Supporting Information

Asymmetric Hydrogenation of α-Hydroxy Ketones with Iridium/f-Amphox Catalyst: Efficient Access to Chiral 1,2-Diols

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I. General Remarks

All reactions and manipulations which are sensitive to moisture or air were performed in an argon-filled glovebox or using standard Schlenk techniques. Hydrogen gas (99.999%) was purchased from Shanghai Regulator Factory Co., Ltd. Simple ketones, were purchased from Aldrich or Alfa Aesar chemical company, and they were further purified by distilled. Anhydrous THF, 1,4-dioxane and toluene distilled was from sodium benzophenone ketyl. Anhydrous i-PrOH, EA, CH₂Cl₂ were freshly distilled from calcium hydride. Anhydrous MeOH and EtOH were freshly distilled from Mg. Anhydrous CF₃CH₂OH were purchased from Sigma-Aldrich. Solvents were transferred by syringe. [Ir(COD)Cl]₂ was prepared according to the literature.¹⁻² ¹H, ¹³C and ³¹P NMR spectra were recorded with a Bruker ADVANCE III (400 MHz) spectrometer with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the CDCl₃ at 7.26 ppm (for ¹H NMR) or 77.0 ppm (for ¹³C NMR). Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz) and signal area integration in natural numbers. ¹³C NMR and ³¹P NMR analyses were run with decoupling. Optical rotations $[\alpha]_D$ were determined using a PERKIN ELMER polarimeter 343 instrument. GC analyses were performed using SHIMADZU Lab Solution instrument. HPLC analyses were performed using Daicel chiral column. Aliphatic α -hydroxy ketones were purchased from Sigma-Aldrich and all the aromatic α -hydroxy ketones were prepared according the literature.³⁻⁷ The characterization data of compounds **2a-2c**, **2e**, **2j**, 21, 2n, 2o, 2r are in accordance with the reported data in the literature.⁶ The characterization data of compounds 2d, 2g, 2i, 2q, 2m are in accordance with the reported data in the literature.^{5, 11} The characterization data of compounds 2f, 2h, 2k, 2p, 2s are in accordance with the reported data in the literature.¹²⁻¹⁶

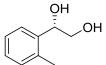
II. General procedure for asymmetric hydrogenation

General procedure for S/C = 10,000: To a 4.0 mL vial was added the catalyst precursor [Ir(COD)Cl]₂ (1.4 mg, 2.0×10^{-3} mmol), ligand L3 (2.4 mg, 4.2×10^{-3} mmol) and anhydrous ⁱPrOH (2.0 mL) under argon atmosphere. The mixture was stirred for 2.0 h at 25 °C giving orange red solution in the argon-filled glovebox. The resulting solution (10 µL) and a solution of K₂CO₃ (10 µL, c = 0.02 mmol/mL) transferred by syringe into a 5.0 mL vial charged with fresh distilled substrate ketones (0.2 mmol) in 1.0 mL anhydrous ⁱPrOH. The vials were transferred to an autoclave, which was then charged with 20 atm of H₂ and stirred at room temperature for 2 h. The hydrogen gas was released slowly in a well-ventilated hood and the solution was concentrated and passed through a short column of silica gel to remove the metal complex. The product was analyzed by chiral GC or chiral HPLC for ee values. The characterization data of compounds **2a-2s** are in accordance with the reported data in the literature.⁵⁻¹⁰

OH T OH

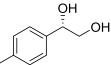
Colorless solid, 27.4 mg, 99% yield; >99% ee; $[\alpha]_D^{25} = +34.8$ (c = 0.50, MeOH). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 220 nm; $t_R(R) = 33.61$ min (minor), $t_R(S) = 37.82$ min (major). ¹H NMR (400 MHz, CD₃OD) δ 7.36-7.24 (m, 4H), 7.23-7.17 (m, 1H), 4.64 (dd, J = 7.1, 5.0 Hz, 1H), 3.57 (dd, J = 6.1, 2.6 Hz, 2H); ¹³C NMR (101 MHz, CD₃OD) δ 141.91, 127.88, 127.15, 126.03, 74.59, 67.39.

(S)-1-(2-Methylphenyl)-1,2-ethanediol 2b



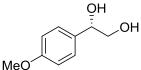
Colorless solid, 30.1 mg, 99% yield; 99% ee; $[\alpha]_D^{25} = +33.4$ (c = 0.35, CHCl₃). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R(*R*) = 29.23 min (minor), t_R(*S*) = 39.62 min (major). ¹H NMR (400 MHz, d-DMSO) δ 7.40 (d, *J* = 4.0 Hz, 1H), 7.19-7.06 (m, 3H), 5.14 (d, *J* = 4.0 Hz, 1H), 4.76-4.74 (m, 1H), 3.39 (dt, *J* = 9.4, 3.8 Hz, 1H), 3.34-3.30 (m, 1H), 2.28 (s, 3H); ¹³C NMR (101 MHz, d-DMSO) δ 141.84, 134.84, 130.16, 126.99, 126.46, 126.06, 71.0, 67.04, 19.28.

(S)-1-(4-Methylphenyl)-1,2-ethanediol 2c



Colorless solid, 30.1 mg, 99% yield; >99% ee; $[\alpha]_D^{25} = +57.8$ (c = 0.225, CHCl₃). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 210 nm; $t_R(R) = 29.15$ min (minor), $t_R(S) = 33.59$ min (major). ¹H NMR (400 MHz, CD₃OD) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.70-4.62 (m, 1H), 3.64-3.57 (m, 2H), 2.33 (s, 3H). ¹³C NMR (101 MHz, CD₃OD) δ 138.82, 136.85, 128.48, 125.97, 74.45, 67.38, 19.79.

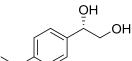
(S)-1-(4-Methoxyphenyl)-1,2-ethanediol 2d



MeO Colorless solid, 33.3 mg, 99% yield; >99% ee; $[\alpha]_D^{25} = +63.8$ (c = 0.24, CHCl₃). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate

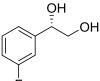
= 1.0 mL/min; UV detection at 220 nm; $t_R(R) = 50.37$ min (minor), $t_R(S) = 58.49$ min (major). ¹H NMR (400 MHz, CD₃OD) δ 7.18 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 4.52 (t, *J* = 6.1 Hz, 1H), 3.67 (s, 3H), 3.48 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 159.25, 133.88, 127.21, 113.24, 74.16, 67.31, 54.25.

(S)-1-(4-Ethylphenyl)-1,2-ethanediol **2e**



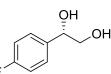
Colorless solid, 32.9 mg, 99% yield; >99% ee; $[\alpha]_D^{25} = +20.2$ (c = 0.50, MeOH). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R(*R*) = 26.75 min (minor), t_R(*S*) = 30.13 min (major). ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 4.80 (dd, *J* = 8.0, 3.4 Hz, 1H), 3.80-3.59 (m, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.54 (brs, 1H), 2.17 (brs, 1H), 1.24 (t, *J* = 8.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.22, 137.74, 128.10, 126.12, 74.60, 68.10, 28.58, 15.62.

(S)-1-(3-Fluorophenyl)-1,2-ethanediol 2f



F Colorless solid, 30.9 mg, 99% yield; >99% ee; $[\alpha]_D^{25} = +19.2$ (c = 0.50, MeOH). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 220 nm; $t_R(R) = 28.39$ min (minor), $t_R(S) = 32.53$ min (major). ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.29 (m, 1H), 7.12-7.08 (m, 2H), 7.01-6.96 (m, 1H), 4.81 (dd, J = 8.1, 3.2 Hz, 1H), 3.77-3.74 (m, 1H), 3.64-3.59 (m, 1H), 3.07 (brs, 1H), 2.54 (brs, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 162.97 (d, J = 246.3 Hz), 143.11 (d, J = 6.9 Hz), 130.10 (d, J = 8.1 Hz), 121.62 (d, J = 2.9 Hz), 114.85 (d, J = 21.1 Hz), 113.08 (d, J = 22.1 Hz), 74.04 (d, J = 1.6 Hz), 67.90.

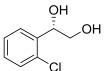
(S)-1-(4-Fluorophenyl)-1,2-ethanediol **2g**



F Colorless solid, 30.9 mg, 99% yield; >99% ee; $[\alpha]_D^{25} = +56.4$ (c = 0.225, CHCl₃). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 210 nm; $t_R(R) = 31.60$ min (minor), $t_R(S) = 35.53$ min (major). ¹H NMR (400 MHz, CD₃OD) δ 7.30-7.26 (m, 2H), 6.97-6.93 (m, 2H), 4.57 (t, *J* = 8.0 Hz, 1H), 3.50-3.48 (m, 2H). ¹³C NMR (101 MHz,

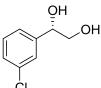
CD₃OD) δ 162.24 (d, *J* = 243.6 Hz), 138.05 (d, *J* = 3.0 Hz), 127.87 (d, *J* = 8.1 Hz), 114.44 (d, *J* = 21.5 Hz), 73.79, 67.23.

(S)-1-(2-Chlorophenyl)-1,2-ethanediol **2h**



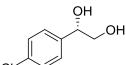
Cl Colorless solid, 34.2 mg, 99% yield; 95% ee; $[\alpha]_D^{25} = +32.4$ (c = 0.50, MeOH). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 205 nm; t_R(*R*) = 24.34 min (minor), t_R(*S*) = 33.78 min (major). ¹H NMR (400 MHz, d-DMSO) δ 7.58-7.55 (m, 1H), 7.41-7.30 (m, 2H), 7.29-7.26 (m, 1H), 5.47 (d, *J* = 4.0 Hz, 1H), 4.92-4.87 (m, 1H), 3.51-3.47 (m, 1H), 3.36-3.26 (m, 1H). ¹³C NMR (101 MHz, d-DMSO) δ 140.82, 131.52, 129.26, 128.99, 128.80, 127.50, 71.02, 66.09.

(S)-1-(3-Chlorophenyl)-1,2-ethanediol 2i



Cl Colorless solid, 34.2 mg, 99% yield; >99% ee; $[\alpha]_D^{25} = +50.8$ (c = 0.24, CHCl₃). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 220 nm; $t_R(R) = 33.02 \text{ min (minor)}$, $t_R(S) = 39.22 \text{ min (major)}$. ¹H NMR (400 MHz, CD₃OD) δ 7.43 (s, 1H), 7.38-7.21 (m, 3H), 4.70-4.67 (m, 1H), 3.63-3.61 (m, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 144.61, 133.77, 129.37, 127.07, 126.11, 124.46, 73.76, 67.10.

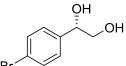
(S)-1-(4-Chlorophenyl)-1,2-ethanediol 2j



Cl Colorless solid, 34.2 mg, 99% yield; >99% ee; $[\alpha]_D^{25} = +11.8$ (c = 0.50, MeOH). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 220 nm; $t_R(R) = 33.41$ min (minor), $t_R(S) = 37.63$ min (major). ¹H NMR (400 MHz, CD₃OD) δ 7.36-7.25 (m, 4H), 4.64-4.61 (m, 1H), 3.59-3.51 (m, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 140.91, 132.72, 127.89, 127.68, 73.75, 67.11.

Br Colorless solid, 42.9 mg, 99% yield; >99% ee; $[\alpha]_D^{25} = +14.8$ (c = 0.50, MeOH). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 210 nm; $t_R(R) = 37.16$ min (minor), $t_R(S) = 45.84$ min (major). ¹H NMR (400 MHz, d-DMSO) δ 7.53 (t, *J* = 1.7 Hz, 1H), 7.42 (ddd, *J* = 7.8, 2.0, 1.2 Hz, 1H), 7.36-7.32 (m, 1H), 7.27 (t, *J* = 7.7 Hz, 1H), 5.42 (brs, 1H), 4.80 (brs, 1H), 4.54 (t, *J* = 5.8 Hz, 1H), 3.53-3.44 (m, 1H), 3.43-3.40 (m, 1H). ¹³C NMR (101 MHz, d-DMSO) δ 146.93, 130.50, 130.04, 129.52, 125.92, 121.80, 73.47, 67.55.

(S)-1-(4-Bromophenyl)-1,2-ethanediol 2l

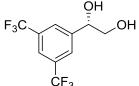


OH

OH

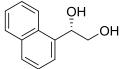
Br Colorless solid, 42.6 mg, 98% yield; >99% ee; $[\alpha]_D^{25} = +31.8$ (c = 0.50, CHCl₃). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 220 nm; $t_R(R) = 39.54$ min (minor), $t_R(S) = 42.78$ min (major). ¹H NMR (400 MHz, CD₃OD) δ 7.46-7.43 (m, 2H), 7.27-7.25 (m, 2H), 4.62-4.60 (m, 1H), 3.56–3.54 (m, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 141.41, 130.90, 128.02, 120.70, 73.79, 67.06.

(S)-1-(3,5-bis(trifluoromethyl)phenyl)-1,2-ethanediol 2m



CF₃ Colorless solid, 54.3 mg, 99% yield; >99% ee; $[\alpha]_D^{25} = +35.8$ (c = 0.50, CHCl₃). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 220 nm; t_R(*R*) = 18.64 min (minor), t_R(*S*) = 20.74 min (major). ¹H NMR (400 MHz, CD₃OD) δ 7.90 (s, 2H), 7.76 (s, 1H), 4.75 (t, *J* = 8.0 Hz, 1H), 3.57 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 143.03, 131.80 (q, *J* = 33.0 Hz), 126.27, 121.86, 99.99, 73.39, 67.58. ¹⁹F NMR (377 MHz, CDCl₃) δ -62.89.

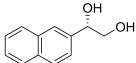
(S)-1-(1-Naphtyl)-1,2-ethanediol **2n**



Colorless solid, 37.3 mg, 99% yield; 97% ee; $[\alpha]_D^{25} = +35.8$ (c = 0.50, MeOH). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 70:30; flow rate

= 0.5mL/min; UV detection at 254 nm; $t_R(R)$ = 10.54 min (minor), $t_R(S)$ = 14.83 min (major). ¹H NMR (400 MHz, CD₃OD) δ 8.17 (d, *J* = 8.0 Hz, 1H), 7.92-7.90 (m, 1H), 7.83-7.81 (m, 1H), 7.59 (d, *J* = 7.1 Hz, 1H), 7.74-7.72 (m, 1H), 7.56-7.49 (m, 3H), 5.57-5.55 (m, 1H), 3.90-3.86 (m, 1H), 3.73-3.68 (m, 1H). ¹³C NMR (101 MHz, CD₃OD) δ 137.30, 133.83, 130.65, 128.47, 127.53, 125.62, 125.09, 125.01, 123.29, 122.60, 71.37, 67.02.

(S)-1-(2-Naphtyl)-1,2-ethanediol 20



Colorless solid, 37.3 mg, 99% yield; 99% ee; $[\alpha]_D^{25} = +13.6$ (c = 0.50, MeOH). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 70:30; flow rate = 0.5 mL/min; UV detection at 254 nm; $t_R(R) = 11.18$ min (minor), $t_R(S) = 12.39$ min (major). ¹H NMR (400 MHz, CD₃OD) δ 7.87-7.84 (m, 4H), 7.48-7.46 (m, 3H), 4.91-4.83 (m, 1H), 3.75-3.72 (m, 2H). ¹³C NMR (101 MHz, CD₃OD) δ 139.43, 133.39, 133.12, 127.53, 127.51, 127.24, 125.66, 125.38, 124.84, 124.17, 74.65, 67.24.

