

Supporting Information for

Enantioselective Synthesis of Planar Chiral Ferrocenes *via*
Palladium-catalyzed Direct Coupling with Aryl Boronic Acids

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General Methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. ^1H and ^{13}C NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz, 400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ , ppm).

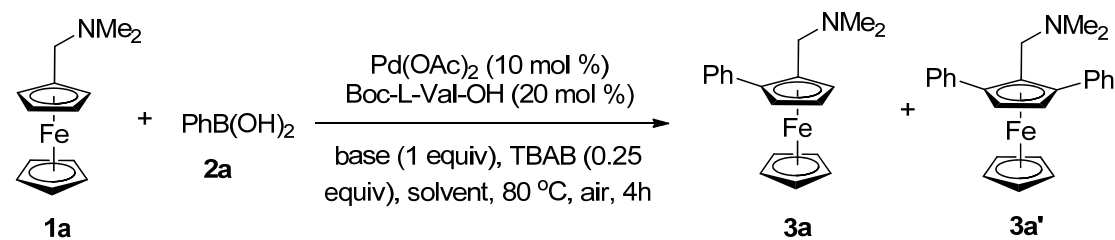
Compounds **1a-d**¹⁻³ were prepared by reductive amination of ferrocene aldehyde with the corresponding amines. (*S*, *R*_p)-**7** was prepared according to the reported procedure.⁴

Complete optimization data

Table 1. Examination of oxidants^a

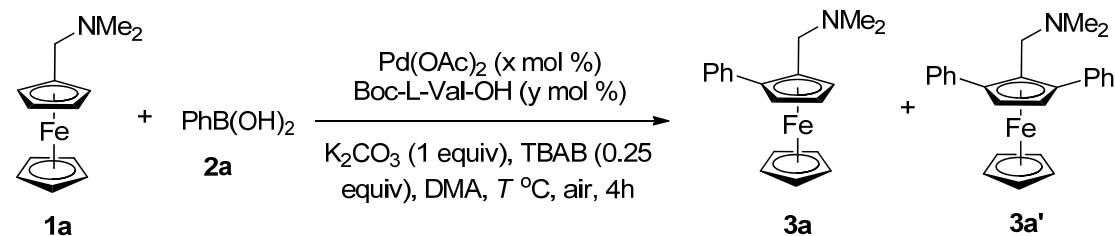
<p>Reaction scheme: Ferrocene aldehyde 1a (with NMe_2 group) reacts with benzaldehyde 2a (PhB(OH)_2) in the presence of Pd(OAc)_2 (10 mol %), Boc-L-Val-OH (20 mol %), K_2CO_3 (1 equiv), TBAB (0.25 equiv), in DMA at 80 °C for 4 h, to yield ferrocene products 3a and 3a'.</p>				
entry	oxidant	3a:3a' ^b	yield (%) ^c	ee (%) ^d
1	Air	8.3:1	74^c	98
2	Ag_2O	-	7	-
3	AgOAc	-	< 5	-
4	Ag_2CO_3	-	15	-
5	Ag_3PO_4	-	15	-
6	Cu(OAc)_2	-	14	-
7	Cu(OTf)_2	-	24	-
8 ^e	O_2	15:1	69(80)	95

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Pd(OAc)_2 (10 mol %), Boc-L-Val-OH (20 mol %), K_2CO_3 (1 equiv), TBAB (0.25 equiv) and oxidant (2 equiv for entries 2-7) in DMA at 80 °C. ^b Determined by ^1H NMR with CH_2Br_2 as an internal standard. ^c Isolated yield. ^d Ee of **3a** was determined by HPLC analysis. ^e Oxygen balloon was used.

Table 2. Examination of base and solvent^a

entry	solvent	base	3a:3a' ^b	yield (%) ^c	ee (%) ^d
1	DMA	K₂CO₃	8.3:1	74	98
2	DMA	KHCO ₃	9.5:1	46 ^b	-
3	DMA	Na ₂ CO ₃	8:1	24 ^b	-
4	DMA	NaOAc	5.6:1	23 ^b	-
5	DMA	Cs ₂ CO ₃	7.7:1	70	99
6	DMF	K ₂ CO ₃	22:1	39	97
7	2-methyl-2-butanol	K ₂ CO ₃	4.3:1	12 ^b	-
8	NMP	K ₂ CO ₃	20:1	55	92

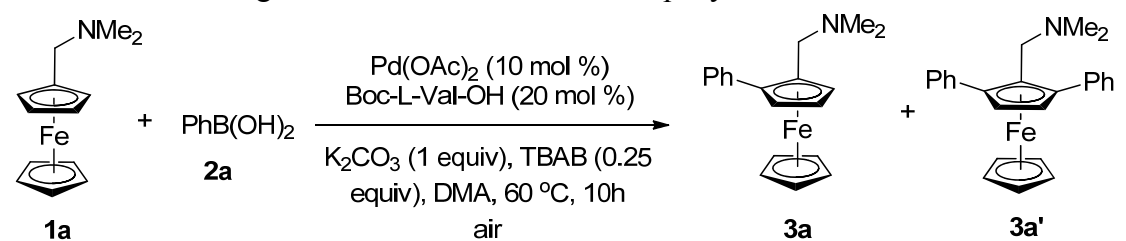
^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $\text{Pd}(\text{OAc})_2$ (10 mol %), Boc-L-Val-OH (20 mol %), base (1 equiv), TBAB (0.25 equiv) in 1.5 mL solvent at 80 °C. ^b Determined by ¹H NMR with CH₂Br₂ as an internal standard. ^c Isolated yield. ^d Ee of **3a** was determined by HPLC analysis.

Table 3. Examination of the amount of phenylboronic acid, catalyst loading and temperature^a

entry	equiv of 2a	x	y	T (°C)	3a:3a' ^b	yield (%) ^c	ee (%) ^d
1	1.1	10	20	80	25:1	60	97
2	1.5	10	20	80	8.3:1	71	98
3	2	10	20	80	8.3:1	74	98
4	3	10	20	80	9.5:1	23	90
5	2	5	10	60	33:1	45	97
6	2	2.5	5	60	-	29	95
7	2	1	2	60	-	9 ^b	-
8	2	10	11	60	12:1	71	96

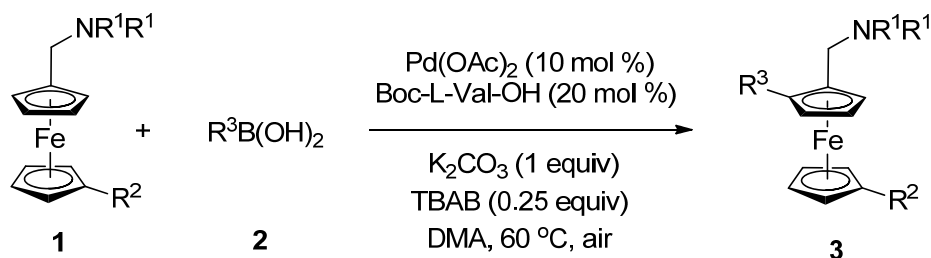
^a Reaction conditions: **1a** (0.2 mmol), **2a**, $\text{Pd}(\text{OAc})_2$ (x mol %), Boc-L-Val-OH (y mol %), K₂CO₃ (1 equiv), TBAB (0.25 equiv) in 1.5 mL DMA under air. ^b Determined by ¹H NMR with CH₂Br₂ as an internal standard. ^c Isolated yield. ^d Ee of **3a** was determined by HPLC analysis.

Table 4. Monitoring kinetic resolution effect of bisphenylation^a

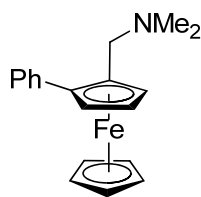
			
entry	time (h)	3a:3a' ^b	ee of 3a (%) ^c
1	2	33:1	94
2	4	28:1	95
3	6	17:1	98
4	8	9:1	99
5	10	7:1	99

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Pd(OAc)₂ (10 mol %), Boc-L-Val-OH (20 mol %), K₂CO₃ (1 equiv), TBAB (0.25 equiv) in 1.5 mL DMA under air at 60 °C. The ratio of **3a/3a'** and ee of **3a** were determined every two hours. ^b Determined by ¹H NMR analysis. ^c Determined by HPLC analysis.

General procedure for the enantioselective synthesis of planar chiral ferrocene

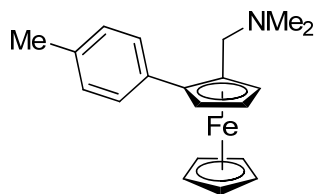


To a solution of boronic acid **2** (0.4 mmol) in DMA (1.5 mL) was added Boc-L-Val-OH (8.7 mg, 0.04 mmol), Pd(OAc)₂ (4.5 mg, 0.02 mmol), K₂CO₃ (27.6 mg, 0.2 mmol), TBAB (tetrabutyl ammonium bromide) (16.1 mg, 0.05 mmol) and ferrocene **1** (0.2 mmol) successively. The mixture was stirred at 60 °C under air (open flask). After the reaction was complete (monitored by TLC), it was then quenched with saturated aqueous NaHCO₃ solution and extracted with EtOAc three times. The combined organic layers were washed with H₂O and brine successively, then dried over anhydrous Na₂SO₄ and filtrated. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether = 1/10, v/v, 2% Et₃N) to afford desired product **3**.



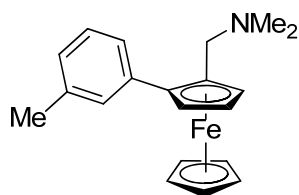
(*S_p*)-1-Dimethylaminomethyl-2-phenyl ferrocene (**3a**)

Yellow oil (50.7 mg, 79% yield, 98% *ee*). Analytical data for **3a**: $[\alpha]_{\text{D}}^{20} = +182.3^\circ$ (*c* = 0.25 Acetone, 98% *ee*). ^1H NMR (400 MHz, CDCl_3) δ 2.17 (s, 6H), 3.15 (AB, $J_{AB} = 12.8$ Hz, 1H), 3.64 (BA, $J_{BA} = 12.8$ Hz, 1H), 4.05 (s, 5H), 4.23-4.24 (m, 1H), 4.30-4.31 (m, 1H), 4.46-4.47 (m, 1H), 7.23-7.30 (m, 1H), 7.31-7.34 (m, 2H), 7.70-7.73 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.0, 57.9, 67.1, 69.9, 70.0, 71.5, 82.2, 88.1, 126.0, 127.9, 129.3, 138.9; IR (film) 3070, 2932, 2762, 1725, 1600, 1452, 1357, 1255, 1171, 1105, 1014, 816, 761, 697 cm^{-1} ; HRMS (ESI) exact mass calcd for ($\text{C}_{19}\text{H}_{21}\text{NFe}$) requires *m/z* 317.1065, found *m/z* 317.1073. The enantiomeric excess was determined by phenomenex cellulose-4 (25 cm), Hexanes / IPA = 29 / 1, 0.3 mL/min, $\lambda = 254$ nm, *t* (minor) = 15.35 min, *t* (major) = 15.93 min.



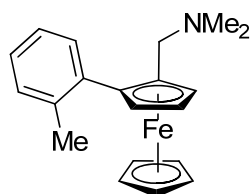
(*S_p*)-1-Dimethylaminomethyl-2-(4-methylphenyl) ferrocene (**3b**)

Yellow oil (47.0 mg, 70% yield, 97% *ee*). Analytical data for **3b**: $[\alpha]_{\text{D}}^{20} = +157.9^\circ$ (*c* = 0.25 Acetone, 97% *ee*). ^1H NMR (400 MHz, CDCl_3) δ 2.16 (s, 6H), 2.34 (s, 3H), 3.15 (AB, $J_{AB} = 12.4$ Hz, 1H), 3.63 (BA, $J_{BA} = 12.4$ Hz, 1H), 4.03 (s, 5H), 4.19-4.21 (m, 1H), 4.27-4.28 (m, 1H), 4.42-4.43 (m, 1H), 7.12 (d, $J = 8.0$ Hz, 2H), 7.59 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1, 45.0, 57.8, 66.9, 69.6, 69.9, 71.3, 82.0, 88.3, 128.6, 129.2, 135.5, 135.6; IR (film) 3092, 2935, 2811, 2762, 1726, 1524, 1454, 1301, 1258, 1173, 1105, 1016, 815, 721 cm^{-1} ; HRMS (ESI) exact mass calcd for ($\text{C}_{20}\text{H}_{23}\text{NFe}$) requires *m/z* 331.1221, found *m/z* 331.1213. The enantiomeric excess was determined by phenomenex cellulose-4 (25 cm), Hexanes / IPA = 29 / 1, 0.3 mL/min, $\lambda = 254$ nm, *t* (minor) = 14.36 min, *t* (major) = 15.40 min.



(*S_p*)-1-Dimethylaminomethyl-2-(3-methylphenyl) ferrocene (**3c**)

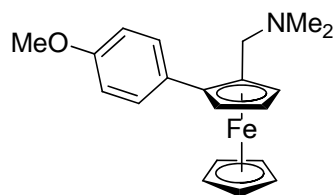
Yellow oil (54.3 mg, 81% yield, 99% *ee*). Analytical data for **3c**: $[\alpha]_{\text{D}}^{20} = +168.1^{\circ}$ (*c* = 0.25 Acetone, 99% *ee*). ^1H NMR (400 MHz, CDCl_3) δ 2.19 (s, 6H), 2.39 (s, 3H), 3.15 (AB, $J_{AB} = 12.4$ Hz, 1H), 3.65 (BA, $J_{BA} = 12.4$ Hz, 1H), 4.06 (s, 5H), 4.06-4.23 (m, 1H), 4.30-4.31 (m, 1H), 4.46-4.47 (m, 1H), 7.05 (d, $J = 7.6$ Hz, 1H), 7.21-7.24 (m, 1H), 7.52-7.54 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.5, 44.9, 57.8, 66.9, 69.8, 69.9, 71.3, 82.1, 88.2, 126.4, 126.8, 127.7, 130.0, 137.2, 138.7; IR (film) 3093, 2936, 2811, 2762, 1727, 1605, 1499, 1454, 1354, 1258, 1173, 1105, 1020, 1000, 807, 785, 705 cm^{-1} ; HRMS (ESI) exact mass calcd for ($\text{C}_{20}\text{H}_{23}\text{NFe}$) requires m/z 331.1221, found m/z 331.1214. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 29 / 1, 0.3 mL/min, $\lambda = 254$ nm, *t* (minor) = 14.95 min, *t* (major) = 16.31 min.



(*S_p*)-1-Dimethylaminomethyl-2-(2-methylphenyl) ferrocene (**3d**)

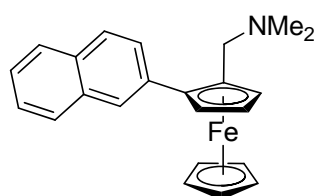
Yellow oil (22.4 mg, 33% yield, 94% *ee*). Analytical data for **3d**: $[\alpha]_{\text{D}}^{20} = -128.1^{\circ}$ (*c* = 0.25 Acetone, 94% *ee*). ^1H NMR (400 MHz, CDCl_3) δ 1.91 (s, 6H), 2.15 (s, 3H), 3.21 (AB, $J_{AB} = 12.8$ Hz, 1H), 3.47 (BA, $J_{BA} = 12.8$ Hz, 1H), 4.19 (s, 5H), 4.28-4.31 (m, 2H), 4.39-4.30 (m, 1H), 7.14-7.25 (m, 3H), 7.82-7.84 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.7, 30.9, 44.3, 56.1, 66.5, 69.2, 69.7, 83.8, 90.0, 124.9, 126.6, 129.8, 132.9, 136.0, 137.7; IR (film) 3093, 2926, 2812, 2763, 2322, 1676, 1498, 1454, 1247, 1175, 1106, 1018, 1001, 814, 762, 726 cm^{-1} ; HRMS (ESI) exact mass calcd for ($\text{C}_{20}\text{H}_{23}\text{NFe}$) requires m/z 331.1221, found m/z 331.1216. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 29 / 1, 0.3

mL/min, $\lambda = 254$ nm, t (major) = 16.13 min, t (minor) = 17.49 min.



(*S_p*)-1-Dimethylaminomethyl-2-(4-methoxyphenyl) ferrocene (**3e**)

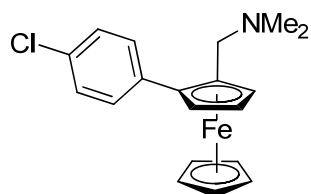
Yellow oil (59% yield, 96% *ee*). Analytical data for **3e**: $[\alpha]_D^{20} = +173.5^\circ$ (*c* = 0.25 Acetone, 96% *ee*). ^1H NMR (400 MHz, CDCl_3) δ 2.15 (s, 6H), 3.12 (AB, $J_{AB} = 12.4$ Hz, 1H), 3.61 (BA, $J_{BA} = 12.4$ Hz, 1H), 3.82 (s, 3H), 4.03 (s, 5H), 4.18-4.19 (m, 1H), 4.25-4.26 (m, 1H), 4.39-4.40 (m, 1H), 6.85-6.88 (m, 2H), 7.62-7.65 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.0, 55.2, 57.9, 66.8, 69.5, 69.9, 71.2, 82.0, 88.3, 113.3, 130.3, 130.9, 158.0; IR (film) 3092, 2934, 2812, 2764, 1610, 1574, 1521, 1455, 1364, 1288, 1244, 1176, 1105, 1034, 830 cm^{-1} ; HRMS (ESI) exact mass calcd for ($\text{C}_{20}\text{H}_{23}\text{NOFe}$) requires m/z 347.1170, found m/z 347.1162. The enantiomeric excess was determined by phenomenex cellulose-4 (25 cm), Hexanes / IPA = 29 / 1, 0.3 mL/min, $\lambda = 254$ nm, t (minor) = 18.79 min, t (major) = 20.32 min.



(*S_p*)-1-Dimethylaminomethyl-2-(2-naphthyl) ferrocene (**3f**)

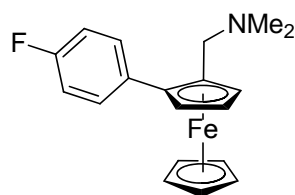
Yellow oil (55.8 mg, 75% yield, 96% *ee*). Analytical data for **3f**: $[\alpha]_D^{20} = -42.6^\circ$ (*c* = 0.25 Acetone, 96% *ee*). ^1H NMR (400 MHz, CDCl_3) δ 2.24 (s, 6H), 3.15 (AB, $J_{AB} = 12.4$ Hz, 1H), 3.73 (BA, $J_{BA} = 12.4$ Hz, 1H), 4.05 (s, 5H), 4.27-4.28 (m, 1H), 4.33-4.34 (m, 1H), 4.58-4.59 (m, 1H), 7.41-7.47 (m, 2H), 7.78-7.84 (m, 4H), 8.24 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.1, 58.2, 67.4, 70.0, 70.1, 71.9, 82.3, 87.8, 125.4, 126.0, 127.2, 127.3, 127.6, 127.9, 128.0, 132.0, 133.5, 136.4; IR (film) 3090, 2934, 2852, 2811, 2763, 1724, 1628, 1599, 1508, 1454, 1354, 1253, 1173, 1104, 1016, 999, 963, 813, 746 cm^{-1} ; HRMS (ESI) exact mass calcd for ($\text{C}_{23}\text{H}_{23}\text{NFe}$) requires m/z

367.1221, found m/z 367.1217. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 29 / 1, 0.3 mL/min, λ = 254 nm, t (minor) = 16.88 min, t (major) = 18.28 min.



(S_P)-1-Dimethylaminomethyl-2-(4-chlorophenyl) ferrocene (**3g**)

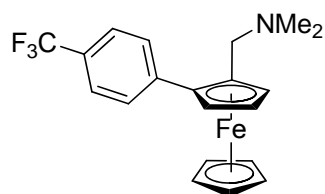
Yellow oil (50.9 mg, 72% yield, 97% *ee*). Analytical data for **3g**: $[\alpha]_D^{20}$ = +185.7° (c = 0.25 Acetone, 97% *ee*). ^1H NMR (300 MHz, CDCl_3) δ 2.19 (s, 6H), 3.09 (AB, J_{AB} = 12.8 Hz, 1H), 3.61 (BA, J_{BA} = 12.8 Hz, 1H), 4.04 (s, 5H), 4.04-4.25 (m, 1H), 4.30-4.31 (m, 1H), 4.46-4.47 (m, 1H), 7.27-7.30 (m, 2H), 7.68-7.71 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.0, 58.0, 67.3, 70.0, 70.1, 71.9, 82.1, 86.8, 128.1, 130.4, 131.6, 137.6; IR (film) 3092, 2936, 2812, 2765, 1725, 1503, 1454, 1257, 1174, 1091, 1014, 971, 817, 726 cm^{-1} ; HRMS (ESI) exact mass calcd for ($\text{C}_{19}\text{H}_{20}\text{NClFe}$) requires m/z 351.0675, found m/z 351.0668. The enantiomeric excess was determined by phenomenex cellulose-4 (25 cm), Hexanes / IPA = 29 / 1, 0.3 mL/min, λ = 254 nm, t (minor) = 13.94 min, t (major) = 14.70 min.



(S_P)-1-Dimethylaminomethyl-2-(4-fluorophenyl) ferrocene (**3h**)

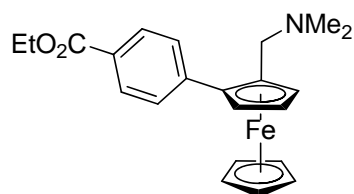
Yellow oil (37.5 mg, 55% yield, 97% *ee*). Analytical data for **3h**: $[\alpha]_D^{20}$ = +153.1° (c = 0.25 Acetone, 97% *ee*). ^1H NMR (400 MHz, CDCl_3) δ 2.16 (s, 6H), 3.09 (AB, J_{AB} = 12.8 Hz, 1H), 3.68 (BA, J_{BA} = 12.8 Hz, 1H), 4.03 (s, 5H), 4.20-4.21 (m, 1H), 4.26-4.27 (m, 1H), 4.41-4.42 (m, 1H), 6.97-7.02 (m, 2H), 7.68-7.72 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.0, 57.9, 67.0, 69.9, 70.0, 71.6, 82.1, 87.3, 114.7 (d, J = 21.0 Hz), 130.6 (d, J = 7.2 Hz), 134.7 (d, J = 3.2 Hz), 161.3 (d, J = 243.6 Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -116.8; IR (film) 3093, 2935, 2813, 2766, 1604, 1519,

1455, 1364, 1301, 1221, 1159, 1105, 1016, 811 cm^{-1} ; HRMS (ESI) exact mass calcd for $(\text{C}_{19}\text{H}_{20}\text{NFFe})$ requires m/z 335.0970, found m/z 335.0961. The enantiomeric excess was determined by phenomenex cellulose-4 (25 cm), Hexanes / IPA = 29 / 1, 0.3 mL/min, λ = 254 nm, t (minor) = 14.23 min, t (major) = 15.06 min.



