

Supporting Information

One-pot synthesis of chiral alcohols from alkynes by CF₃SO₃H/Ruthenium tandem catalysis

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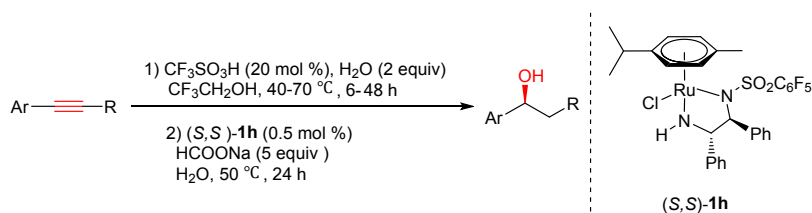
1. General information

Unless otherwise stated, all reagents, catalysts and solvents were purchased from commercial suppliers and used without further purification. Column Chromatography was performed with silica gel (200-300 mesh). **NMR** spectra were recorded on Bruker ADVANCE III (400 MHz) spectrometers. CDCl₃ was the solvent used for the **NMR** analysis, with tetramethylsilane as the internal standard. Chemical shifts were reported up field to TMS (0.00 ppm) for ¹H **NMR** and relative to CDCl₃ (77.0 ppm) for ¹³C **NMR**. Optical rotations were measured on a MCP-500. Melting point were determined using a X-4 made by Peking Taike Apparatus Co., Ltd. HPLC analysis was conducted on a Waters 2489 Series instrument with chiral column OJ-H, AD-H, AS-H and OD-H.

2. General procedure for the synthesis of racemic alcohols

The corresponding aryl ketone (0.2 mmol) was dissolved in 1.0 mL MeOH, and NaBH₄ solid (0.4 mmol) was added slowly. The mixture was stirred until the starting material was disappeared. And then 5.0 mL of H₂O was added slowly, the residue was extracted 3 times with ethyl acetate. The combined organic layer was dried over Na₂SO₄ and evaporated in vacuo. The product was further purified by silica gel column.

3. General procedure for the hydration-ATH of alkynes



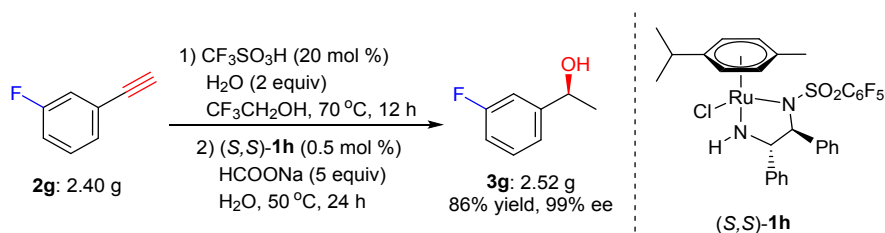
Under nitrogen atmosphere, the corresponding alkyne (5 mmol), CF₃SO₃H (1 mmol, 88 μL), H₂O (10 mmol, 180 uL), and CF₃CH₂OH (2 mL) were added to a 30 mL Schlenk tube. The reaction mixture was stirred at 40-70 °C for 6-48 h. After the hydration was completed monitored by gas chromatography, (*S,S*)-**1h** (0.025 mmol, 17.8 mg), HCOONa (25 mmol, 1.7 g) and H₂O (2 mL) were added, the reaction mixture was stirred at 50 °C for 24 h. The mixture was extracted 3 times with ethyl acetate, and the combined organic layer was dried over Na₂SO₄ and evaporated in vacuo. The product was further purified by silica gel column.

4. General procedure for the hydration-ATH of diethynylbenzene **2t** and **2u**



Under nitrogen atmosphere, the diethynylbenzene **2t** or **2u** (5 mmol), CF₃SO₃H (2 mmol, 176 μL), H₂O (20 mmol, 360 μL), and CF₃CH₂OH (4 mL) were added to a 30 mL Schlenk tube. The reaction mixture was stirred at 70 °C for 48 h. After the hydration was complete monitored by gas chromatography, (*S,S*)-**1h** (0.05 mmol, 35.6 mg), HCOONa (50 mmol, 3.4 g) and H₂O (4 mL) were added, the reaction mixture was stirred at 50 °C for 48 h. The mixture was extracted 3 times with ethyl acetate, and the combined organic layer was dried over Na₂SO₄ and evaporated in vacuo. The product was further purified by silica gel column.

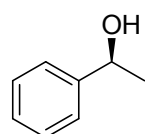
5. Procedure for gram scale reaction



Under nitrogen atmosphere, 3-fluorophenylacetylene **2g** (20 mmol, 2.4 g), CF₃SO₃H (4 mmol, 0.35 mL), H₂O (40 mmol, 0.72 mL), and CF₃CH₂OH (5 mL) was added to a 50 mL Schlenk flask. The reaction mixture was stirred at 70 °C for 12 h. After the reaction was complete, (*S,S*)-**1h** (0.1 mmol, 71.2 mg), HCOONa (100 mmol, 6.8 g) and H₂O (5 mL) were added. The reaction mixture was stirred at 50 °C for 24 h, The mixture was extracted 3 times with ethyl acetate, and the combined organic layer was dried over Na₂SO₄ and evaporated in vacuo. The product was further purified by silica gel column.

6. Analytical Data of the Products

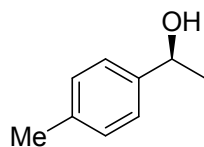
(*S*)-1-phenylethanol (**3a**, CAS: 1445-91-6, known compound)^[1]



Colourless oil; 95% yield (580 mg), 97% ee. Purified by flash column chromatography (PE: EA = 10:1). ([α]_D²⁰ -54.2 (c 0.8, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 7.43-7.38 (m, 4H), 7.34-7.32 (m, 1H), 4.94 (q, *J* = 6.4 Hz, 1H), 2.03 (s, 1H), 1.54 (d, *J* = 6.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 145.8, 128.5, 127.5,

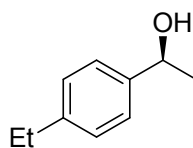
125.4, 70.5, 25.2. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, 30 °C), t_R = 11.59 min (minor), t_S = 13.82 min (major).

(*S*)-1-(*p*-tolyl)ethanol (**3b**, CAS: 51154-54-2, know compound)^[1]



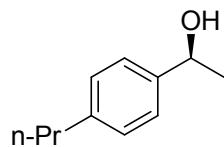
Yellow oil; 83% yield (565 mg), 98% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -58.6 (*c* 1.0, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 7.31 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.91 (q, *J* = 6.4 Hz, 1H), 2.40 (s, 3H), 1.97 (br s, 1H), 1.53 (d, *J* = 6.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 142.9, 137.2, 129.2, 125.4, 70.3, 25.1, 21.1. HPLC (Chiralcel OJ-H column, n-hexane/2-propanol = 95:5 (v/v), 1.0 mL/min, 220 nm, 30 °C), t_S = 10.69 min (major), t_R = 12.46 min (minor).

(*S*)-1-(4-ethylphenyl)ethanol (**3c**, CAS: 101219-72-1, know compound)^[1]



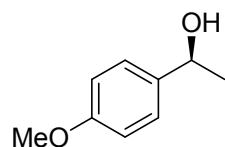
Yellow oil; 84% yield (630 mg), 93% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -48.2 (*c* 1.0, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 7.35 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.93 (q, *J* = 6.4 Hz, 1H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.79 (br s, 1H), 1.54 (d, *J* = 6.4 Hz, 3H), 1.28 (t, *J* = 7.6 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 143.7, 143.1, 128.0, 125.5, 70.3, 28.6, 25.1, 15.7. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 99:1 (v/v), 1.0 mL/min, 254 nm, 30 °C), t_R = 18.78 min (minor), t_S = 19.89 min (major).

(*S*)-1-(4-propylphenyl)ethanol (**3d**, CAS: 473700-93-5, know compound)^[1]



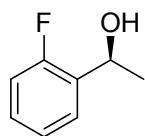
Yellow oil; 74% yield (608 mg), 95% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -47.8 (*c* 1.0, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 7.33 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.92 (q, *J* = 6.4 Hz, 1H), 2.63 (t, *J* = 7.2 Hz, 2H), 1.92 (s, 1H), 1.73-1.66 (m, 3H), 1.54 (d, *J* = 6.4 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 143.1, 142.0, 128.6, 125.4, 70.3, 37.7, 25.0, 24.6, 13.9. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, 30 °C), t_R = 8.17 min (minor), t_S = 8.90 min (major).

(*S*)-1-(4-methoxyphenyl)ethanol (**3e**, CAS: 1572-97-0, know compound)^[1]



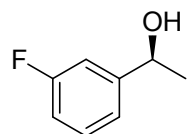
Colourless oil; 77% yield (586 mg), 92% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -50.6 (*c* 1.0, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 7.33 (dd, J_1 = 2.8 Hz, J_2 = 11.2 Hz, 2H), 6.92 (dd, J_1 = 2.8 Hz, J_2 = 11.2 Hz, 2H), 4.86 (q, J = 6.4 Hz, 1H), 3.84 (s, 3H), 2.23 (s, 1H), 1.50 (d, J = 6.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 158.9, 138.1, 126.7, 113.8, 69.9, 55.3, 25.1. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254nm, 30 °C), t_R = 15.98 min (minor), t_S = 17.12min (major).

(*S*)-1-(2-fluorophenyl)ethanol (**3f**, CAS: 171032-87-4, know compound)^[2]



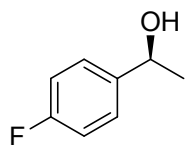
Colourless oil; 82% yield (575 mg), 90% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -41.8 (*c* 0.9, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 7.52-7.49 (m, 1H), 7.29-7.27 (m, 1H), 7.20-7.16 (m, 1H), 7.07-7.03 (m, 1H) 5.21 (q, J = 4.0 Hz, 1H), 2.48 (br s, 1H), 1.54 (d, J = 6.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 159.7 (d, J_{C-F} = 243 Hz), 132.7 (d, J_{C-F} = 14 Hz), 128.8 (d, J_{C-F} = 8.0 Hz), 126.7 (d, J_{C-F} = 4 Hz), 124.3 (d, J_{C-F} = 3 Hz), 115.3 (d, J_{C-F} = 22Hz), 64.5 (d, J_{C-F} = 3 Hz), 24.0. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 98:2 (v/v), 1.0 mL/min, 254 nm, 30 °C), t_R = 10.72 min (minor), t_S = 11.57 min (major).

(*S*)-1-(3-fluorophenyl)ethanol (**3g**, CAS: 126534-32-5, know compound)^[1]



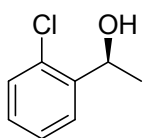
Light yellow oil; 80% yield (561 mg), 99.6% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -48.7 (*c* 1.0, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 7.35-7.30 (m, 1H), 7.17-7.11 (m, 2H), 7.02-6.96 (m, 1H), 4.92 (q, J = 6.4 Hz, 1H), 2.14 (br s, 1H), 1.52 (d, J = 6.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 163.0 (d, J_{C-F} = 244.3Hz), 148.5 (d, J_{C-F} = 6.5 Hz), 130.0 (d, J_{C-F} = 8.0 Hz), 120.9 (d, J_{C-F} = 2.8 Hz), 114.2 (d, J_{C-F} = 21.0 Hz), 112.3 (d, J_{C-F} = 21.7Hz), 69.8 (d, J_{C-F} = 1.5 Hz), 25.2. HPLC (Chiralcel AD-H column, n-hexane/2-propanol = 95:5 (v/v), 1.0 mL/min, 254 nm, 30 °C), t_S = 6.71 min (major), t_R = 8.58min (minor).

(*S*)-1-(4-fluorophenyl)ethanol (**3h**, CAS: 101219-73-2, know compound)^[1]



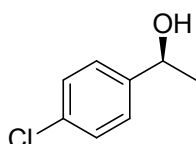
Light yellow oil; 90% yield (631 mg), 91% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -64.0 (*c* 1.0, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 7.38-7.34 (m, 2H), 7.08-7.04 (m, 2H), 4.90 (q, *J* = 6.8 Hz, 1H), 2.27 (br s, 1H), 1.50 (d, *J* = 6.8 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 162.1 (d, *J*_{C-F} = 243 Hz), 141.6 (d, *J*_{C-F} = 3 Hz), 127.1 (d, *J*_{C-F} = 8.0 Hz), 115.3 (d, *J*_{C-F} = 21.0 Hz), 69.7, 25.3. HPLC (Chiralcel AS-H column, n-hexane/2-propanol = 98:2 (v/v), 1.0 mL/min, 254nm, 30 °C), *t*_R = 12.61 min (minor), *t*_S = 14.07 min (major).

(*S*)-1-(2-chlorophenyl)ethanol (**3i**, CAS:131864-71-6, know compound)^[3]



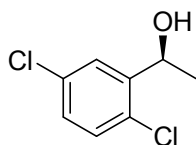
Colourless oil; 88% yield (689 mg), 87% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -64.3 (*c* 1.0, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 7.64 (dd, *J*₁ = 1.6 Hz, *J*₂ = 7.6 Hz, 1H), 7.38-7.32 (m, 2H), 7.27-7.23 (m, 1H), 5.35 (q, *J* = 6.4 Hz, 1H), 2.05 (s, 1H), 1.54 (d, *J* = 6.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 143.1, 131.7, 129.4, 128.5, 127.3, 126.4, 67.0, 23.5. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 99:1 (v/v), 1.0 mL/min, 254 nm, 30 °C), *t*_R = 20.65 min (minor), *t*_S = 22.28 min (major).

(*S*)-1-(4-chlorophenyl)ethanol (**3j**, CAS: 99528-42-4, know compound)^[1]



Colourless oil; 85% yield (666 mg), 92% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -60.0 (*c* 1.0, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 7.37-7.32 (m, 4H), 4.91 (q, *J* = 6.4 Hz, 1H), 2.06 (s, 1H), 1.50 (d, *J* = 6.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 144.3, 133.1, 128.6, 126.8, 69.8, 25.3. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 220 nm, 30 °C), *t*_S = 10.73 min (major), *t*_R = 11.91 min (minor).

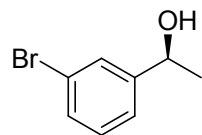
(*S*)-1-(2,5-dichlorophenyl)ethanol (**3k**, CAS: 691881-93-3, know compound)^[3]



Colourless oil; 79% yield (755 mg), 86% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -72.0 (*c* 0.8, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 7.51 (d, *J* = 8.4 Hz, 1H), 7.35 (s, 1H), 7.28 (dd, *J*₁ = 2.0 Hz, *J*₂ = 8.4 Hz, 1H), 5.22 (q, *J* = 6.4 Hz, 1H), 2.78 (s, 1H), 1.46 (d, *J* = 6.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 141.7, 133.4, 132.1, 129.1, 127.5, 127.4, 66.5, 23.6. HPLC (Chiralcel OD-H

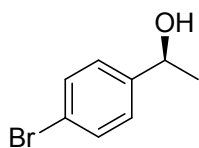
column, n-hexane/2-propanol = 99:1 (v/v), 1.0 mL/min, 220 nm, 30 °C), t_S = 19.90 min (major), t_R = 21.43 min (minor).

(*S*)-1-(3-bromophenyl)ethanol (**3l**, CAS: 134615-22-8, know compound)^[1]



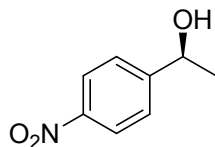
Colourless oil; 78% yield (784 mg), 92% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -46.7 (*c* 1.0, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 7.54 (s, 1H), 7.44-7.41 (m, 1H), 7.30-7.28 (d, *J* = 7.6, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 4.85 (q, *J* = 6.4 Hz, 1H), 2.56 (s, 1H), 1.48 (d, *J* = 6.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 148.2, 130.5, 130.1, 128.6, 124.1, 122.6, 69.7, 25.2. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 95:5 (v/v), 1.0 mL/min, 220 nm, 30 °C), t_S = 8.74 min (major), t_R = 9.67 min (minor).

(*S*)-1-(4-bromophenyl)ethanol (**3m**, CAS: 100760-04-1, know compound)^[1]



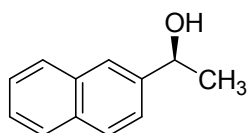
Colourless oil; 68% yield (68 mg), 91% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -30.2 (*c* 0.9, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 7.51(d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.90 (q, *J* = 6.4 Hz, 1H), 2.04 (br s, 1H), 1.51 (d, *J* = 6.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 144.8, 131.6, 127.2, 121.2, 69.8, 25.3. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 95:5 (v/v), 1.0 mL/min, 254 nm, 30 °C), t_S = 8.41 min (major), t_R = 9.29 min (minor).

(*S*)-1-(4-nitrophenyl)ethanol (**3n**, CAS: 6531-13-1, know compound)^[1]



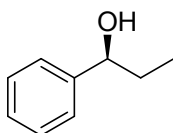
Colourless oil; 66% yield (552 mg), 86% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -24.1 (*c* 0.8, CHCl₃)). **¹H NMR** (400 MHz, CDCl₃): δ = 8.21 (dd, *J*₁ = 2.0 Hz, *J*₂ = 6.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 5.05 (q, *J* = 6.4 Hz, 1H), 2.37 (s, 1H), 1.54 (d, *J* = 6.8 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ = 153.2, 147.2, 126.2, 123.8, 69.5, 25.5. HPLC (Chiralcel OJ-H column, n-hexane/2-propanol = 95:5 (v/v), 1.0 mL/min, 254 nm, 30 °C), t_S = 30.88 min (major), t_R = 34.17 min (minor).

(*S*)-1-(naphthalen-2-yl)ethanol (**3o**, CAS: 27544-18-9, know compound)^[1]



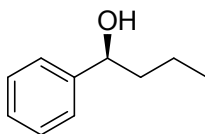
White solid; 88% yield (76 mg), 88% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -40.6 (*c*, 0.70, acetone)). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.89-7.85 (m, 4H), 7.55-7.50 (m, 3H), 5.11 (q, J = 2.8 Hz 1H), 2.09 (s, 1H), 1.63 (d, J = 6.4 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 143.2, 133.4, 133.0, 128.4, 128.0, 127.7, 126.2, 125.8, 123.9, 123.9, 70.6, 25.1. HPLC (Chiralcel OJ-H column, n-hexane/2-propanol = 95:5 (v/v), 1.0 mL/min, 230 nm, 30 °C), t_S = 23.63 min (major), t_R = 31.74 min (minor).

(*S*)-1-phenylpropan-1-ol (**3p**, CAS: 613-87-6, know compound) ^[4]



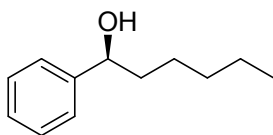
Colourless oil; 67% yield (456 mg), 76% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -38.5 (*c* 1.0, CHCl_3)). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.40-7.38 (m, 4H), 7.34-7.31 (m, 1H), 4.65 (t, J = 6.8 Hz, 1H), 1.91-1.78 (m, 3H), 0.97 (t, J = 7.2 Hz 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 144.6, 128.5, 127.6, 126.0, 76.1, 31.9, 10.2. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 95:5 (v/v), 1.0 mL/min, 254 nm, 30 °C), t_S = 8.66 min (major), t_R = 9.30 min (minor).

(*S*)-1-phenylbutan-1-ol (**3q**, CAS: 22135-49-5, know compound) ^[4]



Colourless oil; 74% yield (556 mg), 89% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -45.7 (*c* 0.8, CHCl_3)). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.40-7.39 (m, 4H), 7.34-7.30 (m, 1H), 4.73 (t, J = 5.6 Hz, 1H), 1.90-1.81(m, 2H), 1.80-1.74 (m, 1H), 1.50-1.47 (m, 1H), 1.38-1.34(m, 1H), 1.00 (t, J = 7.2 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 144.9, 128.5, 127.5, 125.9, 74.5, 41.3, 19.1, 14.0. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 98:2 (v/v), 1.0 mL/min, 254 nm, 30 °C), t_R = 12.65 min (minor), t_S = 13.37 min (major).

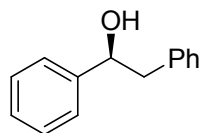
(*S*)-1-phenylhexan-1-ol (**3r**, CAS: 138381-77-8, know compound) ^[5]



Colourless oil; 67% yield (597 mg), 81% ee. Purified by flash column chromatography (PE: EA = 10:1). ($[\alpha]_D^{20}$ -41.9 (*c* 1.0, CHCl_3)). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.42-7.37 (m, 4H), 7.34-7.31 (m, 1H), 4.68 (t, J = 6.4 Hz, 1H), 2.14 (s, 1H), 1.87-1.71 (m, 2H), 1.48-1.43(m, 1H), 1.36-1.34 (m, 5H),

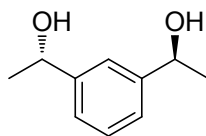
0.93 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 145.0, 128.4, 127.5, 126.0, 74.7, 39.10, 31.8, 25.6, 22.6, 14.1$. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 99:1 (v/v), 1.0 mL/min, 254 nm, 30 °C), $t_R = 20.75$ min (minor), $t_S = 23.75$ min (major).

(*S*)-1,2-diphenylethanol (**3s**, CAS: 5773-56-8, known compound)^[6]



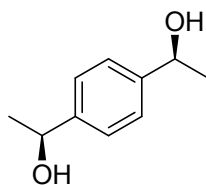
White solid, m. p. = 60-61 °C; 64% yield (634 mg), 82% ee. Purified by flash column chromatography (PE: EA = 5:1). ($[\alpha]_D^{20} -47.3$ (c 1.0, CHCl_3)). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.41-7.24$ (m, 10H), 4.97-4.93 (m, 1H), 3.12-3.00 (m, 2H), 2.00 (d, $J = 2.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 143.8, 138.1, 129.5, 128.5, 128.5, 127.7, 126.7, 125.9, 75.4, 46.1$. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 95:5 (v/v), 1.0 mL/min, 220 nm, 30 °C), $t_R = 11.89$ min (minor), $t_S = 13.58$ min (major).

(1*S*,1'*S*)-1,1'-(1,3-phenylene)diethanol (**3t**, CAS: 143329-81-1, known compound)^{[7], [8]}



Colourless oil; 72% yield (598 mg, de = 76%), 83% ee, Purified by flash column chromatography (PE: EA = 5:1). ($[\alpha]_D^{20} -52.6$ (c , 1.0, acetone)). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.38$ (d, $J = 6.0$ Hz, 1H), 7.33 (t, $J = 7.4$ Hz, 1H), 7.24 (d, $J = 7.2$ Hz, 2H), 4.86 (q, $J = 6.8$ Hz, 2H), 2.78 (s, 2H), 1.48 (d, $J = 6.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 146.1, 146.1, 128.6, 128.6, 124.6, 124.5, 122.5, 122.4, 70.3, 70.3, 25.2, 25.1$. HPLC (Chiralcel OJ-H column, n-hexane/2-propanol = 95:5 (v/v), 1.0 mL/min, 254 nm, 30 °C), $t_{S,S} = 17.89$ min (minor), $t_{R,R} = 21.80$ min (major), $t_{S,R} = 29.62$ min.