(*R*)-1-(2-Furyl)-1,2-ethanediol **2p**



Colorless solid, 25.4 mg, 99% yield; >99% ee; $[\alpha]_D^{25} = +4.4$ (c = 0.50, MeOH). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5; flow rate = 0.8 mL/min; UV detection at 230 nm; t_R(*S*) = 25.36 min (minor), t_R(*R*) = 29.82 min (major). ¹H NMR (400 MHz, CDCl₃) δ 7.37 (s, 1H), 6.34-6.29 (m, 2H), 4.79–4.77 (m, 1H), 3.87-3.79 (m, 2H), 3.74 (brs, 1H), 3.29 (brs, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 153.55, 142.32, 110.34, 107.02, 68.34, 65.04.

(R)-1-(2-Thienyl)-1,2-ethanediol **2q**

OH

OH

Colorless solid, 28.6 mg, 99% yield; >99% ee; $[\alpha]_D^{25} = +36.9$ (c = 0.52, CHCl₃). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 220 nm; $t_R(S) = 7.59$ min (minor), $t_R(R) = 9.02$ min (major). ¹H NMR (400 MHz, CDCl₃) δ 7.27-7.25 (m, 1H), 6.99-6.97 (m, 2H), 5.01 (dd, *J* = 7.6, 3.6 Hz, 1H), 3.81-3.68 (m, 2H), 3.68 (brs, 1H), 3.20 (brs, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.86, 126.89, 125.10, 124.46, 70.70, 67.69.

^COH Colorless oil, 15.1 mg, 99% yield; 93% ee; $[\alpha]_D^{25} = +7.0$ (c = 0.50, MeOH). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 205 nm; $t_R(R) = 41.36$ min (minor), $t_R(S) = 43.34$ min (major). HPLC conditions (To the corresponding *p*-Toluenesulfonyl derivatives). ¹H NMR (400 MHz, d-DMSO) δ 4.39-4.37 (m, 1H), 4.32 (d, *J* = 4.5 Hz, 1H), 3.50-3.38 (m, 1H), 3.20-3.11 (m, 1H), 3.07-3.03 (m, 1H), 0.89 (d, *J* = 6.3 Hz, 3H). ¹³C NMR (101 MHz, d-DMSO) δ 67.69, 67.64, 20.42.

(R)-1,2-Butanediol 2s

OH

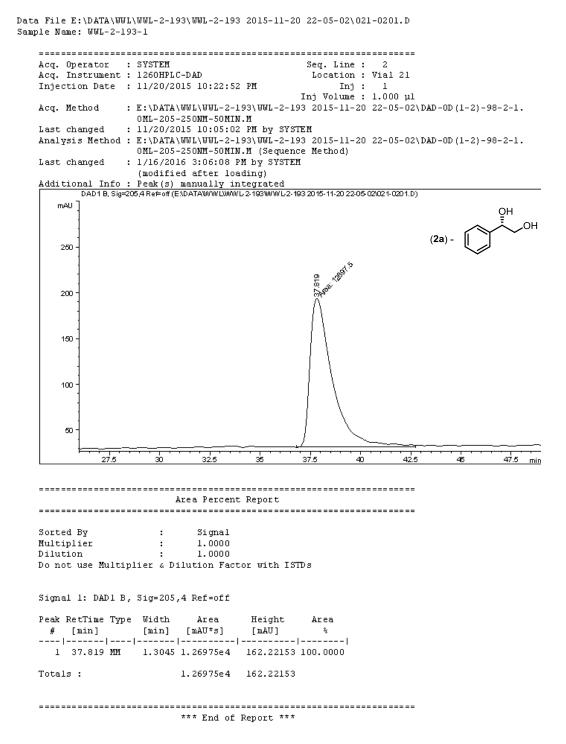
OH OH Colorless oil, 17.8 mg, 99% yield; 96% ee; $[\alpha]_D^{25} = +0.8$ (c = 0.28, MeOH). The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UV detection at 205 nm; $t_R(S) = 28.2$ min (minor), $t_R(R) = 32.37$ min (major). HPLC conditions (To the corresponding *p*-Toluenesulfonyl derivatives). ¹H NMR (400 MHz, CD₃OD) δ 3.41-3.22 (m, 3H), 1.45-1.43 (m, 1H), 1.32-1.26 (m, 1H), 0.86 (t, *J* = 8.0 Hz, 3H). ¹³C NMR (101 MHz, CD₃OD) δ 73.30, 65.60, 25.81, 8.94.

Asymmetric Hydrogenation of acetophenone at S/C = 1 000 000

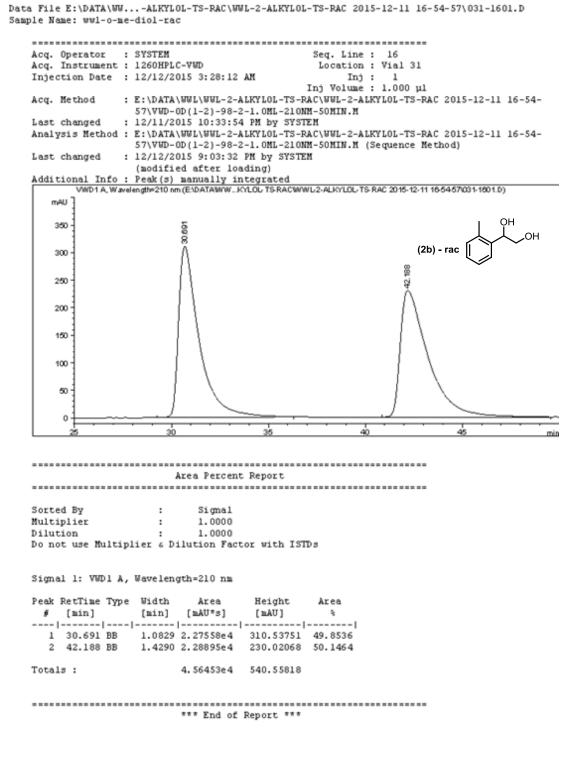
To a 4 mL vial was added the catalyst precursor $[Ir(COD)CI]_2$ (1.4 mg, 2.0×10⁻³ mmol), ligand L3 (2.4 mg, 4.2×10⁻³ mmol) and anhydrous ^{*i*}PrOH (2.0 mL) under argon atmosphere. The mixture was stirred for 2.0 h at 25 °C giving orange red solution in the argon-filled glovebox. The resulting solution (50 µL) and K₂CO₃ (13.8 mg) transferred by syringe into a 100 mL vial charged with recrystallized α -hydroxyacetophenone (100 mmol) in 25 mL anhydrous ^{*i*}PrOH. The vial was transferred to an autoclave, which was then charged with 50 atm of H₂ and stirred at room temperature for 24 h. The hydrogen gas was released slowly in a well-ventilated hood and the solution was concentrated and passed through a column of silica gel to remove the metal complex. The product (*S*)-1-Phenyl-1,2-ethanediol **2a** was analyzed by chiral HPLC, >99% yield and >99% ee.

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                                                Inj: 1
                                          Inj Volume : 1.000 µl
                : E:\DATA\WWL\XY-1-23\XY-1-23 2015-12-12 13-39-51\DAD-0D(1-2)-98-2-1.0ML-
   Acg. Method
                  205-250NM-60MIN.M
   Last changed : 12/12/2015 3:21:25 PM by SYSTEM
                  (modified after loading)
   Analysis Method : E:\DATA\WWL\XY-1-23\XY-1-23 2015-12-12 13-39-51\DAD-0D(1-2)-98-2-1.0ML-
                  205-250NM-60MIN.M (Sequence Method)
   Last changed
                : 12/12/2015 8:56:24 PM by SYSTEM
                  (modified after loading)
   Additional Info : Peak(s) manually integrated
DAD1B, Sig=205,4 Refront (E:DATAWWUXX-1-23XX/1-23 2015-12-12 13-39-51/043-0501.D)
      mAU
                                                                        └_он
      400
                                                           (2a) - rac
      350
                                   33.471
                                                 5
      300
                                                 g
      250
      200
      150
      100
       50
        0
                                                     -áo
                                                                   45
                         30
                                       35
                                                                               min
            25
   Area Percent Report
   Sorted By
                           Signal
                     :
                    :
                           1.0000
   Multiplier
                           1.0000
   Dilution
                     :
   Do not use Multiplier & Dilution Factor with ISTDs
   Signal 1: DAD1 B, Sig=205,4 Ref=off
   Peak RetTime Type Width
                           Area
                                    Height
                                             Area
    # [min]
                   [min]
                         [mAU*s]
                                    [ nAU ]
                                              4
   1 33.471 BB 0.9290 2.02411e4 311.96320 49.0873
2 38.521 BB 1.0839 2.09938e4 274.60208 50.9127
   Totals :
                         4.12349e4 586.56528
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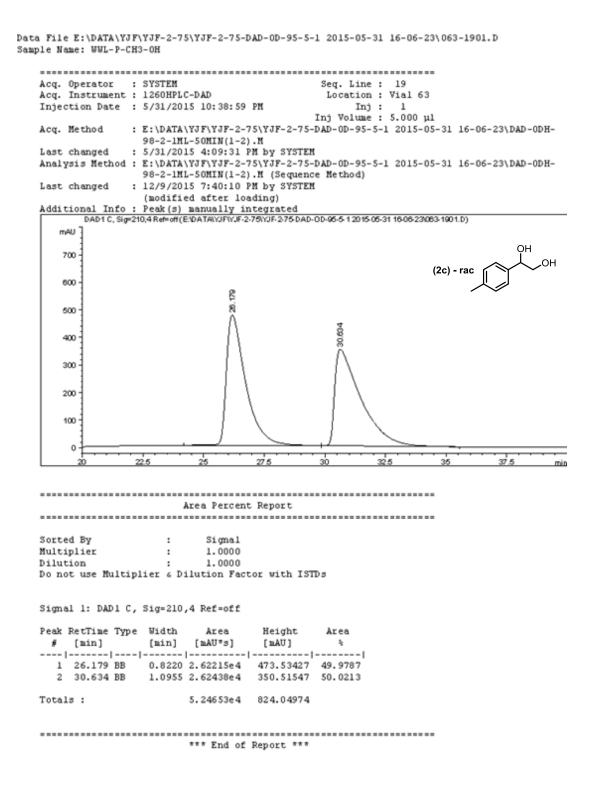


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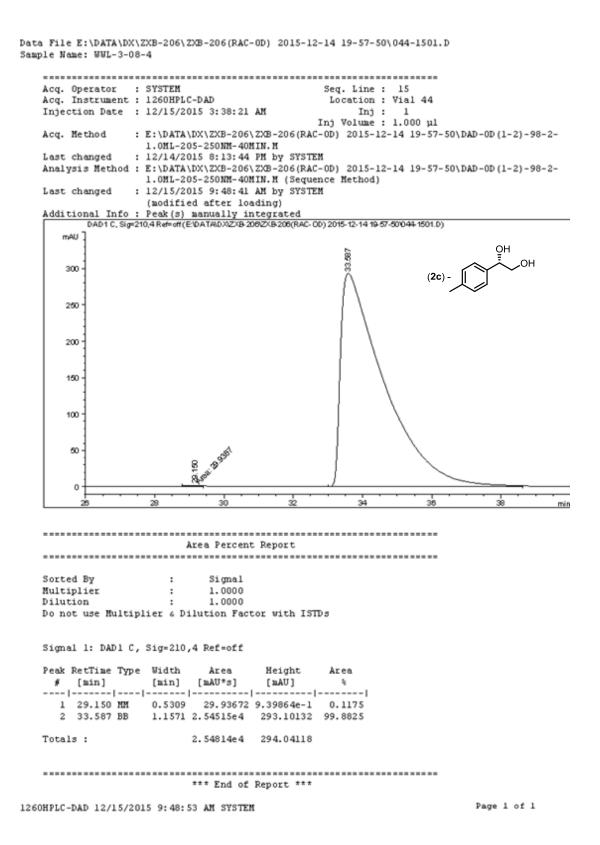


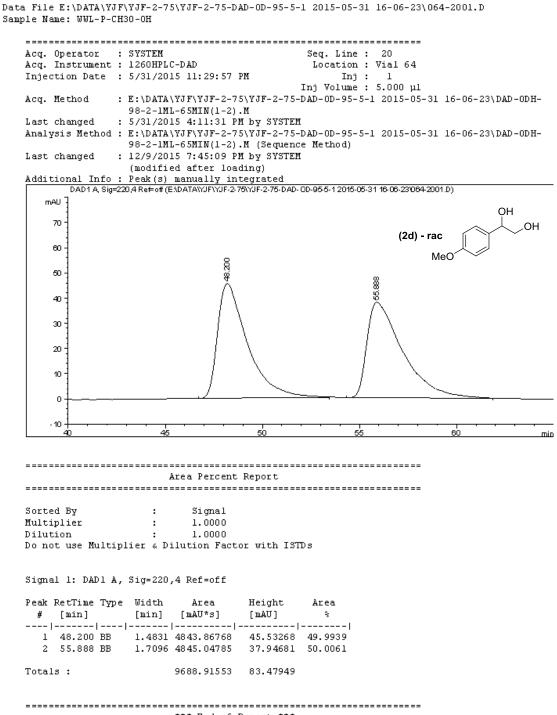
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Data File E:\DATA\DX\ZXB-206\ZXB-206(RAC-0D) 2015-12-14 19-57-50\041-1201.D Sample Name: WWL-3-08-1 Acq. Operator : SYSTEM Seq. Line : 12 Acq. Instrument : 1260HPLC-DAD Location : Vial 41 Injection Date : 12/15/2015 1:05:43 AM Inj: 1 Inj Volume : 1.000 µl : E:\DATA\DX\ZXB-206\ZXB-206(RAC-0D) 2015-12-14 19-57-50\DAD-0D(1-2)-98-2-Acg. Method 1.0ML-205-250NM-50MIN.M Last changed : 12/14/2015 8:13:46 PM by SYSTEM Analysis Method : E:\DATA\DX\ZXB-206(ZXB-206(RAC-OD) 2015-12-14 19-57-50\DAD-OD(1-2)-98-2-1.0ML-205-250NM-50MIN.M (Sequence Method) : 1/21/2016 12:50:11 PM by SYSTEM Last changed (modified after loading) Additional Info : Peak(s) manually integrated DAD1D, Sig=220,4 Ref=off(E:DATALDXZXB-206(RAC-OD)2015-12-14 19-57-50/041-1201.D) mAU ,ОН 175 (**2b**) -150 125 100 Assid 1378 75 8 50 N13812 25 8 She^{de} n 25 зò 35 40 46 20 min Area Percent Report Sorted By : Signal 1.0000 Multiplier : 1.0000 Dilution : Do not use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 D, Sig=220,4 Ref=off Peak RetTime Type Width Area Height Area [min] [mAU*s] [mAU] # [min] * ----|-----|-----|------| 1 29.226 MM 0.4380 17.38722 6.61577e-1 0.4149 2 39.624 MM 1.2267 4173.24707 56.70223 99.5851 4190.63429 57.36381 Totals : _____ *** End of Report *** Page 1 of 1 1260HPLC-DAD 1/21/2016 12:50:19 PM SYSTEM