(*S_p*)-1-Dimethylaminomethyl-2-(4-trifluoromethylphenyl) ferrocene (3i**)**

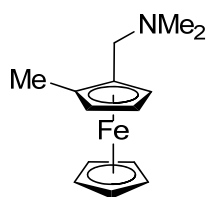
Yellow oil (47.0 mg, 61% yield, 94% *ee*). Analytical data for **3i**: $[\alpha]_{\text{D}}^{20}$ = +198.1° (c = 0.25 Acetone, 94% *ee*). ^1H NMR (400 MHz, CDCl_3) δ 2.21 (s, 6H), 3.09 (AB, J_{AB} = 12.8 Hz, 1H), 3.63 (BA, J_{BA} = 12.8 Hz, 1H), 4.05 (s, 5H), 4.28-4.30 (m, 1H), 4.34-4.35 (m, 1H), 4.4-4.55 (m, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.0, 58.0, 67.6, 70.2, 70.6, 72.4, 82.2, 85.9, 124.4 (q, J = 270.7 Hz), 124.8 (q, J = 3.8 Hz), 127.7 (q, J = 31.6 Hz), 129.1, 143.4 (q, J = 1.3 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -62.3; IR (film) 3094, 2767, 2330, 1615, 1529, 1456, 1409, 1322, 1258, 1160, 1117, 1069, 1016, 973, 819, 689, 655 cm^{-1} ; HRMS (ESI) exact mass calcd for $(\text{C}_{20}\text{H}_{20}\text{NF}_3\text{Fe})$ requires m/z 385.0939, found m/z 385.0930. The enantiomeric excess was determined by phenomenex cellulose-4 (25 cm), Hexanes / IPA = 98 / 2, 0.3 mL/min, λ = 210 nm, t (minor) = 13.08 min, t (major) = 13.74 min.



(*S_p*)-1-Dimethylaminomethyl-2-(4-ethoxycarbonylphenyl) ferrocene (3j**)**

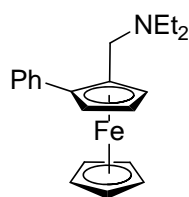
Yellow oil (56.3 mg, 72% yield, 95% *ee*). Analytical data for **3j**: $[\alpha]_{\text{D}}^{20}$ = +207.9° (c = 0.25 Acetone, 95% *ee*). ^1H NMR (400 MHz, CDCl_3) δ 1.39 (t, J = 7.2 Hz, 3H), 2.17 (s, 6H), 3.08 (AB, J_{AB} = 12.8 Hz, 1H), 3.62 (BA, J_{BA} = 12.8 Hz, 1H), 4.01 (s, 5H), 4.26-4.28 (m, 1H), 4.32-4.33 (m, 1H), 4.37 (q, J = 7.2 Hz, 2H), 4.52-4.54 (m, 1H),

7.79 (d, $J = 8.4$ Hz, 2H), 7.97 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.4, 45.0, 58.1, 60.8, 67.8, 70.3, 70.6, 72.5, 82.3, 86.2, 127.8, 128.8, 129.2, 144.8, 166.7; IR (film) 2976, 2935, 2855, 2813, 1709, 1606, 1520, 1456, 1365, 1269, 1175, 1098, 1018, 817, 774, 709 cm^{-1} ; HRMS (ESI) exact mass calcd for $(\text{C}_{22}\text{H}_{25}\text{NO}_2\text{Fe})$ requires m/z 389.1276, found m/z 389.1265. The enantiomeric excess was determined by Diacel Chiralcel OD-H (25 cm), Hexanes / IPA = 29 / 1, 0.3 mL/min, $\lambda = 254$ nm, t (major) = 19.35 min, t (minor) = 22.20 min.



(S_p)-1-Dimethylaminomethyl-2-methyl ferrocene (3k**)**

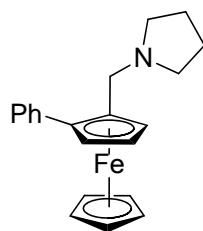
Yellow oil (7.3 mg, 14% yield). Analytical data for **3k**: $[\alpha]_{\text{D}}^{20} = -40.0^\circ$ ($c = 0.25$ Acetone). ^1H NMR (400 MHz, CDCl_3) δ 1.99 (s, 3H), 2.18 (s, 6H), 3.27 (AB, $J_{AB} = 12.8$ Hz, 1H), 3.36 (BA, $J_{BA} = 12.8$ Hz, 1H), 3.99 (t, $J = 2.8$ Hz, 1H), 4.01 (s, 5H), 4.06 (t, $J = 1.6$ Hz, 1H), 4.12 (q, $J = 1.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.4, 44.8, 57.2, 65.8, 69.0, 69.5, 69.7, 82.3, 84.0; IR (film) 3402, 3089, 2922, 2473, 2324, 1727, 1633, 1475, 1383, 1262, 1104, 1036 927, 810 cm^{-1} ; HRMS (ESI) exact mass calcd for $(\text{C}_{14}\text{H}_{19}\text{NFe})$ requires m/z 255.0908, found m/z 255.0906.



(S_p)-1-Diethylaminomethyl-2-phenyl ferrocene (3l**)**

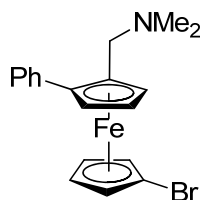
Yellow oil (46.3 mg, 67% yield, 90% *ee*). Analytical data for **3l**: $[\alpha]_{\text{D}}^{20} = +178.4^\circ$ ($c = 0.25$ Acetone, 90% *ee*). ^1H NMR (400 MHz, CDCl_3) δ 0.94 (t, $J = 7.2$ Hz, 6H), 2.41 (q, $J = 7.2$ Hz, 2H), 2.53 (q, $J = 7.2$ Hz, 2H), 3.42 (AB, $J_{AB} = 13.2$ Hz, 1H), 3.72 (BA, $J_{BA} = 13.2$ Hz, 1H), 4.06 (s, 5H), 4.21-4.23 (m, 1H), 4.31-4.32 (m, 1H), 4.44-4.45 (m, 1H), 7.22-7.25 (m, 1H), 7.29-7.33 (m, 2H), 7.76-7.79 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 11.5, 46.0, 51.4, 66.9, 69.7, 70.0, 71.6, 83.0, 88.4, 126.0, 127.8, 129.6,

138.9; IR (film) 3092, 3057, 2966, 2931, 2792, 2349, 2322, 1601, 1506, 1456, 1369, 1286, 1195, 1167, 1105, 1033, 1000, 807, 763, 700, 650 cm^{-1} ; HRMS (ESI) exact mass calcd for $(\text{C}_{21}\text{H}_{25}\text{NFe})$ requires m/z 345.1378, found m/z 345.1370. The enantiomeric excess was determined by phenomenex cellulose-1 (25 cm), CH_3OH / IPA = 9 / 1, 0.7 mL/min, λ = 214 nm, t (minor) = 5.51 min, t (major) = 5.85 min.



(S_p)-1-(Pyrrolidin-1-yl-methyl)-2-phenyl ferrocene (3m**)**

Yellow oil (49.0 mg, 71% yield, 98% *ee*). Analytical data for **3m**: $[\alpha]_D^{20} = +162.4^\circ$ (c = 0.25 Acetone, 98% *ee*). ^1H NMR (400 MHz, CDCl_3) δ 1.71 (t, J = 6.4 Hz, 4H), 2.44 (t, J = 8.0 Hz, 4H), 3.33 (AB, J_{AB} = 12.8 Hz, 1H), 3.83 (BA, J_{BA} = 12.8 Hz, 1H), 4.05 (s, 5H), 4.22 (t, J = 2.4 Hz, 1H), 4.33 (t, J = 2.0 Hz, 1H), 4.45 (t, J = 2.0 Hz, 1H), 7.23-7.25 (m, 1H), 7.30-7.34 (m, 2H), 7.70-7.72 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 23.5, 53.9, 54.1, 67.0, 69.8, 70.0, 71.0, 83.0, 87.8, 126.0, 127.9, 129.4, 139.0; IR (film) 3091, 3056, 2959, 2925, 2777, 1730, 1601, 1506, 1459, 1343, 1317, 1260, 1105, 1033, 1000, 933, 877, 808, 764, 701 cm^{-1} ; HRMS (ESI) exact mass calcd for $(\text{C}_{21}\text{H}_{23}\text{NFe})$ requires m/z 343.1221, found m/z 343.1216. The enantiomeric excess was determined by phenomenex cellulose-1 (25 cm), CH_3CN / IPA = 95 / 5, 0.5mL/min, λ = 214 nm, t (major) = 10.123 min, t (minor) = 10.700 min.



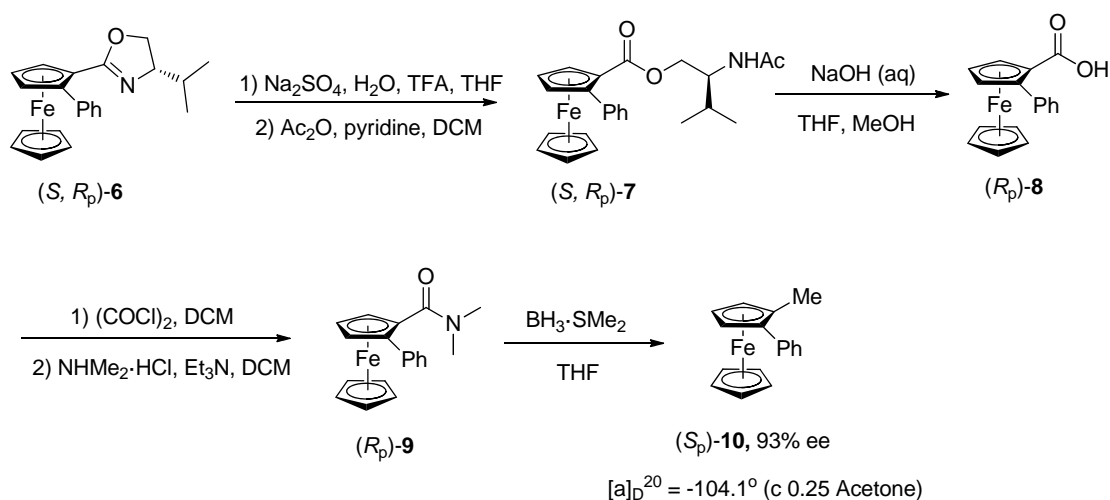
(S_p)-1-Dimethylaminomethyl-2-phenyl -1'-bromo ferrocene (3n**)**

Yellow oil (54.9 mg, 69% yield, 97% *ee*). Analytical data for **3n**: $[\alpha]_D^{20} = +173.6^\circ$ (c = 0.25 Acetone, 97% *ee*). ^1H NMR (400 MHz, CDCl_3) δ 2.17 (s, 6H), 3.18 (AB, J_{AB} = 12.8 Hz, 1H), 3.60 (BA, J_{BA} = 12.8 Hz, 1H), 3.95-3.98 (m, 2H), 4.20-4.21 (m, 1H),

4.26-4.27 (m, 1H), 4.31-4.32 (m, 2H), 4.48-4.49 (m, 1H), 7.24-7.35 (m, 3H), 7.72-7.74 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.0, 56.9, 69.3, 69.7, 70.0, 71.6, 72.2, 72.3, 74.5, 78.4, 83.4, 89.4, 126.3, 128.0, 129.4, 137.8; IR (film) 3084, 3056, 2938, 2812, 2763, 2322, 1727, 1601, 1506, 1456, 1409, 1351, 1258, 1174, 1151, 1017, 871, 804, 764, 700 cm^{-1} ; HRMS (ESI) exact mass calcd for $(\text{C}_{19}\text{H}_{20}\text{NBrFe})$ requires m/z 395.0170, found m/z 395.0158. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 98 / 2, 0.3 mL/min, λ = 210 nm, t (minor) = 17.10 min, t (major) = 19.41 min.

Determination of the absolute configuration of product 3a

Synthesis of 1-Methyl-2-phenyl-ferrocene (S_p)-**8**



A solution of $(S, R_p)\text{-6}^{[4]}$ (424.0 mg, 1.14 mmol) in freshly distilled THF (100 mL) was successively treated with water (1.1 mL) and sodium sulfate (8.3 g, 58.4 mmol). Then the mixture was cooled to 0 °C before trifluoroacetic acid (0.5 mL) was added *via* a syringe. The reaction mixture was stirred for 60 h at room temperature, and then sodium sulfate (2.4 g, 16.9 mmol) was added before the reaction mixture was filtered. The organic solvent was removed under reduced pressure to leave a dark oil, which was immediately dissolved in freshly distilled 30 mL dichloromethane. The resulting solution was cooled to 0 °C, and acetic anhydride (4 mL, 42.3 mmol) was added followed by pyridine (6.3 mL, 80.2 mmol). The mixture was stirred overnight at room temperature. Then the resulting dark solution was quenched with 3 N HCl, washed

with saturated sodium bicarbonate solution, dried over anhydrous MgSO_4 and filtrated. After the solvent was removed under reduced pressure, the residue amide (S, R_p)-**7** was obtained and used directly in the next step.

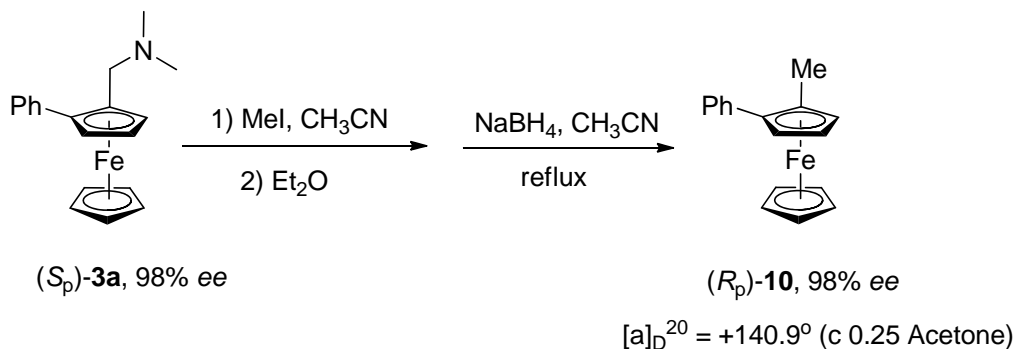
To a solution of the above amide (S, R_p)-**7** (344.5 mg, 0.79 mmol) in THF (5 mL) and CH_3OH (15 mL) was added aqueous NaOH (7.9 mL, 2.5 N). The reaction was refluxed for 2 h, then the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was acidified with hydrochloric acid to pH = 1, then extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the crude carboxylic acid (R_p)-**8** was obtained and used directly in the next step.

To a solution of (R_p)-**8** (246.8 mg, 0.81 mmol) in CH_2Cl_2 (20 mL) was added oxalyl chloride (154.2 mg, 1.22 mmol). The reaction was stirred for 4 h at room temperature, and then the solvent was removed under reduced pressure. The residue was dissolved with 20 mL CH_2Cl_2 , and triethylamine (163.9 mg, 1.62 mmol) and dimethylamine hydrochloride (66.0 mg, 0.81 mmol) were then added. After the resulting mixture was stirred for 4 h, it was quenched with saturated sodium bicarbonate solution, extracted with CH_2Cl_2 , washed with brine, dried over anhydrous Na_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/8) to afford amide (R_p)-**9** (220.3 mg, 82% yield). Analytical data for (R_p)-**9**: $[\alpha]_D^{20} = +51.8$ (c = 0.25 Acetone). ^1H NMR (300 MHz, CDCl_3) δ 2.41 (s, 3H), 2.95 (s, 3H), 4.24 (s, 5H), 4.32 (t, $J = 2.1$ Hz, 1H), 4.54 (s, 2H), 7.22-7.31 (m, 3H), 7.49 (d, $J = 6.9$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 35.2, 38.1, 65.8, 67.4, 70.7, 71.3, 85.0, 85.6, 126.4, 127.5, 128.2, 138.1, 169.6; IR (film) 2963, 1634, 1412, 1260, 1090, 1019, 866, 798 cm^{-1} ; HRMS (ESI) exact mass calcd for ($\text{C}_{20}\text{H}_{23}\text{NFe}$) requires m/z 331.0857, found m/z 331.0863.

Under argon, to a solution of amide (R_p)-**9** (220.3 mg, 0.66 mmol) in THF (4 mL) was added $\text{BH}_3 \cdot \text{Me}_2\text{S}$ (150.4 mg, 1.98 mmol, 3 equiv). After the reaction was refluxed for 4 h, the mixture was quenched with water, extracted with

dichloromethane. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/50) to give (*S_p*)-**10** (36.5 mg, 20% yield). Analytical data for (*S_p*)-**10**: $[\alpha]_{\text{D}}^{20} = -104.1$ ($c = 0.25$ Acetone, 93% *ee*); ^1H NMR (300 MHz, CDCl_3) δ 2.81 (s, 3H), 4.03 (s, 5H), 4.13 (s, 1H), 4.20 (s, 1H), 4.38 (s, 1H), 7.23-7.34 (m, 3H), 7.53-7.56 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.8, 66.1, 69.0, 70.1, 70.5, 81.8, 86.7, 125.9, 127.8, 128.8, 139.0; IR (film) 3087, 3057, 2920, 1946, 1740, 1600, 1504, 1438, 1376, 1265, 1103, 1031, 999, 808, 761, 696, 660, 638 cm^{-1} ; HRMS (ESI) exact mass calcd for ($\text{C}_{17}\text{H}_{16}\text{Fe}$) requires m/z 274.0643, found m/z 274.0635. The enantiomeric excess was determined by Diacel Chiralcel OD-H (25 cm), Hexanes / IPA = 29 / 1, 0.3 mL/min, $\lambda = 254$ nm, t (minor) = 17.32 min, t (major) = 18.72 min.

Synthesis of 1-methyl-2-phenyl-ferrocene (*R_p*)-**10**

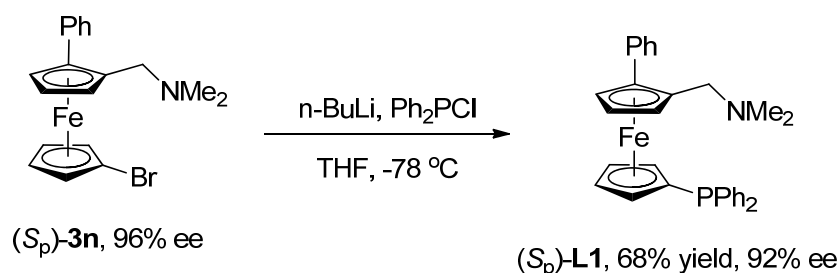


To a solution of product **3a** (220.3 mg, 0.69 mmol) in acetonitrile (20 mL) was added CH_3I (293.8 mg, 2.07 mmol). After the reaction was stirred for 1 h at room temperature, diethyl ether was added and the reaction mixture was filtrated. The solid was washed with diethyl ether three times. The combined organic filtrate was concentrated under reduced pressure. The solid was dissolved in acetonitrile, NaBH_4 (52.2 mg, 1.38 mmol) was added in portions. After the reaction was refluxed for 4 h, the reaction mixture was cooled to room temperature, quenched with H_2O and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (ethyl

acetate/petroleum ether = 1/10) to give (*R_p*)-**10** (142.9 mg, 75% yield). Analytical data for (*R_p*)-**10**: $[\alpha]_D^{20} = +140.9$ (*c* = 0.25 Acetone, 98% *ee*); The enantiomeric excess was determined by Diacel Chiralcel OD-H (25 cm), Hexanes / IPA = 29 / 1, 0.3 mL/min, λ = 254 nm, *t* (major) = 17.20 min, *t* (minor) = 18.68 min.

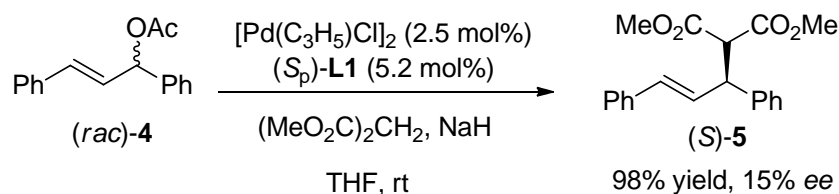
Synthesis of **L1** and Pd-catalyzed asymmetric allylic alkylation

Synthesis of 1-dimethylaminomethyl-2-phenyl -1'-diphenylphosphine ferrocene (**L1**)



To a solution of compound (*S_p*)-**3n** (473 mg, 1.1 mmol) in THF (8.8 mL) was added *n*-BuLi (0.55 mL, 1.3 mmol, 2.4 M in *n*-hexane) at -78°C under argon. The resulting deep red solution was stirred for 30 min. Then chlorodiphenylphosphine (0.29 mL, 1.5 mmol) was added. The mixture was warmed slowly to 0°C and stirred for 1 h. Then the reaction mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na₂SO₄, and filtrated. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum = 1/15 v/v, 2% Et₃N) to give (*S_p*)-**L1** (406 mg, 68% yield, 92% *ee*) as an orange solid. Analytical data for (*S_p*)-**L1**: $[\alpha]_D^{20} = +24.8^\circ$ (*c* = 0.25 Acetone, 92% *ee*). ¹H NMR (400 MHz, CDCl₃) δ 2.13 (s, 6H), 2.88 (AB, *J_{AB}* = 12.8 Hz, 1H), 3.52 (AB, *J_{BA}* = 12.8 Hz, 1H), 4.05 (s, 2H), 4.11-4.13 (m, 2H), 4.20 (s, 1H), 4.24 (s, 1H), 4.41 (s, 1H), 7.19-7.41 (m, 13H), 7.63-7.65 (m, 2H); ³¹P NMR (CDCl₃ 161 MHz) δ -16.91; IR (film) 3055, 2930, 2819, 2772, 2361, 1598, 1504, 1455, 1434, 1303, 1250, 1158, 1091, 1065, 1017, 970, 921, 886, 825, 765, 744 cm⁻¹; HRMS (ESI) exact mass calcd for (C₃₁H₃₀NPFe) requires *m/z* 501.1507, found *m/z* 501.1523. The enantiomeric excess was determined by Diacel Chiralcel OD-H (25 cm), Hexanes / IPA = 98 / 2, 0.3 mL/min, λ = 210 nm, *t* (minor) = 18.78 min, *t* (major) = 22.80 min.

