Electronic Supplementary Information

Design and Synthesis of a New Family of Planar and Central Chiral Ferrocenyl Phosphine Ligands

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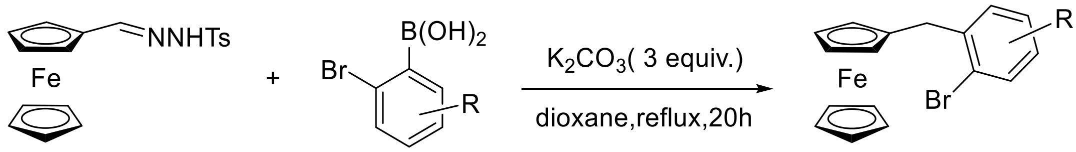
1. General Information

All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere by use of standard Schlenk techniques or a nitrogen atmosphere in a MBRAUN LabMaster PRS314/10-164-2 glovebox. All ^{1}H NMR, ^{13}C NMR, ^{31}P NMR spectra were recorded on a Bruker Avance (500 MHz) instrument. The ^{1}H NMR chemical shifts were measured relative to tetramethylsilane as an internal standard (TMS: $\delta = 0$ ppm). The ^{13}C NMR chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: $\delta = 77.00$ ppm). The ^{31}P NMR chemical shifts were measured relative to 85% H_3PO_4 as external standard (85% H_3PO_4: $\delta = 0$ ppm). High-resolution mass spectra (HRMS) were obtained on a Bruker QTOF mass spectrometer. Optical rotation was measured on a Anton Paar MCP100 polarimeter. Enantiomeric excess was determined by a Shimadzu LC-20A liquid chromatograph, using chiralpak® OD-H column, chiralpak® AD-H column, or chiralpak® OJ-H column with hexane and i-PrOH as solvent.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification.

2. General procedure for preparation of substrates (1a-1f)

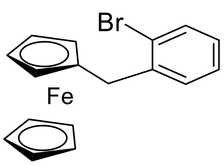


1

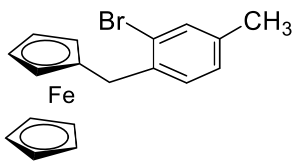
R= H, $-CH_3$, $-OCH_3$, -Cl

30 mmol substituted 2-bromobenzene boric acid, 10 mmol *N*-Tosylhydrazone and 30 mmol of K_2CO_3 were charged into 500 mL oven-dried flasks, and backfilled with Argon three times. 120 mL freshly distilled 1,4-dioxane was then injected into the flask, which were heated up to reflux for 20 h. The solvent was eliminated under vacuum pump. Water and dichloromethane was added and the layers were separated. The aqueous phase was extracted three times with dichloromethane. The combined organic phase was dried over $MgSO_4$. The concentrated residue was purified by column chromatography over silica gel using petroleum ether as eluent to get the product **1**.

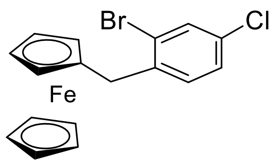
Table S1. preparation of substrates 1.



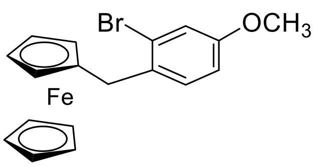
1a
69% yield



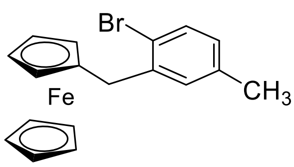
1b
64% yield



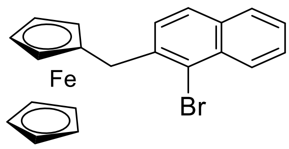
1c
49% yield



1d
61% yield

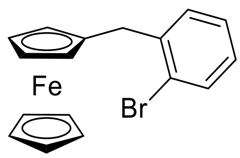


1e
60% yield



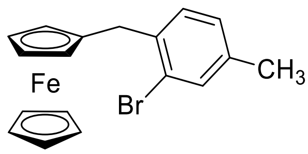
1f
57% yield

[a]Three compounds in 1,4-Dioxane, heating reflux, 20 h. [b]Isolated yield.



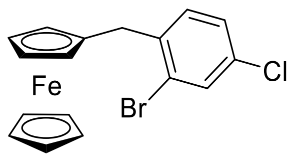
2-bromophenylmethylene ferrocene (**1a**)

Yellow solid, yield 69%. mp 70-71 ^{o}C. Rf (petroleum ether/ethyl acetate 50: 1) = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.3 Hz, 1H), 4.17 (s, 7H), 4.12 (s, 2H), 3.83 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.22 (s), 132.46 (s), 130.14 (s), 127.56 (s), 127.30 (s), 124.13 (s), 86.25 (s), 69.03 (s), 68.71 (s), 67.60 (s), 36.08 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{15}BrFe$ 353.9703; Found: 353.9695.



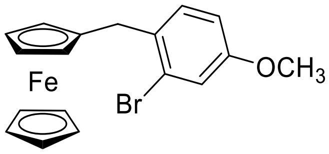
(2-bromo-4-methylphenyl)methylene ferrocene (**1b**)

Yellow solid, yield 64%. mp 91-92 ^{o}C. Rf (petroleum ether/ethyl acetate 50: 1) = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.00 (d, *J* = 0.9 Hz, 2H), 4.16 (s, 7H), 4.10 (t, *J* = 1.8 Hz, 2H), 3.78 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.10 (s), 137.51 (s), 132.87 (s), 129.86 (s), 128.10 (s), 123.83 (s), 86.63 (s), 68.97 (s), 68.69 (s), 67.53 (s), 35.60 (s), 20.52 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{17}BrFe$ 367.9859; Found: 367.9834.



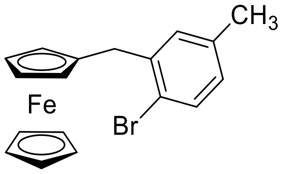
(2-bromo-4-chlorophenyl) methylene ferrocene (**1c**)

Yellow solid, yield 49%. mp 116-117 °C. Rf (petroleum ether/ethyl acetate 80: 1) = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 1.9 Hz, 1H), 6.94 – 6.87 (m, 2H), 4.07 (d, J = 3.9 Hz, 5H), 4.05 (s, 2H), 4.03 (s, 2H), 3.68 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.84 (s), 138.10 (s), 132.86 (s), 132.31 (s), 131.93 (s), 130.78 (s), 127.49 (s), 85.72 (s), 68.96 (s), 68.72 (d, J = 7.8 Hz), 67.76 (s), 67.53 (s), 35.55 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{14}BrClFe$ 387.9317; Found: 387.9292.



(2-bromo-4-methoxyphenyl) methylene ferrocene (**1d**)

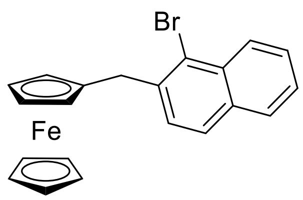
Yellow solid, yield 61%. mp 78-79 °C. Rf (petroleum ether/ethyl acetate 80: 1) = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.7 Hz, 1H), 6.68 (d, J = 2.9 Hz, 1H), 6.61 (dd, J = 8.7, 3.0 Hz, 1H), 4.18 (s, 7H), 4.13 (s, 2H), 3.79 (s, 2H), 3.72 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.59 (s), 143.91 (s), 138.71 (s), 138.01 (s), 122.84 (s), 84.78 (s), 69.05 (s), 68.86 (s), 67.99 (s), 35.37 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{17}BrFeO$ 383.9826; Found: 383.9812.



(2-bromo-5-methylphenyl)methylene ferrocene (**1e**)

Yellow solid, yield 60%. mp 57-58 °C. Rf (petroleum ether/ethyl acetate 50: 1) = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 8.1 Hz, 1H), 6.92 (d, J = 1.6 Hz, 1H), 6.85

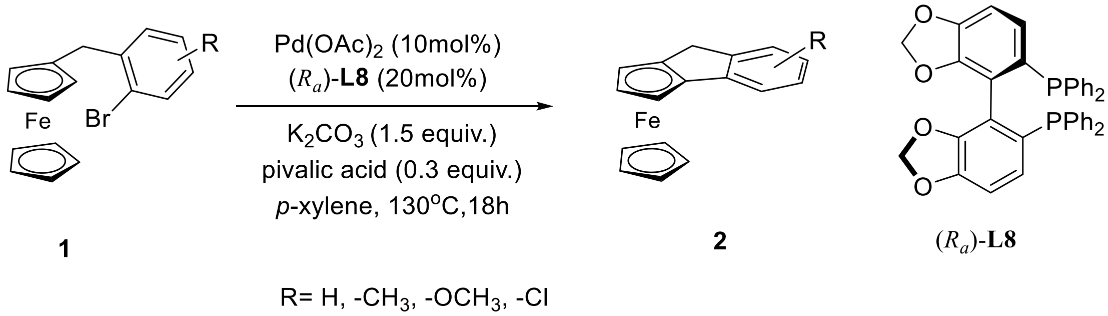
(dd, J = 8.1, 1.8 Hz, 1H), 4.20 – 4.18 (m, 2H), 4.17 (s, 5H), 4.12 – 4.11 (m, 2H), 3.79 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.81 (s), 137.13 (s), 132.17 (s), 130.90 (s), 128.42 (s), 120.73 (s), 86.50 (s), 69.05 (s), 68.72 (s), 67.56 (s), 35.98 (s), 20.93 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{17}BrFe$ 367.9859; Found: 367.9873.



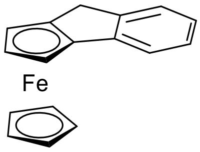
(3-bromo-2-naphthyl)methylene ferrocene (**1f**)

Yellow solid, yield 57%. mp 104-105 °C. Rf (petroleum ether/ethyl acetate 50: 1) = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.74 - 7.69 (m, 2H), 7.53 (s, 1H), 7.45 (dd, J = 5.4, 3.7 Hz, 2H), 4.26 (s, 2H), 4.23 (s, 5H), 4.18 (s, 2H), 4.01 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.63 (s), 132.93 (s), 132.32 (s), 130.86 (s), 128.33 (s), 127.42 (s), 126.41 (s), 126.10 (d, J = 5.7 Hz), 122.76 (s), 86.15 (s), 69.21 (s), 68.72 (s), 67.66 (s), 36.25 (s). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{17}BrFe$ 426.9743; Found: 426.9751.

3. General procedure for preparation of substrates (2a-2k)

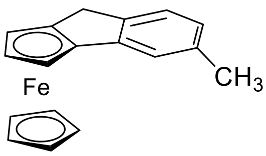


2-Bromophenylmethyl ferrocene (0.2 mmol), $Pd(OAc)_2$ (10% mol), *R*-Segphos (20% mol), K_2CO_3 (1.5 equiv.), pivalic acid (0.3 equiv.), and 1.5 mL *p*-xylene were mixed in a 10 mL Schlenk-type sealed tube. The mixture was stirred at 130 ^{o}C under argon atmosphere for 18 hours. When the reaction was completed, the solvent was eliminated under vacuum pump and water and dichloromethane was added and the layers were separated. The aqueous phase was extracted three times with dichloromethane. The combined organic phase was dried over anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum / DCM = 20 / 1, v / v) to get the product **2**.



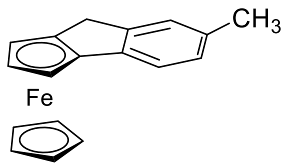
(S_p)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a, 8a-η)-1,8-dihydrocyclopent[*a*]inden-1-yl] iron (**2a**)

Orange solid, (99% yield, >99% *ee*). mp 50-51 ^oC. Rf (hexane) = 0.8. $[\alpha]_D^{20}$ = +490 (c = 0.001, CH_2Cl_2, 99% *ee*). ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 7.4 Hz, 1H), 7.33 (d, J = 7.4 Hz, 1H), 7.23 (t, J = 7.4 Hz, 1H), 7.16 (t, J = 7.4 Hz, 1H), 4.55 (d, J = 1.9 Hz, 1H), 4.49 (d, J = 1.7 Hz, 1H), 4.18 (t, J = 1.9 Hz, 1H), 3.88 (s, 5H), 3.75 (d, J = 19.9 Hz, 1H), 3.52 (d, J = 19.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 120.28 (s), 70.26 (s), 63.28 (s), 58.97 (s), 33.14 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{14}Fe$ 274.0440; Found: 274.0450. The enantiomeric excess was determined by Daicel Chiralpak OJ-H (0.46 cm × 25 cm), Hexane / IPA = 98 / 2, 1.0 mL / min, λ = 254 nm, t (major) = 10.065 min, t (minor) = 14.053 min.



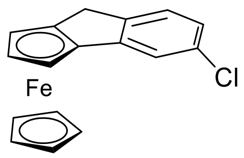
(S_p)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-4–methyl-1,8-dihydrocyclopent[*a*] inden-1-yl]iron **(2b)**

Orange oil, (99% yield, 95% *ee*). Rf (hexane) = 0.8. $[\alpha]_D^{20}$ = +1020 (c = 0.001, CH_2Cl_2, 95% *ee*). ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 - 7.15 (m, 1H), 7.01 - 6.92 (m, 2H), 4.52 - 4.41 (m, 2H), 4.18 - 4.11 (m, 1H), 3.87 - 3.80 (m, 5H), 3.74 - 3.62 (m, 1H), 3.50 - 3.37 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 142.2, 136.2, 125.5, 124.8, 121.1, 93.3, 92.5, 70.2, 69.5, 63.2, 58.8, 32.7, 21.6. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{16}Fe$ 288.0601; Found: 288.0624. The enantiomeric excess was determined by Daicel Chiralpak OJ-H (0.46 cm × 25 cm), Hexane / IPA = 98 / 2, 1.0 mL / min, λ = 254 nm, t (major) = 9.942 min, t (minor) = 10.983 min.



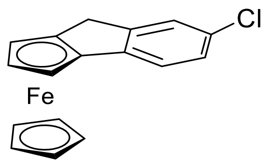
(S_p)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-5-methyl-1,8-dihydrocyclopent[*a*]inden-1-yl]iron **(2c)**

Yellow oil, (97% yield, >99% *ee*). Rf (hexane) = 0.8. $[\alpha]_D^{20}$ = +218 (c = 0.001, CH_2Cl_2, 99% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 27.4 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 4.46 (d, *J* = 21.8 Hz, 1H), 4.20 (d, *J* = 15.5 Hz, 1H), 4.14 (s, 2H), 3.85 (s, 3H), 3.70 (d, *J* = 19.3 Hz, 1H), 3.46 (d, *J* = 19.9 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.57 (s), 138.95 (s), 134.18 (s), 131.25 (s), 130.74 (s), 127.21 (s), 126.74 (s), 126.09 (s), 119.79 (s), 92.61 (s), 70.46 (d, *J* = 19.3 Hz), 70.10 (s), 69.80 (s), 69.27 (d, *J* = 20.0 Hz), 62.95 (s), 58.55 (s), 34.12 (s), 32.86 (s), 22.33 (s), 21.48 (s), 14.06 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{16}Fe$ 288.0601; Found: 288.0624. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 99 / 1, 1.0 mL / min, λ = 254 nm, t (major) = 7.180 min, t (minor) = 9.441 min.



(S_p)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-4–chloro-1,8-dihydrocyclopent[*a*]inden-1-yl]iron **(2d)**

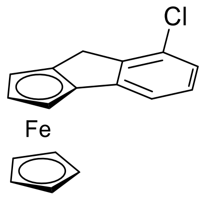
Orange oil, (97% yield, 98% *ee*). Rf (hexane) = 0.4. $[\alpha]_D^{20}$ = +579 (c = 0.001, CH_2Cl_2, 98% *ee*). ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 - 7.32 (m, 1H), 7.23 - 7.15 (m, 1H), 7.15 - 7.04 (m, 1H), 4.54 - 4.43 (m, 2H), 4.22 - 4.15 (m, 1H), 3.98 - 3.76 (m, 5H), 3.76 - 3.58 (m, 1H), 3.51 - 3.36 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 144.6, 132.6, 126.0, 124.6, 120.4, 93.4, 91.1, 70.4, 70.1, 63.6, 59.2, 32.8. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{13}ClFe$ 308.0050; Found: 308.0061. The enantiomeric excess was determined by Daicel Chiralpak OJ-H (0.46 cm × 25 cm), Hexane / IPA = 98 / 2, 1.0 mL / min, λ = 254 nm, t (major) = 38.937 min, t (minor) = 42.084 min.



(S_p)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-5-chloro-1,8-dihydrocyclopent[*a*]inden-1-yl]iron **(2e)**

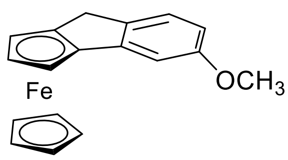
Yellow solid, (77% yield, 99% *ee*). Rf (hexane) = 0.35. $[\alpha]_D^{20}$ = -990 (c = 0.001, CH_2Cl_2, 99% *ee*). ^1H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 1H), 7.28 (s, 1H), 7.19 (d, J = 7.9 Hz, 1H), 4.51 (s, 1H), 4.48 (s, 1H), 4.18 (s, 1H), 3.86 (s, 5H), 3.72 (d, J = 20.0 Hz, 1H), 3.48 (d, J = 20.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.96 (s), 140.91 (s), 130.23 (s), 126.76 (s), 125.50 (s), 120.69 (s), 92.61 (s), 91.14 (s), 70.20 (s), 69.82 (s), 63.32 (s), 58.93 (s), 33.00 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{13}ClFe$

308.0050; Found: 308.0062. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 99 / 1, 1.0 mL / min, λ = 254 nm, t (major) = 6.682 min, t (minor) = 7.143 min.



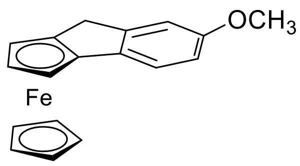
(S_p)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-6–chloro-1,8-dihydrocyclopent[*a*] inden-1-yl]iron **(2f)**

Orange oil, (97% yield, 91.2% *ee*). m.p. = 72 °C. Rf (hexane) = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 7.1 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.15 – 7.12 (m, 1H), 4.53 (t, J = 2.6 Hz, 2H), 4.19 (t, J = 2.3 Hz, 1H), 3.87 (d, J = 12.5 Hz, 5H), 3.78 (d, J = 20.5 Hz, 1H), 3.50 (d, J = 20.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.78 (s), 144.46 (s), 130.63 (s), 128.32 (s), 124.73 (s), 118.37 (s), 92.15 (s), 91.64 (s), 70.24 (s), 69.92 (s), 63.48 (s), 59.22 (s), 32.71 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{13}ClFe$ 308.0050; Found: 308.0047. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 98 / 2, 1.0 mL / min, λ = 254 nm, t (major) = 6.680min, t (minor) = 8.100 min.



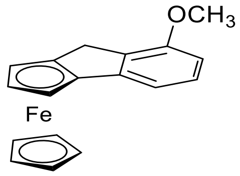
(S_p)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-4-methoxy-1,8-dihydrocyclopent[*a*] inden-1-yl]iron **(2g)**

Orange oil, (98% yield, >99% *ee*). Rf (hexane) = 0.5. $[\alpha]_D^{20}$ = +693(c = 0.001, CH_2Cl_2, 99% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 - 7.27 (m, 1H), 6.97 - 6.87 (m, 1H), 6.82 - 6.71 (m, 1H), 4.50 - 4.35 (m, 2H), 4.12 - 4.10 (m, 1H), 3.90 - 3.83 (m, 5H), 3.83 (s, 3H), 3.74 - 3.66 (m, 1H), 3.53 - 3.40 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 149.3, 142.4, 120.5, 112.1, 111.9, 92.8, 92.4, 70.2, 69.1, 63.0, 58.4. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{16}FeO$ 304.0551; Found: 304.0567. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 99 / 1, 1.0 mL / min, λ = 254 nm, t (major) = 15.614 min, t (minor) = 16.336 min.



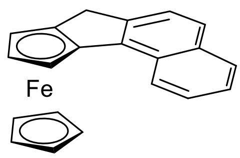
(S_p)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-5–methoxy-1,8-dihydrocyclopent[*a*] inden-1-yl]iron **(2h)**

Orange solid, (79% yield, 97% *ee*). mp 131-132 ºC. Rf (hexane) = 0.3. $[\alpha]_D^{20}$ = -812 (c = 0.001, CH_2Cl_2, 97% *ee*). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.2 Hz, 1H), 6.92 (s, 1H), 6.77 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.45 (d, *J* = 1.7 Hz, 1H), 4.42 (d, *J* = 1.6 Hz, 1H), 4.12 (s, 1H), 3.86 (s, 5H), 3.84 (s, 3H), 3.71 (d, *J* = 19.8 Hz, 1H), 3.48 (d, *J* = 19.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.70 (s), 149.11 (s), 134.25 (s), 120.35 (s), 111.98 (s), 111.70 (s), 92.65 (s), 92.20 (s), 70.04 (s), 68.94 (s), 62.84 (s), 58.22 (s), 55.43 (s), 33.18 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{16}FeO$ 304.0551; Found: 304.0567. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 99 / 1, 1.0 mL / min, λ = 254 nm, t (major) = 9.251 min, t (minor) = 10.189 min.



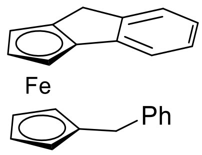
(S_p)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-6-methoxy-1,8-dihydrocyclopent[*a*] inden-1-yl]iron **(2i)**

Orange oil, (94% yield,92.5% *ee*). Rf (hexane) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 4.52 (d, *J* = 11.0 Hz, 2H), 4.17 (s, 1H), 3.91 (d, *J* = 7.3 Hz, 8H), 3.73 (d, *J* = 20.3 Hz, 1H), 3.44 (d, *J* = 20.3 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 155.76 (s), 143.71 (s), 133.91 (s), 128.13 (s), 113.32 (s), 107.22 (s), 93.01 (s), 92.42 (s), 70.16 (s), 69.49 (s), 63.27 (s), 58.98 (s), 55.17 (s), 30.14 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{16}FeO$ 304.0551; Found: 304.0567. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 99 / 1, 1.0 mL / min, λ = 254 nm, t (major) = 9.944 min, t (minor) = 10.341 min.



(S_p)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,10a-η)-1,10-dihydro-10-oxopentaleno [1,2 -b] naphthalen-1-yl] iron **(2j)**

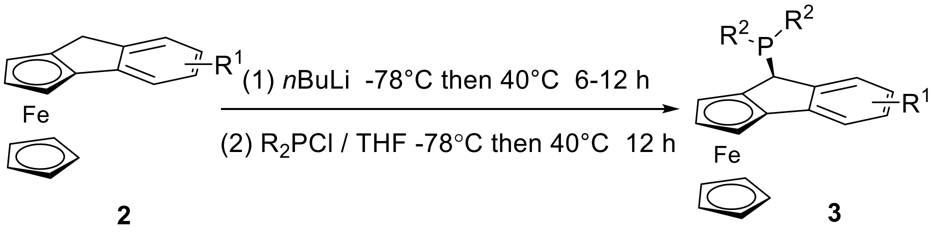
Yellow oil, (88% yield, 99% *ee*). Rf (hexane) = 0.7. $[\alpha]_D^{20}$ = +48 (c = 0.001, CH_2Cl_2, 99% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.9 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 4.89 (s, 1H), 4.64 (s, 1H), 4.32 (d, J = 1.8 Hz, 1H), 3.90 (s, 5H), 3.84 (d, J = 23.2 Hz, 1H), 3.67 (d, J = 20.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.38 (s), 138.50 (s), 132.91 (s), 128.43 (s), 125.71 (s), 125.07 (s), 124.82 (s), 124.43 (s), 123.76 (s), 93.11 (s), 91.84 (s), 73.22 (s), 70.43 (s), 69.90 (d, J = 7.9 Hz), 63.29 (s), 60.77 (s), 33.76 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{16}FeO$ 324.0596; Found: 324.0587. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 99 / 1, 1.0 mL / min, λ = 254 nm, t (major) =10.205 min, t (minor) =11.720 min.



(S_p)-(2-phenylmethylene-η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-1,8-dihydrocyc-lopent[*a*] inden-1-yl] iron **(2k)**

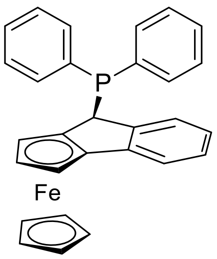
Yellow oil, (63% yield, 90% *ee*). Rf (hexane) = 0.4. $[\alpha]_D^{20}$ = -479 (c = 0.001, CH_2Cl_2, 90% *ee*). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, J = 7.4 Hz, 1H), 7.33 (d, J = 7.4 Hz, 1H), 7.24 (s, 1H), 7.17 (dd, J = 23.5, 7.2 Hz, 3H), 7.11 (s, 1H), 6.99 (d, J = 7.2 Hz, 2H), 4.46 (d, J = 23.7 Hz, 2H), 4.16 (s, 1H), 3.89 – 3.83 (m, 3H), 3.71 – 3.62 (m, 2H), 3.49 (d, J = 20.0 Hz, 1H), 3.23 (d, J = 15.4 Hz, 1H), 3.08 (d, J = 15.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.32 (s), 141.73 (s), 141.46 (s), 128.17 (d, J = 4.9 Hz), 126.57 (s), 125.73 (s), 125.13 (s), 124.64 (s), 120.54 (s), 92.83 (d, J = 5.0 Hz), 88.06 (s), 71.32 (s), 70.26 (s), 69.87 (s), 69.62 (s), 69.24 (s), 63.56 (s), 59.37 (s), 33.97 (s), 32.67 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{24}H_{20}Fe$ 364.0909; Found: 364.0891. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 99 / 1, 1.0 mL / min, λ = 254 nm, t (major) = 9.577 min, t (minor) = 10.619 min.

4. General procedure for preparation of substrates (3a-3r)



R^1= H, $-CH_3$, $-OCH_3$, -Cl
R^2 = Phenyl, Isopropyl, Tert-butyl, Cyclohexyl
Adamantyl

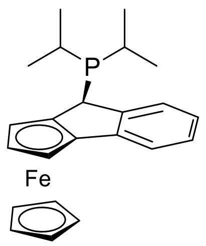
Ferrocenyl indene (1.0 equiv.) was dissolved in THF under argon. The mixture was cooled to -78 ℃ and n-BuLi in hexanes (1.6 M, 1.1 equiv.) was added drop wise. The addition was complete then the mixture was stirred at 40 ℃ for 6-12 h. Cooled to -78 ℃ and R_2PCl (1.1 equiv.) or trimethylchlorosilane (1.1 equiv.) in THF was added drop wise. After the addition was complete, the mixture was stirred at 40 ℃ for 12 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum / DCM = 15 / 1, v / v) to get the product **3**.



(R_p,*S*)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-(8a*S*)-8-(diphenylphosphine)-1,8-dihydrocyclopent[*a*] inden-1-yl]-iron (**3a**)

Yellow oil, (70% yield, 99.9% ee ; 99% de). Rf (petroleum ether) = 0.4. ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.54 (s, 2H), 7.39 (s, 3H), 7.29 (t, J = 8.0 Hz, 4H), 7.19 (s, 2H), 7.13 (t,

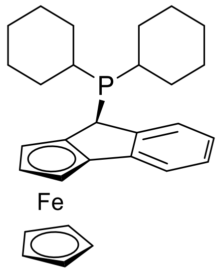
J = 7.4 Hz, 1H), 6.98 (s, 1H), 6.88 (s, 1H), 4.86 (s, 1H), 4.42 (s, 1H), 4.00 (s, 1H), 3.86 (s, 1H), 3.85 (d, J = 12.9 Hz, 5H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 147.26 (d, J = 7.5 Hz), 141.83 (d, J = 3.3 Hz), 137.69 (d, J = 17.8 Hz), 135.32 (d, J = 16.5 Hz), 134.01 (s), 133.84 (s), 133.24 (d, J = 18.4 Hz), 128.98 (s), 128.74 (s), 128.23 (d, J = 6.3 Hz), 127.79 (d, J = 7.2 Hz), 126.76 (d, J = 2.1 Hz), 125.22 (d, J = 6.1 Hz), 124.22 (d, J = 2.0 Hz), 120.03 (s), 93.82 (d, J = 6.4 Hz), 91.50 (s), 70.10 (s), 69.66 (s), 63.22 (d, J = 2.7 Hz), 59.10 (s), 44.03 (s), 43.87 (s). ^{31}P NMR (202 MHz, CDCl$_3$) δ -1.81 (s). HRMS (ESI-TOF) m/z: [M]$^+$ calcd for $C_{29}H_{23}FeP$ 458.0882; Found: 458.0909. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm × 25 cm), Hexane / IPA = 98 / 2, 1.0 mL / min, λ = 254 nm, t (major) = 13.810 min, t (minor) = 10.219 min.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-(8aS)-8-(diisopropylphosphane)-1,8-dihydrocyclopent[*a*] inden-1-yl]-iron (**3b**)

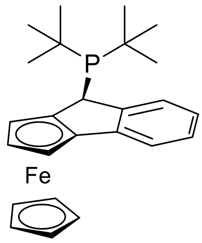
Yellow oil, (76% yield). Rf (petroleum ether) = 0.45. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.47 (d, J = 7.5 Hz, 1H), 7.22 (t, J = 7.9 Hz, 2H), 7.11 (d, J = 6.0 Hz, 1H), 4.95 (d, J = 2.0 Hz, 1H), 4.67 (d, J = 2.2 Hz, 1H), 4.36 (t, J = 2.3 Hz, 1H), 3.99 (s, 5H), 3.85 (s, 1H), 1.84 (dd, J = 9.4, 7.9 Hz, 2H), 1.45 (s, 1H), 1.42 – 1.26 (m, 4H), 1.14 (dd, J = 15.0, 7.0 Hz, 2H), 0.89 (t, J = 7.7 Hz, 3H), 0.66 (dd, J = 11.0, 7.2 Hz, 1H), 0.56 (dd, J = 14.4, 7.2 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 151.86 (s), 140.99 (s), 126.89 (s), 124.77

(s), 124.05 (s), 120.03 (s), 96.45 (s), 91.66 (s), 70.49 – 70.09 (m), 69.95 (s), 63.97 (s), 59.35 (s), 43.85 (s), 39.99 (s). ^{31}P NMR (202 MHz, C_6D_6) δ 22.27 (s).HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{28}FeP$ 391.1273; Found:391.0682.



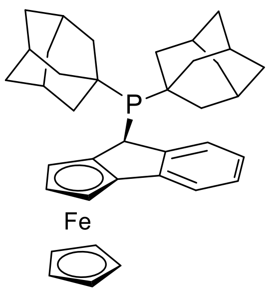
(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-(8a*S*)-8-(dicyclohexylphosphine)-1,8-dihydrocyclopent[*a*] inden-1-yl]-iron (**3c**)

Yellow oil, (76% yield). Rf (petroleum ether) = 0.4. ^{1}H NMR (500 MHz, $cdcl_3$) δ 7.45 (d, J = 7.3 Hz, 1H), 7.40 (d, J = 7.3 Hz, 1H), 7.19 (t, J = 7.3 Hz, 1H), 7.14 (t, J = 7.4 Hz, 1H), 4.55 (s, 1H), 4.43 (s, 1H), 4.29 (d, J = 3.5 Hz, 1H), 4.17 (s, 1H), 3.82 (s, 5H), 2.09 (d, J = 9.4 Hz, 1H), 1.94 (d, J = 10.3 Hz, 1H), 1.74 (d, J = 36.9 Hz, 3H), 1.42 (d, J = 9.7 Hz, 5H), 1.28 (d, J = 18.7 Hz, 5H), 1.10 (d, J = 9.6 Hz, 2H), 0.89 (s, 2H), 0.80 – 0.68 (m, 3H). ^{13}C NMR (126 MHz, $cdcl_3$) δ 149.57 (d, J = 7.2 Hz), 141.23 (d, J = 2.9 Hz), 126.24 (d, J = 1.6 Hz), 124.99 (d, J = 7.9 Hz), 124.56 (s), 119.83 (s), 95.20 (s), 91.60 (s), 70.43 (s), 70.19 (s), 69.50 (s), 62.84 (d, J = 1.5 Hz), 58.87 (s), 40.40 (s), 40.19 (s), 31.84 (dd, J = 16.6, 14.1 Hz), 31.18 (dd, J = 17.1, 9.3 Hz), 30.17 (d, J = 7.9 Hz), 29.60 (d, J = 7.8 Hz), 27.50 – 27.20 (m), 26.97 (d, J = 12.0 Hz), 26.49 (s), 26.20 (s). ^{31}P NMR (202 MHz, C_6D_6) δ 14.28 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{35}FeP$ 470.1899; Found:470.1908.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-(8aS)-8-(ditertbutyl-phosphine)-1,8-dihydrocyclopent[*a*] inden-1-yl]-iron (**3d**)

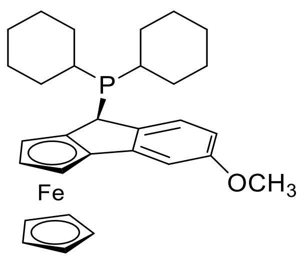
Yellow oil, (76% yield). Rf (petroleum ether) = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 1H), 7.43 – 7.39 (m, 1H), 7.21 (dd, J = 6.0, 2.7 Hz, 2H), 4.69 (d, J = 2.4 Hz, 1H), 4.64 (d, J = 2.3 Hz, 1H), 4.34 (s, 1H), 4.20 (t, J = 2.3 Hz, 1H), 4.00 (s, 1H), 3.84 (s, 5H), 1.52 (d, J = 11.2 Hz, 9H), 0.80 (d, J = 11.5 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.19 – 151.59 (m), 140.87 (s), 140.41 (s), 126.79 (s), 125.99 (dd, J = 12.0, 7.9 Hz), 124.60 (d, J = 16.3 Hz), 123.94 (s), 119.91 (s), 119.43 (s), 96.33 (s), 95.65 (d, J = 6.0 Hz), 92.68 (s), 91.54 (s), 70.36 (d, J = 16.6 Hz), 69.01 (s), 65.72 (s), 58.98 (s), 42.10 (s), 41.81 (s), 33.85 (s), 33.62 (s), 32.04 (s), 31.85 (s), 30.97 (d, J = 13.5 Hz), 29.86 (d, J = 13.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 50.83 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{31}FeP$ 419.1586; Found:419.1566.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-(8aS)-8-(di(1-adamantyl)phosphi-ne) -1,8-dihydrocyclopent[*a*]inden-1-yl]-iron (**3e**)

Yellow oil, (79% yield). Rf (petroleum ether) = 0.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59

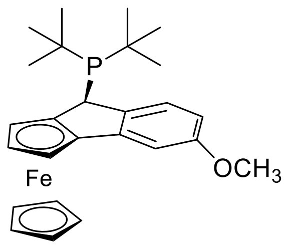
(d, J = 6.2 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.19 – 7.17 (m, 2H), 4.69 (d, J = 1.5 Hz, 1H), 4.61 (d, J = 1.7 Hz, 1H), 4.26 (s, 1H), 4.17 (t, J = 2.3 Hz, 1H), 3.82 (s, 5H), 2.21 (d, J = 56.9 Hz, 10H), 1.88 (s, 6H), 1.68 (d, J = 11.9 Hz, 3H), 1.59 (s, 3H), 1.46 (s, 5H), 1.36 (d, J = 11.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 129.04 (s), 128.23 (s), 125.90 (t, J = 6.8 Hz), 125.31 (s), 124.54 (s), 96.36 (d, J = 5.9 Hz), 92.97 (s), 70.44 (s), 68.87 (s), 66.36 (s), 58.94 (s), 42.41 (d, J = 10.7 Hz), 40.34 (d, J = 10.8 Hz), 39.84 (s), 39.57 (s), 39.24 – 39.14 (m), 38.93 (d, J = 28.0 Hz), 37.16 (s), 36.84 – 35.63 (m), 35.83 – 35.63 (m), 28.92 (d, J = 7.8 Hz), 28.44 (d, J = 8.1 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 48.03 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{37}H_{44}FeP$ 575.2525; Found: 574.8700.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-4-methoxyl-(8a*S*)-8-(dicyclohexy-lphosphine)-1,8-dihydrocyclopent [*a*]inden-1-yl] iron (**3f**)

Yellow oil, (61% yield). Rf (petroleum ether) = 0.31. $[\alpha]_D^{20}$ = +506 (c = 0.001, *n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, J = 8.2 Hz, 1H), 6.97 (s, 1H), 6.70 (d, J = 8.1 Hz, 1H), 4.53 (s, 1H), 4.42 (s, 1H), 4.23 (d, J = 4.2 Hz, 1H), 4.16 (d, J = 1.6 Hz, 1H), 3.86 (d, J = 1.1 Hz, 3H), 3.83 (d, J = 1.3 Hz, 5H), 2.06 (d, J = 6.2 Hz, 1H), 1.93 (d, J = 7.4 Hz, 1H), 1.76 (t, J = 31.7 Hz, 10H), 1.32 – 1.24 (m, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.80 (s), 142.67 (d, J = 2.4 Hz), 141.59 (d, J = 7.3 Hz), 125.28 (d, J

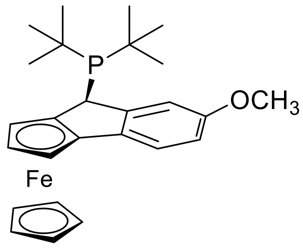
= 7.6 Hz), 109.97 (s), 106.01 (s), 96.29 (d, J = 2.5 Hz), 91.41 (s), 70.27 (s), 69.50 (s), 63.02 (d, J = 1.2 Hz), 58.84 (s), 55.41 (s), 39.61 (s), 39.40 (s), 31.87 (dd, J = 16.4, 4.2 Hz), 31.34 (dd, J = 34.2, 19.2 Hz), 30.22 (d, J = 8.2 Hz), 29.69 (d, J = 7.8 Hz), 27.63 – 26.88 (m), 26.88 – 26.81 (m), 26.54 (s), 26.39 (d, J = 34.8 Hz), 22.61 (d, J = 3.7 Hz), 14.08 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 13.48 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{30}H_{37}FeOP$ 500.1931; Found:500.1959.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-4-methoxyl-(8aS)-8-(ditertbutyl-phosphine) -1,8-dihydrocyclopent [*a*]inden-1-yl] iron **(3g)**

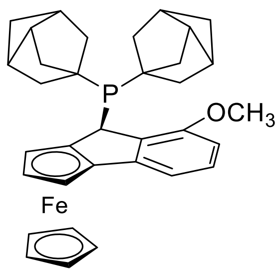
Yellow oil, (68% yield). Rf (petroleum ether) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 8.3 Hz, 1H), 6.95 (d, J = 2.5 Hz, 1H), 6.72 (dd, J = 8.4, 2.5 Hz, 1H), 4.65 (d, J = 2.2 Hz, 1H), 4.59 (d, J = 2.1 Hz, 1H), 4.26 (s, 1H), 4.17 (t, J = 2.3 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 5H), 1.47 (d, J = 11.1 Hz, 9H), 0.77 (d, J = 11.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.63 (d, J = 2.1 Hz), 143.94 (d, J = 15.6 Hz), 141.74 (d, J = 4.0 Hz), 126.28 (d, J = 13.4 Hz), 110.00 (s), 105.48 (s), 96.67 (d, J = 6.1 Hz), 92.48 (s), 70.51 (s), 69.05 (s), 65.90 (s), 58.97 (s), 55.38 (s), 41.27 (s), 40.99 (s), 33.81 (s), 33.59 (s), 32.03 (s), 31.84 (s), 31.00 (d, J = 13.3 Hz), 30.78 (s), 30.18 – 30.08 (m), 29.84 (t, J = 19.6 Hz), 27.81 (d, J = 16.9 Hz), 22.66 (d, J = 13.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 49.55 (s). HRMS (ESI-TOF) m/z: $[M-H]^+$ calcd for $C_{26}H_{33}FeOP$ 447.1534;

Found:447.1739.



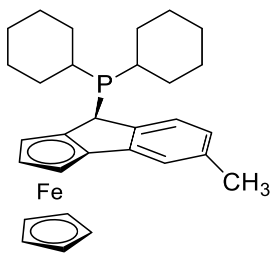
(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-5-methoxyl-(8aS)-8-(ditertbutyl-phosphine)-1,8-dihydrocyclopent [*a*]inden-1-yl] iron **(3h)**

Yellow oil, (69% yield). Rf (petroleum ether / ethyl acetate = 20/1, v/v) = 0.5.$[\alpha]_D^{20}$ = +194 (c = 0.001, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, J = 8.2 Hz, 1H), 7.22 (s, 1H), 6.75 (dd, J = 8.2, 2.4 Hz, 1H), 4.61 (d, J = 2.2 Hz, 1H), 4.54 (d, J = 1.9 Hz, 1H), 4.27 (s, 1H), 4.12 (t, J = 2.3 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 5H), 1.48 (d, J = 11.1 Hz, 9H), 0.78 (d, J = 11.4 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.20 (d, J = 15.4 Hz), 137.37 (d, J = 3.9 Hz), 134.22 (s), 126.83 (dd, J = 10.3, 7.8 Hz), 119.17 (s), 95.40 (d, J = 6.2 Hz), 93.05 (s), 70.44 (s), 70.04 (s), 68.74 (s), 65.66 (s), 58.77 (s), 41.94 (s), 41.66 (s), 33.88 (s), 33.66 (s), 32.19 – 32.08 (m), 31.96 (d, J = 23.2 Hz), 31.00 (d, J = 13.4 Hz), 29.89 (d, J = 13.4 Hz), 27.81 (d, J = 16.8 Hz), 27.36 (d, J = 15.0 Hz), 21.51 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 51.27 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{33}FeOP$ 449.1691; Found: 449.1694.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-6-methoxyl-(8aS)-8-(di(1-adama-ntyl)phosphi-ne)-1,8-dihydrocyclopent [*a*]inden-1-yl] iron (**3i**)

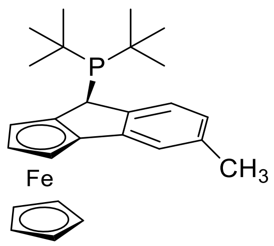
Yellow solid, (69% yield). m.p. = 60 ℃. Rf (petroleum ether) = 0.22. ^{31}P NMR (202 MHz, C_6D_6) δ 41.41 (s). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 4.67 (d, *J* = 2.2 Hz, 1H), 4.60 (d, *J* = 2.4 Hz, 1H), 4.32 (s, 1H), 4.16 (s, 1H), 3.92 (s, 3H), 3.78 (s, 5H), 2.28 (q, *J* = 13.1 Hz, 6H), 2.17 – 2.12 (m, 3H), 1.93 – 1.83 (m, 7H), 1.70 (d, *J* = 12.7 Hz, 4H), 1.62 – 1.57 (m, 3H), 1.52 (d, *J* = 12.6 Hz, 3H), 1.37 (d, *J* = 11.2 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 155.8, 142.4, 139.5, 139.4, 127.44, 113.0, 108.9, 95.6, 95.6, 93.0, 70.4, 68.8, 66.0, 59.2, 56.0, 42.1, 42.0, 40.1, 40.0, 38.9, 38.6, 38.5, 38.2, 37.3, 37.2, 37.1, 36.8, 29.0, 28.9, 28.5, 28.5, 26.9..



(R_p,S)-(η5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-4-methyl-(8aS)-8-(dicyclohexyl-phosphine)-1,8-dihydrocyclopent[a] inden-1-yl]-iron (**3j**)

Yellow oil, (69% yield). Rf (petroleum ether) = 0.4. $[\alpha]_D^{20}$ = +638 (c = 0.001, *n*-hexane).

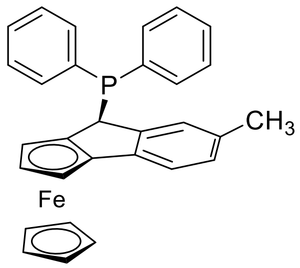
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.7 Hz, 1H), 7.23 (s, 1H), 6.96 (dd, *J* = 7.7, 0.7 Hz, 1H), 4.52 (d, *J* = 2.4 Hz, 1H), 4.42 (d, *J* = 2.2 Hz, 1H), 4.25 (d, *J* = 3.9 Hz, 1H), 4.15 (t, *J* = 2.3 Hz, 1H), 3.82 (s, 5H), 2.40 (s, 3H), 2.12 – 1.70 (m, 8H), 1.53 – 1.36 (m, 6H), 1.29 (dd, *J* = 19.5, 6.2 Hz, 6H), 1.14 – 1.07 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.66 (d, *J* = 7.5 Hz), 141.25 (d, *J* = 3.1 Hz), 135.73 (d, *J* = 1.6 Hz), 125.54 (s), 124.65 (d, *J* = 7.7 Hz), 120.70 (s), 95.64 (d, *J* = 2.6 Hz), 91.82 (s), 70.25 (s), 69.40 (s), 62.89 (s), 58.78 (s), 40.08 (s), 39.87 (s), 32.19 – 31.76 (m), 31.32 (dd, *J* = 17.3, 8.9 Hz), 30.25 (d, *J* = 7.8 Hz), 29.68 (d, *J* = 7.7 Hz), 27.38 (dd, *J* = 9.2, 5.3 Hz), 27.05 (d, *J* = 12.0 Hz), 26.58 (s), 26.30 (s), 21.53 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 13.67 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{30}H_{37}FeP$ 484.1994; Found: 484.1982.



(R_p,S)-(η5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-4-methyl-(8aS)-8-(ditertbutylphosphine)-1,8-dihydrocyclopent[a] inden-1-yl]-iron (**3k**)

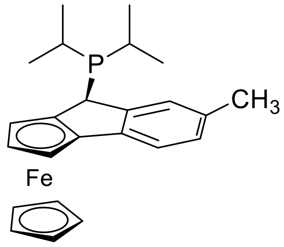
Yellow oil, (79% yield). Rf (petroleum ether) = 0.55. $[\alpha]_D^{25}$ = +324(c = 0.002, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.7 Hz, 1H), 7.22 (s, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 4.65 (d, *J* = 2.2 Hz, 1H), 4.59 (d, *J* = 2.2 Hz, 1H), 4.28 (s, 1H), 4.17 (t, *J* = 2.3 Hz, 1H), 3.83 (s, 5H), 2.41 (s, 3H), 1.50 (d, *J* = 11.2 Hz, 9H), 0.79 (d, *J* = 11.4 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.07 (d, *J* = 15.4 Hz), 140.43 (d, *J* = 4.0 Hz), 135.57 (d, *J* = 1.9 Hz), 125.81 – 125.46 (m), 120.35 (s), 96.10 (d, *J* = 6.0 Hz), 92.92 (s), 70.53

(s), 68.98 (s), 65.80 (s), 58.94 (s), 41.78 (s), 41.49 (s), 33.92 (s), 33.69 (s), 32.11 (s), 31.92 (s), 31.08 (d, *J* = 13.5 Hz), 30.01 (d, *J* = 13.5 Hz), 27.90 (d, *J* = 17.1 Hz), 27.45 (d, *J* = 14.9 Hz), 26.74 (s), 21.52 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 50.13 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{26}H_{33}FeP$ 432.1664; Found:432.1642.



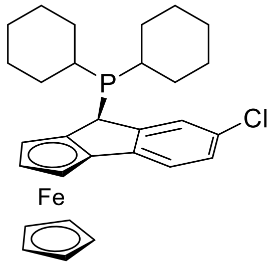
(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-5-methyl-(8a*S*)-8-(diphenyl-phosphine)-1,8-dihydrocyclopent [*a*]inden-1-yl] iron **(3l)**

Yellow solid, (72% yield). mp. 62 ^{o}C. Rf (petroleum ether / ethyl acetate = 20/1, v/v) = 0.437. $[\alpha]_D^{20}$ = +740 (c = 0.001, CH_2Cl_2, 98% de). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.39 (s, 3H), 7.30 (t, *J* = 7.5 Hz, 3H), 7.19 (dd, *J* = 16.0, 7.5 Hz, 3H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.62 (s, 1H), 4.79 (s, 1H), 4.39 (s, 1H), 4.12 (s, 1H), 3.97 (s, 1H), 3.84 (s, 5H), 2.21 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.43 (s), 138.66 (s), 133.86 (d, *J* = 19.7 Hz), 133.29 (d, *J* = 18.0 Hz), 128.90 (s), 128.68 (s), 128.17 (s), 127.75 (s), 127.44 (s), 126.34 (s), 119.65 (s), 93.68 (s), 91.79 (s), 69.69 (d, *J* = 107.4 Hz), 68.36 – 67.12 (m), 63.01 (s), 58.82 (s), 43.88 (d, *J* = 20.3 Hz), 21.46 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 1.72 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{30}H_{25}FeP$ 473.1116; Found: 473.1119.



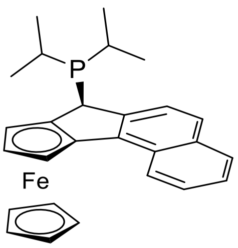
(R_p,S)-(η5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-5-methyl-(8aS)-8-(diisopropylph-osphine)-1,8-dihydrocyclopent[a]inden-1-yl]-iron **(3m)**

Yellow oil, (72% yield). Rf (petroleum ether / ethyl acetate = 20/1, v/v) = 0.4. $[\alpha]_D^{20}$ = +443 (c = 0.001, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 4.52 (d, *J* = 2.2 Hz, 1H), 4.46 (d, *J* = 2.2 Hz, 1H), 4.25 (d, *J* = 3.5 Hz, 1H), 4.15 (t, *J* = 2.3 Hz, 1H), 3.82 (s, 5H), 2.36 (s, 3H), 1.43 (s, 1H), 1.36 (dd, *J* = 10.9, 7.0 Hz, 3H), 1.15 (dd, *J* = 15.3, 6.9 Hz, 4H), 0.64 (dd, *J* = 10.9, 7.1 Hz, 3H), 0.52 (dd, *J* = 14.5, 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.33 (s), 138.36 (s), 134.86 (s), 128.25 (s), 127.60 (s), 119.87 (s), 92.22 (s), 89.65 (s), 70.43 (s), 69.87 (s), 63.46 (s), 59.46 (s), 45.02 (s), 44.60 (s), 25.51 (s), 25.02 (s), 24.11 (s), 23.62 (s), 21.53 (s), 16.54 (d, *J* = 2.6 Hz), 16.33 (dd, *J* = 4.5, 3.2 Hz), 15.67 (d, *J* = 3.5 Hz). ^{31}P NMR (202 MHz, C_6D_6) δ 22.30 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{24}H_{29}FeOP$ 404.1351; Found: 404.1411.



(*R_p*,*S*)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-5-chloro-8-(dicyclohexylphosphi-ne)-1,8-dicyclohexylphosphine[*a*]inden-1-yl] iron (**3n**)

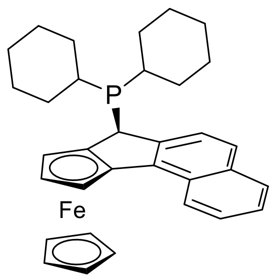
Yellow oil, (74% yield). Rf (petroleum ether / ethyl acetate = 20/1, v/v) = 0.5.$[\alpha]_D^{20}$ = +553 (c = 0.001, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.17 (dd, *J* = 8.0, 1.7 Hz, 1H), 4.54 (d, *J* = 2.2 Hz, 1H), 4.44 (d, *J* = 1.9 Hz, 1H), 4.25 (s, 1H), 4.19 (t, *J* = 2.3 Hz, 1H), 3.83 (s, 5H), 2.07 (d, *J* = 9.5 Hz, 1H), 1.95 (d, *J* = 9.6 Hz, 1H), 1.89 – 1.68 (m, 5H), 1.43 (s, 5H), 1.29 (dd, *J* = 14.0, 10.3 Hz, 5H), 0.85 (ddd, *J* = 38.4, 13.6, 8.7 Hz, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.70 (s), 140.02 (s), 130.32 (s), 126.53 (s), 125.44 (s), 120.46 (d, *J* = 2.8 Hz), 95.24 (s), 90.47 (d, *J* = 2.1 Hz), 70.35 (d, *J* = 2.9 Hz), 69.87 (d, *J* = 3.1 Hz), 63.15 (d, *J* = 5.1 Hz), 59.06 (d, *J* = 3.1 Hz), 40.40 (d, *J* = 3.5 Hz), 29.58 (d, *J* = 11.2 Hz), 27.26 (s), 26.86 – 26.78 (m), 26.51 (d, *J* = 3.5 Hz), 26.21 (d, *J* = 3.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.04 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{34}ClFeP$ 505.1509; Found: 505.1507.



(R$_p$,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,10a-η)-(10a*S*)-10-(diisopropylphosphine)-1,10-dihydro-10-oxopenthaleno [1,2-b] naphthalen-1-yl] iron **(3o)**

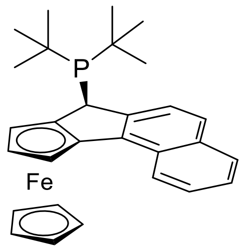
Yellow oil, (74% yield). Rf (petroleum ether) = 0.28. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 1H), 7.93 (t, *J* = 7.0 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.60 (t, *J* = 7.1 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 1H), 4.89 (d, *J* = 1.9 Hz, 1H), 4.63 (d, *J* = 1.6 Hz, 1H), 4.40 (s, 1H), 4.29 (t, *J* = 2.0 Hz, 1H), 3.85 – 3.81 (m, 5H), 1.42 (d, *J* = 3.8 Hz, 1H), 1.40 (d, *J* = 7.7 Hz, 1H), 1.18 (dd, *J* = 15.3, 6.9 Hz, 3H), 0.91 – 0.84 (m, 3H), 0.62 (dd,

J = 10.7, 7.2 Hz, 3H), 0.50 (dd, J = 14.7, 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.45 – 174.29 (m), 173.88 (s), 146.74 (s), 132.86 (s), 128.54 (s), 128.14 (s), 125.69 (s), 125.00 (d, J = 14.8 Hz), 124.61 – 124.24 (m), 124.08 – 123.37 (m), 91.23 (s), 71.86 (s), 70.30 (s), 70.02 (d, J = 13.6 Hz), 63.07 (s), 61.04 (s), 42.23 (d, J = 1.6 Hz), 42.01 (s), 31.89 (s), 31.55 (s), 29.66 (s), 29.33 (s), 26.88 (s), 22.75 – 22.40 (m), 22.05 – 21.74 (m), 21.55 (s), 21.35 (s), 21.29 – 20.83 (m), 20.77 – 20.36 (m), 19.40 (t, J = 7.9 Hz), 16.42 (s), 14.08 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 20.04 (s). HRMS (ESI-TOF) m/z: $[M-H]^+$ calcd for $C_{27}H_{29}FeP$ 439.1272; Found:439.1219.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,10a-η)-(10aS)-10-(dicyclohexylphosphine)-1,10-dihydro-10-oxopenthaleno [1,2-b] naphthalen-1-yl] iron **(3p)**

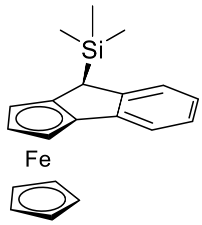
Yellow oil, (77% yield). Rf (petroleum ether / ethyl acetate = 20/1, v/v) = 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 8.3 Hz, 1H), 7.66 (d, J = 8.3 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.49 (t, J = 7.4 Hz, 1H), 4.88 (d, J = 2.1 Hz, 1H), 4.56 (d, J = 2.0 Hz, 1H), 4.37 (s, 1H), 4.28 (t, J = 2.2 Hz, 1H), 3.81 (s, 5H), 2.18 (d, J = 11.4 Hz, 1H), 2.00 – 1.93 (m, 2H), 1.78 (s, 4H), 1.57 – 1.39 (m, 4H), 1.34 (d, J = 7.3 Hz, 4H), 1.06 (dd, J = 23.6, 8.7 Hz, 2H), 0.84 (t, J = 9.7 Hz, 2H), 0.77 – 0.65 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.00 (d, J = 7.3 Hz), 137.50 (d, J = 3.5 Hz), 132.83 (s), 128.54 (s), 128.17 (s), 125.61 (s), 124.93 (d, J = 9.9 Hz), 124.41 (s), 123.67 (d, J = 8.0 Hz), 95.80 (d, J = 2.5 Hz), 91.20 (s), 69.98 (d, J = 17.2 Hz), 63.12 (s), 60.94 (s), 41.40 (s), 41.19 (s), 32.07 – 31.64 (m), 31.31 (dd, J = 17.7, 6.2 Hz), 30.16 (d, J = 6.8 Hz), 29.86 – 29.25 (m), 27.76 – 26.68 (m), 26.52 (s), 26.13 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 11.70 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{33}H_{37}FeP$ 520.1977; Found:520.1859.



(R$_{p,}$S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,10a-η)-(10a*S*)-10-(ditertbutylphosphine) -1,10-dihydro-10-oxopenthaleno [1,2-b] naphthalen-1-yl] iron **(3q)**

Brown solid, (80% yield). mp 172-173 ^{o}C. Rf (petroleum ether / ethyl acetate = 20/1, v/v) = 0.27. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 4.94 (d, J = 2.2 Hz, 1H), 4.79 (d, J = 2.1 Hz, 1H), 4.38 (d, J = 1.3 Hz, 1H), 4.29 (t, J = 2.3 Hz, 1H), 3.80 (s, 5H), 1.54 (d, J = 11.2 Hz, 9H), 0.76 (d, J = 11.5 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.11 (s), 149.14 (s), 136.58 (s), 132.82 (s), 128.56 (s), 128.00 (s), 125.61 (s), 125.14 – 125.04 (m), 124.73 (dd, J = 32.6, 18.8 Hz), 124.31 (s), 96.32 (s), 92.32 (s), 70.32 (s), 69.47 (s), 65.95 (s), 61.16 (s), 43.11 (s), 42.82 (s), 41.35 (s), 36.07 (s), 34.66 (s), 31.58 (s), 31.03 (d, J = 13.5 Hz), 29.89 (d, J = 13.6 Hz), 29.05 (s), 27.66 (s), 26.90 (s), 25.27 (s), 22.62 (d, J = 6.4 Hz), 20.67 (s), 20.43 (s), 19.41 (s), 18.73 (s), 14.29 (s), 14.08 (s), 11.40 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 47.47

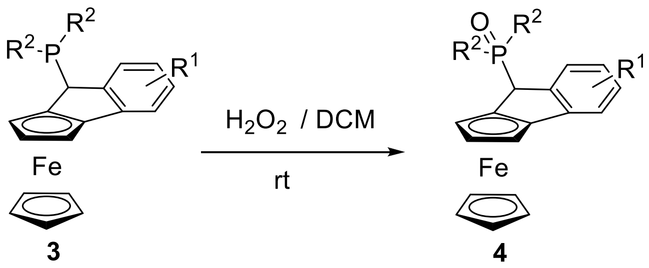
(s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{29}H_{33}FeP$ 468.1664; Found:468.1599.



(R_p, S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-(8aS)-8-(trimethylsilyl)-1,8-dihydrocyclopent[*a*]-inden-1-yl]-iron (**3r**)

Orange solid, (71% yield). mp 87 - 88 °C. Rf (petroleum ether) = 0.8. $[\alpha]_D^{20}$ = +936 (c = 0.001, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 7.4 Hz, 1H), 7.27 (s, 1H), 7.19 (d, J = 7.3 Hz, 1H), 7.14 (d, J = 7.3 Hz, 1H), 4.57 (d, J = 1.9 Hz, 1H), 4.36 (d, J = 1.8 Hz, 1H), 4.13 (t, J = 2.1 Hz, 1H), 3.79 (s, 5H), 3.44 (s, 1H), -0.10 (s, 9H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 149.89 (s), 141.49 (s), 125.13 (s), 124.04 (s), 123.87 (s), 120.11 (s), 95.92 (s), 91.47 (s), 74.96 (s), 74.50 (s), 74.06 (d, J = 18.4 Hz), 69.97 (s), 69.09 (s), 60.93 (s), 58.41 (s), 37.85 (s), -3.07 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{22}FeSi$: 347.0913; Found: 347.0892.

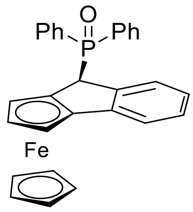
5. General procedure for preparation of substrates (4a-4q)



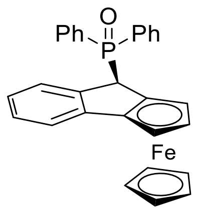
R^1= H, $-CH_3$, $-OCH_3$,
R^2 = Phenyl, Isopropyl, Tert-butyl, Cyclohexyl
Adamantyl

Ferrocenyl phosphine ligands (1.0 equiv.) was dissolved in CH_2Cl_2, then aqueous H_2O_2 solution (excess amount) was added dropwise. After the reaction was complete (monitored by TLC) and the reaction mixture extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Mg_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum / ethyl acetate = 1 / 20, v / v) to get the product **4**.

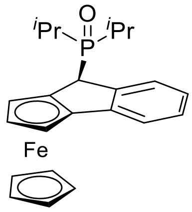
Table S2. Synthesis of novel ferrocenyl phosphine oxide with planar and central chirality [a,b,c]



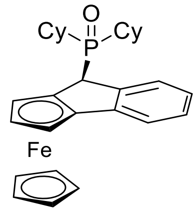
(R_p, S)-**4a**
70%;99%*ee*;99%*de*



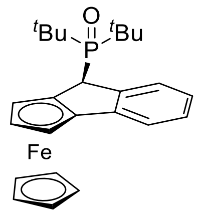
(S_p, R)-**4a**
71%;



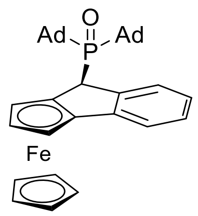
(R_p, S)-**4b**
67%;99%*ee*;90%*de*



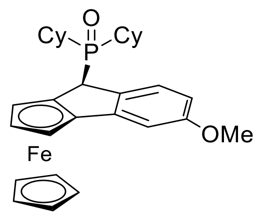
(R_p, S)-**4c**
73%;99%*ee*;98%*de*



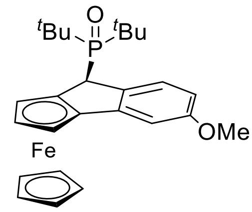
(R_p, S)-**4d**
70%;99%*ee*;98%*de*



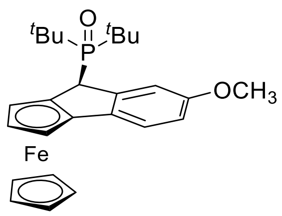
(R_p, S)-**4e**
69% yield



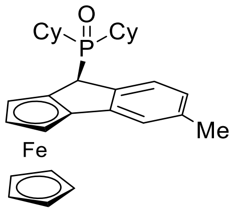
(R_p, S)-**4f**
71%;99%*ee*;97%*de*



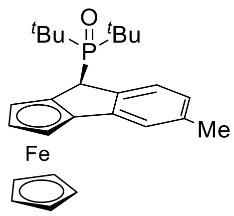
(R_p, S)-**4g**
76%;99%*ee*;95%*de*



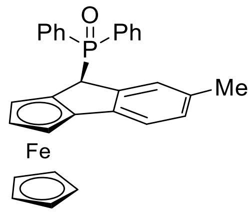
(R_p, S)-**4h**
70%;99%*ee*;92%*de*



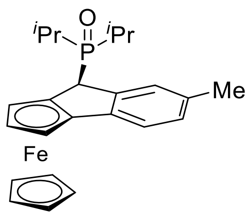
(R_p, S)-**4j**
51%;99%*ee*;89%*de*



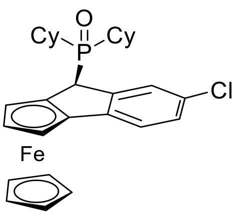
(R_p, S)-**4k**
52%;93%*ee*;99%*de*



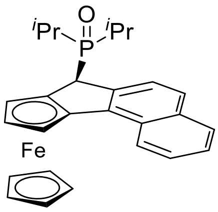
(R_p, S)-**4l**
70%;97.4%*ee*;99.1%*de*



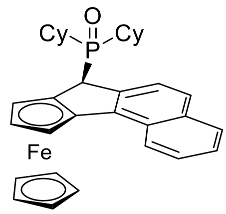
(R_p, S)-**4m**
70%;99%*ee*;96%*de*



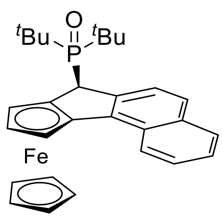
(R_p, S)-**4n**
75%;90%*ee*;95%*de*



(R_p, S)-**4o**
55%;99%*ee*;99%*de*

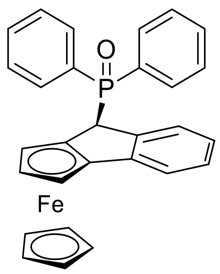


(R_p, S)-**4p**
59%;99%*ee*;91%*de*



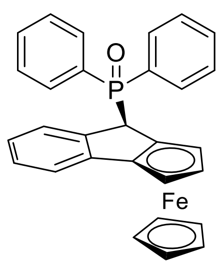
(R_p, S)-**4q**
50%;96%*ee*;99%*de*

[a]3 (1.0 equiv.) in DCM, H_2O_2 (excess), rt, 2 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis.



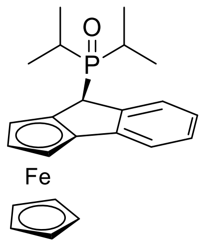
(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-(8aS)-8-(diphenylphosphinyl)-1,8-dihydrocyclopent[*a*] inden-1-yl]-iron (**4a**)

Brown yellow solid, (70% yield; 99% *ee*, 99% *de*). mp 90-91 ^{o}C. Rf (ethyl acetate / petroleum ether = 20/1, v/v) = 0.2. $[\alpha]_D^{20}$ = +804 (c = 0.001, CH_2Cl_2, 93% *de*). ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.61 – 7.53 (m, 3H), 7.45 – 7.37 (m, 3H), 7.35 – 7.28 (m, 3H), 7.22 (dt, *J* = 7.7, 5.2 Hz, 3H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 5.03 (d, *J* = 21.2 Hz, 1H), 4.44 (d, *J* = 2.2 Hz, 1H), 4.06 (t, *J* = 2.2 Hz, 1H), 3.96 (d, *J* = 2.0 Hz, 1H), 3.84 (s, 5H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 142.72 (d, *J* = 4.9 Hz), 142.02 (d, *J* = 5.0 Hz), 132.07 – 131.42 (m), 128.25 (d, *J* = 11.6 Hz), 127.85 – 127.37 (m), 126.32 (s), 124.63 (s), 119.99 (s), 91.82 (s), 89.20 (s), 70.26 (s), 63.92 (s), 59.53 (s), 47.96 (s), 47.45 (s). ^{31}P NMR (202 MHz, CDCl$_3$) δ 31.85 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{23}FeOP$ 475.0909; Found: 475.0905. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm×25 cm), Hexane / IPA = 95 / 5, 1.0 mL / min, λ = 254 nm, t (major) = 14.118 min, t (minor) = 12.393 min.



(S$_p$,*R*)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-(8a*S*)-8-(diphenylphosphinyl)-1,8-dihydrocyclopent[*a*] inden-1-yl]-iron (**4a**)

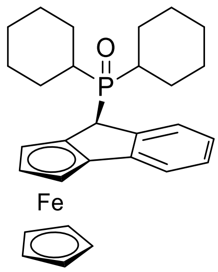
Brown yellow solid, (71% yield). mp 90 - 91 ^{o}C. Rf (ethyl acetate / petroleum ether = 20/1, v/v) = 0.2. ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.61 – 7.53 (m, 3H), 7.45 – 7.37 (m, 3H), 7.35 – 7.28 (m, 3H), 7.22 (dt, *J* = 7.7, 5.2 Hz, 3H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 5.03 (d, *J* = 21.2 Hz, 1H), 4.44 (d, *J* = 2.2 Hz, 1H), 4.06 (t, *J* = 2.2 Hz, 1H), 3.96 (d, *J* = 2.0 Hz, 1H), 3.84 (s, 5H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 142.72 (d, *J* = 4.9 Hz), 142.02 (d, *J* = 5.0 Hz), 132.07 – 131.42 (m), 128.25 (d, *J* = 11.6 Hz), 127.85 – 127.37 (m), 126.32 (s), 124.63 (s), 119.99 (s), 91.82 (s), 89.20 (s), 70.26 (s), 63.92 (s), 59.53 (s), 47.96 (s), 47.45 (s). ^{31}P NMR (202 MHz, CDCl$_3$) δ 31.85 (s). HRMS (ESI-TOF) m/z: [M]$^+$ calcd for $C_{29}H_{23}FeOP$ 474.0861; Found: 474.0863.



(*R$_p$*,*S*)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-(8a*S*)-8-(diisopropylphosphanyl)-1,8-dihydrocyclopent[*a*] inden-1-yl]-iron (**4b**)

Brown yellow solid, (67% yield, > 99% *ee*, 89.6% *de*). mp 95-96 ^{o}C. Rf (ethyl acetate / petroleum ether = 20/1, v/v) = 0.2. $[\alpha]_D^{20}$ = +281 (c = 0.001, CH_2Cl_2, 89.6% *de*). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.72 (s, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 6.9 Hz, 1H), 4.67 (d, *J* = 21.9 Hz, 1H), 4.62 (s, 1H), 4.56 (d, *J* = 6.6 Hz, 1H), 4.22 (s, 1H), 3.85 (s, 1H), 2.22 (d, *J* = 6.8 Hz, 1H), 1.73 (s, 1H), 1.39 (dd, *J* =

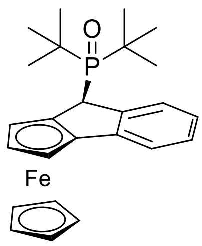
13.7, 5.9 Hz, 1H), 1.10 (dd, J = 14.3, 6.7 Hz, 1H), 0.81 (dd, J = 14.8, 7.0 Hz, 1H), 0.62 – 0.54 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.83 – 143.12 (m), 141.50 – 140.56 (m), 124.99 (s), 120.08 (d, J = 11.8 Hz), 75.13 (s), 65.85 (dd, J = 100.6, 29.6 Hz), 65.38 (s), 43.24 (d, J = 252.9 Hz), 41.26 (s), 34.48 (s), 32.81 (s), 30.61 (s), 29.77 (s), 28.25 (s), 26.69 (s), 25.74 (s), 21.38 (d, J = 114.0 Hz), 19.21 (s), -0.01 (s), -13.34 (s). ^{31}P NMR (243 MHz, $CDCl_3$) δ 55.74 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{27}FeOP$ 407.1222;Found:407.1249.The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 90 / 10, 1.0 mL / min, λ = 254 nm, t (major) = 5.967 min, t (minor) = 9.599 min.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-(8aS)-8-(dicyclohexylphosphinyl)-1,8-dihydrocyclopent[a]inden-1-yl]-iron (**4c**)

Brown yellow solid, (73% yield, > 99% *ee*, 97.8% *de*). mp 81-82 °C .Rf (ethyl acetate / petroleum ether = 20/1, v/v) = 0.2. $[\alpha]_D^{20}$ = +2000 (c = 0.001, CH_2Cl_2, 97.8% *de*). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 7.4 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.19 – 7.13 (m, 1H), 4.66 (d, J = 21.9 Hz, 1H), 4.61 (d, J = 2.3 Hz, 1H), 4.47 (d, J = 2.3 Hz, 1H), 4.22 – 4.18 (m, 1H), 3.83 (s, 5H), 2.07 (dd, J = 13.7, 1.8 Hz, 1H), 1.98 – 1.88 (m, 2H), 1.78 (dd, J = 12.2, 4.4 Hz, 1H), 1.72 (d, J = 12.1 Hz, 1H), 1.67 – 1.60 (m, 2H), 1.57 – 1.52 (m, 2H), 1.45 (dd, J = 14.1, 6.9 Hz, 3H), 1.38 – 1.29

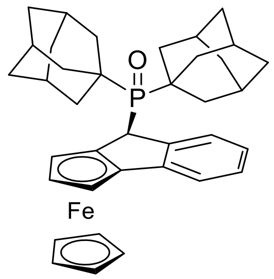
(m, 2H), 1.27 – 1.15 (m, 3H), 0.86 (tdd, J = 28.7, 13.0, 2.9 Hz, 4H), 0.56 (ddd, J = 15.8, 11.7, 3.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.91 (s), 141.53 (s), 127.53 (s), 126.62 (s), 125.05 (s), 120.11 (s), 91.79 (s), 89.53 (s), 70.43 (s), 70.18 (s), 63.66 (s), 59.65 (s), 44.32 (s), 43.97 (s), 35.76 (s), 35.35 (s), 34.26 (s), 33.85 (s), 26.81 (dd, J = 24.7, 12.1 Hz), 26.38 (d, J = 11.9 Hz), 26.14 (d, J = 15.5 Hz), 25.75 (d, J = 5.4 Hz), 25.44 (d, J = 2.4 Hz), 25.12 (s). ^{31}P NMR (243 MHz, $CDCl_3$) δ 51.13 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{29}H_{34}FeOP$ 486.1807; Found: 486.1813. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 98 / 2, 1.0 mL / min, λ = 254 nm, t (major) = 10.979 min, t (minor) = 19.181 min.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-(8aS)-8-(ditertbutylphosphinyl)-1,8-dihydrocyclopent[*a*]inden-1-yl]-iron(**4d**)

Brown yellow solid, (70% yield, > 99% *ee*, 98.4% *de*). mp 88-89 °C Rf (ethyl acetate / petroleum ether = 20/1, v/v) = 0.2. $[\alpha]_D^{20}$ = +1588 (c = 0.001, CH_2Cl_2, 98.4% *de*). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.40 (d, J = 7.2 Hz, 1H), 7.23 (t, J = 7.1 Hz, 1H), 7.14 (t, J = 7.0 Hz, 1H), 4.77 (d, J = 20.6 Hz, 1H), 4.64 (d, J = 14.0 Hz, 2H), 4.19 (s, 1H), 3.79 (s, 5H), 1.54 (s, 9H), 0.72 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.10 (s), 140.50 (s), 128.04 (s), 126.98 (s), 124.52 (s), 119.36 (s), 92.55 (s), 90.21 (s), 70.38 (s), 69.52 (s), 64.74 (s), 59.55 (s), 44.59 (s), 44.29 (s), 37.84 (d, J = 53.7 Hz), 36.45 (s), 36.08 (s), 27.32 (s), 26.78 (s), 22.04 (s), 20.79 (s), 13.96 (s).

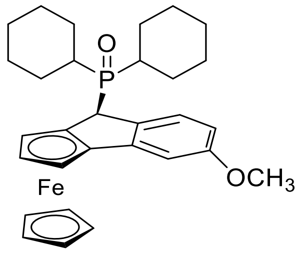
^{31}P NMR (202 MHz, cdcl$_3$) δ 60.27 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{25}H_{31}FeOP$ 434.1457; Found: 434.1474. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm × 25 cm), Hexane / IPA = 98 / 2, 1.0 mL / min, λ = 254 nm, t (major) = 14.581 min, t (minor) = 20.821 min.



(R_p,*S*)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-(8a*S*)-8-(di(1-adamantyl)phosphinyl)-1,8-dihydrocyclopent[*a*]inden-1-yl]-iron (**4e**)

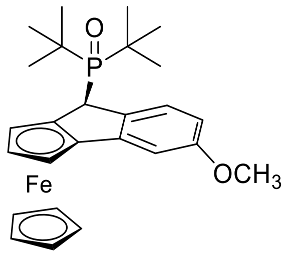
Brown yellow solid, (69% yield). mp 198-199 °C. Rf (ethyl acetate / petroleum ether = 20/1, v/v) = 0.2. $[\alpha]_D^{20}$ = +714 (c = 0.001, CH_2Cl_2). ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.93 (d, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 6.7 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.14 – 7.09 (m, 1H), 4.69 (d, *J* = 19.9 Hz, 1H), 4.66 – 4.58 (m, 2H), 4.17 (d, *J* = 2.2 Hz, 1H), 3.78 (d, *J* = 5.6 Hz, 5H), 2.36 (d, *J* = 20.1 Hz, 6H), 2.16 (s, 3H), 1.86 (s, 6H), 1.69 (s, 3H), 1.59 (d, *J* = 14.0 Hz, 6H), 1.37 (d, *J* = 24.7 Hz, 6H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 145.68 (d, *J* = 4.3 Hz), 140.39 (d, *J* = 4.3 Hz), 128.09 (s), 126.81 (s), 124.65 (s), 119.40 (s), 93.05 (d, *J* = 2.4 Hz), 90.21 (t, *J* = 2.6 Hz), 70.42 (s), 69.37 (s), 65.58 (s), 59.56 (s), 43.12 (s), 42.69 (s), 42.51 (s), 42.15 (s), 40.84 (s), 40.40 (s), 37.23 (s), 36.67 (s), 36.24 (d, *J* = 22.8 Hz), 36.14 – 35.70 (m), 28.00 (d, *J* = 8.7 Hz), 27.40 (d, *J* = 8.9 Hz). ^{31}P NMR (202 MHz, cdcl$_3$) δ 51.58 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{37}H_{43}FeOP$ 590.2396;

Found: 590.2418.



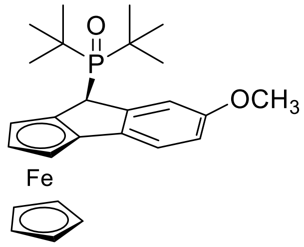
(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-4-methoxyl-(8aS)-8-(dicyclohexy-lphosphinyl)-1,8-dihydrocyclopent [*a*]inden-1-yl] iron **(4f)**

Brown oil, (71% yield, > 99% *ee*, 97% *de*). Rf (ethyl acetate) = 0.28. $[\alpha]_D^{20}$ = +635 (c = 0.0002, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 8.3 Hz, 1H), 6.98 (d, J = 2.1 Hz, 1H), 6.69 (dd, J = 8.4, 2.2 Hz, 1H), 4.58 (d, J = 21.6 Hz, 2H), 4.44 (d, J = 1.5 Hz, 1H), 4.17 (s, 1H), 3.84 (s, 3H), 3.82 (s, 5H), 1.89 (dd, J = 31.1, 12.6 Hz, 3H), 1.78 – 1.50 (m, 8H), 1.44 (s, 3H), 1.29 (d, J = 9.2 Hz, 3H), 0.88 – 0.77 (m, 4H), 0.62 – 0.54 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.57 (s), 142.92 (d, J = 4.5 Hz), 135.62 (d, J = 4.2 Hz), 126.87 (d, J = 2.1 Hz), 110.07 (d, J = 1.3 Hz), 106.30 (s), 91.42 (d, J = 1.7 Hz), 90.34 (s), 70.41 (s), 70.12 (s), 63.73 (s), 59.59 (s), 55.31 (s), 43.33 (s), 42.91 (s), 35.52 (s), 35.03 (s), 34.17 (s), 33.68 (s), 26.60 (ddd, J = 43.0, 30.5, 12.1 Hz), 26.31 (d, J = 11.9 Hz), 26.38 – 25.88 (m), 25.67 (d, J = 2.8 Hz), 25.37 (s), 25.34 – 24.76 (m), 20.93 (s), 14.08 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 51.4 6 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{30}H_{37}FeO_2P$ 517.1953; Found: 517.1979. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm × 25 cm), Hexane / IPA = 80 / 20, 1.0 mL / min, λ = 254 nm, t (major) = 7.668 min, t (minor) = 8.215 min.



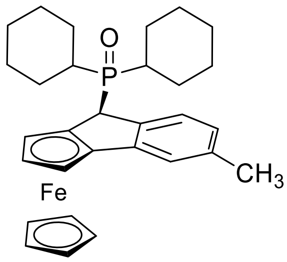
(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-4-methoxyl-(8aS)-8-(ditertbutylphosphinyl)-1,8-dihydrocyclopent [*a*]inden-1-yl] iron **(4g)**

Yellow solid, (76% yield, > 99% *ee*, 94.5% *de*). mp 183-185 ^oC. Rf (petroleum ether / ethyl acetate = 10/1, v/v) = 0.3. $[\alpha]_D^{20}$ = +457 (c = 0.001, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 6.98 (d, J = 2.4 Hz, 1H), 6.70 (dd, J = 8.5, 2.4 Hz, 1H), 4.69 (s, 1H), 4.63 (d, J = 2.0 Hz, 2H), 4.19 (t, J = 2.3 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 5H), 1.55 (d, J = 10.6 Hz, 9H), 0.74 (d, J = 11.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.34 (s), 141.95 (d, J = 4.3 Hz), 137.27 (d, J = 5.0 Hz), 128.55 (s), 109.86 (s), 105.63 (s), 92.45 (s), 91.43 (d, J = 5.0 Hz), 70.52 (s), 69.55 (s), 64.98 (s), 59.57 (s), 55.22 (s), 43.88 (d, J = 47.8 Hz), 37.80 (d, J = 51.8 Hz), 29.89 (d, J = 4.4 Hz), 29.49 (d, J = 4.8 Hz), 27.64 – 27.52 (m), 27.20 (d, J = 61.3 Hz), 26.35 (s), 25.59 (s), 22.67 (s), 22.51 (s), 13.95 (d, J = 4.1 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 59.53 (s). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{26}H_{33}FeO_2P$ 487.1460; Found: 487.1400. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm × 25 cm), Hexane / IPA = 95 / 5, 1.0 mL / min, λ = 254 nm, t (major) = 6.987 min, t (minor) = 9.200 min.



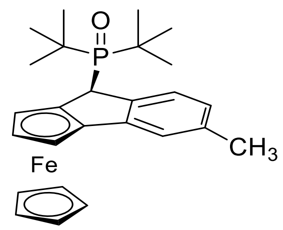
(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-5-methoxyl-(8a*S*)-8-(ditertbutyl-phosphinyl)-1,8-dihydrocyclopent [*a*]inden-1-yl] iron **(4h)**

Yellow oil, (70% yield, > 99% *ee*, 92% *de*). Rf (petroleum ether / ethyl acetate = 10/1, v/v) = 0.2. $[\alpha]_D^{20}$ = +432 (c = 0.001, CH_2Cl_2, 92% *de*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 - 7.67 (m, 1H), 7.33 (d, J = 8.3 Hz, 1H), 6.86 (dd, J = 8.5, 2.2 Hz, 1H), 4.76(s, 0.5H), 4.72(s, 0.5H) 4.61 (m, 2H), 4.17 (t, J = 2.4 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 5H), 1.59 (d, J = 13.5 Hz, 9H), 0.78 (d, J = 13.6 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 146.6, 131.7, 120.1, 114.7, 113.3, 92.6, 89.8, 70.6, 69.2, 64.6, 59.2, 55.5, 41.3, 36.1, 34.7, 33.7, 31.6, 29.1, 27.7, 27.6, 27.1, 25.3, 22.7, 22.6, 20.7, 20.5, 19.5, 18.8. ^{31}P NMR (202 MHz, $CDCl_3$) δ 60.06. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{33}FeO_2P$ 465.1640; Found: 465.1676. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm × 25 cm), Hexane / IPA = 98 / 2, 1.0 mL / min, λ = 254 nm, t (major) = 6.149 min, t (minor) = 7.175 min.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-4-methyl-(8a*S*)-8-(dicyclohexyl-phosphinyl)-1,8-dicyclohexylphosphine[*a*]inden-1-yl] iron (**4j**)

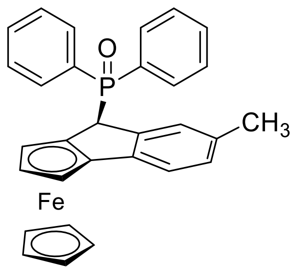
Brown solid, (51% yield, 99.2% *ee*, 88.5% *de*). mp 60-61 ºC. Rf (ethyl acetate) = 0.25. $[\alpha]_D^{25}$ = +29 (c = 0.0018, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 6.8 Hz, 1H), 7.29 (d, J = 11.2 Hz, 1H), 6.99 (d, J = 6.3 Hz, 1H), 4.66 (d, J = 21.8 Hz, 1H), 4.59 (s, 1H), 4.47 (s, 1H), 4.20 (s, 1H), 3.85 (s, 5H), 2.41 (s, 3H), 2.10 (d, J = 25.3 Hz, 2H), 1.94 (s, 3H), 1.85 – 1.75 (m, 3H), 1.72 (d, J = 10.7 Hz, 2H), 1.61 – 1.54 (m, 3H), 1.53 – 1.45 (m, 3H), 0.97 – 0.82 (m, 5H), 0.68 – 0.59 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 129.9, 127.8, 125.0, 120.0, 71.9, 69.5, 69.1, 64.6, 62.7, 58.6, 38.8, 38.6, 38.5, 30.9, 29.5, 28.7, 28.6, 28.3, 26.0, 25.8, 25.7, 25.1, 24.9, 24.7, 24.4, 24.1, 21.7, 20.6, 18.2, 13.2, 13.1, 12.7.^{31}P NMR (202 MHz, $CDCl_3$) δ 52.09. MS (MALDI-TOF) m/z: $[M]^+$ calcd for $C_{30}H_{37}FeOP$ 500.4; Found:500.4, $[M+H]^+$ calcd for $C_{30}H_{37}FeOP$ 501.5; Found:501.5. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm × 25 cm), Hexane / IPA = 90 /10, 1.0 mL / min, λ = 254 nm, t (major) = 9.161 min, t (minor) = 7.711 min.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-4-methyl-(8aS)-8-(ditertbutylphosphinyl)-1,8-dicyclohexylphosphine[*a*]inden-1-yl] iron (**4k**)

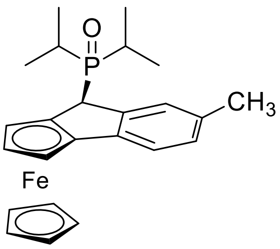
Yellow solid, (52% yield, 93% *ee,* 98.9% *de*). Rf (petroleum ether / ethyl acetate = 10/1, v/v) = 0.2. $[\alpha]_D^{20}$ = +86(c = 0.0005, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.25 (s, 1H), 6.98 (d, J = 7.6 Hz, 1H), 4.70 (d, J = 20.4 Hz, 1H), 4.63 (d, J = 2.1

Hz, 2H), 4.19 (t, J = 2.3 Hz, 1H), 3.82 (s, 5H), 2.40 (s, 3H), 1.56 (d, J = 10.0 Hz, 9H), 0.75 (d, J = 9.2 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.47 (s), 140.58 (s), 136.75 (s), 127.87 (s), 125.69 (s), 120.31 (s), 92.92 (s), 90.94 (s), 70.55 (s), 69.49 (s), 64.91 (d, J = 8.5 Hz), 59.52 (s), 44.42 (dd, J = 46.3, 1.4 Hz), 29.60 (s), 27.54 (s), 27.05 (s), 26.44 (s), 22.60 (s), 21.40 (s), 18.85 (s), 14.04 (s), 13.67 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 59.77 (s). HRMS (ESI-TOF) m/z: $[M-H]^+$ calcd for $C_{26}H_{33}FeOP$ 447.1534; Found: 447.1572. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm × 25 cm), Hexane / IPA = 95 / 5, 1.0 mL / min, λ = 254 nm, t (major) = 5.597 min, t (minor) = 6.638 min.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-5-methyl-(8aS)-8-(diphenylphosp-hinyl) -1,8- dihydrocyclopent[*a*] inden-1-yl]-iron (**4l**)

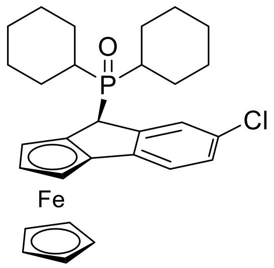
Yellow solid, (70% yield, 97.4% ee, 99.1% de). mp 105 °C. Rf (petroleum ether / ethyl acetate = 5/1, v/v) = 0.115. $[\alpha]_D^{20}$ = +484 (c = 0.001, CH_2Cl_2, 98% de). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.53 (d, J = 7.4 Hz, 1H), 7.44 (d, J = 7.0 Hz, 2H), 7.37 (d, J = 7.0 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.22 (t, J = 6.9 Hz, 2H), 7.14 (s, 2H), 6.95 (d, J = 7.3 Hz, 1H), 4.96 (d, J = 21.4 Hz, 1H), 4.41 (s, 1H), 4.02 (s, 1H), 3.88 (s, 1H), 3.83 (s, 5H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.11 – 131.27 (m), 128.17 (dd, J = 38.0, 31.9 Hz), 127.69 (s), 127.32 (s), 119.70 (s), 92.19 (s), 89.13 (s), 70.28 (s), 69.91 (s), 63.74 (d, J = 1.5 Hz), 59.31 (s), 48.02 (s), 47.51 (s), 21.45 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 31.63 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{30}H_{25}FeOP$ 489.1065; Found: 489.1063. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 90 / 10, 1.0 mL / min, λ = 254 nm, t (major) = 7.345min, t (minor) = 10.900 min.



