

Supporting Information

for

Enantioselective synthesis of planar chiral ferrocenes via palladium-catalyzed annulation with diarylethynes

Yan-Chao Shi¹, Rong-Fei Yang^{1,2}, De-Wei Gao¹ and Shu-Li You*¹

Address: ¹State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China and ²Process Development and Manufacturing Department, Pharmaron (Beijing) Co. Ltd., 6 Taihe Road, BDA, Beijing, 100176, China

Email: Shu-Li You* - E-mail: slyou@sioc.ac.cn

* Corresponding author

Experimental, characterization data and spectra.

Content

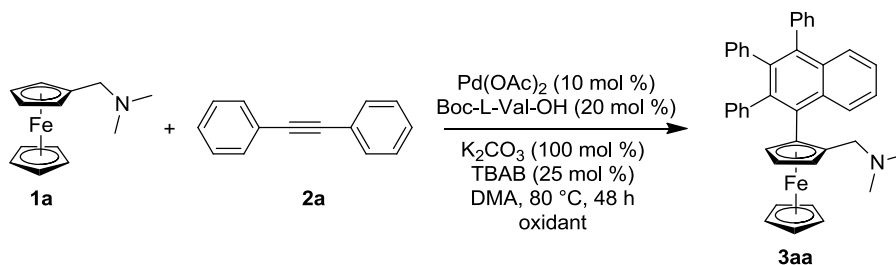
General methods	S3
Complete optimization data	S4
Enantioselective synthesis of planar chiral ferrocenes	S4
Synthesis of (<i>S</i> _p)- L1	S15
Pd-catalyzed allylic amination reaction	S16
Pd-catalyzed allylic alkylation reaction	S17
References	S17
Copies of NMR spectra and HPLC chromatographs	S19

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–c** [1-3] were prepared by reductive amination of ferrocene aldehyde with the corresponding amines. Compound **2a** was purchased from Alfa. Compounds **2b–d** were synthesized following the reported procedures [4].

Complete optimization data

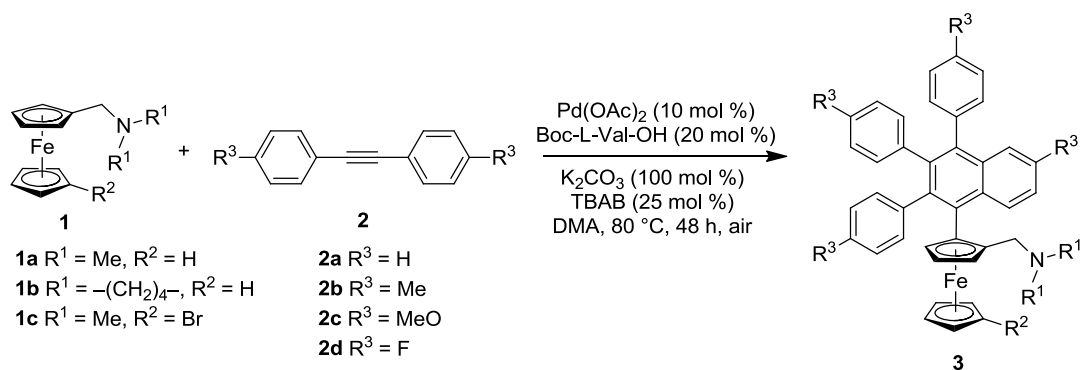
Table S1: Examination of oxidants^a



Entry	Oxidant	Yield (%) ^b	ee (%) ^c
1	air	42	98%
2	Cu(OAc) ₂	trace	-
3	Cu(OTf) ₂	trace	-
4	Ag ₂ CO ₃	<5	-
5	Ag ₂ O	<5	-
6	AgOAc	<5	-
7	BQ	14	-

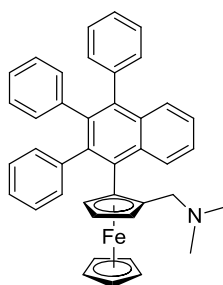
^aReaction conditions: **1a** (0.2 mmol), **2a** (2.3 equiv), Pd(OAc)₂ (10 mol %), Boc-L-Val-OH (20 mol %), K₂CO₃ (100 mol %), TBAB (25 mol %) and oxidant (2 equiv for entries 2–7 under argon) in 1.5 mL DMA. ^bIsolated yield. ^cDetermined by HPLC analysis.

General procedure for the enantioselective synthesis of planar chiral ferrocenes



To a solution of alkyne **2** (0.46 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

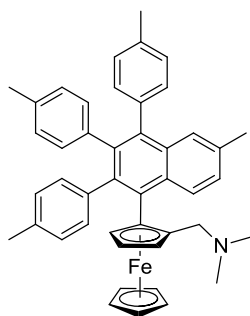
mg, 0.2 mmol), TBAB (tetrabutyl ammonium bromide) (16.1 mg, 0.05 mmol) and ferrocene **1** (0.02 mmol) successively. The mixture was stirred at 80 °C under air (open flask) for 48 h. After the reaction was complete, it was then quenched with saturated aqueous NaHCO₃ solution and extracted with EtOAc for 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 silica gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v, 3% Et₃N) to afford the desired product **3**.



(*S_p*)-1-[(*N,N*-Dimethylamino)methyl]-2-(2,3,4-triphenylnaphthalen-1-yl)ferrocene

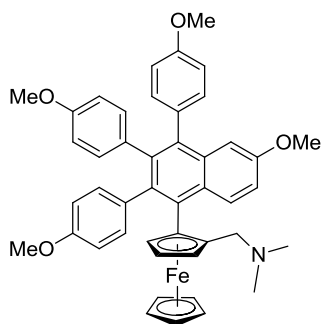
(3aa)

Yellow solid (50 mg, 42% yield, 98% ee). Analytical data for **3aa**: Mp = 78–80 °C; [α]_D²⁰ = –91.7° (*c* = 0.26 chloroform, 98% ee). ¹H NMR (400 MHz, CDCl₃) δ 2.23 (s, 6H), 3.13 (d, *J* = 14.0 Hz, 1H), 3.64 (d, *J* = 14.0 Hz, 1H), 3.73 (dd, *J*₁ = 2.4 Hz, *J*₂ = 1.6 Hz, 1H), 3.85 (t, *J* = 2.1 Hz, 1H), 4.21 (s, 5H), 4.50 (dd, *J*₁ = 2.8 Hz, *J*₂ = 1.6 Hz, 1H), 6.50–6.52 (m, 1H), 6.59–6.62 (m, 1H), 6.73–6.97 (series of m, 9H), 7.09 (td, *J*₁ = 7.2 Hz, *J*₂ = 0.8 Hz, 1H), 7.18 (tt, *J*₁ = 7.6 Hz, *J*₂ = 1.2 Hz, 1H), 7.36 (td, *J*₁ = 7.2 Hz, *J*₂ = 0.8 Hz, 1H), 7.43–7.50 (m, 2H), 7.63–7.70 (m, 2H), 10.18 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 45.7, 58.2, 65.2, 69.1, 70.1, 71.9, 86.0, 86.9, 123.8, 125.14, 125.18, 125.7, 126.20, 126.31, 126.4, 126.6, 127.0, 127.1, 127.8, 129.0, 130.97, 131.19, 131.28, 131.39, 131.9, 132.0, 132.2, 138.4, 138.9, 139.7, 140.8, 142.1, 142.4; The enantiomeric excess was determined by phenomenex cellulose-3 (25 cm), MeOH/IPA = 90/10, 0.7 mL/min, λ = 214 nm, *t* (major) = 5.577 min, *t* (minor) = 9.827 min.



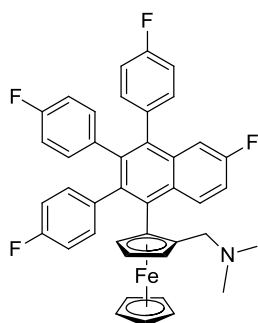
(*S_p*)-1-[(*N,N*-Dimethylamino)methyl]-2-(6-methyl-2,3,4-tri-*p*-tolynaphthalen-1-yl)ferrocene (**3ab**)

Yellow solid (46 mg, 35% yield, 97% ee). Analytical data for **3ab**: Mp = 81–83 °C; $[\alpha]_D^{20} = -176.3^\circ$ ($c = 0.29$ chloroform, 97% ee). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 2.10 (s, 3H), 2.14 (s, 3H), 2.22 (s, 6H), 2.33 (s, 3H), 2.45 (s, 3H), 3.05 (d, $J = 13.8$ Hz, 1H), 3.65–3.70 (m, 2H), 3.84 (t, $J = 2.4$ Hz, 1H), 4.17 (s, 5H), 4.50 (s, 1H), 6.35 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 6.41 (d, $J = 7.8$ Hz, 1H), 6.55 (d, $J = 7.8$ Hz, 1H), 6.60–6.68 (m, 3H), 6.71–6.74 (m, 2H), 6.80 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz, 1H), 6.89 (d, $J = 8.1$ Hz, 1H), 7.15 (d, $J = 7.8$ Hz, 1H), 7.33 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.5$ Hz, 1H), 7.37 (s, 1H), 7.48 (dd, $J_1 = 8.7$ Hz, $J_2 = 1.5$ Hz, 1H), 10.00 (d, $J = 9.0$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 21.05, 21.09, 21.3, 21.8, 45.8, 58.3, 65.1, 68.7, 69.9, 71.8, 86.3, 87.1, 125.78, 125.89, 126.98, 127.00, 127.07, 127.11, 127.7, 128.4, 129.0, 129.5, 130.8, 131.0, 131.14, 131.20, 131.31, 131.59, 131.74, 132.5, 134.0, 134.2, 134.9, 135.4, 137.0, 137.8, 138.1, 139.1, 139.3, 141.7; The enantiomeric excess was determined by phenomenex cellulose-4 (25 cm), $\text{CH}_3\text{CN/IPA} = 95/5$, 0.5 mL/min, $\lambda = 254$ nm, t (major) = 10.318 min, t (minor) = 9.552 min.



(*S_p*)-1-[(*N,N*-Dimethylamino)methyl]-2-(6-methoxy-2,3,4-tris(4-methoxyphenyl)naphthalen-1-yl)ferrocene (**3ac**)

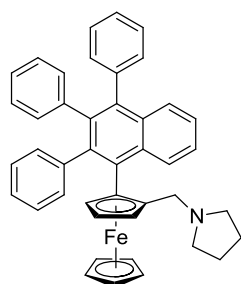
Yellow solid (64 mg, 45% yield, 99% ee). Analytical data for **3ac**: Mp = 84–86 °C; $[\alpha]_D^{20} = -154.4^\circ$ ($c = 0.29$ chloroform, 99% ee). ^1H NMR (300 MHz, CDCl_3) δ 2.23 (s, 6H), 3.08 (d, $J = 13.5$ Hz, 1H), 3.62 (s, 3H), 3.66 (s, 3H), 3.62–3.70 (m, 2H), 3.74 (s, 3H), 3.79 (s, 3H), 3.88 (t, $J = 2.4$ Hz, 1H), 4.17 (s, 5H), 4.51 (s, 1H), 6.30–6.47 (series of m, 6H), 6.62–6.65 (m, 2H), 6.75 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.1$ Hz, 1H), 6.80 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.1$ Hz, 1H), 6.90 (dd, $J_1 = 8.1$ Hz, $J_2 = 2.4$ Hz, 1H), 6.95 (d, $J = 2.7$ Hz, 1H), 7.30 (dd, $J_1 = 9.3$ Hz, $J_2 = 2.7$ Hz, 1H), 7.37 (dd, $J_1 = 8.7$ Hz, $J_2 = 2.1$ Hz, 1H), 10.06 (d, $J = 9.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.5, 54.87, 54.98, 55.06, 55.11, 58.1, 65.4, 68.9, 70.0, 71.9, 86.3, 105.7, 111.86, 111.89, 112.01, 112.06, 112.7, 113.3, 115.6, 126.7, 130.7, 131.82, 132.00, 132.13, 132.17, 132.22, 132.36, 132.9, 133.7, 133.9, 134.8, 137.2, 139.6, 140.2, 156.7, 156.9, 157.1, 157.7; The enantiomeric excess was determined by phenomenex cellulose-4 (25 cm), $\text{CH}_3\text{CN}/\text{IPA} = 95/5$, 0.5 mL/min, $\lambda = 254$ nm, t (major) = 9.818 min, t (minor) = 8.218 min.