Palladium-Catalyzed Allylic Alkylation with (*S_p*)-**L1**



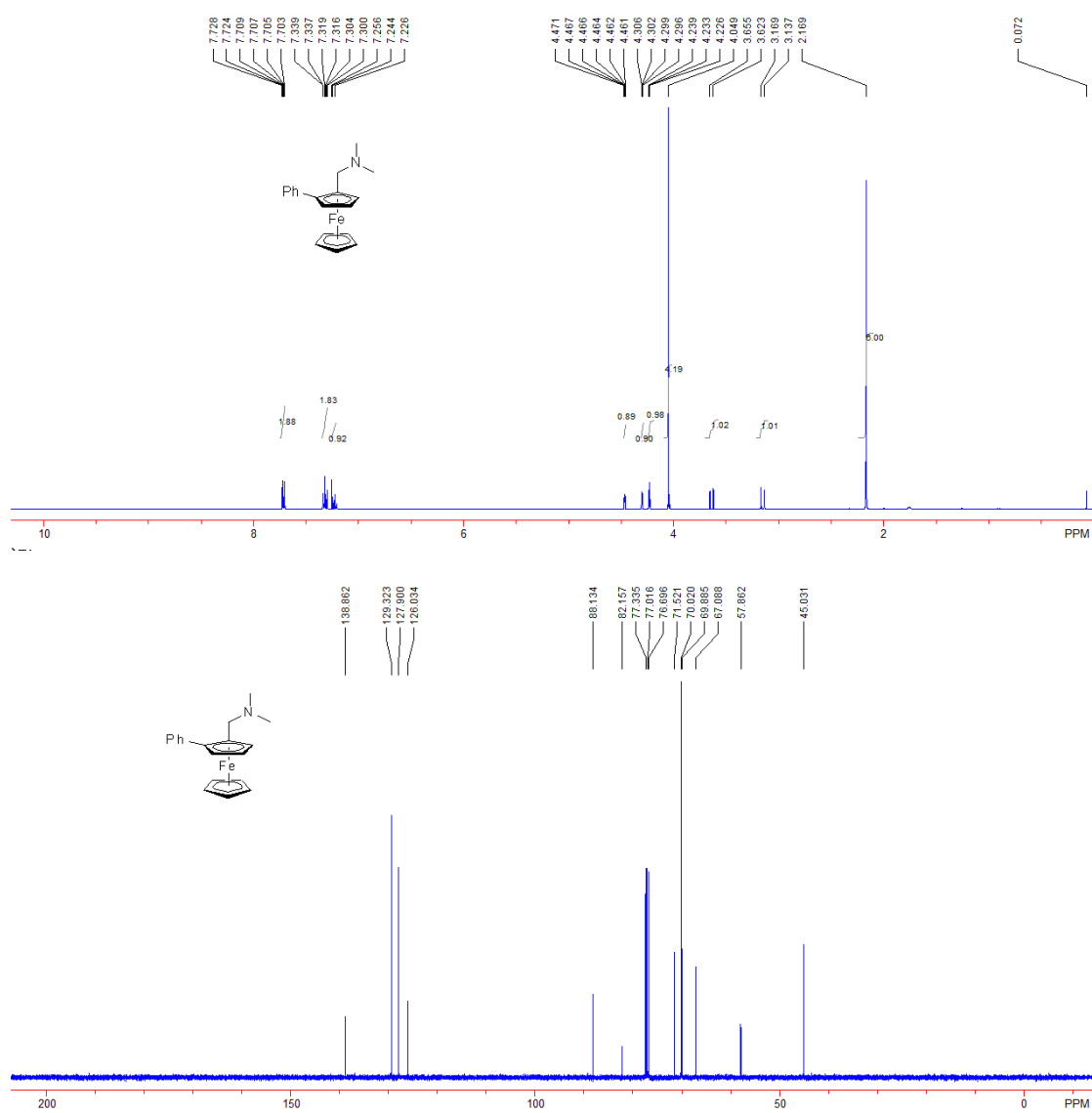
A mixture of ligand (*S_p*)-**L1** (92% ee, 10.1 mg, 0.02 mmol) and $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (3.7 mg, 0.01 mmol) in dry THF (2 mL) was stirred at room temperature for 0.5 h, and to the resulting yellow solution was added **4** (100.9 mg, 0.4 mmol). After an additional stirring for 10 min, sodium dimethyl malonate [generated in situ by mixture dimethyl malonate (0.08 mL, 0.8 mmol) with sodium hydride (19.2 mg, 0.8 mmol) in 2 mL THF] was added. The reaction was stirred at room temperature. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with NH_4Cl (aq.) and extracted with ether. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (ethyl acetate / petroleum = 10/1) to give **10** (126 mg, 98% yield, 15% ee). Analytical data for (*S*)-**10**^[5]: $[\alpha]_{\text{D}}^{20} = -0.51^\circ$ (c = 1.4 Chloroform, 15% ee). ^1H NMR (400 MHz, CDCl_3) δ 3.51 (s, 3H), 3.70 (s, 3H), 3.96 (d, J = 11.2 Hz, 1H), 4.27 (dd, J = 8.8, 10.4 Hz, 1H), 6.33 (dd, J = 8.8, 15.8 Hz, 1H), 6.48 (d, J = 16.0 Hz, 1H), 7.17-7.33 (m, 10H); The enantiomeric excess was determined by Diacel Chiralcel OD-H (25 cm), Hexanes / IPA = 90 / 10, 0.7 mL/min, λ = 254 nm, t (minor) = 8.12 min, t (major) = 8.71 min. The absolute configuration of the product **10** was assigned as (*S*) by comparing the optical rotation with that reported in the literature.^[6]

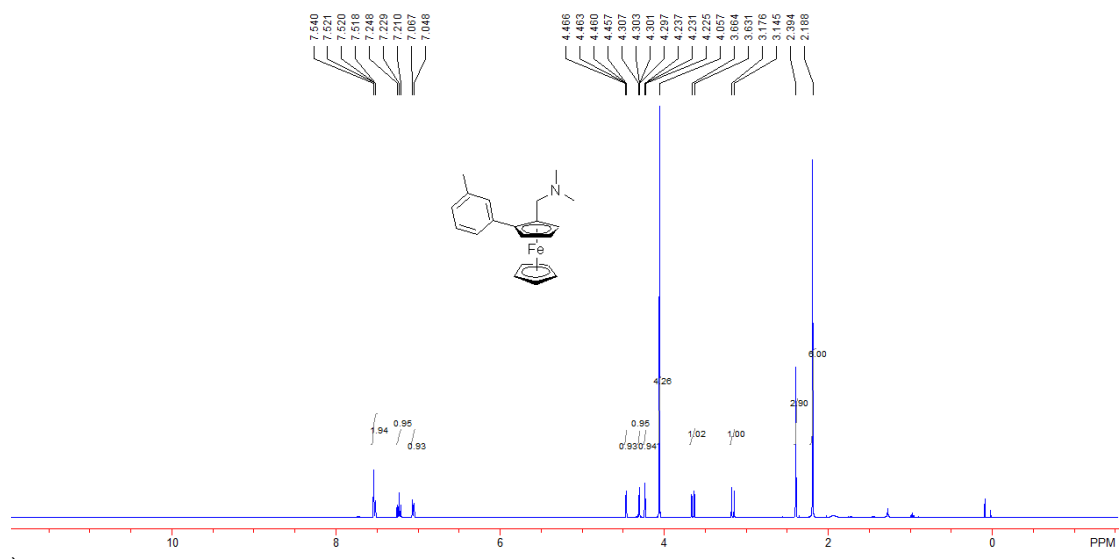
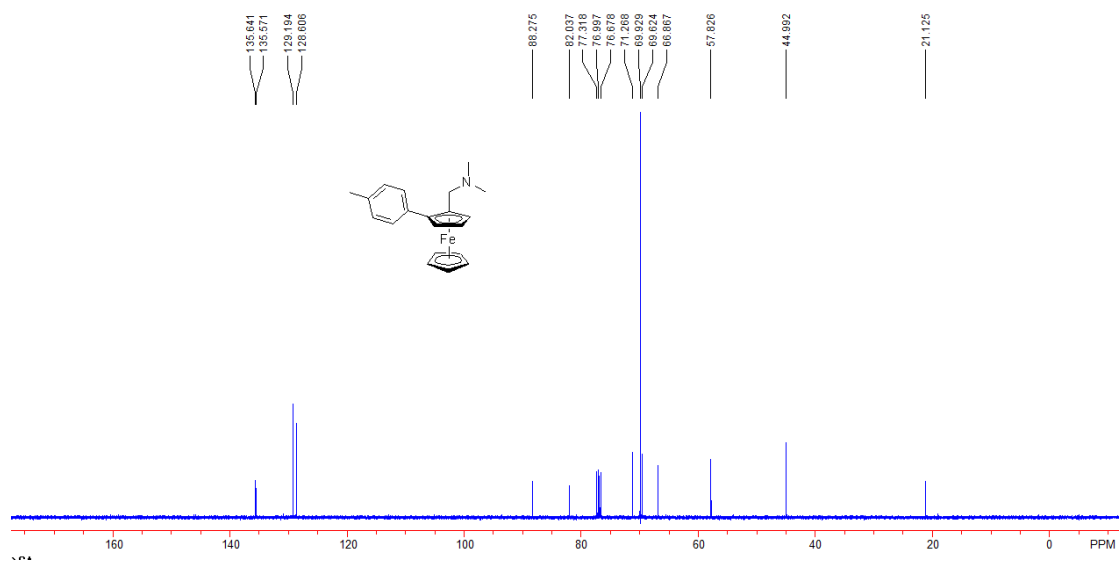
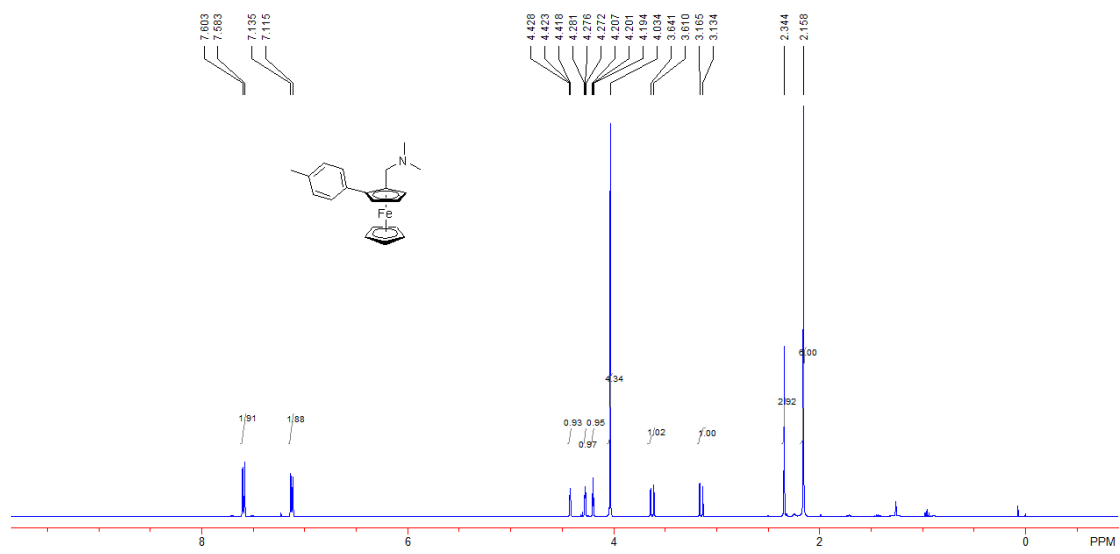
References

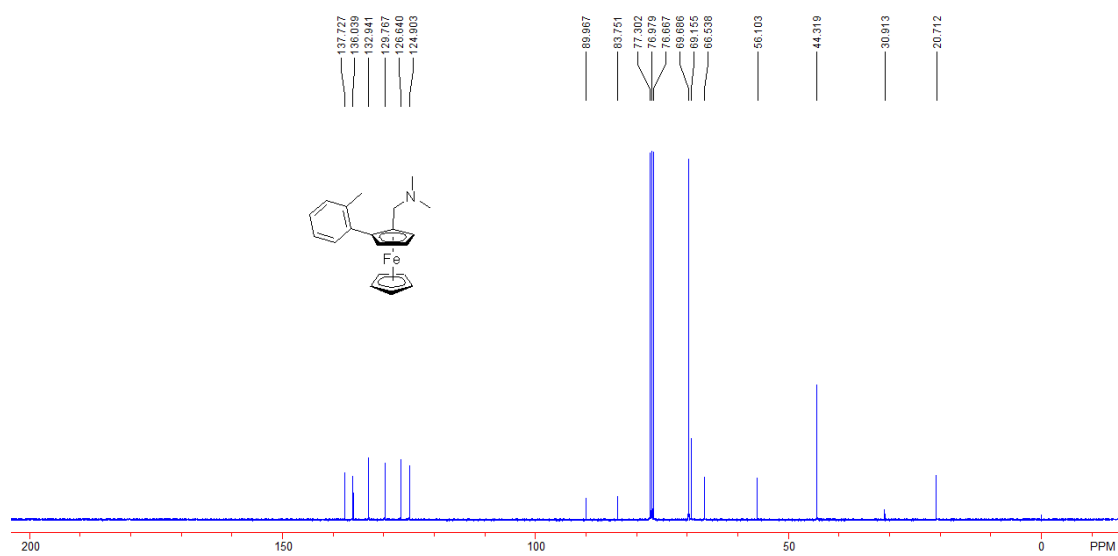
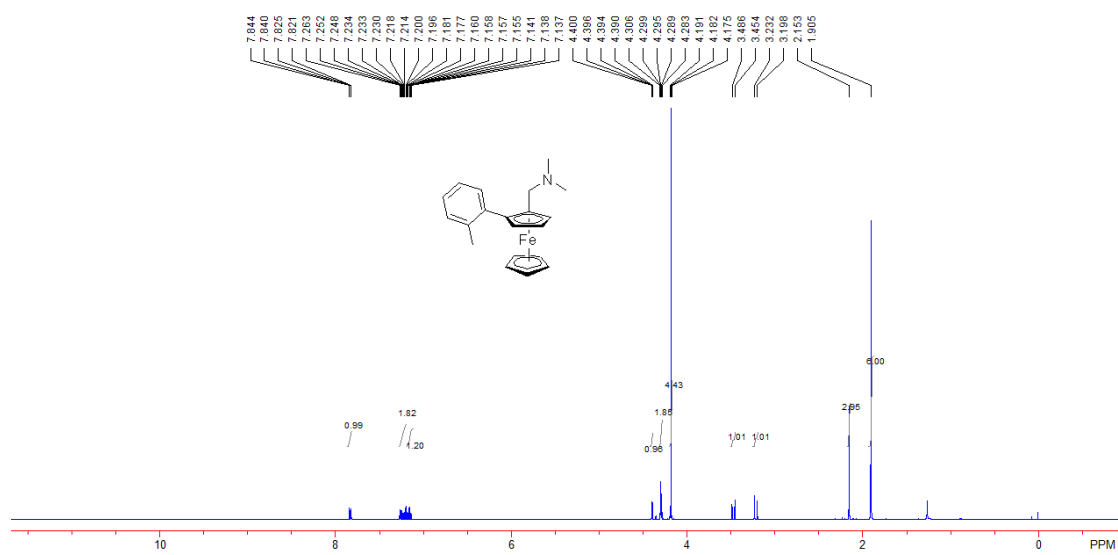
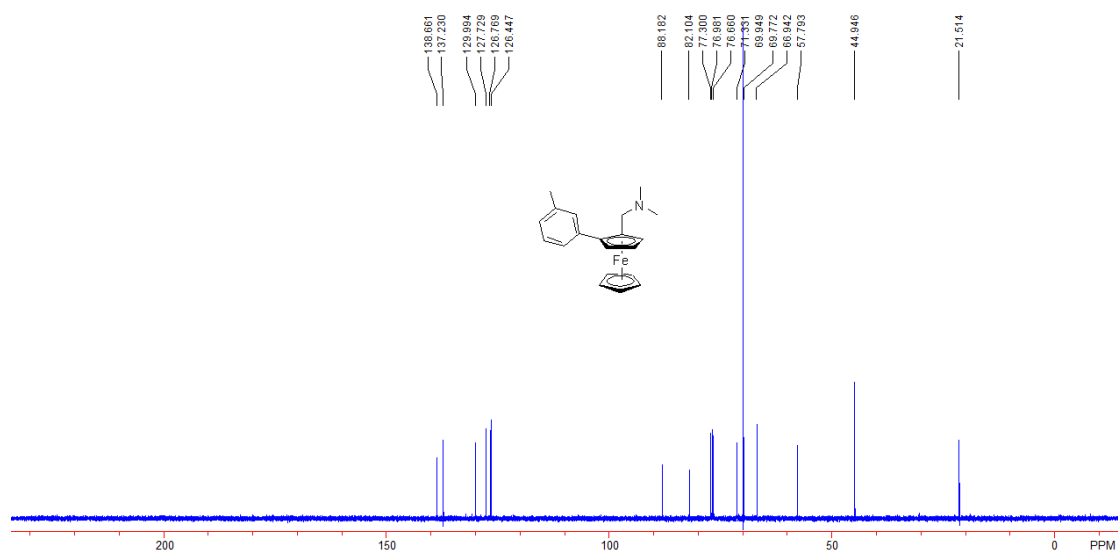
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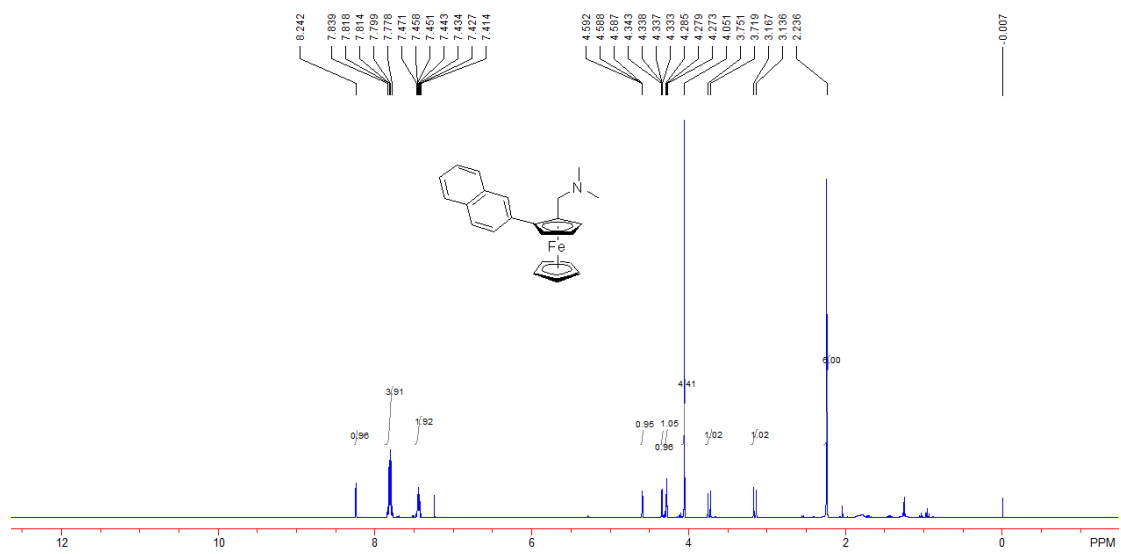
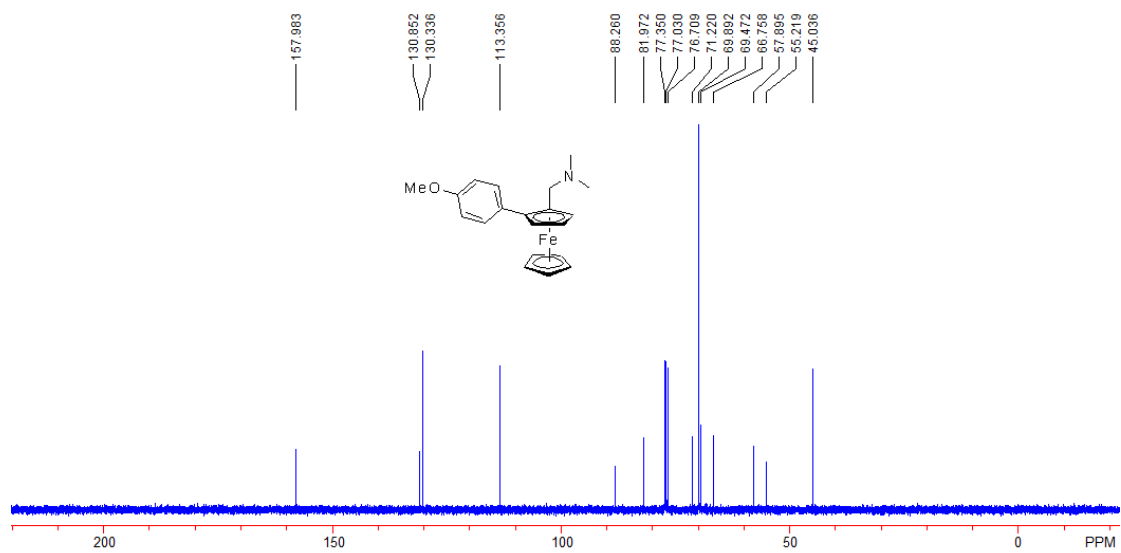
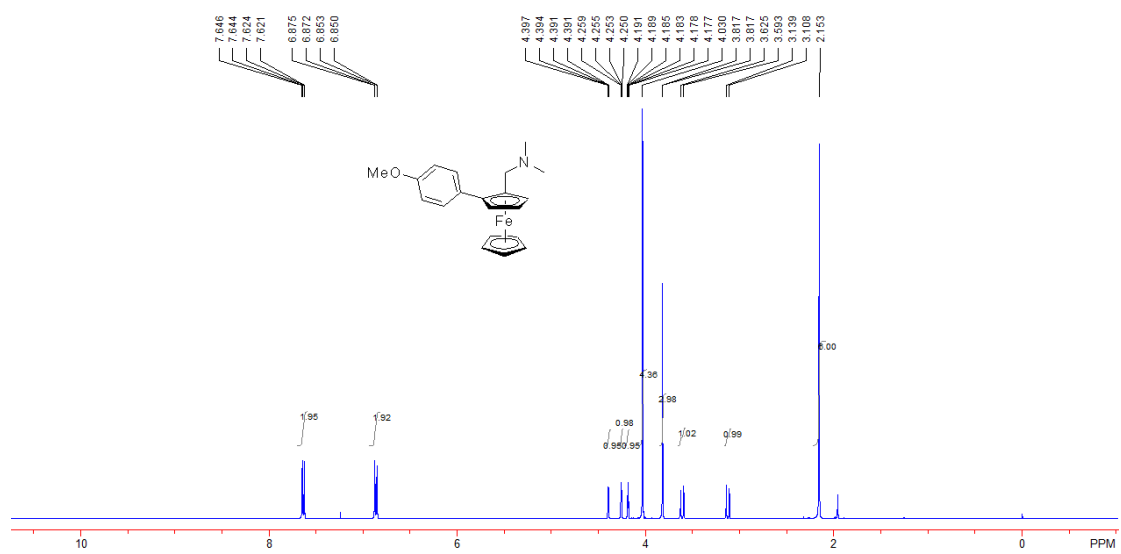
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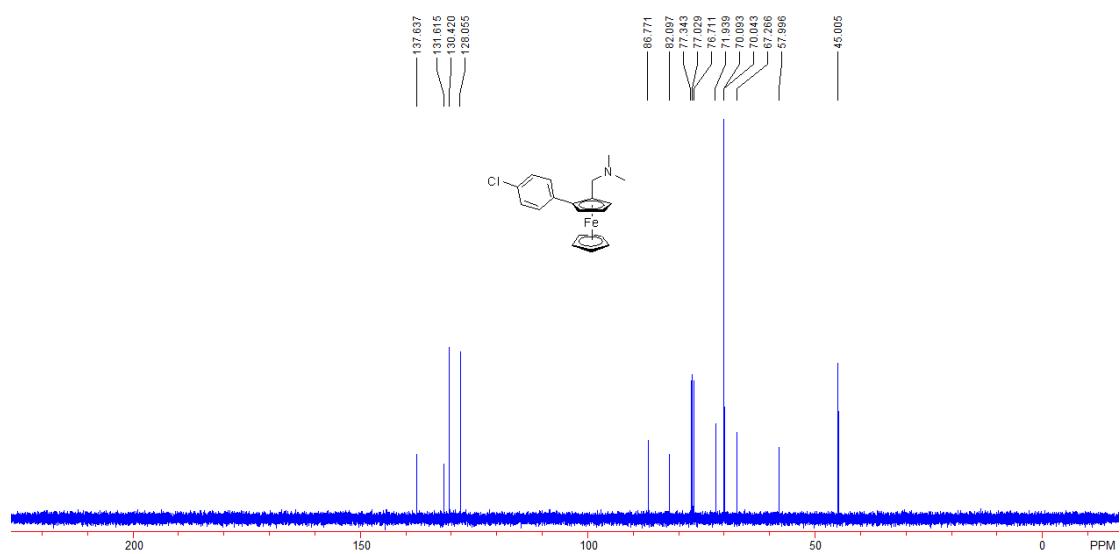
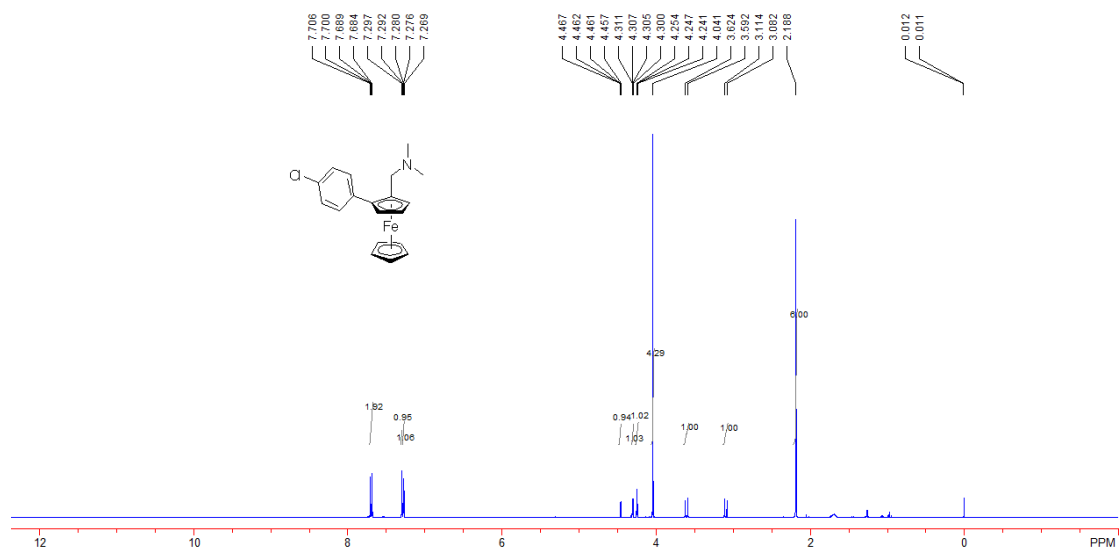
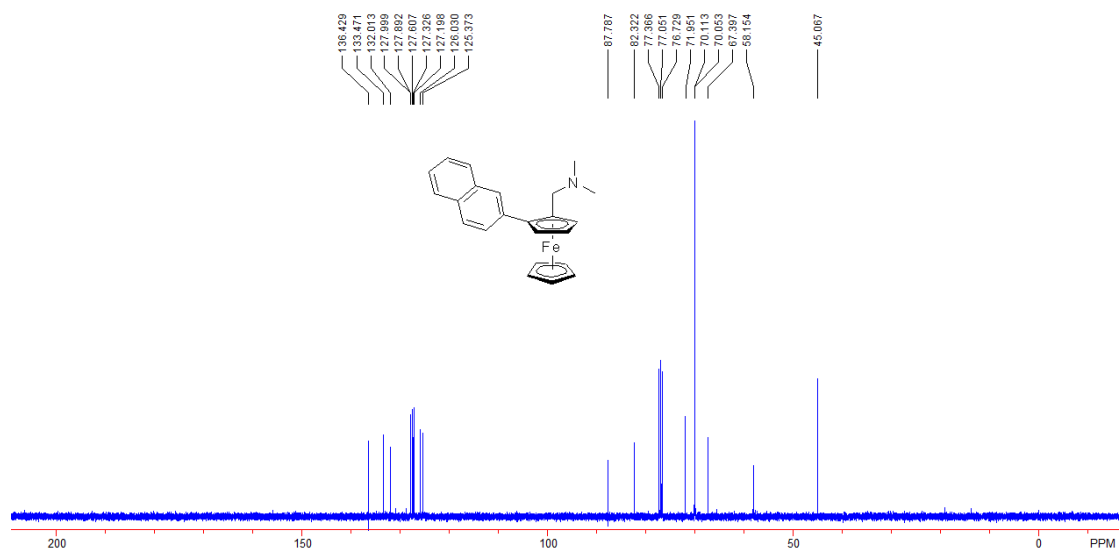
NMR and HPLC Spectra

