Supplementary Material

A Ferrocene Nucleic Acid Oligomer as an Organometallic Structural Mimic of DNA

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1. Monomer Synthetic Procedures

(*R*),(*R*),(*pS*),(*pS*)-2,2'-Bis(iodo)-1,1'-bis(*N*,*N*-dimethylaminoethyl)ferrocene 2

In a 200 ml schlenk tube, the starting bis-amine **1** (2.01 g, 5.62 mmol) was dissolved in diethyl ether (30 ml) at room temperature, *n*-BuLi (8.99 ml, 22.46 mmol) was added and the mixture then stirred overnight under argon. The reaction mixture was then cooled to -78°C and iodine (6.41 g, 25.27 mmol) dissolved in THF (60 ml) was added over the course of 10 mins. The reaction was stirred at -78°C for 90 mins before allowing to warm to room temperature, at which point it was allowed to stirred for an additional 90 mins before quenching at 0°C with sodium thiosulfate$_{(aq)}$ (50 ml, 25% w/v). After dilution with diethyl ether (30 ml), the layers were separated and the aqueous layer was further extracted with ether (50 ml). The combined organic fractions were dried over $MgSO_4$, the solvent removed *in vacuo* and purified *via* flash column chromatography (5% EtOAc in hexane, 5% Et_3N) to yield the product (2.61 g, 80%). ^{1}H-NMR ($CDCl_3$, 300 MHz), δ: 4.17 (6H, m), 3.58 (2H, q, 7 Hz), 2.14 (12H, s), 1.43 (6H, d, J 7 Hz). ^{13}C-NMR ($CDCl_3$, 400 MHz), δ: 90.8(ipso Cp), 82.2(CH-Cp), 72.2(CH-Cp), 67.8(CH-Cp), 56.9(CH), 45.6(ipso Cp), 41.1(Me), 15.6 (Me). MS (ES) (m/z) calcd for $C_{18}H_{26}I_2FeN_2$ 579.95, found 580.9619 (M^++ H). Mp = 66-68°C. IR (cm^{-1}): 2967, 2930, 2897, 2853, 2815, 2770, 1469, 1445, 1270, 1269, 1257, 1230, 1198, 1156, 1071, 1058, 1009, 963, 816, 770, 716.

(*R*),(*R*),(*pS*),(*pS*)-2,2'-Bis(iodo)-1,1'-bis(ethylacetate)ferrocene 3

In a 100 ml schlenk tube, **2** (1.52 g, 2.49 mmol) and acetic anhydride (5ml, 52.99mmol) were heated at 50°C under argon for 2.5 hrs. The excess acetic anhydrides were removed under high vacuum (0.1 mm Hg) and the residue purified *via* flash column chromatography (25% EtOAc in hexane) to yield the product (1.18 g, 78%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.83 (2 H, q, *J* 6.5), 4.39 – 4.35 (2 H, m), 4.32 (2 H, dd, *J* 2.6, 1.4), 4.25 – 4.22 (2 H, m), 2.04 (6 H, s), 1.63 (6 H, d, *J* 6.5). ^{13}C-NMR ($CDCl_3$, 400 MHz), δ: 170.1(C=O), 88.9(ipso Cp), 82.2(CH-Cp), 73.2(CH-Cp), 68.6(CH-Cp), 67.8(CH), 45.5(ipso Cp), 21.1(Me), 18.8(Me). MS (ES) (m/z) calcd for $C_{18}H_{20}O_4I_2Fe^{56}Na$ 632.8698, found 632.8688 (M^+ + Na). Mp = 126-128°C. IR (cm^{-1}): 3098, 2988, 2935, 1723, 1454, 1390, 1229, 1112, 1044, 1019, 948, 928, 823, 719.

(*R*),(*R*),(*p*S),(*p*S)-2,2'-bis(iodo)-1,1'-bis(ethanol)ferrocene 4

In a 250 ml round bottom flask, **3** (1.24 g, 2.36 mmol) was dissolved in ethanol (20ml). $NaOH_{(aq)}$ (40 ml, 10% w/v) was added and the reaction was heated to 95°C for 10 mins. The reaction was allowed to cool to room temperature and the organic layer was extracted with EtOAc (50 ml x 2). The organic layers were dried over

Na_2SO_4, the solvent removed *in vacuo* and the residue purified *via* flash column chromatography (25% EtOAc in hexane) to yield the product (1.19 g, 96%) ^{1}H-NMR ($CDCl_3$, 300 MHz), δ: 4.78 (2H, m), 4.29 (4H, m), 4.19 (2H, q, J=2Hz), 2.08 (2H, d, J=4Hz), 1.57 (6H, d, J=6Hz). ^{13}C-NMR ($CDCl_3$, 400 MHz), δ: 92.8(ipso Cp), 80.6(CH-Cp), 72.5(CH-Cp), 67.2(CH-Cp), 65.6(CH), 45.0(ipso Cp), 21.7(Me). MS (ES) (m/z) calcd for $C_{14}H_{16}O_2I_2{}^{56}FeNa$ 548.8487, found 548.8493 (M^++ Na). Mp = 98-100^{o}C. IR (cm^{-1}): 3385-3120 (br), 2978, 2965, 2928, 1406, 1371, 1270, 1241, 1096, 1058, 1030, 1006, 940, 869, 809, 707.

(*R*),(*R*),(*pS*),(*pS*)-2,2'-Bis(iodo)-1,1'-bis(1-methoxyethyl)ferrocene 5

In a 100 ml round bottom flask, **4** (2.12,g, 4.03 mmol) was dissolved in a MeOH/AcOH (20 ml, 9:1) mixture and the reaction was then stirred at room temperature for 48 hr. The reaction was quenched with water (10 ml) and extracted with DCM (20 ml × 2). The combined organic fractions were dried over $MgSO_4$, the solvent removed *in vacuo* and the residue purified *via* flash column chromatography (20% EtOAc in hexane) to yield the product (2.05 g, 81%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 4.43 (1 H, q, *J* 6.5), 4.35 (2 H, dd, *J* 2.5, 1.5), 4.29 (2 H, dd, *J* 2.7, 1.4), 4.19 – 4.14 (2 H, m), 3.27 (6 H, s), 1.63 (6 H, d, *J* 6.5). ^{13}C-NMR ($CDCl_3$, 400 MHz), δ: 90.8(ipso Cp), 81.5(CH-Cp), 73.5(CH-Cp), 72.7(CH-Cp), 67.4(CH), 56.2(Me), 47.1(ipso Cp), 19.4(Me). MS (ES) (m/z) calcd for $C_{16}H_{20}O_2I_2{}^{56}FeNa$ 576.8800, found 576.8810 (M^++ Na). Mp = 65-67^{o}C. IR (cm^{-1}): 3002, 2978, 2936, 2921, 2880, 2865, 2816, 1454, 1447, 1370, 1322, 1275, 1240, 1195, 1161, 1111, 1083, 1077, 1062, 1051, 996, 710.

(*S*),(*S*),(*pS*),(*pS*)-2,2'-Bis(iodo)-1,1'-bis(ethylbutanoate-3-)ferrocene 6

In a 250 ml schlenk tube, **5** (2.05 g, 3.92 mmol) and silyl ketene acetal (2.53 g, 15.68 mmol) were dissolved in DCM (100 ml) under argon. The mixture was cooled to -78^{o}C and $BF_3.OEt_2$ (1.11 ml, 8.62 mmol) was added dropwise. The reaction mixture was stirred for 15 mins at -78^{o}C before it was warmed to room temperature. After quenching with saturated $NaHCO_3$ (40 ml), the organic layer was separated and the aqueous layer was further extracted with DCM (40 ml). The combined organic fractions were dried over $MgSO_4$, the solvent removed *in vacuo* and the residue purified *via* flash column chromatography (20% EtOAc in hexane) to yield the product (2.40 g, 92%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 4.21 – 4.09 (10 H, m), 3.14 – 2.99 (2 H, m), 2.53 (2 H, dd, *J* 15.0, 3.7), 2.12 (2 H, q, *J* 15.0, 10.1), 1.40 (6 H, d, *J* 6.8), 1.26 (6 H, t, *J* 7.1). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.84(C=O), 94.59(ipso Cp), 81.12(CH-Cp), 71.78(CH-Cp), 66.38(CH-Cp), 60.30(CH_2), 46.19(ipso Cp), 42.80(CH_2), 29.91(CH), 18.84(Me), 14.25(Me). IR (cm^{-1}): 2965, 1725, 1370, 1105. MS (ES) (m/z) calcd for $C_{22}H_{28}O_4I_2{}^{56}FeNa$ 688.9324, found 688.9321 (M^++ Na). Mp = 62-64^{o}C.

(*S*),(*S*),(*pS*),(*pS*)-2,2'-Bis(iodo)-1.1'-bis(butanol-3-)ferrocene 7

In a 100 ml schlenk tube, **6** (2.01 g, 3.02 mmol) was dissolved in diethyl ether (50 ml) under argon, cooled to 0^{o}C and left to stand for 5 mins. Diisobutylalumminum

hydride (18.1 ml, 18.12 mmol) was added to the reaction slowly at that temperature. The reaction was allowed to stir at 0°C for 1 hr before being quenched with aqueous sodium potassium tartrate (30ml). The layers were separated and the aqueous layer was further extracted with diethyl ether (30 ml). The combined organic fractions were dried over Na_2SO_4, the solvent removes *in vacuo* and the residue purified *via* flash column chromatography (30% EtOAc in hexane) to yield the product (1.56 g, 89%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 4.26 – 4.06 (6 H, m), 3.61 (4 H, dd, *J* 10.8, 6.3), 2.82 – 2.62 (2 H, m), 1.81 – 1.48 (4 H, m), 1.37 (6 H, d, *J* 10.0), 1.27 (2 H, s). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 96.3(ipso Cp), 80.8(CH-Cp), 71.6(CH-Cp), 66.0(CH-Cp), 60.8(CH_2), 46.9(ipso Cp), 41.8(CH_2), 29.1(CH), 19.6(Me). IR (cm^{-1}): 3406-3110 (br), 2963, 1029. MS (ES) (m/z) calcd for $C_{18}H_{24}O_2I_2{}^{56}FeNa$ 604.9113, found 604.9112 (M^++ Na). Mp = 87-89°C.

(*S, S*),(*pS, pS*)-2,2'-Diiodo-1,1'-(4-(benzyloxy)butan-2-yl)ferrocene 8

A 100 ml two-necked round bottom flask was filled with argon and **7** (1.01 g, 1.74 mmol) dissolved in DMF (20 ml). NaH (0.35 g, 8.70 mmol, 60% w/w in mineral oil) was then slowly added, followed by benzyl bromide (0.45 ml, 3.83 mmol). The reaction was stirred at room temperature for 1 hr, after which time it was quenched with water (100 ml) and extracted with diethyl ether (40 ml × 3). The combined ethereal fractions were washed with brine (60 ml), dried over $MgSO_4$, the solvent removed *in vacuo* and the residue purified *via* flash column chromatography (10% EtOAC in hexane) to yield the product (1.06 g, 80%). ^{1}H-NMR δ_H (300 MHz, $CDCl_3$) δ: 7.31 (10 H, dd, *J* 7.8, 4.1), 4.50 (4 H, dd, *J* 30.8, 11.9), 4.20 – 4.08 (6 H, m), 3.53 – 3.41 (4 H, m), 2.80 – 2.65 (2 H, m), 1.91 – 1.76 (2 H, m), 1.63 – 1.47 (2 H, m), 1.37 (6 H, d, *J* 6.9). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 138.7(ipso Ph), 128.3(CH-Ph), 127.6(CH-Ph), 127.4(CH-Ph), 96.4(ipso Cp), 80.8(CH-Cp), 72.7(CH_2), 71.6(CH-Cp), 68.3(CH_2), 66.2(CH-Cp), 46.7(ipso Cp), 38.4(CH_2), 29.7(CH), 19.5(Me). IR (cm^{-1}): 2930, 2854, 1092. MS (ES) (m/z) calcd for $C_{32}H_{36}O_2I_2{}^{56}FeNa$ 785.0052, found 785.0055 (M^++ Na).

(*S, S*),(*pS, pS*)-2,2'-Bisformyl-1,1'-bis(4-(benzyloxy)butan-2-yl)ferrocene 9

In a 100 ml schlenk tube, **8** (0.80 g, 1.05 mmol) was dissolved in diethyl ether (30 ml), the mixture cooled to -78°C and *n*-BuLi (1.47 ml, 3.66 mmol) was added. After 30 mins, DMF (0.34 ml, 4.40 mmol) was added and the reaction was stirred at -78°C for another 30 mins before it was allowed to warm to room temperature, at which point it was quenched with water (10 ml). The phases were separated and the aqueous layer was extracted with more diethyl ether (10 ml). The combined ethereal fractions were dried over Na_2SO_4, the solvent removed *in vacuo* and the residue purified *via* flash column chromatography (20% EtOAc in hexane) to yield the product (0.54 g, 91%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 10.07 (2 H, s), 7.34 (10 H, td, *J* 8.9, 4.9), 4.84 (2 H, t, *J* 2.0), 4.55 – 4.33 (8 H, m), 3.47 – 3.25 (4 H, m), 3.20 – 3.07 (2 H, m), 1.78 – 1.62 (4 H, m), 1.38 (6 H, d, *J* 6.9). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 193.1 (C=O), 138.3 (ipso Ph), 128.4 (CH-Ph), 127.8 (CH-Ph), 127.6 (CH-Ph), 99.4 (ipso Cp), 77.7 (ipso Cp), 72.9 (CH2), 72.7 (CH-Cp), 72.0 (CH-Cp), 71.5 (CH-Cp), 67.8 (CH2), 39.9 (CH2), 27.6 (CH), 19.4 (Me). IR (cm^{-1}): 2928, 2864, 1716, 1097. MS (ES) (m/z) calcd for $C_{34}H_{38}O_4Fe^{56}Na$ 589.2017, found 589.2024 (M^++ Na).

(*S*, *S*),(*pS*, *pS*)-2,2'-Bis((*Z*)-3-benzoyl-5-methyl-1-vinylpyrimidine-2,4(1H,3H)-dione)-1,1'-bis(4-(benzyloxy)butan-2-yl)ferrocene 10

In a 200 ml schlenk tube, 3-benzoyl-1-(2-phenylethenyl)thymine (1.39 g, 3.13 mmol) was dissolved in dry pyridine (10 ml) with gentle heating under argon. The pyridine was evaporated and mixture was re-dissolved in dry DMF (15 ml). NaH (119 mg, 4.69 mmol, 95%) was added and the mixture was then stirred under argon at room temperature for 1 hr before **9** (508 mg, 0.89 mmol), dissolved in DMF (20 ml), was added. After 16 hr, the reaction mixture was quenched with water (100 ml), and extracted with EtOAc (30 ml × 3). The combined organic fractions were dried over $MgSO_4$, the solvent removed *in vacuo* and the residue purified *via* flash column chromatography (20% EtOAc in hexane) to yield the product (579 mg, 65%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.96 (4 H, d, *J* 7.4), 7.66 (2 H, t, *J* 7.4), 7.52 (4 H, t, *J* 7.6), 7.39 – 7.23 (10 H, m), 6.92 (2 H, s), 6.51 (2 H, d, *J* 8.4), 6.33 (2 H, d, *J* 8.5), 4.42 (4 H, d, *J* 3.6), 4.26 (2 H, brs), 4.19 (2 H, brs), 3.88 (2 H, brs), 3.36 (4 H, t, *J* 6.5), 2.83 – 2.61 (2 H, m), 1.85 (6 H, s), 1.62 (4 H, brs), 1.34 (6 H, d, *J* 6.6). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.7(C=O), 163.2(C=O), 148.9(C=O), 140.6(CH-Thymine), 138.5(ipso Ph), 135.0(CH-Ar), 131.7(ipso-Ar), 130.5(CH-Ar), 129.2(CH-Ar), 128.4(CH-Ar), 127.6(CH-Ar), 124.4(CH-Alkene), 121.6(CH-Alkene), 110.6(ipso thymine), 97.5 (ipso-Cp), 76.9 (ipso-Cp), 72.9 (CH_2), 70.1 (CH-Cp), 69.8 (CH-Cp), 68.3 (CH_2), 67.2 (CH-Cp), 39.8 (CH_2), 28.1 (CH), 19.4 (Me), 12.3 (Me). IR (cm^{-1}): 2927, 2858, 1746, 1702, 1651, 1598, 1092. MS (ES) (m/z) calcd for $C_{60}H_{58}N_4O_8{}^{56}FeNa$ 1041.3502, found 1041.3519 (M^++ Na). Mp = 76-78°C.

