Iron(II)-catalyzed enantioselective *meso*-epoxide-opening with anilines

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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. CH_2Cl_2 was distilled from CaH_2. Aniline derivatives were used as received and *meso*-epoxides were prepared by known procedures.[1] Iron(II) perchlorate was purchased from Alfa Aesar® (reagent grade purity) and Bolm's ligand **1** was synthesized according to known procedures.[2] ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400 MHz spectrometer in $CDCl_3$. For ^1H 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 [3] 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.

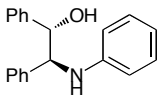
Caution: Perchlorate salts can be explosive and should be handled with care. Conversion to lower hydrates by unintentional dehydration may cause explosion. Use due caution in handling, as for all perchlorates.[4]

General procedure for the *meso*-epoxide opening reaction with aniline derivatives

A mixture of $Fe(ClO_4)_2 \cdot 6H_2O$ (9.1 mg, 0.025 mmol) and Bolm's ligand **1** (9.9 mg, 0.030 mmol) in distilled CH_2Cl_2 (0.5 mL) was stirred at room temperature for 1 h. The epoxide (0.5 mmol) and the aniline derivative (0.5 mmol) were then subsequently added to the mixture. The reaction mixture was stirred at room temperature until the starting materials disappeared (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 desired amino alcohol. The enantiomeric excess of the product was determined by chiral HPLC analysis.

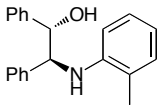
Characterization data of the chiral amino alcohols

(1*S*,2*S*)-1,2-Diphenyl-2-(phenylamino)ethanol (Table 2, entry 1)[5]



According to the general procedure with 98.1 mg *cis*-stilbene oxide and 45.6 μL aniline, the product was isolated as a white solid (m.p. = 85–86 °C). Reaction time = 16 h. Rf = 0.43 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.32–7.20 (m, 10H), 7.10–7.03 (m, 2H), 6.69–6.63 (m, 1H), 6.57–6.51 (m, 2H), 4.89 (dd, J = 5.8, 2.5 Hz, 1H), 4.68 (brs, 1H), 4.54 (d, J = 5.8 Hz, 1H), 2.50 (d, J = 2.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.6, 140.9, 140.5, 129.4, 128.8, 128.5, 128.2, 127.8, 127.6, 126.9, 118.2, 114.5, 78.4, 65.1. IR (neat): 3408, 3046, 3028, 2874, 2831, 1601, 1504, 1455, 1429, 1318, 1265, 1041, 753, 701, 694 cm^{-1}. $[\alpha]_D^{24}$ –51.4 (c = 0.53, CH_2Cl_2, 95% ee). HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min) t_R = 13.4 min (minor), t_R = 17.5 min (major).

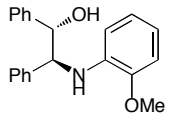
(1*S*,2*S*)-1,2-Diphenyl-2-(*o*-tolylamino)ethanol (Table 2, entry 2)[5]



According to the general procedure with 98.1 mg *cis*-stilbene oxide and 53.4 μL *o*-toluidine, the product was isolated as a white pasty solid (foam). Reaction time = 72 h. Rf = 0.49 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.35–7.21 (m, 10H), 7.02 (d, J = 7.4 Hz, 1H), 6.93–6.87 (m, 1H), 6.62–6.56 (m, 1H), 6.29 (d, J = 8.0 Hz, 1H), 4.97 (dd, J = 5.2, 2.2 Hz, 1H), 4.60 (brs, 1H), 4.58 (d, J = 5.2 Hz, 1H), 2.40 (d, J = 2.2

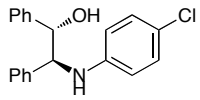
Hz, 1H), 2.21 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 145.5, 141.0, 140.6, 130.3, 128.9, 128.6, 128.2, 127.8, 127.5, 127.2, 126.8, 123.1, 117.6, 111.8, 78.4, 64.8, 17.9. IR (neat): 3420, 3061, 3029, 2888, 2855, 1607, 1587, 1508, 1453, 1316, 1266, 1048, 749, 700 cm^{-1}. HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 80/20, flow rate = 0.5 mL/min) t_R = 10.8 min (minor), t_R = 14.2 min (major).

(1*S*,2*S*)-2-(2-Methoxyphenylamino)-1,2-diphenylethanol (Table 2, entry 3)[5]



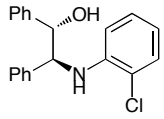
According to the general procedure with 98.1 mg *cis*-stilbene oxide and 56.4 μL *o*-anisidine, the product was isolated as a white pasty solid (foam). Reaction time = 72 h. Rf = 0.44 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.30–7.15 (m, 10H), 6.75 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.70–6.59 (m, 2H), 6.40 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.27 (brs, 1H), 4.89 (dd, *J* = 6.3, 2.0 Hz, 1H), 4.52 (d, *J* = 6.3 Hz, 1H), 3.88 (s, 3H), 2.72 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.7, 141.0, 140.5, 137.5, 128.7, 128.4, 128.1, 127.7, 127.6, 127.1, 121.4, 117.5, 112.1, 109.9, 78.6, 65.2, 55.9. IR (neat): 3401, 3062, 3029, 2937, 2833, 1602, 1511, 1454, 1429, 1343, 1248, 1225, 1176, 1125, 1049, 1028, 910, 769, 737, 700 cm^{-1}. HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min) t_R = 23.2 min (minor), t_R = 28.3 min (major).

(1*S*,2*S*)-2-(4-Chlorophenylamino)-1,2-diphenylethanol (Table 2, entry 4)[5]



According to the general procedure with 98.1 mg *cis*-stilbene oxide and 63.8 mg 4-chloroaniline, the product was isolated as a pale yellow pasty solid (foam). Reaction time = 16 h. Rf = 0.42 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.33–7.18 (m, 10H), 7.02–6.96 (m, 2H), 6.45–6.40 (m, 2H), 4.89 (dd, *J* = 5.6, 2.6 Hz, 1H), 4.75 (brs, 1H), 4.49 (d, *J* = 5.6 Hz, 1H), 2.38 (d, *J* = 2.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.2, 140.7, 140.1, 129.2, 128.9, 128.6, 128.3, 127.9, 127.5, 126.8, 122.7, 115.5, 78.3, 65.0. IR (neat): 3403, 3061, 3029, 2882, 1598, 1497, 1453, 1400, 1316, 1295, 1260, 1177, 1090, 1050, 816, 768, 700 cm^{-1}. HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min) t_R = 15.0 min (major), t_R = 18.0 min (minor).

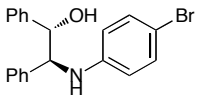
(1*S*,2*S*)-2-(2-Chlorophenylamino)-1,2-diphenylethanol (Table 2, entry 5)[6]



According to the general procedure with 98.1 mg *cis*-stilbene oxide and 52.6 μL 2-chloroaniline, the product was isolated as a white pasty solid (foam). Reaction time = 48 h. Rf = 0.54 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.35–7.22 (m, 10H), 7.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.93–6.87 (m, 1H), 6.58–6.53 (m, 1H), 6.35 (dd, *J* =

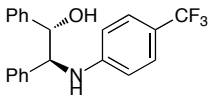
8.2, 1.6 Hz, 1H), 5.45 (d, J = 5.5 Hz, 1H), 4.97 (dd, J = 5.5, 2.7 Hz, 1H), 4.58 (dd, J = 5.5, 5.5 Hz, 1H), 2.36 (d, J = 2.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 143.4, 140.8, 140.0, 129.3, 128.9, 128.6, 128.3, 128.0, 127.8, 127.5, 126.8, 120.2, 117.9, 113.1, 78.3, 64.6. IR (neat): 3403, 3062, 3030, 2884, 1597, 1503, 1453, 1432, 1323, 1052, 1033, 769, 742, 700 cm^{-1}. HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min) t_R = 19.2 min (minor), t_R = 22.4 min (major).

(1*S*,2*S*)-2-(4-Bromophenylamino)-1,2-diphenylethanol (Table 2, entry 6)[5]



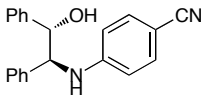
According to the general procedure with 98.1 mg *cis*-stilbene oxide and 86.0 mg 4-bromoaniline, the product was isolated as a pale yellow pasty solid (foam). Reaction time = 16 h. Rf = 0.37 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.33–7.19 (m, 10H), 7.15–7.10 (m, 2H), 6.41–6.36 (m, 2H), 4.89 (dd, J = 5.5, 2.8 Hz, 1H), 4.76 (brs, 1H), 4.49 (d, J = 5.5 Hz, 1H), 2.34 (d, J = 2.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.6, 140.7, 140.0, 132.0, 128.9, 128.6, 128.3, 128.0, 127.5, 126.8, 115.9, 109.8, 78.2, 64.8. IR (neat): 3406, 3062, 3028, 2882, 1593, 1494, 1453, 1396, 1316, 1295, 1260, 1179, 1073, 1051, 814, 768, 700 cm^{-1}. HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 80/20, flow rate = 0.5 mL/min) t_R = 18.5 min (major), t_R = 22.9 min (minor).

(1*S*,2*S*)-1,2-Diphenyl-2-(4-(trifluoromethyl)phenylamino)ethanol (Table 2, entry 7)



According to the general procedure with 98.1 mg *cis*-stilbene oxide and 62.8 μL 4-(trifluoromethyl)aniline, the product was isolated as a pale yellow pasty solid (foam). Reaction time = 24 h. Rf = 0.34 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.36–7.22 (m, 12H), 6.50 (d, J = 8.6 Hz, 2H), 5.11 (d, J = 5.1 Hz, 1H), 4.94 (d, J = 5.1 Hz, 1H), 4.59 (dd, J = 5.1, 5.1 Hz, 1H), 2.25 (brs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 150.1, 140.6, 139.8, 129.0, 128.7, 128.4, 128.1, 127.5, 126.7 (q, J = 3.8 Hz), 125.3 (q, J = 270.8 Hz), 119.4 (q, J = 32.6 Hz), 113.4, 78.1, 64.2. IR (neat): 3414, 3064, 3032, 2888, 1618, 1532, 1491, 1454, 1327, 1274, 1188, 1163, 1110, 1064, 826, 769, 701 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{21}H_{19}F_3NO^+$ ($[M+H]^+$): 358.1413, found: 358.1411. HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 80/20, flow rate = 0.5 mL/min) t_R = 15.6 min (major), t_R = 24.9 min (minor).

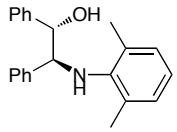
(1*S*,2*S*)-2-(4-Cyanophenylamino)-1,2-diphenylethanol (Table 2, entry 8)



According to the general procedure with 98.1 mg *cis*-stilbene oxide and 59.1 mg 4-cyanoaniline, the product was isolated as a white pasty solid (foam). Reaction time = 24 h. Rf = 0.12 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.36–7.22 (m,

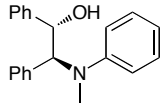
12H), 6.44 (d, J = 8.4 Hz, 2H), 5.33 (d, J = 5.4 Hz, 1H), 4.95 (dd, J = 5.4, 2.9 Hz, 1H), 4.58 (dd, J = 5.4, 5.4 Hz, 1H), 2.26 (d, J = 2.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 151.0, 140.7, 139.5, 133.7, 129.0, 128.7, 128.4, 128.1, 127.4, 126.6, 120.8, 113.6, 98.9, 77.9, 63.9. IR (neat): 3426, 3061, 3030, 2883, 2214, 1607, 1521, 1453, 1339, 1274, 1175, 1054, 826, 700 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{21}H_{19}N_2O^+$ ([M+H]$^+$): 315.1492, found: 315.1486. HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 70/30, flow rate = 0.5 mL/min) t_R = 17.2 min (major), t_R = 21.9 min (minor).

(1*S*,2*S*)-2-(2,6-Dimethylphenylamino)-1,2-diphenylethanol (Table 2, entry 9)



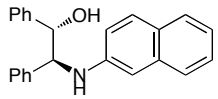
According to the general procedure with 98.1 mg *cis*-stilbene oxide and 61.8 μL 2,6-dimethylaniline, the product was isolated as a colorless oil. Reaction time = 72 h. Rf = 0.54 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.29–7.24 (m, 2H), 7.24–7.14 (m, 6H), 7.06–7.01 (m, 2H), 6.90 (d, J = 7.3 Hz, 2H), 6.77 (t, J = 7.3 Hz, 1H), 5.07 (d, J = 8.6 Hz, 1H), 4.24 (d, J = 8.6 Hz, 1H), 2.14 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 143.8, 141.1, 140.8, 129.6, 129.5, 128.6, 128.3, 128.0, 127.9, 127.2, 122.5, 76.9, 69.2, 19.5. IR (neat): 3403, 3062, 3031, 2950, 2925, 2859, 1594, 1492, 1475, 1454, 1396, 1256, 1211, 1190, 1099, 1056, 1027, 910, 869, 768, 733, 699 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{22}H_{24}NO^+$ ([M+H]$^+$): 318.1852, found: 318.1857. HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min) t_R = 7.9 min (major), t_R = 25.5 min (minor).

(1*S*,2*S*)-2-(*N*-Methyl-*N*-phenylamino)-1,2-diphenylethanol (Table 2, entry 10)[7]



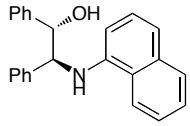
According to the general procedure with 98.1 mg *cis*-stilbene oxide and 54.2 μL *N*-methylaniline, the product was isolated as a colorless oil. Reaction time = 24 h. Rf = 0.52 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.43–7.38 (m, 2H), 7.33–7.12 (m, 8H), 7.05–6.97 (m, 4H), 6.96–6.91 (m, 1H), 5.30 (d, J = 10.0 Hz, 1H), 4.88 (d, J = 10.0 Hz, 1H), 3.98 (s, 1H), 2.72 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 151.7, 141.1, 135.2, 129.5, 129.1, 128.6, 128.4, 128.2, 128.1, 128.0, 120.6, 117.9, 73.9, 71.9, 33.1. IR (neat): 3418, 3061, 3030, 2953, 2885, 2811, 1598, 1500, 1452, 1385, 1320, 1191, 1081, 1056, 1031, 911, 756, 736, 697 cm^{-1}. HPLC (Daicel Chiralpak® AS-H, hexane/*i*-PrOH = 95/5, flow rate = 0.8 mL/min) t_R = 14.7 min (minor), t_R = 20.7 min (major).

(1*S*,2*S*)-2-(Naphthalen-2-ylamino)-1,2-diphenylethanol (Table 2, entry 11)



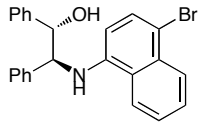
According to the general procedure with 98.1 mg *cis*-stilbene oxide and 71.6 mg 2-naphthylamine, the product was isolated as a pale orange pasty solid (foam). Reaction time = 16 h. Rf = 0.38 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.62 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.36–7.20 (m, 11H), 7.18–7.12 (m, 1H), 6.93 (dd, J = 9.0, 2.4 Hz, 1H), 6.62 (d, J = 2.4 Hz, 1H), 4.96 (d, J = 5.6, 1H), 4.88 (brs, 1H), 4.69 (d, J = 5.6 Hz, 1H), 2.47 (brs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 145.2, 140.9, 140.3, 135.2, 129.1, 128.9, 128.6, 128.3, 128.0, 127.9, 127.6, 127.0, 126.5, 126.4, 122.5, 118.8, 106.9, 78.3, 64.9. IR (neat): 3403, 3059, 3028, 2885, 1630, 1602, 1521, 1483, 1453, 1396, 1359, 1274, 1228, 1190, 1051, 1019, 832, 747, 700 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{24}H_{22}NO^+$ ([M+H]$^+$): 340.1696, found: 340.1701. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min) t_R = 30.6 min (minor), t_R = 33.8 min (major).

(1*S*,2*S*)-2-(Naphthalen-1-ylamino)-1,2-diphenylethanol (Table 2, entry 12)[5]



According to the general procedure with 98.1 mg *cis*-stilbene oxide and 71.6 mg 1-naphthylamine, the product was isolated as a pale pink pasty solid (foam). Reaction time = 16 h. Rf = 0.47 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.02–7.97 (m, 1H), 7.79–7.74 (m, 1H), 7.53–7.43 (m, 2H), 7.40–7.21 (m, 10H), 7.20–7.08 (m, 2H), 6.30 (d, J = 7.2 Hz, 1H), 5.55 (brs, 1H), 5.05 (dd, J = 5.4, 2.8 Hz, 1H), 4.73 (d, J = 5.4 Hz, 1H), 2.46 (d, J = 2.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 142.5, 141.0, 140.3, 134.6, 129.0, 128.9, 128.7, 128.3, 127.9, 127.6, 126.9, 126.8, 126.1, 125.2, 124.3, 120.4, 118.1, 107.0, 78.6, 64.8. IR (neat): 3423, 3060, 3030, 2886, 1582, 1526, 1479, 1454, 1409, 1345, 1281, 1051, 768, 700 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min) t_R = 10.2 min (minor), t_R = 18.7 min (major).

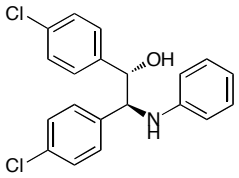
(1*S*,2*S*)-2-(4-Bromonaphthalen-1-ylamino)-1,2-diphenylethanol (Table 2, entry 13)[7]



According to the general procedure with 98.1 mg *cis*-stilbene oxide and 111.0 mg 1-amino-4-bromonaphthalene, the product was isolated as a pale grey pasty solid (foam). Reaction time = 16 h. Rf = 0.40 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.19–8.15 (m, 1H), 8.02–7.97 (m, 1H), 7.61–7.52 (m, 2H), 7.40–7.20 (m, 11H), 6.13 (d, J = 8.2 Hz, 1H), 5.64 (brs, 1H), 5.05 (dd, J = 5.2, 3.0 Hz, 1H), 4.68 (d, J = 5.2 Hz, 1H), 2.35 (d, J = 3.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 142.5, 140.8, 139.7, 132.5,

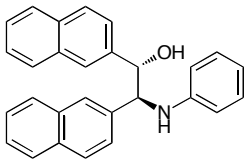
130.5, 129.0, 128.7, 128.5, 128.2, 128.1, 127.5, 127.4, 126.9, 125.9, 125.6, 120.9, 110.7, 107.6, 78.5, 64.7. IR (neat): 3424, 3063, 3029, 2886, 1590, 1570, 1523, 1476, 1453, 1381, 1339, 1268, 1053, 916, 769, 752, 700 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min) t_R = 15.3 min (minor), t_R = 20.4 min (major).

(1*S*,2*S*)-1,2-bis(4-chlorophenyl)-2-(phenylamino)ethanol (Table 3, entry 1)[8]



According to the general procedure with 132.6 mg *cis*-1,2-bis-(*p*-chlorophenyl)ethane oxide and 45.6 μL aniline, the product was isolated as a pale yellow pasty solid (foam). Reaction time = 72 h. Rf = 0.39 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.29–7.21 (m, 4H), 7.19–7.05 (m, 6H), 6.72–6.66 (m, 1H), 6.54–6.49 (m, 2H), 4.80 (dd, *J* = 6.2, 2.4 Hz, 1H), 4.63 (brs, 1H), 4.45 (d, *J* = 6.2 Hz, 1H), 2.53 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.0, 139.0, 138.6, 134.1, 133.6, 129.4, 129.0, 128.9, 128.7, 128.3, 118.7, 114.5, 77.6, 64.6. IR (neat): 3403, 3052, 3025, 2885, 1602, 1503, 1491, 1431, 1409, 1315, 1263, 1092, 1053, 1013, 835, 752, 692 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min) t_R = 20.5 min (minor), t_R = 31.1 min (major).

(1*S*,2*S*)-1,2-di(naphtalen-2-yl)-2-(phenylamino)ethanol (Table 3, entry 2)[5]



According to the general procedure with 148.2 mg *cis*-1,2-bis-(2'-naphthyl)ethane oxide and 45.6 μL aniline, the product was isolated as a white solid (m.p. = 150–151 °C). Reaction time = 36 h. Rf = 0.36 (20% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.86–7.70 (m, 8H), 7.50–7.42 (m, 4H), 7.42–7.36 (m, 2H), 7.07–7.01 (m, 2H), 6.66–6.61 (m, 1H), 6.59–6.53 (m, 2H), 5.18 (d, *J* = 5.6 Hz, 1H), 4.83 (d, *J* = 5.6 Hz, 1H), 4.82 (brs, 1H), 2.61 (brs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.5, 138.3, 138.1, 133.7, 133.4, 133.3, 133.2, 129.4, 128.7, 128.4, 128.3, 128.0, 126.6, 126.5, 126.4, 126.3, 126.2, 125.9, 125.6, 124.7, 118.3, 114.5, 78.2, 65.0. IR (neat): 3551, 3421, 3050, 3019, 2883, 1602, 1506, 1428, 1359, 1302, 1128, 1058, 857, 826, 752, 690 cm^{-1}. HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min) t_R = 22.3 min (minor), t_R = 31.0 min (major).

Crystallization of $[Fe(ClO_4)_2•1]•(H_2O)•2MeCN$ complexes

Crystallization of **$[Fe(ClO_4)_2•1]•(H_2O)•2MeCN$** was carried out as follows: A mixture of $Fe(ClO_4)_2•6H_2O$ (5.4 mg, 15.0 μmol) and Bolm's ligand **1** (4.9 mg, 15.0 μmol) was dissolved in MeCN (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 850236 ($[\mathbf{1}•Fe•2MeCN•H_2O]^{2+}•2ClO_4^-$) 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.

