Supporting information

Linear β-Amino Alcohol Catalyst Anchored to Functionalized Magnetite Nanoparticles for Enantioselective Addition of Dialkyl Zinc to Aromatic Aldehydes

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Synthesis of magnetite/silica coreshell nanoparticles: 3.82 mmol (1.5 g) of Mohr salt ($(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$), 3.82 mmol (1.5 g) of $Fe_2(SO_4)_3$ and 19 mmol (2.12 g) of polyvinylpyrrolidone (PVP) were dissolved in 200 mL of distilled water. The Fe^{2+}/Fe^{3+} solution thus prepared was filtered and added into a filtered solution of 19 mmol (2.12 g) of PVP and 150 ml of NH_3 (33 wt % aqueous solution) in 500 mL of water under mechanical stirring and continuously flowing argon gas. The solution was reacted for 30 min at room temperature, then it was heated to 80 °C for 30 min. After cooling down the reaction mixture, the product was separated by magnetic decantation and dialyzed overnight. The magnetite nanoparticles were dispersed in 30 ml of water by sonication and a solution of 0.4 ml of TEOS and 3.25 ml of in NH_3 (33 wt % aqueous solution) in 150 ml of 2-PrOH was added dropwise under vigorous mechanical stirring. The reaction was stirred at room temperature for three hours and the product was separated by magnetic decantation and repeatedly washed with 2-PrOH and water. The as-synthesized silica-coated magnetite nanoparticles were stored in 20 ml of water. Obtained 770 mg. Diameter 10-15 nm determined by TEM images. HR-TEM images showed lattice fringes both of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) phases. FTIR (neat/ν cm^{-1}): 3341, 1634, 1049, 965, 813, 551.

Synthesis of 3-azidopropyltrimethoxysilane:

In a flame-dried pear shaped flask 4.5 mmol (0.88 ml) of 3-iodopropyltrimethoxysilane were dissolved under inert atmosphere in 15 ml of anhydrous DMSO. 9 mmol of NaN_3 were added and the reaction was stirred at 60 °C for 12 h. 10 ml of hexane were injected under argon gas and the mixture was vigorously stirred for 1 h. The hexane layer was then collected *via canula* and this procedure was repeated twice. The combined hexane layers were concentrated *in vacuo* under inert atmosphere to give 766 mg the product (83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.57 (s, 9H, OCH_3 x3); 3.26 (t, 2H, J = 7.0 Hz, N_3CH_2); 1.71 (m, 2H, $C\underline{H}_2CH_2Si$); 0,69 (m, 2H, $CH_2C\underline{H}_2Si$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 54.0; 50.8; 22.7; 6.5. FTIR (neat/ν cm^{-1}): 2941, 2840, 2092, 1080, 809.

Surface modification with azidosilane (4a): 750 mg of silica-coated magnetite nanoparticles were dispersed in 36 ml of deionized water. A solution of 2.6 ml of 3-azidopropyltrimethoxysilane in 80 ml of EtOH was added under mechanical stirring. 64 µl of NH_3 (33 wt % aqueous solution) were added and the reaction was mechanically stirred for three hours. The product was separated by magnetic decantation and repeatedly washed with 2-PrOH and water. The azido-modified silica-coated magnetite nanoparticles were stored in 20 ml of water. Obtained 760 mg. Loading 0.44 mmol/g calculated by elemental analysis: N 1.87%, C 2.16 %. FTIR (neat/ν cm^{-1}): 3394, 2928, 2868, 2100, 1627, 1444, 1030, 807, 551

End-capping of the free silanols (4b): 390 mg of azido functionalized silica-coated magnetic nanopartcicles were dispersed in 10 ml of toluene. A solution of 9.5 mmol (2 ml) of hexamethildisilazane in 8 ml of toluene was then added under mechanical stirring. The solution was heated to 110 °C and stirred at this temperature for three hours. The product was separated by magnetic decantation and repeatedly washed with toluene and acetone. The dispersibility of the as-synthesized nanoparticles in organic solvents appeared remarkably increased. The sililated azido-modified silica-coated magnetite nanoparticles were stored in 20 ml of toluene. Obtained 290 mg. Elemental analysis: N 1.89%, C 3.52%. FTIR (neat/ν cm^{-1}): 3421, 2948, 2094, 1627, 1444, 1260, 1030, 846, 800, 551.

Immobilization via click reaction. 150 mg of the azido functionalized silica-coated magnetic nanoparticles **4a** or **4b** were dispersed in 10 ml of THF. 0.3 mmol of the terminal alkyne **3** (140 mg), 0.09 mmol (19 mg) of CuI were added under mechanical stirring. 0.4 ml of DIPEA were injected

dropwise into the mixture and the reaction was mechanically stirred for 48 h at room temperature. The product was separated by magnetic decantation and repeatedly washed with THF and toluene. The functionalized silica-coated magnetite nanoparticles were stored in 20 ml of toluene:

1a) Obtained 200 mg. Loading: 0.28 mmol/g calculated by elemental analysis: N 1.95% C 8.69%. FTIR (neat/ν cm^{-1}): 3421, 2934, 2849, 1510, 1056, 551.

1b) Obtained 280 mg. Loading: 0.41 mmol/g calculated by elemental analysis: N 2.89% 13.94%. FTIR (neat/ν cm^{-1}): 3315, 2928, 2849, 1614, 1510, 1450, 1246, 1037, 840, 551.

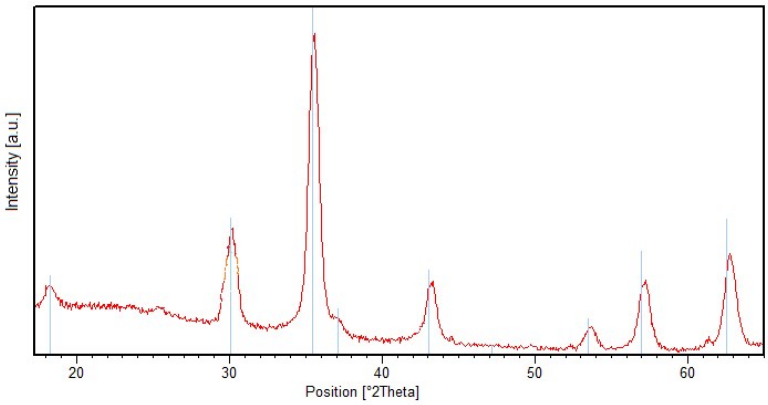
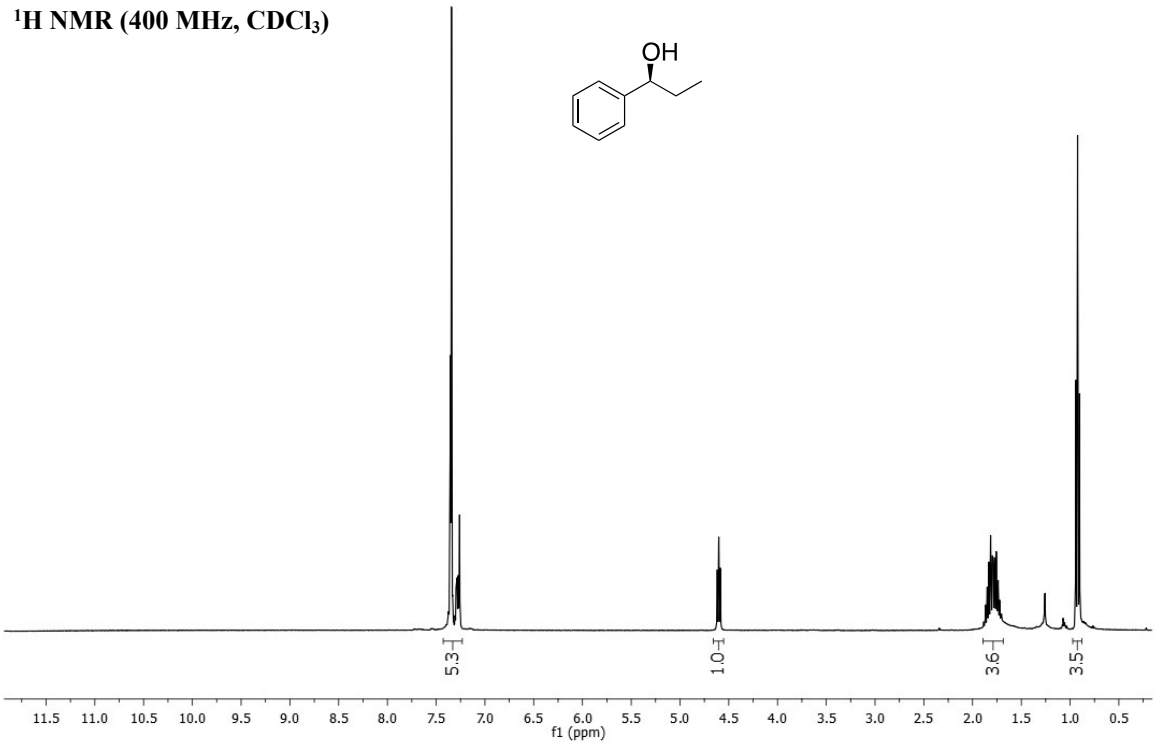


Figure 1S. XRD pattern of sample **1b**

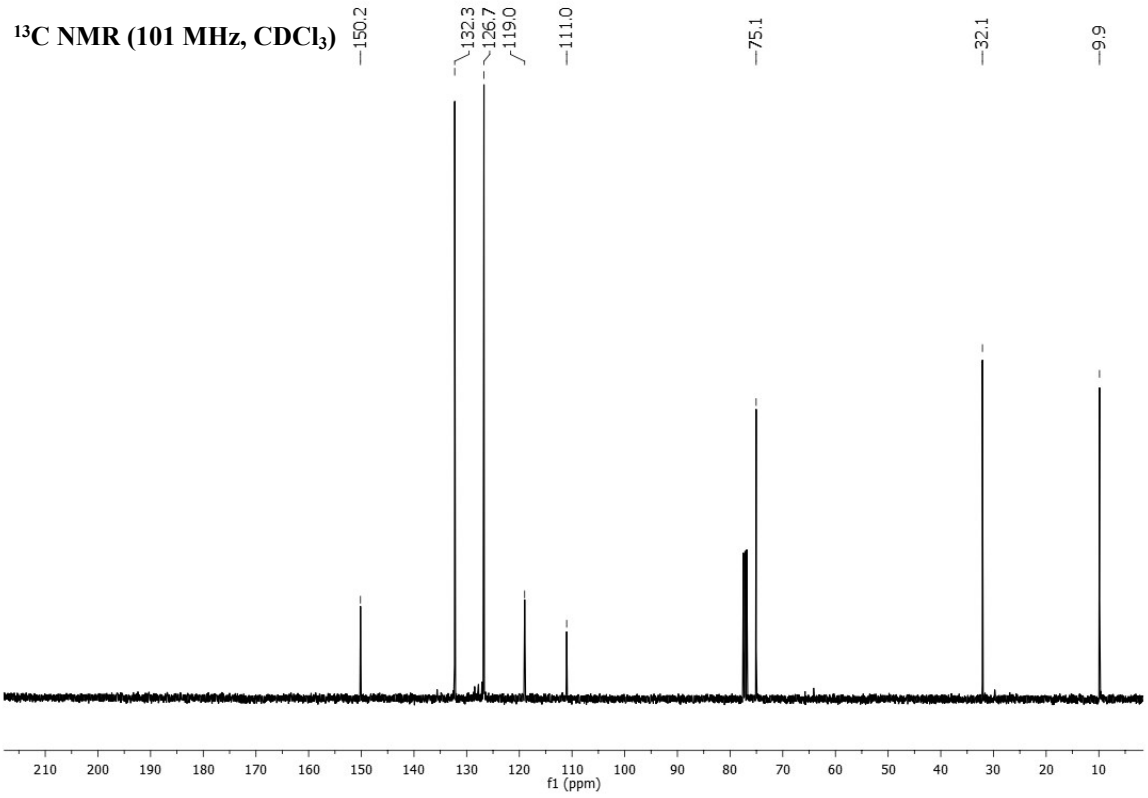
^{1}H and ^{13}C NMR spectra of dialkylzinc addition products

(*S*)-1-phenylpropan-1-ol (10a)

^{1}H NMR (400 MHz, $CDCl_3$)

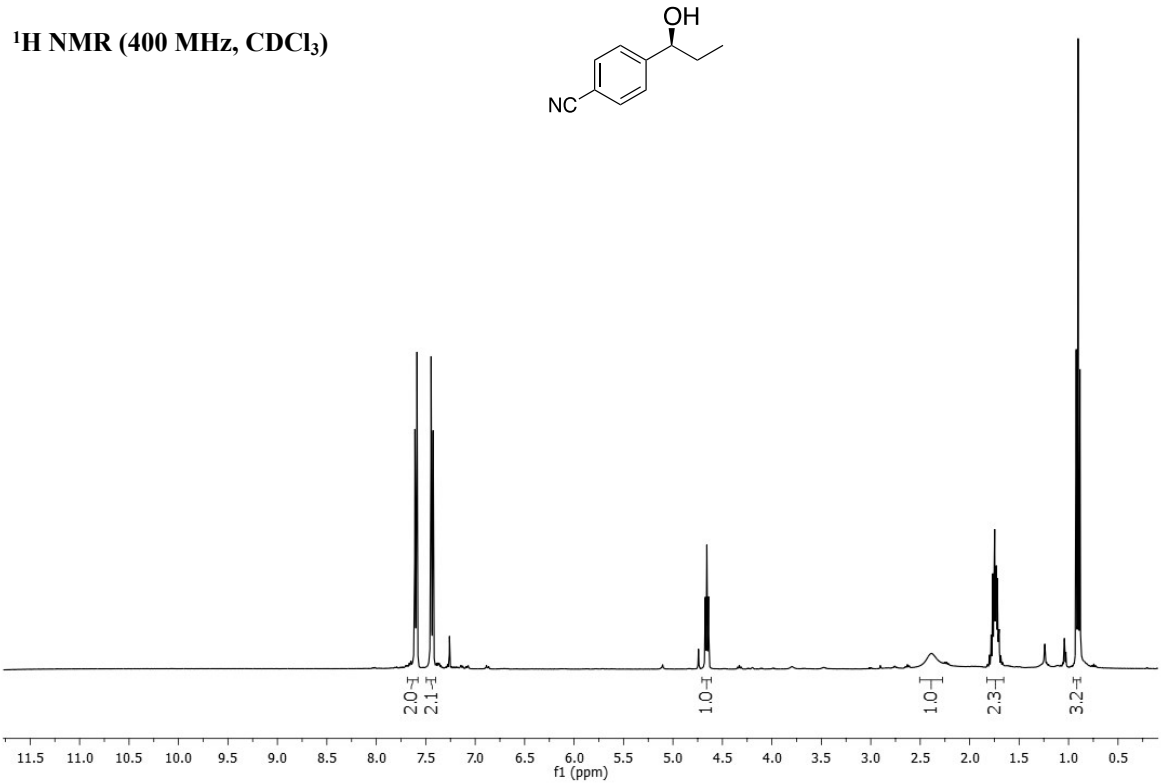


^{13}C NMR (101 MHz, $CDCl_3$)

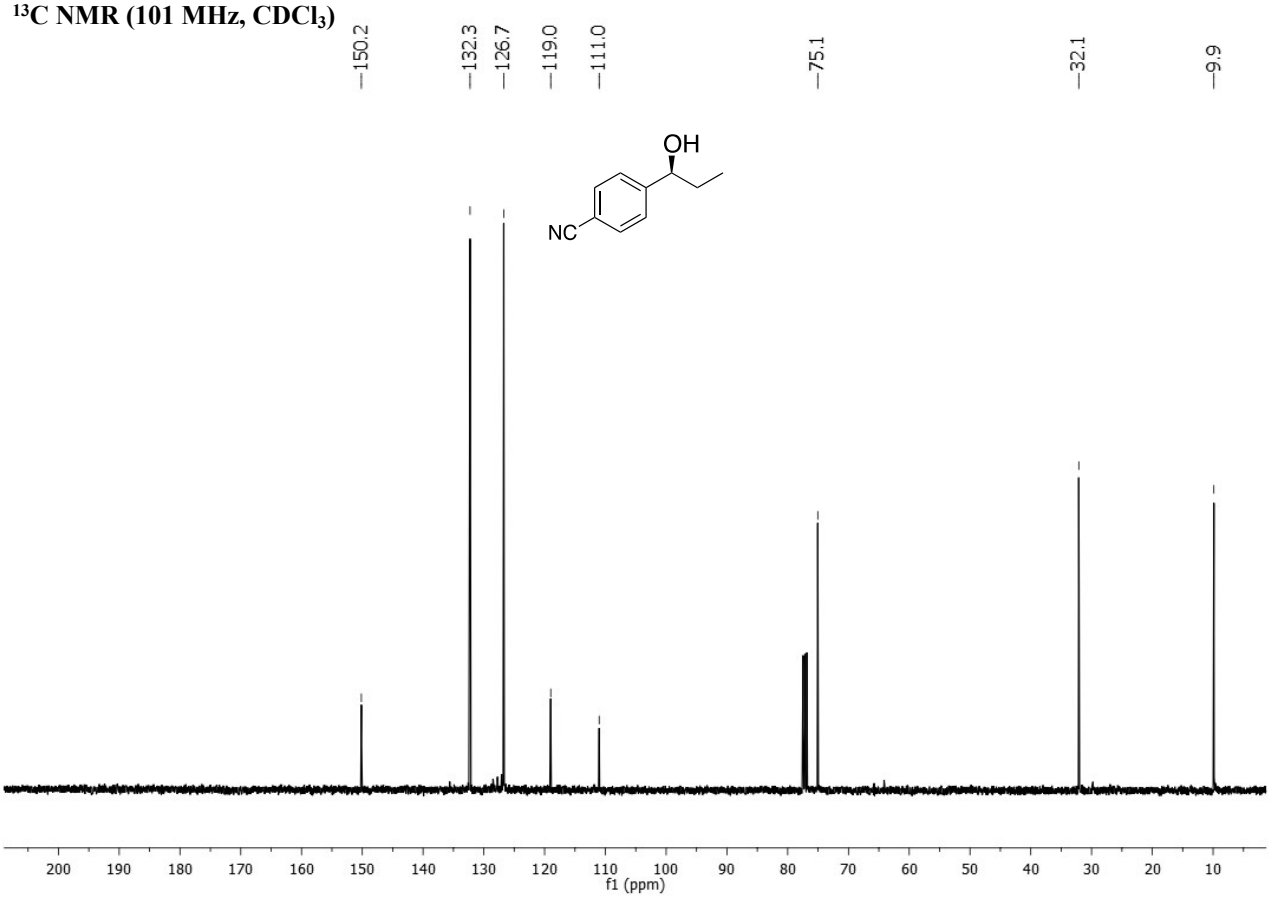


(*S*)-4-(1-hydroxypropyl)benzonitrile (10b)

^{1}H NMR (400 MHz, $CDCl_3$)

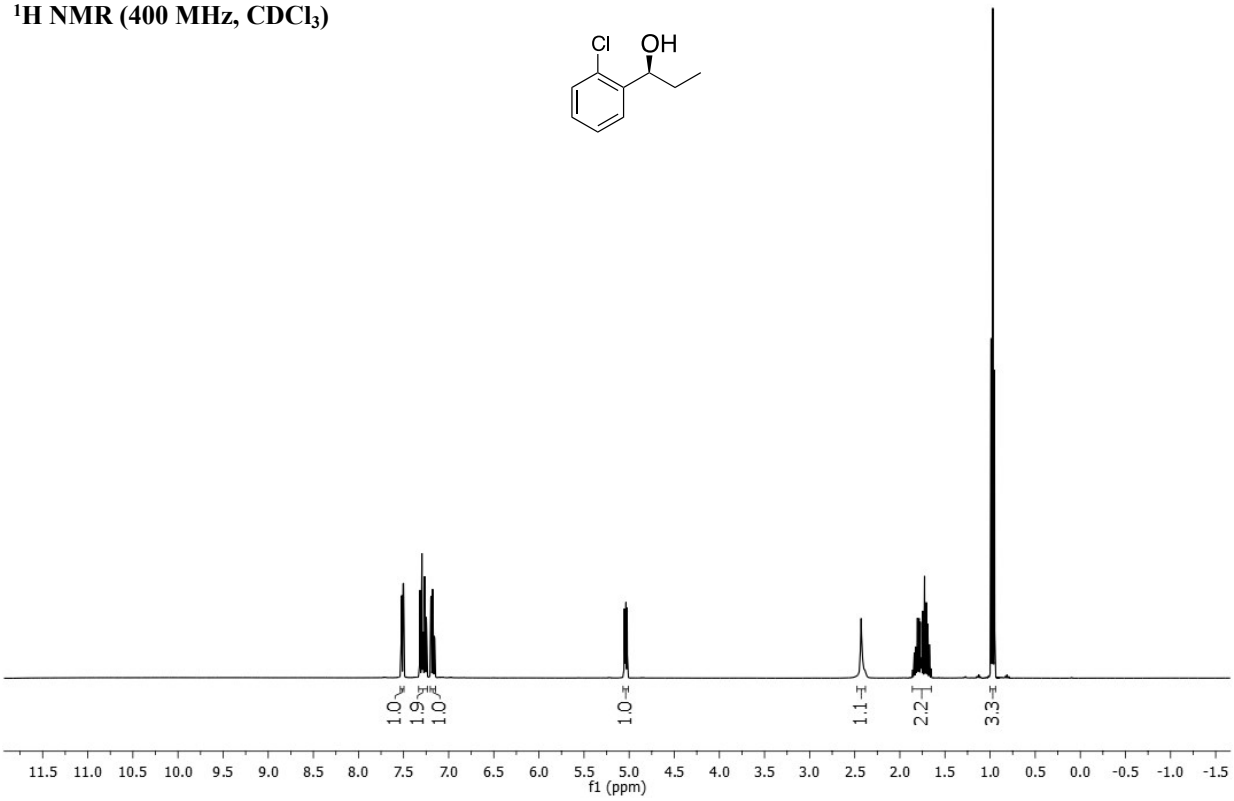


^{13}C NMR (101 MHz, $CDCl_3$)

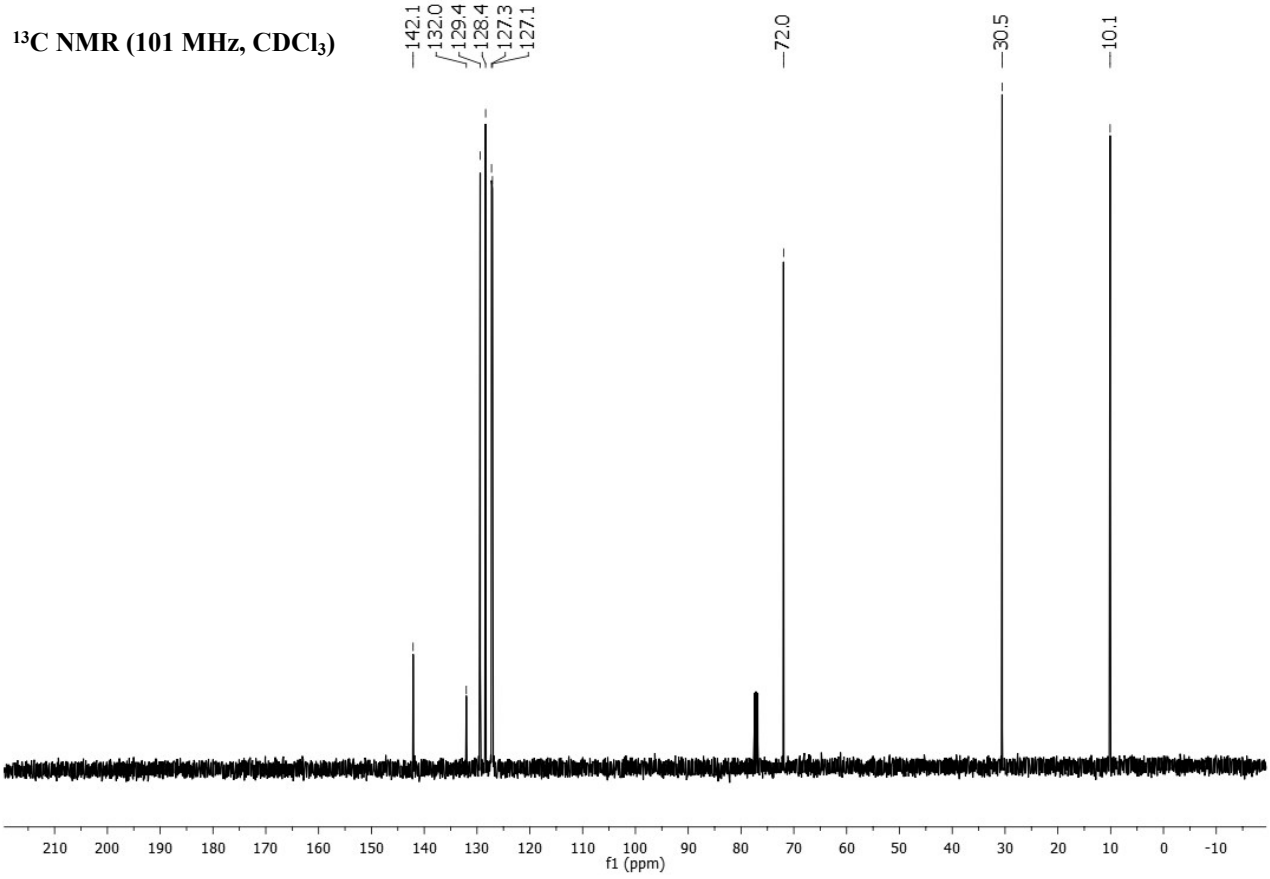


(*S*)-1-(2-chlorophenyl)propan-1-ol (10c)