(1*S*,1'*S*)-1,1'-(1,4-phenylene)diethanol (**3u**, CAS: 143394-10-9, known compound)^{[7], [8]}

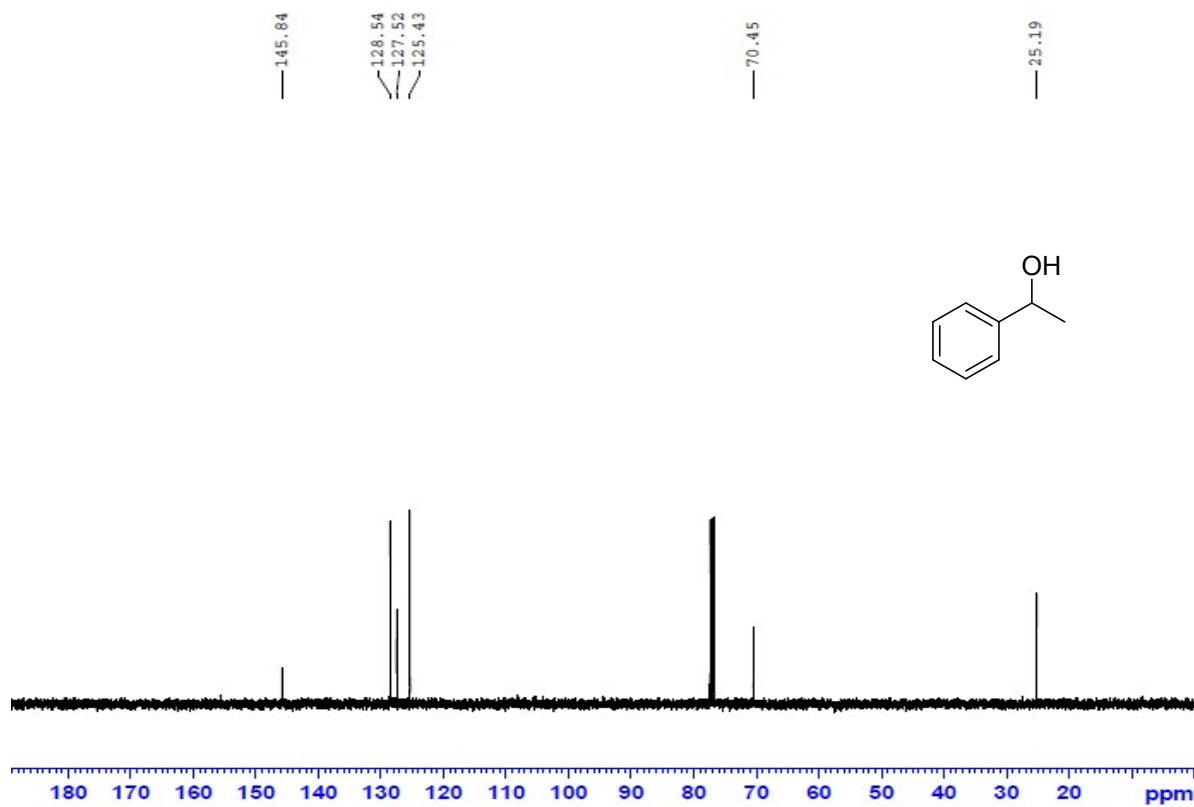
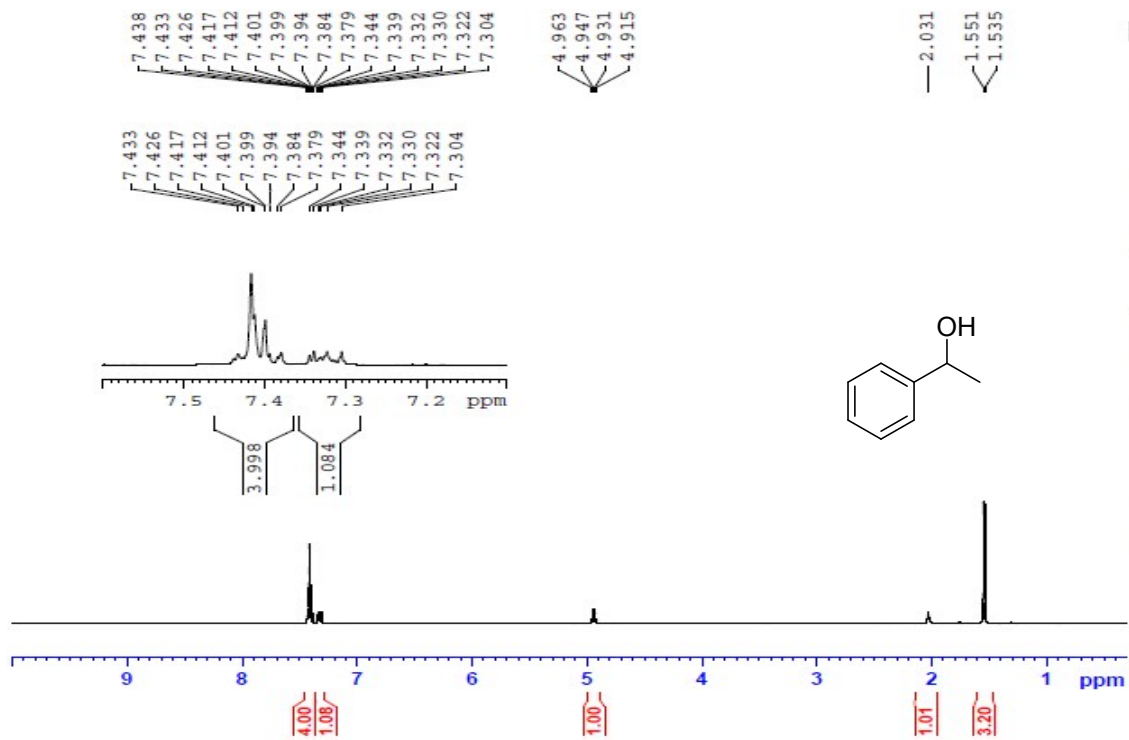
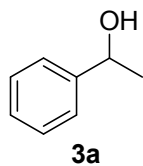


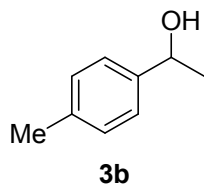
White solid, m.p = 128-130 °C, 75% yield (623 mg, de = 80%), 99% ee, Purified by flash column chromatography (PE: EA = 5:1). ($[\alpha]_D^{20} -89.8$ (c 1.0, acetone)). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.39$ (s, 4H), 4.93 (q, $J = 6.4$ Hz, 2H), 2.03 (s, 2H), 1.53 (d, $J = 6.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 145.1, 125.6, 70.2, 70.2, 25.2$. HPLC (Chiralcel OD-H column, n-hexane/2-propanol = 90:10 (v/v), 1.0 mL/min, 210 nm, 30 °C), $t_{R,R} = 12.25$ min (minor), $t_{S,S} = 13.72$ min (major), $t_{meso} = 18.64$ min (minor).

Reference:

- [1] Li, F.; Wang, N.; Lu, L.; Zhu, G. J. *J. Org. Chem.* **2015**, *80*, 3538–3546.
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- [8] Uchiyama, M.; Katoh, N.; Mimura, R., Yokota, N., Shimogaichi, Y., Shimazaki, M., Ohta, A. *Tetrahedron: Asymmetry*, **1997**, *8*, 3467–3474.

7. ¹H NMR & ¹³C NMR Spectra of the Products

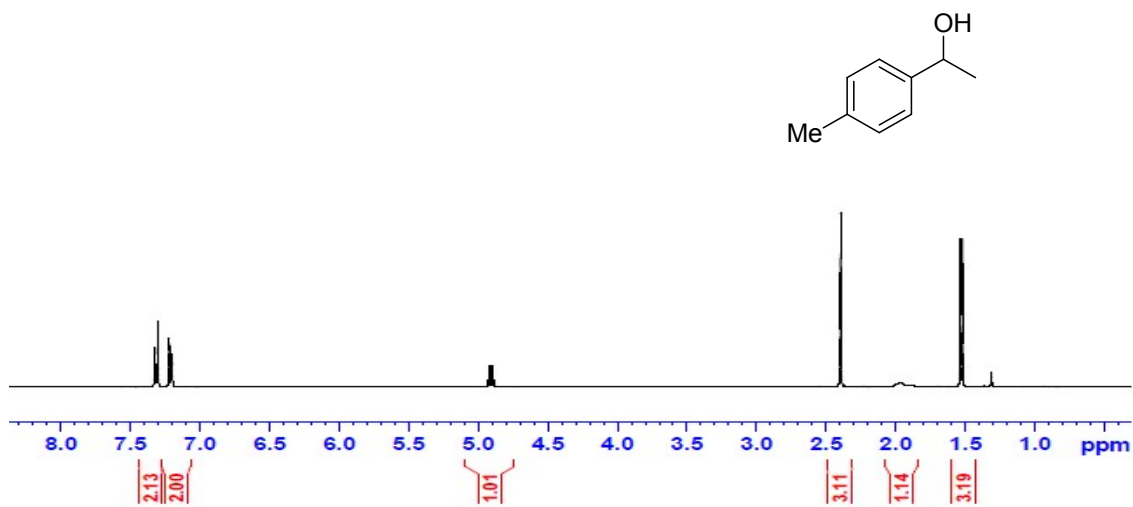




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7.303
7.220
7.201

4.933
4.916
4.900
4.884

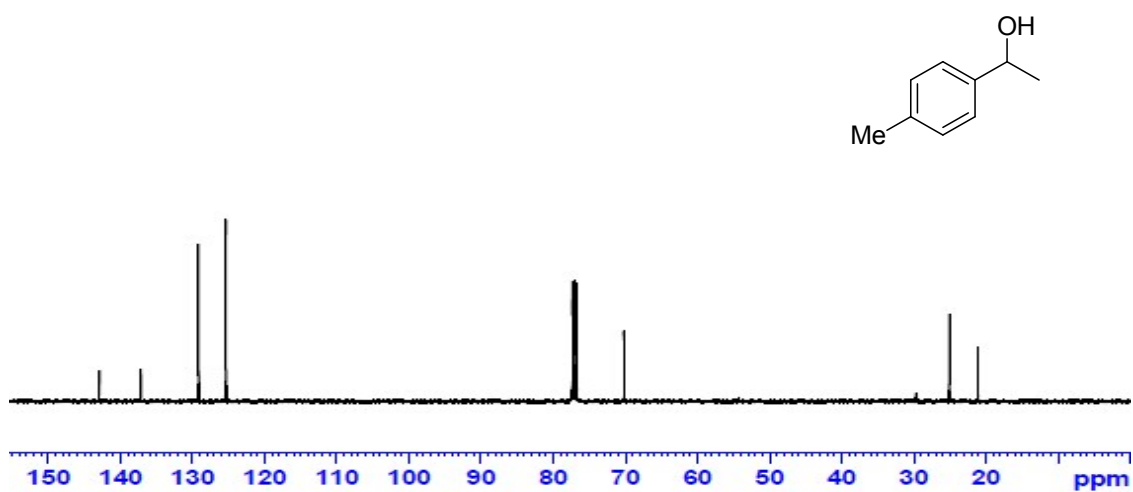
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1.972
1.538
1.522

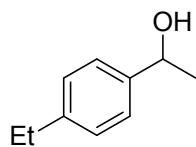


142.910
137.174
129.192
125.390

70.274

25.104
21.122





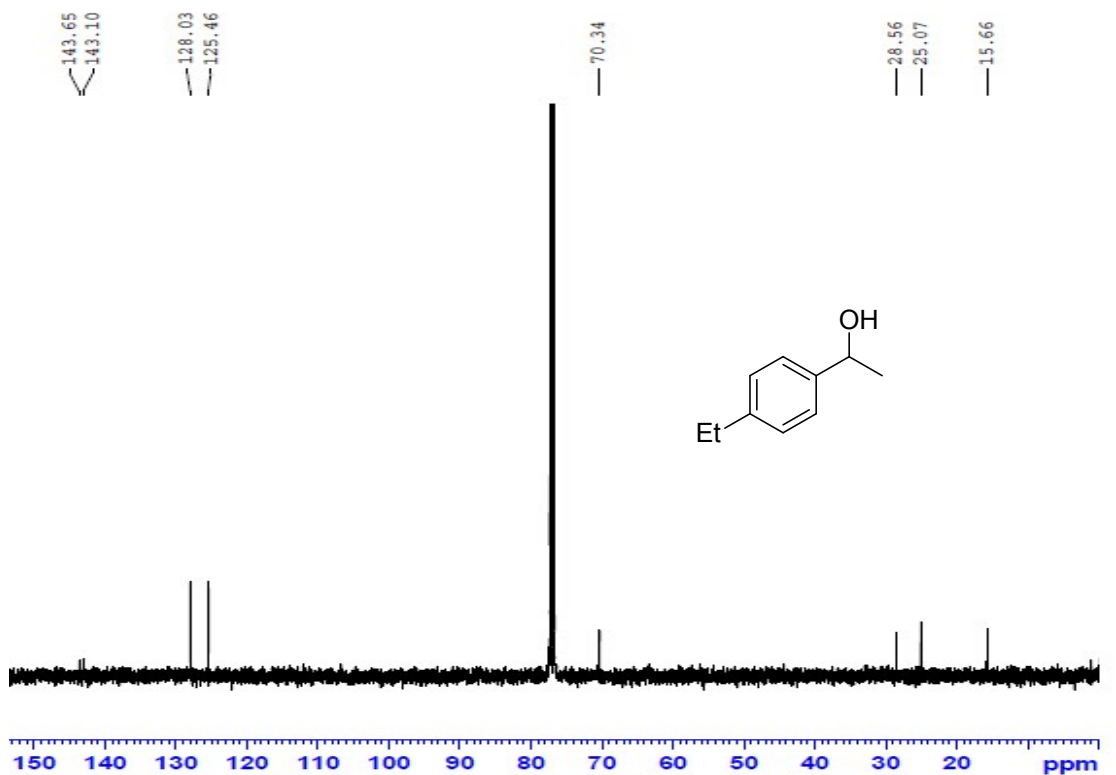
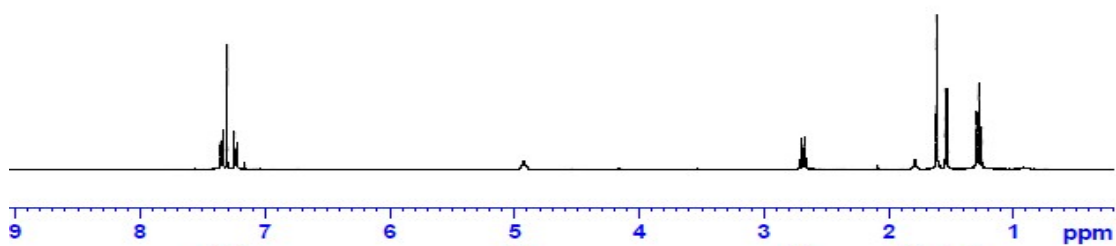
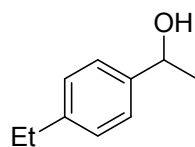
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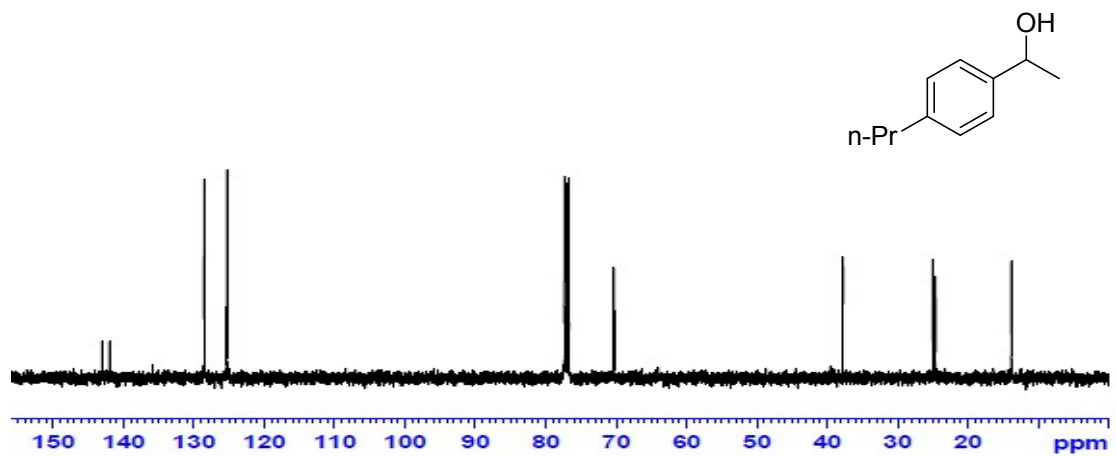
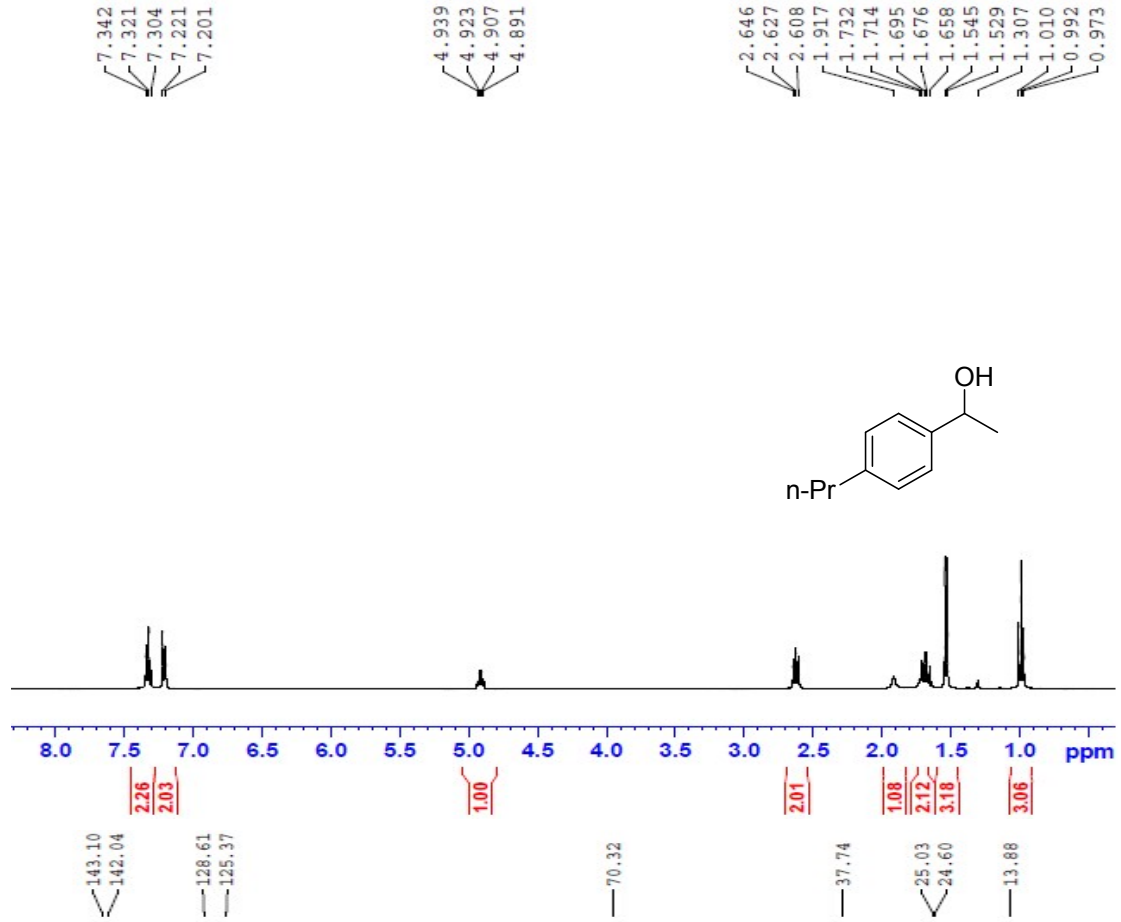
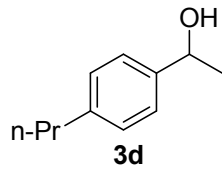
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7.335
7.305
7.246
7.226

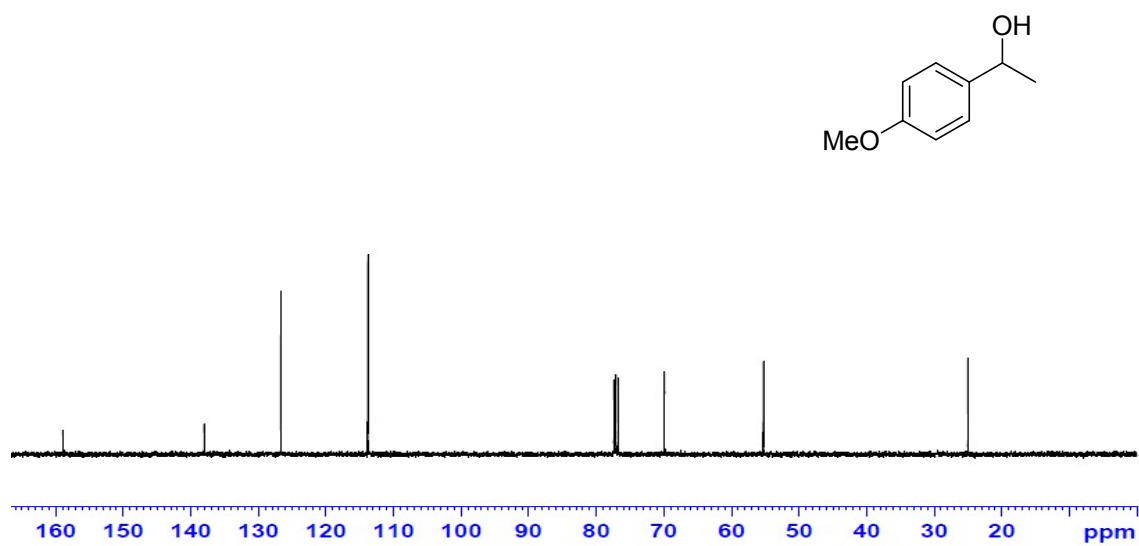
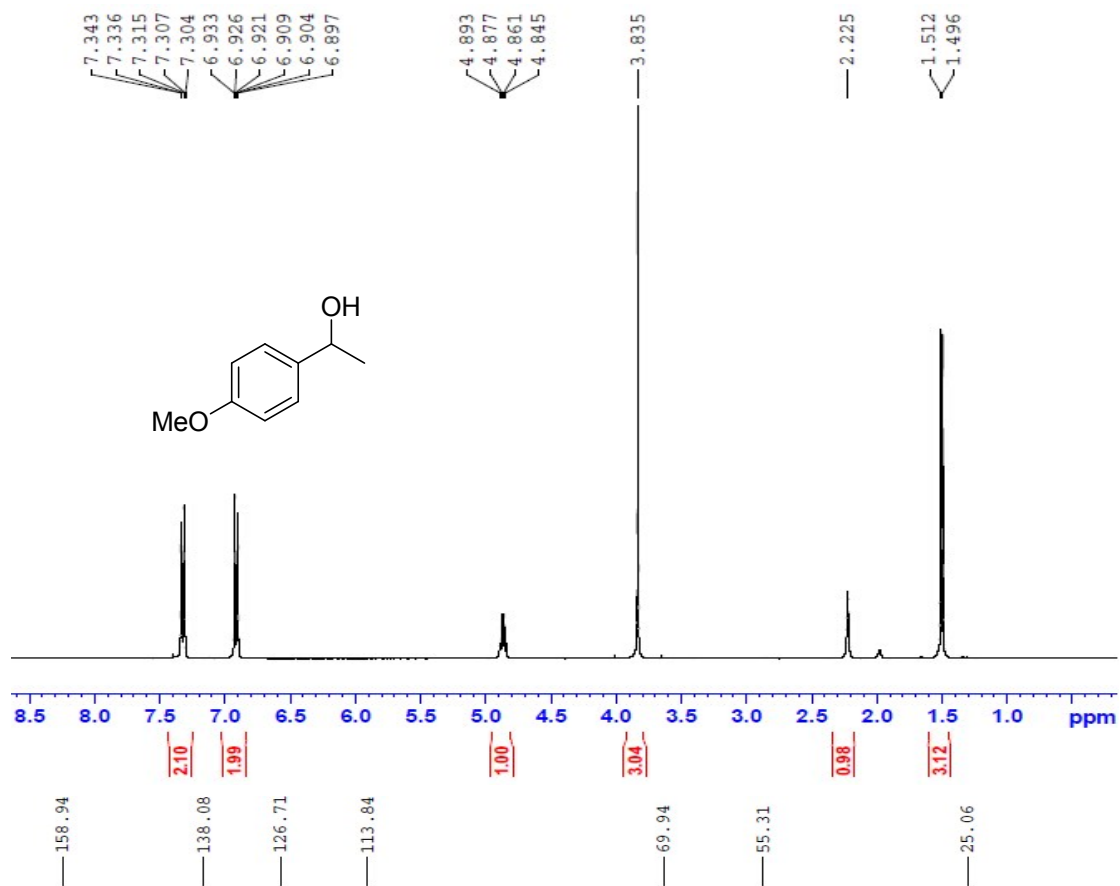
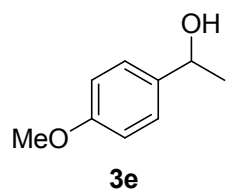
4.952
4.936
4.920
4.904