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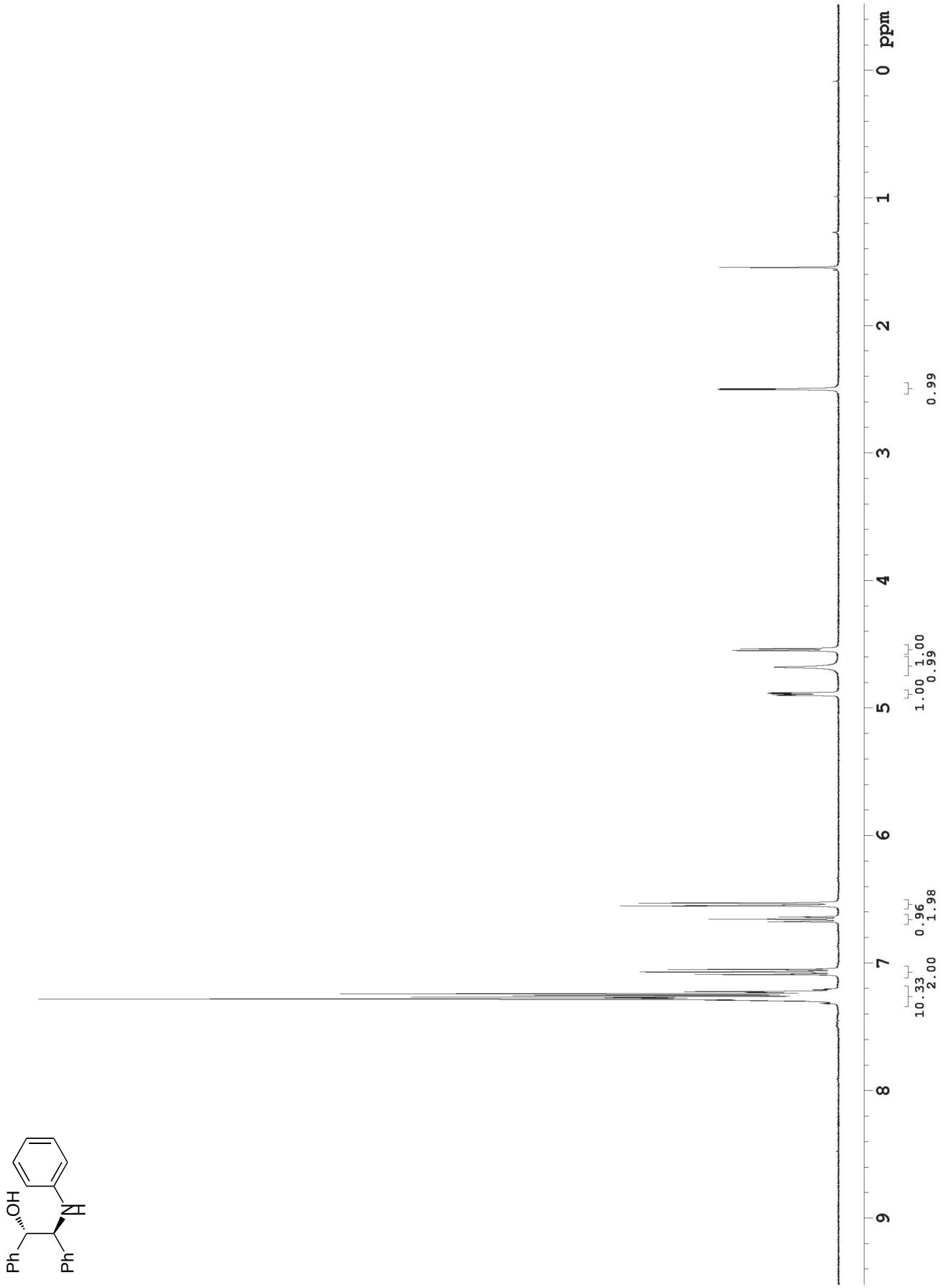
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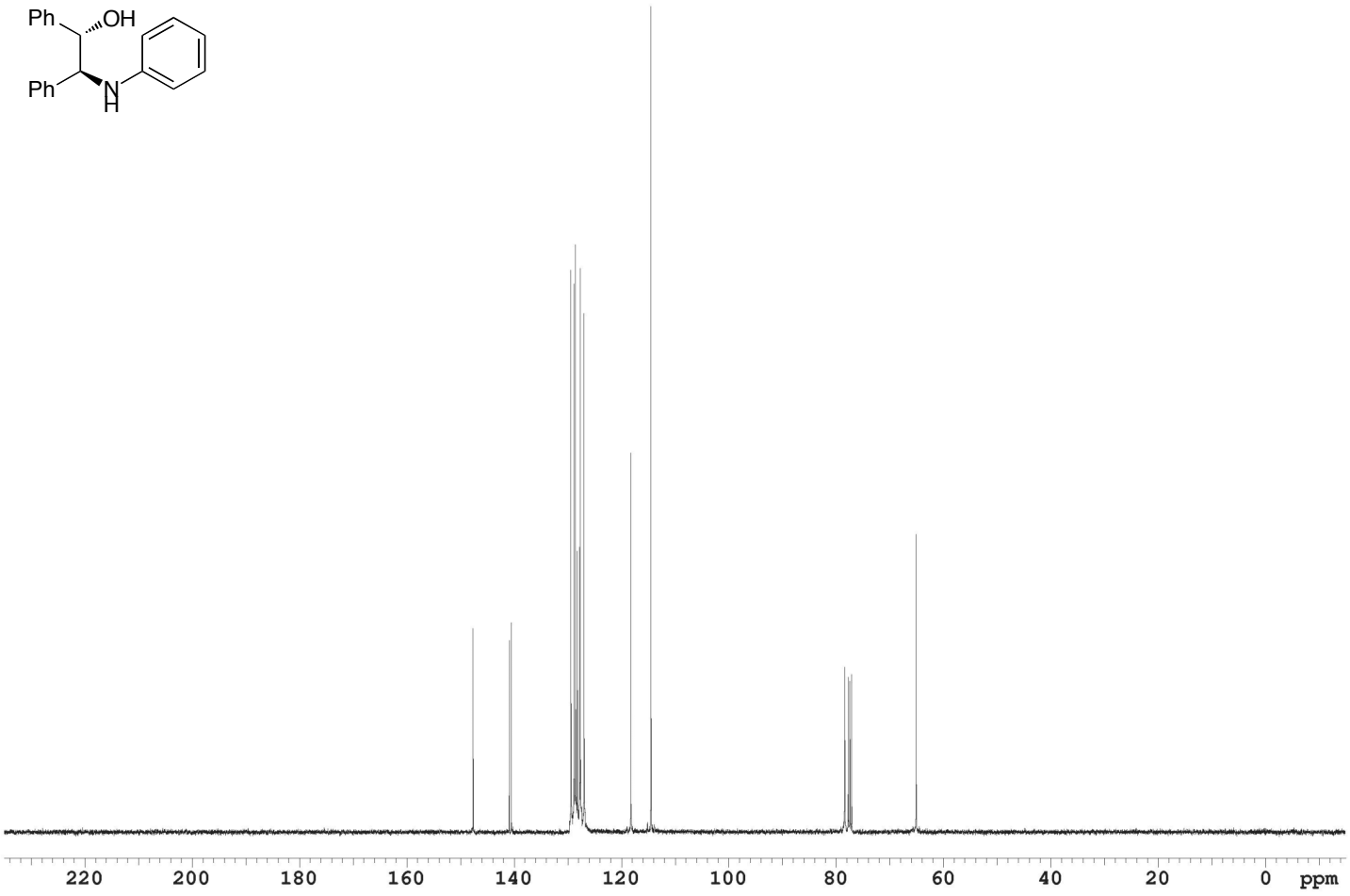

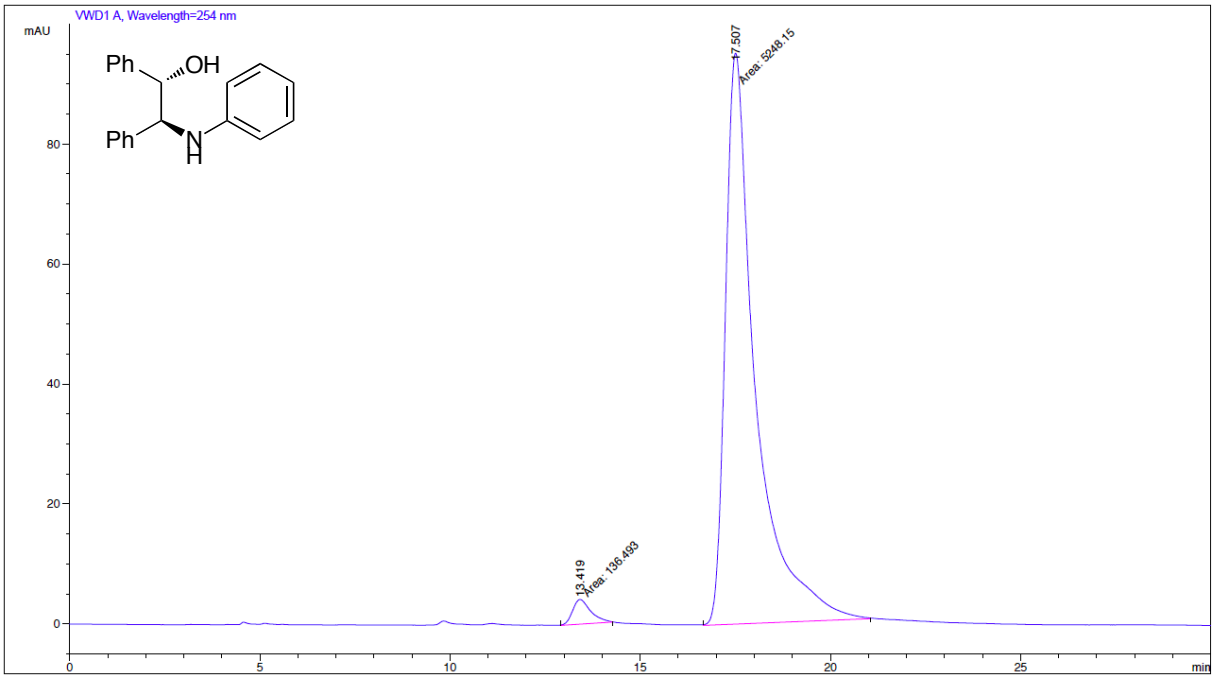

Signal 1: VWD1 A, Wavelength=254 nm

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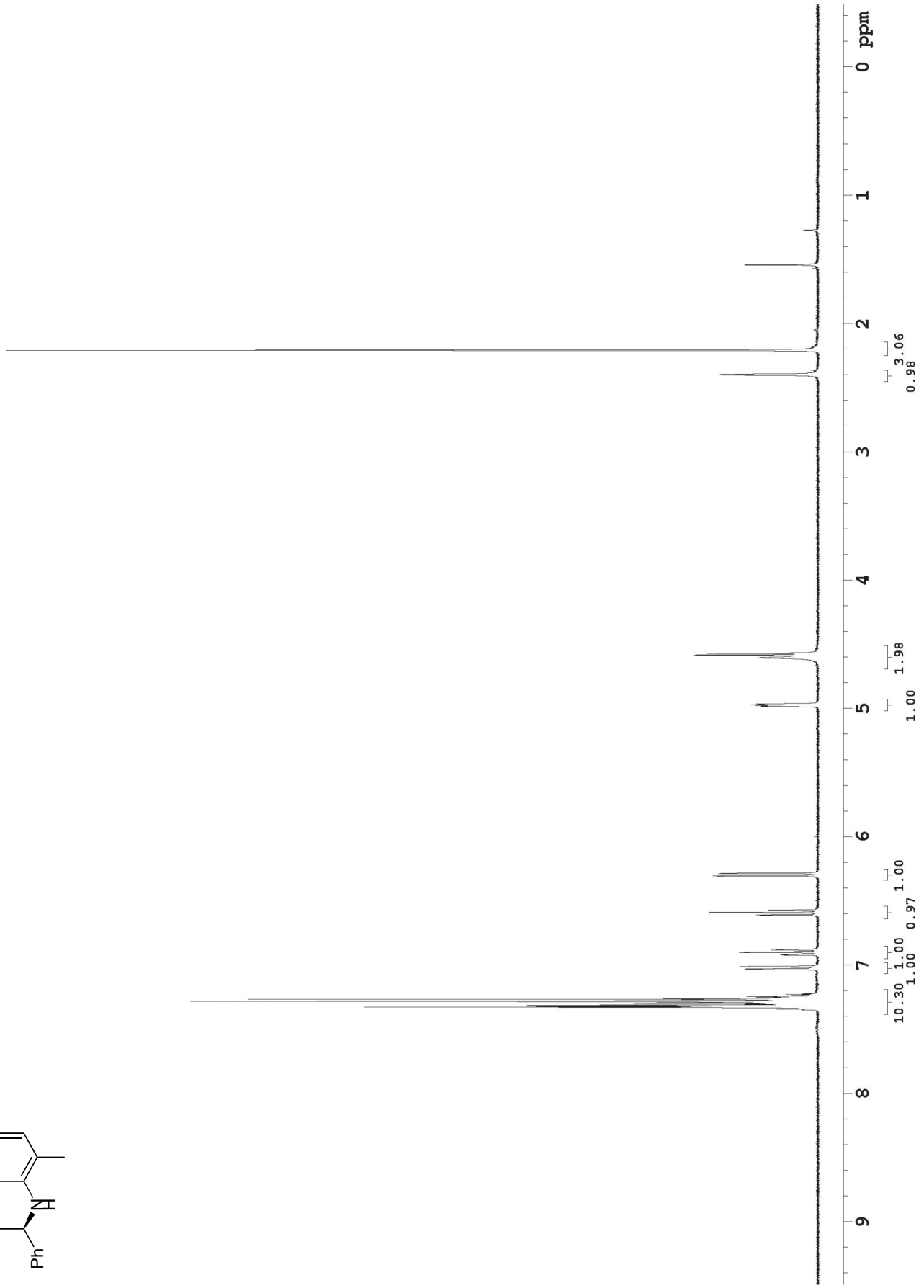
2	17.507	MM	0.9188	5248.14648	95.19704	97.4651
Totals :				5384.63965	99.31461	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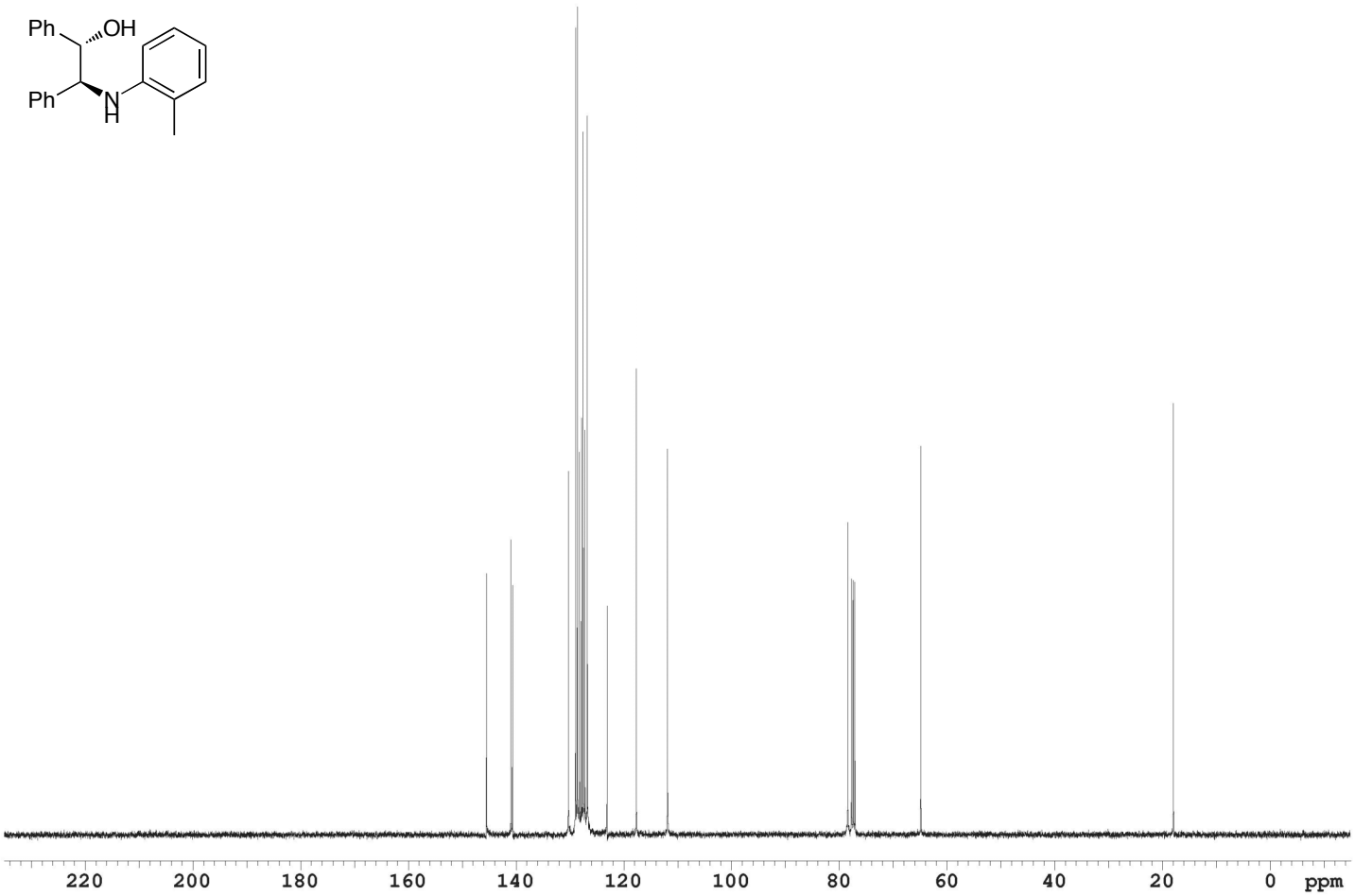