^{1}H NMR (400 MHz, $CDCl_3$)

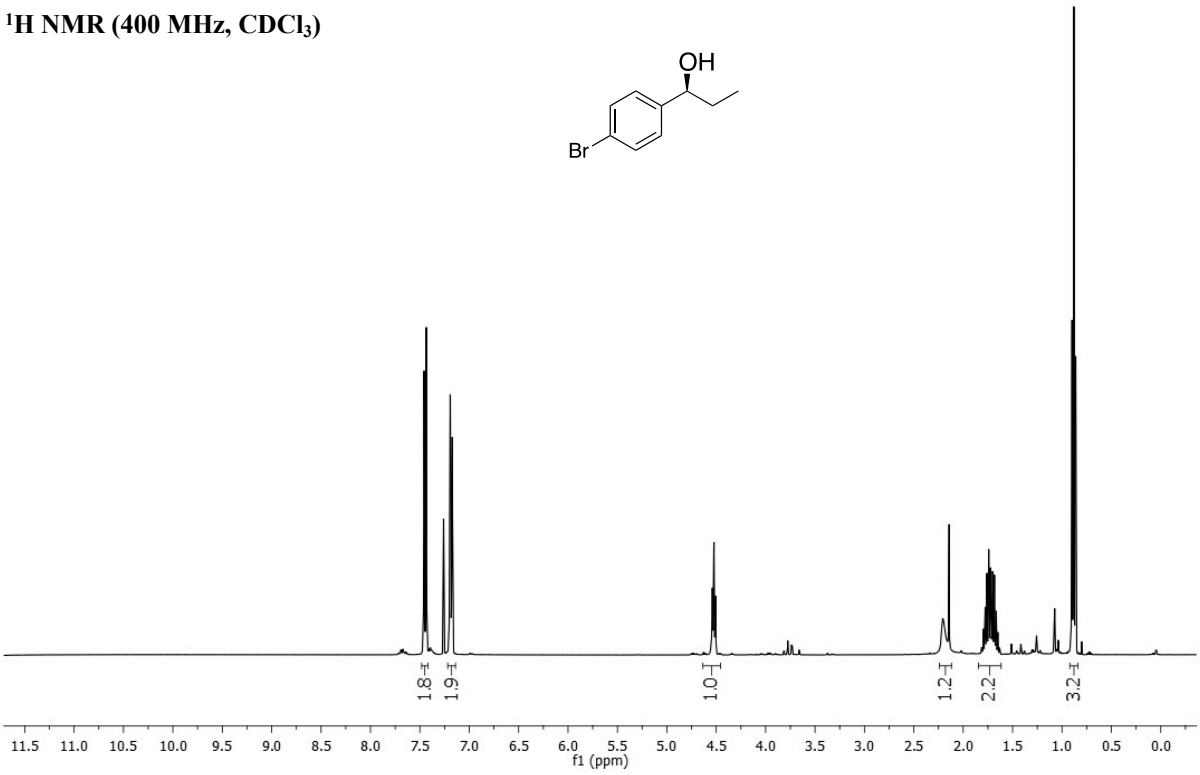


^{13}C NMR (101 MHz, $CDCl_3$)

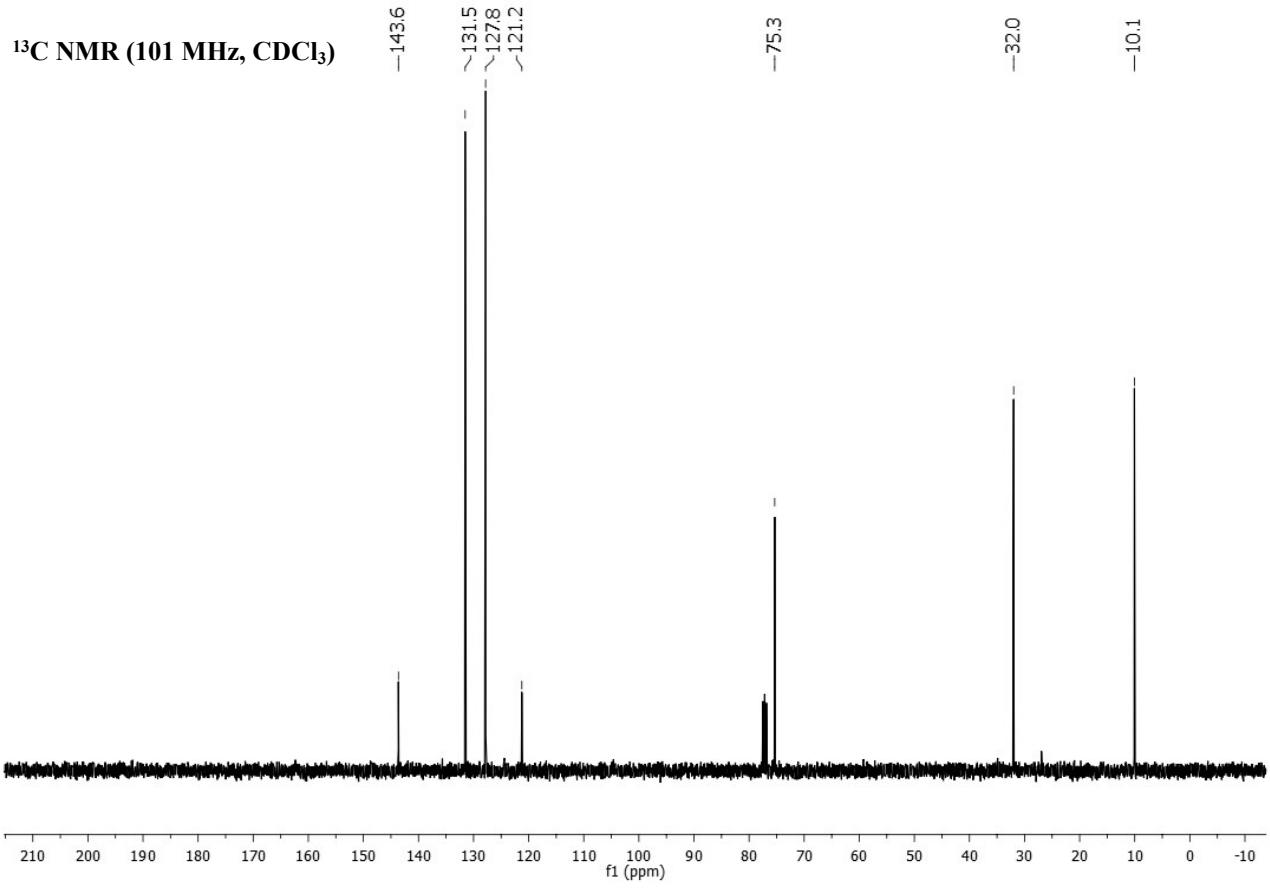


(*S*)-1-(4-bromophenyl)propan-1-ol (10d)

^{1}H NMR (400 MHz, $CDCl_3$)

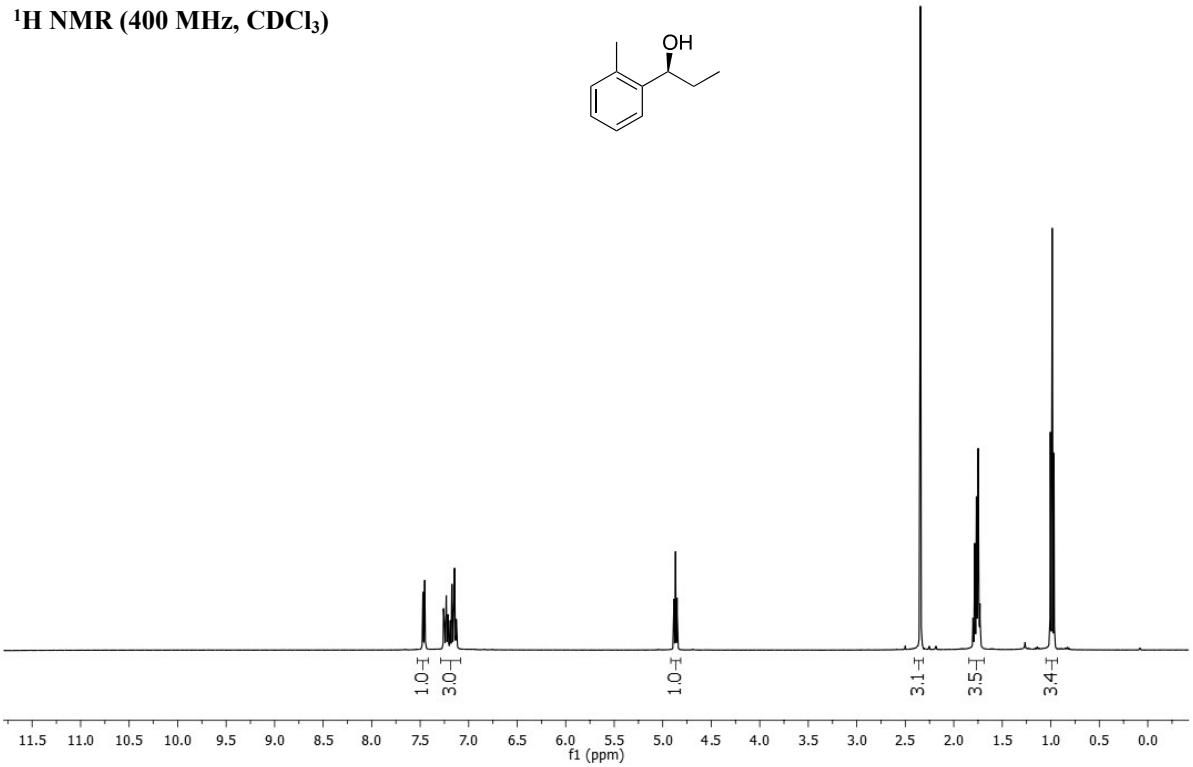


^{13}C NMR (101 MHz, $CDCl_3$)

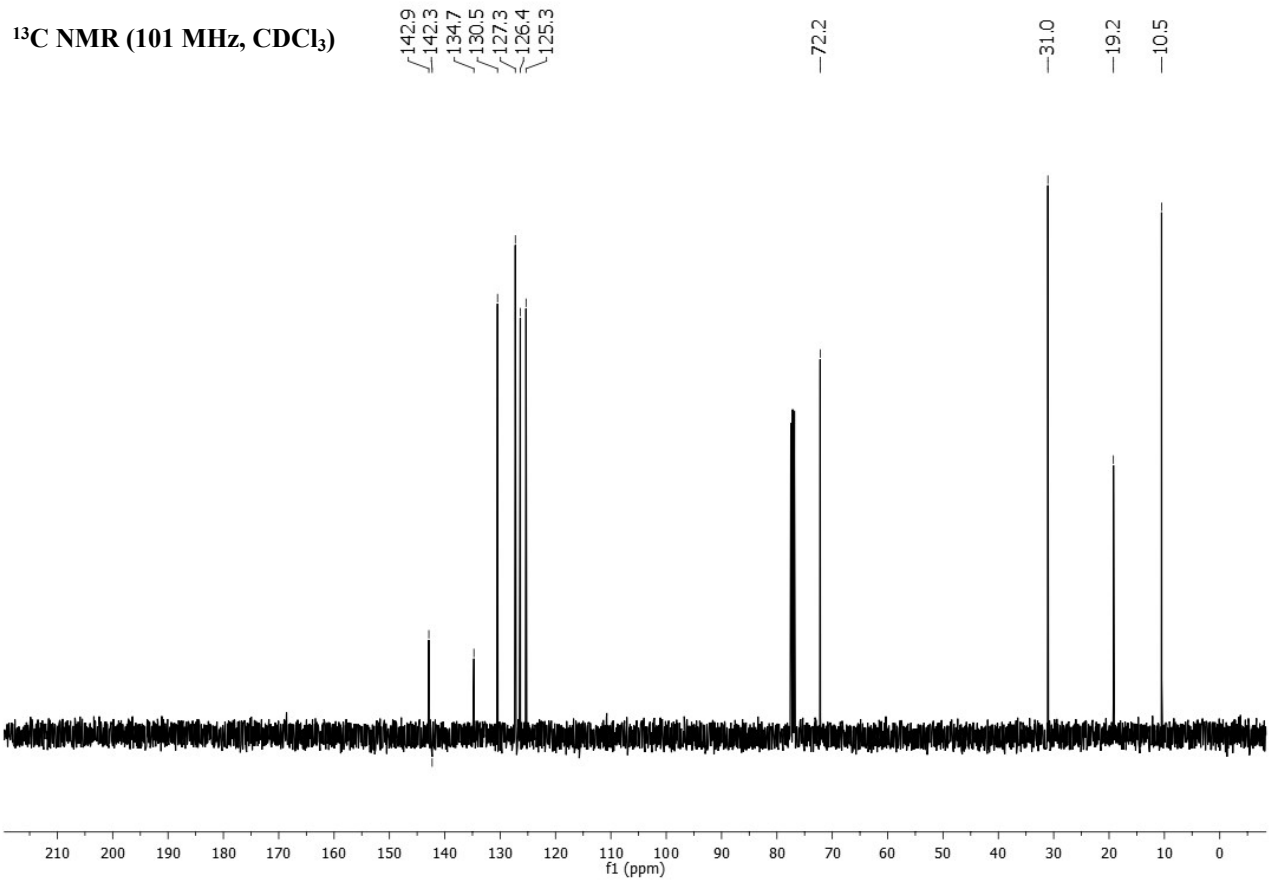


(*S*)-1-(*o*-tolyl)propan-1-ol (10e)

^{1}H NMR (400 MHz, $CDCl_3$)

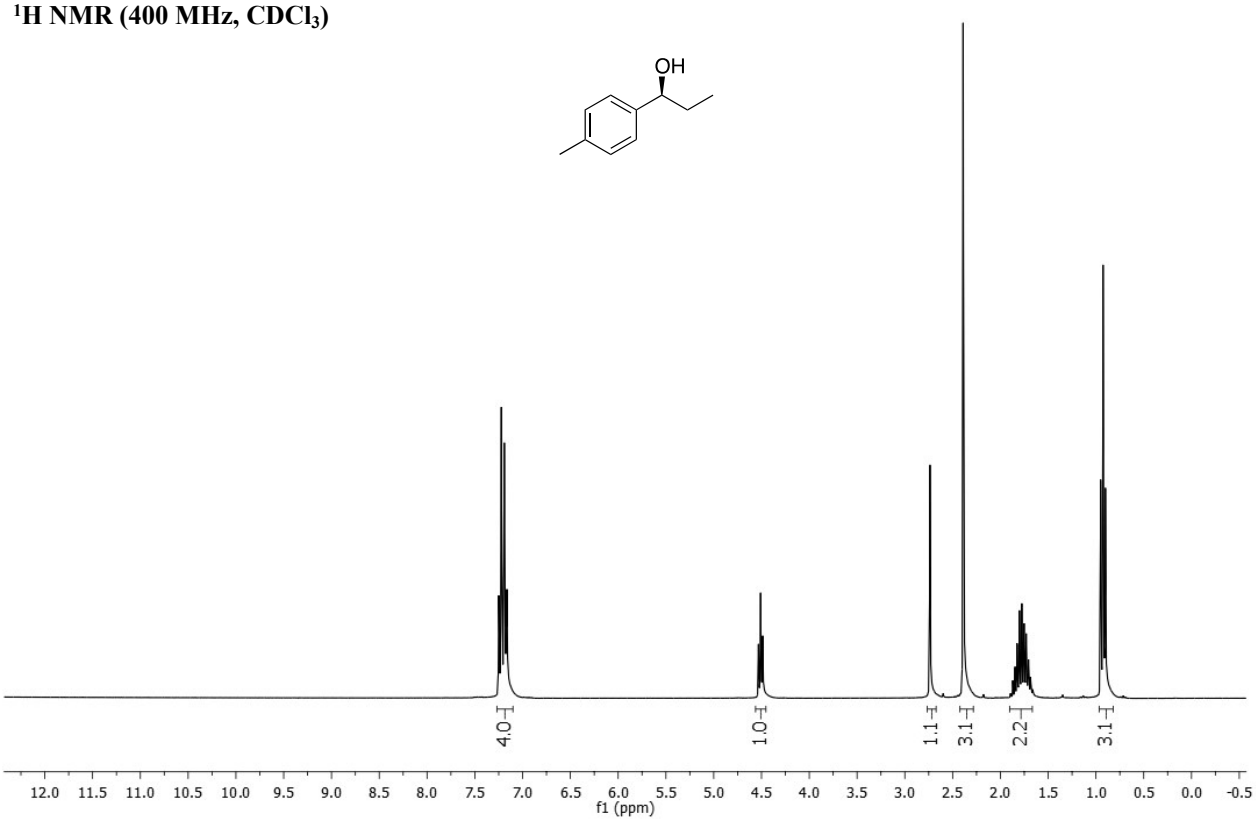


^{13}C NMR (101 MHz, $CDCl_3$)

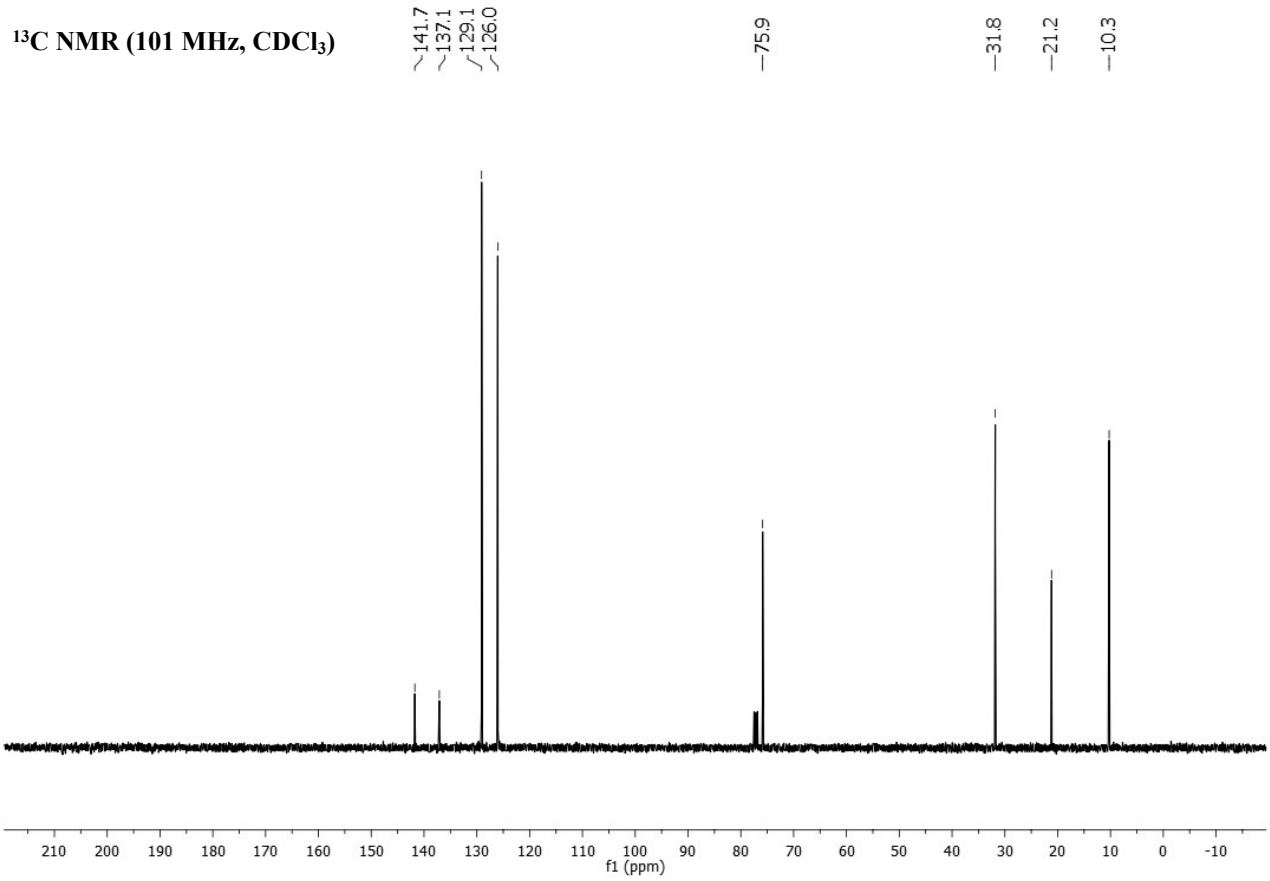


(*S*)-1-(*p*-tolyl)propan-1-ol (10f)

^{1}H NMR (400 MHz, $CDCl_3$)

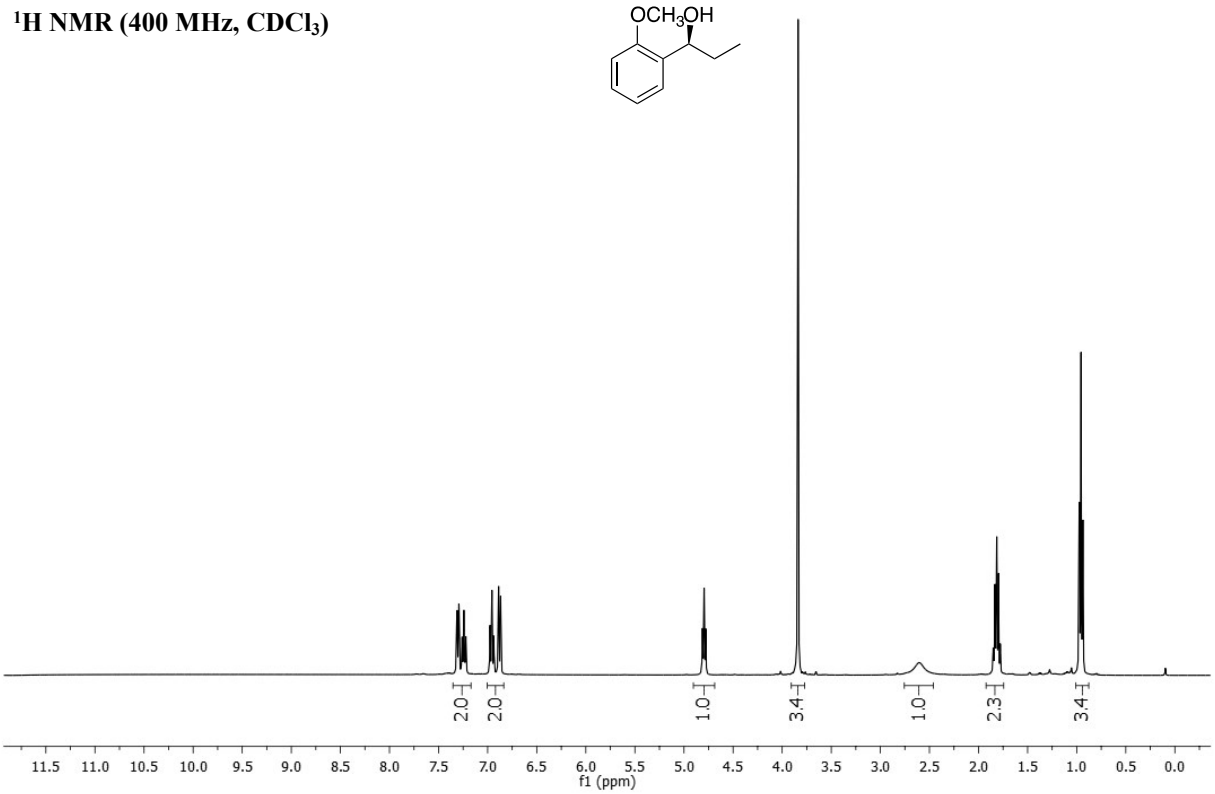


^{13}C NMR (101 MHz, $CDCl_3$)

