

Supporting Information:

Highly Enantioselective Hydrogenation of 2-Substituted-2-Alkenols Catalysed by ChenPhos-Rh Complex

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II. General Procedure and Analytical Data of Hydrogenation Products

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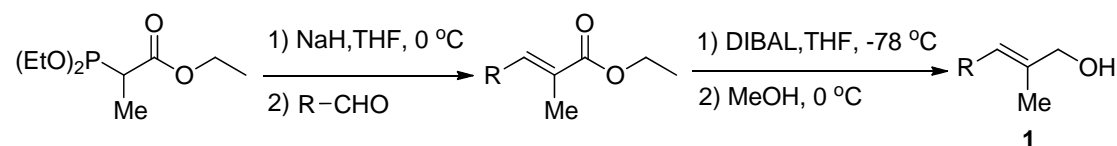
IV. The preparation of (-)-Amorolfine hydrochloride

V. NMR Spectra

VI. HPLC Charts of Hydrogenation Products

General: All the air or moisture sensitive reactions and manipulations were performed under a nitrogen atmosphere by using standard Schlenk techniques. Melting points were measured on a RY-I apparatus and uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 300 spectrometer in CDCl_3 or CD_3OD . Enantiomeric excesses of the asymmetric hydrogenation products were determined by chiral HPLC and chiral GC. Optical rotations were measured on a Perkin–Elmer 343 polarimeter. Anhydrous Et_2O , THF and TBME were distilled from sodium benzophenone ketyl. Anhydrous CH_2Cl_2 , NEt_3 and DMF were freshly distilled from calcium hydride under nitrogen atmosphere. Anhydrous MeOH was distilled from magnesium under nitrogen atmosphere. $\text{Rh}(\text{NBD})_2\text{BF}_4$ was purchased from Aldrich Co. and used as received. Hydrogen gas (99.9%) was purchased from Ally Gas Inc., Xi'an.

I. Preparation and Analytical Data of Substrates

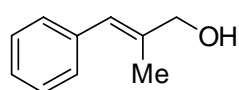


Typical procedure: Most of the allylic alcohols were prepared from corresponding ester according to literature method with modifications.

To a dispersion of sodium hydride (60% in mineral oil, 1.2 g, 0.03 mol) in THF (30 mL), was added Triethyl 2-phosphonopropionate (6.73 g, 0.03 mol) slowly to maintain 0 °C. The reaction was stirred for another 1 h at this temperature. The reaction was cooled to -78 °C and aldehyde (0.02 mol) was added dropwise. The reaction mixture was stirred for another 3 h at ambient atmosphere, and was poured on saturated NH_4Cl (5 mL). The phases were separated and the aqueous phase was extracted with Et_2O ($3 \times$

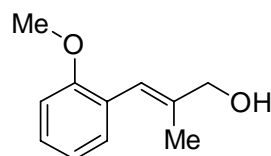
20 mL). The combined organic phases were washed with brine, dried over MgSO₄, and evaporated in vacuo. The residue was purified by chromatography on silica gel (petroleum ether /ethyl acetate = 10:1, v/v) to give product as colorless or red oil. This oil was dissolved in THF (30 mL), and the solution was cooled to -78 °C. To the solution was added 1 M solution of diisobutylaluminum hydride in hexane (40 mL, 0.04 mol) slowly with a syringe at such a rate that the temperature did not exceed -50 °C. After 30 min at -78 °C, the reaction was quenched by addition of methanol (5 mL). The reaction mixture was allowed to warm to room temperature and poured on saturated NH₄Cl with stirring. The aqueous phase was separated and extracted with ether. The organic extracts were sequentially washed with water and brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether /ethyl acetate = 3:1, v/v) to give the product.

(E)-2-methyl-3-phenylprop-2-en-1-ol (1a) ^[1]



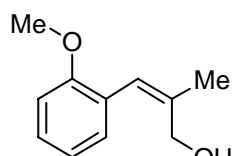
colorless oil, 74% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.35–7.19 (m, 5H), 6.52 (s, 1H), 4.17 (s, 2H), 2.00 (s, 1H), 1.89 (s, 3H).

(E)-3-(2-methoxyphenyl)-2-methylprop-2-en-1-ol (1b) ^[2]



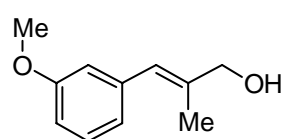
colorless oil, 43% yield. ¹H NMR (500 MHz, CDCl₃): 7.30–7.25 (m, 1H), 7.17–7.15 (m, 1H), 6.98–6.91 (m, 2H), 6.47 (s, 1H), 4.19 (s, 2H), 3.87 (s, 3H), 2.06 (d, *J* = 1.5 Hz, 3H), 1.71 (s, 1H). ¹³C NMR (500 MHz, CDCl₃): 156.8, 138.0, 130.5, 128.3, 126.2, 123.8, 120.4, 110.6, 62.9, 55.5, 21.6.

(Z)-3-(2-methoxyphenyl)-2-methylprop-2-en-1-ol (1s) ^[2]



colorless oil, 21% yield. ¹H NMR (500 MHz, CDCl₃): 7.30–7.25 (m, 2H), 7.00–6.91 (m, 2H), 6.64 (s, 1H), 4.26 (s, 2H), 3.87 (s, 3H), 1.89 (d, *J* = 1 Hz, 3H), 1.74 (s, 1H). ¹³C NMR (500 MHz, CDCl₃): 157.1, 137.9, 130.3, 128.0, 126.3, 120.7, 120.1, 110.3, 69.0, 55.4, 15.3.

(E)-3-(3-methoxyphenyl)-2-methylprop-2-en-1-ol (1c) ^[1]

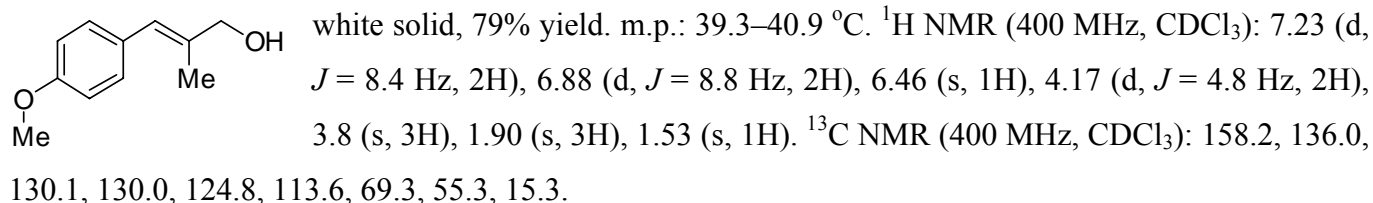


colorless oil, 72% yield. ¹H NMR (500 MHz, CDCl₃): 7.31–7.27 (m, 1H), 6.93–6.81 (m, 3H), 6.54 (s, 1H), 4.22 (s, 2H), 3.85 (s, 3H), 1.95 (d, *J* = 1 Hz, 3H), 1.77 (s, 1H). ¹³C NMR (500 MHz, CDCl₃): 159.4, 139.0, 138.0, 129.1, 124.9, 121.5, 114.5, 112.0, 69.0, 55.2, 15.4.

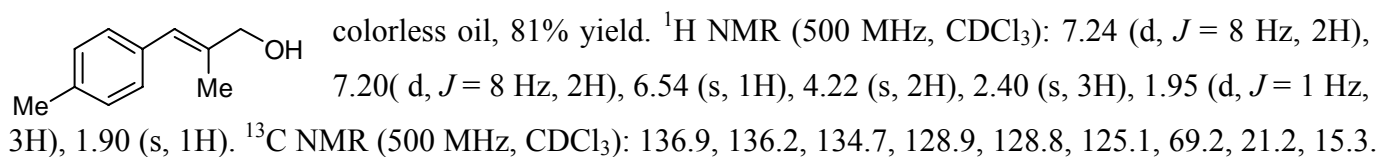
[1] Bausch C. C. *Angew. Chem. Int. Ed.* **2011**, 50, 5687-5690.

[2] Lee, Y. J. *Am. Chem. Soc.* **2008**, 130, 446–447.

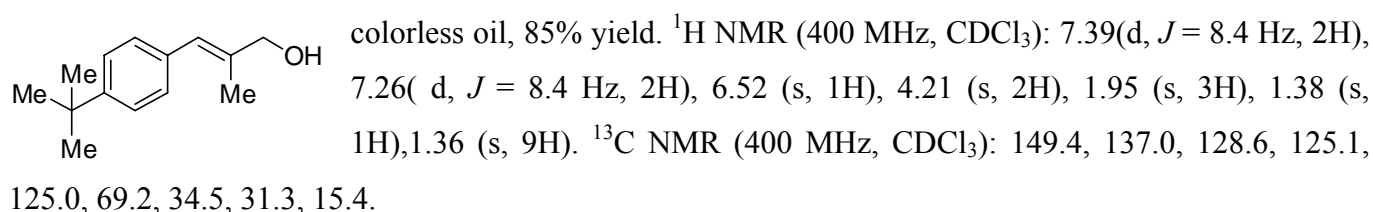
(E)-3-(4-methoxyphenyl)-2-methylprop-2-en-1-ol (1d) ^[1]



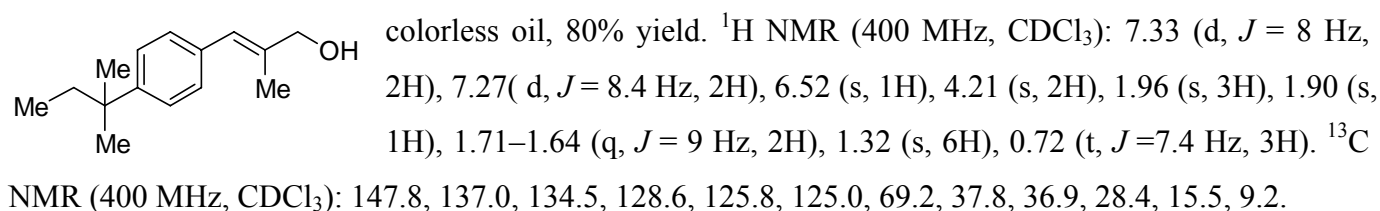
(E)-2-methyl-3-p-tolylprop-2-en-1-ol (1e) ^[1]



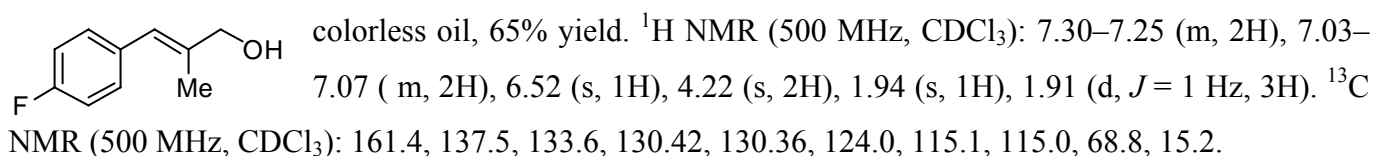
(E)-3-(4-(tert-butyl)phenyl)-2-methylprop-2-en-1-ol (1f) ^[3]



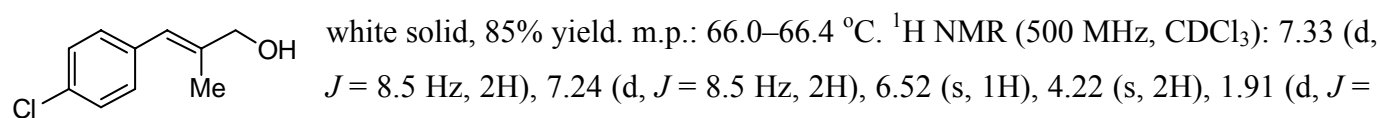
(E)-2-methyl-3-(4-tert-pentylphenyl)prop-2-en-1-ol (1g) ^[4]



(E)-3-(4-fluorophenyl)-2-methylprop-2-en-1-ol (1h) ^[5]



(E)-3-(4-chlorophenyl)-2-methylprop-2-en-1-ol (1i) ^[1]



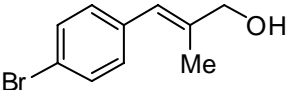
[3] Lölsberg, W. *Adv. Synth. Catal.* **2010**, 352, 2023–2031.

[4] Hoffmann-La Roche Inc. US4202894 A1, **1980**.

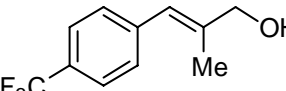
[5] Malkov, A. V. *J. Org. Chem.* **2009**, 74, 3350–3355.

1 Hz, 3H), 1.75 (s, 1H). ^{13}C NMR (500 MHz, CDCl_3): 138.4, 136.0, 132.1, 130.2, 128.3, 123.7, 68.7, 15.3.

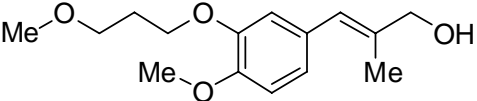
(E)-3-(4-bromophenyl)-2-methylprop-2-en-1-ol (1j) ^[5]

 white solid, 86% yield. m.p.: 80.7–81.3 °C. ^1H NMR (500 MHz, CDCl_3): 7.50–7.47 (m, 2H), 7.17 (d, J = 8.5 Hz, 2H), 6.50 (s, 1H), 4.22 (s, 2H), 1.90 (s, 3H), 1.80 (s, 1H). ^{13}C NMR (500 MHz, CDCl_3): 138.5, 136.5, 131.3, 130.5, 123.7, 120.3, 68.7, 15.3.

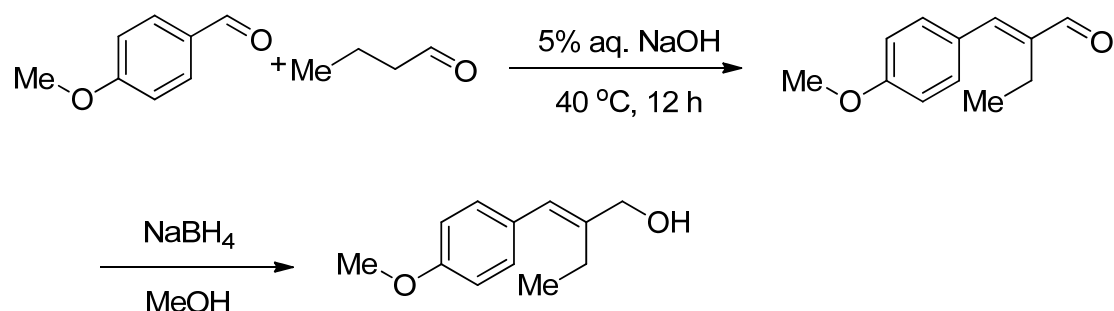
(E)-2-methyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (1k) ^[5]

 colorless oil, 65% yield. ^1H NMR (500 MHz, CDCl_3): 7.61 (d, J = 8 Hz, 2H), 7.40 (d, J = 8 Hz, 2H), 6.60 (s, 1H), 4.25 (s, 2H), 2.22 (s, 1H), 1.92 (d, J = 0.5 Hz, 3H). ^{13}C NMR (500 MHz, CDCl_3): 141.3, 139.9, 129.0, 125.6, 125.1, 123.4, 122.9, 68.4, 15.3.

(E)-3-(4-methoxy-3-(3-methoxypropoxy)phenyl)-2-methylprop-2-en-1-ol (1l) ^[6]

 colorless oil, 65% yield. ^1H NMR (500 MHz, CDCl_3): 6.87 (s, 3H), 6.46 (d, J = 1.2 Hz, 1H), 4.19 (s, 2H), 4.13 (t, J = 6.8 Hz, 2H), 3.88 (s, 3H), 3.59 (t, J = 6 Hz, 2H), 3.37 (s, 3H), 2.16–2.09 (m, 2H), 1.93 (s, 3H), 1.75 (s, 1H).

(E)-2-(4-methoxybenzylidene)butan-1-ol (1m) ^[7]



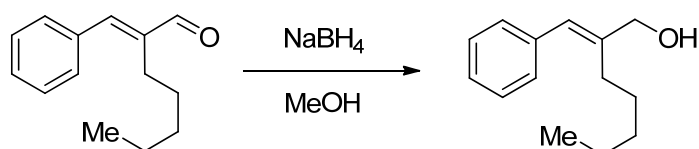
A solution of 4-methoxybenzaldehyde (1.36 g, 10 mmol), butyraldehyde (0.72 g, 10 mmol), EtOH (10 mL) and 5% aq. NaOH (10 mL) was stirred for 12 h at 40 °C. The solution was extracted with acetic ether. The organic extracts were washed with water and brine, dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give the product (E)-2-(4-methoxybenzylidene)butanal as a colorless oil. A solution of (E)-2-(4-methoxybenzylidene)butanal

[6] Pfaltz, A. *Angew. Chem. Int. Ed.* **2013**, 52, 7422–7425.

[7] Fujisawa Pharmaceutical Co., Ltd. US4767768 A1, **1988**.

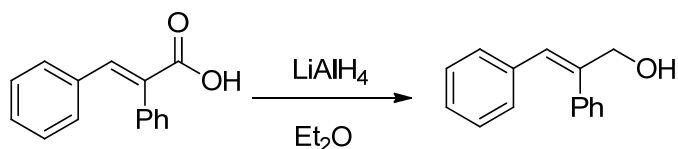
and NaBH₄ (0.42 g, 11 mmol) in MeOH (15 mL) was stirred for 2 h and then quenched by water (5 mL). The solution was extracted with acetic ether. The organic extracts were washed with water and brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether /ethyl acetate = 3:1, v/v) to give the product **1m** (0.86 g, 45% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): 7.22 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.46 (s, 1H), 4.23 (s, 2H), 3.8 (s, 3H), 2.36 (q, *J* = 7.6 Hz, 2H), 1.89 (s, 1H), 1.14 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃): 158.2, 142.0, 130.0, 129.8, 124.7, 113.7, 66.9, 55.3, 21.7, 13.0.

(*E*)-2-benzylideneheptan-1-ol (1n**)** ^[8]



A solution of (*E*)-2-benzylideneheptanal (2.02 g, 10 mmol) and NaBH₄ (0.42 g, 11 mmol) in MeOH (15 mL) was stirred for 2 h and then quenched by water (5 mL). The solution was extracted with acetic ether. The organic extracts were washed with water and brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether /ethyl acetate = 3:1, v/v) to give the product **1n** (1.84 g, 90% yield) as a colorless oil. ¹H NMR (500 MHz, CDCl₃): 7.32 (d, *J* = 7.5 Hz, 2H), 7.25–7.21 (m, 3H), 6.53 (s, 1H), 4.23 (d, *J* = 1 Hz, 2H), 2.29 (t, *J* = 8 Hz, 2H), 1.53–1.47 (m, 2H), 1.32–1.26 (m, 4H), 0.87 (t, *J* = 6.5 Hz, 3H).

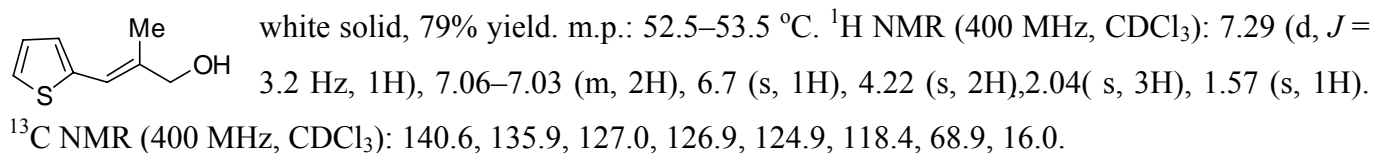
(*E*)-2,3-diphenylprop-2-en-1-ol (1o**)** ^[1]



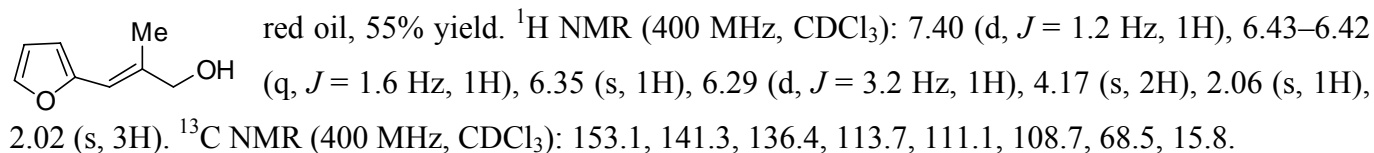
A solution of (*E*)-2,3-diphenylacrylic acid (2.24 g, 10 mmol) and LiAlH₄ (0.76 g, 20 mmol) in Et₂O (15 mL) was stirred for 5 h at 0 °C and then quenched by water (5 mL). The solution was extracted with acetic ether. The organic extracts were washed with water and brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether /ethyl acetate = 3:1, v/v) to give the product **1o** (1.75 g, 83% yield) as a white solid. m.p.: 54–56 °C. ¹H NMR (400 MHz, CDCl₃): 7.36–7.30 (m, 3H), 7.26–7.22 (m, 2H), 7.12–7.10 (m, 3H), 7.00–6.98 (m, 2H), 6.69 (s, 1H), 4.47 (d, *J* = 5.2 Hz, 2H), 1.63 (s, 1H). ¹³C NMR (400 MHz, CDCl₃): 141.5, 138.5, 136.4, 129.2, 128.84, 128.78, 128.0, 127.6, 126.8, 126.5, 68.6.

[8] Du, W.Q. *Chin. Chem. Lett.* **2012**, 23, 773–776.

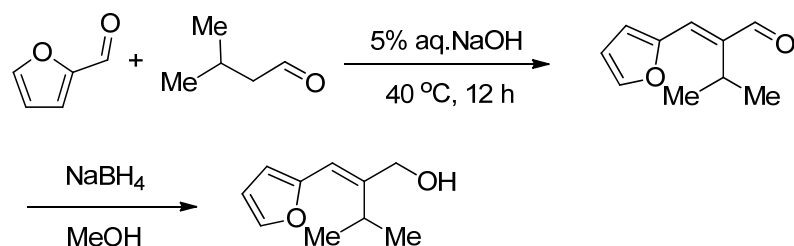
(*E*)-2-methyl-3-(thiophen-2-yl)prop-2-en-1-ol (1p) ^[1]



(*E*)-3-(furan-2-yl)-2-methylprop-2-en-1-ol (1q) ^[9]



(*E*)-2-(furan-2-ylmethylene)-3-methylbutan-1-ol (1r) ^[10]



A solution of furan-2-carbaldehyde (0.96 g, 10 mmol), EtOH (10 mL), 3-methylbutanal (0.86 g, 10 mmol), and 5% aq. NaOH (10 mL) was stirred for 12 h at 40 °C. The solution was extracted with acetic ether. The organic extracts were washed with water and brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give the product (*E*)-2-(furan-2-ylmethylene)-3-methylbutanal as a red oil. A solution of (*E*)-2-(furan-2-ylmethylene)-3-methylbutanal and NaBH₄ (0.42 g, 11 mmol) in MeOH (15 mL) was stirred for 2 h and then quenched by water (5 mL). The solution was extracted with acetic ether. The organic extracts were washed with water and brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether /ethyl acetate = 3:1, v/v) to give the product 1r (0.71 g, 43% yield) as a red oil. ¹H NMR (400 MHz, CDCl₃): 7.38 (d, *J* = 1.2 Hz, 1H), 6.40–6.39 (q, *J* = 1.6 Hz, 1H), 6.30 (s, 1H), 6.28 (d, *J* = 3.2 Hz, 1H), 4.27 (s, 2H), 3.47–3.40 (m, 1H), 1.55 (s, 1H), 1.14 (d, *J* = 7.2 Hz, 6H). ¹³C NMR (400 MHz, CDCl₃): 152.7, 145.7, 141.4, 112.9, 111.1, 108.9, 63.3, 29.0, 20.9.

II. General Procedure and Analytical Data of Asymmetric Hydrogenation

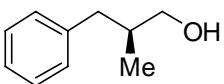
A solution of (*R_C*, *S_{Fc}*, *S_P*)-ChenPhos (3.28 mg, 0.0021 mmol) and Rh(NBD)₂BF₄ (1.50 mg, 0.002 mmol) in DCM (2 mL) was stirred under nitrogen atmosphere. After 30 min, the clear yellow solution was

[9] Huynh, K. *Synlett*, **2013**, 24, 193–196.

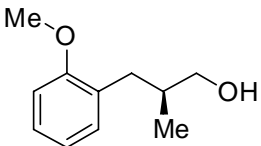
[10] Keilitz, J. *Org. Lett.* **2013**, 15, 1148–1151.

transferred into an autoclave and substrate (0.2 mmol) was added. The air in the autoclave was replaced with hydrogen for three times, and then the autoclave was charged with hydrogen to 25 atm. After stirring for 20 h at room temperature, the hydrogen was carefully released. The mixture was concentrated *in vacuo*, and the residue was purified by flash chromatography on silica gel (petroleum ether /ethyl acetate = 4:1, v/v). The *ee* values of the products were determined by chiral HPLC or chiral GC.

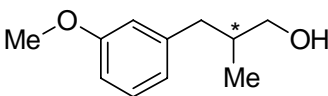
(S)-2-methyl-3-phenylpropan-1-ol (2a) ^[6]

 colorless oil, 98% yield, >99% *ee*, $[\alpha]_D^{15} -12.02$ (*c* 1.47, chloroform), HPLC condition: Chiralpak OD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 214 nm UV detector, t_R = 11.43 min for major isomer (*S*) and t_R = 15.25 min for minor isomer (*R*). ¹H NMR (400 MHz, CDCl₃): 7.30–7.16 (m, 5H), 3.56–3.44 (m, 2H), 2.78–2.73 (dd, *J* = 6.4 Hz, 13.2 Hz, 1H), 2.45–2.39 (dd, *J* = 8 Hz, 13.6 Hz, 1H), 2.00–1.90 (m, 1H), 1.42 (s, 1H), 0.91 (d, *J* = 6.8 Hz, 3H).

(S)-3-(2-methoxyphenyl)-2-methylpropan-1-ol (2b) ^[11]

 colorless oil, 99% yield, 99% *ee*, $[\alpha]_D^{15} -10.9$ (*c* 1.06, chloroform), HPLC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 220 nm UV detector, t_R = 18.21 min for major isomer (*S*) and t_R = 20.59 min for minor isomer (*R*). ¹H NMR (500 MHz, CDCl₃): 7.26–7.16 (m, 2H), 6.97–6.90 (m, 2H), 3.87 (s, 3H), 3.45 (d, *J* = 5.5 Hz, 2H), 2.80–2.76 (dd, *J* = 7 Hz, 13 Hz, 1H), 2.60–2.56 (dd, *J* = 7 Hz, 13.5 Hz, 1H), 2.42 (s, 1H), 2.03–1.99 (m, 1H), 1.01 (d, *J* = 7 Hz, 3H). ¹³C NMR (500 MHz, CDCl₃): 157.5, 131.2, 128.8, 127.3, 120.7, 110.5, 67.0, 55.4, 36.7, 33.2, 16.9.

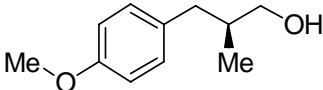
3-(3-methoxyphenyl)-2-methylpropan-1-ol (2c) ^[12]

 colorless oil, 96% yield, >99% *ee*, $[\alpha]_D^{15} -10.2$ (*c* 1.17, chloroform), HPLC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 214 nm UV detector, t_R = 23.72 min for major isomer and t_R = 22.71 min for minor isomer. ¹H NMR (500 MHz, CDCl₃): 7.26–7.22 (m, 1H), 6.82–6.78 (m, 3H), 3.84 (s, 3H), 3.59–3.55 (dd, *J* = 6 Hz, 10.5 Hz, 1H), 3.53–3.50 (dd, *J* = 6 Hz, 10.5 Hz, 1H), 2.80–2.76 (dd, *J* = 6 Hz, 13 Hz, 1H), 2.46–2.42 (dd, *J* = 8 Hz, 13.5 Hz, 1H), 2.02–1.96 (m, 1H), 1.73 (s, 1H), 0.96 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (500 MHz, CDCl₃): 159.6, 142.3, 129.2, 121.6, 114.9, 111.1, 67.7, 55.2, 39.8, 37.7, 16.5.

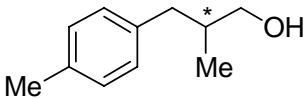
^[11] Nordin, O. *Org. Bio-Org. Chem.* **2000**, 3, 367-376.

^[12] Brenna, E. *J. Mol. Catal. B: Enzym.* **2012**, 84, 94-101.

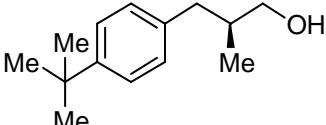
(S)-3-(4-methoxyphenyl)-2-methylpropan-1-ol (2d) ^[13]

 colorless oil, 97% yield, 99% ee, $[\alpha]_{\text{D}}^{15} -10.7$ (*c* 1.8, chloroform), HPLC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 225 nm UV detector, t_{R} = 22.11 min for major isomer (*S*) and t_{R} = 20.84 min for minor isomer (*R*). ¹H NMR (400 MHz, CDCl₃): 7.11 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 3.56–3.46 (m, 2H), 2.74–2.69 (dd, *J* = 6 Hz, 13.6 Hz, 1H), 2.42–2.37 (dd, *J* = 8 Hz, 13.6 Hz, 1H), 1.98–1.86 (m, 1H), 1.69 (s, 1H), 0.93 (d, *J* = 6.8 Hz, 3H).

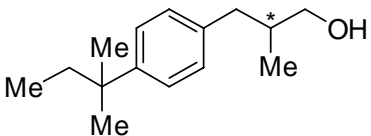
2-methyl-3-p-tolylpropan-1-ol (2e) ^[14]

 colorless oil, 97% yield, >99% ee, $[\alpha]_{\text{D}}^{15} -10.0$ (*c* 1.0, chloroform), HPLC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 214 nm UV detector, t_{R} = 12.56 min for major isomer and t_{R} = 11.92 min for minor isomer. ¹H NMR (400 MHz, CDCl₃): 7.16–7.10 (m, 4H), 3.58–3.54 (dd, *J* = 5.6 Hz, 10.4 Hz, 1H), 3.52–3.47 (dd, *J* = 6 Hz, 10.4 Hz, 1H), 2.78–2.73 (dd, *J* = 6.4 Hz, 13.6 Hz, 1H), 2.45–2.40 (dd, *J* = 8 Hz, 13.6 Hz, 1H), 2.37 (s, 3H), 2.00–1.94 (m, 1H), 1.92 (s, 1H), 0.95 (d, *J* = 6.8 Hz, 1H).

(S)-3-(4-(tert-butyl)phenyl)-2-methylpropan-1-ol (2f) ^[8]

 colorless oil, 98% yield, 95% ee, $[\alpha]_{\text{D}}^{15} -9.3$ (*c* 1.2, chloroform), ¹H NMR (400 MHz, CDCl₃): HPLC condition: Chiralpak OD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 214 nm UV detector, t_{R} = 12.02 min for major isomer (*S*) and t_{R} = 11.00 min for minor isomer (*R*).

2-methyl-3-(4-tert-pentylphenyl)propan-1-ol (2g) ^[4]

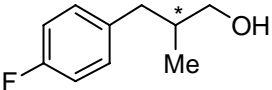
 colorless oil, 99% yield, 99% ee, $[\alpha]_{\text{D}}^{15} -8.78$ (*c* 0.5, chloroform), HPLC condition: Chiralpak OD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 95:5, flow rate = 1.0 mL/min, 225 nm UV detector, t_{R} = 28.20 min for major isomer and t_{R} = 26.70 min for minor isomer. ¹H NMR (500 MHz, CDCl₃): 7.15 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 3.45–3.41 (dd, *J* = 6 Hz, 10.5 Hz, 1H), 3.38–3.34 (dd, *J* = 6 Hz, 10.5 Hz, 1H), 2.64–2.59 (dd, *J* = 6.5 Hz, 13.5 Hz, 1H), 2.34–2.29 (dd, *J* = 8 Hz, 13.5 Hz, 1H), 1.85 (m, 1H),

^[13] Noerder, A. *J. Am. Chem. Soc.* **2012**, *134*, 13524–13531.

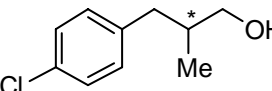
^[14] Meng, X. *Tetrahedron: Asymmetry*, **2009**, *20*, 1402–1406.

1.56–1.51 (q, $J = 7.4$ Hz, 2H), 1.18 (s, 6H), 0.83 (d, $J = 7$ Hz, 3H), 0.59 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (500 MHz, CDCl_3): 147.0, 137.4, 128.7, 125.9, 67.8, 39.3, 37.8, 37.6, 36.9, 28.5, 16.6, 9.2.

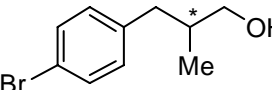
3-(4-fluorophenyl)-2-methylpropan-1-ol (2h) ^[14]

 colorless oil, 98% yield, 98% ee, $[\alpha]_{\text{D}}^{15} -9.37$ (c 0.95, chloroform), HPLC condition: Chiralpak AB column (25 cm \times 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 214 nm UV detector, $t_{\text{R}} = 8.58$ min for major isomer and $t_{\text{R}} = 9.64$ min for minor isomer. ^1H NMR (500 MHz, CDCl_3): 7.17–7.14 (m, 2H), 7.00 (t, $J = 8.5$ Hz, 2H), 3.56–3.49 (m, 2H), 2.80–2.75 (dd, $J = 6$ Hz, 13.5 Hz, 1H), 2.45–2.40 (dd, $J = 8$ Hz, 13.5 Hz, 1H), 1.97–1.91 (m, 1H), 1.79 (s, 1H), 0.93 (d, $J = 6.5$ Hz, 3H), 1.76–1.68 (m, 1H), 1.46–1.35 (m, 2H), 0.97 (t, $J = 7.5$ Hz, 1H).

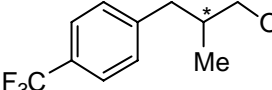
3-(4-chlorophenyl)-2-methylpropan-1-ol (2i) ^[12]

 colorless oil, 99% yield, 99% ee, $[\alpha]_{\text{D}}^{15} -12.6$ (c 1.58, chloroform), HPLC condition: Chiralpak AD-H column (25 cm \times 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 210 nm UV detector, $t_{\text{R}} = 17.79$ min for major isomer and $t_{\text{R}} = 16.51$ min for minor isomer. ^1H NMR (400 MHz, CDCl_3): 7.27 (d, $J = 8$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 3.51 (d, $J = 4$ Hz, 2H), 2.79–2.74 (dd, $J = 6.4$ Hz, 13.6 Hz, 1H), 2.43–2.38 (dd, $J = 8$ Hz, 13.2 Hz, 1H), 1.99–1.87 (m, 1H), 1.50 (s, 1H), 0.92 (d, $J = 6.8$ Hz, 3H).

3-(4-bromophenyl)-2-methylpropan-1-ol (2j) ^[15]

 colorless oil, 99% yield, 99% ee, $[\alpha]_{\text{D}}^{15} -12.8$ (c 2.15, chloroform), HPLC condition: Chiralpak AD-H column (25 cm \times 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 220 nm UV detector, $t_{\text{R}} = 19.51$ min for major isomer and $t_{\text{R}} = 18.01$ min for minor isomer. ^1H NMR (400 MHz, CDCl_3): 7.39 (d, $J = 8.4$ Hz, 2H), 7.05 (d, $J = 8.4$ Hz, 2H), 3.53–3.44 (m, 2H), 2.76–2.71 (dd, $J = 6.4$ Hz, 13.6 Hz, 1H), 2.39–2.34 (dd, $J = 8$ Hz, 13.6 Hz, 1H), 1.96–1.85 (m, 1H), 1.44 (t, $J = 5.2$ Hz, 1H), 0.89 (d, $J = 6.8$ Hz, 3H).

2-methyl-3-(4-(trifluoromethyl)phenyl)propan-1-ol (2k) ^[16]

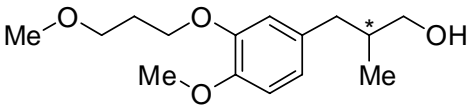
 colorless oil, 98% yield, 93% ee, $[\alpha]_{\text{D}}^{15} -7.82$ (c 1.63, chloroform), HPLC condition: Chiralpak OJ-H column (25 cm \times 0.46 cm ID), hexane/2-propanol = 99:1, flow rate = 1.0 mL/min, 214 nm UV detector, $t_{\text{R}} = 10.03$ min for major

^[15] Chowdari, N. S. *Org. Lett.* **2005**, 7, 867–870.

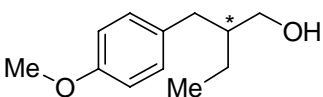
^[16] Du, B. *Org. Lett.* **2003**, 5, 4823–4826.

isomer and $t_R = 9.38$ min for minor isomer. ^1H NMR (500 MHz, CDCl_3): 7.52 (d, $J = 8$ Hz, 2H), 7.27 (d, $J = 8$ Hz, 2H), 3.49–3.47 (m, 2H), 2.86–2.82 (dd, $J = 6$ Hz, 13.5 Hz, 1H), 2.48 (s, 1H), 2.46–2.41 (dd, $J = 8.5$ Hz, 13.5 Hz, 1H), 1.95–1.93 (m, 1H), 0.89 (d, $J = 6.5$ Hz, 1H).

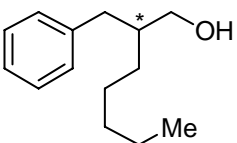
3-(4-methoxy-3-(3-methoxypropoxy)phenyl)-2-methylpropan-1-ol (2l) ^[6]

 colorless oil, 97% yield, 97% ee, $[\alpha]_D^{15} -7.66$ (c 1.24, chloroform), HPLC condition: Chiralpak AD-H column (25 cm \times 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 214 nm UV detector, $t_R = 21.51$ min for major isomer and $t_R = 24.43$ min for minor isomer. ^1H NMR (400 MHz, CDCl_3): 6.80–6.66 (m, 3H), 4.10 (t, $J = 6.4$ Hz, 2H), 3.84 (s, 3H), 3.58 (t, $J = 6$ Hz, 2H), 3.54–3.42 (m, 2H), 3.36 (s, 3H), 2.70–2.65 (dd, $J = 6.4$ Hz, 13.6 Hz, 1H), 2.40–2.33 (m, 1H), 2.13–2.07 (m, 2H), 1.98–1.68 (m, 2H), 0.90 (t, $J = 6.8$ Hz, 3H).

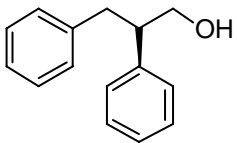
2-(4-methoxybenzyl)butan-1-ol (2m) ^[17]

 colorless oil, 98% yield, 97% ee, $[\alpha]_D^{15} +8.21$ (c 0.86, chloroform), HPLC condition: Chiralpak AD-H column (25 cm \times 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 227 nm UV detector, $t_R = 22.25$ min for major isomer and $t_R = 20.33$ min for minor isomer. ^1H NMR (500 MHz, CDCl_3): 7.13 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 3.82 (s, 3H), 3.56 (d, $J = 5.5$ Hz, 2H), 2.61 (m, 2H), 1.98 (s, 1H), 1.76–1.68 (m, 1H), 1.46–1.35 (m, 2H), 0.97 (t, $J = 7.5$ Hz, 1H). ^{13}C NMR (500 MHz, CDCl_3): 157.7, 132.8, 130.1, 113.7, 64.5, 55.2, 44.2, 36.4, 23.3, 11.3.

2-benzylheptan-1-ol (2n) ^[8]

 colorless oil, 97% yield, >99% ee, $[\alpha]_D^{10} -5.42$ (c 1.5, chloroform), HPLC condition: Chiralpak OD-H column (25 cm \times 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 214 nm UV detector, $t_R = 15.03$ min for major isomer and $t_R = 11.19$ min for minor isomer. ^1H NMR (500 MHz, CDCl_3): 7.30–7.26 (m, 2H), 7.19 (d, $J = 7.5$ Hz, 3H), 3.56–3.50 (m, 2H), 2.64 (d, $J = 7$ Hz, 2H), 1.83–1.75 (m, 1H), 1.39–1.24 (m, 8H), 0.88 (t, $J = 7$ Hz, 3H), 1.56–1.51 (q, $J = 7.4$ Hz, 2H), 1.18 (s, 6H), 0.83 (d, $J = 7$ Hz, 3H), 0.59 (t, $J = 7.5$ Hz, 3H).

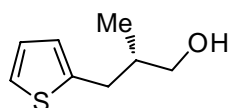
(R)-2,3-diphenylpropan-1-ol (2o) ^[17]

 colorless oil, 99% yield, >99% ee, $[\alpha]_D^{15} -71.5$ (c 2.17, chloroform), HPLC condition: Chiralpak AD-H column (25 cm \times 0.46 cm ID), hexane/2-propanol = 95:5,

^[17] Cano, R. *Chem. Commun.* **2012**, 48, 7628–7630.

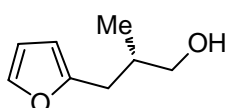
flow rate = 1.0 mL/min, 214 nm UV detector, t_R = 15.45 min for major isomer (*R*) and t_R = 19.58 min for minor isomer (*S*). ^1H NMR (400 MHz, CDCl_3): 7.37–7.12 (m, 10H), 3.82(t, J = 4.8 Hz, 2H), 3.17–3.04 (m, 2H), 2.97–2.92 (dd, J = 7.6 Hz, 13.2 Hz, 1H), 1.41 (d, J = 5.6 Hz, 1H).

(*S*)-2-methyl-3-(thiophen-2-yl)propan-1-ol (2p) ^[18]



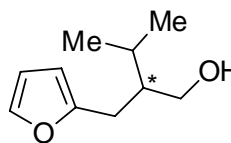
colorless oil, 99% yield, >99% ee, $[\alpha]_D^{15}$ –11.9 (c 0.99, chloroform), HPLC condition: Chiralpak OJ-H column (25 cm \times 0.46 cm ID), hexane/2-propanol = 99:1, flow rate = 1.0 mL/min, 238 nm UV detector, t_R = 12.92 min for major isomer (*S*) and t_R = 12.25 min for minor isomer (*R*). ^1H NMR (500 MHz, CDCl_3): 7.17–7.16 (m, 1H), 6.98–6.96 (m, 1H), 6.84–6.83 (m, 1H), 3.59–3.52 (m, 2H), 3.03–2.99 (dd, J = 6 Hz, 14 Hz, 1H), 2.75–2.70 (dd, J = 8 Hz, 15 Hz, 1H), 2.04–1.97(m, 2H), 1.02–1.00(d, J = 7 Hz, 3H). ^{13}C NMR (500 MHz, CDCl_3): 143.2, 126.8, 125.3, 123.3, 67.2, 38.1, 33.5, 16.5.

(*S*)-3-(furan-2-yl)-2-methylpropan-1-ol (2q) ^[19]



red oil, 99% yield, >99% ee, $[\alpha]_D^{15}$ –2.05 (c 0.5, chloroform), HPLC condition: Chiralpak AD-H column (25 cm \times 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 214 nm UV detector, t_R = 16.9 min for major isomer (*S*) and t_R = 16.45 min for minor isomer (*R*). ^1H NMR (400 MHz, CDCl_3): 7.31 (s, 1H), 6.29 (t, J = 2 Hz, 1H), 6.02 (d, J = 2.8 Hz, 1H), 3.49 (d, J = 6 Hz, 2H), 2.76–2.70 (dd, J = 6 Hz, 14.8Hz, 1H), 2.56–2.51 (dd, J = 7.2 Hz, 14.8 Hz, 1H), 2.08–1.94(m, 1H), 1.66 (s, 1H), 0.94 (d, J = 6.8 Hz, 3H).

2-(furan-2-ylmethyl)-3-methylbutan-1-ol (2r) ^[20]



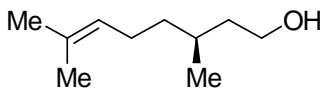
red oil, 97% yield, >99% ee, $[\alpha]_D^{15}$ –1.95 (c 1.0, chloroform), HPLC condition: Chiralpak AD-H column (25 cm \times 0.46 cm ID), hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 220 nm UV detector, t_R = 16.26 min for major isomer and t_R = 17.45 min for minor isomer. ^1H NMR (400 MHz, CDCl_3): 7.33 (d, J = 1 Hz, 1H), 6.31–6.30 (m, 1H), 6.05 (d, J = 3.5 Hz, 1H), 3.65–3.57 (m, 2H), 2.78–2.73 (dd, J = 5.2 Hz, 15.2 Hz, 1H), 2.68–2.63 (dd, J = 8 Hz, 14.8 Hz, 1H), 1.86–1.71(m, 2H), 1.58 (s, 1H), 0.98–0.95 (t, J = 6.4 Hz, 6H). ^{13}C NMR (400 MHz, CDCl_3): 155.1, 141.0, 110.2, 106.0, 63.4, 46.3, 28.0, 26.9, 19.8, 19.5.

