Highly enantioselective Mukaiyama aldol reaction in aqueous conditions using a chiral iron(II) bipyridine catalyst

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Supporting Information

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Experimental

General

All reactions were performed in flame-dried 12x75 mm culture tubes under an atmosphere of nitrogen or argon. Dimethoxyethane (DME) was distilled from [Na, benzophenone]. Distilled solvents (DME and water) were degassed prior to use (freeze-pump-thaw method). Solid aldehydes were used as received and liquid aldehydes were distilled prior to use. Propiophenone-derived silyl enol ether (*Z*/*E* > 99.5:0.5) and 3-pentanone-derived silyl enol ether (*Z*/*E* 93:7) were prepared by known procedures using diphenylamide as base and TMSCl as electrophile.[1] Bolm's ligand **1** was synthesized according to known procedures.[2] Iron(II) perchlorate was purchased from Alfa Aesar® (reagent grade purity) and iron(II) triflate was synthesized from iron metal (Alfa Aesar®, 99.9+% (metals basis)) and triflic acid.[3] ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 400 MHz spectrometer in $CDCl_3$. For ^{1}H NMR (400 MHz), tetramethylsilane (TMS) served as internal standard (δ = 0 ppm) and data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (in Hz), and integration. For ^{13}C NMR (100 MHz), $CDCl_3$ was used as internal standard (δ = 77.23 ppm) and spectra were obtained with complete proton decoupling. IR spectra were recorded on a BOMEM Arid-Zone™ FT-IR spectrometer or a NICOLET 380 FT-IR spectrometer with ZnSe ATR accessory and are reported in reciprocal centimeter (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on an Agilent 6210 ESI TOF (time of flight) mass spectrometer. Melting points (m.p.) are uncorrected and were recorded on a MEL-TEMP® melting

point apparatus. Flash column chromatography [4] was performed on silica gel (230–400 mesh) and analytical thin-layer chromatography was carried out using 250 μm commercial silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance and/or aqueous potassium permanganate.

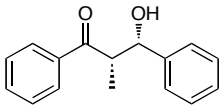
Caution: Perchlorate salts can be explosive and should be handled with care. Conversion to lower hydrates by unintentional dehydration may cause explosion. Use due caution in handling, as for all perchlorates.[5]

General Procedure for the Mukaiyama Aldol Reaction of Silyl Enol Ethers with Various Aldehydes

A mixture of $Fe(ClO_4)_2 \cdot 6H_2O$ (5.4 mg, 0.015 mmol) and Bolm's ligand **1** (14.8 mg, 0.045 mmol) in degassed DME [6] (0.7 mL) was stirred at room temperature for 1 h. The catalyst solution was then cooled at 0 °C for 10 min and 0.3 mL of degassed water [6] was added. Then the aldehyde (0.30 mmol), benzoic acid (2.2 mg, 0.018 mmol) and the silyl enol ether (0.36 mmol) were subsequently added to the mixture. The reaction mixture was stirred at 0 °C until the aldehyde disappeared completely (monitored by TLC). The reaction was quenched with 5 mL saturated aqueous $NaHCO_3$. The resulting mixture was extracted with ether (3x10 mL), and the combined organic layers were dried over anhydrous $MgSO_4$. The solvents were evaporated under reduced pressure (rotary evaporator), and the residue was purified by column chromatography (hexane/ethyl acetate) to give the aldol product. The enantiomeric excess of the product was determined by chiral HPLC analysis.

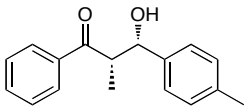
Characterization data of the aldol products

3-Hydroxy-2-methyl-1,3-diphenylpropan-1-one (Table 2, entry 1)[7]



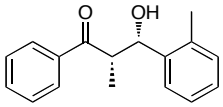
According to the general procedure with 30.5 μL benzaldehyde, the product was isolated as a white solid (m.p. = 44–45 °C). Reaction time = 16 h. Rf (*syn*) = 0.43; Rf (*anti*) = 0.39 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.95 (d, J = 7.2 Hz, 2H), 7.63–7.57 (m, 1H), 7.51–7.46 (m, 2H), 7.44–7.40 (m, 2H), 7.39–7.33 (m, 2H), 7.30–7.25 (m, 1H), 5.26 (dd, J = 2.9, 1.8 Hz, 1H), 3.71 (dq, J = 7.2, 2.9 Hz, 1H), 3.67 (d, J = 1.8 Hz, 1H), 1.20 (d, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 206.0, 142.1, 135.9, 133.9, 129.1, 128.7, 128.5, 127.6, 126.3, 73.4, 47.3, 11.5. IR (neat): 3464, 3061, 3030, 2975, 2934, 2876, 1674, 1596, 1578, 1493, 1449, 1346, 1215, 971, 702 cm^{-1}. $[\alpha]_D^{24}$ +9.3 (c = 1.0, $CHCl_3$, 97% ee). HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min) t_R = 28.2 min (minor), t_R = 36.6 min (major).

3-Hydroxy-2-methyl-3-(4-methylphenyl)-1-phenylpropan-1-one (Table 2, entry 2)[8]



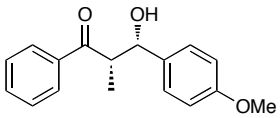
According to the general procedure with 35.5 μL *p*-tolualdehyde, the product was isolated as a colorless oil. Reaction time = 16 h. Rf (*syn*) = 0.48; Rf (*anti*) = 0.44 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.96–7.92 (m, 2H), 7.62–7.57 (m, 1H), 7.51–7.45 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.22 (dd, *J* = 3.1, 2.0 Hz, 1H), 3.69 (dq, *J* = 7.2, 3.1 Hz, 1H), 3.57 (d, *J* = 2.0 Hz, 1H), 2.35 (s, 3H), 1.20 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 206.0, 139.1, 137.2, 135.9, 133.8, 129.2, 129.0, 128.7, 126.2, 73.3, 47.4, 21.4, 11.6. IR (neat): 3466, 3056, 3024, 2976, 2932, 2875, 1674, 1596, 1578, 1514, 1448, 1346, 1215, 971, 817, 706 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min) t_R = 24.8 min (minor), t_R = 30.2 min (major).

3-Hydroxy-2-methyl-3-(2-methylphenyl)-1-phenylpropan-1-one (Table 2, entry 3)



According to the general procedure with 34.7 μL *o*-tolualdehyde, the product was isolated as a white solid (m.p. = 110–111 °C). Reaction time = 24 h. Rf (*syn*) = 0.43; Rf (*anti*) = 0.41 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.96–7.92 (m, 2H), 7.63–7.58 (m, 2H), 7.52–7.46 (m, 2H), 7.28–7.22 (m, 1H), 7.21–7.12 (m, 2H), 5.43 (dd, *J* = 2.7, 2.1 Hz, 1H), 3.68 (dq, *J* = 7.2, 2.7 Hz, 1H), 3.64 (d, *J* = 2.1 Hz, 1H), 2.32 (s, 3H), 1.24 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 206.3, 139.8, 135.9, 134.0, 133.9, 130.6, 129.1, 128.7, 127.5, 126.9, 126.2, 69.9, 44.7, 19.5, 11.6. IR (neat): 3474, 3061, 3024, 2973, 2933, 2876, 1674, 1596, 1578, 1489, 1448, 1345, 1214, 972, 754, 706 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{17}H_{18}O_2Na^+$ ($[M+Na]^+$): 277.1199, found: 277.1203. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 99.5/0.5, flow rate = 0.5 mL/min) t_R = 66.2 min (minor), t_R = 71.1 min (major).

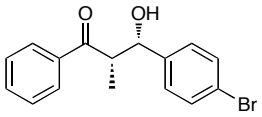
3-Hydroxy-3-(4-methoxyphenyl)-2-methyl-1-phenylpropan-1-one (Table 2, entry 4)[9]



According to the general procedure with 36.5 μL *p*-anisaldehyde, the product was isolated as a white solid (m.p. = 41–43 °C). Reaction time = 16 h. Rf (*syn*) = 0.31; Rf (*anti*) = 0.28 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.96–7.91 (m, 2H), 7.62–7.56 (m, 1H), 7.51–7.45 (m, 2H), 7.35–7.30 (m, 2H), 6.91–6.86 (m, 2H), 5.20 (d, *J* = 3.3 Hz, 1H), 3.81 (s, 3H), 3.68 (dq, *J* = 7.2, 3.3 Hz, 1H), 3.54 (brs, 1H), 1.21 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 206.0, 159.1, 136.0, 134.3, 133.8, 129.0, 128.7, 127.5, 113.9, 73.1, 55.5, 47.4, 11.7. IR (neat): 3482, 3060, 2966, 2934, 2836, 1674, 1612, 1596, 1513, 1449, 1347, 1303, 1248, 1215, 1176, 1033, 971,

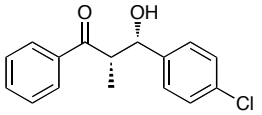
831, 707 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min) t_R = 26.9 min (minor), t_R = 33.6 min (major).

3-(4-Bromophenyl)-3-hydroxy-2-methyl-1-phenylpropan-1-one (Table 2, entry 5)[7]



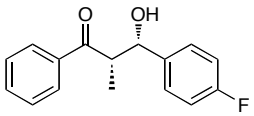
According to the general procedure with 55.5 mg 4-bromobenzaldehyde, the product was isolated as a white solid (m.p. = 43–44 °C). Reaction time = 20 h. Rf (*syn*) = 0.47; Rf (*anti*) = 0.45 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.96–7.92 (m, 2H), 7.64–7.59 (m, 1H), 7.52–7.47 (m, 4H), 7.32–7.27 (m, 2H), 5.22 (dd, *J* = 2.9, 2.0 Hz, 1H), 3.78 (d, *J* = 2.0 Hz, 1H), 3.65 (dq, *J* = 7.2, 2.9 Hz, 1H), 1.17 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 205.8, 141.1, 135.7, 134.0, 131.6, 129.1, 128.7, 128.1, 121.4, 72.7, 47.0, 11.4. IR (neat): 3496, 3082, 2992, 2943, 2865, 1662, 1594, 1577, 1487, 1449, 1396, 1335, 1218, 973, 795, 701 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min) t_R = 34.1 min (minor), t_R = 41.2 min (major).

3-(4-Chlorophenyl)-3-hydroxy-2-methyl-1-phenylpropan-1-one (Table 2, entry 6)[8]



According to the general procedure with 42.2 mg 4-chlorobenzaldehyde, the product was isolated as a white solid (m.p. = 70–71 °C). Reaction time = 24 h. Rf (*syn*) = 0.39; Rf (*anti*) = 0.37 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.96–7.91 (m, 2H), 7.63–7.58 (m, 1H), 7.51–7.46 (m, 2H), 7.37–7.30 (m, 4H), 5.22 (dd, *J* = 3.1, 2.0 Hz, 1H), 3.82 (d, *J* = 2.0 Hz, 1H), 3.66 (dq, *J* = 7.3, 3.1 Hz, 1H), 1.18 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 205.8, 140.6, 135.7, 134.0, 133.2, 129.1, 128.7, 128.6, 127.7, 72.7, 47.1, 11.4. IR (neat): 3497, 3066, 2995, 2947, 2866, 1662, 1594, 1578, 1490, 1449, 1399, 1335, 1218, 973, 798, 701 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min) t_R = 29.4 min (minor), t_R = 36.0 min (major).

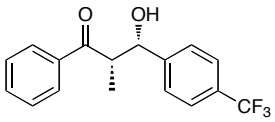
3-(4-Fluorophenyl)-3-hydroxy-2-methyl-1-phenylpropan-1-one (Table 2, entry 7)[10]



According to the general procedure with 32.2 μL 4-fluorobenzaldehyde, the product was isolated as a white solid (m.p. = 78–79 °C). Reaction time = 20 h. Rf (*syn*) = 0.39; Rf (*anti*) = 0.37 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.96–7.92 (m, 2H), 7.63–7.58 (m, 1H), 7.52–7.46 (m, 2H), 7.41–7.35 (m, 2H), 7.08–7.01 (m, 2H), 5.23 (brs, 1H), 3.71 (d, *J* = 2.0 Hz, 1H), 3.66 (dq, *J* = 7.2, 3.1 Hz, 1H), 1.19 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 205.9, 162.3 (d, *J* = 245.4 Hz), 137.8 (d, *J*

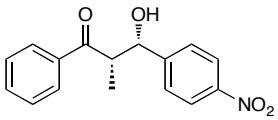
= 3.1 Hz), 135.8, 134.0, 129.1, 128.7, 127.9 (d, *J* = 7.7 Hz), 115.3 (d, J = 20.7 Hz), 72.8, 47.2, 11.5. IR (neat): 3480, 3083, 3060, 2993, 2974, 2955, 2933, 2876, 2851, 1663, 1605, 1592, 1509, 1451, 1372, 1220, 972, 833, 712 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min) t_R = 26.5 min (minor), t_R = 33.5 min (major).

3-Hydroxy-2-methyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (Table 2, entry 8)



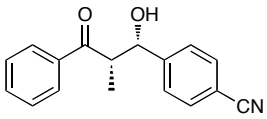
According to the general procedure with 41.0 μL 4-(trifluoromethyl)benzaldehyde, the product was isolated as a white solid (m.p. = 38–39 °C). Reaction time = 20 h. Rf (*syn*) = 0.44; Rf (*anti*) = 0.40 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.97–7.94 (m, 2H), 7.66–7.60 (m, 3H), 7.57–7.48 (m, 4H), 5.33 (brs, 1H), 3.91 (d, *J* = 2.0 Hz, 1H), 3.69 (dq, *J* = 7.4, 2.7 Hz, 1H), 1.17 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 205.8, 146.0, 135.5, 134.1, 129.8 (q, *J* = 32.2 Hz), 129.1, 128.8, 126.6, 125.5 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 272.3 Hz), 72.7, 46.9, 11.2. IR (neat): 3513, 3069, 3004, 2918, 2895, 1667, 1618, 1598, 1579, 1448, 1415, 1323, 1219, 1157, 1123, 1066, 1018, 973, 856, 808, 699 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{17}H_{15}F_3O_2Na^+$ ($[M+Na]^+$): 331.0916, found: 331.0919. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min) t_R = 28.7 min (minor), t_R = 35.5 min (major).

3-Hydroxy-2-methyl-3-(4-nitrophenyl)-1-phenylpropan-1-one (Table 2, entry 9)[8]



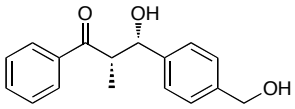
According to the general procedure with 45.3 mg 4-nitrobenzaldehyde, the product was isolated as a white solid (m.p. = 111–113 °C). Reaction time = 20 h. Rf (*syn*) = 0.21; Rf (*anti*) = 0.18 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 8.26–8.22 (m, 2H), 7.98–7.94 (m, 2H), 7.66–7.59 (m, 3H), 7.54–7.48 (m, 2H), 5.37 (dd, *J* = 2.6, 1.8 Hz, 1H), 4.04 (d, *J* = 1.8 Hz, 1H), 3.69 (dq, *J* = 7.3, 2.6 Hz, 1H), 1.16 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 205.5, 149.5, 147.4, 135.3, 134.3, 129.2, 128.8, 127.2, 123.8, 72.5, 46.7, 11.2. IR (neat): 3391, 3110, 3067, 2980, 2942, 2850, 1658, 1598, 1580, 1513, 1447, 1340, 1243, 1217, 1102, 975, 870, 708 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min) t_R = 26.4 min (minor), t_R = 31.9 min (major).

3-(4-Cyanophenyl)-3-hydroxy-2-methyl-1-phenylpropan-1-one (Table 2, entry 10)[10]



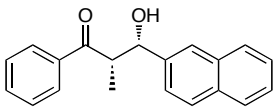
According to the general procedure with 39.3 mg 4-cyanobenzaldehyde, the product was isolated as a white solid (m.p. = 127–129 °C). Reaction time = 24 h. Rf (*syn*) = 0.19; Rf (*anti*) = 0.17 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.97–7.92 (m, 2H), 7.69–7.60 (m, 3H), 7.56–7.47 (m, 4H), 5.31 (d, J = 2.6 Hz, 1H), 3.98 (brs, 1H), 3.67 (dq, J = 7.2, 2.6 Hz, 1H), 1.15 (d, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 205.6, 147.4, 135.4, 134.2, 132.4, 129.2, 128.8, 127.1, 119.1, 111.4, 72.6, 46.7, 11.2. IR (neat): 3492, 3061, 2993, 2923, 2864, 2232, 1661, 1608, 1594, 1578, 1449, 1403, 1336, 1219, 973, 862, 799, 700 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min) t_R = 46.1 min (minor), t_R = 51.2 min (major).

3-hydroxy-3-(4-(hydroxymethyl)phenyl)-2-methyl-1-phenylpropan-1-one (Table 2, entry 11)



According to the general procedure with 40.8 mg 4-(hydroxymethyl)benzaldehyde, the product was isolated as a colorless oil. Reaction time = 16 h. Rf (*syn*) = 0.32; Rf (*anti*) = 0.31 (50% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.97–7.92 (m, 2H), 7.63–7.57 (m, 1H), 7.52–7.45 (m, 2H), 7.43–7.38 (m, 2H), 7.38–7.33 (m, 2H), 5.25 (brs, 1H), 4.69 (d, J = 5.2 Hz, 2H), 3.70 (dq, J = 7.2, 3.1 Hz, 1H), 3.68 (brs, 1H), 1.73 (t, J = 5.2 Hz, 1H), 1.19 (d, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 205.9, 141.5, 140.3, 135.9, 133.8, 129.0, 128.7, 127.2, 126.5, 73.4, 65.1, 47.4, 11.7. IR (neat): 3389, 3060, 2975, 2934, 2876, 1672, 1596, 1578, 1513, 1448, 1420, 1351, 1215, 1035, 1016, 1001, 971, 821, 795, 707 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{17}H_{18}O_3Na^+$ ($[M+Na]^+$): 293.1148, found: 293.1145. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 80/20, flow rate = 0.5 mL/min) t_R = 15.7 min (minor), t_R = 22.5 min (major).

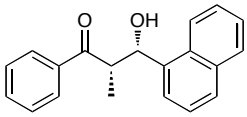
3-Hydroxy-2-methyl-3-(2-naphthyl)-1-phenylpropan-1-one (Table 2, entry 12)[10]



According to the general procedure with 46.9 mg 2-naphthaldehyde, the product was isolated as a white solid (m.p. = 80–81 °C). Reaction time = 20 h. Rf (*syn*) = 0.41; Rf (*anti*) = 0.38 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 8.00–7.92 (m, 3H), 7.89–7.82 (m, 3H), 7.63–7.58 (m, 1H), 7.52–7.45 (m, 5H), 5.44 (d, J = 2.8 Hz, 1H), 3.87 (brs, 1H), 3.82 (dq, J = 7.3, 2.8 Hz, 1H), 1.21 (d, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 206.1, 139.4, 135.8, 133.9, 133.5, 133.0, 129.1, 128.8, 128.3, 128.2, 127.9, 126.4, 126.0, 125.2, 124.3, 73.3, 47.1, 11.4. IR (neat): 3485, 3063, 2982, 2938, 2876, 1652, 1597, 1578, 1509, 1448, 1417, 1341, 1216, 1124, 977, 802, 703 cm^{-1}.

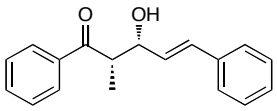
HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min) t_R = 62.5 min (minor), t_R = 67.4 min (major).

3-Hydroxy-2-methyl-3-(1-naphthyl)-1-phenylpropan-1-one (Table 2, entry 13)[7]



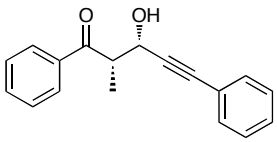
According to the general procedure with 40.7 μL 1-naphthaldehyde, the product was isolated as a colorless oil. Reaction time = 20 h. Rf (*syn*) = 0.45; Rf (*anti*) = 0.37 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.99–7.95 (m, 2H), 7.94–7.88 (m, 2H), 7.88–7.85 (m, 1H), 7.84–7.80 (m, 1H), 7.64–7.59 (m, 1H), 7.58–7.46 (m, 5H), 6.07 (brs, 1H), 4.14 (d, *J* = 2.0 Hz, 1H), 3.94 (dq, *J* = 7.2, 2.2 Hz, 1H), 1.20 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 206.7, 136.9, 135.9, 134.0, 130.0, 129.5, 129.2, 128.8, 128.1, 126.4, 125.7, 125.6, 124.8, 122.6, 69.5, 45.2, 11.7. IR (neat): 3501, 3058, 2980, 2934, 2876, 1665, 1596, 1578, 1510, 1449, 1353, 1215, 973, 909, 794, 732, 706 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min) t_R = 18.3 min (major), t_R = 30.2 min (minor).

(*E*)-3-Hydroxy-2-methyl-1,5-diphenylpent-4-en-1-one (Table 2, entry 14)[7]



According to the general procedure with 37.8 μL cinnamaldehyde, the product was isolated as pale yellow oil. Reaction time = 16 h. Rf (*syn*) = 0.33; Rf (*anti*) = 0.32 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 8.01–7.96 (m, 2H), 7.64–7.58 (m, 1H), 7.53–7.47 (m, 2H), 7.41–7.36 (m, 2H), 7.35–7.29 (m, 2H), 7.27–7.22 (m, 1H), 6.73 (d, *J* = 15.8 Hz, 1H), 6.26 (dd, *J* = 15.8, 5.7 Hz, 1H), 4.81 (brs, 1H), 3.65 (dq, *J* = 7.2, 3.1 Hz, 1H), 3.33 (d, *J* = 2.0 Hz, 1H), 1.32 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 205.5, 137.0, 136.2, 133.8, 131.3, 129.5, 129.1, 128.8, 128.7, 127.9, 126.8, 72.6, 45.8, 12.2. IR (neat): 3514, 3083, 3059, 3029, 3000, 2948, 2875, 1672, 1597, 1578, 1494, 1449, 1401, 1340, 1216, 1131, 1061, 977, 749, 697 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min) t_R = 20.6 min (minor), t_R = 36.1 min (major).

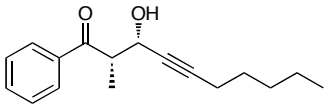
3-Hydroxy-2-methyl-1,5-diphenylpent-4-yn-1-one (Table 2, entry 15)[7]



According to the general procedure with 36.7 μL phenylpropargyl aldehyde, the product was isolated as a white solid (m.p. = 47–49 °C). Reaction time = 24 h. Rf (*syn*) = 0.29; Rf (*anti*) = 0.34 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 8.02–7.97 (m, 2H), 7.64–7.59 (m, 1H), 7.54–7.48 (m, 2H), 7.42–7.37 (m, 2H), 7.33–7.26 (m, 3H),

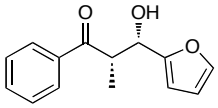
5.09 (d, J = 3.9 Hz, 1H), 3.80 (dq, J = 7.2, 3.9 Hz, 1H), 3.28 (brs, 1H), 1.51 (d, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 204.3, 135.9, 133.9, 132.0, 129.1, 128.8, 128.7, 128.5, 122.6, 88.1, 85.7, 64.0, 46.5, 13.0. IR (neat): 3295, 3062, 2974, 2935, 2876, 2238, 1677, 1596, 1489, 1448, 1346, 1206, 1027, 978, 761, 707, 690 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min) t_R = 19.7 min (minor), t_R = 43.5 min (major).

3-Hydroxy-2-methyl-1-phenyldec-4-yn-1-one (Table 2, entry 16)



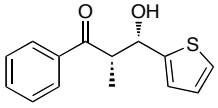
According to the general procedure with 42.8 μL 2-octynal, the product was isolated as a colorless oil. Reaction time = 24 h. Rf (*syn*) = 0.39; Rf (*anti*) = 0.43 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.98–7.93 (m, 2H), 7.62–7.57 (m, 1H), 7.52–7.46 (m, 2H), 4.83 (ddd, J = 4.0, 2.0, 2.0 Hz, 1H), 3.66 (dq, J = 7.2, 4.0 Hz, 1H), 3.06 (brs, 1H), 2.18 (dt, J = 7.2, 2.0 Hz, 2H), 1.46 (tt, J = 7.2, 7.2 Hz, 2H), 1.41 (d, J = 7.2 Hz, 3H), 1.36–1.22 (m, 4H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 204.5, 136.0, 133.8, 129.0, 128.8, 86.7, 79.2, 63.7, 46.7, 31.2, 28.4, 22.4, 18.9, 14.2, 12.8. IR (neat): 3447, 3063, 2933, 2859, 2231, 1679, 1596, 1579, 1449, 1350, 1254, 1212, 1033, 969, 707 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{17}H_{22}O_2Na^+$ ([M+Na]$^+$): 281.1512, found: 281.1516. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 90/10, flow rate = 0.5 mL/min) t_R = 11.6 min (minor), t_R = 16.0 min (major).

3-(2-Furyl)-3-hydroxy-2-methyl-1-phenylpropan-1-one (Table 2, entry 17)[10]



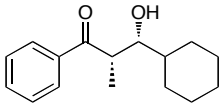
According to the general procedure with 24.8 μL furfural, the product was isolated as a colorless oil. Reaction time = 16 h. Rf (*syn*) = 0.31; Rf (*anti*) = 0.30 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 8.00–7.94 (m, 2H), 7.63–7.57 (m, 1H), 7.52–7.46 (m, 2H), 7.35 (brs, 1H), 6.35–6.30 (m, 2H), 5.23 (d, J = 4.0 Hz, 1H), 3.94 (dq, J = 7.2, 4.0 Hz, 1H), 3.31 (brs, 1H), 1.30 (d, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 204.9, 154.8, 141.9, 135.8, 133.8, 129.0, 128.8, 110.6, 107.0, 68.9, 44.9, 12.7. IR (neat): 3447, 3116, 3062, 2974, 2917, 2877, 2849, 1677, 1596, 1579, 1504, 1449, 1372, 1216, 1148, 1001, 972, 740, 710 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min) t_R = 34.5 min (minor), t_R = 41.8 min (major).

3-Hydroxy-2-methyl-1-phenyl-3-(thiophen-2-yl)propan-1-one (Table 2, entry 18)[9]



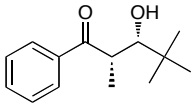
According to the general procedure with 28.0 μL 2-thiophenecarboxaldehyde, the product was isolated as a white solid (m.p. = 45–46 °C). Reaction time = 24 h. Rf (*syn*) = 0.39; Rf (*anti*) = 0.38 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.97–7.93 (m, 2H), 7.63–7.58 (m, 1H), 7.52–7.46 (m, 2H), 7.24 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.02–6.96 (m, 2H), 5.49 (dd, *J* = 3.7, 0.8 Hz, 1H), 3.80 (dq, *J* = 7.2, 3.7 Hz, 1H), 3.60 (brs, 1H), 1.33 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 205.2, 146.1, 135.8, 133.9, 129.1, 128.7, 126.9, 124.5, 123.8, 70.7, 47.9, 12.5. IR (neat): 3458, 3117, 3071, 2985, 2933, 1668, 1593, 1576, 1449, 1376, 1354, 1199, 1180, 1035, 1020, 972, 838, 706 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min) t_R = 36.9 min (minor), t_R = 45.8 min (major).

3-Cyclohexyl-3-hydroxy-2-methyl-1-phenylpropan-1-one (Table 2, entry 19)[11]



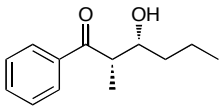
According to the general procedure with 36.1 μL cyclohexanecarboxaldehyde, the product was isolated as a colorless oil. Reaction time = 16 h. Rf (*syn*) = 0.46; Rf (*anti*) = 0.53 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.97–7.91 (m, 2H), 7.62–7.56 (m, 1H), 7.52–7.46 (m, 2H), 3.72–3.65 (m, 2H), 3.09 (d, *J* = 2.3 Hz, 1H), 2.12 (d, *J* = 13.1 Hz, 1H), 1.83–0.92 (m, 10H), 1.24 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 206.2, 136.1, 133.6, 129.0, 128.7, 75.7, 41.5, 40.4, 29.7, 29.4, 26.6, 26.4, 26.1, 10.8. IR (neat): 3497, 3062, 2925, 2852, 1677, 1596, 1579, 1448, 1345, 1313, 1264, 1216, 1079, 971, 709 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min) t_R = 14.7 min (minor), t_R = 17.7 min (major).

3-Hydroxy-2,4,4-trimethyl-1-phenylpentan-1-one (Table 2, entry 20)[12]



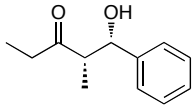
According to the general procedure with 33.3 μL trimethylacetaldehyde, the product was isolated as a white solid (m.p. = 74–75 °C). Reaction time = 24 h. Rf (*syn*) = 0.50; Rf (*anti*) = 0.58 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.99–7.94 (m, 2H), 7.62–7.57 (m, 1H), 7.53–7.47 (m, 2H), 3.81–3.74 (m, 2H), 2.64 (brs, 1H), 1.28 (d, *J* = 6.8 Hz, 3H), 0.99 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 205.6, 135.9, 133.6, 129.0, 128.7, 77.8, 41.2, 35.9, 27.2, 13.4. IR (neat): 3529, 3062, 2970, 2873, 1674, 1596, 1579, 1448, 1365, 1301, 1206, 1064, 967, 710 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 99/1, flow rate = 0.5 mL/min) t_R = 18.8 min (minor), t_R = 23.8 min (major).

3-Hydroxy-2-methyl-1-phenylhexan-1-one (Table 2, entry 21)[13]



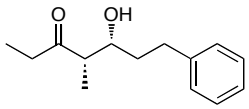
According to the general procedure with 27.0 μL butyraldehyde, the product was isolated as a colorless oil. Reaction time = 16 h. Rf (*syn*) = 0.40; Rf (*anti*) = 0.44 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.99–7.93 (m, 2H), 7.63–7.57 (m, 1H), 7.53–7.47 (m, 2H), 4.10–4.02 (m, 1H), 3.48 (dq, J = 7.2, 2.9 Hz, 1H), 3.09 (brs, 1H), 1.68–1.48 (m, 2H), 1.48–1.34 (m, 2H), 1.27 (d, J = 7.2 Hz, 3H), 0.96 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 206.2, 136.2, 133.7, 129.0, 128.7, 71.3, 44.8, 36.7, 19.5, 14.3, 11.3. IR (neat): 3447, 3064, 2960, 2934, 2873, 1676, 1596, 1579, 1449, 1369, 1308, 1255, 1214, 1120, 1101, 1075, 972, 708 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 99.5/0.5, flow rate = 0.5 mL/min) t_R = 35.1 min (minor), t_R = 45.9 min (major).

1-Hydroxy-2-methyl-1-phenylpentan-3-one (Table 3, entry 1)[14]



According to the general procedure with 30.5 μL benzaldehyde, the product was isolated as a colorless oil. Reaction time = 16 h. Rf (*syn*) = 0.38; Rf (*anti*) = 0.37 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.37–7.24 (m, 5H), 5.07 (d, J = 4.0 Hz, 1H), 3.13 (s, 1H), 2.85 (dq, J = 7.2, 4.0 Hz, 1H), 2.52 (qd, J = 7.2, 18.1 Hz, 1H), 2.35 (qd, J = 7.2, 18.1 Hz, 1H), 1.09 (d, J = 7.2 Hz, 3H), 1.01 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 216.6, 142.0, 128.5, 127.6, 126.2, 73.5, 52.5, 35.7, 10.8, 7.7. IR (neat): 3460, 3063, 3031, 2977, 2938, 2879, 1705, 1604, 1494, 1454, 1408, 1378, 1357, 1197, 1117, 1015, 975, 762, 702 cm^{-1}. HPLC (Daicel Chiralcel® OJ-H, hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min) t_R = 27.0 min (minor), t_R = 29.8 min (major).

5-Hydroxy-4-methyl-7-phenylheptan-3-one (Table 3, entry 2)[11]



According to the general procedure with 39.6 μL 3-phenylpropionaldehyde, the product was isolated as a colorless oil. Reaction time = 16 h. Rf (*syn*) = 0.31; Rf (*anti*) = 0.31 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*syn*): 7.32–7.25 (m, 2H), 7.24–7.17 (m, 3H), 3.97–3.90 (m, 1H), 2.9 (brs, 1H), 2.90–2.80 (m, 1H), 2.71–2.38 (m, 4H), 1.90–1.78 (m, 1H), 1.65–1.54 (m, 1H), 1.15 (d, J = 7.2 Hz, 3H), 1.05 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (*syn*): 217.1, 142.1, 128.7, 128.6, 126.1, 70.5, 50.0, 36.0, 35.3, 32.6, 10.3, 7.8. IR (neat): 3452, 3027, 2977, 2939, 1704, 1603, 1497, 1455, 1410, 1377, 1109, 1030, 974, 749, 700 cm^{-1}. HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min) t_R = 30.7 min (minor), t_R = 32.2 min (major).

Crystallization of $[Fe(ClO_4)_2 \cdot 1] \cdot (H_2O) \cdot DME$ complexes

Crystallization of **$[Fe(ClO_4)_2 \cdot 1] \cdot (H_2O) \cdot DME$** was carried out as follows: A mixture of $Fe(ClO_4)_2 \cdot 6H_2O$ (5.6 mg, 15.4 μmol) and Bolm's ligand **1** (5.1 mg, 15.4 μmol) was dissolved in DME (0.2 mL). This solution was stirred at room temperature for 30 min. Vapor diffusion of diethyl ether into this solution afforded the crystals.
CCDC 828098 ($[\mathbf{1} \cdot Fe \cdot DME \cdot H_2O]^{2+} \cdot 2ClO_4^-$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.au.uk/data_request/cif.