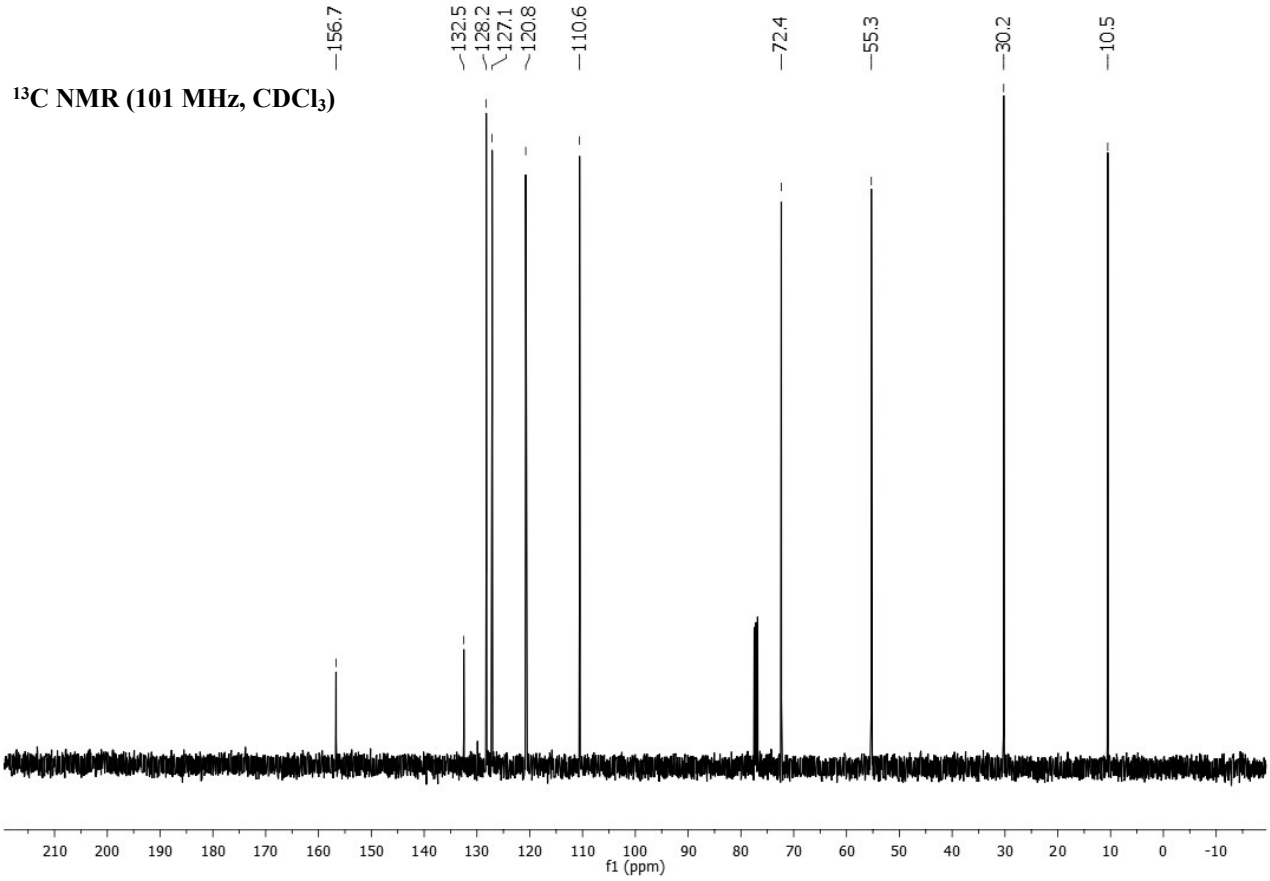


(*S*)-1-(2-methoxyphenyl)propan-1-ol (10g)

^{1}H NMR (400 MHz, $CDCl_3$)

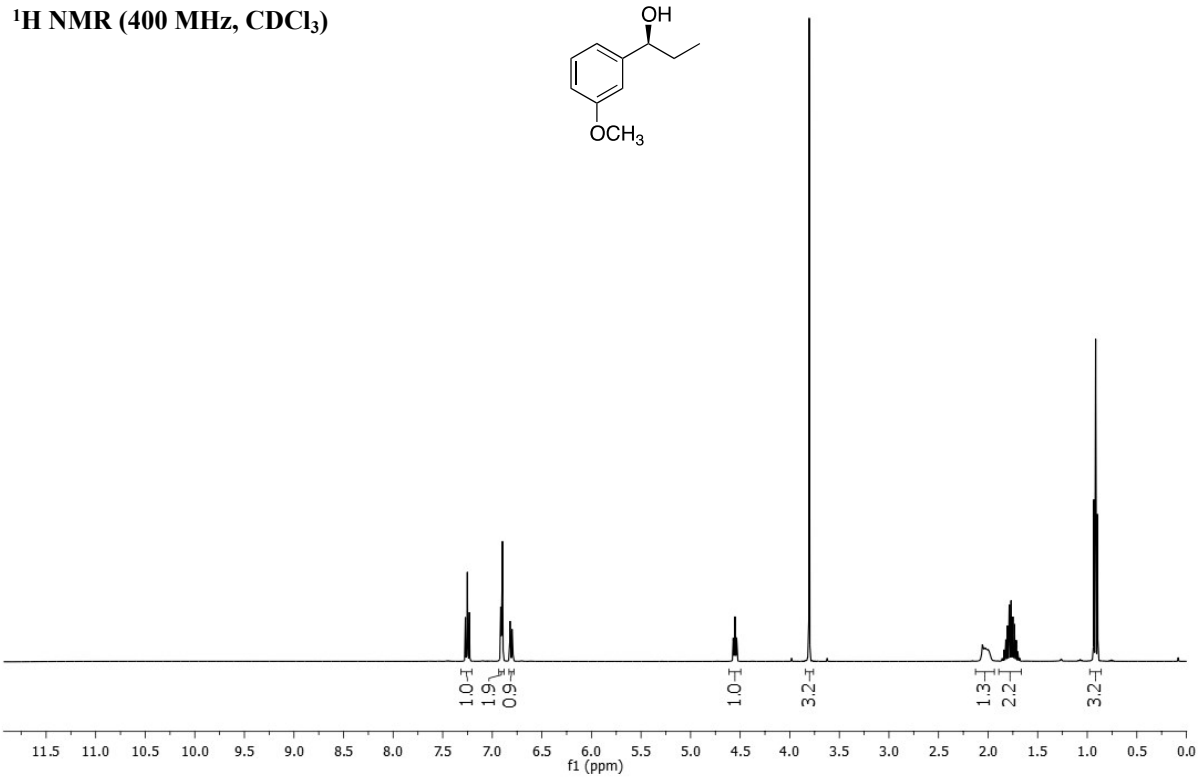


^{13}C NMR (101 MHz, $CDCl_3$)

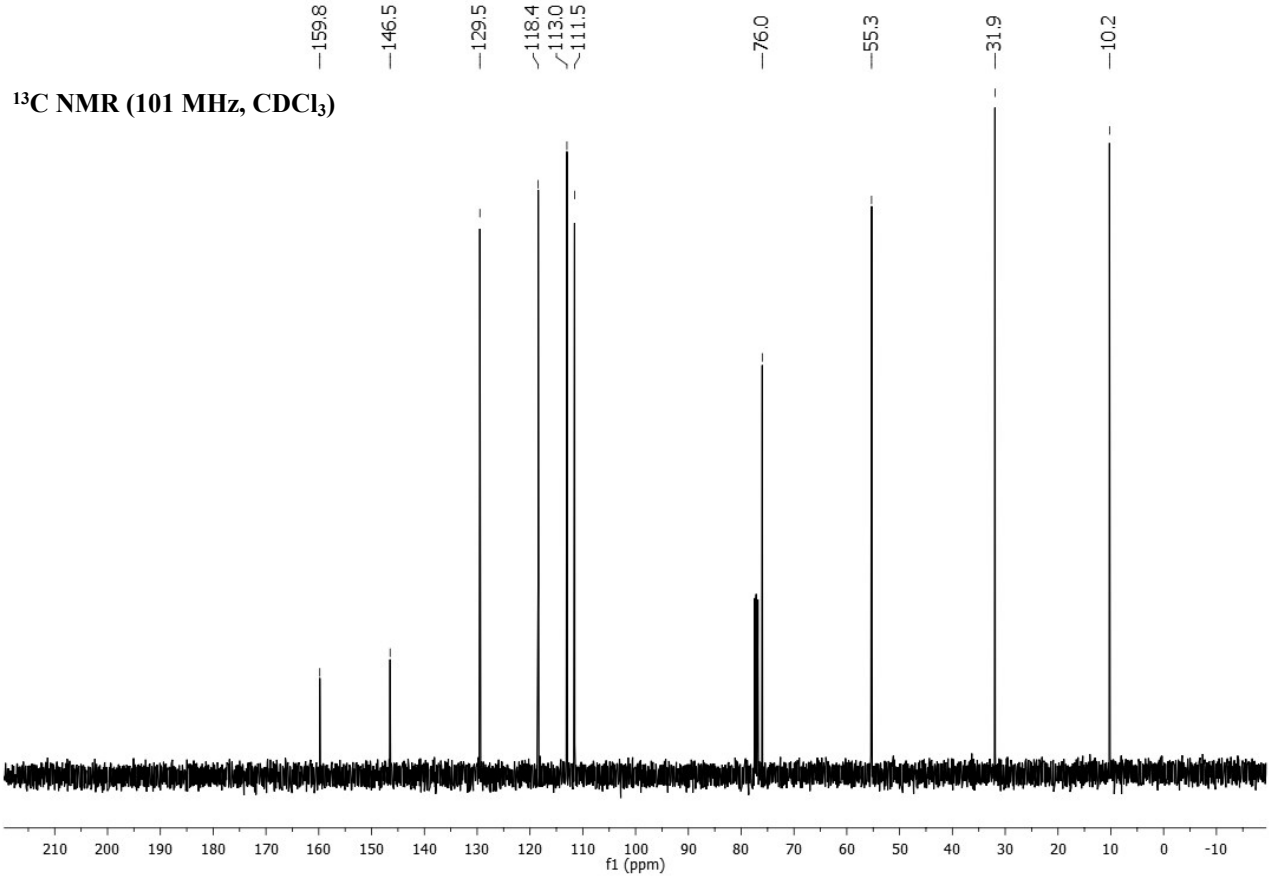


(*S*)-1-(3-methoxyphenyl)propan-1-ol (10h)

^{1}H NMR (400 MHz, $CDCl_3$)

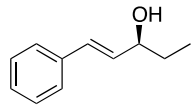


^{13}C NMR (101 MHz, $CDCl_3$)

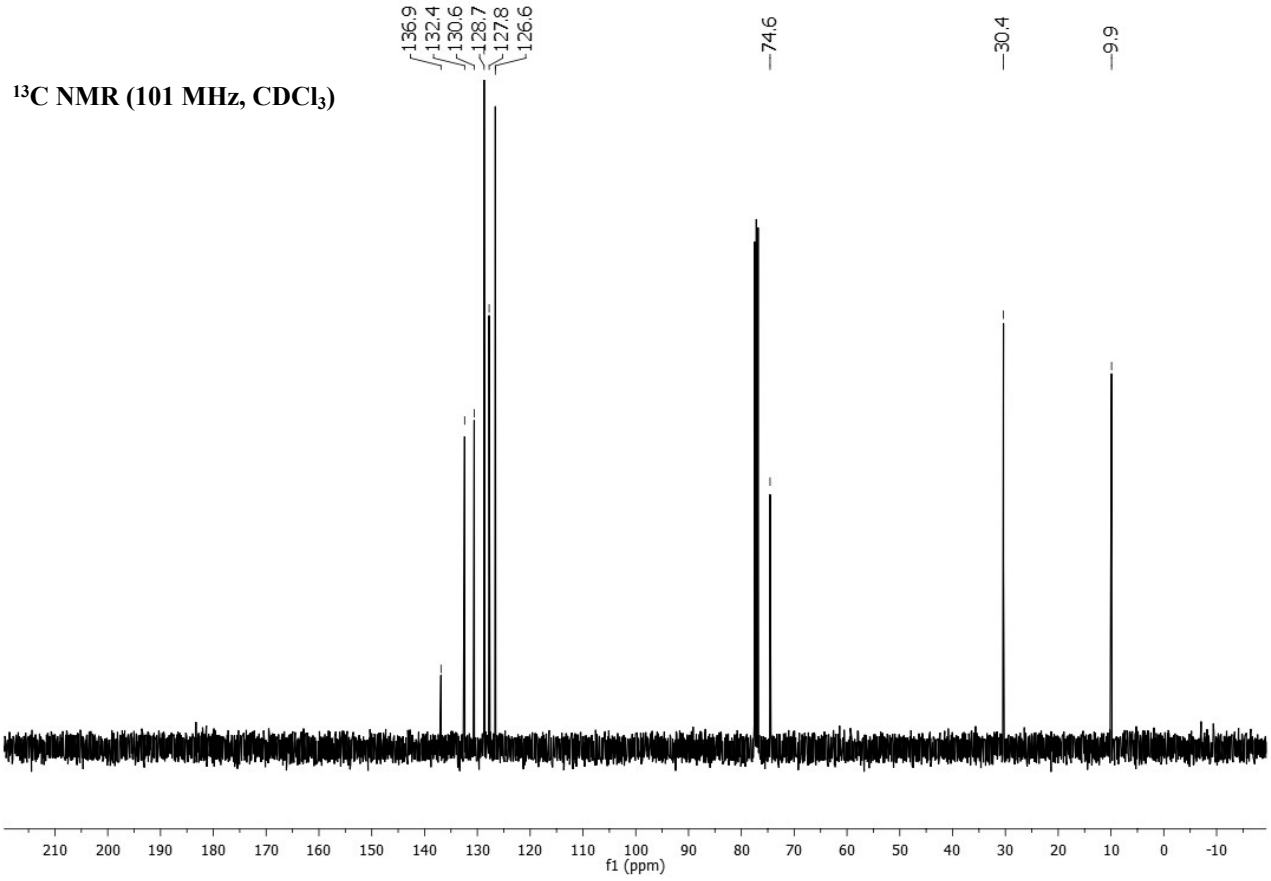


(S,E)-1-phenylpent-1-en-3-ol (10i)

^{1}H NMR (400 MHz, $CDCl_3$)

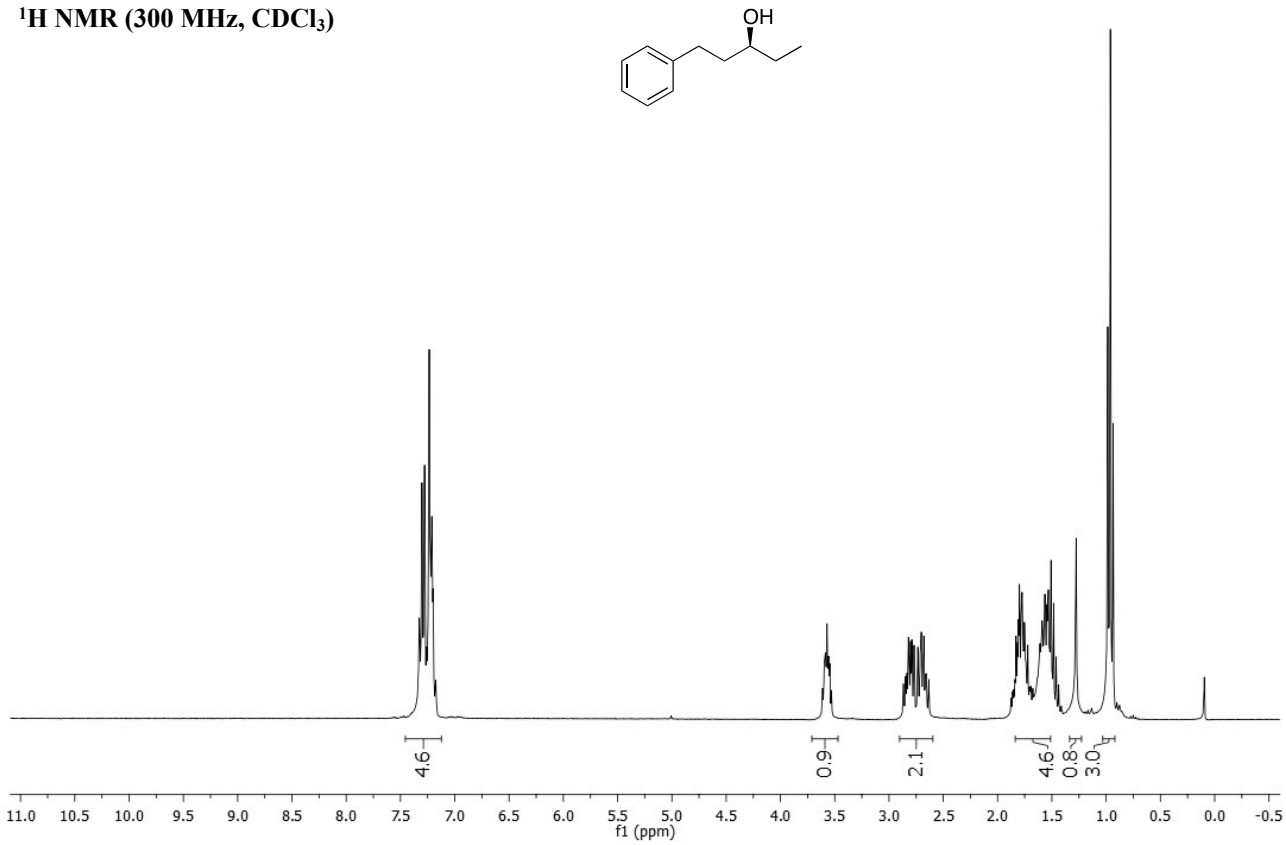


^{13}C NMR (101 MHz, $CDCl_3$)

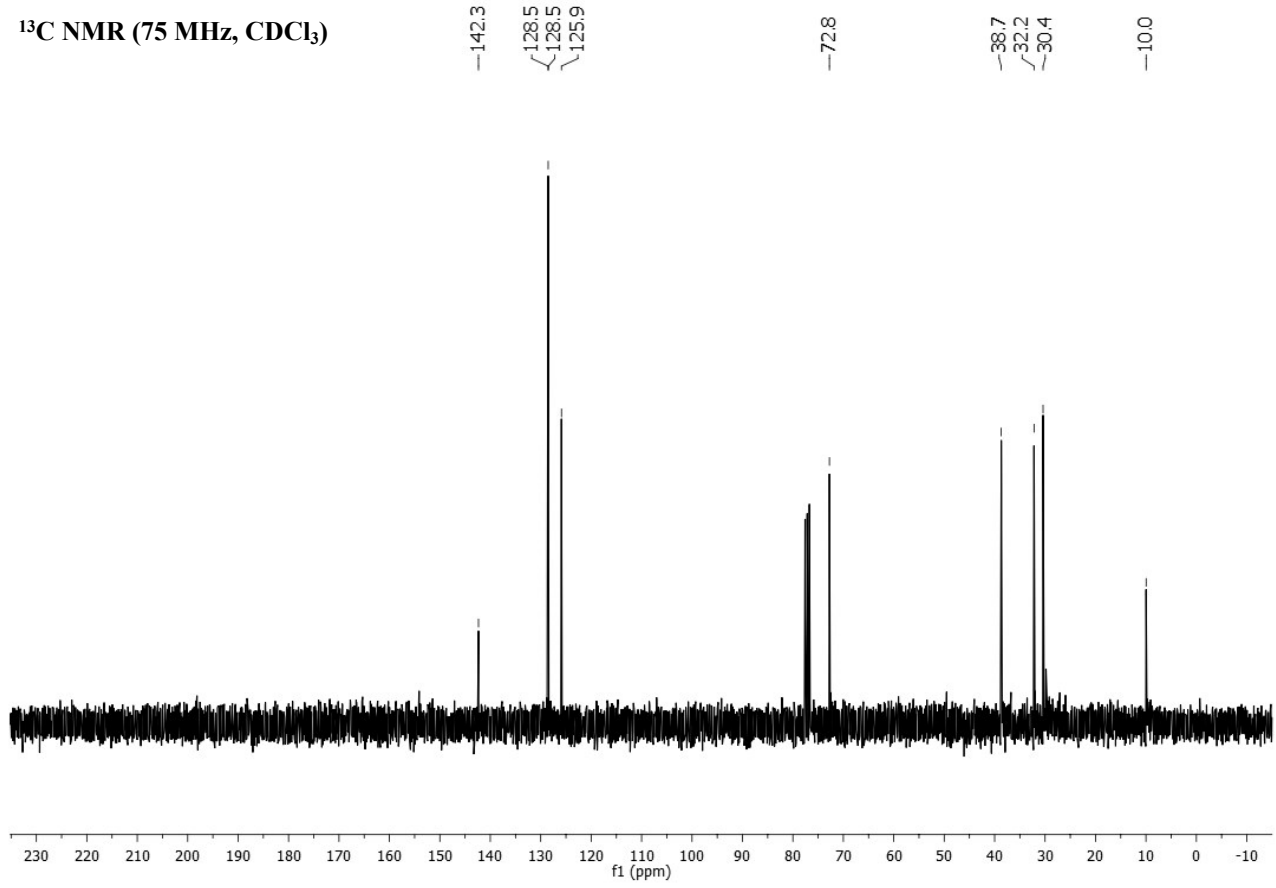


(*S*)-1-phenylpentan-3-ol (10j)

^{1}H NMR (300 MHz, $CDCl_3$)

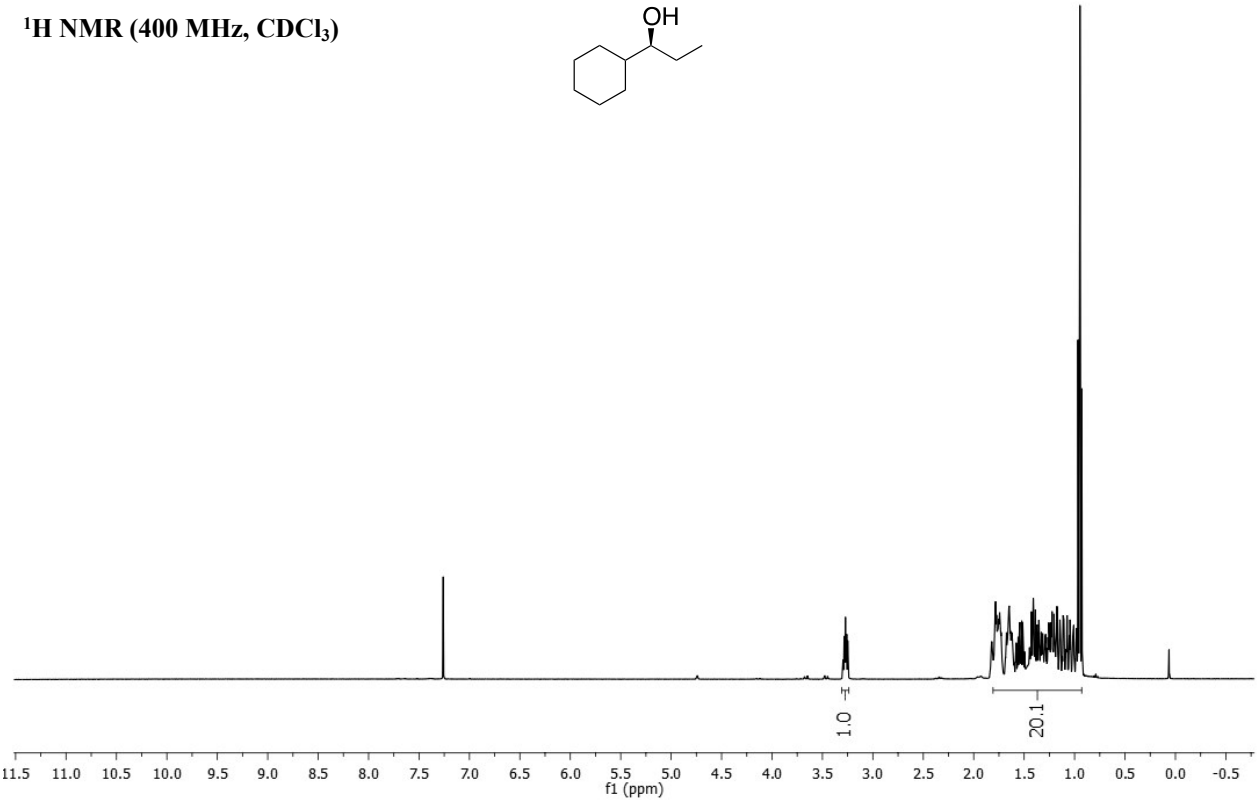


^{13}C NMR (75 MHz, $CDCl_3$)

