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Supplementary Information

Metallocene to Metallocene Conversion. Synthesis of an Oxazoline-Substituted Pentamethyliridocenium Cation from a Ferrocenyloxazoline

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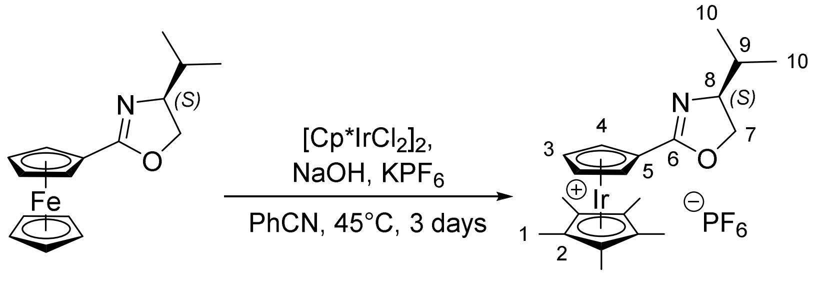
1. Experimental procedures

General information

Diethyl ether and tetrahydrofuran were distilled over sodium and benzophenone ketyl. Acetontirile (LC-MS grade) was dried using 4 Å molecular sieves. Benzonitrile and pivalonitrile were used as received. All reactions involving the use of dry solvents were carried out under an inert atmosphere of either nitrogen or argon. Silica gel (60 Å pore size, 40 - 63 µm technical grade) and neutral aluminium oxide (Brockmann I, 50 - 200 µm) were used for chromatography. All starting materials not commercially available are specifically referenced.

All protons and carbons were assigned using 2D NMR techniques including HSQC, HMBC, NOESY and COESY. Carbons denoted with a prime (*e.g.* $C^{2'}$) indicate the most deshielded carbon when there are two carbons with the same number on the structure. Carbons denoted with two superscripts (*e.g.* $C^{2/3}$) indicate where two environments cannot be distinguished from one another. The following compounds were prepared as described in the literature: (*S*)-2-ferrocenyl-4-(1-methylethyl)oxazoline (**1**)[1].

Preparation of (η^5-(*S*)-2-(4-methylethyl)oxazolinylcyclopentadienyl)(η^5-pentamethylcyclopentadienyl)iridium(III) hexafluorophosphate 3



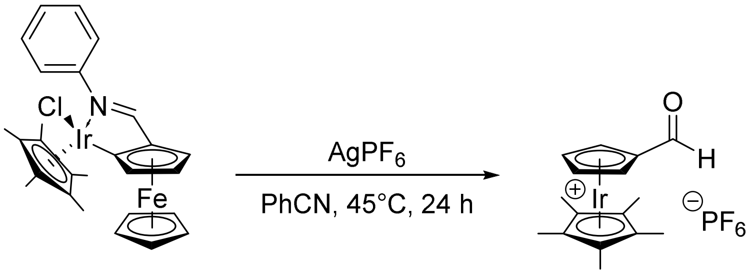
1 **3**

(*S*)-2-Ferrocenyl-4-(1-methylethyl)oxazoline (**1**) (0.019 g, 0.06 mmol), (pentamethylcyclopentadienyl)iridium(III) chloride dimer (0.025 g, 0.03 mmol), NaOH (0.005 g, 0.126 mmol) and potassium hexafluorophosphate (0.047 g, 0.26 mmol) were added to a flame dried Schlenk tube under an inert atmosphere. After the addition of benzonitrile (5 mL) the mixture was stirred at 45 °C for 3 days. Once cooled to room temperature, hexane was added to the reaction mixture and stirred vigorously for 5 mins. The resulting suspension was filtered through Celite® using hexane as the eluent, and the column flushed with hexane twice to remove any remaining benzonitrile. Once all the benzonitrile had been removed, acetonitrile was used to flush the brown precipitate from the top of the Celite®, which was collected and concentrated *in vacuo*. Purification was achieved by filtering through a pad of neutral alumina, using acetonitrile as the eluent, and collecting the first bright yellow fractions (subsequent pale yellow fractions contained small amounts of starting material). Removal of the solvent *in vacuo* yielded the product as a mustard yellow crystalline solid (0.0278 g, 68%): mp 189.7 - 191.2 °C (Found: C, 38.77; H, 4.46; N, 2.22. $C_{21}H_{29}F_6IrNOP$ Requires C, 38.89; H, 4.51; N, 2.16%), HRMS (ES) [cation]$^+$ $C_{21}H_{29}IrNO^+$, Calc. 502.1850, Obs. 502.1843; $[\alpha]_D^{23.0°C}$ = -41.81 (*c* = 0.22, acetonitrile); ν_{max} (film)/cm^{-1} 2962, 2970, 1666 (C=N), 841; ^{1}H NMR (500 MHz, $CDCl_3$) 5.88 (1H, bs, Cp-H^4), 5.84 (1H, bs, Cp-H^4), 5.79 (1H, bs, Cp-H^3), 5.77 (1H, bs, Cp-H^3), 4.41 (1H, dd, *J* = 9.1, 8.5 Hz,C*H*H), 4.06 (1H, t, *J* =

8.5 Hz, CH*H*), 4.03 - 3.97 (1H, m, C*H*), 2.16 (15H, s, Cp*), 1.77 - 1.69 (1H, m, C*H*(CH$_3$)$_2$), 1.03 (3H, d, *J* = 6.7 Hz, C*H*$_3$), 0.92 (3H, d, *J* = 6.7 Hz, C*H*$_3$); ^{1}H NMR (500 MHz, MeCN-d^{3}) 5.89-5.87 (1H, m, Cp-*H*$^{4'}$), 5.87-5.86 (1H, m, Cp-*H*^{4}), 5.65-5.64 (2H, m, Cp-*H*^{3}), 4.45 (1H, dd, *J* = 9.7, 8.5 Hz, C*H*H), 4.08 (1H, t, *J* = 8.7 Hz, CH*H*), 4.03 - 3.95 (1H, m, C*H*), 2.11 (15H, s, Cp*), 1.74 - 1.67 (1H, m, C*H*(CH$_3$)$_2$), 1.01 (3H, d, *J* = 6.7 Hz, C*H*$_3$), 0.90 (3H, d, *J* = 6.7 Hz, C*H*$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 157.02 (C^{6}), 95.84 (C^{2}), 84.79 (C^{5}), 83.22 (C$^{3'}$), 83.12 (C^{3}), 80.74 (C$^{4'}$), 80.64 (C^{4}), 73.61 (C^{8}), 71.43 (C^{7}), 33.46 (C^{9}), 19.28 (C$^{10'}$), 18.69 (C^{10}), 10.05 (C^{1}); ^{13}C NMR (125 MHz, MeCN-d^{3}) δ 157.7 (C^{6}), 99.6 (C^{2}), 85.9 (C^{5}), 83.5 (C$^{3'}$), 83.5 (C^{3}), 81.6 (C$^{4'}$), 81.5 (C^{4}), 74.3 (C^{8}), 72.3 (C^{7}), 34.2 (C^{9}), 19.4 (C$^{10'}$), 18.7 (C^{10}), 10.2 (C^{1}).

Note: When the solvent was changed to pivalonitrile, with exactly the same conditions and work up, the yield was 47%.

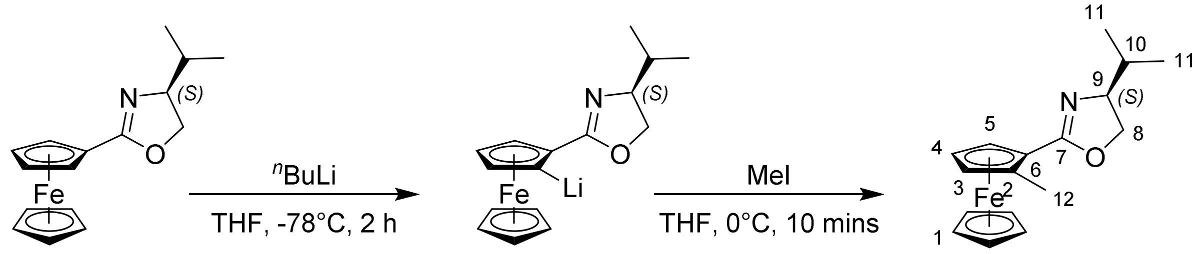
Conversion of iridacycle 5 into iridocenium 6



5 **6**

Iridicycle **5**^{2} (0.039 g, 0.06 mmol) and AgPF$_6$ (0.064 g, 0.25 mmol) was added to a flame dried Schlenk tube under an inert atmosphere and dissolved in benzonitrile (5 mL). This was heated to 45 °C and stirred for 24 h. After cooling to room temperature hexane was added and the resulting suspension was filtered through Celite® using hexane as the eluent, and the column flushed with hexane twice to remove any remaining benzonitrile. Once all the benzonitrile had been removed, acetonitrile was used to flush the brown precipitate from the top of the Celite®, which was subsequently collected and concentrated *in vacuo*. This was redissolved in acetonitrile and filtered through neutral alumina to give a dark brown residue containing iridocinium ion **6**. Further purification was not attempted. HRMS (ES) [cation]$^+$ $C_{16}H_{20}IrO^+$, Calc. 421.1138, Obs. 421.1142; ^{1}H NMR (500 MHz, MeCN-d^3) 9.79 (1H, s, C(O)*H*), 6.01 (2H, t, *J* = 2 Hz) Cp-*H*), 5.76 (2H, t, *J* = 2 Hz, Cp-*H*), 1.57 (15H, s, Cp*).