(*S*, *S*),(*pR*, *pR*)-2,2'-Bis(ethyl-5-methylpyrimidine-2,4(1H,3H)-dione)-1,1'-bis(4-(benzyloxy)butan-2-yl)ferrocene 11

To a 100 ml round bottom flask containing **10** (579 mg, 0.58 mmol) dissolved in EtOAc (10ml) was added $Pd(OH)_2$ (20% wt. on carbon, 465 mg, 1.05 mmol). The reaction was stirred under H_2 (ballon pressure) atmosphere at room temperature for 16hr, after which time the mixture was filtered through a short pad of celite to give a pale yellow solution. The solvent was evaporated and the residue stirred with $MeNH_2$ solution (40% in ethanol, 5 ml) for 10 mins before being evaporated under high vacuum (0.1 mm Hg). Purification *via* flash column chromatography (5% MeOH in DCM) yielded the product (288 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.55 (s, 3H), 6.98 (d, *J* = 1.4 Hz, 3H), 4.10 – 3.84 (m, 12H), 3.83 – 3.52 (m, 6H), 3.06 – 2.73 (m, 7H), 2.65 (ddd, *J* = 14.5, 10.5, 4.7 Hz, 4H), 2.00 – 1.85 (m, 3H), 1.81 (d, *J* = 1.1 Hz, 9H), 1.71 (qd, *J* = 8.4, 4.5 Hz, 2H), 1.43 (d, *J* = 4.5 Hz, 1H), 1.36 (d, *J* = 6.7 Hz, 9H), 7.38 – 7.16 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.5(C=O), 151.6(C=O), 140.9(CH-thymine), 110.4(ipso thymine), 94.3(ipso Cp), 82.1(ipso Cp), 70.1(CH-Cp), 67.4(CH-Cp), 65.3(CH-Cp), 60.3(CH_2), 49.5(CH_2), 42.9(CH_2), 27.0(CH), 26.4(CH_2), 19.1(Me), 12.3(Me). IR (cm^{-1}): 3480, 2928, 2867, 1701, 1651, 1074 (br), 2978. MS (ES) (m/z) calcd for $C_{32}H_{42}N_4O_6{}^{56}FeNa$ 657.2351, found 657.2356 (M^++ Na). Mp = 82-84°C.

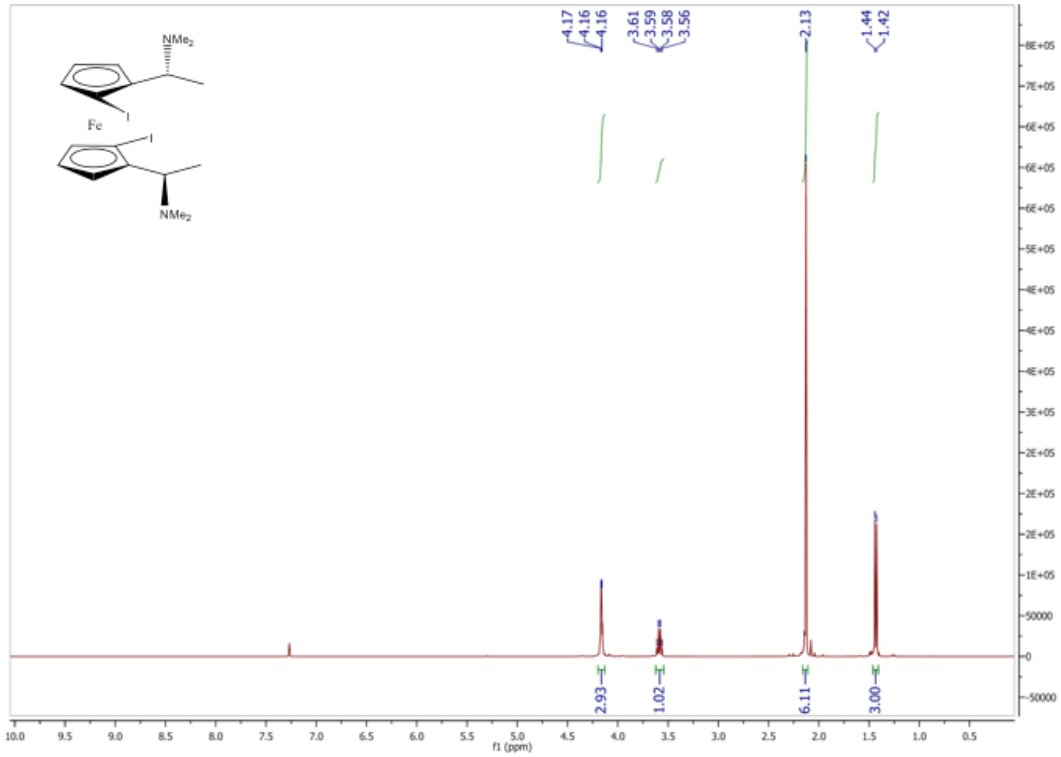
(*S*, *S*),(*pR*, *pR*)-2,2'-Bis(ethyl-5-methylpyrimidine-2,4(1H,3H)-dione)-1,1'-bis(4,4'-dimethoxytrityl)butan-2-yl)ferrocene 12

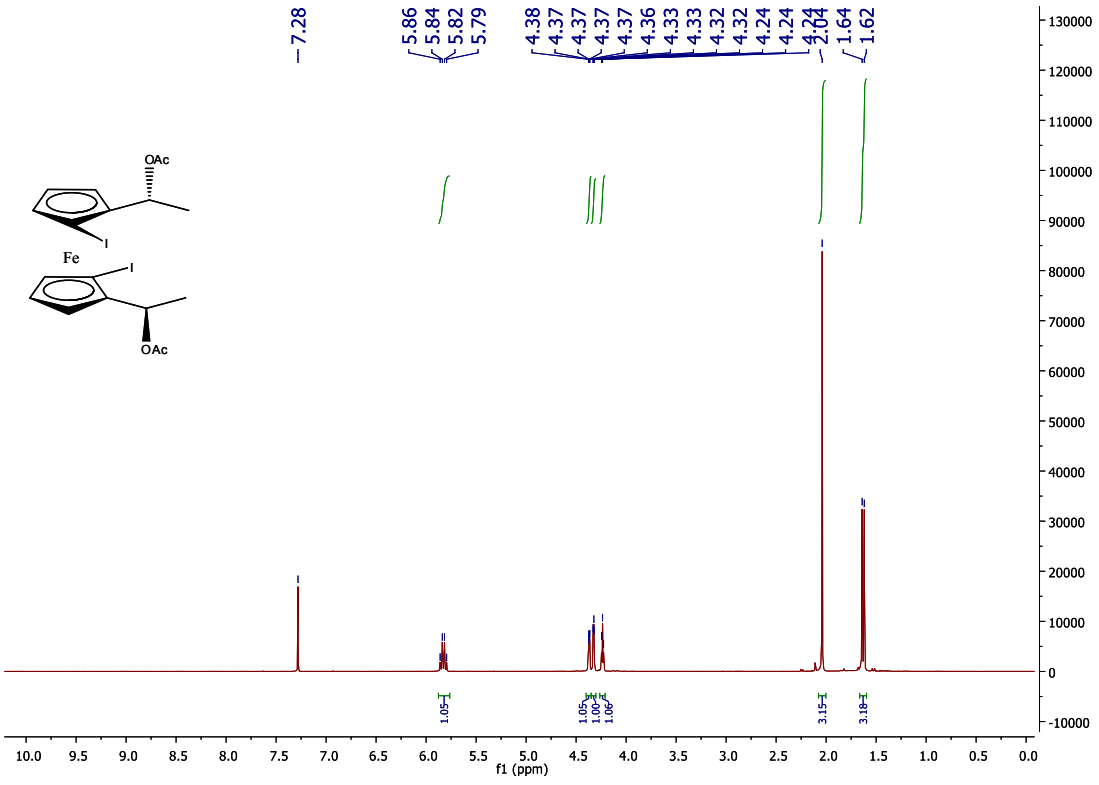
To a 100 ml round bottom flask under argon containing **11** (288 mg, 0.45 mmol) dissolved in THF (15ml) were added DMT-Cl (154 mg, 0.45 mmol), *N*,*N*-Diisopropylethylamine (0.08 ml, 0.45 mmol) and DMAP (11 mg, 0.09 mmol). The reaction was stirred under argon for 16 hr at room temperature, after which time the reaction mixture was quenched with saturated $NaHCO_3$ (10 ml) and extracted with DCM (15 ml × 3). The combined organic fractions were dried over Na_2SO_4, the solvent removed *in vacuo* and the residue purified *via* flash column chromatography (5% MeOH in DCM) to yield the product (193 mg, 45%). ^{1}H NMR (300 MHz, CDC_{l3}) δ: 9.58 (s, 1H), 7.45 – 7.35 (m, 1H), 7.35 – 7.15 (m, 5H), 7.06 (d, *J* = 1.4 Hz, 1H), 6.85 – 6.77 (m, 2H), 6.62 (d, *J* = 1.3 Hz, 1H), 4.04 – 3.87 (m, 3H), 3.79 (s, 3H), 3.77 – 3.49 (m, 2H), 3.08 (t, *J* = 6.4 Hz, 1H), 2.97 – 2.52 (m, 2H), 1.89 (d, *J* = 1.1 Hz, 1H), 1.72 (d, *J* = 1.2 Hz, 1H), 1.35 (d, *J* = 6.7 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.6(C=O), 164.5(C=O), 158.4(ipso-DMT), 151.3(C=O), 151.2(C=O), 145.2(ipso-Ar), 140.8(CH-thymine), 136.5(ipso-Ar), 136.4(ipso-Ar), 130.0(CH-Ar), 128.1(CH-Ar), 127.7(CH-Ar), 126.8(CH-Ar), 113.0(CH-Ar), 110.7(ipso thymine), 110.2(ipso thymine), 94.7(ipso Cp), 94.1(ipso Cp), 86.0(ipso Cp), 81.6(ipso Cp), 70.6(CH-Cp), 67.9(CH-Cp), 65.9(CH-Cp), 65.7(CH-Cp), 61.5(CH_2), 60.2(CH_2), 55.2(OMe), 49.8(CH_2), 49.1(CH_2), 43.3(CH_2), 40.4(CH_2), 27.9(CH), 27.2(CH_2), 27.0(CH_2), 26.9(CH), 20.1(Me), 19.3(Me), 12.3(Me), 12.1(Me) (2 CH-Cp signals and other CH-thymine signal unobserved due to coincidental peaks). MS (ES) (m/z) calcd for $C_{53}H_{60}N_4O_8{}^{56}FeNa$ 959.3658, found 959.3682 (M^++ Na).

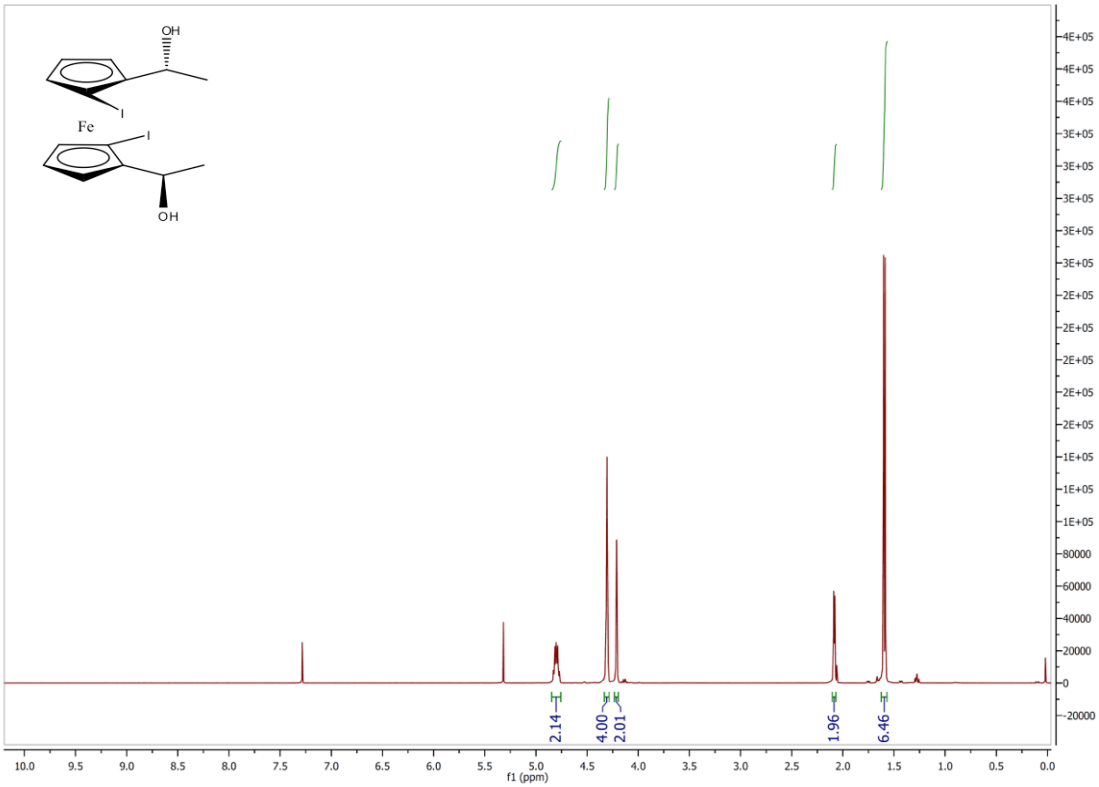
Phosphoramidite (Cpmpound 13)

Compound **12** (192 mg, 0.20 mmol), azeotroped with dry acetonitrile (2 x 10 ml), was re-dissolved in anhydrous dichloromethane (8.0 ml). To the resulting pale yellow solution was added DIPEA (0.70 ml, 4.0 mmol), followed by 2-cyanoethyl *N, N*-diisopropyl chlorophosphoramidite (0.060 ml, 0.27 mmol). The reaction was stirred overnight at room temperature under argon. Degassed ethyl acetate (20 ml) was then added and the mixture washed with degassed sat. $NaHCO_3$ (10 ml), brine (10 ml) and then dried over anhydrous sodium sulphate. The solvents were removed under vacuum and the residue purified on a silica gel column (25 g silica, ethyl acetate with 1% triethylamine) to yield the product as a foam (199 mg, 87%), R_f 0.42 (ethyl acetate and 1% triethylamine). ^{31}P NMR (121 MHz, $CDCl_3$) δ: 147.1 and 146.9 ppm; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.93 (s, br, 2H, NH), 7.38 (d, 2H, Ar-H), 7.32-7.17 (m, 9H, Ar-H), 6.89 (d, 1H), 6.81-6.77 (d, 4H, Ar-H), 6.65 (s, 1H), 3.95-3.77 (m, br, 12H), 3.78 (s, 6H, OCH_3), 3.67-3.47 (br, m, 4H), 3.11-3.01 (br, 2H), 2.91-2.75 (br, 2H), 2.75-2.50 (br, 6H), 1.86 (s, 3H, 5-Me), 1.73 (s, 3H, Me), 1.72-1.61 (m, 2H,), 1.58-1.42 (br, 2H), 1.38-1.10 (m, 20H, CH, Me); m/z (ES), calculated for $C_{62}H_{77}N_6O_9FePNa$, 1159.4734 , found 1159.4737

