Supporting Information

Transfer Hydrogenation in Water: Enantioselective, Catalytic Reduction of *β,β*-Disubstituded Nitroalkenes

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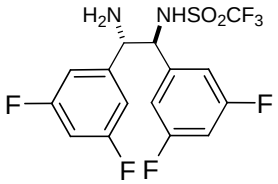
General

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 (H_2O 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}H and ^{13}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, or by chiral GC analysis with HP 6890 apparatus. Optical rotations $[\alpha]_D$ were measured on a Jasco DID-1000 polarimeter. The absolute configurations were assigned by comparison of the $[\alpha]_D$ values of known compounds. For the new compounds, it was assigned based on the established stereochemical outcome of the reaction.

Synthesis of the Ligands:

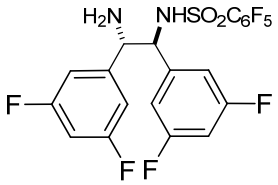
Synthesis of ligands required for the catalysts described below were prepared as outlined in the literature[1,2,3], otherwise commercially available ligands were utilized.

N-((1*S*,2*S*)-2-amino-1,2-bis(3,5-difluorophenyl)ethyl)-1,1,1-trifluoromethanesulfonamide (Ligand for catalyst in Table 1, entry 7)



To a stirred solution of the free diamine[3] (185 mg, 0.65 mmol) in anhydrous THF (6mL) at -78 °C was added *n*-BuLi (0.81mL, 1.3 mmol, 1.6M in Hexane) dropwise. Upon addition of the base the reaction turned pale brown and was aged for 20 min. At this stage a solution of $PhN(Tf)_2$ (255 mg, 0.72 mmol) in THF (1mL) was added dropwise and allowed to stir at -78 °C for 1h. The reaction was then quenched by addition of saturated NH_4Cl (5mL). After extraction with CH_2Cl_2 from H_2O, and drying with Na_2SO_4, the crude was purified by FC ($MeOH/CH_2Cl_2$ = 5/95) to afford pure product 137 mg (51%) as a white powder. NMR Spectroscopy: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.38 (d, *J* = 2.7 Hz, 1H), 4.63 (d, *J* = 2.7 Hz, 1H), 6.79-6-86 (m, 2H), 6.89-6.99 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 59.8, 64.0, 104.0 (dd, *J* = 24.9, 49.8 Hz, 2C), 109.6 (dd, *J* = 17.6, 25.5 Hz, 4C), 142.3, 161.5 (d, *J* = 12.7 Hz), 164.8 (d, *J* = 12.7 Hz). IR-Spectroscopy: (thin film, cm^{-1}) ν 3098, 2927, 1626, 1603, 1466, 1326, 1278, 1198, 1124, 993, 925, 856, 694, 604. MS Spectrometry: HR-MALDI calcd for $C_{15}H_{11}F_7N_2O_2S$ $[M\text{-}CF_3]^+$ 347.0472, found 347.0470. $[\alpha]_D^{26}$ = 3.3° (c = 0.35, $CHCl_3$).

(*S,S*)-$C_6F_5SO_2$-3,5-F-DPEN (Ligand for catalyst Table 1, entry 6)

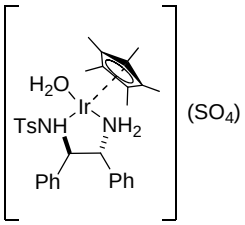


To a stirred solution of diamine[3] (121 mg, 0.43 mmol) and DIPEA (0.18mL, 1.03 mmol) in anhydrous CH_2Cl_2 (4mL) at -50 °C was added a solution of pentafluorophenylsulfonyl chloride (136 mg, 0.51 mmol, in 0.5mL CH_2Cl_2). The reaction was allowed to warm to room temperature and stirred overnight (18h) at room temperature. The reaction was then quenched by addition of saturated NH_4Cl (5mL). After extraction with CH_2Cl_2 from H_2O, and drying with Na_2SO_4, the crude was purified by FC (MeOH/CH_2Cl_2 = 5/95) to afford pure product 42.8 mg (19%) as a white powder. NMR Spectroscopy: ^{1}H-NMR (300 MHz, CD_3OD) δ 4.20 (d, *J* = 7.4 Hz, 1H), 4.61 (d, *J* = 7.4 Hz), 6.73-6.81 (m, 4H), 6.87-6.93 (m, 2H). ^{13}C NMR (150 MHz, CD_3OD) δ 60.7, 65.5, 103.8 (t, *J* = 25.6 Hz, 2C), 111.5 (ddd, *J* = 5.1, 20.8, 26.3 Hz, 2C), 118.7 (t, *J* = 14.1 Hz), 125.6 (d, *J* = 101.9, 2H), 131.6 (*J* = 378 Hz), 138.9 (dm, *J* = 252.5 Hz), 144.5 (d, *J* = 256.7 Hz), 145.4 (dt, *J* = 8.6, 251.6 Hz), 164.3 (dd, *J* = 70.4, 246.0 Hz). IR-Spectroscopy: (thin film, cm^{-1}) ν 3435, 2540, 1624, 1599, 1495, 1172, 1100, 989, 856. MS Spectrometry: HR-MALDI calcd for $C_{20}H_{10}F_9N_2O_2S$ $[M-H]^+$ 513.0325, found 513.0317. $[\alpha]_D^{26}$ = -29.1 (c = 2.0, CH_3OH).

Synthesis of the Catalysts:

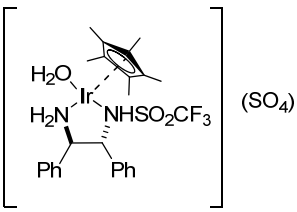
Representative Procedure: To a vial was added $[Cp^*Ir(H_2O)_3](SO_4)$[4] (1 equiv) and monosulfonylated diamine (1 equiv) in a 1:1 mixture of water:methanol (0.5 M) was stirred for 1 h at room temperature. Removal of the solvent *in vacuo* provided the catalyst complex as a red powder in quantitative yield.

{Cp*Ir[(*R,R*)-Ts-DPEN](H$_2$O)}(SO$_4$) (Catalyst in Table 1, entry 1)



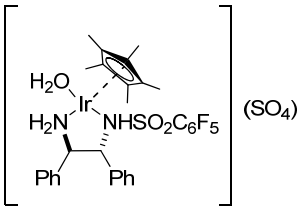
NMR Spectroscopy: ^{1}H-NMR (300 MHz, CD_3OD) δ 1.95 (s, 15H), 2.30 (s, 3H), 4.26 (s, 1H), 4.65 (s, 1H), 6.92-6.95 (m, 2H), 7.10-7.38 (m, 12H). ^{13}C-NMR (75 MHz, CD_3OD) δ 10.3, 21.2, 68.5, 78.5, 92.2, 127.0, 127.6, 127.8, 128.5, 128.6, 129.0, 129.1, 135.8, 137.9, 141.5, 143.8. MS Spectrometry: HR-MALDI calcd for $C_{31}H_{36}IrN_2O_2S$ $[M\text{-}SO_4\text{-}H_2O]^+$ 693.2121, found 693.2109. $[\alpha]_D^{25}$ = -273.92° (c = 1.0, $CHCl_3$).

{Cp*Ir[(*R,R*)-Tf-DPEN](H$_2$O)}(SO$_4$) (Catalyst in Table 1, entry 7)



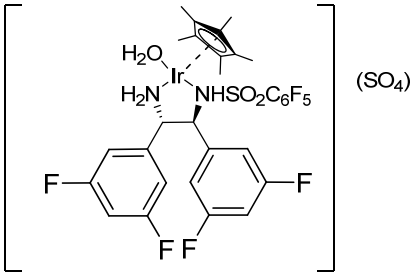
NMR Spectroscopy: ^{1}H-NMR (300 MHz, CD_3OD) δ 1.80 (s, 15H), 4.15 (d, *J* = 6.9 Hz, 1H), 4.74 (d, *J* = 7.2 Hz, 1H), 7.06-7.27 (m, 10H). ^{13}C-NMR (75 MHz, CD_3OD) δ 9.9, 72.6, 73.2, 89.6, 128.5, 129.0, 129.2, 129.4, 129.8. MS Spectrometry: HR-MALDI calcd for $C_{25}H_{29}IrN_2O_2S$ $[M\text{-}SO_4\text{-}H_2O]^+$ 671.1525, found 671.1514. $[\alpha]_D^{28}$ = -293.16° (c = 0.25, CH_3OH).

{Cp*Ir[(*R,R*)- $C_6F_5SO_2$-DPEN](H_2O)}(SO_4) (Catalyst in Table 1, entries 4 and 5)



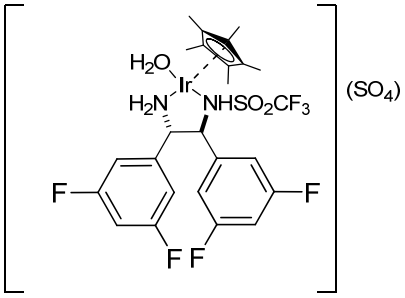
NMR Spectroscopy: ^{1}H-NMR (300 MHz, CD_3OD) δ 1.91 (s, 15H), 4.30 (d, *J* = 3.1 Hz, 1H), 4.67 (d, *J* = 3.1 Hz, 1H), 7.18-7.36 (m, 10H). ^{13}C-NMR (75 MHz, CD_3OD) δ 8.8, 67.2, 75.3, 91.2, 103.4, 126.0, 126.8, 127.7, 127.8, 127.9, 136.0, 136.8, 138.1, 138.9, 142.0, 142.9, 144.02, 145.0. MS Spectrometry: HR-MALDI calcd for $C_{30}H_{29}IrN_2O_2S$ [M-SO_4-H_2O]$^+$ 769.1494, found 769.1479. $[\alpha]_D^{26}$ = -242.22° (c = 1.0, $CHCl_3$).

{Cp*Ir[(*S,S*)-$C_6F_5SO_2$-3,5-F-DPEN](H_2O)}(SO_4) (Catalyst in Table 1, entry 6)



NMR Spectroscopy: ^{1}H-NMR (300 MHz, CD_3OD) δ 1.87 (s, 15H), 4.27-4.31 (m, 1H), 4.64-4.66 (m, 1H), 6.87-6.98 (m, 6H). ^{13}C-NMR (75 MHz, CD_3OD) δ 10.2, 66.9, 75.4, 89.1, 93.0, 104.2, 110.7, 111.3, 141.6, 144.6, 147.1, 162.0, 165.4. MS Spectrometry: HR-MALDI calcd for $C_{30}H_{25}IrN_2O_2S$ [M-SO_4-H_2O]$^+$ 841.1117, found 841.1102. $[\alpha]_D^{26}$ -206.25° (c 0.50, $CHCl_3$).

{Cp*Ir[(*S,S*)-Tf-3,5-F-DPEN](H$_2$O)}(SO$_4$) (Catalyst in Table 1, entry 7)

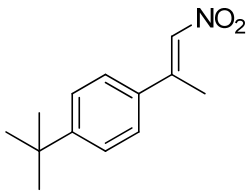


NMR Spectroscopy: ^{1}H-NMR (300 MHz, CD_3OD) δ 1.82 (s, 15H), 4.38 (d, *J* = 4.8 Hz), 4.86 (d, *J* = 4.8 Hz), 6.89-6.98 (m, 5H), 6.99-7.03 (m, 2H). ^{13}C-NMR (150 MHz, CD_3OD) δ 10.3 (s, 5C), 64.2, 72.5, 89.1 (s, 5C), 101.7 (d, *J* = 28.5 Hz), 101.9 (d, *J* = 28.4 Hz, 2C), 110.6 (d, *J* = 31.5 Hz, 2C), 120.8 (q, *J* = 387.1 Hz, CF_3), 164.6 (dd, *J* = 15.5, 269.6 Hz), 164.9 (dd, *J* = 15.2, 295.4 Hz), 167.8, *J* = 13.3, 282.8 Hz). MS Spectrometry: HR-MALDI calcd for $C_{25}H_{25}IrN_2O_2S$ $[M\text{-}SO_4\text{-}H_2O]^+$ 743.1148, found 743.1147. $[\alpha]_D^{26}$ = 18.8° (c = 0.25, CH_3OH).