^[18] Renaudat, A. *Angew. Chem. Int. Ed.* **2010**, 49, 7261 – 7265.

^[19] De A. *Org. Lett.* **2013**, 15, 476–479.

^[20] Schuikin. *Dokl. Chem.* **1960**, 131, 11.

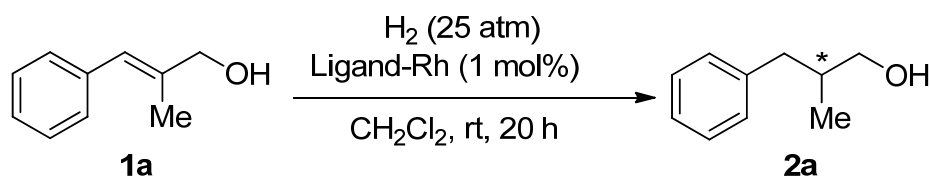
(S)-citronellol (2t) ^[21]

 colorless oil, 99% yield, 99% ee, $[\alpha]_D^{15} -4.9$ (*c* 0.5, chloroform), (¹H NMR (400 MHz, CDCl₃):) HPLC condition for corresponding ester: Chiralpak OD-H column (25 cm × 0.46 cm ID), hexane/2-propanol = 99:1, flow rate = 1.0 mL/min, 225 nm UV detector, *t*_R = 18.86 min for major isomer (*S*) and *t*_R = 16.12 min for minor isomer (*R*).

III. Asymmetric hydrogenation of 2-methyl-3-phenylpropenol with a variety of diphosphine ligands

Some well-known diphosphine ligands were tested in the reaction as well. TriFer was highly enantioselective, giving 98% ee, but the activity was very low. Hydrogenation under 25 atm of hydrogen at rt in DCM for 20 h with S/C ratio of 1,000, full conversion was achieved with ChenPhos, while TriFer with S/C ratio of 100 only gave 50% conversion (Table, entry 1). Taniaphos (SL-T002-1) afforded good results, while all other diphosphine ligands tested were ineffective in the hydrogenation, showing low enantioselectivity and activity (Table, entries 2-7).

Table. Asymmetric hydrogenation of 2-methyl-3-phenylpropenol with a variety of diphosphine ligands.^a



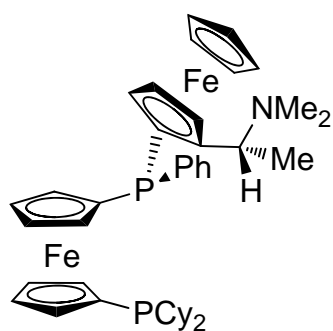
Entry	Ligand	Conv.(%) ^b	ee (%) ^c
1	TriFer	50	98
2	Taniaphos (SL-T002-1)	100	82
3	Walphos (SL-W001-1)	90	61
4	Josiphos (SL-J002-1)	99	33
5	Mandyphos (SL-M004-1)	74	46
6	MeOBIPHEP	92	10
7	BINAP	99	9

^aReaction conditions: 0.2 mmol scale, [substrate] = 0.1 mol/L, solvent = 2 mL, 1.0 mol% of catalyst.

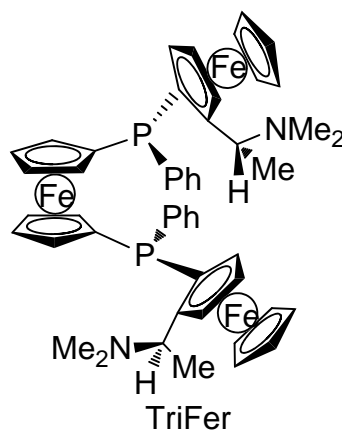
^bDetermined by ¹H NMR analysis. ^cDetermined by chiral HPLC analysis.

^[21] Achard, M. *Green. Chem.*, **2013**, 15, 775–779.

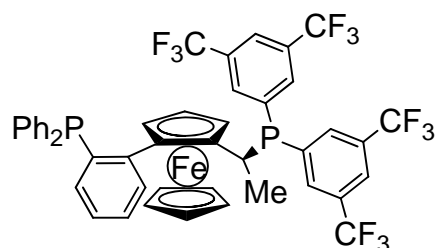
Diphosphine ligands



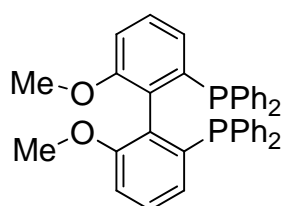
ChenPhos



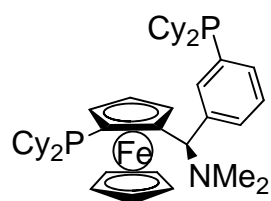
TriFer



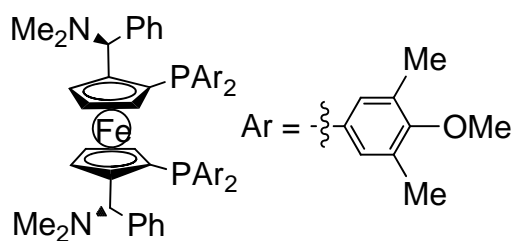
Walphos(SL-W001-1)



MeOBIPHEP(SL-A101-1)



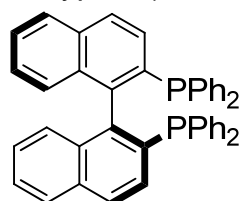
Taniaphos(SL-T002-1)



Mandyphos(SL-M004-1)



Josiphos(SL-J002-1)

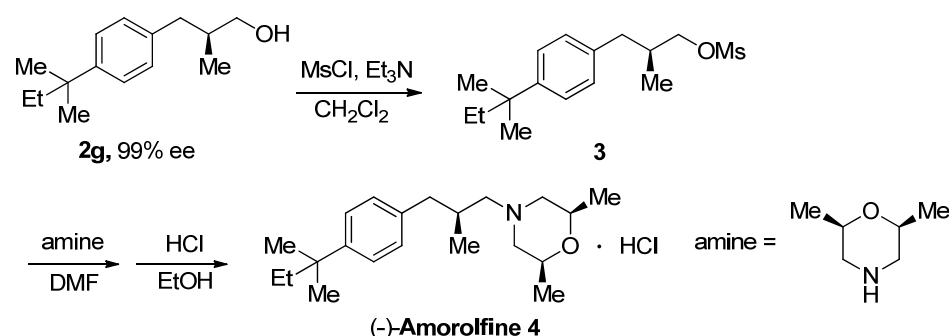


(S)-BINAP

IV. The preparation of (-)-Amorolfine hydrochloric acid

The application of the enantioselective hydrogenation was demonstrated in the first asymmetric synthesis of antifungal agent (-)-amorolfine.^[22]

Thus, 3-(4-tert-amylphenyl)-2-methylpropanol **1g** was hydrogenated, with 1,000 of S/C ratio in dichloromethane (DCM) under 25 atm of hydrogen pressure at room temperature for 20 h, to give (-)-3-(4-tert-amylphenyl)-2-methylpropanol **2g** in 98% yield with 99% ee. Converting **2g** to the corresponding sulfonate **3**, followed by reaction with cis-2,6-dimethylmorpholine afforded (-)-amorolfine in 74% yield. The study on the antifungal activities of (+)-, (-)- and racemic amorolfine is underway, and the results will be reported in due course.



(-)-2-Methyl-3-(4-tert-pentylphenyl)propyl methanesulfonate (**3**)

To a solution of (*S*)-2-methyl-3-(4-tert-pentylphenyl)propan-1-ol **2g** (0.6 g, 2.7 mmol) in CH₂Cl₂ (10 mL) was added MeSO₂Cl (0.37 g, 3.3 mmol) and Et₃N (0.41 g, 4.0 mmol) at 0 °C. The reaction mixture was stirred for 1 h at this atmosphere. The resulting suspension was filtered, and the precipitate was washed with Et₂O. The organic phase was washed with water (2 x 20 mL) and brine (2 x 20 mL), dried over anhydrous MgSO₄, filtered, and concentrated by rotary evaporator *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give product as yellow oil (0.76 g, 95% yield). [α]_D¹⁰ -3.19 (*c* 1.4, chloroform). ¹H NMR (500 MHz, CDCl₃): 7.30–7.25 (m, 2H), 7.14–7.10 (m, 2H), 4.15–4.12 (dd, *J* = 6 Hz, 9.5 Hz, 1H), 4.09–4.06 (dd, *J* = 6 Hz, 9.5 Hz, 1H), 3.01 (s, 3H), 2.77–2.73 (dd, *J* = 6.5 Hz, 13.5 Hz, 1H), 2.57–2.53 (dd, *J* = 7.5 Hz, 13.5 Hz, 1H), 2.28–2.19 (m, 1H), 1.69–1.65 (q, *J* = 7.5 Hz, 3H), 1.31 (s, 6H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.72 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (500 MHz, CDCl₃): 147.5, 135.9, 128.7, 126.0, 73.9, 38.6, 37.6, 37.2, 36.9, 34.9, 28.4, 16.5, 9.2.

2,6-Dimethyl-4-((*S*)-2-methyl-3-(4-*t*-pentylphenyl)propyl)morpholine hydrochloride (**4**)^[23]

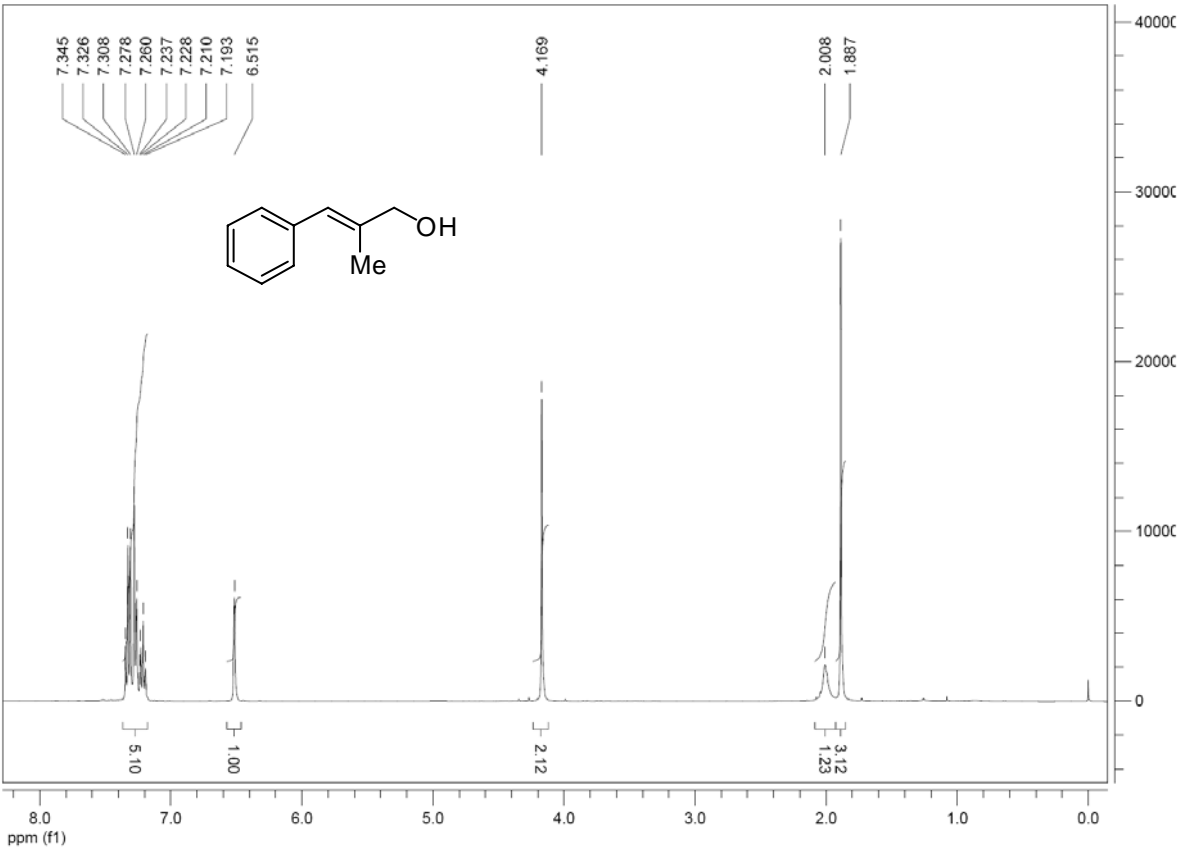
^[22] Haria, H. *Drugs*, **1995**, *49*, 103.

^[23] Kido, Y. *J. Med.Chem.* **2011**, *54*, 4548–4558.

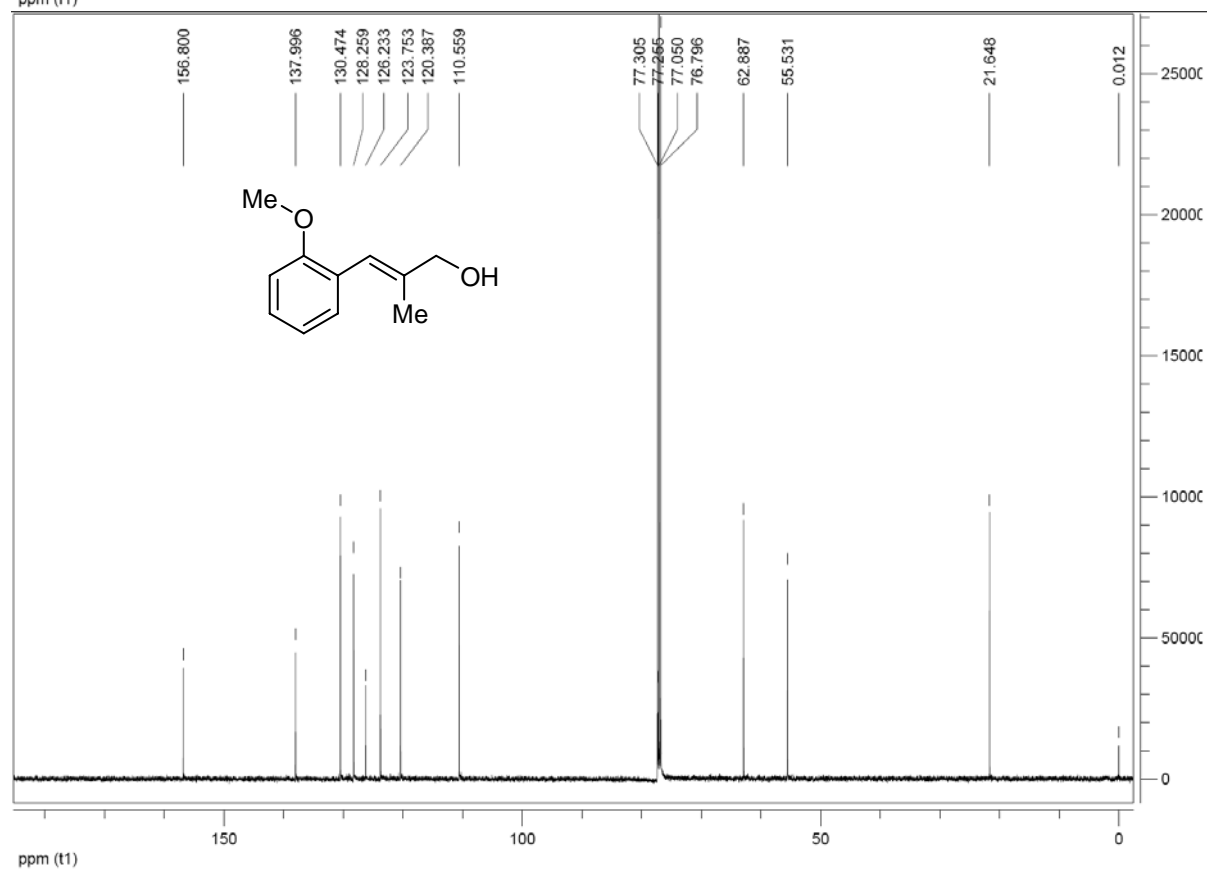
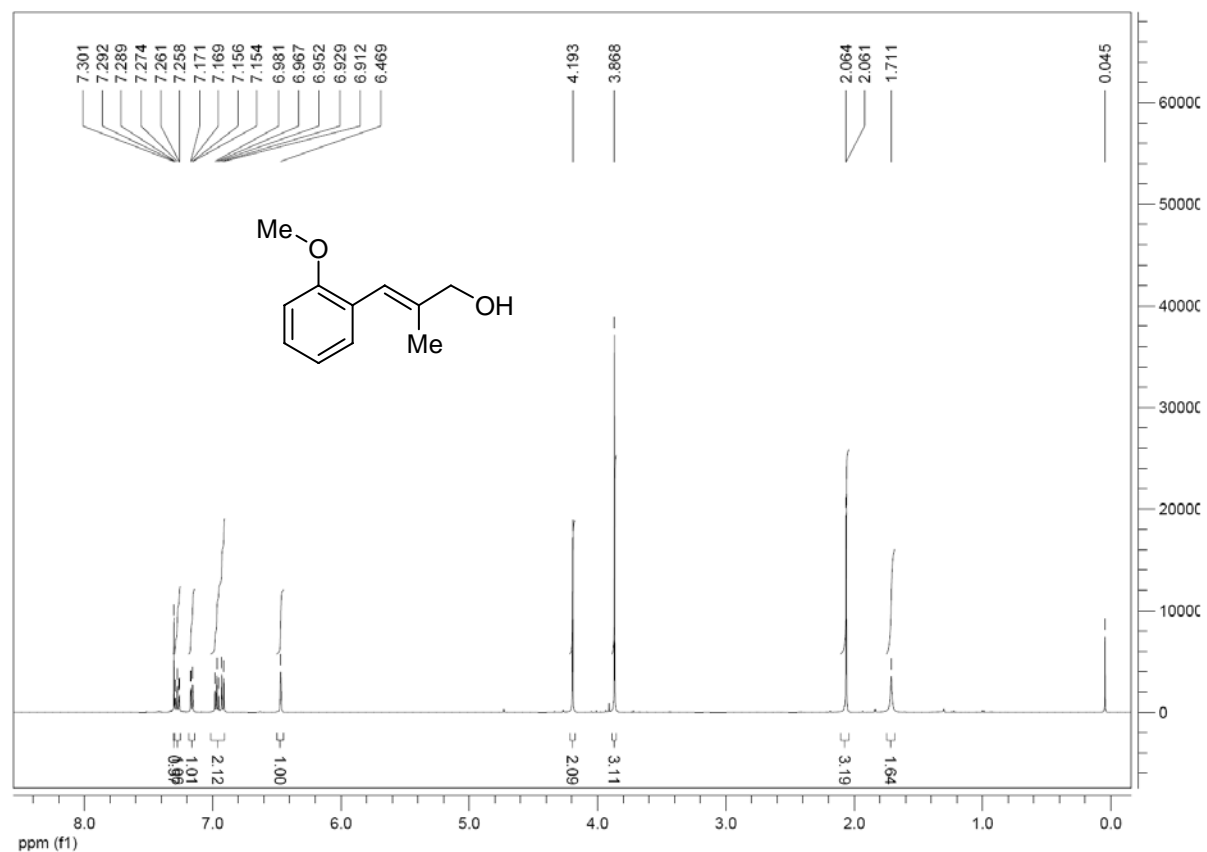
To a solution of (*S*)-2-methyl-3-(4-*tert*-pentylphenyl)propyl methanesulfonate **3** (0.73 g, 2.4 mmol), K₂CO₃ (0.50g, 3.6 mmol) and KI (0.40 g, 2.4 mmol) in DMF (30 mL) was added *cis*-2,6-dimethylmorpholine (0.41g, 3.6 mmol) and the mixture was stirred at 120 °C for 12 h. The reaction mixture was washed with water (2 x 20 mL) and brine (2 x 20 mL), dried over anhydrous MgSO₄, filtered, and concentrated by rotary evaporator *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give product as yellow oil. This oil was dissolved in EtOH (5 mL), and the solution was cooled to 0 °C. To the solution was added hydrochloric acid (12 M, 2 mL). The precipitate was purified by recrystallization with cold EtOH to give the product **4** (0.63 g, 78% yield) as a white solid. m.p.: 210-212 °C. $[\alpha]_D^{15} -7.62$ (c 0.5, methanol), ¹H NMR (400 MHz, CD₃OD): 7.32 (d, *J* = 8 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.99–3.88 (m, 2H), 3.52–3.44 (m, 2H), 3.15–3.04 (m, 2H), 2.77–2.71 (m, 2H), 2.59–2.49 (m, 2H), 2.41–2.33 (m, 1H), 1.68 (q, *J* = 7.2 Hz, 2H), 1.29 (s, 6H), 1.24 (d, *J* = 2.8 Hz, 3H), 1.23 (d, *J* = 3.2 Hz, 3H), 1.06 (d, *J* = 6.4 Hz, 3H), 0.68 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (400 MHz, CD₃OD): 147.4, 135.5, 128.6, 125.8, 69.0, 68.9, 63.5, 57.1, 55.4, 40.0, 37.2, 36.5, 30.0, 27.6, 17.3, 17.2, 16.7, 8.1.

V. NMR Spectra:

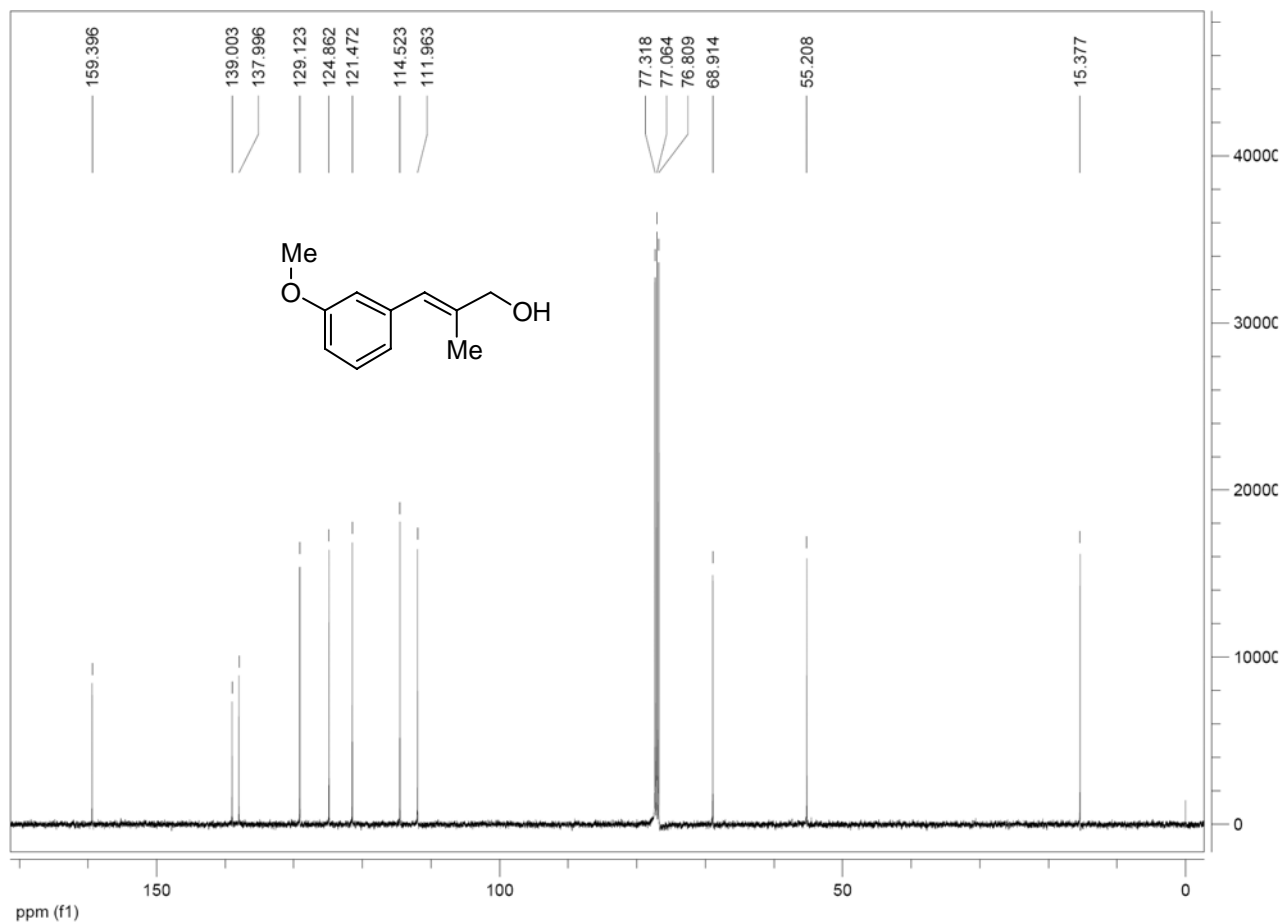
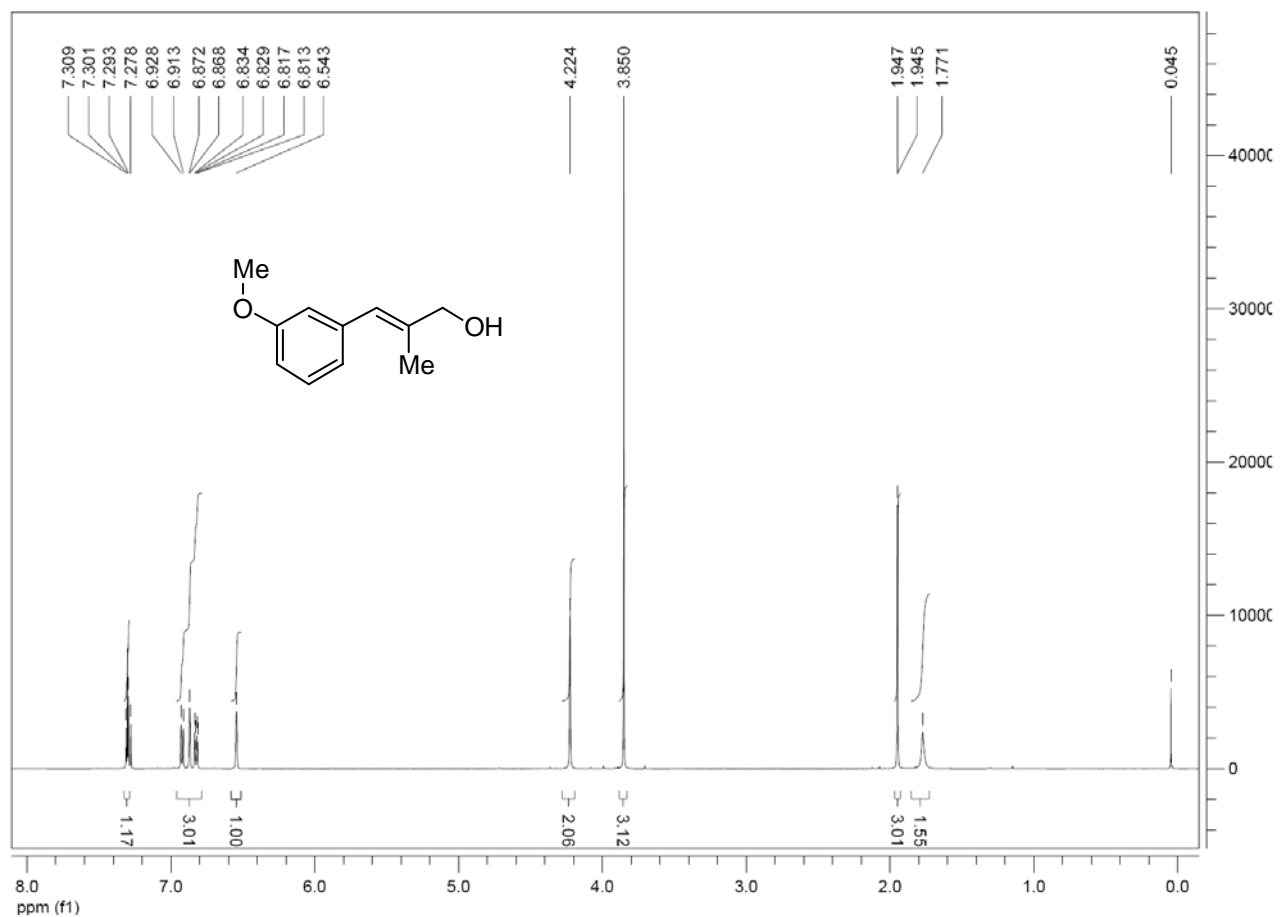
(E)-2-methyl-3-phenylprop-2-en-1-ol (1a)



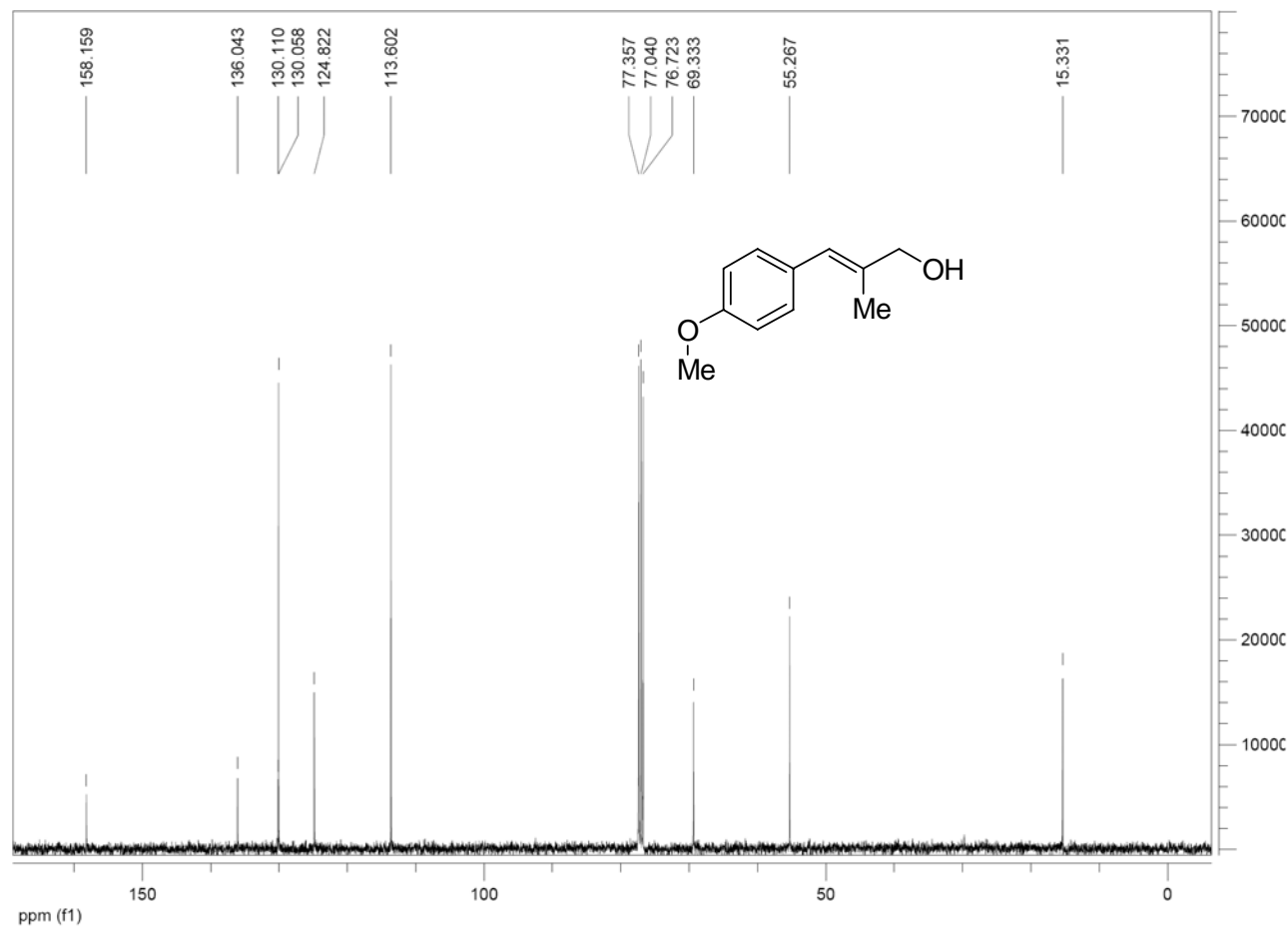
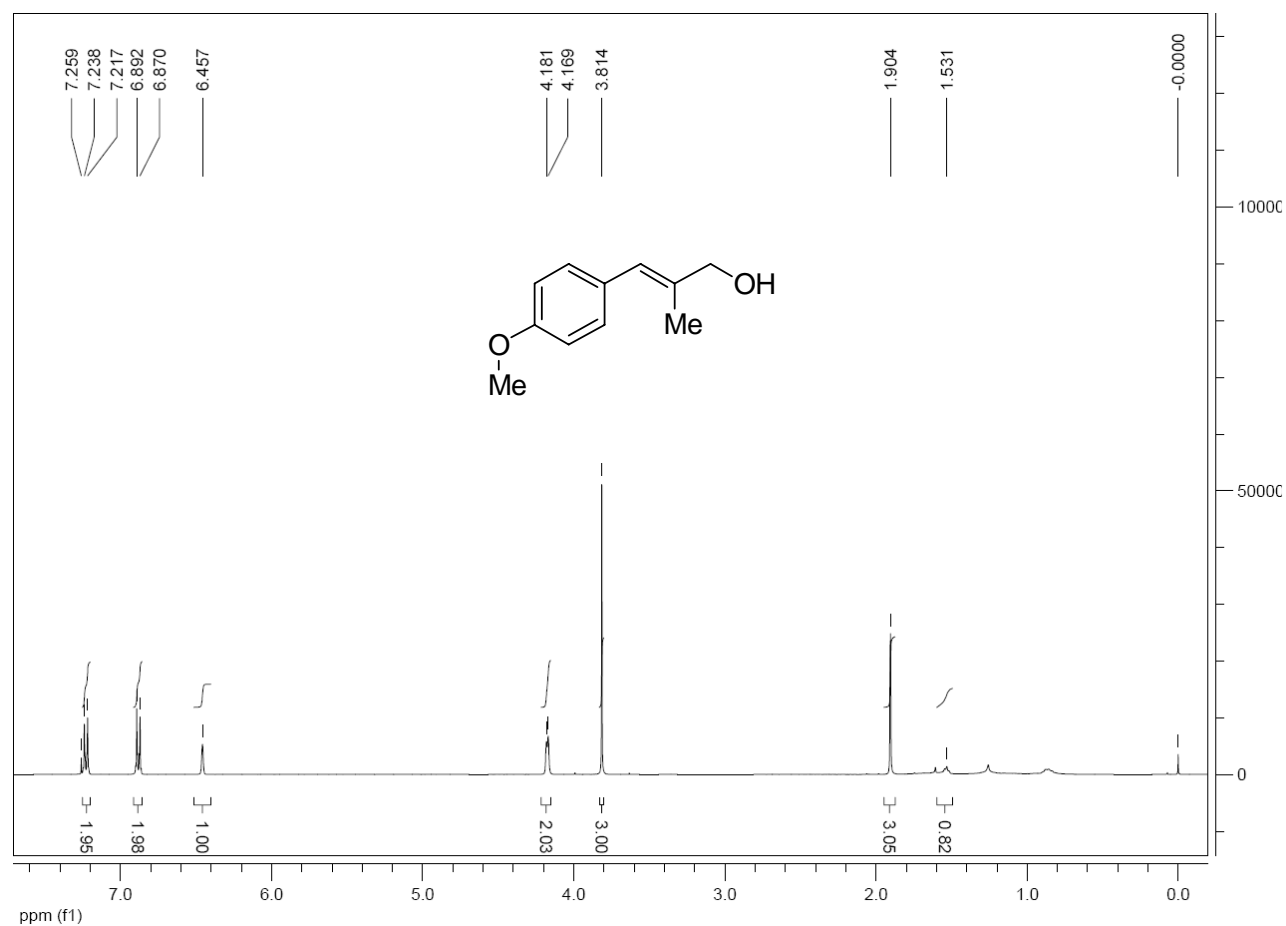
(E)-3-(2-methoxyphenyl)-2-methylprop-2-en-1-ol (1b)



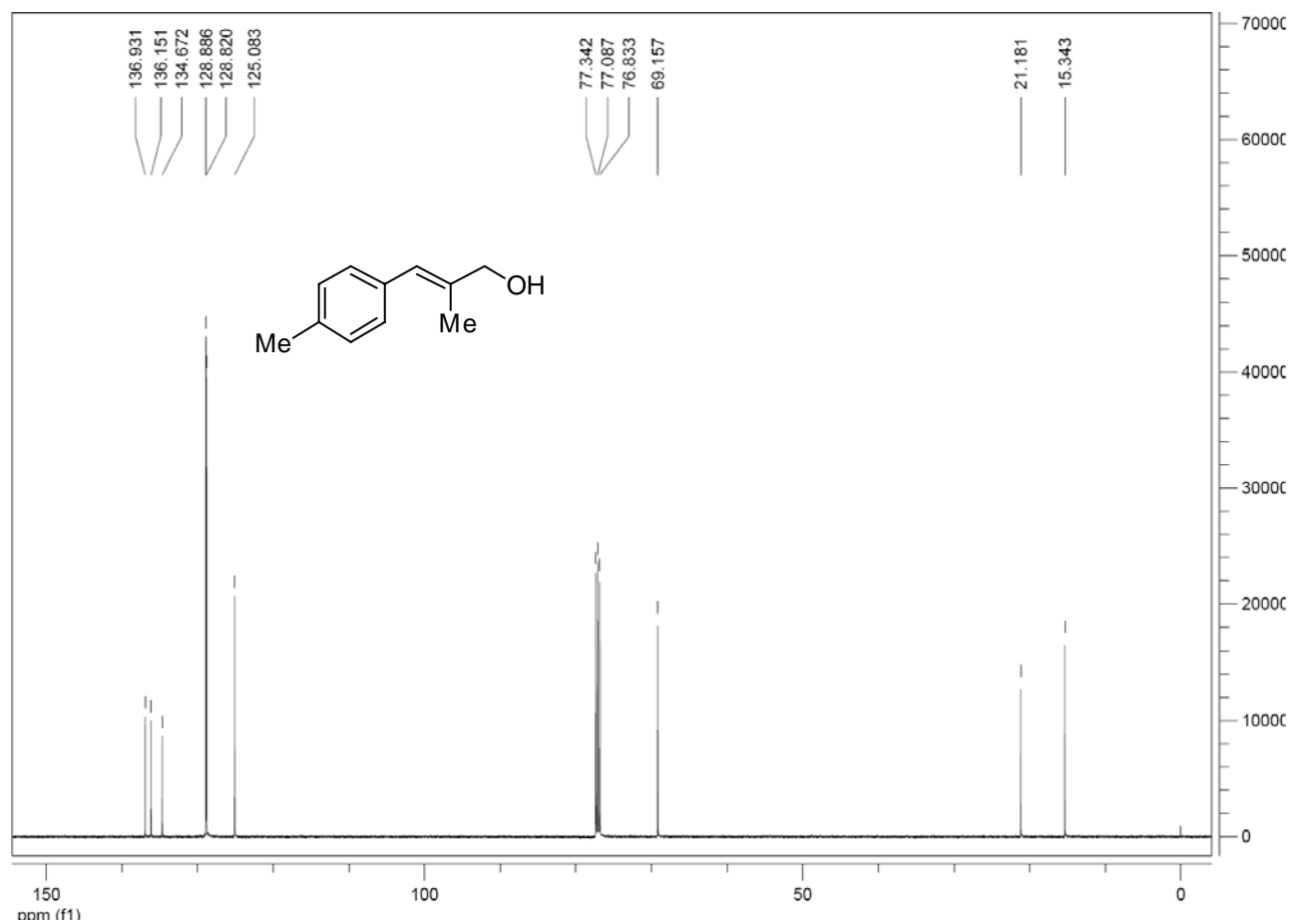
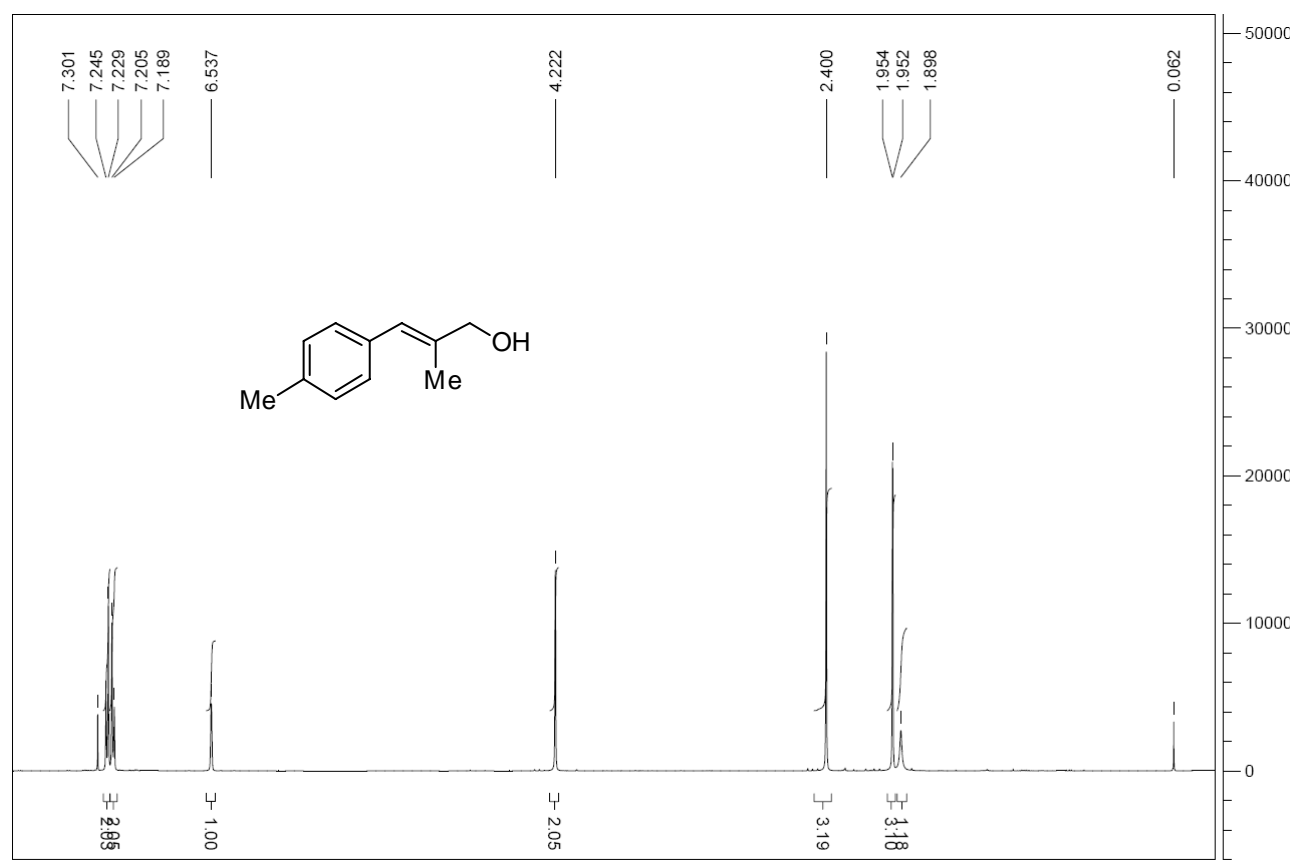
(E)-3-(3-methoxyphenyl)-2-methylprop-2-en-1-ol (1c)



