

## Supporting Information

### Transfer Hydrogenation in Water: Enantioselective, Catalytic Reduction of $\alpha$ -Cyano and $\alpha$ -Nitro Substituted Acetophenones

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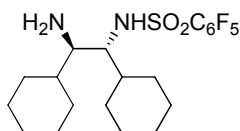
#### General

The following includes general experimental procedures, specific details for representative reactions, and isolation and spectroscopic information for the new compounds prepared. All reactions were performed in oven dried glass ware under argon or nitrogen atmosphere unless noted otherwise. For the reactions, solvents were purified by distillation and dried by passage over activated alumina under an argon atmosphere ( $\text{H}_2\text{O}$  content < 30 ppm, *Karl-Fischer* titration). Commercially available chemicals were used as received unless noted otherwise. Other starting materials were prepared according published procedures and the corresponding syntheses are described below. Buffered formate solutions were prepared from 1M formic acid solutions (pH = 2.0) and the pH was adjusted with 4M NaOH. The pH of these solutions was measured with an inoLab pH Level 1 pH meter.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a VARIAN Mercury 300 MHz or a Gemini 300 MHz spectrometer. Infrared spectra were recorded on a Perkin-Elmer spectrum RX-I FT-IR. Melting points were measured on a Büchi 510 apparatus (all melting points were measured in open capillaries and are uncorrected). High resolution mass spectra were obtained on a VG-TRIBRID for electron impact ionization (EI). Enantiomeric excesses were determined by chiral HPLC analysis with Merck-Hitachi D-7000 system and Daicel columns. Optical rotations  $[\alpha]_{\text{D}}$  were measured on a Jasco DID-1000 polarimeter. The absolute configurations were assigned by comparison of the  $[\alpha]_{\text{D}}$  values of known compounds. For the new compounds, it was assigned based on the established stereochemical outcome of the reaction.

### **Synthesis of the Ligands:**

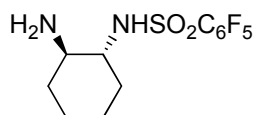
Synthesis of ligands required for the catalysts described below were prepared as outlined in the literature,<sup>1,2,3</sup> otherwise commercially available ligands were utilized.

#### **N-((1*R*,2*R*)-2-amino-1,2-dicyclohexylethyl)-2,3,4,5,6-pentafluorobenzenesulfonamide (Ligand Table 1, Entry 2)**



To a stirred solution of the free diamine<sup>4</sup> (83 mg, 0.37 mmol) and DIPEA (0.13 ml, 0.74 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (10 ml) at 0 °C was added pentafluorophenyl sulfonyl chloride (dropwise) and the resulting mixture was stirred over night. The reaction was then quenched by addition of saturated NH<sub>4</sub>Cl (10 mL). After extraction with CH<sub>2</sub>Cl<sub>2</sub> from H<sub>2</sub>O, and drying with Na<sub>2</sub>SO<sub>4</sub>, the crude was purified by FC (MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 5/95) to afford pure product 51 mg (30%) as a white powder. NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 0.83-1.19 (m, 9H), 1.42 (m, 1H), 1.59-1.72 (m, H), 2.66 (d, *J* = 3.9, 1H), 3.42 (d, *J* = 4.2, 1H), 6.62 (br s, 3H, NH's). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 25.9, 26.1, 26.1, 26.2, 26.2, 29.1, 29.8, 29.8, 118.8 (m, 1C), 137.7 (m, 2C), 143.2 (m, 1C), 144.1 (m, 2C). IR-Spectroscopy: (thin film, cm<sup>-1</sup>) ν 3377, 3089, 2922, 2852, 1646, 1589, 1520, 1494, 1450, 1354, 1314, 1166, 1098, 1032, 988, 932, 909, 889. MS Spectrometry: HR-MALDI calcd for C<sub>20</sub>H<sub>10</sub>F<sub>9</sub>N<sub>2</sub>O<sub>2</sub>S [M-H]<sup>+</sup> 455.1792, found 455.1779. [α]<sub>D</sub><sup>26</sup> = -66.6 (c = 1.0, CH<sub>3</sub>OH).

**N-((1*R*,2*R*)-2-aminocyclohexyl)-2,3,4,5,6-pentafluorobenzenesulfonamide (Ligand Table 1, Entry 3)**

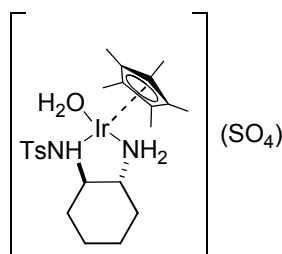


To a stirred solution of the free diamine (300 mg, 2.63 mmol) and DIPEA (0.90 ml, 5.26 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (30 ml) at 0 °C was added pentafluorophenyl sulfonyl chloride (dropwise) and the resulting mixture was stirred over night. The reaction was then quenched by addition of saturated  $\text{NH}_4\text{Cl}$  (10 mL). After extraction with  $\text{CH}_2\text{Cl}_2$  from  $\text{H}_2\text{O}$ , and drying with  $\text{Na}_2\text{SO}_4$ , the crude was purified by FC ( $\text{MeOH}/\text{CH}_2\text{Cl}_2 = 5/95$ ) to afford pure product 383 mg (42%) as a white powder. NMR Spectroscopy:  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.25-1.70 (m, 9H), 2.32 (d,  $J = 8.1$  Hz, 1H), 3.34 (m, 1H), 3.50 (m, 1H), 6.62 (br s, 3H, NH's).  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  23.7, 24.3, 31.0, 31.5, 31.8, 33.1, 118.5 (m, 1C), 137.8 (m, 2C), 143.6 (m, 1C), 144.3 (m, 2C). IR-Spectroscopy: (thin film,  $\text{cm}^{-1}$ )  $\nu$  2940, 2866, 1645, 1520, 1495, 1453, 1355, 1299, 1266, 1169, 1098, 989, 918, 831. MS Spectrometry: HR-MALDI calcd for  $\text{C}_{20}\text{H}_{10}\text{F}_9\text{N}_2\text{O}_2\text{S}$   $[\text{M}-\text{H}]^+$  345.0691, found 345.0690.  $[\alpha]_{\text{D}}^{26} = -46.7$  ( $c = 1.0$ ,  $\text{CH}_3\text{OH}$ ).

### Synthesis of the Catalysts:

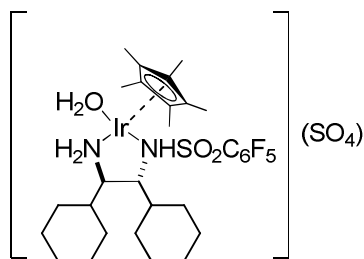
**Representative Procedure:** To a vial was added  $[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3](\text{SO}_4)^5$  (1 equiv) and the monosulfonylated diamine (1 equiv) in a 1:1 mixture of water:methanol (0.5 M) and it was stirred for 1 h at room temperature. Removal of the solvent *in vacuo* provided the catalyst complex as a powder in quantitative yield.

#### **{Cp\*Ir[(*R,R*)-Ts-DACH](H<sub>2</sub>O)}(SO<sub>4</sub>) (Catalyst Table 1, entry 1)**



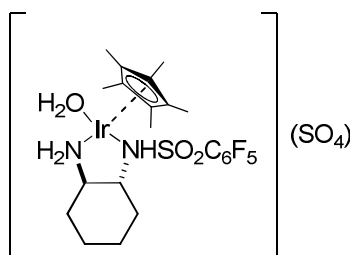
NMR Spectroscopy:  $^1\text{H}$ -NMR (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  0.70-1.66 (m, 9H, Diastereomer A+B), 1.63 (s, 15H, Diastereomer A), 1.76 (s, 15H, Diastereomer B), 1.99-2.16 (m, 2H, Diastereomer A+B), 2.43 (s, 3H, Diastereomer B), 2.45 (s, 3H, Diastereomer A), 2.96-3.03 (m, 1H, Diastereomer B), 2.77-2.92 (m, 1H, Diastereomer A), 7.38 (d,  $J = 6.0$  Hz, 2H, Diastereomer B), 7.41 (d,  $J = 6.0$  Hz, 2H, Diastereomer A), 7.74 (d,  $J = 6.3$  Hz, 2H, Diastereomer B), 7.79 (d,  $J = 6.3$  Hz, 2H, Diastereomer A).  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  8.9, 9.4, 9.4, 10.3, 21.4, 21.5, 24.7, 25.6, 25.8, 26.0, 30.8., 32.0, 33.6, 34.0, 56.1, 56.5, 82.8, 85.1, 90.8, 91.4, 127.8, 128.1, 130.7, 131.0. MS Spectrometry: HR-MALDI calcd for  $\text{C}_{31}\text{H}_{36}\text{IrN}_2\text{O}_2\text{S} [\text{M}-\text{SO}_4-\text{H}_2\text{O}]^+$  693.2121, found 693.2109.  $[\alpha]_{\text{D}}^{25} = -273.92^\circ$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).

**{Cp\*Ir[(*R,R*)-Tf-Dicyclohexyl](H<sub>2</sub>O)}(SO<sub>4</sub>) (Catalyst Table 1, entry 2)**



NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CD<sub>3</sub>OD) δ 1.04-2.22 (m, 37H), 2.86-2.97 (s, 15H). <sup>13</sup>C-NMR (75 MHz, CD<sub>3</sub>OD) δ 9.6, 24.6, 25.4, 25.9, 26.1, 30.2, 32.2, 33.2, 35.2, 55.7, 56.9, 66.0, 85.1, 89.4. <sup>19</sup>F-NMR (282 MHz, CD<sub>3</sub>OD) δ 160.1 (m, 2F), 147.6 (m, 1F), 134.9 (m, 2F). MS Spectrometry: HR-MALDI calcd for C<sub>25</sub>H<sub>29</sub>IrN<sub>2</sub>O<sub>2</sub>S [M-SO<sub>4</sub>-H<sub>2</sub>O]<sup>+</sup> 671.1525, found 671.1514. [α]<sub>D</sub><sup>28</sup> = -293.16° (c = 0.25, CH<sub>3</sub>OH).

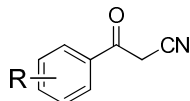
**{Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>-DACH](H<sub>2</sub>O)}(SO<sub>4</sub>) (Catalyst Table 1, entry 3)**



NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CD<sub>3</sub>OD) δ 0.43-0.51 (m, 1H), 0.73-0.61 (m, 5H), 1.02-1.21, 1.81 (s, 15H), 2.86 (d, *J* = 5.1 Hz, 1H), 3.48 (d, *J* = 3.3 Hz, 1H). <sup>13</sup>C-NMR (75 MHz, CD<sub>3</sub>OD) δ 10.4, 27.0, 27.0, 27.4, 27.6, 27.8, 29.4, 30.7, 31.1, 32.3, 41.0, 43.0, 62.0, 73.9, 93.1. <sup>19</sup>F-NMR (282 MHz, CD<sub>3</sub>OD) δ 160.4 (m, 2F), 147.8 (m, 1F), 134.9 (m, 2F). MS Spectrometry: HR-MALDI calcd for C<sub>30</sub>H<sub>29</sub>IrN<sub>2</sub>O<sub>2</sub>S [M-SO<sub>4</sub>-H<sub>2</sub>O]<sup>+</sup> 769.1494, found 769.1479. [α]<sub>D</sub><sup>26</sup> = -242.22° (c = 1.0, CHCl<sub>3</sub>).

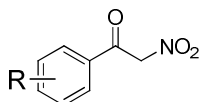
## **Synthesis of Substrates:**

### **Synthesis of $\beta$ -Ketonitriles:<sup>6</sup>**



A solution of KO<sup>t</sup>-Amyl (1.33 mL, 2.61 mmol, 3.00 equiv, 1.7 M in toluene, Fluka) was added dropwise to a room temperature stirred solution of acetonitrile (0.87 mmol, 1.00 equiv) in THF (3.0 mL) followed by dropwise addition of the ester (3.48 mmol, 4.00 equiv). After 20 min at room temperature, the reaction mixture was diluted with HCl (0.25 M, 100 mL) and EtOAc (100 mL). The layers were separated and the organic layer was washed sequentially with H<sub>2</sub>O (2 x 50 mL) and brine (2 x 50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated, and chromatographed (silica gel, EtOAc/Hex) to provide the corresponding  $\beta$ -ketonitrile.

### **Synthesis of $\alpha$ -Nitroketones:<sup>7</sup>**



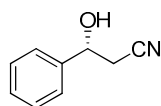
A mixture of nitromethane (0.11 mL, 2.0 mmol, 1 equiv) and KO<sup>t</sup>-butyl (0.5 g, 4.4 mmol, 2.2 equiv) in DMSO (10 mL) was stirred for 10 min. while the temperature was maintained at 10 °C. The corresponding *N*-acetylbenzotriazole<sup>23</sup> (2.0 mmol, 1 equiv) in DMSO (10 mL) was added dropwise to the resulting solution, and the mixture was stirred for 2 h at 10 °C, and then for additional 6 h at room temperature. The mixture was poured into water (40 mL), acidified with acetic acid (10 % in water), and then extracted with ethyl acetate (3 x 30 mL). The combined extracts were washed with water, dried over Na<sub>2</sub>SO<sub>4</sub> concentrated, and chromatographed (silica gel, EtOAc/Hex) to provide the corresponding  $\alpha$ -nitroketone.

## Transfer Hydrogenation Reaction of $\beta$ -Ketonitriles:

### General procedure:

The  $\beta$ -ketonitrile (0.5 mmol, 1.0 equiv), catalyst (0.00125-0.0025 mmol, 0.25-0.5 mol%) and aqueous solution of formic acid (1.0 M formate soln., pH = 3.5, 5.0 equiv, 0.2 M overall concentration) were combined in a glass vial and sealed with a punctured plastic cap. The reaction mixture was then stirred at ambient temperature for 24 h. The reaction mixture was then extracted with dichloromethane (3 x). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The residue was purified by flash chromatography to provide the corresponding  $\beta$ -hydroxynitrile.

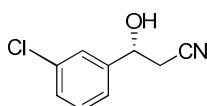
### (*R*)-3-Hydroxy-3-phenylpropanenitrile (Table 2, entry 1)



3-Oxo-3-phenylpropanenitrile (0.55 mmol, 80 mg, 1 equiv) was reduced using the catalyst {Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>DPEN](H<sub>2</sub>O)}(SO<sub>4</sub>) (0.0012 mmol, 1.1 mg, 0.25 mol%) according to general method to give 78 mg (96%) as a colorless oil.

ee = 94% (HPLC: OJ-H, 215 nm, hexane:2-propanol = 90:10, flow rate 1 mL/min,  $t_{r(\text{major})}$  = 26.9 min,  $t_{r(\text{minor})}$  = 22.0 min).  $[\alpha]_D^{24} = +56.93^\circ$  (c 1.0, CHCl<sub>3</sub>), Lit.<sup>5</sup>  $[\alpha]_D^{20} = +56.1^\circ$  (c 0.9, EtOH) for (*R*) enantiomer (99% ee). NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.43 (br s, 1H, OH), 2.78 (d,  $J$  = 6.3 Hz, 2H), 5.03-5.08 (m, 1H), 7.33-7.42 (m, 5H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  28.1, 70.2, 117.6, 125.5, 128.8, 128.9, 139.1. All other spectroscopic data were in agreement with the literature.<sup>8</sup>

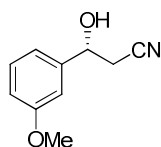
### (*R*)-3-(3-Chlorophenyl)-3-hydroxypropanenitrile (Table 2, entry 2)



3-(3-Chlorophenyl)-3-oxopropanenitrile (1.11 mmol, 200 mg, 1 equiv) was reduced using the catalyst {Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>DPEN](H<sub>2</sub>O)}(SO<sub>4</sub>) (0.0024 mmol, 2.5 mg, 0.25 mol%) according to the general method to give 182 mg (90%) as a pale yellow oil.

ee = 90% (HPLC: OJ-H, 215 nm, hexane:2-propanol = 90:10, flow rate 1 mL/min, *t<sub>r</sub>*(major) = 15.4 min, *t<sub>r</sub>*(minor) = 13.6 min). [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +41.76° (c = 1.0, CHCl<sub>3</sub>). NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.56 (br s, 1H, OH), 2.76 (d, *J* = 6.3 Hz, 2H), 5.04 (ddd, *J* = 3.3, 6.0, 12.0 Hz, 1H), 7.26-7.35 (m, 3H), 7.41 (m, 1H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  27.8, 68.8, 117.4, 123.8, 125.7, 128.6, 130.1, 134.5, 143.1. IR-Spectroscopy: (thin film, cm<sup>-1</sup>)  $\nu$  3436, 2256, 1576, 1478, 1434, 1303, 1193, 1063, 883, 790. MS Spectrometry: HR-EI calcd for C<sub>9</sub>H<sub>8</sub>ClNO [M]<sup>+</sup> 181.0294, found 181.0289.