(*S_p*)-1-[(*N,N*-Dimethylamino)methyl]-2-(6-fluoro-2,3,4-tris(4-fluorophenyl)naphthalen-1-yl)ferrocene (**3ad**)

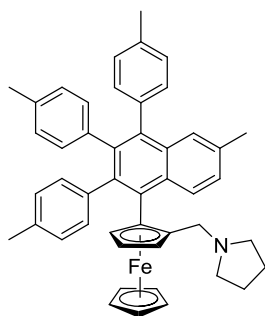
Yellow solid (41 mg, 31% yield, 97% ee). Analytical data for **3ad**: $[\alpha]_D^{20} = -62.2^\circ$ ($c = 0.30$ chloroform, 97% ee). ^1H NMR (300 MHz, CDCl_3) δ 2.18 (s, 6H), 3.10 (d, $J = 13.2$ Hz, 1H), 3.44 (d, $J = 13.5$ Hz, 1H), 3.66 (s, 1H), 3.91 (t, $J = 2.4$ Hz, 1H), 4.18 (s, 5H), 4.45 (s, 1H), 6.39–6.66 (series of m, 7H), 6.79–6.86 (m, 3H), 7.08 (td, $J_1 = 8.4$ Hz, $J_2 = 1.5$ Hz, 1H), 7.18 (dd, $J_1 = 11.1$ Hz, $J_2 = 2.7$ Hz, 1H), 7.36 (td, $J_1 = 6.6$ Hz, $J_2 = 2.1$ Hz, 1H), 7.44 (td, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 1H), 10.7 (dd, $J_1 = 9.3$ Hz, $J_2 = 6.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.6, 57.9, 65.7, 69.6, 70.1, 71.8, 85.6, 86.9,

110.1 (d, $J = 21.5$ Hz), 113.6 (d, $J = 21.2$ Hz), 113.74 (d, $J = 20.8$ Hz), 113.78 (d, $J = 20.9$ Hz), 113.9 (d, $J = 21.0$ Hz), 114.2 (d, $J = 26.7$ Hz), 114.6 (d, $J = 21.4$ Hz), 115.2 (d, $J = 20.6$ Hz), 128.3, 131.7 (d, $J = 8.1$ Hz), 132.30, 132.38, 132.43, 132.50 (d, $J = 8.7$ Hz), 132.62, 133.0 (d, $J = 7.7$ Hz), 133.11, 133.6 (d, $J = 8.0$ Hz), 134.9 (d, $J = 3.4$ Hz), 136.2 (d, $J = 3.1$ Hz), 137.0 (d, $J = 5.1$ Hz), 137.5 (d, $J = 3.7$ Hz), 139.1, 140.6, 160.65 (d, $J = 244$ Hz), 160.74 (d, $J = 246$ Hz), 160.76 (d, $J = 242$ Hz), 161.6 (d, $J = 245$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -116.8, -116.5, -115.2, -114.0; The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), hexanes/IPA = 98/2, 0.3 mL/min, $\lambda = 254$ nm, t (major) = 19.220 min, t (minor) = 16.953 min.



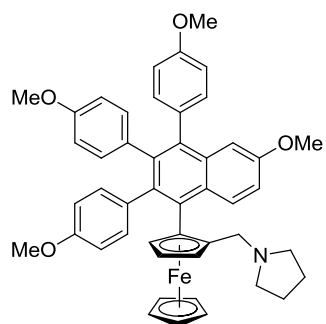
(*S_p*)-1-[(Pyrrolidin-1-yl)-methyl]-2-(2,3,4-triphenylnaphthalen-1-yl)ferrocene (**3ba**)

Yellow solid (44 mg, 35% yield, 95% ee). Analytical data for **3ba**: Mp = 77–79 °C; $[\alpha]_{\text{D}}^{20} = -101.4^\circ$ ($c = 0.31$ chloroform, 95% ee). ^1H NMR (300 MHz, CDCl_3) δ 1.79 (br, 4H), 2.53 (br, 4H), 3.32 (d, $J = 13.8$ Hz, 1H), 3.71 (s, 1H), 3.76 (d, $J = 13.5$ Hz, 1H), 3.85 (s, 1H), 4.22 (s, 5H), 4.50 (s, 1H), 6.50 (d, $J = 7.2$ Hz, 1H), 6.63 (d, $J = 6.0$ Hz, 1H), 6.73–6.98 (series of m, 9H), 7.10 (t, $J = 7.2$ Hz, 1H), 7.18 (t, $J = 7.5$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.42–7.51 (m, 2H), 7.63–7.70 (m, 2H), 10.22 (d, $J = 9.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 23.4, 54.2, 54.5, 65.1, 68.8, 69.6, 70.0, 71.7, 85.8, 123.8, 125.1, 125.6, 126.21, 126.28, 126.38, 126.40, 126.5, 127.0, 127.1, 127.7, 129.0, 130.9, 131.17, 131.25, 131.36, 131.39, 131.8, 132.1, 132.2, 138.3, 138.8, 139.7, 140.7, 142.1, 142.4; IR (film) 3445, 3055, 2959, 2775, 1651, 1601, 1491, 1441, 1373, 1107, 1031, 1002, 819, 754, 699 cm^{-1} ; HRMS (ESI): Exact mass calcd for $\text{C}_{43}\text{H}_{38}\text{FeN}^+$ (M+H) requires m/z 624.2348, found m/z 624.2339. The enantiomeric excess was determined by phenomenex cellulose-3 (25 cm), $\text{CH}_3\text{CN}/\text{IPA} = 95/5$, 0.5 mL/min, $\lambda = 254$ nm, t (major) = 6.917 min, t (minor) = 7.473 min.



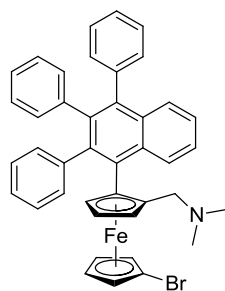
(*S_p*)-1-(Pyrrolidin-1-yl-methyl)-2-(6-methyl-2,3,4-tri-p-tolyl-naphthalen-1-yl)ferrocene
(3bb)

Yellow solid (41 mg, 30% yield, 97% ee). Analytical data for **3bb**: Mp = 84–86 °C; $[\alpha]_D^{20} = -157.7^\circ$ ($c = 0.31$ chloroform, 97% ee). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.77 (br, 4H), 2.10 (s, 3H), 2.14 (s, 3H), 2.33 (s, 3H), 2.45 (s, 3H), 2.52 (br, 4H), 3.25 (d, $J = 13.6$ Hz, 1H), 3.67 (dd, $J_1 = 2.0$ Hz, $J_2 = 1.2$ Hz, 1H), 3.78 (d, $J = 13.6$ Hz, 1H), 3.82–3.83 (m, 1H), 4.18 (s, 5H), 4.49 (s, 1H), 6.36 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 6.43–6.45 (m, 1H), 6.55 (d, $J = 8.0$ Hz, 1H), 6.61–6.65 (m, 3H), 6.69–6.73 (m, 2H), 6.81 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 6.89 (d, $J = 7.2$ Hz, 1H), 7.17 (d, $J = 7.6$ Hz, 1H), 7.37 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.6$ Hz, 1H), 7.38 (s, 1H), 7.48 (dd, $J_1 = 8.8$ Hz, $J_2 = 1.6$ Hz, 1H), 10.04 (d, $J = 8.8$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 21.06, 21.09, 21.3, 21.8, 23.5, 54.3, 54.5, 65.0, 68.5, 69.9, 71.6, 86.2, 125.77, 125.83, 126.94, 127.01, 127.09, 127.11, 127.7, 128.4, 129.0, 129.5, 130.8, 131.0, 131.20, 131.23, 131.34, 131.67, 131.69, 132.5, 134.01, 134.11, 134.9, 135.3, 137.0, 137.7, 138.1, 139.0, 139.3, 141.7; IR (film) 3440, 3020, 2920, 2871, 2776, 1622, 1511, 1447, 1375, 1347, 1183, 1107, 833, 815, 731 cm^{-1} ; HRMS (ESI): Exact mass calcd for $\text{C}_{47}\text{H}_{46}\text{FeN}^+$ ($\text{M}+\text{H}$) requires m/z 680.2974, found m/z 680.2971. The enantiomeric excess was determined by phenomenex cellulose-4 (25 cm), $\text{CH}_3\text{CN}/\text{IPA} = 95/5$, 0.5 mL/min, $\lambda = 254$ nm, t (major) = 11.327 min, t (minor) = 9.835 min.



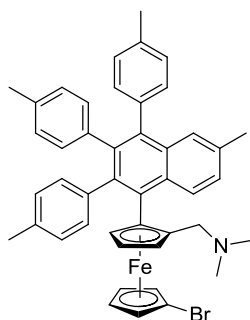
(*S_p*)-1-[(Pyrrolidin-1-yl)-methyl]-2-(6-methoxy-2,3,4-tris(4-methoxyphenyl)naphthalen-1-yl)ferrocene (**3bc**)

Yellow solid (61 mg, 41% yield, 97% ee). Analytical data for **3bc**: Mp = 87–89 °C; $[\alpha]_D^{20} = -174.3^\circ$ ($c = 0.30$ chloroform, 97% ee). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.77 (br, 4H), 2.51 (br, 4H), 3.24 (d, $J = 13.5$ Hz, 1H), 3.62 (s, 3H), 3.66 (s, 3H), 3.74 (s, 3H), 3.79 (s, 3H), 3.69–3.89 (series of m, 3H), 4.17 (s, 5H), 4.47 (s, 1H), 6.31–6.47 (series of m, 6H), 6.60–6.65 (m, 2H), 6.75 (d, $J = 8.7$ Hz, 1H), 6.81 (d, $J = 8.4$ Hz, 1H), 6.91 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 1H), 7.95 (d, $J = 2.4$ Hz, 1H), 7.30 (dd, $J_1 = 9.3$ Hz, $J_2 = 2.4$ Hz, 1H), 7.38 (d, $J = 8.4$ Hz, 1H), 10.11 (d, $J = 9.3$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 23.4, 54.1, 54.5, 54.78, 54.89, 54.97, 55.02, 65.1, 68.5, 69.4, 69.8, 71.5, 86.1, 87.8, 105.5, 111.8, 112.0, 112.6, 113.2, 115.4, 126.7, 130.8, 131.9, 132.11, 132.18, 132.31, 132.34, 132.7, 133.6, 133.8, 134.8, 137.0, 139.4, 140.1, 156.6, 156.8, 157.0, 157.6; IR (film) 3423, 2932, 2833, 2776, 1609, 1509, 1459, 1286, 1245, 1176, 1107, 1035, 827, 774 cm^{-1} ; HRMS (ESI): Exact mass calcd for $\text{C}_{47}\text{H}_{46}\text{FeNO}_4^{+1}$ (M+H) requires m/z 744.2771, found m/z 744.2770. The enantiomeric excess was determined by phenomenex cellulose-4 (25 cm), $\text{CH}_3\text{CN}/\text{IPA} = 95/5$, 0.5 mL/min, $\lambda = 254$ nm, t (major) = 11.677 min, t (minor) = 8.627 min.



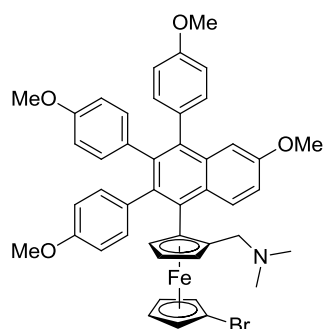
(*S_p*)-1-[(*N,N*-Dimethylamino)methyl]-2-(2,3,4-triphenylnaphthalen-1-yl)-1'-bromoferrocene (**3ca**)

Yellow solid (85 mg, 42% yield, 96% ee). Analytical data for **3ca**: Mp = 82–84 °C; $[\alpha]_D^{20} = -13.3^\circ$ ($c = 0.15$ chloroform, 96% ee). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.31 (s, 6H), 3.12 (d, $J = 14.0$ Hz, 1H), 3.79 (d, $J = 14.0$ Hz, 1H), 3.89 (s, 1H), 3.94 (t, $J = 2.4$ Hz, 1H), 3.86 (d, $J = 1.2$ Hz, 1H), 4.23 (d, $J = 0.8$ Hz, 1H), 4.47 (d, $J = 1.2$ Hz, 1H), 4.49 (d, $J = 0.8$ Hz, 1H), 4.67 (s, 1H), 6.61 (d, $J = 7.6$ Hz, 1H), 6.74 (t, $J = 2.8$ Hz, 1H), 6.80–6.98 (series of m, 8H), 7.05 (d, $J = 8.0$ Hz, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.80 (t, $J = 7.6$ Hz, 1H), 10.01 (d, $J = 8.4$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 46.0, 56.6, 68.4, 68.6, 69.5, 70.3, 71.7, 73.4, 74.3, 79.6, 87.6, 88.6, 124.2, 125.28, 125.39, 125.9, 126.46, 126.54, 126.58, 126.74, 127.2, 127.9, 128.9, 131.0, 131.23, 131.25, 131.35, 131.45, 131.93, 132.23, 138.7, 139.0, 139.7, 140.8, 142.1, 142.6; IR (film) 3056, 2941, 2814, 2765, 1602, 1491, 1442, 1370, 1265, 1152, 1072, 1024, 872, 789, 772, 755, 737, 700, 624 cm^{-1} ; HRMS (ESI): Exact mass calcd for $\text{C}_{41}\text{H}_{35}\text{BrFeN}^{+1}$ ($\text{M}+\text{H}$) requires m/z 676.1297, found m/z 676.1287. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), hexanes/IPA = 98/2, 0.4 mL/min, $\lambda = 254$ nm, t (major) = 16.438 min, t (minor) = 14.545 min.