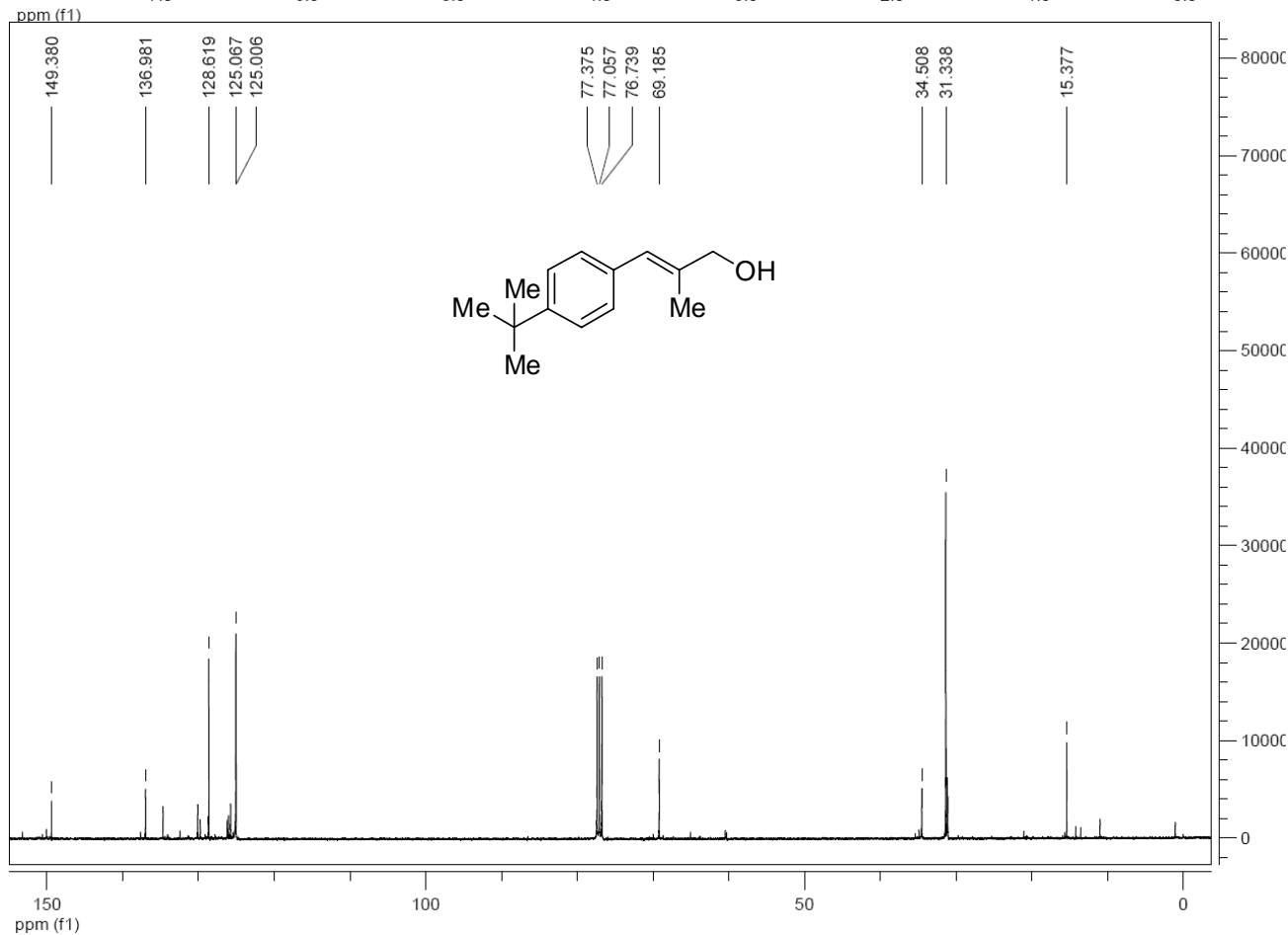
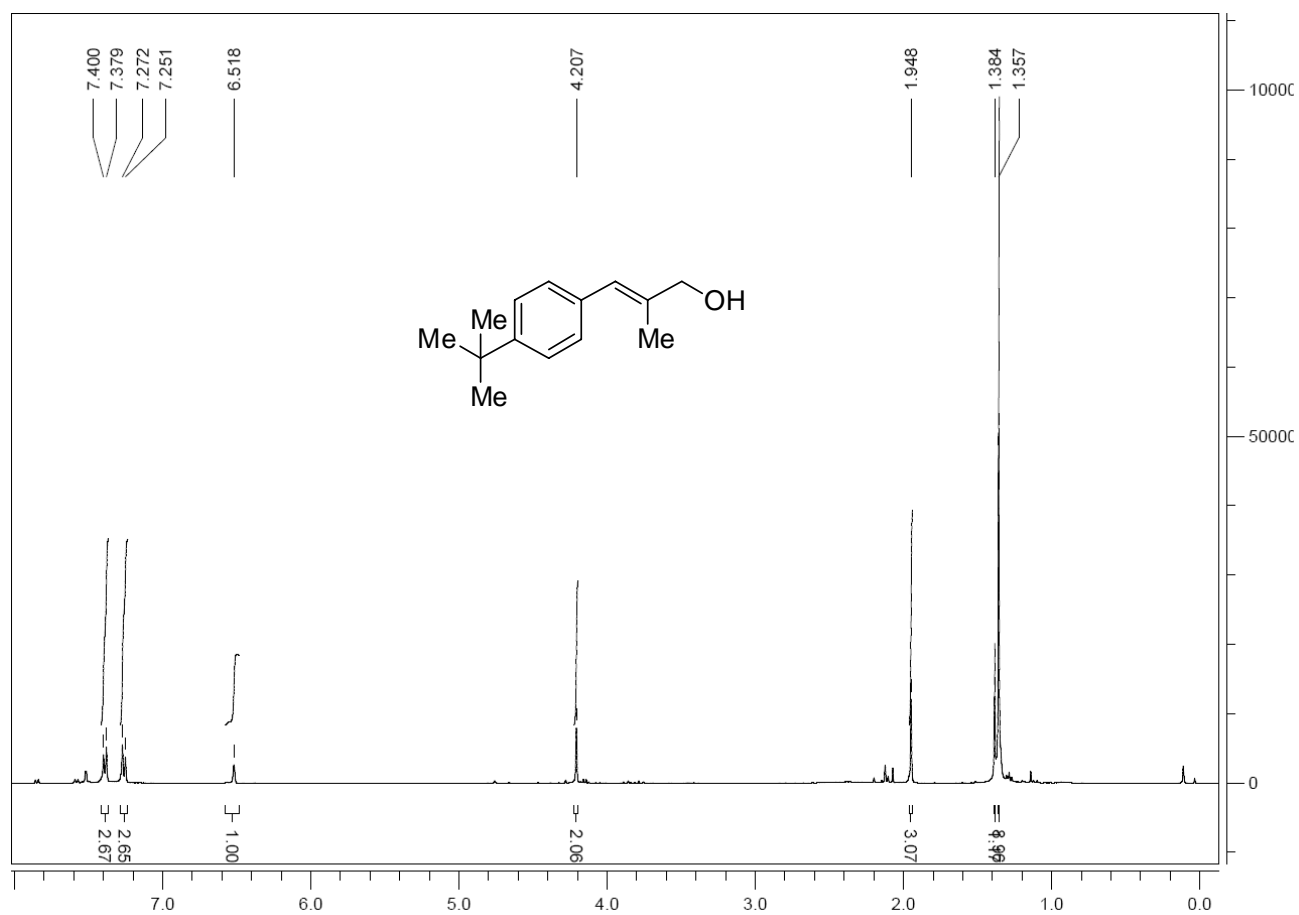
(E)-3-(4-methoxyphenyl)-2-methylprop-2-en-1-ol (1d)



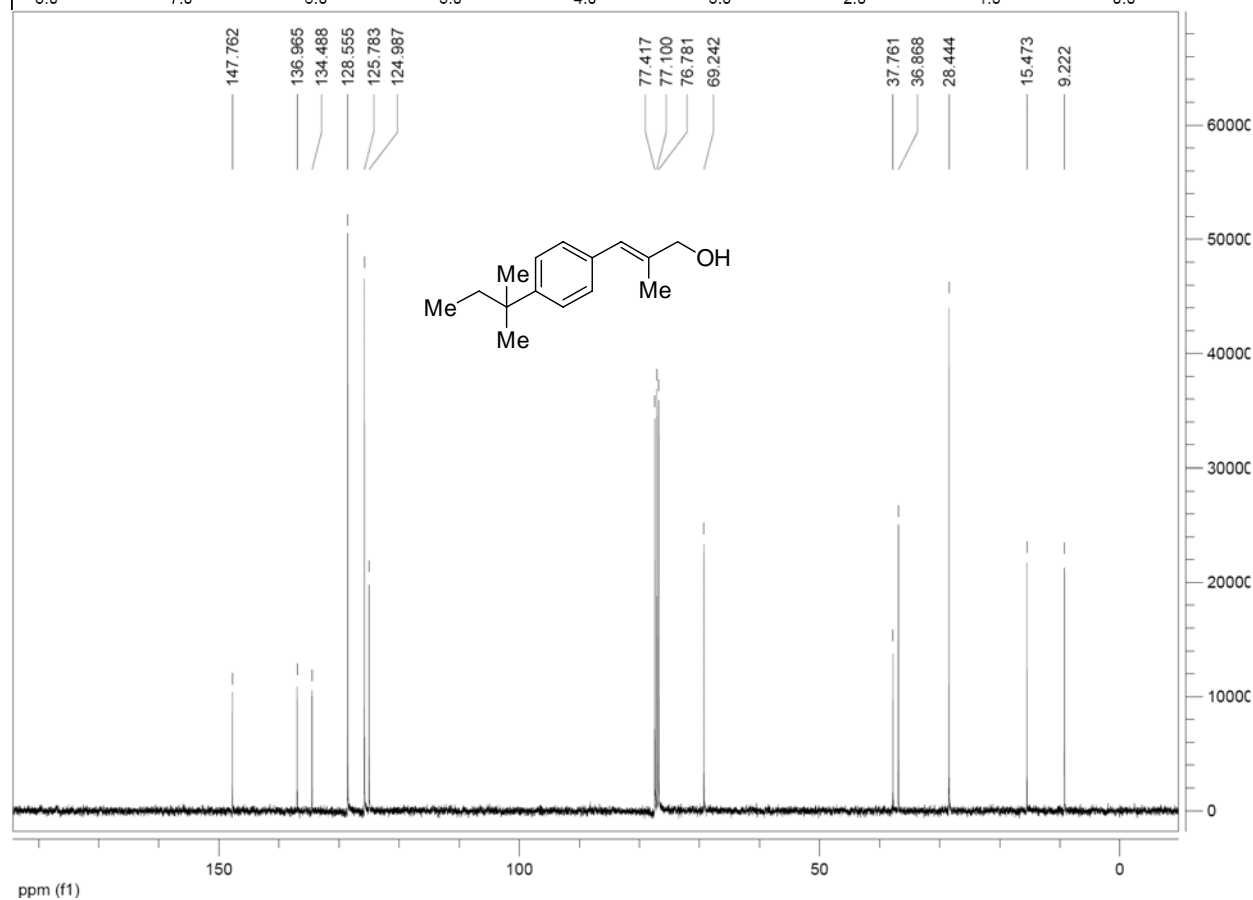
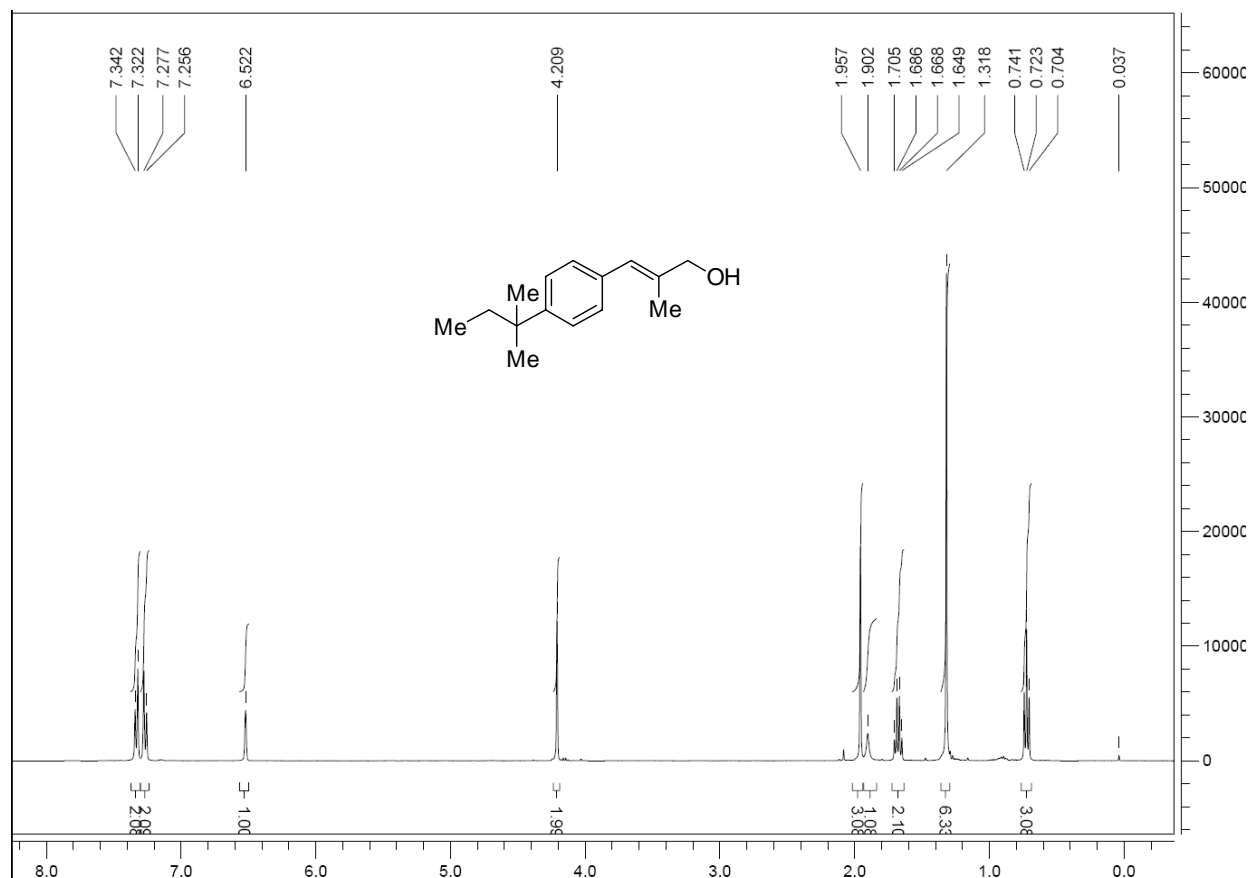
(E)-2-methyl-3-p-tolylprop-2-en-1-ol (1e)



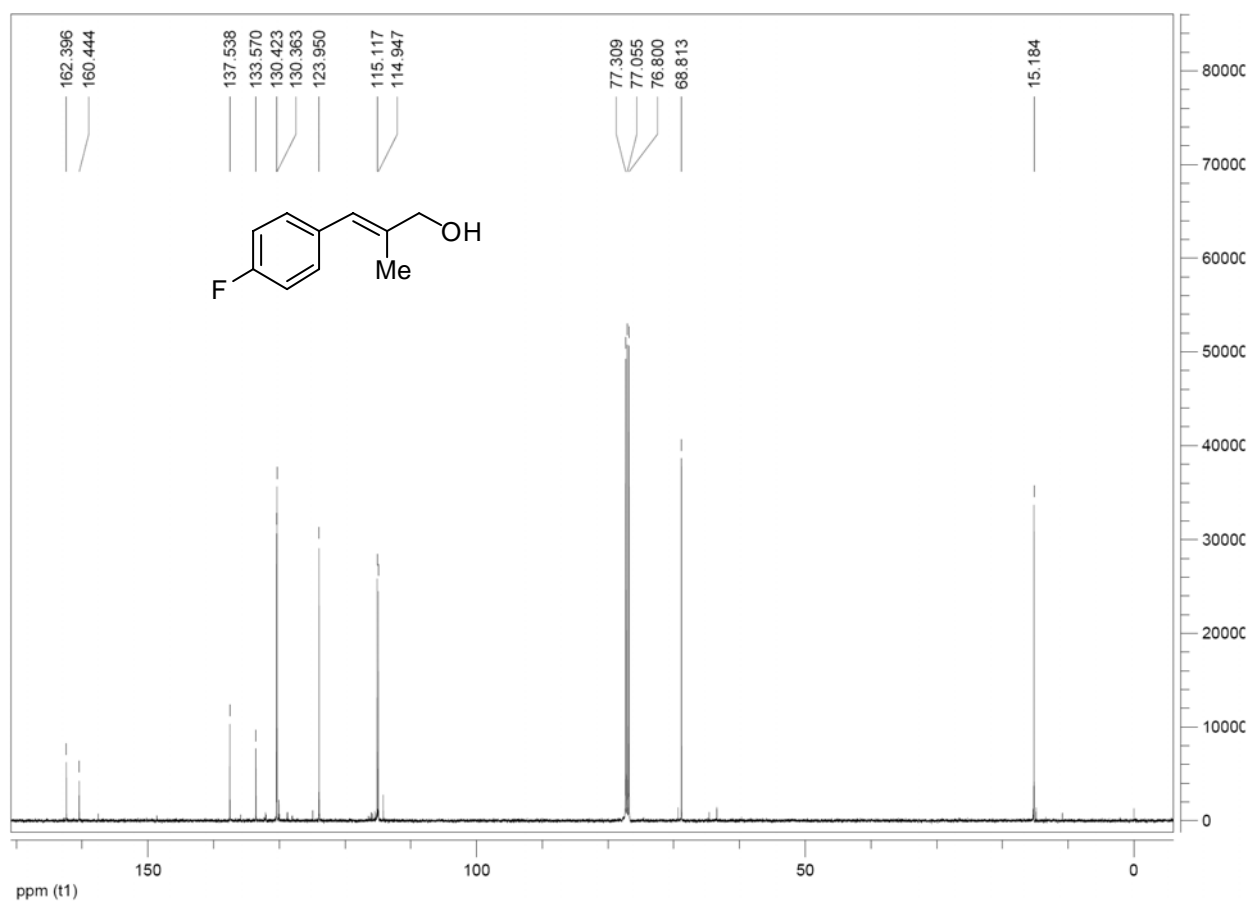
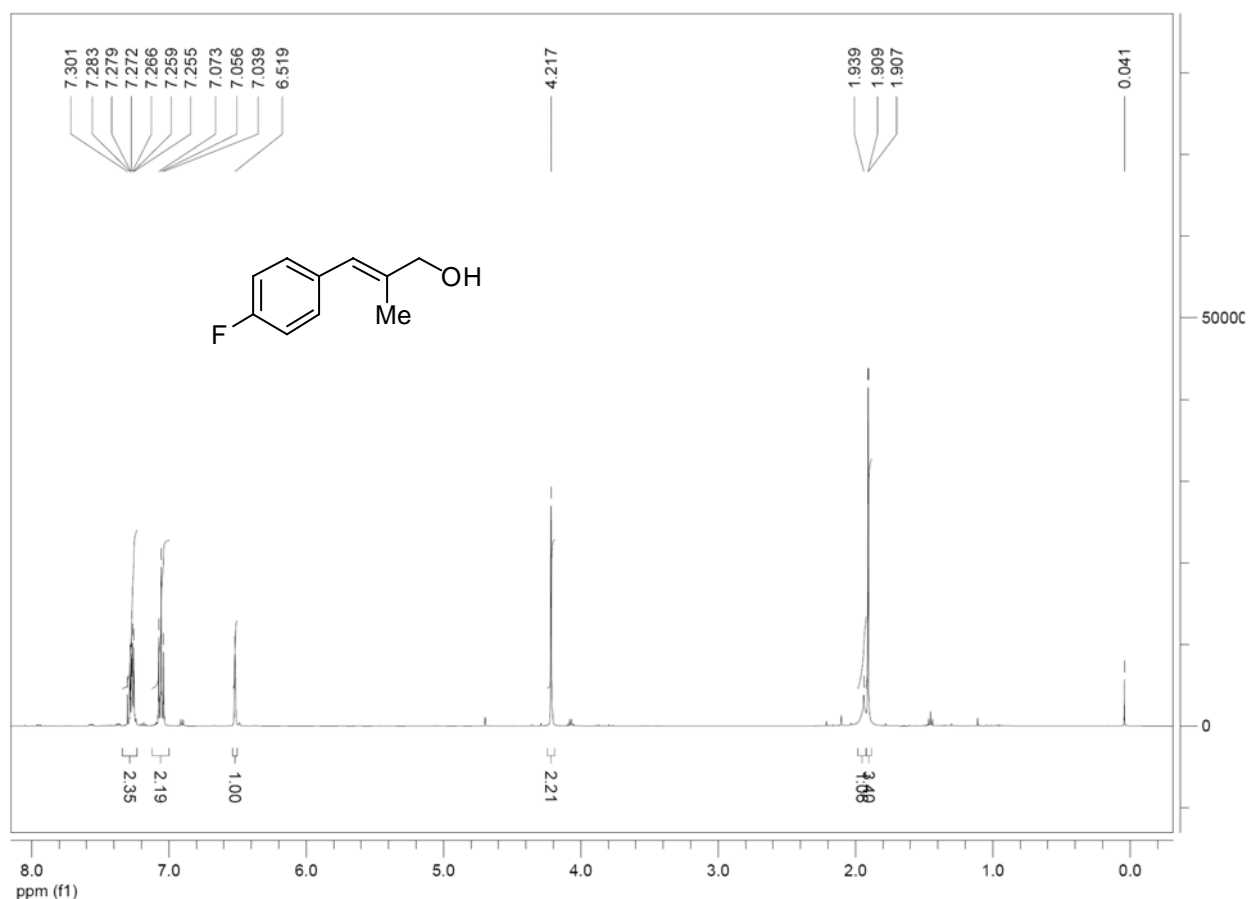
(E)-3-(4-(tert-butyl)phenyl)-2-methylprop-2-en-1-ol (1f)



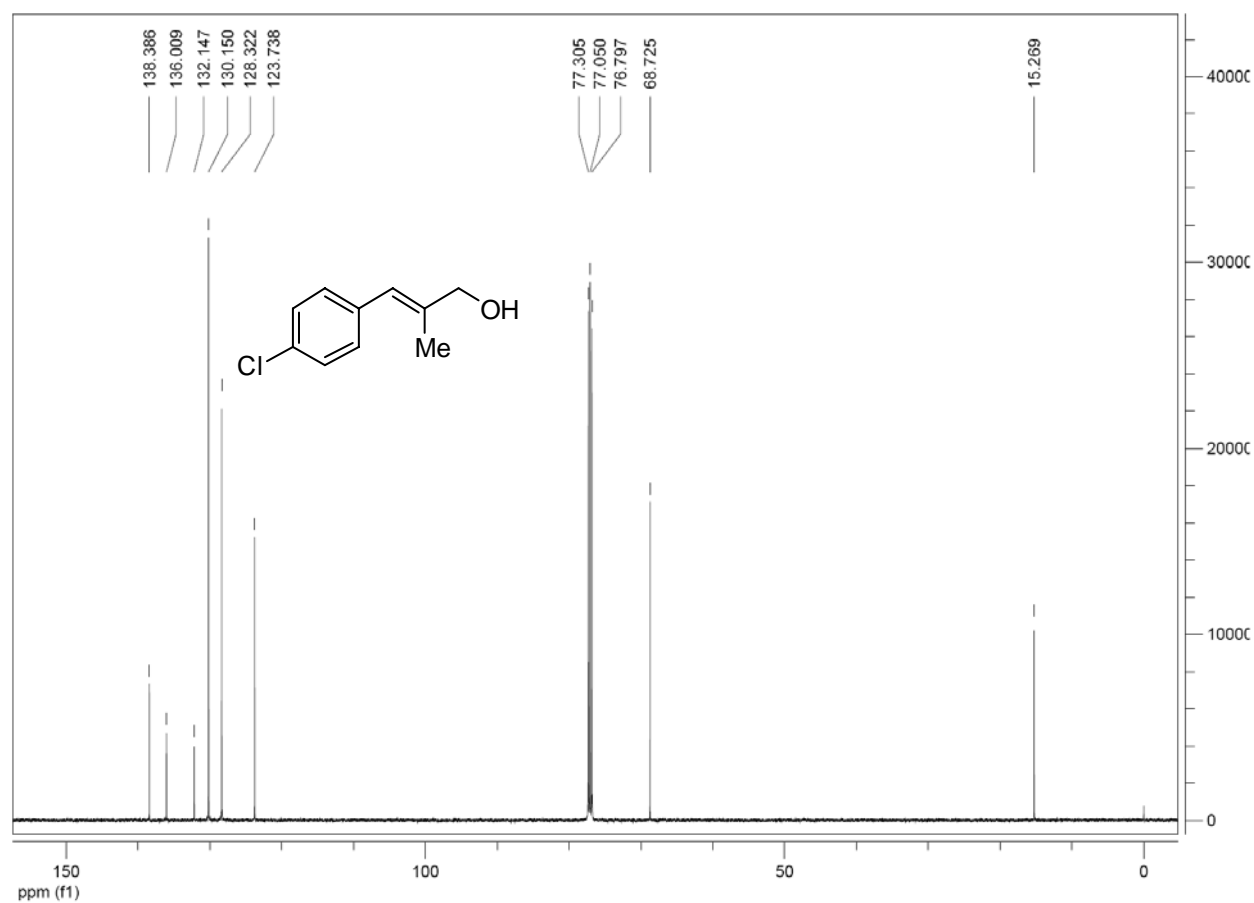
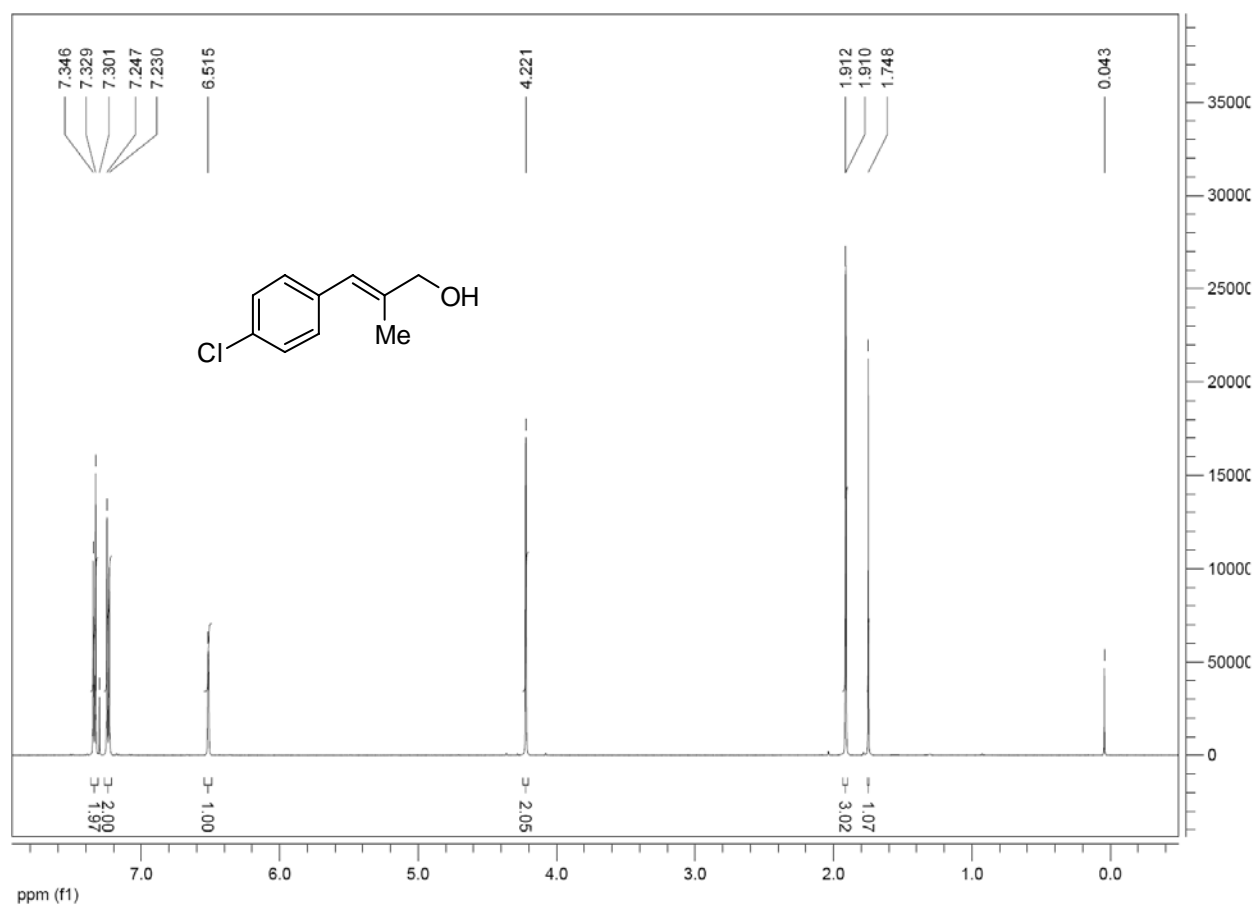
(E)-2-methyl-3-(4-tert-pentylphenyl)prop-2-en-1-ol (1g)



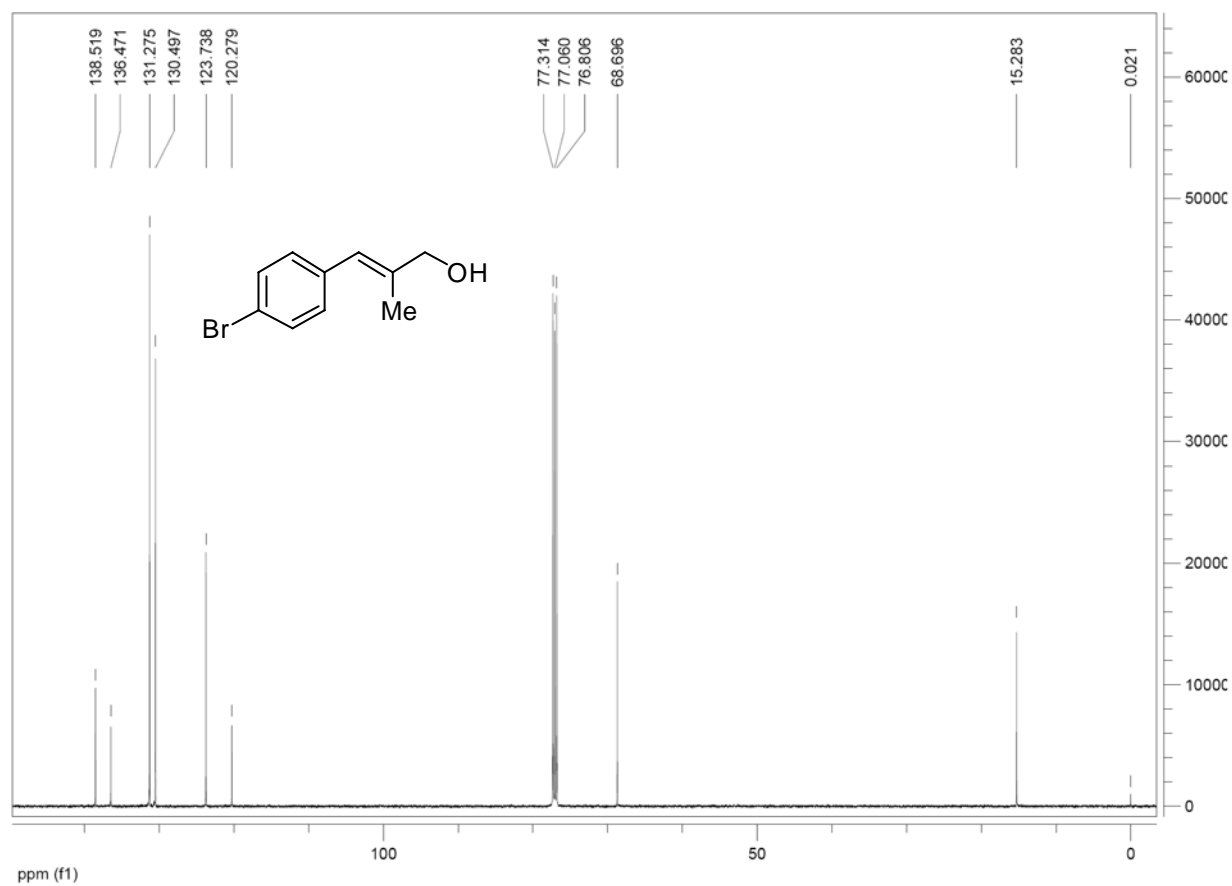
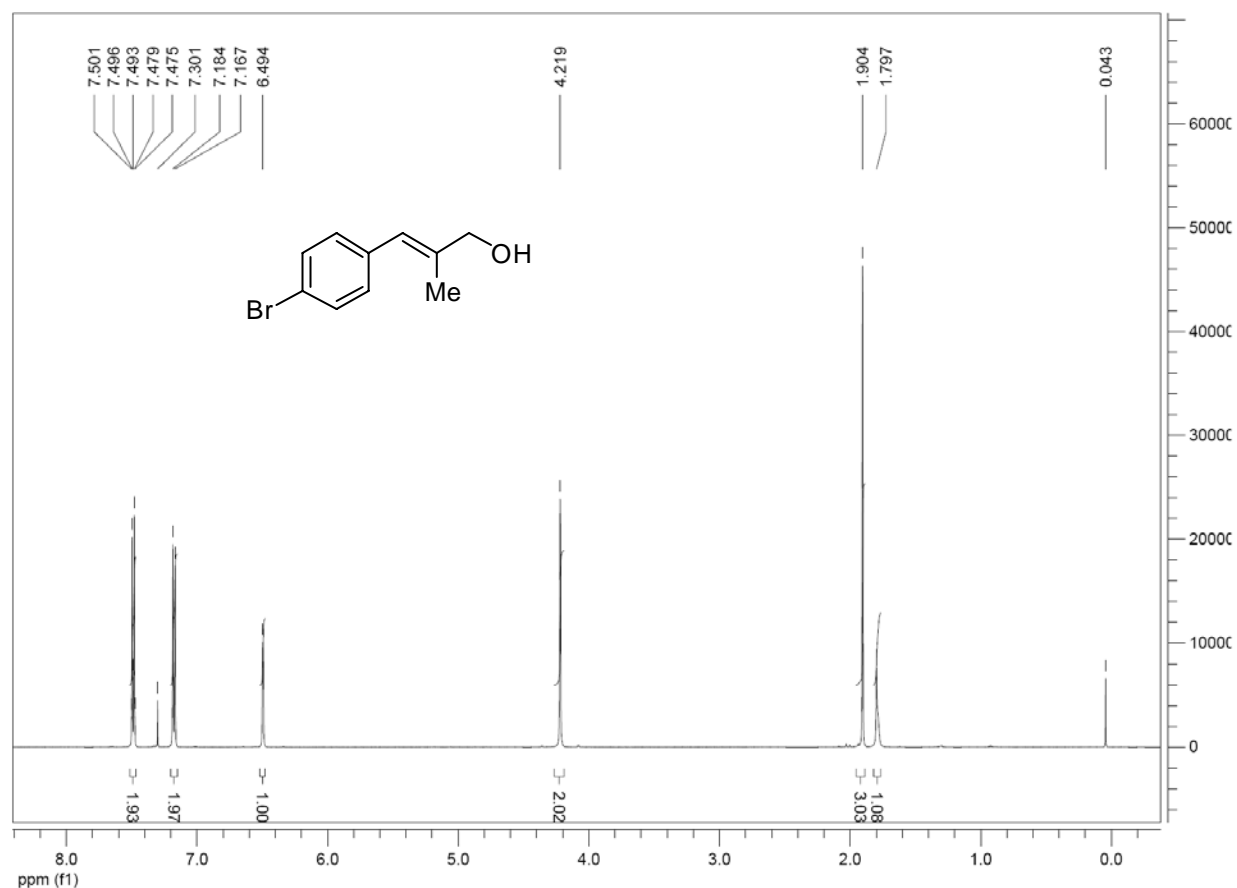
(E)-3-(4-fluorophenyl)-2-methylprop-2-en-1-ol (1h)



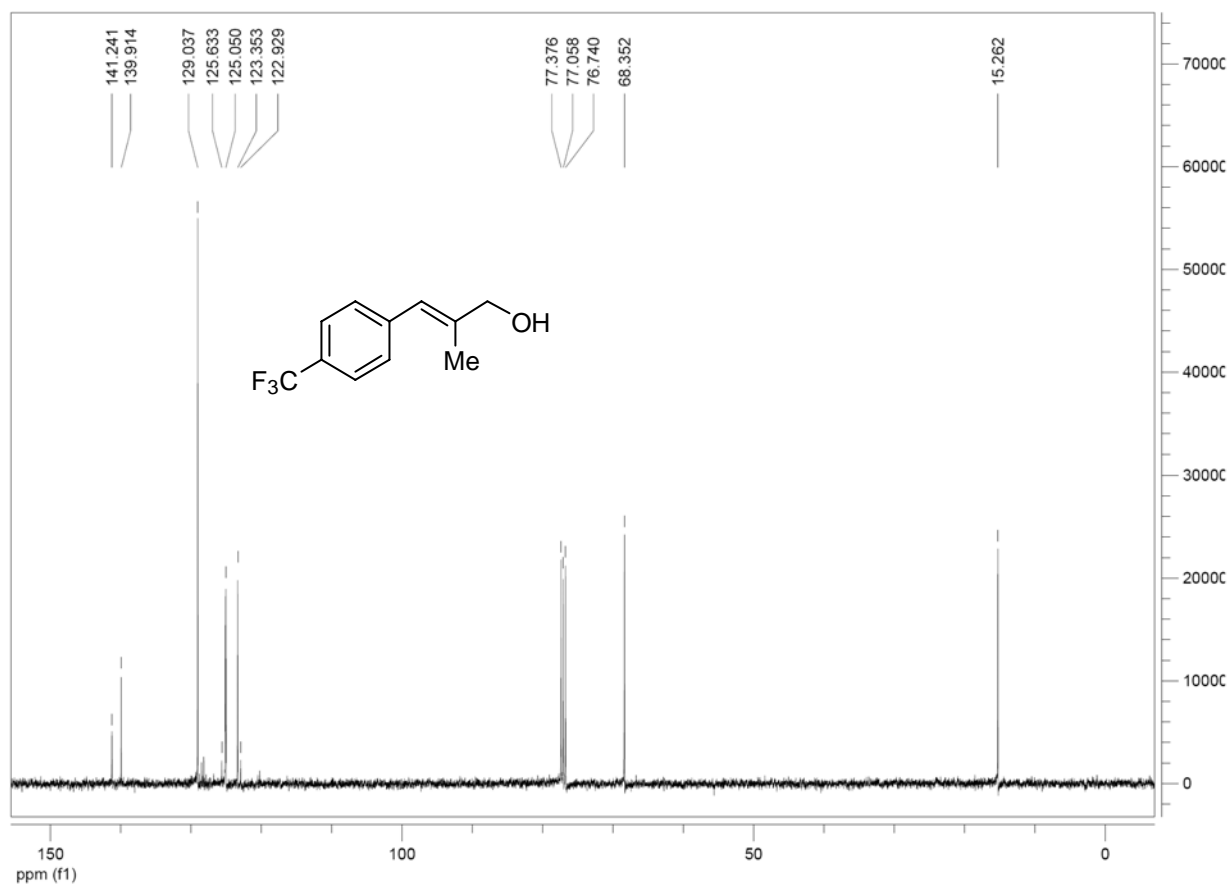
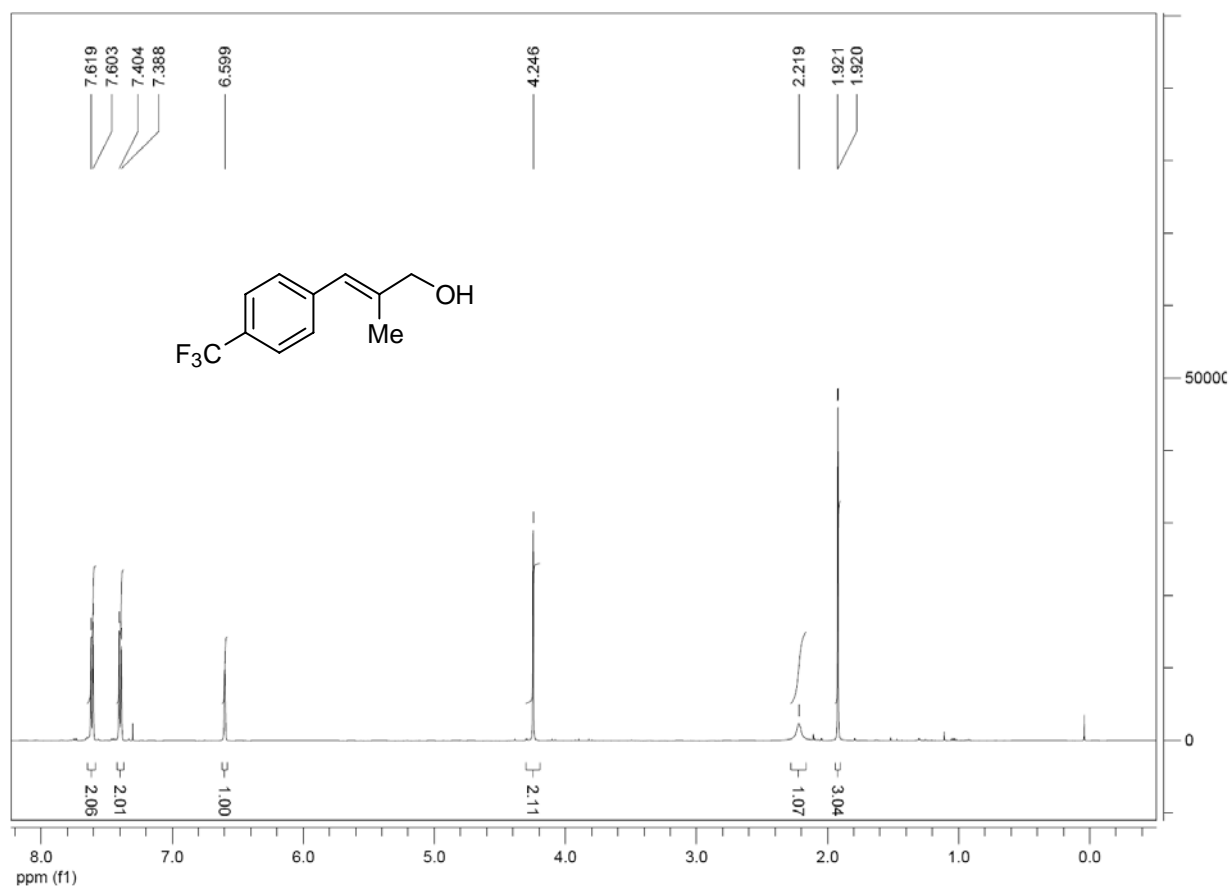
(*E*)-3-(4-chlorophenyl)-2-methylprop-2-en-1-ol (1i)



