Supporting information

Redox of Ferrocene Controlled Asymmetric Dehydrogenative Heck Reaction via Palladium-catalyzed dual C- H Bonds Activation

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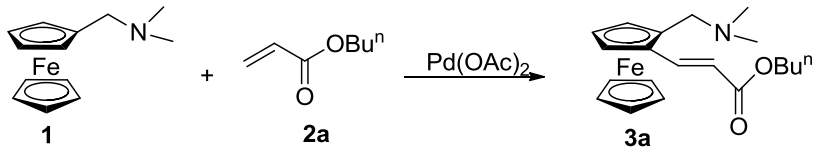
General Information:

All reagents were used directly without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. Monoprotected α-amino acids were purchased from GL Biochem (shanghai) Ltd.. ^{1}H NMR spectra were recorded on a **Bruker DPX-400** (400 MHz) spectrometer with deuteraterated chloroform as solutions. The chemical shifts δ are reported in ppm relative to tetramethylsilane. The multiplicity of signals is designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were recorded at 100 MHz on **Bruker DPX-400**. The chemical shifts δ are reported relative to residual $CHCl_3$ (δ_c=77.00 ppm). High resolution mass spectra (HRMS) were obtained on an **Agilent LC- MSD- Trap-XCT** spectrometer with micromass MS software using electrospray ionisation (ESI). Enantiomeric excesses (ees) were determined on a **Waters 1525** HPLC system using commercially available chiral columns. The optical rotations were measured using a **Perkin-Elmer model 343** polarimeter at the reported temperature.

Experimental Procedure:

Screening of reaction parameter (Table S1)

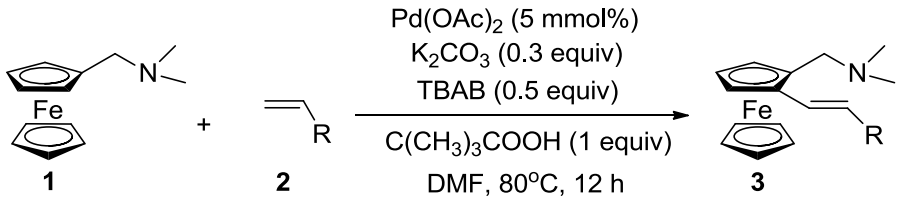


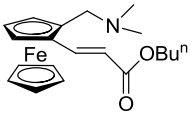
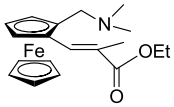
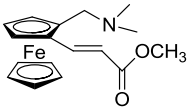
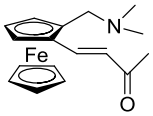
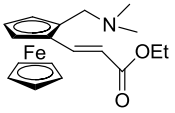
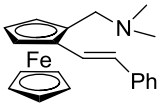
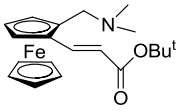
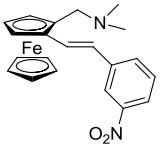
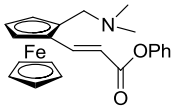
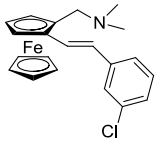
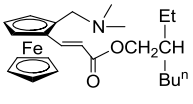
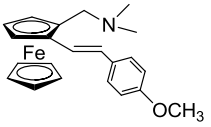
1 **2a** **3a**

Entry	Solvent	Base	Additives	Acid	Yield[%]
1	Toluene	-	-	-	20
2	Toluene	-	TBAB	PivOH	27
3	Toluene	K_2CO_3	-	PivOH	25
4	Toluene	K_2CO_3	TBAB	PivOH	34
5	NMP	K_2CO_3	TBAB	PivOH	60
6	DMF	K_2CO_3	TBAB	PivOH	65
7	DMSO	K_2CO_3	TBAB	PivOH	22
8	EtOH	K_2CO_3	TBAB	PivOH	19
9	$CHCl_3$	K_2CO_3	TBAB	PivOH	19
10	CH_3CN	K_2CO_3	TBAB	PivOH	10
11	DMF	NEt_3	TBAB	PivOH	18
12	DMF	Cs_2CO_3	TBAB	PivOH	28
13	DMF	KOAc	TBAB	PivOH	46
14	DMF	KOBu^t	TBAB	PivOH	64
15[b]	DMF	K_2CO_3	TBAB	PivOH	85

[a] Reaction conditions: **1** 1 mmol, **2a** 1.5 equiv, $Pd(OAc)_2$ 5 mol%, K_2CO_3 0.3 equiv, TBAB 0.5 equiv, PivOH = $C(CH_3)_3CO_2H$ 1 equiv, DMF 2 mL, 80 °C, 12 h. [b] **1** 1 mmol, **2a** 3.0 equiv.

General procedure for ortho alkenylation of N,N-dimethylaminomethyl ferrocene with olefins. (Table S2)



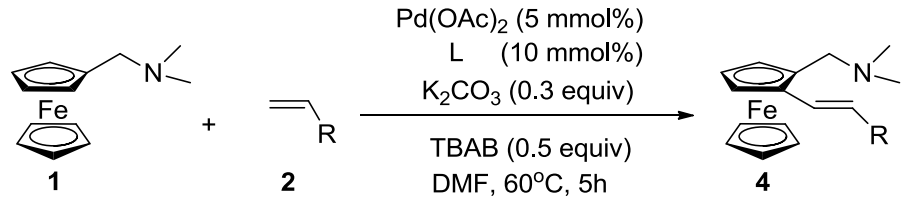
Entry	Product	Yield[%]	Entry	Product	Yield[%]
1	 **3a**	85	7	 **3g**	40
2	 **3b**	70	8	 **3h**	75
3	 **3c**	79	9	 **3i**	72
4	 **3d**	68	10	 **3j**	63
5	 **3e**	92	11	 **3k**	46
6	 **3f**	72	12	 **3l**	50

[a] Reaction Conditions: **1** 1 mmol, **2** 3 mmol, $Pd(OAc)_2$ 5 mmol%, K_2CO_3 0.3 equiv, TBAB 0.5 equiv, $C(CH_3)_3CO_2H$ 1 equiv, DMF 2 mL, 80 °C, 12 h, under air.

3 mmol olefins in 2 mL DMF was added into the 10 mL flask charged with 1 mmol N,N-dimethylaminomethyl ferrocene, 5 mol% $Pd(OAc)_2$ (11.2 mg), 0.3 mmol K_2CO_3, 0.5mmol TBAB, 1mmol PivOH. The mixture was stirred at 80 °C for 12 hours, then

cooled down to room temperature. The desired products were purified by chromatography on silica gel (elute: EtOAc/NEt_3 10/1 v/v).

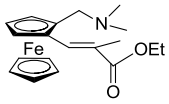
General procedure for enantioselective alkenylation of sp^2 C-H Bonds with olefins.



N,N-Dimethylaminomethyl ferrocene (0.5 mmol, 1 equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Boc-L-Phe-OH (13.3mg, 0.05 mmol, 10 mol%), K_2CO_3 (21.0 mg, 0.15 mmol, 0.3 equiv), TBAB (81.0 mg, 0.25 mmol, 0.5 equiv) were dissolved in 1.5 mL of anhydrous DMF in a 10 mL flask under air. The reaction mixture was stirred at 60 ^oC for 5 h, then cooled down to room temperature. The desired products were purified by chromatography on silica gel (elute: EtOAc/NEt_3 10/1 v/v), and enantiomeric excesses (ees) were determined on a **Waters 1525** HPLC system using commercially available chiral columns as described below.

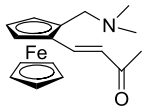
Characterization of new C-H Olefinated Products

(*E*)-Ethyl-2-methyl-3-[2-(N,N-dimethylaminomethylferrocenyl)]acrylate 3g



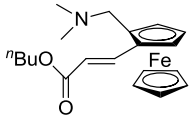
(Table S2, entry 7): Orange solid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1 H), 4.63 (s, 1 H), 4.47 (s, 1 H), 4.42(t, 1 H), 4.29 (q, *J* = 6.70 Hz, 2 H), 4.12 (s, 5 H), 3.65 (d, *J* = 13.10 Hz, 1 H), 3.52 (d, *J* = 12.88 Hz, 1 H), 2.24(s, 6 H), 2.04(s, 3 H), 1.37 (t, *J* = 7.00 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.61, 135.99, 125.06, 79.29, 77.29, 72.55, 69.90, 60.61, 56.59, 44.16, 14.79.

(E)-4-(2-((dimethylamino)methyl)ferrocenyl)but-3-en-2-one 3h[1]



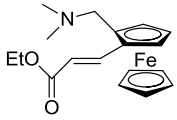
(Table S2, entry 8): Orange solid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 15.85 Hz, 1 H), 6.45 (d, *J* = 15.84 Hz, 1 H), 4.59 (s, 1 H), 4.48 (s, 1 H), 4.43 (s, 1 H), 4.09 (s, 5 H), 3.56 (d, *J* = 12.94 Hz, 1 H), 3.31 (d, *J* = 12.94 Hz, 1 H), 2.31(s, 3 H), 2.18 (s, 6 H). ^{13}C NMR (100MHz, $CDCl_3$): δ 197.75, 142.99, 124.82, 85.39, 78.41, 77.33, 73.82, 70.16, 66.69, 56.97, 44.84, 27.52.

(*E*)-*n*-Butyl-3-[2-(N,N-dimethylaminomethylferrocenyl)]acrylate ($_pS$)**-4a**



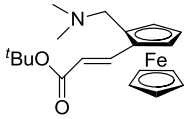
(Table 2, ($_p$*S*)-4a): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 15.64 Hz, 1 H), 6.11 (d, *J* = 15.68 Hz, 1 H), 4.56 (t, *J* = 1.28 Hz, 1 H), 4.43 (t, *J* = 2.32 Hz, 1 H), 4.38 (t, *J* = 2.56 Hz, 1 H), 4.18 (t, *J* = 6.72 Hz, 2 H), 4.09 (s, 5 H), 3.53 (d, *J* = 13.00 Hz, 1 H), 3.29 (d, *J* = 13.00 Hz, 1 H), 2.17 (s, 6 H), 1.68 (m, 2 H), 1.44 (m, 2 H), 0.97 (t, *J* = 7.36 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ 167.44, 143.73, 115.53, 85.22, 78.74, 73.41, 70.16, 69.71, 66.59, 64.13, 57.00, 44.92. 30.85, 19.28, 13.82. HRMS (ESI+): *m/z* calc. for $[C_{20}H_{27}FeNO_2+H]^+$: 370.1464; found $[M+H]^+$: 370.1467. The *ee* was determined by chiral HPLC (IE-3(250*4.6 mm), EtOH : *n*-hexane 2:8, 0.7 mL/min): t_r 10.168 min (major), 14.101 min (minor): > 99% *ee*. $[\alpha]_D^{20.0℃}$ = + 1080^o (*c* = 0.196 in $CHCl_3$, > 99% *ee*).

(*E*)-Ethyl-3-[2-(N,N-dimethylaminomethylferrocenyl)]acrylate ($_p$*S*)-**4b**



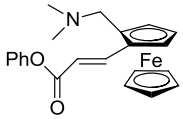
(Table 2, ($_p$*S*)-4b): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 15.68 Hz, 1 H), 6.11 (d, *J* = 15.64 Hz, 1 H), 4.56 (s, 1 H), 4.43 (s, 1 H), 4.38 (s, 1 H), 4.23 (q, 2 H), 4.06 (s, 5 H), 3.53 (d, *J* = 13.00 Hz, 1 H), 3.29 (d, *J* = 13.40 Hz, 1 H), 2.16 (s, 6 H), 1.32(t, *J* = 7.08 Hz, 3 H). ^{13}C NMR (100MHz, $CDCl_3$): δ 167.33, 143.75, 115.50, 85.19, 78.70, 73.41, 70.15, 69.71, 66.61, 60.16, 56.99, 44.91, 14.39. HRMS (ESI+): *m/z* calc. for $[C_{18}H_{23}FeNO_2+H]^+$: 342.1151; found $[M+H]^+$: 342.1151. The *ee* was determined by chiral HPLC (IE-3(250*4.6 mm), EtOH : *n*-hexane 2:8, 0.7 mL/min): t_r 10.718 min (major), 16.386 min (minor): 97% *ee*. $[\alpha]_D^{20.0℃}$ = + 1000^o (*c* = 0.238 in $CHCl_3$, 96% *ee*).

(*E*)-*t*-Butyl-3-[2-(N,N-dimethylaminomethylferrocenyl)]acrylate ($_p$*S*)-**4c**



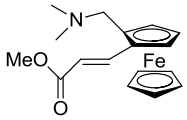
(Table 2, ($_p$*S*)-4c): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 15.64 Hz, 1 H), 6.05 (d, *J* = 15.64 Hz, 1 H), 4.54 (s, 1 H), 4.42 (s, 1 H), 4.36 (s, 1 H), 4.07 (s, 5 H), 3.52 (d, *J* = 12.96 Hz, 1 H), 3.28 (d, *J* = 13.00 Hz, 1 H), 2.17 (s, 6 H), 1.53 (s, 9 H). ^{13}C NMR (100MHz, $CDCl_3$): δ 166.76, 142.52, 117.43, 85.05, 80.01, 73.17, 70.11, 69.51, 68.51, 66.45, 57.00, 44.94, 28.30. HRMS (ESI+): *m/z* calc. for $[C_{20}H_{27}FeNO_2+H]^+$: 370.1464; found $[M+H]^+$: 370.1470. The *ee* was determined by chiral HPLC (IE-3(250*4.6 mm), *i*-PrOH : *n*-hexane 1:13, 0.7 mL/min): t_r 14.010 min (minor), 15.164 min (major): 96% *ee*. $[\alpha]_D^{20.0℃}$ = + 920^o (*c* = 0.184 in $CHCl_3$, 96% *ee*).

(*E*)-Phenyl-3-[2-(N,N-dimethylaminomethylferrocenyl)]acrylate ($_p$*S*)-**4d**



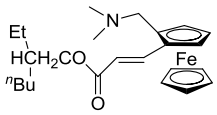
(Table 2, ($_p$*S*)-4d): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 15.60 Hz, 1 H), 7.42 (t, *J* = 7.68 Hz, 2 H), 7.27 (d, *J* = 7.56 Hz, 1 H), 7.17 (d, *J* = 8.12 Hz, 2 H), 6.31 (d, *J* = 15.60 Hz, 1 H), 4.65 (s, 1 H), 4.52 (s, 1 H), 4.47 (d, *J* = 2.12 Hz, 1 H), 4.16 (s, 5 H), 3.58 (d, *J* = 13.08 Hz, 1 H), 3.38 (d, *J* = 13.08 Hz, 1H), 2.22 (s, 6 H). ^{13}C NMR (100MHz, $CDCl_3$): δ 165.70, 151.01, 146.12, 129.39, 125.62, 121.76, 114.38, 85.20, 78.38, 73.95, 70.32, 66.90, 56.90, 44.81. HRMS (ESI+): *m/z* calc. for $[C_{22}H_{23}FeNO_2+H]^+$: 390.1151; found $[M+H]^+$: 390.1158. The *ee* was determined by chiral HPLC (IE-3(250*4.6 mm), EtOH : *n*-hexane 2:8, 0.7 mL/min): t_r 12.697 min (major), 15.657 min (minor): 95% *ee*. $[\alpha]_D^{20.0℃}$ = + 1110^o (*c* = 0.196 in $CHCl_3$, 95% *ee*).

(*E*)-Methyl-3-[2-(N,N-dimethylaminomethylferrocenyl)]acrylate ($_p$*S*)-4e



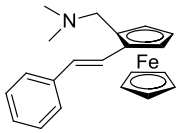
(Table 2, ($_p$*S*)-4e): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 15.68 Hz, 1 H), 6.11 (d, *J* = 15.68 Hz, 1 H), 4.56 (s, 1 H), 4.44 (s, 1 H), 4.38 (s, 1 H), 4.08 (s, 5 H), 3.75 (s, 3 H), 3.54 (d, *J* = 13.00 Hz, 1 H), 3.29 (d, *J* = 13.00 Hz, 1 H), 2.18 (s, 6 H). ^{13}C NMR (100MHz, $CDCl_3$): 167.73, 144.06, 115.07, 85.22, 78.63, 73.51, 70.17, 69.76, 66.70, 57.02, 51.44, 44.92. HRMS (ES+): *m/z* calc. for $[C_{17}H_{21}FeNO_2+H]^+$: 328.0995; found $[M+H]^+$: 328.0996. The *ee* was determined by chiral HPLC (IE-3(250*4.6 mm), EtOH : *n*-hexane 2:8, 0.7 mL/min): t_r 11.293 min (major), 16.700 min (minor): 96% *ee*. $[\alpha]_D^{20.0℃}$ = + 1250^o (*c* = 0.207 in $CHCl_3$, 95% *ee*).

(*E*)-2-ethylhexyl-3-[2-(N,N-dimethylaminomethylferrocenyl)]acrylate ($_p$*S*)-4f



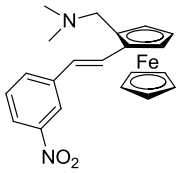
(Table 2, ($_p$*S*)-4f): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 15.64 Hz, 1 H), 6.11 (d, *J* = 15.64 Hz, 1 H), 4.57 (d, *J* = 0.76 Hz, 1 H), 4.44 (s, 1 H), 4.39 (d, *J* = 2.52 Hz, 1 H), 4.10 (s, 5 H), 3.52 (d, *J* = 13.00 Hz, 1 H), 3.29 (d, *J* = 13.00 Hz, 1 H), 2.17 (s, 6 H), 1.65 (m, 1 H), 1.42 (t, 2H), 1.37 (m, 7 H), 0.94 (m, 6 H). ^{13}C NMR (100MHz, $CDCl_3$): δ 167.52, 143.63, 115.57, 85.21, 78.75, 73.39, 70.15, 69.71, 66.56, 57.00, 44.90, 38.92, 30.62, 30.58, 29.01, 24.00, 23.03, 14.10, 11.12. HRMS (ESI+): *m/z* calc. for $[C_{24}H_{35}FeNO_2+H]^+$: 426.2090; found $[M+H]^+$: 426.2095. The *ee* was determined by chiral HPLC (IE-3(250*4.6 mm), *i*-PrOH : *n*-hexane 2:8, 0.6 mL/min): tr 11.328 min (minor), 12.130 min (major): 96% *ee*. $[\alpha]_D^{20.0℃}$ = + 990^o (*c* = 0.216 in $CHCl_3$, 96% *ee*).

(*E*) -1-[2-(N,N-dimethylaminomethylferrocenyl)] -2-Phenyl-ethylene ($_p$*S*)-4g



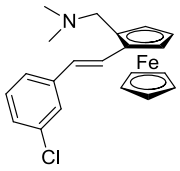
(Table 2, ($_p$*S*)-4g): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.45 (d, *J* = 7.52 Hz, 2 H), 7.33 (t, *J* = 7.44 Hz, 2 H), 7.22 (t, *J* = 7.44 Hz, 1 H), 6.97 (d, *J* = 16.08 Hz, 1 H), 6.78 (d, *J* = 16.12 Hz, 1 H), 4.58 (s, 1 H), 4.33 (s, 1 H), 4.28 (t, *J* = 2.28 Hz, 1 H), 4.07 (s, 5 H), 3.60 (d, *J* = 12.96 Hz, 1 H), 3.36 (d, *J* = 12.96 Hz, 1 H), 2.21 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.06, 128.70, 126.88, 125.93, 125.16, 83.41, 82.46, 71.90, 69.77, 68.12, 65.49, 57.27, 44.90. HRMS (ES+): *m/z* calc. for $[C_{21}H_{23}FeN+H]^+$: 346.1253; found $[M+H]^+$: 346.1256. The *ee* was determined by chiral HPLC (IE-3(250*4.6 mm), *i*-PrOH : *n*-hexane 3:7, 0.5 mL/min): t_r 9.3783 min (major), 10.544 min (minor): 95% *ee*. $[\alpha]_D^{20.0℃}$ = + 740^o (*c* = 0.268 in $CHCl_3$, 95% *ee*).