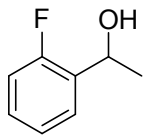
2.719
2.700
2.681
2.662

1.794
1.619
1.548
1.532
1.298
1.279
1.260

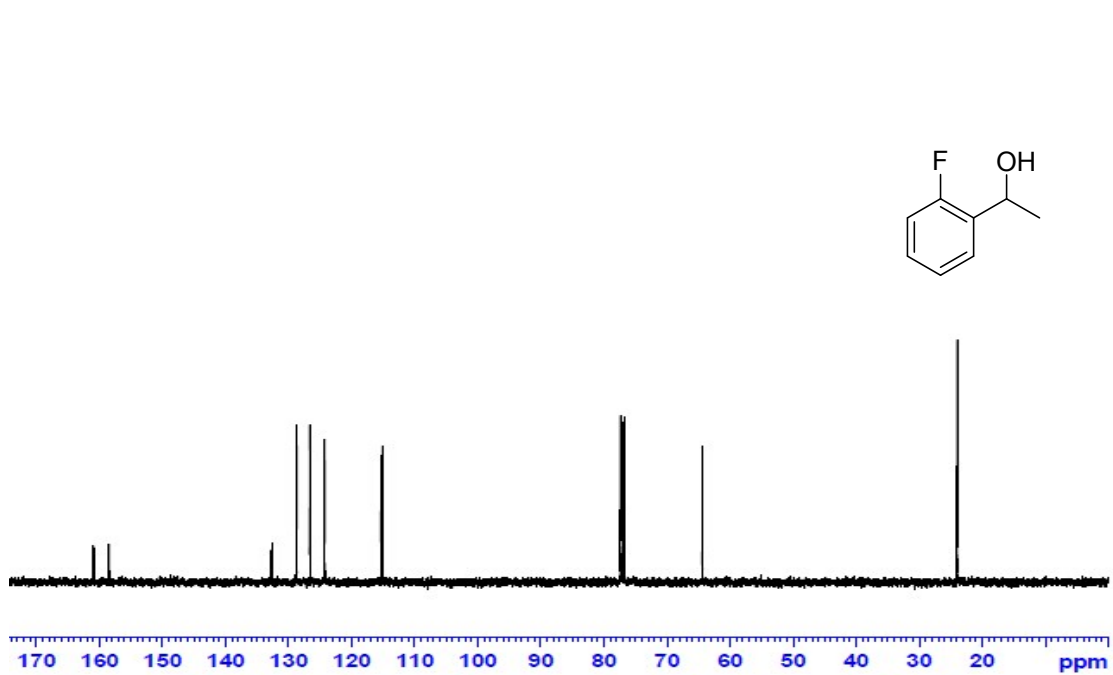
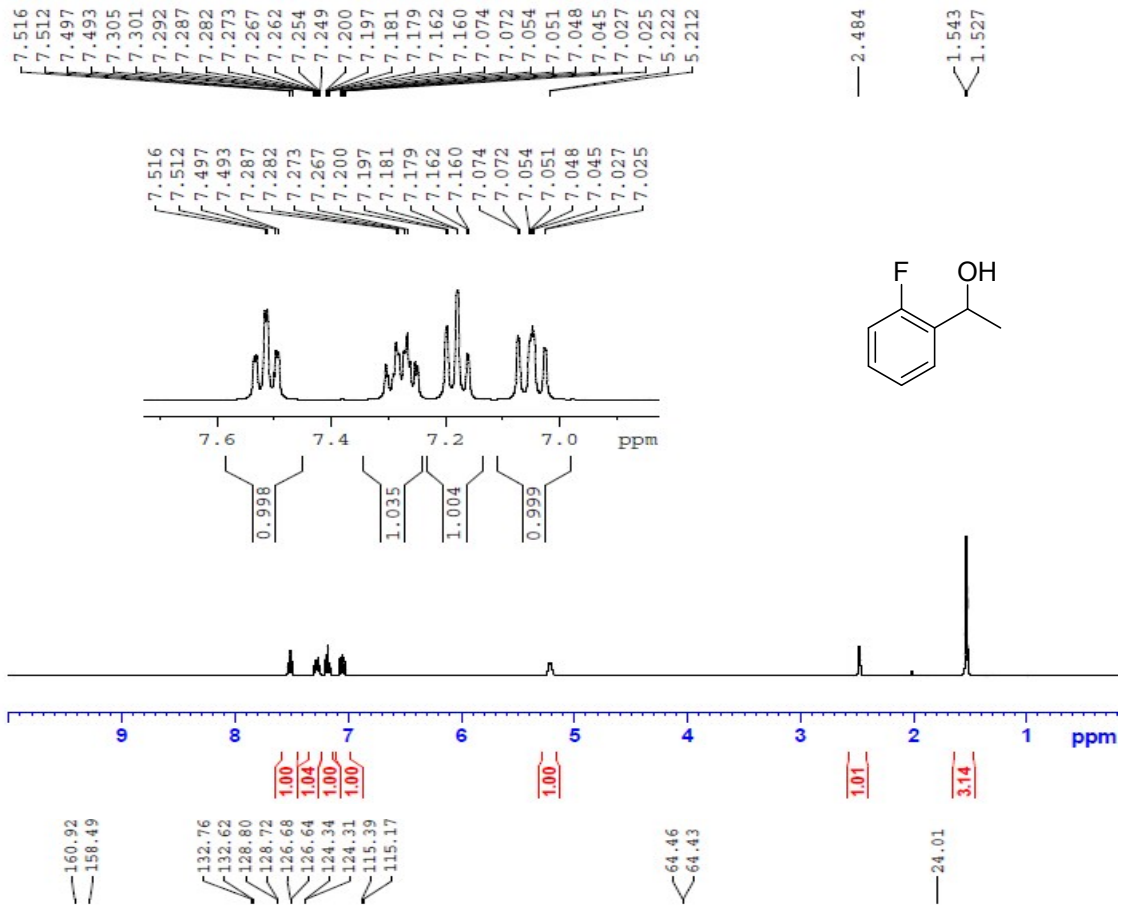


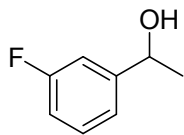




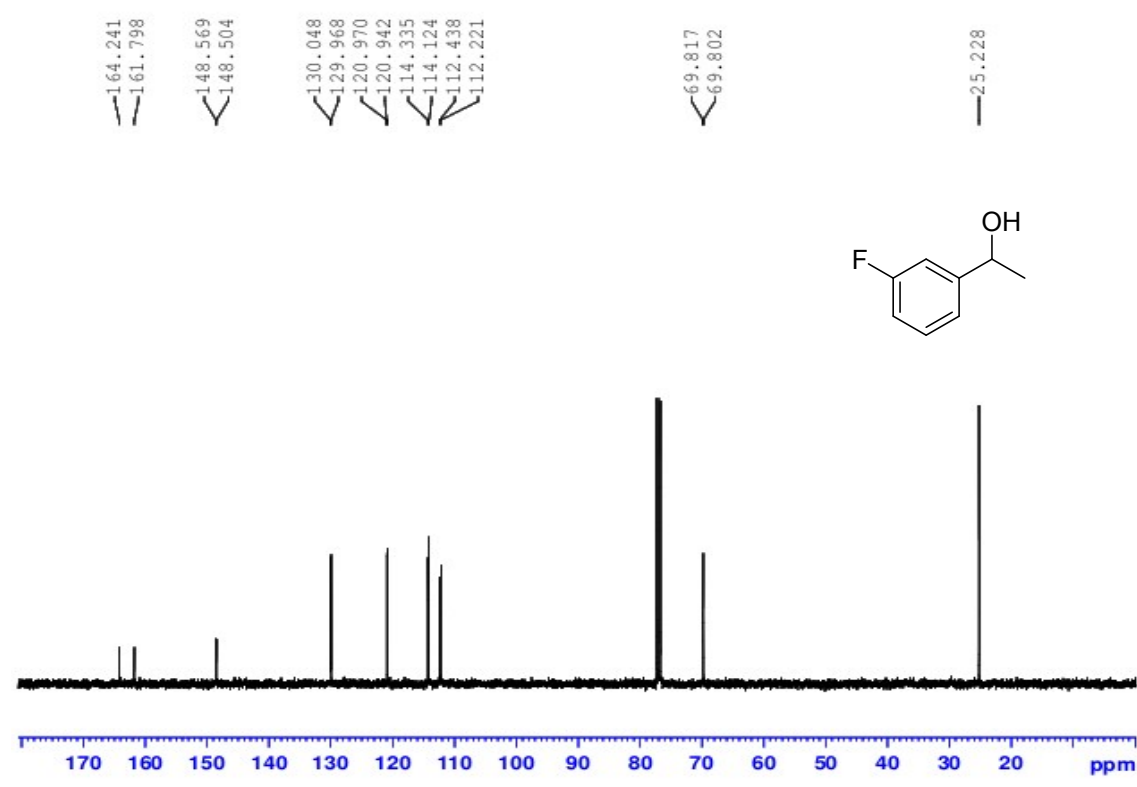
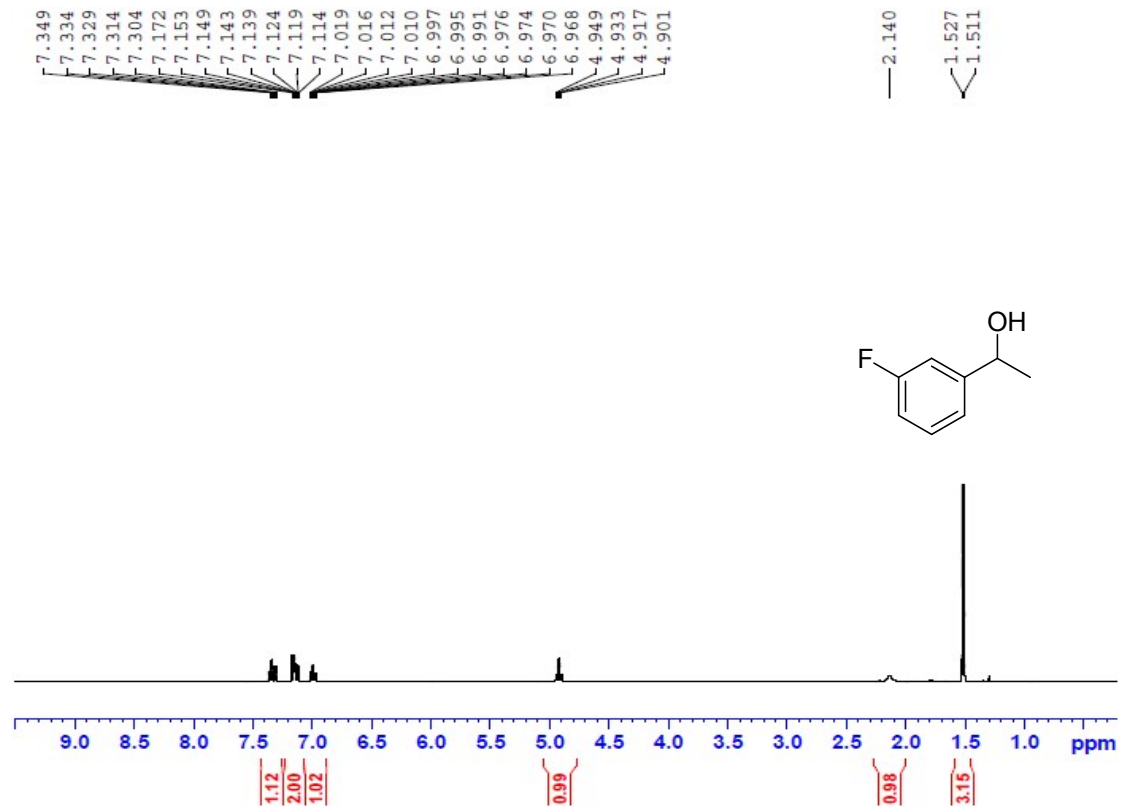


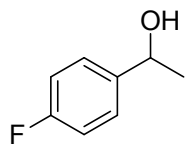
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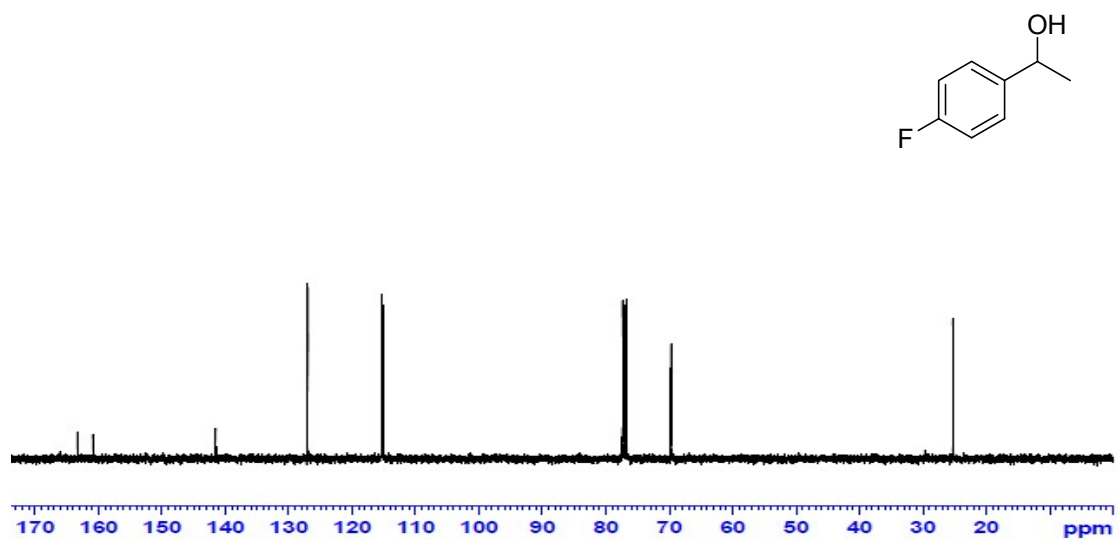
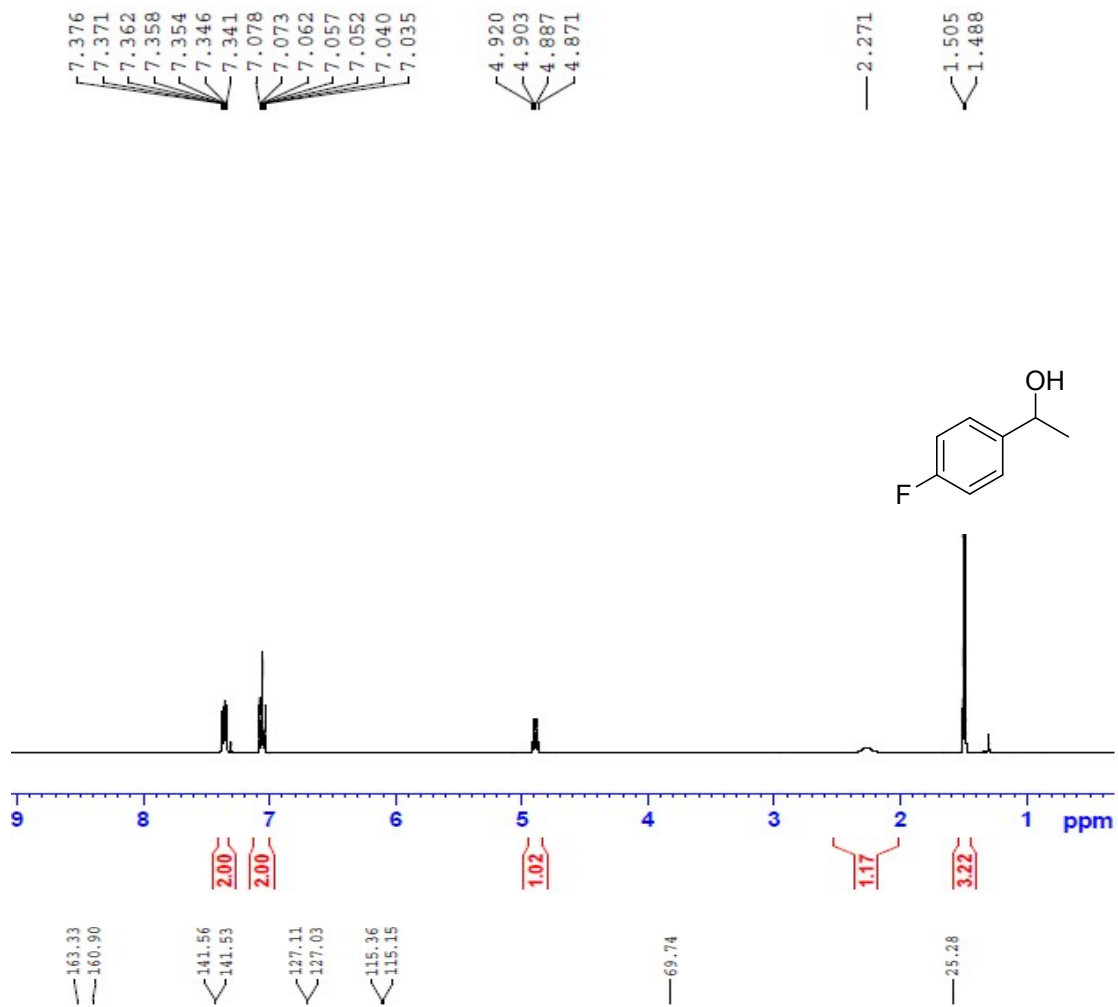


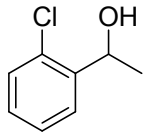
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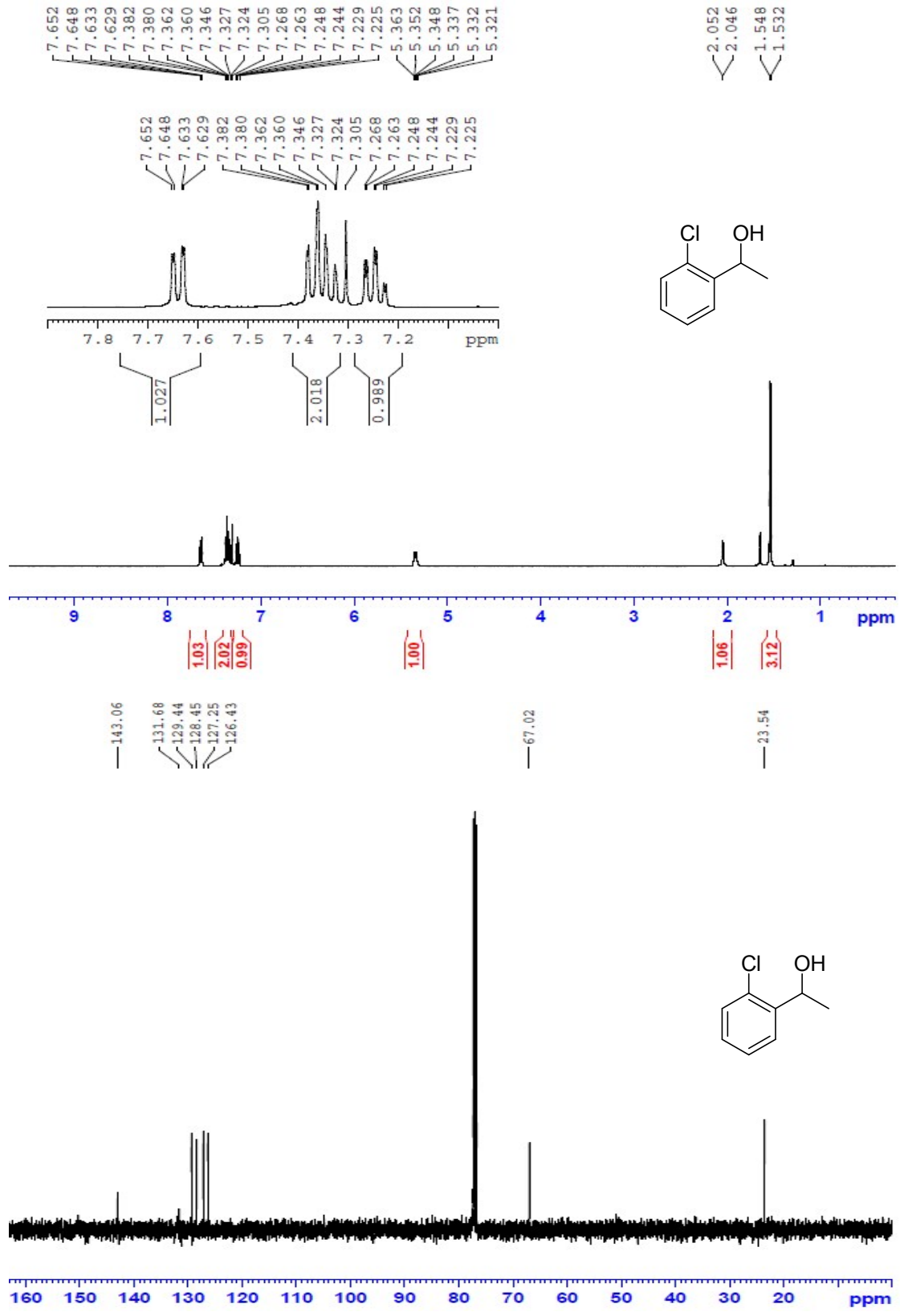