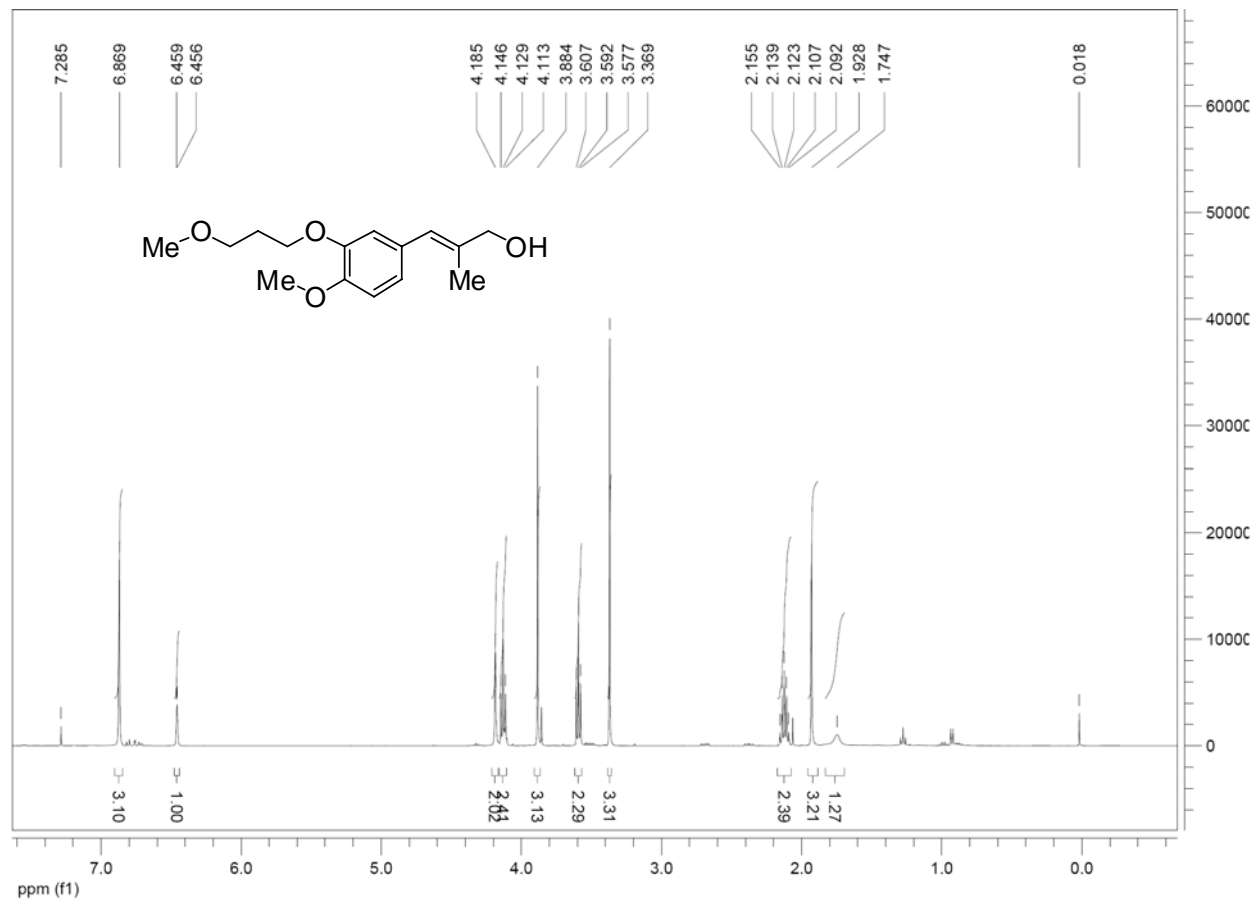
(E)-3-(4-bromophenyl)-2-methylprop-2-en-1-ol (1j)



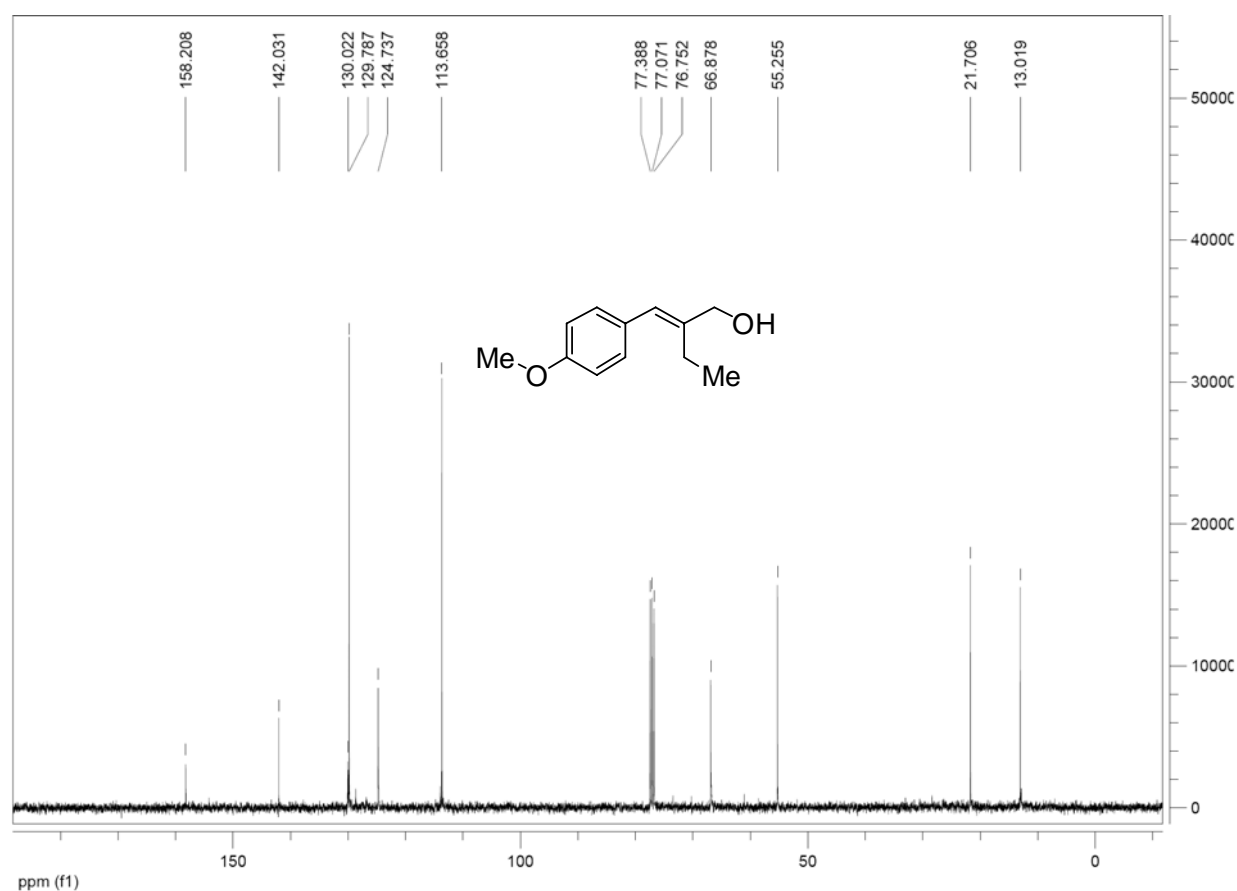
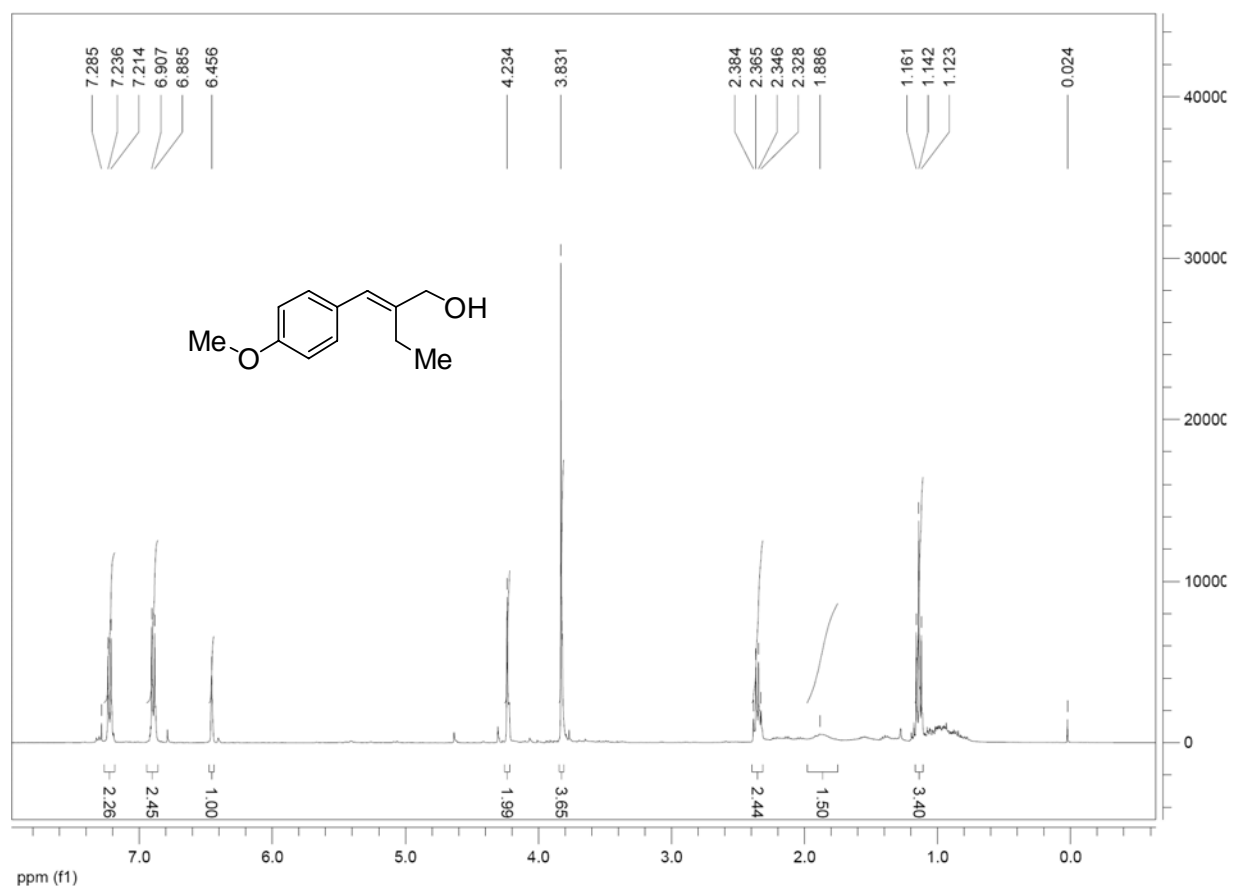
(*E*)-2-methyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (1k)



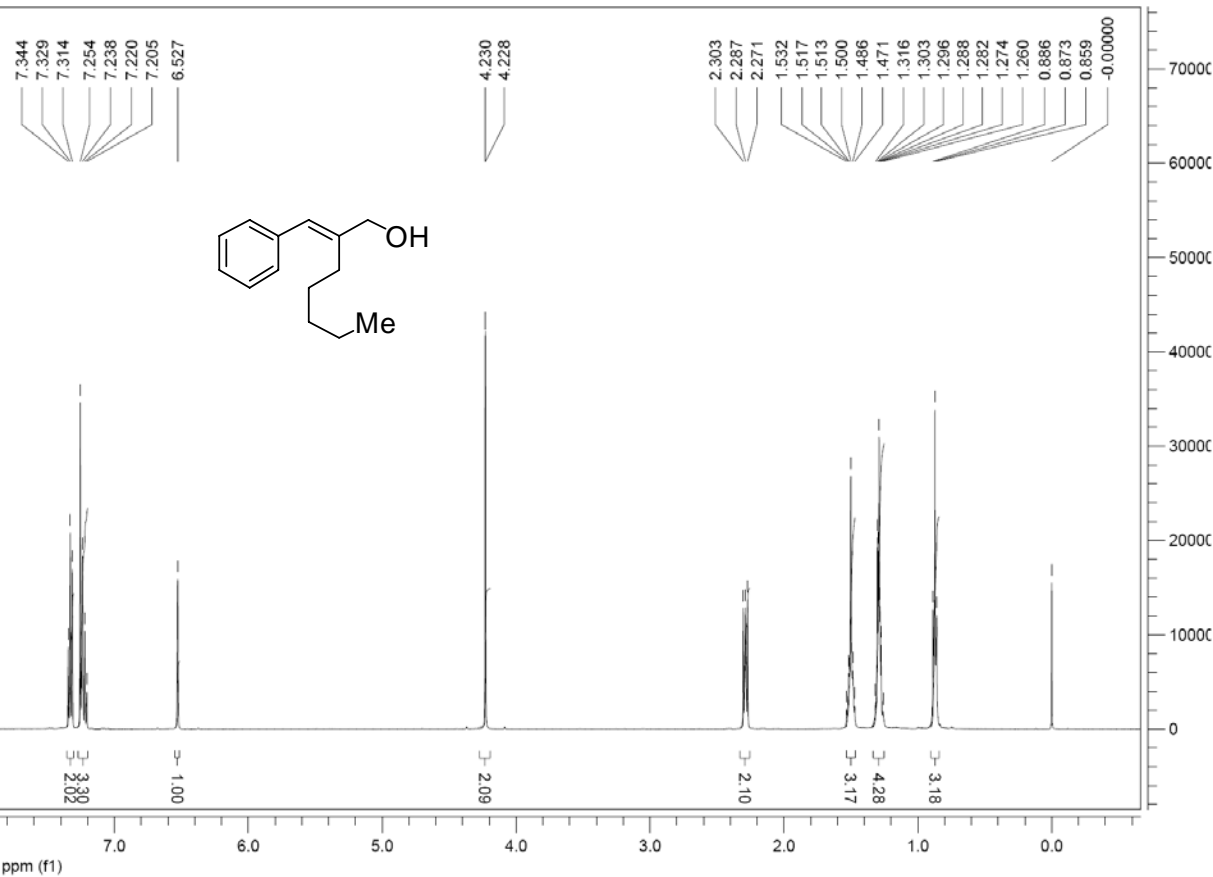
(E)-3-(4-methoxy-3-(3-methoxypropoxy)phenyl)-2-methylprop-2-en-1-ol (1l)



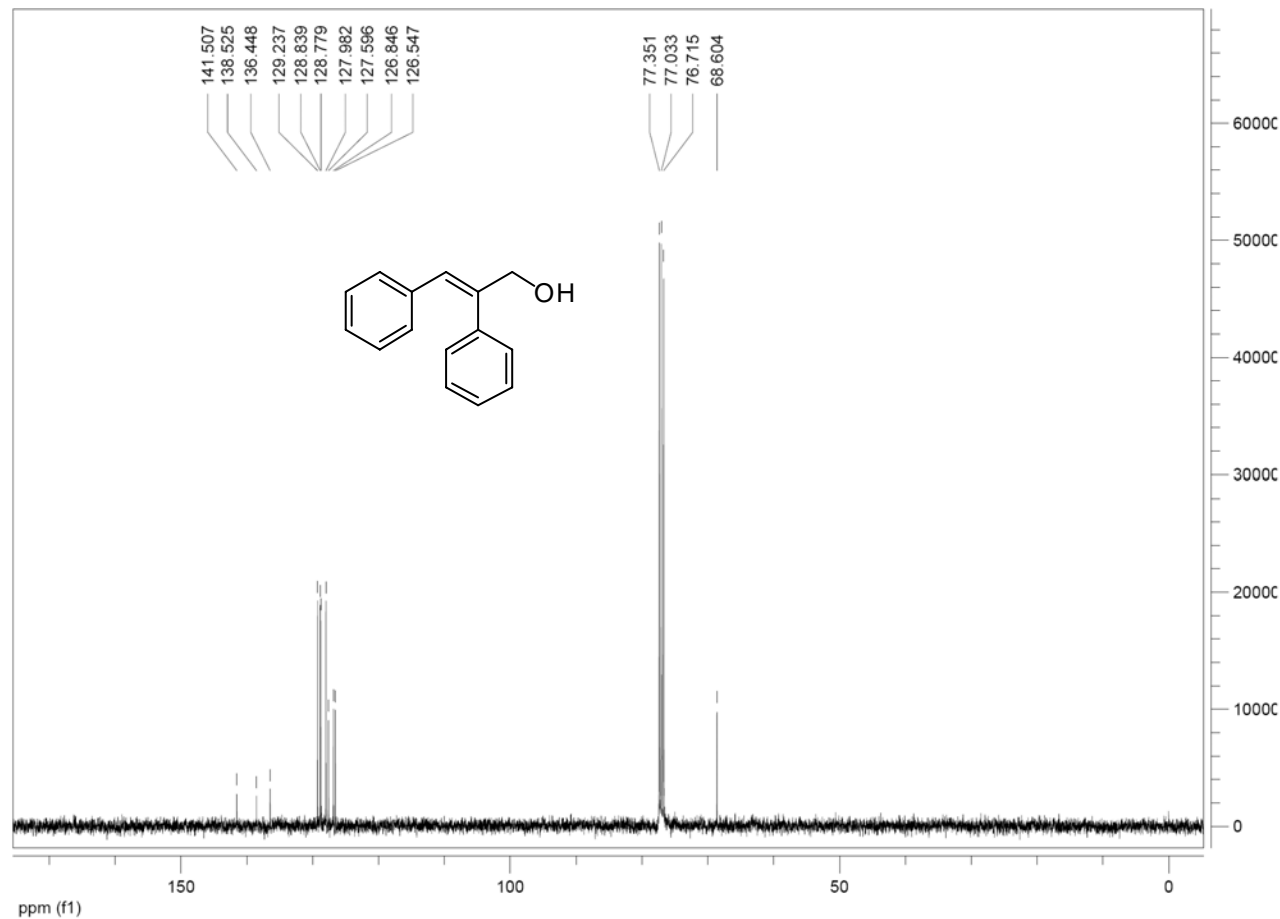
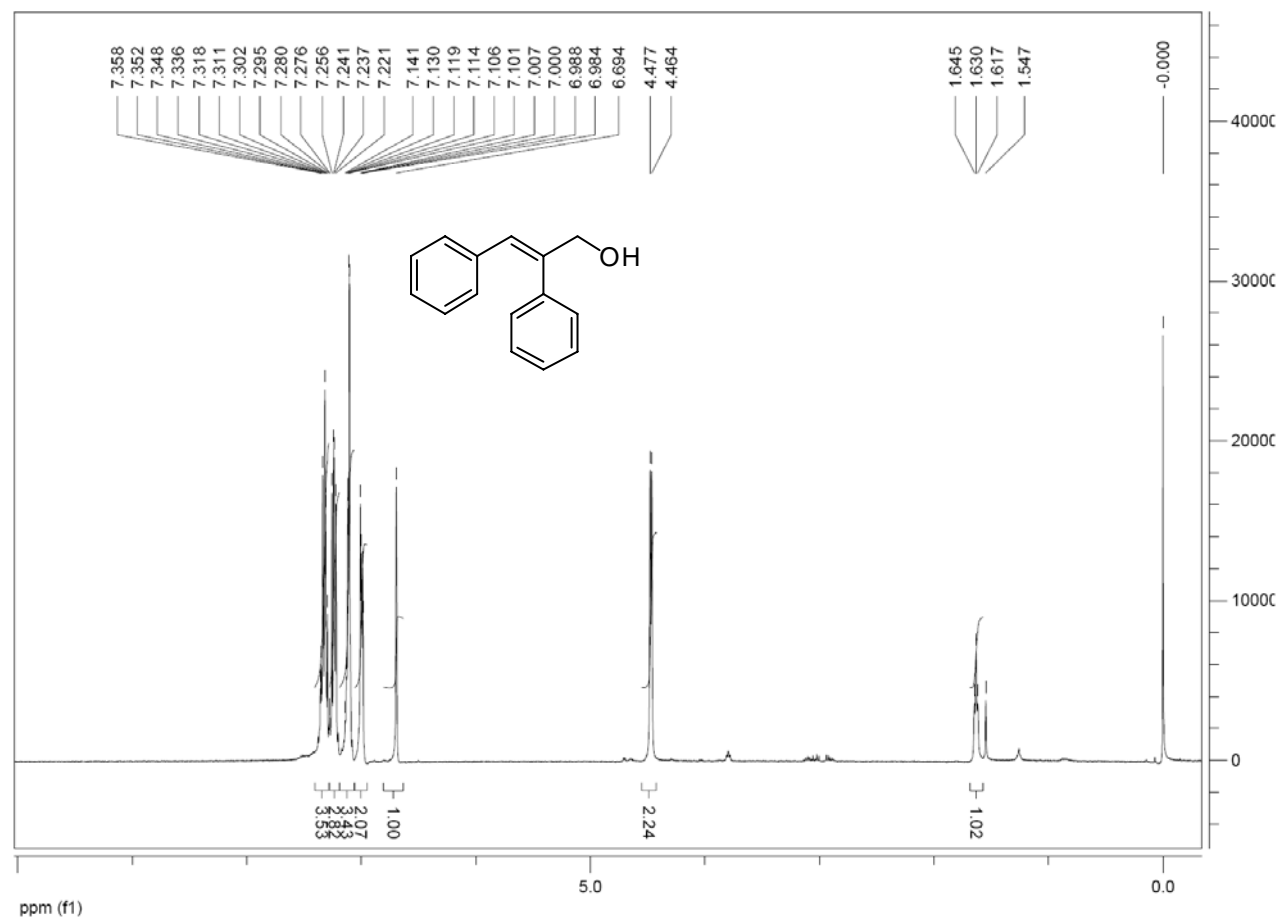
(E)-2-(4-methoxybenzylidene)butan-1-ol (1m)



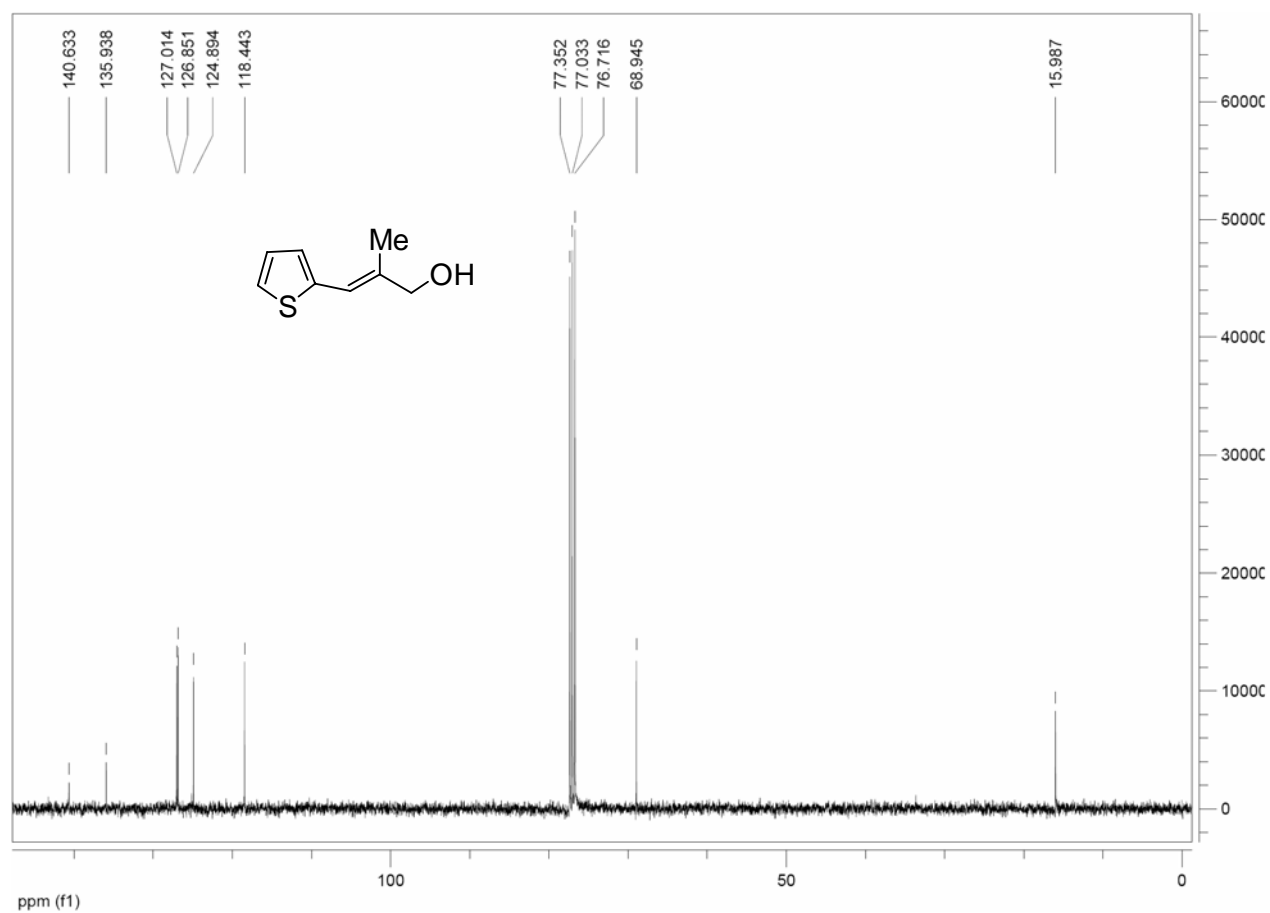
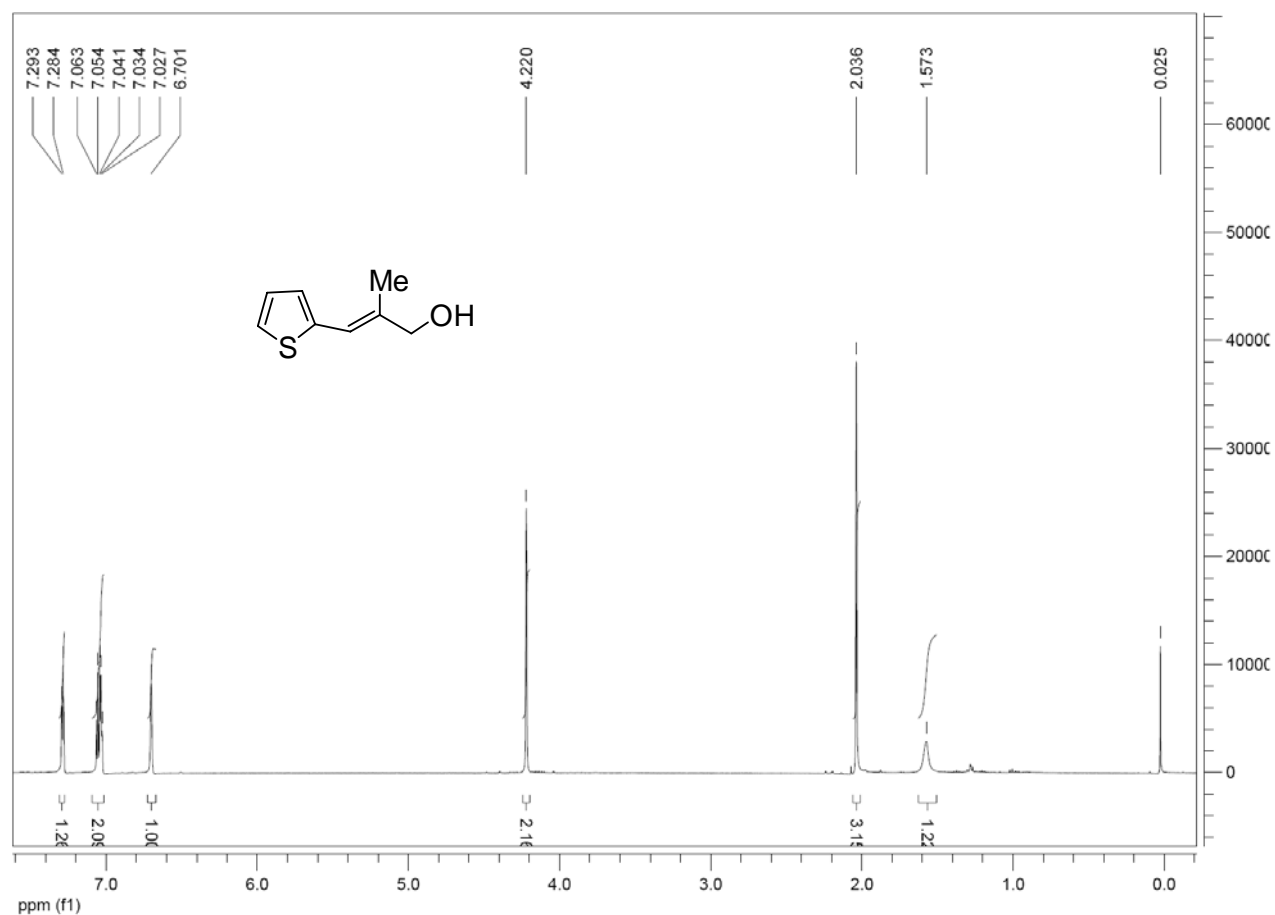
(E)-2-benzylideneheptan-1-ol (1n)



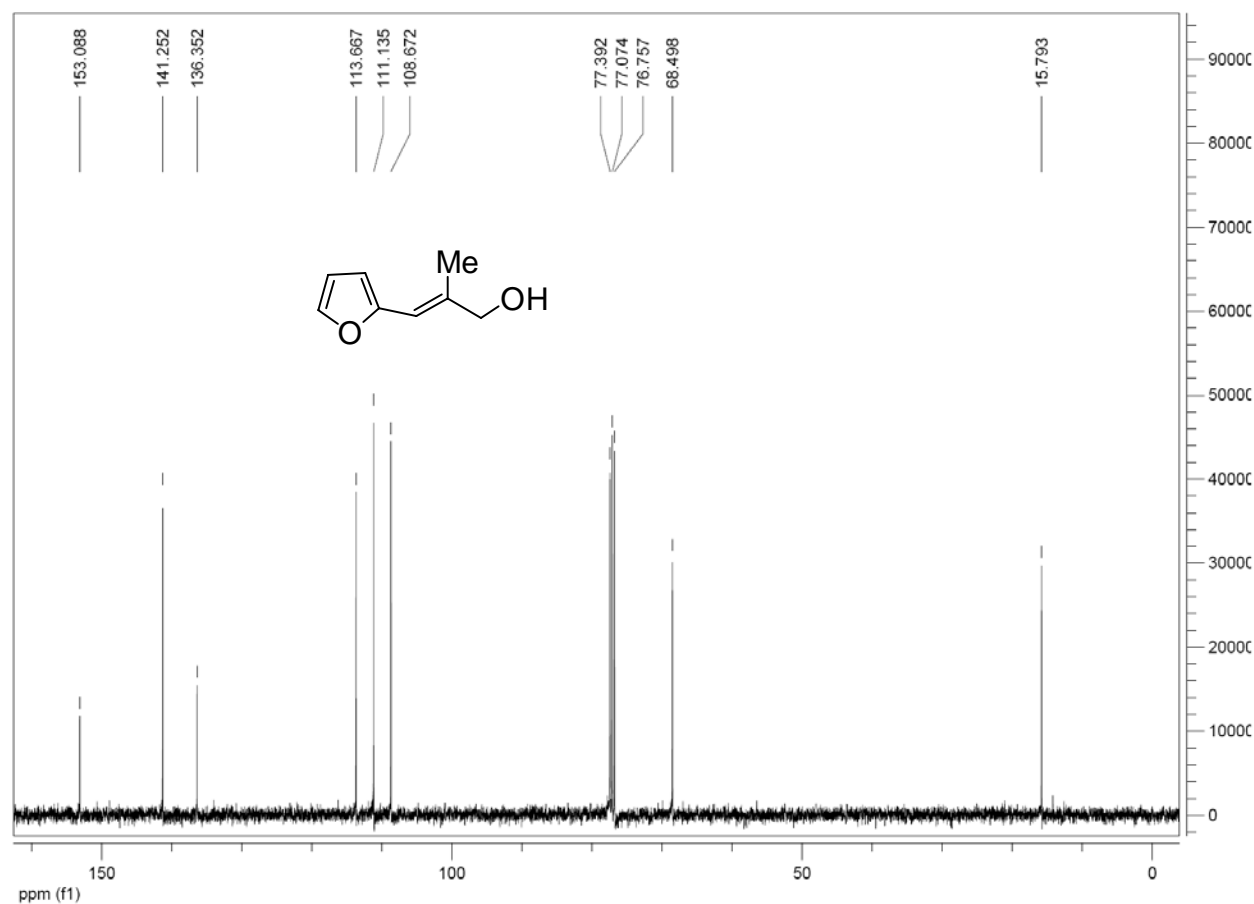
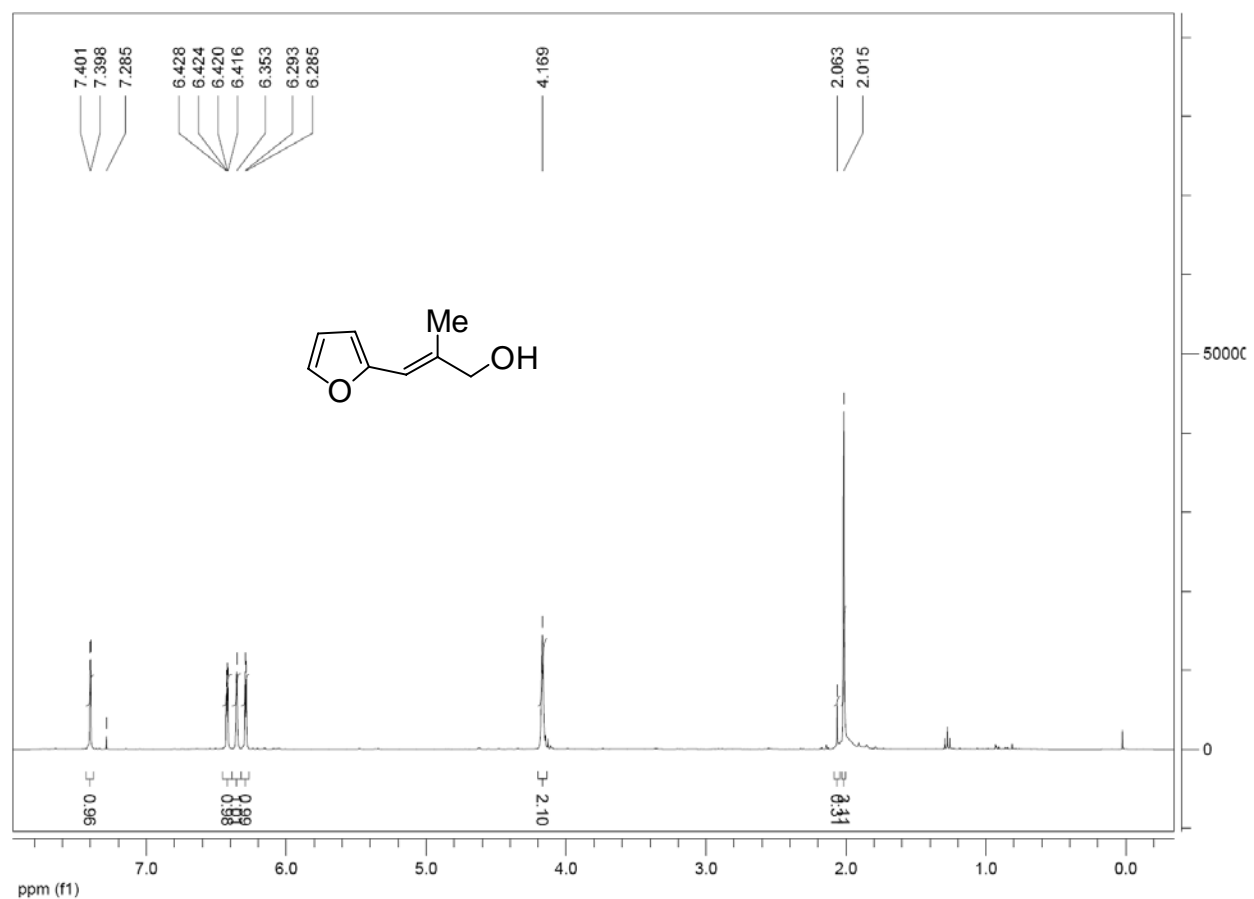
(E)-2,3-diphenylprop-2-en-1-ol (1o)



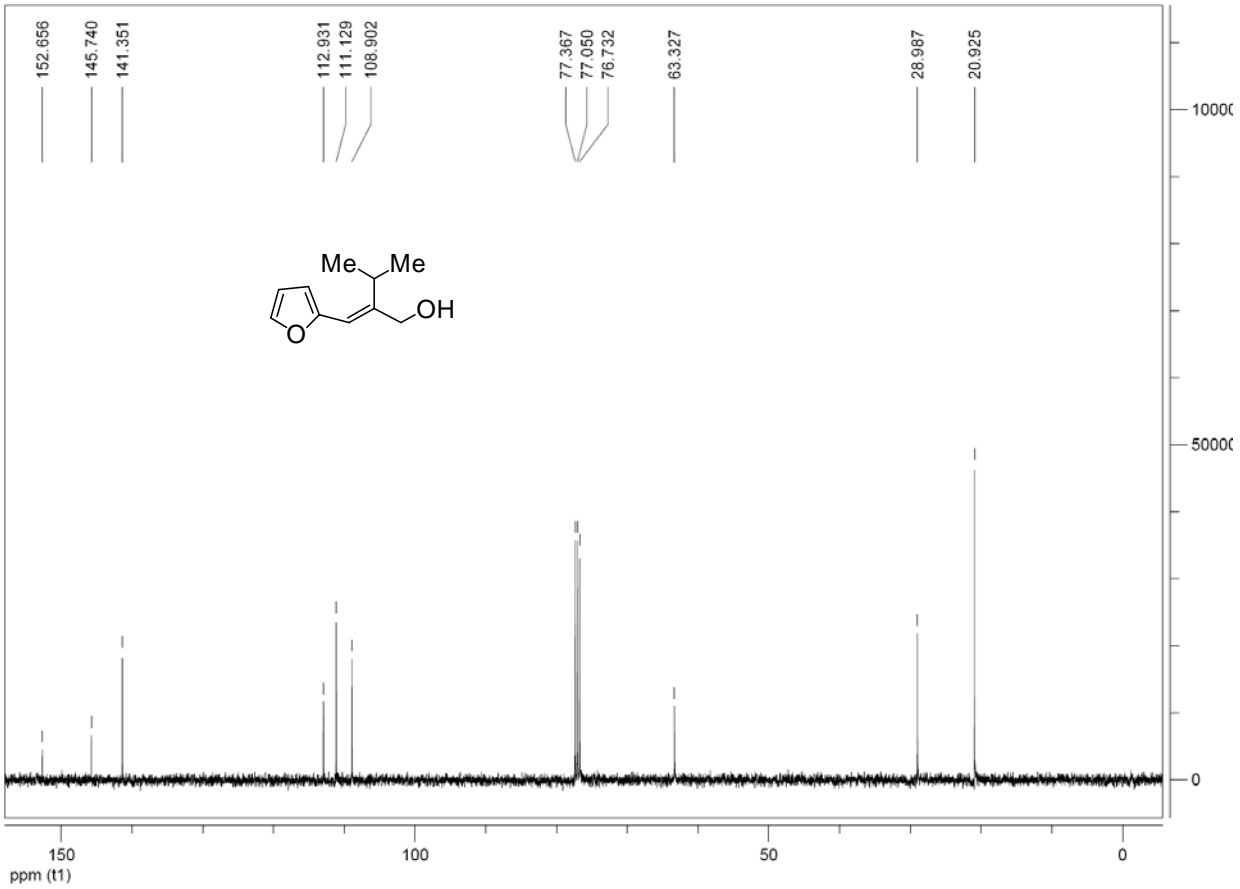
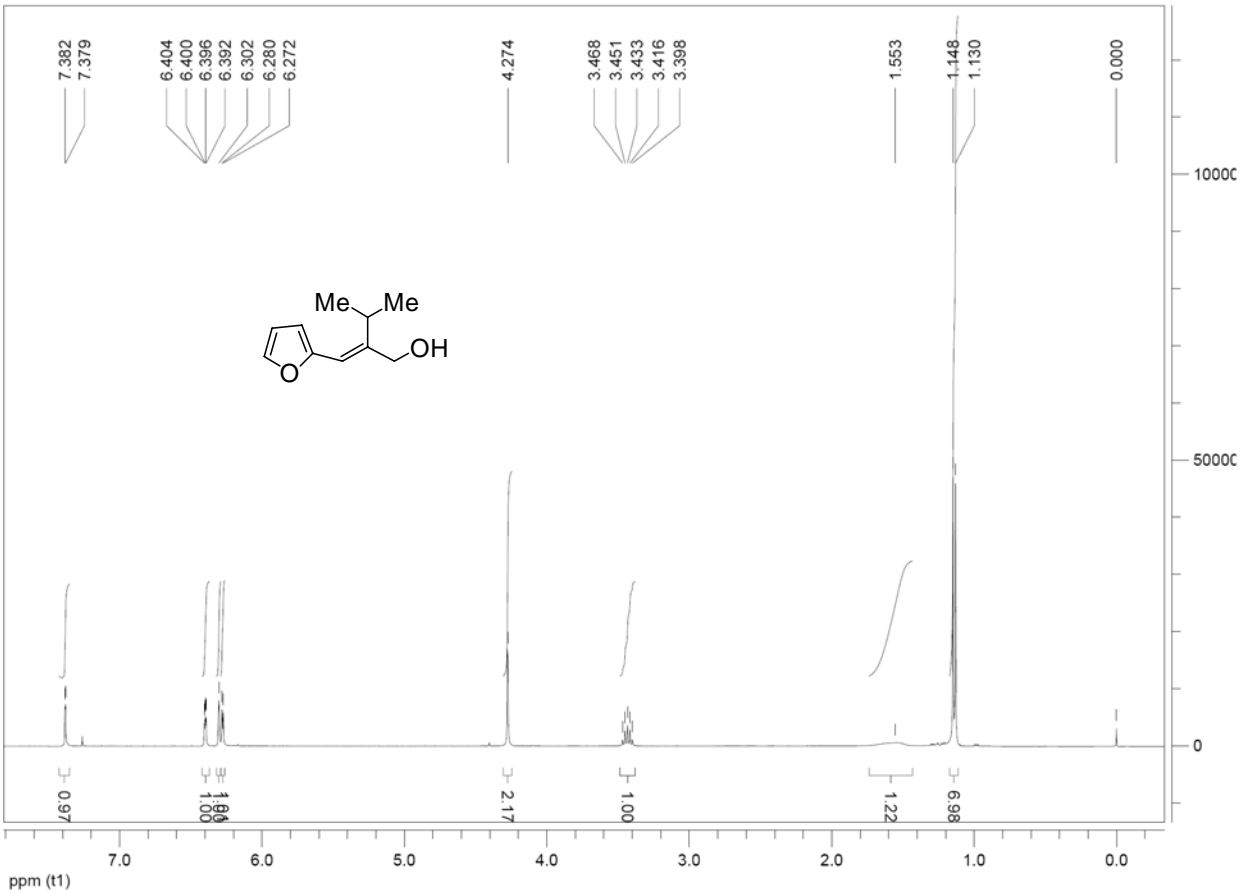
(E)-2-methyl-3-(thiophen-2-yl)prop-2-en-1-ol (1p)