(R_p,S)-(η5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-5-methyl-(8aS)-8-(diisopropylph-osphinyl)-1,8-dihydrocyclopent[a]inden-1-yl]-iron **(4m)**

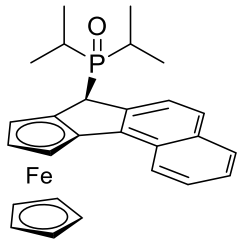
Yellow oil, (70% yield, > 99% *ee*, 96% *de*). Rf (petroleum ether / ethyl acetate = 10/1, v/v) = 0.2. $[\alpha]_D^{20}$ = +291 (c = 0.001, CH_2Cl_2, 96% *de*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 4.63 – 4.56 (m, 2H), 4.50 (d, J = 2.1 Hz, 1H), 4.18 (t, J = 2.3 Hz, 1H), 3.84 (s, 5H), 2.36 (s, 3H), 2.24 – 2.17 (m, 1H), 1.70 (dt, J = 14.0, 7.3 Hz, 1H), 1.41 (dd, J = 14.7, 7.2 Hz, 3H), 1.12 (dd, J = 14.4, 7.1 Hz, 3H), 0.80 (dd, J = 14.9, 7.4 Hz, 3H), 0.58 (dd, J = 15.0, 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.32 (d, J = 4.7 Hz), 138.34 (d, J = 4.5 Hz), 134.87 (d, J = 1.9 Hz), 128.26 (d, J = 1.4 Hz), 127.61 (d, J = 2.1 Hz), 119.87 (s), 92.23 (d, J = 2.2 Hz), 89.66 (d, J = 1.6 Hz), 70.43 (s), 69.87 (s), 63.46 (s), 59.46 (s), 45.02 (s), 44.60 (s), 25.51 (s), 25.02 (s), 24.11 (s), 23.62 (s), 21.53 (s), 16.54 (d, J = 2.6 Hz), 16.33 (dd, J = 4.5, 3.2 Hz), 15.67 (d, J = 3.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 54.74 (s). HRMS

(ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{29}FeOP$ 421.1378; Found: 421.1393. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 90 / 10, 1.0 mL / min, λ = 254 nm, t (major) = 6.833min, t (minor) = 9.868 min.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-5-chloro-8-(dicyclohexylphosphinyl)-1,8-dicyclohexylphosphine[*a*]inden-1-yl] iron (**4n**)

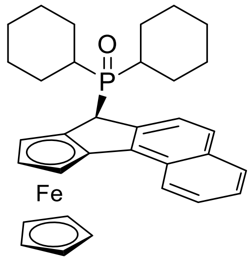
Yellow solid, (75% yield, 90% *ee*, 95% *de*). Rf (petroleum ether / ethyl acetate = 10/1, v/v) = 0.1. $[\alpha]_D^{20}$ = +173 (c = 0.001, CH_2Cl_2, 95% *de*). ^1H NMR (500 MHz, CDCl3) δ 7.72 - 7.71 (m, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.28 (m, 1H), 4.62 - 4.60 (m, 1.5H), 4.56 (s, 1H), 4.47 (d, J = 2.3 Hz, 1H), 4.23 (t, J = 2.4 Hz, 1H), 3.85 (s, 5H), 2.00 - 1.98 (m, 2H), 1.73 - 1.64 (m, 2H), 1.54 - 1.20 (m, J = 101.1 Hz, 12H), 0.96 - 0.71 (m, 5H), 0.60 - 0.49 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.01, 140.27, 130.79, 127.77, 127.05, 120.65, 90.74, 89.76, 70.56, 70.48, 63.79, 59.80, 44.71, 44.30, 36.28, 35.79, 34.43, 33.93, 26.98, 26.88, 26.84, 26.74, 26.69, 26.34, 26.25, 25.81, 25.77, 25.52, 25.14. ^{31}P NMR (202 MHz, $CDCl_3$) δ 49.91. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{34}ClFeOP$ 521.1458; Found: 521.1458. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 98 / 2, 1.0 mL / min, λ = 254 nm, t (major) = 10.113 min, t (minor) = 13.545 min.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,10a-η)-(10a*S*)-10-(diisopropylphosphin-yl)-1,10-dihydro-10-oxopenthaleno [1,2-b] naphthalen9-1-yl] iron **(4o)**

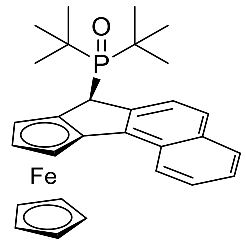
Brown solid, (55% yield, 98.7% *ee*, 98.7% *de*). mp 92-94 ^{o}C. Rf (ethyl acetate) = 0.2. $[\alpha]_D^{25}$ = -78 (c = 0.0005, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.52 (dd, *J* = 9.5, 4.9 Hz, 1H), 4.94 (d, *J* = 2.2 Hz, 1H), 4.76 (s, 1H), 4.67 (d, *J* = 2.0 Hz, 1H), 4.34 – 4.32 (m, 1H), 3.84 (s, 1H), 1.72 – 1.66 (m, 1H), 1.48 (dd, *J* = 14.9, 7.2 Hz, 2H), 1.15 (dd, *J* = 14.6, 7.1 Hz, 3H), 0.93 – 0.89 (m, 1H), 0.80 (dd, *J* = 15.0, 7.4 Hz, 3H), 0.55 (dd, *J* = 15.2, 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.45 – 174.29 (m), 173.88 (s), 146.74 (s), 132.86 (s), 128.54 (s), 128.14 (s), 125.69 (s), 125.00 (d, *J* = 14.8 Hz), 124.61 – 124.24 (m), 124.08 – 123.37 (m), 91.23 (s), 71.86 (s), 70.30 (s), 70.02 (d, *J* = 13.6 Hz), 63.07 (s), 61.04 (s), 42.23 (d, *J* = 1.6 Hz), 42.01 (s), 31.89 (s), 31.55 (s), 29.66 (s), 29.33 (s), 26.88 (s), 22.75 – 22.40 (m), 22.05 – 21.74 (m), 21.55 (s), 21.35 (s), 21.29 – 20.83 (m), 20.77 – 20.36 (m), 19.40 (t, *J* = 7.9 Hz), 16.42 (s), 14.08 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 57.05 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{27}H_{29}FeOP$ 456.3; Found: 456.3, $[M+H]^+$ calcd for $C_{27}H_{29}FeOP$ 457.4; Found: 457.4. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm ×25 cm), Hexane / IPA = 90 / 10, 1.0 mL / min, λ = 254 nm, t (major) = 9,879 min, t (minor) =

11.177 min.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,10a-η)-(10a*S*)-10-(dicyclohexylphosphinyl)-1,10-dihydro-10-oxopenthaleno [1,2-b] naphthalen-1-yl] iron **(4p)**

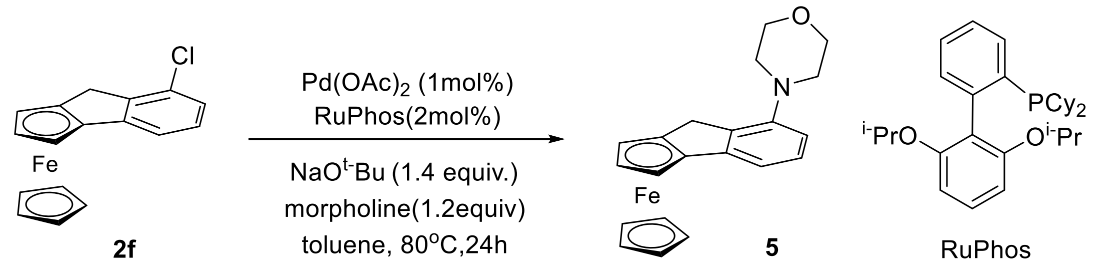
Brown solid, (59% yield, 99.2% *ee*, 91.1% *de*). mp 80-82 ^oC. Rf (ethyl acetate) = 0.2. $[\alpha]_D^{25}$ = +28 (c = 0.0017, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 1H), 7.95 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.54 – 7.50 (m, 1H), 4.94 (d, *J* = 2.2 Hz, 1H), 4.74 (s, 1H), 4.58 (d, *J* = 2.0 Hz, 1H), 4.33 – 4.31 (m, 1H), 3.82 (s, 1H), 2.18 (d, *J* = 13.6 Hz, 1H), 1.99 (d, *J* = 12.1 Hz, 1H), 1.81 (s, 1H), 1.77 – 1.68 (m, 3H), 1.53 (dd, *J* = 39.1, 9.4 Hz, 3H), 1.39 (s, 3H), 1.26 (d, *J* = 7.2 Hz, 2H), 0.83 (d, *J* = 9.8 Hz, 2H), 0.76 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.00 (d, *J* = 7.3 Hz), 137.50 (d, *J* = 3.5 Hz), 132.83 (s), 128.54 (s), 128.17 (s), 125.61 (s), 124.93 (d, *J* = 9.9 Hz), 124.41 (s), 123.67 (d, *J* = 8.0 Hz), 95.80 (d, *J* = 2.5 Hz), 91.20 (s), 69.98 (d, *J* = 17.2 Hz), 63.12 (s), 60.94 (s), 41.40 (s), 41.19 (s), 32.07 – 31.64 (m), 31.31 (dd, *J* = 17.7, 6.2 Hz), 30.16 (d, *J* = 6.8 Hz), 29.86 – 29.25 (m), 27.76 – 26.68 (m), 26.52 (s), 26.13 (s). ^{31}P NMR (202 MHz, $CDCl_3$) δ 51.20. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{33}H_{37}FeOP$ 536.4; Found: 536.3, $[M+H]^+$ calcd for $C_{33}H_{37}FeOP$ 537.5; Found: 537.5. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm × 25 cm), Hexane / IPA = 90 / 10, 1.0 mL / min, λ = 254 nm, t (major) = 15.819 min, t (minor) = 11.244 min.



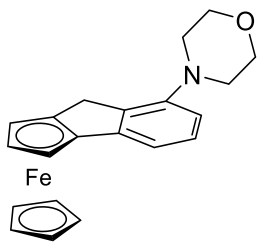
(R_{p},S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,10a-η)-(10aS)-10-(ditertbutylphosphiny-l)-1,10-dihydro-10-oxopenthaleno [1,2-b] naphthalen9-1-yl] iron **(4q)**

Brown solid, (50% yield, 95.5% *ee*, 99.4% *de*). mp 79-80 ^{o}C. Rf (ethyl acetate) = 0.38. $[\alpha]_D^{25}$ = +20 (c = 0.00005, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 5.7 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.50 (dd, *J* = 11.0, 4.0 Hz, 1H), 4.99 (d, *J* = 2.1 Hz, 1H), 4.84 (s, 1H), 4.77 (s, 1H), 4.33 – 4.32 (m, 1H), 3.79 (s, 1H), 1.62 (d, *J* = 11.9 Hz, 8H), 0.74 (d, *J* = 12.4 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.11 (s), 149.14 (s), 136.58 (s), 132.82 (s), 128.56 (s), 128.00 (s), 125.61 (s), 125.14 – 125.04 (m), 124.73 (dd, *J* = 32.6, 18.8 Hz), 124.31 (s), 96.32 (s), 92.32 (s), 70.32 (s), 69.47 (s), 65.95 (s), 61.16 (s), 43.11 (s), 42.82 (s), 41.35 (s), 36.07 (s), 34.66 (s), 31.58 (s), 31.03 (d, *J* = 13.5 Hz), 29.89 (d, *J* = 13.6 Hz), 29.05 (s), 27.66 (s), 26.90 (s), 25.27 (s), 22.62 (d, *J* = 6.4 Hz), 20.67 (s), 20.43 (s), 19.41 (s), 18.73 (s), 14.29 (s), 14.08 (s), 11.40 (s). ^{31}P NMR (202 MHz, C_6D_6) δ 61.98 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{29}H_{33}FeOP$ 484.4; Found: 484.3, $[M+H]^+$ calcd for $C_{29}H_{33}FeOP$ 485.4; Found: 485.4. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm × 25 cm), Hexane / IPA = 95 / 5, 1.0 mL / min, λ = 254 nm, t (major) = 6.066 min, t (minor) = 15.078 min.

6. General procedure for preparation of substrates (5)



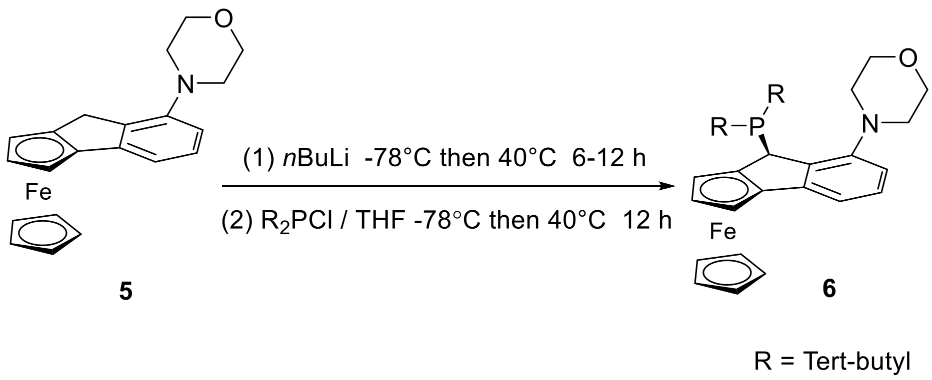
Compound **2f** (2 mmol), Pd(OAc)$_2$ (1% mol), Ruphos (2% mol), NaO^{t-}Bu (1.4 equiv.), morpholine (1.2 equiv.), and 5 mL toluene were mixed in a 25 mL Schlenk-type sealed tube. The mixture was stirred at 80 ^{o}C under argon atmosphere for 24 hours. When the reaction was completed, the solvent was eliminated under vacuum pump and water and dichloromethane was added and the layers were separated. The aqueous phase was extracted three times with dichloromethane. The combined organic phase was dried over anhydrous MgSO$_4$. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum / ethyl acetate = 20 / 1, v / v) to get the product **5**.



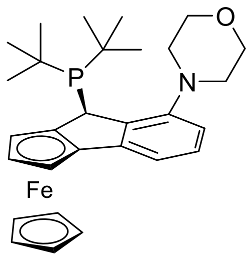
(S_p)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-6-(4-morpholino)-1,8-dihydrocyclo-pent[*a*] inden-1-yl]iron **(5)**

Orange solid, (87% yield). Rf (hexane) = 0.4. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.22 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.0 Hz, 1H), 6.84 (d, J = 7.6 Hz, 1H), 4.52 (d, J = 2.1 Hz, 1H), 4.47 (d, J = 2.0 Hz, 1H), 4.15 (t, J = 2.2 Hz, 1H), 3.90 (t, J = 4.6 Hz, 4H), 3.86 (s, 5H), 3.73 (d, J = 20.1 Hz, 1H), 3.47 (d, J = 20.1 Hz, 1H), 3.12 – 3.05 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.26 (s), 143.39 (s), 139.72 (s), 127.87 (s), 115.55 (s), 114.82 (s), 92.45 (d, J = 16.3 Hz), 70.08 (s), 69.36 (s), 67.45 (s), 62.94 (s), 58.87 (s), 51.67 (s), 31.81 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{22}OFeN$ 360.1045; Found: 360.1049.

7. General procedure for preparation of substrates (6)



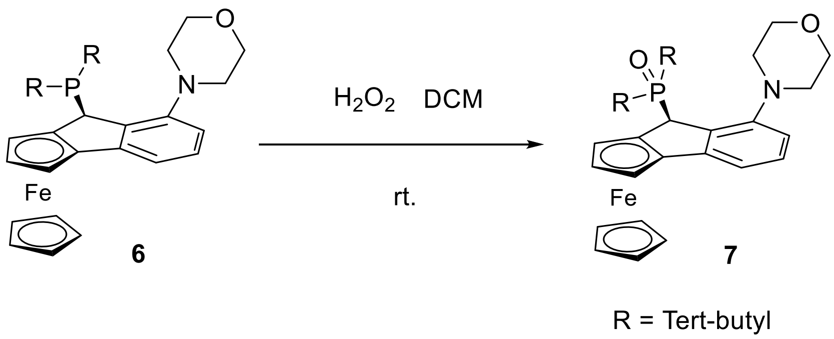
Ferrocenyl indene (1mmol, 1.0 equiv.) was dissolved in THF under argon. The mixture was cooled to -78 ℃ and n-BuLi in hexanes (1.6 M, 1.1 equiv.) was added drop wise. The addition was complete then the mixture was stirred at 40 ℃ for 6-12 h. Cooled to -78 ℃ and R_2PCl (1.1 equiv.) in THF was added drop wise. After the addition was complete, the mixture was stirred at 40 ℃ for 12 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum / DCM = 15 / 2, v / v) to get the product **6**.



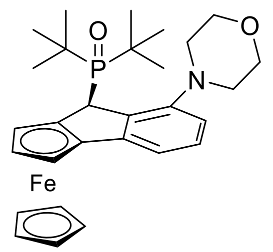
(*R$_p$*,*S*)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-6-(4-morpholino)-(8a*S*)-8-(ditertb-utylphosphine)-1,8-dihydrocyclopent [*a*]inden-1-yl] iron **(6)**

Yellow solid, (70% yield). mp 179 °C. Rf (petroleum ether / ethyl acetate = 20/1, v/v) = 0.4. $[\alpha]_D^{20}$ = +367 (c = 0.001, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.19 (m, 1H), 7.17 (d, J = 6.9 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 4.66 (d, J = 2.0 Hz, 1H), 4.60 (d, J = 2.1 Hz, 1H), 4.43 (s, 1H), 4.16 (t, J = 2.3 Hz, 1H), 3.91 (t, J = 4.6 Hz, 4H), 3.74 (s, 5H), 3.12 – 3.08 (m, 2H), 3.01 – 2.96 (m, 2H), 1.51 (d, J = 10.4 Hz, 9H), 0.66 (d, J = 11.0 Hz, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.88 (d, J = 2.5 Hz), 147.40 (d, J = 11.2 Hz), 142.64 (d, J = 3.9 Hz), 127.47 (s), 119.29 (s), 116.46 (s), 95.02 (d, J = 6.1 Hz), 92.72 (s), 70.43 (s), 69.04 (s), 67.07 (s), 59.16 (s), 53.09 (s), 41.92 (s), 41.63 (s), 33.76 (s), 33.54 (s), 32.81 (s), 32.60 (s), 31.59 (d, J = 13.8 Hz), 29.97 (d, J = 15.9 Hz). ^{31}P NMR (202 MHz, C_6D_6) δ 47.51 (s). HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{29}H_{38}FeNOP$ 503.2035; Found: 503.2024.

8. General procedure for preparation of substrates (7)



Ferrocenyl phosphine ligands (1.0 equiv.) was dissolved in CH_2Cl_2, then aqueous H_2O_2 solution (excess amount) was added dropwise. After the reaction was complete (monitored by TLC) and the reaction mixture extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Mg_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum / ethyl acetate = 1 / 20, v / v) to get the product **7**.



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-6-(4-morpholino)-(8a*S*)-8-(ditertb-u-tylphosphinyl)-1,8-dihydrocyclopent [*a*]inden-1-yl] iron **(7)**

Yellow solid, (76% yield, >99.9% *ee*, >99.9% *de*). mp 186 °C. Rf (ethyl acetate) = 0.3. $[\alpha]_D^{20}$ = +343 (c = 0.001, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, J = 5.7 Hz, 1H), 7.21 (d, J = 7.0 Hz, 1H), 7.17 (d, J = 7.7 Hz, 1H), 4.96 (d, J = 15.6 Hz, 1H), 4.68 (s, 1H), 4.64 (s, 1H), 4.22 (s, 1H), 3.90 (s, 4H), 3.76 (s, 5H), 3.14 (s, 2H), 2.97 (s, 2H), 1.59 (s, 9H), 0.87 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.26 (s), 128.64 (s), 119.79 (s), 116.64 (s), 89.55 (s), 70.51 (s), 69.41 (s), 67.37 (s), 65.93 (s), 60.10 (s), 53.26 (s), 44.07 (s), 43.78 (s), 39.30 (s), 38.95 (s), 37.23 (s), 36.87 (s), 27.73 (s), 27.25 (s). ^{31}P NMR (243 MHz, $CDCl_3$) δ 58.27 (s). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{38}FeNO_2P$ 520.2063; Found: 520.2052. The enantiomeric excess was determined by Daicel Chiralpak OD-H (0.46 cm × 25 cm), Hexane / IPA = 95 / 5, 1.0 mL / min, λ = 254 nm, t (major) = 7.643min, t (minor) = 10.383 min.

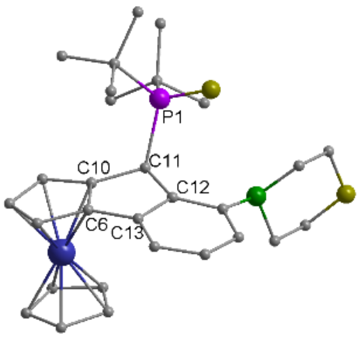


Figure S1. X-ray crystal structure of and (R_p,*S*)-**7**. Selected bond lengths [Å] and bond angles[º] for **7**: Fe1-Cp1 1.665 (av.), Fe1-Cp2 1.646 (av.), C6-C10 1.422(3), C6-C13 1.457(3), C12-C13 1.413(3), C11-C12 1.535(3), C10-C11 1.515(3), C11-P1 1.882(2), C10-C11-C12 100.97(17), C10-C11-P1 117.05(15), C12-C11-P1 112.83(14).

9. ^{1}H, ^{13}C and ^{31}P NMR spectra

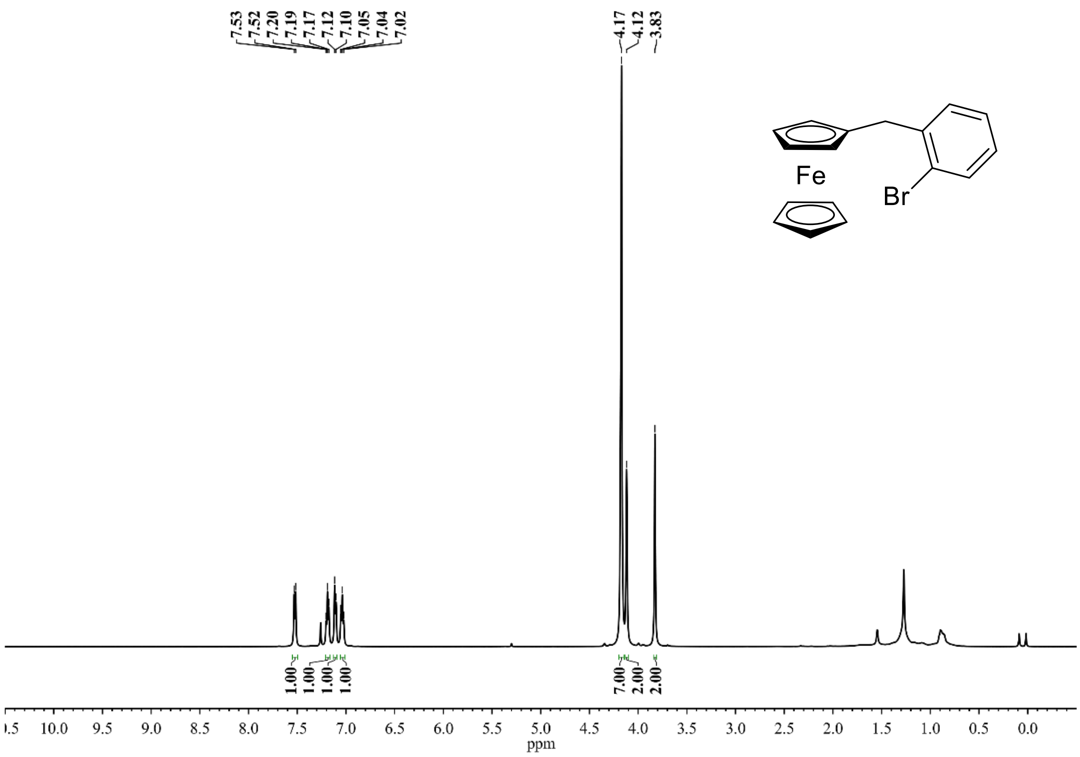


Figure S2. **^{1}H NMR** of **1a** (500 MHz, $CDCl_3$)

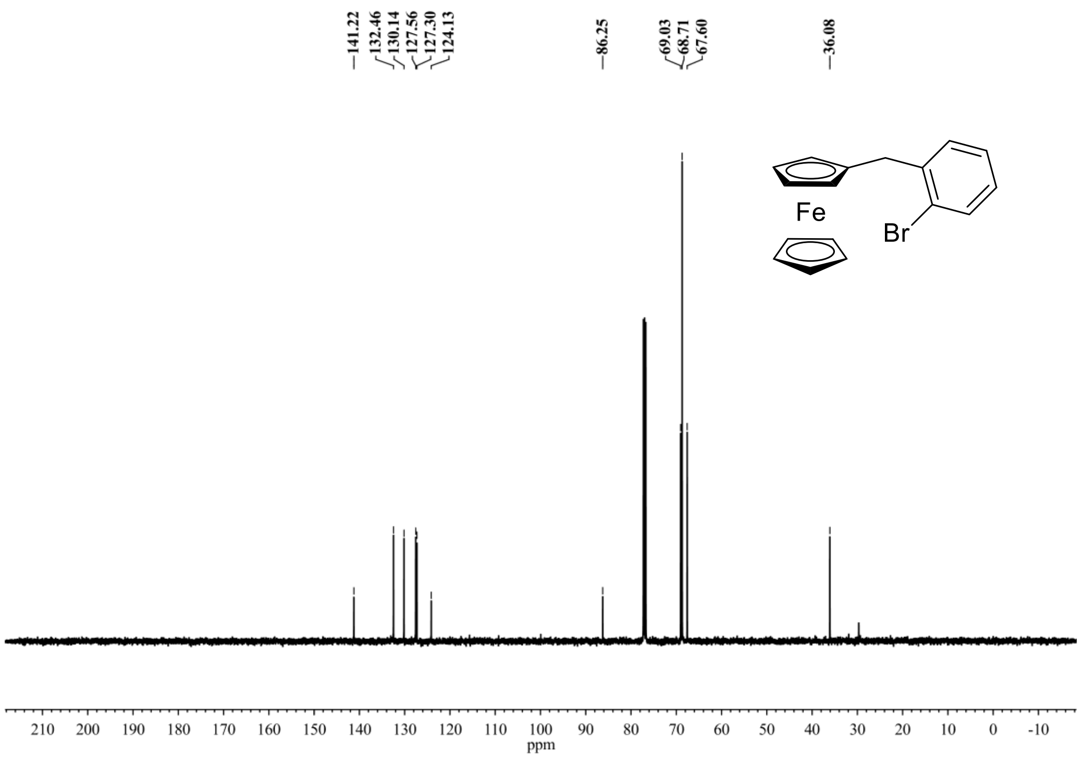


Figure S3. **^{13}C NMR** of **1a** (126 MHz, $CDCl_3$)

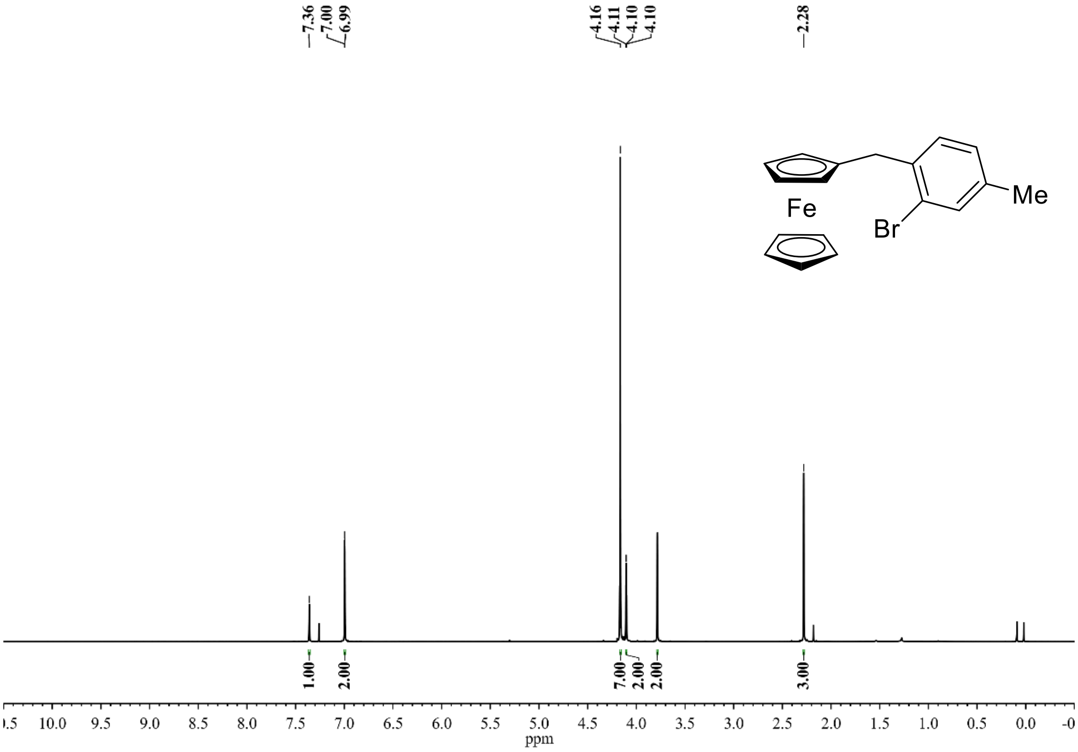


Figure S4. ^{1}**H NMR** of **1b** (500 MHz, $CDCl_3$)

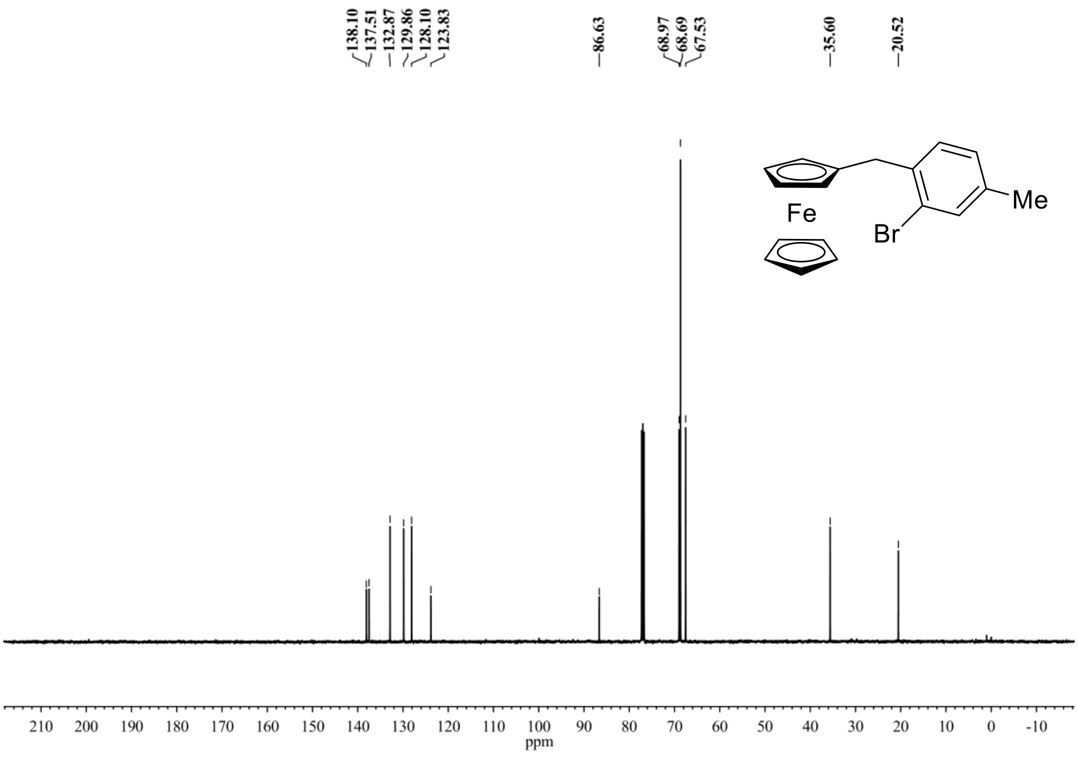


Figure S5. ^{13}**C NMR** of **1b** (126 MHz, $CDCl_3$)

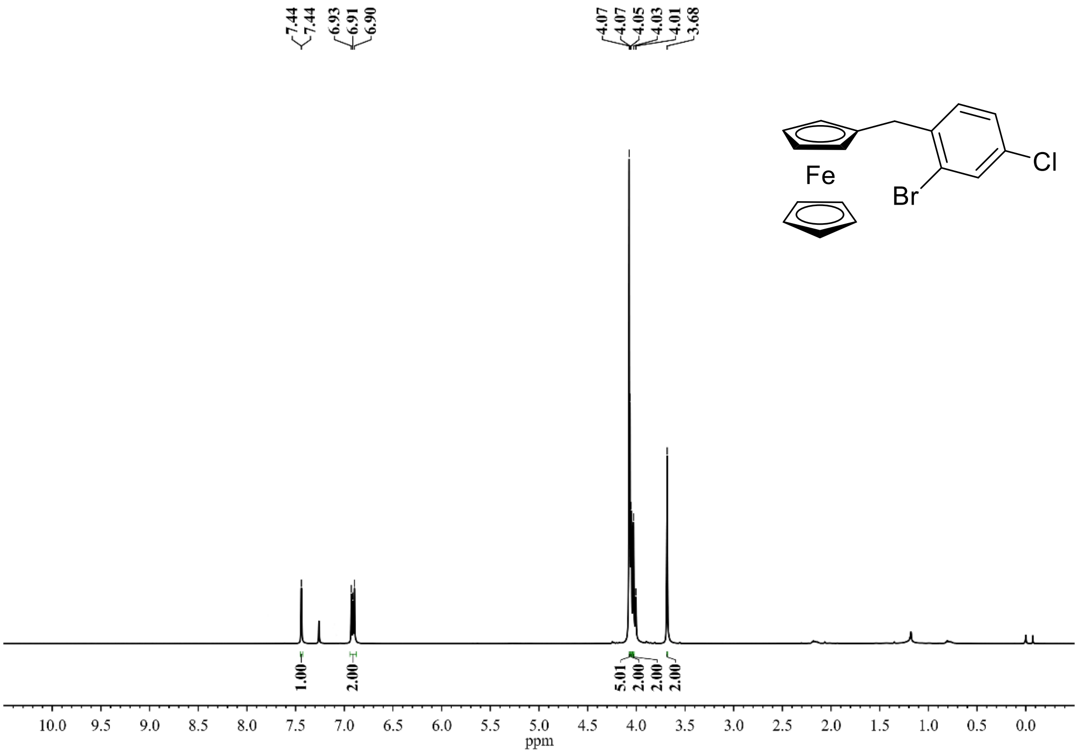


Figure S6. **^{1}H NMR** of **1c** (500 MHz, $CDCl_3$)

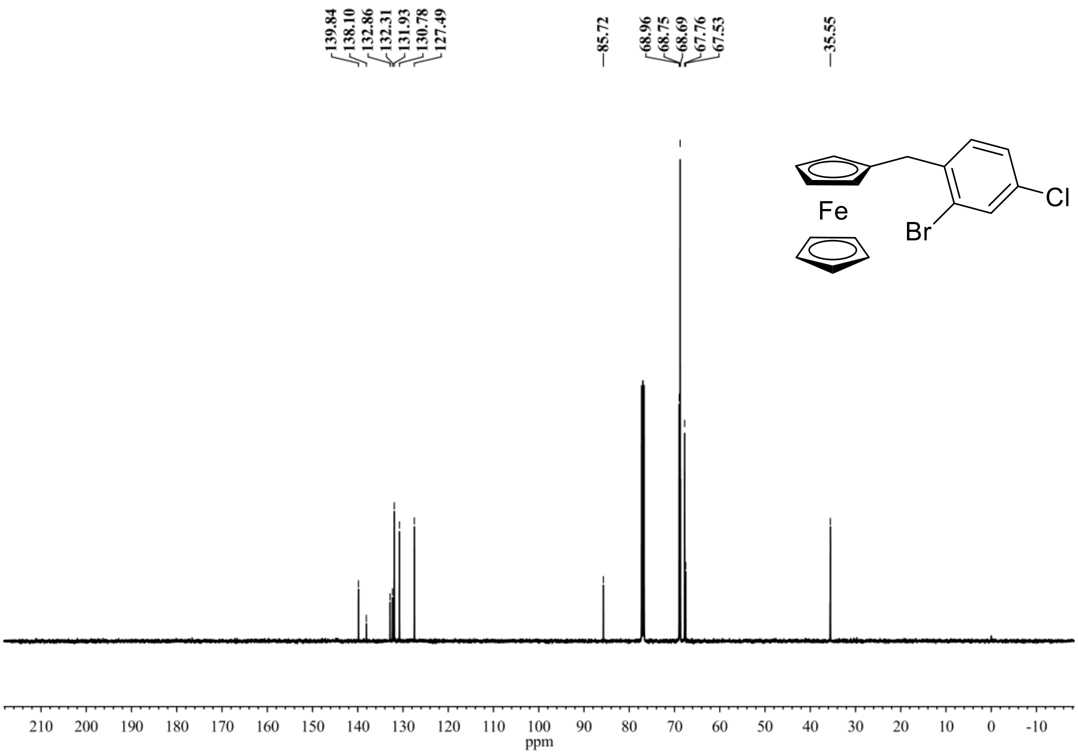


Figure S7. **^{13}C NMR** of **1c** (126 MHz, $CDCl_3$)

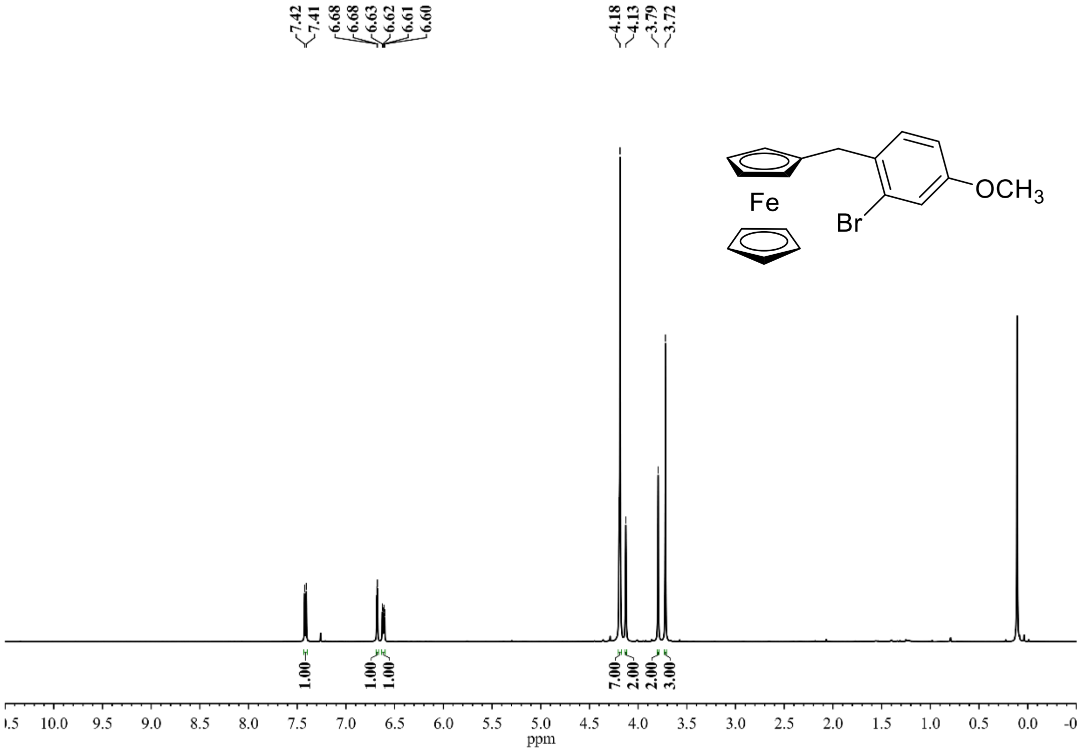


Figure S8. **^{1}H NMR** of **1d** (500 MHz, $CDCl_3$)

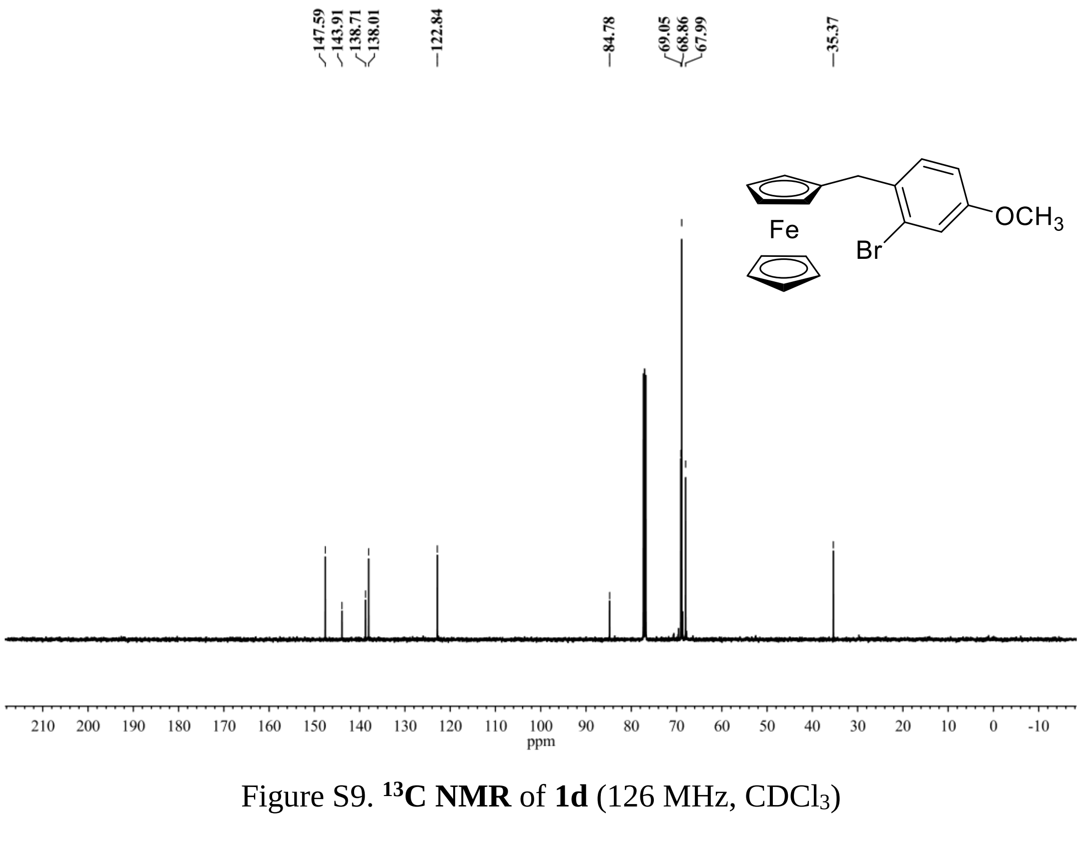


Figure S9. **^{13}C NMR** of **1d** (126 MHz, $CDCl_3$)

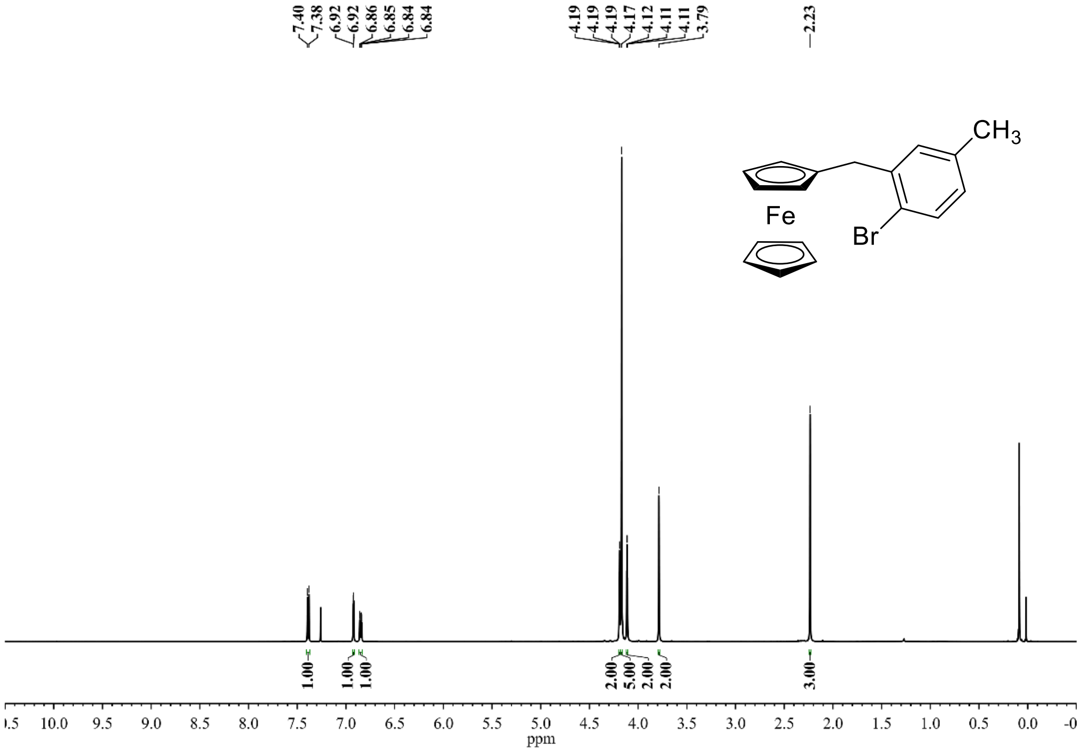


Figure S10. **^{1}H NMR** of **1e** (500 MHz, $CDCl_3$)

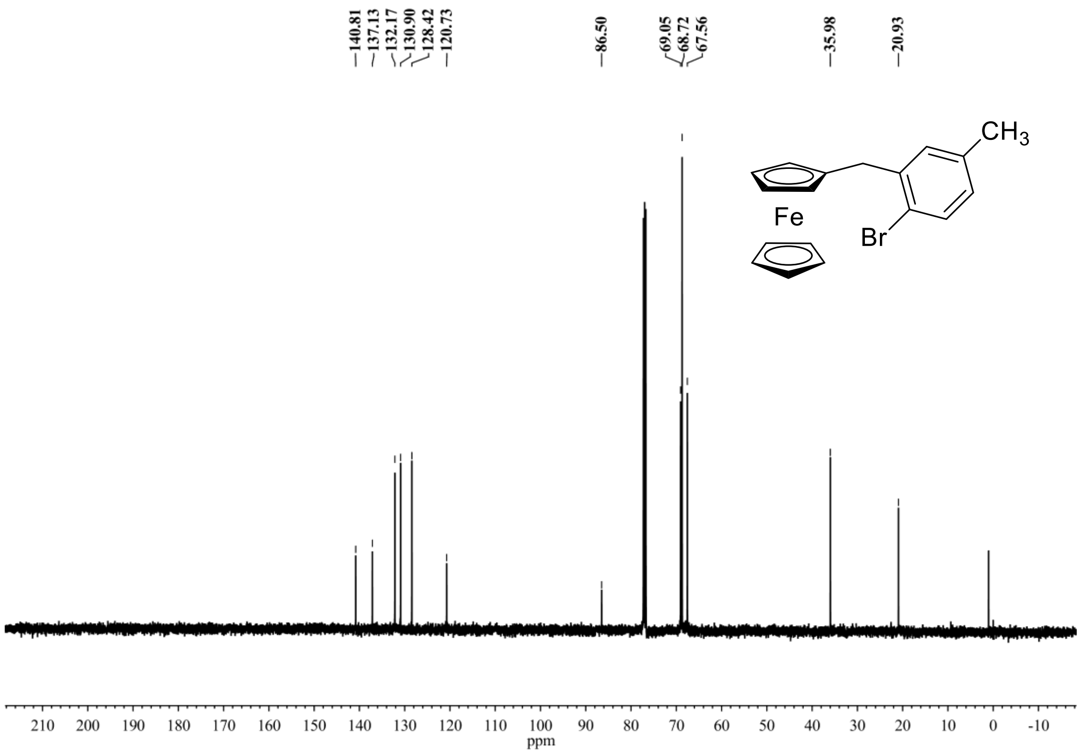


Figure S11. **^{13}C NMR** of **1e** (126 MHz, $CDCl_3$)

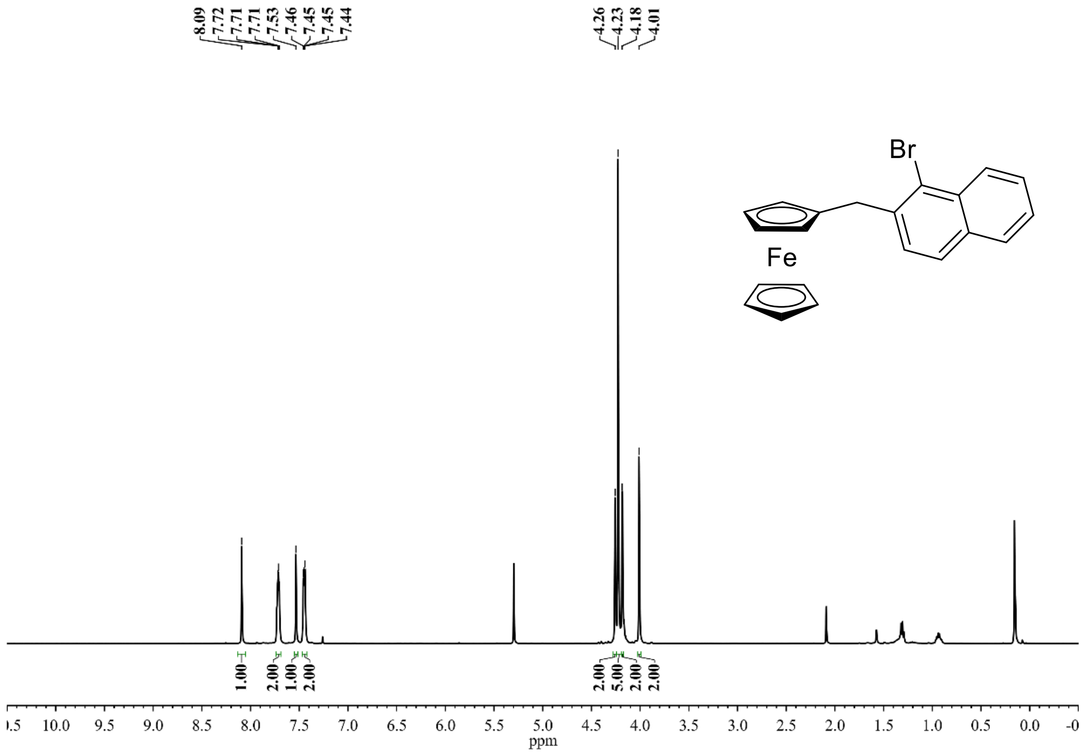


Figure S12. ^{1}**H NMR** of **1f** (500 MHz, $CDCl_3$)

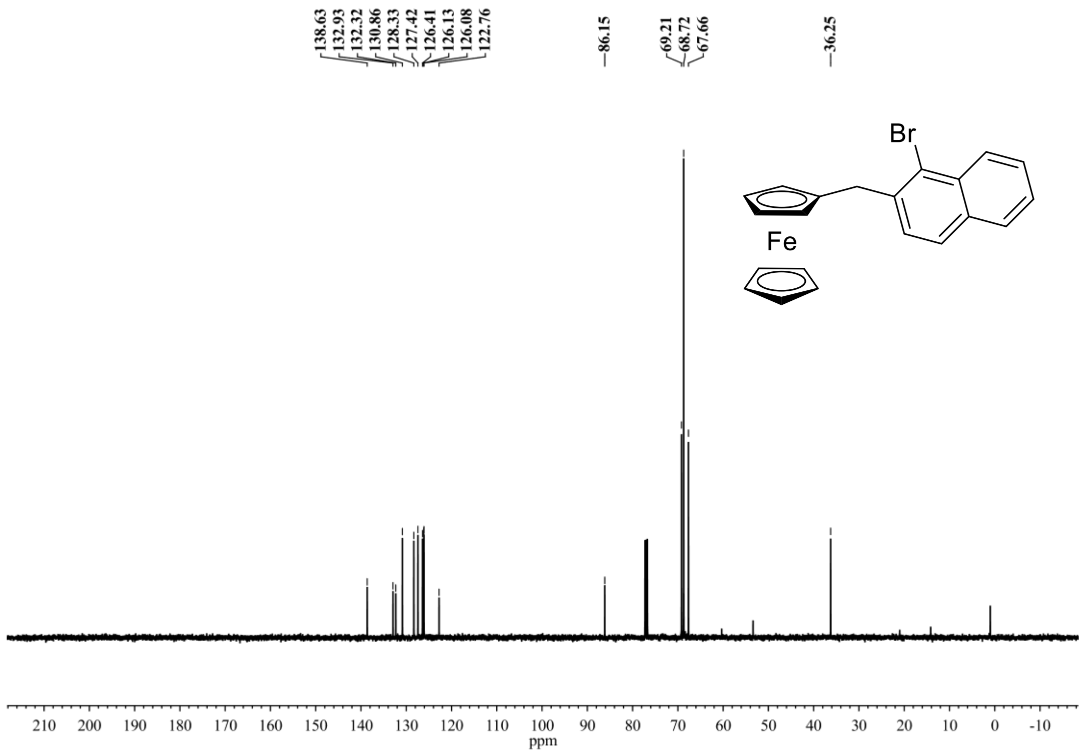


Figure S13. ^{13}**C NMR** of **1f** (126 MHz, $CDCl_3$)

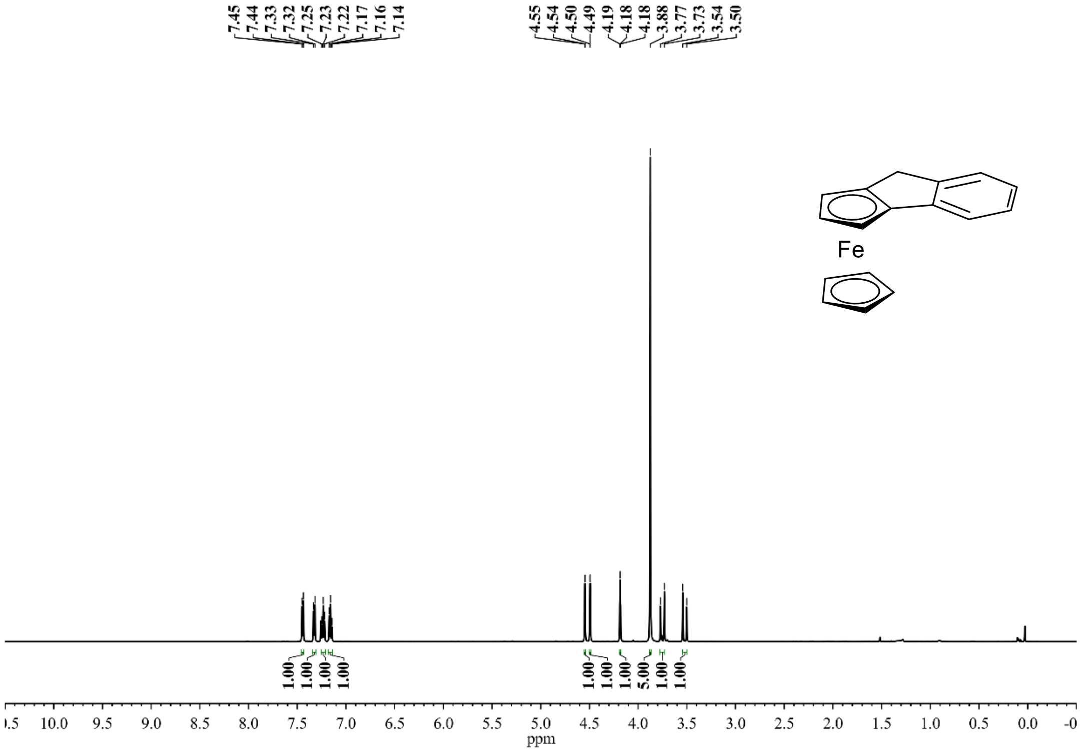


Figure S14. **^{1}H NMR** of **2a** (500 MHz, $CDCl_3$)

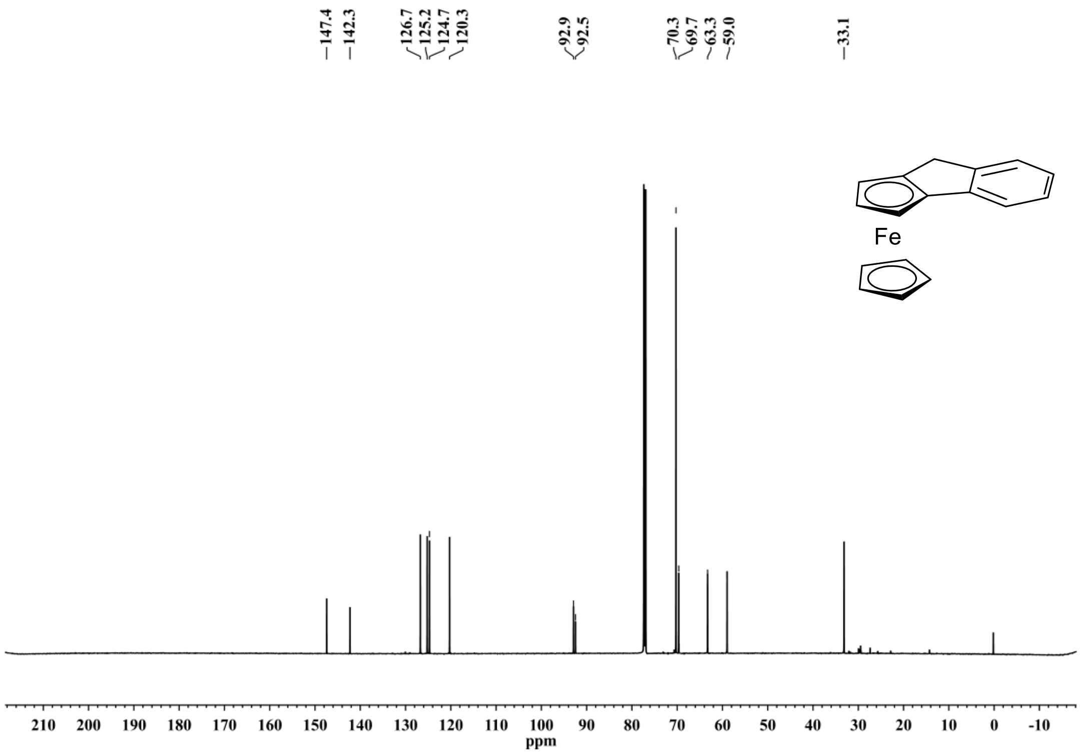


Figure S15. **^{13}C NMR** of **2a** (126 MHz, $CDCl_3$)

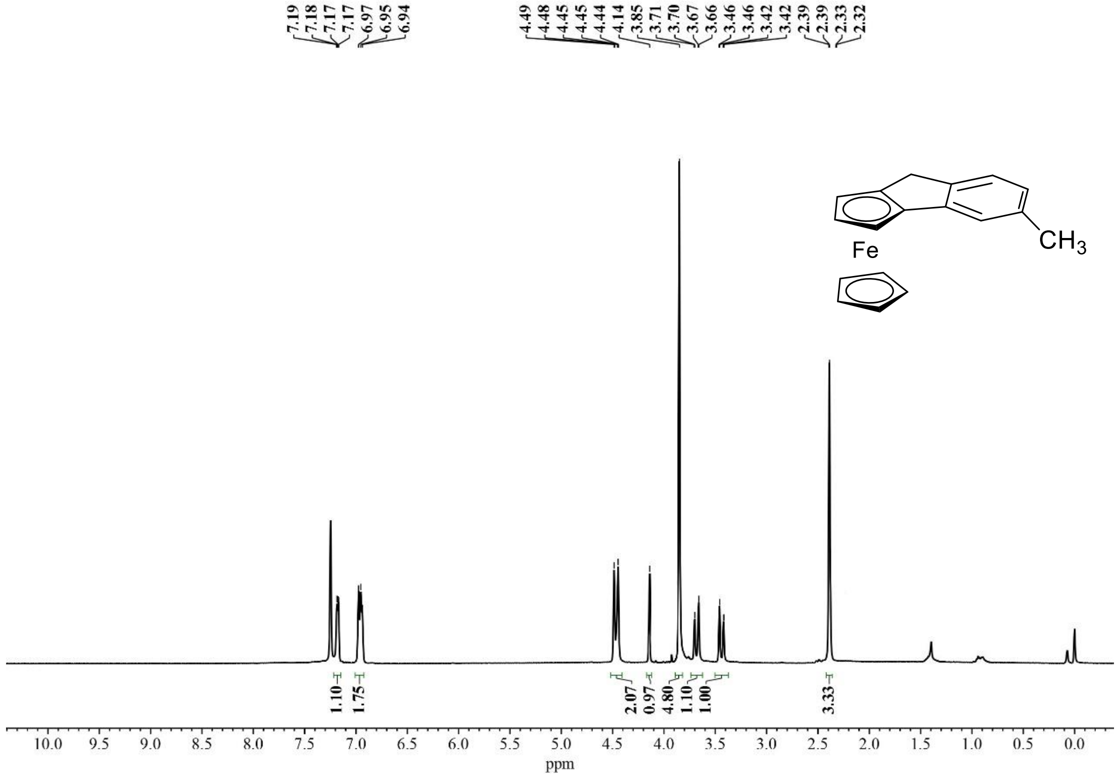


Figure S16. **^{1}H NMR** of **2b** (500 MHz, $CDCl_3$)

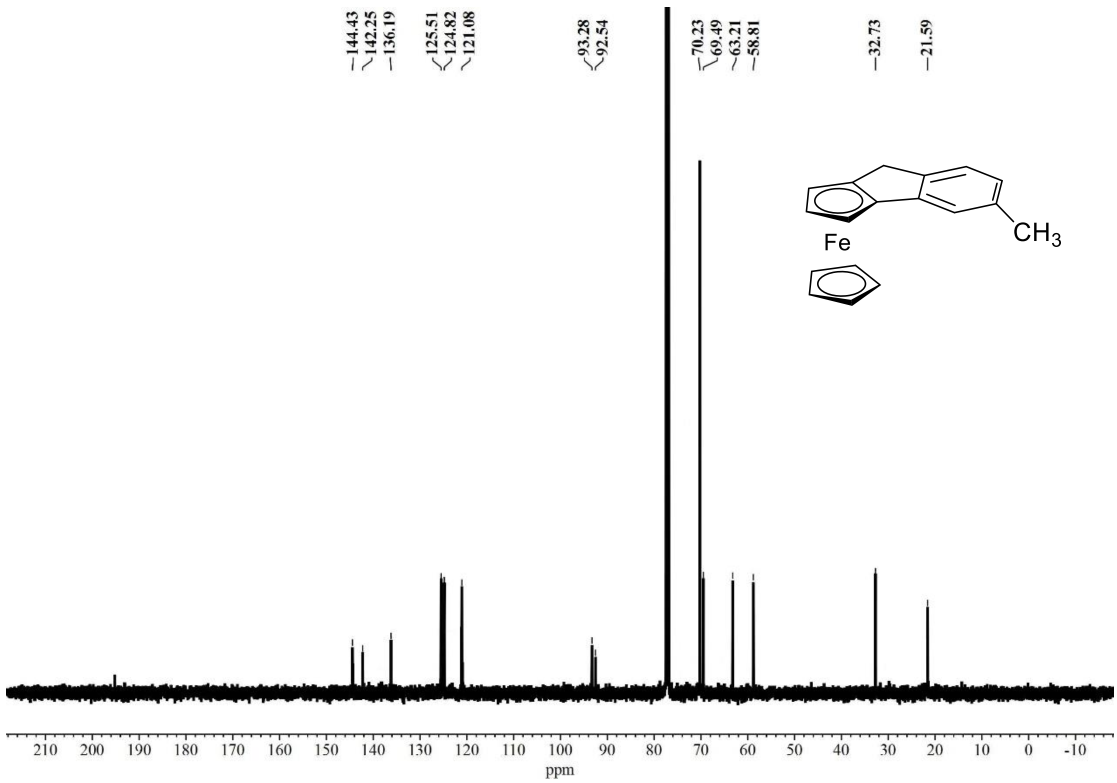


Figure S17. **^{13}C NMR** of **2b** (126 MHz, $CDCl_3$)

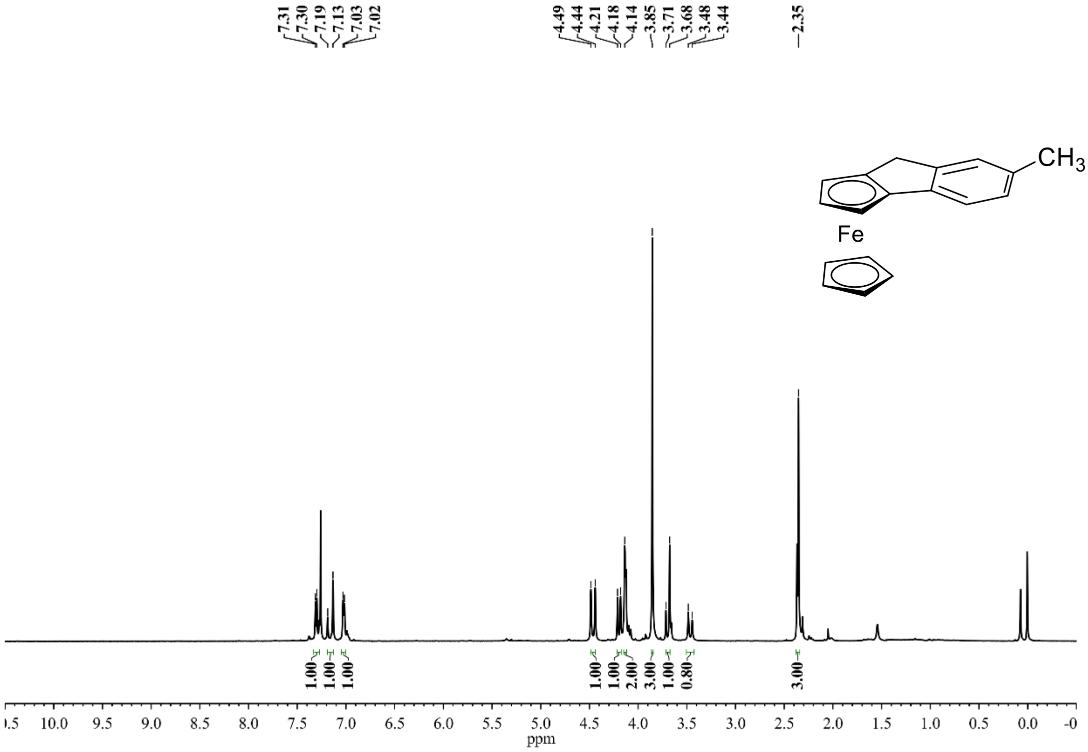


Figure S18. **^{1}H NMR** of **2c** (500 MHz, $CDCl_3$)

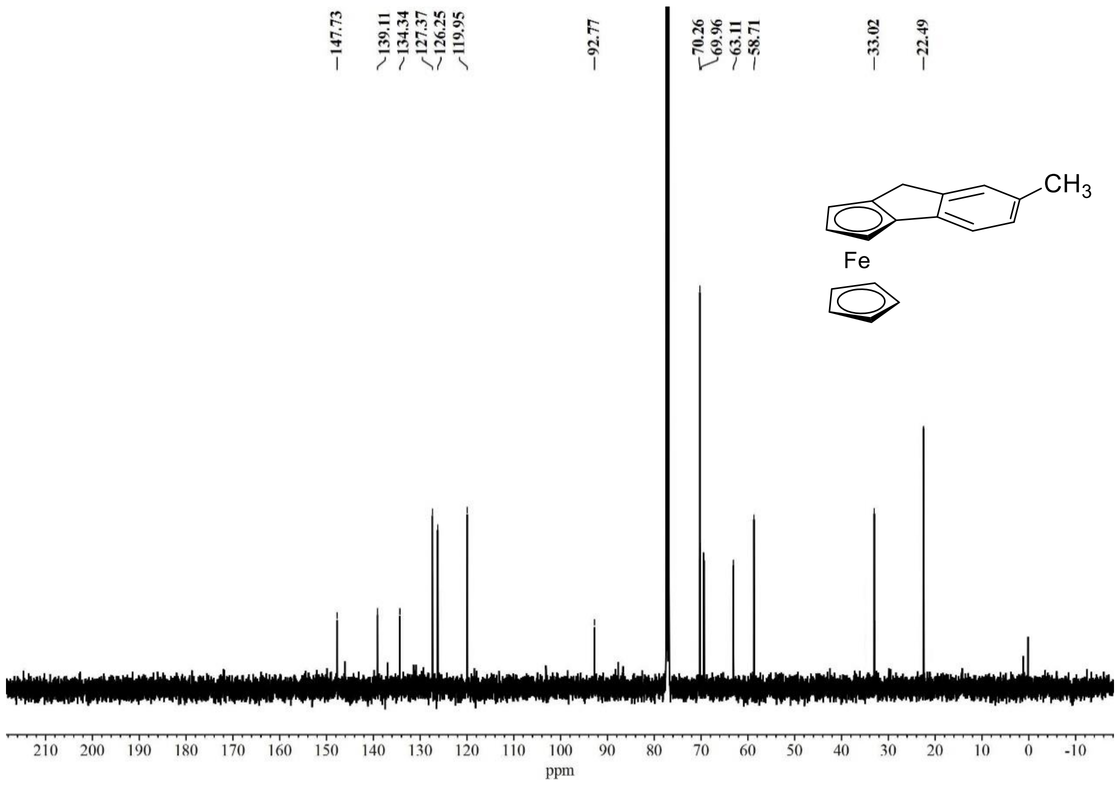


Figure S19. **^{13}C NMR** of **2c** (126 MHz, $CDCl_3$)

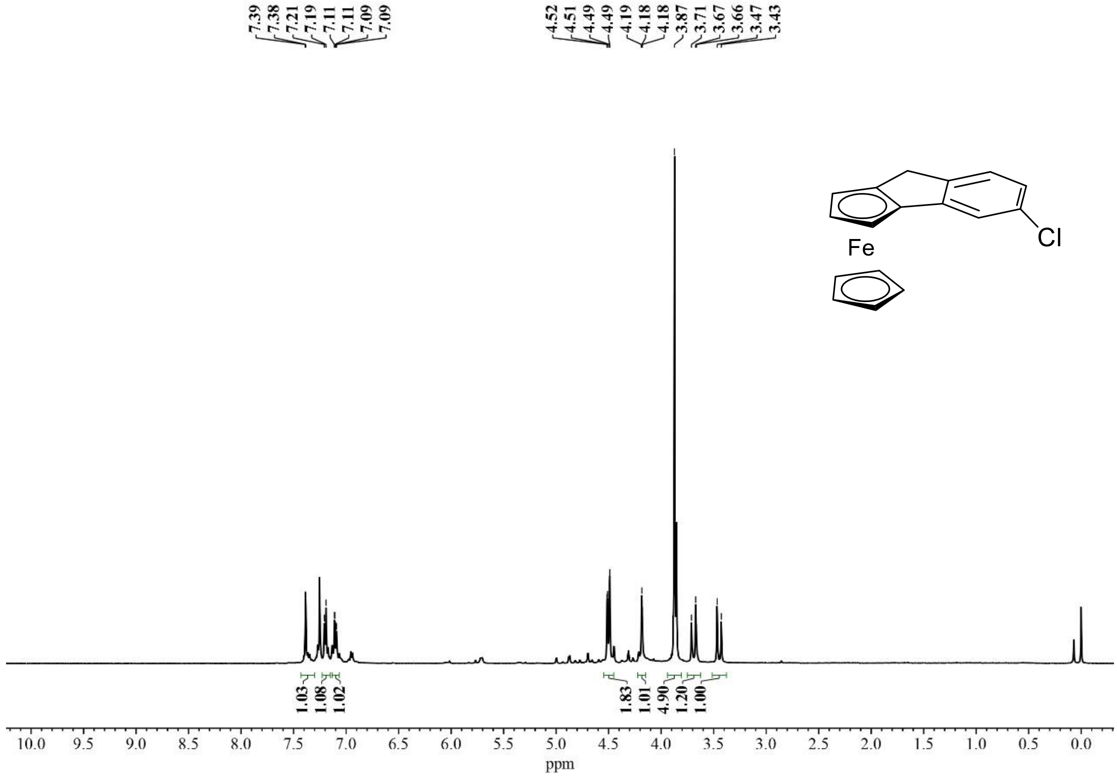


Figure S20. **^{1}H NMR** of **2d** (500 MHz, $CDCl_3$)

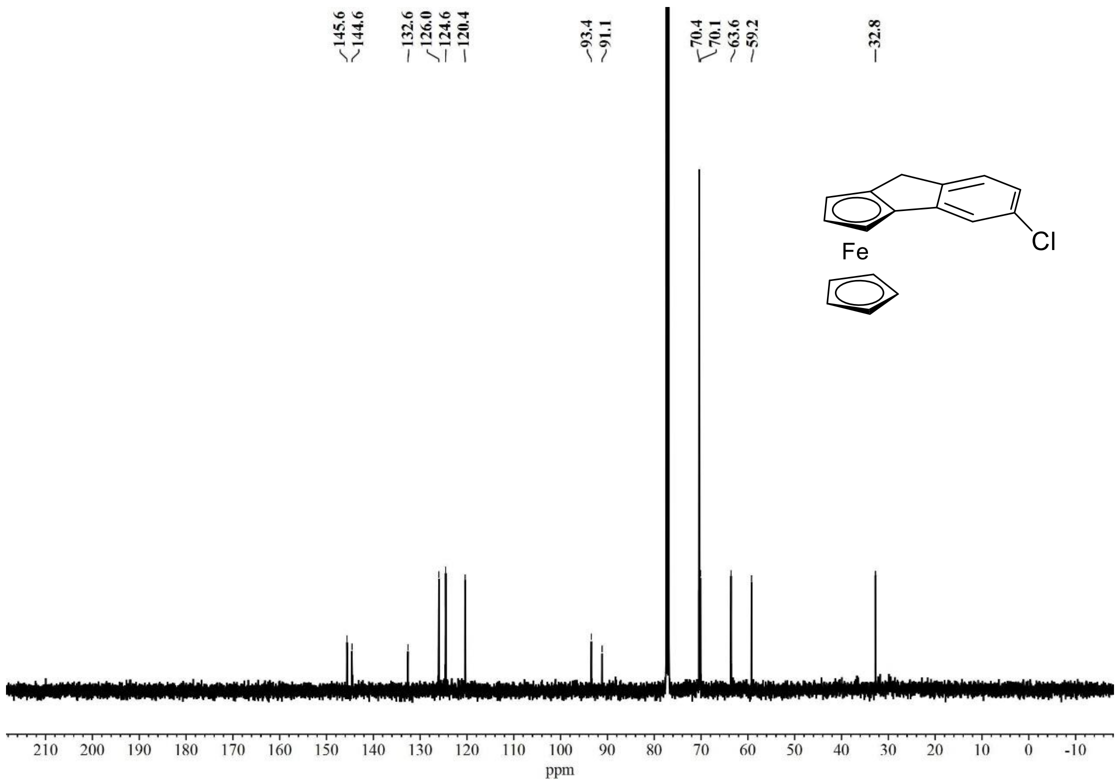


Figure S21. **^{13}C NMR** of **2d** (126 MHz, $CDCl_3$)

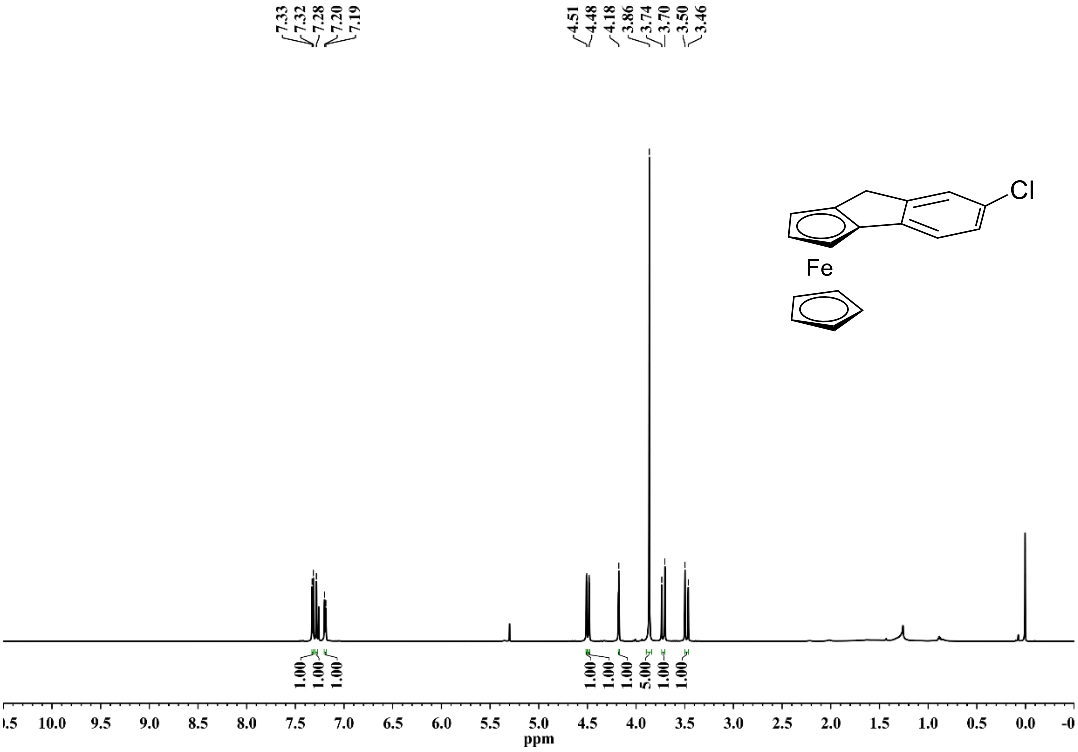


Figure S22. **^{1}H NMR** of **2e** (500 MHz, $CDCl_3$)

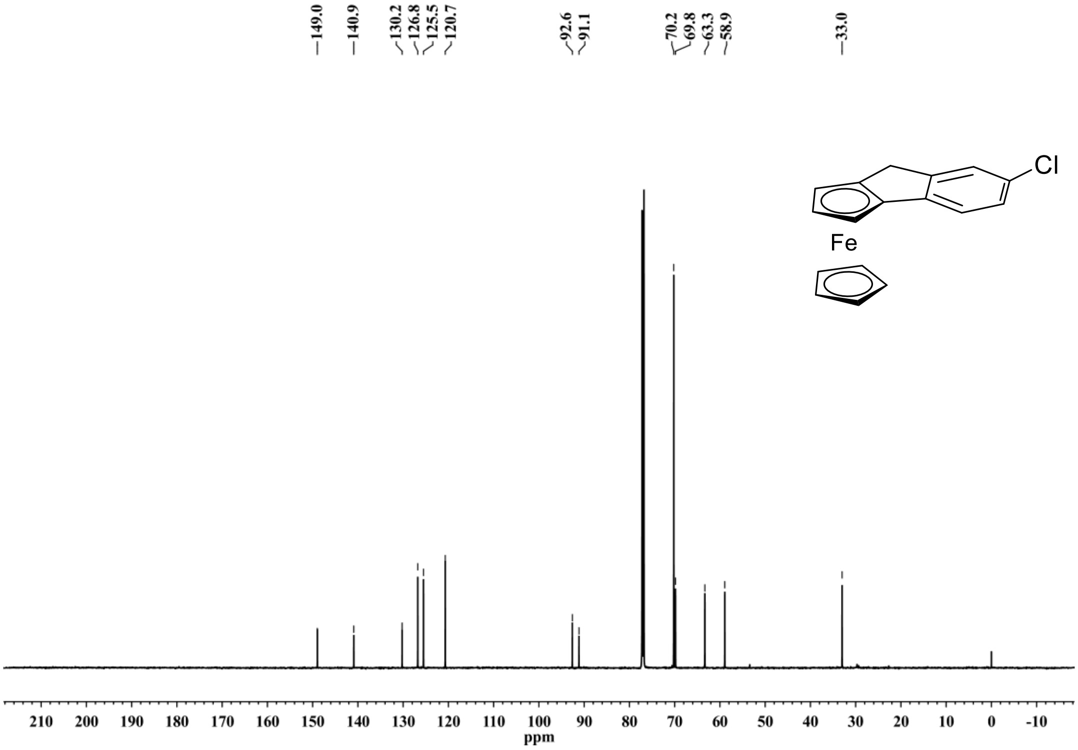


Figure S23. **^{13}C NMR** of **2e** (126 MHz, $CDCl_3$)

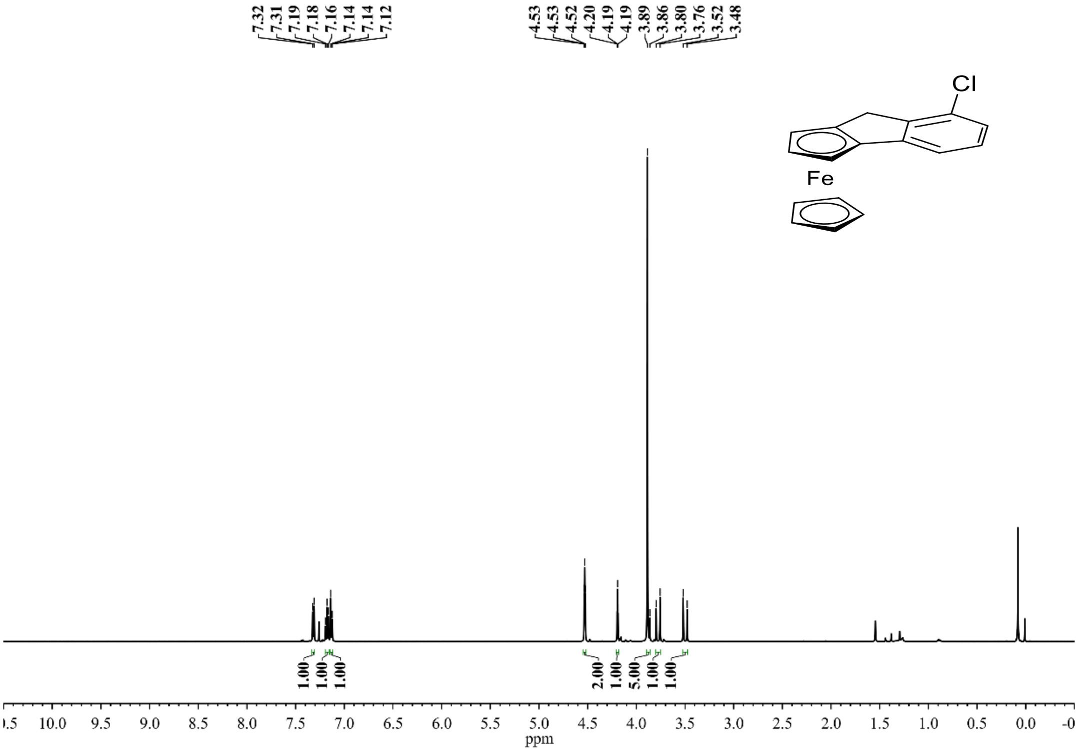


Figure S24. ^{1}**H NMR** of **2f (500 MHz, CDCl$_3$)**

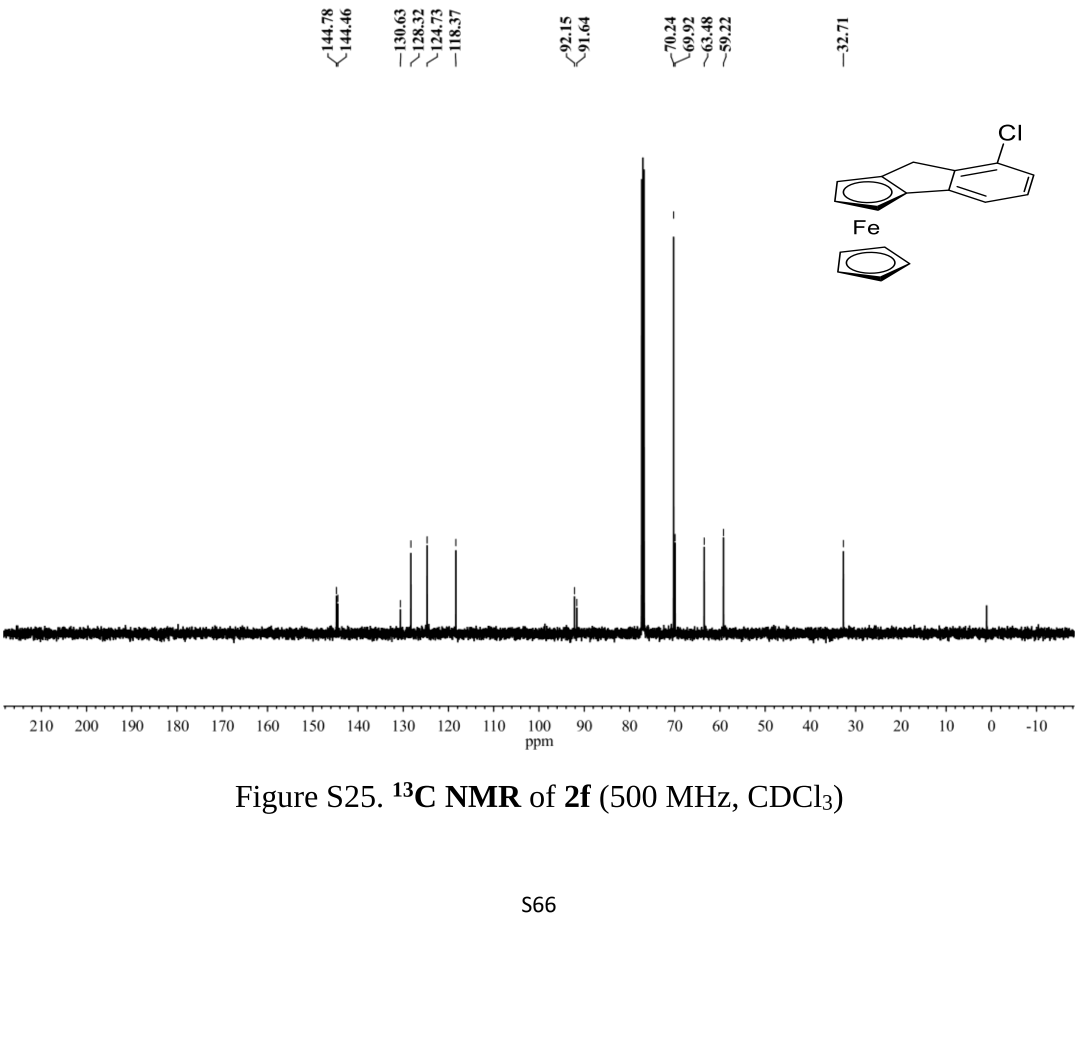


Figure S25. ^{13}**C NMR** of **2f** (500 MHz, CDCl$_3$)

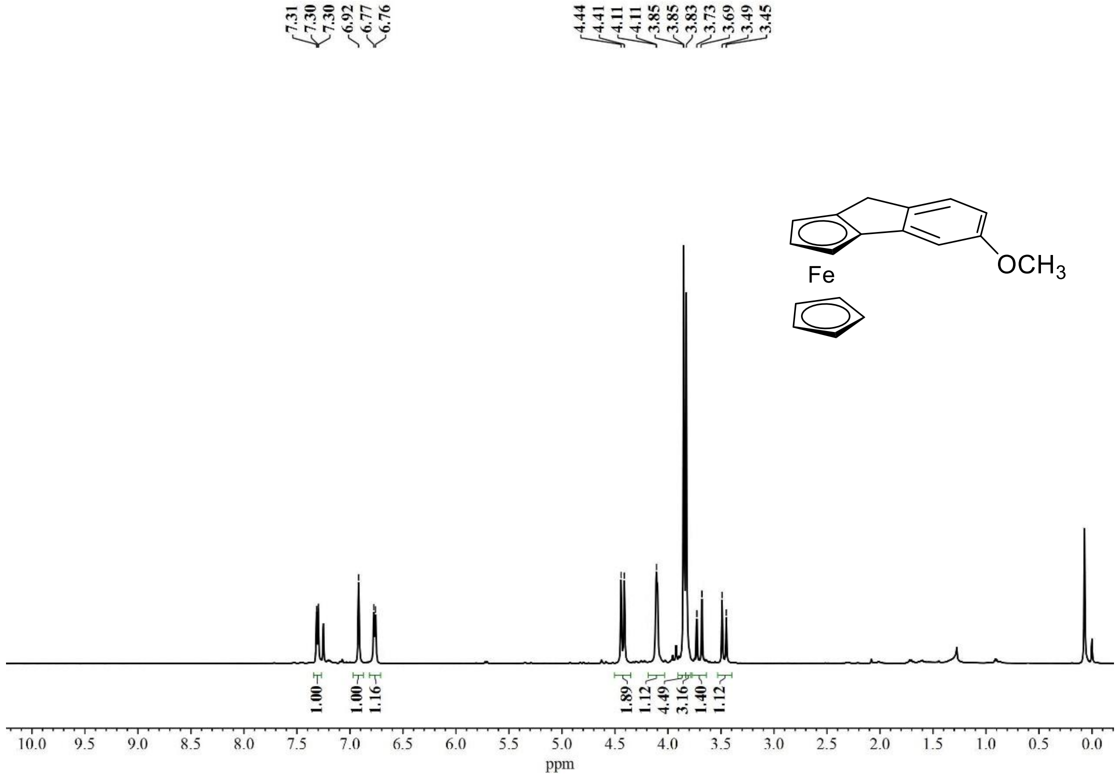


Figure S26. **^{1}H NMR** of **2g** (500 MHz, $CDCl_3$)