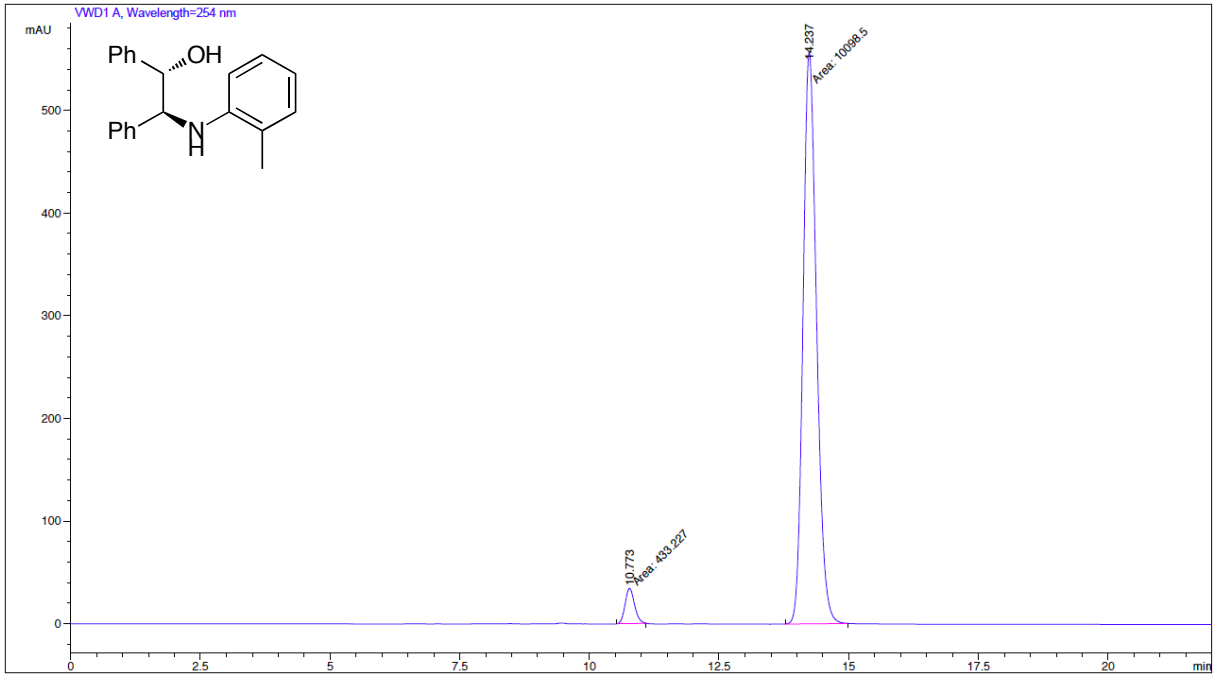

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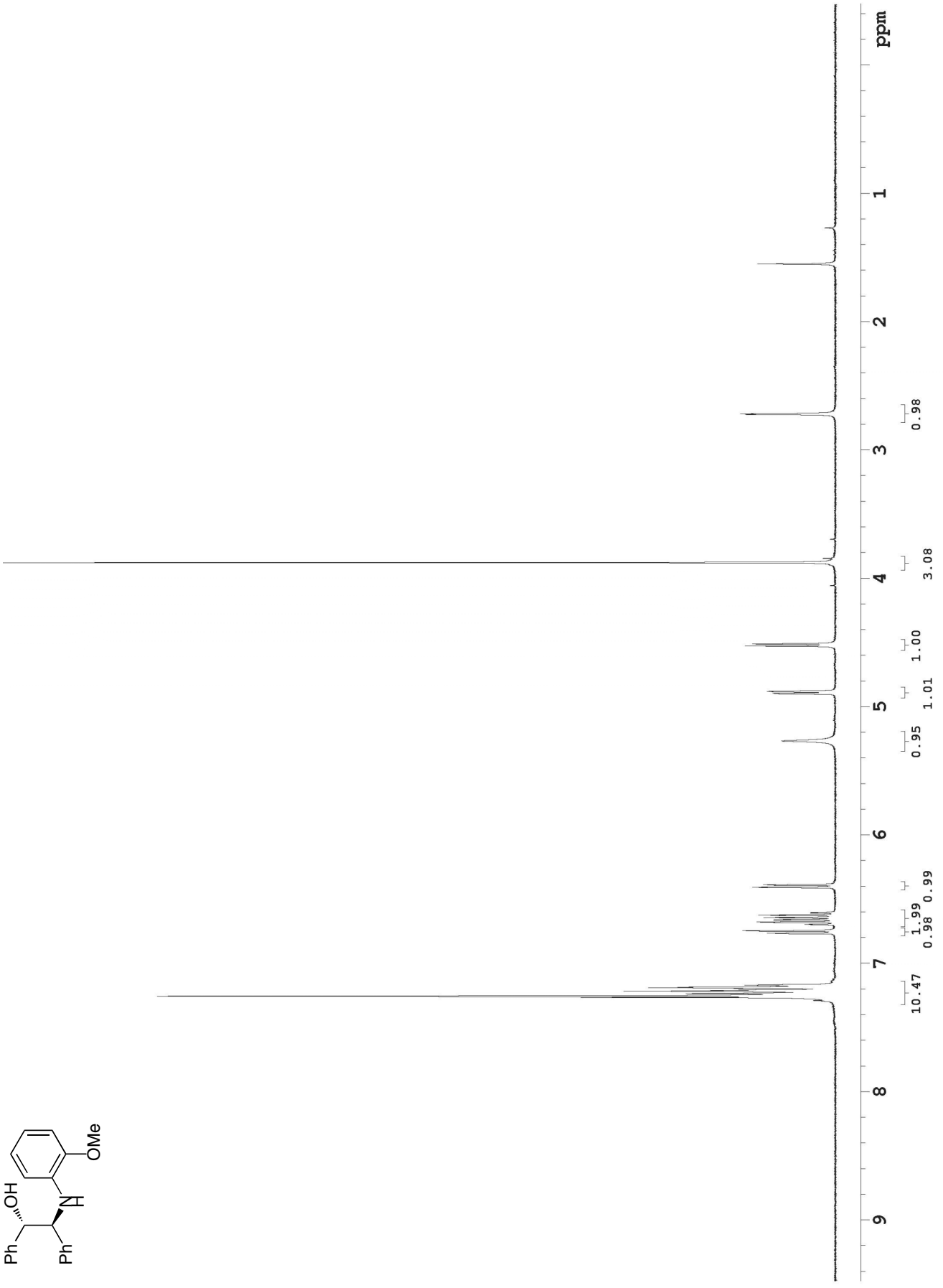
2	14.237	MM	0.3021	1.00985e4	557.10486	95.8865
Totals :				1.05317e4	591.43296	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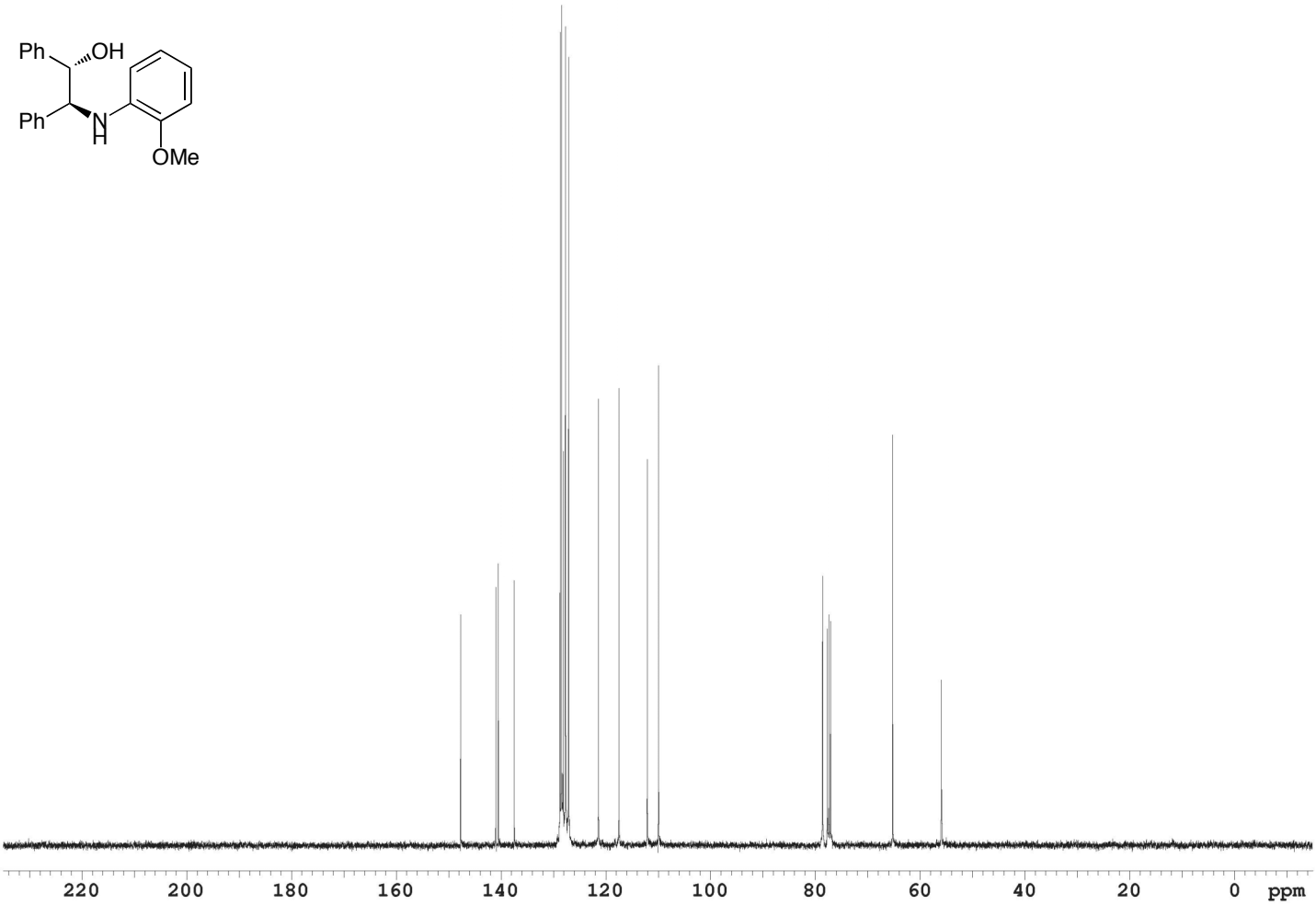

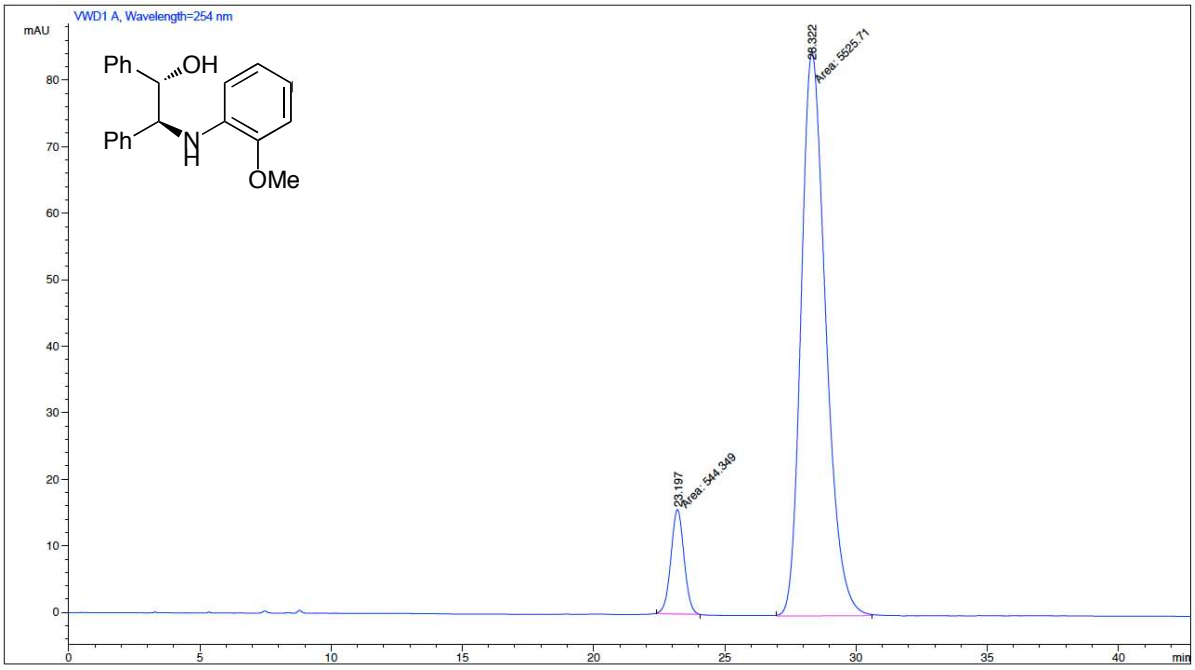

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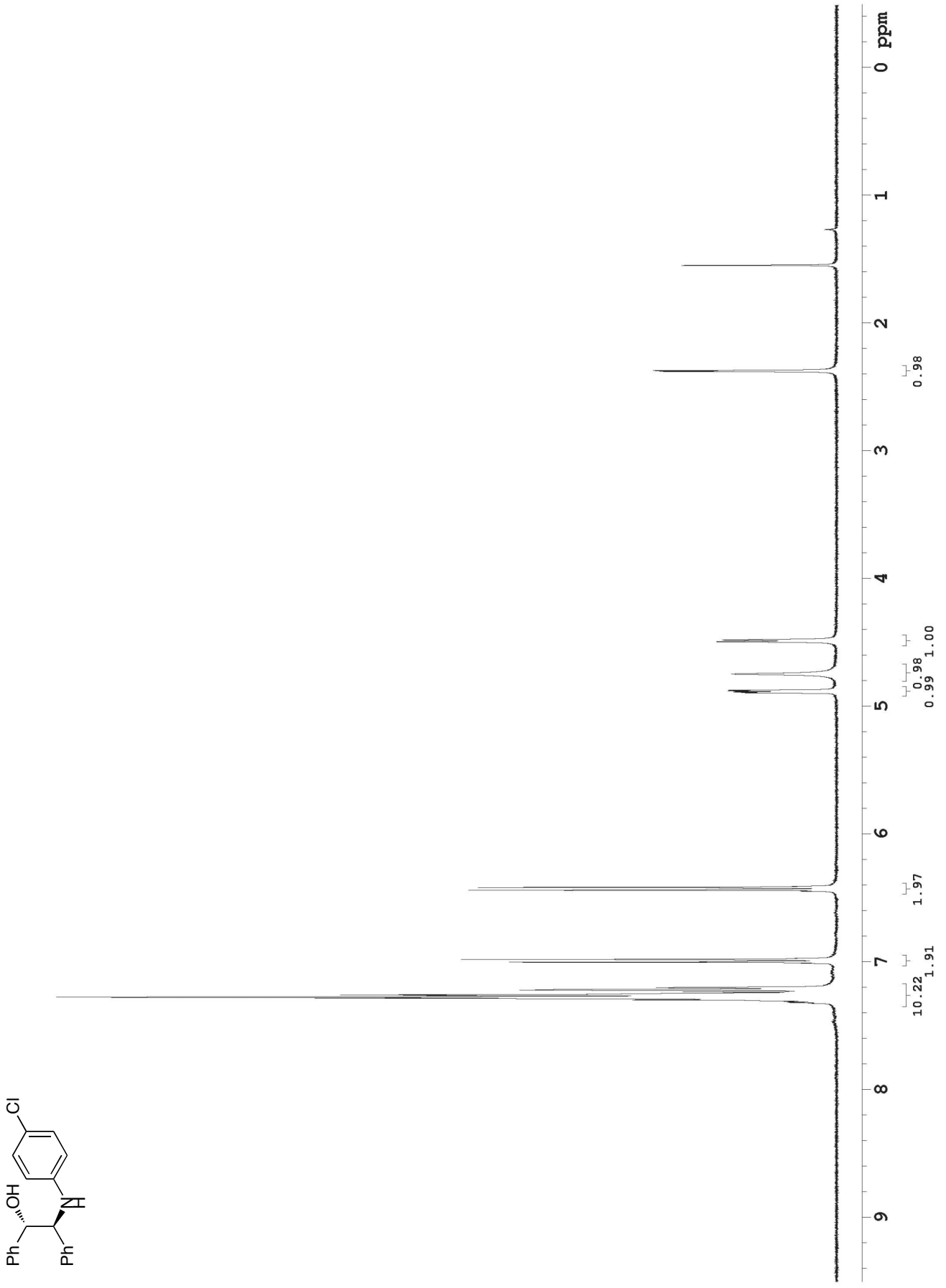
1	23.197	MM	0.5766	544.34882	15.73445	8.9678
2	28.322	MM	1.0872	5525.70801	84.70680	91.0322
Totals :				6070.05682	100.44125	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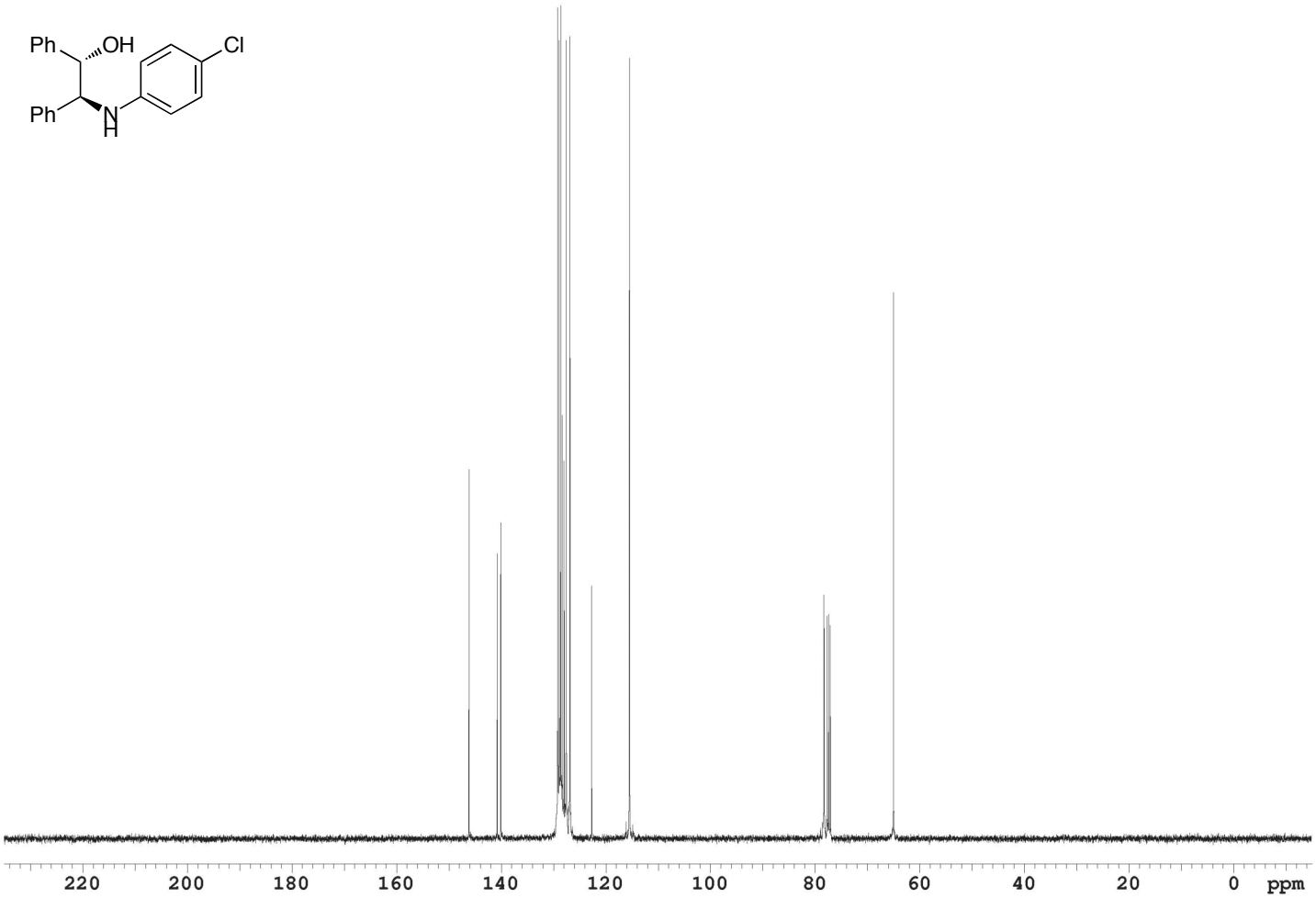