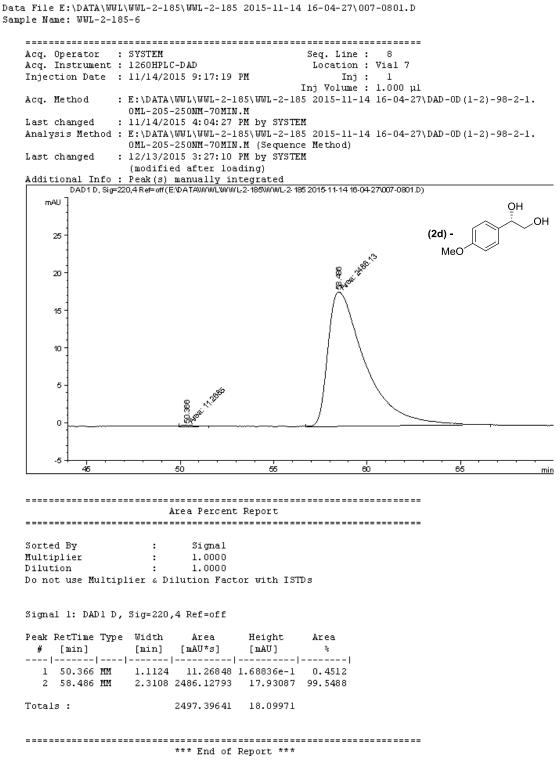
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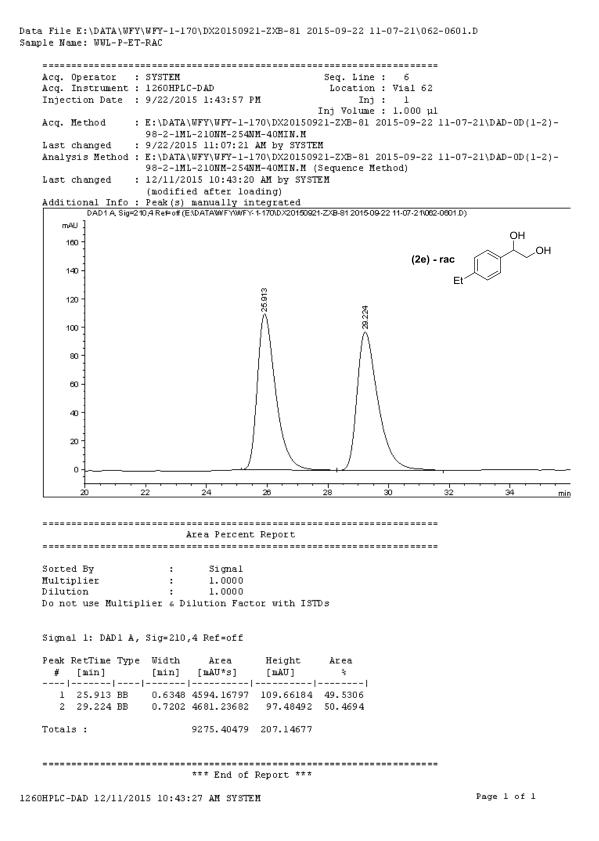


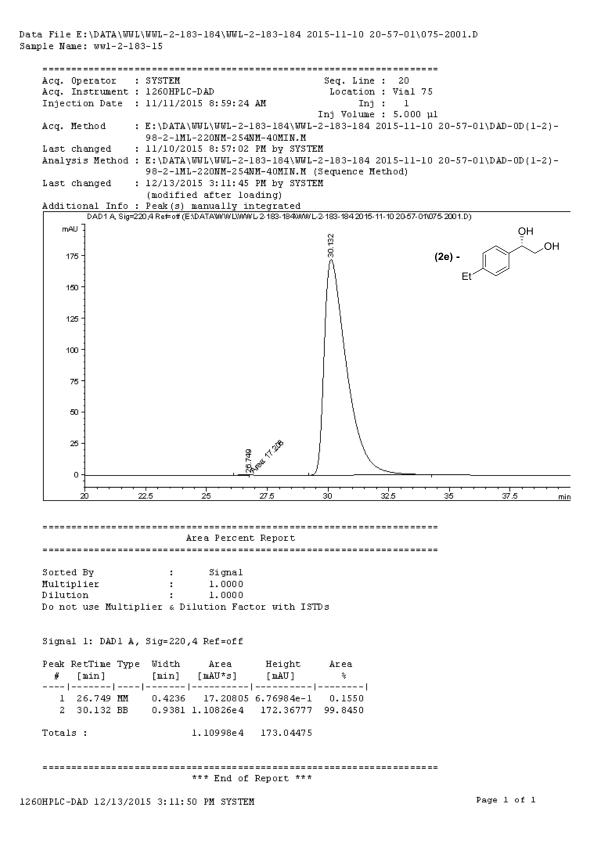
*** End of Report ***

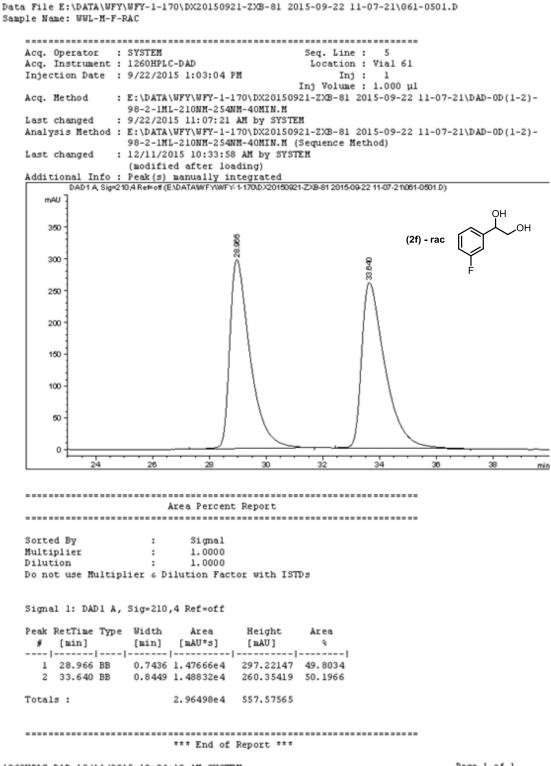
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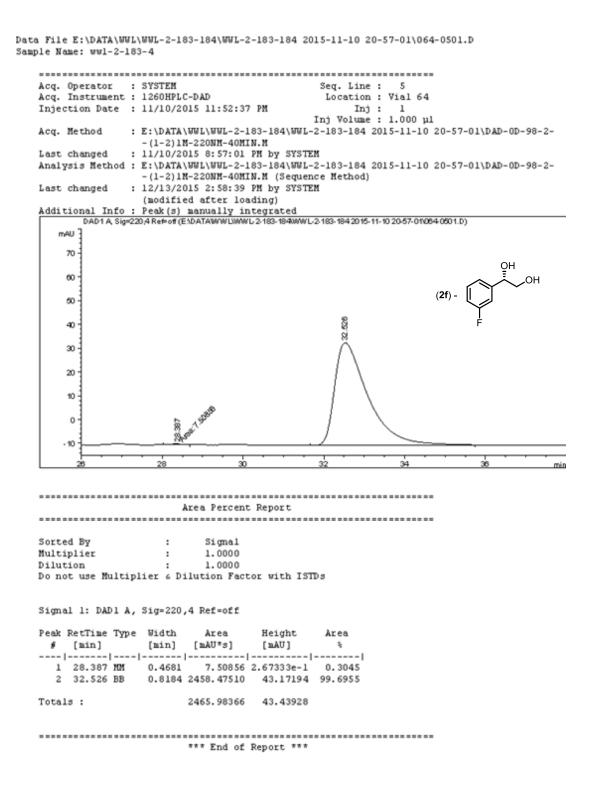
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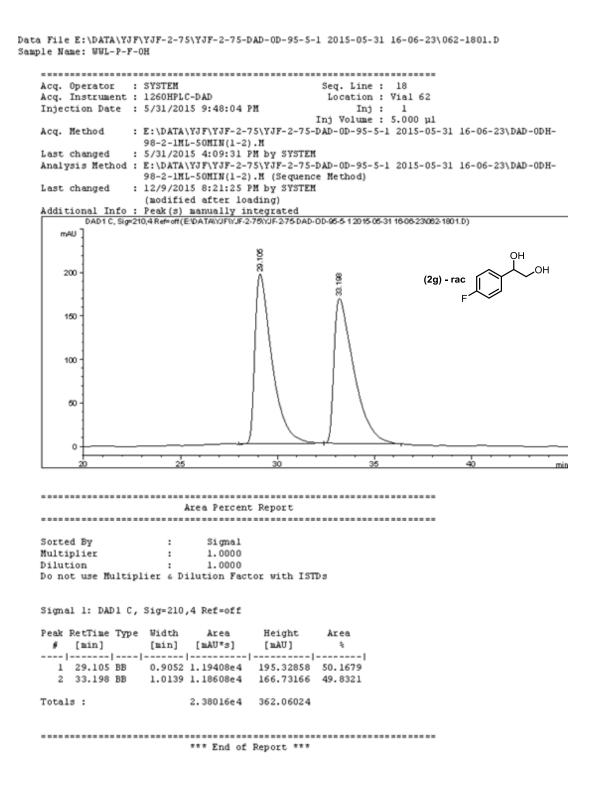




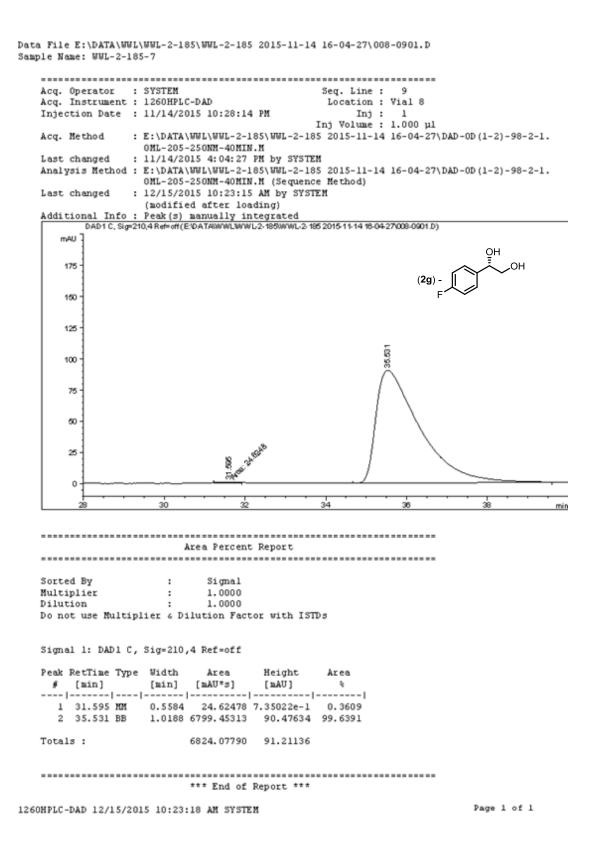
1260HPLC-DAD 12/11/2015 10:34:10 AM SYSTEM

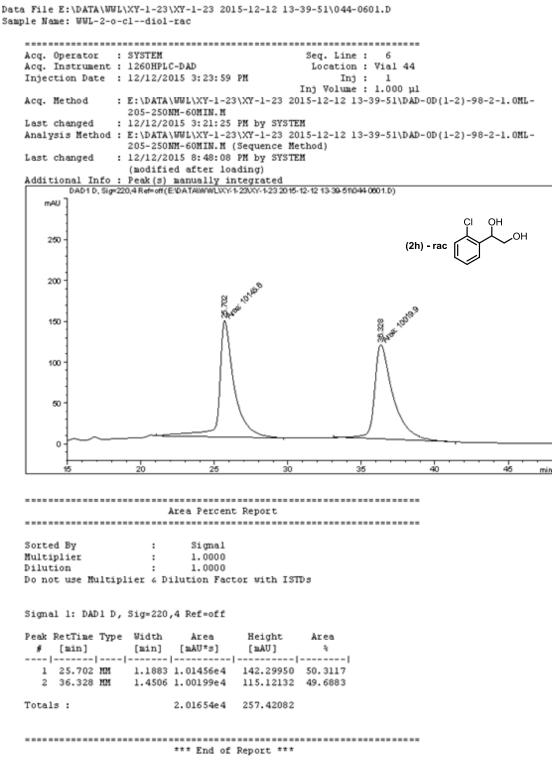


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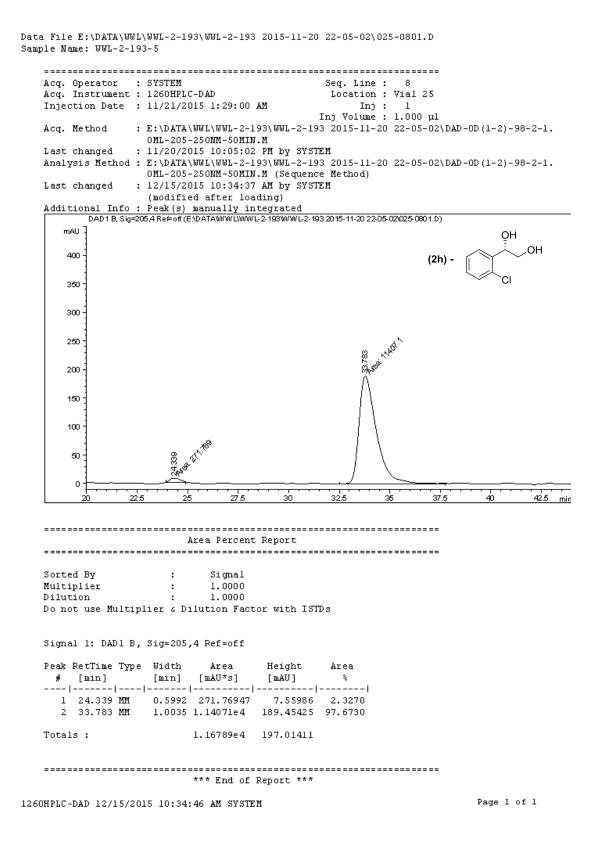