(*E*)-1-[2-(N,N-dimethylaminomethylferrocenyl)]-2-(3-nitrophenyl)-ethylene ($_p$*S*)-4h



(Table 2, ($_p$*S*)-4h): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28(s, 1 H), 8.04 (m, 1 H), 7.71 (d, *J* = 7.76 Hz, 1 H), 7.48 (t, *J* = 7.92 Hz, 1 H), 7.13 (d, *J* = 16.08 Hz, 1 H), 6.82 (d, *J* = 16.08 Hz, 1 H), 4.60 (s, 1 H), 4.38 (d, *J* = 1.28, 1 H), 4.31 (t, *J* = 2.48, 1 H), 4.10 (s, 5 H), 3.63 (d, *J* = 12.88 Hz, 1 H), 3.29 (d, *J* = 12.92 Hz, 1 H), 2.21 (s, 6 H). ^{13}C NMR (100MHz, $CDCl_3$): δ 148.83, 139.91, 131.69, 129.52, 128.97, 124.20, 121.18, 120.20, 83.50, 82.05, 72.53, 69.88, 68.54, 65.88, 57.52, 45.08. HRMS (ES+): *m/z* calc. for $[C_{21}H_{22}FeN_2O_2+H]^+$: 391.1104; found $[M+H]^+$: 391.1105. The *ee* was determined by chiral HPLC (AD-H(250*4.6 mm), *i*-PrOH : *n*-hexane 3:7, 0.7 mL/min): t_r 5.909 min (major), 6.832 min (minor): 94% *ee*. $[\alpha]_D^{20.0℃}$ = + 670° (*c* = 0.214 in $CHCl_3$, 94% *ee*).

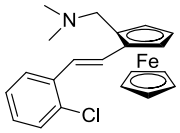
(*E*)-1-[2-(N,N-dimethylaminomethylferrocenyl)]-2-(3-chlorophenyl)-ethylene ($_p$*S*)-4i



(Table 2, ($_p$*S*)-4i): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 1 H), 7.31 (d, *J* = 7.56, 1 H), 7.23-7.27 (m, 1 H), 7.19 (d, *J* = 7.72 Hz, 1 H), 6.99 (d, *J* = 16.08Hz, 1 H), 6.72(d, *J* = 16.04 Hz, 1 H), 4.57 (s, 1 H), 4.35 (s, 1 H), 4.29 (t, *J* = 2.32 Hz, 1 H), 4.07(s, 5 H), 3.60 (d, *J* = 12.96 Hz, 1 H), 3.33 (d, *J* = 12.96 Hz, 1 H), 2.21 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.99, 134.64, 129.88, 126.94, 126.69, 125.63,

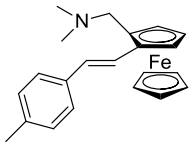
125.34, 124.18, 82.93, 82.72, 72.18, 69.82, 68.31, 65.65, 57.36, 44.97. HRMS (ES+): *m/z* calc. for $[C_{21}H_{22}ClFeN+H]^+$: 380.0863; found $[M+H]^+$: 380.0866. The *ee* was determined by chiral HPLC (AS-H(250*4.6 mm), *i*-PrOH : *n*-hexane 0.1:9.9, 0.5 mL/min): t_r 9.526 min (major), 12.346 min (minor): 96% *ee*. $[\alpha]_D^{20.0℃}$ = + 710° (*c* = 0.21 in $CHCl_3$, 96% *ee*).

(*E*)-1-[2-(N,N-dimethylaminomethylferrocenyl)]-2-(2-chlorophenyl)-ethylene ($_pS$)-**4j**



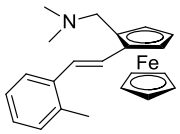
(Table 2, ($_pS$)-4j): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.76, 1 H), 7.36 (d, *J* = 7.88, 1 H), 7.26 (d, *J* = 3.72, 1 H), 7.23-7.14 (m, 2 H), 6.98 (d, *J* = 16.08 Hz, 1 H), 4.64 (s, 1 H), 4.35 (s, 1 H), 4.29 (t, *J* = 2.32 Hz, 1 H), 4.08(s, 5 H), 3.64 (d, *J* = 12.96 Hz, 1 H), 3.35 (d, *J* = 12.96 Hz, 1 H), 2.22 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.14, 132.57, 129.87, 128.17, 127.77, 126.90, 126.12, 122.88, 82.88, 82.63, 72.24, 69.91, 68.39, 66.23, 57.31, 44.89. HRMS (ES+): *m/z* calc. for $[C_{21}H_{22}ClFeN+H]^+$: 380.0863; found $[M+H]^+$: 380.0865. The *ee* was determined by chiral HPLC (IE-3(250*4.6 mm), *i*-PrOH : *n*-hexane 3:7, 0.5 mL/min): t_r 9.549 min (major), 12.438 min (minor): 96% *ee*. $[\alpha]_D^{20.0℃}$ = + 990° (*c* = 0.168 in $CHCl_3$, 96% *ee*).

(*E*)-1-[2-(N,N-dimethylaminomethylferrocenyl)]-2-(4-metheyl)-ethylene ($_pS$)-**4k**



(Table 2, ($_pS$)-4k): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.96 Hz, 2 H), 7.14 (d, *J* = 7.88 Hz, 2 H), 6.91 (d, *J* = 16.12 Hz, 1 H),6.74 (d, *J* = 16.08 Hz, 1 H), 4.57 (s, 1 H), 4.31 (s, 1 H), 4.25 (t, *J* = 2.32 Hz, 1 H), 4.06 (s, 5 H), 3.59 (d, *J* = 12.92 Hz, 1 H), 3.36 (d, *J* = 13.00 Hz, 1 H), 2.34 (s, 3 H), 2.21 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.73, 135.31, 129.40, 126.85, 125.85, 124.08, 83.69, 82.34, 71.77, 69.74, 68.00, 65.39, 57.28, 44.92, 21.28. HRMS (ES+): *m/z* calc. for $[C_{22}H_{25}FeN+H]^+$: 360.1409; found $[M+H]^+$: 360.1410. The *ee* was determined by chiral HPLC (IE-3(250*4.6 mm), *i*-PrOH : *n*-hexane 3:7, 0.5 mL/min): t_r 9.616 min (major), 11.793 min (minor): 96% *ee*. $[\alpha]_D^{20.0℃}$ = + 730° (*c* = 0.232 in $CHCl_3$, 96% *ee*).

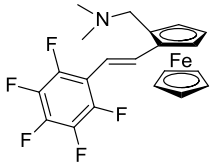
(*E*)-1-[2-(N,N-dimethylaminomethylferrocenyl)]-2-(2-metheyl)-ethylene ($_pS$)-**4l**



(Table 2, ($_pS$)-4l): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.44 Hz,

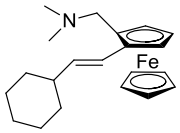
1 H), 7.21 (m, 1 H), 7.15 (d, *J* = 3.92 Hz, 2 H), 7.01 (d, *J* = 15.92 Hz, 1H), 6.87 (d, *J* = 15.92 Hz, 1 H), 4.59 (s, 1 H), 4.34 (s, 1 H), 4.27 (t, *J* = 2,40 Hz, 1 H), 4.08 (s, 5 H), 3.61 (d, *J* = 12.96 Hz, 1 H), 3.38 (d, *J* = 13.00 Hz, 1 H), 2.39 (s, 3 H), 2.22 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.13, 135.05, 130.45, 126.91, 126.43, 126.21, 125.00, 124.71, 83.81, 82.33, 72.00, 69.81, 68.10, 65.72, 57.24, 44.87, 20.04. HRMS (ES+): *m/z* calc. for $[C_{22}H_{25}FeN+H]^+$: 360.1409; found $[M+H]^+$: 360.1411. The *ee* was determined by chiral HPLC (IE-3(250*4.6 mm), *i*-PrOH : *n*-hexane 3:7, 0.5 mL/min): t_r 9.208 min (major), 9.994 min (minor): 96% *ee*. $[\alpha]_D^{20.0℃}$ = + 800^o (*c* = 0.196 in $CHCl_3$, 96% *ee*).

(*E*)-1-[2-(N,N-dimethylaminomethylferrocenyl)]-2-(2,3,4,5,6,fluorine)-ethylene ($_pS$)-**4n**



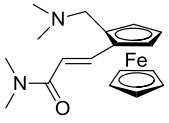
(Table 2, ($_pS$)-4n): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 16.48 Hz, 1 H), 6.66 (d, *J* = 16.48 Hz, 1 H), 4.60 (s, 1 H), 4.39 (s, 1 H), 4.34 (d, *J* = 2.40 Hz, 1 H), 4.09 (s, 5 H), 3.56 (d, *J* = 12.96 Hz, 1 H), 3.27 (d, *J* = 12.96 Hz, 1 H), 2.20 (s, 6 H). ^{13}C NMR (100MHz, $CDCl_3$): δ 135.31, 110.03, 83.80, 82.04, 72.85, 70.00, 68.87, 65.85, 57.43, 44.96. HRMS (ES+): *m/z* calc. for $[C_{21}H_{18}F_5FeN+H]^+$: 436.0782; found $[M+H]^+$: 476.0785. The *ee* was determined by chiral HPLC (IE-3(250*4.6 mm), *i*-PrOH : *n*-hexane 5:5, 0.3 mL/min): t_r 15.183 min (major), 15.936 min (minor): 91% *ee*. $[\alpha]_D^{20.0℃}$ = + 690^o (*c* = 0.18 in $CHCl_3$, 91% *ee*).

(*E*)-1-[2-(N,N-dimethylaminomethylferrocenyl)]-2-cyclohexyl-ethylene ($_pS$)-**4o**



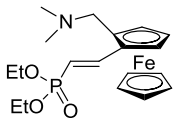
(Table 2, ($_pS$)-4o): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (d, *J* = 15.76 Hz, 1 H), 5.81(m, 1 H), 4.39 (s, 1 H), 4.20 (d, *J* = 2.00 Hz, 1 H), 4.13 (t, *J* = 2.40 Hz, 1 H), 3.99 (s, 5 H), 3.46 (d, *J* = 12.92 Hz, 1 H), 3.29 (d, *J* = 12.96 Hz, 1 H), 2.18 (s, 6 H), 2.02 (m, 1 H), 1.76 (m, 4 H), 1.20 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.24, 122.33, 84.37, 81.52, 70.98, 69.67, 67.28, 65.22, 57.11, 44.87, 41.35, 33.44, 33.12, 29.73, 26.24, 26.11, 26.08. HRMS (ES+): *m/z* calc. for $[C_{21}H_{29}FeN+H]^+$: 352.1722; found $[M+H]^+$: 352.1724. The *ee* was determined by chiral HPLC (AD-H(250*4.6 mm), *i*-PrOH : *n*-hexane 0.3:0.87, 0.9 mL/min): t_r 4.073 min (major), 4.811 min (minor): 94% *ee*. $[\alpha]_D^{20.0℃}$ = + 560^o (*c* = 0.212 in $CHCl_3$, 94% *ee*).

(*E*)-1-[2-(N,N-dimethylaminomethylferrocenyl)]-2-(N,N-dimethylformamide)-ethylene ($_pS$)-**4p**



(Table 2, ($_p$*S*)-4p): Orange solid; 1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 14.64 Hz, 1 H), 6.61 (d, *J* = 14.68 Hz, 1 H), 4.49 (s, 1 H), 4.39 (s, 1 H), 4.31 (s, 1 H), 4.07 (s, 5 H), 3.58 (d, *J* = 12.16 Hz, 1 H), 3.25 (d, *J* = 10.56 Hz, 1 H), 3.09 (s, 3 H), 3.02 (s, 3 H), 2.16 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.01, 140.95, 115.00, 84.30, 80.30, 73.21, 70.00, 69.12, 66.82,57.21, 44.80, 37.28, 35.83. HRMS (ESI+): *m/z* calc. for $[C_{18}H_{24}FeN_2O+H]^+$: 341.1311; found $[M+H]^+$: 341.1313. The *ee* was determined by chiral HPLC (AS-H(250*4.6 mm), EtOH: *n*-hexane 0.06:0.54, 0.6 mL/min): t_r 9.190 min (major), 12.367 min (minor): 97% *ee*. $[\alpha]_D^{20.0℃}$ = + 750^o (*c* = 0.158 in $CHCl_3$, 97% *ee*).

(*E*)-1-[2-(N,N-dimethylaminomethylferrocenyl)]-2-(diethyl phosphite)-ethylene ($_p$*S*)-4q



(Table 2, ($_p$*S*)-4q): Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (m, 1 H), 5.91 (m, 1 H), 4.54 (s, 1 H), 4.43 (s, 1 H), 4.37 (d, *J* = 2.20 Hz, 1 H), 4.13 (d, *J* = 7.36 Hz, 4 H), 4.08 (s, 5 H), 3.53 (d, *J* = 13.00 Hz, 1 H), 3.32 (d, *J* = 13.00 Hz, 1 H), 2.17 (s, 6 H), 1.36 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.60, 109.69, 84.45, 73.36, 70.16, 69.58, 66.48, 61.66, 61.61, 56.80, 44.69, 29.72, 16.46. HRMS (ESI+): *m/z* calc. for $[C_{19}H_{28}FeNO_3P+H]^+$: 406.1229; found $[M+H]^+$: 406.1235. The *ee* was determined by chiral HPLC (AS-H(250*4.6 mm), *i*-PrOH: *n*-hexane 0.2:0.2, 0.4 mL/min): t_r 21.105 min (major), 12.886 min (minor): 93% *ee*. $[\alpha]_D^{20.0℃}$ = + 430^o (*c* = 0.32 in $CHCl_3$, 93% *ee*).

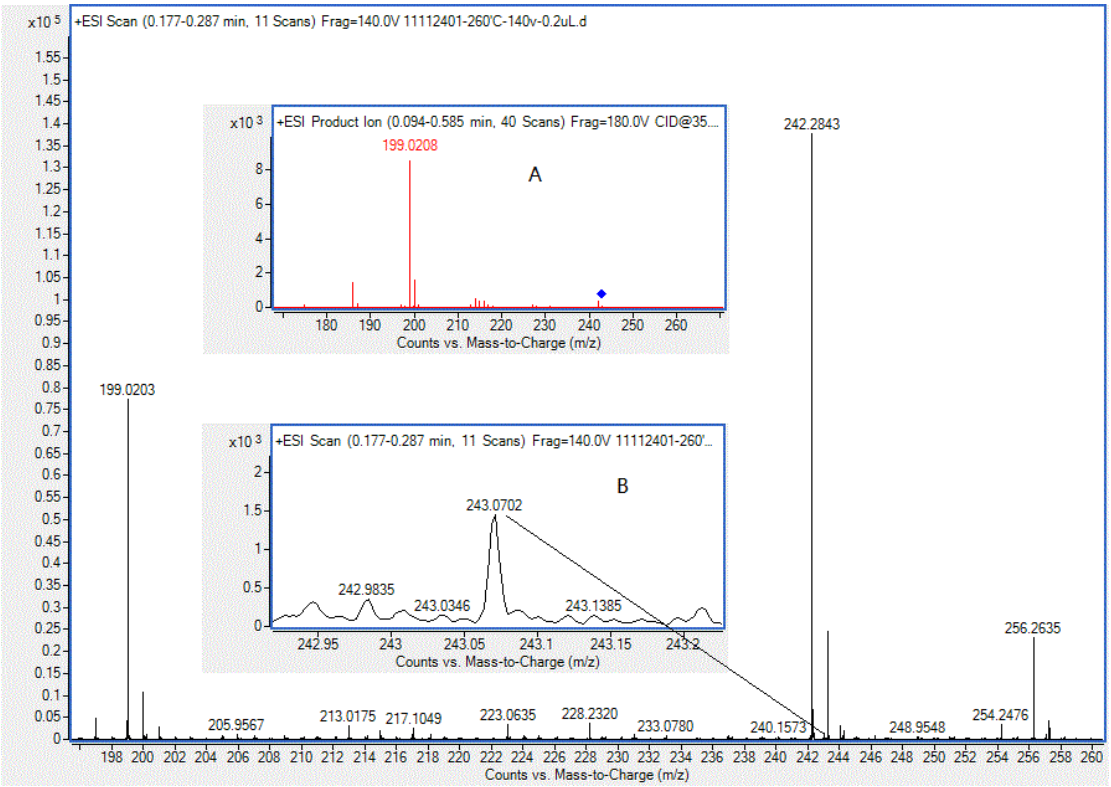


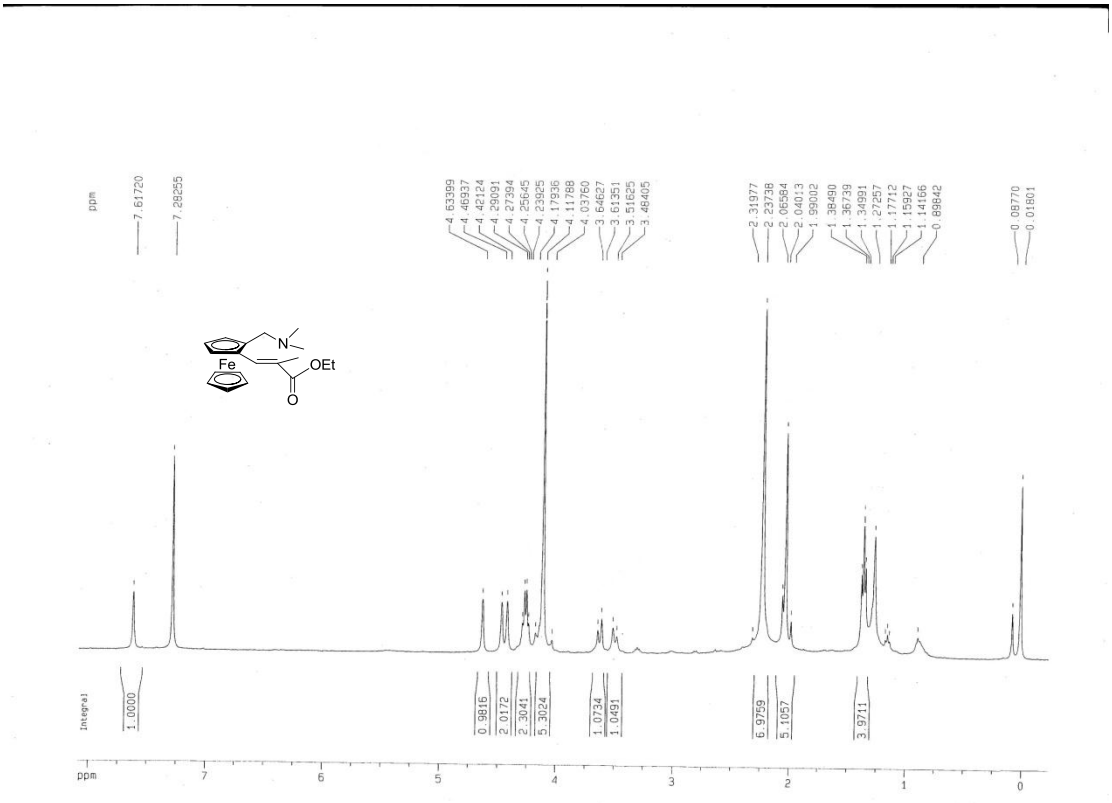
Fig. SI ESI-(+)-MS of the sample taken at 2 h after mixing N, N-dimethyl aminomethyl ferrocene **1** and butyl acrylate **2a** under optimal reaction conditions.