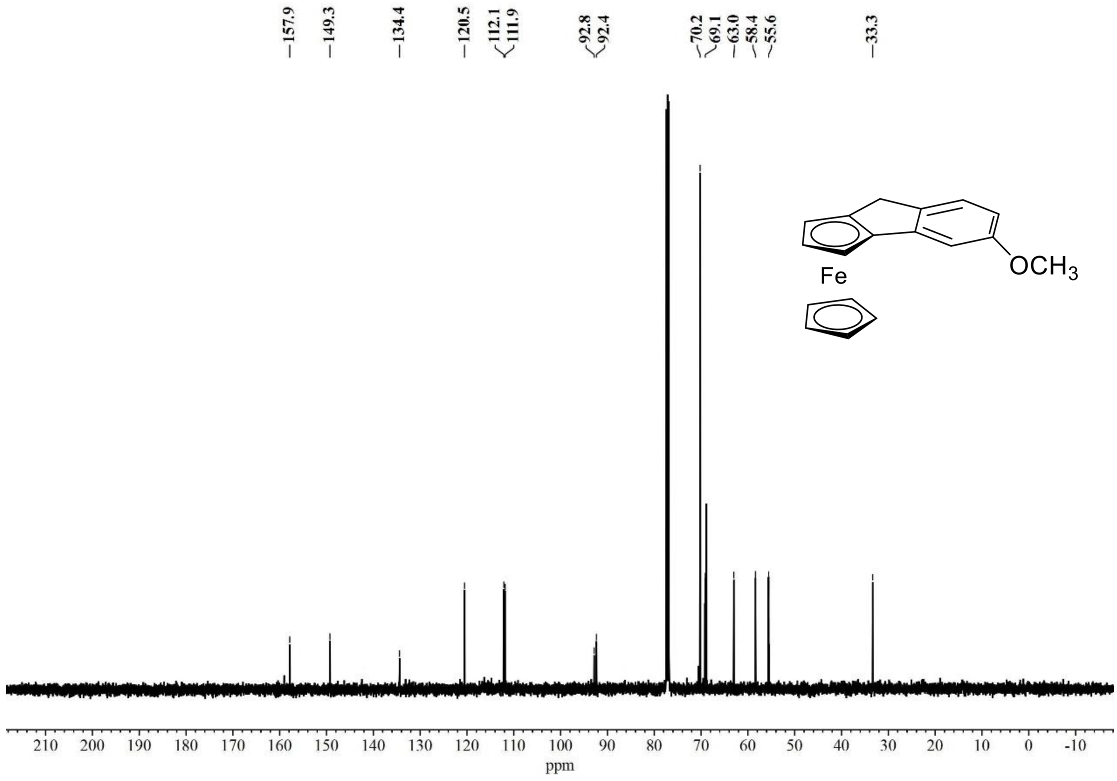


Figure S27. **^{13}C NMR** of **2g** (126 MHz, $CDCl_3$)

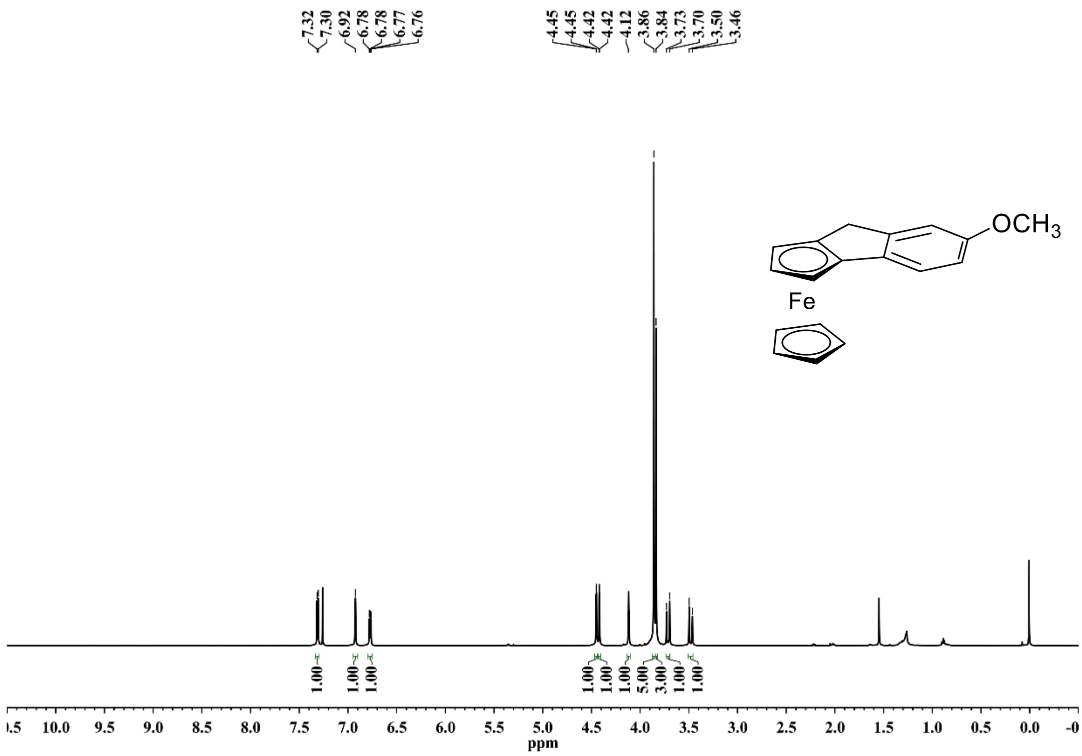


Figure S28. ^{1}**H NMR** of **2h** (500 MHz, $CDCl_3$)

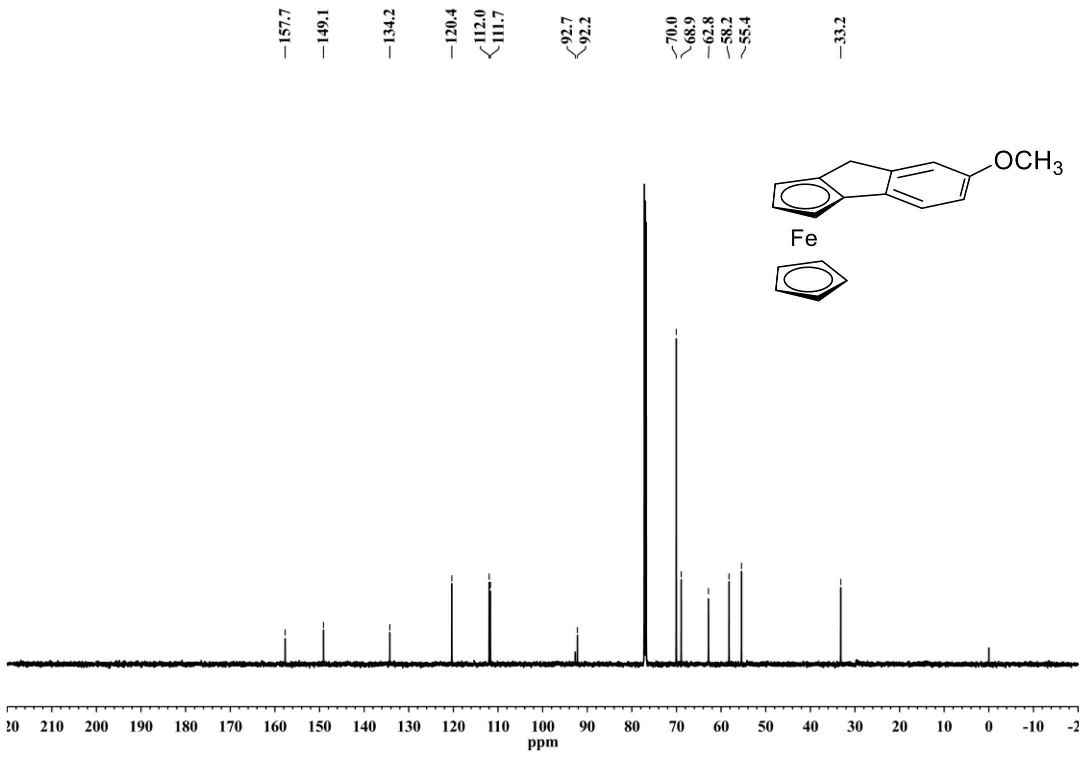


Figure S29. ^{13}**C NMR** of **2h** (126 MHz, $CDCl_3$)

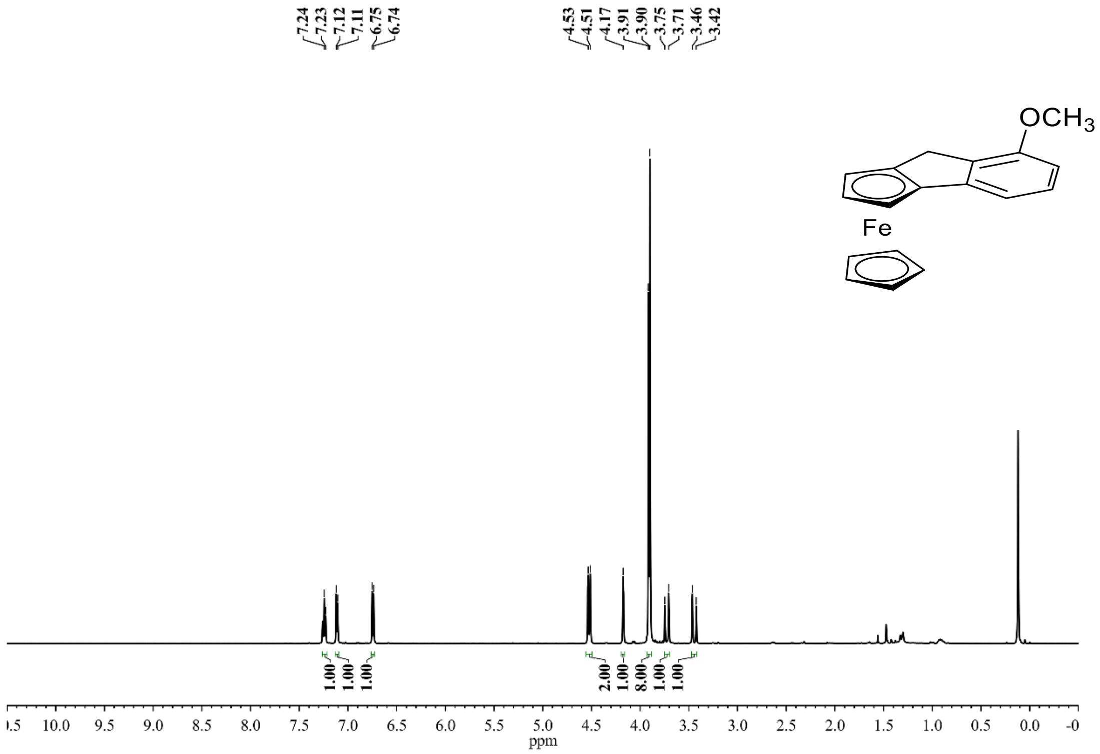


Figure S30. **^{1}H NMR** of **2i** (500 MHz, $CDCl_3$)

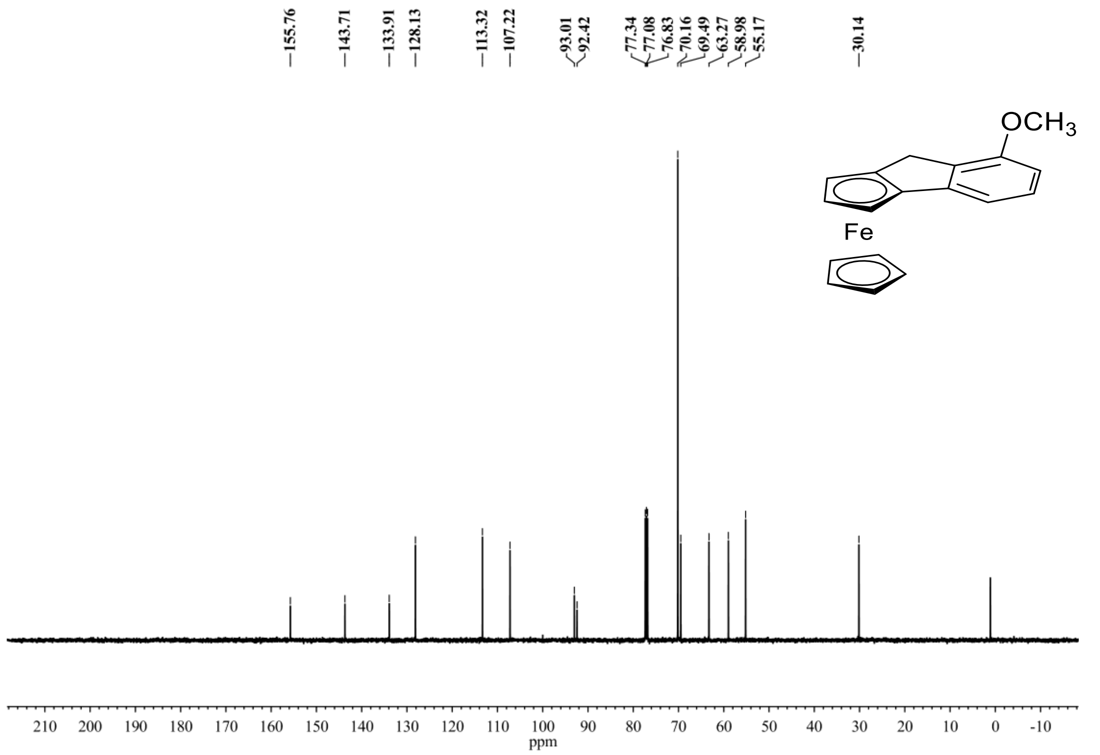


Figure S31. **^{13}C NMR** of **2i** (126 MHz, $CDCl_3$)

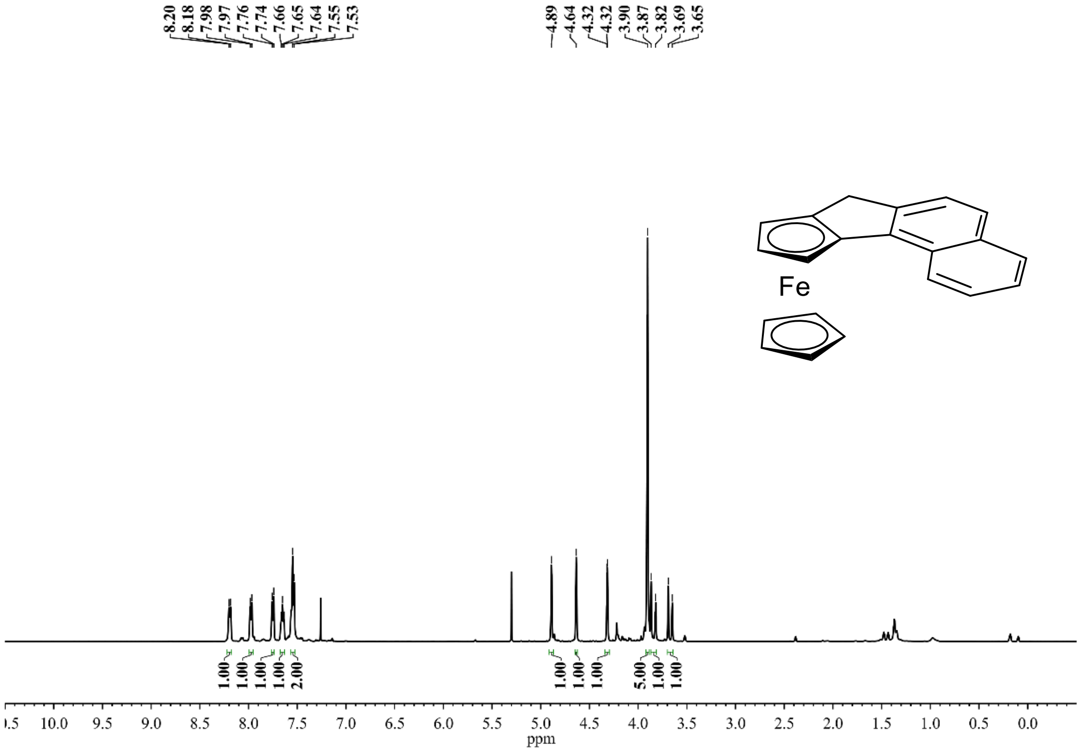


Figure S32. **^{1}H NMR** of **2j** (500 MHz, $CDCl_3$)

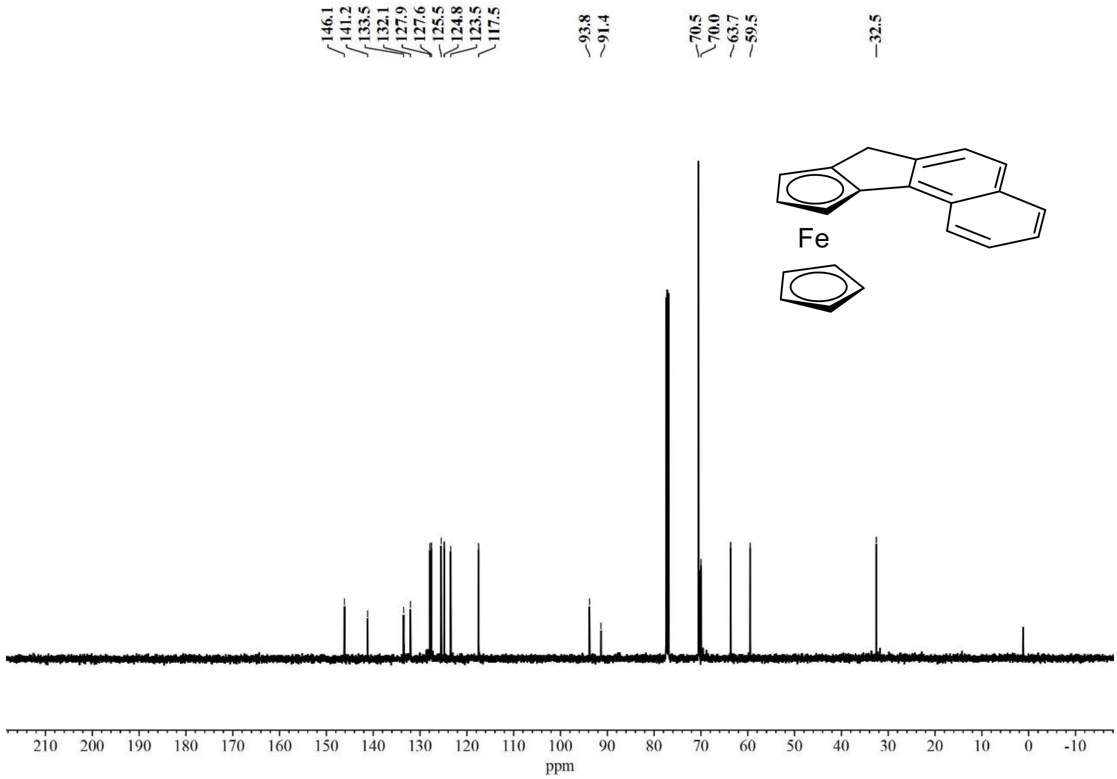


Figure S33. **^{13}C NMR** of **2j** (126 MHz, $CDCl_3$)

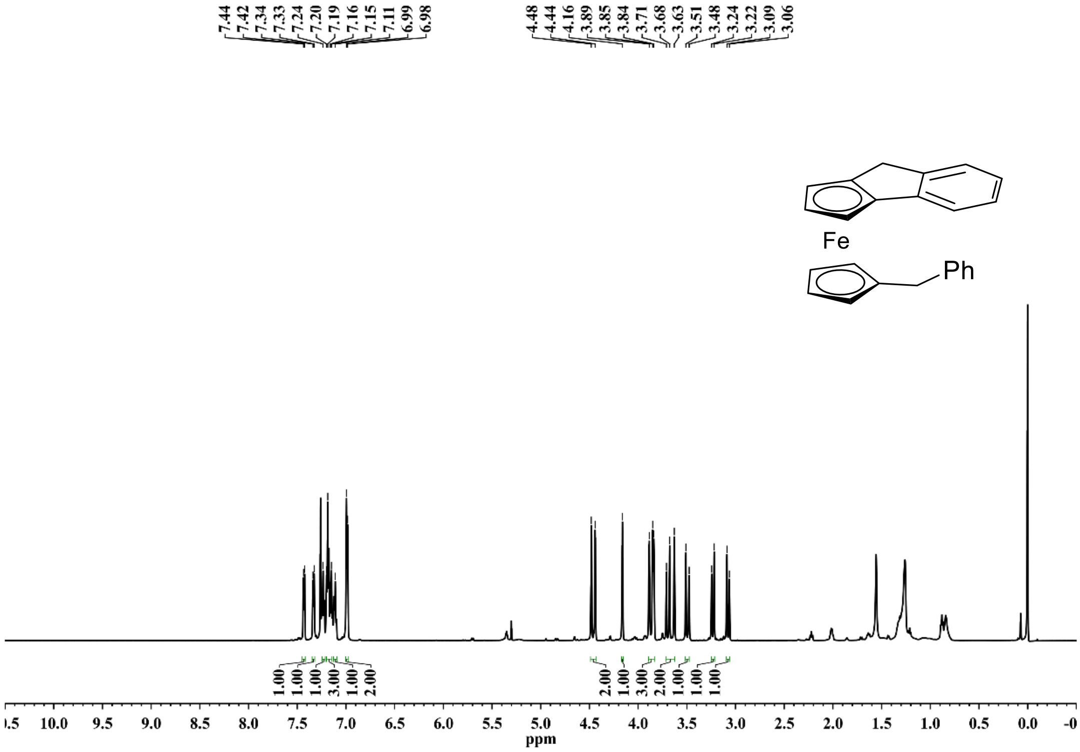


Figure S34. ^{1}**H NMR** of **2k** (500 MHz, $CDCl_3$)

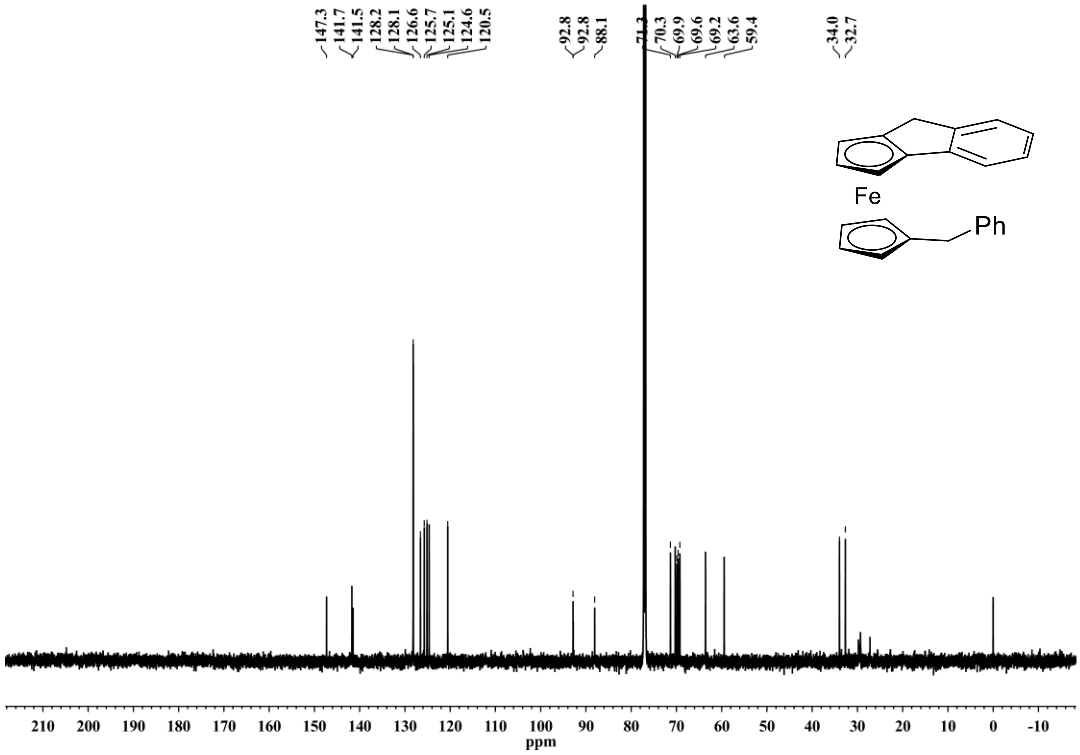


Figure S35. ^{13}**C NMR** of **2k** (126 MHz, $CDCl_3$)

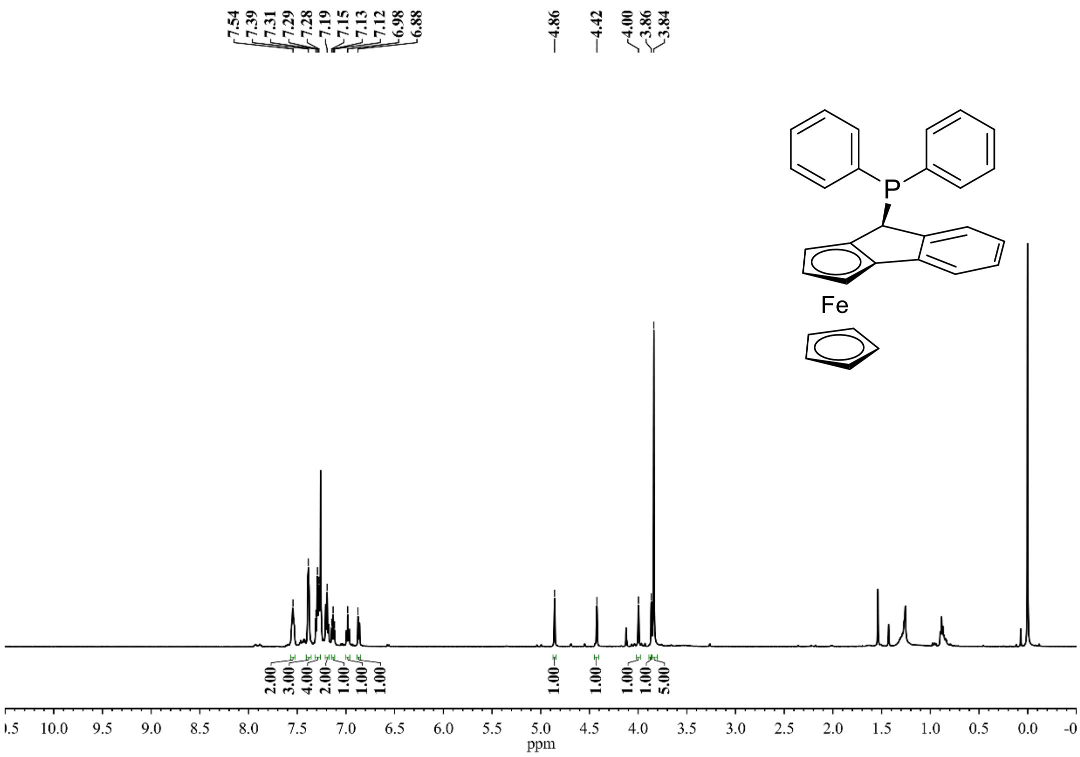


Figure S36. **^{1}H NMR** of **3a** (500 MHz, $CDCl_3$)

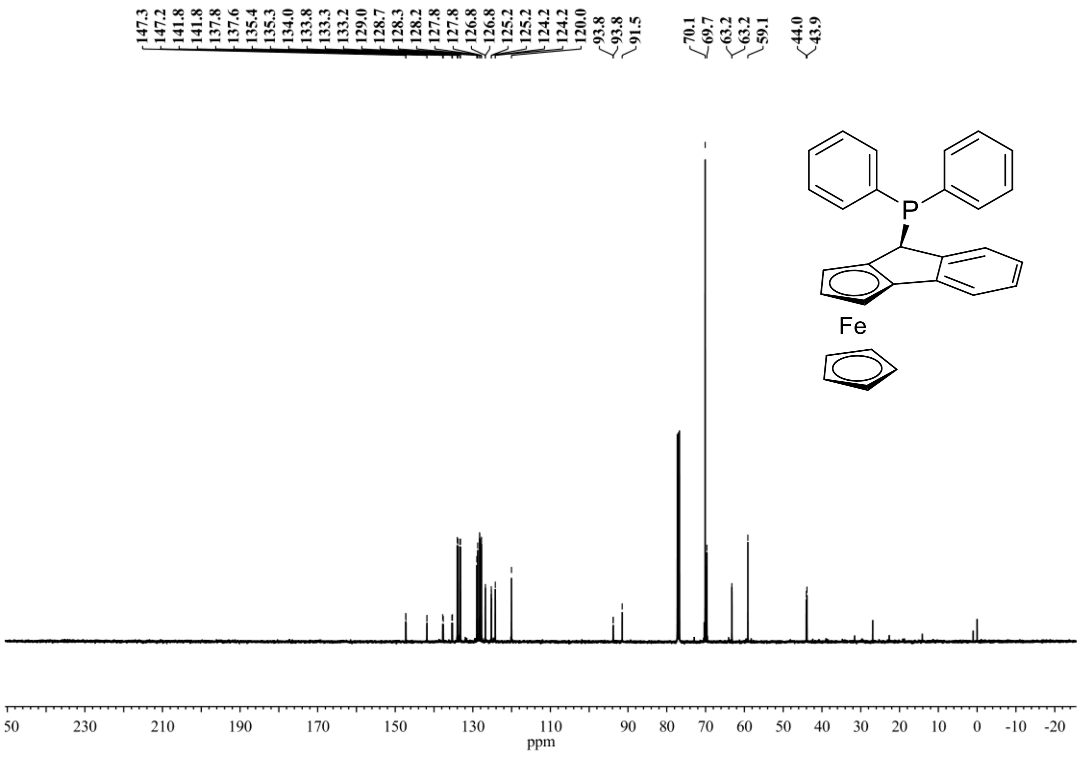


Figure S37. **^{13}C NMR** of **3a** (126 MHz, $CDCl_3$)

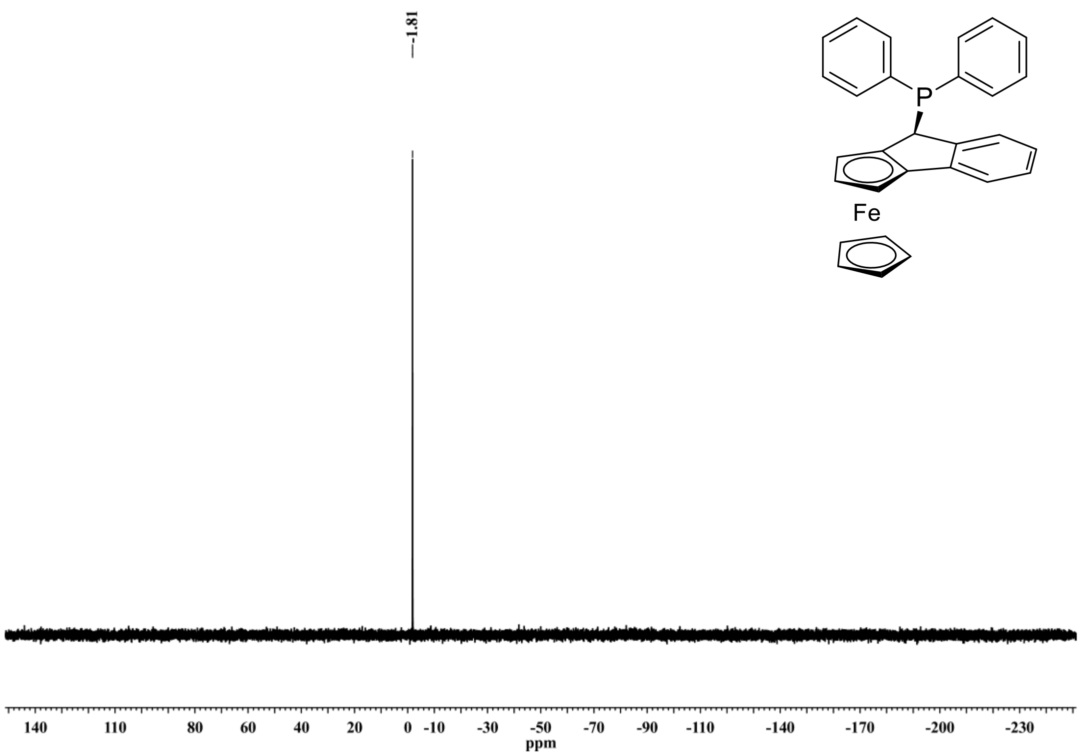


Figure S38. ^{31}**P NMR** of **3a** (202 MHz, $CDCl_3$)

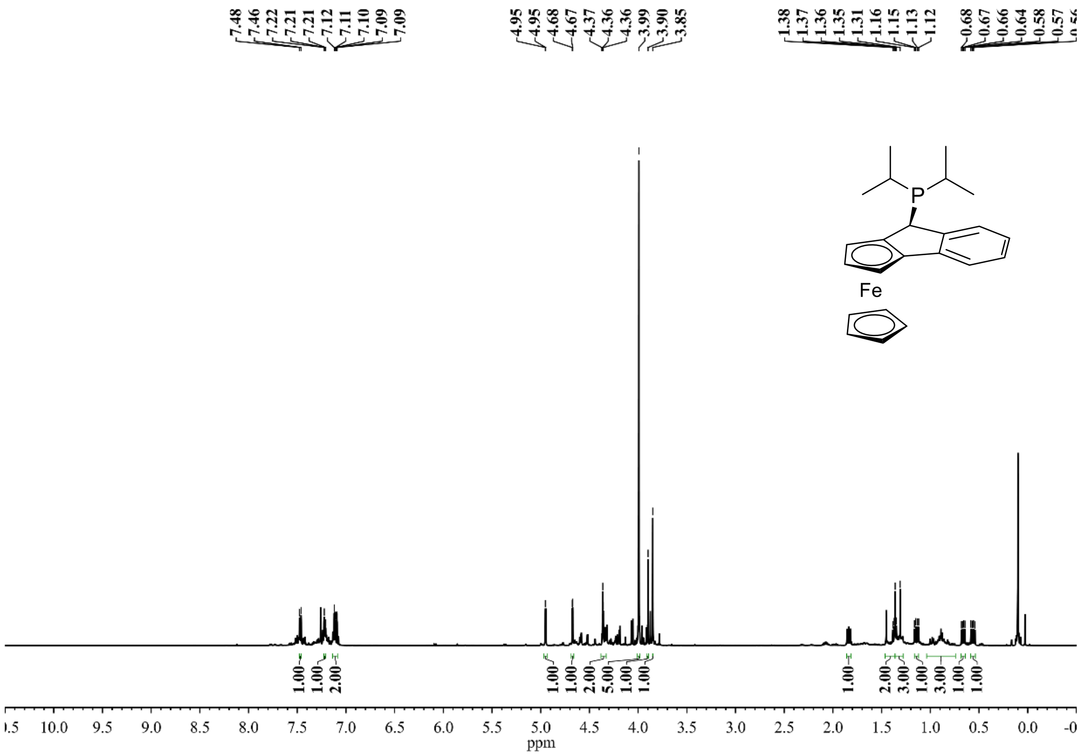


Figure S39. ^{1}**H NMR** of **3b** (500 MHz, $CDCl_3$)

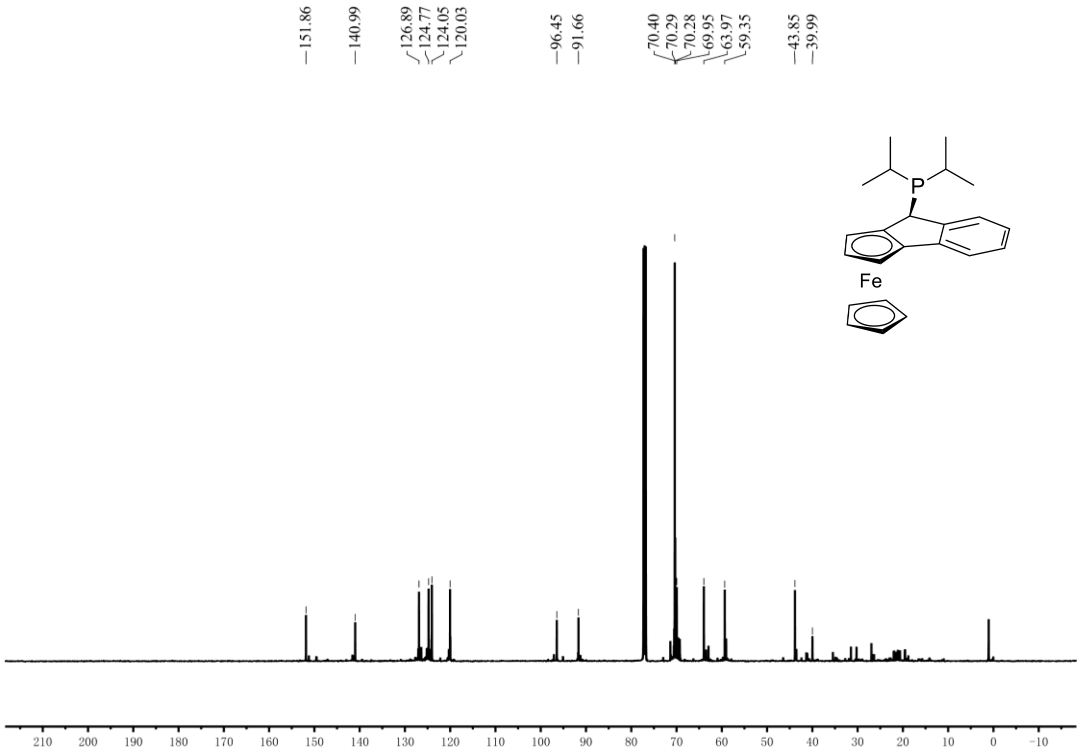


Figure S40. **^{13}C NMR** of **3b** (126 MHz, $CDCl_3$)

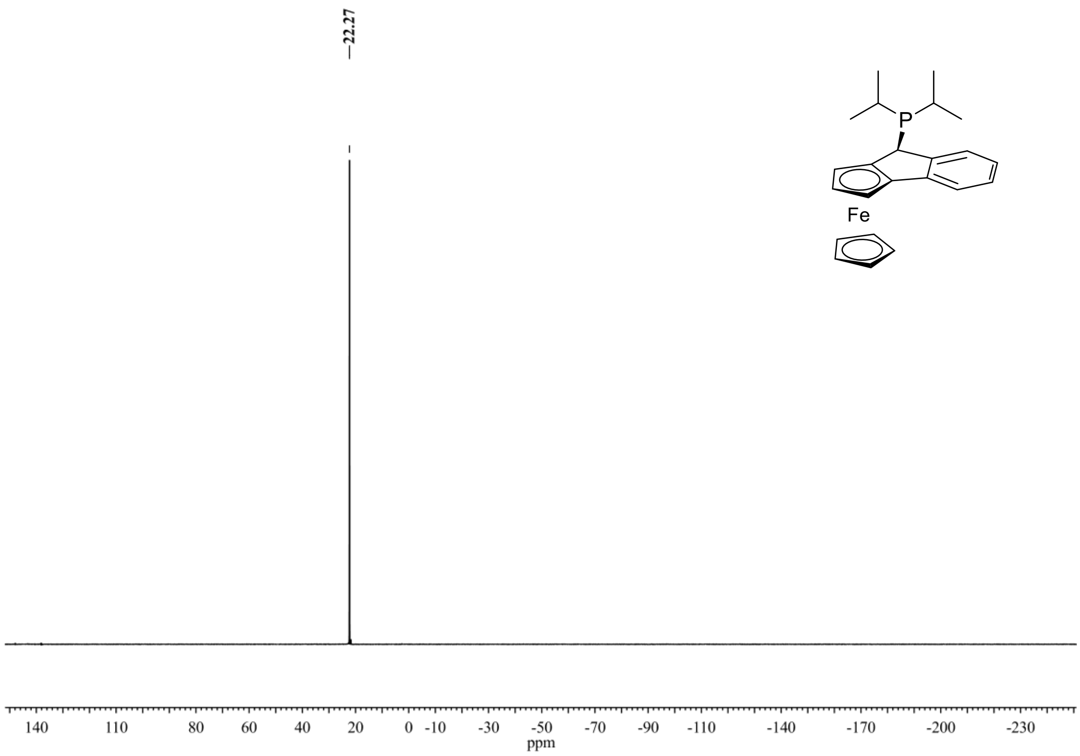


Figure S41. **^{31}P NMR** of **3b** (202 MHz, $CDCl_3$)

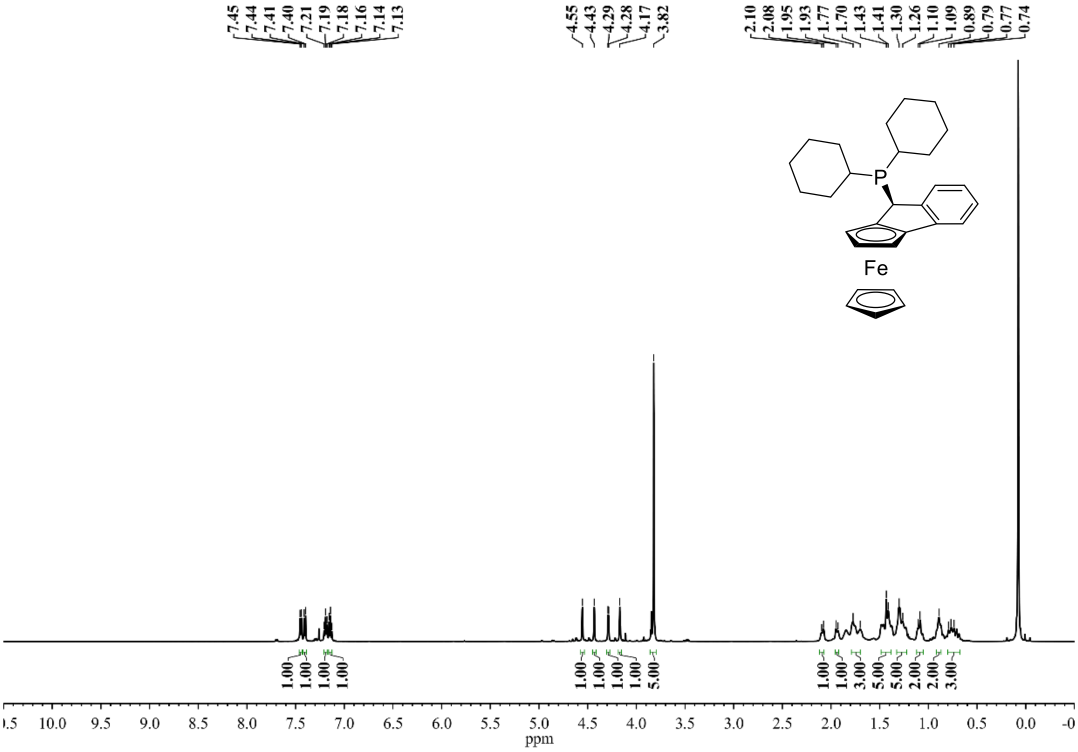


Figure S42. **^{1}H NMR** of **3c** (500 MHz, $CDCl_3$)

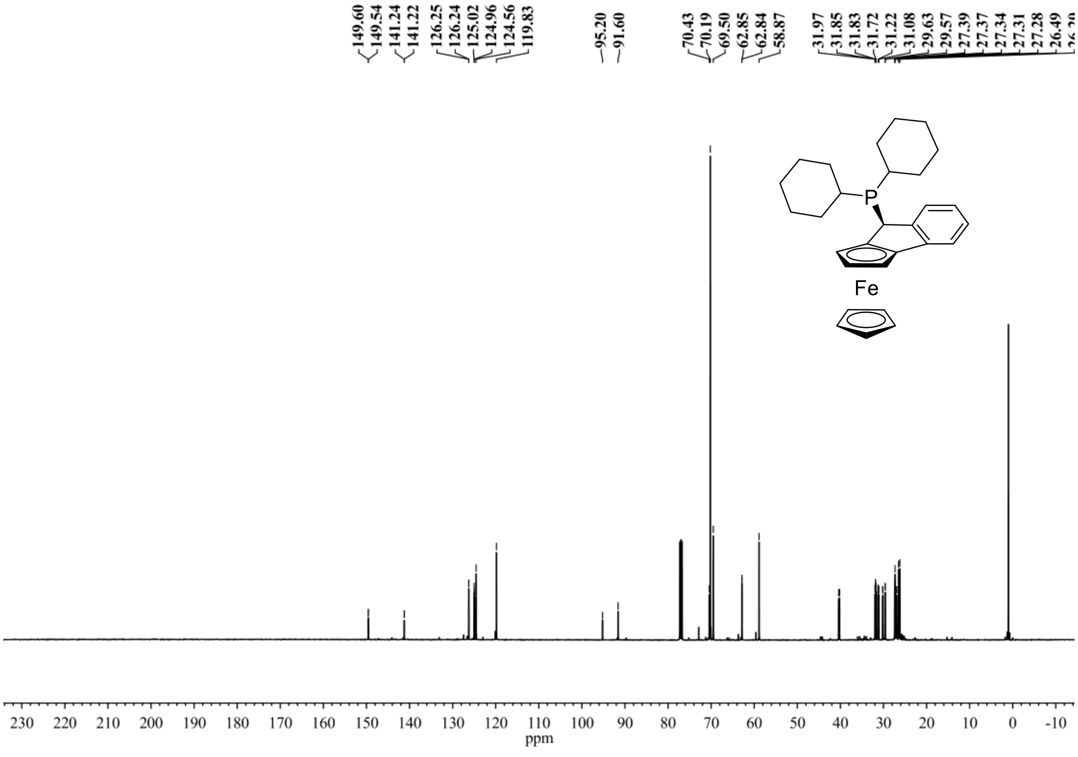


Figure S43. **^{13}C NMR** of **3c** (126 MHz, $CDCl_3$)

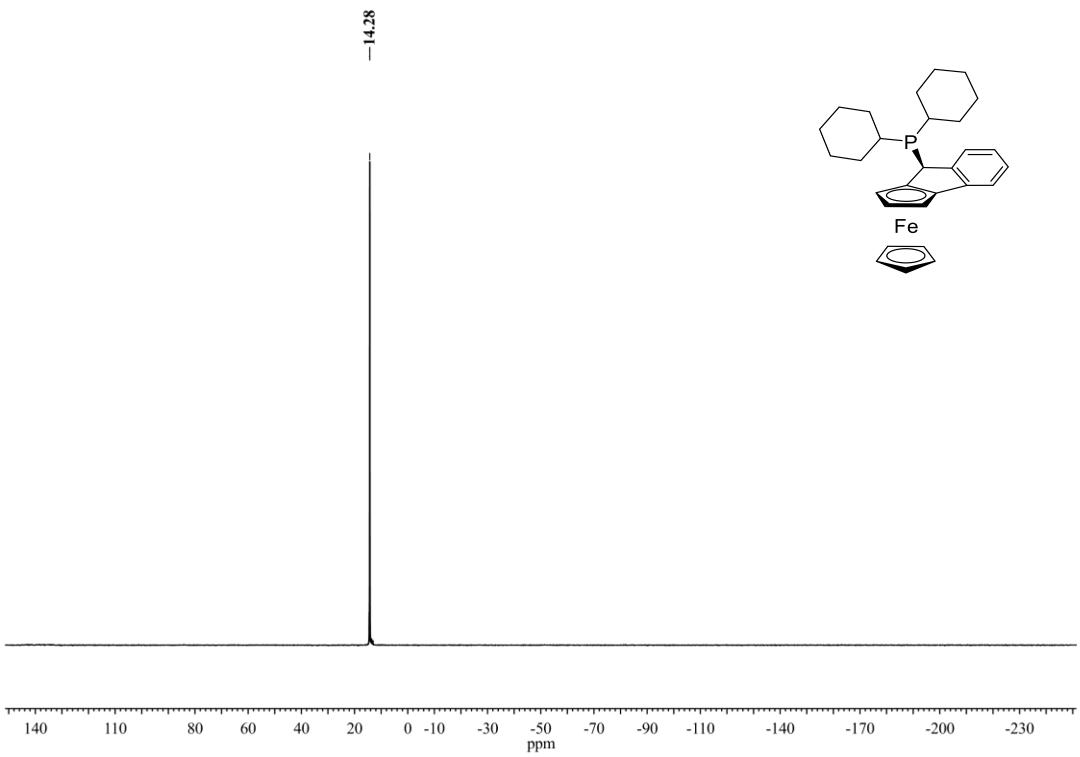


Figure S44. **^{31}P NMR** of **3c** (202 MHz, $CDCl_3$)

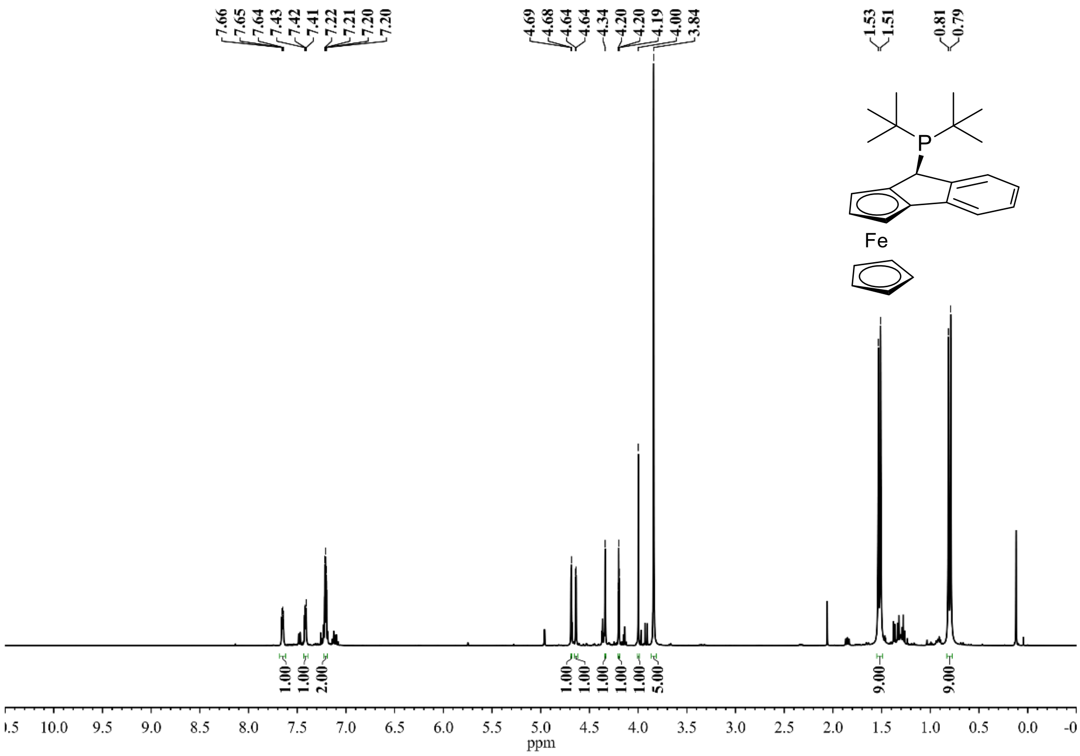


Figure S45. **^{1}H NMR** of **3d** (500 MHz, $CDCl_3$)

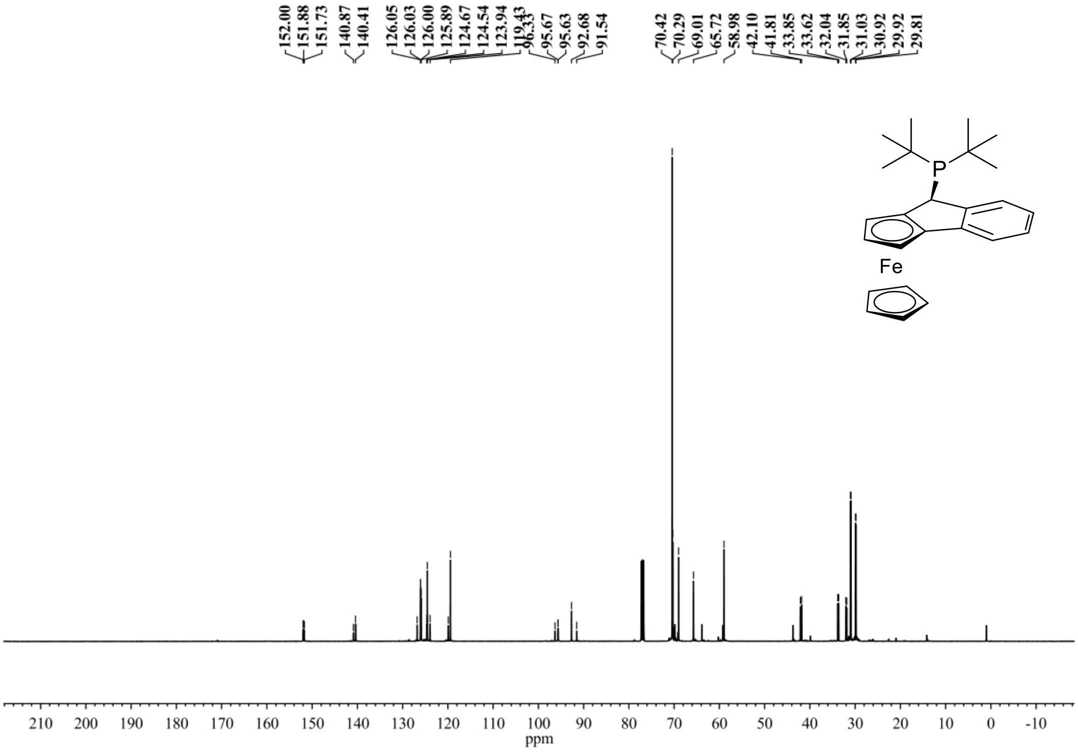


Figure S46. ^{13}**C NMR** of **3d** (126 MHz, $CDCl_3$)

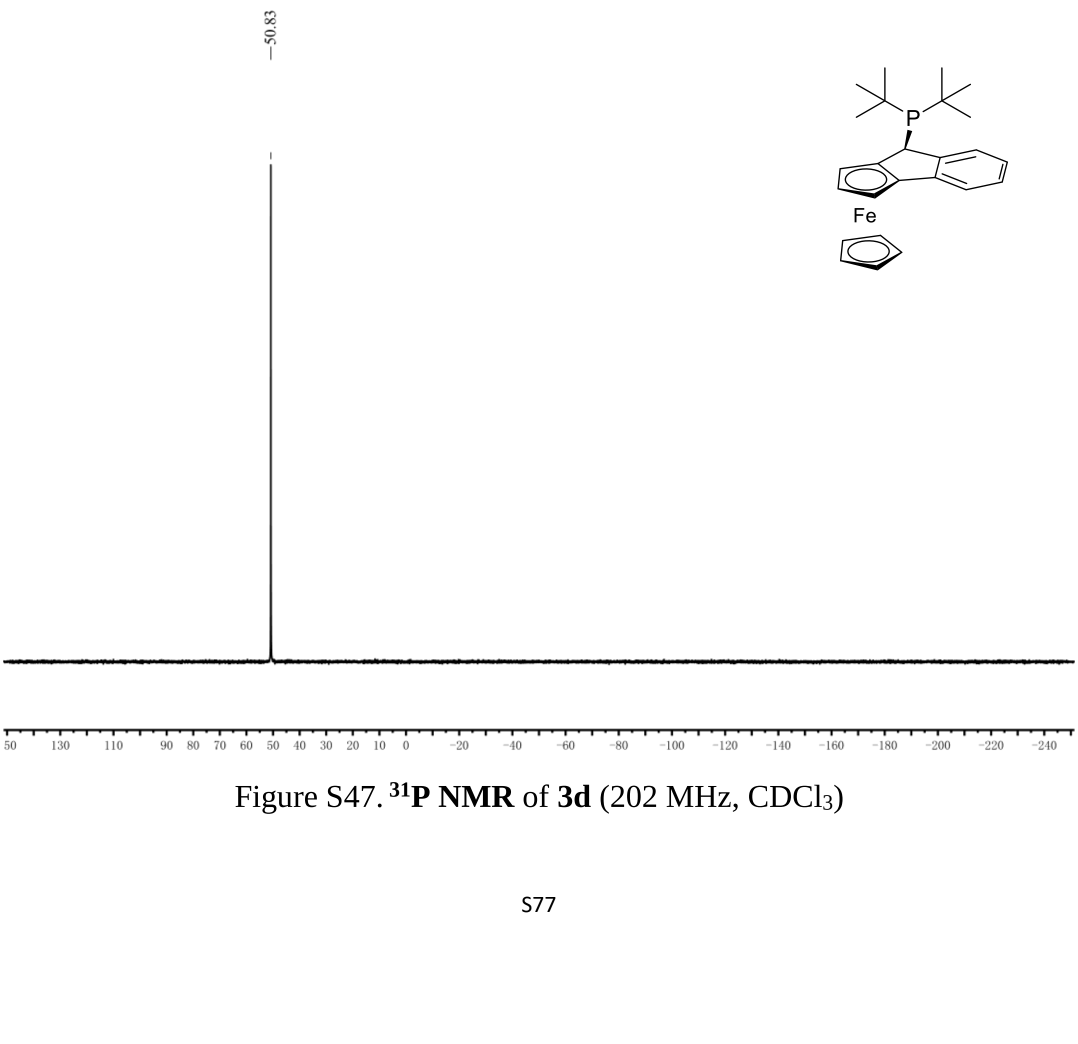


Figure S47. ^{31}**P NMR** of **3d** (202 MHz, $CDCl_3$)

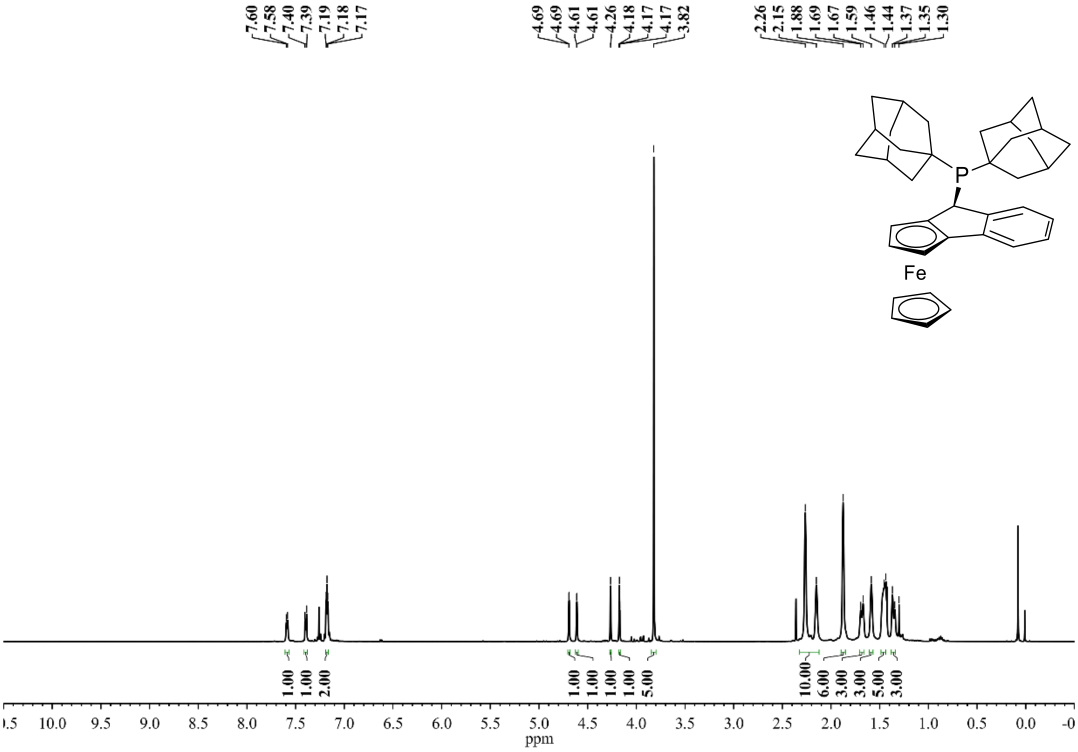


Figure S48. ^{1}**H NMR** of **3e** (500 MHz, $CDCl_3$)

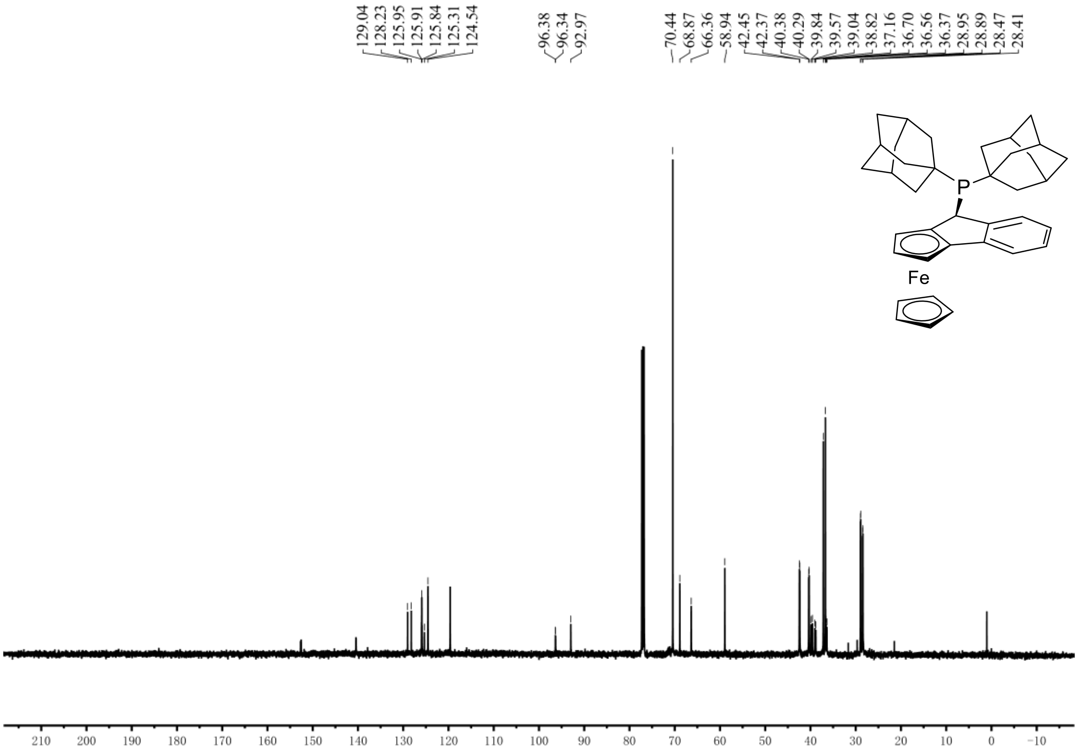


Figure S49. ^{13}**C NMR** of **3e** (126 MHz, $CDCl_3$)

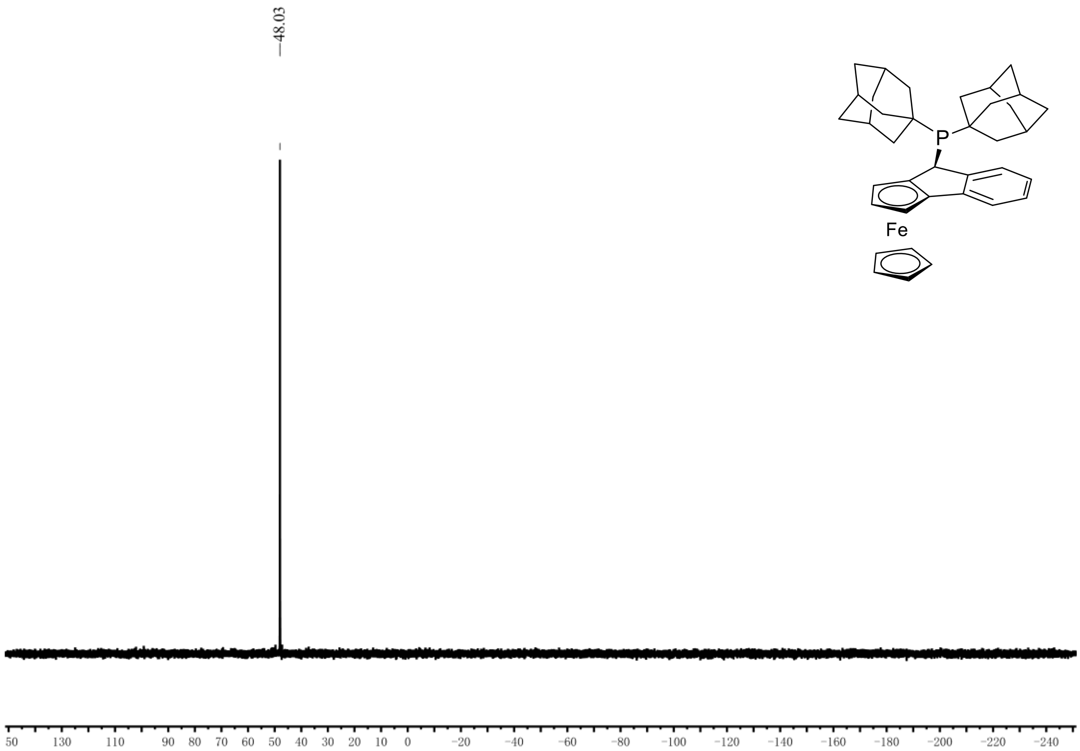


Figure S50. **^{31}P NMR** of **3e** (202 MHz, $CDCl_3$)

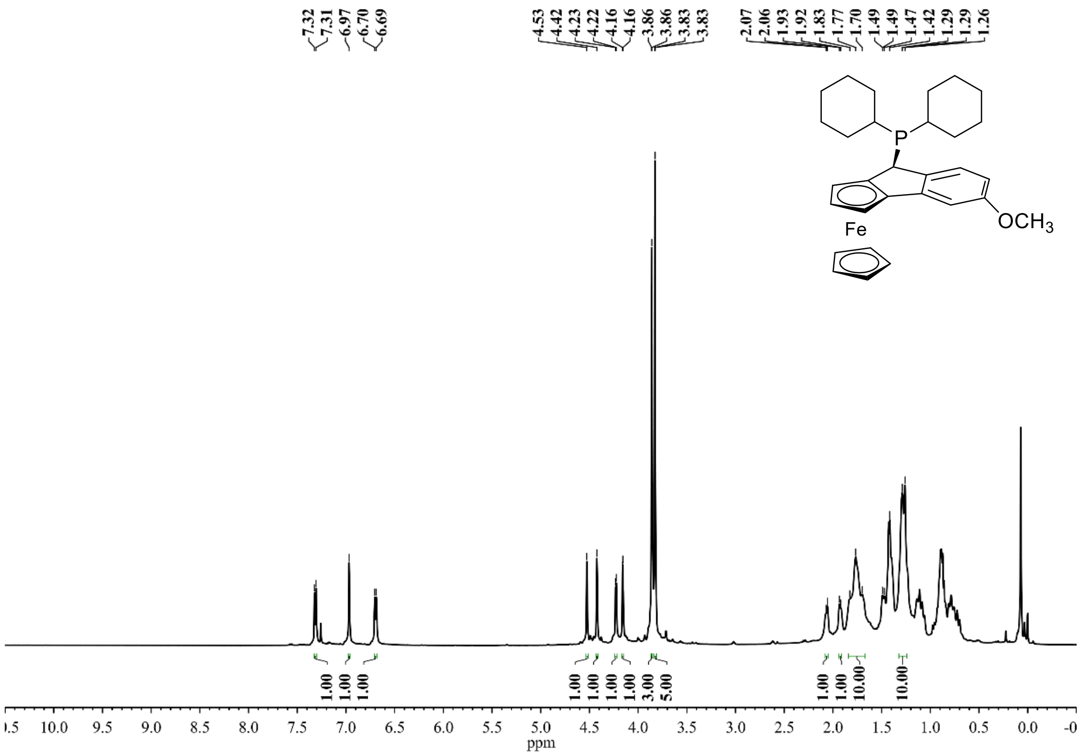


Figure S51. **^{1}H NMR** of **3f** (500 MHz, $CDCl_3$)

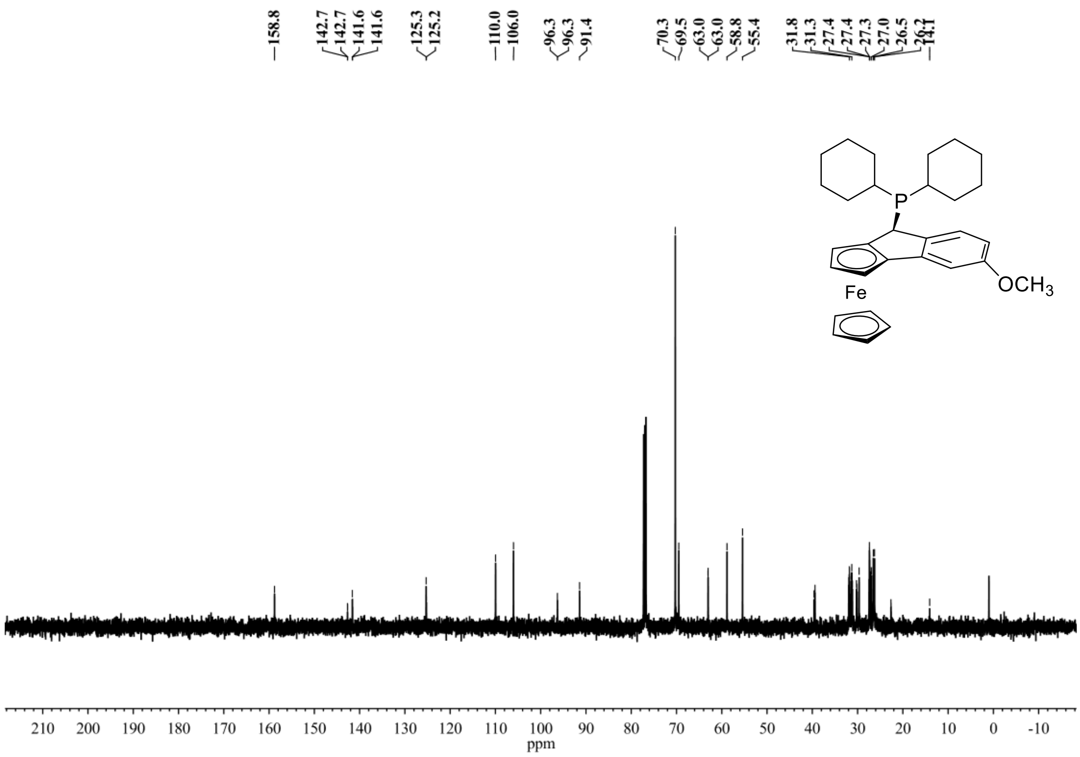


Figure S52. **^{13}C NMR** of **3f** (126 MHz, $CDCl_3$)

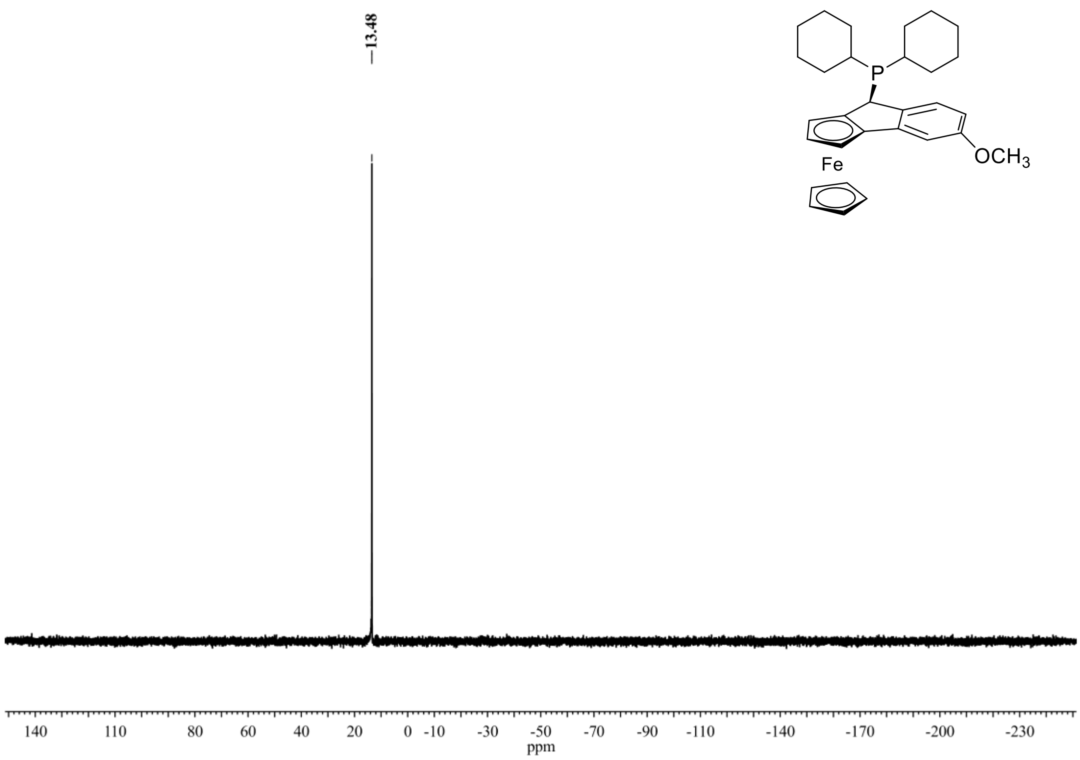


Figure S53. **^{31}P NMR** of **3f** (202 MHz, $CDCl_3$)

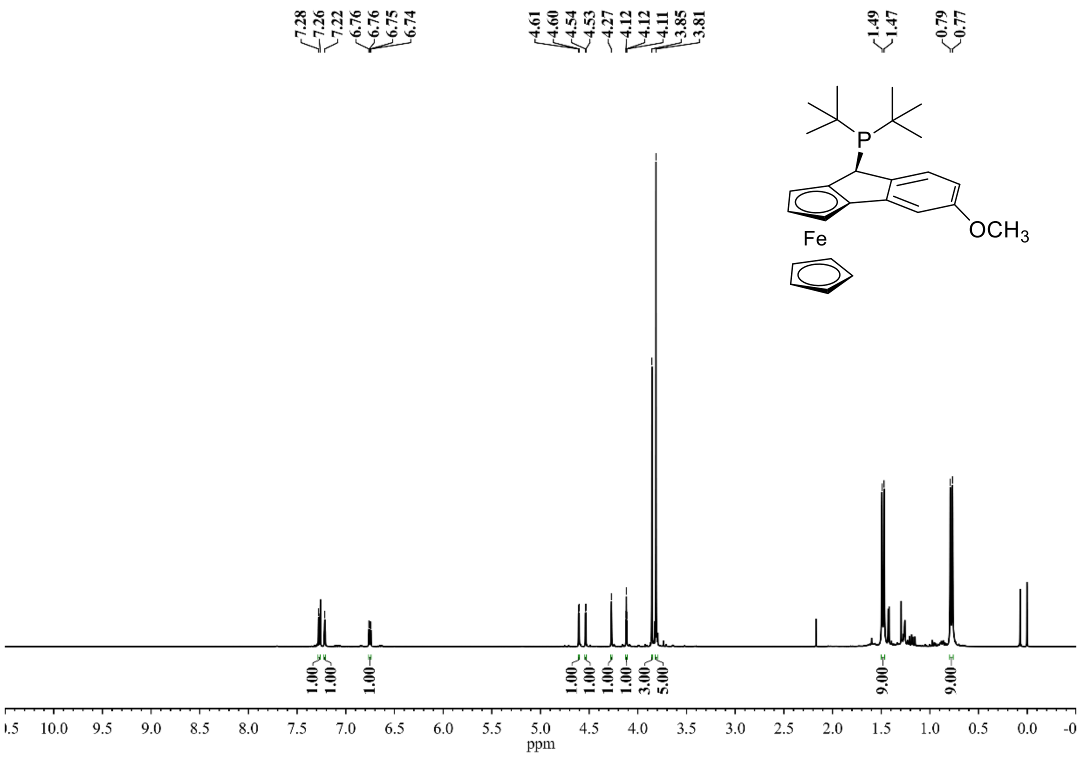


Figure S54. **^{1}H NMR** of **3g** (500 MHz, $CDCl_3$)

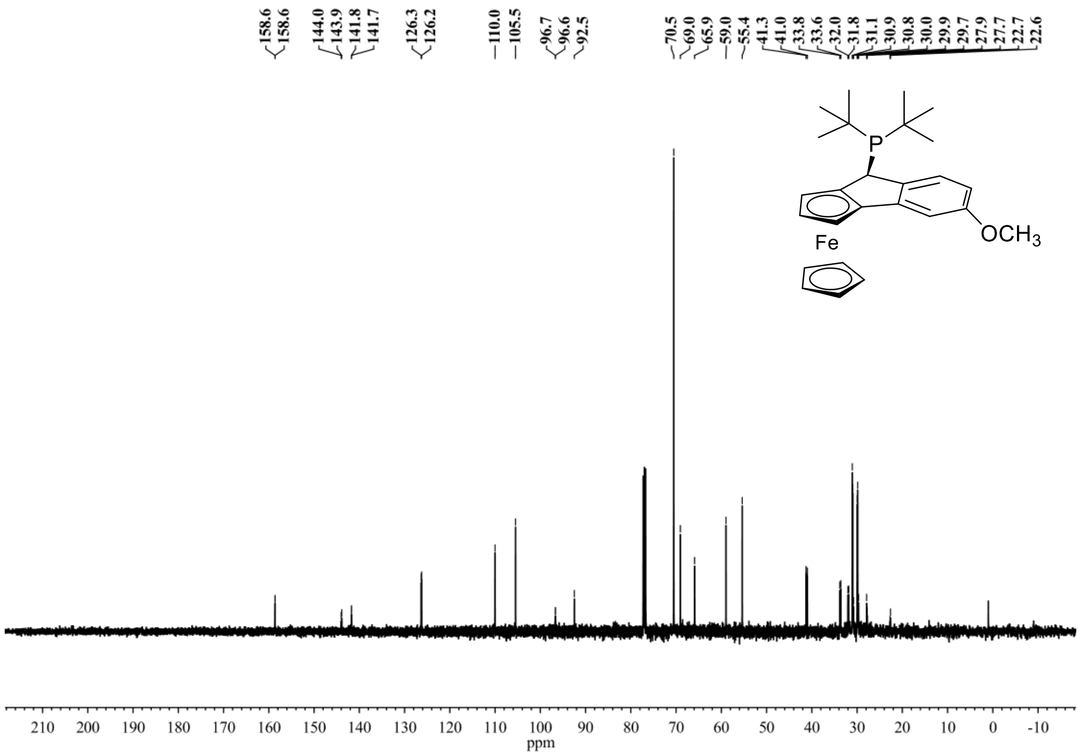


Figure S55. **^{13}C NMR** of **3g** (126 MHz, $CDCl_3$)

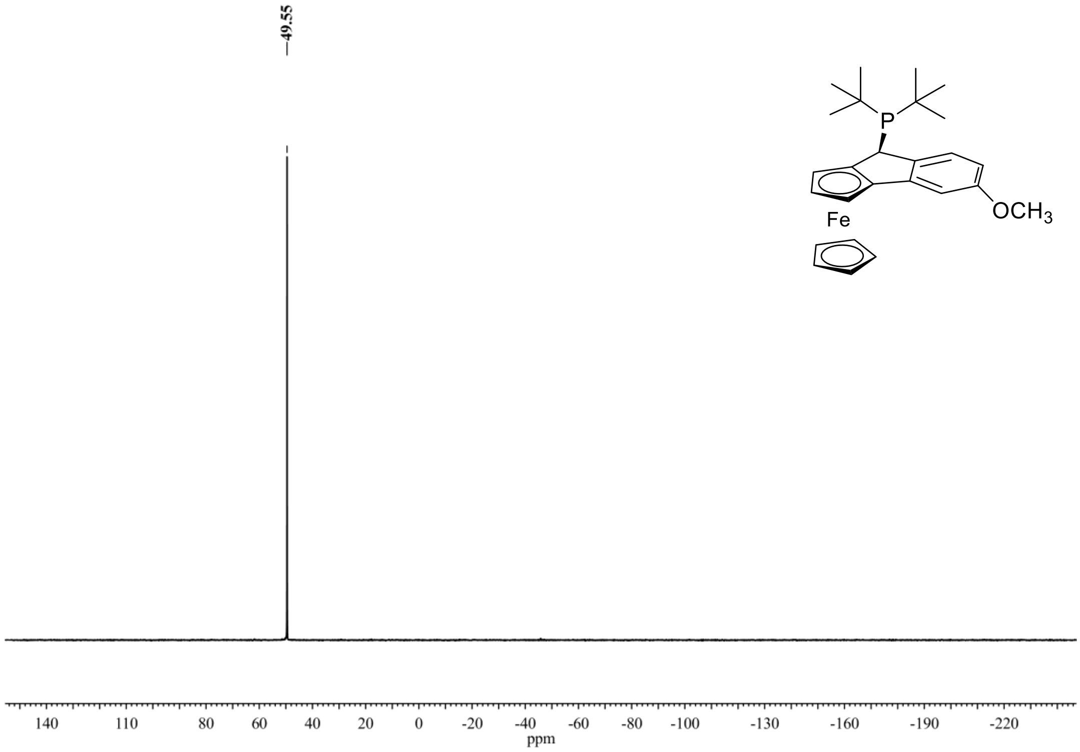


Figure S56. **^{31}P NMR** of **3g** (202 MHz, $CDCl_3$)

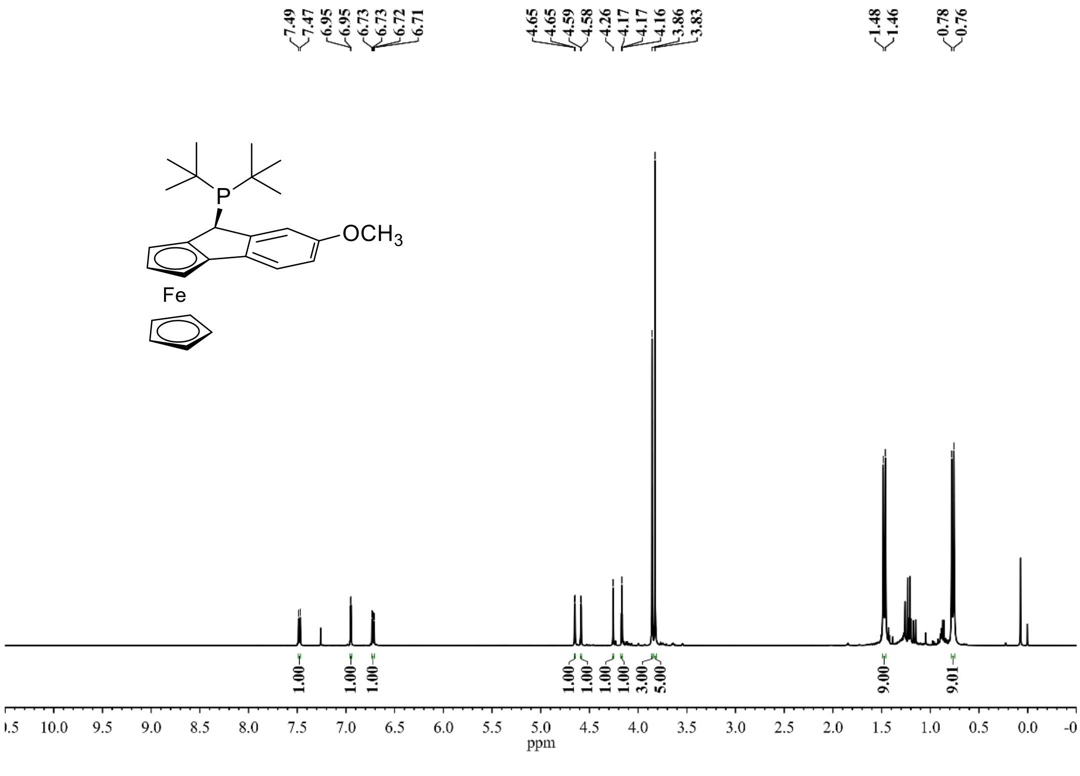


Figure S57. **^{1}H NMR** of **3h** (500 MHz, $CDCl_3$)

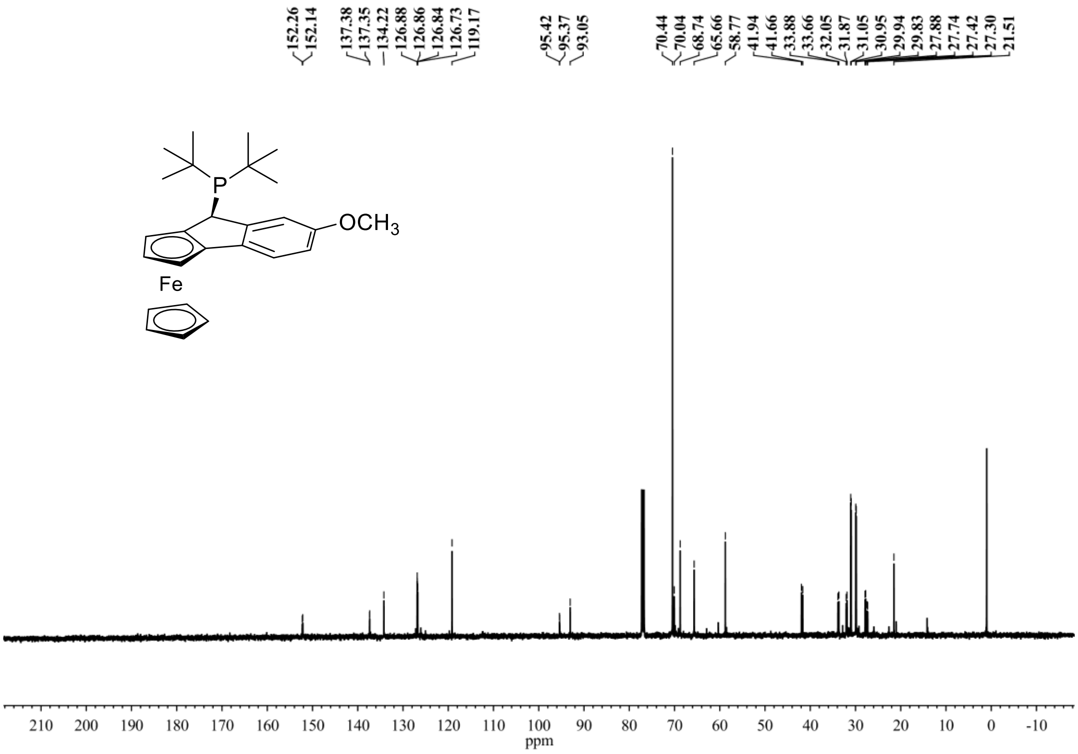


Figure S58. **^{13}C NMR** of **3h** (126 MHz, $CDCl_3$)