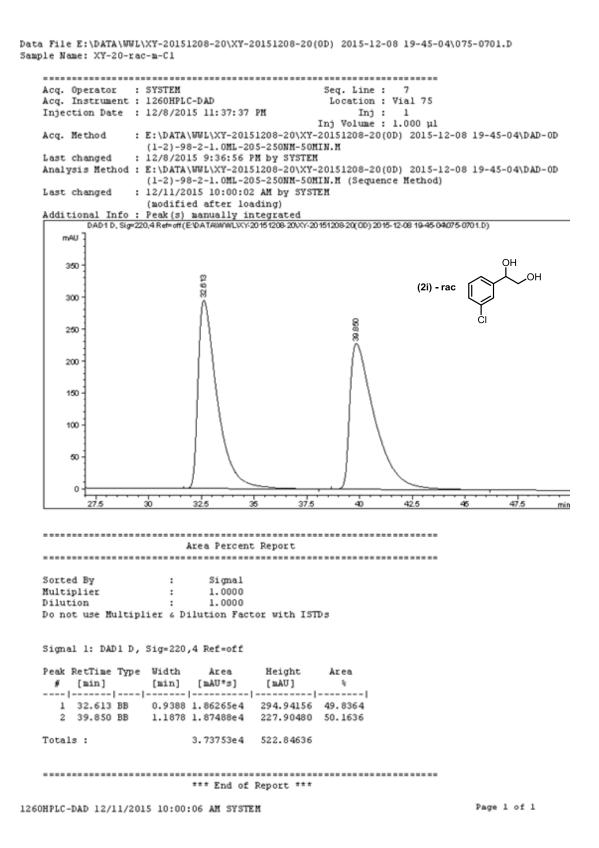
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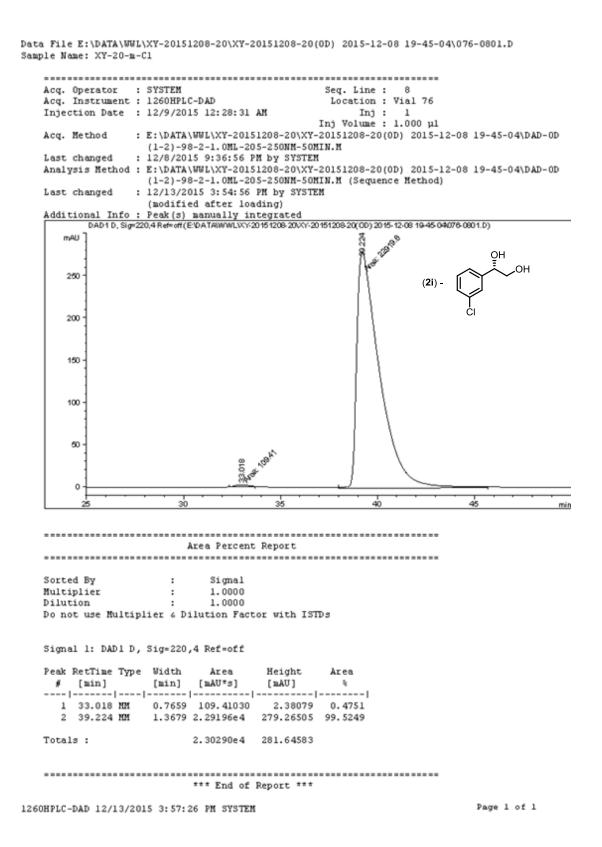


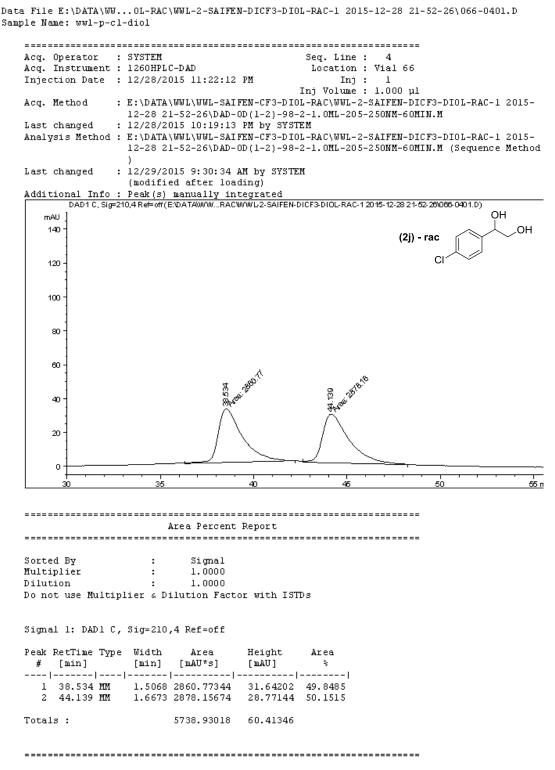


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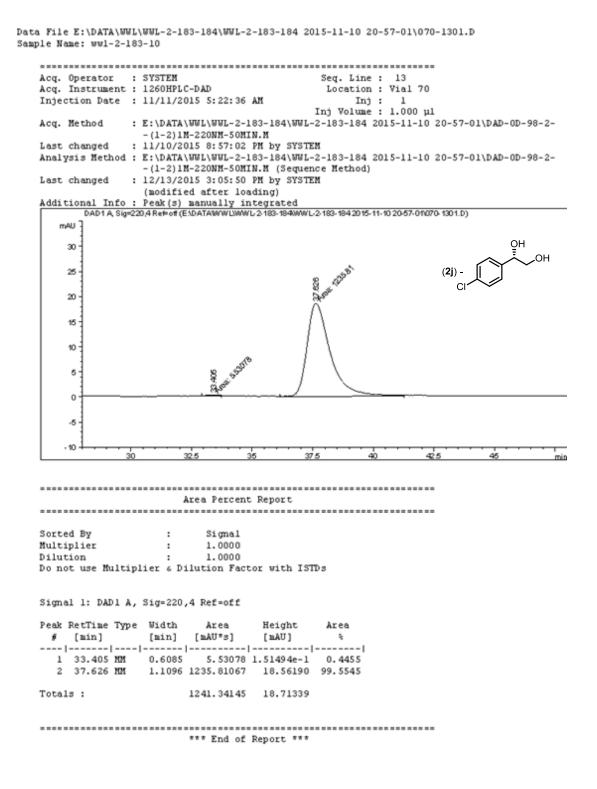




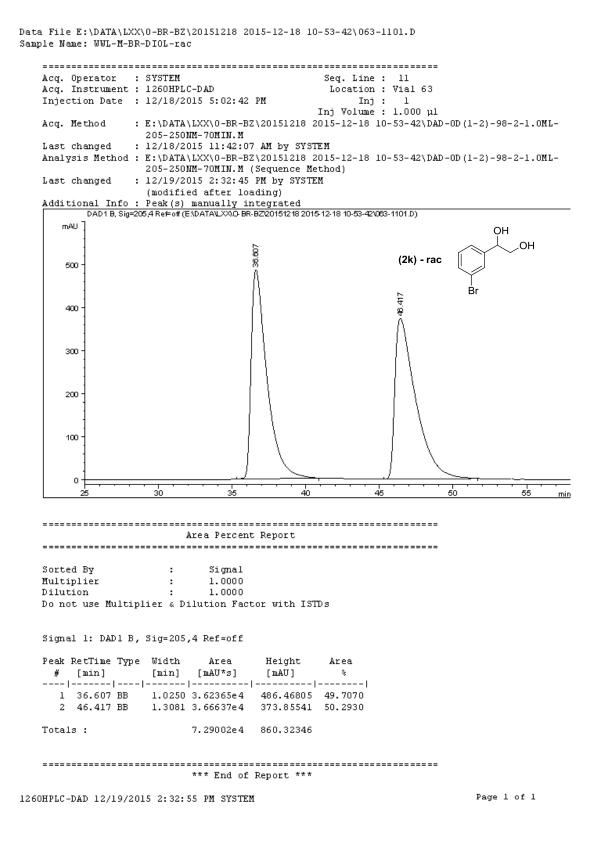


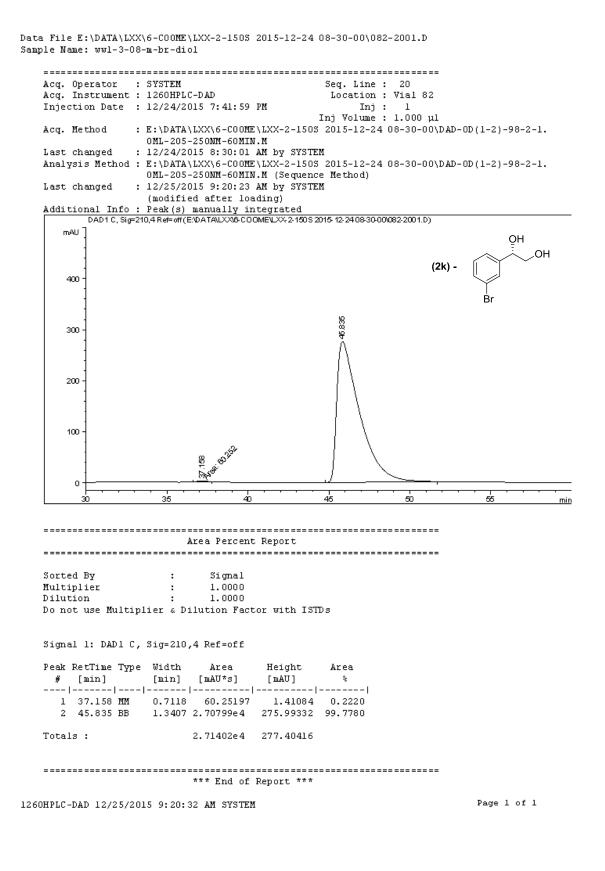


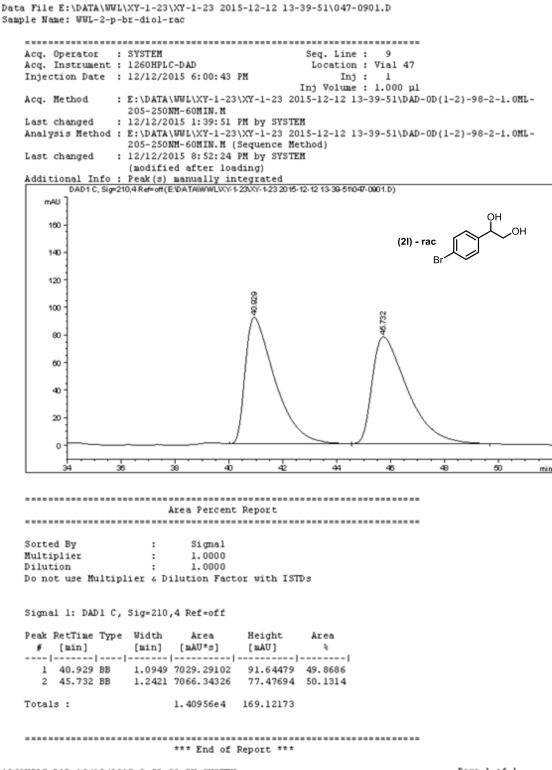
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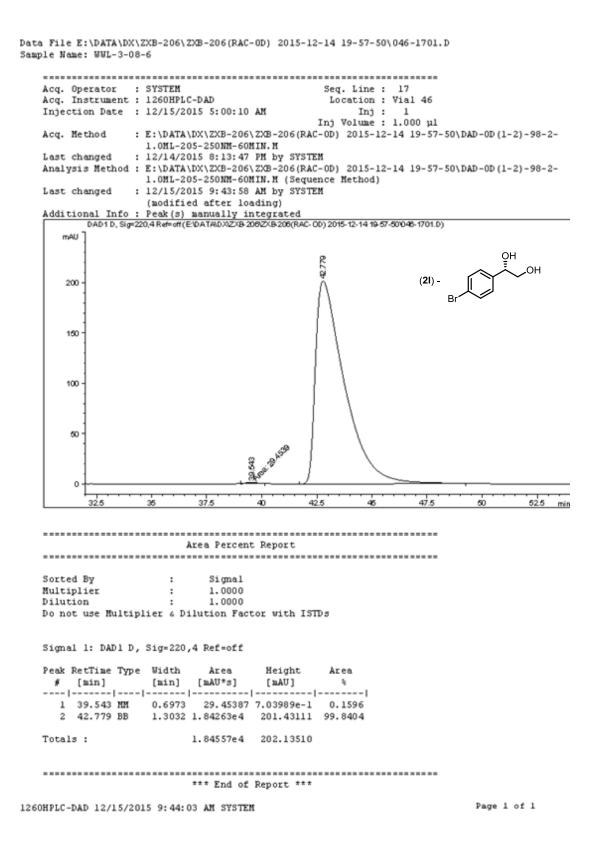
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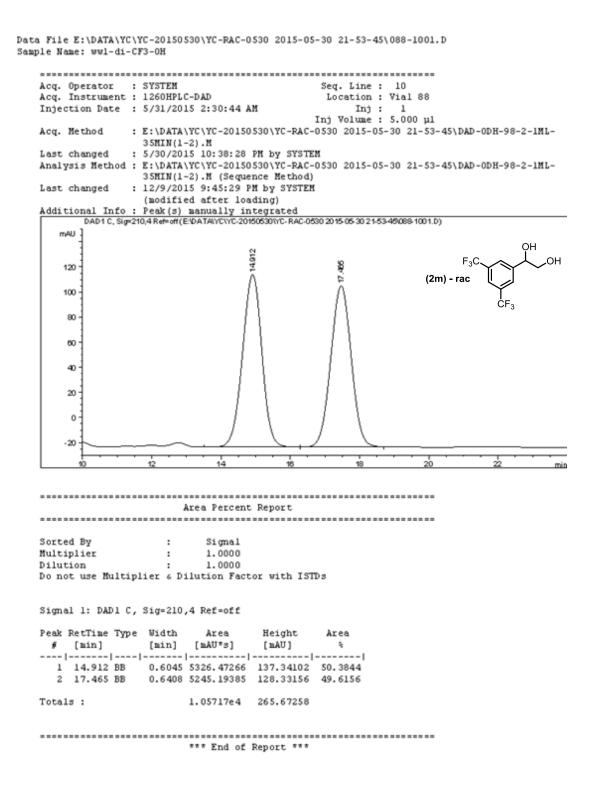




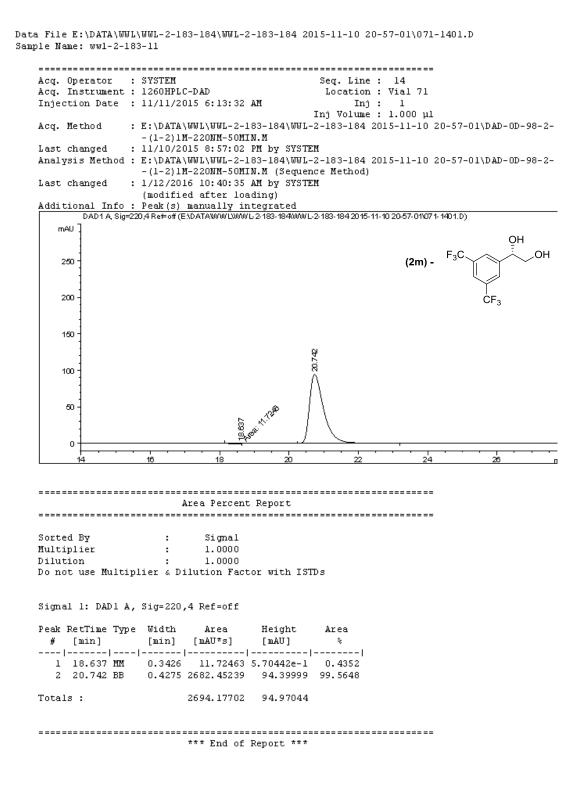


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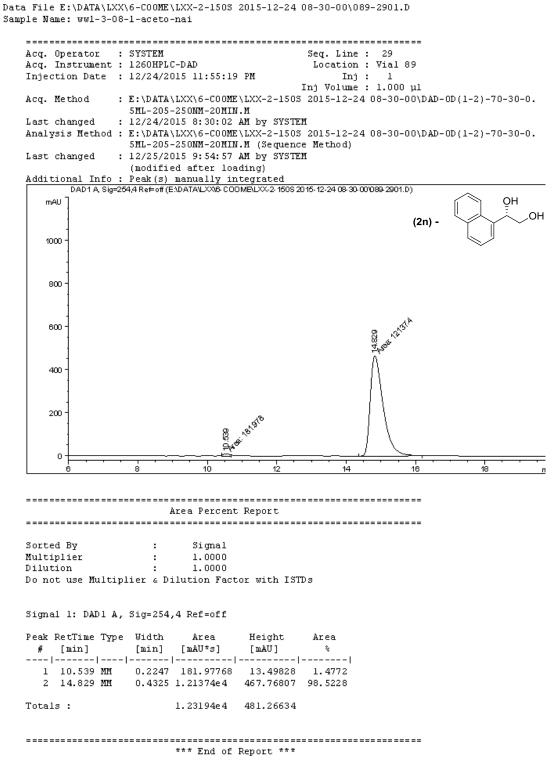
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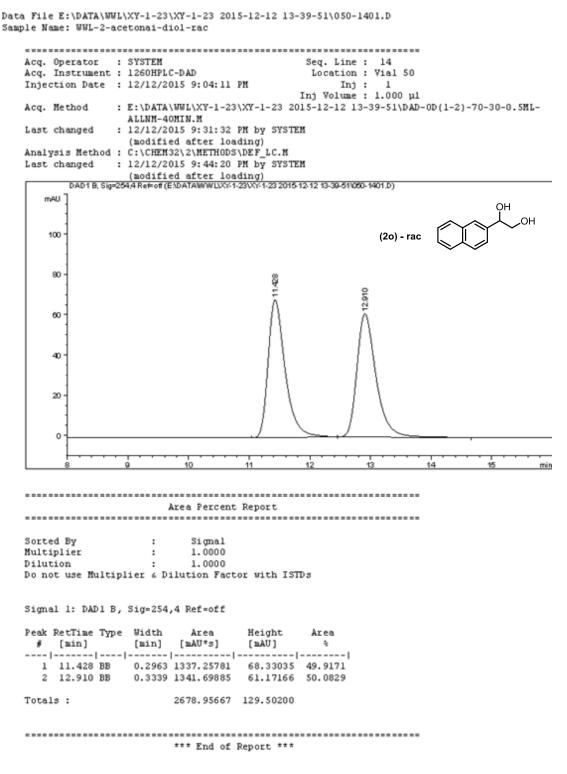
Data File E:\DATA\WWL\WWL-185RAC\WWL-2-185RAC% 2015-11-12 14-23-48\003-0501.D Sample Name: WWL-NAI-RAC