A: MS/MS of principal ion in MS spectrum at m/z 243.0702
B: ESI-(+)-MS/MS of N, N-dimethylaminomethyl ferrocenium (calcd. for $C_{13}H_{17}FeN^+$: m/z 243.0710; $C_{11}H_{11}Fe^+$: m/z 199.0210)

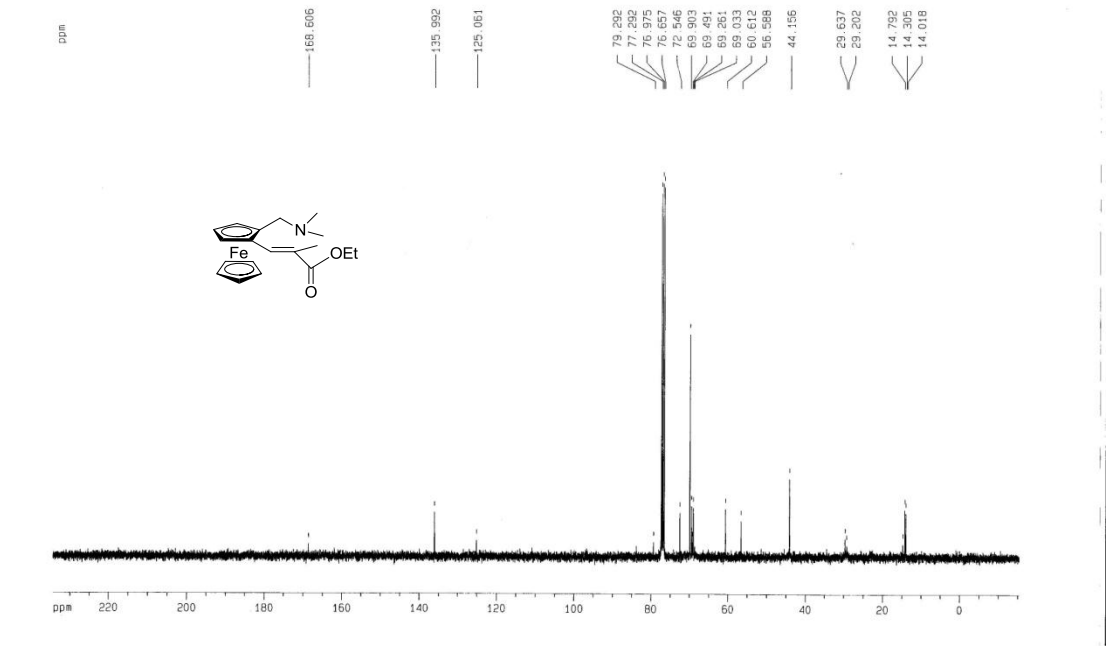
References:

(1) Izumi T.; Endo K.; Saito O.; Shimizu I.; Maemura M.; Kasahara A. *Bull. Chem. Soc. Jpn.*, **1977**, *51*: 663-664

