

Supporting Information

Enantiopure Planar Chiral and Chiral-at-Metal Iridacycles Derived from Bulky Cobalt Sandwich Complexes

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Index

1. Experimental procedures

General information	S3
Cycloiridation of (S)- 3	S4
Cycloiridation of (S)- 4	S6
Cycloiridation of (S)- 9	S7
Cycloiridation of (S)- 1	S8
Decomposition of iridacycle (<i>S,S_p,S_{ir}</i>)- 6 to (S)- 11 & (Z)- 12	S9
Decomposition of iridacycle mixture to (S)- 13	S10
Preparation of (<i>S,S_p,R_{ir}</i>)- 14 by ligand exchange	S11
Preparation of (<i>S,S_p,S_{ir}</i>)- 6 by ligand exchange	S13
Preparation of (<i>S,S_p,R_{ir}</i>)- 18 by ligand exchange	S13
2. ¹H & ¹³C spectra of key compounds	S15-27
3. X-Ray data	S28-32
4. CD Spectra	S33-36
5. References	S37

1. Experimental procedures (compounds are listed in the order they appear in the paper).

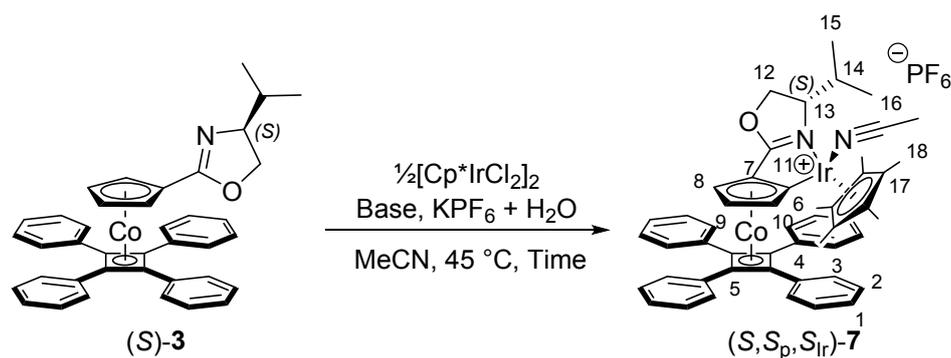
General information

Acetonitrile and dichloromethane were dried by distillation over calcium hydride. Methanol was dried over 4 Å MS. All cycloiridation reactions and 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.

Use was made of ^1H and ^{13}C NMR spectroscopy to confirm compound purity in addition to identity, and copies of these spectra are included below. 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.

For simplicity, in cases where a mixture of diastereoisomers is formed or used as a starting material, only the major isomer will be depicted in the scheme and procedure for this experimental. The supplemental file ColrCycle contains the computed Cartesian coordinates of all of the molecules reported in this study. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modeling program such as Mercury (version 3.3 or later, <http://www.ccdc.cam.ac.uk/pages/Home.aspx>) for visualization and analysis.

Cycloiridation of (S)-3



Oxazoline (S)-3 (0.037 g, 0.06 mmol), (pentamethylcyclopentadienyl)iridium(III) chloride dimer (0.025 g, 0.03 mmol), base (0.06 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 freshly distilled acetonitrile (5 ml) and the introduction (or not) of water via micropipette (10 μl) the mixture was stirred at 45 °C for the desired time. The reaction was allowed to cool to room temperature and separated between hexane and acetonitrile until the hexane layer became colourless. The acetonitrile layer was reduced *in vacuo* and the resulting solid was re-dissolved in a minimum amount of acetonitrile and filtered through a 6 cm pad of neutral alumina using acetonitrile as the eluent to give a bright orange solution. Removal of the solvent *in vacuo* yielded the product as an amorphous orange solid (see table for yields and ratios). Data for major diastereoisomer: mp 138 - 140 °C; ν_{max} (film)/ cm^{-1} 3058, 2967, 2923, 1600 (CN), 842; $[\alpha]_{\text{D}}^{23.3^\circ\text{C}} = -640$ ($c = 0.2$, MeCN)*; HRMS (NS) $[\text{M}-(\text{PF}_6 + \text{MeCN})]^+$ $\text{C}_{49}\text{H}_{48}\text{CoIrNO}^+$, Calc. 918.2693, Obs. 918.2679; ^1H NMR (500 MHz, MeCN- d_3) δ 7.51 - 7.48 (8H, m, *o*-PhH), 7.30 - 7.22 (12H, m, *m+p*-PhH), 5.50 (1H, dd, $J = 2.2, 1.0$ Hz, Cp-H¹⁰), 4.97 (1H, dd, $J = 2.6, 1.0$ Hz, Cp-H⁸), 4.82 (1H, t, $J = 2.5$ Hz, Cp-H⁹), 4.65 (1H, dd, $J = 10.1, 9.1$ Hz, CHH (pointing away from C_4Ph_4)), 4.36 (1H, t, $J = 8.6$ Hz, CHH (pointing towards C_4Ph_4)), 3.90 (1H, ddd, $J = 10.2, 8.3, 3.4$ Hz, CH), 1.70 (15H, s, Cp*), 1.57 - 1.54 (1H, m, ^{*i*}Pr(H)), 0.80 (3H, d, $J = 7.1$ Hz, ^{*i*}Pr(Me) (pointing away from C_4Ph_4)), -0.04 (3H, d, $J = 6.7$ Hz, ^{*i*}Pr(Me) (pointing towards C_4Ph_4)); ^{13}C NMR (125 MHz, MeCN- d_3) δ 178.8 (C¹¹), 136.6 (C⁴), 130.5 (C³), 129.1 (C²), 127.9 (C¹), 107.3 (C⁶), 91.3 (C¹⁷), 91.2 (C⁷), 87.1 (C¹⁰), 86.5 (C⁹), 83.2 (C⁸), 77.8 (C⁵), 73.6 (C¹²), 67.5 (C¹³), 30.0 (C¹⁴), 19.9 (C¹⁵), 15.5 (C¹⁶), 9.5 (C¹⁸).

Note: Protons and carbons relating to the acetonitrile ligand were unable to be observed due to exchange with the solvent. * = in order to weigh out the correct mass of base a glove box

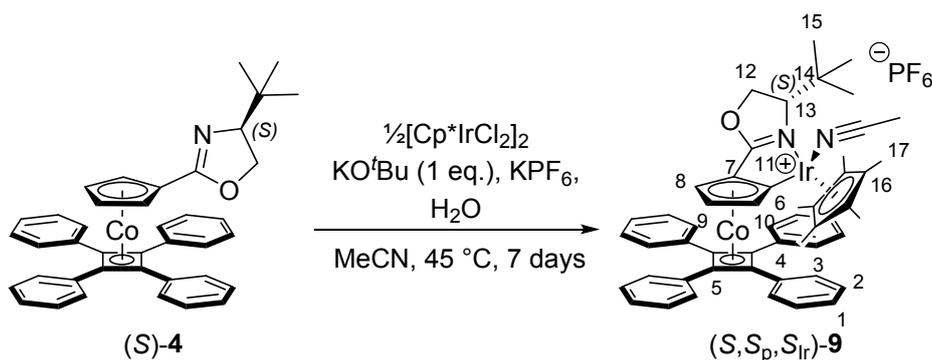
was used as both bases are hygroscopic, * = ratio of 7.6:1. Using D₂O instead of H₂O did not lead to deuterium incorporation onto the iridacycle. See Figure S17 for CD spectra.

Table S1. The effects of base, water and time on the cycloiridation of (S)-3.

Entry	Base	Water?	Time	Ratio ^a	Yield ^b
1	NaOH	×	18 h	1:0.86 (1.2:1)	20.2%
2	NaOH	✓	18 h	1:0.59 (1.7:1)	20.2%
3	KO ^t Bu	×	18 h	1:0.27 (3.7:1)	23.2%
4	KO ^t Bu	✓	18 h	1:0.36 (2.8:1)	41.0%
5	NaOH	×	7 days	1:0.64 (1.6:1)	19.3%
6	NaOH	✓	7 days	1:0.49 (2:1)	56.4%
7	KO ^t Bu	×	7 days	1:0.21 (4.8:1)	39.4%
8	KO ^t Bu	✓	7 days	1:0.35 (2.9:1)	78.1%
9	KO ^t Bu	✓ ^c	3 days	1:0.66 (1.5:1)	35.5%

^a Ratio of diastereoisomers was calculated by averaging three different ratios in the crude NMR (Cp-H^{maj}:Cp-H^{min}, Cp^{*maj}:Cp^{*min} & ⁱPrMe^{maj}:ⁱPr^{min}). ^b Isolated yield of iridacycle mixture. ^c 11 μl of D₂O added to the reaction.

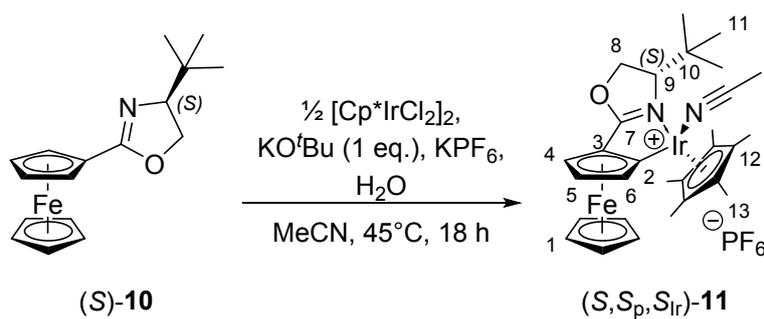
Cycloiridation of (S)-4



Oxazoline (S)-4 (0.038 g, 0.06 mmol), (pentamethylcyclopentadienyl)iridium(III) chloride dimer (0.025 g, 0.03 mmol), potassium *tert*-butoxide (0.007 g, 0.06 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 freshly distilled acetonitrile (5 ml) and the introduction of water via micropipette (10 μl) the mixture was stirred at 45 $^\circ\text{C}$ for the 7 days. The reaction was allowed to cool to room temperature and separated between hexane and acetonitrile until the hexane layer became colourless. The acetonitrile layer was reduced *in vacuo* and resulting solid was re-dissolved in a minimum amount of acetonitrile and filtered through a 6 cm pad of neutral alumina using acetonitrile as the eluent to give a bright orange solution. Removal of the solvent *in vacuo* yielded the product as an amorphous orange solid (0.018 g, 27 %): $[\alpha]_{\text{D}}^{22.2^\circ\text{C}} = -337$ ($c = 0.88$, MeCN); HRMS (NS) $[\text{M}(\text{PF}_6 + \text{MeCN})]^+$ $\text{C}_{50}\text{H}_{50}\text{CoIrNO}^+$, Calc. 932.2852, Obs. 932.2851; ^1H NMR (500 MHz, MeCN- d_3) δ 7.51 - 7.47 (8H, m, *o*-PhH), 7.32 - 7.21 (12H, m, *m+p*-PhH), 5.44 (1H, dd, $J = 2.3, 1.0$ Hz, Cp-H¹⁰), 5.07 (1H, dd, $J = 2.6, 1.0$ Hz, Cp-H⁸), 4.73 (1H, t, $J = 2.5$ Hz, Cp-H⁹), 4.58 (1H, dd, $J = 10.2, 9.3$ Hz, CHH (opposite face as ^tBu)), 4.50 (1H, dd, $J = 9.3, 6.1$ Hz, CHH (same face as ^tBu)), 3.76 (1H, dd, $J = 10.2, 6.1$ Hz, CH), 1.66 (15H, s, Cp*), 0.56 (9H, s, ^tBu); ^{13}C NMR (125 MHz, MeCN- d_3) δ 180.6 (C¹¹), 136.8 (C⁴), 130.5 (C³), 129.2 (C²), 128.0 (C¹), 107.4 (C⁶), 91.7 (C¹⁶), 91.5 (C⁷), 87.3 (C⁸), 86.6 (C¹⁰), 83.1 (C⁹), 77.6 (C⁵), 74.8 (C¹²), 70.6 (C¹³), 35.0 (C¹⁴), 25.9 (C¹⁵), 9.8 (C¹⁷).

Note: Protons and carbons relating to the acetonitrile ligand were unable to be observed due to exchange with the solvent. * = in order to weigh out the correct mass of base a glove box was used. See Figure S18 for CD spectra.

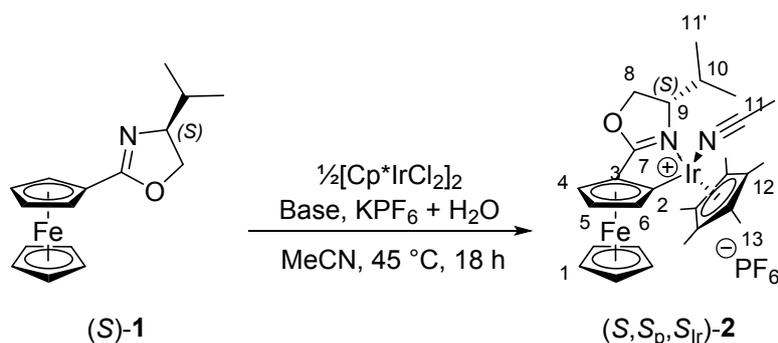
Cycloiridation of (S)-10



Oxazoline (S)-**10** (0.020 g, 0.06 mmol, (pentamethylcyclopentadienyl)iridium(III) chloride dimer (0.025 g, 0.03 mmol), potassium *tert*-butoxide (0.007 g, 0.06 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 freshly distilled acetonitrile (5 ml) and the introduction of water via micropipette (10 μ l) the mixture was stirred at 45 °C overnight. After cooling to room temperature the reaction mixture was separated with hexane until the hexane layer became colourless. The acetonitrile layer was reduced *in vacuo* and the resulting solid was re-dissolved in a minimum amount of acetonitrile and filtered through a 6 cm pad of neutral alumina using acetonitrile as the eluent to give a bright orange solution. Removal of the solvent *in vacuo* yielded the desired product as an amorphous air sensitive orange solid (0.023 g, 45 %): ν_{\max} (film)/ cm^{-1} 2960, 2920, 2877, 1594, 842, 560; $[\alpha]_{\text{D}}^{20.5^\circ\text{C}} = -776$ ($c = 0.3$, acetonitrile); HRMS (NS) $[\text{M-PF}_6\text{-MeCN}]^+ \text{C}_{27}\text{H}_{35}\text{FeIrNO}^+$, Calc. 638.1693, Obs. 638.1672; ^1H NMR (500 MHz, MeCN- d_3) δ 4.83 (1H, dd, $J = 9.4, 5.1$ Hz, CHH), 4.65 (1H, t, $J = 9.7$ Hz, CHH), 4.64 (1H, dd, $J = 2.2, 0.7$ Hz, Cp-H⁶), 4.58 (1H, dd, $J = 2.3, 0.7$ Hz, Cp-H⁴), 4.55 (1H, t, $J = 2.3$ Hz, Cp-H⁵), 4.16 (5H, s, CpH), 3.85 (1H, dd, 10.0, 5.1 Hz, CH^tBu), 1.59 (15H, s, Cp*), 1.01 (9H, s, ^tBu); ^{13}C NMR (125 MHz, MeCN- d_3) δ 185.1 (C⁷), 96.4 (C²), 91.2 (C¹²), 75.0 (C⁸), 74.9 (C⁶), 74.0 (C³), 71.7 (C⁵), 70.4 (C⁹), 70.0 (C¹), 65.5 (C⁴), 35.1 (C¹⁰), 26.0 (C¹¹), 9.4 (C¹³).

