Dynamic Parallel Kinetic Resolution of α-Ferrocenyl Cation Initiated by Chiral Brønsted Acid Catalyst

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Contents:

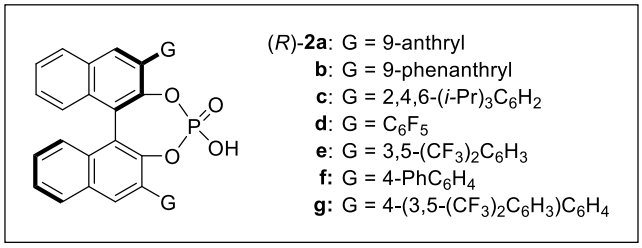
1. General information

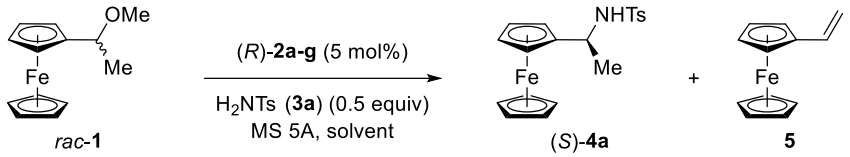
^{1}H NMR spectra were recorded on a JEOL JNM-ECA600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, C_6D_6: 7.16 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, br = broad, m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECA600 (150.9 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm, C_6D_6: 128.0 ppm). Analytical thin layer chromatography (TLC) was performed on Merck pre-coated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on silica gel 60 N (Merck: 0.040-0.063 mm, 230-400 mesh ASTM). Short column chromatography was performed on Al_2O_3 (Merck: alminium oxide 90 standardized). High-performance liquid chromatography (HPLC) was performed on a Jasco equipped with a variable wavelength detector using Daicel chiral column (0.46 × 25 cm). Optical rotations were measured on a Jasco P-1020 digital polarimeter with a sodium lamp and reported as follows; $[\alpha]^{T\,^{\circ}C}{}_{D}$ (*c* = g/100 mL, solvent). Infrared (IR) spectra were recorded on a Jasco FT/IR-4100 spectrometer. Mass spectra analysis was performed on a Bruker Daltonics solariX 9.4T and a JEOL JMS-T100GCV spectrometer at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University. Unless otherwise noted, all reactions were carried out under argon atmosphere in dried glassware. All substrates were purified by column chromatography to use. Toluene, dichloromethane (CH_2Cl_2), diethyl ether (Et_2O) and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as "Dehydrated solvent system". Other solvents were dried over activated MS 4A and used under argon atmosphere. Reagents were purchased from commercial suppliers and used without further purification. The other simple chemicals were used as such.

2. Optimization of reaction conditions

Optimization of reaction conditions is shown in Table S1. We found that MS 5A is necessary for the removal of methanol. It can be considered that the methanol addition to the ferrocenyl cation is competitive to the amination by **3a** in the absence of MS 5A.

Table S1. Optimization of reaction conditions[a]

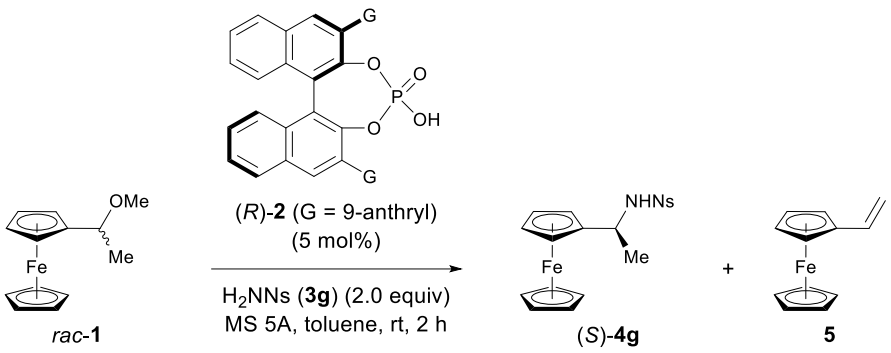




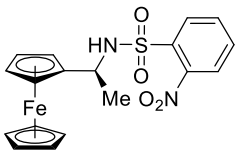
entry	(*R*)-**2**	solvent	MS 5A	temp.	time	% conv.	% yield[b]		% ee[c]
							4a	**5**	
1	**2a**	toluene	+	rt	6 h	100	50	50	40
2	**2a**	toluene	-	rt	1.5 d	20	8	11	nd
3	**2b**	toluene	+	rt	6 h	100	50	50	39
4	**2c**	toluene	+	rt	12 h	100	16	84	-6
5	**2d**	toluene	+	rt	6 h	100	50	50	13
6	**2e**	toluene	+	rt	6 h	100	50	50	<1
7	**2f**	toluene	+	rt	6 h	100	50	50	-3
8	**2g**	toluene	+	rt	6 h	100	50	50	33
9	**2a**	toluene	+	0 °C	8 h	100	50	50	40
10	**2a**	toluene	+	40 °C	4 h	100	47	53	39
11	**2a**	CH_2Cl_2	+	rt	24 h	93	35	49	12
12	**2a**	MeCN	+	rt	24 h	71	6	65	11
13	**2a**	Et_2O	+	rt	24 h	78	23	37	33

[a] Unless otherwise noted, all reactions were performed using 0.20 mmol *rac*-**1**, 5 mol% of catalyst **2**, 0.5 equiv. of **3a** in the indicated solvent (0.2 M). [b] Determined by crude ^{1}H NMR analysis (in C_6D_6) using 1,3-benzodioxole as an internal standard. [c] Determined by chiral stationary phase HPLC analysis.

3. Parallel kinetic resolution of an α-ferrocenyl cation catalyzed by a chiral phosphoric acid



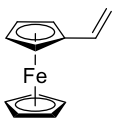
Representative procedure: To a solution of MS 5A (150 mg), **1** (48.8 mg, 200 μmol), and H_2NNs (**3g**) (80.9 mg, 400 μmol) in toluene (1 mL) was added (*R*)-**2** (5 mol%, 7.0 mg, 10 μmol)[1] at room temperature. The atmosphere was replaced with argon (×3), and the mixture was stirred at room temperature for 2 hours. The reaction mixture was quenched by NEt_3, and then passed through a pad of Al_2O_3 with EtOAc. After removing solvents in vacuo, the NMR yield was determined by ^1H NMR spectrum in C_6D_6 using 1,3-benzodioxole as an internal standard. The crude material was purified by flash column chromatography on silica gel (Hexane/EtOAc = 100/1-1/1 as eluent) to give **4g** in 47% yield as a brown solid and vinylferrocene (**5**) in 43% yield as an orange solid. The enantiomeric excess of **4g** was determined by chiral stationary phase HPLC analysis (95% ee).



(*S*)-**4g**

(*S*)-2-Nitro-*N*-(1-ferrocenylethyl)benzenesulfonamide (4g): Brown solid (mp 86-88 °C); R_f = 0.40 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak IB-3 (Hexane/EtOH = 90/10, 0.8 mL/min, 254 nm, 30 °C) 15.1 (minor), 16.8 (major) min, (95% ee); $[\alpha]^{25}_D$ = -124.9 (*c* 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz), δ 1.51 (3H, d, *J* = 6.6 Hz), 3.93-3.94 (1H, m), 3.98-3.99 (1H, m), 4.07-4.09 (2H, m), 4.22 (5H, s), 4.39 (1H, qui, *J* = 6.6 Hz), 5.69 (1H, d, *J* = 6.6 Hz), 7.71-7.75 (2H, m), 7.87-7.91 (1H, m), 8.15-8.19 (1H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ 22.1, 49.3, 65.3, 67.3, 68.0, 68.2, 68.6, 90.2, 125.3, 130.5, 132.9, 133.3, 135.0, 147.7; IR (ATR): 3359, 3097, 2980, 1540, 1393, 1344, 1168, 1106, 1059, 1029, 1002, 964, 905, 853, 821 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{18}FeN_2O_4S$ ($[M+Na]^+$) 437.0229, Found 437.0229.

Configuration assignment: The absolute configuration of **4** was determined to be (*S*) by comparing the optical rotation with the stereochemically known compound; see section 4 for detail.

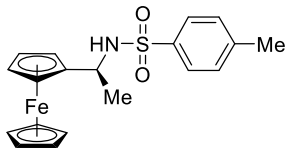


5

Vinylferrocene (5): Orange solid (mp 51-53 °C); R_f = 0.45 (Hexane); ^1H NMR ($CDCl_3$, 600 MHz), δ 4.11 (5H, s), 4.21 (2H, t, *J* = 1.8 Hz), 4.36 (2H, t, *J* = 1.8 Hz), 5.03 (1H, dd, *J* = 10.8, 1.2 Hz), 5.34 (1H, dd, *J* = 17.4, 1.2 Hz), 6.46 (1H, dd, *J* = 17.4, 10.8 Hz); ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ 66.6, 68.6, 69.2, 83.5, 111.0, 134.6; IR (ATR): 3082, 3006, 1632, 1621, 1409, 1386, 1240, 1103, 1045, 1028, 999, 895, 823, 811 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{12}Fe$ ($[M+H]^+$) 213.0361,

(1) Chiral phosphoric acid **2** was prepared according to a known method, see: Terada, M.; Toda, Y. *J. Am. Chem. Soc.* **2009**, *131*, 6354-6355. **2** was purified by the following method: **2** purified with silica gel (Merck: Catalog No.109385) column chromatography was dissolved in MeOH. Next, aqueous HCl solution (2 *M*) was added to the resultant MeOH solution to give a white suspension. The resultant suspension was extracted with CH_2Cl_2 (×3), and then the combined organic layer was washed with water, dried over Na_2SO_4, filtered, and concentrated. The resultant residue was recrystallized from EtOH/hexane, and dried under reduced pressure for more than 12 h to use.

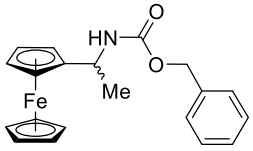
Found 213.0361.



(*S*)-**4a**

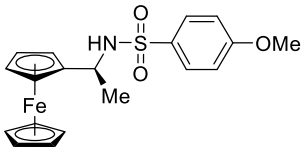
(*S*)-4-Methyl-*N*-(1-ferrocenylethyl)benzenesulfonamide (4a): Orange solid (mp 134-136 °C); R_f = 0.25 (Hexane/EtOAc = 4/1); HPLC analysis Chiralpak IA-3 (Hexane/IPA = 90/10, 1.0 mL/min, 254 nm, 30 °C) 22.8 (minor), 24.3 (major) min, (40% ee); $[\alpha]^{24}_D$ = -4.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz), δ 1.41 (3H, d, *J* = 6.6 Hz), 2.44 (3H, s), 3.93 (1H, brs), 3.96 (1H, brs), 4.09-4.10 (2H, m), 4.14-4.19 (6H, m), 4.63 (1H, d, *J* = 6.6 Hz), 7.32 (2H, d, *J* = 7.8 Hz), 7.80 (2H, d, *J* = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ 21.5, 22.1, 48.4, 65.6, 66.9, 67.9, 68.0, 68.5, 91.0, 127.0, 129.6, 138.0, 143.2; IR (ATR): 3284, 3094, 2979, 2935, 1411, 1328, 1160, 1092, 1028, 966, 906, 815 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{21}FeNO_2S$ ($[M+Na]^+$) 406.0535, Found 406.0535.

Configuration assignment: The absolute configuration was assigned as (*S*) by analogy.



4d

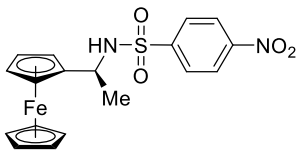
Benzyl 1-ferrocenylethylcarbamate (4d): Orange solid (mp 56-58 °C); R_f = 0.40 (Hexane/EtOAc = 4/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 90/10, 1.0 mL/min, 254 nm, 30 °C) 15.6, 17.6 min, (<1% ee); ^{1}H NMR ($CDCl_3$, 600 MHz), δ 1.47 (3H, d, *J* = 6.6 Hz), 4.12-4.19 (9H, m), 4.64 (1H, qui, *J* = 6.6 Hz), 4.93 (1H, d, *J* = 6.6 Hz), 5.13 (2H, s), 7.31-7.40 (5H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ 21.3, 45.6, 65.7, 66.5, 66.9, 67.6, 67.9, 68.4, 91.5, 128.0, 128.1, 128.5, 136.6, 155.4; IR (ATR): 3429, 3330, 3091, 3033, 2974, 1696, 1497, 1453, 1323, 1221, 1105, 1047, 1026, 1001, 819 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{21}FeNO_2$ ($[M+Na]^+$) 386.0814, Found 386.0814.



(*S*)-**4e**

(*S*)-4-Methoxy-*N*-(1-ferrocenylethyl)benzenesulfonamide (4e): Orange solid (mp 131-133 °C); R_f = 0.50 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak IA-3 (Hexane/IPA = 90/10, 1.0 mL/min, 254 nm, 30 °C) 33.2 (minor), 35.7 (major) min, (28% ee); $[\alpha]^{25}_D$ = -4.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz), δ 1.42 (3H, d, *J* = 6.6 Hz), 3.88 (3H, s), 3.92-3.93 (1H, m), 3.96-3.97 (1H, m), 4.09-4.10 (2H, m), 4.12-4.17 (6H, m), 4.63 (1H, d, *J* = 6.6 Hz), 6.99 (2H, d, *J* = 9.0 Hz), 7.85 (2H, d, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ 22.1, 48.3, 55.6, 65.7, 67.0, 68.0, 68.1, 68.5, 91.1, 114.2, 129.2, 132.7, 162.8; IR (ATR): 3245, 2970, 1596, 1497, 1432, 1316, 1301, 1257, 1155, 1094, 1024, 963, 904, 830, 813 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{21}FeNO_3S$ ($[M+Na]^+$) 422.0484, Found 422.0484.

Configuration assignment: The absolute configuration was assigned as (*S*) by analogy.



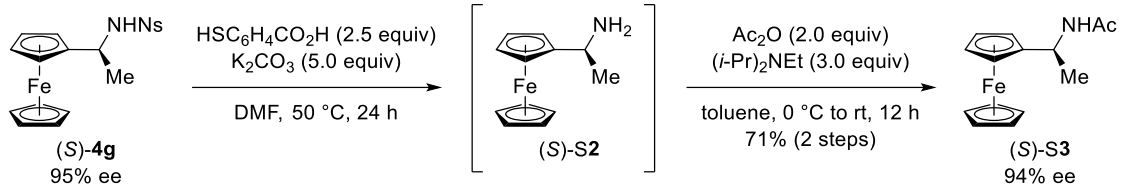
(*S*)-**4f**

(*S*)-4-Nitro-*N*-(1-ferrocenylethyl)benzenesulfonamide (4f): Brown solid (mp 175-177 °C); R_f = 0.20 (Hexane/EtOAc = 4/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 70/30, 1.0 mL/min, 254 nm, 40 °C) 23.6 (minor), 28.0 (major) min, (82% ee); $[\alpha]^{25}_D$ = +6.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz), δ 1.47 (3H, d, *J* = 6.6 Hz), 3.91-3.92 (1H, m), 3.95-3.96 (1H, m), 4.09-4.10 (1H, m), 4.10-4.11 (1H, m), 4.15 (5H, s), 4.29 (1H, qui, *J* = 6.6 Hz), 4.83 (1H, d, *J* = 6.6 Hz), 8.06 (2H, d, *J* = 9.0 Hz), 8.35 (2H, d, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ 22.1, 49.2, 65.4, 67.3, 68.2$_6$, 68.2$_8$, 68.6, 90.1, 124.3, 128.2, 147.1, 149.9; IR (ATR): 3266, 2926, 2856, 1523, 1416, 1348, 1330, 1311, 1154, 1073, 965, 854 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{18}FeN_2O_4S$ ($[M+Na]^+$) 437.0229, Found 437.0229.

Configuration assignment: The absolute configuration was assigned as (*S*) by analogy.

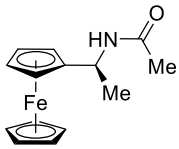
4. Determination of absolute configuration

The absolute configuration of **4g** was determined to be (*S*) by comparing the optical rotation of S**3** with the reported data.



Procedure for the derivatization of 4g to S3: To a solution of **4g** (82.9 mg, 200 μmol) in DMF (2 mL) was added 4-mercaptobenzoic acid (0.44 mg, 0.001 mmol) and K_2CO_3 (67.6 mg, 300 μmol). The mixture was stirred at 50 °C for 24 hours, and then the reaction mixture was cooled to 0 °C. The reaction mixture was treated with aqueous KOH solution (1 *M*), and the mixture was extracted with Et_2O (×3). The combined organic layers were washed with H_2O (×2) and brine, dried over Na_2SO_4, filtered, and concentrated. This material was employed for subsequent *N*-acetyl protection without further purification. Next, to a solution of S**2** in toluene (4 mL) was added (*i*-Pr)$_2$NEt (105 μL, 600 μmol) and Ac_2O (37.8 μL, 400 μmol) at 0 °C. After stirring at room temperature for 12 hours, H_2O was added to the reaction mixture, and then the mixtue was extracted with Et_2O (×3). The combined organic layers were washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography on silica gel (Hexane/EtOAc = 8/1-1/2 as eluent) afforded S**3** in 71% yield over 2 steps as an orange solid. The enantiomeric excess of S**3** was determined by chiral stationary phase HPLC analysis (94% ee).