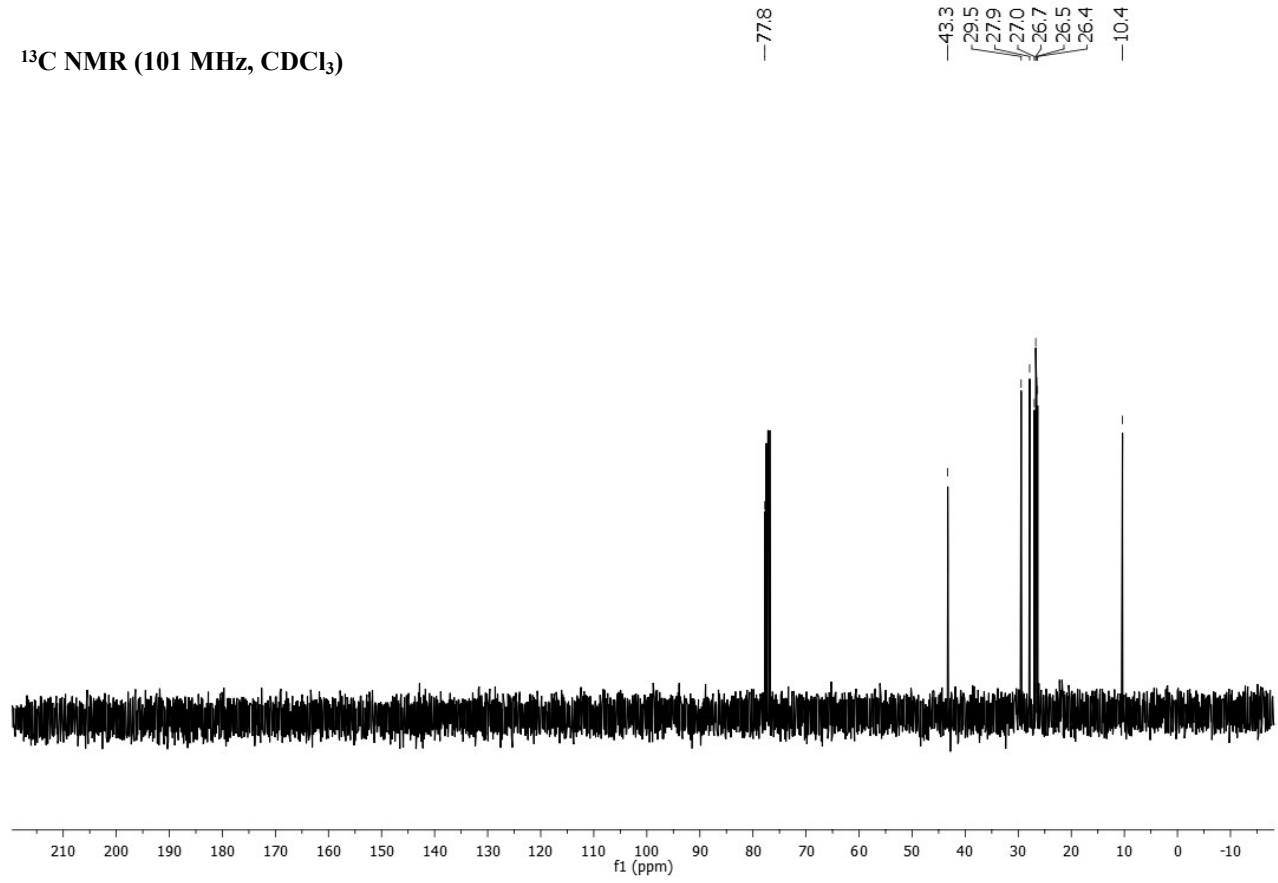


(*S*)-1-cyclohexylpropan-1-ol (10k)

^{1}H NMR (400 MHz, $CDCl_3$)

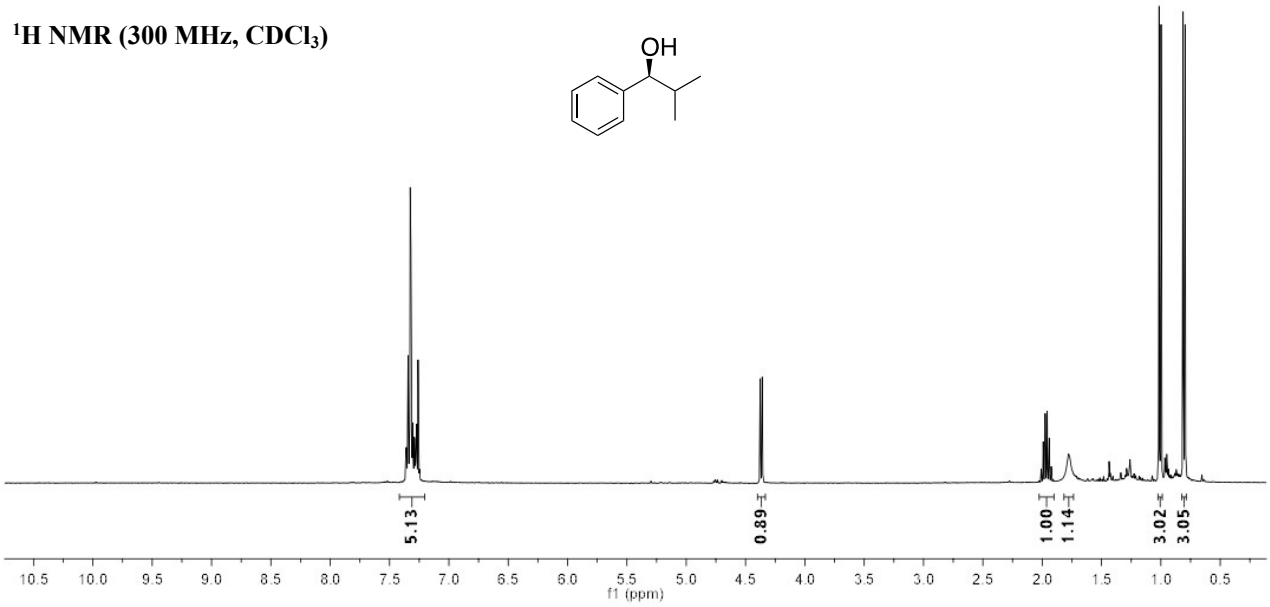


^{13}C NMR (101 MHz, $CDCl_3$)

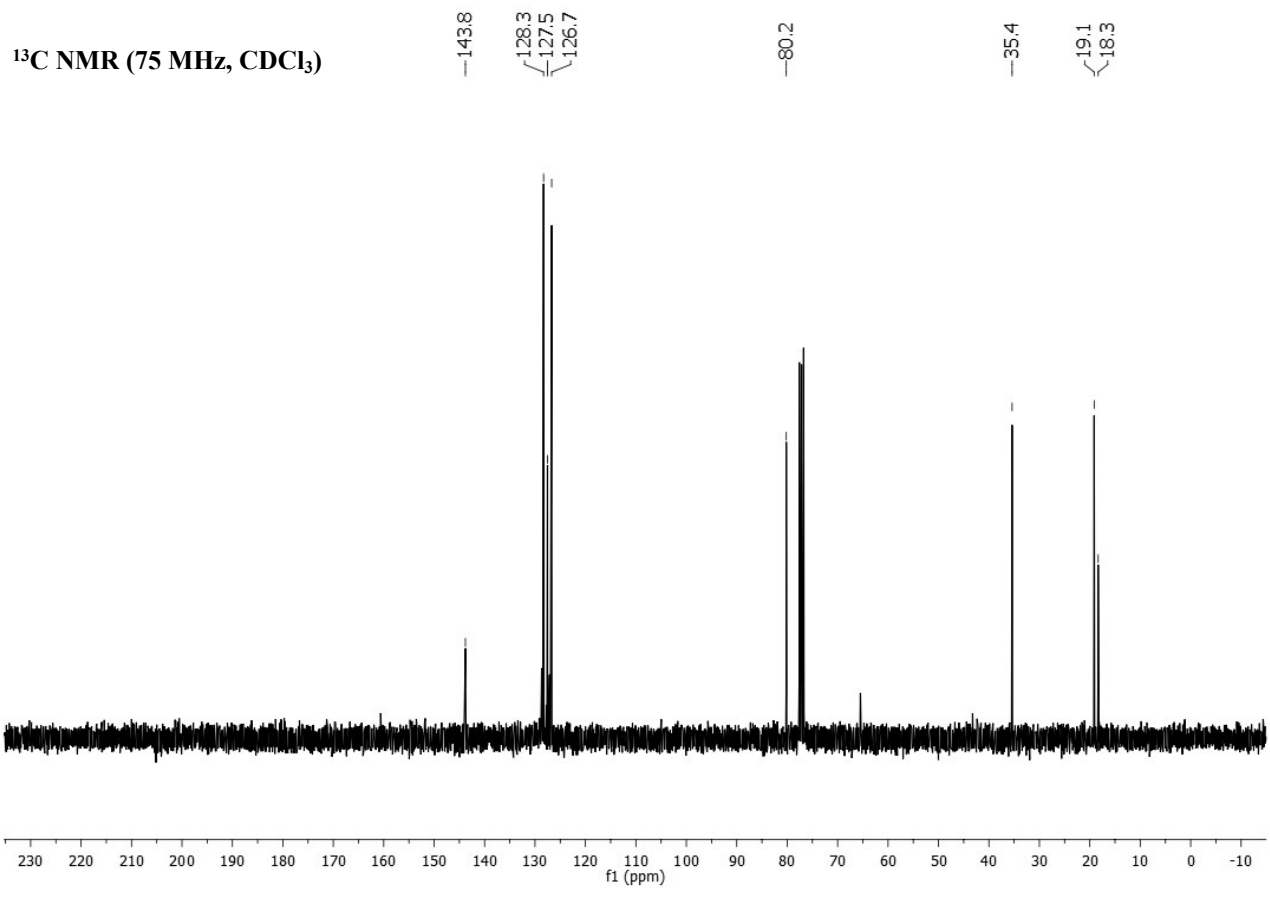


(*S*)-2-methyl-1-phenylpropan-1-ol (11a)

^{1}H NMR (300 MHz, $CDCl_3$)

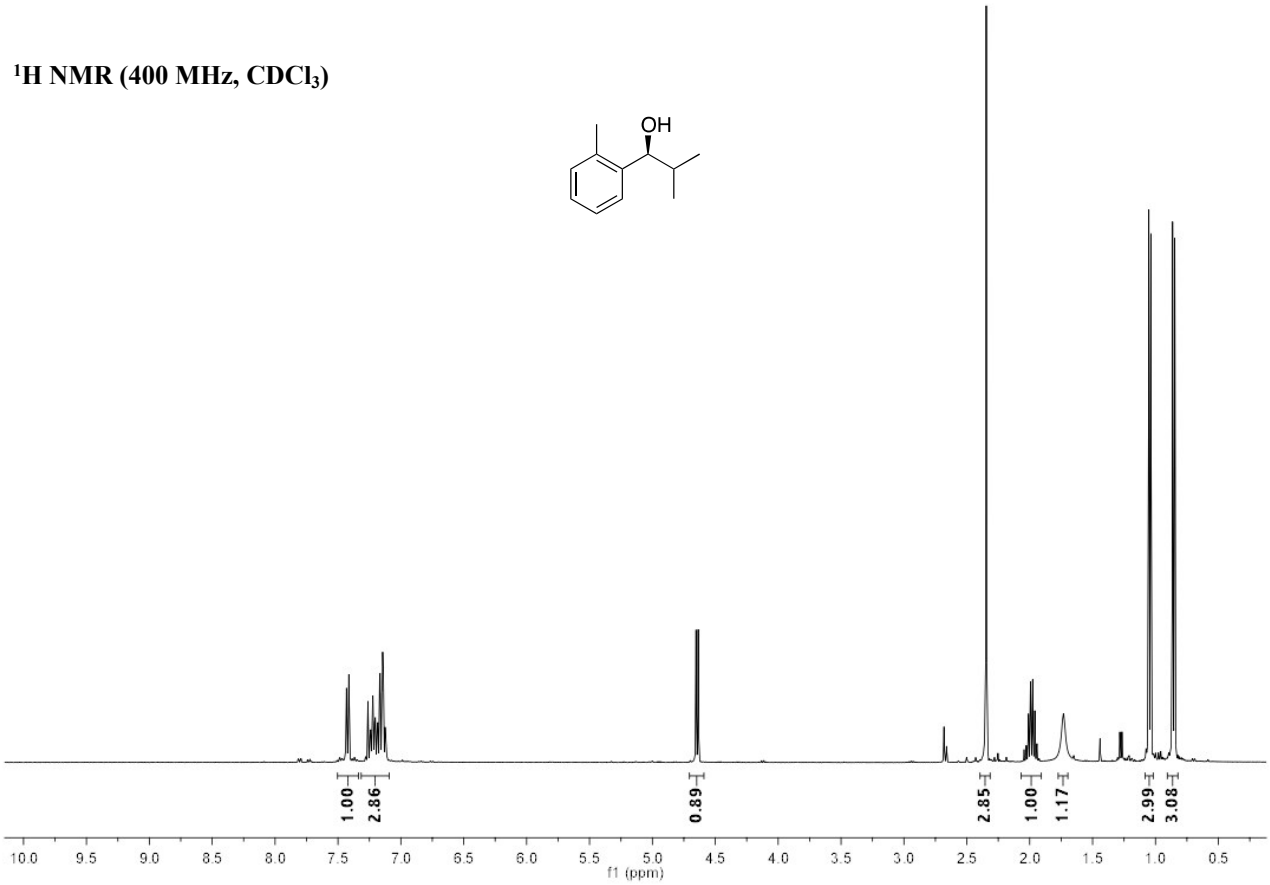


^{13}C NMR (75 MHz, $CDCl_3$)

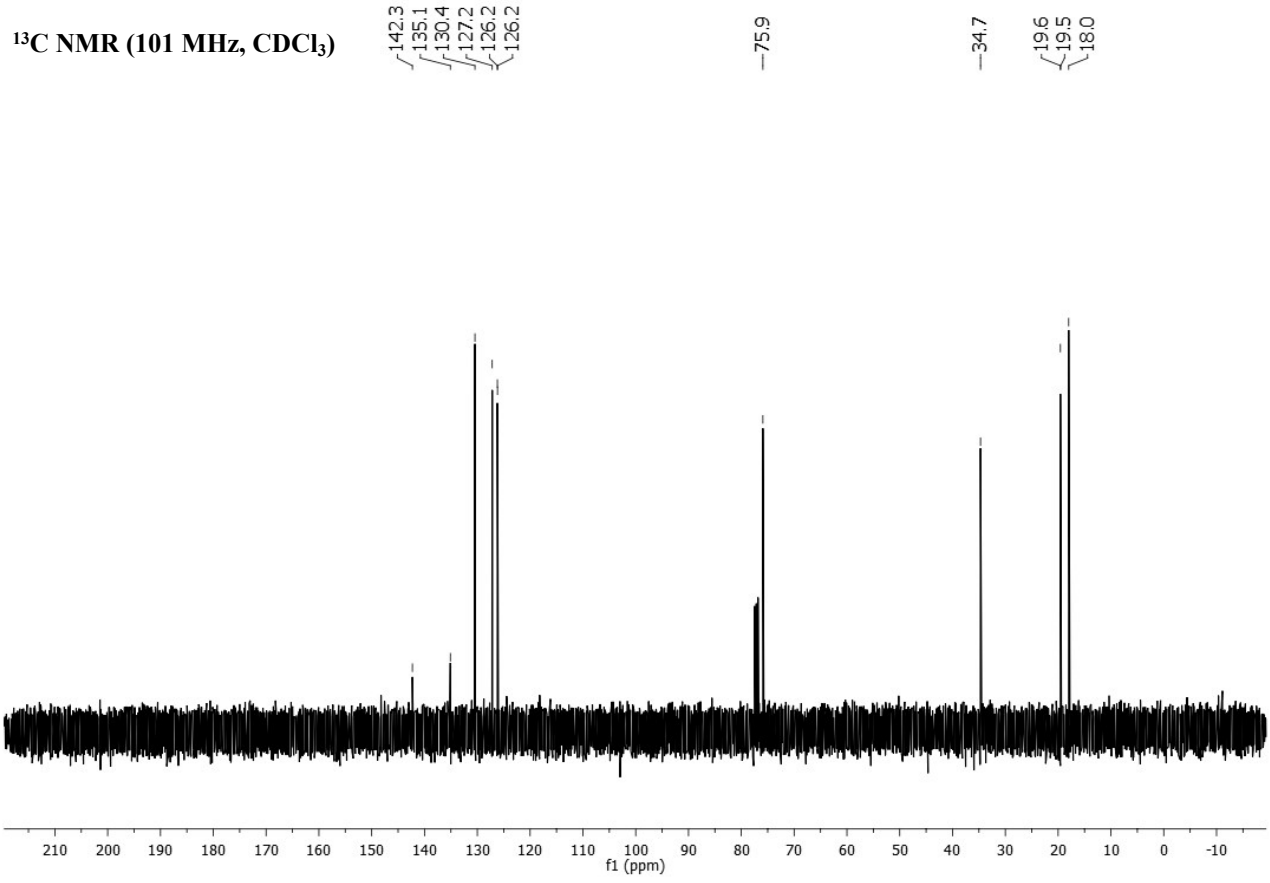


(*S*)-2-methyl-1-(*o*-tolyl)propan-1-ol (11b)

^{1}H NMR (400 MHz, $CDCl_3$)

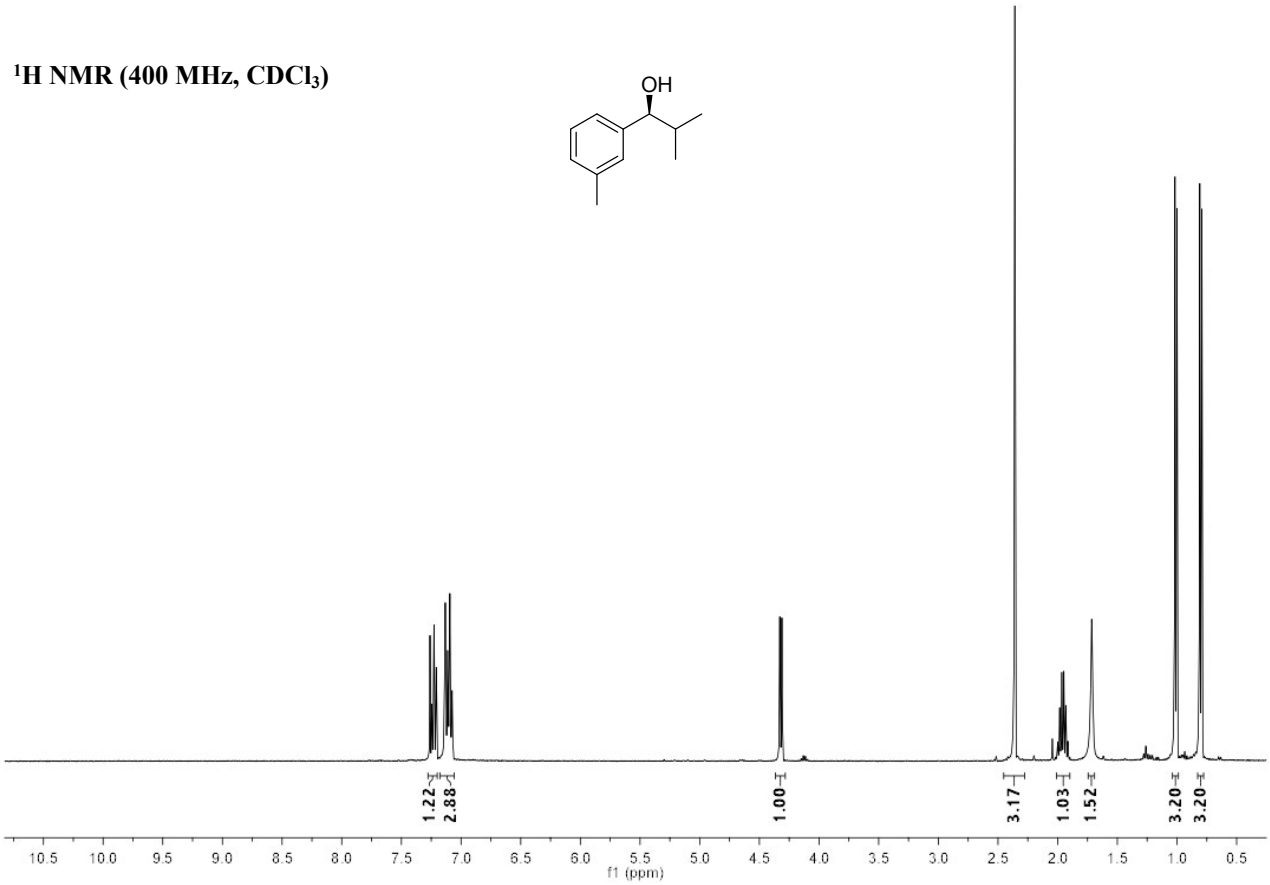


^{13}C NMR (101 MHz, $CDCl_3$)

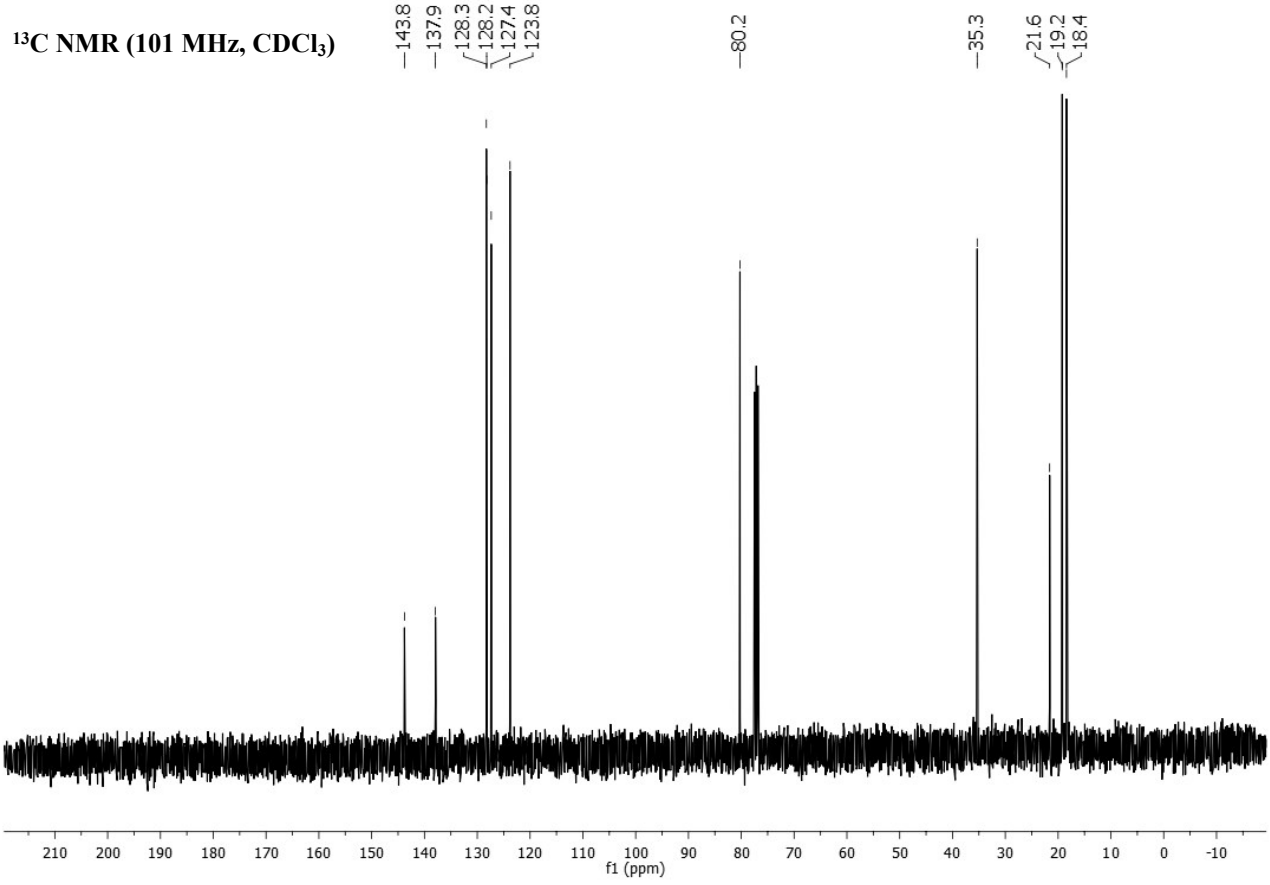


(*S*)-2-methyl-1-(*m*-tolyl)propan-1-ol (11c)

^{1}H NMR (400 MHz, $CDCl_3$)

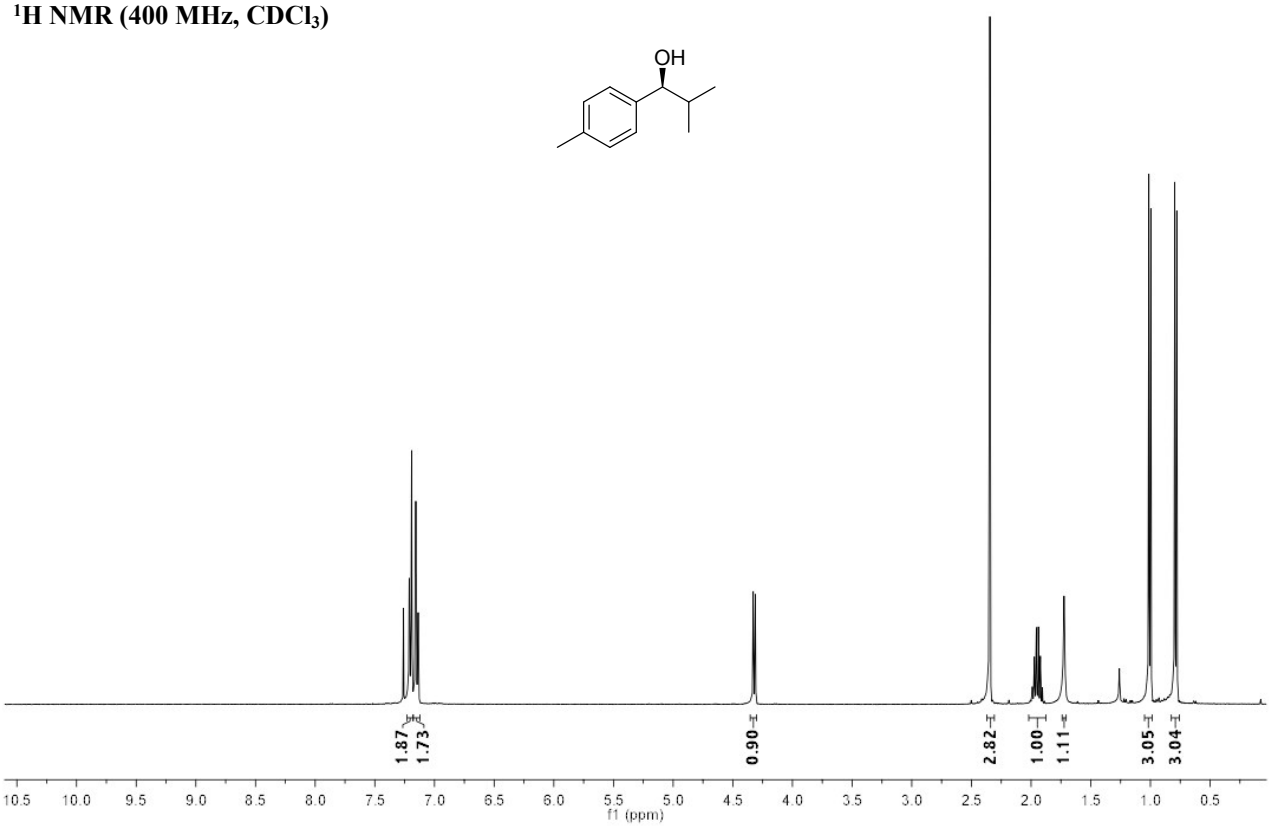


^{13}C NMR (101 MHz, $CDCl_3$)