Note: Protons and carbons relating to the acetonitrile ligand were unable to be observed due to exchange with the solvent. * = in order to weigh out the correct mass of base a glove box was used. See Figure S20 for CD spectra.

Cycloiridation of (S)-1



Oxazoline (S)-1 (0.019 g, 0.06 mmol), (pentamethylcyclopentadienyl)iridium(III) chloride dimer (0.025 g, 0.03 mmol), potassium *tert*-butoxide (0.007 g, 0.06 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 freshly distilled acetonitrile (5 ml) and the introduction (or not) of water via micropipette (10 μ l) the mixture was stirred at 45 $^\circ$ C for the desired time. The reaction was allowed to cool to room temperature and separated between hexane and acetonitrile until the hexane layer became colourless. The acetonitrile layer was reduced *in vacuo* and the resulting solid was re-dissolved in a minimum amount of acetonitrile and filtered through a 6 cm pad of neutral alumina using acetonitrile as the eluent to give a bright orange solution. Removal of the solvent *in vacuo* yielded the product as an amorphous orange solid (see table for yields and ratios). Data for major diastereoisomer: ν_{max} (film)/ cm^{-1} 2961, 2919, 2871, 1600, 1510, 840, 557; $[\alpha]_{\text{D}}^{24.0^\circ\text{C}} = -782$ ($c = 0.2$, acetonitrile); $^1\text{H NMR}$ (500 MHz, MeCN-d_3) δ 4.77 (1H, dd, $J = 9.2, 5.6$ Hz, CHH), 4.71 - 4.67 (1H, m, CHH), 4.65 (1H, dd, $J = 2.3, 0.8$ Hz, Cp-H⁶), 4.56 (1H, dd, $J = 2.3, 0.8$ Hz, Cp-H⁴), 4.54 (1H, t, $J = 2.3$ Hz, Cp-H⁵), 4.15 (5H, s, CpH), 4.02 (1H, ddd, 9.8, 5.6, 2.7 Hz), 2.10 - 2.04 (1H, m, ^{*i*}PrH), 1.67 (15H, s, Cp*), 1.00 (3H, d, $J = 7.1$ Hz, ^{*i*}PrMe^{11'}), 0.97 (3H, d, $J = 6.7$ Hz, ^{*i*}PrMe¹¹); $^{13}\text{C NMR}$ (125 MHz, MeCN-d_3) δ 183.92 (C⁷), 95.30 (C²), 91.01 (C¹²), 74.86 (C⁶), 74.72 (C³), 73.98 (C⁸), 71.76 (C⁵), 69.87 (C¹), 67.41 (C⁹), 65.28 (C⁴), 30.08 (C¹⁰), 19.29 (C^{11'}), 15.26 (C¹¹), 9.33 (C¹³). Matches previously reported data.¹

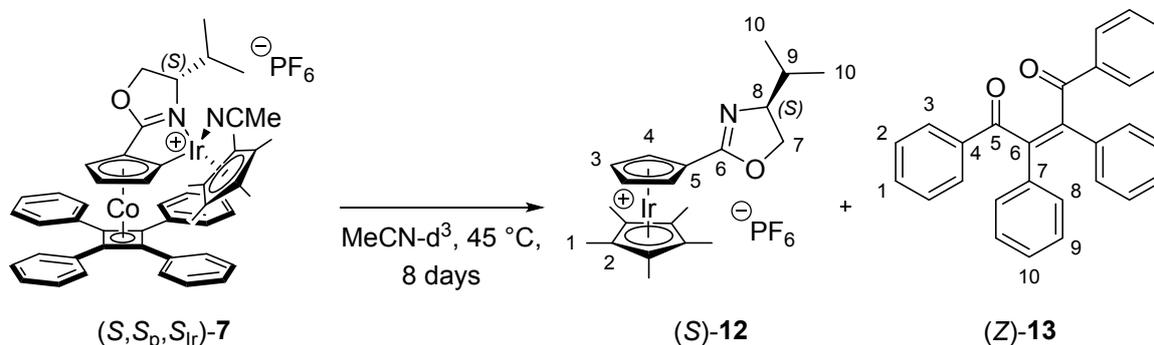
Note: Protons and carbons relating to the acetonitrile ligand were unable to be observed due to exchange with the solvent. HRMS was unable to be performed due to the low stability of the complex. * = in order to weigh out the correct mass of base a glove box was used. See Figure S19 for CD spectra.

Table S2. The effects of water on the cycloiridation of (S)-1.

Entry	Water?	Time	Ratio ^a	Yield ^b
1	×	18 h	1:0.02 (48:1)	37.8%
2	✓	18 h	1:0.7 (14:1)	30.5%

^a Ratio of diastereoisomers was calculated from the ratio of major and minor Cp singlets. ^b Isolated yield of iridacycle mixture.

Decomposition of iridacycle (S,S_p,S_{Ir})-7 to (S)-12 & (Z)-13



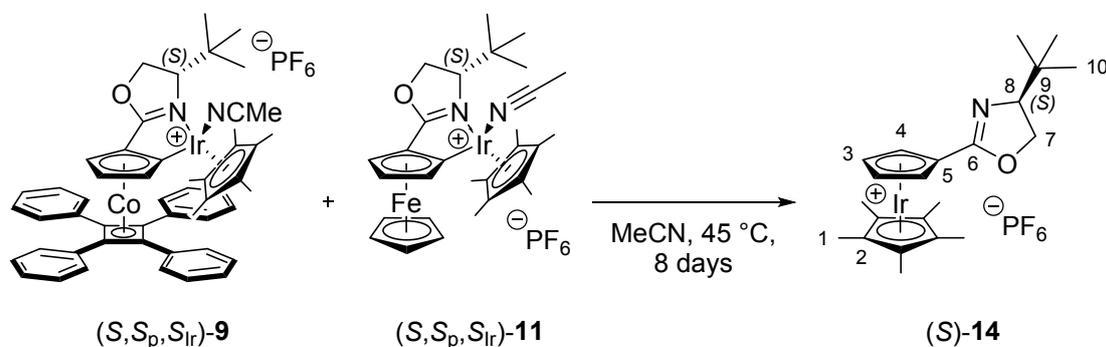
Iridacycle (S,S_p,S_{Ir})-7 (0.031 g, 0.028 mmol) were dissolved in deuterated acetonitrile (not distilled or degassed) and stirred in a schlenk tube at 45 °C for 8 days. Proton NMRs were taken after each day after allowing the reaction to cool to room temperature. Proton NMRs were taken after each day by allowing the reaction to cool to room temperature. After 8 days the reaction mixture showed a mixture of compounds (S)-11 and (Z)-12.

Data for (S)-12: mp 189.7 - 191.2 °C, $[\alpha]_D^{23.0^\circ\text{C}} = -41.81$ (c = 0.22, acetonitrile); ν_{max} (film)/cm⁻¹ 2962, 2970, 1666 (C=N), 841; ¹H NMR (300 MHz, CDCl₃) 5.88 (1H, bs, Cp-H⁴), 5.84 (1H, bs, Cp-H⁴), 5.79 (1H, bs, Cp-H³), 5.77 (1H, bs, Cp-H³), 4.41 (1H, dd, J = 9.1, 8.5 Hz, CHH), 4.06 (1H, t, J = 8.5 Hz, CHH), 4.03 - 3.97 (1H, m, CH), 2.16 (15H, s, Cp*), 1.77 - 1.69 (1H, m, ⁱPrH), 1.03 (3H, d, J = 6.7 Hz, ⁱPrCH₃), 0.92 (3H, d, J = 6.7 Hz, ⁱPrCH₃); ¹³C NMR (125 MHz, CDCl₃) δ 157.02 (C⁶), 95.84 (C²), 84.79 (C⁵), 83.22 (C^{3'}), 83.12 (C³), 80.74 (C^{4'}), 80.64 (C⁴), 73.61 (C⁸), 71.43 (C⁷), 33.46 (C⁹), 19.28 (C^{10'}), 18.69 (C¹⁰), 10.05 (C¹). Matches previously reported data.²

Data for (Z)-13: ν_{max} (film)/cm⁻¹ 3084, 3058, 3025, 2967, 1659 (CO); ¹H NMR (500 MHz, CDCl₃) δ 7.86 - 7.83 (4H, m, PhH³), 7.42 (2H, tt, J = 7.4 + 1.3 Hz, PhH¹), 7.34 - 7.29 (4H, m, PhH⁹), 7.21 - 7.15 (10H, m, PhH^{2,8+10}); ¹³C NMR (125 MHz, CDCl₃) δ 197.1 (C⁵), 144.7 (C⁶), 136.5 (C⁷), 135.4 (C⁴), 133.1 (C¹), 130.2 (C³), 130.0 (C²), 128.8 (C⁸), 128.5 (C¹⁰), 128.4 (C⁹). Matches previously reported data.³

Note: See S7 for a comparison of NMR spectra over 8 days. See Figure S14 for X-ray structure of (Z)-13.

Decomposition of iridacycle mixture to (S)-14

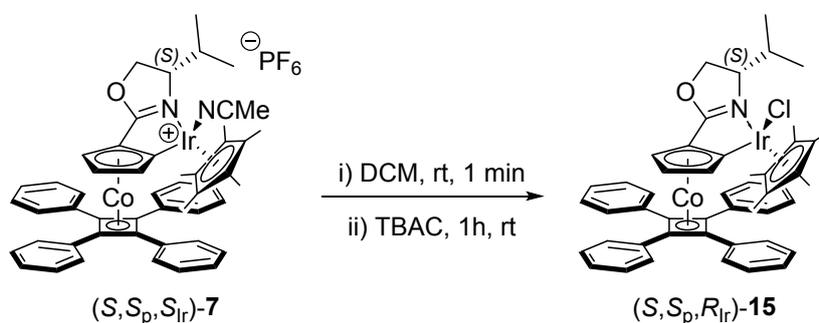


(S,S_p,S_{Ir}) -9 (0.031 g, 0.028 mmol) and (S,S_p,S_{Ir}) -11 (0.015 g, 0.018 mmol) dissolved in acetonitrile (not distilled or degassed) and stirred in a schlenk tube at 45 °C. After 8 days the reaction mixture was reduced *in vacuo* and then purified by column chromatography on neutral alumina using acetonitrile as the eluent resulting isolation of a yellow solid (0.003 g, 11 %): mp 144 - 146 °C, ν_{\max} (film)/ cm^{-1} 2954, 2925, 2871, 2856, 1662 (C=N), 840; $[\alpha]_D^{23.0^\circ\text{C}} = -29.4$ ($c = 0.34$, acetonitrile); HRMS (NS) $[\text{M-PF}_6]^+$ $\text{C}_{22}\text{H}_{31}\text{IrNO}^+$, Calc. 518.2030, Obs. 518.2017; ^1H NMR (500 MHz, MeCN-d_3) 5.89 (1H, dd, $J = 3.6, 1.4$ Hz, Cp-H), 5.85 (1H, dd, $J = 3.3, 1.7$ Hz, Cp-H), 5.64 (2H, t, $J = 1.7$ Hz, Cp-H), 4.38 (1H, dd, $J = 10.2, 8.9$ Hz, CHH), 4.19 (1H, t, $J = 9.0$ Hz, CHH), 4.04 (1H, dd, $J = 10.2, 9.1$ Hz, CH), 2.12 (15H, s, Cp*), 0.91 (9H, s, $t\text{Bu}$); ^{13}C NMR (125 MHz, MeCN-d_3) δ 157.7 (C⁶), 99.6 (C²), 86.1 (C⁵), 83.4 (C³), 81.4 (C⁴), 81.4 (C⁴), 77.4 (C⁸), 70.3 (C⁷), 34.2 (C⁹), 26.1 (C¹⁰), 10.2 (C¹).

Note: crude shows all (S,S_p,S_{Ir}) -11 gone with a 1.1:1 ratio of (S)-14 and (S,S_p,S_{Ir}) -9. Low yield is due to difficulties separating (S,S_p,S_{Ir}) -9 and (S)-14 on the column.

Preparation of (*S,S_p,R_{Ir}*)-15 by ligand exchange

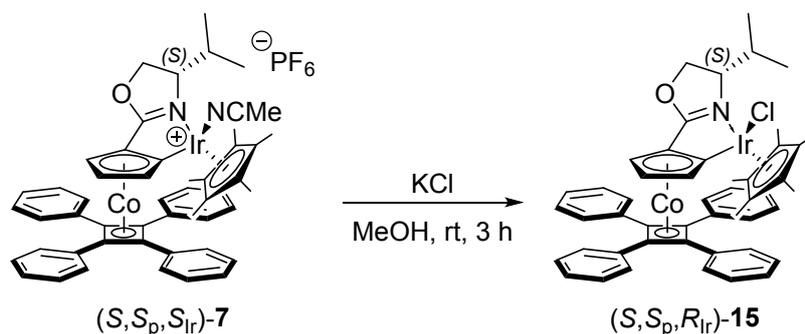
Route 1



Iridacycle (*S,S_p,S_{Ir}*)-7 (0.033 g, 0.03 mmol) was added to a flame dried RBF under an inert atmosphere and dissolved in dry dichloromethane (5 ml). To this, a solution of tetra-*n*-butylammonium chloride (0.008 g, 0.03 mmol) in dry dichloromethane (1 ml) was added causing an immediate colour change from brown green to bright orange. The reaction was allowed to stir at room temperature for 1 h before removing the solvent *in vacuo*. Excess tetra-*n*-butylammonium chloride was removed by re-dissolving the orange residue in hexane/dichloromethane and separating with brine (4 x 50 ml). The organics were dried by filtering through a glass wool pad loaded with magnesium sulphate and removing the solvent *in vacuo* to give a tacky orange solid (0.02 g, 78 %): mp 180 - 182 °C; HRMS (AS) [M+H]⁺ C₄₉H₄₈CoIrNOCl+H⁺, Calc. 954.2453, Obs. 954.2457.

Note: The proton NMR spectrum was very broad and unable to be assigned (see Figure S10 for a comparison between NMR solvents). In addition to this, further data on this compound was unable to be obtained due to the small quantity of pure sample obtained from crystallisation. See Figures S15 & S16 for X-ray structures.

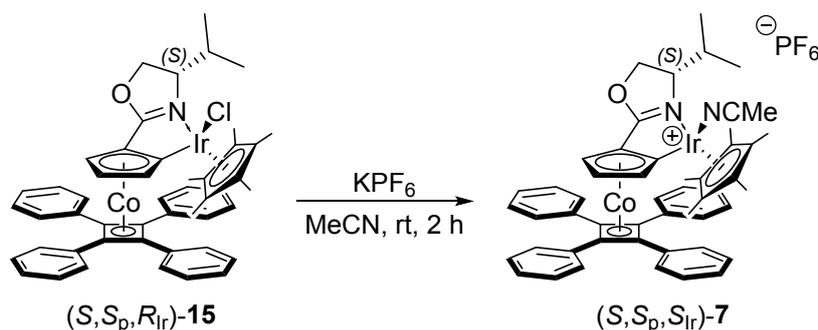
Route 2



To a RBF containing Iridacycle $(S,S_p,S_{Ir})\text{-7}$ (0.027 g, 0.03 mmol) and potassium chloride (0.028 g, 0.38 mmol) was added methanol (3 ml) to give a brown/orange solution. The reaction was allowed to stir at room temperature for 1 h before filtering through neutral alumina using methanol as the eluent. The solvent was removed *in vacuo* to give the crude product. The crude was re-dissolved in ethyl acetate and transferred to an NMR tube whereby hexane was carefully layered on top and the solvents allowed to slowly diffuse and evaporate, yielded crystals suitable for X-ray diffraction (0.02 g, 86 %): mp 180 - 182 °C; HRMS (AS) $[M+H]^+$ $C_{49}H_{48}CoIrNOCl+H^+$, Calc. 954.2453, Obs. 954.2457.