(*S*)-Ferrocenylethylamine (S2): $[\alpha]^{27}_D$ = +23.8 (*c* 1.9, EtOH) {lit.[2] (*R*)-S**2** (>98% ee); $[\alpha]^{25}_D$ = -22.1 (*c* 3.3, EtOH)}; ^{1}H NMR ($CDCl_3$, 600 MHz), δ 1.34 (3H, d, *J* = 6.6 Hz), 1.68 (2H, brs), 3.78-3.81 (1H, m), 4.11-4.16 (9H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ 24.8, 46.0, 65.6$_5$, 65.7$_0$, 67.3, 67.4, 68.3, 96.5.

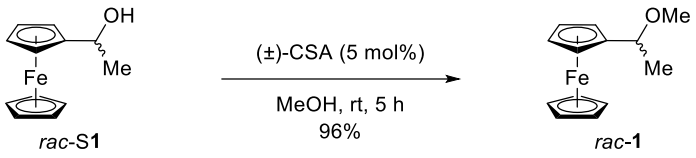


(*S*)-S**3**

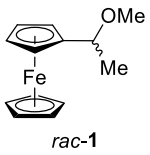
(*S*)-*N*-(1-Ferrocenylethyl)acetamide (S3): Orange solid; R_f = 0.25 (Hexane/EtOAc = 1/1); HPLC analysis Chiralcel OD-3 (Hexane/IPA = 90/10, 1.5 mL/min, 220 nm, 30 °C) 12.1 (major), 17.6 (minor) min, (94% ee); $[\alpha]^{26}_D$ = +68.1 (*c* 1.0, C_6H_6) {lit.[3] (*S*)-S**3** (>99% ee); $[\alpha]^{25}_D$ = +73.5 (*c* 1.0, C_6H_6)}; ^{1}H NMR ($CDCl_3$, 600 MHz), δ 1.46 (3H, d, *J* = 6.6 Hz), 1.98 (3H, s), 4.13-4.16 (3H, m), 4.17 (5H, s), 4.20-4.21 (1H, m), 4.89 (1H, dq, *J* = 8.4, 6.6 Hz), 5.59 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ 20.6, 23.5, 43.8, 65.6, 67.4, 67.6, 68.1, 68.5, 91.1, 168.6; IR (ATR): 3244, 3075, 2974, 2925, 2852, 1631, 1557, 1441, 1374, 1300, 1104, 1039, 818 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{17}FeNO$ ([M+Na]$^+$) 294.0552, Found 294.0551.

(2) Woltersdorf, M.; Kranich, R.; Schmalz, H.-G. *Tetrahedron* **1997**, *53*, 7219-7230.
(3) Fukuda, T.; Takehara, A.; Haniu, N.; Iwao, M. *Tetrahedron: Asymmetry* **2000**, *11*, 4083-4091.

5. Preparation of 1



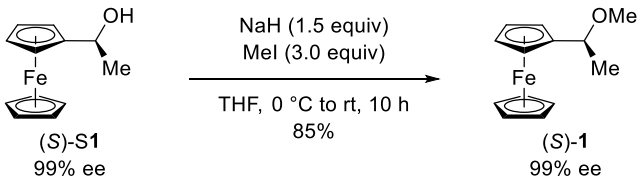
To a solution of 1-ferrocenylethanol (S**1**) (1.15 g, 5.00 mmol)[4] in MeOH (20 mL) was added (±)-CSA (5 mol%, 58.1 mg, 250 μmol) at room temperature, and the mixture was stirred at room temperature for 5 hours. The reaction mixture was quenched by NEt_3, and then the mixture was diluted with saturated aqueous $NaHCO_3$, and extracted with Et_2O (×3). The combined organic layers were washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated. After purification by flash column chromatography on silica gel (Hexane/EtOAc = 50/1-4/1 as eluent), **1** was obtained in 96% yield as an orange oil.



(1-Methoxyethyl)ferrocene (1): Orange oil; R_f = 0.40 (Hexane/EtOAc = 4/1); ^{1}H NMR (C_6D_6, 600 MHz), δ 1.45 (3H, d, *J* = 6.6 Hz), 3.14 (3H, s), 3.96-3.98 (2H, m), 3.99-4.03 (6H, m), 4.07-4.08 (1H, m), 4.10-4.11 (1H, m); ^{13}C NMR (C_6D_6, 150.9 MHz), δ 20.6, 55.5, 66.2, 67.7, 68.1, 68.7, 68.9, 74.9, 90.2; IR (ATR): 3094, 2975, 2934, 2882, 2816, 1448, 1367, 1308, 1236, 1189, 1106, 1085, 1060, 1039, 1022, 1000, 815 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{16}FeO$ ($[M+Na]^+$) 267.0443, Found 267.0442.

(4) Commercially available, purchased from Tokyo Chemical Industry (TCI) Co., Ltd.

6. Preparation of enantio-pure 1



To a solution of (*S*)-1-ferrocenylethanol ((*S*)-S**1**, 99% ee) (690 mg, 3.00 mmol)[5] in THF (30 mL) was added NaH (60% dispersion in mineral oil, 180 mg, 4.50 mmol) at 0 °C, the mixture was stirred at 0 °C for 20 minutes. MeI (560 μL) was added to the mixture at 0 °C, the mixture was allowed to warm to room temperature for 10 hours. The reaction mixture was quenched by H_2O at 0 °C, and then extracted with Et_2O (×3). The combined organic layers were washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated. After purification by flash column chromatography on silica gel (Hexane/EtOAc = 50/1-4/1 as eluent, add 1% NEt_3), enantio-pure **1** was obtained in 96% yield as an orange oil. The enantiomeric excess of **1** was determined by chiral stationary phase HPLC analysis (99% ee).

(*S*)-(1-Methoxyethyl)ferrocene (1): Orange oil; HPLC analysis Chiralpak AD-3 (Hexane/IPA = 98/2, 1 mL/min, 220 nm, 15 °C) 5.8 (major), 6.8 (minor) min, (99% ee); $[\alpha]^{25}_D$ = -33.9 (*c* 0.4, $CHCl_3$) {lit.[6] (*S*)-**1** (86% ee); $[\alpha]_D$ = -20.0 (*c* 0.2, $CHCl_3$)}.

(5) The preparation of enantio-pure S**1**, see: Tappe, K.: Knochel, P. *Tetrahedron: Asymmetry* **2004**, *15*, 91-102.
(6) Vicennati, P.; Cozzi, P. G. *Eur. J. Org. Chem.* **2007**, 2248-2253.

7. Theoretical studies of transition state analysis

All calculations were conducted using Gaussian 09, Revision C.01: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

7-1. C-N bond formation (amination) step: Cartesian coordinates

TSs

Optimization at the B3LYP/6-31G(d)

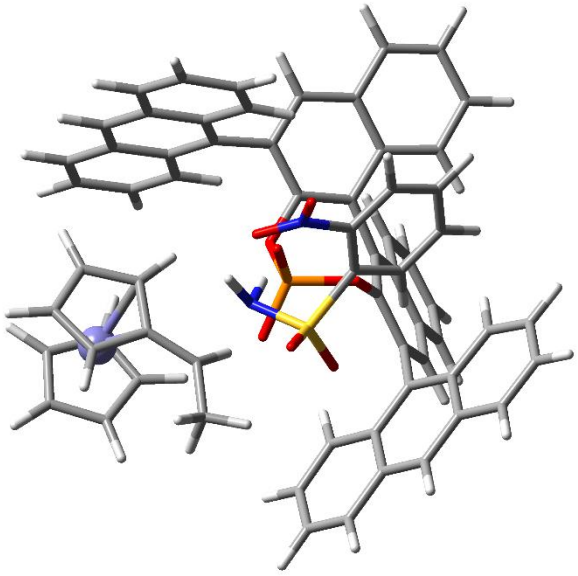
E(RB3LYP) = -5257.74455651 Hartree

Thermal correction to Gibbs Free Energy = 0.863682 Hartree

Sum of electronic and thermal Free Energies = -5256.880874 Hartree

Single point calculation at the M062X/6-311+g(d,p)

E(RM062X) = -5257.29542276 Hartree



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4	8	0	-0.028924	1.909144	-0.292253
5	8	0	-0.126251	-0.196261	-1.683197
6	6	0	0.543186	2.677244	0.695457
7	6	0	1.915159	2.901477	0.678362
8	6	0	0.243175	4.051591	2.646028
9	6	0	2.502359	3.648000	1.757552
10	6	0	-0.322899	3.269423	1.660777
11	6	0	1.644604	4.241176	2.740679
12	6	0	2.676208	0.963869	-0.685172
13	6	0	2.738663	2.327840	-0.426815
14	6	0	4.360249	1.106329	-2.394048
15	6	0	3.572177	3.147048	-1.264503
16	6	0	3.507047	0.320871	-1.648209
17	6	0	4.399533	2.516584	-2.250512
18	6	0	2.212860	4.992899	3.804611
19	6	0	3.907818	3.798145	1.924346
20	6	0	4.428396	4.519833	2.975831
21	6	0	3.575698	5.135953	3.921996
22	6	0	3.587265	4.568330	-1.193660
23	6	0	5.234659	3.314999	-3.077833
24	6	0	5.240413	4.685913	-2.966499
25	6	0	4.396936	5.315096	-2.020970
26	1	0	-0.399208	4.521938	3.386345
27	1	0	5.010330	0.636280	-3.127873
28	1	0	1.544289	5.444872	4.533747
29	1	0	4.576383	3.326189	1.213805
30	1	0	5.506018	4.613078	3.081827
31	1	0	3.999124	5.708571	4.742684
32	1	0	2.939739	5.068088	-0.482476
33	1	0	5.863458	2.816988	-3.812264
34	1	0	5.879080	5.286402	-3.608535
35	1	0	4.383221	6.399497	-1.949713
36	6	0	3.488529	-1.165363	-1.828531
37	6	0	4.177101	-1.987144	-0.905386
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43	6	0	5.545911	-2.279011	1.099991
44	1	0	4.875560	-0.385848	0.388495
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47	6	0	2.242879	-3.739707	-4.284366
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73	6	0	-3.774570	0.732782	4.578081
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79	1	0	-2.293792	5.779995	-2.106206
80	1	0	-4.266155	0.138746	5.343877
81	1	0	-4.782564	5.572289	-2.057340
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85	6	0	-3.474542	-1.871339	-1.078957
86	6	0	-4.774369	-2.295315	-1.569294
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112	6	0	0.013921	-3.865248	3.860177
113	6	0	0.510133	-3.610914	2.570528
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119	1	0	3.528675	-2.316568	3.437339
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121	1	0	-2.268910	-3.034729	1.417982
122	1	0	-1.092634	-1.917990	0.859732
123	1	0	2.644378	-2.812802	5.723688
124	7	0	-1.348120	-4.365402	4.117697
125	8	0	-1.511348	-5.070689	5.107843
126	8	0	-2.251360	-4.005280	3.361705

TSr

Optimization at the B3LYP/6-31G(d)

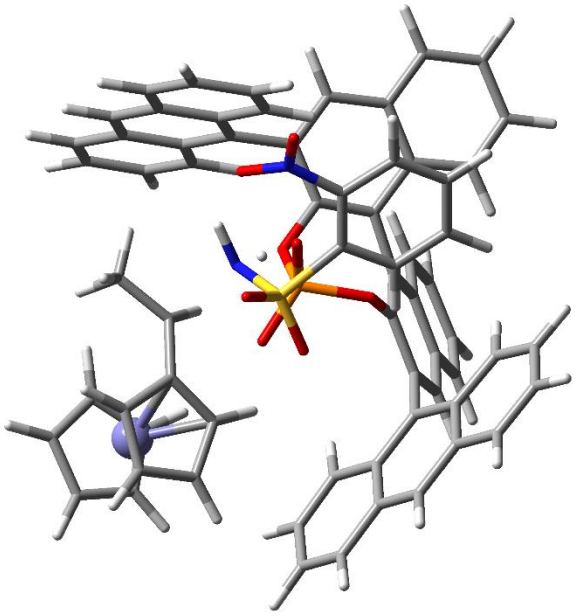
E(RB3LYP) = -5257.74190987 Hartree

Thermal correction to Gibbs Free Energy = 0.864716 Hartree

Sum of electronic and thermal Free Energies = -5256.877194 Hartree

Single point calculation at the M062X/6-311+g(d,p)

E(RM062X) = -5257.29278678 Hartree



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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11	6	0	-5.033691	-2.228086	0.517961
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13	6	0	-3.538015	1.287326	-0.051861
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15	6	0	-4.530187	2.193177	-0.565556
16	6	0	-2.104729	3.217261	0.529889

17	6	0	−4.305013	3.605227	−0.461868
18	6	0	−6.134688	−2.846953	1.169152
19	6	0	−5.776013	−0.084059	1.433737
20	6	0	−6.824438	−0.716250	2.065353
21	6	0	−7.017118	−2.110619	1.925070
22	6	0	−5.719783	1.756524	−1.213136
23	6	0	−5.285120	4.509069	−0.953800
24	6	0	−6.434286	4.050653	−1.554640
25	6	0	−6.643224	2.658499	−1.694159
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27	1	0	−2.948710	5.150744	0.207543
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32	1	0	−5.892451	0.693943	−1.337796
33	1	0	−5.100078	5.576319	−0.855647
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35	1	0	−7.539233	2.295991	−2.191055
36	6	0	−0.828268	3.738346	1.111028
37	6	0	−0.580693	3.605818	2.498672
38	6	0	0.112200	4.393954	0.281629
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53	1	0	2.466876	5.194882	2.662623
54	6	0	2.014349	5.776019	−1.320134
55	1	0	3.140123	6.052542	0.479167
56	1	0	0.671176	5.318473	−2.971567
57	1	0	0.161116	3.281306	6.345739
58	1	0	2.718101	6.322059	−1.943745
59	6	0	−2.009430	−3.247041	−1.582698
60	6	0	−1.054129	−4.045605	−0.912442
61	6	0	−2.072071	−3.246687	−2.996406
62	6	0	−0.933856	−4.072976	0.514631
63	6	0	−0.142092	−4.864327	−1.681260
64	6	0	−1.159471	−4.072654	−3.753568
65	6	0	−3.020747	−2.460921	−3.726326
66	6	0	0.008424	−4.851199	1.133980
67	1	0	−1.587009	−3.440639	1.102718
68	6	0	0.828492	−5.661043	−0.993192
69	6	0	−0.221369	−4.857776	−3.076772
70	6	0	−1.239322	−4.071115	−5.181458
71	1	0	−3.715453	−1.835976	−3.176199
72	6	0	−3.063257	−2.485110	−5.095775
73	6	0	0.905038	−5.657764	0.374325
74	1	0	0.081998	−4.848062	2.218000
75	1	0	1.502925	−6.276025	−1.585216
76	1	0	0.461790	−5.481555	−3.650582
77	6	0	−2.161555	−3.300888	−5.837098
78	1	0	−0.547505	−4.701146	−5.736146
79	1	0	−3.791774	−1.876459	−5.624579
80	1	0	1.649700	−6.261086	0.885972
81	1	0	−2.211708	−3.309140	−6.922673
82	26	0	4.095349	1.282659	−2.714344
83	6	0	4.712521	2.282997	−1.006350
84	6	0	5.371014	0.140186	−1.572698
85	6	0	4.007858	0.083366	−1.076725
86	6	0	3.609233	1.441746	−0.752666
87	6	0	5.788187	1.491111	−1.521812
88	1	0	4.721799	3.357251	−0.878970
89	1	0	5.963704	−0.697841	−1.913386
90	1	0	2.627127	1.718316	−0.395679
91	1	0	6.751573	1.866266	−1.841678
92	6	0	3.092093	−0.989869	−1.196796
93	1	0	2.047218	−0.691279	−1.209031
94	6	0	3.463256	−2.315087	−1.786933
95	1	0	2.685505	−3.062190	−1.612139
96	1	0	3.563448	−2.196391	−2.873875
97	1	0	4.418899	−2.682516	−1.402486
98	6	0	2.934104	0.545447	−4.258645
99	6	0	4.249566	0.824042	−4.729528
100	6	0	4.505946	2.210786	−4.501882
101	6	0	3.344263	2.778868	−3.895165
102	6	0	2.372633	1.748615	−3.731124
103	1	0	2.443145	−0.419183	−4.273973
104	1	0	4.933098	0.114255	−5.177018
105	1	0	5.421607	2.735932	−4.741081
106	1	0	3.235954	3.803882	−3.566130
107	1	0	1.415026	1.833071	−3.233207
108	6	0	1.407199	−0.596905	4.082150
109	6	0	0.608932	−0.852160	5.198936
110	6	0	0.670723	−2.089323	5.836340
111	6	0	1.519815	−3.081562	5.348292
112	6	0	2.286955	−2.834787	4.211949
113	6	0	2.250816	−1.584692	3.573352
114	16	0	3.315484	−1.069606	2.188776
115	7	0	2.597410	−1.756104	0.813043
116	8	0	4.641882	−1.654180	2.366229
117	8	0	3.134944	0.374310	2.066080
118	1	0	1.388045	0.373250	3.599942
119	1	0	−0.052091	−0.072143	5.563062
120	1	0	1.589133	−4.052595	5.823958
121	1	0	2.704757	−2.772302	0.867159
122	1	0	1.562230	−1.491349	0.762036
123	1	0	0.059325	−2.290993	6.710492
124	7	0	3.073284	−3.974634	3.709016
125	8	0	3.528087	−4.755420	4.537491
126	8	0	3.180383	−4.111900	2.488473

