Highly Enantioselective Iron(II)-catalyzed Opening Reaction of Aromatic *meso*-Epoxides with Indoles

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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. Dichloromethane was distilled from CaH_2. Indoles were used as received and *meso*-epoxides were prepared by known procedures.[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 $CDCl_3$. Chemical shifts for ^{1}H NMR spectra (400 MHz) are recorded in parts per million from tetramethylsilane (TMS) with the solvent resonance as the internal standard (chloroform, δ = 7.27 ppm). 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. Chemical shifts for ^{13}C NMR spectra (100 MHz) are recorded in parts per million from tetramethylsilane using the solvent resonance as the internal standard (chloroform, δ = 77.23 ppm). All ^{13}C NMR spectra were obtained with complete proton decoupling. IR spectra were recorded on 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 ceric ammonium molybdate solution (CAM). Thermogravimetric analysis was performed on a Mettler Toledo® apparatus. Chiral High Performance Liquid Chromatography were performed on an Agilent 1100 Series LC system and data are reported as follows: column type, eluent, flow rate, wavelength, retention time t_R. To confirm the retention times of both enantiomers, all racemic 2-(indol-3-yl)ethanol derivatives were prepared and injected on chiral HPLC.

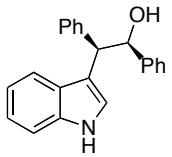
Caution: Perchlorate salts can be explosive and should be handled with care. Conversion to lower hydrates by unintentional dehydration may cause explosion. Use due caution in handling, as for all perchlorates.[5]

General Procedure for the *meso*-Epoxide Opening Reaction with Various Indoles

A mixture of $Fe(ClO_4)_2 \cdot 6H_2O$ (18.1 mg, 0.05 mmol), Bolm's ligand **1** (19.7 mg, 0.06 mmol) and 4Å MS (50 mg) in distilled CH_2Cl_2 (0.5 mL) was stirred at room temperature for 0.5 h. The indole derivative (0.6 mmol) and the epoxide (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), and was then directly poured onto silica-gel column and eluted with CH_2Cl_2 to give the desired product. The enantiomeric excess of the product was determined by chiral HPLC analysis.

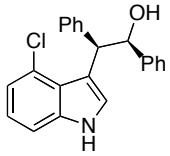
Characterization Data of the 2-(indol-3-yl)ethanol derivatives

(1*R*,2*R*)-2-(3-Indolyl)-1,2-diphenylethanol (Table 2, entry 1)[6,7]



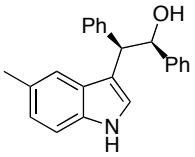
According to the general procedure with 98.1 mg *cis*-stilbene oxide and 70.3 mg indole, the product was isolated as a white solid (m.p. = 158–159 °C). Reaction time = 18 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.49 (d, J = 2.8 Hz, 1H), 4.60 (d, J = 7.9 Hz, 1H), 5.35 (dd, J = 2.8, 7.9 Hz, 1H), 7.02-7.26 (m, 12H), 7.34-7.37 (m, 2H), 7.45 (dd, J = 1.1, 8.0 Hz, 1H), 8.18 (brs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.3, 77.9, 111.4, 115.5, 119.6, 119.9, 122.6, 122.7, 126.6, 127.0, 127.6, 127.8, 128.2, 128.4, 128.9, 136.6, 142.0, 142.6. IR (neat): 3535, 3306, 3058, 3025, 2880, 1598, 1455, 1422, 1338, 1224, 1032, 1018, 987, 740. HRMS (ESI-TOF) calcd for $C_{22}H_{20}NO^+$ ($[M+H]^+$): 314.1539, found: 314.1540. $[\alpha]_D^{24}$ –77.5 (c = 1.0, $CHCl_3$, > 99% ee). HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 85/15, flow rate = 0.8 mL/min, λ = 220 nm) t_R = 36.9 min (major), t_R = 44.2 min (minor).

(1*R*,2*R*)-2-(4-Chloro-3-indolyl)-1,2-diphenylethanol (Table 2, entry 2)



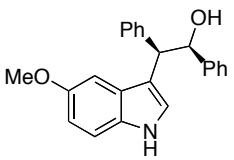
According to the general procedure with 98.1 mg *cis*-stilbene oxide and 72.2 μL 4-chloroindole, the product was isolated as a white solid (m.p. = 96–101 °C). Reaction time = 45 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.55 (brs, 1H), 5.22 (d, *J* = 8.0 Hz, 1H), 5.44 (d, *J* = 8.0 Hz, 1H), 6.98-7.29 (m, 13H), 7.48 (d, *J* = 2.2 Hz, 1H), 8.32 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 51.0, 78.7, 110.2, 115.8, 121.3, 122.9, 123.7, 124.5, 126.5, 126.6, 127.0, 127.5, 128.2, 128.3, 129.3, 137.8, 142.2, 142.3. IR (neat): 3515, 3354, 3242, 3029, 2916, 1618, 1489, 1453, 1423, 1338, 1266, 1182, 1073, 1033, 979, 936, 867, 817, 777 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{22}H_{19}ClNO^{+}$ ($[M+H]^{+}$): 348.1150, found: 348.1149. $[\alpha]_D^{24}$ –137.3 (*c* = 0.7, MeOH, 97% ee). HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 75/25, flow rate = 0.8 mL/min, λ = 220 nm) t_R = 9.7 min (major), t_R = 15.9 min (minor).