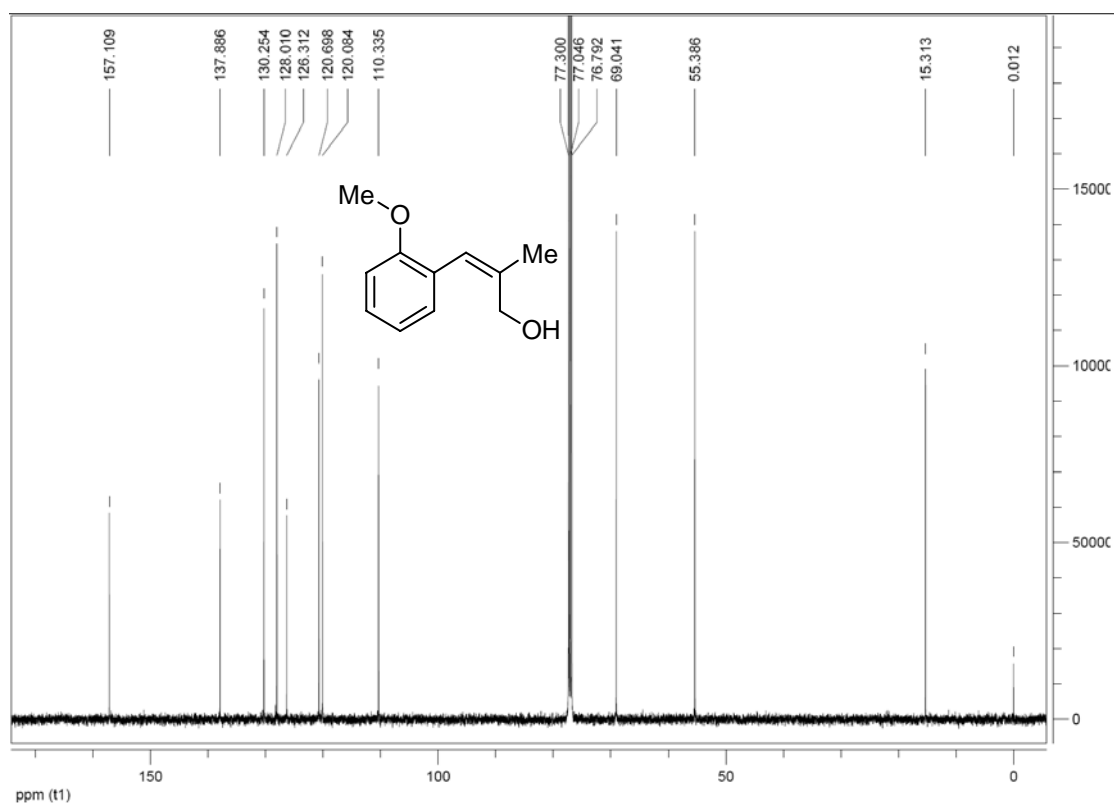
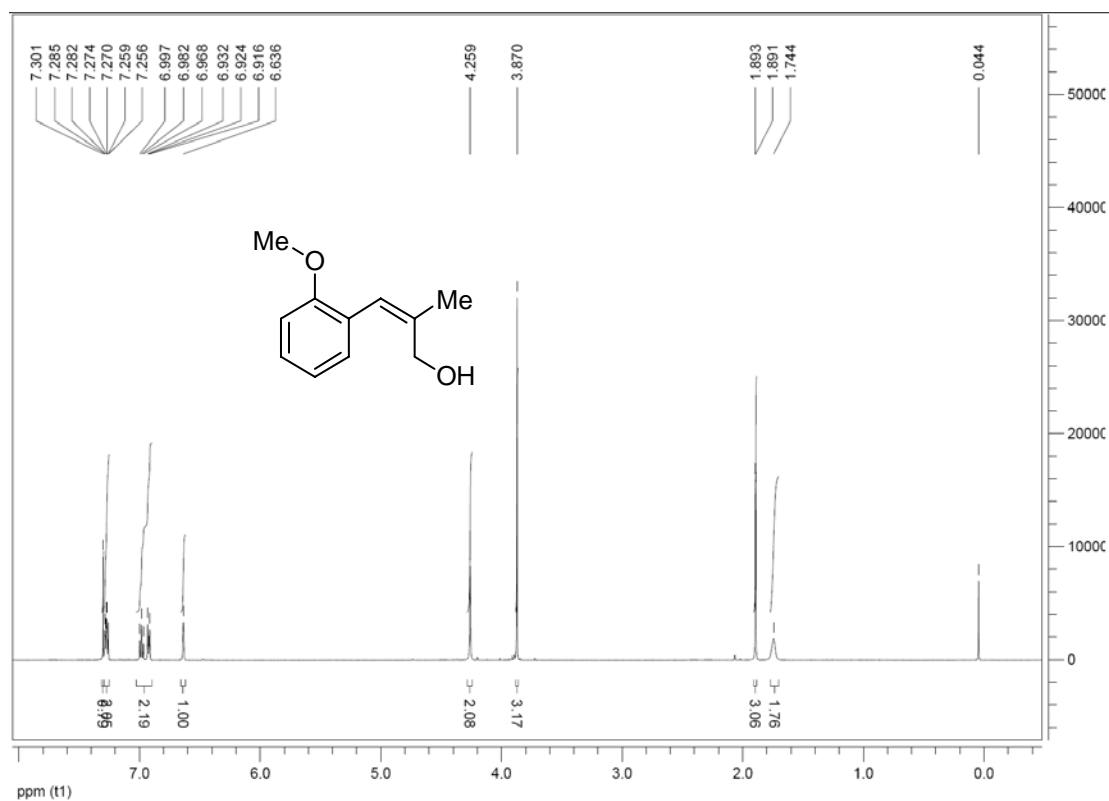
(E)-3-(furan-2-yl)-2-methylprop-2-en-1-ol (1q)



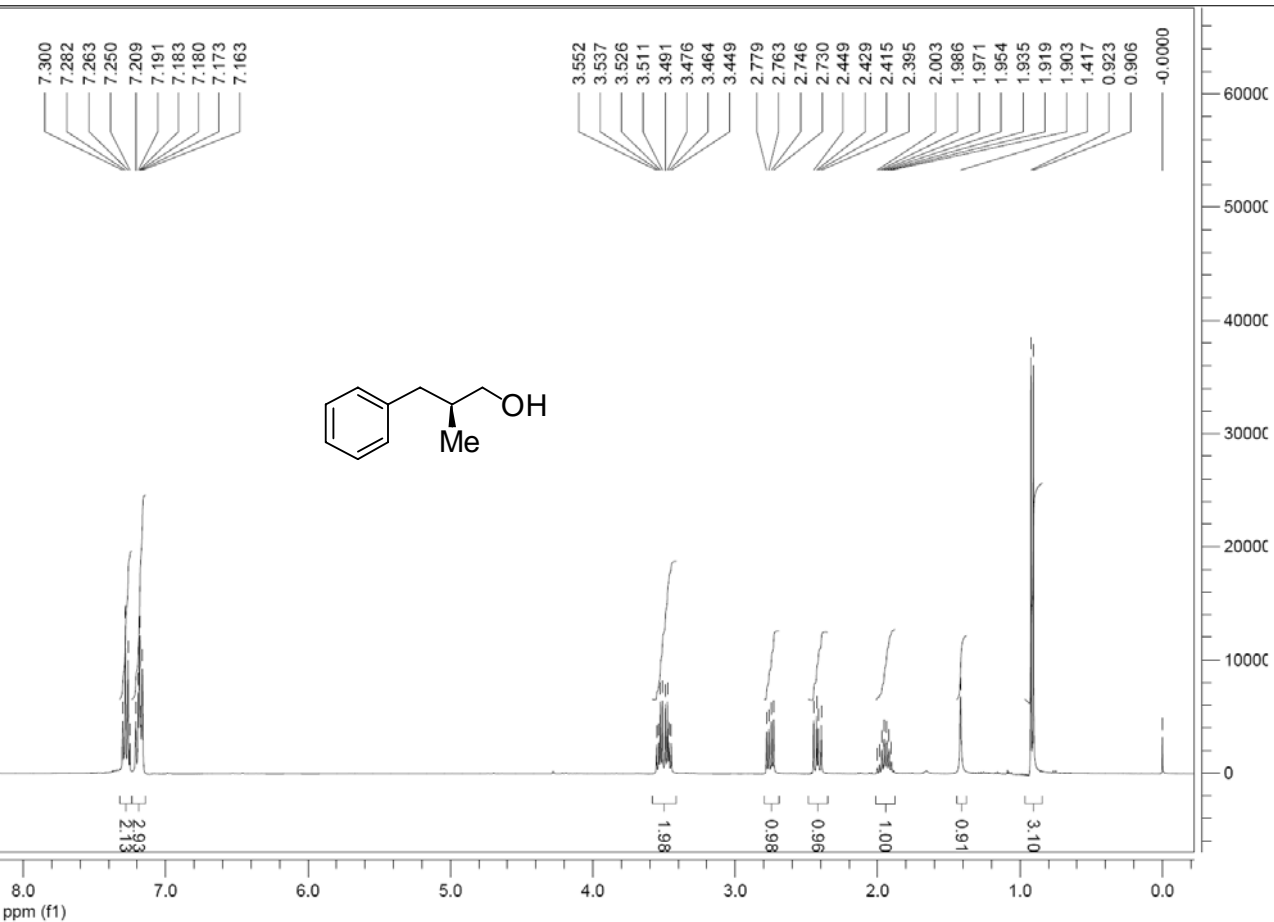
(E)-2-(furan-2-ylmethylene)-3-methylbutan-1-ol (1r)



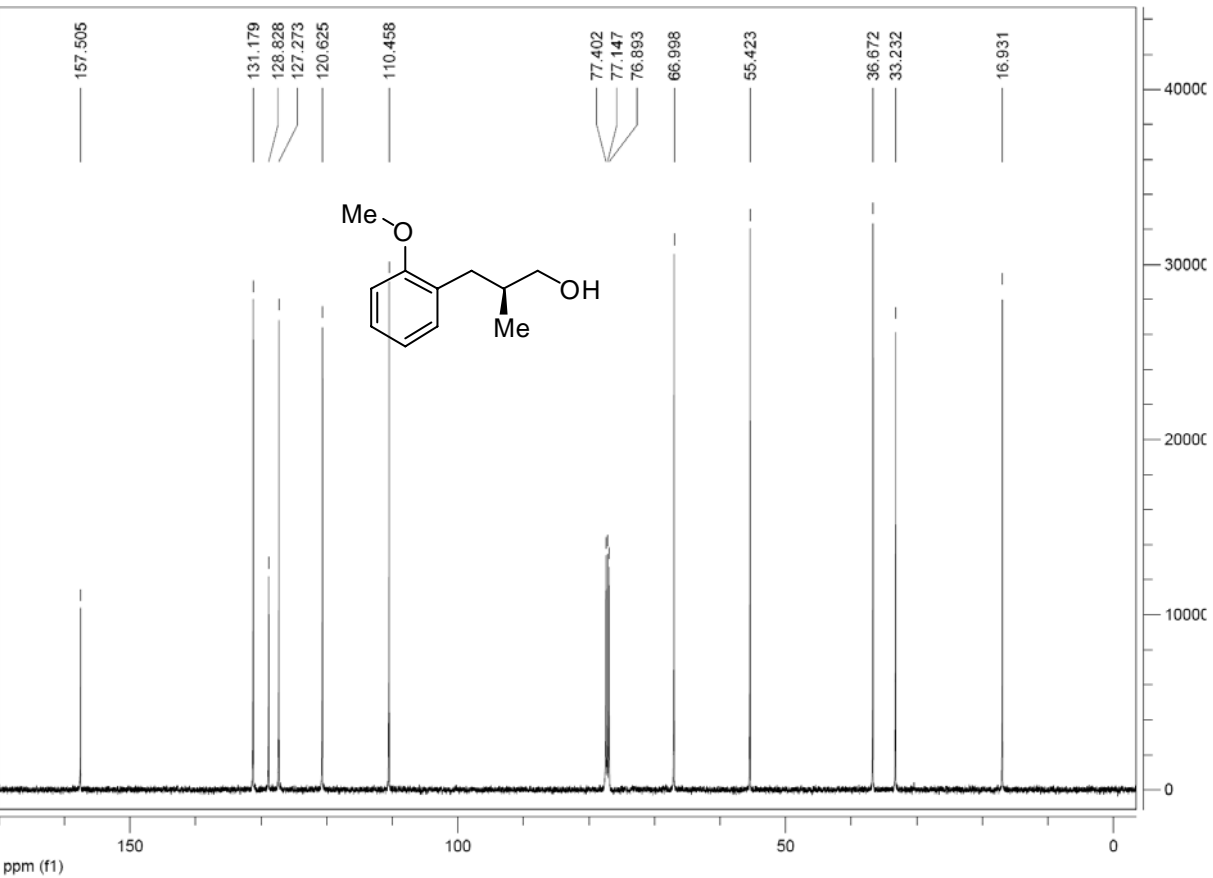
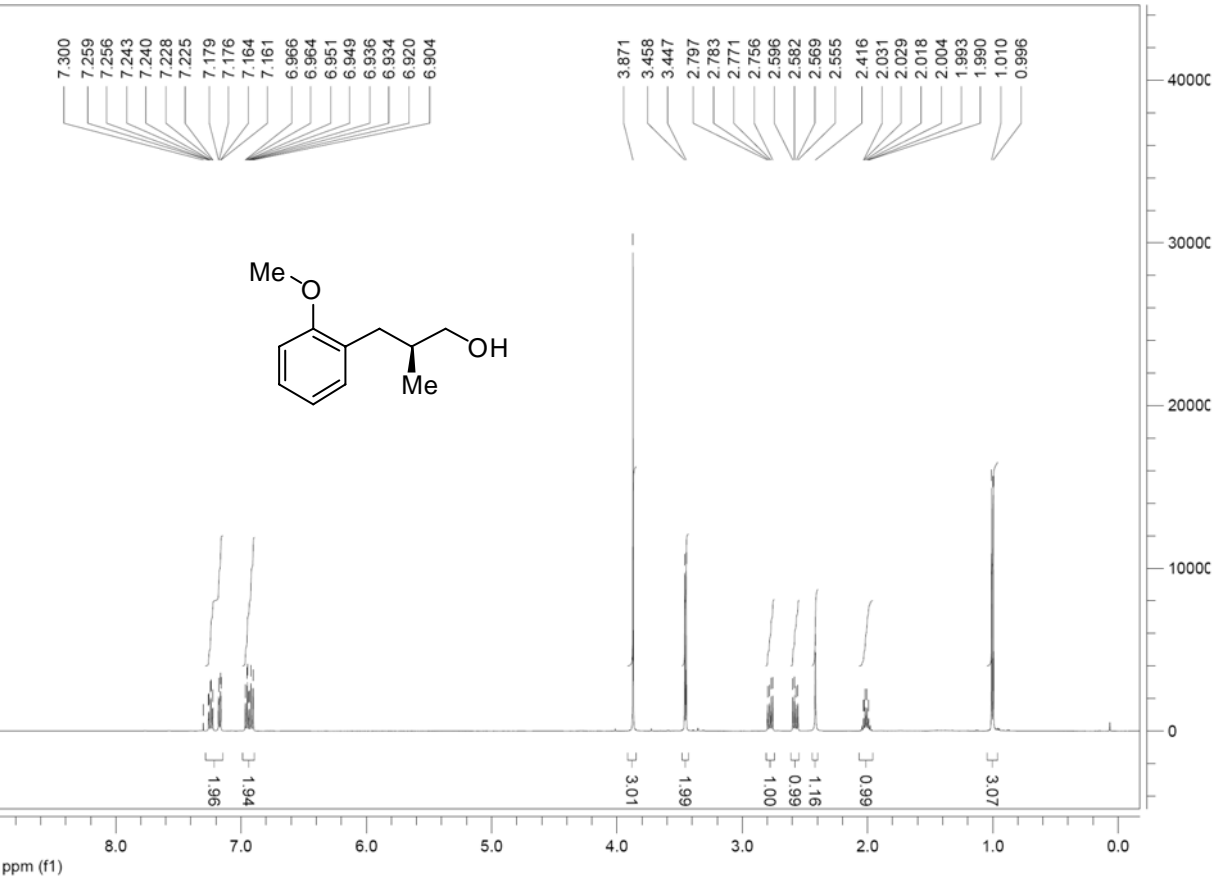
(Z)-3-(2-methoxyphenyl)-2-methylprop-2-en-1-ol (1s)



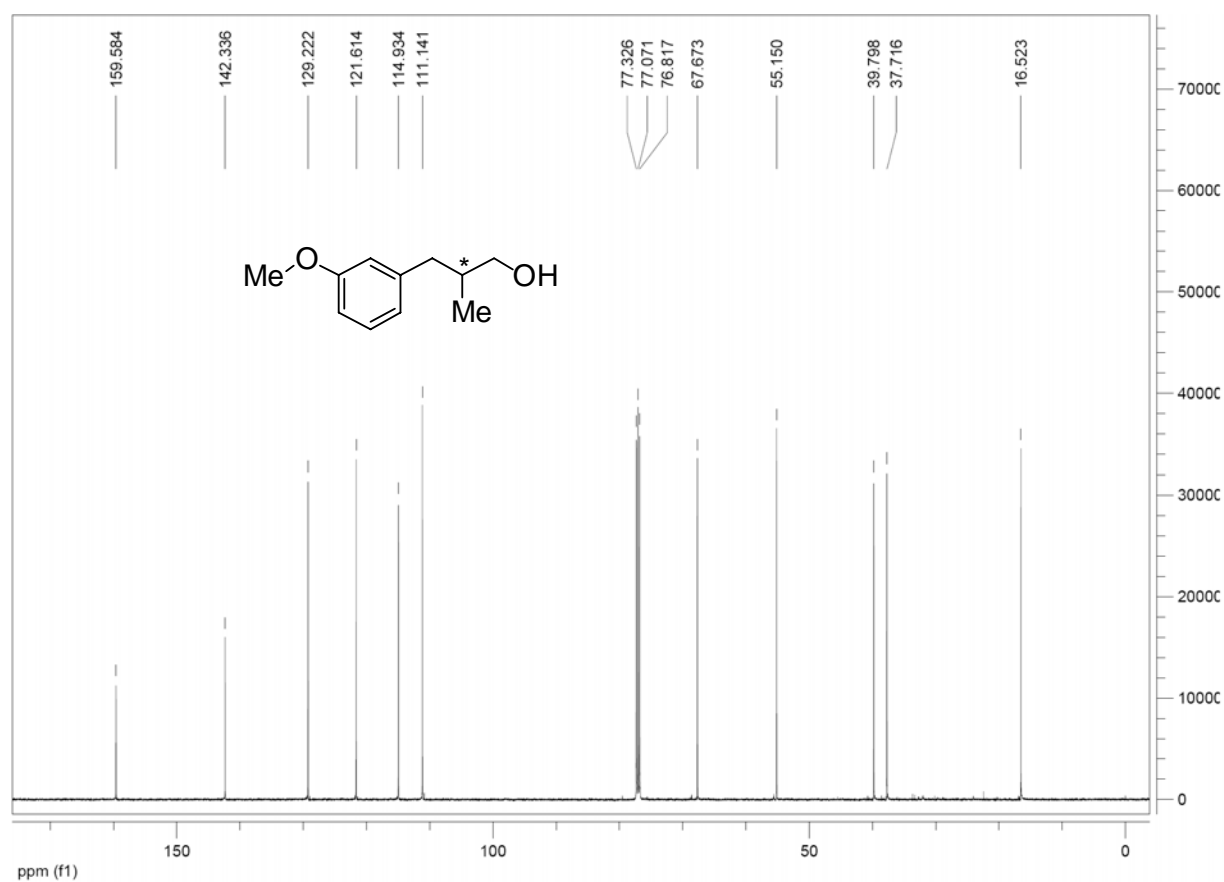
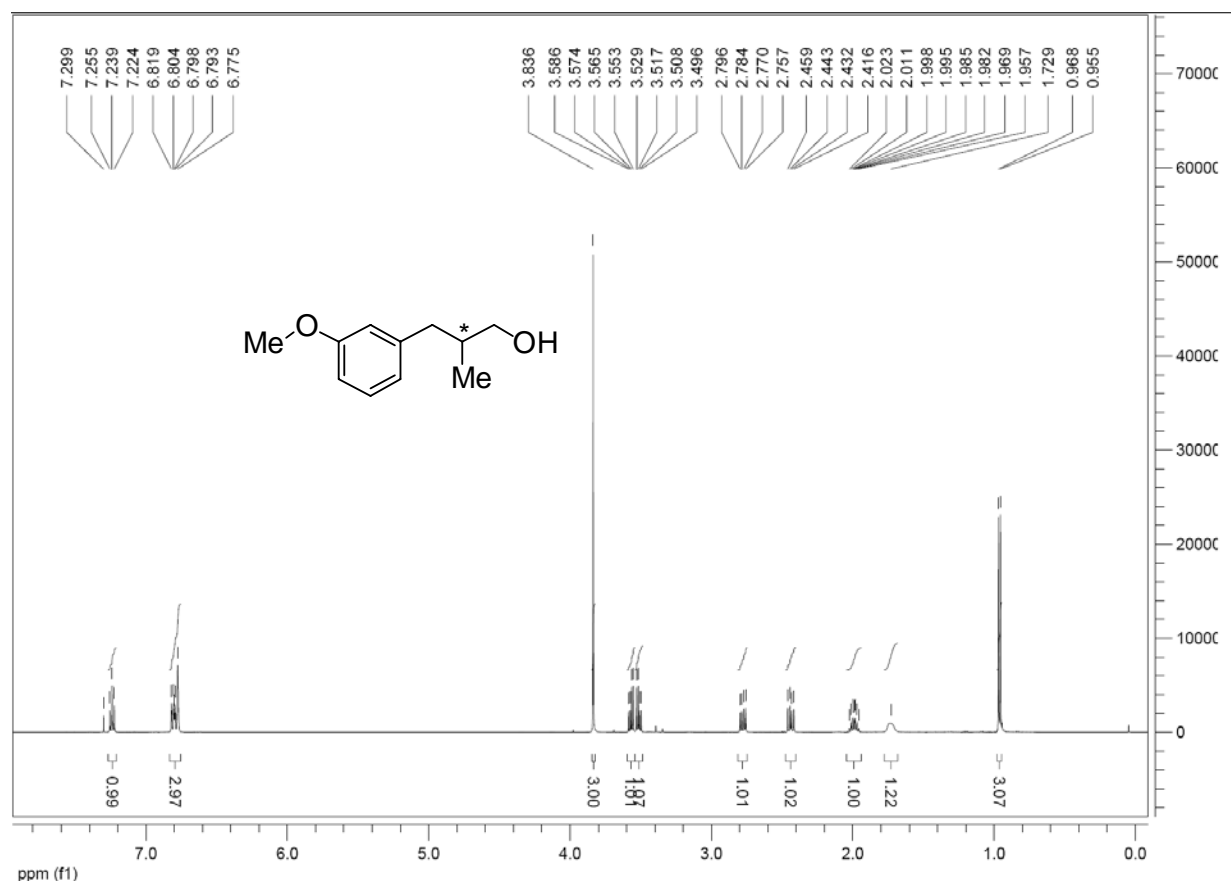
(S)-2-methyl-3-phenylpropan-1-ol(2a)



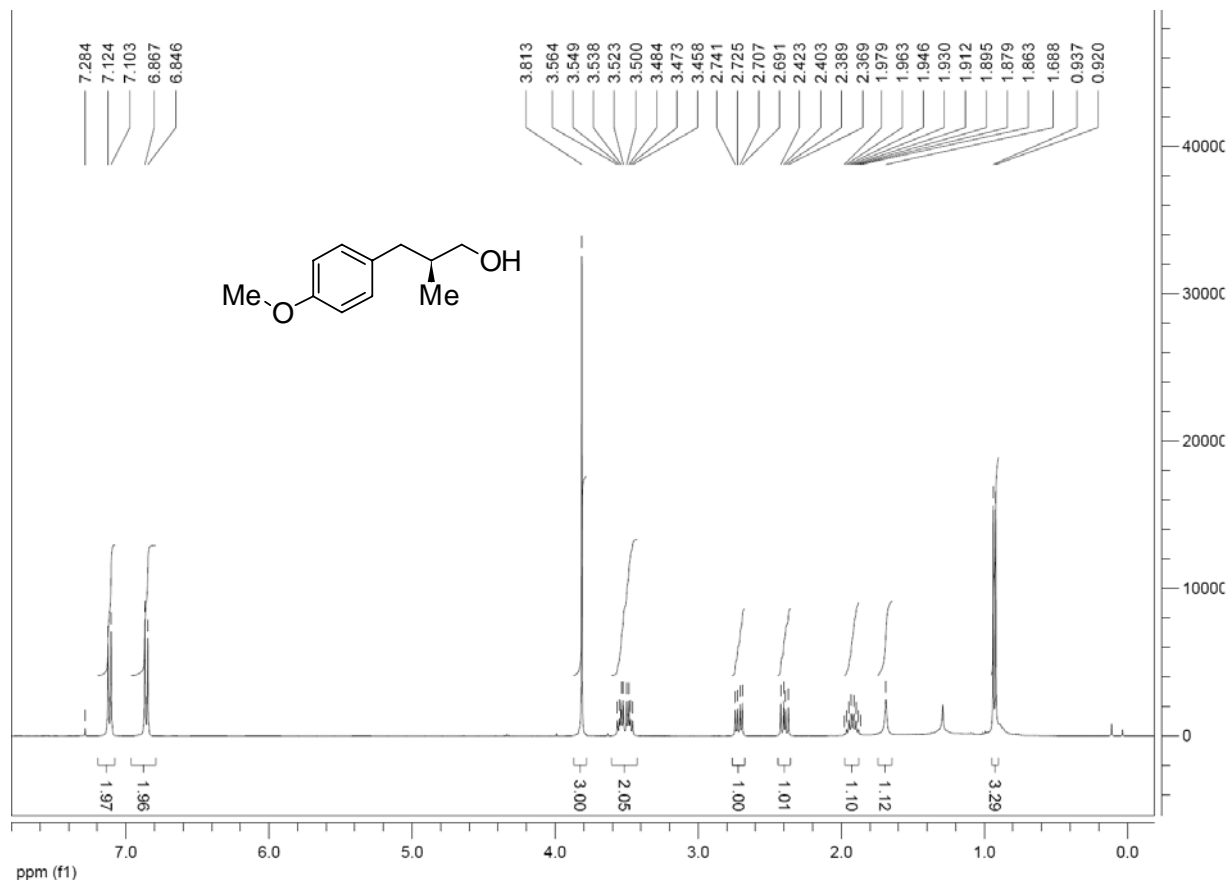
(S)-3-(2-methoxyphenyl)-2-methylpropan-1-ol (2b)



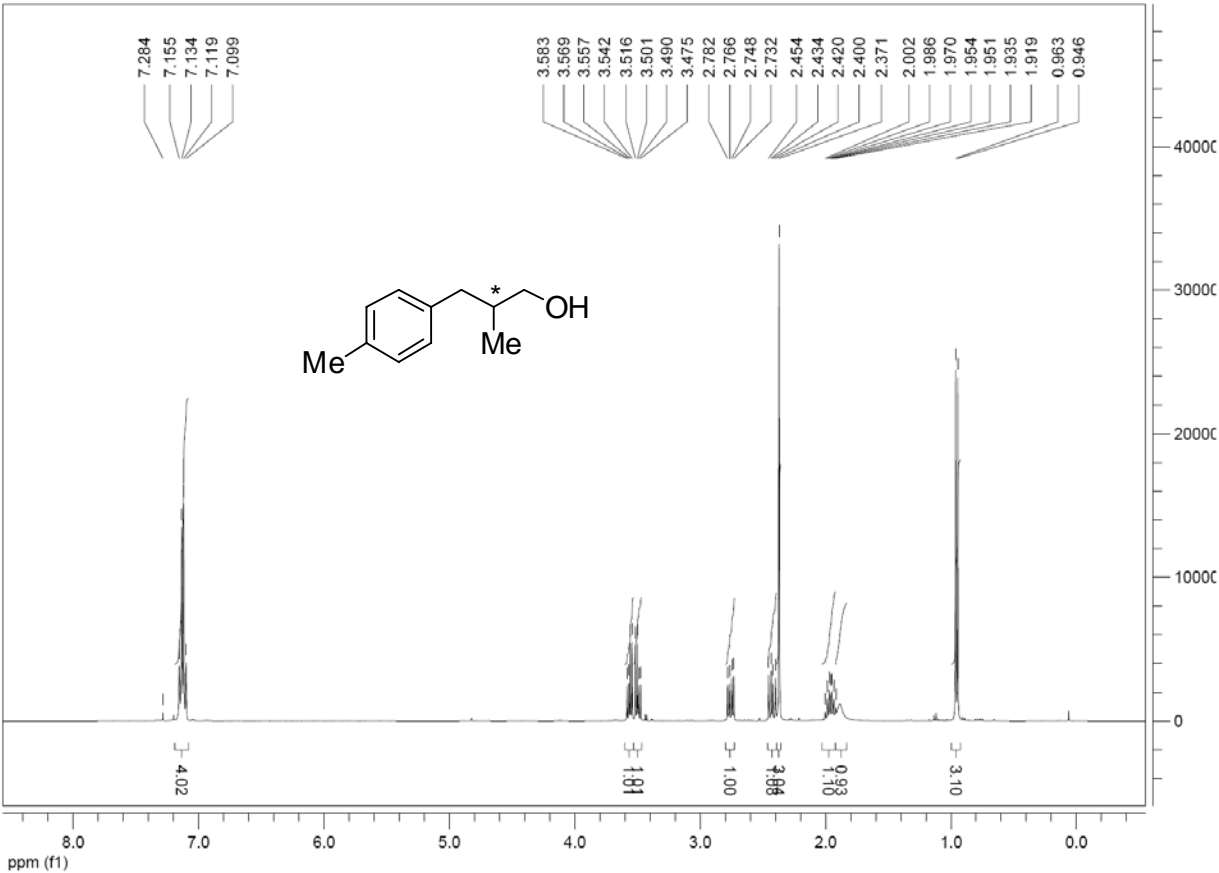
3-(3-methoxyphenyl)-2-methylpropan-1-ol (2c)



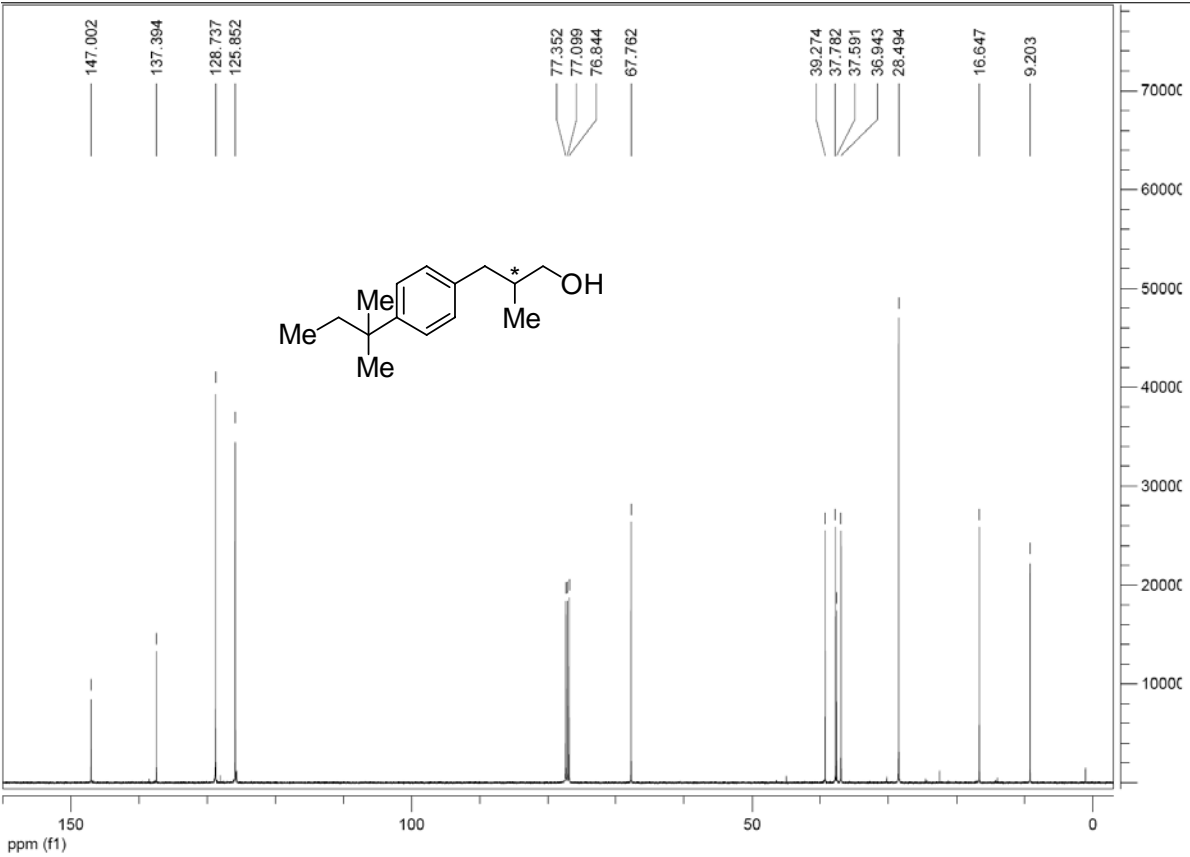
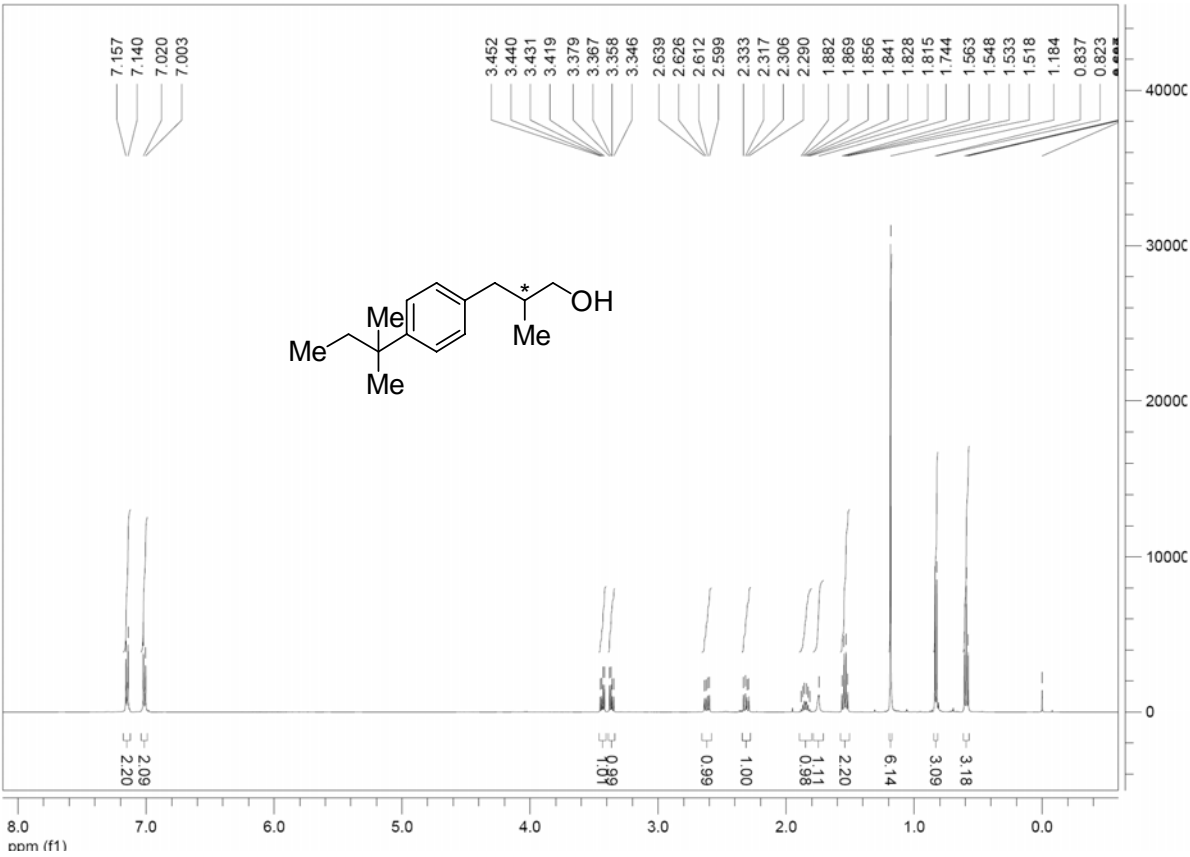
(S)-3-(4-methoxyphenyl)-2-methylpropan-1-ol (2d)



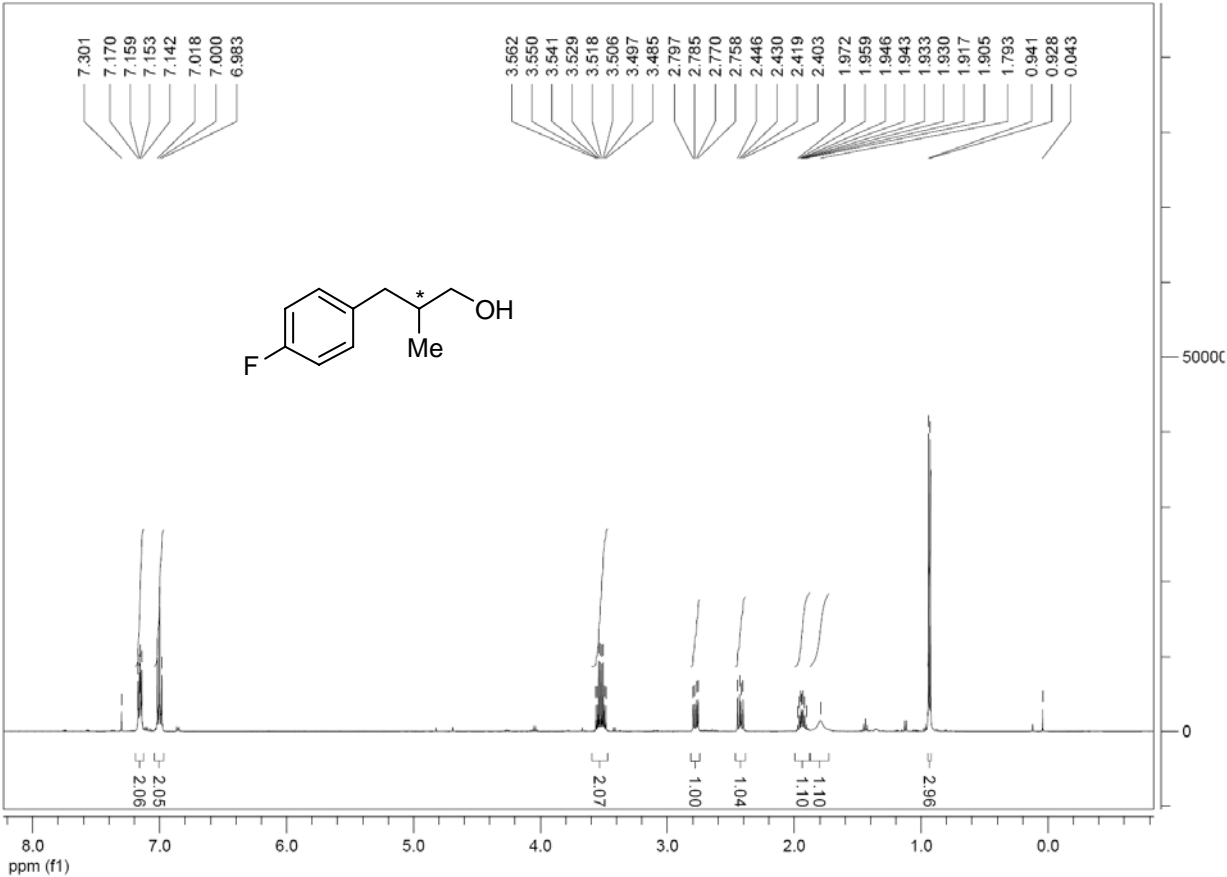
2-methyl-3-p-tolylpropan-1-ol (2e)



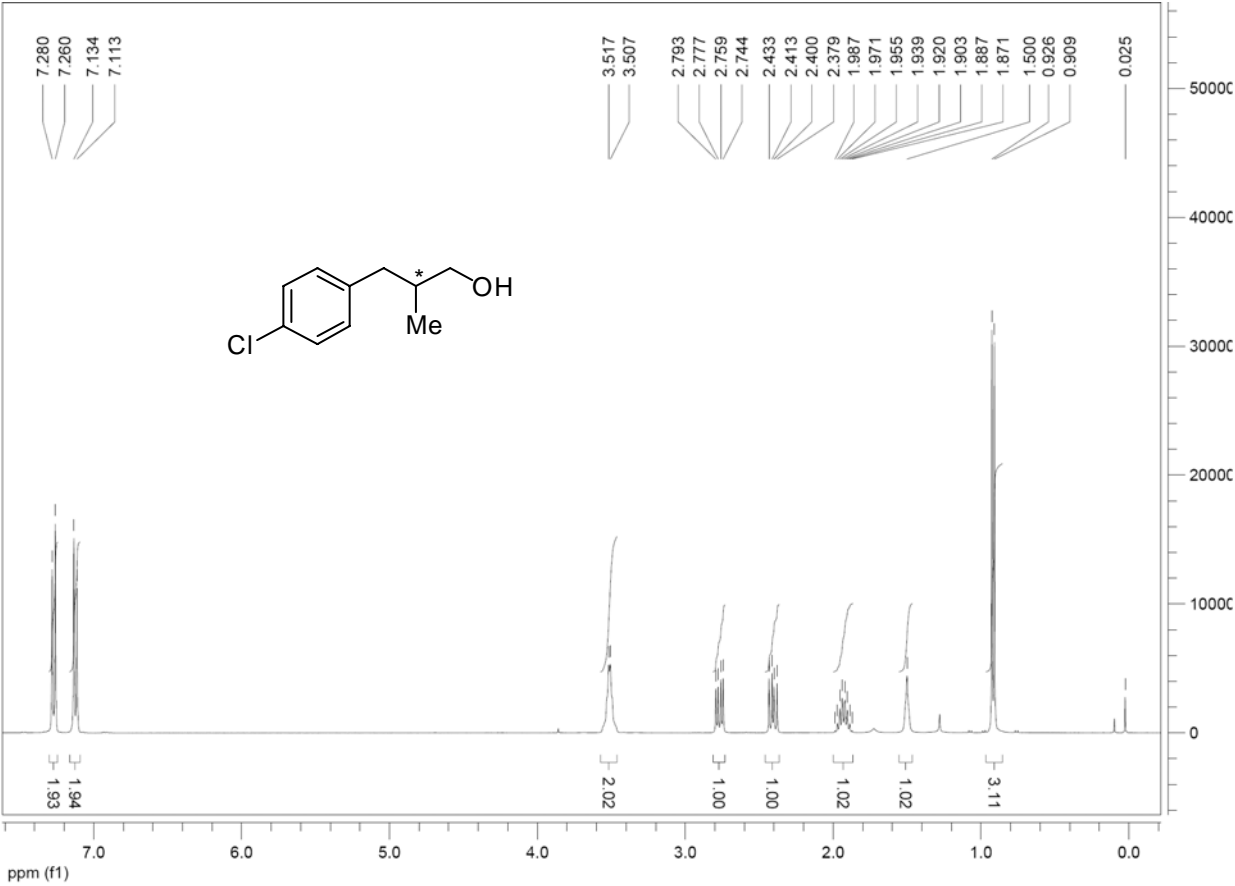
2-methyl-3-(4-tert-pentylphenyl)propan-1-ol (2g)



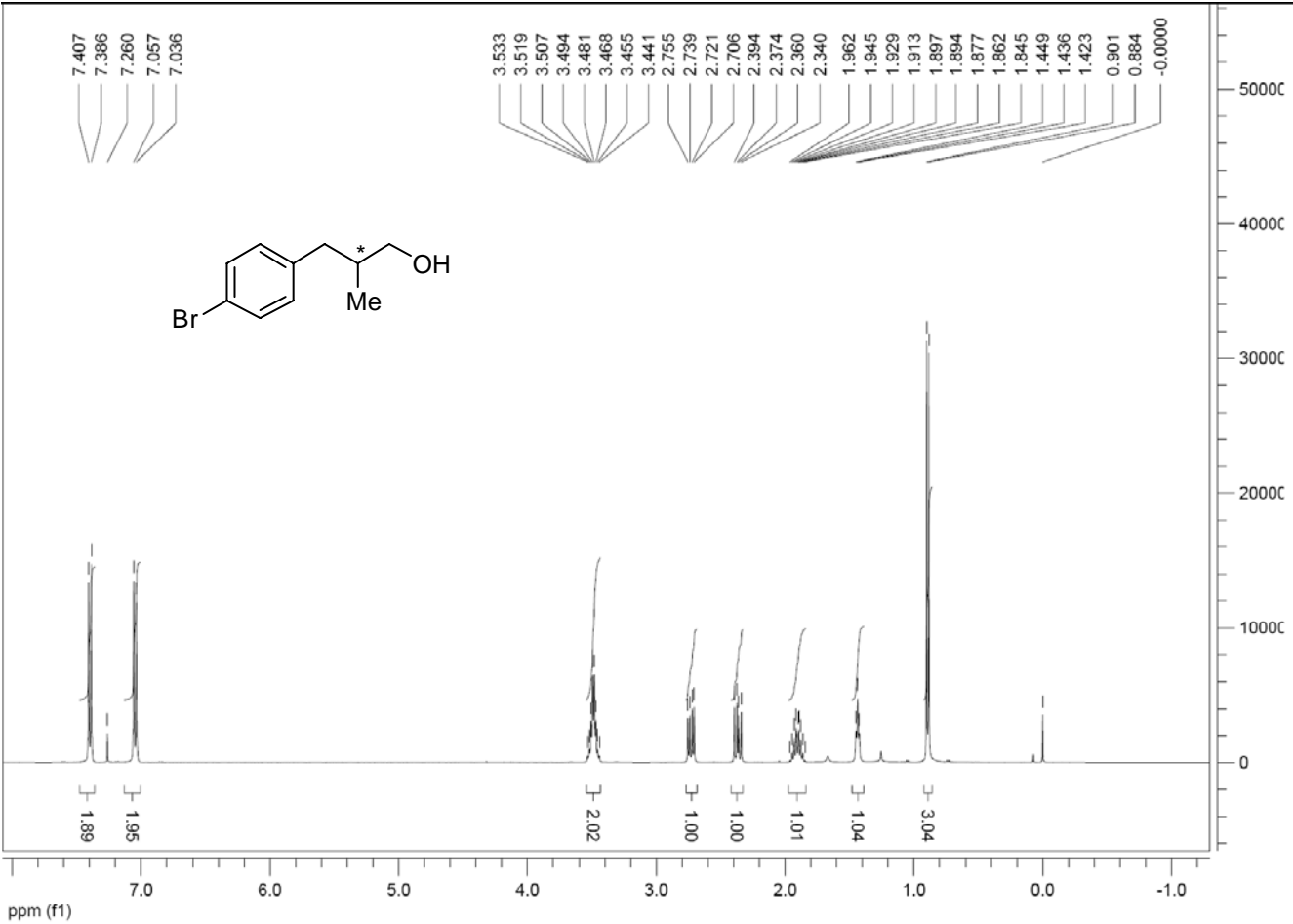
3-(4-fluorophenyl)-2-methylpropan-1-ol (2h)