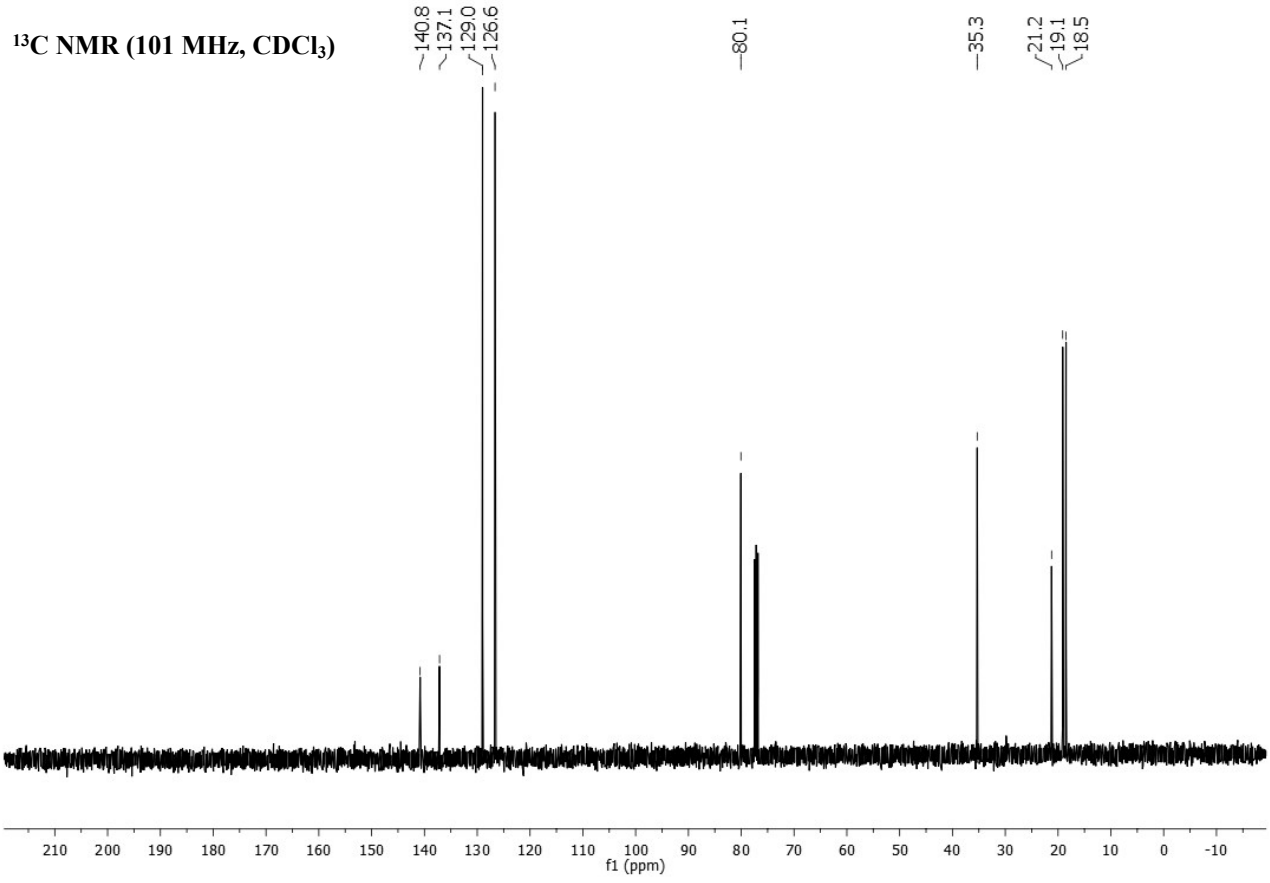


(*S*)-2-methyl-1-(*p*-tolyl)propan-1-ol (11d)

^{1}H NMR (400 MHz, $CDCl_3$)

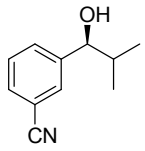


^{13}C NMR (101 MHz, $CDCl_3$)

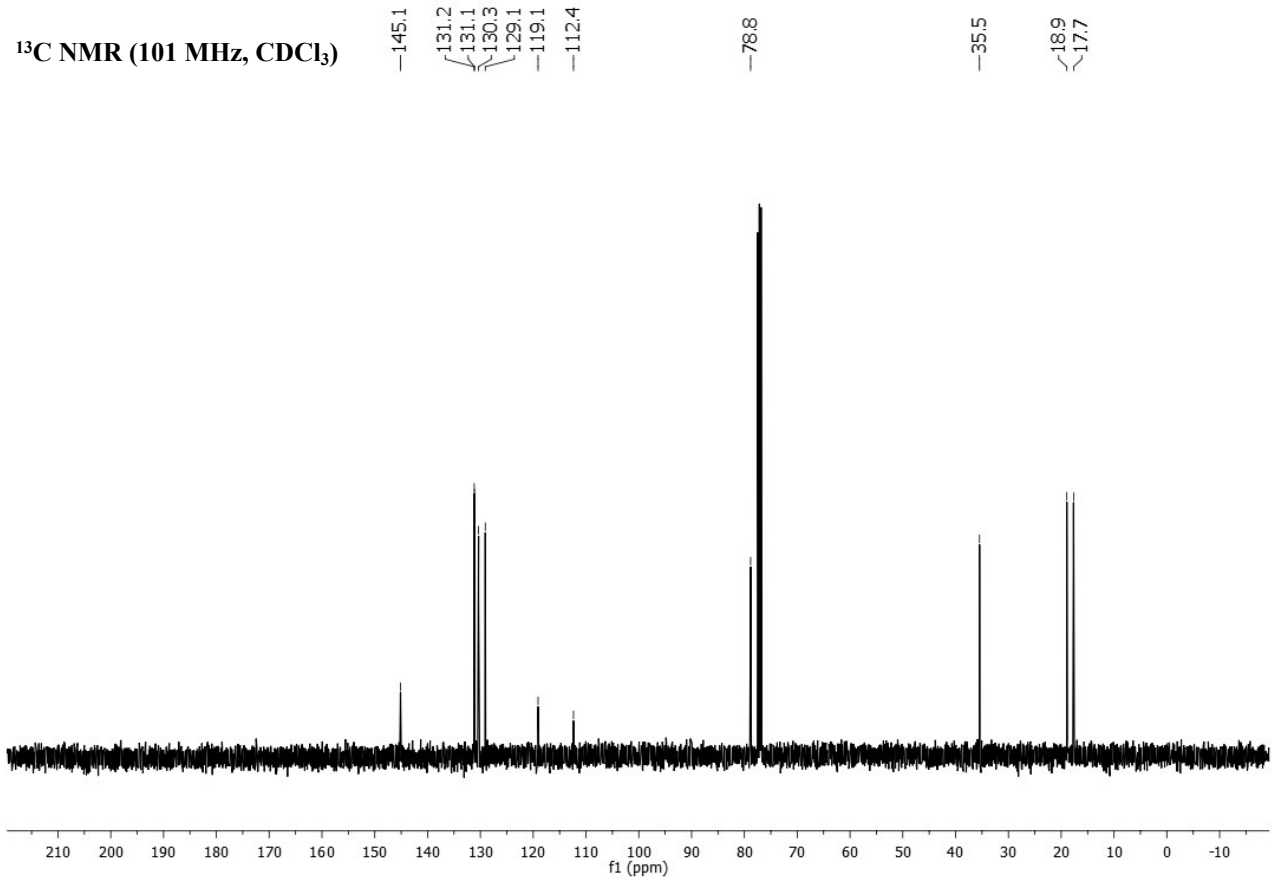


(*S*)-3-(1-hydroxy-2-methylpropyl)benzonitrile (11e)

^{1}H NMR (400 MHz, $CDCl_3$)

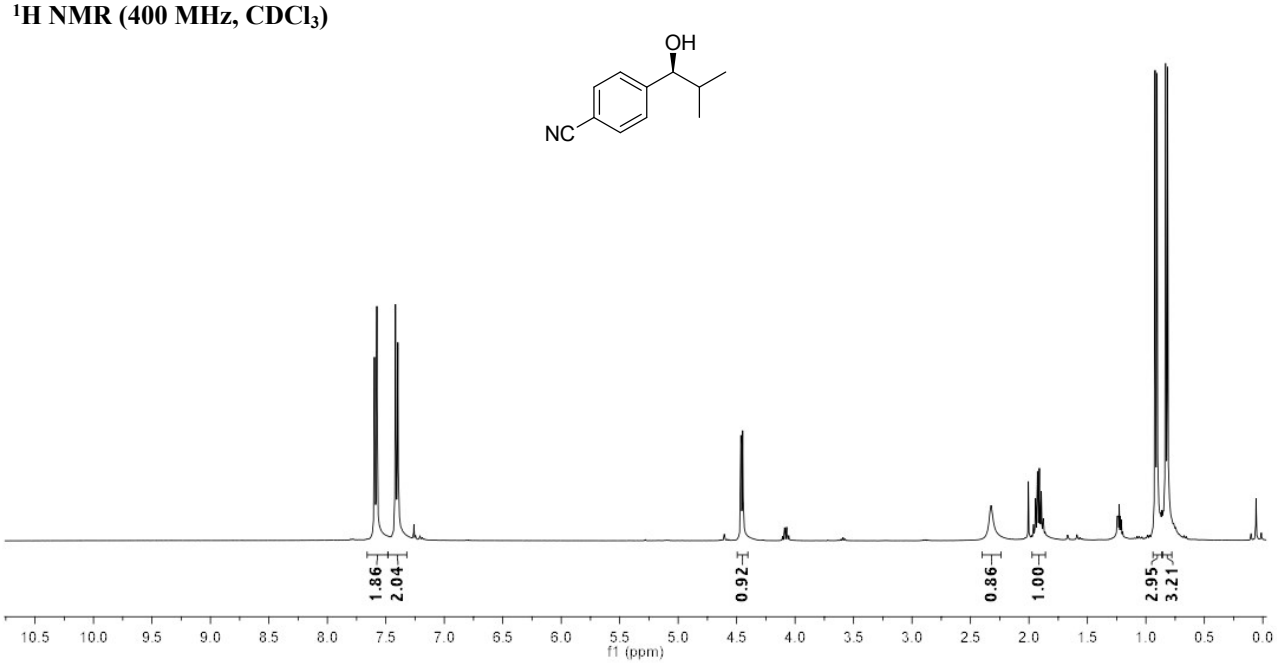


^{13}C NMR (101 MHz, $CDCl_3$)

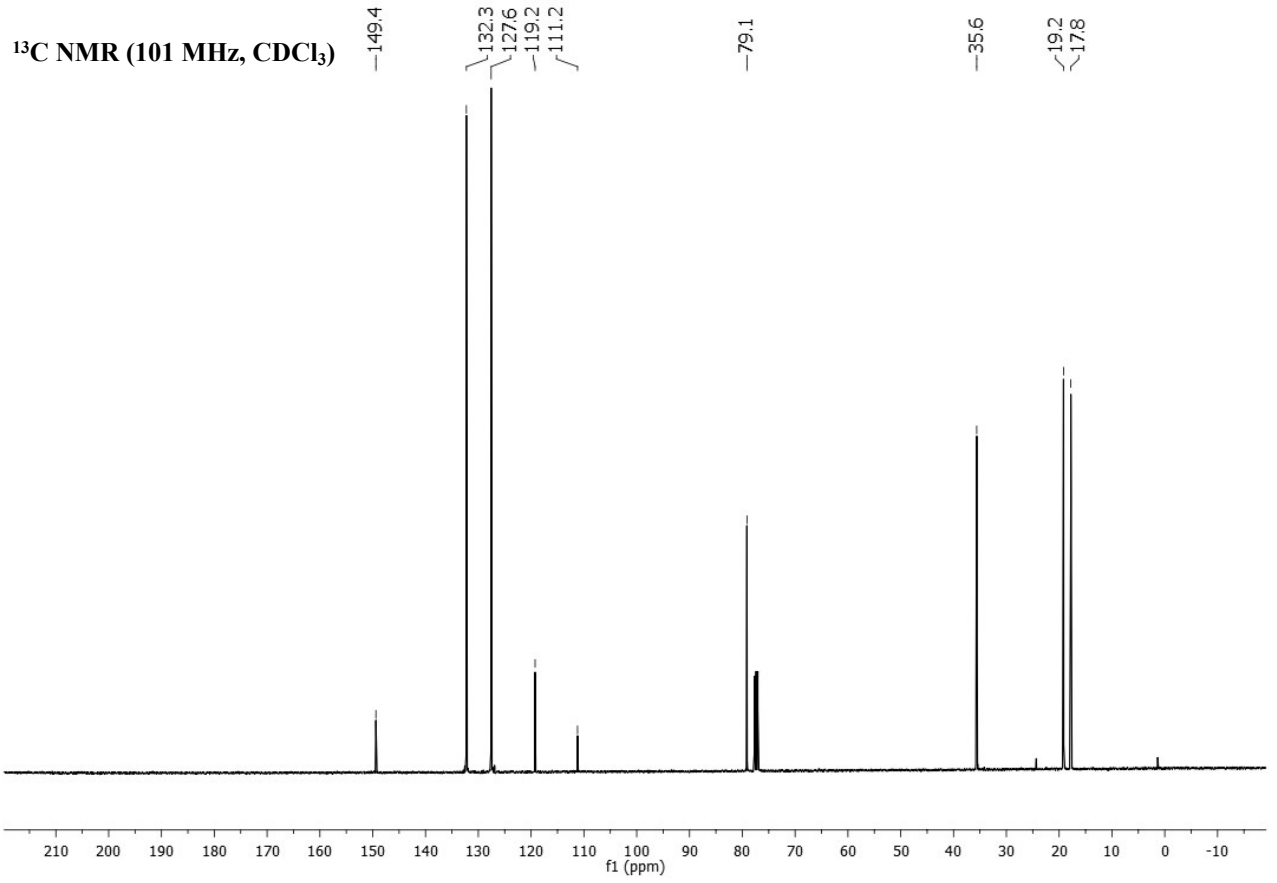


(*S*)-4-(1-hydroxy-2-methylpropyl)benzonitrile (11f):

^{1}H NMR (400 MHz, $CDCl_3$)

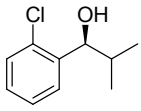


^{13}C NMR (101 MHz, $CDCl_3$)

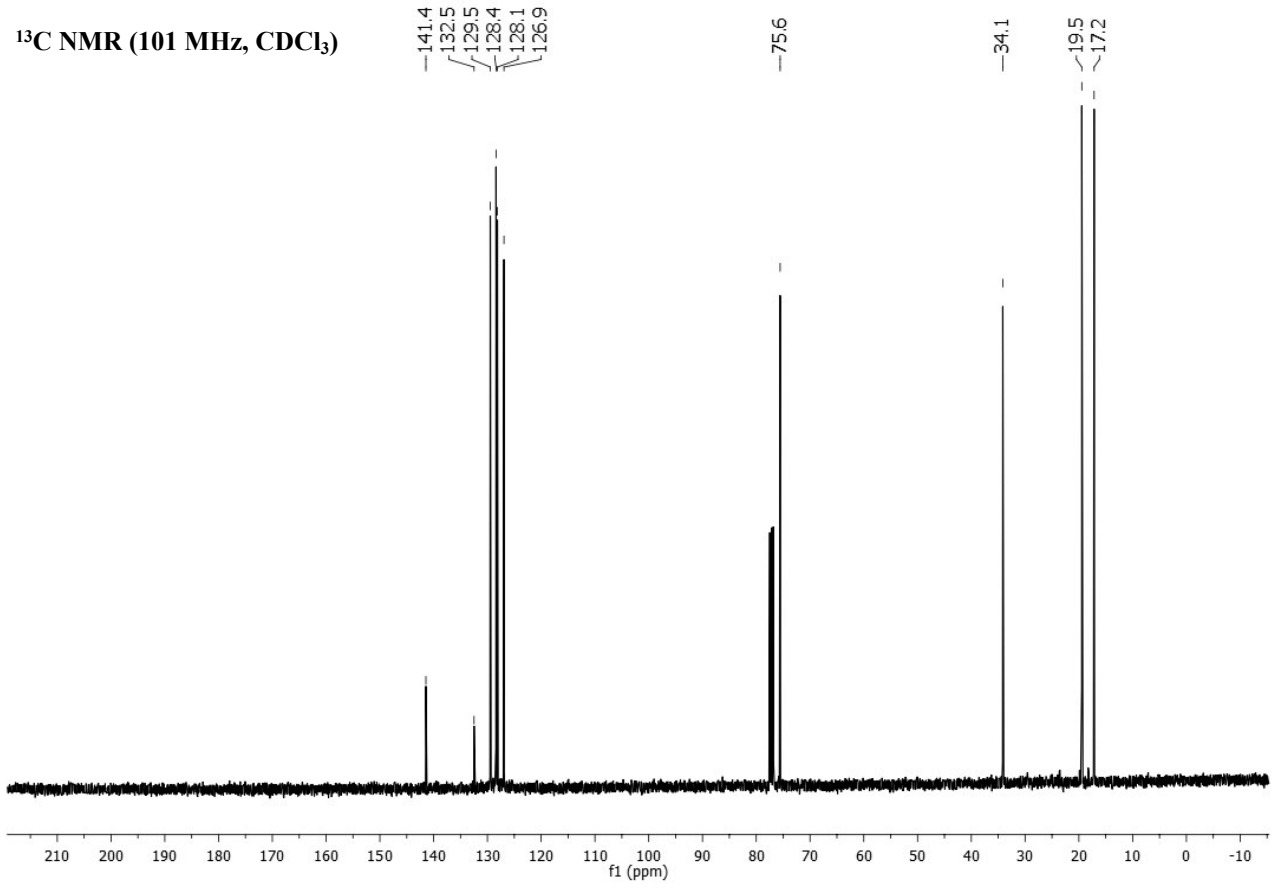


(*S*)-1-(2-chlorophenyl)-2-methylpropan-1-ol (11g)

^{1}H NMR (400 MHz, $CDCl_3$)

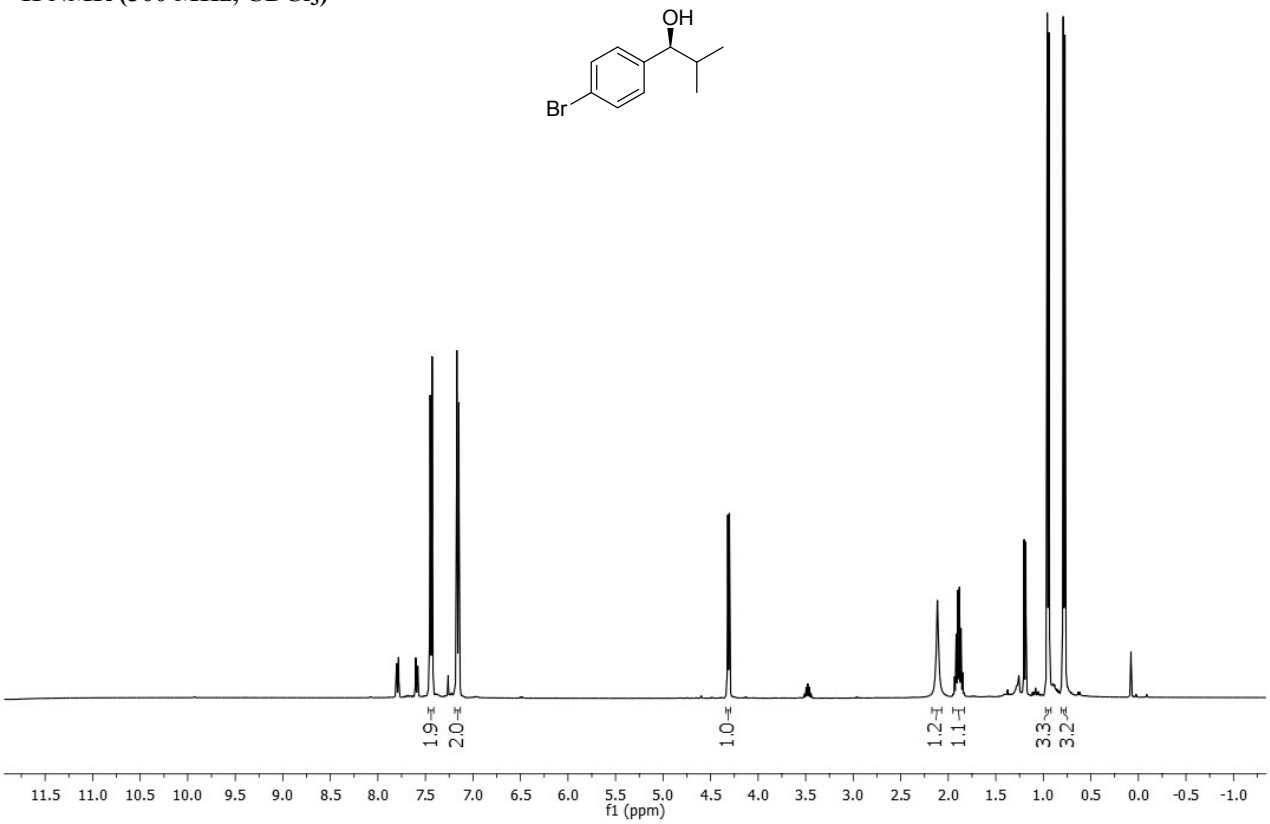


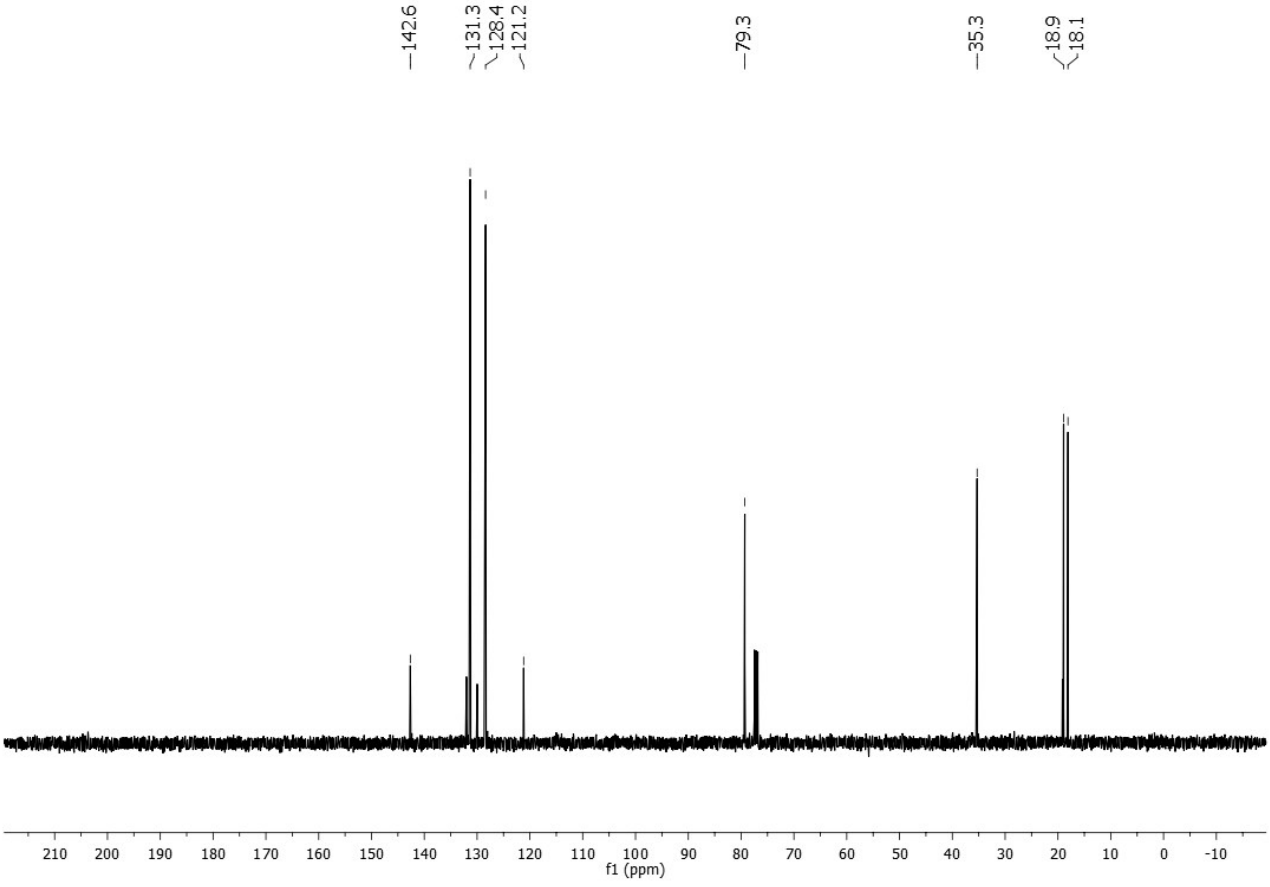
^{13}C NMR (101 MHz, $CDCl_3$)