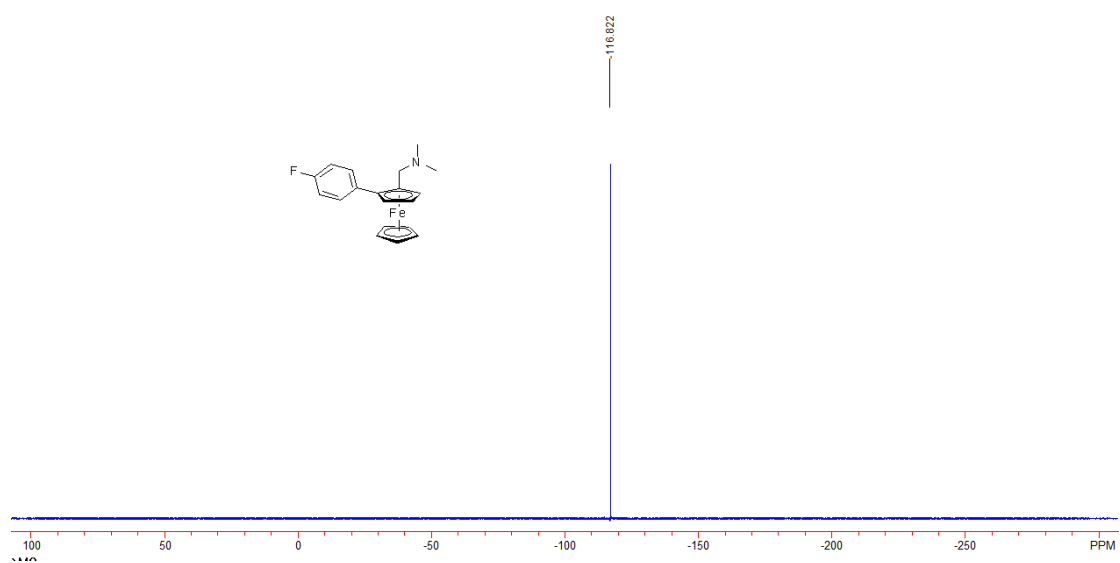
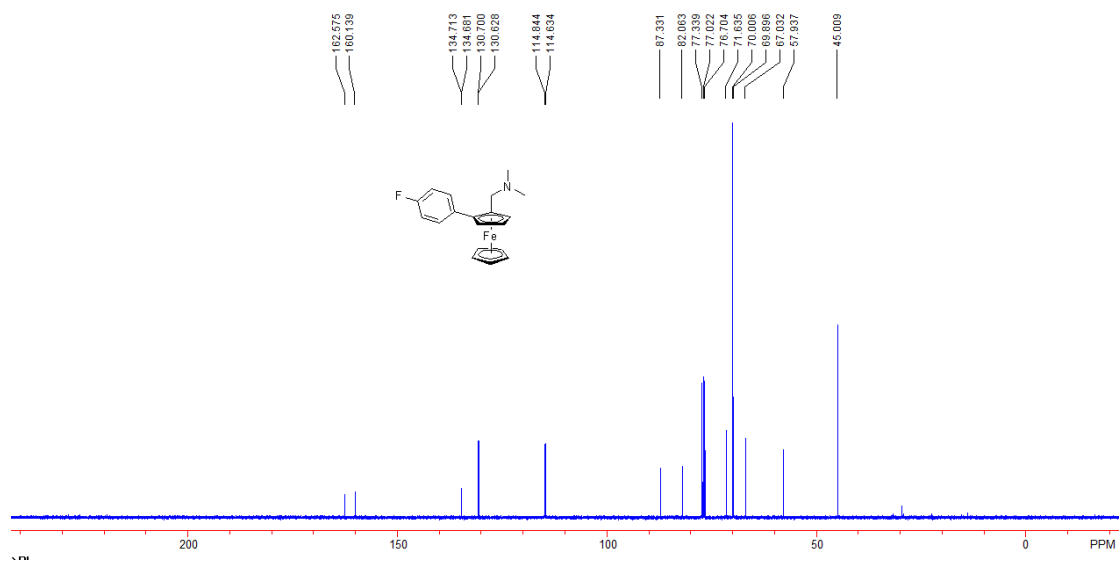
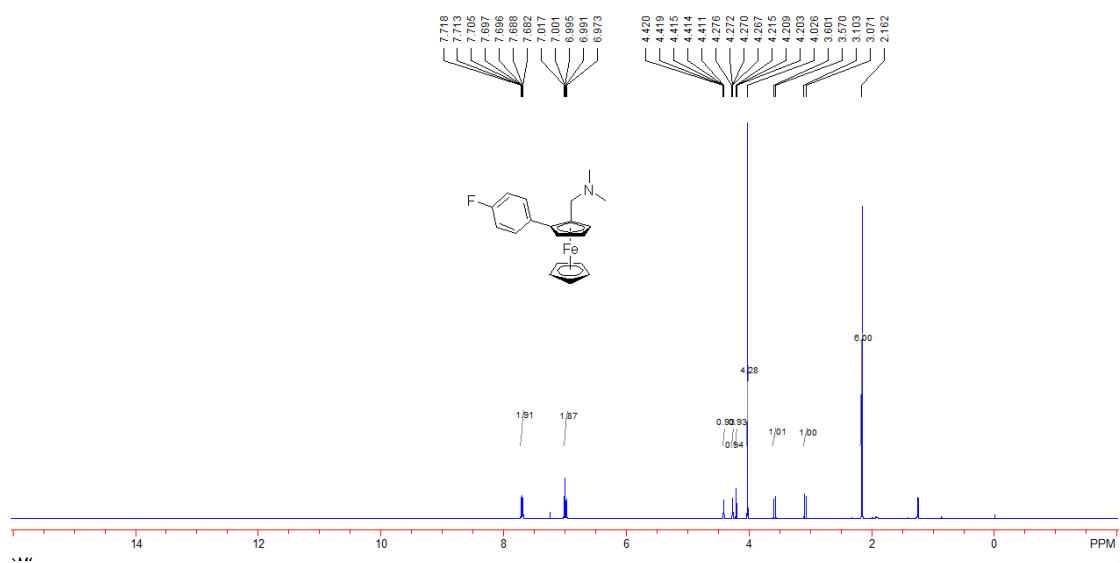


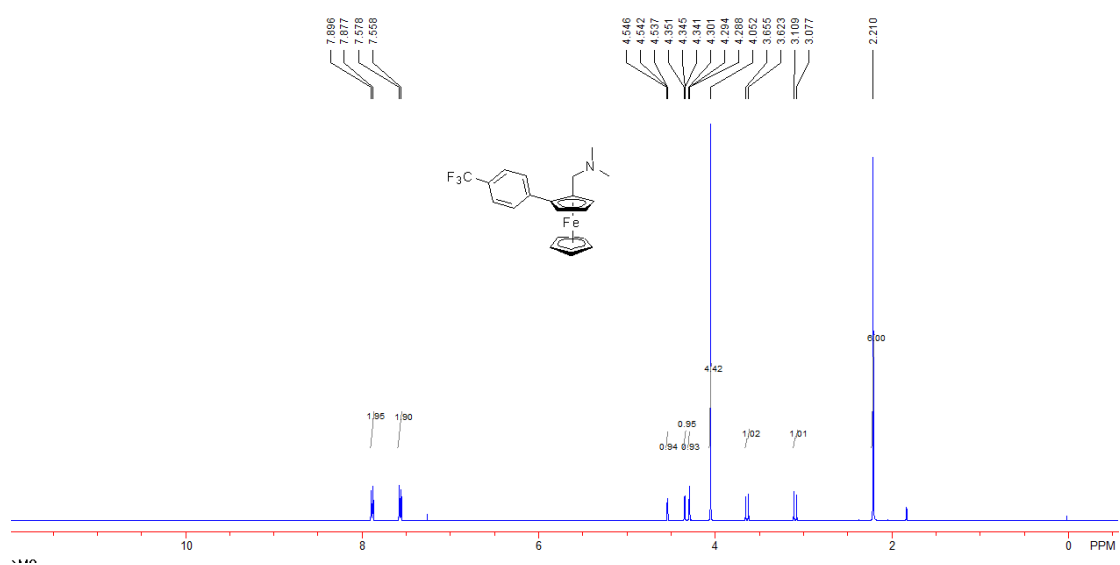
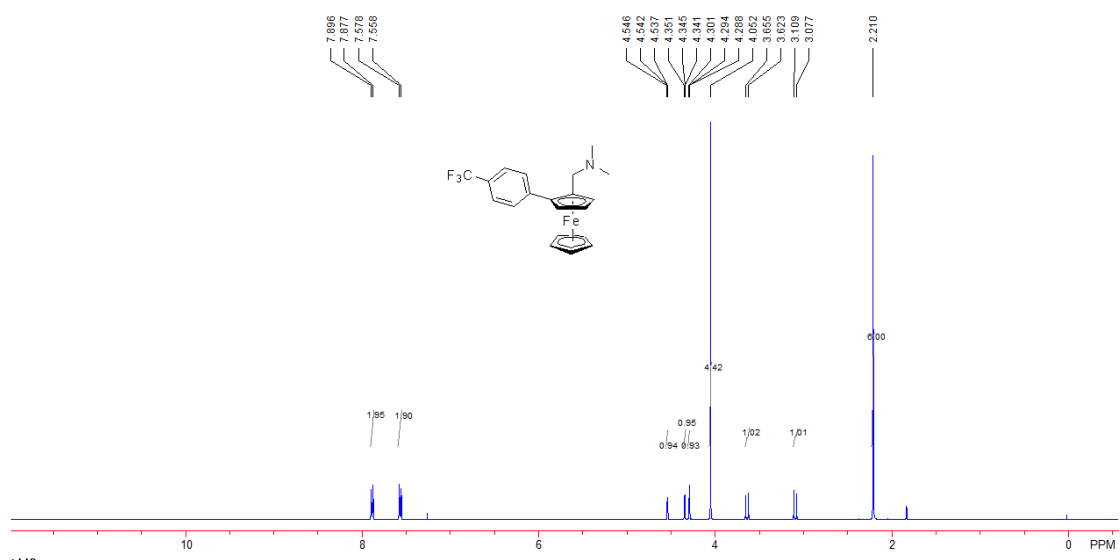
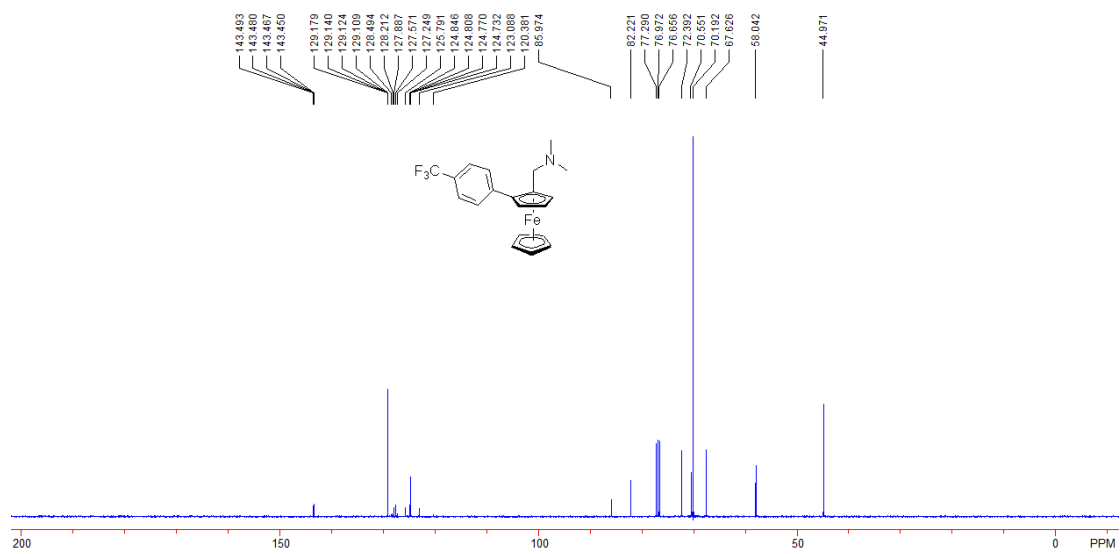