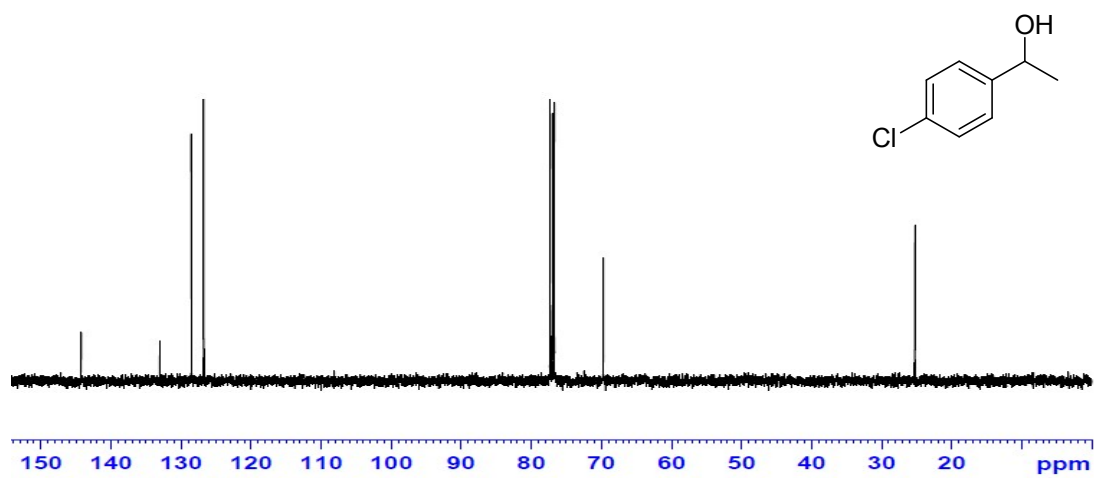
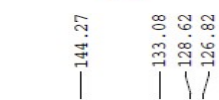
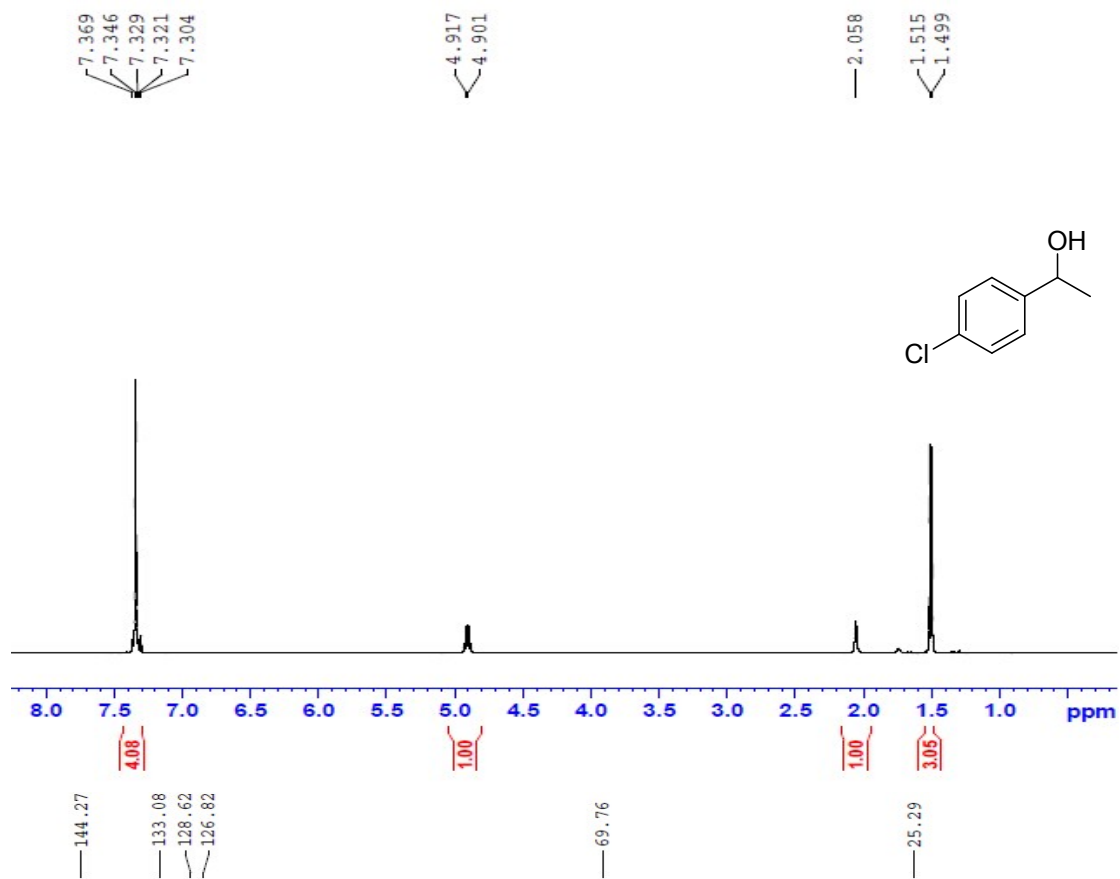
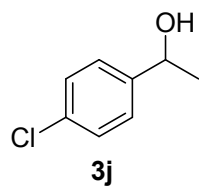
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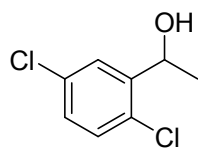




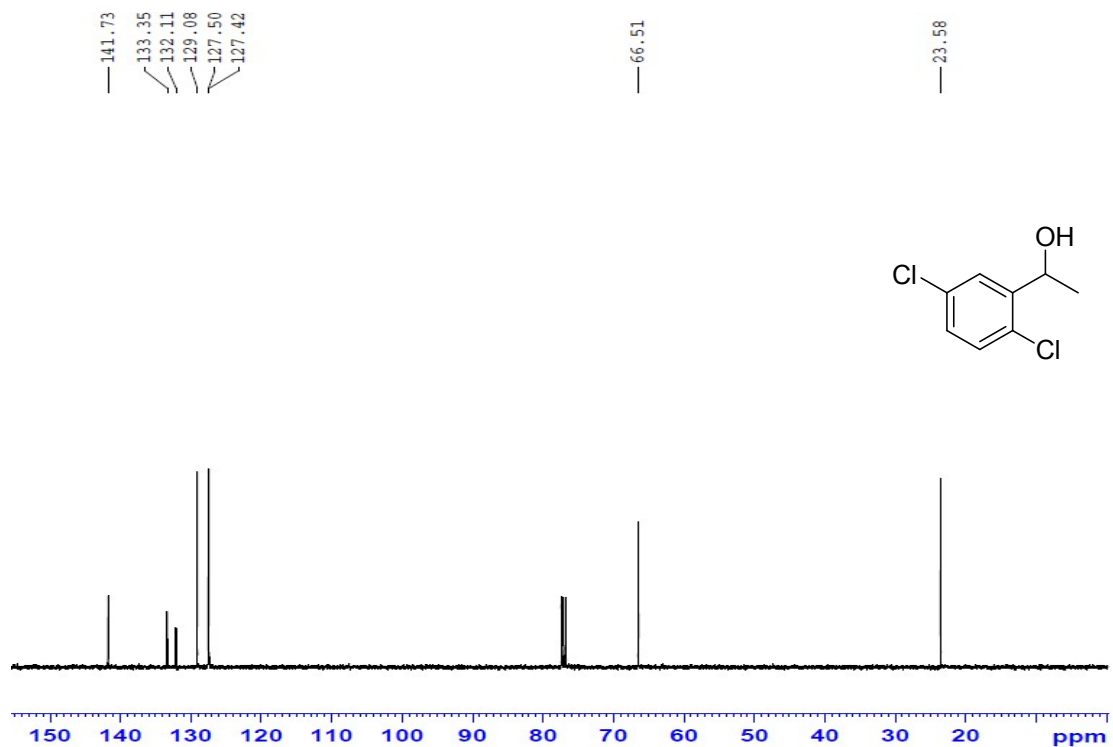
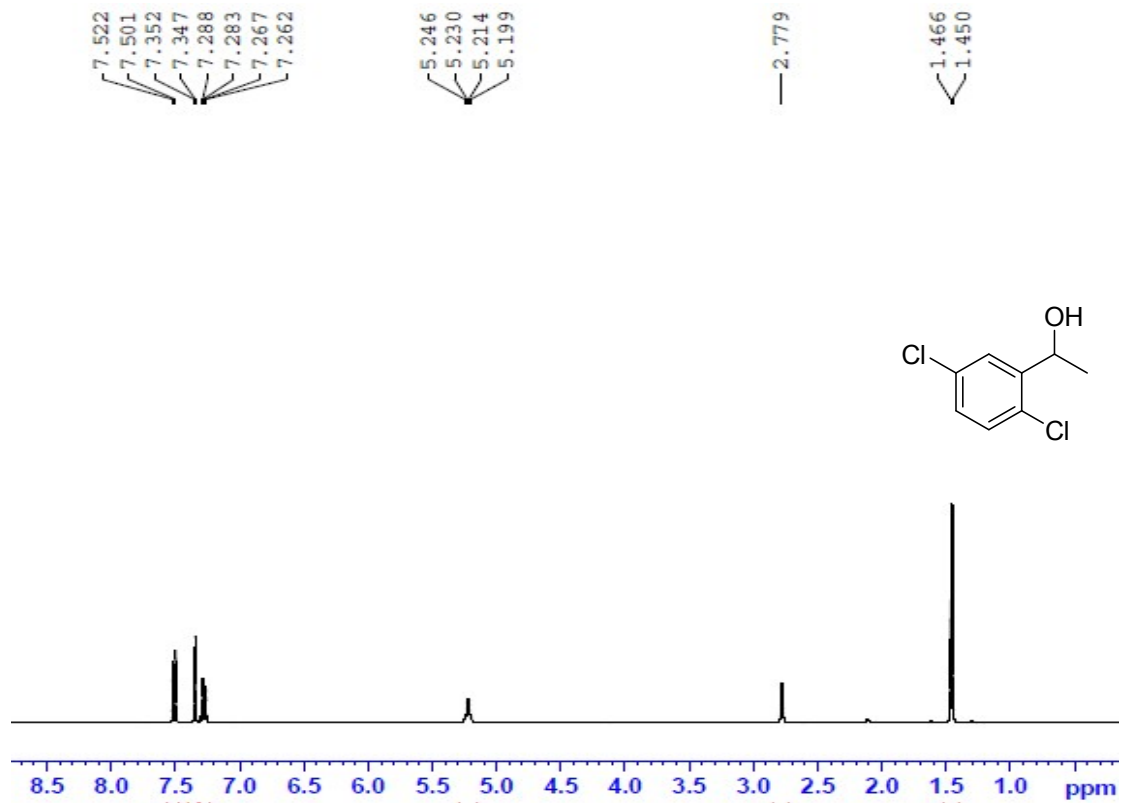
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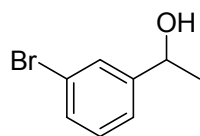




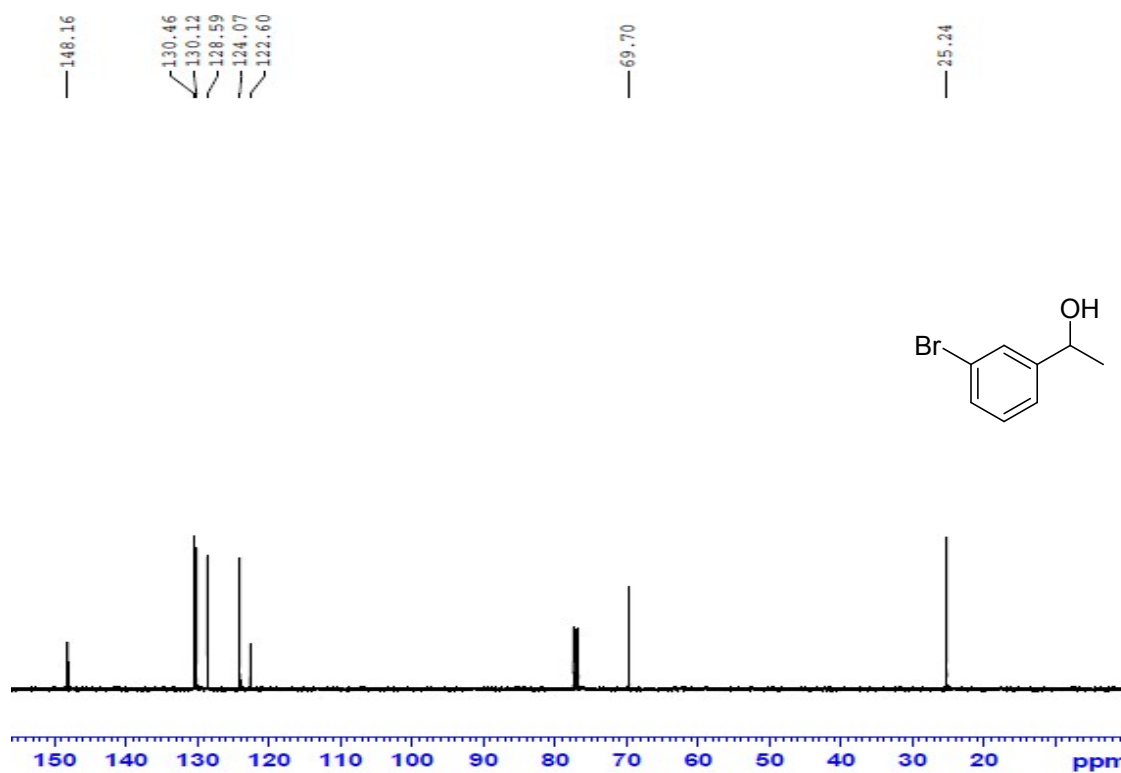
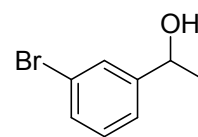
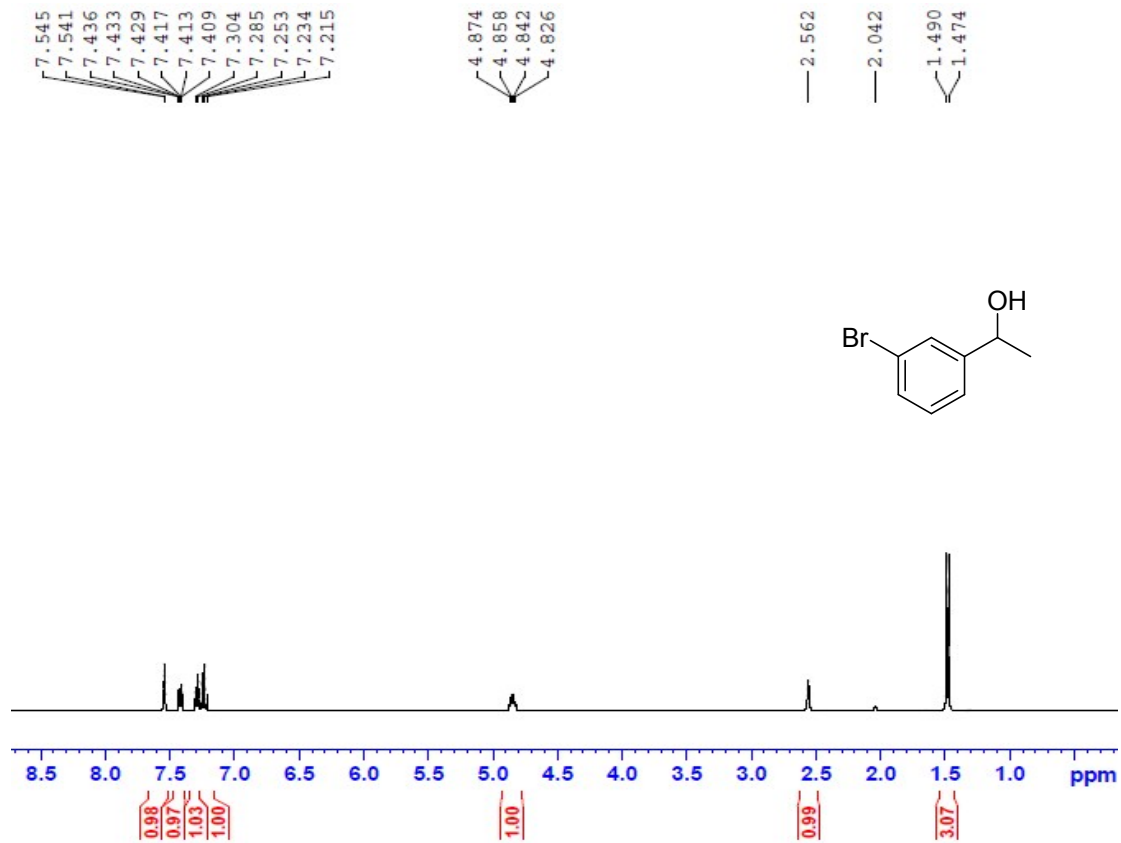


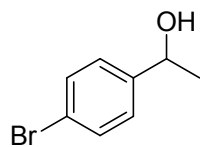
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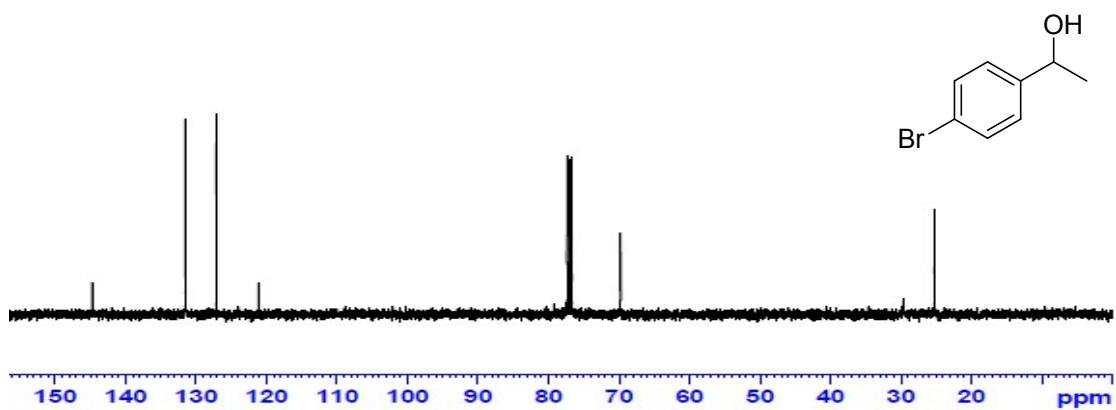
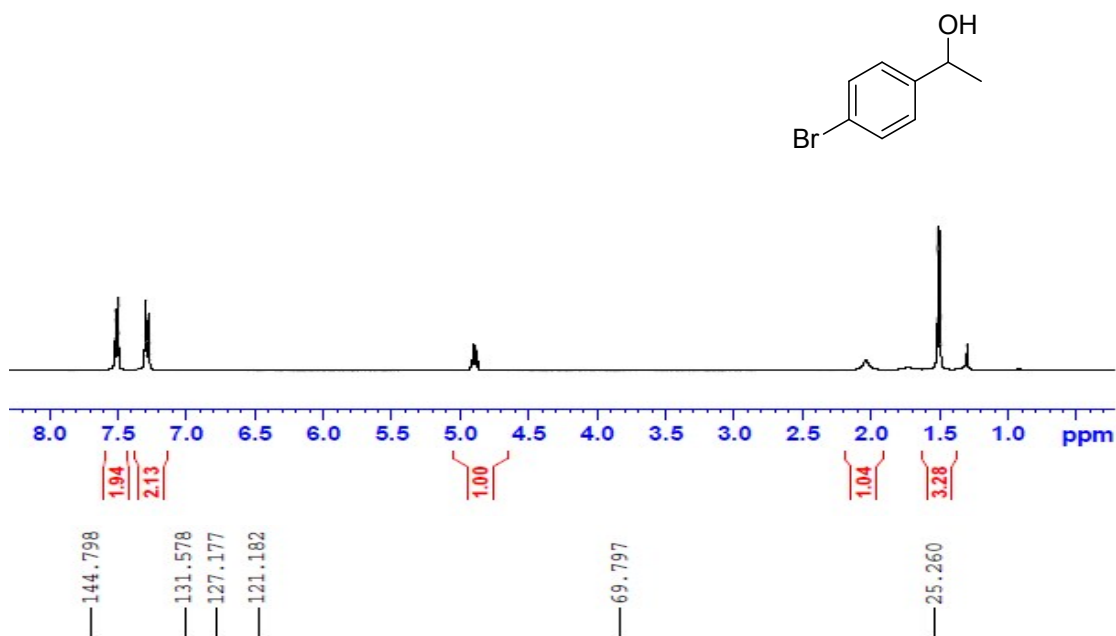
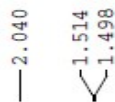
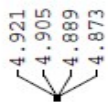
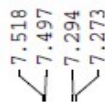


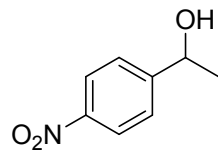
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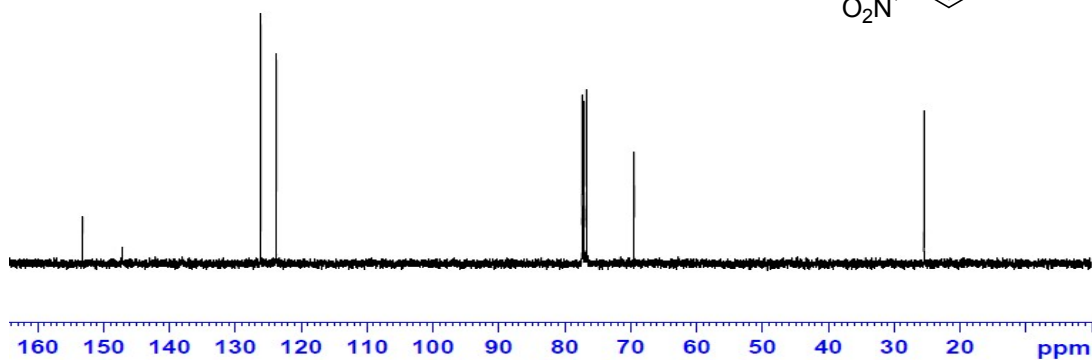
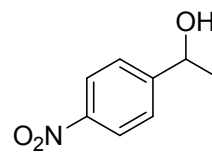
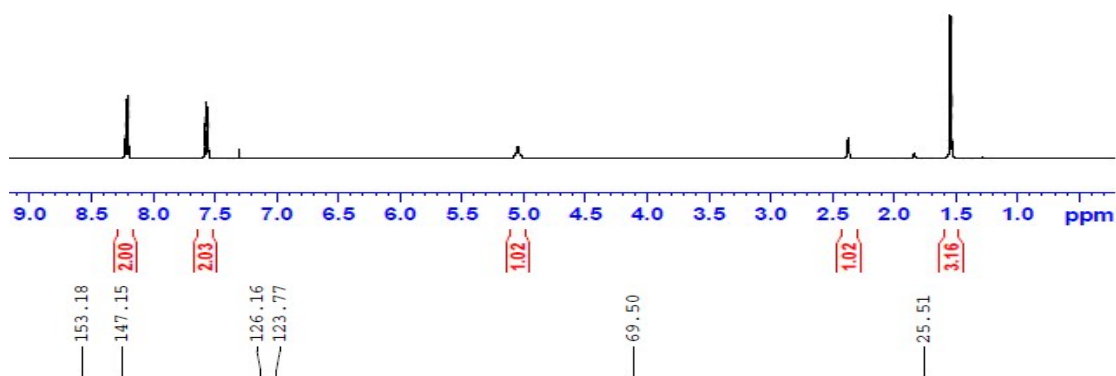
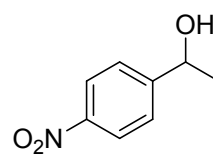
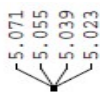
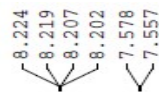