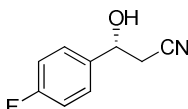
### (*R*)-3-Hydroxy-3-(3-methoxyphenyl)propanenitrile (Table 2, entry 3)



3-(3-Methoxyphenyl)-3-oxopropanenitrile (0.57 mmol, 100 mg, 1 equiv) was reduced using the catalyst {Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>DPEN](H<sub>2</sub>O)}(SO<sub>4</sub>) (0.0014 mmol, 1.26 mg, 0.25 mol%) according to general method to give 97 mg (96%) as a colorless oil.

ee = 95% (HPLC: OJ-H, 215 nm, hexane:2-propanol = 95:5, flow rate 0.5 mL/min, *t<sub>r</sub>*(major) = 152.0 min, *t<sub>r</sub>*(minor) = 137.7 min). [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +44.08° (c = 1.0, CHCl<sub>3</sub>). NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.35 (br s, 1H, OH), 2.75 (d, *J* = 2.4 Hz, 1H), 2.77 (d, *J* = 3.0 Hz, 1H), 3.82 (s, 3H), 4.98-5.03 (m, 1H), 6.86-6.97 (m, 3H), 7.27-7.34 (m, 1H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  28.0, 55.4, 70.1, 111.0, 114.2, 117.2, 117.6, 130.0, 142.5, 159.9. IR-Spectroscopy: (thin film, cm<sup>-1</sup>)  $\nu$  3448, 2940, 2838, 2253, 1603, 1490, 1457, 1436, 1267, 1155, 1043, 771. MS Spectrometry: HR-EI calcd for C<sub>10</sub>H<sub>11</sub>NO<sub>2</sub> [M]<sup>+</sup> 177.0789, found 177.0783.

### (*R*)-3-(4-Fluorophenyl)-3-hydroxypropanenitrile (Table 2, entry 4)

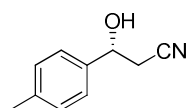




3-(4-Fluorophenyl)-3-oxopropanenitrile (0.61 mmol, 100 mg, 1 equiv) was reduced using the catalyst {Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>DPEN](H<sub>2</sub>O)}(SO<sub>4</sub>) (0.003 mmol, 2.7 mg, 0.5 mol%) according to the general method to give 95 mg (95%) as a pale yellow oil.

ee = 91% (HPLC: OD-H, 215 nm, hexane:2-propanol = 95:5, flow rate 0.5 mL/min,  $t_{r(\text{major})}$  = 93.6 min,  $t_{r(\text{minor})}$  = 77.7 min).  $[\alpha]_{\text{D}}^{29}$  = +43.58° (c = 1.0, CHCl<sub>3</sub>), Lit.<sup>5</sup>  $[\alpha]_{\text{D}}^{20}$  = +53.7° (c = 0.86, EtOH) for (*R*) enantiomer (99% ee). NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 2.44 (br s, 1H, OH), 2.77 (d, *J* = 6.3 Hz, 2H), 5.05 (t, *J* = 6.3 Hz, 1H), 7.06-7.13 (m, 2H), 7.31-7.42 (m, 2H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 28.0, 69.1, 115.4 (d, *J* = 21.2 Hz), 117.2, 127.1 (d, *J* = 8.5 Hz), 136.7 (d, *J* = 3.0 Hz), 160.8 (d, *J* = 245.2 Hz). All other spectroscopic data were in agreement with the literature.<sup>9</sup>

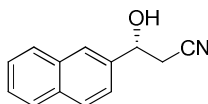
### (*R*)-3-Hydroxy-3-*p*-tolylpropanenitrile (Table 2, entry 5)



3-Oxo-3-*p*-tolylpropanenitrile (0.64 mmol, 103 mg, 1 equiv) was reduced using the catalyst {Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>DPEN](H<sub>2</sub>O)}(SO<sub>4</sub>) (0.003 mmol, 2.8 mg, 0.5 mol%) according to general method to give 99 mg (96%) as a colorless oil.

ee = 93% (HPLC: OJ-H, 215 nm, hexane:2-propanol = 90:10, flow rate 1 mL/min,  $t_{r(\text{major})}$  = 21.3 min,  $t_{r(\text{minor})}$  = 18.6 min).  $[\alpha]_{\text{D}}^{29}$  = +29.68° (c 1.0, CHCl<sub>3</sub>), Lit.<sup>5</sup>  $[\alpha]_{\text{D}}^{20}$  = +65.8° (c 1.09, CHCl<sub>3</sub>) for (*R*) enantiomer (99% ee). NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 2.28 (d, *J* = 3.6 Hz, 1H, OH), 2.36 (s, 3H), 2.76 (d, *J* = 5.7 Hz, 1H), 2.82 (d, *J* = 6.9 Hz, 1H), 4.99-5.05 (ddd, *J* = 3.9, 6.3, 12.3 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 21.4, 28.1, 70.1, 117.7, 125.7, 129.7, 138.3, 138.9. All other spectroscopic data were in agreement with the literature.<sup>10</sup>

### (*R*)-3-Hydroxy-3-(naphthalen-2-yl)propanenitrile (Table 2, entry 6)

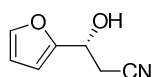


3-(Naphthalen-2-yl)-3-oxopropanenitrile (0.6 mmol, 117 mg, 1 equiv) was reduced using the catalyst {Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>DPEN](H<sub>2</sub>O)}(SO<sub>4</sub>) (0.003 mmol, 2.6 mg, 0.5 mol%)

with a modification to the general method. For this substrate 10% hexafluoroisopropanol was added as a co-solvent to give 111 mg (95%) as a pale yellow solid.

ee = 96% (HPLC: OJ-H, 254 nm, hexane:2-propanol = 90:10, flow rate 1 mL/min,  $t_{r(\text{major})}$  = 65.9 min,  $t_{r(\text{minor})}$  = 60.6 min).  $[\alpha]_{\text{D}}^{25}$  = +43.85° (c = 1.0, CHCl<sub>3</sub>), Lit.<sup>5</sup>  $[\alpha]_{\text{D}}^{20}$  = +59.5° (c 0.5, EtOH) for (*R*) enantiomer (99% ee). NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 2.90 (d, *J* = 3.6 Hz, 2H), 4.61 (dd, *J* = 3.3, 13.5 Hz, 2H), 4.4.71 (dd, *J* = 9.3, 13.5 Hz, 2H), 5.63-5.68 (m, 1H), 7.47-7.55 (m, 3H), 7.85-7.91 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 28.0, 70.2, 117.3, 122.9, 124.7, 126.4, 126.5, 127.7, 128.0, 128.8, 133.0, 133.3, 138.2. All other spectroscopic data were in agreement with the literature.<sup>11</sup>

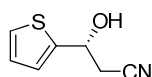
#### (*R*)-3-(Furan-2-yl)-3-hydroxypropanenitrile (Table 2, entry 7)



3-(Furan-2-yl)-3-oxopropanenitrile (0.55 mmol, 75 mg, 1 equiv) was reduced using the catalyst {Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>DPEN](H<sub>2</sub>O)}(SO<sub>4</sub>) (0.0014 mmol, 1.22 mg, 0.25 mol%) according to the general method to give 62.5 mg (83%) as a pale yellow oil.

ee = 96% (HPLC: OJ-H, 220 nm, hexane:2-propanol = 90:10, flow rate 1 mL/min,  $t_{r(\text{major})}$  = 22.6 min,  $t_{r(\text{minor})}$  = 19.9 min).  $[\alpha]_{\text{D}}^{27}$  = +37.16° (c = 1.0, CHCl<sub>3</sub>). NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 2.57 (br s, 1H, OH), 2.91 (d, *J* = 6.0 Hz, 2H), 5.06 (t, *J* = 6.3 Hz, 1H), 6.37-6.42 (m, 2H), 7.41-7.42 (m, 1H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 24.8, 63.6, 107.4, 110.5, 117.0, 142.8, 152.8. IR-Spectroscopy: (thin film, cm<sup>-1</sup>) ν 3426, 2931, 2255, 1504, 1416, 1233, 1057, 1013, 748, 598, 348. MS Spectrometry: HR-EI calcd for C<sub>7</sub>H<sub>7</sub>NO<sub>2</sub> [M]<sup>+</sup> 137.0477, found 137.0472.

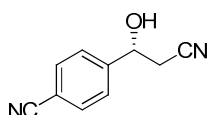
#### (*R*)-3-Hydroxy-3-(thiophen-2-yl)propanenitrile (Table 2, entry 8)



3-Oxo-3-(thiophen-2-yl)propanenitrile (0.50 mmol, 76 mg, 1 equiv) was reduced using the catalyst {Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>DPEN](H<sub>2</sub>O)}(SO<sub>4</sub>) (0.0025 mmol, 2.2 mg, 0.5 mol%) in pH = 3.5 formic acid buffer (2.5 mL, 5 equiv) at 50 °C for 24 h to give 72.5 mg (94%) as a pale yellow oil.

ee = 92% (HPLC: OJ-H, 215 nm, hexane:2-propanol = 90:10, flow rate 1 mL/min, *t<sub>r</sub>*(major) = 33.4 min, *t<sub>r</sub>*(minor) = 28.8 min). [ $\alpha$ ]<sub>D</sub><sup>26</sup> = +33.23° (c = 1.0, CHCl<sub>3</sub>). NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.62 (d, *J* = 3.9 Hz, 1H, OH), 2.88 (d, *J* = 0.9 Hz, 1H), 2.90 (d, *J* = 1.2 Hz, 1H), 5.28-5.34 (m, 1H), 7.01 (dd, *J* = 3.6, 5.1 Hz, 1H), 7.10 (td, *J* = 0.9, 3.9 Hz, 1H), 7.7.33 (dd, *J* = 1.2, 4.8 Hz, 1H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  28.3, 66.4, 116.8, 124.7, 125.8, 127.1, 144.3. All other spectroscopic data were in agreement with the literature.<sup>12</sup>

**(*R*)-4-(2-Cyano-1-hydroxyethyl)benzonitrile (Table 2, entry 9)**



4-(2-Cyanoacetyl)benzonitrile (0.59 mmol, 100 mg, 1 equiv) was reduced using the catalyst {Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>DPEN](H<sub>2</sub>O)}(SO<sub>4</sub>) (0.0015 mmol, 1.3 mg, 0.25 mol%) according to the general method to give 98 mg (97%) as a pale yellow oil.

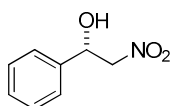
ee = 86% (HPLC: OJ-H, 215 nm, hexane:2-propanol = 90:10, flow rate 1 mL/min, *t<sub>r</sub>*(major) = 62.4 min, *t<sub>r</sub>*(minor) = 51.9 min). [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +48.16° (c = 1.0, CHCl<sub>3</sub>). NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.52-2.78 (br s, 1H, OH), 2.79 (d, *J* = 5.7 Hz, 2H), 5.11-5.17 (m, 1H), 7.56 (d, *J* = 8.1, 2H), 7.70 (d, *J* = 8.1, 2H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  28.1, 69.1, 112.3, 116.6, 118.3, 126.3, 132.6, 146.0. IR-Spectroscopy: (thin film, cm<sup>-1</sup>)  $\nu$  3448, 2230, 1610, 11505, 1413, 1071, 842, 567. MS Spectrometry: HR-EI calcd for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>O [M]<sup>+</sup> 172.0637, found 172.0630.

## Transfer Hydrogenation Reaction of $\alpha$ -Nitroketones:

### General procedure:

The  $\alpha$ -nitroketone (0.5 mmol, 1.0 equiv), catalyst (0.0025 mmol, 0.5 mol%), and aqueous formic acid solution (1.0M formate soln., pH = 2.0, 5.0 equiv, 0.2M overall concentration) were combined in a glass vial which was then sealed with a punctured plastic cap. The reaction mixture was then stirred at ambient temperature for 24 h. The reaction mixture was then extracted with  $\text{CH}_2\text{Cl}_2$  (3 x). The combined organic layer was washed, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. The residue was purified by flash chromatography to give the corresponding  $\alpha$ -nitroalcohol.

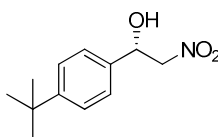
### (S)-2-Nitro-1-phenylethanol (Table 2, entry 10)



2-Nitro-1-phenylethanone (0.51 mmol, 85 mg, 1 equiv) was reduced using the catalyst  $\{\text{Cp}^*\text{Ir}[(R,R)\text{-C}_6\text{F}_5\text{SO}_2\text{DPEN}](\text{H}_2\text{O})\}(\text{SO}_4)$  (0.0025 mmol, 2.2 mg, 0.5 mol%) according to general method to give 84 mg (94%) as a pale yellow oil.

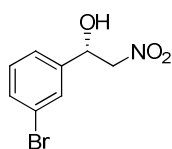
ee = 93% (HPLC: OD-H, 215 nm, hexane:2-propanol = 97:3, flow rate 1 mL/min,  $t_{r(\text{major})}$  = 42.6 min,  $t_{r(\text{minor})}$  = 36.5 min).  $[\alpha]_{\text{D}}^{24}$  = 42.99° (c = 1.0,  $\text{CHCl}_3$ ), Lit.<sup>11</sup>  $[\alpha]_{\text{D}}^{20}$  = -20.2° (c = 1.00, EtOH) for (R) enantiomer (98% ee). NMR Spectroscopy:  $^1\text{H}$ -NMR: (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.82 (d,  $J$  = 3.9 Hz, 1H, OH), 4.52 (dd,  $J$  = 3.3, 13.5 Hz, 1H), 4.62 (dd,  $J$  = 9.3, 13.5 Hz, 1H), 5.47 (dt,  $J$  = 3.3, 9.6 Hz, 1H), 7.34-7.45 (m, 5H).  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  71.4, 81.6, 126.2, 129.3, 129.3, 138.4. All other spectroscopic data were in agreement with the literature.<sup>13</sup>

### (S)-1-(4-*tert*-Butylphenyl)-2-nitroethanol (Table 2, entry 11)



1-(4-*tert*-Butylphenyl)-2-nitroethanone (0.500 mmol, 109 mg, 1 equiv) was reduced using the catalyst {Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>DPEN](H<sub>2</sub>O)}(SO<sub>4</sub>) (0.0025 mmol, 2.2 mg, 0.5 mol%) according to general method to give 103 mg (92%) as a white solid. Melting Point: 70 to 72°C. ee = 99% (HPLC: OD-H, 215 nm, hexane:2-propanol = 90:10, flow rate 1 mL/min,  $t_{r(\text{major})}$  = 16.0 min,  $t_{r(\text{minor})}$  = 11.6 min).  $[\alpha]_D^{28}$  = +38.32 (c = 1.0, CHCl<sub>3</sub>). NMR Spectroscopy: <sup>1</sup>H-NMR: (300 MHz, CDCl<sub>3</sub>) δ 1.32 (s, 9H), 2.71 (d, *J* = 3.6 Hz, 1H), 4.51 (dd, *J* = 3.3, 13.5 Hz, 1H), 4.63 (dd, *J* = 9.6, 13.5 Hz, 1H), 5.42-5.48 (m, 1H), 7.32-7.36 (m, 2H), 7.41-7.45 (m, 2H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 31.3, 34.7, 70.8, 81.2, 125.6, 125.9, 134.9, 152.0. IR-Spectroscopy: (thin film, cm<sup>-1</sup>) ν 3546, 2963, 2360, 1555, 1378, 1219, 1078, 836, 772. MS Spectrometry: HR-EI calcd for C<sub>12</sub>H<sub>17</sub>NO<sub>3</sub> [M]<sup>+</sup> 223.1208, found 223.1204.