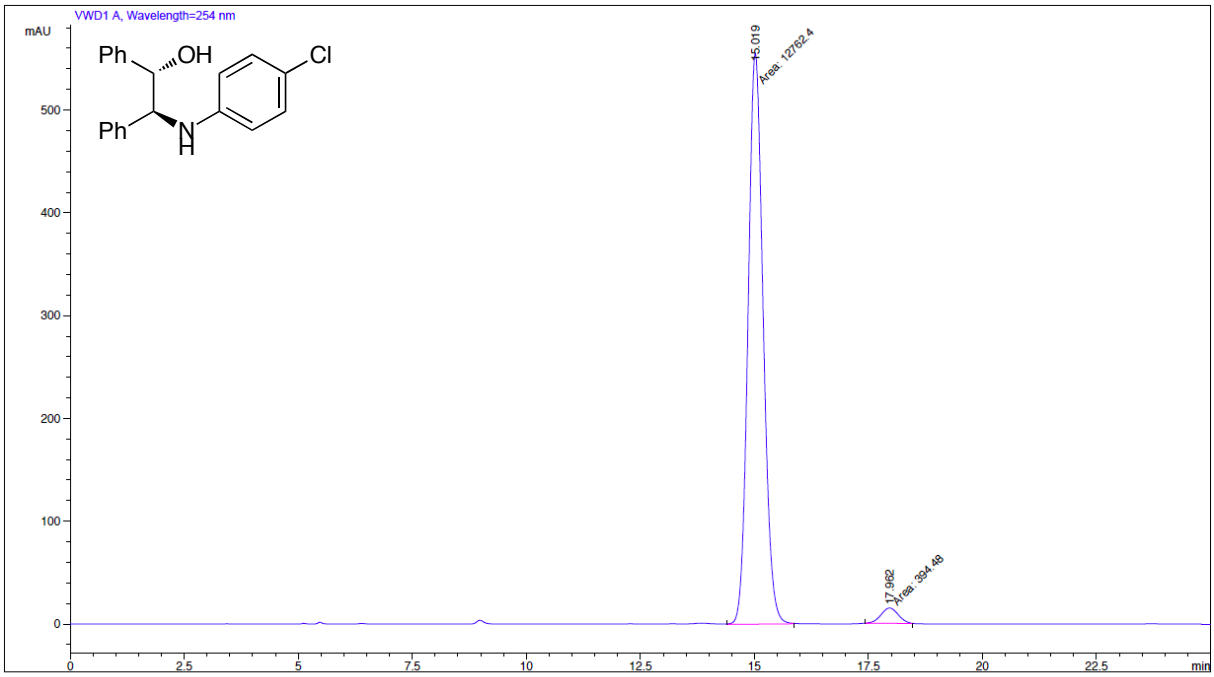

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1	15.019	MM	0.3832	1.27624e4	555.10309	97.0017
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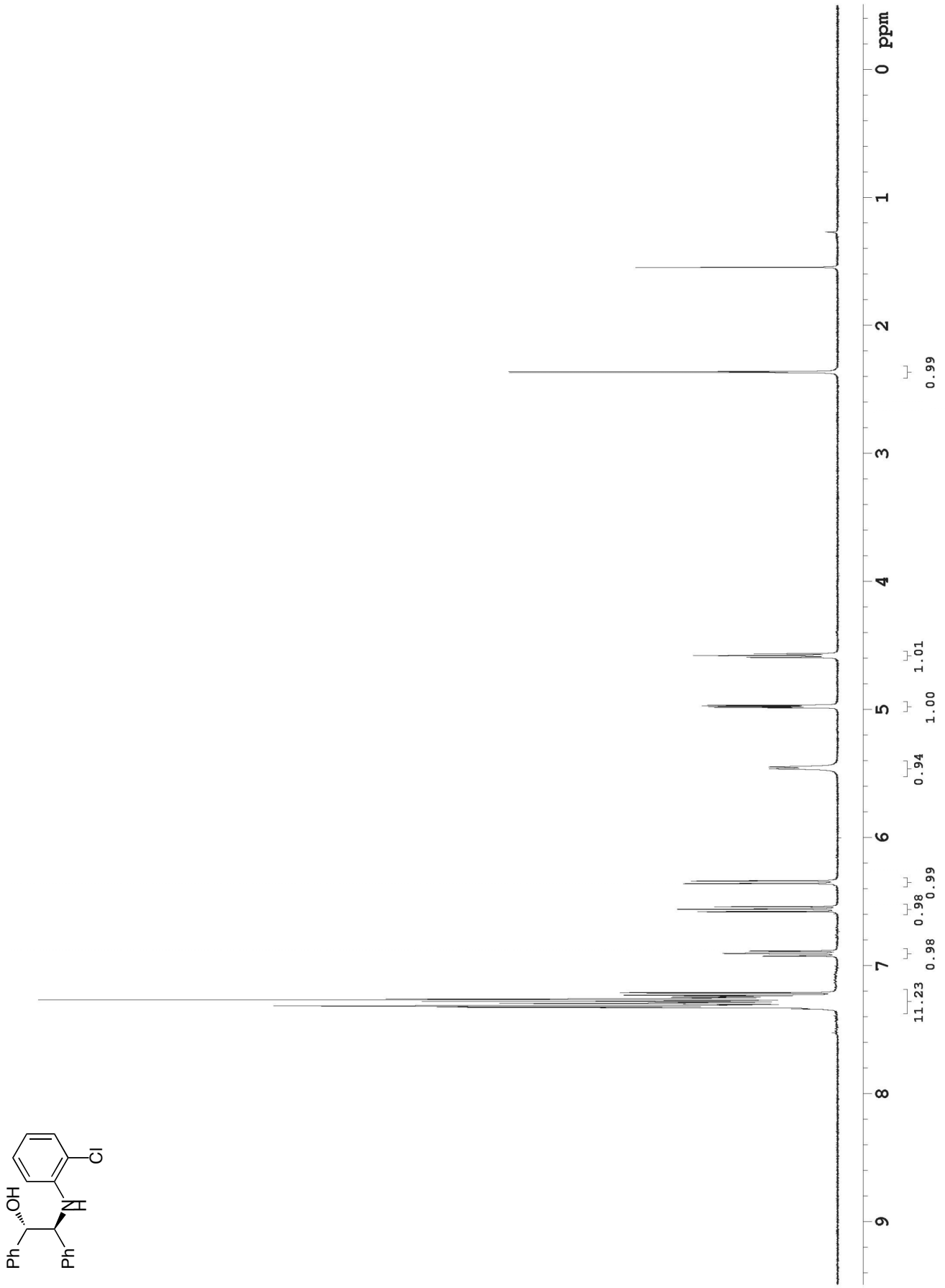
Totals :				1.31569e4	570.03418	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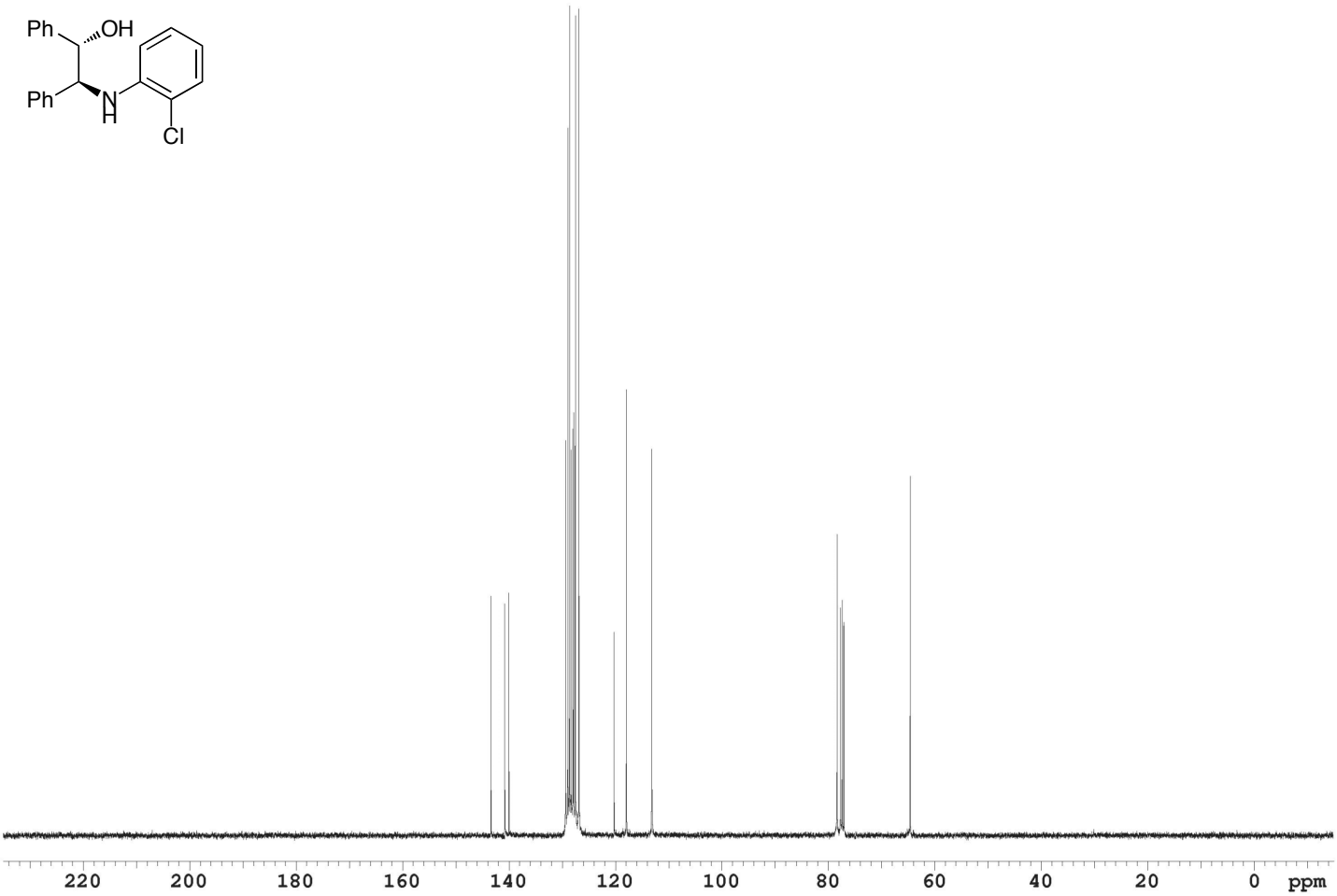

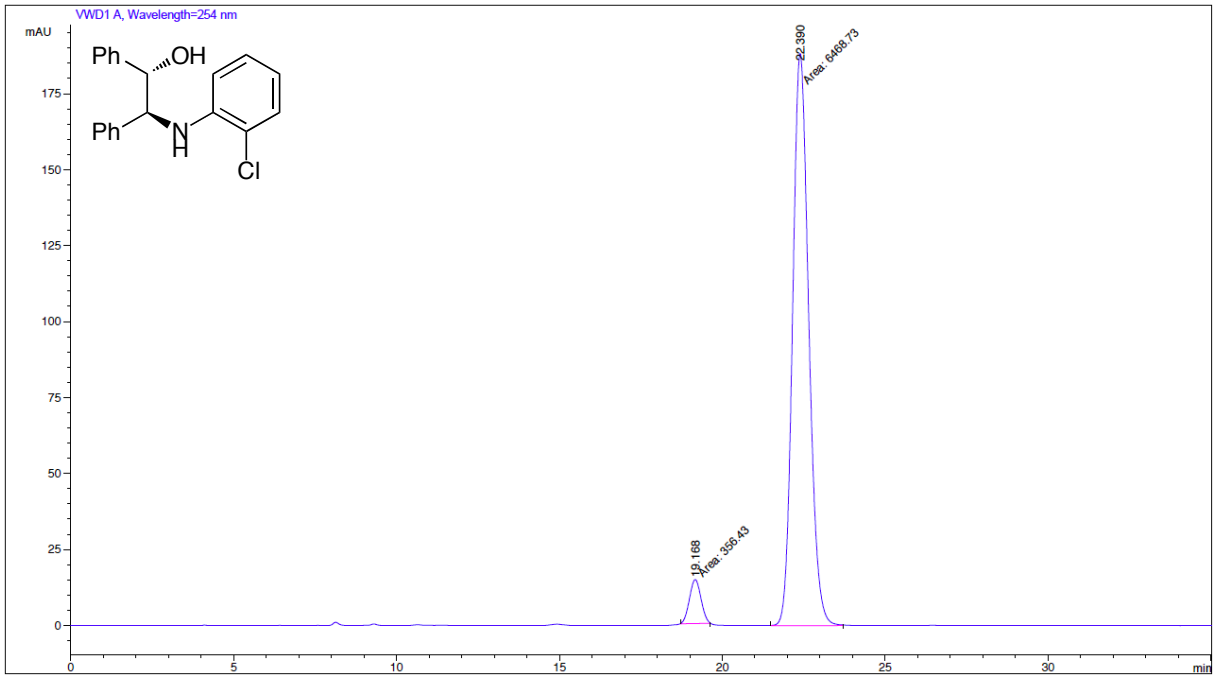

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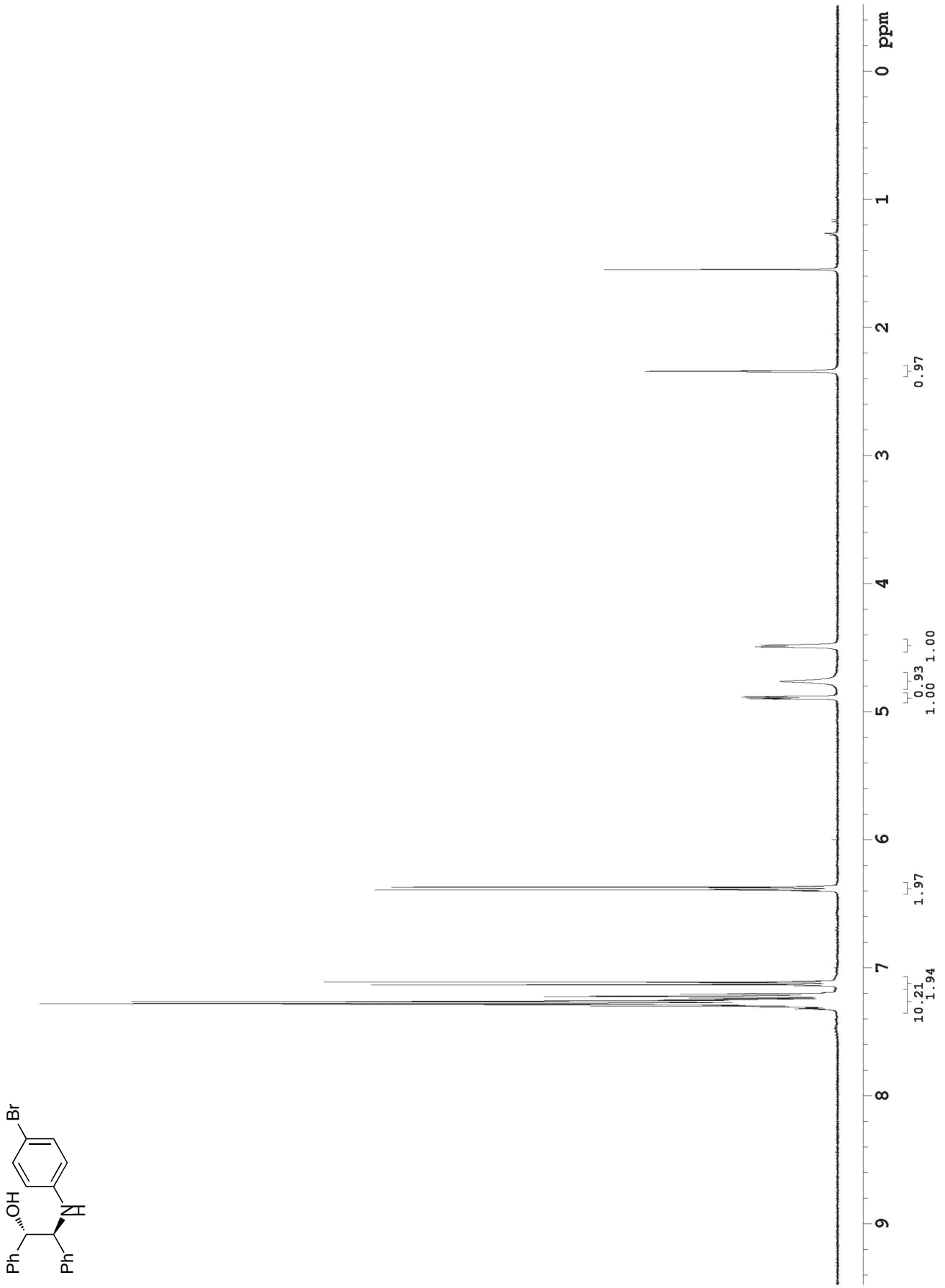
Totals :				6825.16302	202.75220	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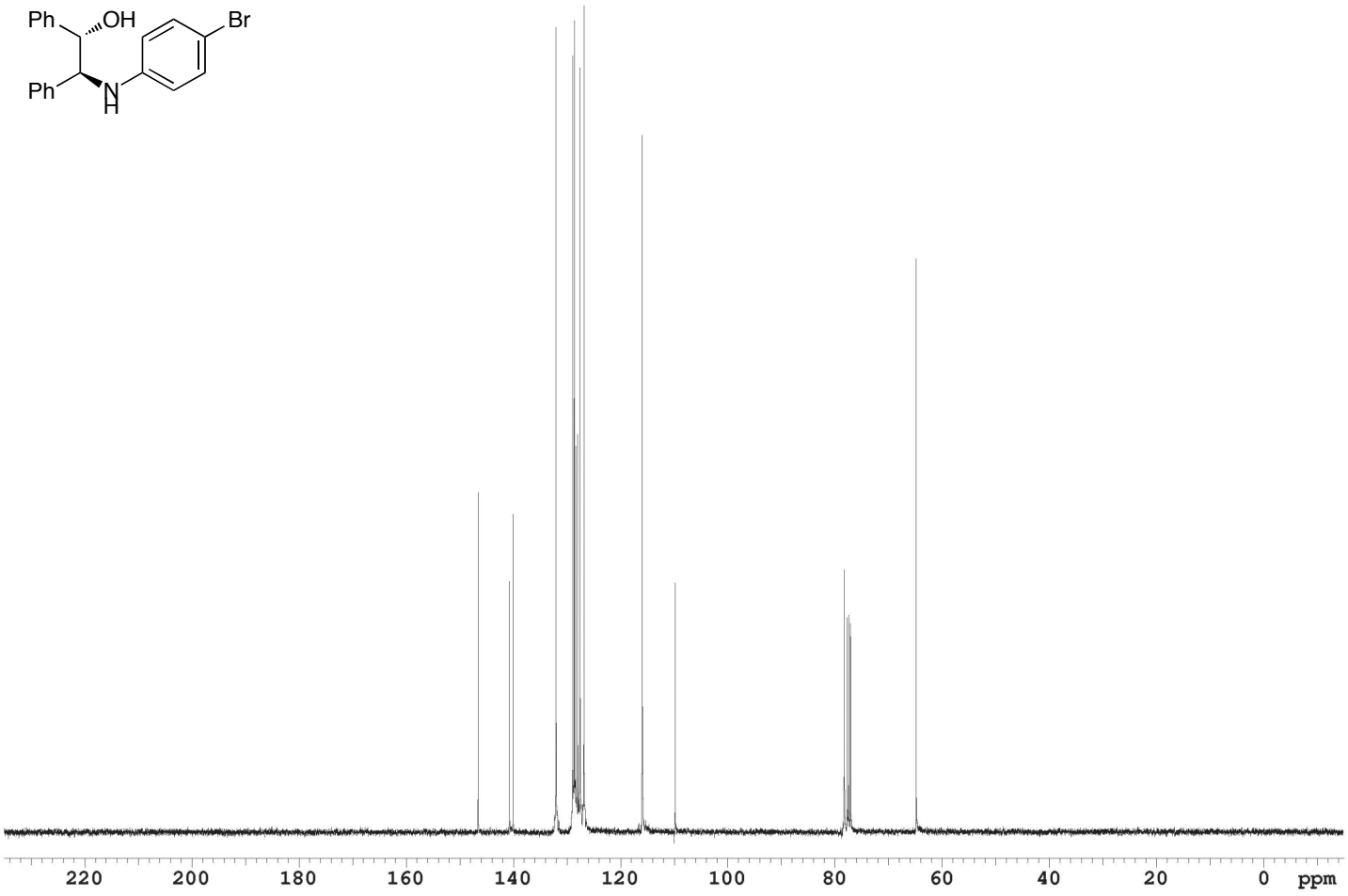