7-2. Deprotonation of cation A (protonation of vinylferrocene): Cartesian coordinates

TS of the deprotonation of (S_p)-cation A by conjugate base (*R*)-2$^-$

Optimization at the B3LYP/6-31G(d)

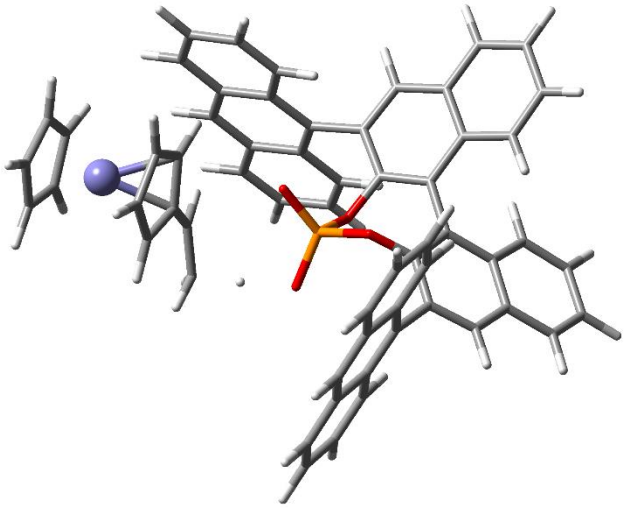
E(RB3LYP) = -4217.05232634 Hartree

Thermal correction to Gibbs Free Energy = 0.743203 Hartree

Sum of electronic and thermal Free Energies = -4216.309123 Hartree

Single point calculation at the M062X/6-311+g(d,p)

E(RM062X) = -4216.65624117 Hartree



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8	6	0	4.749150	1.852667	0.637582
9	6	0	4.795210	-0.586953	0.313128
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12	6	0	1.507223	-2.072679	-0.104701
13	6	0	2.724441	-1.728185	-0.677454
14	6	0	1.317886	-4.060945	-1.438942
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23	6	0	3.002220	-4.533032	-3.184578
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95	6	0	-7.595654	1.852073	-0.547309	102	1	0	-6.148876	0.197485	1.983114
96	6	0	-7.152854	1.816436	0.809742	103	6	0	-2.528634	1.137102	2.163669
97	6	0	-6.591884	0.529959	1.053183	104	1	0	-2.582870	0.439848	3.002586
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99	1	0	-7.509618	0.303380	-2.163647	106	1	0	-2.741403	2.173499	2.429743
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101	1	0	-7.219016	2.627209	1.523295						

TS of the deprotonation of (R_p)-cation A by conjugate base (*R*)-2$^-$

Optimization at the B3LYP/6-31G(d)

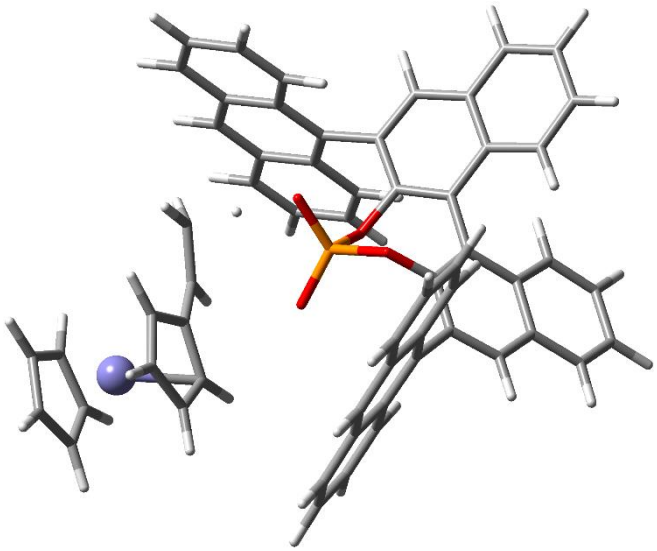
E(RB3LYP) = -4217.05152780 Hartree

Thermal correction to Gibbs Free Energy = 0.744503 Hartree

Sum of electronic and thermal Free Energies = -4216.307025 Hartree

Single point calculation at the M062X/6-311+g(d,p)

E(RM062X) = -4216.65720497 Hartree



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39	6	0	-0.569888	-4.315346	-2.229303
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41	6	0	2.774169	-4.149926	0.422497
42	6	0	1.430830	-3.042651	2.166356
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45	6	0	1.935123	-5.276922	-3.056421
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47	6	0	3.884368	-4.121897	1.324931
48	1	0	0.496723	-2.600285	2.491487
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50	6	0	0.862600	-5.334866	-3.904782
51	1	0	-1.253046	-4.898809	-4.161039
52	1	0	2.908663	-5.650387	-3.366087
53	1	0	3.853397	-5.085437	-1.184582
54	6	0	3.764132	-3.583263	2.578278
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56	1	0	2.439133	-2.581471	3.985518
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61	6	0	-2.575505	3.840622	1.228514
62	6	0	-1.916007	3.531877	-2.484278
63	6	0	-1.327576	5.297307	-0.867534
64	6	0	-1.929467	5.106585	1.489913
65	6	0	-3.196498	3.170613	2.331110
66	6	0	-1.315059	4.249117	-3.485084
67	1	0	-2.343467	2.559942	-2.696936
68	6	0	-0.712891	6.013974	-1.942951
69	6	0	-1.327831	5.800733	0.436174
70	6	0	-1.929647	5.627433	2.821789
71	1	0	-3.691463	2.222004	2.155578
72	6	0	-3.173840	3.702772	3.593668
73	6	0	-0.710125	5.510647	-3.215980
74	1	0	-1.288763	3.847545	-4.494405
75	1	0	-0.250088	6.973708	-1.723423
76	1	0	-0.851850	6.759239	0.635387

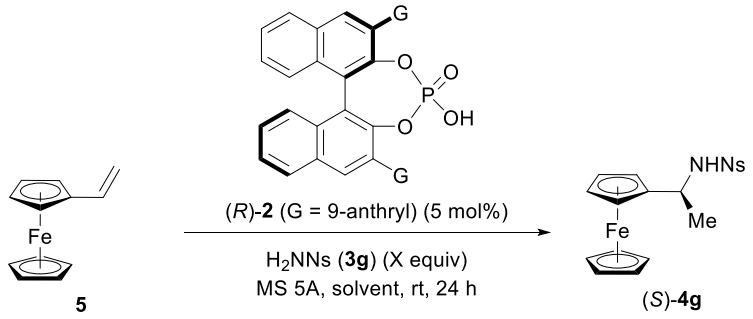
77	6	0	−2.531512	4.948366	3.846558	93	6	0	2.139352	2.517972	−1.335140
78	1	0	−1.439725	6.581995	3.000741	94	1	0	1.694799	3.467199	−1.028376
79	1	0	−3.650421	3.170791	4.412689	95	1	0	2.632478	2.552224	−2.307956
80	1	0	−0.243082	6.067071	−4.024662	96	1	0	2.389206	1.860339	0.695677
81	1	0	−2.524699	5.355692	4.854123	97	6	0	6.066061	2.248616	1.852145
82	26	0	5.705592	1.173624	0.137364	98	6	0	7.162055	1.381046	1.567281
83	6	0	5.653895	−0.331761	−1.284564	99	6	0	7.678012	1.725378	0.282055
84	6	0	4.201264	−0.157223	0.501256	100	6	0	6.905236	2.812875	−0.227220
85	6	0	3.797242	0.805791	−0.502602	101	6	0	5.913391	3.136167	0.742694
86	6	0	4.731505	0.694603	−1.602416	102	1	0	5.457758	2.234945	2.746816
87	6	0	5.320300	−0.860052	0.002392	103	1	0	7.524019	0.584305	2.203953
88	1	0	6.486003	−0.647273	−1.900326	104	1	0	8.503514	1.240305	−0.222208
89	1	0	3.667204	−0.346761	1.421647	105	1	0	7.040108	3.297679	−1.185130
90	1	0	4.727095	1.291989	−2.503859	106	1	0	5.158281	3.905465	0.644963
91	1	0	5.841980	−1.655610	0.516414	107	1	0	1.137332	1.826932	−1.501687
92	6	0	2.776932	1.772838	−0.313650						

8. Dynamic Parallel Kinetic Resolution

8-1. Hydroamination of vinylferrocene (5)

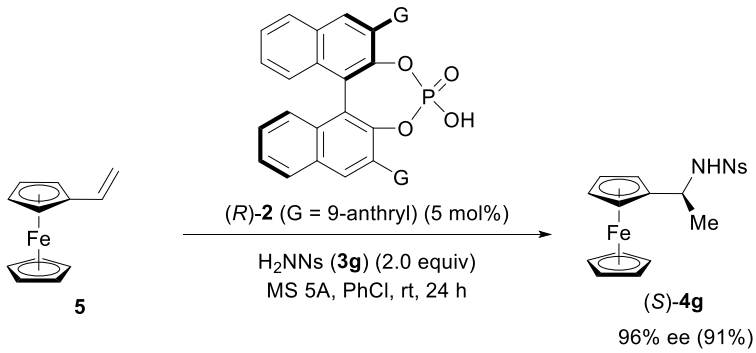
Screening of reaction conditions is shown in Table S2.

Table S2. Screening of reaction conditions[a]



entry	solvent	equivalent of **3g**	% yield[b]	% ee[c]
1[d]	toluene	2.0	15	95
2	toluene	2.0	24	94
3	PhCl	2.0	91	96
4	PhCl	3.0	77	96
5	PhCl	4.0	89	94
6	$PhCF_3$	2.0	83	92

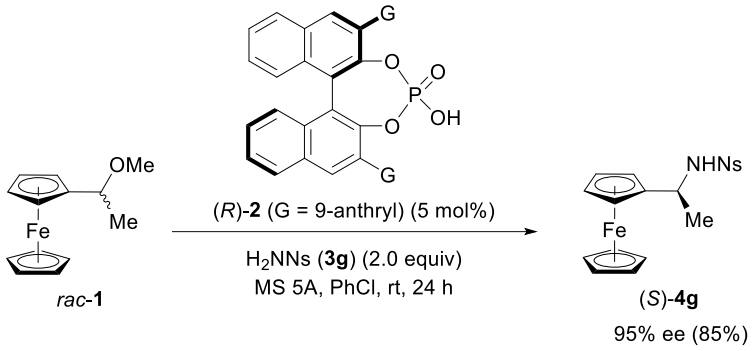
[a] Unless otherwise noted, all reactions were performed using 0.20 mmol of **5**, 5 mol% of catalyst **2** (G = 9-anthryl), X equivalent of **3g**, and MS 5A in the indicated solvent (0.2 M) at room temperature for 24 h. [b] Isolated yield. [c] Determined by chiral stationary phase HPLC analysis. [d] For 2 h (Fig. 3d).



To a solution of MS 5A (150 mg), **5** (42.4 mg, 200 μmol), and H_2NNs (**3g**) (80.9 mg, 400 μmol) in chlorobenzene (1 mL) was added (*R*)-**2** (5 mol%, 7.0 mg, 10 μmol) at room temperature. The atmosphere was replaced with argon (×3), and the mixture was stirred at room temperature for 24 hours. The reaction mixture was quenched by NEt_3, and then passed through a pad of Al_2O_3 with EtOAc. After removing solvents in vacuo, the crude material was purified by flash column chromatography on silica gel (Hexane/EtOAc = 100/1-1/1

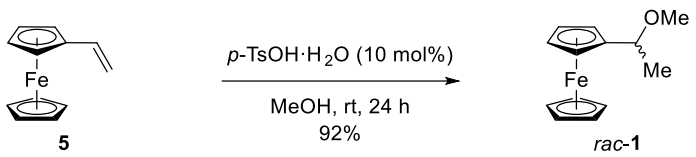
as eluent) to give **4g** in 91% yield as a brown solid. The enantiomeric excess of **4g** was determined by chiral stationary phase HPLC analysis (96% ee).

8-2. Substitution reaction of racemic 1



To a solution of MS 5A (150 mg), *rac*-**1** (48.8 mg, 200 μmol), and H_2NNs (**3g**) (80.9 mg, 400 μmol) in chlorobenzene (1 mL) was added (*R*)-**2** (5 mol%, 7.0 mg, 10 μmol) at room temperature. The atmosphere was replaced with argon (×3), and the mixture was stirred at room temperature for 24 hours. The reaction mixture was quenched by NEt_3, and then passed through a pad of Al_2O_3 with EtOAc. After removing solvents in vacuo, the crude material was purified by flash column chromatography on silica gel (Hexane/EtOAc = 100/1-1/1 as eluent) to give **4g** in 85% yield as a brown solid. The enantiomeric excess of **4g** was determined by chiral stationary phase HPLC analysis (95% ee).

9. Regeneration of 1 (formal dynamic kinetic resolution)

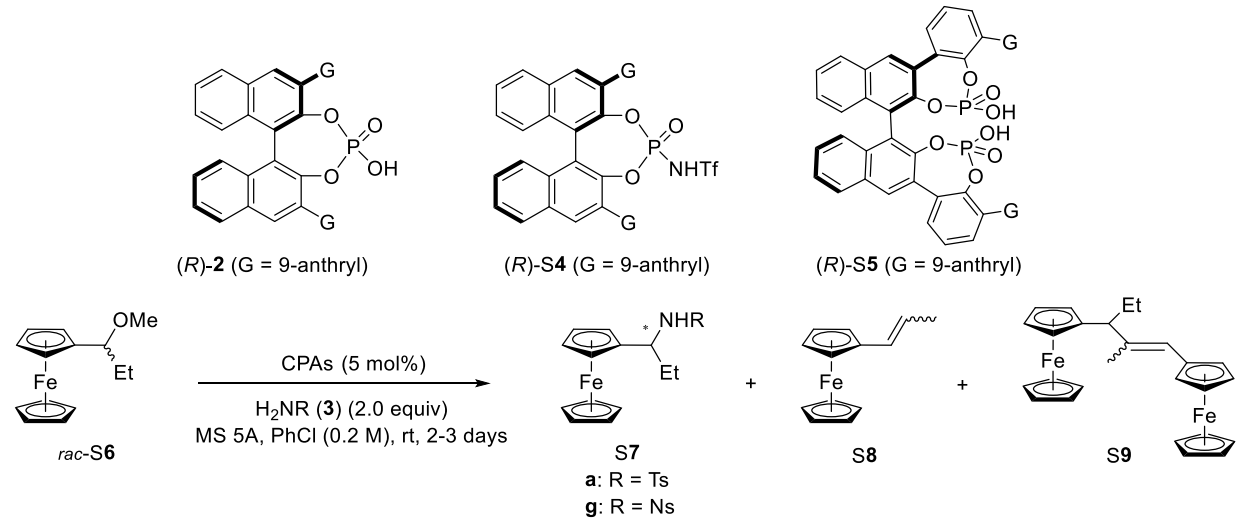


To a solution of vinylferrocene (**5**) (42.4 mg, 200 μmol) in MeOH (4 mL) was added *p*-TsOH (10 mol%, 3.4 mg, 20 μmol) at room temperature. The mixture was stirred at room temperature for 24 hours, and then the reaction mixture was quenched by NEt_3. The mixture was diluted with saturated aqueous $NaHCO_3$, and extracted with Et_2O (×3). The combined organic layers were washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated. After purification by flash column chromatography on silica gel (Hexane/EtOAc = 50/1-4/1 as eluent), **1** was obtained in 92% yield as an orange oil.