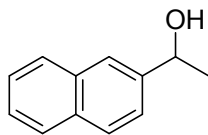
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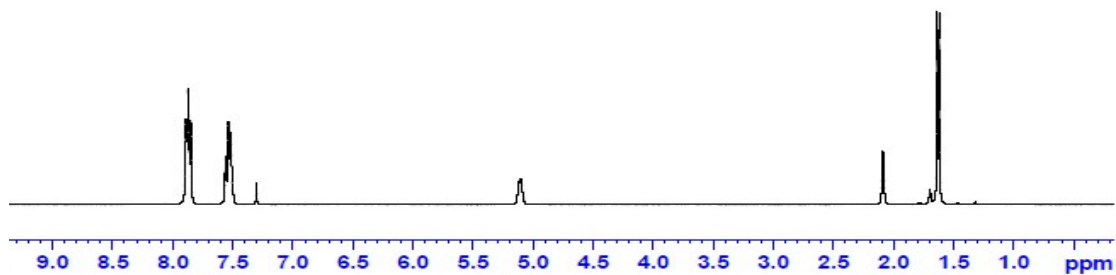
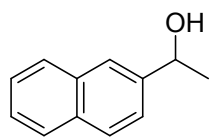
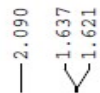
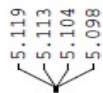
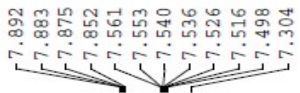


3n





3o



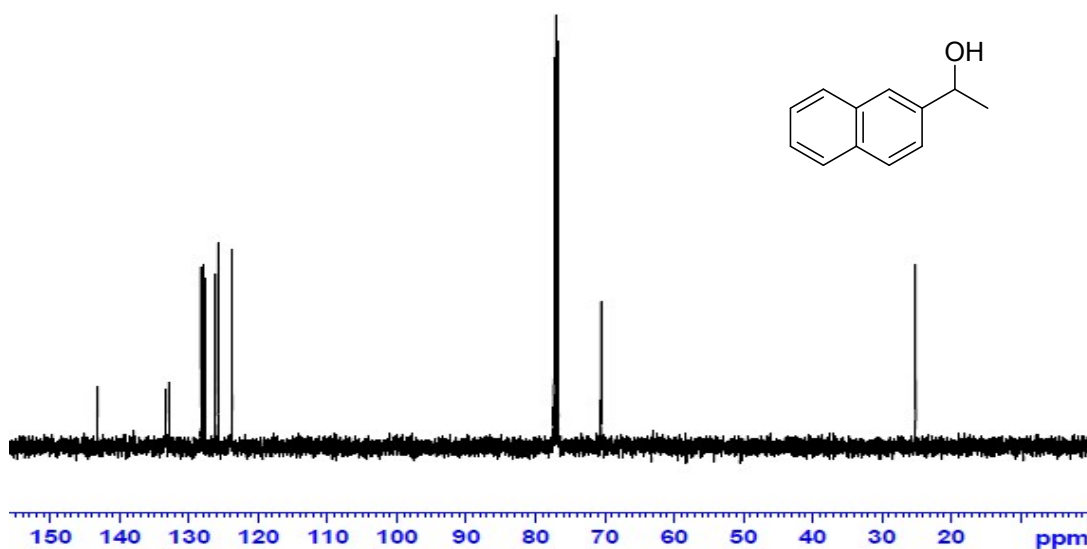
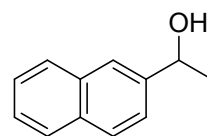
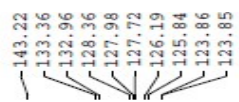
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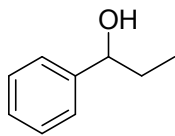
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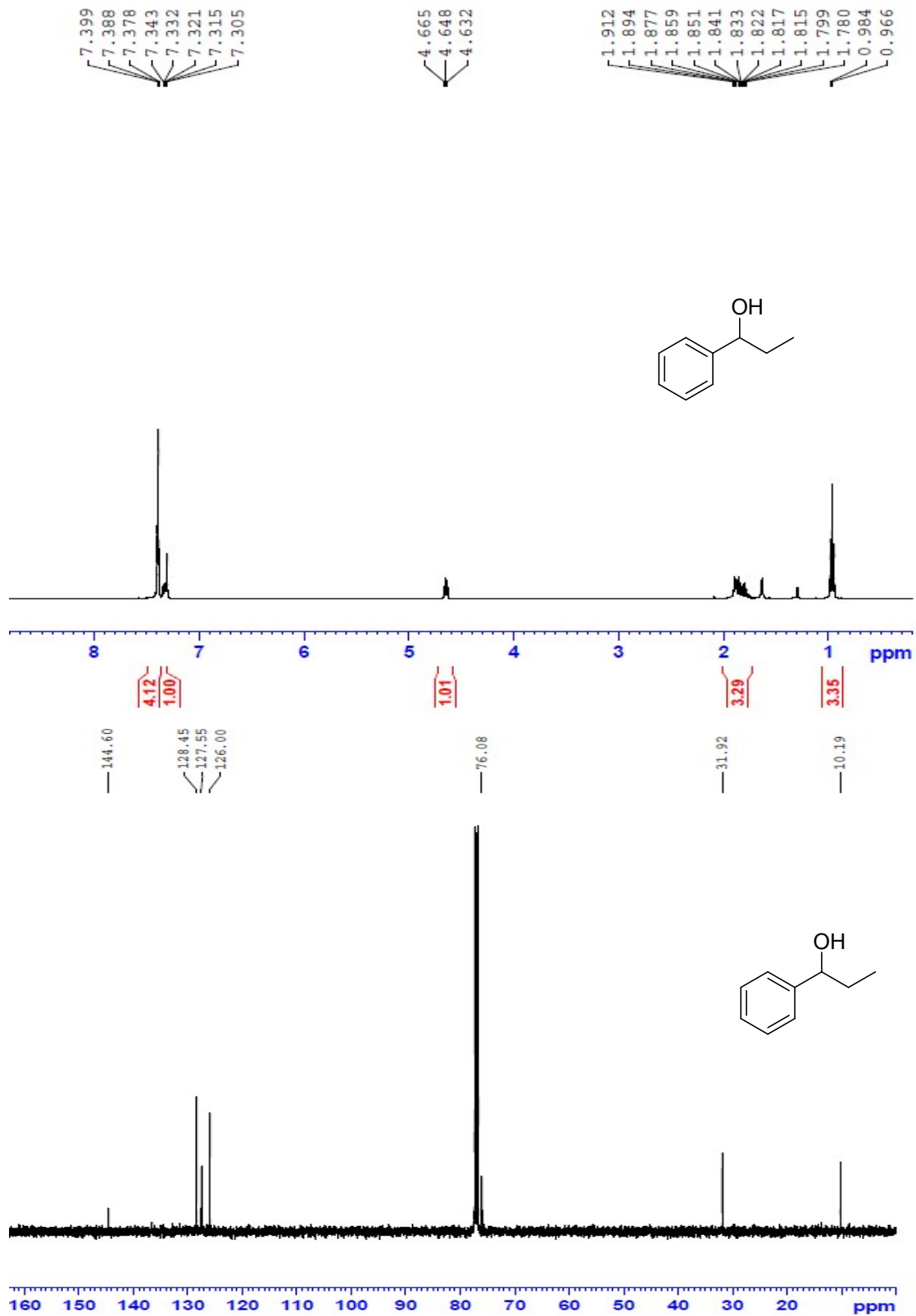
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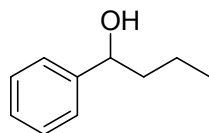
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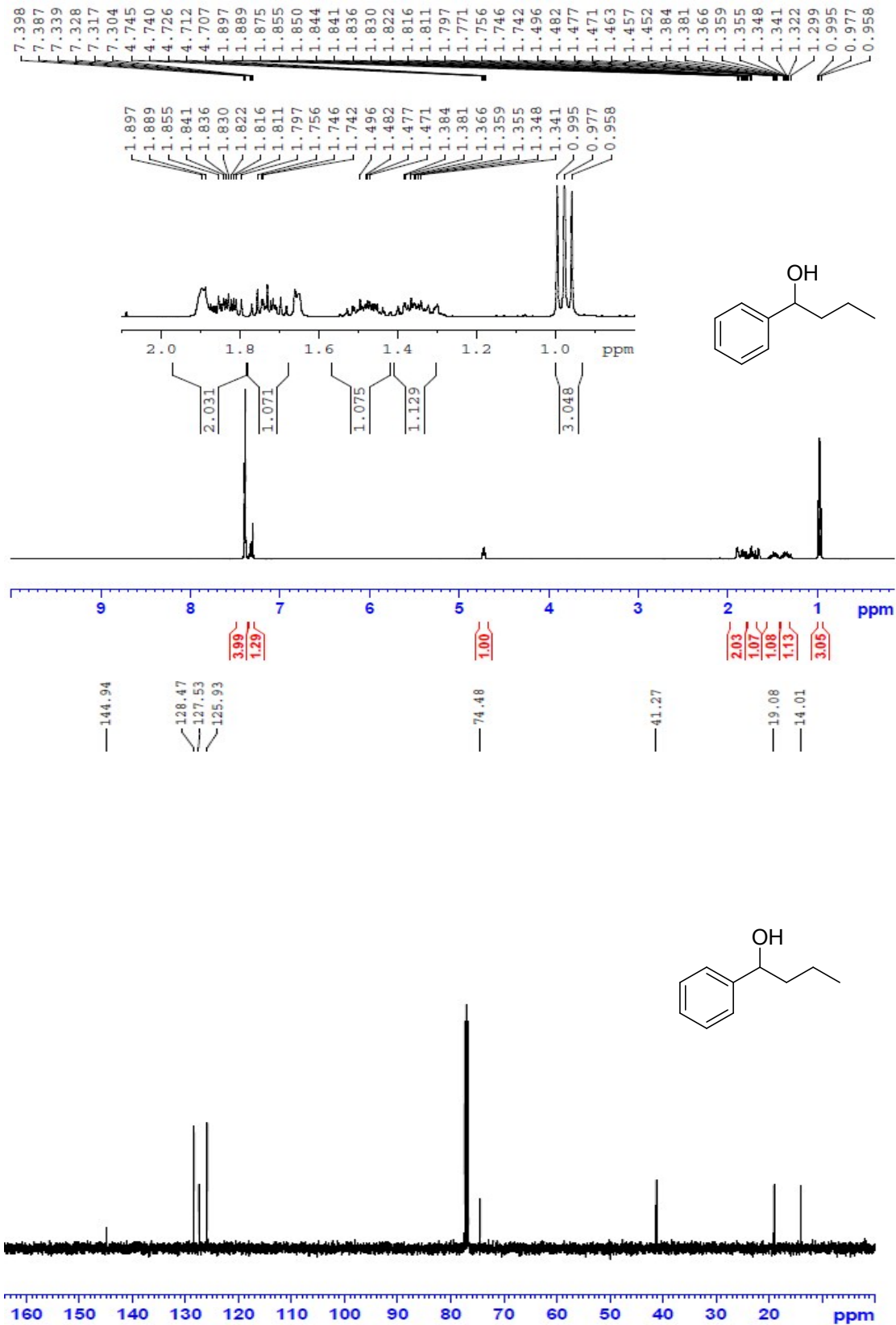


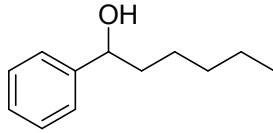
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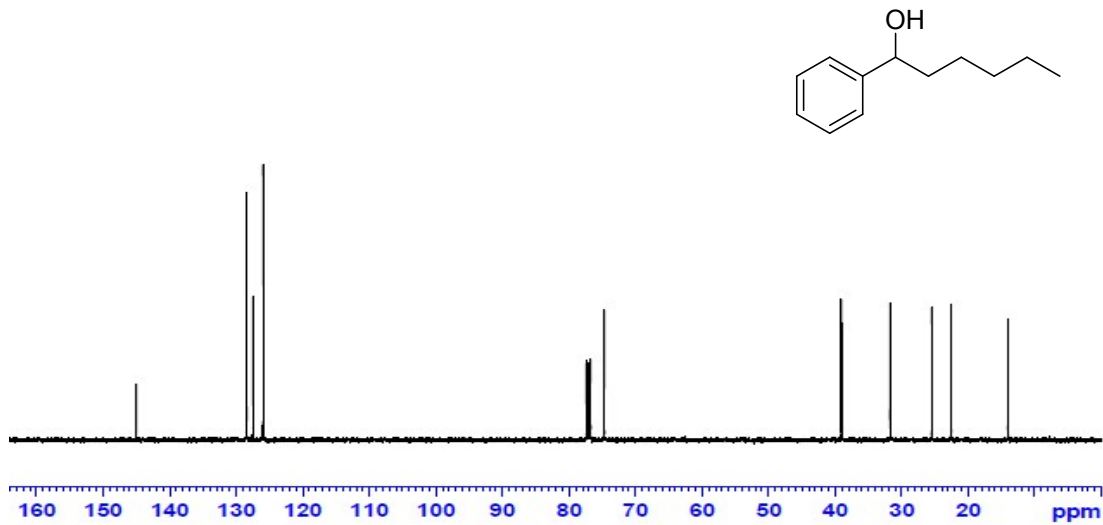
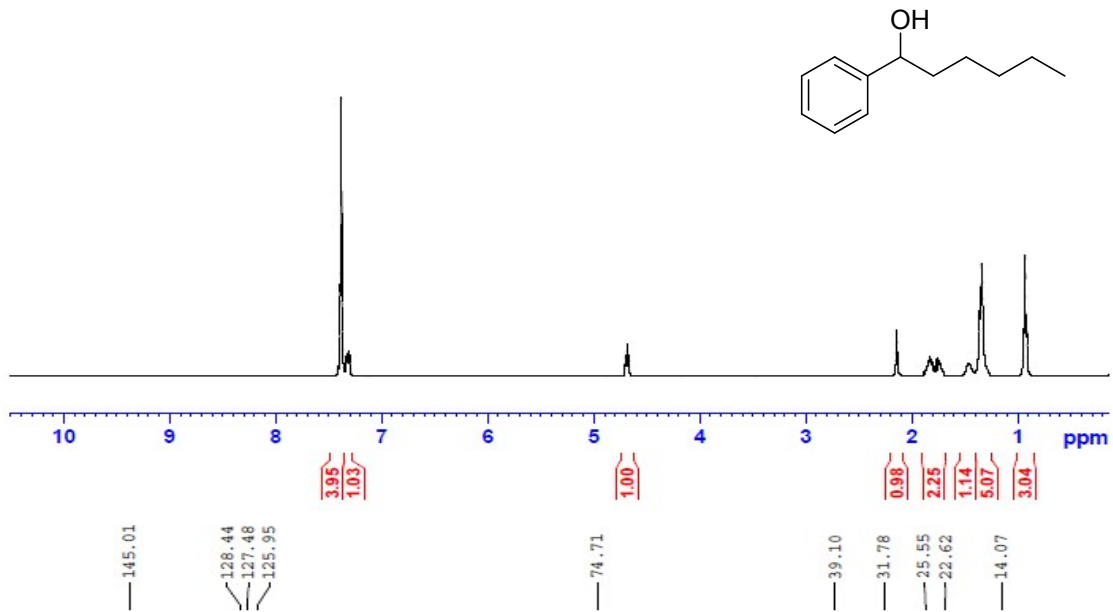
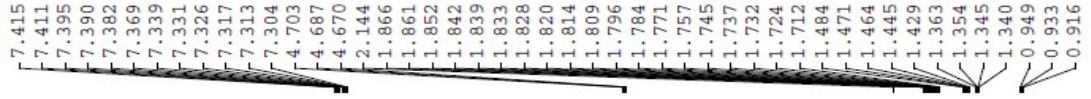


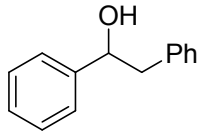
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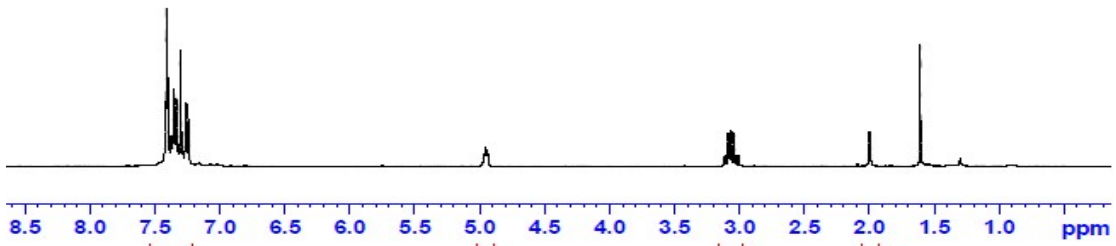
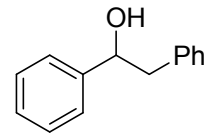
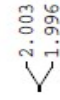
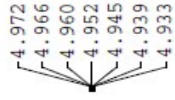
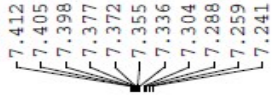


3r





3s

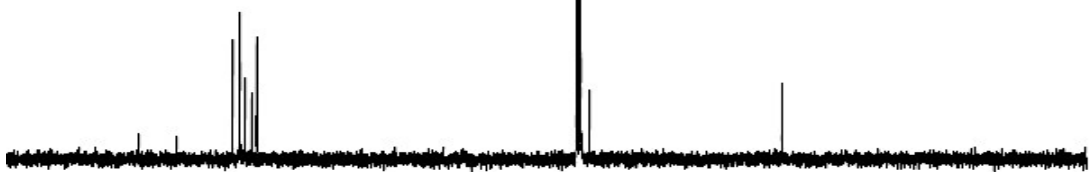
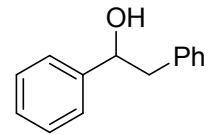
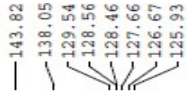


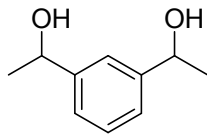
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1.00

2.03

0.97





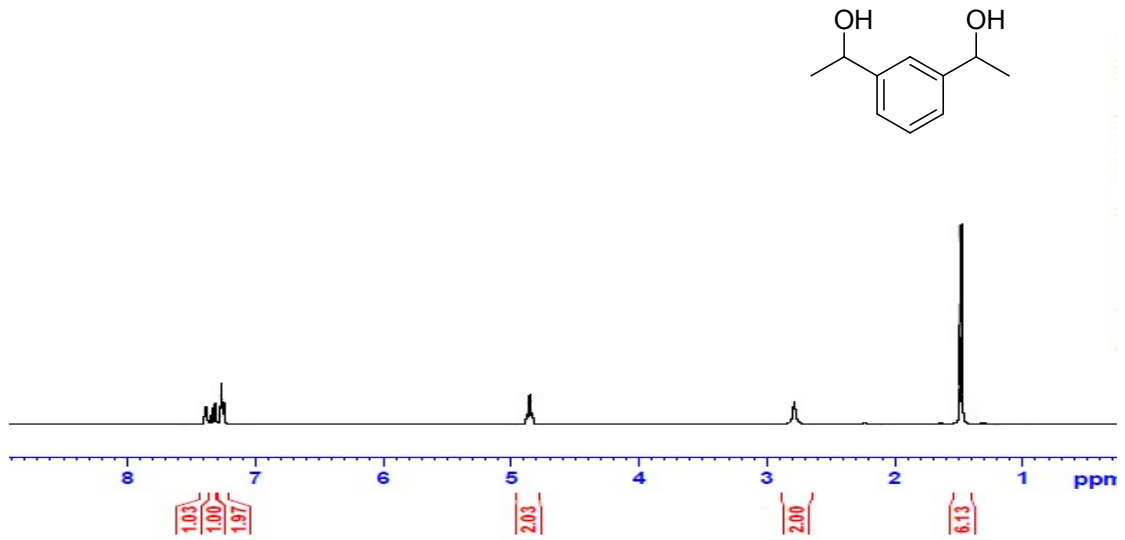
3t

7.393
7.378
7.350
7.330
7.313
7.304
7.265
7.247
7.244

4.881
4.865
4.849
4.833

2.789

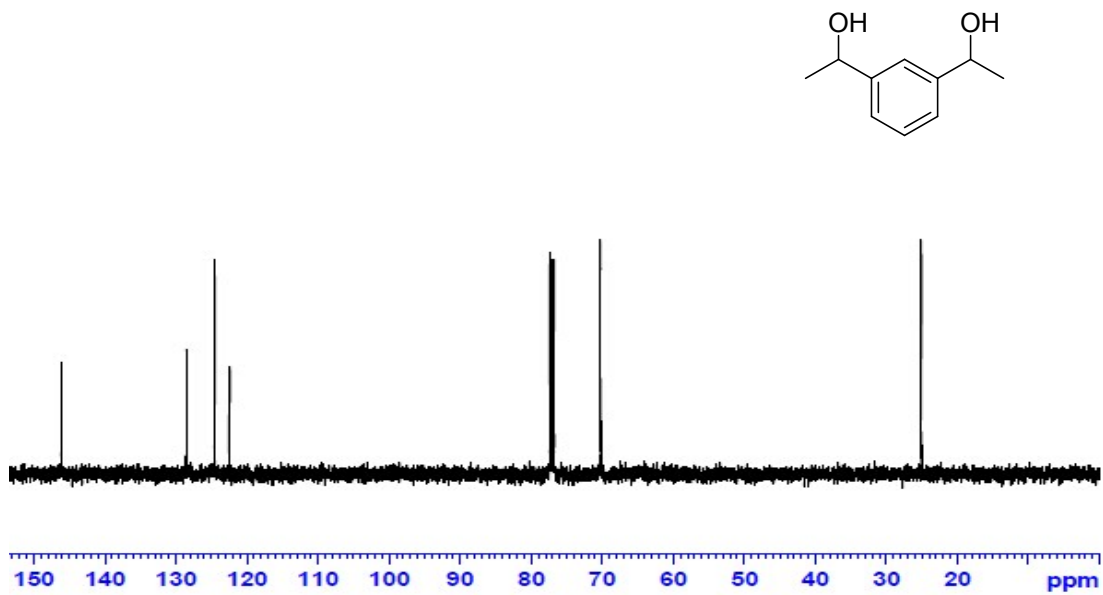
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1.478

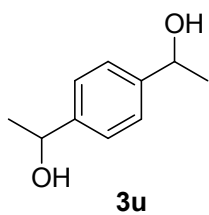


146.13
146.10
128.56
128.55
124.56
124.52
122.51
122.39

70.29
70.26

25.15
25.10

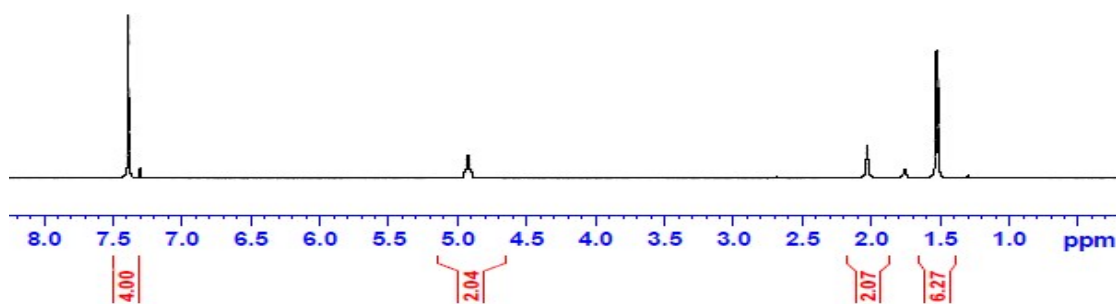
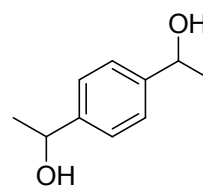