Acq. Operator : SYSTEM Acq. Instrument : 1260HPLC-DAD Seq. Line : 5 Location : Vial 3 1 Injection Date : 11/12/2015 4:39:33 PM Inj : Inj Volume : 1.000 µl Acq. Method : E:\DATA\WWL\WWL-185RAC\WWL-2-185RAC% 2015-11-12 14-23-48\DAD-0D(1-2)-70-30-0.5ML-ALLNM-40MIN.M Last changed : 11/12/2015 2:23:48 PM by SYSTEM Analysis Method : E:\DATA\WWL\WWL-185RAC\WWL-2-185RACS 2015-11-12 14-23-48\DAD-OD(1-2)-70-30-0.5ML-ALLNM-40MIN.M (Sequence Method) : 12/11/2015 4:04:59 PM by SYSTEM Last changed (modified after loading) Additional Info : Peak(s) manually integrated DAD1C, Sig=210,4 Ref=off(E:DATAWWLUWWL185RACWWL-2-185RACS 2015-11-12 14-23-481003-0501.D) mAU 8 OH ē 1400 OH (2n) - rac ĥ 1200 15.682 1000 800 600 400 200 0 10 12 14 16 18 20 _____ Area Percent Report _____ Sorted By : Signal Multiplier 1.0000 : 1.0000 Dilution : Do not use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 C, Sig=210,4 Ref=off Peak RetTime Type Width Area Height Area [min] [mAU*s] # [min] [mAU] * 1 10.783 VV 0.2765 2.49964e4 1359.38037 49.4576 2 15.562 BB 0.4220 2.55446e4 919.91034 50.5424 Totals : 5.05410e4 2279.29071

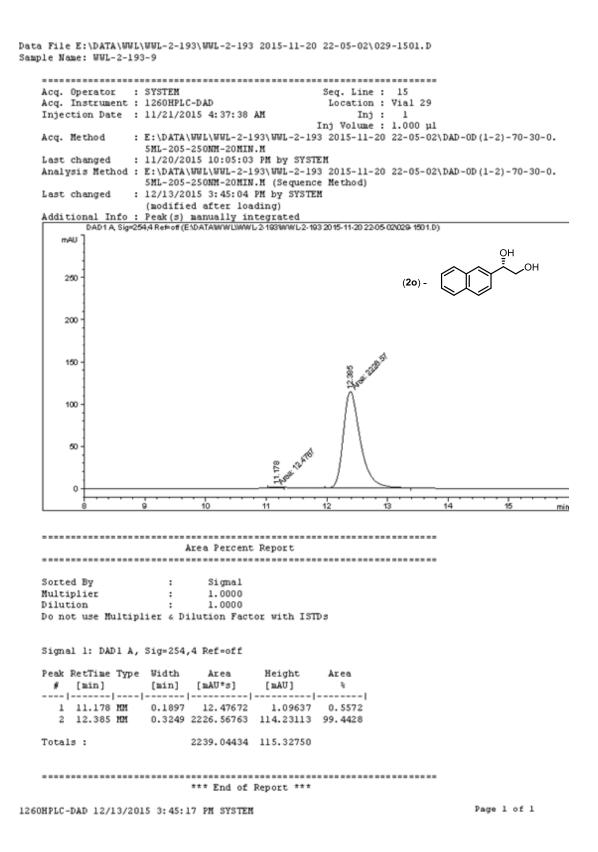
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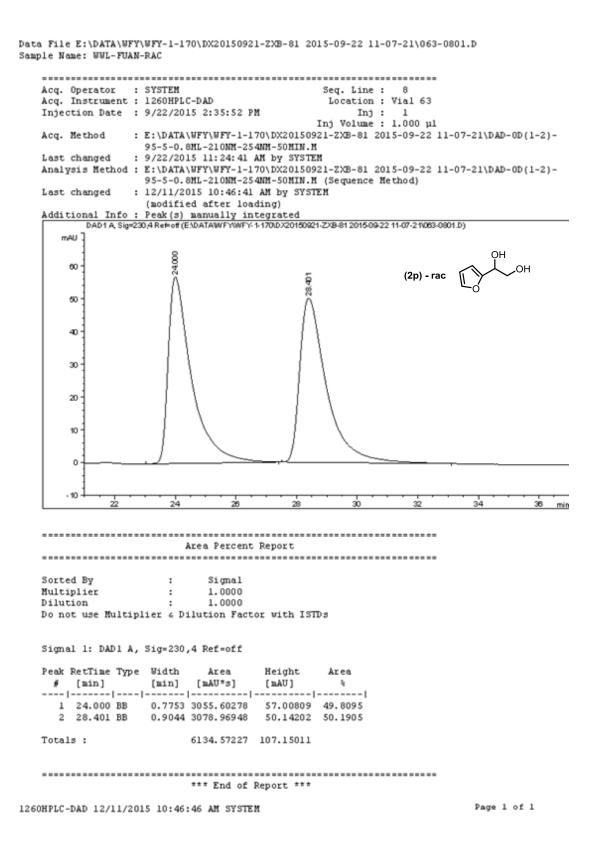


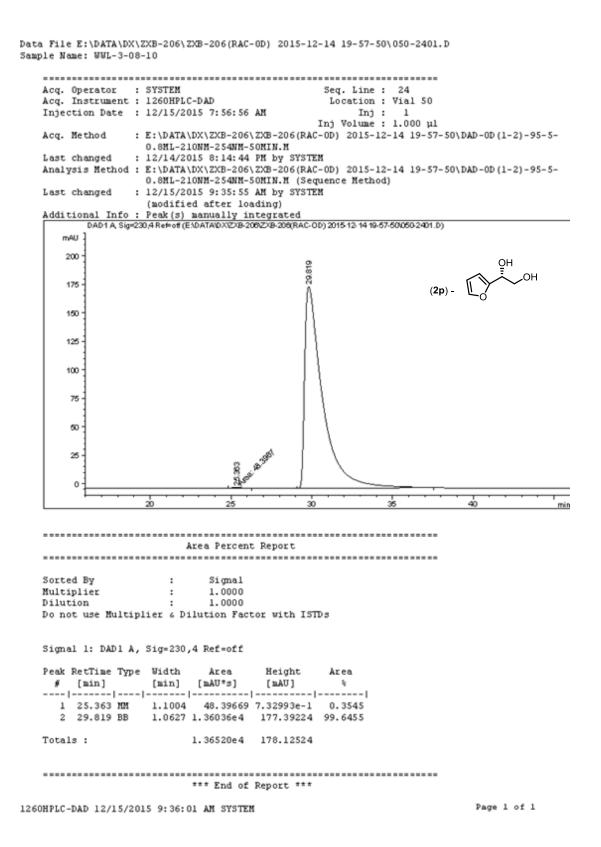
1260HPLC-VWD 12/25/2015 9:55:17 AM SYSTEM



1260HPLC-DAD 12/12/2015 9:44:24 PM SYSTEM







Sample Name: wwl-saifen-OH Acq. Operator : SYSTEM Acq. Instrument : 1260HPLC-DAD Seq. Line : 37 Location : Vial 69 Injection Date : 5/30/2015 8:36:24 AM Inj : 1 Inj Volume : 5.000 µl Acq. Method : E:\DATA\LP\LP20150529\LP20150529-1 2015-05-29 19-00-52\DAD-0DH-95-5-1ML-30MIN(1-2).M Last changed : 5/30/2015 8:57:11 AM by SYSTEM (modified after loading) Analysis Method : E:\DATA\LP\LP20150529\LP20150529-1 2015-05-29 19-00-52\DAD-0DH-95-5-1ML-30MIN(1-2).M (Sequence Method) Last changed : 1/16/2016 3:54:56 PM by SYSTEM (modified after loading) Additional Info : Peak(s) manually integrated DAD1 B, Sig=210,4 Re≑off (E:DATALP:LP:201505294120150529 1 201505 29 19-00-52'069-3701.D) mALL OH .OH (2q) -rac 800 600 4 10.665 400 200 0 · · · 10 11 13 Area Percent Report Sorted By Signal : 1.0000 : Multiplier Dilution Do not use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 B, Sig=210,4 Ref=off Peak RetTime Type Width Area Height Area # [min] [mAU*s] [mAU] % 1 9.174 BV 0.3086 7663.20947 365.43793 49.2618 2 10.655 VB 0.3598 7892.88867 324.47595 50.7382 1.55561e4 689.91388 Totals : *** End of Report ***

Data File E:\DATA\LP\LP20150529\LP20150529-1 2015-05-29 19-00-52\069-3701.D

1260HPLC-DAD 1/16/2016 3:55:02 PM SYSTEM

Data File E:\DATA\YJF\YJF-2-167\YJF-2-167RE-DAD-0D-95-5-1 2015-10-05 10-00-06\011-0201.D Sample Name: YJF-2-167 Acq. Operator : SYSTEM Acq. Instrument : 1260HPLC-DAD Seq. Line : 2 Location : Vial 11

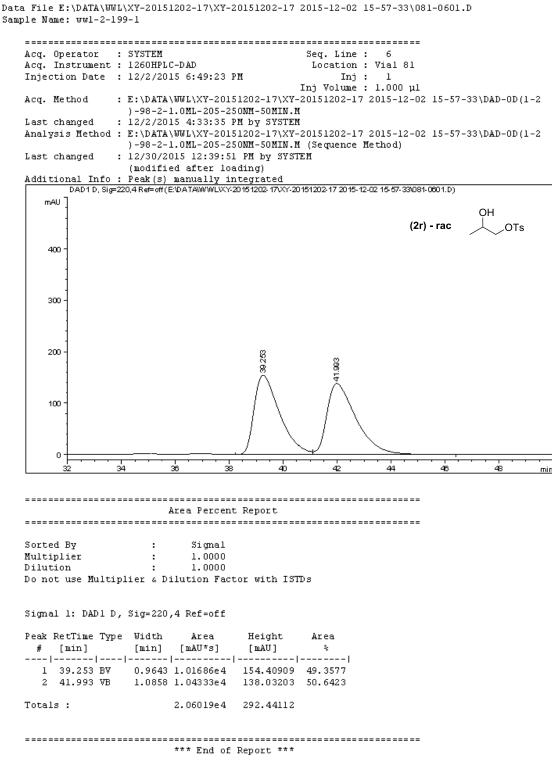
Injection Date : 10/5/2015 10:21:57 AM Inj: 1 Inj Volume : 5.000 µl Acq. Method : E:\DATA\YJF\YJF-2-167\YJF-2-167RE-DAD-0D-95-5-1 2015-10-05 10-00-06\DAD-0D(1-2)-95-5-1ML-220NM-254NM-20MIN.M Last changed : 10/5/2015 10:00:06 AM by SYSTEM Analysis Method : E:\DATA\YJF\YJF-2-167\YJF-2-167RE-DAD-0D-95-5-1 2015-10-05 10-00-06\DAD-OD(1-2)-95-5-1ML-220NM-254NM-20MIN.M (Sequence Method) Last changed : 1/15/2016 10:43:43 PM by SYSTEM (modified after loading) Additional Info : Peak(s) manually integrated DAD1A Sig=220.4 Re≠off (E:DATAWJ...F-2-167WJF-2-167RE-DAD-OD-95-5-1 2015-10-05 10-00-060011-0201.D) - πΔ11 T ∕он 800 (2q) -600 9.018 400 200 887 1 80 Baylor 0. 12 ż 10 11 6 8 min Area Percent Report -Sorted By Sional : 1.0000 Multiplier : 1.0000 Dilution : Do not use Multiplier & Dilution Factor with ISTDs Signal 1: DAD1 A, Sig=220,4 Ref=off Peak RetTime Type Width Area Height Area ÷ # [min] [min] [mAU*s] [mAU]
 1
 7.588 MM
 0.2018
 28.94666
 2.39117
 0.4627

 2
 9.018 VB
 0.2177
 6227.20752
 443.84637
 99.5373
 --- | ------ | ---------1

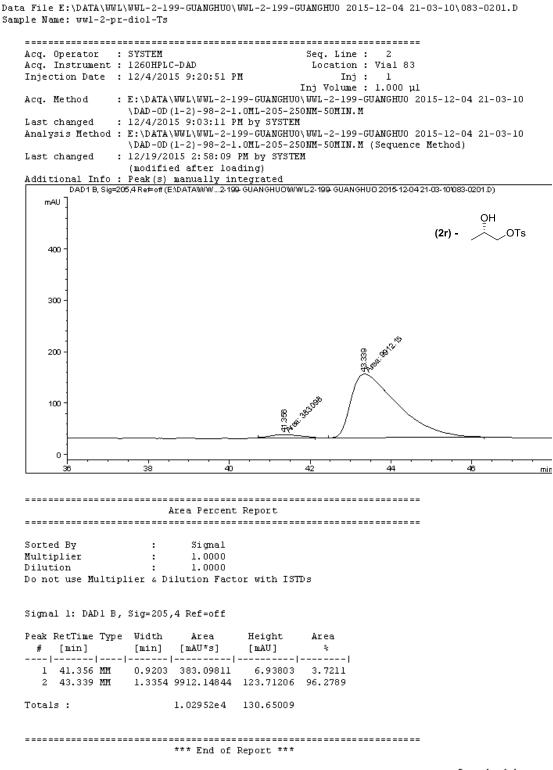
6256.15418 446.23755 Totals :