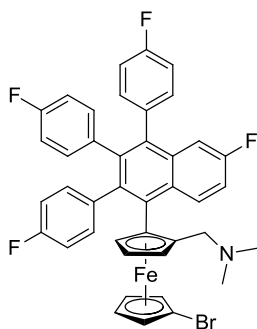
(*S*)-1-[(*N,N*-Dimethylamino)methyl]-2-(6-methyl-2,3,4-tri-*p*-tolyl-naphthalen-1-yl)-1'-bromo ferrocene (**3cb**)

Yellow solid (41 mg, 28% yield, 96% ee). Analytical data for **3cb**: Mp = 87–89 °C; $[\alpha]_D^{20} = -59.7^\circ$ ($c = 0.29$ chloroform, 96% ee). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.09 (s, 3H), 2.15 (s, 3H), 2.25 (s, 6H), 2.32 (s, 3H), 2.45 (s, 3H), 3.00 (d, $J = 14.0$ Hz, 1H), 3.77–3.80 (m, 2H), 3.85 (t, $J = 2.8$ Hz, 1H), 4.00 (dd, $J_1 = 4.0$ Hz, $J_2 = 2.4$ Hz, 1H), 4.15 (dd, $J_1 = 4.0$ Hz, $J_2 = 2.4$ Hz, 1H), 4.38–4.39 (m, 2H), 4.64 (br, 1H), 6.35 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.6$ Hz, 1H), 6.41 (d, $J = 7.2$ Hz, 1H), 6.55 (d, $J = 8.0$ Hz, 1H), 6.62–6.74 (series of m, 5H), 6.80 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 6.89 (dt, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H), 7.16 (d, $J = 7.6$ Hz, 1H), 7.32 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 7.38 (s, 1H), 7.52 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz, 1H), 9.73 (d, $J = 8.8$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 21.00, 21.04, 21.21, 21.7, 45.5, 56.4, 68.2, 68.6, 69.3, 70.2, 71.3, 73.2, 74.3, 79.5, 87.8, 126.0, 126.1, 127.00, 127.08, 127.10, 127.12, 127.7, 128.4, 128.6, 129.2, 130.69, 130.92, 130.99, 131.16, 131.24, 131.7, 132.4, 134.1, 134.4, 135.0, 135.4, 136.8, 137.9, 138.1, 139.07, 139.16, 141.8; IR (film) 3421, 3021, 2920, 1814, 2761, 2602, 2496, 1508, 1151, 1107, 1022, 869, 834, 815, 742, 668 cm^{-1} ; HRMS (ESI): Exact mass calcd for $\text{C}_{45}\text{H}_{43}\text{BrFeN}^+$ ($\text{M}+\text{H}$) requires m/z 732.1923, found m/z 732.1919. The enantiomeric excess was determined by phenomenex cellulose-4 (25 cm), $\text{CH}_3\text{CN}/\text{IPA} = 95/5$, 0.5 mL/min, $\lambda = 254$ nm, t (major) = 17.027 min, t (minor) = 16.227 min.



(*S_p*)-1-[(*N,N*-Dimethylamino)methyl]-2-(6-methoxy-2,3,4-tris(4-methoxyphenyl)naphthalen-1-yl)-1'-bromo ferrocene (**3cc**)

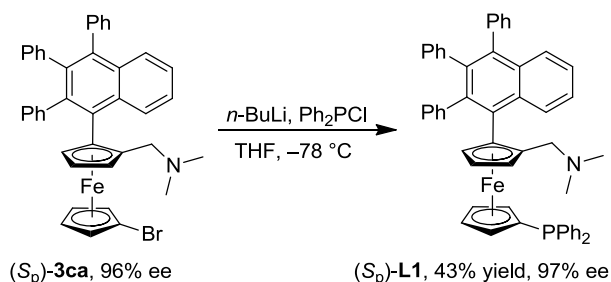
Yellow solid (64 mg, 40% yield, 96% ee). Analytical data for **3cc**: Mp = 90–92 °C; $[\alpha]_D^{20} = -80.7^\circ$ ($c = 0.30$ chloroform, 96% ee). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.22 (s, 6H), 2.98 (d, $J = 13.6$ Hz, 1H), 3.62 (s, 3H), 3.66 (s, 3H), 3.68 (d, $J = 18.4$ Hz, 1H), 3.75 (s, 3H), 3.76 (dd, $J_1 = 2.4$ Hz, $J_2 = 1.6$ Hz, 1H), 3.79 (s, 3H), 3.88 (t, $J = 2.8$ Hz, 1H), 4.00 (td, $J_1 = 2.8$ Hz, $J_2 = 1.2$ Hz, 1H), 4.14 (td, $J_1 = 2.8$ Hz, $J_2 = 1.2$ Hz, 1H), 4.36–4.38 (m, 2H), 4.58 (s, 1H), 6.31–6.48 (series of m, 6H), 6.63 (t, $J = 2.4$ Hz, 1H), 6.65 (t, $J = 2.0$ Hz, 1H), 6.76 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 1H), 6.81 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 1H), 6.90 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 1H), 7.96 (d, $J = 2.8$ Hz, 1H), 7.34–7.38 (m, 2H), 9.80 (d, $J = 9.6$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 45.6, 54.84, 54.96, 55.03, 55.11, 56.4, 68.2, 68.7, 69.3, 70.2, 71.4, 73.1, 74.2, 79.4, 87.8, 105.7, 111.9, 112.1, 112.7, 113.3, 115.8, 126.5, 130.5, 131.1, 131.96, 132.10, 132.12, 132.21, 132.28, 132.9, 133.6, 133.8, 134.7, 137.4, 139.6, 140.3, 156.7, 157.0, 157.2, 157.7; IR (film) 3384, 2934, 2833, 2762, 1735, 1610, 1577, 1509, 1459, 1370, 1286, 1286, 1244, 1176, 1035, 828 cm^{-1} ; HRMS (ESI): Exact mass calcd for $\text{C}_{45}\text{H}_{43}\text{BrFeNO}_4^{+1}$ (M+H) requires m/z 796.1719, found m/z 796.1714. The enantiomeric excess was determined by phenomenex cellulose-4 (25 cm), $\text{CH}_3\text{CN}/\text{IPA} = 95/5$, 0.5 mL/min, $\lambda = 254$ nm, t (major) = 9.277 min, t (minor) = 8.377 min.



(*S_p*)-1-[(*N,N*-Dimethylamino)methyl]-2-(6-methoxy-2,3,4-tris(4-methoxyphenyl)naphthalen-1-yl)ferrocene (**3cd**)

Yellow solid (45 mg, 30% yield, 92% ee). Analytical data for **3cd**: Mp = 94–96 °C; $[\alpha]_D^{20} = -9.7^\circ$ ($c = 0.31$ chloroform, 92% ee). ^1H NMR (300 MHz, CDCl_3) δ 2.27 (s, 6H), 3.11 (d, $J = 13.5$ Hz, 1H), 3.71–3.75 (m, 2H), 3.97 (br, 1H), 4.05 (br, 1H), 4.18 (br, 1H), 4.35 (d, $J = 0.9$ Hz, 1H), 4.44 (br, 1H), 4.68 (br, 1H), 6.43–6.71 (series of m, 7H), 6.80–6.86 (m, 3H), 7.08 (td, $J_1 = 8.1$ Hz, $J_2 = 1.2$ Hz, 1H), 7.20 (dd, $J_1 = 10.8$ Hz, $J_2 = 2.7$ Hz, 1H), 7.34–7.39 (td, $J_1 = 6.9$ Hz, $J_2 = 1.5$ Hz, 1H), 7.48–7.55 (td, $J_1 = 8.4$ Hz, $J_2 = 2.7$ Hz, 1H), 9.98 (dd, $J_1 = 9.3$ Hz, $J_2 = 6.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.68, 45.80, 56.3, 68.3, 68.8, 69.2, 70.1, 70.5, 72.0, 73.3, 74.1, 79.4, 87.2, 110.1 (d, $J = 21.8$ Hz), 113.7 (d, $J = 21.4$ Hz), 113.8 (d, $J = 21.2$ Hz), 113.9 (d, $J = 21.3$ Hz), 114.5 (d, $J = 24.8$ Hz), 114.6 (d, $J = 21.5$ Hz), 115.2 (d, $J = 21.2$ Hz), 128.1, 131.5 (d, $J = 8.3$ Hz), 132.28, 132.33, 132.37, 132.45, 132.52, 132.6 (d, $J = 7.8$ Hz), 133.0 (d, $J = 7.7$ Hz), 133.6 (d, $J = 8.2$ Hz), 134.8 (d, $J = 3.4$ Hz), 136.1 (d, $J = 3.3$ Hz), 137.3, 137.4 (d, $J = 3.1$ Hz), 139.2, 140.7, 160.7 (d, $J = 244$ Hz), 160.815 (d, $J = 247$ Hz), 160.824 (d, $J = 244$ Hz), 161.6 (d, $J = 245$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -116.2, -116.1, -115.0, -113.3; IR (film) 2941, 2814, 2765, 2604, 2498, 1625, 1604, 1513, 1368, 1228, 1156, 1093, 1039, 1015, 872, 847, 831, 819, 785 cm^{-1} ; HRMS (ESI): Exact mass calcd for $\text{C}_{41}\text{H}_{31}\text{BrF}_4\text{FeN}^+$ ($\text{M}+\text{H}$) requires m/z 748.0920, found m/z 748.0920. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), hexanes/IPA = 98/2, 0.3 mL/min, $\lambda = 254$ nm, t (major) = 20.938 min, t (minor) = 17.655 min.