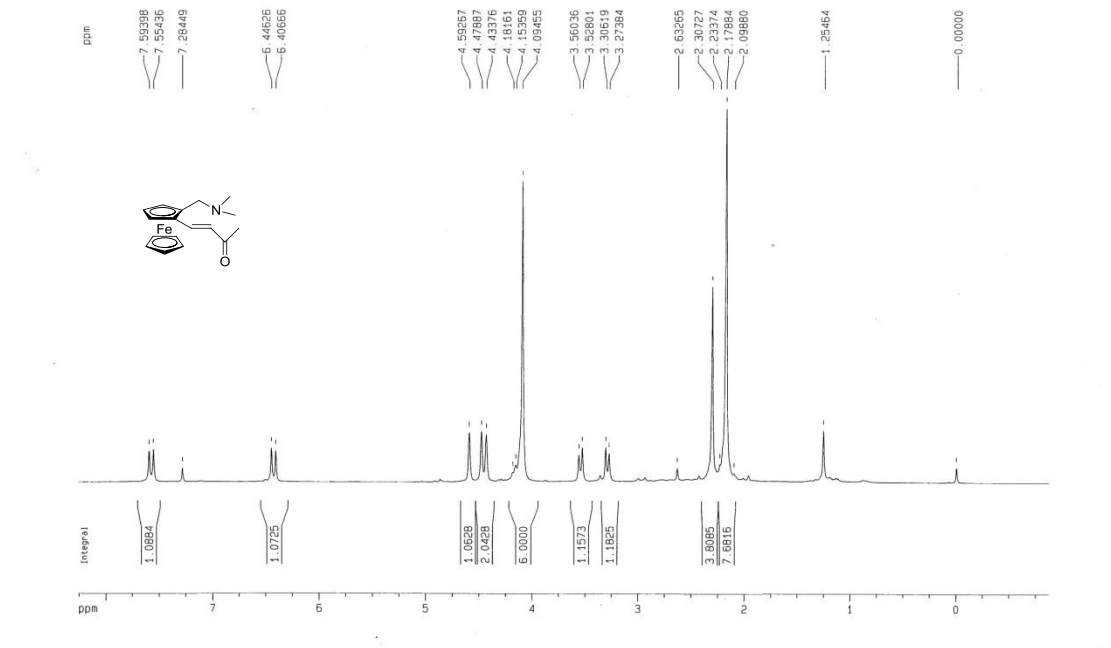
NMR Data



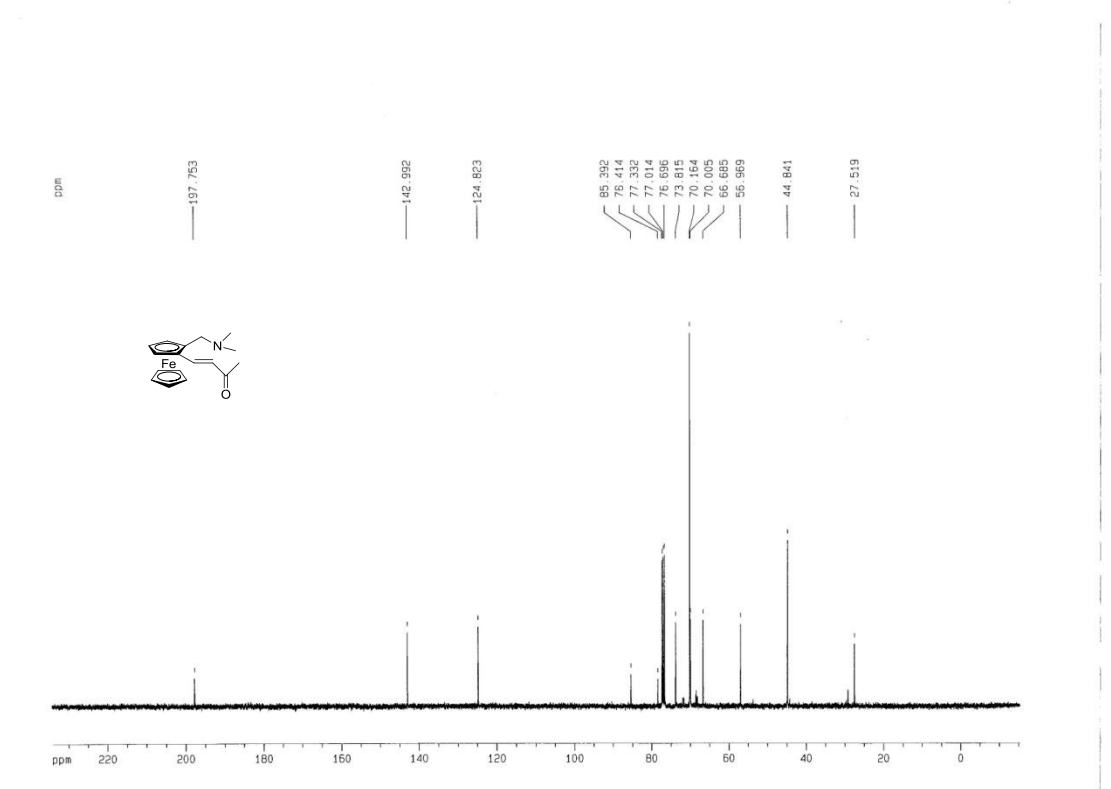
^{1}H NMR spectrum of compound 3g



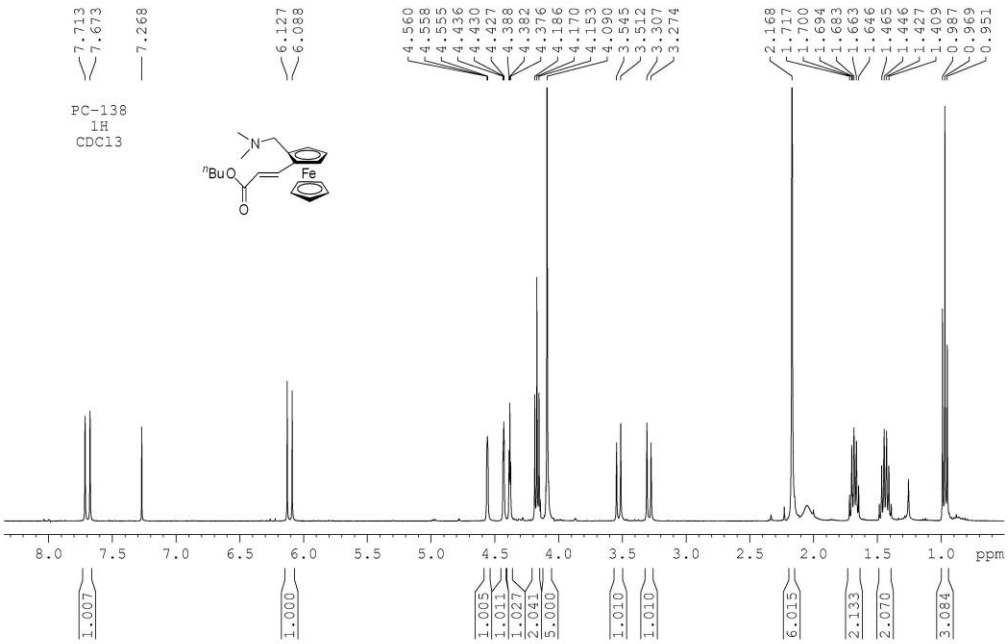
^{13}C NMR spectrum of compound 3g



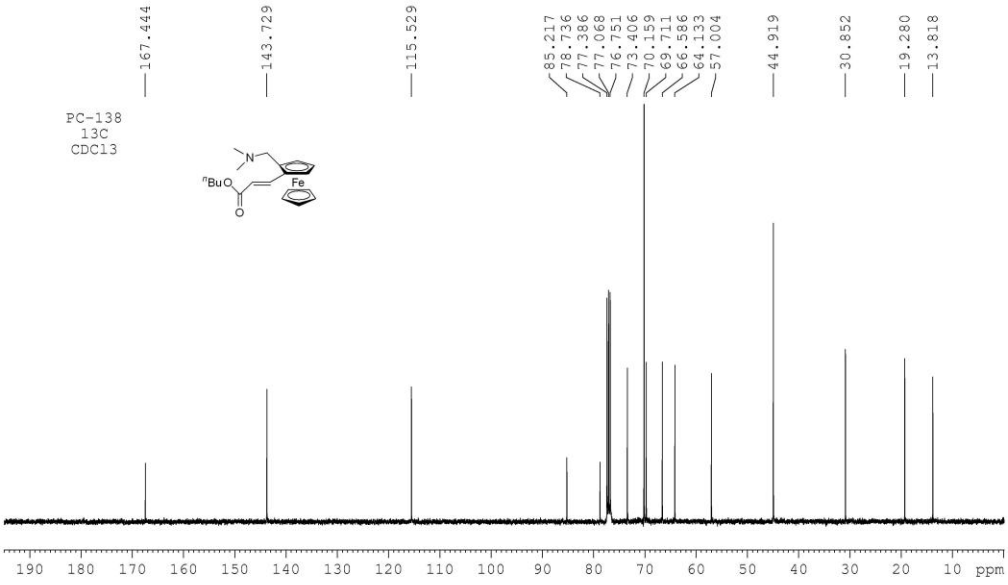
^{1}H NMR spectrum of compound 3h



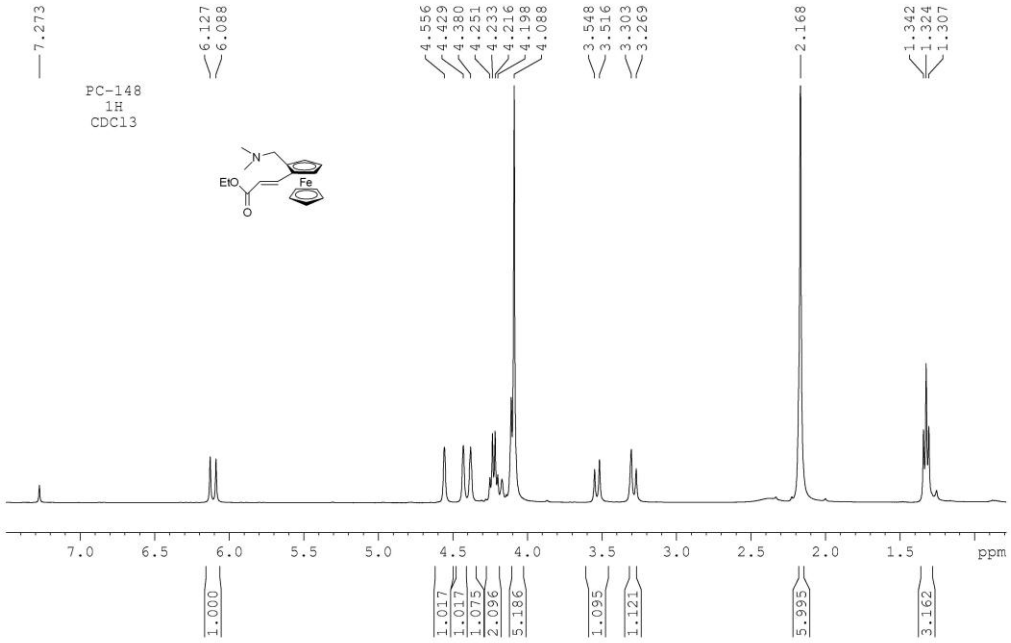
^{13}C NMR spectrum of compound 3h



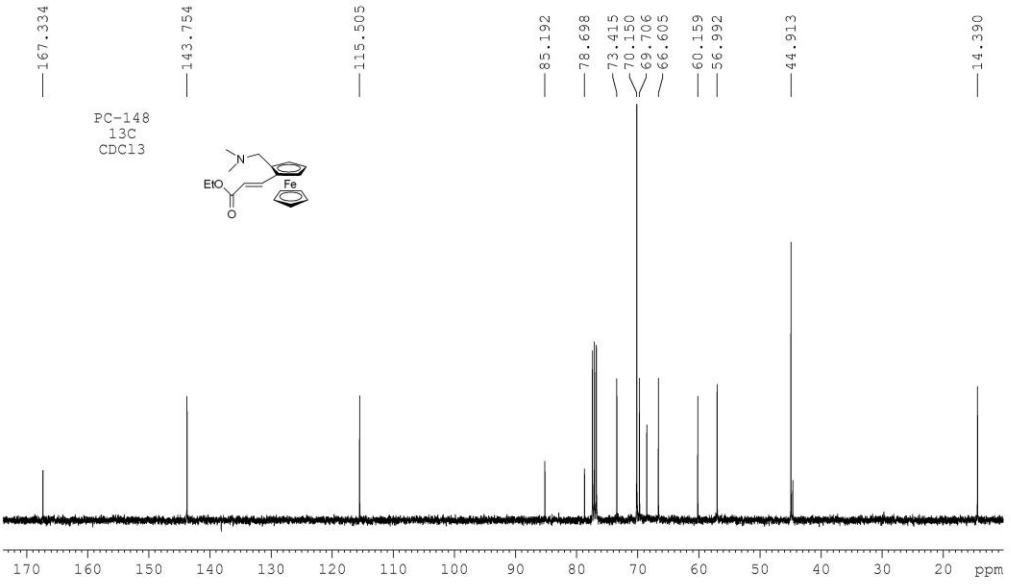
^{1}H NMR spectrum of compound 4a



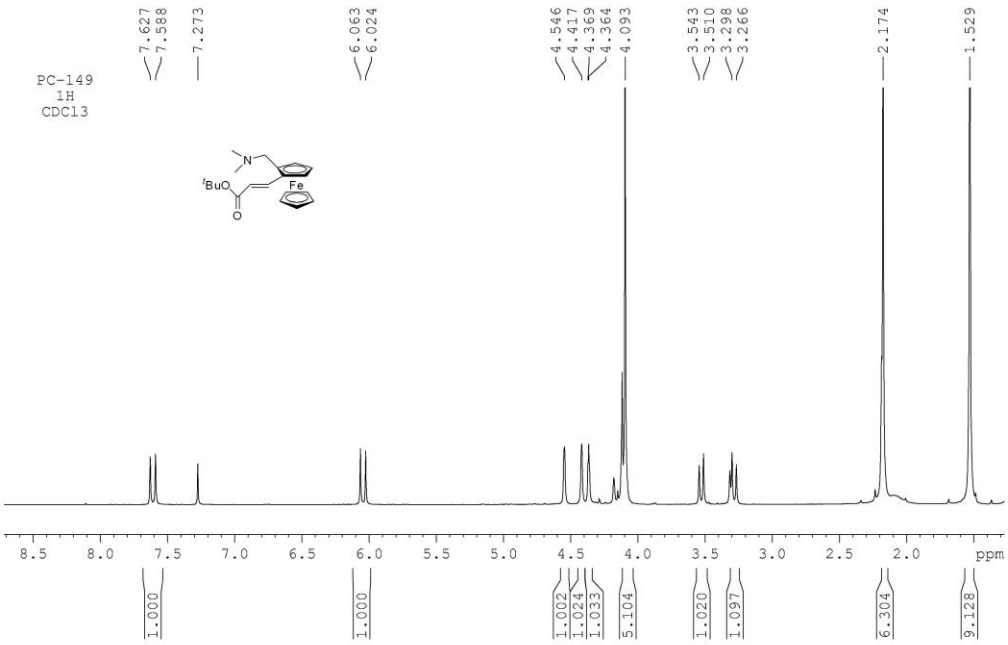
^{13}C NMR spectrum of compound 4a



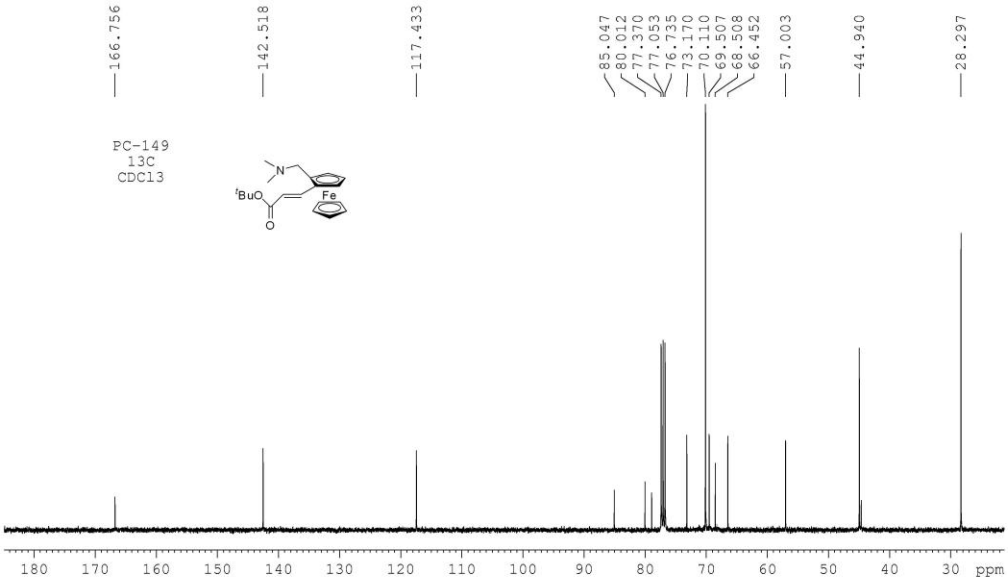
^{1}H NMR spectrum of compound 4b



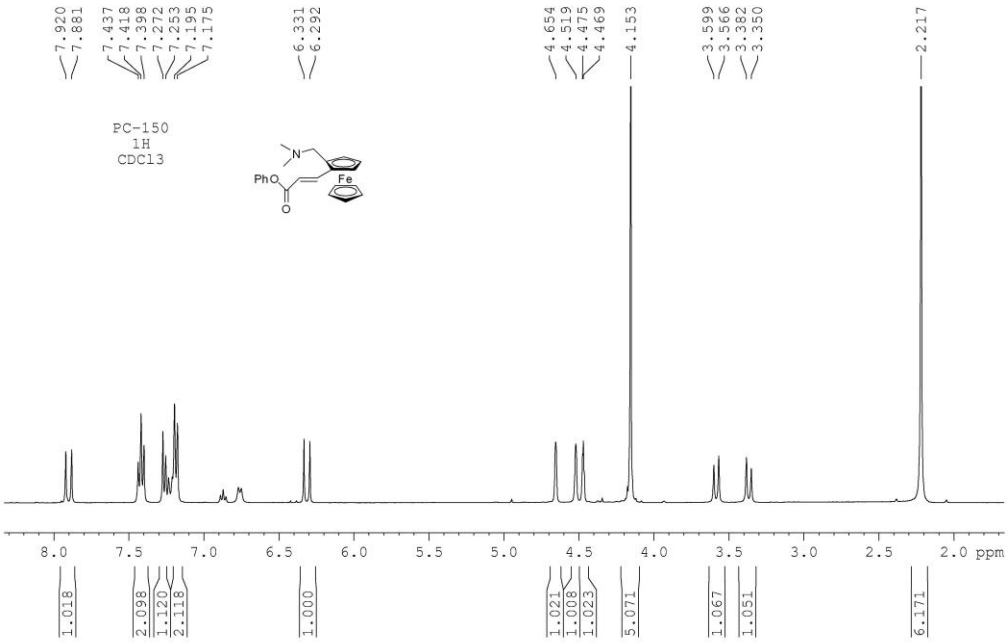
^{13}C NMR spectrum of compound 4b



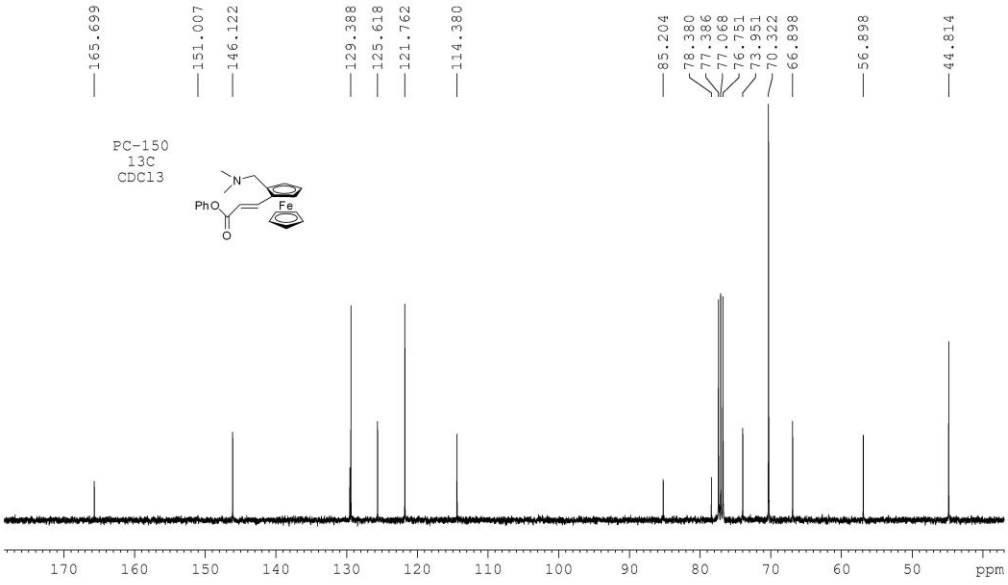
^{1}H NMR spectrum of compound 4c



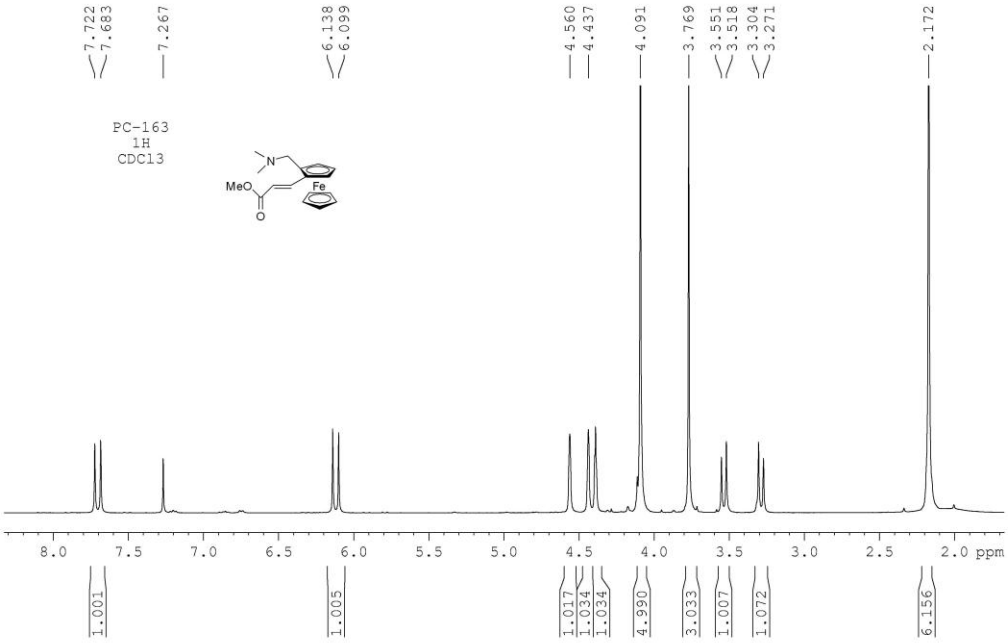
^{13}C NMR spectrum of compound 4c



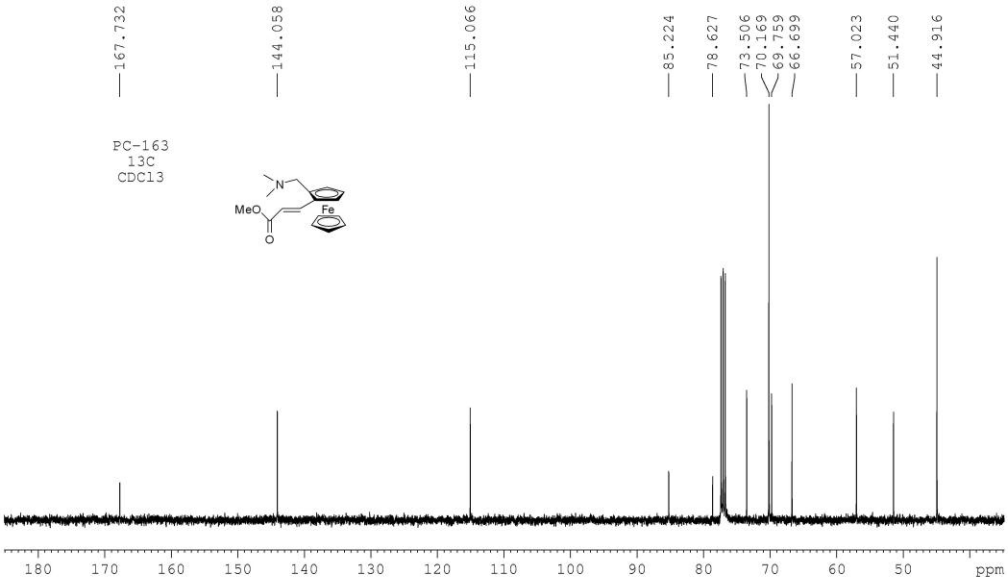
^{1}H NMR spectrum of compound 4d



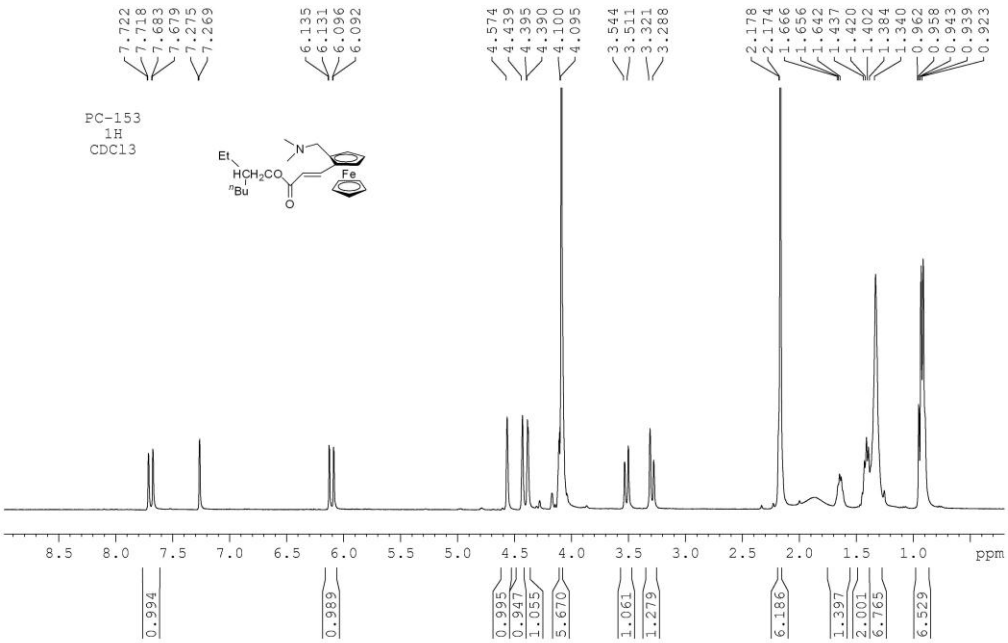
^{13}C NMR spectrum of compound 4d



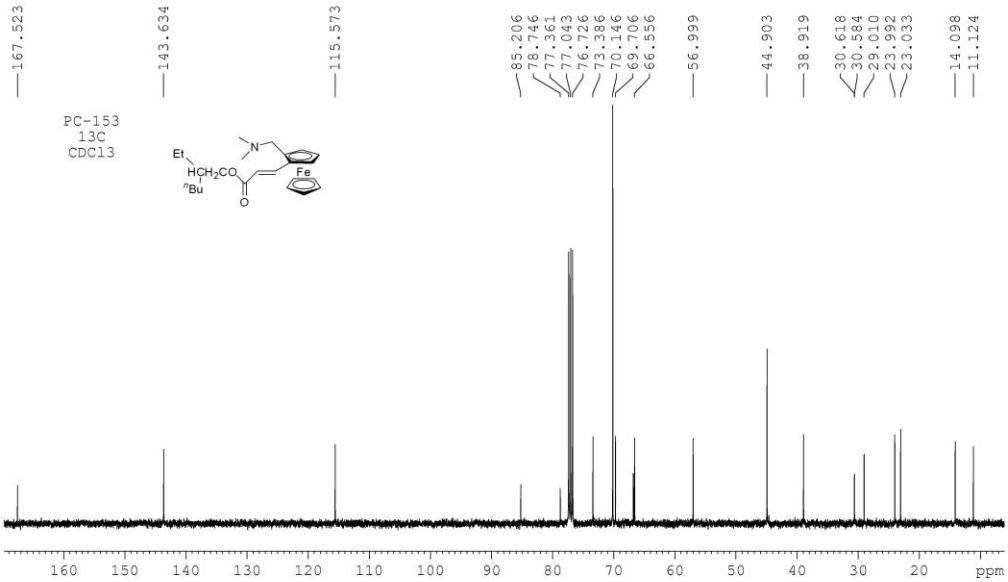
^{1}H NMR spectrum of compound 4e



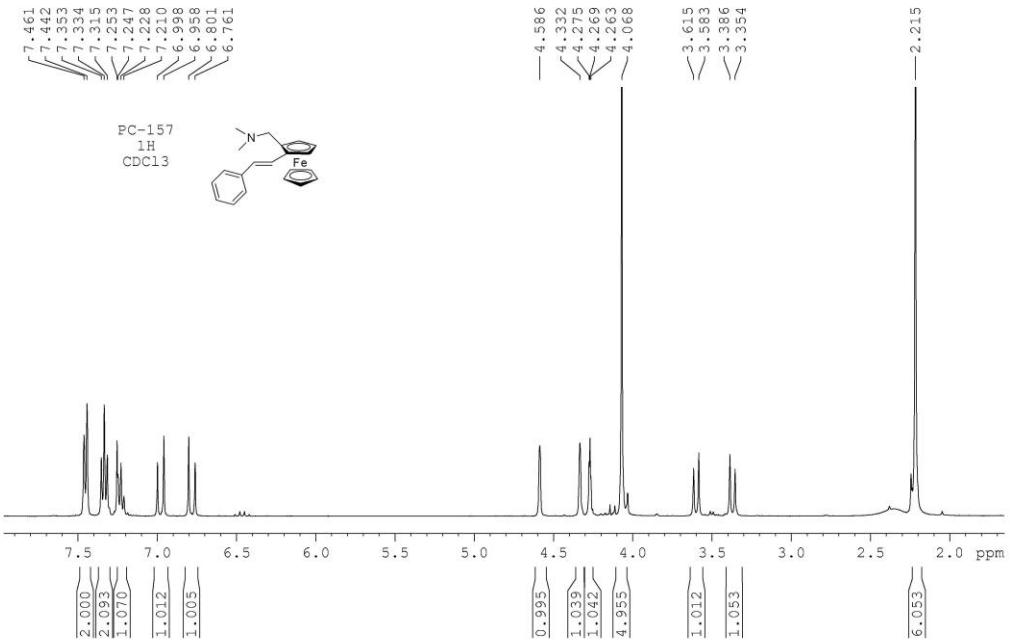
^{13}C NMR spectrum of compound 4e



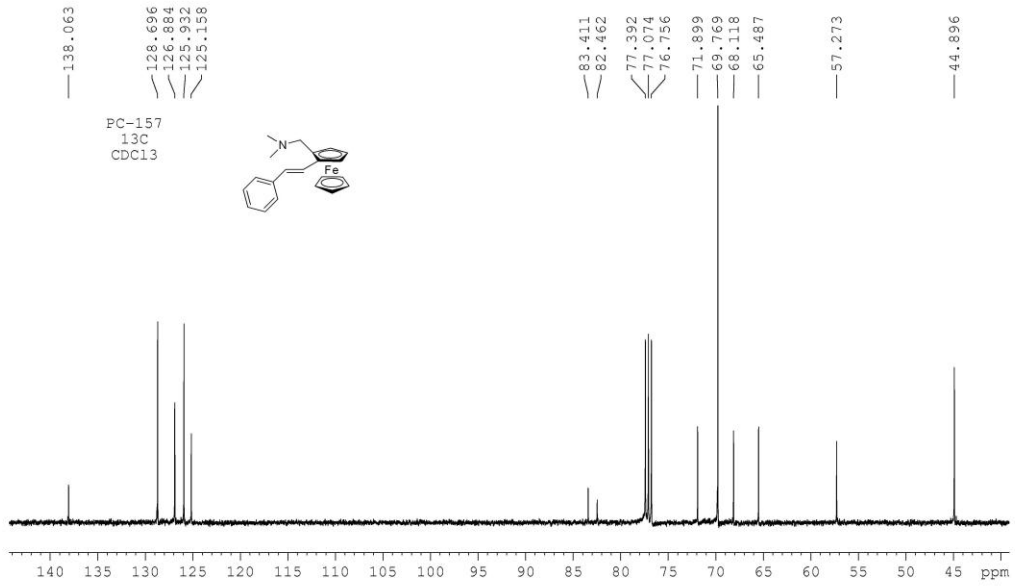
^{1}H NMR spectrum of compound 4f



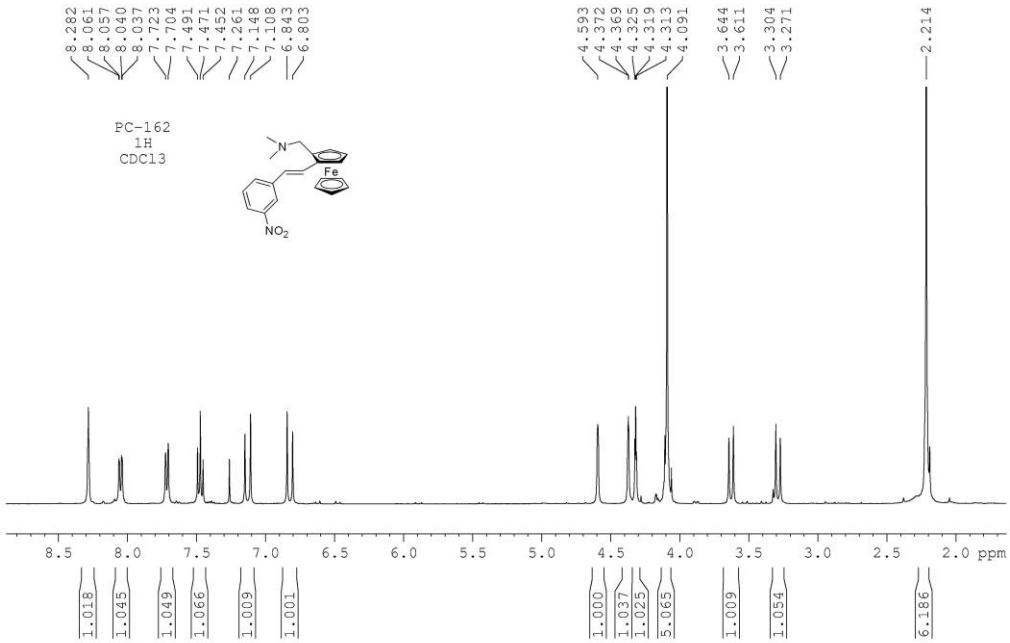
^{13}C NMR spectrum of compound 4f



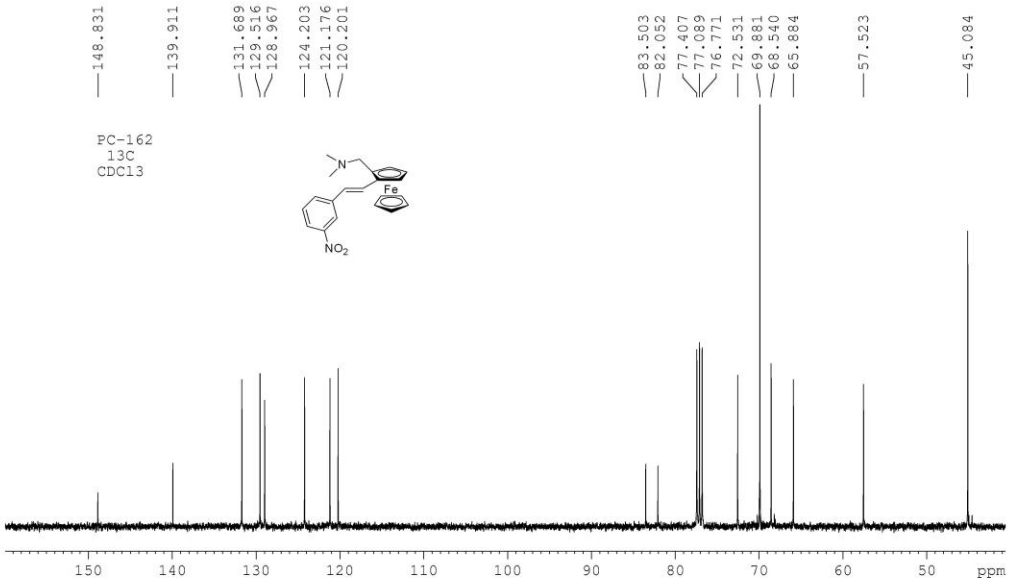
^{1}H NMR spectrum of compound 4g



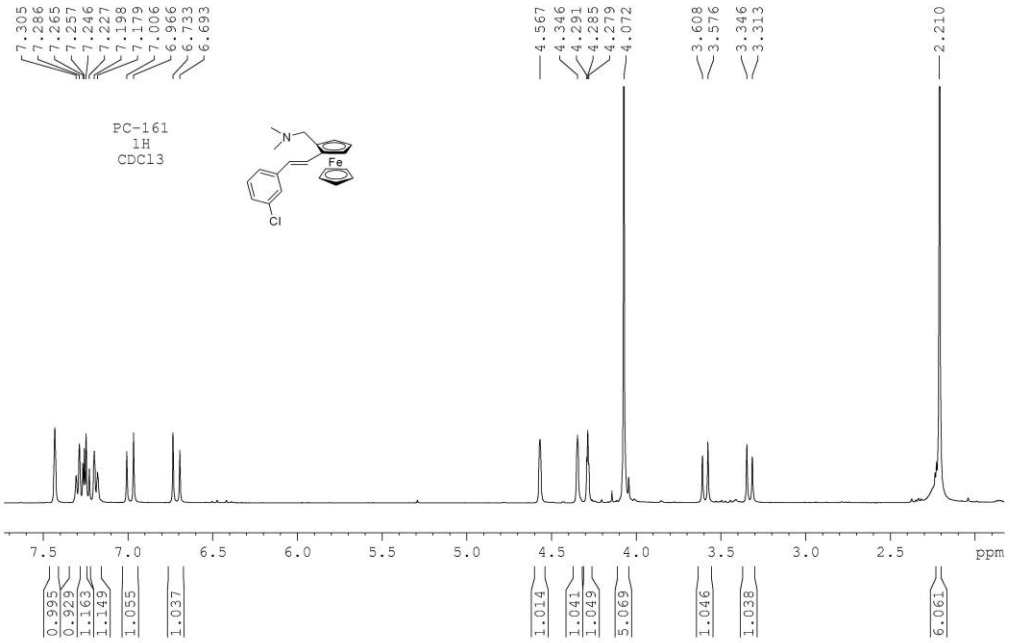
^{13}C NMR spectrum of compound 4g



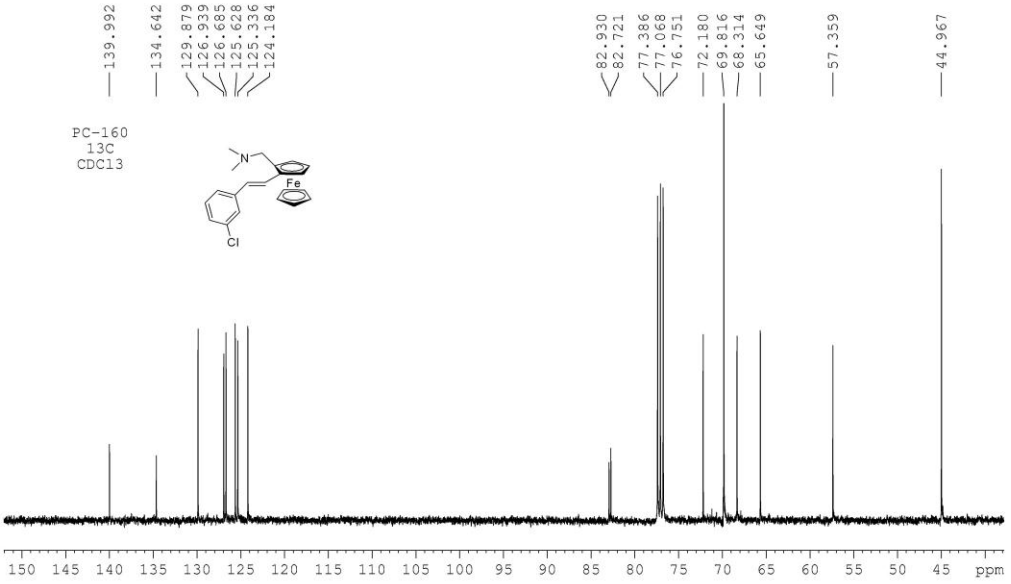
^{1}H NMR spectrum of compound 4h



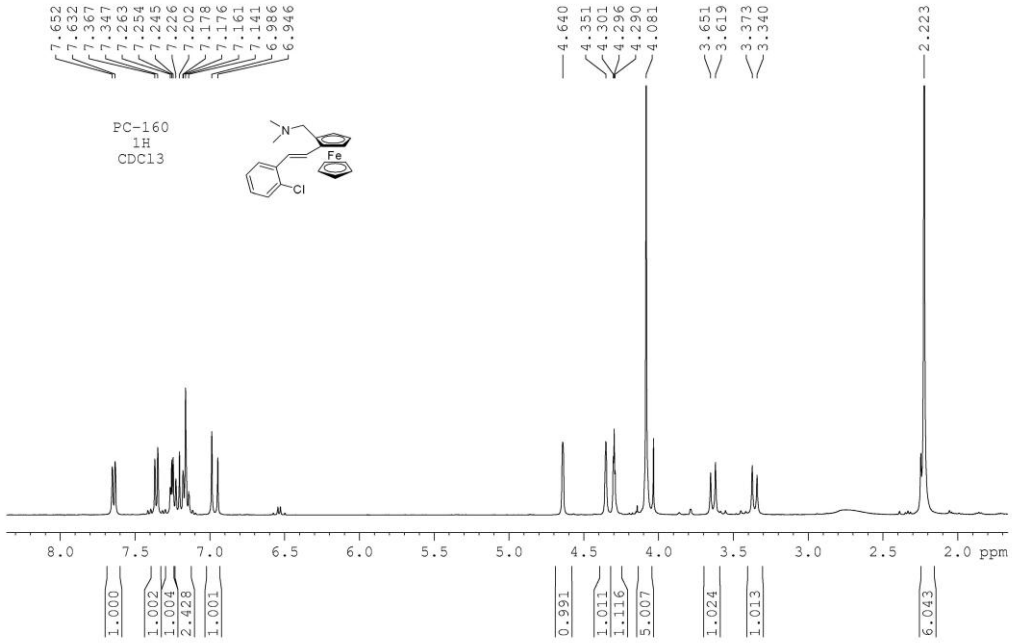
^{13}C NMR spectrum of compound 4h



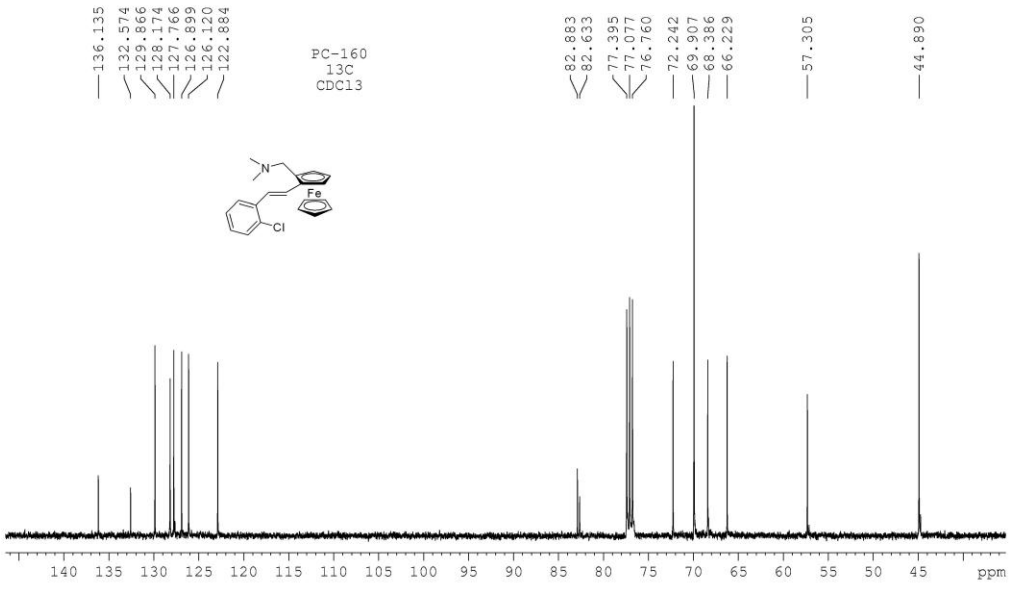
^{1}H NMR spectrum of compound 4i



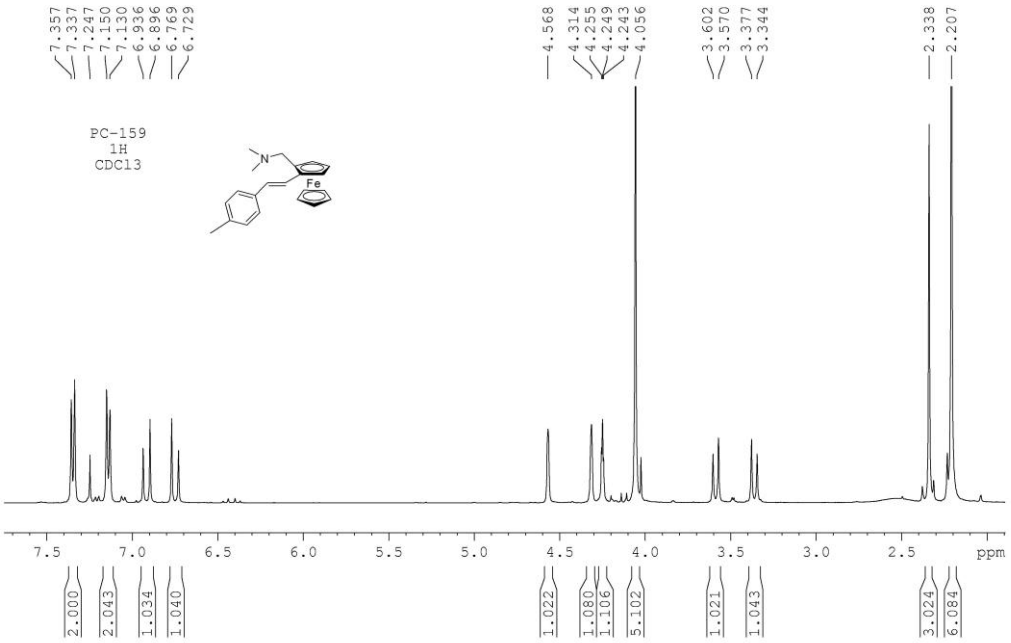
^{13}C NMR spectrum of compound 4i



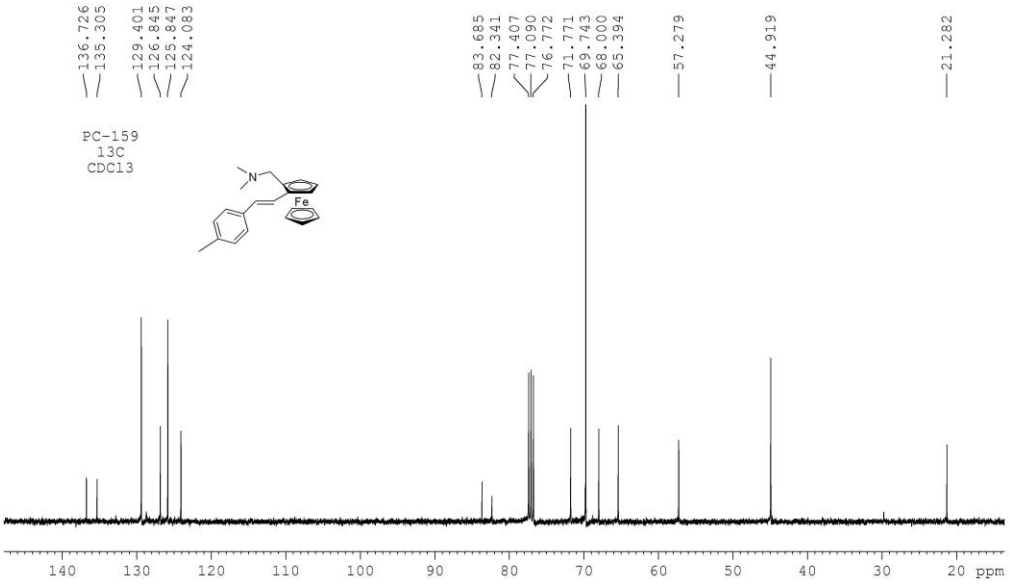