Preparation of 1-methyl-2-(4'-isopropyloxazolinyl)ferrocene 7 as a 2:1 ratio of (*S*,*R*$_p$) : (*S*,*S*$_p$) diastereoisomers[3]



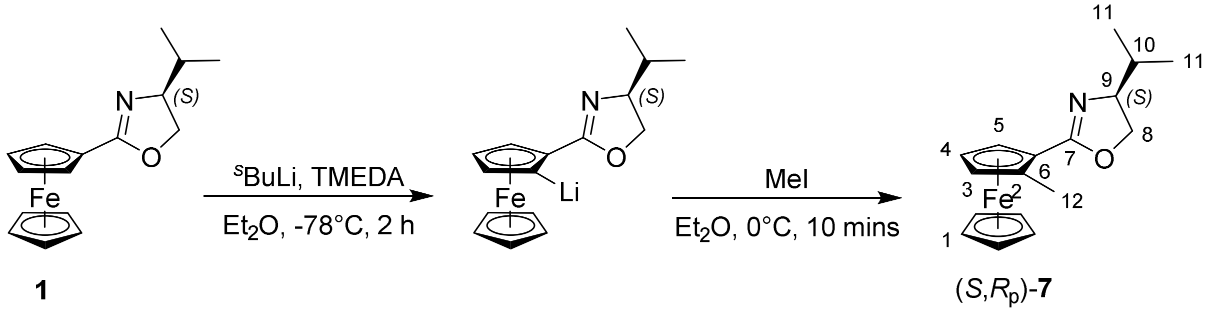
1

(*S*,*R*$_p$)-**7** + (*S*,*S*$_p$)-**7**
(2 : 1 ratio)

(*S*)-2-Ferrocenyl-4-(1-methylethyl)oxazoline (**1**) (0.100 g, 0.34 mmol) was added to a flame dried Schlenk tube under an atmosphere of argon and dissolved in dry THF. The subsequent orange solution was cooled to -78 °C and stirred for 5 mins after which *n*-butyllithium (2.5 M in hexanes) (0.17 mL, 0.44 mmol) was slowly added. After stirring for 2 hours the mixture was warmed to 0 °C, methyl iodide (0.22 mL, 0.67 mmol) added and stirred for 10 mins. The reaction was allowed to warm to room temperature, and after an additional 10 mins, was diluted with diethyl ether and then quenched with saturated sodium hydrogen carbonate. The organics were separated with H_2O, washed with brine, dried over $MgSO_4$ and upon removal of the solvent *in vacuo* gave the crude product. Column chromatography (SiO_2, 10% EtOAc in hexane) yielded an orange oil as a 2:1 mixture of diastereoisomers (0.085 g, 81%). Data for major diastereoisomer: R_f 0.35 (15% EtOAc in hexane); ν_{max}(film)/cm^{-1} 1652 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.61 (1H, m, Cp-*H*), 4.28 - 4.22 (2H, m, Cp-*H* & C*H*H), 4.17 (1H, m, Cp-*H*), 4.10 (5H, s, Cp-*H*), 4.09 - 4.05 (1H, m, C*H*), 4.02 - 3.96 (1H, m, CH*H*), 2.28

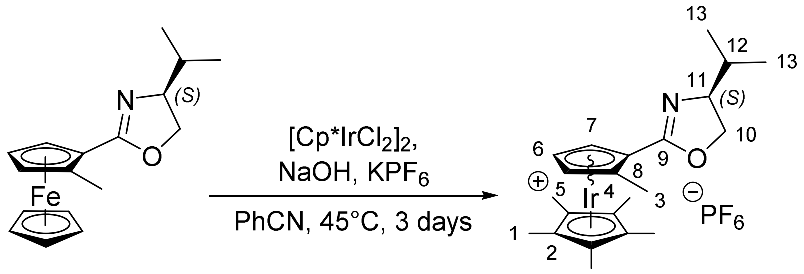
(3H, s,CH_3), 1.83 - 1.82 (1H, m, CH(CH$_3$)$_2$), 1.03 (3H, d, J = 6.8 Hz, CH_3), 0.97 (3H, d, J = 6.8 Hz, CH_3); ^{13}C NMR (125 MHz, CDCl$_3$) δ 165.87 (C^7), 85.35 (C^2), 77.60 (C^6), 72.45 (C^9), 72.24 (C^3), 70.12 (C^1), 69.34 (C^5), 68.86 (C^8), 67.81 (C^4), 32.58 (C^{10}), 18.83 (C$^{11'}$), 18.06 (C^{11}), 14.76 (C^{12}). Data for minor diastereoisomer: R_f 0.28 (15% EtOAc in hexane); ν_{max}(film)/cm^{-1} 1652 (C=N); ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.67 (1H, m, Cp-H), 4.28 - 4.22 (2H, m, Cp-H & CHH), 4.17 (1H, m, Cp-H), 4.11 (5H, s, Cp-H), 4.09 - 4.05 (1H, m, CH), 4.02 - 3.96 (1H, m, CHH), 2.25 (3H, s, CH_3), 1.83 - 1.82 (1H, m, CH(CH$_3$)$_2$), 1.01 (3H, d, J = 6.8 Hz, CH_3), 0.94 (3H, d, J = 6.8 Hz, CH_3); ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.14 (C^7), 85.42 (C^2), 78.00 (C^6), 72.22 (C^9), 72.15 (C^3), 70.12 (C^1), 69.14 (C^5), 69.03 (C^8), 67.88 (C^4), 32.46 (C^{10}), 18.90 (C$^{11'}$), 17.84 (C^{11}), 14.67 (C^{12}). Matches previously reported data.[4]

Preparation of 1-methyl-2-(4'-isopropyloxazolinyl)ferrocene 7 as a >100 :1 ratio of (*S*,*R*p) : (*S*,*S*p) diastereoisomers.[3]



(*S*)-2-Ferrocenyl-4-(1-methylethyl)oxazoline (**1**) (0.100 g, 0.34 mmol) was added to a flame dried Schlenk tube under an atmosphere of argon and dissolved in dry diethyl ether. TMEDA (0.07 mL, 0.44 mmol) was added and the subsequent orange solution was cooled to -78 °C and stirred for 5 mins after which *sec*-butyllithium (2.5 M in hexanes) (0.31 mL, 0.44 mmol) was slowly added. After stirring for 2 hours the mixture was warmed to 0 °C, methyl iodide (0.03 mL, 0.44 mmol) added and stirred for 5 mins. The reaction was allowed to warm to room temperature, and after an additional 30 mins, was diluted with diethyl ether and then quenched with saturated sodium hydrogen carbonate. The organics were separated with H_2O, washed with brine, dried over $MgSO_4$ and upon removal of the solvent *in vacuo* gave the crude product. Column chromatography (SiO_2, 10% EtOAc in hexane) yielded an orange oil as a single diastereoisomer (0.083 g, 80%): R_f 0.35 (15% EtOAc in hexane); $[\alpha]_D^{23.0°C}$= -22 (*c* = 0.2, ethanol); ν_{max}(film)/cm^{-1} 1652 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.61 (1H, m, Cp-*H*), 4.28 - 4.22 (2H, m, Cp-*H* & C*H*H), 4.17 (1H, m, Cp-*H*), 4.10 (5H, s, Cp-*H*), 4.09 - 4.05 (1H, m, C*H*), 4.02 - 3.96 (1H, m, CH*H*), 2.28 (3H, s, C*H*$_3$), 1.83 - 1.82 (1H, m, C*H*(CH_3)$_2$), 1.03 (3H, d, *J* = 6.8 Hz, C*H*$_3$), 0.97 (3H, d, *J* = 6.8 Hz, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.87 (C^7), 85.35 (C^2), 77.60 (C^6), 72.45 (C^9), 72.24 (C^3), 70.12 (C^1), 69.34 (C^5), 68.86 (C^8), 67.81 (C^4), 32.58 (C^{10}), 18.83 (C$^{11'}$), 18.06 (C^{11}), 14.76 (C^{12}). Matches previously reported data.[4] Note: Optical rotation has not been reported previously.

