Electronic Supplementary Information

Cp*Ir(III)/Chiral Carboxylic Acid-Catalyzed Enantioselective C–H Alkylation of Ferrocene Carboxamides with Diazomalonates

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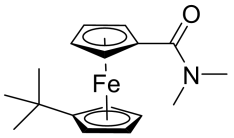
1. General Information

All anhydrous reactions were carried out in a flame-dried glassware under nitrogen atmosphere unless otherwise noted or in an nitrogen-filled glove box. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance (400 MHz and 100 Hz respectively) or Bruker Avance (500 MHz and 125 Hz respectively). ^{19}F NMR spectra were recorded on a Bruker Avance (376 MHz), The chemical shifts (δ) were recorded in parts per million (ppm). The coupling constants (*J*) were shown in Hertz (Hz). Chemical shifts in $CDCl_3$ were reported the residual $CHCl_3$ (7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR). HRMS measurements were performed on an Ultima Global spectrometer with an ESI source. **1a**,[S1] **1b-1j**,[S2] **2a-2i**,[S3] **4b**,[S4] **4c-4d**[S5] were reported previously. All other reagents were commercially available and used as received unless otherwise noted.

2. Experimental Section

2.1 Preparation of Ferrocene Carboxamides

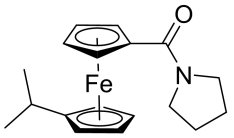
1-(N,N-dimethyl-1-carbonyl)-1'-tertbutyl-ferrocene (1k)



1k

1k (700mg) was obtained according to the reported method.[S6] The total yield was 44% for 2 steps; Red solid; m.p.: 110-112 °C; IR: ν 2957, 1617, 1392, 1273, 1106, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.61 (s, 2H), 4.29 (s, 2H), 4.16 (s, 2H), 4.05 (s, 2H), 3.10 (s, 6H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 103.2, 78.0, 70.9, 69.8, 69.3, 66.8, 31.4, 30.4; HRMS (ESI): m/z calculated for $C_{17}H_{24}FeNO^+$ $[M+H]^+$: 314.1202, found: 314.1212.

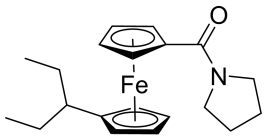
1-(pyrrolidine-1-carbonyl)-1'-isopropyl-ferrocene (1l)



1l

1l (600mg) was obtained according to the reported method.[S2] The total yield was 48% for 3 steps; Red solid; m.p.: 116-118 °C; IR: ν 2959, 1607, 1407, 1028, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.69 (s, 2H), 4.28 (s, 2H), 4.15-4.02 (m, 4H), 3.74-3.53 (m, 4H), 2.66-2.56 (m, 1H), 2.01-1.81 (m, 4H), 1.15 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 98.1, 77.9, 70.7, 70.4, 68.8, 67.6, 48.1, 47.1, 27.2, 26.8, 24.0, 23.5; HRMS (ESI): m/z calculated for $C_{18}H_{24}FeNO^+$ $[M+H]^+$: 326.1202, found: 326.1209.

1-(pyrrolidine-1-carbonyl)-1'-pentan-3-yl-ferrocene (1m)



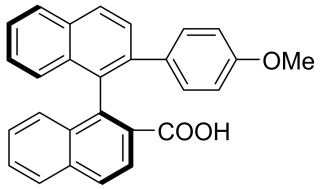
1m

1m (510mg) was obtained according to the reported method.[S2] The total yield was 36% for 3 steps; Red solid; m.p.: 119-121 °C; IR: ν 2962, 1704, 1410, 1214, 1028, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.67 (s, 2H), 4.25 (s, 2H), 4.13-3.98 (m, 4H), 3.75-3.50 (m, 4H), 2.22-2.12 (m, 1H), 2.02-1.80 (m, 4H), 1.68-1.42 (m, 4H), 0.83 (t, J = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 96.3, 77.8, 70.7, 70.6, 68.6, 68.6, 48.1, 47.1, 40.3, 26.8, 26.5, 24.0, 11.3; HRMS (ESI): m/z calculated for

$C_{20}H_{28}FeNO^+$ $[M+H]^+$: 354.1515, found: 354.1526.

2.2 Preparation of CCA

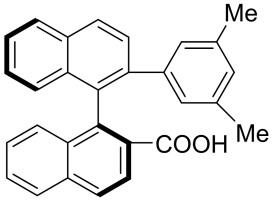
(*S*)-2'-[4-methoxyl-phenyl]-[1,1'-binaphthalene]-2-carboxylic acid (4e)



4e

4e (570 mg) was synthesized according to the reported method.[S5] The total yield was 48% for 4 steps; White solid; m.p.: 121-123 °C; IR: ν 2925, 1638, 1460, 1246, 1176, 817, 770, 750, 621 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04-7.91 (m, 3H), 7.87-7.81 (m, 2H), 7.57-7.38 (m, 3H), 7.38-7.32 (m, 1H), 7.32-7.18 (m, 2H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.85-6.74 (m, 2H), 6.49-6.40 (m, 2H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 158.0, 140.8, 138.5, 135.1, 134.0, 133.9, 133.4, 132.9, 132.4, 129.9, 128.4, 128.3, 128.0, 128.0, 127.9, 127.9, 127.9, 126.8, 126.3, 126.2, 126.2, 125.5, 112.9, 55.0; $[\alpha]_D^{23.6}$ = –73.7 (*c* = 0.20, $CHCl_3$); HRMS (ESI): m/z calculated for $C_{28}H_{21}O_3^+$ $[M+H]^+$: 405.1485, found: 405.1487.

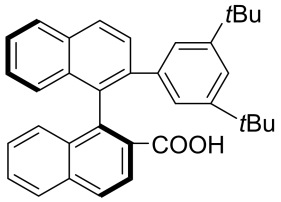
(*S*)-2'-[3,5-dimethyl-phenyl]-[1,1'-binaphthalene]-2-carboxylic acid (4f)



4f

4f (430 mg) was synthesized according to the reported method.[S5] The total yield was 43% for 4 steps; White solid; m.p.: 197-199 °C; IR: ν 2924, 1639, 1384, 813, 771, 744, 619 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.95-7.89 (m, 1H), 7.88-7.78 (m, 2H), 7.55-7.43 (m, 3H), 7.41-7.35 (m, 1H), 7.34-7.20 (m, 2H), 7.15-7.08 (m, 1H), 6.62 (s, 1H), 6.49 (s, 2H), 1.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 141.4, 140.9, 139.0, 136.7, 135.0, 134.0, 133.7, 132.9, 132.5, 128.5, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 126.7, 126.4, 126.3, 126.1, 125.5, 21.0; $[\alpha]_D^{24.1}$ = –87.0 (*c* = 0.20, $CHCl_3$); HRMS (ESI): m/z calculated for $C_{29}H_{23}O_2^+$ $[M+H]^+$: 403.1693, found: 403.1690.

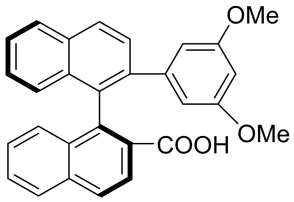
(*S*)-2'-[3,5-ditertbutyl-phenyl]-[1,1'-binaphthalene]-2-carboxylic acid (4g)



4g

4g (240 mg) was synthesized according to the reported method.[S5] The total yield was 29% for 4 steps; White solid; m.p.: 142-144 °C; IR: ν 2962, 1691, 1363, 1248, 819, 769, 747, 716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (t, *J* = 7.8 Hz, 2H), 7.95-7.87 (m, 1H), 7.87-7.74 (m, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.54-7.38 (m, 3H), 7.35-7.21 (m, 2H), 7.18-7.11 (m, 1H), 7.02-6.97 (m, 1H), 6.78-6.70 (m, 2H), 0.93 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 149.4, 141.2, 140.6, 140.0, 135.1, 134.2, 133.8, 132.9, 132.4, 128.7, 128.1, 128.0, 127.9, 127.8, 127.8, 127.5, 126.7, 126.4, 126.4, 126.2, 125.4, 123.3, 119.9, 34.4, 31.1; $[\alpha]_D^{24.6}$ = –88.4 (*c* = 0.20, $CHCl_3$); HRMS (ESI): m/z calculated for $C_{35}H_{35}O_2^+$ $[M+H]^+$: 487.2632, found: 487.2641.

(*S*)-2'-[3,5-methoxyl-phenyl]-[1,1'-binaphthalene]-2-carboxylic acid (4h)

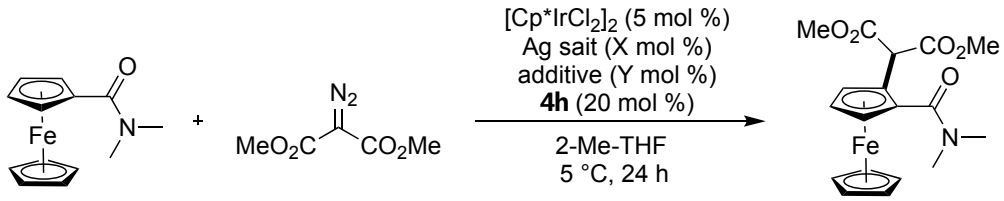


4h

4h (1.5 g) was synthesized according to the reported method.[S5] The total yield was 46% for 4 steps; White solid; m.p.: 162-164 °C; IR: ν 2953; 1680, 1459, 1285, 1153, 815, 773, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03-7.93 (m, 3H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.53-7.42 (m, 2H), 7.38-7.34 (m, 1H), 7.33-7.27 (m, 1H), 7.25-7.21 (m, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 6.14-6.08 (m, 3H), 3.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 159.7, 143.5, 140.8, 138.7, 135.0, 134.0, 133.7, 132.9, 132.6, 128.4, 128.0, 127.9, 127.9, 127.9, 127.8, 126.8, 126.4, 125.7, 106.8, 99.8, 54.9; $[\alpha]_D^{25.3}$ = –109.1 (*c* = 0.20, $CHCl_3$); HRMS (ESI): m/z calculated for $C_{29}H_{23}O_4^+$ $[M+H]^+$: 435.1591, found: 435.1600.

2.3 Effects of Silver Salts in Optimization Studies

Table S1. Effects of Silver Salts[a]

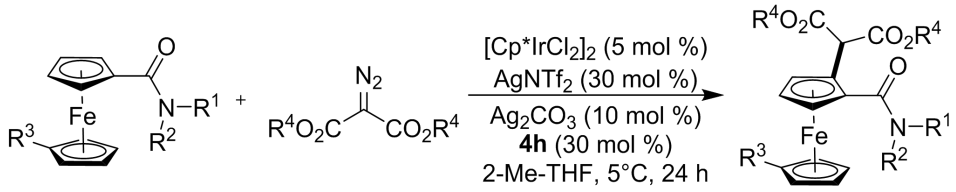


1a **2a** **3aa**

Entry	Ag sait (X mol%)	additive (Y mol %)	Yield (%)	er
1	$AgPF_6$ (20)	-	42	84:16
2	$AgBF_4$ (20)	-	trace	-
3	$AgSbF_6$ (20)	-	62	89:11
4	$AgNTf_2$ (20)	-	57	91:9
5[b]	$AgNTf_2$ (20)	Ag_2CO_3 (5)	74	91:9
6[b]	$AgNTf_2$ (20)	Ag_2CO_3 (10)	68	93:7
7[b]	$AgNTf_2$ (30)	Ag_2CO_3 (10)	84	92:8

[a]Reaction conditions: **1** (0.1 mmol), **2a** (0.13 mmol), $[Cp^*IrCl_2]_2$ (5 mol %), $AgNTf_2$ (X mol %), additive (Y mol %), **4h** (30 mol %) in 2-Me-THF 1 mL at 5 °C under N_2 for 24 h. [b]**4h** (30 mol %), 2-Me-THF(0.5 mL).

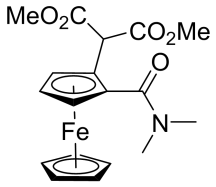
2.4 General Procedure of Cp*Ir(III)/CCA-catalyzed Enantioselective C-H Alkylation of Ferrocenes



1 **2**, (1.3 eq.) **3**

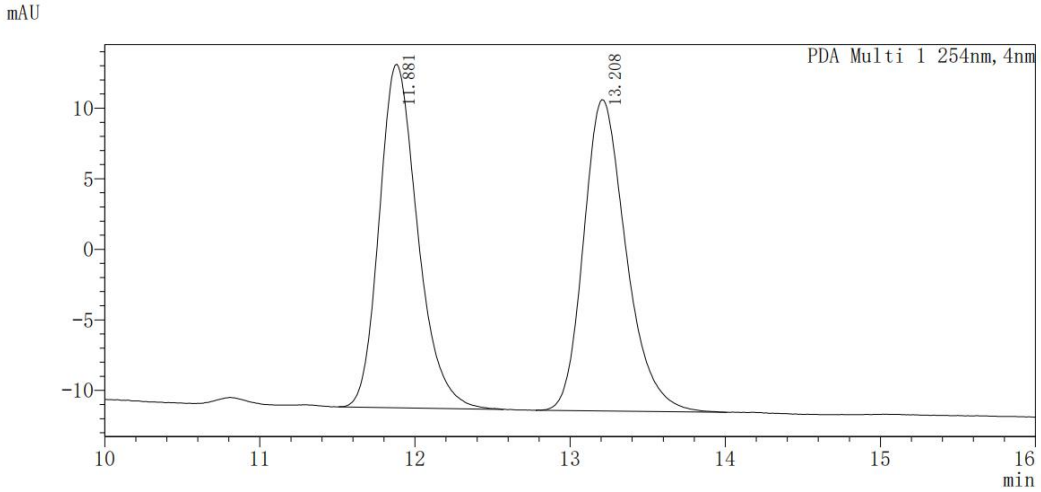
To a dried screw-capped vial added ferrocene carboxamides **1** (0.10 mmol), diazomalonates **2** (0.13 mmol, 1.3 eq.), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $AgNTf_2$ (11.7 mg, 0.03 mmol), Ag_2CO_3 (2.8 mg, 0.01 mmol), **4h** (13.1 mg, 0.03 mmol) and 2-Me-THF (0.5 mL) under nitrogen atmosphere. The vial was capped, and the mixture was cooled at 5 °C for 24 h with stirring. The resulting mixture directly purified by silica gel column chromatography (petroleum ether:acetone = 8:1-4:1) to give product **3**.

(S_p)-2-Dimethyl malonate-(dimethyl-1-carbonyl)ferrocene (3aa):



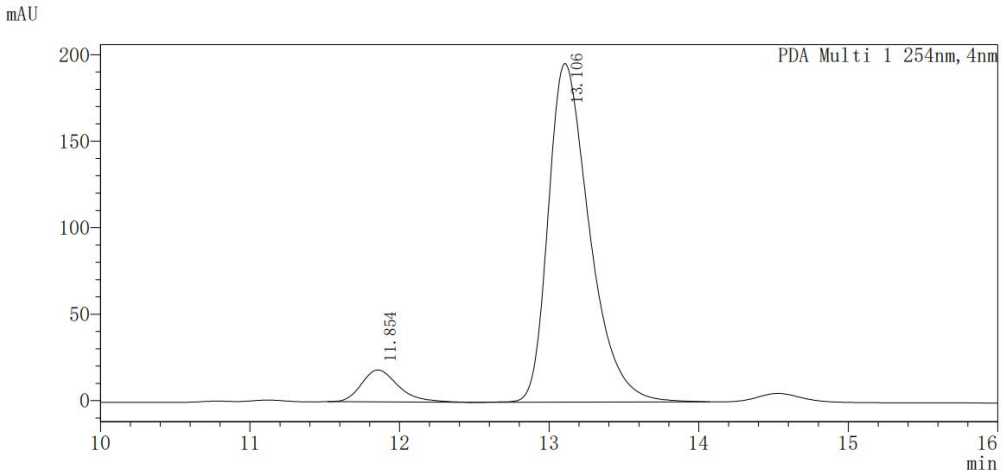
3aa

Compound **3aa** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3aa** (32.5 mg, 84%); Yellow solid; m.p.: 105-107 °C; IR: ν 2952, 1734, 1618, 1501, 1156, 822 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.18 (s, 1H), 4.56 (s, 1H), 4.36 (s, 1H), 4.25 (t, J = 2.4 Hz, 1H), 4.20 (s, 5H), 3.89 (s, 3H), 3.63 (s, 3H), 3.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 168.7, 168.7, 82.2, 80.5, 70.8, 68.8, 68.2, 67.4, 52.7, 52.4, 50.3, 29.7; HRMS (ESI): m/z calculated for $C_{18}H_{22}FeNO_5^+$ $[M+H]^+$: 388.0842, found: 388.0855; HPLC separation (DAICEL CHIRALPAK IA, hexane:2-propanol = 90:10, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 13.1 min, t_R(minor) = 11.9 min, 92:8 er.



PDA Ch1 254nm

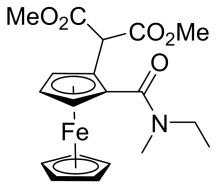
Peak No	Ret. time	Area/%
1	11.881	49.947
2	13.208	50.053



PDA Ch1 254nm

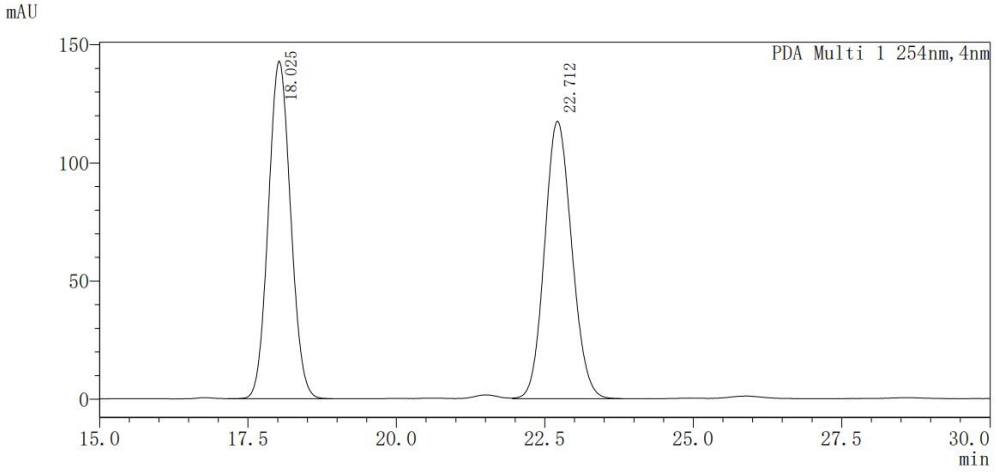
Peak No	Ret. time	Area/%
1	11.854	7.794
2	13.106	92.206

(S_p)-2-Dimethyl malonate-(methyl-ethyl-1-carbonyl)ferrocene (3ba):



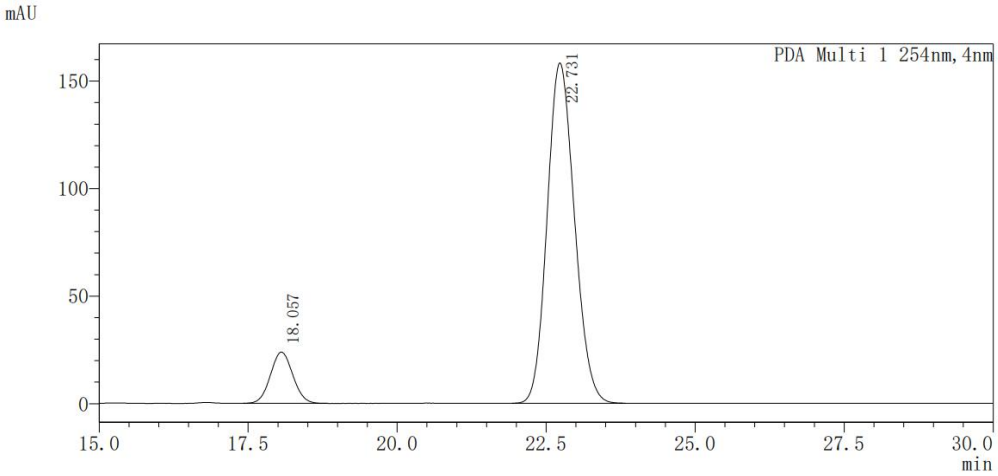
3ba

Compound **3ba** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ba** (32.9 mg, 82%); Yellow solid; m.p.: 104-106 °C; IR: ν 2953, 1737, 1618, 1492, 1196, 822 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.17 (s, 1H), 4.55 (s, 1H), 4.35 (s, 1H), 4.24 (s, 1H), 4.20 (s, 5H), 3.89 (s, 3H), 3.62 (s, 3H), 3.59-3.24 (m, 2H), 2.95 (s, 3H), 1.12 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 168.6, 82.3, 81.2, 70.8, 68.6, 67.3, 52.6, 52.3, 50.3, 29.8, 13.9; HRMS (ESI): m/z calculated for $C_{19}H_24FeNO_5^+$ $[M+H]^+$: 402.0998, found: 402.1001; HPLC separation (DAICEL CHIRALPAK AD, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 22.7 min, t_R(minor) = 18.1 min, 89:11 er.



PDA Ch1 254nm

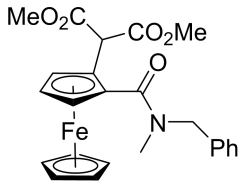
Peak No	Ret. time	Area/%
1	18.025	49.942
2	22.712	50.058



PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	18.057	10.993
2	22.731	89.007

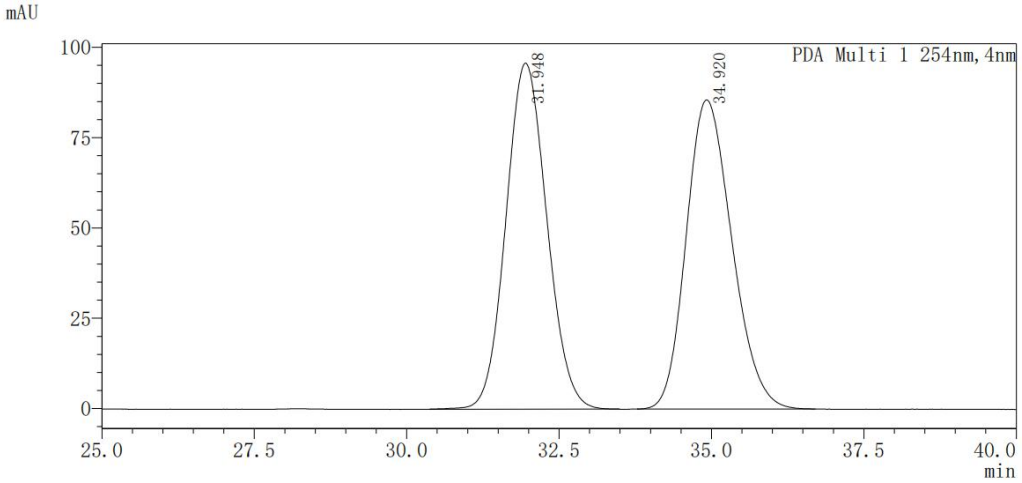
(S_p)-2-Dimethyl malonate-(methyl-benzyl-1-carbonyl)ferrocene (3ca):



3ca

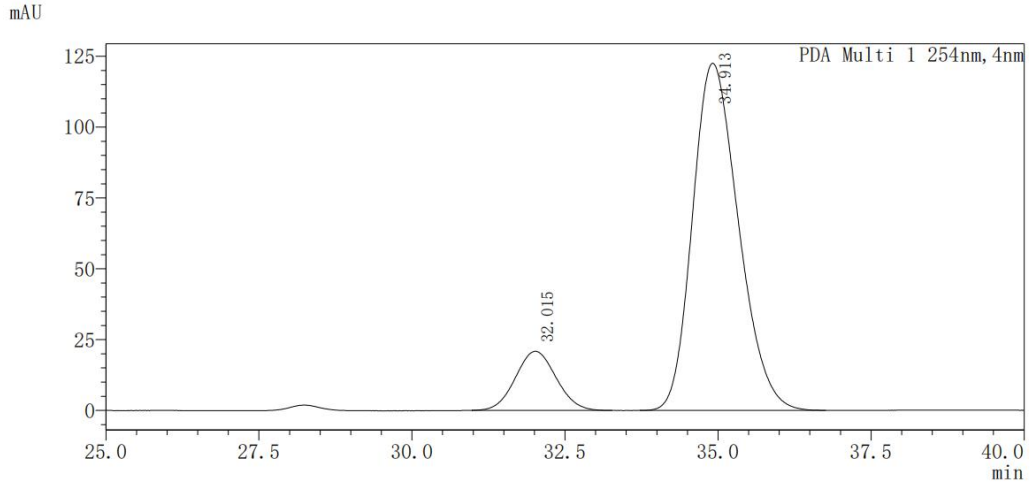
Compound **3ca** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ca** (35.2 mg, 76%); Yellow solid; m.p.: 93-95 °C; IR: ν 2923, 1726, 1612, 1264, 1142, 823 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.15 (m, 5H), 5.30 (s, 1H), 4.83 (d, J = 15 Hz, 1H), 4.58 (s, 1H), 4.54-4.06 (m, 8H), 3.91 (s, 3H), 3.79-3.43 (m, 3H), 2.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 168.6, 137.4, 128.7, 127.3, 82.7, 81.6, 70.9, 67.7, 67.6, 52.6, 52.4, 50.3, 29.7; HRMS (ESI): m/z calculated for $C_{24}H_{26}FeNO_5^+$ $[M+H]^+$: 464.1155, found: 464.1165; HPLC separation (DAICEL

CHIRALPAK AD, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 34.9 min, t_R(minor) = 32.0 min, 87:13 er.



PDA Ch1 254nm

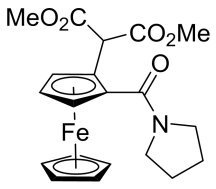
Peak No	Ret. time	Area/%
1	31.948	50.093
2	34.920	49.907



PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	32.015	13.106
2	34.913	86.894

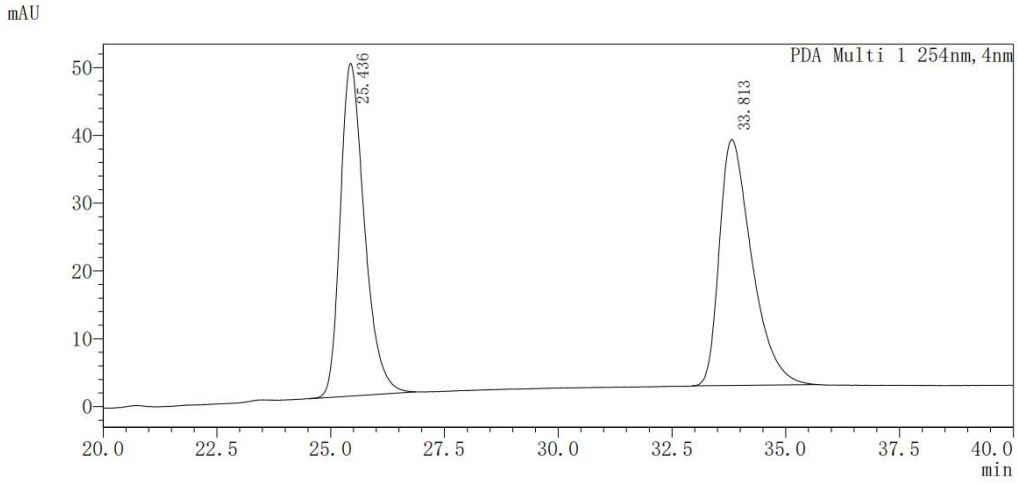
(S_p)-2-Dimethyl malonate-(pyrrolidine-1-carbonyl)ferrocene (3da):



3da

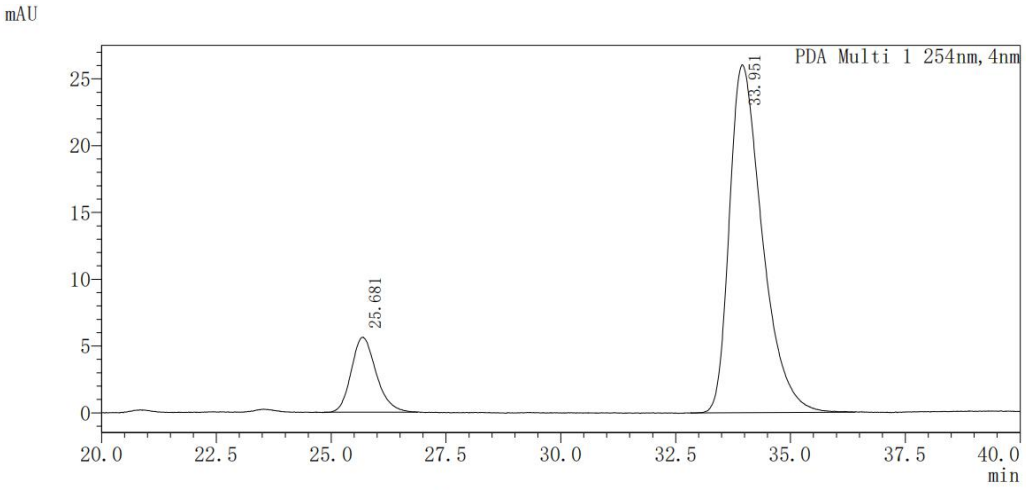
Compound **3da** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3da** (33.9 mg, 82%); Yellow solid; m.p.: 117-119 °C; IR: ν 2927, 1734, 1608, 1435, 1214, 825 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.39 (s, 1H), 4.53 (s, 1H),

4.44 (s, 1H), 4.29-4.23 (m, 1H), 4.18 (s, 5H), 3.88 (s, 3H), 3.62 (s, 3H), 3.60-3.37 (m, 4H), 1.97-1.74 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 168.8, 168.8, 82.4, 79.4, 70.7, 69.2, 68.1, 68.0, 52.6, 52.3, 50.7, 48.8, 46.4, 29.7, 26.6, 24.2; HRMS (ESI): m/z calculated for $C_{20}H_{24}FeNO^{5+}$ $[M+H]^+$: 414.0998, found: 414.0999; HPLC separation (DAICEL CHIRALPAK IA, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 34.0 min, t_R(minor) = 25.7 min, 86:14 er.



PDA Ch1 254nm

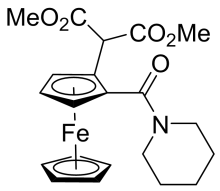
Peak No	Ret. time	Area/%
1	25.436	50.123
2	33.813	49.877



PDA Ch1 254nm

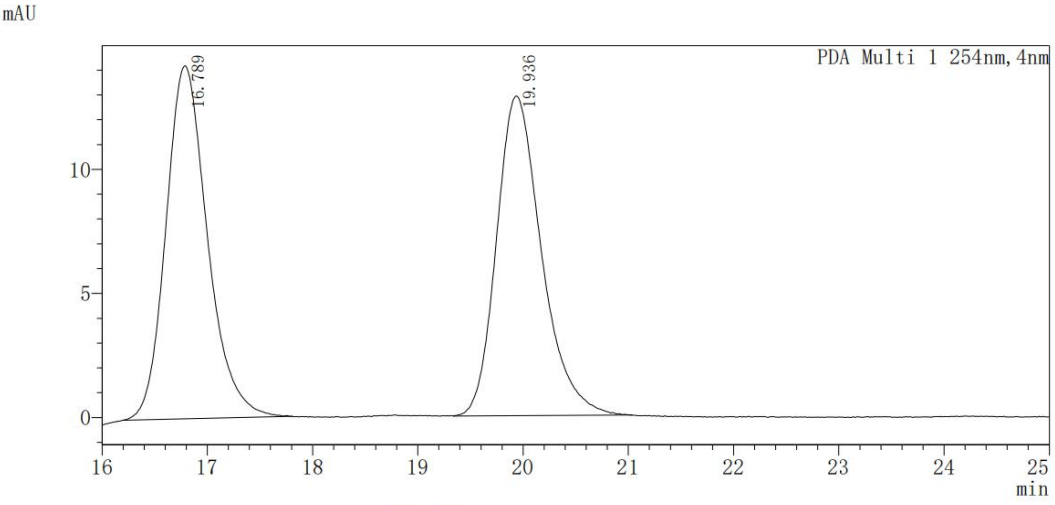
Peak No	Ret. time	Area/%
1	25.681	14.020
2	33.951	85.980

(S_p)-2-Dimethyl malonate-(pyrrolidine-1-carbonyl)ferrocene (3ea):



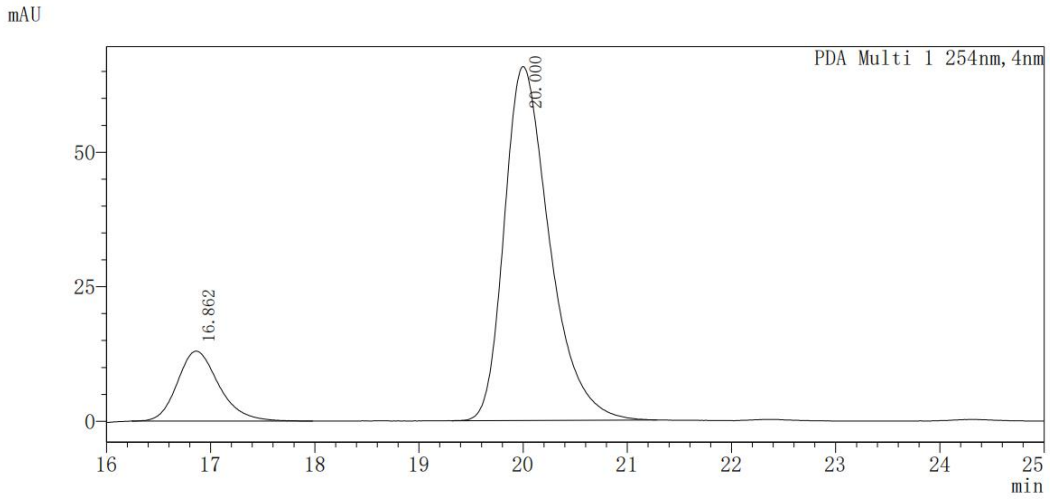
3ea

Compound **3ea** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ea** (29.9 mg, 70%); Yellow solid; m.p.: 115-117 °C; IR: ν 2937, 1736, 1615, 1215, 1026, 821 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.14 (s, 1H), 4.56 (s, 1H), 4.30 (s, 1H), 4.25-4.22 (m, 1H), 4.20 (s, 5H), 3.89 (s, 3H), 3.63 (s, 3H), 3.58-3.45 (m, 4H), 1.67-1.59 (m, 2H), 1.56-1.45 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 168.4, 82.2, 81.1, 70.9, 68.7, 67.8, 67.3, 52.7, 52.4, 50.2, 29.7, 26.1, 24.7; HRMS (ESI): m/z calculated for $C_{21}H_{26}FeNO_5^+$ $[M+H]^+$: 428.1155, found: 428.1166; HPLC separation (DAICEL CHIRALPAK IA, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 20.0 min, t_R(minor) = 16.9 min, 85:15 er.