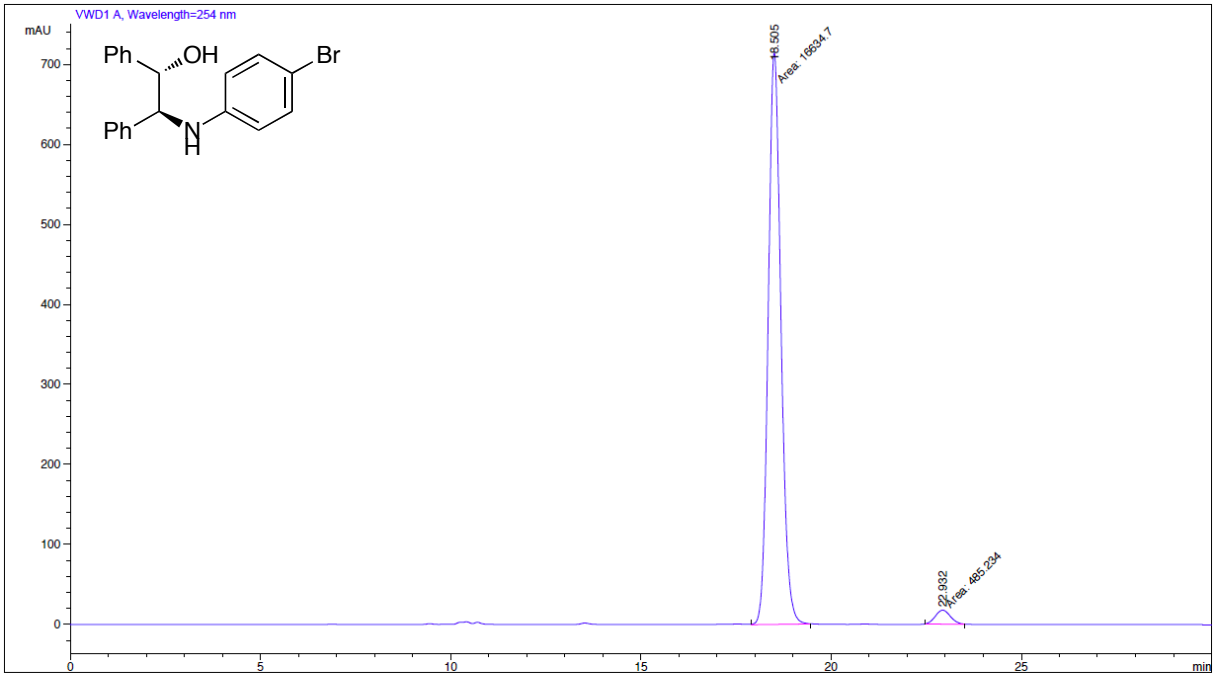

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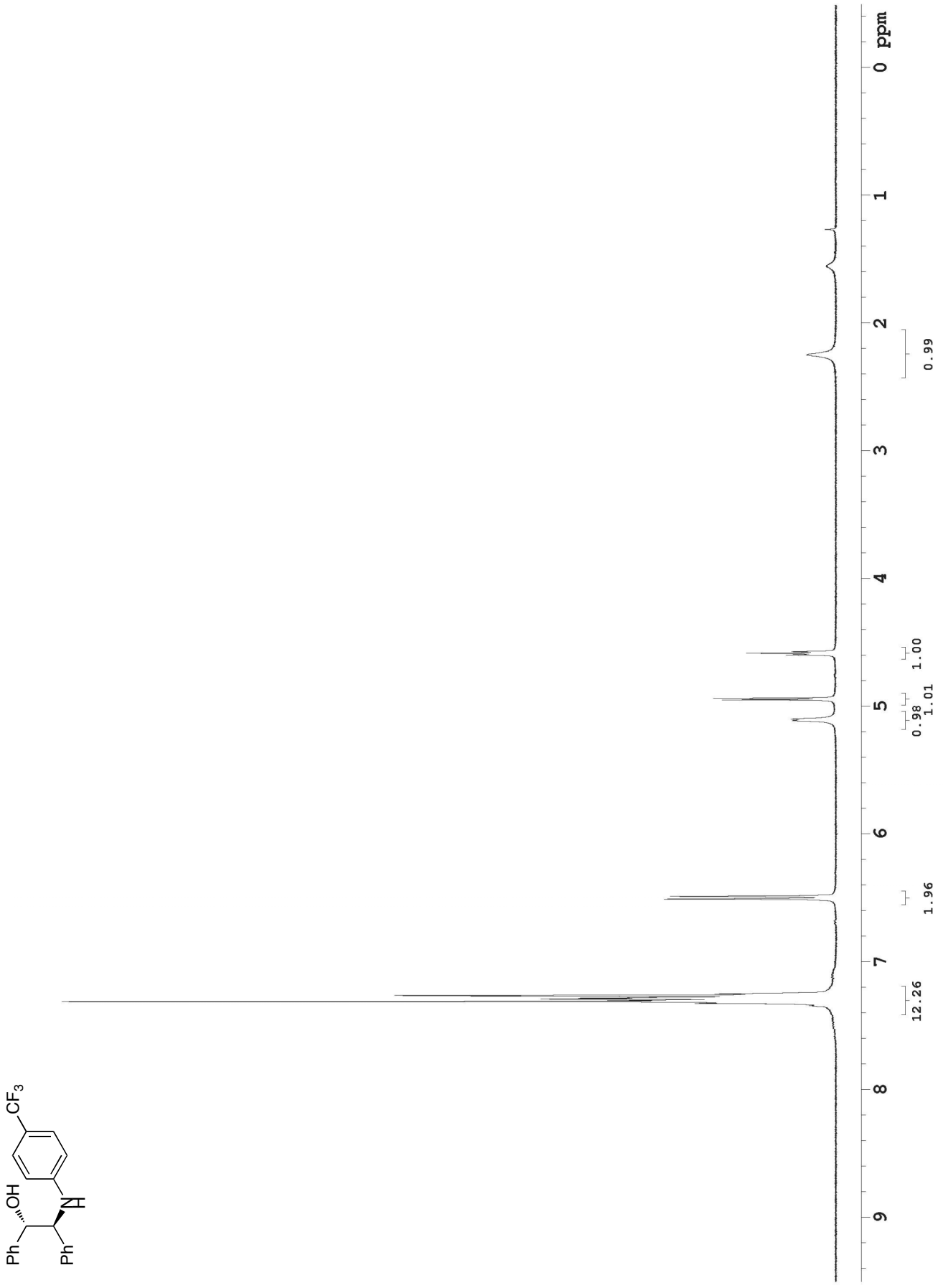
Totals :				1.71200e4	732.33491	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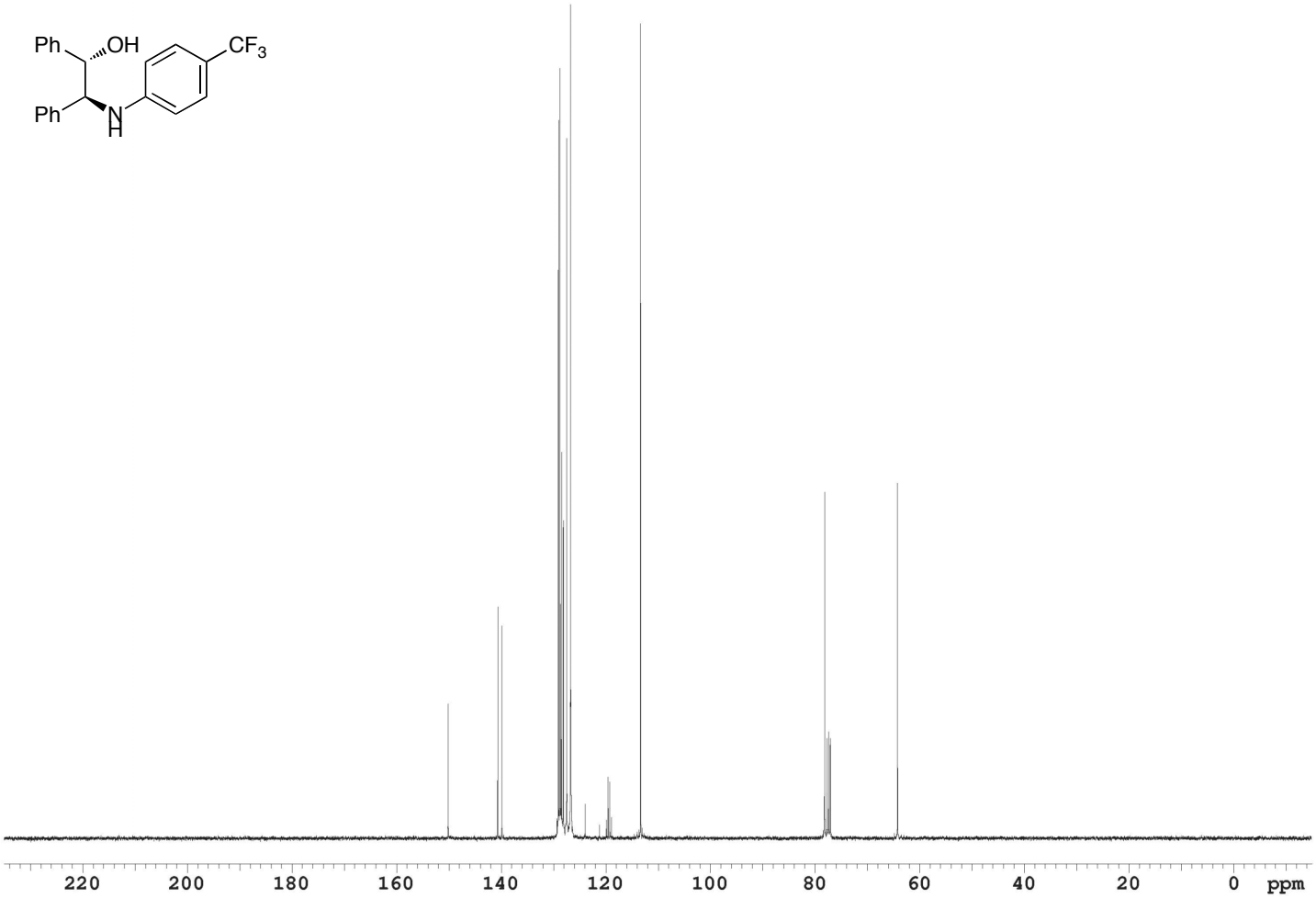

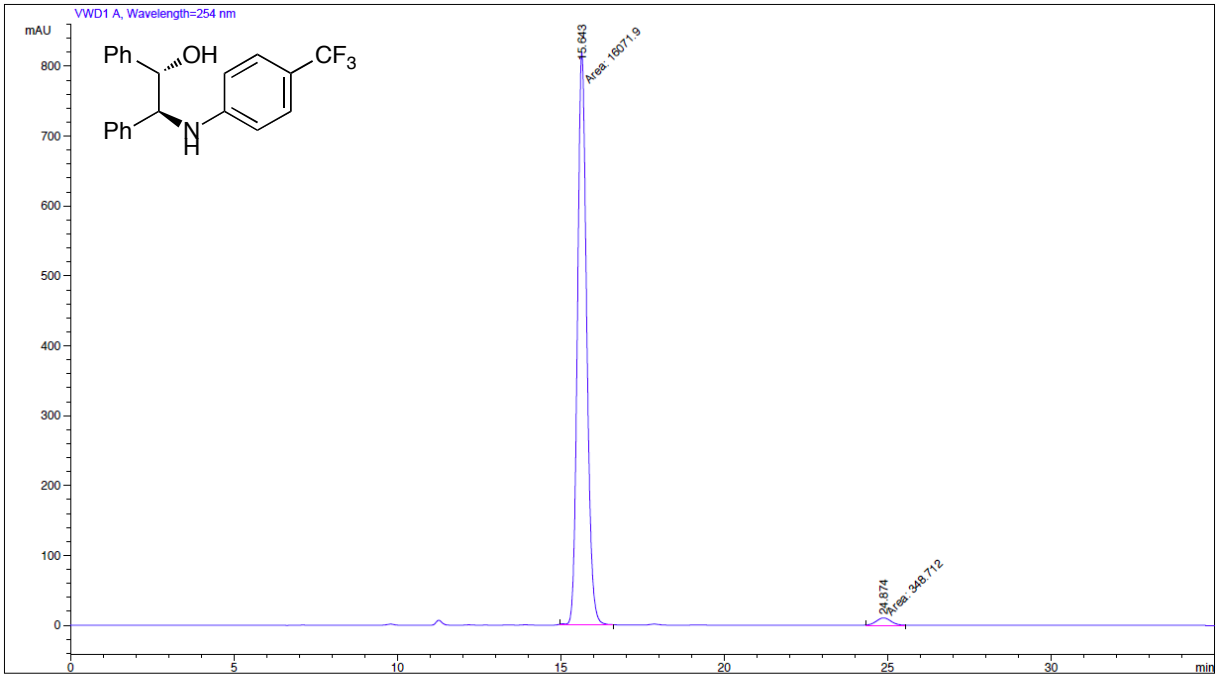

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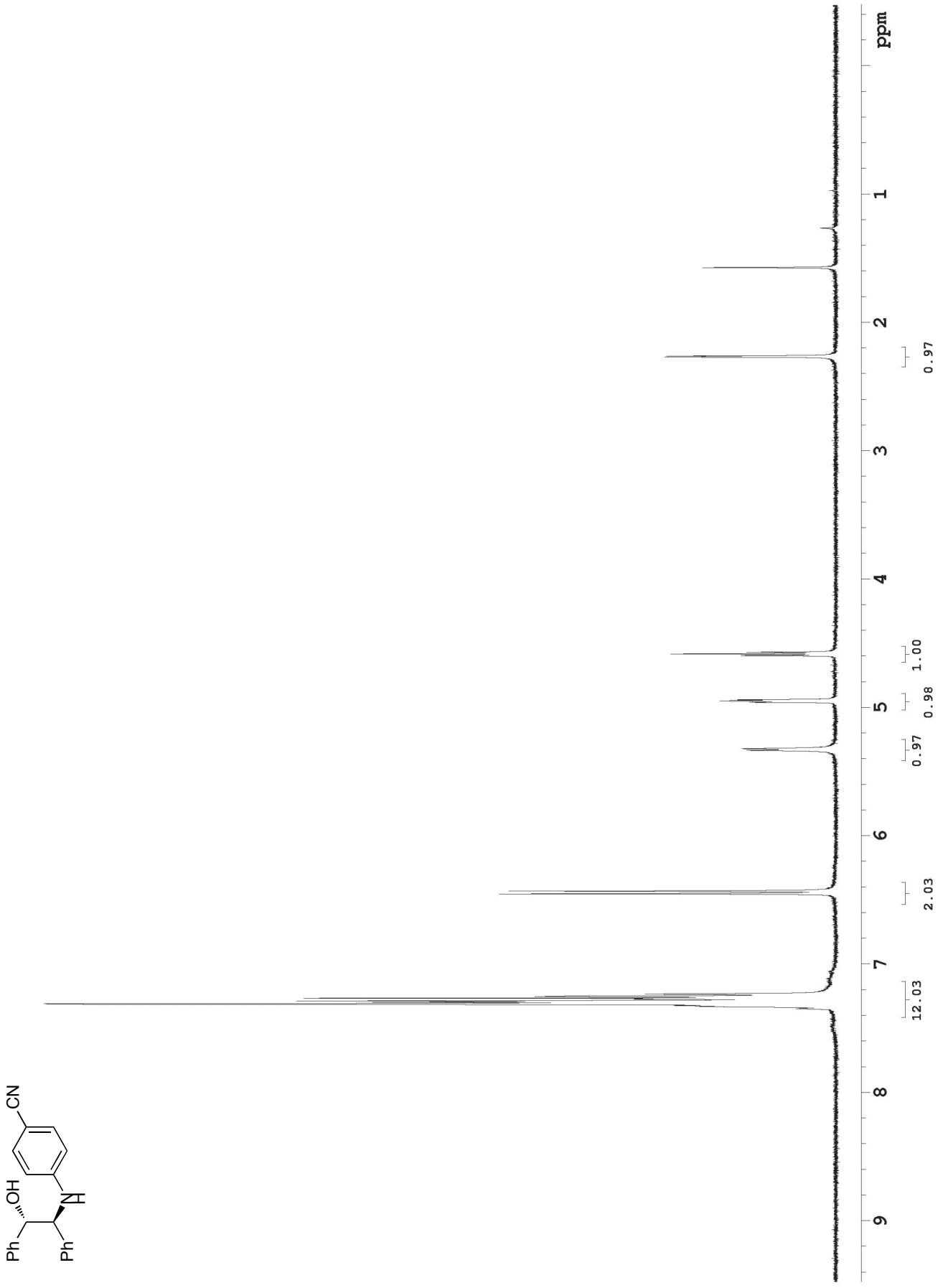
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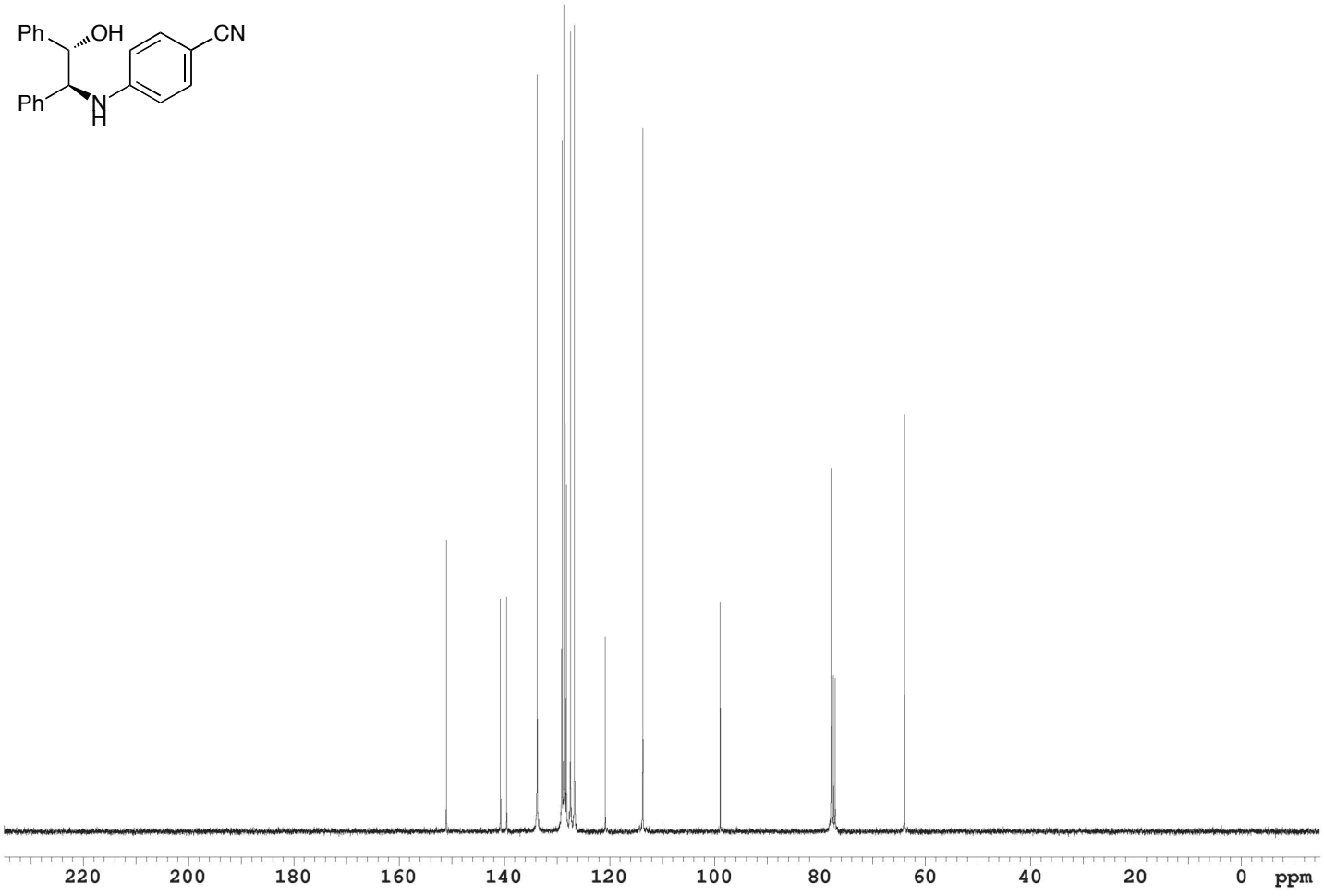

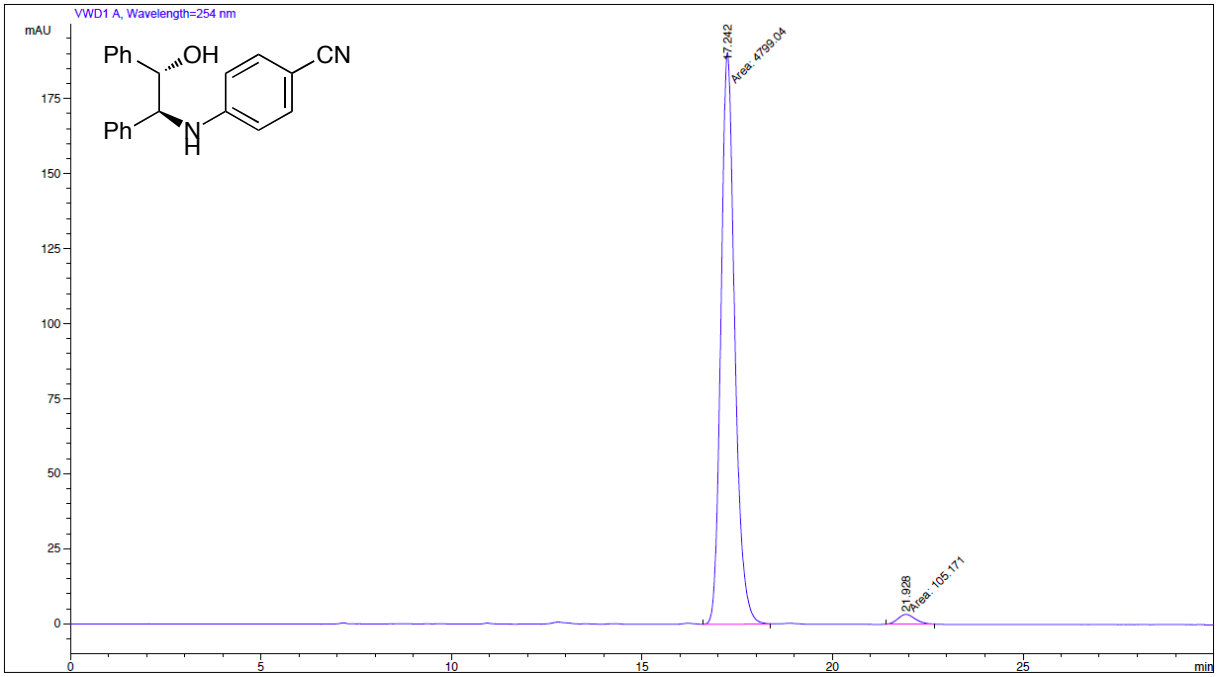

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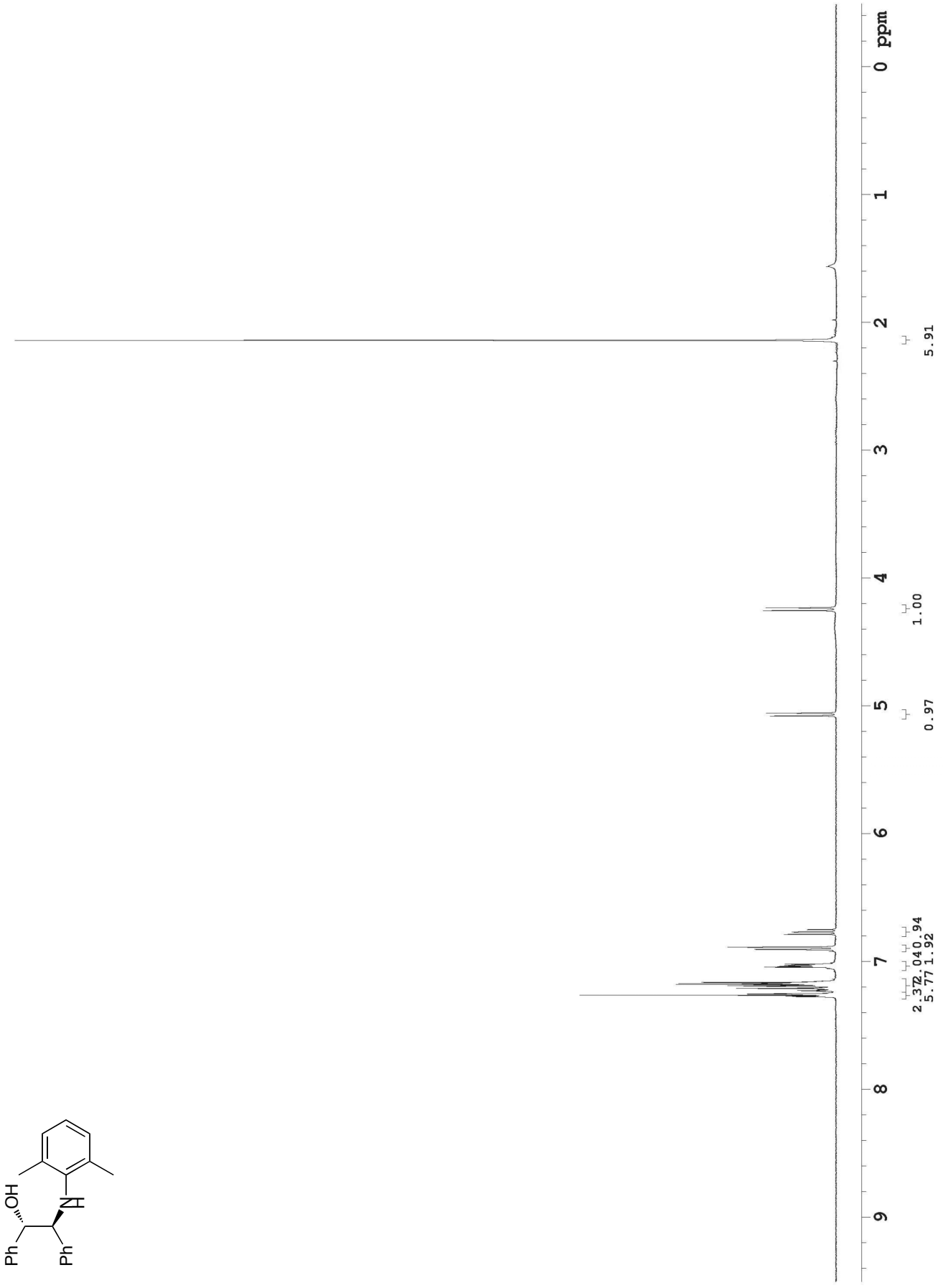
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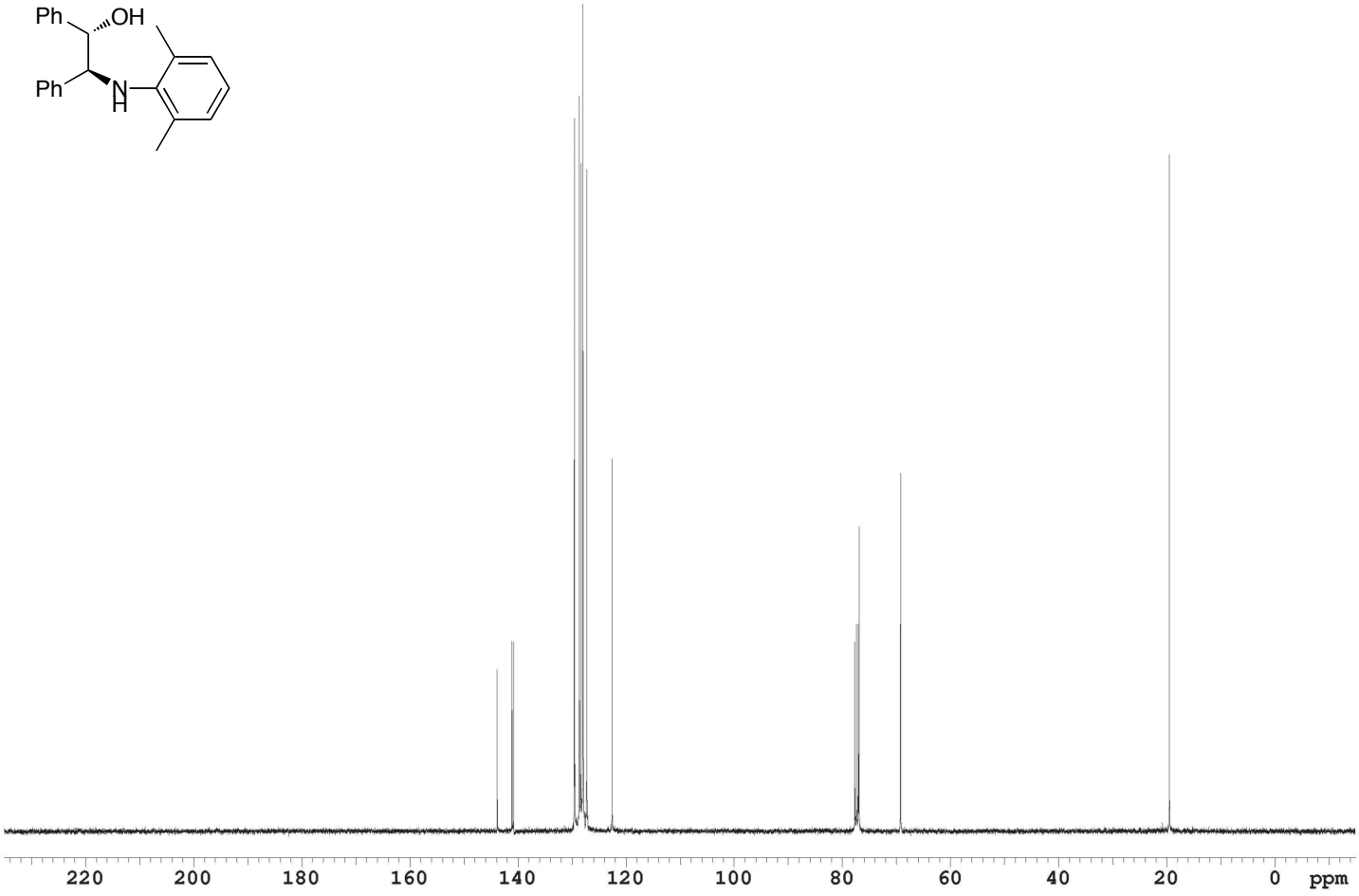