7.389

4.951
4.935
4.919
4.903

2.033
1.535
1.519

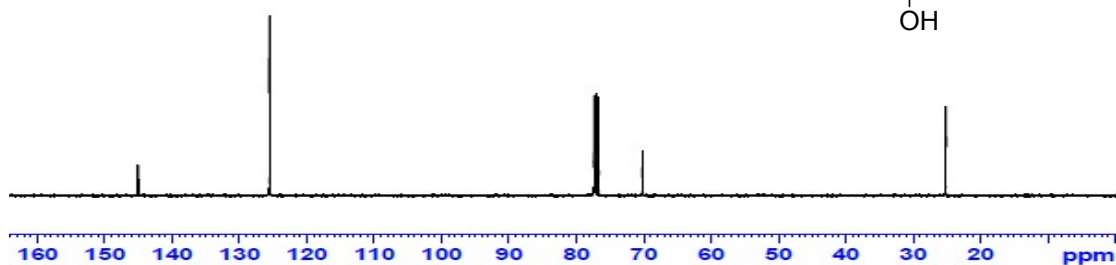
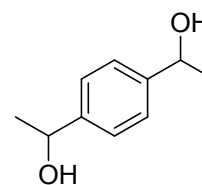


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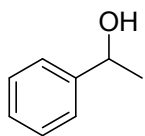
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70.188
70.167

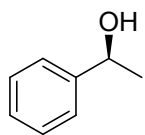
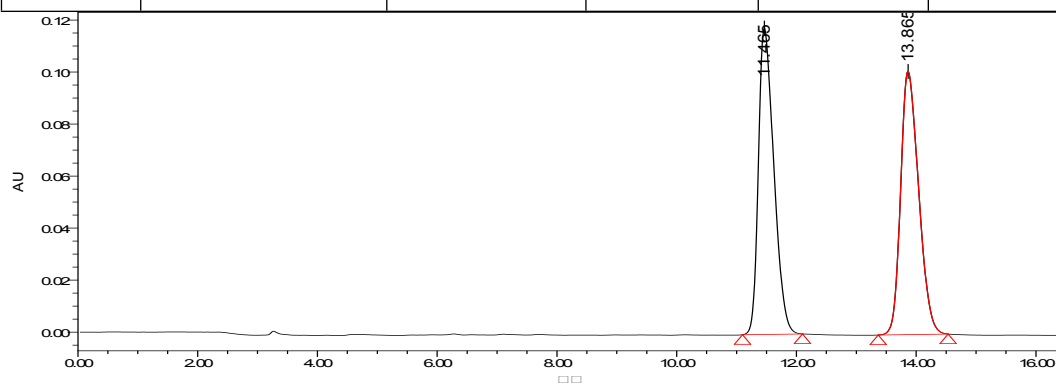
25.158

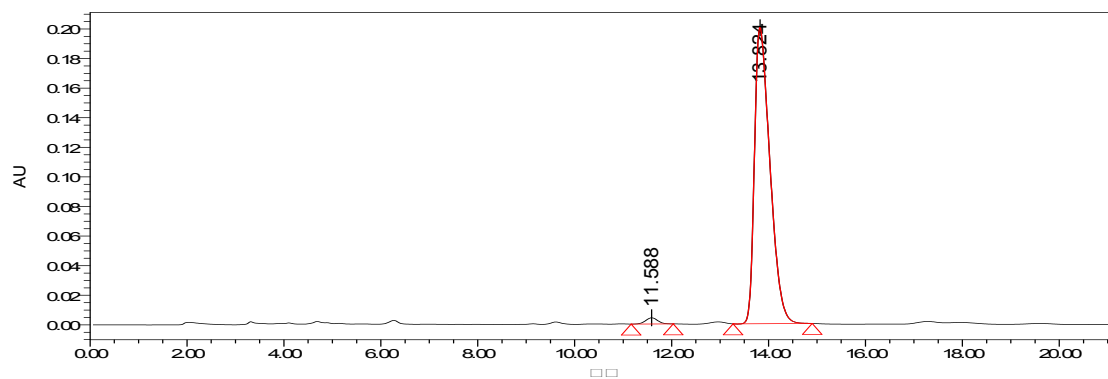


8. HPLC Spectra of the Products

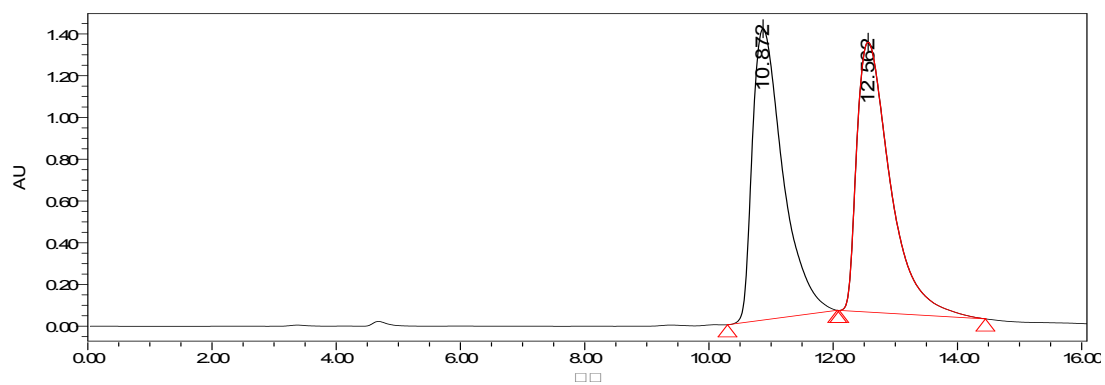
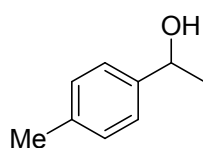


Peak	Ret Time [min]	Area	% Area	Height	Type
1	11.465	2112025	50.01	117887	bb
2	13.865	2117372	49.99	101264	bb

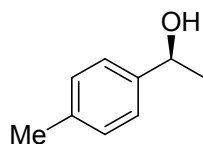


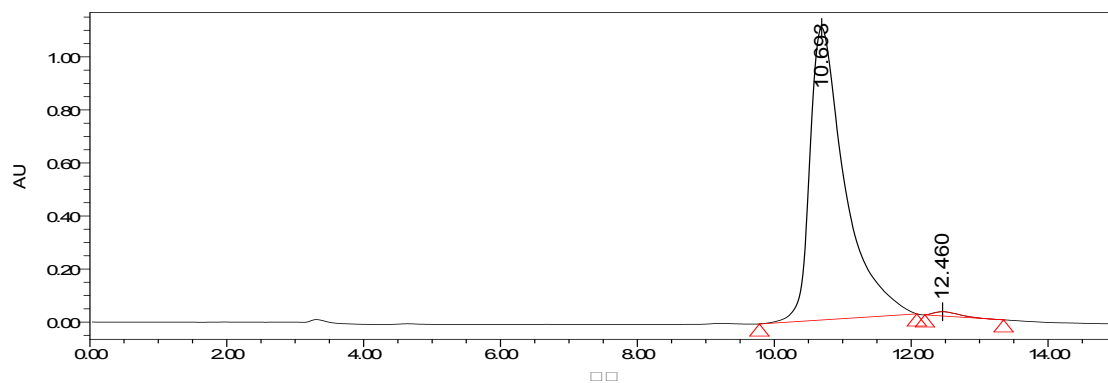


Peak	Ret Time [min]	Area	% Area	Height	Type
1	11.588	71718	1.59	4175	bb
2	13.824	4439245	98.41	200542	bb

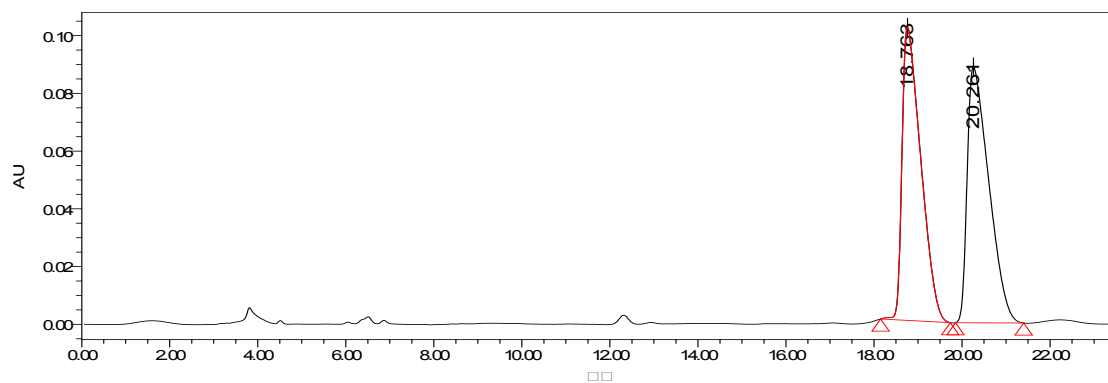
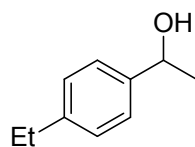


Peak	Ret Time [min]	Area	% Area	Height	Type
1	10.872	47797307	49.64	1396857	bb
2	12.562	48496006	50.36	1293156	bb

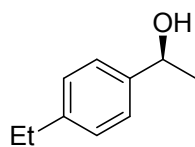


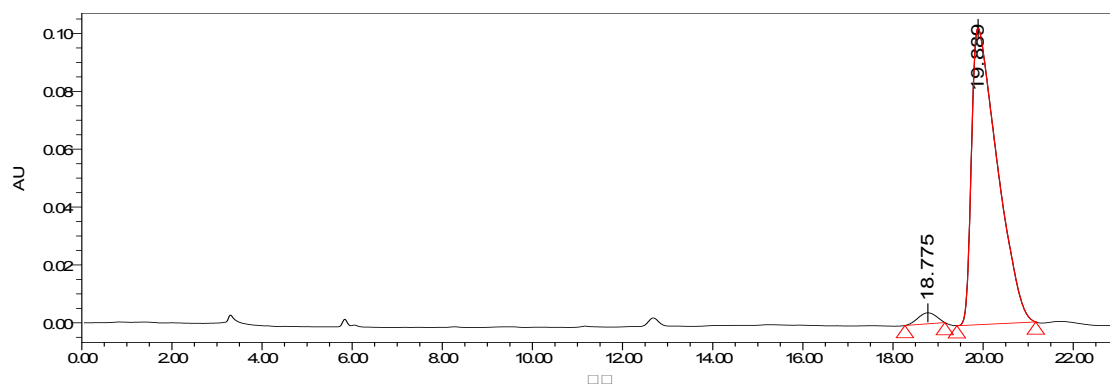


Peak	Ret Time [min]	Area	% Area	Height	Type
1	10.693	39225918	98.96	1103203	bb
2	12.460	414183	1.04	16069	bb

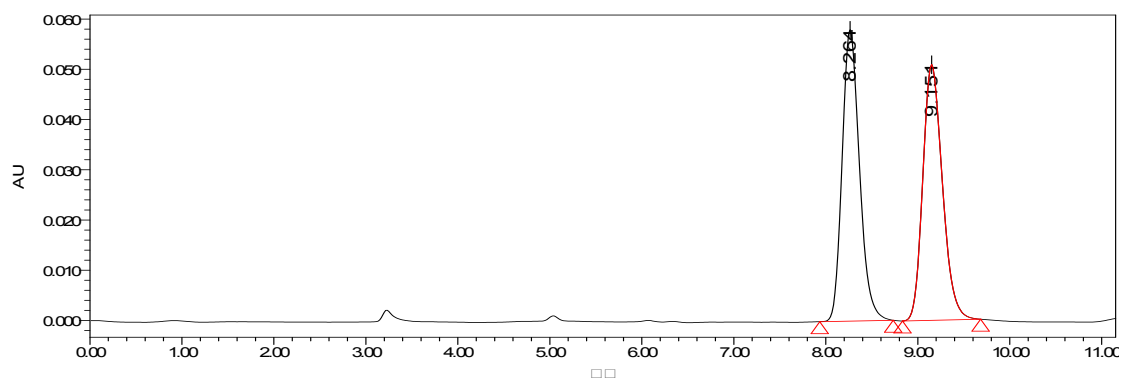
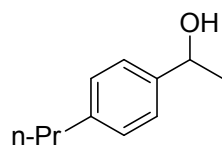


Peak	Ret Time [min]	Area	% Area	Height	Type
1	18.763	2965481	49.56	101097	bb
2	20.261	3017731	50.44	88696	bb

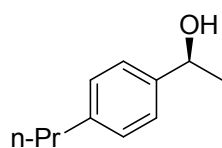


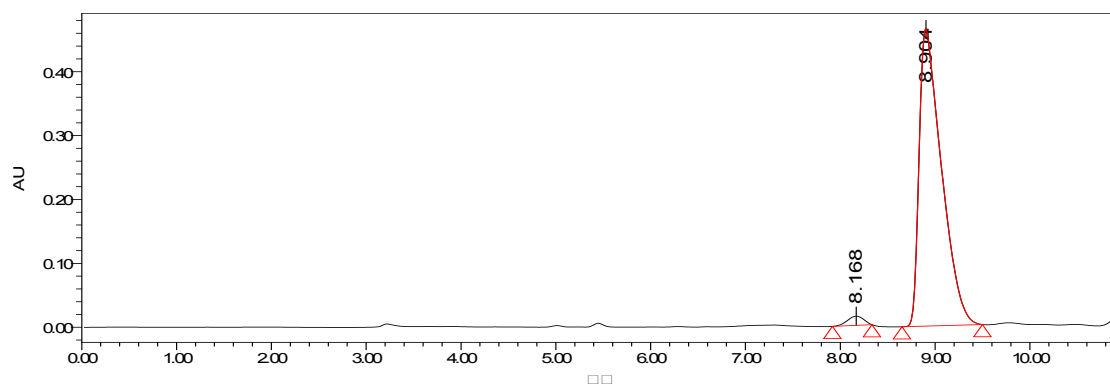


	Ret Time [min]	Area	% Area	Height	Type
1	18.775	142626	3.38	4444	bb
2	19.889	4078714	96.62	102607	bb

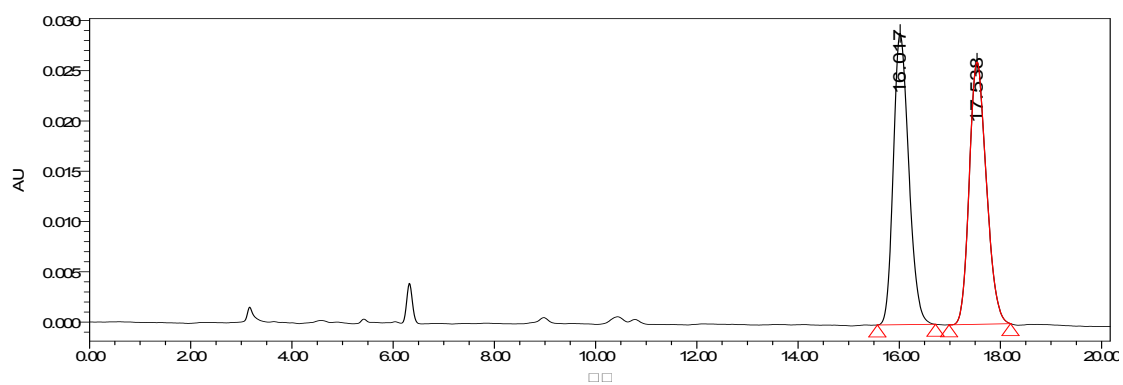
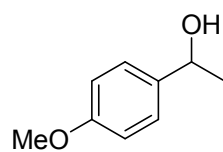


Peak	Ret Time [min]	Area	% Area	Height	Type
1	8.264	763658	49.94	58071	bb
2	9.151	765462	50.06	51064	bb

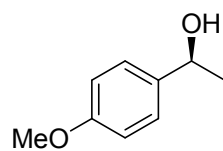


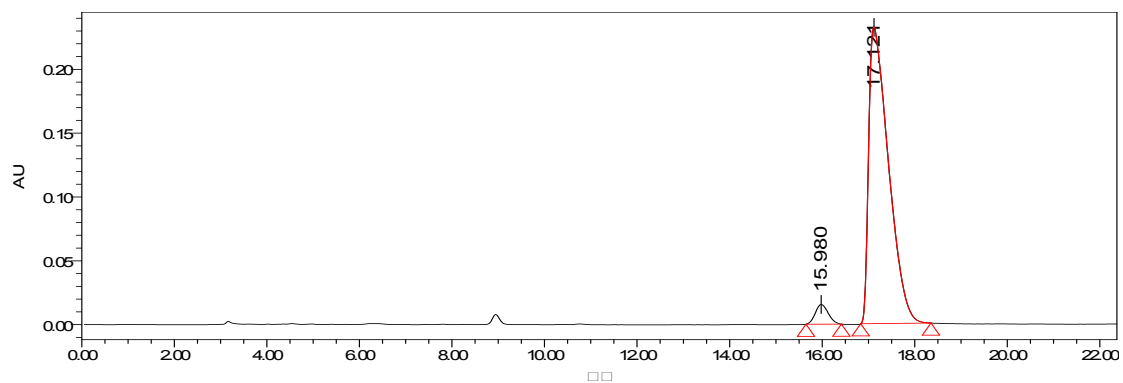


Peak	Ret Time [min]	Area	% Area	Height	Type
1	8.168	213466	2.74	16206	bb
2	8.904	7588006	97.26	466505	bb

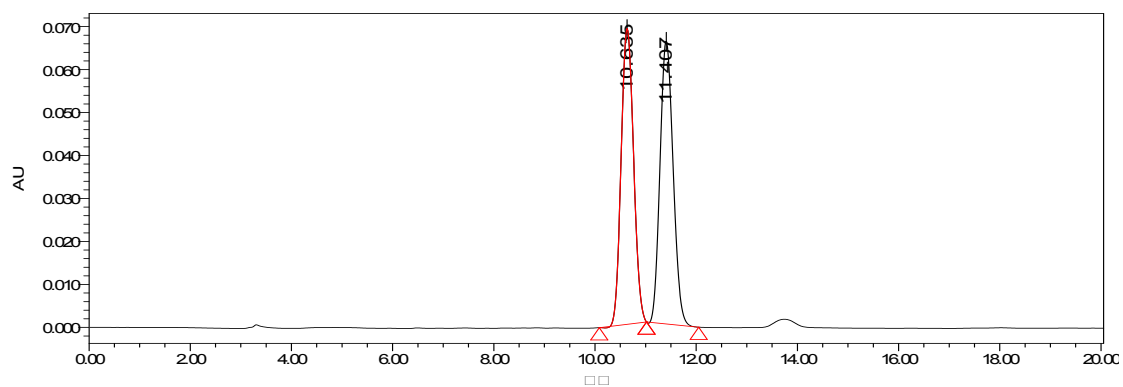
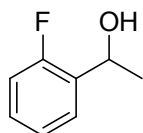


Peak	Ret Time [min]	Area	% Area	Height	Type
1	16.017	613243	49.81	28964	bb
2	17.538	617984	50.19	26171	bb

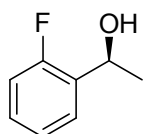


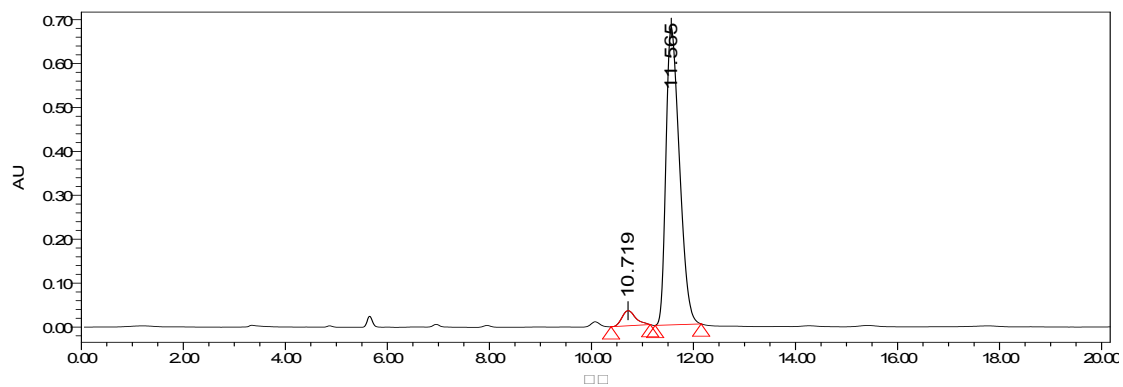


Peak	Ret Time [min]	Area	% Area	Height	Type
1	15.980	291644	4.04	15260	bb
2	17.121	6926491	95.96	232829	bb

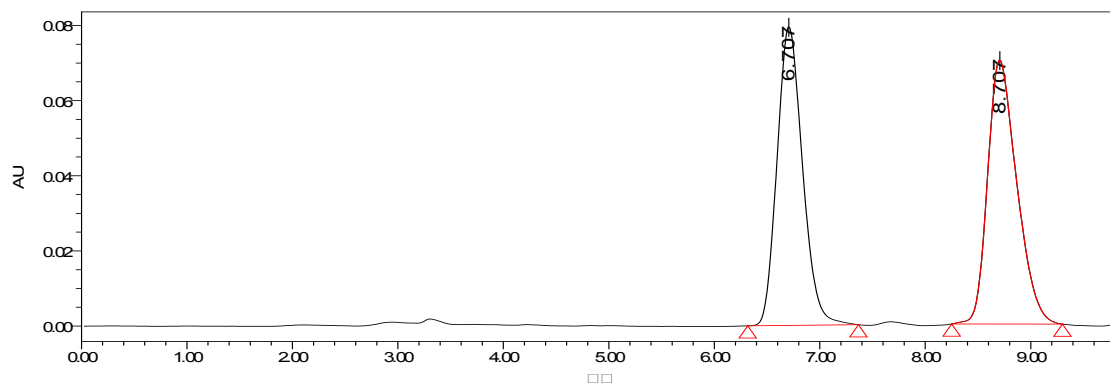
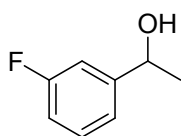


Peak	Ret Time [min]	Area	% Area	Height	Type
1	10.635	1175759	49.76	68837	bb
2	11.407	1187210	50.24	65875	bb

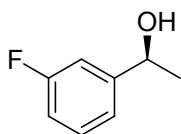


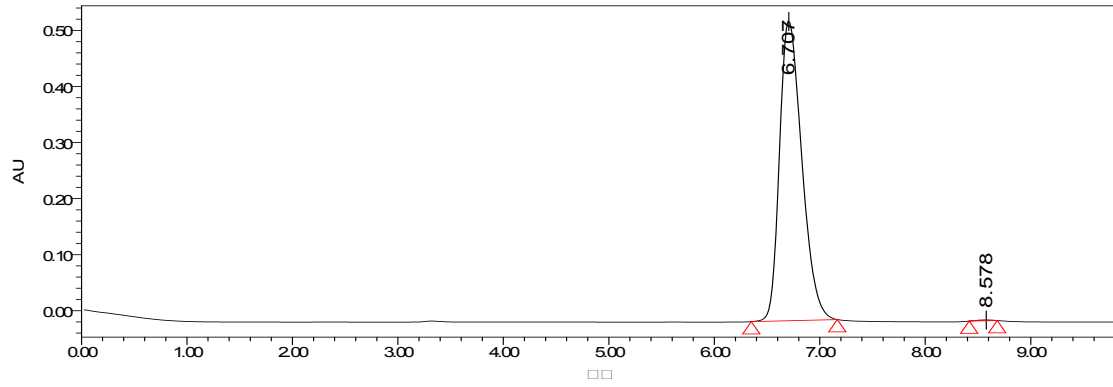


Peak	Ret Time [min]	Area	% Area	Height	Type
1	10.719	636640	4.81	34249	bb
2	11.565	12606704	95.19	678865	bb