^{1}H NMR spectrum of compound 4j



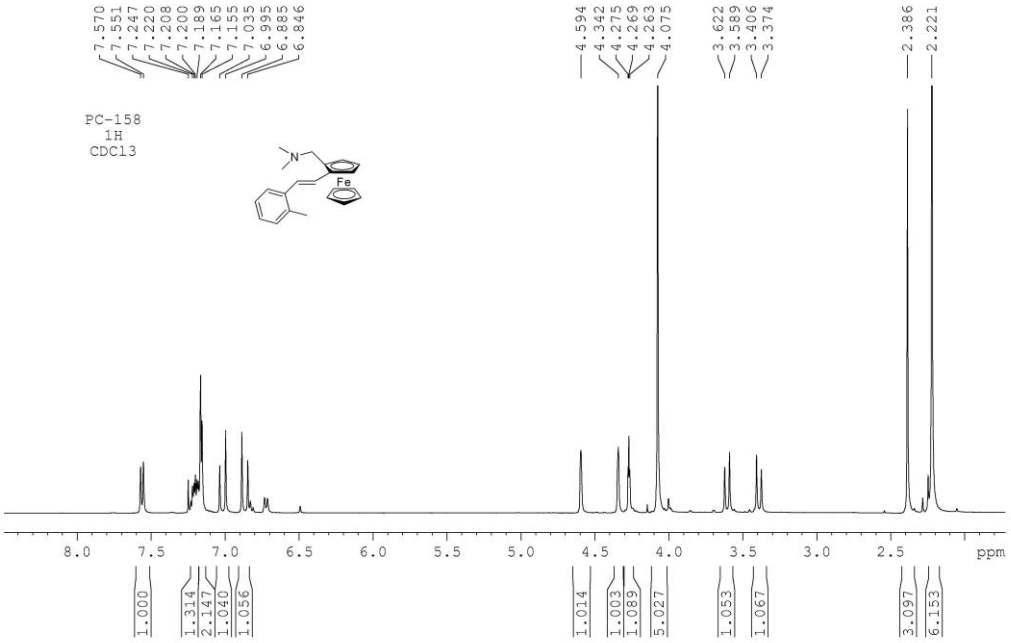
^{13}C NMR spectrum of compound 4j



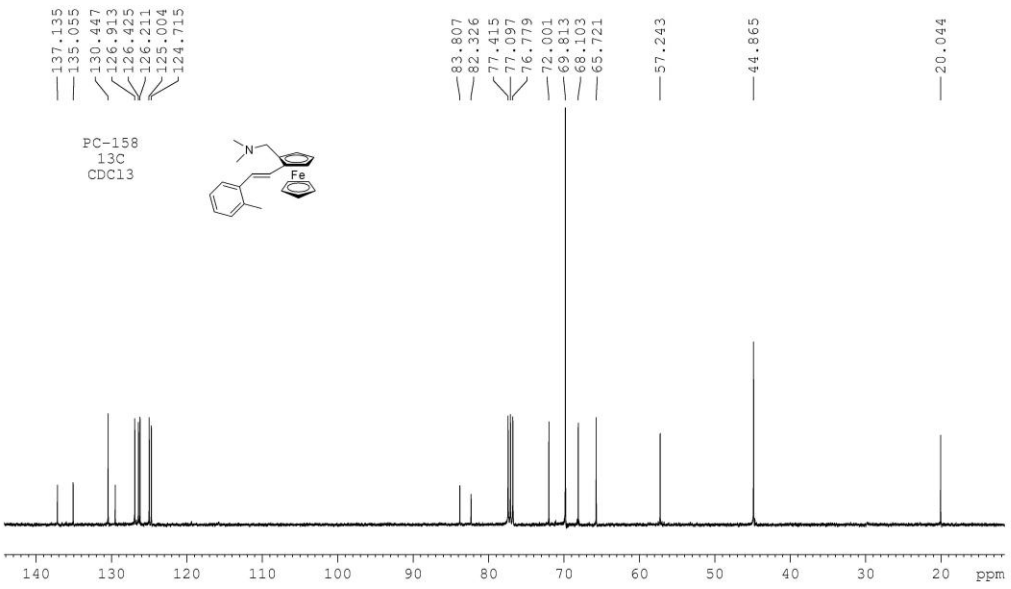
^{1}H NMR spectrum of compound 4k



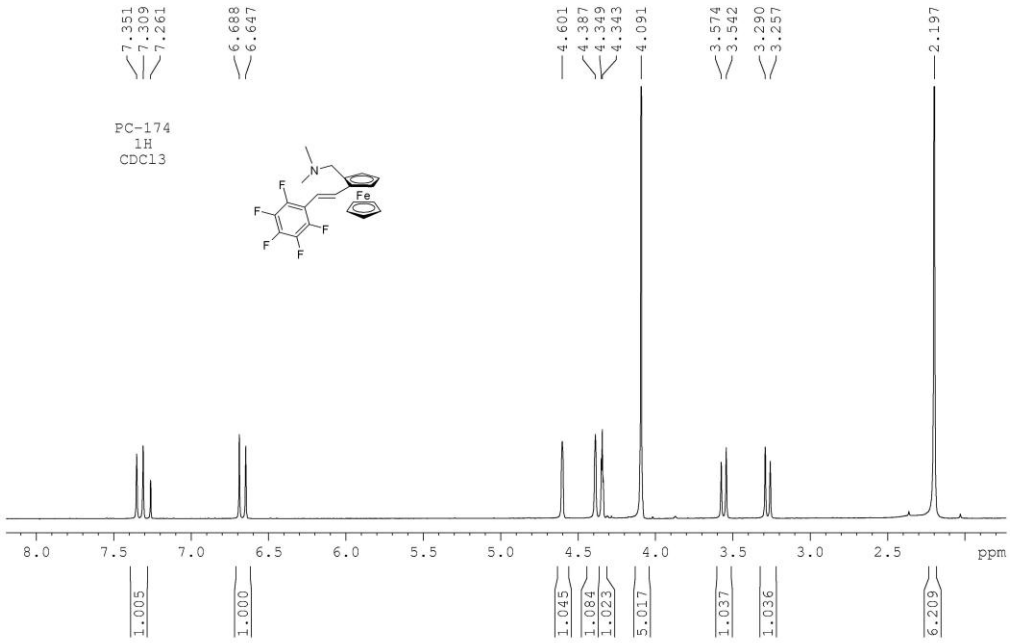
^{13}C NMR spectrum of compound 4k



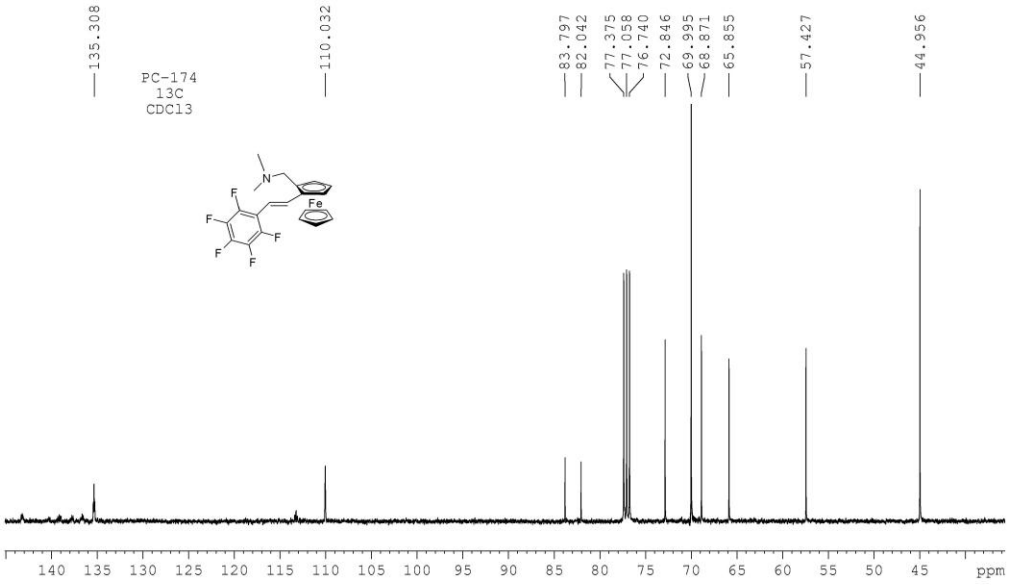
^{1}H NMR spectrum of compound 4l



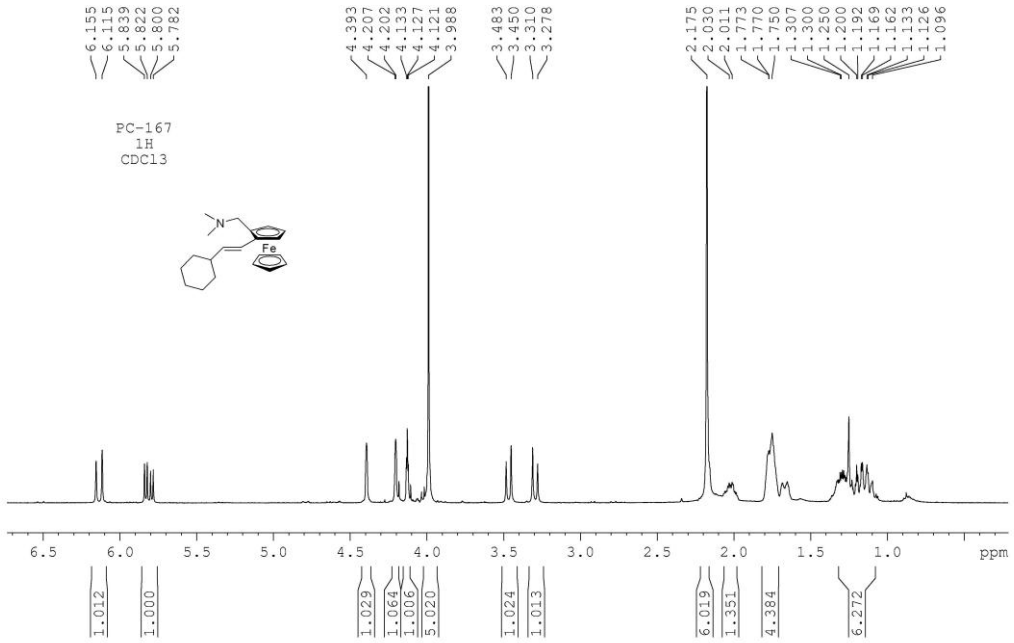
^{13}C NMR spectrum of compound 4l



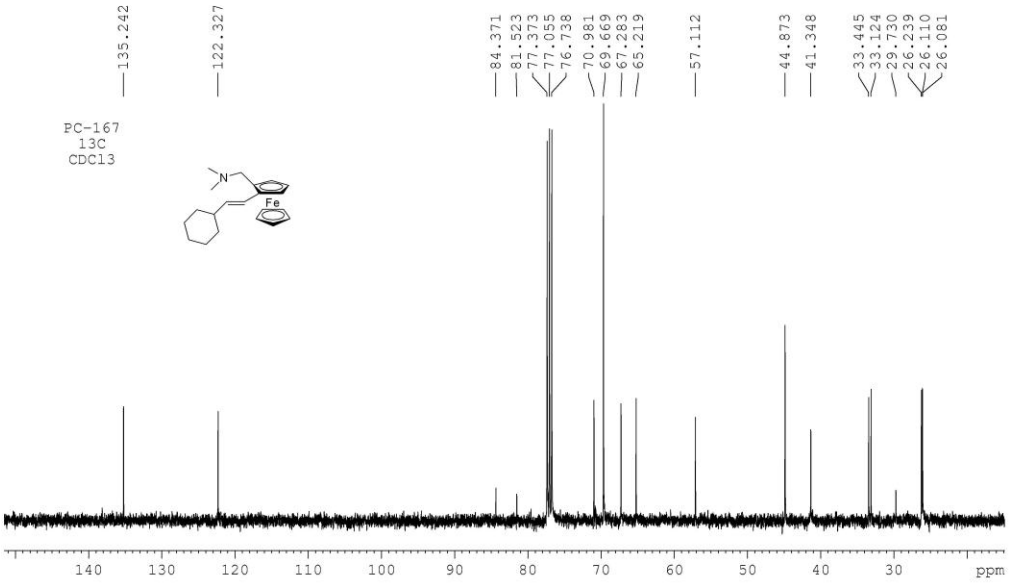
^{1}H NMR spectrum of compound 4n



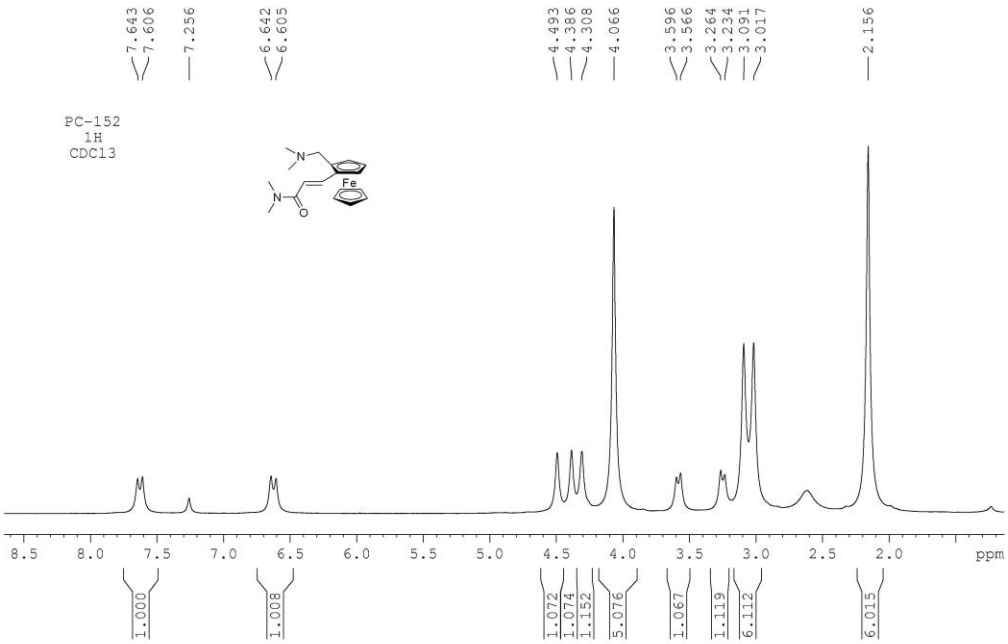
^{13}C NMR spectrum of compound 4n



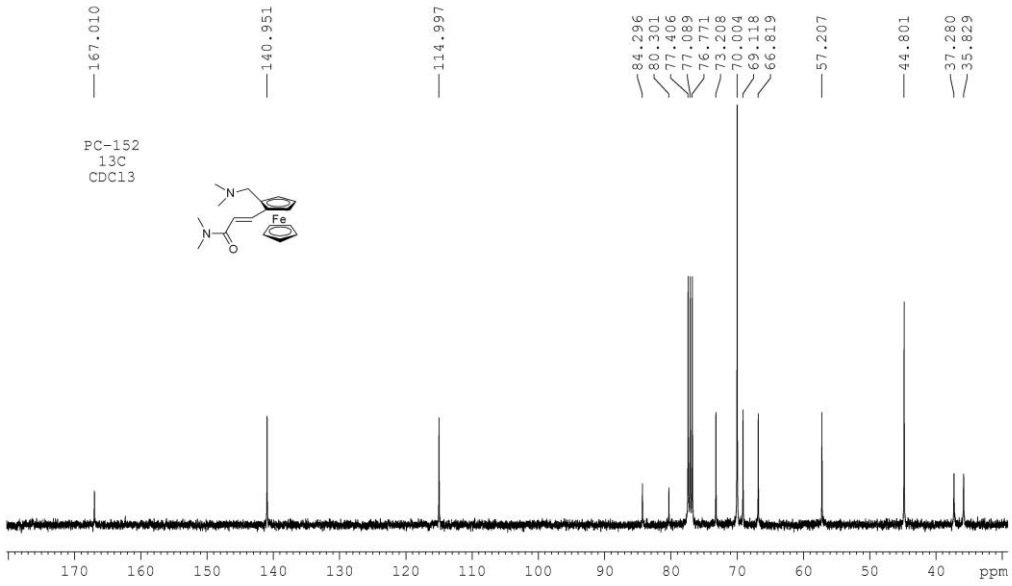
^{1}H NMR spectrum of compound 4o



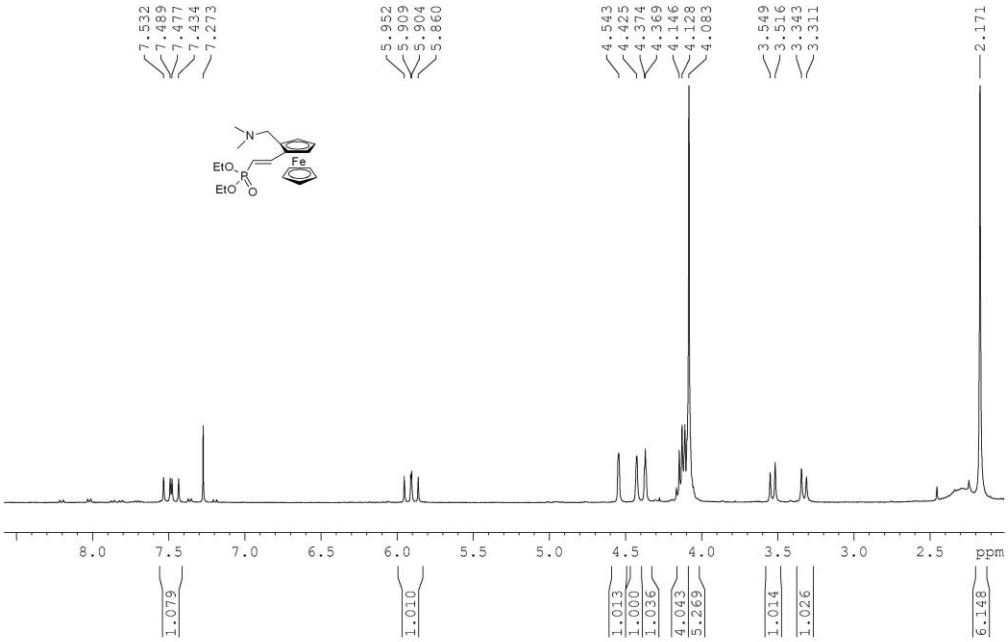
^{13}C NMR spectrum of compound 4o



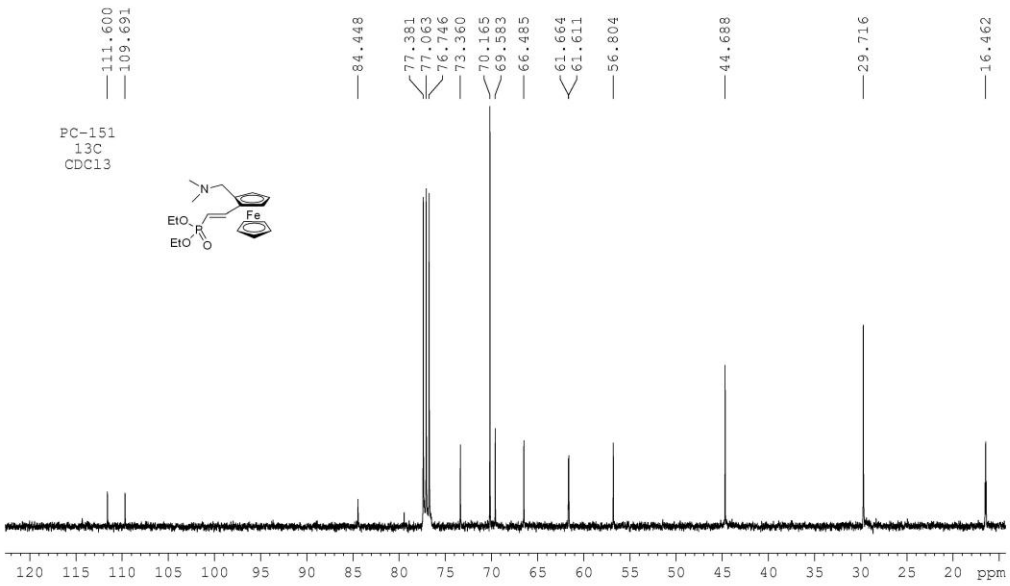
^{1}H NMR spectrum of compound 4p



^{13}C NMR spectrum of compound 4p

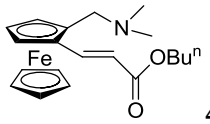


^{1}H NMR spectrum of compound 4q



^{13}C NMR spectrum of compound 4q

Chiral HPLC Data:



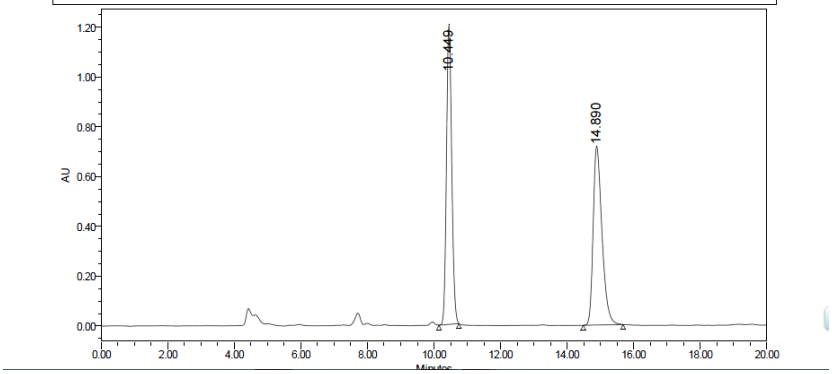
4a

HPLC chiralcel IE-3 (EtOH : *n*-hexane 2:8, 0.7 mL/min), > 99% *ee*

Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	34	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	6/28/2012 8:34:02 PM CST
Vial:	2	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 11:30:55 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



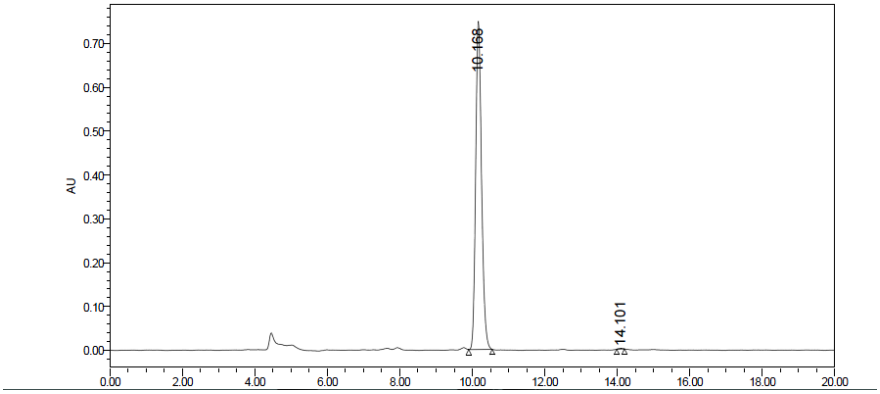
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.449	13221371	50.01	1204776	62.61
2	14.890	13217873	49.99	719375	37.39

Reported by User: Breeze ÓÃ»§ (Breeze)

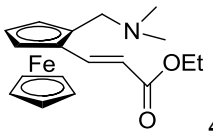
HPLC System

SAMPLE INFORMATION

Sample Name:	141	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/3/2012 11:17:29 AM CST