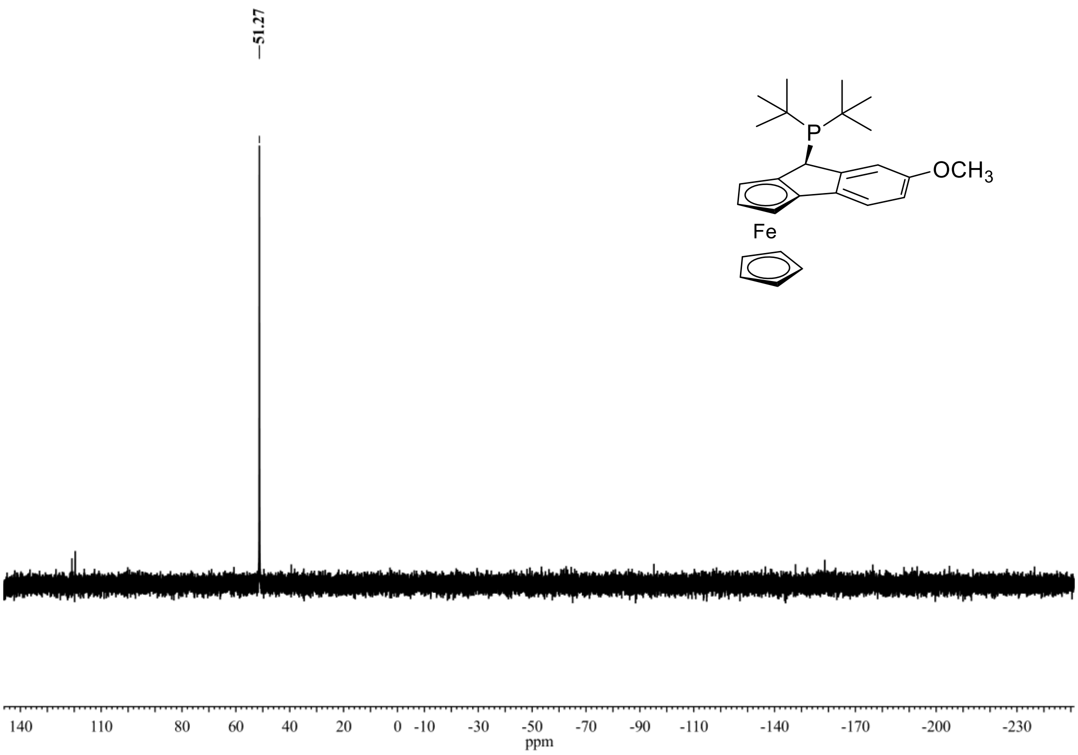


Figure S59. **^{31}P NMR** of **3h** (202 MHz, $CDCl_3$)

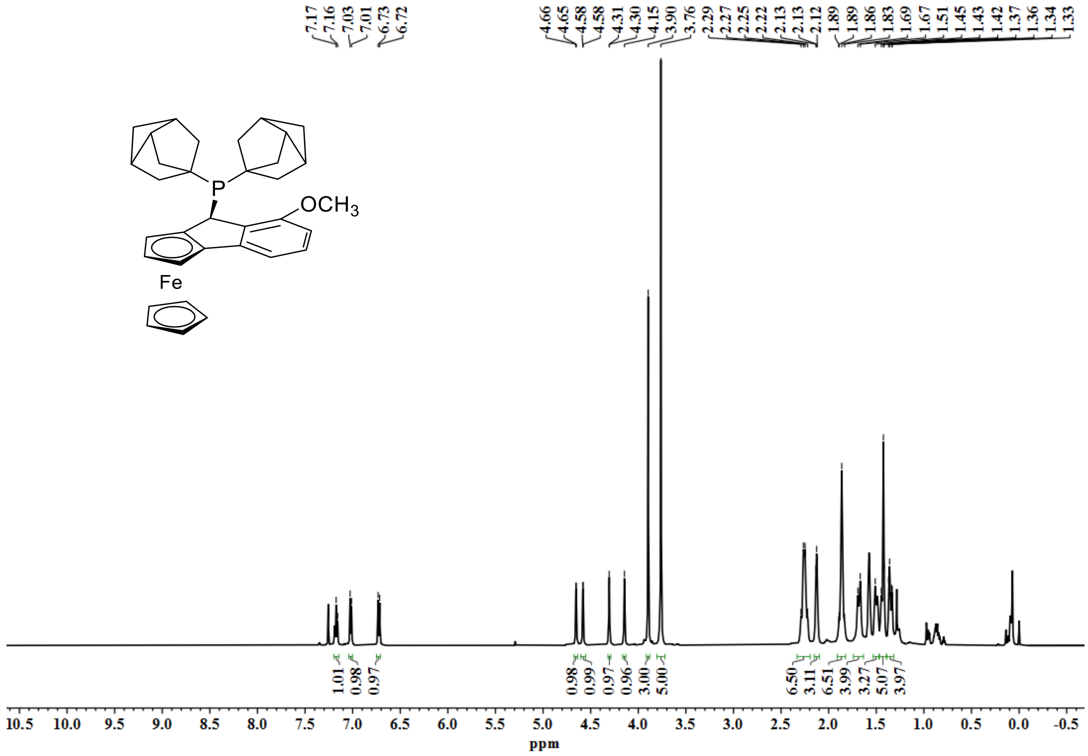


Figure S60. **^{1}H NMR** of **3i** (500 MHz, $CDCl_3$)

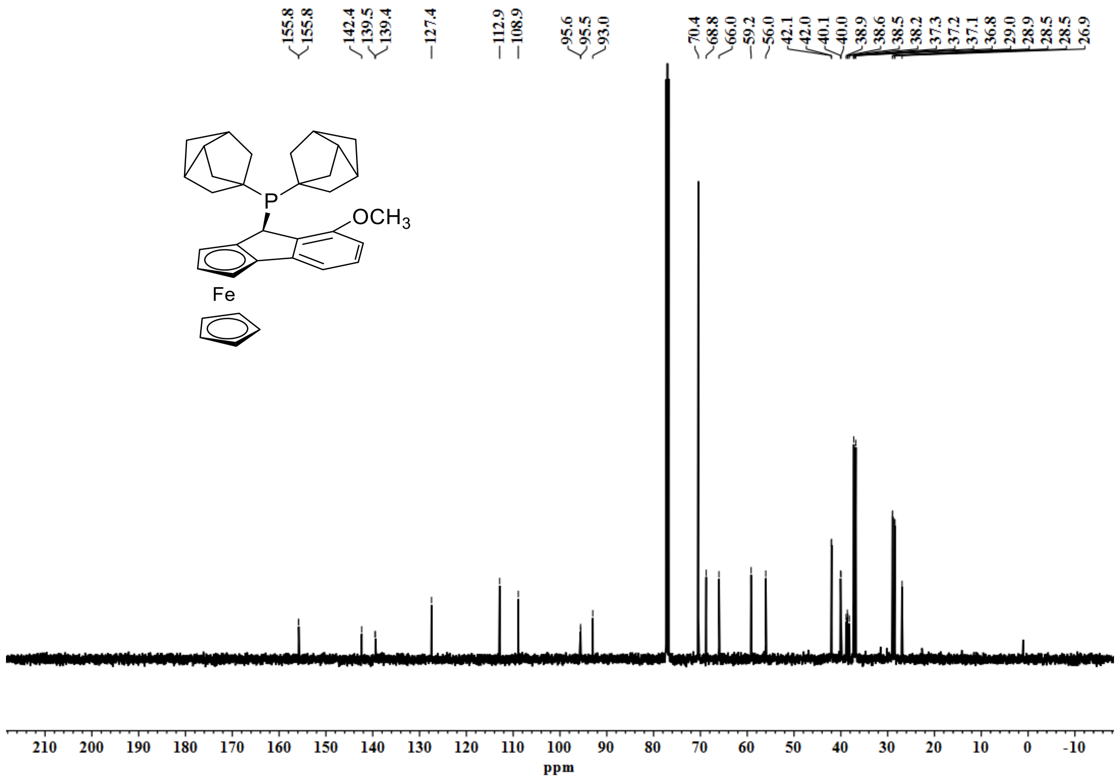


Figure S61. **^{13}C NMR** of **3i** (126 MHz, $CDCl_3$)

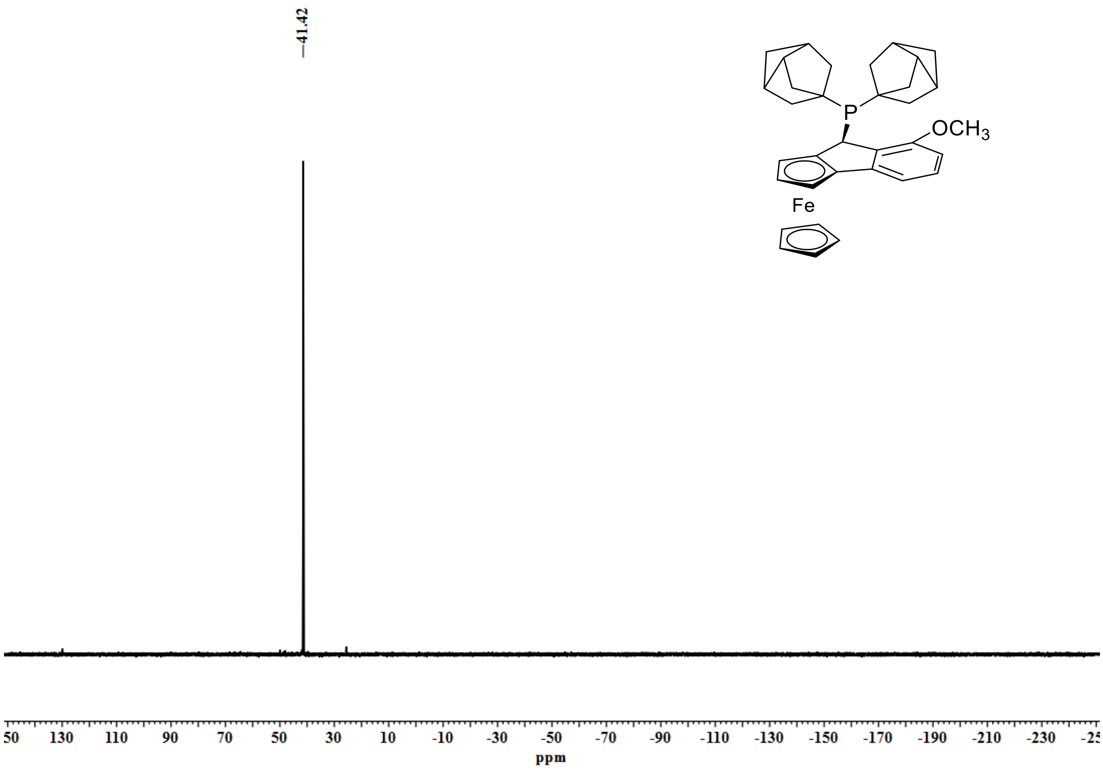


Figure S62. ^{31}**P NMR** of **3i** (202 MHz, CDCl3)

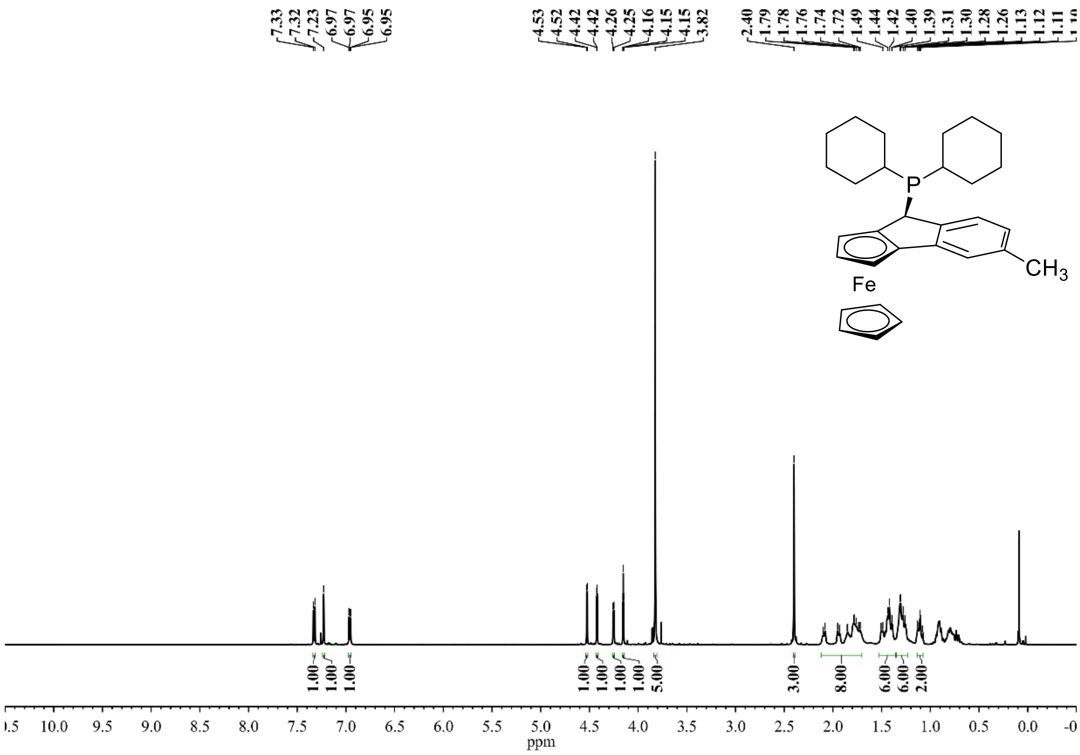


Figure S63. ^{1}**H NMR** of **3j** (500 MHz, $CDCl_3$)

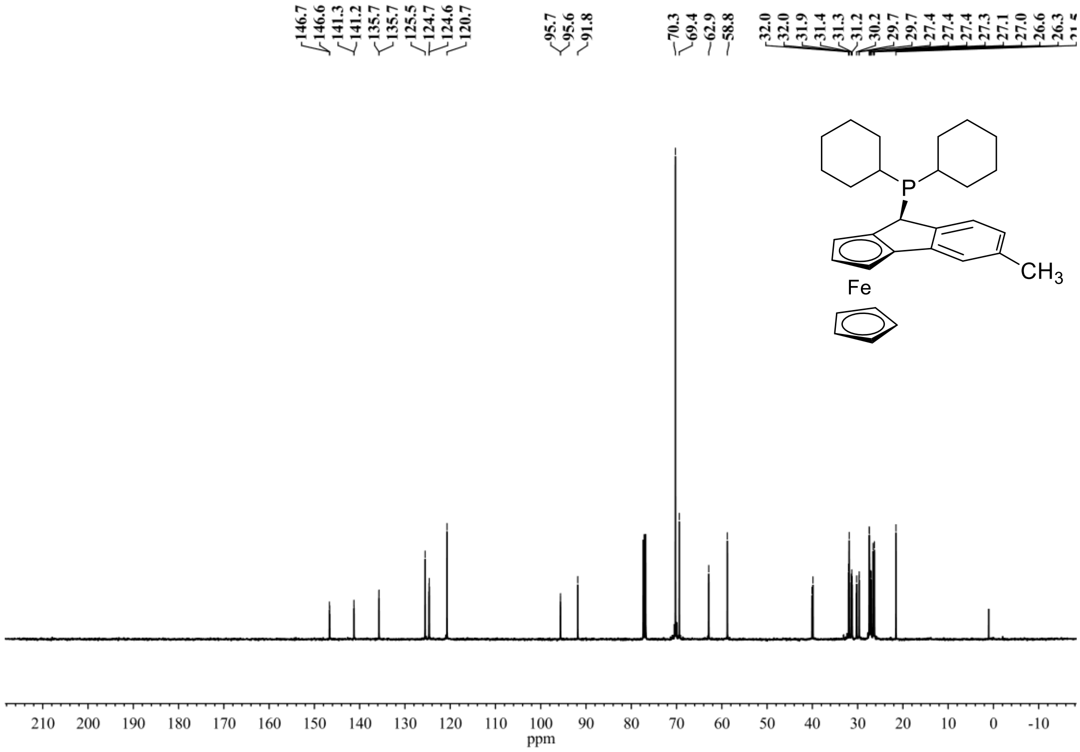


Figure S64. **^{13}C NMR** of **3j** (126 MHz, $CDCl_3$)

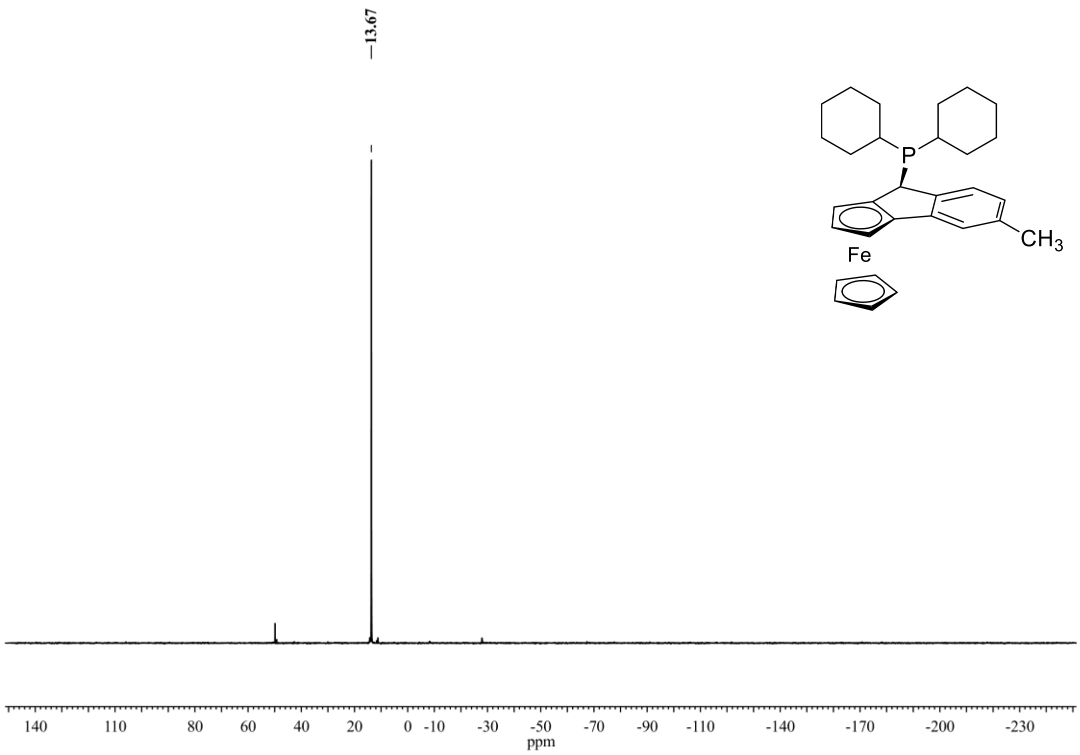


Figure S65. **^{31}P NMR** of **3j** (202 MHz, $CDCl_3$)

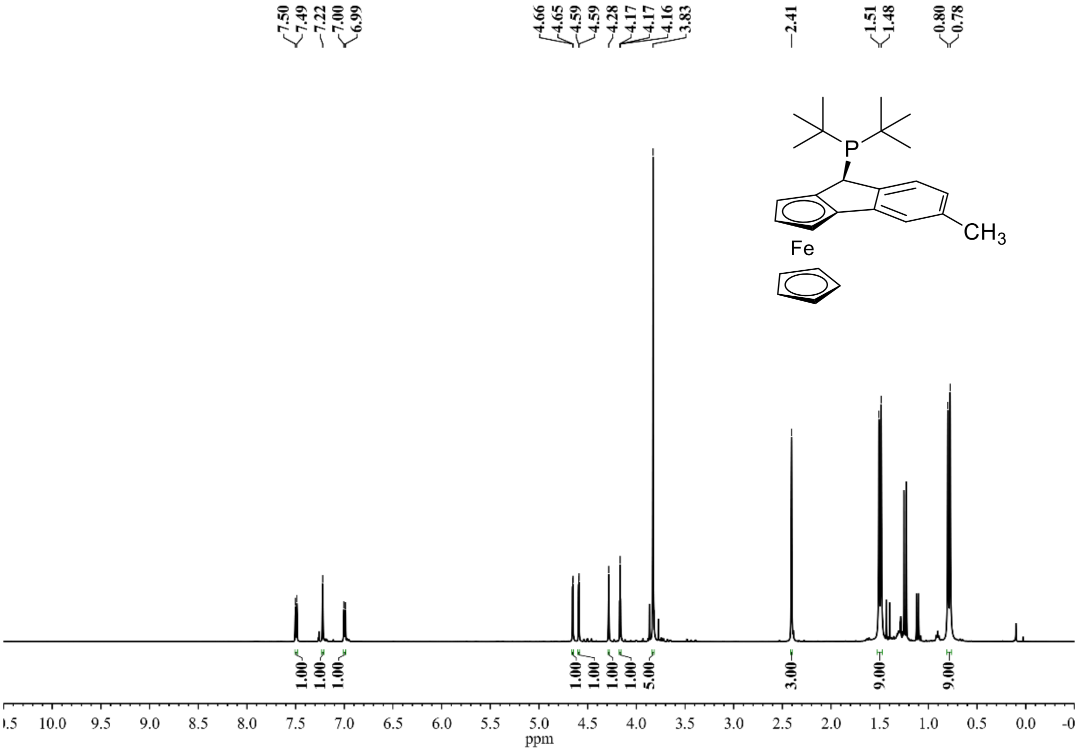


Figure S66. **^{1}H NMR** of **3k** (500 MHz, $CDCl_3$)

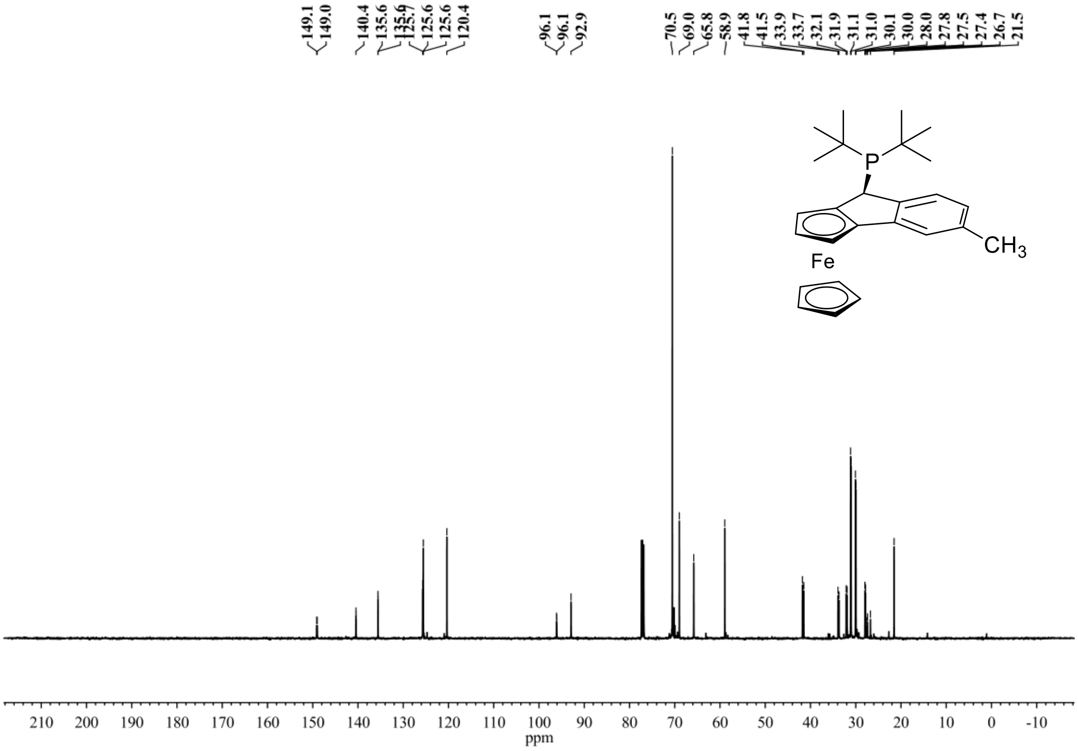


Figure S67. **^{13}C NMR** of **3k** (126 MHz, $CDCl_3$)

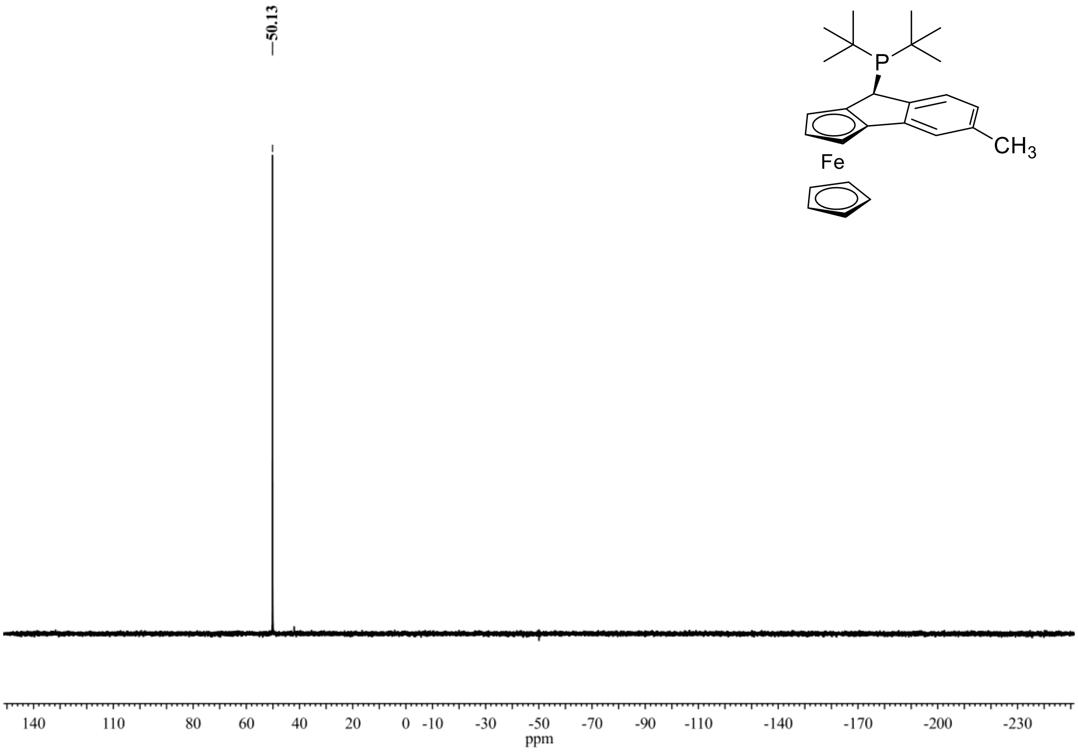


Figure S68. **^{31}P NMR** of **3k** (202 MHz, $CDCl_3$)

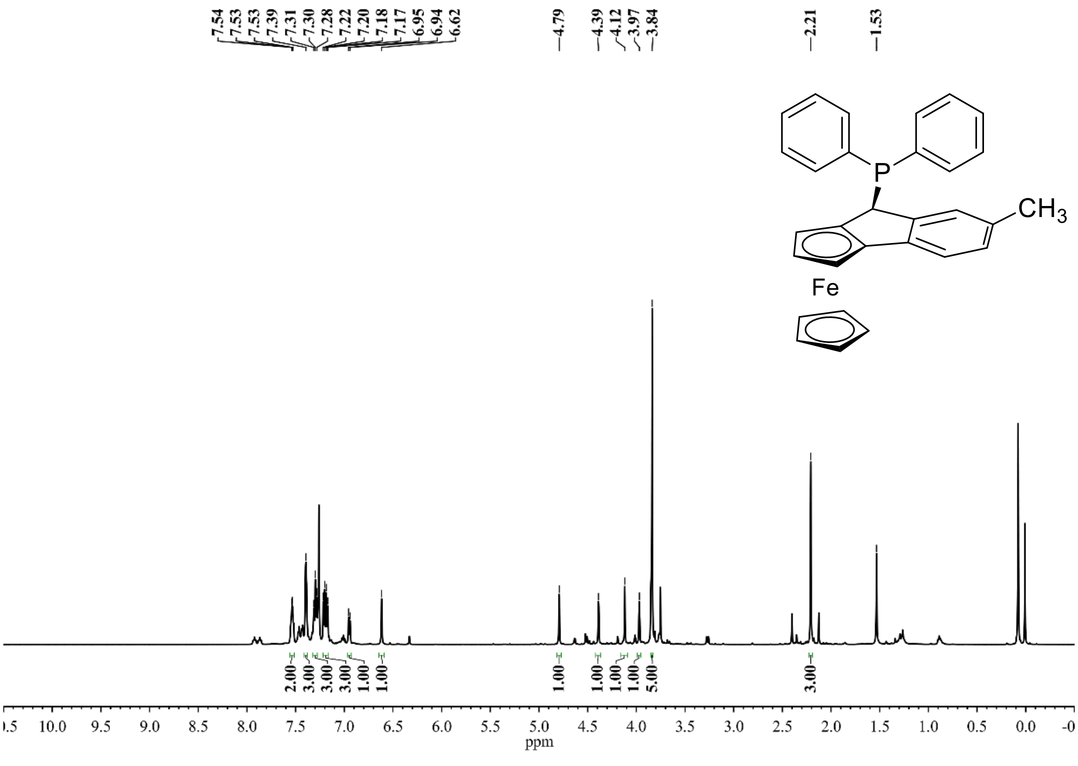


Figure S69. **^{1}H NMR** of **3l** (500 MHz, $CDCl_3$)

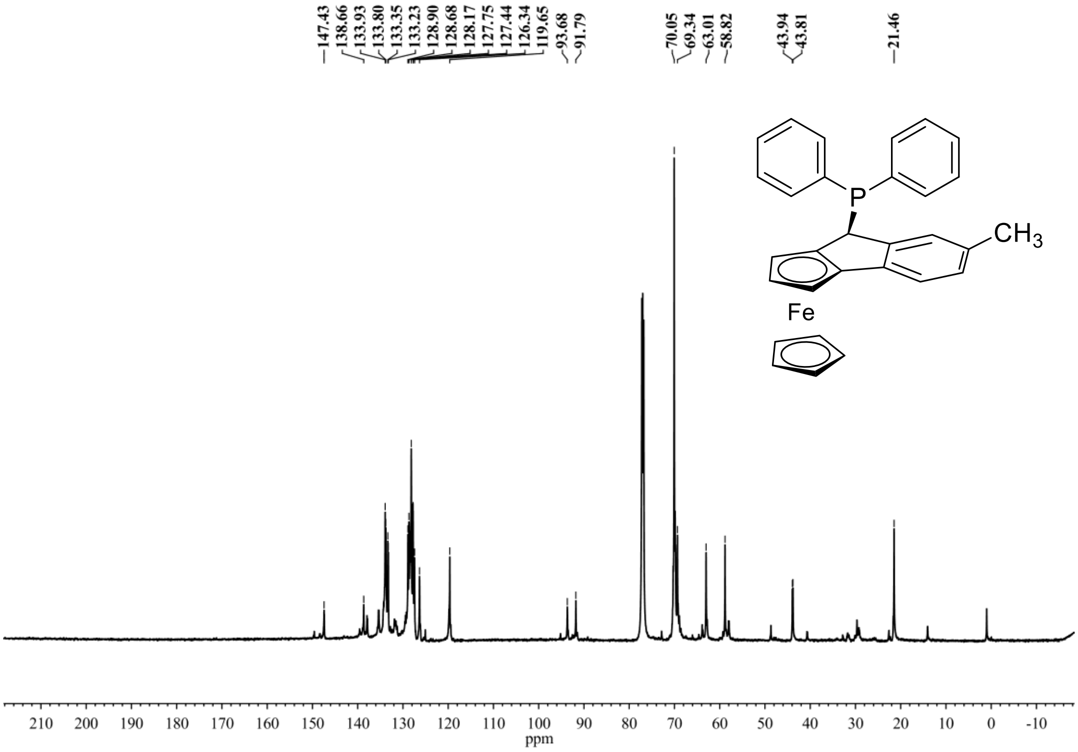


Figure S70. **^{13}C NMR** of **3l** (126 MHz, $CDCl_3$)

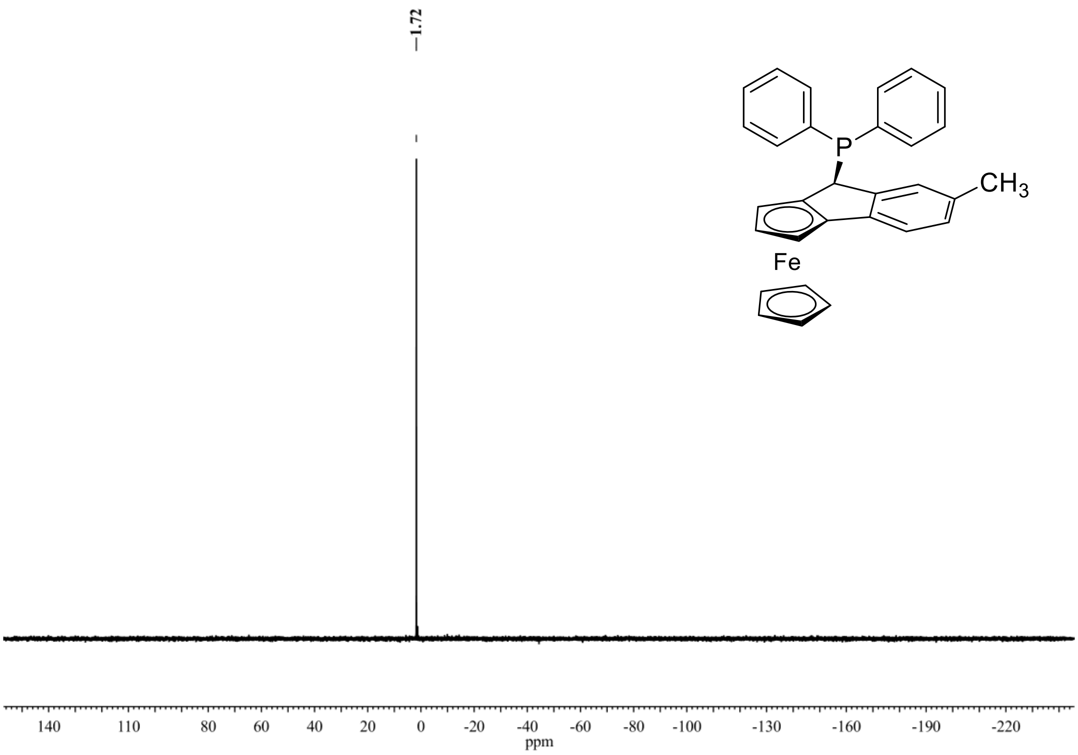


Figure S71. **^{31}P NMR** of **3l** (202 MHz, $CDCl_3$)

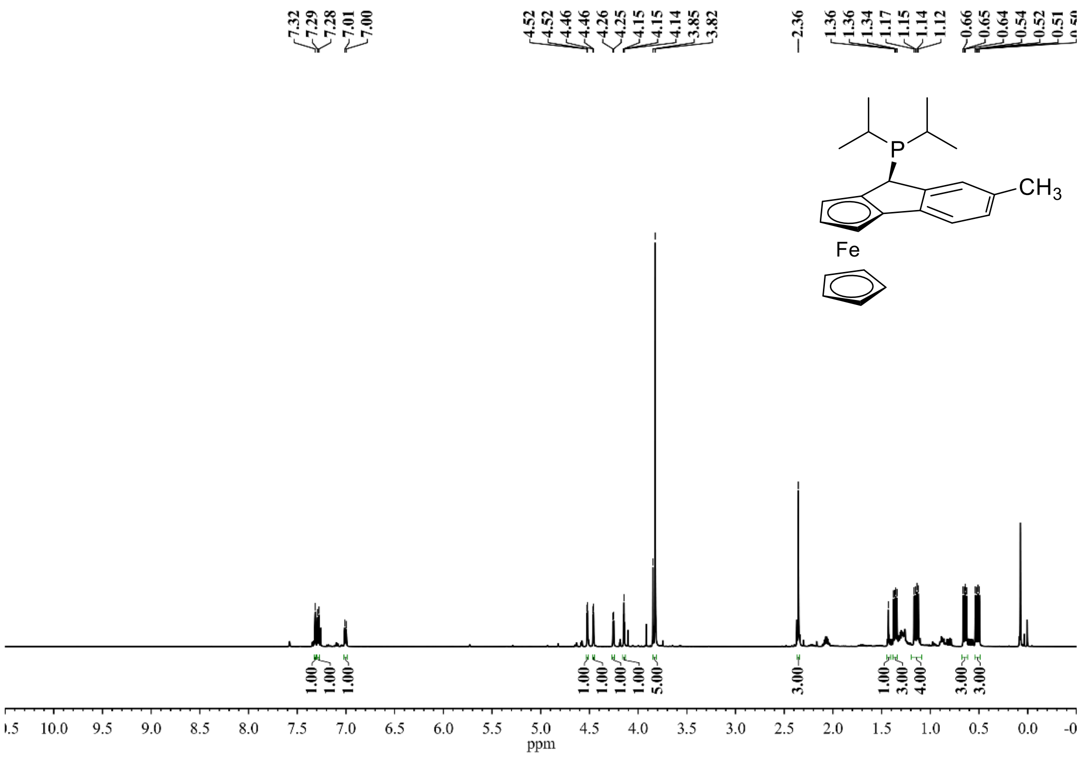


Figure S72. **^{1}H NMR** of **3m** (500 MHz, $CDCl_3$)

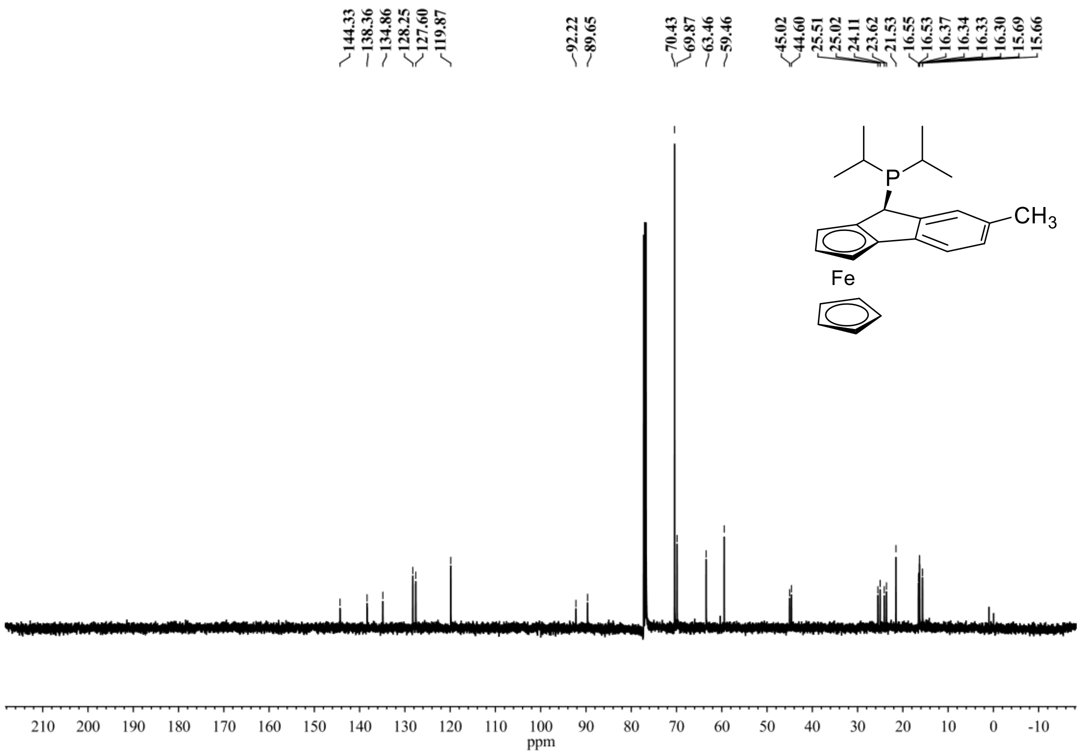


Figure S73**. ^{13}C NMR** of **3m** (126 MHz, $CDCl_3$)

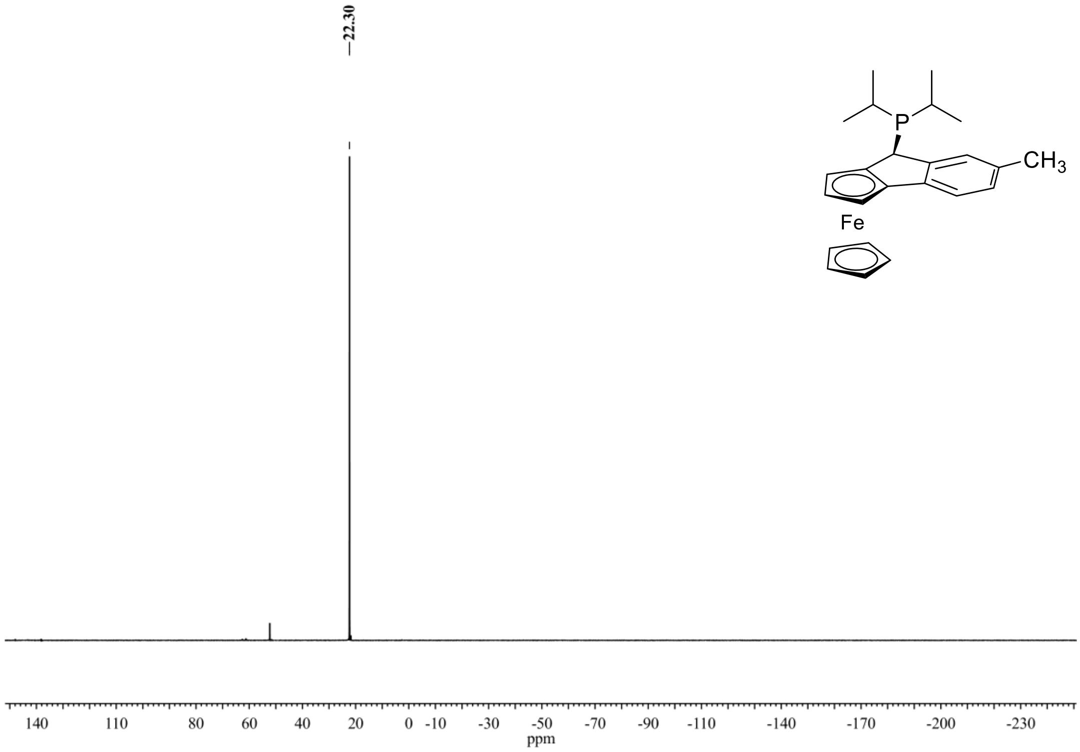


Figure S74. **^{31}P NMR** of **3m** (202 MHz, $CDCl_3$)

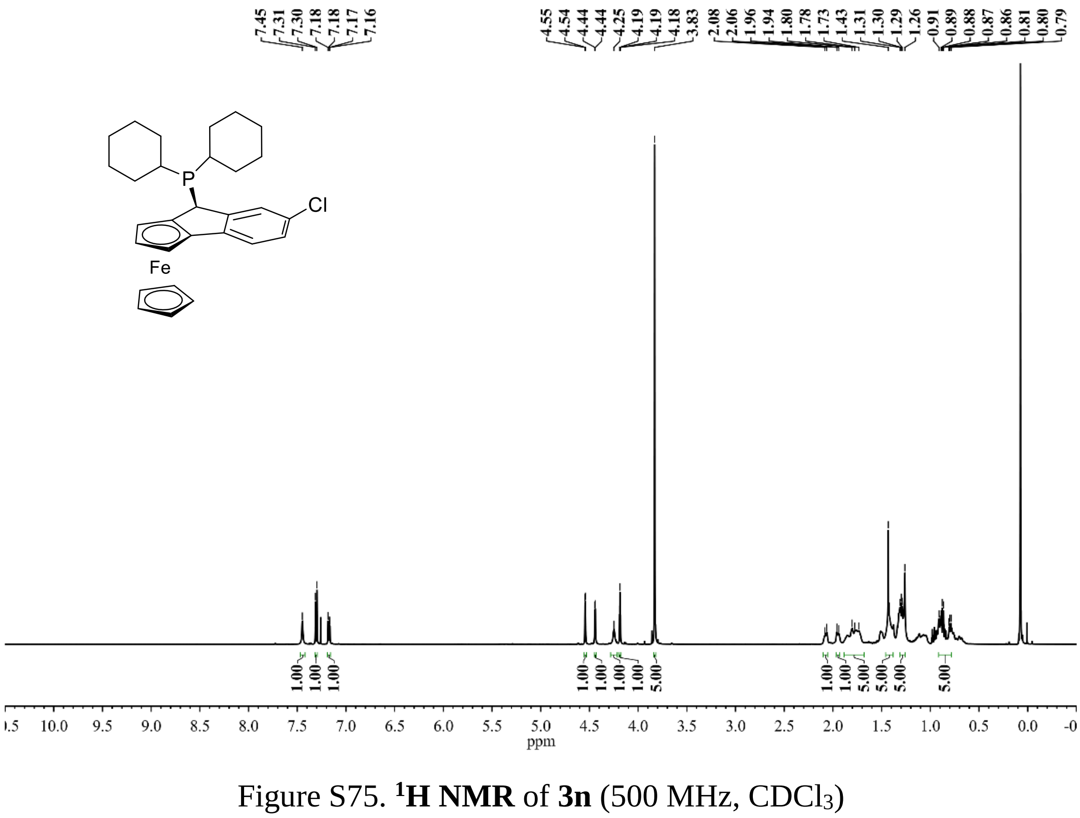


Figure S75. **^{1}H NMR** of **3n** (500 MHz, $CDCl_3$)

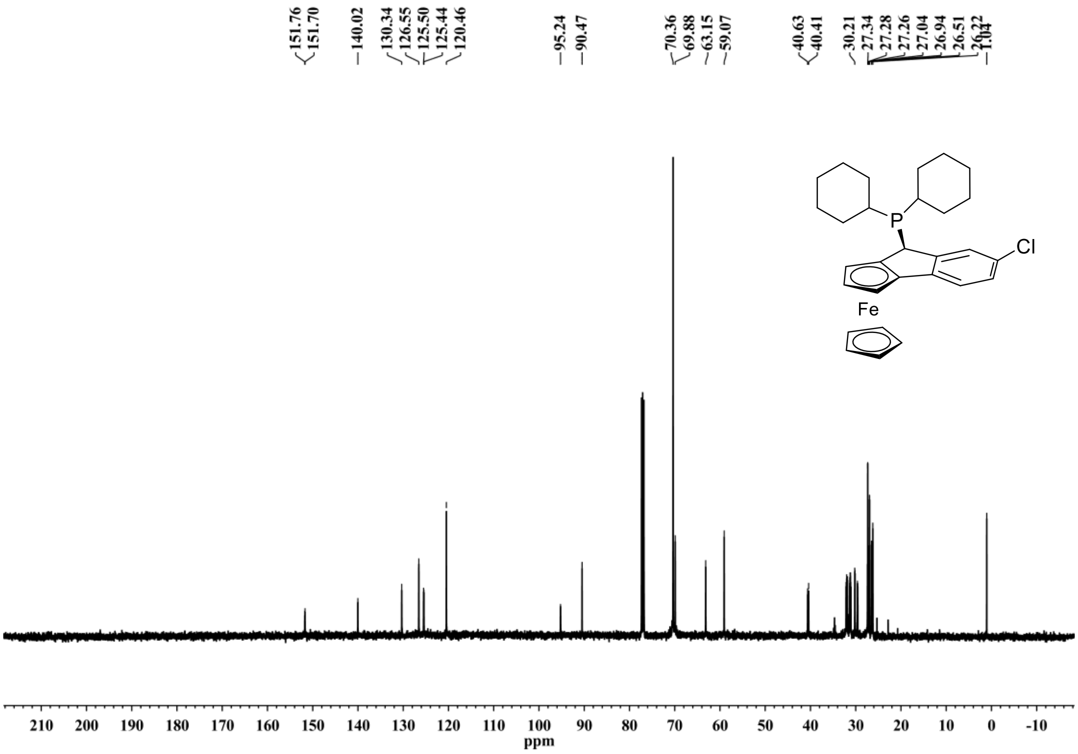


Figure S76. ^{13}**C NMR** of **3n** (126 MHz, $CDCl_3$)

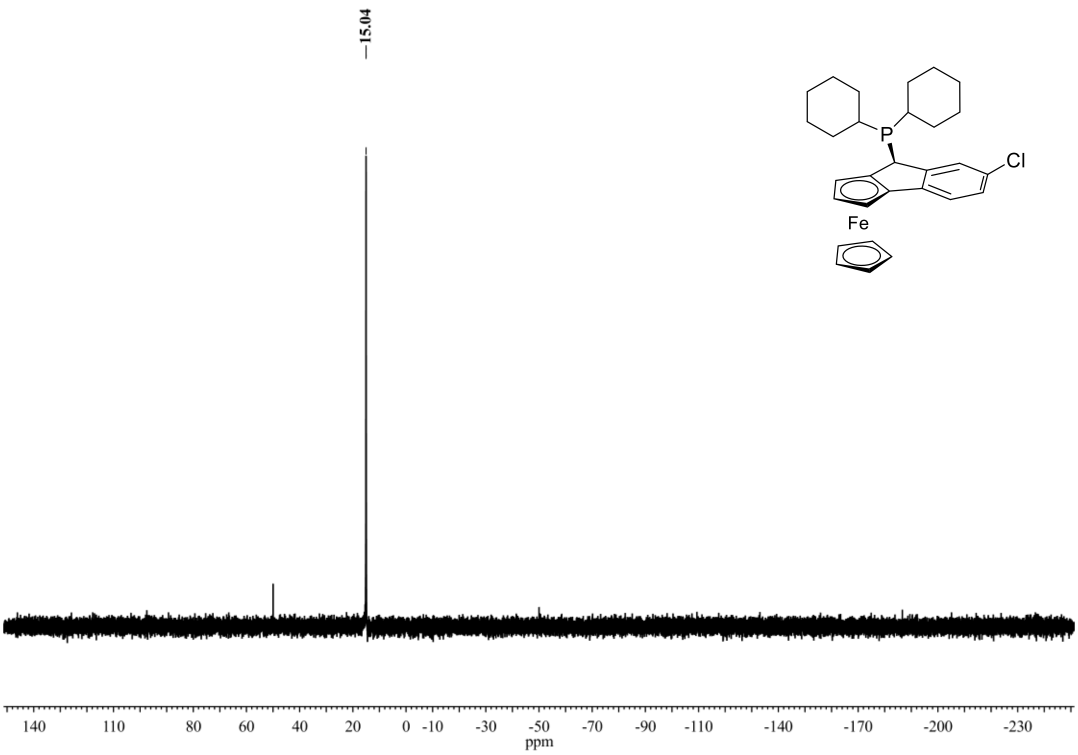


Figure S77. ^{31}**P NMR** of **3n** (202 MHz, $CDCl_3$)

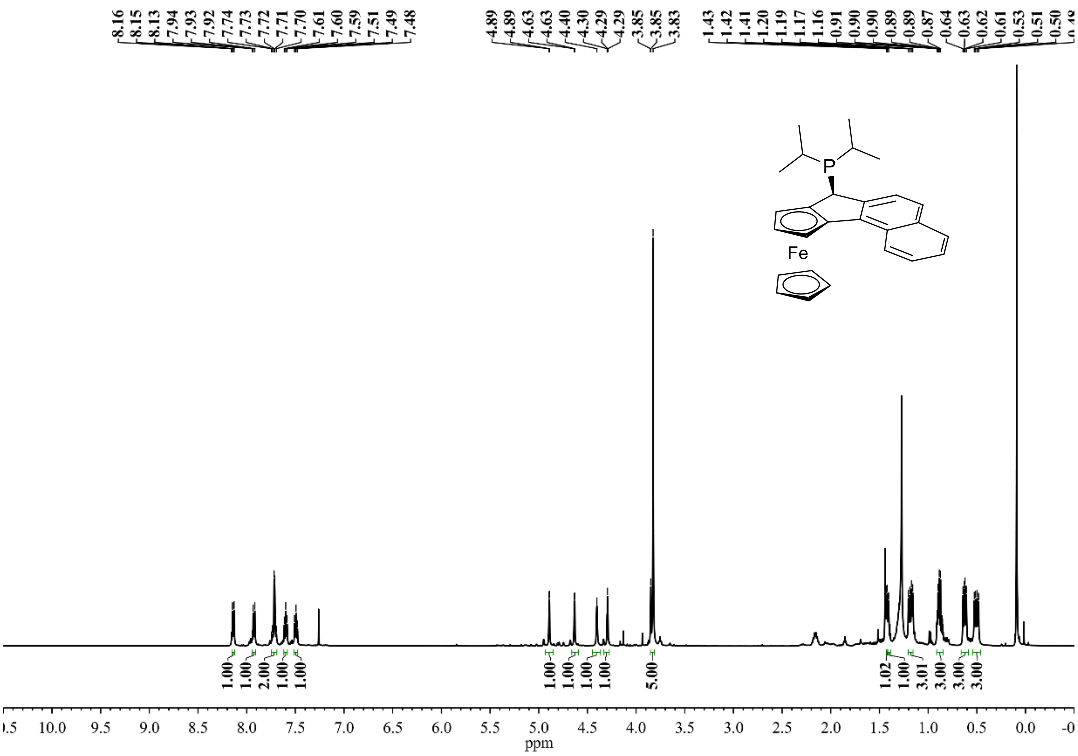


Figure S78. **^{1}H NMR** of **3o** (500 MHz, $CDCl_3$)

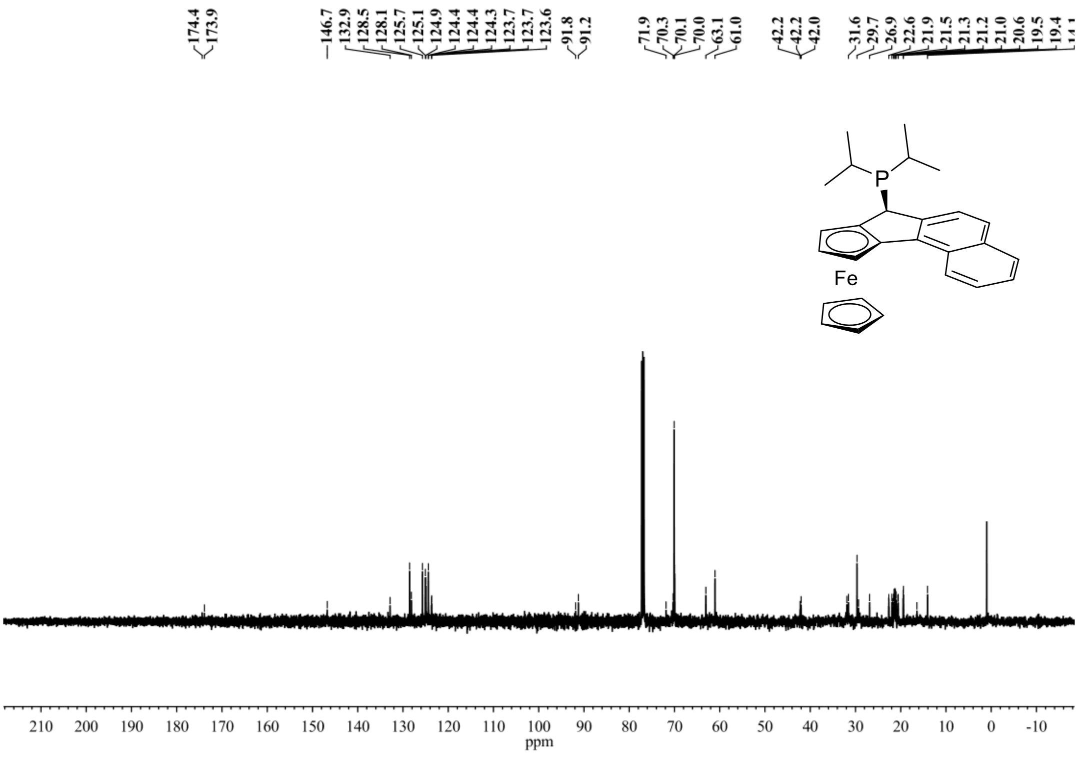


Figure S79. **^{13}C NMR** of **3o** (126 MHz, $CDCl_3$)

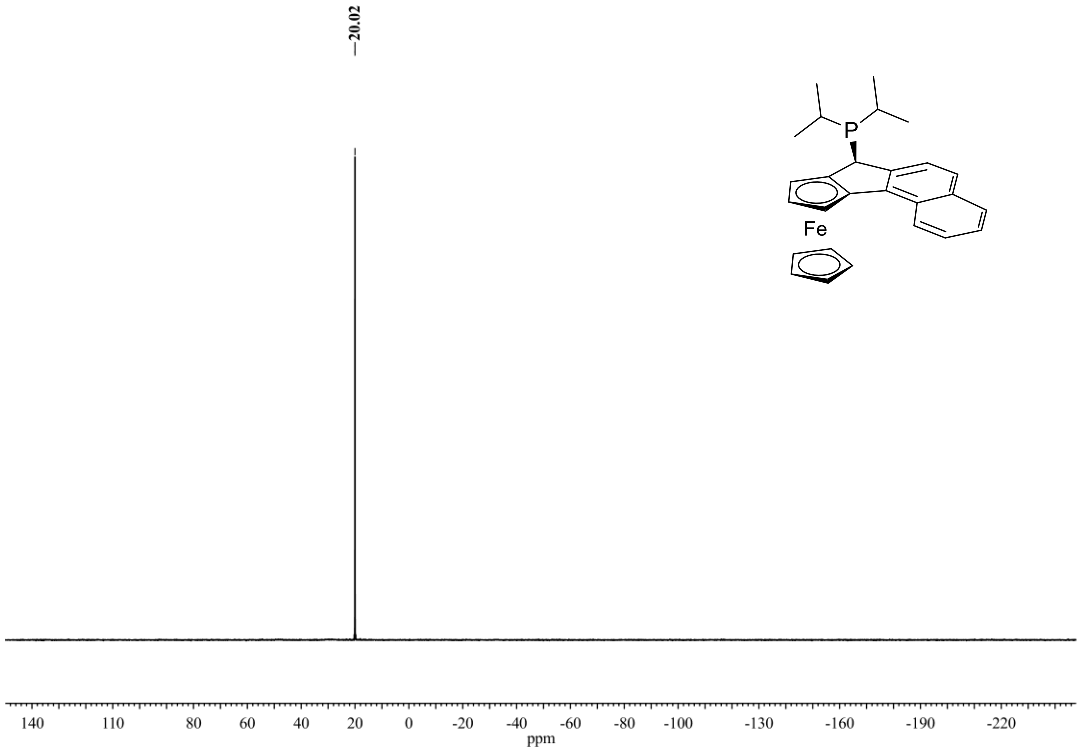


Figure S80. **^{31}P NMR** of **3o** (202 MHz, $CDCl_3$)

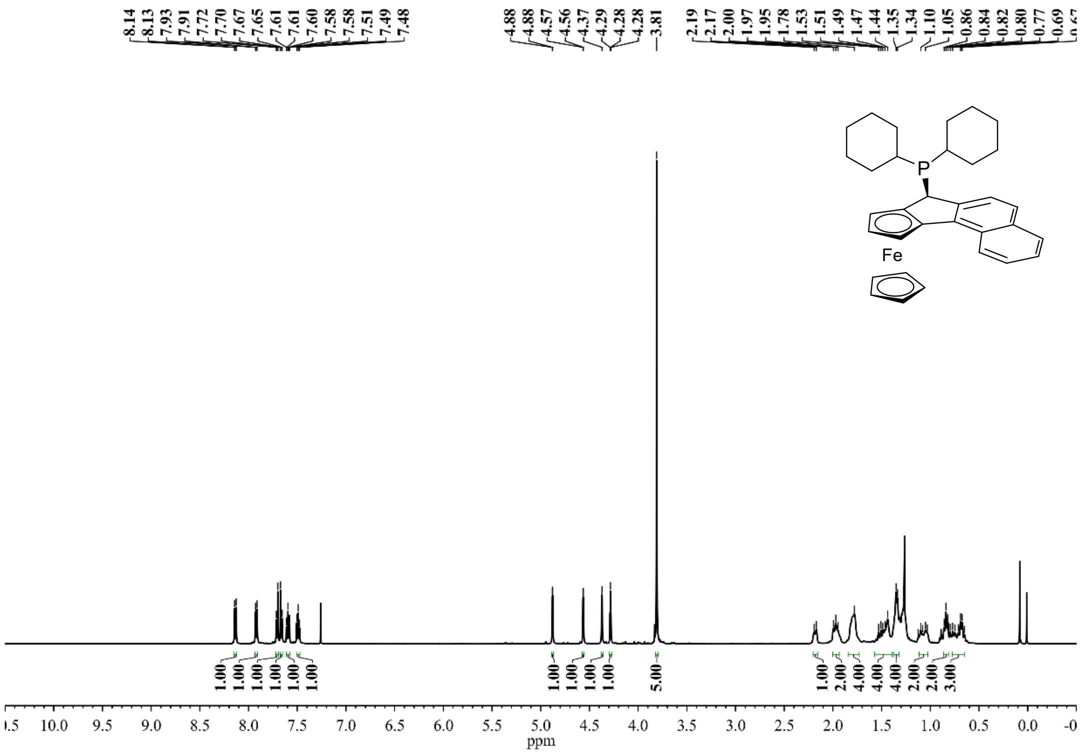


Figure S81. **^{1}H NMR** of **3p** (500 MHz, $CDCl_3$)

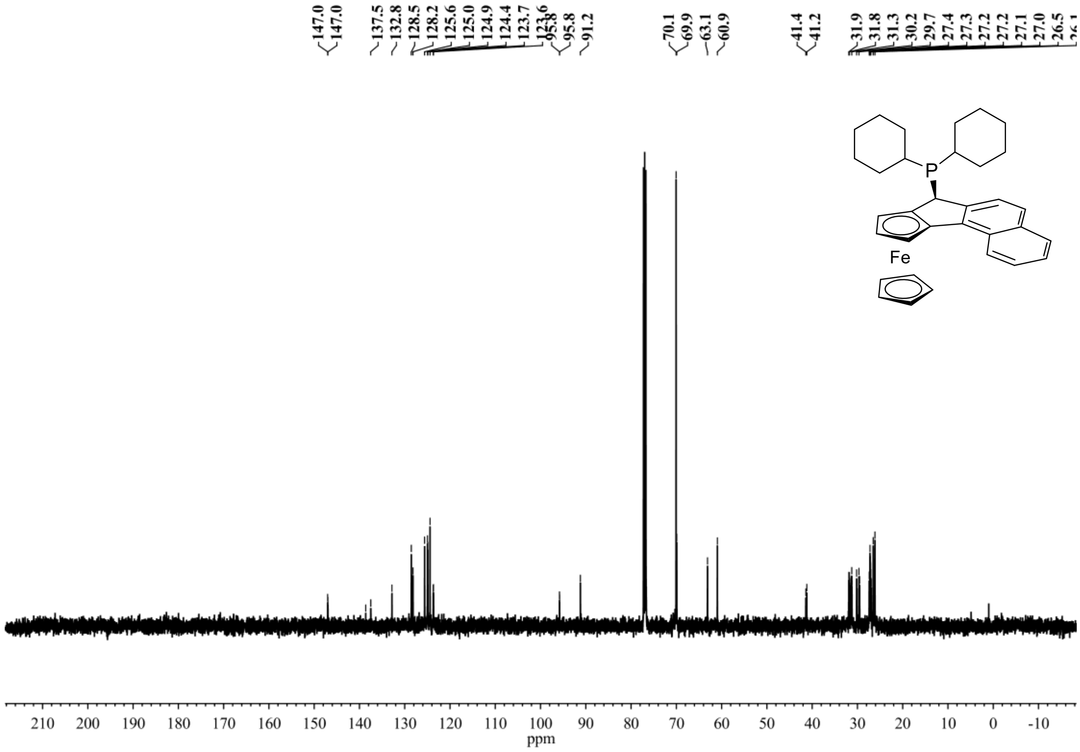


Figure S82. **^{13}C NMR** of **3p** (126 MHz, $CDCl_3$)

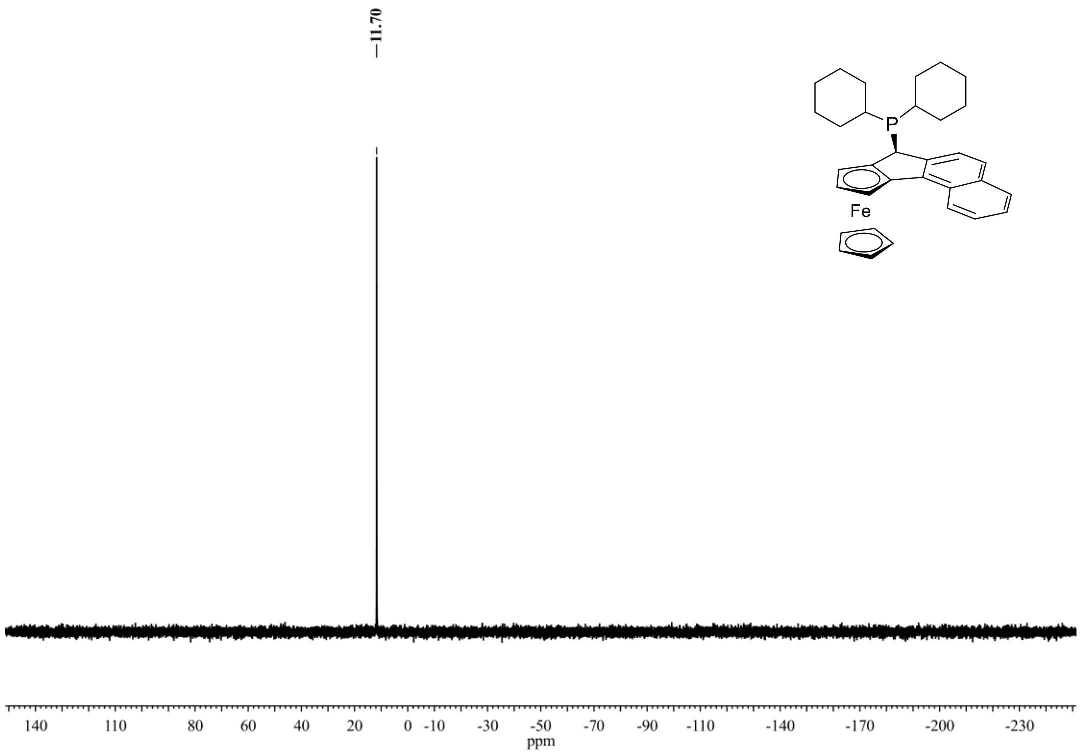


Figure S83**.** **^{31}P NMR** of **3p** (202 MHz, $CDCl_3$)

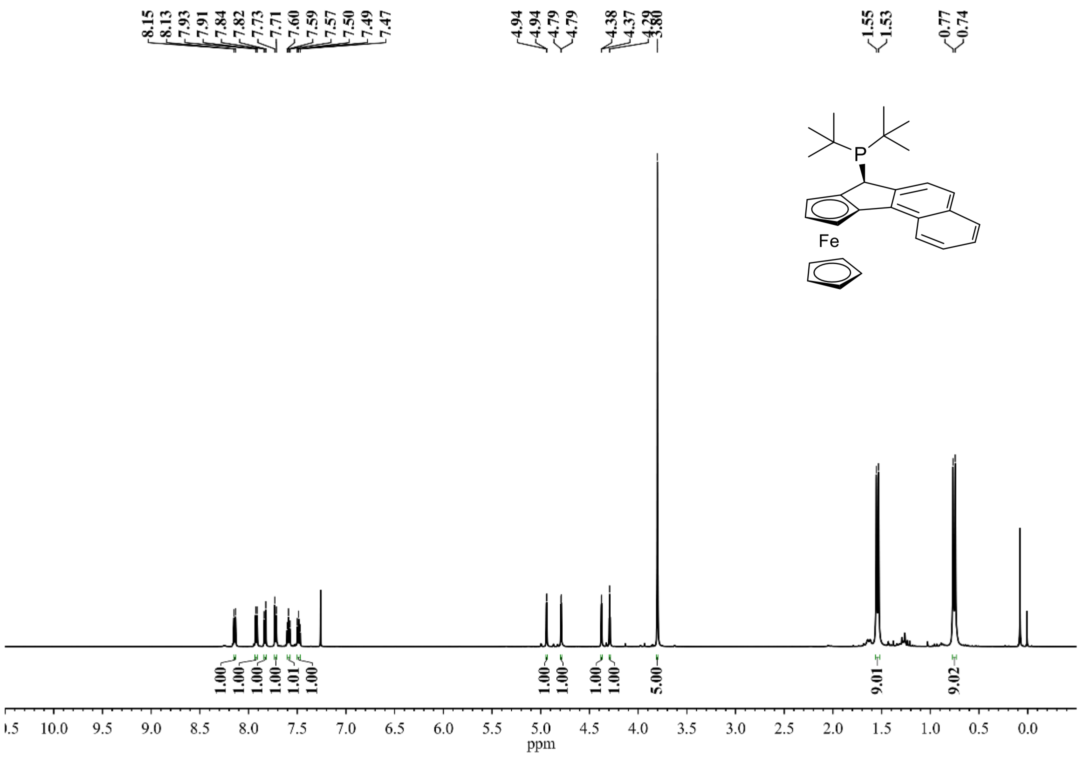


Figure S84. **^{1}H NMR** of **3q** (500 MHz, $CDCl_3$)

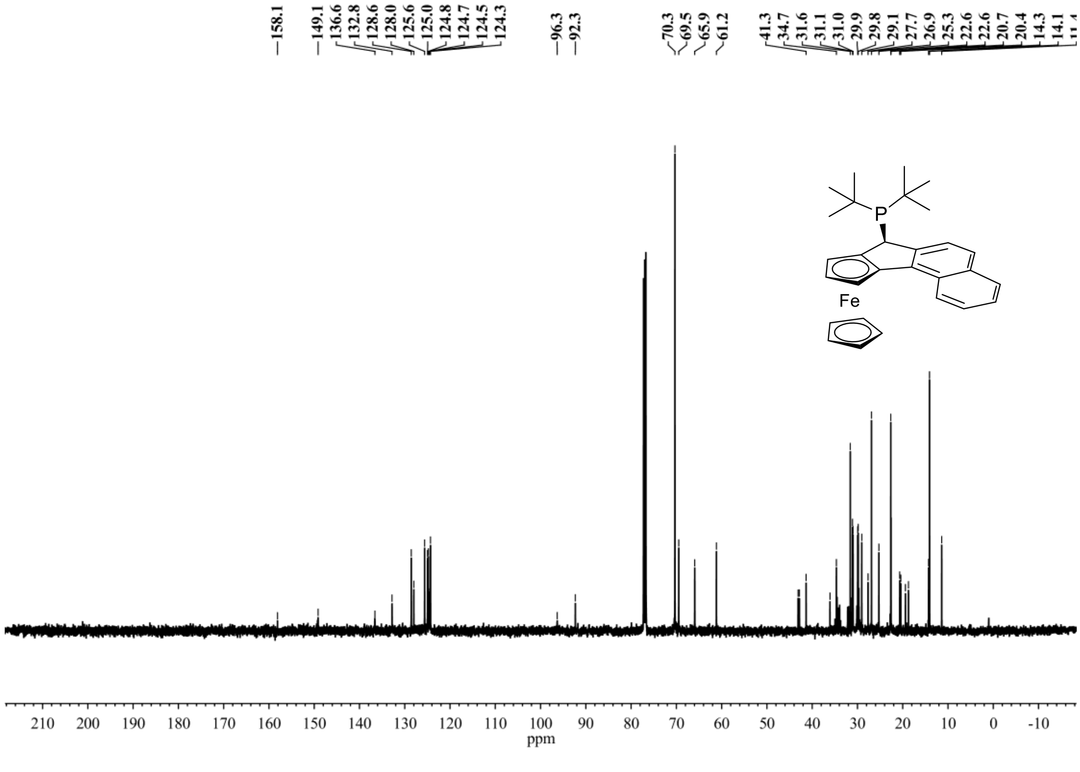


Figure S85. **^{13}C NMR** of **3q** (126 MHz, $CDCl_3$)

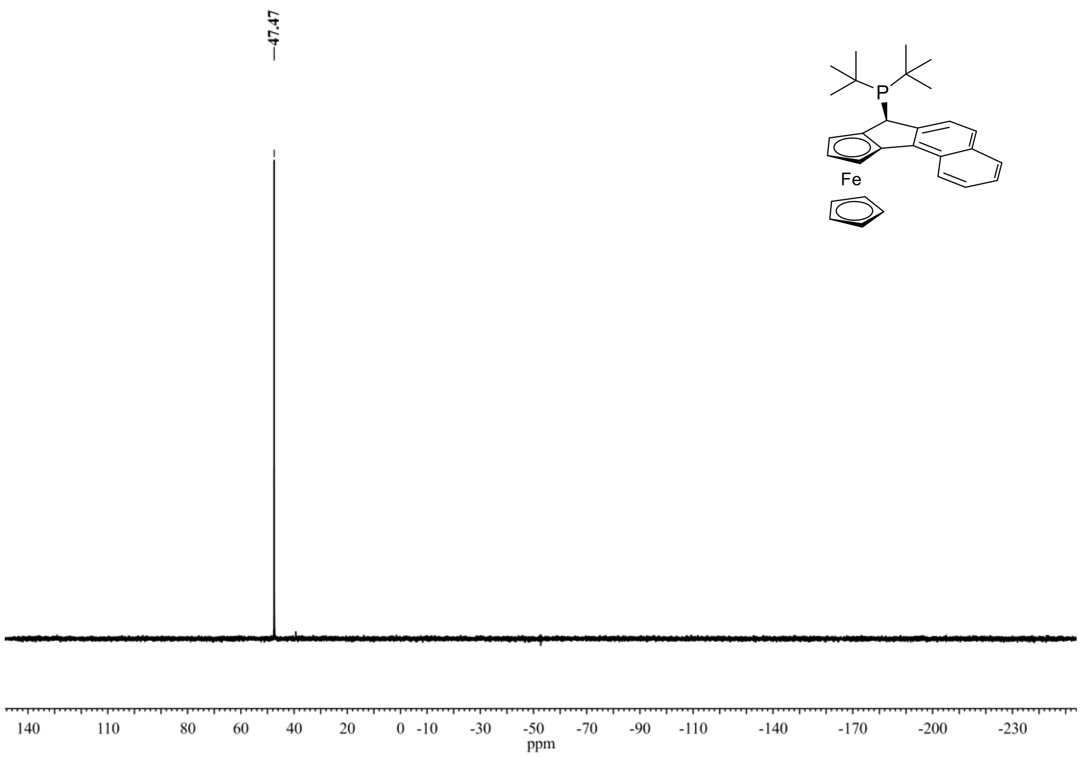


Figure S86. **^{31}P NMR** of **3q** (202 MHz, $CDCl_3$)

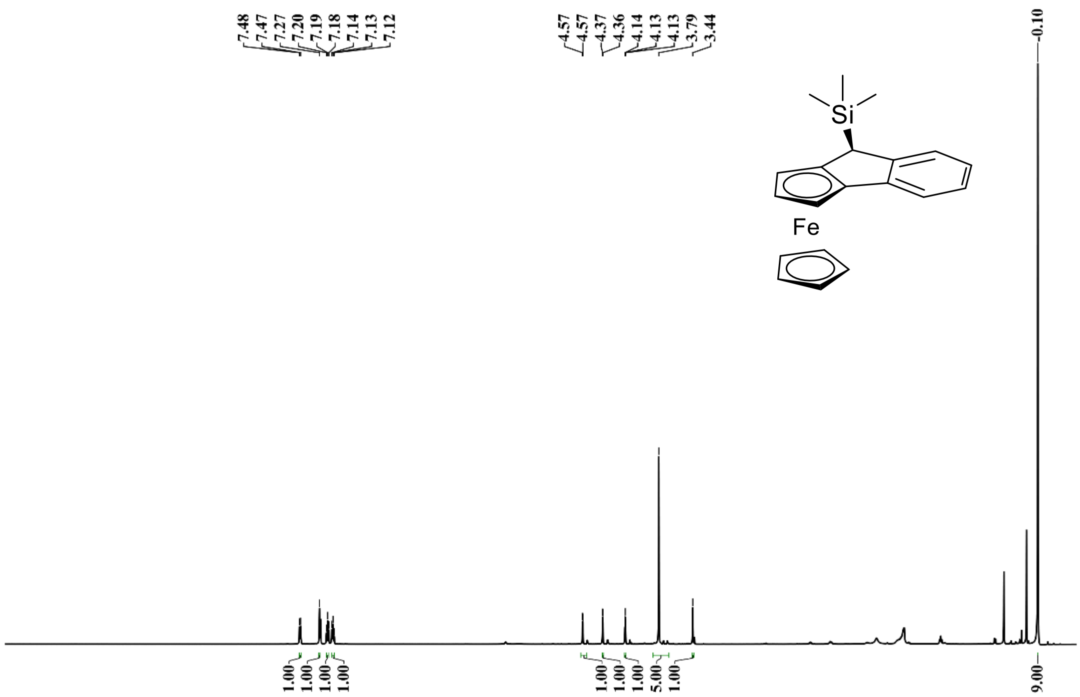


Figure S87. **^{1}H NMR** of **3r** (500 MHz, $CDCl_3$)

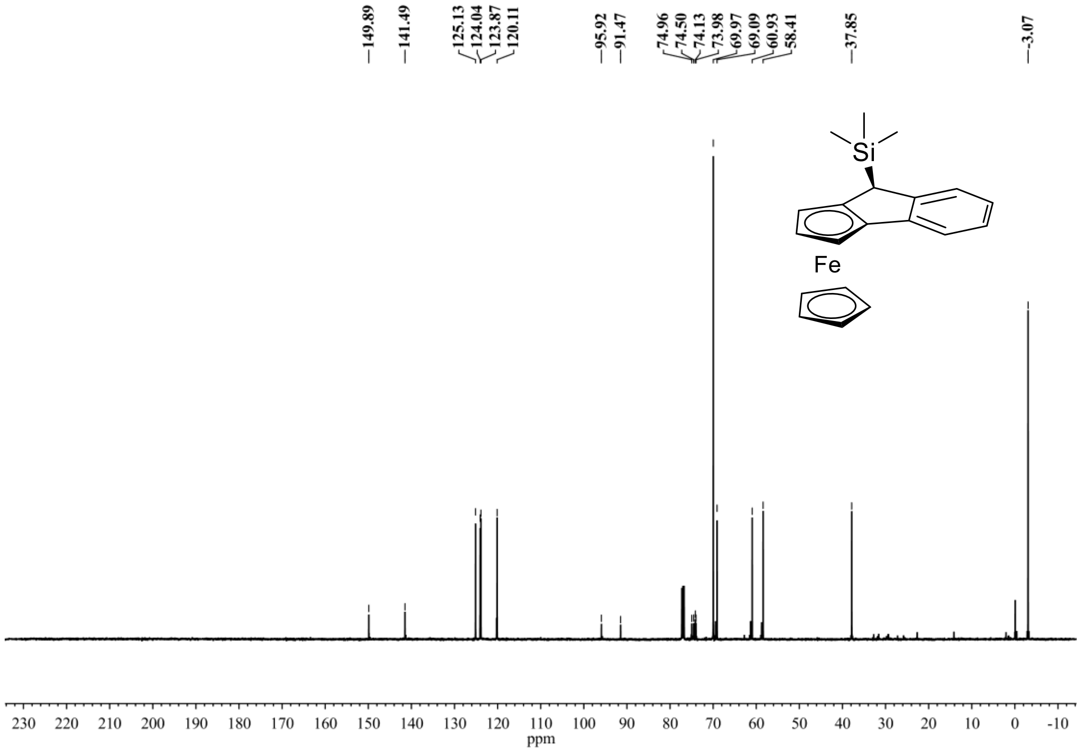


Figure S88. **^{13}C NMR** of **3r** (126 MHz, $CDCl_3$)

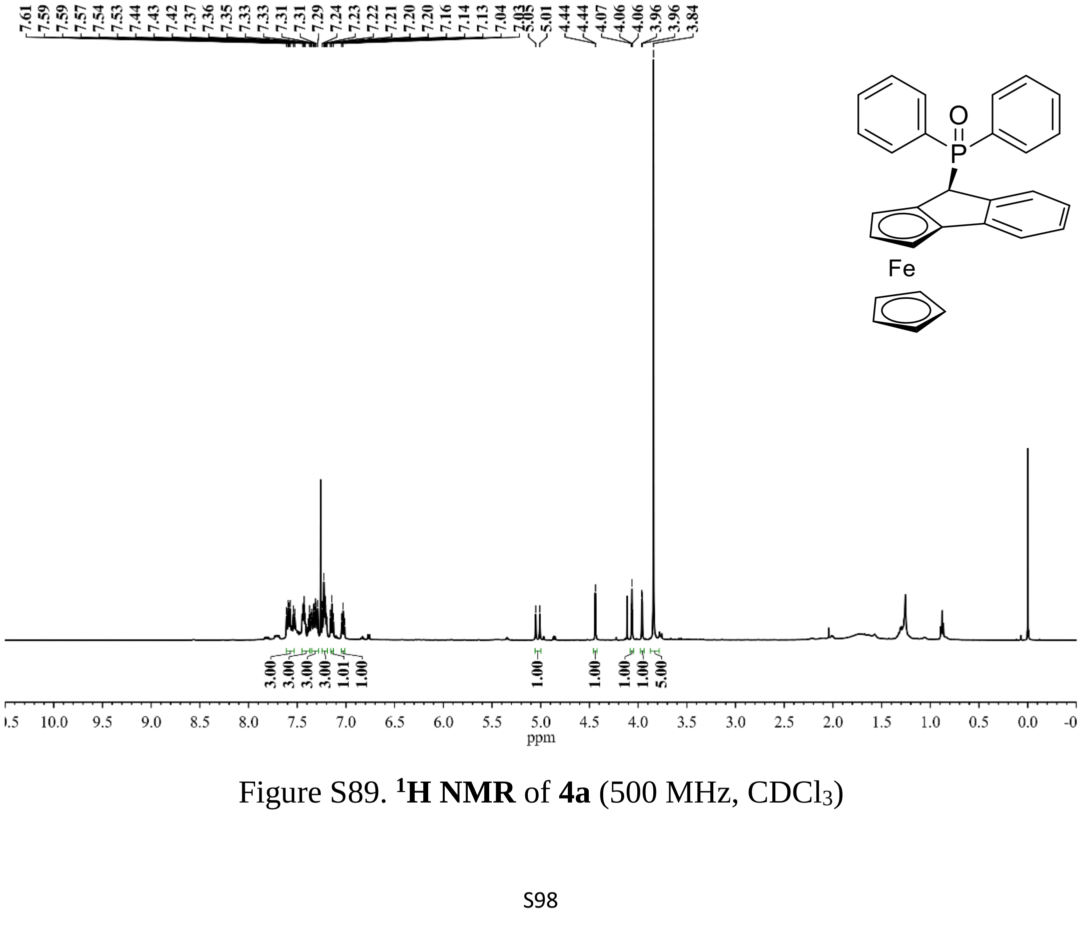


Figure S89. **^{1}H NMR** of **4a** (500 MHz, $CDCl_3$)

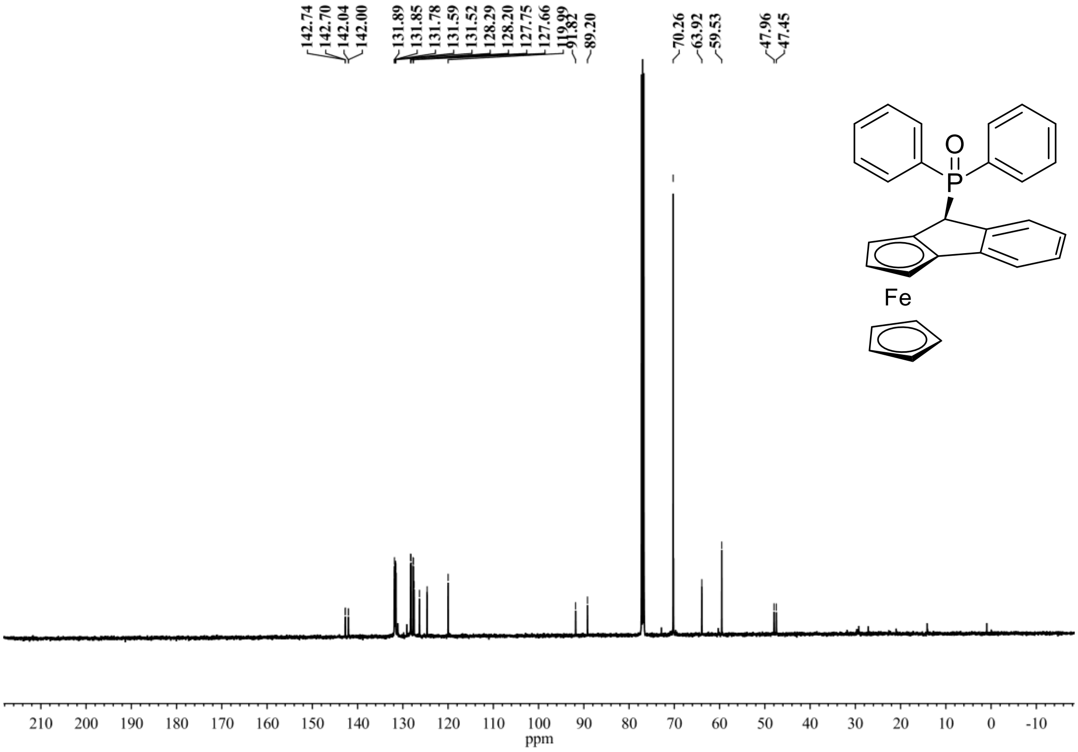


Figure S90. **^{13}C NMR** of **4a** (126 MHz, $CDCl_3$)

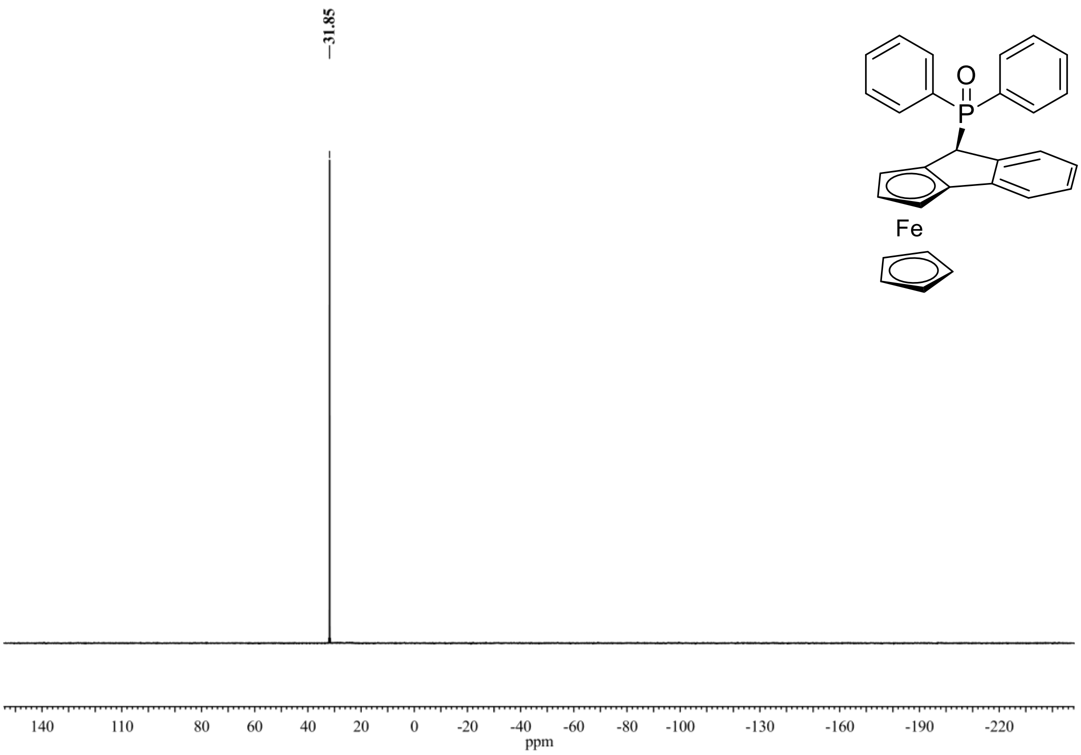


Figure S91. **^{31}P NMR** of **4a** (202 MHz, $CDCl_3$)

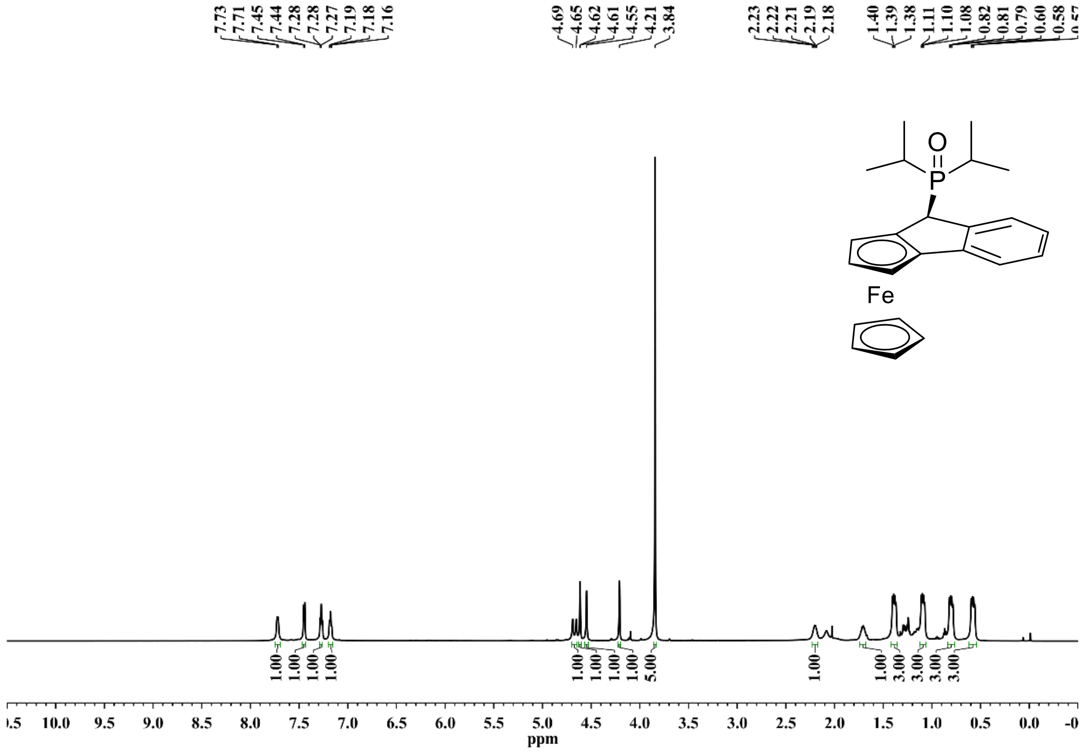


Figure S92. **^{1}H NMR** of **4b** (500 MHz, $CDCl_3$)