2. ^{1}H NMR spectra of compounds 2-12



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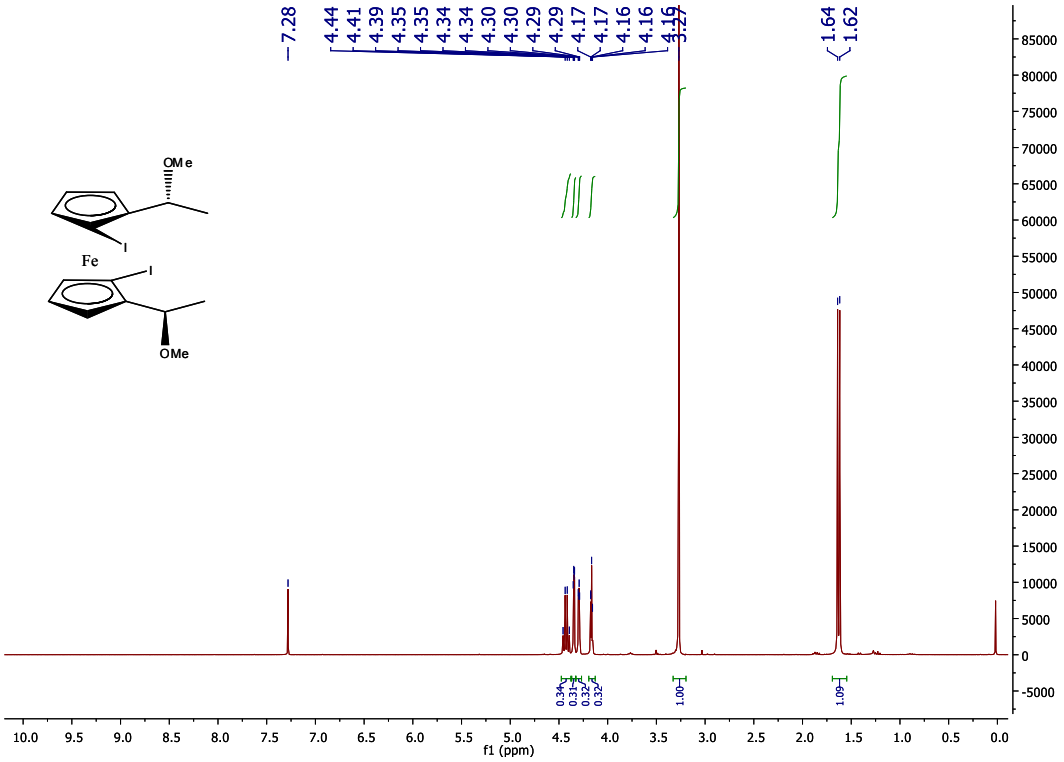
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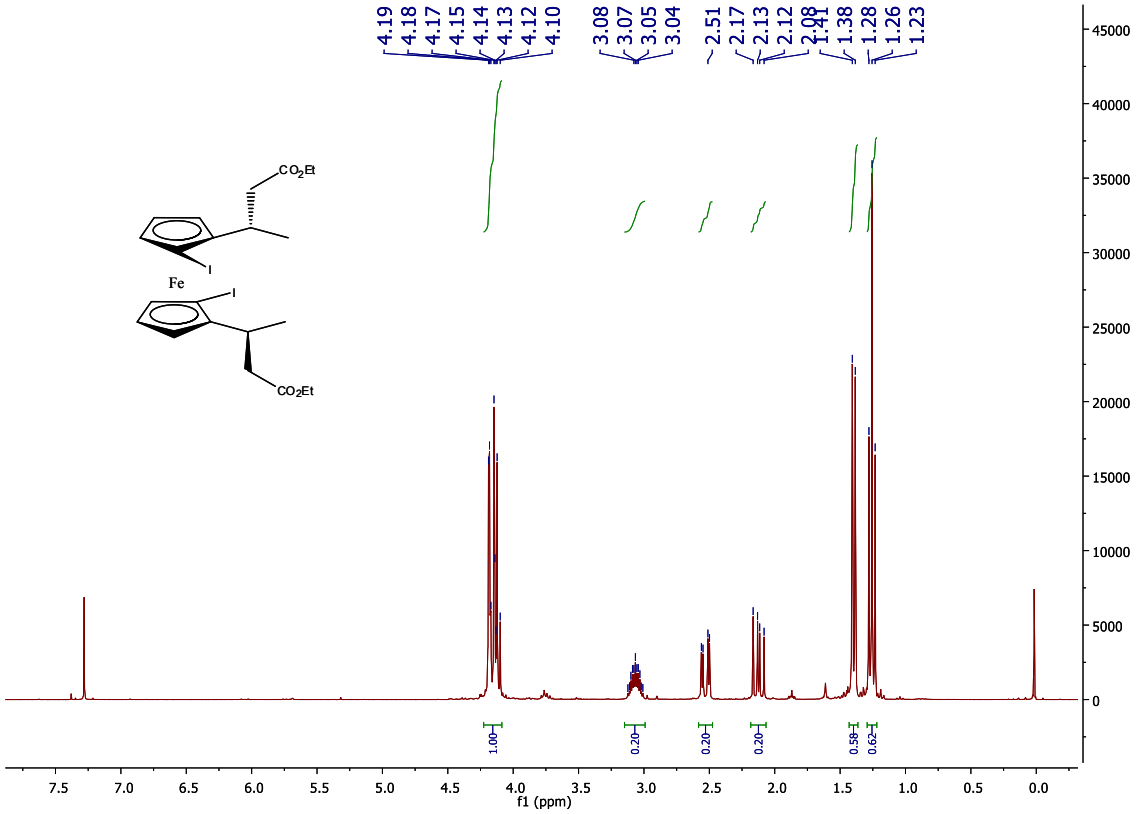
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CO2Et
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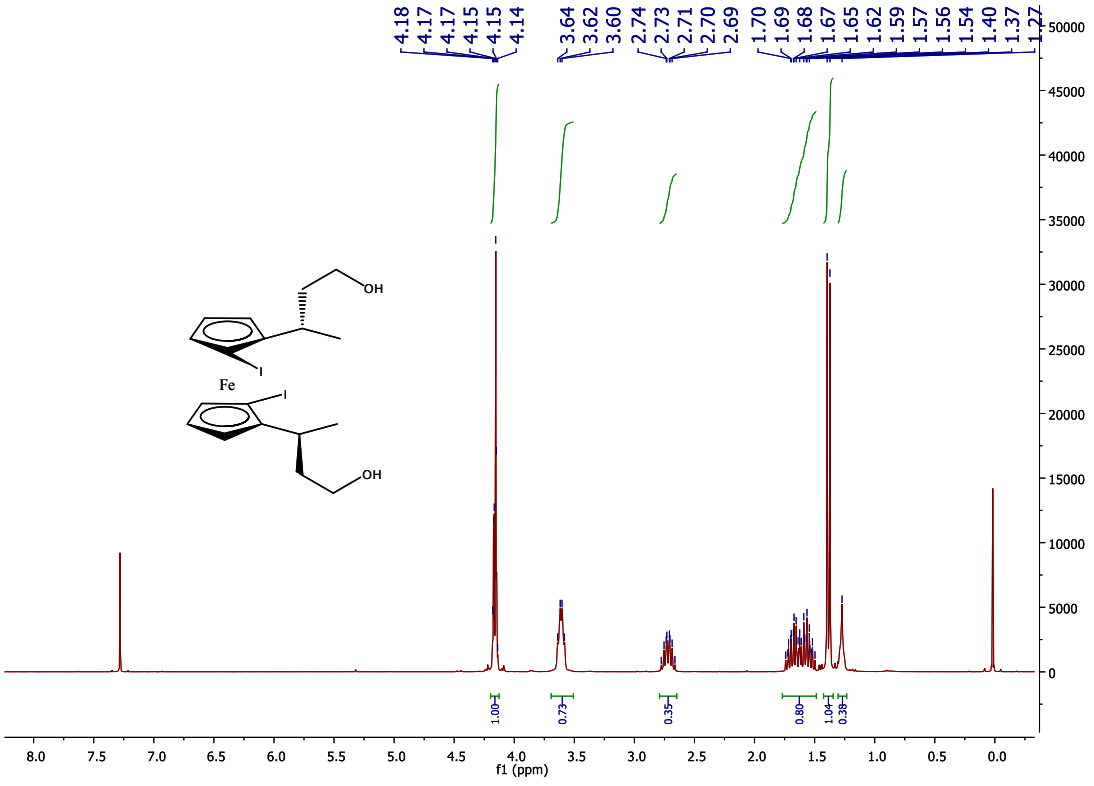
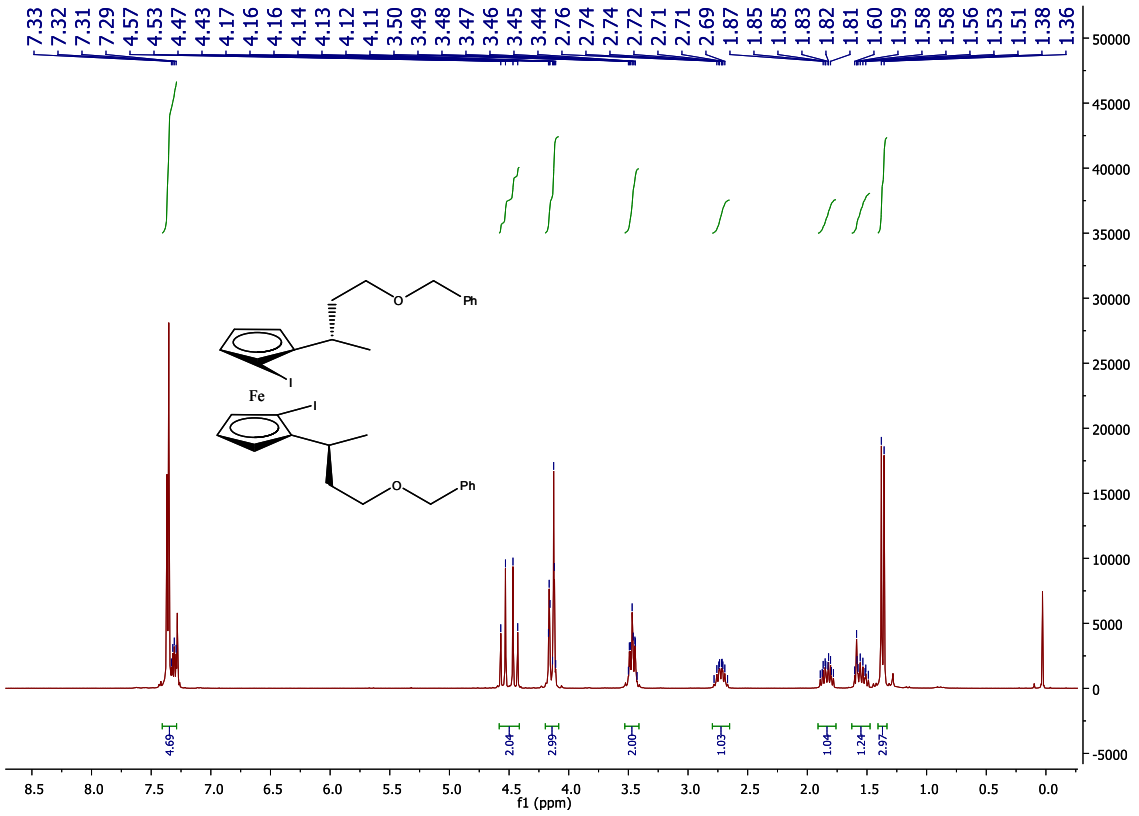
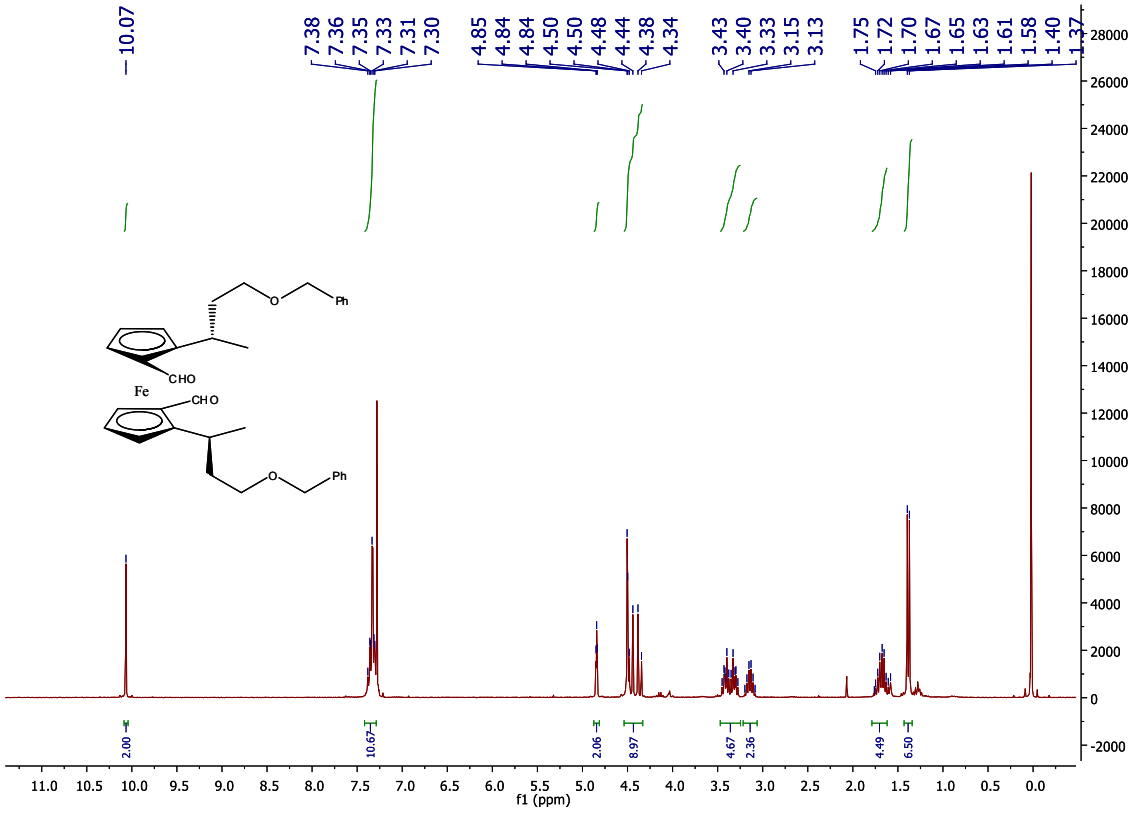
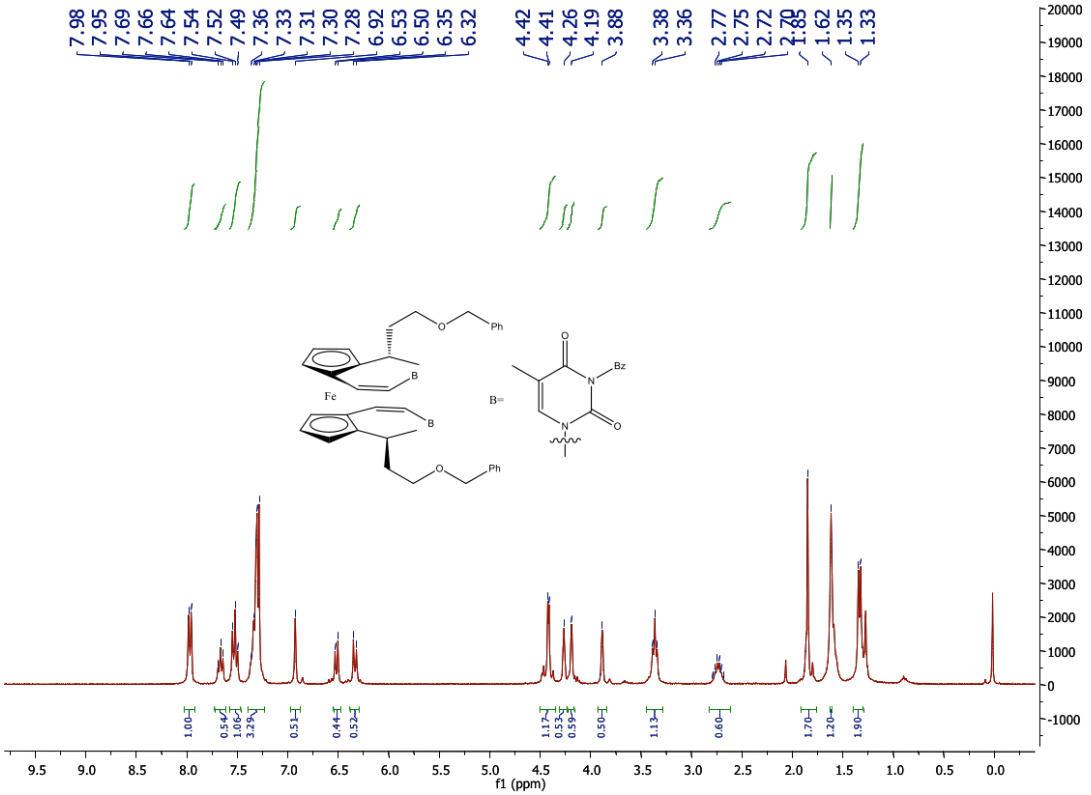
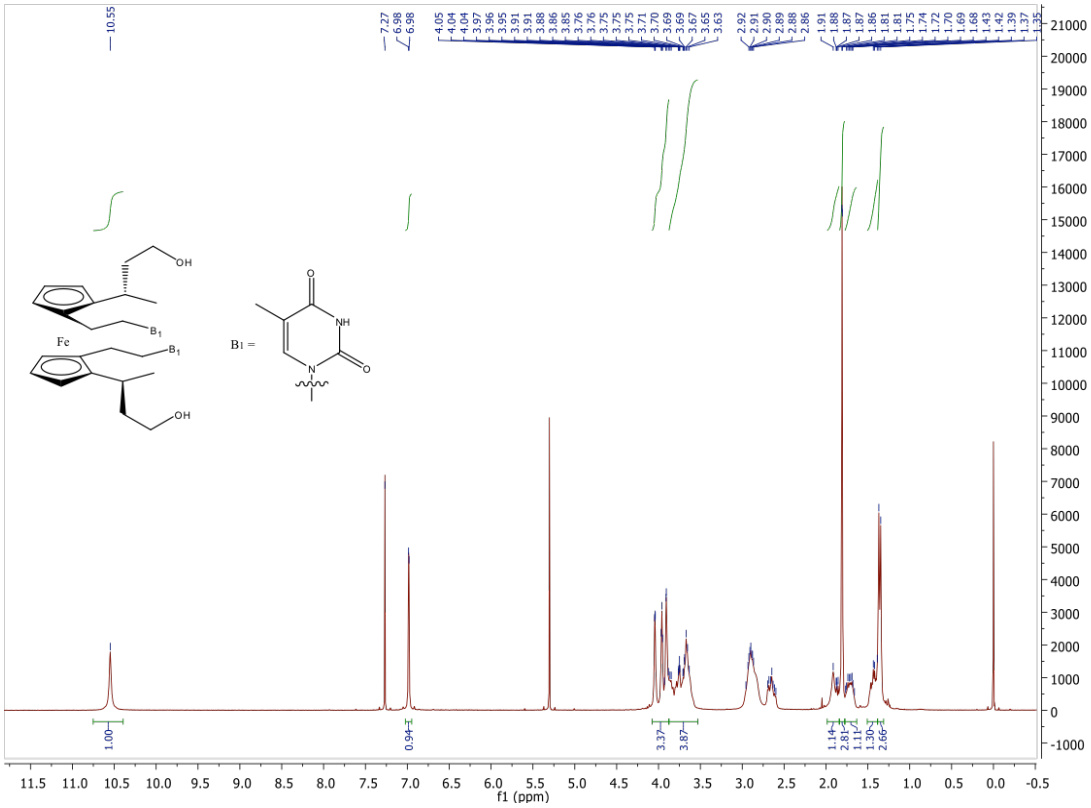
0.20
0.20
0.20
0.58
0.62
f1 (ppm)