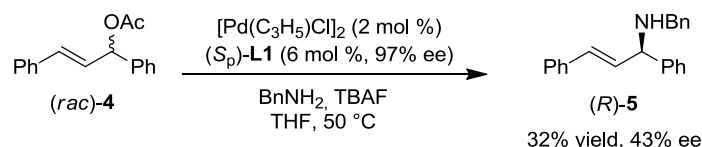
Synthesis of (*S_p*)-L1



To a solution of compound (*S_p*)-**3ca** (610 mg, 0.90 mmol) in THF (10 mL) was added *n*-BuLi (0.68 mL, 1.08 mmol, 1.6 M in *n*-hexane) at $-78\text{ }^\circ\text{C}$ under argon. The resulting deep red solution was stirred for 30 min. Then chlorodiphenylphosphine (0.194 mL, 1.08 mmol) was added. The mixture was warmed slowly to $0\text{ }^\circ\text{C}$ and stirred for 1 h. Then the reaction mixture was quenched with water, extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 , and filtrated. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (dichloromethane/methanol = 1/100, v/v) to give (*S_p*)-**L1** (306 mg, 43% yield, 97% ee) as an orange solid. Analytical data for (*S_p*)-**L1**: Mp = $93\text{--}95\text{ }^\circ\text{C}$; $[\alpha]_{\text{D}}^{20} = -130.6^\circ$ ($c = 0.63$ chloroform, 97% ee). ^1H NMR (400 MHz, CDCl_3) δ 2.18 (s, 6H), 3.11 (d, $J = 13.6$ Hz, 1H), 3.62 (d, $J = 13.6$ Hz, 1H), 3.76 (br, 1H), 3.78 (t, $J = 2.4$ Hz, 1H), 4.04 (s, 1H), 4.13 (br, 1H), 4.39 (br, 1H), 4.48 (br, 1H), 4.52 (br, 1H), 6.47 (d, $J = 7.6$ Hz, 1H), 6.53 (d, $J = 7.2$ Hz, 1H), 6.72 (td, $J_1 = 7.6$ Hz, $J_2 = 0.8$ Hz, 1H), 6.76–6.90 (series of m, 7H), 6.96 (d, $J = 7.6$ Hz, 1H), 7.02–7.08 (m, 3H), 7.11–7.31 (series of m, 9H), 7.33–7.38 (m, 2H), 7.48 (d, $J = 7.6$ Hz, 1H), 7.534 (td, $J_1 = 9.4$ Hz, $J_2 = 1.2$ Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 1H), 9.86 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 45.2, 57.8, 66.8, 70.6, 73.3, 73.51, 73.58, 73.62, 74.07, 74.10, 74.19, 74.95, 75.07, 76.55, 76.61, 86.7, 123.8, 125.17, 125.32, 123.6, 126.36, 126.42, 126.44, 126.46, 126.6, 127.09, 127.16, 127.74, 127.79, 127.80, 128.10, 128.17, 128.24, 128.56, 128.75, 130.97, 131.00, 131.18, 131.27, 131.33, 132.0, 132.2, 133.3 (d, $J = 18.6$ Hz), 133.5 (d, $J = 19.2$ Hz), 138.45, 138.54, 138.74, 138.83, 138.94, 139.7, 140.7, 142.0, 142.4; ^{31}P NMR (161 MHz, CDCl_3) δ -18.05 ; IR (film) 3054, 2941, 2854, 2813, 2765, 1737, 1601, 1434, 1370, 1265, 1160, 1071, 1027, 846, 789, 772, 739, 698 cm^{-1} ; HRMS (ESI): Exact mass

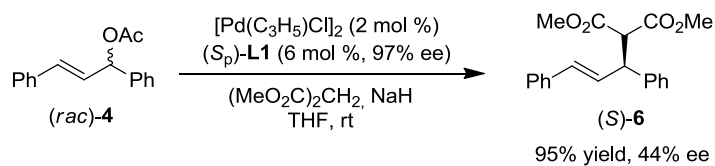
calcd for $C_{53}H_{45}FeNP^{+1}$ (M+H) requires m/z 782.2634, found m/z 782.2643. The enantiomeric excess was determined by phenomenex cellulose-2 (25 cm), hexanes/EtOH = 94/6, 0.7 mL/min, λ = 254 nm, t (major) = 8.690 min, t (minor) = 7.317 min.

Pd-catalyzed allylic amination reaction with (*S_p*)-**L1**



[Pd(C₃H₅)Cl]₂ (1.5 mg, 0.004 mmol) and ligand (*S_p*)-**L1** (9.4 mg, 0.012 mmol, 99% ee) were dissolved in dry THF (0.5 mL), and the mixture was stirred for 30 min at rt under argon. To this solution were successively added (*rac*)-**4** (50.4 mg, 0.2 mmol), BnNH₂ (42.8 mg, 0.4 mmol), and TBAF (1 M in THF, 0.4 mL, 0.4 mmol). The reaction mixture was stirred at 50 °C for 14 h. After completion, the reaction mixture was diluted with Et₂O (20 mL) and washed twice with ice-cold saturated aqueous ammonium chloride. The organic phase was dried over anhydrous Na₂SO₄ and then concentrated under reduced pressure. The residue was purified by preparative TLC (ethyl acetate/petroleum = 1/10) to give (*R*)-**5** (19.1 mg, 32% yield, 43% ee). Analytical data for (*R*)-**5**: $[\alpha]_D^{20} = -14.24^\circ$ ($c = 0.25$ chloroform, 43% ee). ¹H NMR (300 MHz, CDCl₃) δ 1.84 (s, 1H), 3.78 (s, 2H), 4.39 (d, $J = 6.9$ Hz, 1H), 6.31 (dd, $J_1 = 15.9$ Hz, $J_2 = 7.2$ Hz, 1H), 6.57 (d, $J = 15.9$ Hz, 1H) 7.20–7.42 (series of m, 15H); The enantiomeric excess was determined by Diacel Chiralcel OJ-H (25 cm), hexanes/IPA = 90/10, 0.6 mL/min, λ = 254 nm, t (minor) = 18.40 min, t (major) = 22.07 min. The absolute configuration of the product (*R*)-**5** was assigned as (*R*) by comparing the optical rotation with that reported in the literature [5].

Pd-catalyzed allylic alkylation reaction with (*S_p*)-**L1**

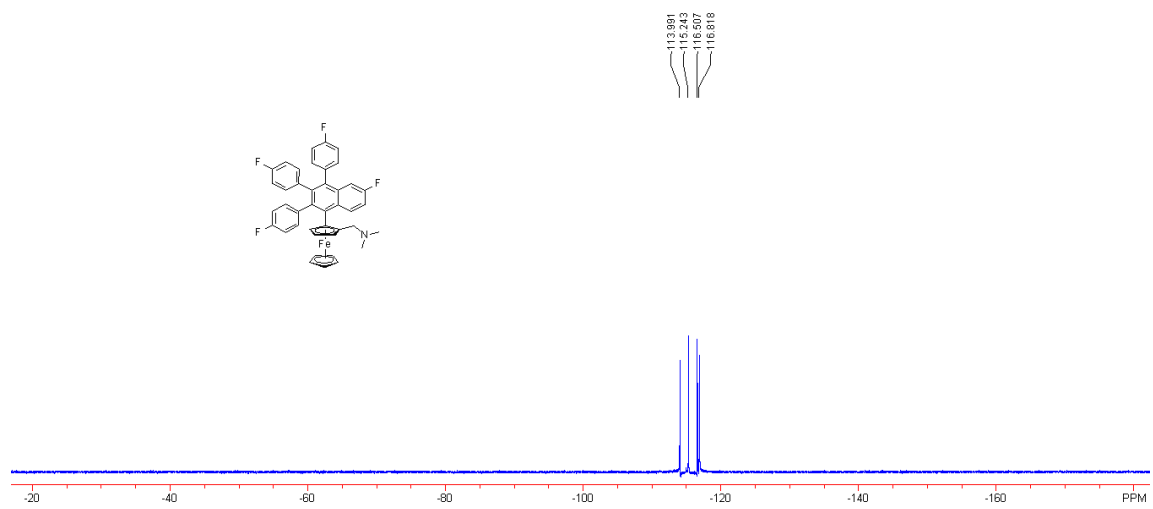
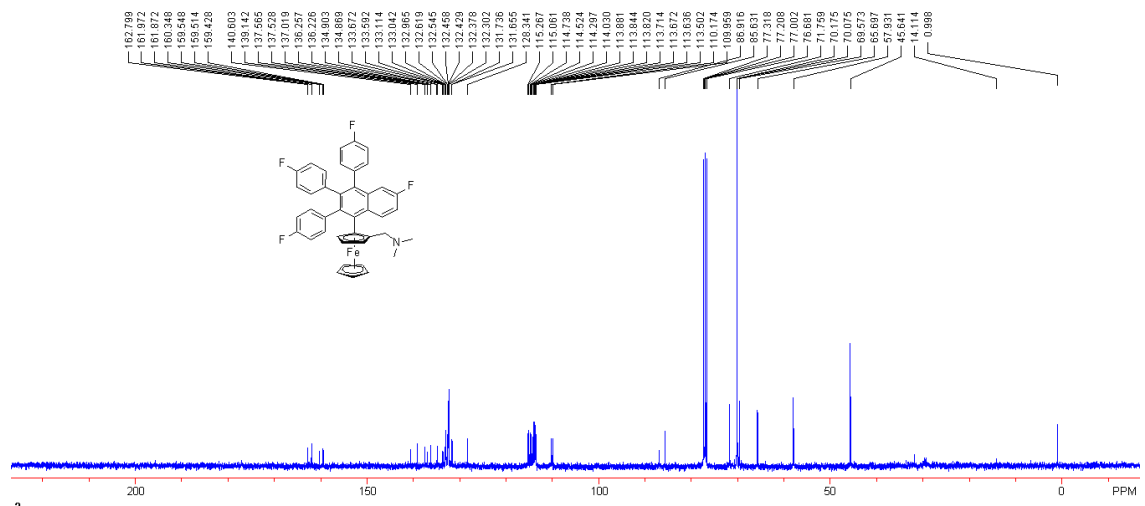
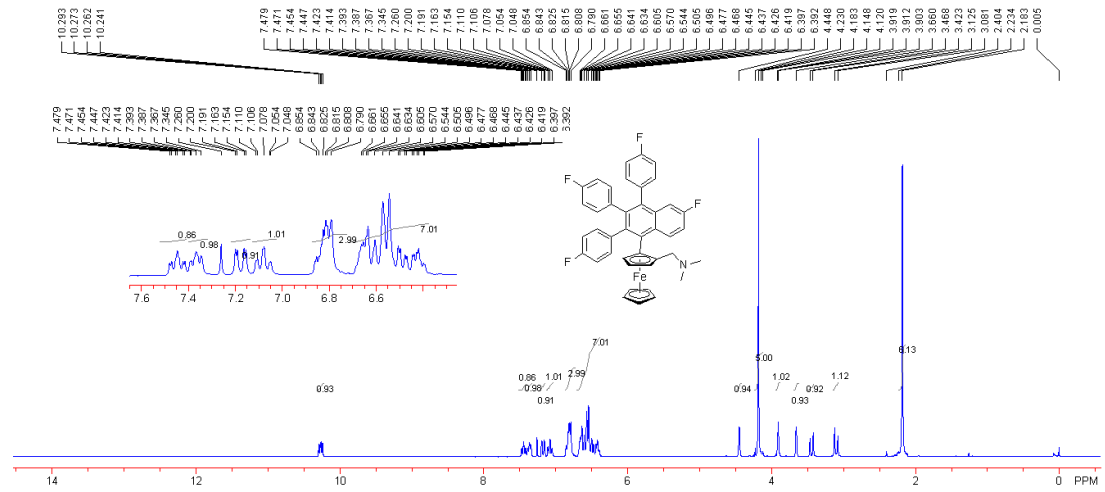