Preparation of iridoceninium isomers (*S*,*R*$_p$) and (*S*,*S*$_p$)-8

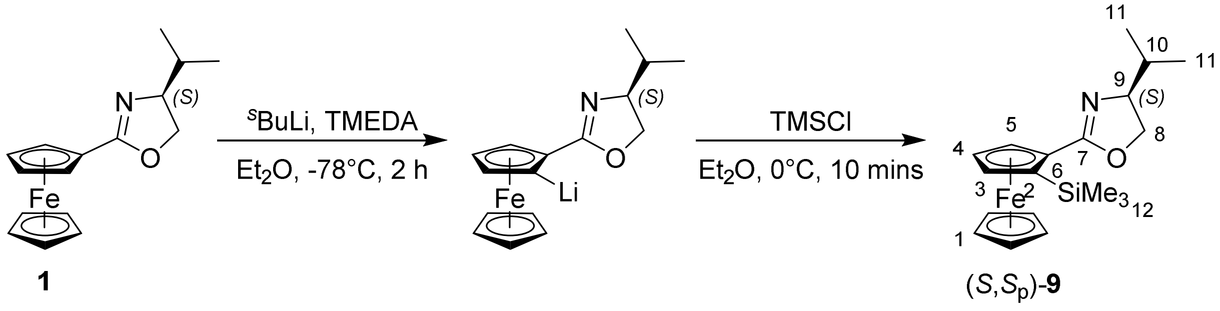


7

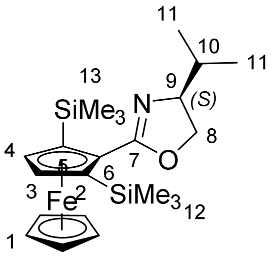
(*S*,*R*$_p$)/(*S*,*S*$_p$)-**8**

((*S*,*R*$_p$)-1-Methyl-2-(4'-isopropyloxazolinyl)ferrocene (**7**) (either 2:1 or >100:1 ratio of diastereoisomers) (0.0195 g, 0.06 mmol), (pentamethylcyclopentadienyl)iridium(III) chloride dimer (0.025 g, 0.03 mmol), NaOH (0.005 g, 0.13 mmol) and potassium hexafluorophosphate (0.047 g, 0.25 mmol) were added to a flame dried Schlenk tube under an inert atmosphere. After the addition of benzonitrile (5 mL) the mixture was stirred at 45 °C for 3 days. Once cooled to room temperature, hexane was added to the reaction mixture and stirred vigorously for 5 mins. The resulting suspension was filtered through Celite® using hexane as the eluent and the column flushed with hexane twice to remove any remaining benzonitrile. Once all benzonitrile had been removed, acetonitrile was used to flush the brown precipitate from the top of the Celite®, which was subsequently collected and concentrated *in vacuo*. Purification was achieved by filtering through a pad of neutral alumina, using acetonitrile as the eluent, and collecting the first bright yellow fractions (subsequent pale yellow fractions contained small amounts of starting material). Removal of the solvent *in vacuo* yielded the desired product as a mustard yellow crystalline solid as a 1:0.86 ratio of diastereoisomers (0.0322 g, 77%): mp 80.2 - 82.0 °C, HRMS (ES) [cation]$^+$ $C_{22}H_{31}IrNO^+$, Calc. 516.2006, Obs. 516.1993; $[\alpha]_D^{24.4°C}$ = -13.91 (*c* = 0.23, acetonitrile); ν_{max} (film)/cm^{-1} 3124, 2965, 2925, 2876, 1662 (C=N), 838. Data specific for major diastereoisomer: ^{1}H NMR (500 MHz, MeCN-d^3) 5.75 -5.73 (1H, m, Cp-*H*^{7}), 5.56 - 5.54 (1H, m, Cp-*H*^{5}), 5.50-5.49 (1H, m, Cp-*H*^{6}), 4.43 (1H, dd, *J* = 9.7, 8.5 Hz, C*H*H), 4.08 - 3.99 (1H, m, CH*H*), 3.95 - 3.89 (1H, m, C*H*), 2.21 (3H, s, -C*H*$_3$), 2.05 (15H, s, Cp*), 1.77 - 1.73 (1H, m, C*H*(CH$_3$)$_2$), 1.04 (3H, d, *J* = 6.7 Hz, C*H*$_3$), 0.92 (3H, d, *J* = 6.7 Hz, C*H*$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 157.78 (C^9), 96.95 (C^4), 95.59 (C^2), 84.64 (C^5), 84.16 (C^8), 81.49 (C^7), 81.34 (C^6), 74.15 (C^{11}), 71.52 (C^{10}), 34.27 (C^{12}), 19.23 (C$^{13'}$), 18.84 (C^{13}), 10.98 (C^3), 9.39 (C^1). Data specific for minor diastereoisomer: ^{1}H NMR (500 MHz, MeCN-d^3) 5.75 - 5.73 (1H, m, Cp-*H*^{7}), 5.56 - 5.54 (1H, m, Cp-*H*^{5}), 5.50-5.49 (1H, m, Cp-*H*^{6}), 4.39 (1H, dt, *J* = 7.6, 3.7 Hz, C*H*H), 4.08 - 3.99 (2H, m, CH*H* + C*H*), 2.22 (3H, s, -C*H*$_3$), 2.04 (15H, s, Cp*), 1.77 - 1.73 (1H, m, C*H*(CH$_3$)$_2$), 0.99 (3H, d, *J* = 6.7 Hz, C*H*$_3$), 0.90 (3H, d, *J* = 6.7 Hz, C*H*$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 157.66 (C^9), 97.07 (C^4), 95.60 (C^2), 84.64 (C^5), 83.86 (C^8), 81.56 (C^7), 81.31 (C^6), 73.83 (C^{11}), 70.99 (C^{10}), 33.53 (C^{12}), 18.74 (C$^{13'}$), 18.37 (C^{13}), 10.87 (C^3), 9.31 (C^1).

Preparation of (S,S_p)-1-trimethylsilyl-2-(4'-isopropyloxazolinyl)ferrocene 9 as a single diastereoisomer[3] and isolation of byproduct 10.



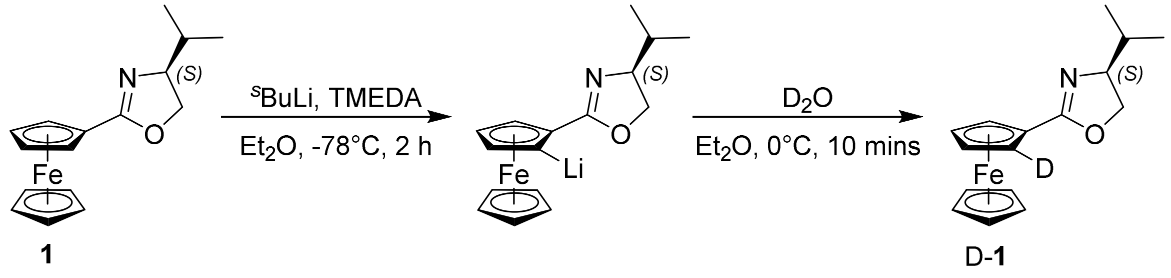
(S)-2-Ferrocenyl-4-(1-methylethyl)oxazoline (**1**) (0.100 g, 0.34 mmol) was added to a flame dried Schlenk tube under an atmosphere of argon and dissolved in dry diethyl ether (5 mL). TMDEA (0.07 mL, 0.44 mmol) was added and the subsequent orange solution was cooled to -78 °C and stirred for 5 mins after which *n*-butyllithium (2.5 M in hexanes) (0.31 mL, 0.44 mmol) was slowly added. After stirring for 2 hours the mixture was warmed to 0 °C, trimethylsilyl chloride (0.056 mL, 0.44 mmol) added and stirred for 10 mins. The reaction was allowed to warm to room temperature, and after an additional 10 mins, was diluted with diethyl ether and then quenched with saturated sodium hydrogen carbonate solution. The organics were separated with H_2O, washed with brine, dried over $MgSO_4$ and upon removal of the solvent *in vacuo* gave the crude product. Column chromatography (SiO_2, 10% EtOAc in hexane) yielded an orange oil as a single diastereoisomer (0.104 g, 84%): R_f 0.50 (10% EtOAc in hexane); $[\alpha]_D^{23.6°C} = +285$ (c = 0.2, ethanol); ν_{max} (film)/cm^{-1} 1655 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.89 (1H, dd, J = 2.4, 1.4 Hz, Cp-H), 4.43 (1H, t, J = 2.5 Hz, Cp-H), 4.29 – 4.24 (2H, m, Cp-H & CHH), 4.18 (5H, s, Cp-H), 4.01 (1H, t, J = 7.9 Hz, CHH), 3.95 - 3.91 (1H, m, CH), 1.84 - 1.77 (1H, m, CH(CH_3)$_2$), 1.02 (3H, d, J = 6.8 Hz, CH_3), 0.92 (3H, d, J = 6.8 Hz, CH_3), 0.32 (9H, s, Si(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.93 (C^7), 77.13 (C^3), 75.58 (C^6), 73.34 (C^5), 73.20 (C^2), 73.04 (C^9), 71.71 (C^4), 69.64 (C^1), 69.52 (C^8), 32.75 (C^{10}), 19.29 ($C^{11'}$), 18.20 (C^{11}) , 0.65 (C^{12}).



10

A byproduct included the disubstituted oxazoline **10** which was collected by column chromatography (SiO_2, 10% EtOAc in hexane) as an orange oil (0.030 g, 20%): R_f 0.95 (10 % EtOAc in hexane); $[\alpha]_D^{19.1°C}$ = -6 (c = 0.25, ethanol); HRMS (ES) $[M+H]^+$ $C_{22}H_{35}FeNOSi_2+H^+$, Calc. 442.1679, Obs. 442.1678; ν_{max} (film)/cm^{-1} 3097, 2959, 1652 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36 (1H, d, J = 2.3 Hz, Cp-H), 4.34 (1H, d, J = 2.3 Hz, Cp-H), 4.31 (1H, dd, J = 9.3, 8.0 Hz, CHH), 4.17 (5H, s, Cp-H), 3.90 (1H, dd, J = 9.3, 8.0 Hz, CHH), 3.83 (1H, td, J = 9.1, 7.0 Hz, CH), 1.75 - 1.69 (1H, m, CH(CH_3)$_2$), 1.05 (3H, d, J = 6.7 Hz, CH_3), 0.93 (3H, d, J = 6.7 Hz, CH_3), 0.30 (9H, s, Si(CH_3)$_3$), 0.30 (9H, s, Si(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.96 (C^7), 80.93 (C^6), 78.62 ($C^{3/4}$), 78.46 ($C^{4/3}$), 77.73 ($C^{2/5}$), 77.22 ($C^{5/2}$), 73.60 (C^9), 70.110 (C^8), 69.68 (C^1), 33.23 (C^{10}), 19.52 ($C^{11'}$), 19.07 (C^{11}), 0.89 ($C^{12/13}$), 0.83 ($C^{13/12}$).

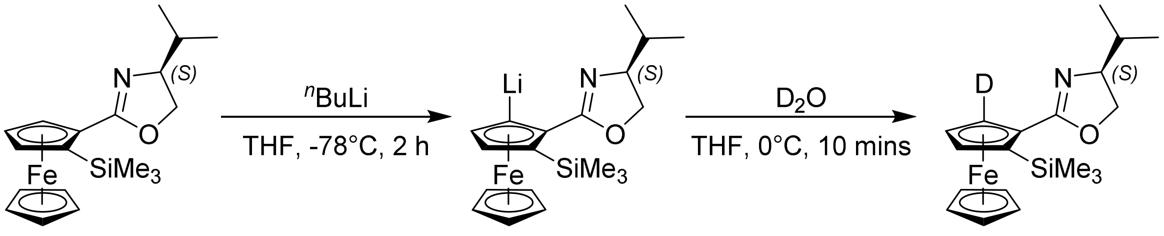
Deuteration of (*S*)-2-ferrocenyl-4-(1-methylethyl)oxazoline to give D-1



(*S*)-2-Ferrocenyl-4-(1-methylethyl)oxazoline (**1**) (0.100 g, 0.34 mmol) was added to a flame dried Schlenk tube under an atmosphere of argon and dissolved in dry diethyl ether (5 mL). TMDEA (0.07 mL, 0.44 mmol) was added and the subsequent orange solution was cooled to

-78 °C and stirred for 5 mins after which *s*-butyllithium (1.4 M in hexanes) (0.31 mL, 0.44 mmol) was slowly added. After stirring for 2 hours the mixture was warmed to 0 °C, D_2O (0.01 mL, 0.44 mmol) was added and stirred for 10 mins. The reaction was allowed to warm to room temperature, and after an additional 10 mins, was diluted with diethyl ether and then quenched with saturated sodium hydrogen carbonate solution. The organics were separated with H_2O, washed with brine, dried over $MgSO_4$ and upon removal of the solvent *in vacuo* gave a crude product. Column chromatography (SiO_2, 20% EtOAc in hexane) yielded an orange solid with 50% deuterium incorporation (see proton spectrum for comparison with starting material).

