Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Synthesis, coordination behavior and structural features of chiral iron(II) PNP diferrocene complexes

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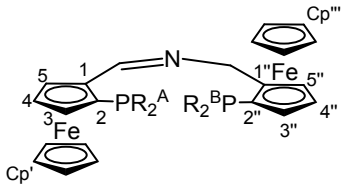
General considerations

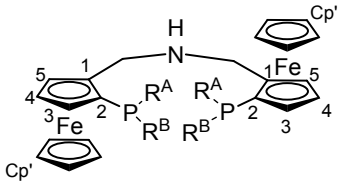
All reactions were carried out under an argon atmosphere using standard Schlenk techniques and dry solvents. Solvents were dried according to standard procedures under argon atmosphere and distilled freshly prior to use. Tetrahydrofuran (THF) was dried over sodium/benzophenone, dichloromethane (DCM) was dried over P_2O_5, diethyl ether (Et_2O) over $LiAlH_4$, ethanol (EtOH) over magnesiumalkoxide. Column chromatography was performed either on silica gel (Merck, 40–63 μm) or on aluminium oxide (Merck, aluminium oxide 90). Petroleum ether (PE, boiling range 60–80 °C), ethyl acetate (EA) and triethyl amine (TEA) were used as the eluents.

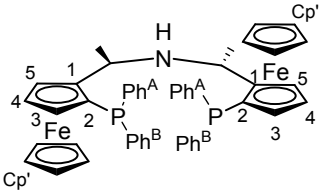
NMR spectra were recorded either on a Bruker DRX-400 and Bruker DRX-600 spectrometer in $CDCl_3$, CD_2Cl_2. Chemical shifts are referenced to: $CHCl_3$ (^1H: 7.26 ppm) and $CDCl_3$ (^{13}C: 77.0 ppm); $CDHCl_2$ (^1H: 5.32 ppm) and CD_2Cl_2 (^{13}C: 53.7 ppm). ^{31}P NMR spectra were referenced to 85% H_3PO_4 (^{31}P: 0 ppm). For the assignment of peaks, the following abbreviations were used: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. Coupling constants in ^{13}C NMR are due to ^{31}P-^{13}C coupling. High resolution mass spectra were recorded on a Bruker ESI-Qq aoTOF MS spectrometer. Optical rotations were measured on a Perkin Elmer 241 or a Jasko P-1020 polarimeter in CH_2Cl_2. Melting points were measured either on a Kofler or on a Boif X-4 melting point apparatus.

The ^{57}Fe Mössbauer spectrum was recorded in transmission mode at 78 K using a conventional constant-acceleration spectrometer and a 50 mCi ^{57}Co source in a Rh matrix. The measurement was performed using a liquid nitrogen flow cryostat with a temperature stability of ±0.5 K. The velocity scale was calibrated using an α-Fe foil. The spectrum was fitted to Lorentzian lines using the WinNormos software program, and the isomer shifts reported are relative to metallic α-Fe at room temperature.

General atom numbering schemes for NMR assignment:







Synthesis of the compounds:

(S_{Fc},S_{Fc})-1a

A mixture of (S_{Fc})-**6a** (0.289 g, 0.726 mmol) and (S_{Fc})-**8a** (0.290 mg, 0.726 mmol) in ethanol (10 mL) was refluxed for 90 minutes. Then, the mixture was cooled down to 0 °C and stirred overnight. The product was precipitated as a yellow powder and was isolated by filtration (0.359 g, 0.682 mmol, 94% yield). Single crystals suitable for X-ray structure determination were grown from Toluene/Hexane by slow evaporation of the solvent. M.p.: 165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.63–3.67 (m, 1H, H3″/H5″), 3.77–3.81 (m, 1H, H3/H5), 3.92 (s, 5H, Cp‴), 4.02 (s, 5H, Cp′), 4.16 (t, J = 2.4 Hz, 1H, H4″), 4.31–4.34 (m, 1H, H3″/5″), 4.37, 4.52 (AB, J_{AB} = 14.2 Hz, 2H, CH_2), 4.40 (t, J = 2.4 Hz, 1H, H4), 4.82–4.86 (1H, H3/H5), 7.10–7.25 (m, 10H, Ph^{A}), 7.34–7.44 (m, 6H, Ph^{B}-*meta* + Ph^{B}-*para*), 7.49–7.61 (m, 4H, Ph^{B}-*ortho*), 8.44 (bs, 1H, CHN). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 59.2 (d, J = 10.2 Hz, 2C, CH_2), 68.9 (C4″), 69.5 (5C, Cp‴), 70.0 (d, J = 3.3 Hz, C3/C5), 70.2 (5C, Cp′), 70.7 (d, J = 4.2 Hz, C3″/5″), 71.1 (d, J = 3.9 Hz, C3/5), 71.4 (C4), 73.4 (C3″/5″), 127.6–135.4 (Ph), 161.2 (d, J = 9.1 Hz, CHN), C1, C2, C1″, C2″ and Ph-*ipso* not observed. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ –21.17, –21.14. HR-MS (ESI, MeOH/MeCN): *m/z* $[M+H]^+$ calcd. 780.1335 for $C_{46}H_{40}Fe_2NP_2$; found: 780.1311. $[\alpha]^{20}_{\lambda}$ (nm): –15.6 (589) (*c* 0.26, CH_2Cl_2).

(S_{Fc},S_{Fc})-1b

Starting from (S_{Fc})-**6b** (0.698 g, 2.11 mmol) and (S_{Fc})-**8b** (0.700 g, 2.11 mmol) and following the procedure of (S_{Fc},S_{Fc})-**1a**, the desired product was obtained as a red oil after removing of the solvent in vacuum and was used without further purification in the next step. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.74 (dd, J = 9.5 Hz, J = 7.1 Hz, 3H, CH(CH_3)(CH$_3$)^{A}), 0.91–0.98 (m, 6H, CH(CH_3)$_2^{A}$), 1.05 (dd, J = 13.4 Hz, J = 7.1 Hz, 3H, CH(CH$_3$)(CH_3)^{A}), 1.19–1.32 (m, 6H, CH(CH_3)$_2^{B}$), 1.41–1.53 (m, 6H, CH(CH_3)$_2^{B}$), 1.74–1.82 (m, 1H, CH(CH$_3$)$_2^{A}$),

1.85–1.93 (m, 1H, C*H*$(CH_3)_2{}^A$), 2.19–2.32 (m, 2H, C*H*$(CH_3)_2{}^B$), 4.10–4.13 (m, 1H, H3″), 4.17 (s, 5H, Cp‴), 4.19 (s, 5H, Cp′), 4.25–4.27 (m, 1H, H4″), 4.29–4.32 (m, 1H, H3), 4.33–4.34 (m, 1H, H5″), 4.46, 4.63 (AB, J = 13.9 Hz, 2H, CH_2), 4.51 (t, J = 2.5 Hz, 1H, H4), 5.03–5.08 (m, 1H, H5), 8.59 (bs, 1H, CH=N).$^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$): δ 18.4 (d, J = 4.4 Hz, CH(*C*H_3)$(CH_3)^A$), 19.9 (d, J = 12.3 Hz, CH(CH_3)(*C*$H_3)^A$), 20.1–20.2 (m, 3C, CH(*C*$H_3)_2{}^A$ + CH(*C*H_3)$(CH_3)^B$), 20.5 (d, J = 16.0 Hz, CH(CH_3)(*C*$H_3)^B$), 22.3 (d, J = 9.2 Hz, CH(*C*H_3)$(CH_3)^B$), 22.4 (d, J = 19.8 Hz, CH(CH_3)(*C*$H_3)^B$), 22.9 (d, J = 21.3 Hz, *C*H$(CH_3)_2{}^B$), 23.3 (d, J = 9.9 Hz, *C*H$(CH_3)_2{}^B$), 25.6–25.9 (2C, *C*H$(CH_3)_2{}^A$), 59.7 (d, J = 10.6 Hz, CH_2), 68.2 (d, J = 2.3 Hz, C5), 68.3 (C4″), 69.4 (d, J = 3.7 Hz, C3″), 69.7 (d, J = 3.2 Hz, C5″), 69.8 (5C, Cp‴), 70.2 (5C, Cp'), 70.7 (C4), 71.5 (d, J = 4.8 Hz, C3), 78.9 (d, J = 15.2 Hz, C1), 85.7 (d, J = 23.6 Hz, C2), 92.0 (d, J = 20.9 Hz, C2″), 160.5 (d, J = 10.7 Hz, CH=N), C1″ not observed. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ –7.5, –6.5. HR-MS (ESI, MeOH/MeCN): *m/z* $[M+H]^+$ calcd. 644.1961 for $C_{34}H_{48}Fe_2NP_2$; found: 644.1933.

(S_{Fc},S_{Fc})-2a

To a solution of (S_{Fc},S_{Fc})-**1a** (0.600 g, 0.770 mmol) in ethanol (40 mL) was added $NaBH_4$ (0.88 g, 2.33 mmol) in portions at 0° C. The mixture was refluxed for 3 hours and stirred further overnight at r.t. After cooling to 0° C, the reaction mixture was quenched by dropwise addition of water, and then the phases were separated and the aqueous phase extracted with diethyl ether (3×50 mL), and the organic phase was washed with water and dried over $MgSO_4$ and then the solvents were removed under reduced pressure. The crude product was chromatographed on aluminium oxide 90 using PE/EA/TEA = 4/1/1 as eluent giving the pure compound as a yellow powder (0.511 g, 0.654 mmol, 85% yield). Mp.: 74 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 3.52–3.71 (6H, CH_2 + H3), 3.87 (s, 10H, Cp′), 4.16 (t, J = 2.4 Hz, 2H, H4), 4.29–4.33 (m, 2H, H5), 7.13–7.21 (m, 4H, Ph^A-*ortho*), 7.22–7.25 (m, 6H, Ph^A-*meta* + Ph^A-*para*), 7.33–7.41 (m, 6H, Ph^B-*meta* + Ph^B-*para*), 7.48–7.56 (m, 4H, Ph^B-*ortho*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 48.3 (d, J = 9.9 Hz, 2C, CH_2), 68.9 (2C, C4), 69.4 (10C, Cp′), 70.9 (d, J = 3.8 Hz, 2C, C5), 71.2 (d, J = 4.3 Hz, 2C, C3), 75.1 (2C, C1), 92.4 (d, J = 23.8 Hz, 2C, C2), 127.8 (2C, Ph^A-*para*), 128.0–128.3 (8C, Ph-*meta*), 129.1 (2C, Ph^B-*para*), 132.2 (d, J = 17.6 Hz, 4C, Ph^A-*ortho*), 135.0 (d, J = 21.4 Hz, 4C, Ph^B-*ortho*), 137.6 (d, J = 9.0 Hz, 2C, Ph^B-*ipso*), 140.2 (d, J = 10.2 Hz, 2C, Ph^A-*ipso*). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ –21.9. HR-MS (ESI, MeOH/MeCN): *m/z* $[M+H]^+$ calcd. 782.1491 for $C_{46}H_{42}Fe_2NP_2$; found: 782.1483. $[\alpha]^{20}_{\lambda}$ (nm): –20.3 (589) (*c* 0.27, CH_2Cl_2).