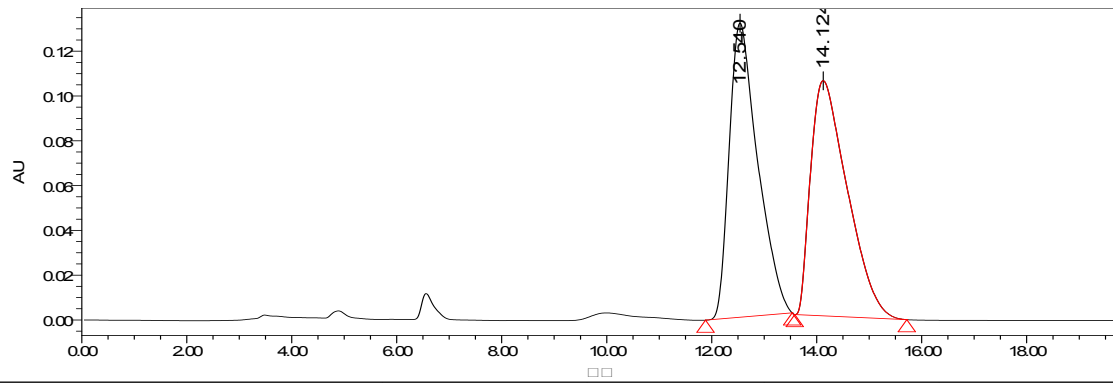
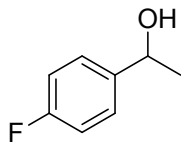


Peak	Ret Time [min]	Area	% Area	Height	Type
1	6.707	1334049	49.68	79580	bb
2	8.707	1351358	50.32	70314	bb

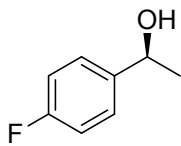


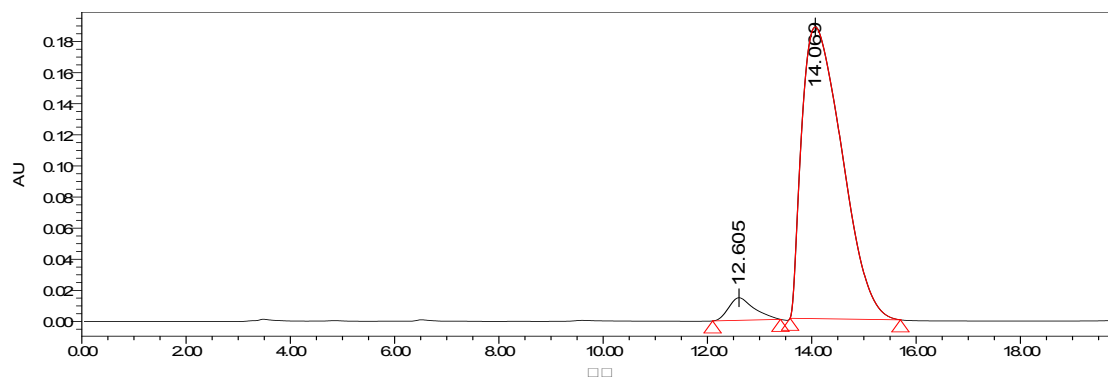


Peak	Ret Time [min]	Area	% Area	Height	Type
1	6.707	7926951	99.78	537269	bb
2	8.577	17115	0.22	1494	bb

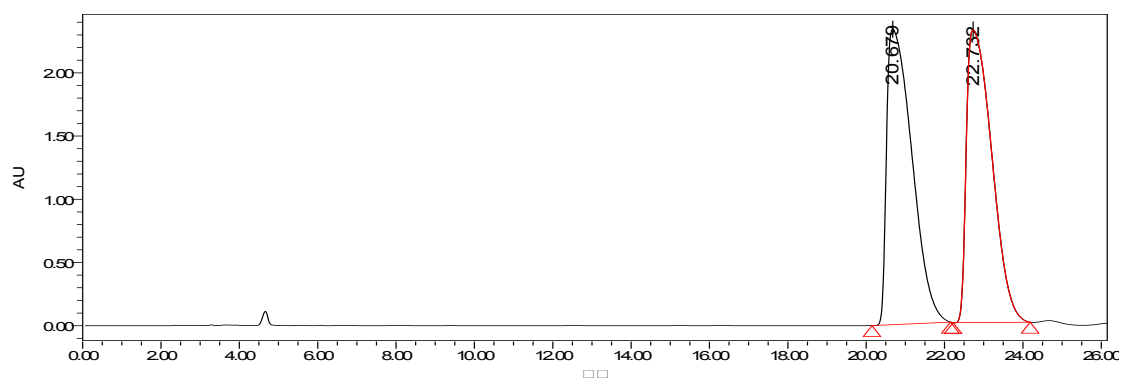
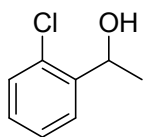


Peak	Ret Time [min]	Area	% Area	Height	Type
1	12.540	5000295	49.76	131758	bb
2	14.124	5049143	50.24	104537	bb

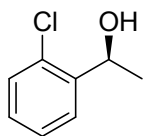


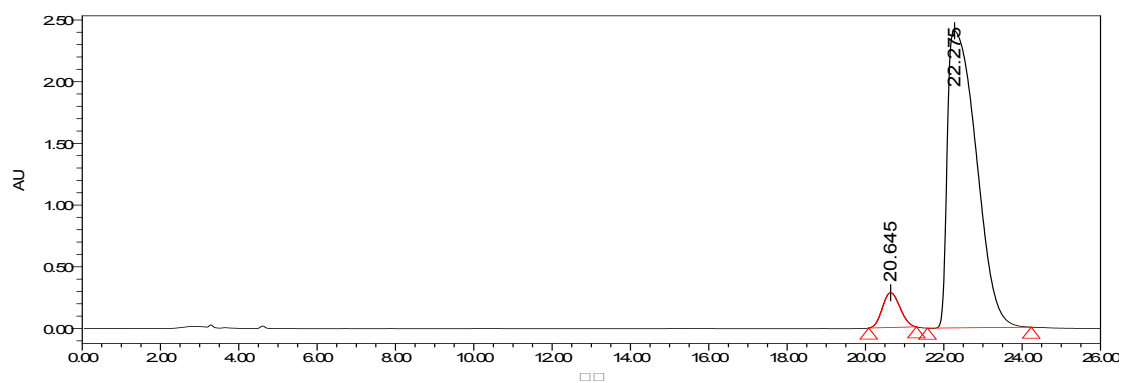


Peak	Ret Time [min]	Area	% Area	Height	Type
1	12.605	500459	4.69	14593	bb
2	14.069	10167108	95.31	188649	bb

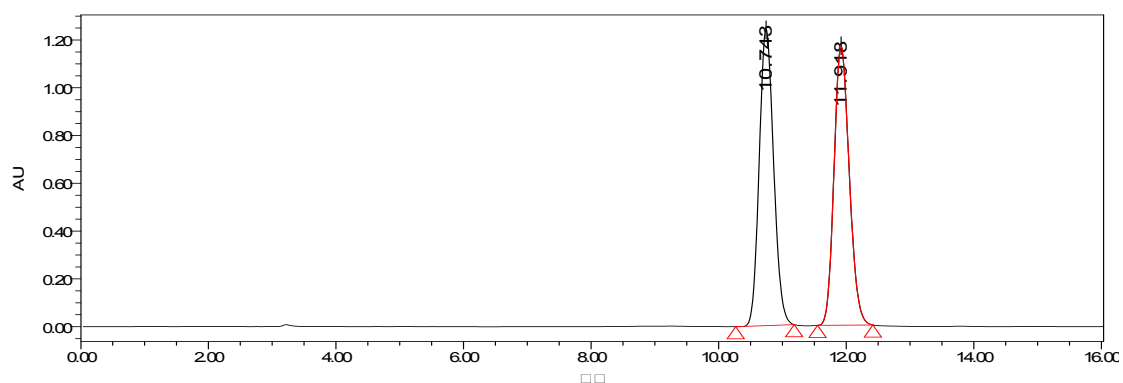
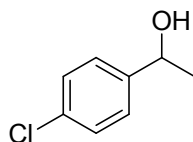


Peak	Ret Time [min]	Area	% Area	Height	Type
1	20.679	104915368	50.37	2337424	bb
2	22.732	103378528	49.63	2308887	bb

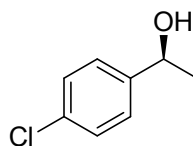


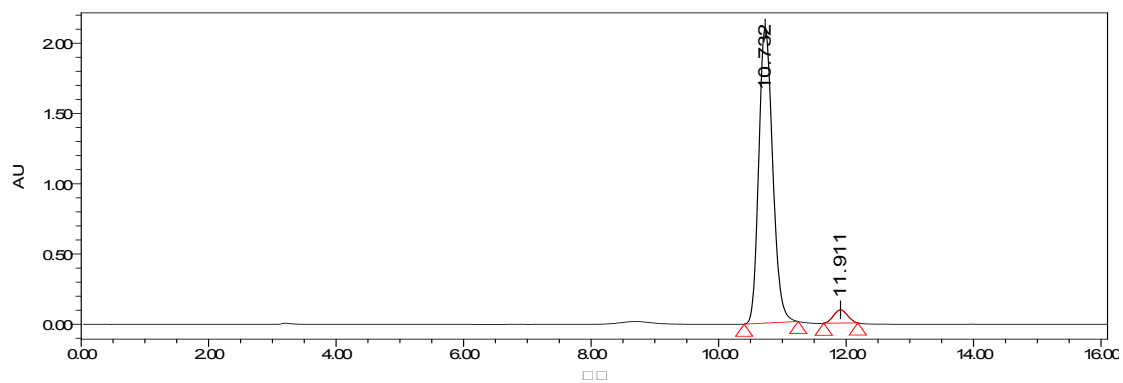


Peak	Ret Time [min]	Area	% Area	Height	Type
1	20.645	8838023	6.71	282273	bb
2	22.275	122951433	93.29	2408508	bb

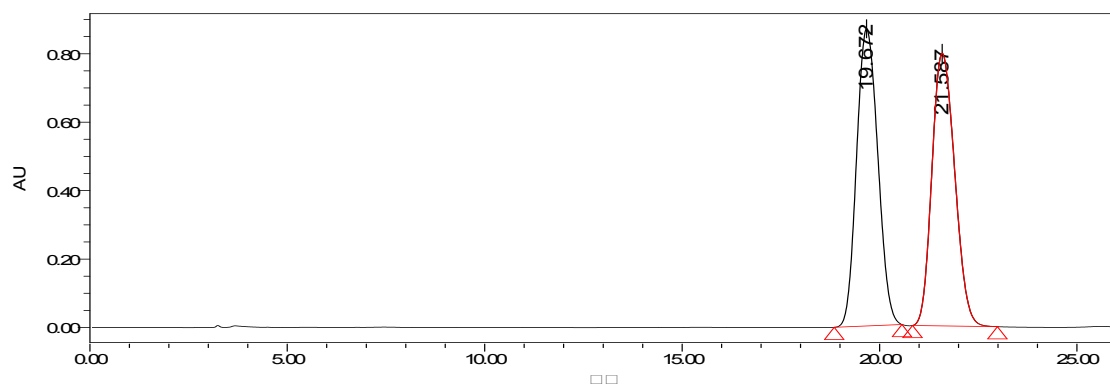
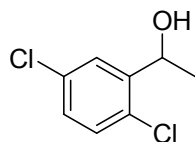


Peak	Ret Time [min]	Area	% Area	Height	Type
1	10.743	19596416	50.17	1242675	bb
2	11.918	19462000	49.83	1170966	bb

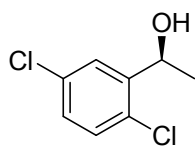


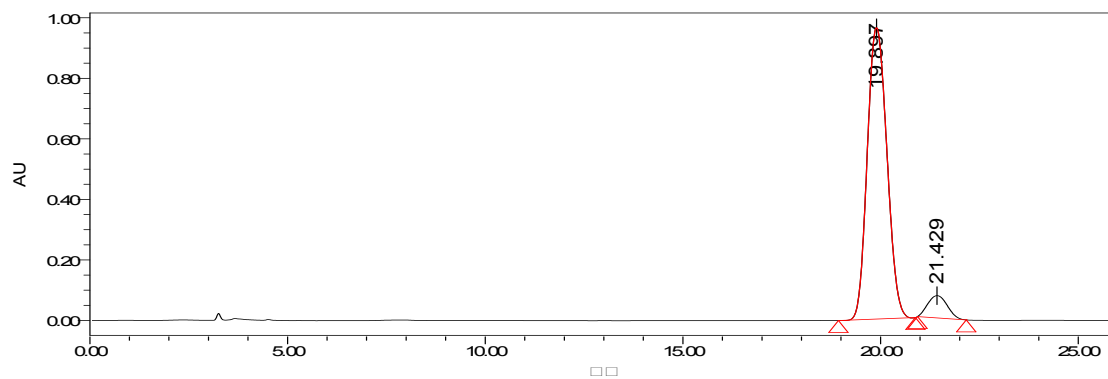


Peak	Ret Time [min]	Area	% Area	Height	Type
1	10.732	31867460	95.74	2101674	bb
2	11.911	1417644	4.26	93739	bb

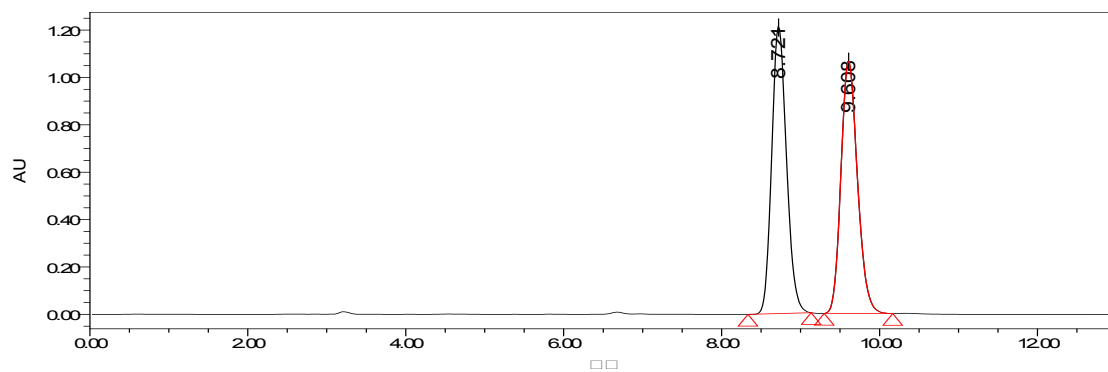
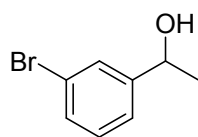


Peak	Ret Time [min]	Area	% Area	Height	Type
1	19.672	32428901	50.34	868765	bb
2	21.587	31986547	49.66	796697	bb

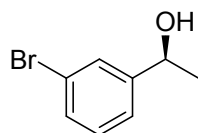


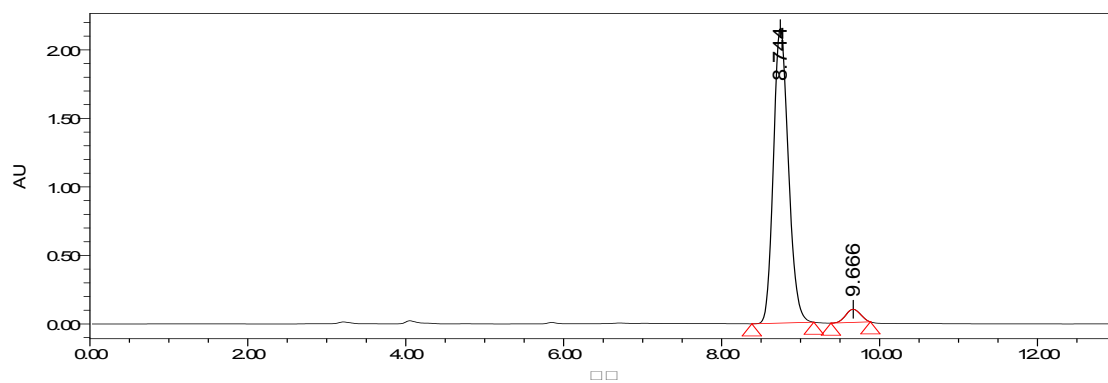


Peak	Ret Time [min]	Area	% Area	Height	Type
1	19.897	33194269	92.92	962608	bb
2	21.429	2527357	7.08	73709	bb

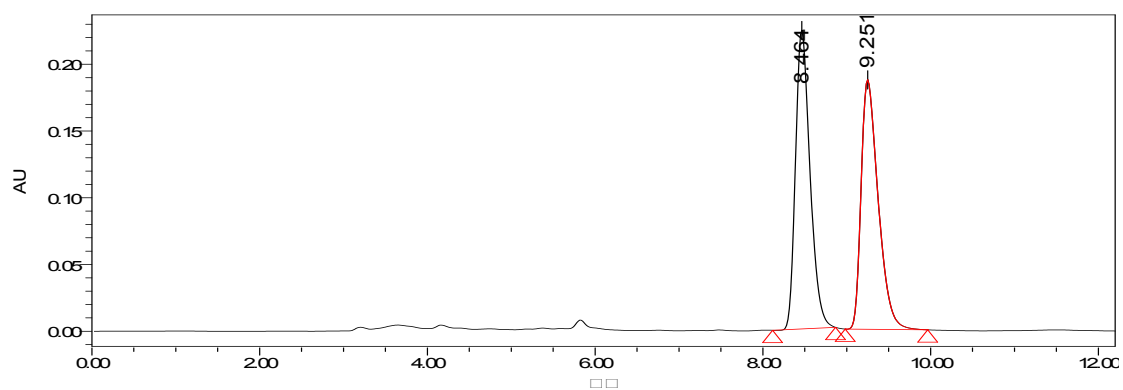
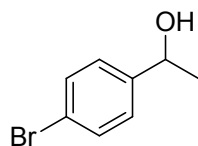


Peak	Ret Time [min]	Area	% Area	Height	Type
1	8.721	15787884	50.50	1212522	bb
2	9.608	15476214	49.50	1067116	bb

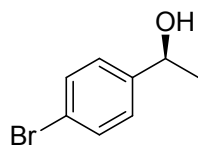


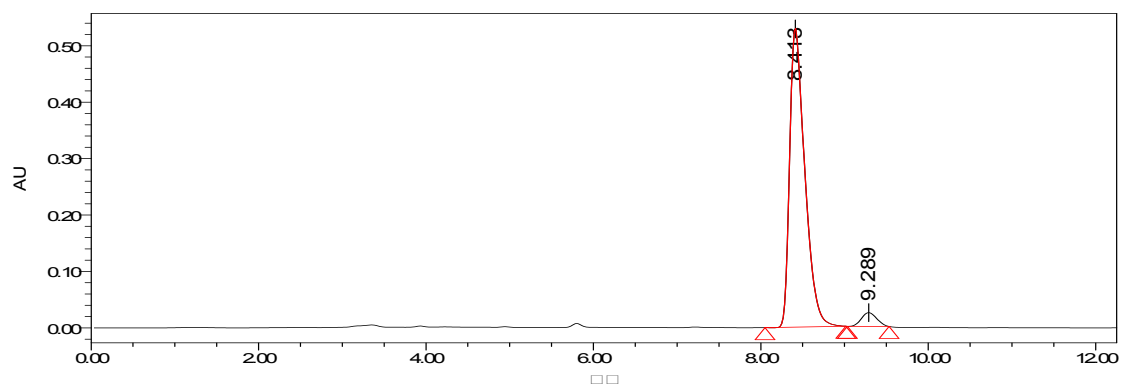


Peak	Ret Time [min]	Area	% Area	Height	Type
1	8.744	28360804	95.76	2155054	bb
2	9.666	1254970	4.24	96080	bb

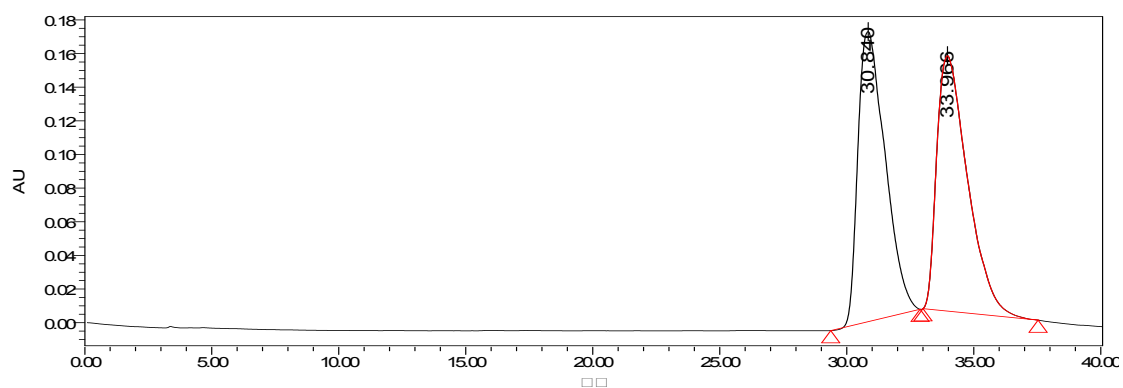
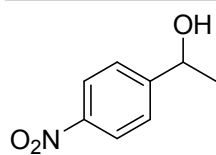


Peak	Ret Time [min]	Area	% Area	Height	Type
1	8.464	2696239	50.55	223904	bb
2	9.251	2637677	49.45	187004	bb

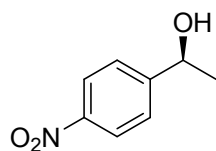


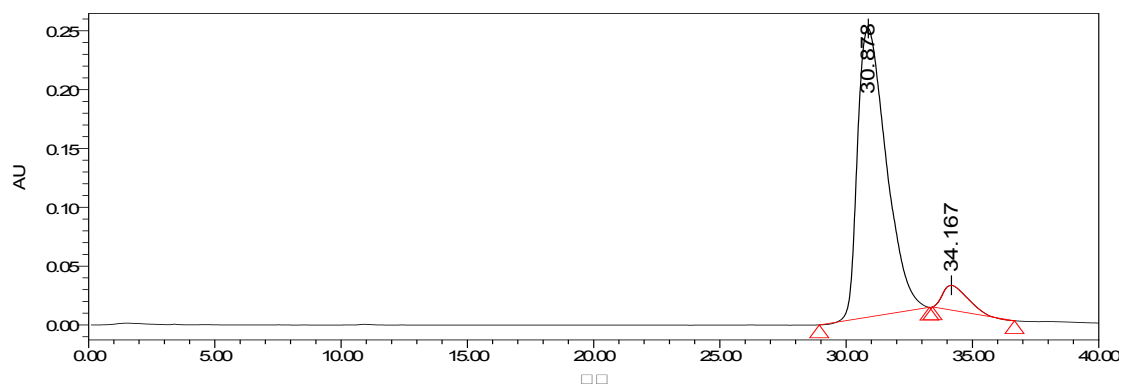


Peak	Ret Time [min]	Area	% Area	Height	Type
1	8.413	6675249	95.55	529580	bb
2	9.289	310669	4.45	24391	bb