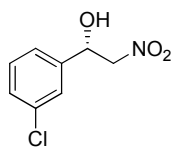
**(S)-1-(3-Bromophenyl)-2-nitroethanol (Table 2, entry 12)**



1-(3-Bromophenyl)-2-nitroethanone (0.50 mmol, 122 mg, 1 equiv) was reduced using the catalyst {Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>DPEN](H<sub>2</sub>O)}(SO<sub>4</sub>) (0.0025 mmol, 2.2 mg, 0.5 mol%) according to general method to give 66 mg (54%) as a colorless oil.

ee = 91% (HPLC: OD-H, 215 nm, hexane:2-propanol = 90:10, flow rate 1 mL/min,  $t_{r(\text{major})}$  = 21.4 min,  $t_{r(\text{minor})}$  = 15.9 min).  $[\alpha]_D^{26}$  = +25.76° (c = 1.0, CHCl<sub>3</sub>). NMR Spectroscopy: <sup>1</sup>H-NMR: (300 MHz, CDCl<sub>3</sub>) δ 2.90 (d, *J* = 3.9 Hz, 1H, OH), 4.51 (dd, *J* = 3.3, 13.5 Hz, 1H), 4.59 (dd, *J* = 9.0, 13.5 Hz, 1H), 5.43-5.48 (m, 1H), 7.25-7.35 (m, 2H), 7.48-7.52 (m, 1H), 7.59-7.60 (m, 1H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 70.3, 80.9, 123.1, 124.5, 129.0, 130.5, 132.0, 140.1. All other spectroscopic data were in agreement with the literature.<sup>14</sup>

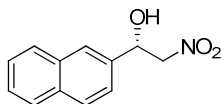
**(S)-1-(3-Chlorophenyl)-2-nitroethanol (Table 2, entry 13)**



1-(3-Chlorophenyl)-2-nitroethanone (0.50 mmol, 100 mg, 1 equiv) was reduced using the catalyst {Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>DPEN](H<sub>2</sub>O)}(SO<sub>4</sub>) (0.0025 mmol, 2.2 mg, 0.5 mol%) according to general method to give 96 mg (95%) as a colorless oil.

ee = 95% (HPLC: OD-H, 215 nm, hexane:2-propanol = 90:10, flow rate 1 mL/min, *t<sub>r</sub>*(major) = 17.8 min, *t<sub>r</sub>*(minor) = 14.1 min). [ $\alpha$ ]<sub>D</sub><sup>27</sup> = 31.17° (c 1.0, CHCl<sub>3</sub>). NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.91 (d, *J* = 3.9, 1H), 4.51 (dd, *J* = 3.6, 13.5 Hz, 1H), 4.59 (dd, *J* = 9.0, 13.5 Hz, 1H), 5.43-5.49 (m, 1H), 7.26-7.36 (m, 3H), 7.43-7.45 (m, 1H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  70.3, 80.9, 109.9, 124.0, 126.1, 129.1, 130.2, 135.0, 139.9. All other spectroscopic data were in agreement with the literature.<sup>15</sup>

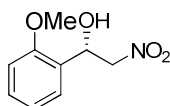
#### (*S*)-1-(Naphthalen-2-yl)-2-nitroethanol (Table 2, entry 14)



1-(Naphthalen-2-yl)-2-nitroethanone (0.53 mmol, 113 mg, 1 equiv) was reduced using the catalyst {Cp\*Ir[(*R,R*)-C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>DPEN](H<sub>2</sub>O)}(SO<sub>4</sub>) (0.0025 mmol, 2.2 mg, 0.5 mol%) according to general method to give 66 mg (58%) as a pale yellow oil.

ee = 93% (HPLC: OD-H, 215 nm, hexane:2-propanol = 90:10, flow rate 1 mL/min, *t<sub>r</sub>*(major) = 59.2 min, *t<sub>r</sub>*(minor) = 43.0 min). [ $\alpha$ ]<sub>D</sub><sup>28</sup> = +37.52° (c = 1.0, CHCl<sub>3</sub>). NMR Spectroscopy: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.91 (d, *J* = 3.6 Hz, 1H, OH), 4.61 (dd, *J* = 3.3, 13.5 Hz, 1H), 4.71 (dd, *J* = 9.3, 13.5 Hz, 1H), 5.65 (td, *J* = 3.6, 9.0 Hz, 1H), 7.47-7.56 (m, 3H), 7.85-7.91 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  71.2, 81.2, 123.1, 125.3, 126.3, 126.7, 127.7, 128.0, 128.9, 133.1, 133.3, 135.3. All other spectroscopic data were in agreement with the literature.<sup>16</sup>

#### (*S*)-1-(2-methoxyphenyl)-2-nitroethanol (Table 2, entry 15)





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- <sup>10</sup> Dehli, J. R.; Gotor, V. *Tet: Asymm.* **2000**, *11*, 3693-3700.
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- <sup>17</sup> Imuta, M.; Kawai, K.; Ziffer, H. *J. Org. Chem.* **1980**, *45*, 3352-3355.



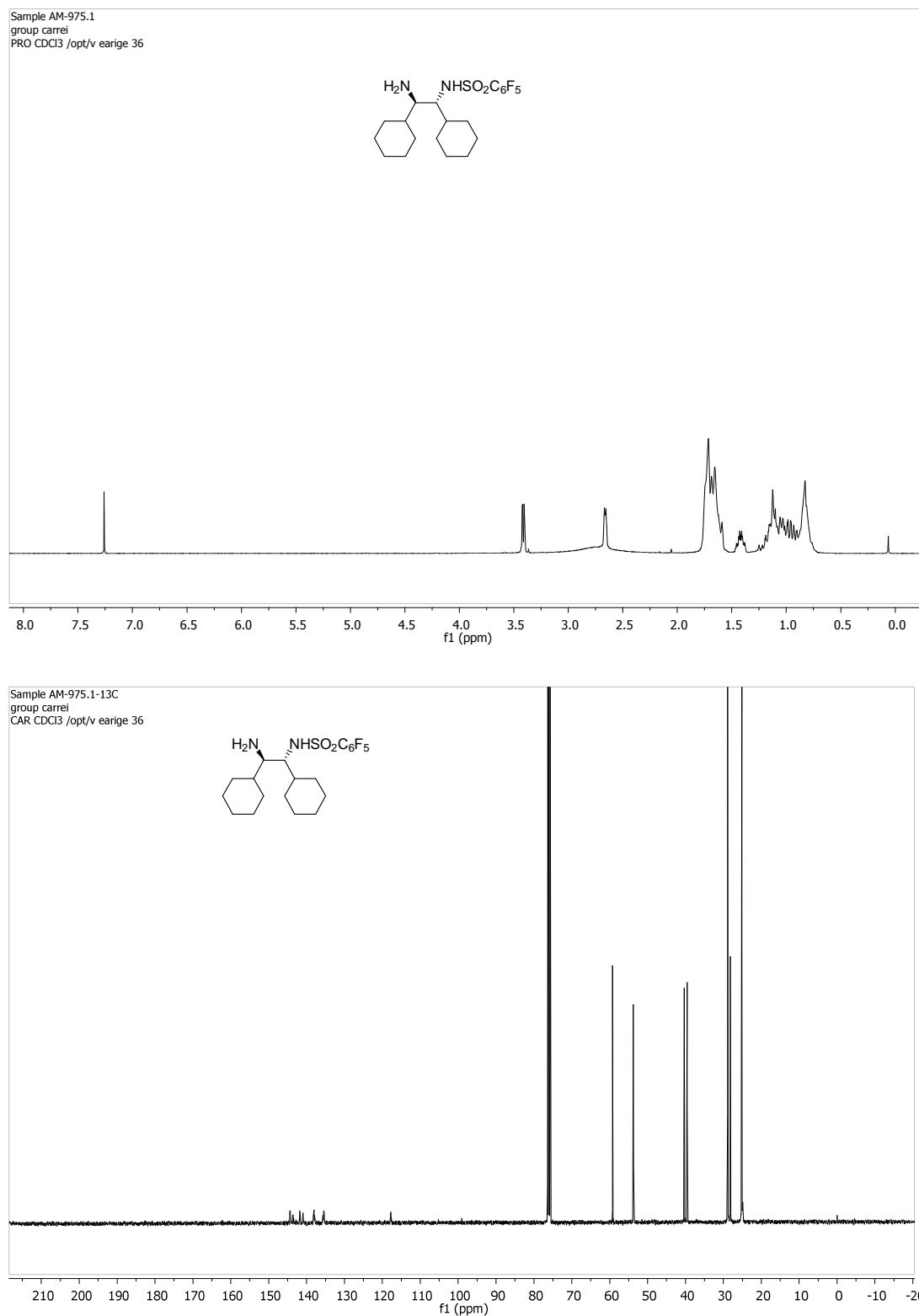


Figure 1: <sup>1</sup>H- and <sup>13</sup>C-NMR of N-((1*R*,2*R*)-2-amino-1,2-dicyclohexylethyl)-2,3,4,5,6-pentafluorobenzenesulfonamide ( Ligand Table 1, Entry 2)

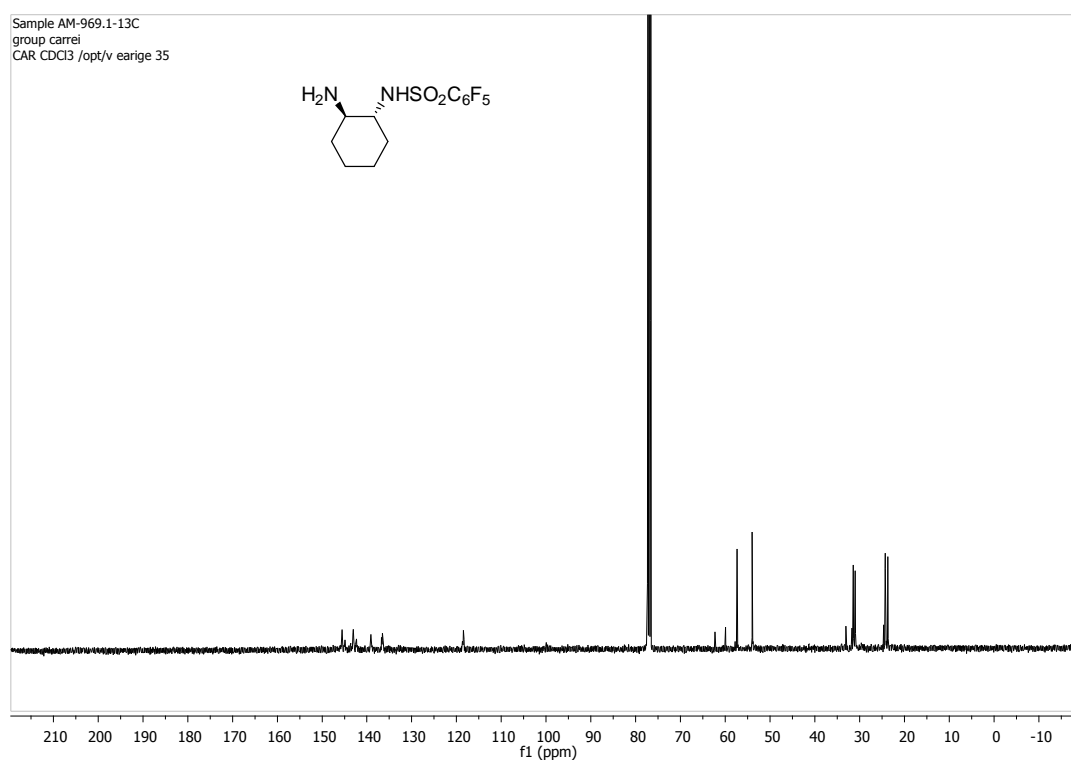
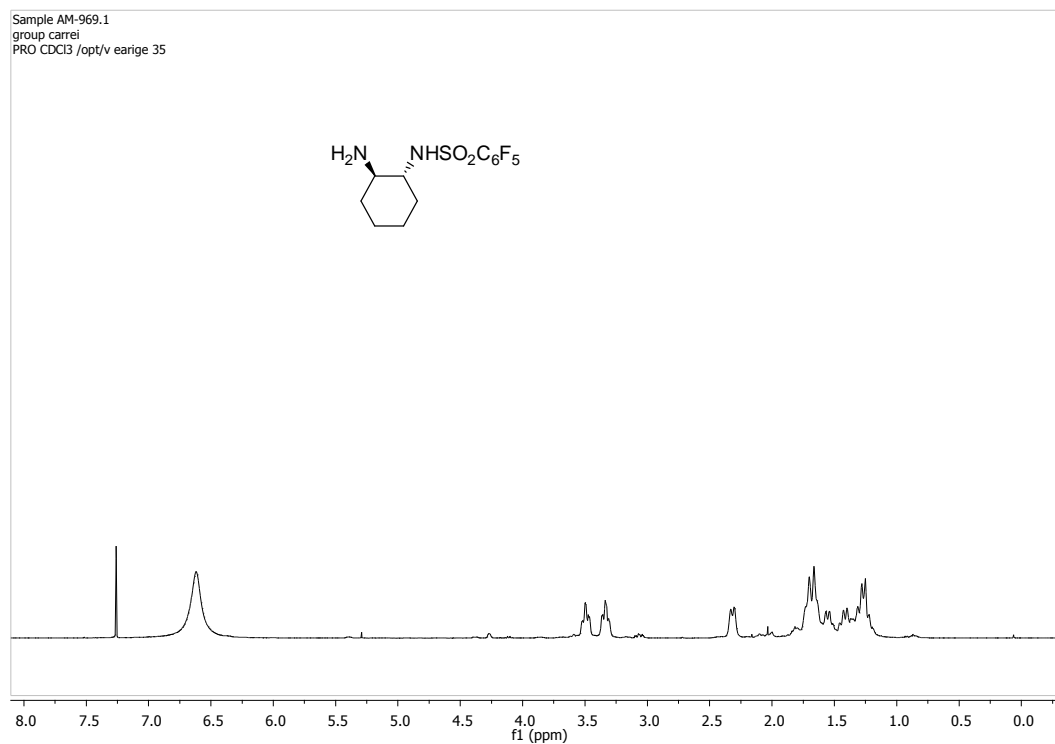


Figure 2:  $^1\text{H}$  and  $^{13}\text{C}$ -NRM of N-((1*R*,2*R*)-2-aminocyclohexyl)-2,3,4,5,6-pentafluorobenzenesulfonamide (Ligand Table 1, Entry 3)