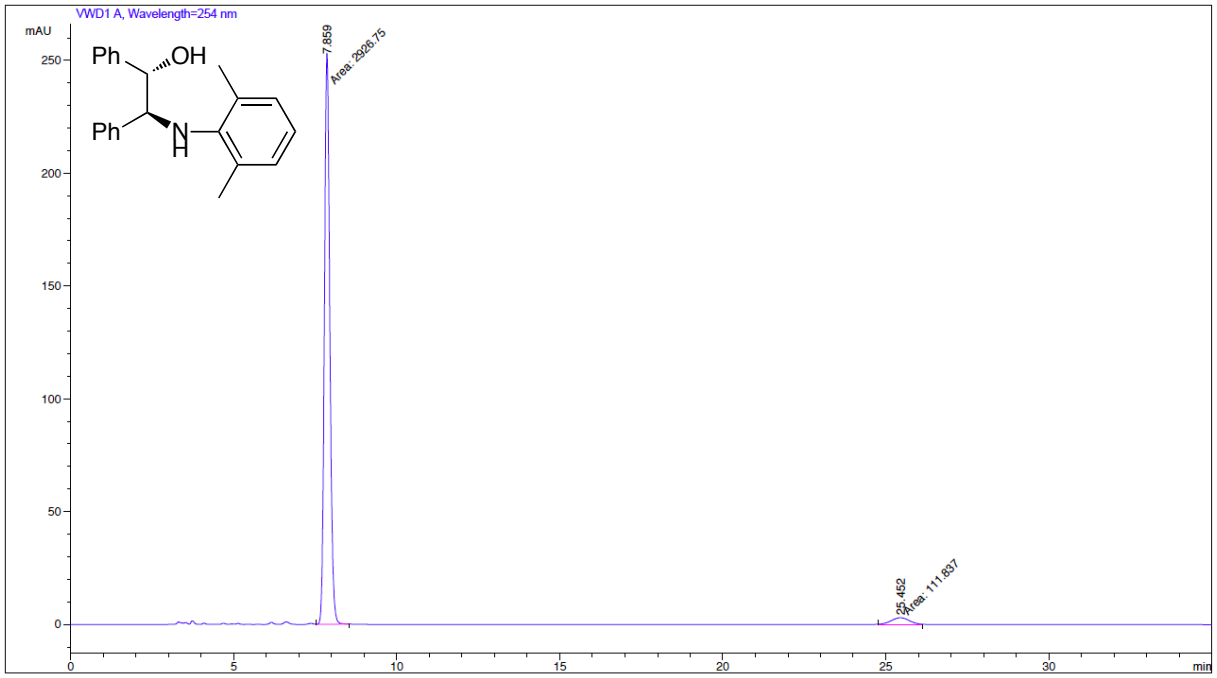

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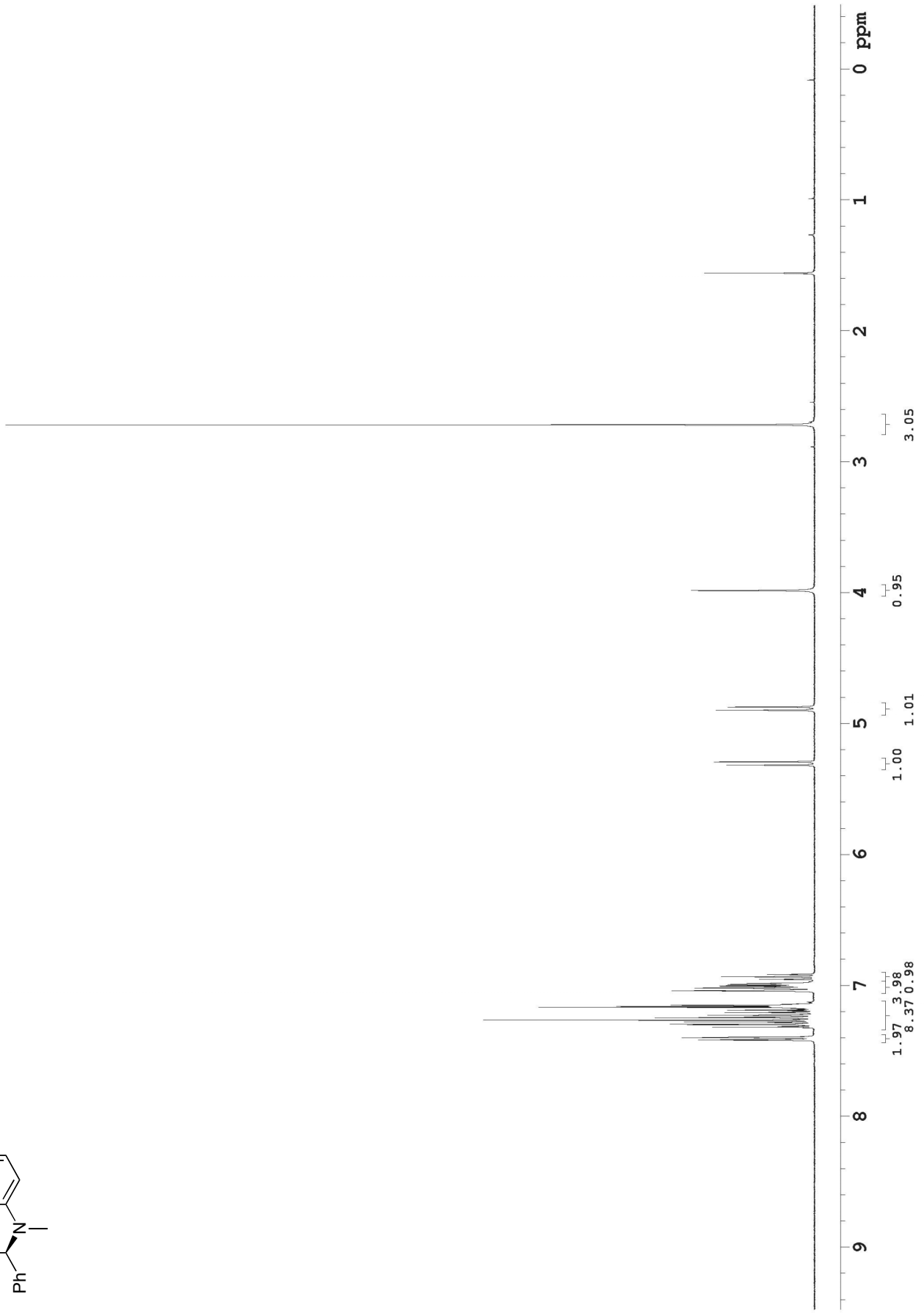
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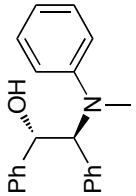
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Ph
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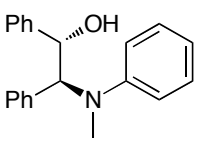
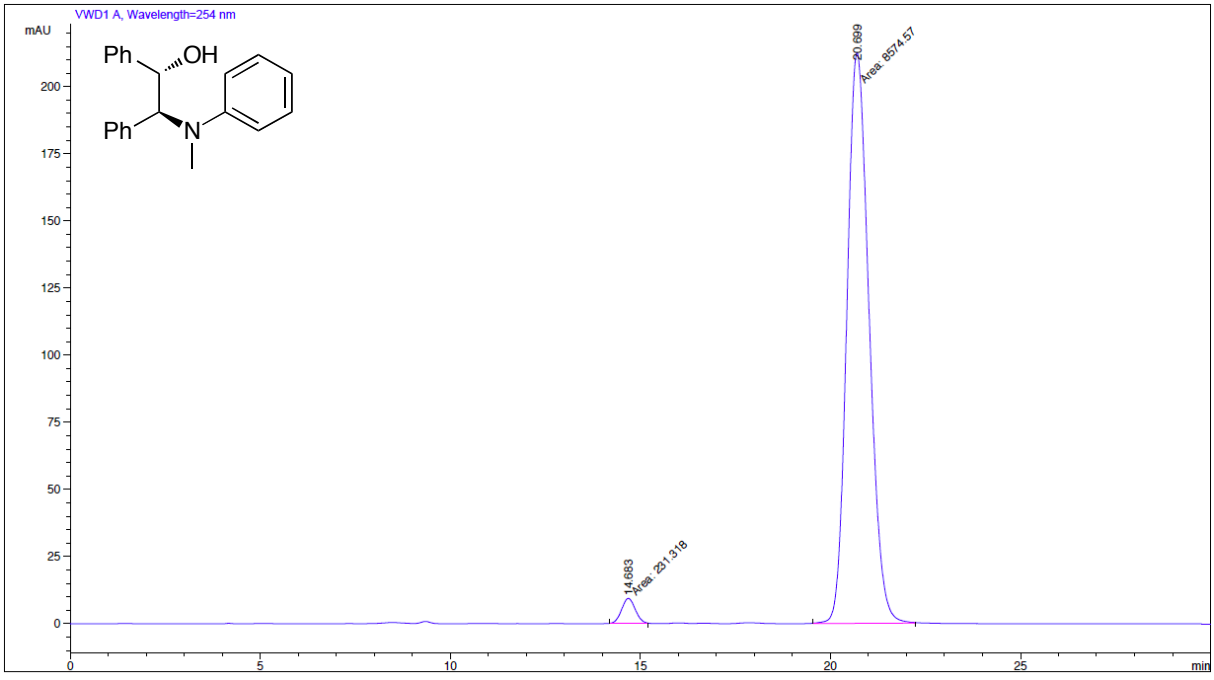
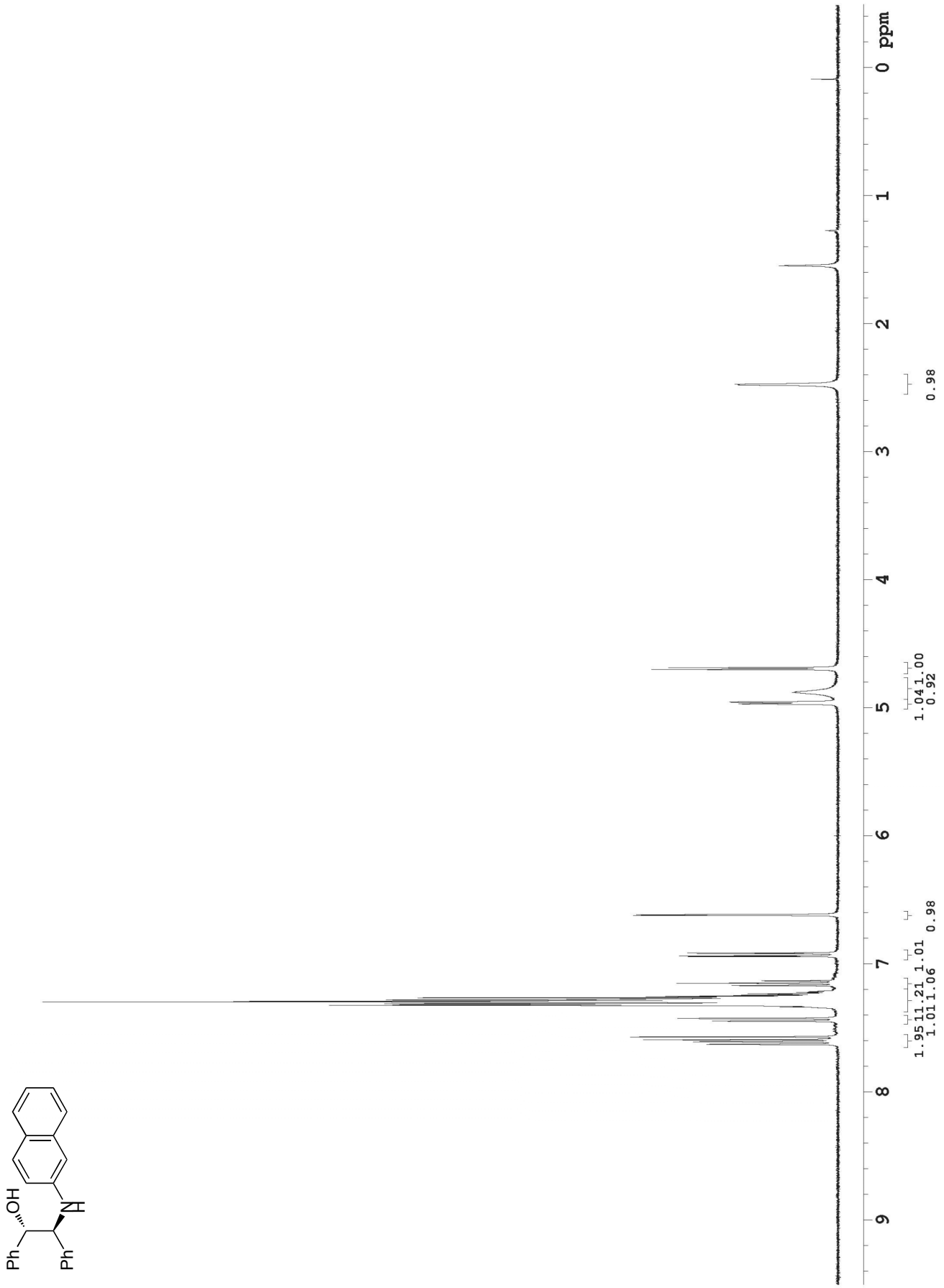
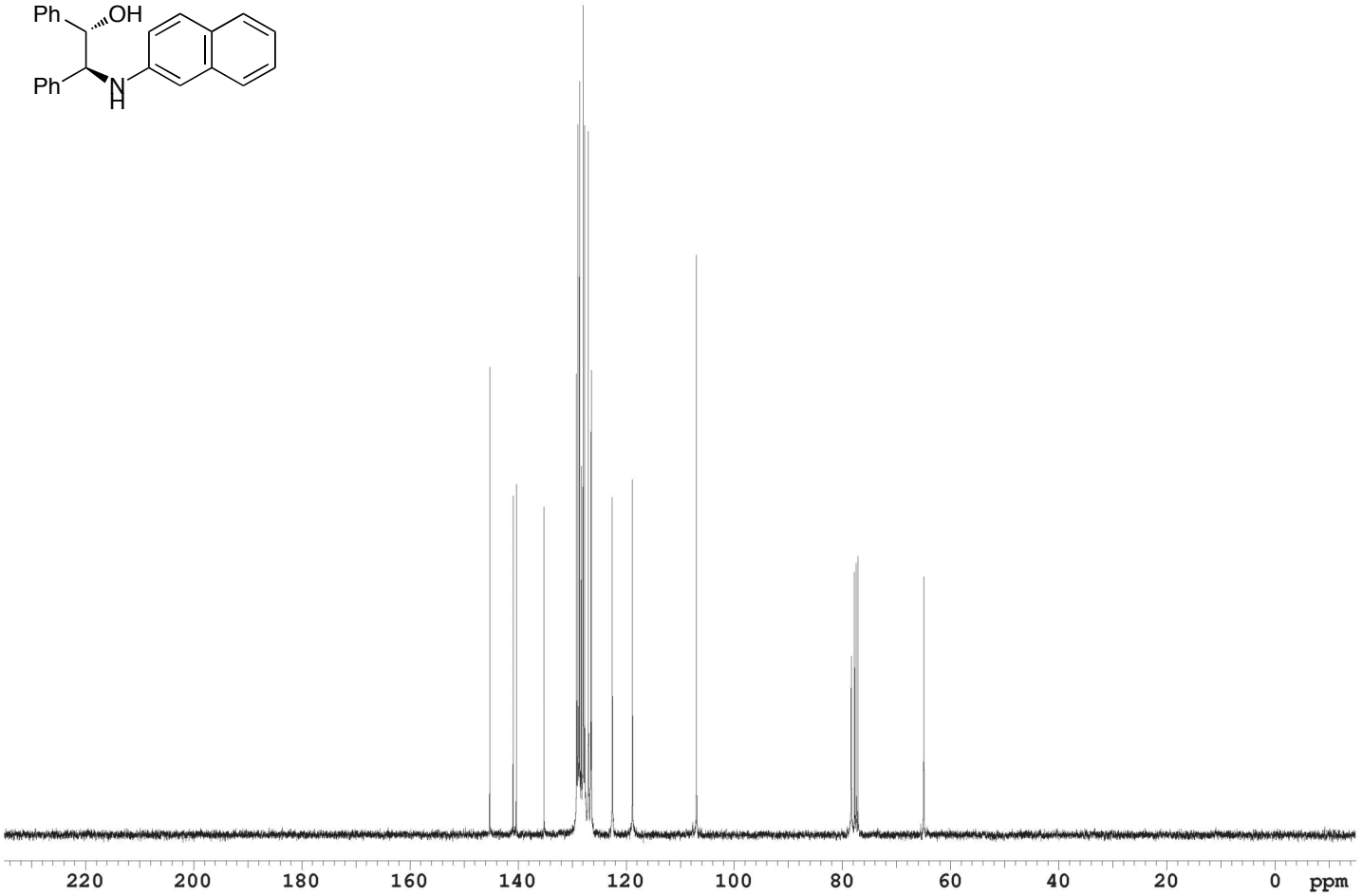


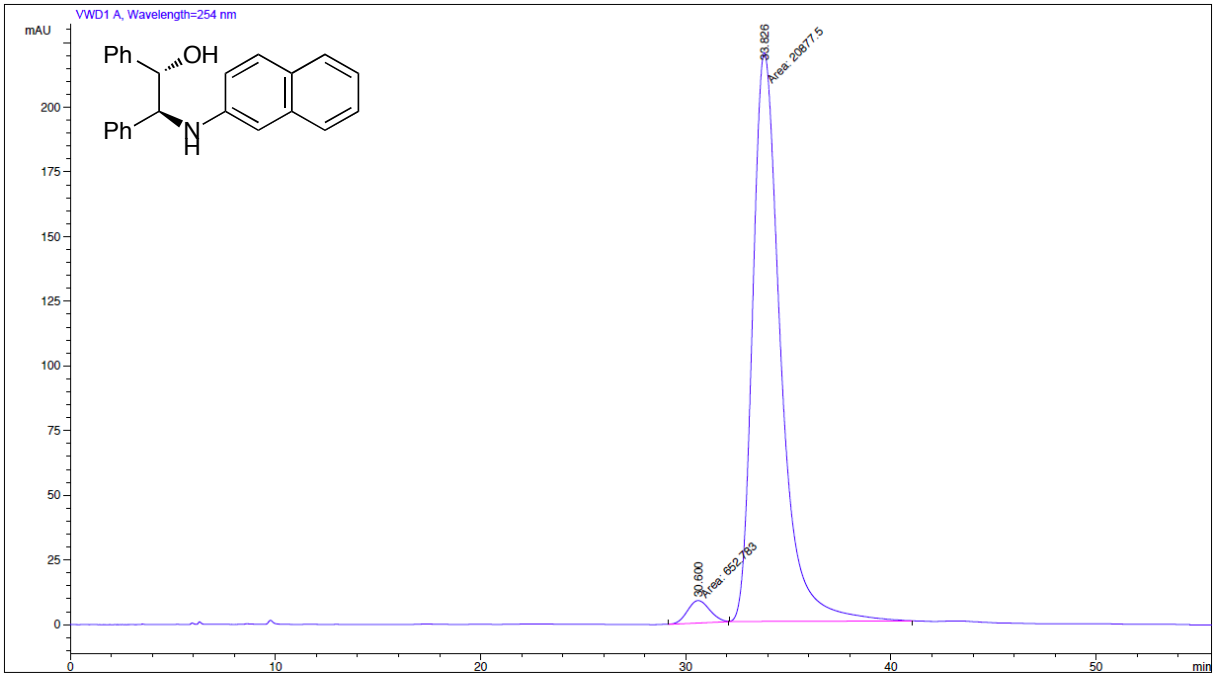


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.683	MM	0.4159	231.31760	9.27047	2.6269
2	20.699	MM	0.6723	8574.57324	212.56267	97.3731
Totals :				8805.89084	221.83314	