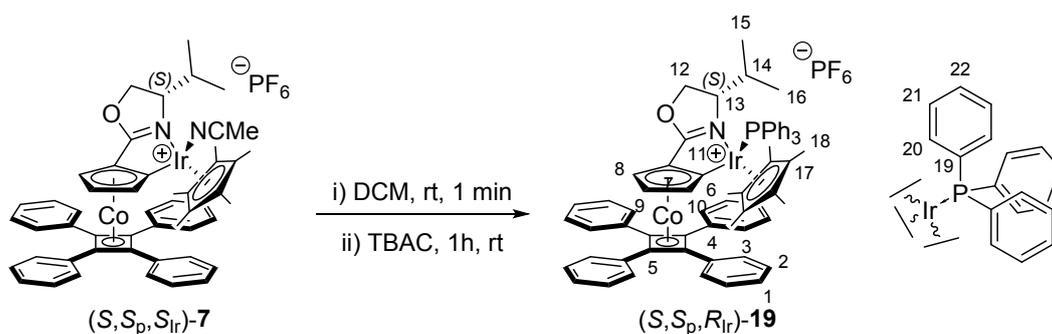
Note: The proton NMR spectrum was very broad and unable to be assigned (see Figure S10 for a comparison between NMR solvents). In addition to this, further data on this compound was unable to be obtained due to the small quantity of pure sample obtained from crystallisation. See Figures S15 & S16 for X-ray structures.

Preparation of (*S,S_p,S_{Ir}*)-7 by ligand exchange



(*S,S_p,R_{Ir}*)-15 (0.021 g, 0.02 mmol) and potassium hexafluorophosphate (0.016 g, 0.09 mmol) was added to a flame dried schlenk tube under an inert atmosphere. After the dissolving in acetonitrile the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was separated with hexane until the hexane layer became colourless. The acetonitrile layer was reduced *in vacuo*. Purification was achieved by filtering through a 30 cm pad of neutral alumina, using acetonitrile as the eluent, and collecting the first bright orange fractions. Removal of the solvent *in vacuo* yielded the desired product as an amorphous orange solid (0.017 g, 69 %).

Preparation of (*S,S_p,R_{Ir}*)-19 by ligand exchange



(*S,S_p,S_{Ir}*)-7 (0.022 g, 0.02 mmol) was added to a flame dried RBF under an inert atmosphere and dissolved in dry dichloromethane (2 ml). To this, a solution of triphenylphosphine (0.053 g, 0.20 mmol) in dichloromethane (1 ml) was added causing an immediate colour change from brown green to bright orange. The reaction was allowed to stir at room temperature for 1 h before concentrating under reduced pressure. Addition of hexane caused a precipitate to form which was collected via filtration and washed with copious amounts of hexane to remove excess triphenylphosphine. Drying in air yielded a red powder (0.03 g, 85 %): mp 182

- 183 °C; ν_{\max} (film)/ cm^{-1} 3058, 2963, 2923, 2868, 1586 (C=N), 838; $[\alpha]_{\text{D}}^{23.9^\circ\text{C}} = -504$ (c = 0.1, chloroform)*; HRMS (NS) $[\text{M-PF}_6]^+ \text{C}_{67}\text{H}_{63}\text{CoIrNOP}^+$, Calc. 1180.3608, Obs. 1180.3597; ^1H NMR (500 MHz, CDCl_3) δ 7.46 - 7.08 (15H, m, PPh_3), 7.40 - 7.36 (8H, m, *o*-PhH), 7.29 - 7.27 (4H, m, *p*-PhH), 7.22 - 7.18 (8H, *m*-PhH), 5.32 (1H, brs, Cp-H¹⁰), 4.54 (1H, dd, $J = 9.3, 5.0$ Hz, CHH (pointing towards C_4Ph_4)), 4.37 (1H, d, $J = 9.7$ Hz, CHH (pointing away from C_4Ph_4)), 4.33 (1H, brs, Cp-H⁹), 4.29 (1H, brs, Cp-H⁸), 3.76 - 3.70 (1H, m, CH), 1.97 - 1.90 (1H, m, ^{*i*}Pr(H)), 1.31 (15H, d, $J = 1.5$ Hz, Cp*), 0.96 (3H, d, $J = 7.0$ Hz, ^{*i*}Pr(Me) (pointing away from C_4Ph_4)), 0.43 (3H, d, $J = 6.7$ Hz, ^{*i*}Pr(Me) (pointing towards C_4Ph_4)); ^{13}C NMR (125 MHz, CDCl_3) δ 179.3 (C¹¹), 135.7 (C⁴), 134.0 (C²²), 132.2 (d, $J = 10.0$ Hz, C¹⁹), 129.5 (d, $J = 18.5$ Hz, C²⁰), 129.1 (C³), 128.5 (C²), 128.3 (C²¹), 127.2 (C¹), 122.4 (d, $J = 9.8$ Hz, C⁷), 95.8 (d, $J = 2.2$ Hz, C¹⁷), 90.8 (C¹⁰), 90.5 (C⁶), 90.4 (C⁹), 77.5 (C⁸), 75.9 (C⁵), 71.8 (C¹²), 69.4 (C¹³), 29.3 (C¹⁴), 19.1 (C¹⁵), 15.4 (C¹⁶), 9.9 (C¹⁸), ^{31}P NMR (202 MHz, CDCl_3) δ 7.13 (PPh_3).

Note: * = ratio of 7.4:1.

2. ^1H and ^{13}C spectra for new compounds

Figure S1. (*S,S*_p,*S*_{ir})-**7** (inlays show peaks for (*S,R*_p,*R*_{ir})-**8**) - ^1H NMR (500 MHz, MeCN- d_3).

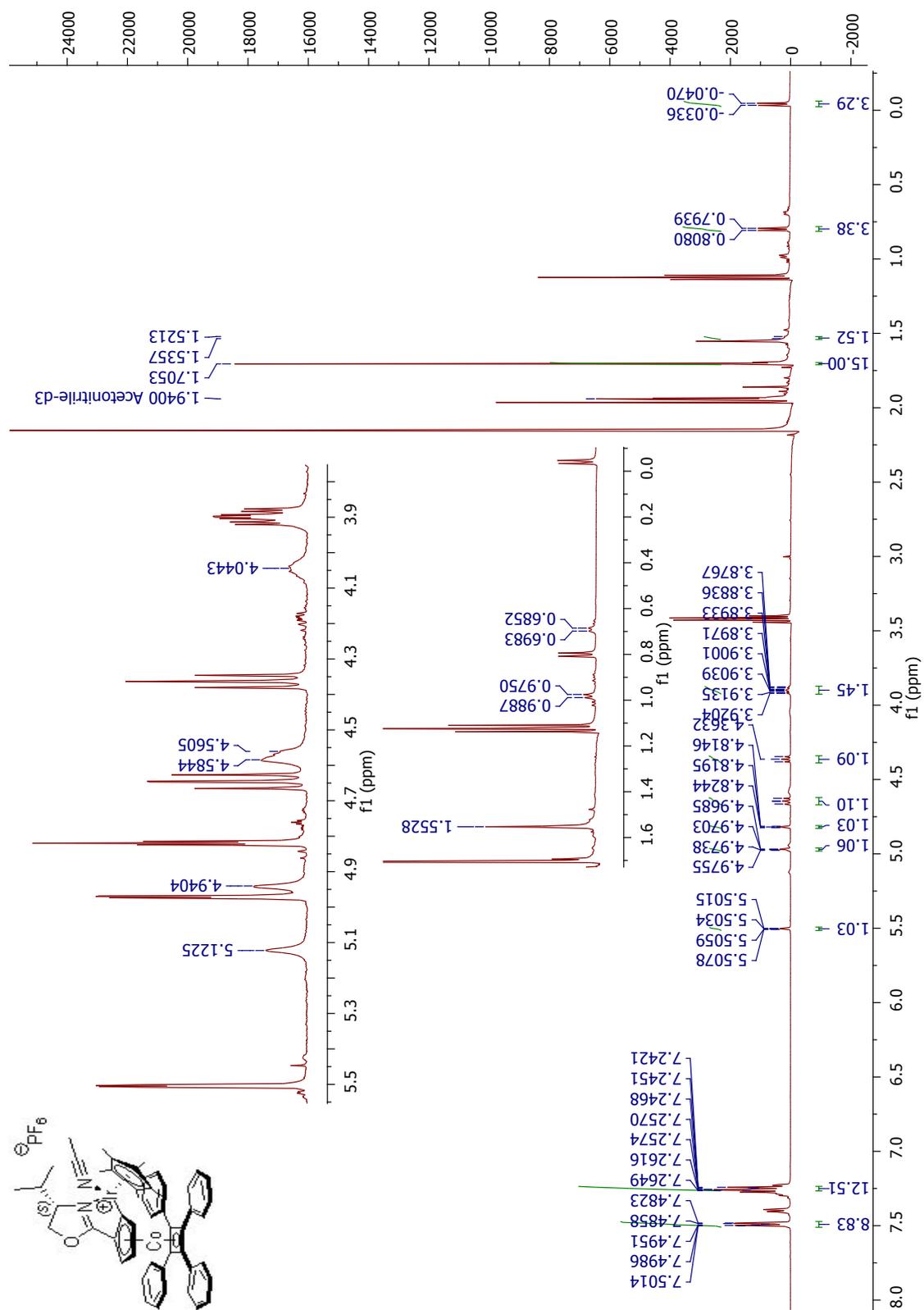


Figure S2. (*S,S*_p,*S*_{ir})-**7** - ¹³C NMR (125 MHz, MeCN-d³).

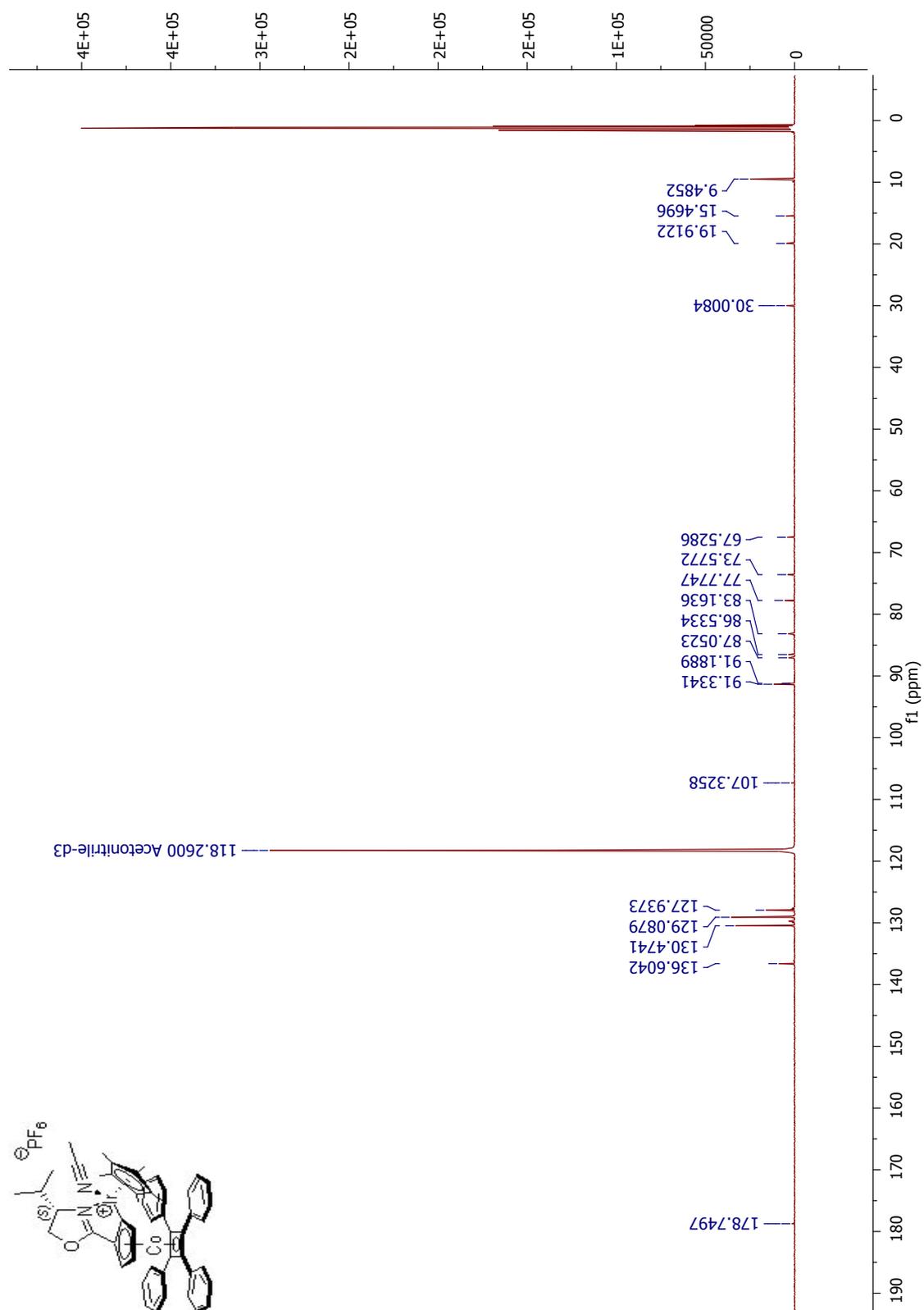


Figure S3. (*S,S*_p,*S*_r)-**9** - ¹H NMR (500 MHz, MeCN-d³).