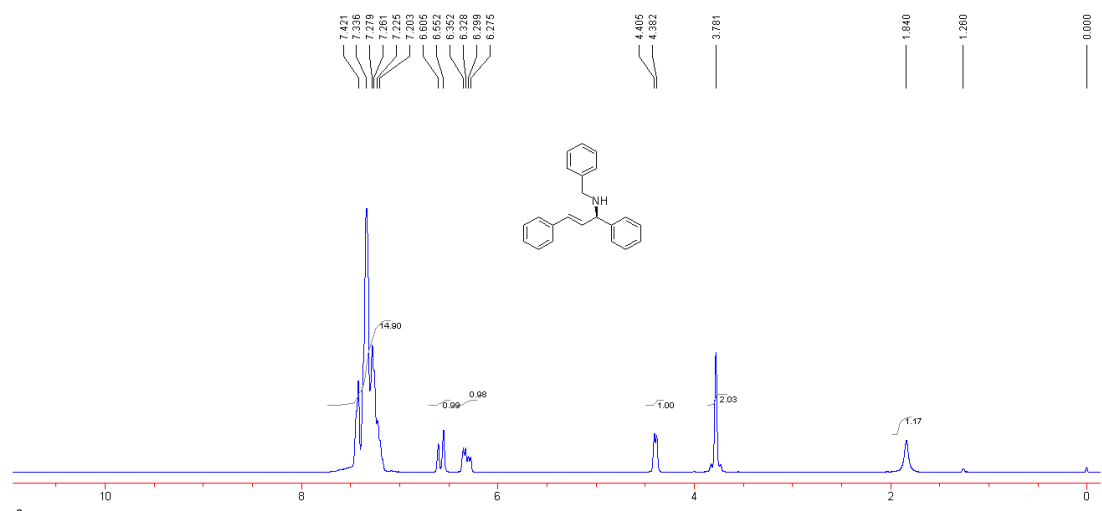
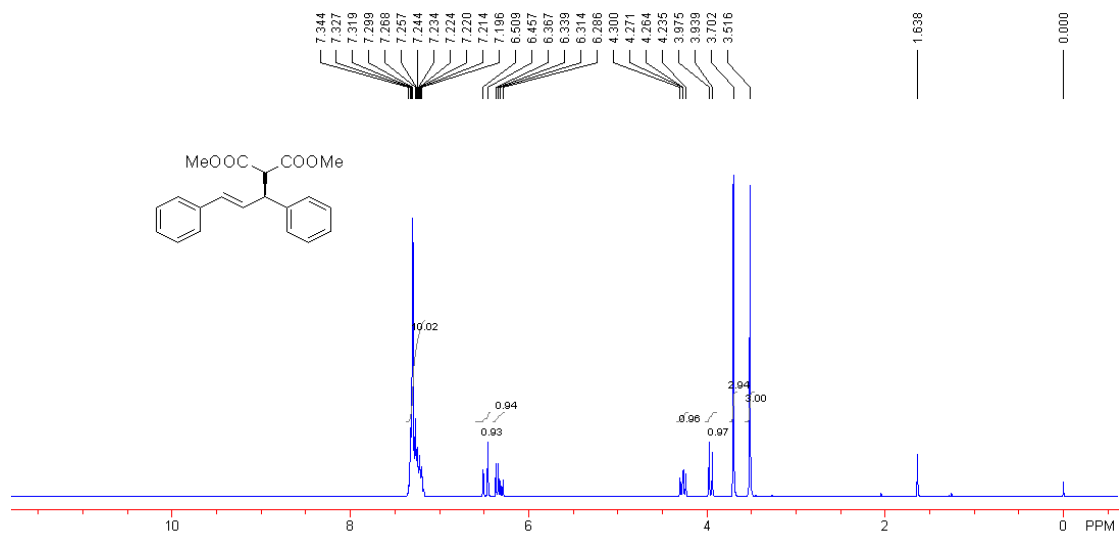
A mixture of ligand (*S_p*)-**L1** (9.4 mg, 0.012 mmol, 97% ee) and [Pd(C₃H₅)Cl]₂ (1.5 mg, 0.004 mmol) in dry THF (2 mL) was stirred at room temperature for 0.5 h, and to the resulting yellow solution was added **4** (50.4 mg, 0.2 mmol). After an additional stirring for 10 min, sodium dimethyl malonate [generated in situ by adding dimethyl malonate (79.2 mg, 0.6 mmol) and sodium hydride (14.4 mg, 0.6 mmol) in 1 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 NH₄Cl (aq.) and extracted with ether. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and filtrated. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum = 1/15) to give (*S*)-**6** (61 mg, 94% yield, 44% ee). Analytical data for (*S*)-**6**^[6]: [α]_D²⁰ = -8.8° (*c* = 1.4 chloroform, 44% ee). ¹H NMR (300 MHz, CDCl₃) δ 3.52 (s, 3H), 3.70 (s, 3H), 3.96 (d, *J* = 10.8 Hz, 1H), 4.27 (dd, *J* = 8.8, 10.4 Hz, 1H), 6.33 (dd, *J* = 8.4, 15.9 Hz, 1H), 6.48 (d, *J* = 15.6 Hz, 1H), 7.17–7.33 (series of 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) = 8.507 min, *t* (major) = 9.140 min. The absolute configuration of the product (*S*)-**6** was assigned as (*S*) by comparing the optical rotation with that reported in the literature [6].

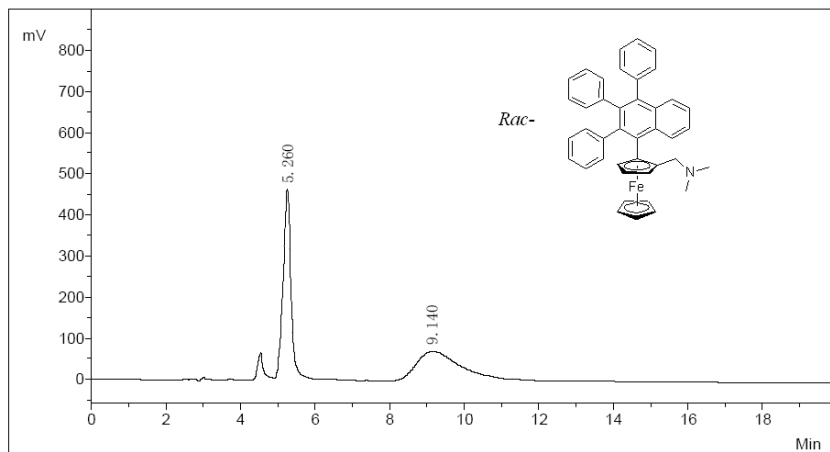
References

- (1) Khrushcheva, N. S.; Sokolov, V. I. *Russ. Chem. Bull.* **2004**, *53*, 830–833.
- (2) Bhat, A. R.; Bhat, A. I.; Athar, F.; Azam, A. *Helv. Chim. Act.* **2009**, *92*, 1644–1656.
- (3) Michael, W.; Ulrike, N.; Kurt, M. *Tetrahedron: Asymmetry* **1999**, *10*, 4369–4391.
- (4) Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett.* **2002**, *4*, 3199–3202

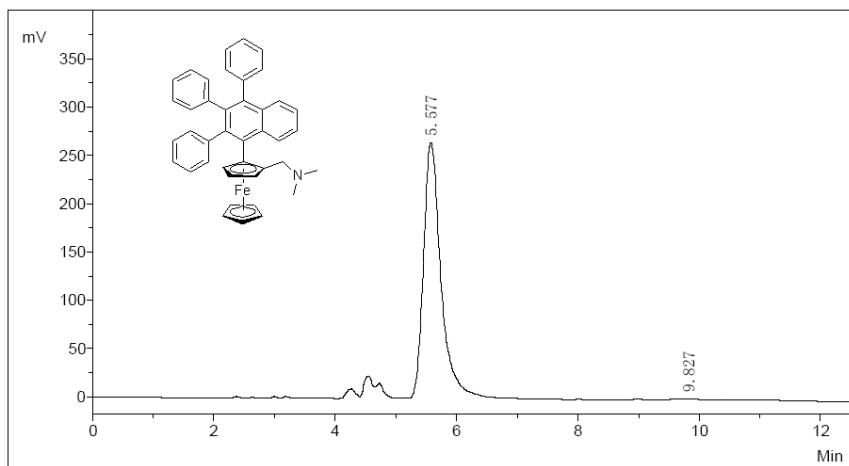
- (5) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301–6311.
- (6) Hayashi, T.; Yamamoto, A.; Hagihara, T.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 191–194.



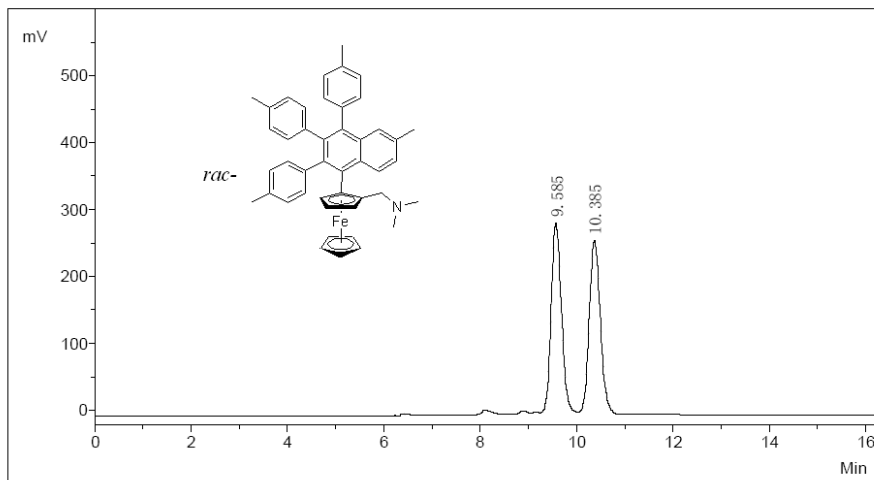




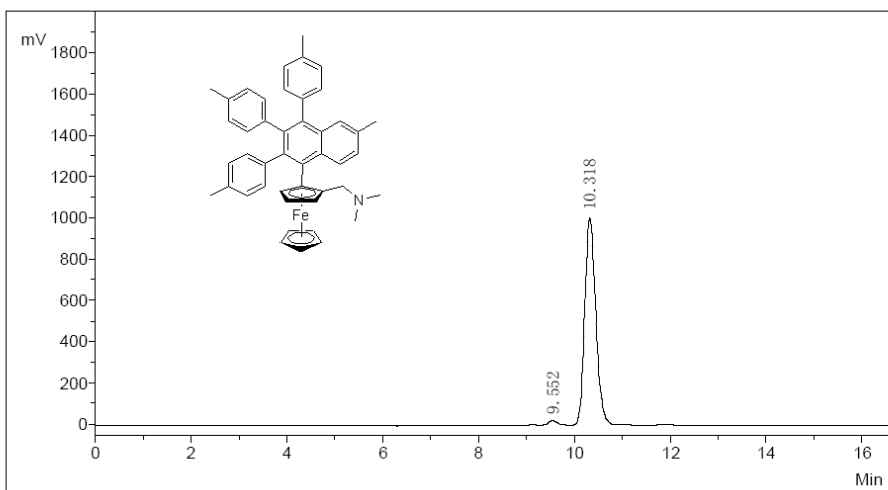
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		5.260	455177.3	6524683.9	51.0654
2	2		9.140	71564.6	6252421.1	48.9346
Total				526741.9	12777105.0	100.0000



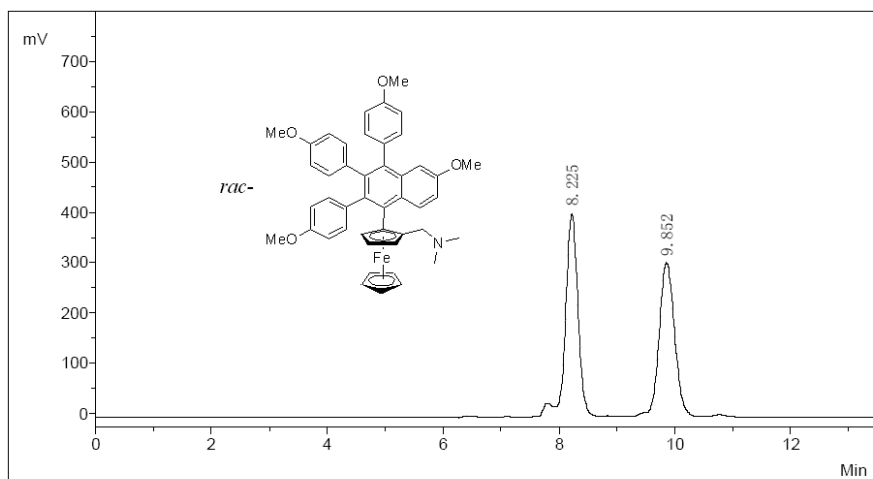
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		5.577	264324.1	5263154.8	99.0179
2	2		9.827	1280.4	52201.6	0.9821
Total				265604.5	5315356.5	100.0000



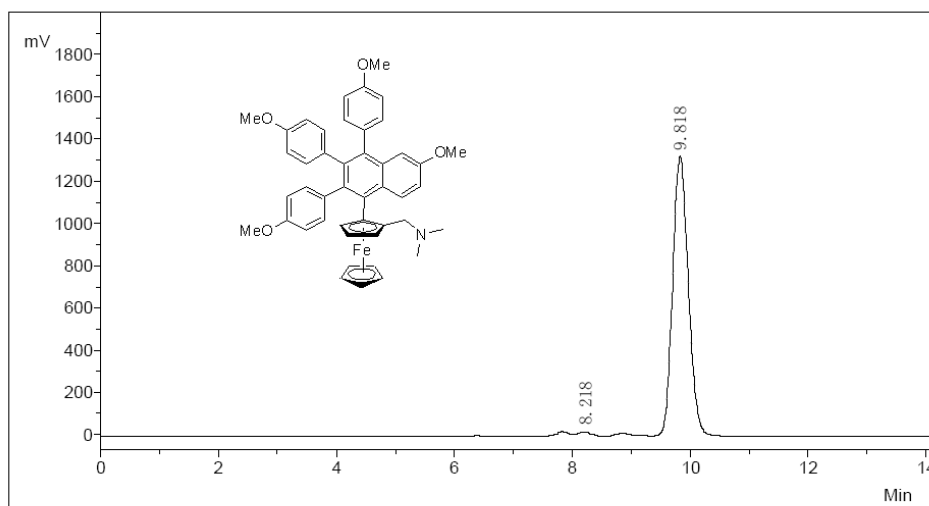
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		9.585	282080.5	4217669.7	50.9092
2	2		10.385	256623.8	4067027.2	49.0908
Total				538704.3	8284697.0	100.0000