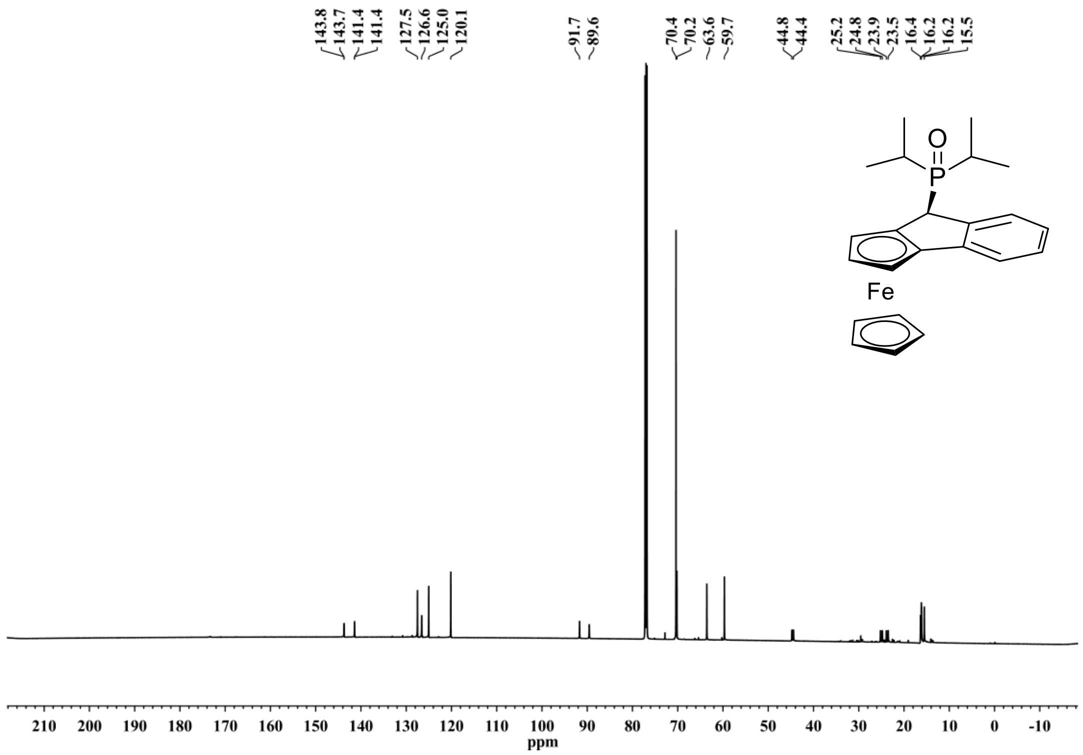


Figure S93. **^{13}C NMR** of **4b** (126 MHz, $CDCl_3$)

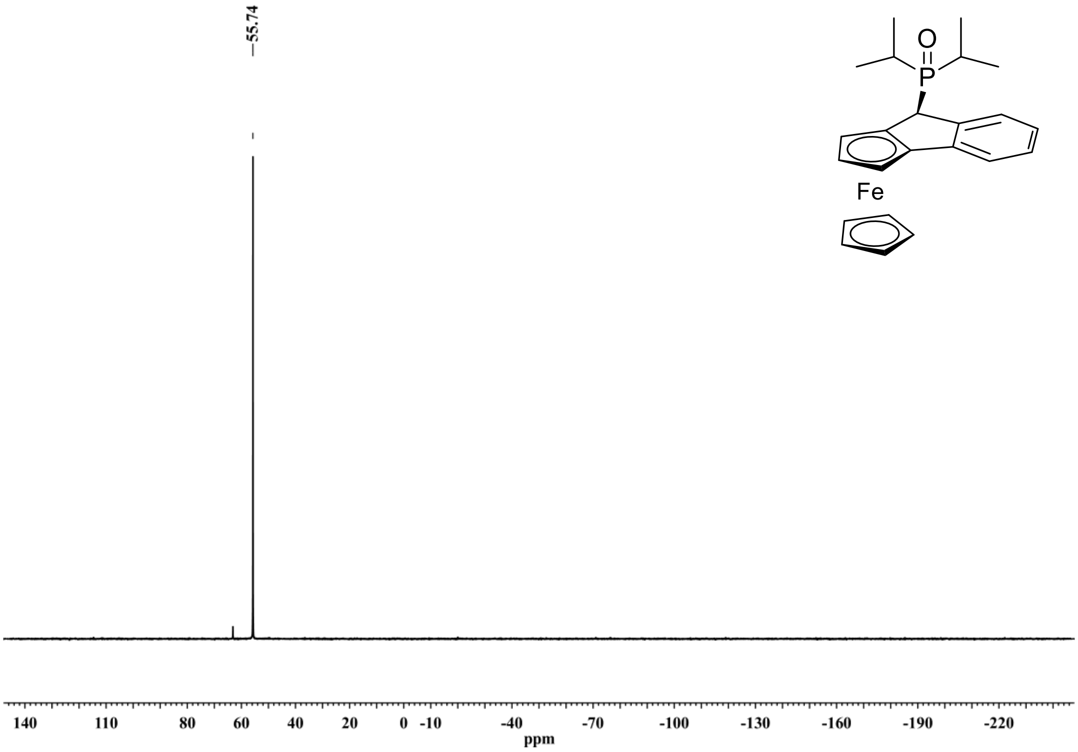


Figure S94. **^{31}P NMR** of **4b** (202 MHz, $CDCl_3$)

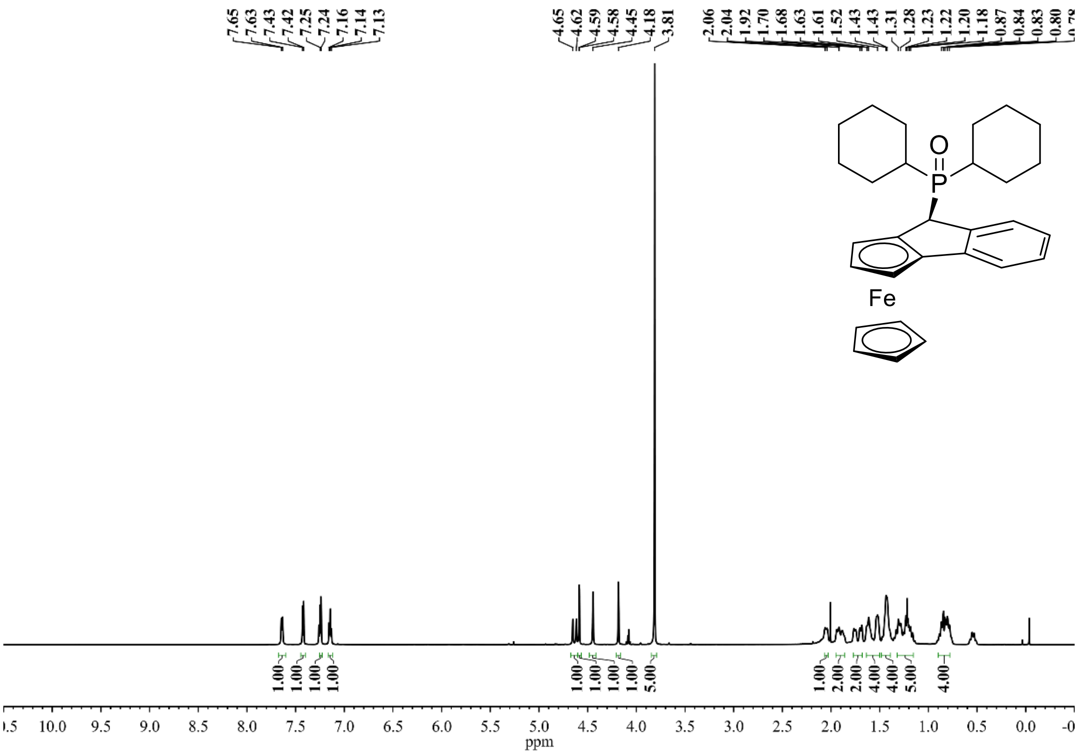


Figure S95. **^{1}H NMR** of **4c** (500 MHz, $CDCl_3$)

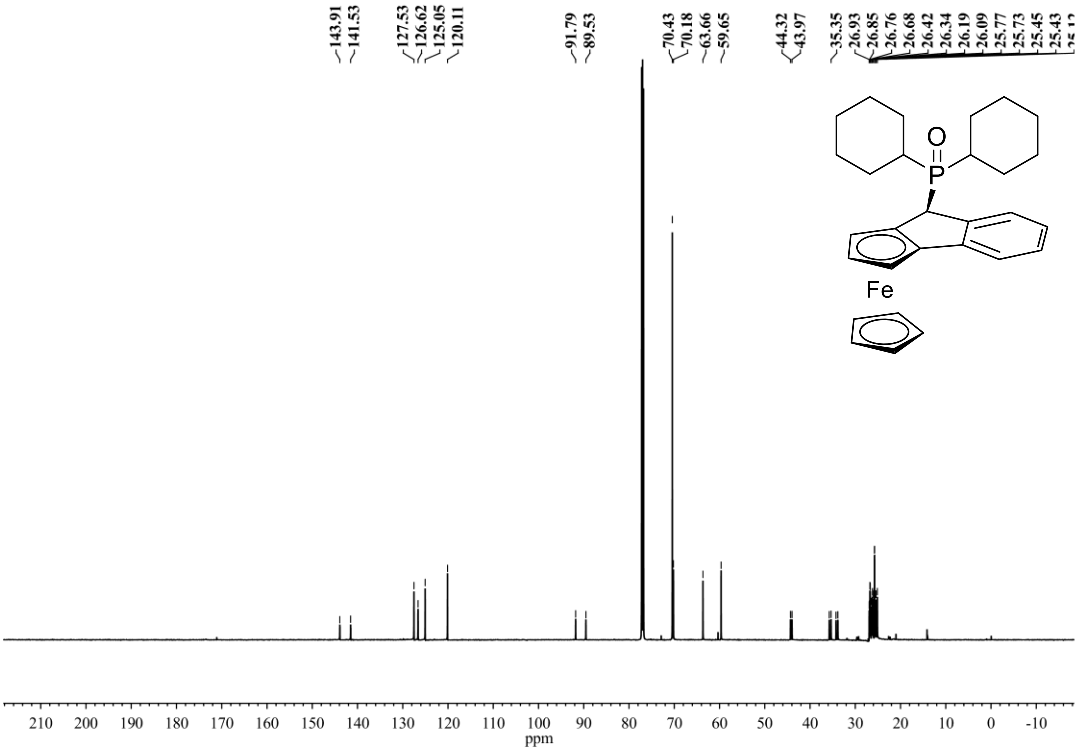


Figure S96. **^{13}C NMR** of **4c** (126 MHz, $CDCl_3$)

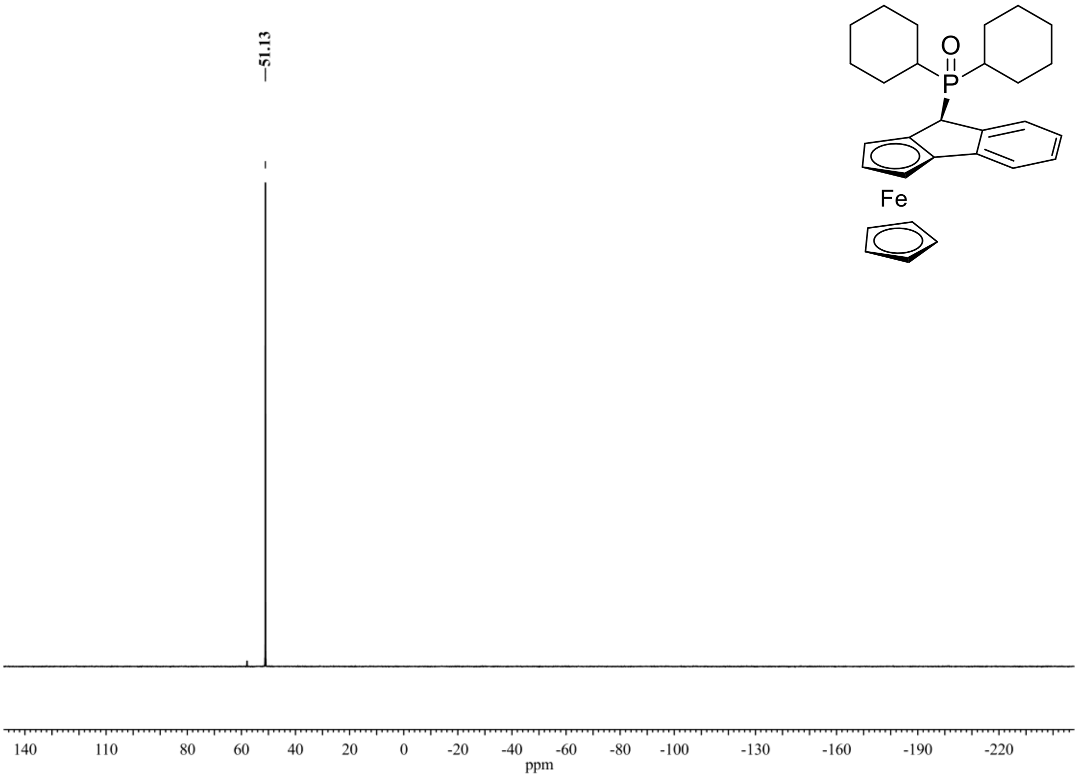


Figure S97. **^{31}P NMR** of **4c** (202 MHz, $CDCl_3$)

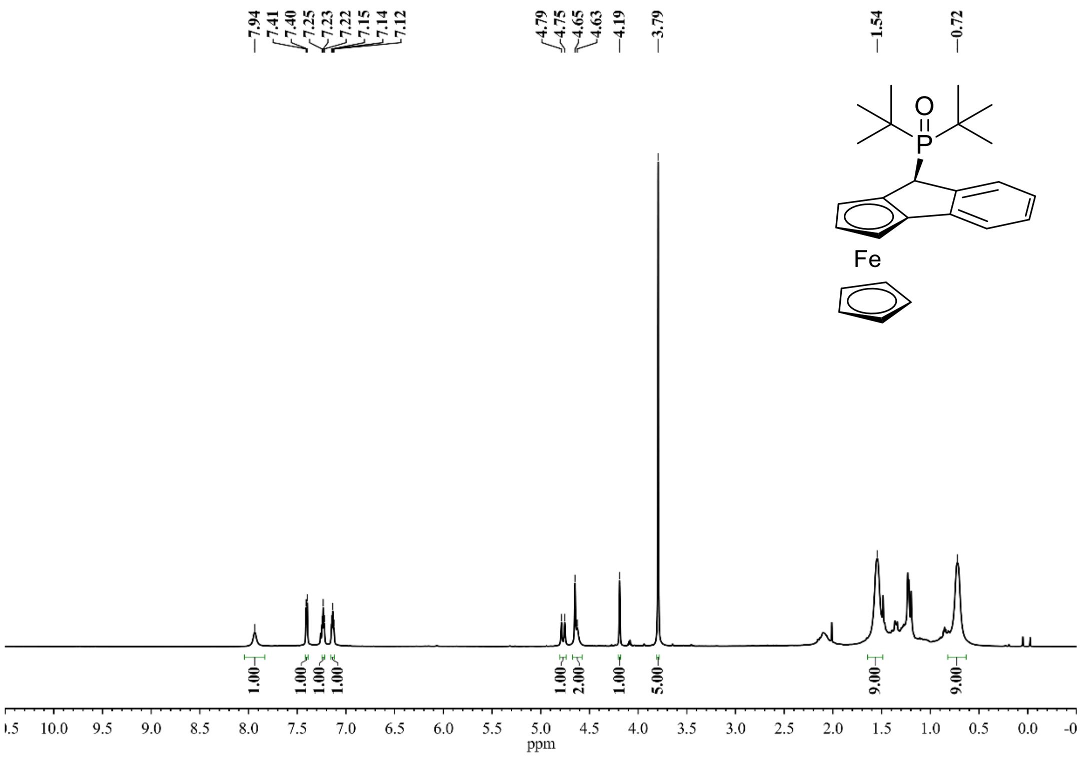


Figure S98. ^{1}**H NMR** of **4d** (500 MHz, $CDCl_3$)

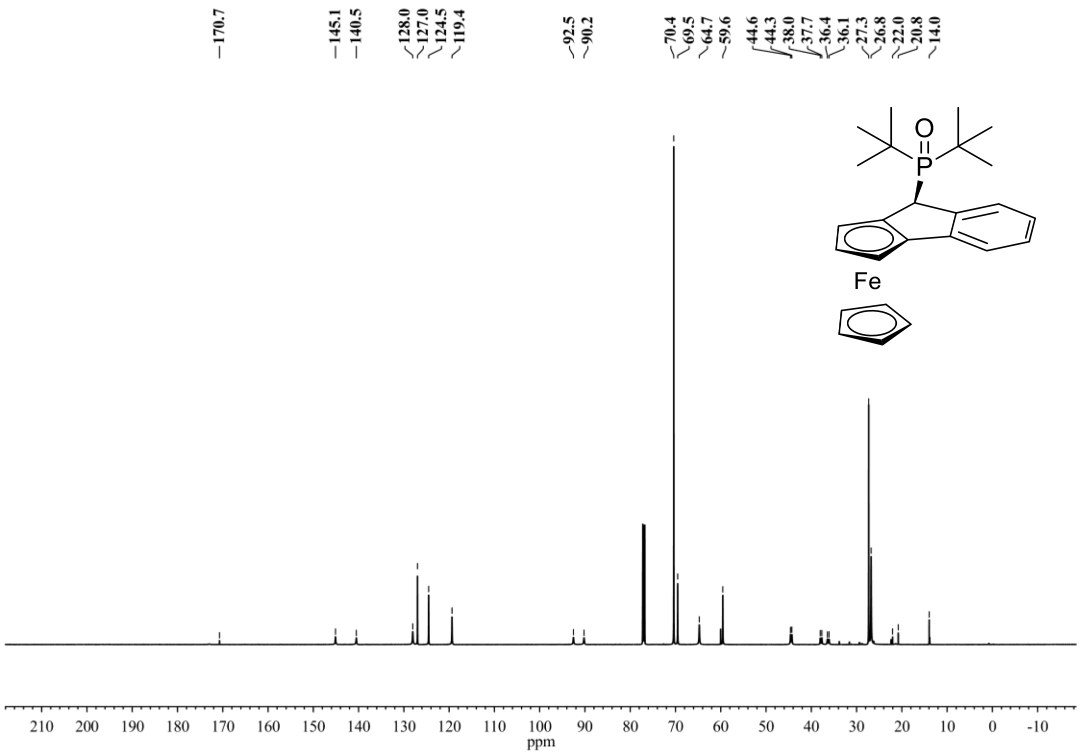


Figure S99**.** ^{13}**C NMR** of **4d** (126 MHz, $CDCl_3$)

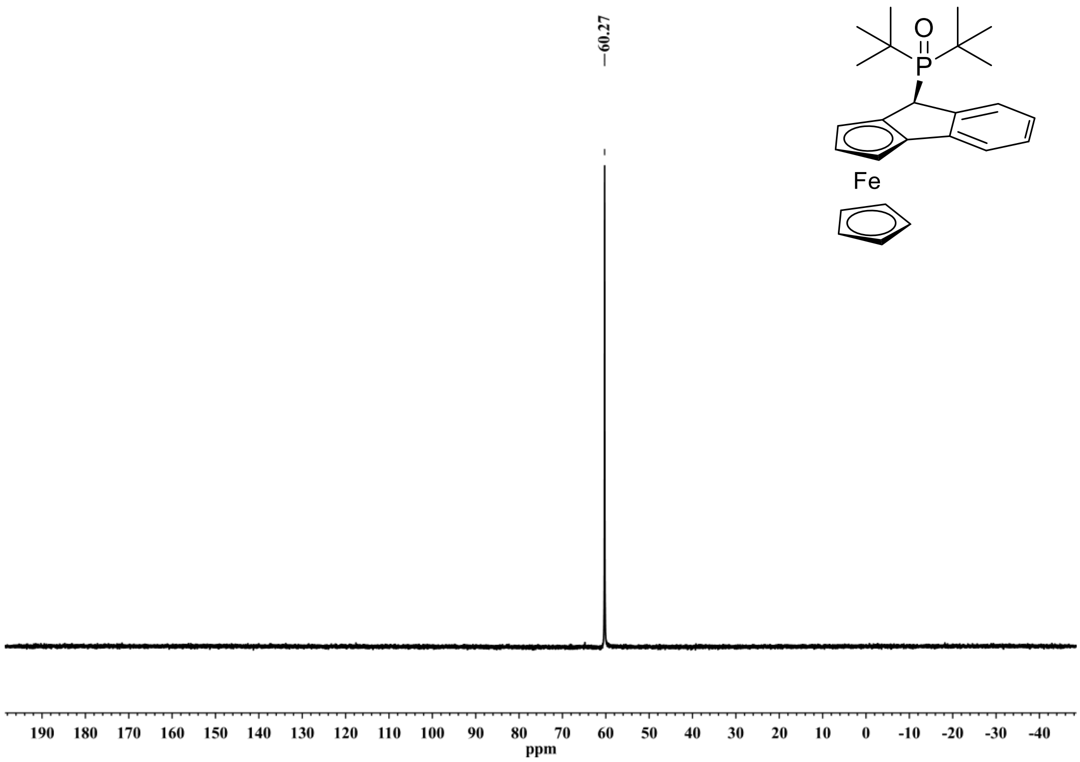


Figure S100. ^{31}**P NMR** of **4d** (202 MHz, $CDCl_3$)

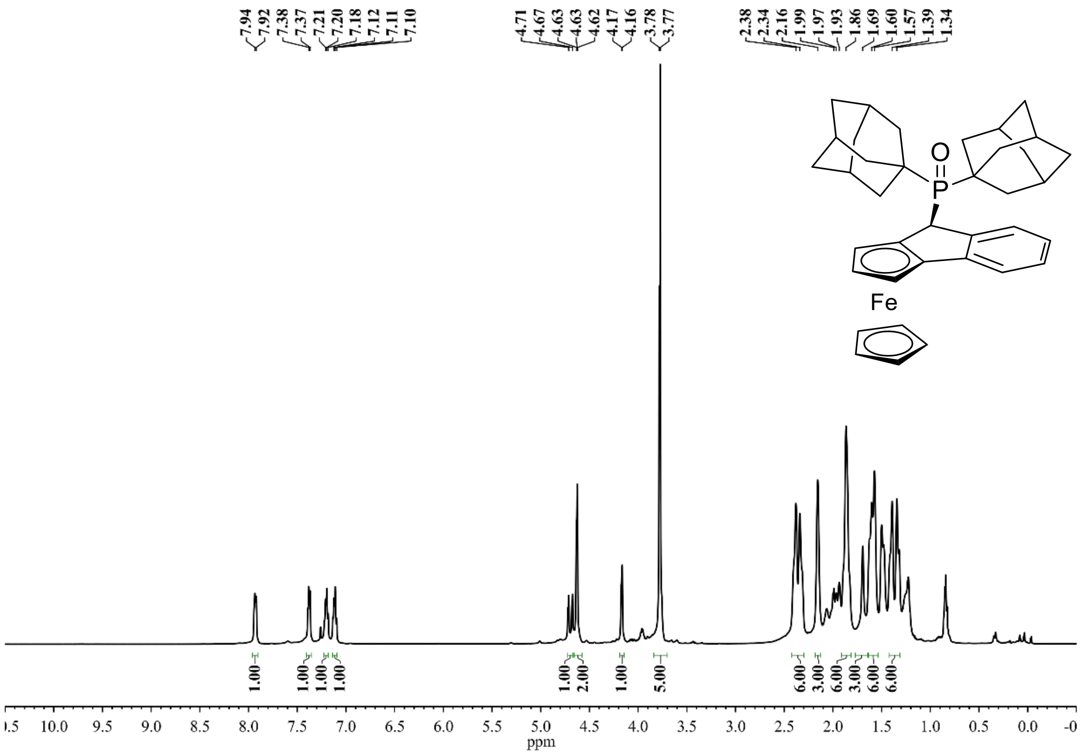


Figure S101. ^{1}**H NMR** of **4e** (500 MHz, $CDCl_3$)

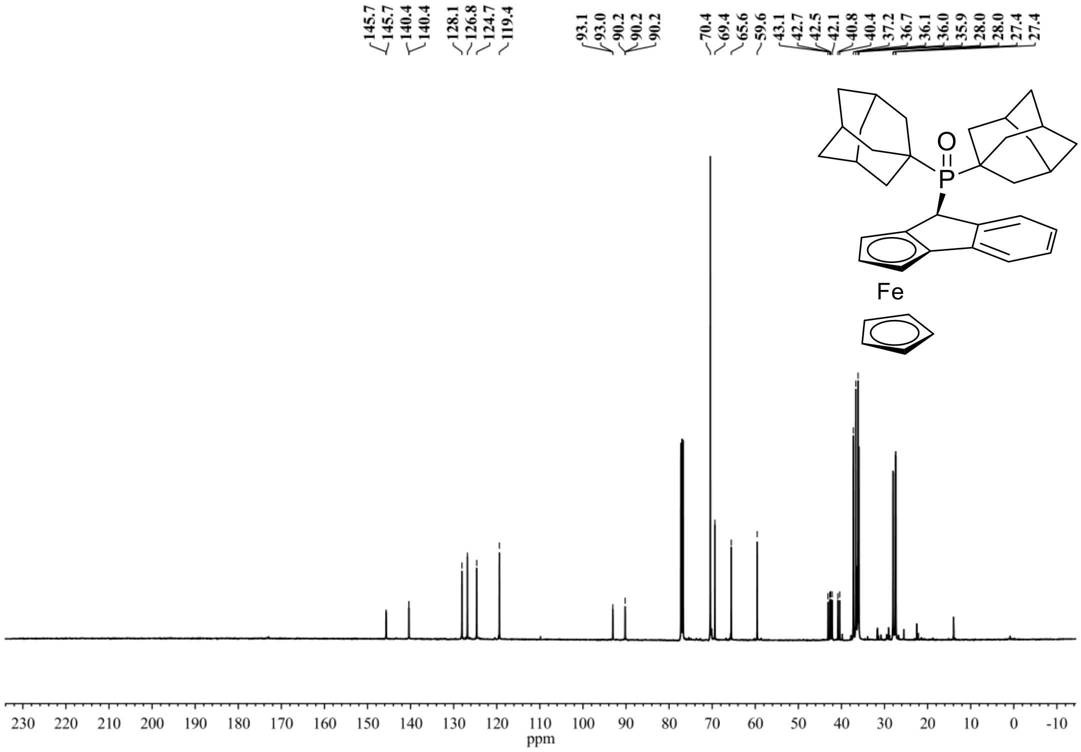


Figure S102**. ^{13}C NMR** of **4e** (126 MHz, $CDCl_3$)

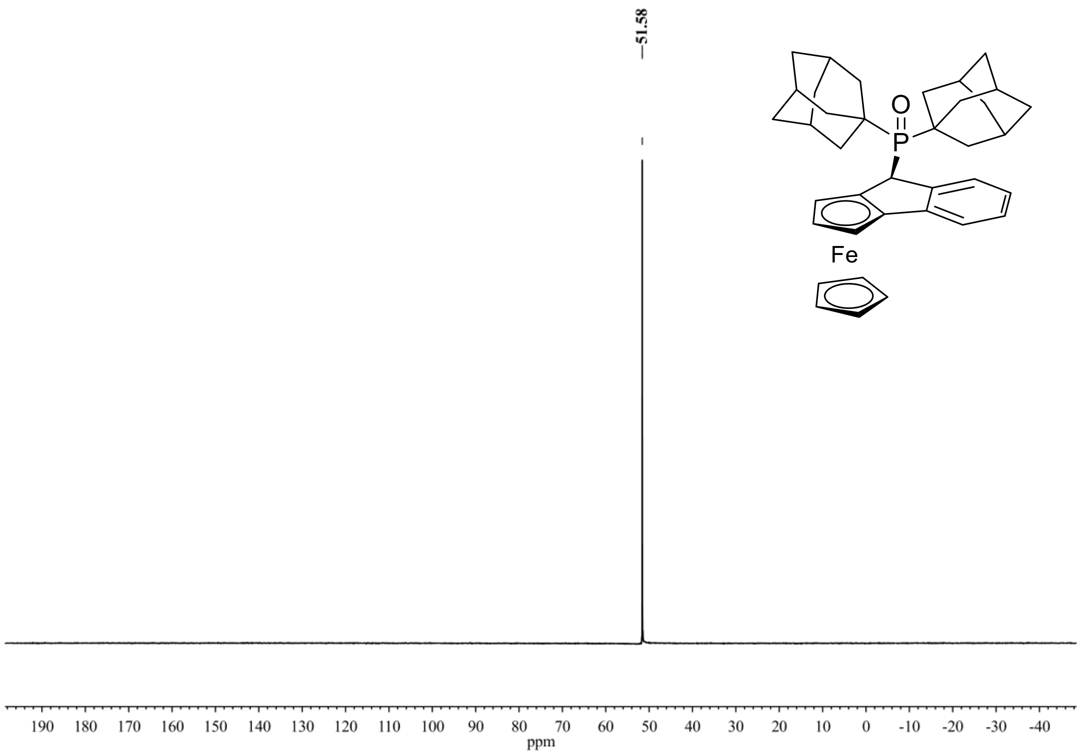


Figure S103. **^{31}P NMR** of **4e** (202 MHz, $CDCl_3$)

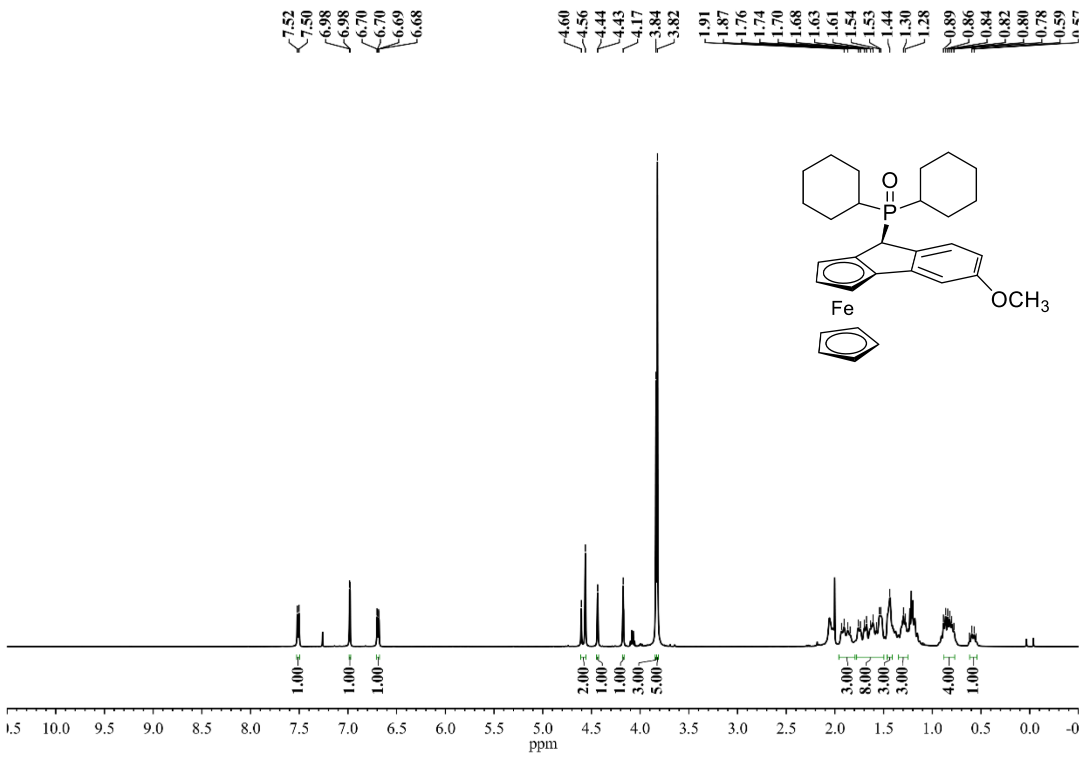


Figure S104. **^{1}H NMR** of **4f** (500 MHz, $CDCl_3$)

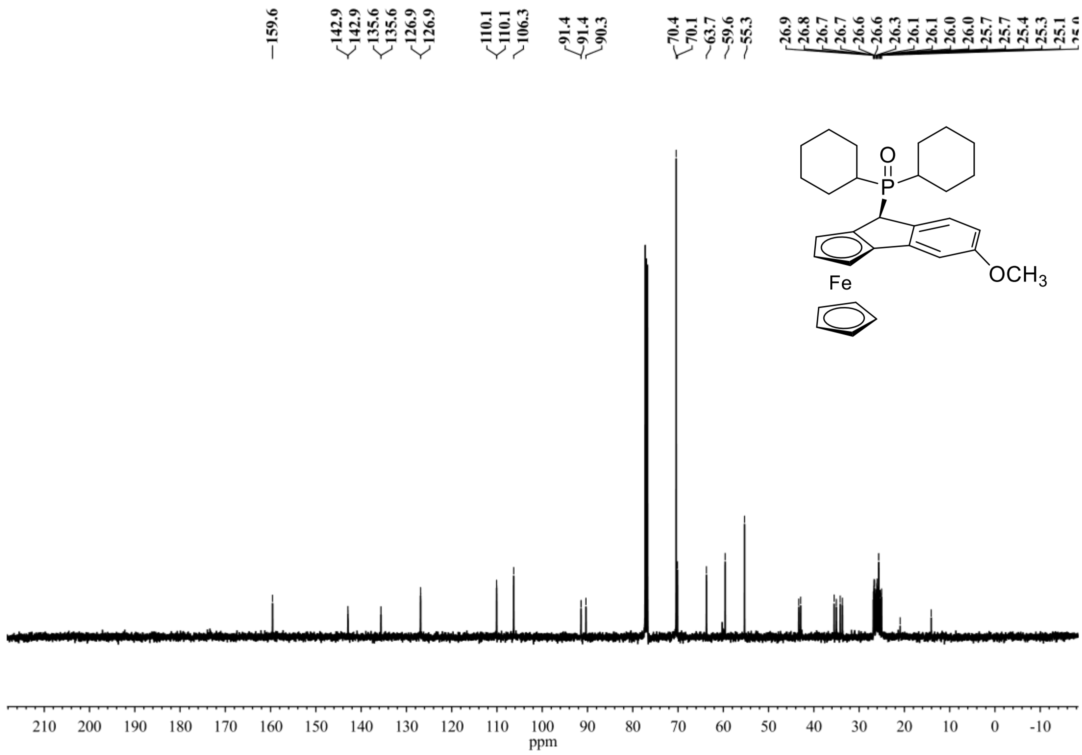


Figure S105. **^{13}C NMR** of **4f** (126 MHz, $CDCl_3$)

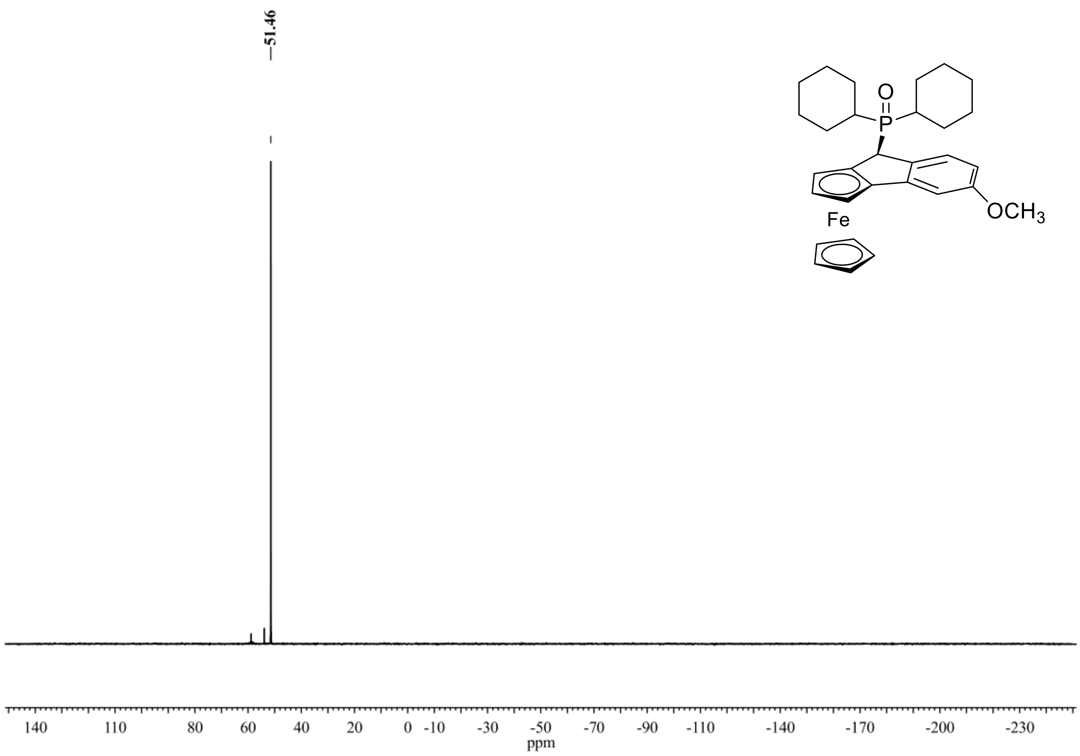


Figure S106. **31P NMR** of **4f** (202 MHz, $CDCl_3$)

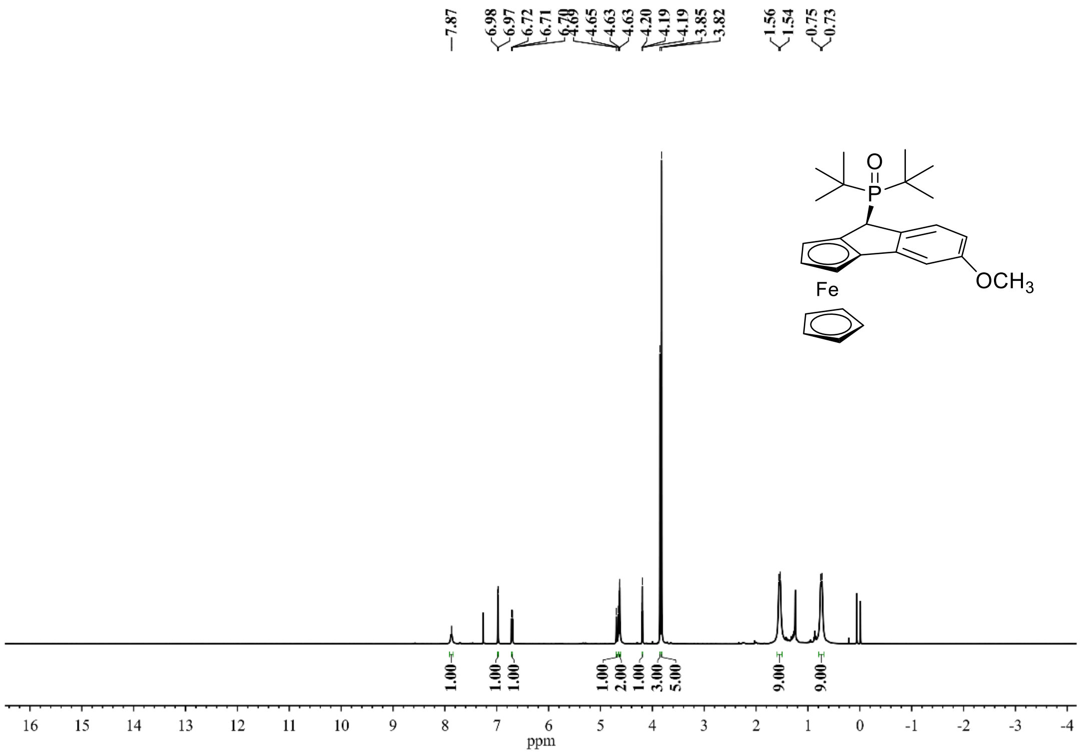


Figure S107. **1H NMR** of **4g** (500 MHz, $CDCl_3$)

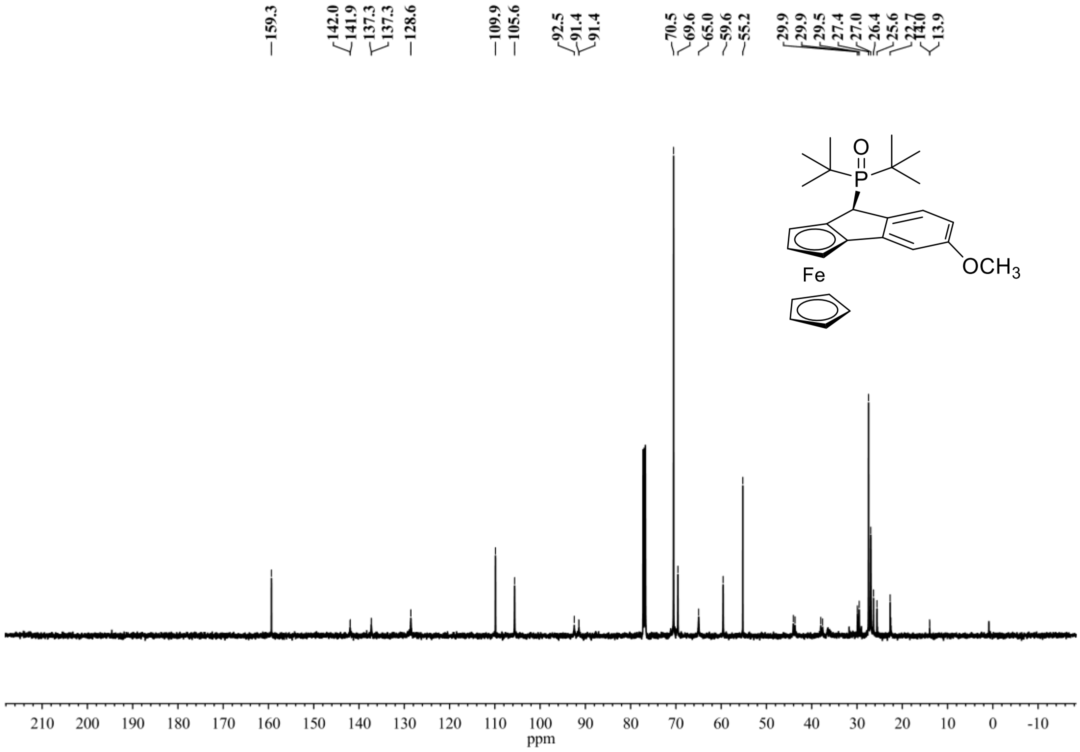


Figure S108. **^{13}C NMR** of **4g** (126 MHz, $CDCl_3$)

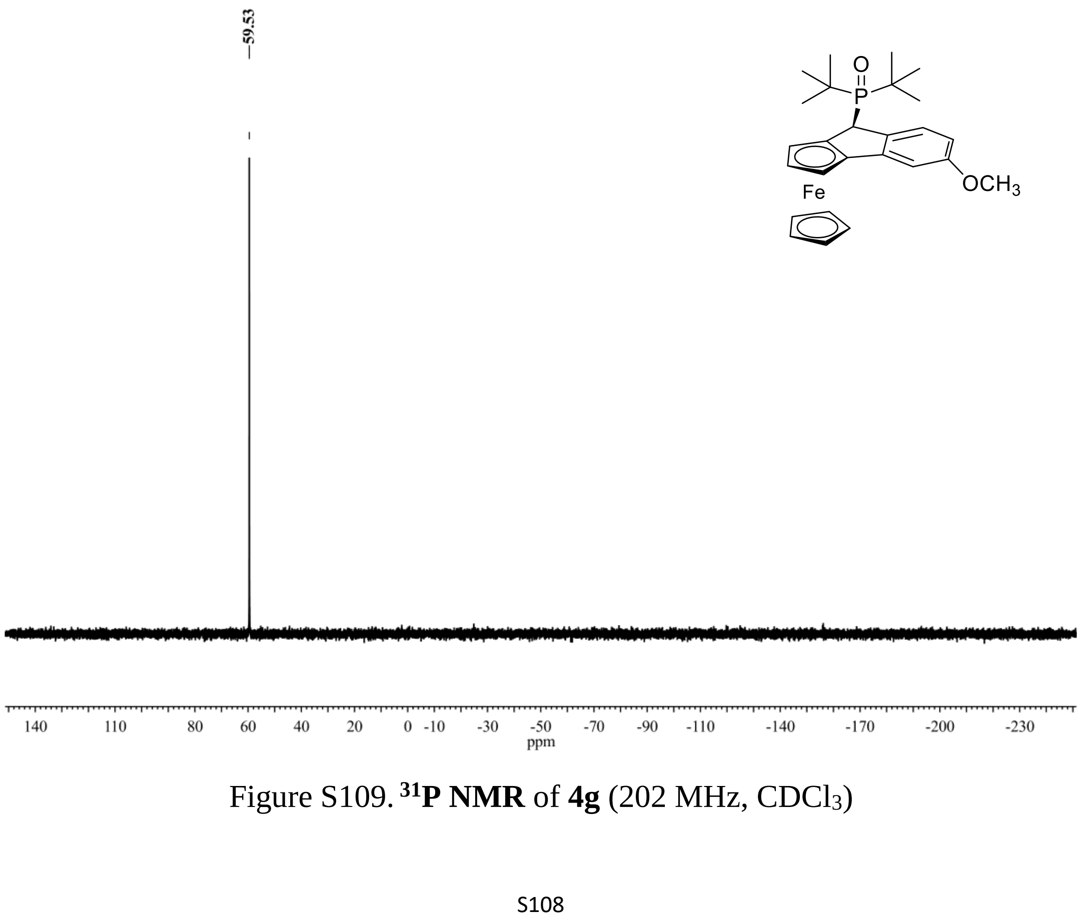


Figure S109. **^{31}P NMR** of **4g** (202 MHz, $CDCl_3$)

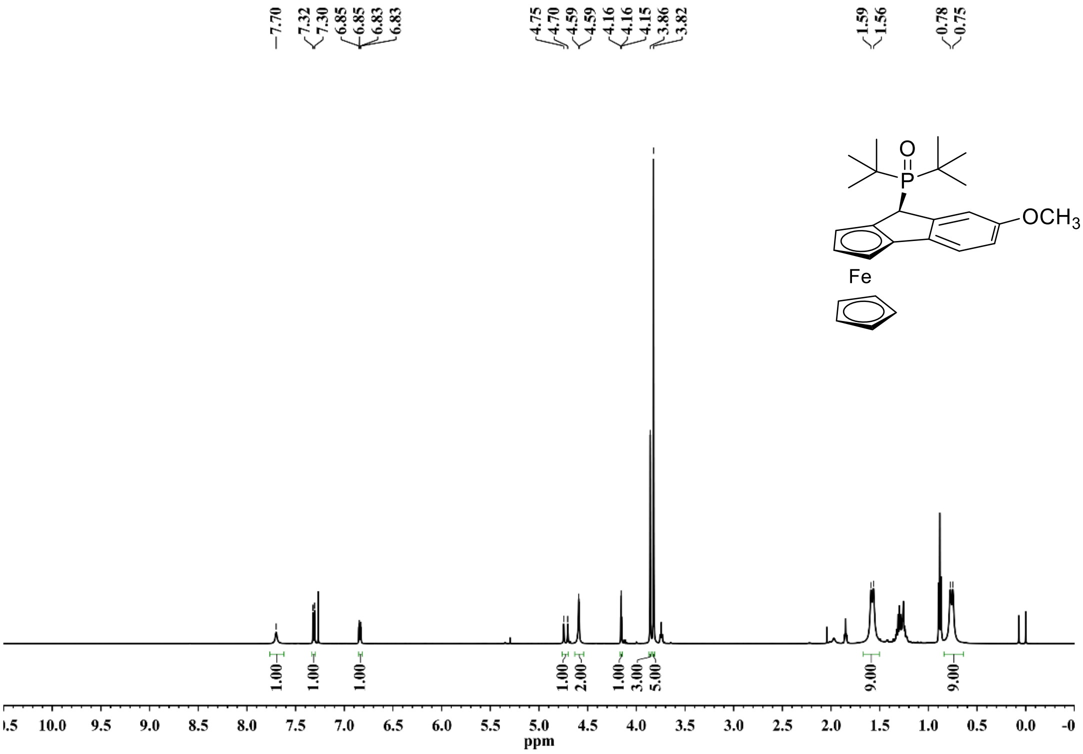


Figure S110. **^{1}H NMR** of **4h** (500 MHz, $CDCl_3$)

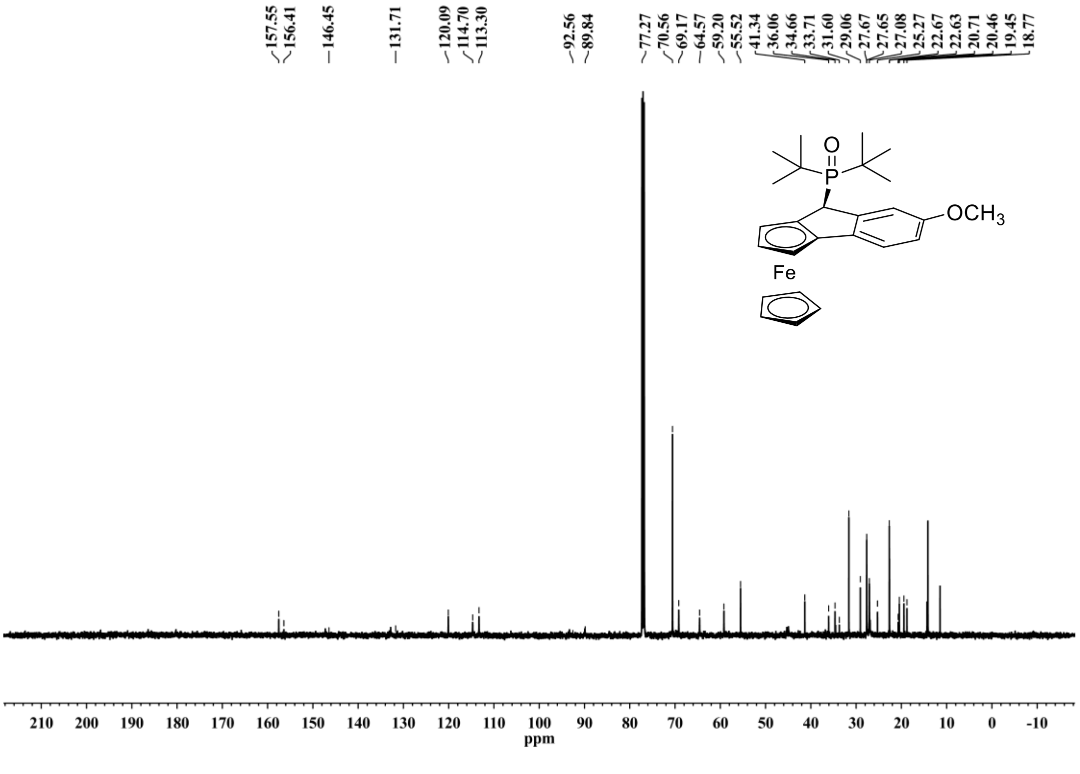


Figure S111. **^{13}C NMR** of **4h** (126 MHz, $CDCl_3$)

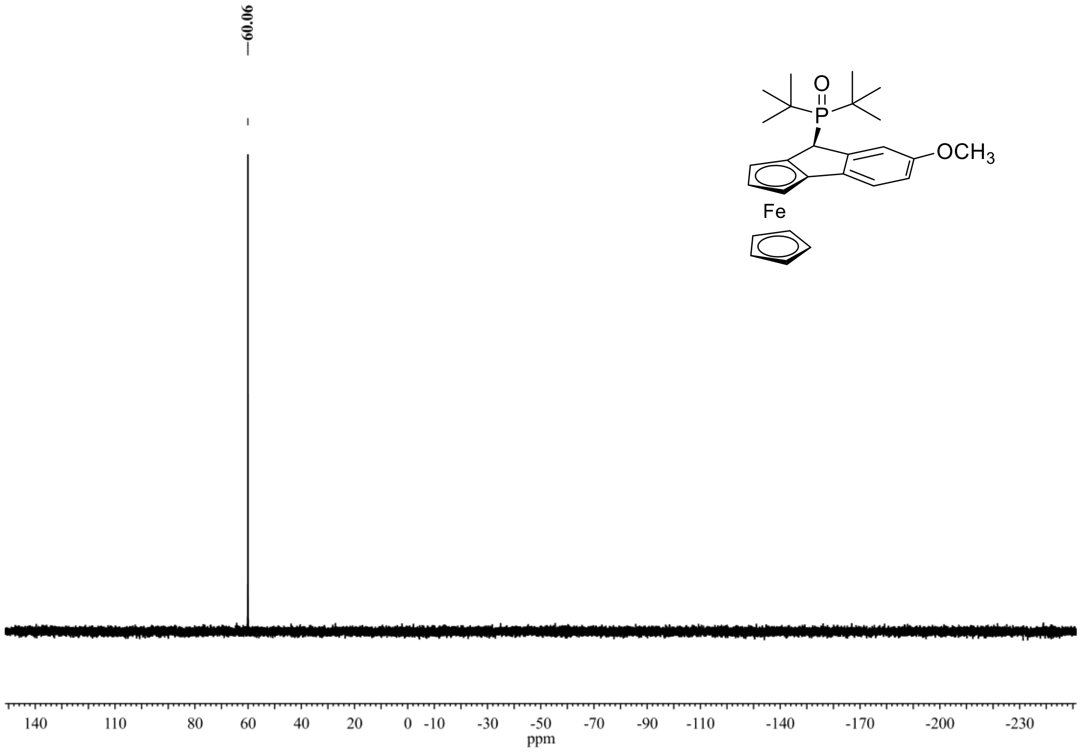


Figure S112. **^{31}P NMR** of **4h** (202 MHz, $CDCl_3$)

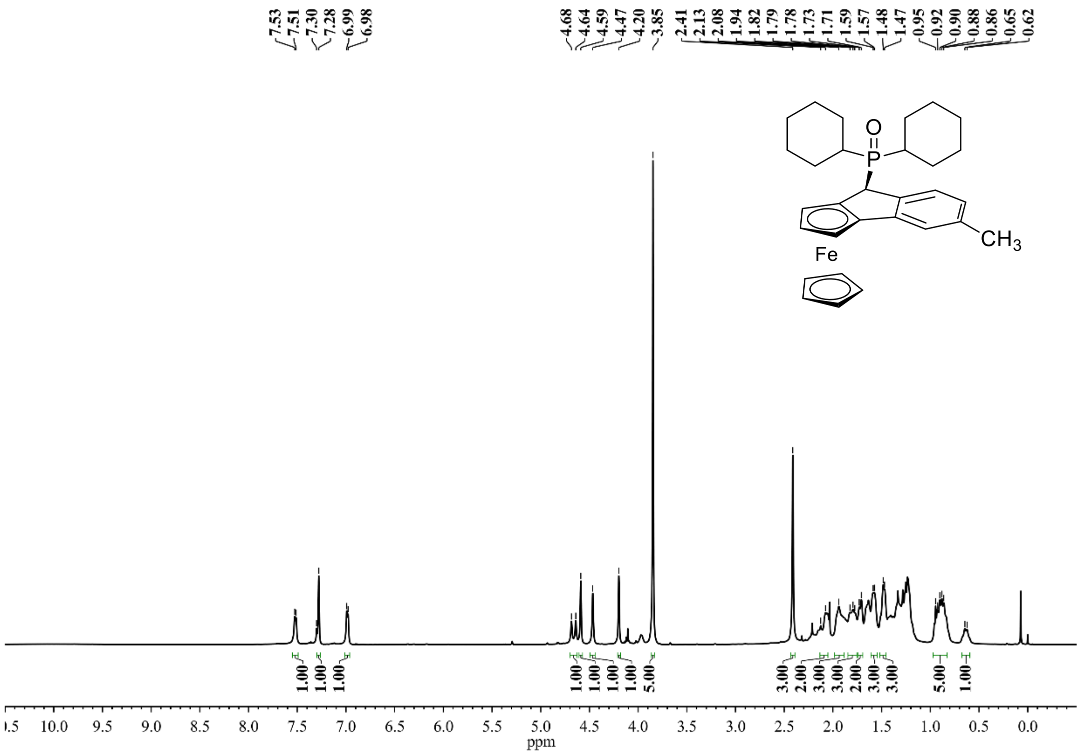


Figure S113. **^{1}H NMR** of **4j** (500 MHz, $CDCl_3$)

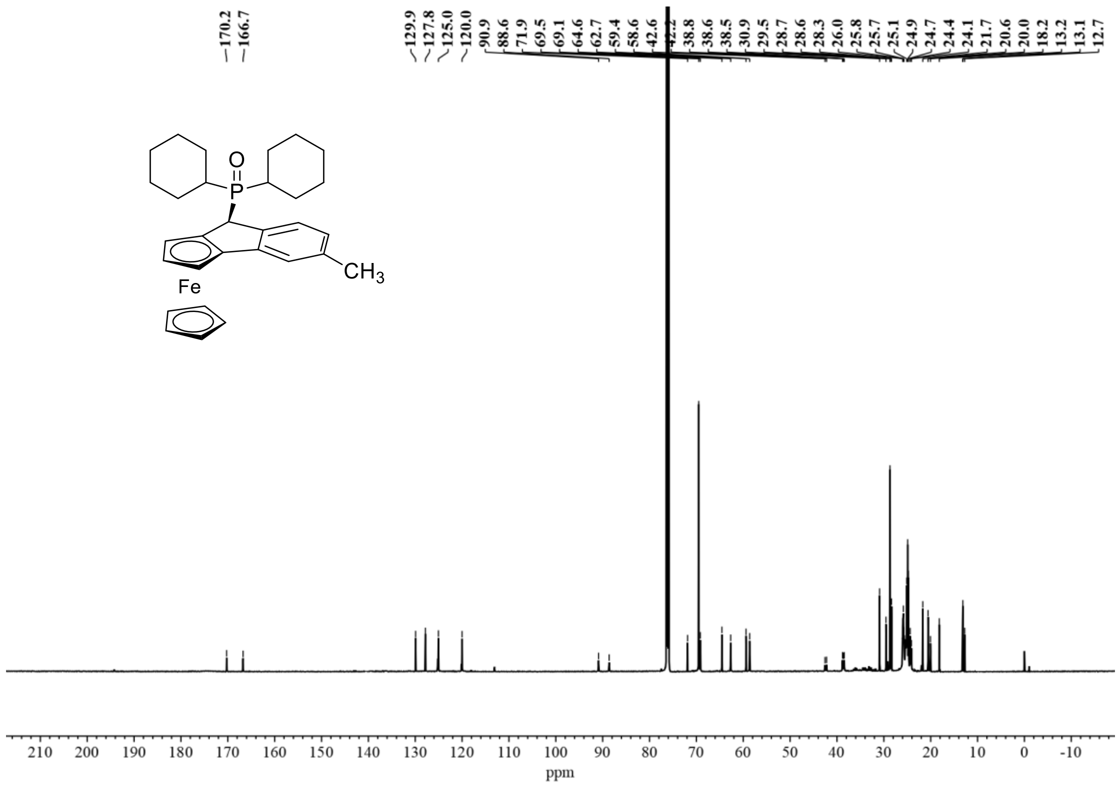


Figure S114. **^{13}C NMR** of **4j** (151 MHz, $CDCl_3$)

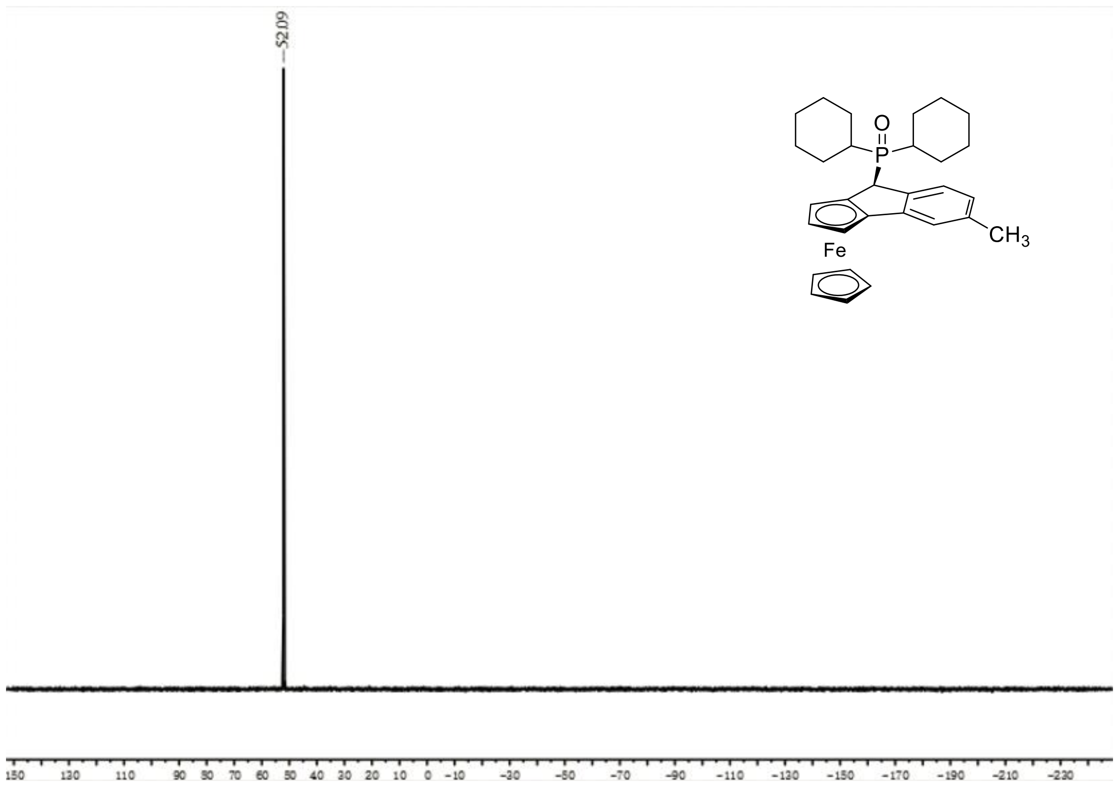


Figure S115. **^{31}P NMR** of **4j** (202 MHz, $CDCl_3$)

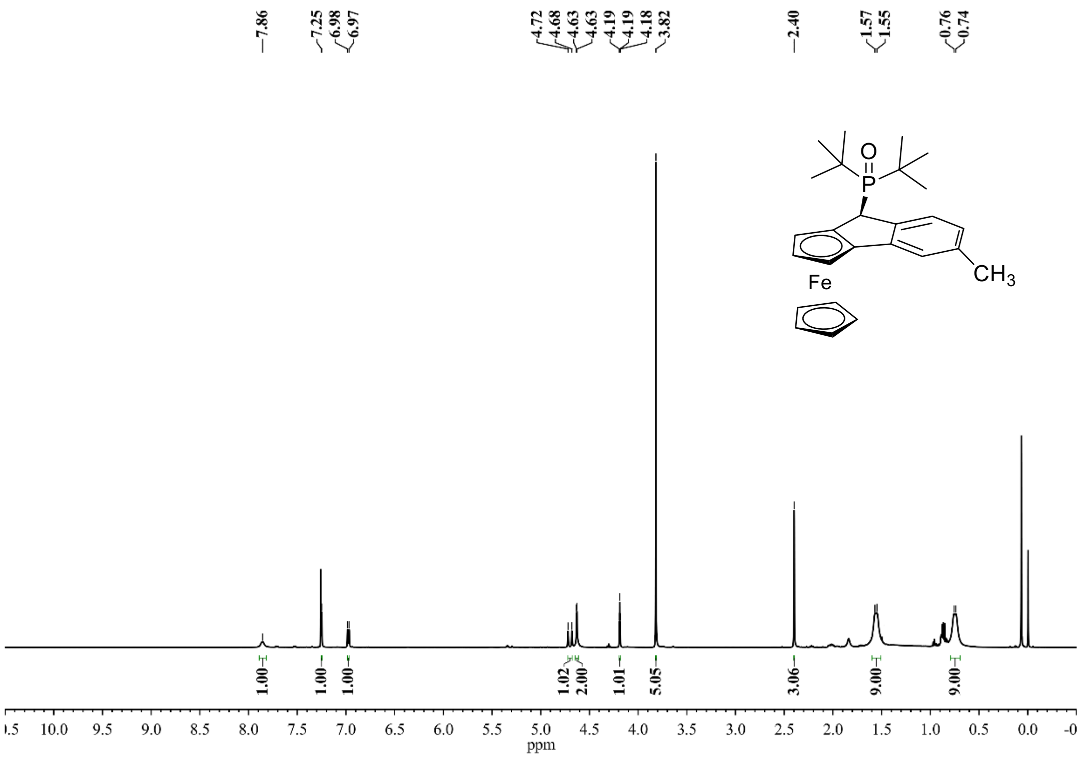


Figure S116. ^{1}**H NMR** of **4k** (500 MHz, $CDCl_3$)

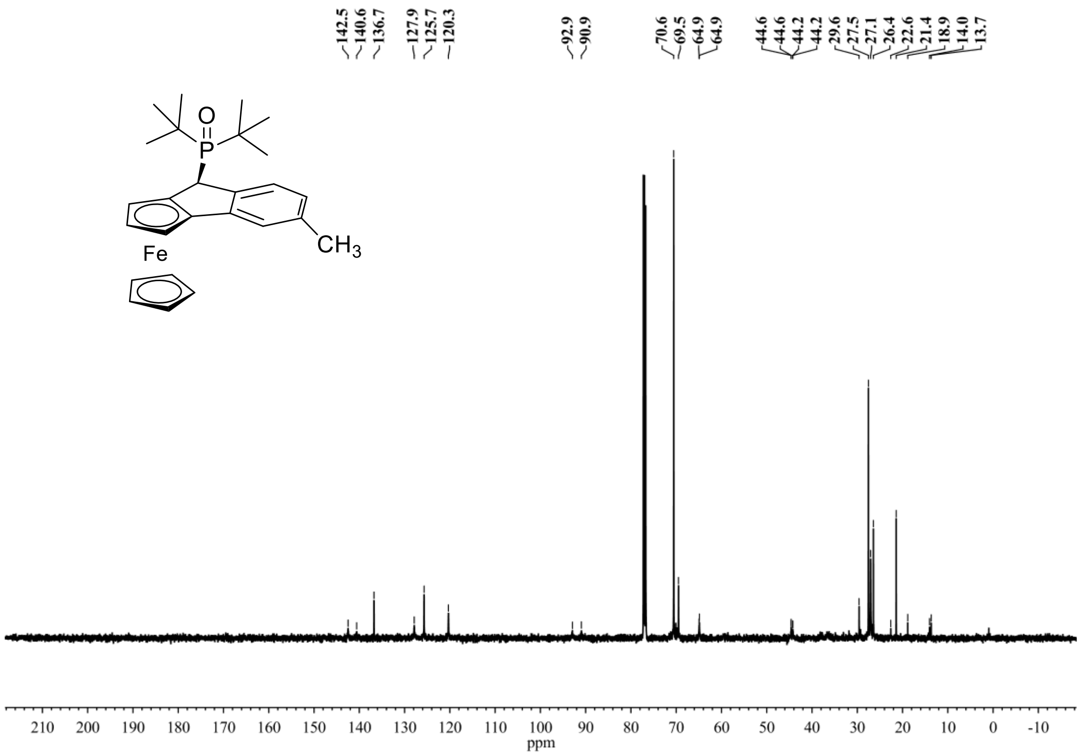


Figure S117. ^{13}**C NMR** of **4k** (126 MHz, $CDCl_3$)

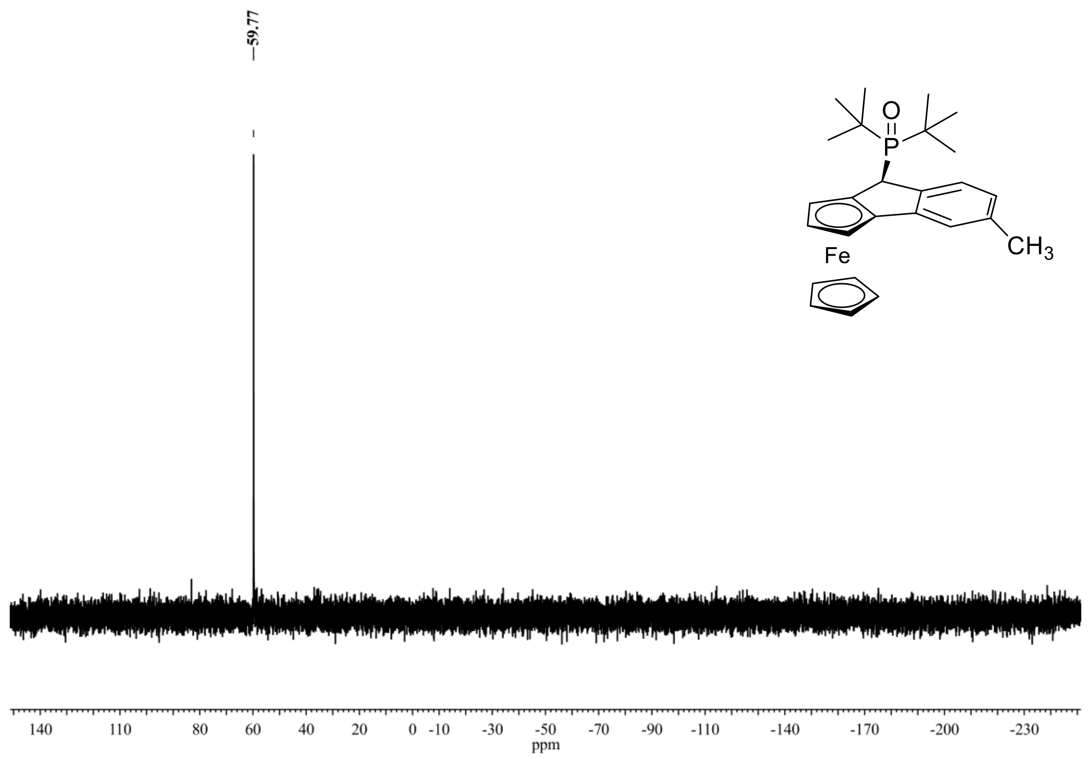


Figure S118. **^{31}P NMR** of **4k** (202 MHz, $CDCl_3$)

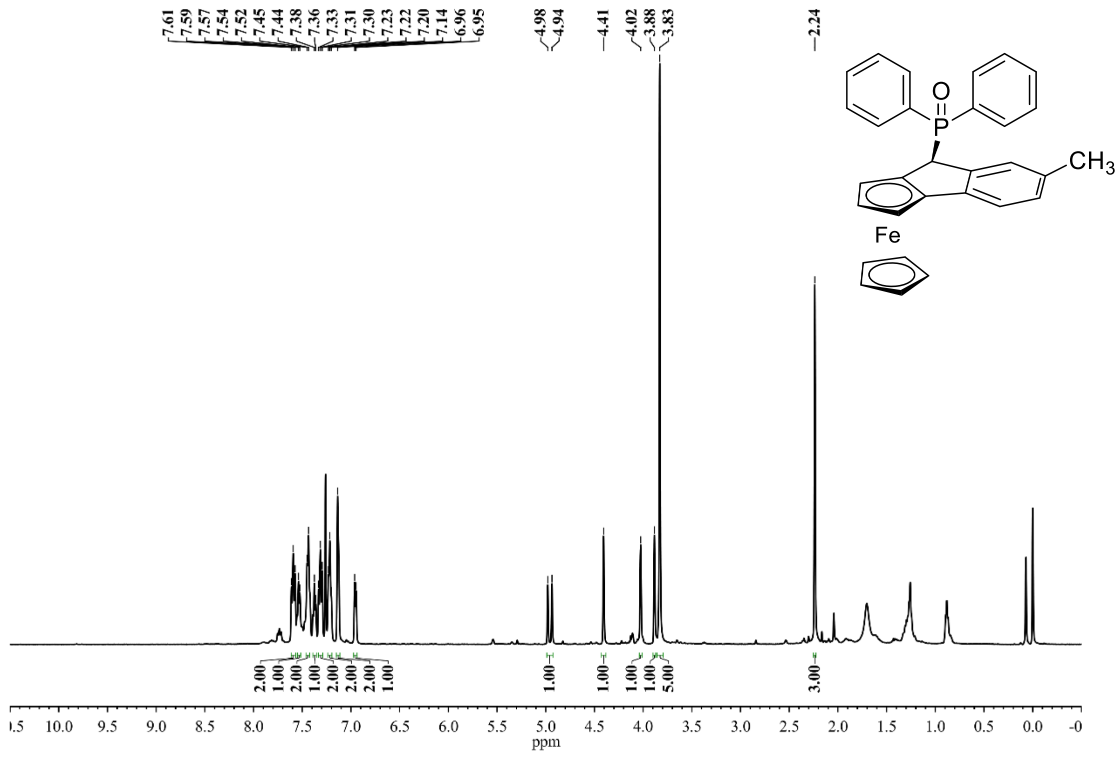


Figure S119. **^{1}H NMR** of **4l** (500 MHz, $CDCl_3$)

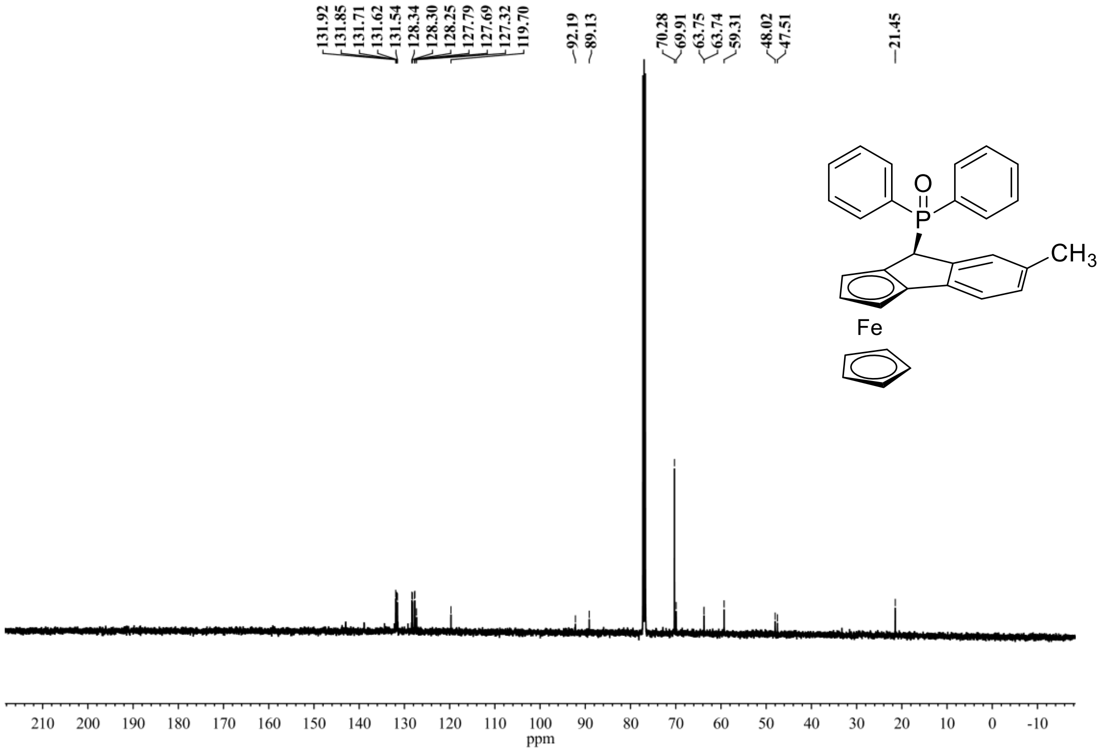


Figure S120. **^{13}C NMR** of **4l** (126 MHz, $CDCl_3$)

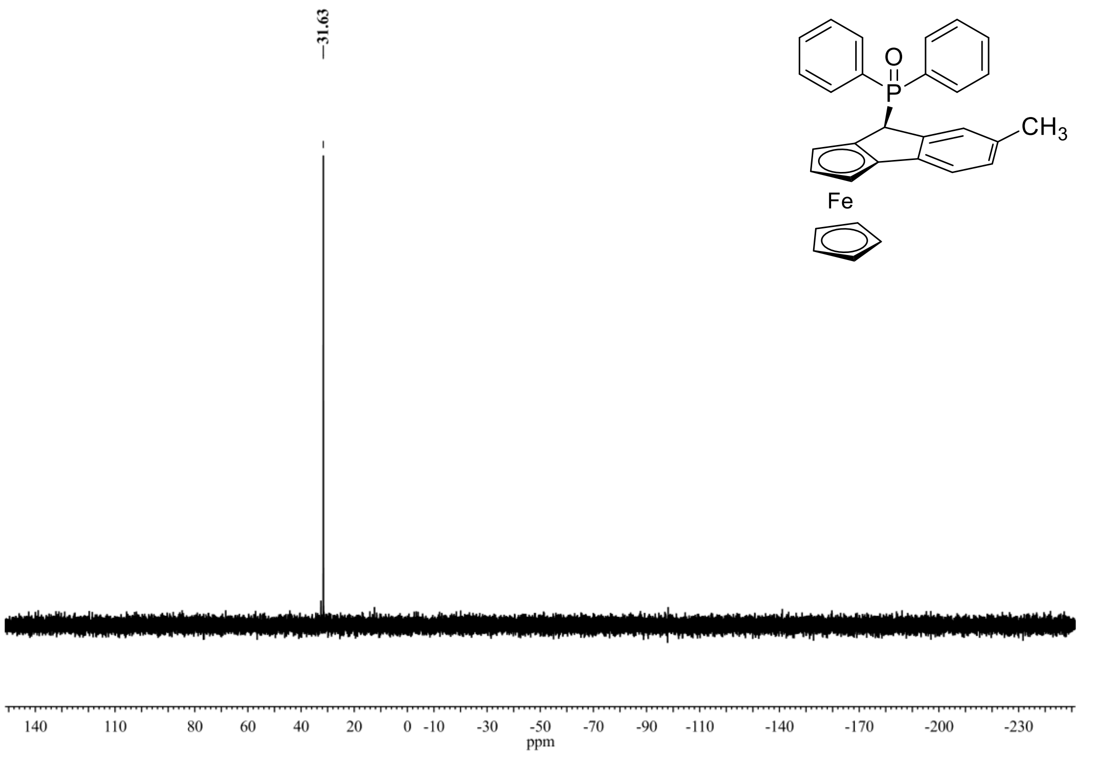


Figure S121. **^{31}P NMR** of **4l** (202 MHz, $CDCl_3$)

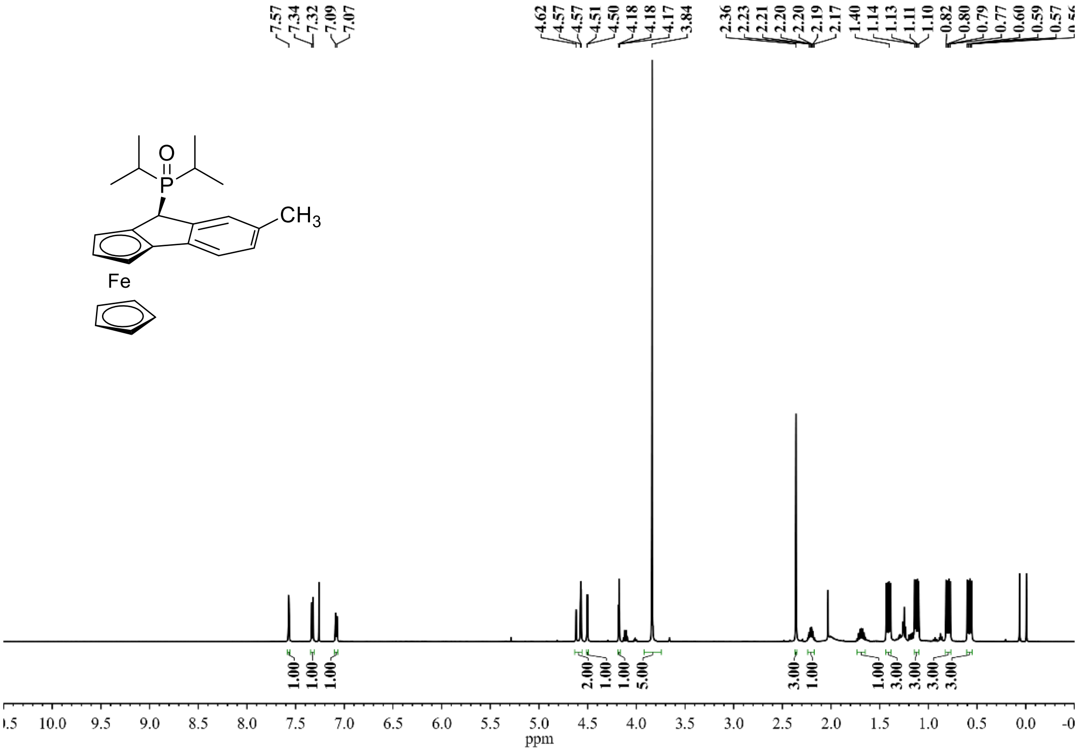


Figure S122. **^{1}H NMR** of **4m** (500 MHz, $CDCl_3$)

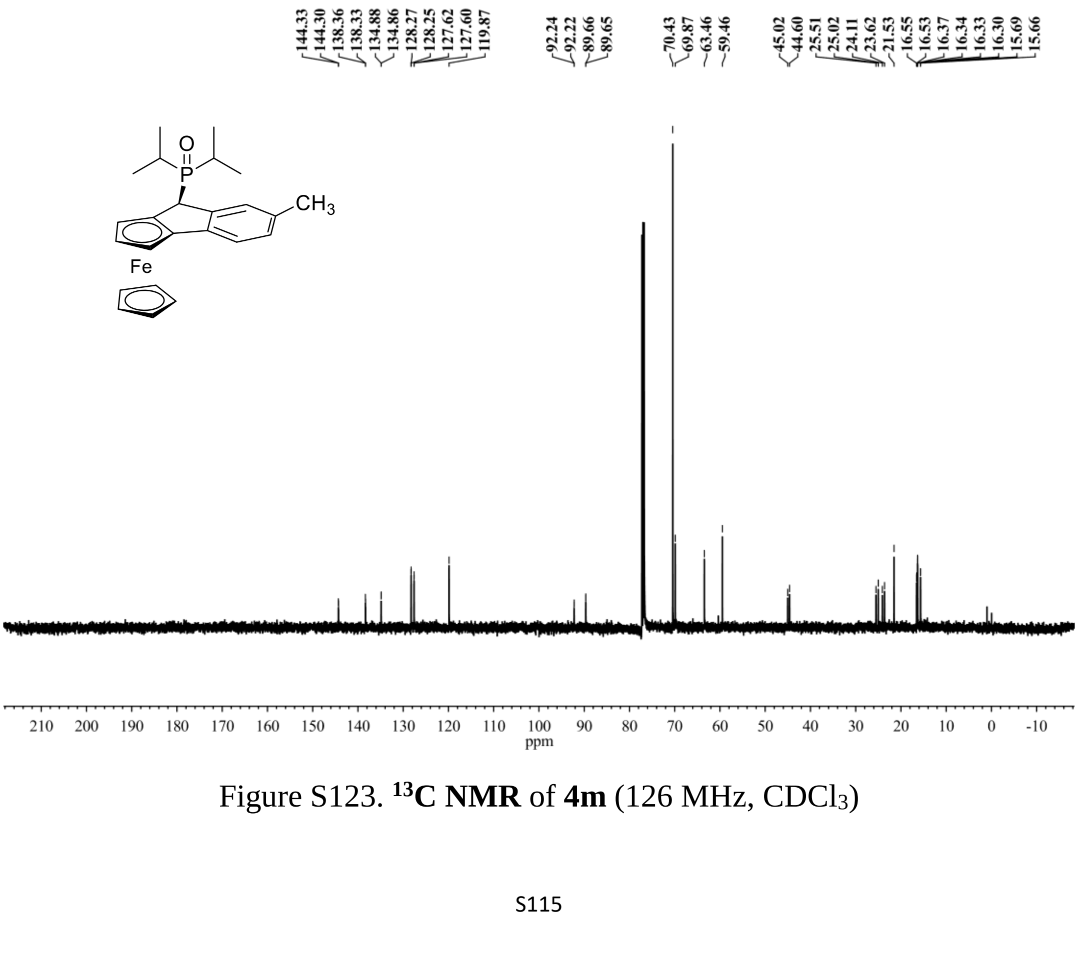


Figure S123. **^{13}C NMR** of **4m** (126 MHz, $CDCl_3$)

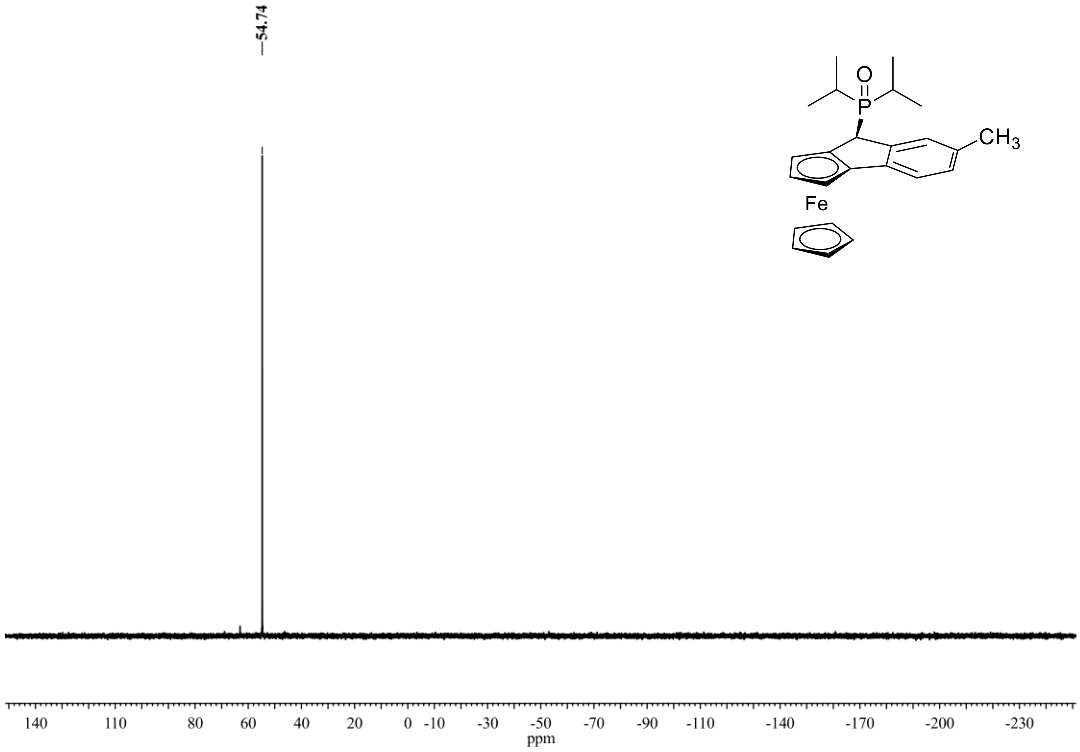


Figure S124. **^{31}P NMR** of **4m** (202 MHz, $CDCl_3$)