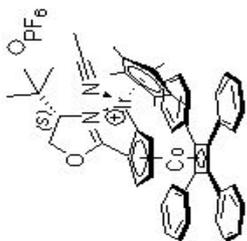
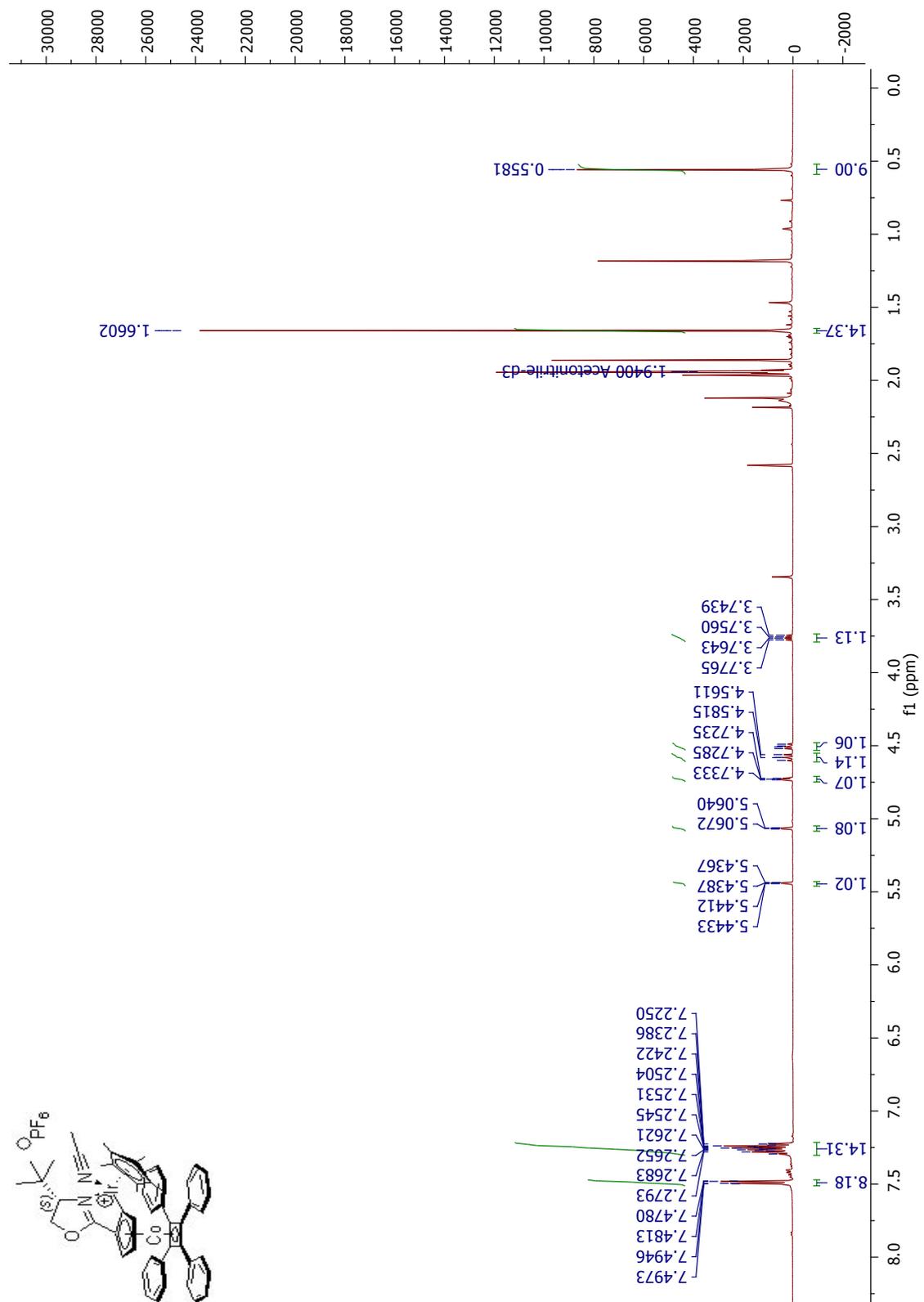


Figure S4. (*S,S*_p,*S*_{ir})-**9** - ¹³C NMR (125 MHz, MeCN-d³).

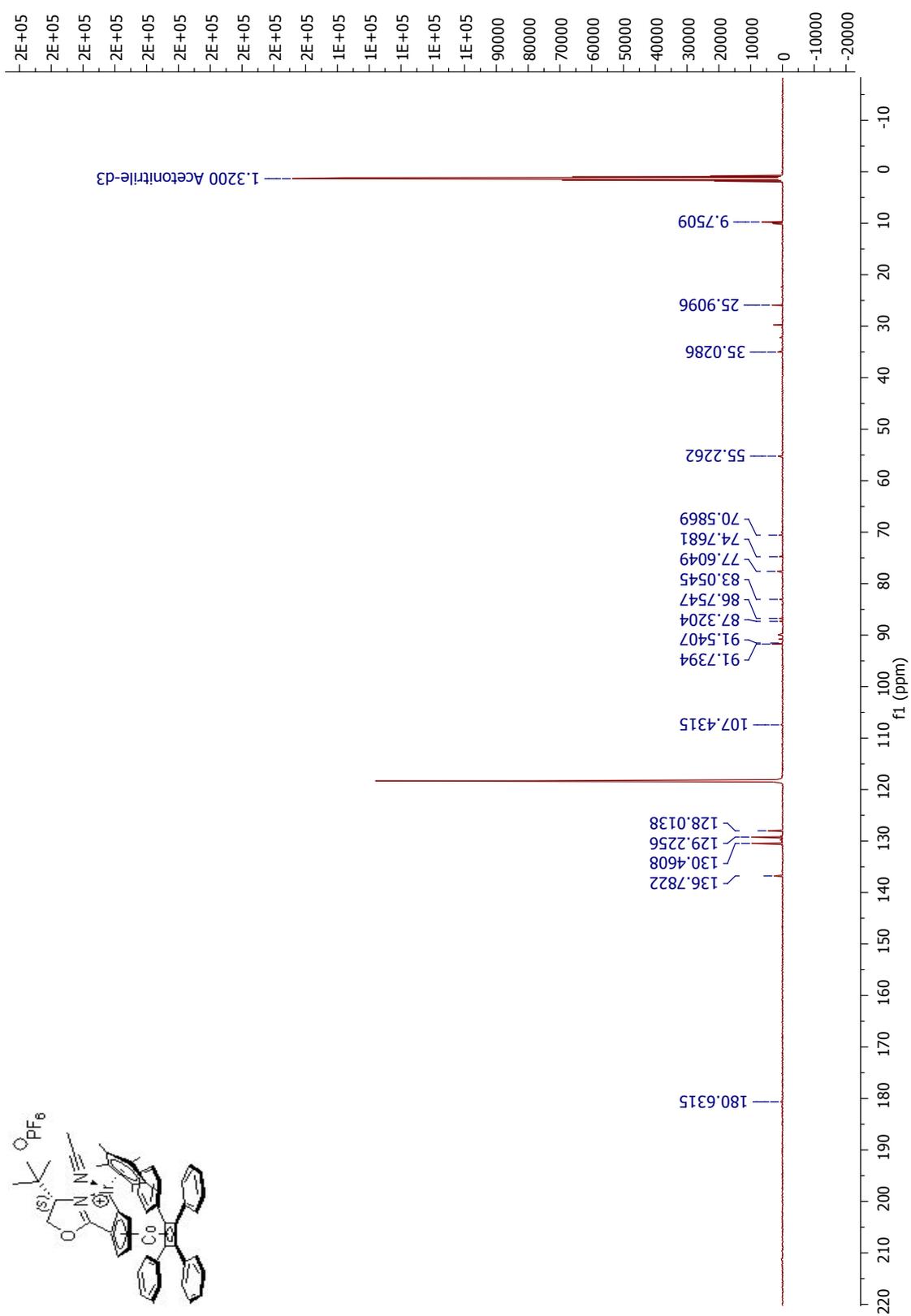


Figure S5. (*S,S*_p,*S*_{ir})-**11** - ¹H NMR (500 MHz, MeCN-d₃).

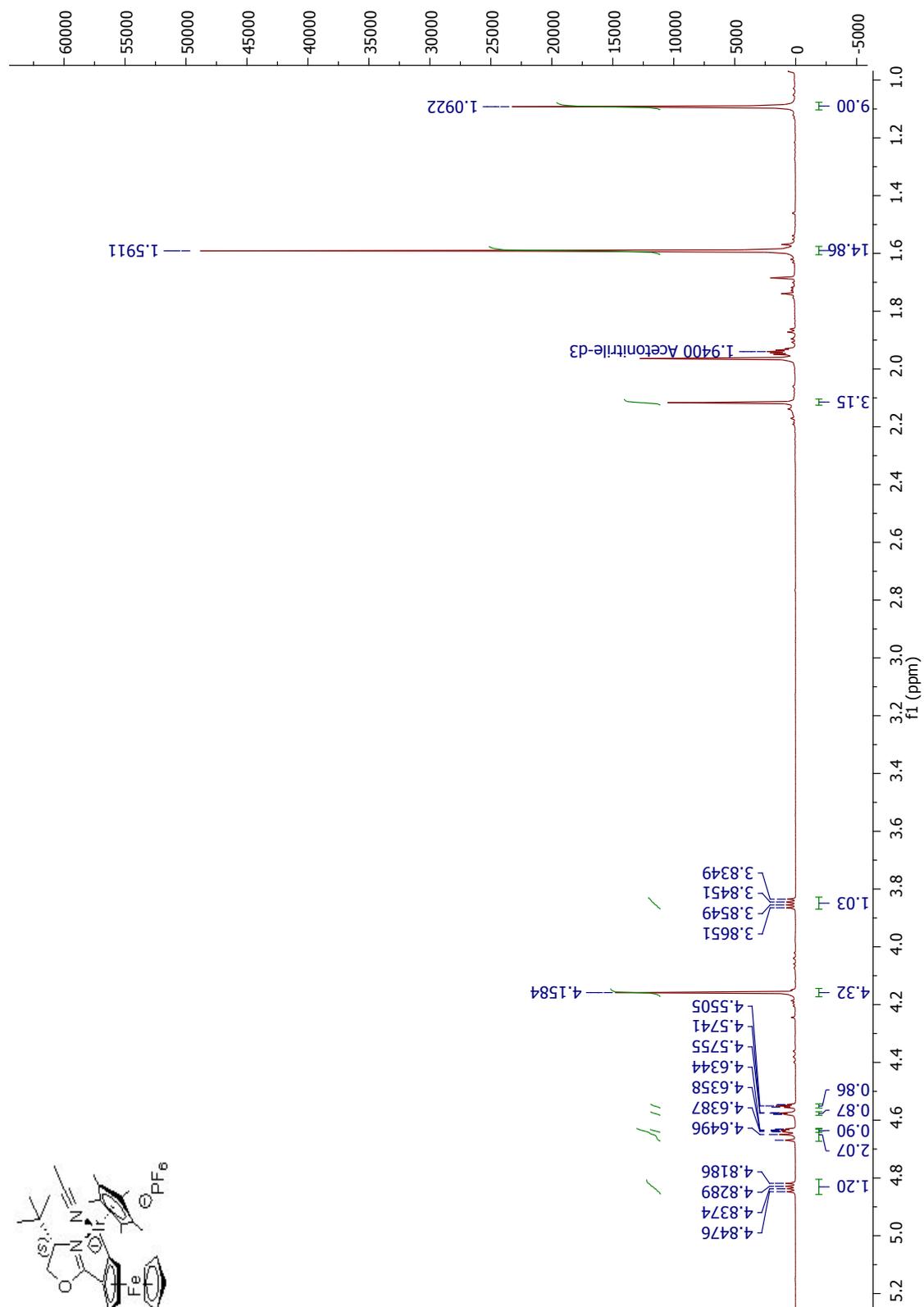


Figure S6. (*S,S_p,S_{ir}*)-**11** - ¹³C NMR (125 MHz, MeCN-d³).

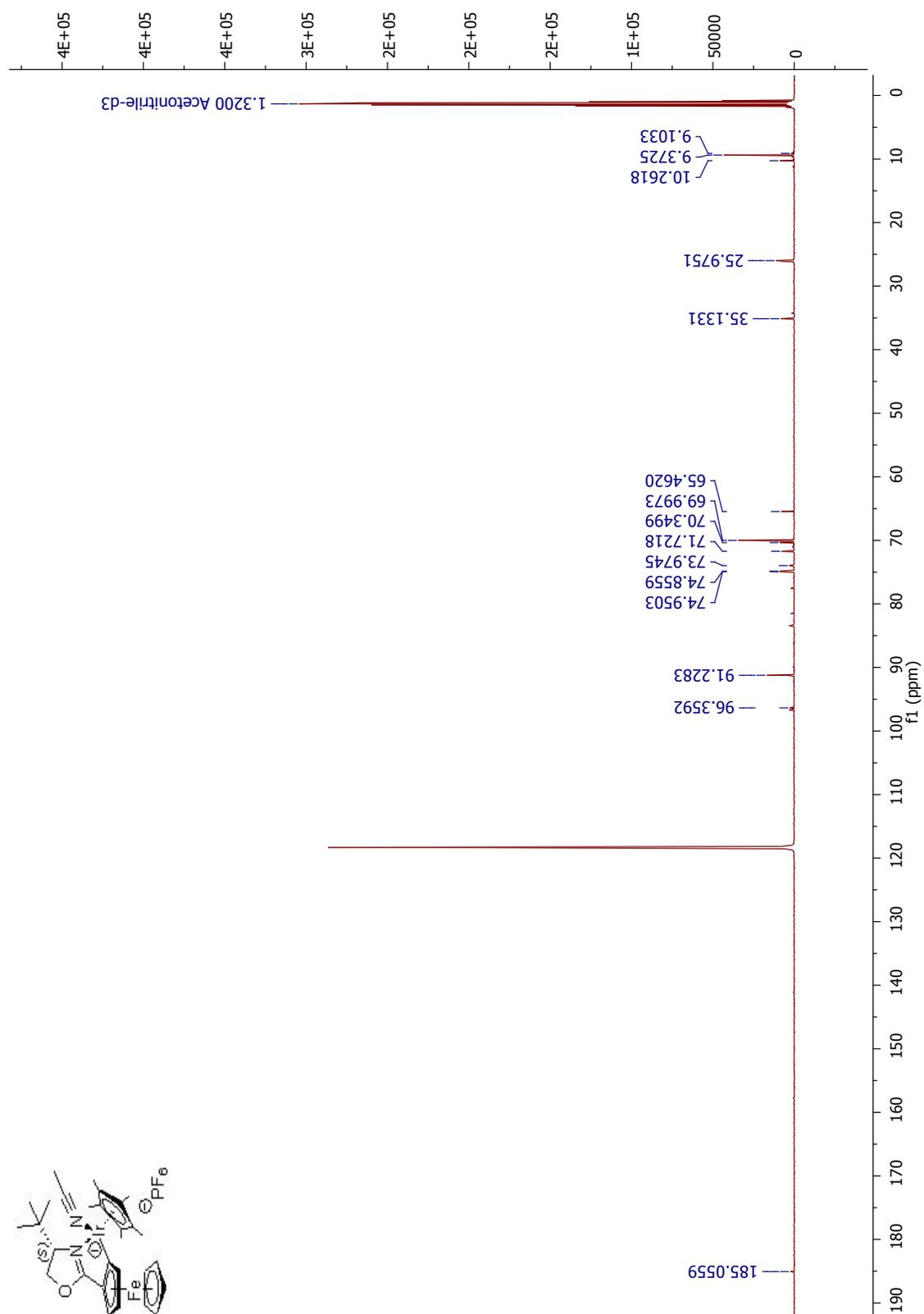


Figure S7. Heating (*S,S*_p,*S*_{Ir})-**7** for 8 days - ¹H NMR (500 MHz, MeCN-d³).