References

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[3] Iron powder (111.7 mg, 2 mmol) was suspended in 2 mL distilled water and freshly distilled triflic acid (354 μL, 4 mmol) was added. The mixture was refluxed for 30 minutes and the resulting solution was filtered and evaporated. The white solid obtained was dried under high vacuum to afford $Fe(OTf)_2 \bullet H_2O$ quantitatively. Thermogravimetric analysis confirmed the presence of one hydration water molecule.
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[6] A control experiment with propiophenone-derived silyl enol ether and benzaldehyde using non degassed solvents afforded the product with the same yield and selectivities as the same reaction using oxygen-free solvents. This result adds further evidence that Fe(III) catalysis is not involved in our reaction conditions.
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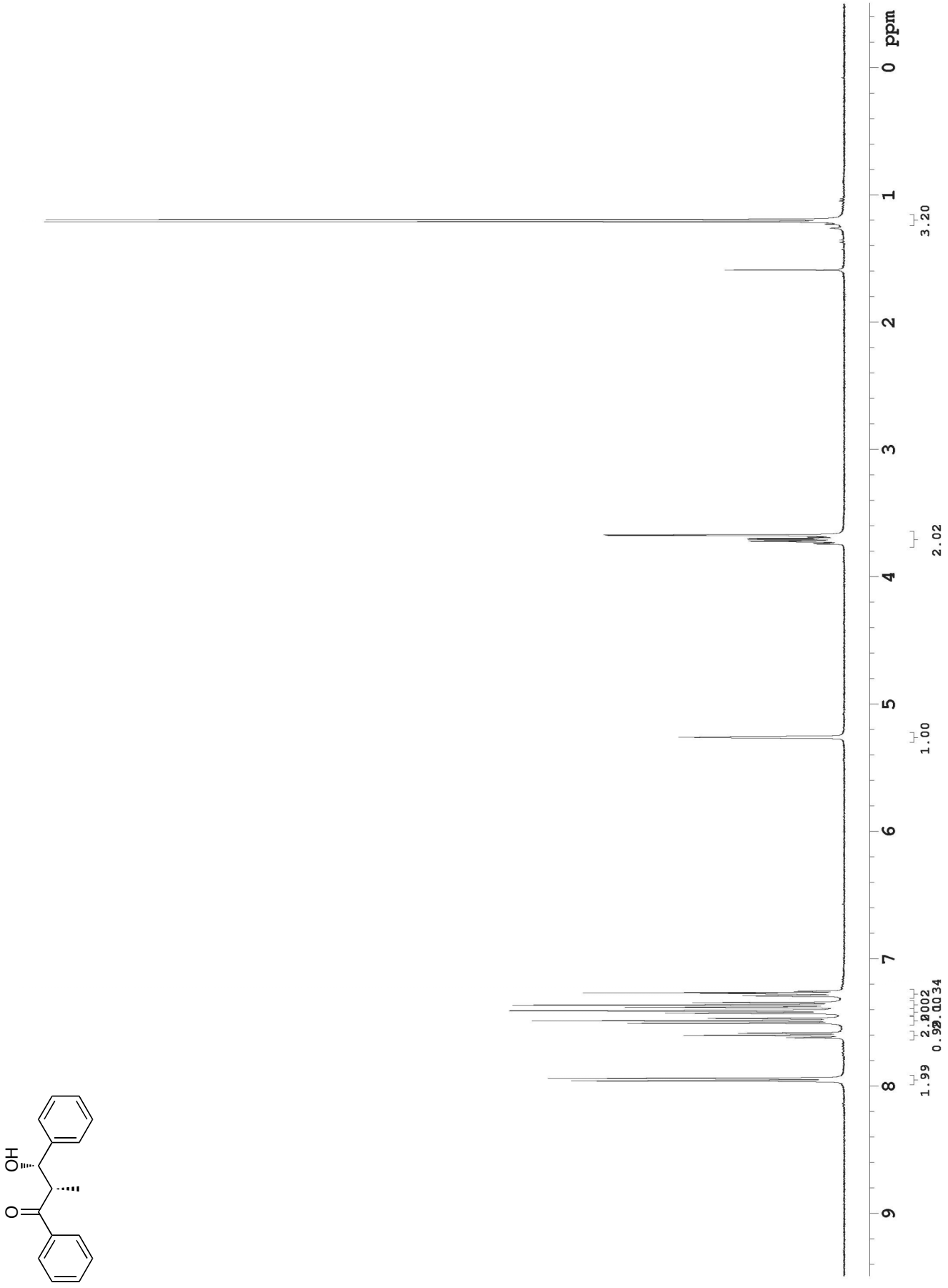
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1.00
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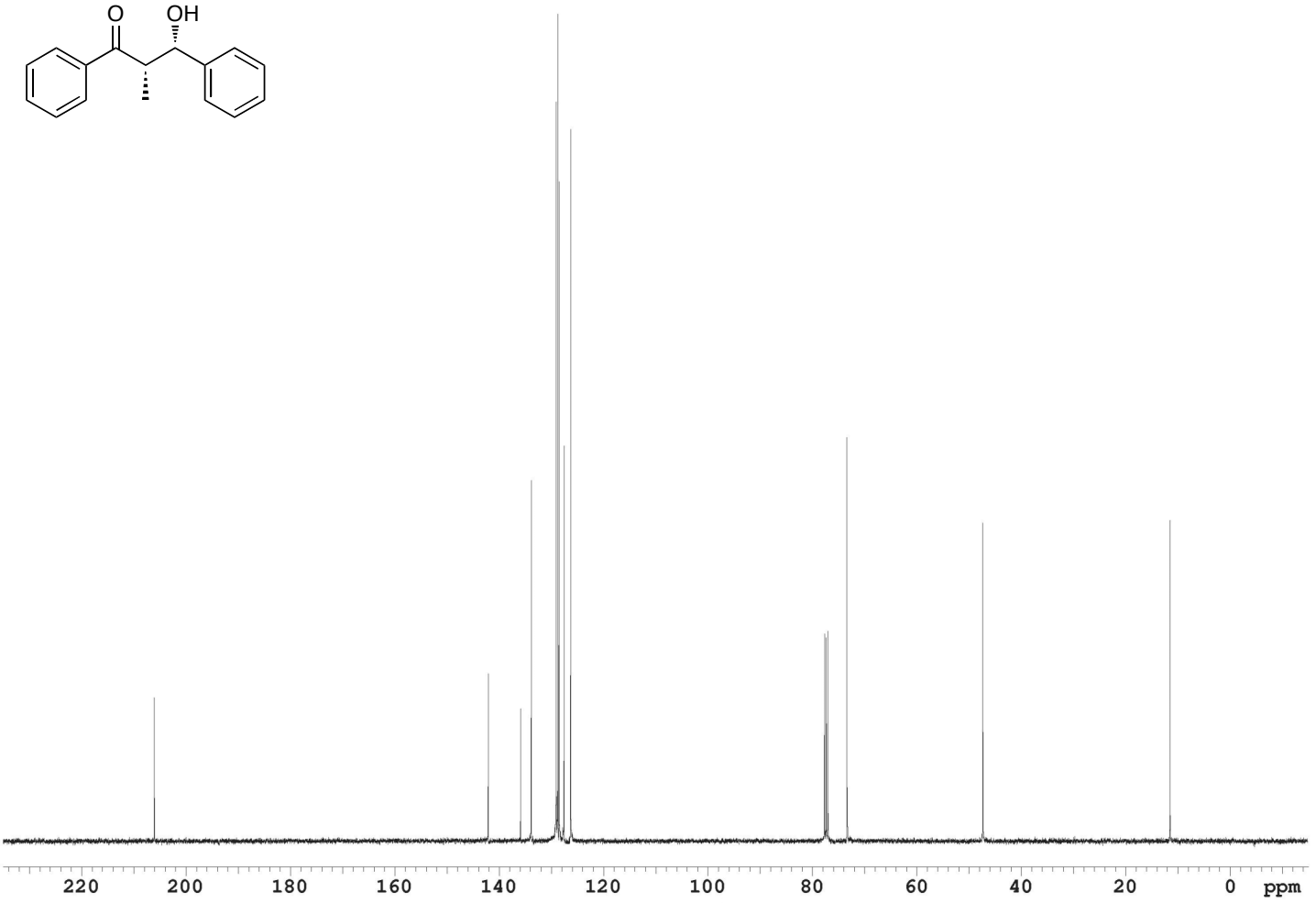
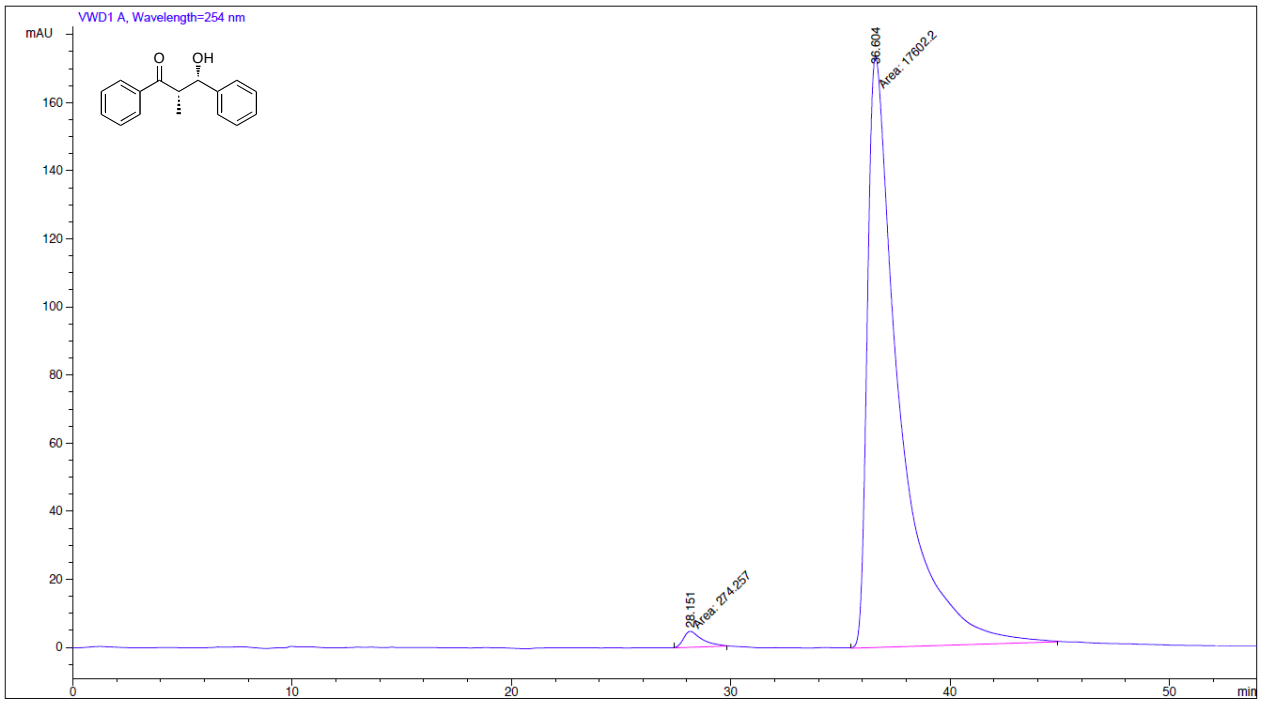
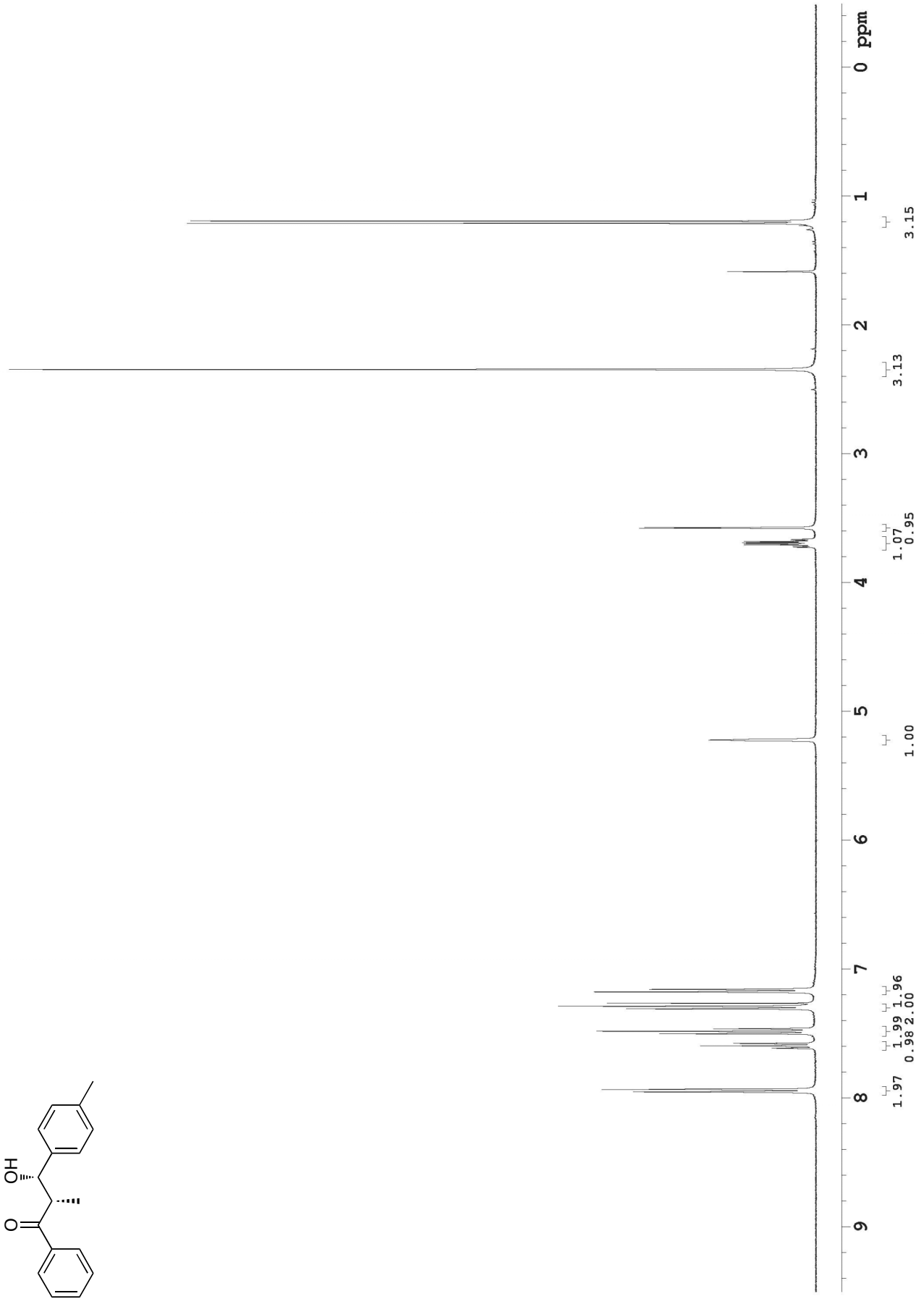
OH
O





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.151	MM	0.9738	274.25662	4.69370	1.5342
2	36.604	MM	1.6895	1.76022e4	173.64651	98.4658
Totals :				1.78764e4	178.34021	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2.00
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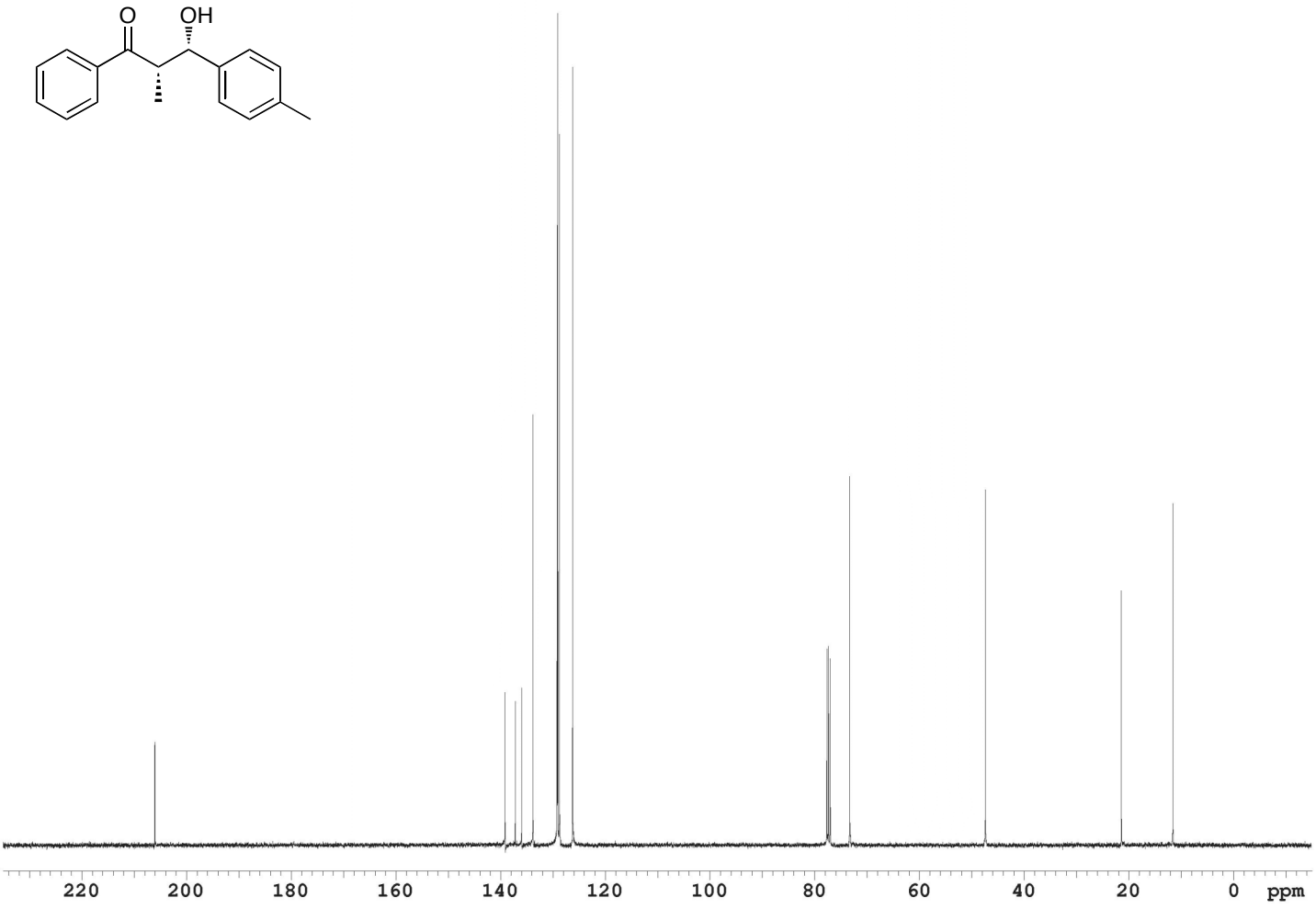
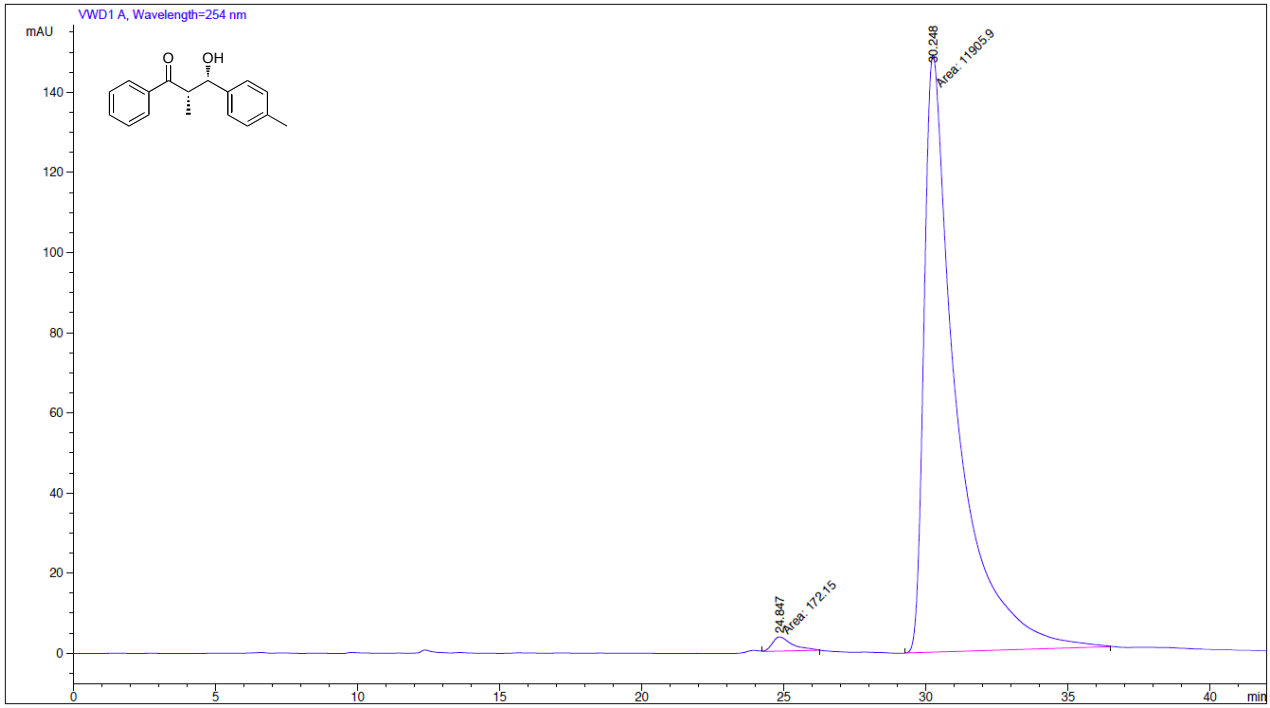
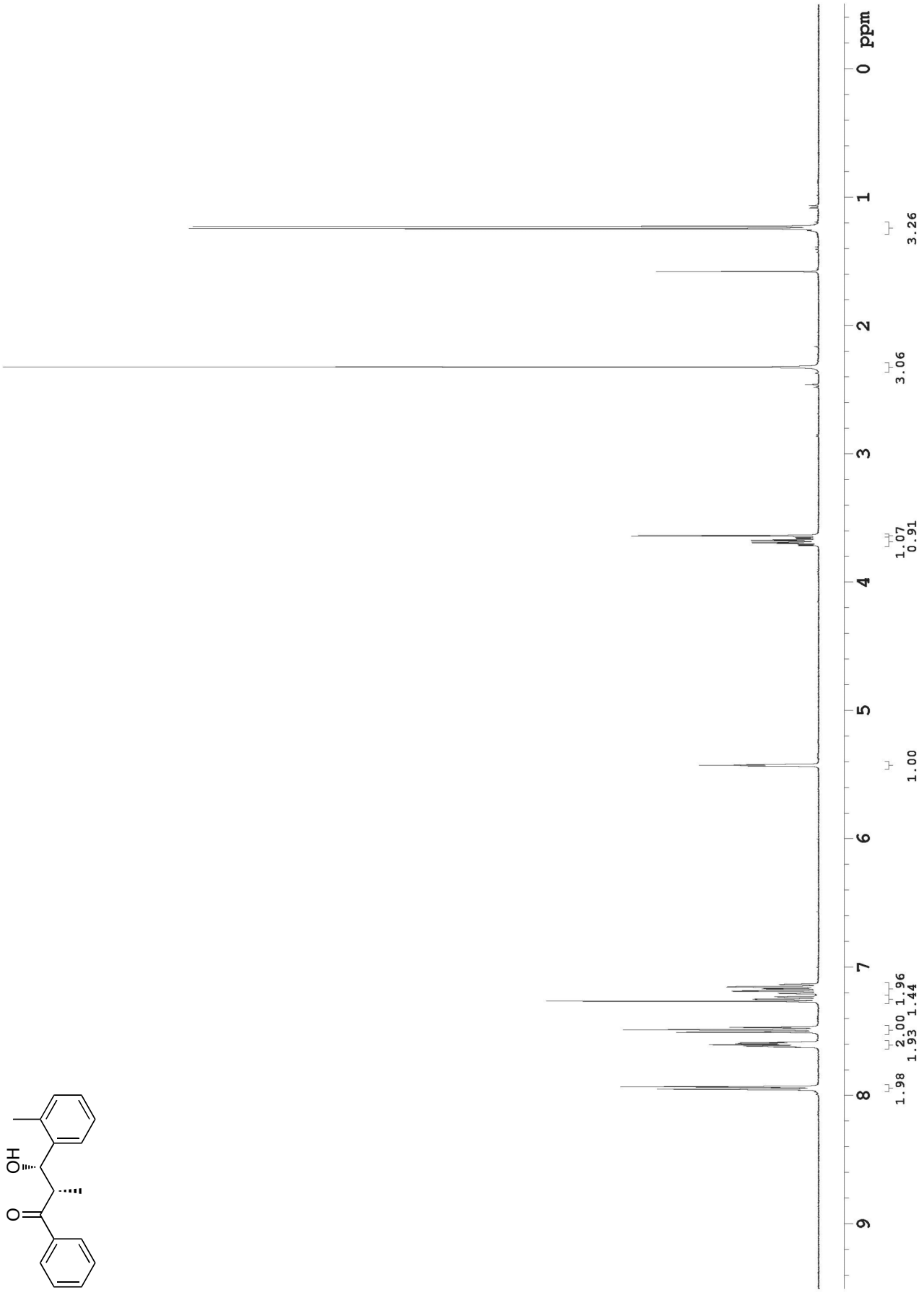
OH
O





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.847	MM	0.8069	172.15022	3.55566	1.4253
2	30.248	MM	1.3313	1.19059e4	149.05525	98.5747
Totals :				1.20780e4	152.61091	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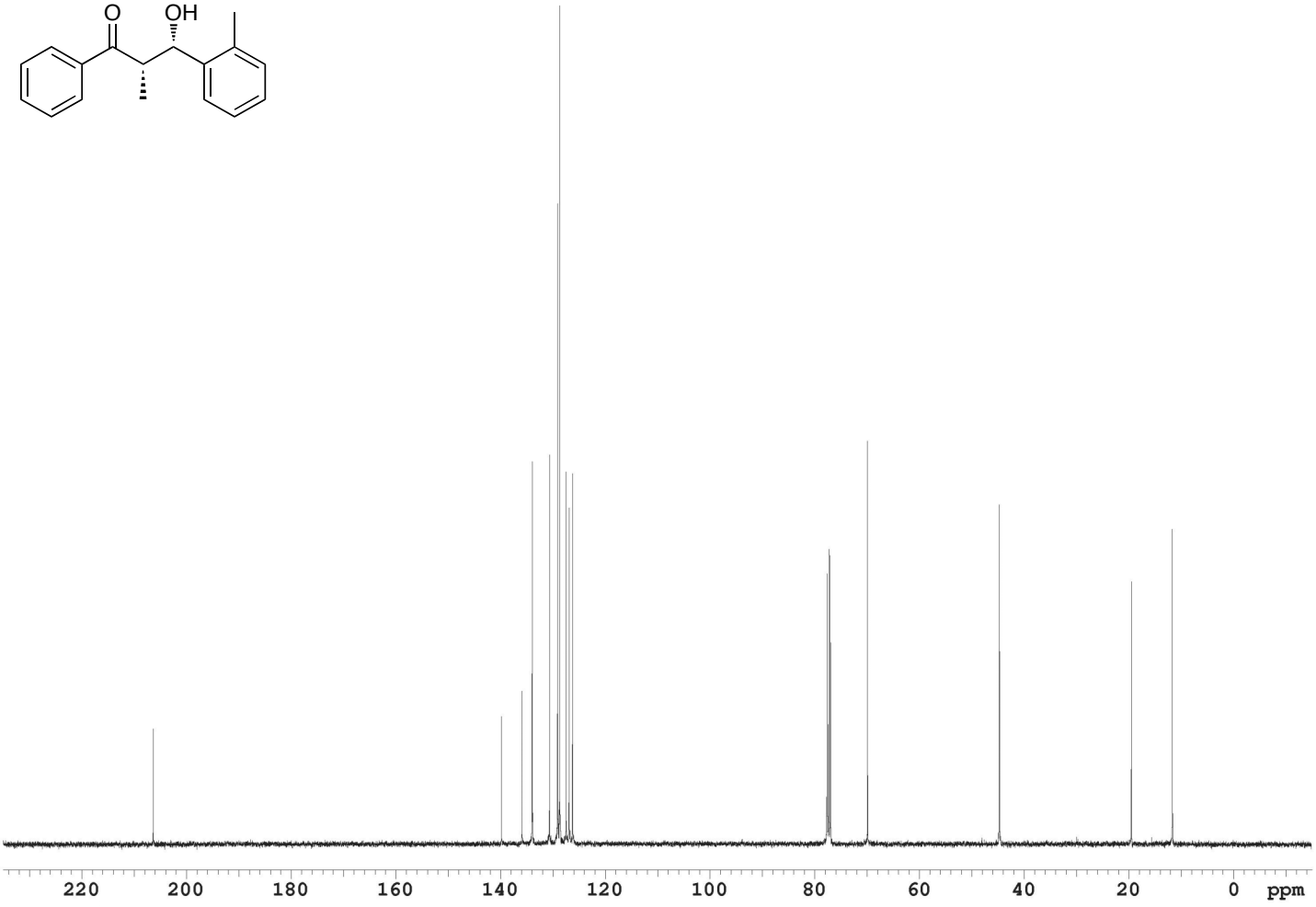
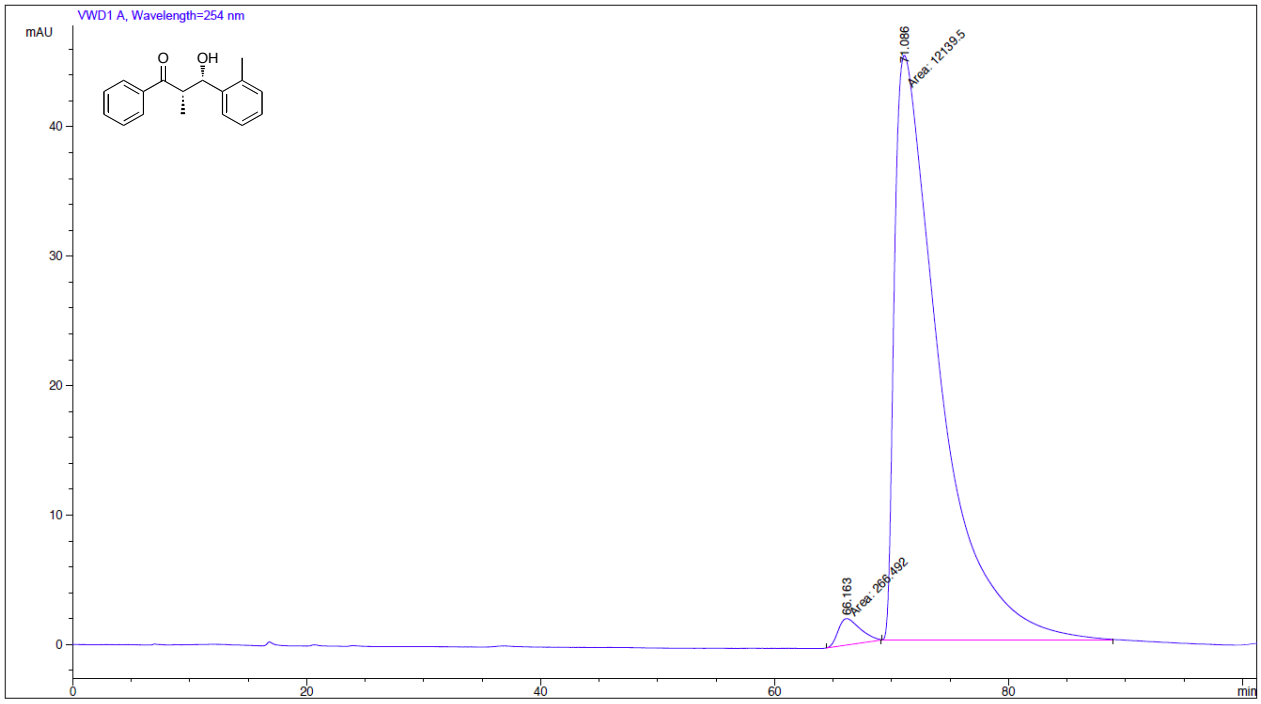
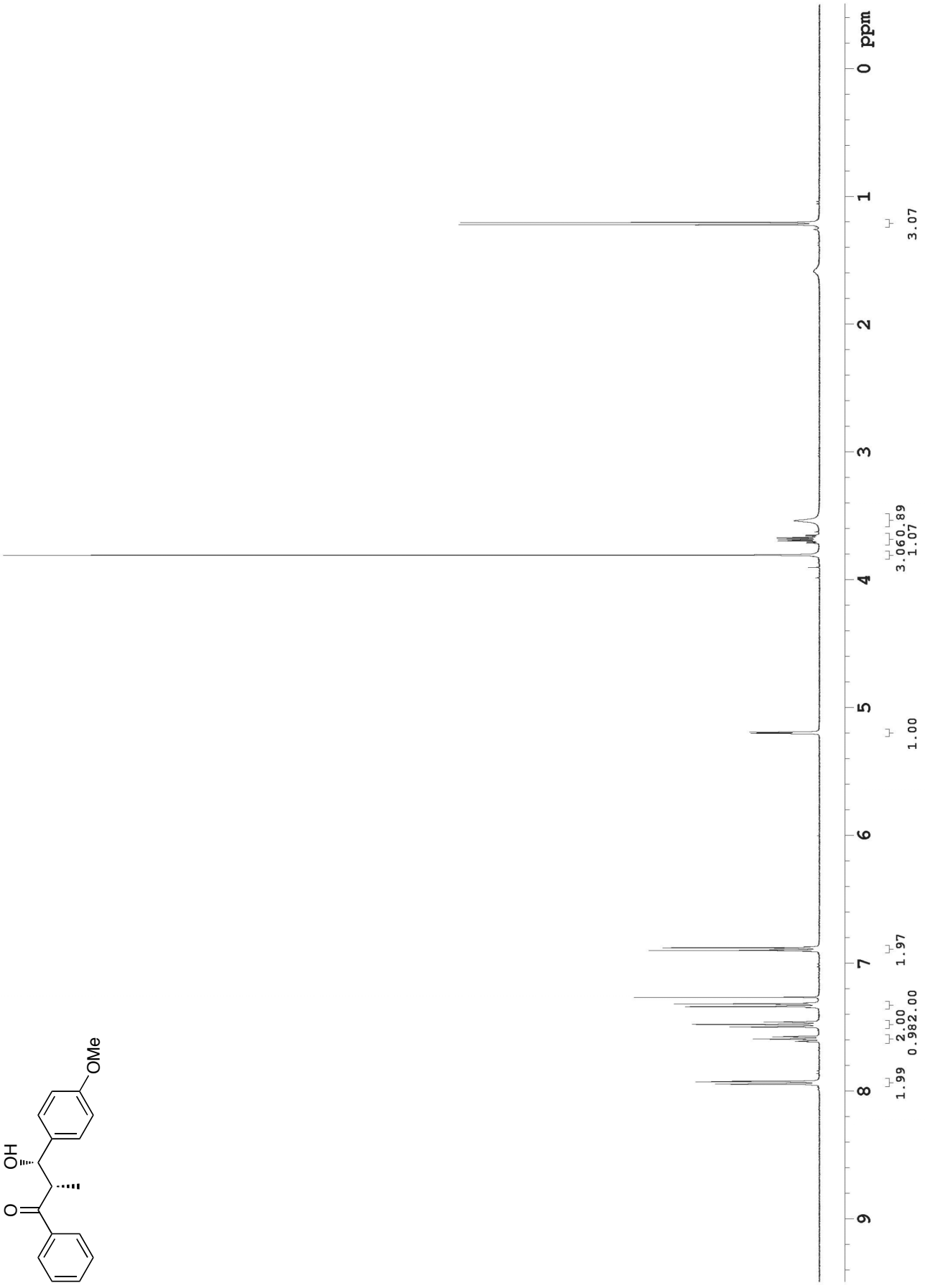
1.93
1.44
OH
O