Deuteration of 1-trimethylsilyl-2-(4'-isopropyloxazolinyl)ferrocene 9 to give D-9



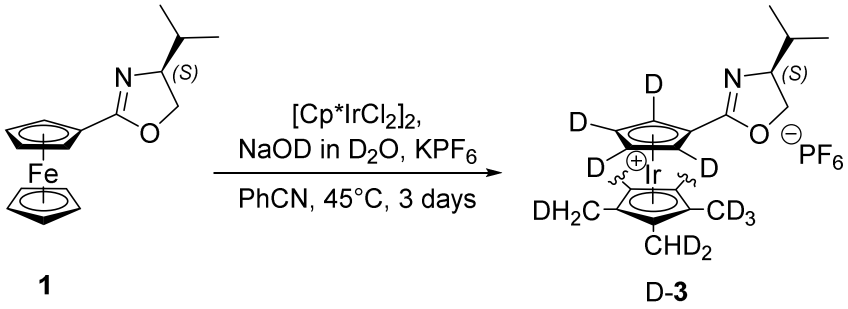
9

D-**9**

A diastereomerically pure sample of (**9**) (0.0696 g, 0.19 mmol) was added to a flame dried Schlenk tube under an atmosphere of argon and dissolved in dry THF (5 mL). The subsequent orange solution was cooled to -78 °C and stirred for 5 mins after which *n*-butyllithium (2.5 M in hexanes) (0.15 mL, 0.38 mmol) was slowly added. After stirring for 2 hours the mixture was warmed to 0 °C, D_2O (0.01 mL, 0.38 mmol) added and stirred for 10 mins. The reaction was allowed to warm to room temperature, and after an additional 10 mins, was diluted with diethyl ether and then quenched with saturated sodium hydrogen carbonate solution. The organics were separated with H_2O, washed with brine, dried over $MgSO_4$. Purification by column chromatography (SiO_2, 10% EtOAc in hexane) yielded an orange oil with 45% deuterium incorporation (see proton spectrum for comparison with starting material).

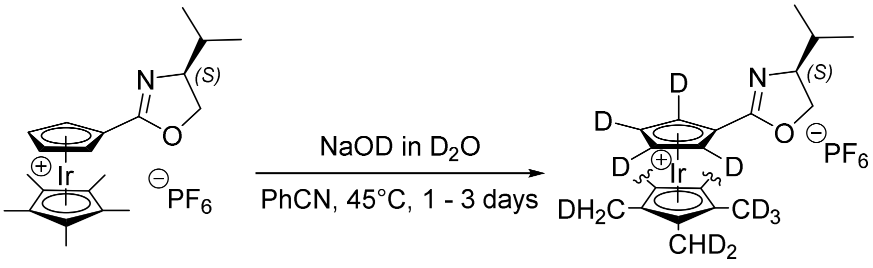
Deuterium incorporation into give iridoconium ion D-3

Route 1



(*S*)-2-Ferrocenyl-4-(1-methylethyl)oxazoline (**1**) (0.019 g, 0.06 mmol), (pentamethylcyclopentadienyl)iridium(III) chloride dimer (0.025 g, 0.03 mmol) and potassium hexafluorophosphate (0.047 g, 0.25 mmol) were added to a flame dried Schlenk tube under an inert atmosphere. After the addition of benzonitrile (5 mL), NaOD (in D_2O 40 wt%) (0.13 mL, 1.85 mmol) was added and the mixture was stirred at 45 °C for 3 days. Once cooled to room temperature, hexane was added to the reaction mixture and stirred vigorously for 5 mins. The resulting suspension was filtered through Celite® using hexane as the eluent and the column flushed with hexane twice to remove any remaining benzonitrile. Once all the benzonitrile had been removed, acetonitrile was used to flush the brown precipitate from the top of the Celite®, which was subsequently collected and concentrated *in vacuo*. Purification was achieved by filtering through a pad of neutral alumina, using acetonitrile as the eluent, and collecting the first bright yellow fractions (subsequent pale yellow fractions contained small amounts of starting material). Removal of the solvent *in vacuo* yielded the desired product as a mustard yellow crystalline solid showing deuterium incorporation (seen proton spectrum).

Route 2



3 D-**3**

Iridocenium ion (**3**) (0.010 g, 0.016 mmol) was dissolved in benzonitrile (1 mL). To this, NaOD (in D_2O 40 wt%) (0.02 mL, 0.3 mmol) was added using a micro pipette and the solution stirred at 45 °C for 1 or 3 days. Once cooled to room temperature, hexane was added to the reaction mixture and stirred vigorously for 5 mins. The resulting suspension was filtered through Celite® using hexane as the eluent and the column flushed with hexane twice to remove any remaining benzonitrile. Once all the benzonitrile had been removed, acetonitrile was used to flush the brown precipitate from the top of the Celite®, which was subsequently collected and concentrated *in vacuo*. Purification was achieved by filtering through a pad of neutral alumina, using acetonitrile as the eluent, and collecting the first bright yellow fractions. Removal of the solvent *in vacuo* yielded the desired product as a mustard yellow crystalline solid with varying deuterium incorporation (see proton spectrum for comparison with starting material).

2. ^{1}H and ^{13}C spectra

Figure S1.Complex **3** - ^{1}H NMR (500 MHz, MeCN-d^3).

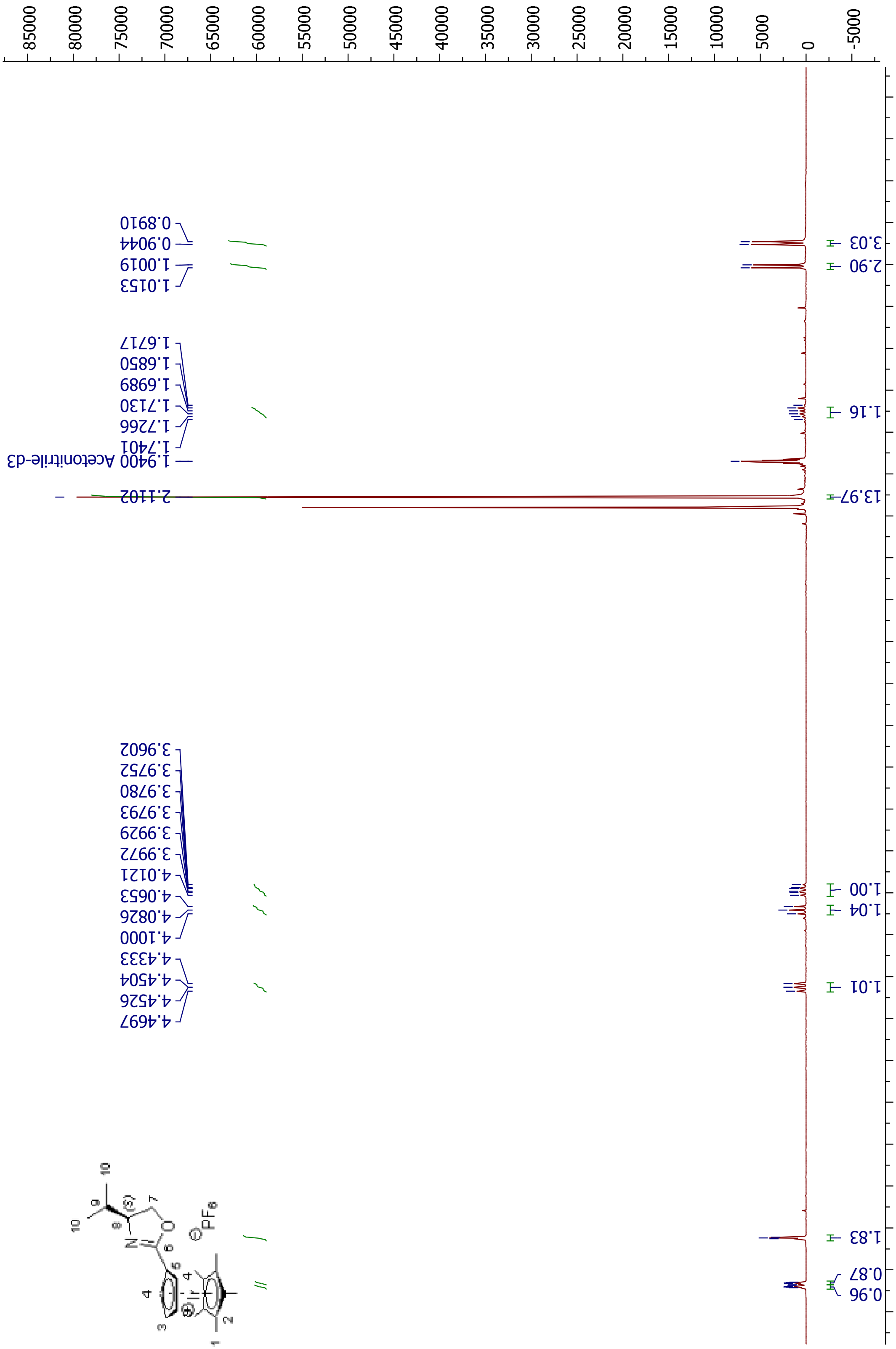


Figure S2. Complex **3** - ^{13}C NMR (125 MHz, MeCN-d^3).