*** End of Report ***

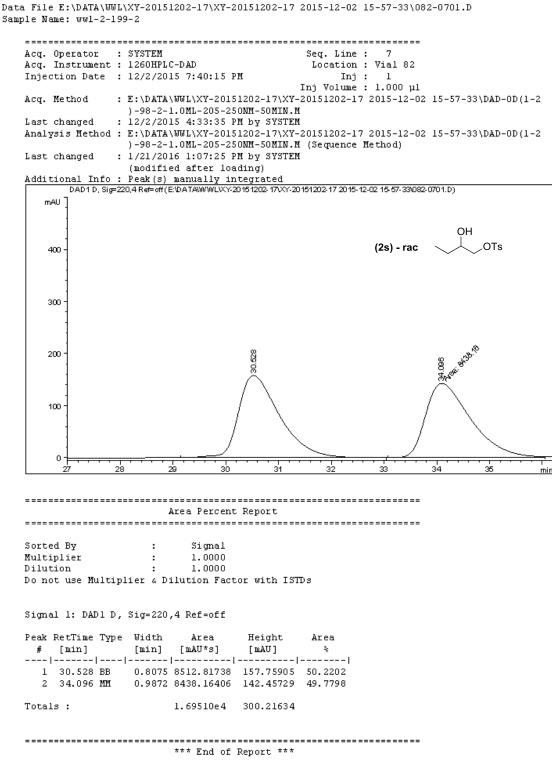
1260HPLC-DAD 1/15/2016 10:43:51 PM SYSTEM



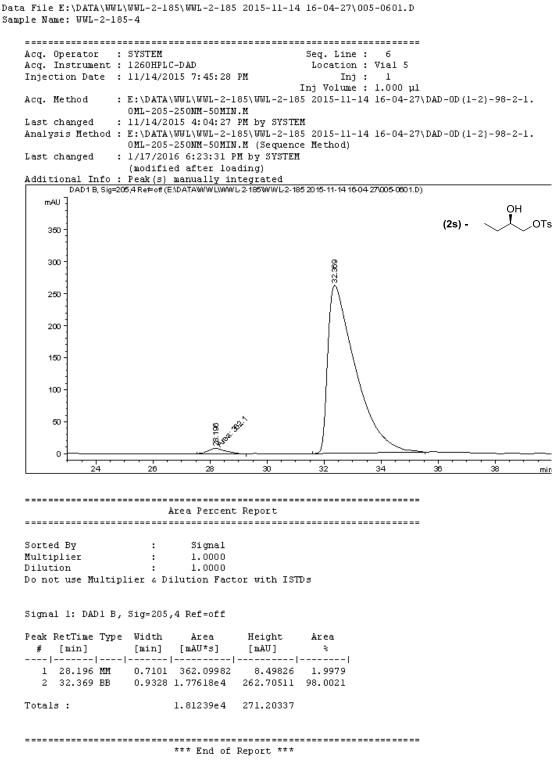
1260HPLC-DAD 12/30/2015 12:39:55 PM SYSTEM



1260HPLC-DAD 12/19/2015 2:58:12 PM SYSTEM

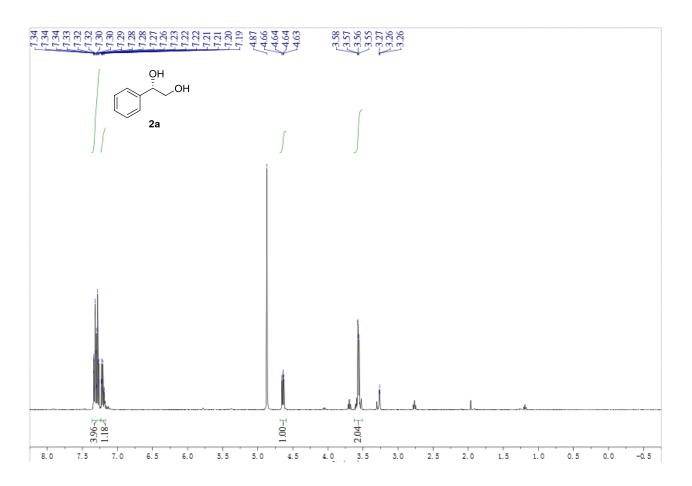


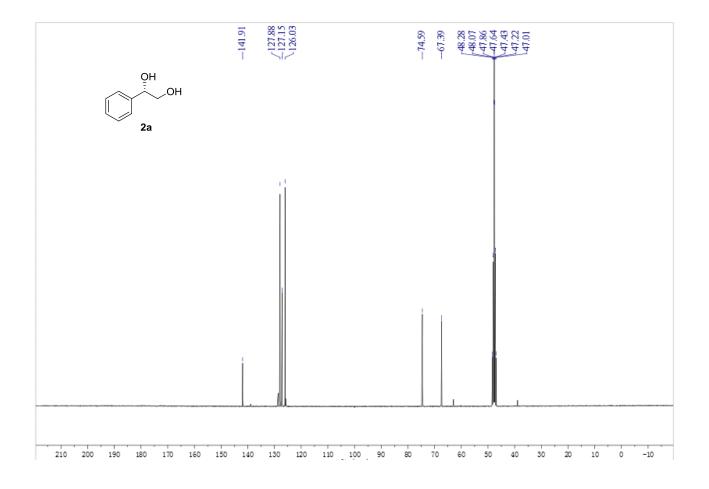
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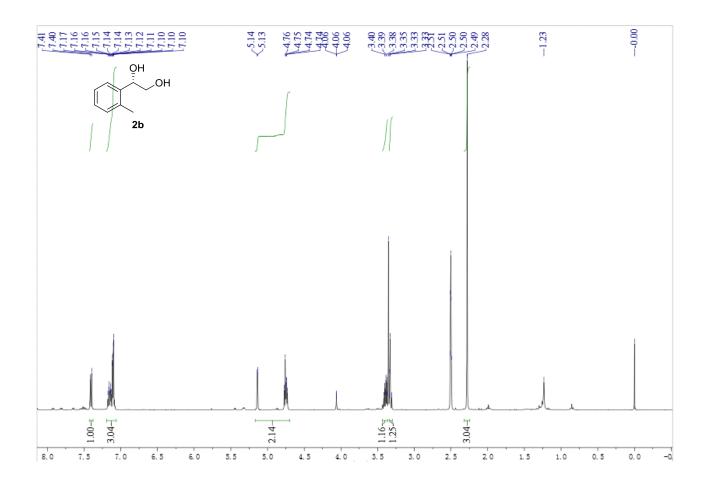


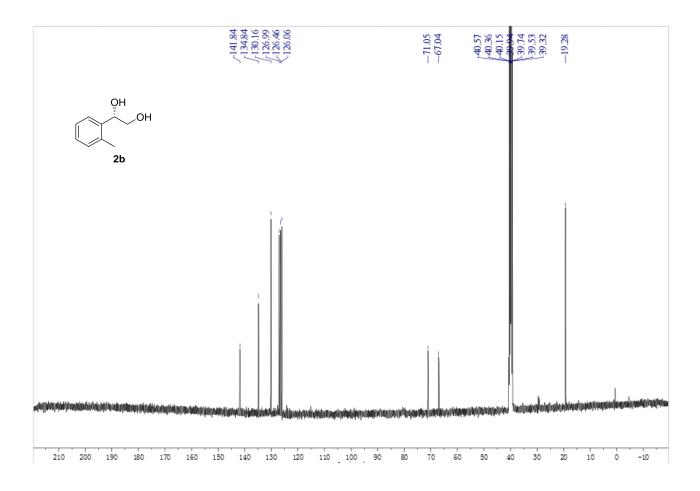
1260HPLC-DAD 1/17/2016 6:23:36 PM SYSTEM