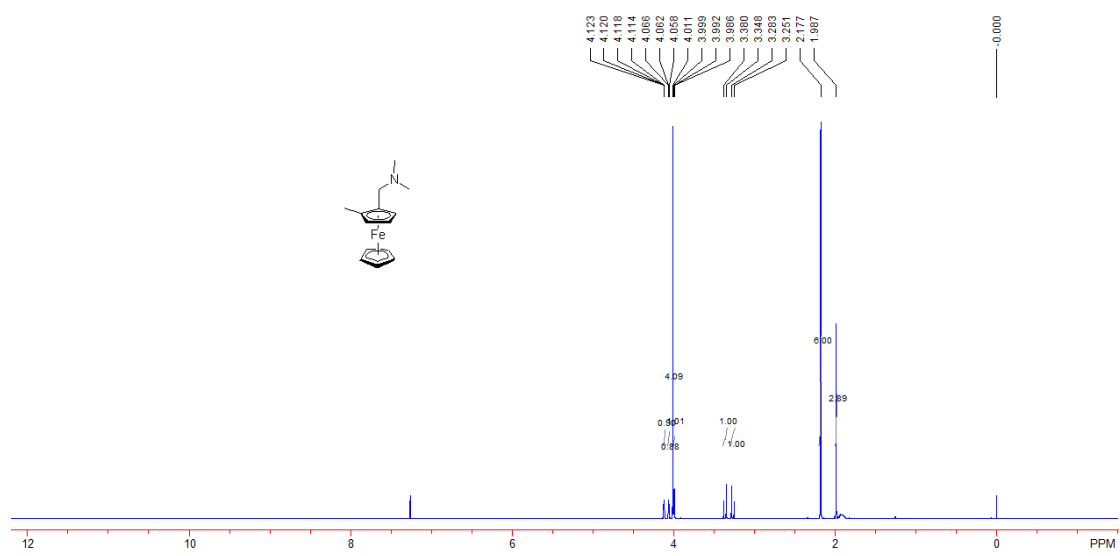
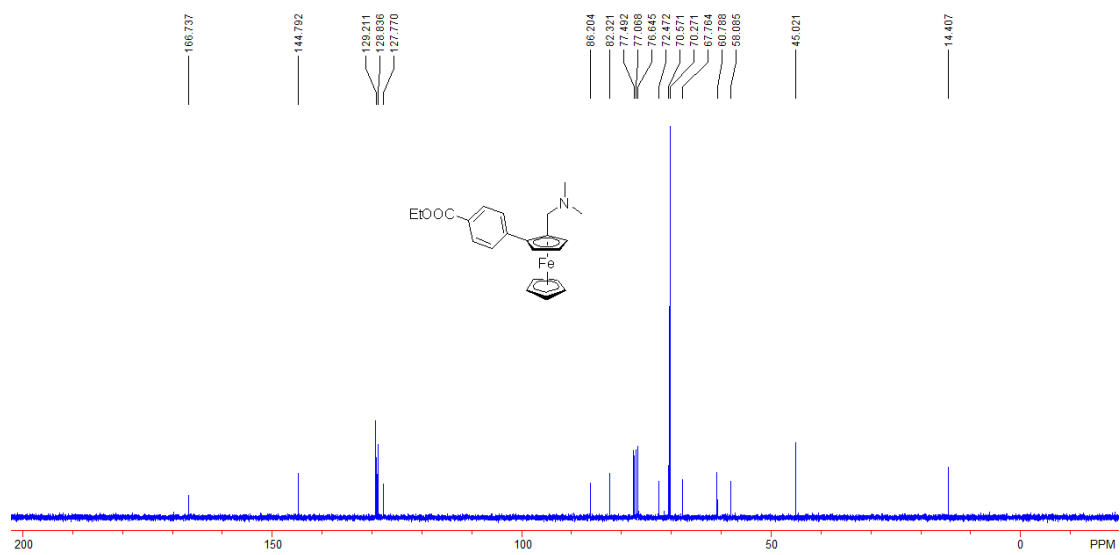
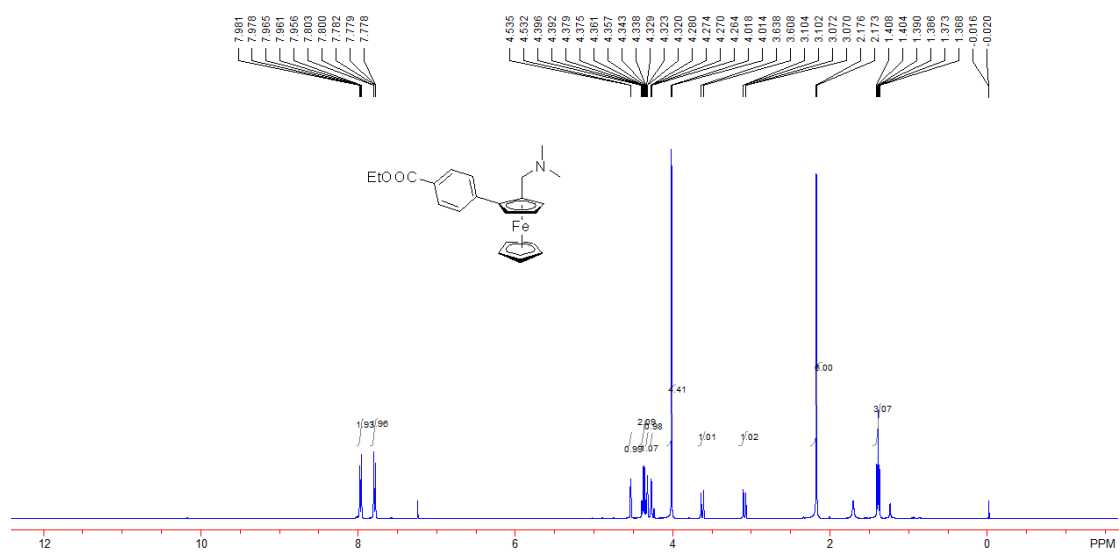


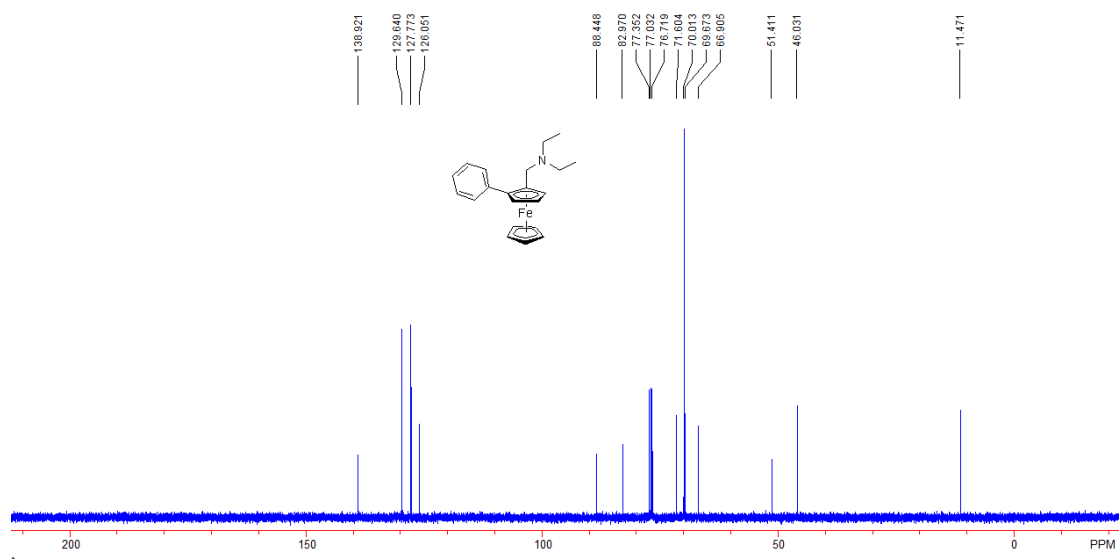
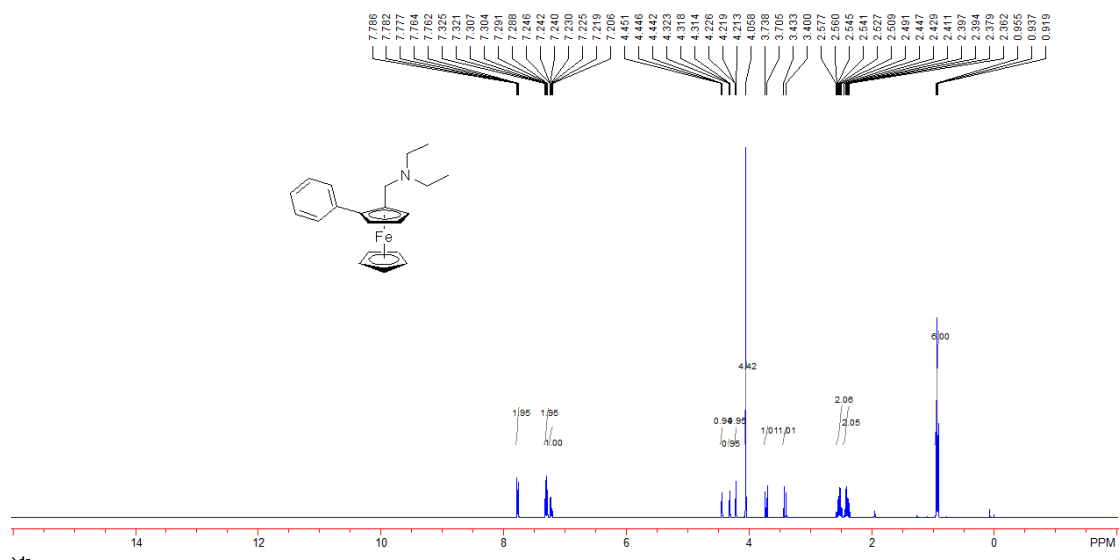
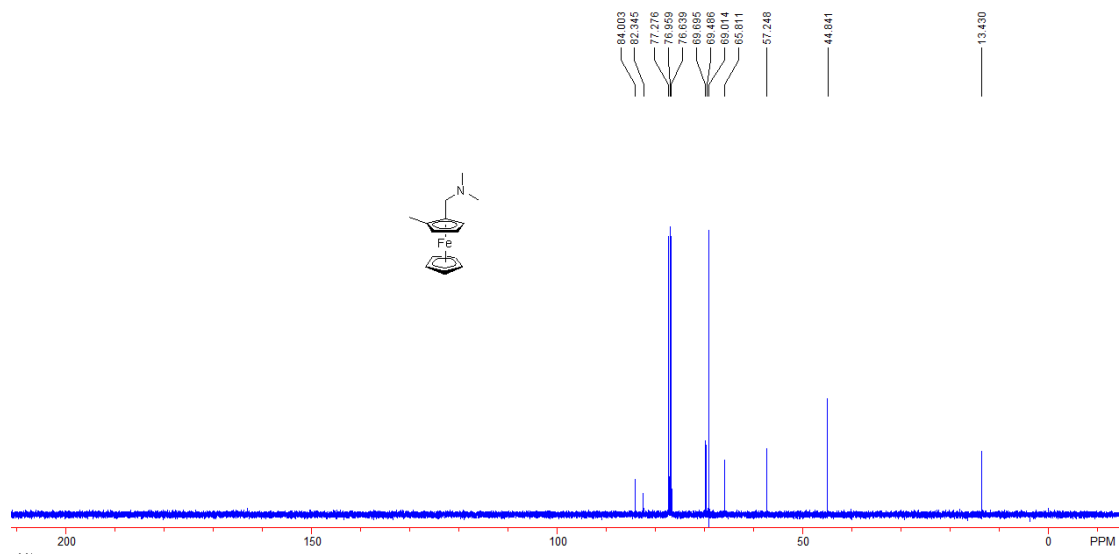


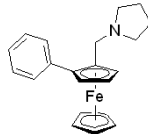
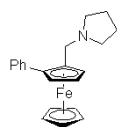


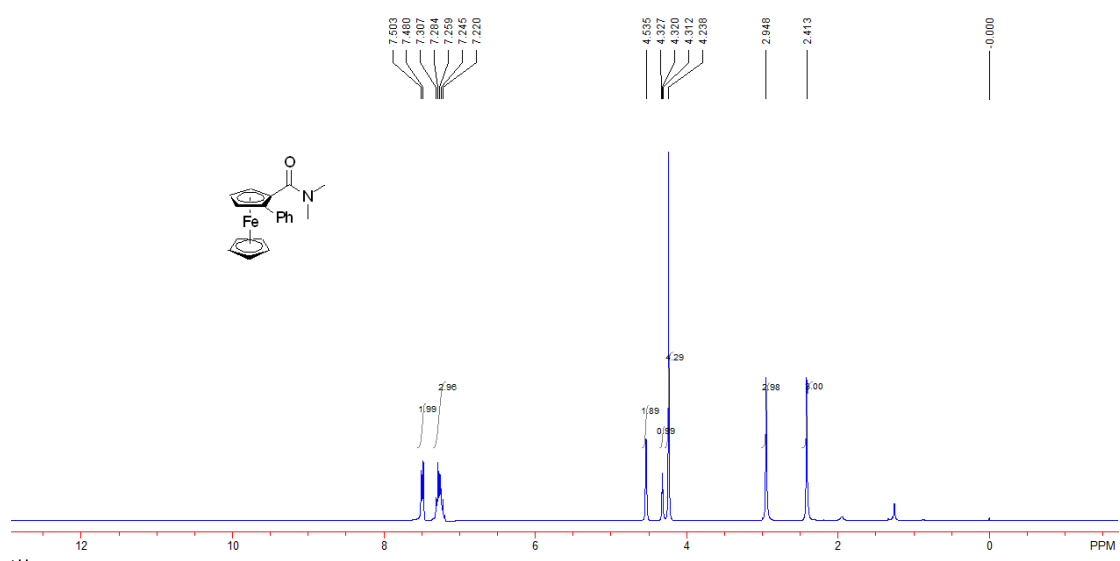
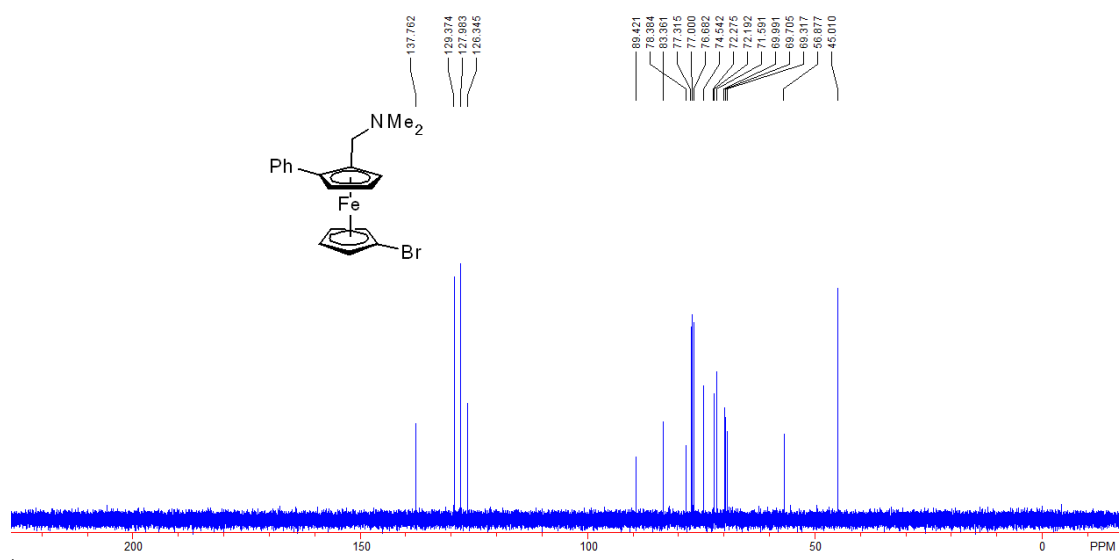
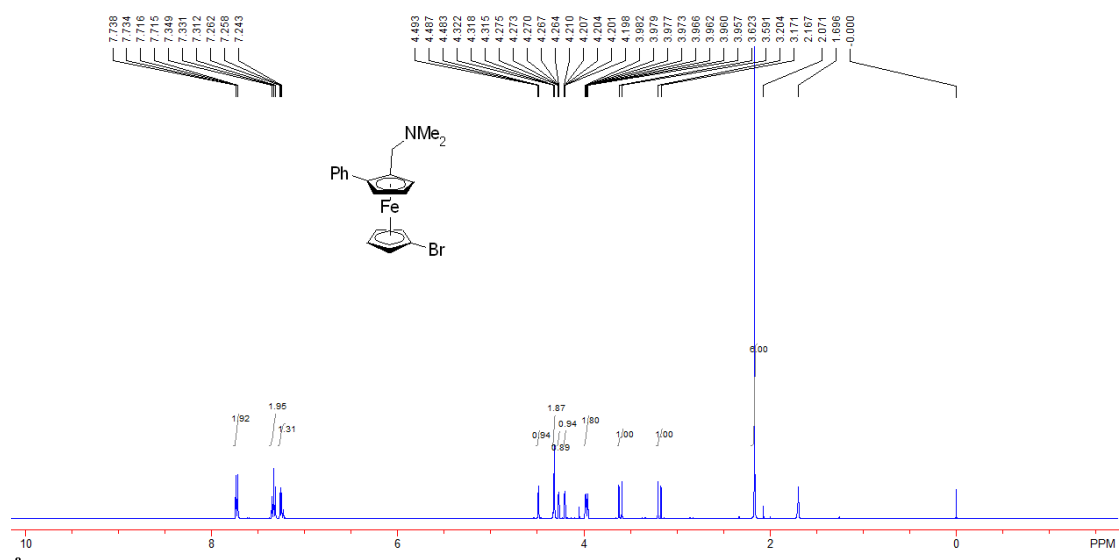


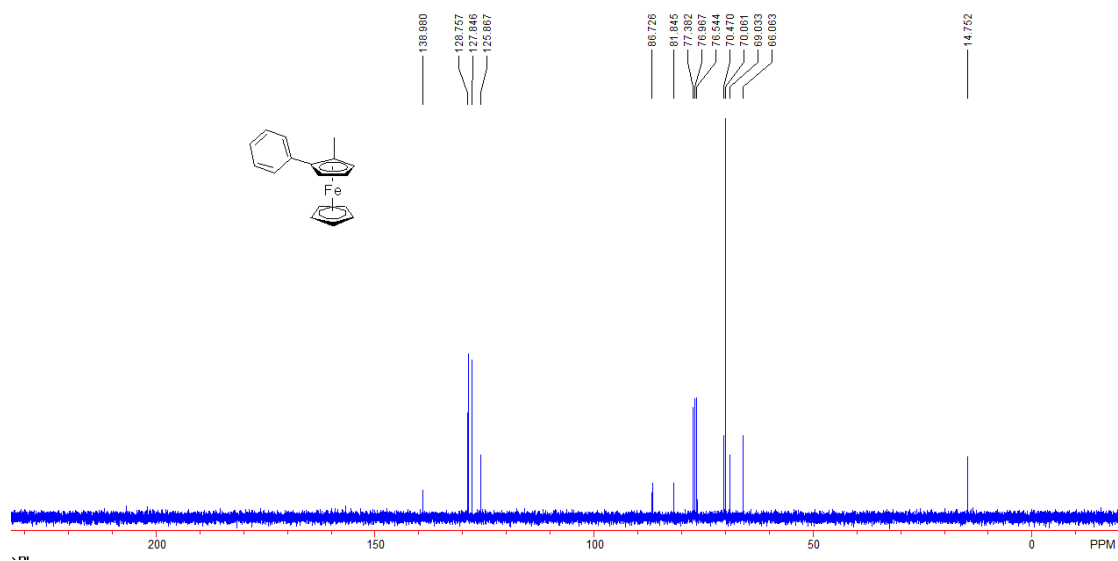
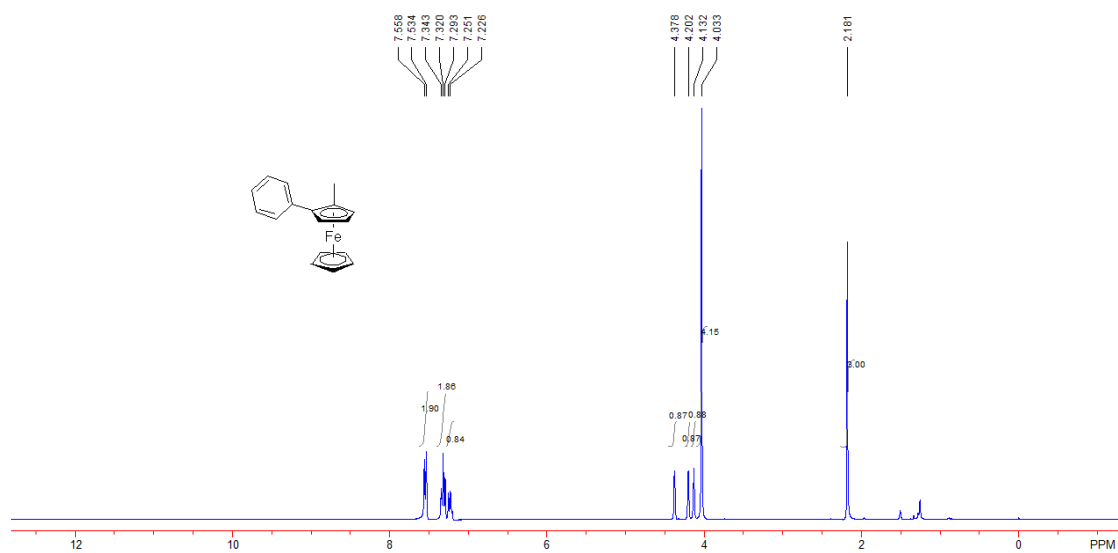
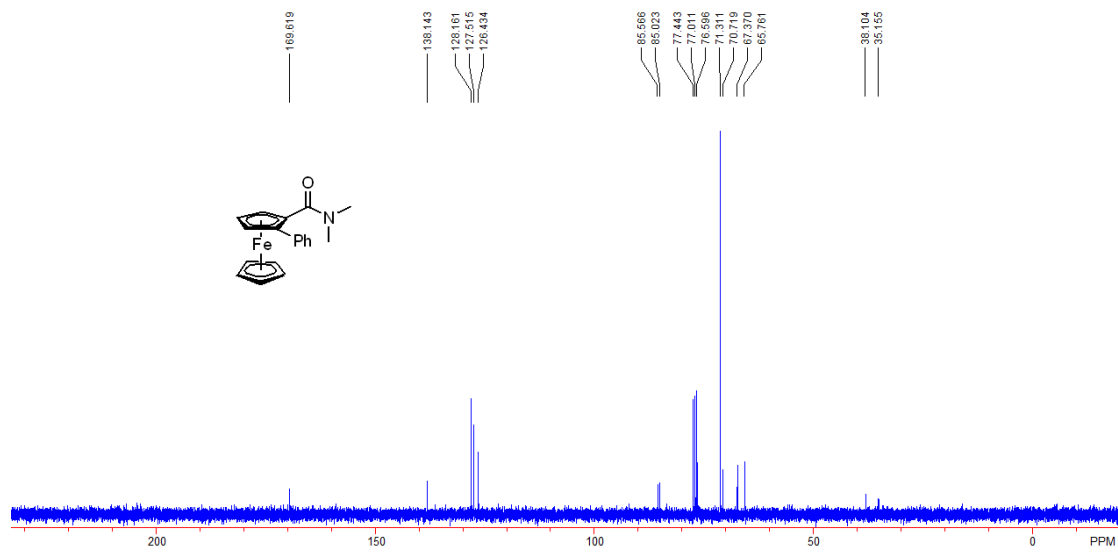