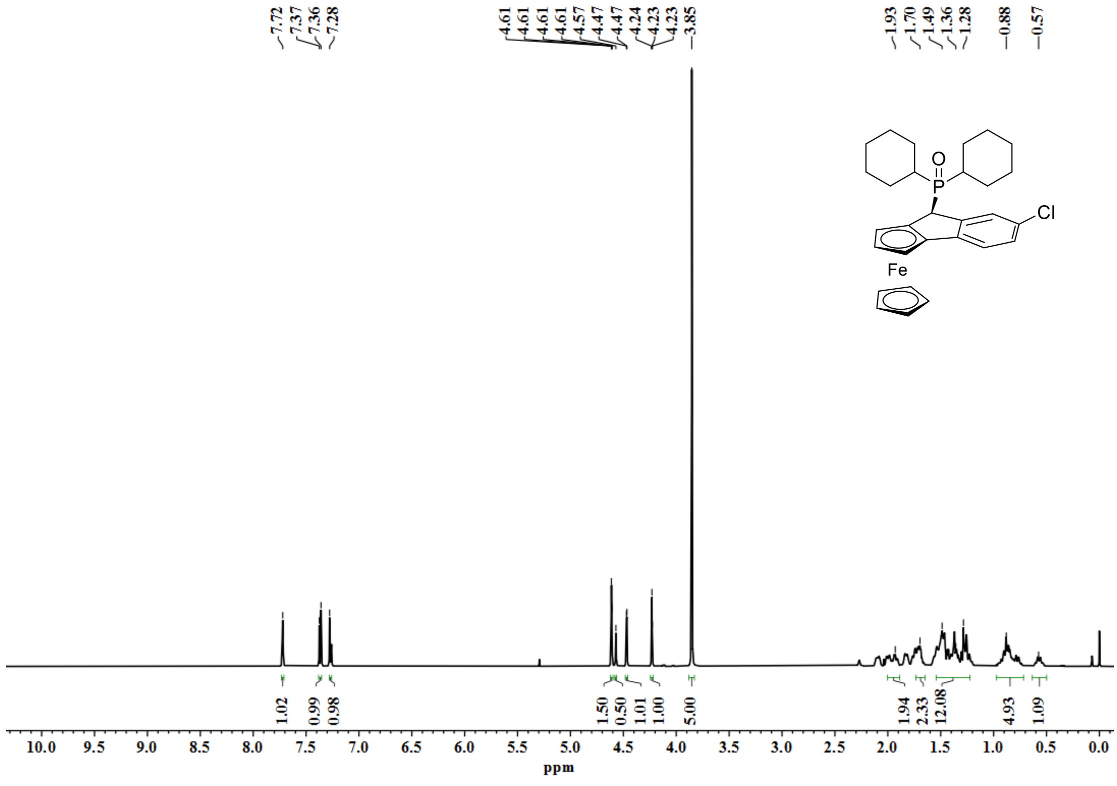


Figure S125. **^{1}H NMR** of **4n** (500 MHz, $CDCl_3$)

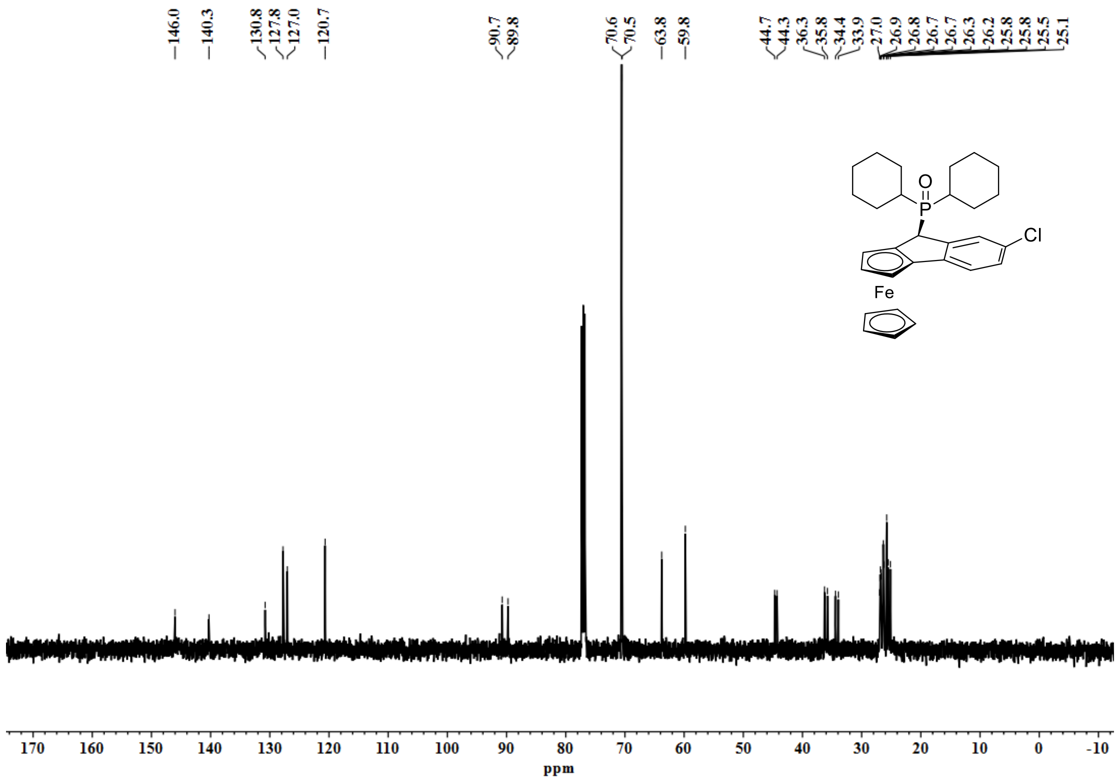


Figure S126. ^{13}**C NMR** of **4n** (126 MHz, $CDCl_3$)

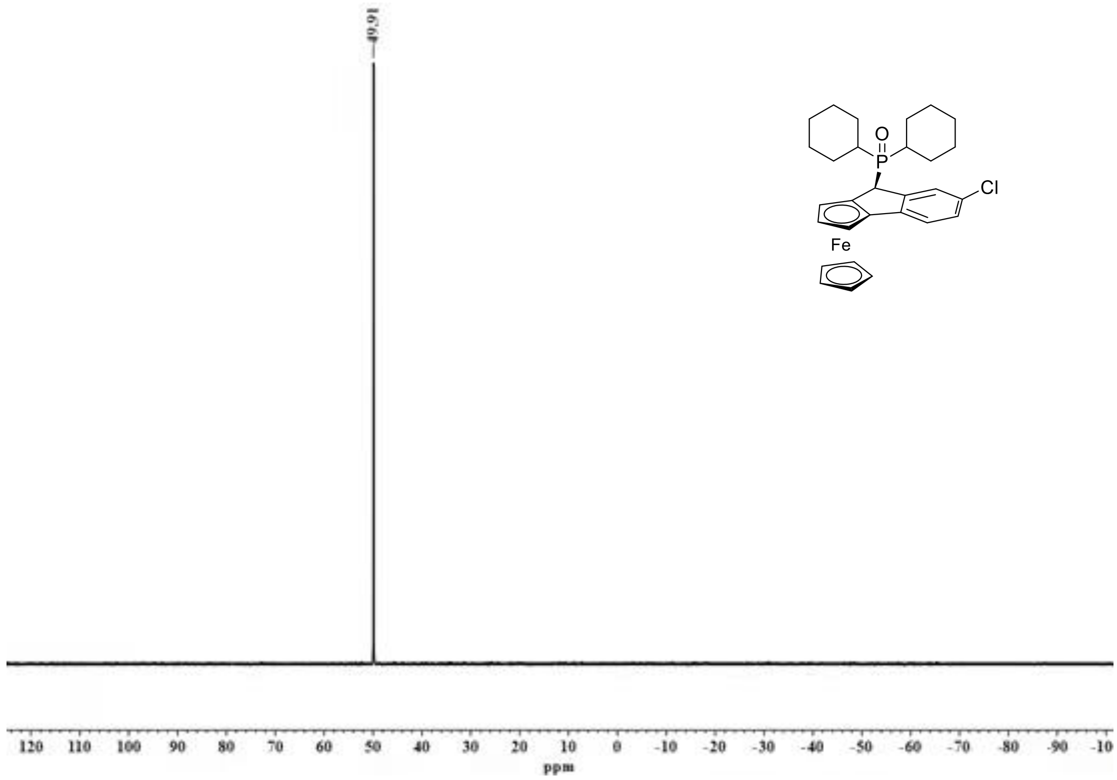


Figure S127. ^{31}**P NMR** of **4n** (202 MHz, $CDCl_3$)

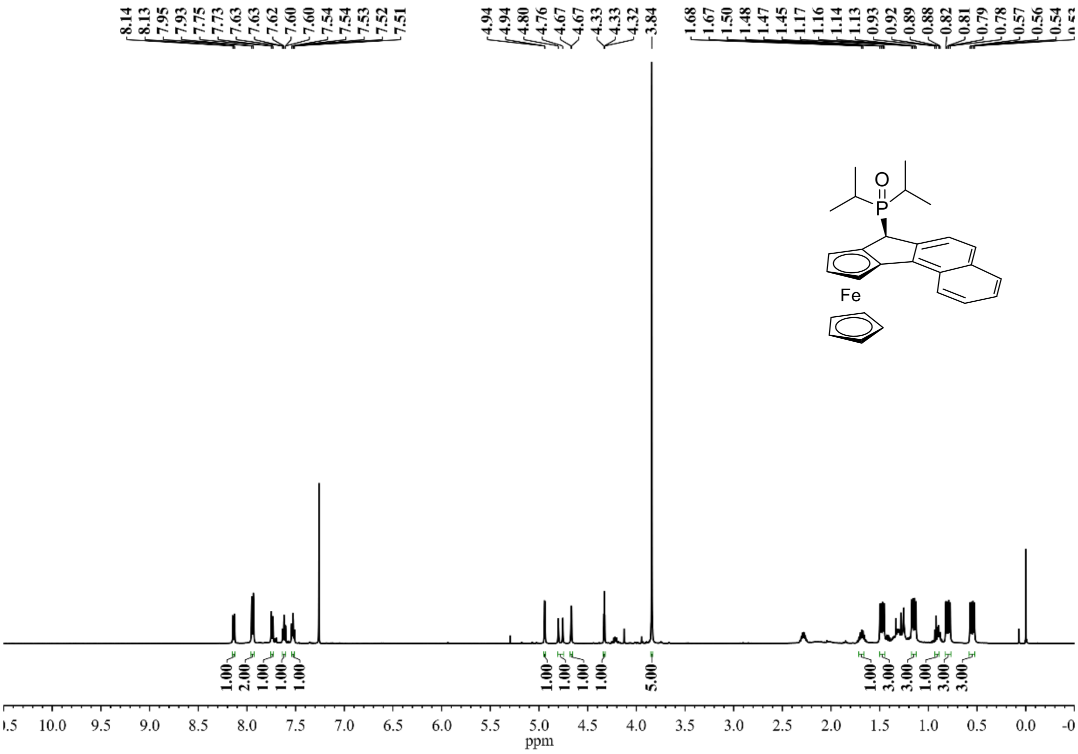


Figure S128. **^{1}H NMR** of **4o** (500 MHz, $CDCl_3$)

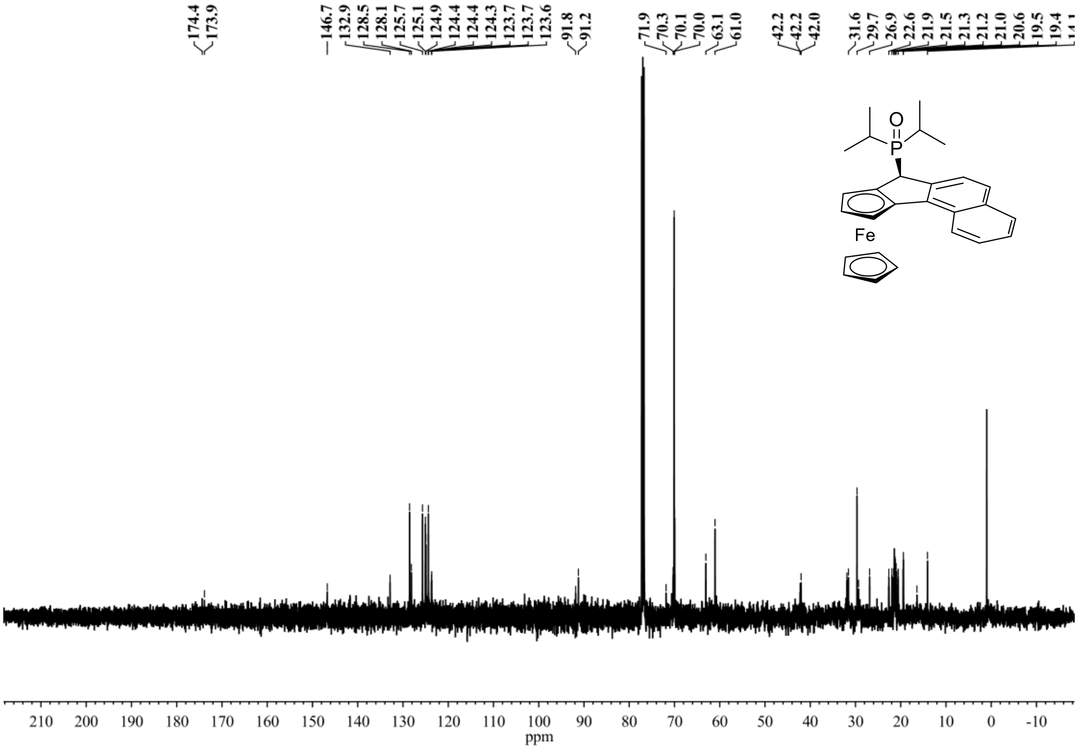


Figure S129. **^{13}C NMR** of **4o** (151 MHz, $CDCl_3$)

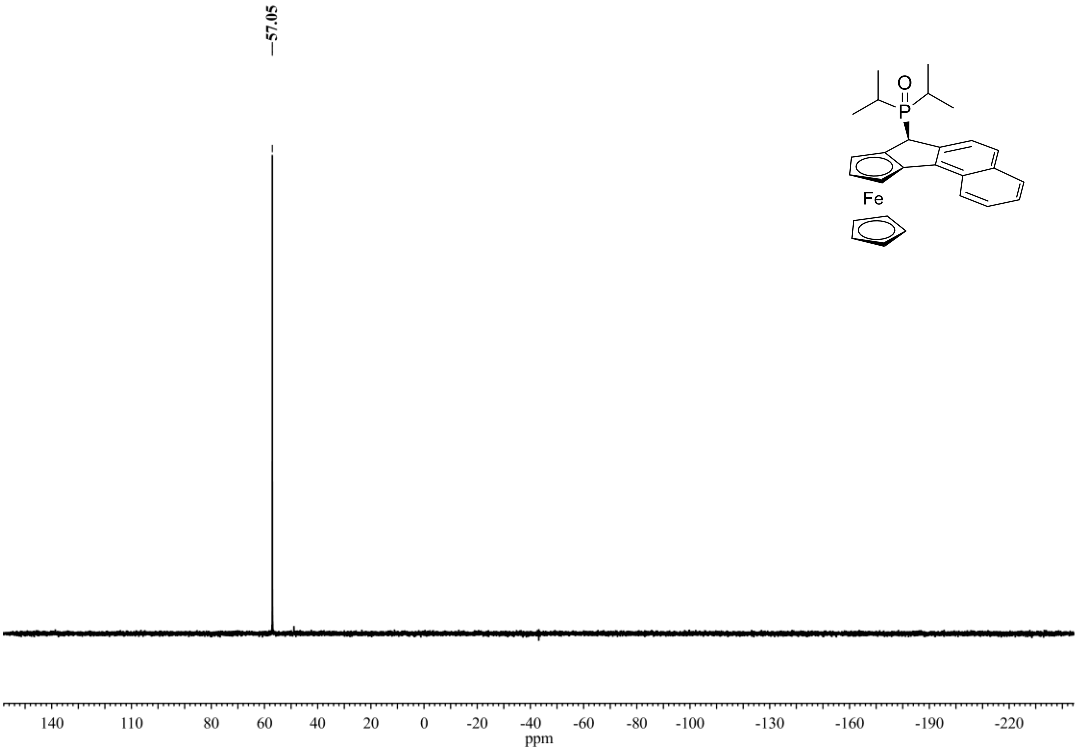


Figure S130. **^{31}P NMR** of **4o** (202 MHz, $CDCl_3$)

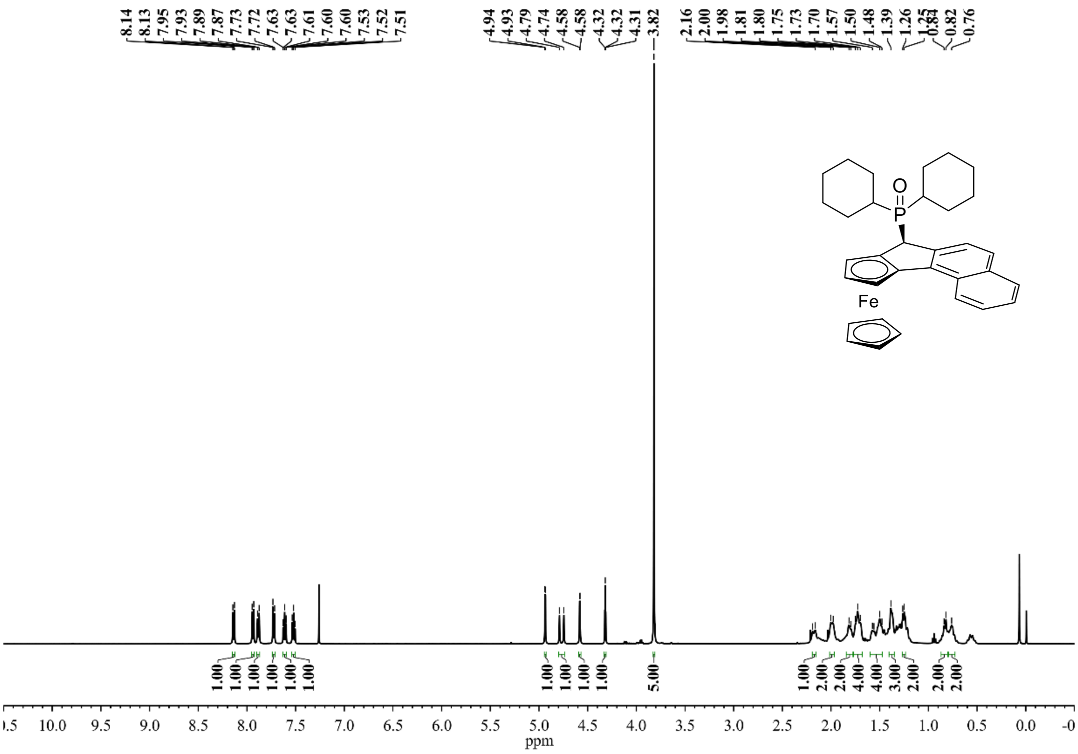


Figure S131. **^{1}H NMR** of **4p** (500 MHz, $CDCl_3$)

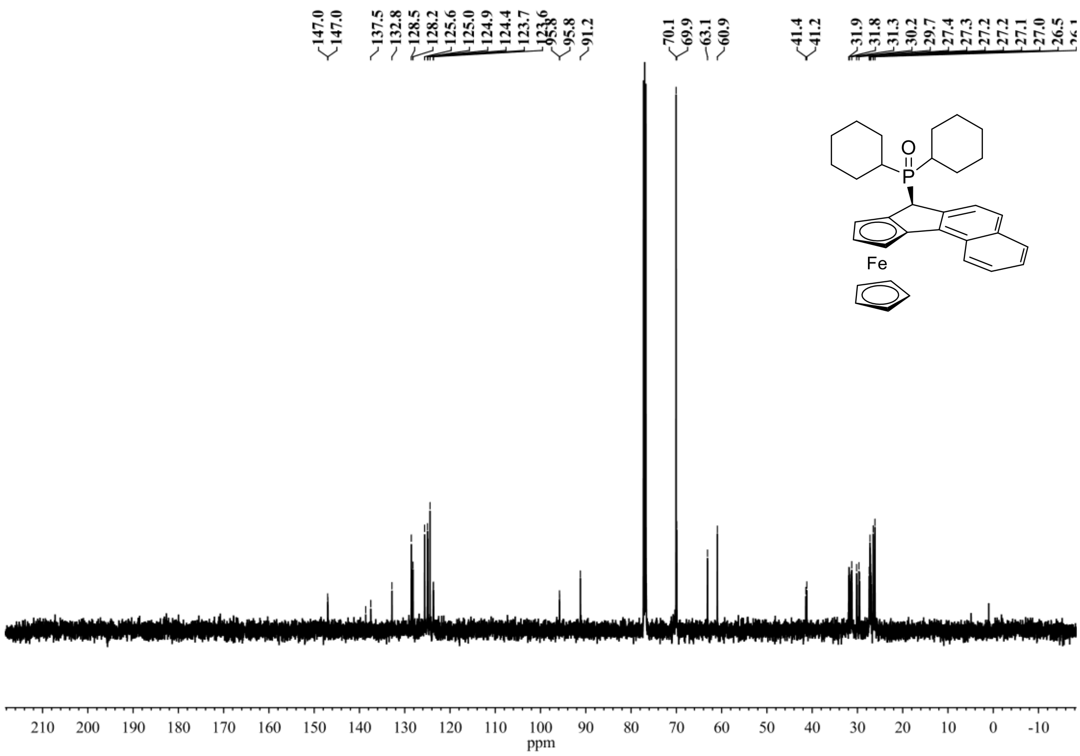


Figure S132. **^{13}C NMR** of **4p** (151 MHz, $CDCl_3$)

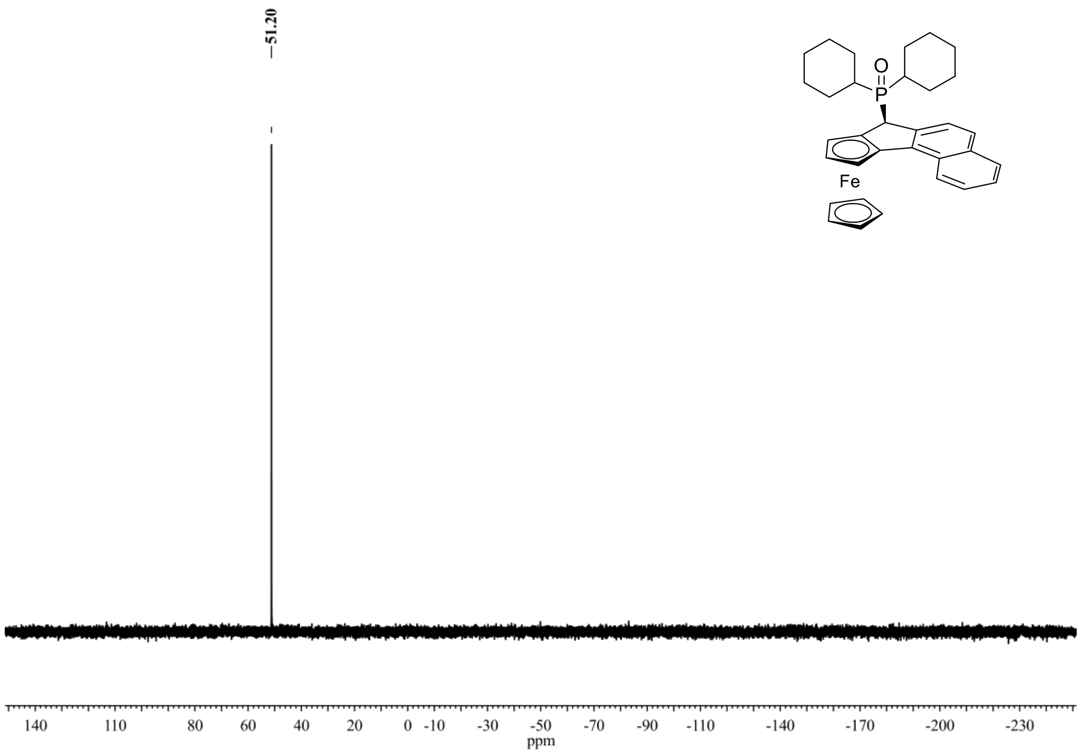


Figure S133**.** **^{31}P NMR** of **4p** (202 MHz, $CDCl_3$)

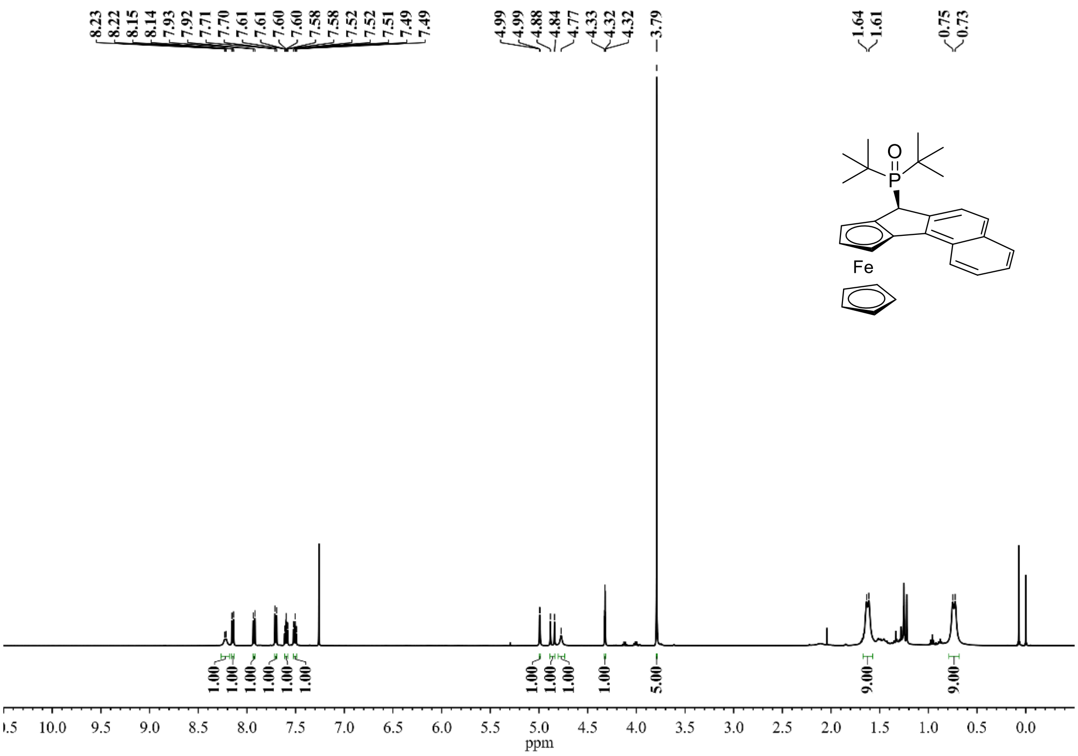


Figure S134. **^{1}H NMR** of **4q** (500 MHz, $CDCl_3$)

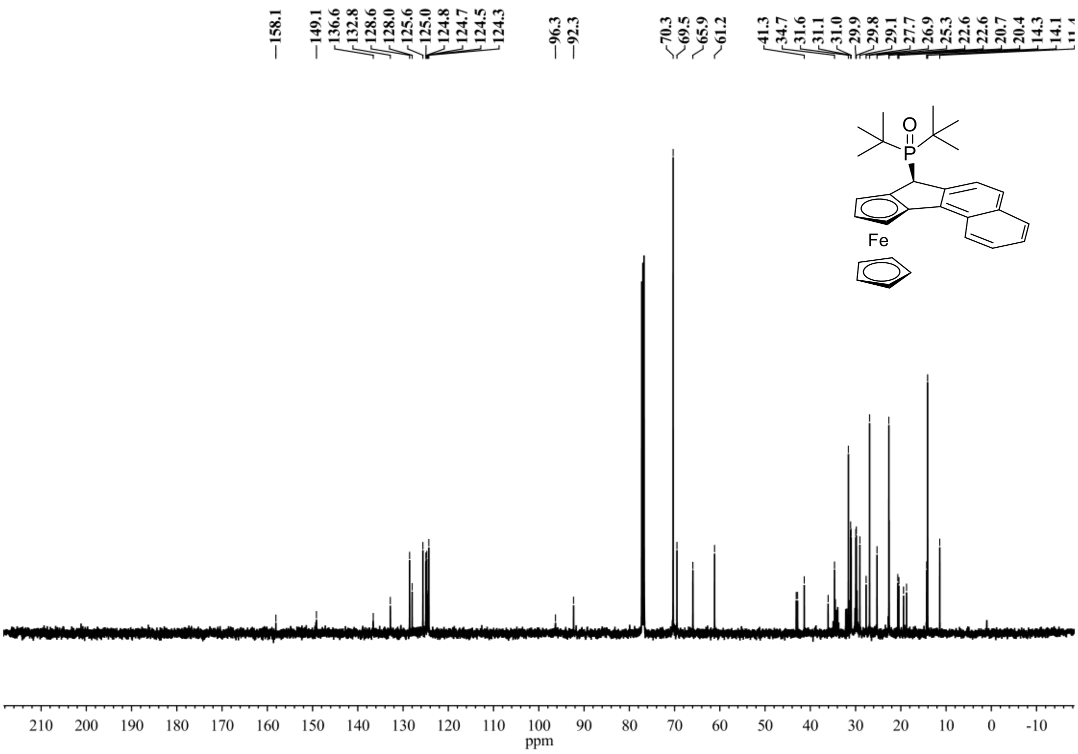


Figure S135. **^{13}C NMR** of **4q** (151 MHz, $CDCl_3$)

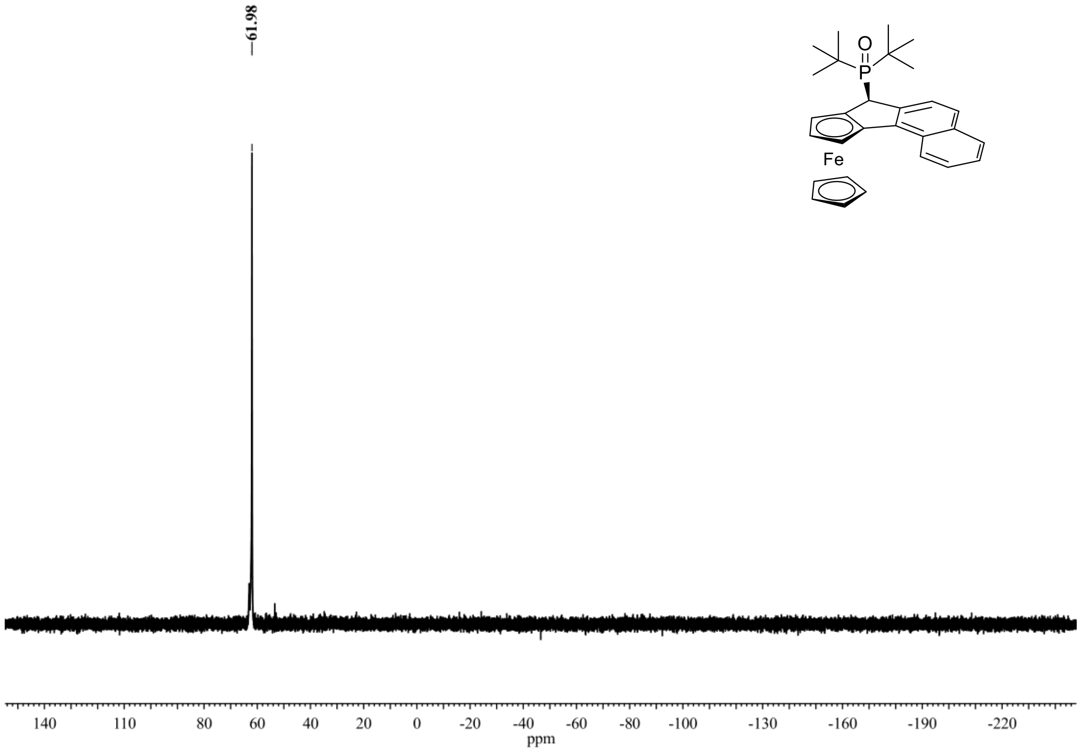


Figure S136. ^{31}**P NMR** of **4q** (202 MHz, $CDCl_3$)

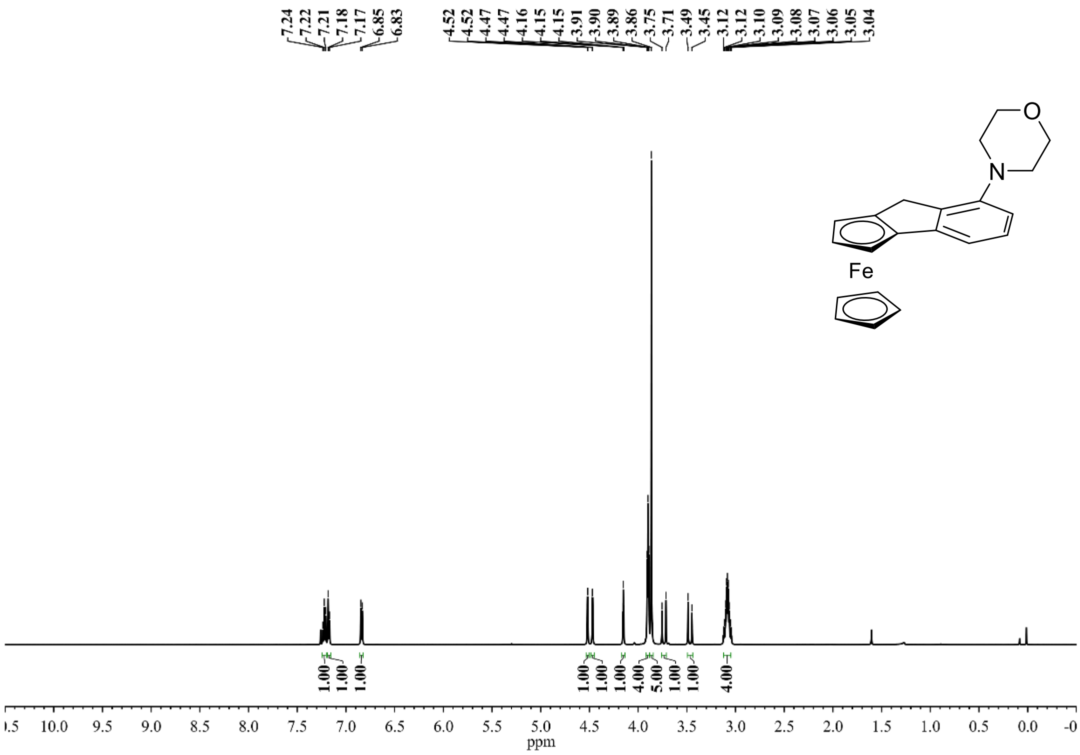


Figure S137. ^{1}**H NMR** of **5** (500 MHz, $CDCl_3$)

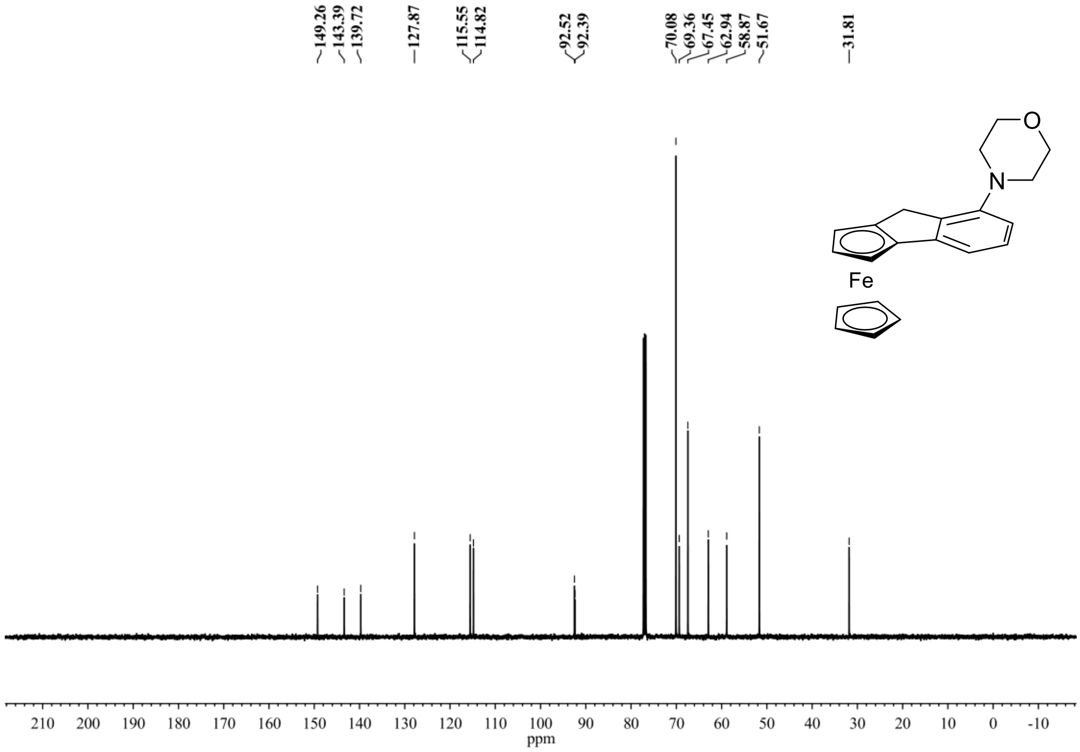


Figure S138. ^{13}**C NMR** of **5** (126 MHz, $CDCl_3$)

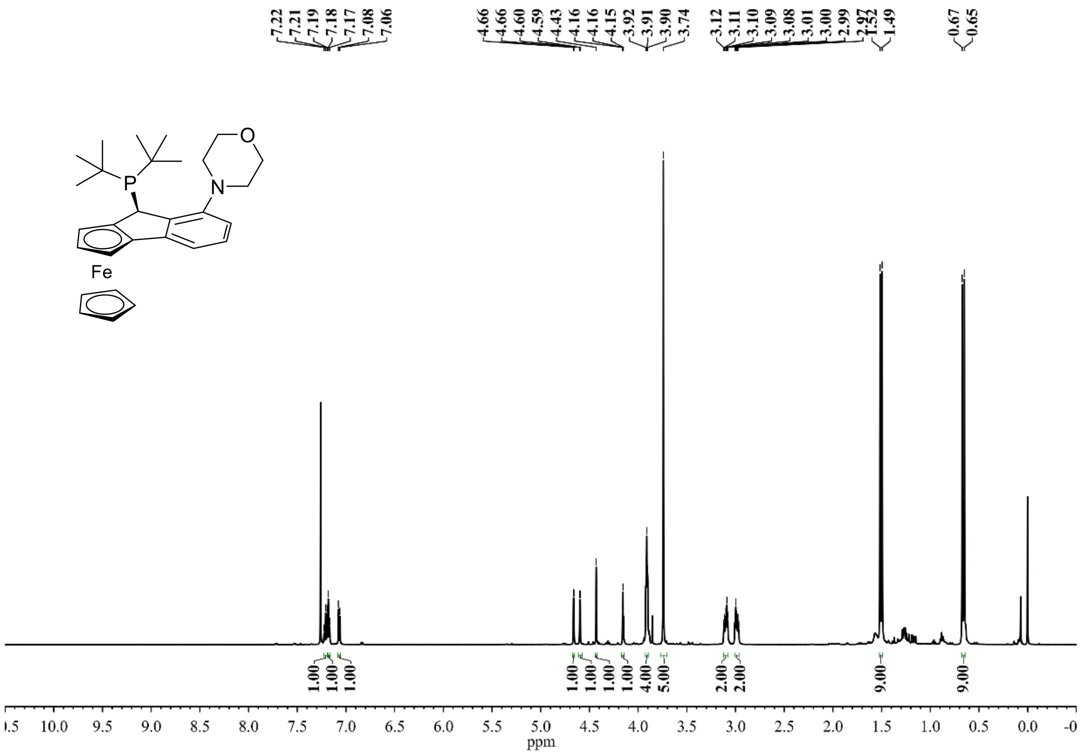


Figure S139**.** ^{1}**H NMR** of **6** (500 MHz, $CDCl_3$)

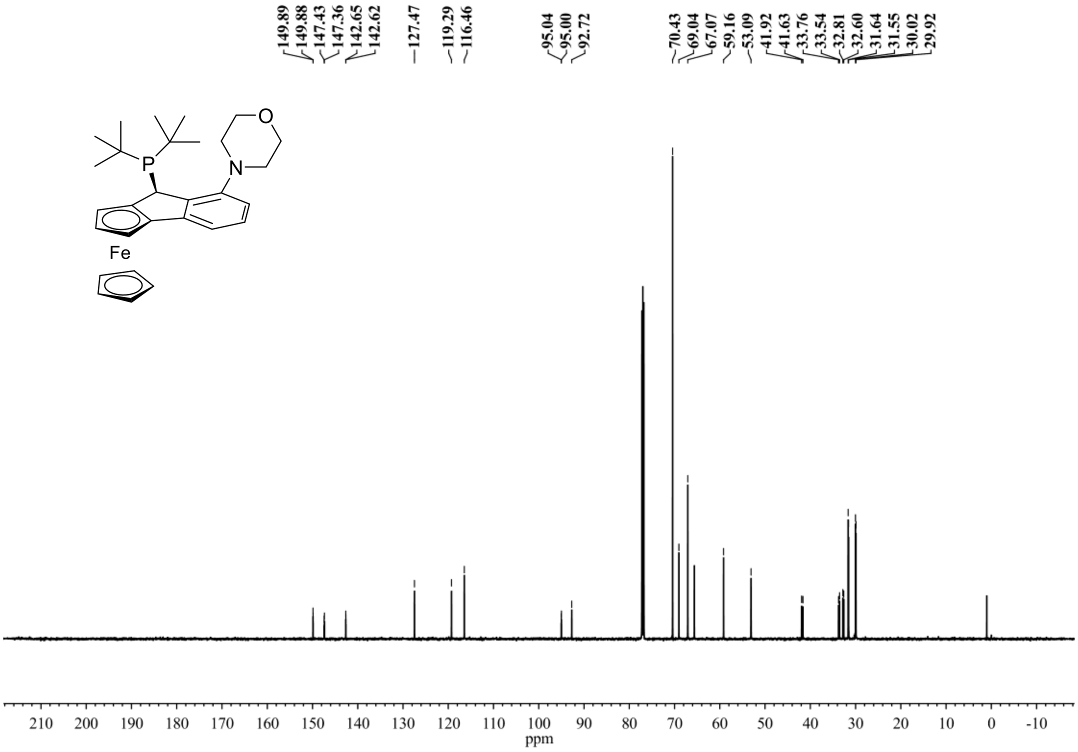


Figure S140**. ^{13}C NMR** of **6** (126 MHz, $CDCl_3$)

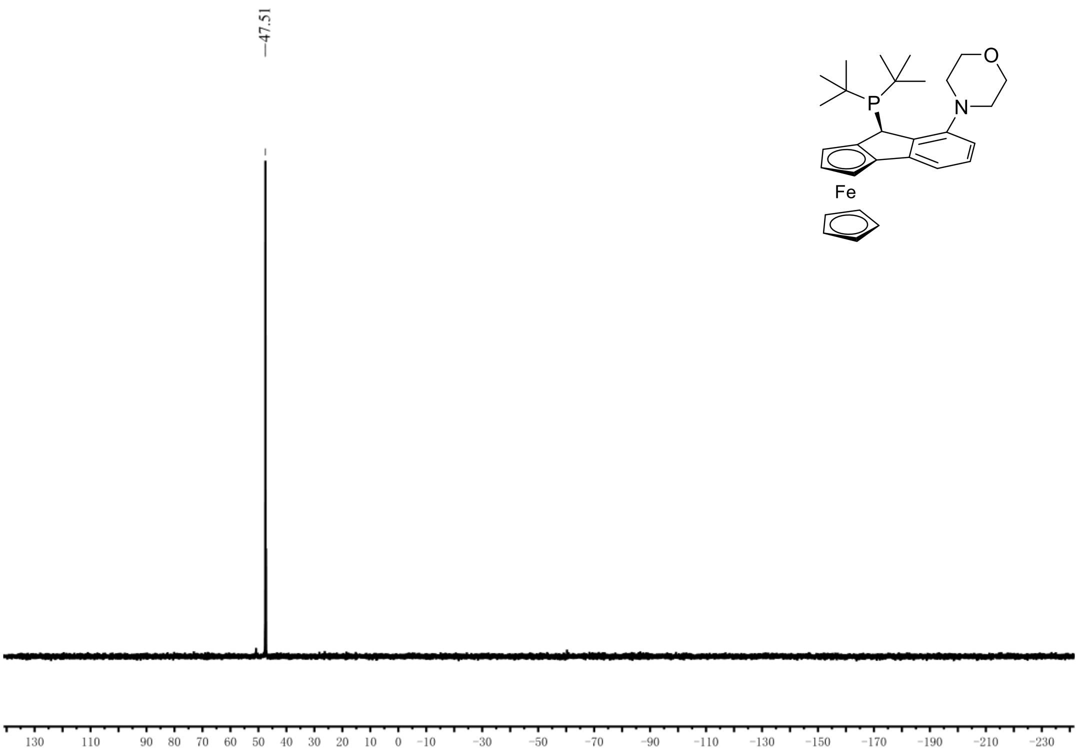


Figure S141**. ^{31}P NMR** of **6** (202 MHz, $CDCl_3$)

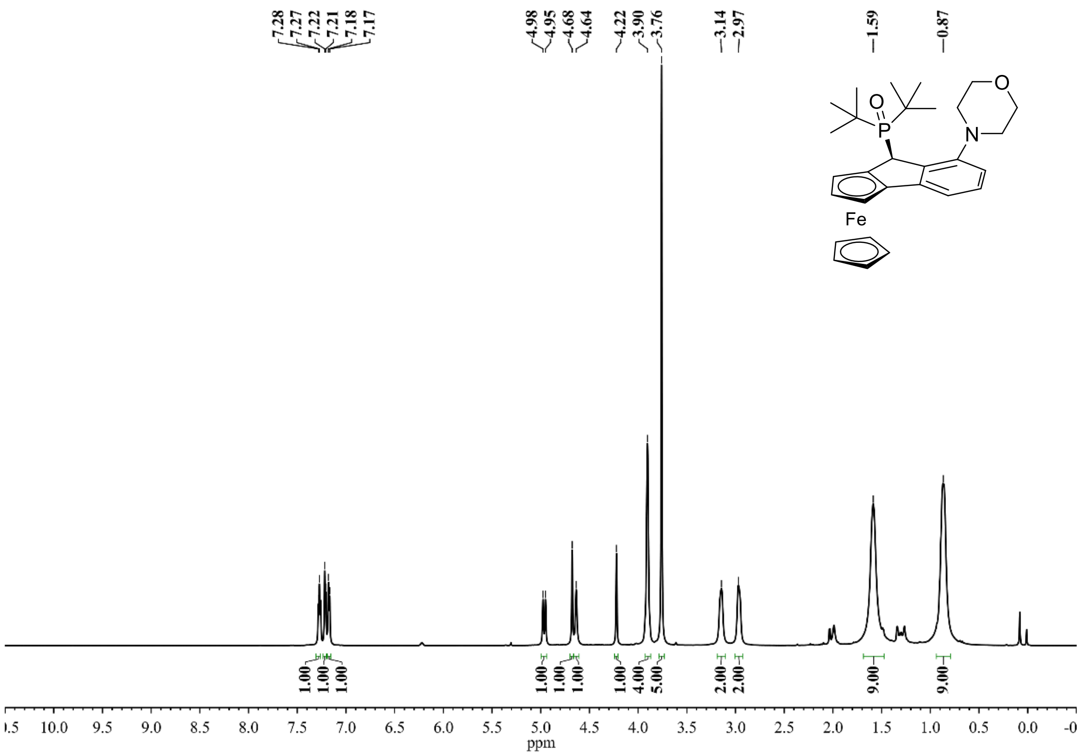


Figure S142**. ^{1}H NMR** of **7** (500 MHz, $CDCl_3$)

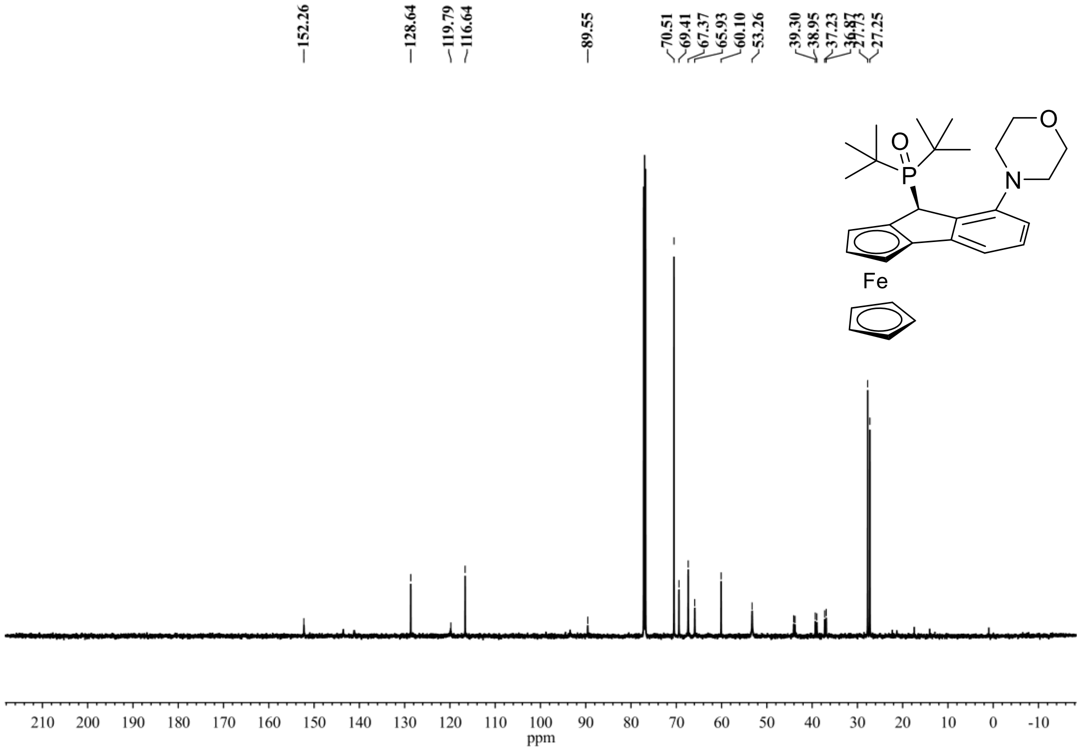


Figure S143. **^{13}C NMR** of **7** (126 MHz, $CDCl_3$)

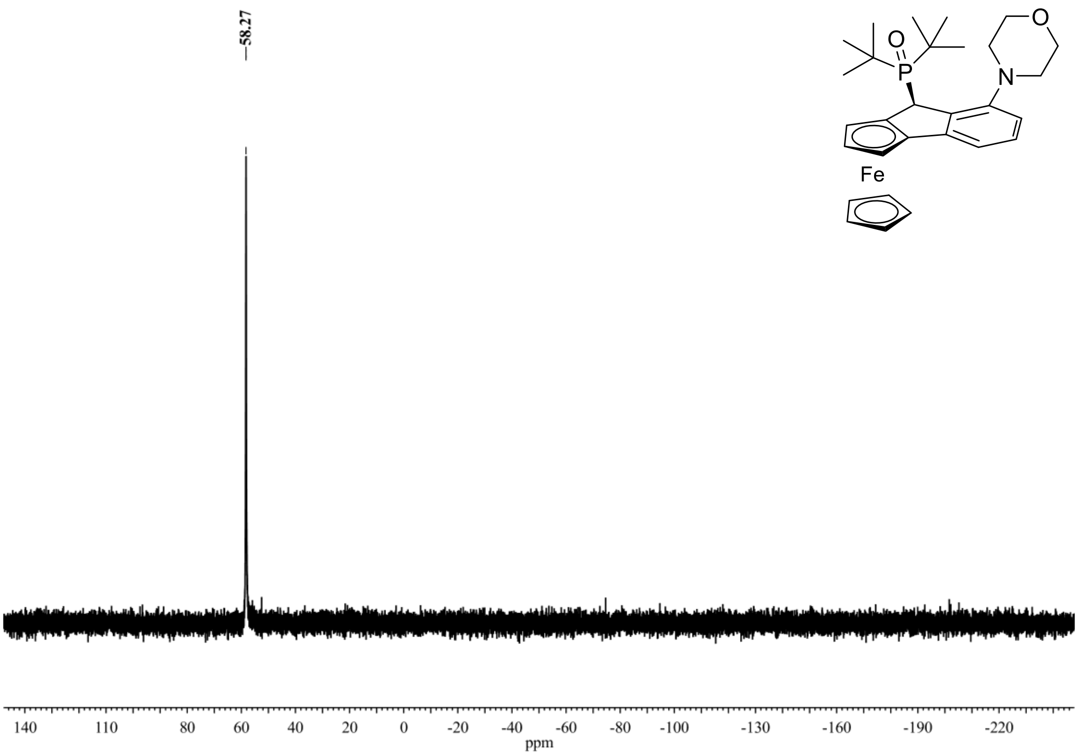
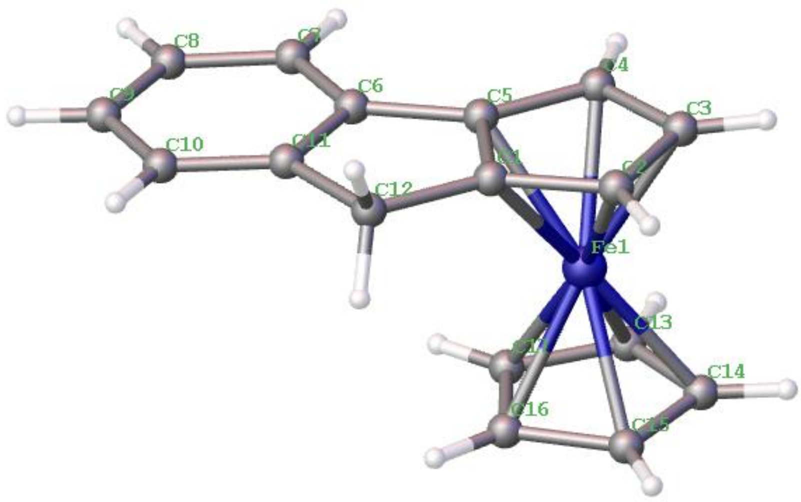


Figure S144. ^{31}**P NMR** of **7** (202 MHz, $CDCl_3$)

10. Crystal data for compound



(S_p)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a, 8a-η)-1,

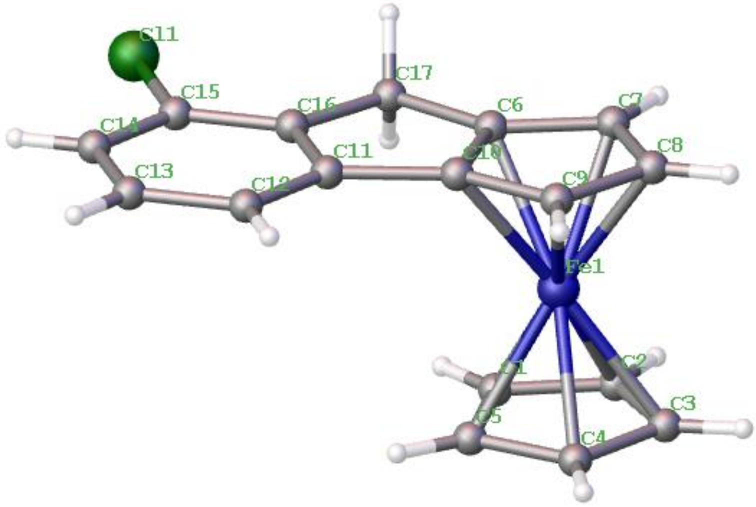
8-dihydrocyclopent[*a*]inden-1-yl] iron (**2a**)

Table S3. Sample and crystal data for 2a.

Identification code	2a	
Chemical formula	$C_{17}H_{14}Fe$	
Formula weight	274.13 g/mol	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal size	0.200 x 0.200 x 0.200 mm	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.700(2) Å	α = 90°
	b = 10.814(3) Å	β = 90°
	c = 29.940(8) Å	γ = 90°
Volume	2493.0(12) Å^3	
Z	8	
Density (calculated)	1.461 g/cm^3	
Absorption coefficient	1.185 mm^{-1}	
F(000)	1136	

Table S4. Data collection and structure refinement for 2a.

Theta range for data collection	2.00 to 25.00 °	
Index ranges	-9<=h<=9, -12<=k<=12, -34<=l<=33	
Reflections collected	13144	
Independent reflections	3899 [R(int) = 0.0492]	
Max. and min. transmission	0.7970 and 0.7970	
Structure solution technique	direct methods	
Structure solution program	SUPERFLIP (Palatinus & Chapuis,2007)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	Σ w(F_o^2 - F_c^2)^2	
Data / restraints / parameters	3899 / 0 / 326	
Goodness-of-fit on F^2	1.030	
Δ/σ_{max}	0.001	
Final R indices	3579 data; I>2σ(I)	R1 = 0.0467, wR2 = 0.1215
	all data	R1 = 0.0513, wR2 = 0.1270
Weighting scheme	w=1/[$\sigma^2(F_o^2)+(0.0907P)^2+0.4100P$] where P=($F_o^2+2F_c^2$)/3	
Absolute structure parameter	0.0(0)	
Largest diff. peak and hole	0.633 and -0.687 eÅ^{-3}	
R.M.S. deviation from mean	0.092 eÅ^{-3}	

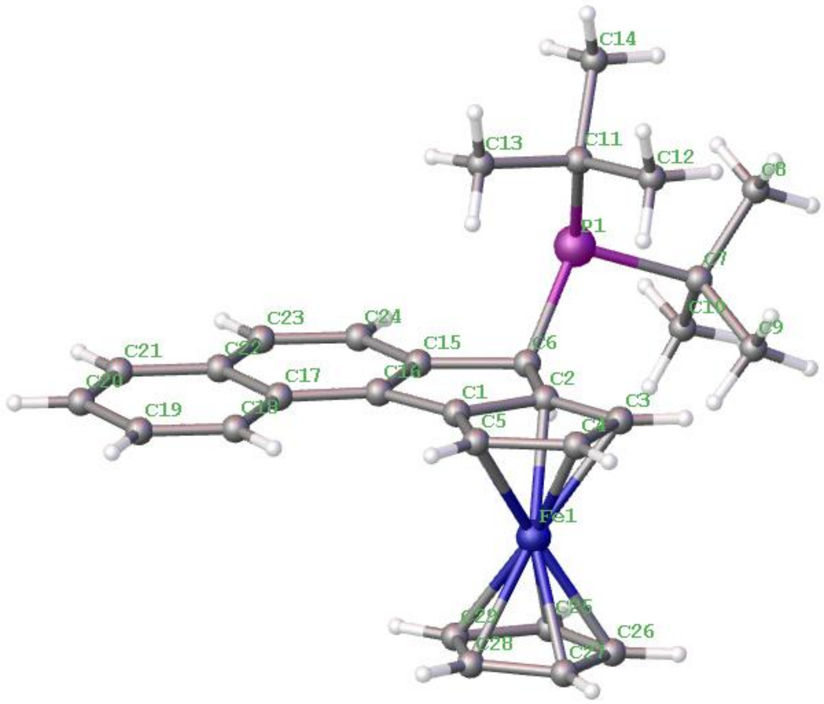


(R_p)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-6–chloro-1,8-dihydrocyclopent[*a*] inden-1-yl]iron **(2f)**

Table S5 Crystal data and structure refinement for 2f.

Identification code	2f
Empirical formula	$C_{17}ClFeH_{13}$
Formula weight	308.57
Temperature/K	273.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.2854(6)
b/Å	20.4848(10)
c/Å	10.5744(4)
α/°	90
β/°	90.403(2)
γ/°	90
Volume/Å^3	2661.1(2)
Z	8
ρ_{calc}g/cm^3	1.540
μ/mm^{-1}	1.314
F(000)	1264.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.178 to 49.998
Index ranges	$-14 \le h \le 14$, $-24 \le k \le 24$, $-12 \le l \le 11$
Reflections collected	48421

Independent reflections	4679 [R_{int} = 0.0295, R_{sigma} = 0.0147]
Data/restraints/parameters	4679/12/331
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0854, wR_2 = 0.2454
Final R indexes [all data]	R_1 = 0.0924, wR_2 = 0.2503
Largest diff. peak/hole / e Å^{-3}	2.98/-1.27



(R$_p$,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,10a-η)-(10a*S*)-10-(ditertbutylphosphine) -1,10-dihydro-10-oxopenthaleno [1,2-b] naphthalen-1-yl] iron **(3q)**

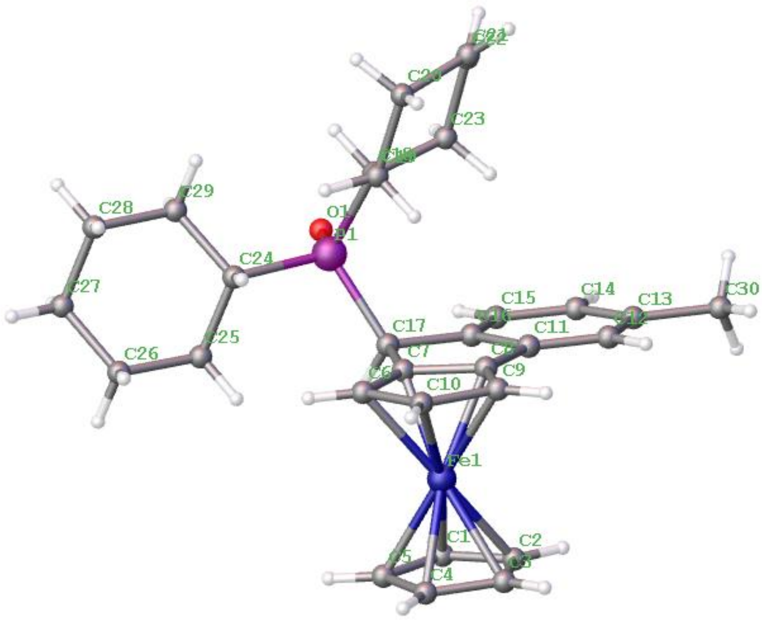
Table S6. Sample and crystal data for 3q.

Identification code	shanhe20201217
Chemical formula	$C_{29}H_{33}FeP$
Formula weight	468.37 g/mol
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P 1 21/c 1

Unit cell dimensions	a = 7.7863(12) Å	α = 90°
	b = 16.223(3) Å	β = 91.630(3)°
	c = 19.281(3) Å	γ = 90°
Volume	2434.5(7) $Å^3$	
Z	4	
Density (calculated)	1.278 g/cm^3	
Absorption coefficient	0.699 mm^{-1}	
F(000)	992	

Table S7. Data collection and structure refinement for 35.

Theta range for data collection	1.64 to 28.25 °	
Index ranges	-9<=h<=10, -21<=k<=12, -25<=l<=25	
Reflections collected	16614	
Independent reflections	6011 [R(int) = 0.0339]	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	Σ w(F_o^2 - F_c^2)^2	
Data / restraints / parameters	6011 / 0 / 286	
Goodness-of-fit on F^2	1.051	
Final R indices	4026 data; I>2σ(I)	R1 = 0.0558, wR2 = 0.1479
	all data	R1 = 0.0877, wR2 = 0.1664
Weighting scheme	w=1/[σ^2(F_o^2)+(0.0754P)^2+1.4616P] where P=(F_o^2+2F_c^2)/3	
Largest diff. peak and hole	0.540 and -0.316 e$Å^{-3}$	
R.M.S. deviation from mean	0.065 e$Å^{-3}$	



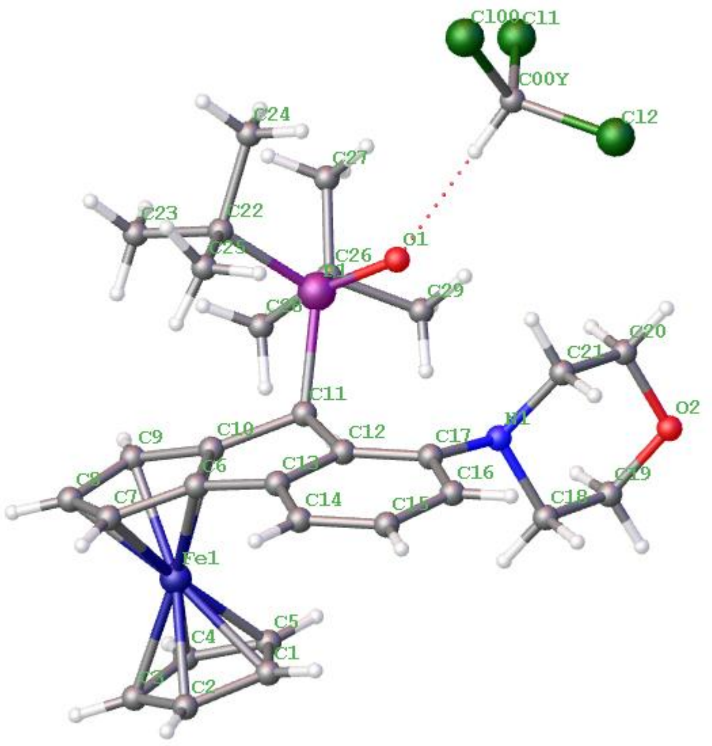
(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-5-methyl-(8a*S*)-8-(dicyclohexyl-phosphinyl)-1,8-dicyclohexylphosphine[*a*]inden-1-yl] iron (**4j**)

Table S8. Sample and crystal data for 4j.

Identification code	S4j	
Chemical formula	$C_{30}H_{35}FeOP$	
Formula weight	498.40 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.4885(9) Å	α = 88.962(2) °
	b = 10.5604(10) Å	β = 79.165(2)°
	c = 15.0107(15) Å	γ = 79.812(2)°
Volume	1453.8(2) Å^3	
Z	2	
Density (calculated)	1.139 g/cm^3	
Absorption coefficient	0.591 mm^{-1}	
F(000)	528	

Table S9. Data collection and structure refinement for 4j.

Theta range for data collection	1.96 to 25.00 °	
Index ranges	-11<=h<=11, -12<=k<=12, -17<=l<=17	
Reflections collected	15766	
Independent reflections	5098 [R(int) = 0.0176]	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5098 / 10 / 297	
Goodness-of-fit on F^2	1.042	
Δ/σ_{max}	0.001	
Final R indices	4418 data; $I>2\sigma(I)$	R1 = 0.0485, wR2 = 0.1364
	all data	R1 = 0.0553, wR2 = 0.1442
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0926P)^2+0.6842P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.914 and -0.407 $eÅ^{-3}$	
R.M.S. deviation from mean	0.062 $eÅ^{-3}$	



(R_p,S)-(η^5-2,4-cyclopentadien-1-yl)[(1,2,3,3a,8a-η)-6-(4-morpholino)-(8A*s*)-8-(ditertb-u-tylphosphinyl)-1,8-dihydrocyclopent [*a*]inden-1-yl] iron **(7b)**

Table S10 Crystal data and structure refinement for 7b

Identification code	mo_211231a_0m_a
Empirical formula	$C_{30}H_{39}NO_2PFeCl_3$
Formula weight	638.79
Temperature/K	273.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.2416(3)
b/Å	19.7855(6)
c/Å	14.5494(4)
α/°	90
β/°	107.3950(10)
γ/°	90
Volume/Å^3	3088.09(15)
Z	4
ρ_{calc}g/cm^3	1.374
μ/mm^{-1}	0.827

F(000)	1336.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/ °	5.056 to 52.832
Index ranges	$-14 \leq h \leq 14$, $-24 \leq k \leq 24$, $-18 \leq l \leq 18$
Reflections collected	62603
Independent reflections	6316 [R_{int} = 0.0455, R_{sigma} = 0.0243]
Data/restraints/parameters	6316/23/337
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.1024
Final R indexes [all data]	R_1 = 0.0627, wR_2 = 0.1125
Largest diff. peak/hole / e Å^{-3}	0.64/-0.47