10. Reaction of ferrocenyl derivative having different substituent

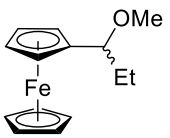
In order to enhance the utility of the developed DPKR, we attempted the reaction of ferrocenyl derivative methyl ether *rac*-S**6** having ethyl substituent, instead of methyl substituent of **1**, with $NsNH_2$ **3g** was conducted. As shown in Table S3, entry 1, however, substitution product S**7g** was not formed at all under the optimized reaction conditions [(*R*)-**2**, chlorobenzene, MS 5A, rt] despite the complete consumption of starting methyl ether S**6**. Meanwhile demethoxylation product 1-propenyl ferrocene S**8** was formed as the sole product. Similarly, the use of more nucleophilic $TsNH_2$ **3a** than $NsNH_2$ **3g** was also unsuccessful, affording S**8** in a nearly quantitative manner (entry 2). These results suggest that the acidity of parent CPA (*R*)-**2** (G = 9-anthryl) is insufficient to protonate S**8**. Therefore CPAs having strong acidity, such as triflylamide derivative (*R*)-S**4** and bisphosphoric acid (*R*)-S**5**, were further investigated. Although, in the presence of MS 5A, a significant amount of unexpected dimer S**9** was formed using (*R*)-S**4** (G = 9-anthryl) even by using **3a** (entry 3), desired substitution product S**7a** was obtained in fairly good yield without using MS 5A, albeit in a racemic form (entry 4). In order to improve the enantioselectivity of S**7a**, we further employed bisphosphoric acid (*R*)-S**5** (G = 9-anthryl) (entries 5 and 6). Desired S**7a** was formed in moderate yield, irrespective of using MS 5A or not. However, enantioselectivity was not markedly improved. Currently, we have not succeeded in the formation of S**7** in a highly enantioselective manner. The present intriguing DPKR is established by the well-balanced system between the deprotonation of cation **A** and the selective introduction of a nucleophile to enantiomeric cations **A**. Hence it is considered that optimization of CPAs and reaction conditions would be strictly required to achieve the efficient DPKR with high enantioselectivity for each substrate.

Table S3. Screening of reaction conditions using ferrocenyl derivative methyl ether S**6**[a]



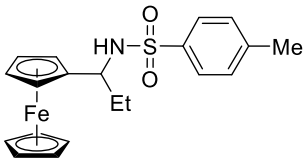
entry	CPAs	**3**	% conv.	% yield[b]			% ee of S**7**[c]
				S**7**	S**8**	S**9**	
1	**2**	**3g** (R = Ns)	100	-	>98	-	-
2	**2**	**3a** (R = Ts)	100	<1	>99	-	-
3	S**4**	**3a**	100	<5	4	45	-
4[d]	S**4**	**3a**	100	75 (67)	10	7	<1
5	S**5**	**3a**	100	39 (29)	34	2	15
6[d]	S**5**	**3a**	93	45 (21)	30	-	21

[a] Unless otherwise noted, all reactions were performed using 0.20 mmol of *rac*-S**6**, 5 mol% of CPAs (G = 9-anthryl), 2.0 equiv. of **3**, and MS 5A in chlorobenzene (0.2 M) at room temperature for 2-3 days. [b] Determined by crude ^1H NMR analysis (in $CDCl_3$) using 1,1-dibromomethane as the internal standard. Isolated yields are shown in parentheses. [c] Determined by chiral stationary phase HPLC analysis. [d] Without using MS 5A.



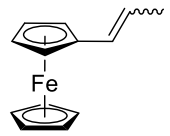
rac-**S6**

(1-Methoxypropyl)ferrocene (S6): Orange oil; R_f = 0.74 (Hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 600 MHz), δ 1.02 (3H, t, *J* = 7.8 Hz), 1.73-1.81 (1H, m), 1.91-1.99 (1H, m), 3.29 (3H, s), 3.92 (1H, dd, *J* = 9.0, 1.8 Hz), 4.11-4.15 (8H, m), 4.19-4.20 (1H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ 10.6, 27.9, 56.0, 66.1, 67.2, 67.6, 68.1, 68.5, 80.4, 89.0; IR (ATR): 3095, 2969, 2931, 2875, 2816, 1462, 1320, 1236, 1120, 1105, 1094, 1079, 1024, 1000, 817 cm^{-1}; HRMS (FD+) Calcd for $C_{14}H_{18}FeO$ [M] 258.0707, Found 258.0704.



S**7a**

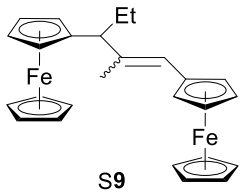
4-Methyl-*N*-(1-ferrocenylpropyl)benzenesulfonamide (S7a): Yellow solid (mp 163-169 °C); R_f = 0.40 (Hexane/EtOAc = 4/1); HPLC analysis Chiralpak IC-3 (Hexane/IPA = 90/10, 1.0 mL/min, 254 nm, 30 °C) 33.4 (major), 35.9 (minor) min, (21% ee); $[\alpha]^{24}_D$ = -1.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz), δ 0.83 (3H, t, *J* = 7.8 Hz), 1.63-1.70 (1H, m), 1.76-1.83 (1H, m), 2.44 (3H, s), 3.91-3.94 (2H, m), 3.97-4.01 (1H, m), 4.06-4.09 (2H, m), 4.10-4.13 (5H, m), 4.73 (1H, d, *J* = 7.2 Hz), 7.32 (2H, d, *J* = 7.8 Hz), 7.80 (2H, d, *J* = 8.4Hz); ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ 10.2, 21.5, 28.9, 54.3, 66.5, 66.7, 67.8, 67.9, 68.6, 90.6, 127.1, 129.6, 138.3, 143.3; IR (ATR): 3398, 3296, 3086, 2965, 2927, 2873, 1597, 1456, 1411, 1378, 1328, 1161, 1093, 1002, 907, 814 cm^{-1}; HRMS (FD+) Calcd for $C_{20}H_{23}FeNO_2S$ $[M]^+$ 397.0799, Found 397.0798.



S**8**

2-Propenylferrocene (S8): Orange oil; R_f = 0.40 (Hexane); ^{1}H NMR ($CDCl_3$, 600 MHz) for *E*-isomer (*major*), δ 1.73 (3H, dd, *J* = 6.6, 1.8 Hz), 4.08-4.11 (5H, m), 4.14 (2H, t, *J* = 1.8 Hz), 4.27 (2H, t, *J* = 1.8 Hz), 5.81 (1H, dq, *J* = 15.0, 6.6 Hz), 6.09 (1H, dd, *J* = 15.6, 1.8 Hz); ^{13}C NMR ($CDCl_3$, 150.9 MHz) for *E*-isomer (*major*), δ 18.5, 66.2, 68.0, 68.96, 68.99, 84.4, 122.9, 127.6, one carbon was not found due to overlapping.; ^{1}H NMR ($CDCl_3$, 600 MHz) for *Z*-isomer (*minor*), δ 1.82 (3H, dd, *J* = 7.2, 1.8 Hz), 4.08-4.11 (5H, m), 4.19 (2H, t, *J* = 1.8 Hz), 4.33 (2H, t, *J* = 1.8 Hz), 5.57 (1H, dq, *J* = 11.4, 7.2 Hz), 6.07-6.12 (1H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) for *Z*-isomer (*minor*), δ 14.8, 68.2, 69.1, 123.5, 126.8, some carbons could not be assigned due to the low intensity of minor isomer.; IR (ATR): 3094, 2958, 2927, 2854, 1608, 1473, 1411, 1376, 1260, 1105, 1042, 1024, 1000, 958, 910, 815 cm^{-1}; HRMS (FD+) Calcd for $C_{13}H_{14}Fe$ [M] 226.0445, Found 226.0440.

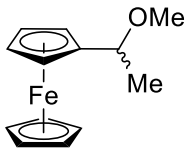
(2-methylpent-1-ene-1,3-diyl)diferrocene (S9): Orange oil; R_f = 0.15 (Hexane); ^{1}H NMR ($CDCl_3$, 600 MHz) for major isomer, δ 0.96 (3H, t, *J* = 7.2 Hz), 1.53 (3H, d, *J* = 0.6 Hz), 1.58-1.66 (1H, m), 1.87-1.95 (1H, m), 3.07 (1H, dd, *J* = 11.4, 3.6 Hz), 4.05-4.18 (16H, m), 4.28-4.32 (2H, m), 5.99 (1H, s); IR (ATR): 3093, 2959, 2926, 2871, 1747, 1697, 1679, 1456, 1410, 1375, 1260, 1260, 1217, 1104, 1023, 999, 866 cm^{-1}; HRMS (FD+) Calcd for $C_{26}H_{28}Fe_2$ [M] 452.0890, Found 452.0889.



S**9**

11. ^{1}H and ^{13}C NMR spectra, HPLC trace

^{1}H NMR (C_6D_6, 600 MHz) and ^{13}C NMR (C_6D_6, 150.9 MHz) spectra of **1**



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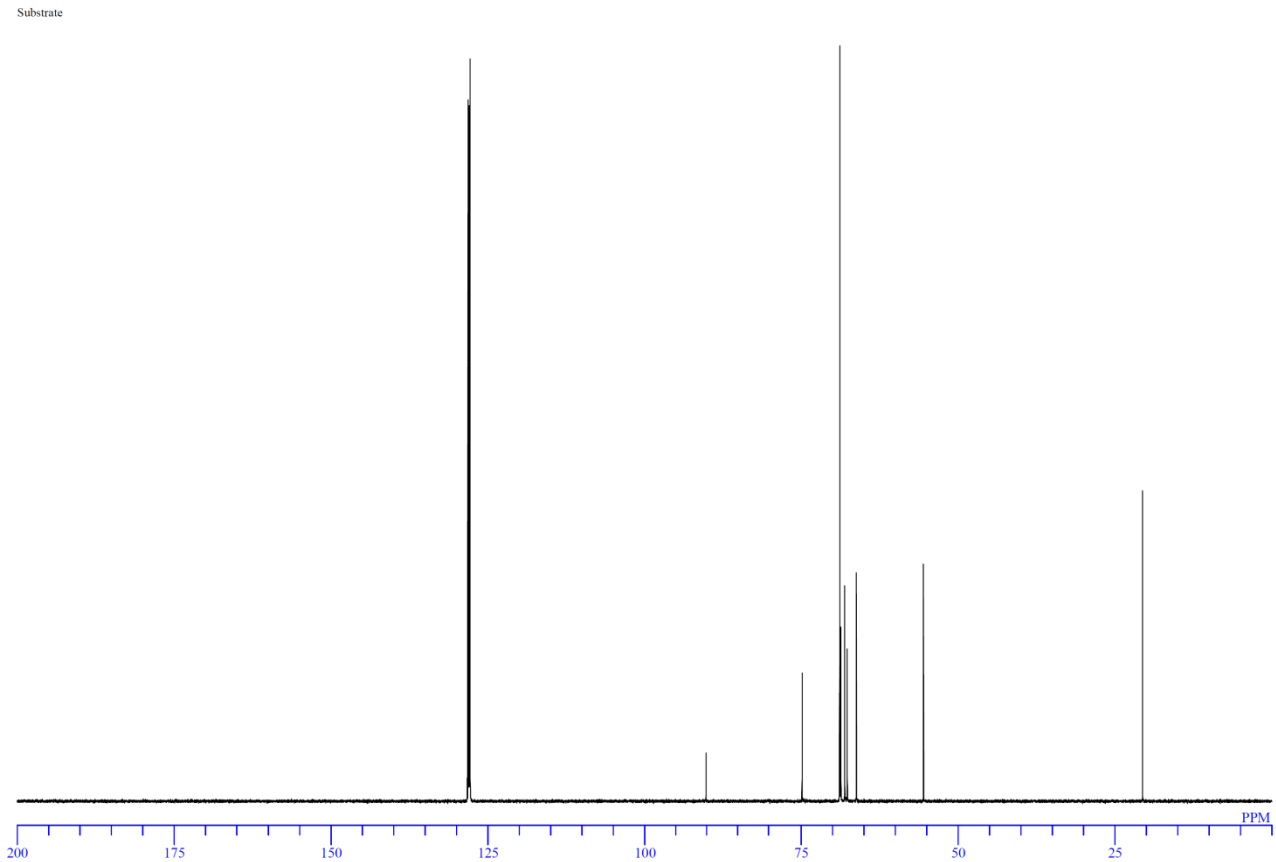
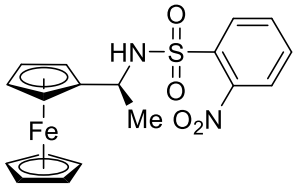
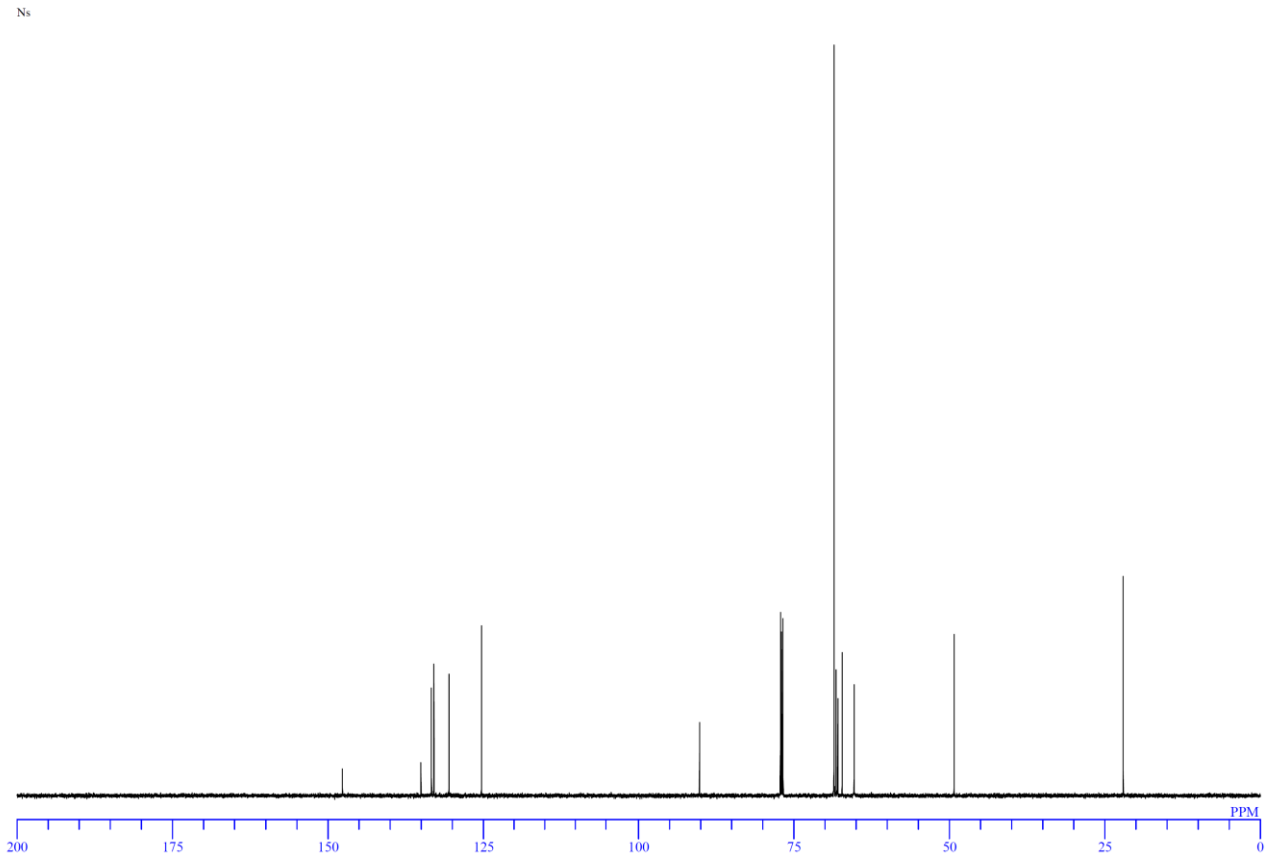


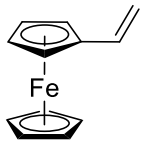
^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150.9 MHz) spectra of **4g**