(*S*)-1-(4-bromophenyl)-2-methylpropan-1-ol (11h)

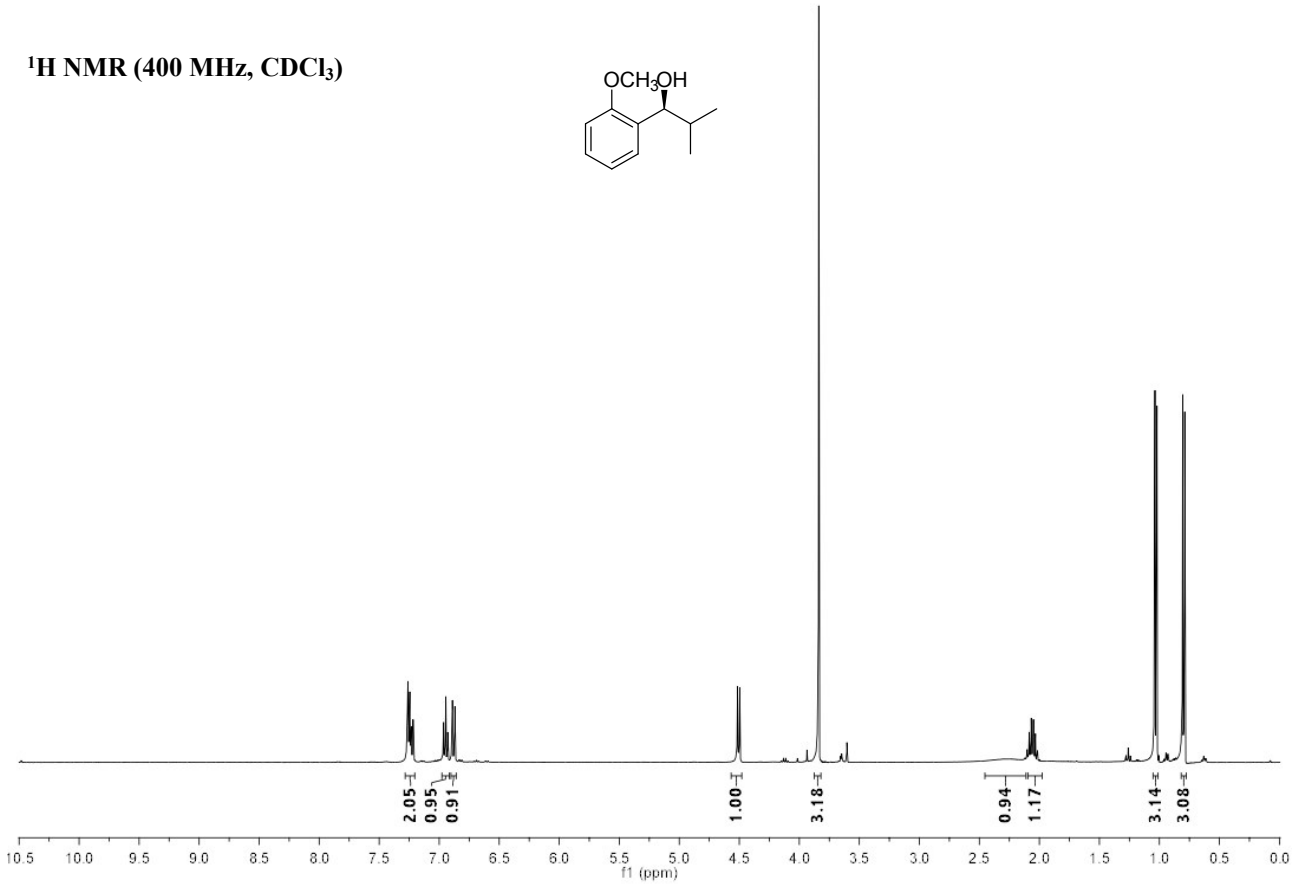
^{1}H NMR (300 MHz, $CDCl_3$)



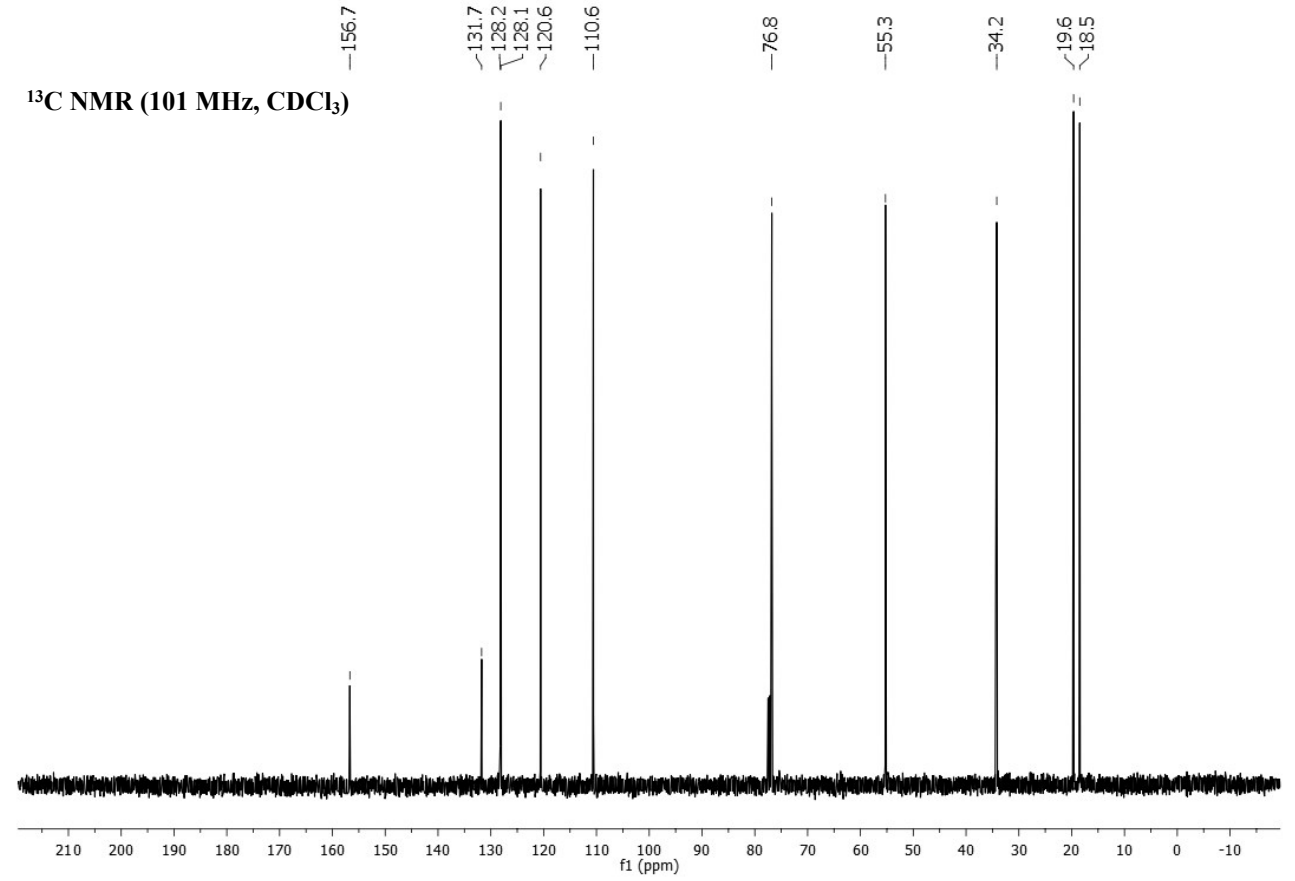


(*S*)-1-(2-methoxyphenyl)-2-methylpropan-1-ol (11i)

^{1}H NMR (400 MHz, $CDCl_3$)

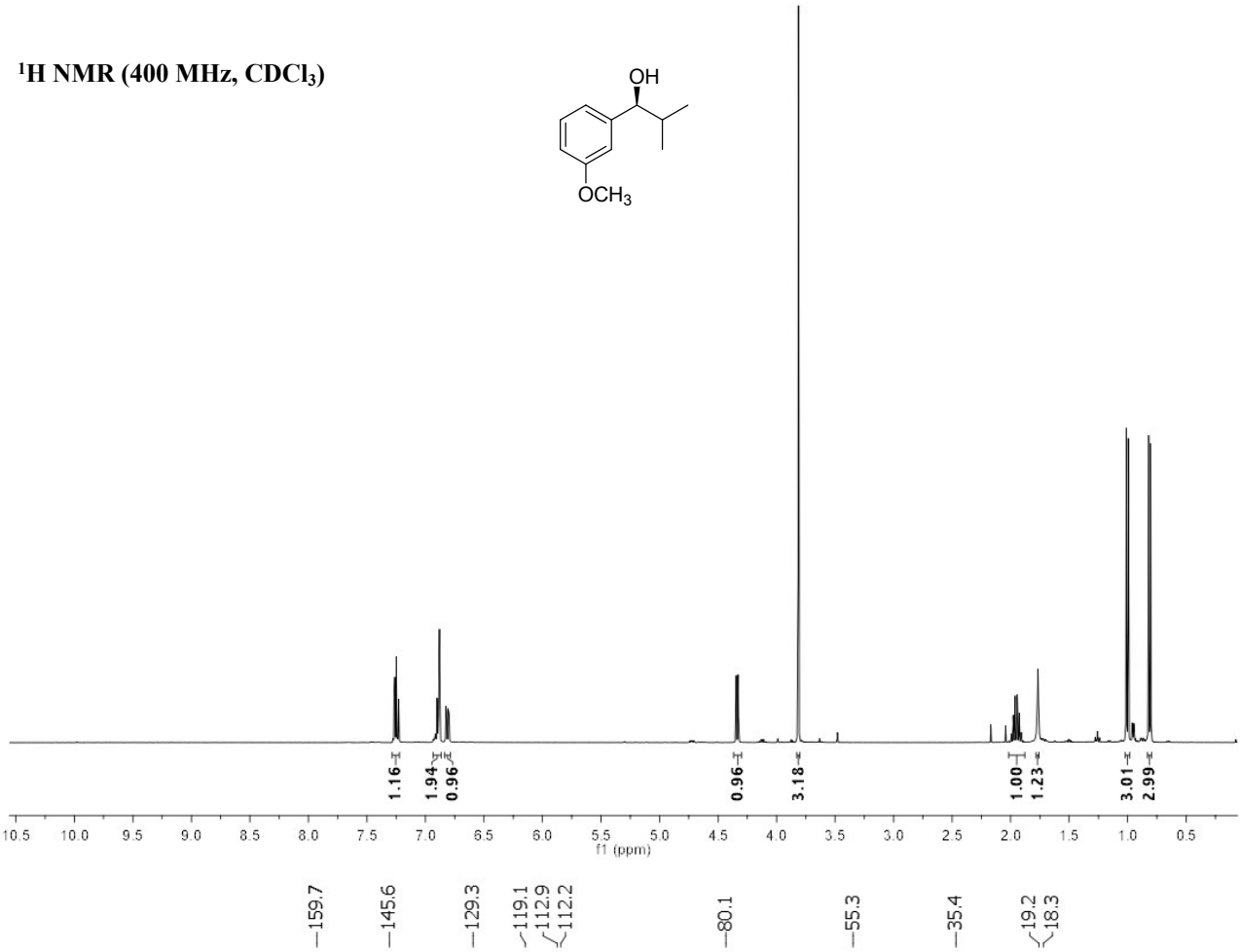


^{13}C NMR (101 MHz, $CDCl_3$)

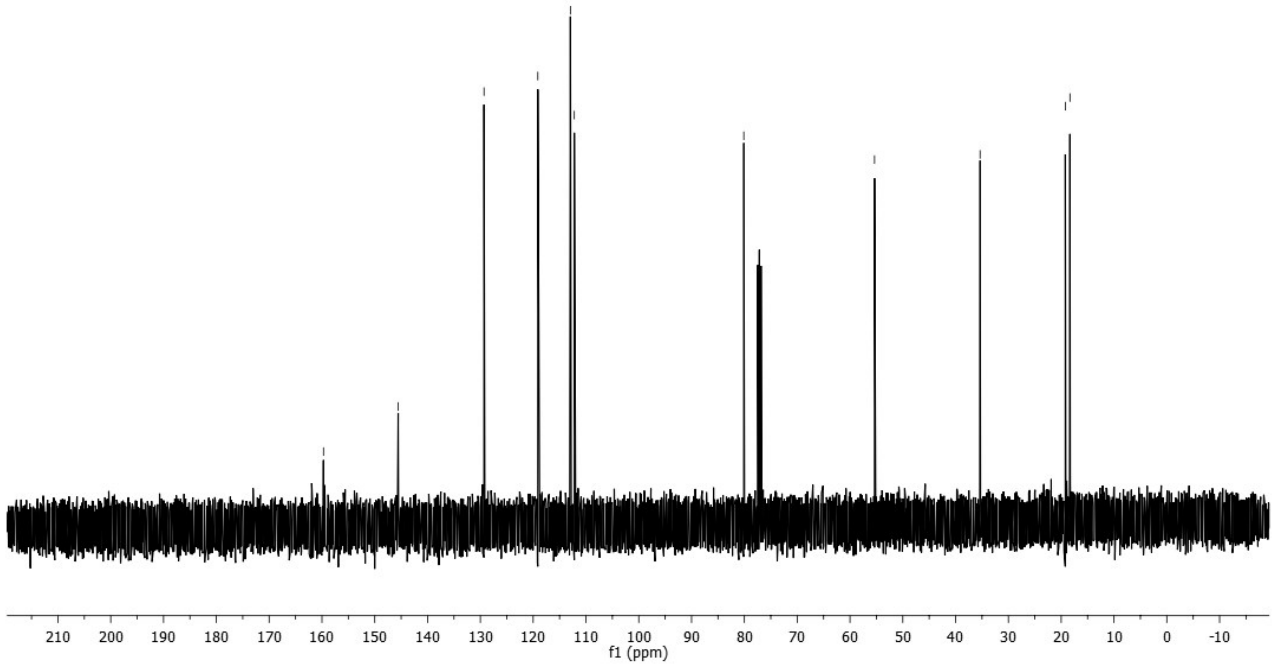


(*S*)-1-(3-methoxyphenyl)-2-methylpropan-1-ol (11j)

^{1}H NMR (400 MHz, $CDCl_3$)

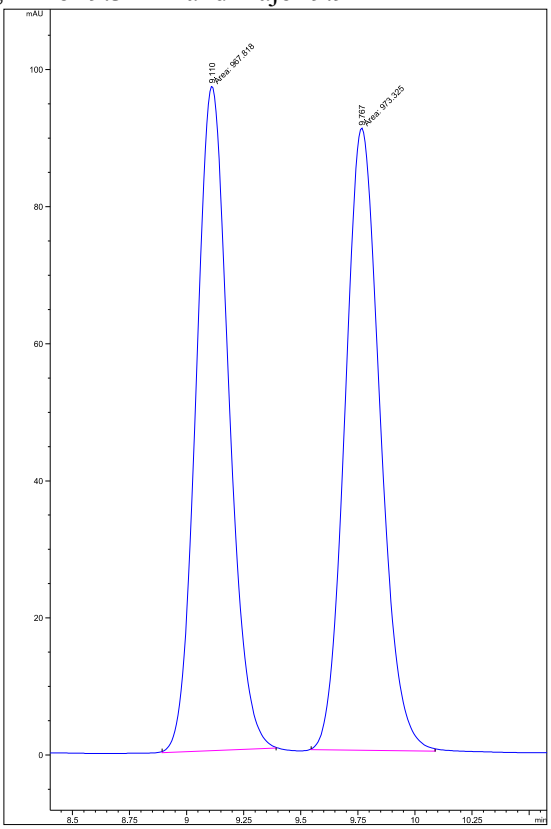


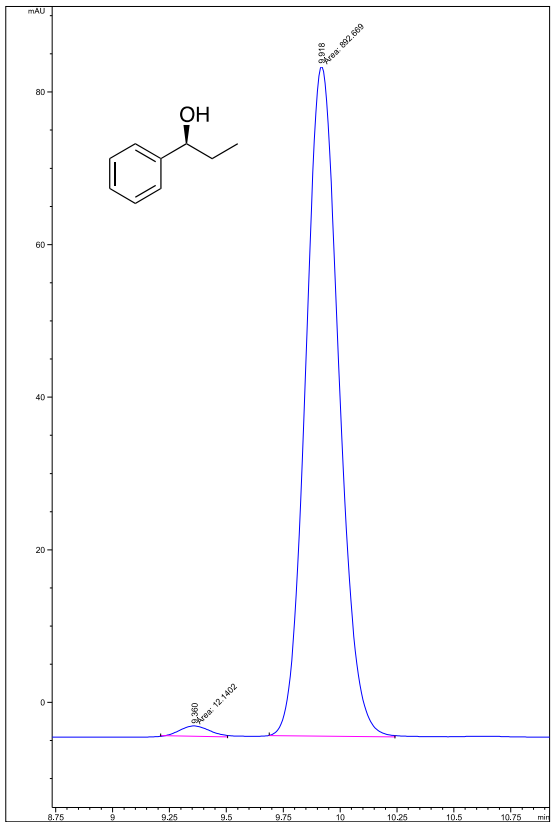
^{13}C NMR (101 MHz, $CDCl_3$)



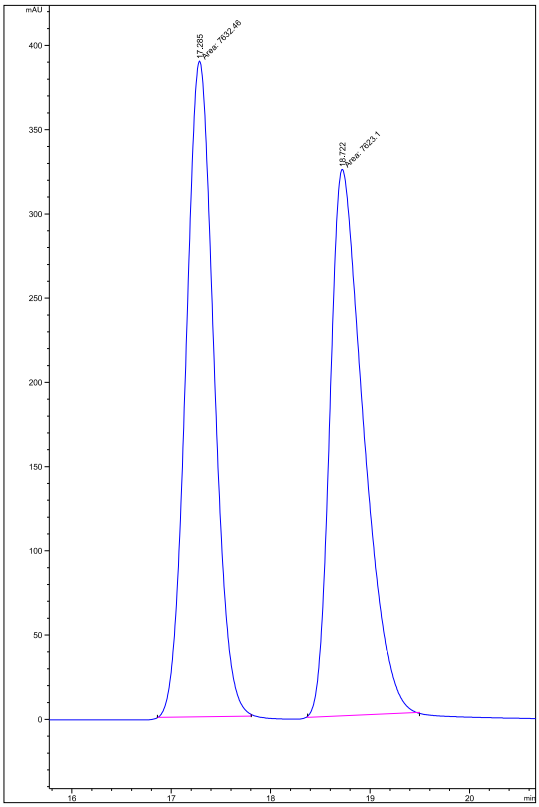
Chiral HPLC chromatograms of dialkylzinc addition products

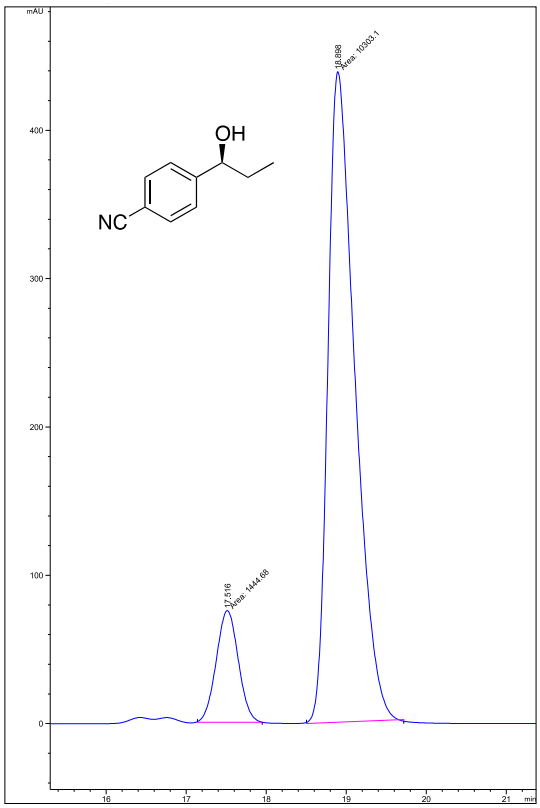
(*S*)-1-phenylpropan-1-ol (10a): *ee* = 97.4%. HPLC: Chiralpak IB, hexane/i-PrOH = 98:2, 1 mL/min, 258 nm, minor 9.3 min and major 9.9 min



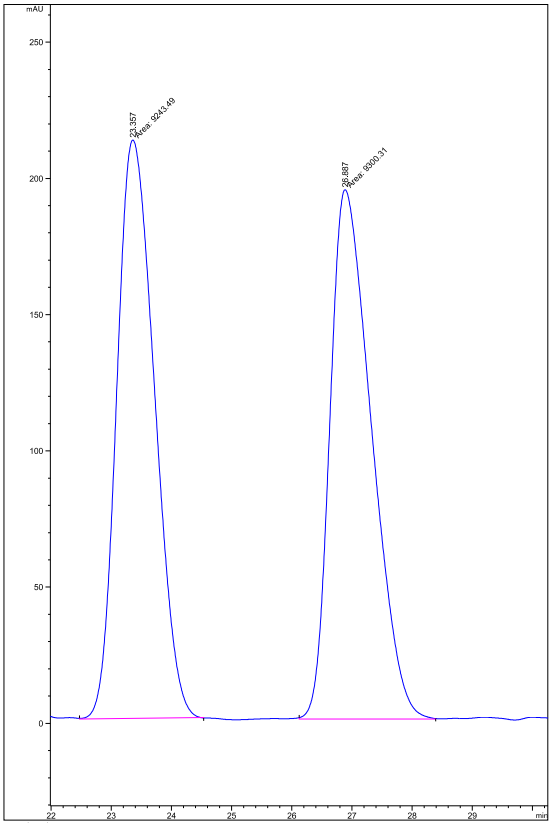


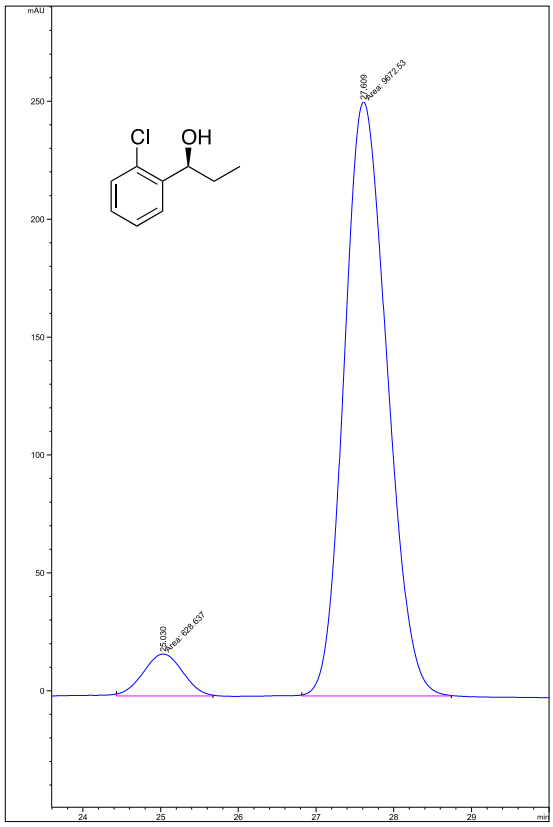
(*S*)-4-(1-hydroxypropyl)benzonitrile (10b): *ee* = 75.4%. HPLC: Chiralpak IA, hexane/i-PrOH = 95:5, 0.8 mL/min, 220 nm, minor 17.5 min and major 18.9 min.