11. HRMS (ESI-TOF) spectra

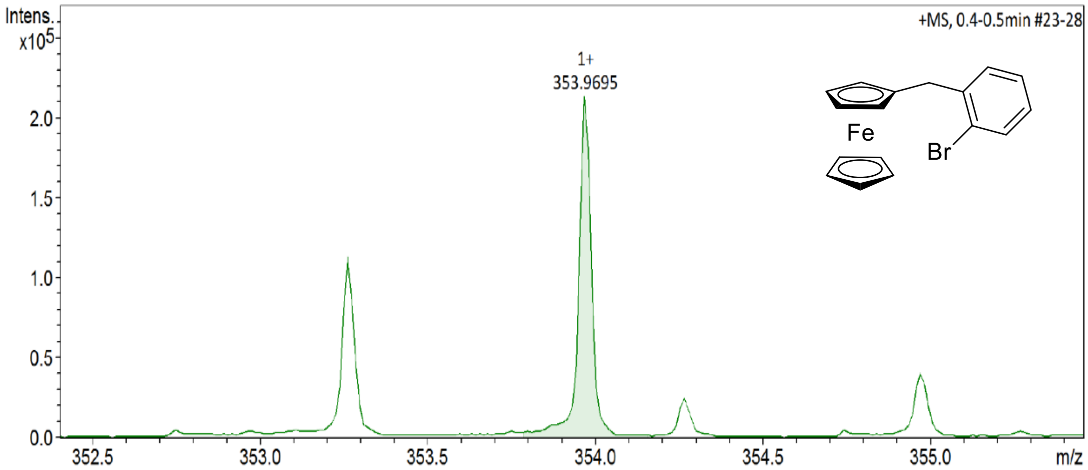


Figure S145. **HRMS** spectra of **1a**

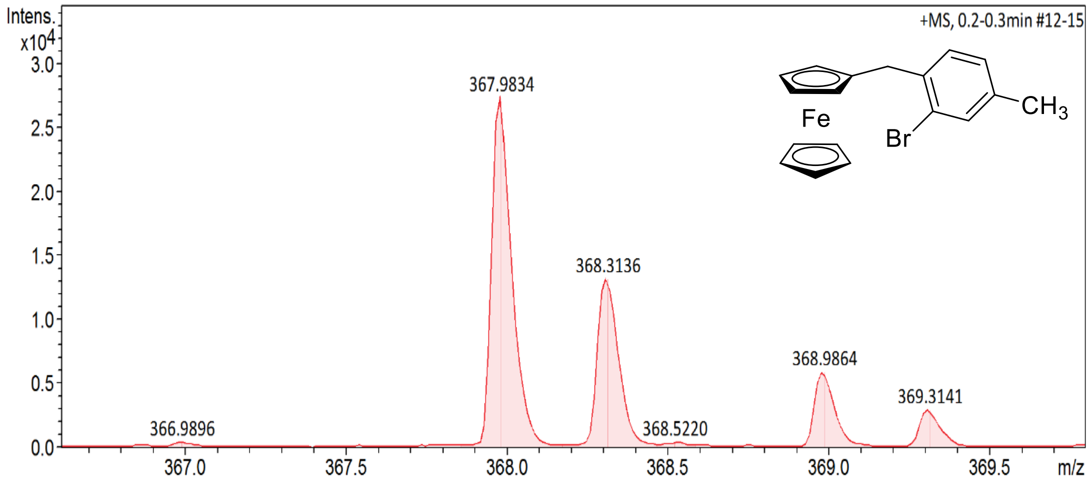


Figure S146. **HRMS** spectra of **1b**

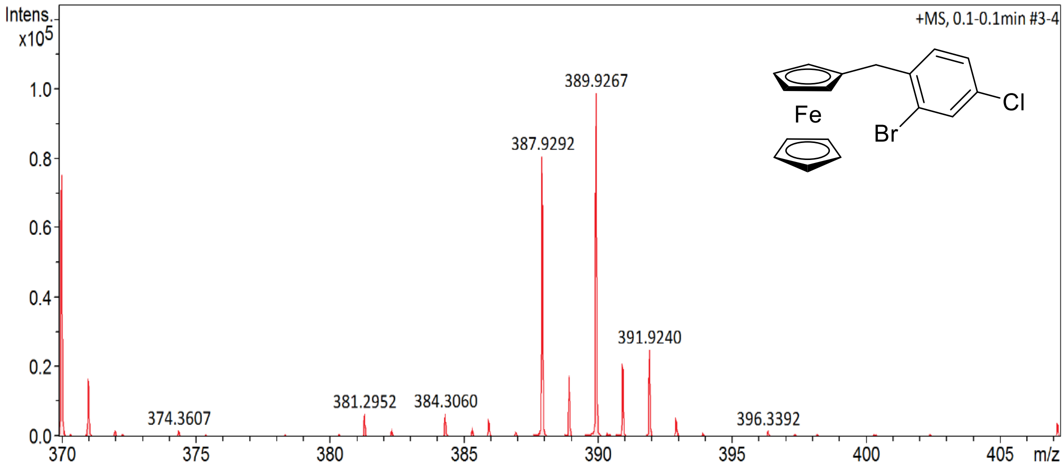


Figure S147**. HRMS** spectra of **1c**

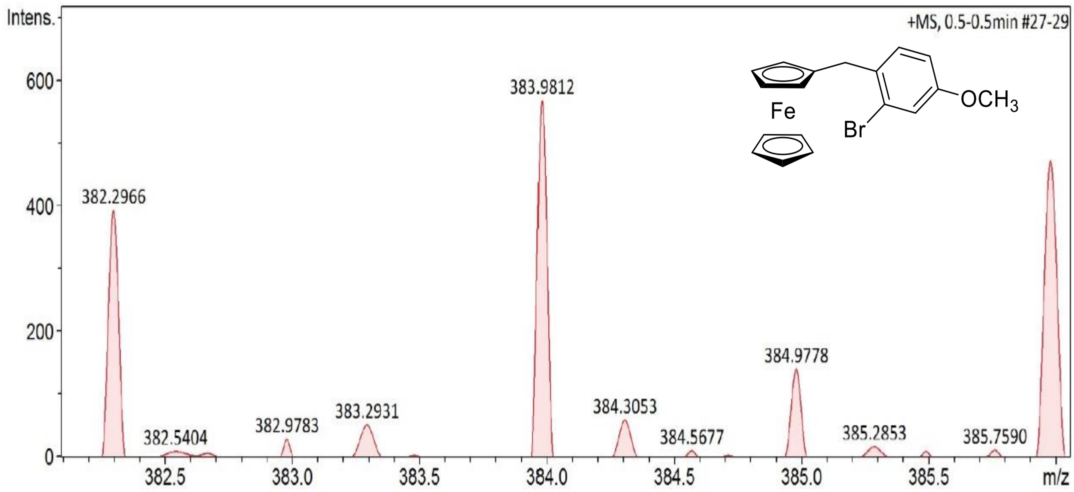


Figure S148. **HRMS** spectra of **1d**

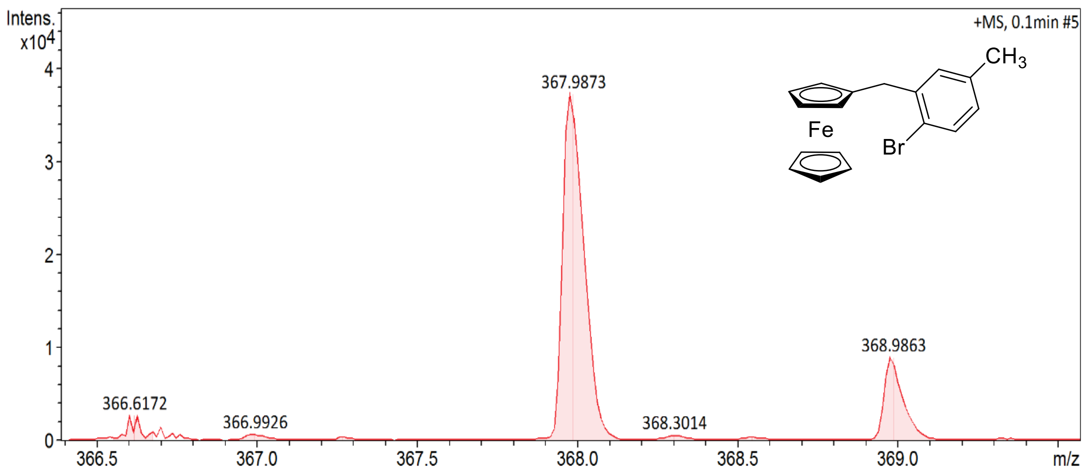


Figure S149**. HRMS** spectra of **1e**

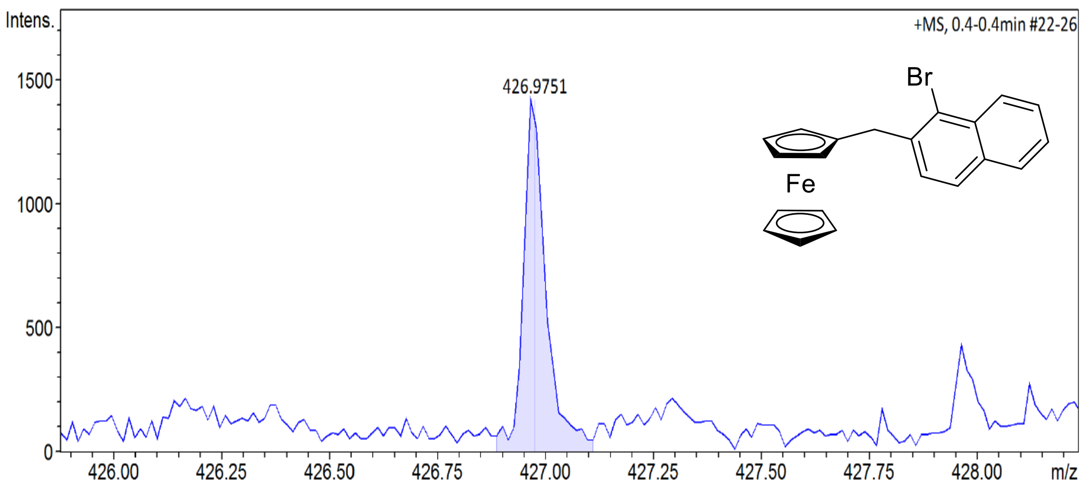


Figure S150**. HRMS** spectra of **1f**

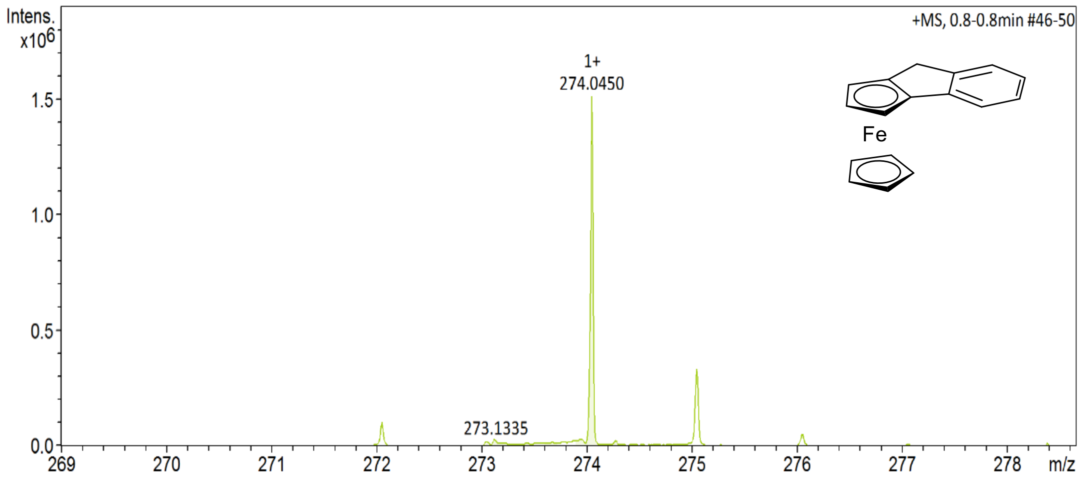


Figure S151**. HRMS** spectra of **2a**

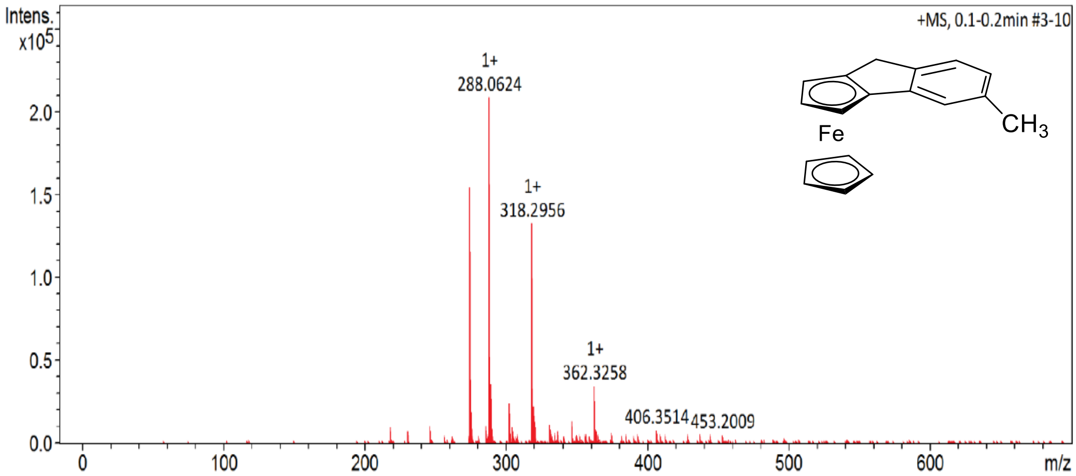


Figure S152. **HRMS** spectra of **2b**

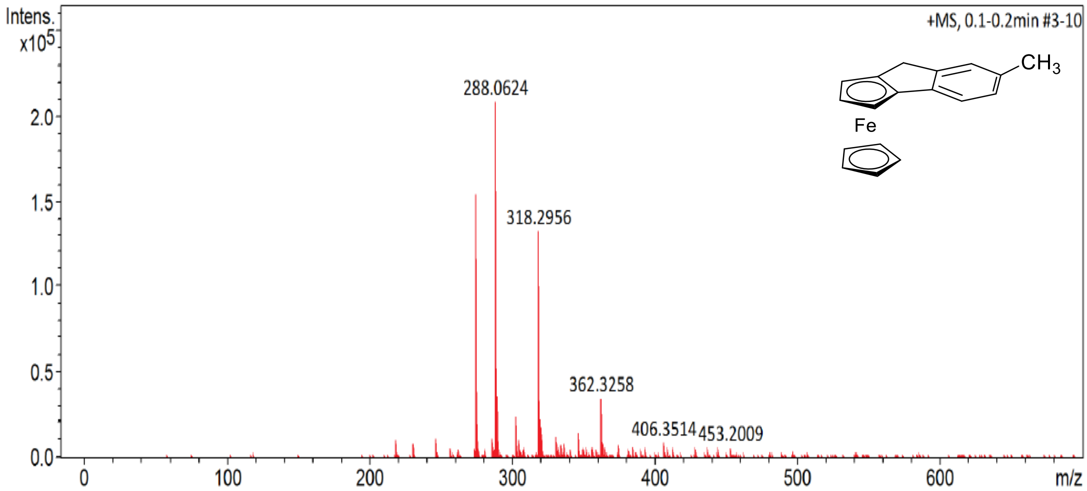


Figure S153**. HRMS** spectra of **2c**

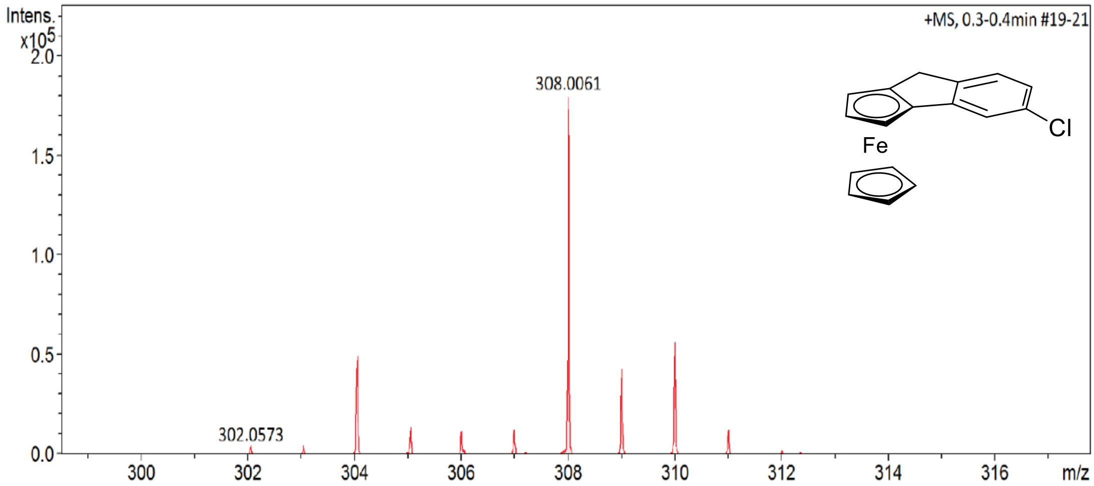


Figure S154. **HRMS** spectra of **2d**

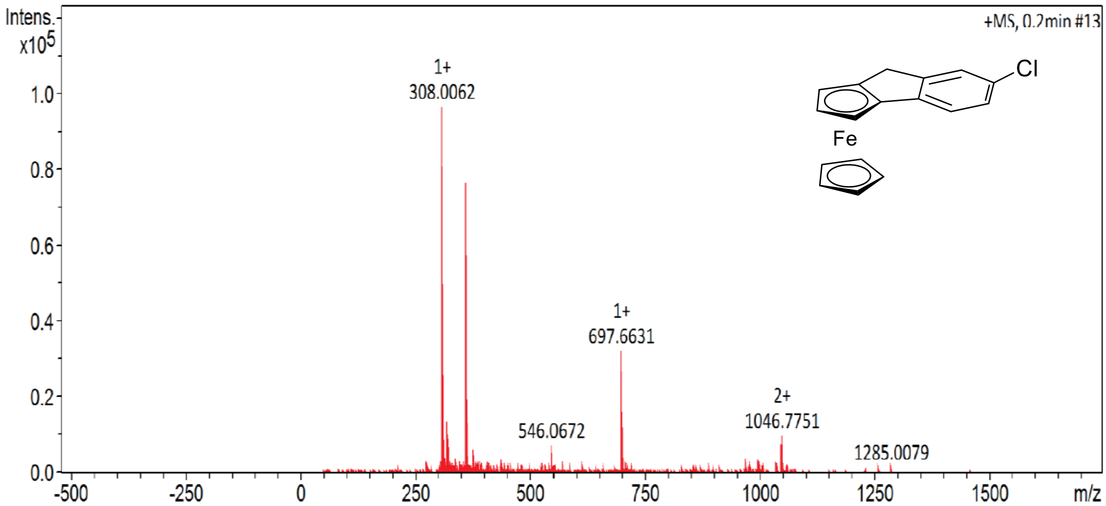


Figure S155. **HRMS** spectra of **2e**

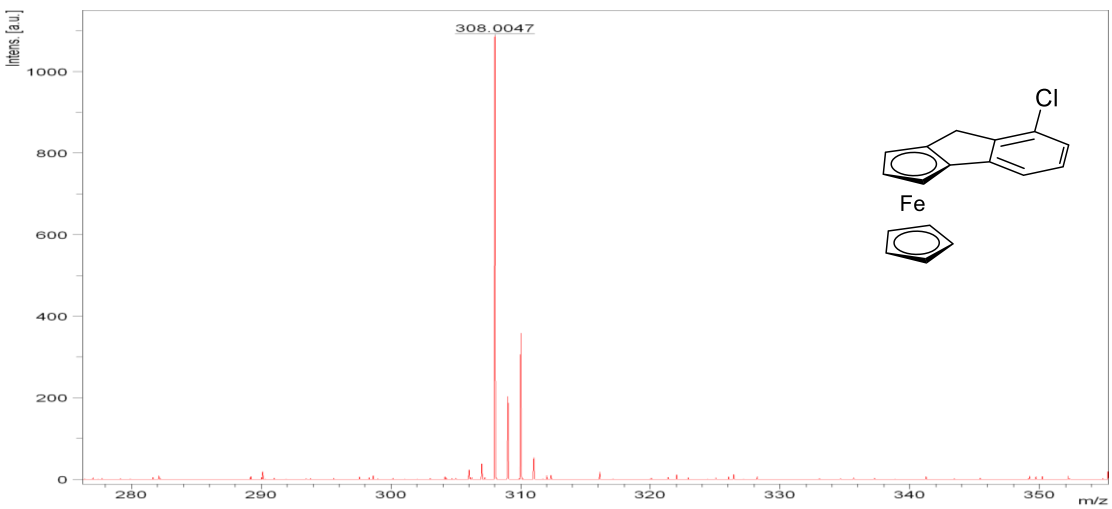


Figure S156. **HRMS** spectra of **2f**

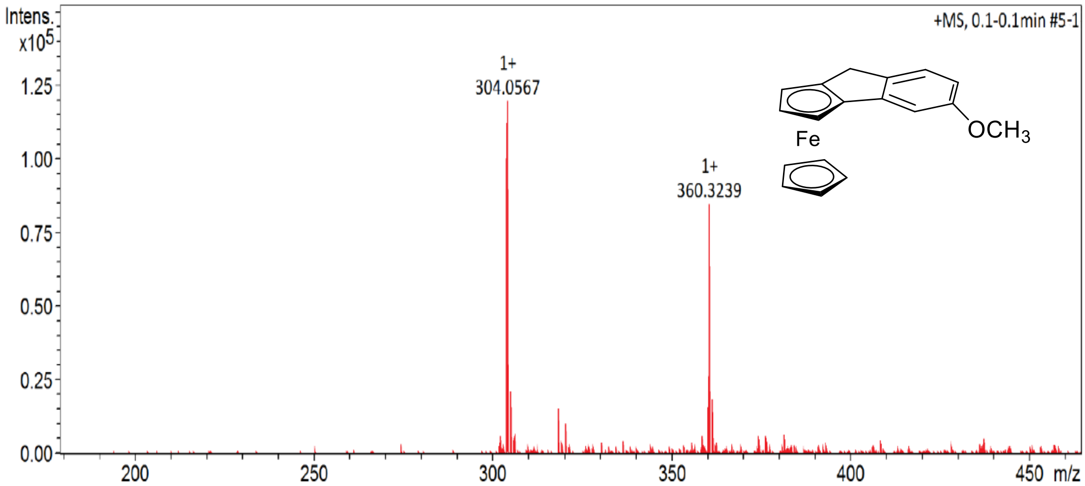


Figure S157. **HRMS** spectra of **2g**

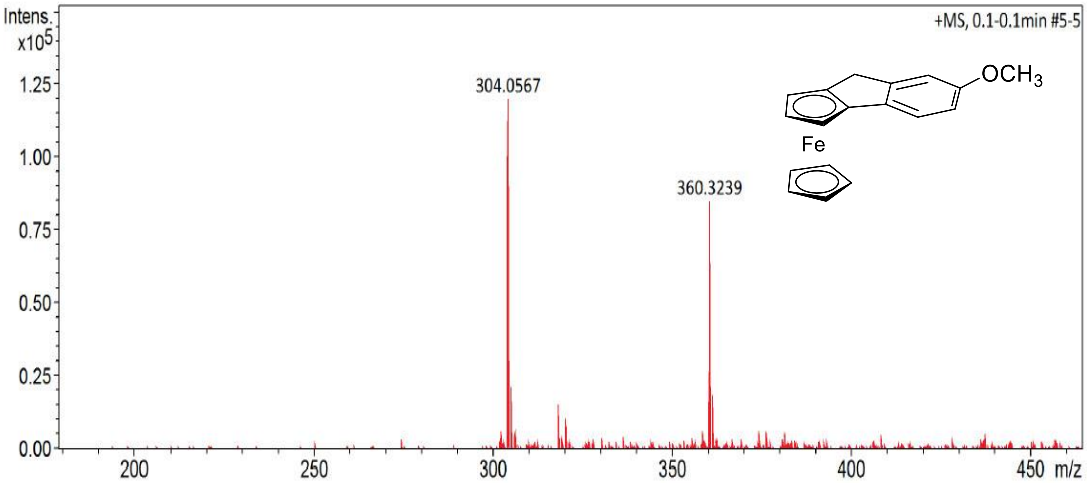


Figure S158. **HRMS** spectra of **2h**

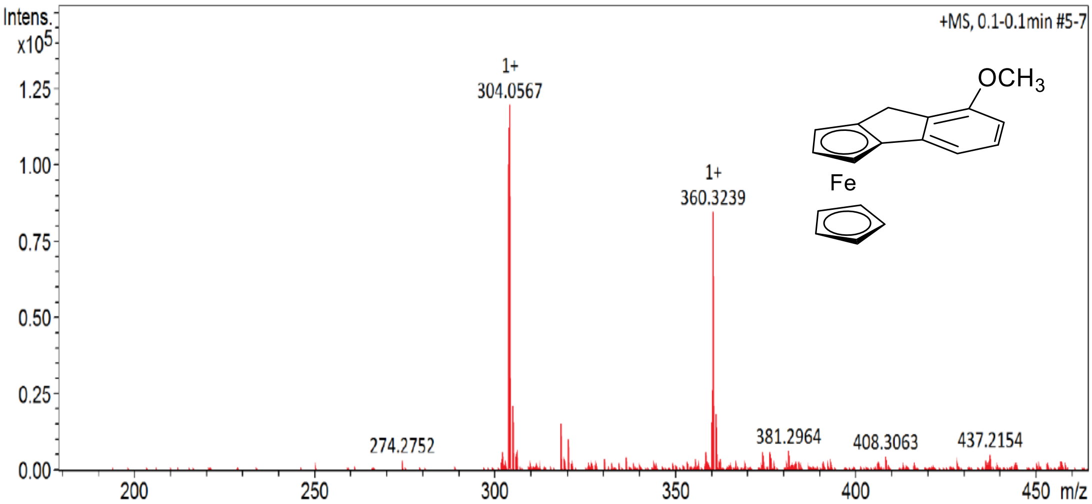


Figure S159. **HRMS** spectra of **2i**

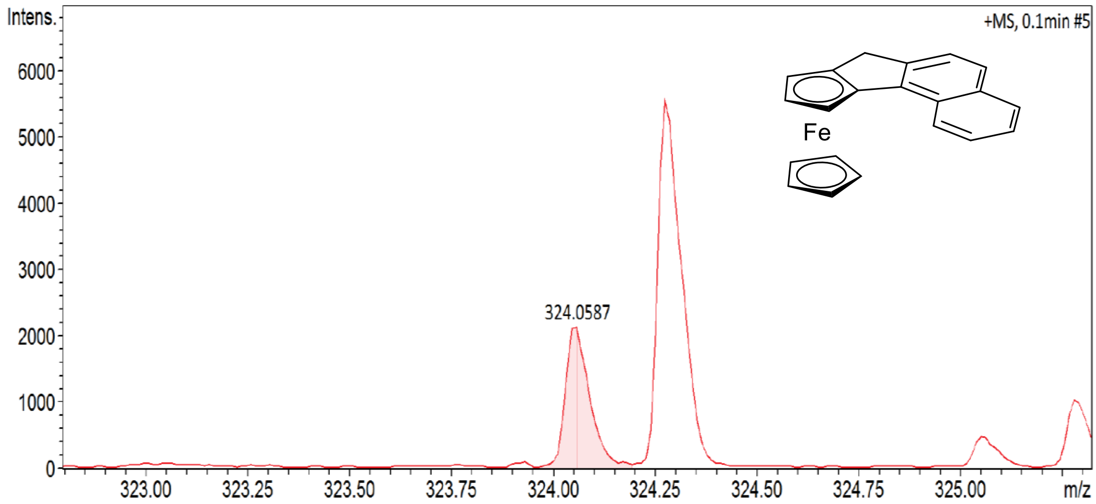


Figure S160. **HRMS** spectra of **2j**

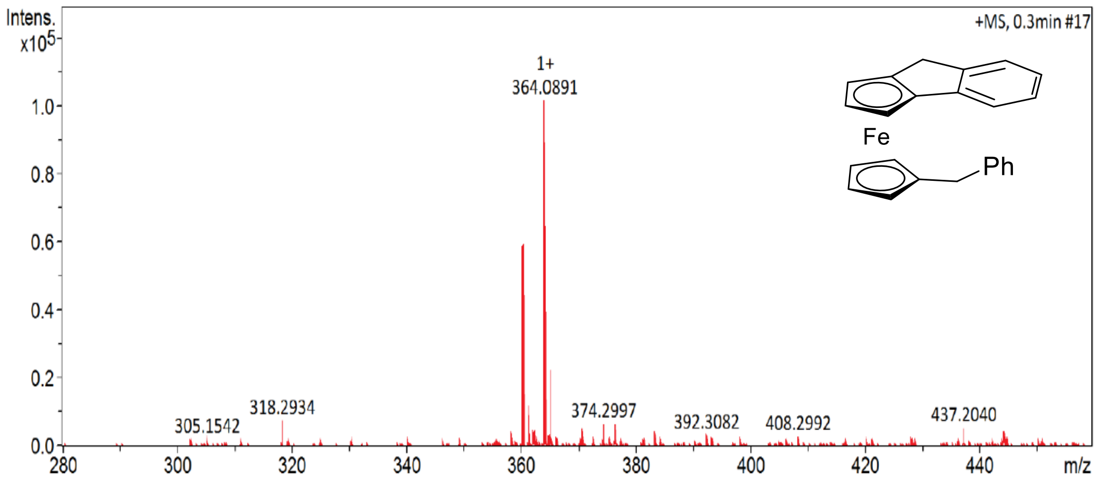


Figure S161. **HRMS** spectra of **2k**

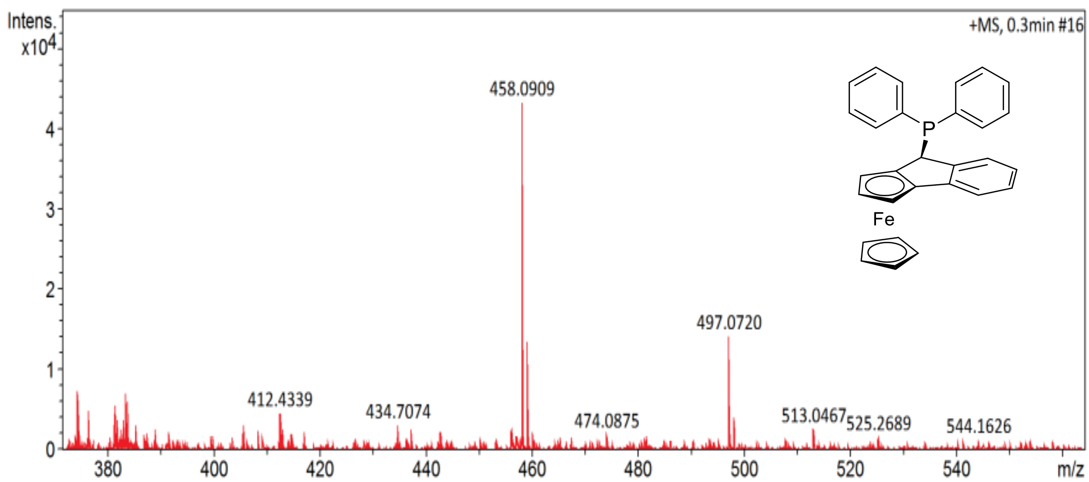


Figure S162. **HRMS** spectra of **3a**

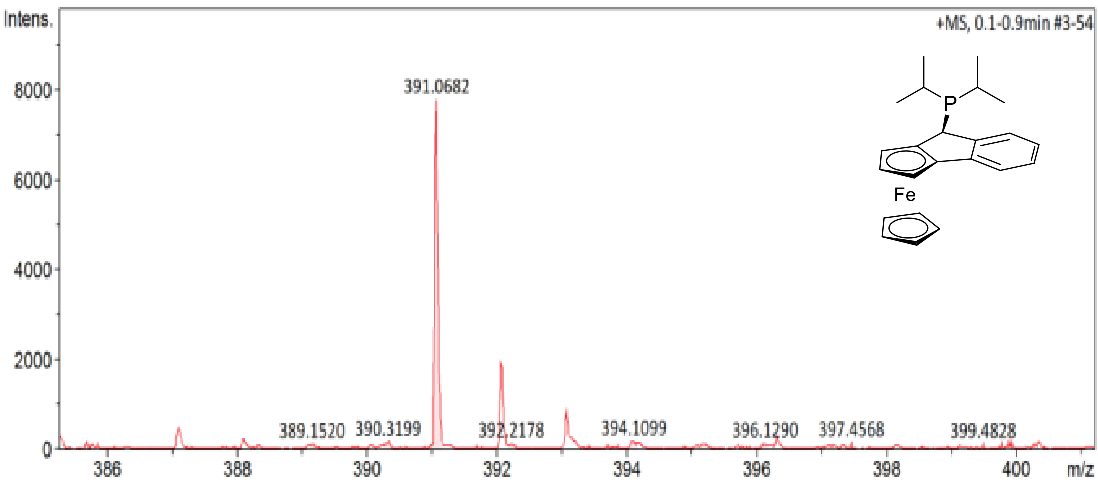


Figure S163. **HRMS** spectra of **3b**

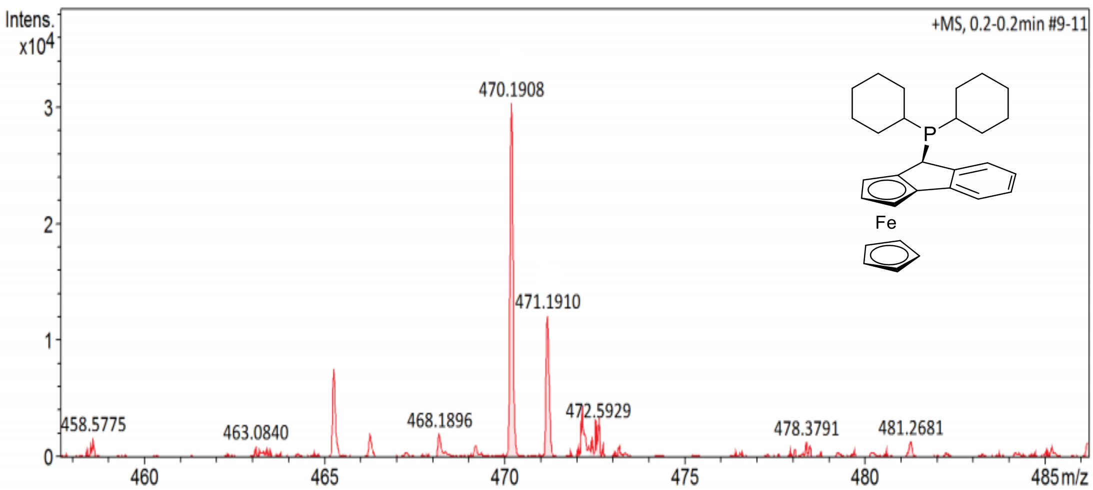


Figure S164. **HRMS** spectra of **3c**

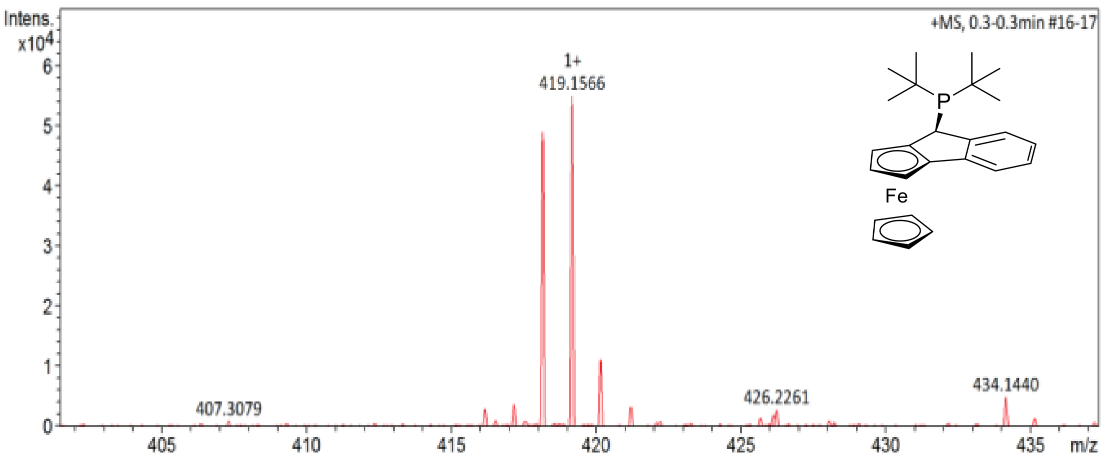


Figure S165. **HRMS** spectra of **3d**

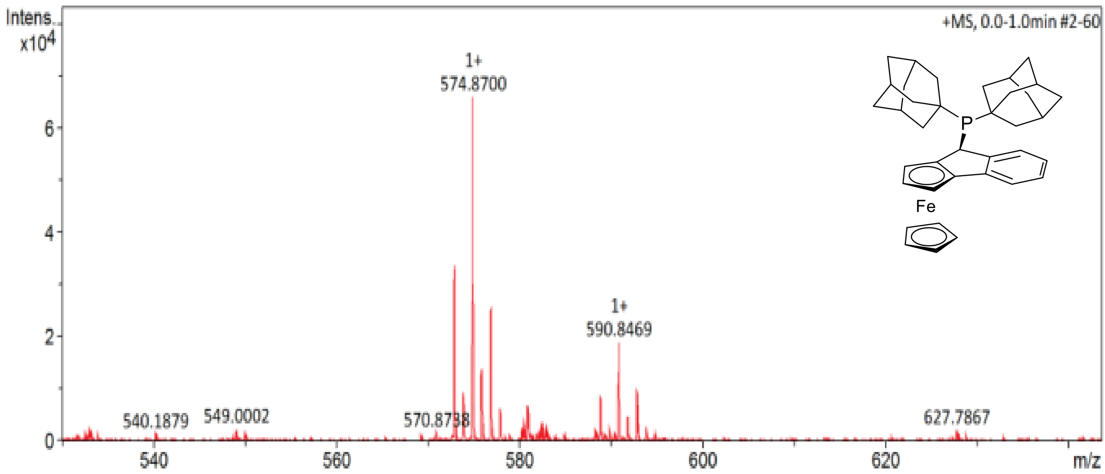


Figure S166. **HRMS** spectra of **3e**

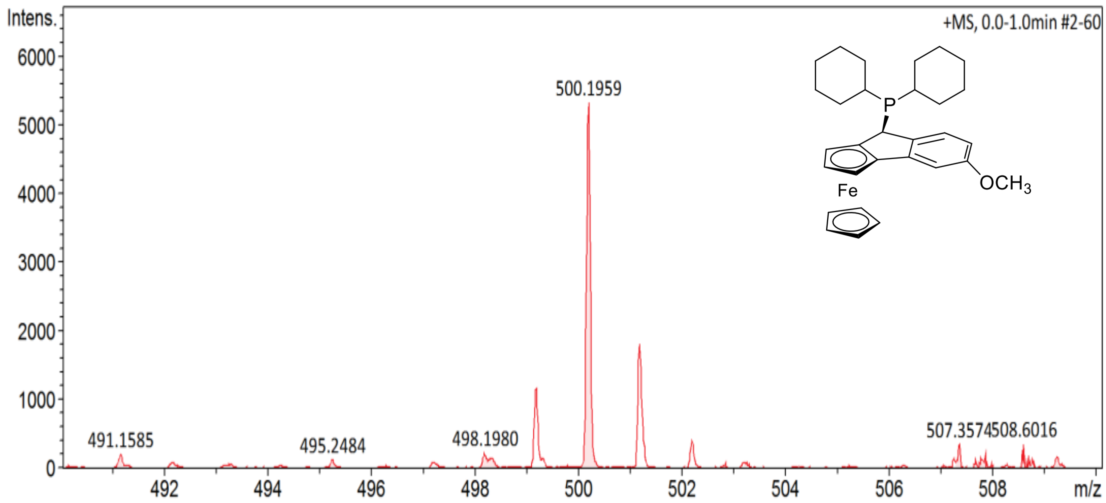


Figure S167. **HRMS** spectra of **3f**

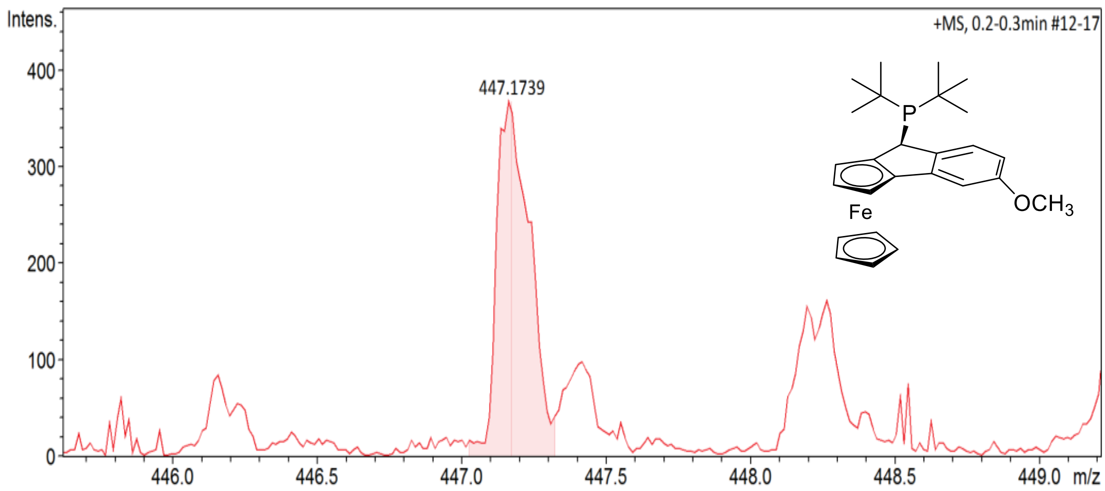


Figure S168. **HRMS** spectra of **3g**

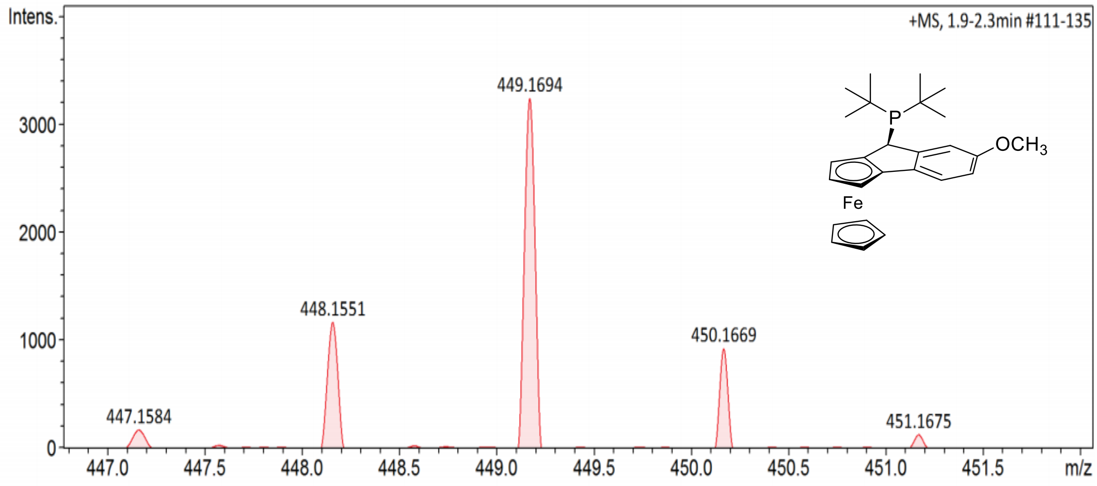


Figure S169. **HRMS** spectra of **3h**

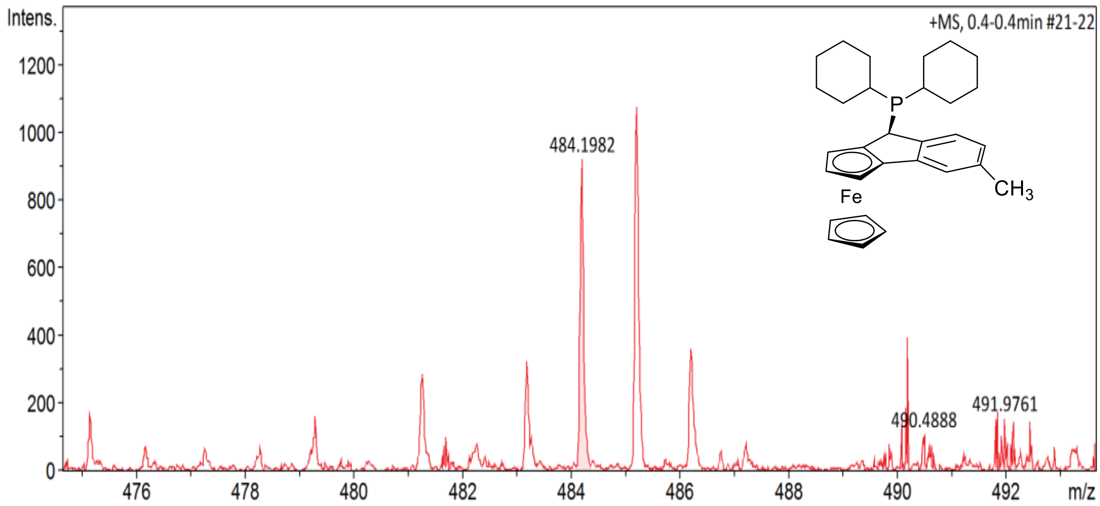


Figure S170. **HRMS** spectra of **3j**

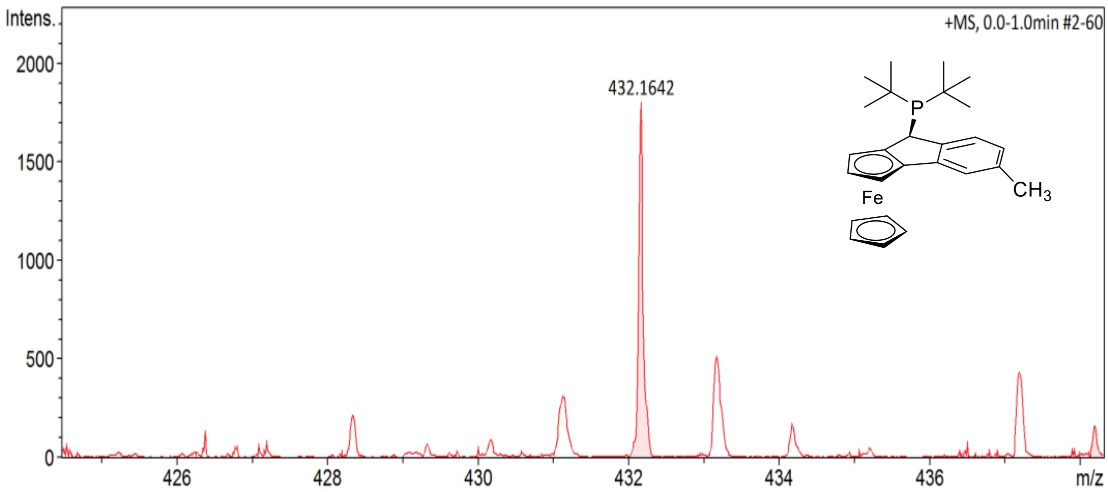


Figure S171. **HRMS** spectra of **3k**

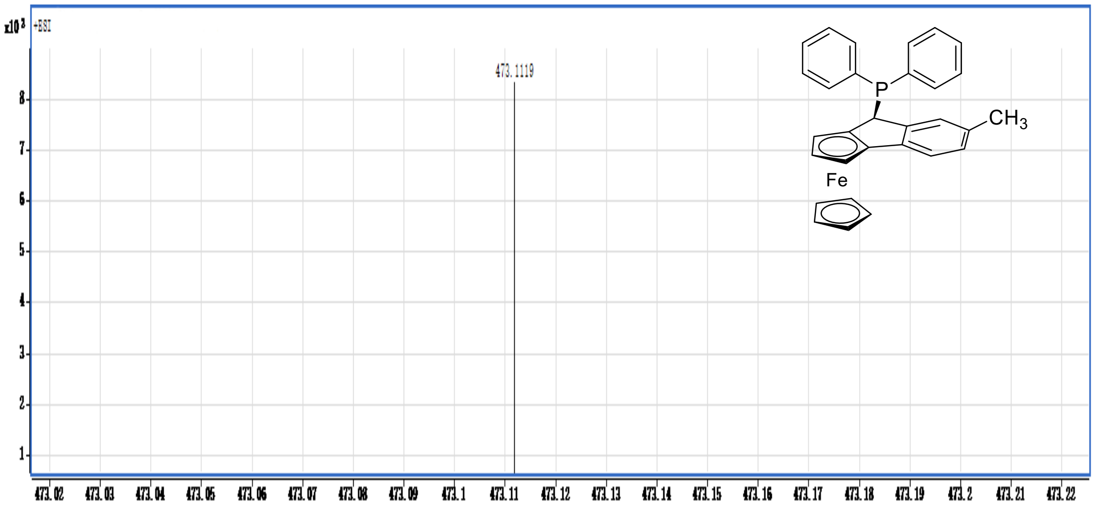


Figure S172. **HRMS** spectra of **3l**

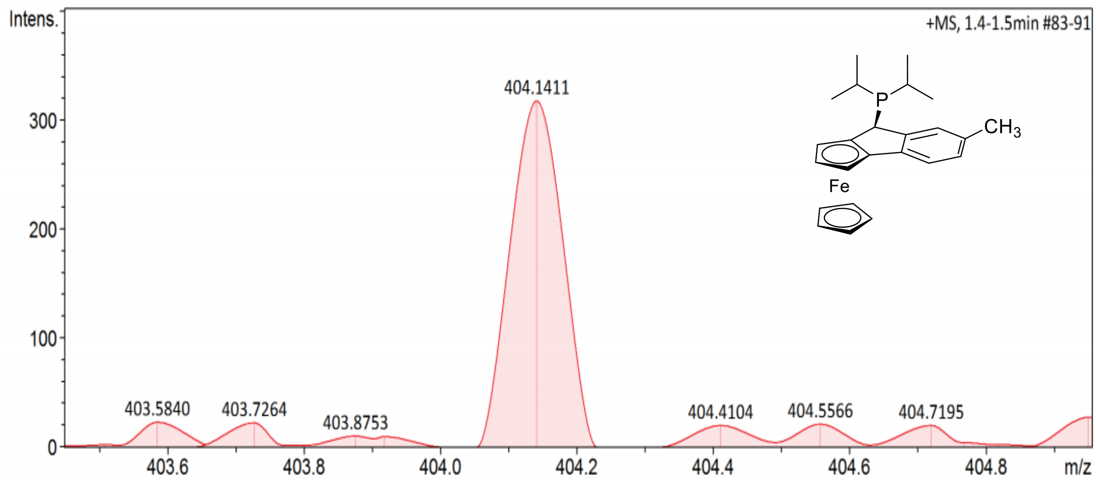


Figure S173. **HRMS** spectra of **3m**

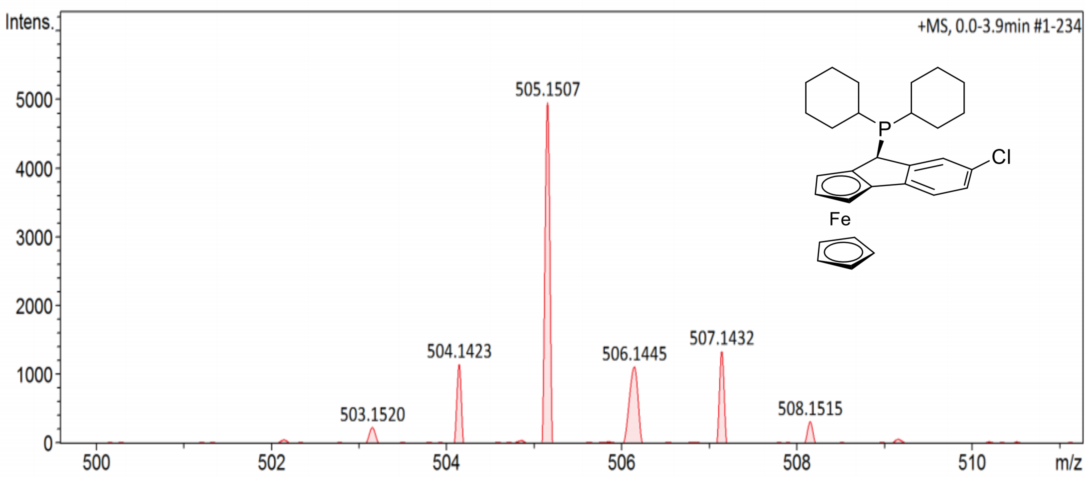


Figure S174. **HRMS** spectra of **3n**

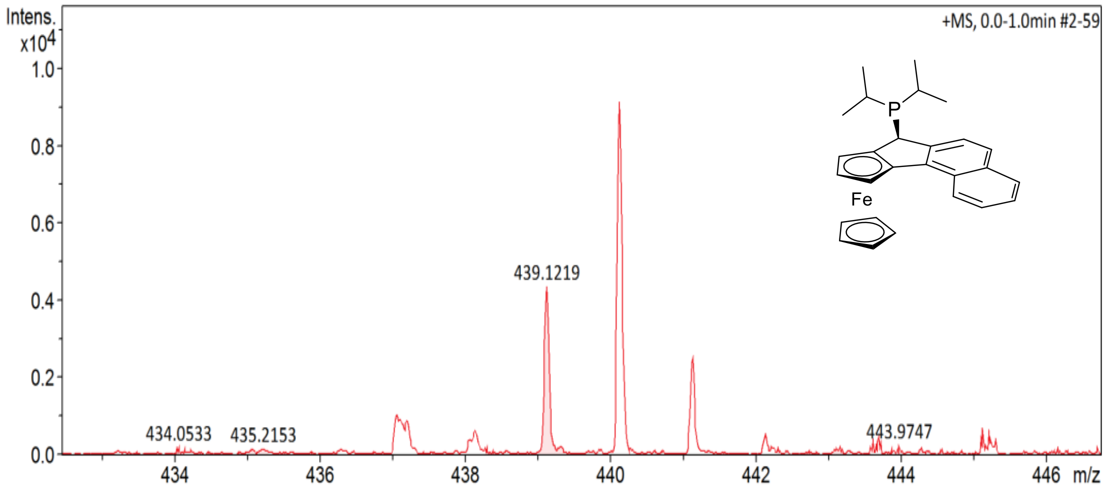


Figure S175. **HRMS** spectra of **3o**

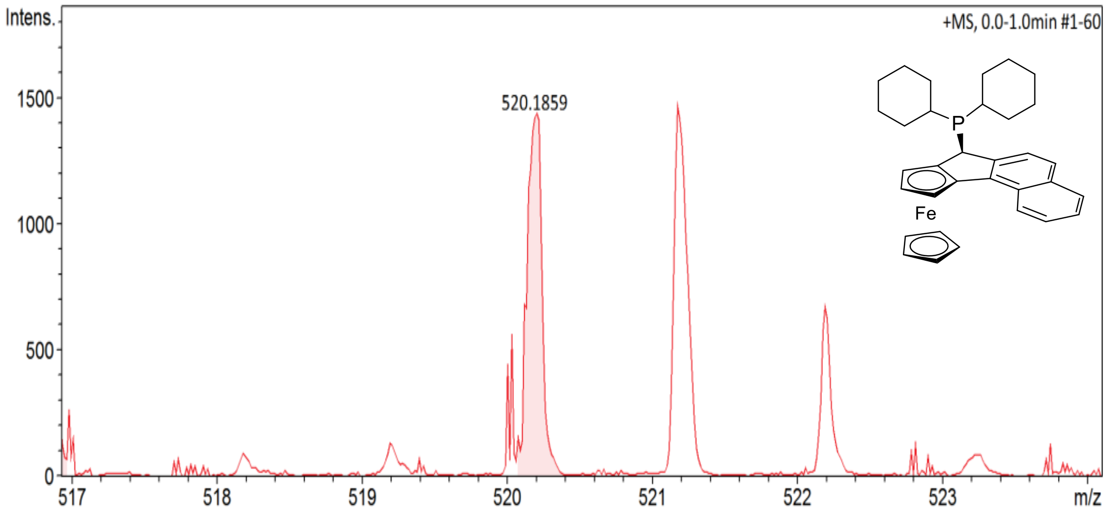


Figure S176. **HRMS** spectra of **3p**

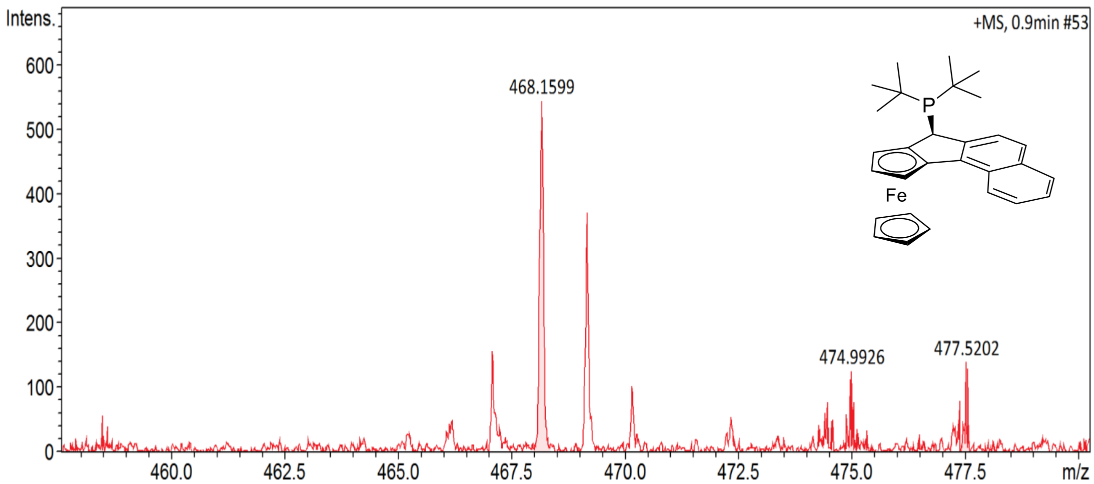


Figure S177. **HRMS** spectra of **3q**

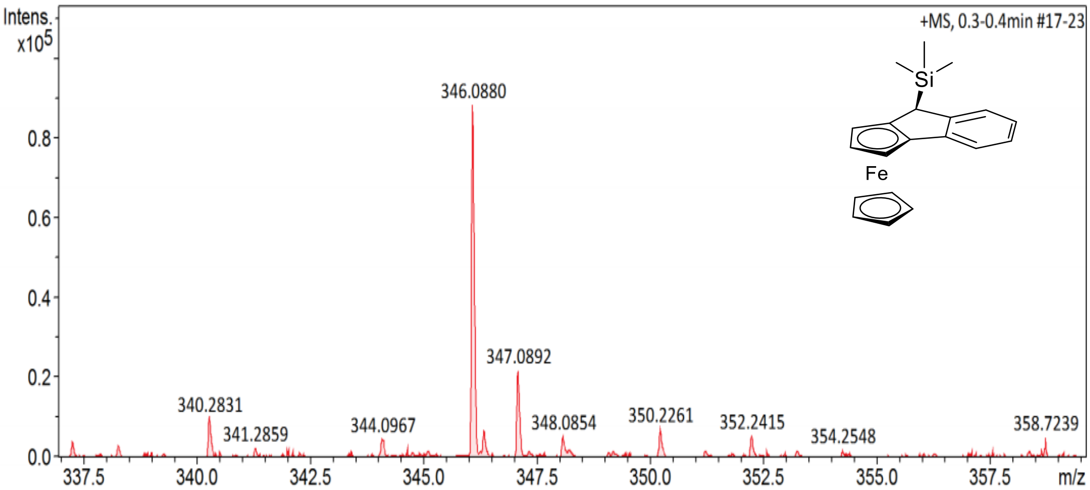


Figure S178. **HRMS** spectra of **3r**

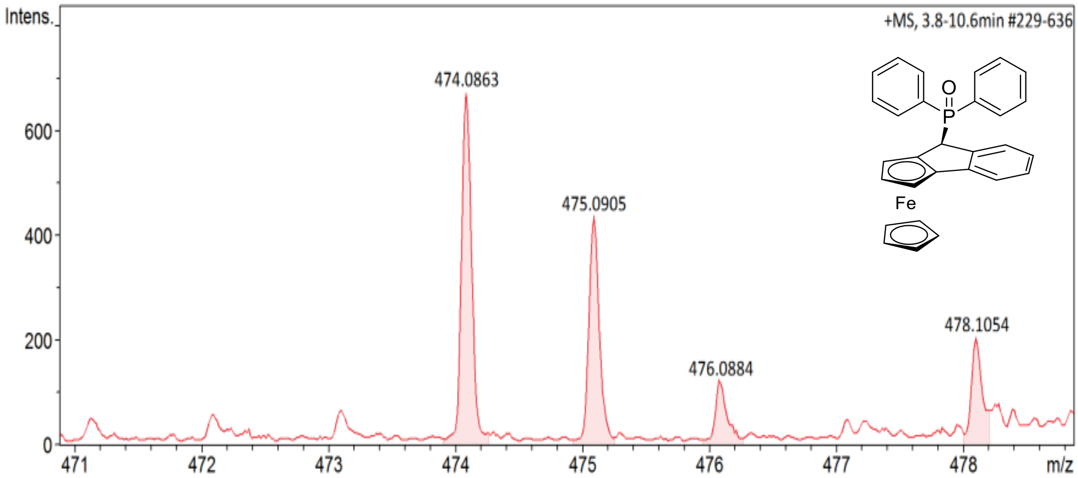


Figure S179. **HRMS** spectra of **4a**

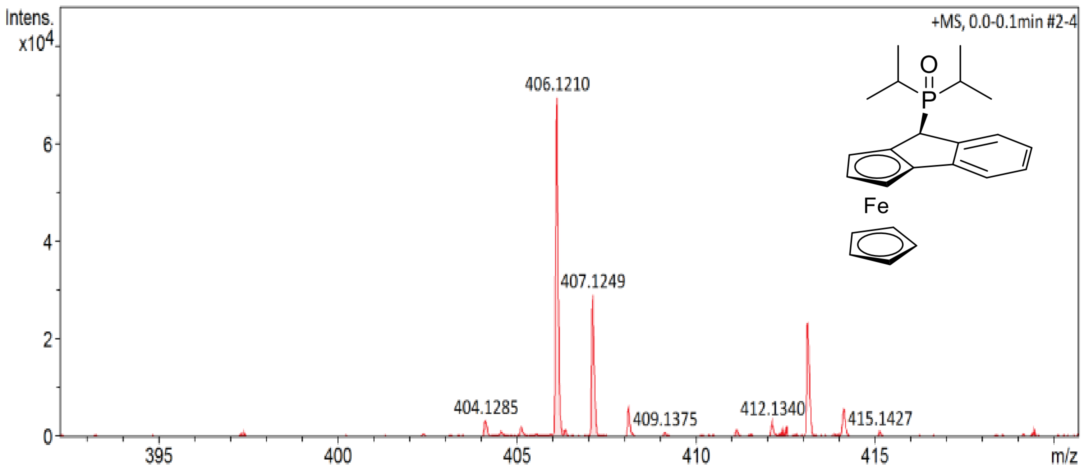


Figure S180. **HRMS** spectra of **4b**

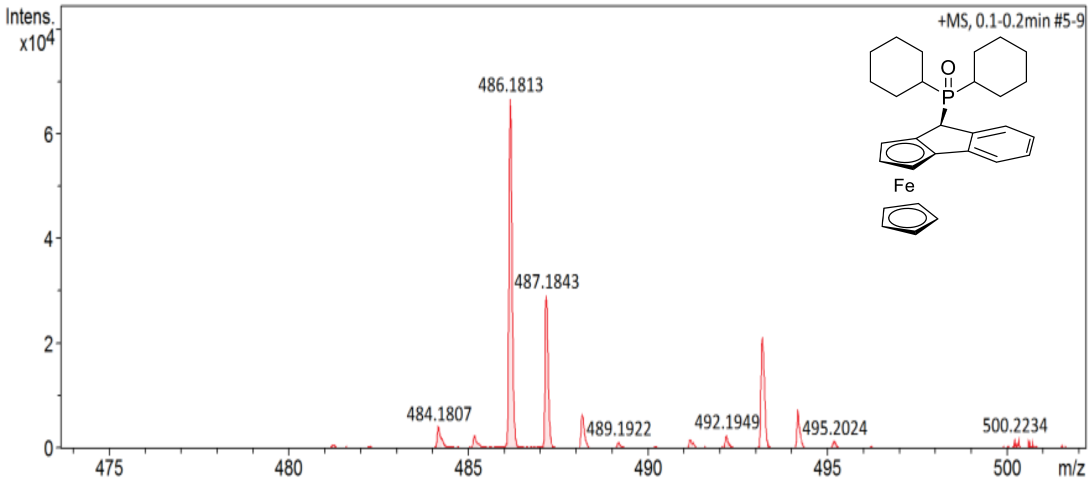


Figure S181. **HRMS** spectra of **4c**

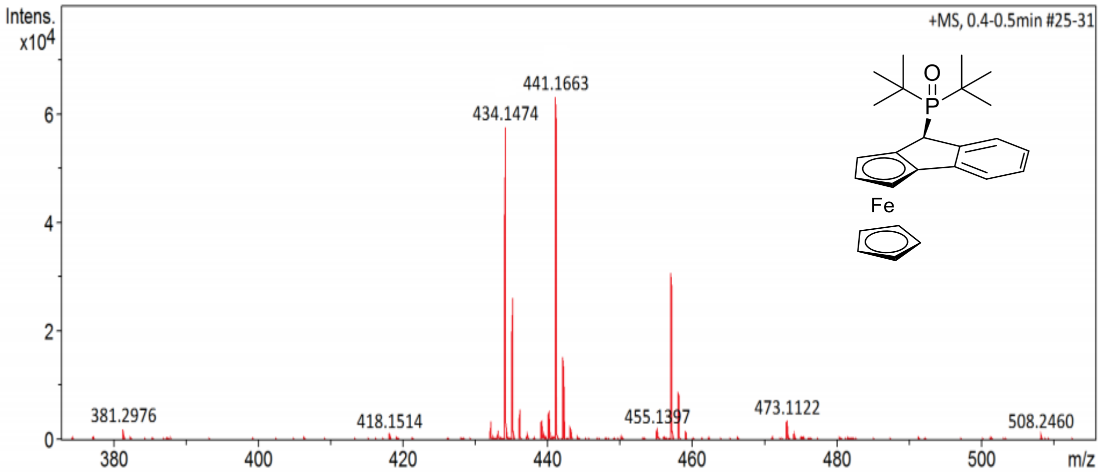


Figure S182. **HRMS** spectra of **4d**

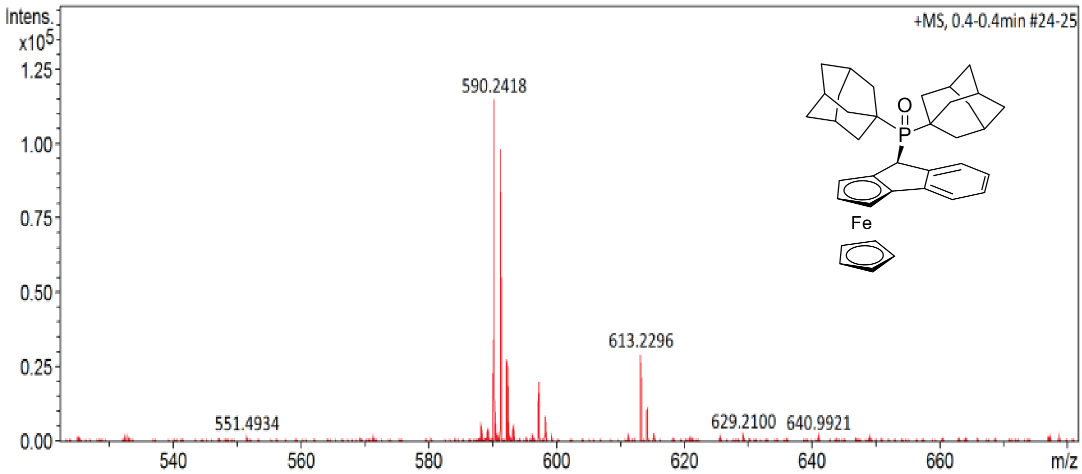


Figure S183. **HRMS** spectra of **4e**

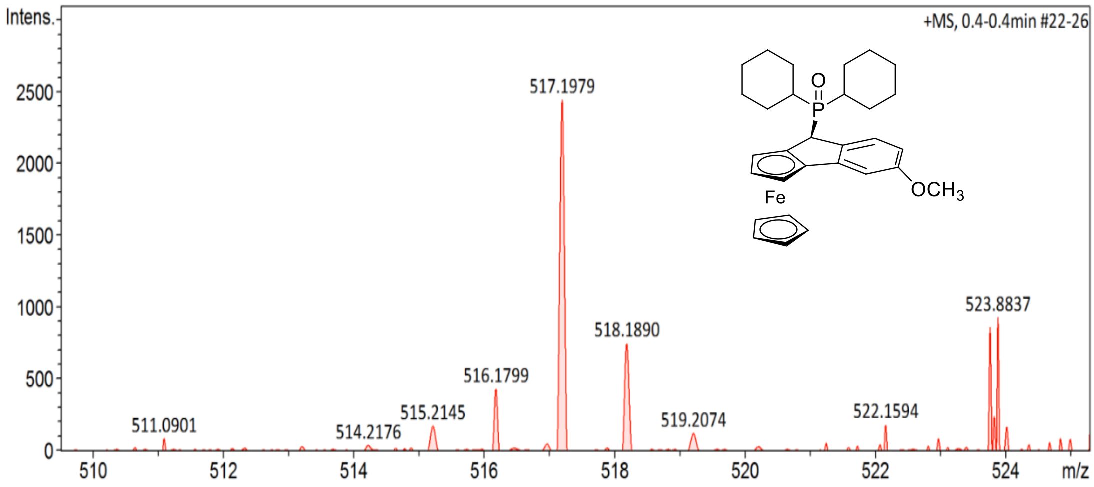


Figure S184. **HRMS** spectra of **4f**

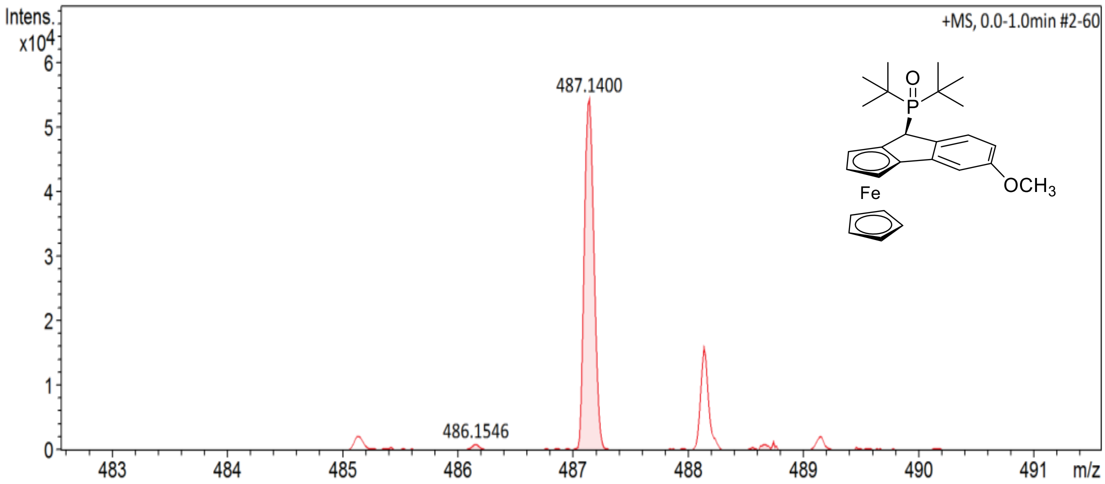


Figure S185. **HRMS** spectra of **4g**

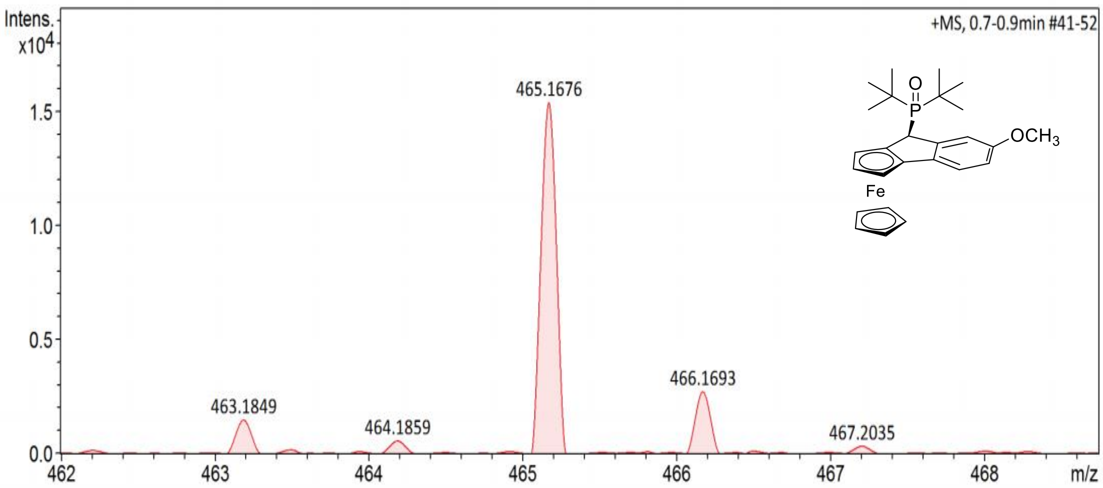


Figure S186. **HRMS** spectra of **4h**

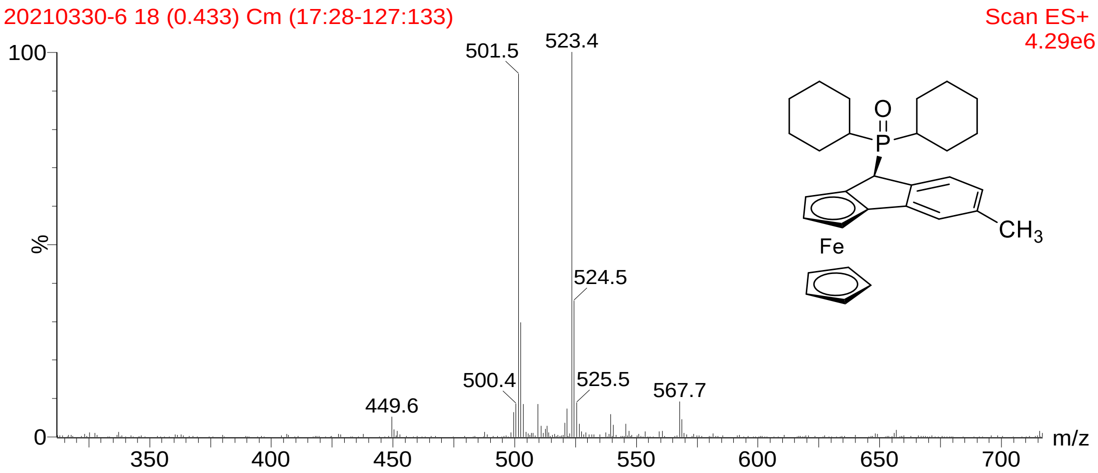


Figure S187. **MS** spectra of **4j**

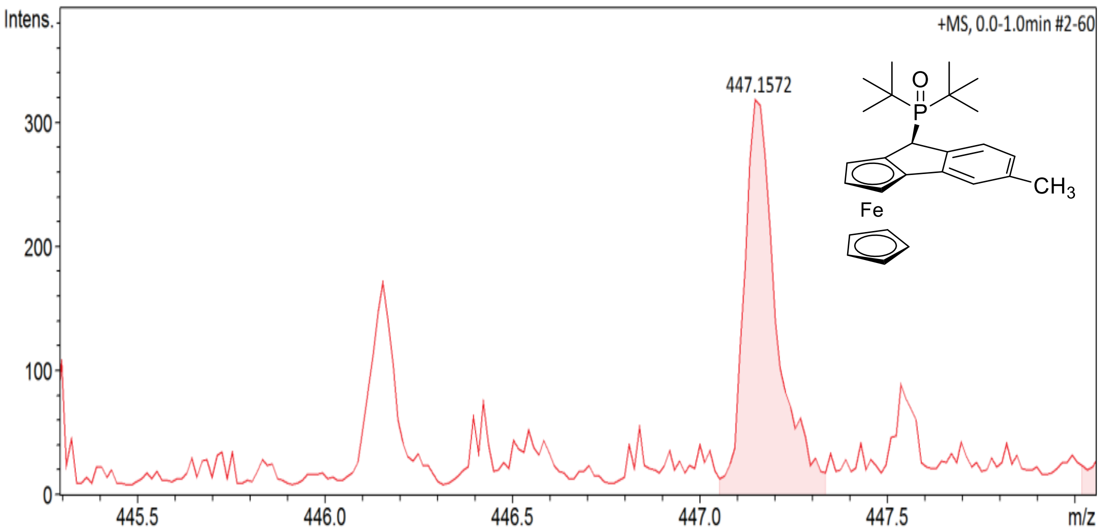


Figure S188. **HRMS** spectra of **4k**

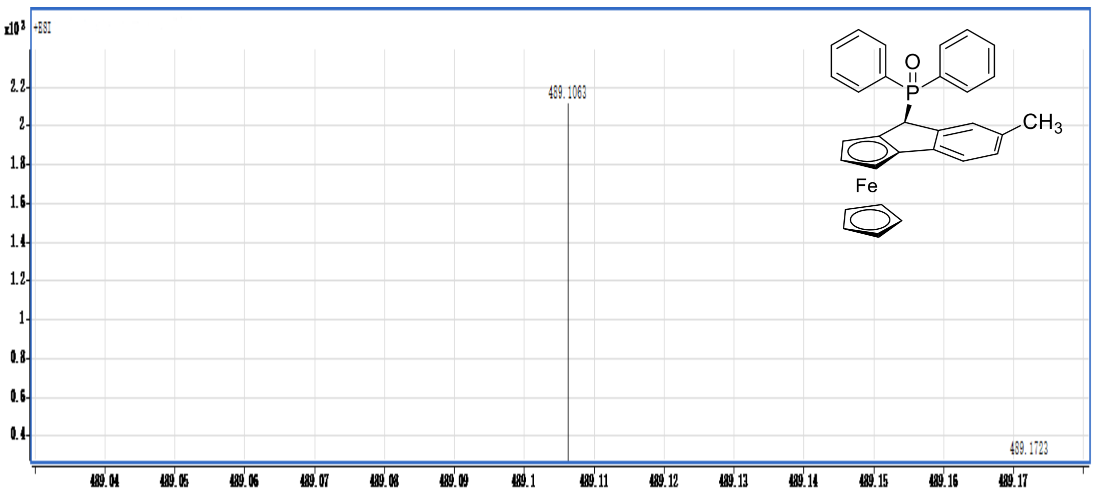


Figure S189. **HRMS** spectra of **4l**

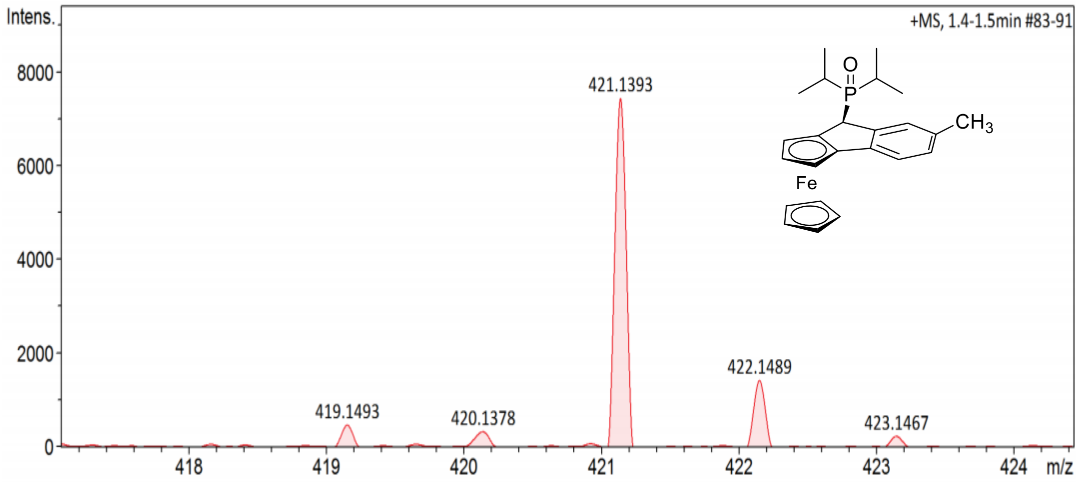


Figure S190. **HRMS** spectra of **4m**

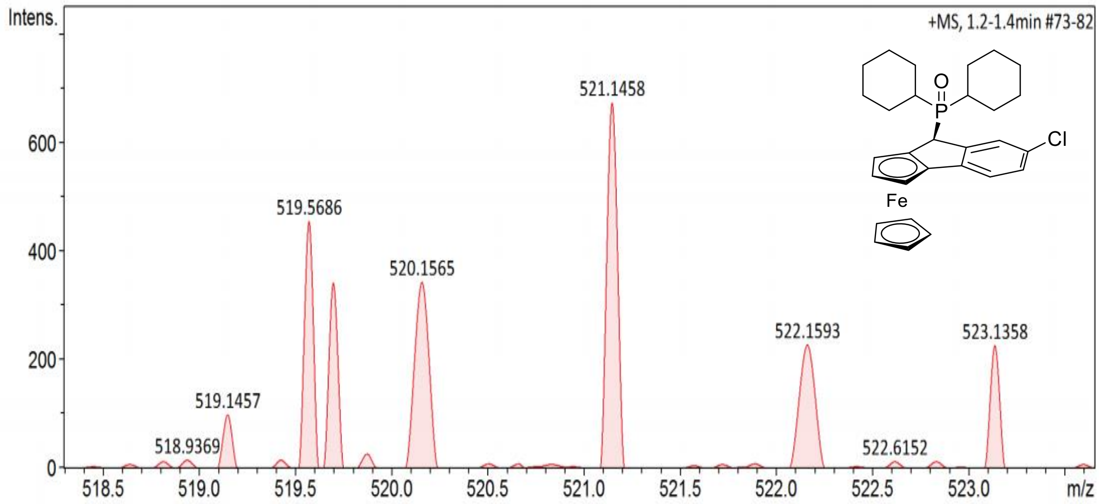


Figure S191. **HRMS** spectra of **4n**

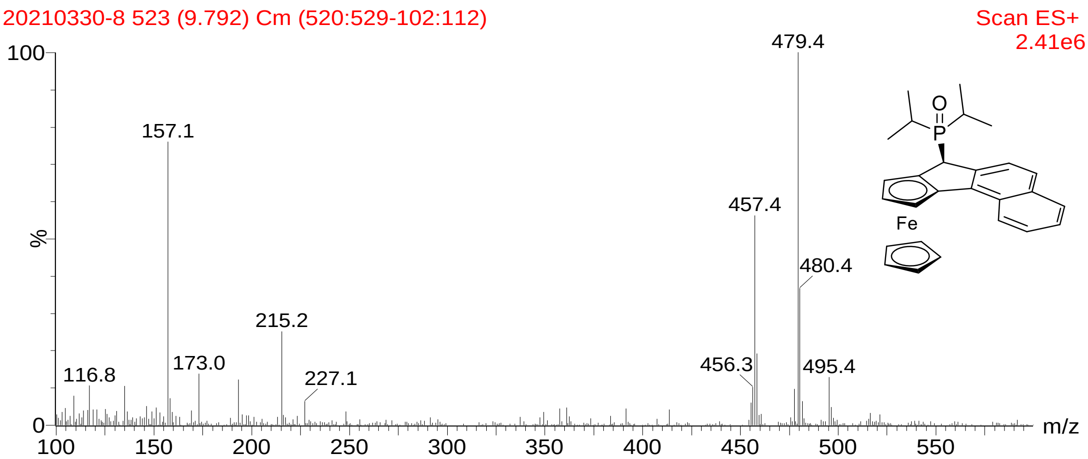


Figure S192. **MS** spectra of **4o**

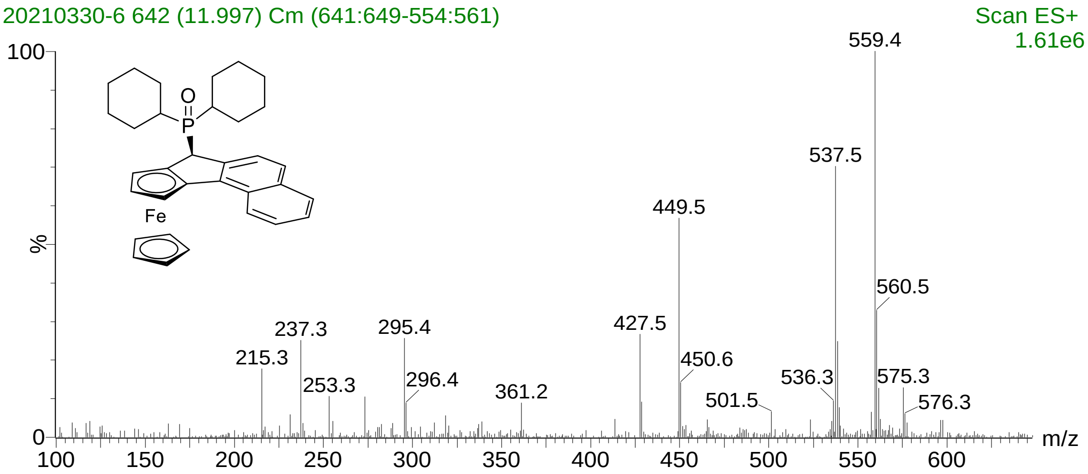


Figure S193. **MS** spectra of **4p**

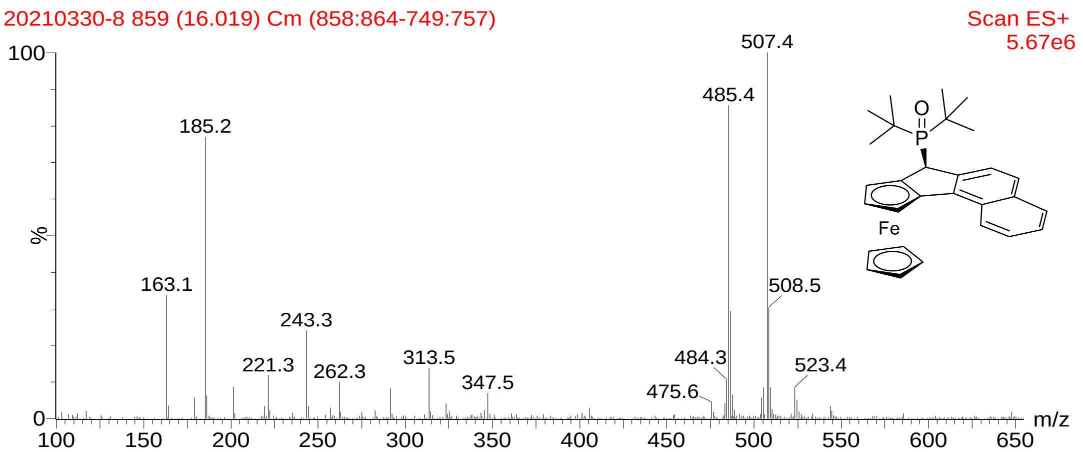


Figure S194. **MS** spectra of **4q**

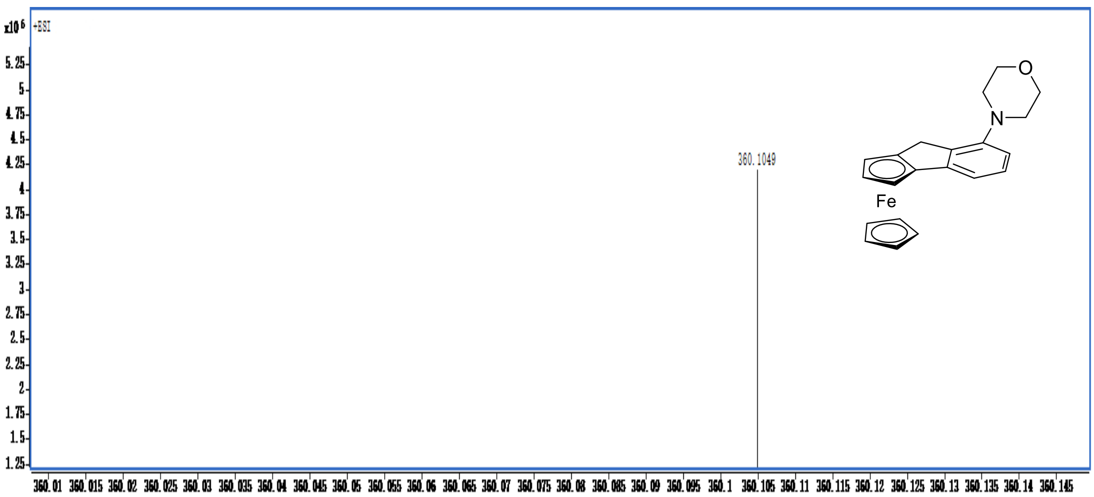


Figure S195. **HRMS** spectra of **5**

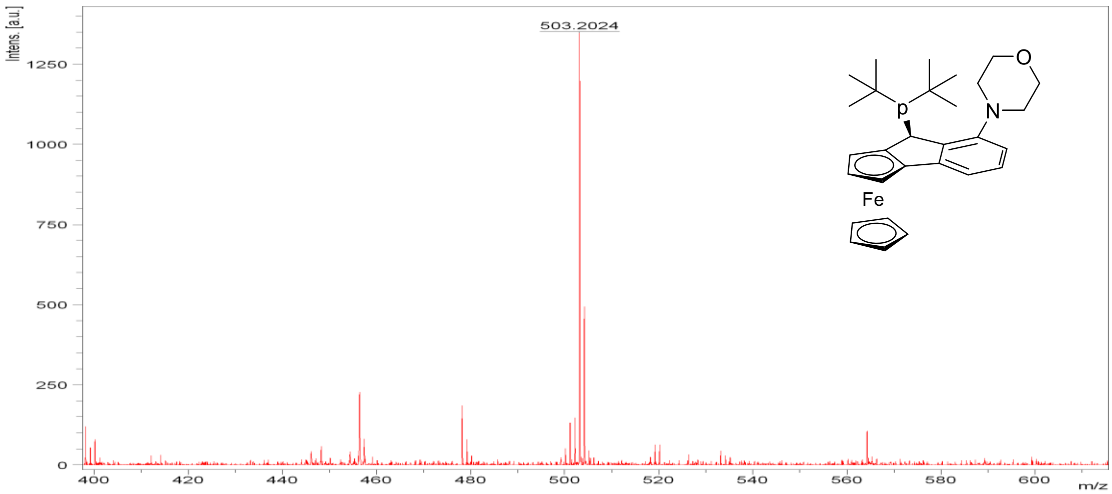


Figure S196. **HRMS** spectra of **6**

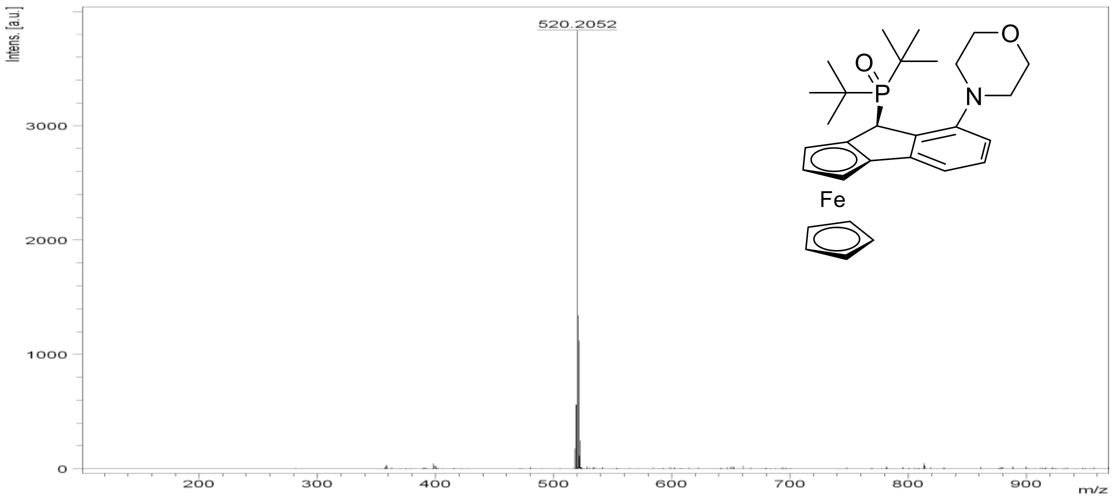
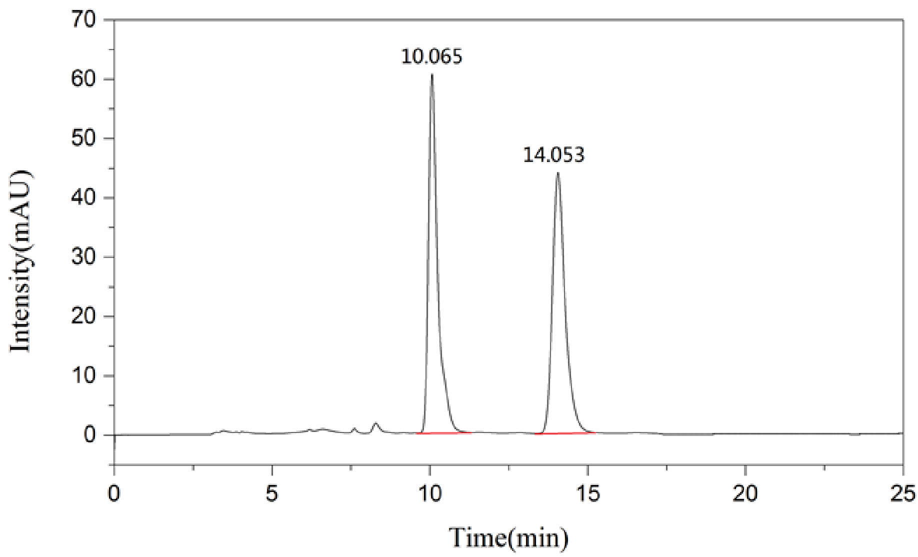
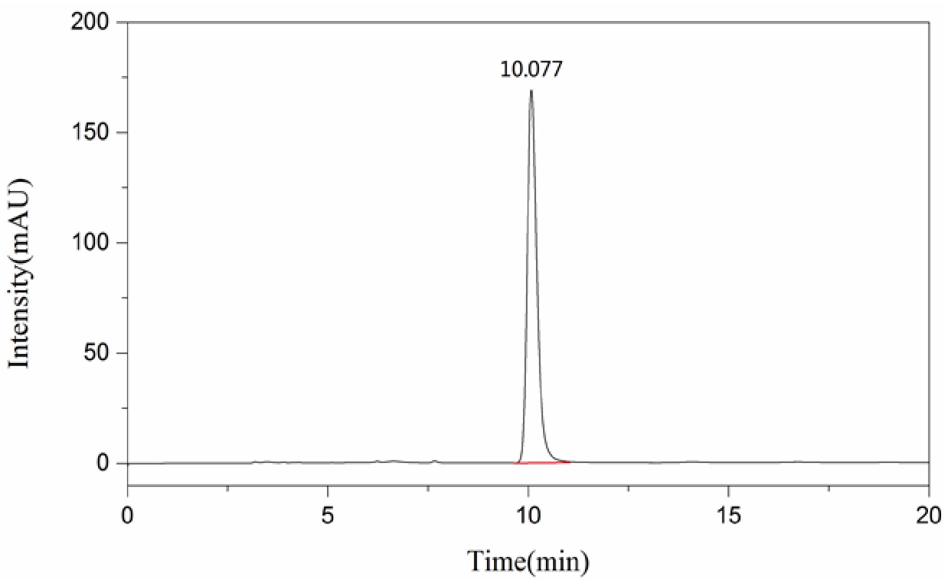


Figure S197. **HRMS** spectra of **7**

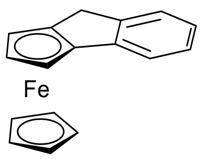
12. HPLC spectra



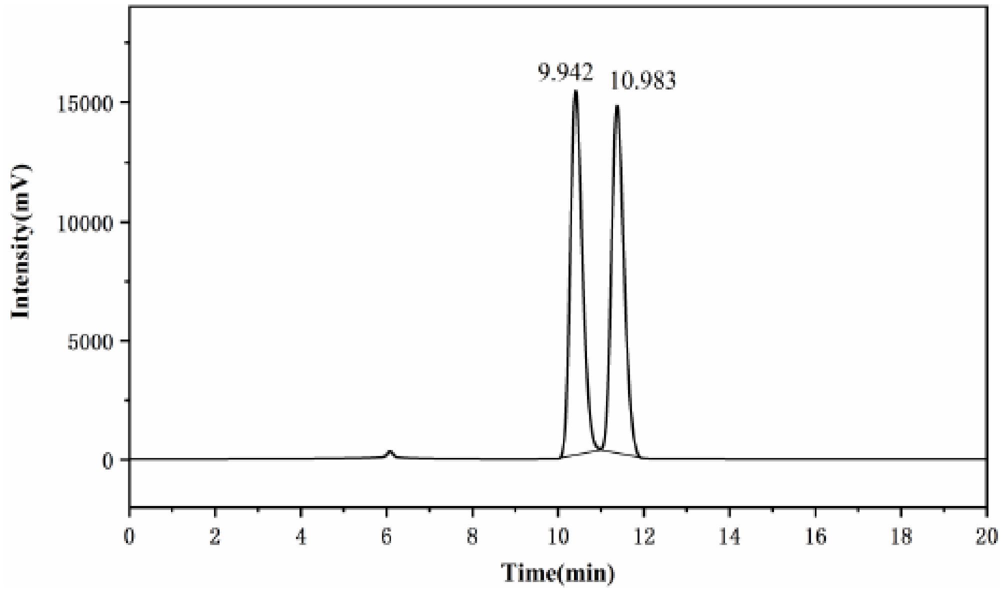
	RT(min)	Area	Area%	Height	Height%
1	10.065	1230062	50.0932	60500	57.9352
2	14.053	1225485	49.9068	43927	42.0648



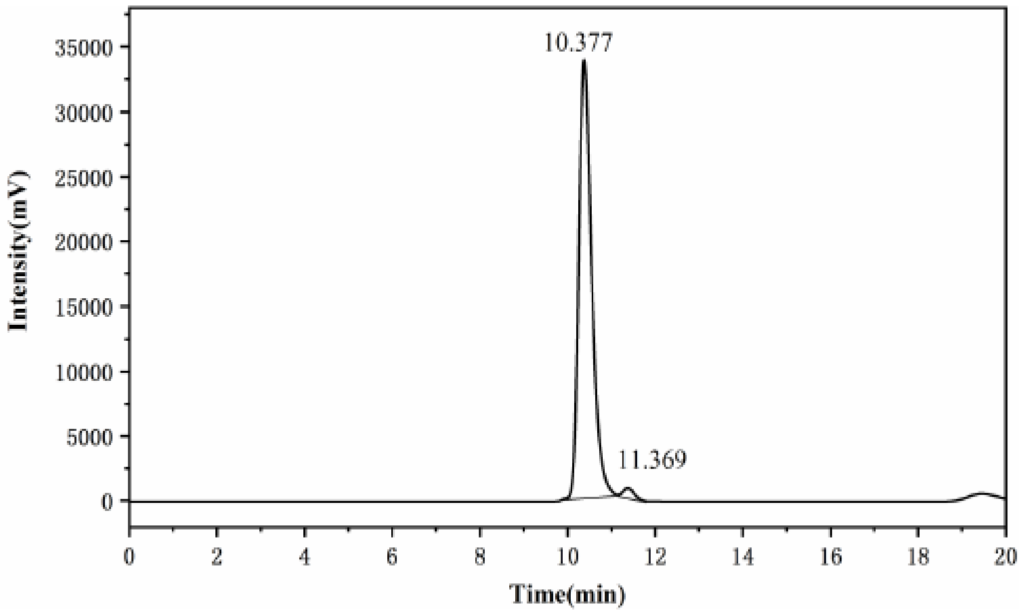
	RT(min)	Area	Area%	Height	Height%
1	10.077	2846011	99.6745	168976	99.8021
2	14.090	9294	0.3255	335	0.1979



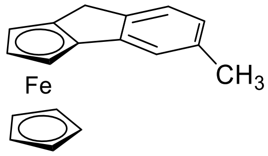
(S_p)-(**2a**)
yield 99%;ee>99%



	RT(min)	Area	Area%	Height	Height%
1	9.942	316125	50.4512	15482	51.0014
2	10.983	310470	49.05488	14874	48.9986

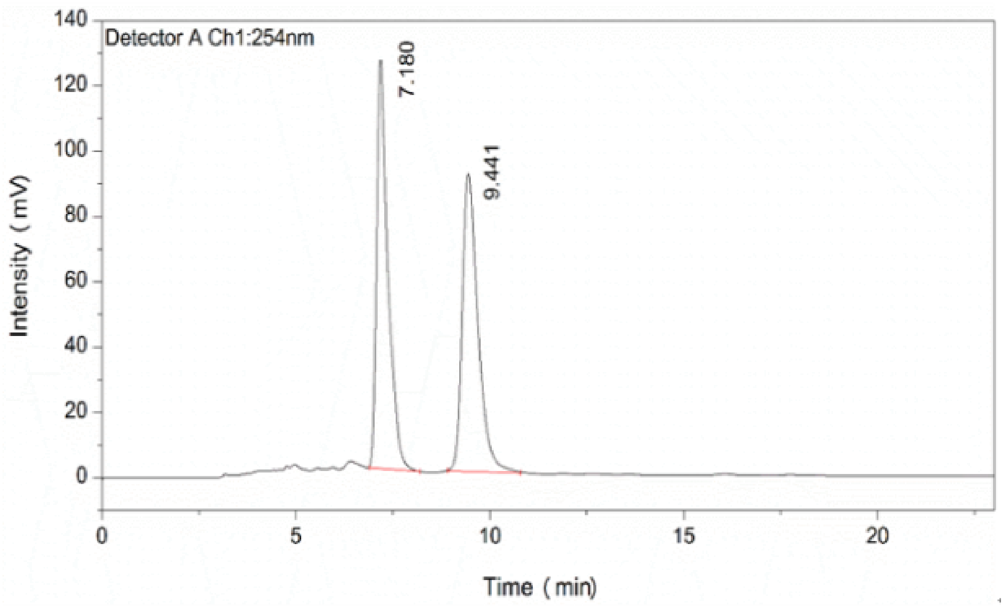


	RT(min)	Area	Area%	Height	Height%
1	10.377	704524	97.2917	33883	97.2448
2	11.369	19611	2.7083	960	2.7552

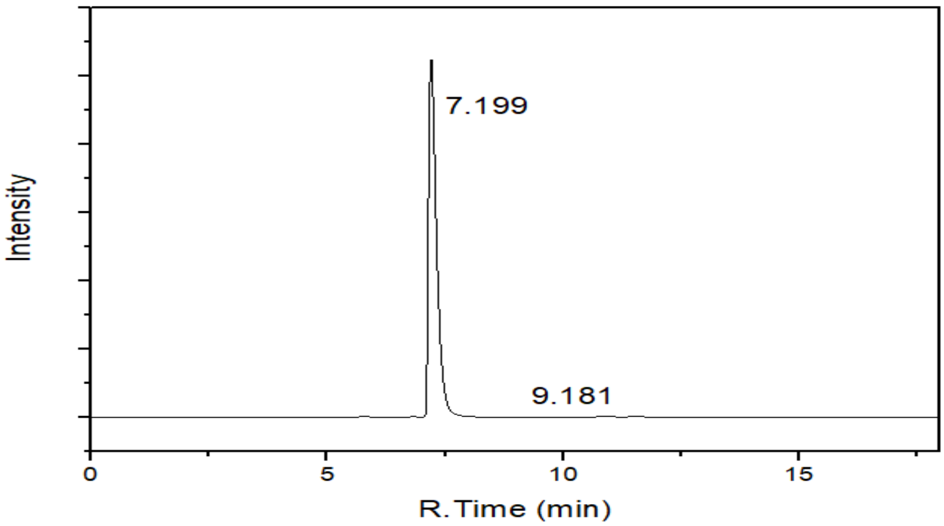


(S_p)- **(2b)**

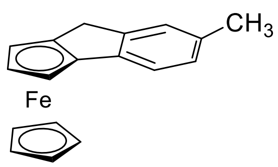
yield 99% ; ee=95%



	RT(min)	Area	Area%	Height	Height%
1	7.180	2510189	49.3895	125195	57.8559
2	9.441	2572242	50.6105	91196	42.1441

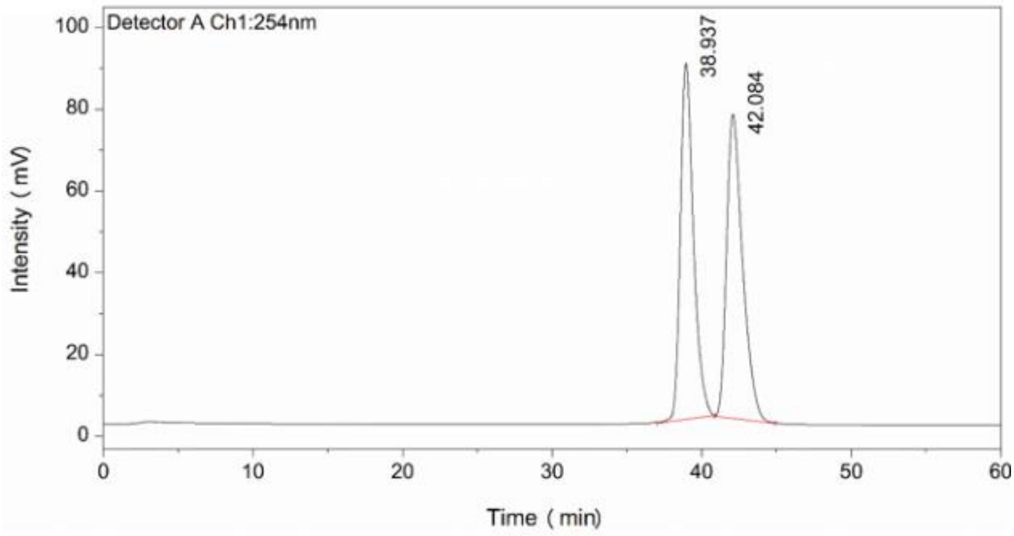


	RT(min)	Area	Area %	Height	Height %
1	7.199	31465766	99.9821	2619176	99.9831
2	9.181	5619	0.0179	444	0.0169

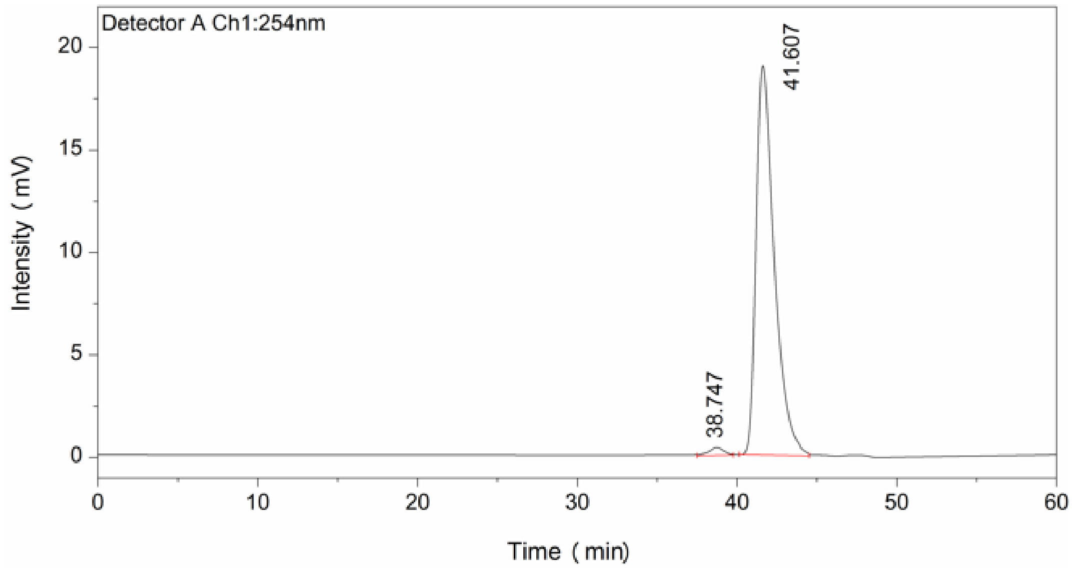


(S_p)- **(2c)**

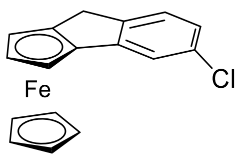
yield 97% ; ee>99.9%



	RT(min)	Area	Area%	Height	Height%
1	38.937	509585	49.1891	8574	54.0878
2	42.084	526388	50.8109	7278	45.9122