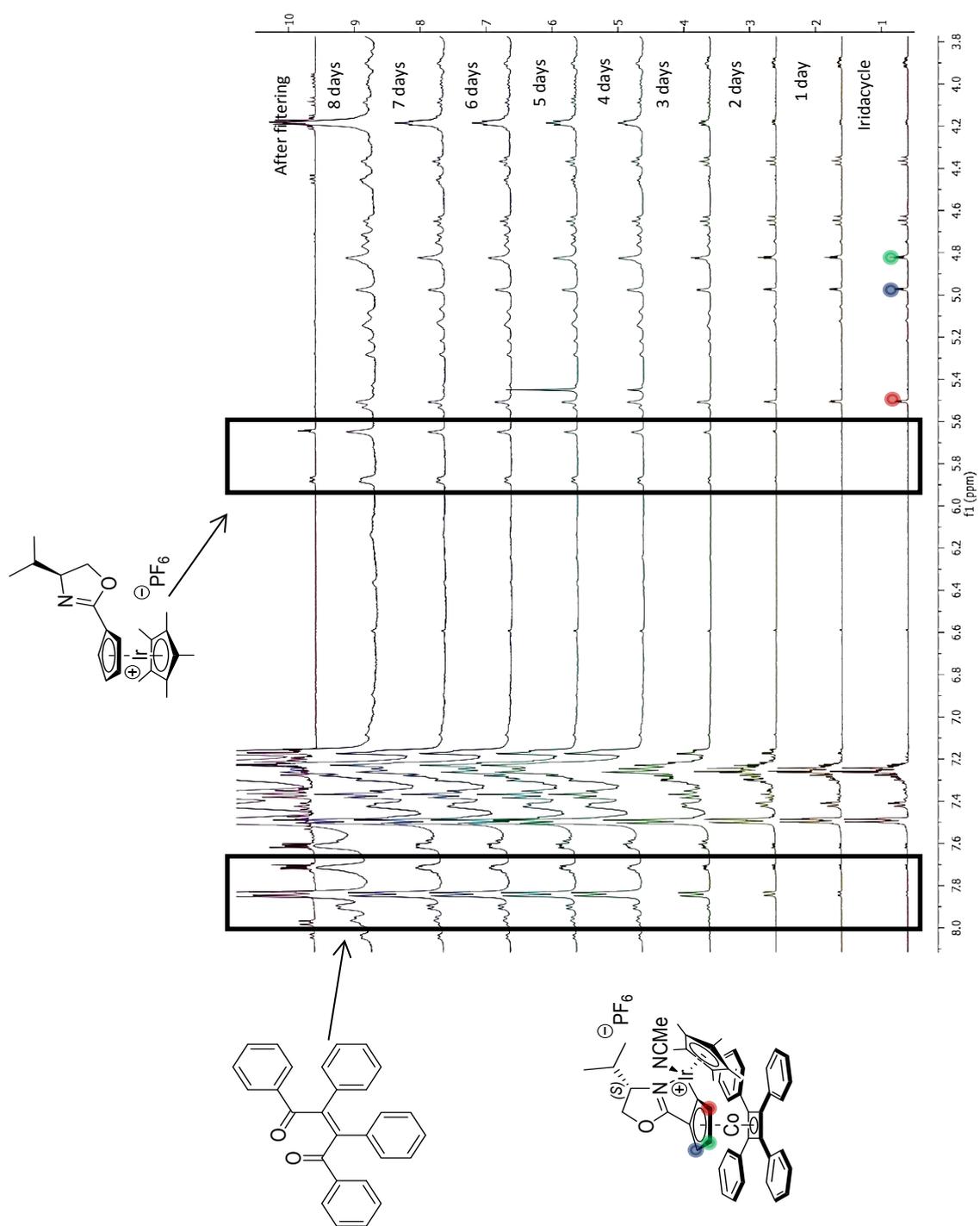


Figure S8. (S)-14 - ^1H NMR (500 MHz, MeCN-d_3).

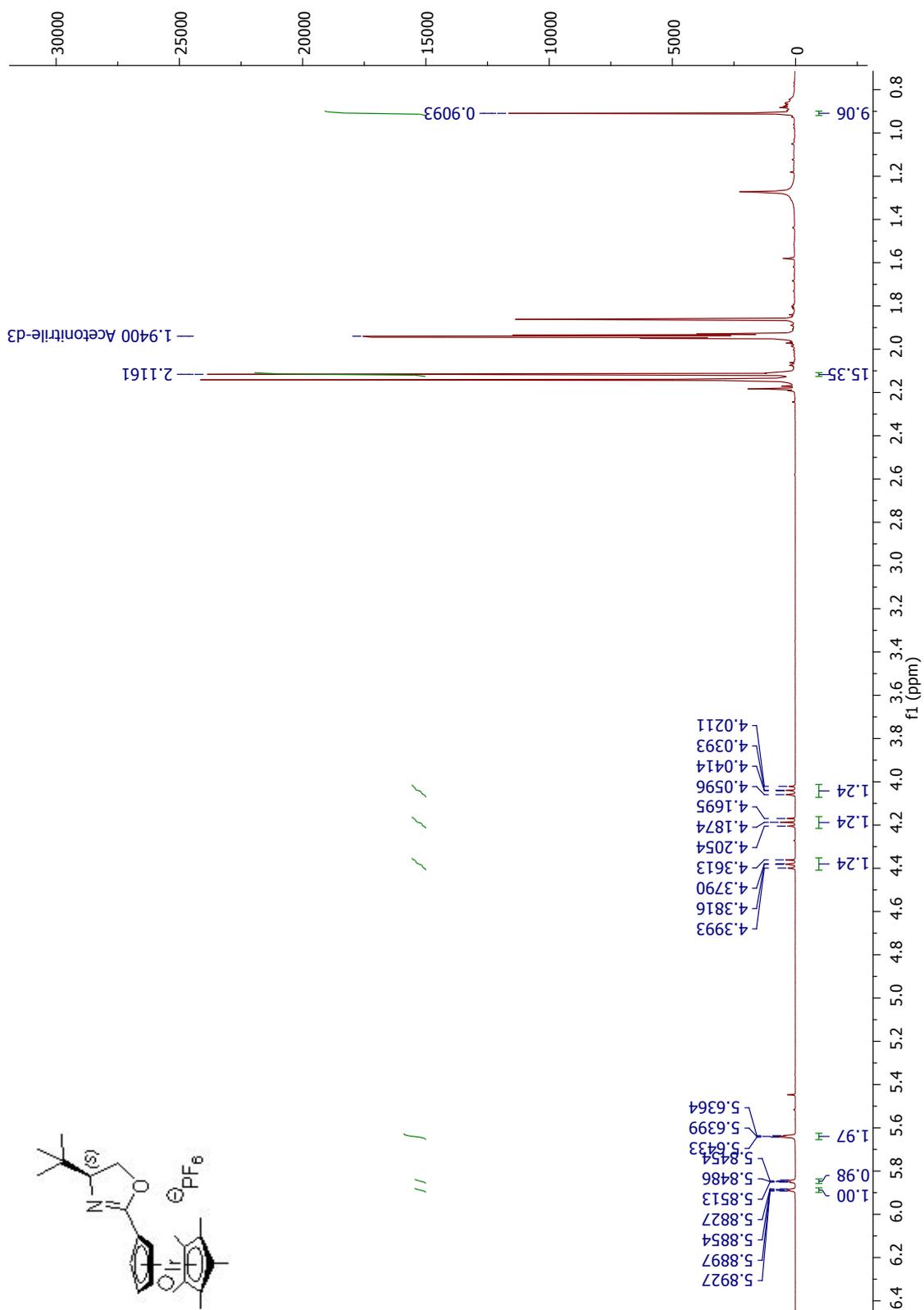


Figure S9. (S)-**14** - ^{13}C NMR (125 MHz, MeCN- d_3).

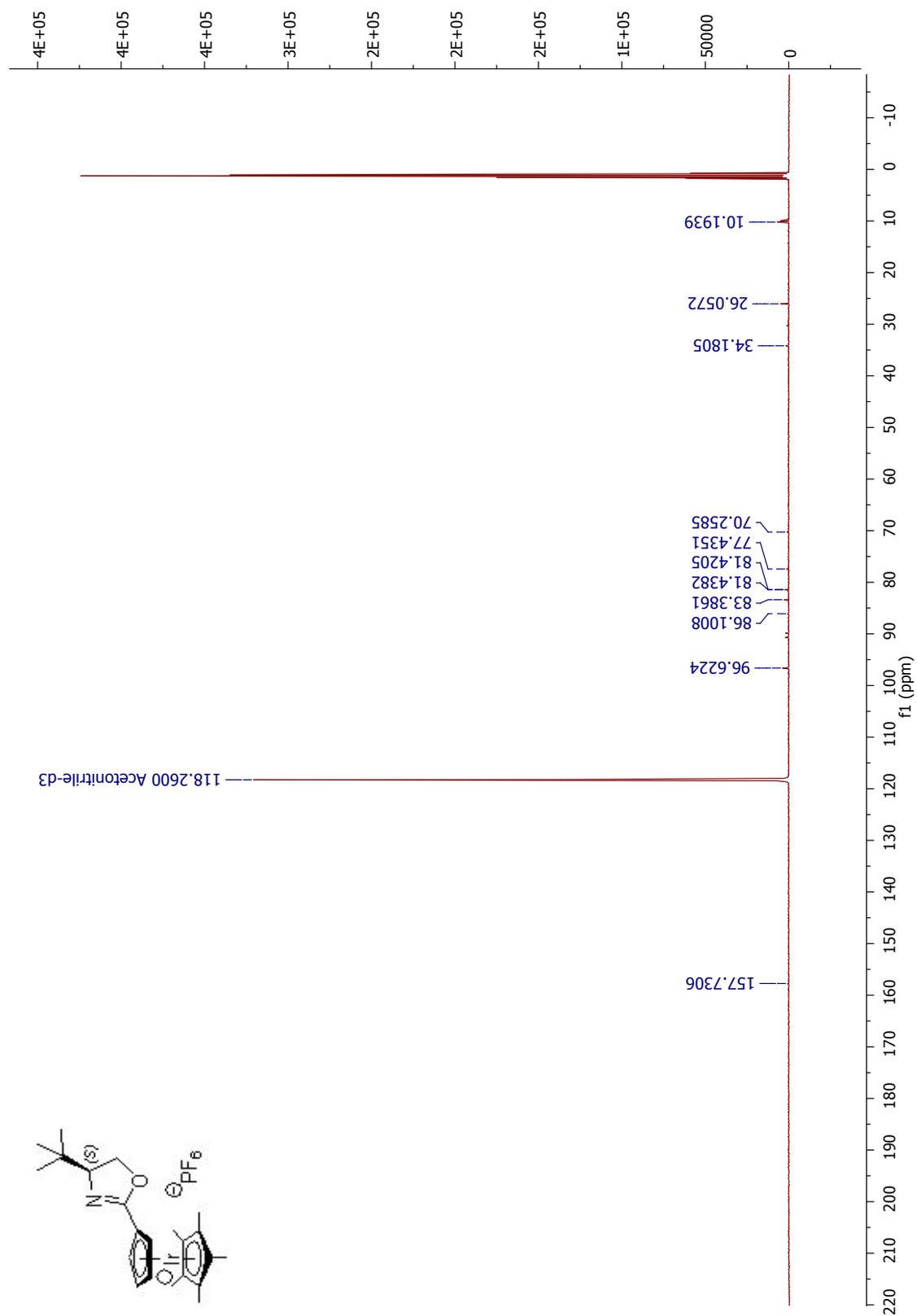


Figure S10. (*S,S*_p,*R*_{ir})-**15**/*(S,R*_p,*S*_{ir})-**16** - ¹H NMR (500 MHz, CDCl₃ (red), then THF-d⁸ (green), then Acetone-d⁶ (blue) and then CDCl₃ again (purple)).

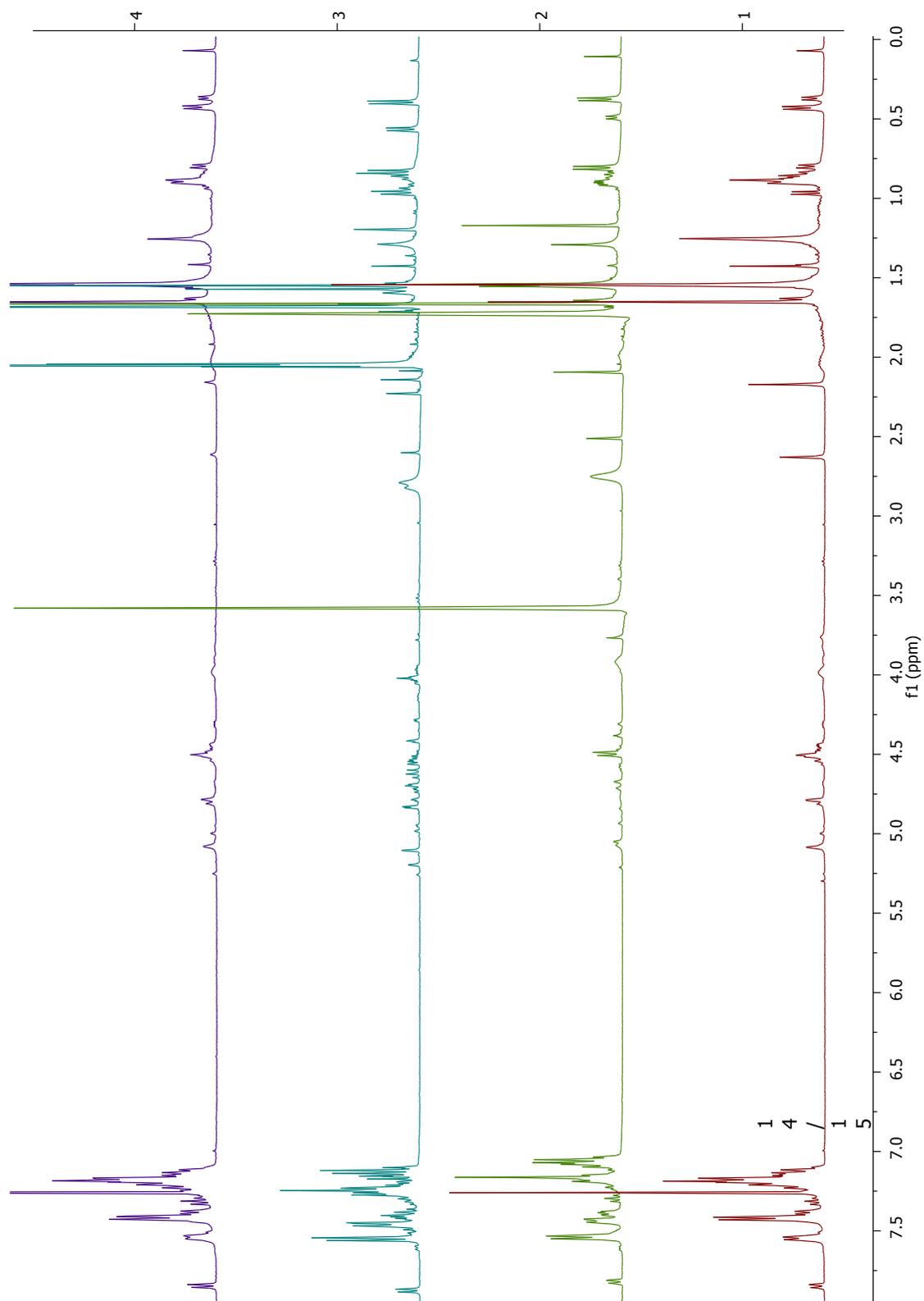


Figure S11. (*S,S*_p,*R*_{ir})-**19** - ¹H NMR (500 MHz, CDCl₃).