Synthesis of Substrates:

The Substrates were synthesized according to a known procedure.[5]

(E)-1-*tert*-butyl-4-(1-nitroprop-1-en-2-yl)benzene (Table 2, entry 9)



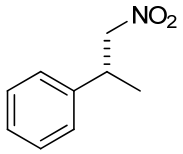
NMR Spectroscopy: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ 1.34 (s, 9H), 2.65 (d, *J* = 1.5 Hz, 3H), 7.34 (q, *J* = 1.5 Hz, 1H), 7.39 - 7.47 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.4, 31.1, 34.8, 126.0, 126.7, 135.3, 135.9, 149.9, 154.1. IR-Spectroscopy: (thin film, cm^{-1}) ν 2964, 2869, 1619, 1513, 1402, 1339, 1271, 1202, 1116, 1015, 922, 826. MS Spectrometry: HR-EI calcd for $C_{13}H_{17}NNaO_2$ $[M+Na]^+$ 242.1151, found 242.1149.

Transfer hydrogenation of β,β-Nitroalkenes:

General procedure:

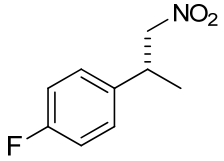
The β,β-nitroalkene (0.50 mmol, 1.0 equiv) and {Cp*Ir[(*S,S*)-Tf-3,5-F-DPEN](H_2O)}(SO_4) (0.005 mmol, 1.0 mol%) were combined in a glass vial, followed by addition of an aqueous formic acid solution (1.0M formate soln., pH = 2.0, 0.2M overall concentration). The reaction mixture was stirred at ambient temperature for 24 h. The reaction mixture was then extracted with CH_2Cl_2 (3X) from H_2O and dried over Na_2SO_4. The organic phase was then filtered, concentrated and purified by FC (EtOAc/Hex). The nitroalkane products were analyzed by standard spectroscopic methods and found to be in agreement with the literature reported values for all known compounds. Enantiomeric excess was determined by chiral HPLC.

(*R*)-(1-Nitropropan-2-yl)benzene (Table 2, entry 1)



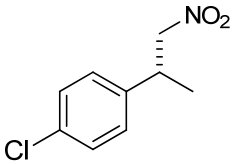
90% Yield, ee = 90% (HPLC: OD-H, 215 nm, hexane:2-propanol = 99:1, flow rate 0.5 mL/min, $t_{r(major)}$ = 28.4 min, $t_{r(minor)}$ = 36.9 min). $[\alpha]_D^{22}$ = +44.2° (c = 1.0, $CHCl_3$) Lit.[6] $[\alpha]_D^{25}$ = +44.3° (c = 3.4, $CHCl_3$) 98% ee. NMR Spectroscopy: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ 1.39 (d, *J* = 6.9 Hz, 3H), 3.60-3.68 (m, 1H), 4.45-4.59 (m, 2H), 7.22-7.38 (m, 5H). All other spectroscopic data were in agreement with the literature.[6]

(*R*)-1-Fluoro-4-(1-nitropropan-2-yl)benzene (Table 2, entry 2)



82% Yield, ee = 94% (HPLC: OD-H, 215 nm, hexane, flow rate 0.2 mL/min, $t_{r(major)}$ = 89.0 min, $t_{r(minor)}$ = 108.2 min). $[\alpha]_D^{22}$ = +44.0° (c = 1.0, $CHCl_3$) Lit.[5] $[\alpha]_D^{30}$ = +48.4° (c = 0.52, $CHCl_3$) 99% ee. NMR Spectroscopy: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ 1.37 (d, *J* = 6.9 Hz, 3H), 3.57-3.70 (m, 1H), 4.44-4.55 (m, 2H), 6.99-7.07 (m, 2H), 7.17-7.23 (m, 2H). All other spectroscopic data were in agreement with the literature.[5]

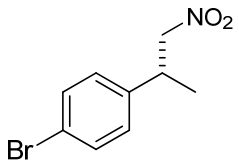
(*R*)-1-Chloro-4-(1-nitropropan-2-yl)benzene (Table 2, entry 3)



92% Yield, ee = 90% (HPLC: OD-H, 215 nm, hexane:2-propanol = 99:1, flow rate 0.5 mL/min, $t_{r(major)}$ = 30.2 min, $t_{r(minor)}$ = 43.0 min). $[\alpha]_D^{25}$ = +42.0° (c = 1.0, $CHCl_3$) Lit.[5] $[\alpha]_D^{30}$ = +51.3 (c = 0.60, $CHCl_3$) 99% ee. NMR Spectroscopy: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ

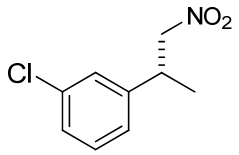
1.37 (d, *J* = 6.6 Hz, 3H), 3.56-3.69 (m, 1H), 4.44-4.56 (m, 2H), 7.14-7.19 (m, 2H), 7.29-7.34 (m, 2H). All other spectroscopic data were in agreement with the literature.[5]

(*R*)-1-Bromo-4-(1-nitropropan-2-yl)benzene (Table 2, entry 4)



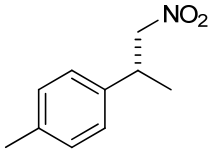
92% Yield, ee = 92% (HPLC: OD-H, 215 nm, hexane:2-propanol = 99:1, flow rate 0.5 mL/min, $t_{r(major)}$ = 35.7 min, $t_{r(minor)}$ = 59.1 min). $[\alpha]_D^{24}$ = +39.4° (c = 1.0, $CHCl_3$) Lit.[5] $[\alpha]_D^{30}$ = +43.2° (c 0.58, $CHCl_3$) 99% ee. NMR Spectroscopy: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ 1.45 (d, *J* = 7.2 Hz, 3H), 3.55-3.67 (m, 1H), 4.43-4.55 (m, 2H), 7.09-7.13 (m, 2H), 7.45-7.49 (m, 2H). All other spectroscopic data were in agreement with the literature.[5]

(*R*)-1-Chloro-3-(1-nitropropan-2-yl)benzene (Table 2, entry 5)



94% Yield, ee = 91% (HPLC: OD-H, 215 nm, hexane:2-propanol = 99:1, flow rate 0.5 mL/min, $t_{r(major)}$ = 30.5 min, $t_{r(minor)}$ = 45.6 min). $[\alpha]_D^{26}$ = +37.3° (c = 1.0, $CHCl_3$). NMR Spectroscopy: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ 1.38 (d, *J* = 7.2 Hz, 3H), 3.56-3.68 (m, 1H), 4.45-4.58 (m, 2H), 7.10-7.13 (m, 1H), 7.22-7.28 (m, 3H). All other spectroscopic data were in agreement with the literature.[7]

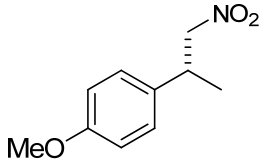
(*R*)-1-Methyl-4-(1-nitropropan-2-yl)benzene (Table 2, entry 6)



78% Yield, ee = 90% (HPLC: OD-H, 215 nm, hexane:2-propanol = 99:1, flow rate 0.5 mL/min, $t_{r(major)}$ = 23.7 min, $t_{r(minor)}$ = 38.0 min). $[\alpha]_D^{25}$ = +34.5° (c = 0.5, $CHCl_3$). NMR

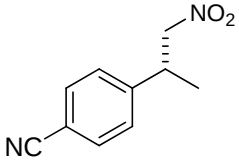
Spectroscopy: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ 1.45 (d, *J* = 7.2 Hz, 3H), 3.55-3.67 (m, 1H), 4.43-4.55 (m, 2H), 7.09-7.13 (m, 2H), 7.45-7.49 (m, 2H). NMR Spectroscopy: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ 1.37 (d, *J* = 6.6 Hz, 3H), 2.33 (s, 3H), 3.54-3.66 (m, 1H), 4.43-4.57 (m, 2H), 7.10-7.17 (m, 4H). All other spectroscopic data were in agreement with the literature.[7]

(*R*)-1-Methoxy-4-(1-nitropropan-2-yl)benzene (Table 2, entry 7)



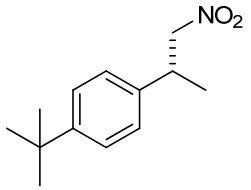
Reaction with 1.5 mol% catalyst gives 94% Yield, ee = 92% (HPLC: OD-H, 215 nm, hexane:2-propanol = 99:1, flow rate 0.5 mL/min, $t_{r(major)}$ = 33.7 min, $t_{r(minor)}$ = 58.3 min). $[\alpha]_D^{27}$ +50.2 (c 0.5, $CHCl_3$) Lit.[5] $[\alpha]_D^{30}$ = +66.2° (c = 0.99, $CHCl_3$) 97% ee. NMR Spectroscopy: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ 1.36 (d, *J* = 7.2 Hz, 3H), 3.53-3.65 (m, 1H), 3.80 (s, 3H), 4.41-4.54 (m, 2H), 6.85-6.90 (m, 2H), 7.12-7.17 (m, 2H). All other spectroscopic data were in agreement with the literature.[5]

(*R*)-1-Cyano-4-(1-nitropropan-2-yl)benzene (Table 2, entry 8)



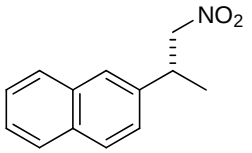
87% Yield, ee = 92% (HPLC: IC, 215 nm, hexane:2-propanol = 9:1, flow rate 1.0 mL/min, $t_{r(major)}$ = 36.1 min, $t_{r(minor)}$ = 44.0 min). $[\alpha]_D^{30}$ = +53.8° (c = 0.5, $CHCl_3$). NMR Spectroscopy: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ 1.40 (d, *J* = 6.9 Hz, 3H), 3.65-3.77 (m, 1H), 4.49-4.60 (m, 2H), 7.34-7.37 (m, 2H), 7.63-7.66 (m, 2H). All other spectroscopic data were in agreement with the literature.[7]

(*R*)-1-*tert*-Butyl-4-(1-nitropropan-2-yl)benzene (Table 2, entry 9)



77% Yield, ee = 89% (HPLC: OD-H, 215 nm, hexane:2-propanol = 99:1, flow rate 0.5 mL/min, $t_{r(major)}$ = 14.9 min, $t_{r(minor)}$ = 29.4 min). $[\alpha]_D^{24}$ = +40.5° (c = 0.5, $CHCl_3$). NMR Spectroscopy: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ 1.31 (s, 9H), 1.37 (d, *J* = 7.2 Hz, 3H), 3.55-3.68 (m, 1H), 4.43-4.58 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.6, 31.2, 34.4, 38.0, 81.9, 125.8, 126.5, 137.7, 150.4. IR-Spectroscopy: (thin film, cm^{-1}) ν 2965, 1553, 1382, 1270, 1130, 1016, 833, 653, 575. MS Spectrometry: HR-EI calcd for $C_{13}H_{19}NO_2$ $[M]^+$ 221.1416, found 221.1412.