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	66.163	MM	1.5389	266.49164	2.04552	2.1481
2	71.086	MM	4.4819	1.21395e4	45.14259	97.8519
Totals :				1.24060e4	47.18812	


OMe
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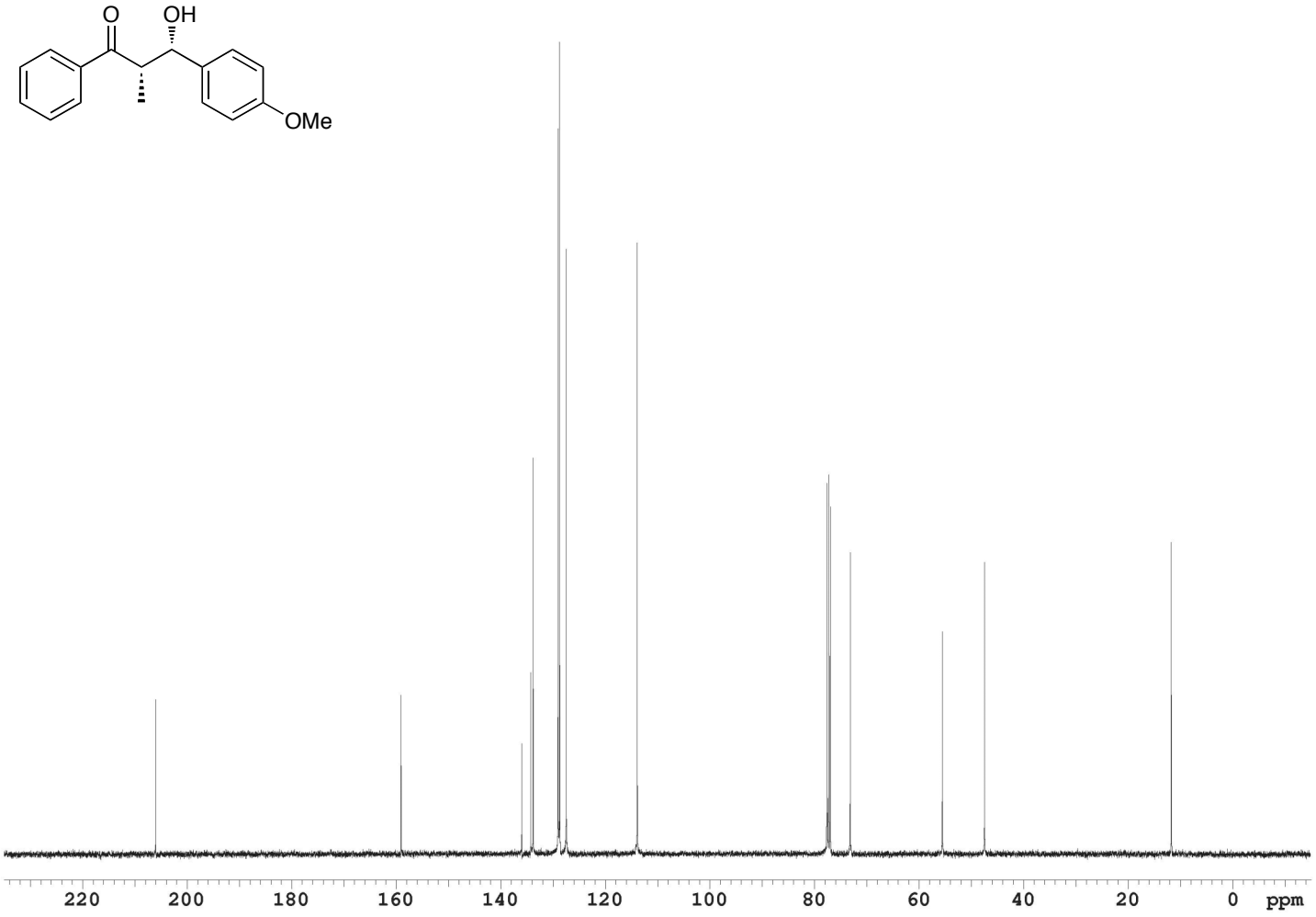
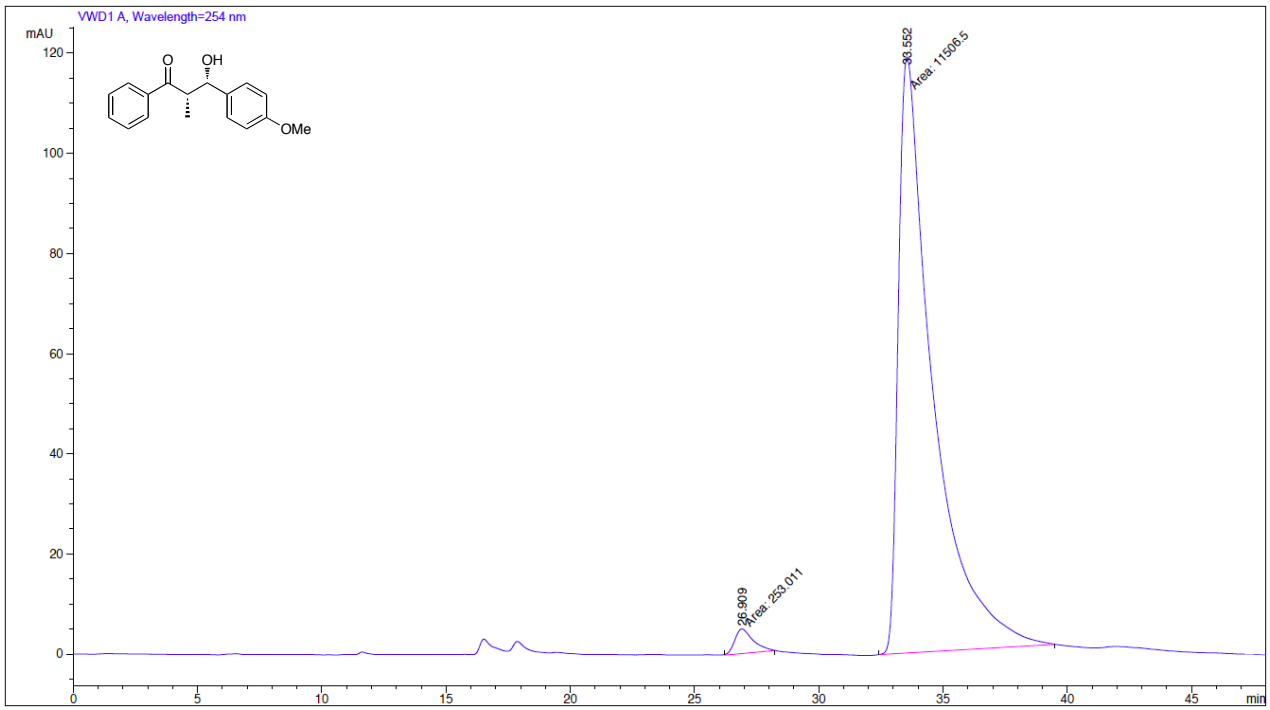
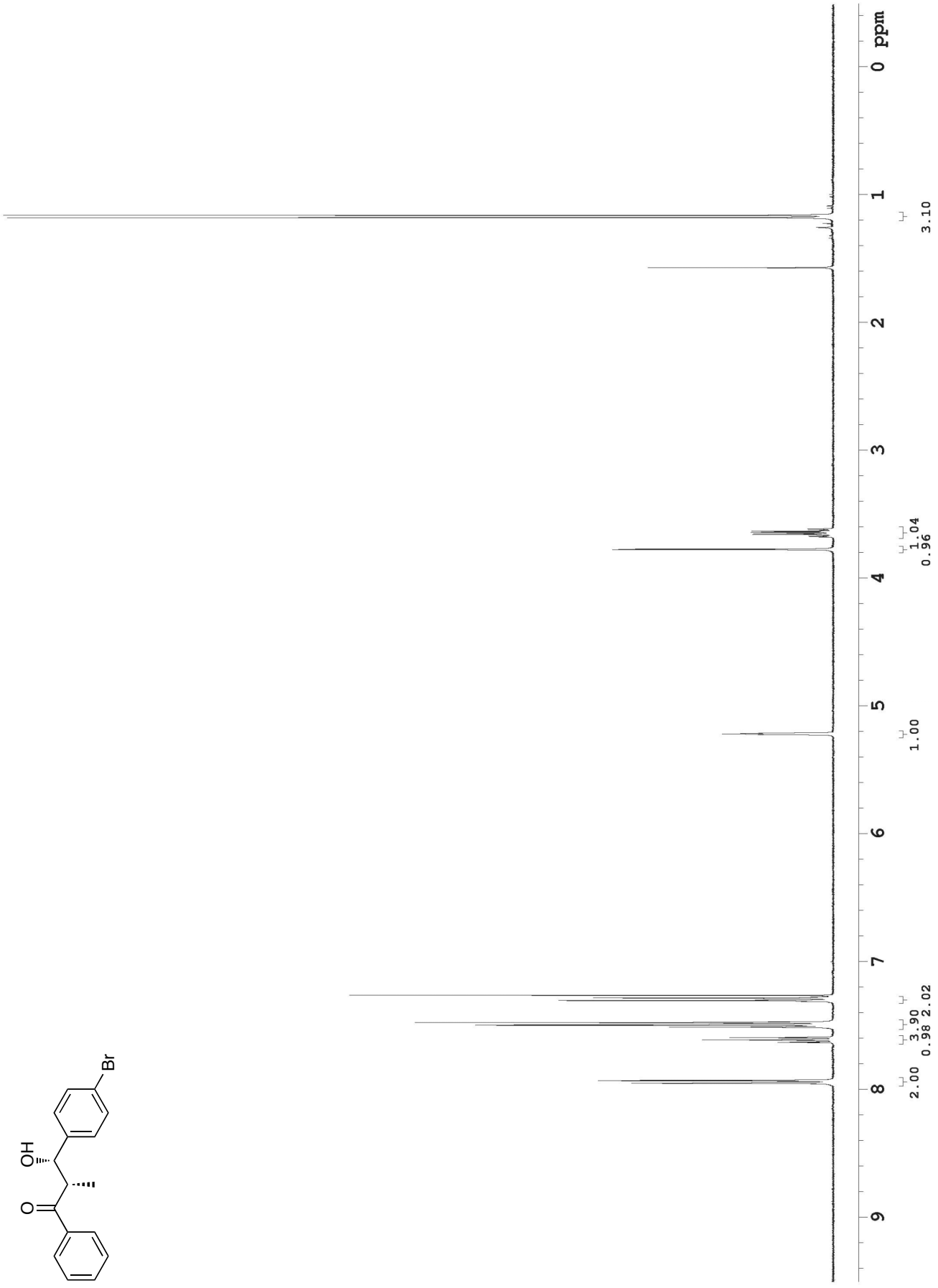




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.909	MM	0.8576	253.01126	4.91680	2.1515
2	33.552	MM	1.6112	1.15065e4	119.02736	97.8485
Totals :				1.17595e4	123.94416	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0.98
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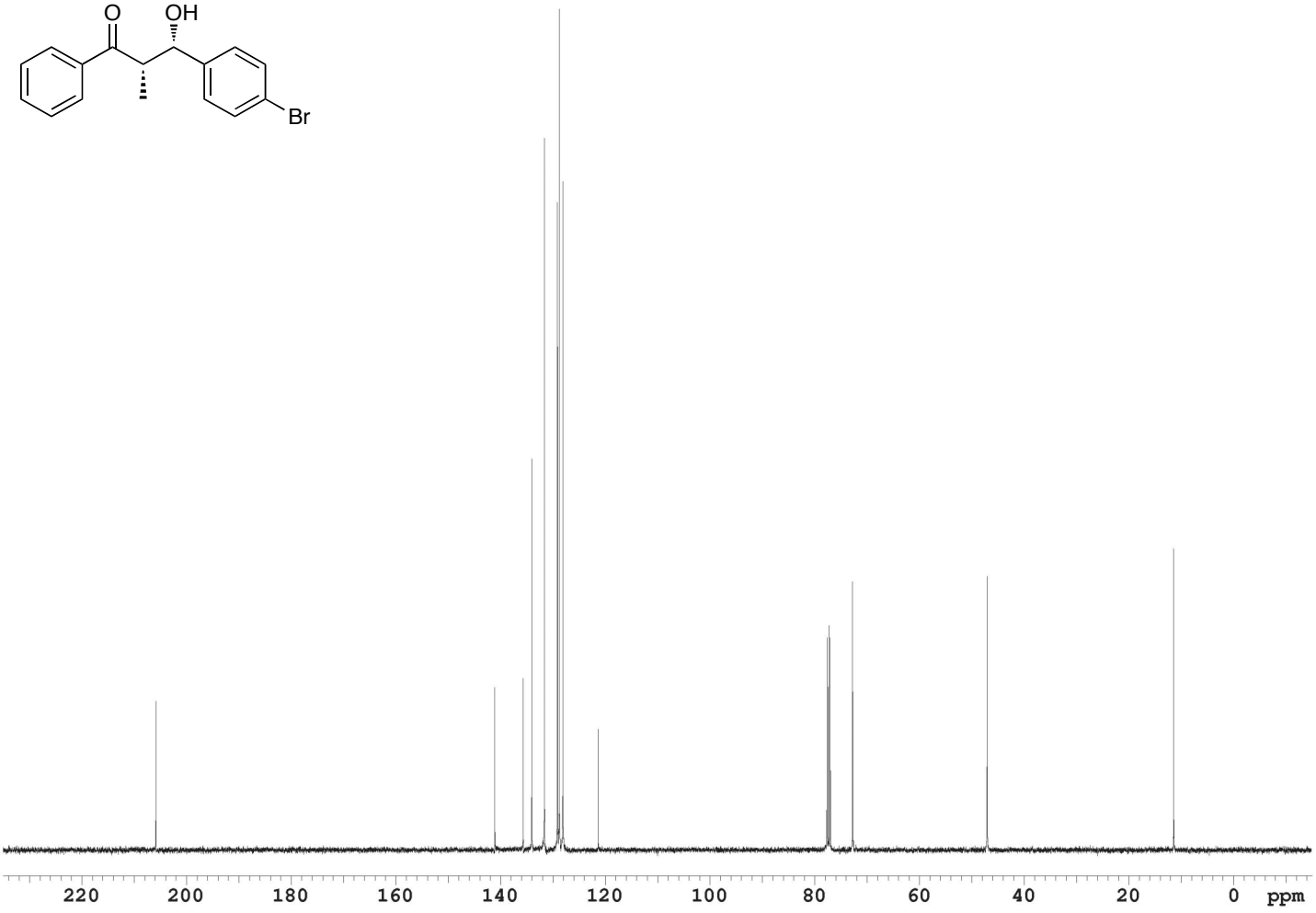
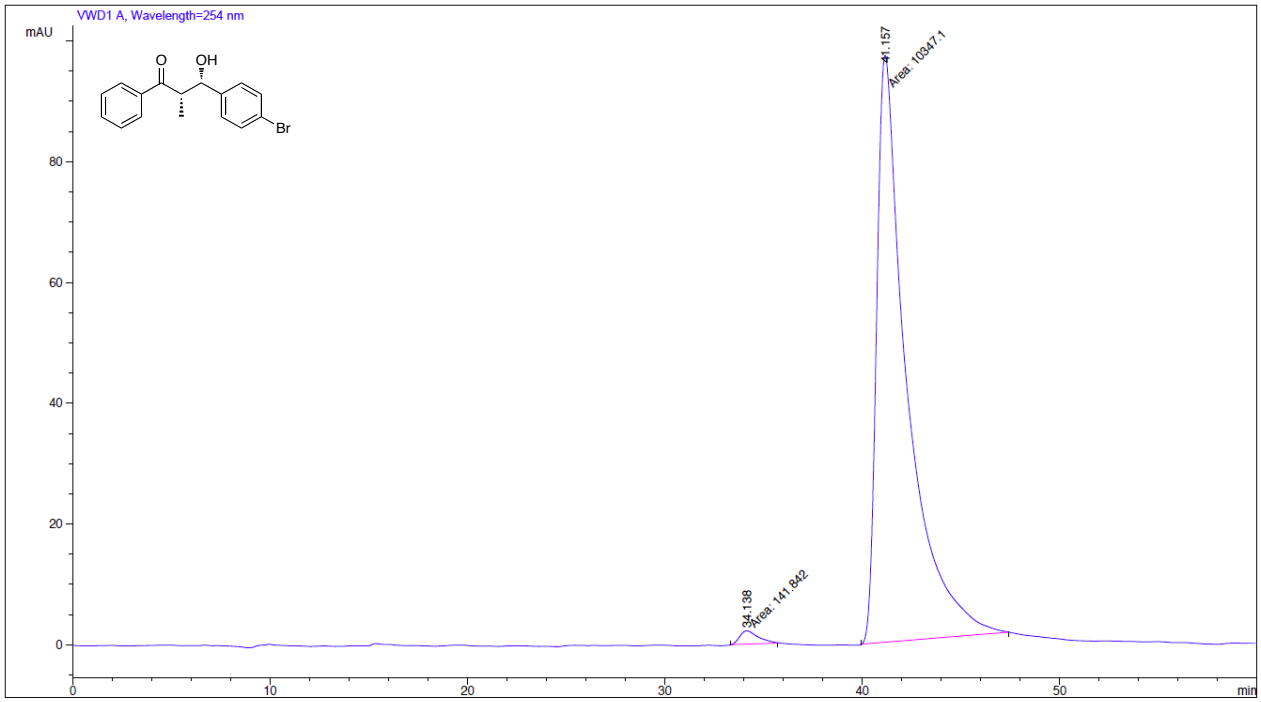
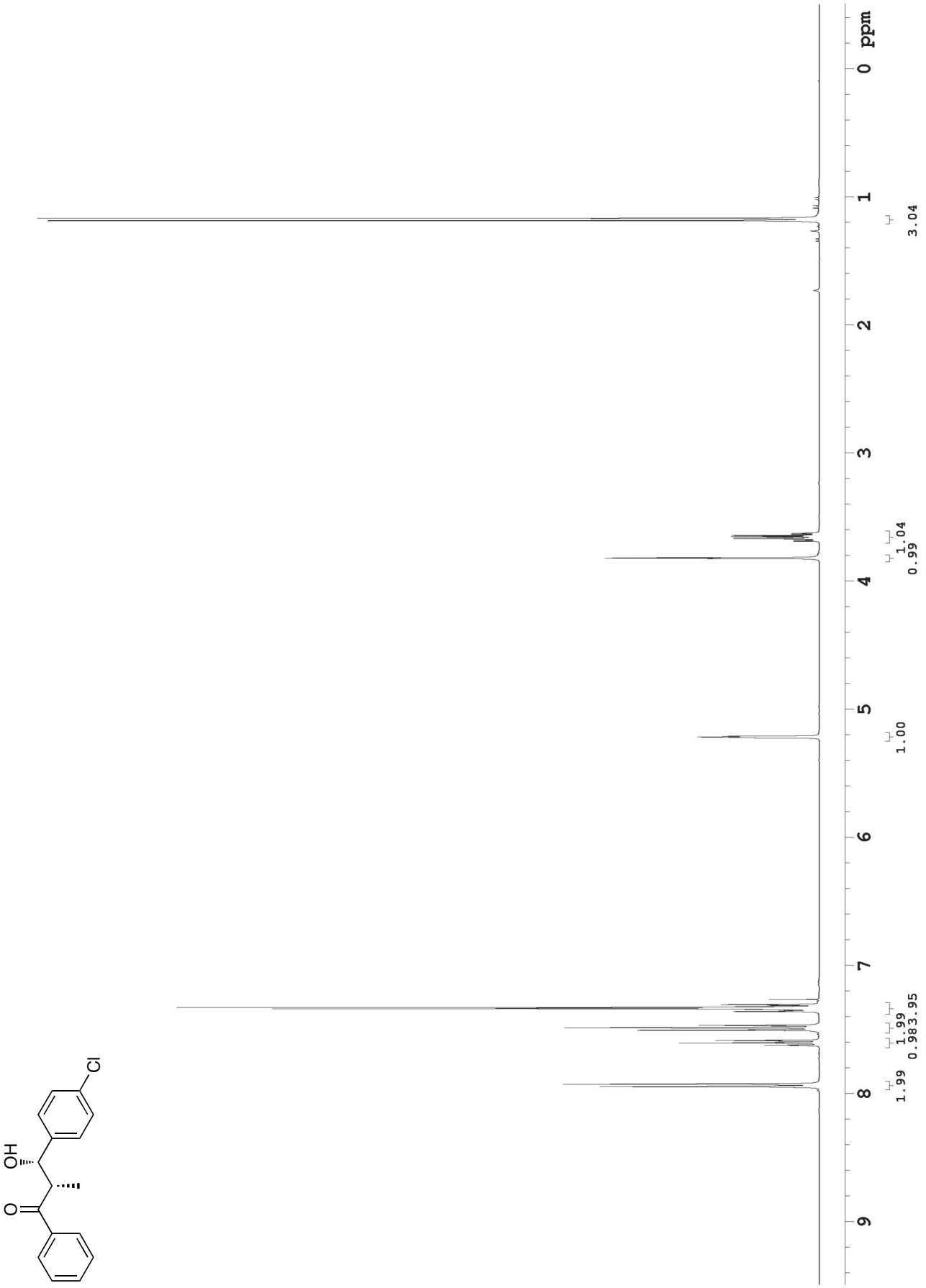
2.00
Br
OH
O





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.138	MM	1.0763	141.84200	2.19642	1.3523
2	41.157	MM	1.7747	1.03471e4	97.17222	98.6477
Totals :				1.04890e4	99.36863	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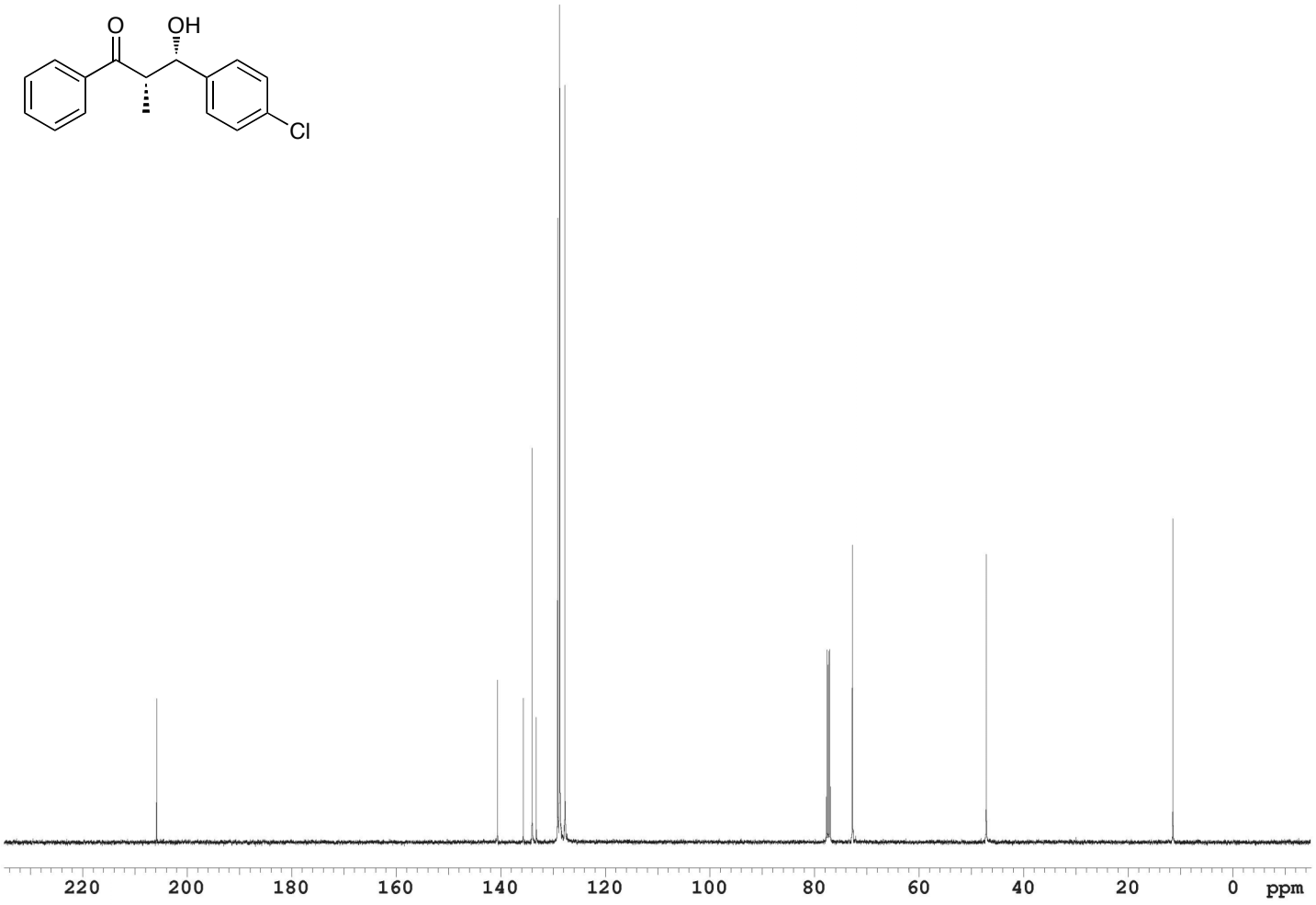
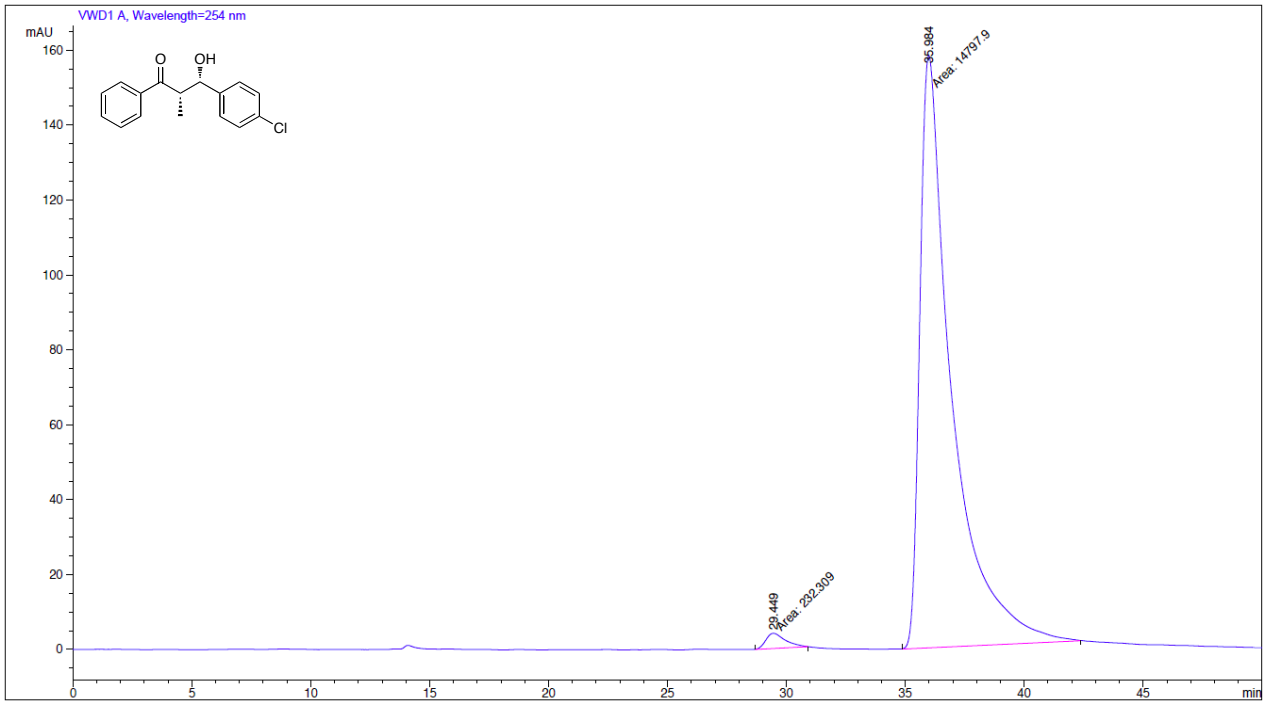
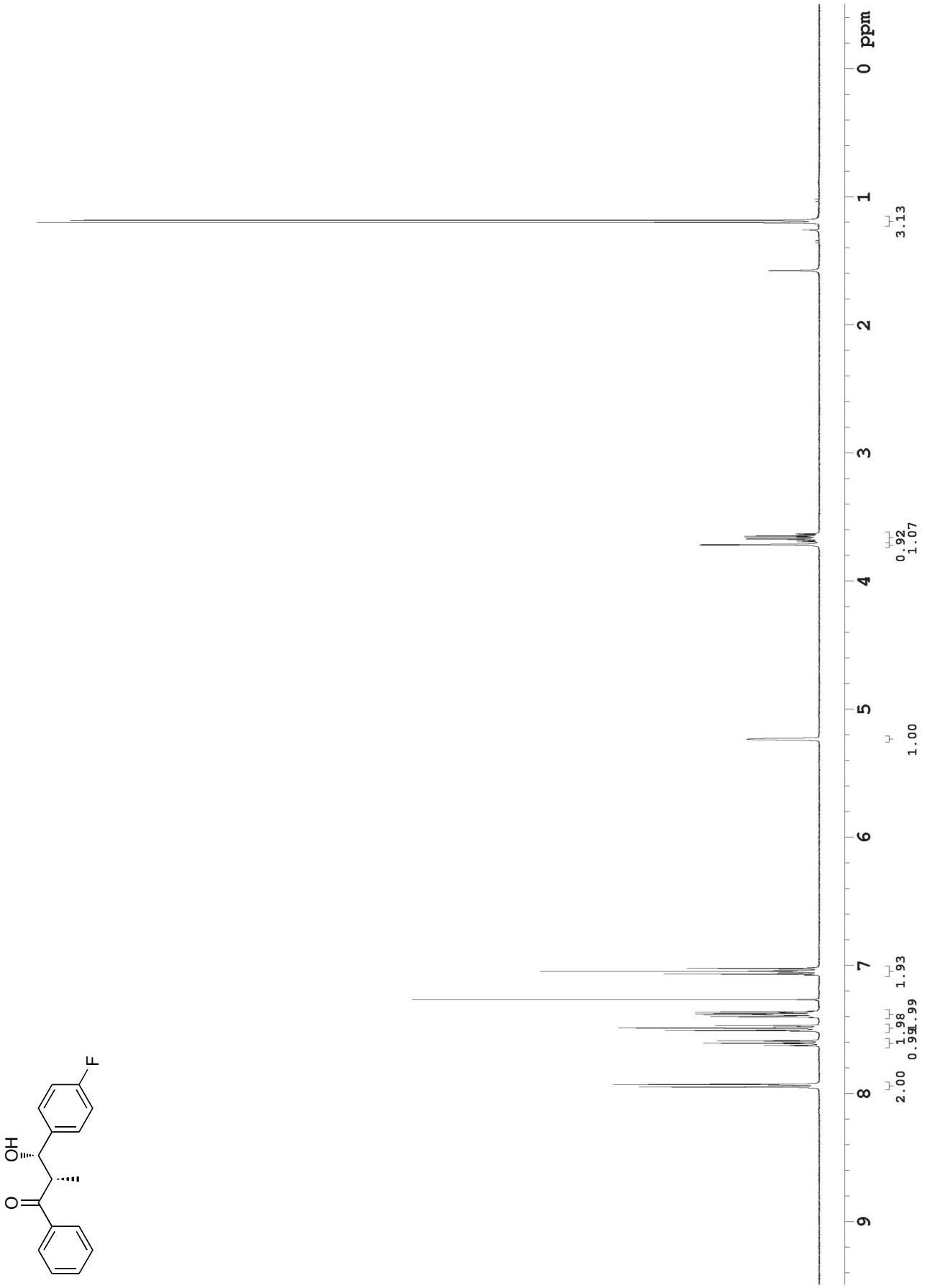
1.99
OH
O
Cl





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.449	MM	0.9510	232.30858	4.07152	1.5456
2	35.984	MM	1.5597	1.47979e4	158.13118	98.4544
Totals :				1.50302e4	162.20270	