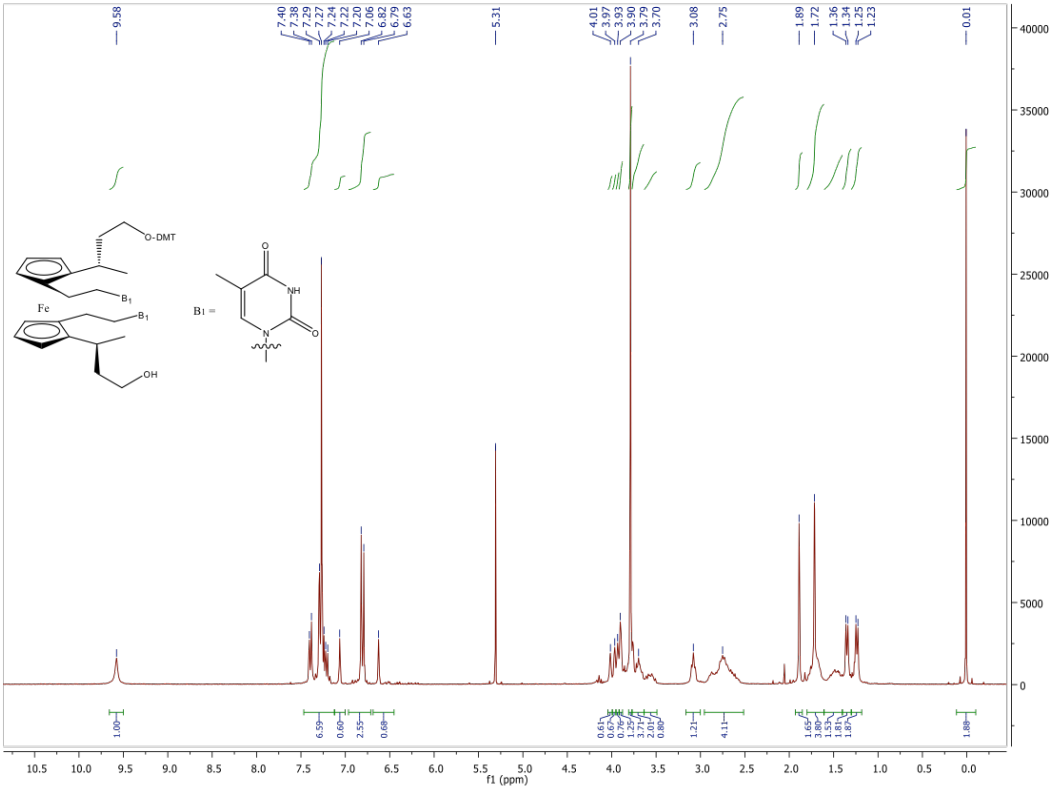

4.18
4.17
4.17
4.15
4.15
4.14
3.64
3.62
3.60
2.74
2.73
2.71
2.70
2.69
1.70
1.69
1.68
1.67
1.65
1.62
1.59
1.57
1.56
1.54
1.40
1.37
1.22
OH
Fe
I
OH
1.00
0.73
0.35
0.80
1.04
0.38
f1 (ppm)


7.33
7.32
7.31
7.29
4.57
4.53
4.47
4.43
4.17
4.16
4.16
4.14
4.13
4.12
4.11
3.50
3.49
3.48
3.47
3.46
3.45
3.44
2.76
2.74
2.74
2.72
2.71
2.71
2.69
1.87
1.85
1.85
1.83
1.82
1.81
1.60
1.59
1.58
1.58
1.56
1.53
1.51
1.38
1.36
Ph
O
I
Fe
I
O
Ph
4.69
2.04
2.99
2.00
1.03
1.04
1.24
2.97
f1 (ppm)

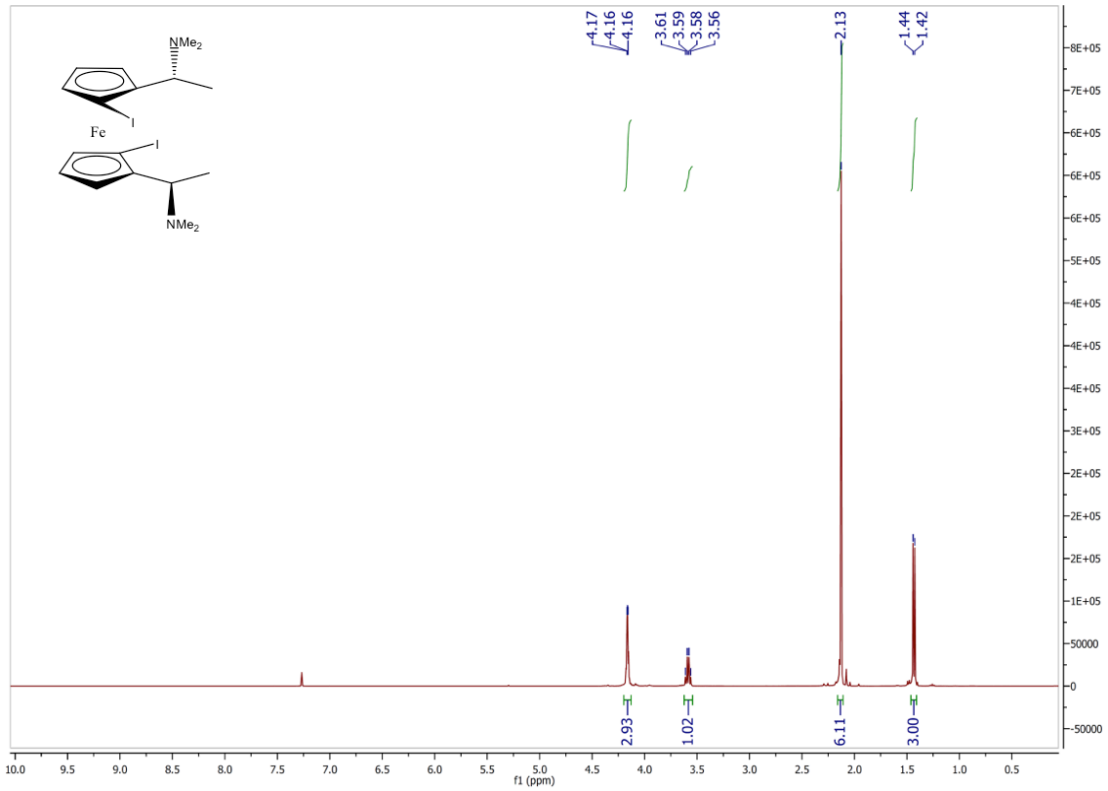

10.07
7.38
7.36
7.35
7.33
7.31
7.30
4.85
4.84
4.84
4.50
4.48
4.44
4.38
4.34
3.43
3.40
3.33
3.15
3.13
1.75
1.72
1.70
1.67
1.65
1.63
1.61
1.58
1.40
1.37
O
Ph
CHO
Fe
CHO
O
Ph
2.00
10.67
2.06
8.97
4.67
2.36
4.49
6.50
f1 (ppm)

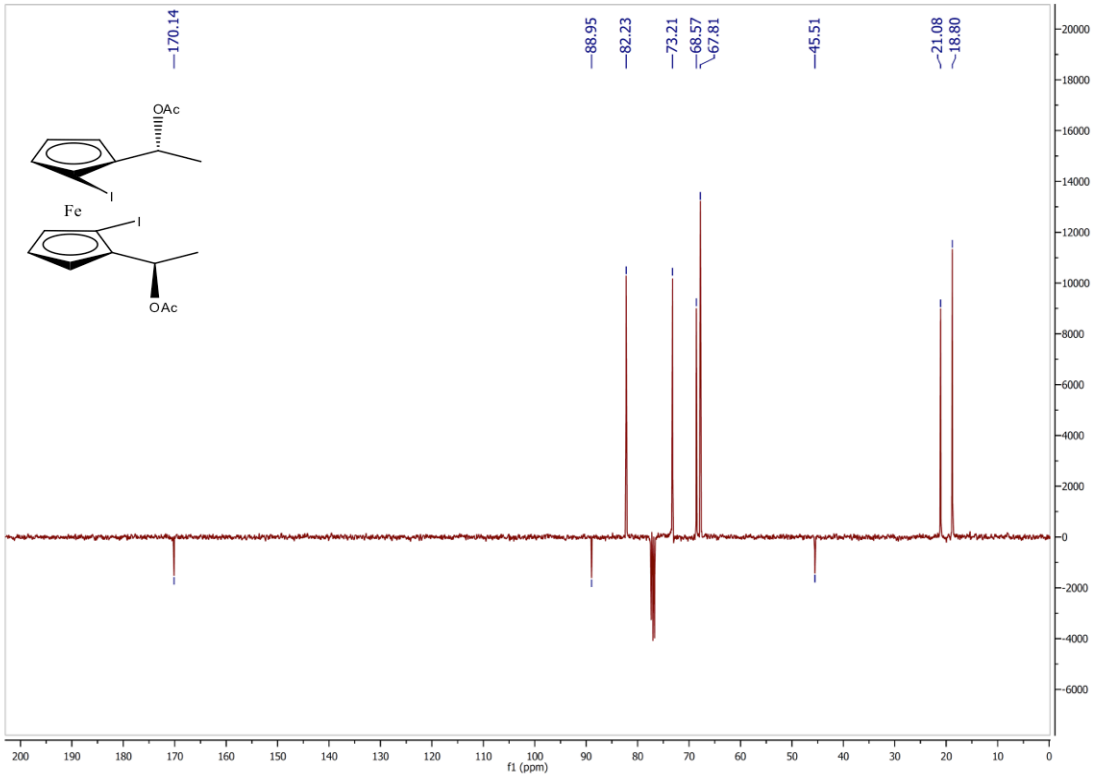

7.98
7.95
7.69
7.66
7.64
7.54
7.52
7.49
7.36
7.33
7.31
7.30
7.28
6.92
6.53
6.50
6.35
6.32
4.42
4.41
4.26
4.19
3.88
3.38
3.36
2.77
2.75
2.72
1.62
1.35
1.33
Fe
B=
Bz
Ph
f1 (ppm)