(*R*)-2-(1-Nitropropan-2-yl)naphthalene (Table 2, entry 10)



Reaction with 1.5 mol% catalyst at 40 °C gives 56% Yield, ee = 92% (HPLC: OD-H, 215 nm, hexane:2-propanol = 99:1, flow rate 1.0 mL/min, $t_{r(major)}$ = 53.9 min, $t_{r(minor)}$ = 79.2 min). $[\alpha]_D^{28}$ = +46.4 (c = 0.5, $CHCl_3$). NMR Spectroscopy: ^{1}H-NMR: (300 MHz, $CDCl_3$) δ 1.48 (d, *J* = 7.2 Hz, 3H), 3.78-3.85 (m, 1H), 4.54-7.70 (m, 2H), 7.36 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.45-7.52 (m, 2H), 7.68 (m, 1H) 7.79-7.85 (m, 2H). All other spectroscopic data were in agreement with the literature.[7]

[1] Hashiguchi, S.; Fujii, A.; Takehara, J.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 7562-7563.
[2] Mohar, B.; Valleix, A.; Desmus, J-R.; Felemez, M.; Wagner, A.; Mioskowski, C. *Chem. Comm.* **2001**, *24*. 2572-2573.
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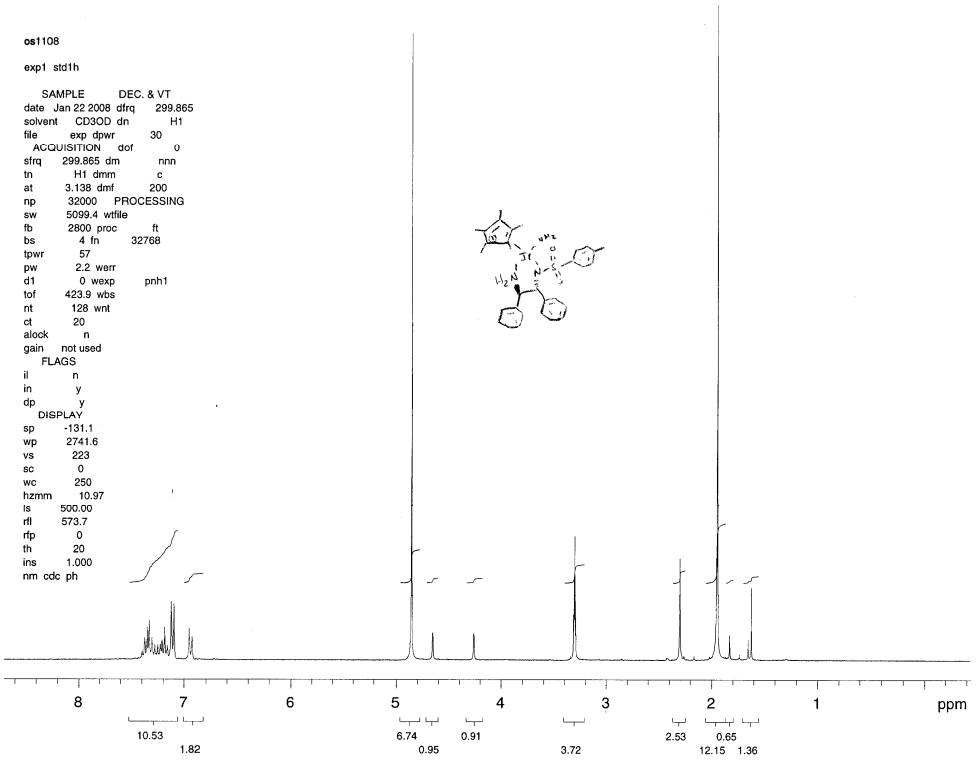
[6] Ohta, H.; Kobayashi, N.; Ozaki, K.; *J. Org. Chem.* **1989**, *54*, 1802-1804.
[7] Martin, N. J. A.; Ozores, L.; List, B.; *J. Am. Chem. Soc.* **2007**, *129*, 8976-8977.

Catalyst from Table 1, entry 1



Catalyst from Table 1, entry 1

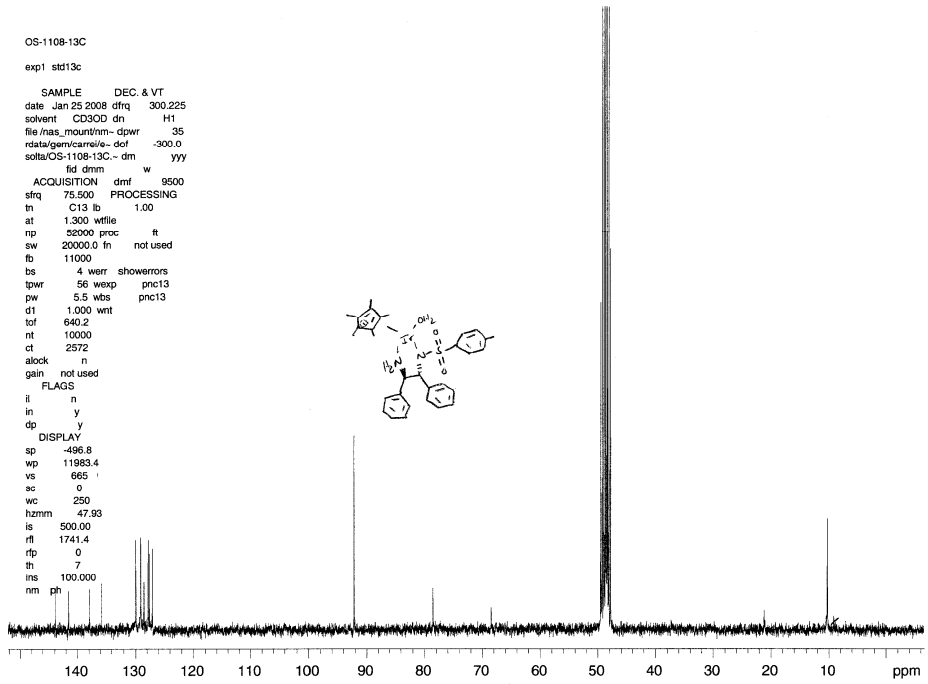
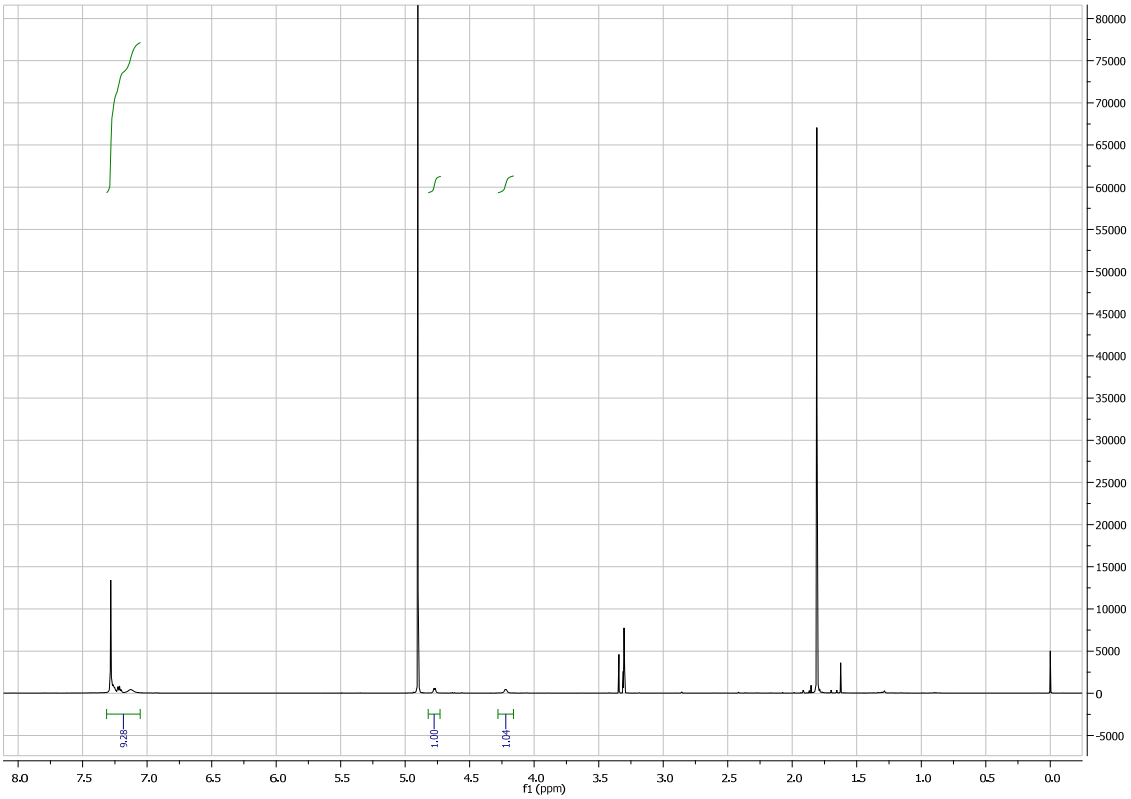


Figure 1: ^{1}H- and ^{13}C-NMR of {Cp*Ir[(*R*,*R*)-Ts-DPEN](H$_2$O)}(SO$_4$)

Catalyst from Table 1, entries 2 and 3



Catalyst from Table 1, entries 2 and 3

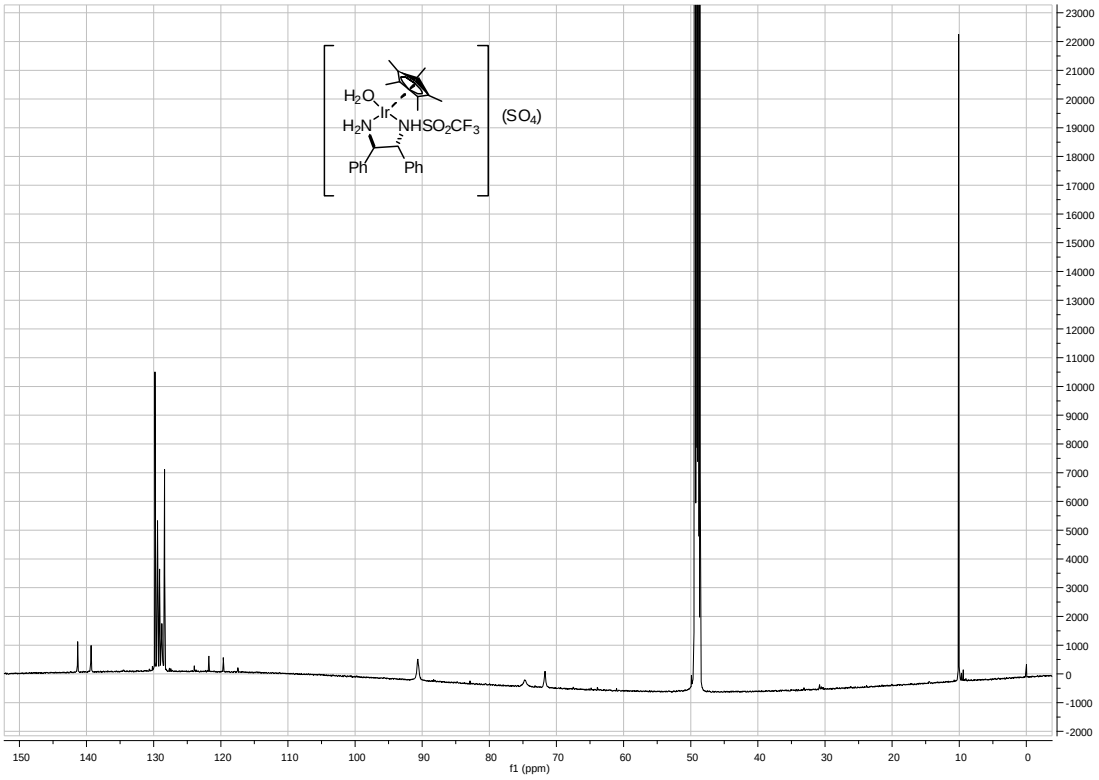
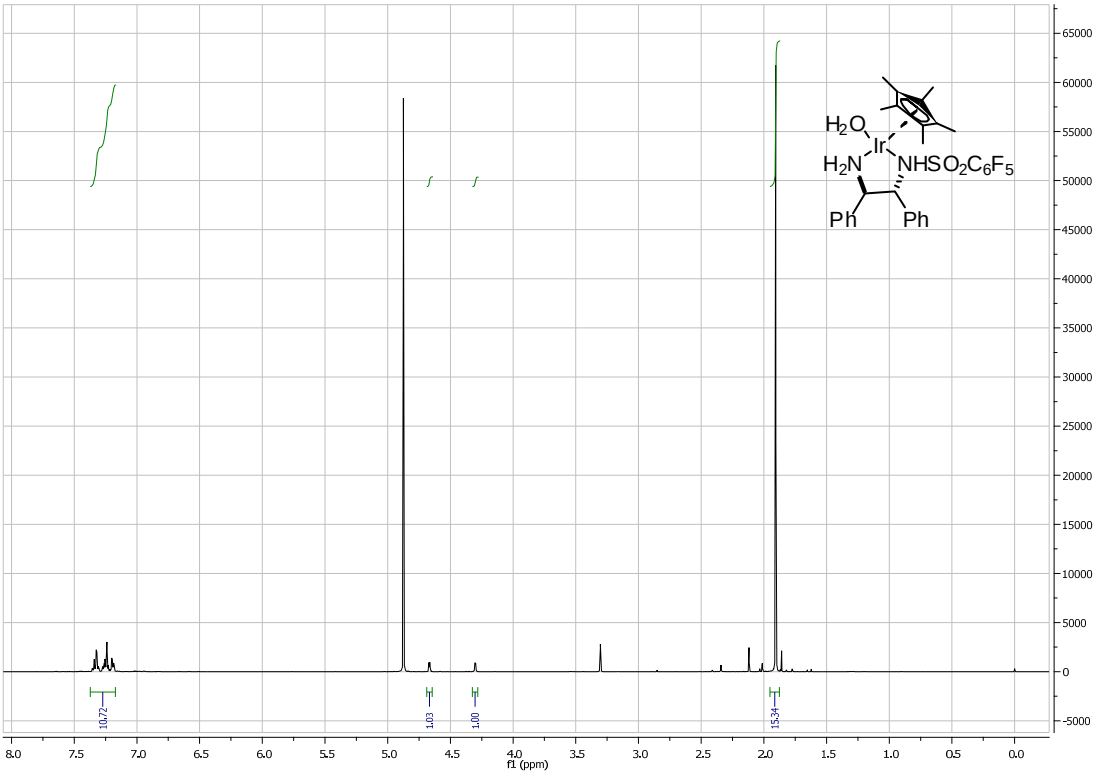