(S_{Fc},S_{Fc})-2b

Starting from (S_{Fc},S_{Fc})-**1b** (0.200 g, 0.311 mmol) and $NaBH_4$ (35.24 mg, 0.931 mmol) in ethanol (20 mL) following the procedure of (S_{Fc},S_{Fc})-**2a**, the desired product was obtained as a red oil (0.140 g, 0.218 mmol, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.88 (dd, J = 12.4 Hz, J = 7.1 Hz, 6H, CH(CH_3)$_2^A$), 1.01 (dd, J = 13.2 Hz, J = 7.1 Hz, 6H, CH(CH_3)$_2^A$), 1.27 (dd, J = 10.7 Hz, J = 7.1 Hz, 6H, CH(CH_3)$_2^B$), 1.45 (dd, J = 16.3 Hz, J = 7.3 Hz, 6H, CH(CH_3)$_2^B$), 1.78–1.90 (m, 2H, CH(CH$_3$)$_2^A$), 2.19–2.31 (m, 2H, CH(CH$_3$)$_2^B$), 3.67–3.81 (m, 4H, CH_2), 4.09–4.11 (m, 2H, H3), 4.13 (s, 10H, Cp′), 4.23–4.25 (m, 2H, H4), 4.45–4.48 (m, 2H, H5). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): δ 19.2–20.3 (6C, CH(CH$_3$)$_2^A$ + CH(CH$_3$)$_2^B$), 22.9 (d, J = 21.7 Hz, 2C, CH(CH$_3$)$_2^B$), 23.5 (d, J = 10.4 Hz, 2C, CH(CH$_3$)$_2^B$), 25.7 (d, J = 12.3 Hz, 2C, CH(CH$_3$)$_2^A$), 48.9 (d, J = 10.0 Hz, 2C, CH_2), 68.2 (2C, C4), 69.5 (d, J = 3.5 Hz, 2C, C5), 69.5 (d, J = 3.8 Hz, 2C, C3), 69.6 (10C, Cp′), 77.6 (d, J = 18.9 Hz, 2C, C1), 92.3 (d, J = 20.6 Hz, 2C, C2). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ –6.8, HR-MS (ESI, MeOH/MeCN): m/z [M+H]$^+$ calcd. 646.2117 for $C_{34}H_{50}Fe_2NP_2$; found: 646.2088. $[\alpha]^{20}_{\lambda}$ (nm): +46.3 (589) (c 0.32, CH_2Cl_2).

(R,R,S_{Fc},S_{Fc})-3

To a mixture of (R,S_{Fc})-**11** (1.60 g, 3.51 mmol) and (R,S_{Fc})-**12** (1.45 g, 3.51 mmol) was added degassed acetonitrile (50 mL) and water (6 mL). The reaction mixture was refluxed for 30 hours. After cooling to room temperature, the phases were separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water and brine, and dried over $MgSO_4$. After filtration and evaporation of the solvents, the crude product was purified by column chromatography on aluminium oxide 90 using PE/EA = 9/1 as eluent giving the pure compound as a yellow powder (1.73 g, 2.14 mmol, 61% yield). Mp.: 104 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 1.12 (d, J = 6.3 Hz, 6H, CHCH_3), 3.56–3.60 (m, 2H, H3), 3.72–3.76 (m, 2H, H5), 3.90 (s, 10H, Cp′), 3.92–3.98 (m, 2H, CHCH$_3$), 4.02 (t, J = 2.5 Hz, 2H, H4), 7.12–7.19 (m, 4H, Ph^A-*ortho*), 7.19–7.24 (m, 6H, Ph^A-*meta* + Ph^A-*para*), 7.31–7.38 (m, 6H, Ph^B-*meta* + Ph^B-*para*), 7.47–7.56 (m, 4H, Ph^B-*ortho*). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 18.3 (2C, CHCH$_3$), 47.5 (d, J = 9.2 Hz, 2C, CHCH$_3$), 68.4 (2C, C4), 68.7 (d, J = 4.1 Hz, 2C, C5), 69.3 (10C, Cp′), 70.5 (d, J = 4.7 Hz, 2C, C3), 74.2 (d, J = 6.4 Hz, 2C, C1), 99.2 (d, J = 24.0 Hz, 2C, C2), 127.7 (2C, Ph^A-*para*), 127.7–128.0 (8C, Ph-*meta*), 128.8 (2C, Ph^B-*para*), 132.8 (d, J = 18.4 Hz, 4C, Ph^A-*ortho*), 135.2 (d, J = 21.4 Hz, 4C, Ph^B-*ortho*), 137.8 (d, J = 9.2 Hz, 2C, Ph^B-*ipso*), 140.5 (d, J = 9.9 Hz, 2C, Ph^A-*ipso*).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ –22.0. HR-MS (ESI, MeOH/MeCN): *m/z* $[M+H]^+$ calcd. 810.1804 for $C_{48}H_{46}Fe_2NP_2$; found: 810.1795. $[\alpha]^{20}_{\lambda}$ (nm): +57.3 (589) (*c* 0.28, CH_2Cl_2).

(2*S*,4*S*,S_{Fc})-4-(Methoxymethyl)-2-[α-(diisopropylphosphino)ferrocenyl]-1,3-dioxane (2*S*,4*S*,S_{Fc})-5b

To a degassed solution of (2*S*,4*S*)-**4** (4.40 g, 13.92 mmol) in dry diethyl ether (90 mL) was added dropwise a solution of ^{t}BuLi (9.54 mL, 1.6 M, 15.31 mmol) at –78 °C. The reaction mixture was stirred for 20 minutes at –78 °C and for an additional 90 minutes at r.t. The resulting orange suspension was cooled to –78 °C and neat chlorodiisopropylphosphine (2.55 g, 16.70 mmol) was added. The reaction mixture was stirred for an additional 30 minutes at –78 °C and for 16 hours at r.t. The reaction mixture was quenched by the addition of saturated solution of $NaHCO_3$ (30 mL) and the aqueous phase was extracted with diethyl ether (3 × 30 mL). The combined organic phases were washed with brine (3 × 20 mL) and dried over $MgSO_4$. Column chromatography on silica gel using PE/EA = 5/1 as eluent gave desired product as a red oil (5.41 g, 12.52 mmol, 90% yield). This compound can be used in the next step without any further purification. ^{1}H NMR (400MHz, $CDCl_3$): δ 0.63–0.74 (m, 6H, $CH(CH_3)_2^A$), 0.94 (dd, *J* = 11.8 Hz, *J* = 6.9 Hz, 3H, $CH(CH_3)(CH_3)^B$), 1.15 (dd, *J* = 15.9 Hz, *J* = 7.2 Hz, 3H, $CH(CH_3)(CH_3)^B$), 1.18–1.24 (m, 1H, CHH), 1.37–1.54 (m, 1H, CHH), 1.54–1.67 (m, 1H, $CH(CH_3)_2^A$), 1.88–2.06 (m, 1H, $CH(CH_3)_2^B$), 3.02 (s, 3H, OCH_3), 3.03–3.19 (m, 2H, MeO-CH_2), 3.61–3.76 (m, 2H, CH + CHO), 3.76–3.82 (m, 1H, H3), 3.84 (s, 5H, Cp′), 3.94–4.05 (m, 2H, H4 + CHO), 4.26–4.33 (m, 1H, H5), 5.34 (d, *J* = 2.5 Hz, 1H, CH). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 18.7 (d, *J* = 9.2 Hz, $CH(CH_3)(CH_3)^A$), 20.5 (d, *J* = 11.5 Hz, $CH(CH_3)(CH_3)^B$), 20.9 (d, *J* = 15.3 Hz, $CH(CH_3)(CH_3)^A$), 22.5–23.0 (2C, $CH(CH_3)_2^B$ + $CH(CH_3)(CH_3)^B$), 26.3 (d, *J* = 12.3 Hz, $CH(CH_3)_2^A$), 28.2 (CH_2), 59.2 (OCH_3), 67.0 (OCH_2), 68.2 (d, *J* = 2.6 Hz, C5), 68.8 (C4), 69.5 (d, *J* = 4.4 Hz, C3), 70.1 (5C, Cp′), 75.4 (MeO-CH_2), 75.6 (CH), 77.8 (d, *J* = 19.8 Hz, C2), 89.8 (d, *J* = 18.5 Hz, C1), 99.7 (d, *J* = 10.7 Hz, CH). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ –4.1. HR-MS (ESI, MeOH/MeCN): *m/z* $[M+H]^+$ calcd. 433.1595 for $C_{22}H_{34}FeO_3P$; found: 433.1590. $[\alpha]^{20}_{\lambda}$ (nm): +68.7 (589) (*c* 0.27, CH_2Cl_2).