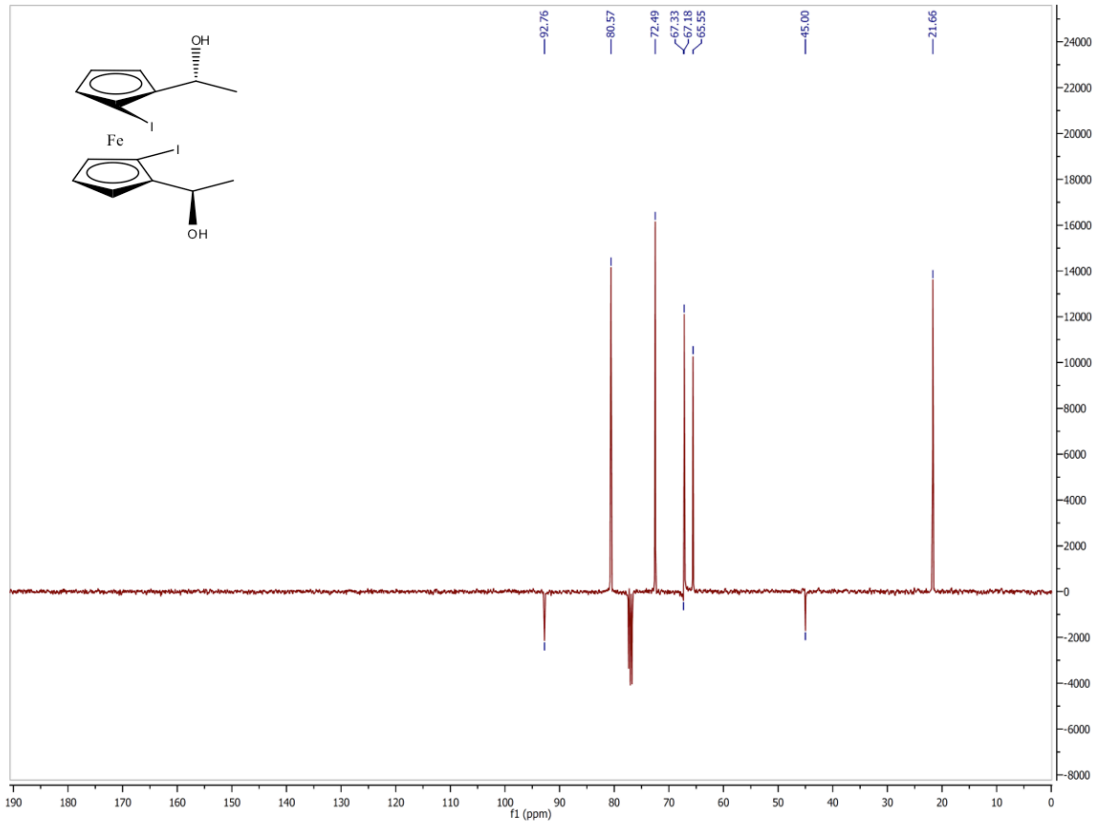

10.55
7.27
6.98
6.98
Fe
B1 =
OH
NH
f1 (ppm)

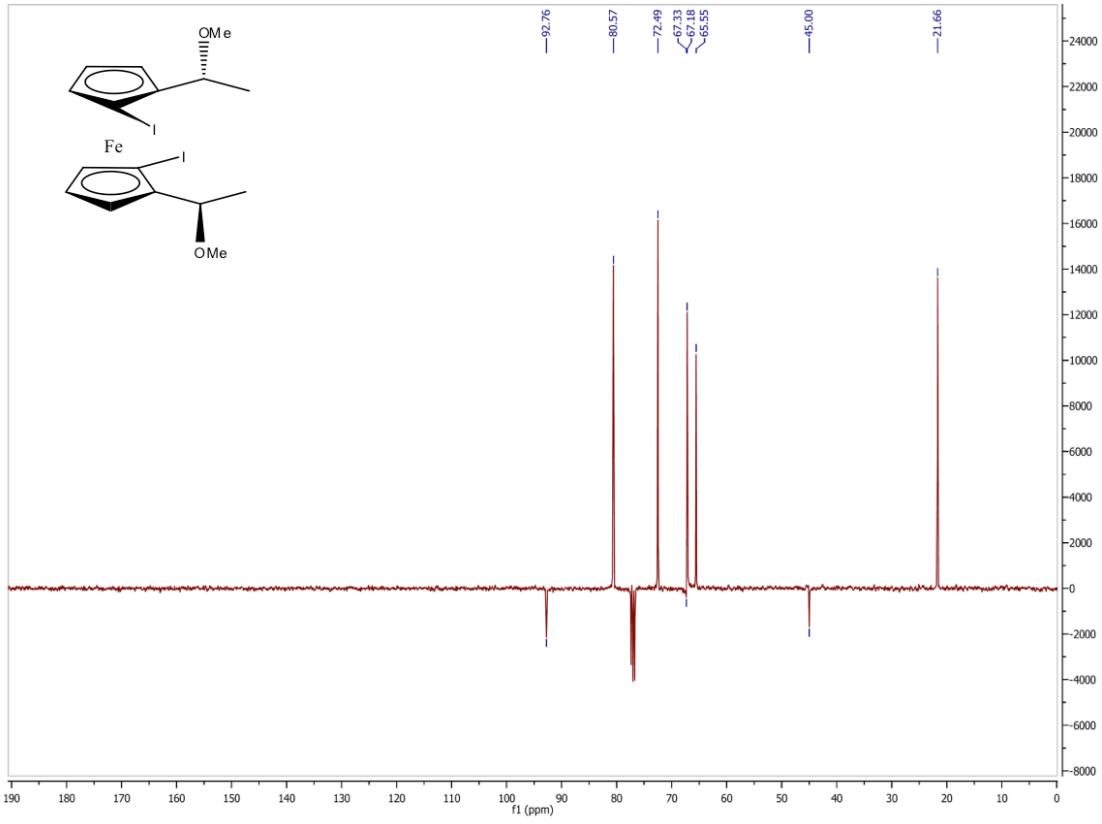

9.58
7.40
7.38
7.29
7.27
7.24
7.22
7.20
7.06
6.82
6.79
6.63
5.31
4.01
3.97
3.93
3.90
3.79
3.70
3.08
2.75
1.89
1.72
1.36
1.34
1.25
1.23
0.01
O-DMT
Fe
B1
B1 =
NH
N
O
OH
f1 (ppm)

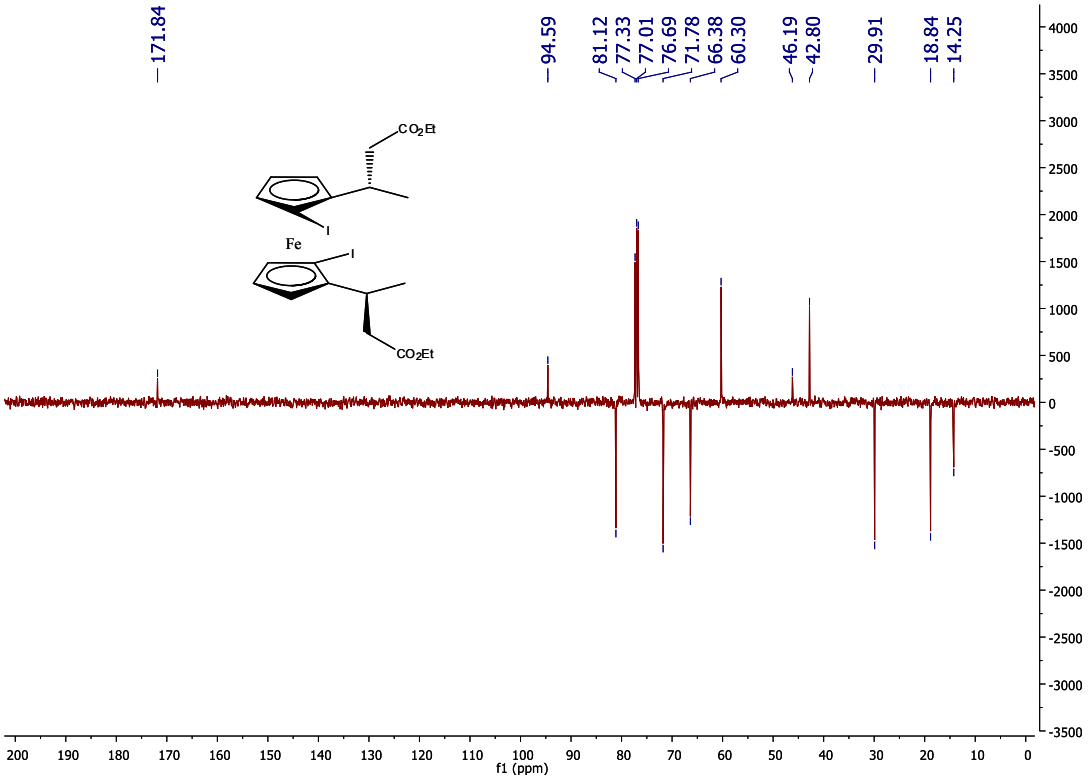
3. ^{13}C NMR spectra of compounds 2-12

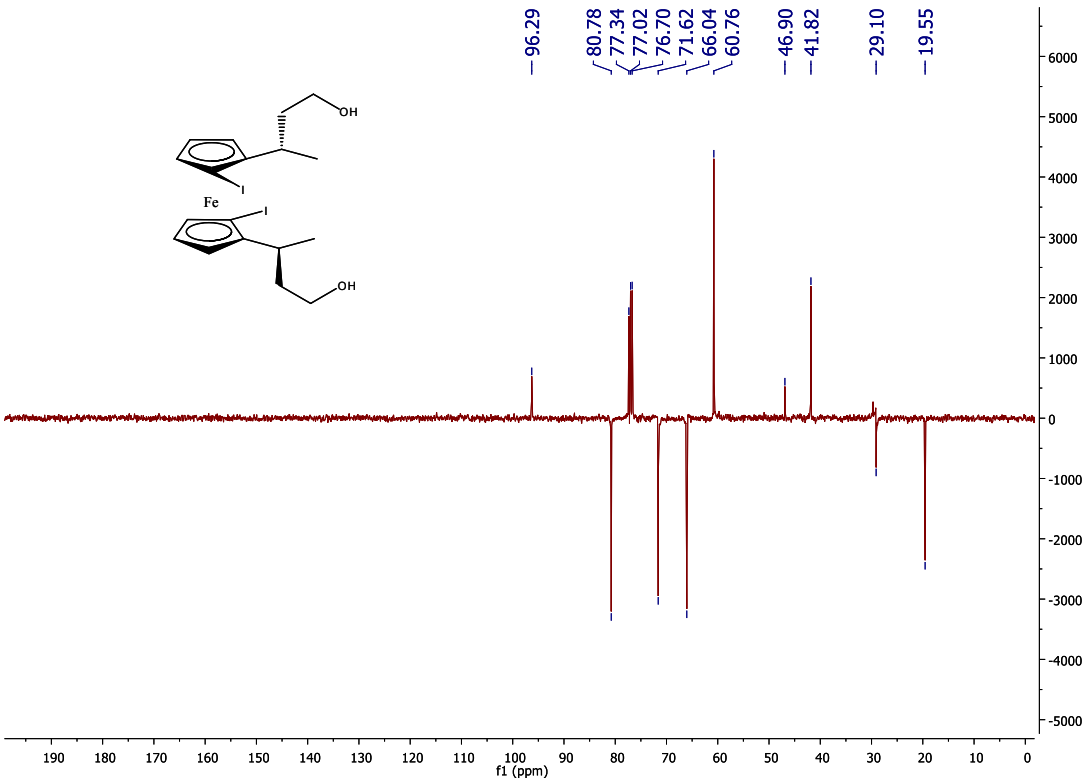


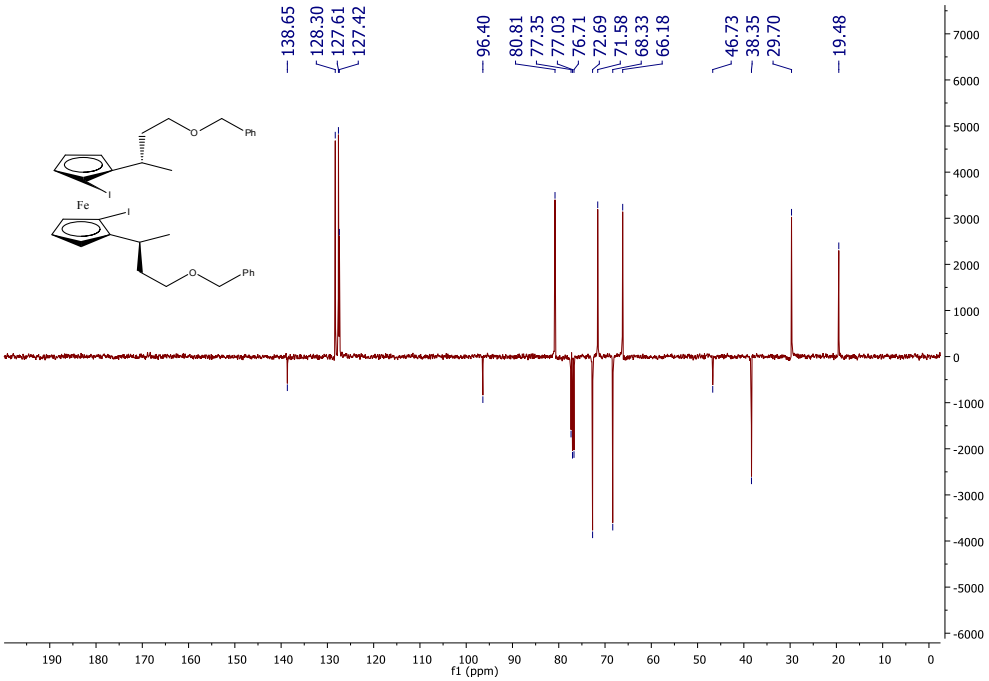


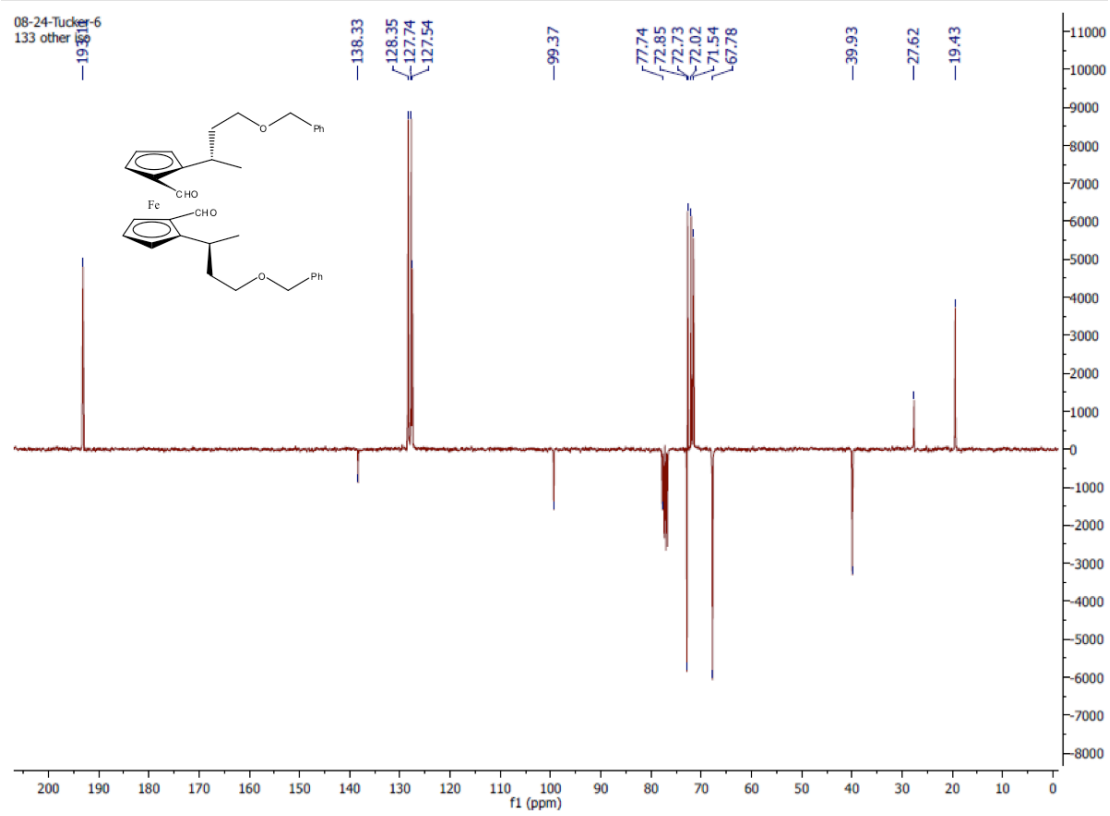

OH
I
Fe
I
OH
92.76
80.57
72.49
67.33
67.18
65.55
45.00
21.66
f1 (ppm)