Figure 2: ^{1}H- and ^{13}C-NMR of {Cp*Ir[(*R*,*R*)-Tf-DPEN](H$_2$O)}(SO$_4$)

Catalyst from Table 1, entries 4 and 5



Catalyst from Table 1, entries 4 and 5

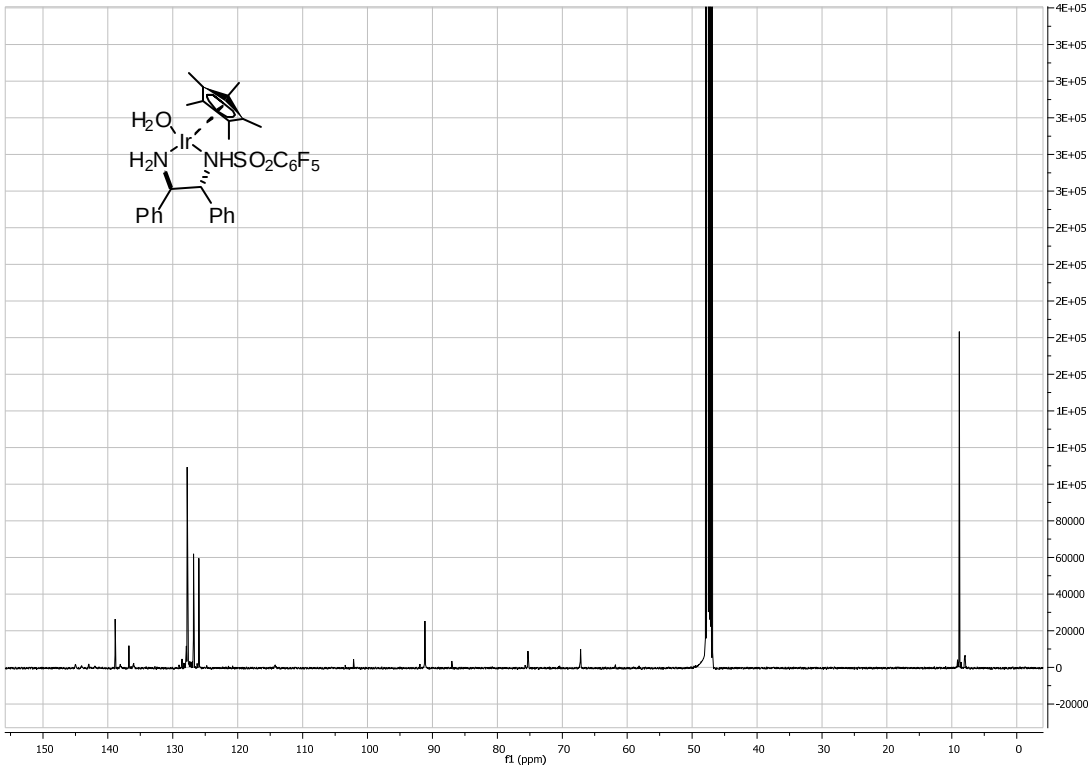
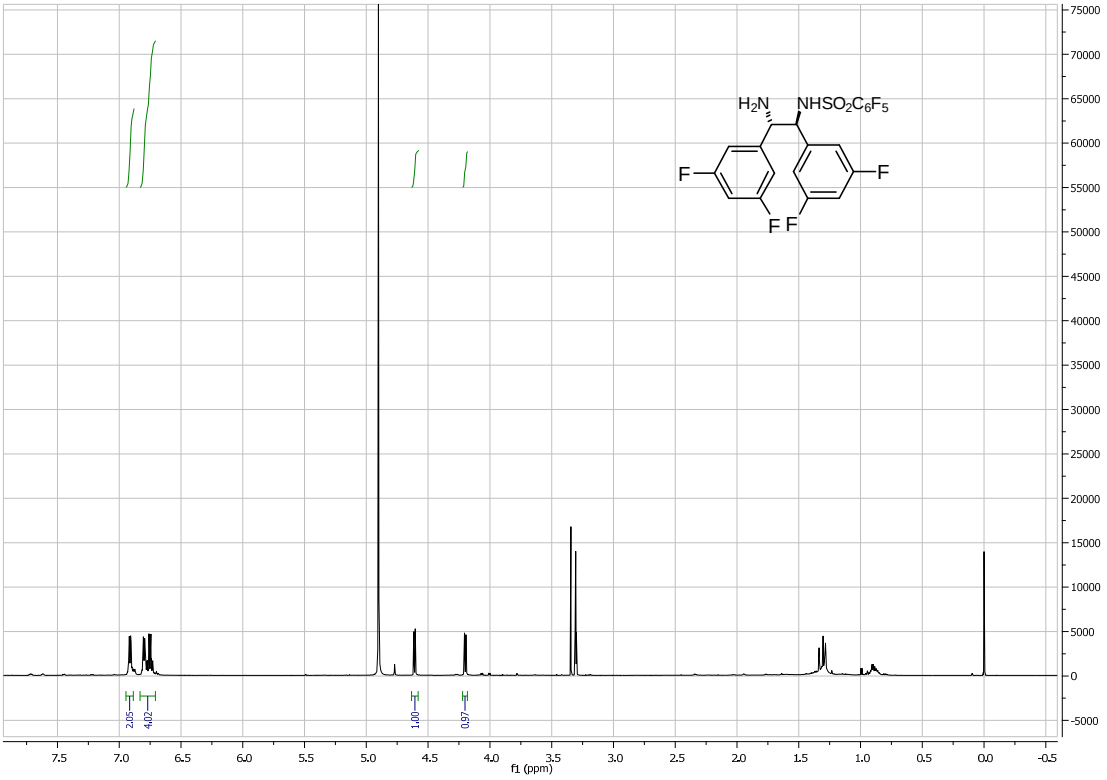


Figure 3: ^{1}H- and ^{13}C-NMR of {Cp*Ir[(*R*,*R*)- $C_6F_5SO_2$-DPEN](H_2O)}(SO_4)

Ligand used in catalyst from Table 1, entry 6



Ligand used in catalyst from Table 1, entry 6

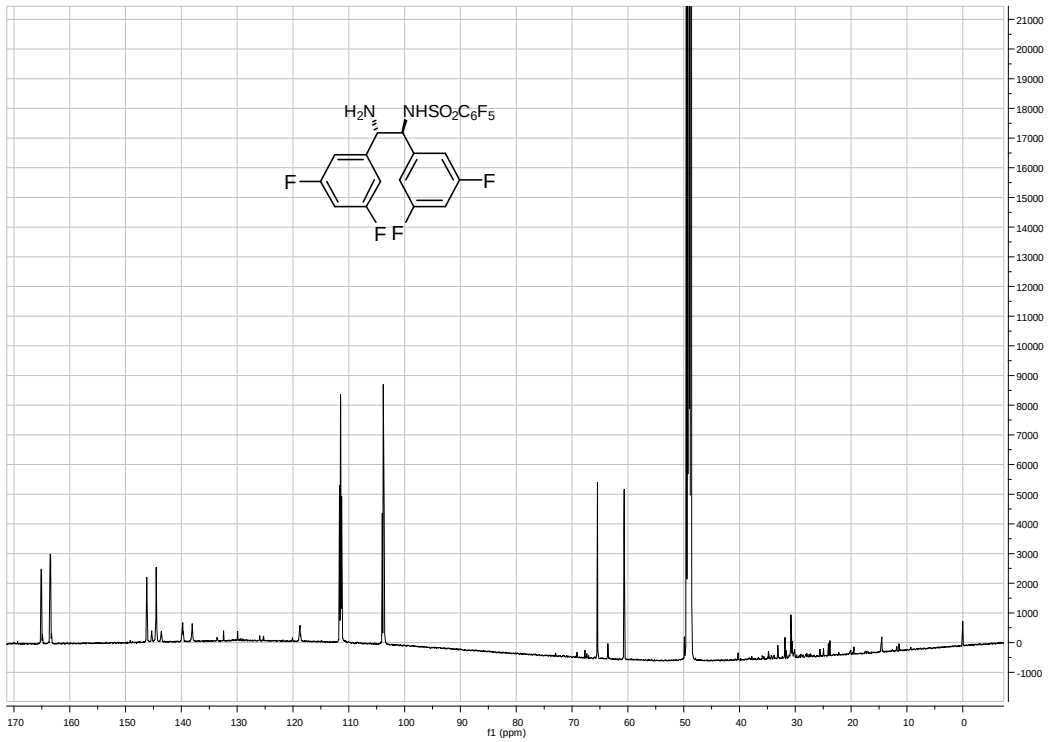
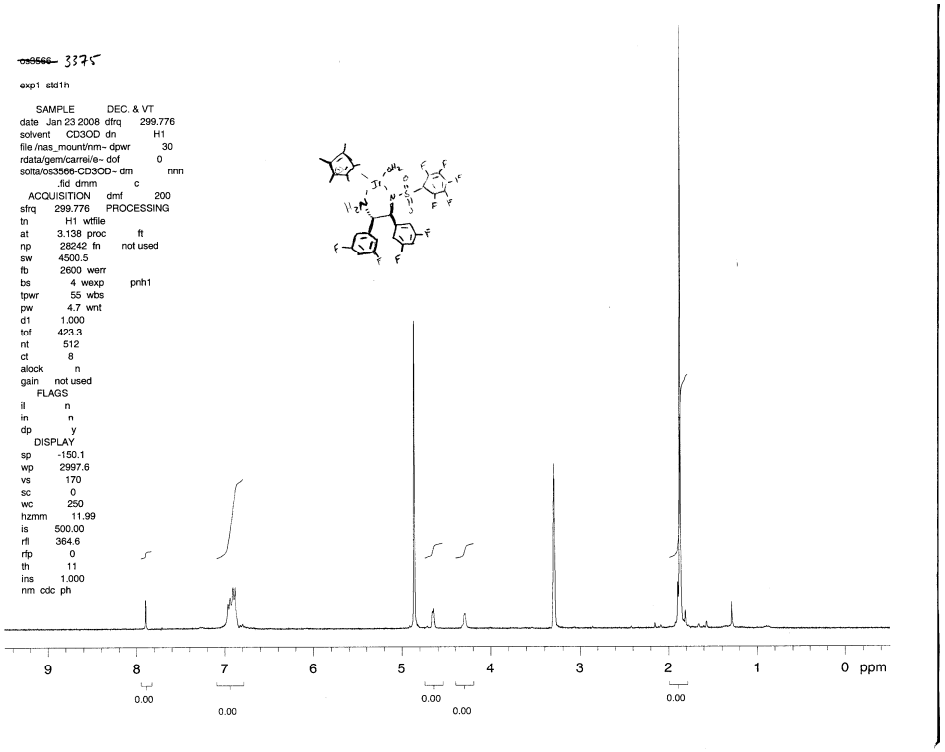