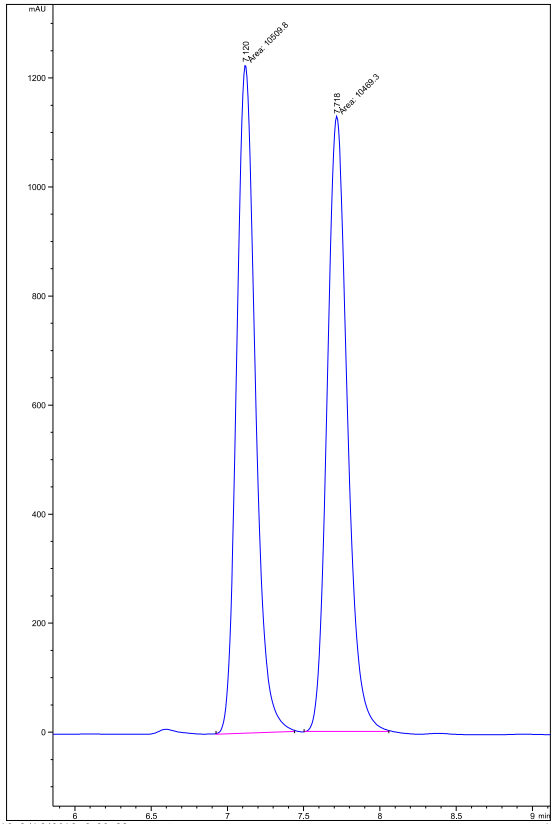


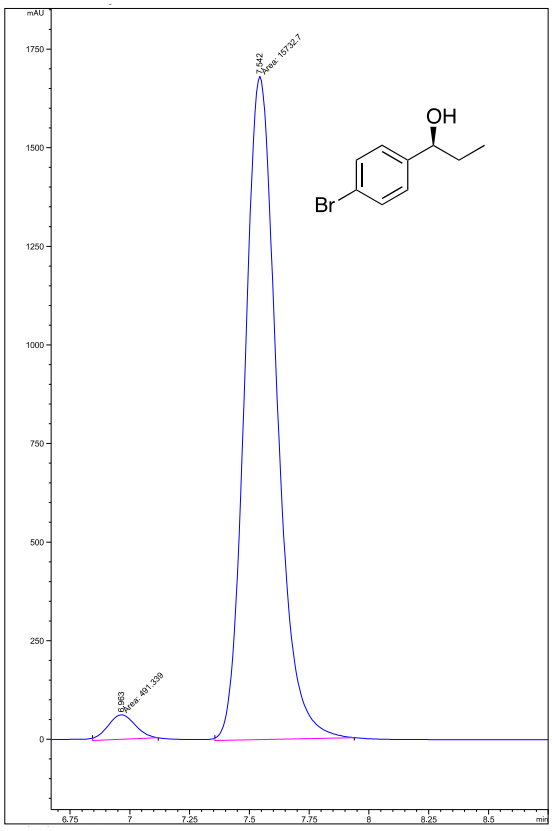
(*S*)-1-(2-chlorophenyl)propan-1-ol (10c): *ee* = 87.8%. HPLC: Chiralpak IA, hexane/i-PrOH = 99.5:0.5, 1 mL/min, 225 nm, minor 25.0 min and major 27.6 min



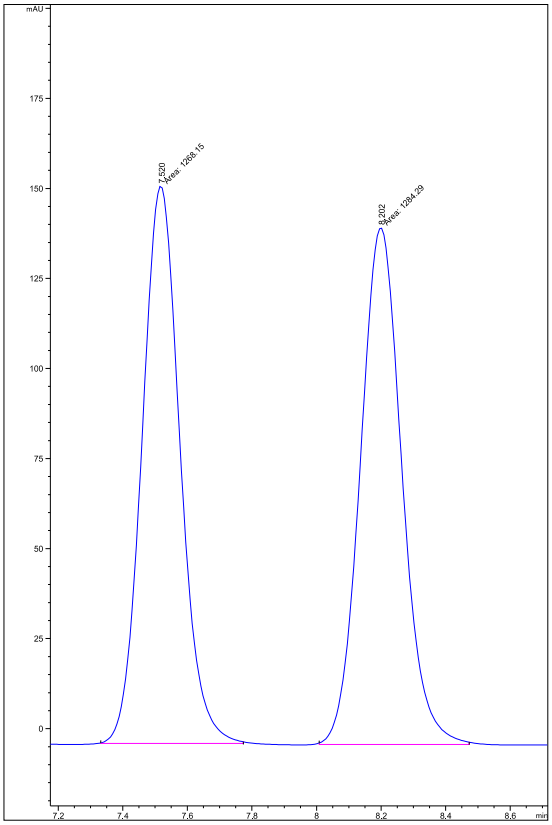


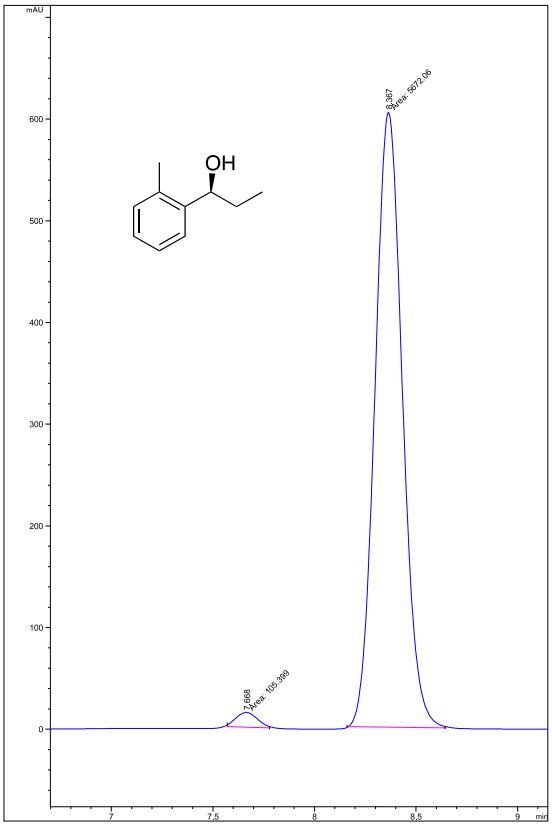
(*S*)-1-(4-bromophenyl)propan-1-ol (10d): *ee* = 94%. HPLC: Chiralpak IC, hexane/i-PrOH = 99:1, 1.5 mL/min, 220 nm, minor 6.9 min and major 7.5 min.



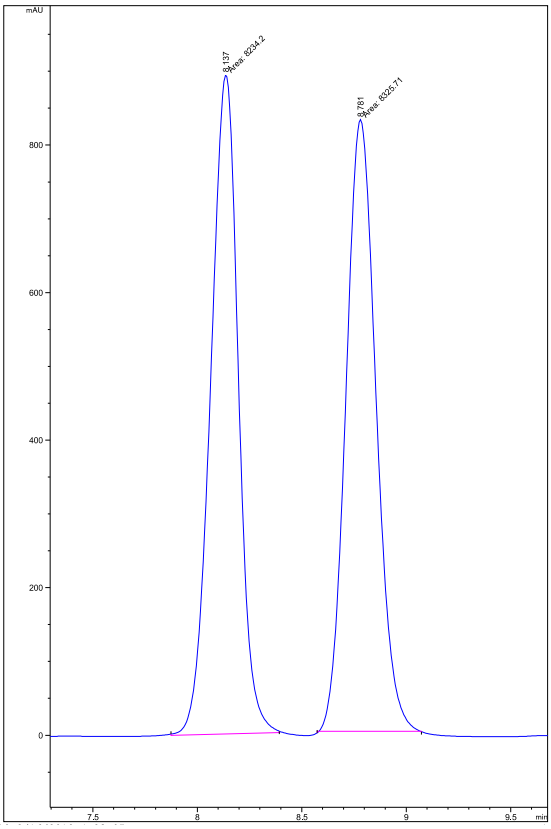


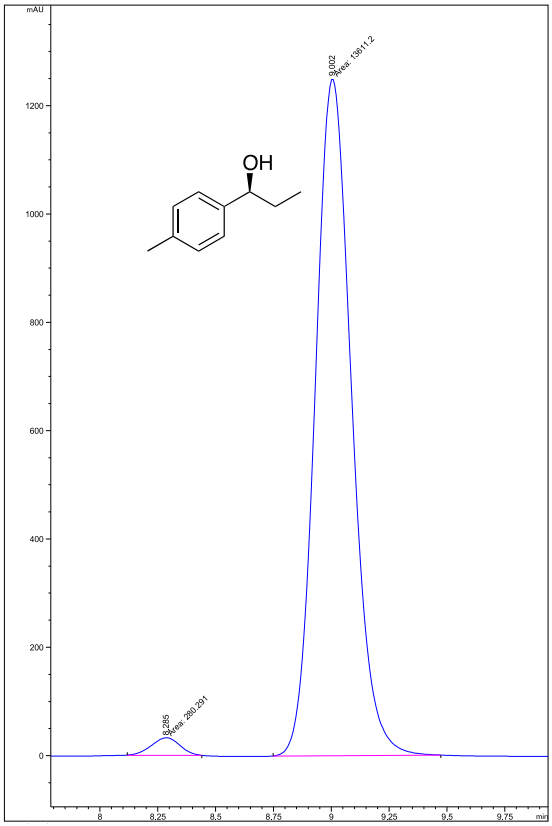
(*S*)-1-(*o*-tolyl)propan-1-ol (10e): *ee* = 96.4%. HPLC: Chiralpak IA, hexane/i-PrOH = 95:5, 0.8 mL/min, 220 nm, minor 7.6 min and major 8.3 min.



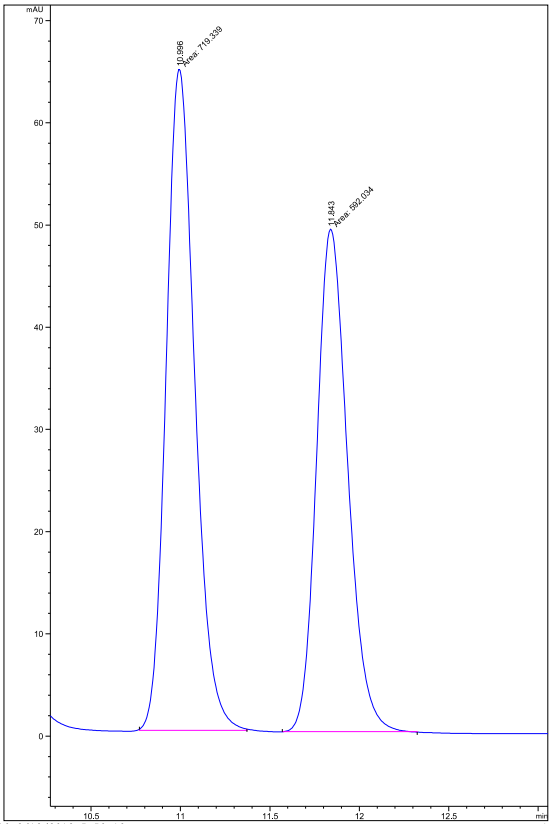


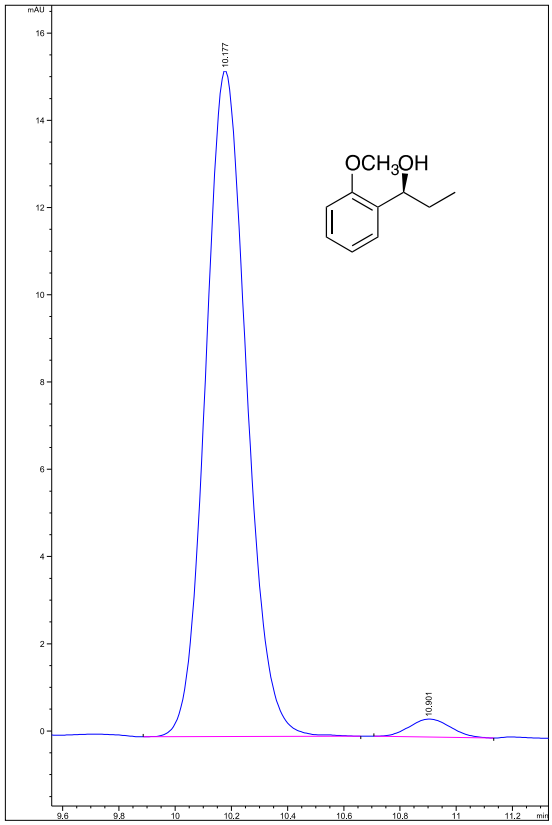
(*S*)-1-(*p*-tolyl)propan-1-ol (10f): *ee* = 96%. HPLC: Chiralpak IA, hexane/i-PrOH = 98:2, 1 mL/min, 220 nm, minor 8.3 min and major 9 min.



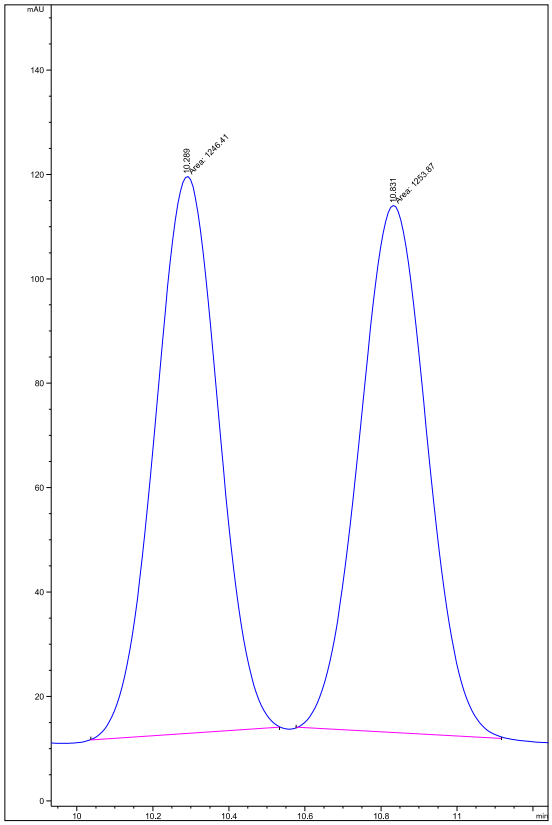


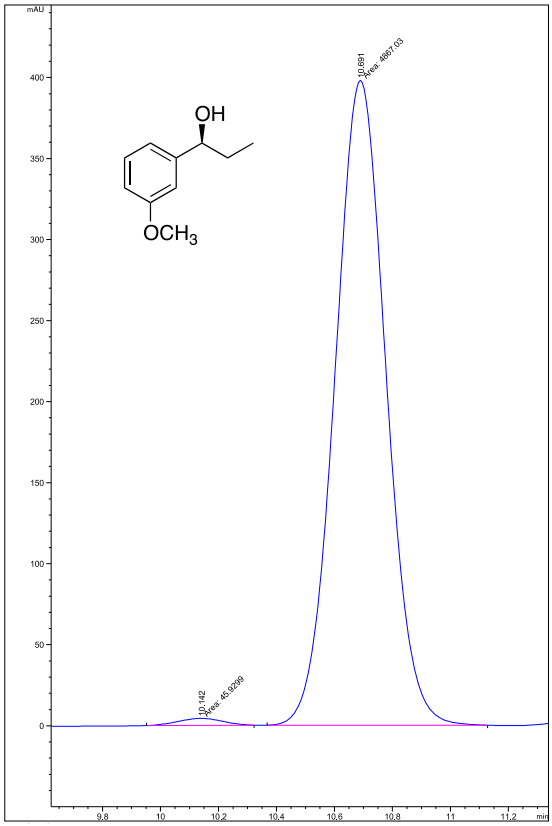
(*S*)-1-(2-methoxyphenyl)propan-1-ol (10g): *ee* = 94.8%. HPLC: Chiralpak IB, hexane/i-PrOH = 97:3, 0.8 mL/min, 220 nm, major 10.1 min and minor 10.9 min.



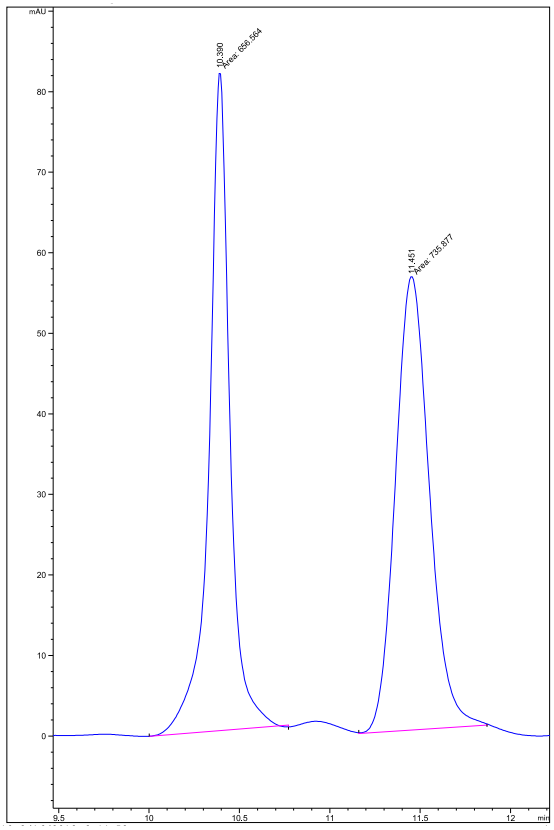


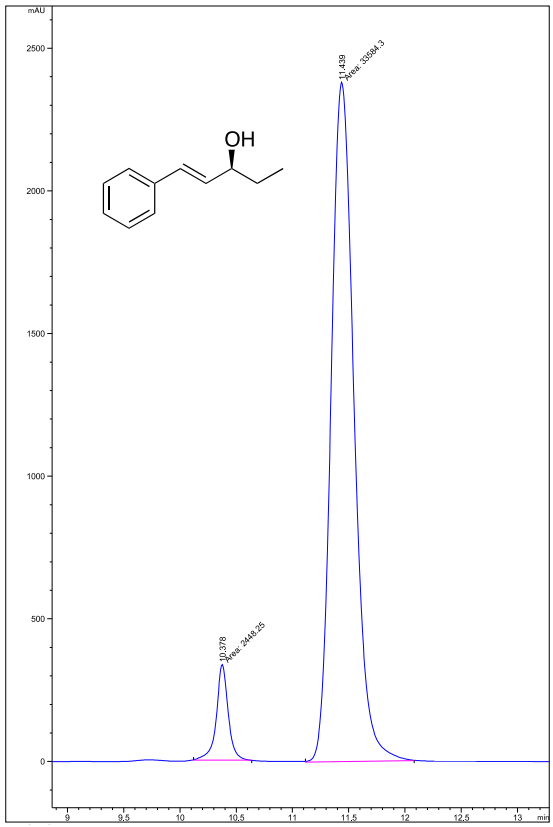
(*S*)-1-(3-methoxyphenyl)propan-1-ol (10h): *ee* = 98.2%. HPLC: Chiralpack IA, hexane/i-PrOH 95:5, 1 mL/min, 220 nm, minor 10.1 min and major 10.6 min.



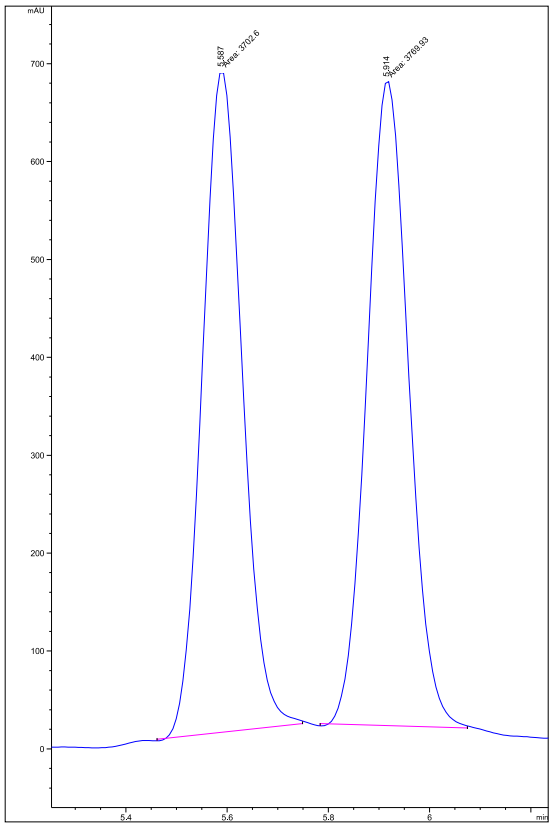


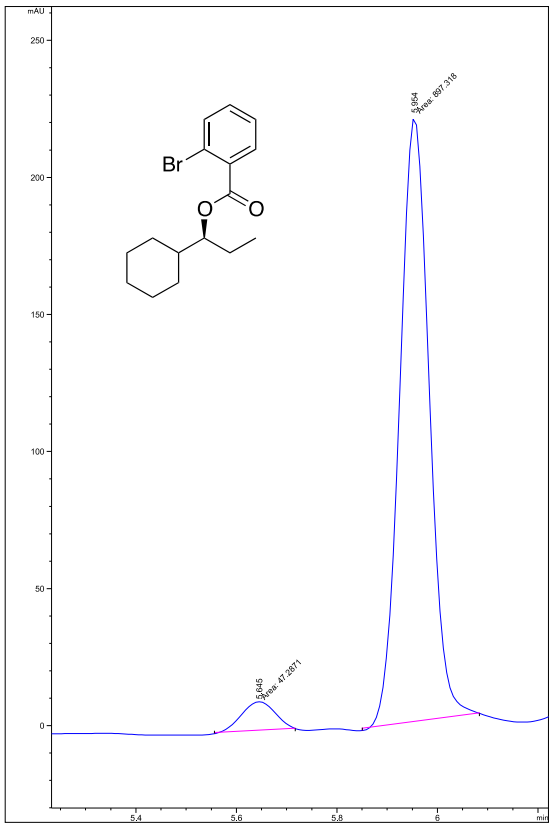
(*S*,*E*)-1-phenylpent-1-en-3-ol (10i): *ee* = 85.2%. HPLC: Chiralpak IC, hexane/i-PrOH = 98:2, 1 mL/min, 254 nm, minor 10.4 min and major 11.4 min.



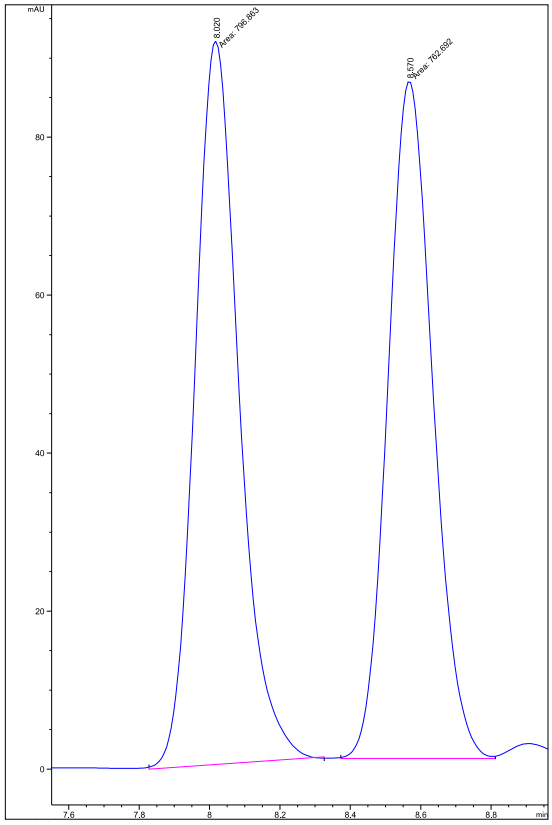


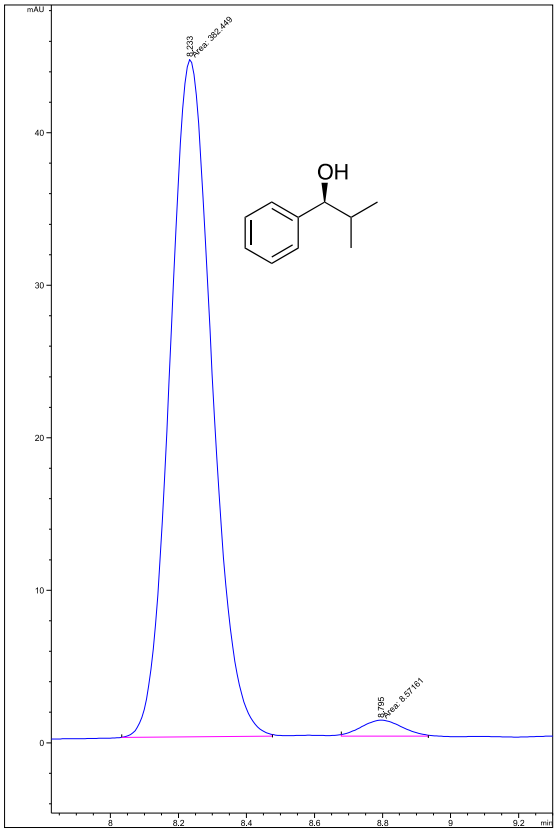
(*S*)-1-cyclohexylpropan-1-ol (10k): *ee* = 90%. HPLC on the *o*-bromo benzoyl ester derivative: Chiralpak IA, hexane/EtOH = 99:1, 0.8 mL/min, 220 nm, minor 5.6 min and major 5.9 min.