Vial:	2	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 11:38:36 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.168	8372507	99.86	749014	99.81
2	14.101	11554	0.14	1409	0.19



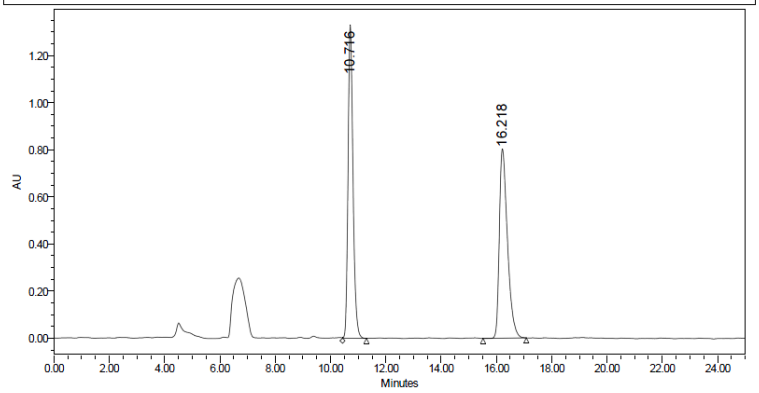
4b

HPLC chiralcel IE-3 (EtOH : *n*-hexane 2:8, 0.7 mL/min), 96% *ee*

Reported by User: Breeze OA»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	148xx	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/20/2012 10:55:01 AM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 11:44:10 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	25.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample

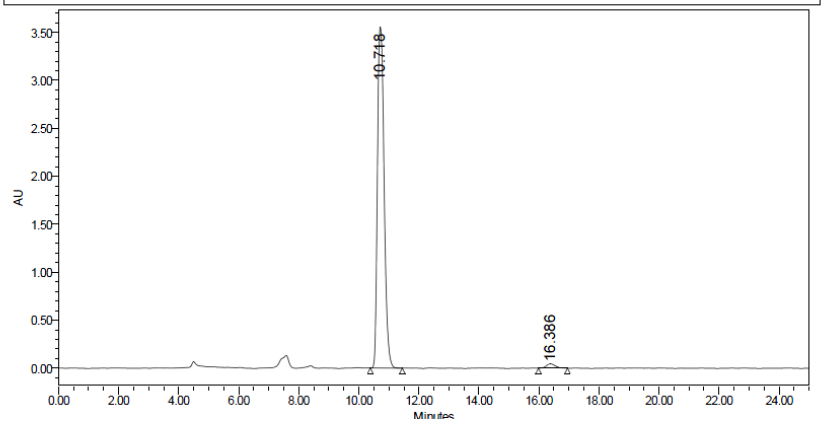


	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	10.716	16523943	50.21	1329739	62.29
2	16.218	16386882	49.79	804845	37.71

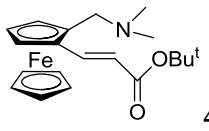
Reported by User: Breeze OÄ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	148	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/20/2012 11:20:42 AM CST
Vial:	2	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 11:46:06 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	25.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	10.718	54727066	98.31	3557347	98.75
2	16.386	940953	1.69	44975	1.25



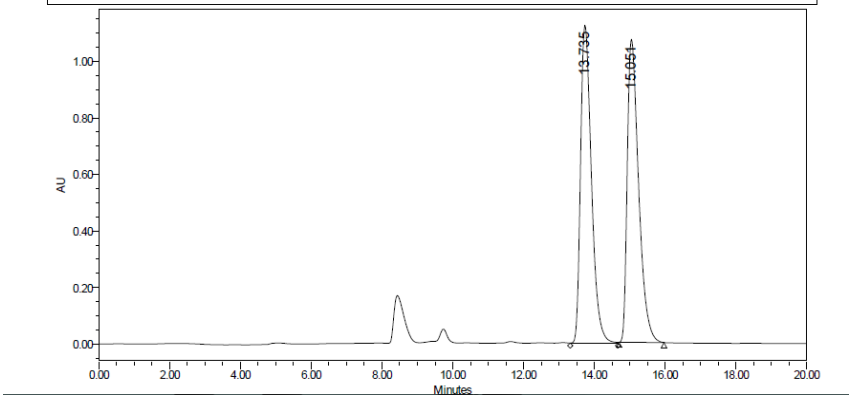
4c

HPLC chiralcel IE-3 (*i*-PrOH : *n*-hexane 1:13, 0.7 mL/min), 96% *ee*

Reported by User: Breeze ÓA»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	149xx 0.05:0.65 d	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/6/2012 10:19:01 AM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 11:55:44 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample

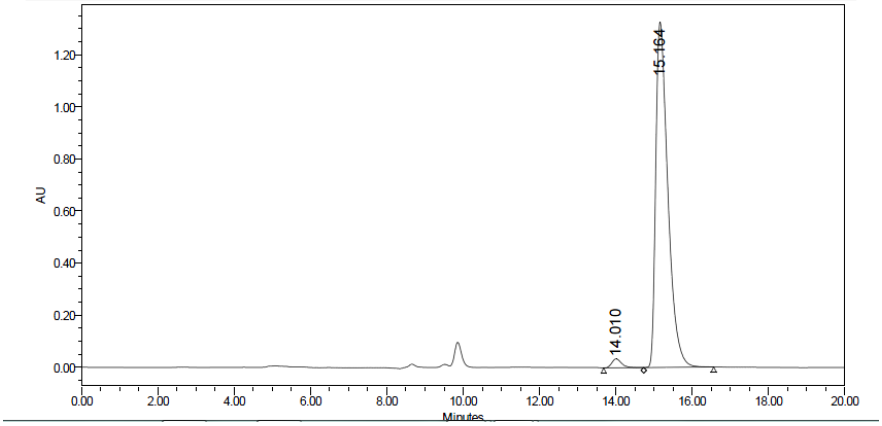


	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	13.735	23889700	50.04	1124626	51.19
2	15.051	23850912	49.96	1072352	48.81