Figure 4: ^{1}H- and ^{13}C-NMR of (*S*,*S*)-$C_6F_5SO_2$-3,5-F-DPEN

Catalyst used in Table 1, entry 6



Catalyst used in Table 1, entry 6

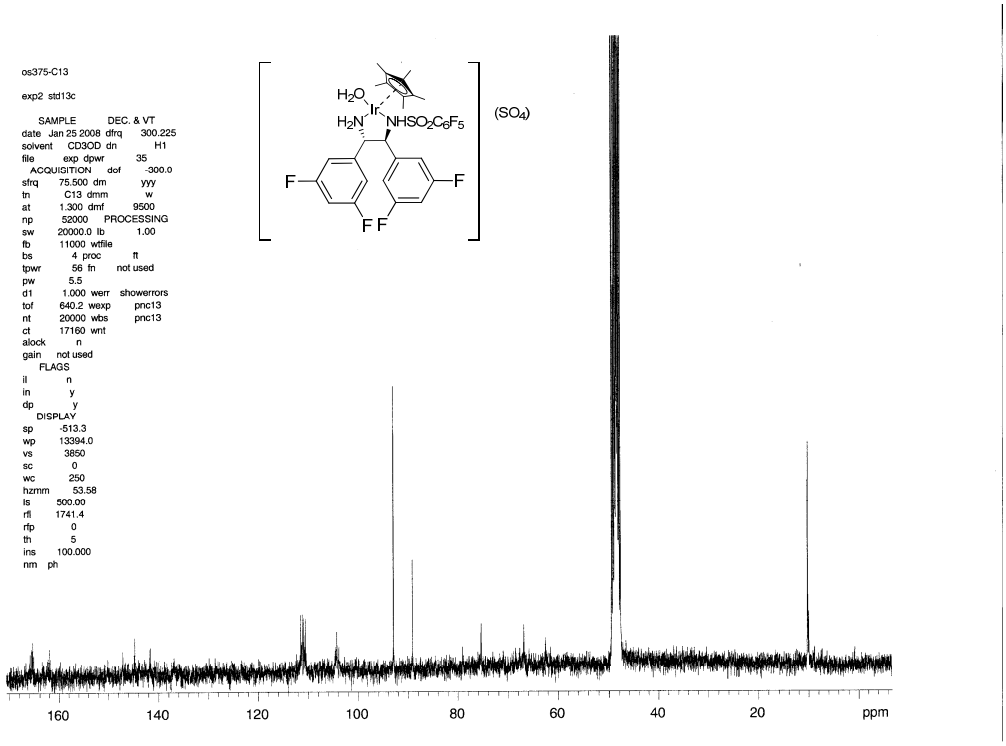
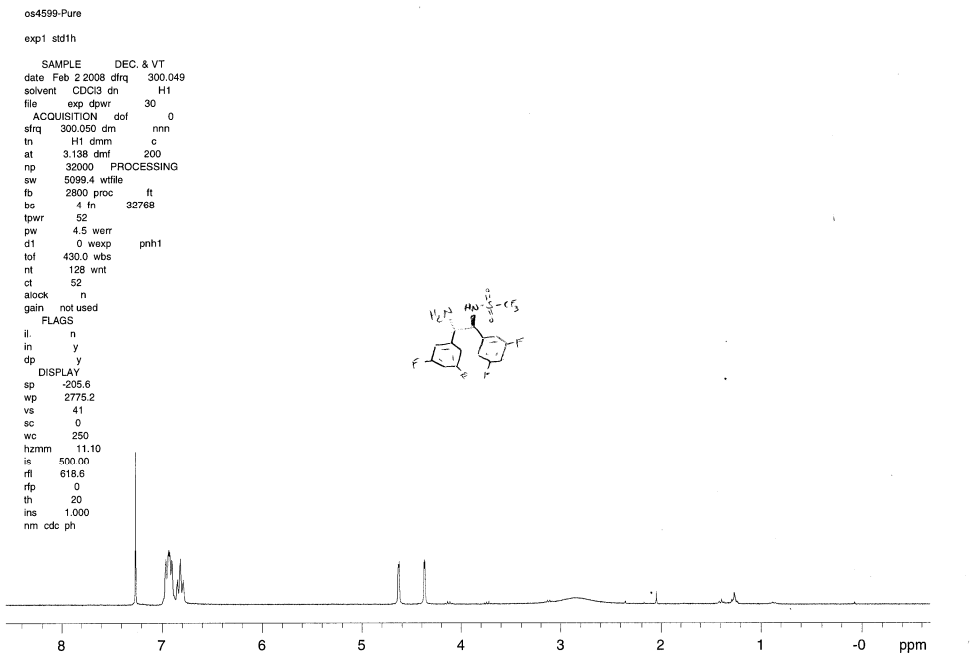


Figure 5: ^{1}H- and ^{13}C-NMR of {Cp*Ir[(*S*,*S*)-$C_6F_5SO_2$-3,5-F-DPEN](H_2O)}(SO_4)

Ligand used in Table 1, entry 7



Ligand used in Table 1, entry 7

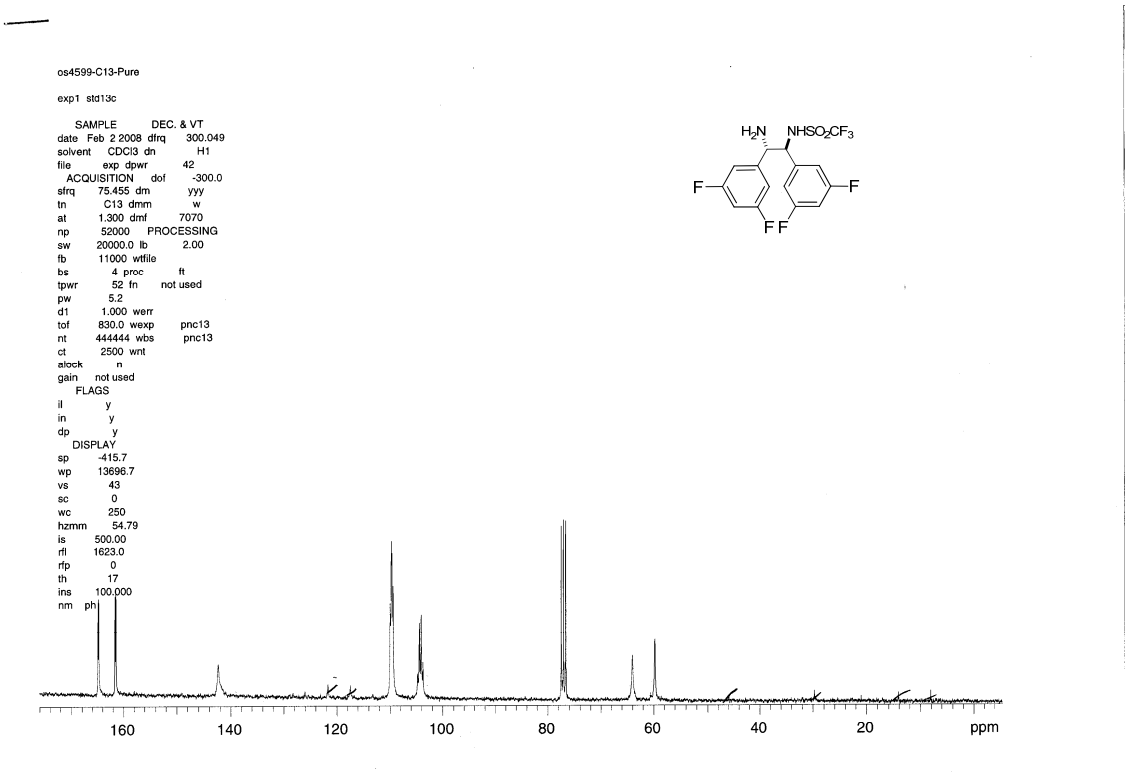
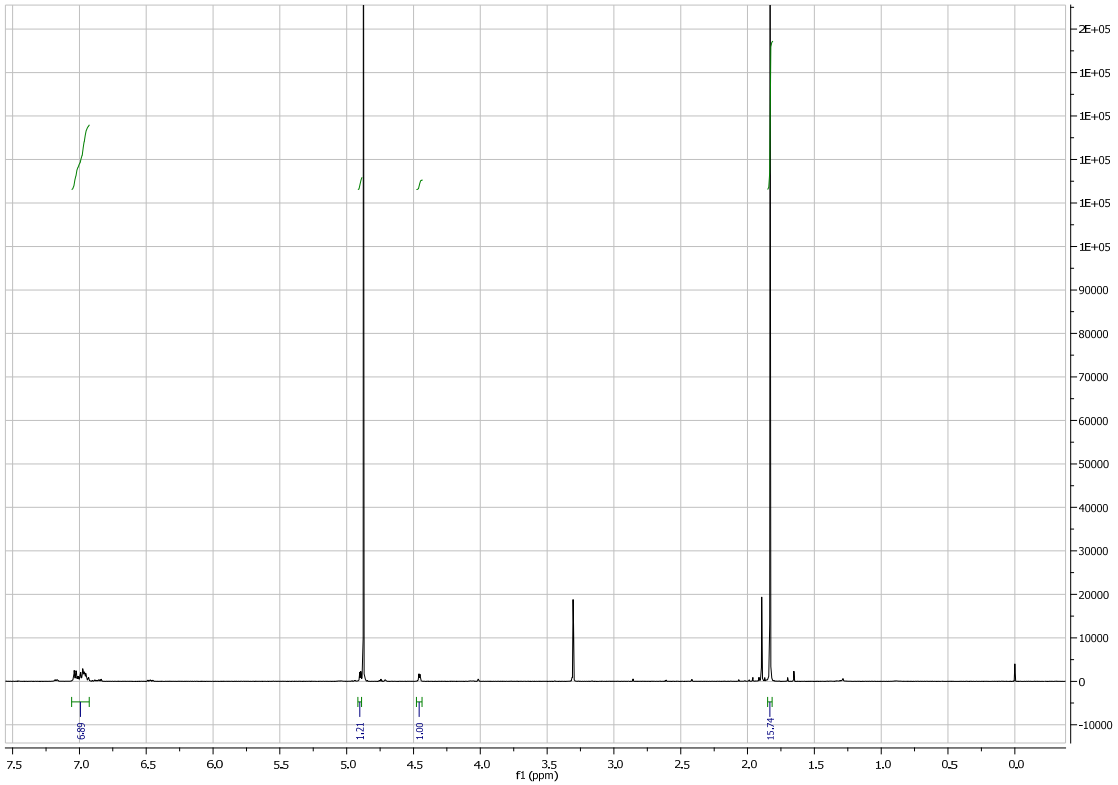


Figure 6: ^{1}H- and ^{13}C-NMR of *N*-((1*S*,2*S*)-2-amino-1,2-bis(3,5-difluorophenyl)ethyl)-1,1,1-trifluoromethanesulfonamide