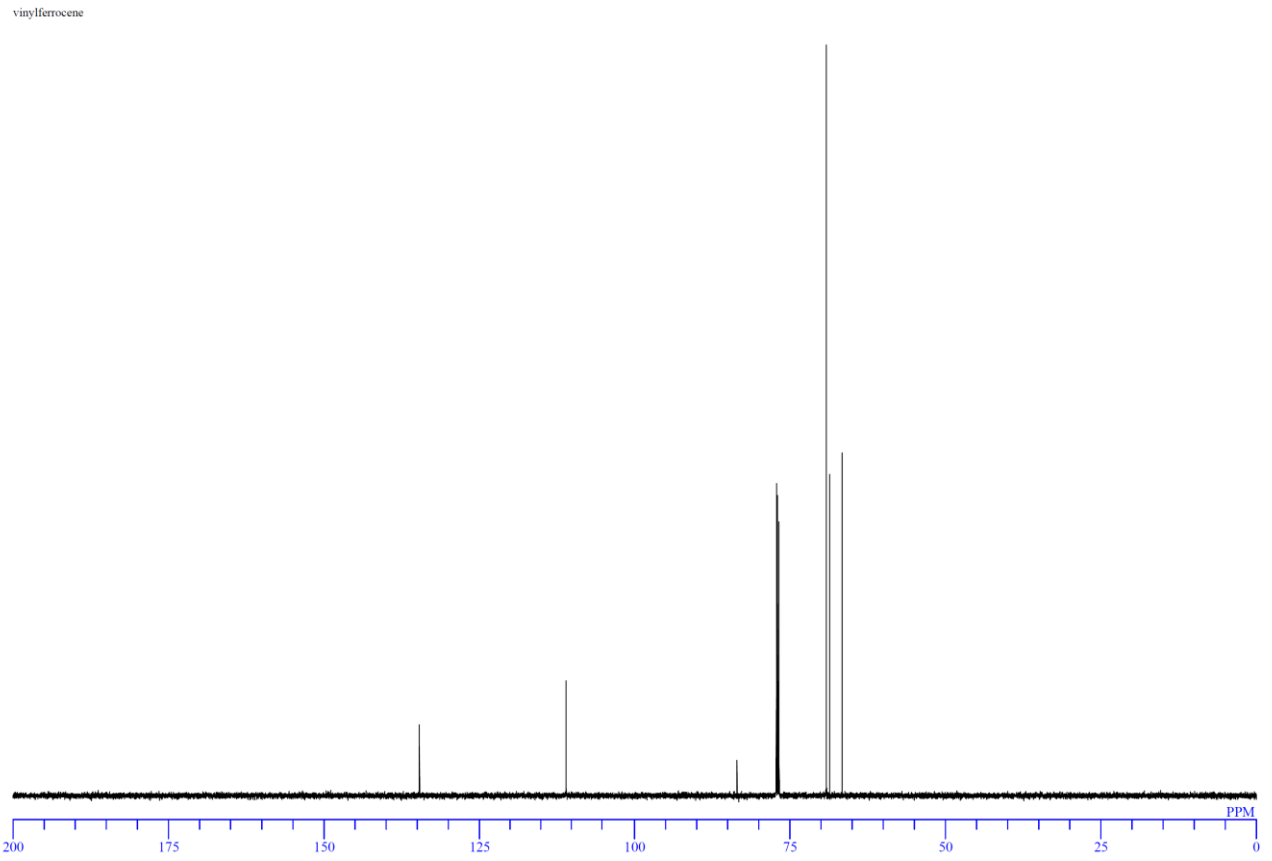
(*S*)-**4g**



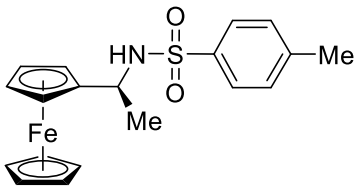
^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150.9 MHz) spectra of **5**



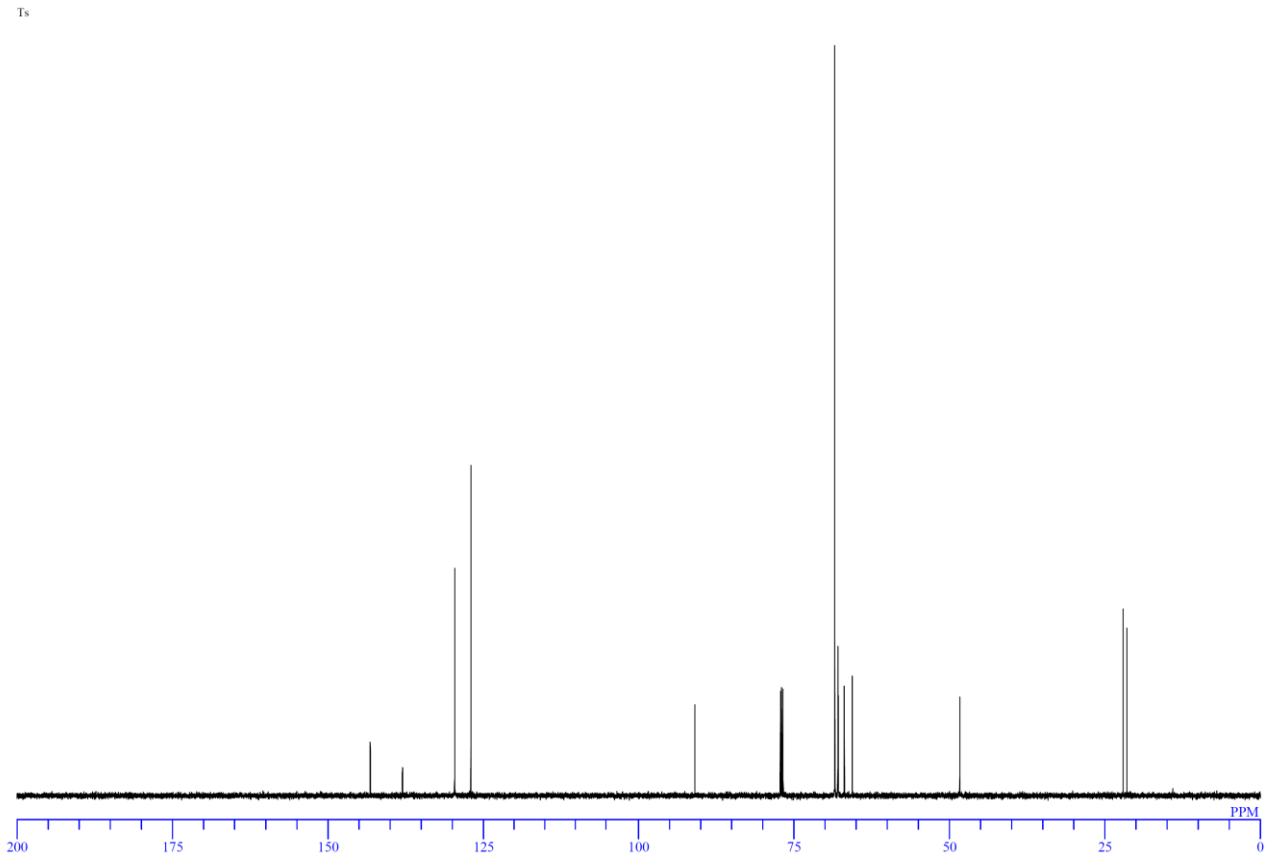
5



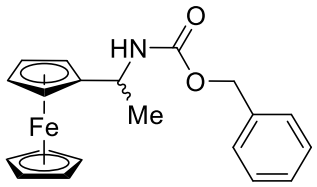
^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150.9 MHz) spectra of **4a**



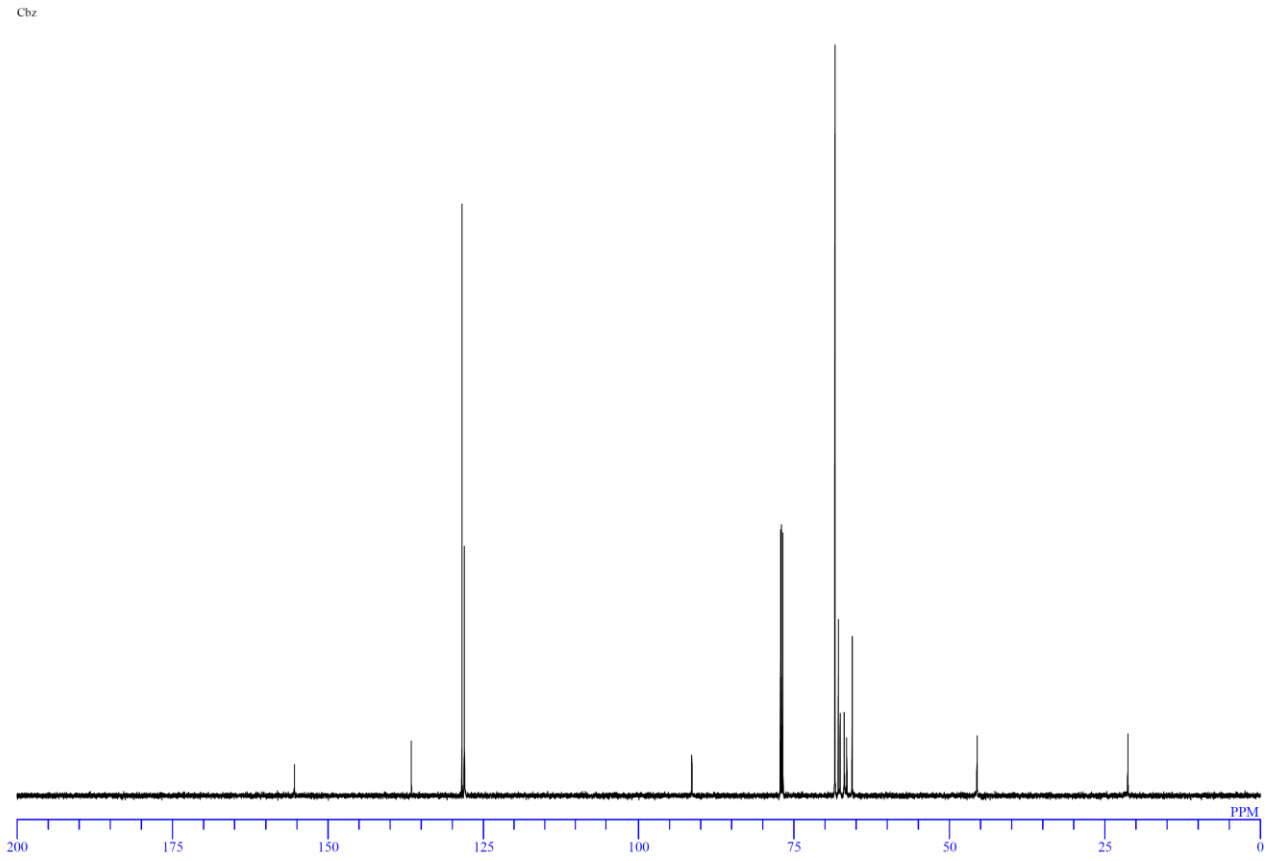
(*S*)-**4a**



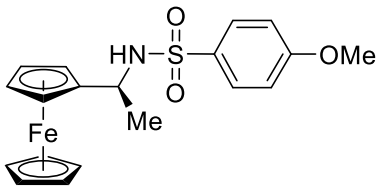
^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150.9 MHz) spectra of **4d**



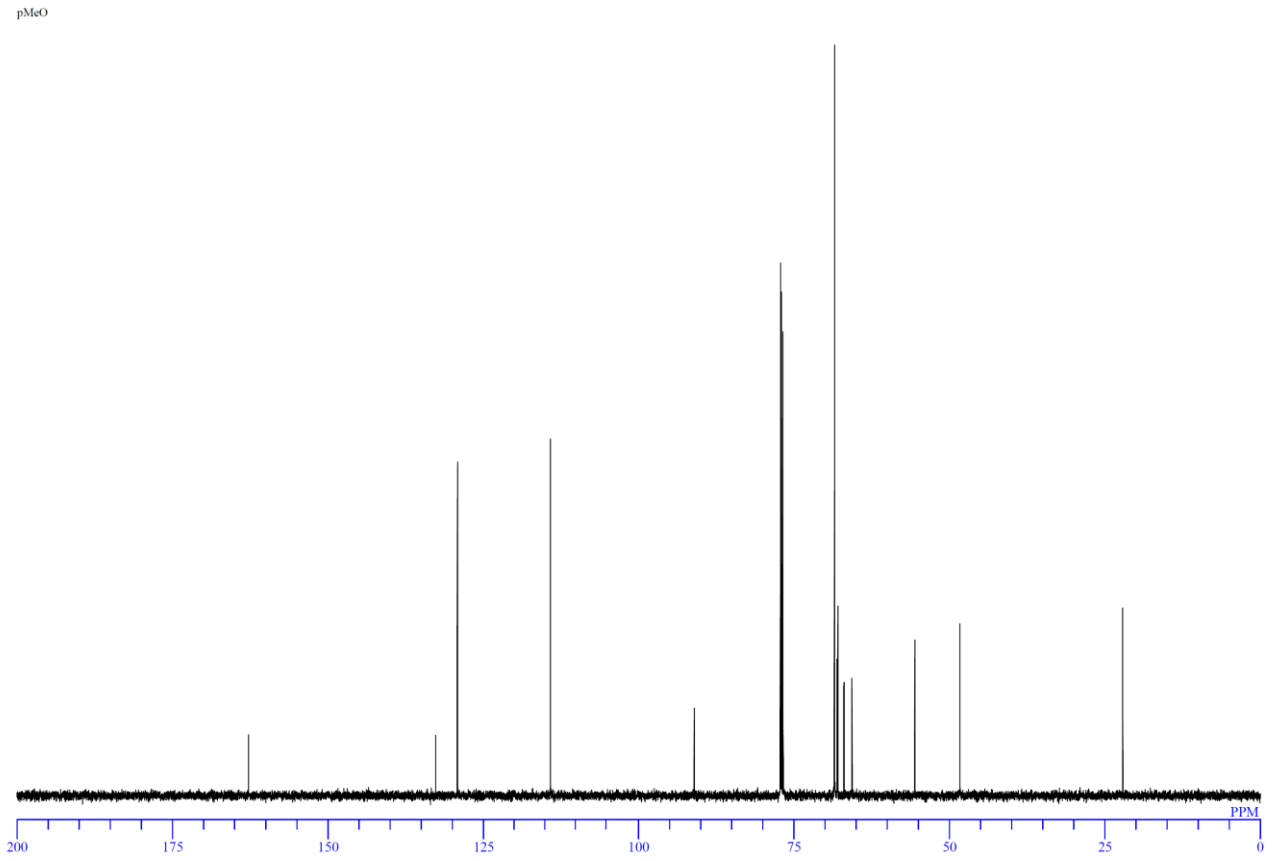
4d



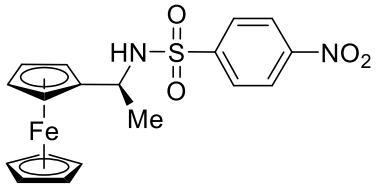
^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150.9 MHz) spectra of **4e**



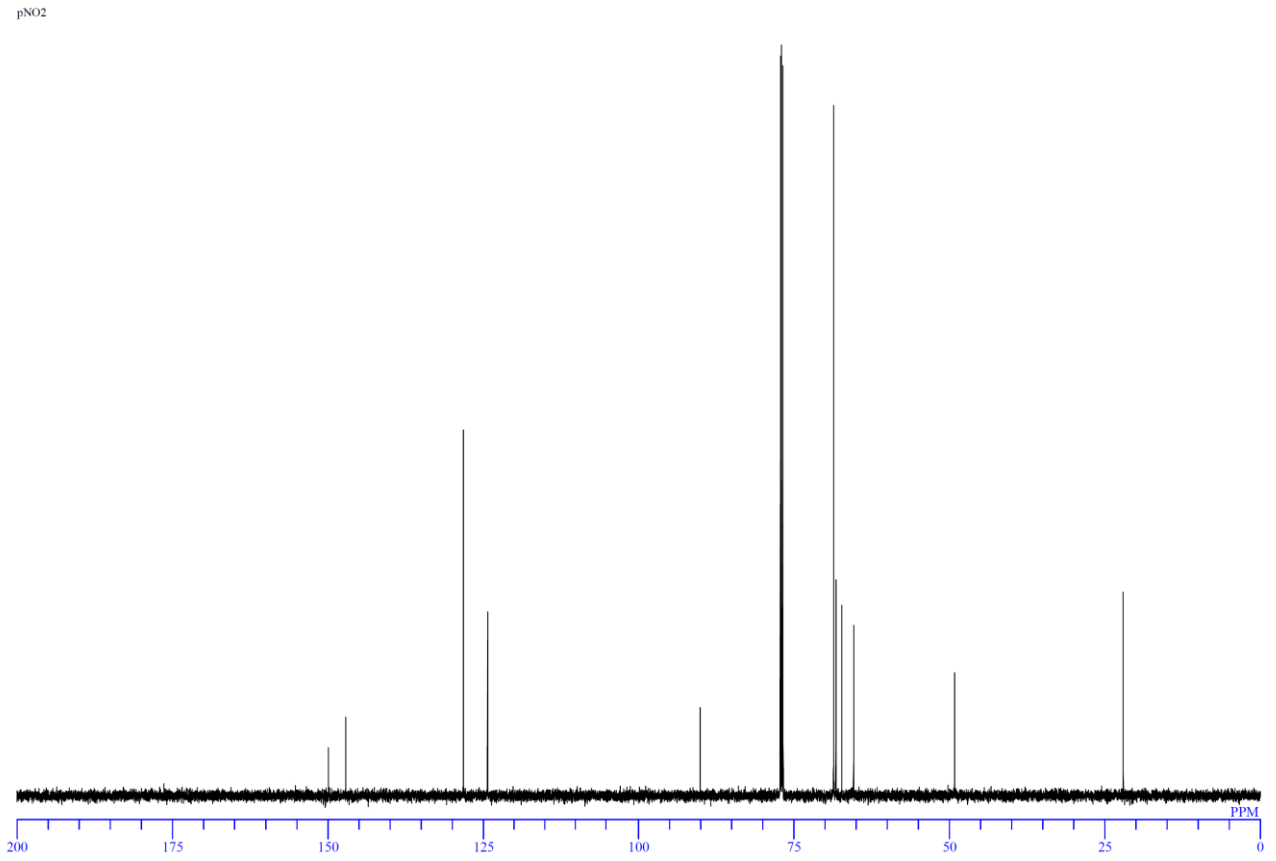
(*S*)-**4e**



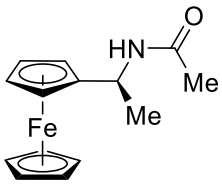
^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150.9 MHz) spectra of **4f**