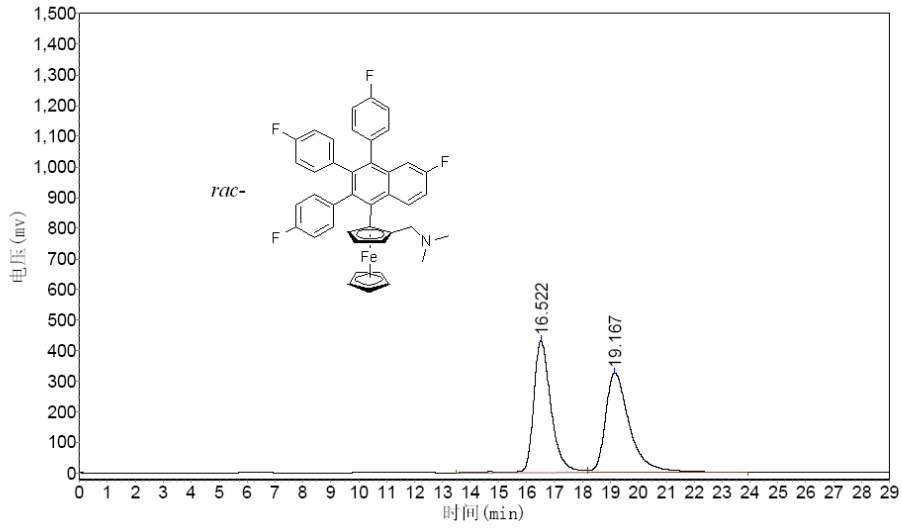
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		9.552	20173.1	283294.8	1.7260
2	2		10.318	1004494.0	16129919.7	98.2740
Total				1024667.0	16413214.5	100.0000



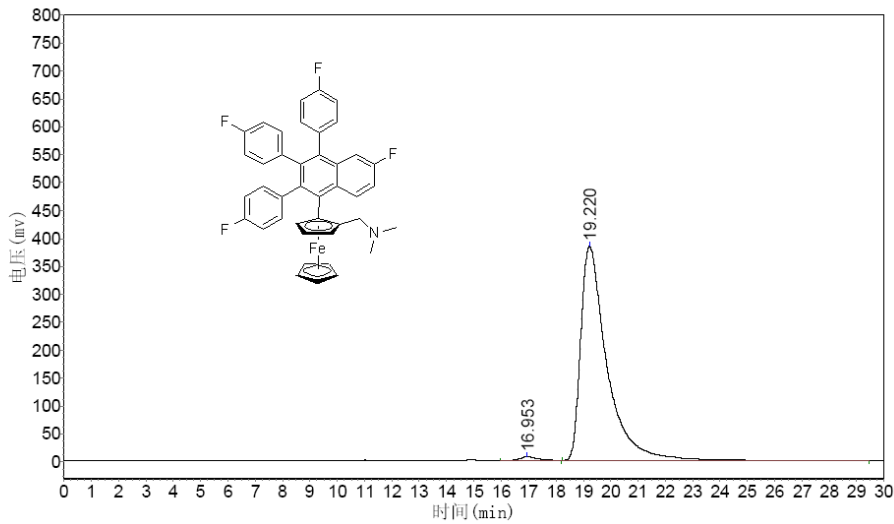
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		8.225	392907.1	5355204.4	48.5611
2	2		9.852	306171.9	5672562.1	51.4389
Total				699079.1	11027766.5	100.0000



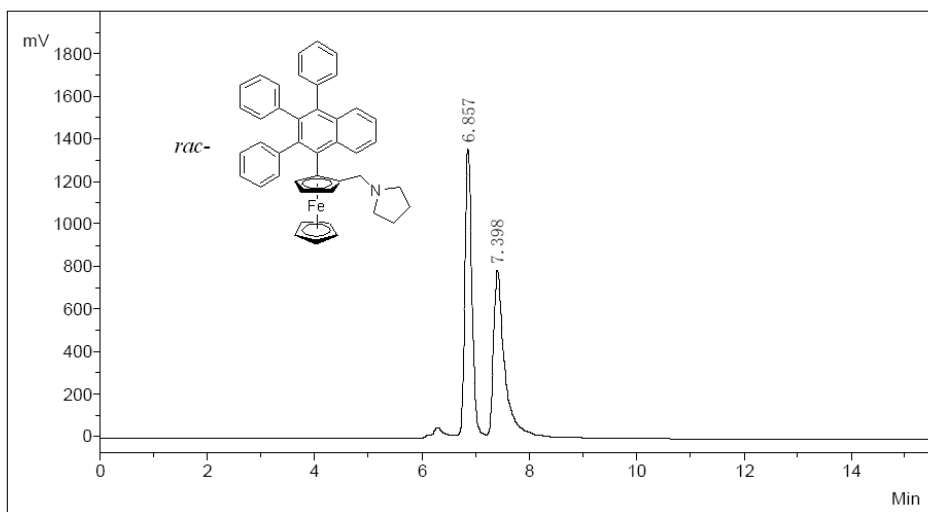
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		8.218	13115.0	143279.9	0.5833
2	2		9.818	1317328.3	24422418.8	99.4167
Total				1330443.3	24565698.7	100.0000



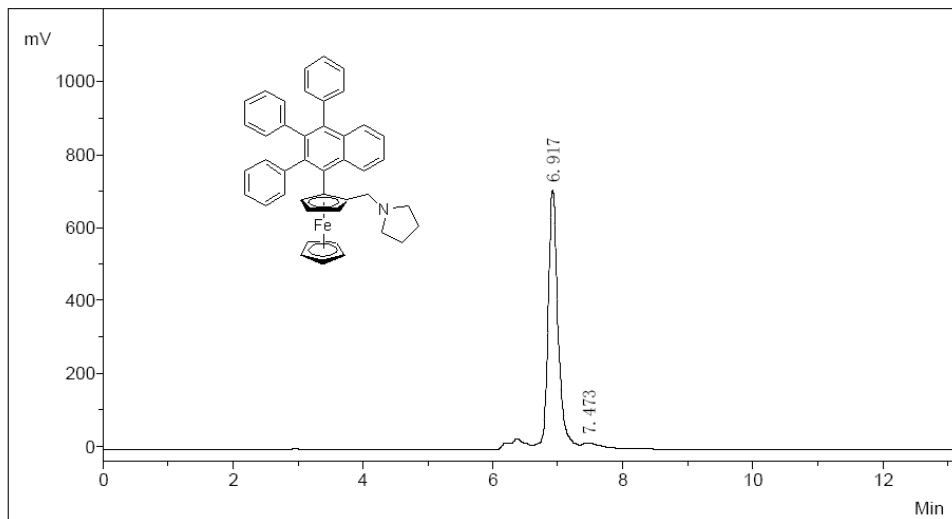
PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	16.522	432494.094	18804770.000	49.0590
2	19.167	325761.031	19526184.000	50.9410
Total		758255.125	38330954.000	100.0000



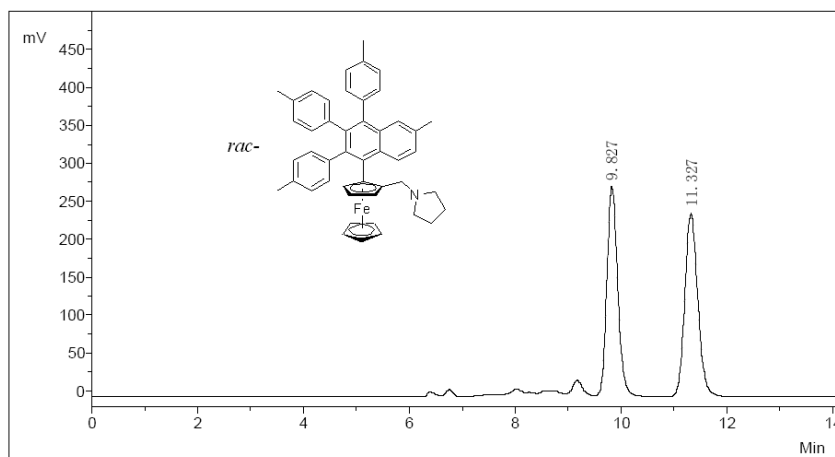
PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	16.953	6457.522	361496.344	1.3749
2	19.220	384619.594	25931188.000	98.6251
Total		391077.116	26292684.344	100.0000



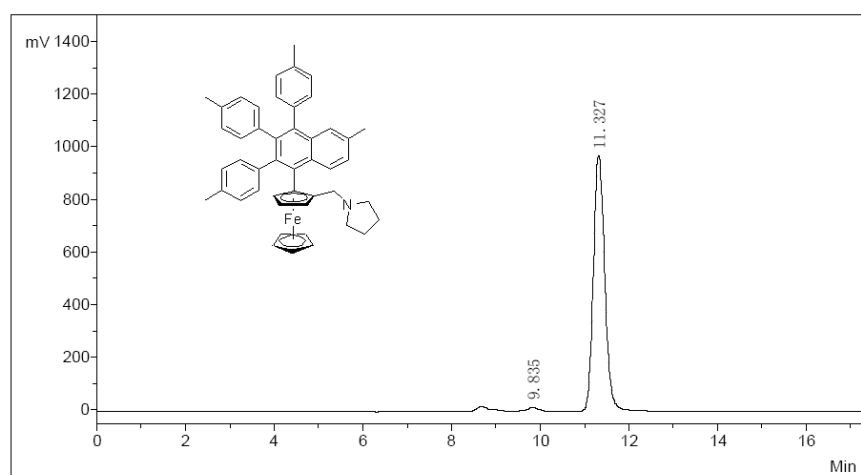
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		6.857	1341416.0	11818219.4	51.5591
2	2		7.398	772948.8	11103491.1	48.4409
Total				2114364.8	22921710.5	100.0000



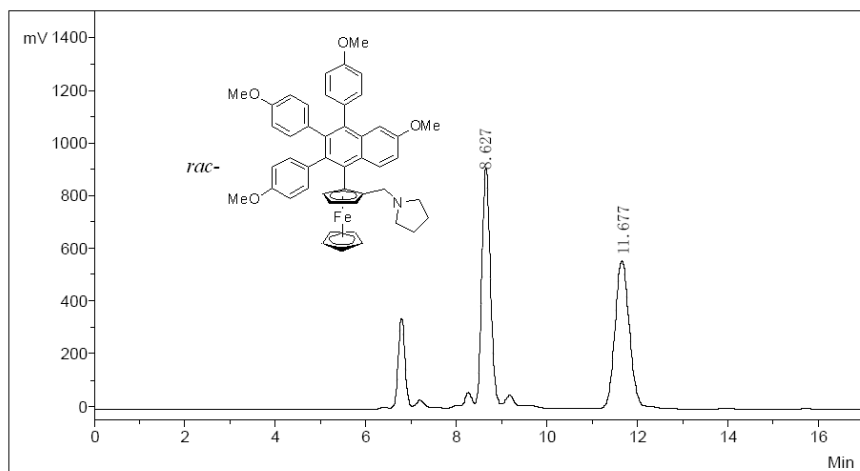
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		6.917	699828.0	7169651.8	97.6677
2	2		7.473	12231.9	171210.5	2.3323
Total				712059.9	7340862.4	100.0000



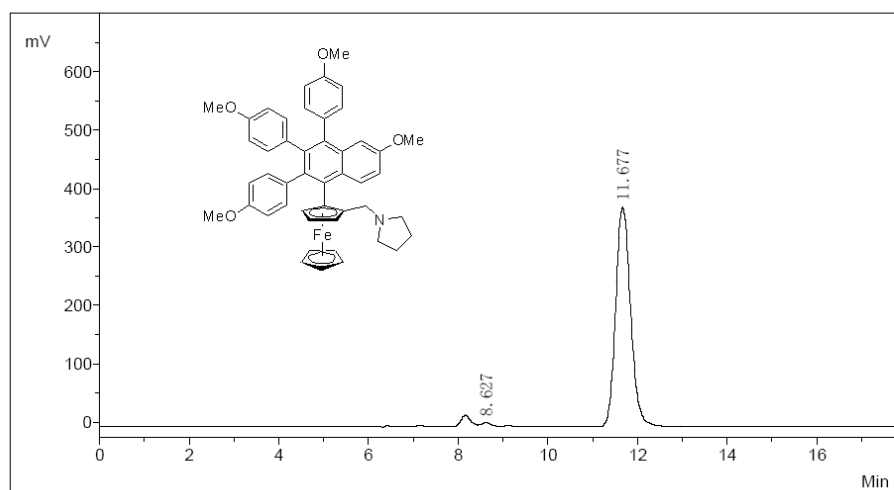
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		9.827	275220.9	3882593.2	48.7036
2	2		11.327	240766.1	4089283.3	51.2964
Total				515987.0	7971876.6	100.0000