(S_{Fc})-2-(Diisopropylphosphino)ferrocenecarboxaldehyde (S_{Fc})-6b

To a degassed solution of (2*S*,4*S*,S_{Fc})-**5b** (4.00 g, 9.25 mmol) in DCM (60 mL) was added a solution of PTSA (1.70 g, 9.90 mmol) in degassed water (30 mL). The reaction mixture was stirred at r.t. overnight. After adding water (50 mL), the aqueous phase was extracted with

DCM (3 x 20 mL); the organics were combined, washed with water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude product dissolved in DCM (4 mL) and the product was precipitated by addition of PE (30 mL). The precipitate was separated from the supernatant solution, washed with PE (3 × 10 mL), and dried under vacuum to afford an orange powder (2.41 g, 7.31 mmol, 79% yield). Mp.: 123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.73 (dd, J = 8.5 Hz, J = 7.3 Hz, 3H, CH(CH_3)(CH$_3$)^{A}), 0.97 (dd, J = 15.3 Hz, J = 7.3 Hz, 3H, CH(CH$_3$)(CH_3)^{A}), 1.24 (dd, J = 13.3 Hz, J = 7.0 Hz, 3H, CH(CH_3)(CH$_3$)^{B}), 1.50 (dd, J = 15.5 Hz, J = 7.1 Hz, 3H, CH(CH$_3$)(CH_3)^{B}), 1.75–1.90 (m, 1H, CH(CH$_3$)$_2{}^{A}$), 2.14–2.32 (m, 1H, CH(CH$_3$)$_2{}^{B}$), 4.28 (s, 5H, Cp′), 4.53–4.58 (m, 1H, H3/H5), 4.73–4.81 (m, 1H, H4), 5.03–5.09 (m, 1H, H3/H5), 10.24 (d, J = 3.4 Hz, CHO). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 17.9 (d, J = 9.1 Hz, CH(*C*H$_3$)(CH$_3$)^{A}), 19.9 (d, J = 13.5 Hz, CH(CH$_3$)(*C*H$_3$)^{A}), 20.3 (d, J = 15.3 Hz, CH(*C*H$_3$)(CH$_3$)^{B}), 21.8–22.3 (2C, *C*H(CH$_3$)$_2{}^{B}$ + CH(CH$_3$)(*C*H$_3$)^{B}), 25.3 (dd, J = 12.3 Hz, *C*H(CH$_3$)$_2{}^{A}$), 69.4 (bs, C3/C5), 70.1 (5C, Cp′), 73.4 (C4), 74.7 (bs, C3/C5), 193.3 (d, J = 12.3 Hz, CHO), C1 and C2 not observed. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ –6.4. HR-MS (ESI, MeOH/MeCN): *m/z* [M+H]$^{+}$ calcd. 331.0914 for $C_{17}H_{24}FeOP$; found: 331.0913. [α]$^{20}_{\lambda}$ (nm): +30.8 (589) (*c* 0.32, $CHCl_3$).

(*S*)-2-(Diphenylphosphino) ferrocenecarbaldehyde oxime, (S_{Fc})-7a

A mixture of (S_{Fc})-**6a** (2.00 g, 5.02 mmol), Sodium hydroxide (1.19 g, 29.75 mmol) and Hydroxylamine hydrochloride (0.698 g, 10.04 mmol) in ethanol (35 mL) was refluxed for 3 hours. After cooling to r.t. and adding water (50 mL), the aqueous phase was extracted with DCM (3 x 30 mL); the organics were combined, washed with water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure to give 2.00 g of the title compound as an orange-yellow solid and was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83–3.91 (m, 1H, H3), 4.13 (s, 5H, Cp′), 4.47 (t, J = 2.5 Hz, 1H, H4), 4.88–4.91 (m, 1H, H5), 7.07–7.16 (m, 2H, Ph^{A}-*ortho*), 7.19–7.25 (m, 3H, Ph^{A}-*meta* + Ph^{A}-*para*), 7.34–7.43 (m, 3H, Ph^{B}-*meta* + Ph^{B}-*para*), 7.50–7.60 (m, 2H, Ph^{B}-*ortho*), 8.25 (d, J = 2.3 Hz, 1H, CHN). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 69.6 (d, J = 3.1 Hz, C5), 70.8 (5C, Cp′), 70.9 (C4), 73.6 (d, J = 4.2 Hz, C3), 81.9 (d, J = 20.5 Hz, C2), 128.4 (Ph^{A}-*para*), 128.5–128.8 (4C, Ph-*meta*), 129.8 (Ph^{B}-*para*), 132.5 (d, J = 17.8 Hz, 2C, Ph^{A}-*ortho*), 135.6 (d, J = 21.3 Hz, 2C, Ph^{B}-*ortho*), 137.3 (d, J = 9.2 Hz, Ph^{B}-*ipso*), 139.8 (d, J = 9.9 Hz, Ph^{A}-*ipso*), 149.5 (d, J = 9.2 Hz, CHN), C1 not obsereved. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ –21.3. HR-MS (ESI, MeOH/MeCN): *m/z* [M+H]$^{+}$ calcd. 414.0710 for $C_{23}H_{21}FeNOP$; found: 414.0696.

(*S*)-2-(Diisopropylphosphino) ferrocenecarbaldehyde oxime, (S_{Fc})-7b

Starting from (S_{Fc})-**6b** (1.00 g, 3.03 mmol), Sodium hydroxide (0.714 g, 17.88 mmol) and Hydroxylamine hydrochloride (0.421 g, 6.06 mmol) in ethanol (35 mL) and following the procedure of (S_{Fc},S_{Fc})-**7a**, the desired product was obtained as a orange solid after removing of the solvent under reduced pressure and was used without further purification. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.73 (dd, J = 9.4 Hz, J = 7.0 Hz, 3H, CH(CH_3)(CH_3)^{A}), 0.94 (dd, J = 14.8 Hz, J = 7.2 Hz, 3H, CH(CH_3)(CH_3)^{A}), 1.21 (dd, J = 12.5 Hz, J = 7.0 Hz, 3H, CH(CH_3)(CH_3)^{B}), 1.47 (dd, J = 15.6 Hz, J = 7.2 Hz, 3H, CH(CH_3)(CH_3)^{B}), 1.72–1.79 (m, 1H, CH(CH_3)$_2^{A}$), 2.16–2.24 (m, 1H, CH(CH_3)$_2^{B}$), 4.19 (s, 5H, Cp′), 4.28–4.31 (m, 1H, H3), 4.49 (t, J = 2.5 Hz, 1H, H4), 4.84–4.87 (m, 1H, H5), 7.77 (bs, 1H, OH), 8.33 (d, J = 2.5 Hz, 1H, CH=N).^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): δ 18.3 (d, J = 4.3 Hz, CH(*C*H_3)(CH_3)^{A}), 19.9 (d, J = 12.7 Hz, CH(CH_3)(*C*H_3)^{A}), 20.4 (d, J = 16.0 Hz, CH(*C*H_3)(CH_3)^{B}), 22.2–22.4 (2C, *C*H(CH_3)$_2^{B}$ + CH(CH_3)(*C*H_3)^{B}), 25.6 (dd, J = 13.4 Hz, *C*H(CH_3)$_2^{A}$), 67.1 (d, J = 2.3 Hz, C5), 70.4 (5C, Cp′), 70.6 (C4), 71.3 (d, J = 4.8 Hz, C3), 78.4 (d, J = 16.9 Hz, C1), 80.8 (d, J = 24.1 Hz, C2). 150.1 (d, J = 10.2 Hz, CH=N). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ –7.2. HR-MS (ESI, MeOH/MeCN): *m/z* $[M+H]^+$ calcd. 346.1023 for $C_{17}H_{25}FeNOP$; found: 346.1002.

(*S*)-2-(Diphenylphosphino) ferrocenylmethylamine, (S_{Fc})-8a

A solution of (S_{Fc})-**7a** (2.13 g, 5.15 mmol) in dry THF (30 mL) was added dropwise to a solution of $LiAlH_4$ (1.17 g, 30.93 mmol) in dry THF (20 mL) at r.t. The mixture was refluxed for 6 Hours. After cooling to 0 °C and quenching with water, the aqueous phase was extracted with diethyl ether (3 x 30 mL); the combined organic phases were washed with water, dried over $MgSO_4$. After filtration and evaporation of the solvents, the crude product was purified by column chromatography on aluminum oxide 90 using EA as eluent and then change to ethanol giving the pure compound as an orange-brown solid (1.80 mg, 4.51 mmol, 88% yield). Mp.: 132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.59–3.76 (m, 3H, CH_2 + H3), 4.06 (s, 5H, Cp′), 4.25 (t, J = 2.5 Hz, 1H, H4), 4.43–4.48 (m, 1H, H5), 7.18–7.28 (m, 5H, Ph^{A}), 7.34–7.41 (m, 3H, Ph^{B}-*meta* + Ph^{B}-*para*), 7.47–7.55 (m, 2H, Ph^{B}-*ortho*). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 40.5 (d, J = 9.9 Hz, CH_2), 69.0 (C4), 69.4 (5C, Cp′), 70.7 (d, J = 3.6 Hz, C5), 71.2 (d, J = 3.8 Hz, C3), 75.4 (d, J = 6.9 Hz, C1), 95.3 (d, J = 24.2 Hz, C2), 128.0–128.4 (5C, Ph^{A}-*meta* + Ph^{B}-*meta* + Ph^{A}-*para*), 129.1 (Ph^{B}-*para*), 132.5 (d, J = 18.9 Hz, 2C, Ph^{A}-*ortho*), 134.8 (d, J = 20.8 Hz, 2C, Ph^{B}-*ortho*), 137.1 (d, J = 9.3 Hz, Ph^{B}-*ipso*), 139.7 (d, J

= 10.7 Hz, Ph^A-*ipso*). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ –21.9. HR-MS (ESI, MeOH/MeCN): *m/z* $[M+H]^+$ calcd. 400.0918 for $C_{23}H_{23}FeNP$; found: 400.0905. $[\alpha]^{20}_{\lambda}$ (nm): –130.6 (589) (*c* 0.42, $CHCl_3$).