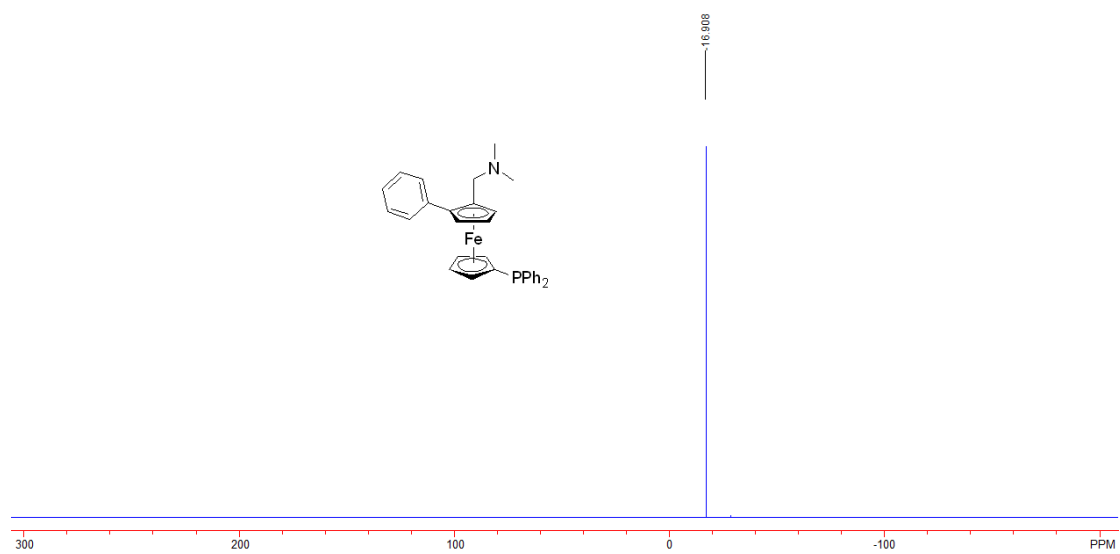
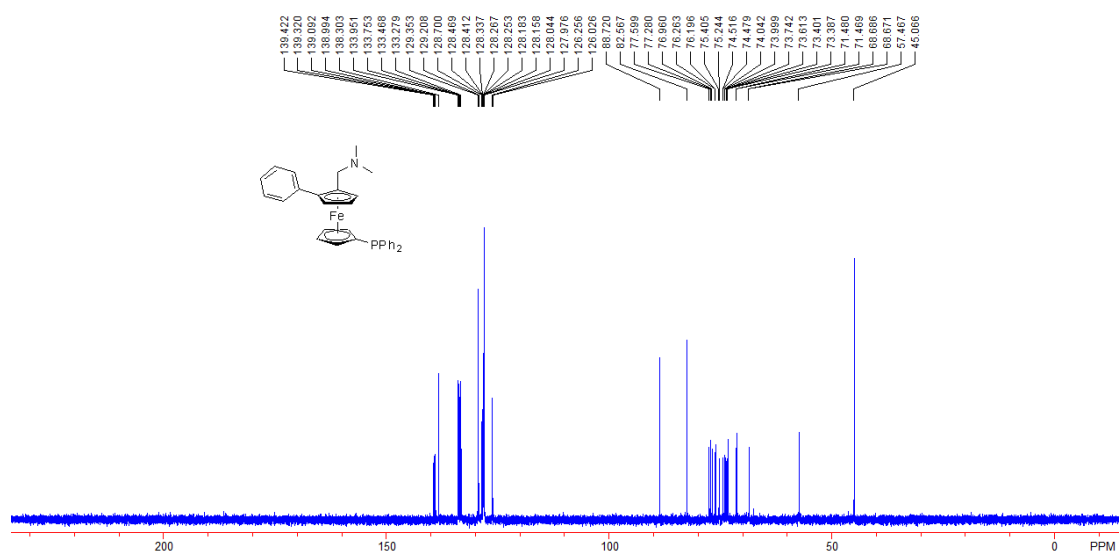
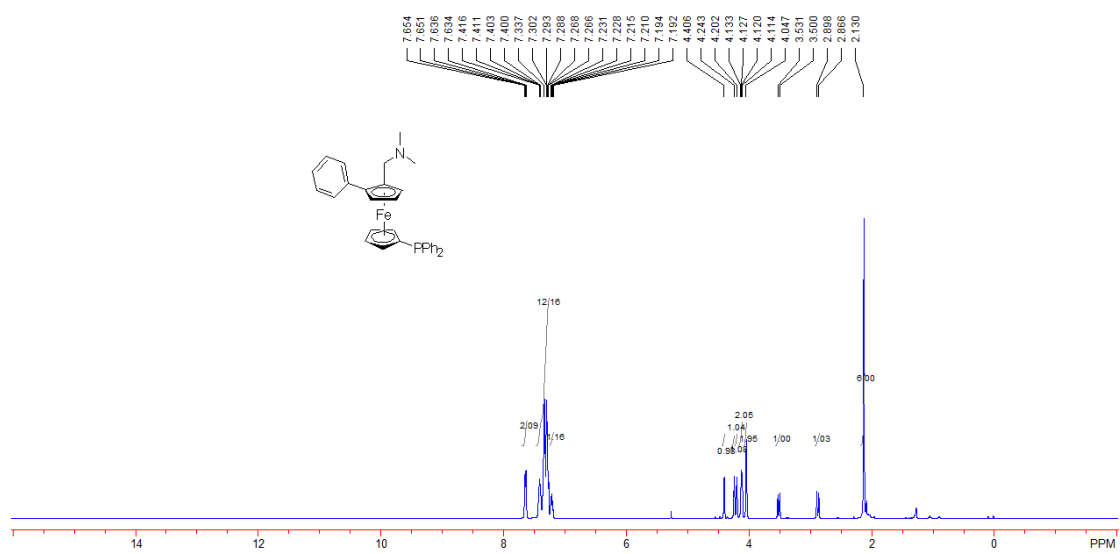


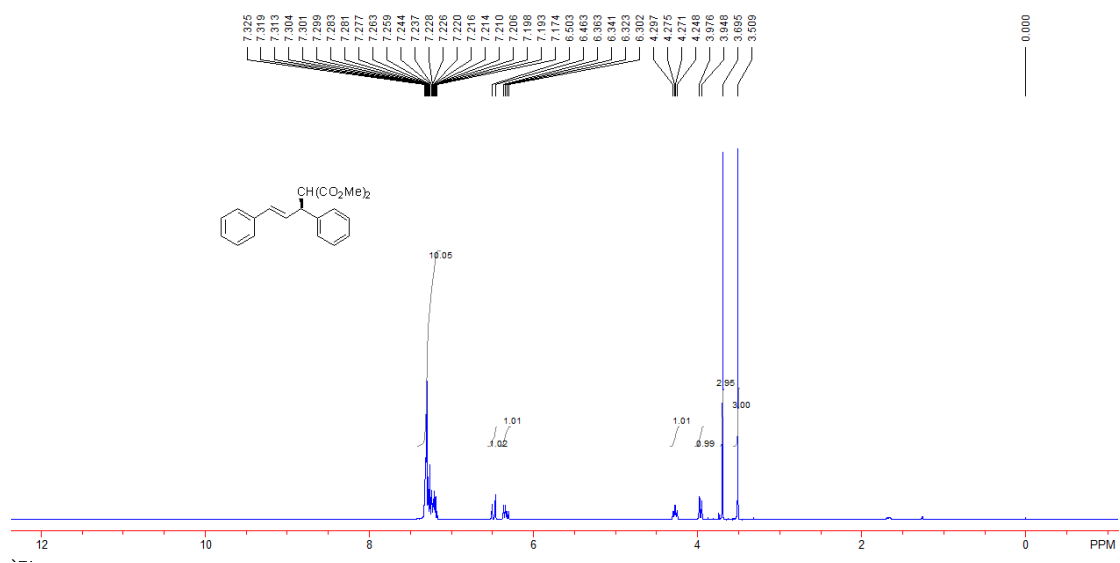


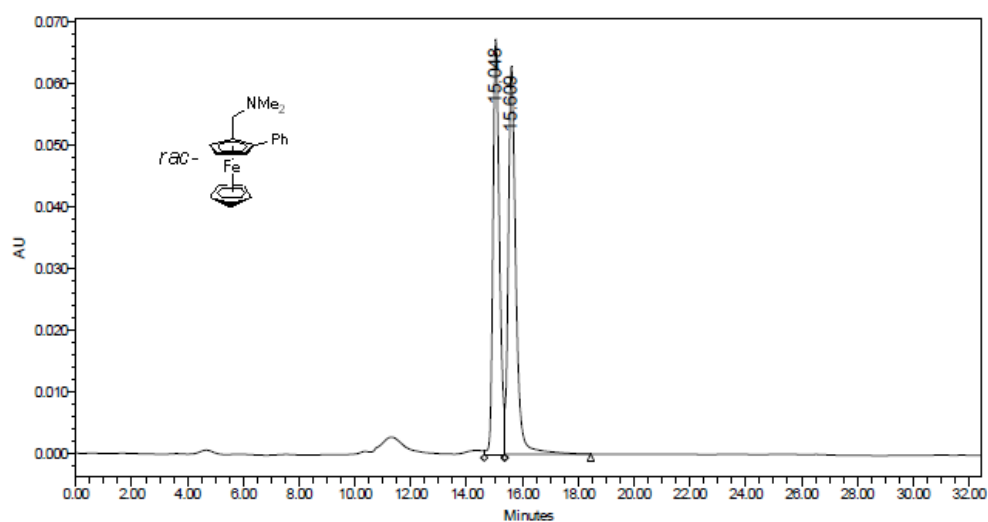




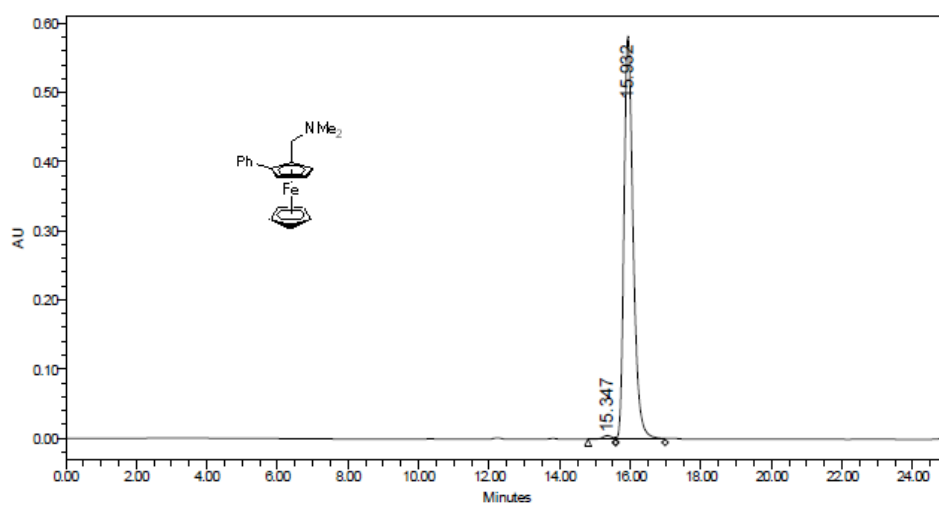




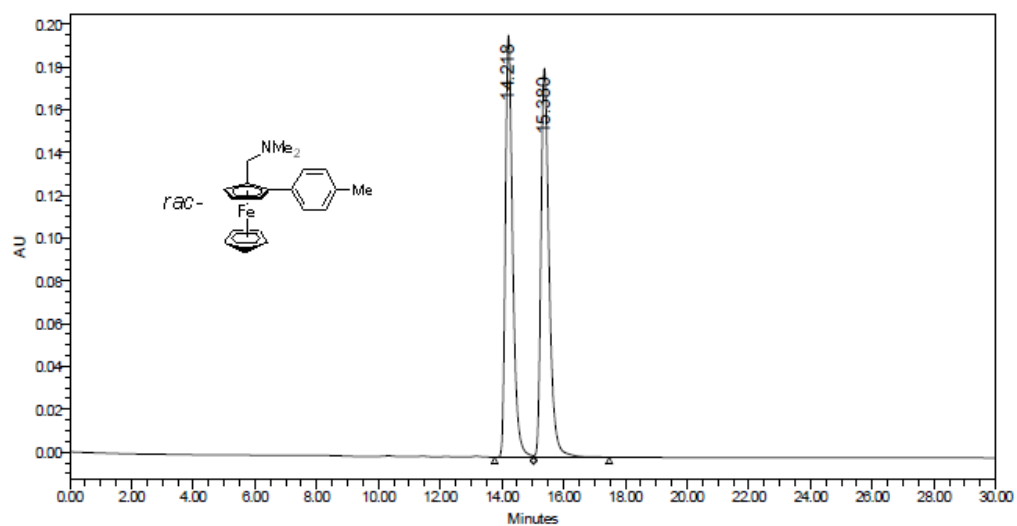




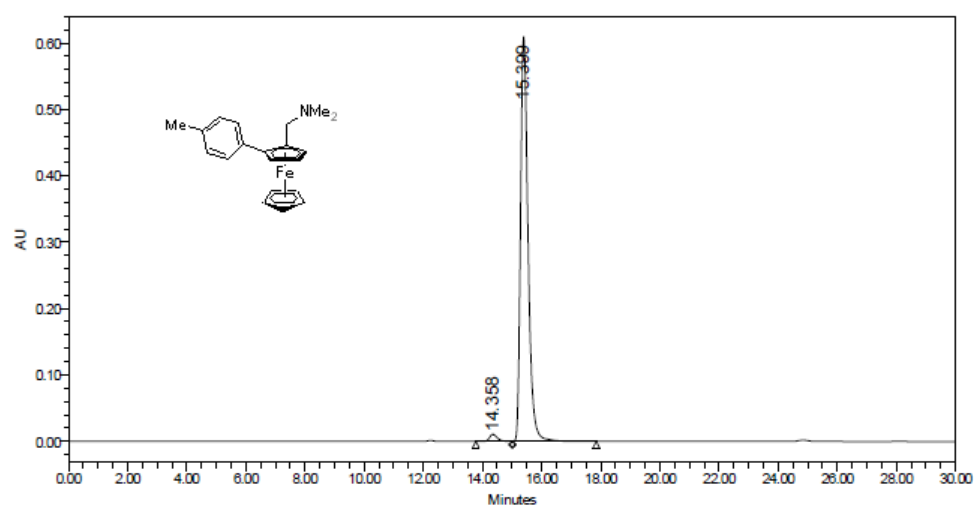
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	15.048	1082616	47.50	67307	51.64
2	15.609	1196341	52.50	63025	48.36



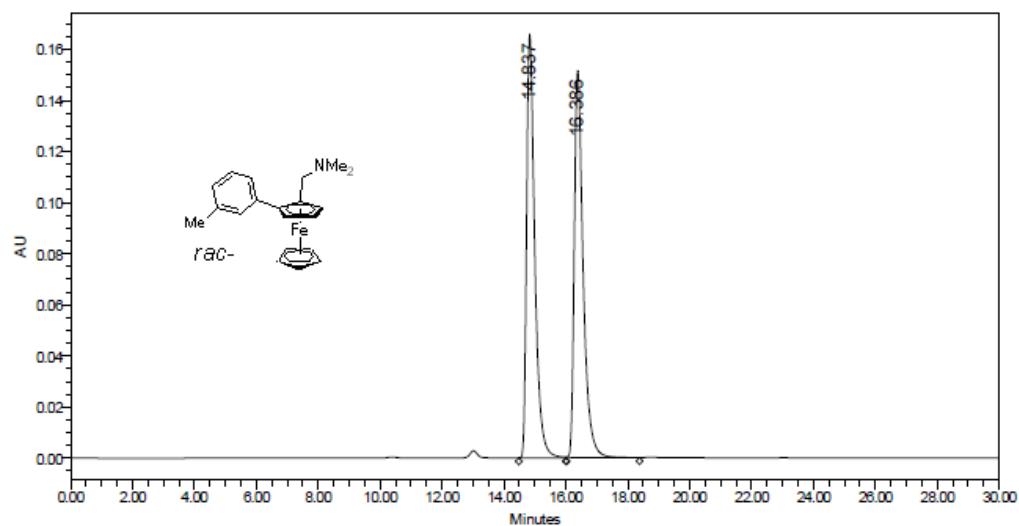
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	15.347	95079	0.90	5192	0.88
2	15.932	10507655	99.10	582706	99.12



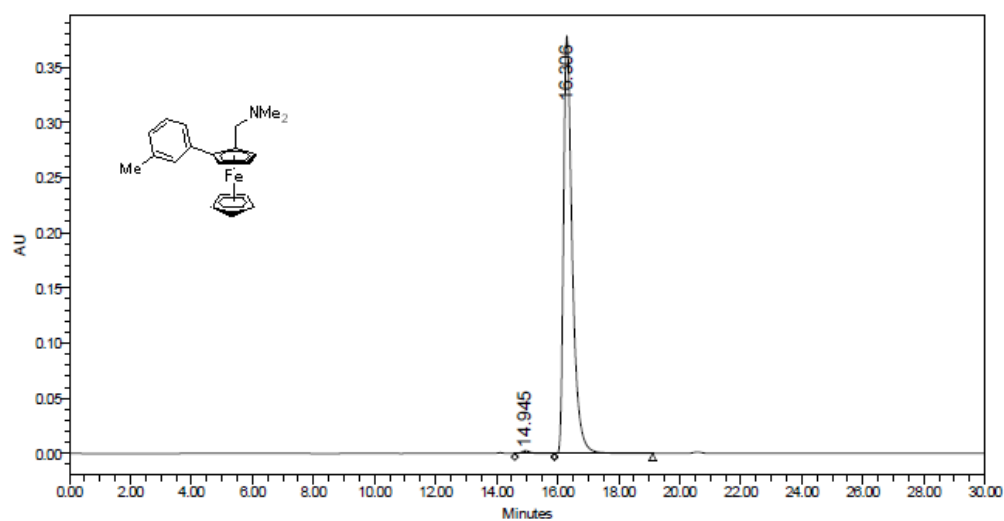
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	14.218	3246202	49.30	197158	52.04
2	15.380	3338075	50.70	181716	47.96



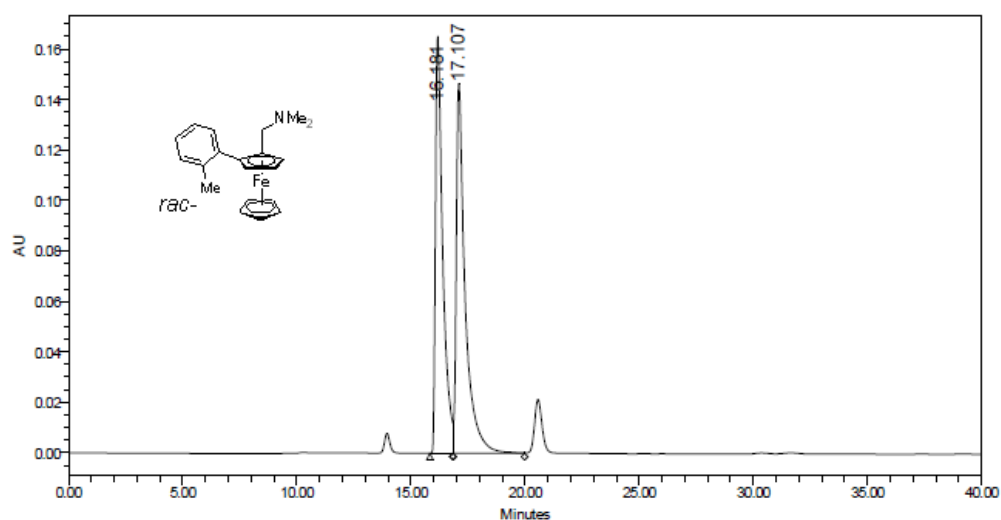
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	14.358	191614	1.75	10688	1.72
2	15.399	10743350	98.25	609479	98.28



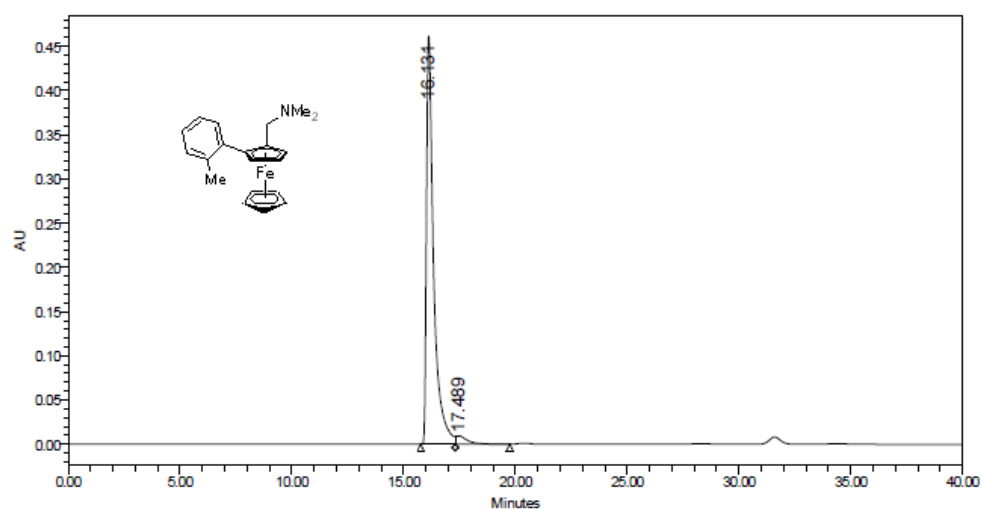
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	14.837	3036002	50.15	165870	52.26
2	16.386	3018105	49.85	151544	47.74