PDA Ch1 254nm

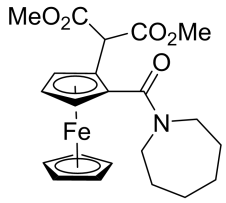
Peak No	Ret. time	Area/%
1	16.789	50.448
2	19.936	49.552



PDA Ch1 254nm

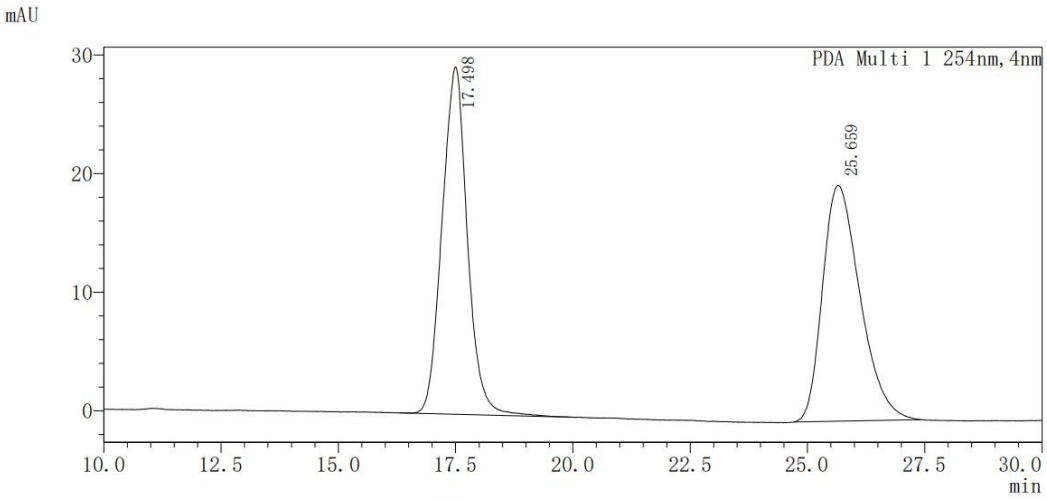
Peak No	Ret. time	Area/%
1	16.862	15.372
2	20.000	84.628

(S_p)-2-Dimethyl malonate-(azetane-1-carbonyl)ferrocene (3fa):



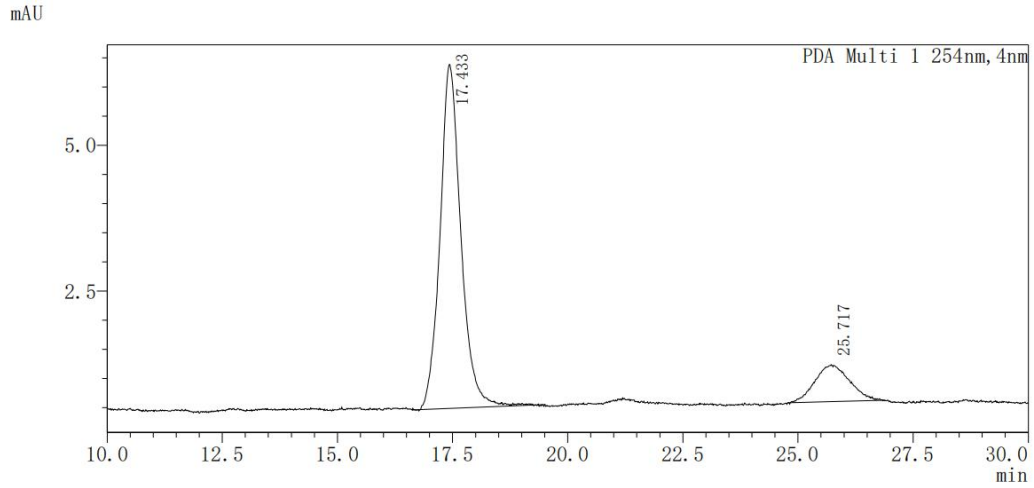
3fa

Compound **3fa** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3fa** (31.8 mg, 72%); Yellow solid; m.p.: 115-117 °C; IR: ν 2928, 1734, 1607, 1208, 1156, 819 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.21 (s, 1H), 4.53 (s, 1H), 4.35 (s, 1H), 4.24-4.21 (m, 1H), 4.19 (s, 5H), 3.89 (s, 3H), 3.62 (s, 3H), 3.57-3.34 (m, 4H), 1.72-1.54 (m, 6H), 1.46-1.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 168.7, 168.6, 82.5, 81.5, 70.9, 68.7, 67.5, 67.3, 52.6, 52.3, 50.3, 49.4, 46.3, 29.7, 28.2, 27.4, 26.3; HRMS (ESI): m/z calculated for $C_{22}H_{28}FeNO_5^+$ $[M+H]^+$: 442.1311, found: 442.1310; HPLC separation (DAICEL CHIRALPAK OD, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 17.4 min, t_R(minor) = 25.7 min, 85:15 er.



PDA Ch1 254nm

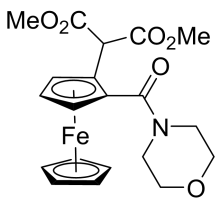
Peak No	Ret. time	Area/%
1	17.498	49.852
2	25.659	50.148



PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	17.433	84.976
2	25.717	15.024

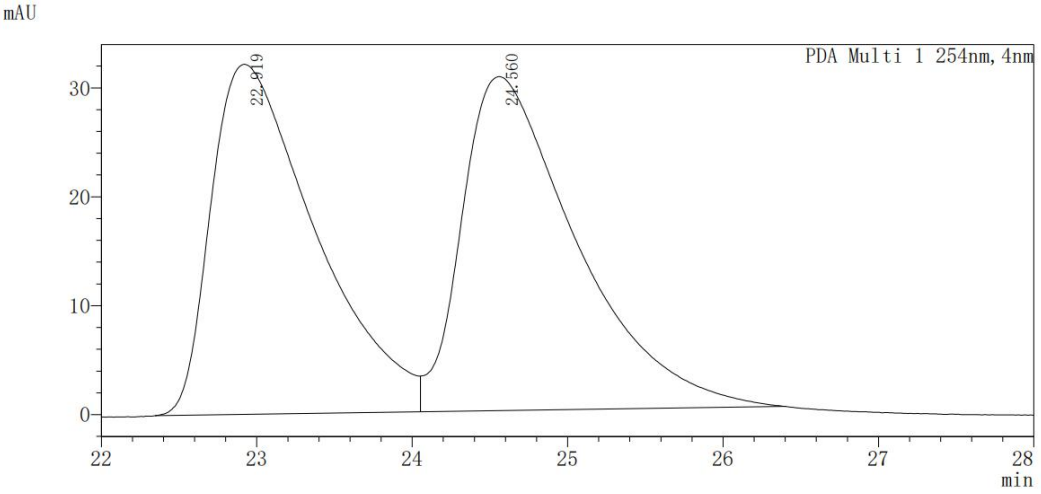
(S_p)-2-Dimethyl malonate-(morpholine-1-carbonyl)ferrocene (3ga):



3ga

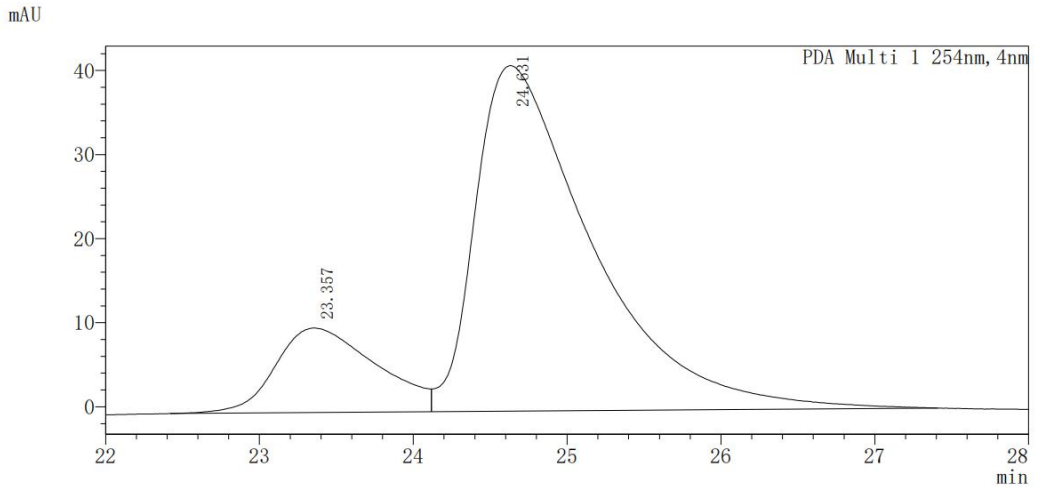
Compound **3ga** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ga** (25.7 mg, 60%); Yellow solid; m.p.: 128-130 °C; IR: ν 2923, 1736, 1614, 1469, 1108, 825 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.12 (s, 1H), 4.56 (s, 1H), 4.28 (s, 1H), 4.26-4.23 (m, 1H), 4.21 (s, 5H), 3.89 (s, 3H), 3.71-3.45 (m, 11H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 168.9, 168.5, 168.5, 82.5, 80.2, 71.0, 68.9, 67.6, 67.5, 66.91, 52.8, 52.4, 50.2; HRMS (ESI): m/z calculated for $C_{20}H_{24}FeNO_6^+$ $[M+H]^+$: 430.0948, found: 430.0966; HPLC separation (DAICEL CHIRALPAK IB, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 24.6 min, t_R(minor) = 23.4 min, 83:17 er.



PDA Ch1 254nm

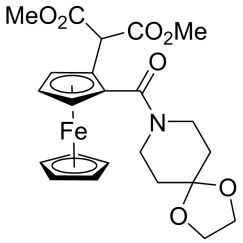
Peak No	Ret. time	Area/%
1	22.919	48.859
2	24.560	51.141



PDA Ch1 254nm

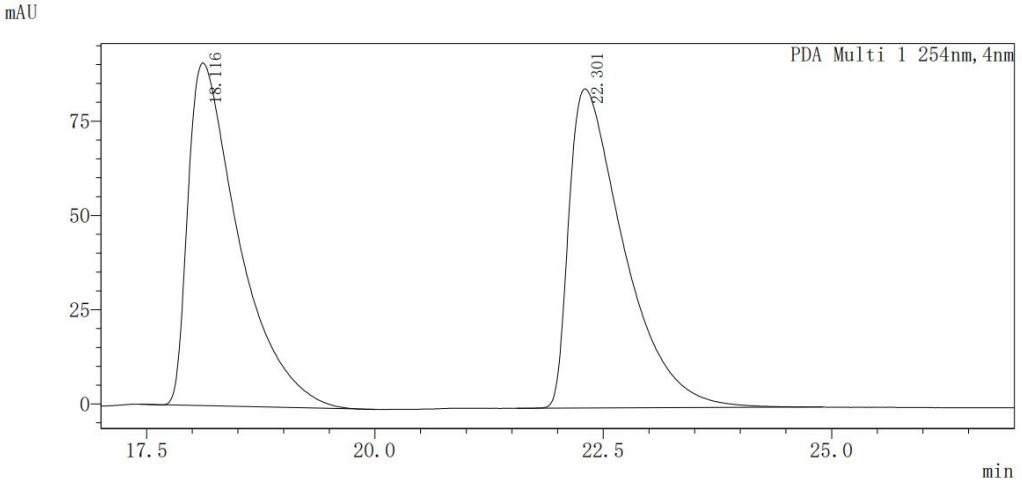
Peak No	Ret. time	Area/%
1	23.357	17.385
2	24.631	82.615

(S_p)-2-Dimethyl malonate-(4-piperidine-1-carbonyl)ferrocene (3ha):



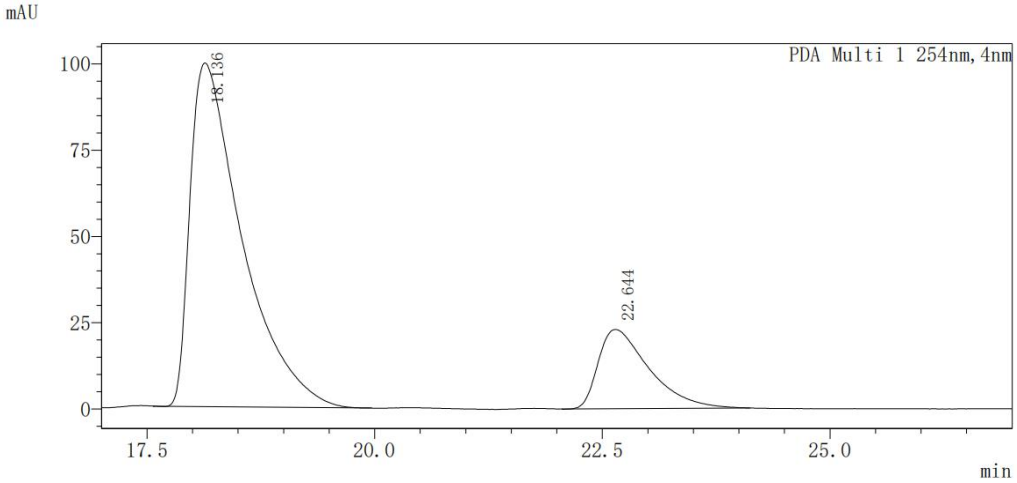
3ha

Compound **3ha** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ha** (31.0 mg, 64%); Yellow solid; m.p.: 132-134 °C; IR: ν 2956, 1736, 1621, 1452, 1144, 822 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.14 (s, 1H), 4.56 (s, 1H), 4.30 (s, 1H), 4.27-4.22 (m, 1H), 4.20 (s, 5H), 3.95 (s, 4H), 3.89 (s, 3H), 3.79-3.53 (m, 7H), 1.72-1.56 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 168.5, 107.1, 82.5, 80.5, 70.9, 68.9, 67.7, 67.4, 64.4, 52.7, 52.4, 50.2, 47.3, 44.9, 35.2; HRMS (ESI): m/z calculated for $C_{23}H_{28}FeNO_7^+$ $[M+H]^+$: 486.1210, found: 486.1226; HPLC separation (DAICEL CHIRALPAK IB, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 18.1 min, t_R(minor) = 22.6 min, 82:18 er.



PDA Ch1 254nm

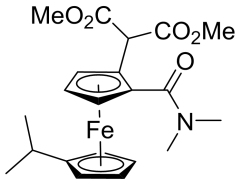
Peak No	Ret. time	Area/%
1	18.116	49.744
2	22.301	50.256



PDA Ch1 254nm

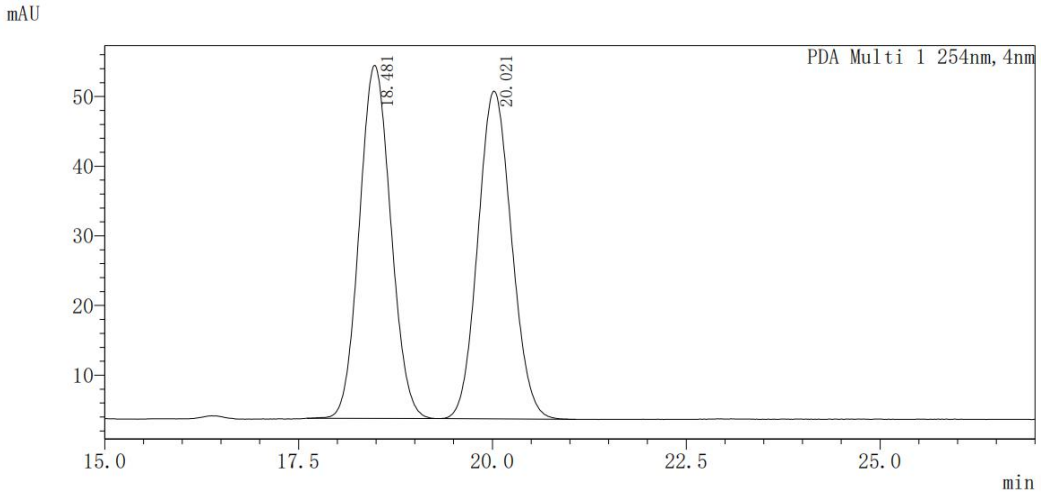
Peak No	Ret. time	Area/%
1	18.136	81.565
2	22.644	18.435

(S_p)-2-Dimethyl malonate-(dimethyl-1-carbonyl)-1'-ispropyl-ferrocene (3ia):



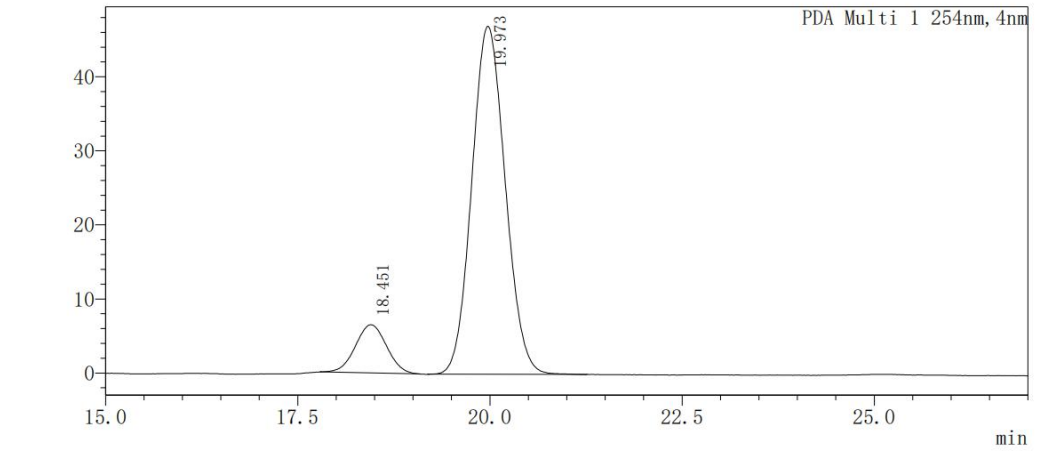
3ia

Compound **3ia** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ia** (33.9 mg, 79%); Yellow solid; m.p.: 102-104 °C; IR: ν 2958, 1741, 1621, 1435, 1261, 831 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.24 (s, 1H), 4.52 (s, 1H), 4.30 (s, 1H), 4.22-4.07 (m, 4H), 4.02 (s, 1H), 3.88 (s, 3H), 3.62 (s, 3H), 2.99 (s, 6H), 2.51-2.60 (m, 1H), 1.10 (d, J = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 168.7, 98.4, 82.2, 80.0, 71.3, 70.6, 69.5, 69.1, 68.9, 68.4, 67.6, 52.6, 52.3, 50.2, 39.2, 35.7, 27.0, 23.6, 23.5; HRMS (ESI): m/z calculated for $C_{21}H_{28}FeNO_5^+$ $[M+H]^+$: 430.1311, found: 430.1321; HPLC separation (DAICEL CHIRALPAK AD, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 20.0 min, t_R(minor) = 18.5 min, 89:11 er.



PDA Ch1 254nm

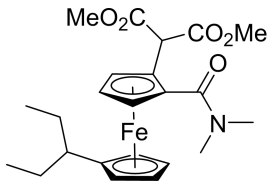
Peak No	Ret. time	Area/%
1	18.481	50.111
2	20.021	49.889



PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	18.451	11.443
2	19.973	88.557

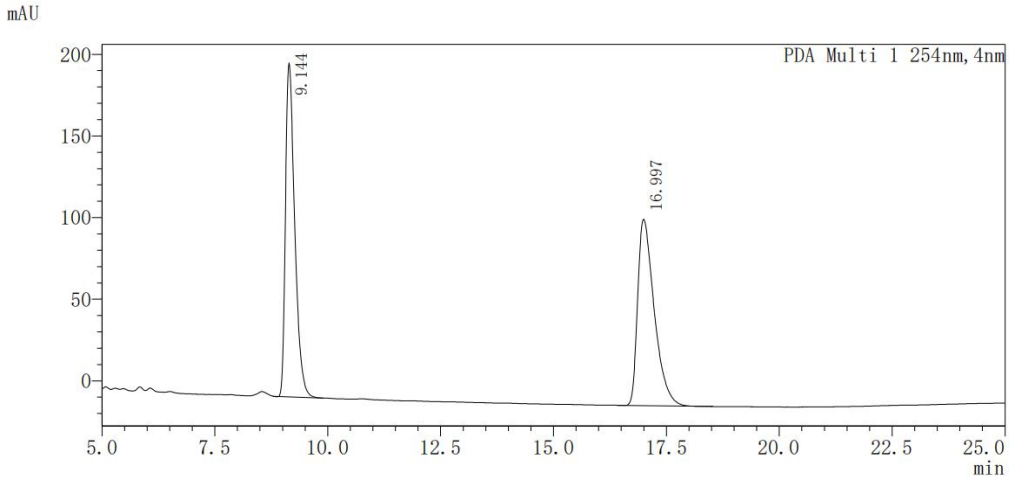
(S_p)-2-Dimethyl malonate-(dimethyl-1-carbonyl)-1'-pentan-3-yl-ferrocene (3ja):



3ja

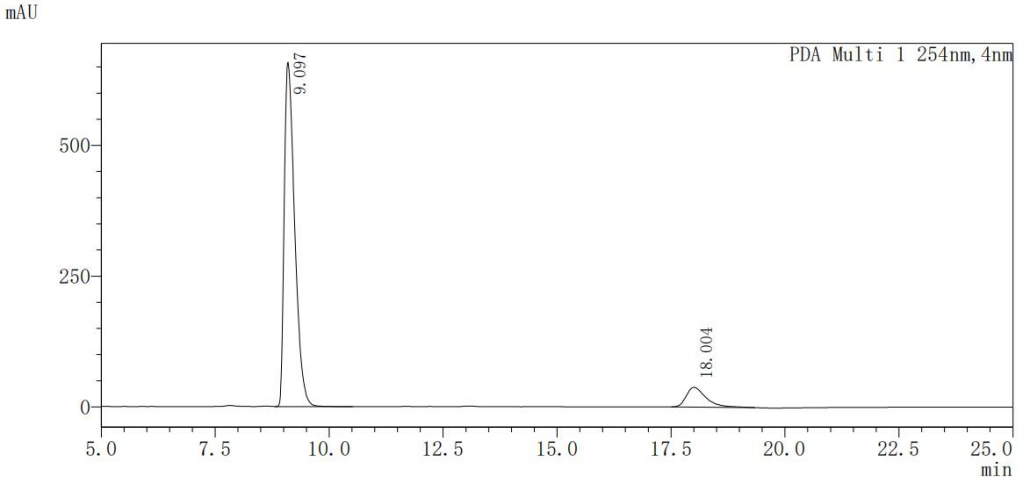
Compound **3ja** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ja** (34.7 mg, 76%); Yellow solid; m.p.: 107-109 °C; IR: ν 2961, 1743, 1600, 1436, 1260, 1108, 835 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.24 (s, 1H), 4.50 (s, 1H), 4.28 (s, 1H), 4.19-4.12 (m, 2H), 4.12-4.04 (m, 2H), 3.98 (s, 1H), 3.88 (s, 3H), 3.62 (s, 3H), 2.99 (s, 6H), 2.19-2.08 (m, 1H), 1.58-1,41 (m, 4H), 0.86-0.74 (m, 6H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 168.8, 96.7, 82.2, 79.8, 71.0, 70.4, 70.4, 69.3, 69.1, 68.6, 68.6, 52.6, 52.3, 50.3, 40.0, 39.3, 35.7, 26.6, 26.5, 11.3, 11.2; HRMS (ESI): m/z calculated for $C_{23}H_{32}FeNO_5^+$ $[M+H]^+$: 458.1624, found: 458.1623; HPLC separation (DAICEL CHIRALPAK IB, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 9.1 min, t_R(minor) = 18.0 min, 90:10 er.



PDA Ch1 254nm

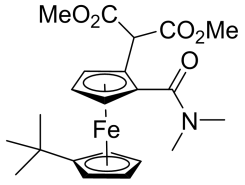
Peak No	Ret. time	Area/%
1	9.144	50.017
2	16.997	49.983



PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	9.097	90.253
2	18.004	9.747

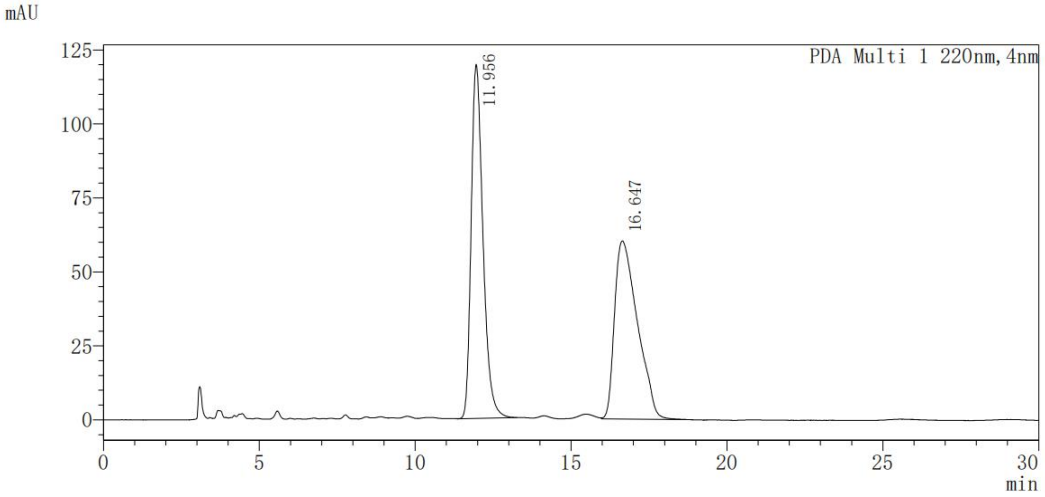
(S_p)-2-Dimethyl malonate-(dimethyl-1-carbonyl)-1'-tertbutyl -ferrocene (3ka):



3ka

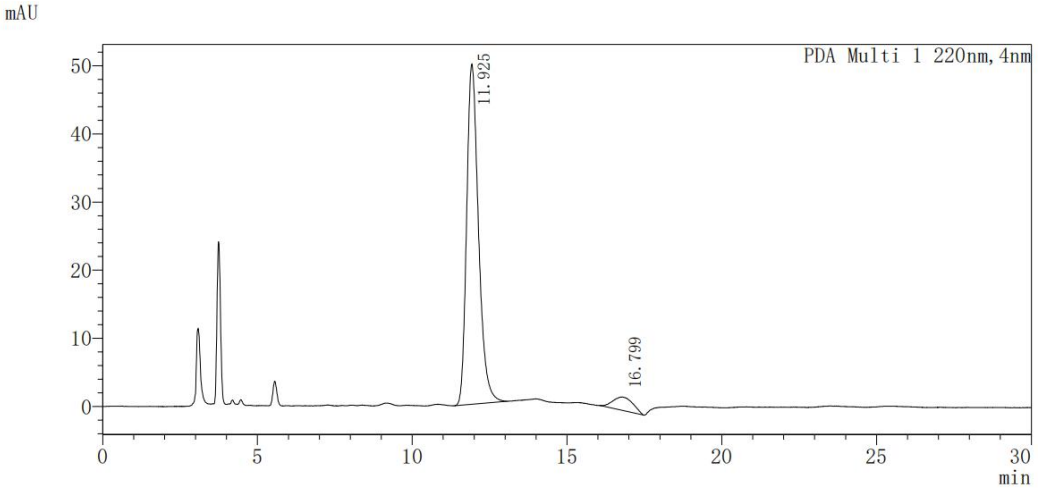
Compound **3ka** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1)

to provide **3ka** (37.2 mg, 84%); Yellow solid; m.p.: 110-112 °C; IR: ν 2924, 1737, 1620, 1434, 1259, 832 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.25 (s, 1H), 4.55 (s, 1H), 4.36 (s, 1H), 4.24 (s, 1H), 4.20 (s, 1H), 4.17 (s, 1H), 4.11 (s, 1H), 3.97 (s, 1H), 3.89 (s, 3H), 3.63 (s, 3H), 3.00 (s, 6H), 1.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 168.7, 103.2, 82.1, 80.0, 72.0, 70.9, 68.8, 68.6, 68.3, 66.5, 52.7, 52.3, 50.2, 31.4, 30.3; HRMS (ESI): m/z calculated for $C_{22}H_{30}FeNO_5^+$ $[M+H]^+$: 444.1468, found: 444.1471; HPLC separation (DAICEL CHIRALPAK OD, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 220nm): t_R(major) = 11.9 min, t_R(minor) = 16.8 min, 94:6 er.



PDA Ch1 220nm

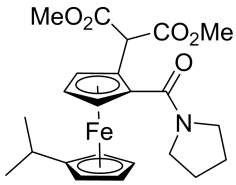
Peak No	Ret. time	Area/%
1	11.956	50.592
2	16.647	49.408



PDA Ch1 220nm

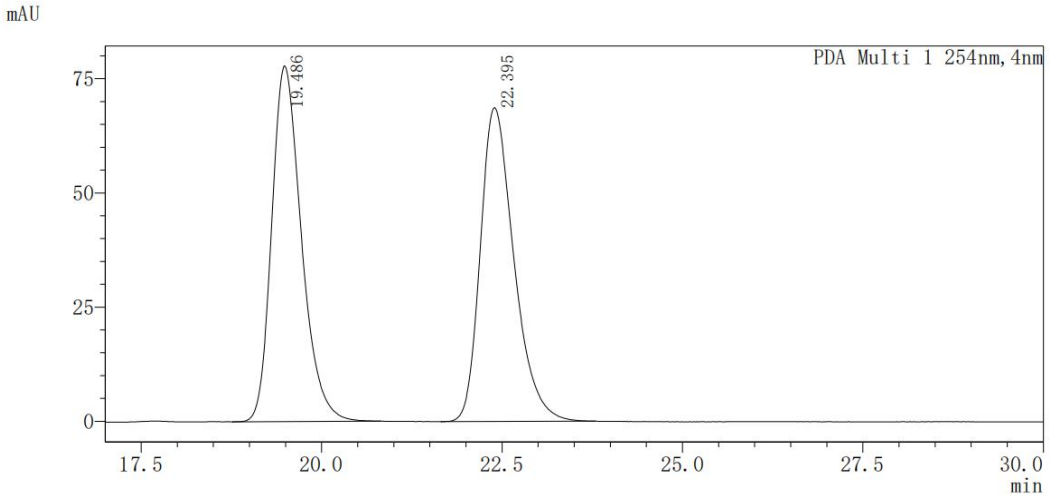
Peak No	Ret. time	Area/%
1	11.925	93.770
2	16.799	6.230

(S_p)-2-Dimethyl malonate-(dimethyl-1-carbonyl)-1'-ispropyl-ferrocene (3la):



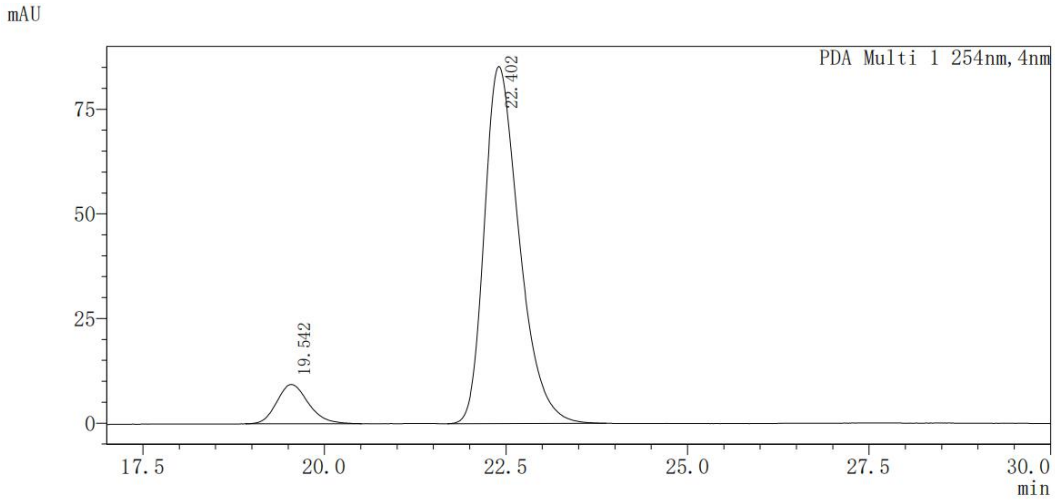
3la

Compound **3la** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3la** (34.1 mg, 75%); Yellow solid; m.p.: 116-118 °C; IR: ν 2956, 1736, 1603, 1456, 1215, 835 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.45 (s, 1H), 4.49 (s, 1H), 4.40 (s, 1H), 4.21 (s, 1H), 4.16-4.06 (m, 3H), 4.03 (s, 1H), 3.88 (s, 3H), 3.62 (s, 3H), 3.56-3.43 (m, 4H), 2.59-2.51 (m, 1H), 1.96-1,74 (m, 4H), 1.10 (d, J = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 168.9, 98.3, 82.4, 79.0, 70.9, 70.5, 69.6, 69.2, 68.9, 68.8, 67.7, 52.6, 52.3, 50.6, 48.9, 46.4, 27.0, 26.6, 24.2, 23.6, 23.5; HRMS (ESI): m/z calculated for $C_{23}H_{30}FeNO_5^+$ $[M+H]^+$: 456.1468, found: 456.1475; HPLC separation (DAICEL CHIRALPAK IA, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 22.4 min, t_R(minor) = 19.5 min, 91:9 er.



PDA Ch1 254nm

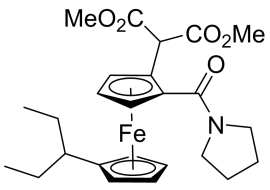
Peak No	Ret. time	Area/%
1	19.486	50.024
2	22.395	49.976



PDA Ch1 254nm

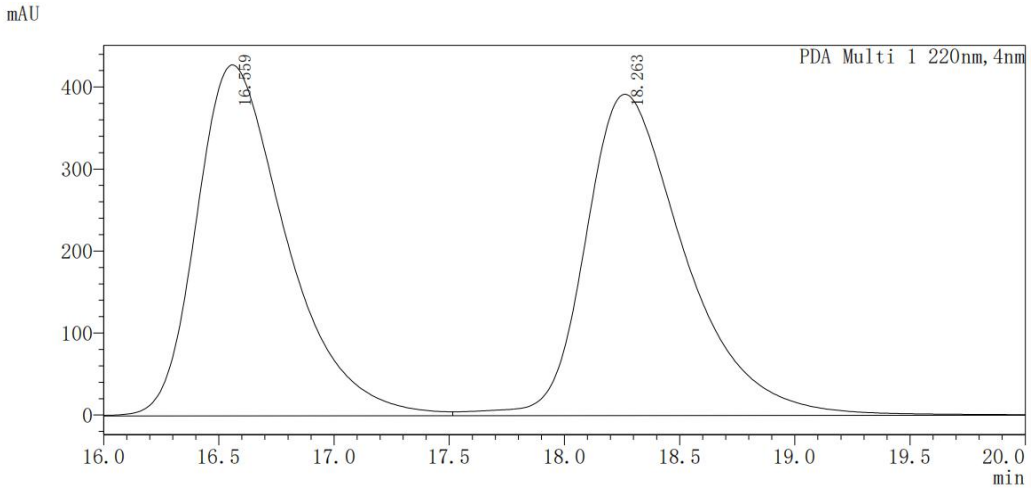
Peak No	Ret. time	Area/%
1	19.542	9.065
2	22.402	90.935

(S_p)-2-Dimethyl malonate-(dimethyl-1-carbonyl)-1'-pentan-3-yl-ferrocene (3ma):



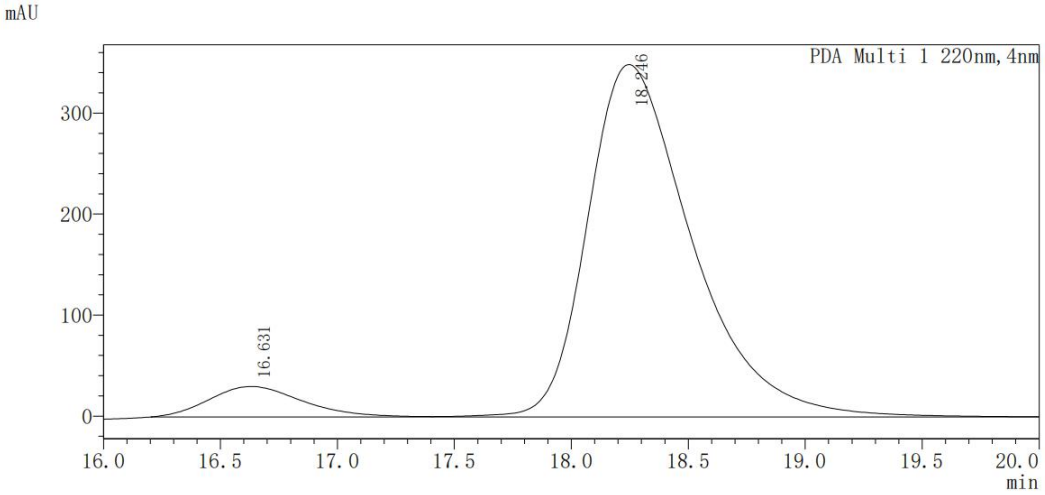
3ma

Compound **3ma** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ma** (34.8 mg, 72%); Yellow solid; m.p.: 119-121 °C; IR: ν 2959, 1737, 1604, 1456, 1251, 835 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.47 (s, 1H), 4.49 (s, 1H), 4.39 (s, 1H), 4.18 (s, 1H), 4.13-4.05 (m, 3H), 3.99 (s, 1H), 3.88 (s, 3H), 3.63 (s, 3H), 3.58-3.43 (m, 4H), 2.17-2.12 (m, 1H), 1.93-1.76 (m, 4H), 1.59-1.41 (m, 4H), 0.85-0.76 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 168.9, 96.7, 82.4, 78.8, 70.6, 70.2, 70.1, 69.7, 69.1, 68.9, 68.7, 52.6, 52.3, 50.7, 48.9, 46.4, 39.9, 26.6, 26.5, 24.2, 11.3, 11.2; HRMS (ESI): m/z calculated for $C_{25}H_{34}FeNO_5^+$ $[M+H]^+$: 484.1781, found: 484.1783; HPLC separation (DAICEL CHIRALPAK IG, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 220nm): t_R(major) = 18.2 min, t_R(minor) = 16.6 min, 93:7 er.