F
OH
O
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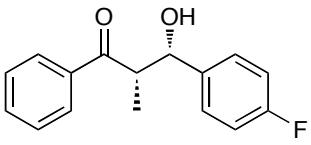
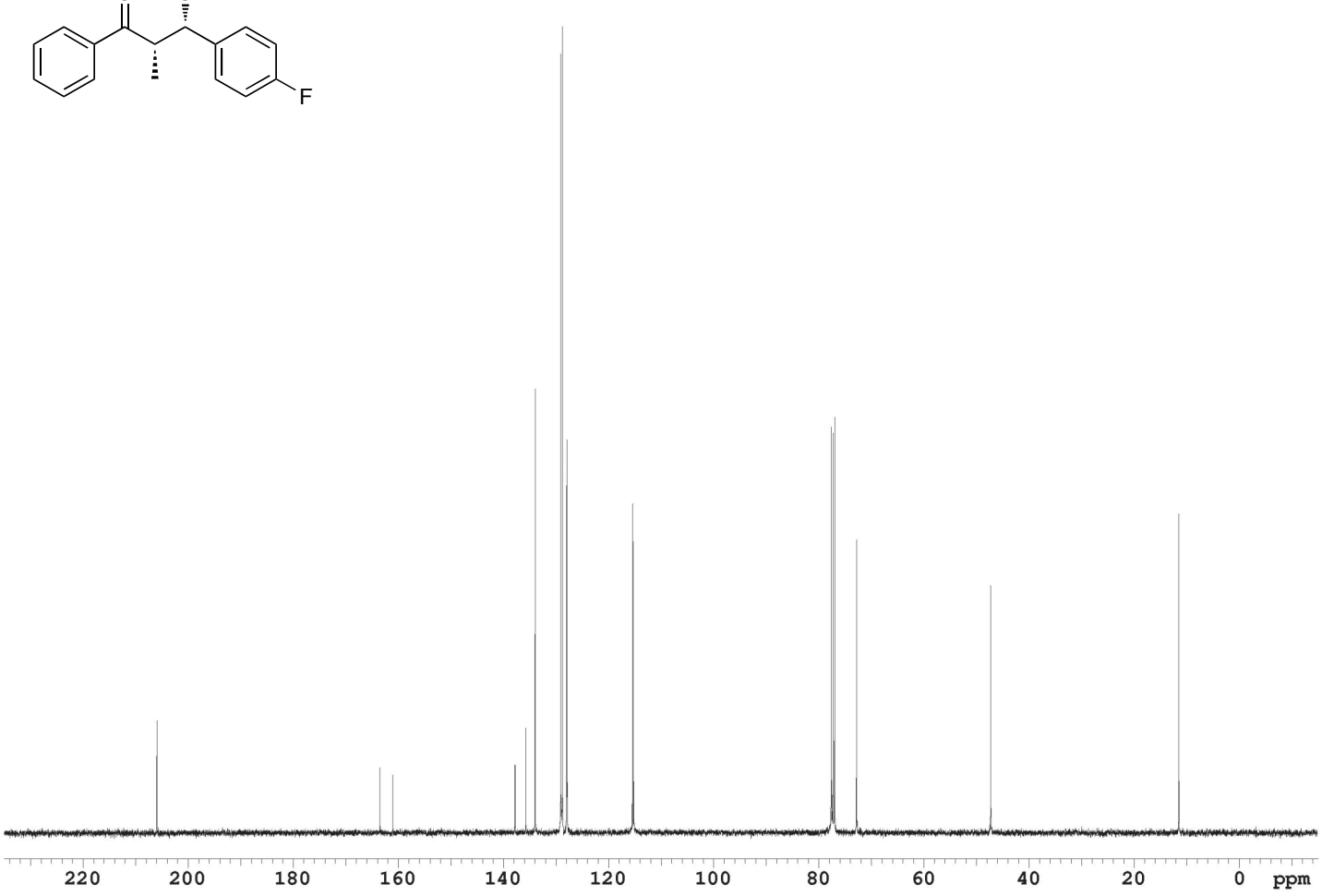
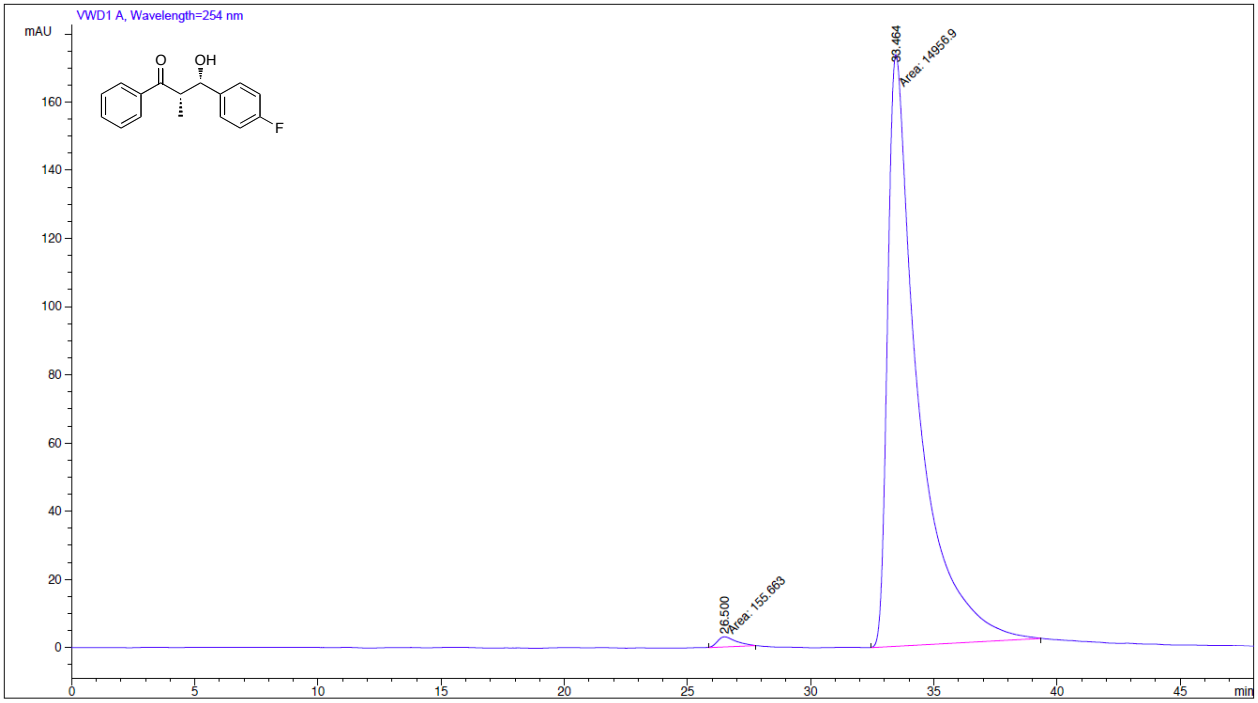
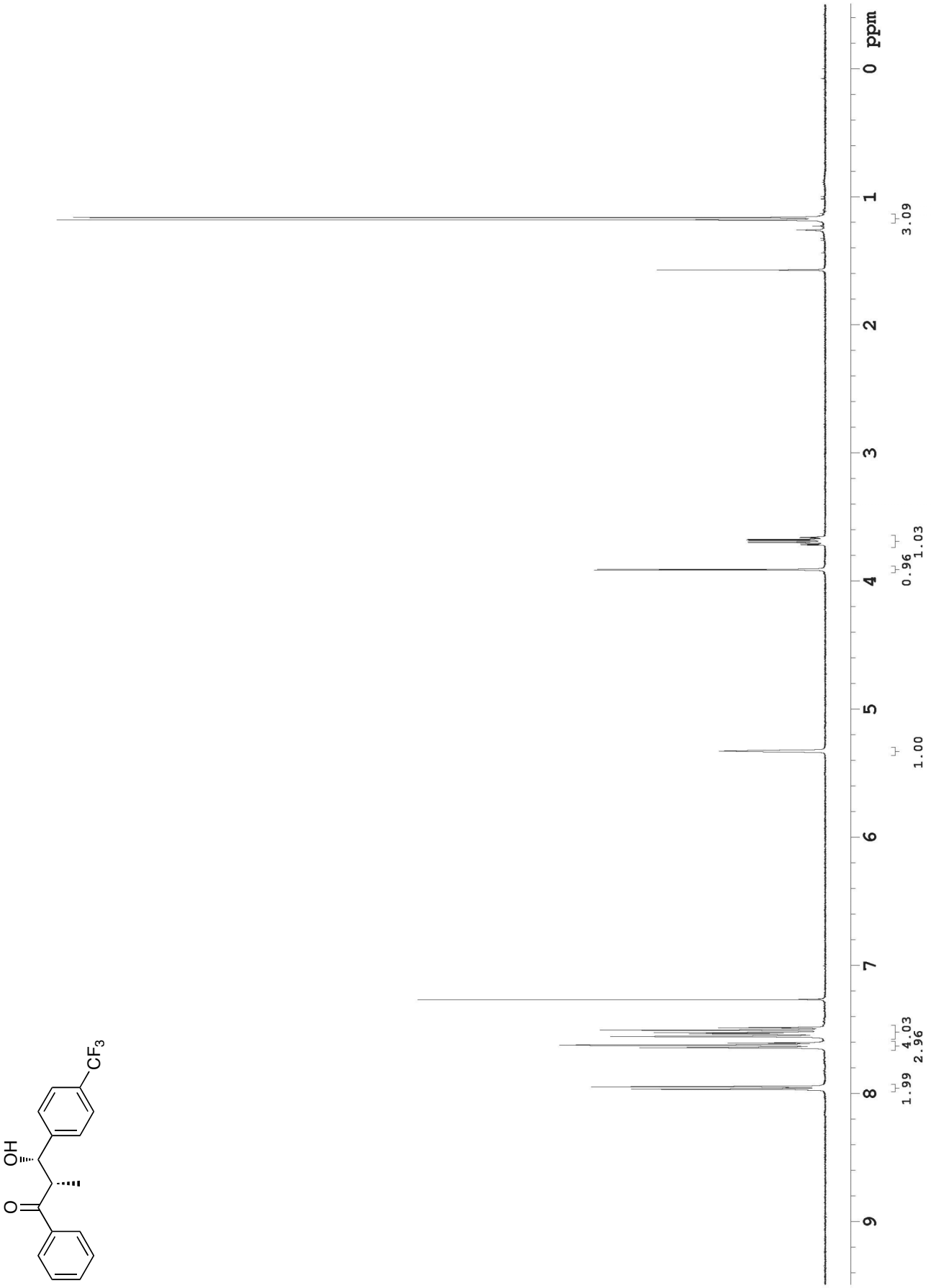
1.99
2.00







Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.500	MM	0.8738	155.66269	2.96900	1.0300
2	33.464	MM	1.4362	1.49569e4	173.56775	98.9700
Totals :				1.51126e4	176.53675	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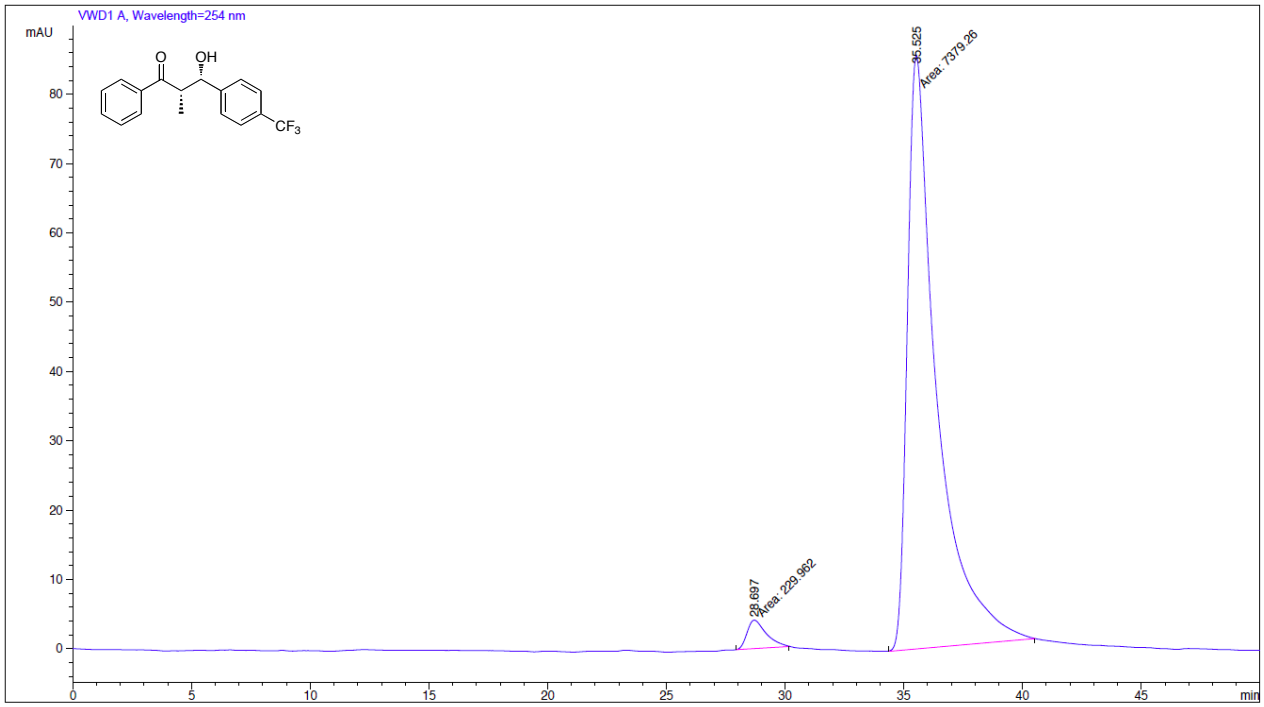
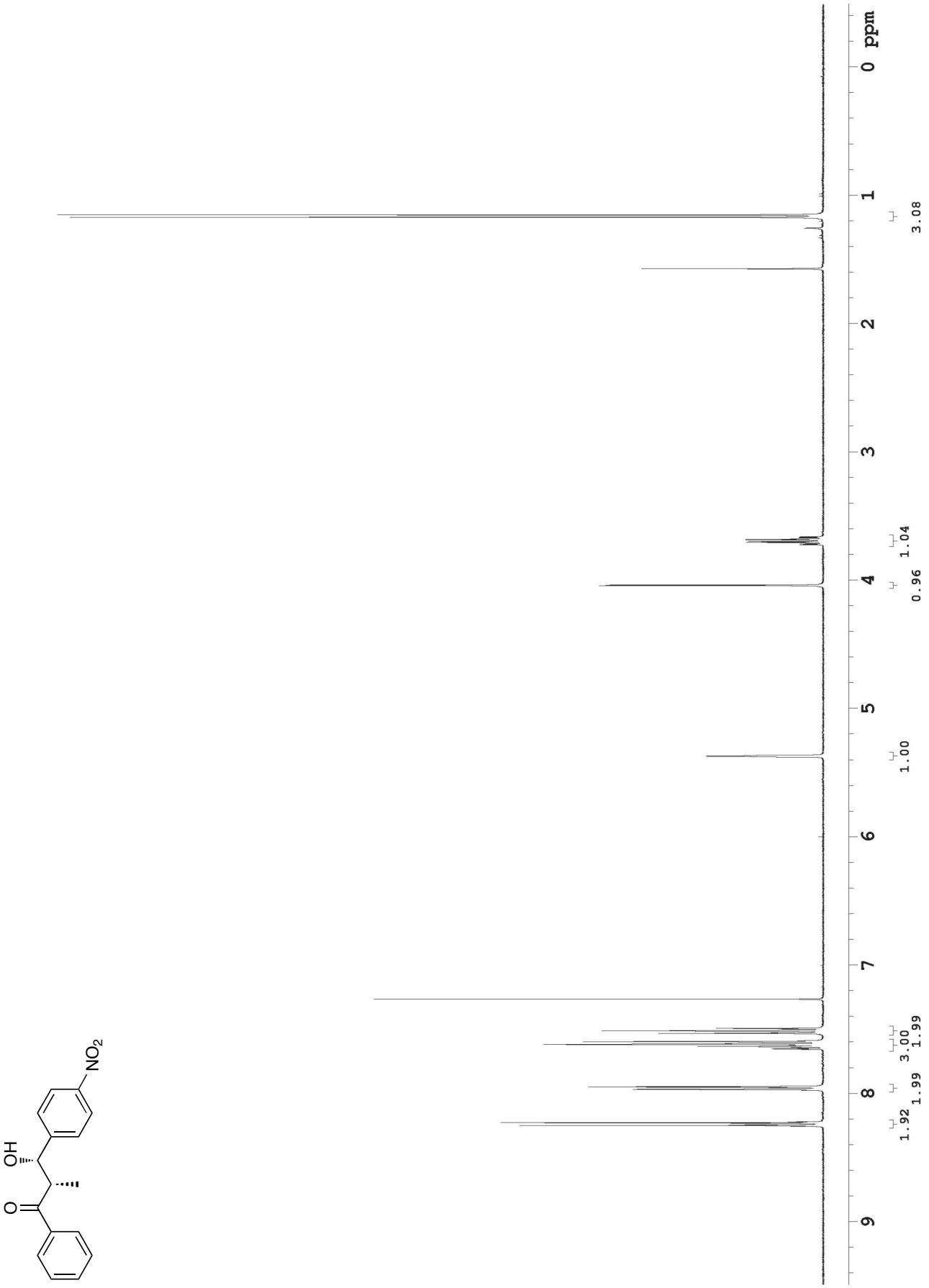
OH
O
CF3



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.697	MM	0.9330	229.96230	4.10810	3.0222
2	35.525	MM	1.4371	7379.25879	85.58334	96.9778
Totals :				7609.22108	89.69144	


NO2
OH
O
ppm
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1.04
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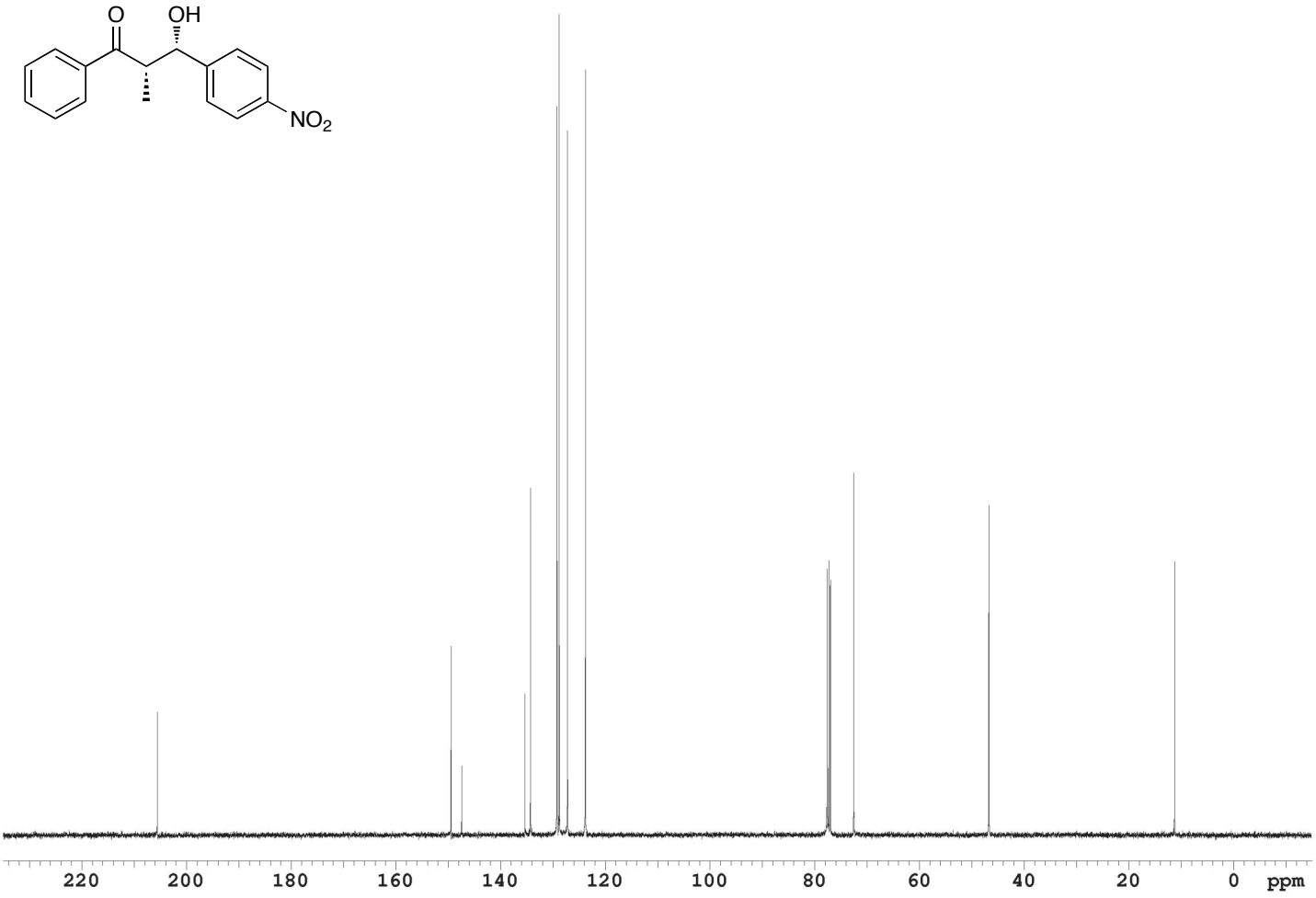
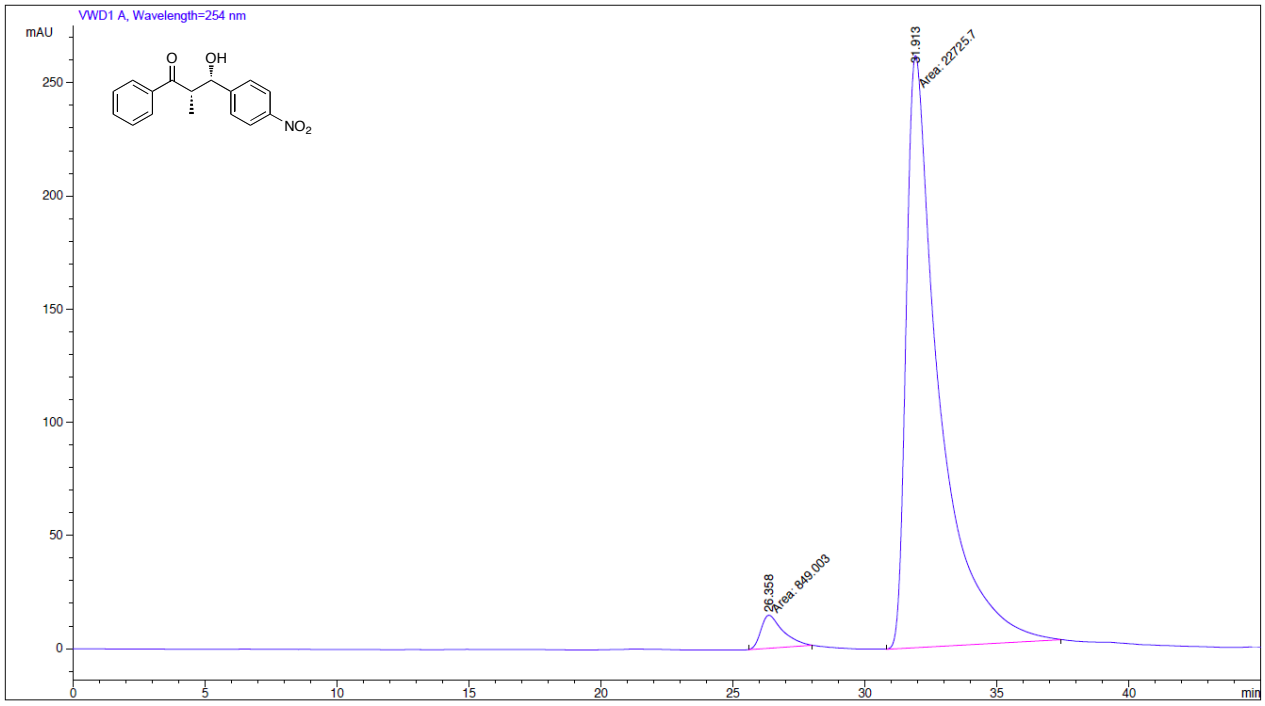
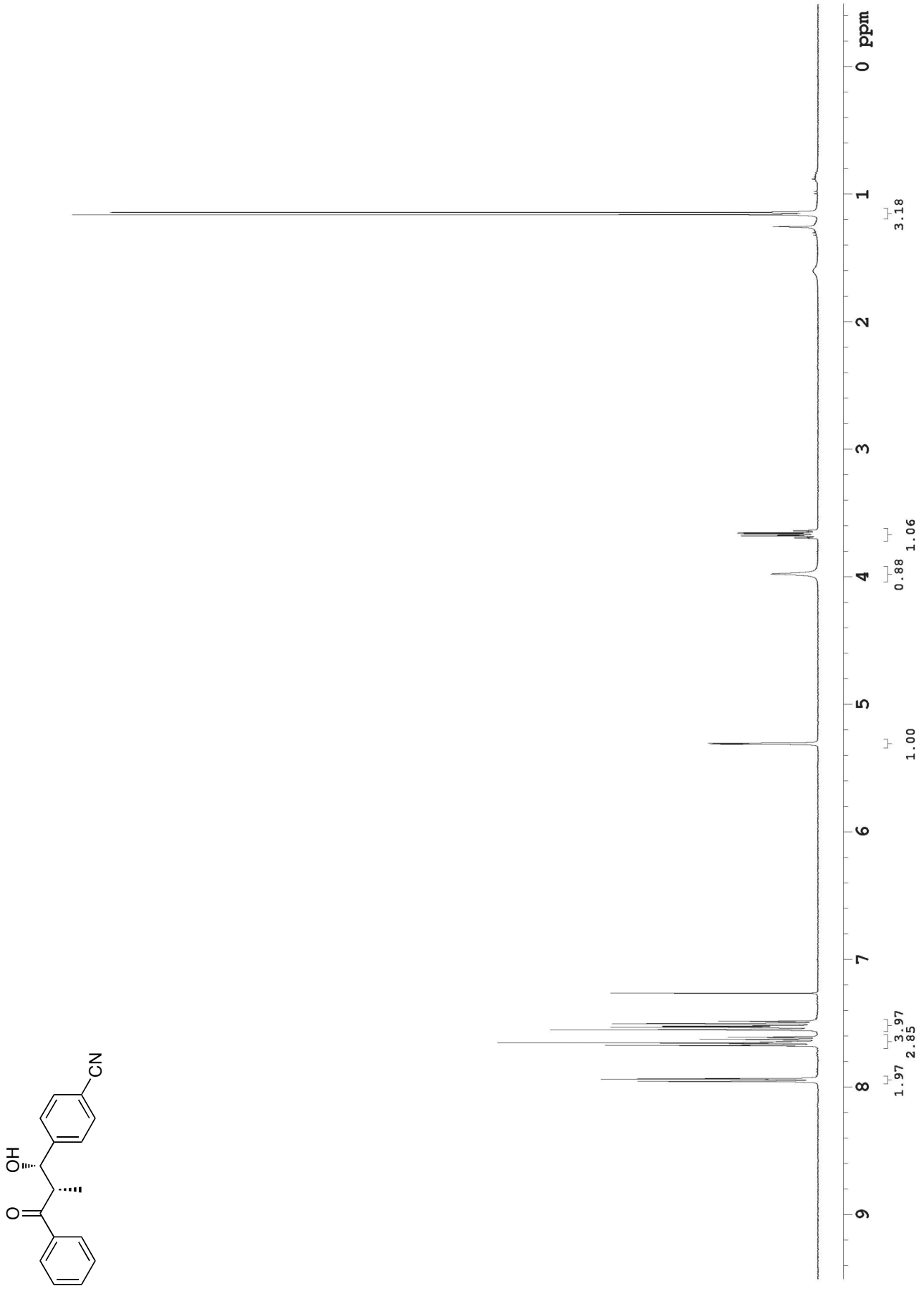
1.00
3.00
1.99
1.99
1.92





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.358	MM	0.9675	849.00342	14.62575	3.6013
2	31.913	MM	1.4480	2.27257e4	261.57864	96.3987
Totals :				2.35747e4	276.20440	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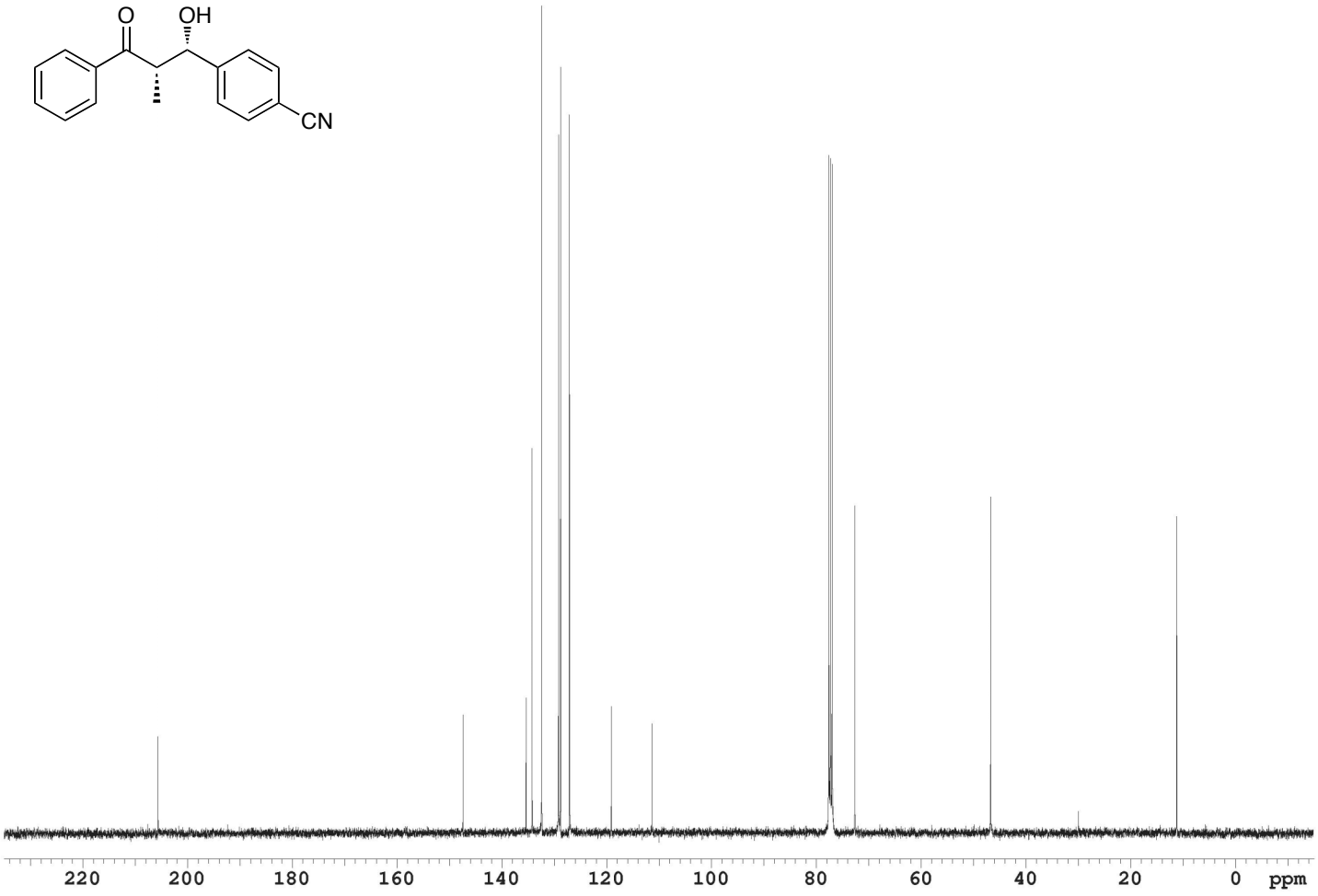
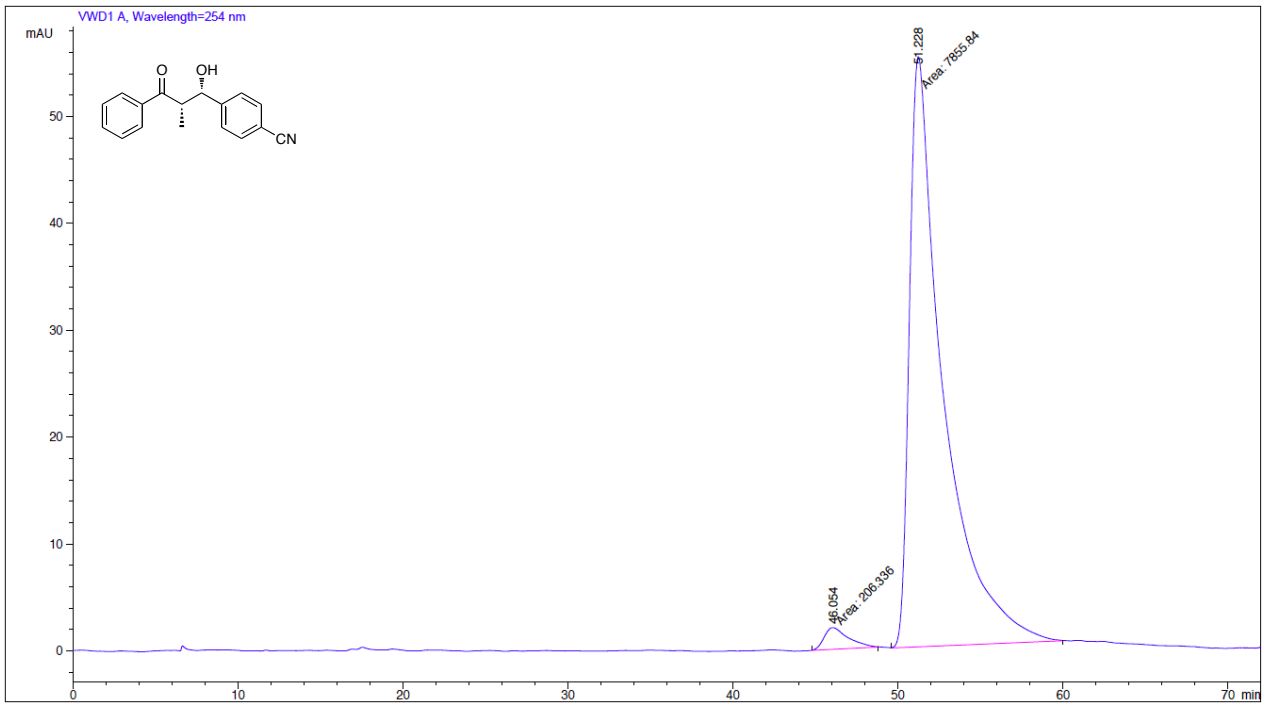
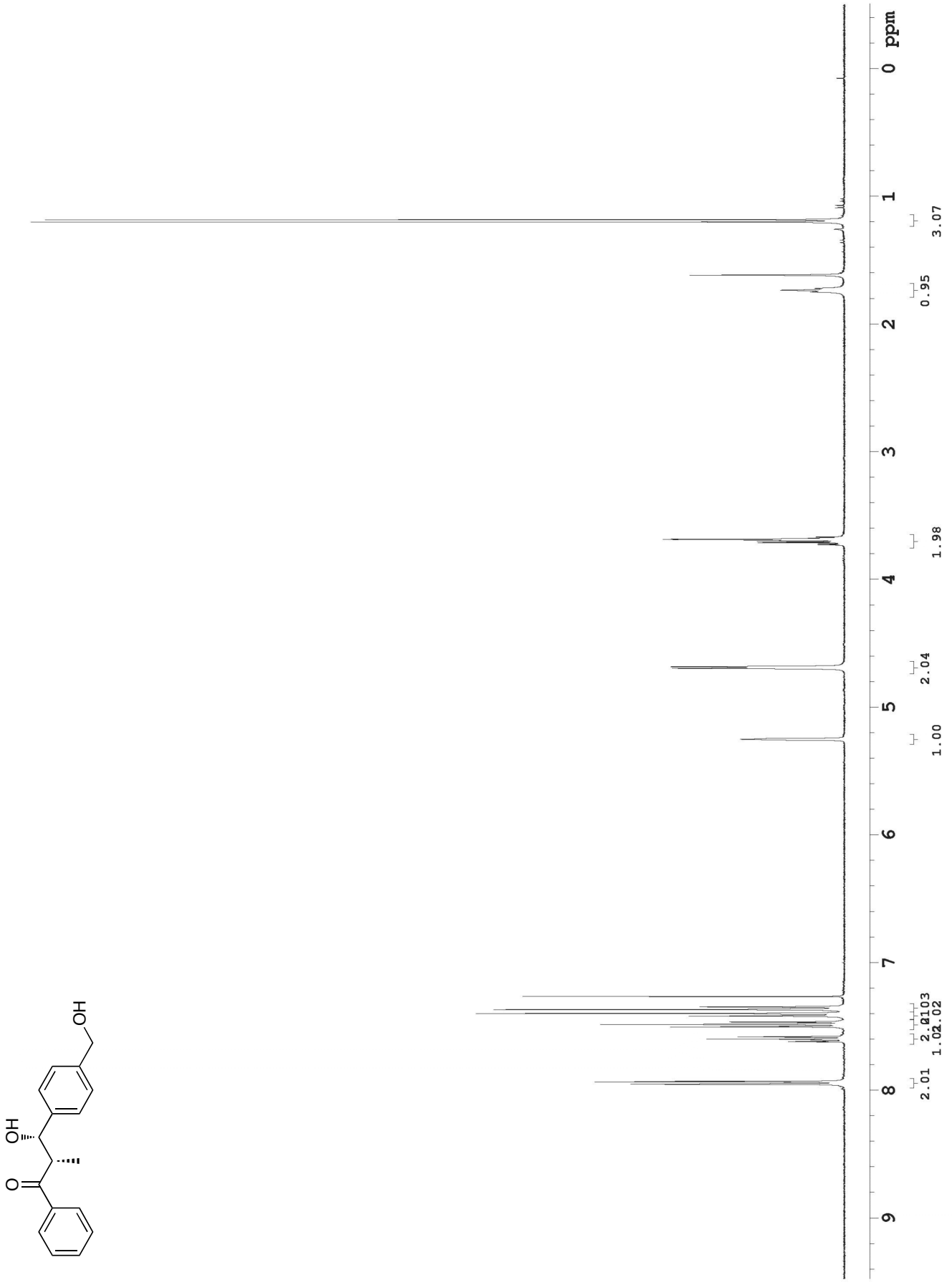
1.97
CN
OH
O