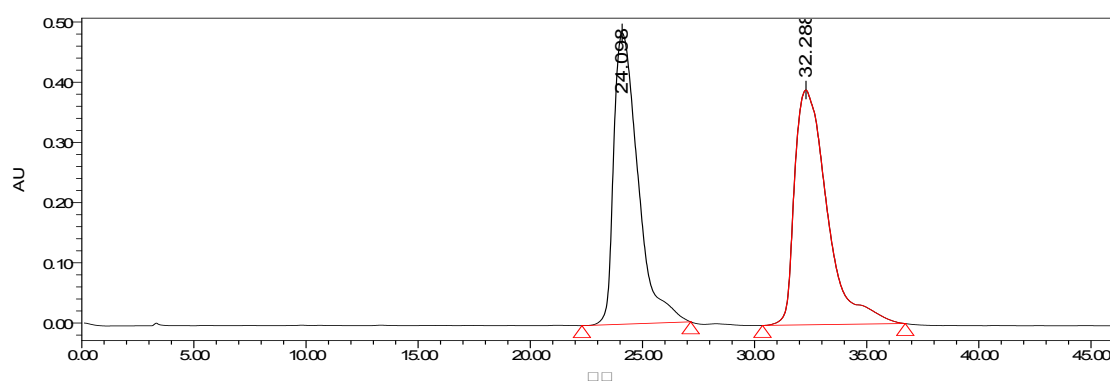
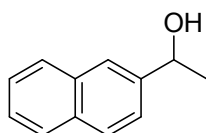


Peak	Ret Time [min]	Area	% Area	Height	Type
1	30.840	12842757	50.04	1724443	bb
2	33.966	12824508	49.96	151823	bb

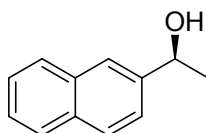


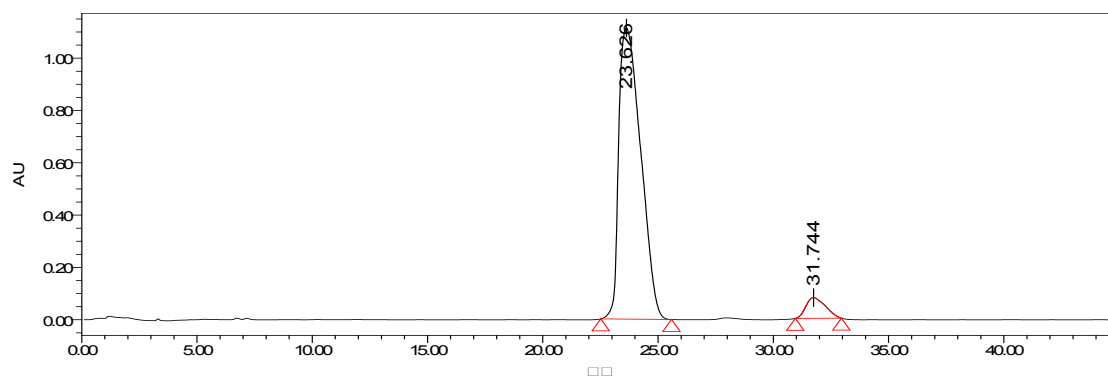


Peak	Ret Time [min]	Area	% Area	Height	Type
1	30.878	19391229	92.89	245366	bb
2	34.167	1483753	7.11	21101	bb

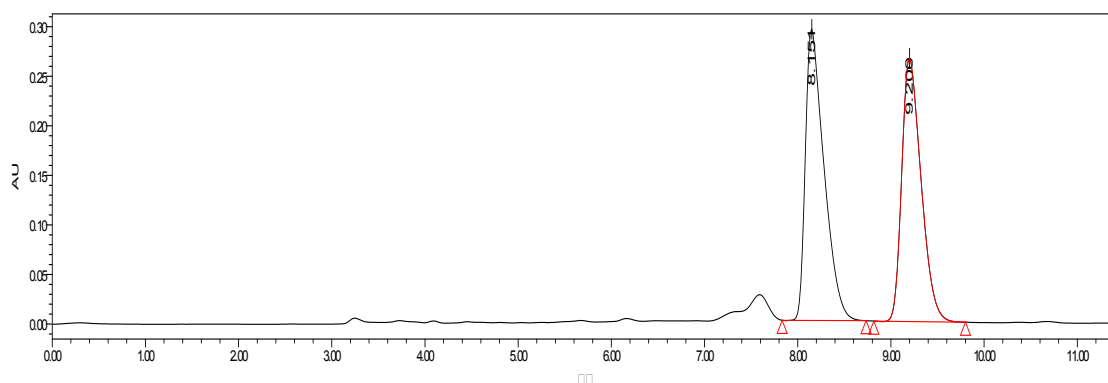
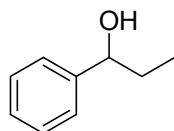


Peak	Ret Time [min]	Area	% Area	Height	Type
1	24.098	36872753	48.60	484977	bb
2	32.288	38994136	51.40	388819	bb

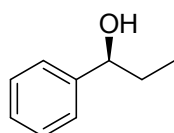


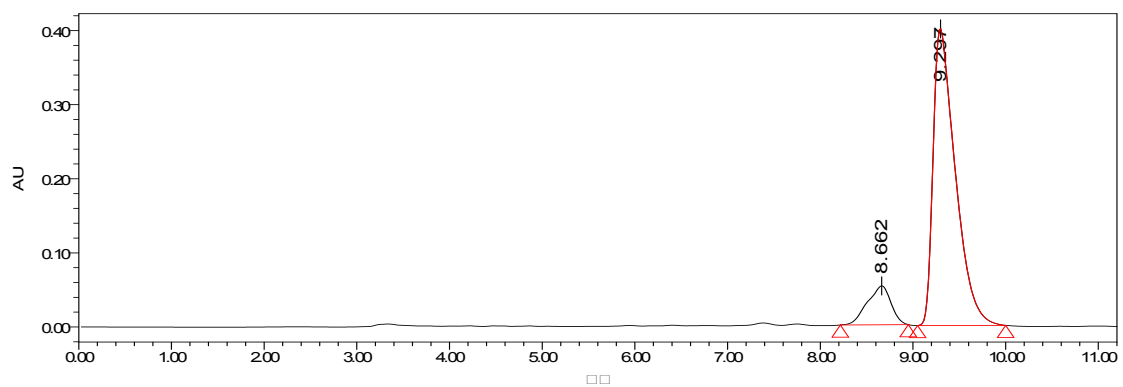


Peak	Ret Time [min]	Area	% Area	Height	Type
1	23.626	73451283	94.07	1113344	bb
2	31.744	4627879	5.93	79206	bb

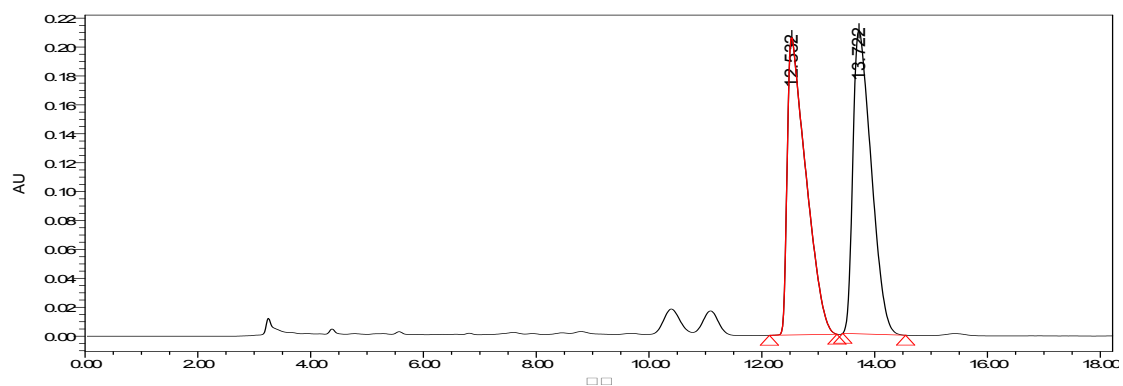
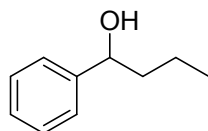


Peak	Ret Time [min]	Area	% Area	Height	Type
1	8.151	4088101	51.68	294285	bb
2	9.200	3823016	48.32	265718	bb

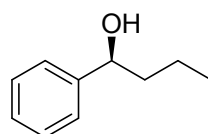


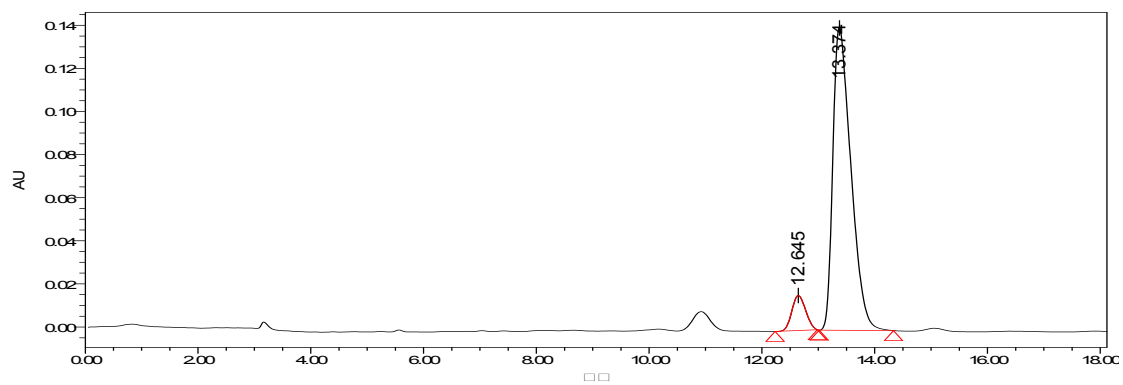


Peak	Ret Time [min]	Area	% Area	Height	Type
1	8.662	929952	12.25	52621	bb
2	9.297	6662504	87.75	400736	bb

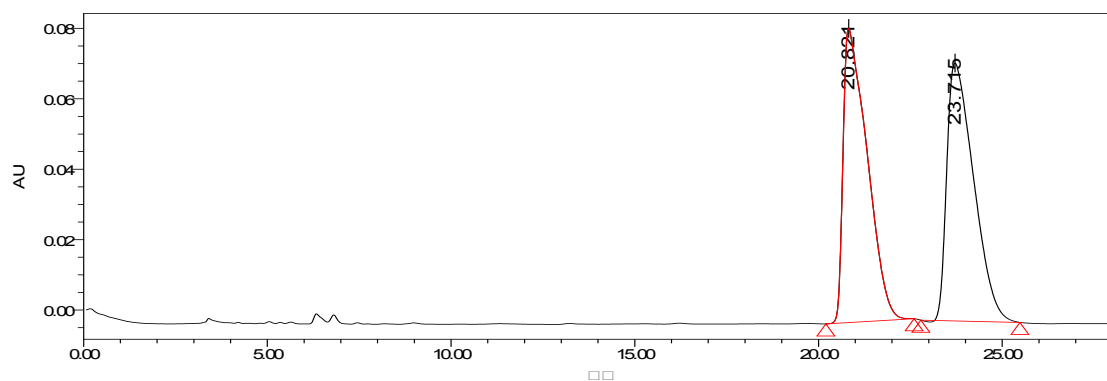
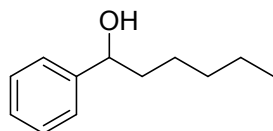


Peak	Ret Time [min]	Area	% Area	Height	Type
1	12.532	4727313	49.90	205680	bb
2	13.722	4745623	50.10	210010	bb

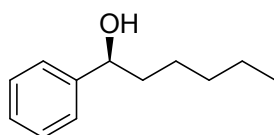


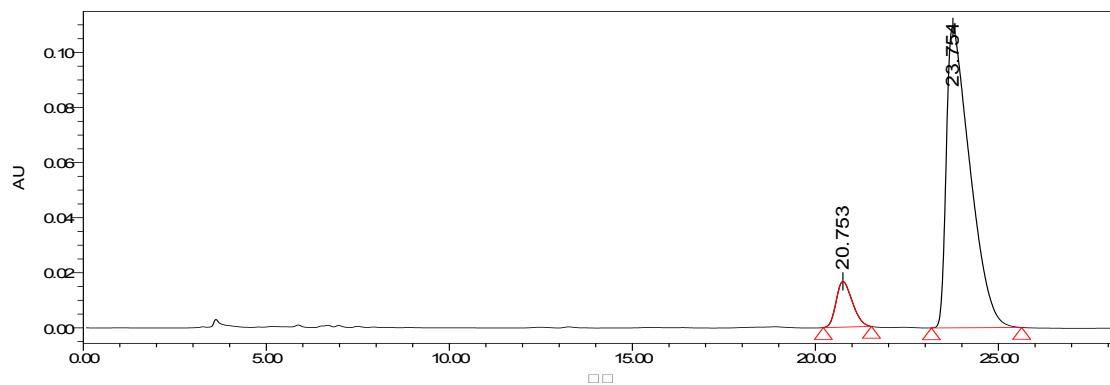


Peak	Ret Time [min]	Area	% Area	Height	Type
1	12.645	275356	8.10	16249	bb
2	13.374	3122263	91.90	140592	bb

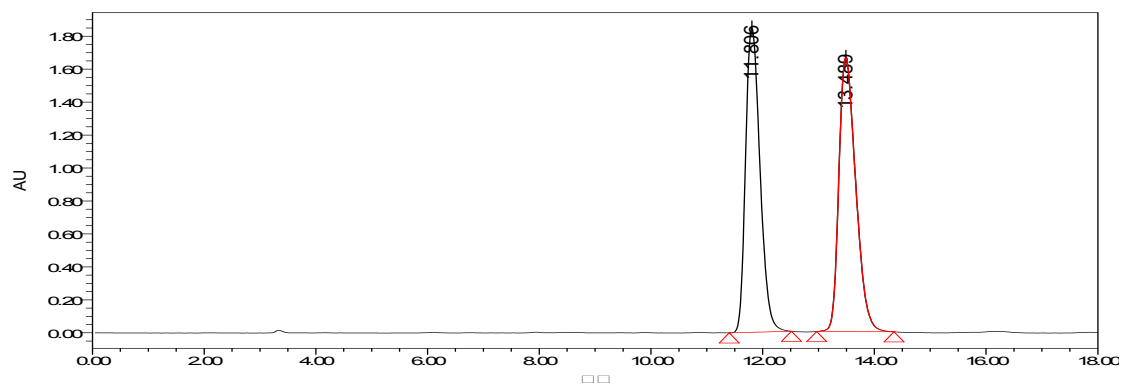
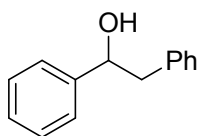


Peak	Ret Time [min]	Area	% Area	Height	Type
1	20.821	3776543	50.34	83616	bb
2	23.715	3725105	49.66	73235	bb

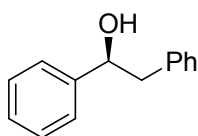


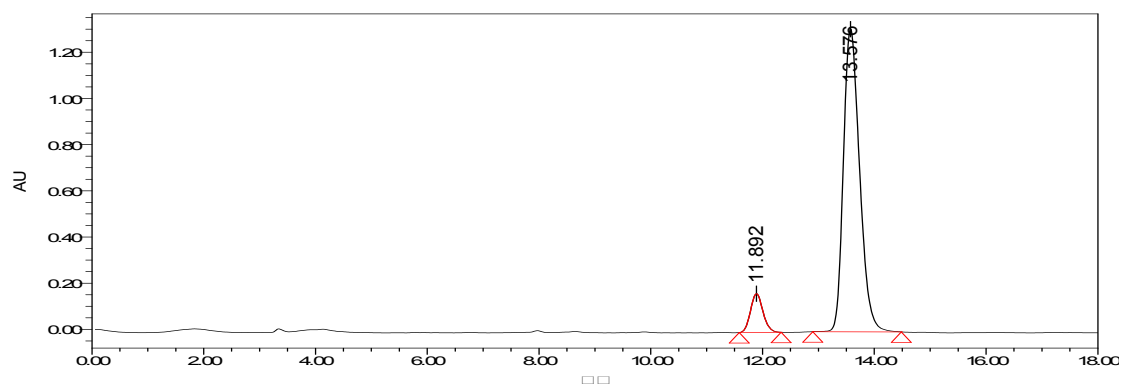


Peak	Ret Time [min]	Area	% Area	Height	Type
1	20.753	511496	9.45	16581	bb
2	23.754	4902090	90.55	109355	bb

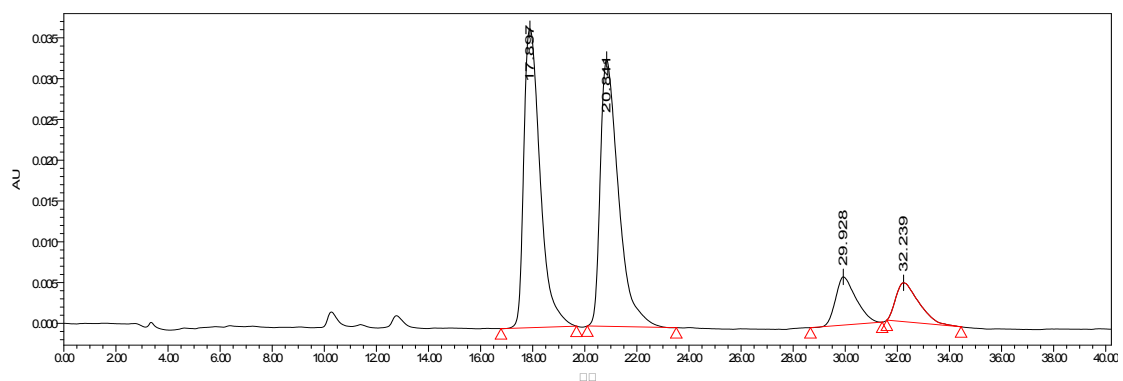
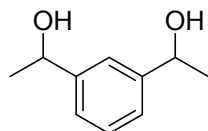


Peak	Ret Time [min]	Area	% Area	Height	Type
1	11.806	33244408	48.80	1848723	bb
2	13.489	34877277	51.20	1664852	bb

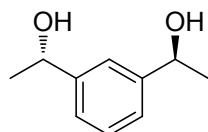


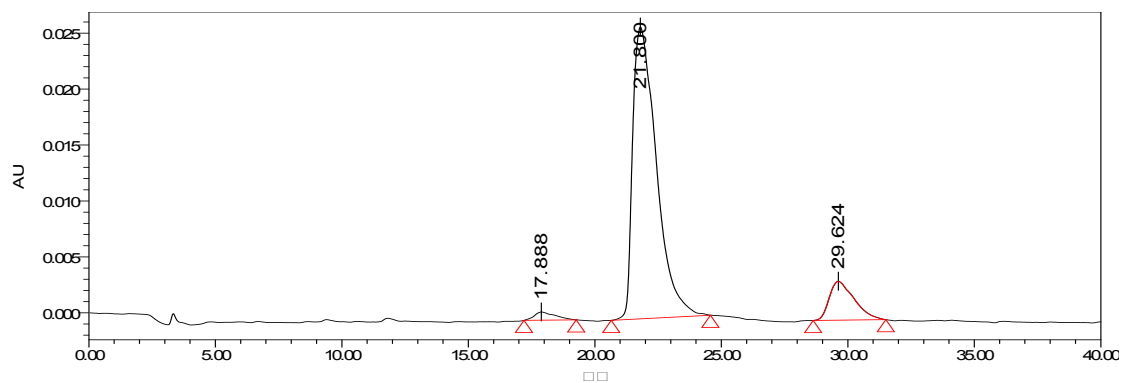


Peak	Ret Time [min]	Area	% Area	Height	Type
1	11.892	2609658	8.99	168012	bb
2	13.576	26418066	91.01	1312893	bb

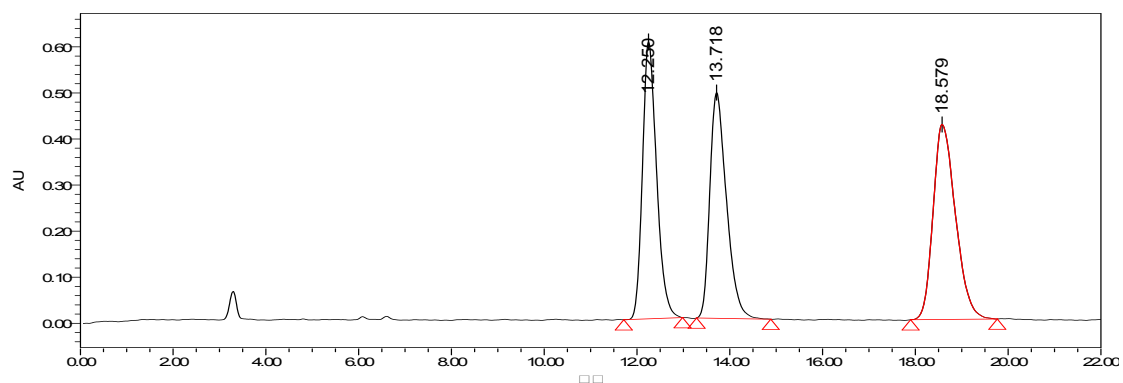
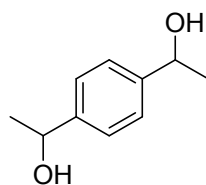


Peak	Ret Time [min]	Area	% Area	Height	Type
1	17.897	1598497	42.08	36650	bb
2	20.841	1586914	41.77	32729	bb
3	29.928	321781	8.47	5918	bb
4	32.239	291888	7.68	4754	bb

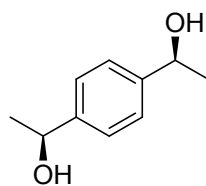


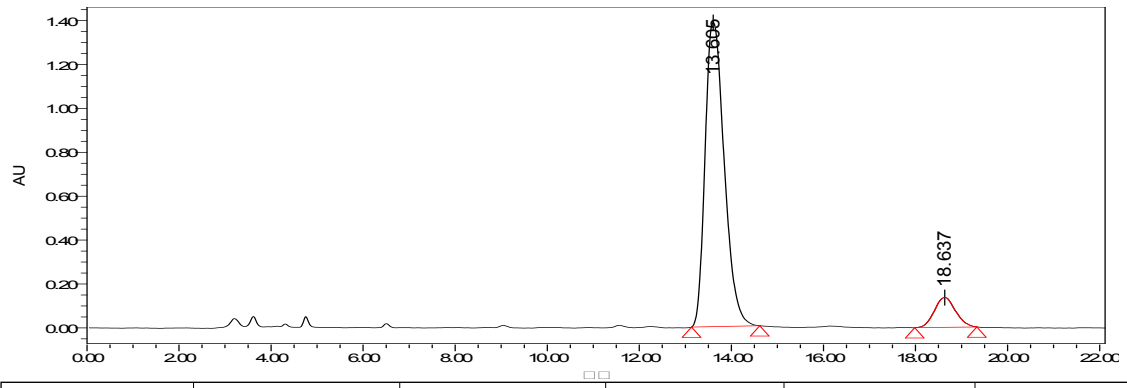


Peak	Ret Time [min]	Area	% Area	Height	Type
1	17.888	48219	2.41	787	bb
2	21.800	1711728	85.46	26113	bb
3	29.624	243103	12.14	3509	bb



Peak	Ret Time [min]	Area	% Area	Height	Type
1	12.250	12705689	32.49	601947	BV
2	13.718	12210893	31.22	490167	VB
3	18.579	14193679	36.29	423458	BB





Peak	Ret Time [min]	Area	% Area	Height	Type
1	13.605	40100638	90.22	1386482	bb
2	18.637	4348180	9.78	135834	bb