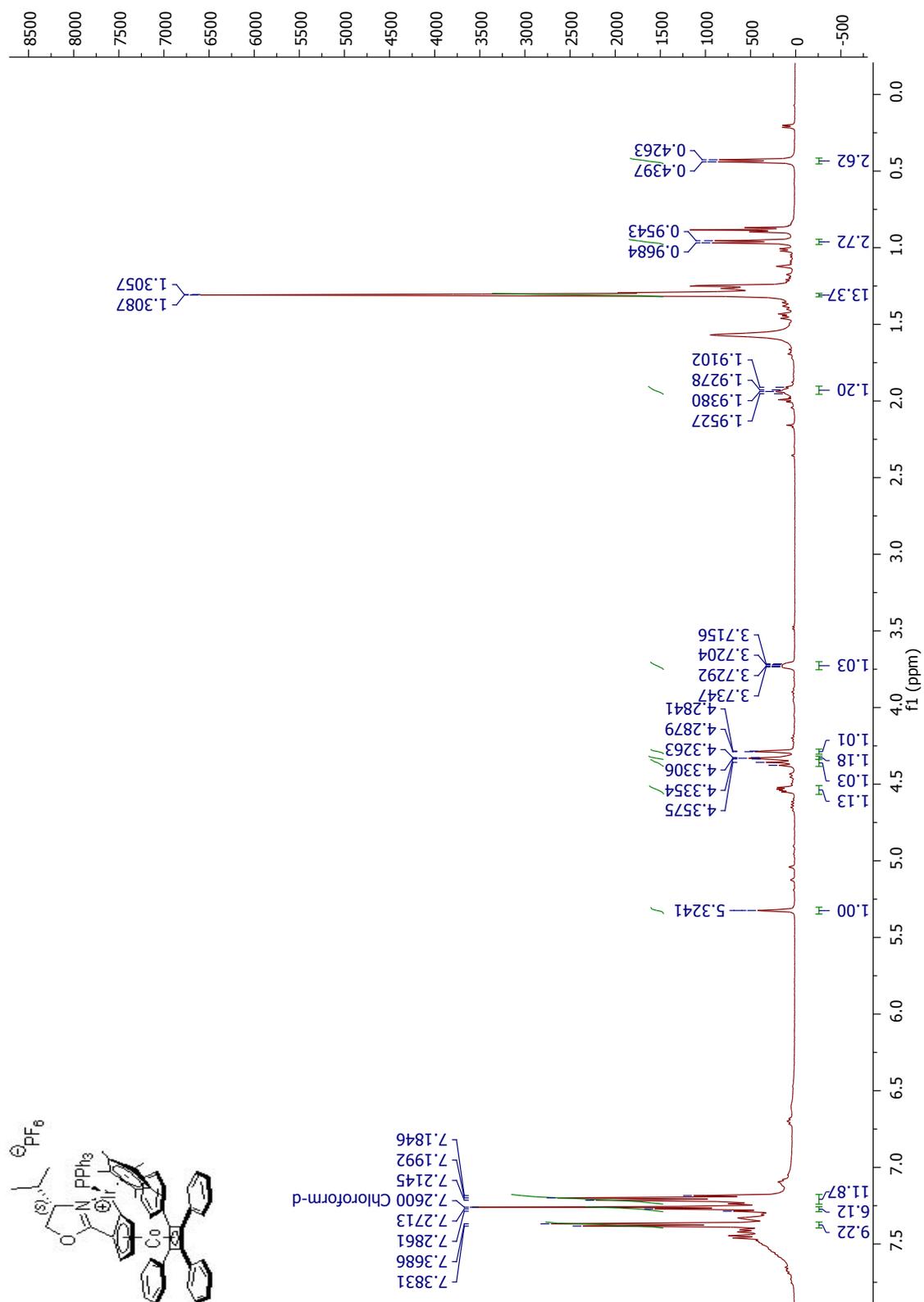


Figure S12. (*S,S*,*R,R*)-**19** - ^{13}C NMR (125 MHz, CDCl_3).

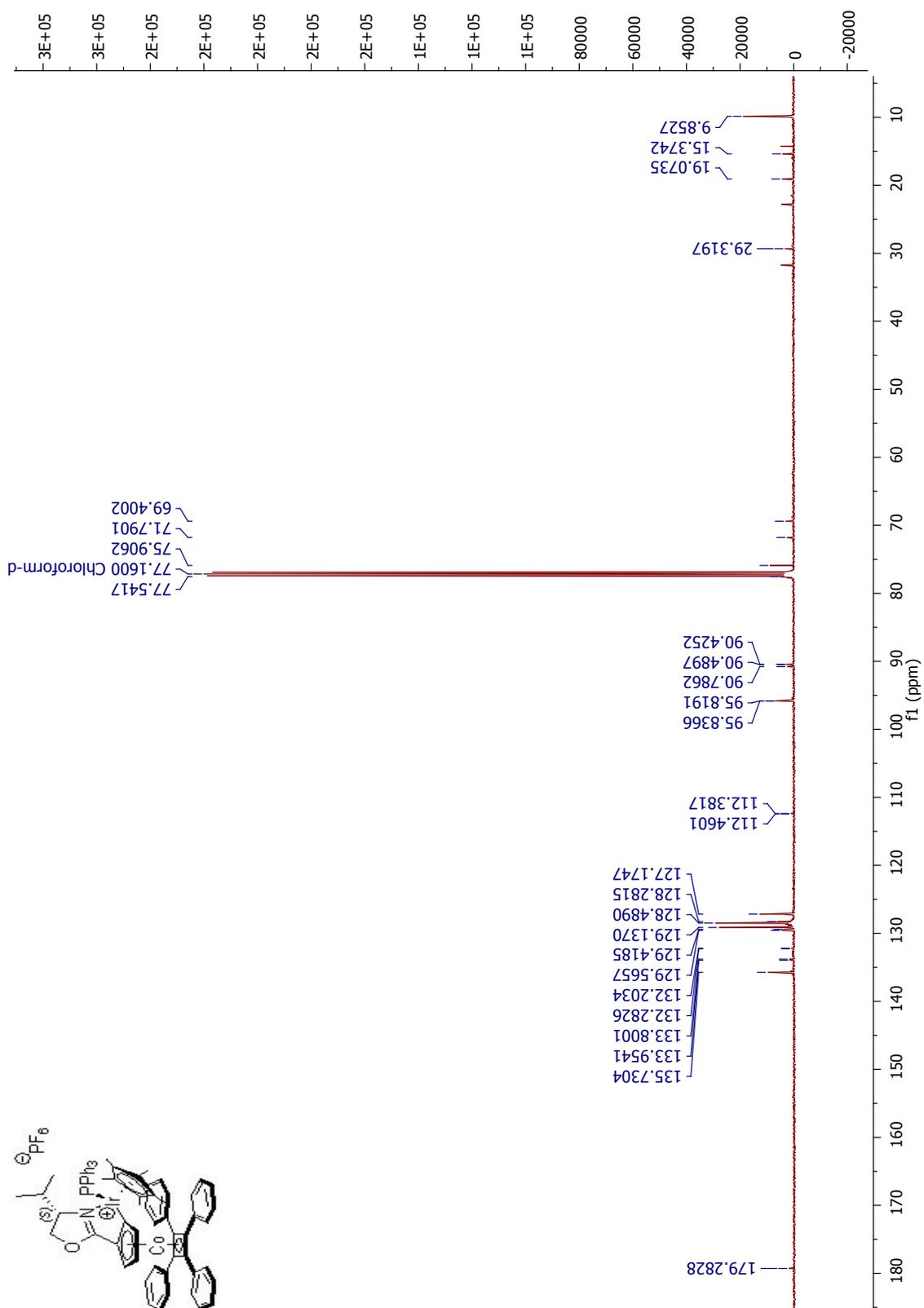
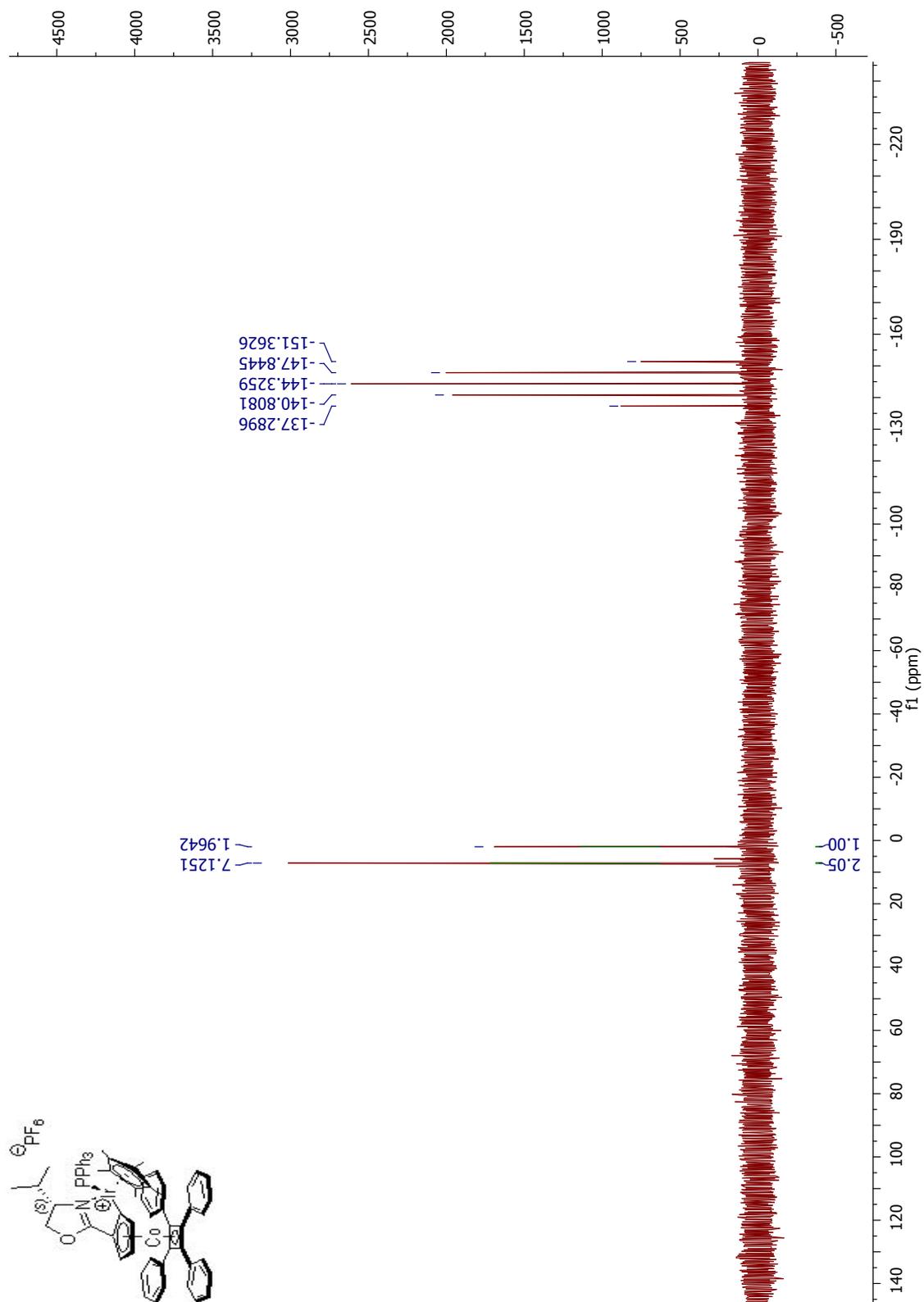


Figure S13. (*S,S*_p,*R*_{lr})-**19** (minor peak is (*S*,*R*_p,*S*_{lr})-**20**) - ³¹P NMR (202 MHz, CDCl₃).



3. X-ray structures

Crystal structure analysis of (*S,S*_p,*R*_{Ir})-15

Crystal data: C₄₉H₄₈ClCoIrNO, M = 953.46. Monoclinic, space group P2₁ (no. 4), a = 10.0619(2), b = 12.0816(3), c = 17.0228(4) Å, β = 105.350(2) °, V = 1995.54(8) Å³. Z = 2, D_c = 1.587 g cm⁻³, F(000) = 956, T = 140(1) K, μ(Mo-Kα) = 38.5 cm⁻¹, λ(Mo-Kα) = 0.71069 Å. Crystals are pink-orange rectangular prisms. One, ca 0.40 x 0.11 x 0.045 mm, was mounted in oil on a glass fibre and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-Kα radiation and graphite monochromator. Intensity data were measured by thin-slice ω- and φ-scans. Total no. of reflections recorded, to θ_{max} = 30°, was 38619 of which 11599 were unique (R_{int} = 0.036); 10981 were 'observed' with I > 2σ_I. Data were processed using the CrysAlisPro-CCD and -RED⁴ programs. The structure was determined by the direct methods routines in the SHELXS program⁵ and refined by full-matrix least-squares methods, on F²'s, in SHELXL⁶. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. At the conclusion of the refinement, wR₂ = 0.062 and R₁ = 0.030 (28) for all 11599 reflections weighted w = [σ²(F_o²) + (0.0346P)² + 0.291P]⁻¹ with P = (F_o² + 2F_c²)/3; for the 'observed' data only, R₁ = 0.027. In the final difference map, the highest peaks (to ca 1.5 eÅ⁻³) were close to the iridium atom. Scattering factors for neutral atoms were taken from reference⁷. Computer programs used in this analysis have been noted above, and were run through WinGX⁸ on a Dell Optiplex 755 PC at the University of East Anglia.

Crystal structure analyses of (*S,R*_p,*S*_{Ir})-16 and (*Z*)-13

The analyses of (*S,R*_p,*S*_{Ir})-16 and (*Z*)-13 followed very similar procedures to (*S,S*_p,*R*_{Ir})-15, but the limit of reliable intensity data and the quality of those data were rather lower than values normally required for publication. However, the results from these compounds showed clearly the structures and, indeed, the absolute configurations of the molecules involved, and we wish to record some details of this work; the crystal data and the refinement results from all three structures are collated below Figures S14-16.

Notes on the structure, (*S,S*_p,*R*_{Ir})-15

From calculations of the centroids of the three, planar, π-coordinated rings [Ct1 is the centroid of the ring C(1-4), Ct2 of ring C(51-55) and Ct3 of ring C(71-75)], the metal centroid distances

are: Co – Ct1 1.699, Co – Ct2 1.700, and Ir – Ct3 1.819 Å, and the angle subtended at Co by Ct1 and Ct2 is 172.58°. The angle between the normals to the rings of C(1-4) and C(51-55) is 10.8(3)°. The cobalt atom is sandwiched between the almost parallel C(1-4) and C(51-55) rings. The Ir atom is π -coordinated to the Cp* ring of C(71-75) and to the Cl, C(55) and N(62) atoms in a three-legged piano-stool pattern. Three of the phenyl rings in the (CPh)₄ ligand follow the normal propeller pattern around the ring with similar rotations about the C(n)-C(n1) bonds, but the fourth phenyl ring, of C(11-16), is rotated in the opposite direction about the C(1)-C(11) bond. All the molecules in this polar space group are of the same chirality and all point in the same direction along the *b*-axis.