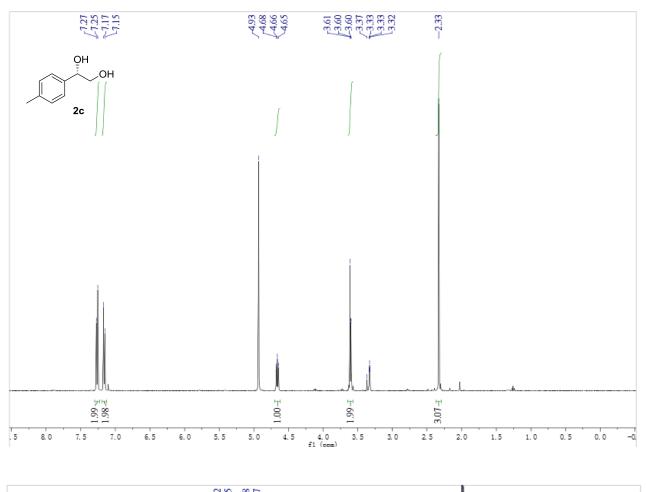
IV. NMR spectra

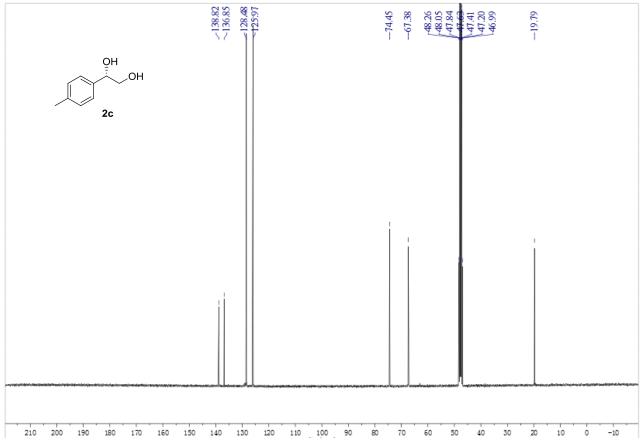


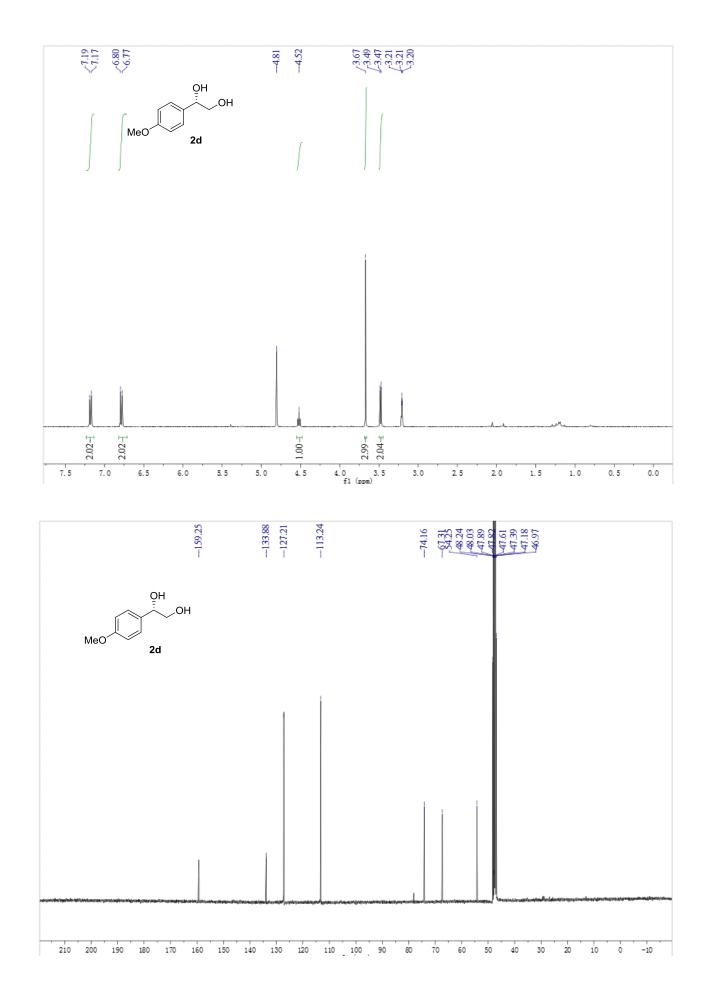


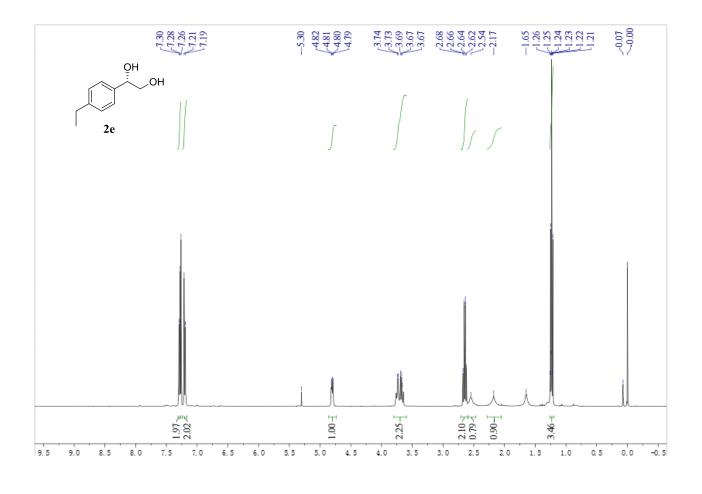


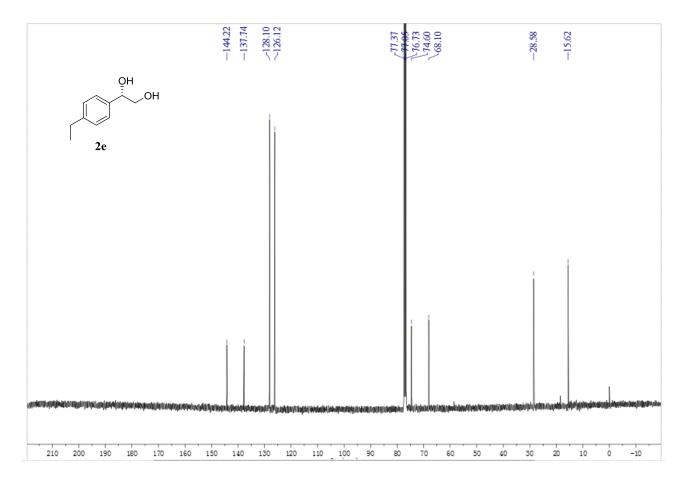


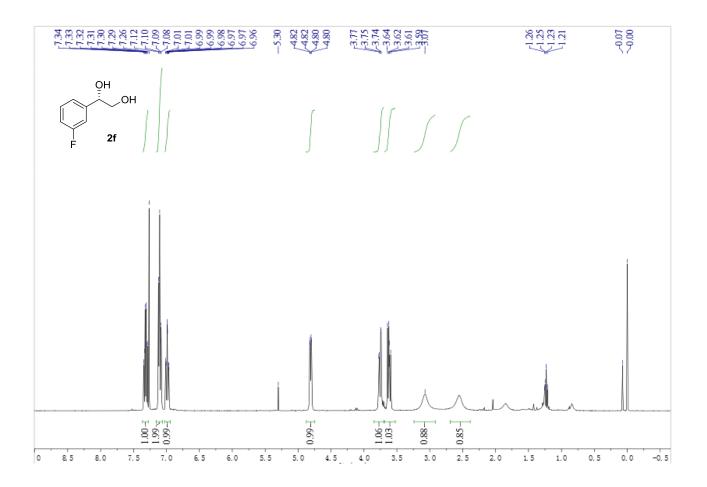


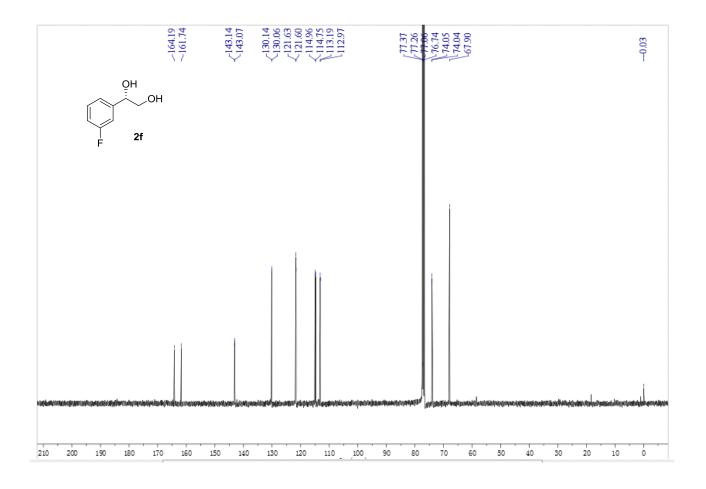


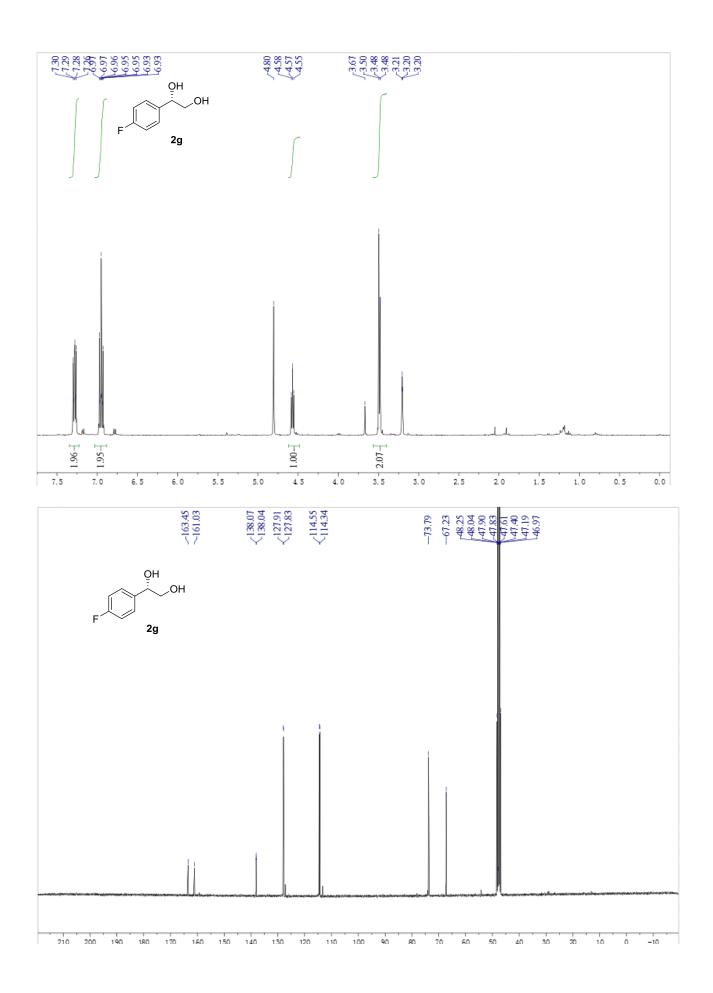


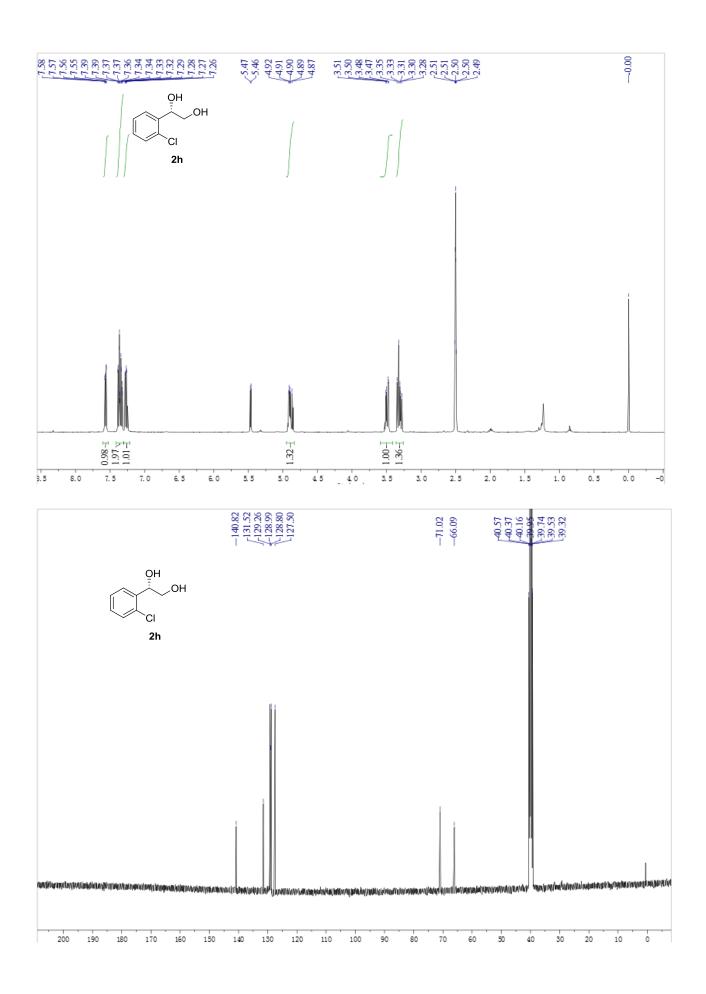


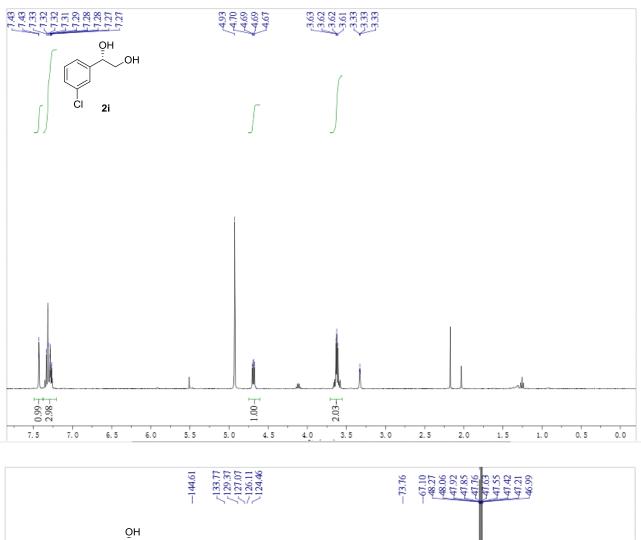


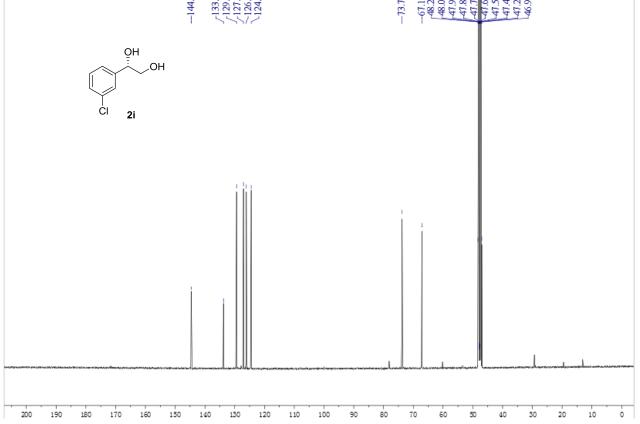


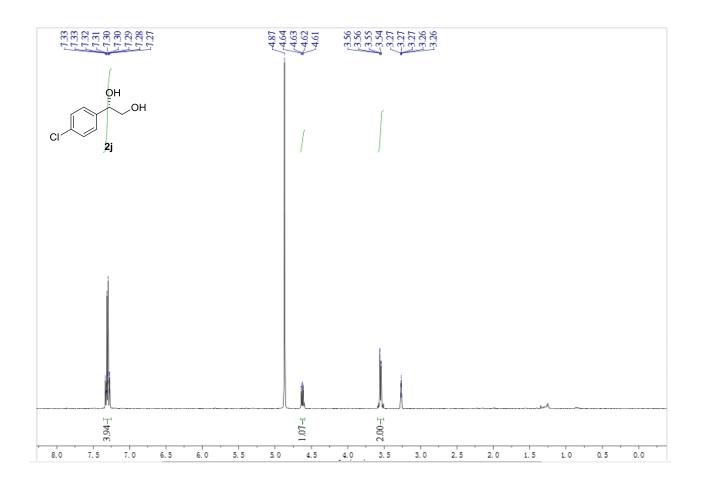


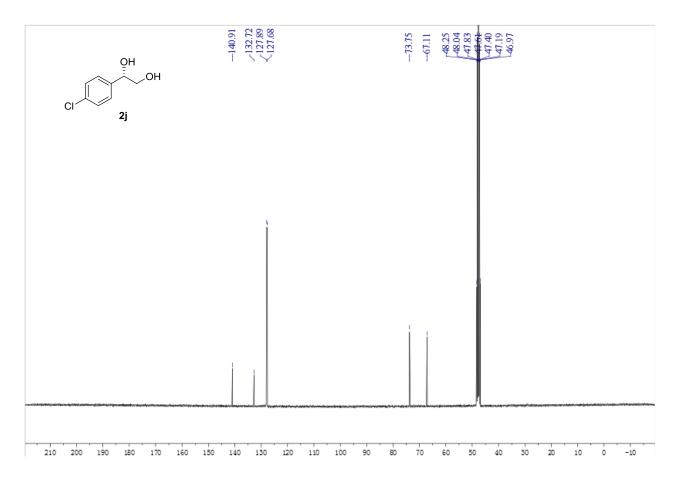


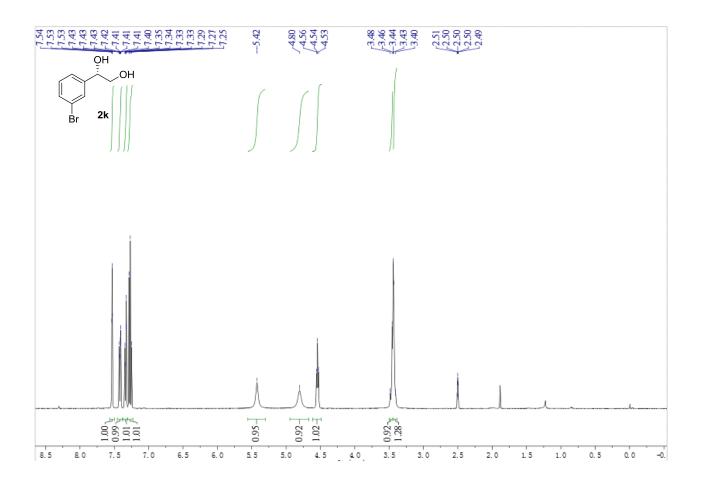