(*S*)-2-(Diisopropylphosphino) ferrocenylmethylamine, (S_{Fc})-8b

Starting from (S_{Fc})-**7b** (1.00 g, 2.897 mmol) and $LiAlH_4$ (0.658 g, 17.38 mmol) and following the procedure of (S_{Fc})-**8a**, the desired product was obtained as a red oil. Due to decomposition of this compound on the column was used without further purification. ^1H NMR (600 MHz, $CDCl_3$): δ 0.81 (dd, *J* = 11.7 Hz, *J* = 6.9 Hz, 3H, $CH(CH_3)(CH_3)^A$), 0.99 (dd, *J* = 14.0 Hz, *J* = 7.1 Hz, 3H, $CH(CH_3)(CH_3)^A$), 1.24 (dd, *J* = 10.4 Hz, *J* = 7.0 Hz, 3H, $CH(CH_3)(CH_3)^B$), 1.40 (dd, *J* = 16.2 Hz, *J* = 7.3 Hz, 3H, $CH(CH_3)(CH_3)^B$), 1.70–1.81 (m, 1H, $CH(CH_3)_2^A$), 2.18–2.28 (m, 1H, $CH(CH_3)_2^B$), 3.56, 3.78 (AB, *J* = 14.3 Hz, 2H, CH_2), 4.09–4.13 (m, 1H, H3/H5), 4.13 (s, 5H, Cp′), 4.25 (t, *J* = 2.4 Hz, 1H, H4), 4.38–4.41 (m, 1H, H3/H5), $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$): δ 19.8–20.0 (2C, $CH(CH_3)_2^A$), 20.4 (d, *J* = 16.3 Hz, $CH(CH_3)(CH_3)^B$), 22.9 (d, *J* = 22.0 Hz, $CH(CH_3)(CH_3)^B$), 23.5 (d, *J* = 10.1 Hz, $CH(CH_3)_2^B$), 25.7 (dd, *J* = 12.3 Hz, $CH(CH_3)_2^A$), 68.2 (C4), 68.5 (bs, C3/C5), 69.4 (5C, Cp′), 69.8 (bs, C3/C5), 78.4 (d, *J* = 16.9 Hz, C1), 96.1 (d, *J* = 20.5 Hz, C2). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ –7.0. HR-MS (ESI, MeOH/MeCN): *m/z* $[M+H]^+$ calcd. 332.1231 for $C_{17}H_{26}FeNP$; found: 332.1212.

(S_{Fc},S_{Fc})-13a

$FeBr_2(THF)_2$, free of iron (III), was prepared by stirring $FeBr_2$ (68.34 mg, 0.317 mmol) and excess Fe powder (0.500 g, 8.93 mmol) in THF (10 mL) under argon until it turned colorless. The suspension was filtered through a frit and a solution of (S_{Fc},S_{Fc})-**1a** (0.260 g, 0.333 mmol) in THF (10 mL) was slowly added to it. The immediately formed orange suspension was stirred overnight. Then the solvent was removed under vacuum and the remaining solid dissolved in CH_2Cl_2 (5mL) and filtered through a short pad of celite and concentrated to 1 mL and the product was precipitated by addition of *n*-pentane (40 mL). The precipitate was separated from the supernatant solution, washed with n-pentane (3 × 10 mL), and dried under vacuum to afford an orange powder (0.315 g, 0.317 mmol, 93% yield). Single crystals suitable for X-ray structure determination were grown from CH_2Cl_2/ACN/Et_2O by slow evaporation of the solvent. Mp.> 170 °C (dec.). ESI-MS (m/z, ACN); pos. ion: 914.0 $[M-Br]^+$.

(S_{Fc},S_{Fc})-13b

Starting from (S_{Fc},S_{Fc})-**1b** (0.250 mg, 0.389 mmol) and $FeBr_2$ (79.60 mg, 0.369 mmol) and following the procedure of (S_{Fc},S_{Fc})-**13a** the desired product was obtained as a red powder (0.267 g, 0.311 mmol, 80% yield). Mp.> 170 °C (dec.). ESI-MS (m/z, ACN); pos. ion: 778.1 $[M-Br]^+$.

(S_{Fc},S_{Fc})-13c

Starting from (S_{Fc},S_{Fc})-**1a** (0.250 g, 0.321 mmol) and $FeCl_2$ (38.62 g, 0.305 mmol) and following the procedure of (S_{Fc},S_{Fc})-**13a**, the desired product was obtained as an orange powder (0.264 g, 0.291 mmol, 91% yield). Single crystals suitable for X-ray structure determination were grown from DCM/ACN/Et_2O by slow evaporation of the solvent. Mp.> 170 °C (dec.). ESI-MS (m/z, ACN); pos. ion: 870.0 $[M-Cl]^+$.

(S_{Fc},S_{Fc})-14

To a degassed solution of (S_{Fc},S_{Fc})-**13a** (50.00 mg, 0.050 mmol) in dry DCM (3 mL) was added dropwise to a solution of Borane tetrahydrofuran complex (55.00 µL, 1 M, 0.055 mmol) at 0 °C. After stirring for 30 minutes at r.t. was filtered through a short pad of celite and then the solvents were removed under reduced pressure to afford an orange powder. Single crystals suitable for X-ray structure determination were grown from DCM/Et_2O by slow evaporation of the solvent. ESI-MS (m/z, ACN); pos. ion: 928.0 $[M-Br]^+$.

(S_{Fc},S_{Fc})-16a

a)

A glass Autoclave was charged with (S_{Fc},S_{Fc})-**13a** (0.200 g, 0.201 mmol) in DCM (10 mL) and then was exposed to an atmosphere of CO (~2 bar). The reaction was allowed to stir overnight at r.t. The color changed from orange to red. The solvent was removed under reduced pressure and was concentrated to 1 mL. The product was precipitated by addition of diethyl ether (20 mL). The precipitate was separated from the supernatant solution, washed with diethyl ether (3 × 5 mL), and dried under vacuum to afford a deep orange powder. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 21.9 (d, J = 164.0 Hz), 24.7 (d, J = 173.8 Hz), 27.9 (d, J = 176.6 Hz), 29.4 (d, J = 176.6 Hz), 33.3 (d, J = 173.8 Hz), 34.4 (d, J = 164.0 Hz). IR (ATR, cm^{-1}): 1990 (ν_{CO}), 2038 (ν_{CO}). HR-MS (ESI, MeOH/MeCN): *m/z* $[M]^+$ calcd. 969.9688 for $C_{48}H_{39}BrFe_3NO_2P_2$; found: 969.9684.

b)

A degassed solution of (S_{Fc},S_{Fc})-**13b** (0.200 g, 0.257 mmol) in dry THF (5 mL) was added dropwise to a solution of $Fe(CO)_4Br_2$ (80.0 mg, 0.244 mmol) in THF (5 mL) at –78 °C and stirred overnight at r.t. Then solvent was removed under reduced pressure and the residue was taken up in DCM (2 mL), and the product was precipitated by addition of diethyl ether (20 mL). The precipitate was separated from the supernatant solution, washed with diethyl ether (3 × 5 mL), and dried under vacuum to afford an orange powder (182.00 mg, 0.186 mmol, 73% yield).

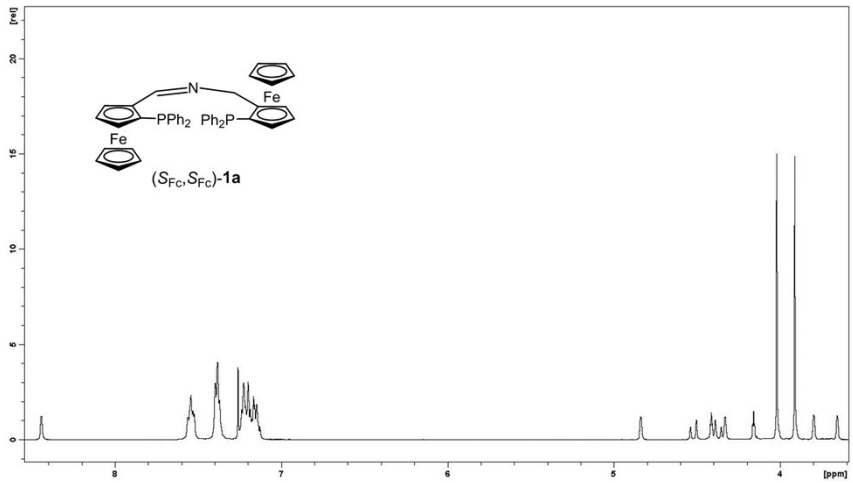
(S_{Fc},S_{Fc})-16b

Starting from (S_{Fc},S_{Fc})-**1b** (0.150 g, 0.202 mmol) and following the procedure (a) of (S_{Fc},S_{Fc})-**16a**, the desired product was obtained as a red powder (0.121 g, 0.152 mmol, 75% yield). Mp.> 170 °C (dec.). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 20.0 (d, J = 179.6 Hz), 21.7 (d, J = 158.9 Hz), 24.6 (d, J = 172.7 Hz), 27.9 (d, J = 172.7 Hz), 28.6 (d, J = 175.9 Hz), 30.2 (d, J = 175.9 Hz), 33.9 (d, J = 164.5 Hz). IR (ATR, cm^{-1}): 1988 (ν_{CO}), 2037 (ν_{CO}). HR-MS (ESI, MeOH/MeCN): *m/z* $[M]^+$ calcd. 834.0314 for $C_{36}H_{47}BrFe_3NO_2P_2$; found: 834.0309.