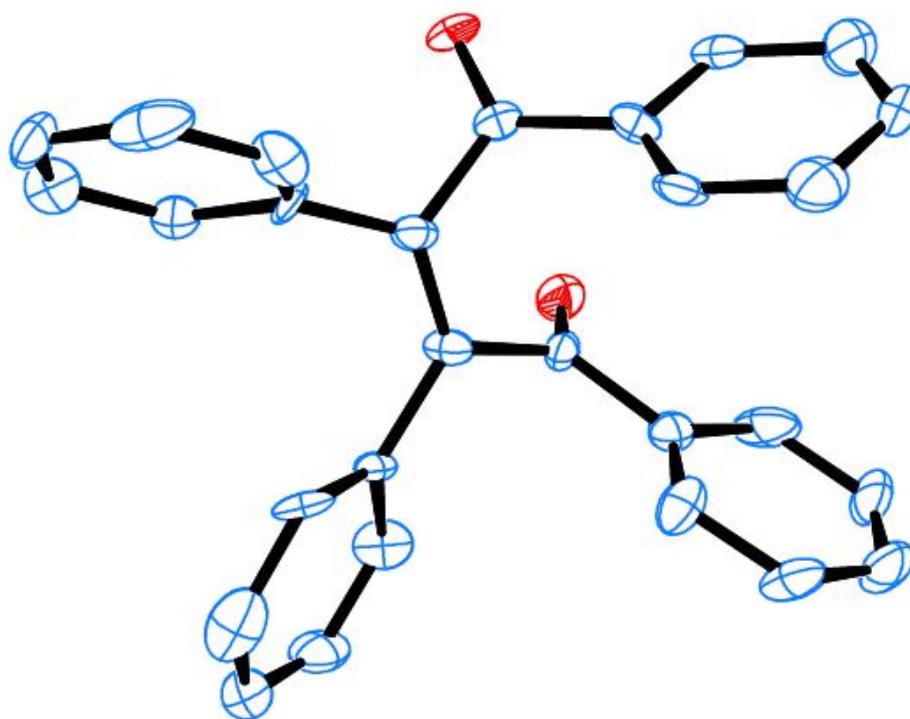
Notes on the structure of (*S*,*R*_p,*S*_{Ir})-16

There are two very similar molecules in the asymmetric unit. The principal difference in the conformations of the molecules is in the degree of rotation of the Cp* ligand about the Ir...Ct vector (where Ct is the centroid of the Cp ring). The quality of the X-ray data did not allow for anisotropic refinement of the lighter atoms, and the precision of the molecular dimensions is rather less than ideal. However, the structures of both molecules are well defined and the chiralities in the two molecules are clear and unequivocal and the same. Molecules are arranged in spirals around 2₁ screw axes parallel to the *b* axis. The columns of the Ir(1) molecules are pointed in the opposite direction from those of the Ir(2) molecular columns.

Notes on the structure of (*Z*)-13

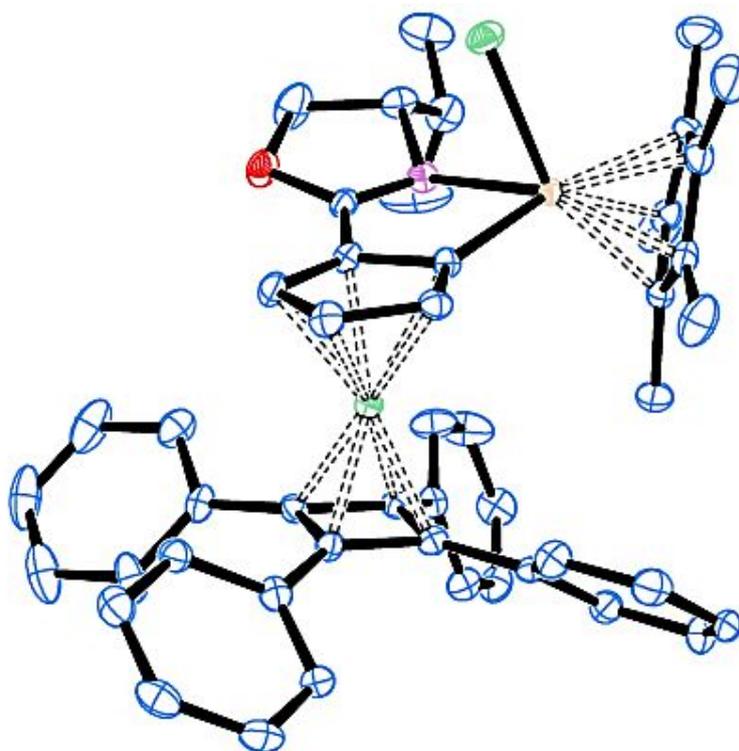
The four carbon atoms of the main chain, C(1)-C(4), all have trigonal planar conformations and the central bond, C(2)-C(3), with bond distance 1.362(14) Å is a double-bond; this bond is significantly shorter than the other bonds along this chain.

Figure S14. (Z)-13



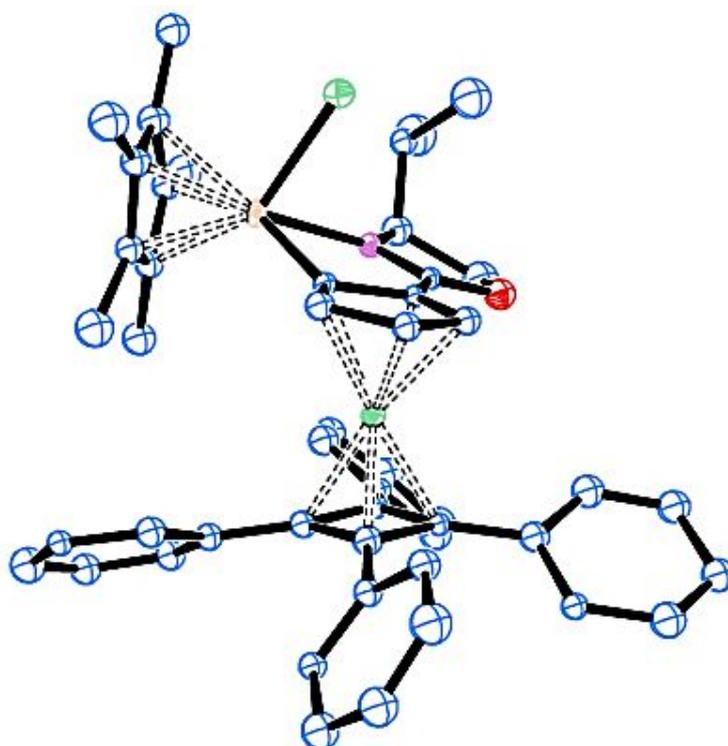
Identification code	rossa4 / RAA5.292g / (Z)-13	
Empirical formula	$C_{28}H_{20}O_2$	
Formula weight	388.4	
Crystal system, Space Group	Monoclinic, $P2_1$	
Unit cell dimensions	$a = 5.9297(11) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 17.204(3) \text{ \AA}$	$\beta = 100.39(2)^\circ$
	$c = 10.128(2) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$1016.2(4) \text{ \AA}^3$	
Z, Density (calculated)	2, 1.269 Mg / m^3	
$F(000)$	408	
Absorption coefficient	0.079 mm^{-1}	
Temperature	140(1) K	
Wavelength	0.71073 \AA	
Crystal colour, shape	Colourless, Needle	
Crystal size	$0.88 \times 0.04 \times 0.025 \text{ mm}^3$	
Crystal mounting	on a glass fibre, in oil, fixed in cold N_2 stream	
θ range for data collection	$3.13 - 22.50^\circ$	
Limiting indices: h, k, l	$-6 \leq h \leq 6, -18 \leq k \leq 18, -10 \leq l \leq 10$	
Completeness of data: θ , %	$22.50^\circ, 99.8\%$	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0 and 0.4626	
Reflections collected	10057	
No. of unique reflections, R(int)	2665, 0.131	
No. of 'obsd' reflections ($I > 2\sigma I$)	1758	
Structure determined by:	direct methods, SHELXS	
Refinement	Full-matrix least-squares on F^2 , in SHELXS	
Data / restraints / parameters	2665 / 1 / 261	
Goodness-of-fit on F^2	1.066	
Final R indices ('obsd' data)	$R I = 0.122, wR2 = 0.289$	
Final R indices (all data)	$R I = 0.170, wR2 = 0.321$	
Reflections weighted: $w =$ where $P = (F_o^2 + 2F_c^2)/3$	$[\sigma^2(F_o^2) + (0.1882P)^2]^{-1}$	
Absolute structure parameter	0(6)	
Largest diff. peak and hole	0.75 and -0.32 e \AA^{-3}	
Location of largest difference peaks	near H(46)	

Figure S15. (*S,S*_p,*R*_{Ir})-15



Identification code	rossa1 / RAA1.130c / (<i>S,S</i>_p,<i>R</i>_{Ir})-15	
Empirical formula	C ₄₉ H ₄₈ ClCoIrNO	
Formula weight	953.46	
Crystal system, Space Group	Monoclinic, <i>P</i> 2 ₁	
Unit cell dimensions	<i>a</i> = 10.0619(2) Å	<i>α</i> = 90°
	<i>b</i> = 12.0816(3) Å	<i>β</i> = 105.350(2)°
	<i>c</i> = 17.0228(4) Å	<i>γ</i> = 90°
Volume	1995.54(8) Å ³	
Z, Density (calculated)	2, 1.587 Mg / m ³	
<i>F</i> (000)	956	
Absorption coefficient	3.852 mm ⁻¹	
Temperature	140(1) K	
Wavelength	0.71073 Å	
Crystal colour, shape	Pink/Orange, Rectangular prism	
Crystal size	0.40 × 0.11 × 0.045 mm ³	
Crystal mounting	on a glass fibre, in oil, fixed in cold N ₂ stream	
<i>θ</i> range for data collection	3.19 – 30.00°	
Limiting indices: <i>h</i> , <i>k</i> , <i>l</i>	–14 ≤ <i>h</i> ≤ 14, –16 ≤ <i>k</i> ≤ 16, –23 ≤ <i>l</i> ≤ 23	
Completeness of data: <i>θ</i> , %	30.00°, 99.8%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.667	
Reflections collected	38637	
No. of unique reflections, <i>R</i> (int)	11604, 0.036	
No. of 'obsd' reflections (<i>I</i> > 2σ _{<i>I</i>})	10981	
Structure determined by:	direct methods, SHELXS	
Refinement	Full-matrix least-squares on <i>F</i> ² , in SHELXL	
Data / restraints / parameters	11604 / 1 / 492	
Goodness-of-fit on <i>F</i> ²	1.022	
Final <i>R</i> indices ('obsd' data)	<i>R</i> 1 = 0.027, <i>wR</i> 2 = 0.060	
Final <i>R</i> indices (all data)	<i>R</i> 1 = 0.030, <i>wR</i> 2 = 0.062	
Reflections weighted: <i>w</i> =	[σ ² (<i>F</i> _o ²) + (0.0346 <i>P</i>) ² + 0.291 <i>P</i>] ⁻¹	
where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3		
Absolute structure parameter	–0.019(4)	
Largest diff. peak and hole	1.52 and –0.89 e Å ⁻³	
Location of largest difference peaks	close to the iridium atom	

Figure S16. (*S,R_p,S_{Ir}*)-16



Identification code	rossa3b / RAA1.130d / (<i>S,R_p,S_{Ir}</i>)-16	
Empirical formula	C ₄₉ H ₄₈ ClCoIrNO	
Formula weight	953.46	
Crystal system, Space Group	Monoclinic, <i>P</i> 2 ₁	
Unit cell dimensions	<i>a</i> = 11.1202(4) Å	<i>α</i> = 90°
	<i>b</i> = 15.1873(7) Å	<i>β</i> = 101.855(4)°
	<i>c</i> = 24.5875(13) Å	<i>γ</i> = 90°
Volume	4063.9(3) Å ³	
Z, Density (calculated)	4, 1.558 Mg / m ³	
<i>F</i> (000)	1912	
Absorption coefficient	3.783 mm ⁻¹	
Temperature	140(1) K	
Wavelength	0.71073 Å	
Crystal colour, shape	Pale pink, Thin prism	
Crystal size	0.25 × 0.045 × 0.025 mm ³	
Crystal mounting	on a glass fibre, in oil, fixed in cold N ₂ stream	
<i>θ</i> range for data collection	3.078 – 24.999°	
Limiting indices: <i>h</i> , <i>k</i> , <i>l</i>	–13 ≤ <i>h</i> ≤ 13, –18 ≤ <i>k</i> ≤ 18, –29 ≤ <i>l</i> ≤ 29	
Completeness of data: <i>θ</i> , %	25.24°, 97.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.947	
Reflections collected	54364	
No. of unique reflections, <i>R</i> (int)	14297, 0.108	
No. of 'obsd' reflections (<i>I</i> > 2σ _{<i>I</i>})	12355	
Structure determined by:	heavy atom methods, SHELXS	
Refinement	Full-matrix least-squares on <i>F</i> ² , in SHELXL	
Data / restraints / parameters	14297 / 1 / 472	
Goodness-of-fit on <i>F</i> ²	1.138	
Final <i>R</i> indices ('obsd' data)	<i>R</i> 1 = 0.096, <i>wR</i> 2 = 0.217	
Final <i>R</i> indices (all data)	<i>R</i> 1 = 0.110, <i>wR</i> 2 = 0.223	
Reflections weighted: <i>w</i> =	[σ ² (<i>F</i> _o ²) + (0.0259 <i>P</i>) ² + 195.9 <i>P</i>] ⁻¹	
where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²) / 3		
Absolute structure parameter	0.036(7)	
Largest diff. peak and hole	7.20 and –3.38 e Å ⁻³	
Location of largest difference peaks	close to the iridium atom	

4. CD Spectra

Figure S17. CD spectra for (S,S_p,S_{lr}) -**7**. The CD spectra for (S,S_p,S_{lr}) -**7** was obtained from a sample containing a 3.7 : 1 ratio of **7** & **8** at two different concentrations in acetonitrile. X2 UV = 0.2 $\mu\text{mol ml}^{-1}$ 190 - 520 nm range, X15 Vis = 1.5 $\mu\text{mol ml}^{-1}$ 480 - 850 nm range.