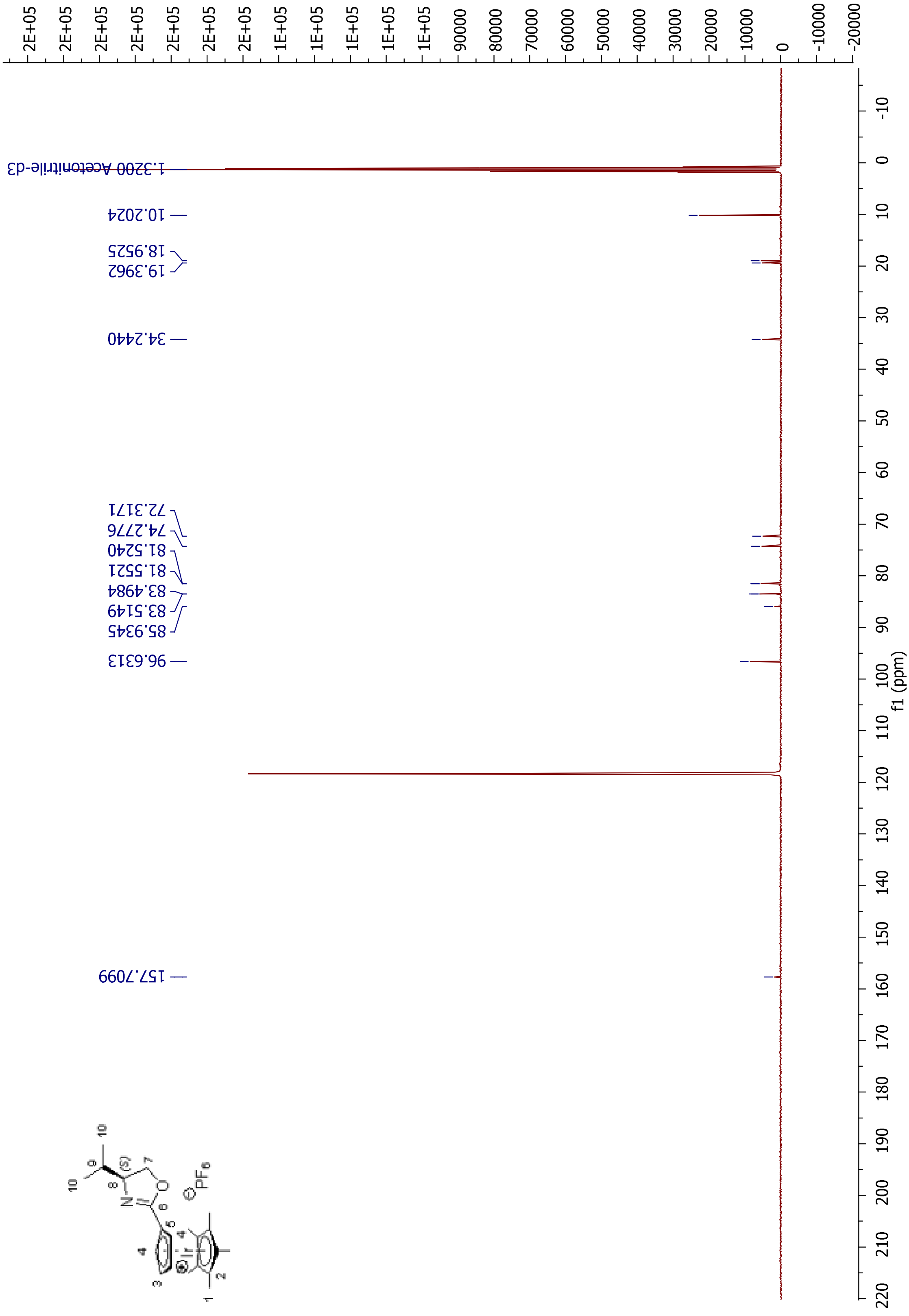


Figure S3. Complex **6** - ^{1}H NMR (500 MHz, MeCN-d^3).

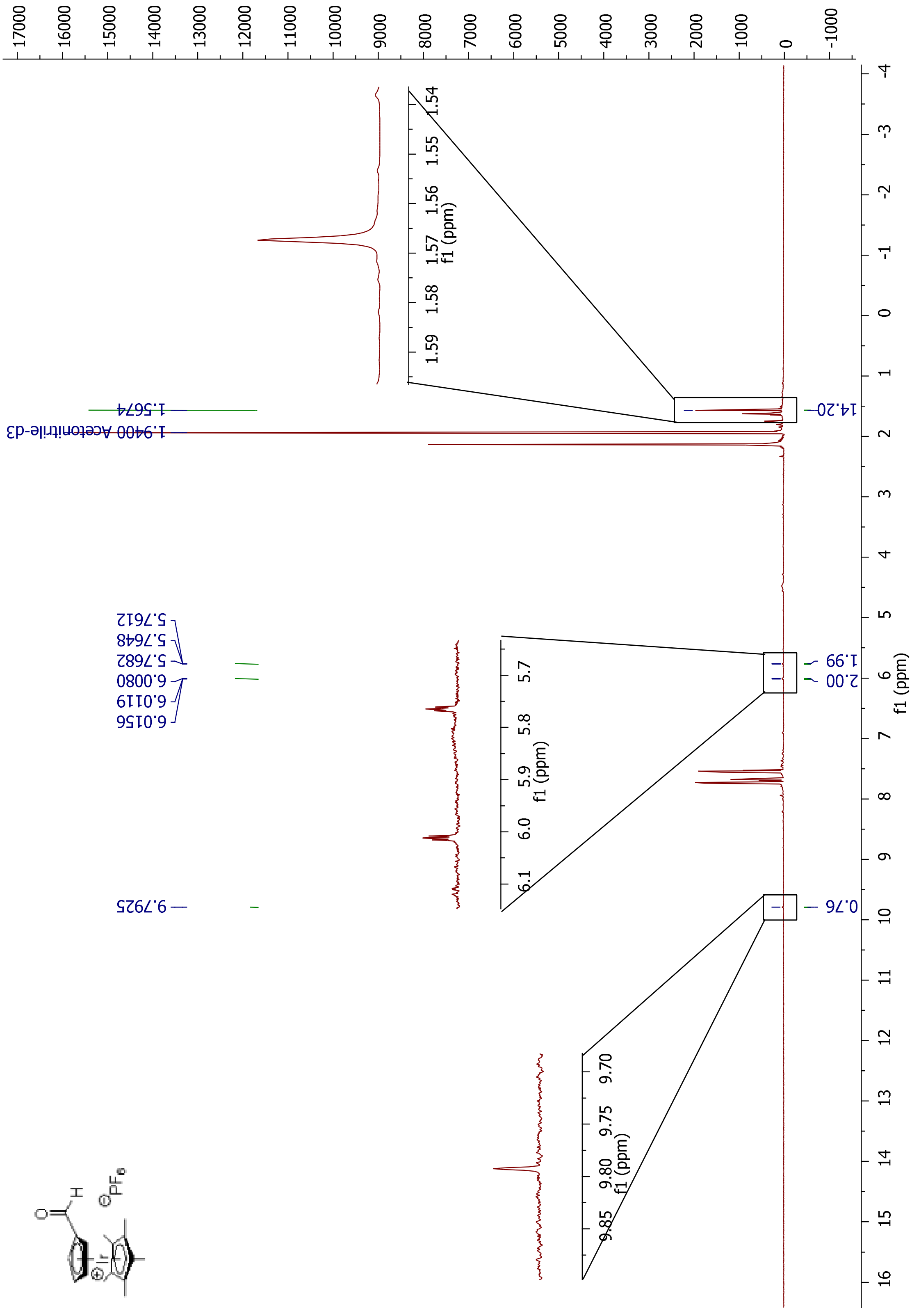


Figure S4.Complexes **8** - ^{1}H NMR (500 MHz, MeCN-d^3).

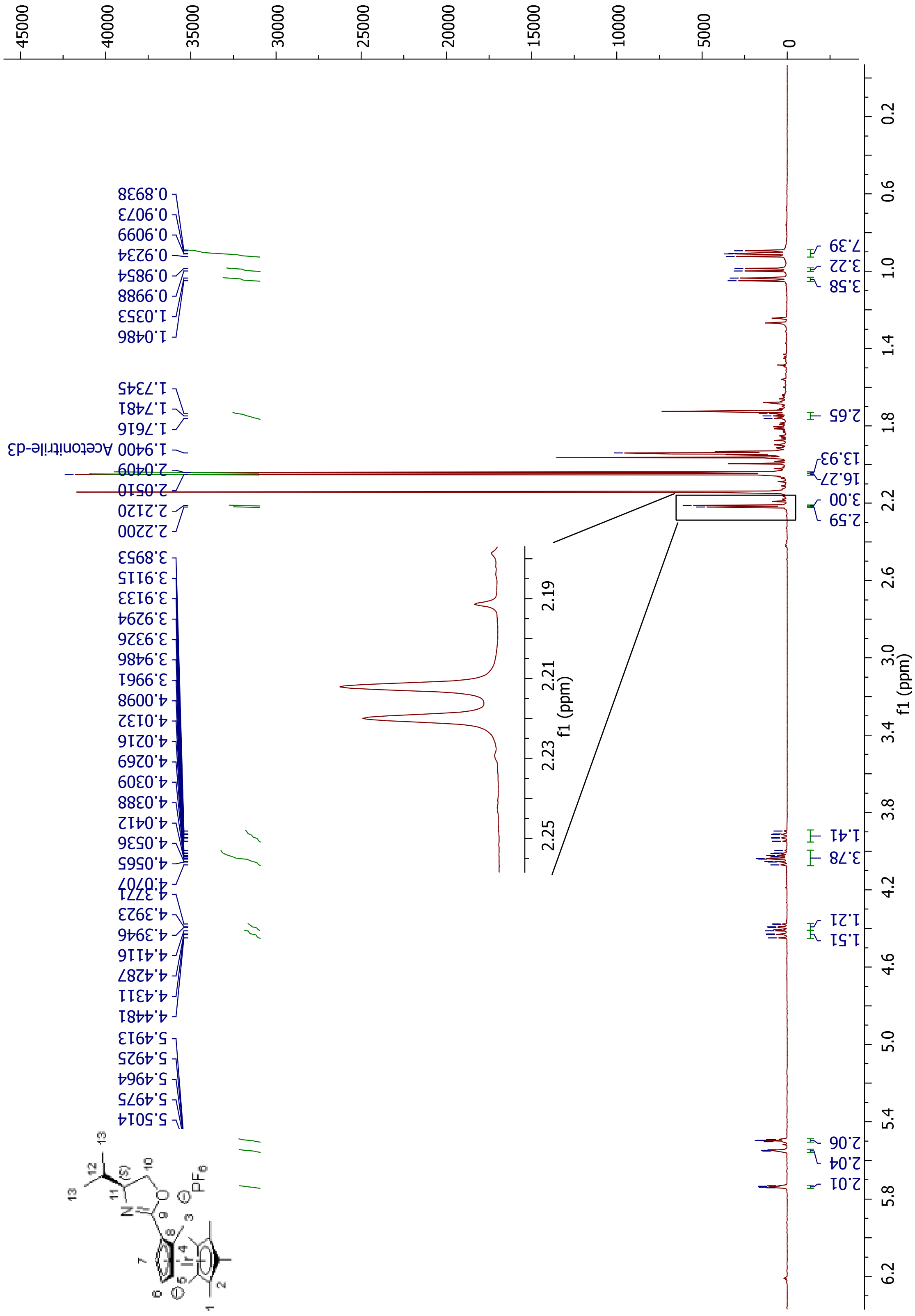


Figure S5. Complexes **8** - ^{13}C NMR (125 MHz, MeCN-d^3).