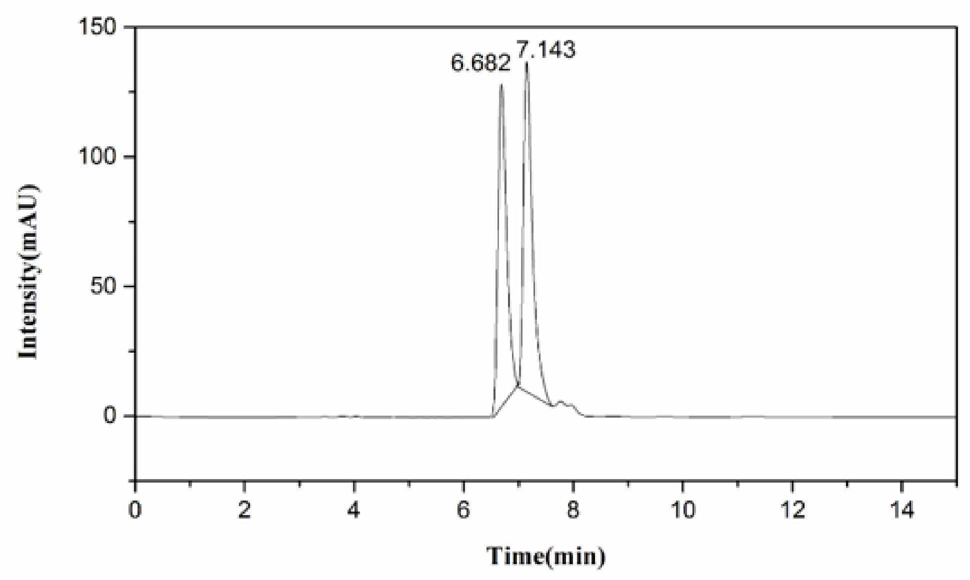


	RT(min)	Area	Area%	Height	Height%
1	38.747	13781	0.9562	292	1.5355
2	41.607	1427449	99.0438	18724	98.4645

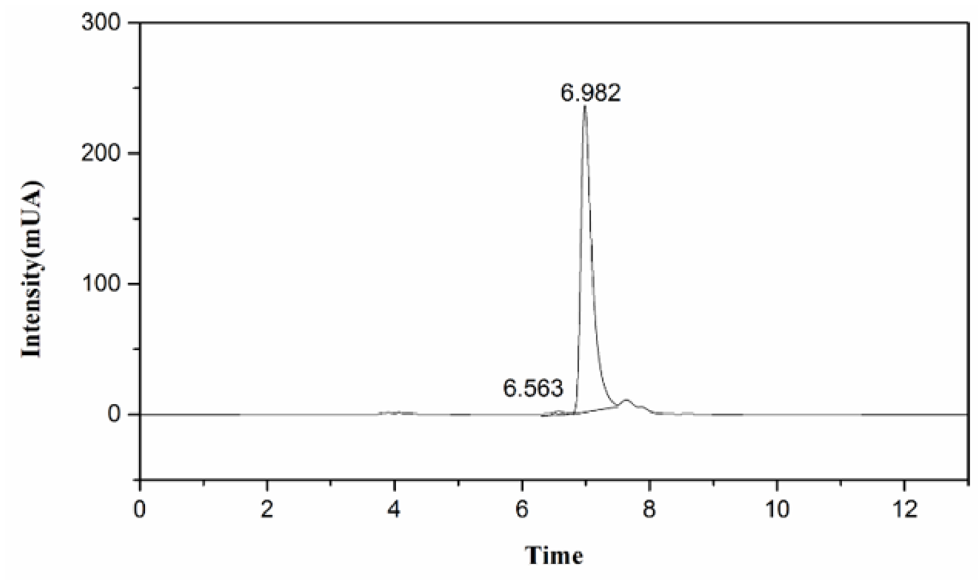


(S_p)- **(2d)**

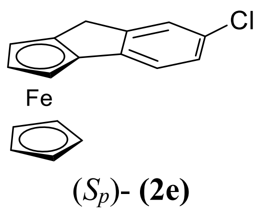
yield 97% ; ee=98.1%



	RT(min)	Area	Area%	Height	Height%
1	6.682	1512775	47.5138	127971	48.66
2	7.143	1671088	52.4862	135013	51.34

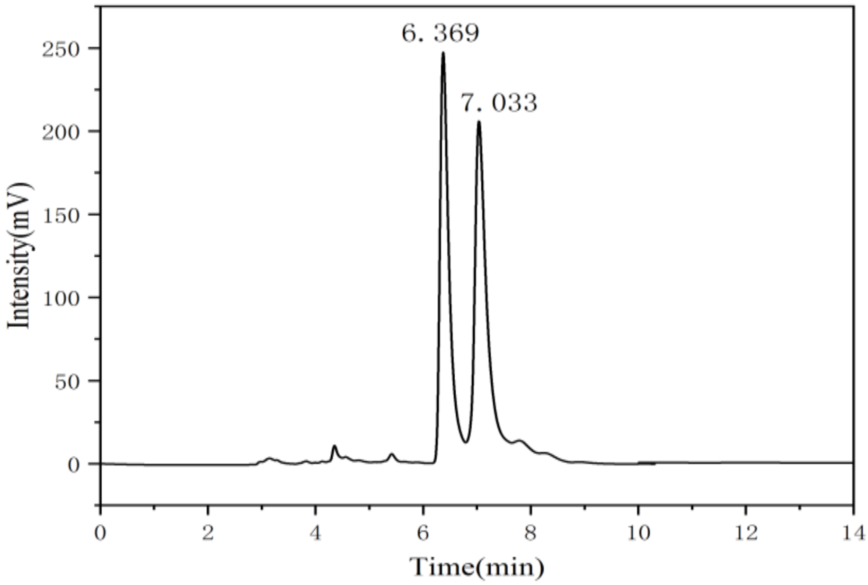


	RT(min)	Area	Area%	Height	Height%
1	6.563	17312	0.5951	1810	0.77
2	6.982	2891864	99.4049	234366	99.23

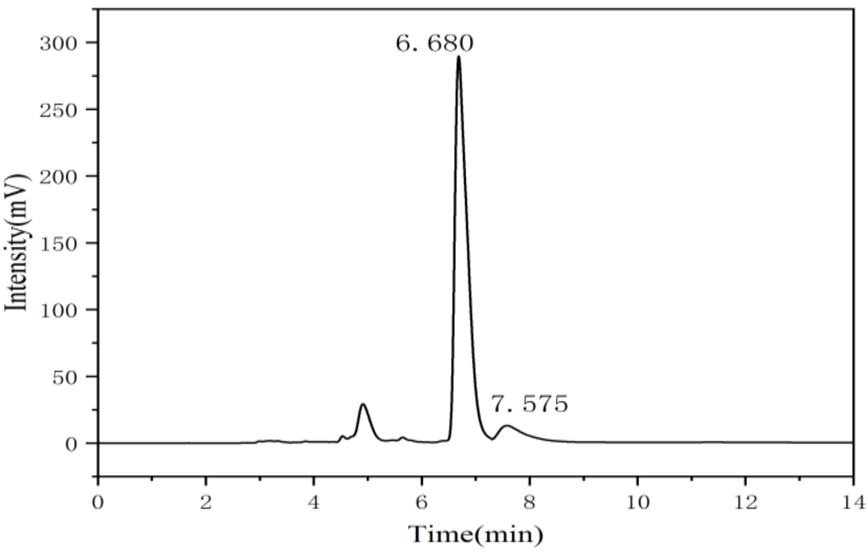


(S_p)- **(2e)**

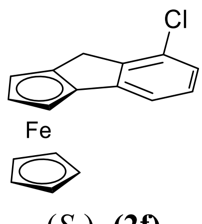
yield 77% ; ee=99%



	RT(min)	Area	Area%	Height	Height%
1	6.369	2896639	49.7043	245851	55.3061
2	7.033	2931101	50.2957	198677	44.6939

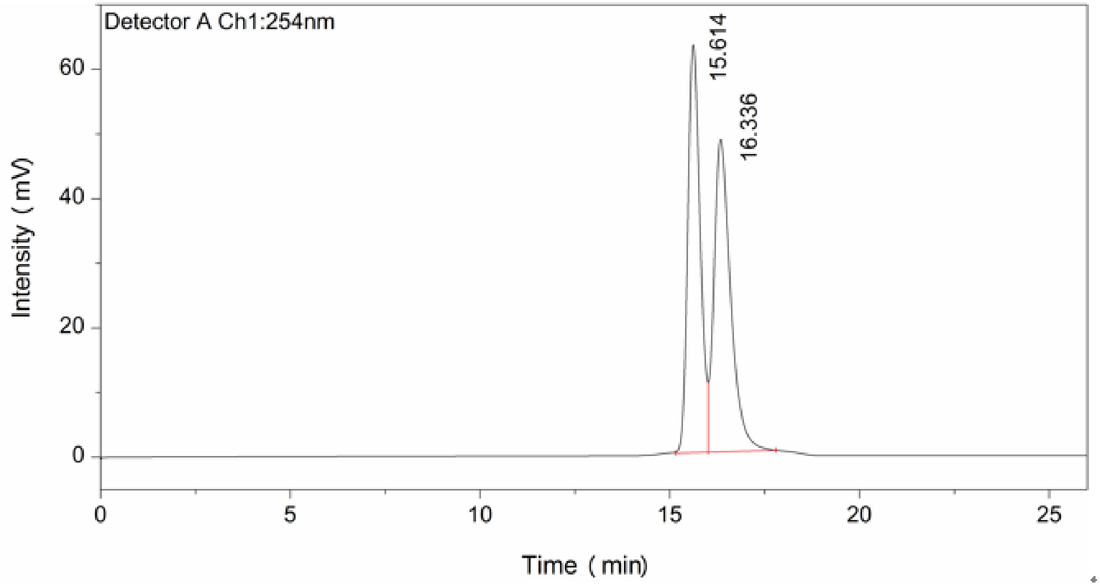


	RT(min)	Area	Area%	Height	Height%
1	6.680	4683240	95.5967	289072	96.8129
2	7.575	215717	4.4033	9516	3.1871

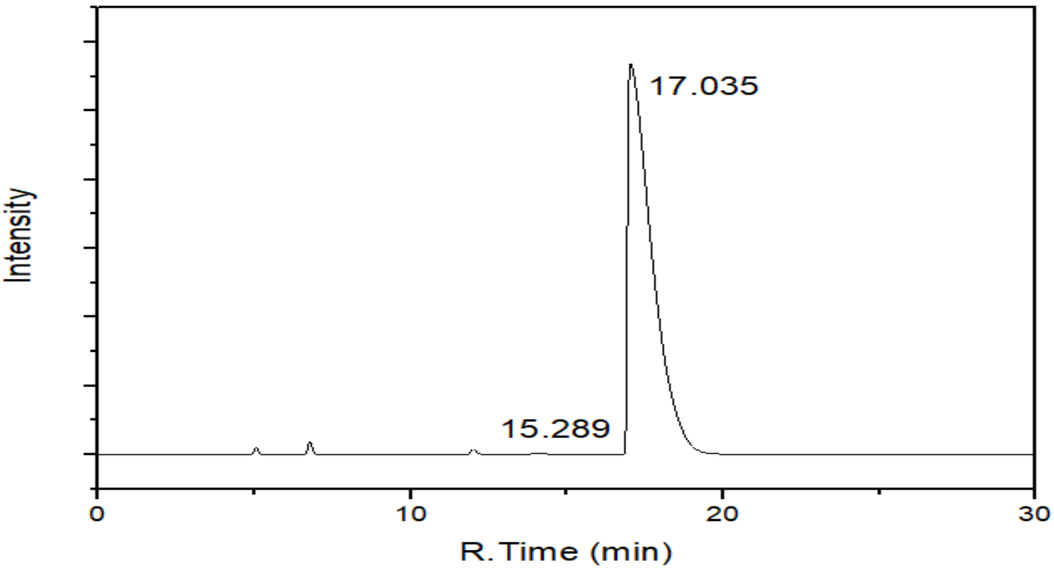


(S_p)- **(2f)**

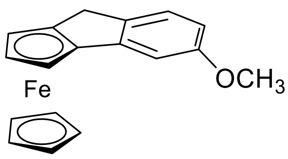
yield 97% ; ee=91.2%



	RT(min)	Area	Area%	Height	Height%
1	15.614	1430109	48.1044	63178	56.5194
2	16.336	1542818	51.8956	48603	43.4806

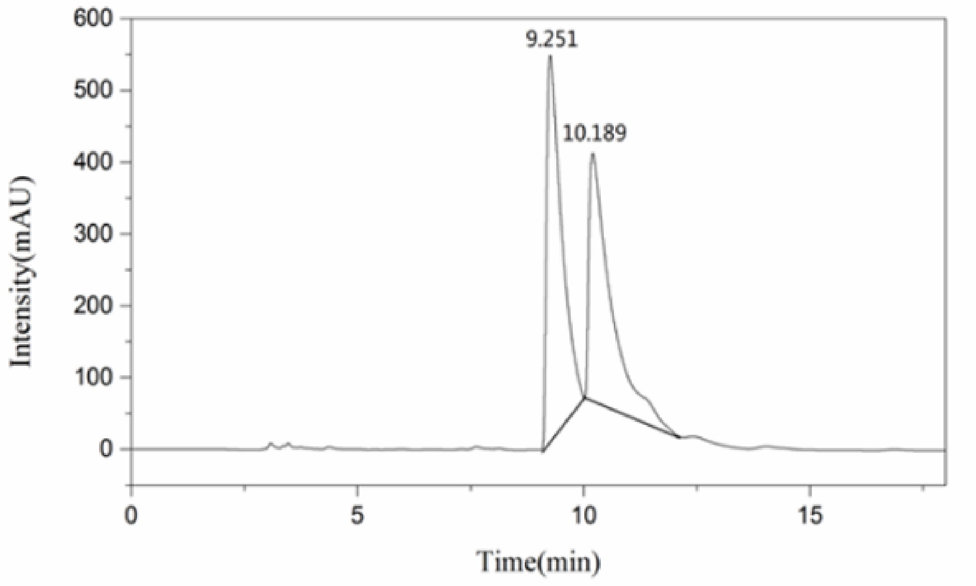


	RT(min)	Area	Area%	Height	Height%
1	15.289	45491	0.0297	1988	0.0700
2	17.035	153050734	99.9703	2839304	99.9300

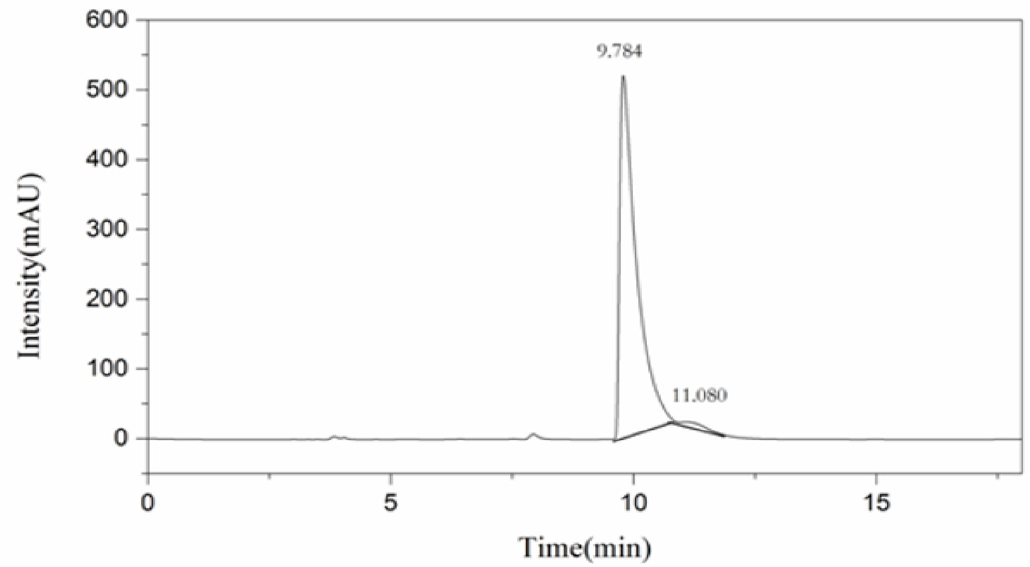


(S_p)- **(2g)**

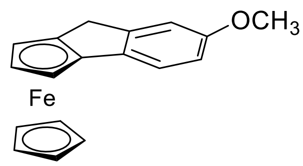
yield 98% ; ee>99%



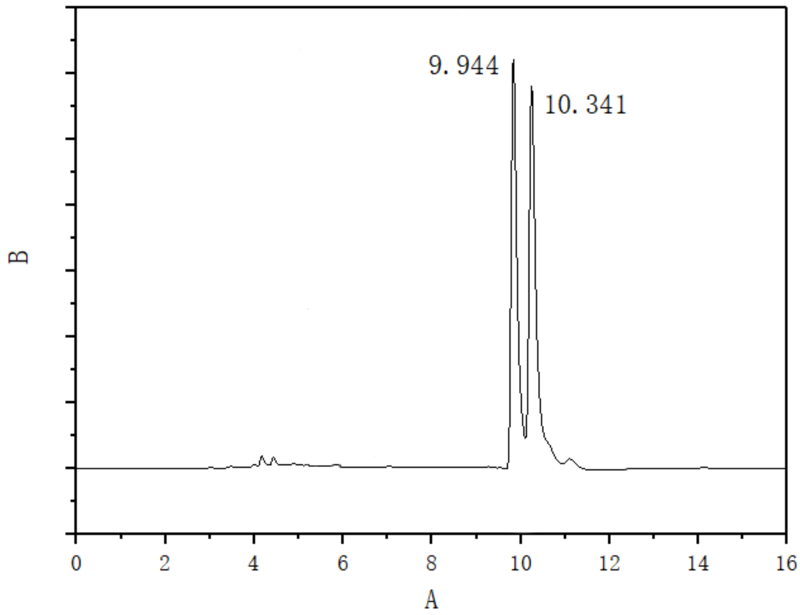
	RT(min)	Area	Area%	Height	Height%
1	9.251	14376278	47.3568	548740	57.3879
2	10.189	15981120	52．6432	407454	42.6121



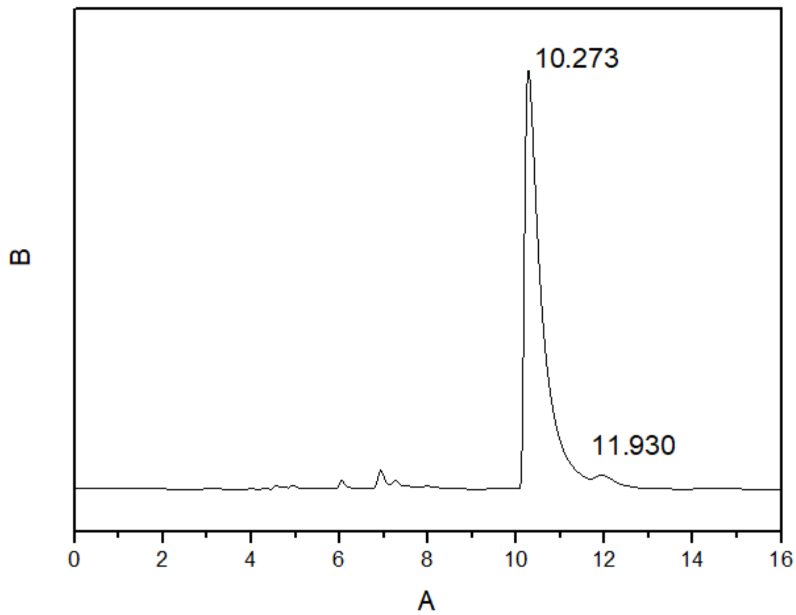
	RT(min)	Area	Area%	Height	Height%
1	9.784	12564397	98.7194	518552	99.2672
2	11.080	162991	1.2806	3828	0.7328



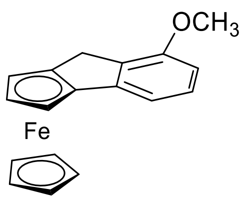
(S_p)- **(2h)**
yield 79% ; ee=97.4%



	RT(min)	Area	Area%	Height	Height%
1	9.944	212471	47.8130	12141	50.3525
2	10.341	231629	52.1570	11971	49.6475

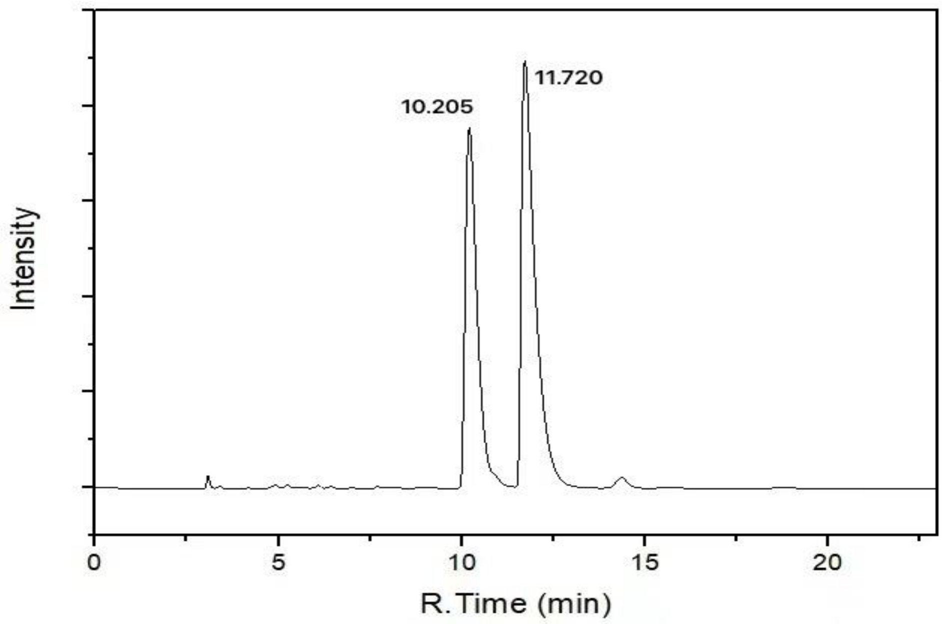


	RT(min)	Area	Area%	Height	Height%
1	10.273	13074603	96.2335	480547	97.6210
2	11.930	511725	3.7665	11711	2.3790

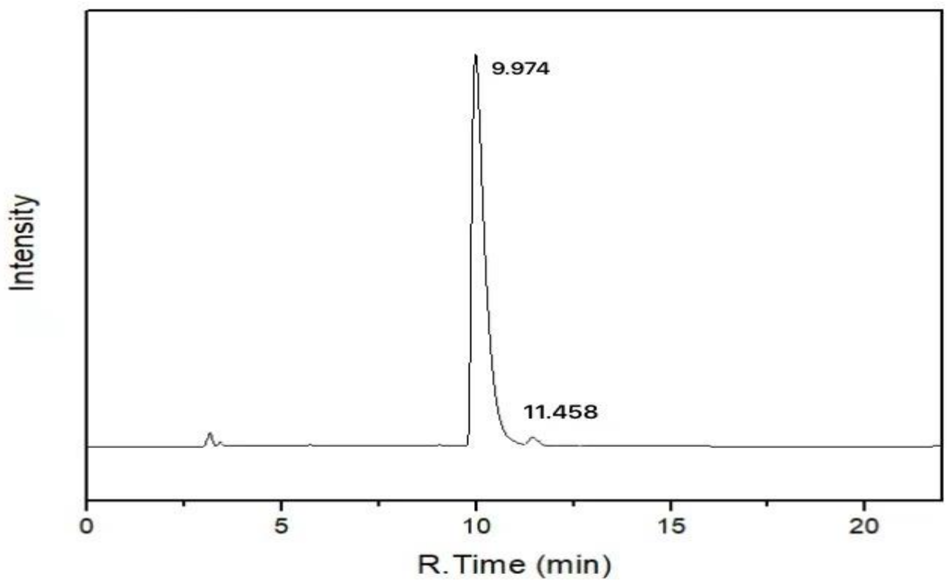


(S_p)- **(2i)**

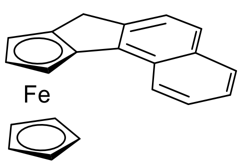
yield 94% ; ee=92.5%



	RT(min)	Area	Area%	Height	Height%
1	10.205	8592583	42.4232	378060	45.8104
2	11.720	11661843	57.5768	447211	54.1896

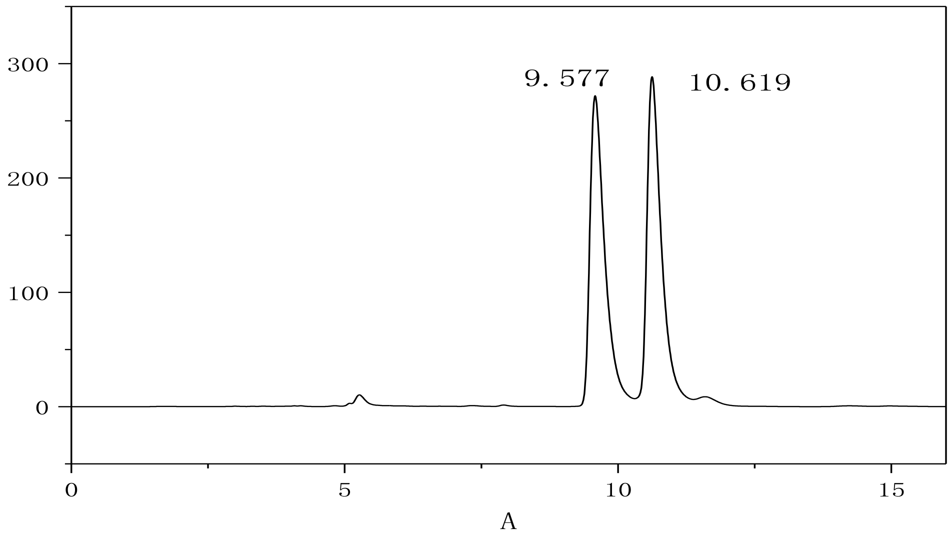


	RT(min)	Area	Area%	Height	Height%
1	9.974	34112161	99.4988	1436756	98.9155
2	11.458	171834	0.5012	15753	1.0845

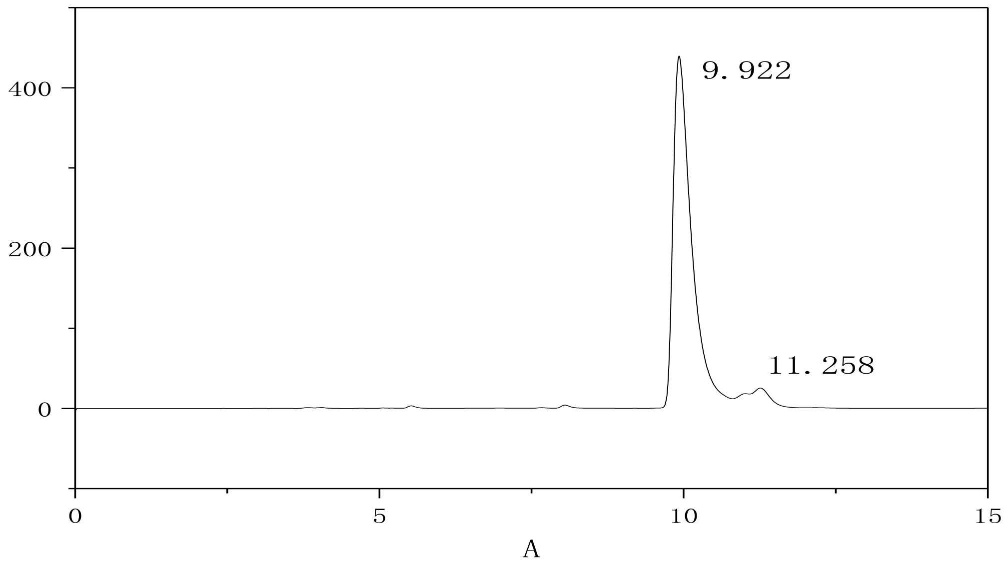


(S_p)- **(2j)**

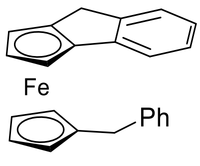
yield 88% ; ee=99%



	RT(min)	Area	Area%	Height	Height%
1	9.577	5137001	49.9329	270621	48.7633
2	10.619	5150808	50.0671	284348	51.2367

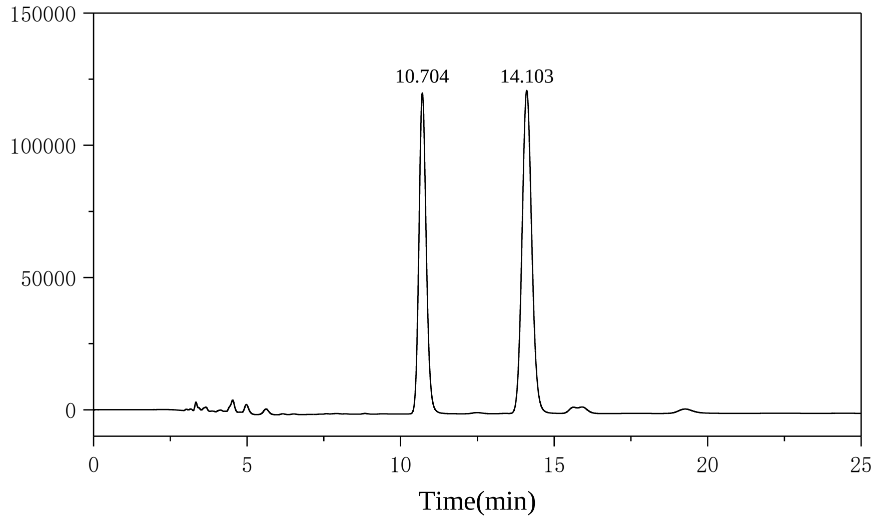


	RT(min)	Area	Area%	Height	Height%
1	9.922	8964164	94.8359	436177	95.6336
2	11.258	488128	5.1641	19915	4.3664

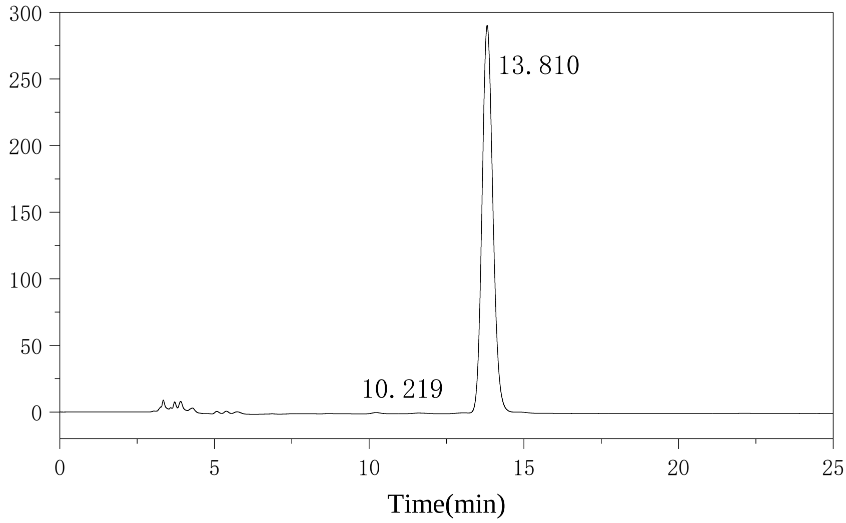


(S_p)- **(2k)**

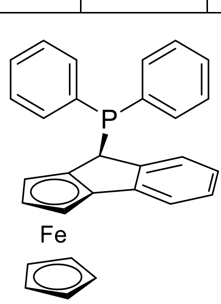
yield 63% ; ee=90%



	RT(min)	Area	Area%	Height	Height%
1	10.704	2009545	42.6986	121434	49.8405
2	14.103	2696805	57.3014	122211	50.1595

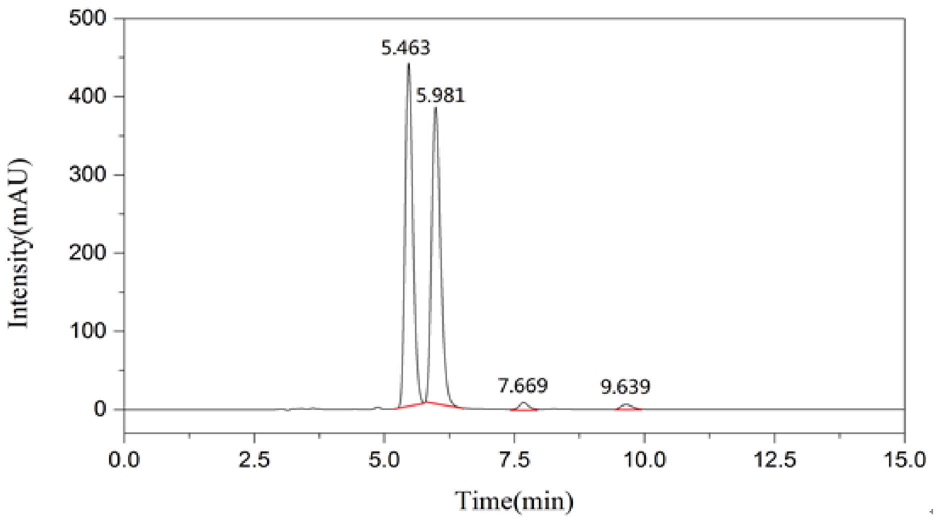


	RT(min)	Area	Area%	Height	Height%
1	10.219	16629	0.2358	917	0.3143
2	13.810	7036226	99.7642	290847	99.6857

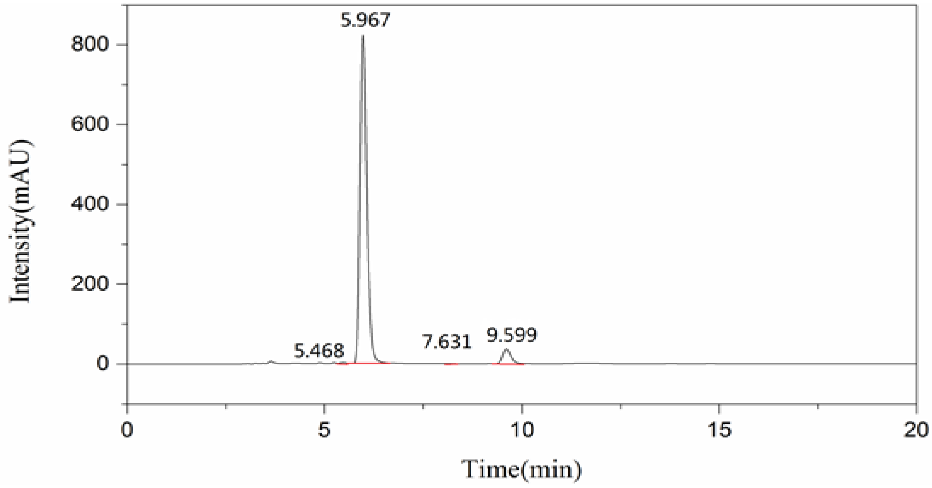


(R_p,S)- **(3a)**

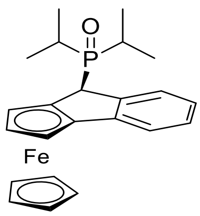
yield 70% ; ee>99% ; de>99%



	RT(min)	Area	Area%	Height	Height%
1	5.463	4686923	48.6263	443185	52.4447
2	5.981	4754637	49.3288	386680	45.7581
3	7.669	98934	1.0264	8829	1.0448
4	9.639	98165	1.0185	6358	0.7524

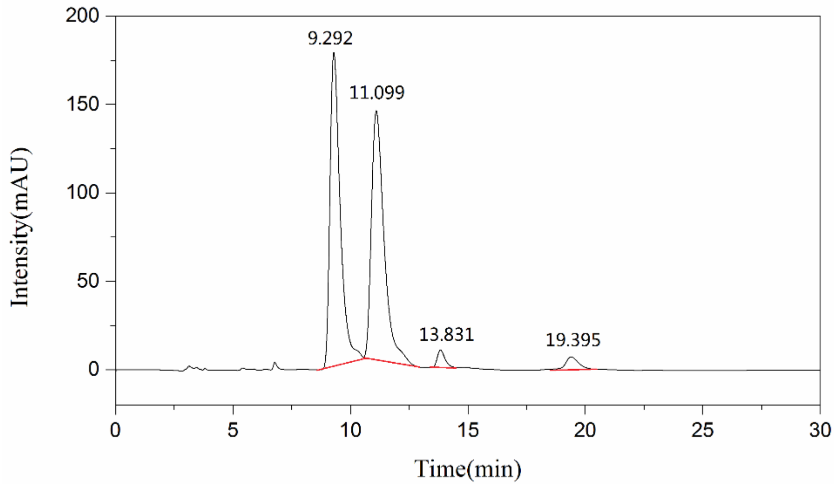


	RT(min)	Area	Area%	Height	Height%
1	5.468	22562	0.2118	2679	0.3099
2	5.967	10046878	94.5479	823955	95.3145
3	7.631	4038	0.0380	447	0.0517
4	9.599	552818	5.2024	37378	4.3239

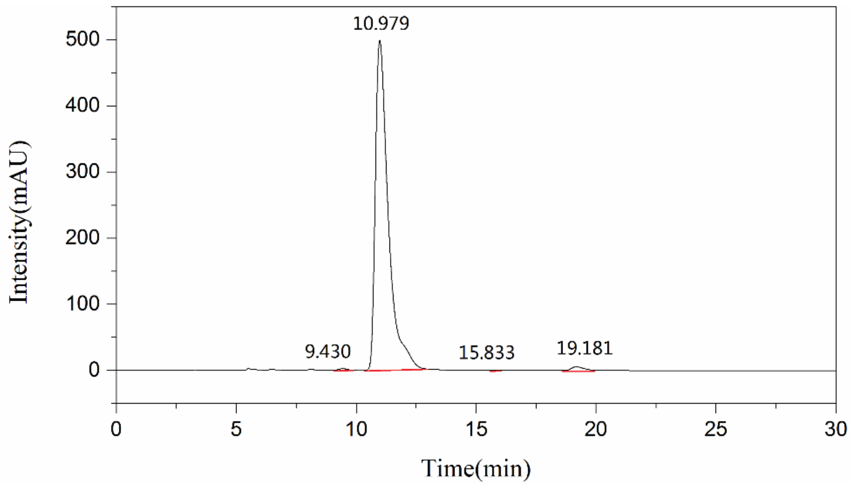


(R_p,S)- **(4b)**

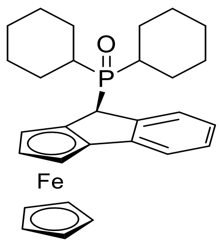
67% yield, ee > 99.6%; de =90.38%



	RT(min)	Area	Area%	Height	Height%
1	9.292	5709658	47.8134	179417	52.4769
2	11.099	5763673	48.2657	145819	42.6500
3	13.831	224809	1.8826	9865	2.8854
4	19.395	243415	2.0384	6796	1.9877

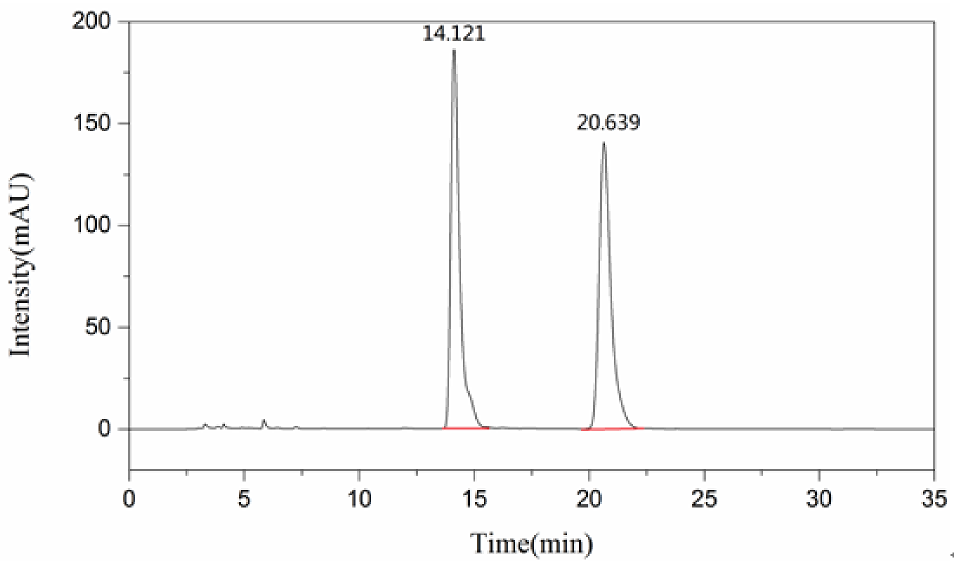


	RT(min)	Area	Area%	Height	Height%
1	9.430	50445	0.2650	2252	0.4445
2	10.979	18779021	98.6421	498645	98.4278
3	15.833	567	0.0030	87	0.0172
4	19.181	207507	1.0900	5626	1.1105

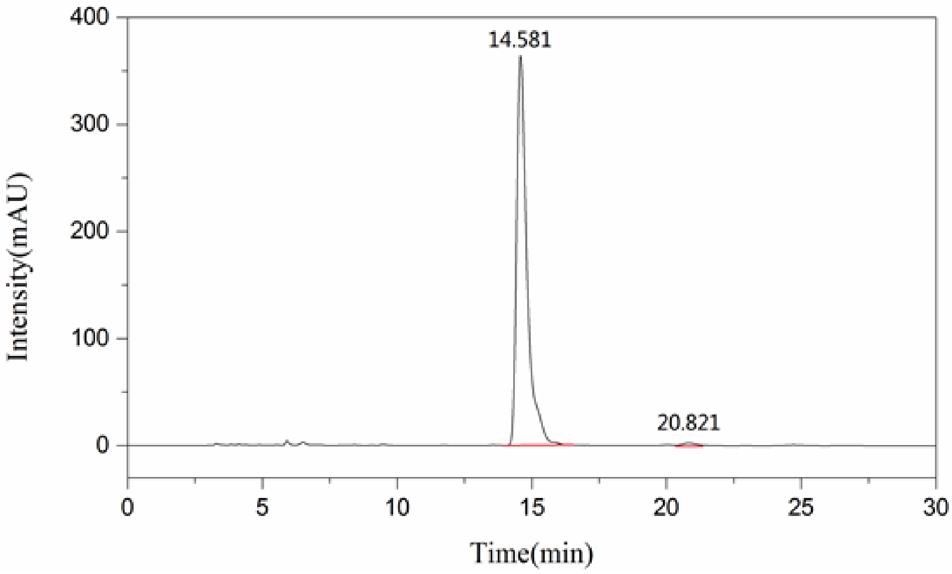


(R_p,S)- **(4c)**

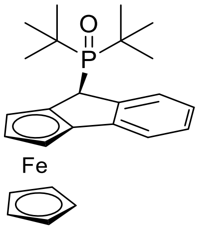
yield 73% ; ee = 99.5% ; de=97.8%



	RT(min)	Area	Area%	Height	Height%
1	14.121	5033245	49.8006	186003	56.9824
2	20.639	5073555	50.1994	140419	43.0176

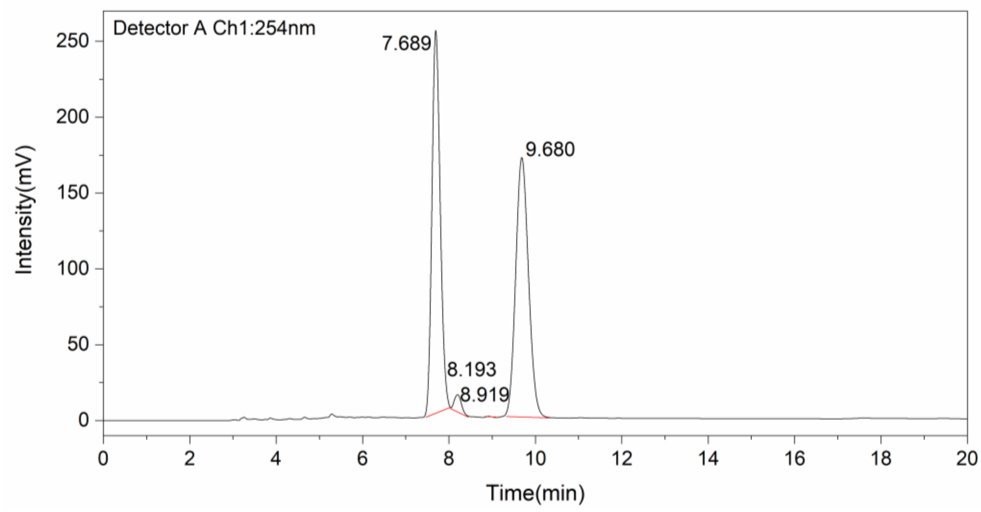


	RT(min)	Area	Area%	Height	Height%
1	14.581	9571110	99.2108	363172	82.6693
2	20.821	76135	0.7892	76135	17.3307

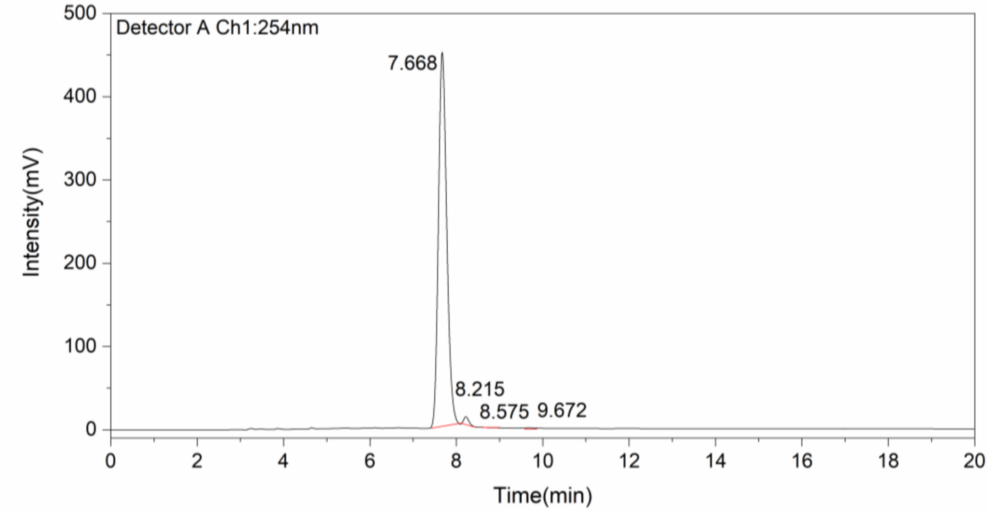


(R_p,S)- **(4d)**

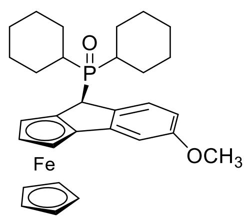
yield 70% ; ee > 99% ; de=98.4%



	RT(min)	Area	Area%	Height	Height%
1	7.689	3481317	47.9108	255554	57.6695
2	8.193	216459	2.9790	15100	3.4076
3	8.919	6526	0.0898	768	0.1733
4	9.680	3561946	49.0204	171713	38.7495

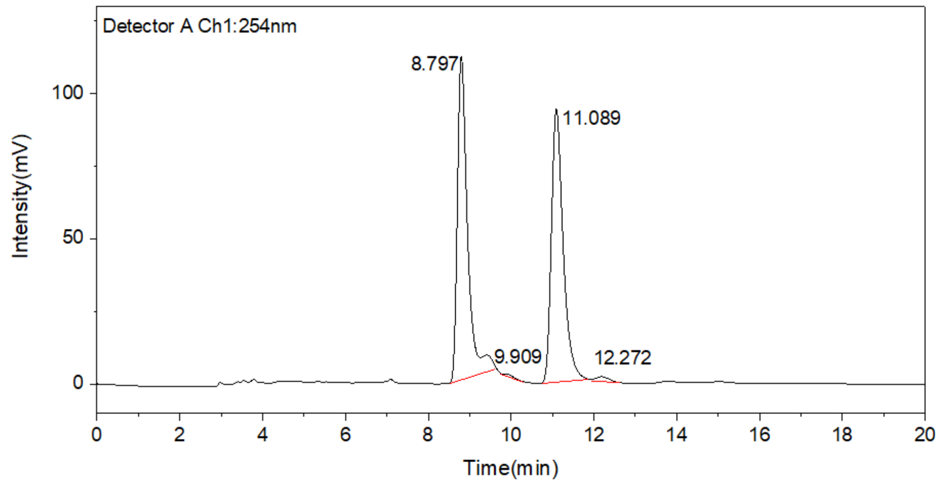


	RT(min)	Area	Area%	Height	Height%
1	7.668	6200270	98.4810	451910	97.6792
2	8.215	85217	1.3535	10059	2.1743
3	8.575	1273	0.0202	193	0.0417
4	9.672	9146	0.1453	485	0.1048

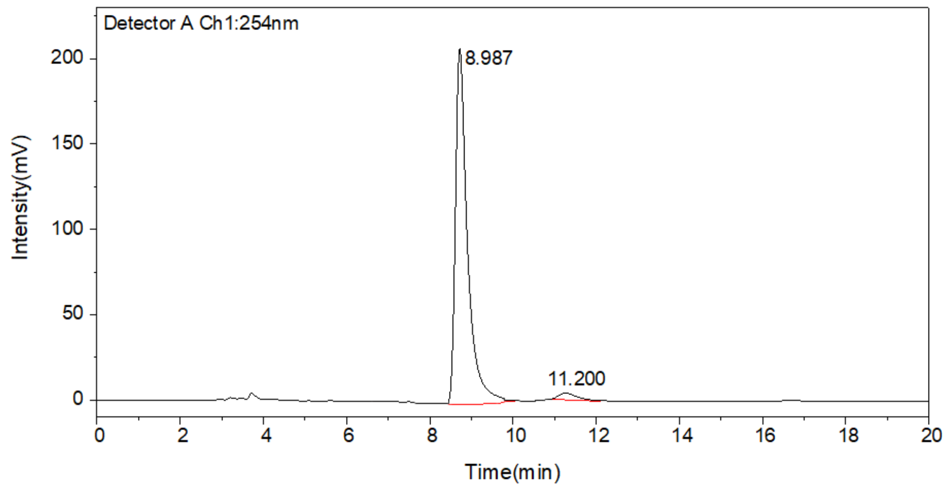


(R_p,S)- **(4f)**

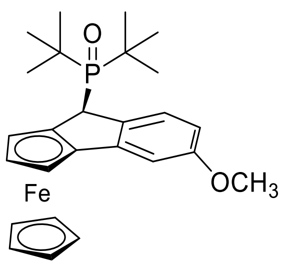
yield 71%, ee > 99.7%, de = 97.3%



	RT(min)	Area	Area%	Height	Height%
1	8.797	1675977	47.3242	109186	53.0828
2	9.909	911	0.0257	480	0.2334
3	11.089	1860769	52.5421	94152	45.7737
3	12.272	3826	0.1080	1872	0.9101

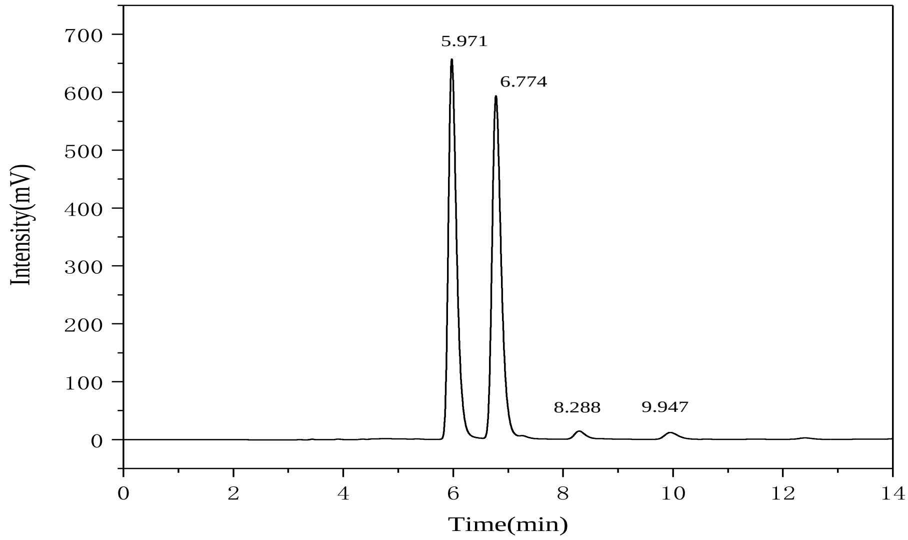


	RT(min)	Area	Area%	Height	Height%
1	8.987	4453756	97.4923	208553	98.1537
2	11.200	114560	2.5077	3923	1.8463

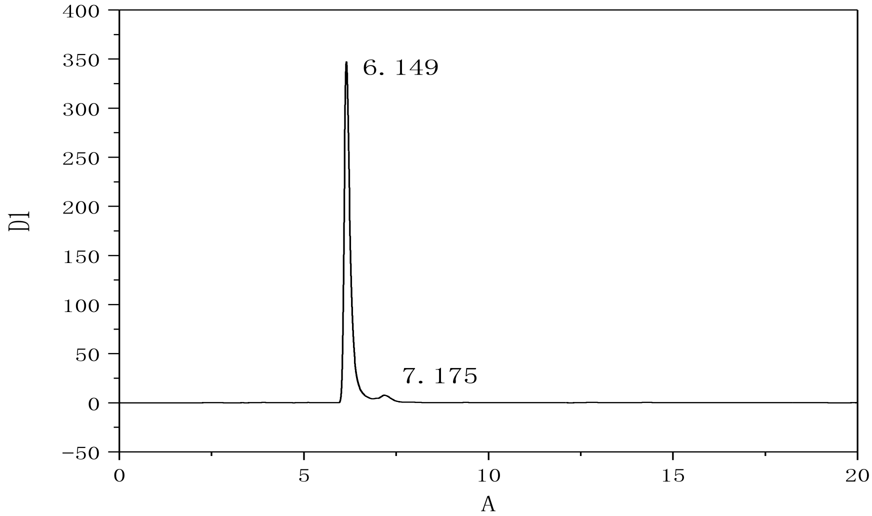


(R_p,S)- **(4g)**

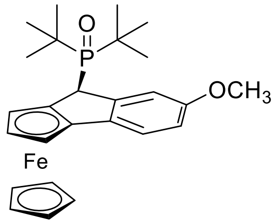
yield 76% ; ee > 99% ; de = 95.0%.



	RT(min)	Area	Area%	Height	Height%
1	5.971	10324152	49.0715	985846	51.6580
2	6.774	10182210	48.3969	885624	46.4064
3	8.288	249790	1.1873	19707	1.0326
4	9.947	282838	1.3444	17232	0.9029

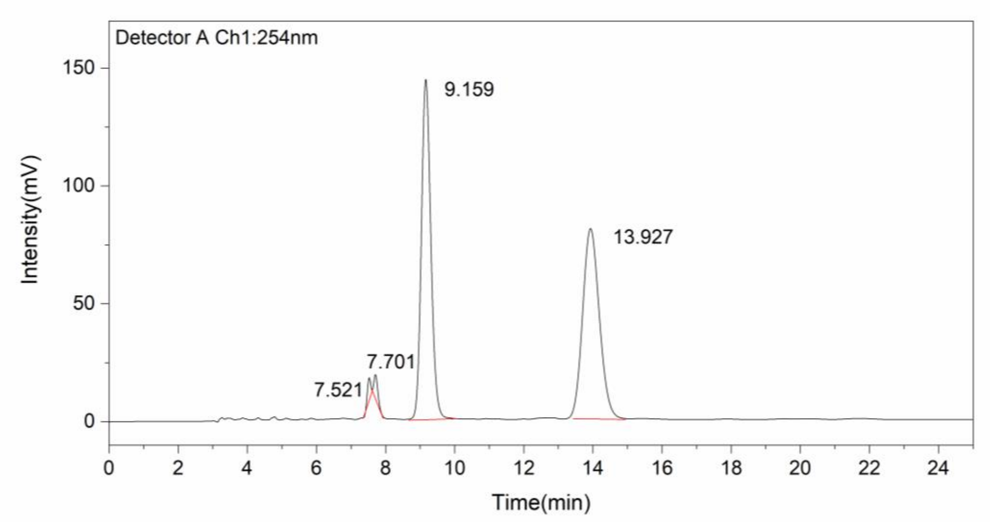


	RT(min)	Area	Area%	Height	Height%
1	6.149	8306983	95.8406	695508	97.9598
2	7.175	360517	4.1594	14485	2.0402

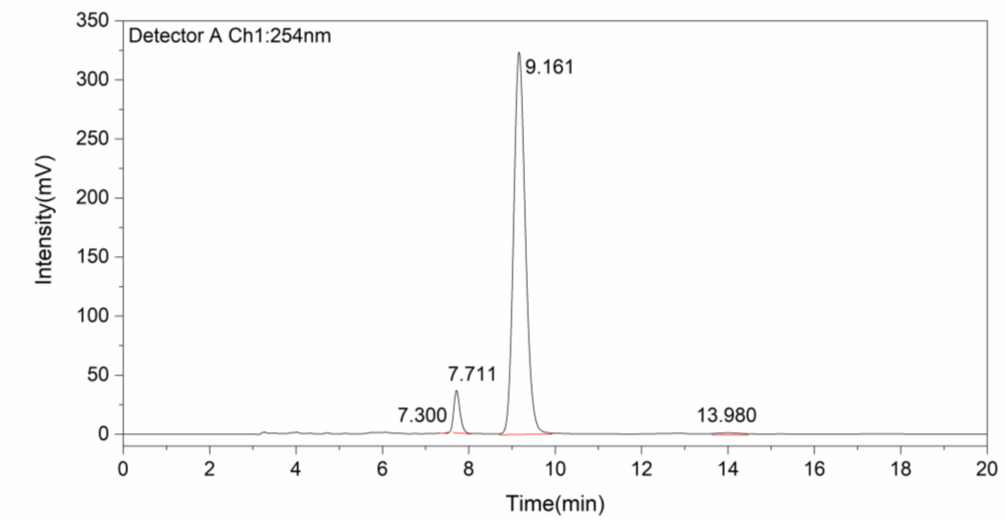


(R_p,S)- **(4h)**

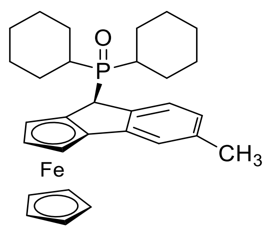
yield 70% ; ee > 99% ; de = 91.7%



	RT(min)	Area	Area%	Height	Height%
1	7.521	149550	2.5753	17192	6.5909
2	7.701	194351	3.3468	18612	7.1354
3	9.159	2748714	47.3342	144251	55.3021
4	13.927	2714420	46.7436	80787	30.9716

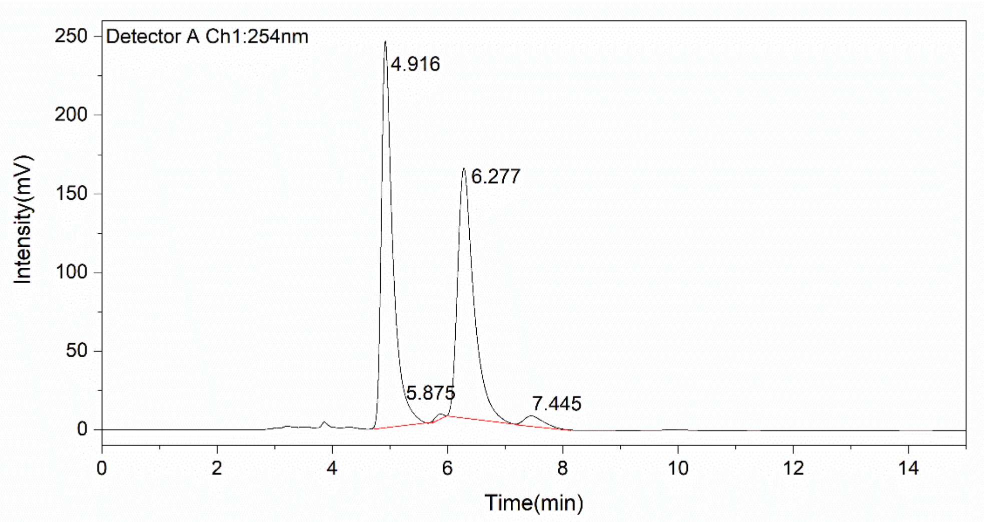


	RT(min)	Area	Area%	Height	Height%
1	7.300	2451	0.0376	253	0.0700
2	7.711	373145	5.7213	36637	10.1532
3	9.161	6122892	93.8794	323174	89.5616
4	13.980	23597	0.3618	777	0.2152

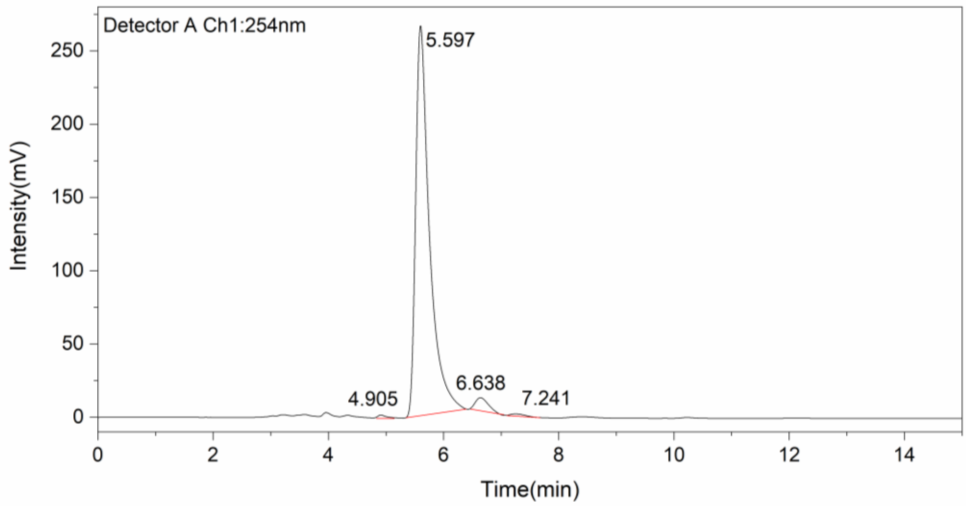


(R_p,S)- **(4j)**

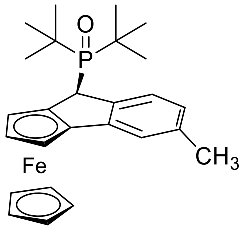
yield 51% ; ee = 99.2% ; de =88.5%



	RT(min)	Area	Area%	Height	Height%
1	4.916	3648805	48.7149	247249	58.4987
2	5.875	26821	0.3581	2692	0.6369
3	6.277	3670810	49.0087	166413	39.3731
4	7.445	143685	1.9183	6304	1.4914

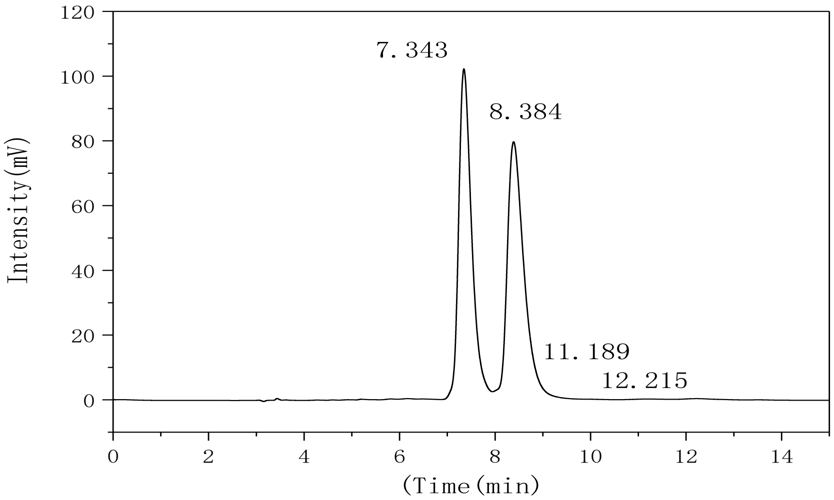


	RT(min)	Area	Area%	Height	Height%
1	5.597	4832669	96.4019	268070	96.1038
2	6.638	154872	3.0894	9386	3.3649
3	7.241	25500	0.5087	1482	0.5313

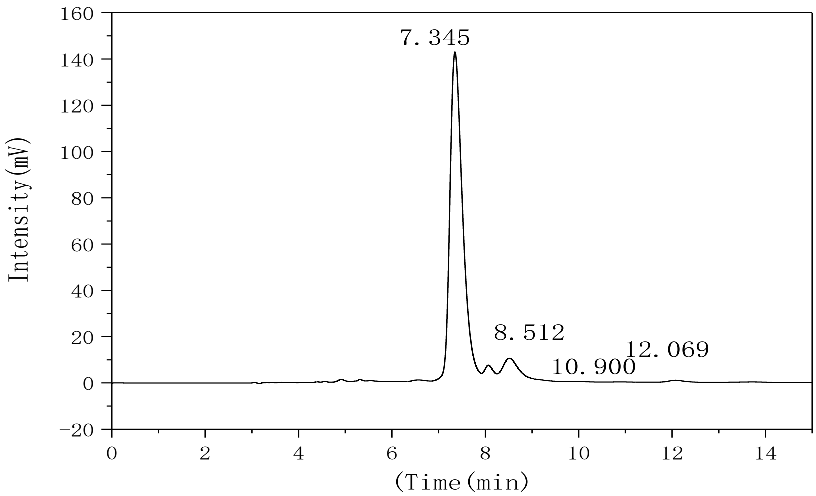


(R_p,S)- **(4k)**

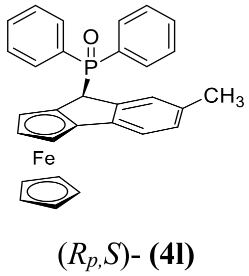
yield 52% ; ee =93.4% ; de= 99.0%



	RT(min)	Area	Area%	Height	Height%
1	7.343	19393499	49.1409	1022516	56.0034
2	8.384	1975708	50.1347	797181	43.6618
3	11.189	107847	0.2733	2262	0.1239
4	12.215	178071	0.4512	3851	0.2109

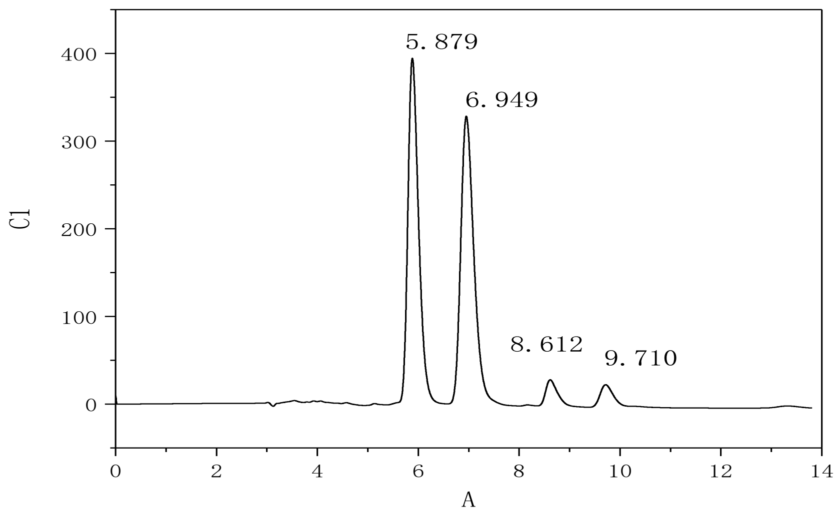


	RT(min)	Area	Area%	Height	Height%
1	7.345	25907338	93.9359	1407944	94.4067
2	8.512	1457397	5.2843	74092	4.9681
3	10.900	20620	0.0748	844	0.0566
4	12.069	194463	0.7051	8481	0.5687

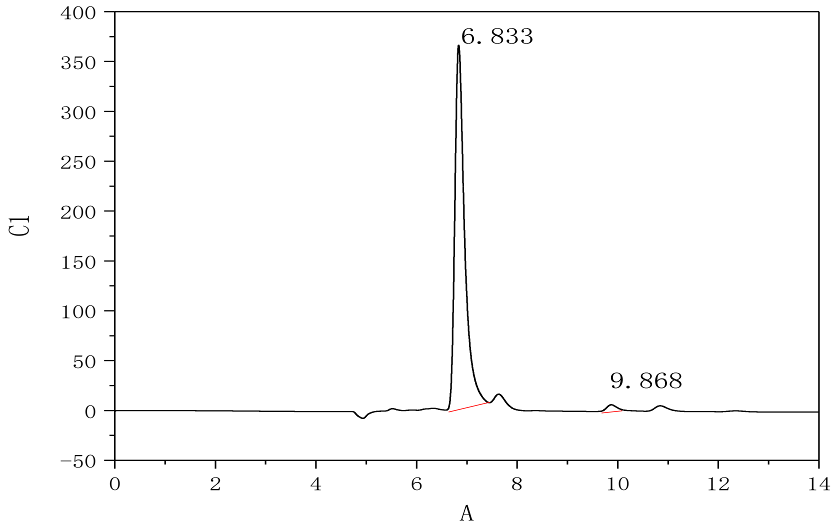


(R_p,S)- **(4l)**

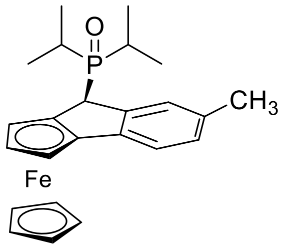
yield 70%, ee =89.3%, de = 98.4%



	RT(min)	Area	Area%	Height	Height%
1	5.879	2975888	45.9813	198155	50.6743
2	6.949	3021907	46.6923	165113	42.2246
3	8.612	247119	3.8183	15100	3.8617
4	9.710	227045	3.5081	12667	3.2394

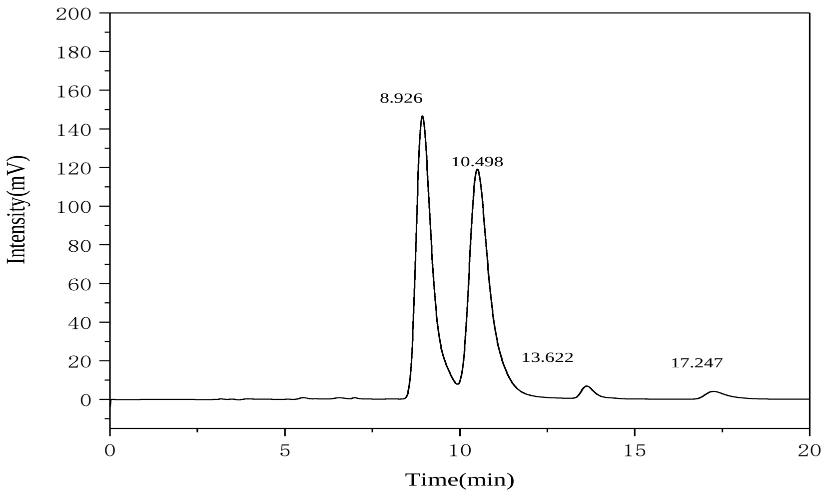


	RT(min)	Area	Area%	Height	Height%
1	5.892	1291	0.0512	152	0.0816
2	6.833	2465470	97.7771	182281	98.1387
3	8.617	90	0.0036	2	0.0008
4	9.868	54670	2.1682	3307	1.7805

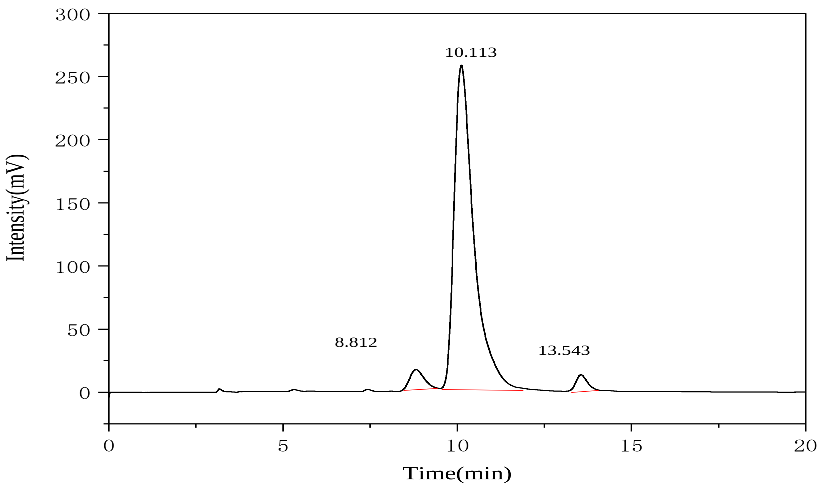


(R_p,S)- **(4m)**

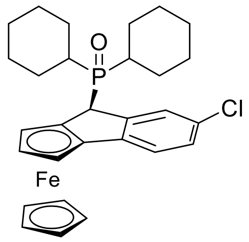
yield 70% ; ee > 99% ; de = 96%



	RT(min)	Area	Area%	Height	Height%
1	8.926	2427348	47.8134	73244	53.0962
2	10.498	2550328	48.2657	59447	43.0950
3	13.622	89966	1.8826	3234	2.3446
4	17.247	92765	2.0384	2020	1.4643

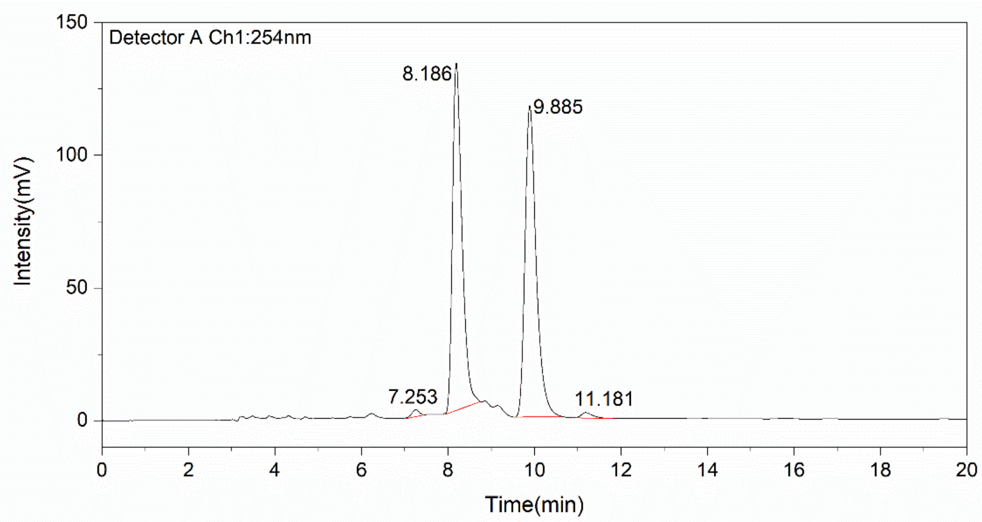


	RT(min)	Area	Area%	Height	Height%
1	8.812	278512	4.9677	8614	5.9797
2	10.113	5181307	92.4163	129062	89.5893
3	13.543	146676	2.6162	6383	4.4310
4	17.258	0	0.000	0	0.0000

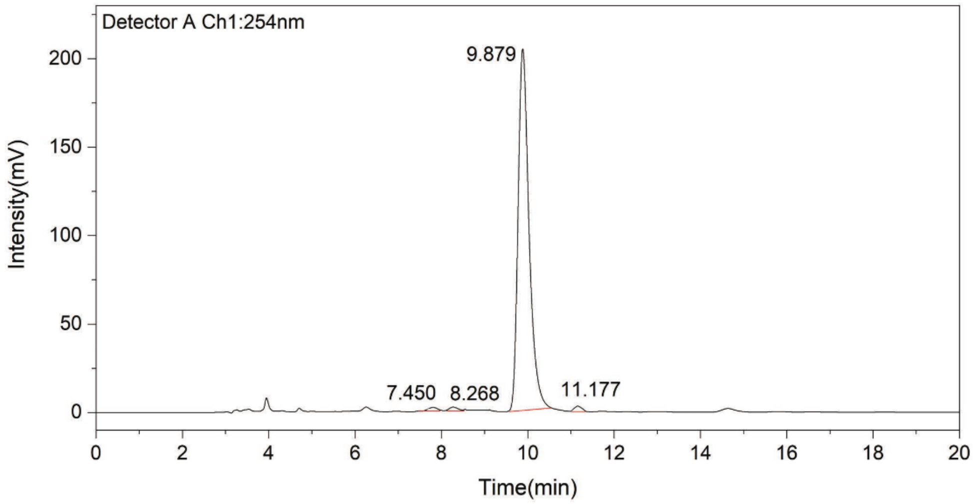


(R_p,S)- **(4n)**

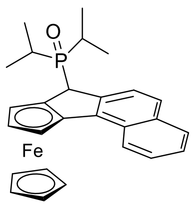
yield 75% ; ee = 89.8% ; de = 94.8%



	RT(min)	Area	Area%	Height	Height%
1	7.253	30191	0.7199	2572	1.0155
2	8.186	1995653	47.5829	131014	51.7224
3	9.885	2131186	50.8144	117659	46.4501
4	11.181	37025	0.8828	2057	0.8119

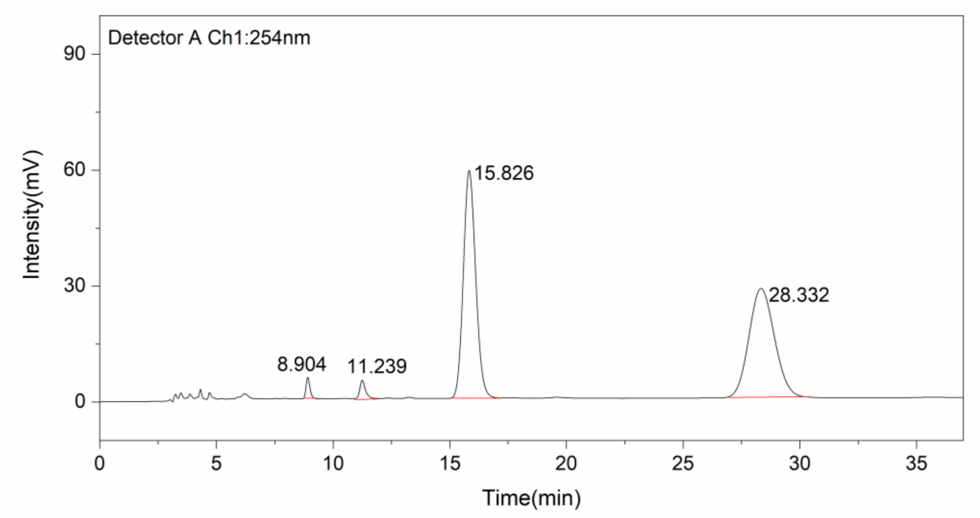


	RT(min)	Area	Area%	Height	Height%
1	7.450	912	0.0242	147	0.0702
2	8.268	23418	0.6225	1865	0.8912
3	9.879	3710843	98.6382	205331	98.1149
4	11.177	26901	0.7151	1933	0.9237

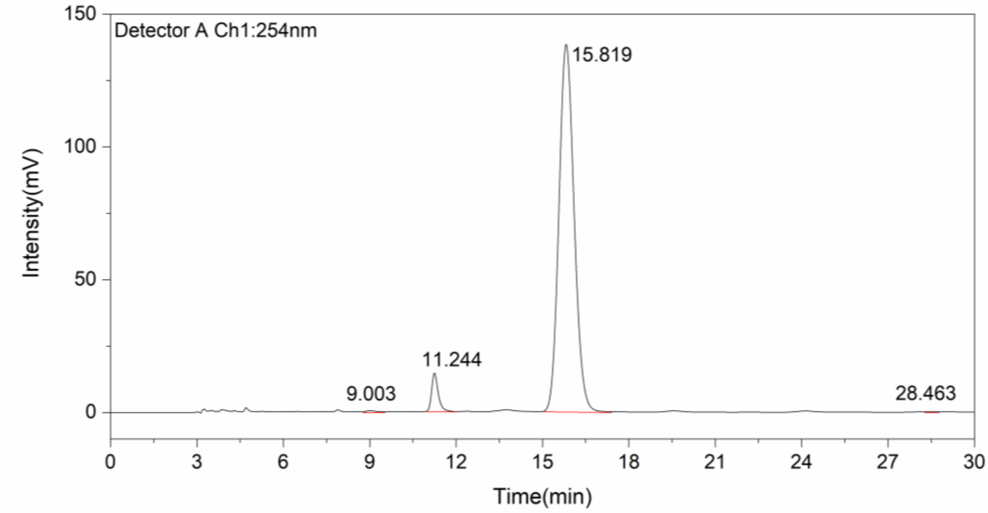


(R_p,S)- **(4o)**

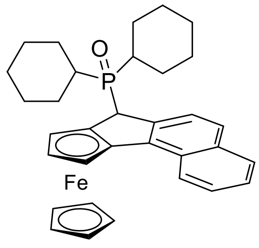
yield 55%, ee =98.7%, de =98.5%



	RT(min)	Area	Area%	Height	Height%
1	8.904	66008	1.4901	5589	5.7409
2	11.239	77649	1.7528	4734	4.8633
3	15.826	2160816	48.7780	58926	60.5322
4	28.332	2125426	47.9791	28098	28.8636

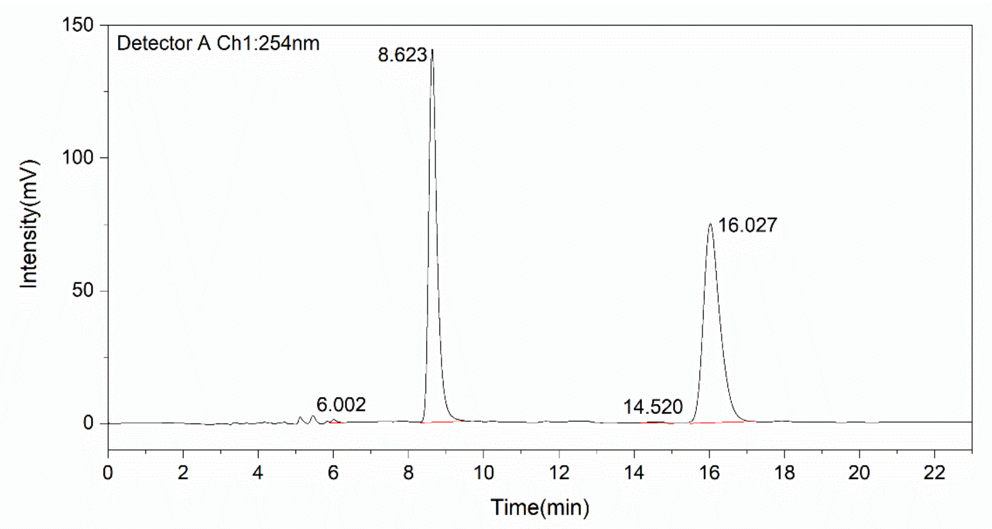


	RT(min)	Area	Area%	Height	Height%
1	9.003	7458	0.1403	403	0.2626
2	11.244	228440	4.2961	14437	9.4174
3	15.819	5062127	95.1992	138282	90.2034
4	28.463	19380	0.3645	179	0.1166

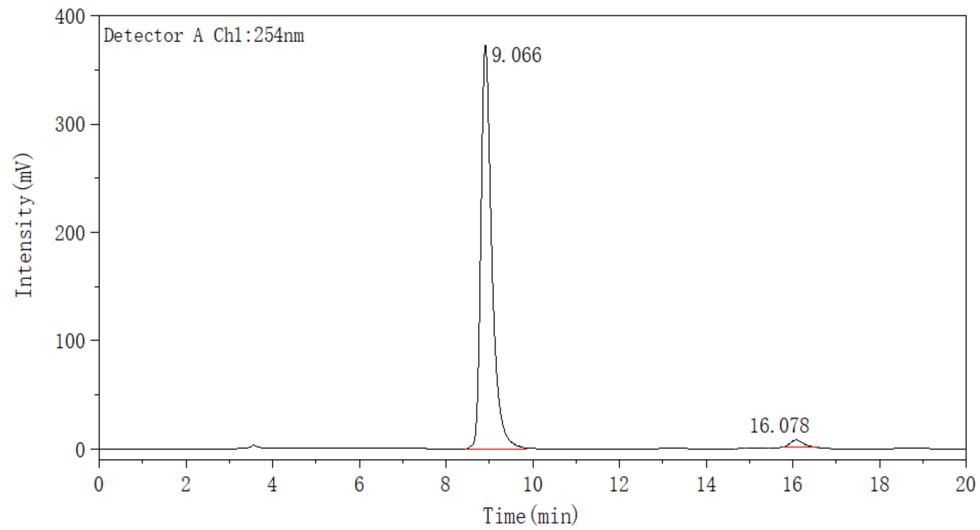


(R_p,S)- **(4p)**

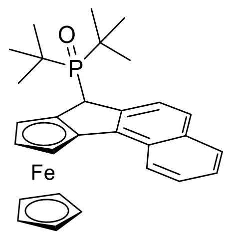
yield 59%, ee > 99.2%, de = 91.1%



	RT(min)	Area	Area%	Height	Height%
1	6.002	7213	0.1607	998	0.4606
2	8.623	2177957	48.5197	140666	64.8968
3	14.520	5012	0.1116	177	0.0817
4	16.027	2298626	51.2079	74912	34.5610

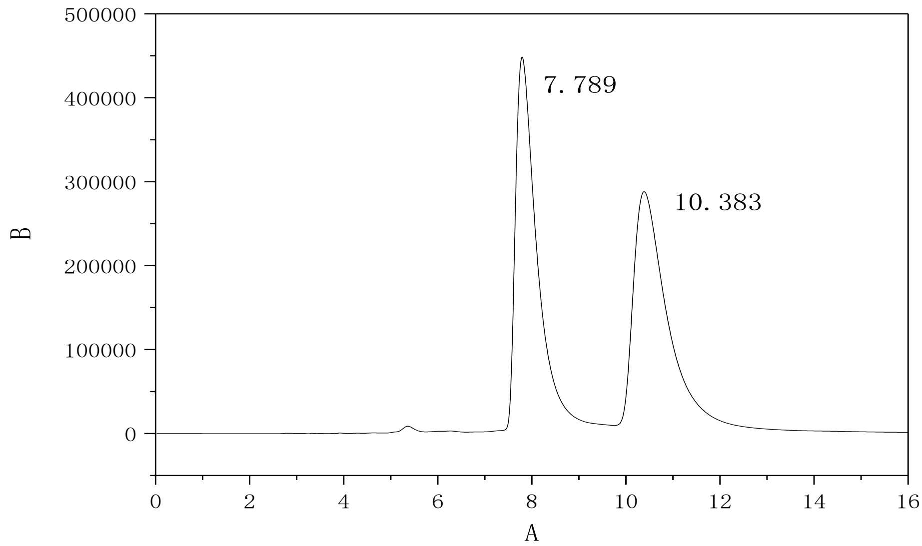


	RT(min)	Area	Area%	Height	Height%
1	9.066	6650204	97.7714	374060	98.1785
2	16.078	151585	2.2286	6940	1.8215

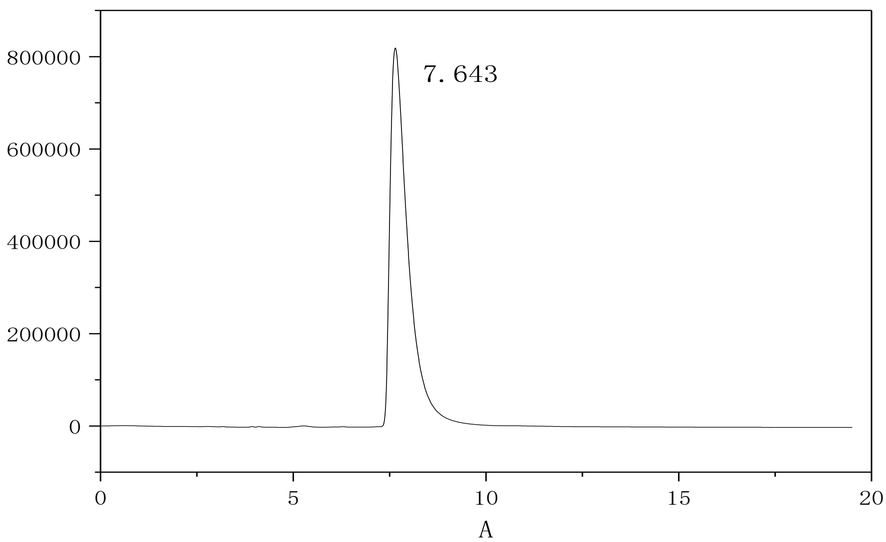


(R_p,S)- **(4q)**

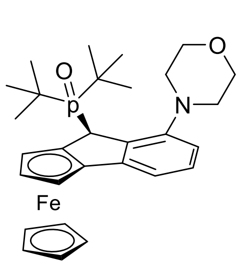
yield 50%, ee =95.5%, de > 99.9%



	RT(min)	Area	Area%	Height	Height%
1	7.789	13887019	50.9693	442387	61.4888
2	10.383	13358851	49.0307	277073	38.5112



	RT(min)	Area	Area%	Height	Height%
1	7.643	26791330	100.0000	819518	100.0000



(R_p,S)- **(7)**

yield 76% ; ee > 99.9% ; de >99.9%