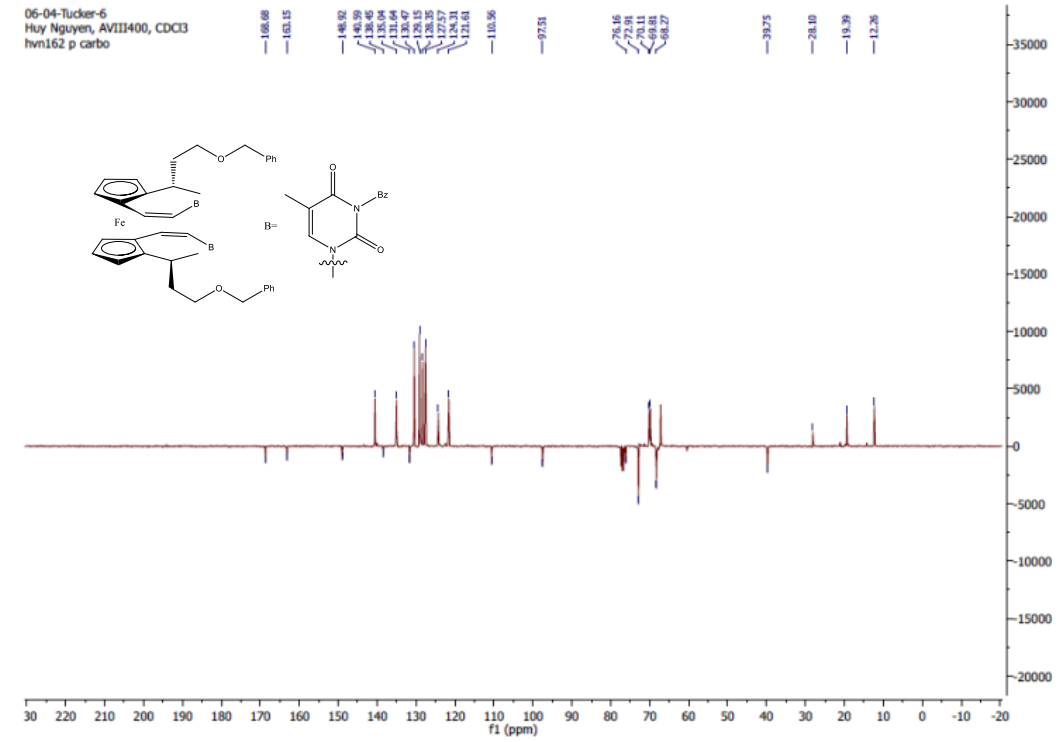

OMe
I
Fe
I
OMe
92.76
80.57
72.49
67.33
67.18
65.55
45.00
21.66
f1 (ppm)

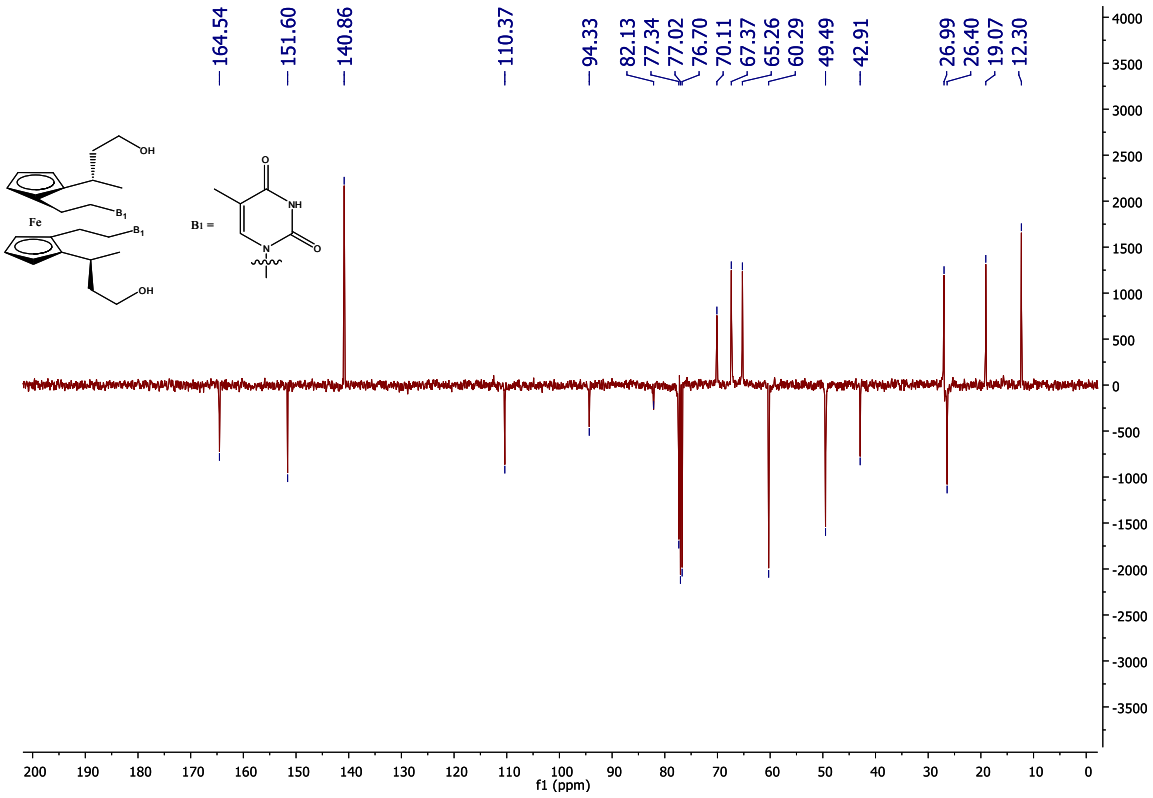

171.84
94.59
81.12
77.33
77.01
76.69
71.78
66.38
60.30
46.19
42.80
29.91
18.84
14.25
CO2Et
Fe
I
CO2Et
f1 (ppm)

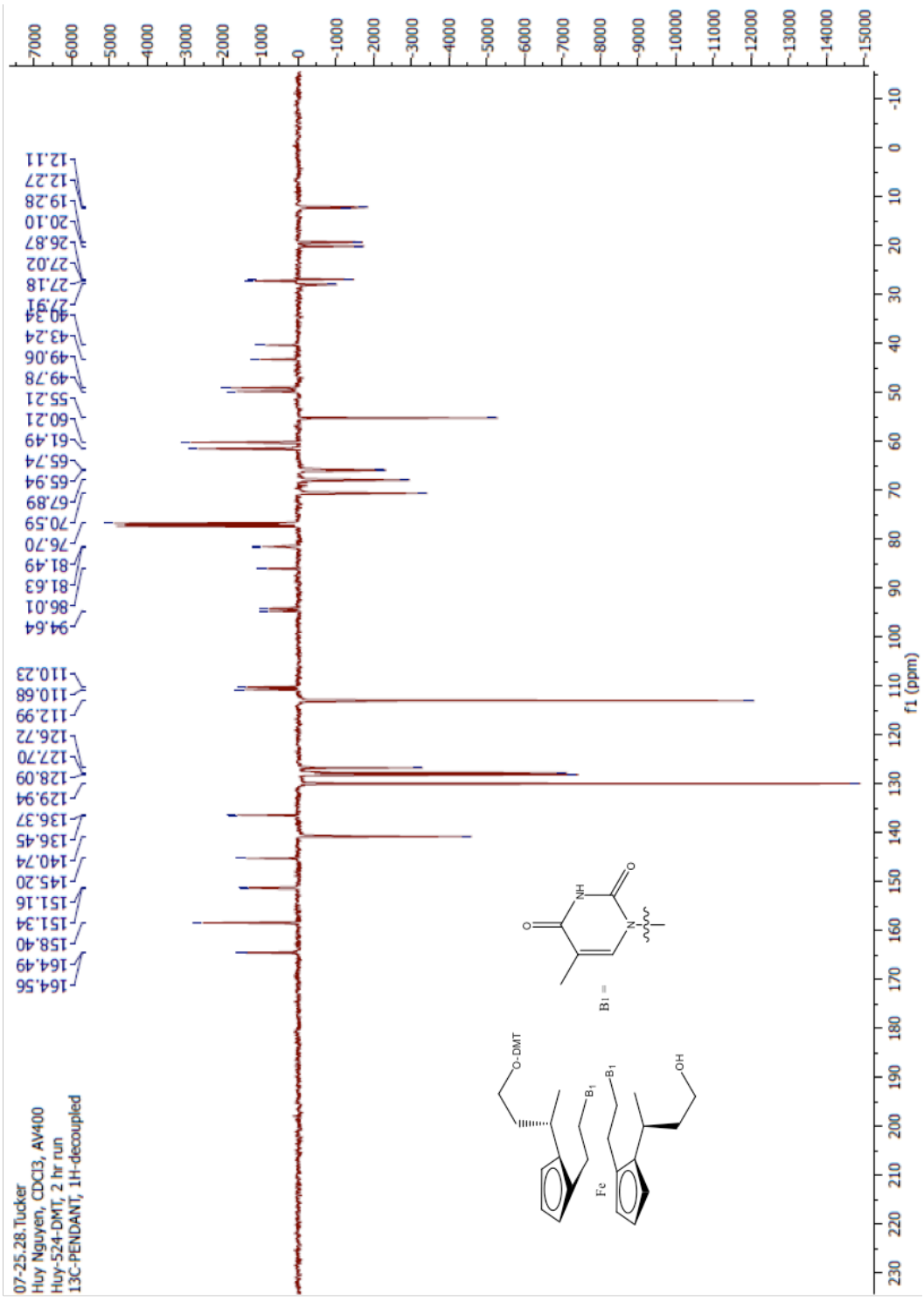

96.29
80.78
77.34
77.02
76.70
71.62
66.04
60.76
46.90
41.82
29.10
19.55
OH
Fe
I
OH
f1 (ppm)


138.65
128.30
127.61
127.42
96.40
80.81
77.35
77.03
76.71
72.69
71.58
68.33
66.18
46.73
38.35
29.70
19.48
Ph
I
Fe
I
O
Ph
f1 (ppm)


08-24-Tucker-6
133 other
138.33
128.35
127.74
127.54
99.37
77.74
72.85
72.73
72.02
71.54
67.78
39.93
27.62
19.43
Ph
O
CHO
Fe
CHO
O
Ph
f1 (ppm)

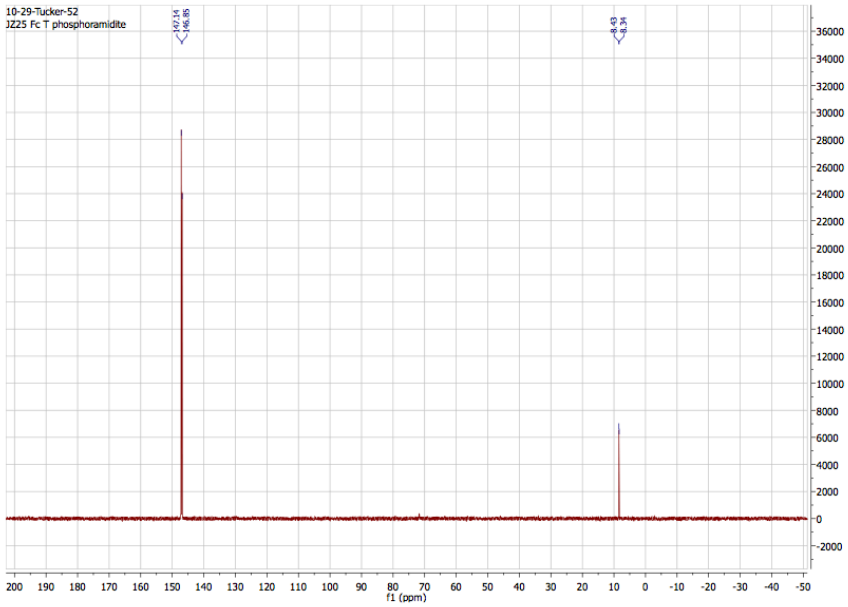

06-04-Tucker-6
Huy Nguyen, AVIII400, CDCl3
hvn162 p carbo
168.68
163.15
148.92
140.59
138.45
135.04
131.64
130.47
128.35
127.57
124.31
121.61
110.96
97.51
76.16
73.91
70.11
69.81
68.27
39.75
28.10
19.39
12.26
Fe
B=
Bz
Ph
f1 (ppm)


164.54
151.60
140.86
110.37
94.33
82.13
77.34
77.02
76.70
70.11
67.37
65.26
60.29
49.49
42.91
26.99
26.40
19.07
12.30
Fe
B1 =
OH
NH
f1 (ppm)

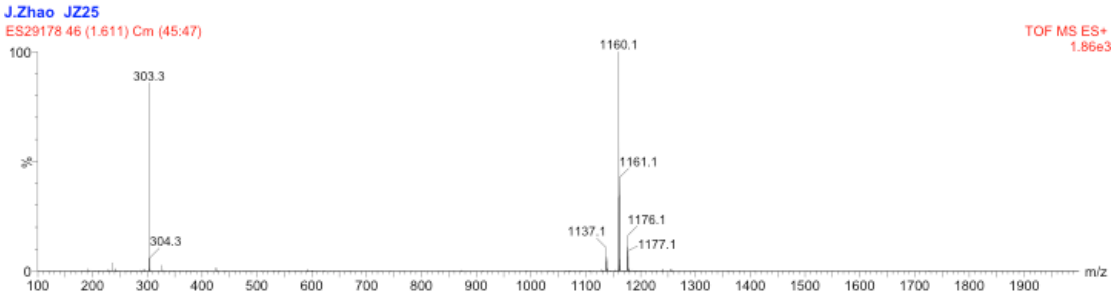

12.11
12.27
19.28
20.10
26.87
27.02
27.18
27.91
40.34
43.24
49.06
49.78
55.21
60.21
61.49
65.74
65.94
67.89
70.59
76.70
81.49
81.63
86.01
94.64
110.23
110.68
112.99
126.72
127.70
128.09
129.94
136.37
136.45
140.74
145.20
151.16
151.34
158.40
164.49
164.56
07-25.28.Tucker
Huy Nguyen, CDCl3, AV400
Huy-524-DMT, 2 hr run
13C-PENDANT, 1H-decoupled
f1 (ppm)
O-DMT
OH
Fe
B1

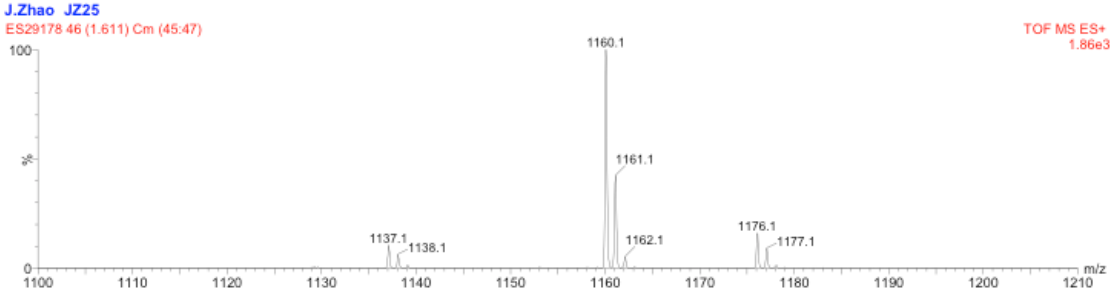
4. Compound 13 –Characterisation

(a) ^{31}P NMR spectrum:



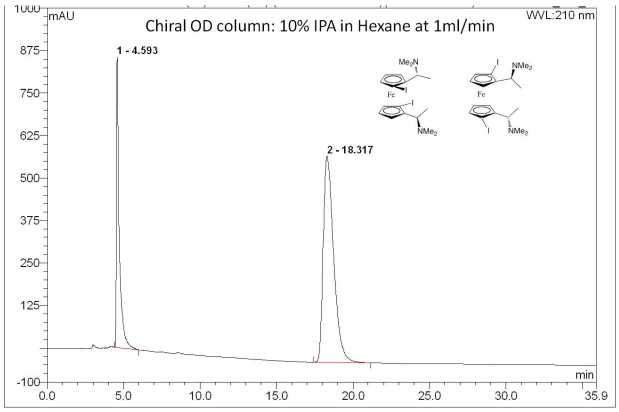
(b) ESMS – low resolution



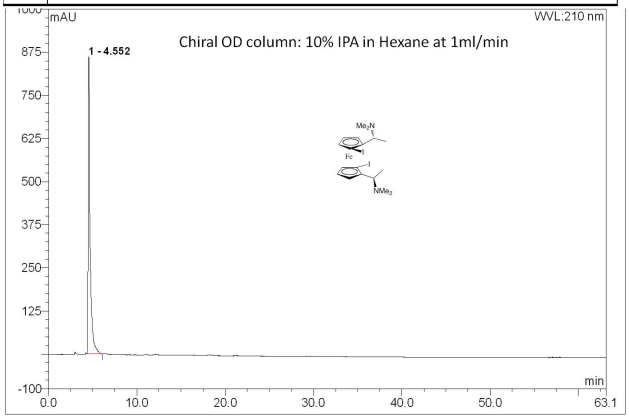


5. Chiral HPLC traces

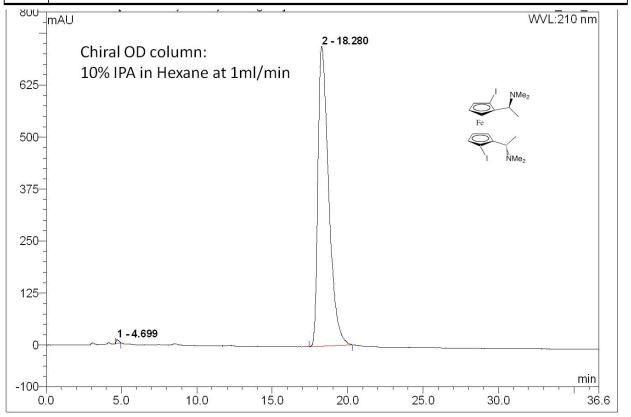
Compound **2** and enantiomer



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	4.59	n.a.	856.722	187.937	28.15	n.a.	BMB
2	18.32	n.a.	608.371	479.647	71.85	n.a.	BMB
Total:			1465.093	667.584	100.00	0.000	

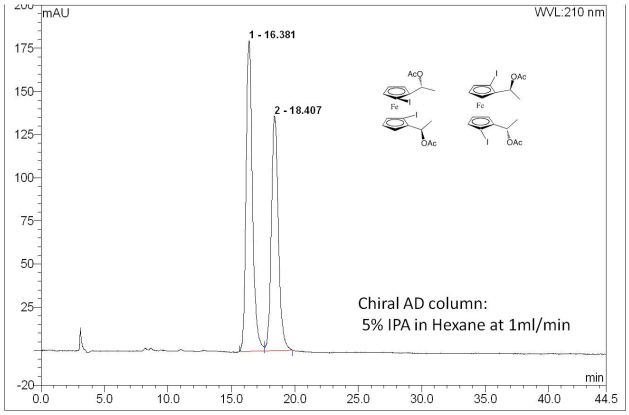


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	4.55	n.a.	859.945	206.296	100.00	n.a.	BMB
Total:			859.945	206.296	100.00	0.000	

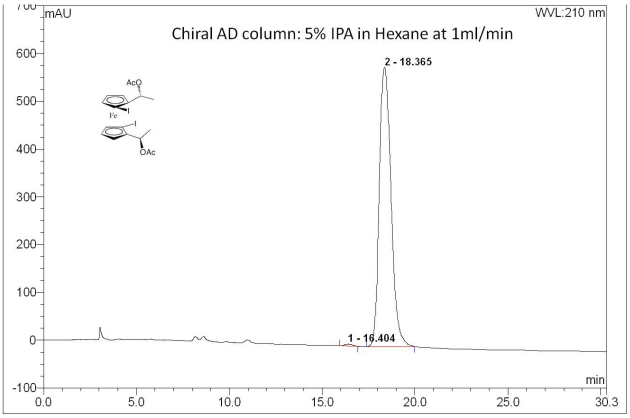


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	4.70	n.a.	9.575	1.849	0.31	n.a.	BMB*
2	18.28	n.a.	720.530	593.685	99.69	n.a.	BMB
Total:			730.105	595.534	100.00	0.000	

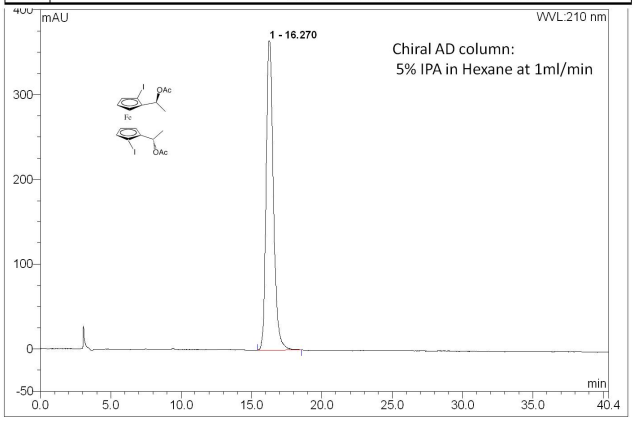
Compound **3** and enantiomer



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.38	n.a.	179.899	104.832	54.69	n.a.	BM
2	18.41	n.a.	135.914	86.847	45.31	n.a.	MB
Total:			315.813	191.678	100.00	0.000	

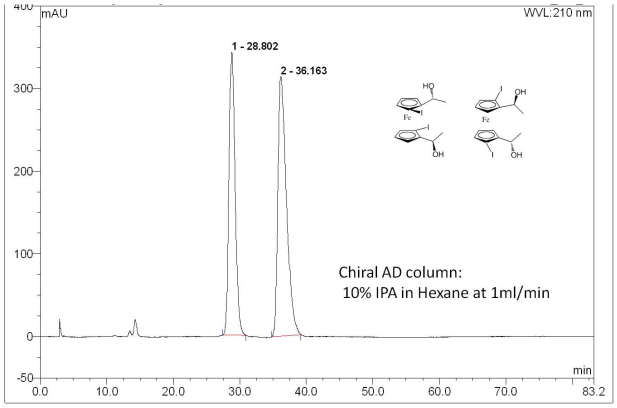


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.40	n.a.	4.212	1.963	0.46	n.a.	BMB*
2	18.36	n.a.	583.896	428.726	99.54	n.a.	BMB
Total:			588.108	430.689	100.00	0.000	

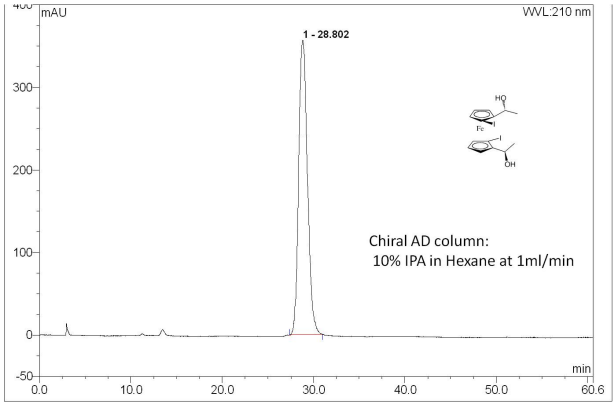


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.27	n.a.	364.843	215.757	100.00	n.a.	BMB
Total:			364.843	215.757	100.00	0.000	

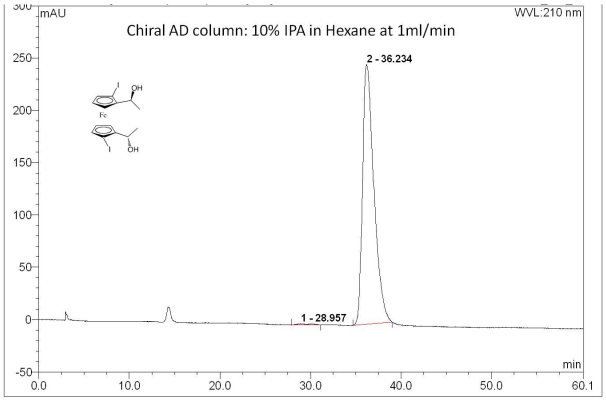
Compound **4** and enantiomer



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	28.80	n.a.	342.160	372.365	44.34	n.a.	BMB
2	36.16	n.a.	314.034	467.339	55.66	n.a.	BMB
Total:			656.193	839.704	100.00	0.000	

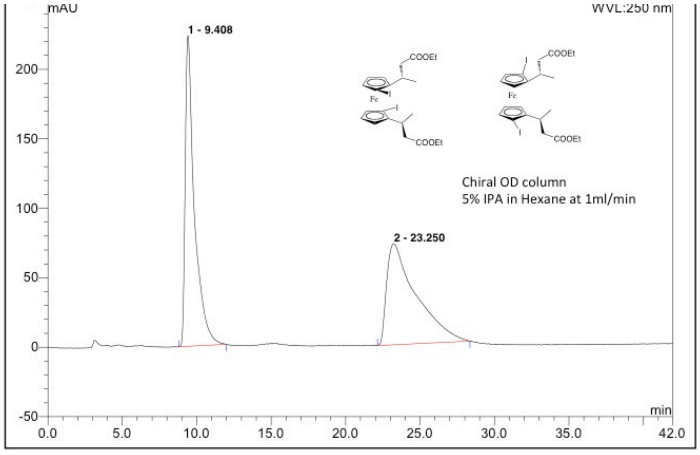


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	28.80	n.a.	356.756	395.734	100.00	n.a.	BMB
Total:			356.756	395.734	100.00	0.000	

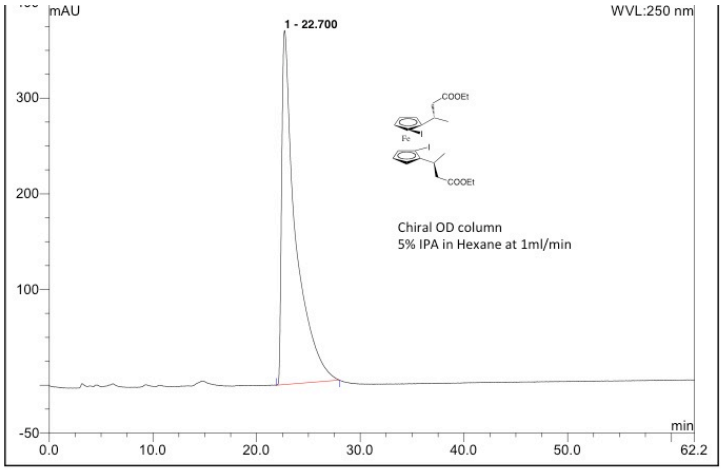


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	28.96	n.a.	0.902	1.617	0.44	n.a.	BMB*
2	36.23	n.a.	248.288	361.857	99.56	n.a.	BMB
Total:			249.190	363.475	100.00	0.000	

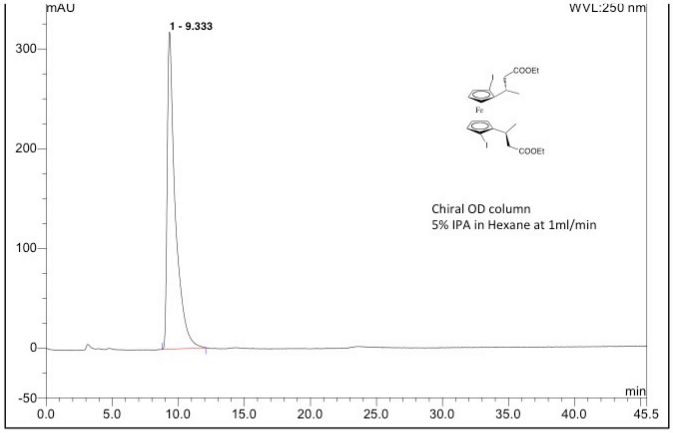
Compound **6** and enantiomer



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.41	n.a.	223.599	159.973	49.04	n.a.	BMB
2	23.25	n.a.	72.685	166.214	50.96	n.a.	BMB
Total:			296.284	326.186	100.00	0.000	

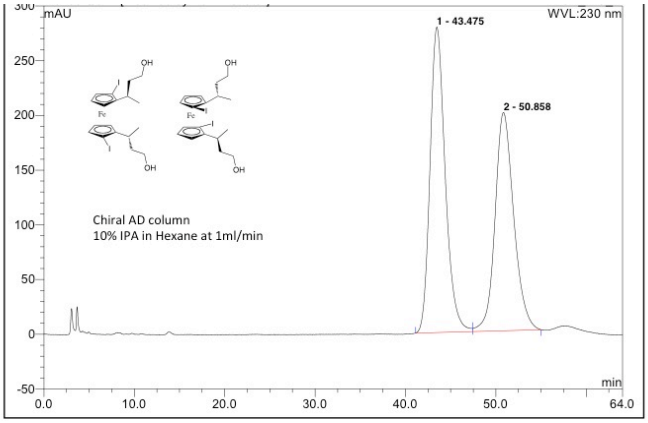


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.70	n.a.	370.104	574.686	100.00	n.a.	BMB
Total:			370.104	574.686	100.00	0.000	

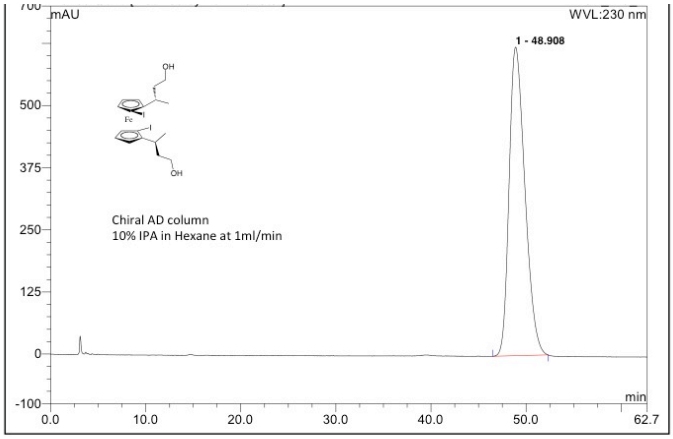


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.33	n.a.	318.089	226.195	100.00	n.a.	BMB
Total:			318.089	226.195	100.00	0.000	

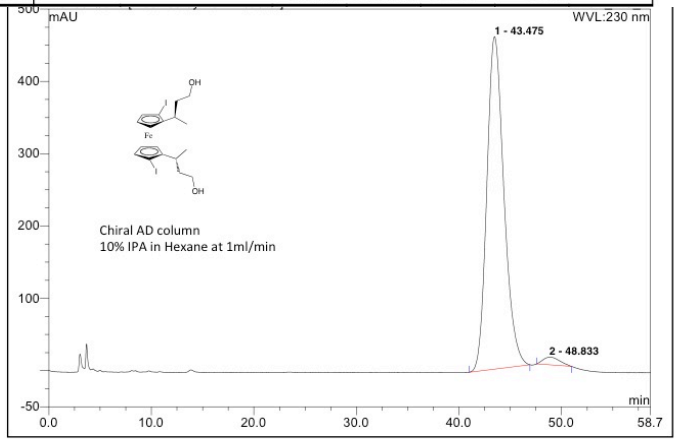
Chiral HPLC Compound **7** and enantiomer



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	43.48	n.a.	279.315	543.909	53.24	n.a.	BM
2	50.86	n.a.	199.498	477.627	46.76	n.a.	MB
Total:			478.813	1021.536	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	48.91	n.a.	620.842	1195.063	100.00	n.a.	BMB*
Total:			620.842	1195.063	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	43.48	n.a.	459.681	886.055	97.78	n.a.	BMB
2	48.83	n.a.	10.715	20.160	2.22	n.a.	BMB*
Total:			470.396	906.215	100.00	0.000	

6. Preparation and Characterisation of $(FcTT)_8$

The phosphoramidite **13** was dissolved in anhydrous acetonitrile (2.0 ml, Link Technologies) and filtered through a 0.2 micron PTFE syringe filter (Watman). The solvents were removed and the residue re-dissolved in anhydrous dichloromethane (2.0 ml) and dispensed into two vials fitted to DNA synthesiser (Applied Biosystems 394 DNA synthesiser). The solvents were removed under high vacuum overnight. The compound (0.1 M in dry acetonitrile) was oligomerised *via* solid phase synthesis on a 1.0 μmol scale with a stepwise coupling yield of over 99.5%. Specifically for the synthesis of **$(FcTT)_8$** oligomer, an 1.0 mmol CPG phosphate column (Links) was used and an extended coupling time (10 mins) was applied. The standard coupling conditions were applied, *i.e.* detritylation with 3% trichloroacetic acid in DCM (ABI reagents), activation with 0.25 M ETT in acetonitrile (Link) and capping with acetic anhydride and methylimidazole (Link), oxidation with 0.02 M iodine in water (Link). The product was then cleaved from the solid support by treatment with concentrated aqueous ammonia (30%) (Sigma-Aldrich) at room temperature for 1 hour, followed by heating at 55°C for 3 hours. The solvents were removed on a speed vac (Thermo Scientific) and the residue purified by C18 RP-HPLC and desalted with a NAP 10 column (GE Healthcare) to give a product (50 OD at 260 nm), which was characterised by ES MS, UV/Vis spectrometry and analytical HPLC. The sample was kept in the freezer (-20 °C) for a few months without any apparent changes.