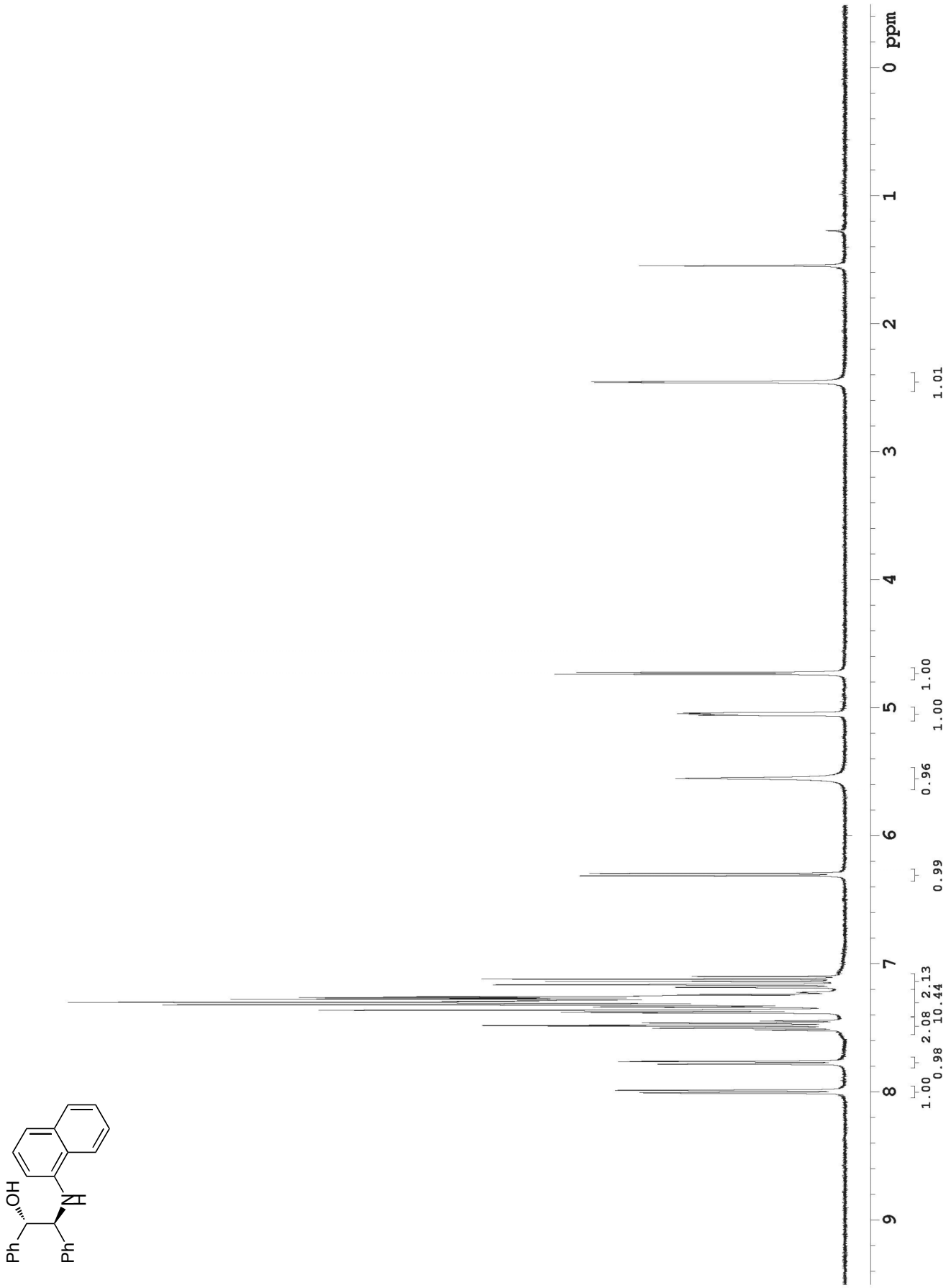

OH
N
H
Ph
Ph
ppm
0
1
2
3
4
5
6
7
8
9
0.98
1.04
1.00
0.92
1.95
11.21
1.01
1.01
1.06
0.98

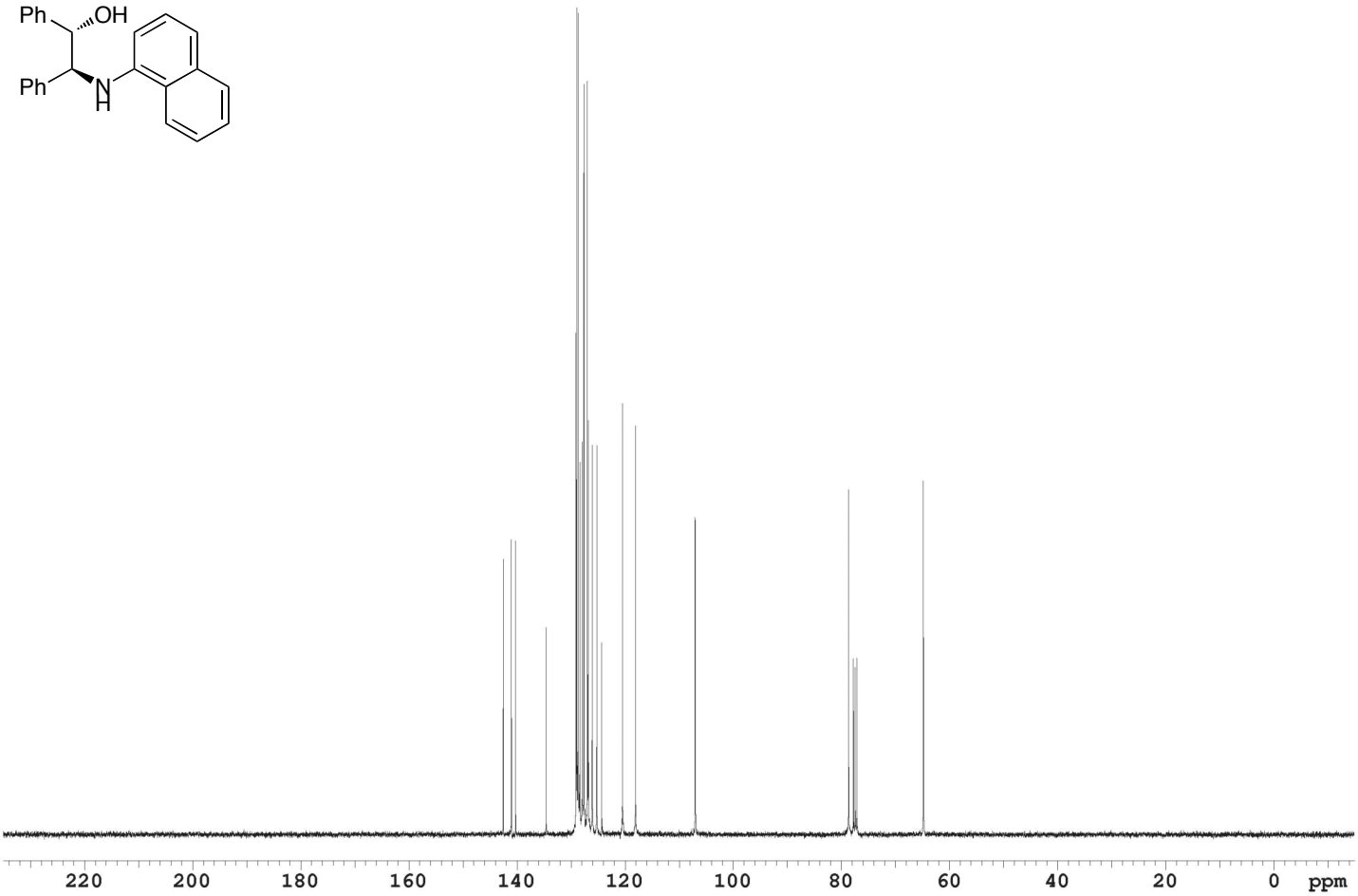


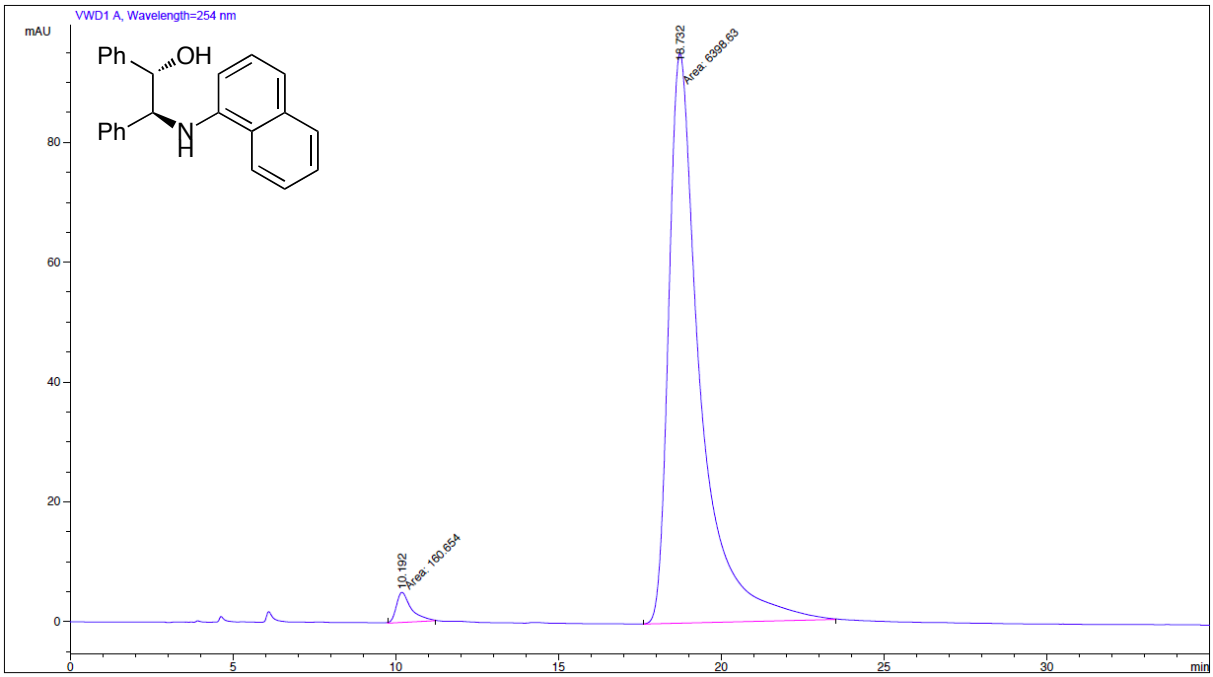


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.600	MM	1.2521	652.78339	8.68936	3.0319
2	33.826	MM	1.5828	2.08775e4	219.83984	96.9681
Totals :				2.15303e4	228.52921	

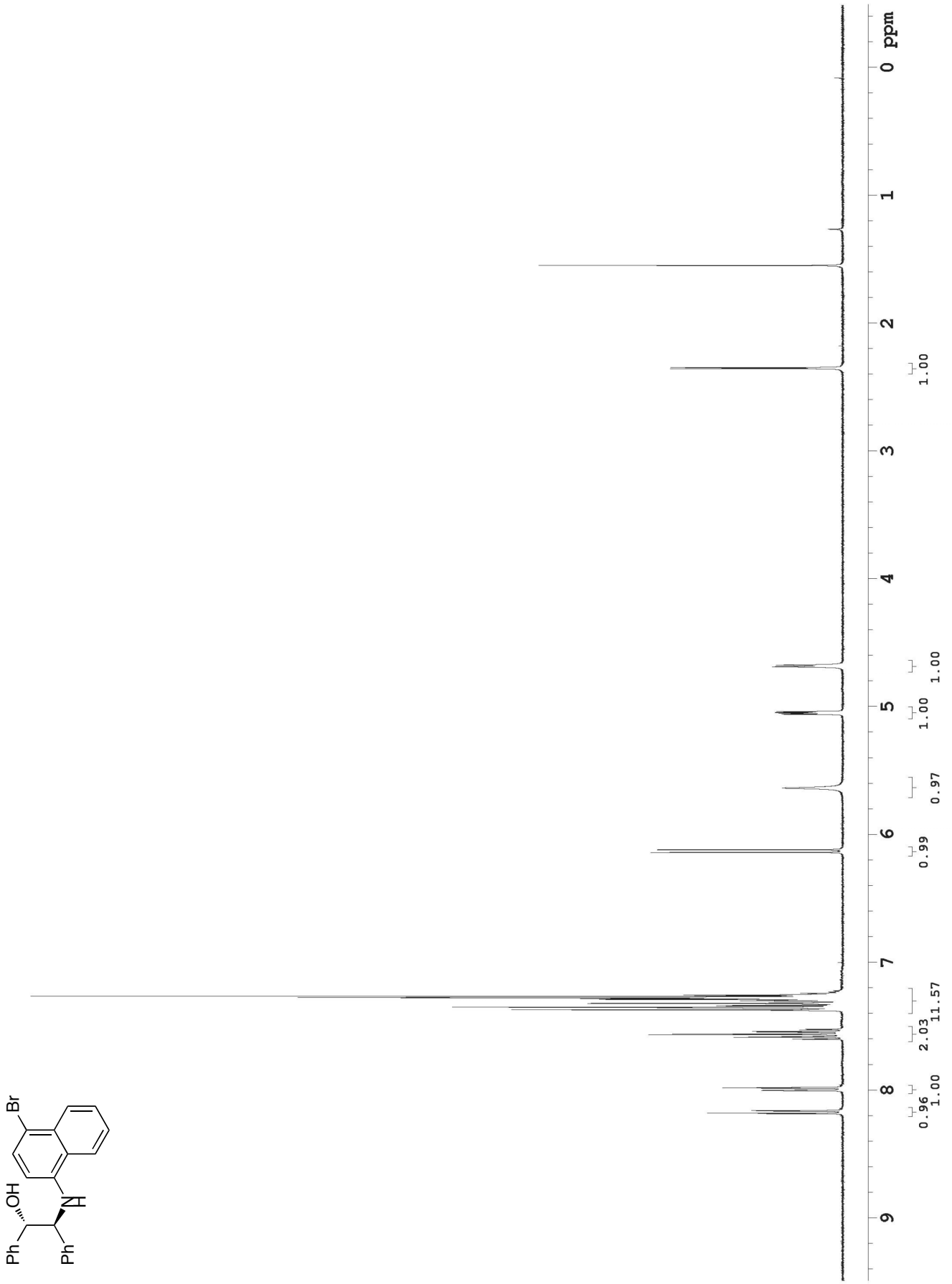

OH
N
H
Ph
Ph
ppm
0
1
2
3
4
5
6
7
8
9
1.01
1.00
1.00
0.96
0.99
1.00
0.98
2.08
10.44
2.13

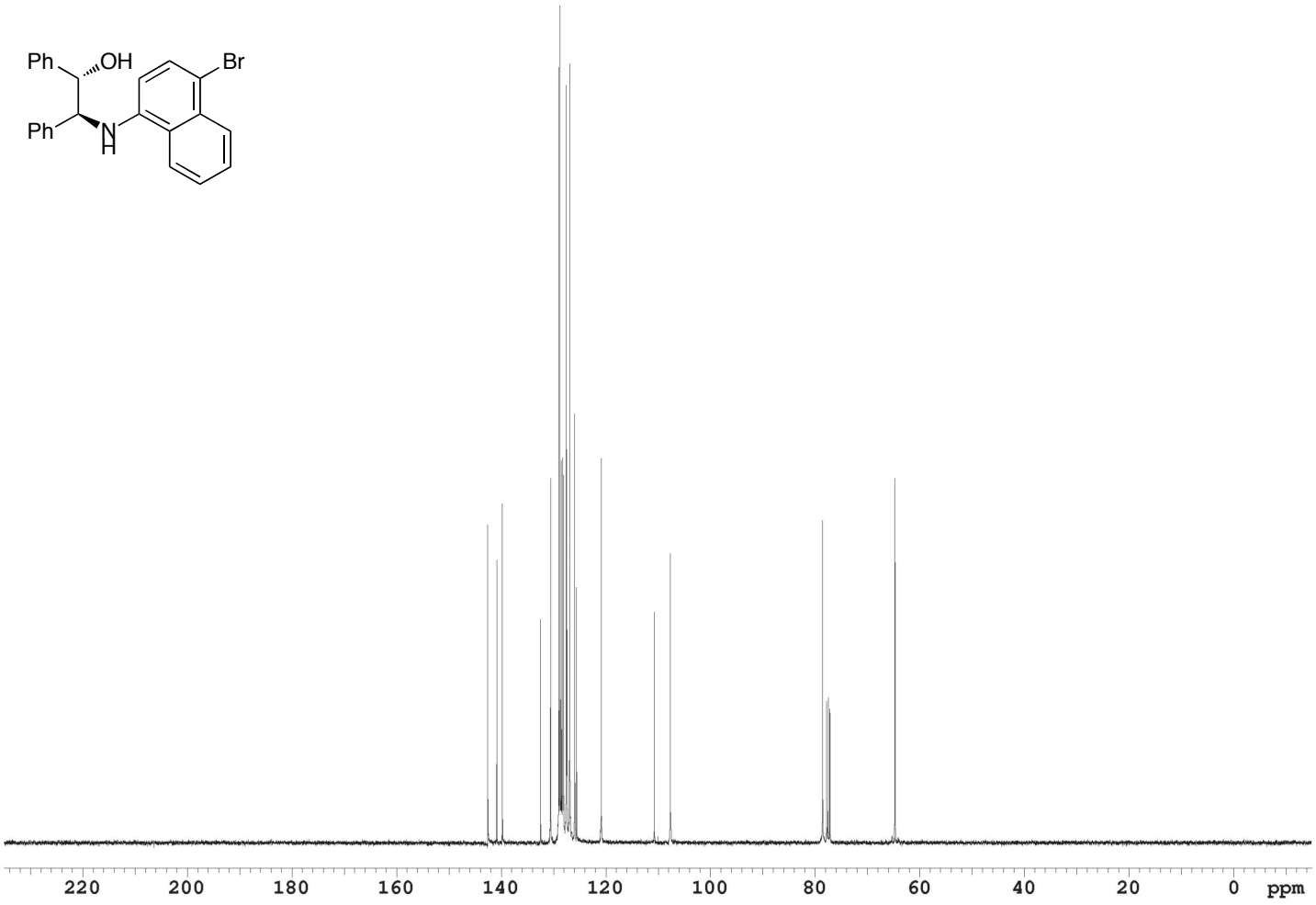


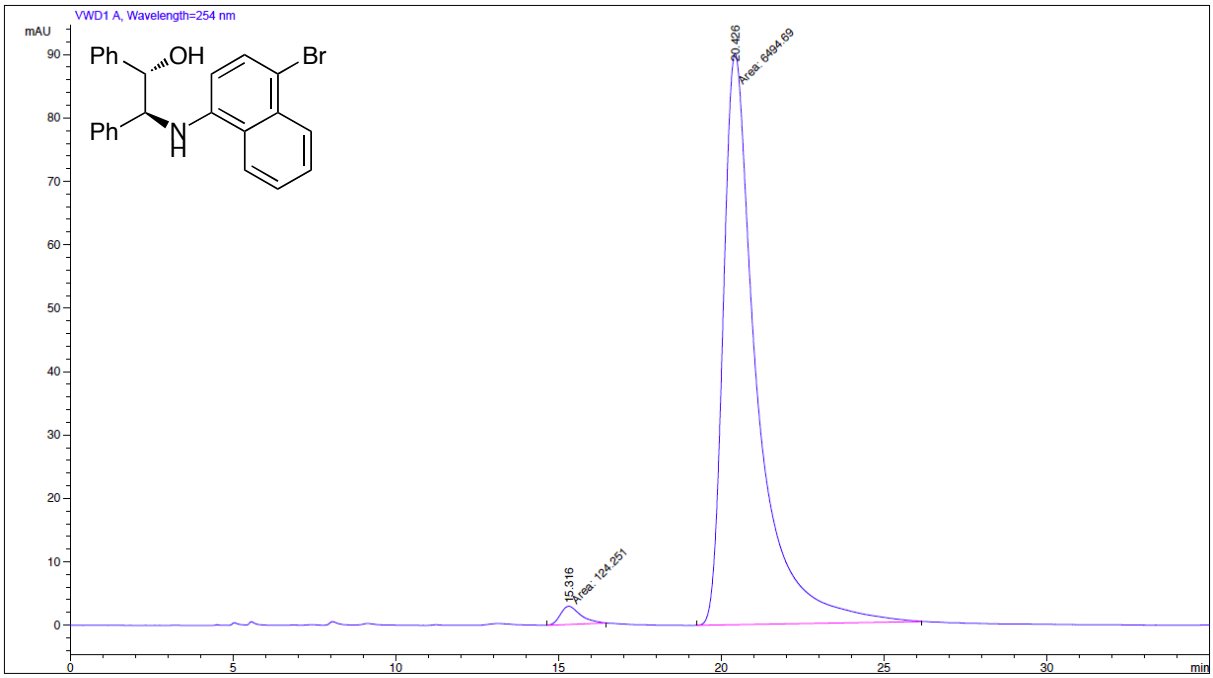


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.192	MM	0.5328	160.65446	5.02566	2.4493
2	18.732	MM	1.1214	6398.63086	95.10046	97.5507
Totals :				6559.28532	100.12612	