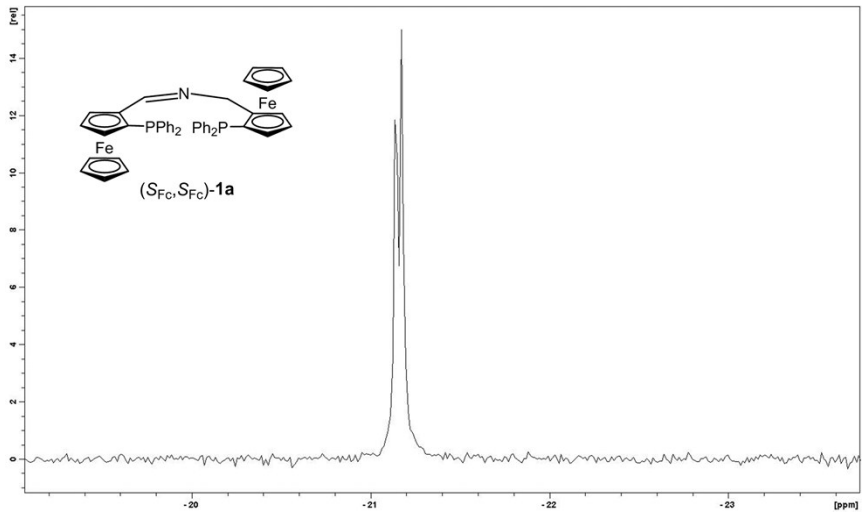
Computational Details. Calculations were performed using the GAUSSIAN 09 software package, and the B3LYP functional without symmetry constraints. The optimized geometries were obtained with the Stuttgart/Dresden ECP (SDD) basis set to describe the electrons of the iron atom. For all other atoms a standard 6-31G** basis set was employed. Frequency calculations were performed to confirm the nature of the stationary points yielding no imaginary frequency for the minima.

Figures of ^{1}H and ^{13}P NMR spectra:

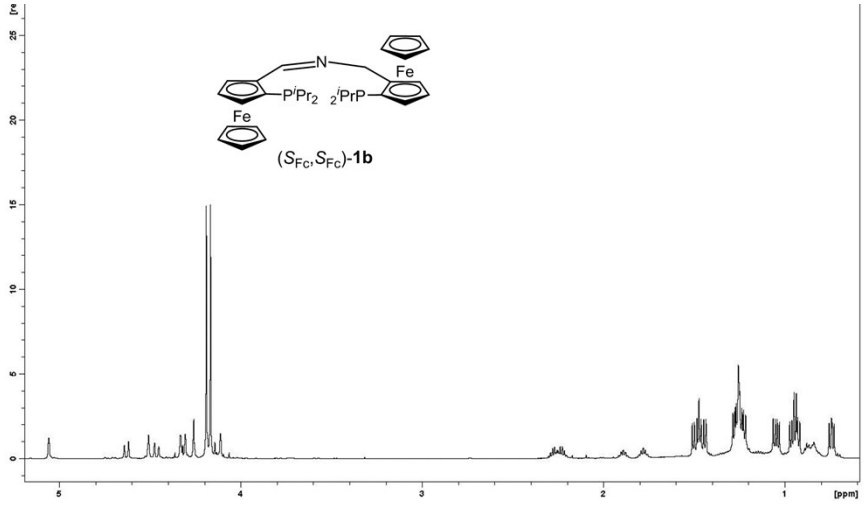
^{1}H NMR (400 MHz, $CDCl_3$) of (S_{Fc},S_{Fc})-**1a**



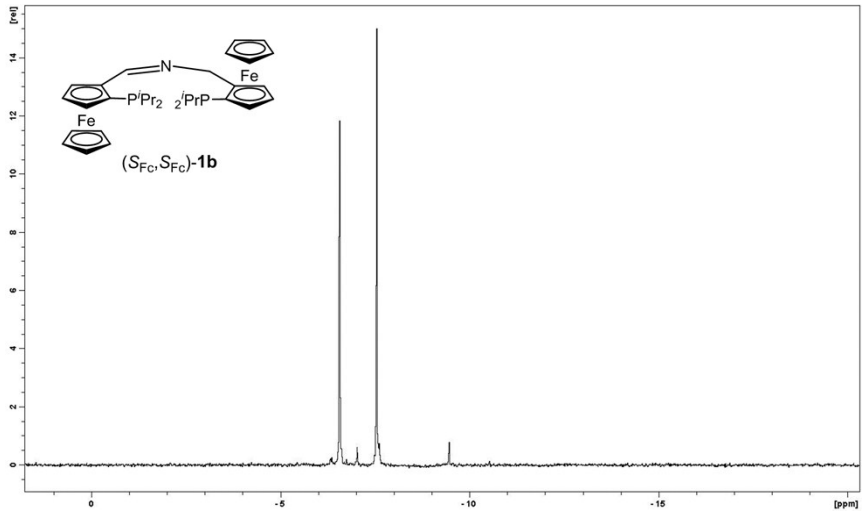
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) of (S_{Fc},S_{Fc})-**1a**



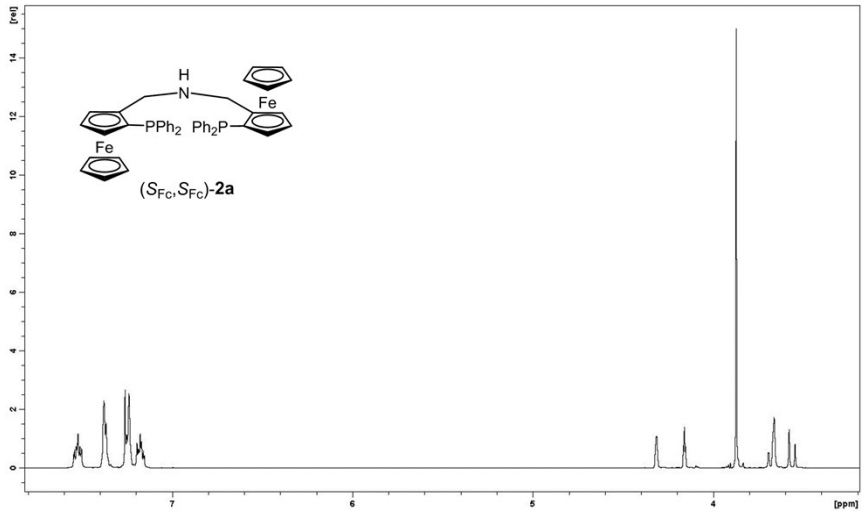
^{1}H NMR (600 MHz, $CDCl_3$) of (S_{Fc},S_{Fc})-**1b**



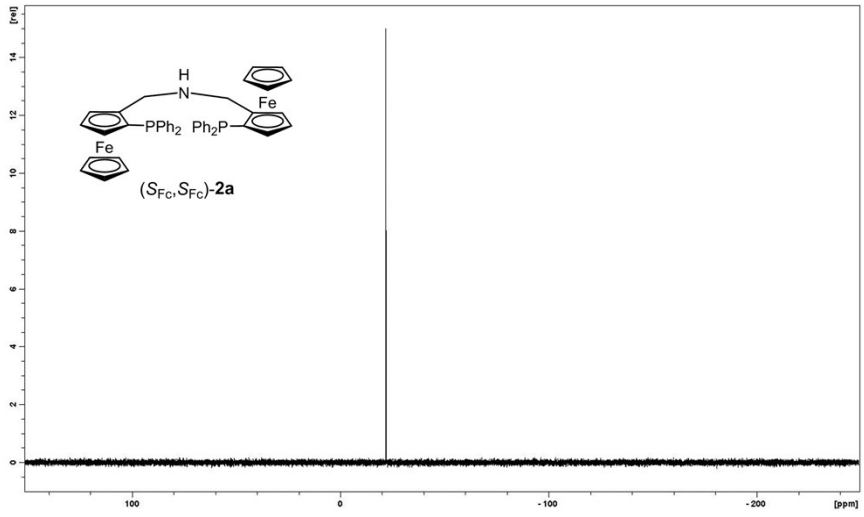
$^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$) of (S_{Fc},S_{Fc})-**1b**



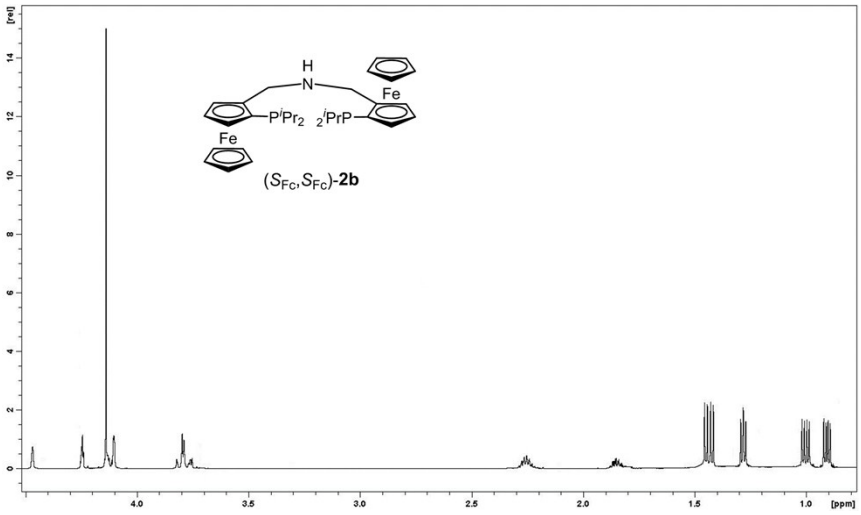
^{1}H NMR (400 MHz, $CDCl_3$) of (S_{Fc},S_{Fc})-**2a**



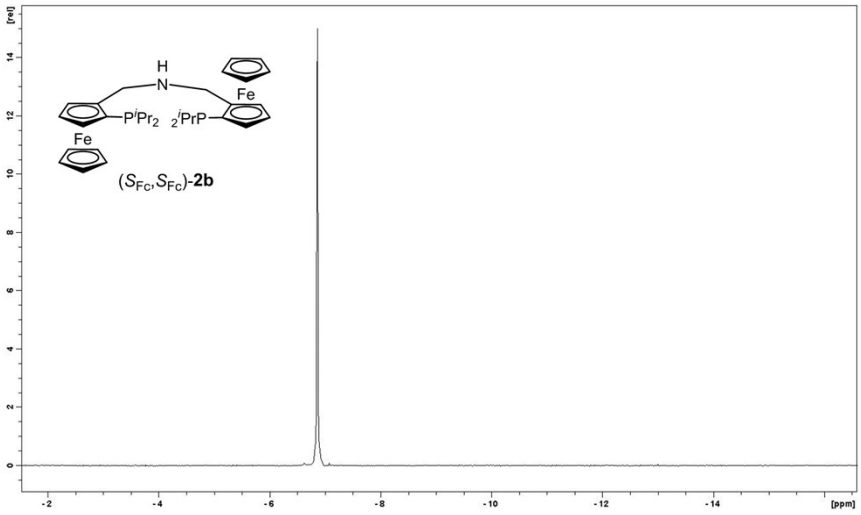
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) of (S_{Fc},S_{Fc})-**2a**