Mass Spec Conditions (Waters LCT ESI-TOF mass spectrometer): A 20 mL oligomer sample (ca. 70 mM) was mixed with 50 ml Buffer (50% 1% TEA in water/acetonitrile), 10 ml of which were injected.
Molecular mass: $C_{256}H_{330}Fe_8N_{32}O_{65}P_8$: 5587.6197 g/mol
Observed mass (ESI): 5590 (see also raw data)

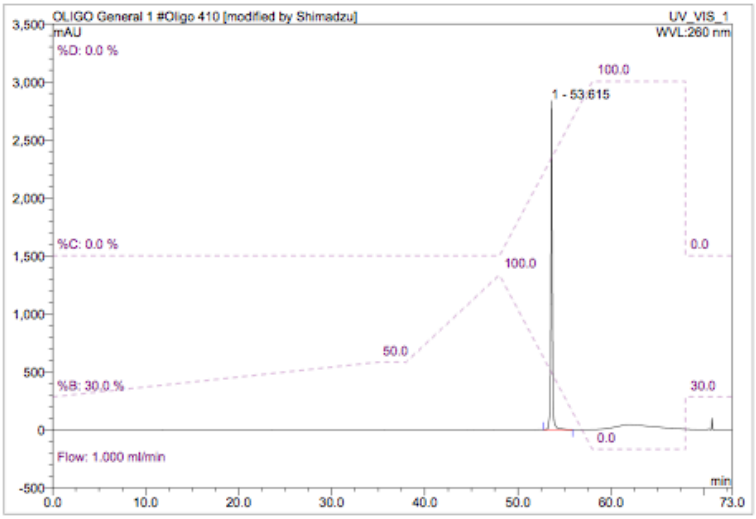
HPLC conditions (Dionex system with Summit P580 pump and Summit UVD 170s UV/VIS Multi-Channel Detector with prep flow cell, Phenomenex Clarity Oligo-RP columns, 150 mm x 4.60 mm 5 micron and 150 mm x 10 mm 5 micron were used for analytical and preparative HPLC respectively): Solvent system **A**: 5% MeCN/0.1M TEAA, pH 7.0; Solvent system **B**: 15% MeCN/0.1M TEAA, pH 7.0, Solvent system **C:** MeCN. Gradient (linear increase): 0-35 min, 30% B - 50% B (remainder A); 35-38 min, 50% B hold; 38-48 min, 50% B - 100% B; 48-58 mins, 100% B - 100% C; 58 to 68 min, 100% C hold; 68-73 min, revert to initial 30% B (remainder A).

$(Fc\text{-}TT)_8$ Analytical HPLC data:

Operator:Shimadzu Timebase:LC_System2 Sequence:OLIGO General 1 Page 1-1
18/1/2011 10:18 AM

121 Oligo 410

Sample Name:	**Oligo 410**	*Injection Volume:*	**30.0**
Vial Number:	**51**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**260**
Control Program:	**OLIGO General 1**	*Bandwidth:*	**n.a.**
Quantif. Method:	**OLIGO General 1**	*Dilution Factor:*	**1.0000**
Recording Time:	**11/11/2010 20:48**	*Sample Weight:*	**1.0000**
Run Time (min):	**73.00**	*Sample Amount:*	**1.0000**

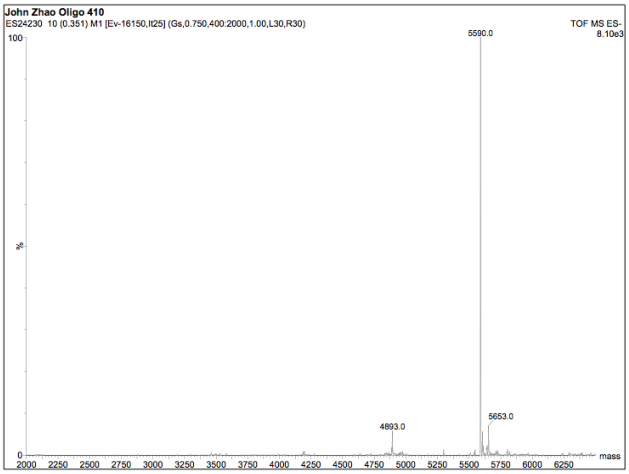


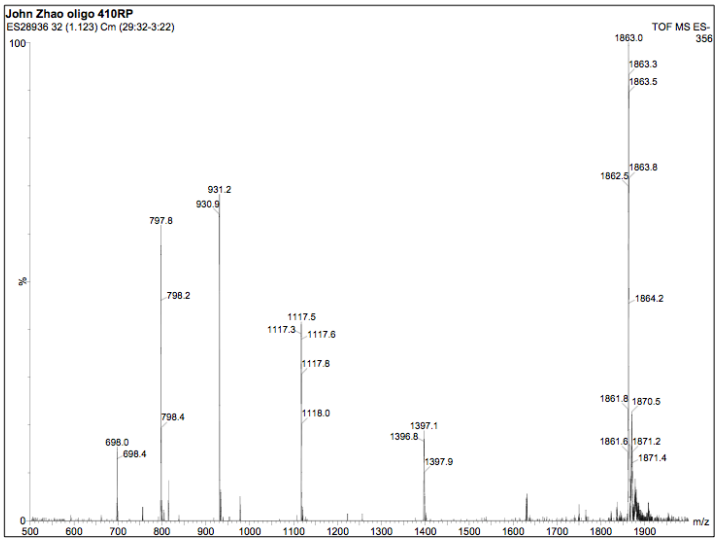
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	53.62	n.a.	2833.577	455.814	100.00	n.a.	BMB
Total:			2833.577	455.814	100.00	0.000	

DEFAULT/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR9 Build 2673 (161349)

$(Fc\text{-}TT)_8$ MS data:



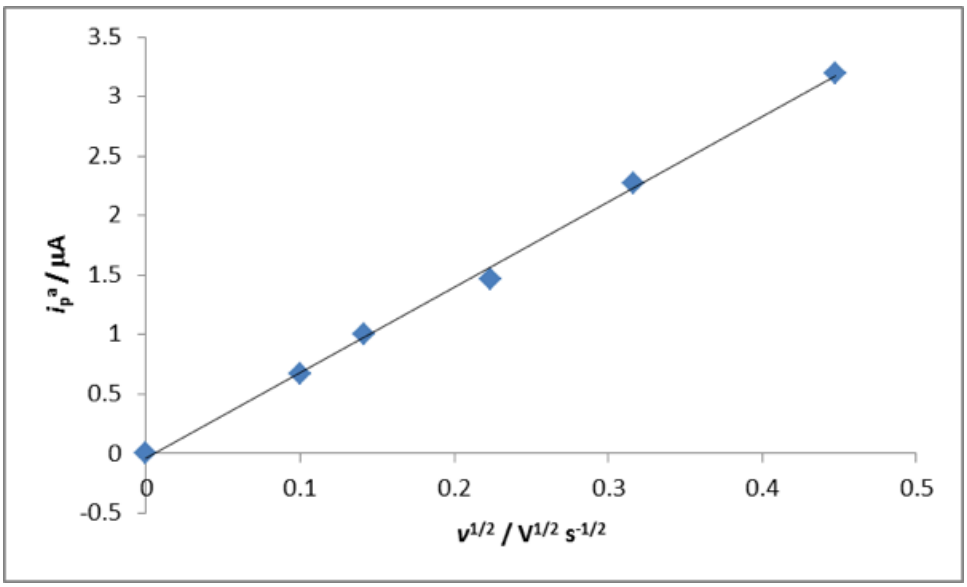


7. Electrochemistry of $(FcTT)_8$:

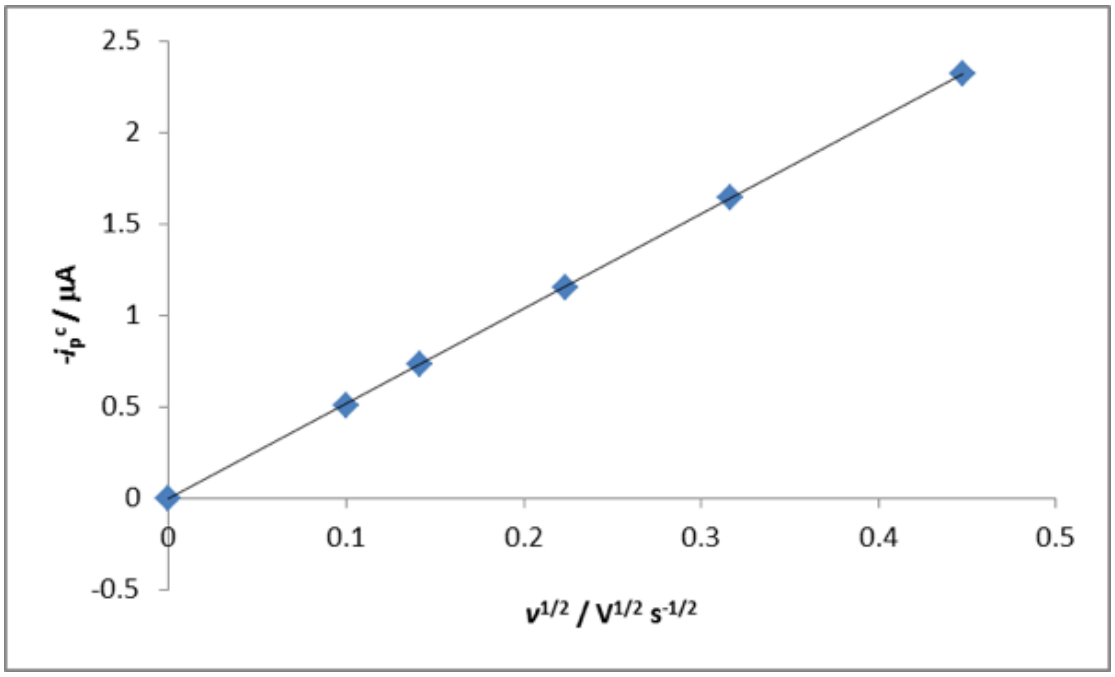
The cyclic voltammograms were recorded using a three-electrode cell consisting of a gold working electrode of 1.6 mm diameter, a platinum wire as auxiliary electrode and a Ag|AgCl reference electrode. All potentials are quoted w.r.t. Ag|AgCl. The working electrode was immersed in 100 mL of a 0.1 mM solution of FcTT in buffer (10 mM phosphate, 100 mM NaCl, pH 7.0), which was separated from the electrolyte solution of the same buffer with a glass holder terminating in a glass frit. Solutions were saturated with argon before measurements. Glassware and cells were cleaned prior to use with a 1:1 mixture of ammonia and hydrogen peroxide solution, followed by rinsing with copious quantities of ultrapure water. Ultrapure water, purified with a Millipore Elix-Gradient A10 system (18 MΩ cm, toc≤5 ppb, Millipore, France) was used throughout. The working electrode was cleaned by mechanical polishing with aqueous slurries of successively finer grades of alumina, followed by potential cycling. Measurements were carried out with a BioAnalytical Systems Inc. (BASi) EC epsilon potentiostat. The voltammograms were recorded at different scan rates, varying from 10 mV s^{-1} to 200 mV s^{-1}.

Scan Rate (mV s^{-1})	i_p^a (A)	i_p^c (A)	i_p^a/i_p^c	E_p^a (mV)	E_p^c (mV)	$E_p^a - E_p^c$ (mV)	$E^{0'}$ (mV)
10	6.73×10^{-7}	-5.09×10^{-7}	1.32	236	181	55	208
20	1.00×10^{-6}	-7.31×10^{-7}	1.37	241	179	62	210
50	1.46×10^{-6}	-1.15×10^{-6}	1.27	255	174	81	214
100	2.27×10^{-6}	-1.65×10^{-6}	1.37	255	170	85	212
200	3.20×10^{-6}	-2.32×10^{-6}	1.38	269	164	105	216

Dependence of anodic peak height (i_p^a) on sweep rate (v):



Dependence of cathodic peak height (i_p^c) on sweep rate (v):



8. X-ray diffraction data for compound 6:

$C_{22}H_{28}Fe\ I_2O_4$, M = 666.09, Monoclinic, a = 14.1877(7), b = 8.3380(2), c = 20.9652(9) Å, β= 101.305(2)°, U= 2432.00(17) Å3, T = 120(2) K, space group $P2_1$, Z = 4, 29532 reflections measured, 10419 unique (R_{int} = 0.0542) which were used in all calculations. The final $R1$ was 0.0464 ($I>2\sigma(I)$) and $wR(F_2)$ was 0.1054 (all data). CCDC 896623

A suitable crystal was selected and a dataset was measured[1] on a Bruker FR591 rotating anode ($\lambda_{Mo\text{-}K_\alpha}$ = 0.71073 Å). The data collection was driven by COLLECT[2] and was processed by DENZO[3]. An absorption correction was applied using SADABS[4]. The structure was solved using SIR92[5] and was refined by a full-matrix least-squares procedure on F^2 in ShelXL-97.[6] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. Figures were produced using OLEX2.[7]

The structure contains two crystallographically independent molecules.
There are two halogen bonds: I(101)…O(101)^{i} = 3.08 (1) Å, I(101)…O(01')^{i} = 3.04 (2) Å and I(102)…O(1)^{ii} = 3.263 (6) Å (symmetry codes: (i) x, y-1, z; (ii) x+1, y-1, z). The methyl group C(16) / C(16') is disordered over two positions at a percentage occupancy ratio of 73(3):27(3), respectively. The groups C(114)-C(116), O(101), O(102) / C(04')-C(06'), O(01'), O(02') and C(120)-C(122), O(103), O(104) / C(20')-C(22'), O(03'), O(04') are disordered over two positions both at the percentage occupancy ratio of 70(2):30(2).

(1) Coles, S. J.; Gale, P. A., *Chem. Sci.*, 2012, **3** (3), 683-689.
(2) Hooft, R. W. W. 1998, *COLLECT Data Collection Software*, Nonius B. V., Delft.
(3) Otwinowski, Z.; Minor, W. in *Methods in Enzymology*, ed. C. W. Carter and R. M. Sweet, Academic Press, New York, 1997, **276**, 307-326.
(4) Sheldrick, G. M. 2007, *SADABS,* Bruker AXS Inc., Madison, Wisconsin, USA.
(5) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.*, 1994, **27**, 435-388.
(6) Sheldrick, G. M. *Acta Cryst.*, 2008, **A64**, 112-122.
(7) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.*, 2009, **42**, 339-341.