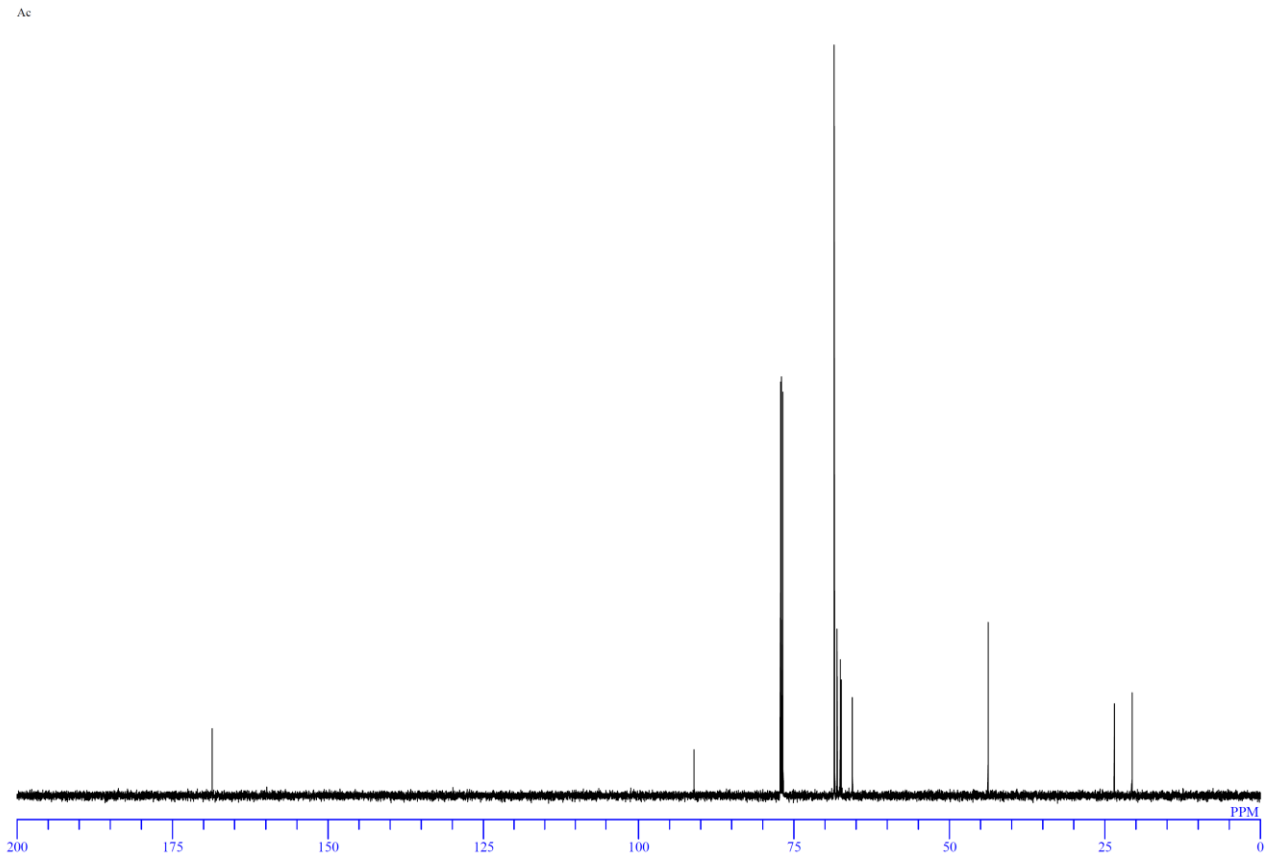
(*S*)-**4f**



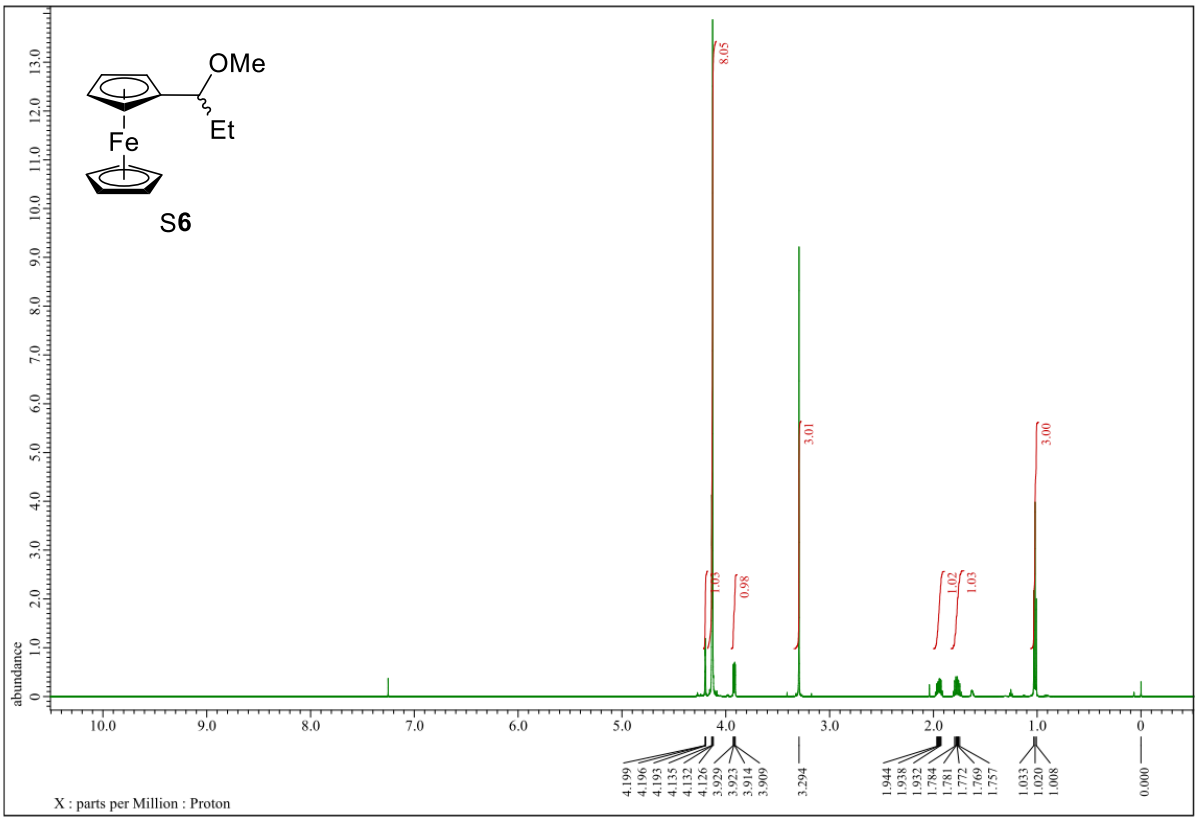
^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150.9 MHz) spectra of S**3**

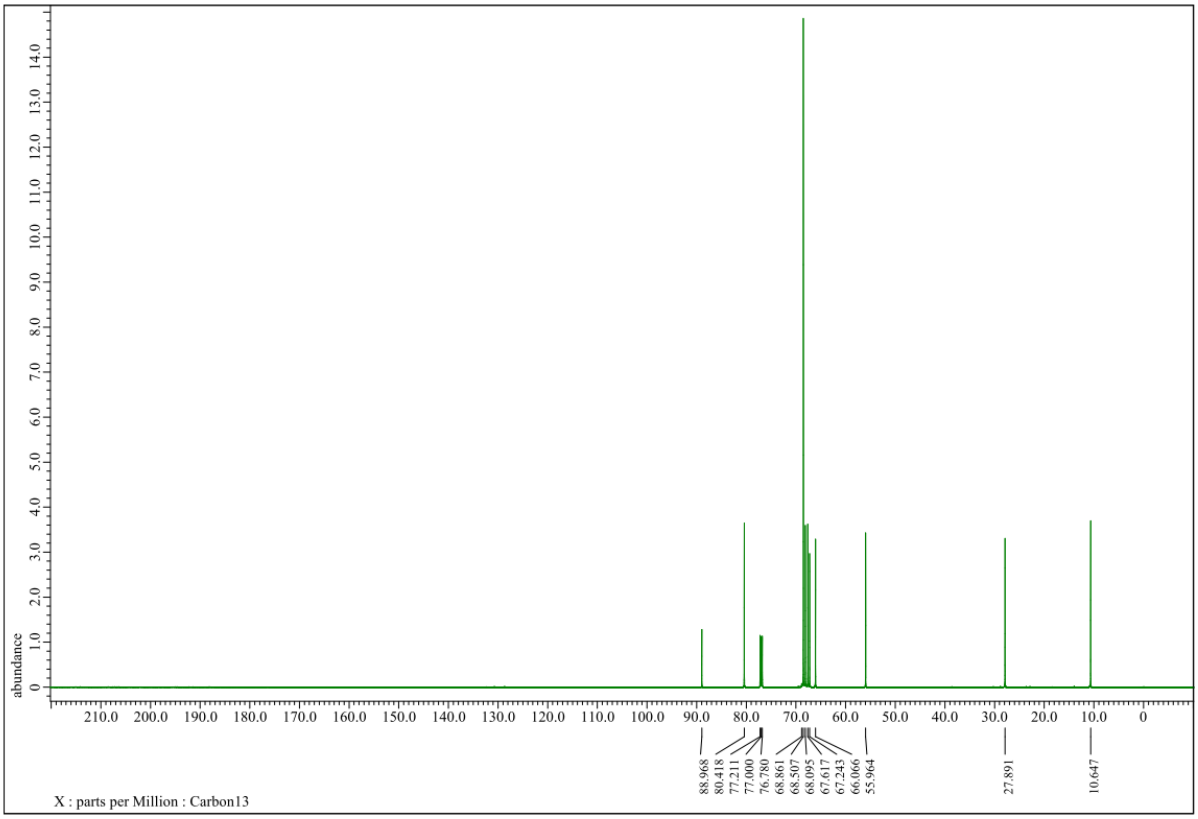


(*S*)-S**3**

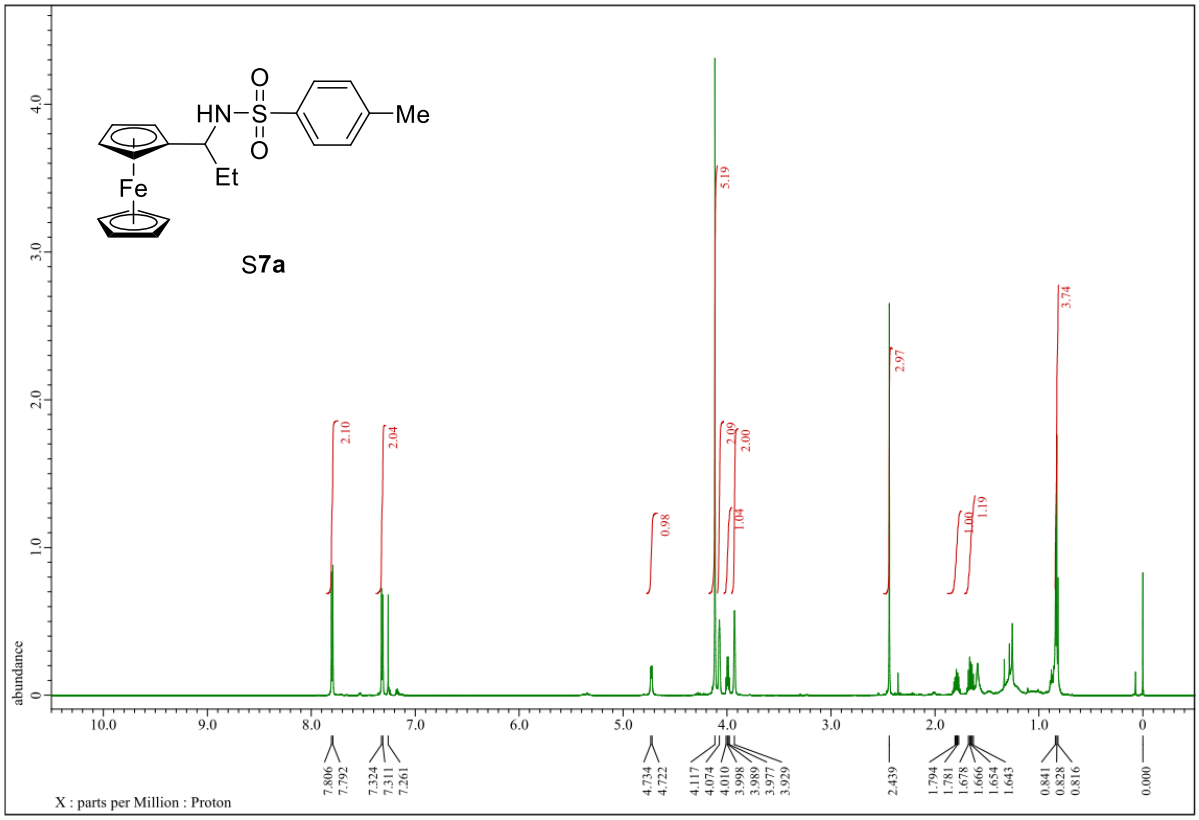


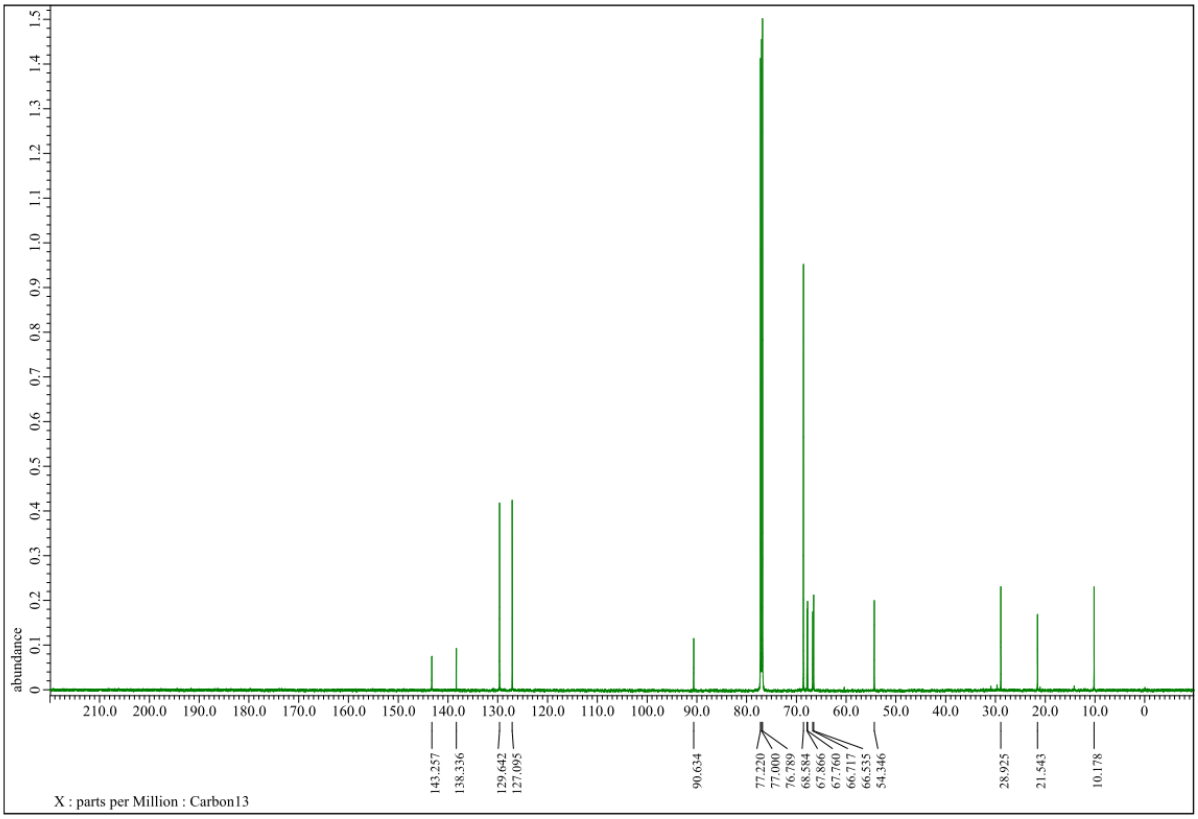
^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150.9 MHz) spectra of S**6**