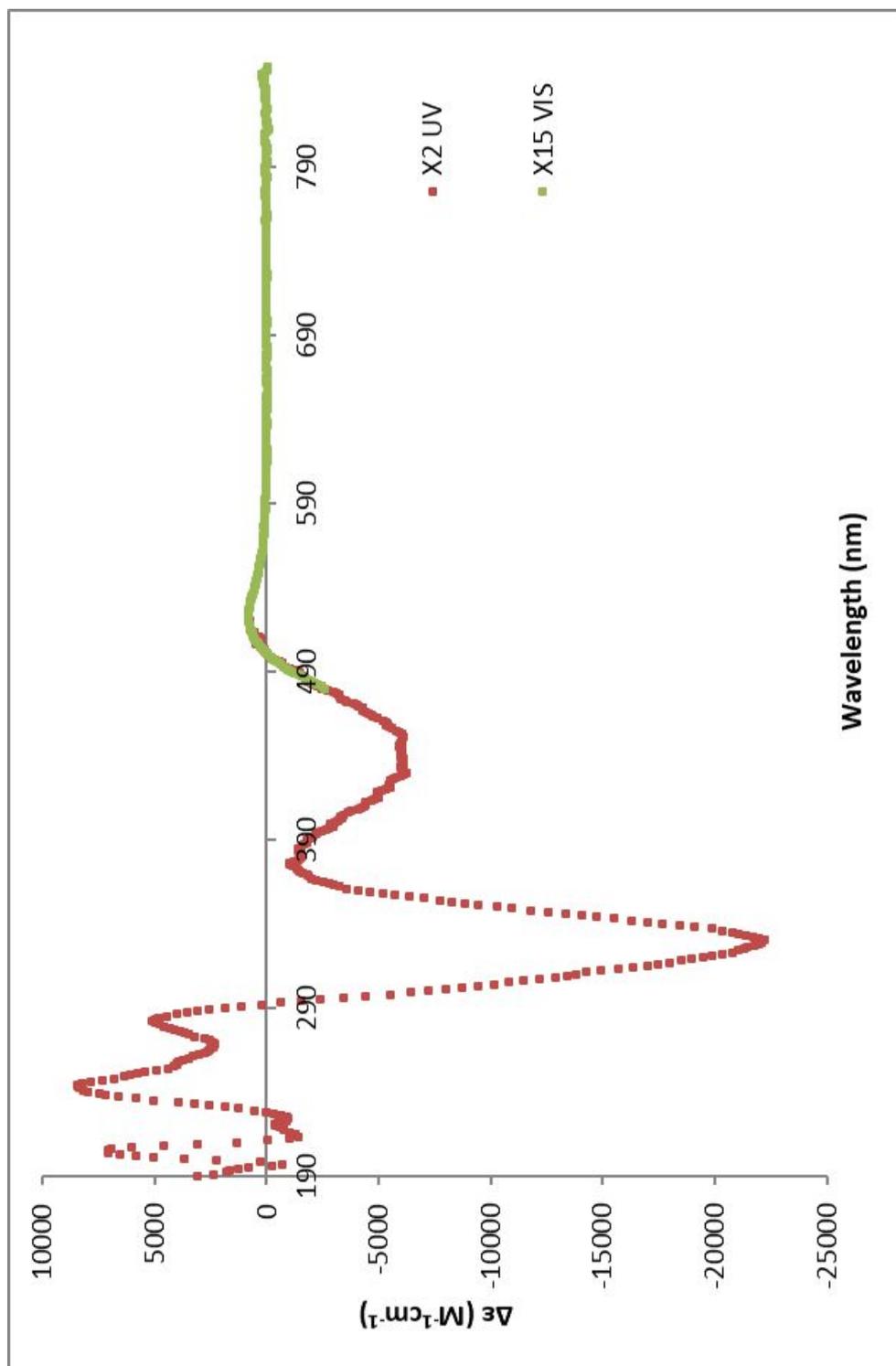


Figure S18. CD spectra for (*S,S_p,S_{ir}*)-**9**. The CD spectra for (*S,S_p,S_{ir}*)-**9** was obtained at two different concentrations in acetonitrile. X2 UV = 0.2 $\mu\text{mol ml}^{-1}$ 190 - 520 nm range, X15 Vis = 1.5 $\mu\text{mol ml}^{-1}$ 480 - 850 nm range.

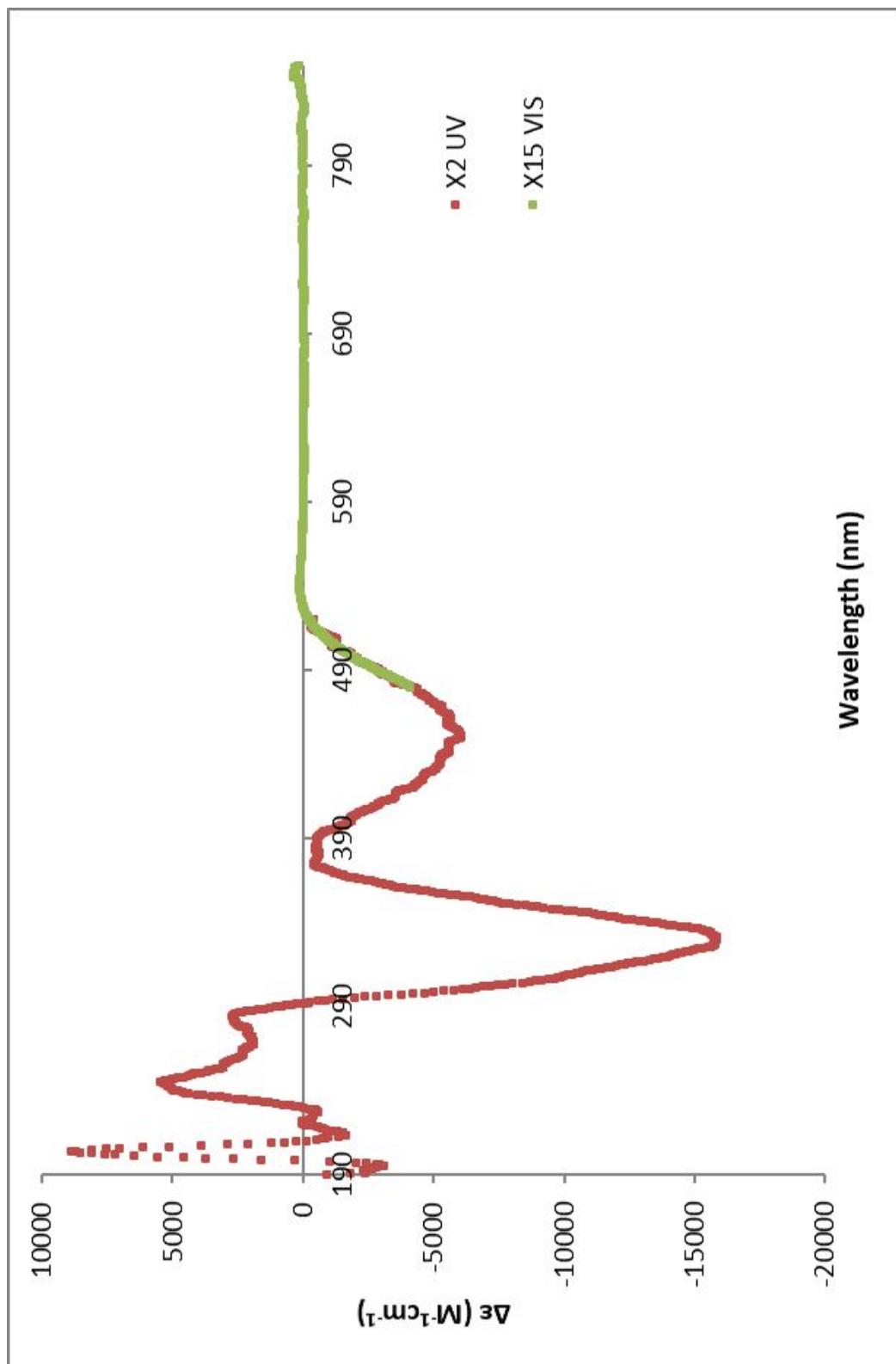


Figure S19. CD spectra for (*S,S_p,S_{ir}*)-**2**. The CD spectra for (*S,S_p,S_{ir}*)-**2** was obtained from a sample containing a 48 : 1 ratio of diastereoisomers at two different concentrations in acetonitrile. X2 UV = 0.2 $\mu\text{mol ml}^{-1}$ 190 - 520 nm range, X15 Vis = 1.5 $\mu\text{mol ml}^{-1}$ 480 - 850 nm range.

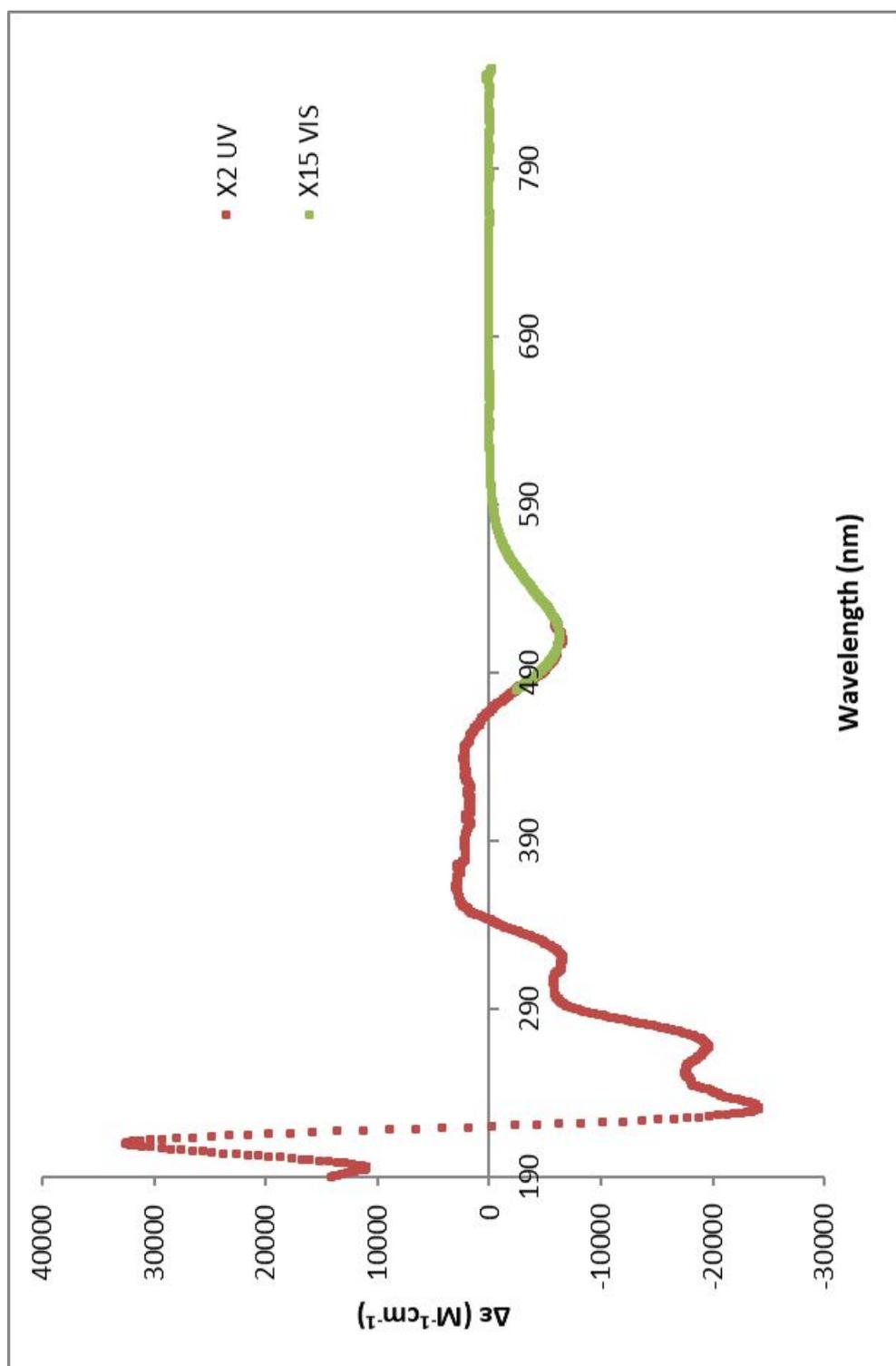
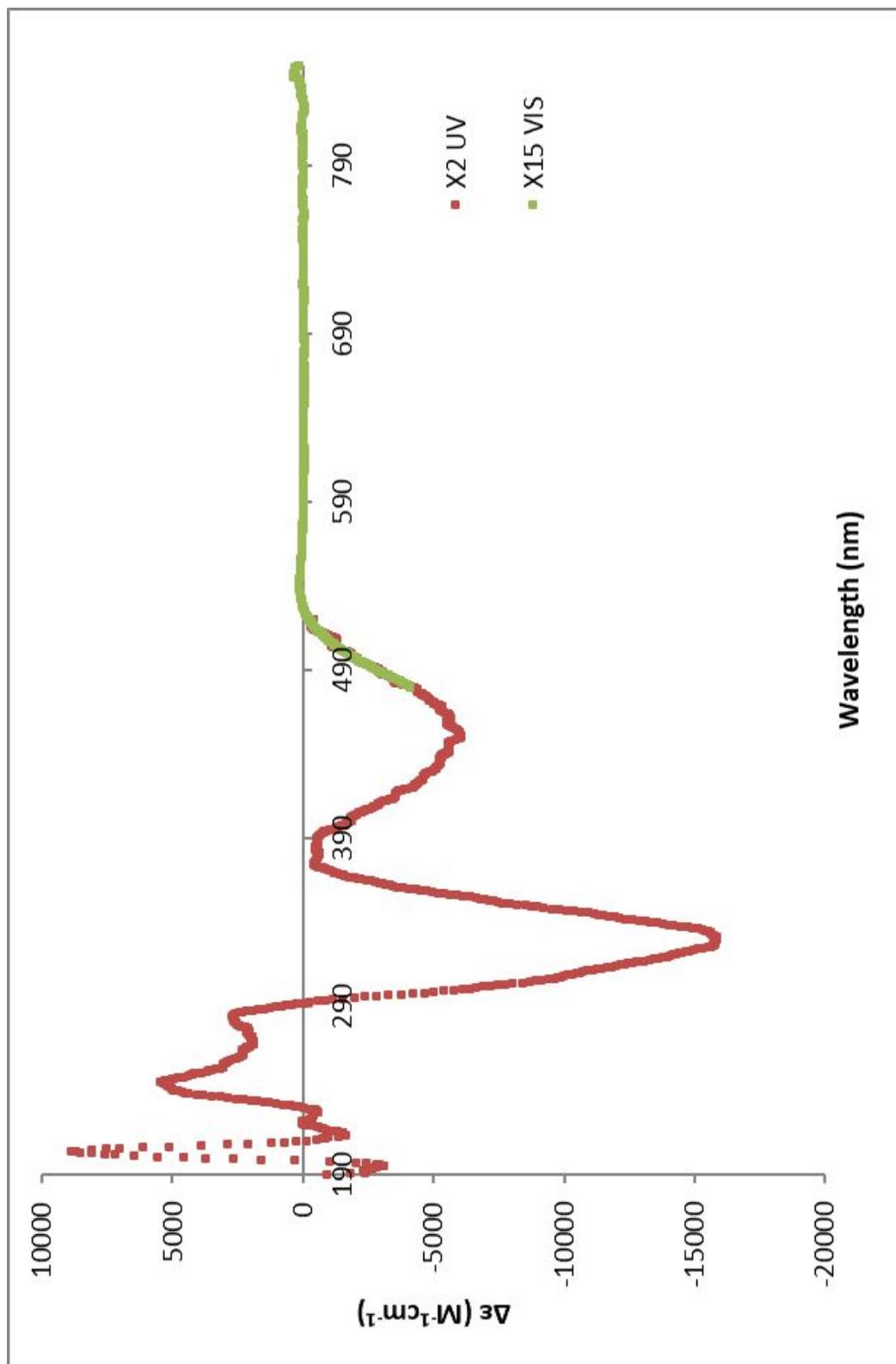


Figure S20. CD spectra for (*S,S_p,S_{lr}*)-**11**. The CD spectra for (*S,S_p,S_{lr}*)-**11** was obtained at two different concentrations in acetonitrile. X2 UV = 0.2 $\mu\text{mol ml}^{-1}$ 190 - 520 nm range, X15 Vis = 1.5 $\mu\text{mol ml}^{-1}$ 480 - 850 nm range.



5. References

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