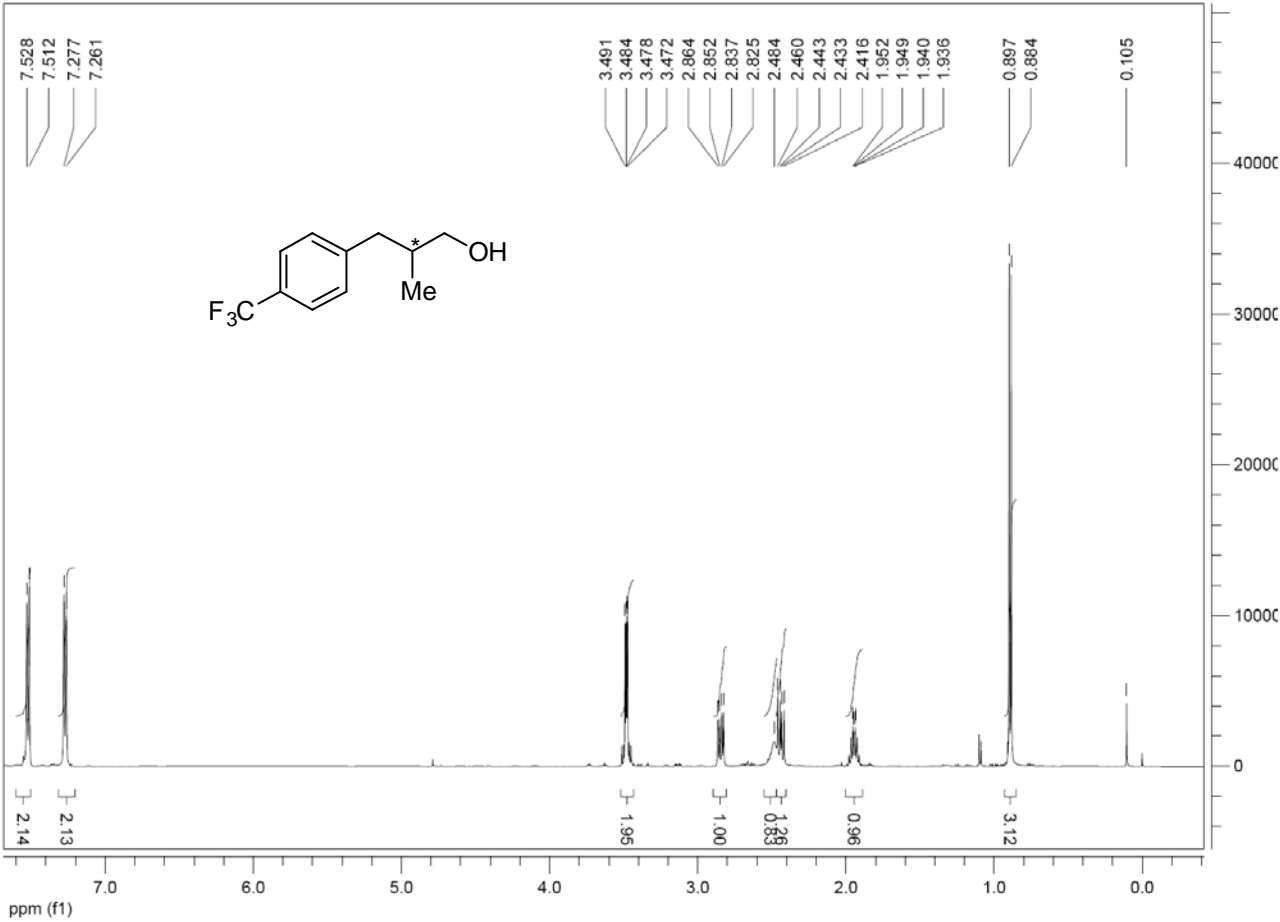
3-(4-chlorophenyl)-2-methylpropan-1-ol (2i)



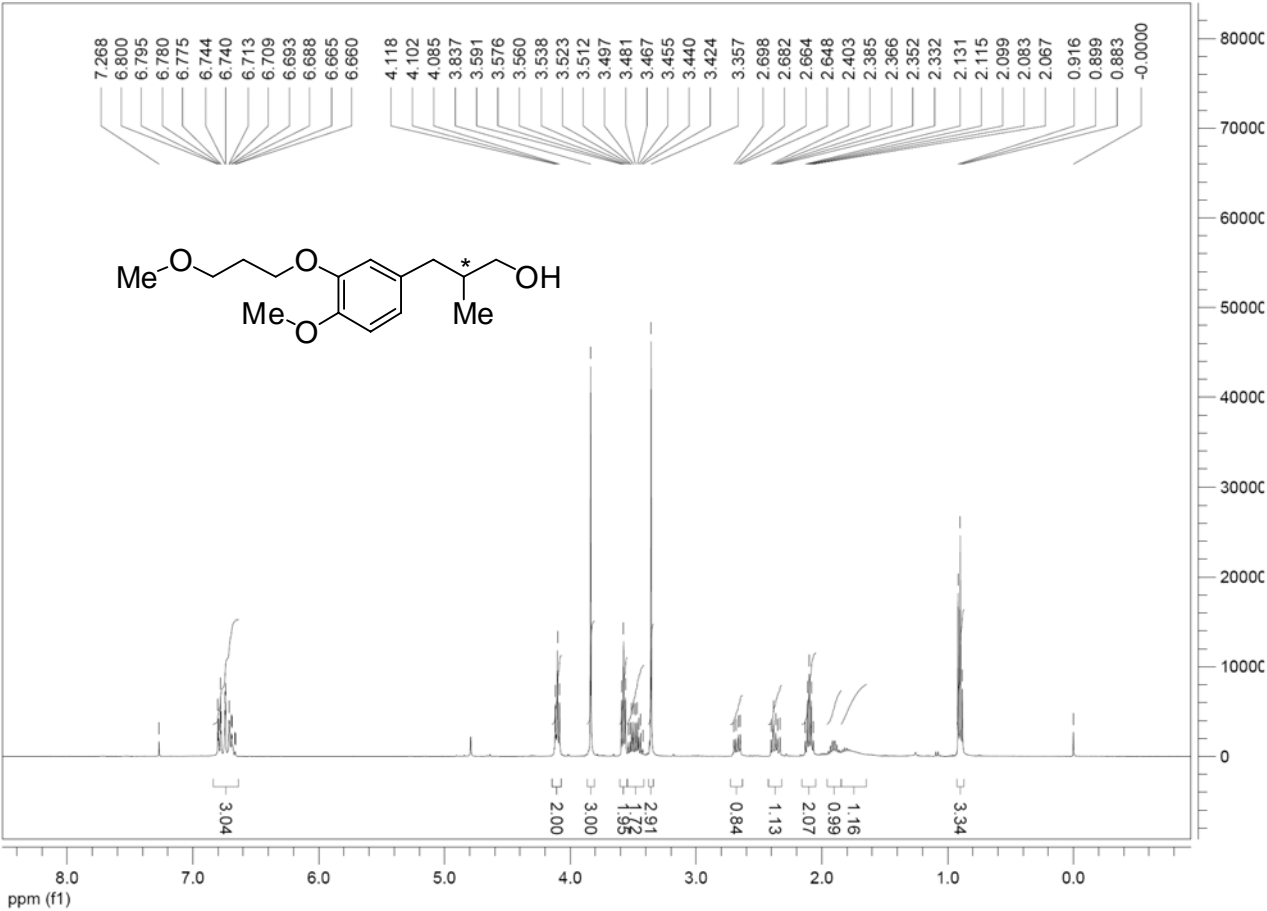
3-(4-bromophenyl)-2-methylpropan-1-ol (2j)



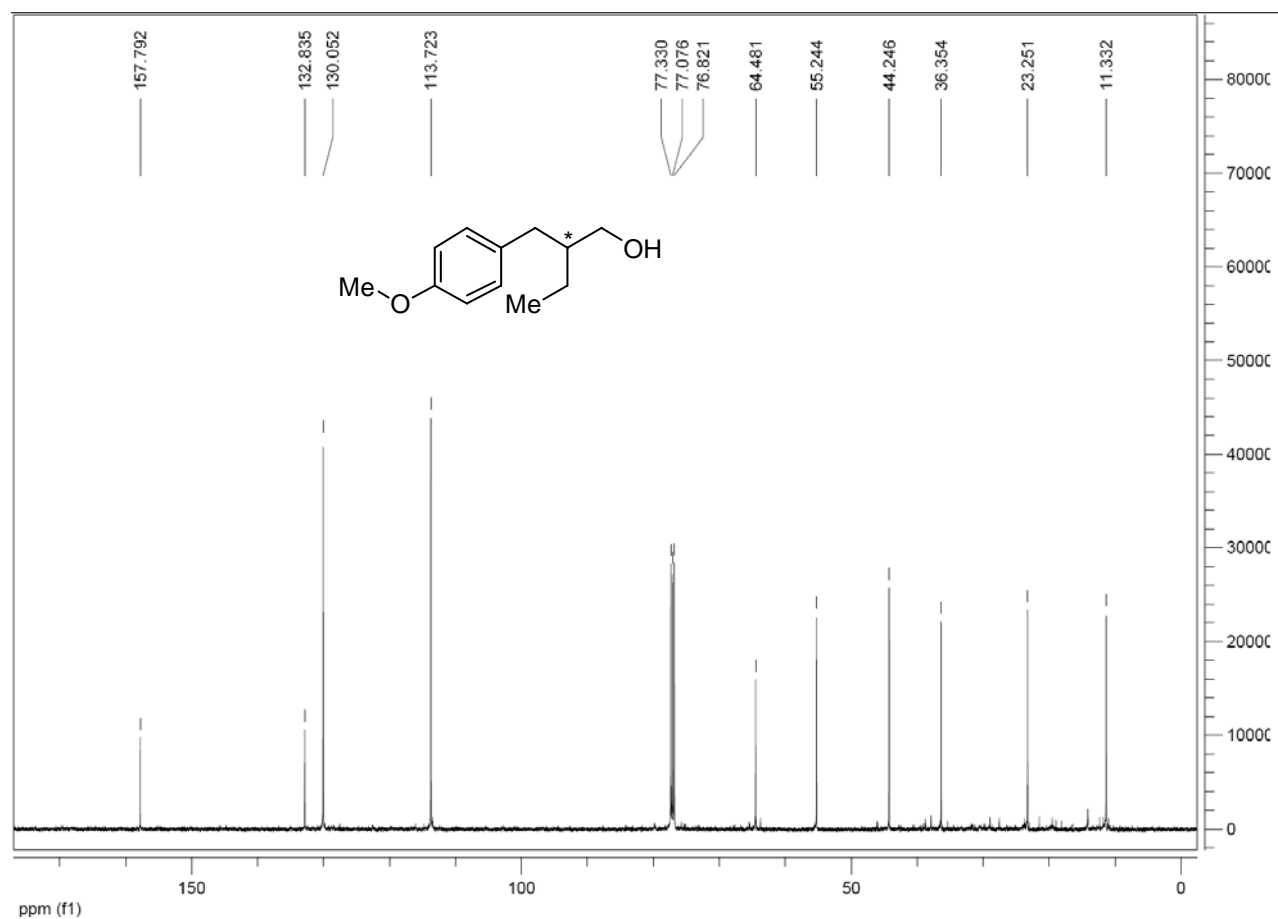
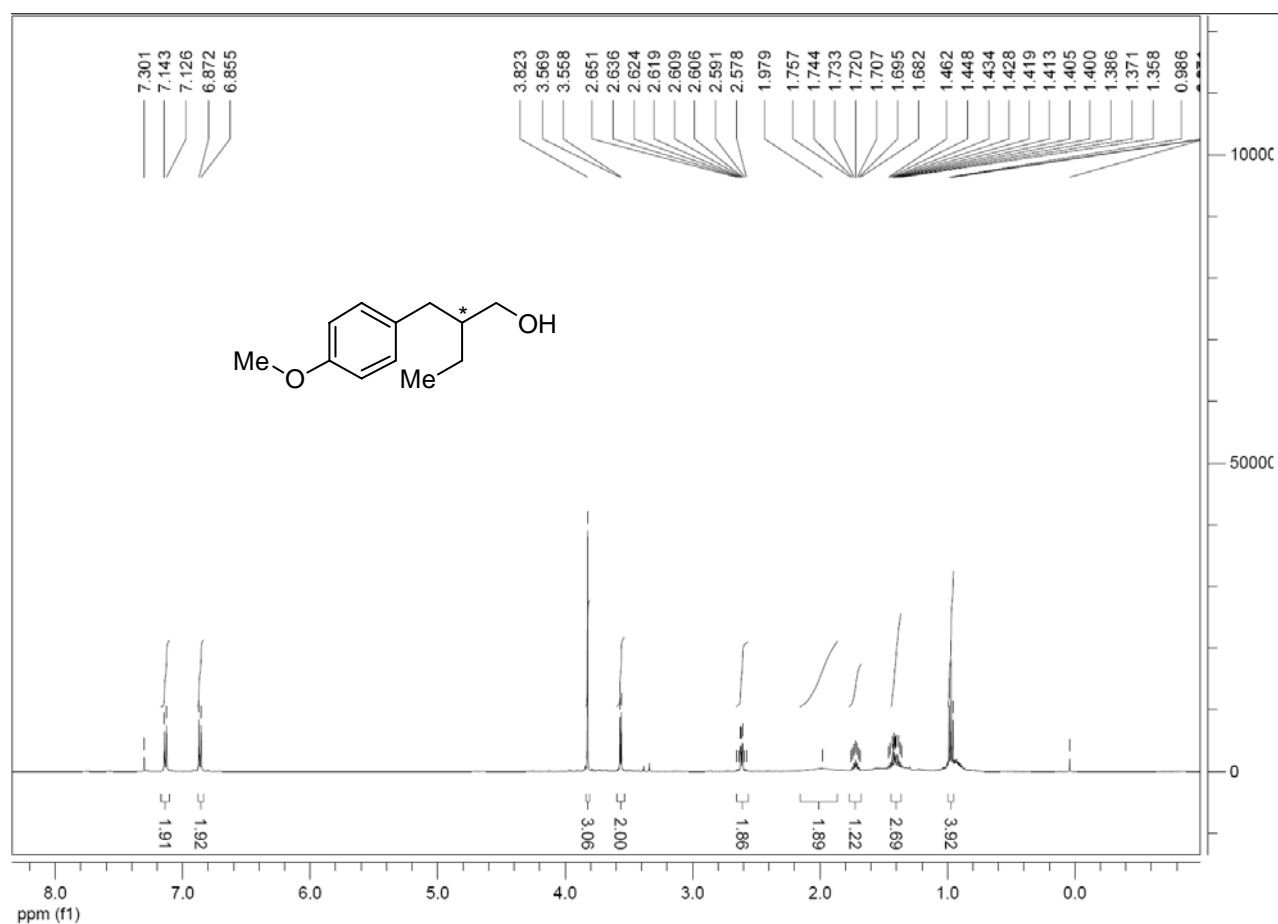
2-methyl-3-(4-(trifluoromethyl)phenyl)propan-1-ol (2k)



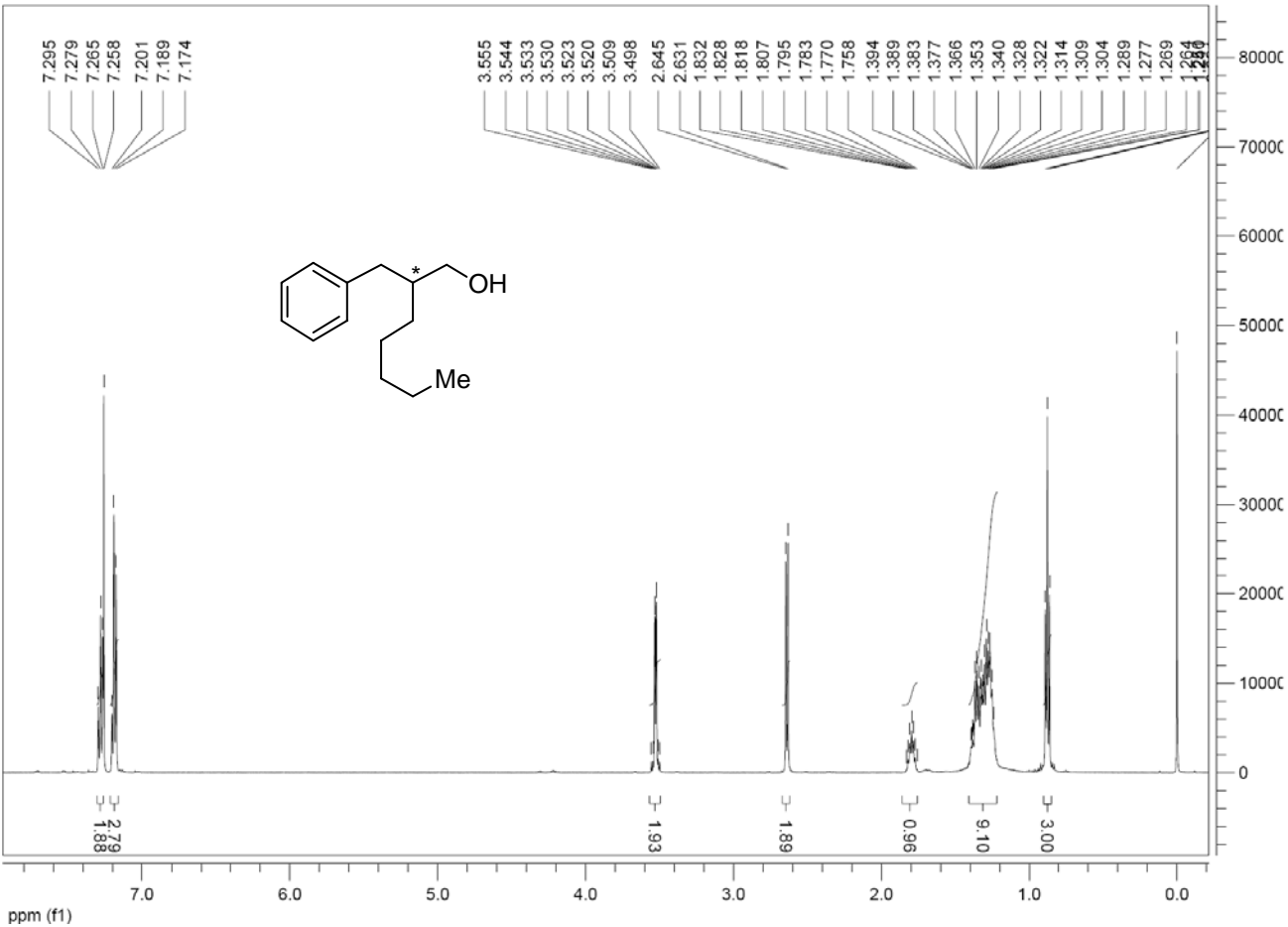
3-(4-methoxy-3-(3-methoxypropoxy)phenyl)-2-methylpropan-1-ol (2l)



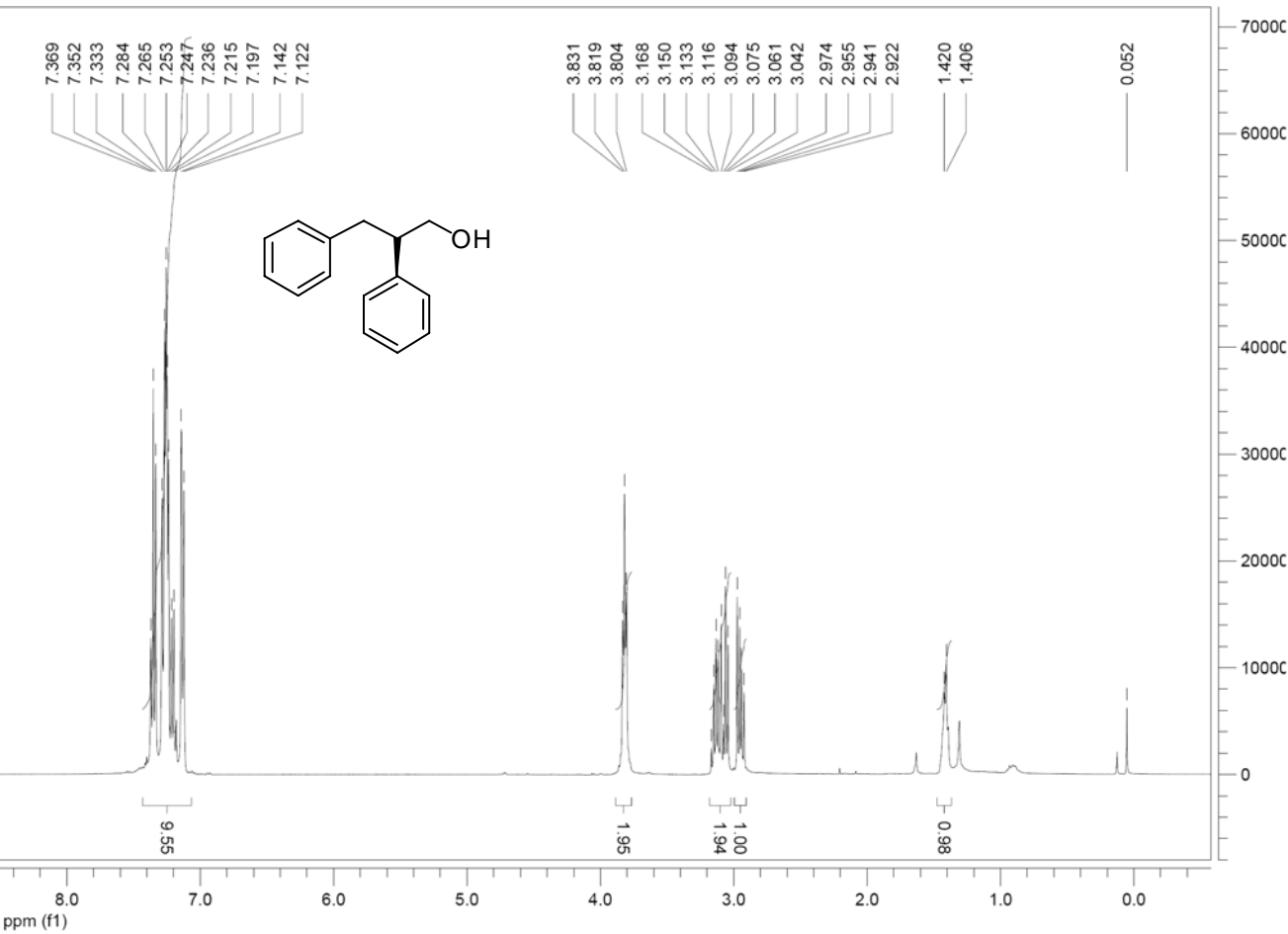
2-(4-methoxybenzyl)butan-1-ol (2m)



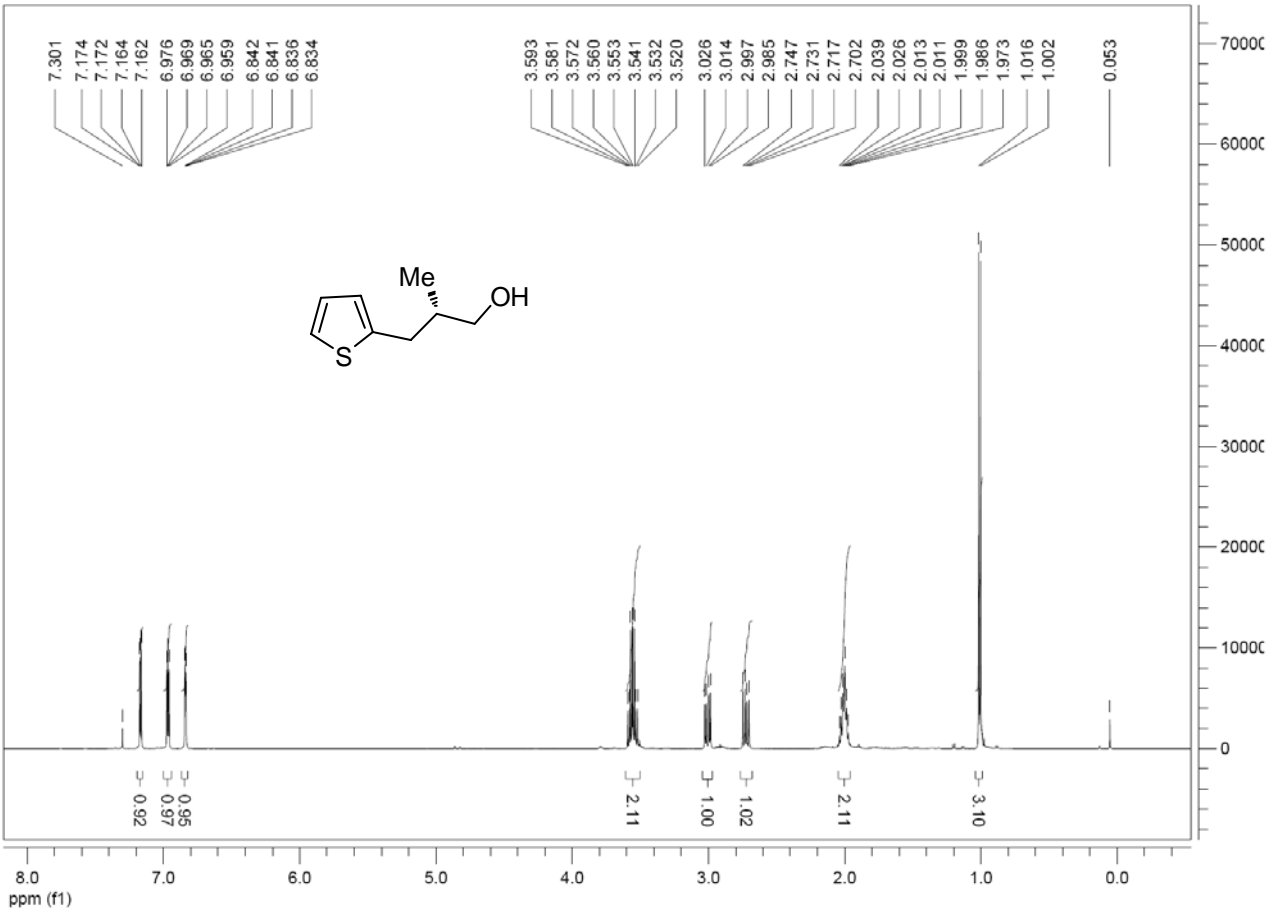
2-benzylheptan-1-ol (2n)



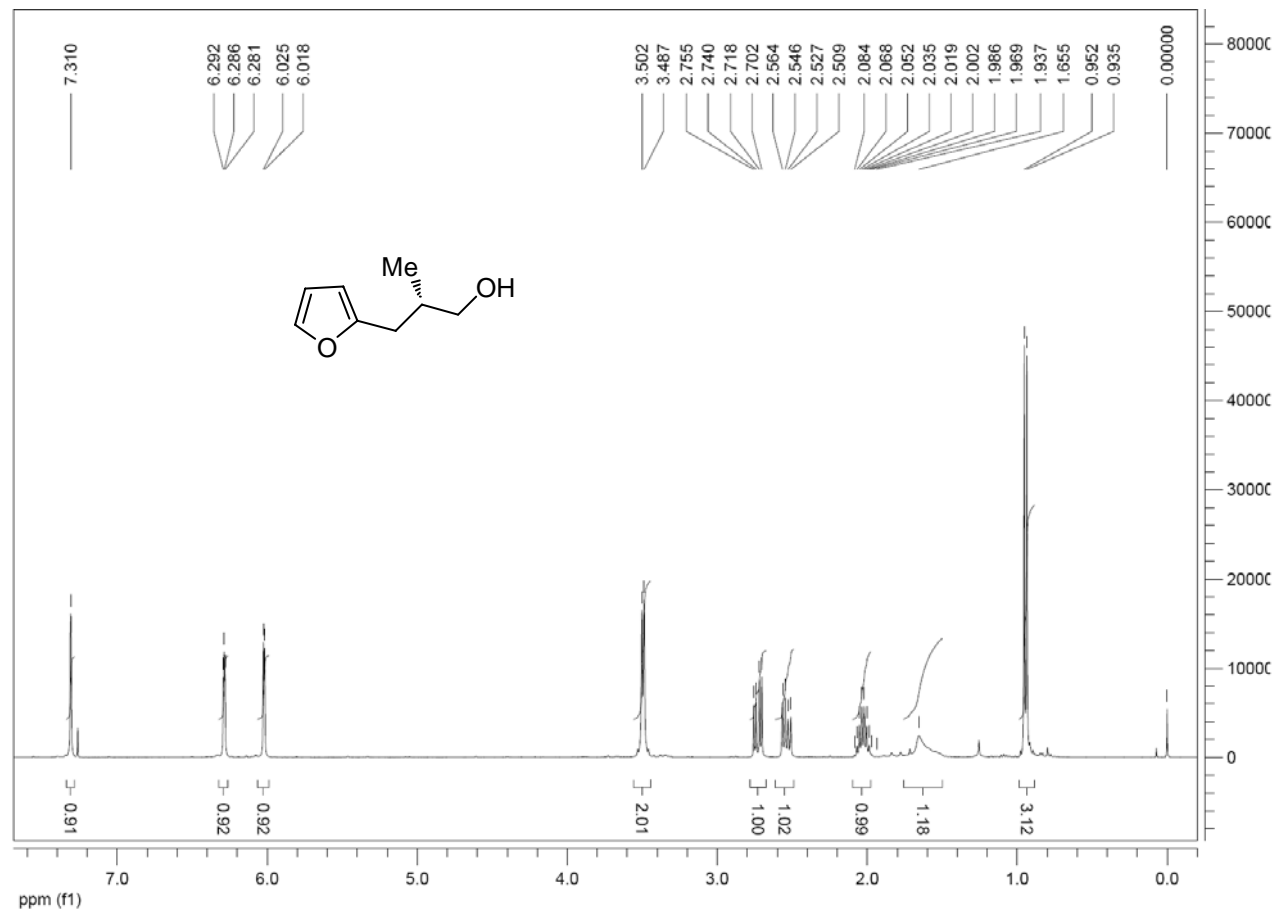
(R)-2,3-diphenylpropan-1-ol (2o)



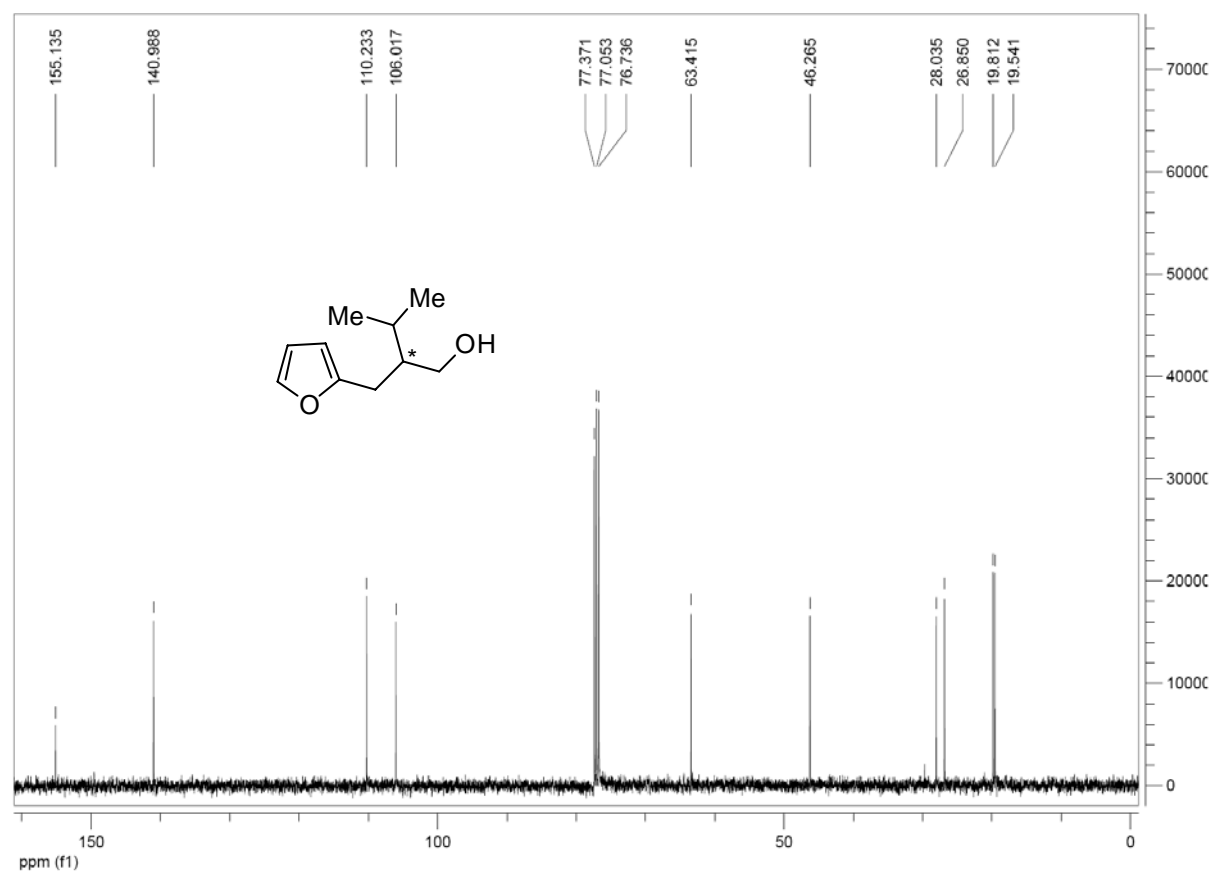
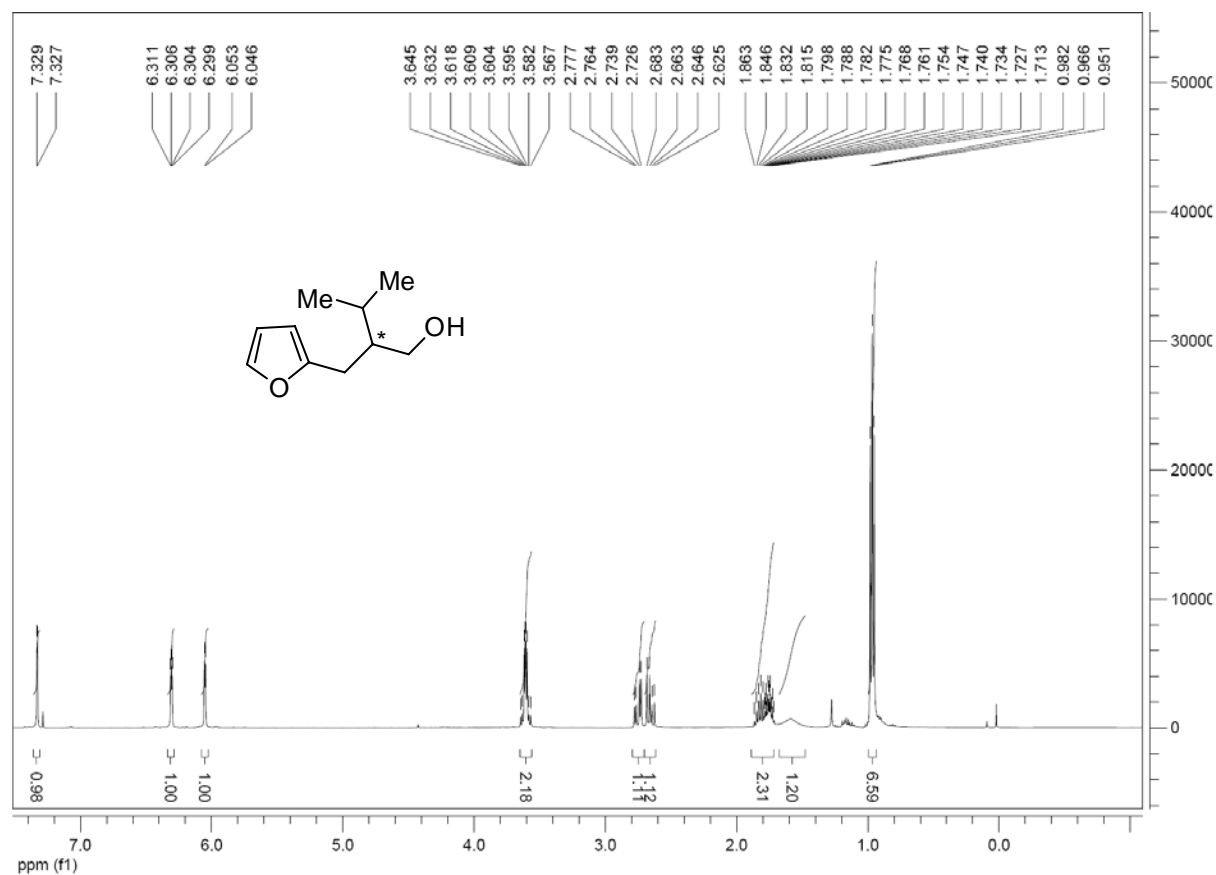
(S)-2-methyl-3-(thiophen-2-yl)propan-1-ol (2p)



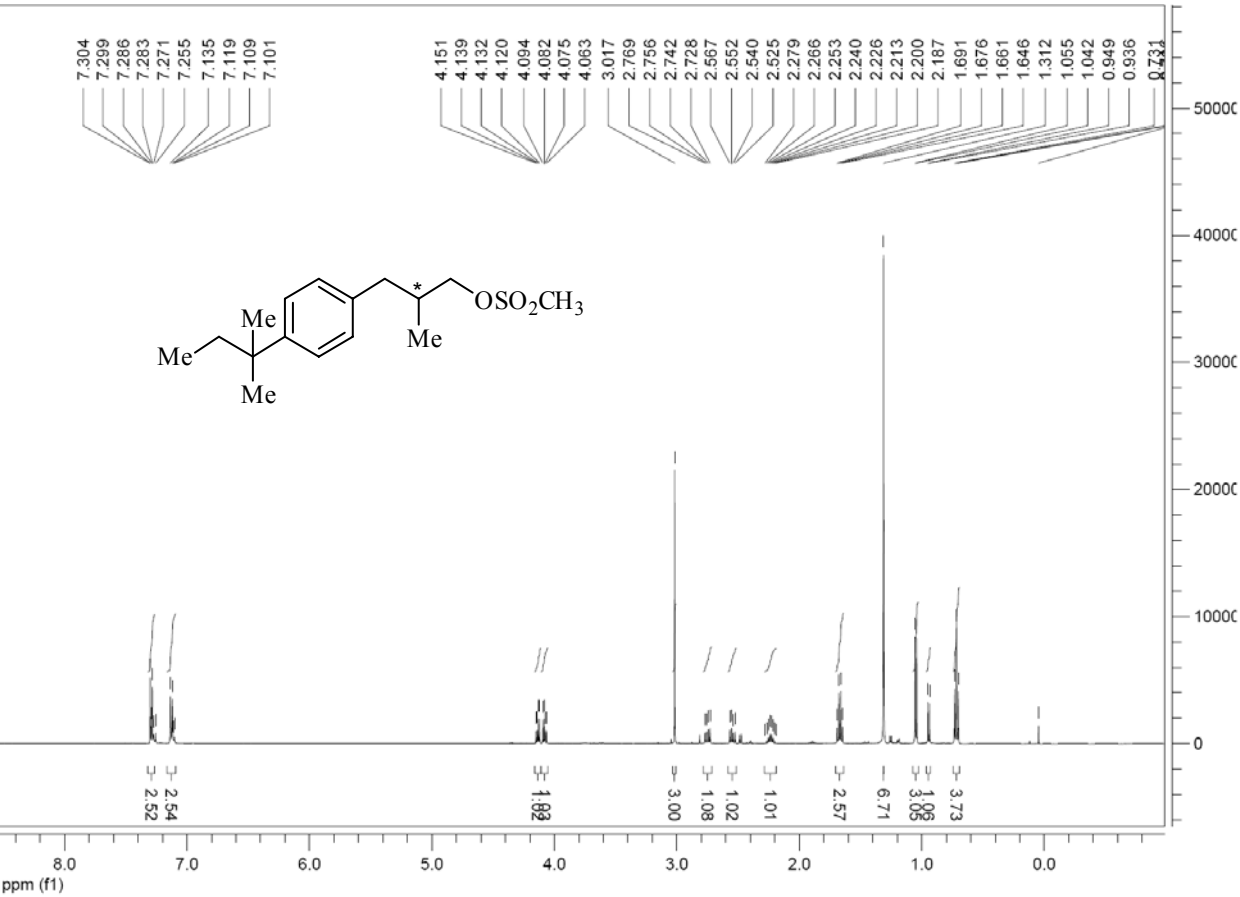
(S)-3-(furan-2-yl)-2-methylpropan-1-ol (2q)