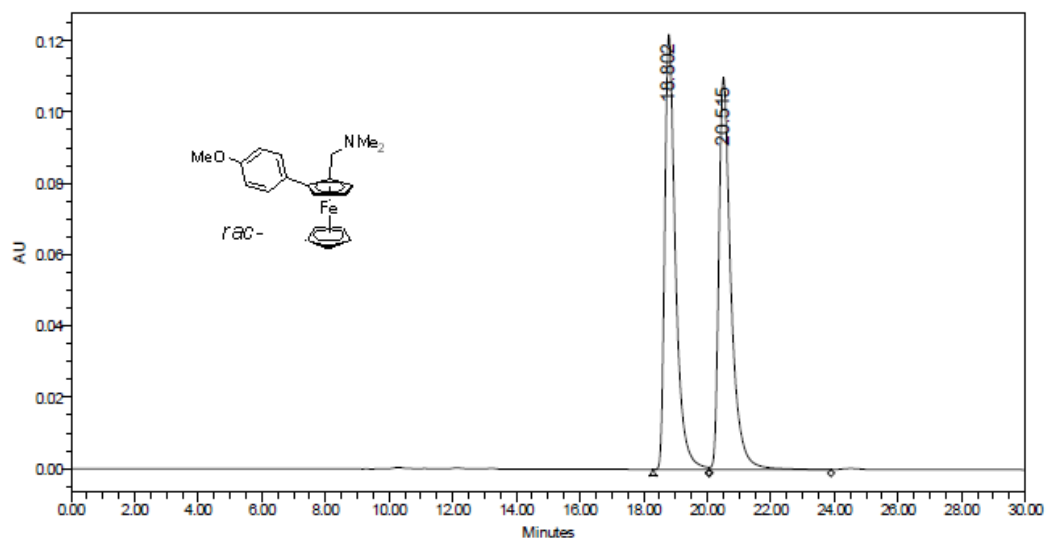
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	14.945	48952	0.65	2569	0.67
2	16.306	7524140	99.35	378712	99.33



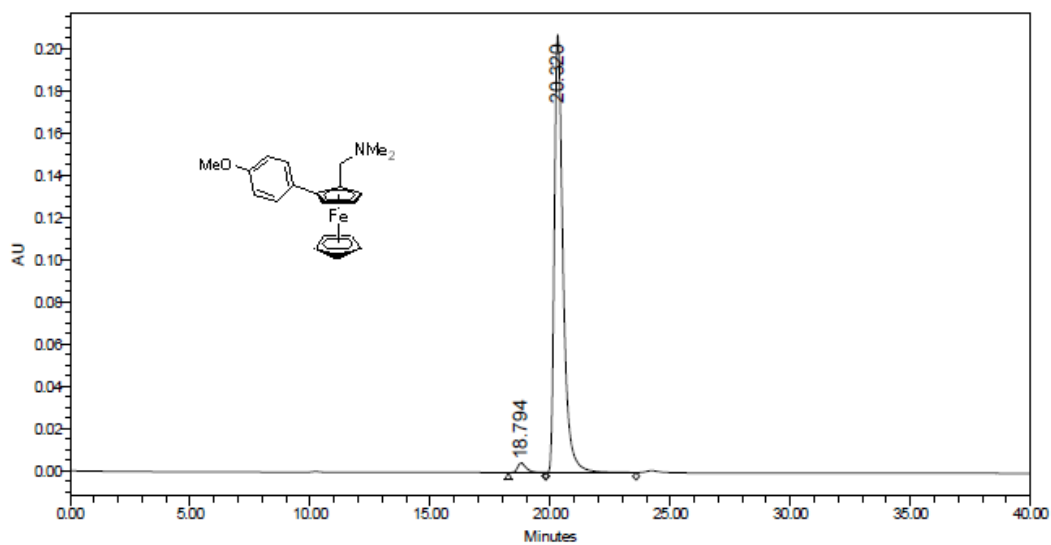
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	16.181	3683893	48.12	165245	52.97
2	17.107	3972143	51.88	146692	47.03



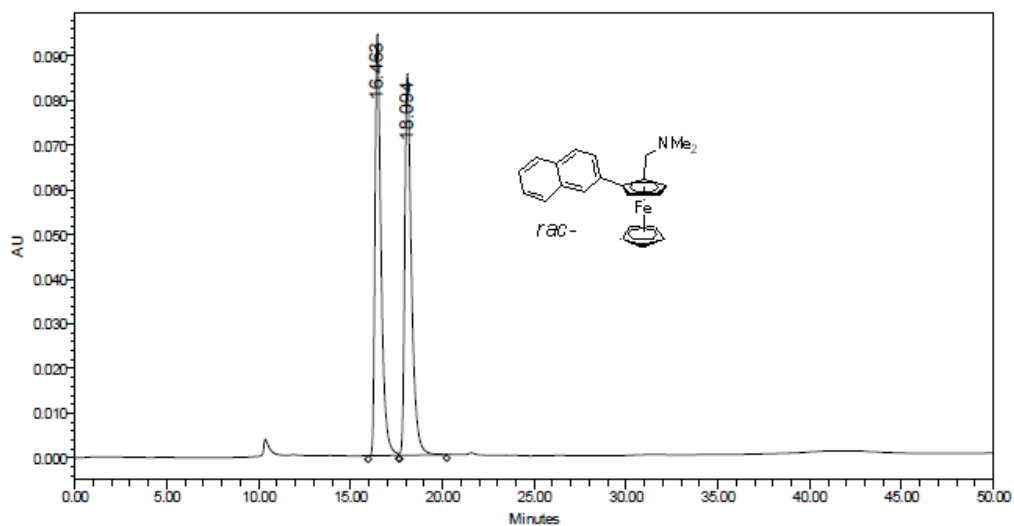
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	16.131	10273430	96.82	461685	97.99
2	17.489	337344	3.18	9476	2.01



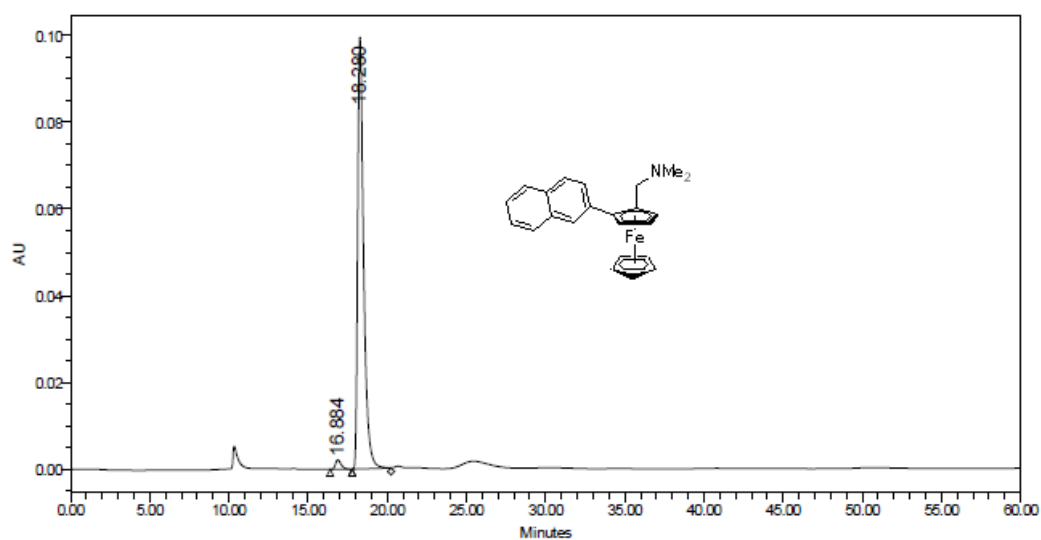
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	18.802	2864542	49.70	121924	52.62
2	20.515	2898851	50.30	109799	47.38



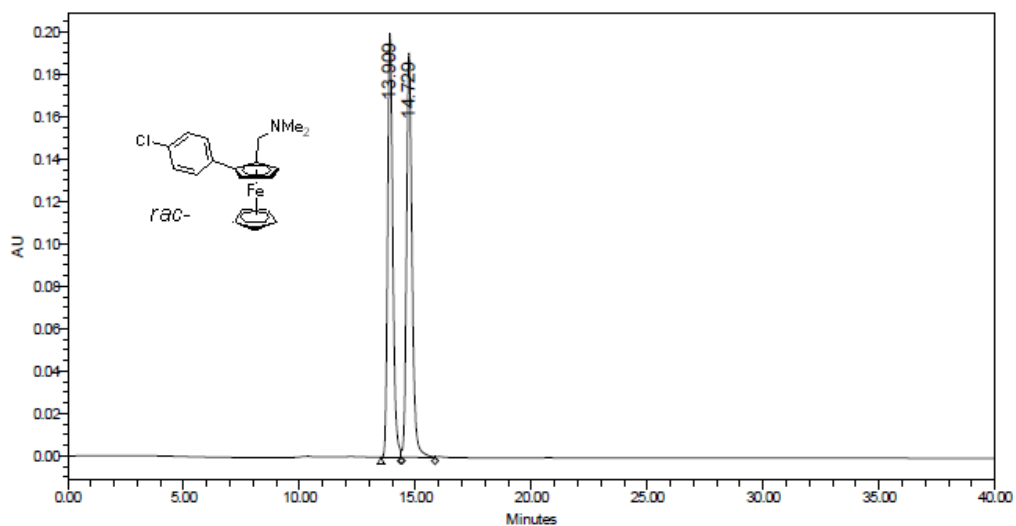
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	18.794	116096	2.16	4485	2.12
2	20.320	5260322	97.84	207483	97.88



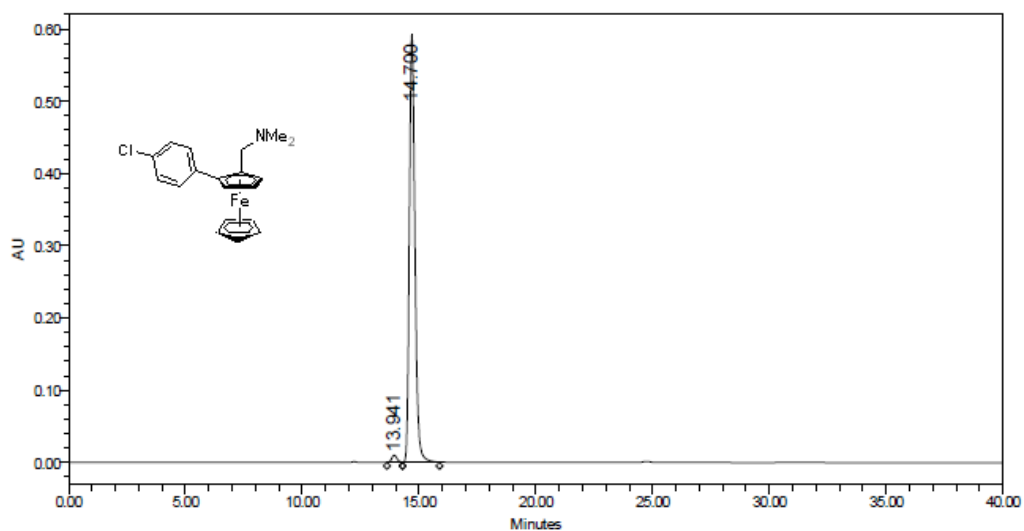
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	16.463	2160276	49.93	94476	52.52
2	18.094	2166318	50.07	85408	47.48



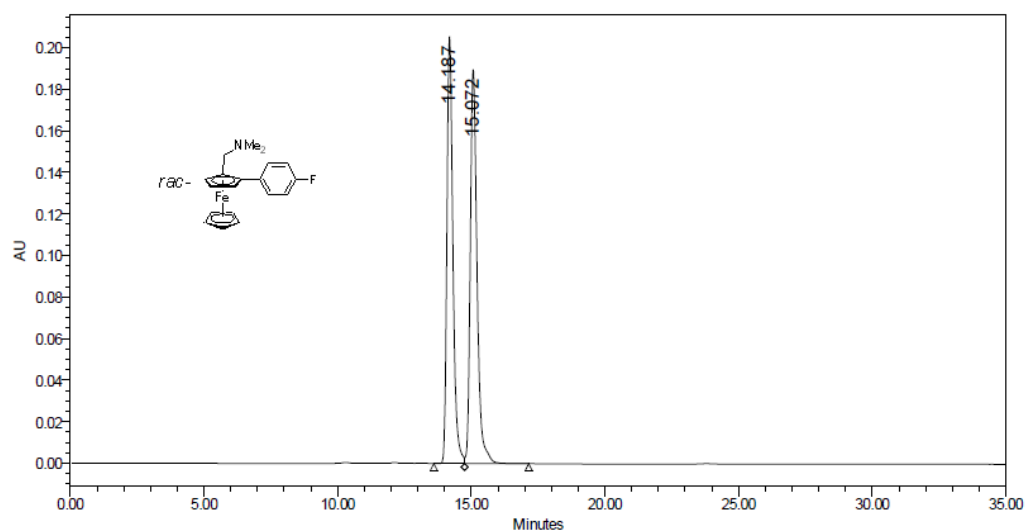
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	16.884	53752	2.02	2173	2.14
2	18.280	2603002	97.98	99454	97.86



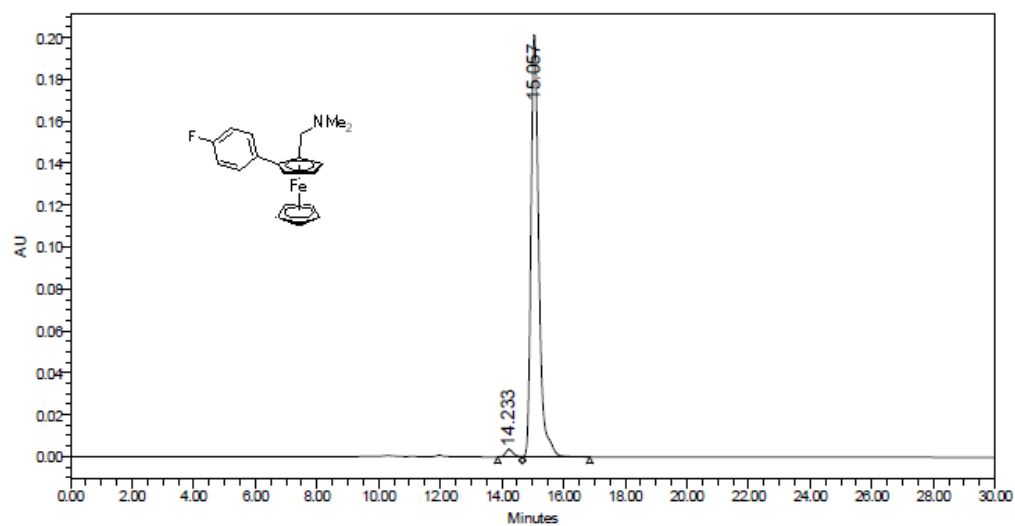
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.909	3081433	49.08	200261	51.21
2	14.729	3196877	50.92	190801	48.79



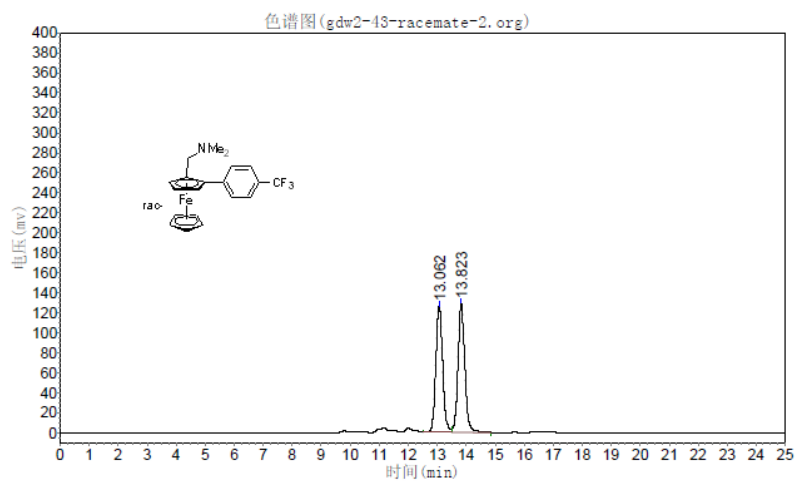
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.941	162507	1.62	10116	1.68
2	14.700	9878645	98.38	591525	98.32



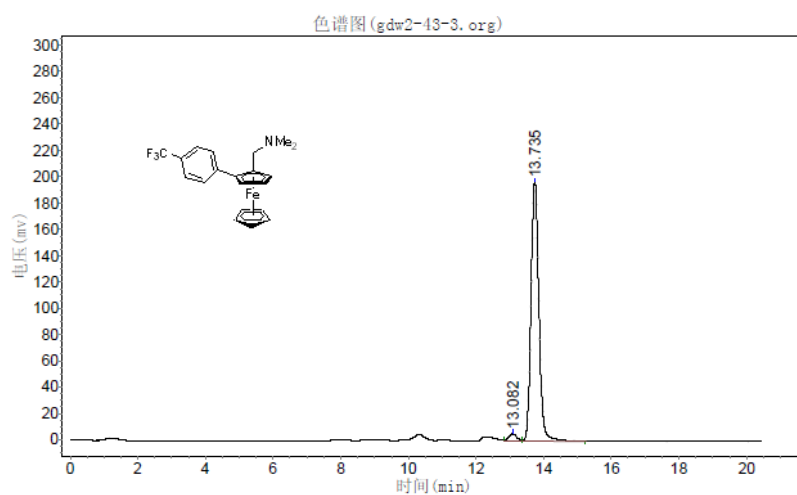
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	14.187	3206840	48.96	205700	52.01
2	15.072	3342871	51.04	189823	47.99



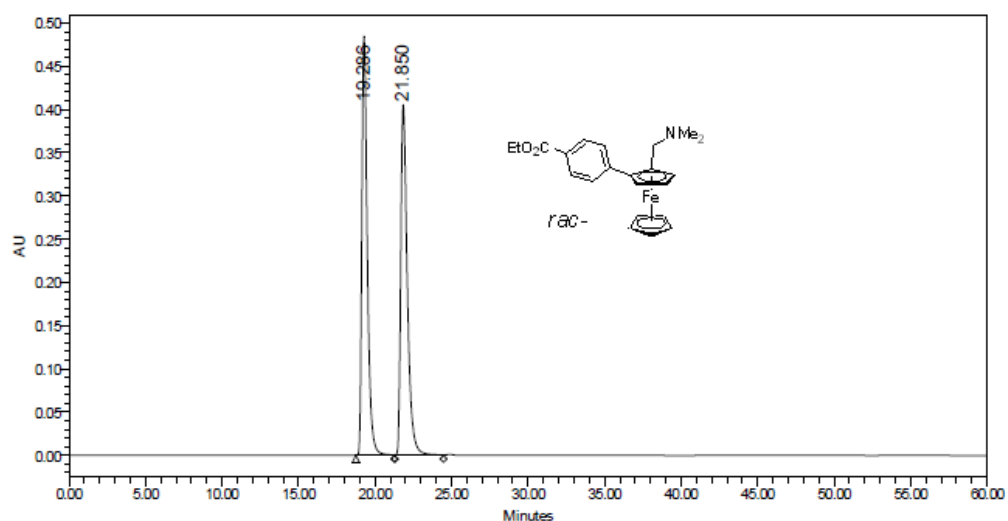
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	14.233	61140	1.69	3539	1.72
2	15.057	3567058	98.31	201826	98.28



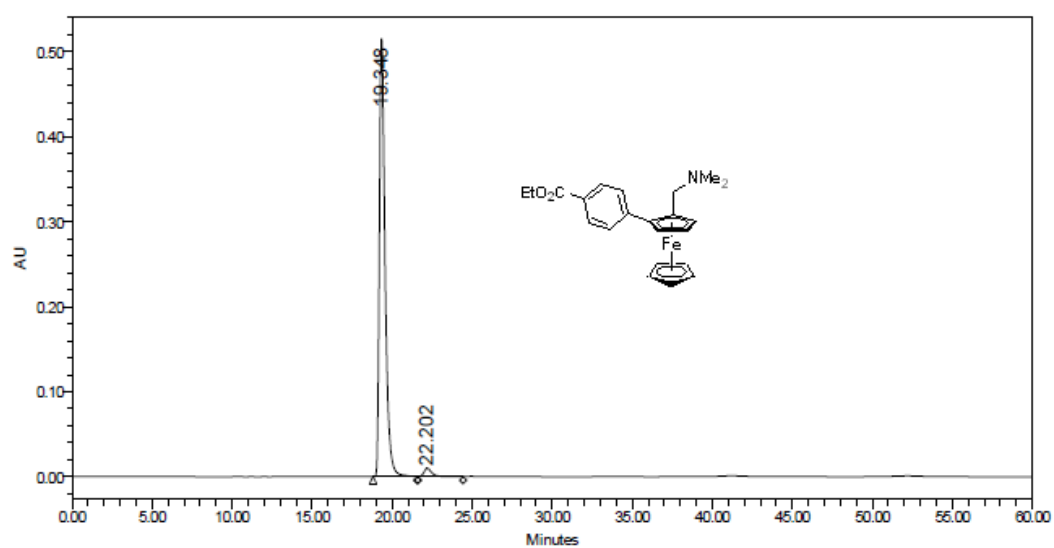
NO.	Time	Height	Area	Percent
1	13.062	126262.297	2059025.750	49.2573
2	13.823	129310.391	2121119.750	50.7427
		255572.688	4180145.500	100.0000