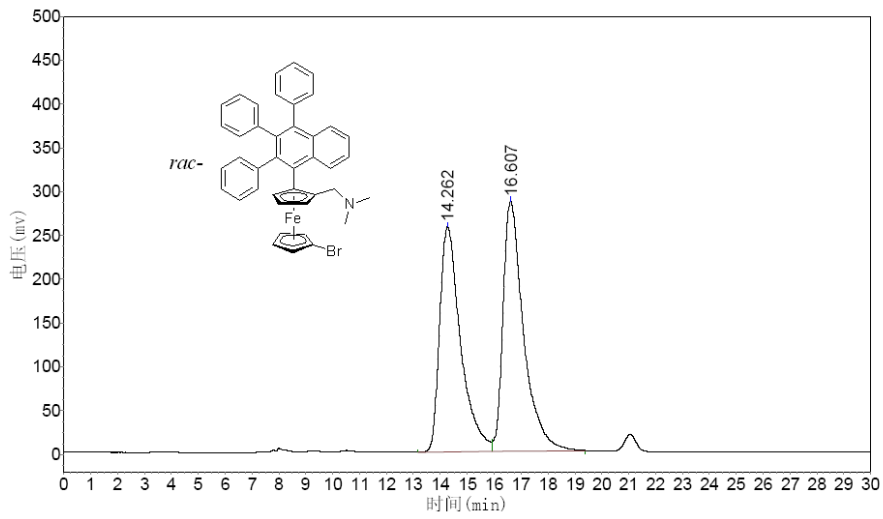
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		9.835	15306.8	247486.5	1.4074
2	2		11.327	970572.0	17337145.5	98.5926
Total				985878.8	17584632.0	100.0000



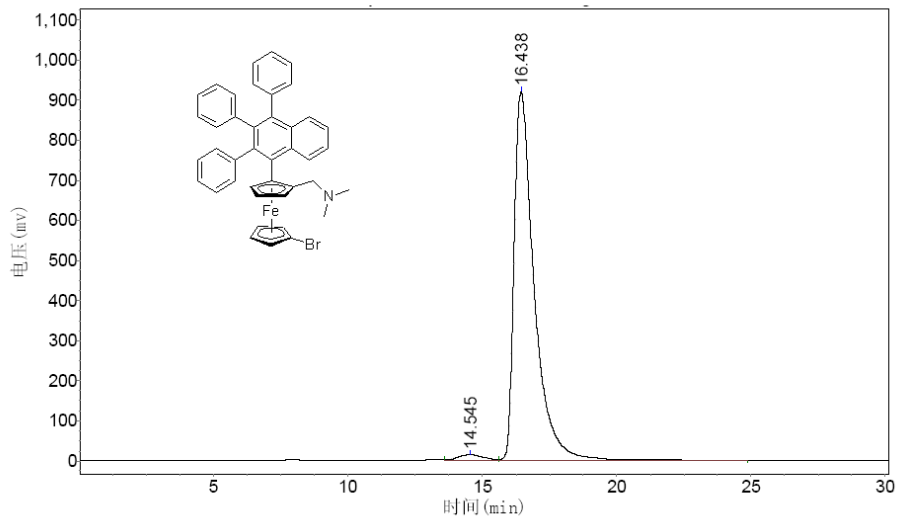
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		8.627	858645.1	11436145.9	48.8049
2	2		11.677	549721.2	11996248.2	51.1951
Total				1408366.3	23432394.1	100.0000



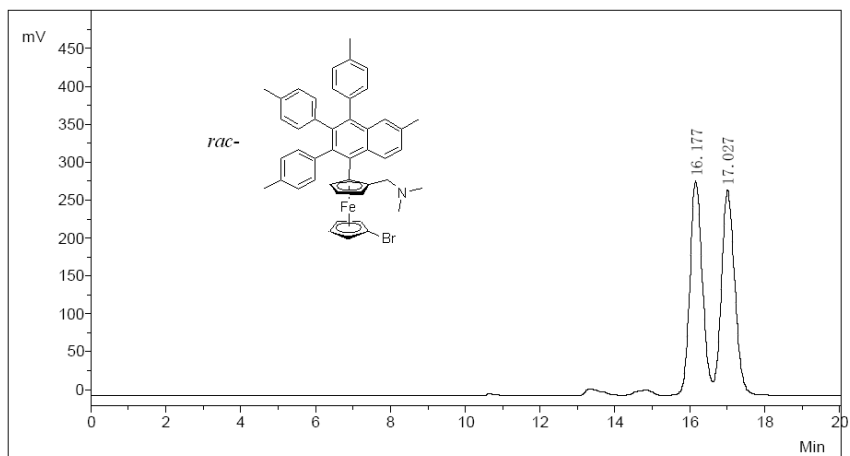
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		8.627	3837.3	45509.4	0.5188
2	2		11.677	375535.7	8725694.8	99.4812
Total				379373.0	8771204.2	100.0000



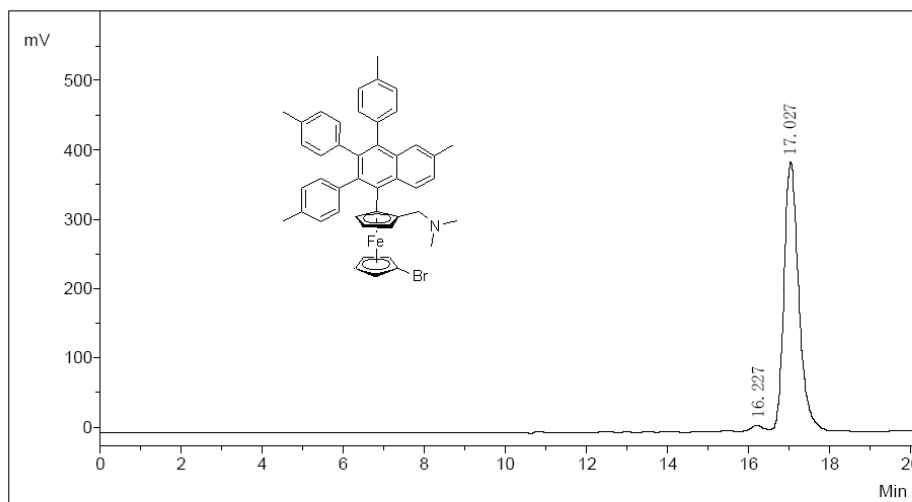
PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	14.262	257082.922	13896266.000	48.0055
2	16.607	285364.188	15050990.000	51.9945
Total		542447.109	28947256.000	100.0000



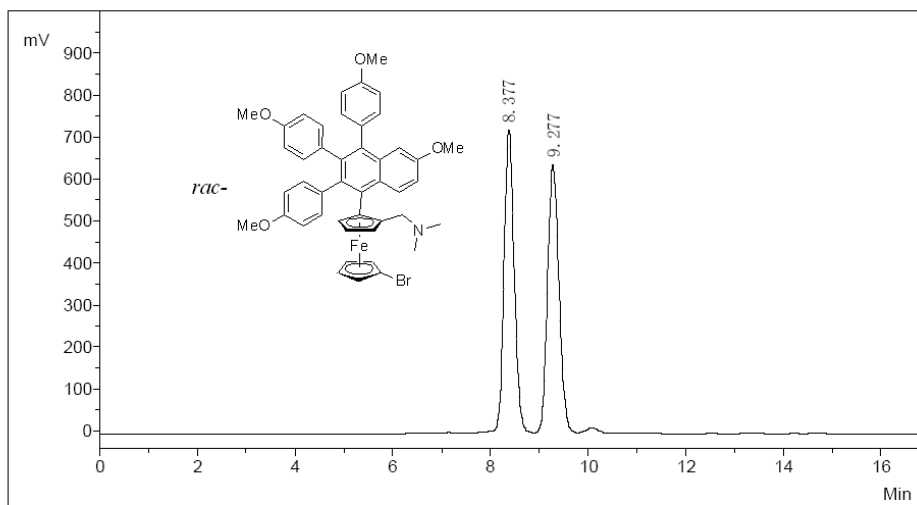
PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	14.262	257082.922	13896266.000	48.0055
2	16.607	285364.188	15050990.000	51.9945
Total		542447.109	28947256.000	100.0000



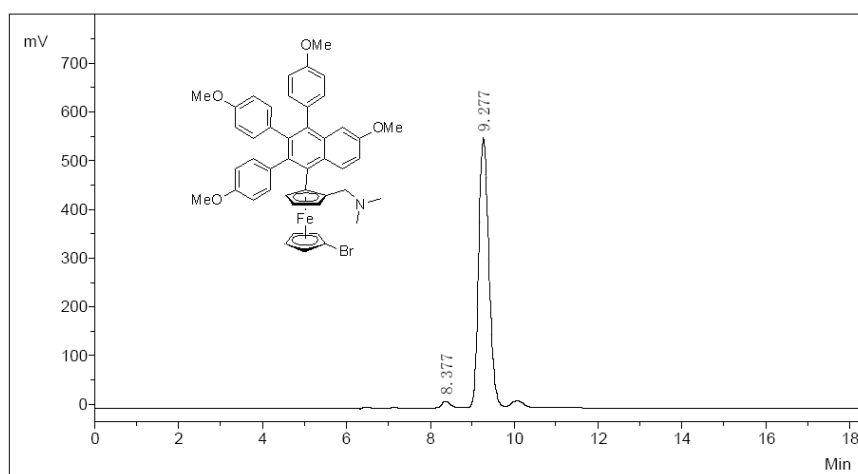
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		16.177	279914.6	6534434.8	49.2680
2	2		17.027	269295.8	6728597.1	50.7320
Total				549210.4	13263031.9	100.0000



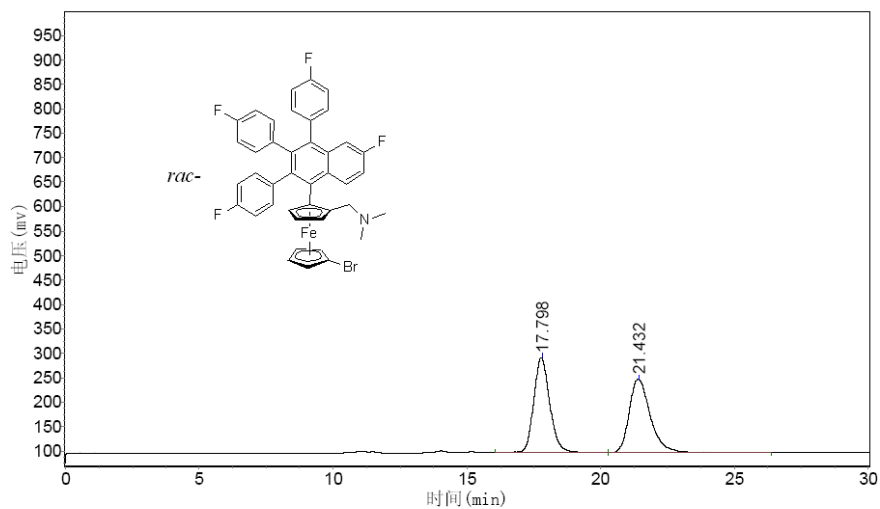
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		16.227	8941.5	213167.7	2.0942
2	2		17.027	388019.3	9965877.3	97.9058
Total				396960.7	10179045.0	100.0000



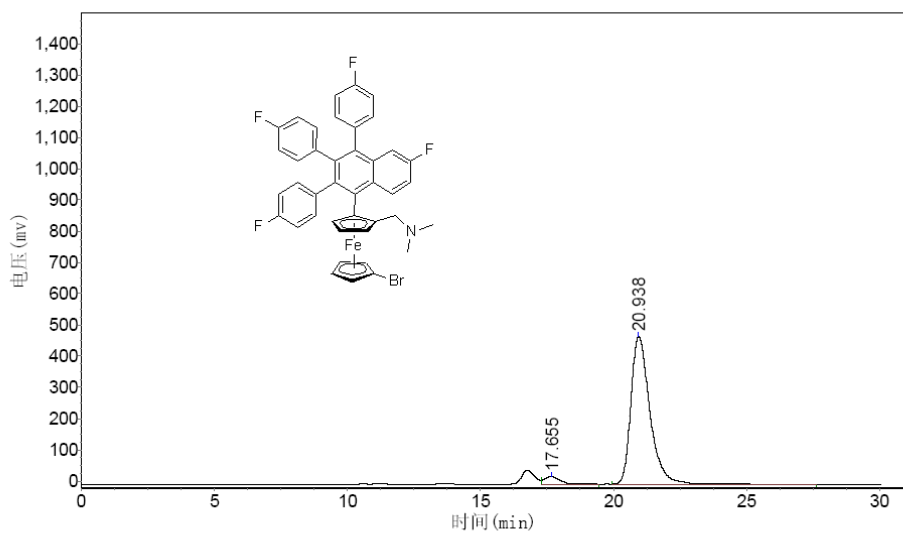
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		8.377	721269.0	10584821.6	50.4867
2	2		9.277	639616.7	10380726.0	49.5133
Total				1360885.7	20965547.6	100.0000