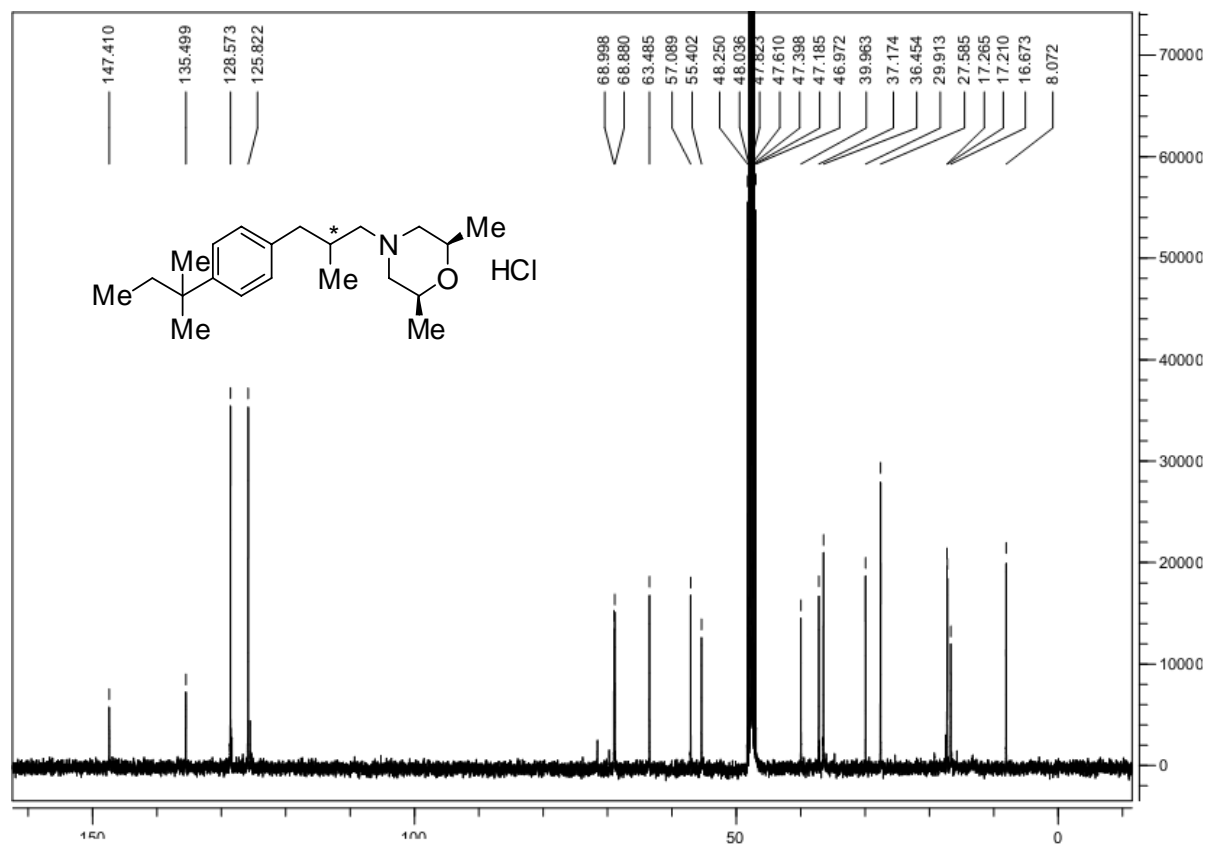
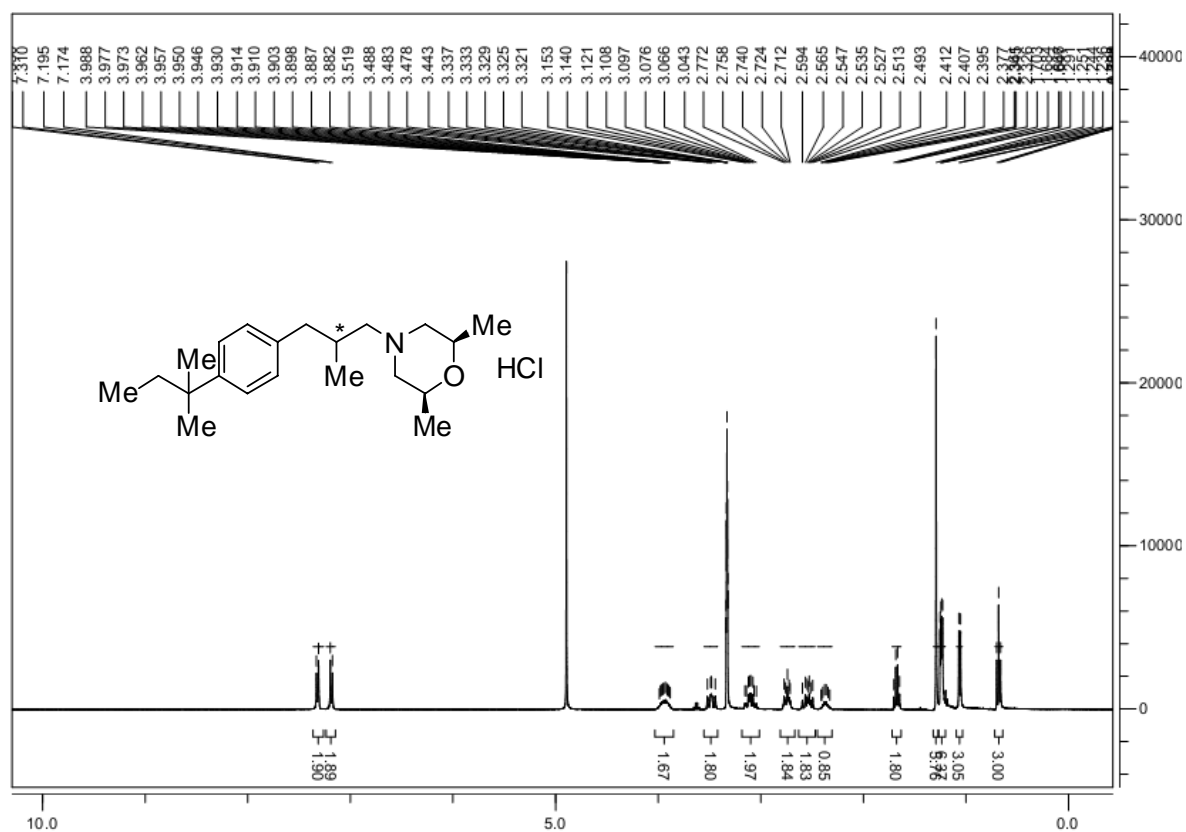
2-(furan-2-ylmethyl)-3-methylbutan-1-ol (2r)



(-)-2-methyl-3-(4-tert-pentylphenyl)propyl methanesulfonate (3)

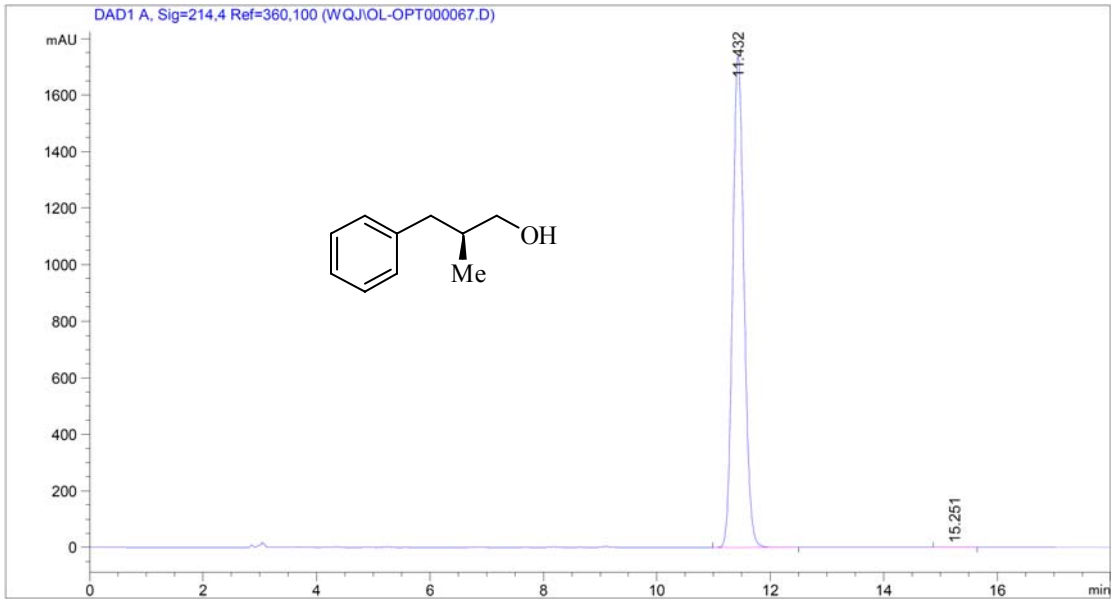
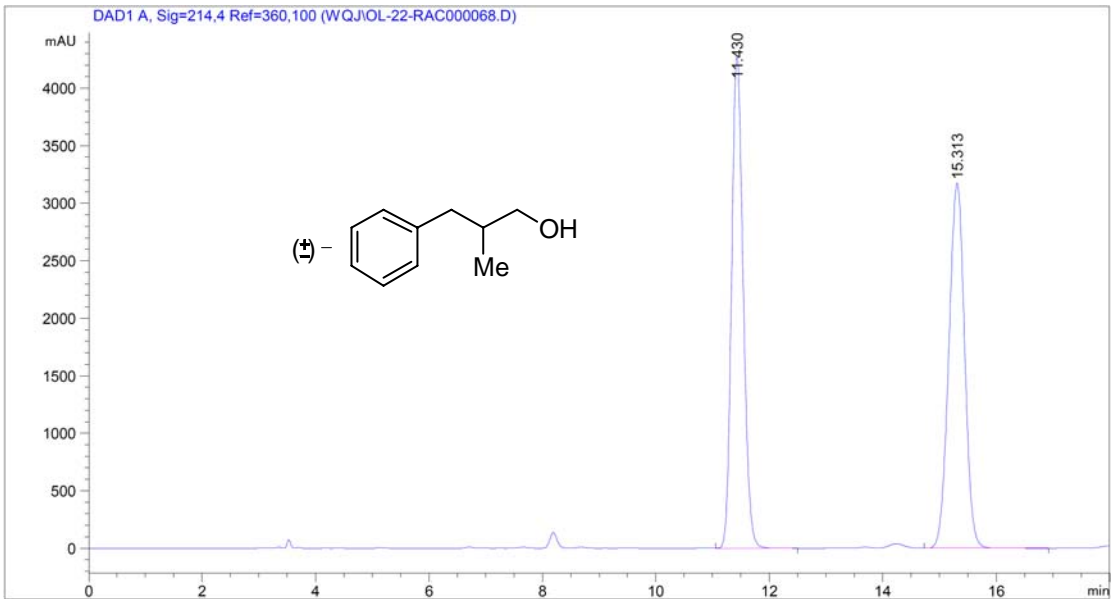


2,6-dimethyl-4-(2-methyl-3-(4-tert-pentylphenyl)propyl)morpholine hydrochloride (4)



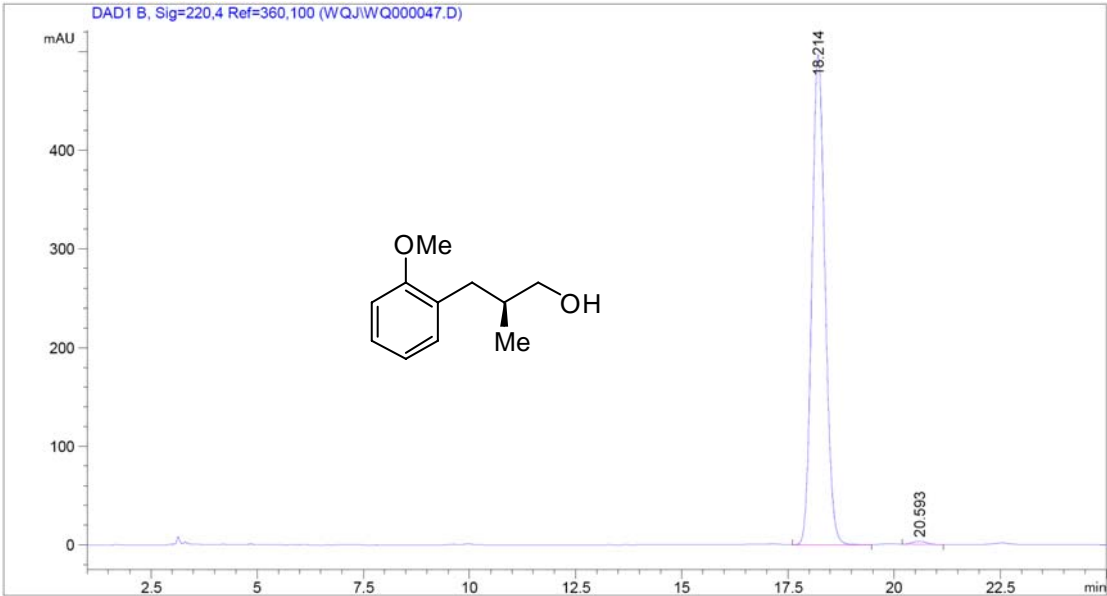
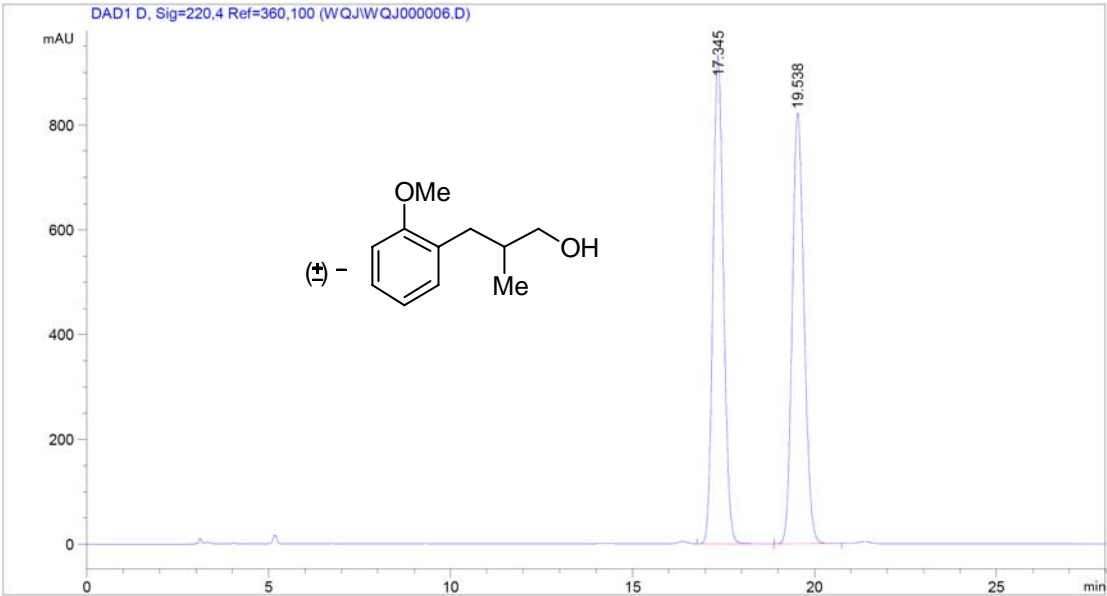
VI. HPLC Charts of Hydrogenation Products and Derivatives:

2-methyl-3-phenylpropan-1-ol (2a)



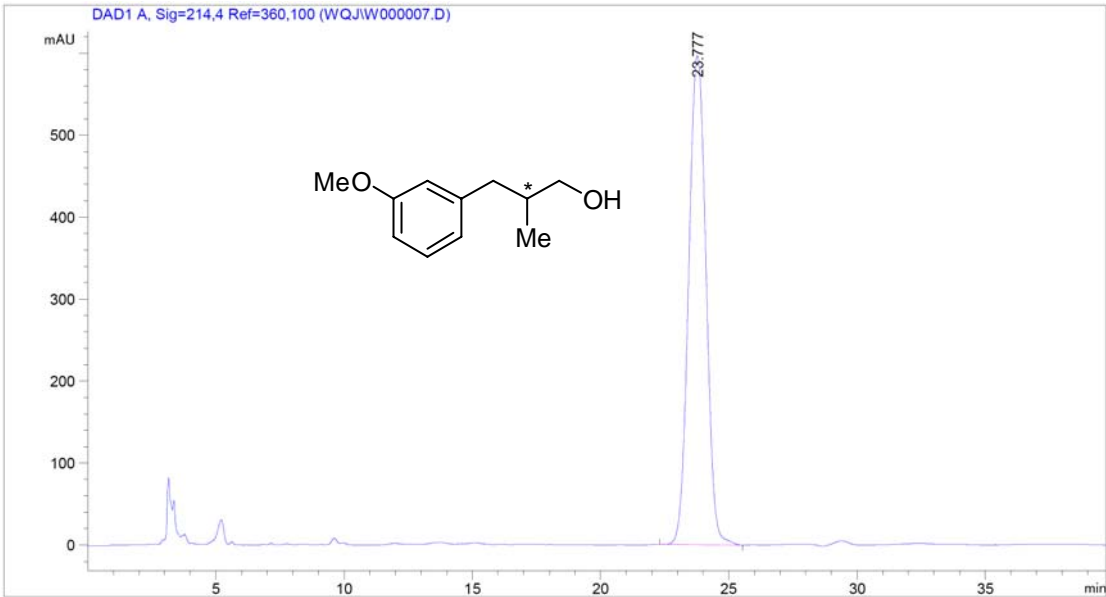
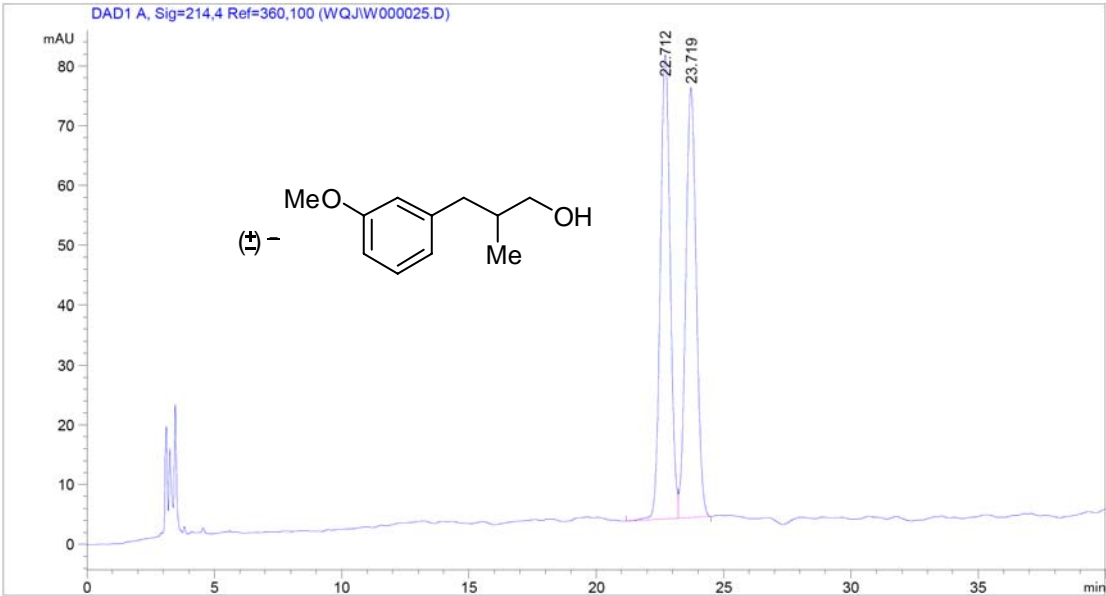
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.432	BB	0.2165	2.42081e4	1738.45056	99.9816
2	15.251	BB	0.2872	4.44749	2.38851e-1	0.0184

3-(2-methoxyphenyl)-2-methylpropan-1-ol (2b)



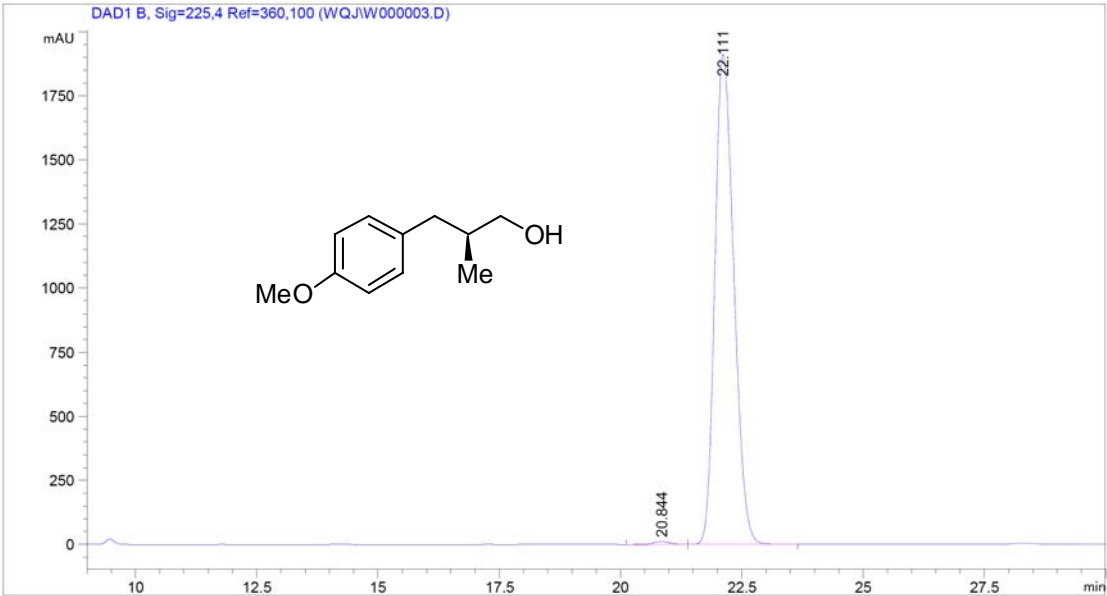
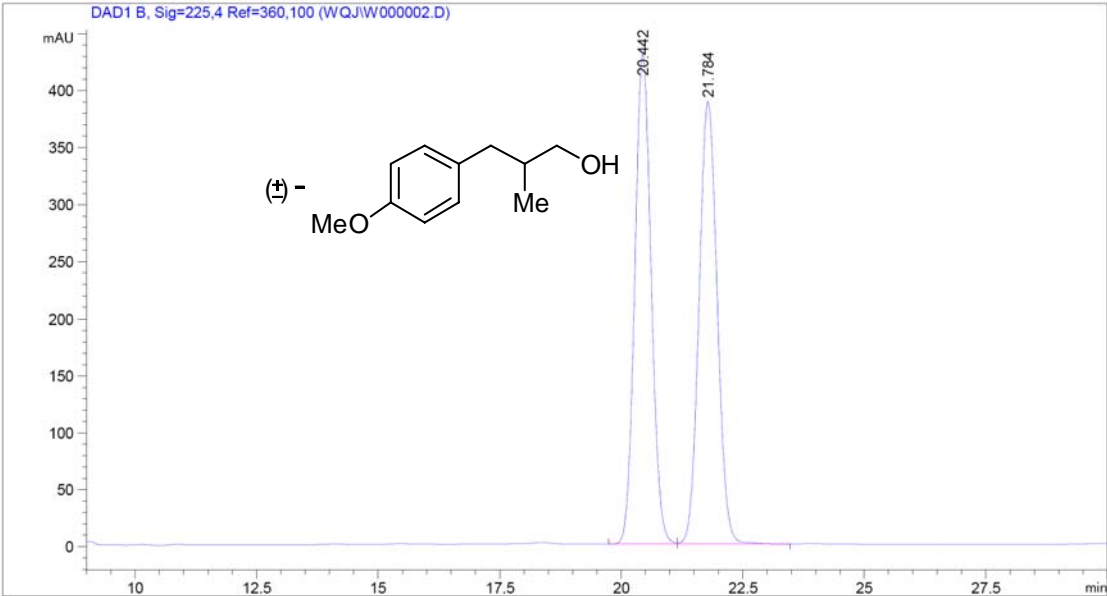
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.214	BB	0.3334	1.07040e4	496.66928	99.3171
2	20.593	BB	0.3604	73.60270	3.24790	0.6829

3-(3-methoxyphenyl)-2-methylpropan-1-ol (2c)



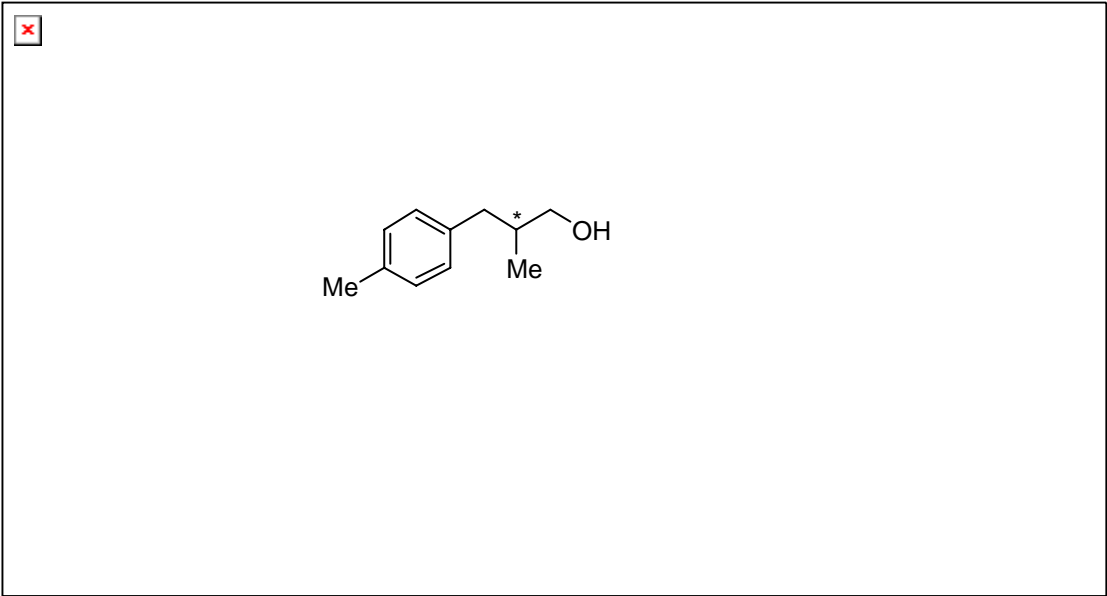
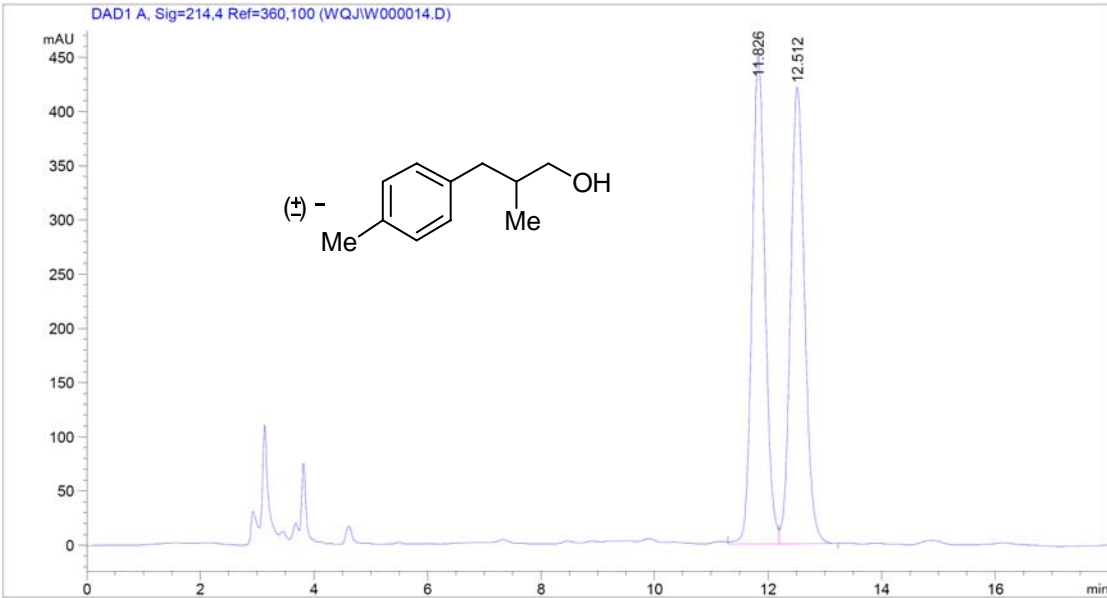
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3-(4-methoxyphenyl)-2-methylpropan-1-ol (2d)



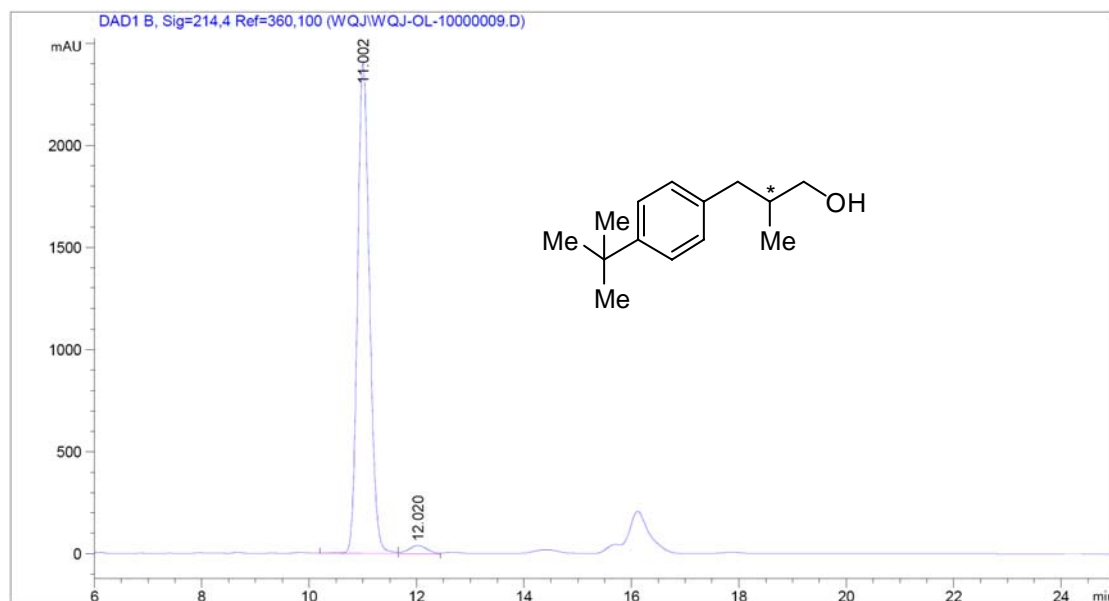
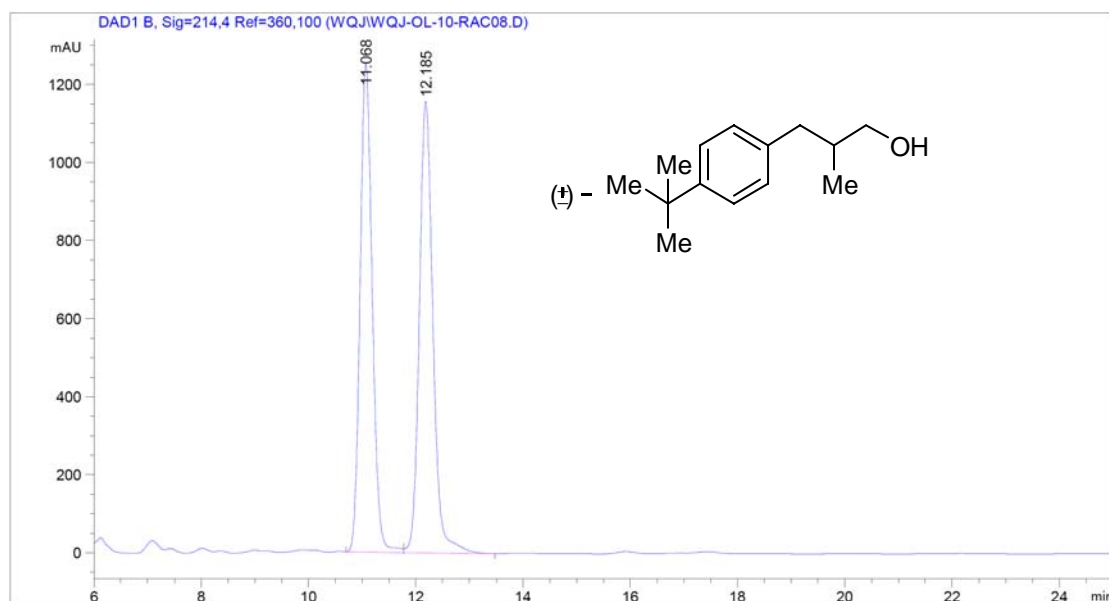
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.844	BV	0.3665	266.23770	11.31565	0.5090
2	22.111	VB	0.4258	5.20390e4	1910.46411	99.4910

2-methyl-3-p-tolylpropan-1-ol (2e)



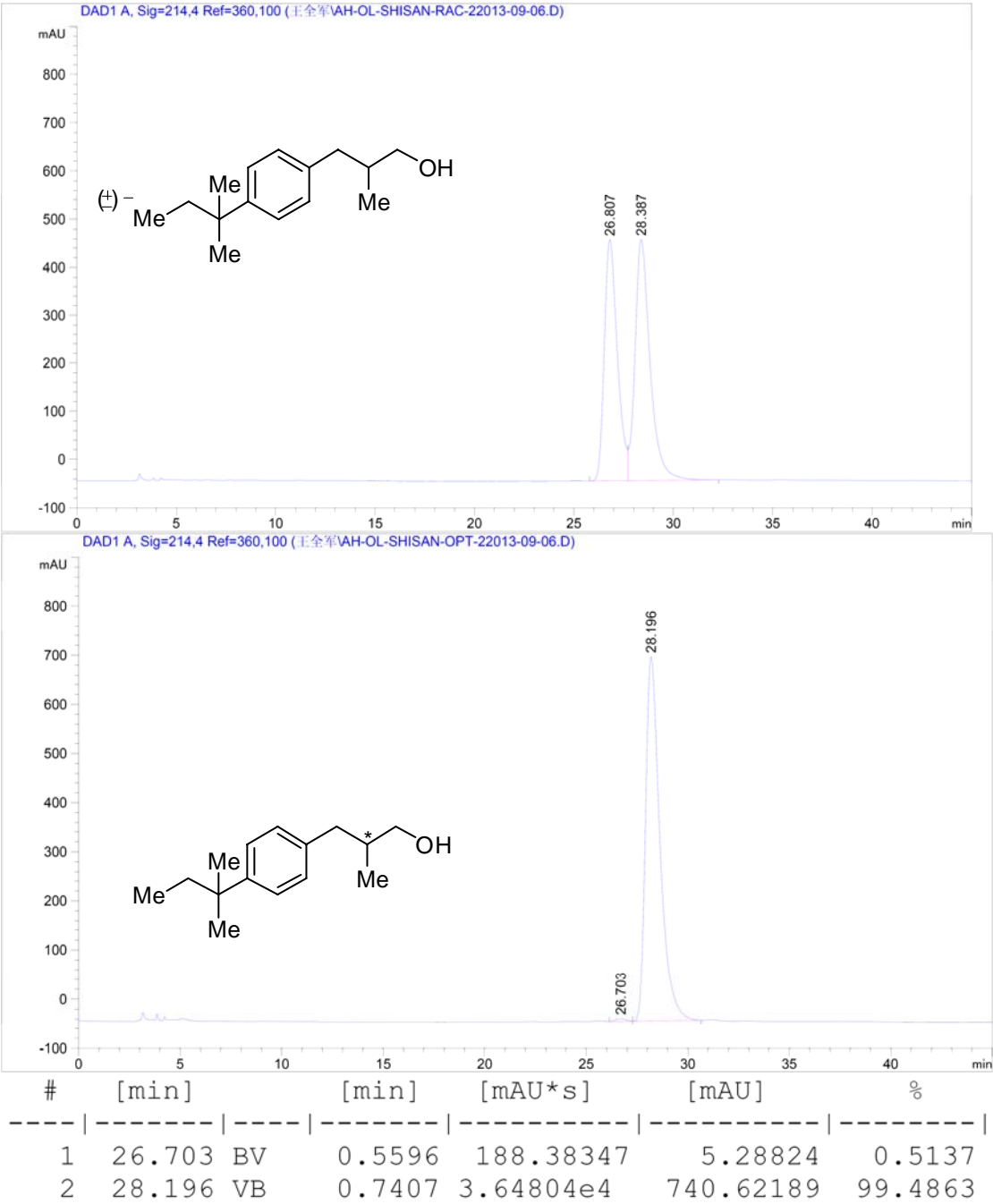
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.923	BV	0.2427	162.05525	9.91289	0.4270
2	12.559	VB	0.2401	3.77901e4	2420.48193	99.5730

(S)-3-(4-tert-butylphenyl)-2-methylpropan-1-ol (2f)

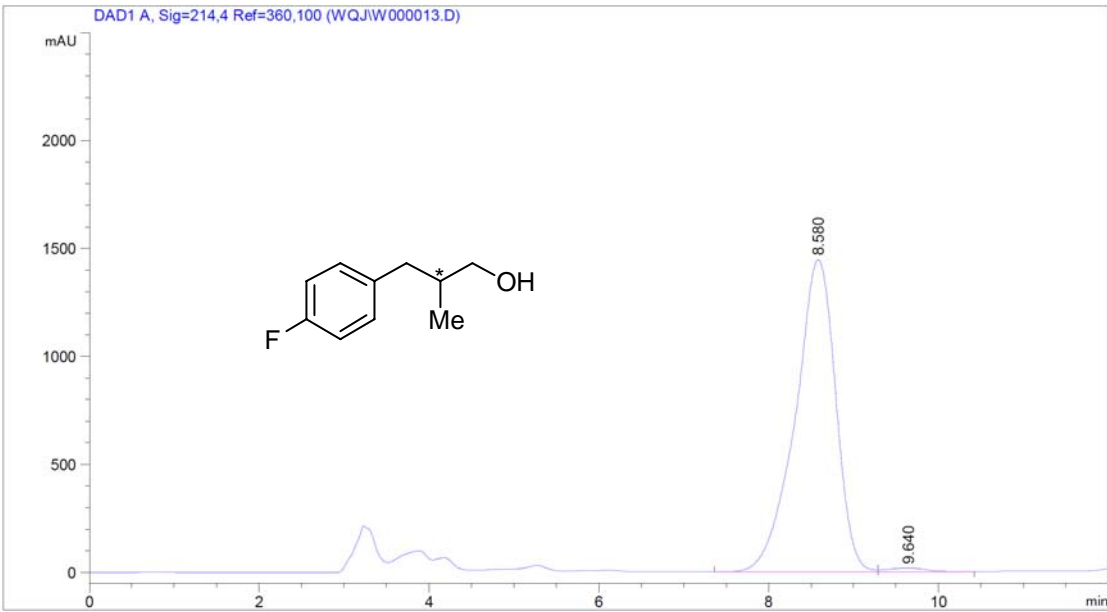
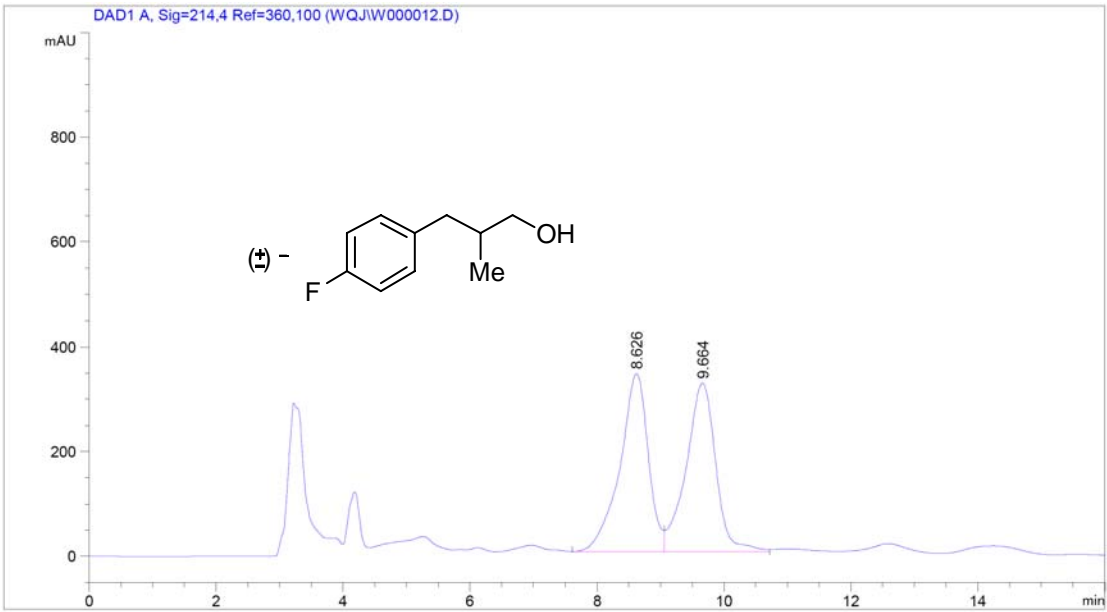


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.002	BV	0.2402	3.71239e4	2402.93628	97.6467
2	12.020	VV	0.3664	894.68335	38.59523	2.3533

2-methyl-3-(4-tert-pentylphenyl)propan-1-ol (2g)

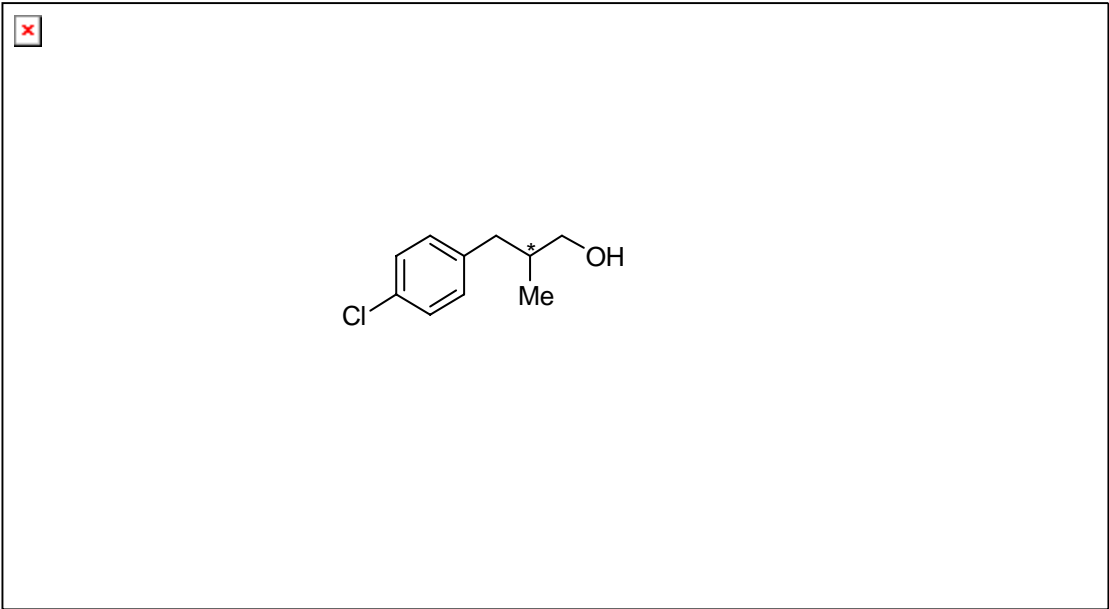
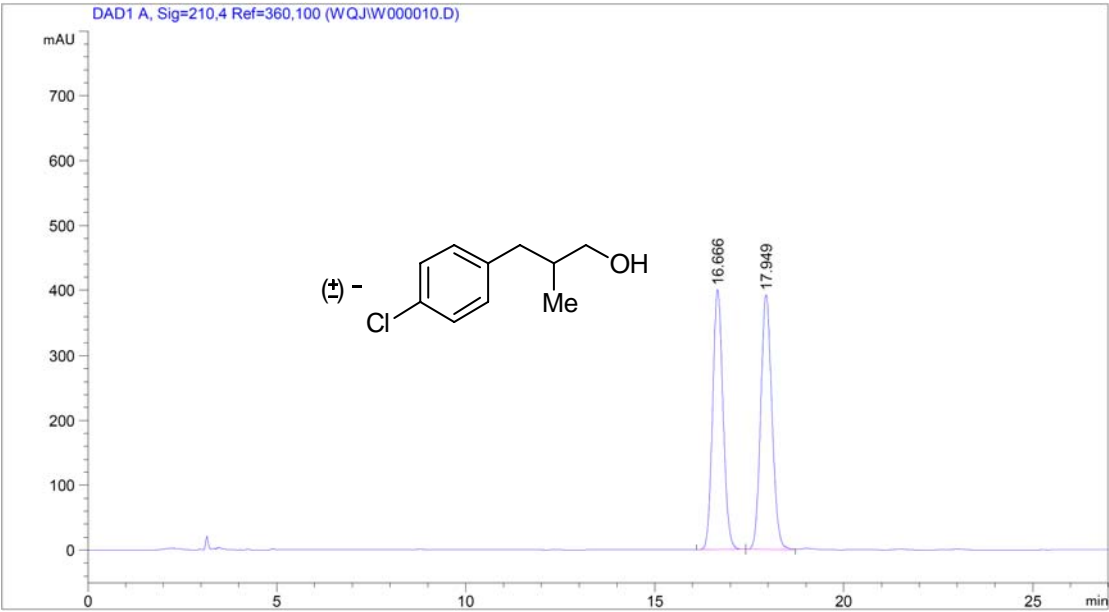


3-(4-fluorophenyl)-2-methylpropan-1-ol (2h)



