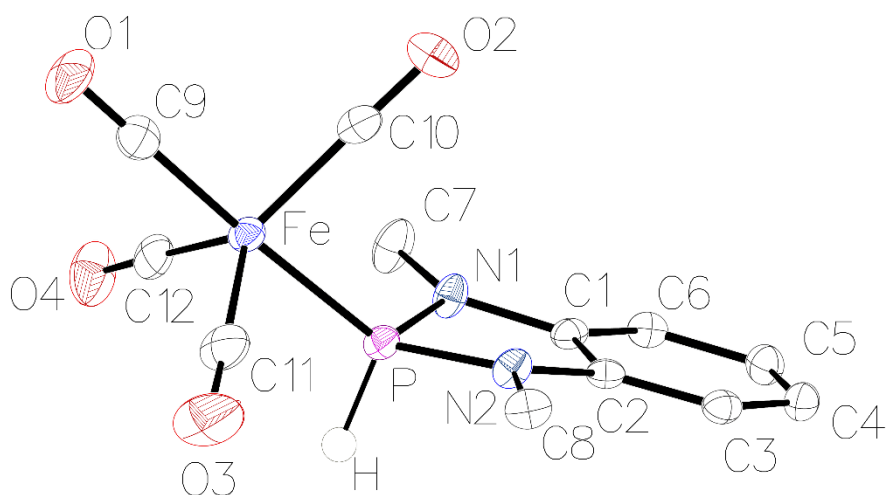
Single crystal X-ray diffraction studies of
1b^{Fe}



Crystal Habitus	clear light yellow block	Crystal size/mm ³	0.2 × 0.15 × 0.12
Device Type	STOE STADIVARI	Absorption correction	multi-scan
Empirical formula	C ₈ H ₁₀ ClFeN ₂ O ₄ P	Tmin; Tmax	1.0000; 1.0000
Moiety formula	C ₈ H ₁₀ Cl Fe N ₂ O ₄ P	Radiation	MoKα (λ = 0.71073)
Formula weight	320.45	2θ range for data collection/°	5.788 to 61.59°
Temperature/K	120.0	Completeness to theta	1.000
Crystal system	monoclinic	Index ranges	-9 ≤ h ≤ 9, -9 ≤ k ≤ 9, -20 ≤ l ≤ 20
Space group	Pc	Reflections collected	14397
a/Å	6.9354(6)	Independent reflections	3349 [R _{int} = 0.0155, R _{sigma} = 0.0151]
b/Å	6.4697(10)	Data/restraints/parameters	3349/2/156
c/Å	14.1938(17)	Goodness-of-fit on F ²	1.049
α/°	90	Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0189, wR ₂ = 0.0420
β/°	97.364(8)	Final R indexes [all data]	R ₁ = 0.0210, wR ₂ = 0.0429
γ/°	90	Largest diff. peak/hole / e Å ⁻³	0.25/-0.28
Volume/Å ³	631.62(14)	Flack parameter	-0.004(6)
Z	2	CCDC Deposition Number	2350418
ρ _{calc} /cm ³	1.685		
μ/mm ⁻¹	1.534		
F(000)	324.0		

4c^{Fe}

Crystal Habitus	clear colourless plate	Crystal size/mm ³	0.35 × 0.26 × 0.08
Device Type	Bruker X8-KappaApexII	Absorption correction	empirical
Empirical formula	C ₁₀ H ₅ O ₆ PFe	Tmin; Tmax	0.5417; 0.7461
Moiety formula	C ₁₀ H ₅ Fe O ₆ P	Radiation	MoKα (λ = 0.71073)
Formula weight	307.96	2θ range for data collection/°	7.572 to 50.46°
Temperature/K	100	Completeness to theta	0.995
Crystal system	orthorhombic	Index ranges	-18 ≤ h ≤ 19, -12 ≤ k ≤ 12, -8 ≤ l ≤ 5
Space group	Pca ₂₁	Reflections collected	7821
a/Å	16.151(2)	Independent reflections	1918 [R _{int} = 0.0646, R _{sigma} = 0.0551]
b/Å	10.4300(12)	Data/restraints/parameters	1918/1/166
c/Å	6.8190(8)	Goodness-of-fit on F ²	1.024
α/°	90	Final R indexes [I >= 2σ (I)]	R ₁ = 0.0345, wR ₂ = 0.0702
β/°	90	Final R indexes [all data]	R ₁ = 0.0400, wR ₂ = 0.0725
γ/°	90	Largest diff. peak/hole / e Å ⁻³	0.37/-0.24
Volume/Å ³	1148.7(2)	Flack parameter	0.01(2)
Z	4	CCDC Deposition Number	2350419
ρ _{calc} /cm ³	1.781		
μ/mm ⁻¹	1.467		
F(000)	616.0		

6C^{Fe}

Crystal Habitus	clear brownish colourless block	Crystal size/mm ³	0.12 × 0.1 × 0.09
Device Type	STOE IPDS-2T	Absorption correction	integration
Empirical formula	C ₁₂ H ₁₁ FeN ₂ O ₄ P	Tmin; Tmax	0.6213; 0.9091
Moiety formula	C ₁₂ H ₁₁ Fe N ₂ O ₄ P	Radiation	MoKα (λ = 0.71073)
Formula weight	334.05	2θ range for data collection/°	5.334 to 50.5°
Temperature/K	123	Completeness to theta	0.999
Crystal system	trigonal	Index ranges	-22 ≤ h ≤ 22, -22 ≤ k ≤ 22, -24 ≤ l ≤ 24
Space group	R-3	Reflections collected	20708
a/Å	19.0115(5)	Independent reflections	2584 [R _{int} = 0.1008, R _{sigma} = 0.0473]
b/Å	19.0115(5)	Data/restraints/parameters	2584/0/187
c/Å	20.4834(6)	Goodness-of-fit on F ²	0.940
α/°	90	Final R indexes [I >= 2σ(I)]	R ₁ = 0.0236, wR ₂ = 0.0547
β/°	90	Final R indexes [all data]	R ₁ = 0.0332, wR ₂ = 0.0563
γ/°	120	Largest diff. peak/hole / e Å ⁻³	0.40/-0.32
Volume/Å ³	6411.6(4)		
Z	18		
ρ _{calc} /cm ³	1.557		
μ/mm ⁻¹	1.183	CCDC Deposition Number	2350420
F(000)	3060.0		