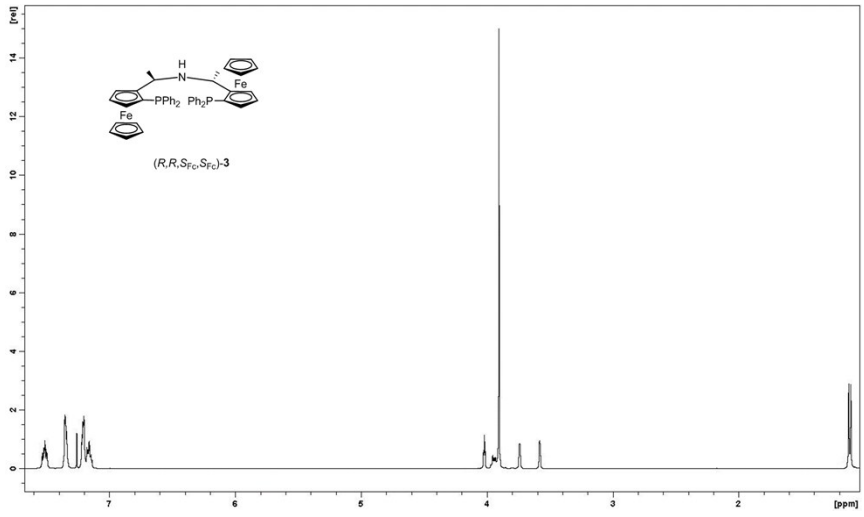
^{1}H NMR (600 MHz, $CDCl_3$) of (S_{Fc},S_{Fc})-**2b**



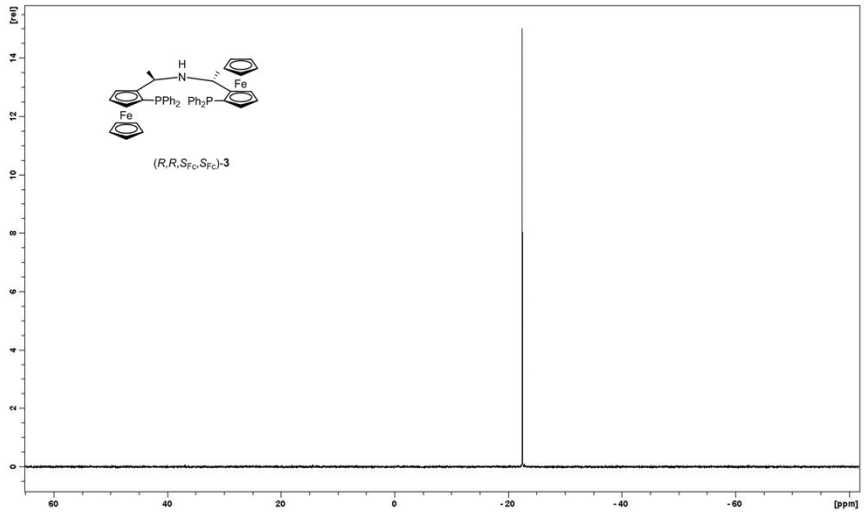
^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) of (S_{Fc},S_{Fc})-**2b**



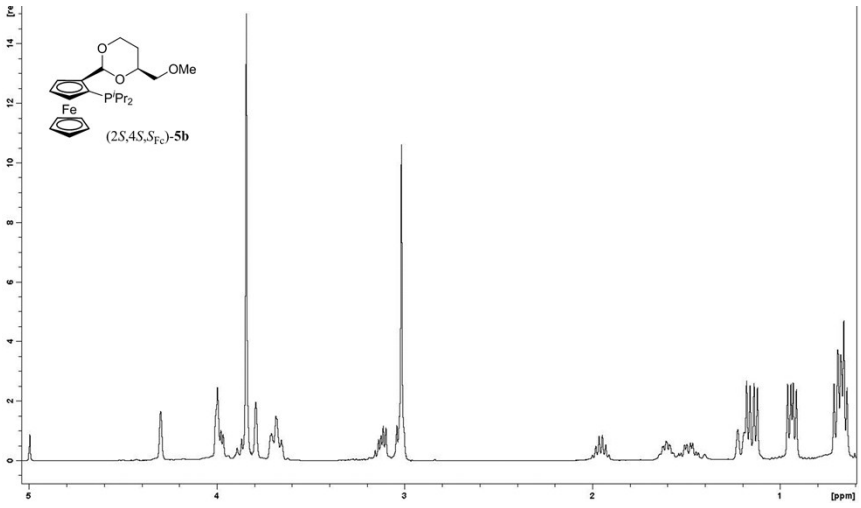
H NMR (400 MHz, $CDCl_3$) of (R,R,S_{Fc},S_{Fc})-**3**



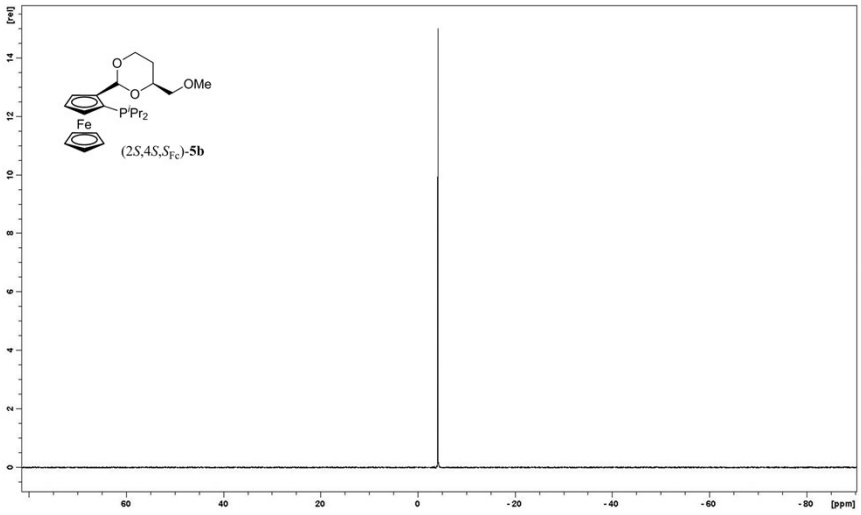
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) of (R,R,S_{Fc},S_{Fc})-**3**



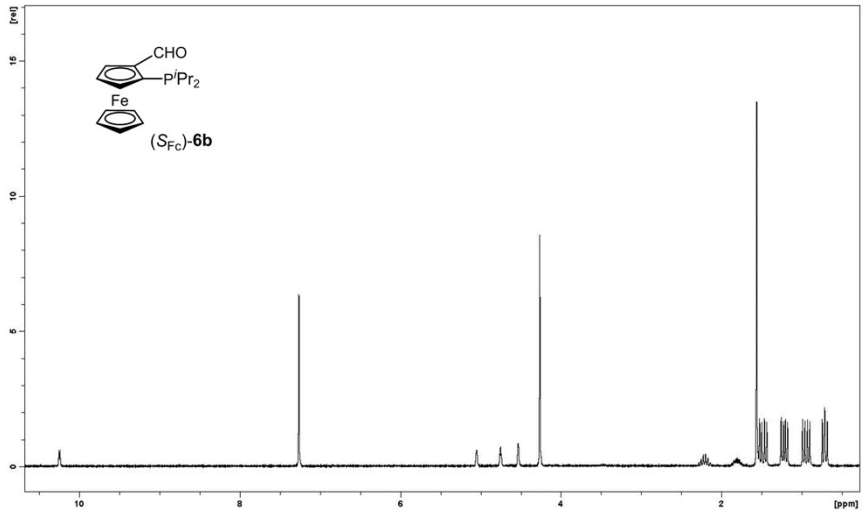
^{1}H NMR (400 MHz, $CDCl_3$) of (2*S*,4*S*,S_{Fc})-**5b**



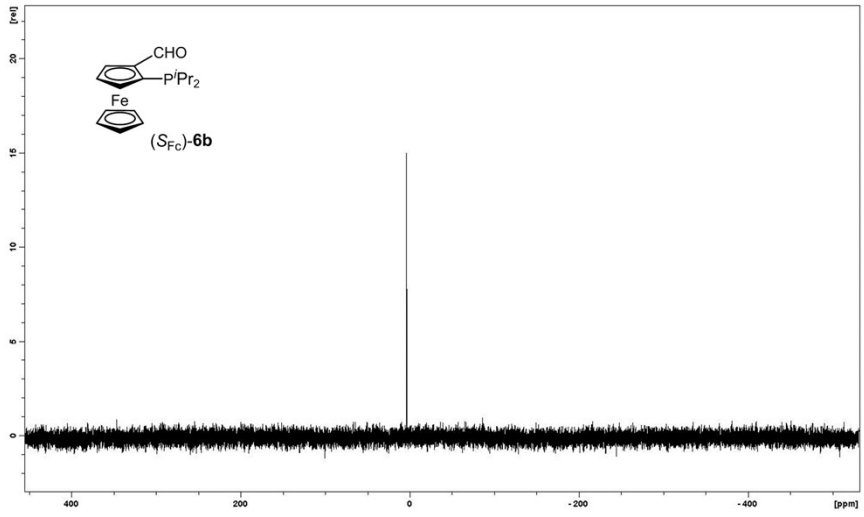
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) of (2*S*,4*S*,S_{Fc})-**5b**