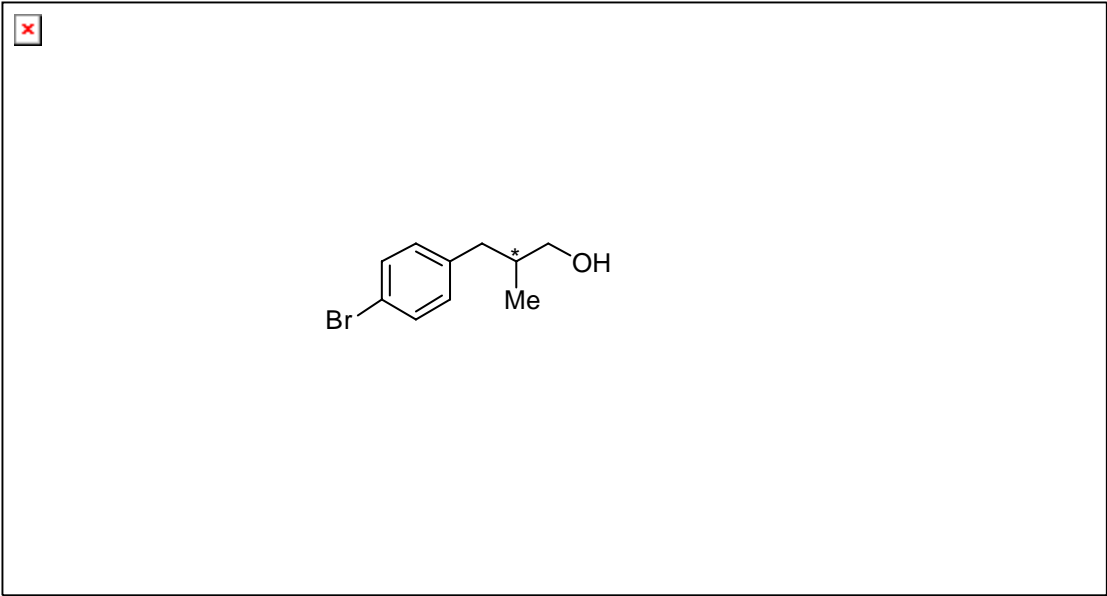
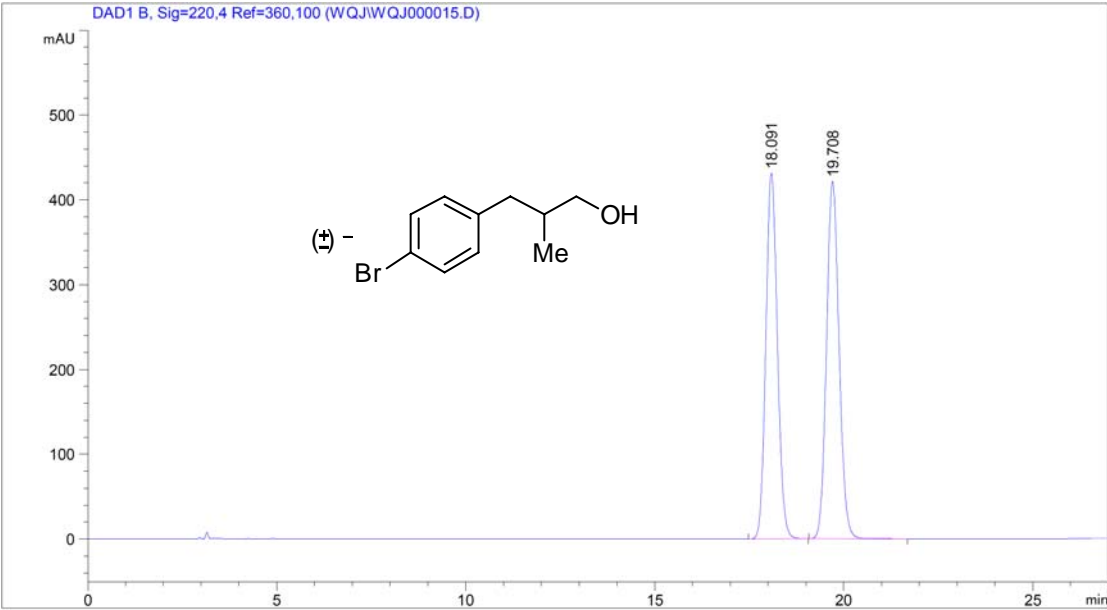
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.580	BV	0.4970	4.76924e4	1445.06726	99.0207
2	9.640	VB	0.4999	471.65475	15.03904	0.9793

3-(4-chlorophenyl)-2-methylpropan-1-ol (2i)



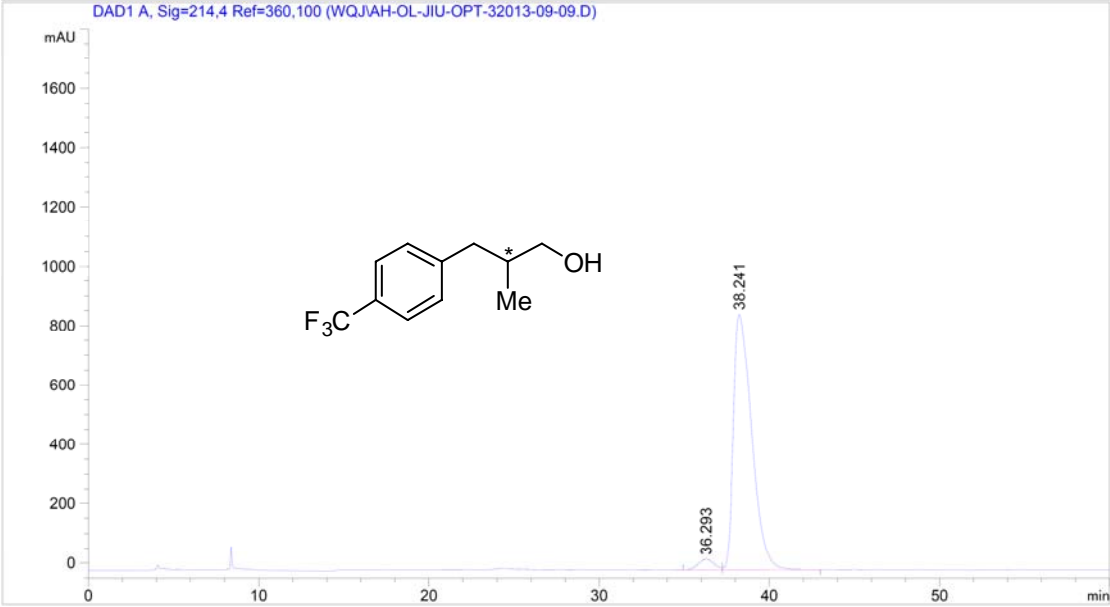
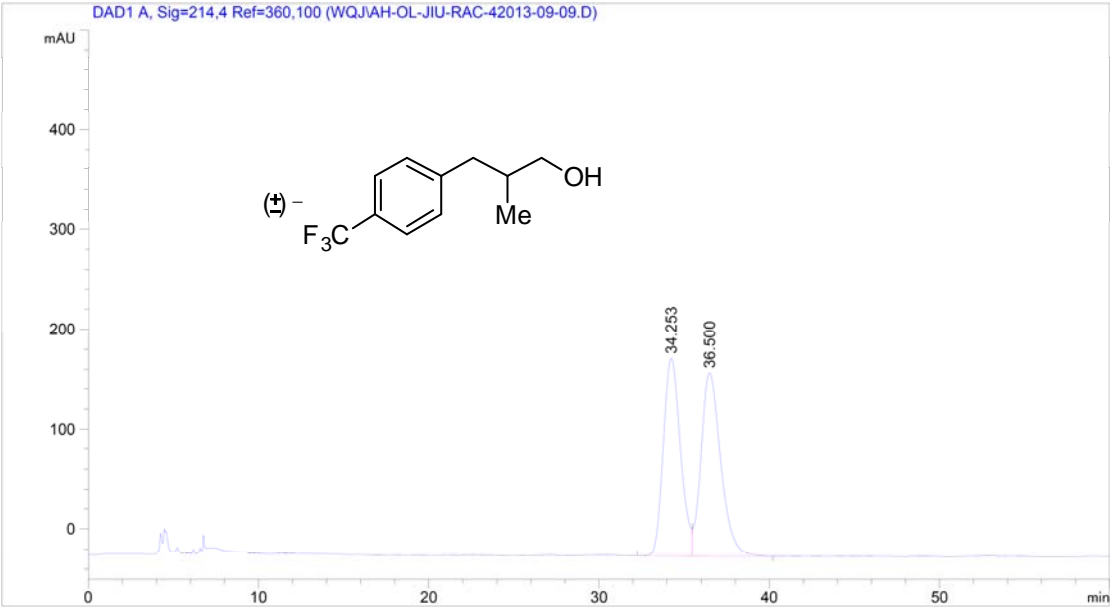
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.514	BB	0.3270	180.85136	8.54309	0.5517
2	17.790	BV	0.3480	3.25987e4	1451.79126	99.4483

3-(4-bromophenyl)-2-methylpropan-1-ol (2j)



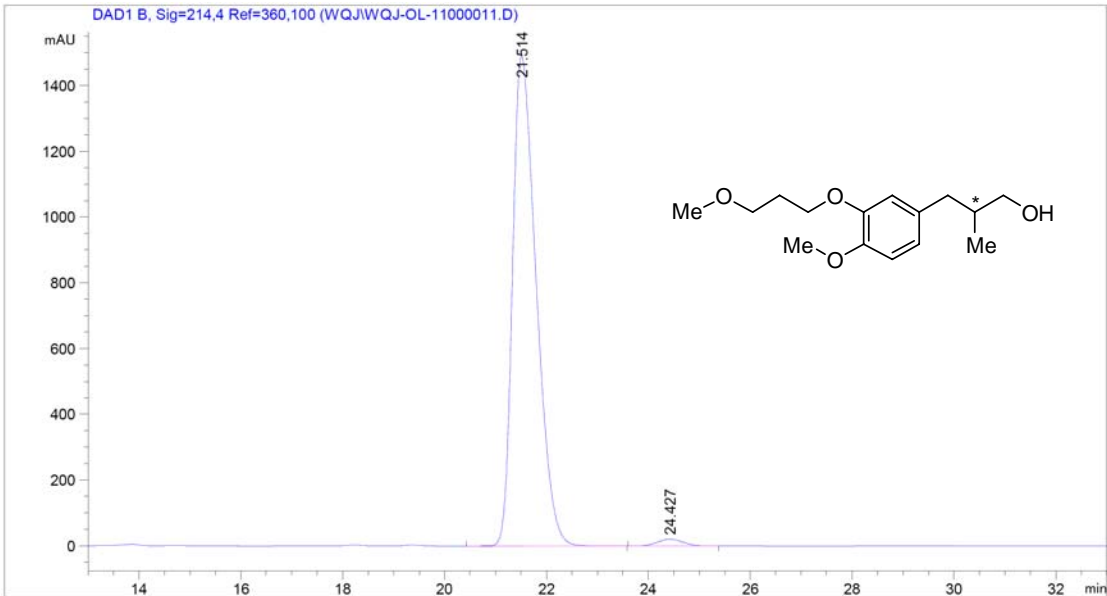
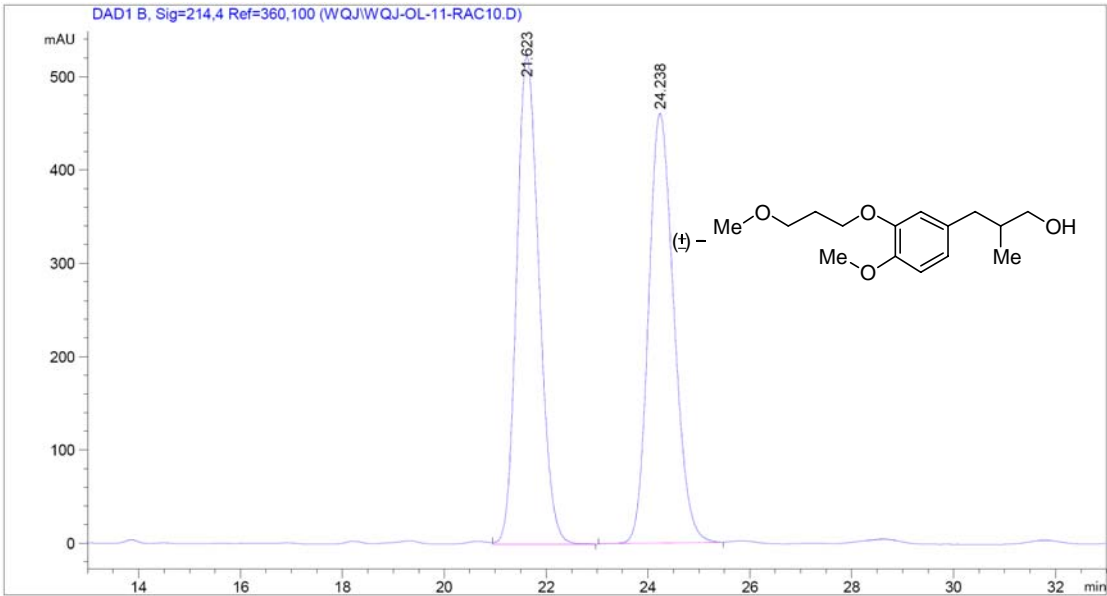
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.006	BB	0.2923	196.87523	10.15052	0.6416
2	19.509	BB	0.3592	3.04886e4	1321.36609	99.3584

2-methyl-3-(4-(trifluoromethyl)phenyl)propan-1-ol (2k)



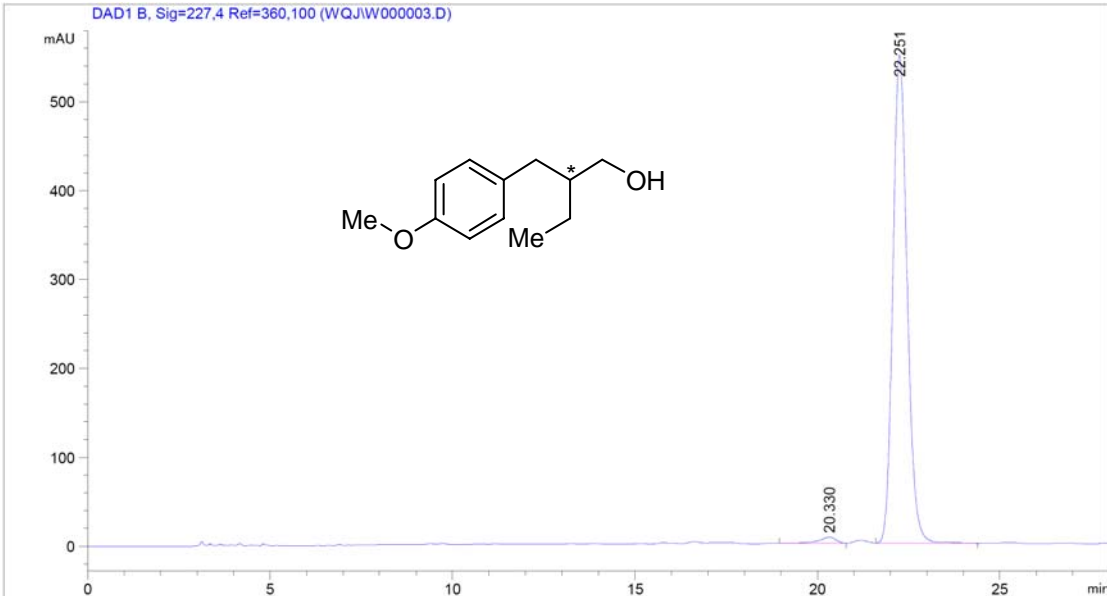
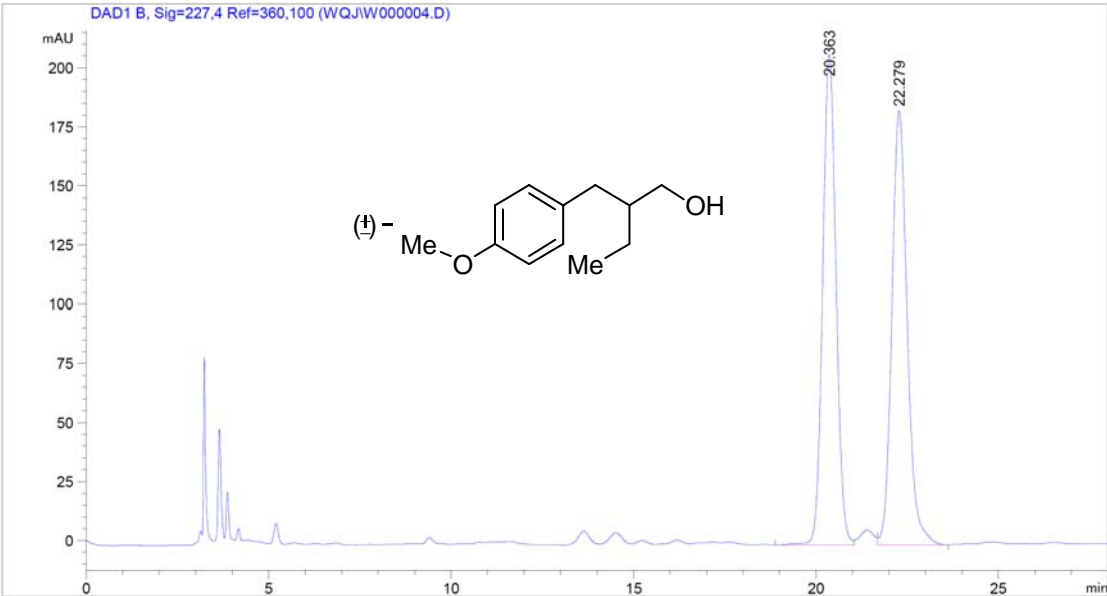
#	[min]		[min]	[mAU*s]	[mAU]	%
1	36.293	BV	0.9783	2252.62720	35.78900	3.3902
2	38.241	VB	1.0560	6.41923e4	860.83679	96.6098

3-(4-methoxy-3-(3-methoxypropoxy)phenyl)-2-methylpropan-1-ol (2l)



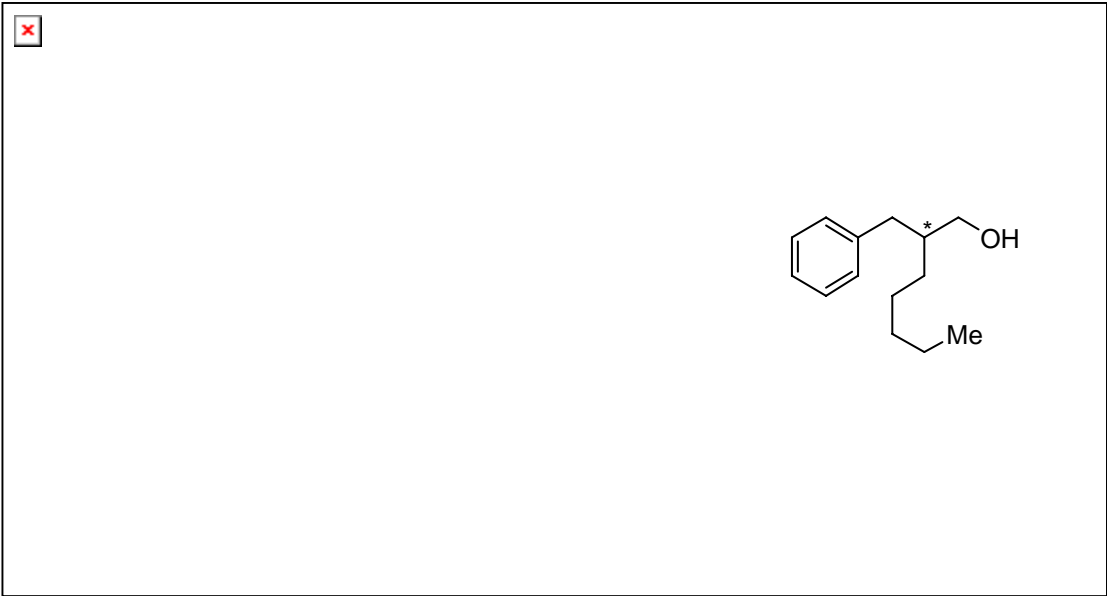
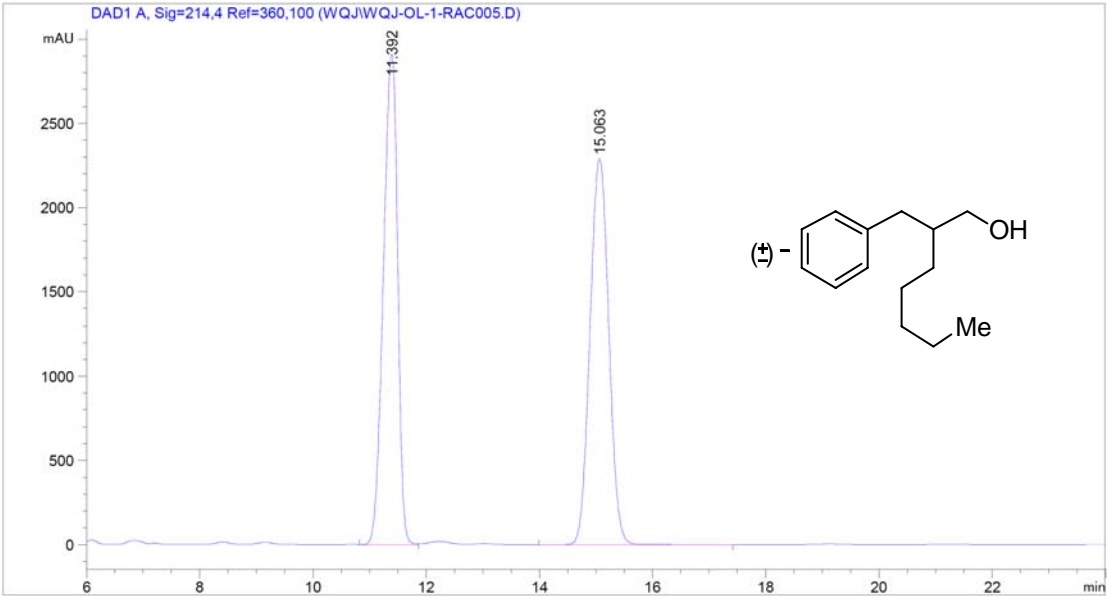
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.514	BB	0.4954	4.79836e4	1491.39587	98.4807
2	24.427	BB	0.5494	740.27338	21.09338	1.5193

2-(4-methoxybenzyl)butan-1-ol (2m)



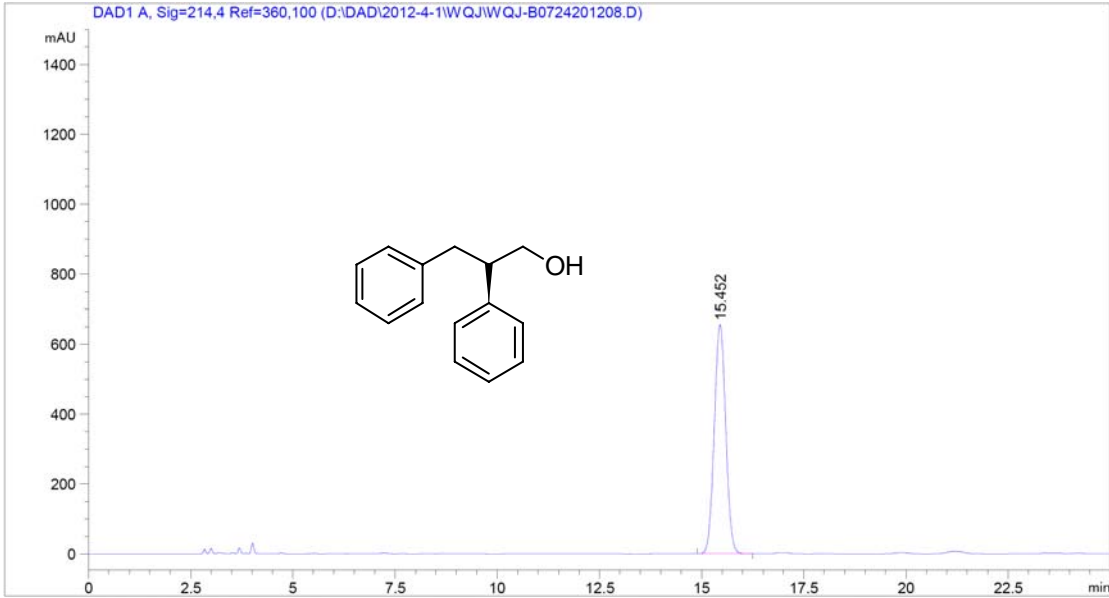
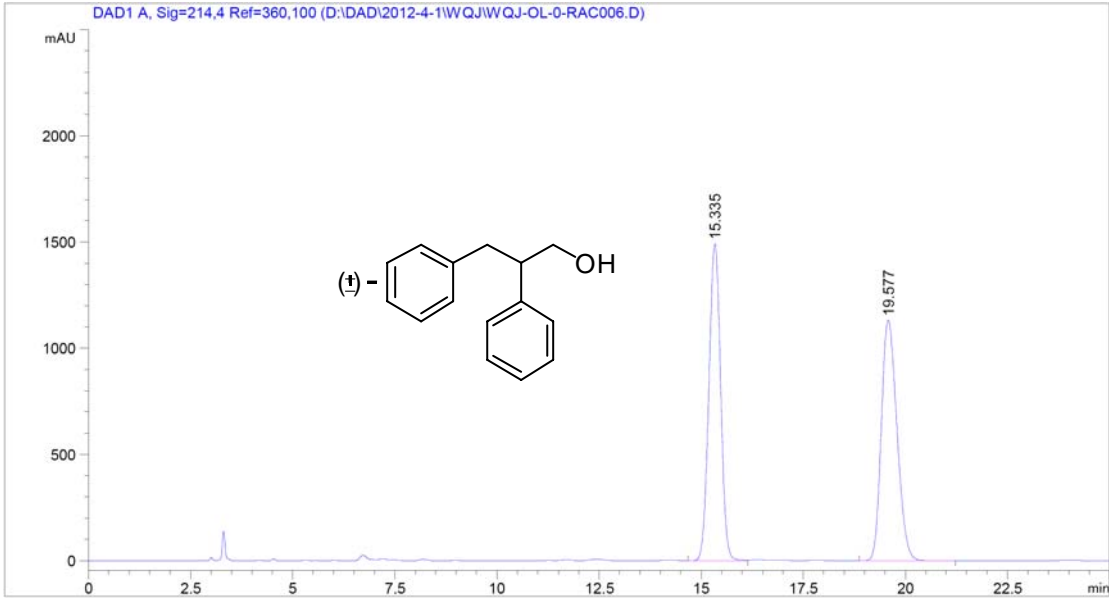
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.330	BB	0.4748	218.24777	6.79329	1.4390
2	22.251	VB	0.4215	1.49482e4	549.35406	98.5610

2-benzylheptan-1-ol (2n)



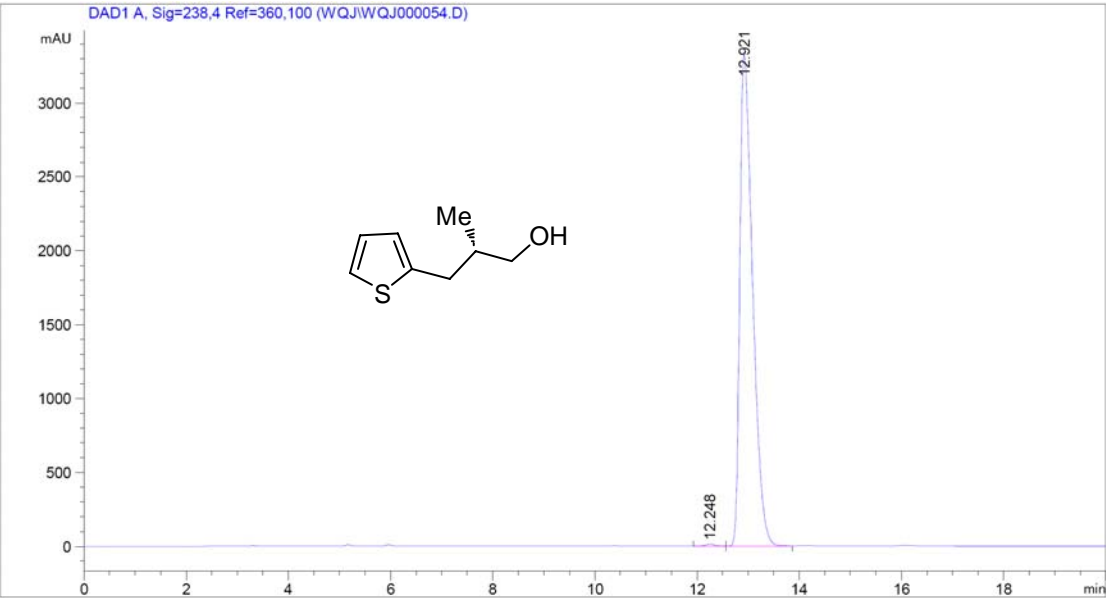
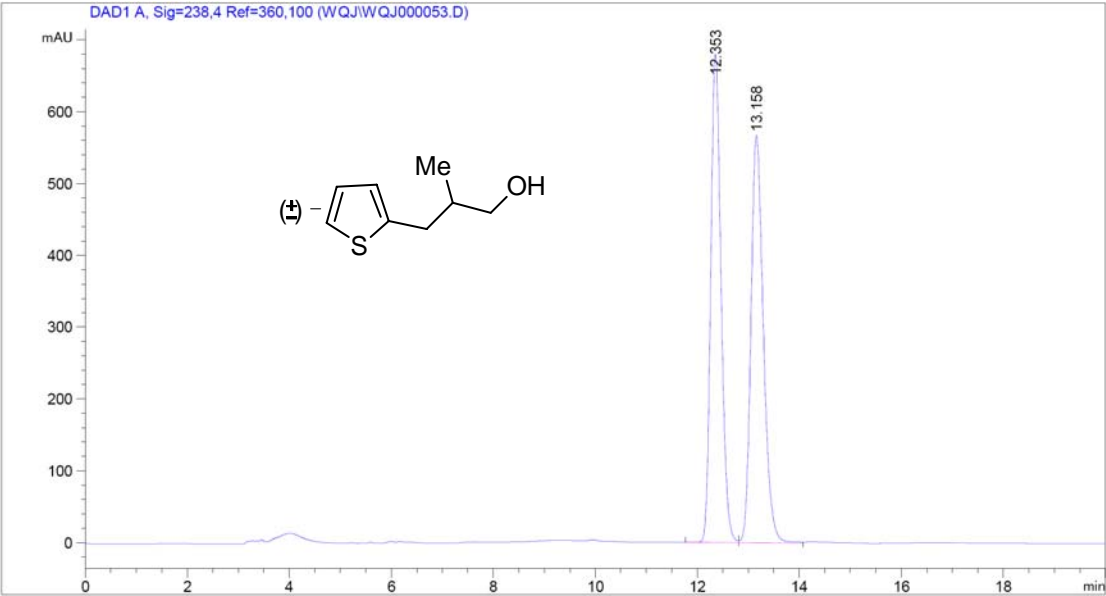
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.194	BB	0.2521	171.79895	10.65418	0.4227
2	15.034	BB	0.3709	4.04732e4	1717.76685	99.5773

2,3-diphenylpropan-1-ol (2o)



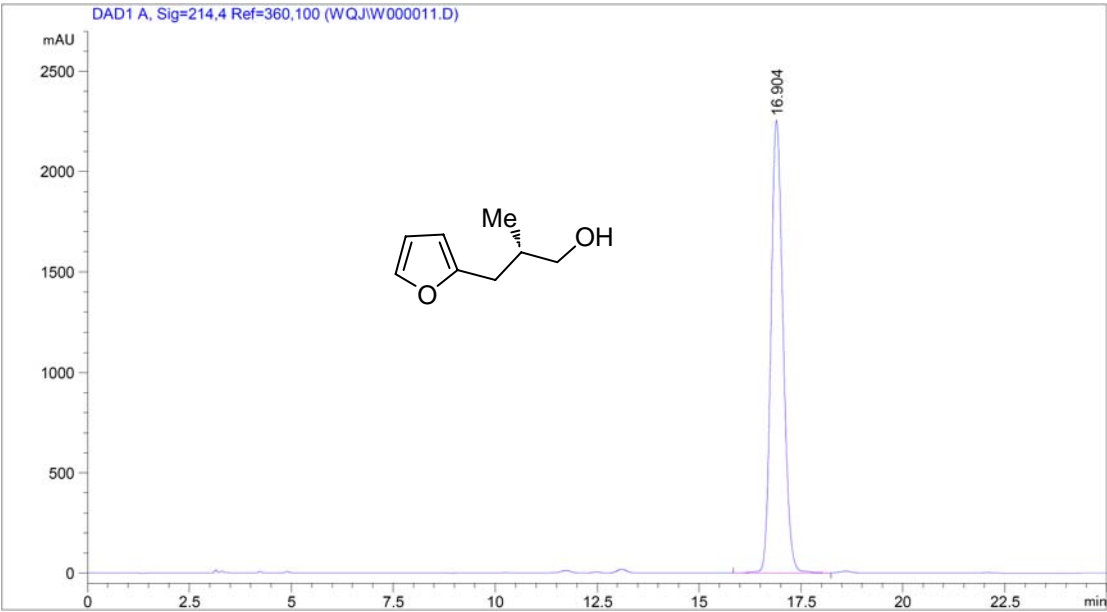
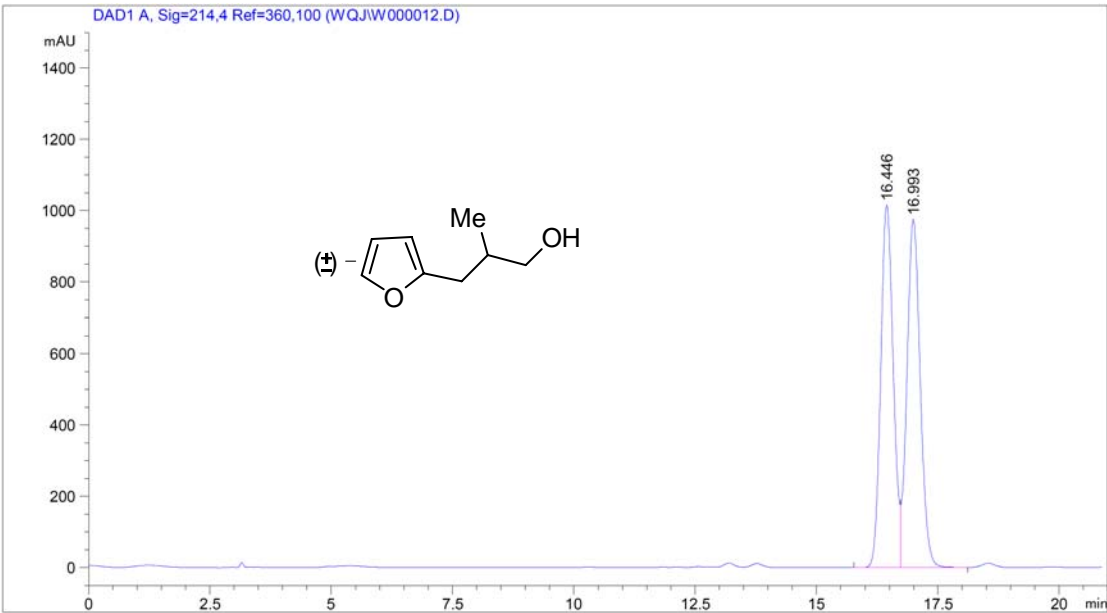
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.452	BB	0.3030	1.27728e4	656.44110	100.0000

(S)-2-methyl-3-(thiophen-2-yl)propan-1-ol (2p)



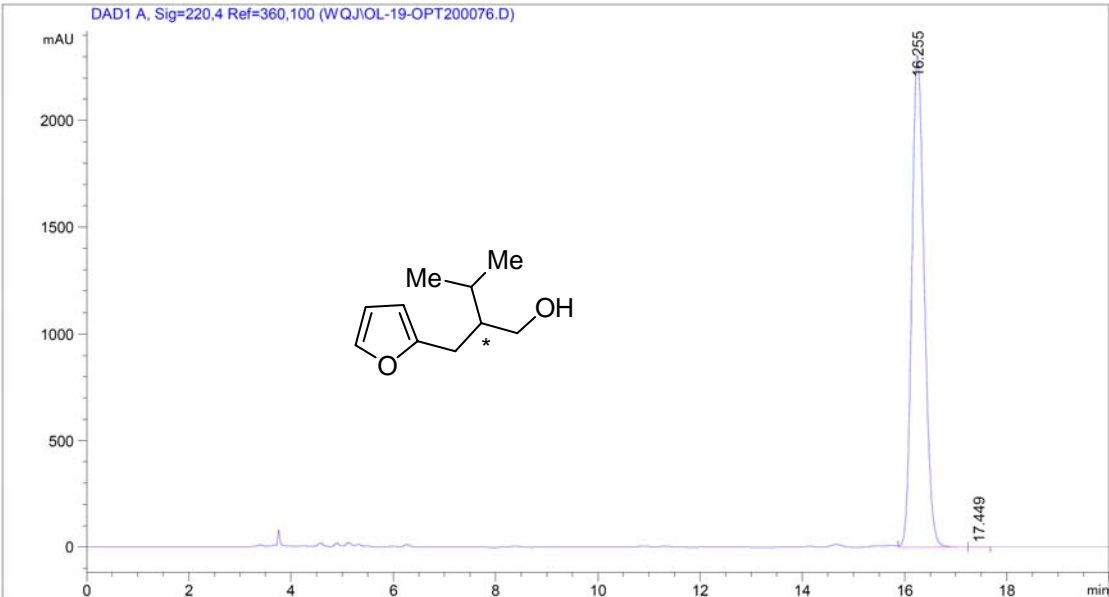
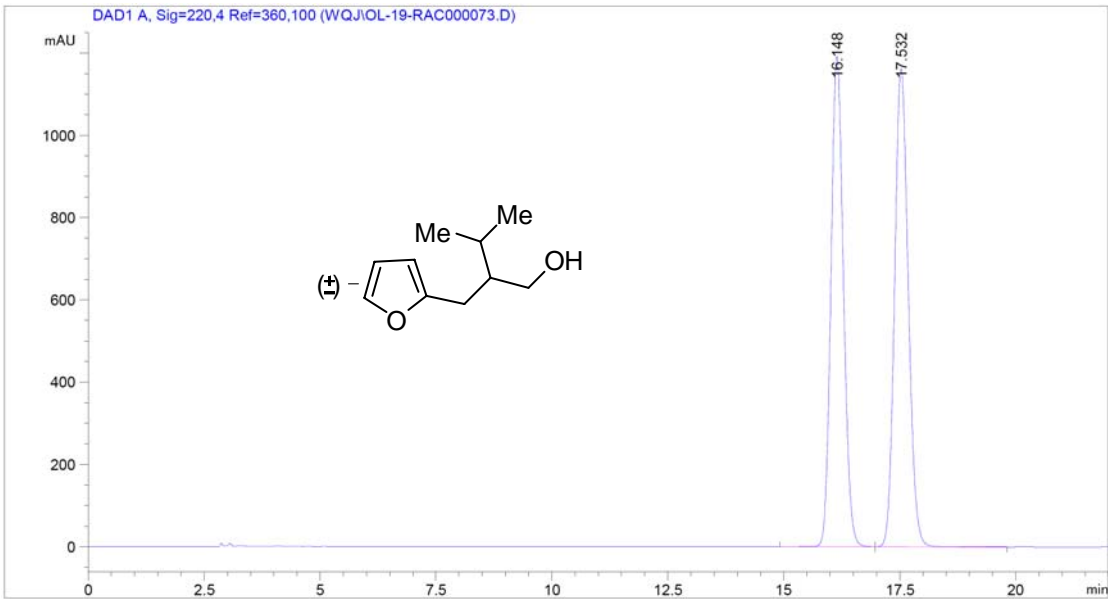
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.248	BB	0.2024	184.75371	14.33477	0.3179
2	12.921	BV	0.2675	5.79339e4	3321.54956	99.6821

3-(furan-2-yl)-2-methylpropan-1-ol (2q)



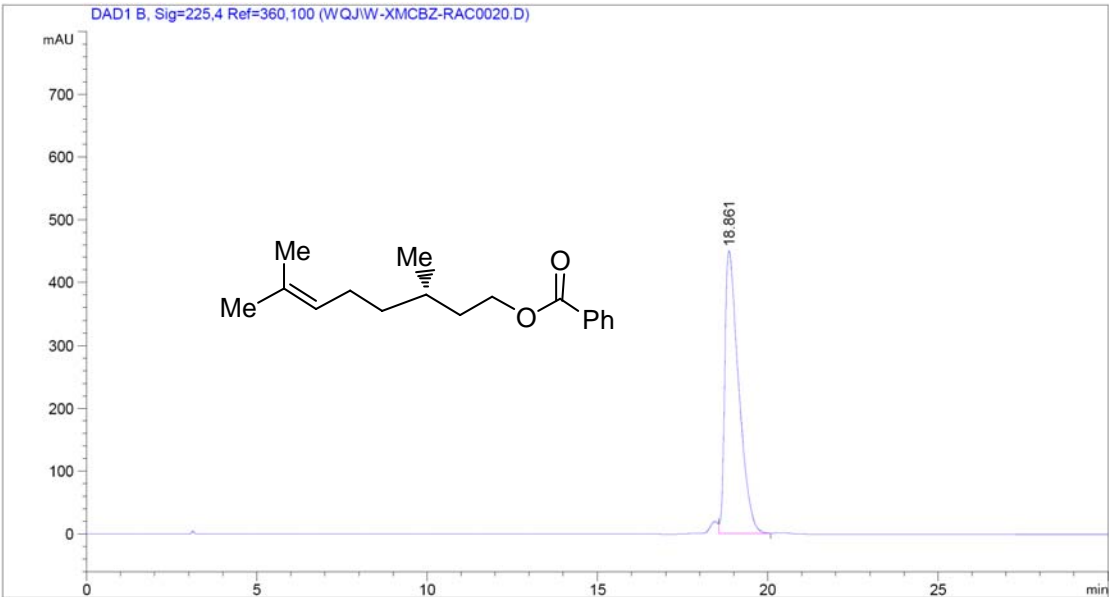
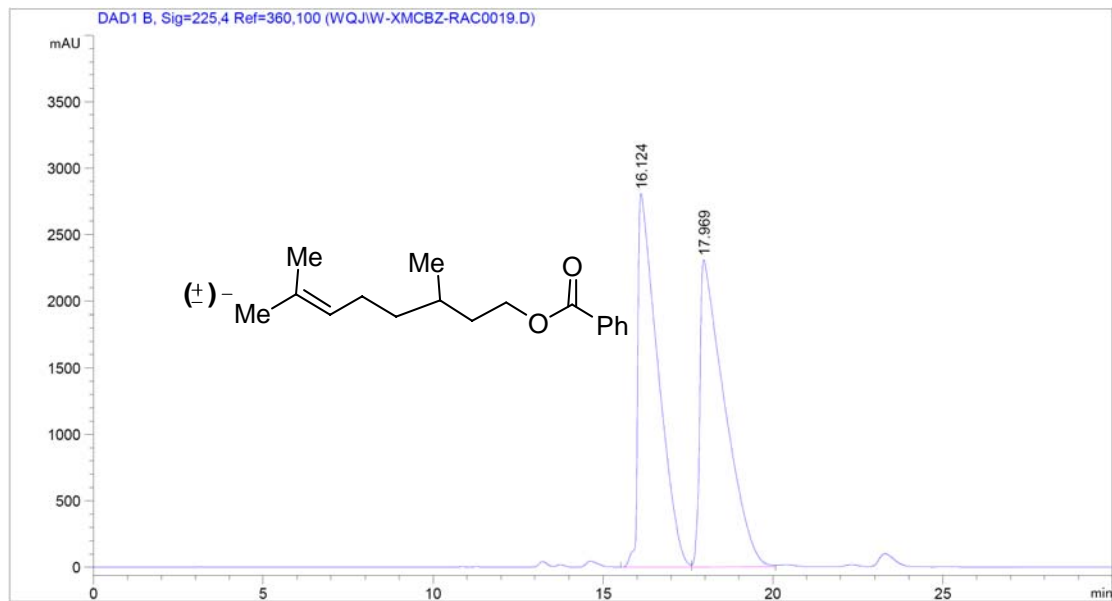
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.904	BV	0.3216	4.67223e4	2256.23120	100.0000

2-(furan-2-ylmethyl)-3-methylbutan-1-ol (2r)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.255	VB	0.2632	3.89768e4	2306.17358	99.9843
2	17.449	BB	0.2103	6.13193	4.75883e-1	0.0157

3,7-dimethyloct-6-enyl benzoate



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.861	VB	0.4230	1.27454e4	449.25998	100.0000