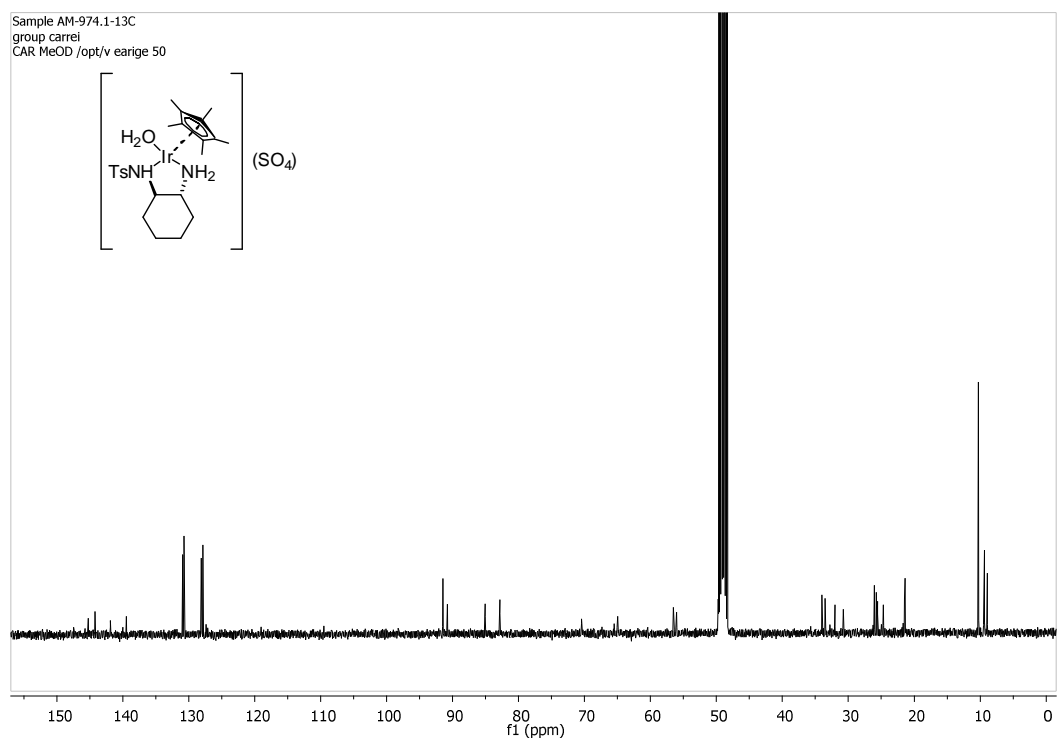
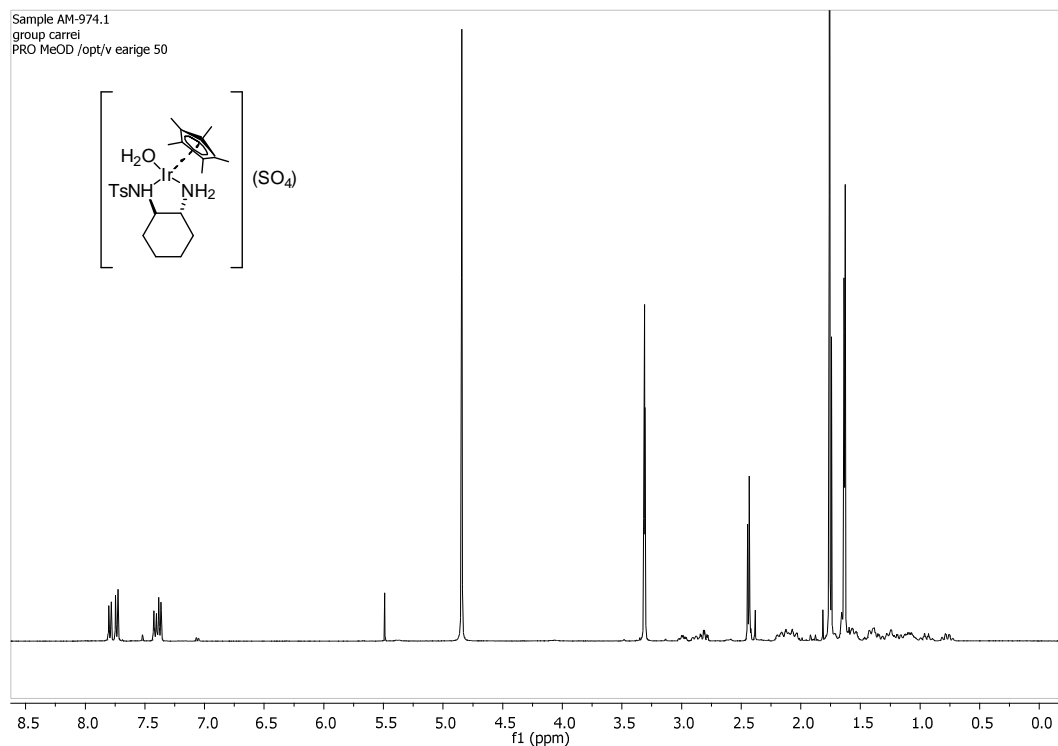


Figure 3:  $^1H$ - and  $^{13}C$ -NMR of  $\{Cp^*Ir[(R,R)\text{-Ts-DACH}](H_2O)\}(SO_4)$  (Catalyst Table 1, Entry 1)

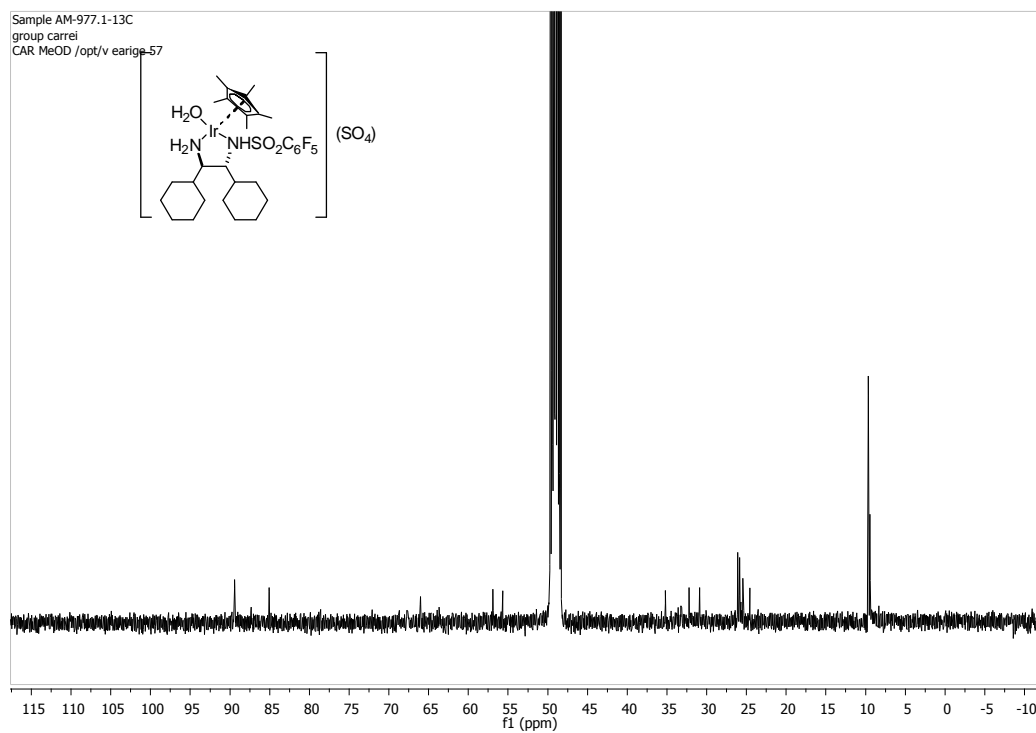
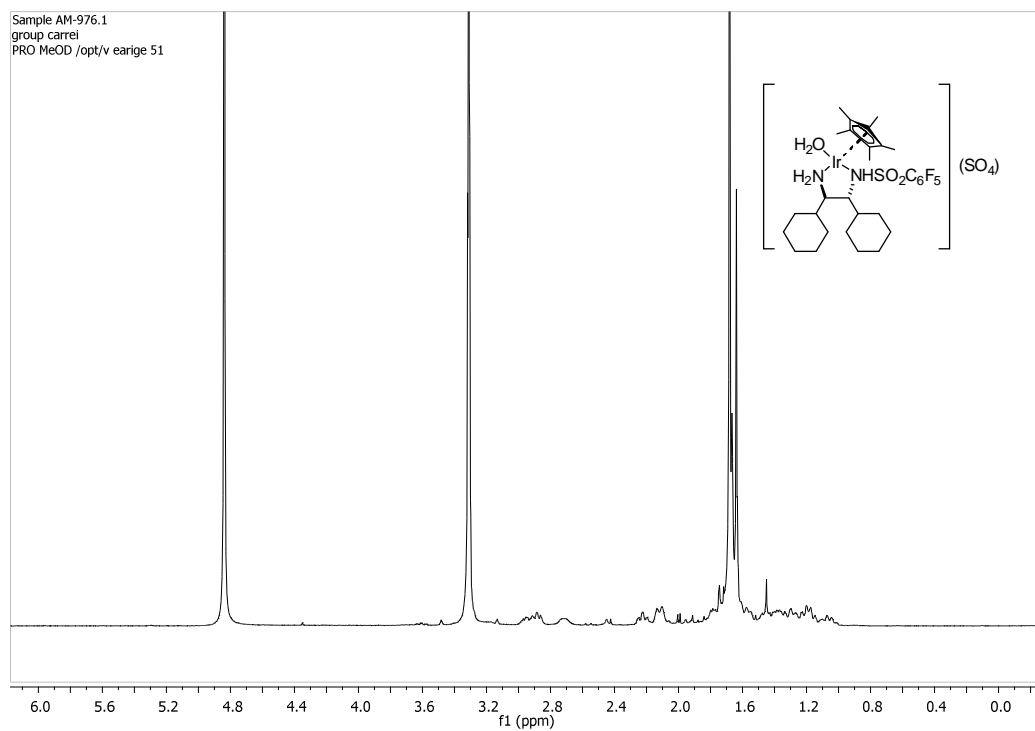


Figure 4:  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR of  $\{\text{Cp}^*\text{Ir}[(R,R)\text{-Tf-dicyclohexyl}](\text{H}_2\text{O})\}(\text{SO}_4)$  (Catalyst Table 1, Entry 2)

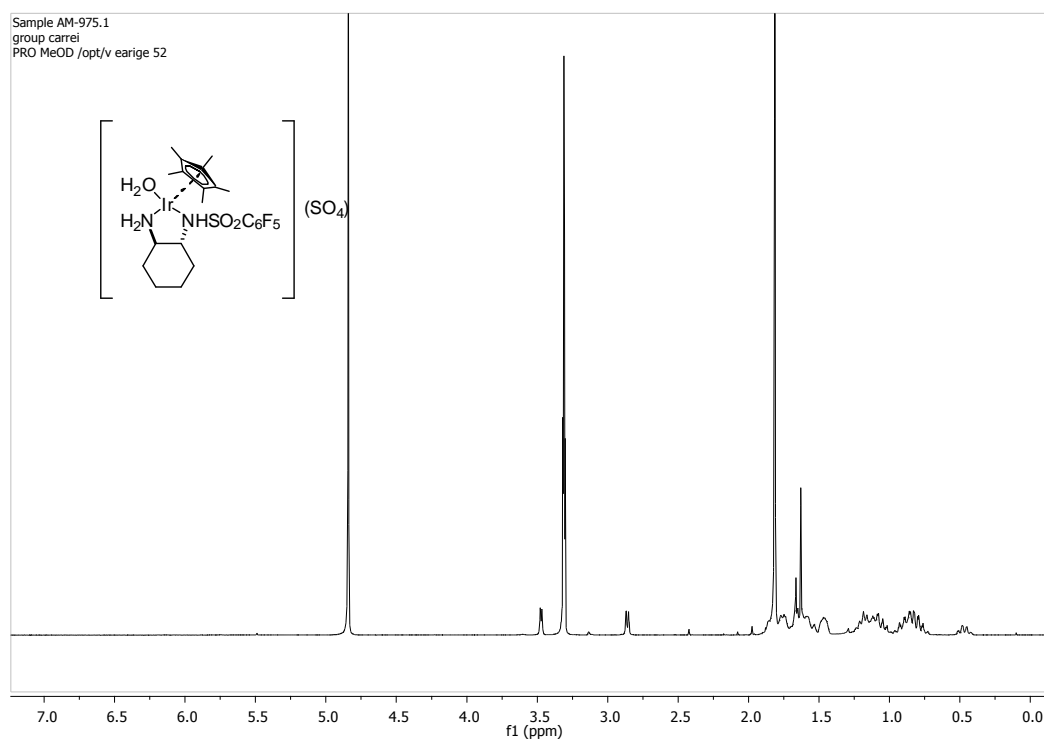
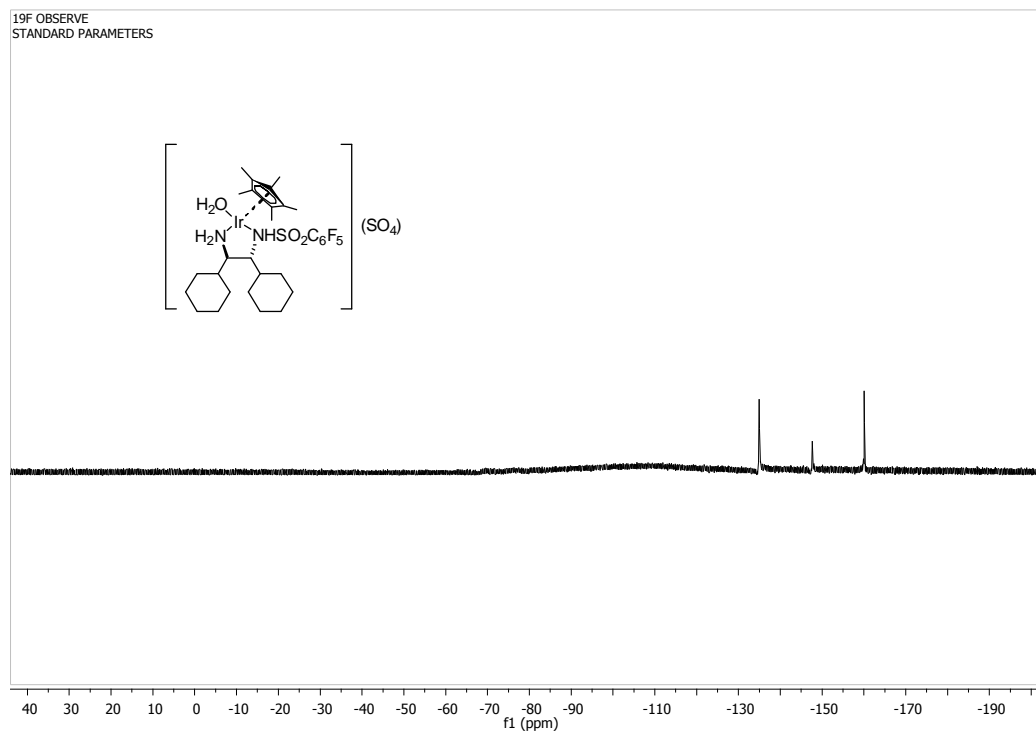


Figure 5:  $^{19}\text{F}$ -NMR of  $\{\text{Cp}^*\text{Ir}[(R,R)\text{-Tf-dicyclohexyl}](\text{H}_2\text{O})\}(\text{SO}_4)$  (Catalyst Table 1, Entry 2) and  $^1\text{H}$ -NMR of  $\{\text{Cp}^*\text{Ir}[(R,R)\text{-C}_6\text{F}_5\text{SO}_2\text{-DACH}](\text{H}_2\text{O})\}(\text{SO}_4)$  (Catalyst Table 1, entry 3)