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	46.054	MM	1.6909	206.33623	2.03384	2.5593
2	51.228	MM	2.3713	7855.84082	55.21507	97.4407
Totals :				8062.17705	57.24891	


OH
OH
O
ppm
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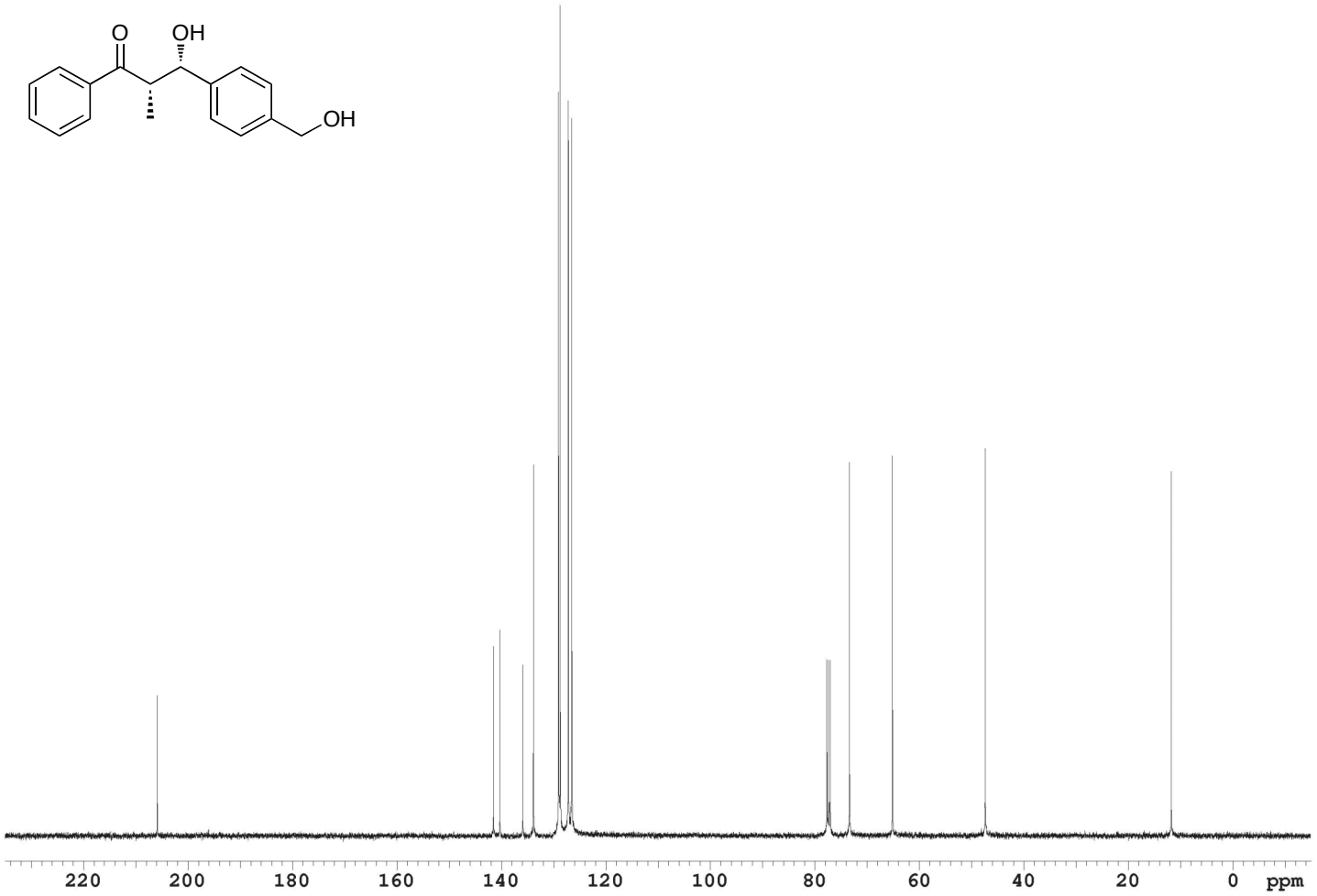
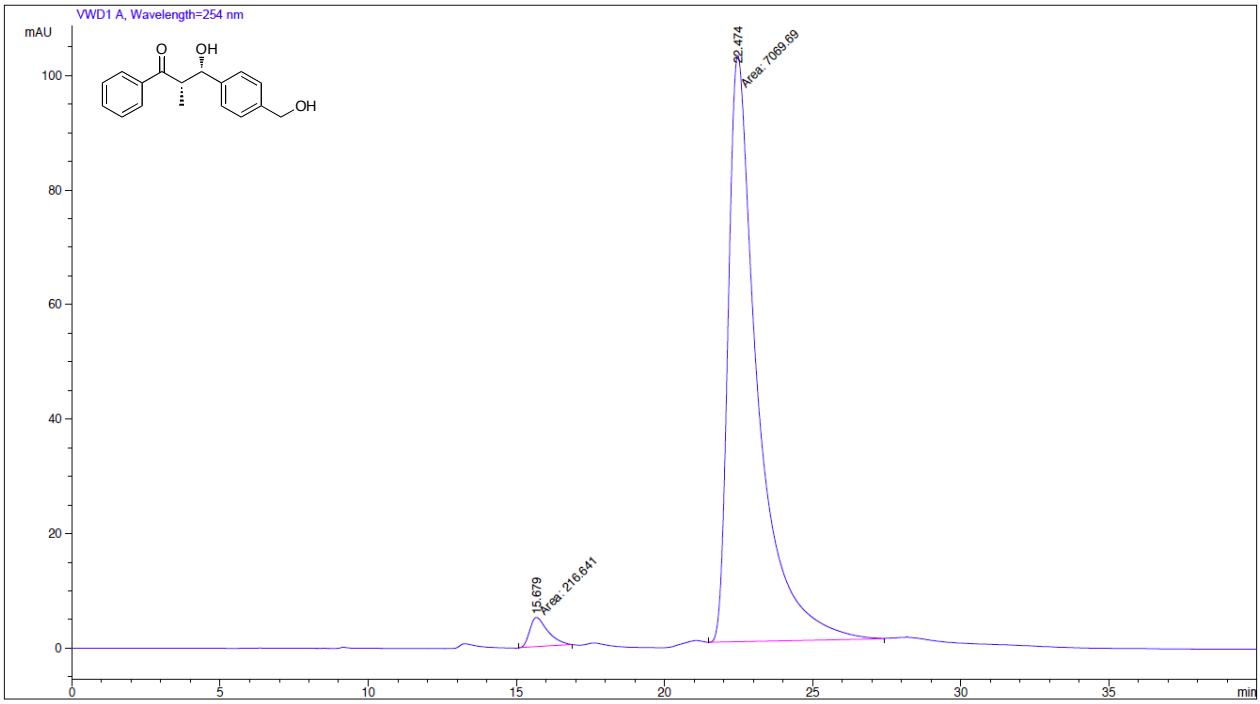
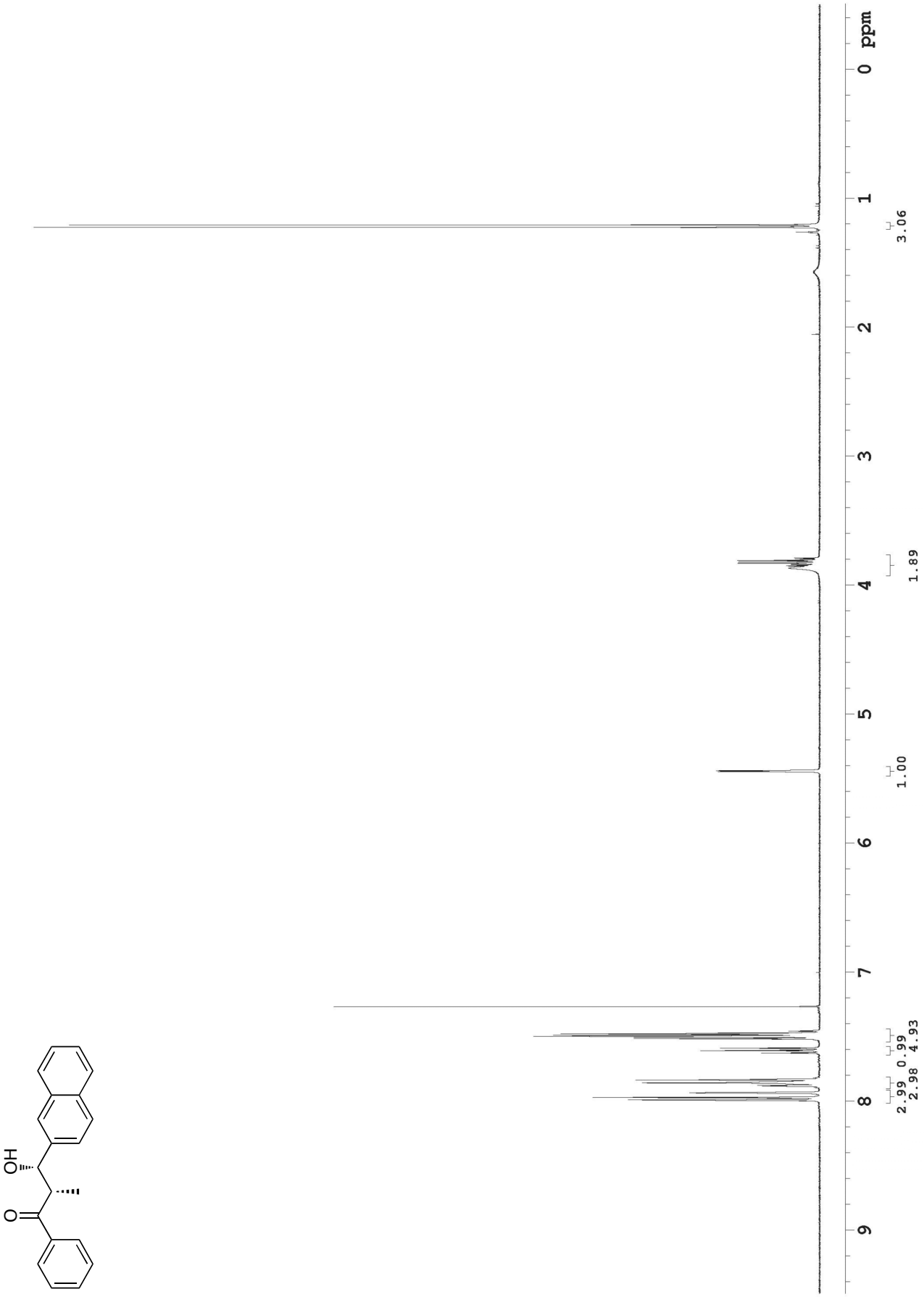
1.02.02





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.679	MM	0.7081	216.64139	5.09930	2.9733
2	22.474	MM	1.1508	7069.68799	102.38390	97.0267
Totals :				7286.32938	107.48321	


OH
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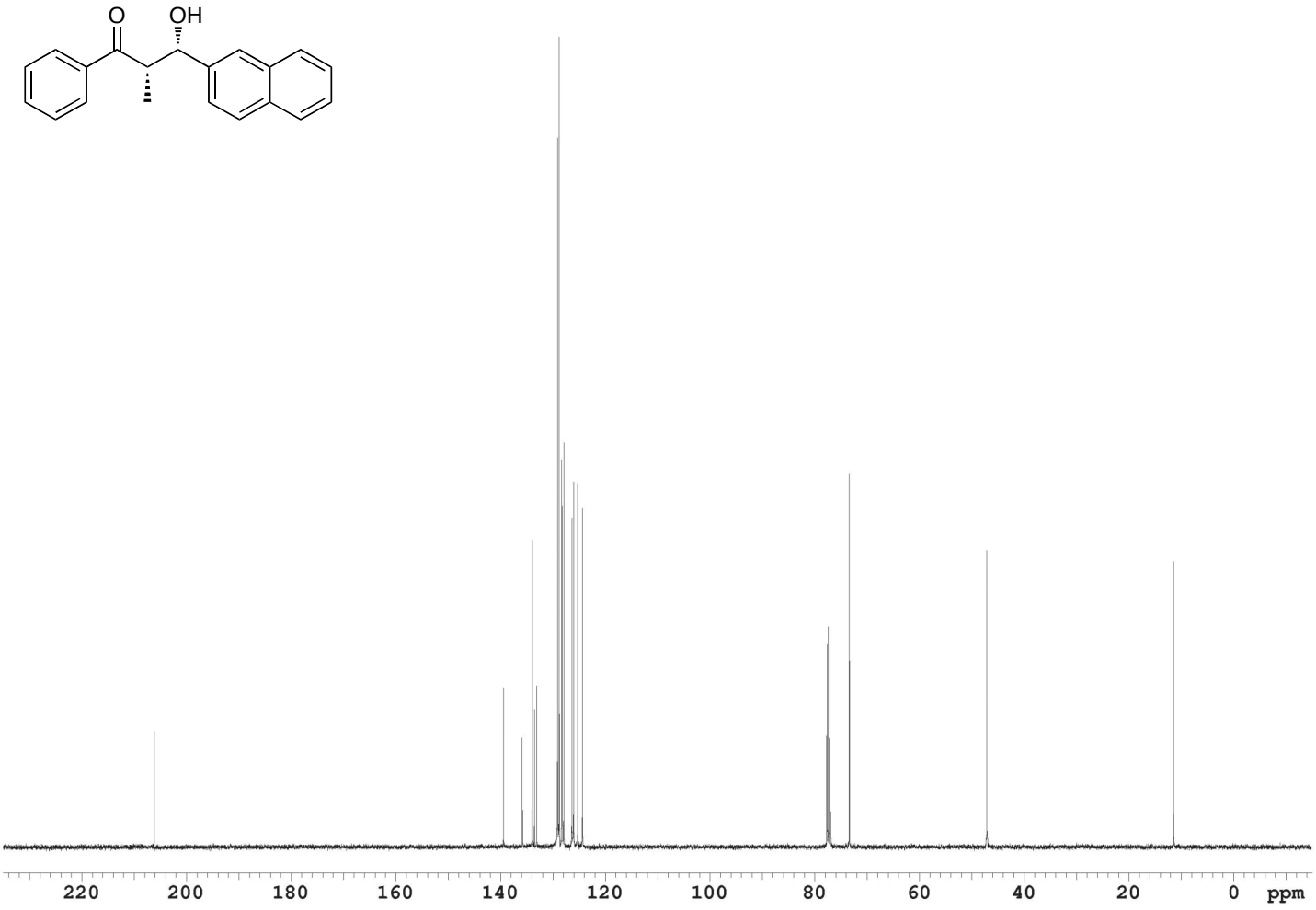
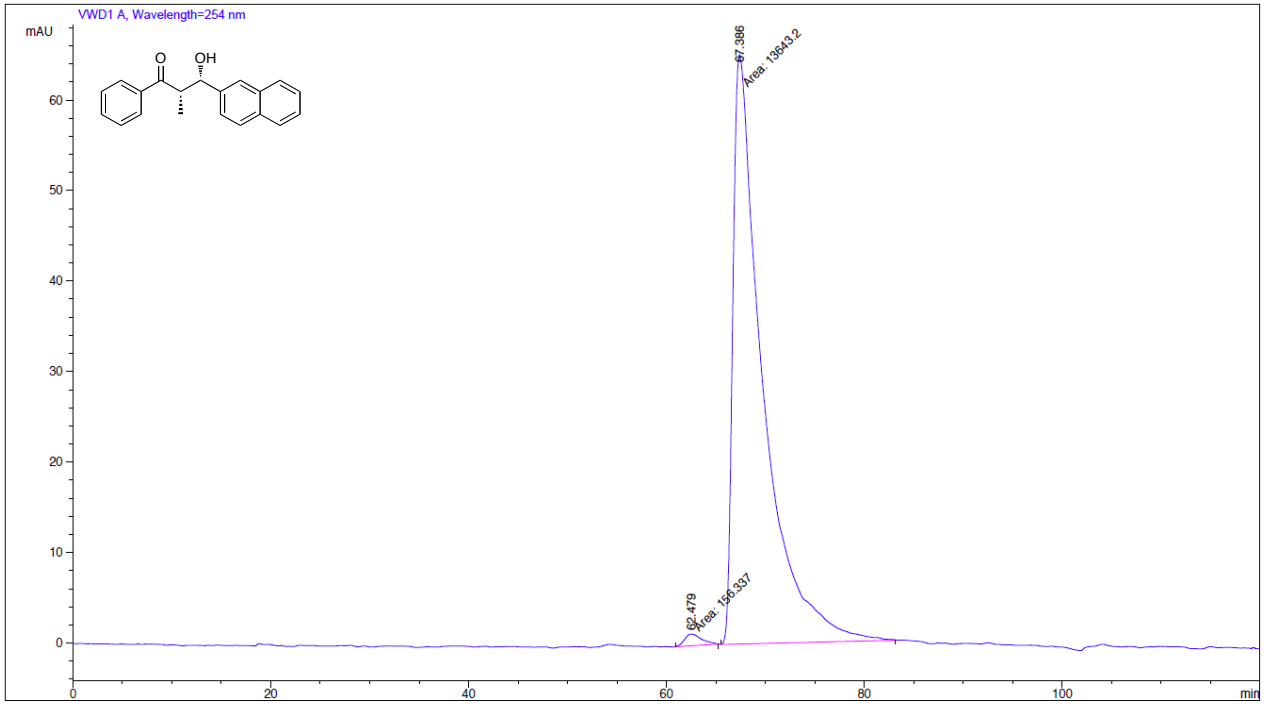
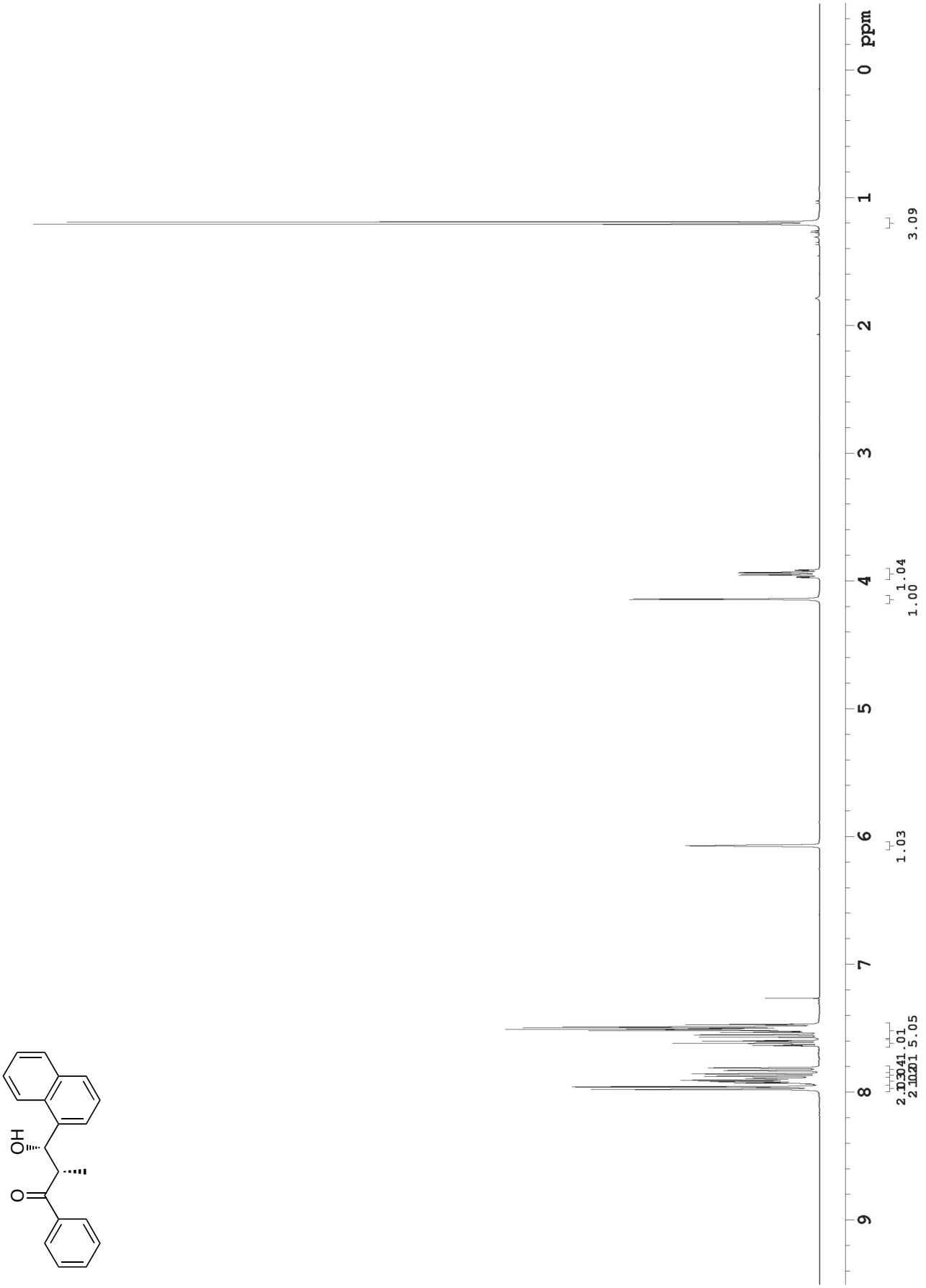
4.93





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	62.479	MM	1.9954	156.33727	1.30578	1.1329
2	67.386	MM	3.4921	1.36432e4	65.11498	98.8671
Totals :				1.37996e4	66.42076	


ppm
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2.02
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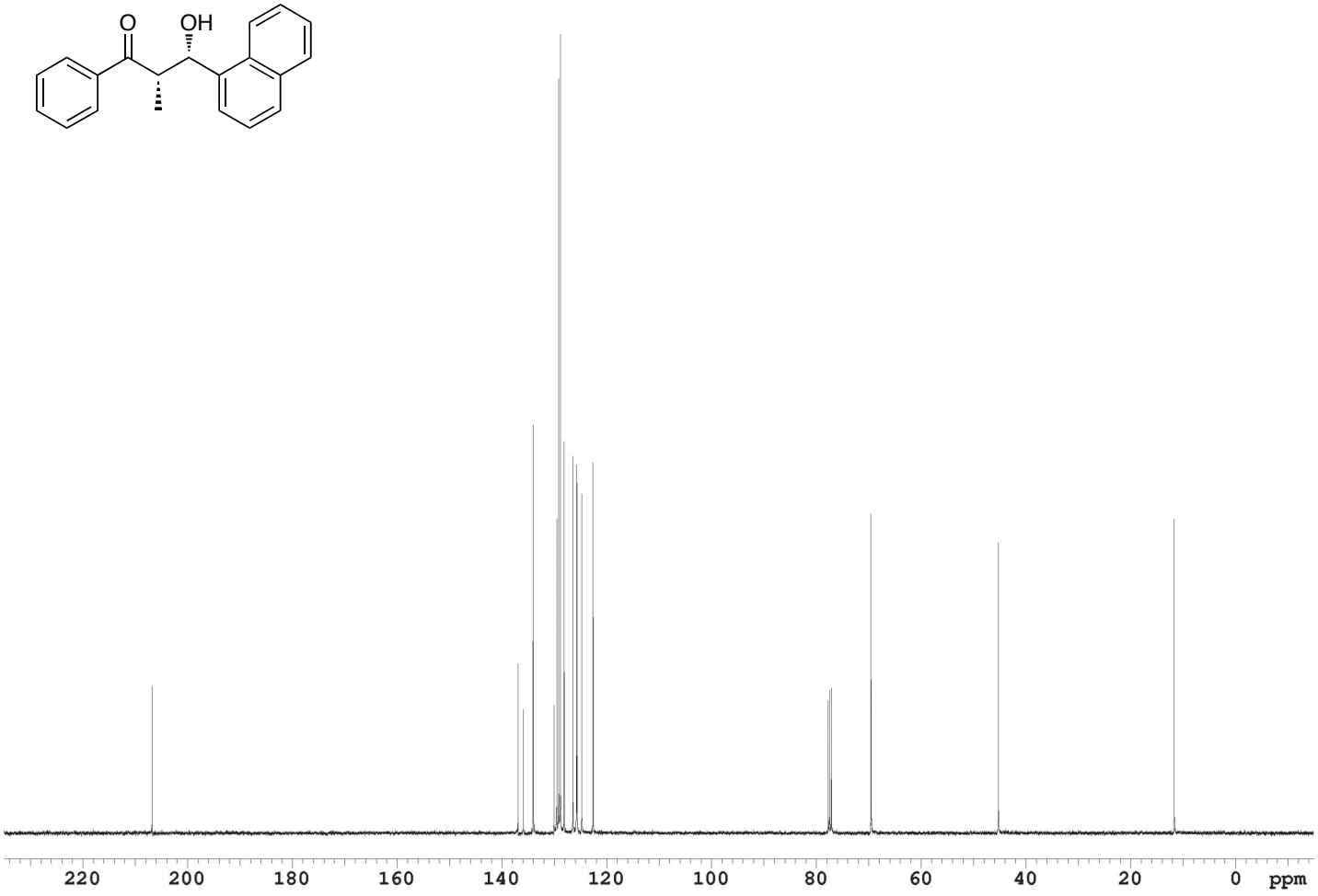
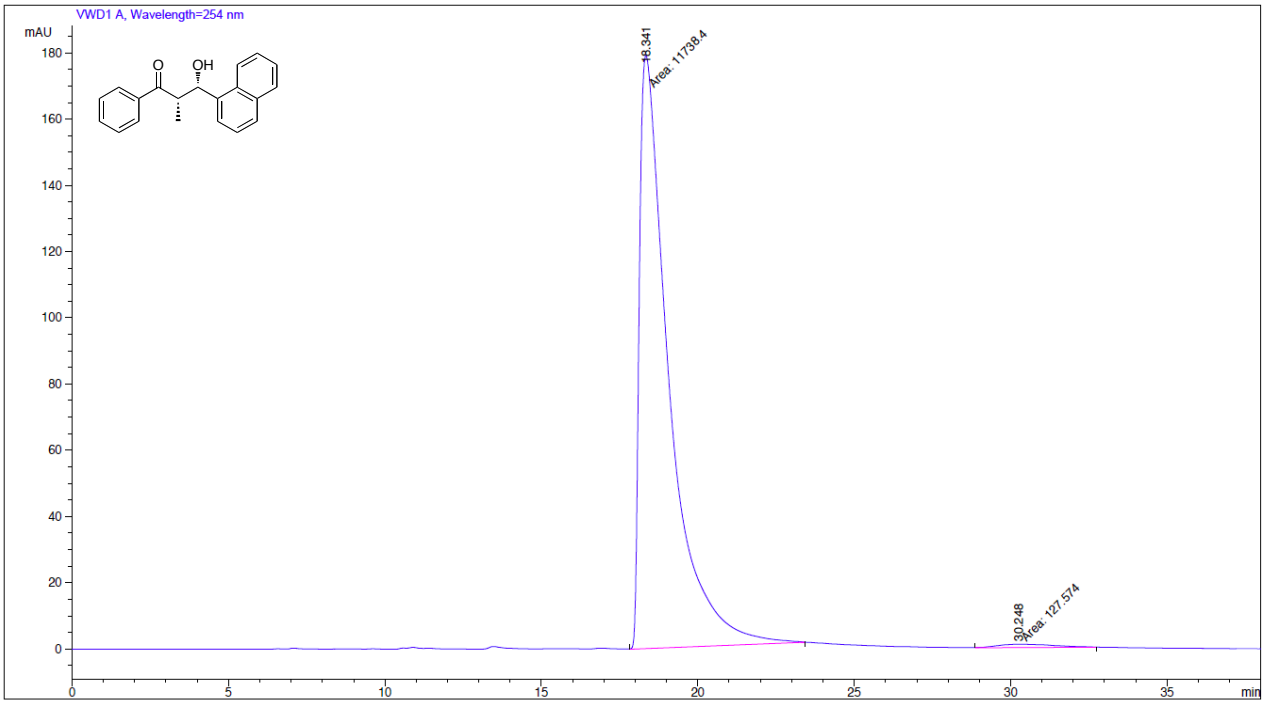
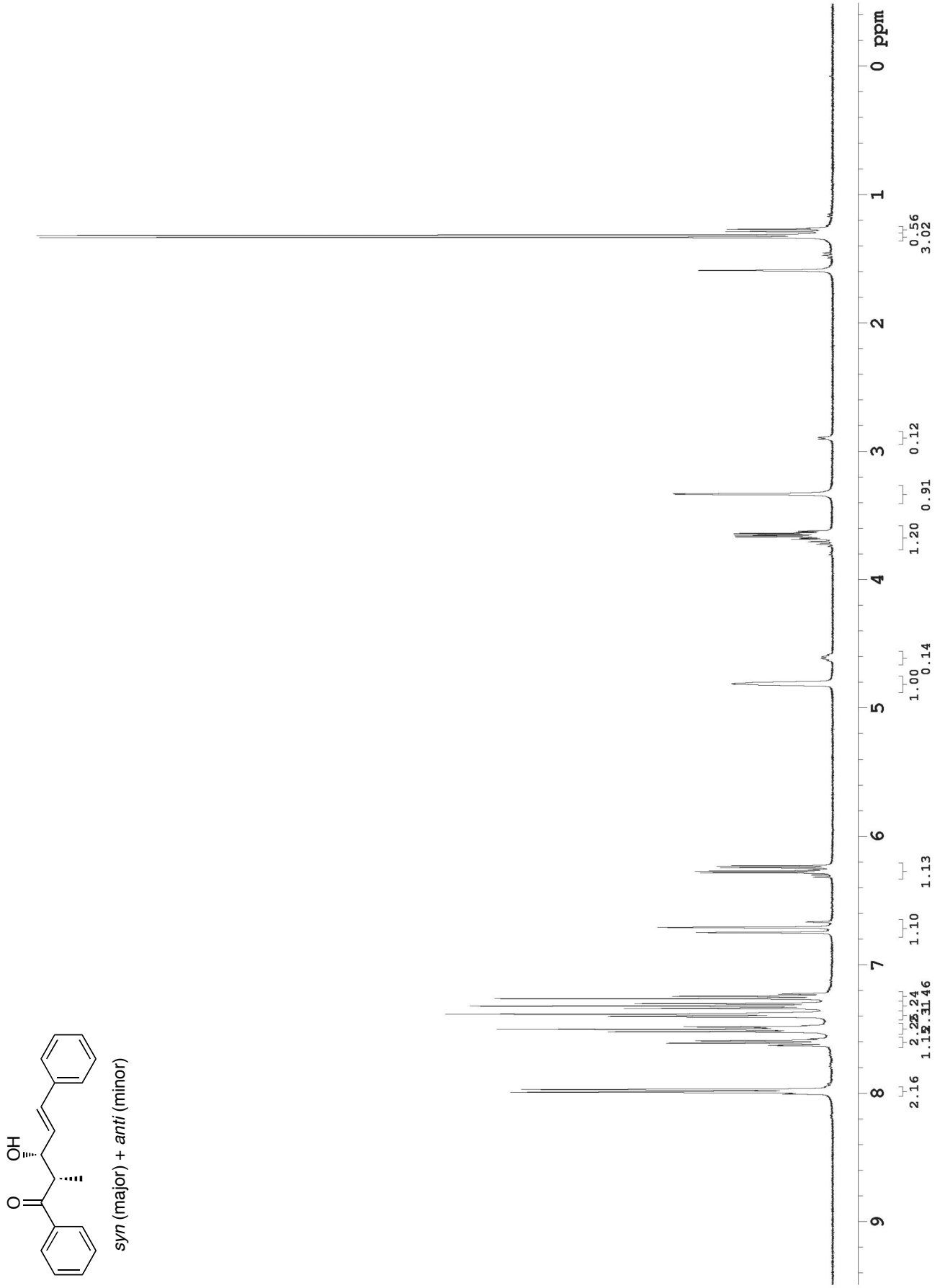
5.05
OH
O