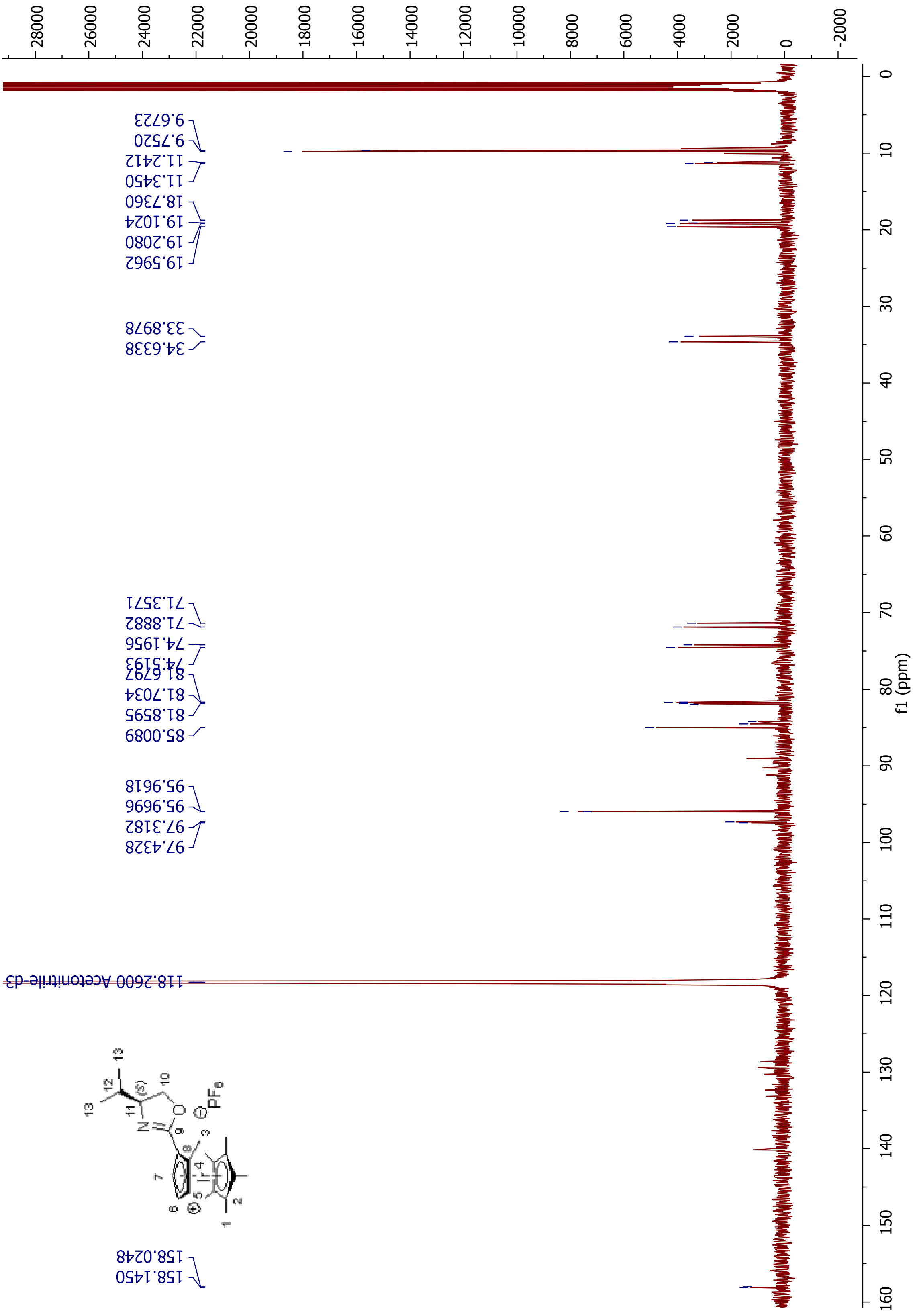


Figure S6.Complex (**D-1**) - ^{1}H NMR (500 MHz, $CDCl_3$).

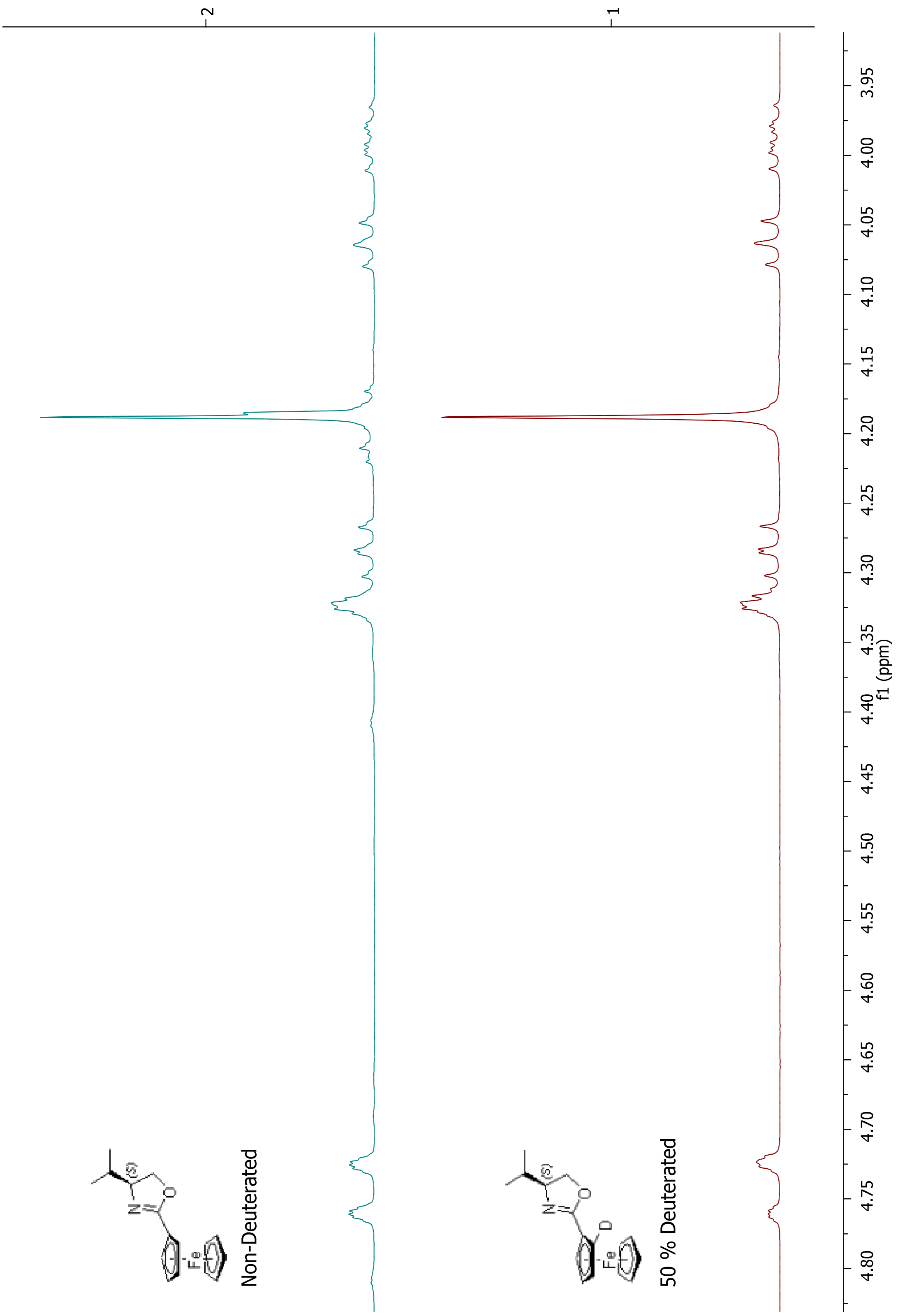


Figure S7. Complex (**D-9**) -^{1}H NMR (500 MHz, CDCl$_3$).

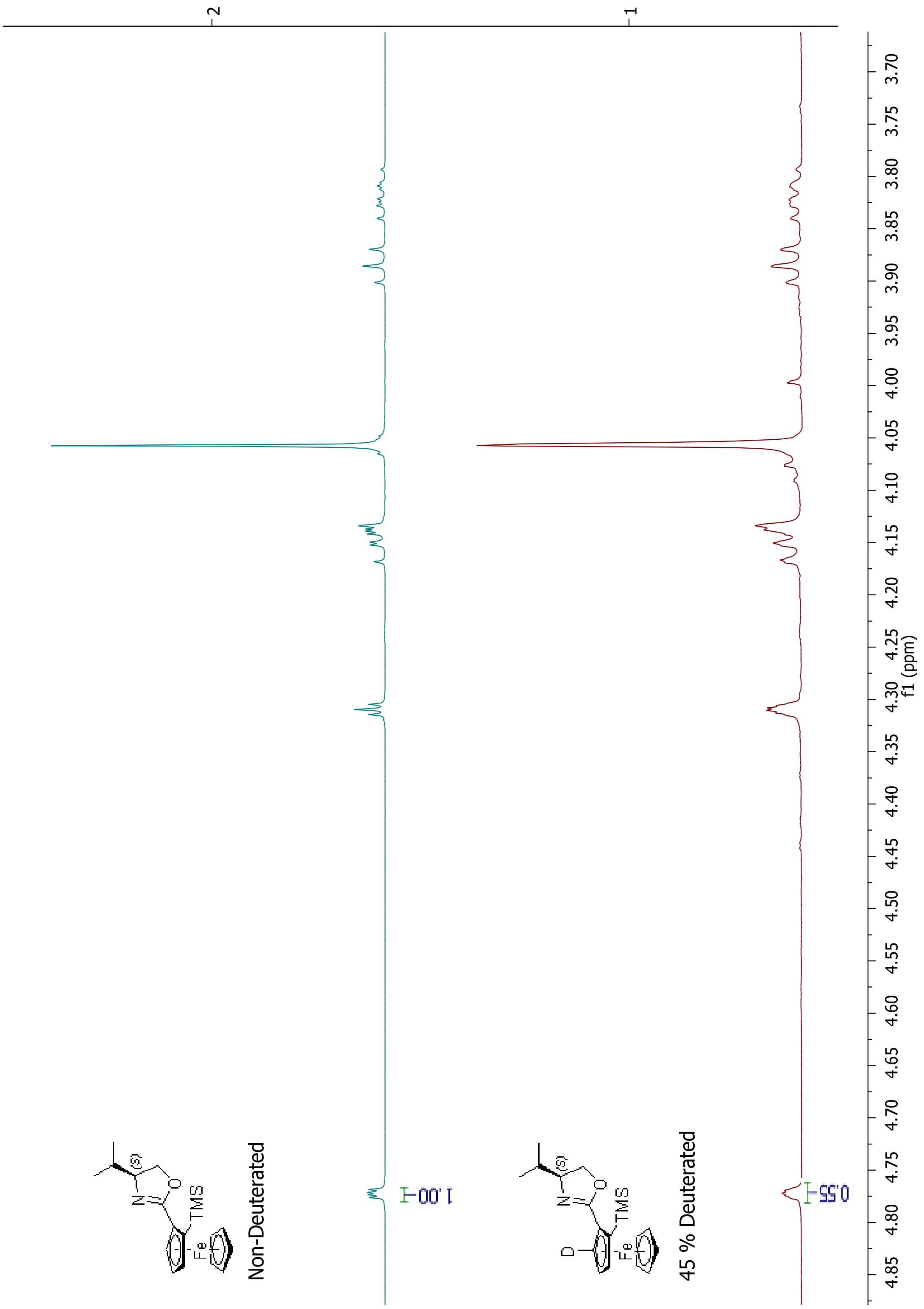


Figure S8. Deuterium incorporation into iridocenium ion to give (**D-3**) Table 1, Entry 1 - ^{1}H NMR (500 MHz, MeCN-d^3).