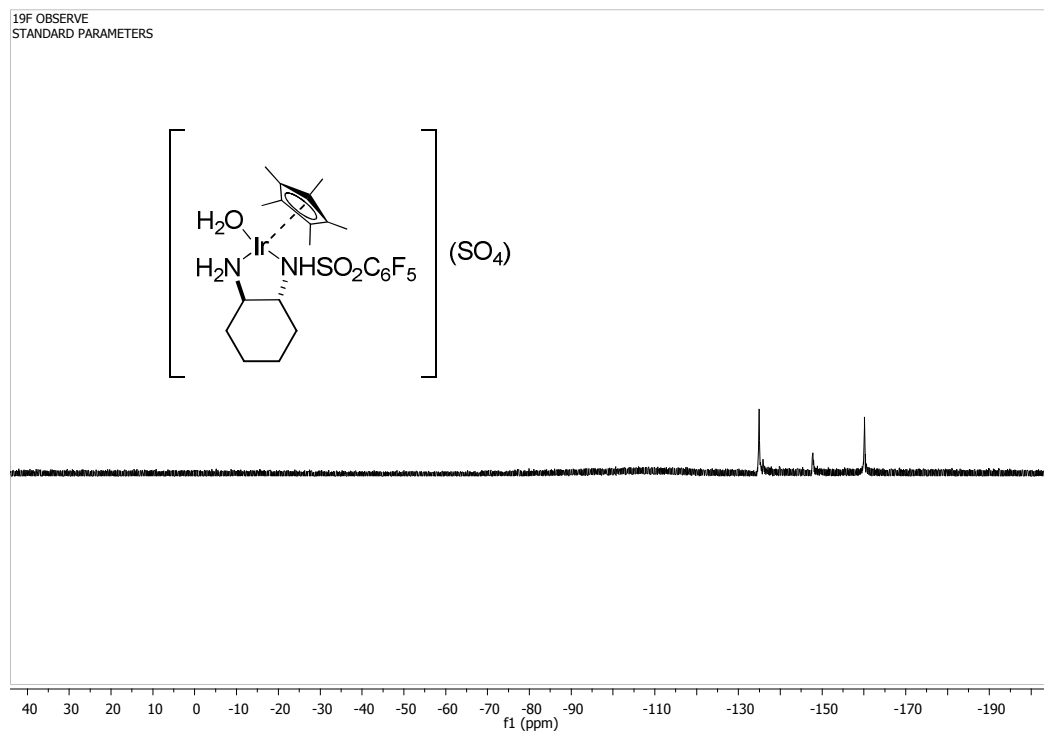
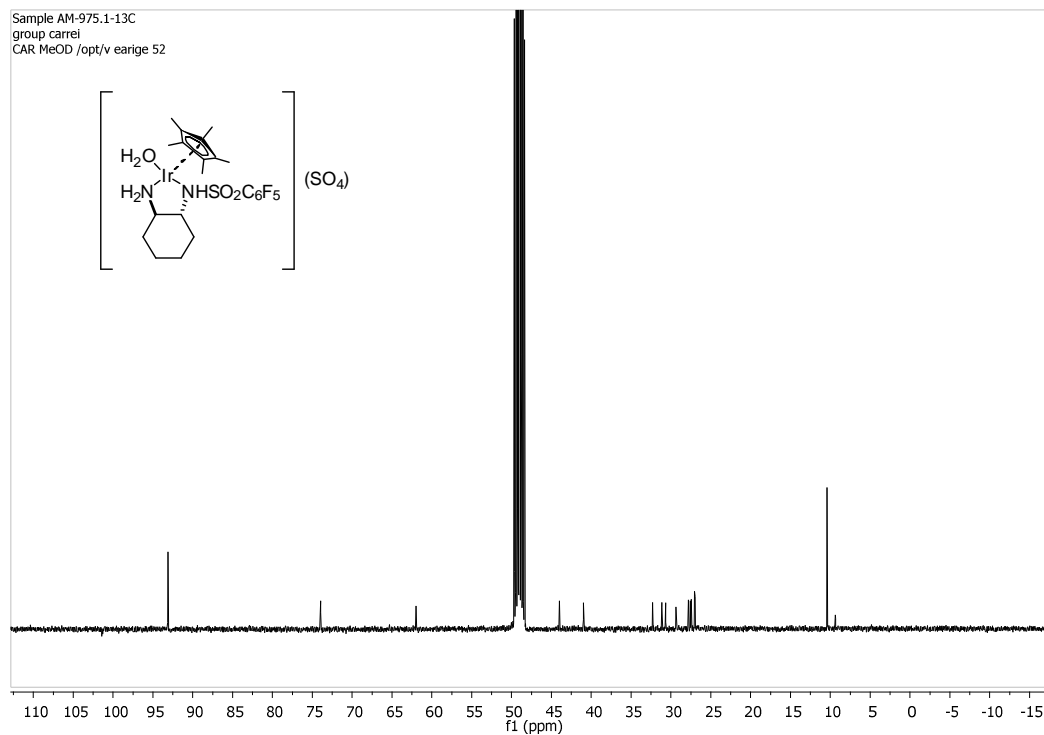


Figure 6:  $^{13}\text{C}$ -NMR and  $^{19}\text{F}$ -NMR of  $\{\text{Cp}^*\text{Ir}[(R,R)\text{-C}_6\text{F}_5\text{SO}_2\text{-DACH}](\text{H}_2\text{O})\}(\text{SO}_4)$  (Catalyst Table 1, entry 3)

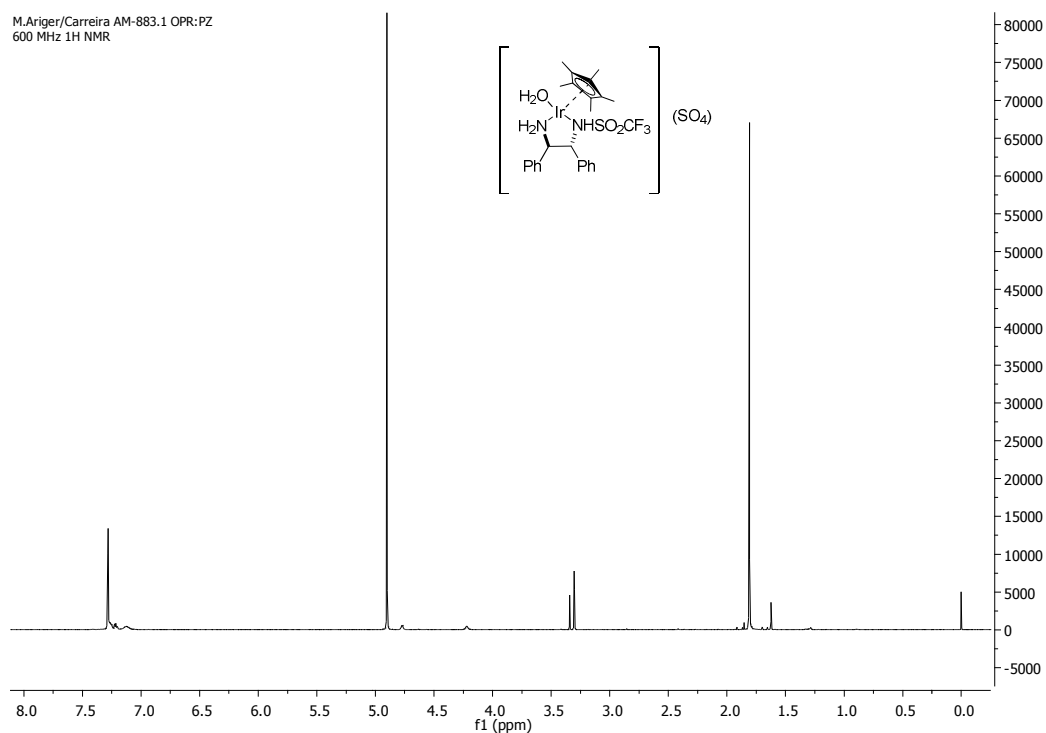
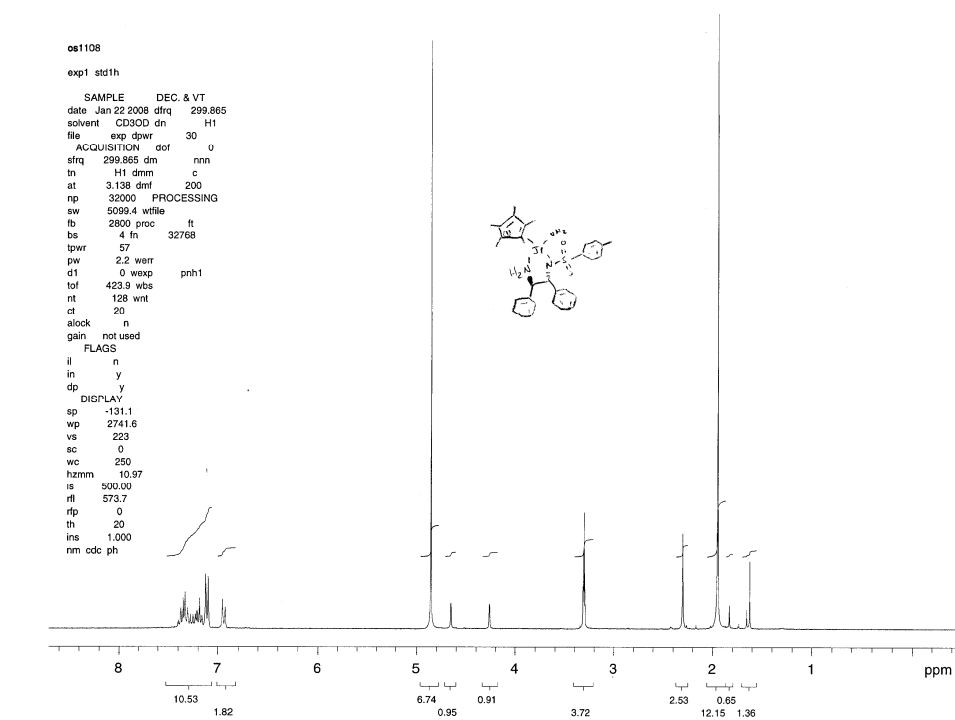


Figure 7:  $^1\text{H}$ -NMR of  $\{\text{Cp}^*\text{Ir}[(R,R)\text{-Ts-DPEN}](\text{H}_2\text{O})\}(\text{SO}_4)$  (Catalyst Table 1, Entry 4) and  $^1\text{H}$ -NMR of  $\{\text{Cp}^*\text{Ir}[(R,R)\text{-Tf-DPEN}](\text{H}_2\text{O})\}(\text{SO}_4)$  (Catalyst Table 1, Entry 5)

Ariger/Carreira AM-863.1 OPR:PZ  
500 MHz  $^1\text{H}$  NMR

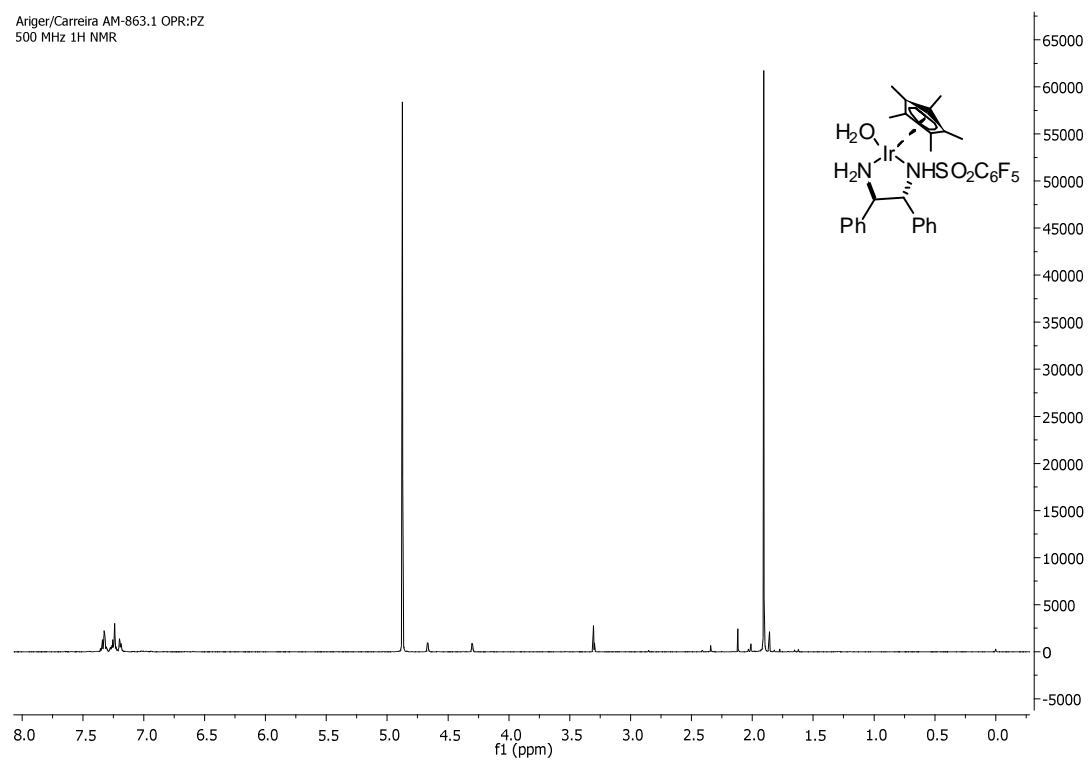


Figure 8:  $^1\text{H}$ -NMR of  $\{\text{Cp}^*\text{Ir}[(R,R)\text{-C}_6\text{F}_5\text{SO}_2\text{-DPEN}](\text{H}_2\text{O})\}(\text{SO}_4)$  (Catalyst Table 1, Entry 6)



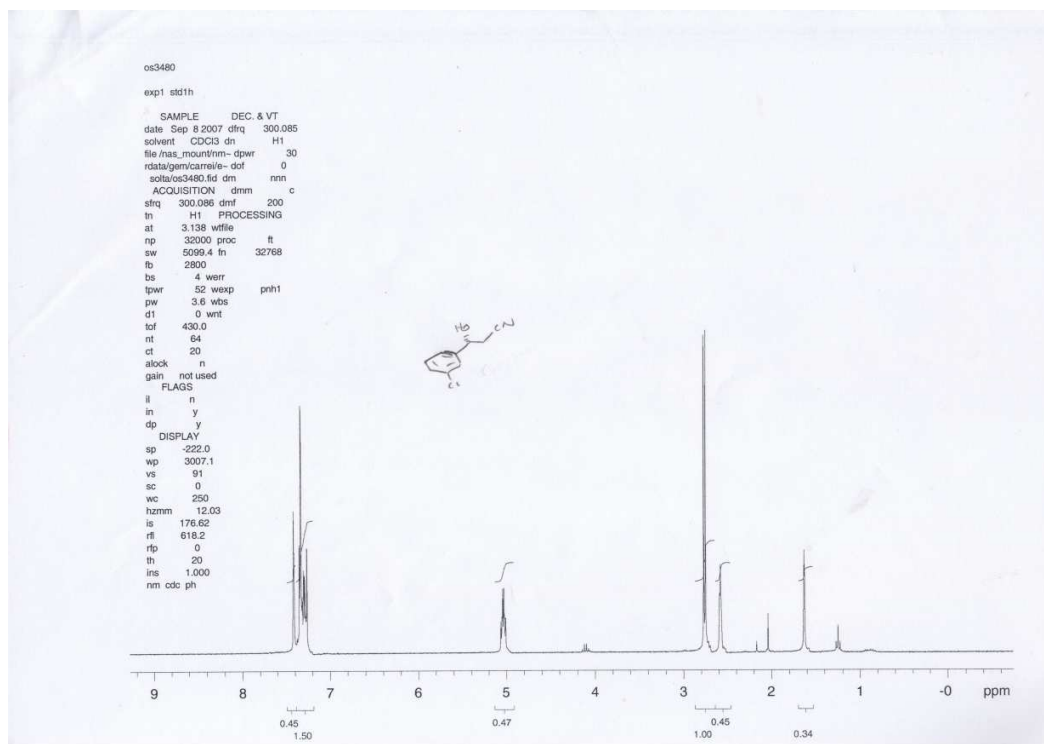
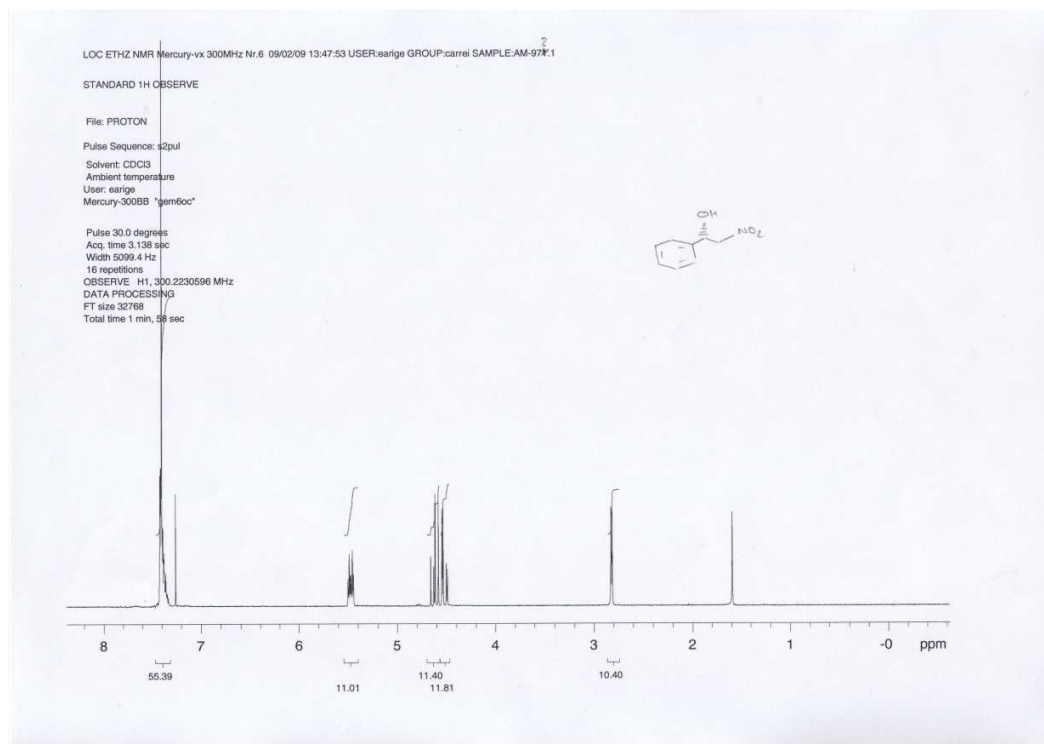