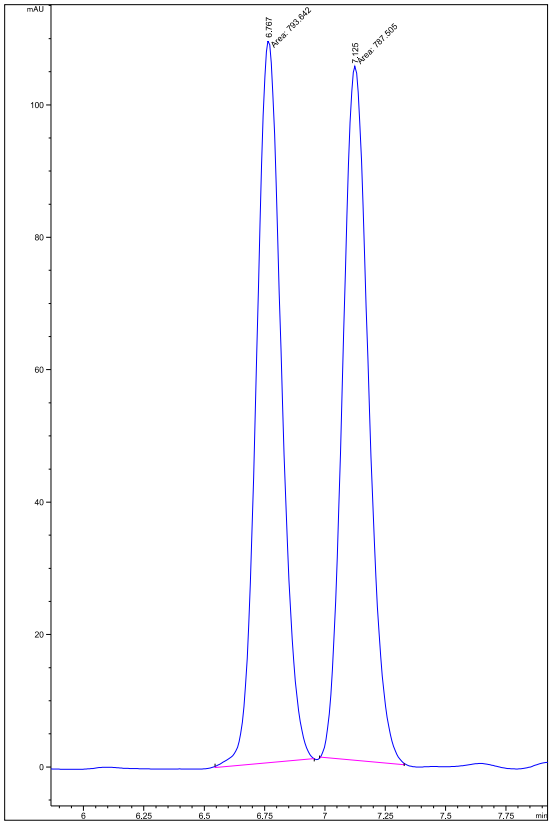


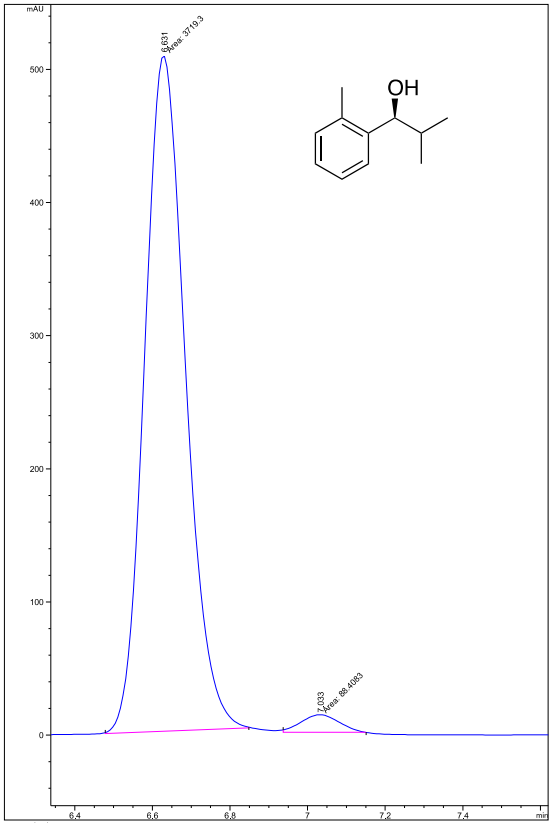
(*S*)-2-methyl-1-phenylpropan-1-ol (11a): *ee* = 95.6%. HPLC: Chiralpak IB, hexane/i-PrOH = 99:1, 1 mL/min, 220 nm, T=30°C, major 8.2 min and minor 8.8 min.



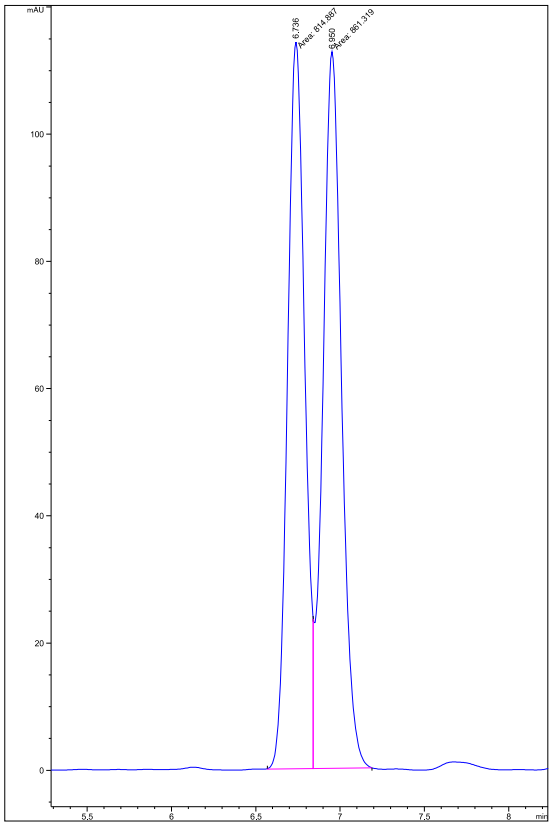


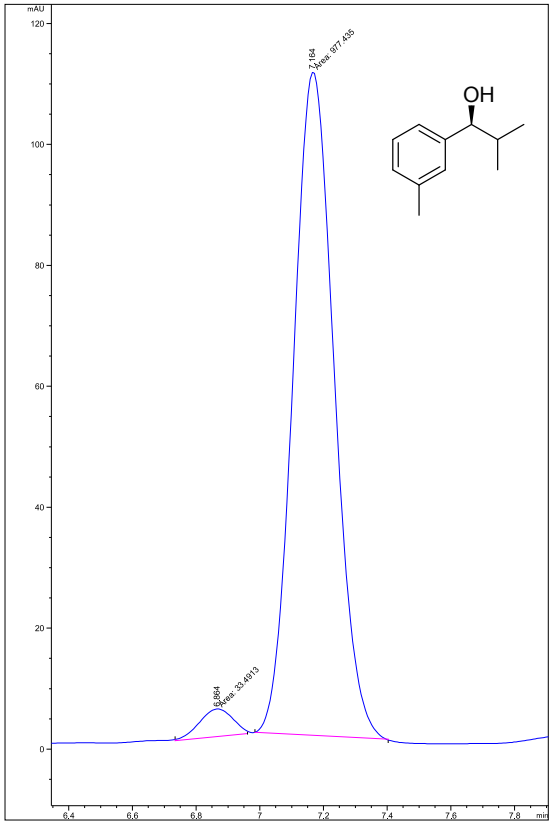
(*S*)-2-methyl-1-(*o*-tolyl)propan-1-ol (11b): *ee* = 95.4%. HPLC: Chiralpak IB, hexane/i-PrOH = 98:2, 1 mL/min, 220 nm, T=30°C, major 6.6 min and minor 7 min.



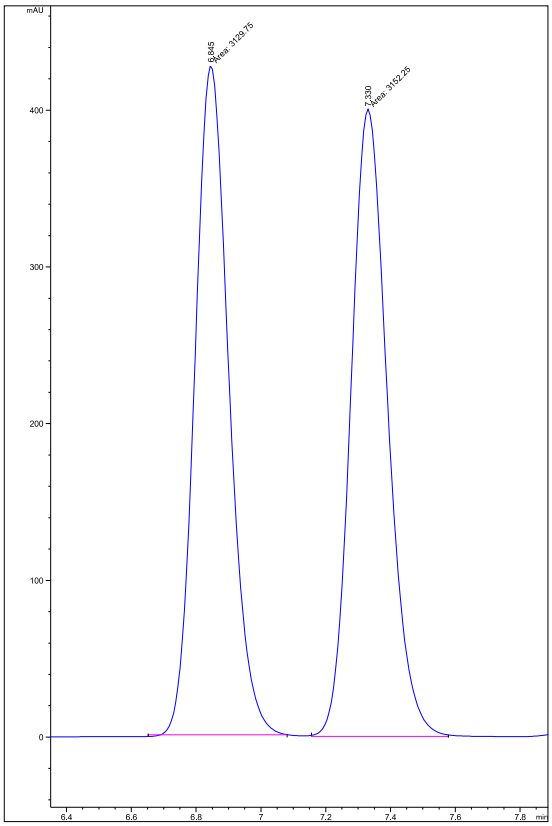


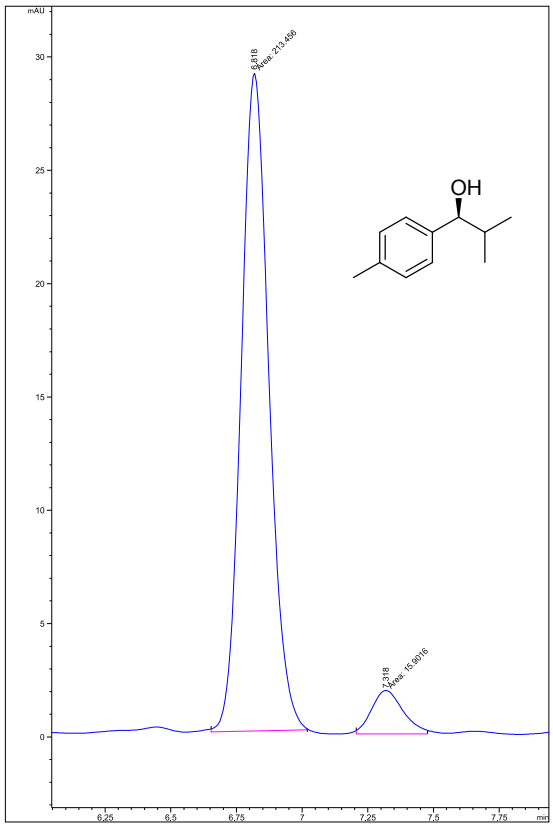
(*S*)-2-methyl-1-(*m*-tolyl)propan-1-ol (11c): *ee* = 93.4%. HPLC: Chiralpak IB, hexane/i-PrOH = 98:2, 1 mL/min, 220 nm, T=30°C, minor 6.8 min and major 7.1 min.



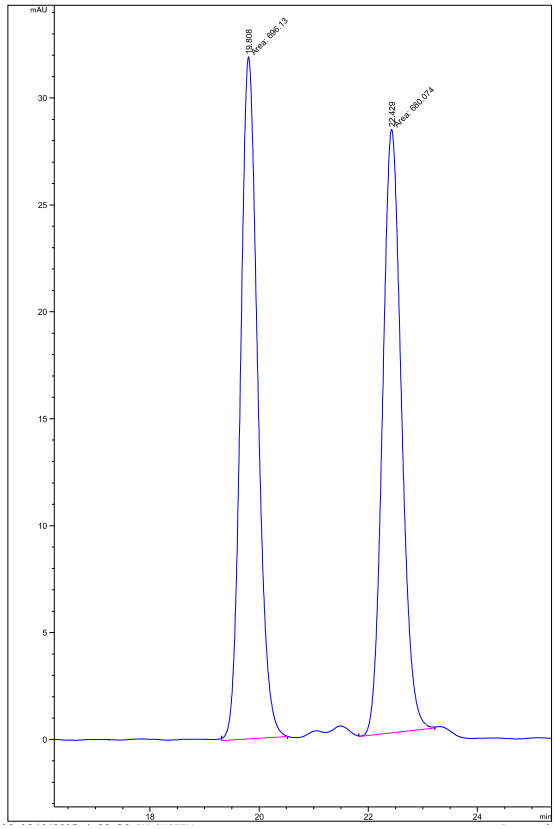


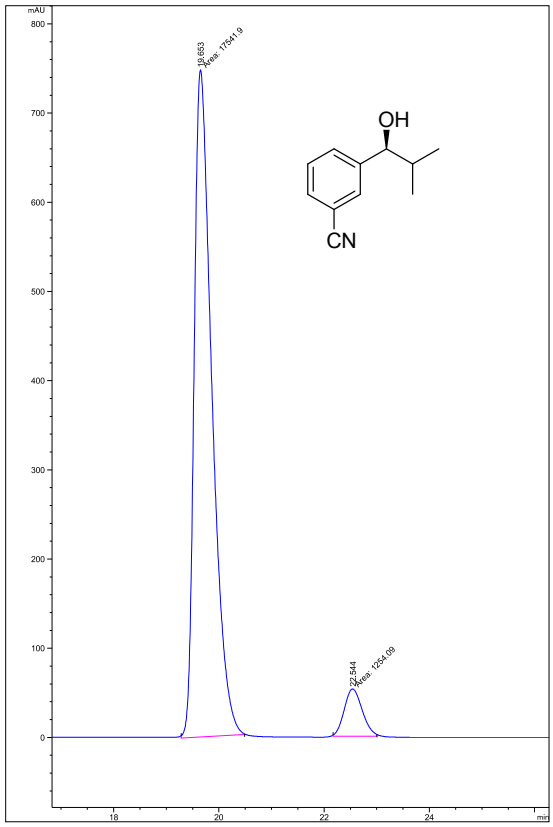
(*S*)-2-methyl-1-(*p*-tolyl)propan-1-ol (11d): *ee* = 86.2%. HPLC: Chiralpak IB, hexane/i-PrOH = 98:2, 1 mL/min, 220 nm, T=30°C, major 6.8 min and minor 7.3 min.



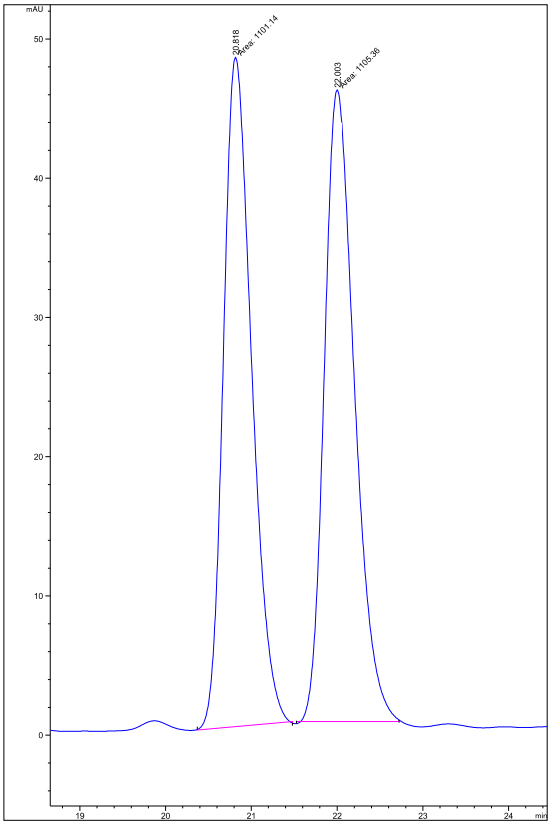


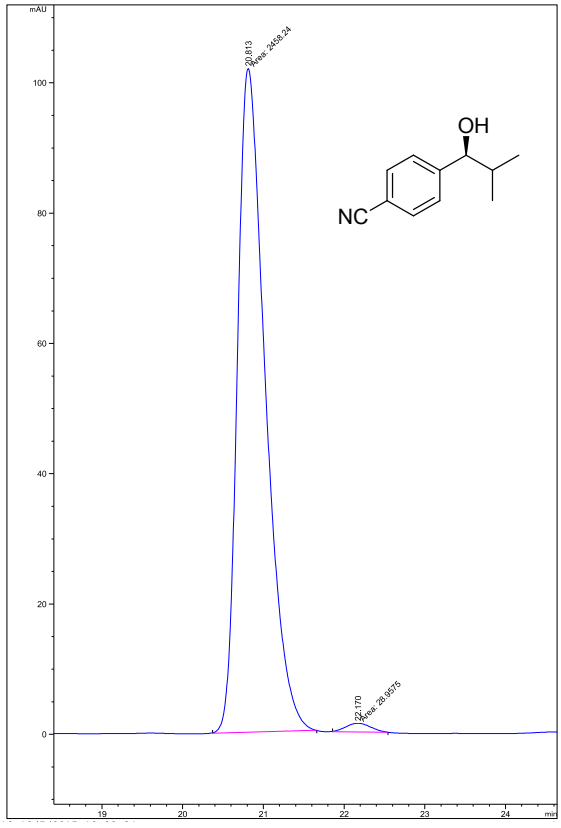
(*S*)-3-(1-hydroxy-2-methylpropyl)benzonitrile (11e): *ee* = 86.6%. HPLC: Chiralpak IB, hexane/i-PrOH = 98:2, 1 mL/min, 220 nm, T=30°C, major 19.6 min and minor 22.5 min.



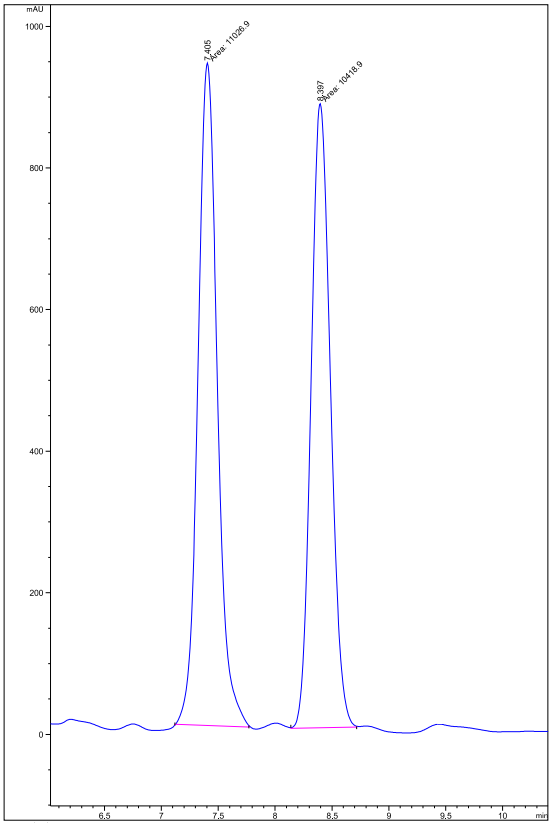


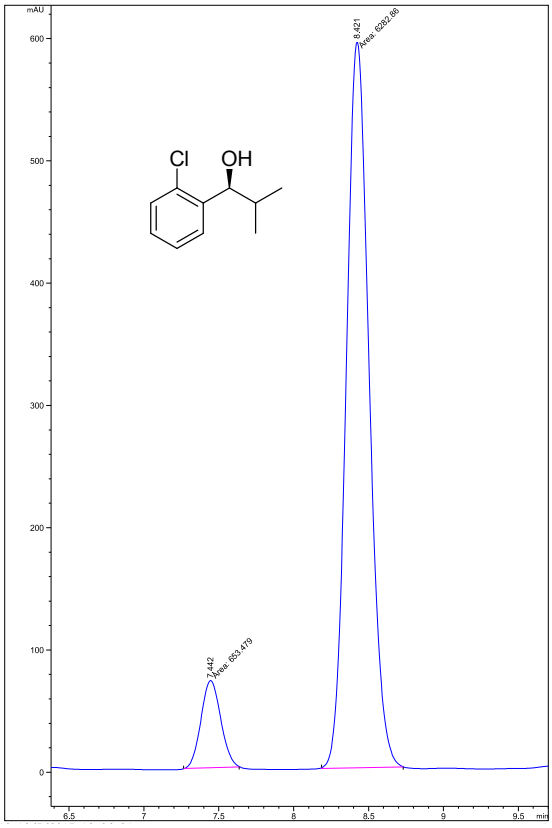
(*S*)-4-(1-hydroxy-2-methylpropyl)benzonitrile (11f): *ee* = 97.7%. HPLC: Chiralpak IB, hexane/i-PrOH = 98:2, 1 mL/min, 220 nm, T=30°C, major 20.8 min and minor 22.1 min.



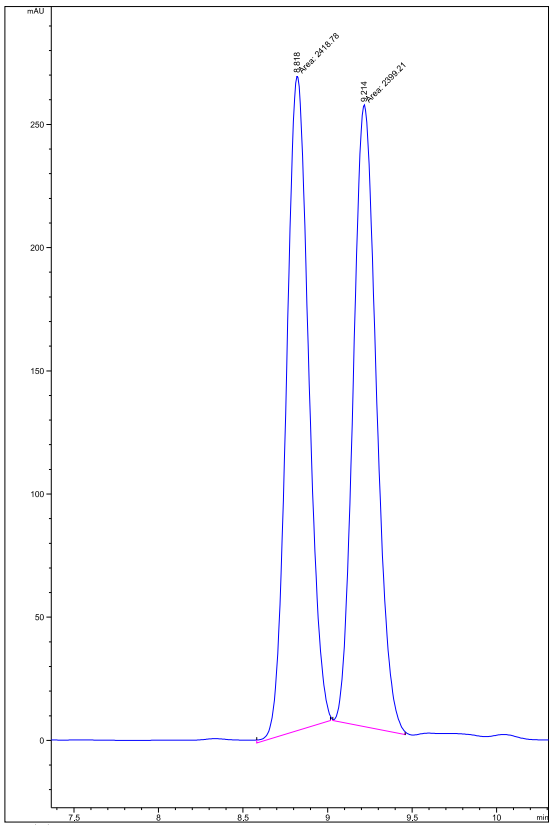


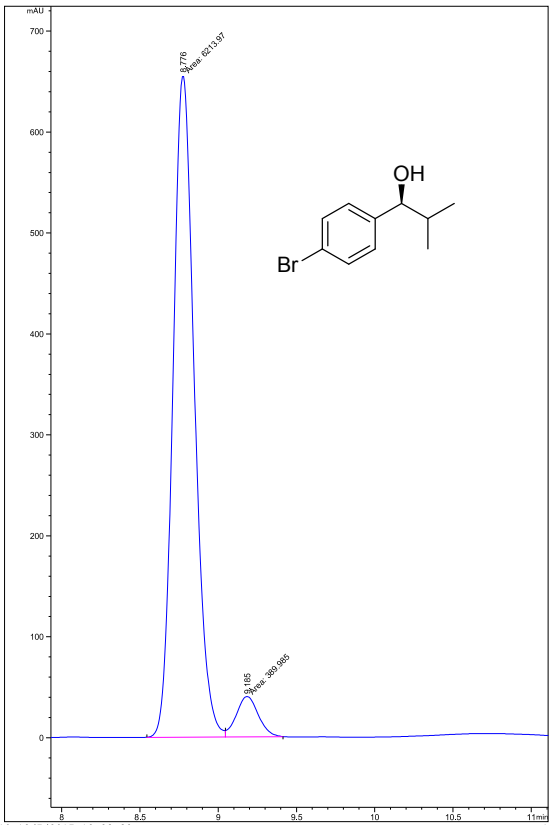
(*S*)-1-(2-chlorophenyl)-2-methylpropan-1-ol (11g): *ee* = 81.2% HPLC: Chiralpak IF, hexane/i-PrOH = 98:2, 1 mL/min, 220 nm, r.t., minor 7.4 min and major 8.4 min.



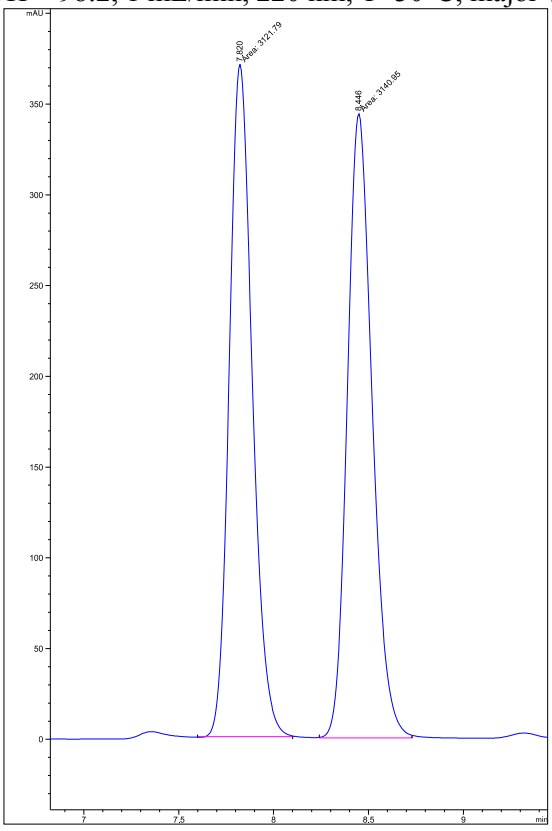


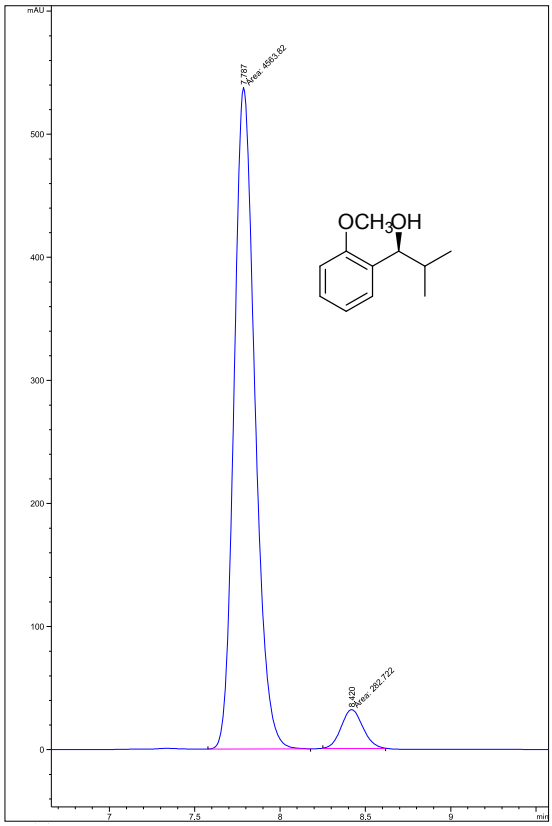
(*S*)-1-(4-bromophenyl)-2-methylpropan-1-ol (11h): *ee* = 88.2%. HPLC: Chiralpak IB, hexane/i-PrOH = 99:1, 1 mL/min, 220 nm, T=30°C, major 8.8 min and minor 9.2 min





(*S*)-1-(2-methoxyphenyl)-2-methylpropan-1-ol (11i): *ee* = 88.4%. HPLC: Chiralpak IB, hexane/i-PrOH = 98:2, 1 mL/min, 220 nm, T=30°C, major 7.8 min and minor 8.4 min.





(*S*)-1-(3-methoxyphenyl)-2-methylpropan-1-ol (11j): *ee* = 91.1%. HPLC: Chiralpak IB, hexane/i-PrOH = 98:2, 1 mL/min, 220 nm, T=30°C, major 13.4 min and minor 17 min.