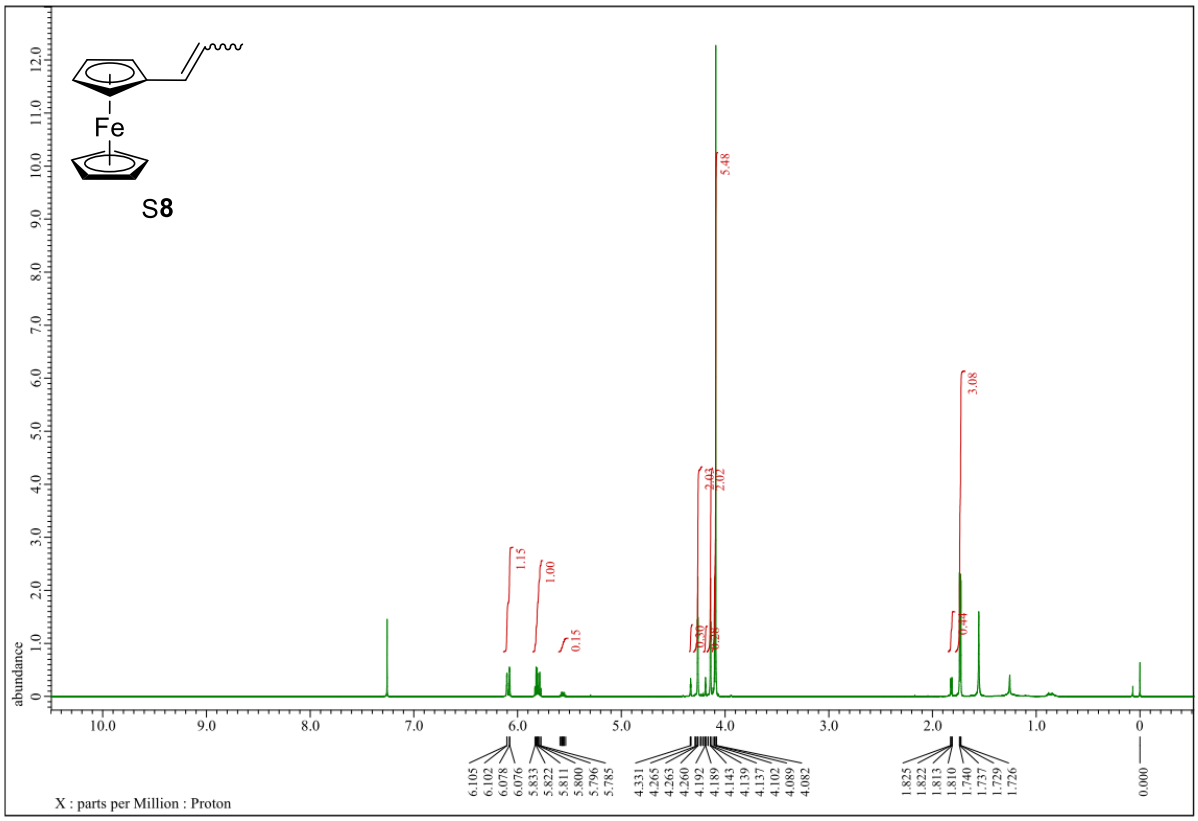


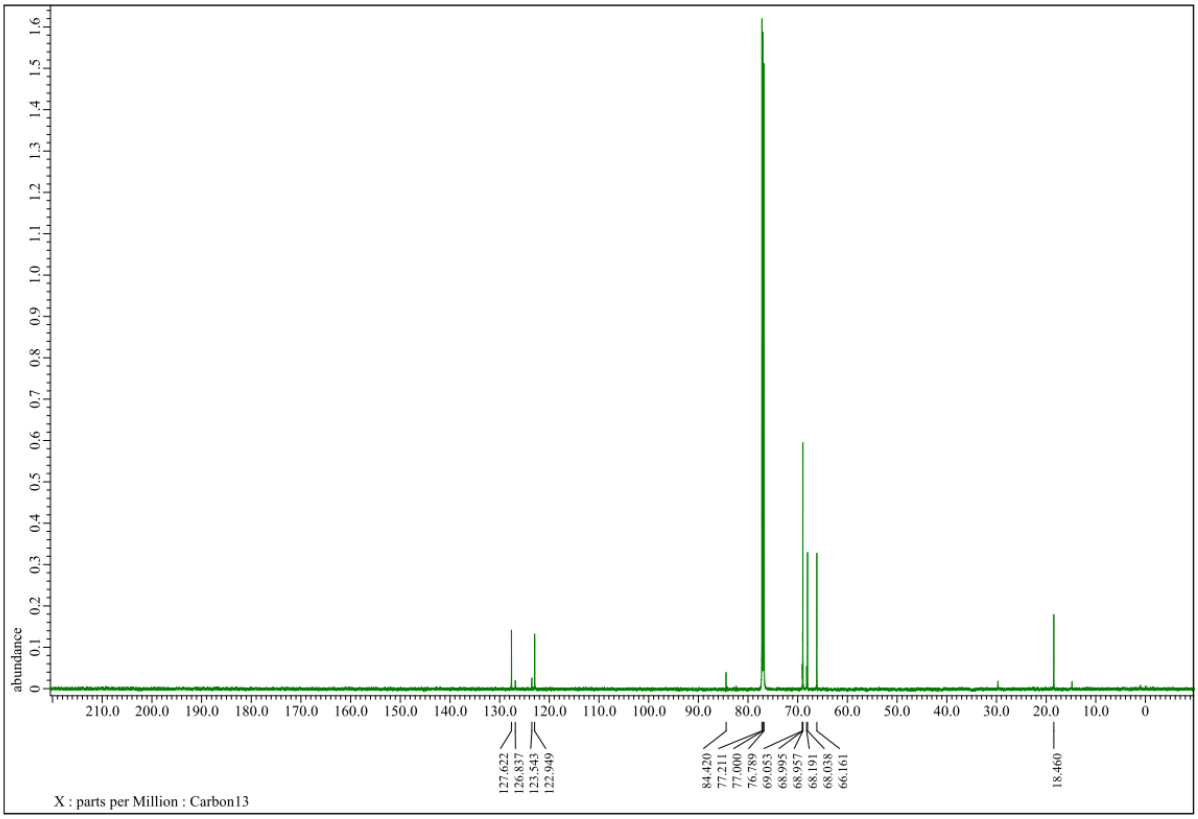
^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150.9 MHz) spectra of **S7a**



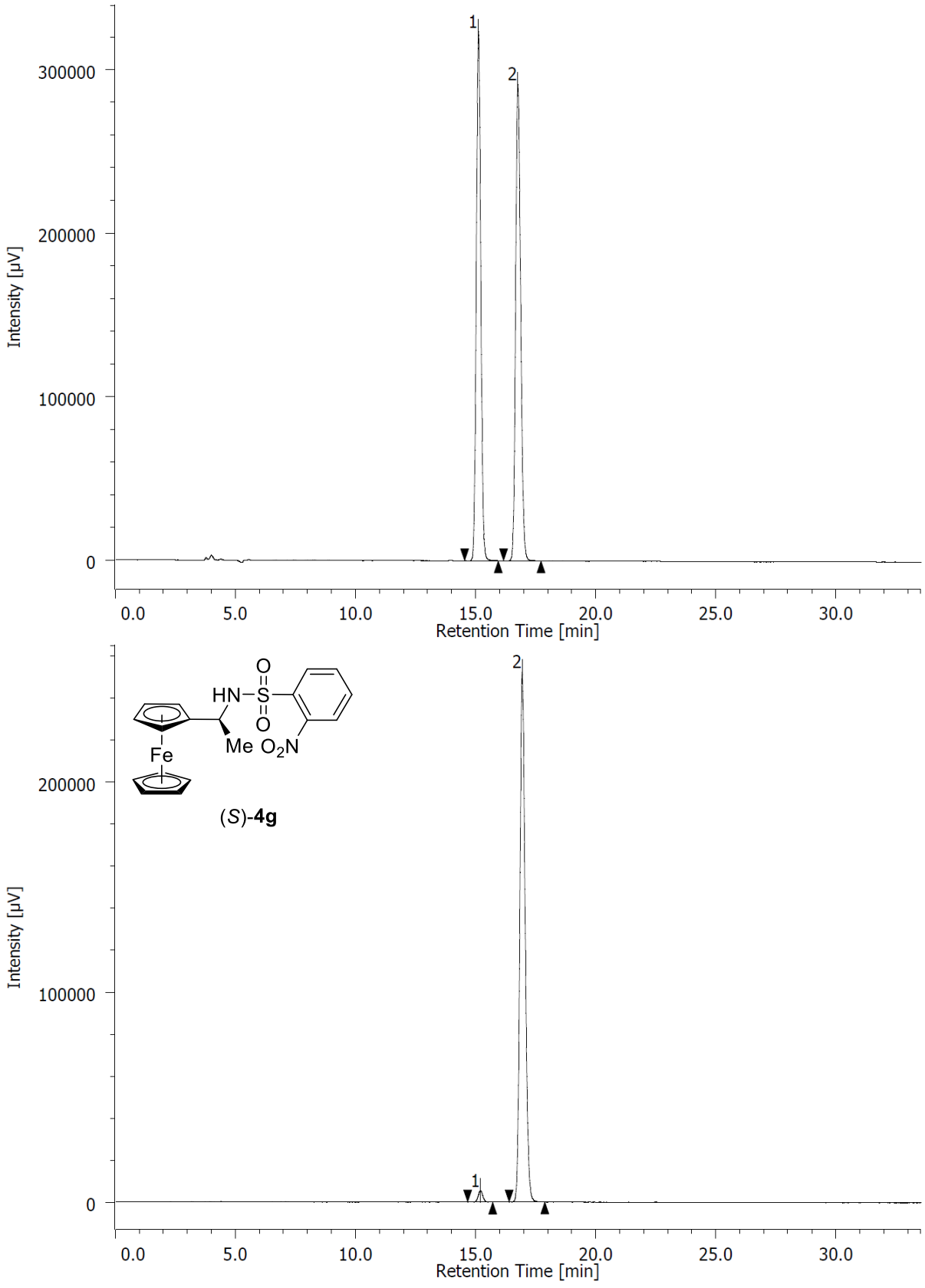


^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 150.9 MHz) spectra of **S8**