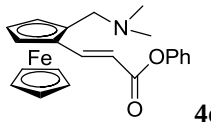
Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	149 0.05:0.65 d	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/6/2012 10:43:30 AM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 11:56:17 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	14.010	621610	2.09	34218	2.51
2	15.164	29148561	97.91	1326484	97.49



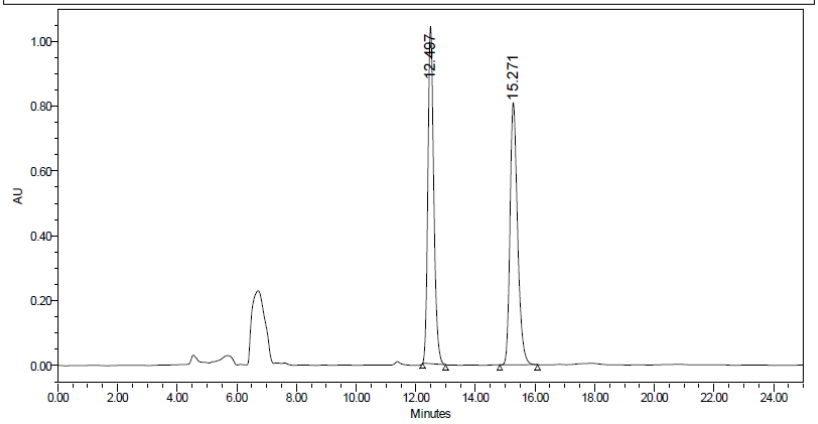
4d

HPLC chiralcel IE-3 (EtOH : *n*-hexane 2:8, 0.7 mL/min), 95% *ee*

Reported by User: Breeze OA»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	150xx	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/20/2012 2:04:57 PM CST
Vial:	4	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 11:49:08 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	25.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample

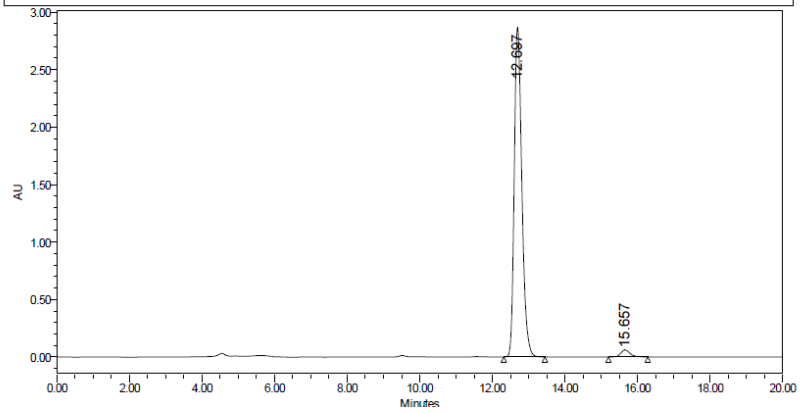


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.497	14237417	49.97	1040957	56.25
2	15.271	14251888	50.03	809602	43.75

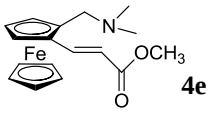
Reported by User: Breeze OA»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	150	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/20/2012 2:36:52 PM CST
Vial:	3	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 11:49:38 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.697	41495971	97.48	2870675	97.94
2	15.657	1073164	2.52	60470	2.06



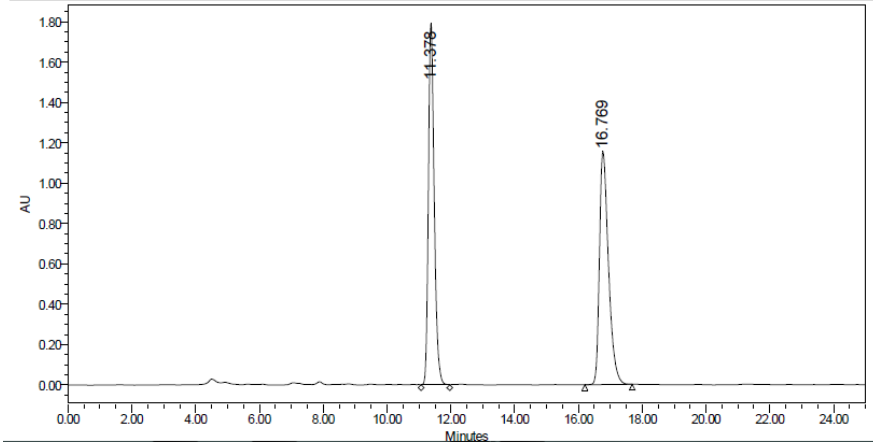
4e

HPLC chiralcel IE-3 (EtOH : *n*-hexane 2:8, 0.7 mL/min), 95% *ee*

Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	163xx	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/20/2012 1:08:38 PM CST
Vial:	4	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 11:47:49 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	25.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample

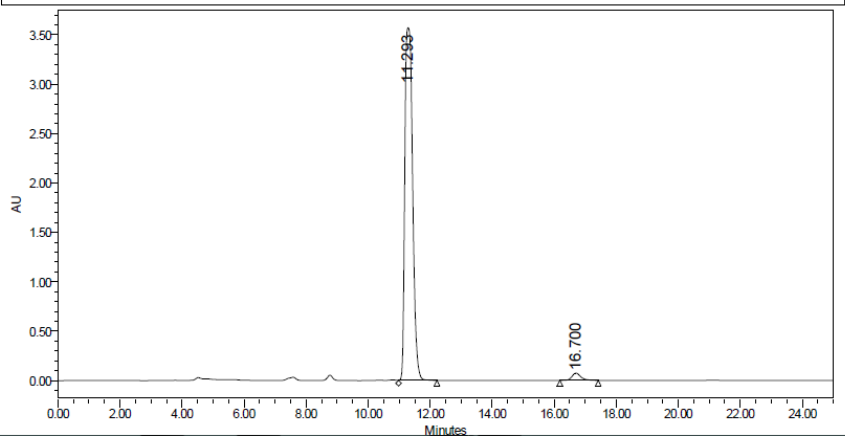


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.378	22668637	49.98	1795495	60.83
2	16.769	22684495	50.02	1156059	39.17

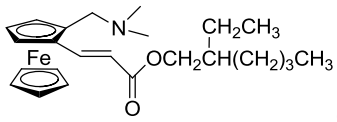
Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	163	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/20/2012 1:37:18 PM CST
Vial:	3	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 11:48:16 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	25.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.293	62056675	97.72	3572498	97.98
2	16.700	1448662	2.28	73668	2.02



4f

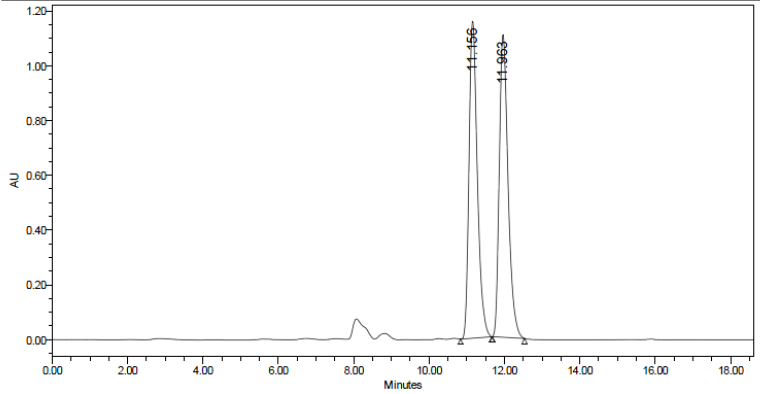
HPLC chiralcel IE-3 (*i*-PrOH : *n*-hexane 2:8, 0.6 mL/min), 96% *ee*

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	153xx	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/23/2012 5:07:52 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 12:10:01 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	25.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



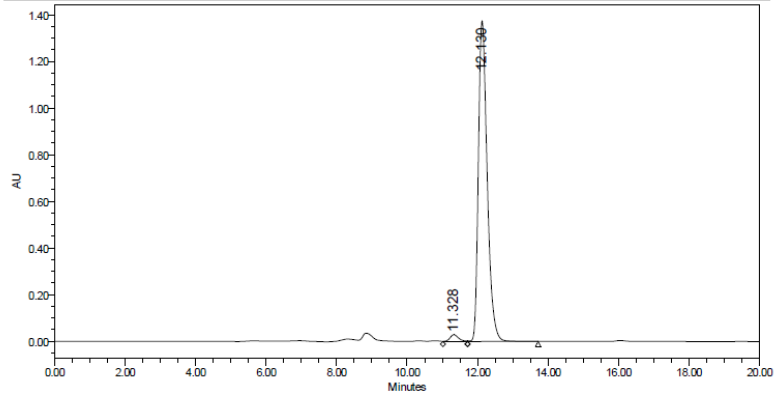
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.156	17736934	49.88	1160403	51.19
2	11.963	17822379	50.12	1106463	48.81

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

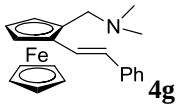
Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	153	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/24/2012 10:23:50 AM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 12:13:21 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.328	503784	2.07	29360	2.09
2	12.130	23859236	97.93	1375531	97.91



4g

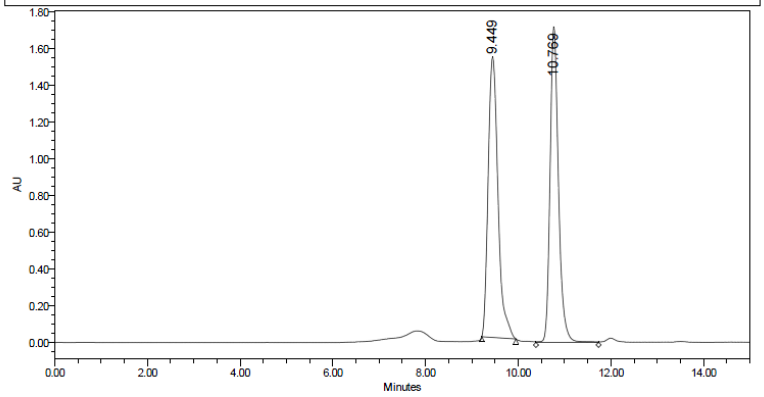
HPLC chiralcel IE-3 (*i*-PrOH : *n*-hexane 3:7, 0.5 mL/min), 95% *ee*

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	157xx	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/9/2012 4:31:33 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 4:53:10 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	15.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



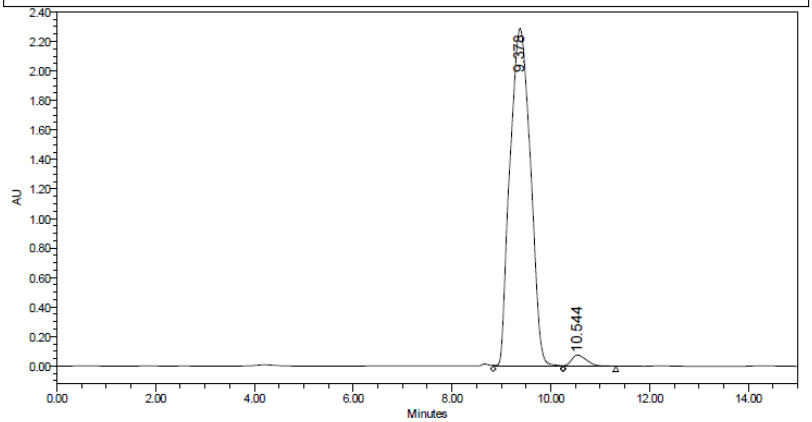
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.449	22534812	51.08	1525796	47.03
2	10.769	21579452	48.92	1718205	52.97

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

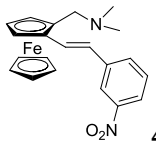
Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	157	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/23/2012 2:38:37 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 4:00:23 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	15.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.378	65687710	97.67	2287353	96.84
2	10.544	1568723	2.33	74639	3.16



4h

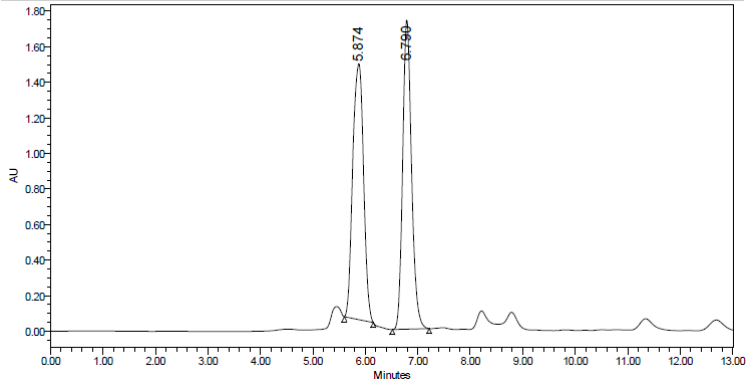
HPLC chiralcel AD-H (*i*-PrOH : *n*-hexane 3:7, 0.7 mL/min), 94% *ee*

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	162xx 0.21:0.52	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/7/2012 9:45:30 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 3:50:53 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	15.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



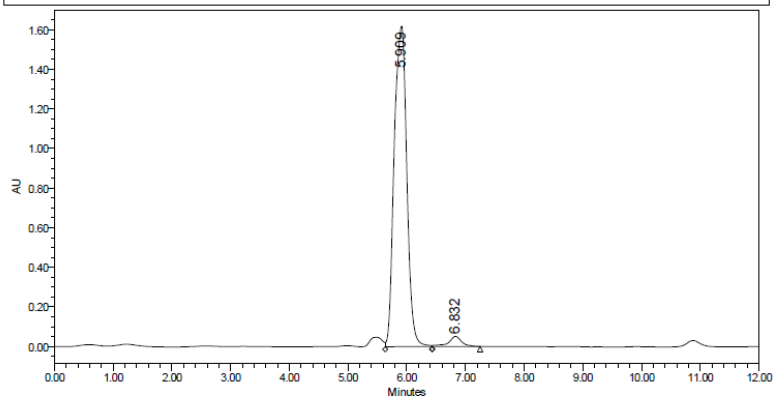
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	5.874	20591074	50.29	1443449	45.27
2	6.790	20349541	49.71	1745234	54.73

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

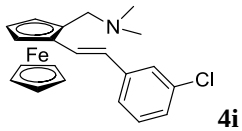
Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	162 0.21:0.52	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/7/2012 10:17:22 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 3:52:06 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	12.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	5.909	24092051	96.80	1623531	96.95
2	6.832	795905	3.20	51161	3.05



4i

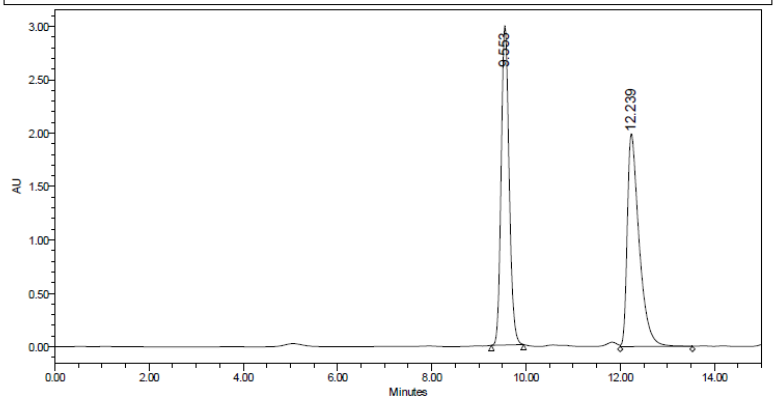
HPLC chiralcel AS-H (*i*-PrOH : *n*-hexane 0.1:9.9, 0.5 mL/min), 96% *ee*

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	161xx	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/23/2012 1:38:40 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 12:23:14 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	15.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



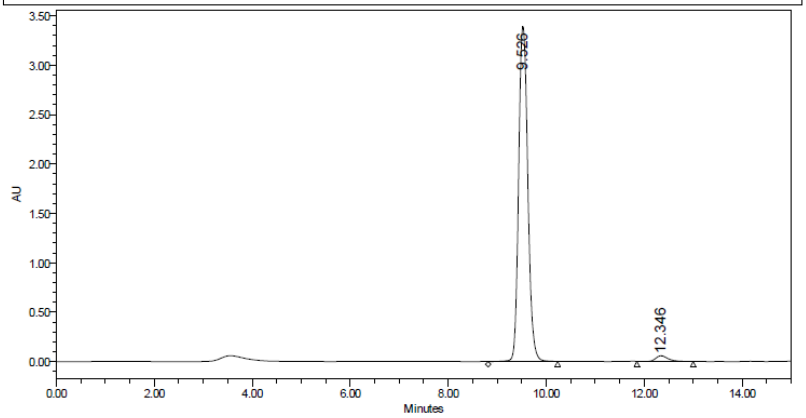
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.553	35047043	50.24	2990278	59.98
2	12.239	34713151	49.76	1994815	40.02

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

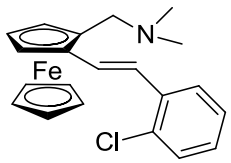
Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	161	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/23/2012 2:01:56 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 12:24:56 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	15.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.526	44069078	97.84	3398706	98.36
2	12.346	972990	2.16	56696	1.64



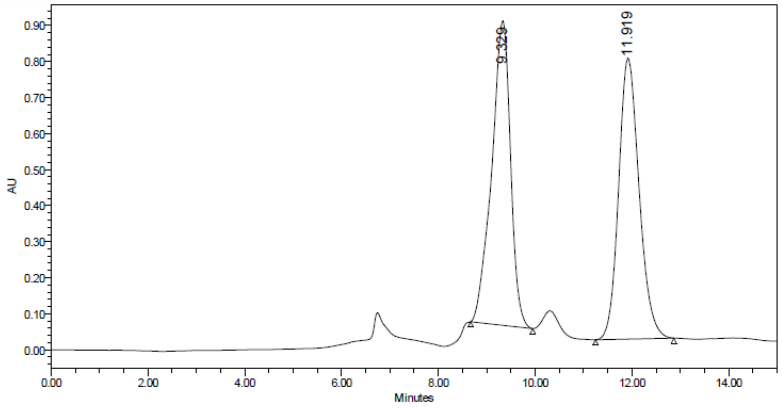
4j

HPLC chiralcel IE-3 (*i*-PrOH : *n*-hexane 3:7, 0.5 mL/min), 96% *ee*

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	160xx 0.01:0.49	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/4/2012 9:42:26 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 11:59:29 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	15.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample

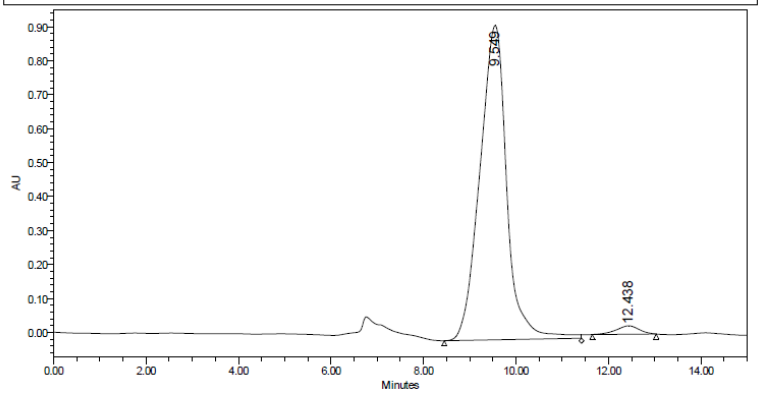


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.329	22879233	49.93	844330	52.01
2	11.919	22943782	50.07	778925	47.99