Catalyst used in Table 1, entry 7



Catalyst used in Table 1, entry 7

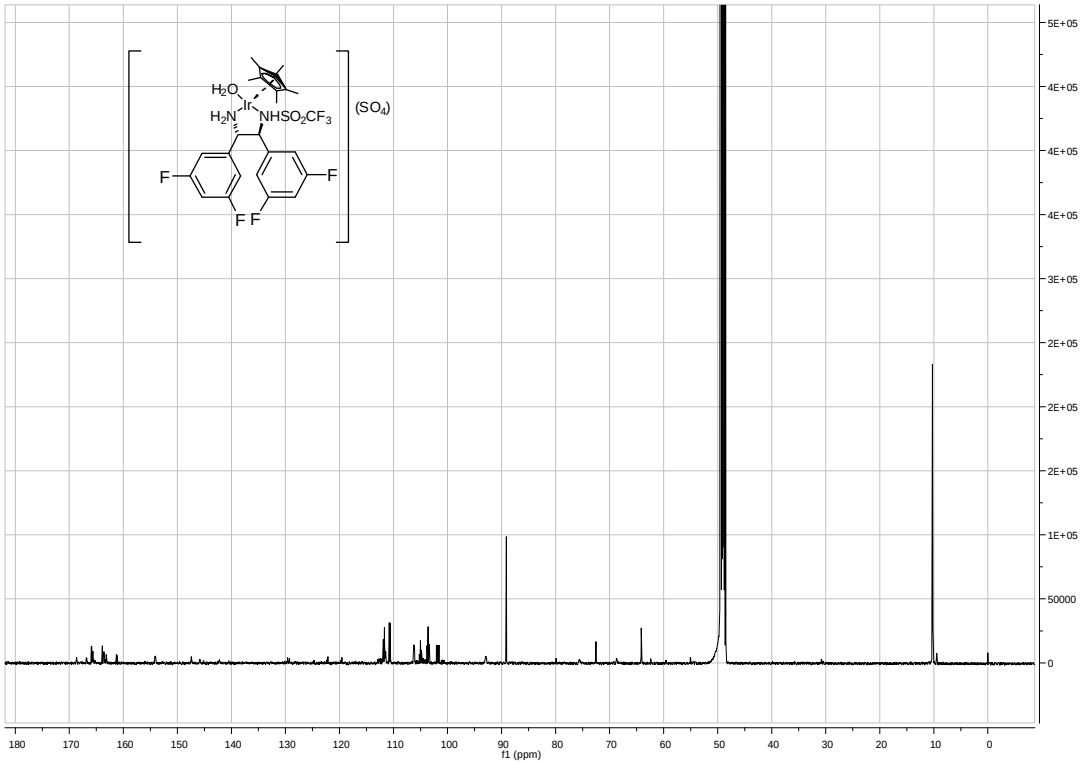
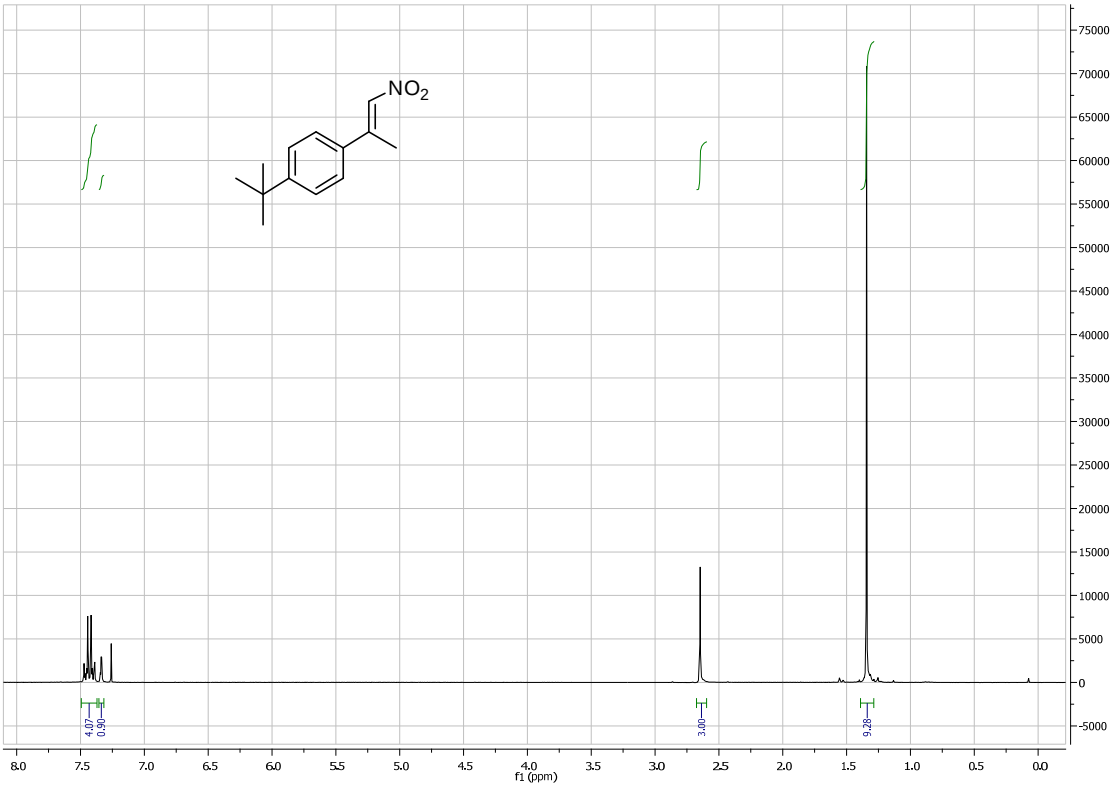


Figure 7: ^{1}H- and ^{13}C-NMR of {Cp*Ir[(*S*,*S*)-Tf-3,5-F-DPEN](H_2O)}(SO_4)

Substrate for Table 2, entry 9



Substrate for Table 2, entry 9

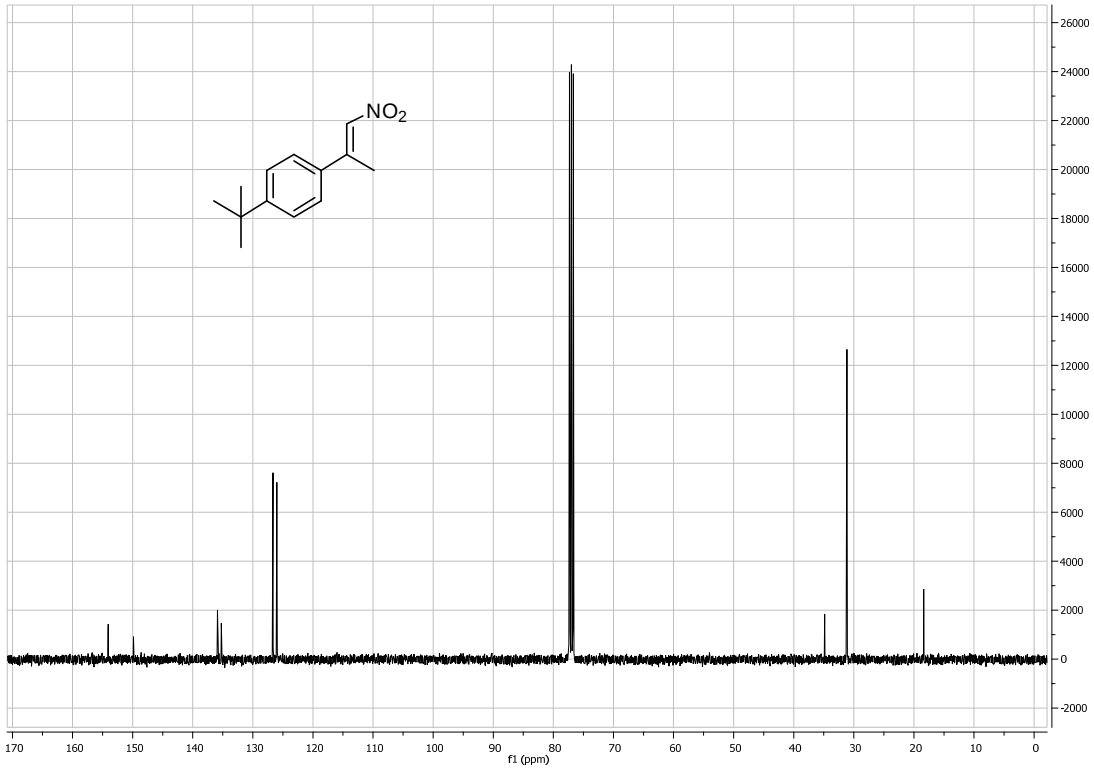
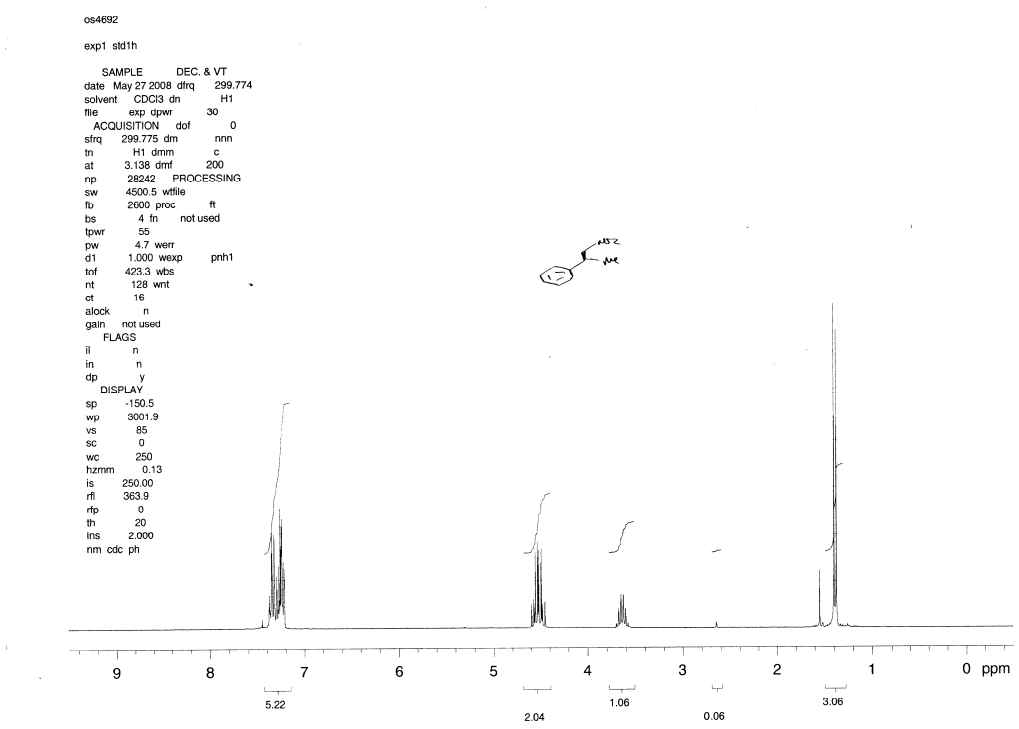
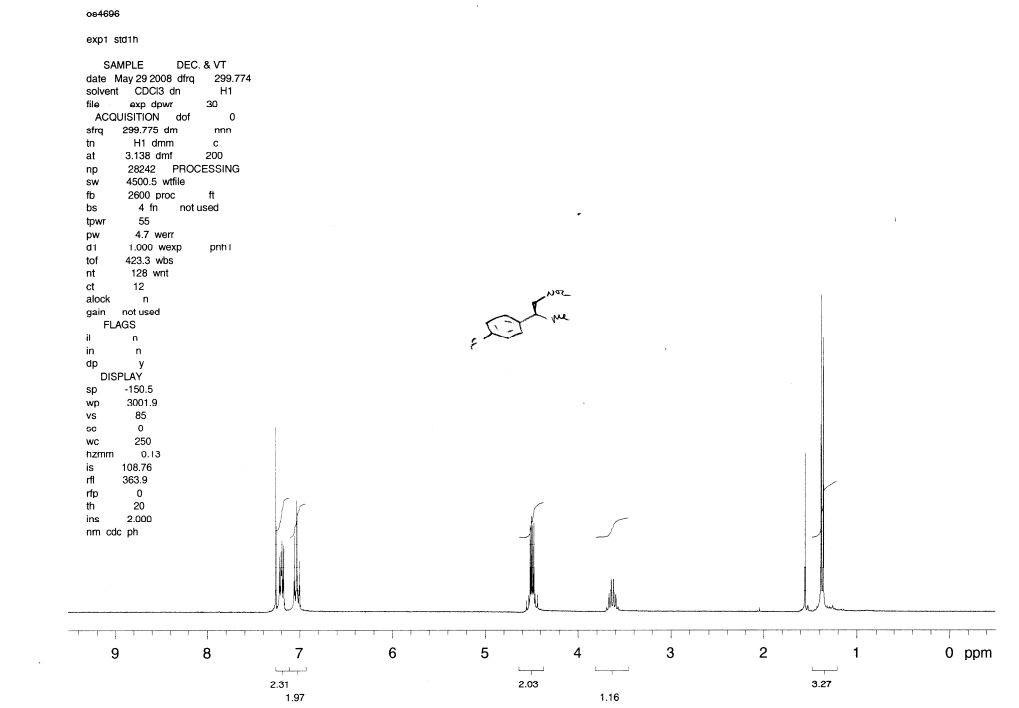