PDA Ch1 220nm

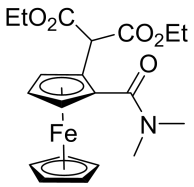
Peak No	Ret. time	Area/%
1	16.559	49.557
2	18.263	50.443



PDA Ch1 220nm

Peak No	Ret. time	Area/%
1	16.631	7.173
2	18.246	92.827

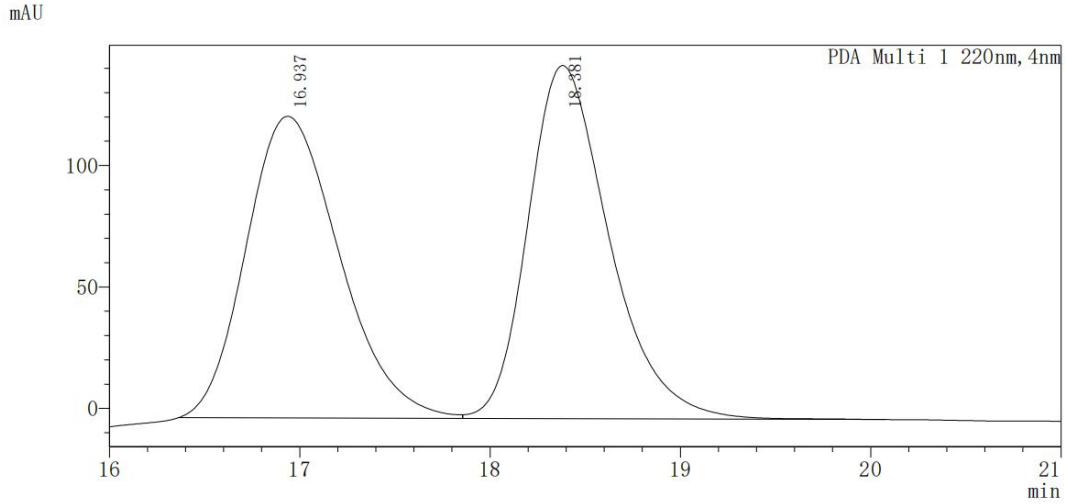
(S_p)-2-Diethyl malonate-(dimethyl-1-carbonyl)ferrocene (3ab):



3ab

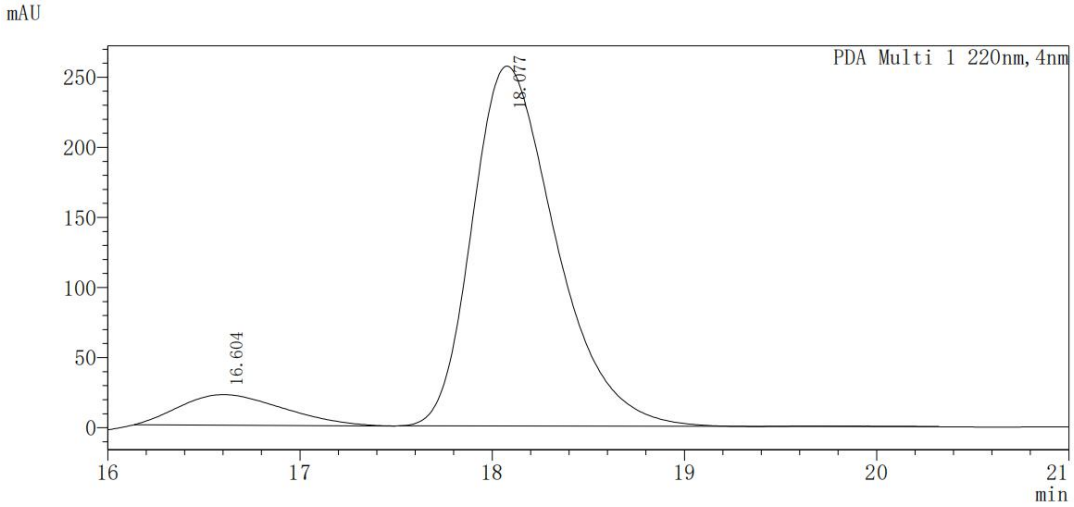
Compound **3ab** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ab** (34.0 mg, 82%); Yellow solid; m.p.: 92-94 °C; IR: ν 2925, 1737, 1626, 1463, 1214, 801 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.16 (s, 1H), 4.58 (s, 1H), 4.41-4.30 (m, 3H), 4.26-4.23 (m, 1H), 4.22 (s, 5H), 4.15-4.01 (m, 2H), 3.00 (s, 6H), 1.40 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

170.0, 168.3, 168.2, 82.4, 80.7, 70.8, 68.7, 68.0, 67.2, 61.5, 61.3, 50.7, 14.2, 14.0; HRMS (ESI): m/z calculated for $C_{20}H_{26}FeNO_5^+$ $[M+H]^+$: 416.1155, found: 416.1160; HPLC separation (DAICEL CHIRALPAK IA, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 220nm): t_R(major) = 18.1 min, t_R(minor) = 16.6 min, 91:9 er.



PDA Ch1 220nm

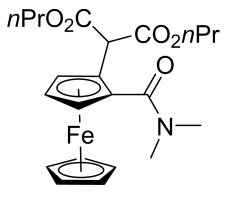
Peak No	Ret. time	Area/%
1	16.937	49.608
2	18.381	50.392



PDA Ch1 220nm

Peak No	Ret. time	Area/%
1	16.604	9.457
2	18.077	90.543

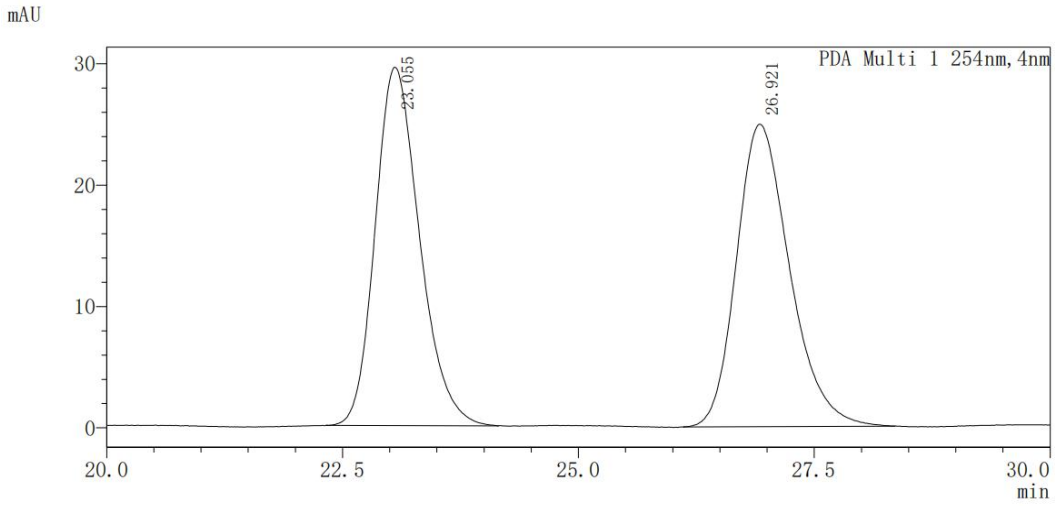
(S_p)-2-Dipropyl malonate-(dimethyl-1-carbonyl)ferrocene (3ac):



3ac

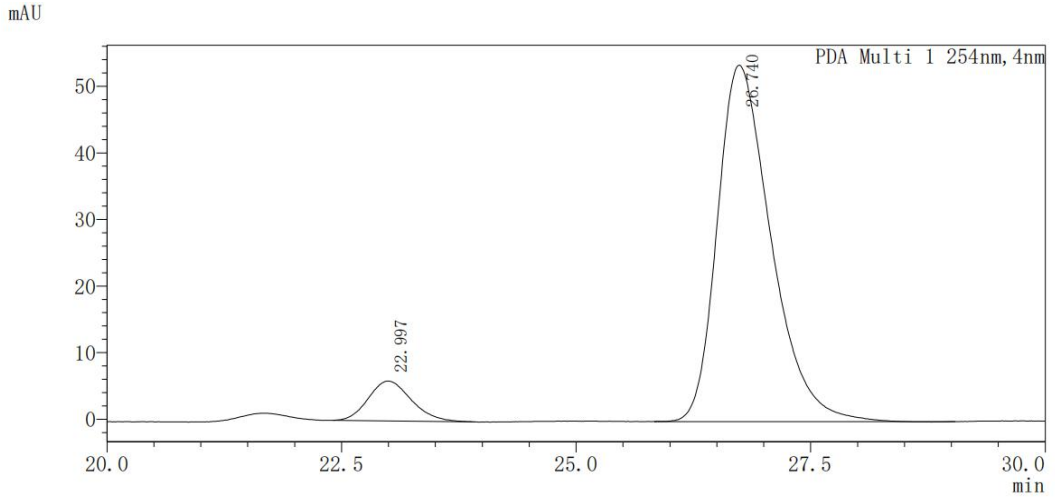
Compound **3ac** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1)

to provide **3ac** (35.0 mg, 79%); Yellow solid; m.p.: 87-89 °C; IR: ν 2968, 1733, 1624, 1460, 1275, 1058, 822 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.17 (s, 1H), 4.57 (s, 1H), 4.34 (s, 1H), 4.28-4.06 (m, 8H), 4.05-3.86 (m, 2H), 2.98 (s, 6H), 1.87-1.70 (m, 2H), 1.62-1,45 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 168.4, 168.3, 82.5, 80.7, 70.8, 68.8, 68.0, 67.3, 67.0, 67.0, 50.6, 22.0, 21.8, 10.5, 10.2; HRMS (ESI): m/z calculated for $C_{22}H_{30}FeNO_5^+$ $[M+H]^+$: 444.1468, found: 444.1469; HPLC separation (DAICEL CHIRALPAK IA, hexane:2-propanol = 98:2, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 26.7 min, t_R(minor) = 23.0 min, 92:8 er.



PDA Ch1 254nm

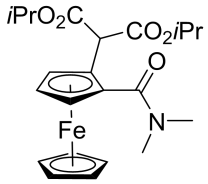
Peak No	Ret. time	Area/%
1	23.055	49.664
2	26.921	50.336



PDA Ch1 254nm

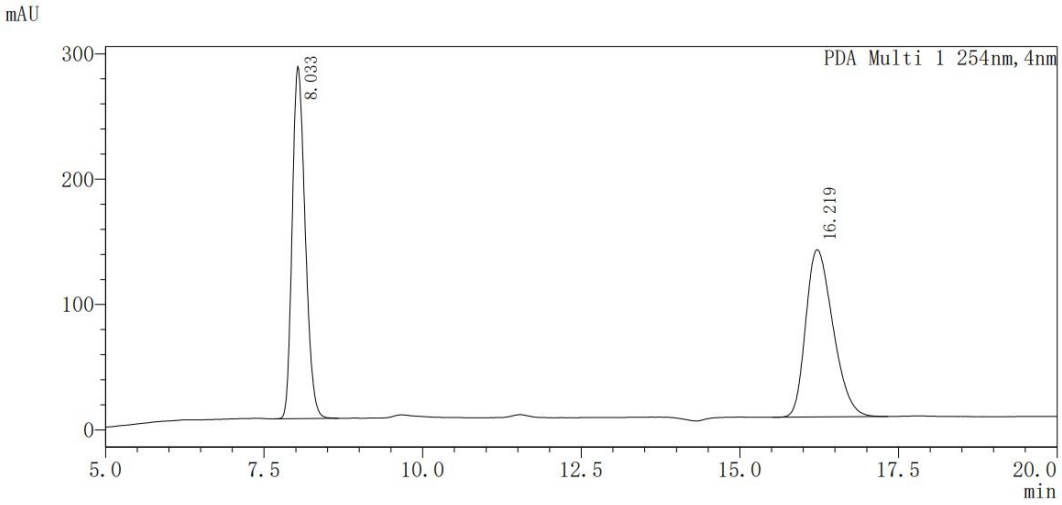
Peak No	Ret. time	Area/%
1	22.997	8.212
2	26.740	91.788

(S_p)-2-Diisopropyl malonate-(dimethyl-1-carbonyl)ferrocene (3ad):



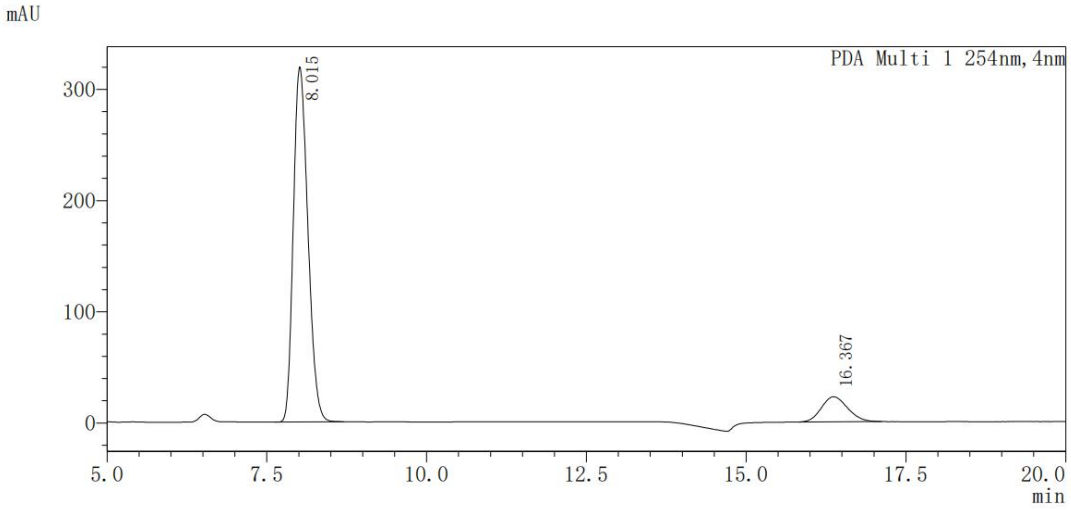
3ad

Compound **3ad** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ad** (31.9 mg, 72%); Yellow solid; m.p.: 84-86 °C; IR: ν 2981, 1727, 1625, 1456, 1277, 1102, 818 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.25-5.17 (m, 1H), 5.10 (s, 1H), 4.95-4.88 (m, 1H), 4.58 (s, 1H), 4.34 (s, 1H), 4.24-4.19 (m, 6H), 2.99 (s, 6H), 1.40-1.35 (m, 6H), 1.19-1.11 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 167.9, 167.6, 82.5, 81.0, 70.8, 69.0, 68.9, 68.6, 67.9, 67.1, 51.1, 25.4, 21.8, 21.6, 21.5; HRMS (ESI): m/z calculated for $C_{22}H_{30}FeNO_5^+$ $[M+H]^+$: 444.1468, found: 444.1473; HPLC separation (DAICEL CHIRALPAK OD, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 8.0 min, t_R(minor) = 16.4 min, 89:11 er.



PDA Ch1 254nm

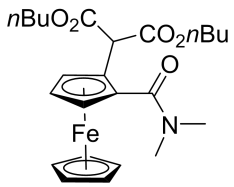
Peak No	Ret. time	Area/%
1	8.033	50.039
2	16.219	49.961



PDA Ch1 254nm

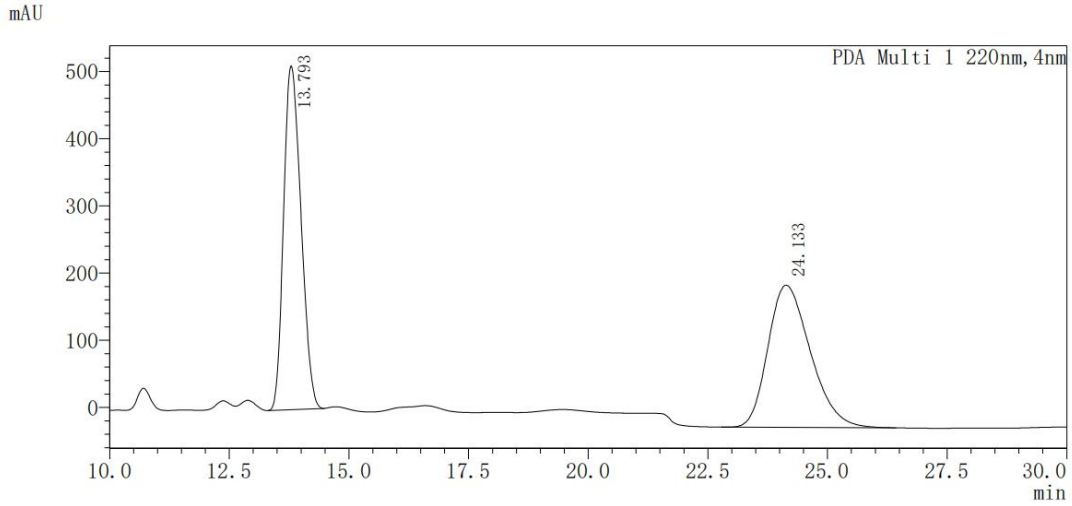
Peak No	Ret. time	Area/%
1	8.015	88.736
2	16.367	11.264

(S_p)-2-Dibutyl malonate-(dimethyl-1-carbonyl)ferrocene (3ae):



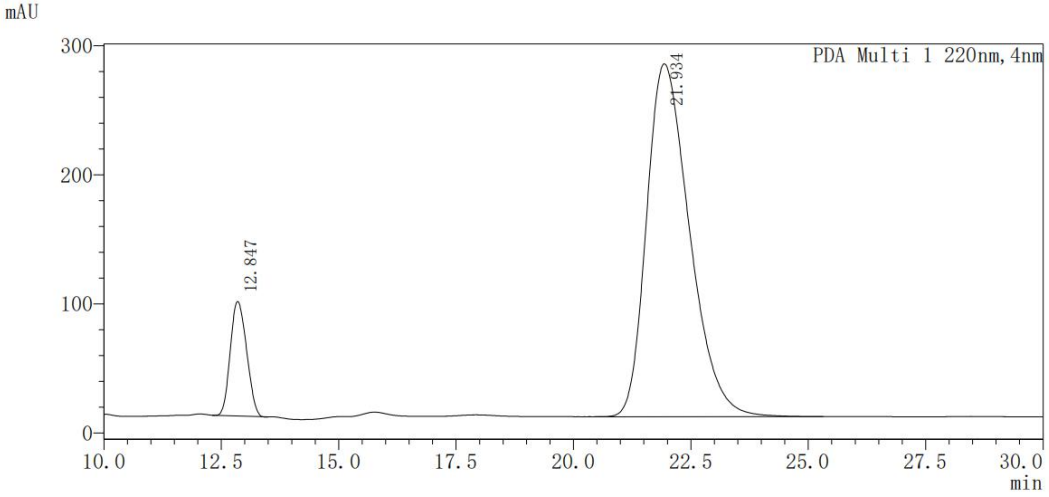
3ae

Compound **3ae** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ae** (36.3 mg, 77%); Yellow solid; m.p.: 86-88 °C; IR: ν 2960, 1732, 1627, 1459, 1277, 1062, 821 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.18 (s, 1H), 4.59 (s, 1H), 4.37-4.29 (m, 2H), 4.27-4.23 (m, 2H), 4.21 (m, 5H), 4.10-3.98 (m, 2H), 3.00 (s, 6H), 1.79-1.70 (m, 2H), 1.58-1.45 (m, 4H), 1.32-1.26 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 168.4, 168.3, 82.5, 80.7, 70.8, 68.8, 68.0, 67.3, 65.3, 65.2, 50.6, 30.6, 30.5, 19.2, 18.9, 13.7, 13.6; HRMS (ESI): m/z calculated for $C_{24}H_{34}FeNO_5^+$ $[M+H]^+$: 472.1781, found: 472.1788; HPLC separation (DAICEL CHIRALPAK AD, hexane:2-propanol = 98:2, flow rate: 1.0 mL/min, detection at 220nm): t_R(major) = 21.9 min, t_R(minor) = 12.8 min, 89:11 er.



PDA Ch1 220nm

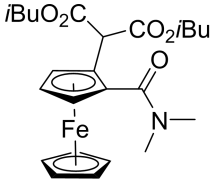
Peak No	Ret. time	Area/%
1	13.793	49.753
2	24.133	50.247



PDA Ch1 220nm

Peak No	Ret. time	Area/%
1	12.847	10.985
2	21.934	89.015

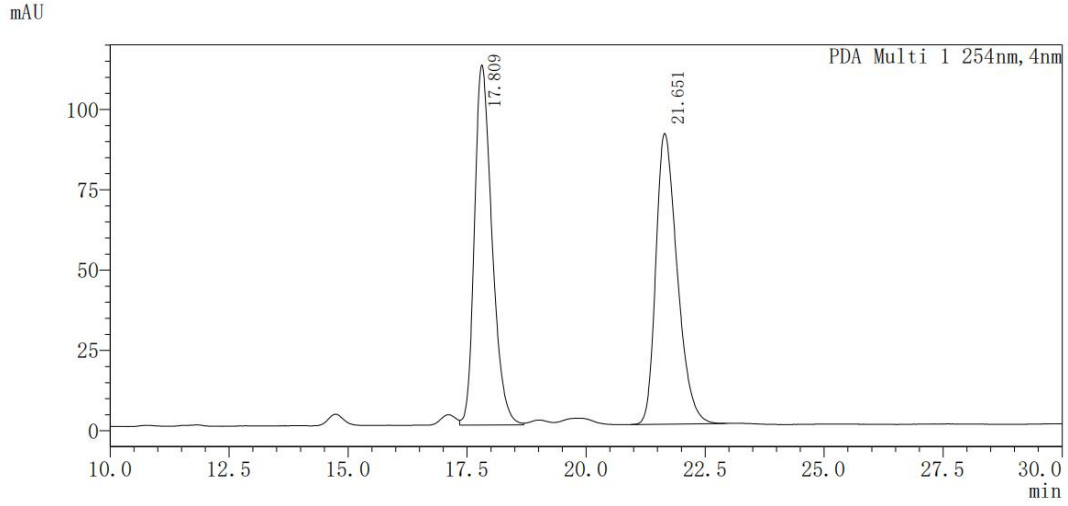
(S_p)-2-Diisobutyl malonate-(dimethyl-1-carbonyl)ferrocene (3af):



3af

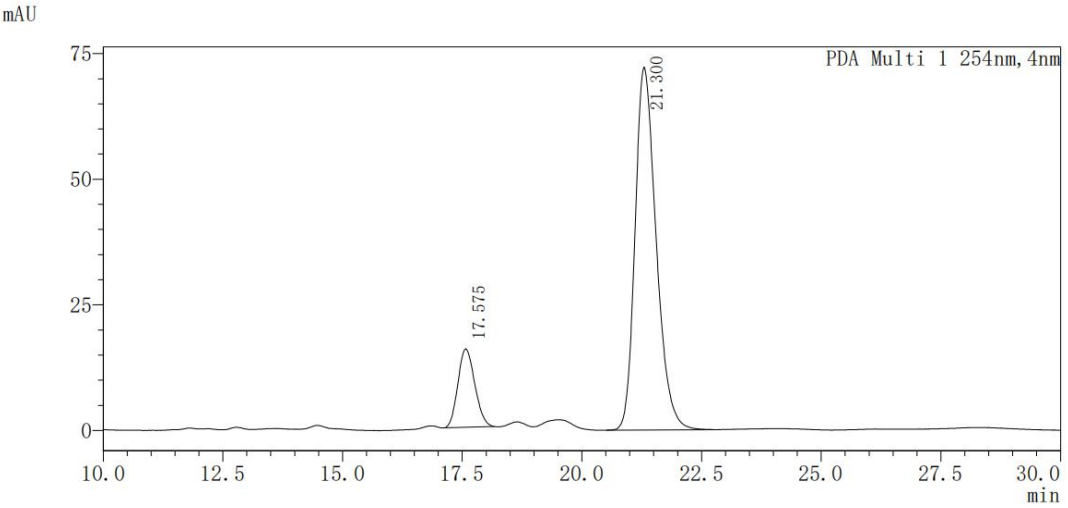
Compound **3af** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3af** (34.4 mg, 73%); Yellow solid; m.p.: 94-96 °C; IR: ν 2961, 1734, 1626, 1470, 1277, 1004, 823 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.22 (s, 1H), 4.61 (s, 1H), 4.37-4.34 (m, 1H), 4.26-4.23 (m, 1H), 4.21 (s, 5H), 4.17-4.12 (m, 1H), 4.02-3.96 (m,

1H), 3.86-3.76 (m, 2H), 2.99 (s, 6H), 2.12-2.01 (m, 1H), 1.90-1.78 (m, 1H), 1.06-1.00 (m, 6H), 0.88-0.81 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 168.3, 82.5, 80.7, 71.6, 71.5, 70.8, 68.9, 68.0, 67.3, 50.5, 27.8, 27.7, 19.2, 18.9; HRMS (ESI): m/z calculated for $C_{24}H_{34}FeNO_5^+$ $[M+H]^+$: 472.1781, found: 472.1794; HPLC separation (DAICEL CHIRALPAK IA, hexane:2-propanol = 98:2, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 21.3 min, t_R(minor) = 17.6 min, 85:15 er.



PDA Ch1 254nm

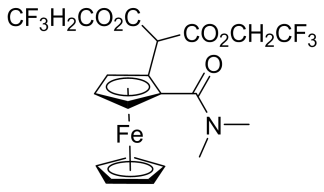
Peak No	Ret. time	Area/%
1	17.809	50.418
2	21.651	49.582



PDA Ch1 254nm

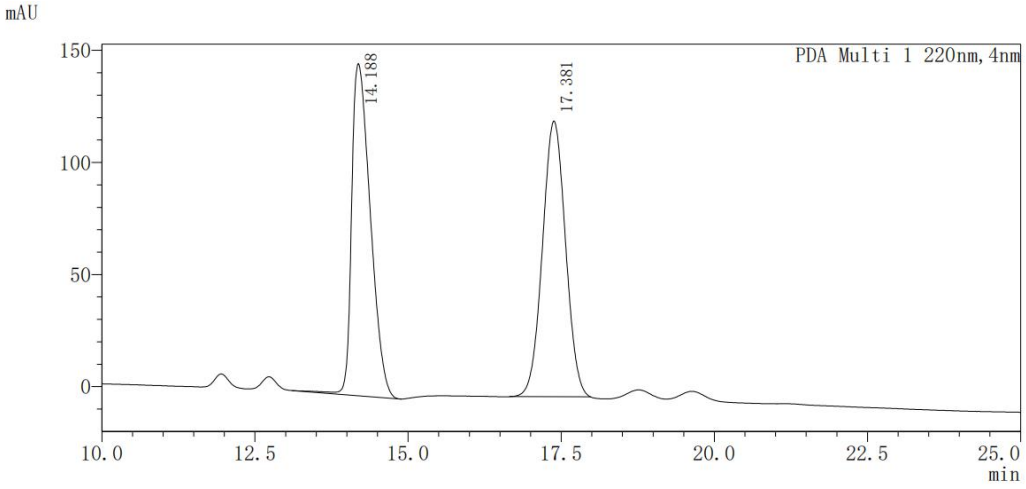
Peak No	Ret. time	Area/%
1	17.575	14.721
2	21.300	85.279

(S_p)-2-Ditrifluoroethyl malonate-(dimethyl-1-carbonyl)ferrocene (3ag):



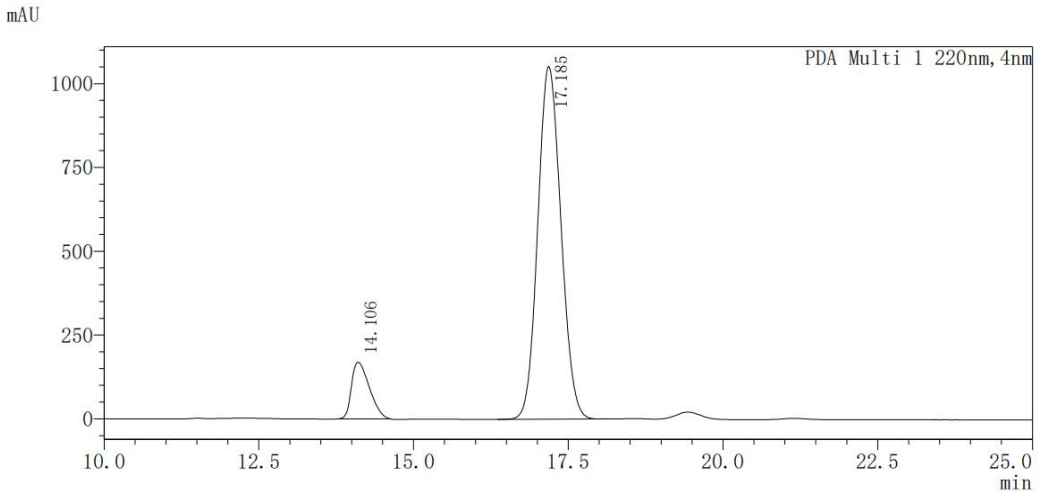
3ag

Compound **3ag** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ag** (45.5 mg, 87%); Yellow solid; m.p.: 84-86 °C; IR: ν 2922, 1758, 1618, 1410, 1165, 1059, 840 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.58 (s, 1H), 4.77-4.58 (m, 2H), 4.54 (s, 1H), 4.50-4.45 (m, 1H), 4.43 (s, 1H), 4.39-4.33 (m, 1H), 4.31 (s, 1H), 4.21 (s, 5H), 3.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 166.1, 165.9, 80.9, 79.2, 71.0, 68.7, 67.9, 61.3 (d, J = 6.1 Hz), 61.0 (d, J = 6.3 Hz), 50.0, 29.7, 29.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.29 (t, J = 8.3 Hz), -73.89 (t, J = 8.2 Hz); HRMS (ESI): m/z calculated for $C_{20}H_{20}F_6FeNO_5^+$ $[M+H]^+$: 524.0590, found: 524.0597; HPLC separation (DAICEL CHIRALPAK AD, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 220nm): t_R(major) = 17.2 min, t_R(minor) = 14.1 min, 89:11 er.



PDA Ch1 220nm

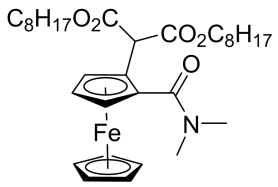
Peak No	Ret. time	Area/%
1	14.188	49.344
2	17.381	50.656



PDA Ch1 220nm

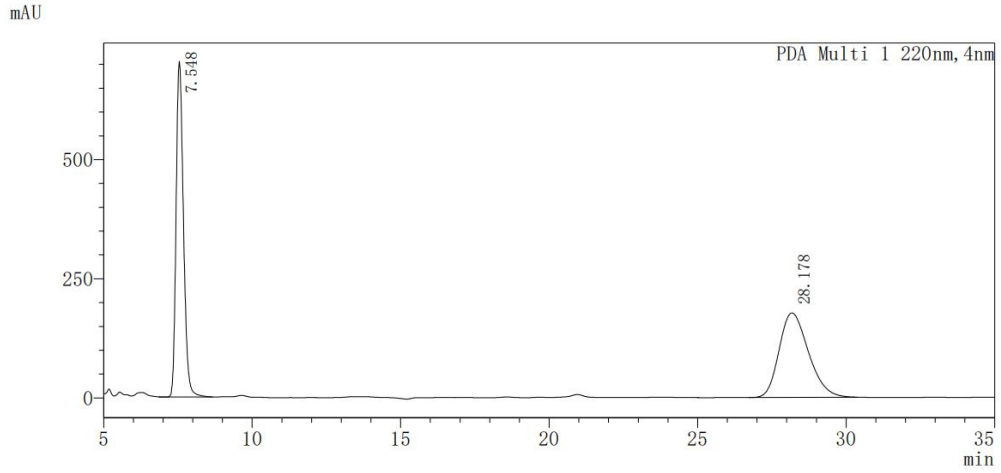
Peak No	Ret. time	Area/%
1	14.106	11.070
2	17.185	88.930

(S_p)-2-Dioctyl malonate-(dimethyl-1-carbonyl)ferrocene (3ah):



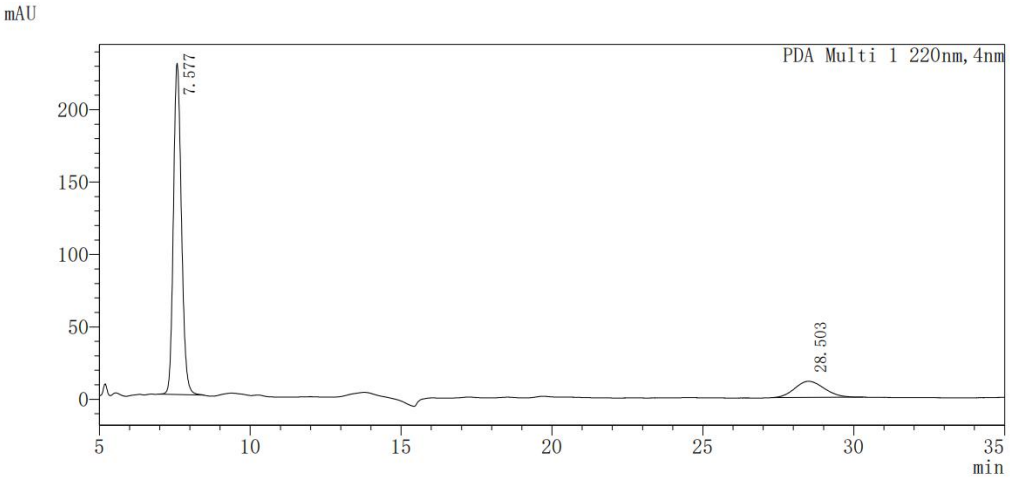
3ah

Compound **3ah** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ah** (43.7 mg, 75%); Yellow solid; m.p.: 103-105 °C; IR: ν 2958, 1733, 1627, 1459, 1276, 1062, 819 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.16 (s, 1H), 4.59 (s, 1H), 4.35 (s, 1H), 4.34-4.27 (m, 1H), 4.25-4.22 (m, 2H), 4.21 (s, 5H), 4.06-3.96 (m, 2H), 2.99 (s, 6H), 1.78-1.72 (m, 2H), 1.58-1.49 (m, 2H), 1.48-1.40 (m, 2H), 1.37-1.28 (m, 16H), 0.94-0.78 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 168.4, 168.3, 82.5, 80.8, 70.8, 68.8, 68.0, 67.3, 65.6, 65.5, 50.6, 31.8, 31.8, 29.2, 29.2, 29.2, 29.2, 28.6, 28.5, 26.0, 25.7, 22.6, 14.1; HRMS (ESI): m/z calculated for $C_{32}H_{50}FeNO_5^+$ $[M+H]^+$: 584.3033, found: 584.3043; HPLC separation (DAICEL CHIRALPAK OD, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 220nm): t_R(major) = 7.6 min, t_R(minor) = 28.5 min, 85:15 er.