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.341	MM	1.0924	1.17384e4	179.09474	98.9249
2	30.248	MM	2.0998	127.57449	1.01261	1.0751
Totals :				1.18660e4	180.10735	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O
syn (major) + anti (minor)
ppm
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6
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1.10
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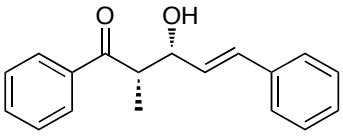
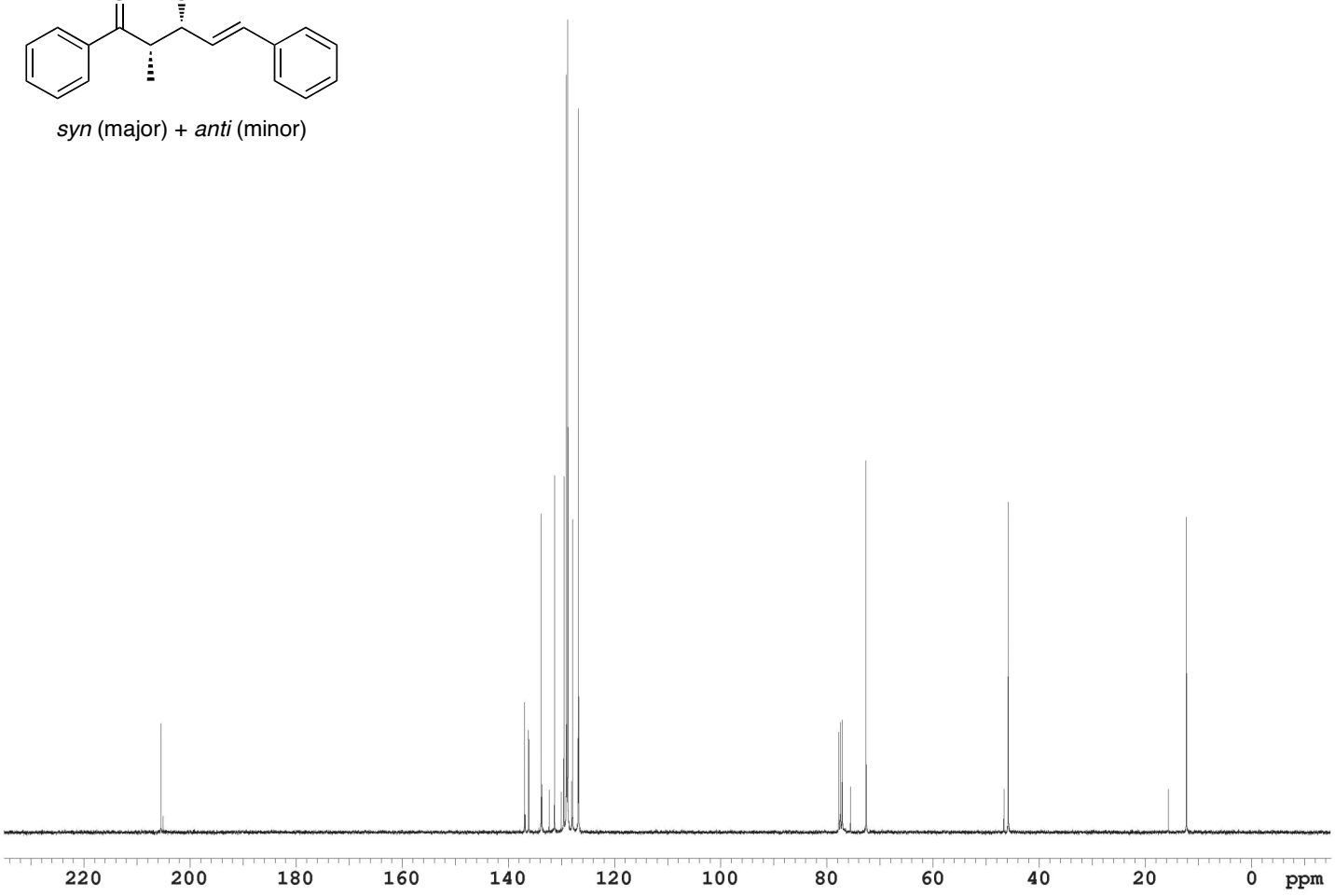
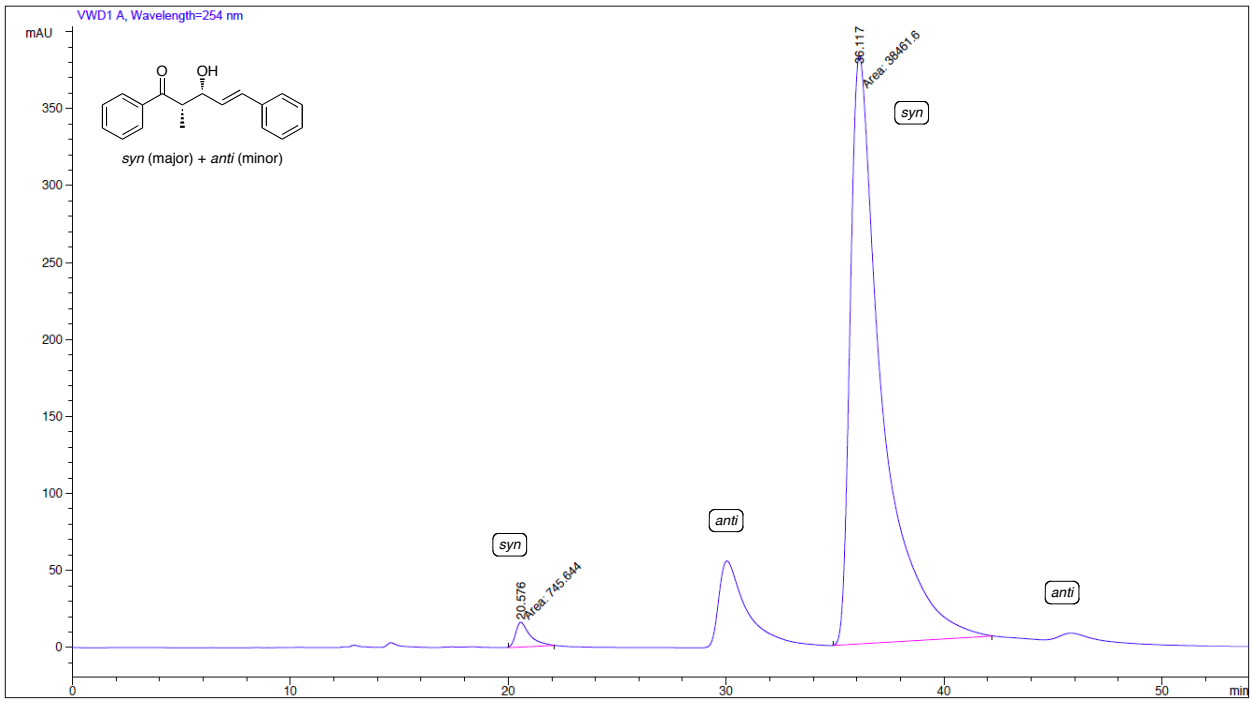
2.16

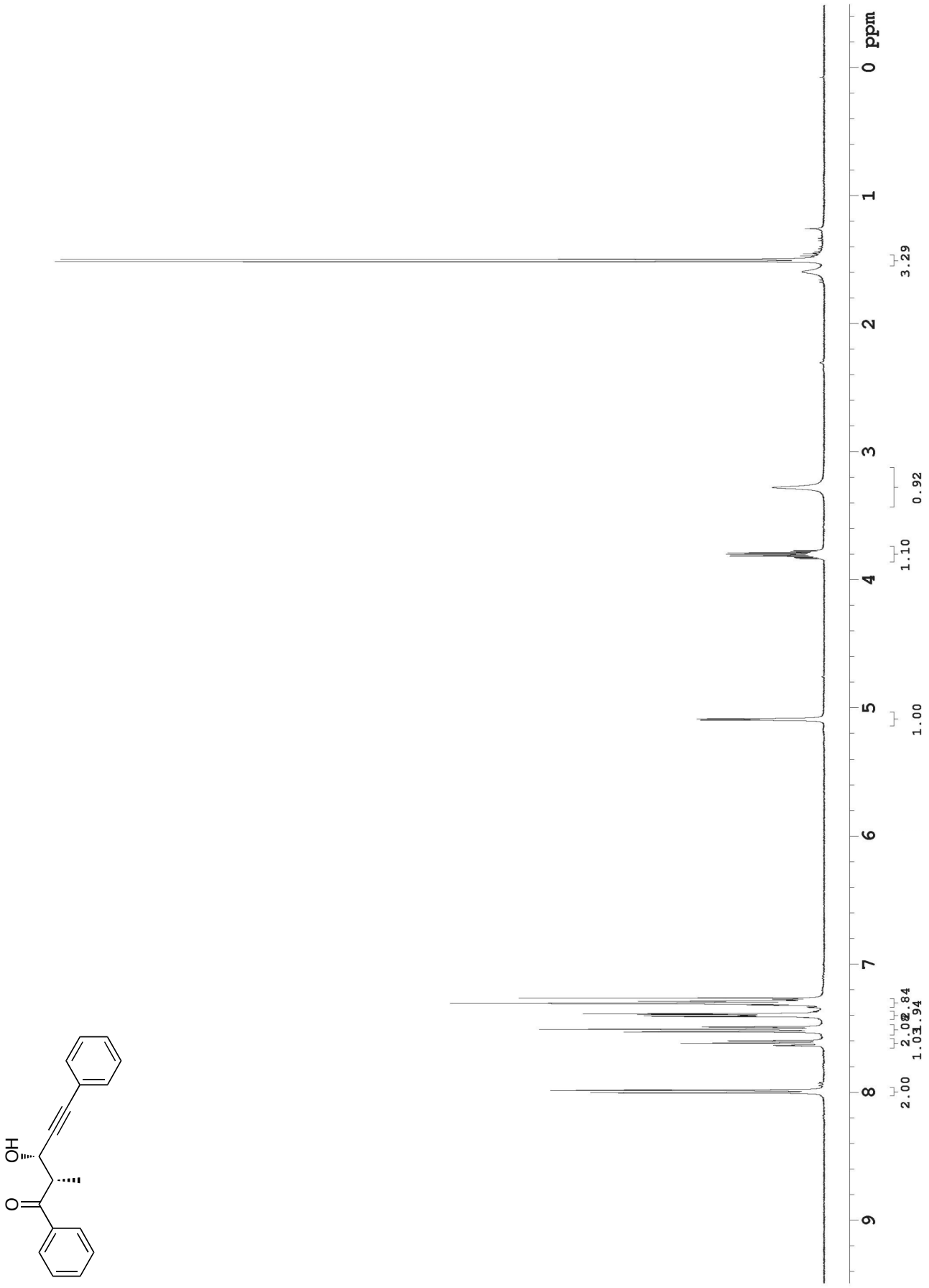


syn (major) + *anti* (minor)





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.576	MM	0.7718	745.64404	16.10189	1.9018
2	36.117	MM	1.6789	3.84616e4	381.81305	98.0982
Totals :				3.92072e4	397.91494	


ppm
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1
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3
4
5
6
7
8
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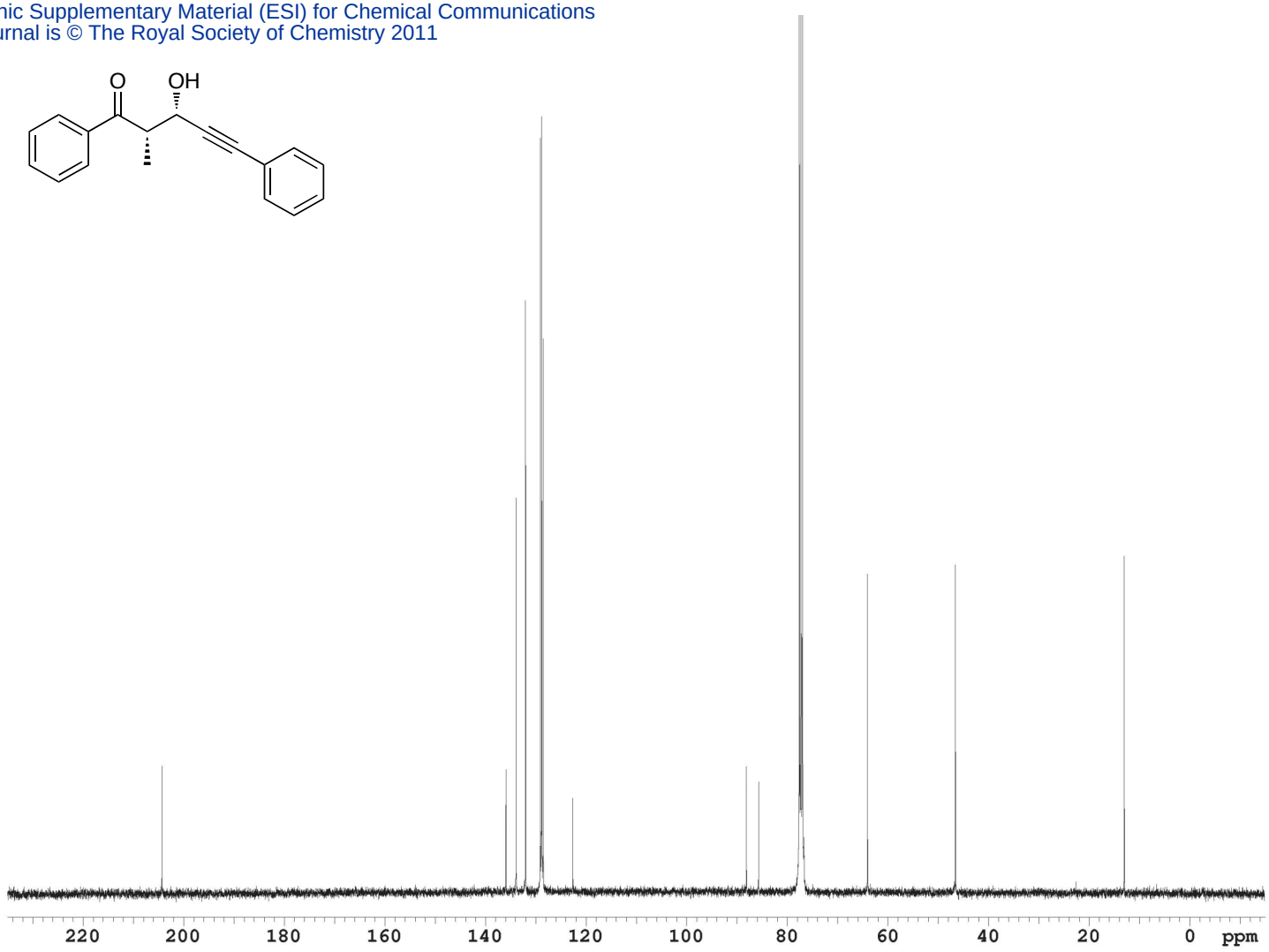
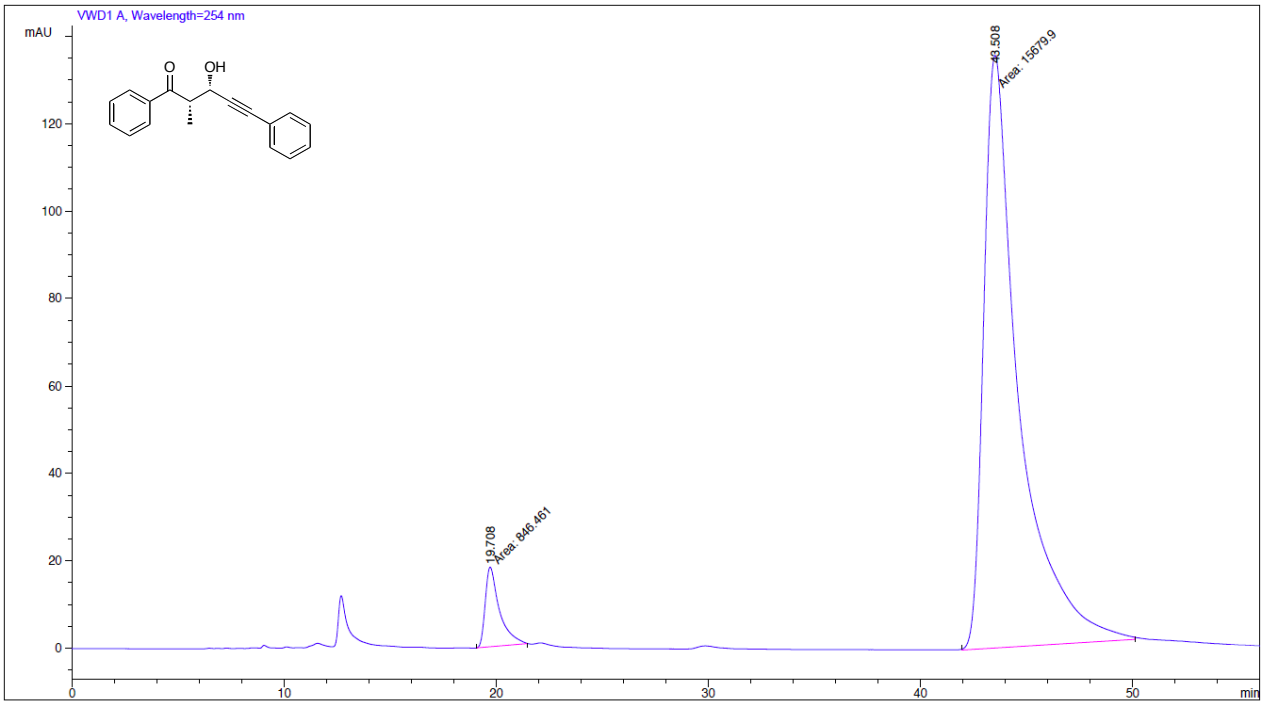
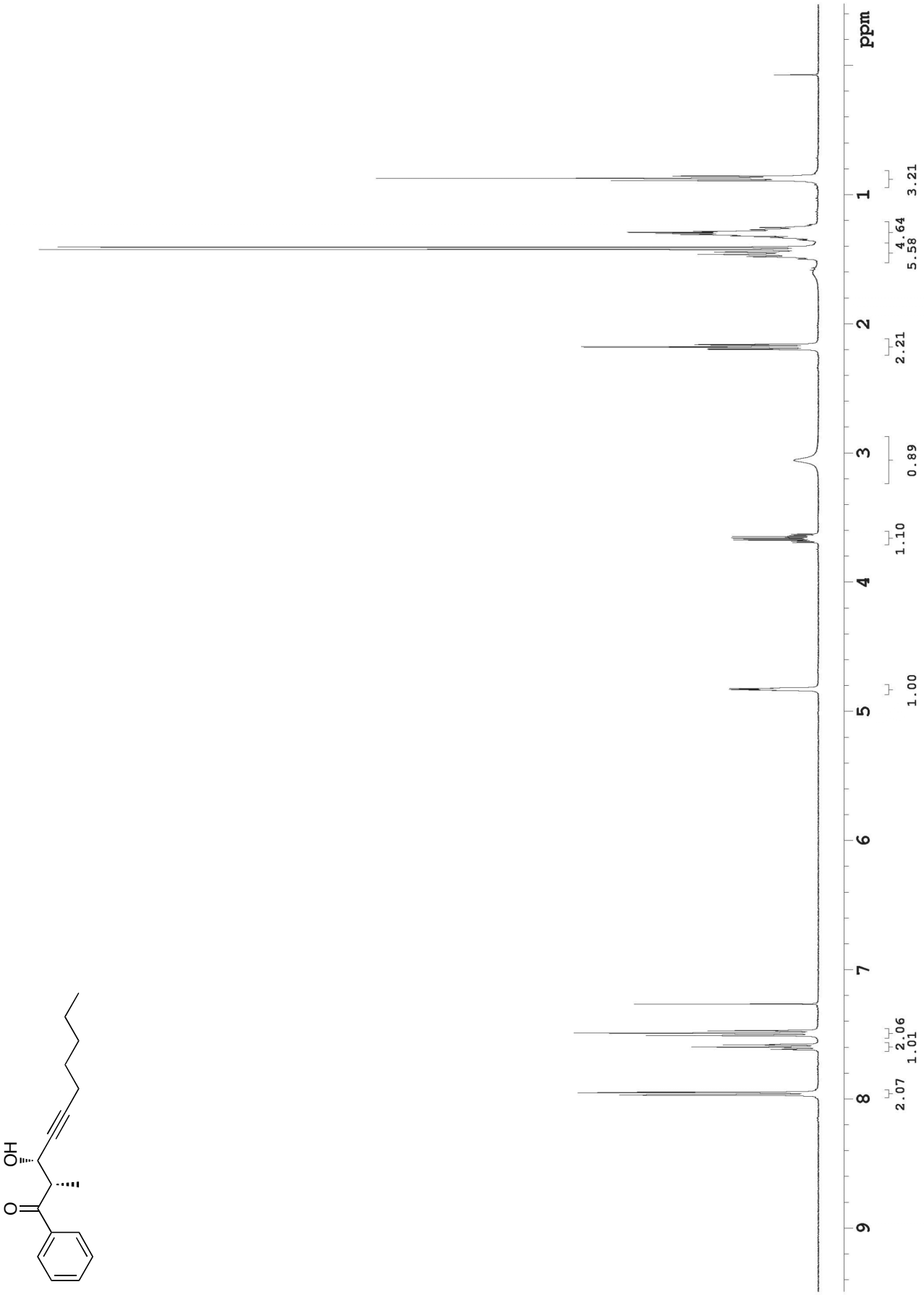
0.92
1.10
1.00
2.08
2.84
1.03
1.94
2.00
OH
O





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.708	MM	0.7749	846.46118	18.20631	5.1219
2	43.508	MM	1.9285	1.56799e4	135.50975	94.8781
Totals :				1.65264e4	153.71606	


ppm
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6
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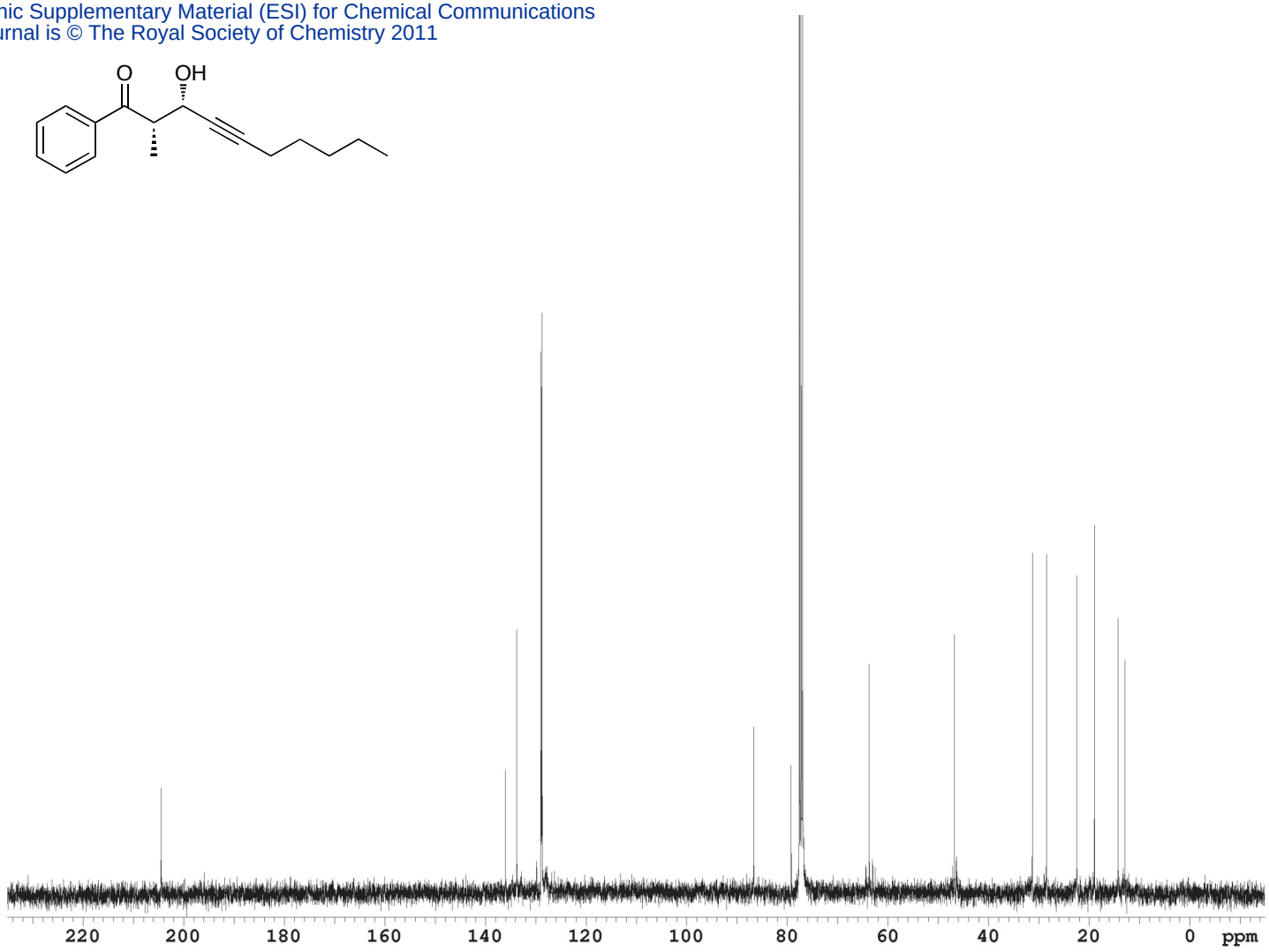
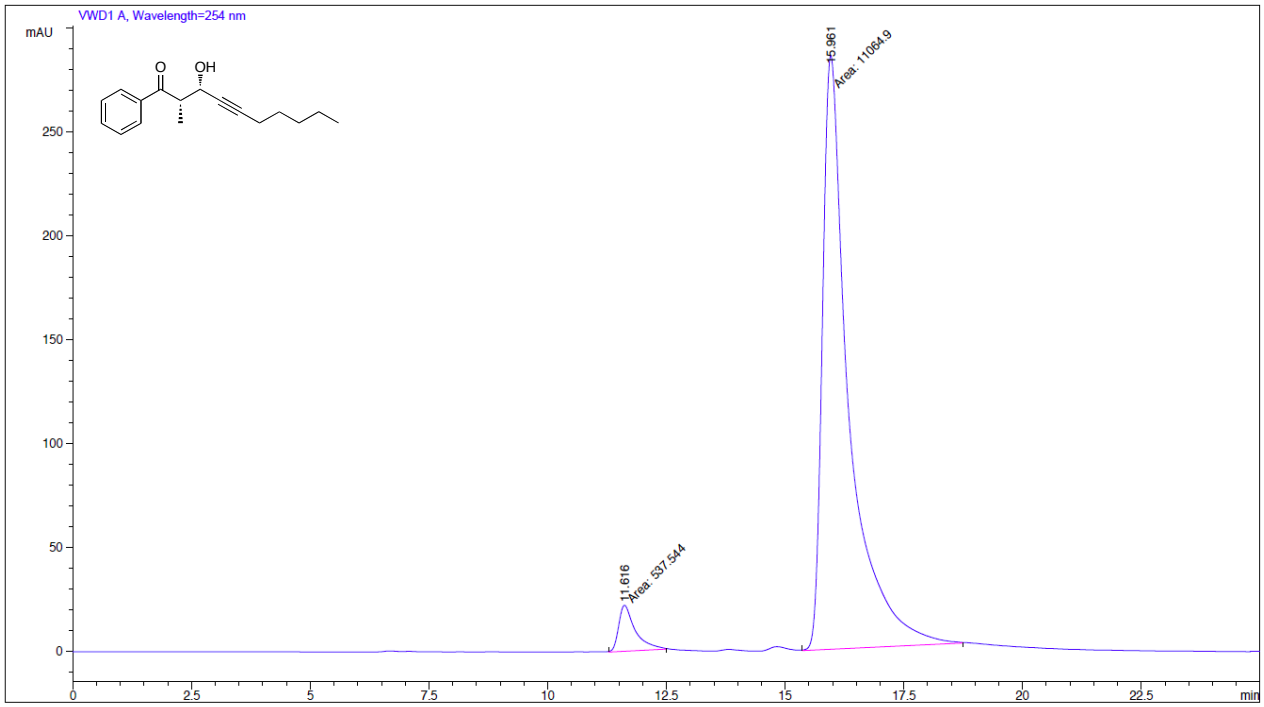
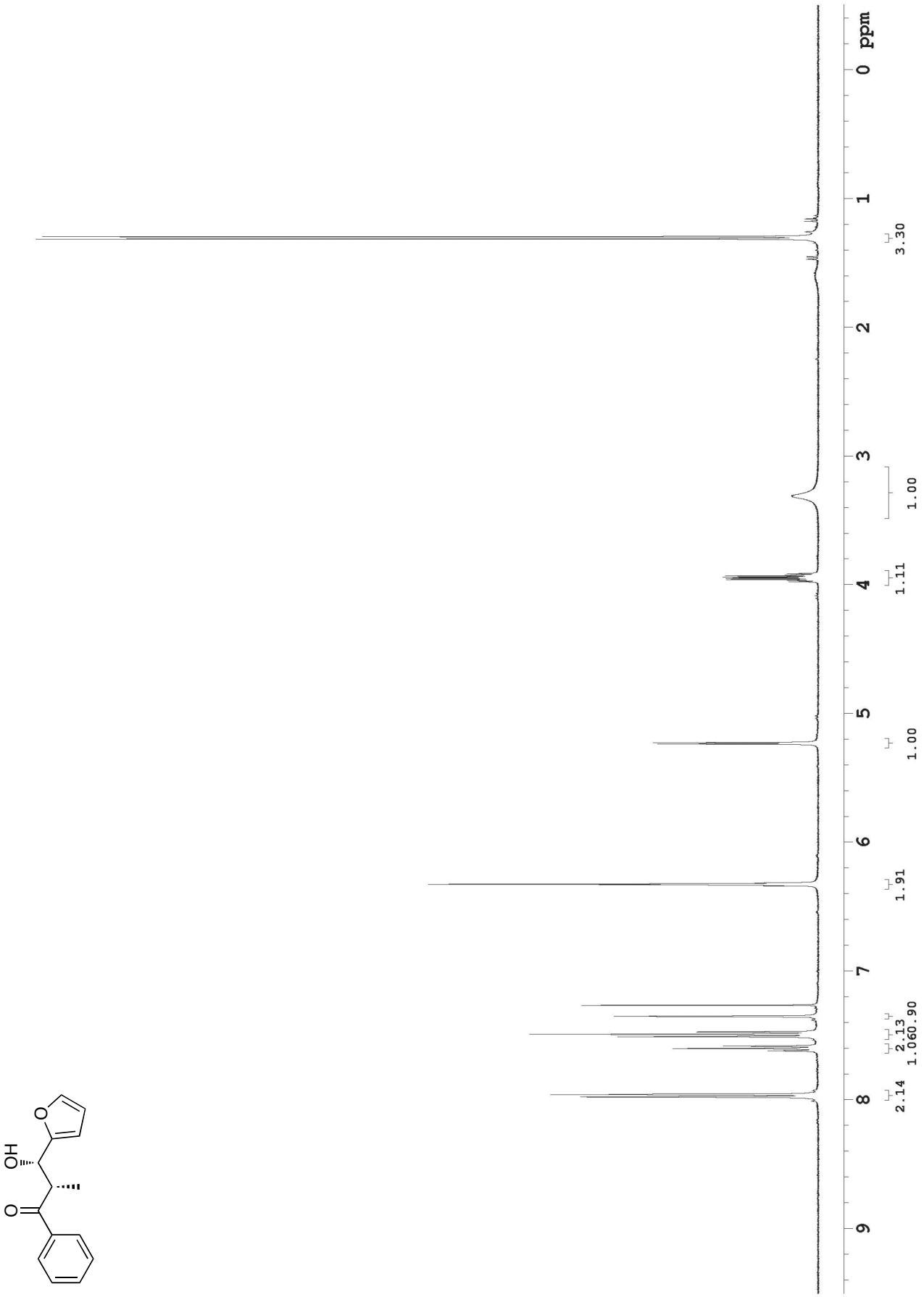
1.10
1.00
2.06
1.01
2.07
OH
O