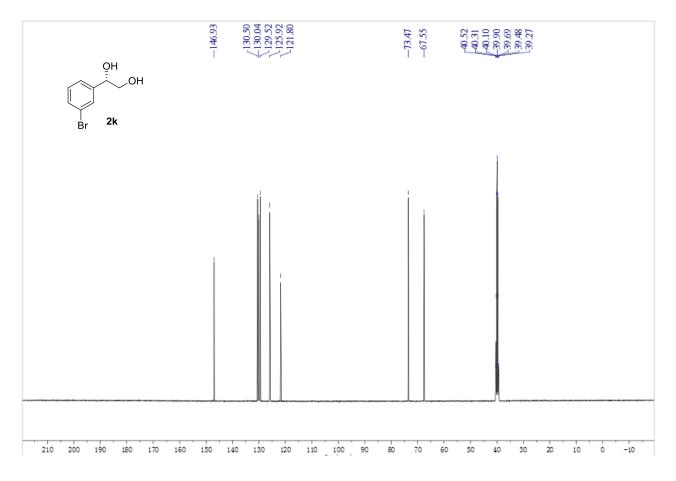


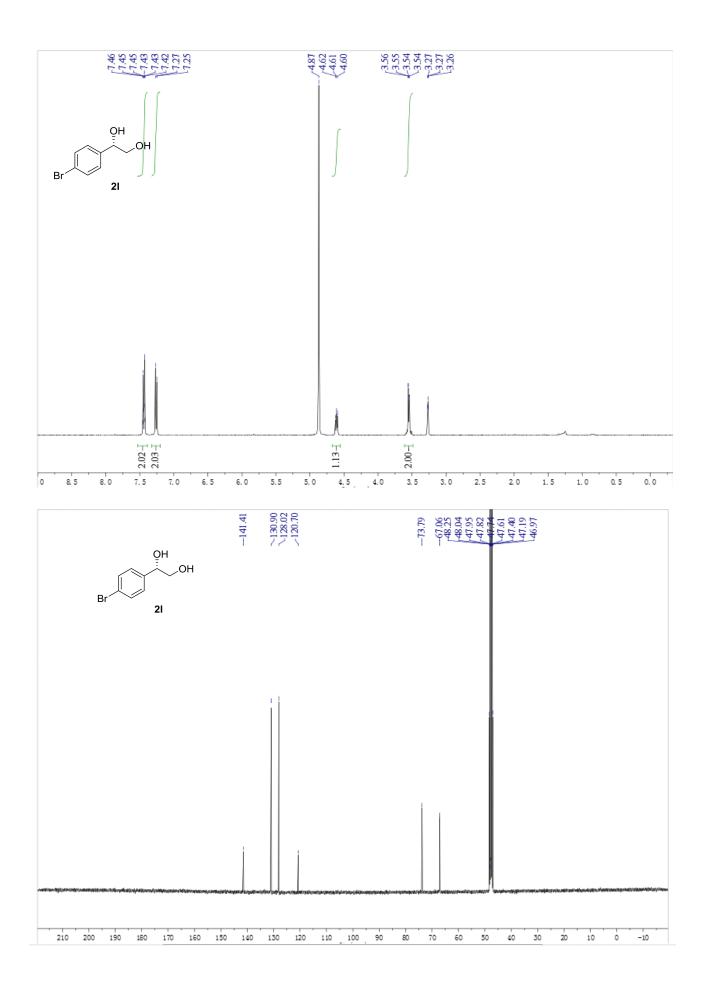


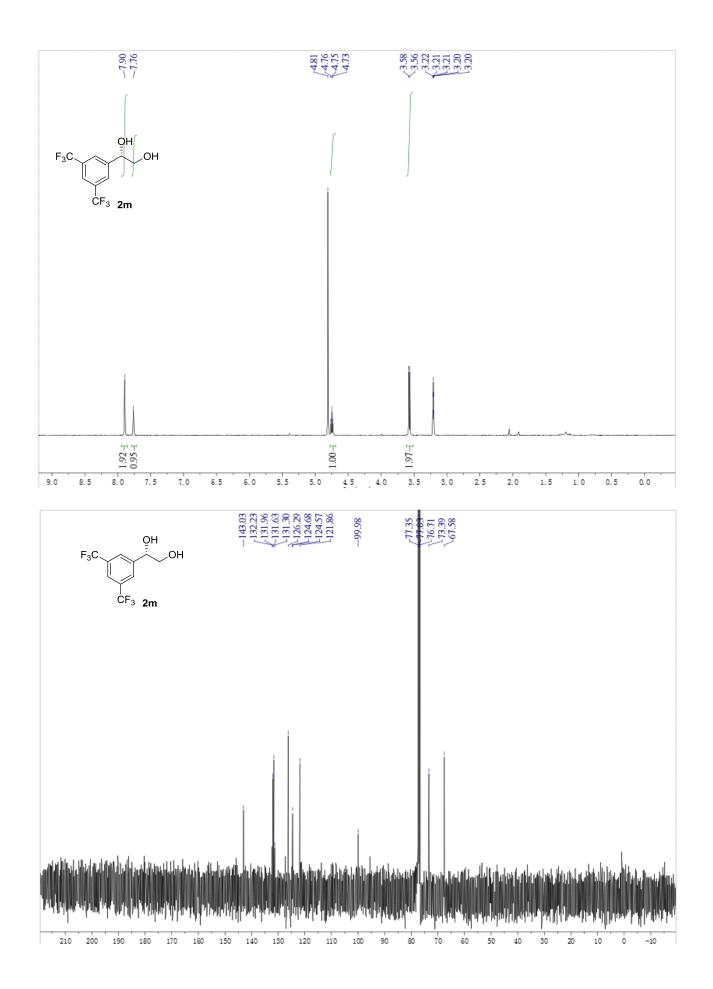


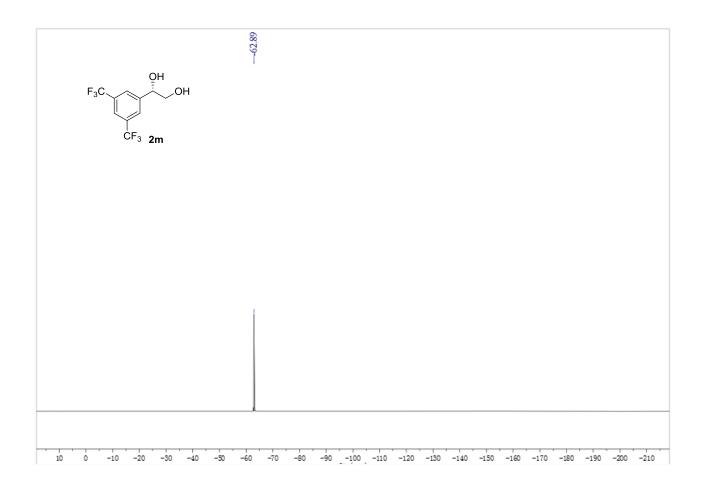


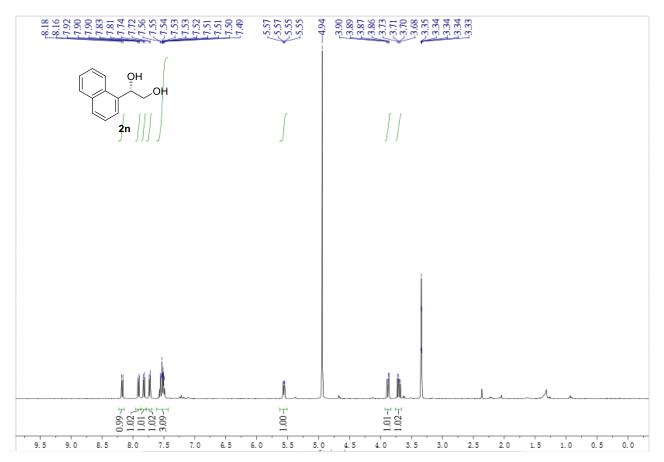


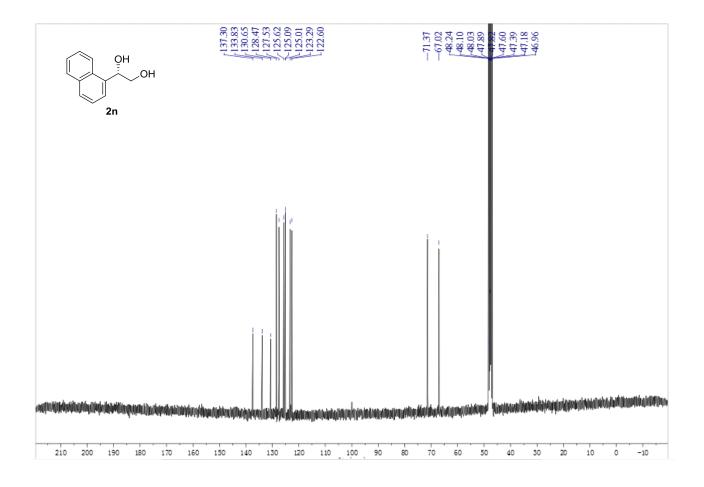


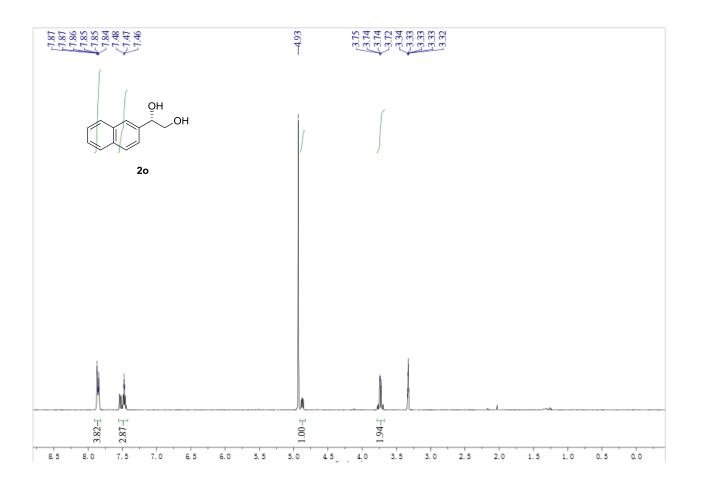


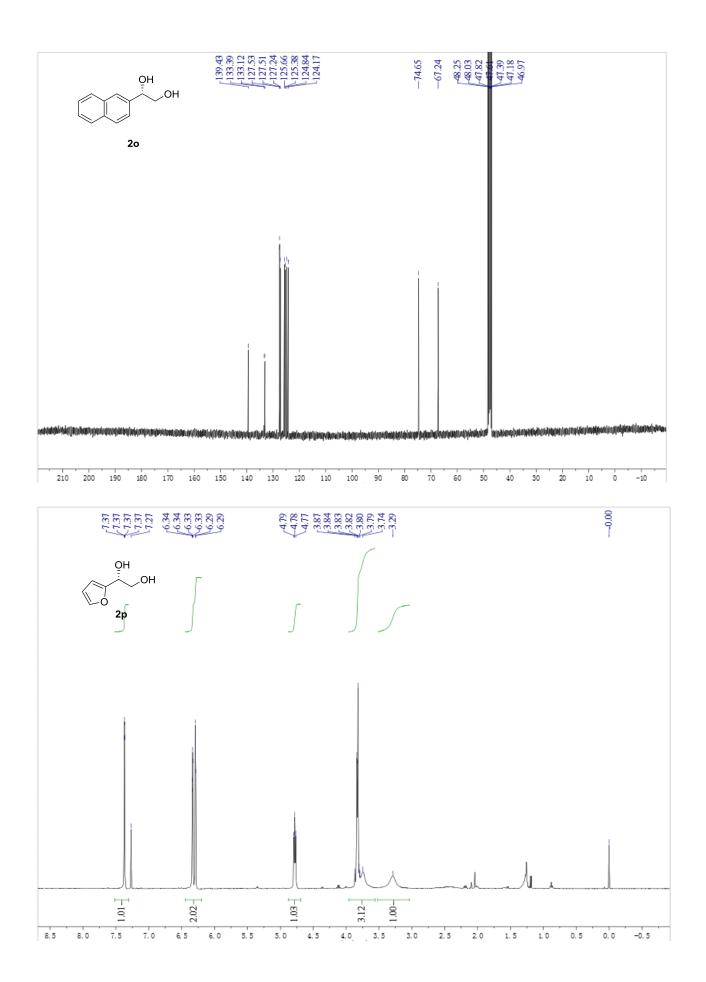


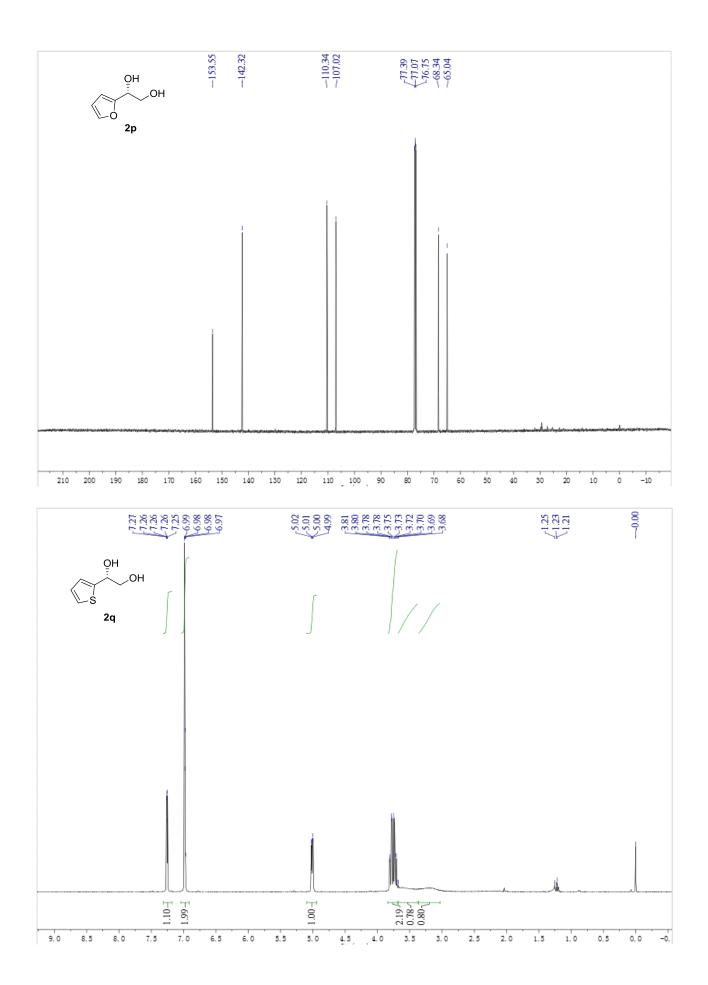


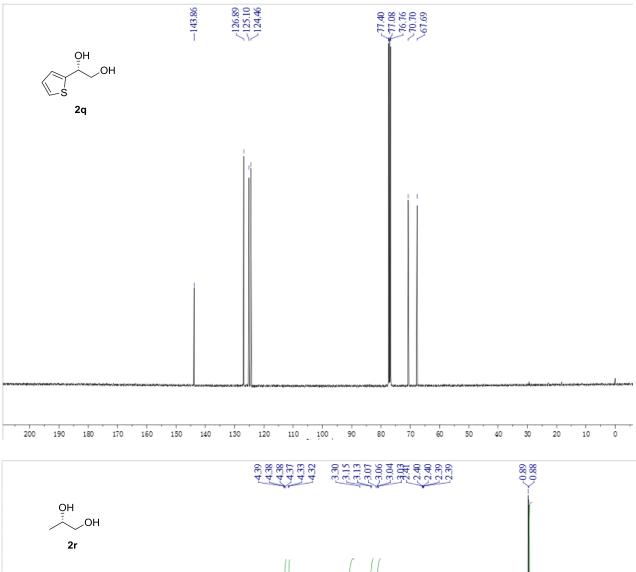


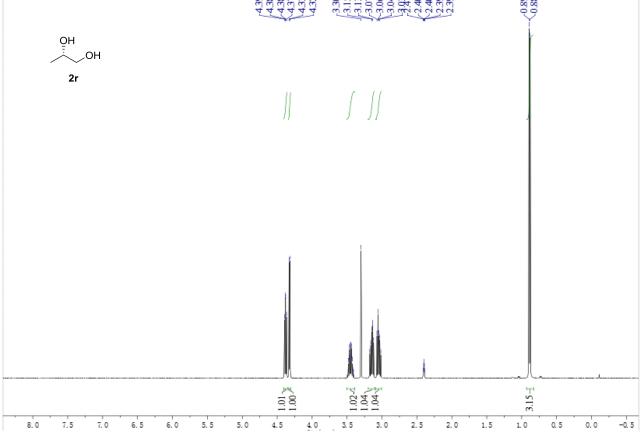


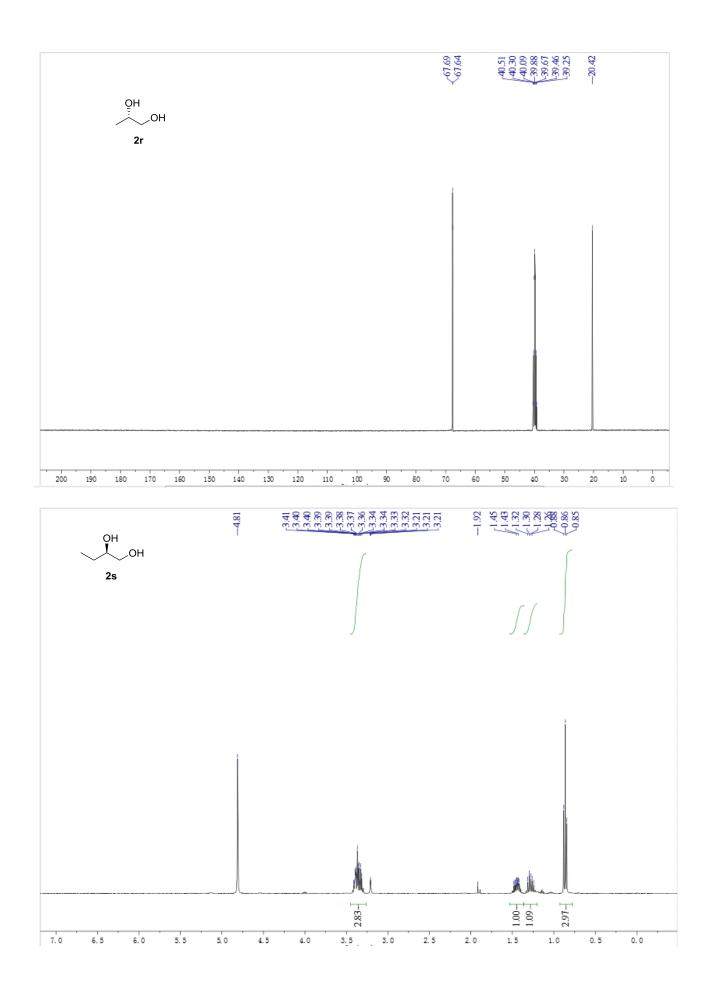


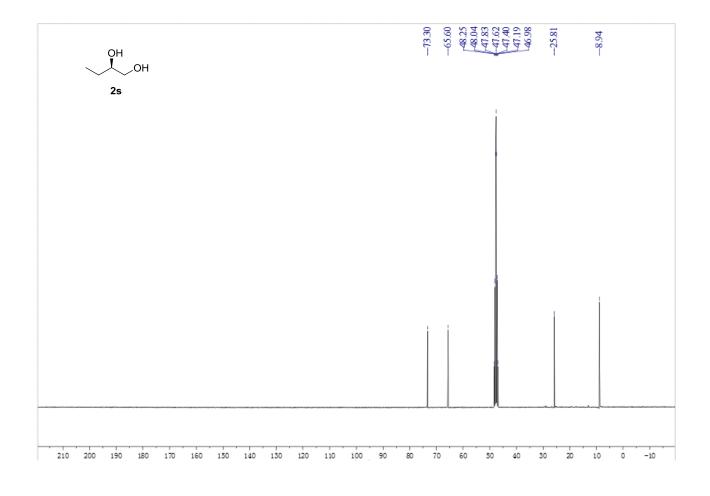












V. References:

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