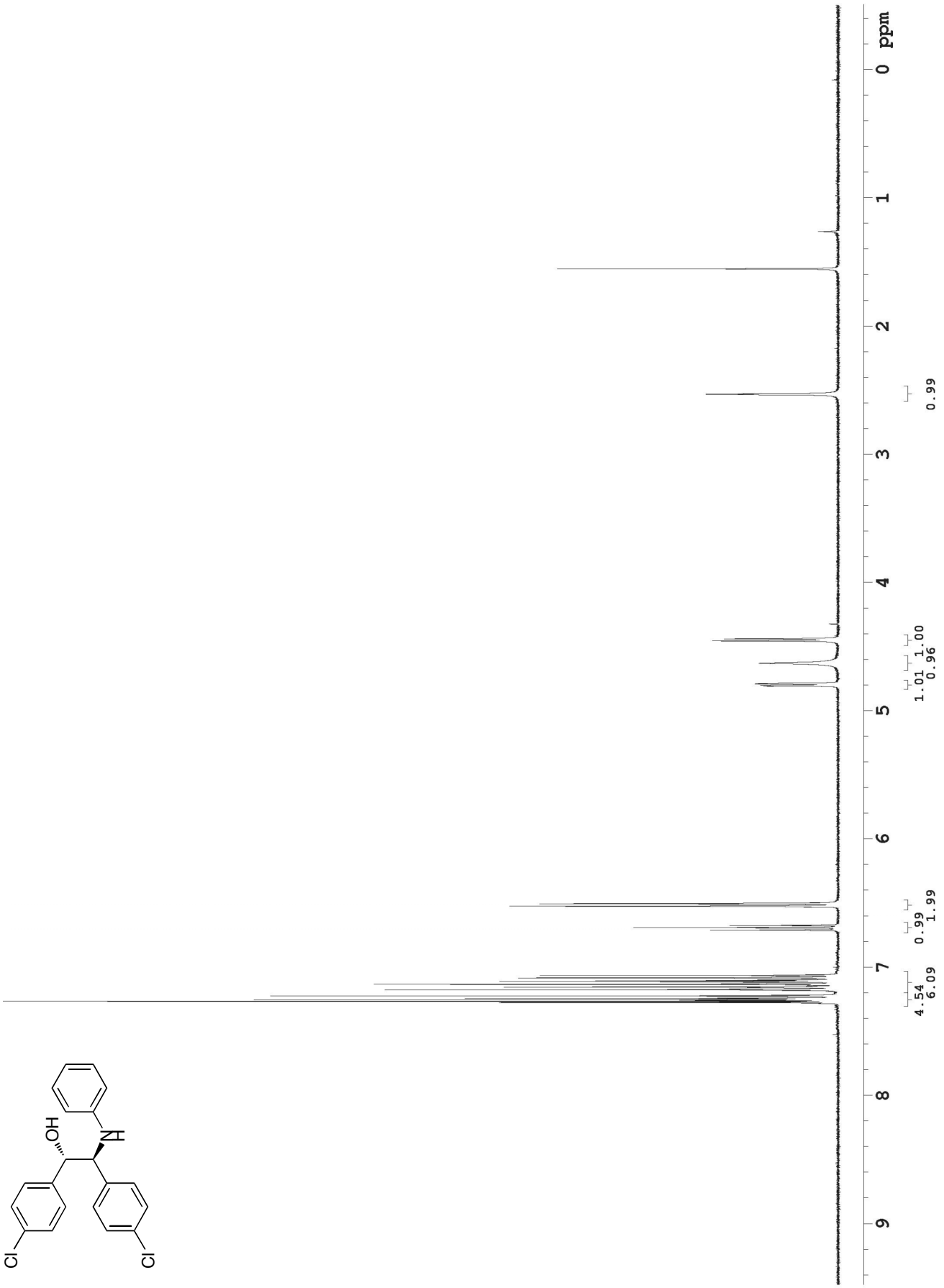

Br
OH
N
H
Ph
Ph
ppm
0
1
2
3
4
5
6
7
8
9
1.00
1.00
1.00
0.97
0.99
11.57
2.03
1.00
0.96

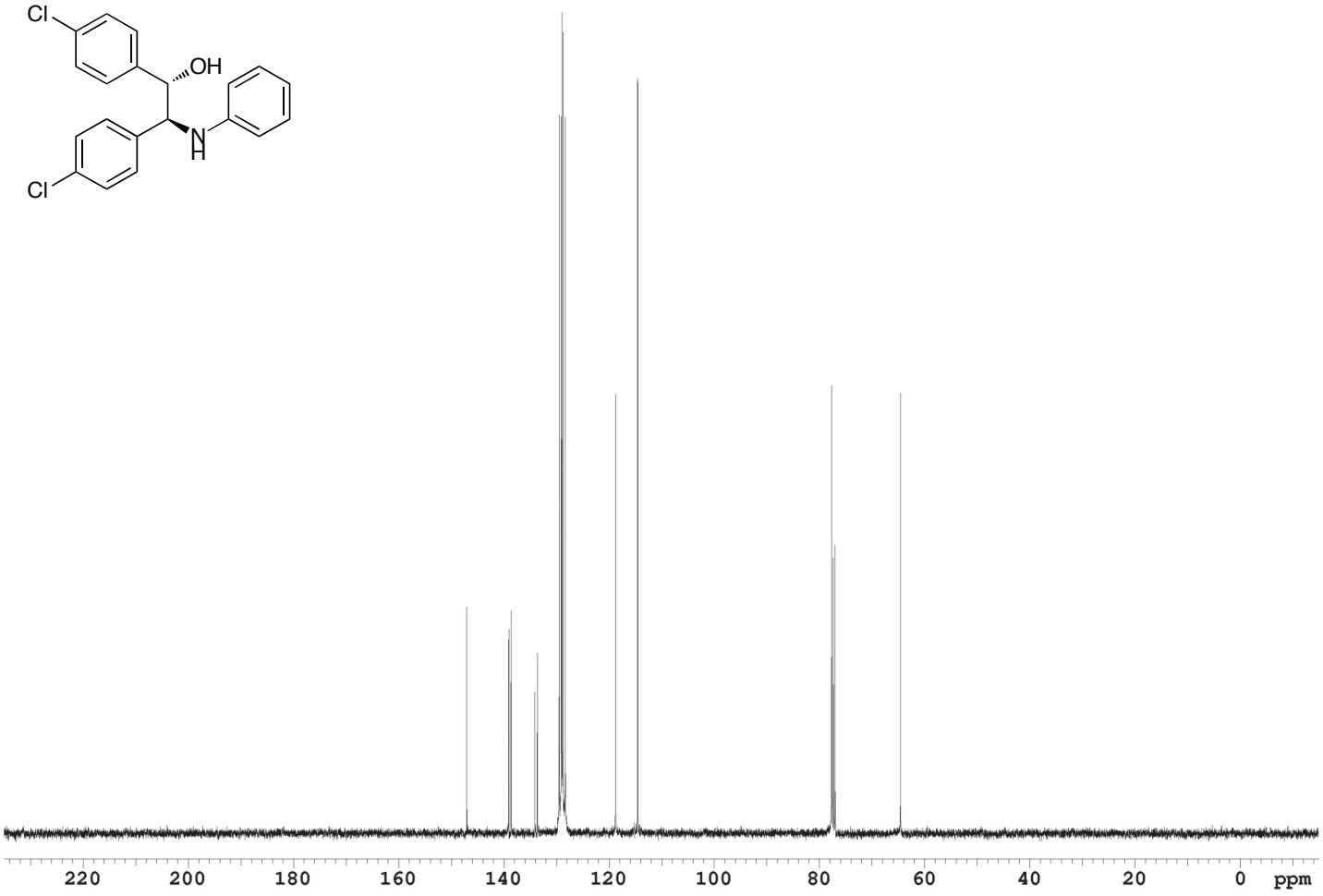


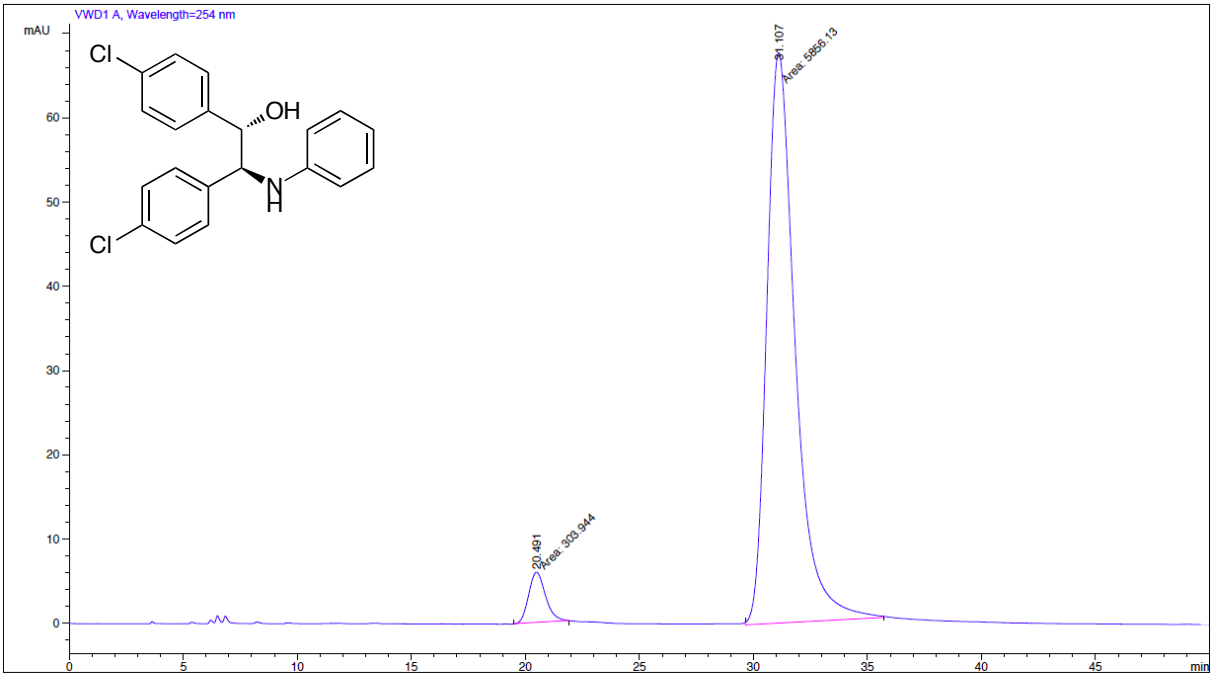


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.316	MM	0.7235	124.25077	2.86234	1.8772
2	20.426	MM	1.2019	6494.68506	90.05785	98.1228
Totals :				6618.93583	92.92019	

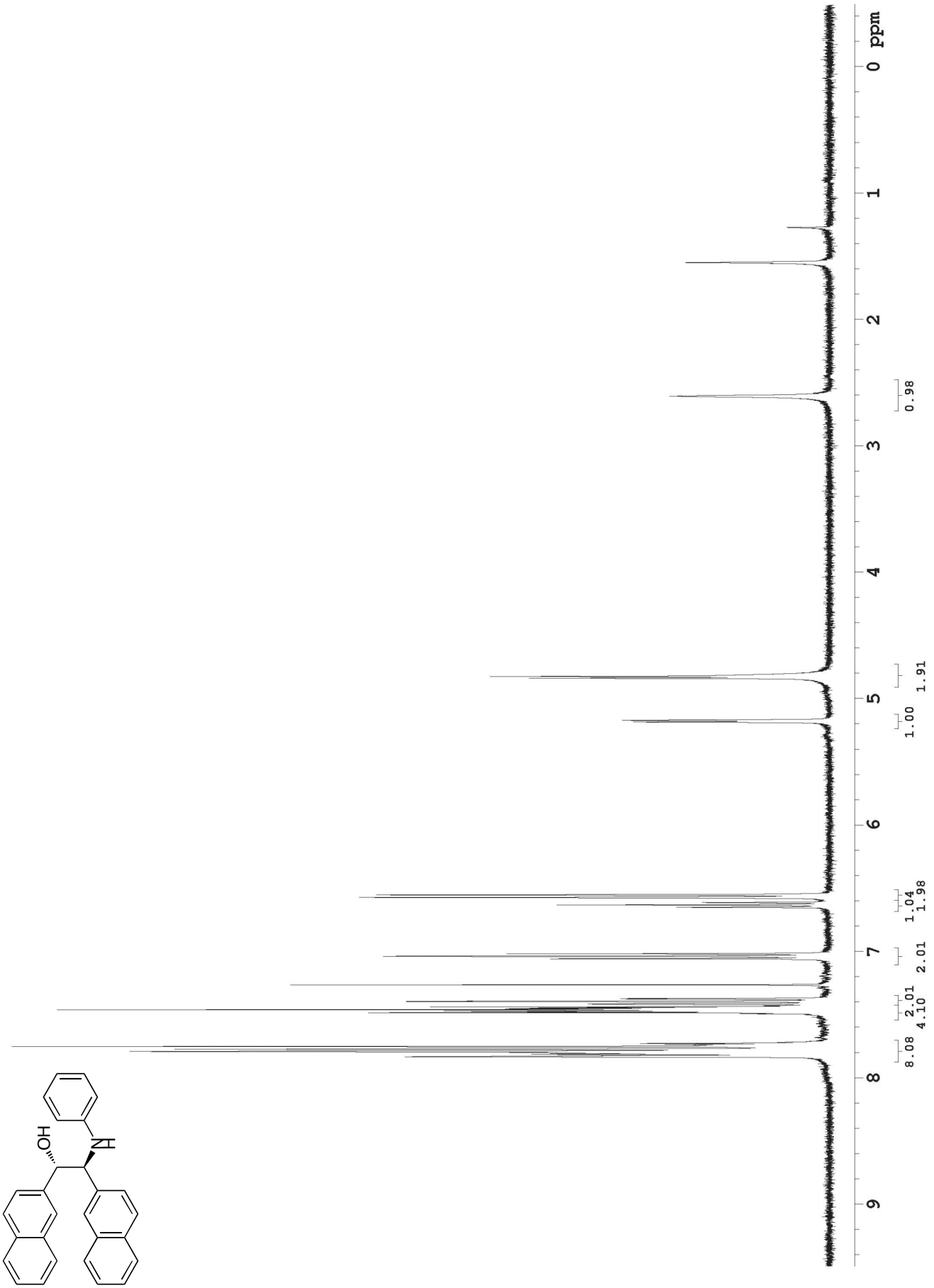

ppm
0
1
2
3
4
5
6
7
8
9
0.99
1.01
1.00
0.96
0.99
1.99
4.54
6.09
OH
H
N
Cl
Cl

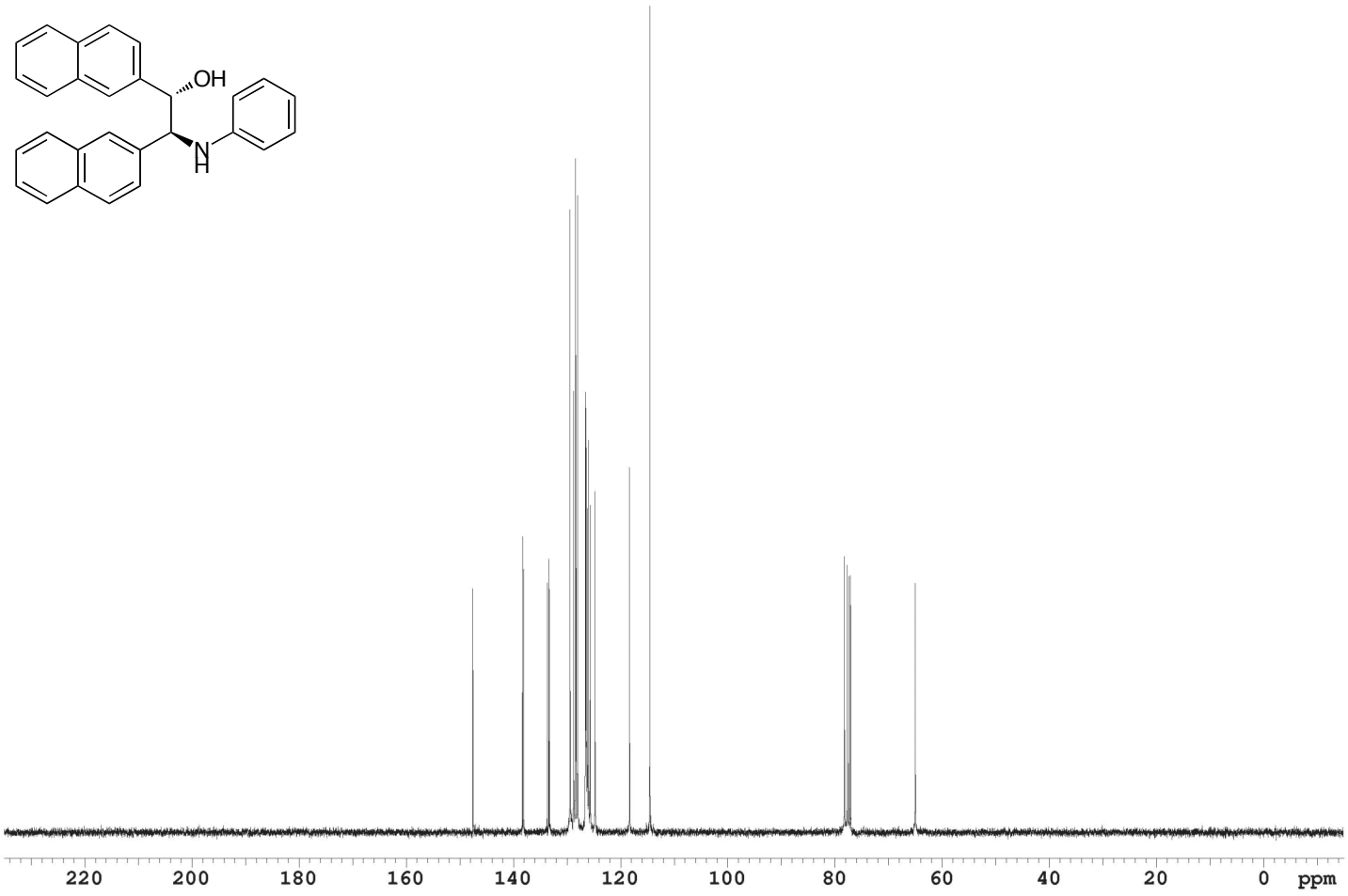


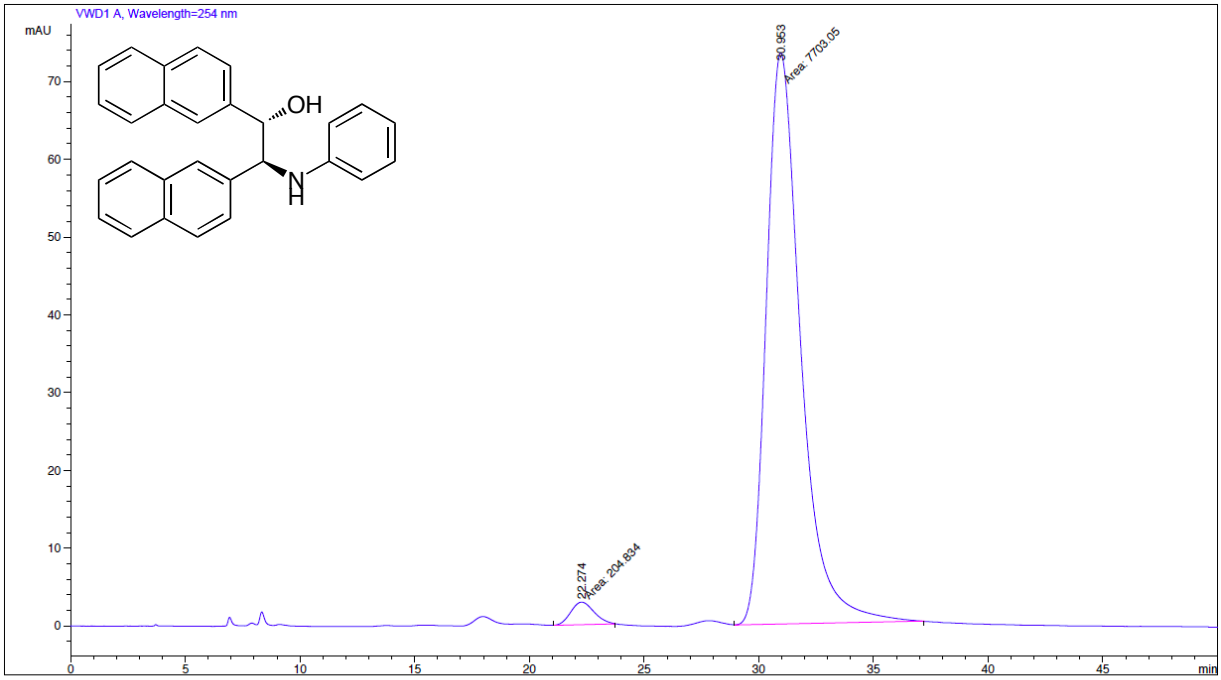


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.491	MM	0.8512	303.94446	5.95124	4.9341
2	31.107	MM	1.4417	5856.13232	67.70043	95.0659
Totals :				6160.07678	73.65168	


ppm
0
1
2
3
4
5
6
7
8
9
0.98
1.91
1.00
1.04
1.98
2.01
2.01
4.10
8.08
OH
H
N





Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.274	MM	1.1770	204.83405	2.90059	2.5902
2	30.953	MM	1.7483	7703.05469	73.43355	97.4098
Totals :				7907.88873	76.33414	