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.616	MM	0.4055	537.54437	22.09576	4.6330
2	15.961	MM	0.6462	1.10649e4	285.40335	95.3670
Totals :				1.16024e4	307.49911	


ppm
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3
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5
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7
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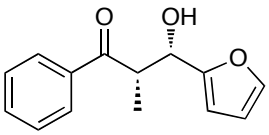
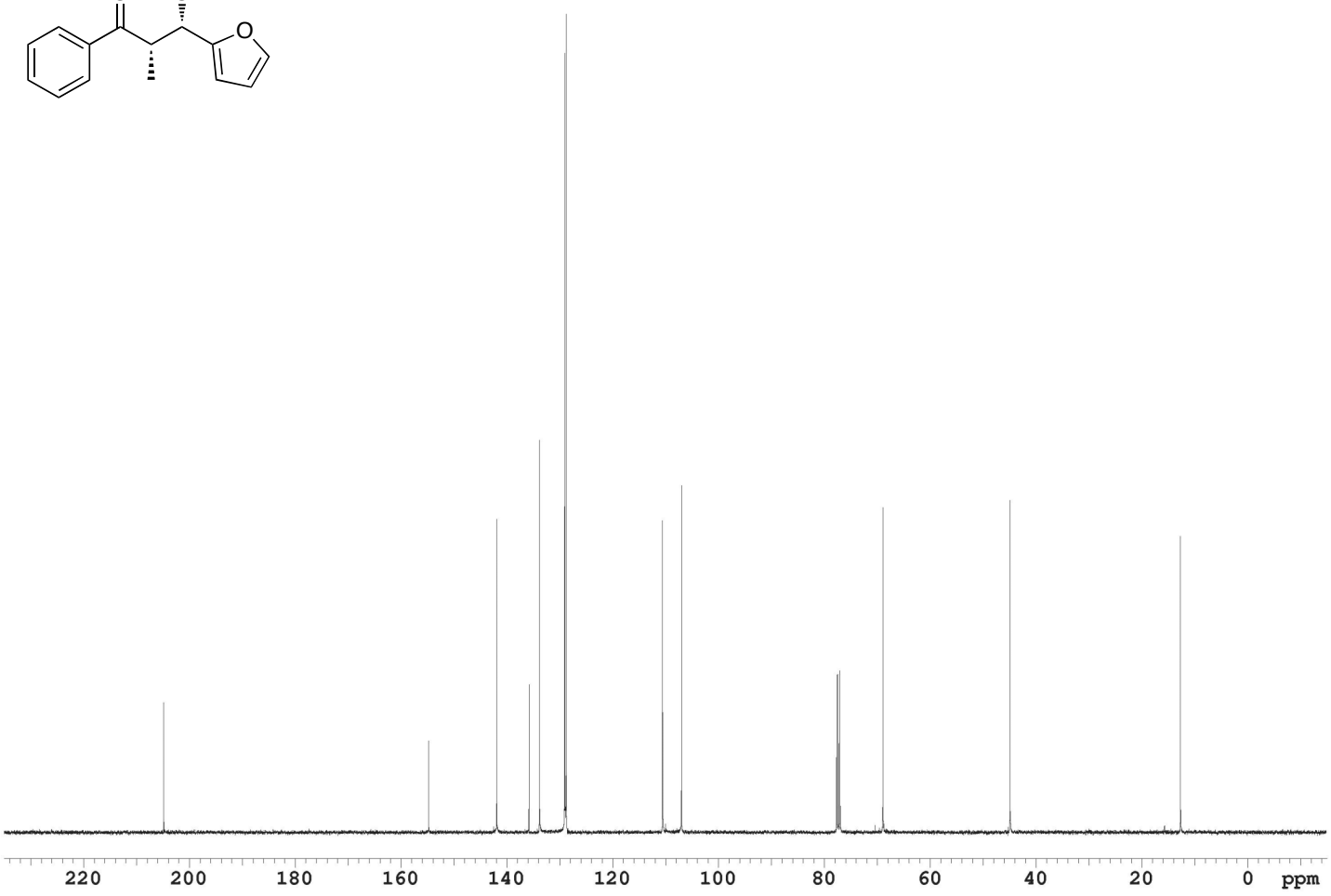
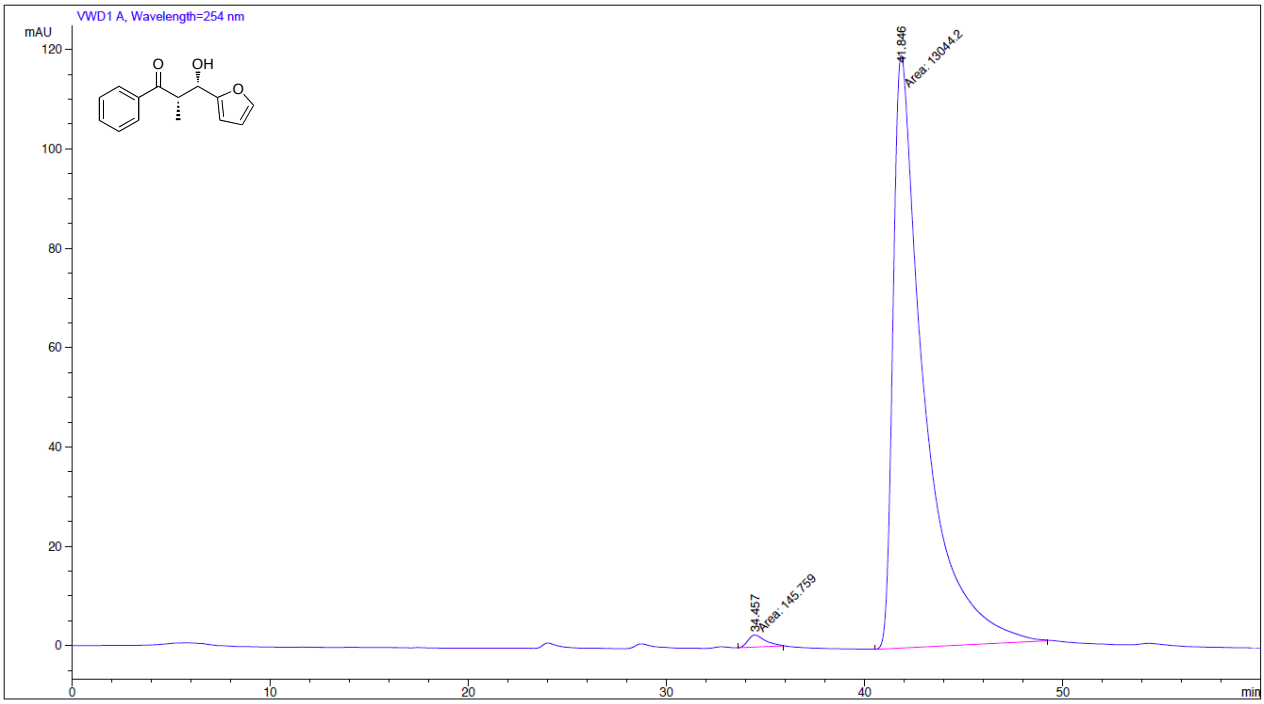
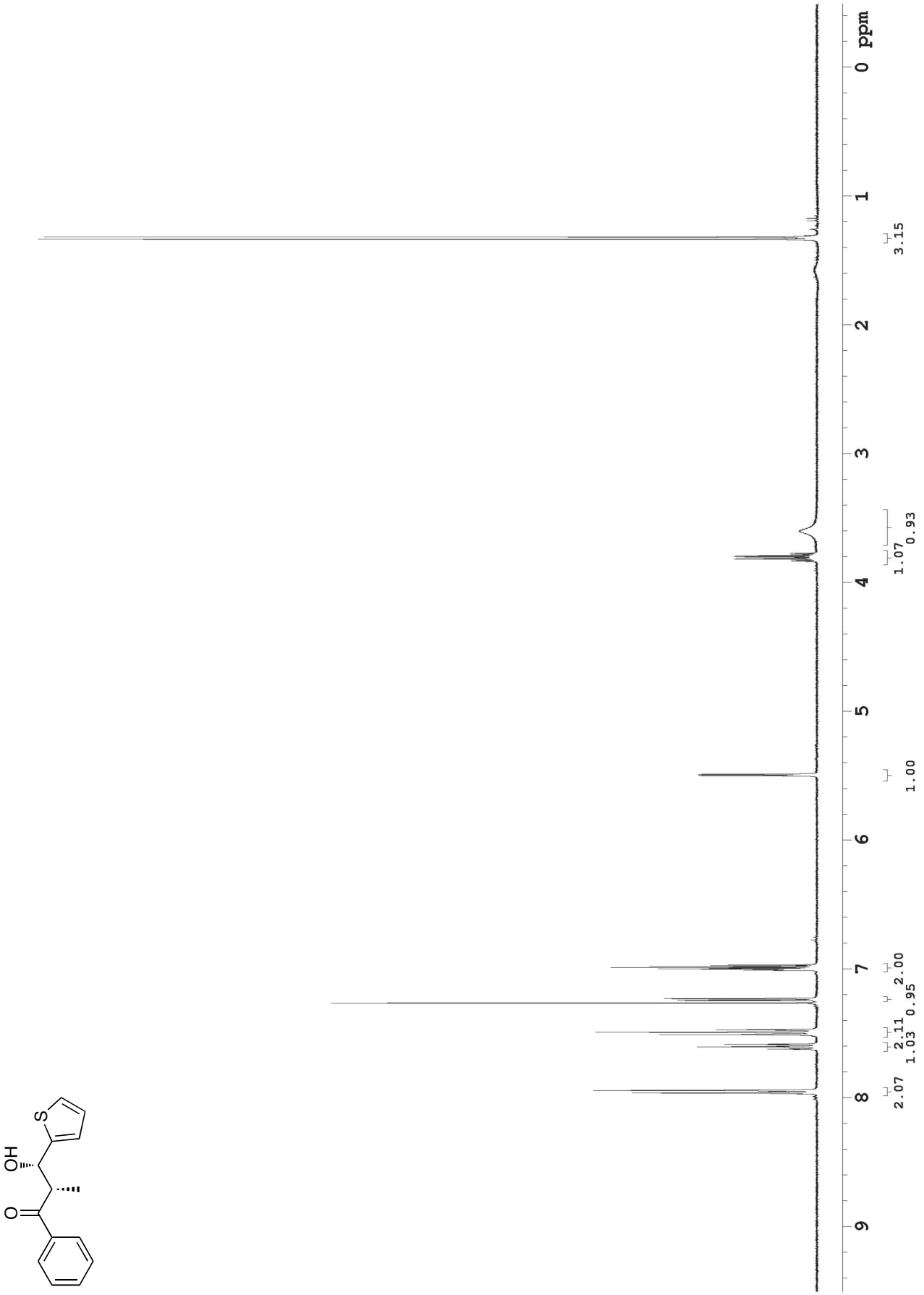
1.11
1.00
1.91
2.13
1.06
0.90
2.14
OH
O
O







Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.457	MM	1.0066	145.75938	2.41339	1.1051
2	41.846	MM	1.8222	1.30442e4	119.30511	98.8949
Totals :				1.31899e4	121.71849	


ppm
0
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3
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6
7
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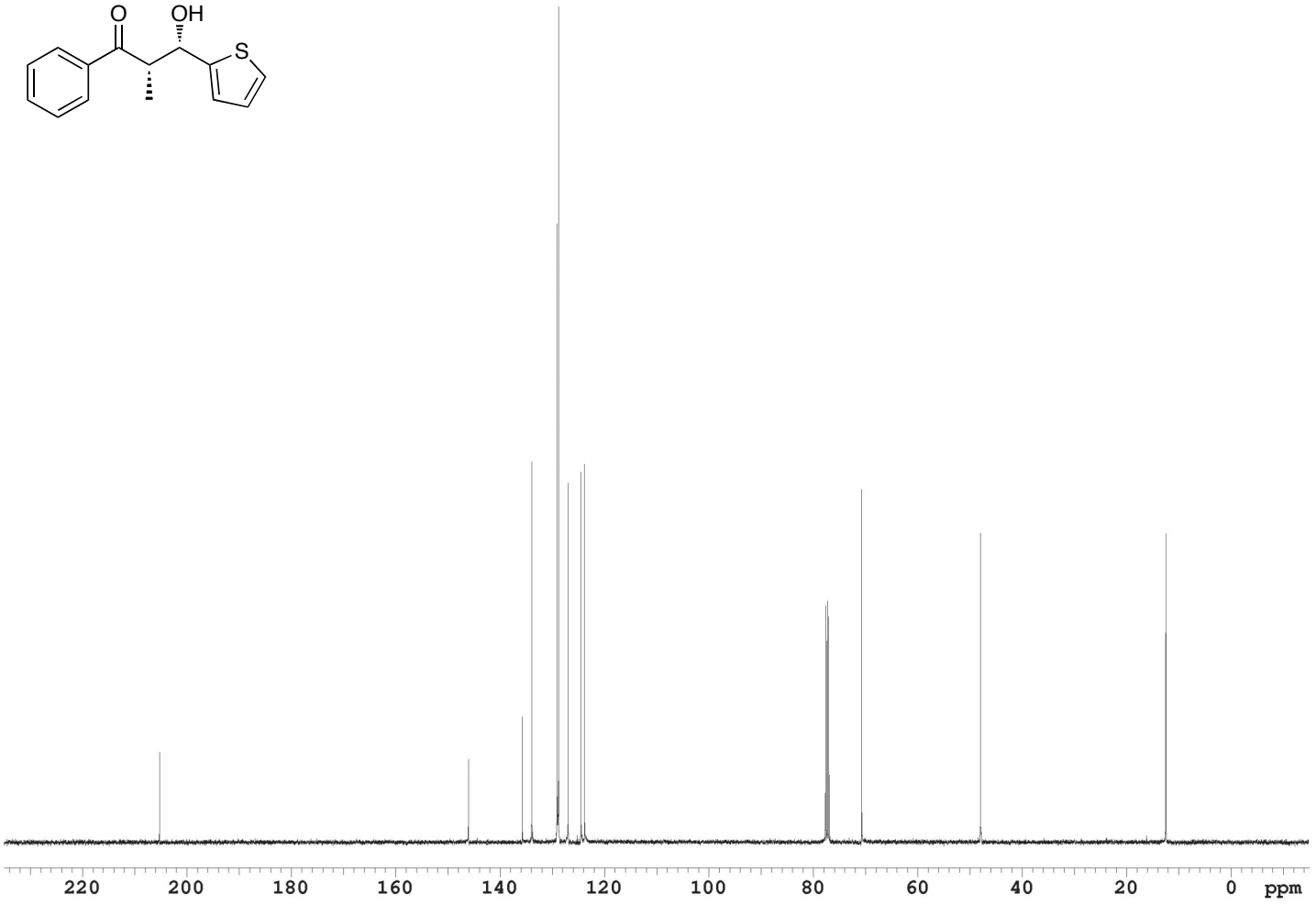
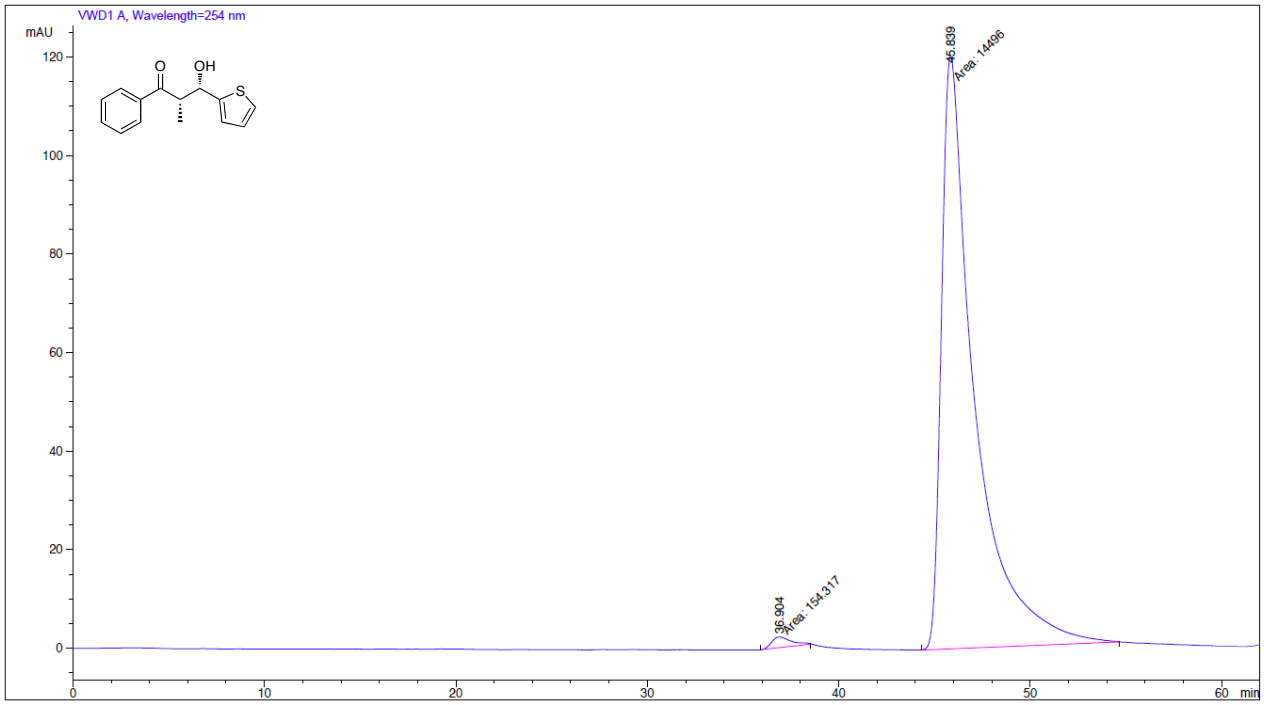
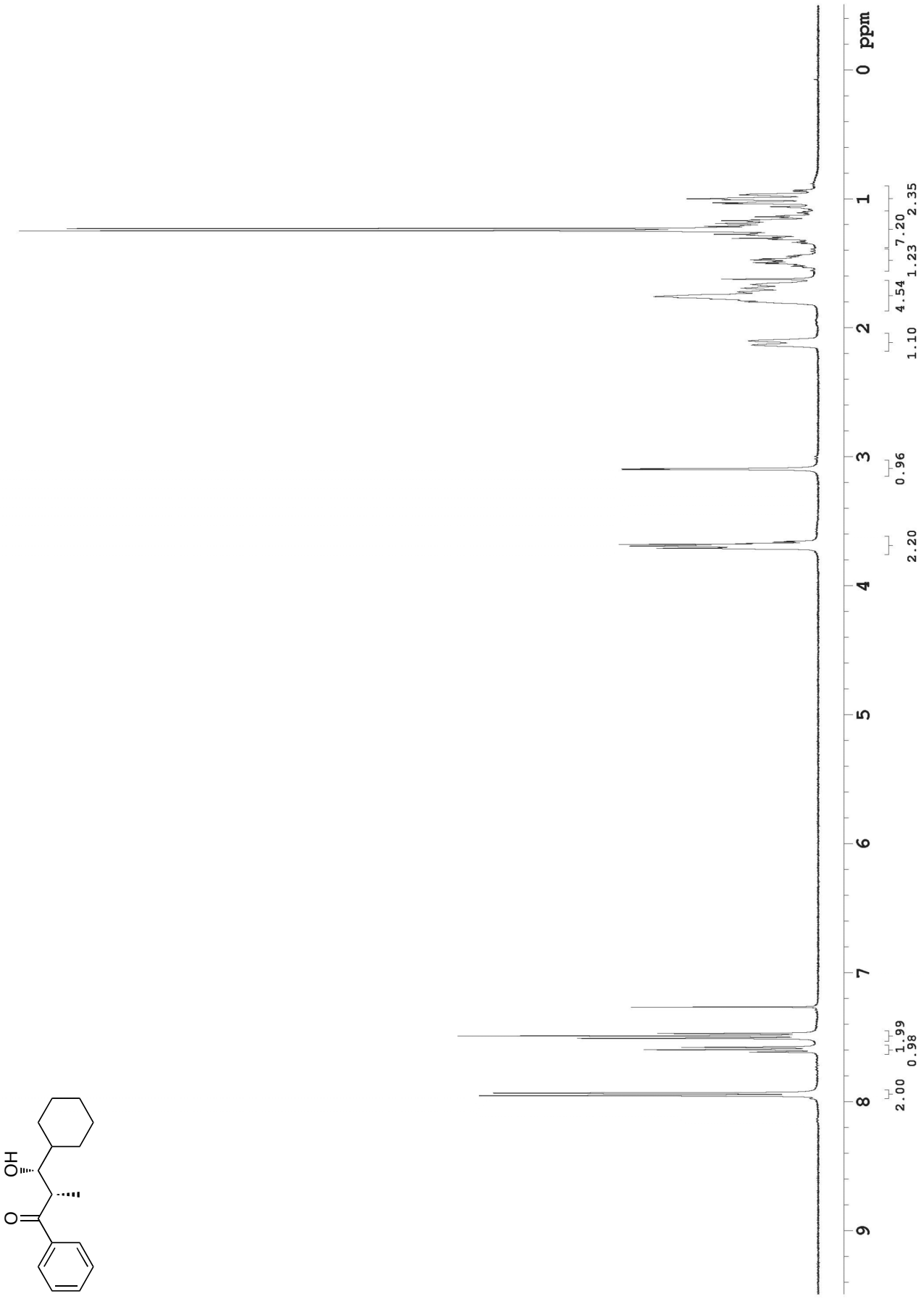
1.07
0.93
1.00
2.00
0.95
2.11
1.03
2.07
OH
O
S





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	36.904	MM	1.1901	154.31725	2.16105	1.0533
2	45.839	MM	2.0069	1.44960e4	120.38651	98.9467
Totals :				1.46503e4	122.54756	


OH
O
ppm
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2
3
4
5
6
7
8
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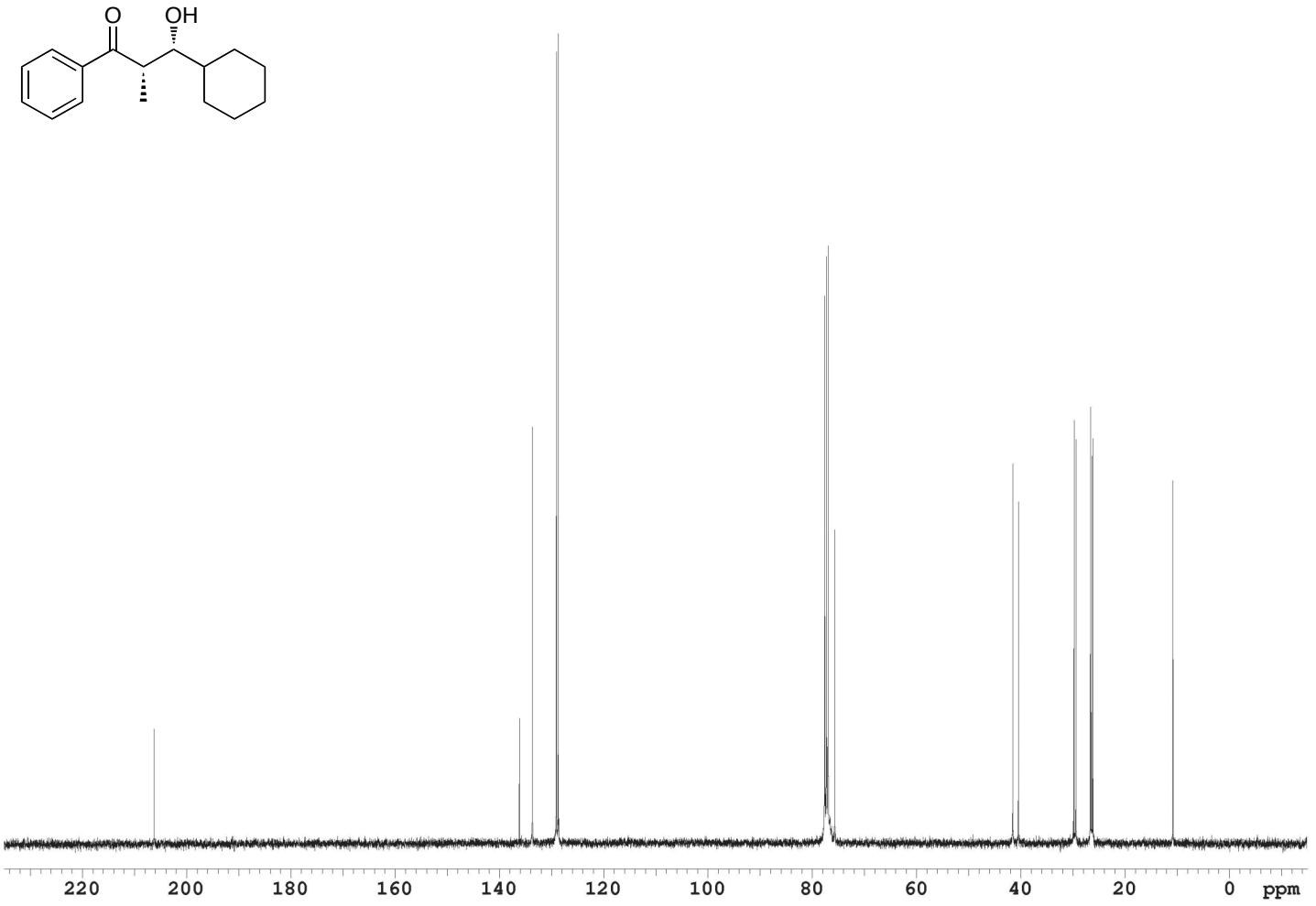
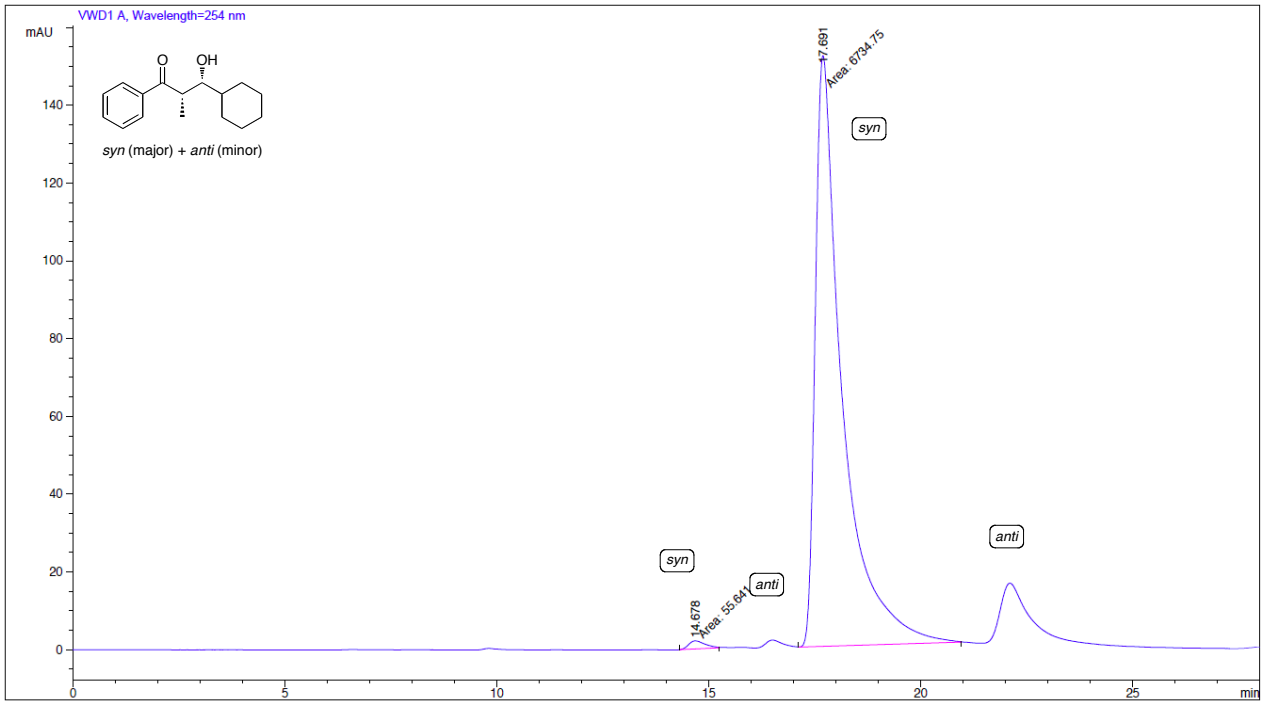
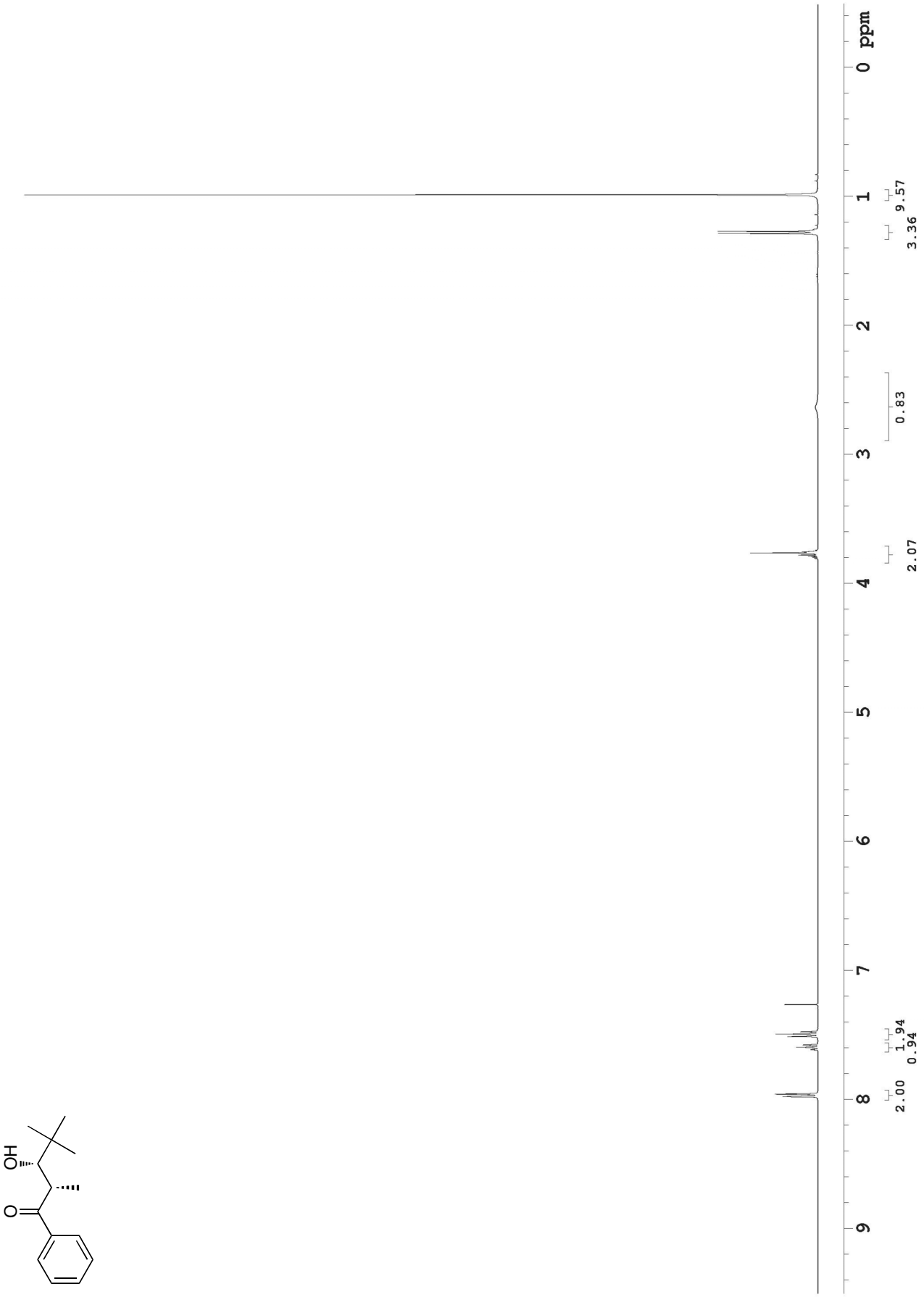
2.35
7.20
1.23
4.54
1.10
0.96
2.20
1.99
0.98
2.00