Figure 9:  $^1\text{H}$ -NMR of (*R*)-3-Hydroxy-3-phenylpropanenitrile (Table 2, Entry 1) and  $^1\text{H}$ -NMR of (*R*)-3-(3-Chlorophenyl)-3-hydroxypropanenitrile (Table 2, Entry 2)

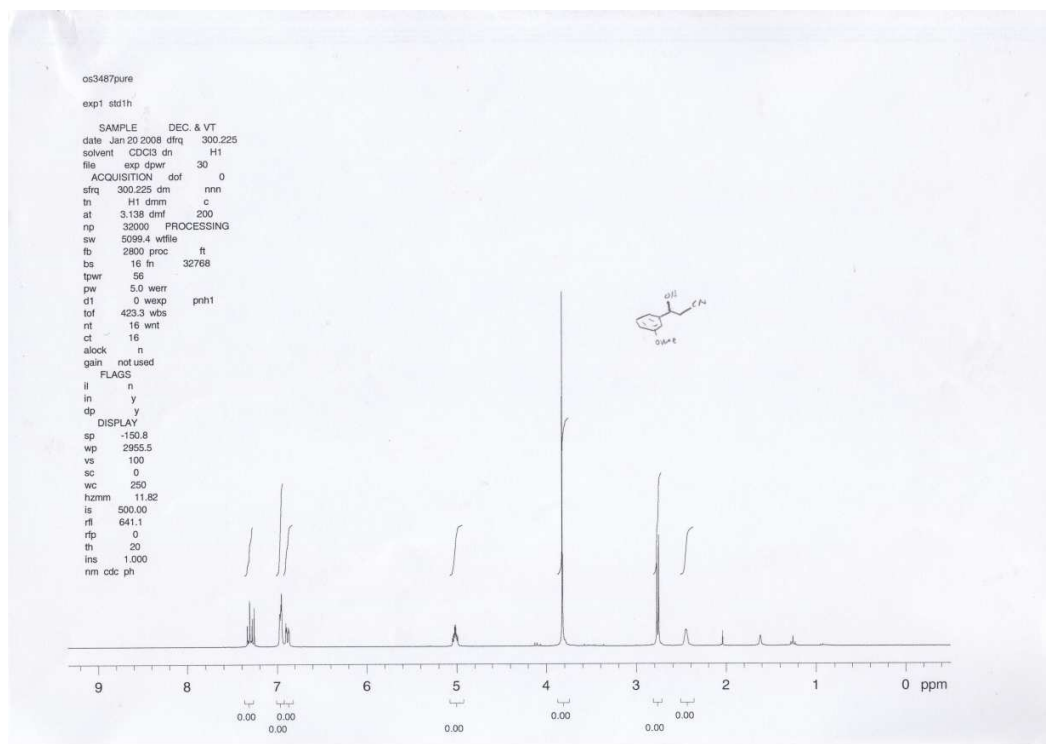
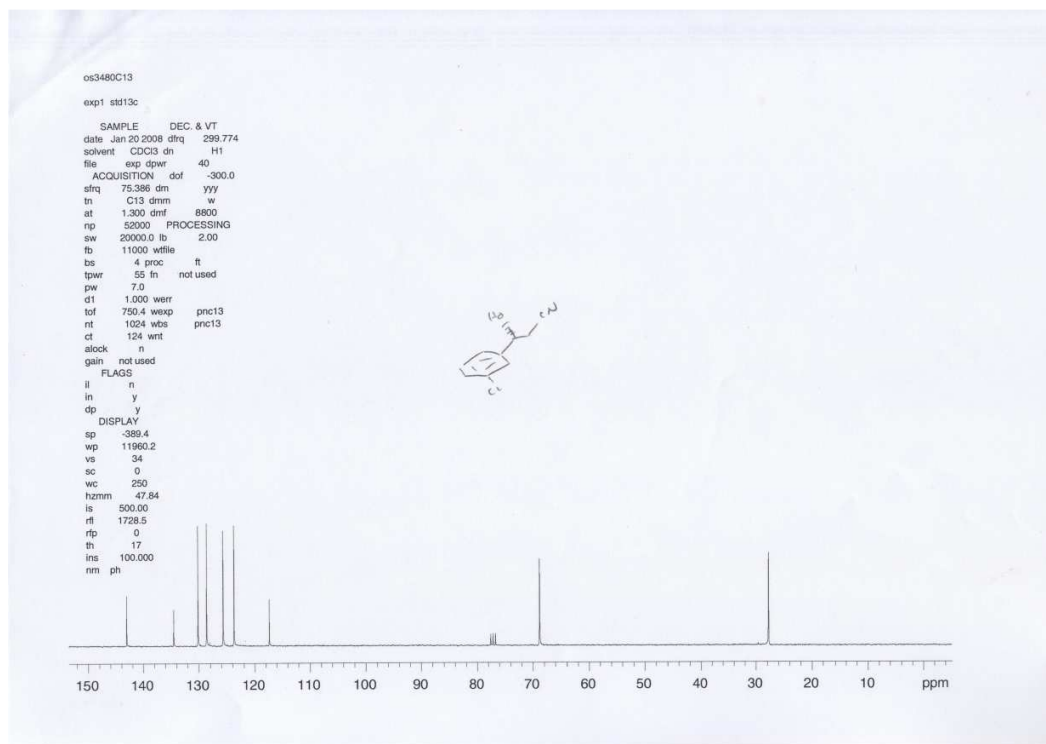


Figure 10:  $^{13}\text{C}$ -NMR of (*R*)-3-(3-Chlorophenyl)-3-hydroxypropanenitrile (Table 2, Entry 2) and  $^1\text{H}$ -NMR of (*R*)-3-Hydroxy-3-(3-methoxyphenyl)propanenitrile (Table 2, Entry 3)

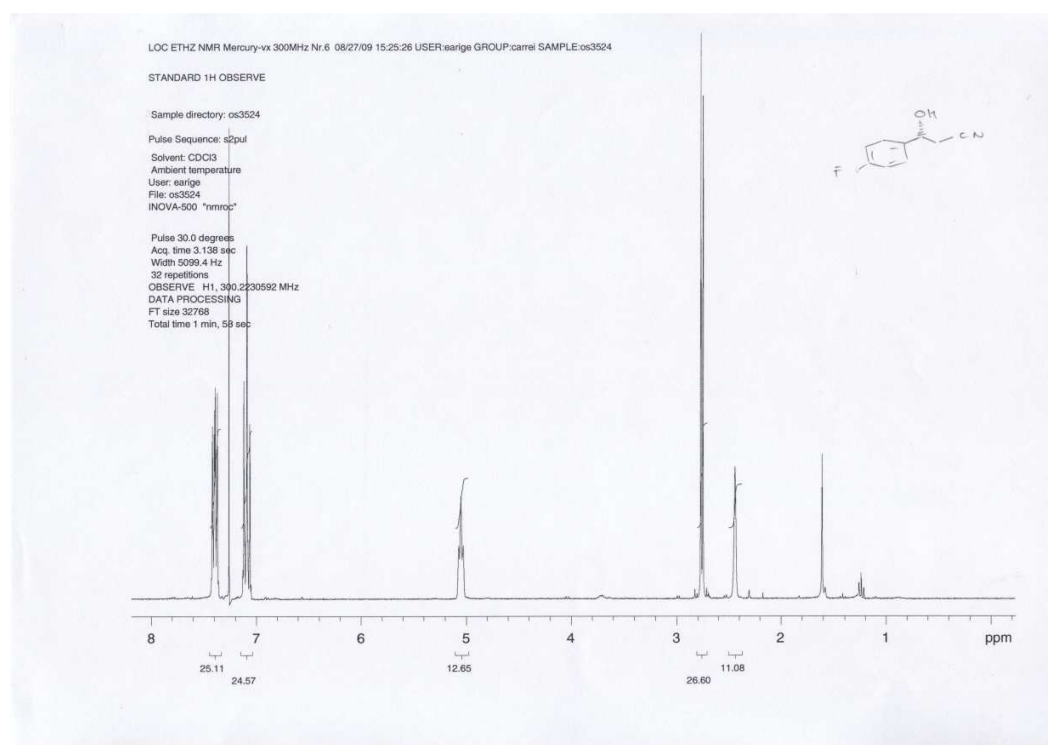
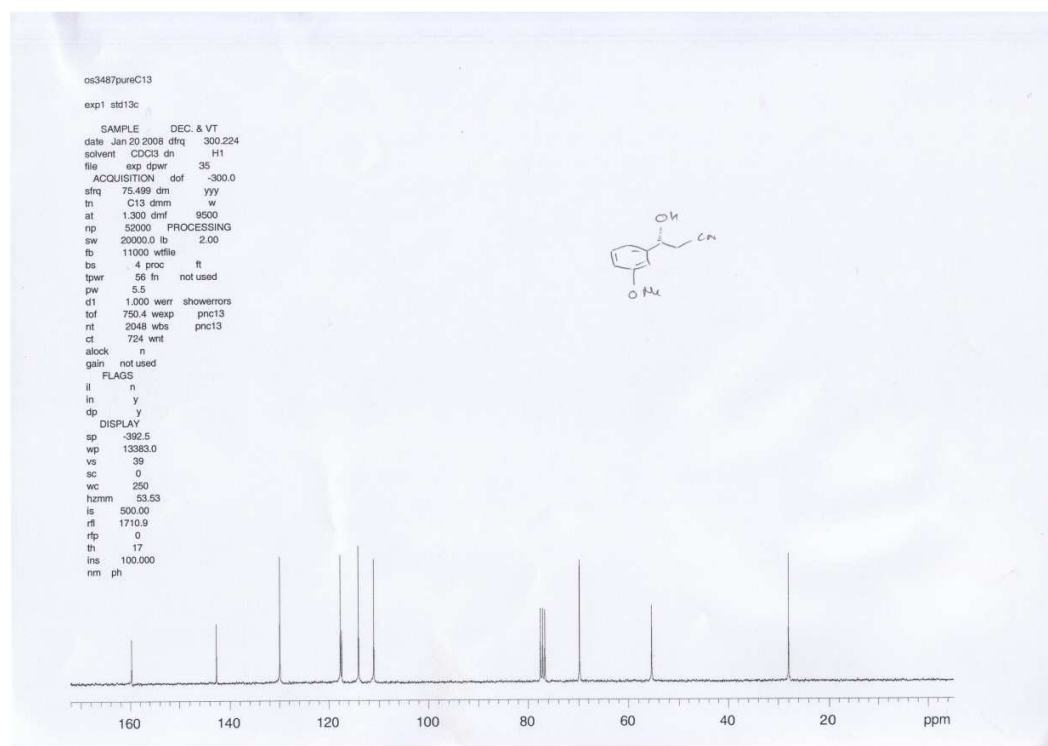


Figure 11:  $^{13}\text{C}$ -NMR of (*R*)-3-Hydroxy-3-(3-methoxyphenyl)propanenitrile (Table 2, Entry 3) and  $^1\text{H}$ -NMR of (*R*)-3-(4-Fluorophenyl)-3-hydroxypropanenitrile (Table 2, Entry 4)

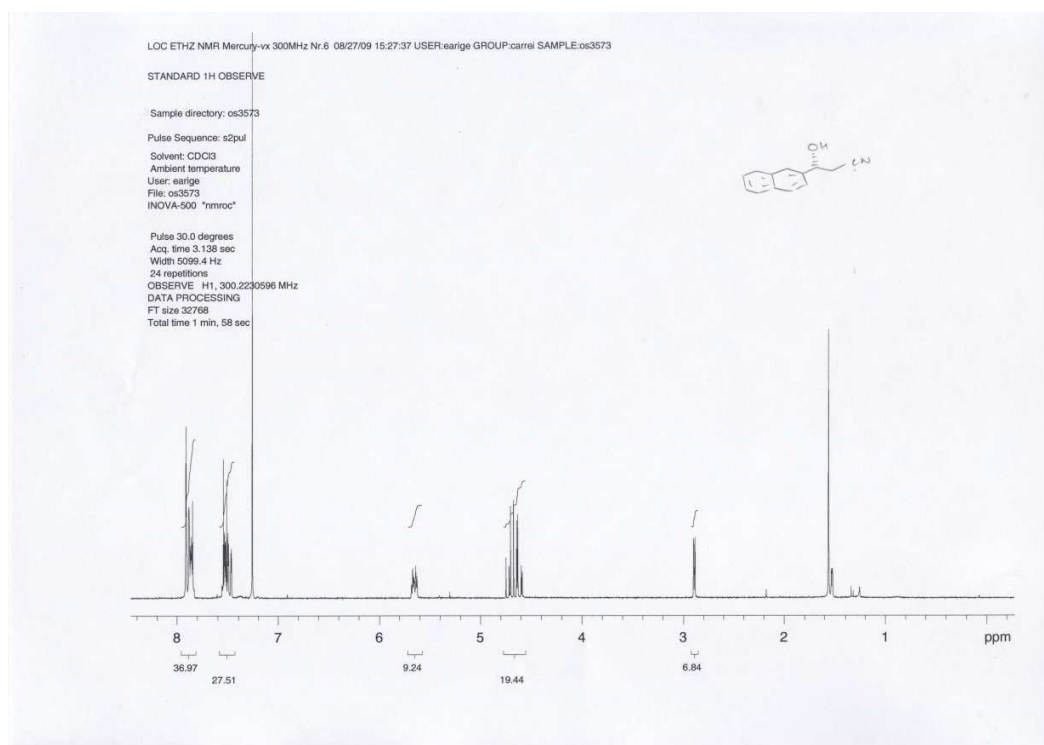
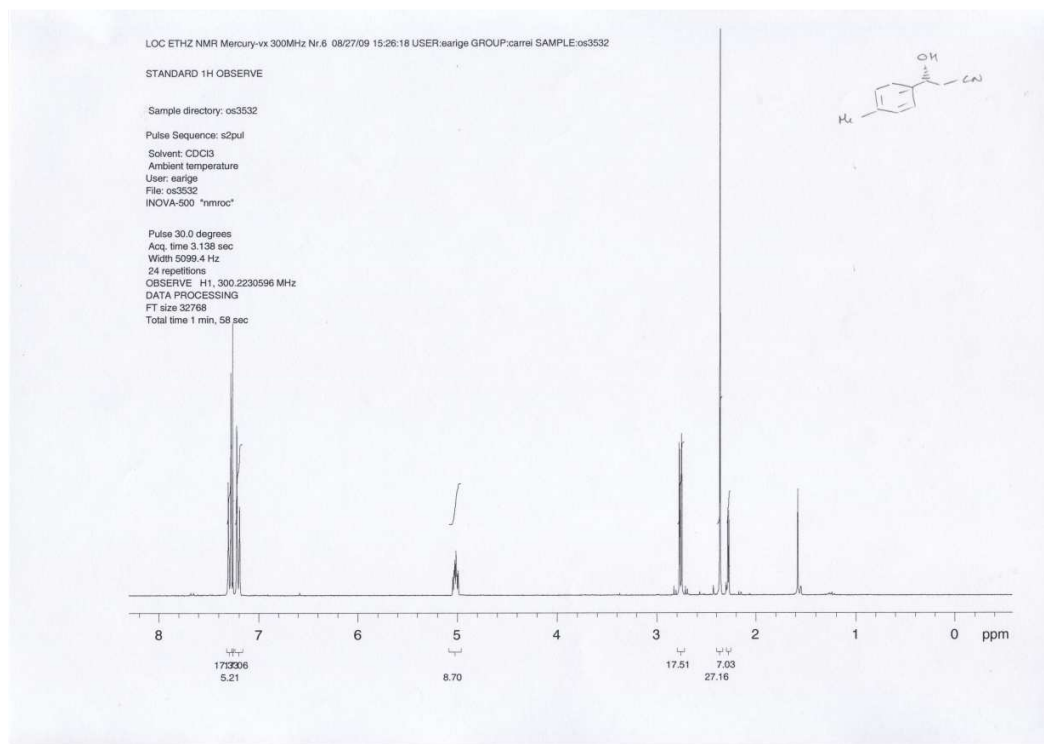