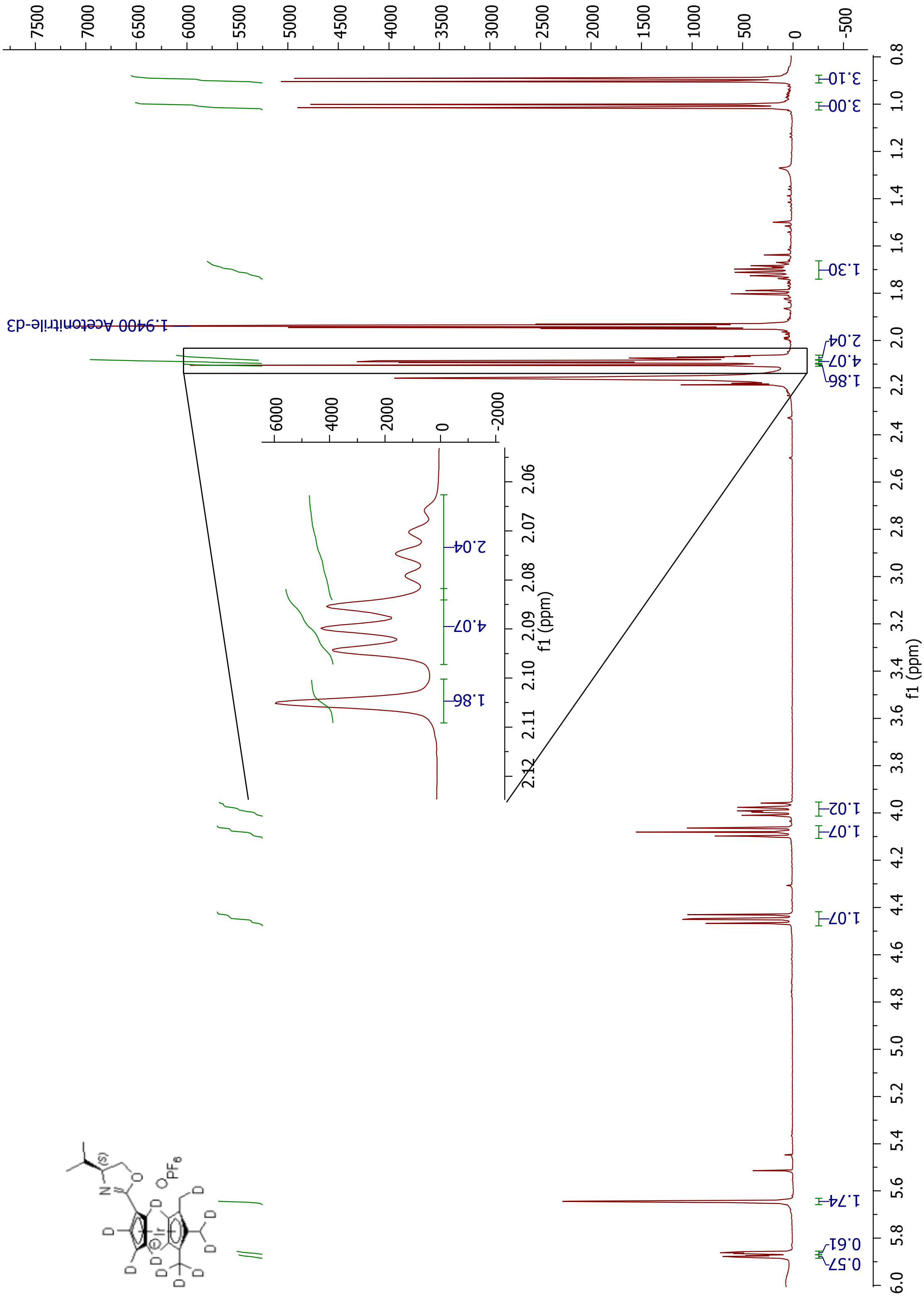


Figure S9. Deuterium incorporation into iridocenium ion to give (**D-3**) Table 1, Entry 2 - (500 MHz, MeCN-d^3).

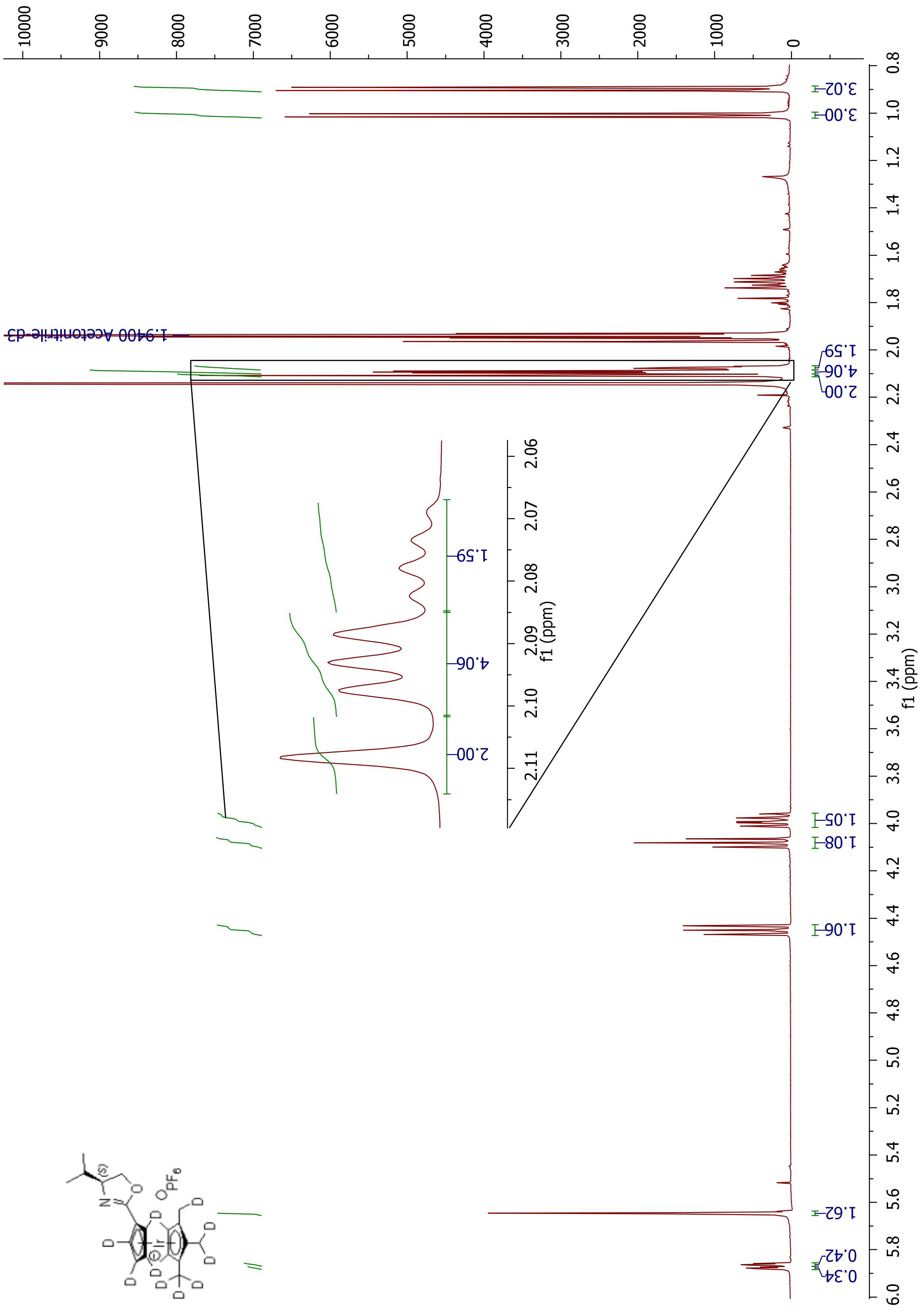
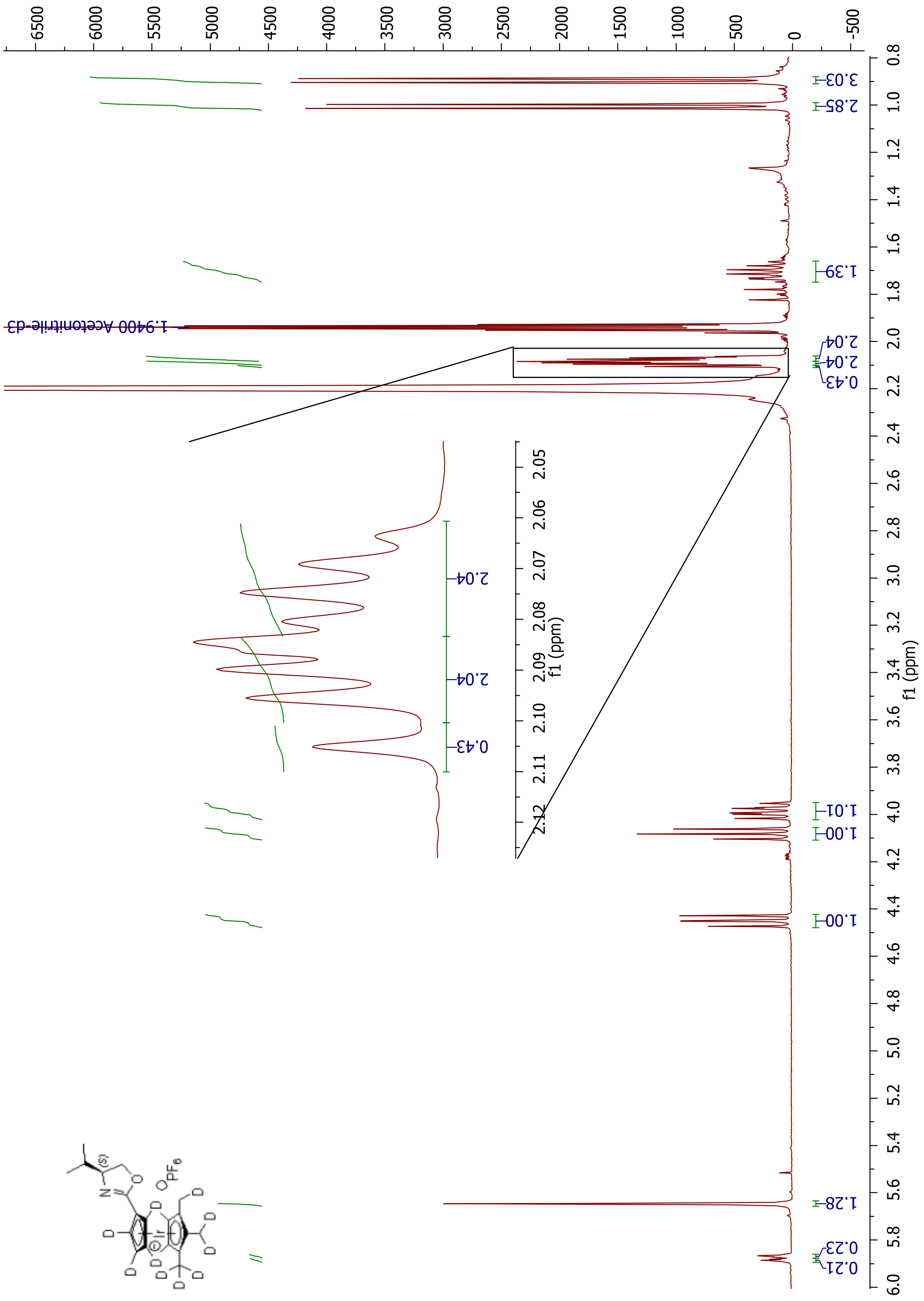
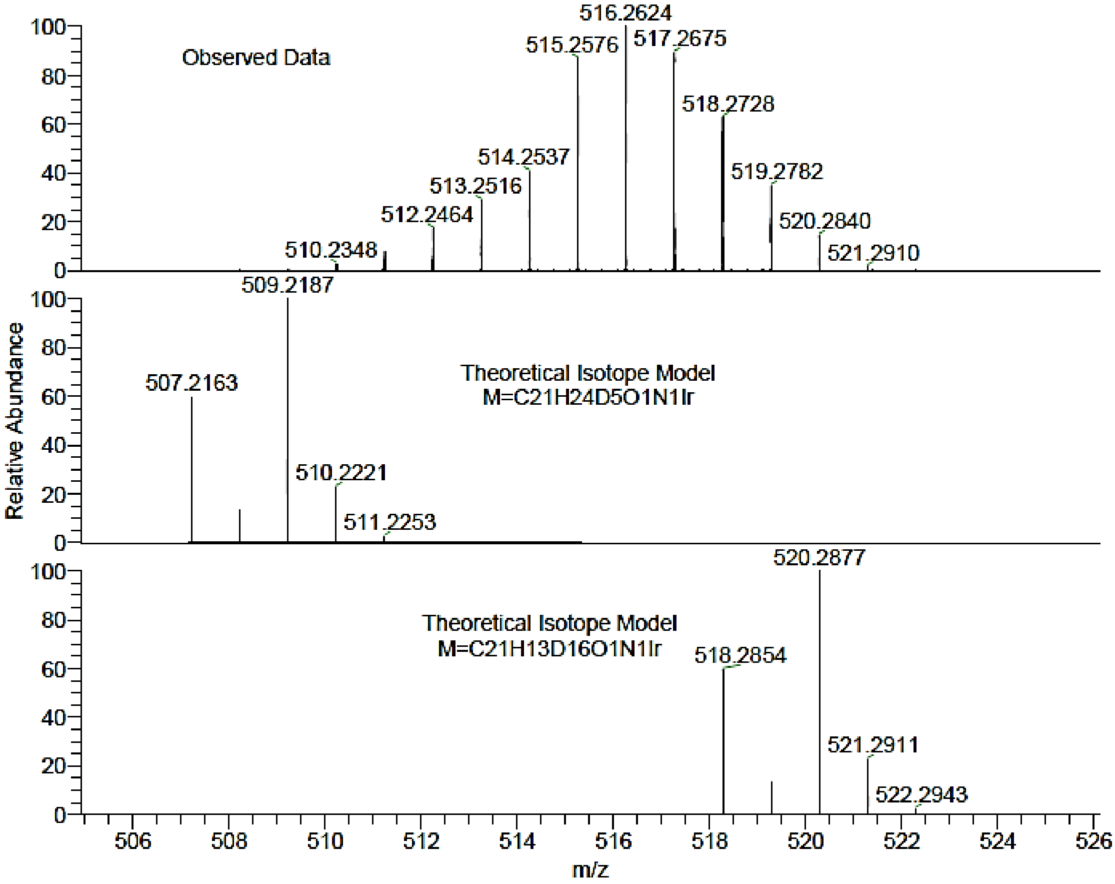