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.678	MM	0.4454	55.64098	2.08224	0.8194
2	17.691	MM	0.7389	6734.74756	151.90036	99.1806
Totals :				6790.38854	153.98260	


ppm
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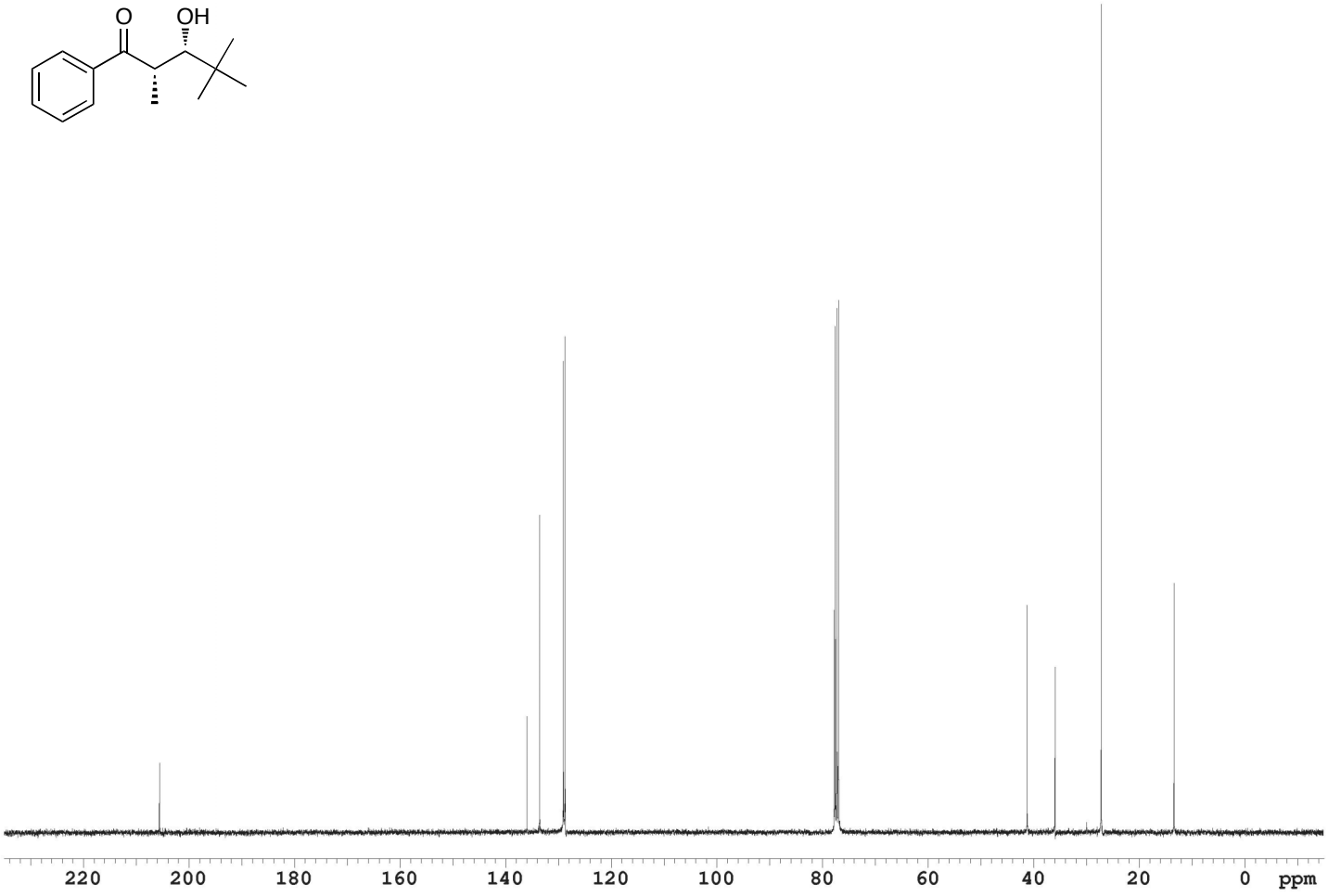
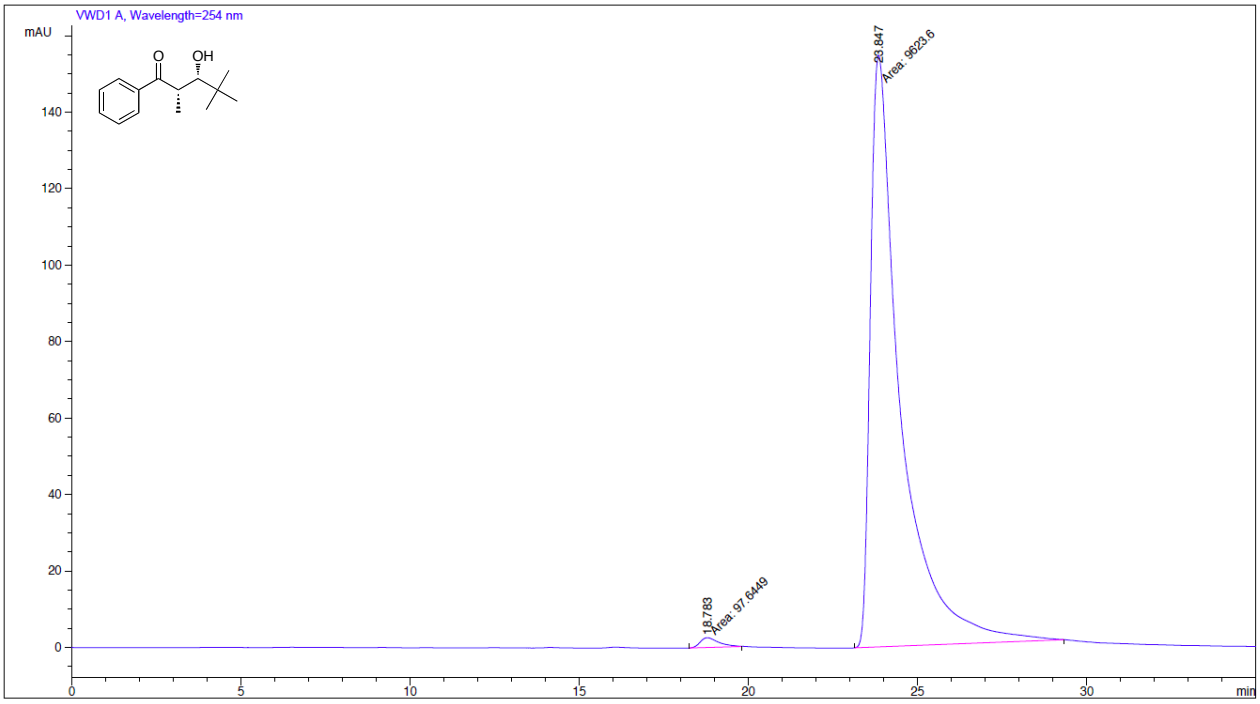
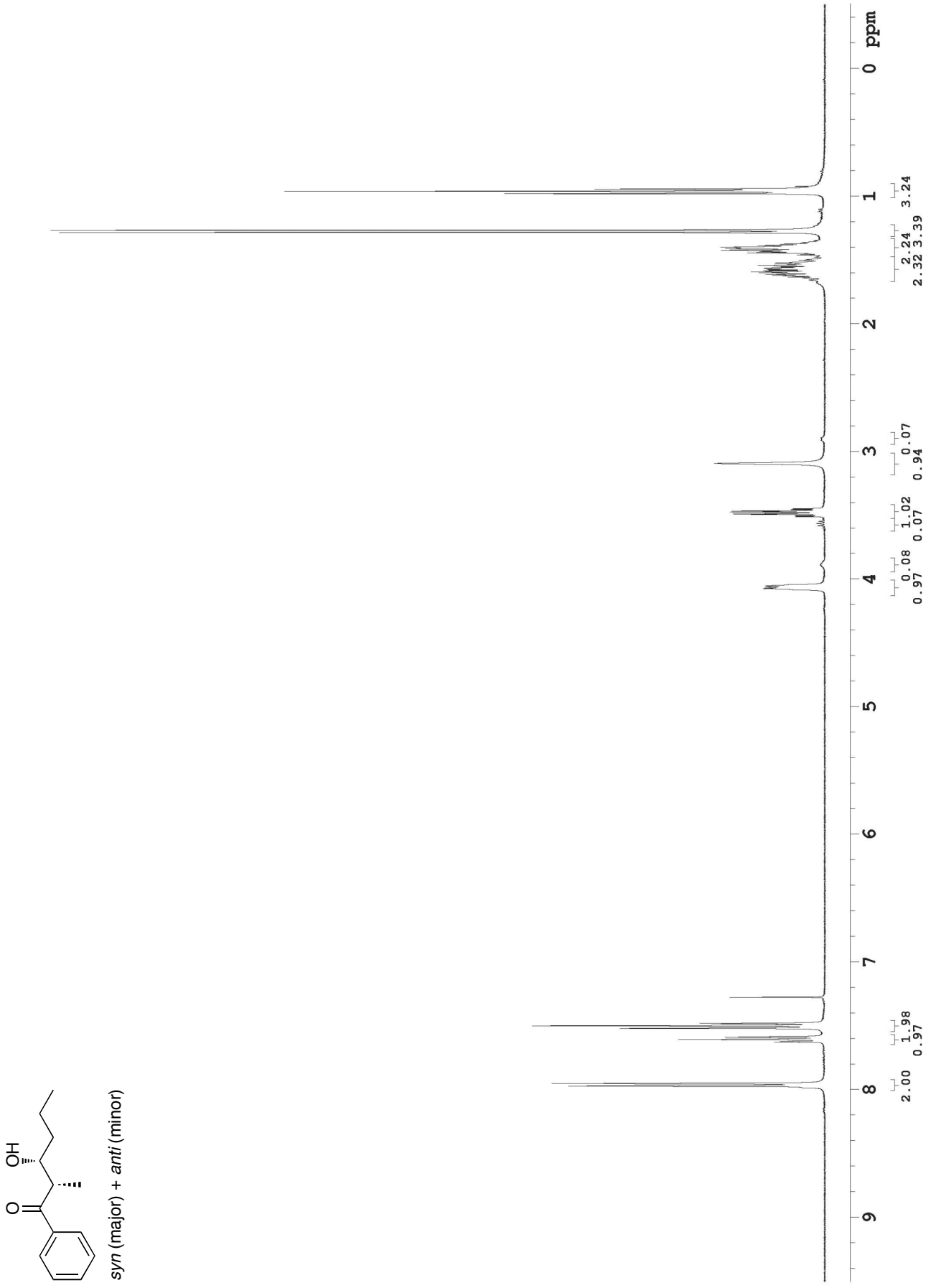
0.94
2.00
OH
O





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.783	MM	0.6346	97.64491	2.56457	1.0044
2	23.847	MM	1.0362	9623.59668	154.79140	98.9956
Totals :				9721.24159	157.35597	


OH
O
syn (major) + anti (minor)
ppm
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2
3
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5
6
7
8
9
3.24
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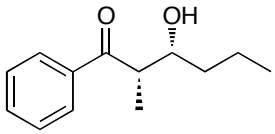
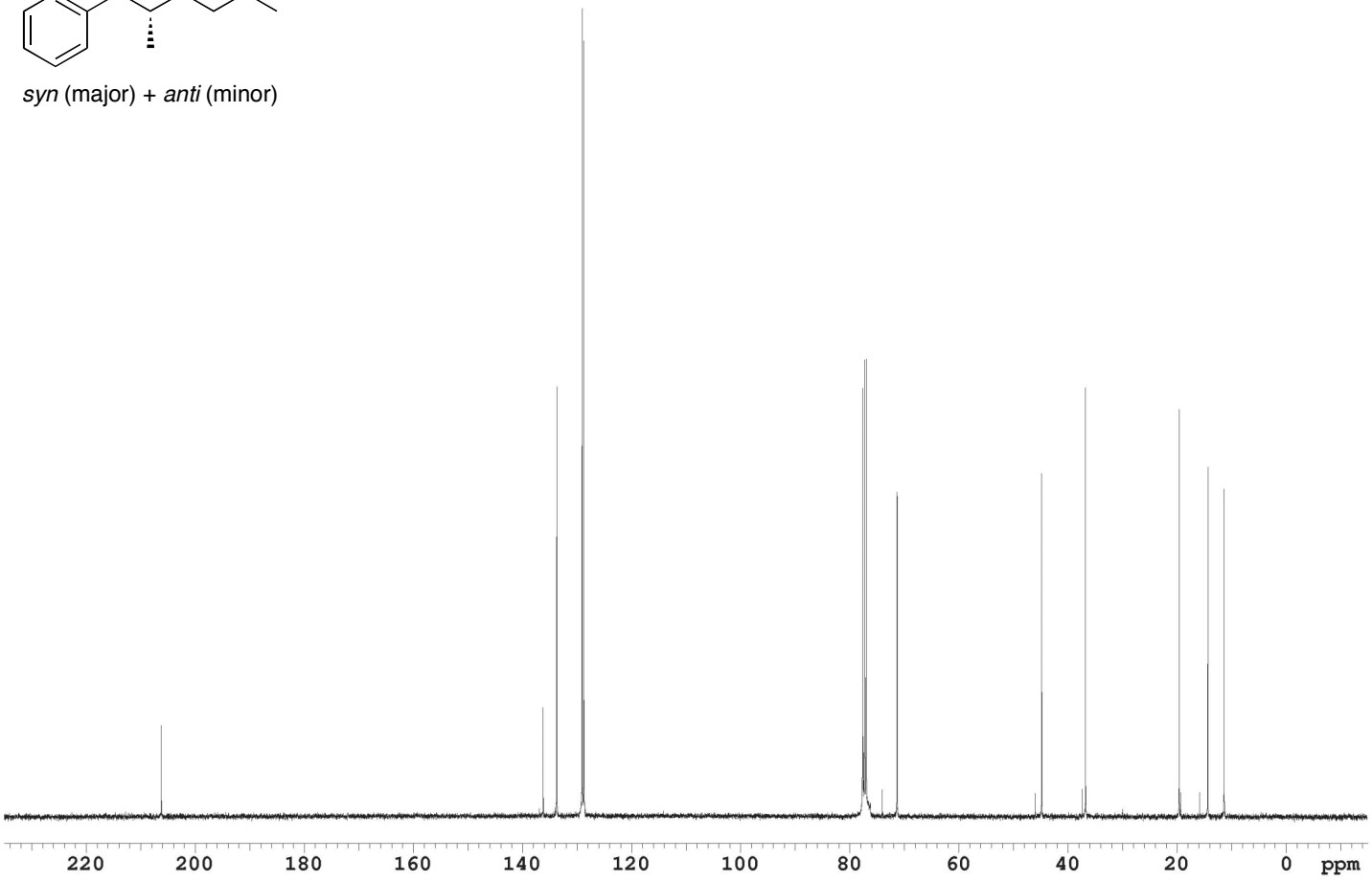
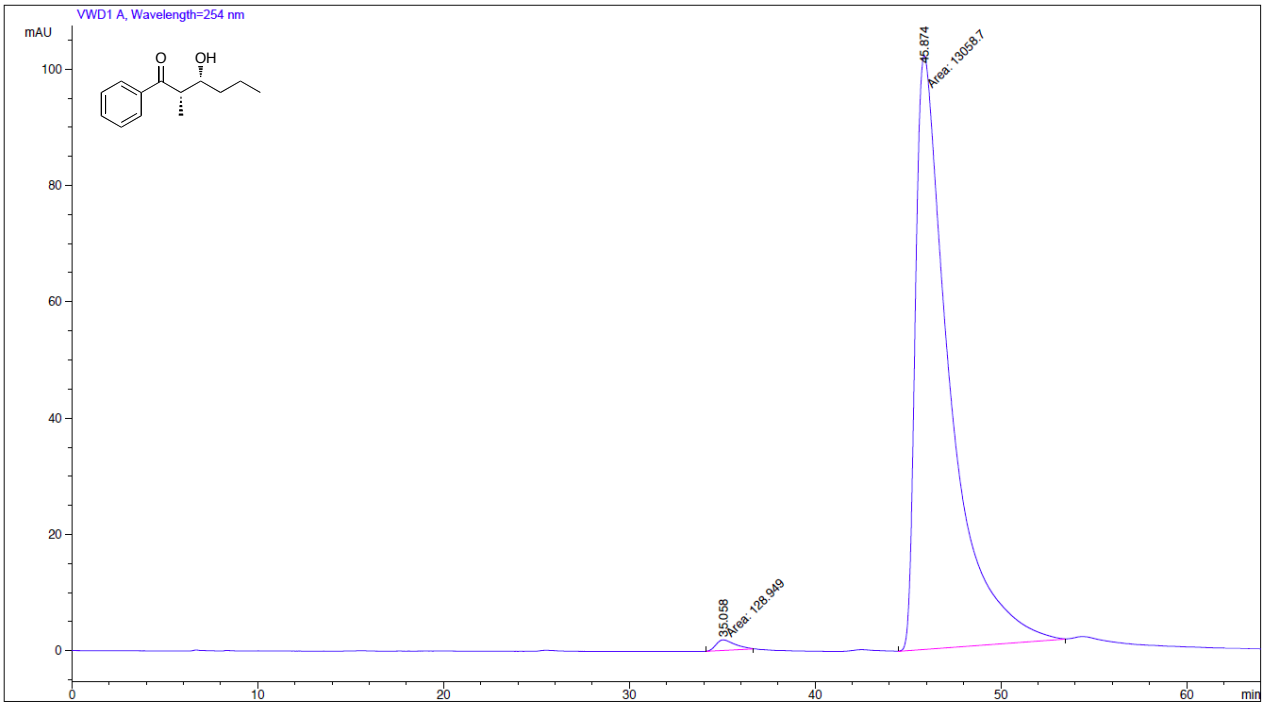
3.39
0.07
0.94
1.02
0.07
0.08
0.97
1.98
0.97
2.00

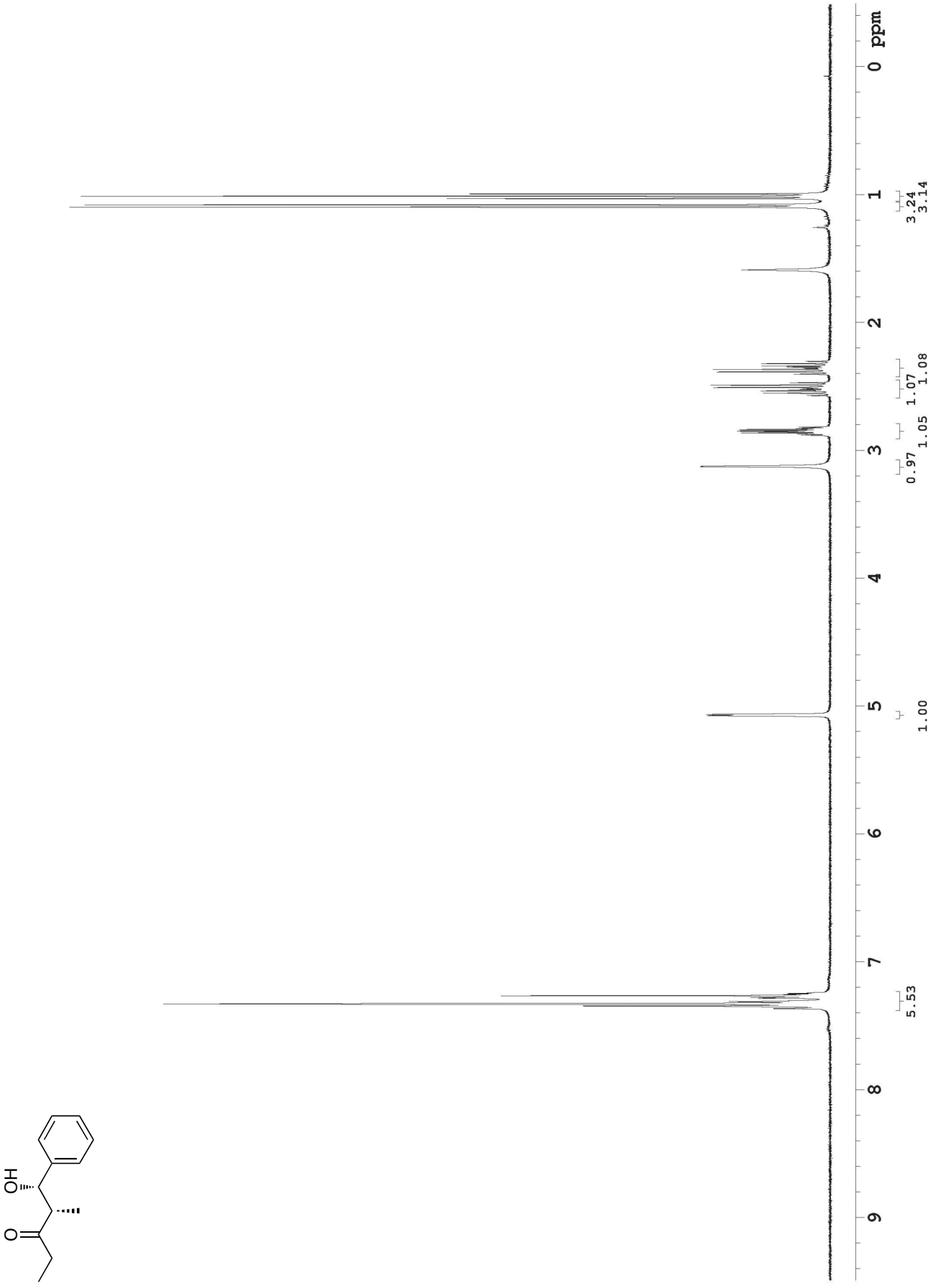


syn (major) + *anti* (minor)





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.058	MM	1.1782	128.94933	1.82407	0.9778
2	45.874	MM	2.1315	1.30587e4	102.10992	99.0222
Totals :				1.31877e4	103.93399	


ppm
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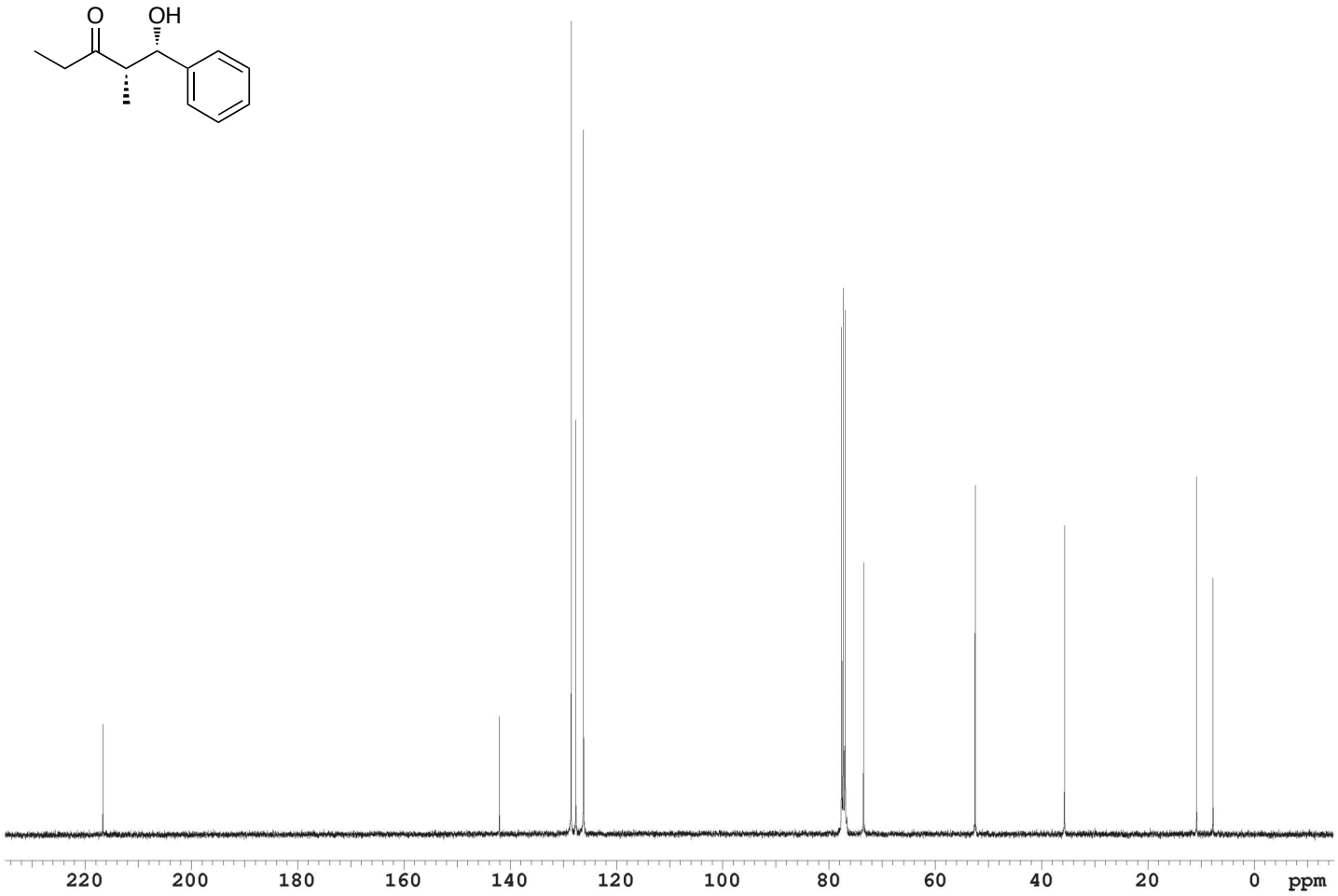
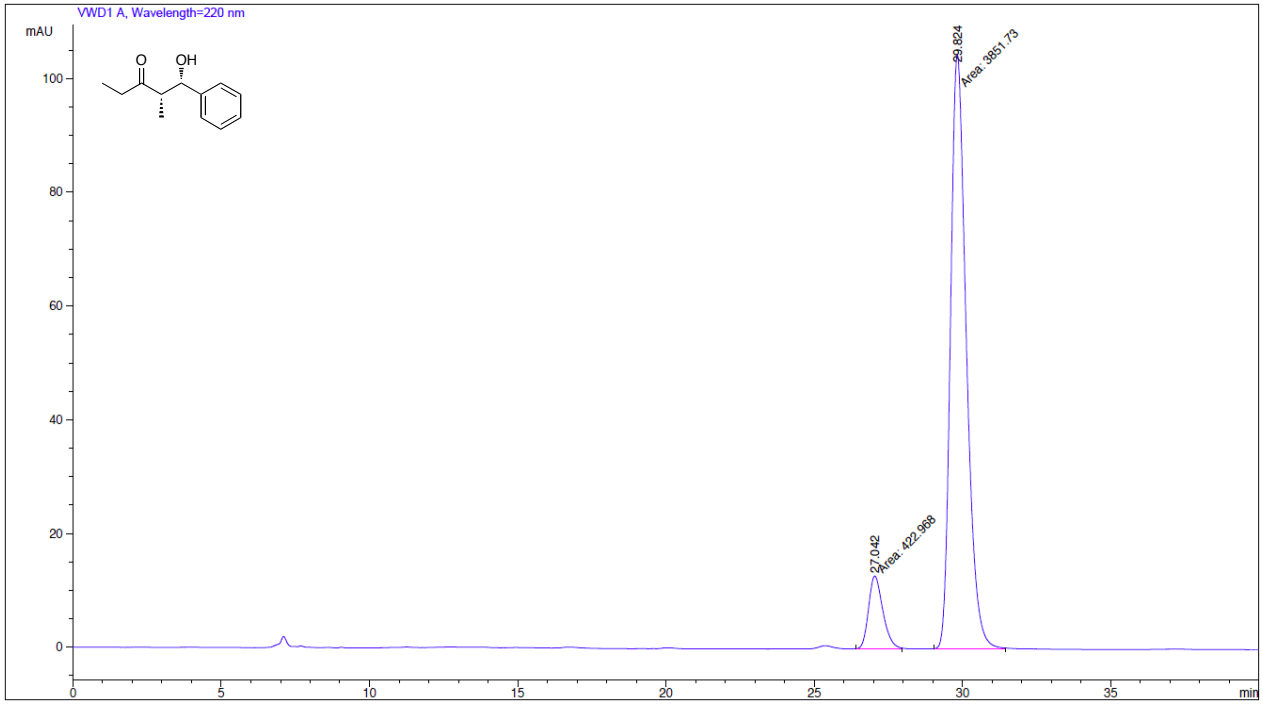
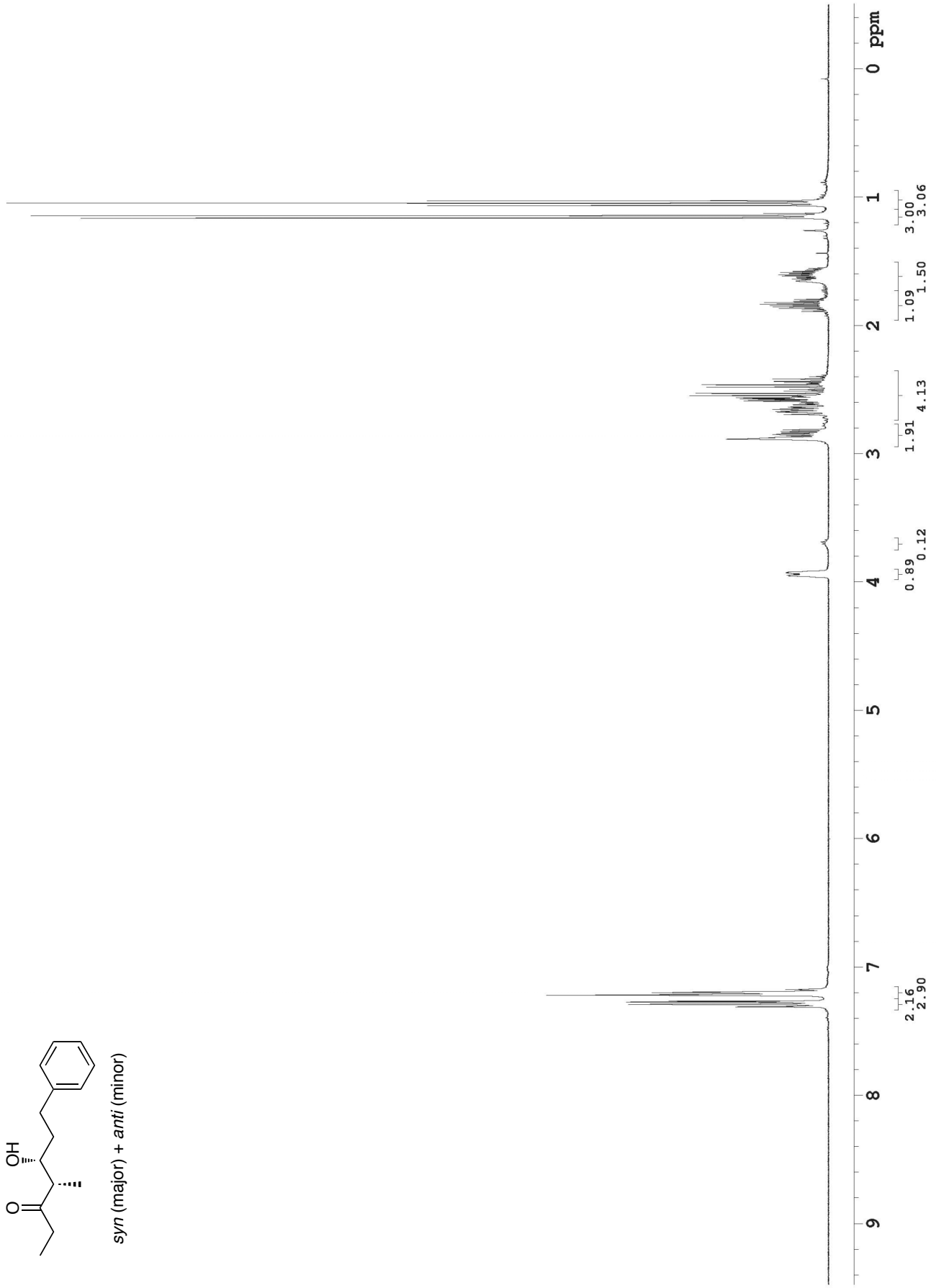
2
3
4
5
6
7
8
9
3.24
3.14
1.07
1.08
0.97
1.05
1.00
5.53
OH
O



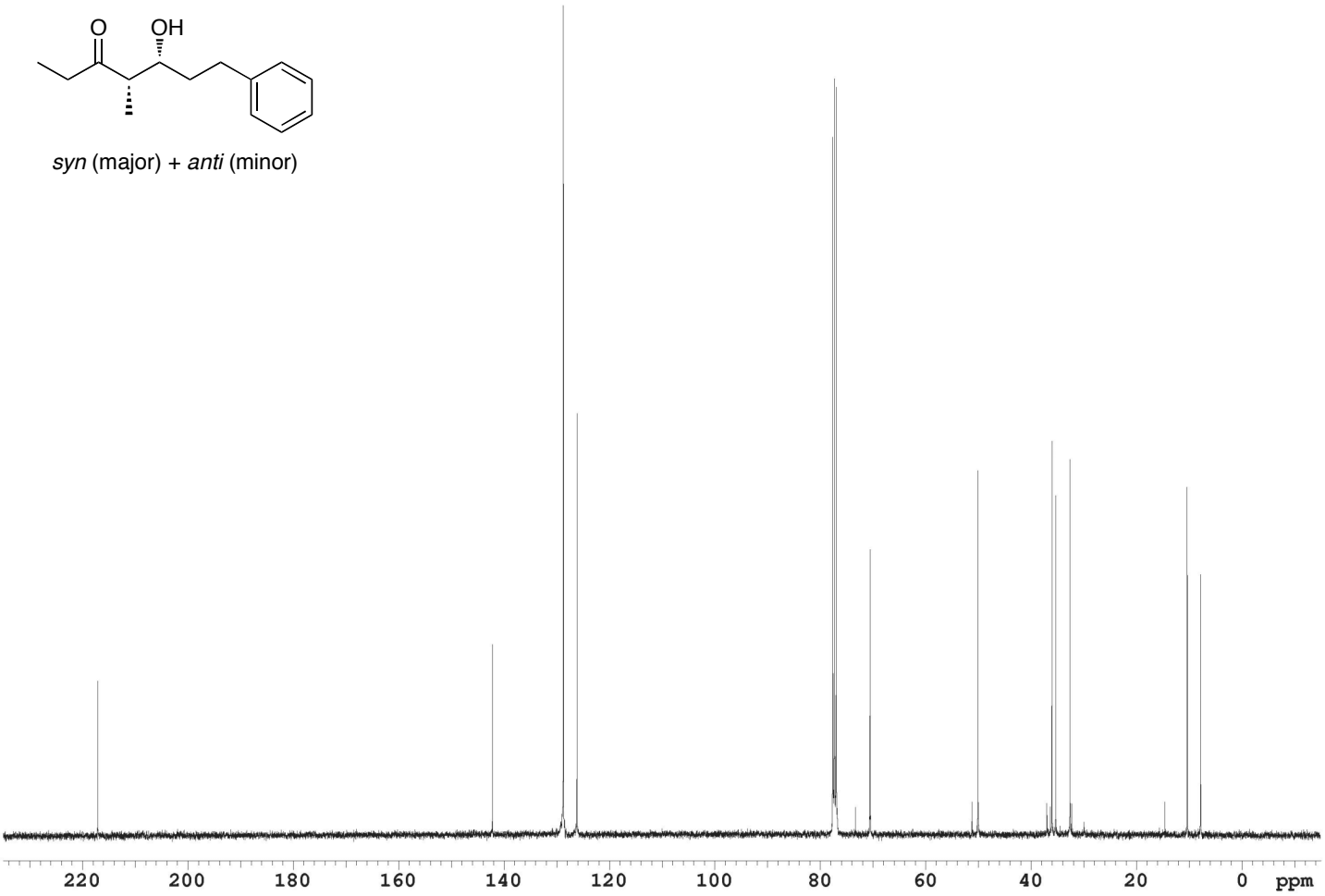


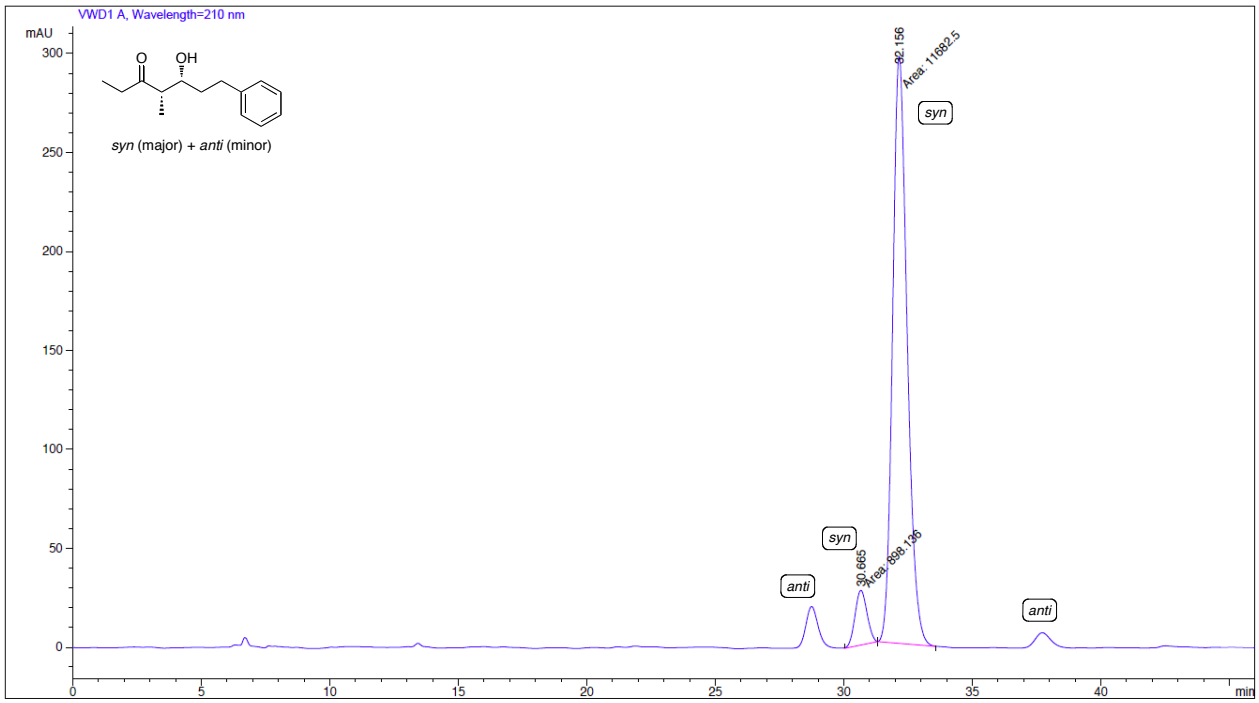
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.042	MM	0.5537	422.96811	12.73160	9.8947
2	29.824	MM	0.6148	3851.72925	104.42204	90.1053
Totals :				4274.69736	117.15363	



syn (major) + *anti* (minor)

syn (major) + *anti* (minor)





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.665	MM	0.5405	898.13586	27.69229	7.1390
2	32.156	MM	0.6564	1.16825e4	296.65283	92.8610
Totals :				1.25807e4	324.34512	