Figure 12: <sup>1</sup>H-NMR of (*R*)-3-Hydroxy-3-*p*-tolylpropanenitrile (Table 2, Entry 5) and <sup>1</sup>H-NMR of (*R*)-3-Hydroxy-3-(naphthalen-2-yl)propanenitrile (Table 2, Entry 6)

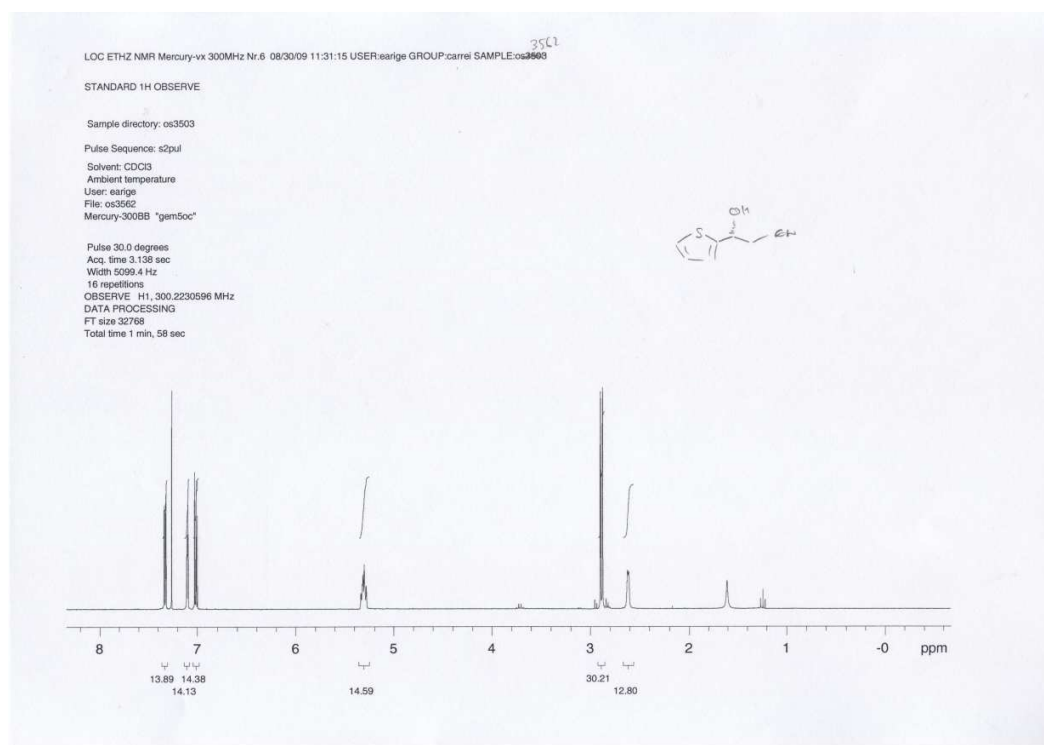
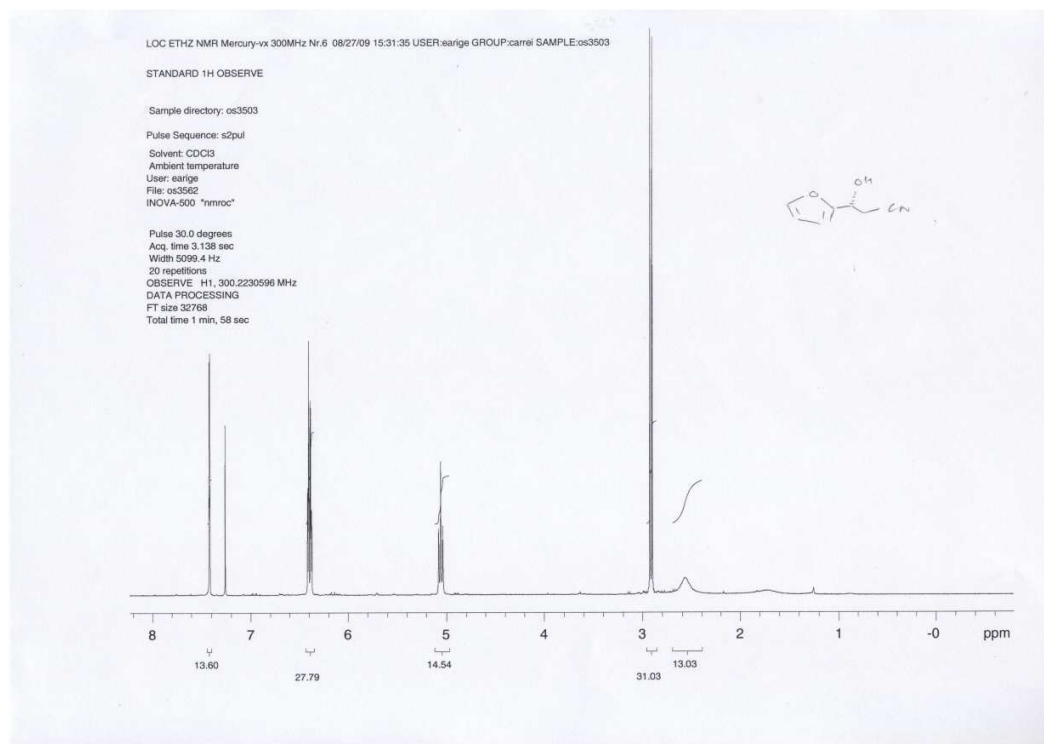


Figure 13: <sup>1</sup>H-NMR of (*R*)-3-(Furan-2-yl)-3-hydroxypropanenitrile (Table 2, Entry 7) and <sup>1</sup>H-NMR of (*R*)-3-Hydroxy-3-(thiophen-2-yl)propanenitrile (Table 2, Entry 8)

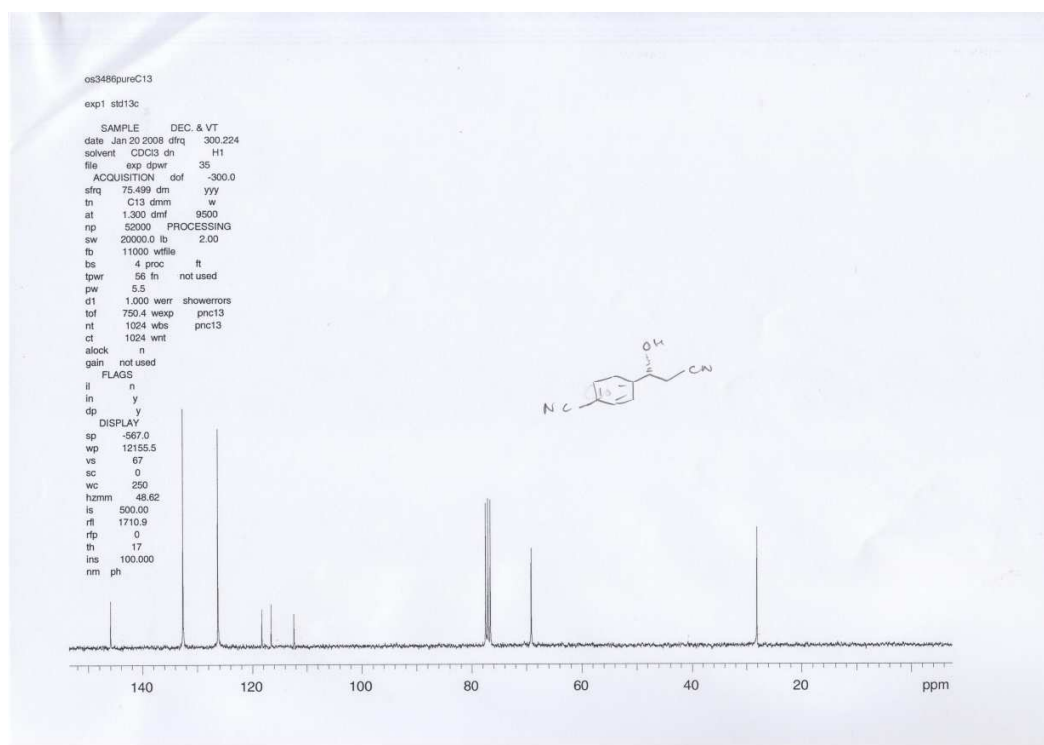
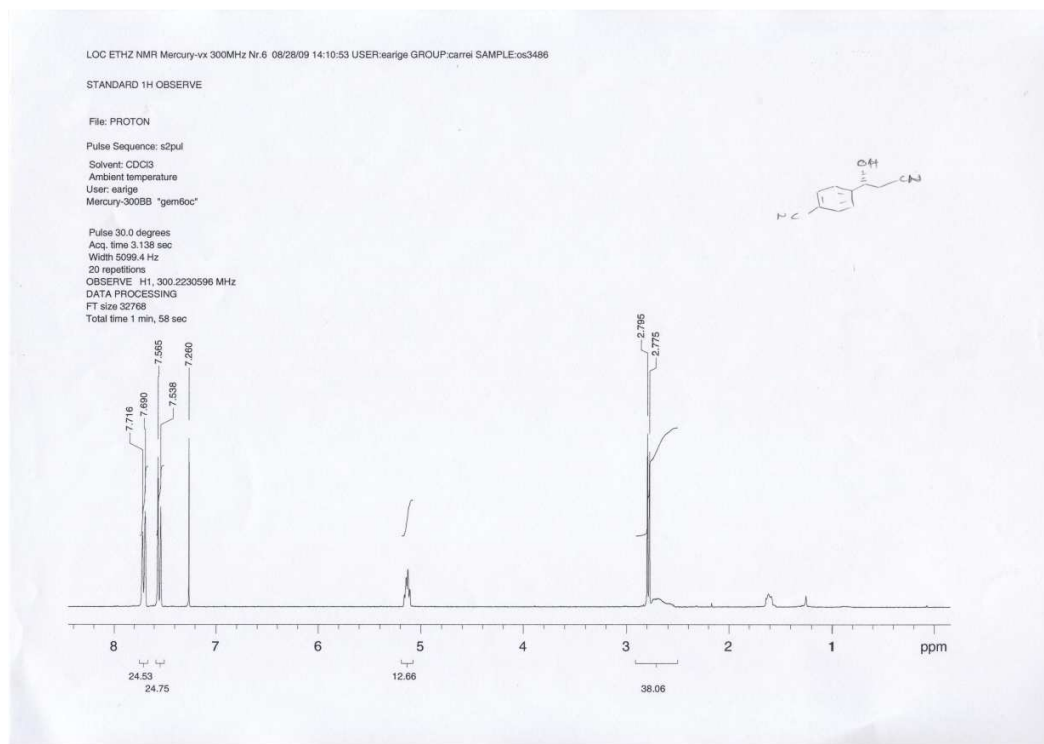


Figure 14:  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR of (*R*)-4-(2-Cyano-1-hydroxyethyl)benzonitrile (Table 2, Entry 9)

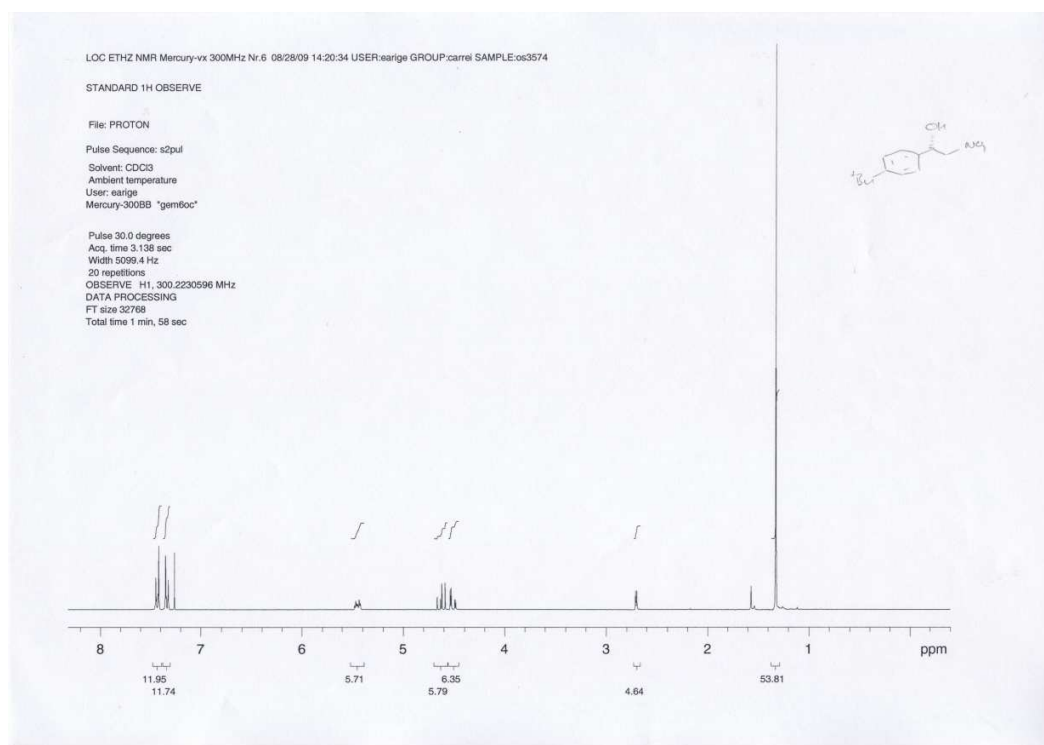
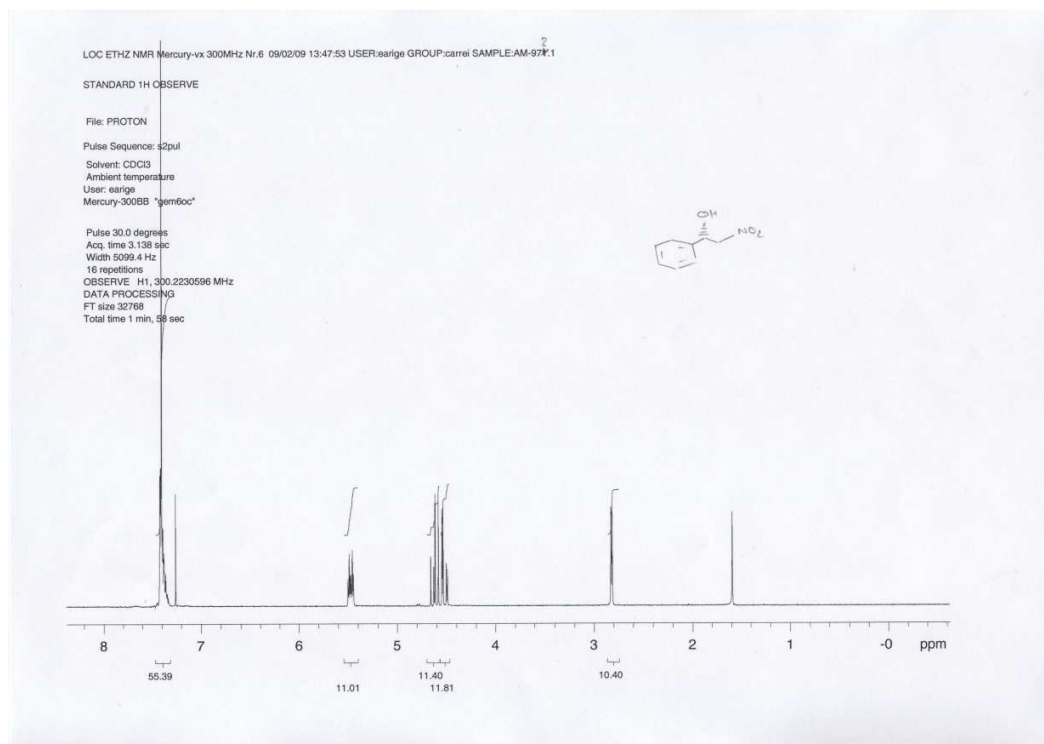