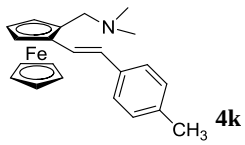
Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	160 0.01:0.49 d	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/4/2012 9:59:14 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 12:01:59 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	15.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.549	37466465	97.77	926261	97.40
2	12.438	856093	2.23	24742	2.60



4k

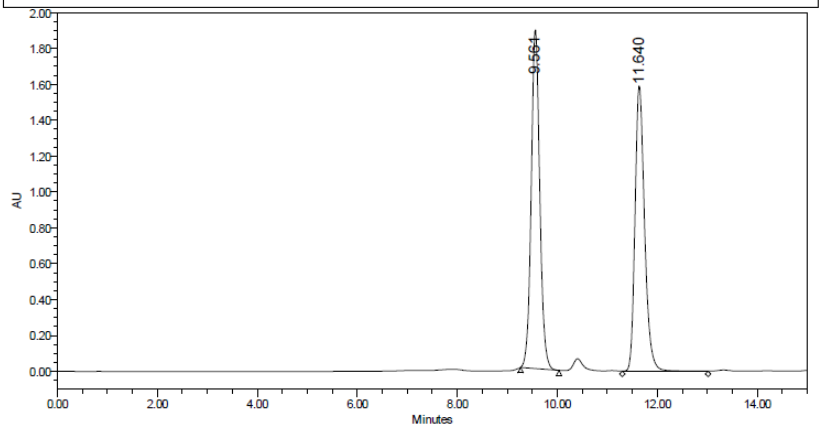
HPLC chiralcel IE-3 (*i*-PrOH : *n*-hexane 3:7, 0.5 mL/min), 96% *ee*

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	159xx	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/23/2012 12:15:49 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 12:31:40 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	15.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



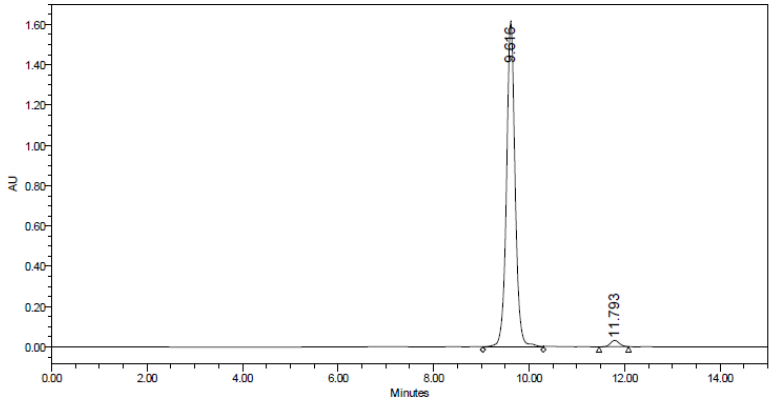
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.561	22377812	51.40	1892583	54.27
2	11.640	21155073	48.60	1594993	45.73

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

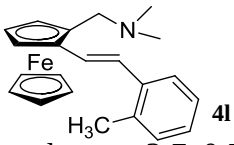
Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	159	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/23/2012 1:02:42 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 12:22:23 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	15.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.616	20216276	98.05	1617874	98.11
2	11.793	402430	1.95	31246	1.89



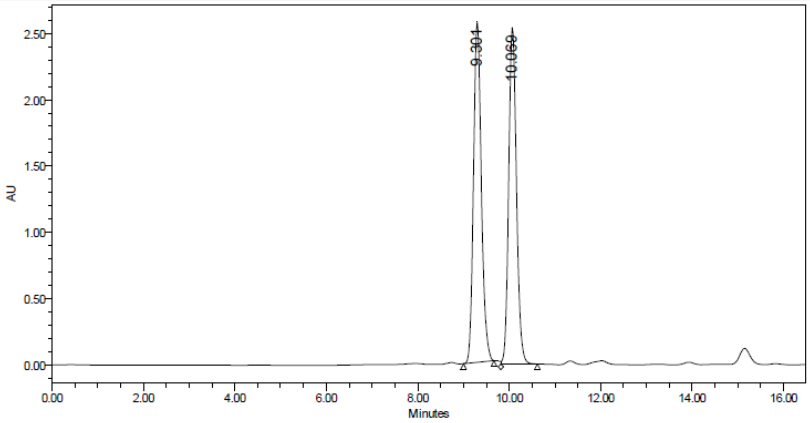
4l

HPLC chiralcel IE-3 (*i*-PrOH : *n*-hexane 3:7, 0.5 mL/min), 96% *ee*

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	158xx	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/23/2012 10:43:39 AM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 12:18:12 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample

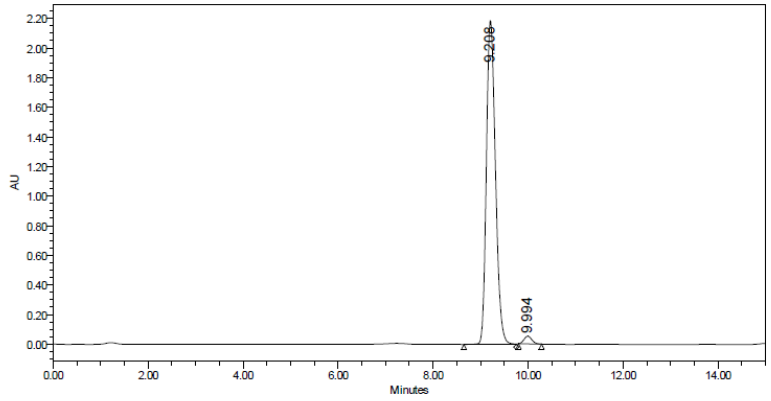


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.301	30504853	50.47	2567777	50.26
2	10.069	29940574	49.53	2540932	49.74

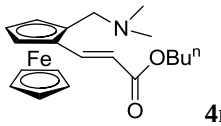
Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	158	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	8/23/2012 11:58:32 AM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 12:19:17 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	15.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.208	28964685	97.96	2194474	97.67
2	9.994	603213	2.04	52295	2.33



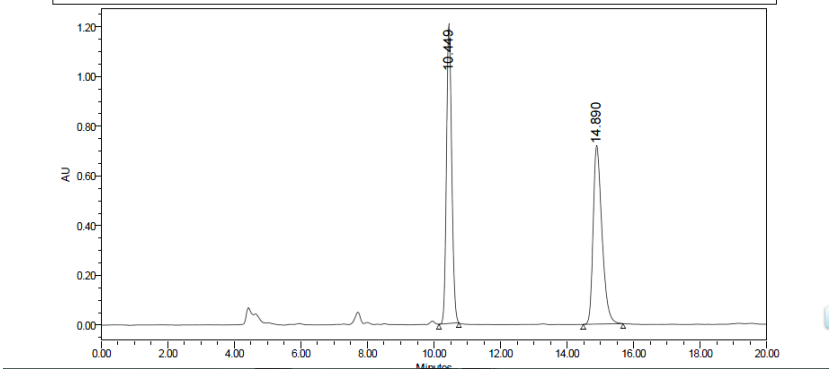
4m

HPLC chiralcel IE-3 (EtOH : *n*-hexane 2:8, 0.7 mL/min), > 99% *ee*

Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	34	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	6/28/2012 8:34:02 PM CST
Vial:	2	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 11:30:55 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample

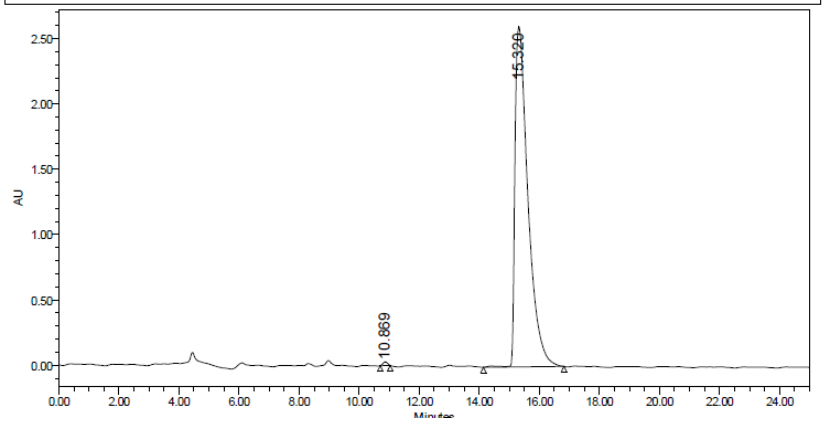


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.449	13221371	50.01	1204776	62.61
2	14.890	13217873	49.99	719375	37.39

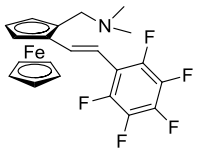
Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	177	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	10/26/2012 11:23:21 AM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	10/26/2012 11:41:01 AM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	25.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.869	299089	0.38	28781	1.09
2	15.320	78162744	99.62	2603918	98.91



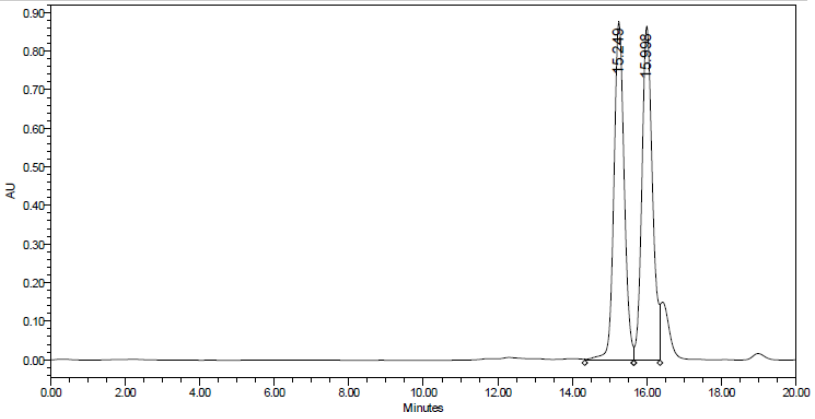
4n

HPLC chiralcel IE-3 (*i*-PrOH : *n*-hexane 5:5, 0.3 mL/min), 91% *ee*

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	174xx d	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/3/2012 4:32:41 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 12:04:38 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample

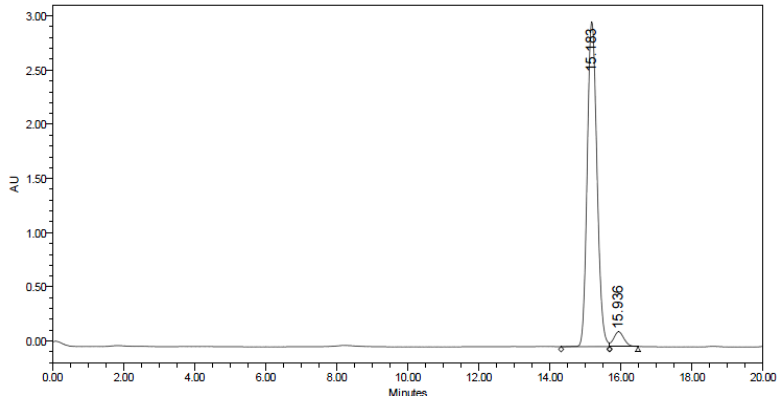


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.249	16747051	49.61	877025	50.32
2	15.998	17011793	50.39	866014	49.68

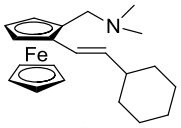
Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	174 d	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/3/2012 4:10:16 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	2/21/2013 4:18:10 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.183	57001971	95.42	2999299	95.64
2	15.936	2737812	4.58	136741	4.36



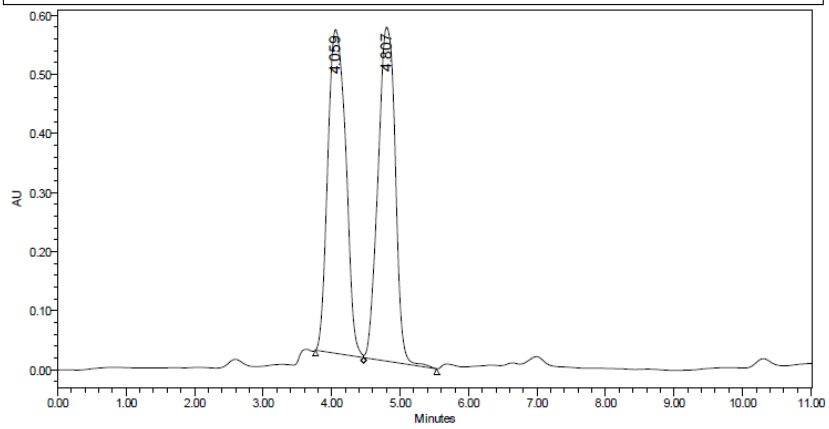
4o

HPLC chiralcel AD-H (*i*-PrOH : *n*-hexane 0.3:0.87, 0.9 mL/min), 94% *ee*

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	167xx 0.03:0.86	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/7/2012 6:35:36 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 3:54:42 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	15.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample

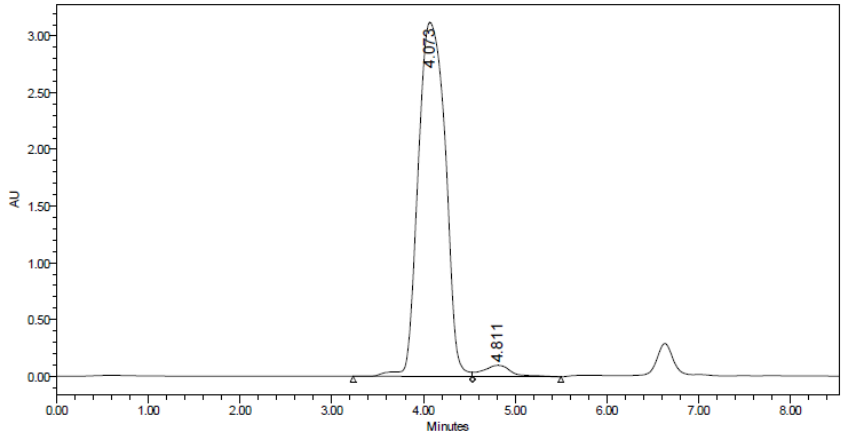


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	4.059	10019811	50.24	548707	49.23
2	4.807	9925280	49.76	565970	50.77

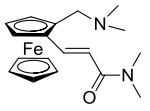
Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

SAMPLE INFORMATION

Sample Name:	167 0.03:0.86	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/7/2012 6:48:13 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 3:55:29 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	15.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	4.073	64167985	96.86	3126915	96.96
2	4.811	2078271	3.14	98120	3.04



4p

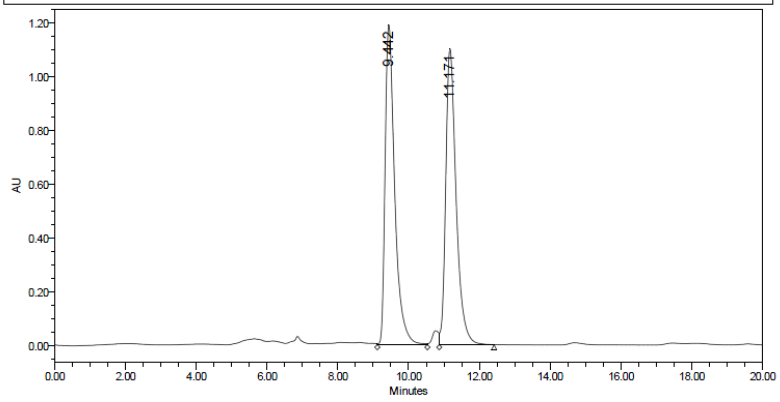
HPLC chiralcel AS-H (EtOH : *n*-hexane 0.06:0.54, 0.6 mL/min), 97% *ee*

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	152xx d	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/4/2012 3:16:59 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/9/2012 3:59:03 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



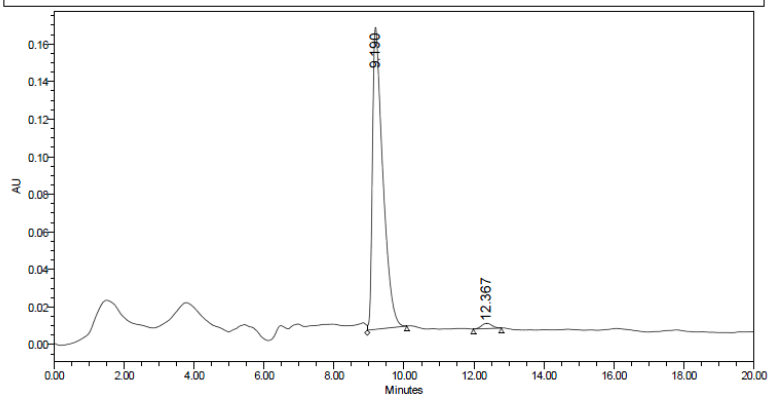
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.442	22480304	50.16	1192804	51.96
2	11.171	22339186	49.84	1102599	48.04

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

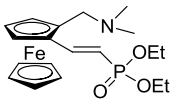
Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	152	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/11/2012 10:12:11 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/11/2012 10:34:30 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.190	3291564	98.27	161077	98.27
2	12.367	58036	1.73	2833	1.73



4q

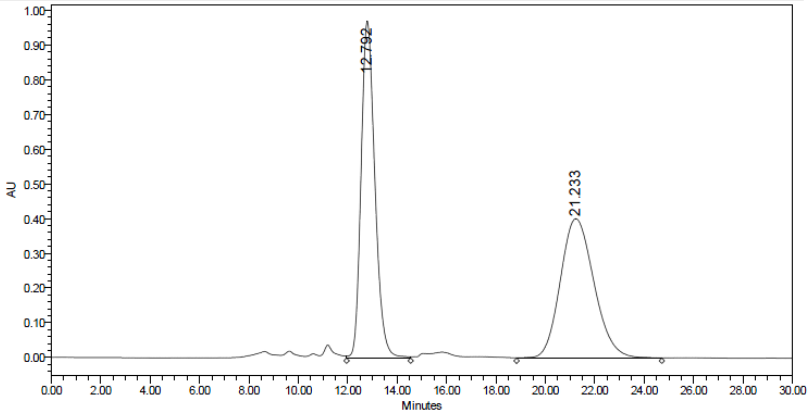
HPLC chiralcel AS-H (*i*-PrOH : *n*-hexane 0.2:0.2, 0.4 mL/min), 93% *ee*

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	151XX	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/11/2012 4:35:14 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/11/2012 8:11:32 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



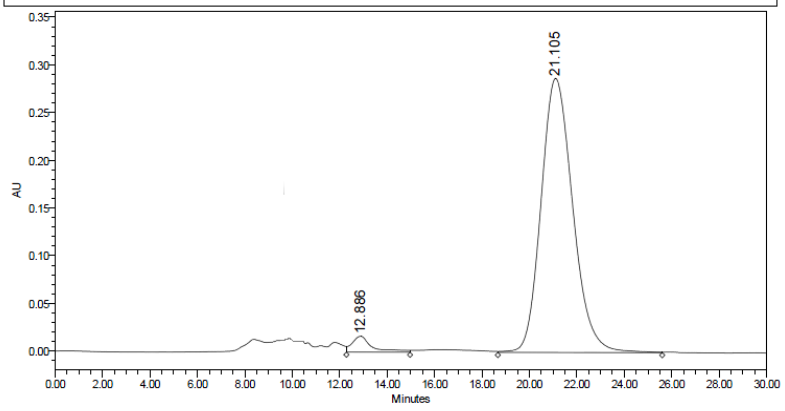
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.792	37649485	49.70	969620	70.72
2	21.233	38111013	50.30	401521	29.28

Project Name siyinchun
Reported by User: Breeze ÓÃ»§ (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	151	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	9/11/2012 5:12:20 PM CST
Vial:	1	Acq. Method:	pc
Injection #:	1	Date Processed:	9/11/2012 8:12:20 PM CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.00 Minutes	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name	pc sample



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.886	989297	3.57	16575	5.46
2	21.105	26708585	96.43	287267	94.54