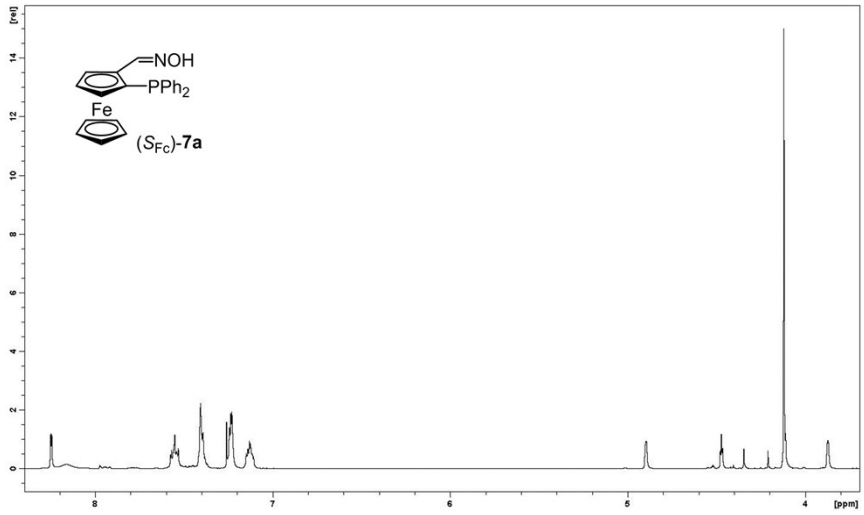
^{1}H NMR (400 MHz, $CDCl_3$) of (S_{Fc})-**6b**



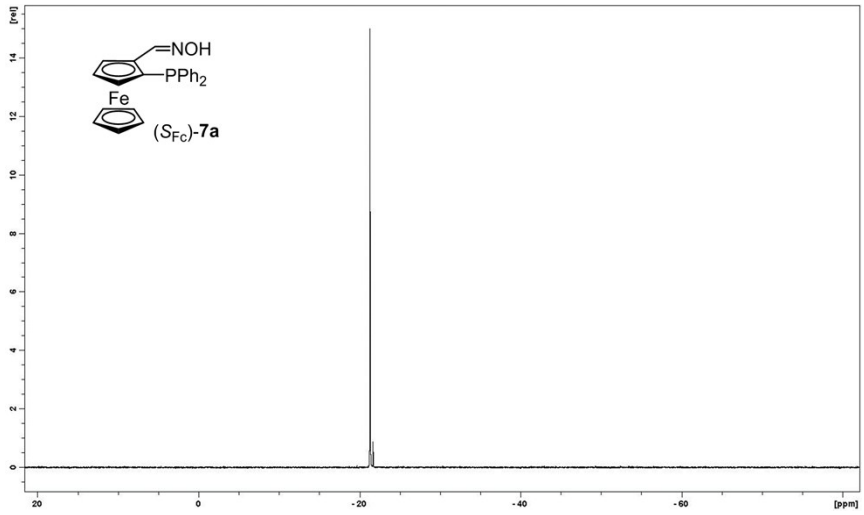
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) of (S_{Fc})-**6b**



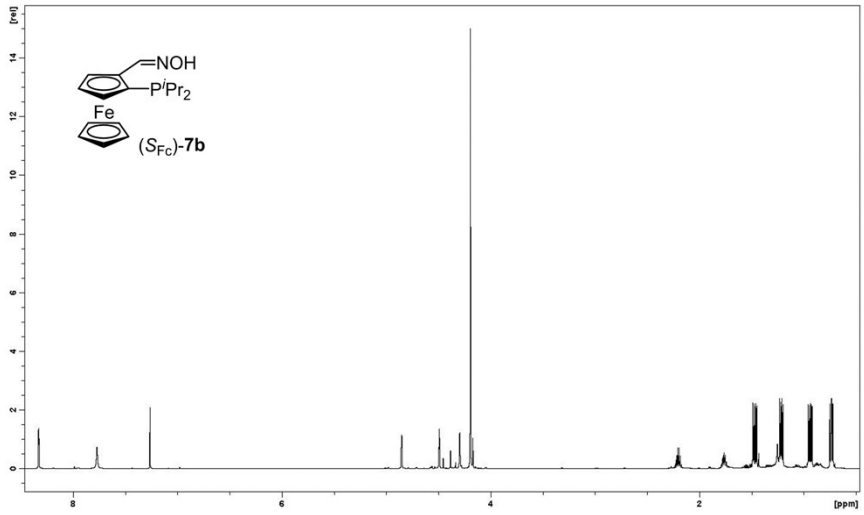
^{1}H NMR (400 MHz, $CDCl_3$) of (S_{Fc})-**7a**



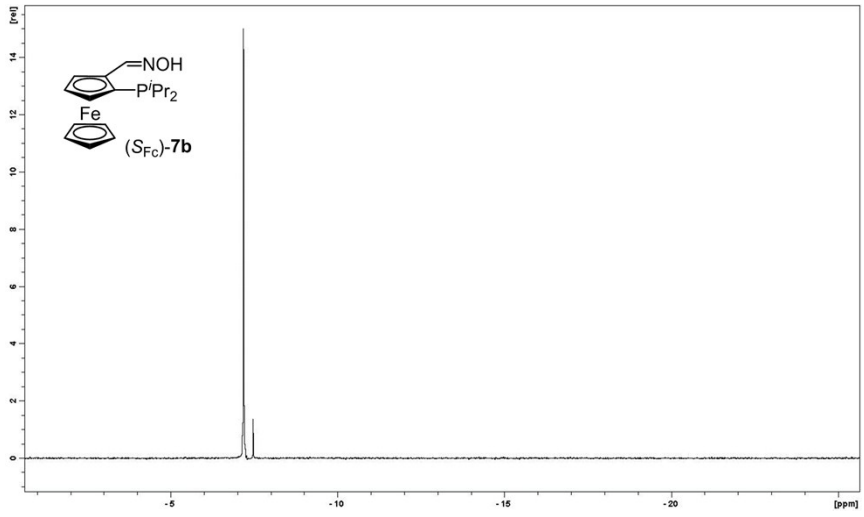
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) of (S_{Fc})-**7a**



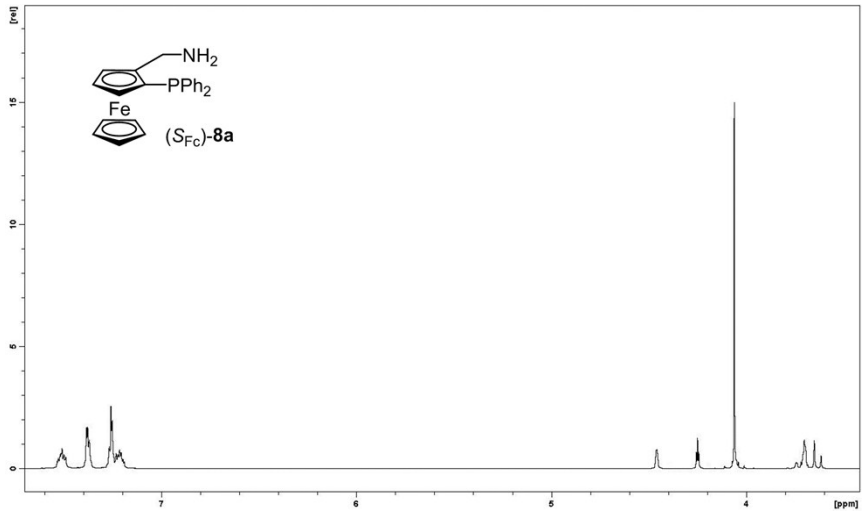
^{1}H NMR (600 MHz, $CDCl_3$) of (S_{Fc})-**7b**



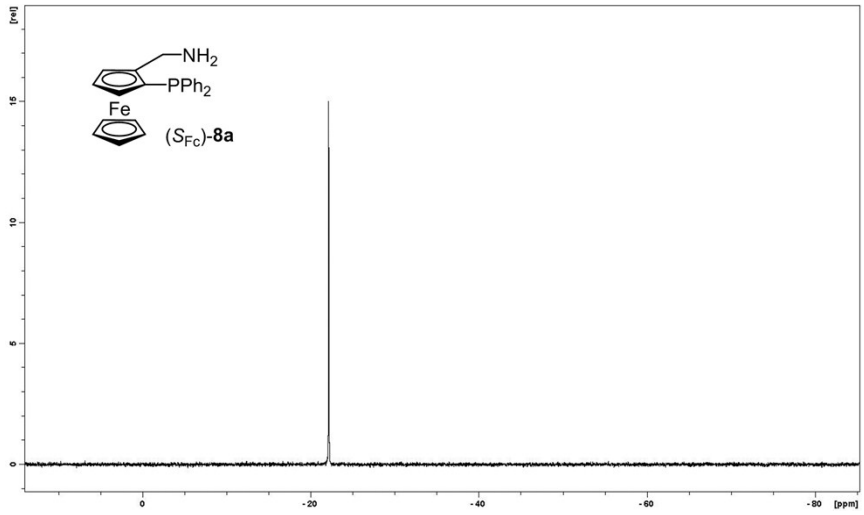
$^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$) of (S_{Fc})-**7b**



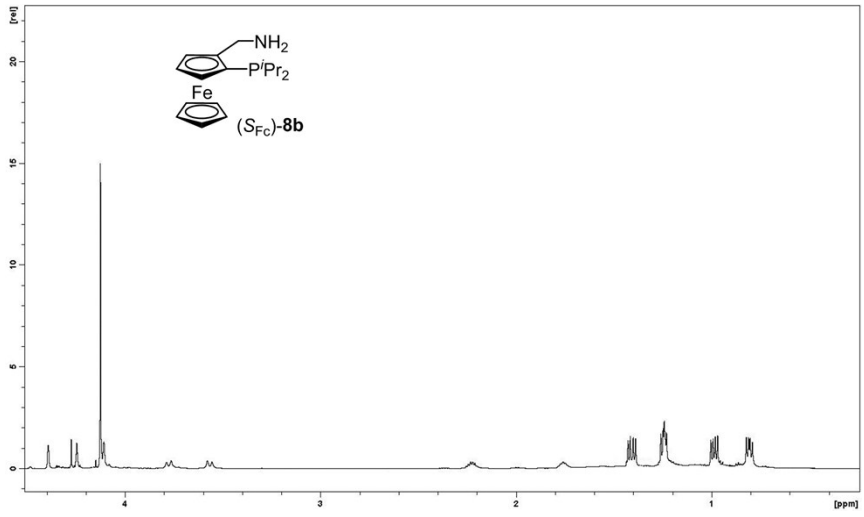
^{1}H NMR (400 MHz, $CDCl_3$) of (S_{Fc})-**8a**