Figure 15:  $^1\text{H}$ -NMR of (S)-2-Nitro-1-phenylethanol (Table 2, Entry 10) and  $^1\text{H}$ -NMR of (S)-1-(4-*tert*-Butylphenyl)-2-nitroethanol (Table 2, Entry 11)



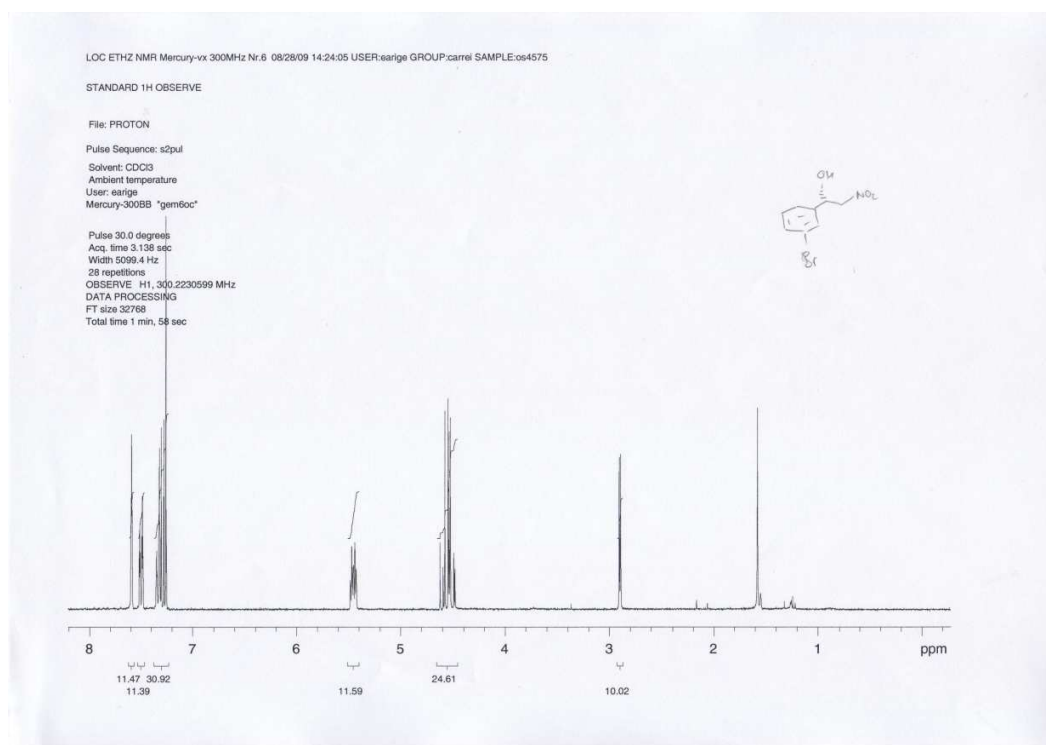
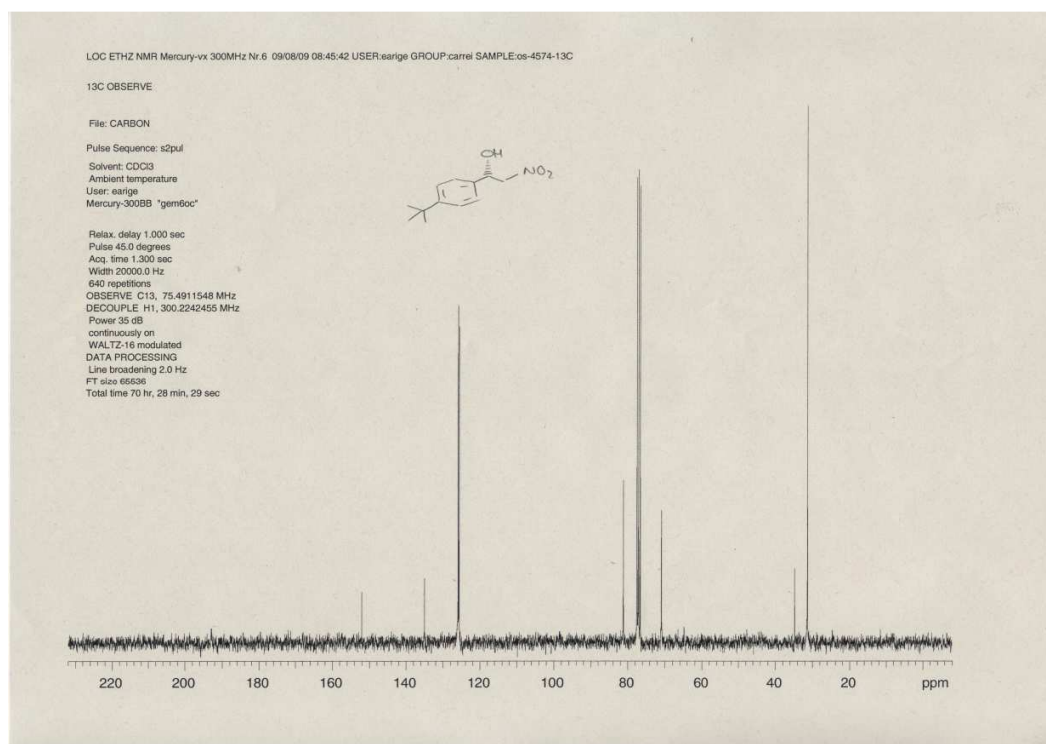


Figure 16:  $^{13}\text{C}$ -NMR of (S)-1-(4-*tert*-Butylphenyl)-2-nitroethanol (Table 2, Entry 11) and  $^1\text{H}$ -NMR of (S)-1-(3-Bromophenyl)-2-nitroethanol (Table 2, Entry 12)



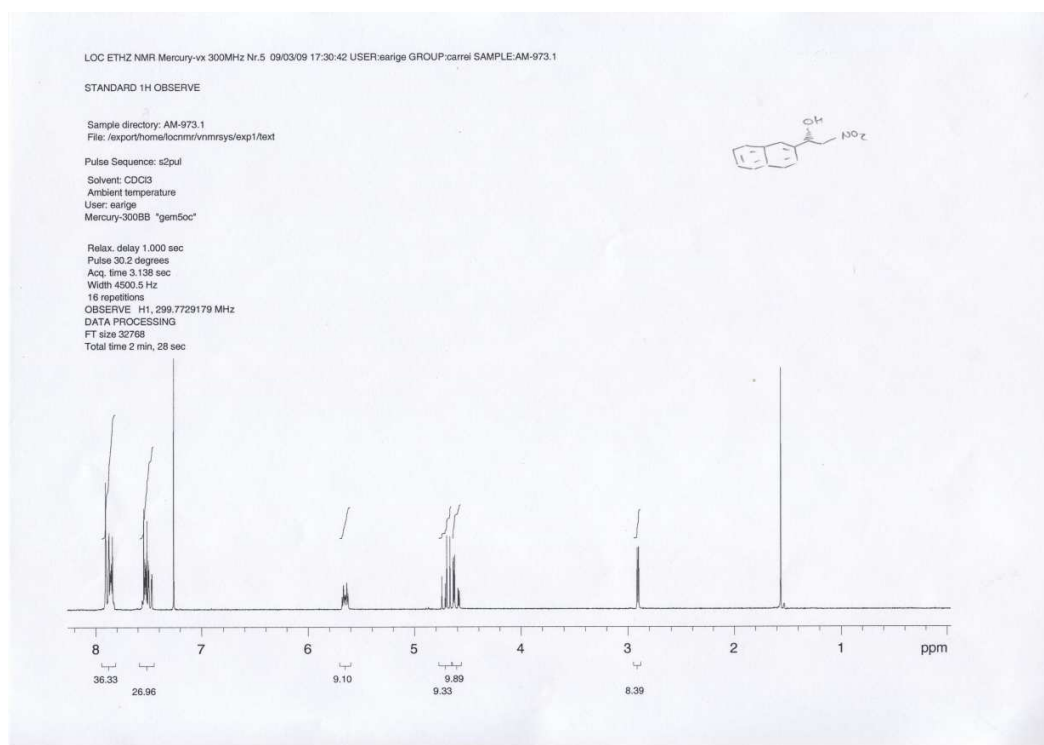
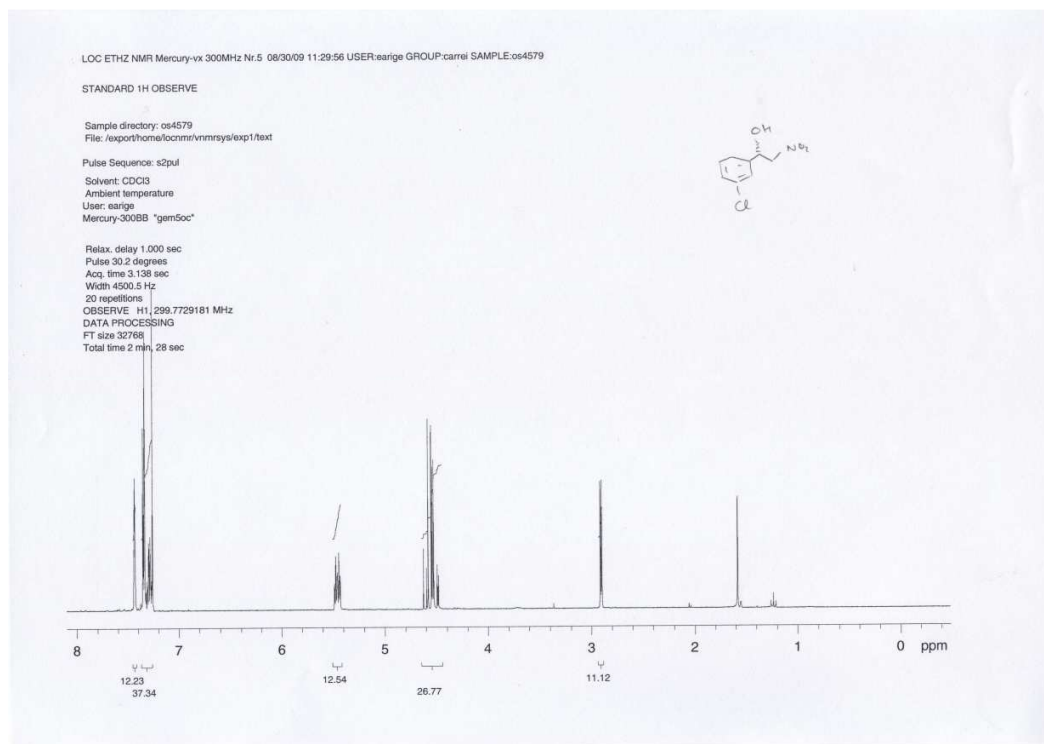


Figure 17:  $^1\text{H}$ -NMR of (S)-1-(3-Chlorophenyl)-2-nitroethanol (Table 2, Entry 13) and  $^1\text{H}$ -NMR of (S)-1-(Naphthalen-2-yl)-2-nitroethanol (Table 2, Entry 14)

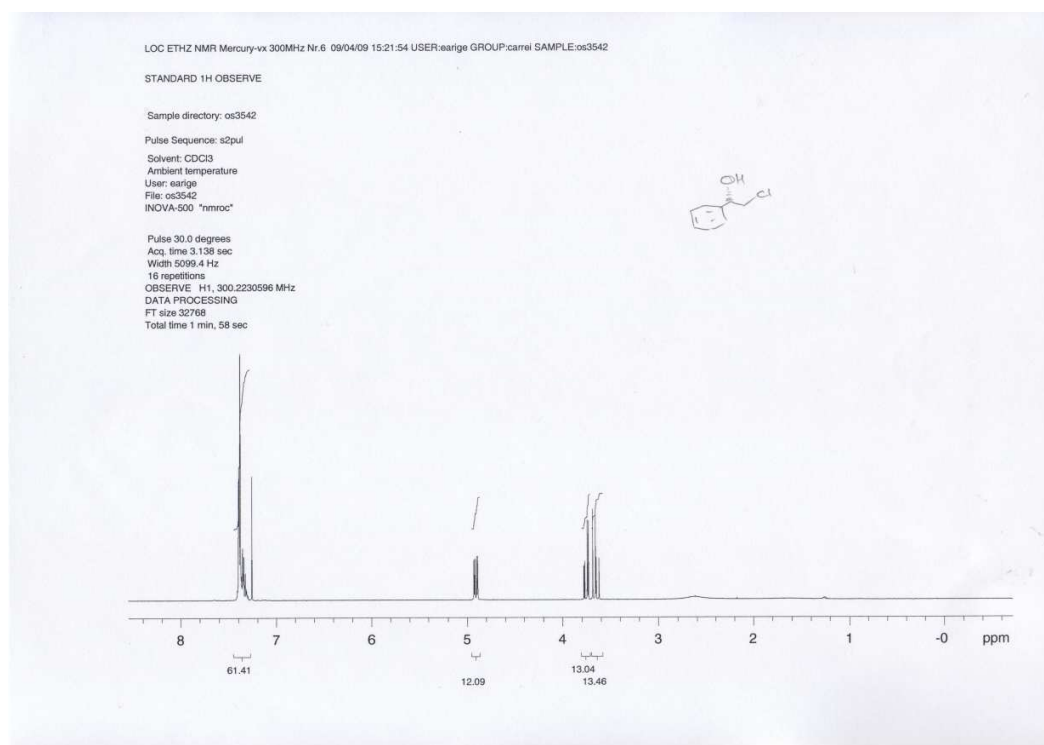
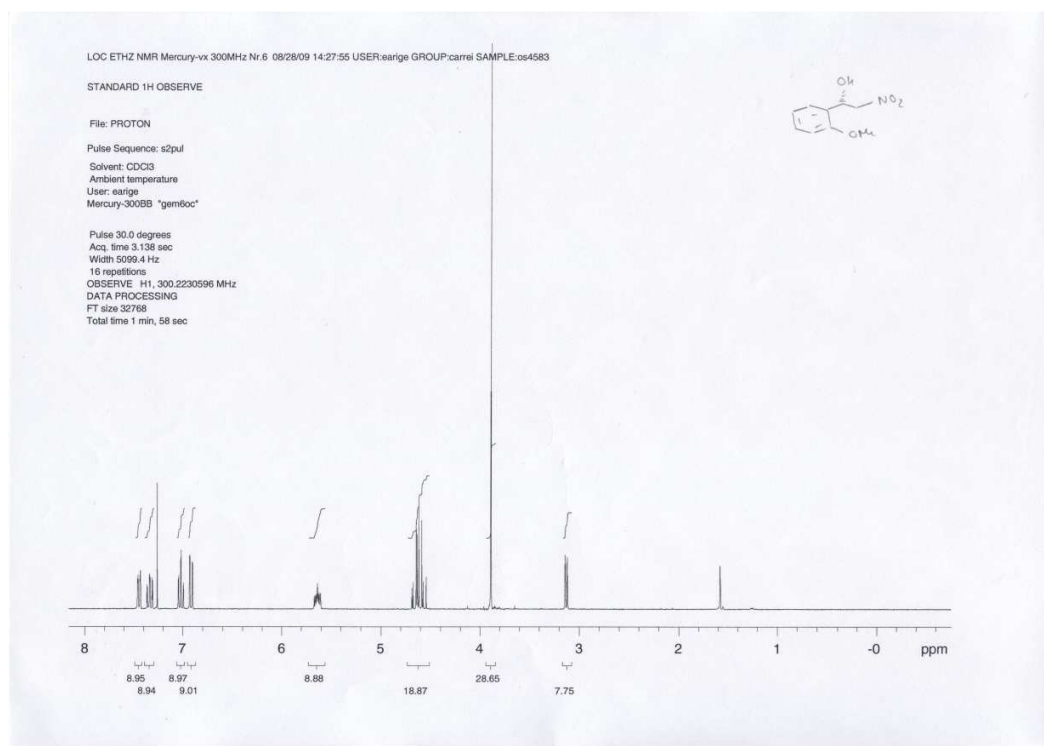


Figure 18:  $^1\text{H}$ -NMR of (S)-1-(2-methoxyphenyl)-2-nitroethano (Table 2, Entry 15) and  $^1\text{H}$ -NMR of (S)-2-Chloro-1-phenylethanol (Table 2, Entry 16)