PDA Ch1 220nm

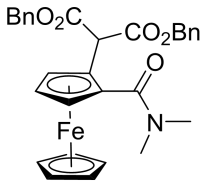
Peak No	Ret. time	Area/%
1	7.548	49.883
2	28.178	50.117



PDA Ch1 220nm

Peak No	Ret. time	Area/%
1	7.577	84.717
2	28.503	15.283

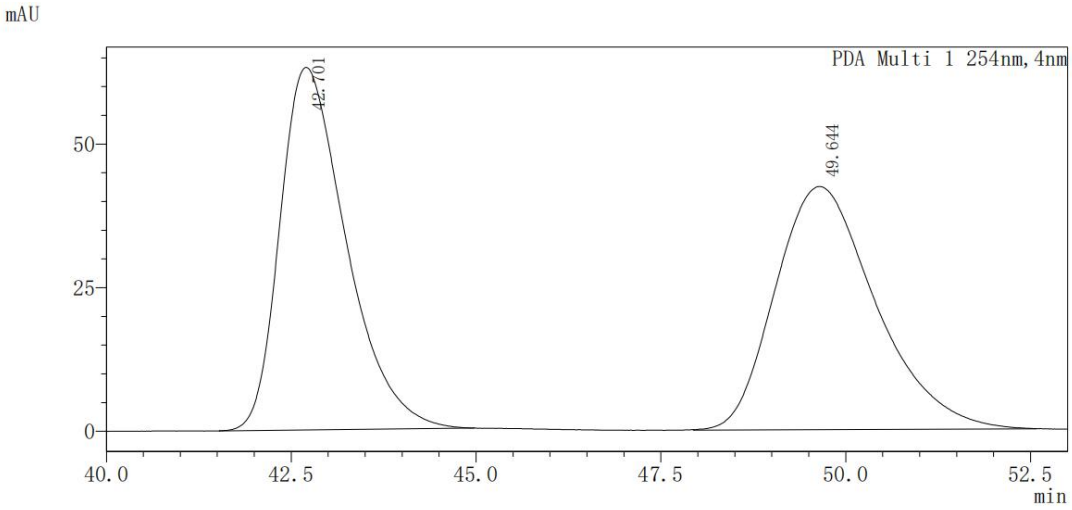
(S_p)-2-Dibenzyl malonate-(dimethyl-1-carbonyl)ferrocene (3ai):



3ai

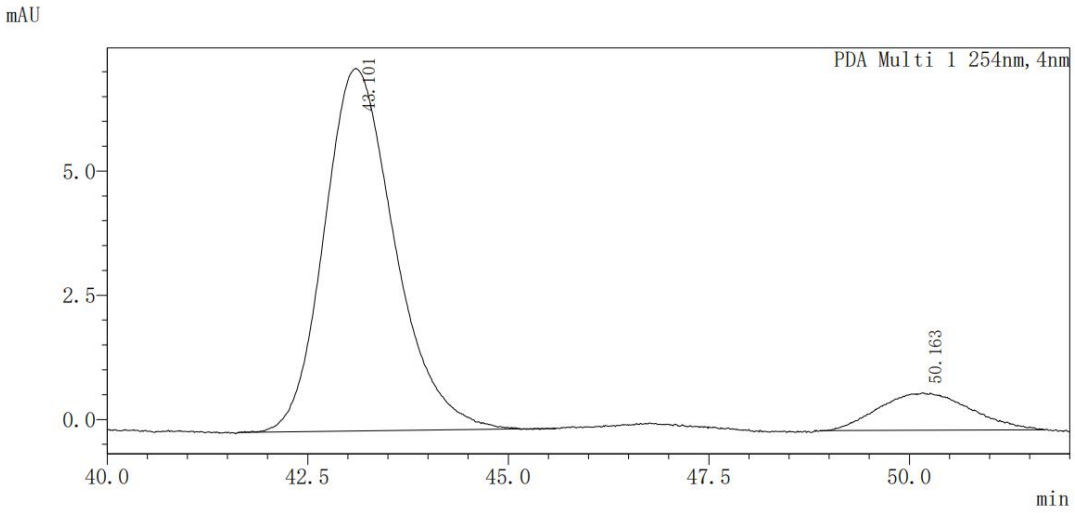
Compound **3ai** was prepared according to the general procedure. The crude product was purified by silica gel chromatography (petroleum ether:acetone = 8:1-4:1) to provide **3ai** (39.9 mg, 74%); Yellow solid; m.p.: 102-104 °C; IR: ν 2921, 1731, 1617, 1455, 1274, 1001, 819 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.47-7.40 (m, 2H), 7.39-7.24 (m, 6H), 7.22-7.15 (m, 2H), 5.35-5.24 (m, 3H), 5.13-5.05 (m, 1H), 5.04-4.97 (m, 1H), 4.57 (s, 1H), 4.31 (s, 1H), 4.23-4.19 (m, 1H), 4.11 (s, 5H), 2.84 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 168.0, 167.8, 135.4, 135.3, 128.7, 128.6, 128.5, 128.5, 128.1, 128.0, 82.2, 80.6, 70.8, 68.7, 68.0, 67.3, 67.1, 50.6, 39.0, 35.6;

HRMS (ESI): m/z calculated for $C_{30}H_{30}FeNO_5^+$ $[M+H]^+$: 540.1468, found: 540.1466; HPLC separation (DAICEL CHIRALPAK IA, hexane:2-propanol = 95:5, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 43.1 min, t_R(minor) = 50.2 min, 88:12 er.



PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	42.701	49.623
2	49.644	50.377

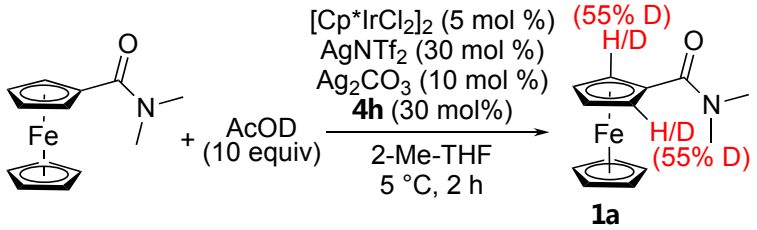


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	43.101	88.182
2	50.163	11.818

2.5 H/D Exchange Experiments

(a) Reaction without **2a**

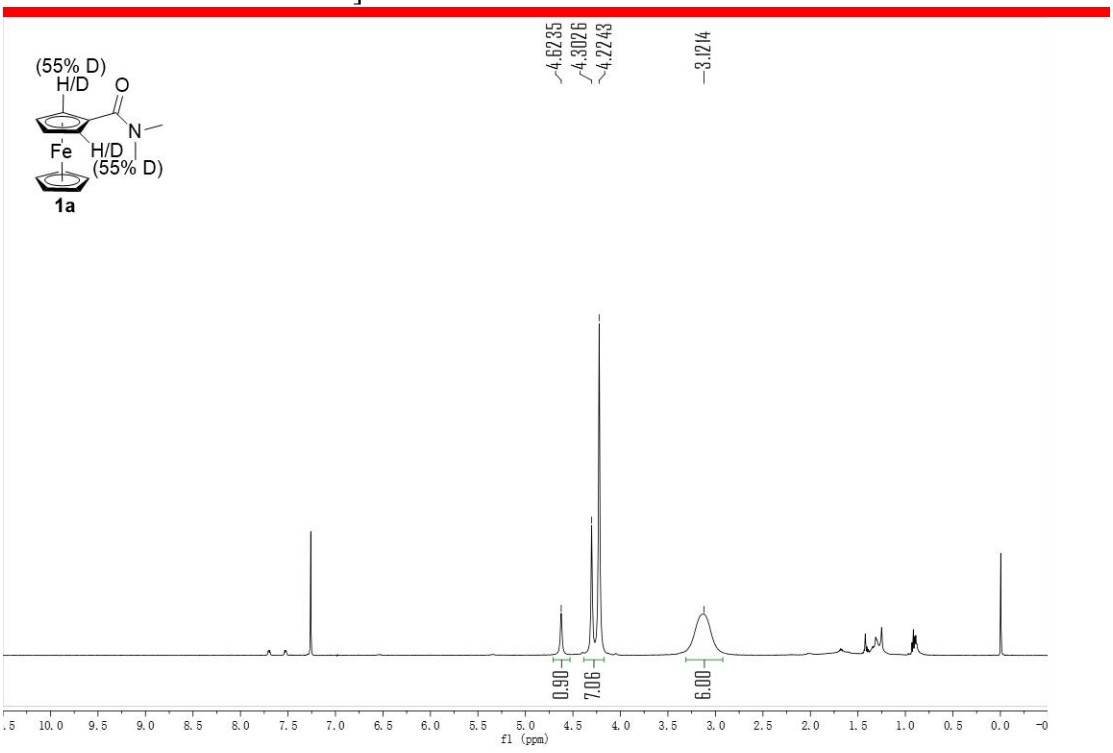


1a

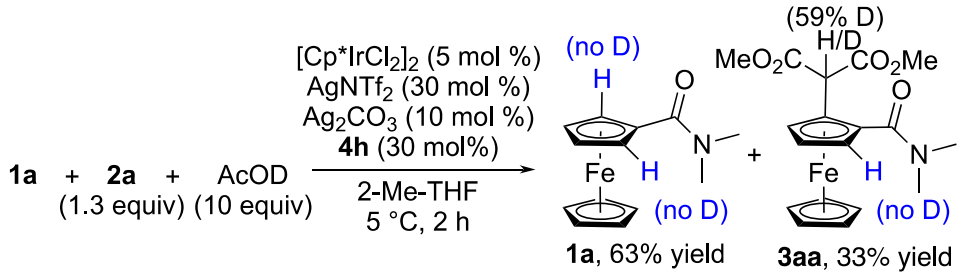
To a dried screw-capped vial were added ferrocene carboxamide **1** (0.10 mmol),

AcOD (57.2 μL, 10 equiv), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $AgNTf_2$ (11.7 mg, 0.03 mmol), Ag_2CO_3 (2.8 mg, 0.01 mmol), **4h** (13.1 mg, 0.03 mmol) and 2-Me-THF (0.5 mL) under nitrogen atmosphere. The vial was capped, and the mixture was cooled at 5 °C for 2 h with stirring. The resulting mixture was directly purified by silica gel column chromatography (petroleum ether:acetone = 4:1) to give **1a**.

[^{1}H NMR chart of recovered **1a**]:

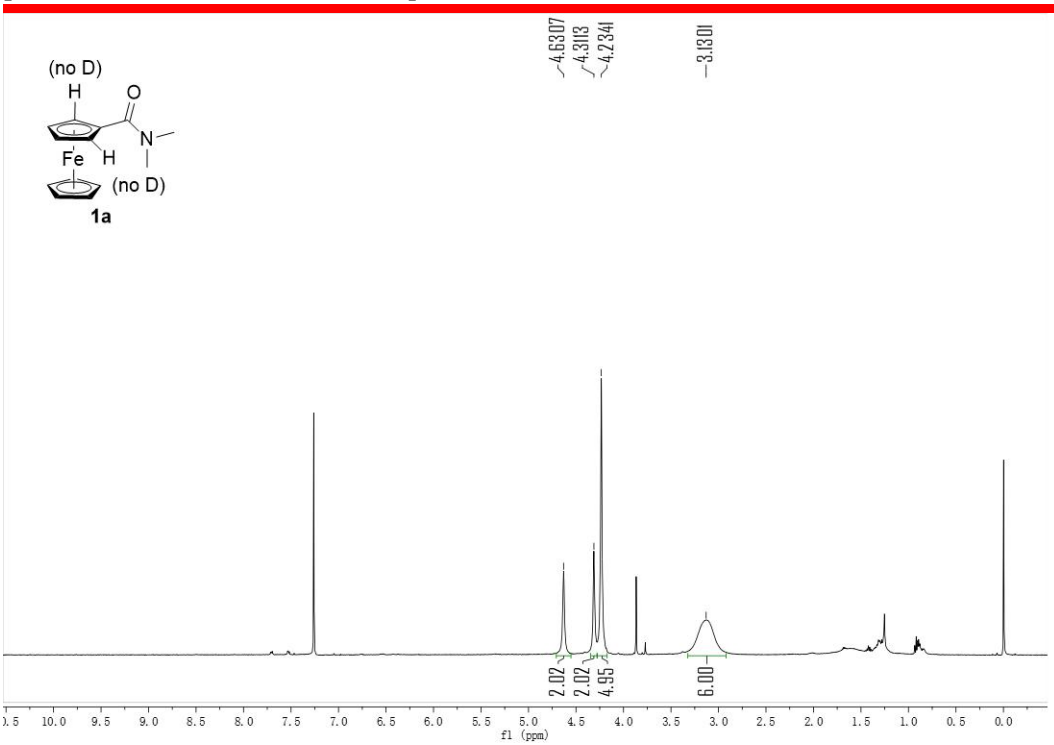


(b) Reaction with **2a**

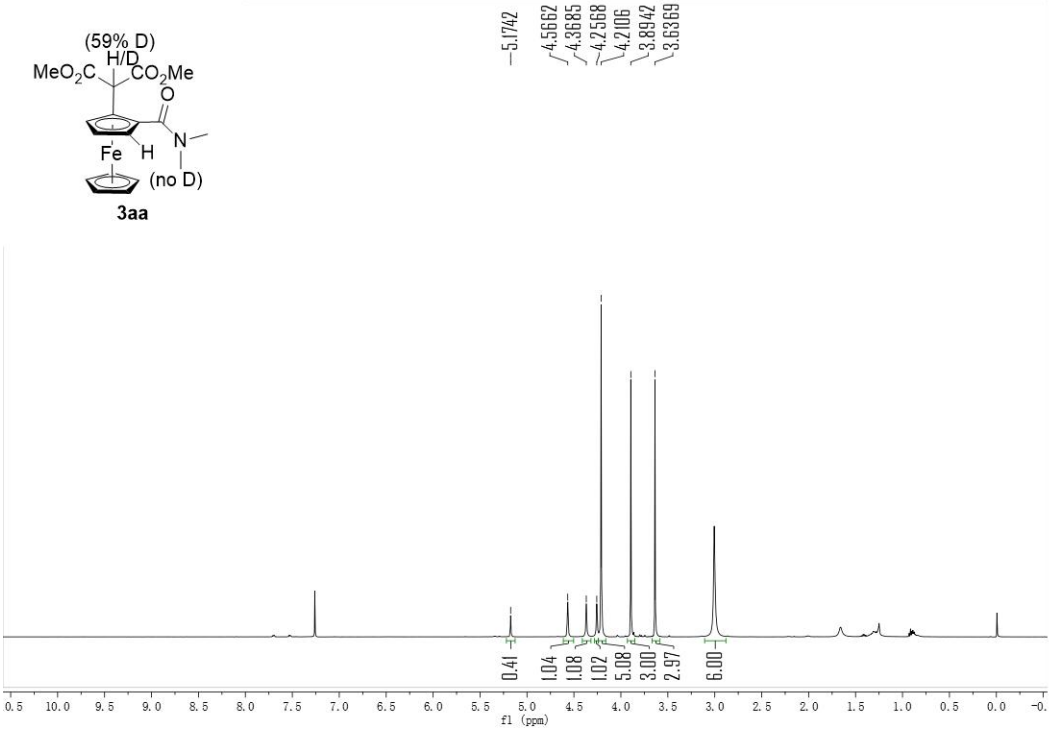


To a dried screw-capped vial were added ferrocene carboxamide **1a** (0.10 mmol), **2** (0.13 mmol, 1.3 equiv), AcOD (57.2 μL, 10 equiv), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $AgNTf_2$ (11.7 mg, 0.03 mmol), Ag_2CO_3 (2.8 mg, 0.01 mmol), **4h** (13.1 mg, 0.03 mmol) and 2-Me-THF (0.5 mL) under nitrogen atmosphere. The vial was capped, and the mixture was cooled at 5 °C for 2 h with stirring. The resulting mixture was directly purified by silica gel column chromatography (petroleum ether:acetone = 4:1) to give **1a** (63% yield) and **3aa** (33% yield).

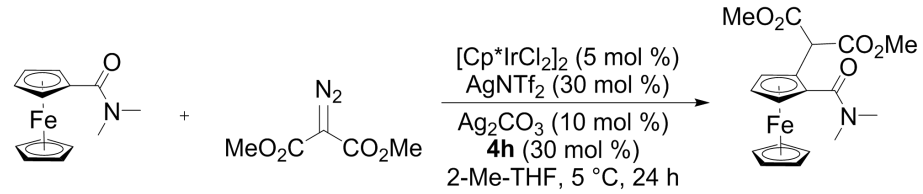
[^{1}H NMR chart of recovered **1a**]



[^{1}H NMR chart of **3aa**]



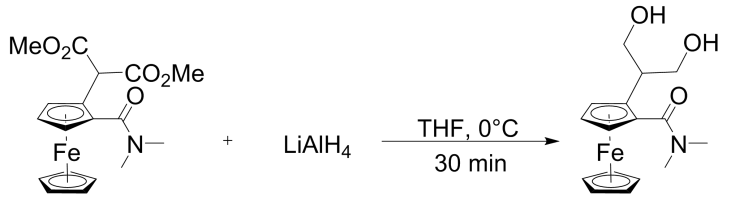
2.6 Preparative Scale Reaction



1a (1.0 mmol) **2a** (1.3 eq.) **3aa**, 82%, 92:8 er

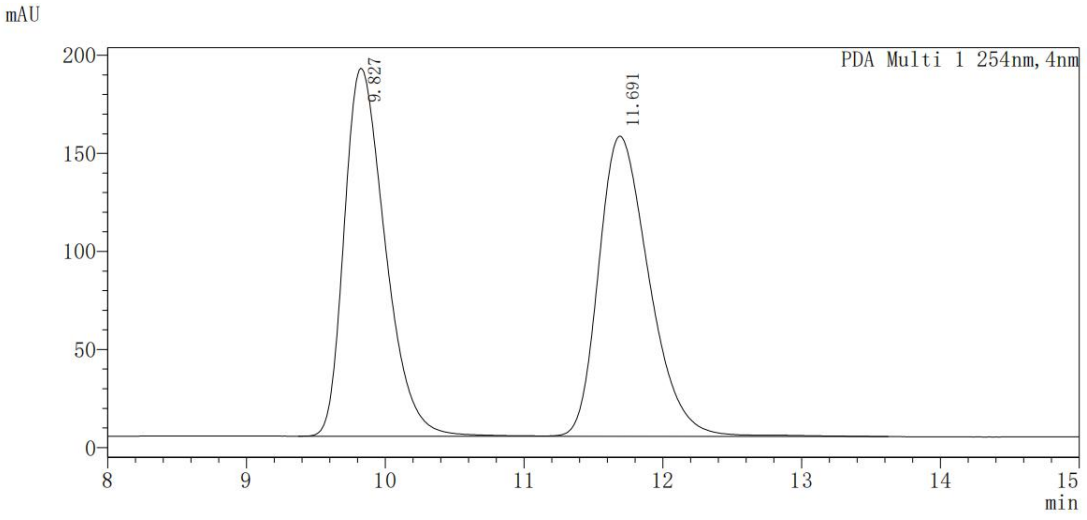
To a 50 mL Schlenk tube was added **1a** (257.1 mg, 1.0 mmol), **2a** (205.4 mg, 1.3 mmol), $[Cp^*IrCl_2]_2$ (40.1 mg, 0.05 mmol), $AgNTf_2$ (116.4 mg, 0.3 mmol), Ag_2CO_3 (27.6 mg, 0.1 mmol), **4h** (130.3 mg, 0.3 mmol), 2-Me-THF (5.0 mL). The mixture was evacuated and refilled with N_2 for three times. Then the reaction was kept stirring at 5 °C for 24 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether:acetone = 8:1-4:1) to afford amide **3aa** (317.4 mg, 82% yield, 92:8 er).

2.7 Derivations of 3aa



3aa, 92:8 er 4.5 eq. **5**, 76%, 92:8 er

3aa (193.5 mg, 0.5 mmol) in THF (2 mL), $LiAlH_4$ (85.4 mg, 2.25 mmol) was added in several times at 0 °C. Then the reaction was kept stirring at room temperature for 30 min. The mixture was quenched with water, extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (dichloromethane:methanol = 30:1) to give **5** as a red solid (125.8 mg, 76%); m.p.: 137-139 °C; IR: ν 3385, 2926, 1608, 1456, 1036, 820 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.31-4.27 (m, 1H), 4.26 (s, 5H), 4.24-4.21 (m, 1H), 4.21-4.15 (m, 2H), 4.02-3.82 (m, 1H), 3.80-3.68 (m, 3H), 3.68-3.57 (m, 1H), 3.25-3.14 (m, 1H), 3.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 90.7, 80.1, 70.6, 67.7, 67.4, 66.9, 66.7, 65.8, 41.3; HRMS (ESI): m/z calculated for $C_{16}H_{22}FeNO_3^+$ $[M+H]^+$: 332.0944, found: 332.0941; HPLC separation (DAICEL CHIRALPAK OD, hexane:2-propanol = 90:10, flow rate: 1.0 mL/min, detection at 254nm): t_R(major) = 9.8 min, t_R(minor) = 11.8 min, 92:8 er.



PDA Ch1 254nm

Peak No	Ret. time	Area/%
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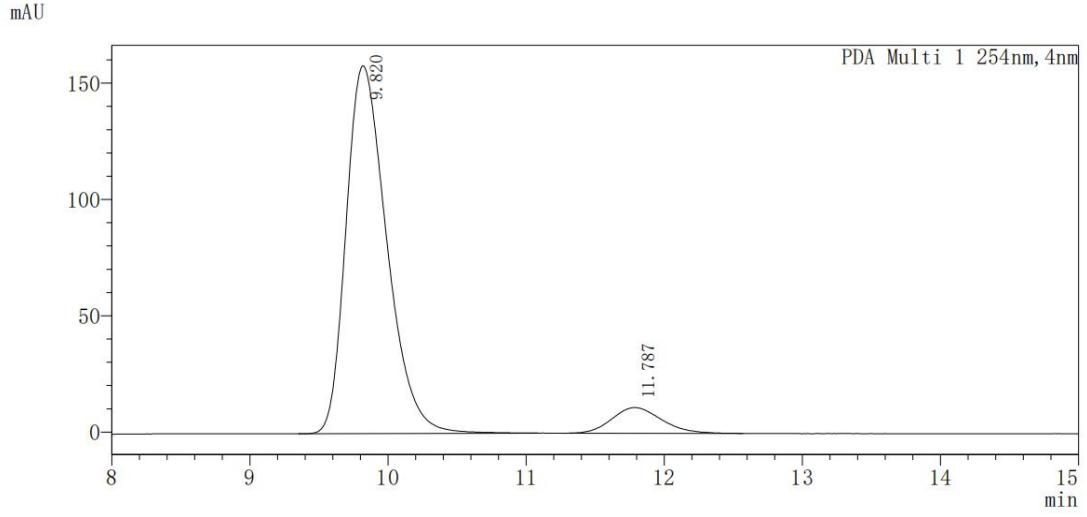
2	11.691	50.124

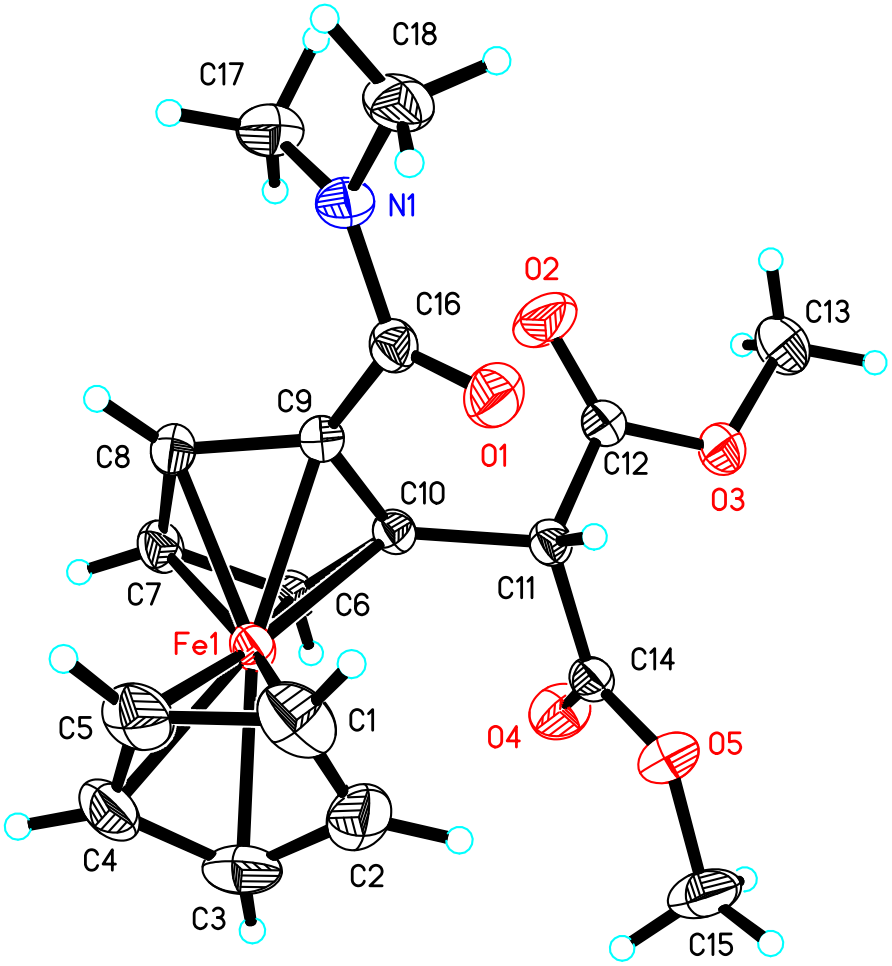


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	9.820	92.136
2	11.787	7.864

3. X-ray Crystallographic Analysis of 3aa

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC Number: 2094161. Copies of the data can be obtained, free of charge from https://www.ccdc.cam.ac.uk.



Bond precision: C-C = 0.0043 A Wavelength=0.71073

Cell: a=7.4884(2) b=14.7146(4) c=8.3630(2)

alpha=90 beta=108.511(1) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	873.83(4)	873.83(4)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C18 H21 Fe N O5	C18 H21 Fe N O5
Sum formula	C18 H21 Fe N O5	C18 H21 Fe N O5
Mr	387.21	387.21
Dx,g cm-3	1.472	1.472
Z	2	2
Mu (mm-1)	0.891	0.891
F000	404.0	404.0
F000'	404.87	
h,k,lmax	9,18,10	9,18,10
Nref	3431[1787]	3382
Tmin,Tmax	0.852,0.899	0.628,0.746
Tmin'	0.837	

Correction method= # Reported T Limits: Tmin=0.628 Tmax=0.746

AbsCorr = MULTI-SCAN

Data completeness= 1.89/0.99 Theta(max)= 25.992

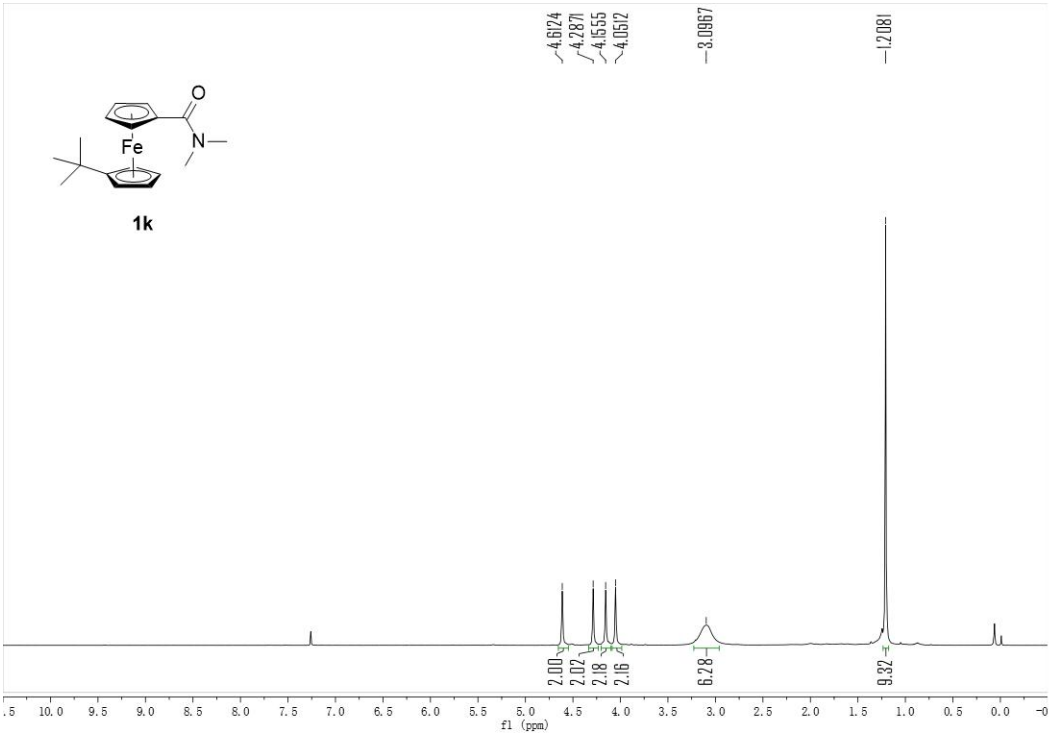
R(reflections)= 0.0211(3305) wR2(reflections)= 0.0556(3382)

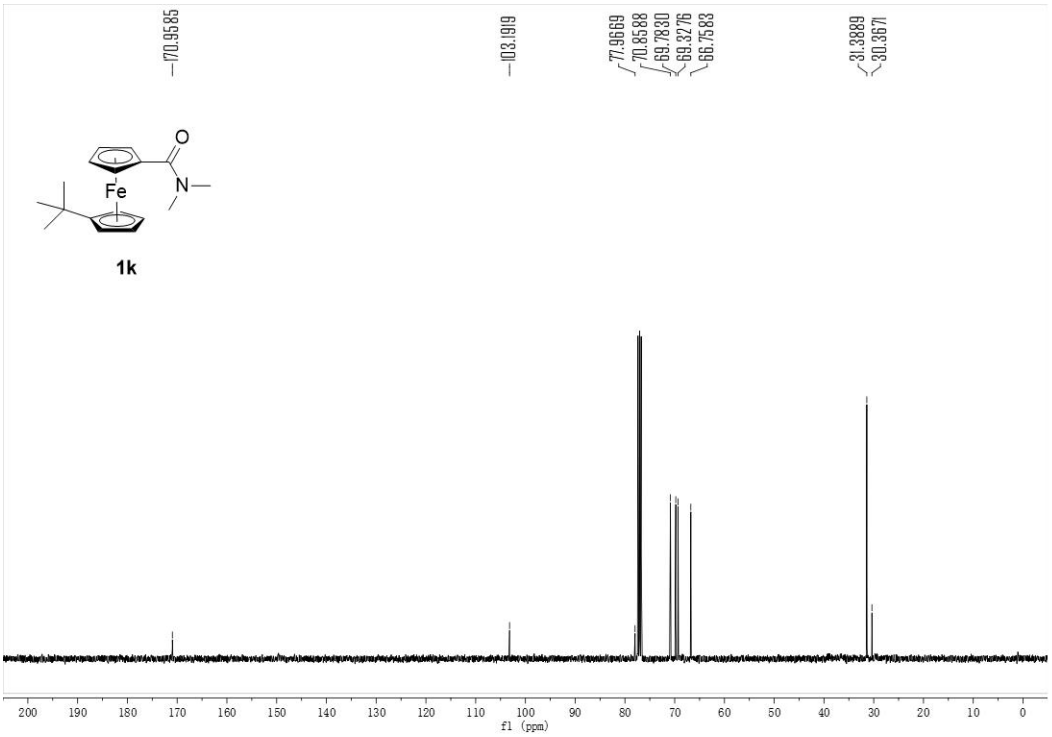
S = 1.055 Npar= 231

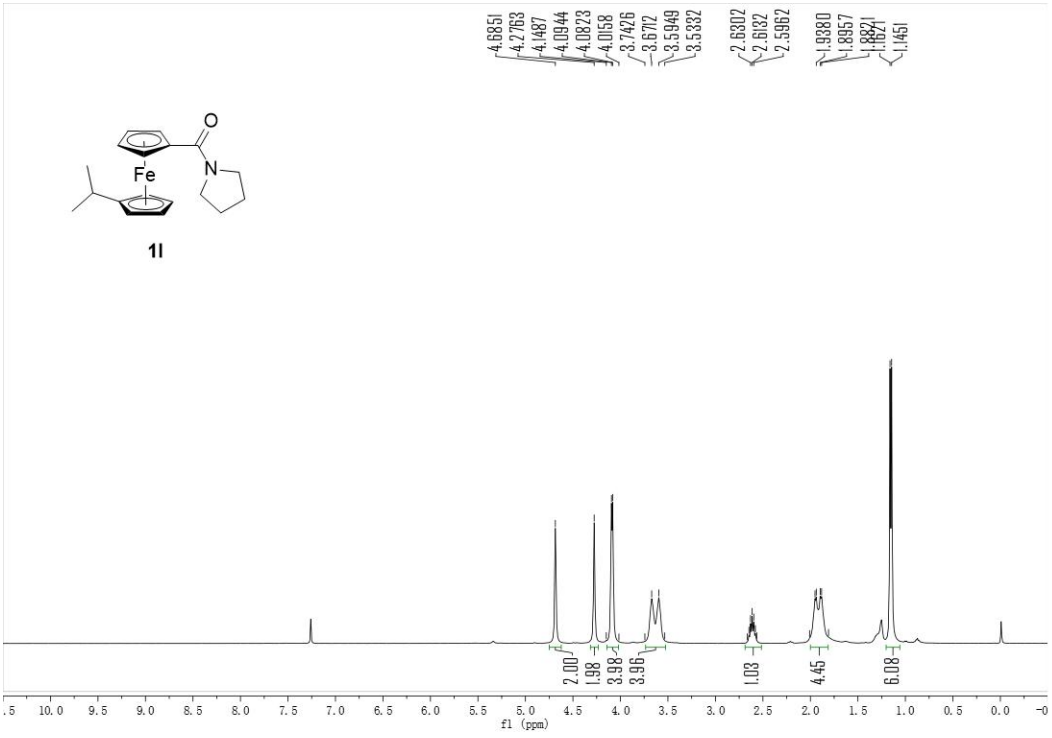
4. References

[S1] M. Tazi, W. Erb, Y. S. Halauko, O. A. Ivashkevich, V. E. Matulis, T. Roisnel, V. Dorcet, F. Mongin, *Organometallics*, 2017, **36**, 4770.
[S2] L. Liu, H. Song, Y.-H. Liu, L.-S. Wu, B.-F. Shi, *ACS Catal*., 2020, **10**, 7117.
[S3] Y. Wu, P. Sun, K. Zhang, T. Yang, H. Yao, A. Lin, *J. Org. Chem.*, 2016, 81, 2166.
[S4] Hoshino, Y. Yamamoto, H. *J. Am. Chem. Soc.*, 2000, **122**, 10452.
[S5] S. Fukagawa, M. Kojima, T. Yoshino, S. Matsunaga, *Angew. Chem., Int. Ed.*, 2019, **58**, 18154.
[S6] X. Ma, Z. Gu, *RSC Adv.*, 2014, **4**, 36241.