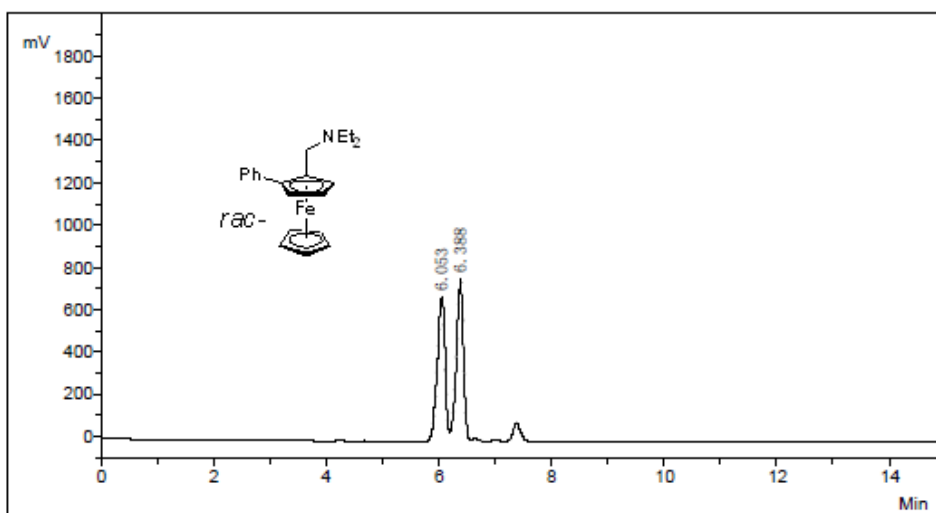
NO.	Time	Height	Area	Percent
1	13.082	5602.569	95153.945	2.9033
2	13.735	197002.766	3182240.500	97.0967
		202605.335	3277394.445	100.0000



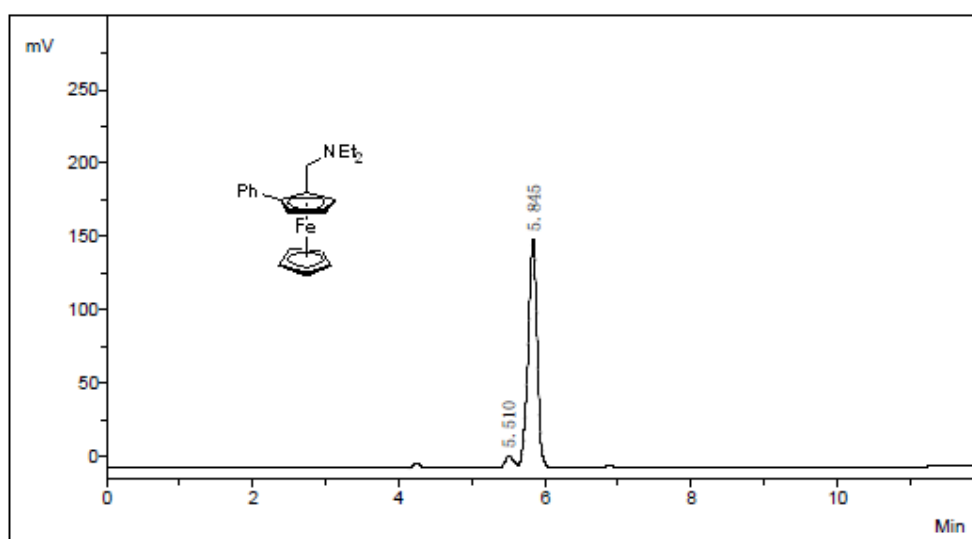
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	19.286	12012204	49.77	485166	54.47
2	21.850	12122879	50.23	405588	45.53



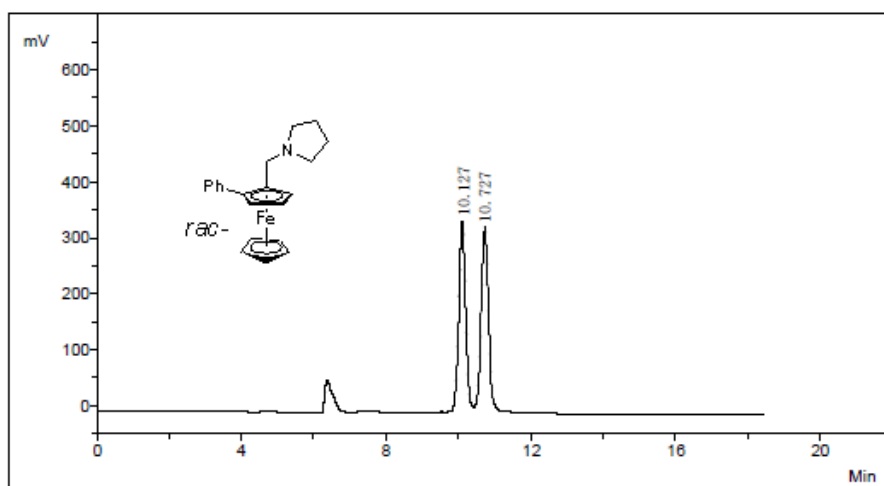
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	19.348	12799916	97.32	515302	98.10
2	22.202	352406	2.68	9972	1.90



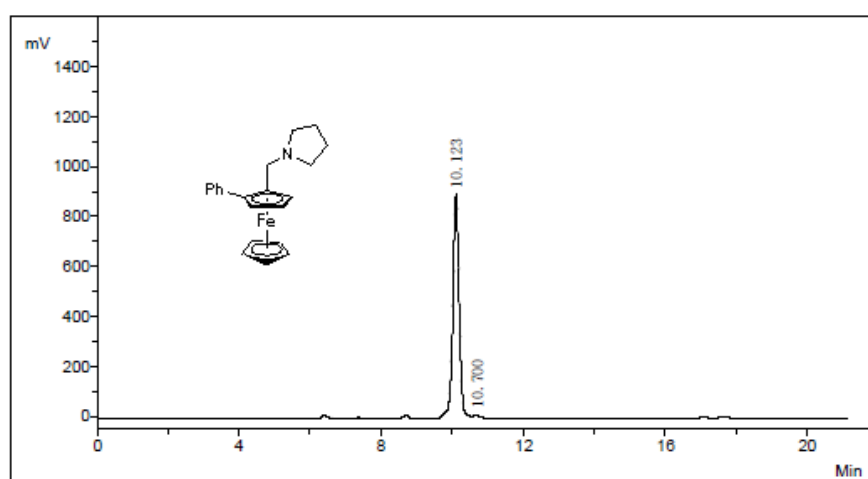
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		6.053	670736.9	6496442.6	49.6486
2	2		6.388	754749.2	6588415.9	50.3514
Total				1425486.1	13084858.5	100.0000



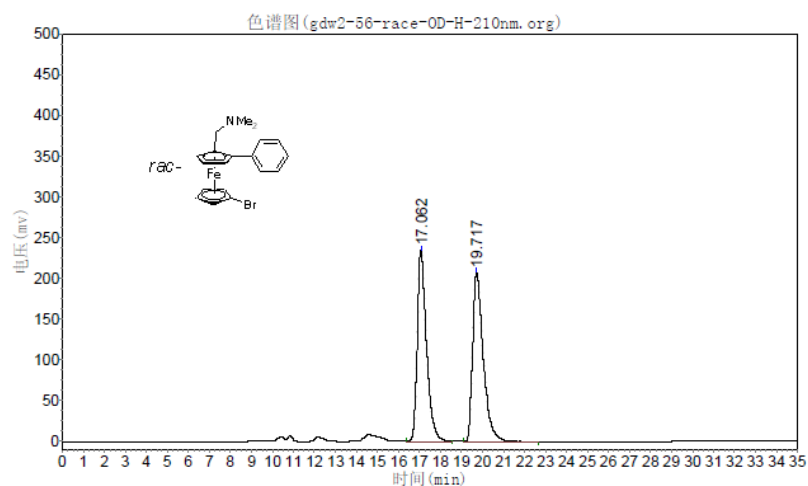
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		5.510	7964.6	63290.5	4.5295
2	2		5.845	155872.8	1333993.5	95.4705
Total				163837.4	1397284.0	100.0000



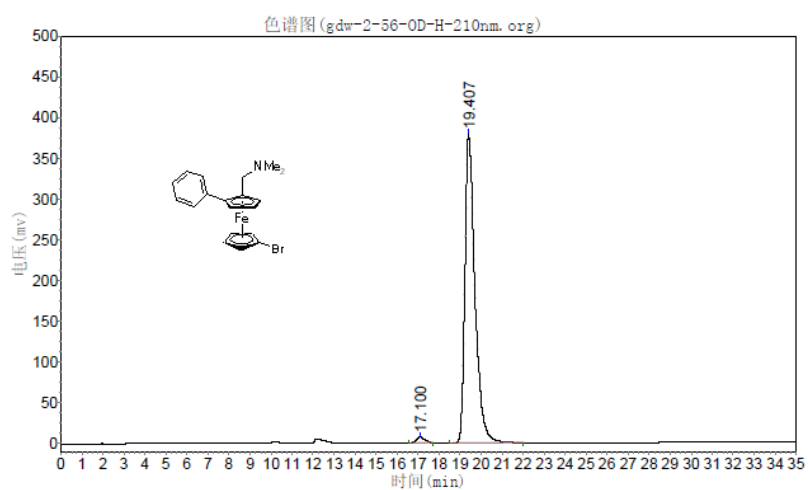
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		10.127	336782.5	4592806.2	49.0314
2	2		10.727	328692.5	4774262.7	50.9686
Total				665475.0	9367068.9	100.0000



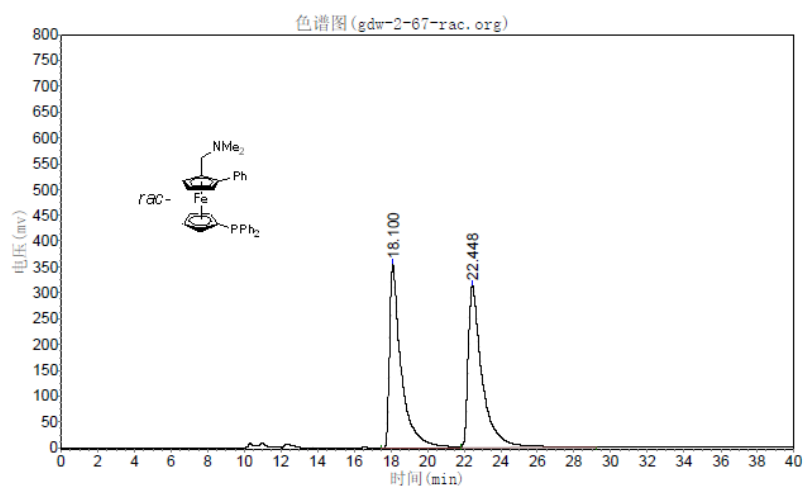
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		10.123	890498.4	11167632.6	98.8684
2	2		10.700	9009.2	127816.4	1.1316
Total				899507.6	11295449.0	100.0000



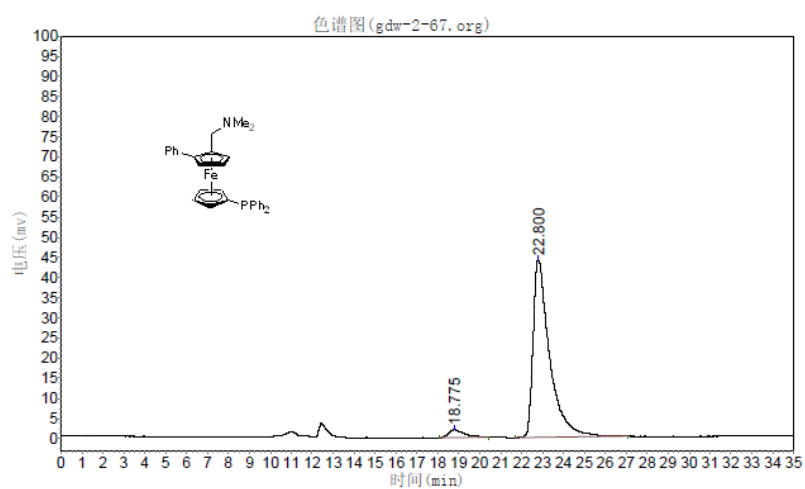
NO.	Time	Height	Area	Percent
1	17.062	235543.578	7248012.000	49.2302
2	19.717	208333.734	7474683.000	50.7698
		443877.313	14722695.000	100.0000



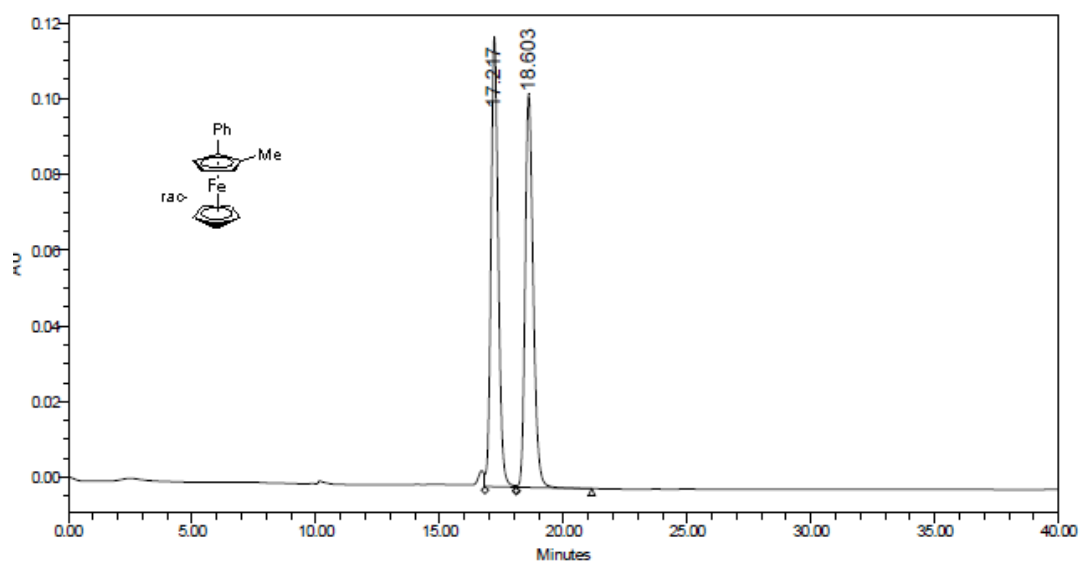
NO.	Time	Height	Area	Percent
1	17.100	6840.289	180528.297	1.4142
2	19.407	379586.875	12584795.000	98.5858
		386427.164	12765323.297	100.0000



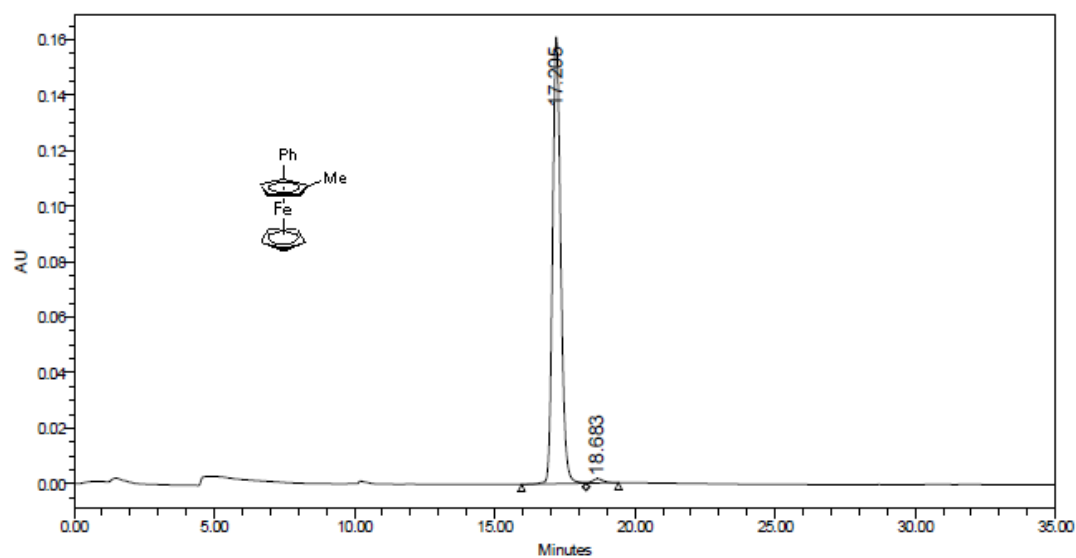
NO.	Time	Height	Area	Percent
1	18.100	357102.250	15758846.000	48.7153
2	22.448	315193.781	16590040.000	51.2847
		672296.031	32348886.000	100.0000



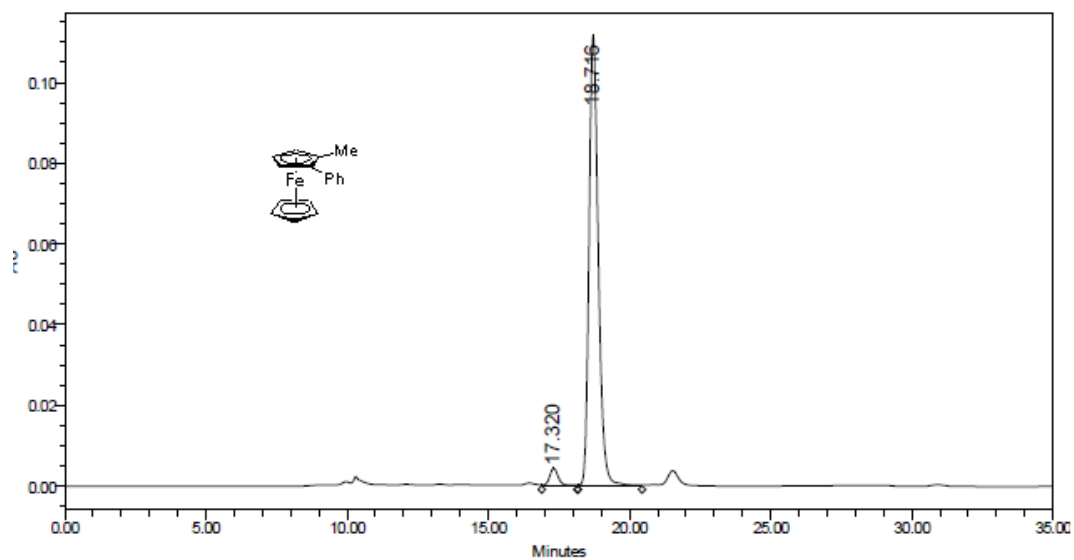
NO.	Time	Height	Area	Percent
1	18.775	1873.883	99021.203	3.9278
2	22.800	44000.984	2422027.000	96.0722
		45874.867	2521048.203	100.0000



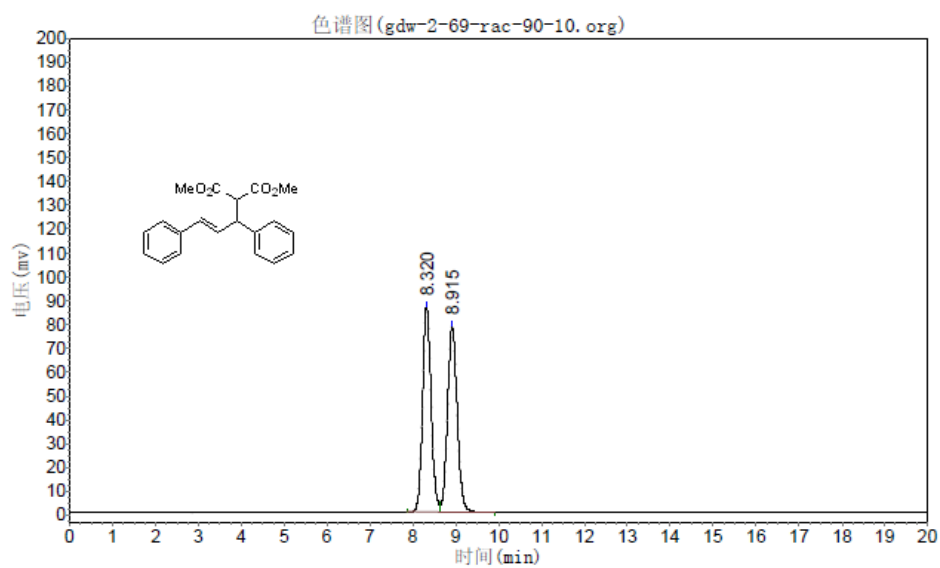
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	17.217	2402009	50.51	118571	53.29
2	18.603	2353490	49.49	103938	46.71



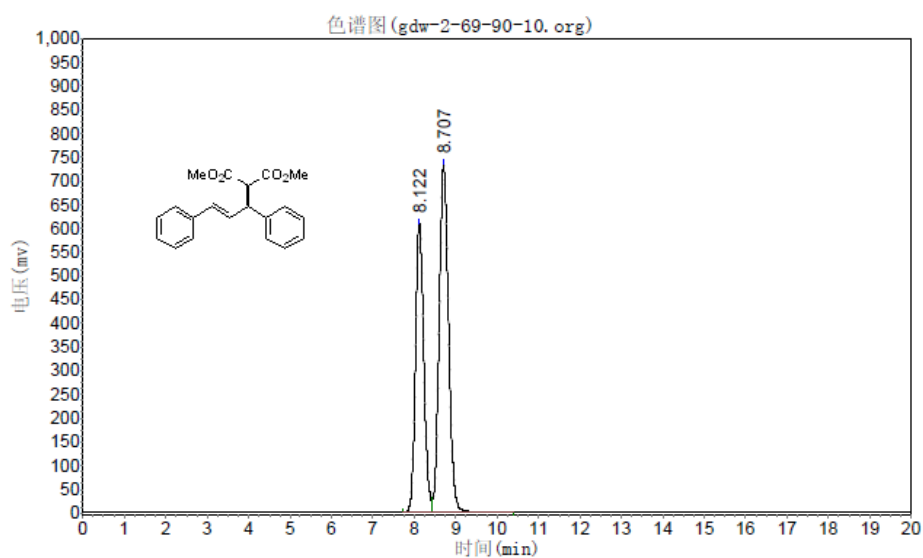
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	17.205	3251971	98.80	161126	99.09
2	18.683	39415	1.20	1488	0.91



	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	17.320	97940	3.70	4358	3.76
2	18.716	2545602	96.30	111562	96.24



No.	Time	Height	Area	Percent
1	8.320	85921.734	1200669.500	49.6353
2	8.915	78175.141	1218312.125	50.3647
		164096.875	2418981.625	100.0000



No.	Time	Height	Area	Percent
1	8.122	608668.500	8568984.000	42.6514
2	8.707	733313.313	11521746.000	57.3486
		1341981.813	20090730.000	100.0000