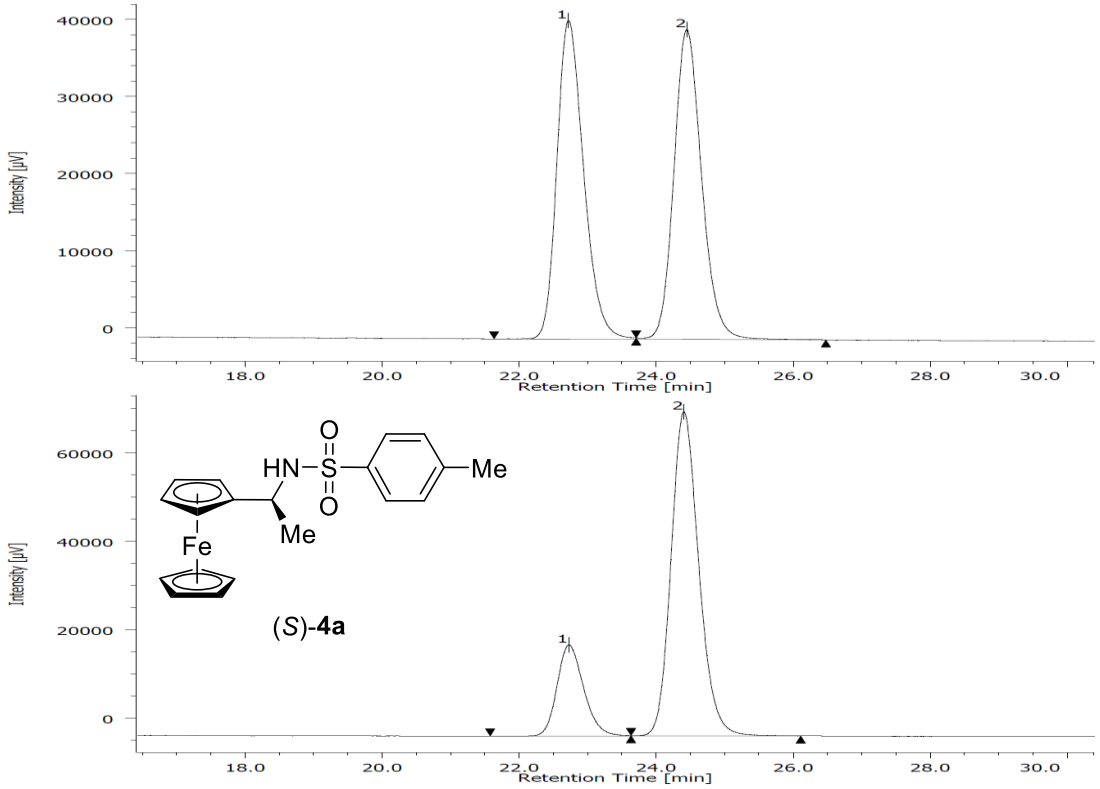




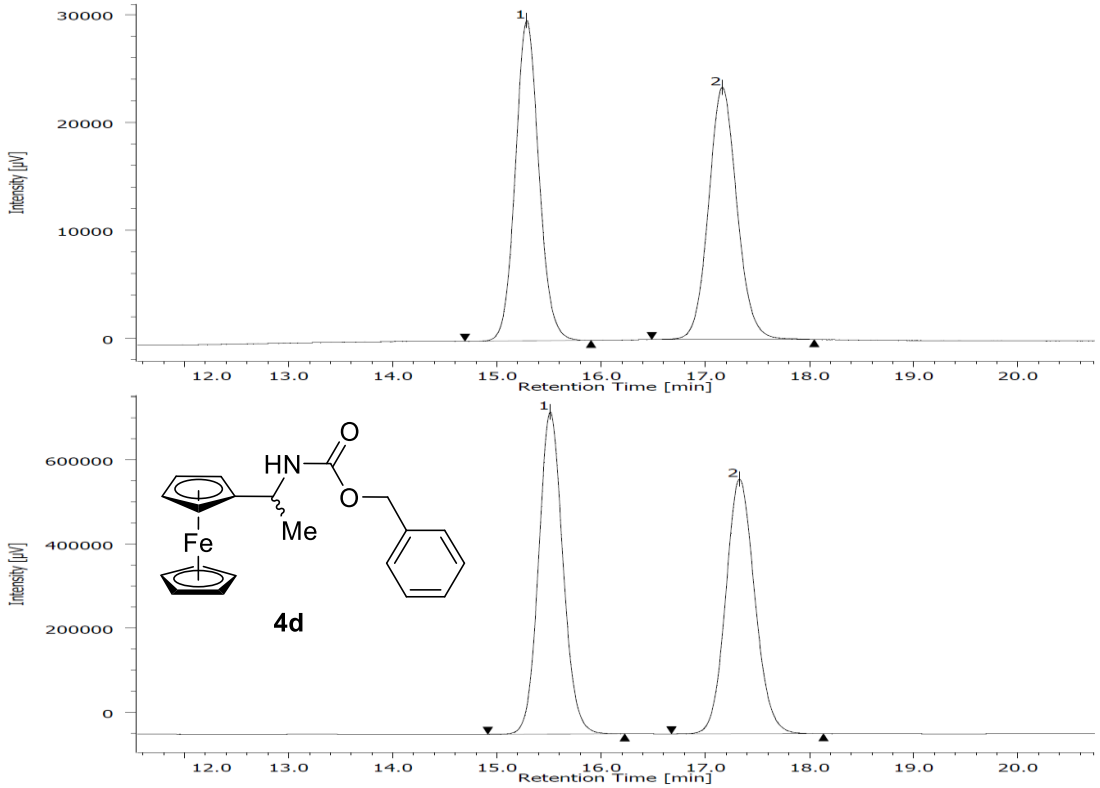
HPLC trace of **4g**



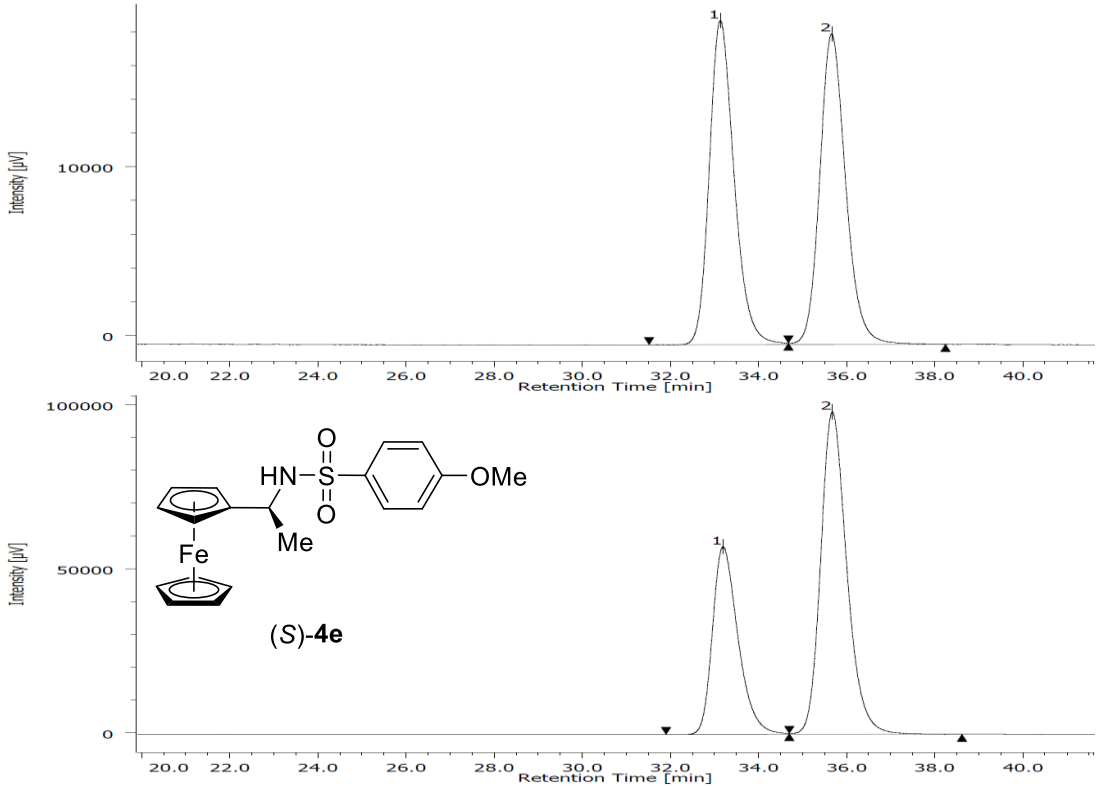
HPLC trace of **4a**



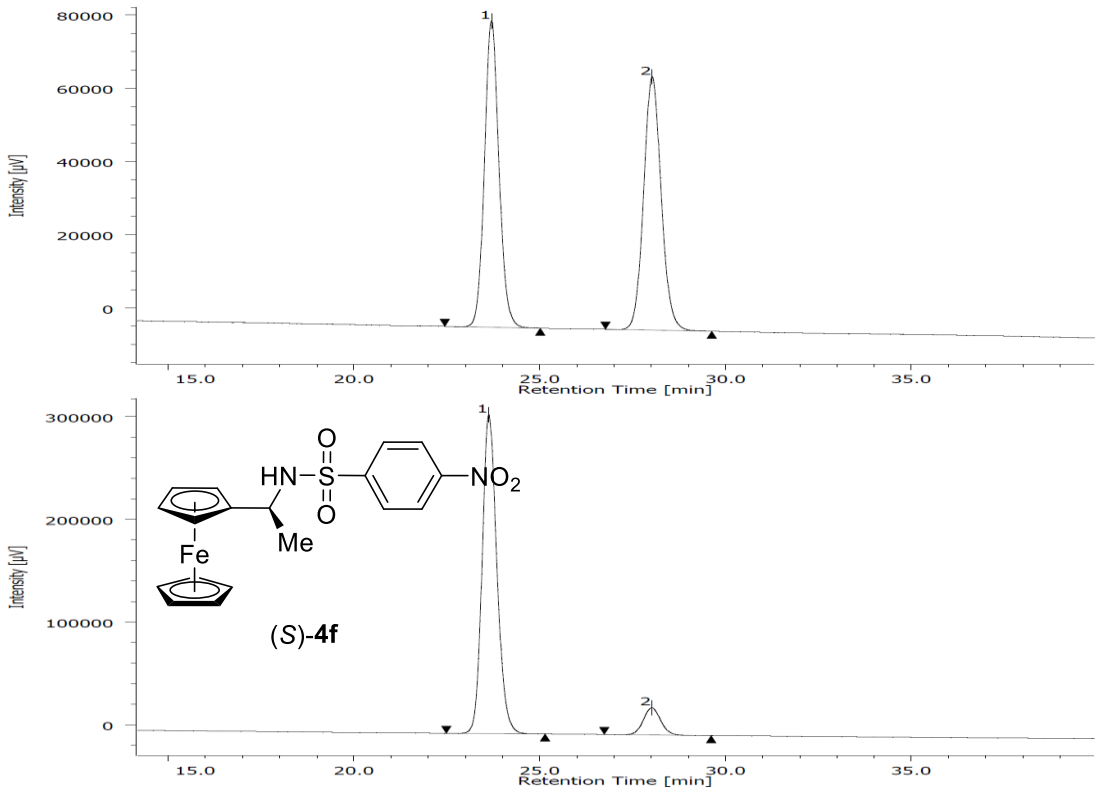
HPLC trace of **4d**



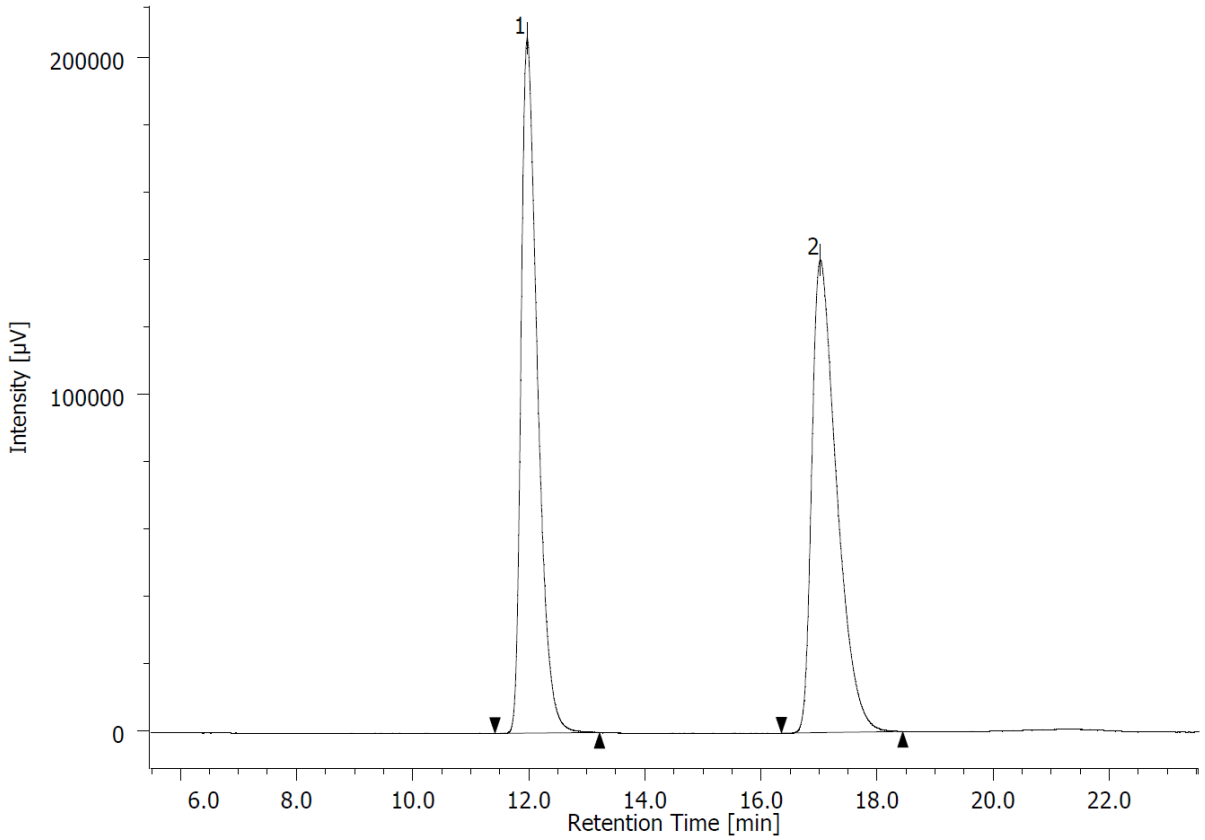
HPLC trace of **4e**

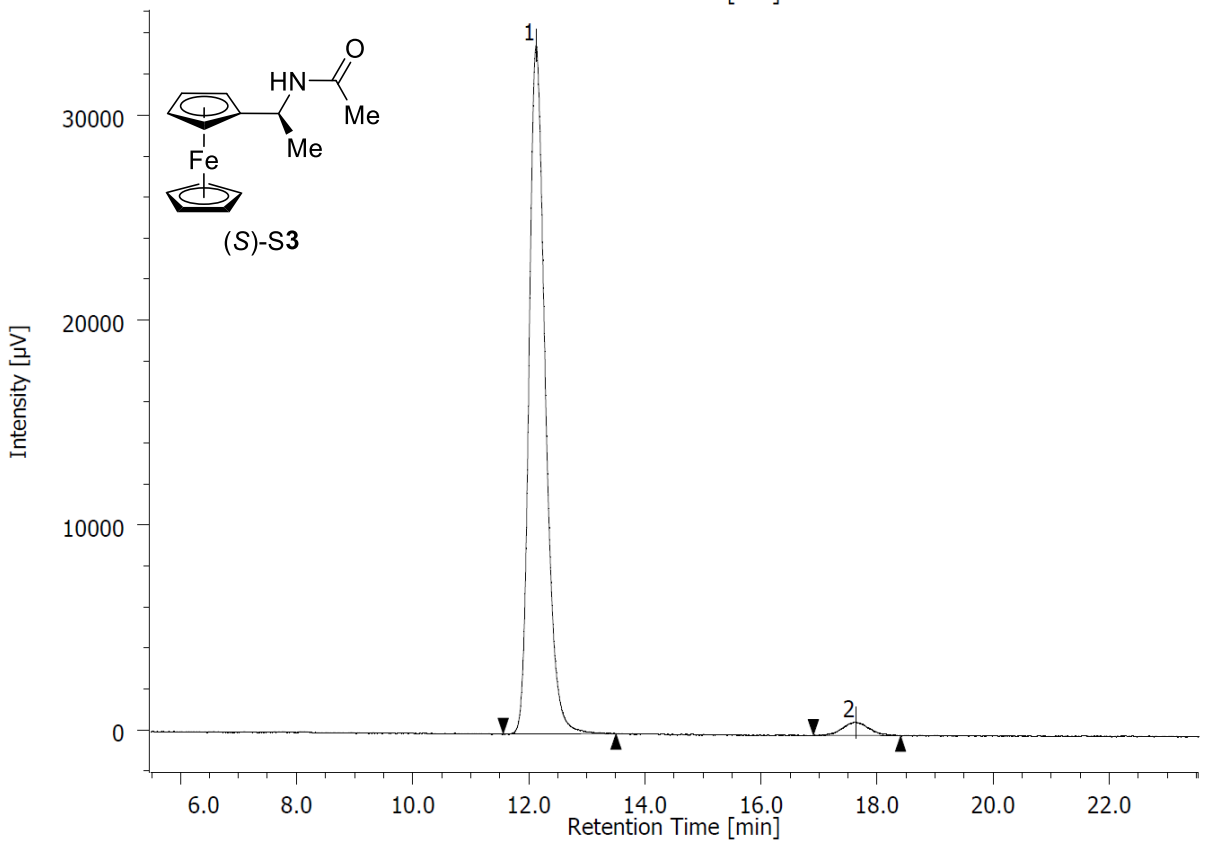


HPLC trace of **4f**

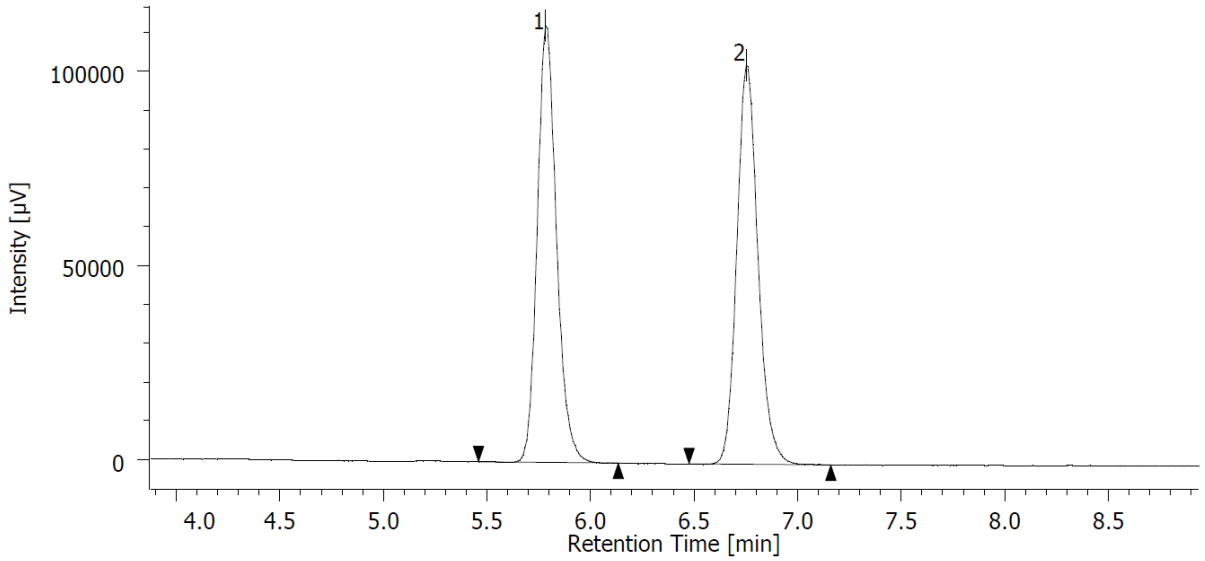


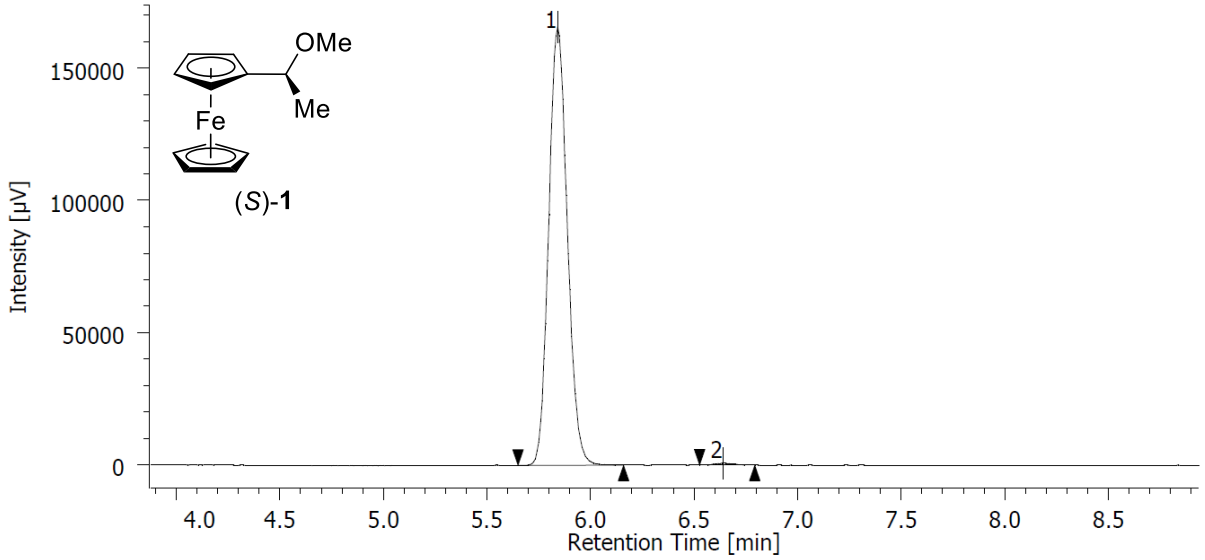
HPLC trace of **S3**

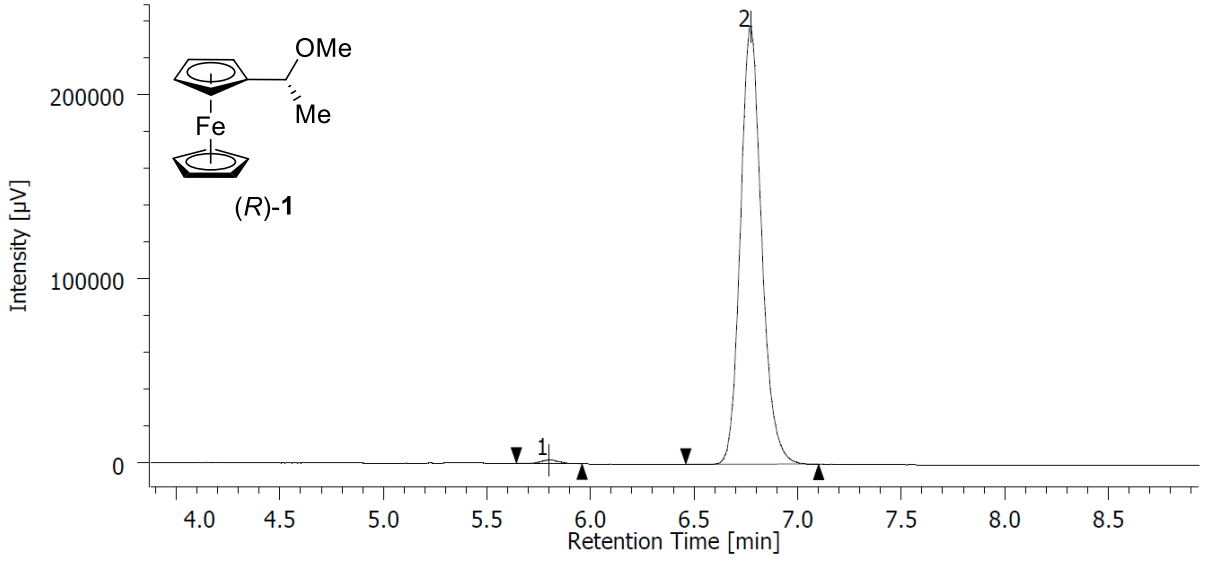




HPLC trace of **1**







HPLC trace of **S7a**