5. NMR Spectra



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4.1487
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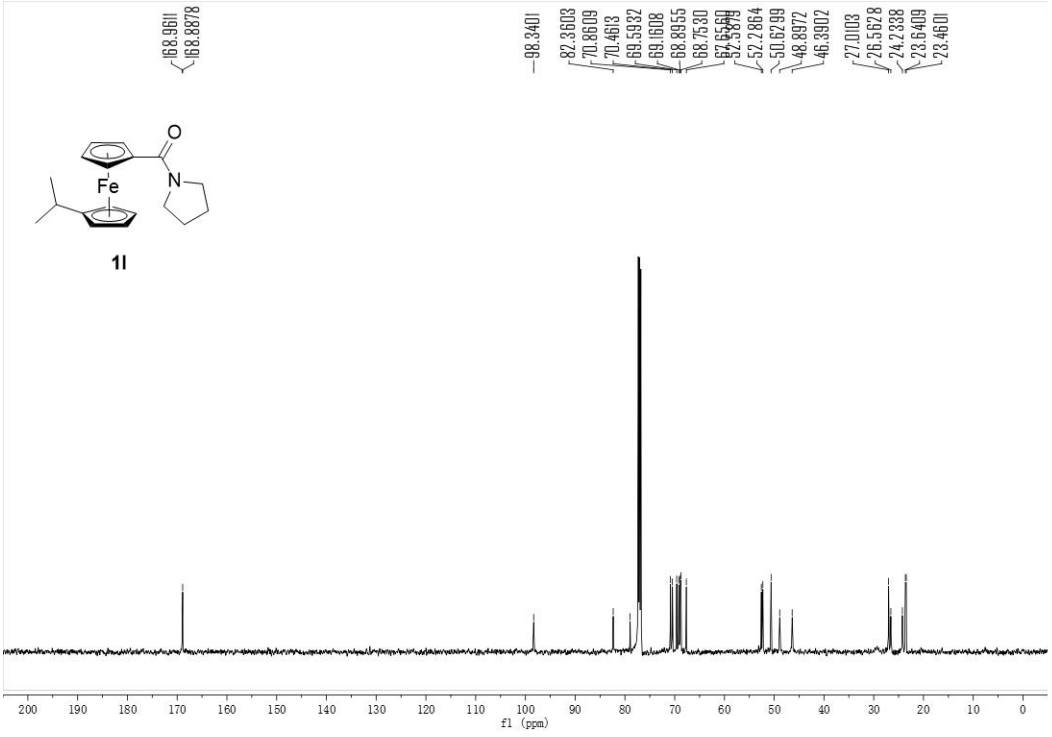
4.0823
4.0158
3.7426
3.6712
3.5949
3.5332
2.6302
2.6132
2.5962
1.9380
1.8957
1.8821
1.1451
O
N
Fe
1l
2.00
1.98
3.98
3.96
1.03
4.45
6.08
f1 (ppm)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168.8878
98.3401
82.3603
70.8809
70.4613
69.5932
69.1608
68.8955
68.7530
52.2864
50.6799
48.8972
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27.0103
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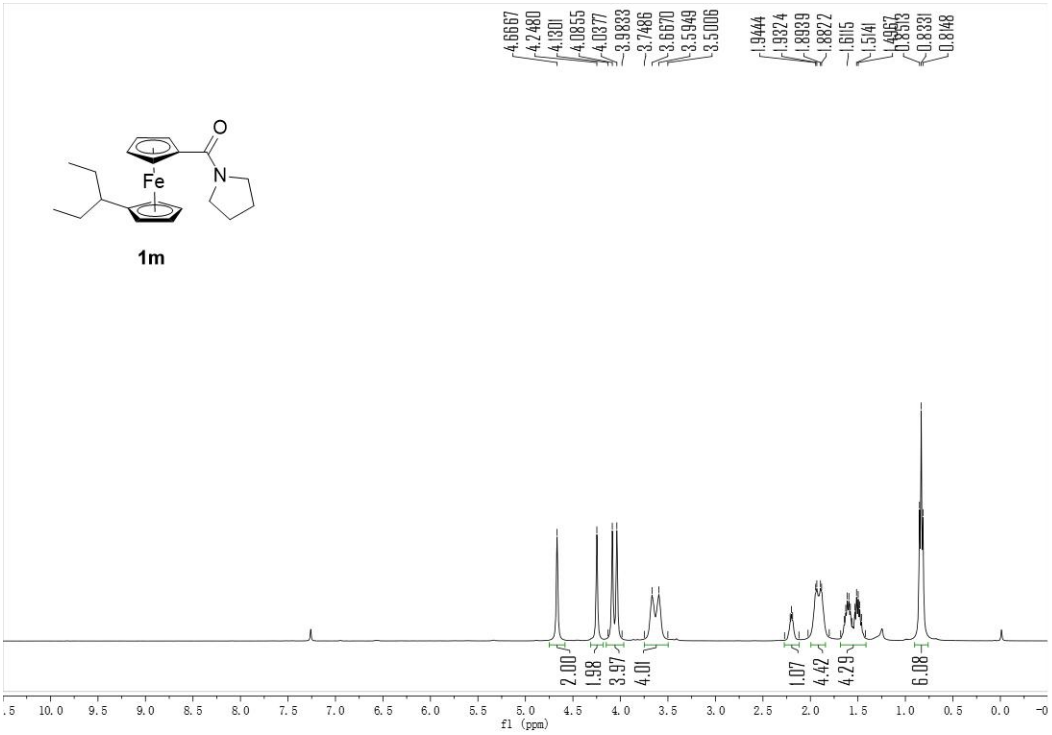
23.6409
23.4601
O
N
Fe
1l
f1 (ppm)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4.0855
4.0377
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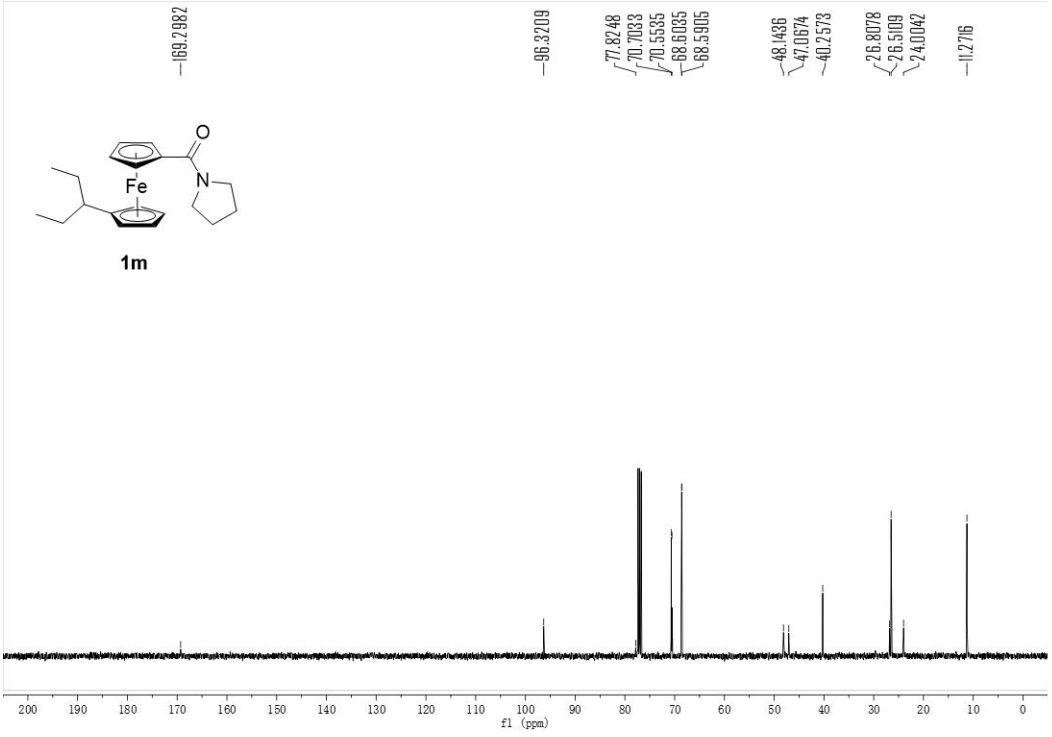
3.7486
3.6670
3.5949
3.5006
1.9444
1.9324
1.8939
1.8822
1.6115
1.5141
1.4967
0.8513
0.8331
0.8148
O
Fe
N
1m
2.00
1.98
3.97
4.01
1.07
4.42
4.29
6.08
f1 (ppm)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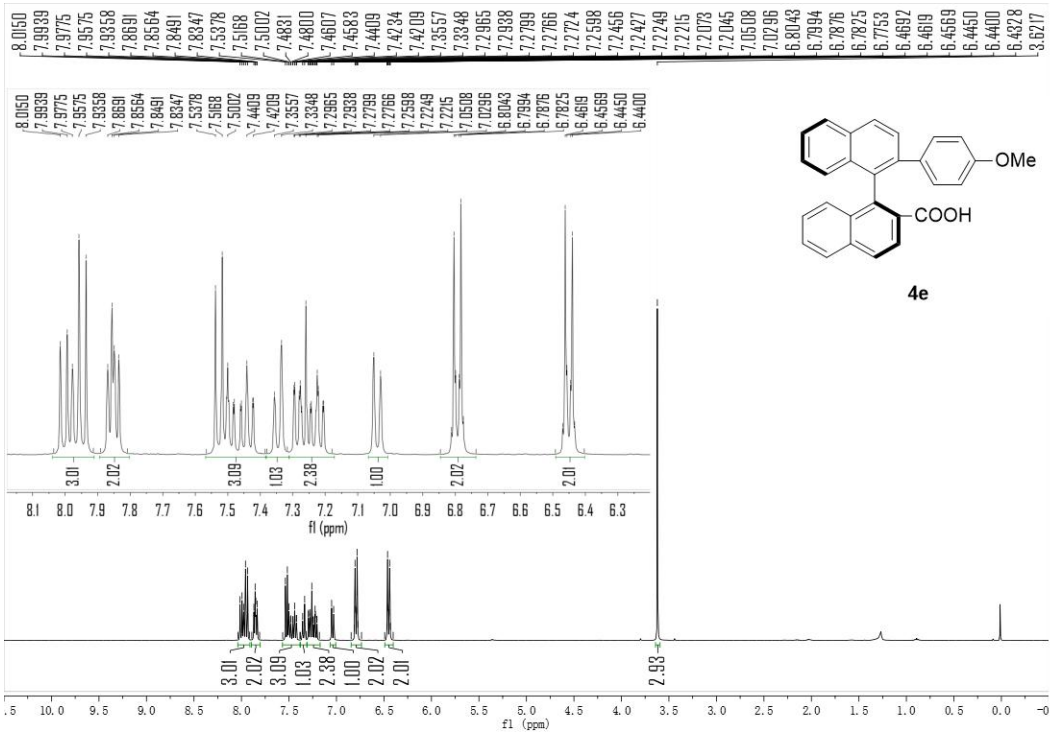
O
Fe
N
1m
f1 (ppm)


OMe
COOH
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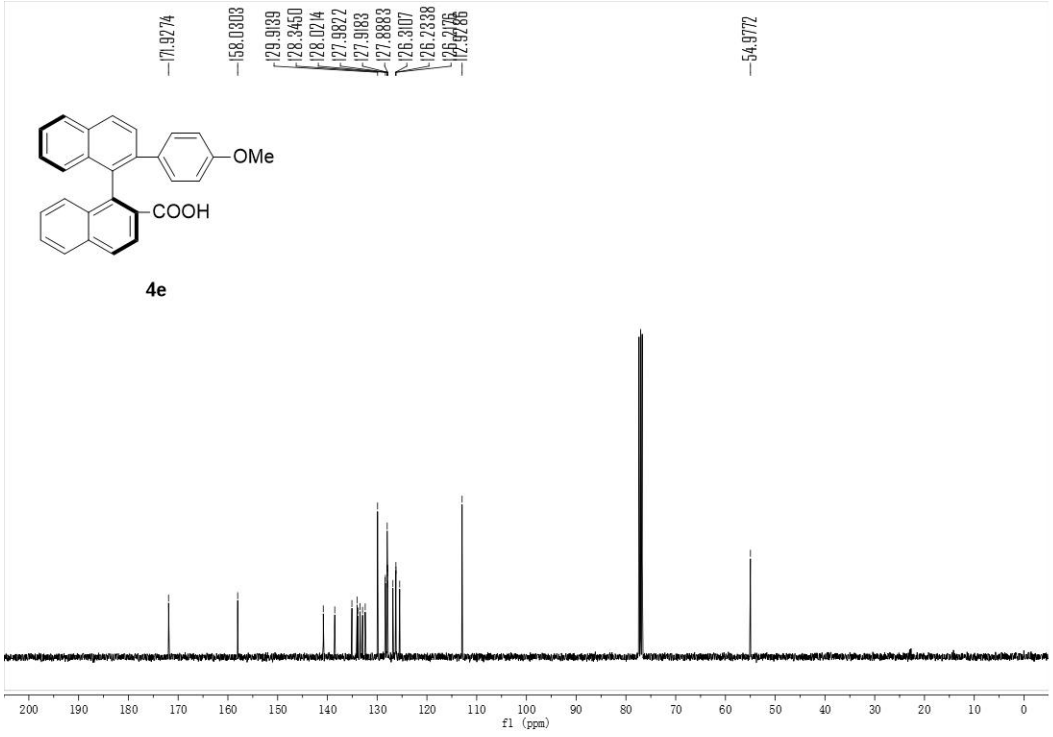
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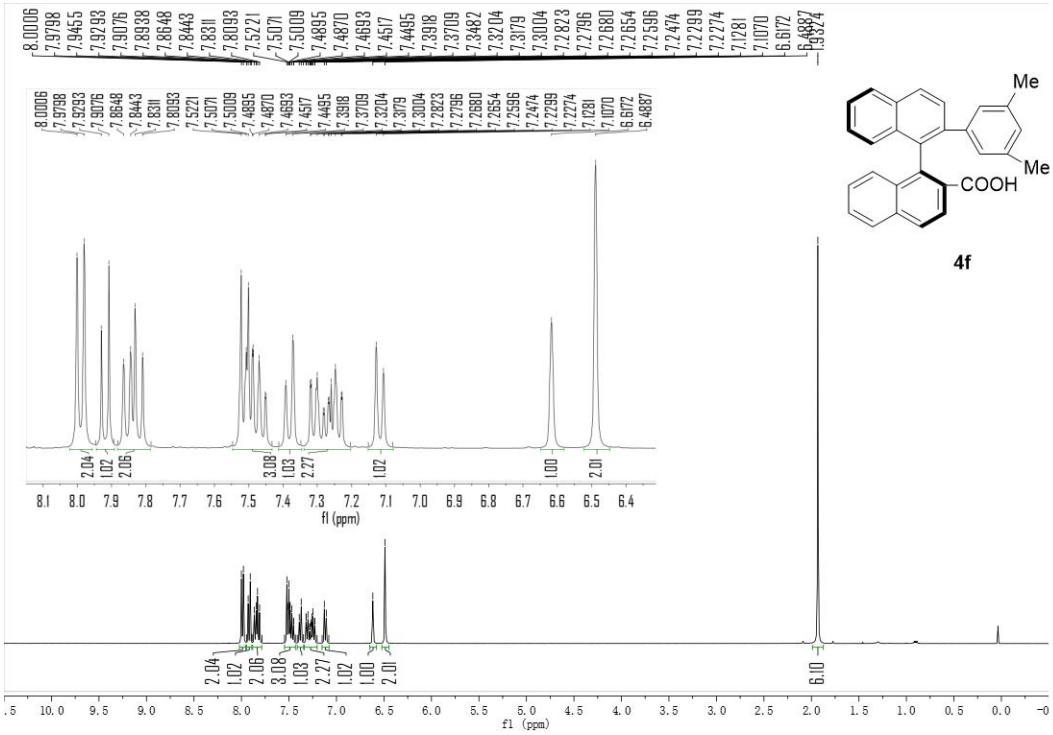
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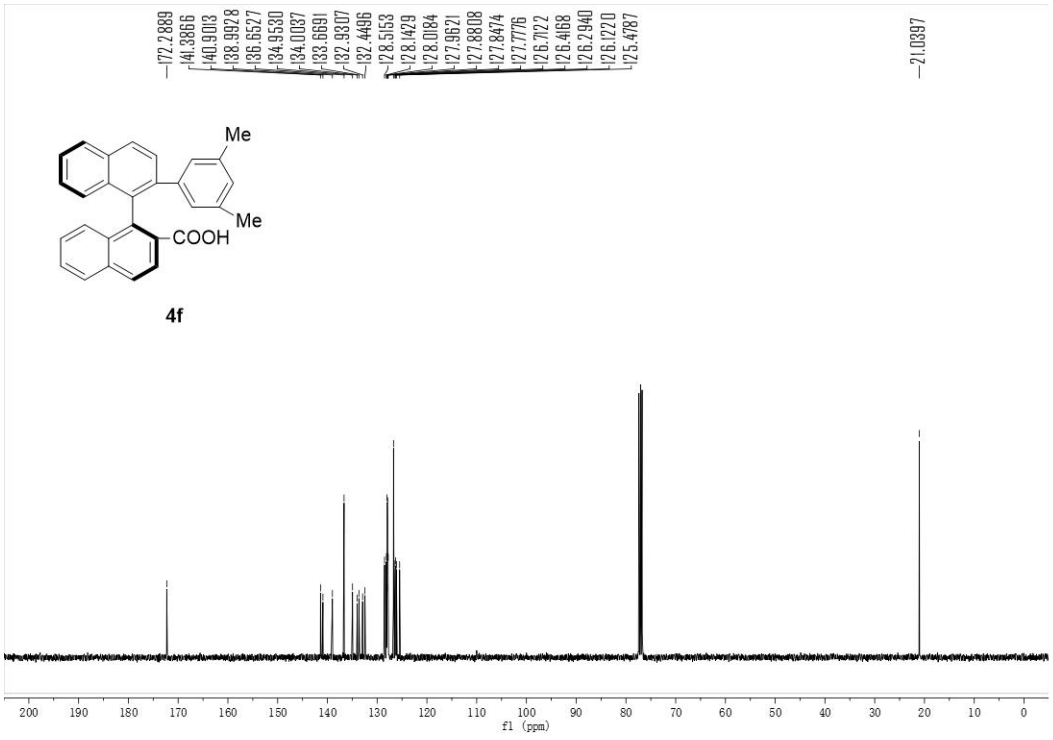
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Me
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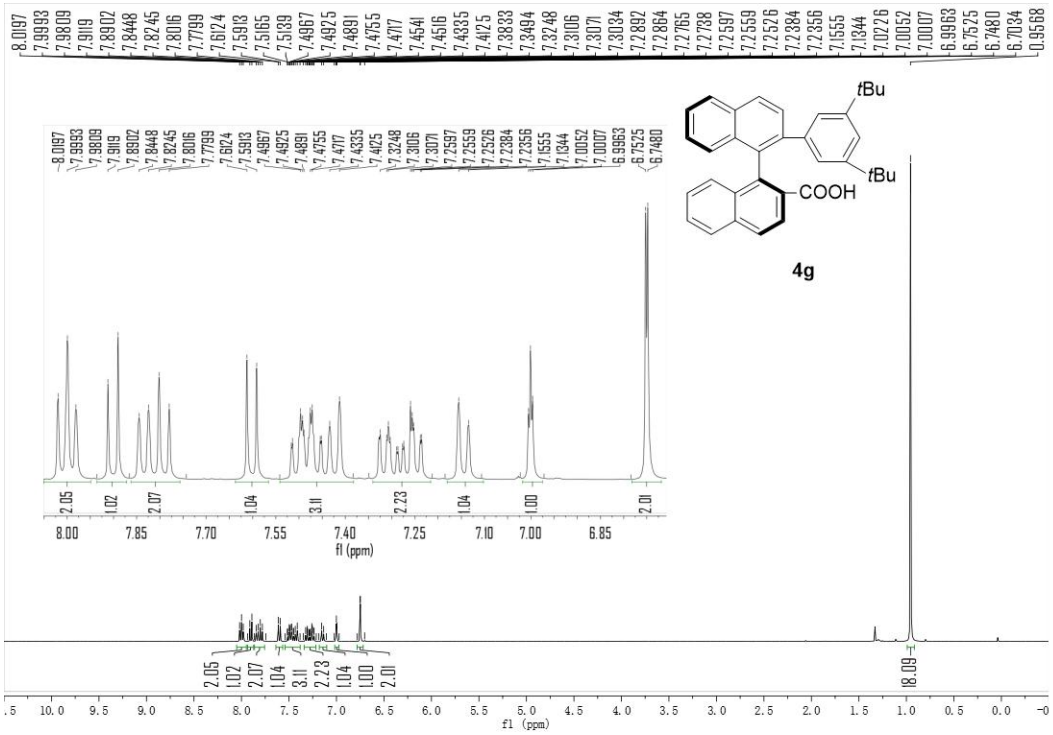
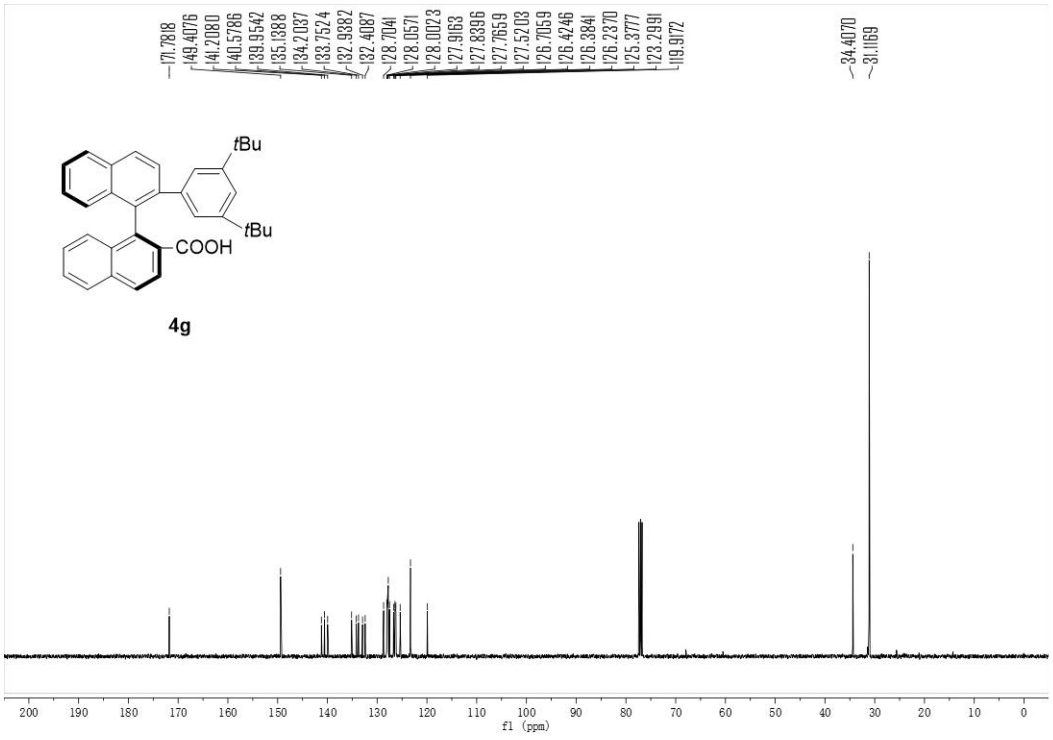
4f
f1 (ppm)


tBu
tBu
COOH
4g
f1 (ppm)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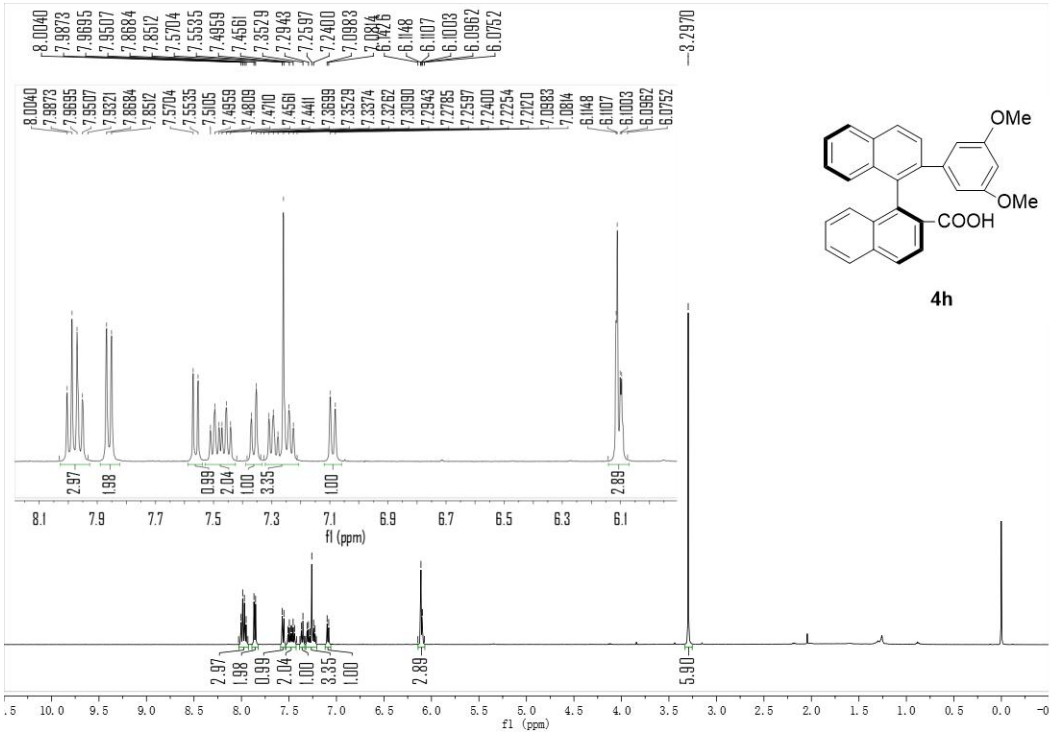
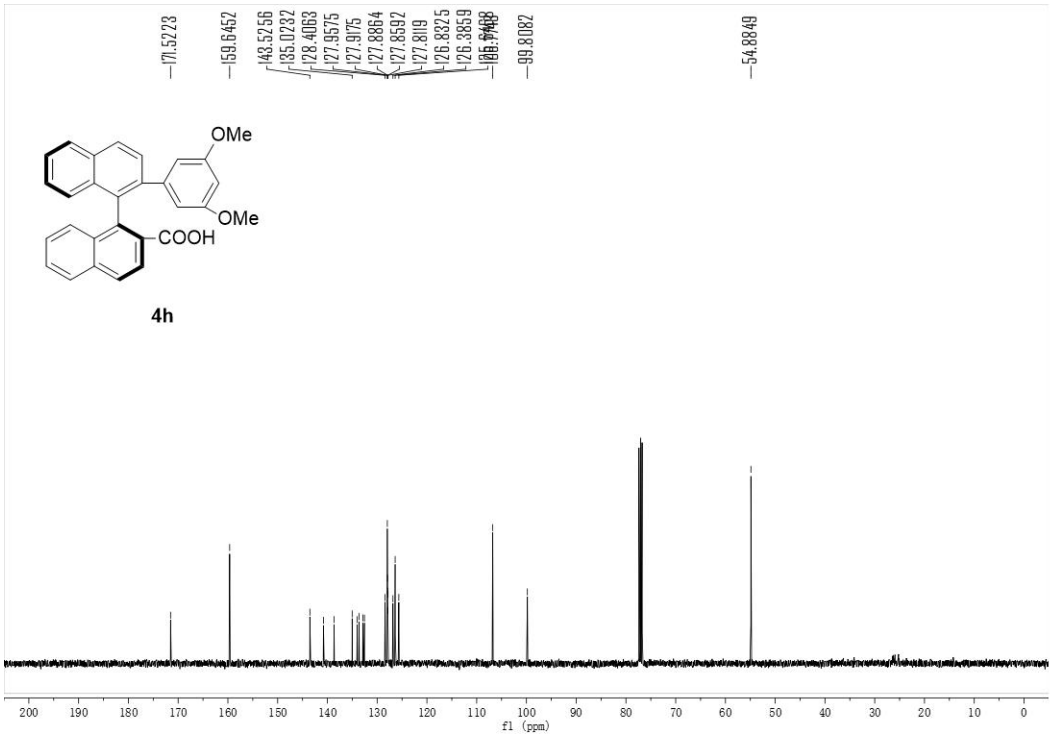
tBu
COOH
4g
f1 (ppm)