Figure 8: ^{1}H- and ^{13}C-NMR of (E)-1-*tert*-butyl-4-(1-nitroprop-1-en-2-yl)benzene

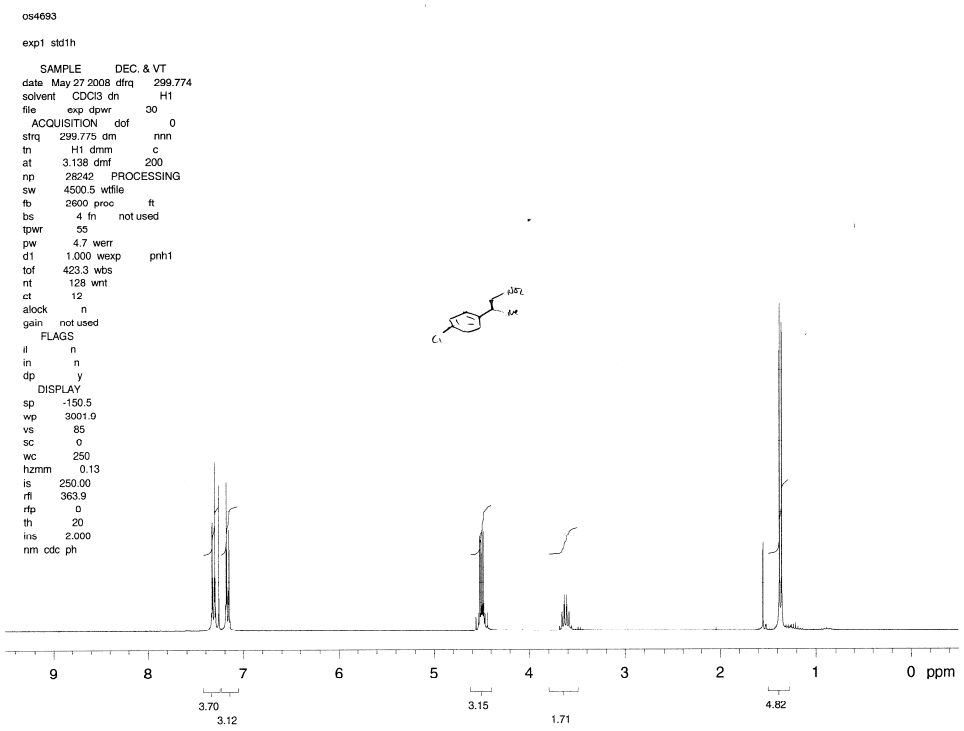
Product Table 2, entry 1 Product Table 2, entry 1



Product Table 2, entry 2



Product Table 2, entry 3



Product Table 2, entry 4

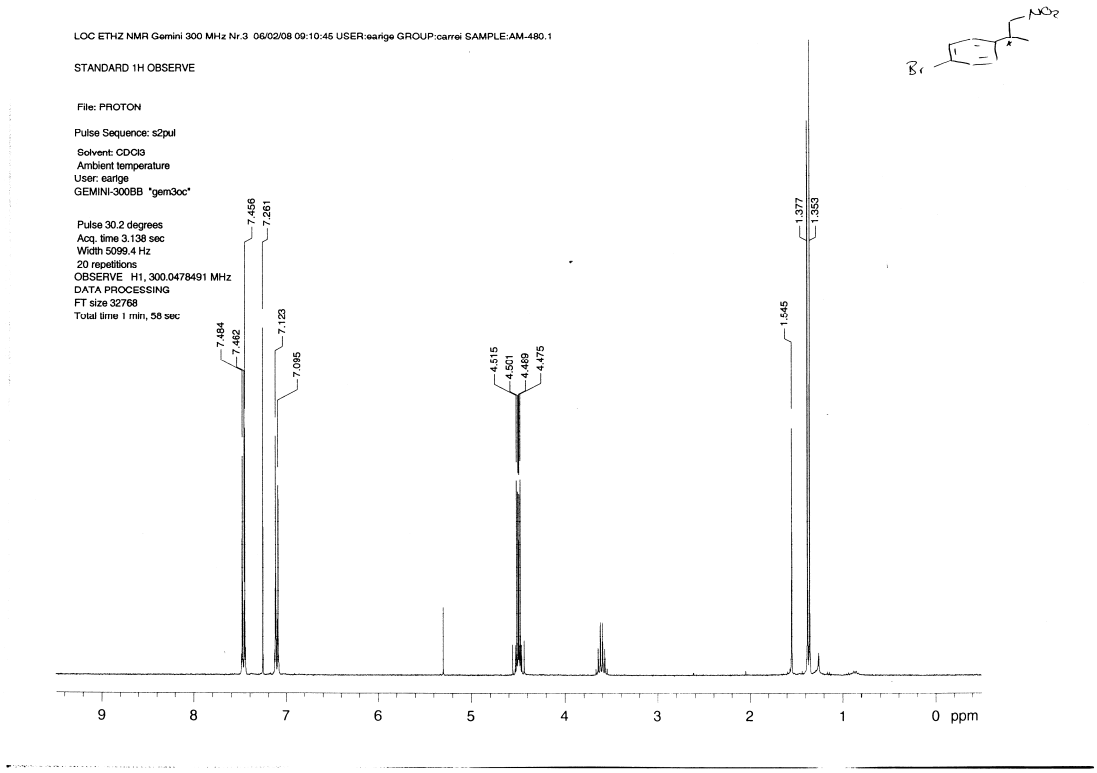
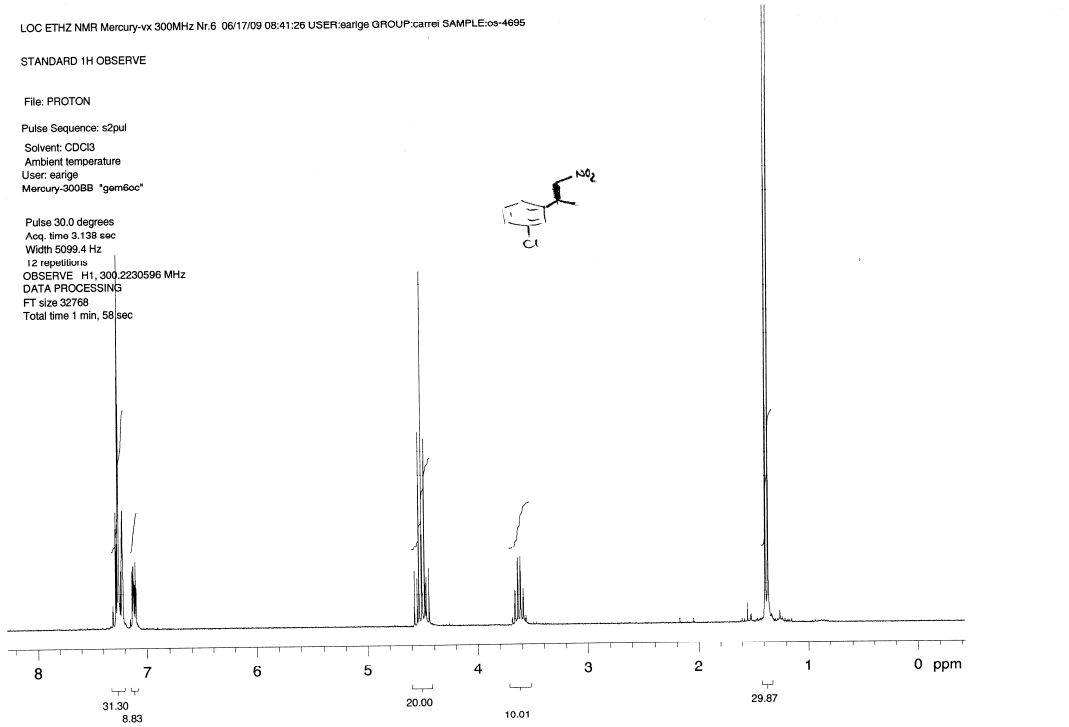


Figure 10: ^{1}H-NMR of (*R*)-1-Chloro-4-(1-nitropropan-2-yl)benzene and ^{1}H-NMR of (*R*)-1-Bromo-4-(1-nitropropan-2-yl)benzene

Product Table 2, entry 5



Product Table 2, entry 6

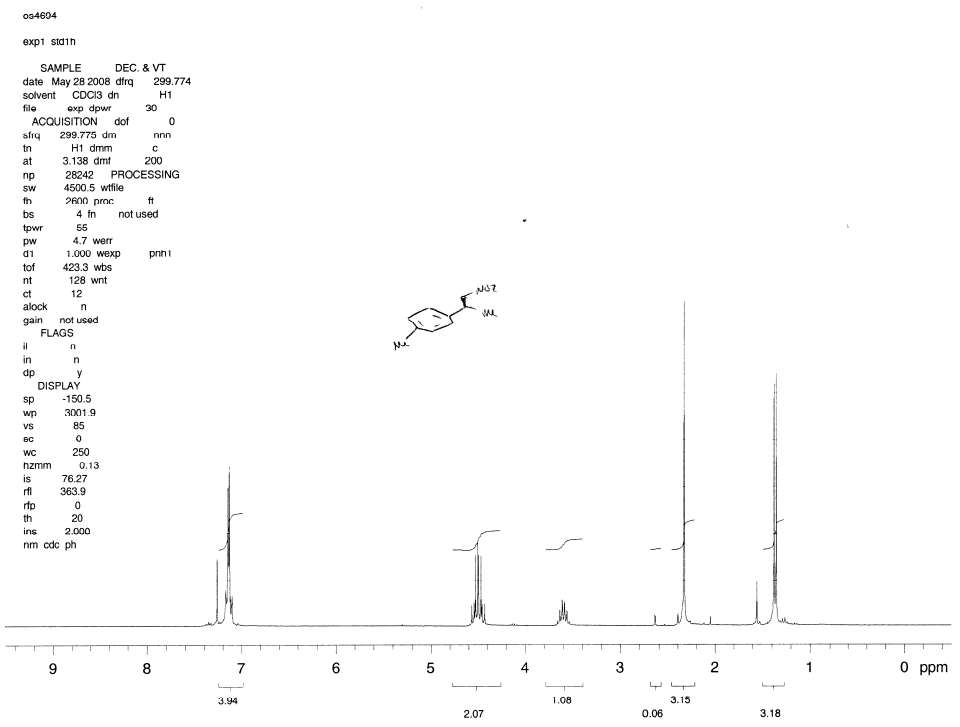
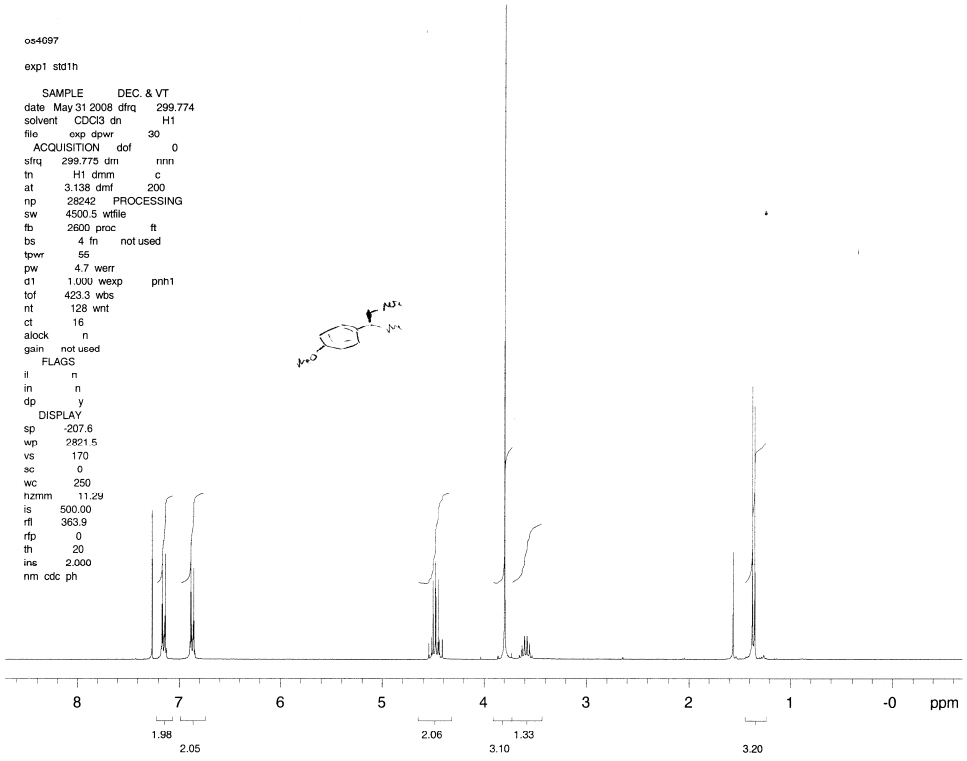