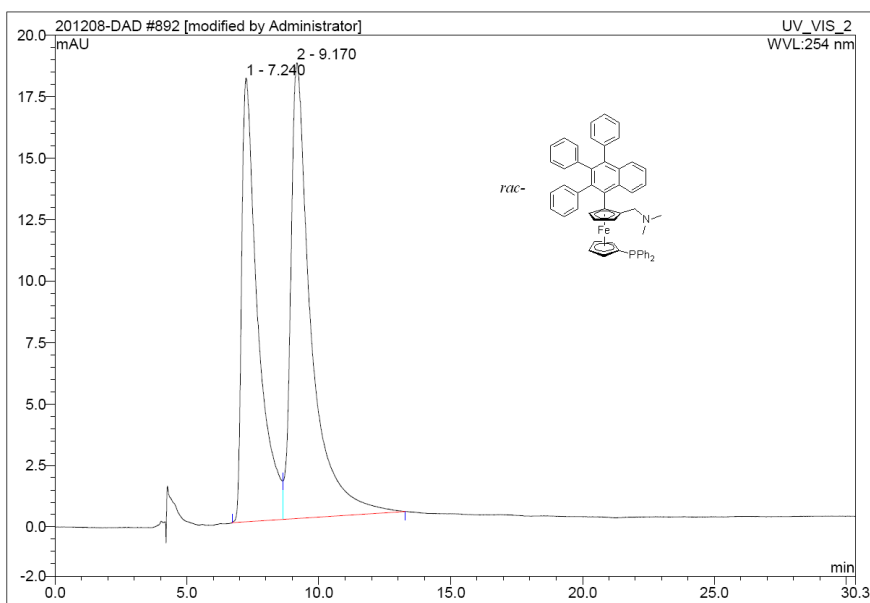
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		8.377	14377.1	208847.4	2.2047
2	2		9.277	550513.7	9264058.5	97.7953
Total				564890.8	9472905.9	100.0000



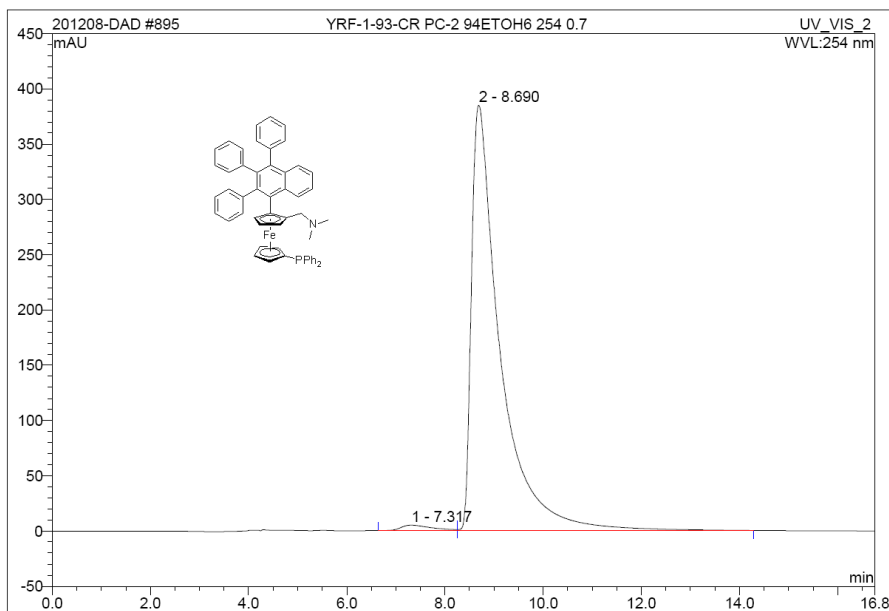
PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	17.798	195255.219	8292356.000	49.7119
2	21.432	150282.000	8388480.000	50.2881
Total		345537.219	16680836.000	100.0000



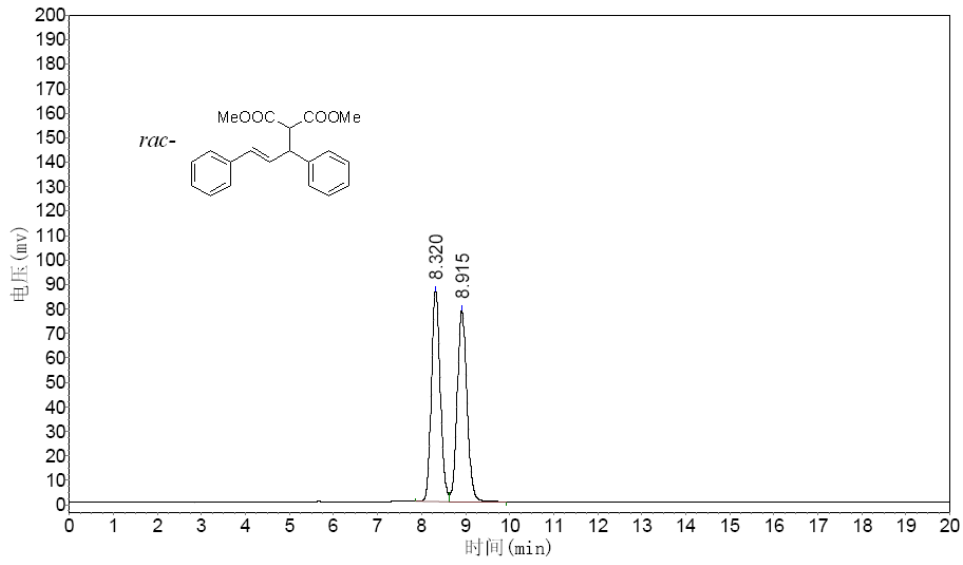
PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	17.655	25205.662	1033276.938	4.2002
2	20.938	471440.938	23567194.000	95.7998
Total		496646.600	24600470.938	100.0000



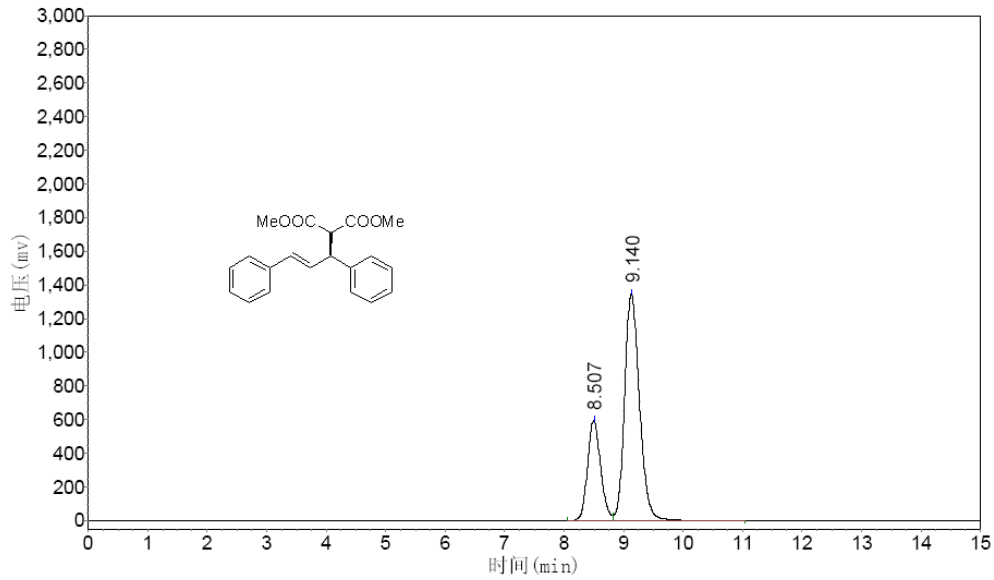
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.24	n.a.	18.048	12.783	43.62	n.a.	BM *
2	9.17	n.a.	18.536	16.521	56.38	n.a.	MB*
Total:			36.584	29.303	100.00	0.000	



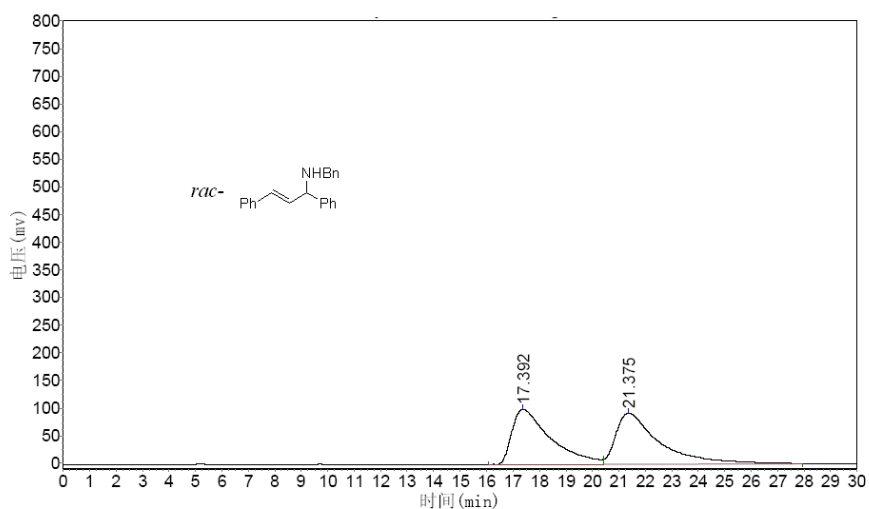
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.32	n.a.	4.900	3.551	1.35	n.a.	BM
2	8.69	n.a.	384.839	259.539	98.65	n.a.	MB
Total:			389.740	263.090	100.00	0.000	



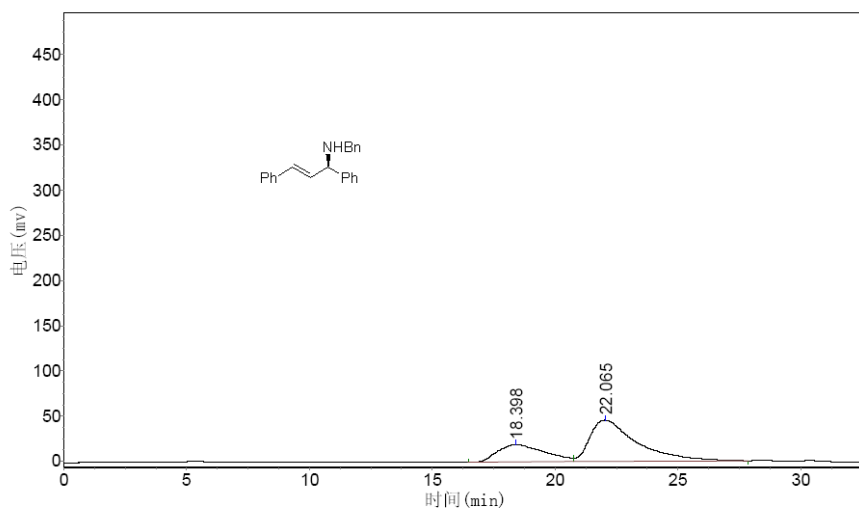
PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	8.320	85921.734	1200669.500	49.6353
2	8.915	78175.141	1218312.125	50.3647
Total		164096.875	2418981.625	100.0000



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	8.507	591039.375	9057392.000	27.8780
2	9.140	1346444.000	23431976.000	72.1220
Total		1937483.375	32489368.000	100.0000



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	17.392	99232.867	10057614.000	48.9027
2	21.375	92170.680	10508958.000	51.0973
Total		191403.547	20566572.000	100.0000



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	18.398	19460.605	2660869.750	28.5714
2	22.065	46957.941	6652172.500	71.4286
Total		66418.547	9313042.250	100.0000