OMe
OMe
COOH
4h
f1 (ppm)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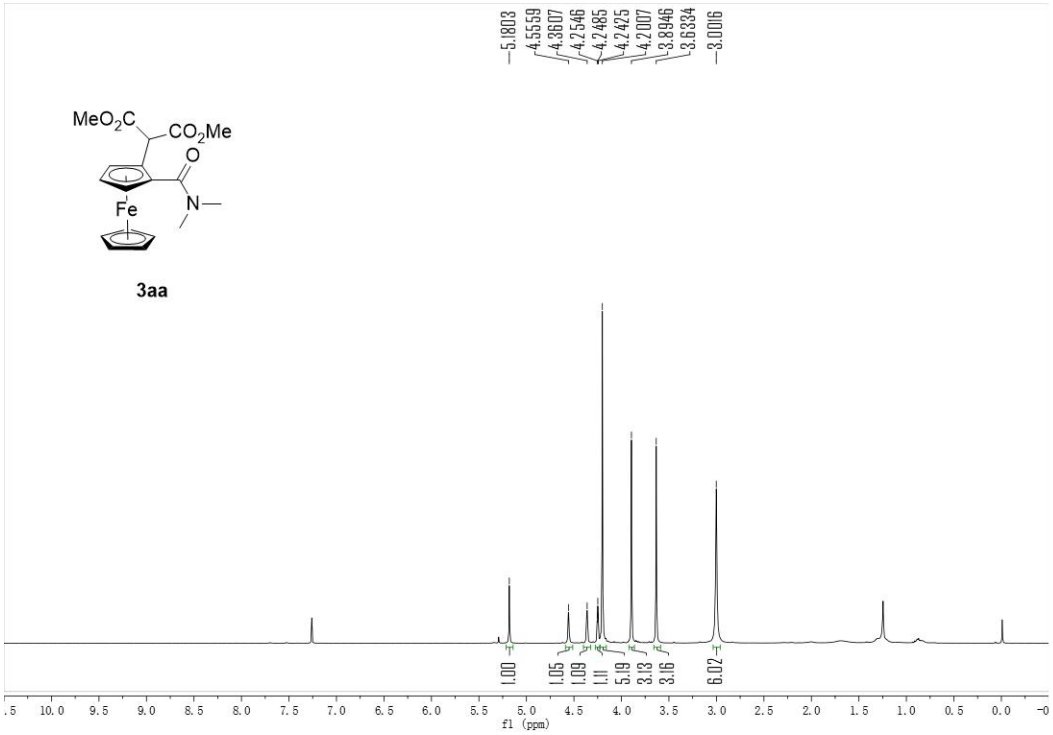
OMe
COOH
4h
f1 (ppm)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3.8334
3.0016
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CO2Me
O
Fe
N
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1.09
1.11
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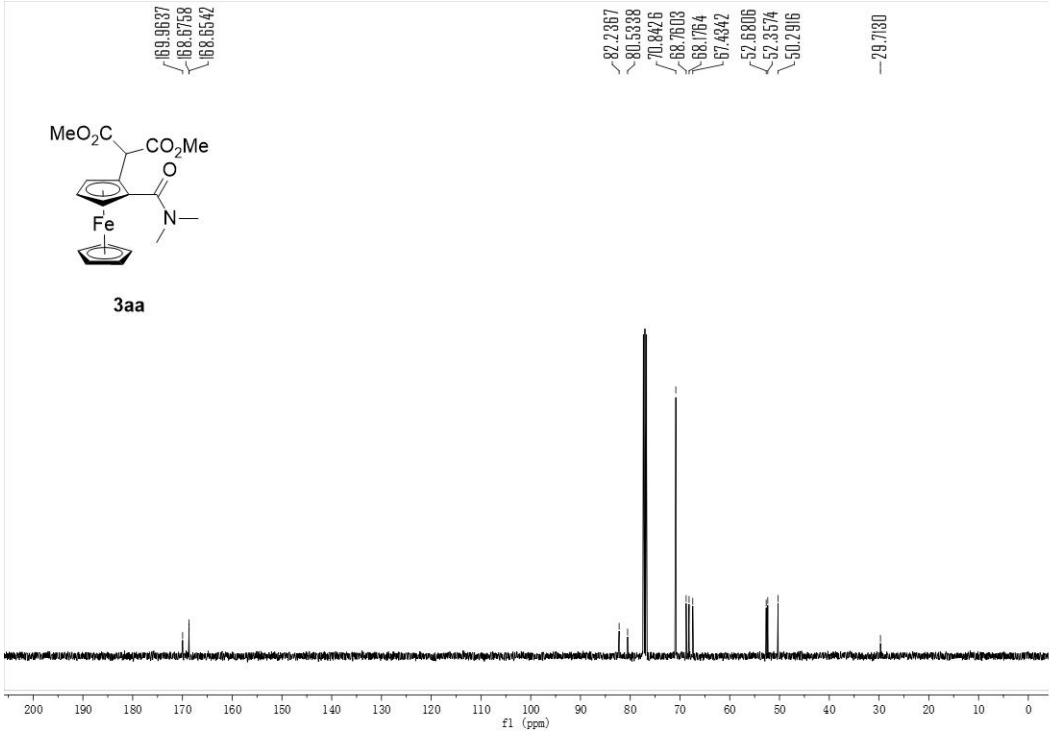
3.13
3.16
6.02
f1 (ppm)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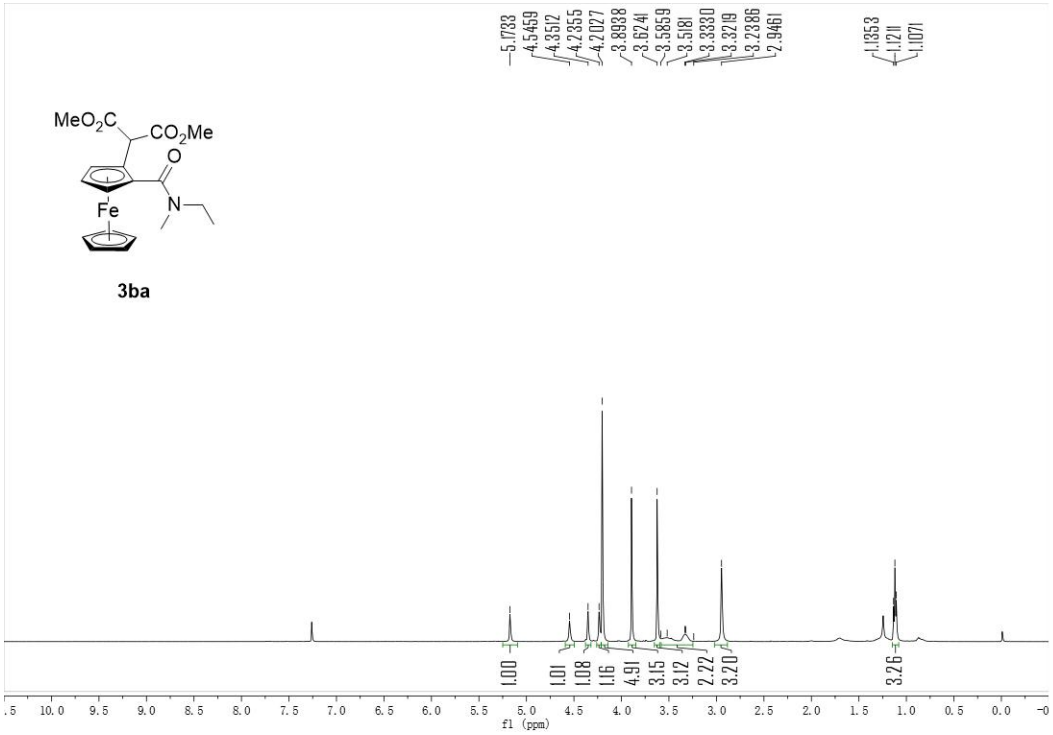
MeO2C
CO2Me
O
Fe
N
3aa
f1 (ppm)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3.3219
3.2386
2.9461
1.1953
1.1211
1.1071
MeO2C
CO2Me
O
Fe
N
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1.08
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4.91
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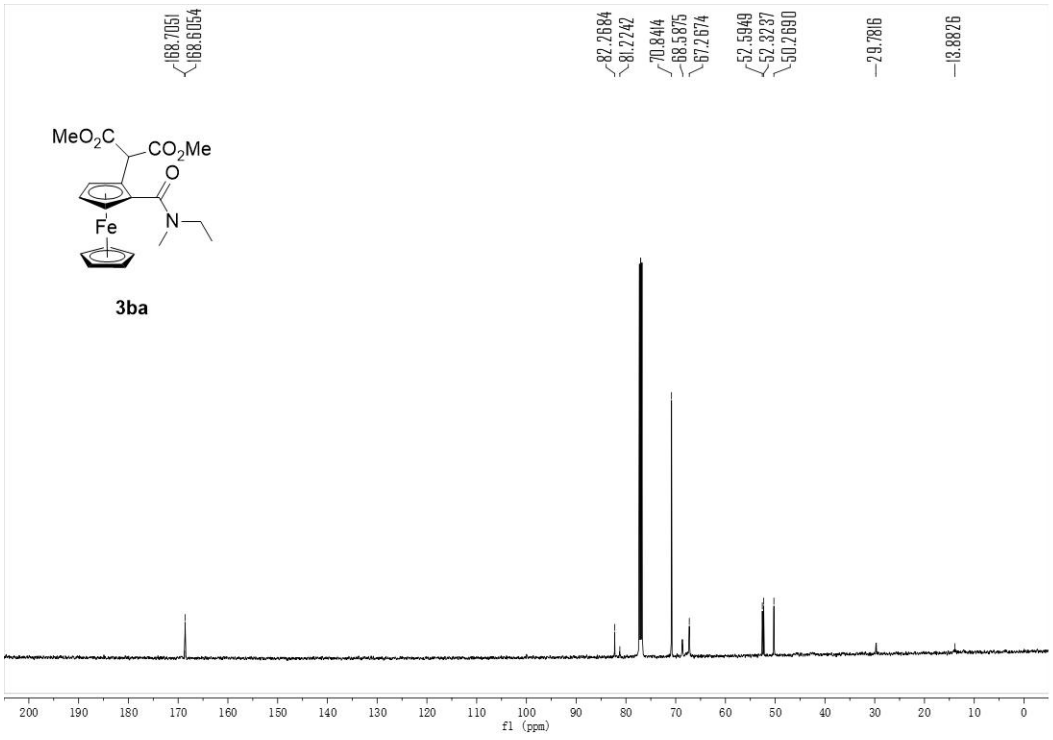
3.26
f1 (ppm)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CO2Me
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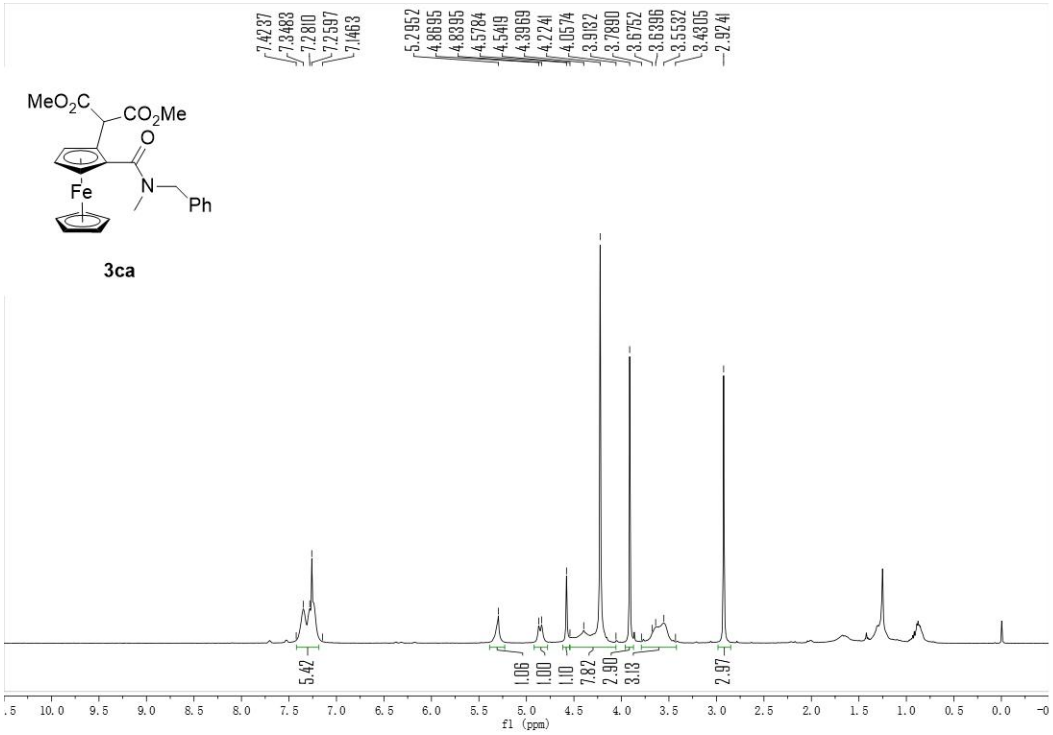
Fe
N
3ba
f1 (ppm)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3.9182
3.7890
3.6752
3.6396
3.5532
3.4305
2.9741
MeO2C
CO2Me
O
N
Ph
Fe
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1.00
1.10
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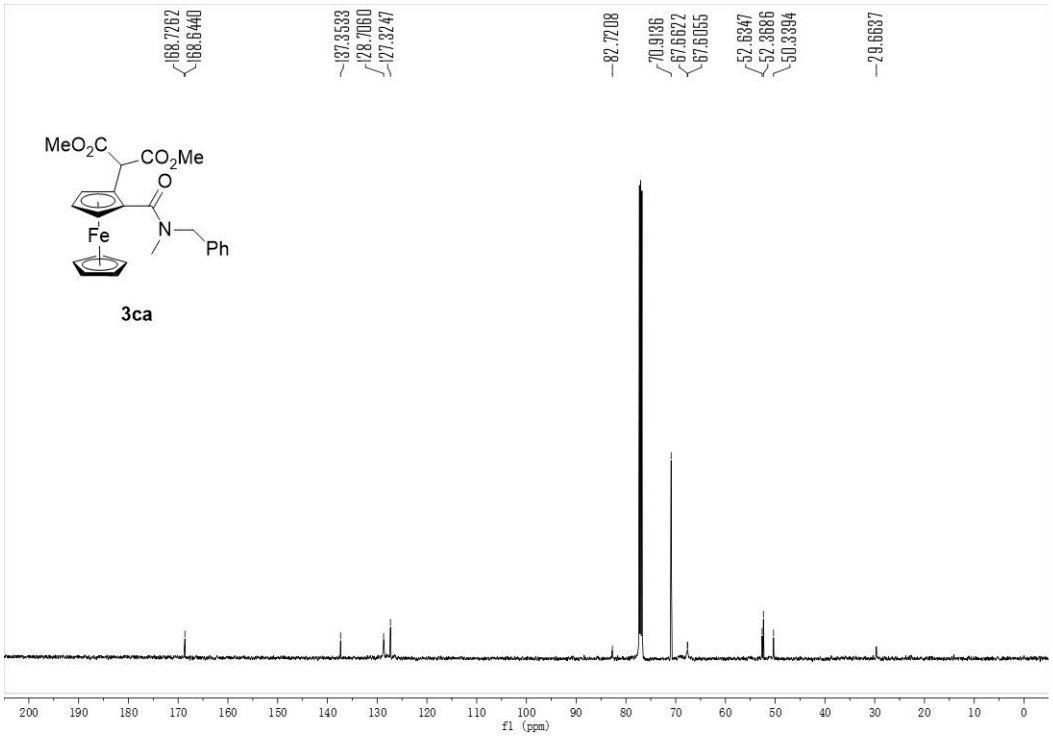
3.13
2.97
f1 (ppm)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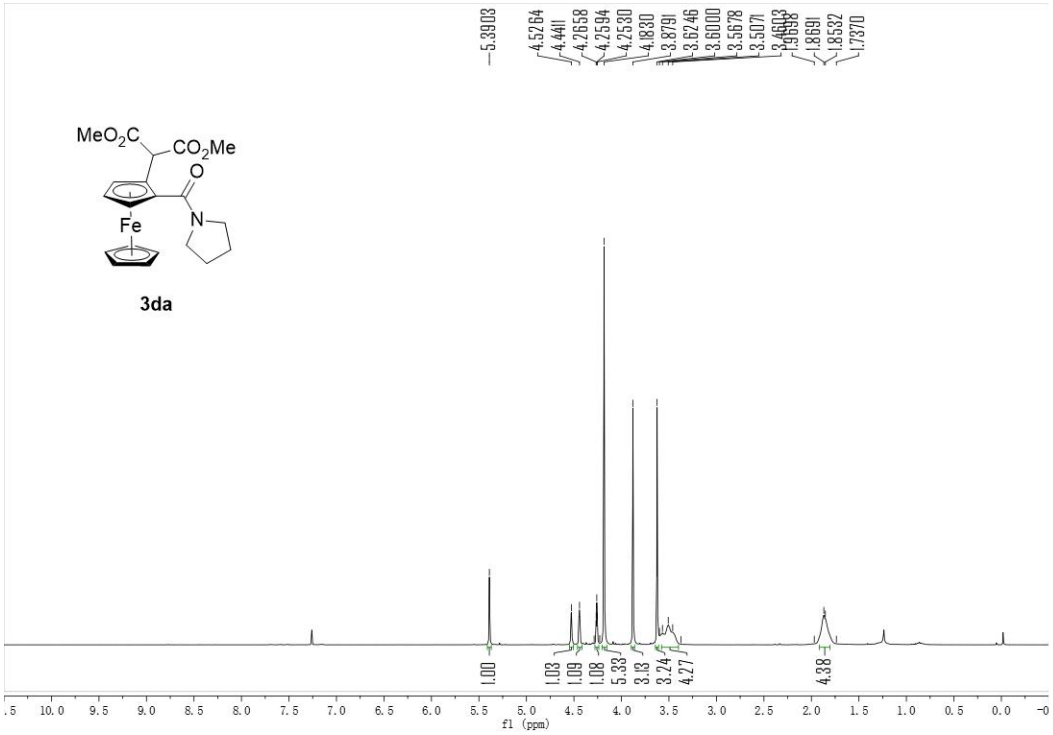
CO2Me
O
N
Ph
Fe
3ca
f1 (ppm)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3.5678
3.5071
1.8691
1.8532
1.7370
MeO2C
CO2Me
O
N
Fe
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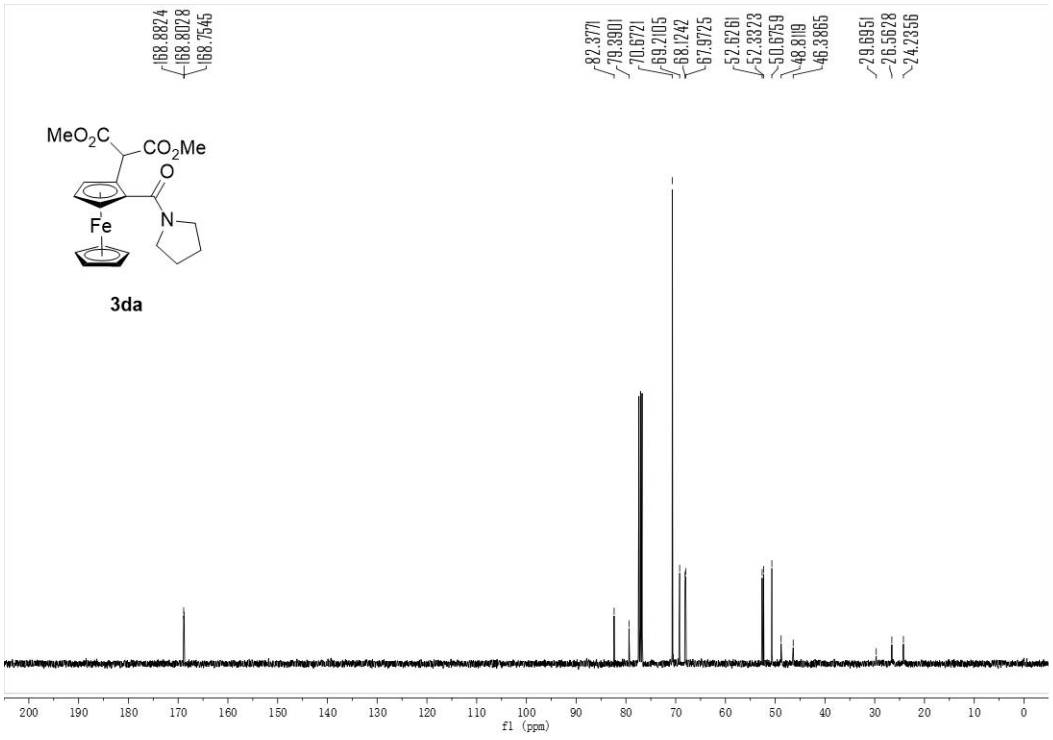
1.09
1.08
5.33
3.13
3.24
4.27
4.38
f1 (ppm)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69.2105
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67.9725
52.6261
52.3323
50.6759
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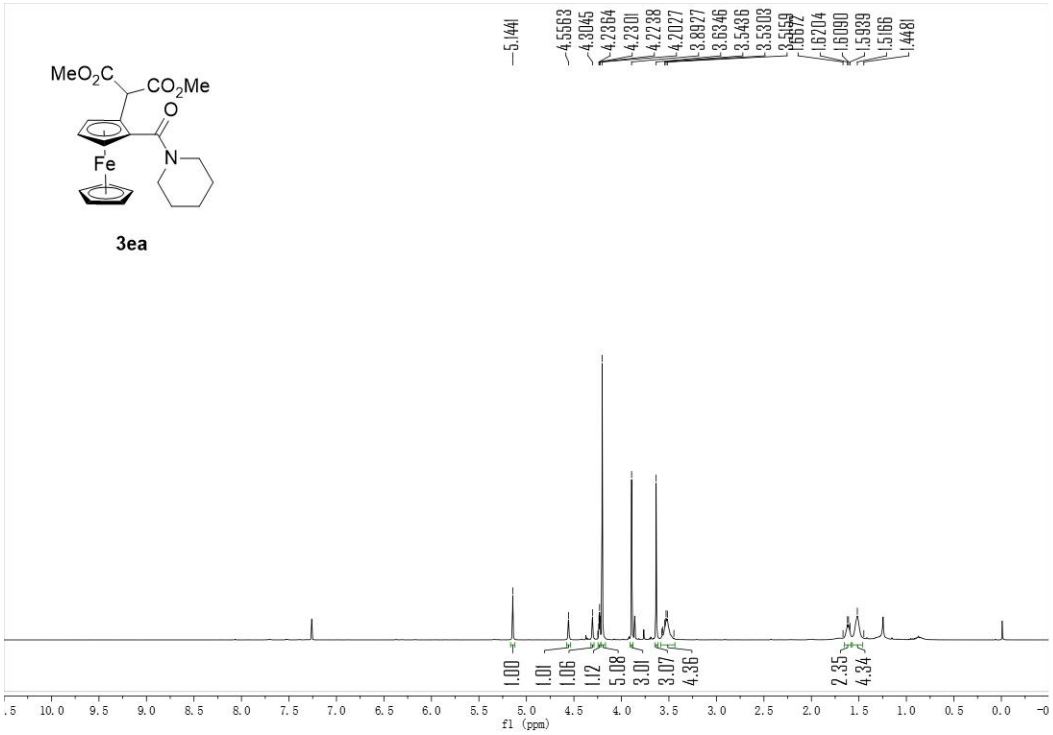
29.6951
26.5628
24.2356
MeO2C
CO2Me
O
N
Fe
3da
f1 (ppm)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4.2027
3.8927
3.6346
3.5436
3.5303
3.5159
1.6204
1.6090
1.5939
1.5166
1.4481
1.00
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1.06
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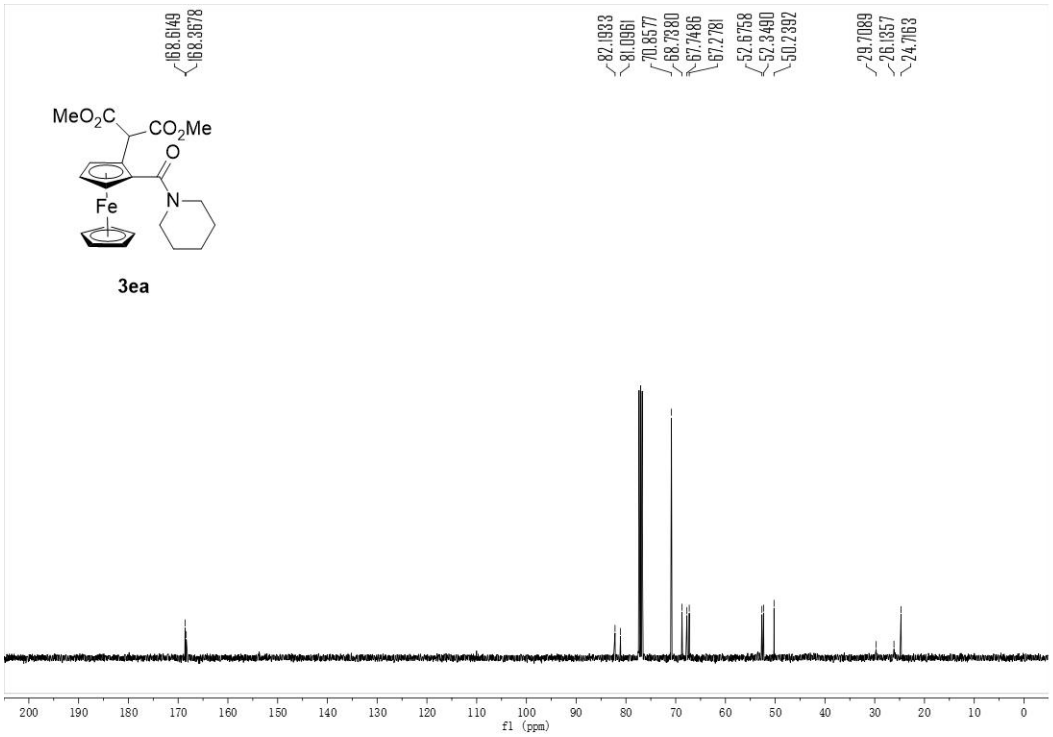
5.08
3.01
3.07
4.36
2.35
4.34
f1 (ppm)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29.7089
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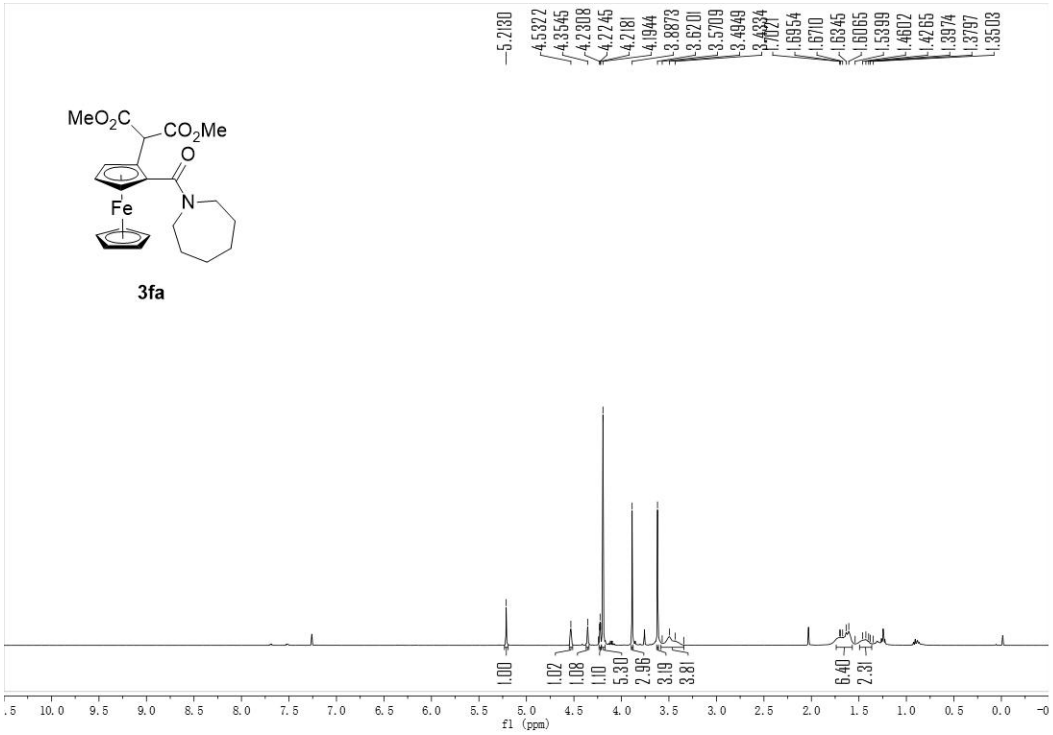
f1 (ppm)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3.4234
1.7021
1.6954
1.6710
1.6345
1.6065
1.5399
1.4602
1.4265
1.3974
1.3797
1.3503
MeO2C
CO2Me
O
Fe
N
1.00
1.02
1.08
1.10
5.30
2.96
3.19
3.81
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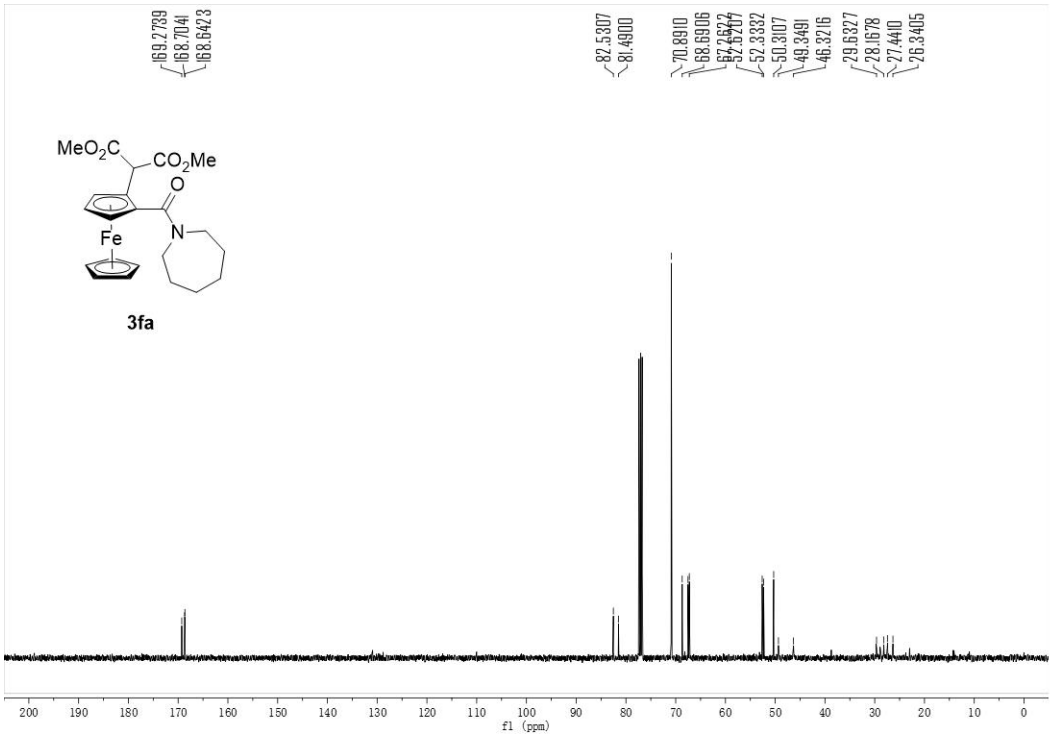
2.31
f1 (ppm)

3fa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50.3107
49.3491
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27.4410
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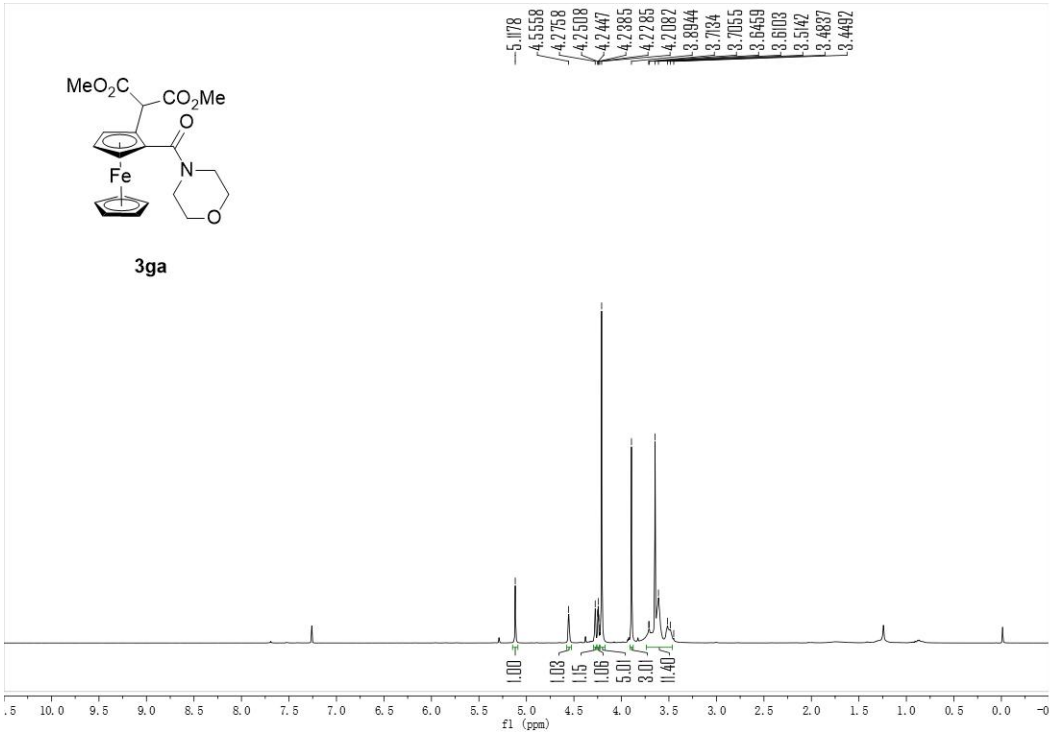
CO2Me
O
Fe
N
f1 (ppm)