Figure 11: ^{1}H-NMR of (*R*)-1-Chloro-3-(1-nitropropan-2-yl)benzene and ^{1}H-NMR of (*R*)-1-Methyl-4-(1-nitropropan-2-yl)benzene

Product Table 2, entry 7



Product Table 2, entry 8

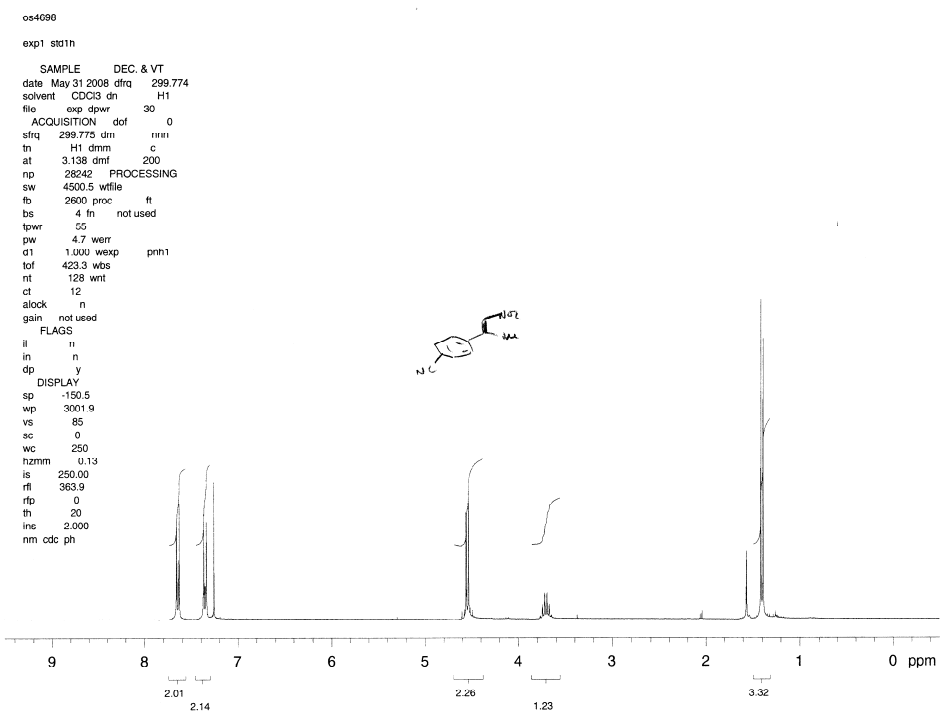


Figure 12: ^{1}H-NMR of (*R*)-1-Methoxy-4-(1-nitropropan-2-yl)benzene and ^{1}H-NMR of (*R*)-1-Cyano-4-(1-nitropropan-2-yl)benzene

Product Table 2, entry 10

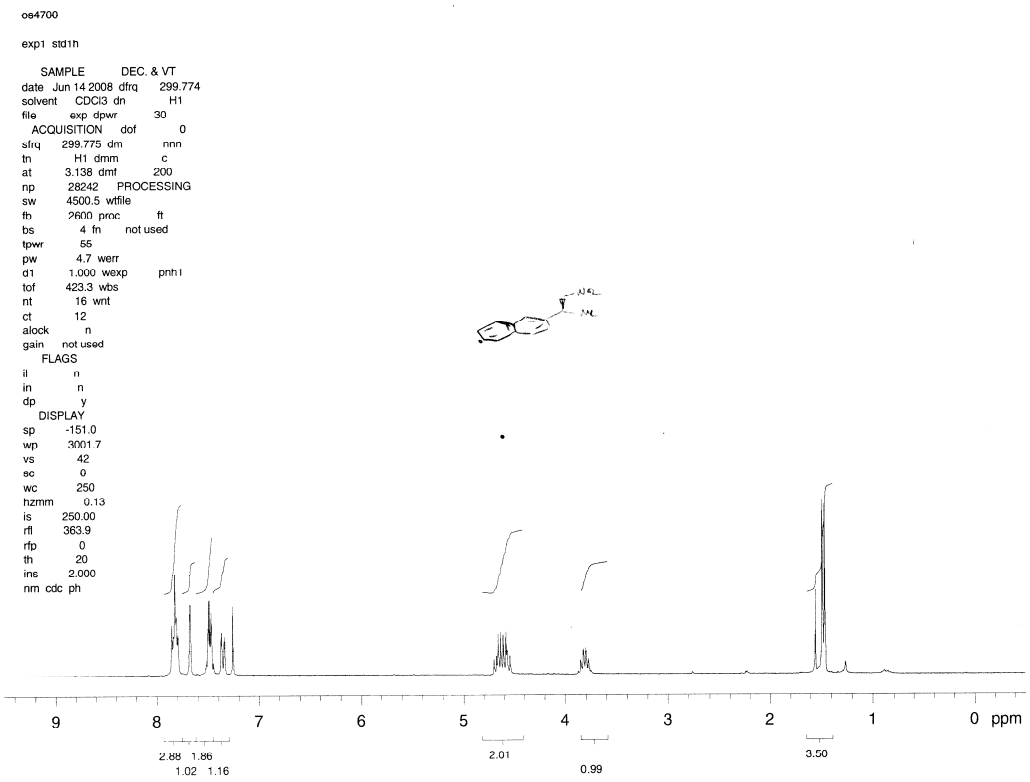
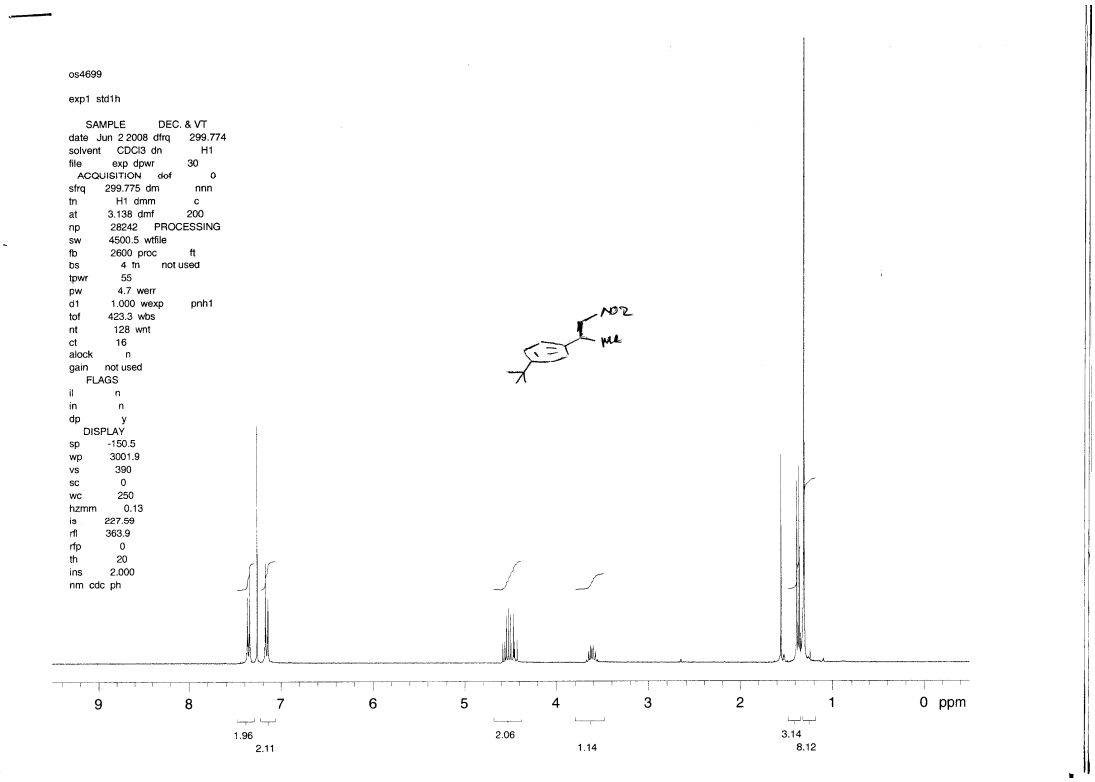


Figure 13: ^{1}H-NMR of (*R*)-2-(1-Nitropropan-2-yl)naphthalene

Product Table 2, entry 9



Product Table 2, entry 9

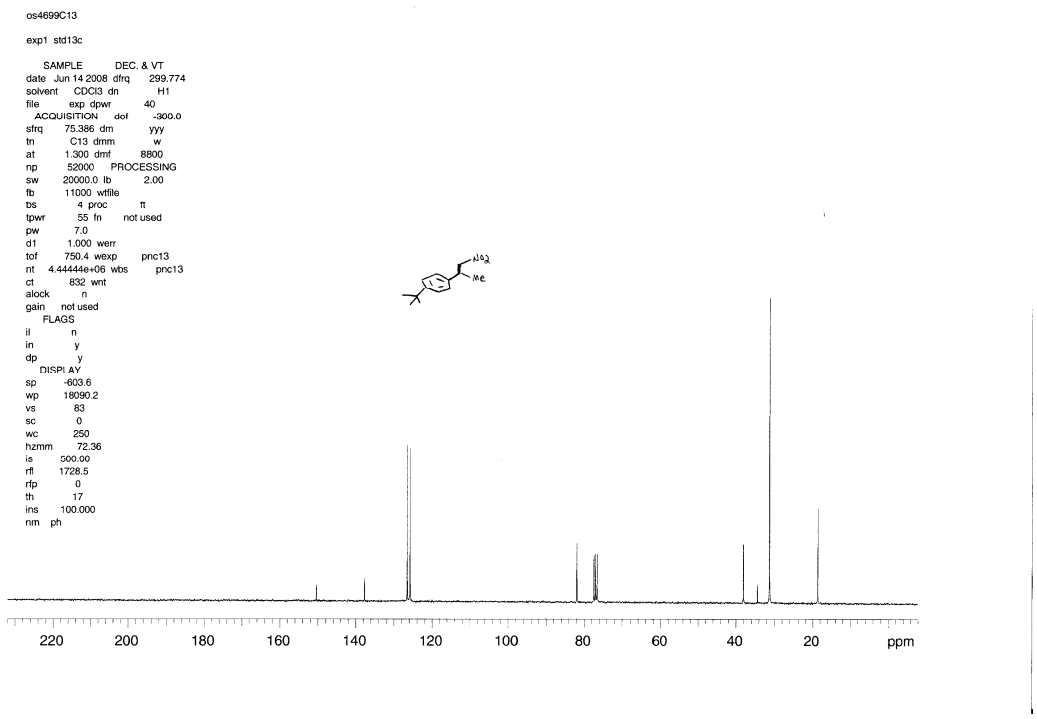


Figure 14: ^{1}H- and ^{13}C-NMR of (R)-1-*tert*-Butyl-4-(1-nitropropan-2-yl)benzene