Figure S10. Deuterium incorporation into iridocenium ion to give (**D-3**) Table 1, Entry 3 - ^{1}H NMR (500 MHz, MeCN-d^3).



3. HRMS of deuterium incorporation

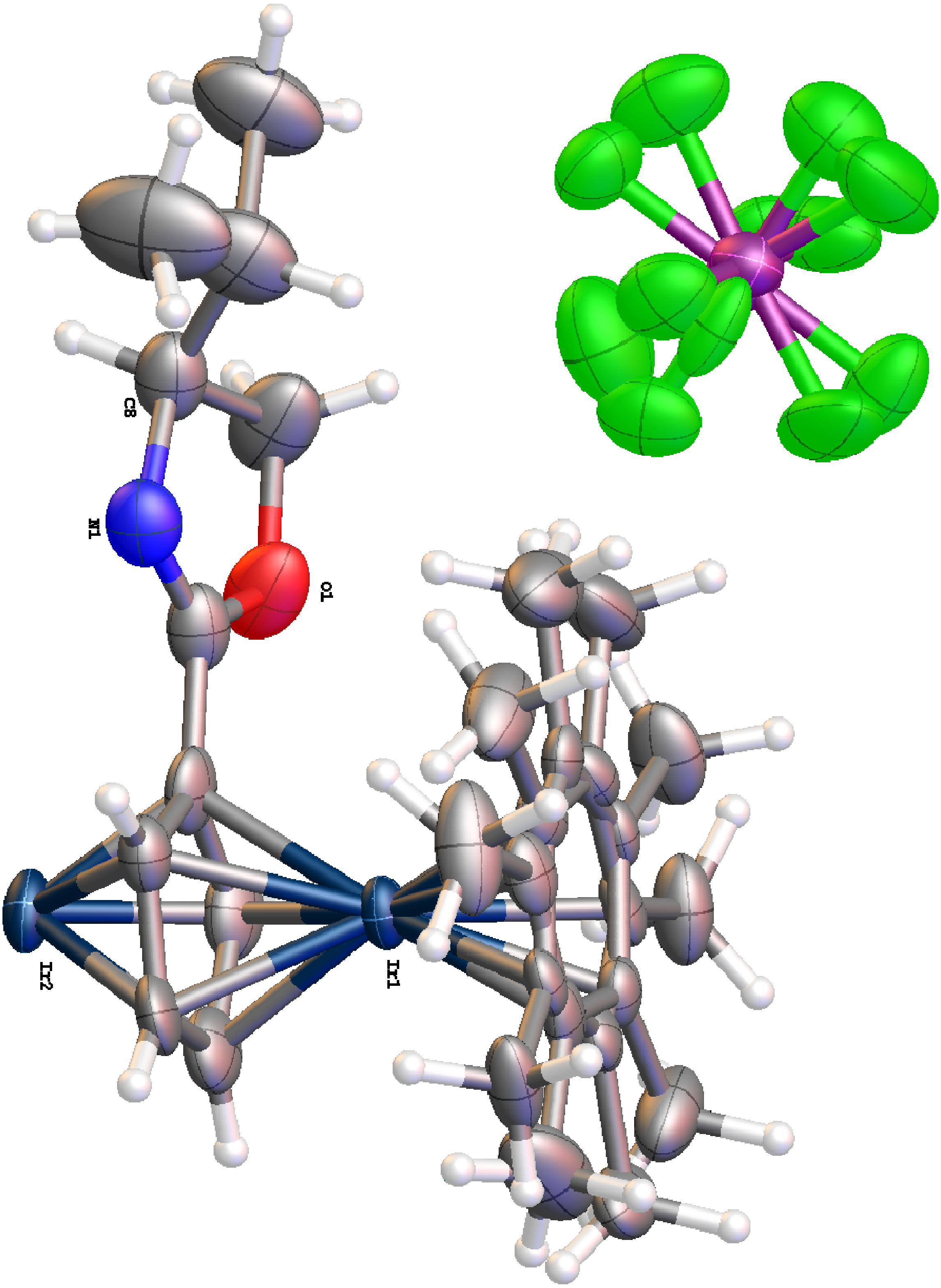
Figure S8. HRMS showing the range of deuterium incorporation into **D-3** (from Table 1, Entry 3 - between 6 and 16 deuteriums incorporated)



4. Single crystal X-ray diffraction

A suitable crystal of **3** was selected and data collected following a standard method,[5] on a Rigaku AFC12 goniometer at 100K equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E-Superbright molybdenum anode generator with VHF Varimax optics (70µm focus).

Cell determination and data collectionwere carried out using CrystalClear.[6] Data reduction, cell refinement and absorption correction were carried out using CrysAlisPro.[7] Structure solutionand refinement using SHELX programs.[8]


C8
N1
O1
Ir1
Ir2

5. References

1. C. J. Richards and A. W. Mulvaney, *Tetrahedron: Asymmetry*, 1996, **7**, 1419.
2. R. A. Arthurs, M. Ismail, C. C. Prior, V. S. Oganesyan, P. N. Horton, S. J. Coles and C. J. Richards, *Chem. Eur. J.*, 2016, **22**, 3065.
3. T. Sammakia and H. A. Latham, *J. Org. Chem.*, 1995, **60**, 6002.
4. Y. Nishibayashi, K. Segawa, Y. Arikawa, K. Ohe, M. Hidai and S. Uemura, *J Organomet. Chem.*, 1997, **545–546**, 381
5. S. J. Coles and P. A. Gale, *Chem. Sci.*, 2012, **3**, 683.
6. Rigaku, *CrystalClear- SM Expert 3.1 b27,* 2013.
7. Rigaku Oxford Diffraction, *CrysAlisPro Version 1.171.38.41*, 2015.
8. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.