3fa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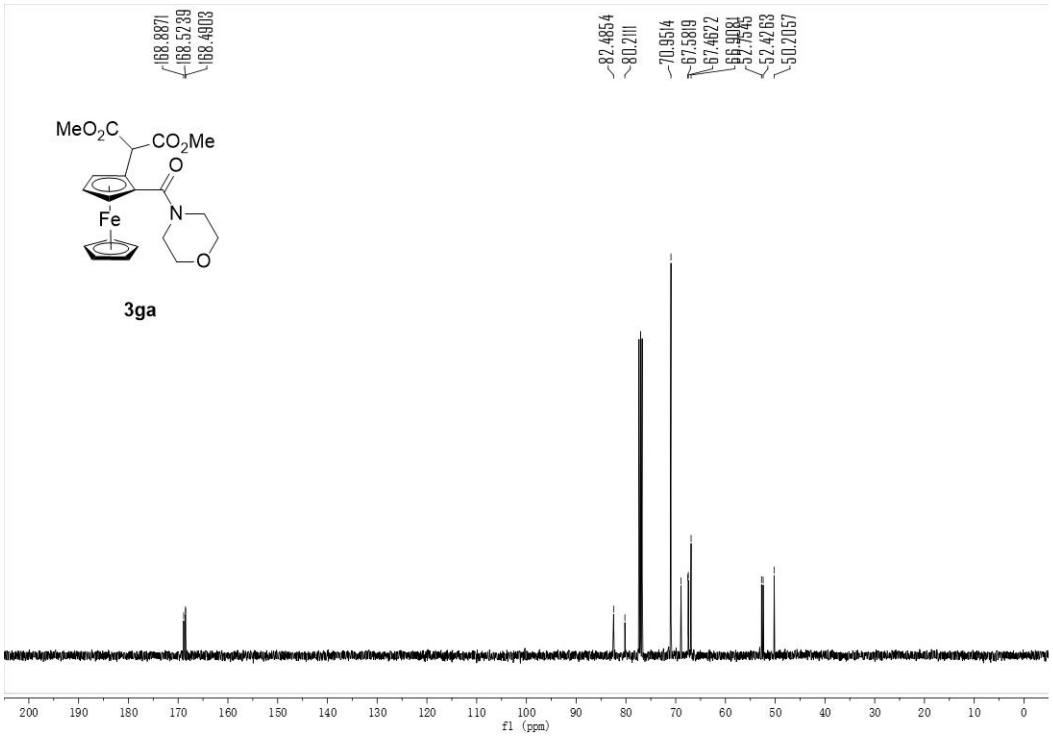
4.2447
4.2385
4.2285
4.2082
3.8944
3.7334
3.7055
3.6459
3.6103
3.5142
3.4837
3.4492
MeO2C
CO2Me
O
Fe
N
O
3ga
1.00
1.03
1.15
1.06
5.01
3.01
11.40
f1 (ppm)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82.4854
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70.9514
67.5819
67.4622
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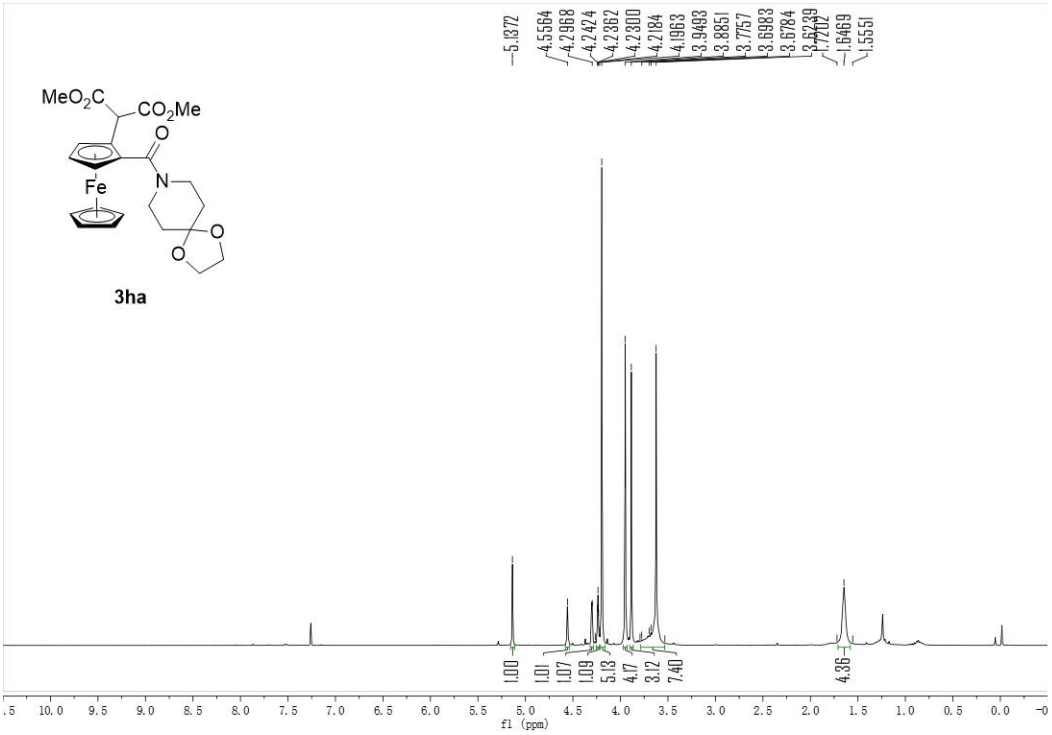
CO2Me
O
Fe
N
O
3ga
f1 (ppm)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4.2362
4.2300
4.2184
4.1963
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3.7757
3.6983
3.6784
3.6239
1.7207
1.6469
1.5551
MeO2C
CO2Me
O
Fe
N
O
O
3ha
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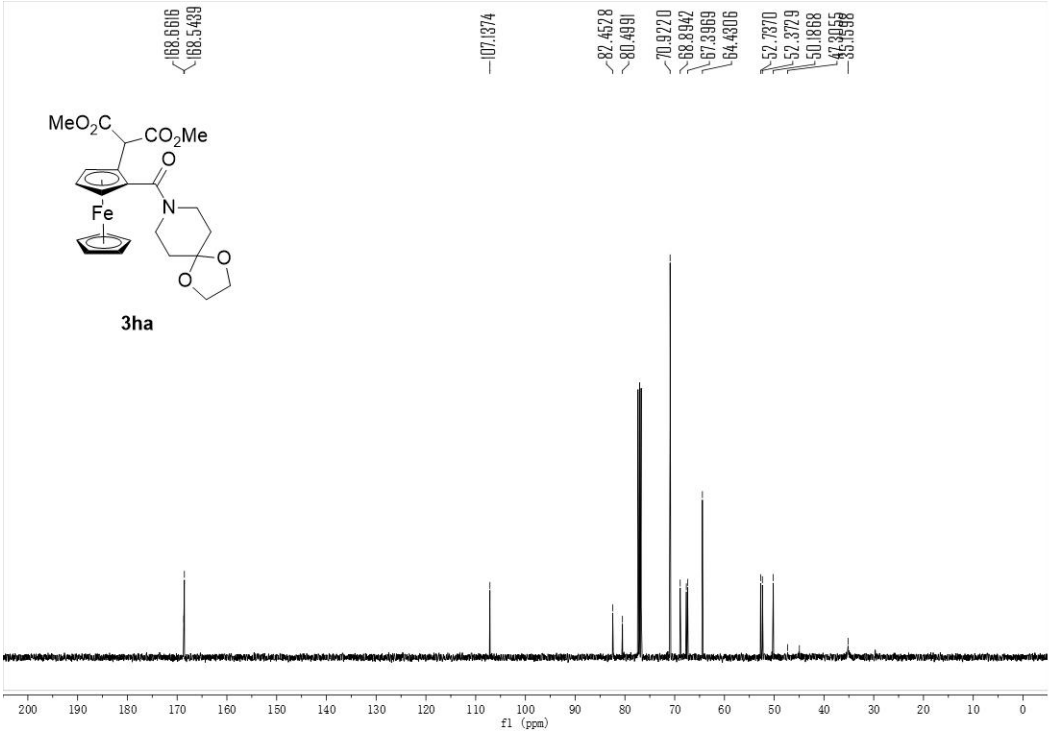
1.01
1.07
1.09
5.13
4.17
8.12
7.40
4.36
f1 (ppm)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68.8942
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64.4306
52.7870
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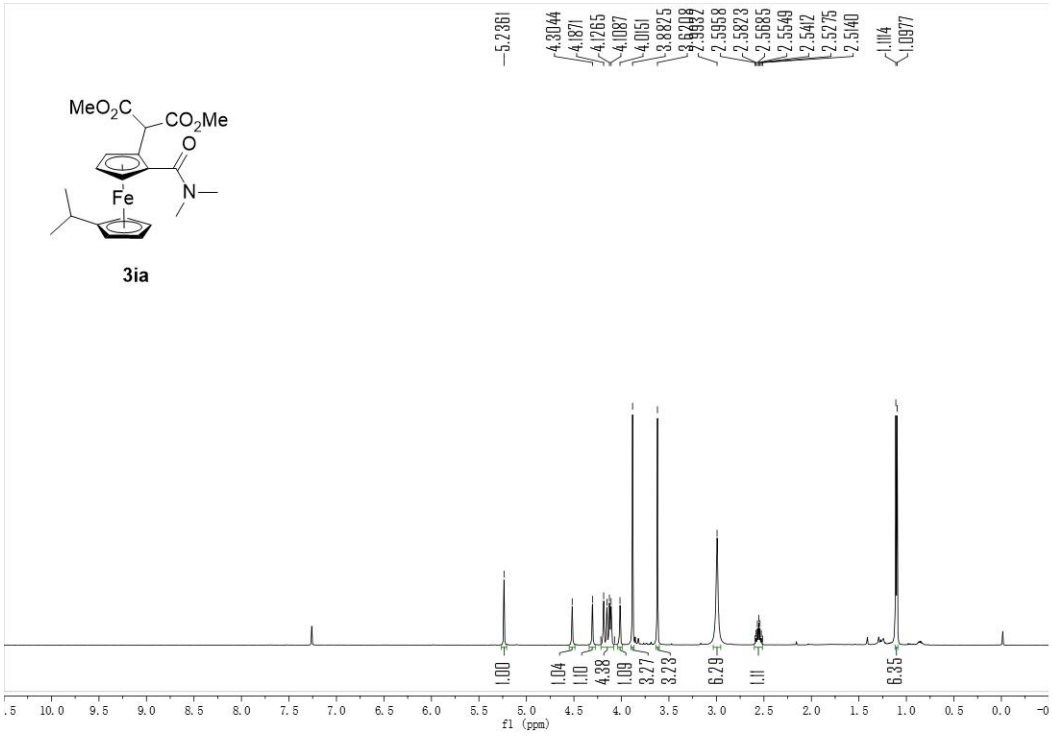
MeO2C
CO2Me
O
Fe
N
O
O
3ha
f1 (ppm)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2.5823
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2.5549
2.5412
2.5275
2.5140
1.1114
1.0977
MeO2C
CO2Me
O
N
Fe
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1.00
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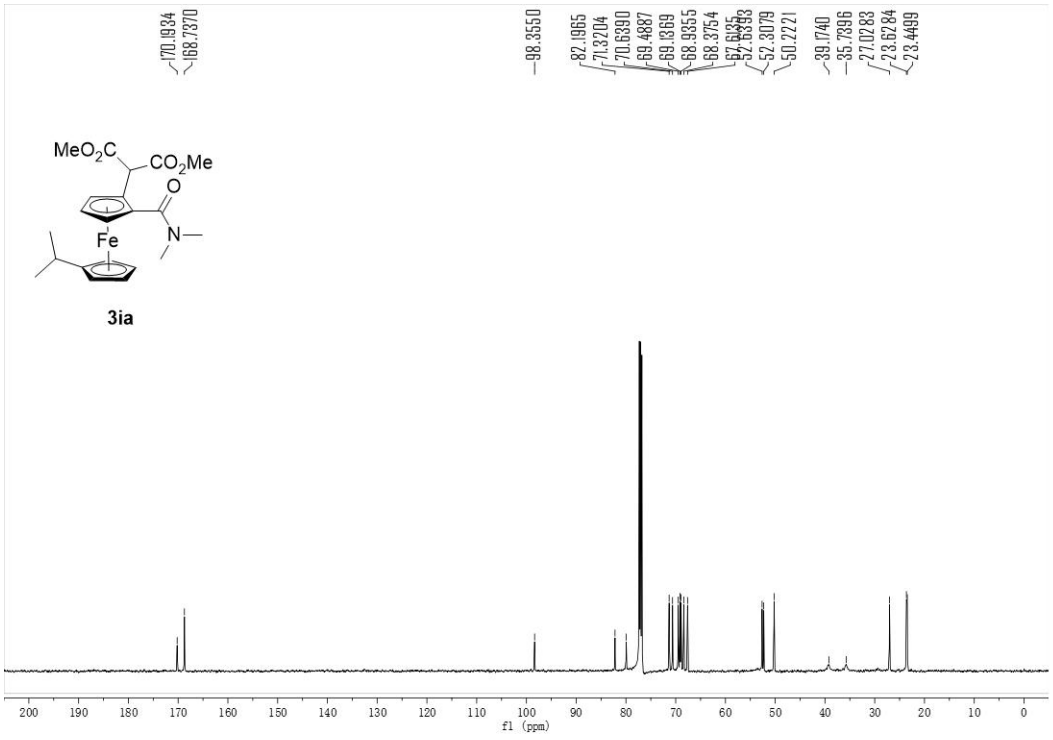
1.10
4.38
1.09
3.27
3.23
6.29
1.11
6.35
f1 (ppm)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52.6393
52.3079
50.2221
39.1740
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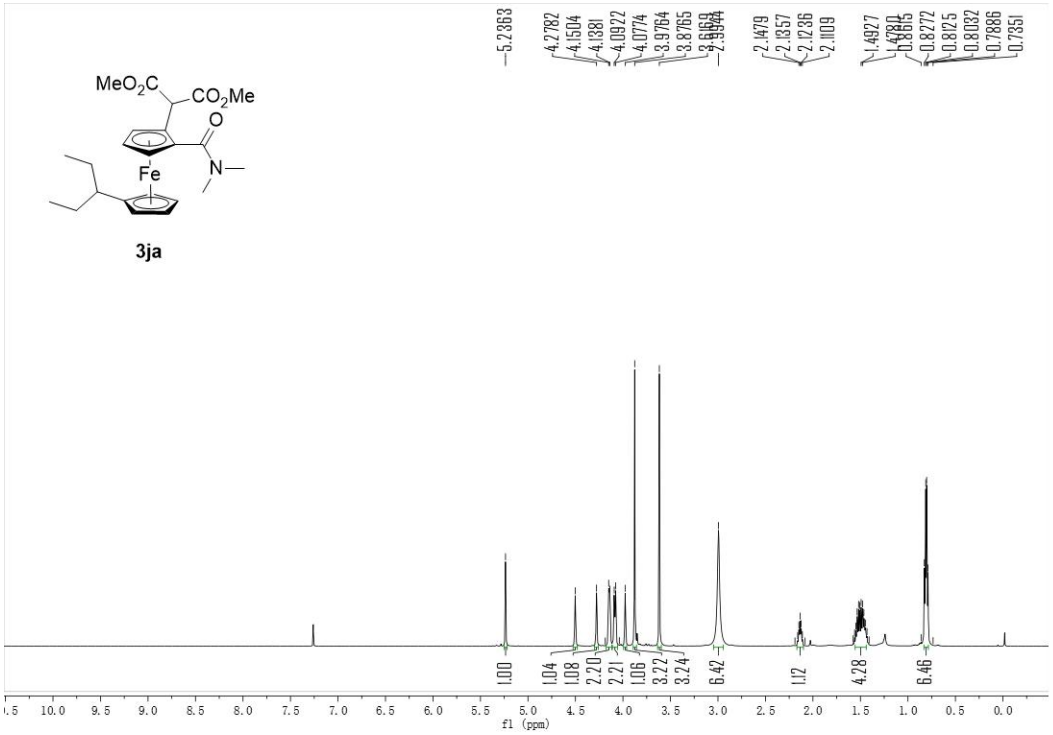
27.0283
23.6284
23.4499
MeO2C
CO2Me
O
N
Fe
3ia
f1 (ppm)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CO2Me
O
N
Fe
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4.1504
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4.0922
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3.9764
3.8765
2.9944
2.4479
2.1357
2.1236
2.1109
1.4927
1.4780
0.8272
0.8125
0.8032
0.7886
0.7351
1.00
1.04
1.08
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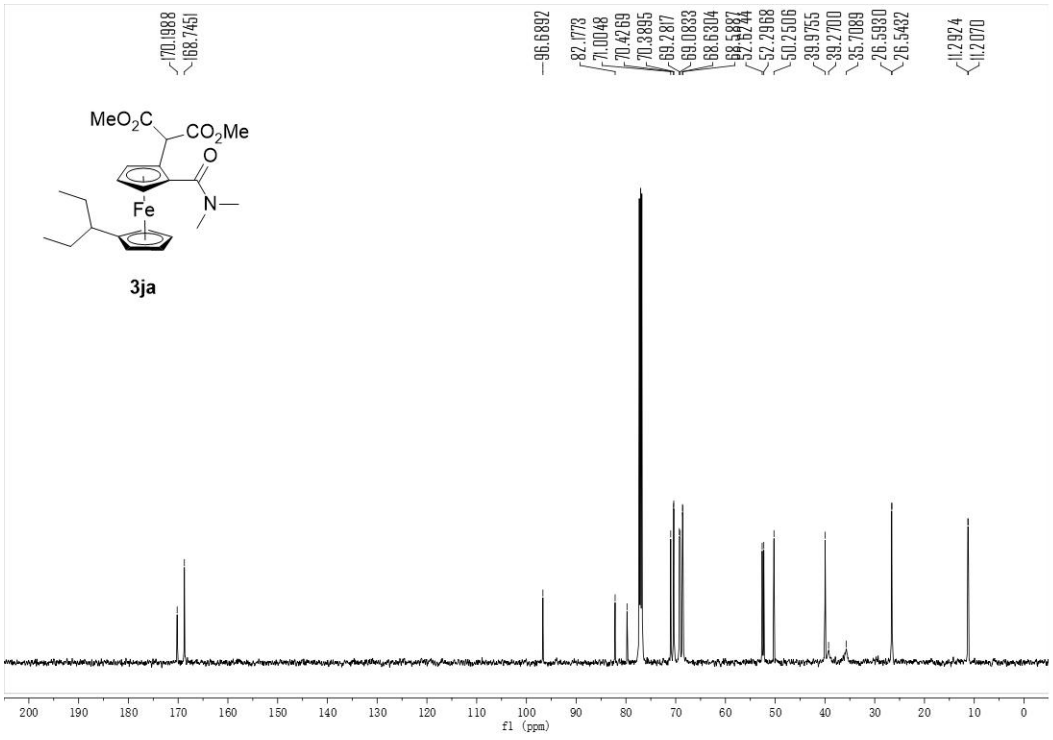
2.21
1.06
3.22
3.24
6.42
1.12
4.28
6.46
f1 (ppm)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O
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Fe
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69.2817
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26.5432
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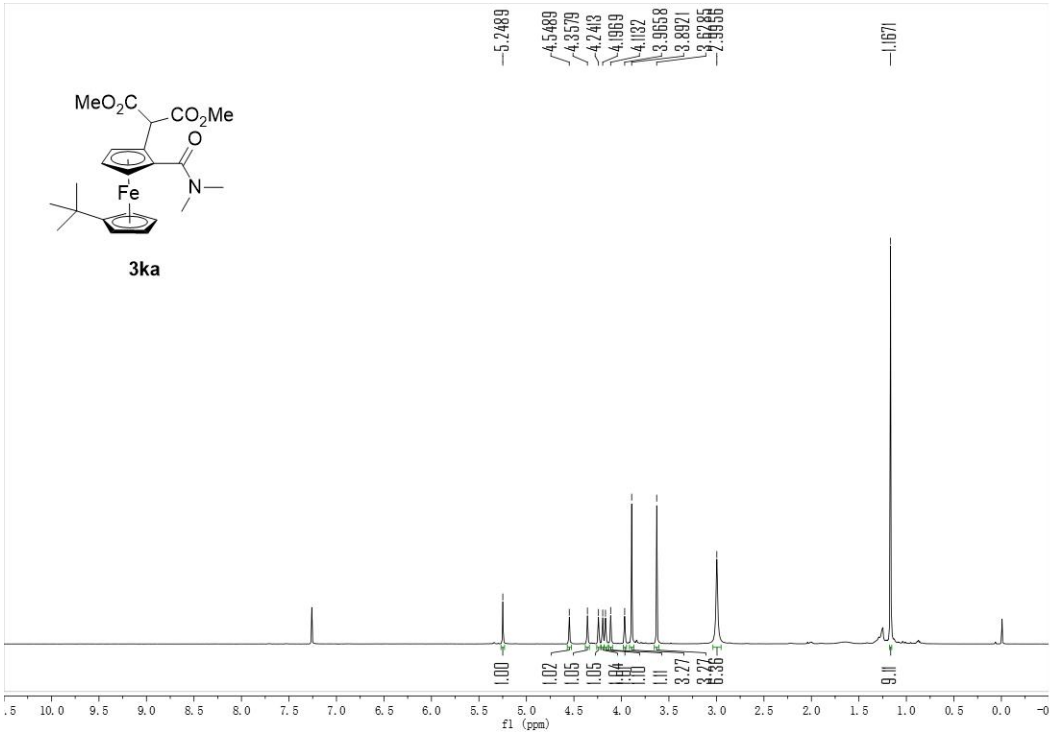
11.2070
f1 (ppm)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2.3956
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MeO2C
CO2Me
O
N
Fe
3ka
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1.05
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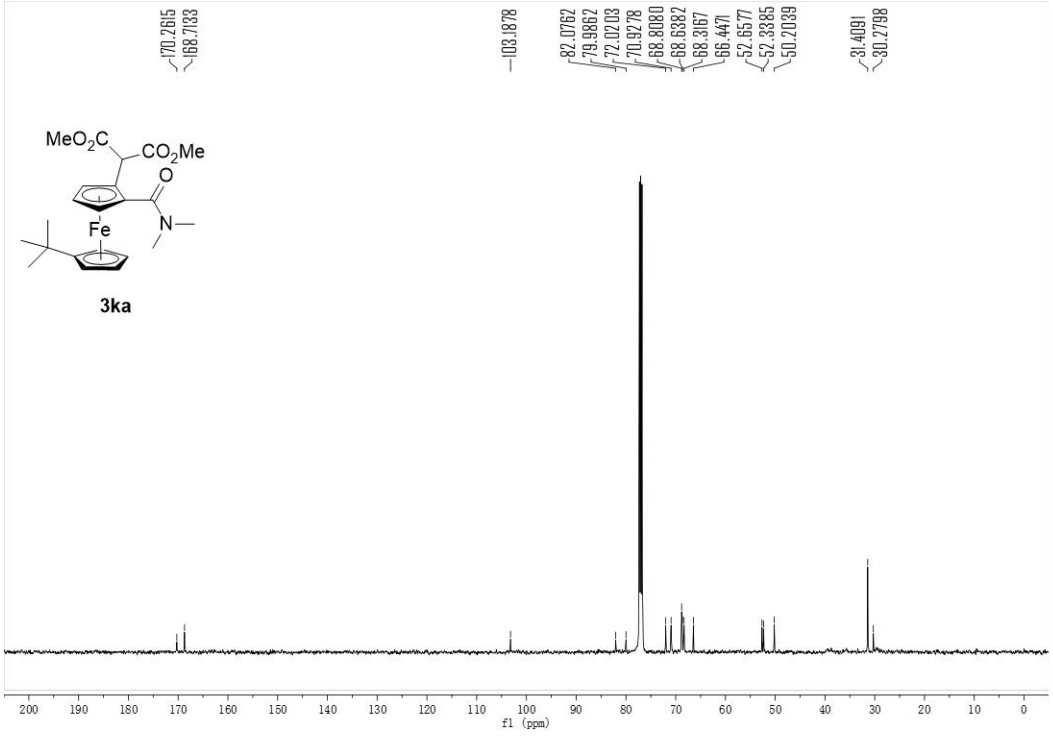
1.10
1.11
3.27
3.27
6.36
9.11
f1 (ppm)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50.2039
31.4091
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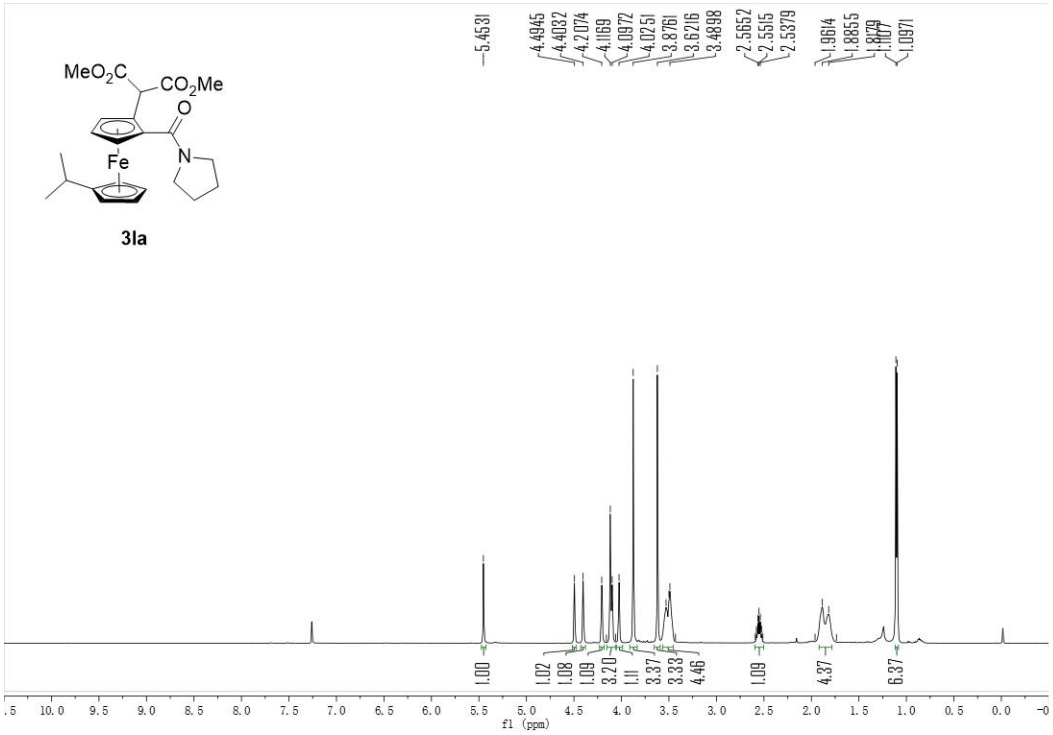
CO2Me
O
N
Fe
3ka
f1 (ppm)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CO2Me
O
Fe
N
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3.6216
3.4898
2.5652
2.5515
2.5379
1.9614
1.8855
1.8679
1.8077
1.0971
1.00
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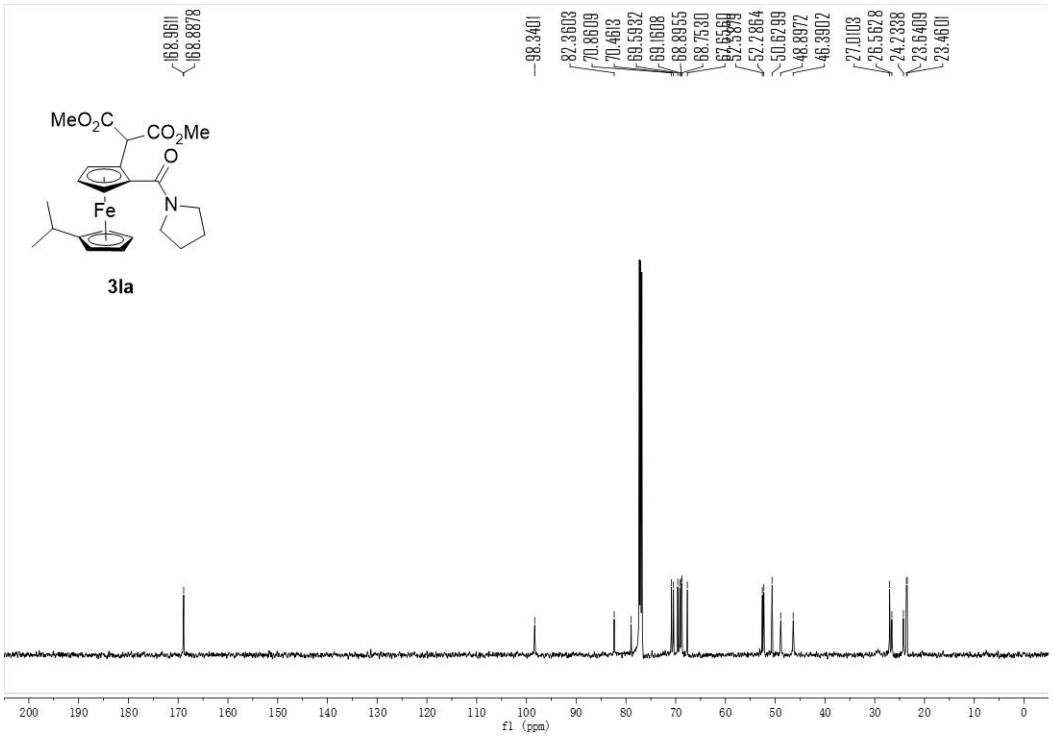
1.09
3.20
1.11
3.37
3.33
4.46
1.09
4.37
6.37
f1 (ppm)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50.6279
48.8972
46.3902
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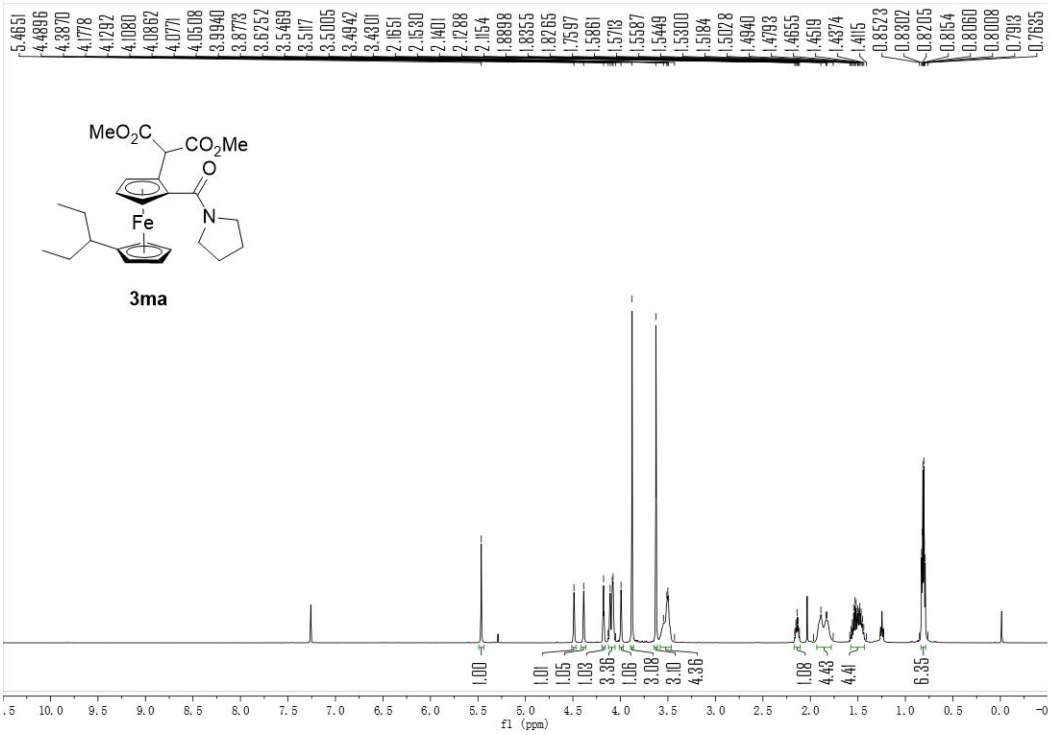
24.2338
23.6409
23.4601
MeO2C
CO2Me
O
Fe
N
3la
f1 (ppm)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CO2Me
O
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Fe
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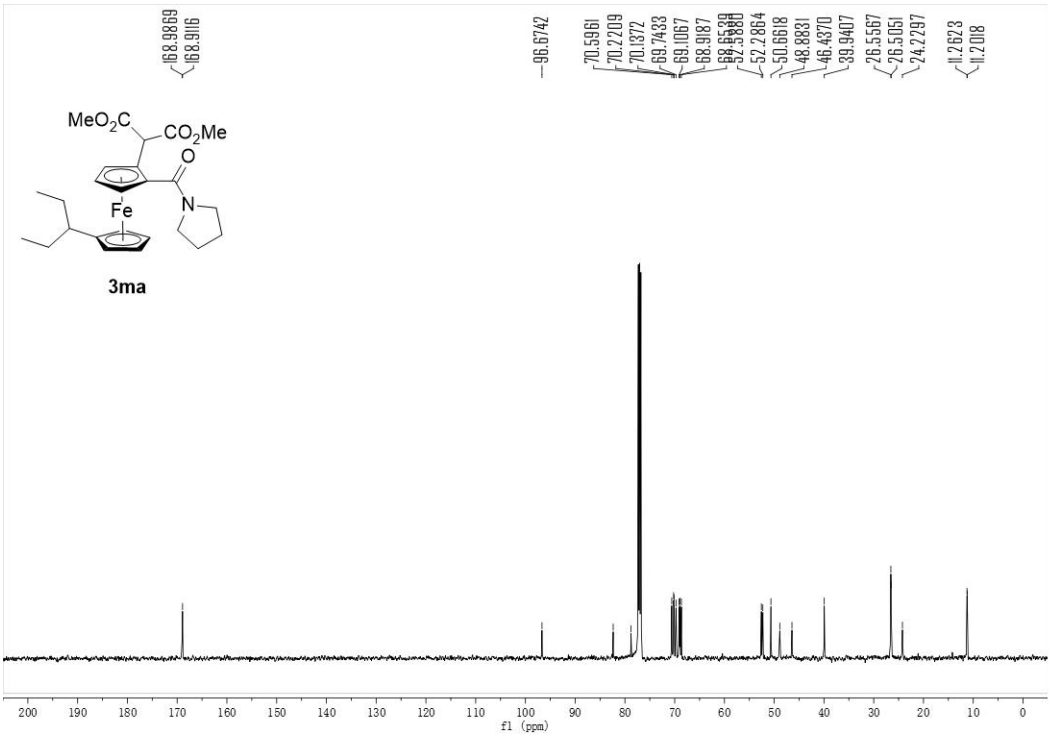
f1 (ppm)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CO2Me
O
N
Fe
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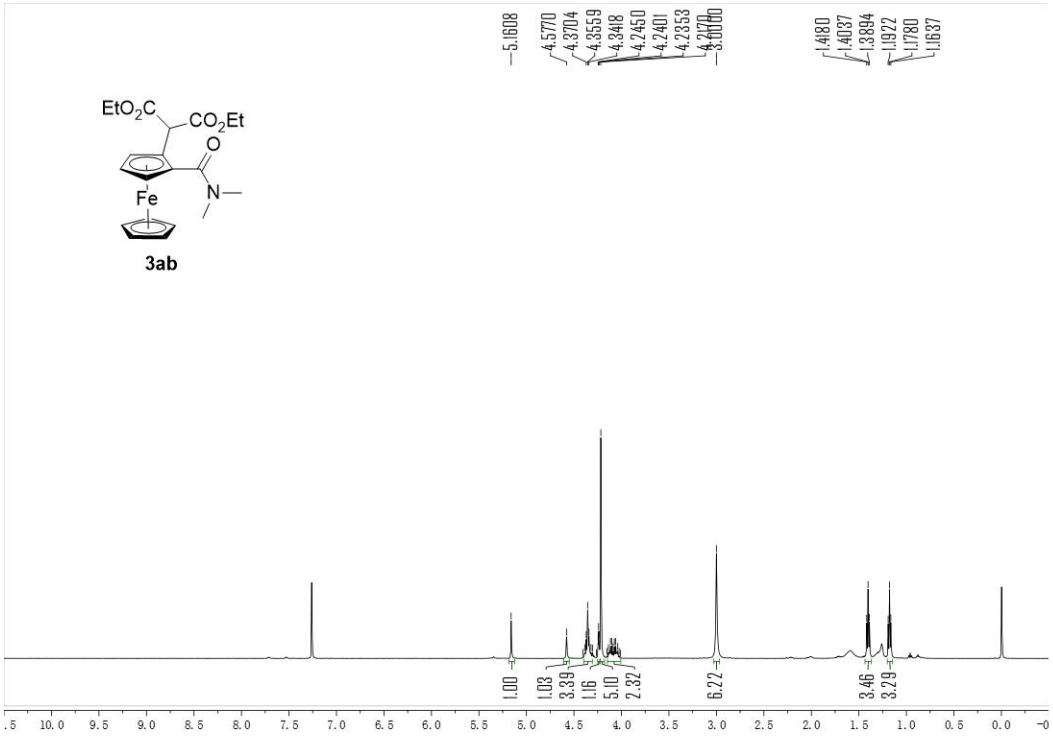
f1 (ppm)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4.2170
4.0000
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1.4037
1.3894
1.1922
1.1780
1.1637
EtO2C
CO2Et
O
N
Fe
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5.10
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6.22
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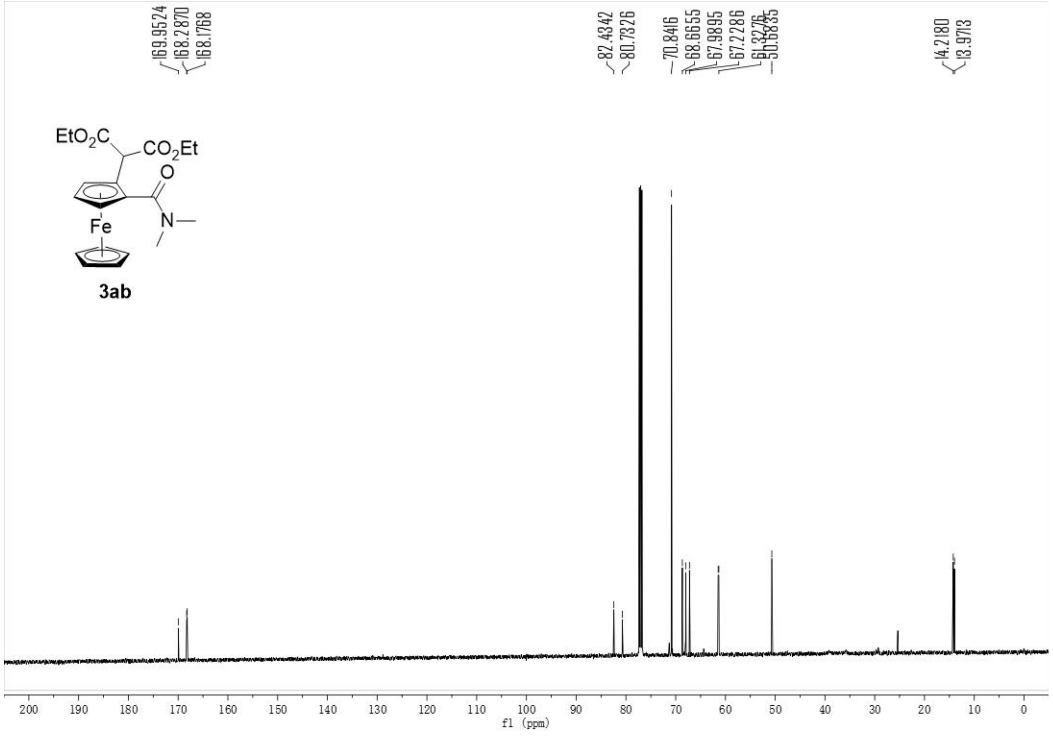
3.29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14.2180
13.9713
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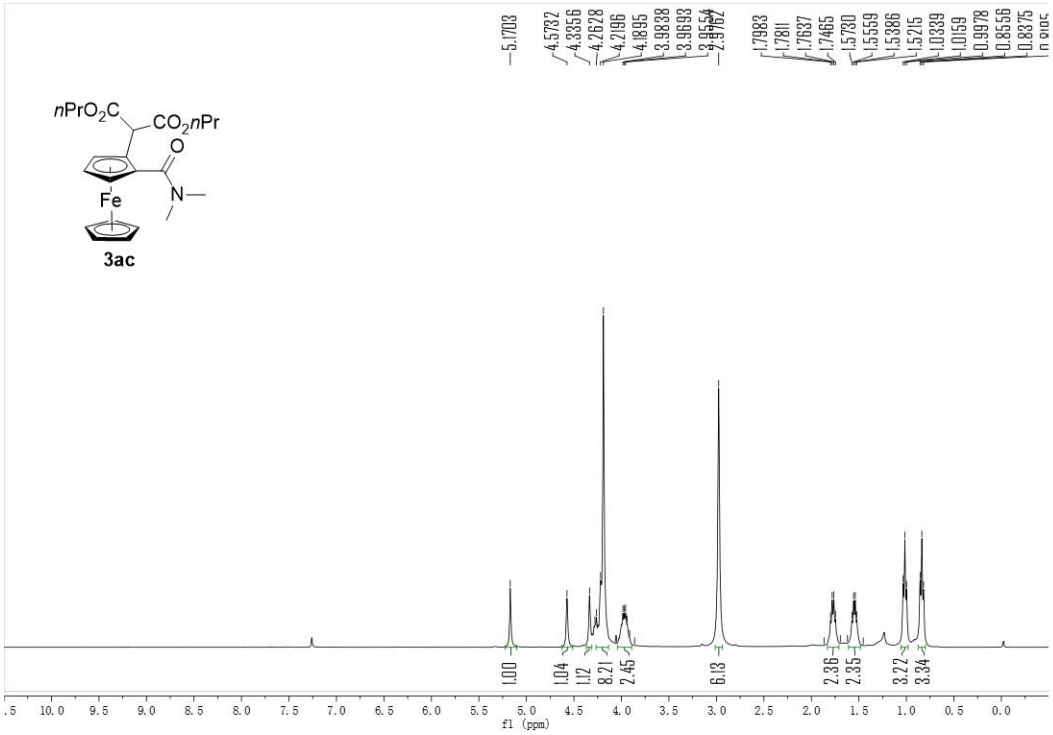
CO2Et
O
N
Fe
3ab
f1 (ppm)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2.9762
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1.7811
1.7637
1.7465
1.5730
1.5559
1.5386
1.5215
1.0339
1.0159
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0.8556
0.8375
nPrO2C
CO2nPr
O
N
Fe
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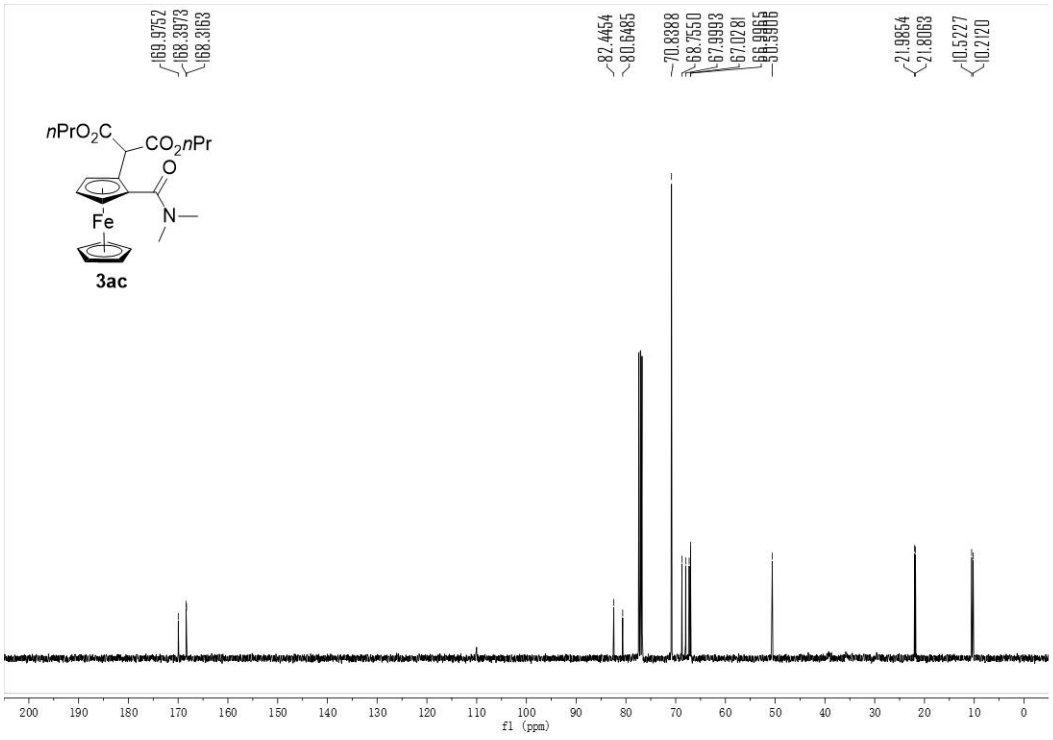
2.35
3.22
3.84
f1 (ppm)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10.5227
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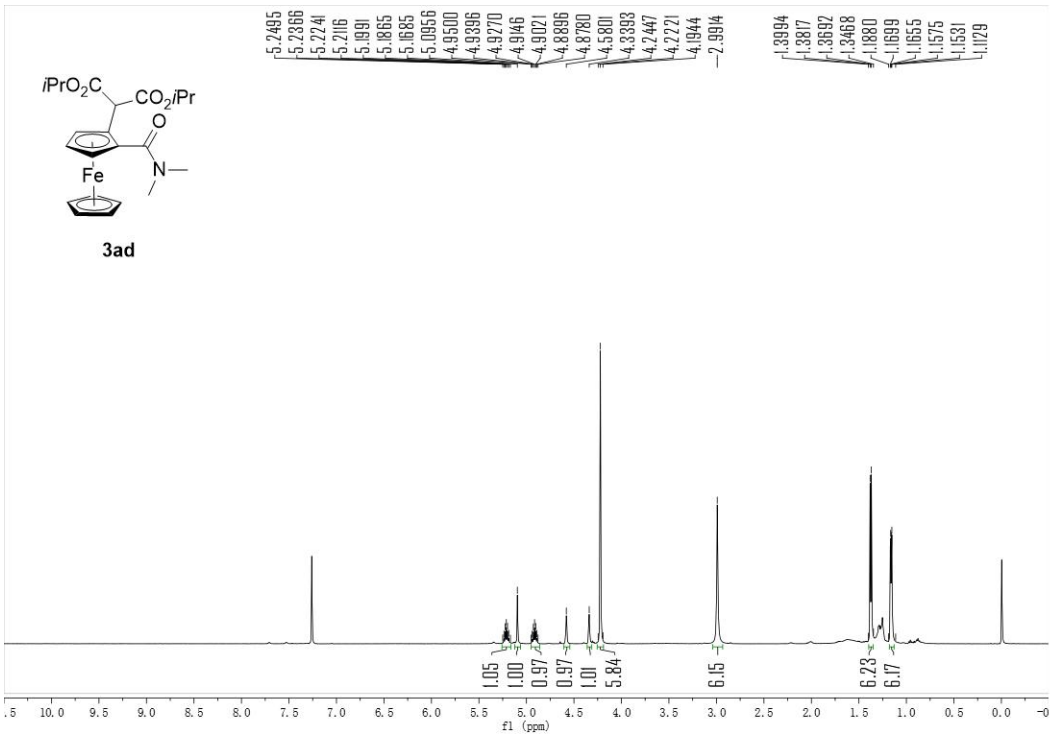
CO2nPr
O
N
Fe
3ac
f1 (ppm)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4.3393
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4.2221
4.1944
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1.3994
1.3817
1.3692
1.3468
1.1880
1.1699
1.1655
1.1575
1.1531
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1.00
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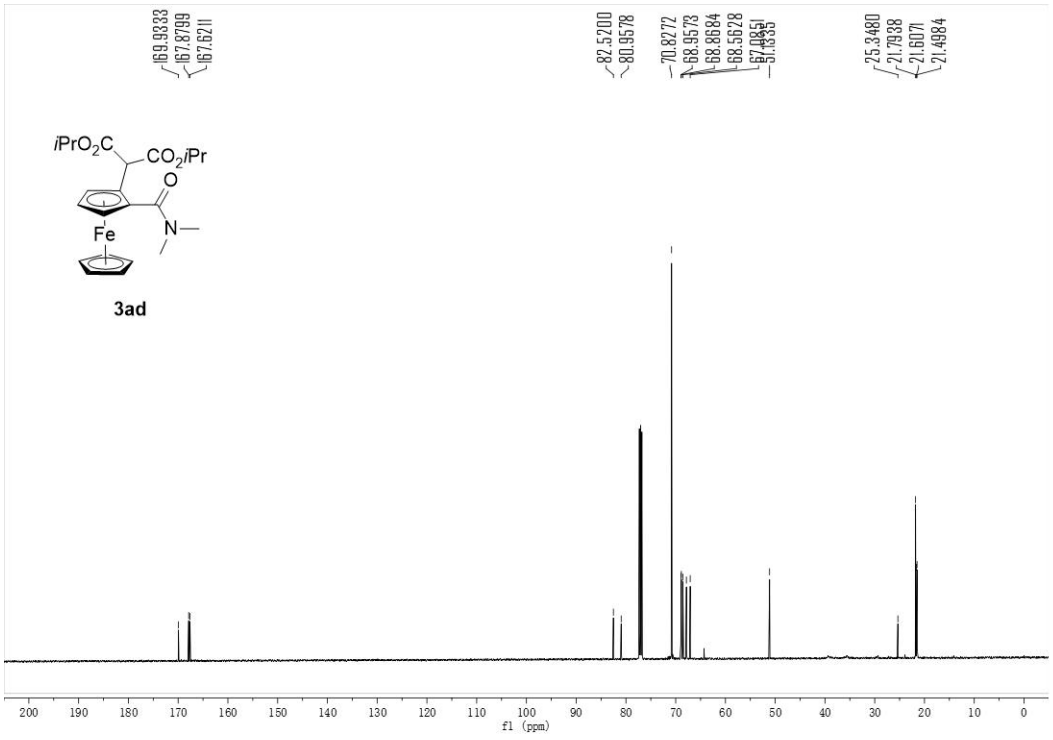
0.97
1.01
5.84
6.15
6.23
6.17
f1 (ppm)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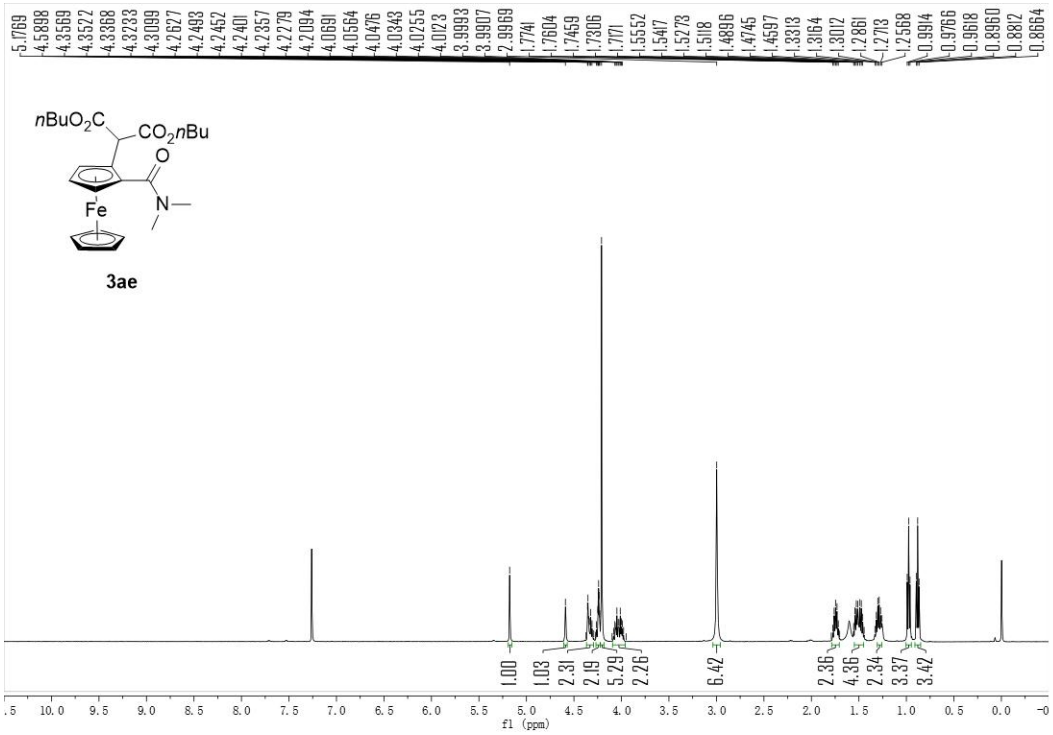
21.7938
21.6071
21.4984
f1 (ppm)