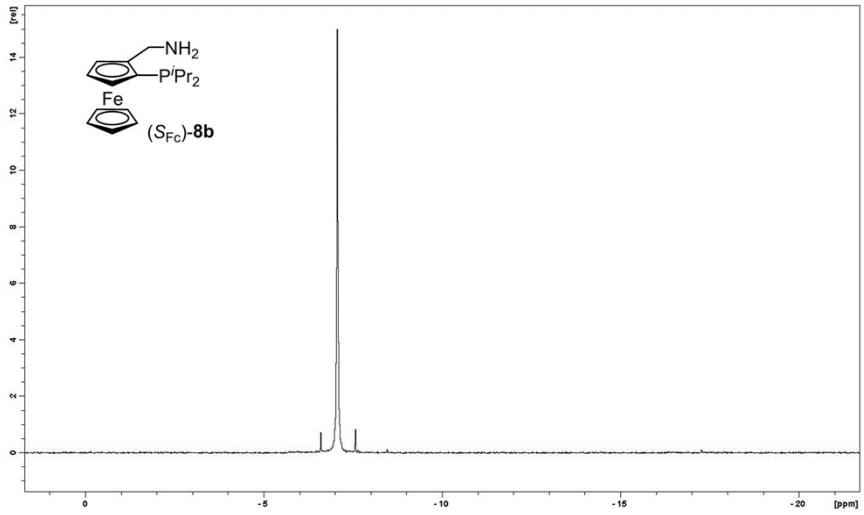
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) of (S_{Fc})-**8a**



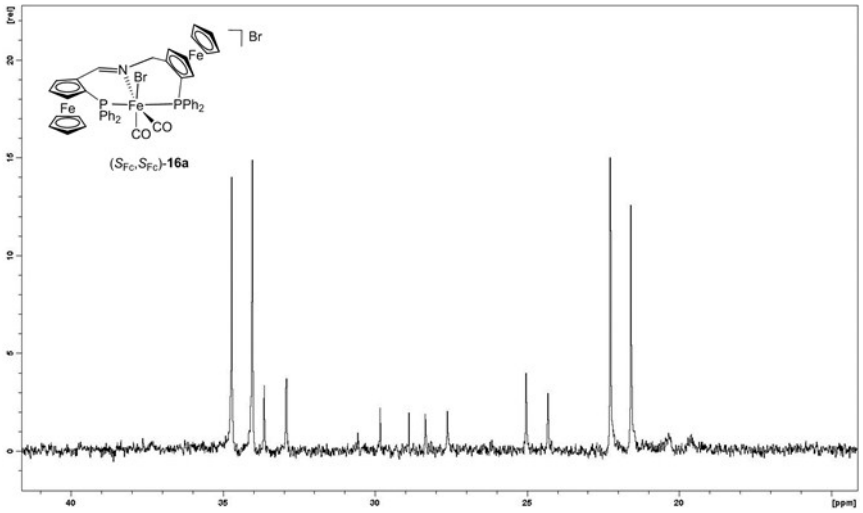
^{1}H NMR (600 MHz, $CDCl_3$) of (S_{Fc})-**8b**



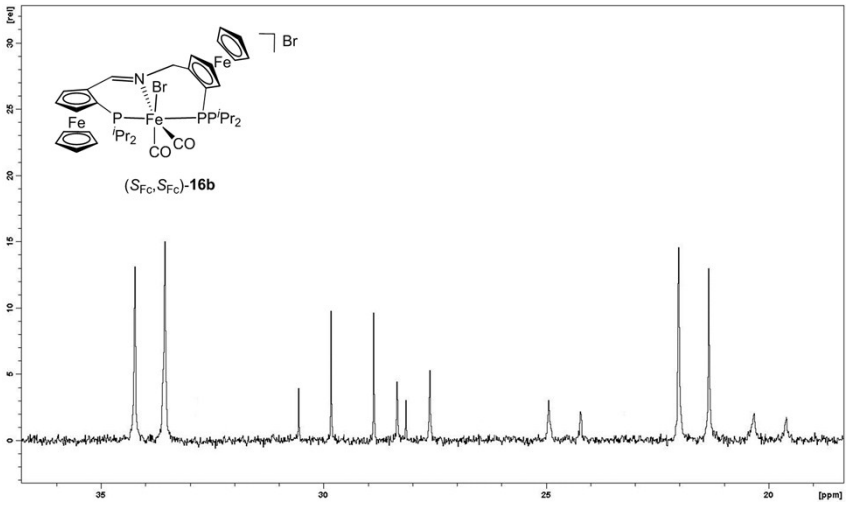
^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) of (S_{Fc})-**8b**



$^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$) of (S_{Fc},S_{Fc})-**16a**



$^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$) of (S_{Fc},S_{Fc})-**16b**



Crystal Structure Determination:

X-ray diffraction data of (S_{Fc},S_{Fc})-**1a**, (S_{Fc},S_{Fc})-**13a**, (S_{Fc},S_{Fc})-**13b**, and (S_{Fc},S_{Fc})-**14** [CCDC entries: 1435577 ((S_{Fc},S_{Fc})-**1a**), 1435448 ((S_{Fc},S_{Fc})-**13a**), 1433174 ((S_{Fc},S_{Fc})-**13b**) and 1433175 ((S_{Fc},S_{Fc})-**14**)] were collected at T = 100 K in a dry stream of nitrogen on Bruker D8 Venture ((S_{Fc},S_{Fc})-**1a** and (S_{Fc},S_{Fc})-**13a**) and Bruker KAPPA APEX II ((S_{Fc},S_{Fc})-**13b** and (S_{Fc},S_{Fc})-**14**) diffractometer systems using graphite-monochromatized Mo-$K\alpha$ radiation (λ = 0.71073 Å) and fine sliced φ- and ω-scans. Data were reduced to intensity values with SAINT and an absorption correction was applied with the multi-scan approach implemented in SADABS.[1] The structures were solved by direct methods implemented in SHELXS [2].Th e structures were refined using SHELXL[3] against F^2. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms connected to C atoms were placed in calculated positions and thereafter refined as riding on the parent atoms. The H atoms of the borane unit were located in difference Fourier maps and freely refined. Molecular graphics were generated with the program MERCURY.[4] Crystal data and experimental details are given in Table S1.

Table S1. Crystal data and structure refinement for the five investigated compounds (S_{Fc},S_{Fc})-**1a**, (S_{Fc},S_{Fc})-**13a**, (S_{Fc},S_{Fc})-**13c**, and (S_{Fc},S_{Fc})-**14**.

	(S_{Fc},S_{Fc})-**1a**	(S_{Fc},S_{Fc})-**13a**.2CH_2Cl_2	(S_{Fc},S_{Fc})-**13c**.2CH_2Cl_2	(S_{Fc},S_{Fc})-**14**.2CH_2Cl_2
formula	$C_{46}H_{39}Fe_2NP_2$	$C_{46}H_{39}Br_2Fe_3NP_2.2CH_2Cl_2$	$C_{46}H_{39}Cl_2Fe_3NP_2.2CH_2Cl_2$	$C_{46}H_{42}BBr_2Fe_3NP_2.2CH_2Cl_2$
fw	779.1257	992.8973	904.9983	1006.9301
cryst.size, mm	0.45 x 0.17 x 0.08	0.27 x 0.13 x 0.02	0.62 x 0.11 x 0.04	0.55 x 0.16 x 0.02
color, shape	clear red block	clear red plate	translucent red rod	translucent red plate
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*P2$_1$2$_1$2$_1$ (no. 19)*	*P*2$_1$ (no. 4)	*P*2$_1$ (no. 4)	*P*2$_1$ (no. 4)
a, Å	7.9187(11)	9.3149(3)	9.1961(5)	9.3238(3)
b, Å	16.357(2)	18.7337(7)	18.5027(10)	18.8630(7)
c, Å	28.737(4)	13.9965(5)	14.0562(8)	13.9040(5)
α/°	90	90	90	90
β, °	90	97.3358(14)	96.081(2)	97.689(2)
γ/°	90	90	90	90
V, Å^3	3722.2(9)	2422.43(15)	2378.2(2)	2423.38(15)
T, K	100	100	100	100
Z, Z'	4, 1	2, 1	2, 1	2, 1
ρ_{calc}, g cm^{-3}	1.391	1.597	1.503	1.615
μ, mm^{-1} (MoKα)	0.900	2.857	1.342	2.856
F(000)	1616.0	1168	1096	1184
absorption corrections,	multi-scan, 0.51–0.74	multi-scan, 0.64–0.75	multi-scan, 0.65–0.75	multi-scan, 0.45–0.75
θ range, deg	2.464 – 25.342	2.174 - 25.242	1.83–30.14	2.20–30.09
no. of rflns measd	13611	54 673	44 762	43 414
R_{int}	0.1033	0.0293	0.0305	0.0585
no. of rflns unique	6795	14 257	13 983	14 056
no. of rflns $I>2\sigma(I)$	4315	13 656	12 641	12 435
no. of params /	418 / 0	556 / 84	555 / 0	563 / 0
R ($I > 2\sigma(I)$) [a]	0.0673	0.0284	0.0313	0.0356
R (all data)	0.1312	0.0311	0.0382	0.0432
wR ($I > 2\sigma(I)$)	0.1082	0.0650	0.0631	0.0767
wR (all data)	0.1326	0.0665	0.0653	0.0790
GooF	0.987	1.025	1.020	0.993
Diff.Four.peaks	-0.50 / 0.43	-0.78 / 1.22	-0.71 / 0.97	-1.34 / 1.45
Flack Parameter	0.00(3)	-0.0114(17)	0.001(4)	0.019(7)
CCDC no.	1435577	1435448	1433174	1433175

[a] $R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2\}^{1/2}$, GooF = $\{\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\}^{½}$

1 Bruker computer programs: APEX2, SAINT and SADABS (Bruker AXS Inc., Madison, WI, 2012).

2 G. Sheldrick, Acta Crystallogr. 2008, A**64**, 112.

3 G. Sheldrick, Acta Crystallogr. 2008, A**64**, 112.

4 C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.* 2006, **39**, 453.