nBuO2C
CO2nBu
O
Fe
N
3ae
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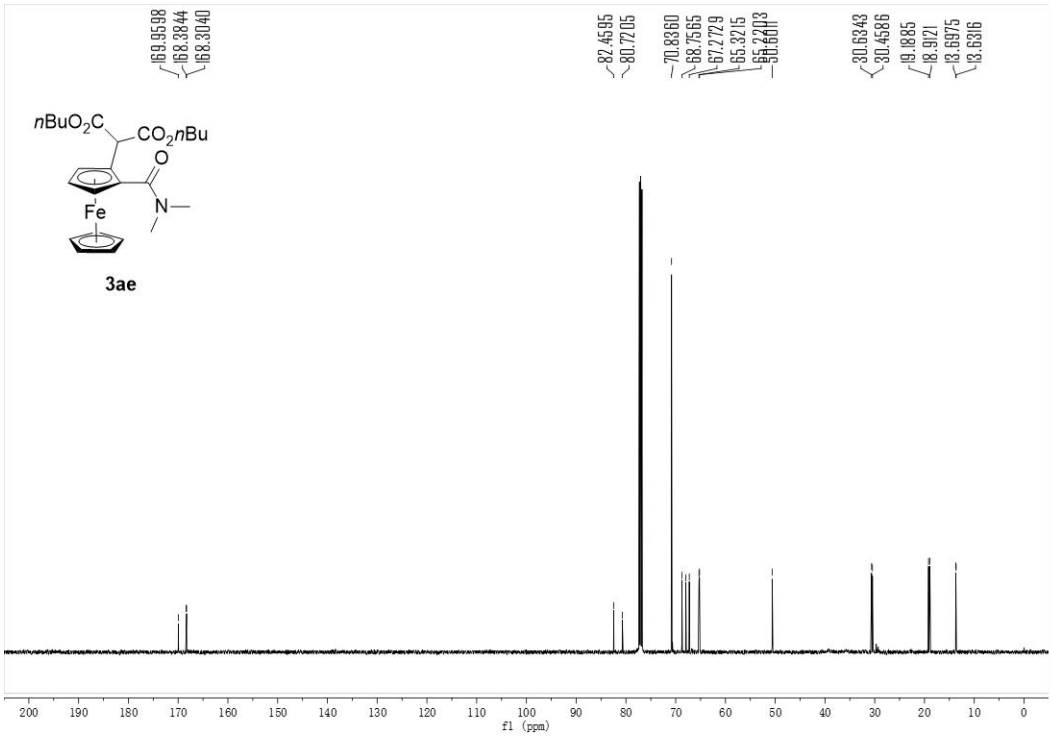
5.29
2.26
6.42
2.36
4.36
2.34
3.37
3.42
f1 (ppm)


nBuO2C
CO2nBu
O
Fe
N
3ae
f1 (ppm)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1.8185
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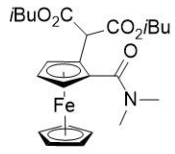
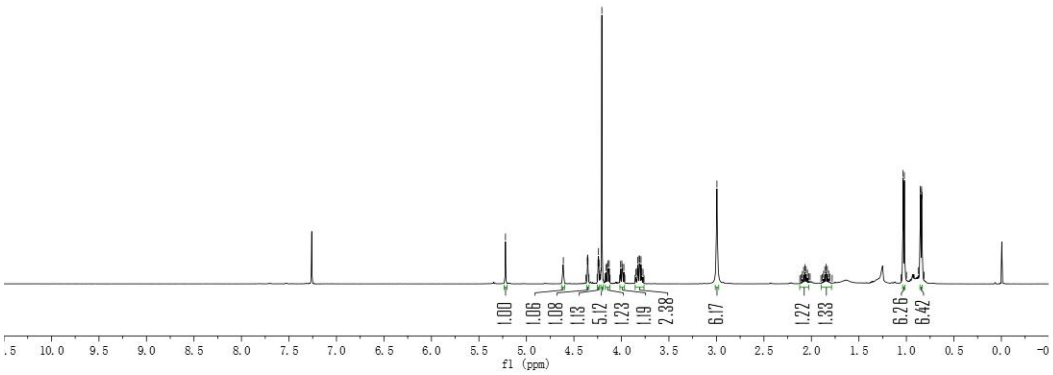
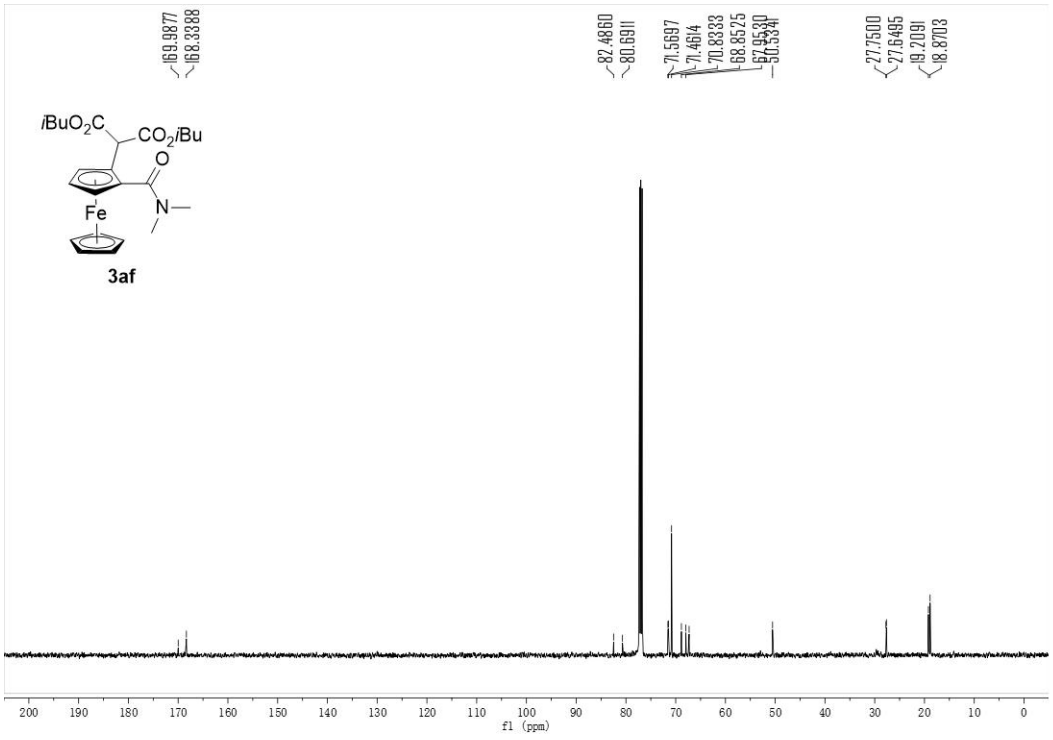
1.0212
0.9991
0.8761
0.8530
0.8493
0.8396
0.8359
0.8140


iBuO2C
CO2iBu
O
N
Fe

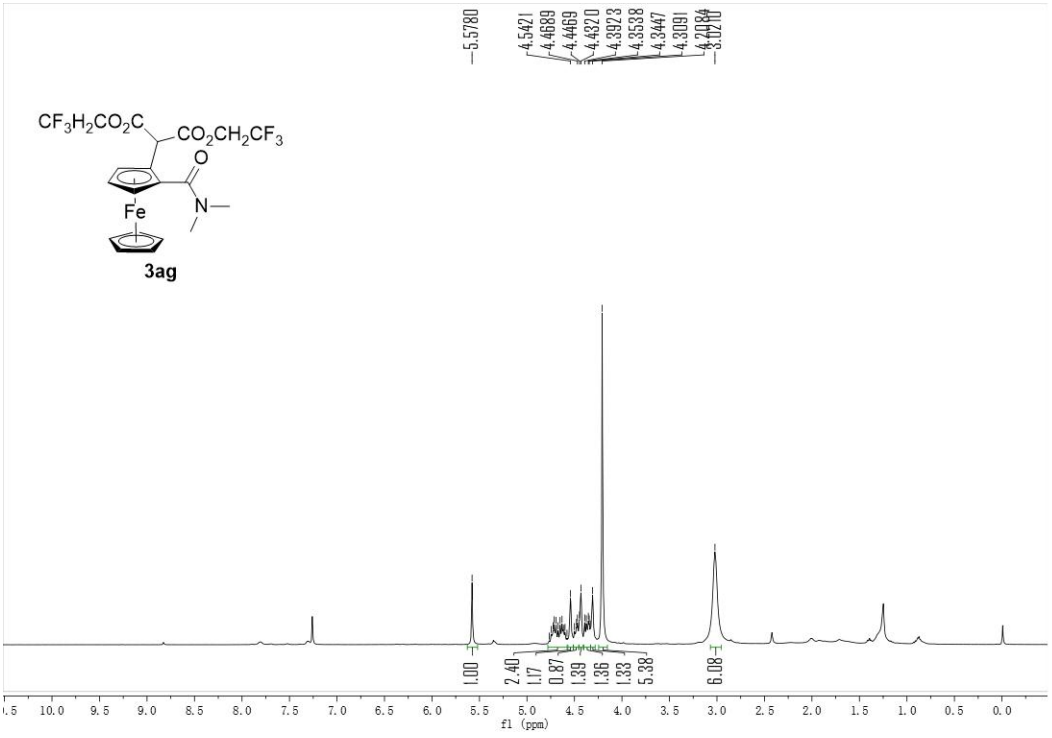
3af

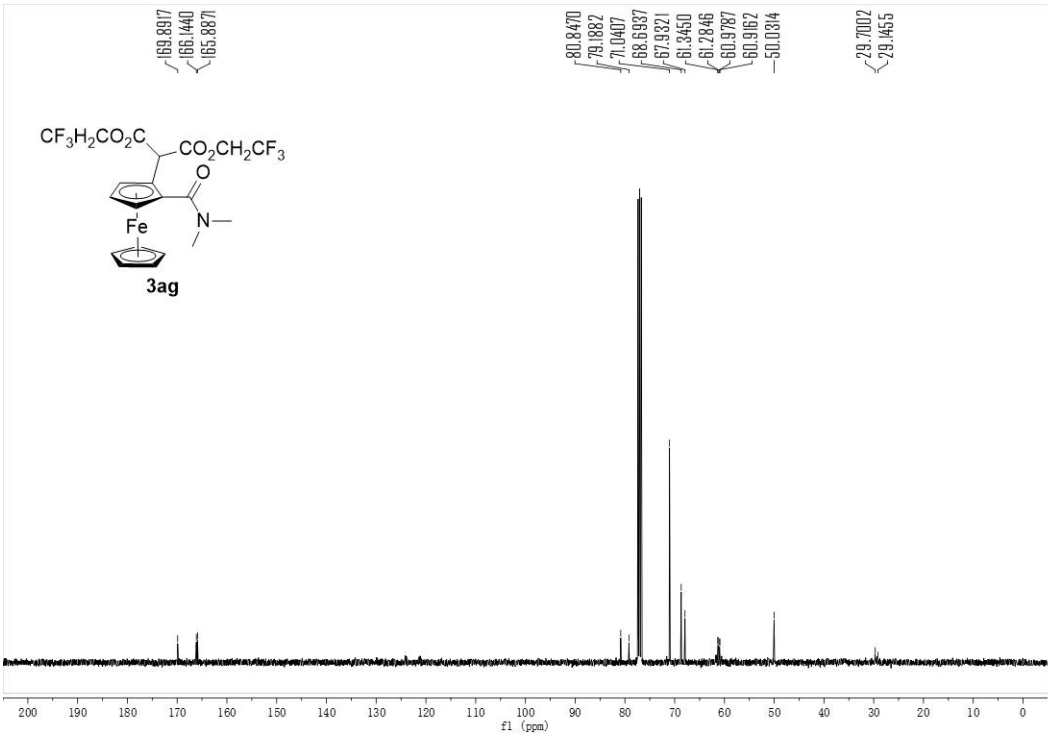

1.00
1.06
1.08
1.13
5.12
1.23
1.19
2.38
6.17
1.22
1.33
6.26
6.42
f1 (ppm)

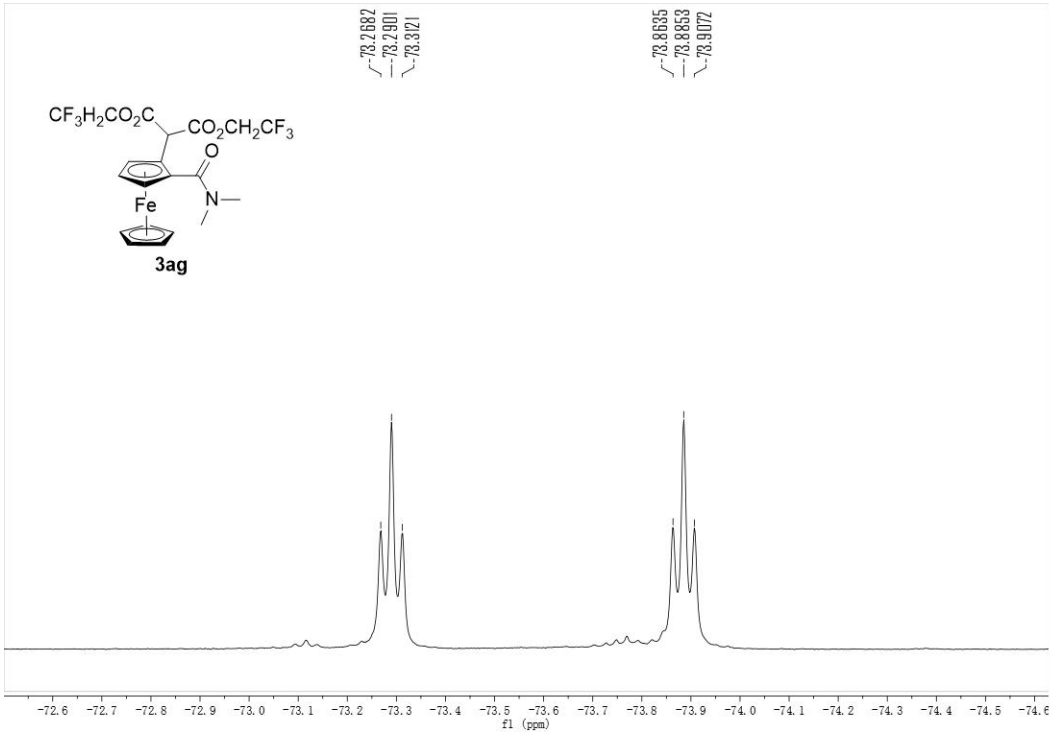

169.9877
168.3388
82.4860
80.6911
71.5697
71.4614
70.8333
68.8525
67.9530
50.3534
27.7500
27.6495
19.2091
18.8703
f1 (ppm)

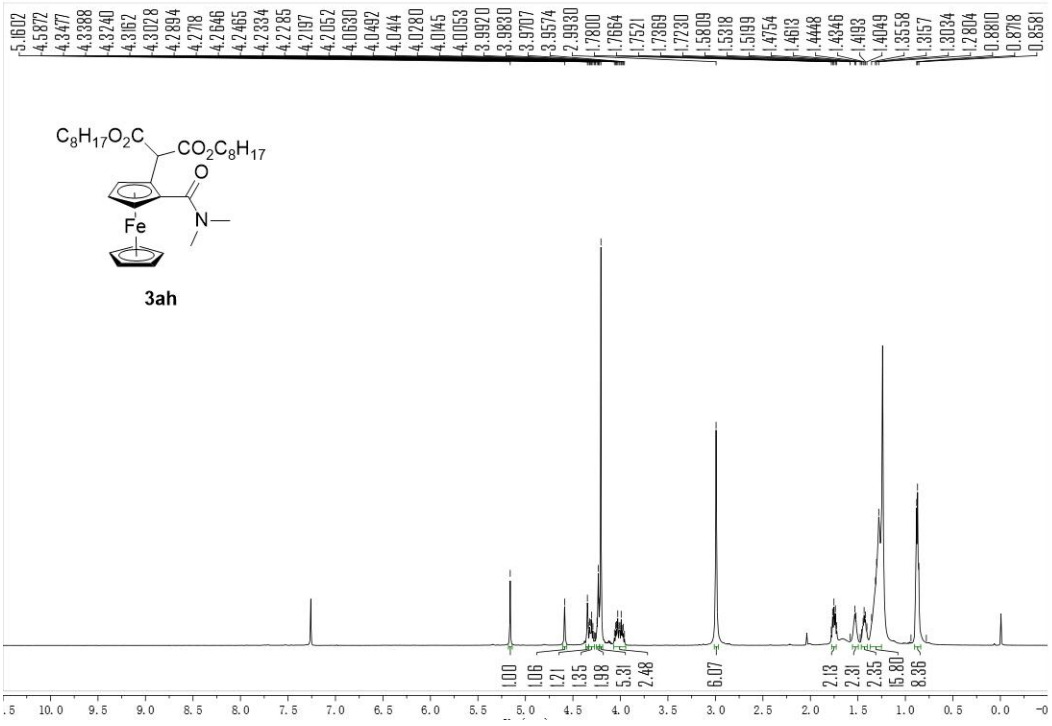
iBuO2C
CO2iBu
O
N
Fe

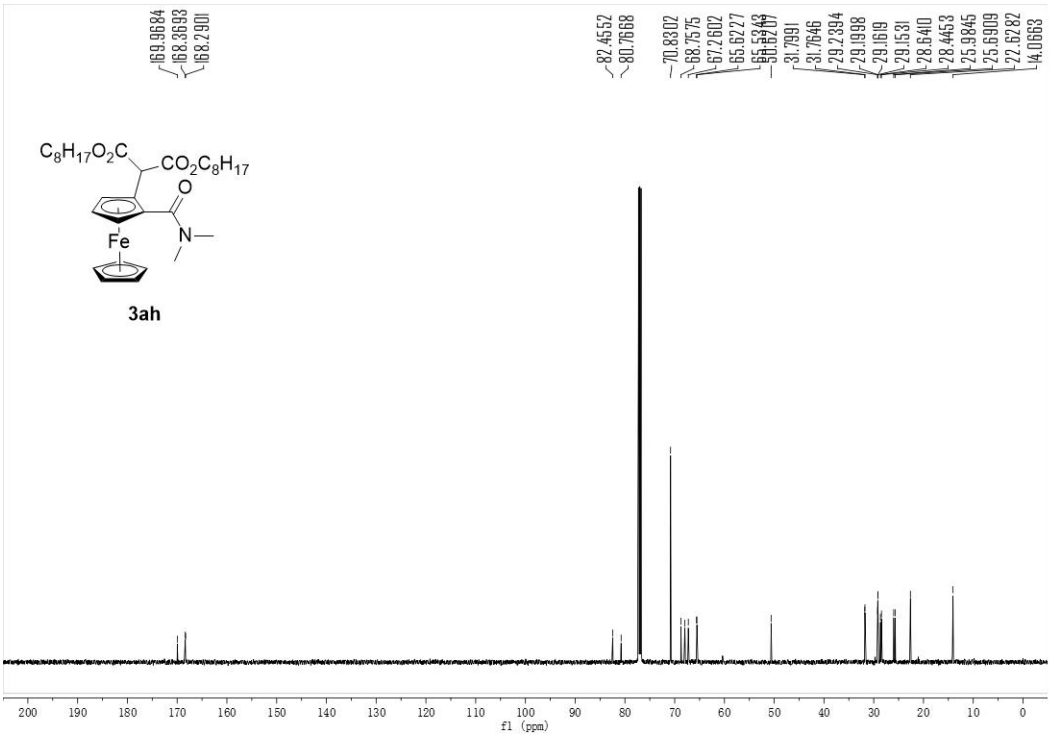
3af

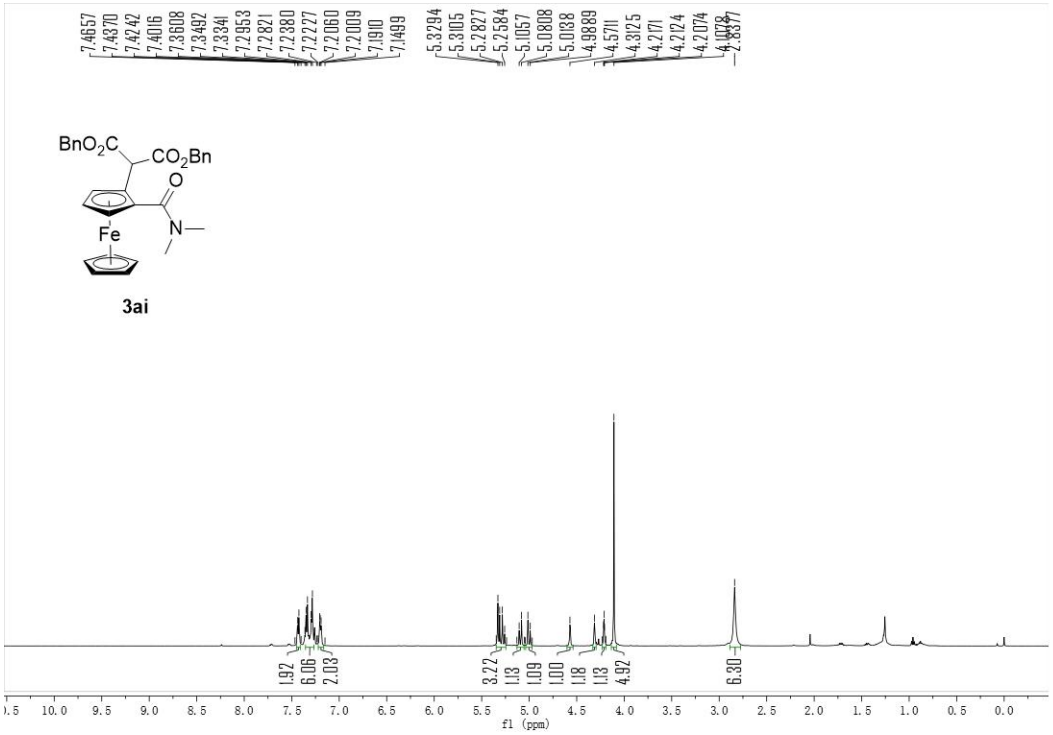

5.5780
4.5421
4.4689
4.4469
4.4321
4.3923
4.3538
4.3447
4.3091
4.2084
4.0210
CF3H2CO2C
CO2CH2CF3
O
Fe
N
3ag
1.00
2.40
1.17
0.87
1.39
1.36
1.33
5.38
6.08
f1 (ppm)


169.8917
166.1440
165.8871
80.8470
79.1882
71.0407
68.6937
67.9321
61.3450
61.2846
60.9787
60.9162
50.0314
29.7002
29.1455
CF3H2CO2C
CO2CH2CF3
O
Fe
N
3ag
f1 (ppm)


-73.2682
-73.2901
-73.3121
-73.8635
-73.8853
-73.9072
CF3H2CO2C
CO2CH2CF3
O
Fe
N
3ag
-72.6 -72.7 -72.8 -72.9 -73.0 -73.1 -73.2 -73.3 -73.4 -73.5 -73.6 -73.7 -73.8 -73.9 -74.0 -74.1 -74.2 -74.3 -74.4 -74.5 -74.6
f1 (ppm)


3ah


3ah
f1 (ppm)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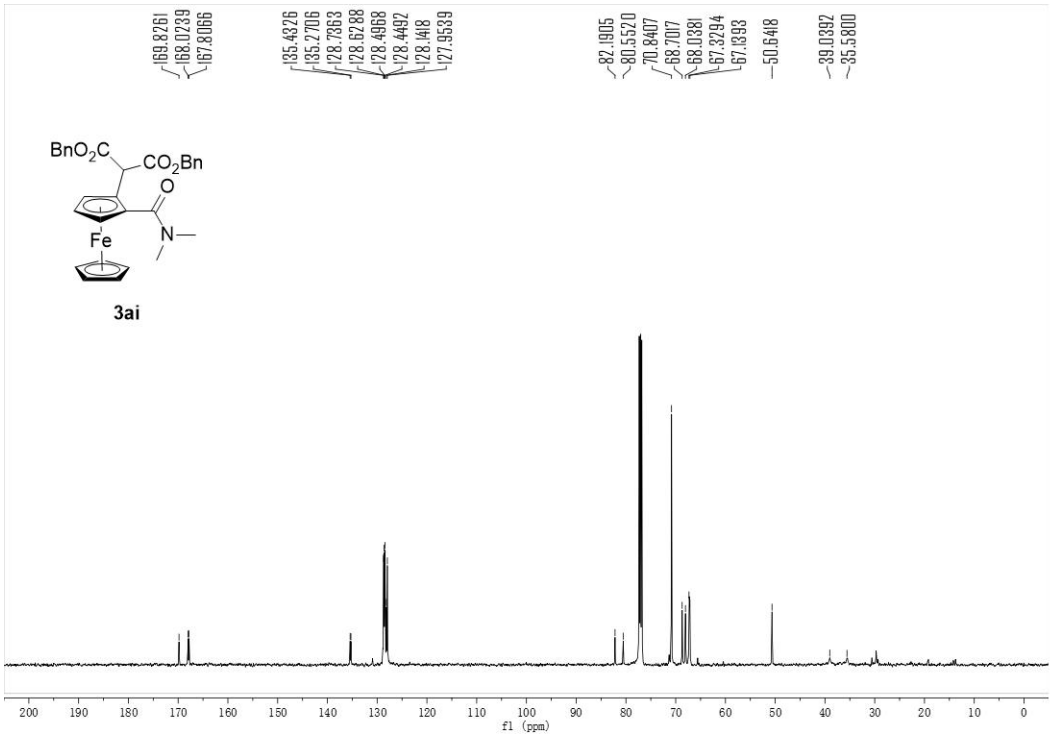
7.4370
7.4242
7.4016
7.3608
7.3492
7.3344
7.2953
7.2821
7.2380
7.2227
7.2060
7.2009
7.1910
7.1499
5.3294
5.3105
5.2827
5.2584
5.1057
5.0808
5.0138
4.9889
4.5711
4.3125
4.2171
4.2124
4.2074
4.1078
2.8877
BnO2C
CO2Bn
O
Fe
N
3ai
1.92
6.06
2.03
3.22
1.13
1.09
1.00
1.18
1.13
4.92
6.30
f1 (ppm)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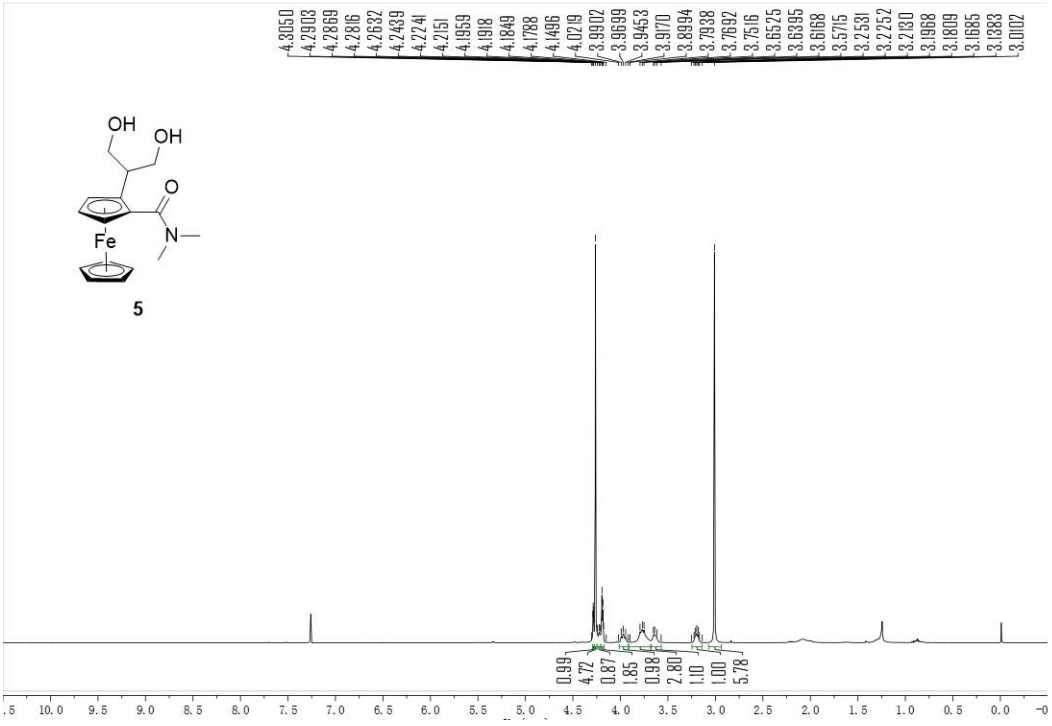
168.0239
167.8066
135.4326
135.2706
128.7863
128.6288
128.4968
128.4492
128.1418
127.9539
82.1905
80.5520
70.8407
68.7017
68.0381
67.3294
67.1393
50.6418
39.0392
35.5800
BnO2C
CO2Bn
O
Fe
N
3ai
f1 (ppm)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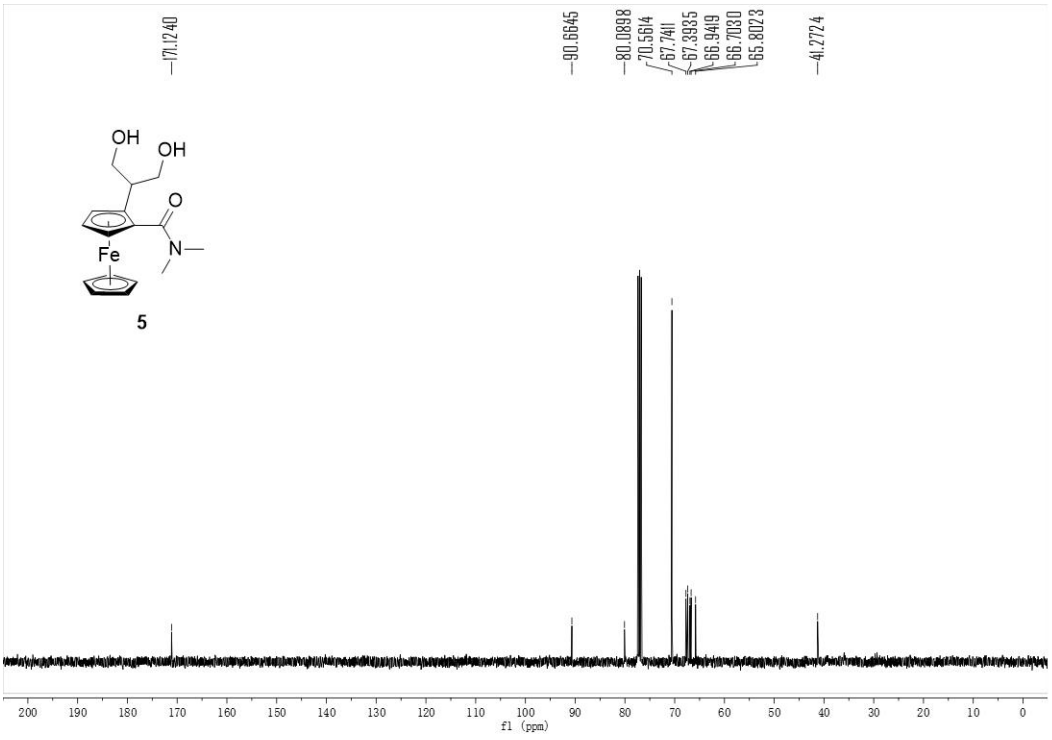
4.2903
4.2869
4.2816
4.2632
4.2439
4.2241
4.2151
4.1959
4.1918
4.1849
4.1788
4.1496
4.0219
3.9902
3.9699
3.9453
3.9370
3.8994
3.7938
3.7692
3.7516
3.6525
3.6395
3.6168
3.5715
3.2531
3.2252
3.2180
3.1968
3.1809
3.1685
3.1383
3.0102
OH
OH
O
N
Fe
5
0.99
4.72
0.87
1.85
0.98
2.80
1.10
1.00
5.78


171.1240
90.6645
80.0898
70.5614
67.7411
67.3935
66.9949
66.7030
65.8023
41.2724
OH
OH
O
N
Fe
5
f1 (ppm)