(1*R*,2*R*)-2-(5-Methyl-3-indolyl)-1,2-diphenylethanol (Table 2, entry 3)[7]



According to the general procedure with 98.1 mg *cis*-stilbene oxide and 78.7 mg 5-methylindole, the product was isolated as a white solid (m.p. = 185–186 °C). Reaction time = 19 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.38 (s, 3H), 2.53 (d, *J* = 2.7 Hz, 1H), 4.57 (d, *J* = 8,0 Hz, 1H), 5.33 (dd, *J* = 2.7, 8.0 Hz, 1H), 7.00 (dd, *J* = 1.4, 8.2 Hz, 1H), 7.07-7.25 (m, 12H), 7.31 (d, *J* = 2.5 Hz, 1H), 8.08 (brs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.8, 52.4, 111.0, 115.0, 119.2, 122.8, 124.3, 126.5, 127.1, 127.6, 128.8, 128.2, 128.4, 129.2, 134.9, 142.0, 142.6. IR (neat): 3523, 3280, 3024, 2881, 2852, 1600, 1485, 1428, 1309, 1226, 1111, 1022, 922, 796 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{23}H_{22}NO^{+}$ ($[M+H]^{+}$): 328.1696, found: 328.1699. $[\alpha]_D^{24}$ –39.8 (*c* = 1.0, $CHCl_3$, > 99% ee). HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 70/30, flow rate = 0.8 mL/min, λ = 220 nm) t_R = 18.4 min (minor), t_R = 23.2 min (major).

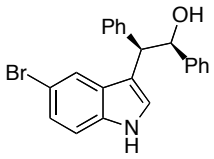
(1*R*,2*R*)-2-(5-Methoxy-3-indolyl)-1,2-diphenylethanol (Table 2, entry 4)[6,7]



According to the general procedure with 98.1 mg *cis*-stilbene oxide and 88.3 mg 5-methoxyindole, the product was isolated as a white solid (m.p. = 173–174 °C). Reaction time = 18 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.52 (d, *J* = 3.3 Hz, 1H), 3.70 (s, 3H), 4.56

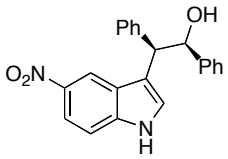
(d, J = 7.5 Hz, 1H), 5.35 (dd, J = 3.3, 7.5 Hz, 1H), 6.78 (d, J = 2.3, 1H), 6.83 (dd, J = 2.3, 7.8 Hz, 1H), 7.09-7.25 (m, 11H), 7.29 (d, J = 2.3Hz, 1H), 8.05 (brs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.3, 56.5, 77.6, 101.5, 112.0, 112.8, 115.1, 123.5, 126.6, 126.9, 127.6, 128.2, 128.2, 128.4, 128.8, 131.7, 142.1, 142.8, 154.2. IR (neat): 3516, 3311, 3130, 3062, 3025, 2878, 2854, 1623, 1583, 1484, 1436, 1264, 1211, 1164, 1055, 1033, 1022, 925, 809, 691 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{23}H_{22}NO_2^+$ ($[M+H]^+$): 344.1645, found: 344.1648. $[\alpha]_D^{24}$ –22.8 (c = 0.9, $CHCl_3$, > 99% ee). HPLC (Daicel Chiralpak® AD-H, hexane/i-PrOH = 70/30, flow rate = 0.8 mL/min, λ = 220 nm) t_R = 23.3 min (minor), t_R = 29.7 min (major).

(1*R*,2*R*)-2-(5-Bromo-3-indolyl)-1,2-diphenylethanol (Table 2, entry 5)[7]



According to the general procedure with 98.1 mg *cis*-stilbene oxide and 117.6 mg 5-bromoindole, the product was isolated as a white solid (m.p. = 129–131 °C). Reaction time = 19 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.37 (d, J = 3.2 Hz, 1H), 4.54 (d, J = 7.2 Hz, 1H), 5.32 (dd, J = 3.2, 7.2 Hz, 1H), 7.10-7.25 (m, 12H), 7.36 (d, J = 2.6 Hz, 1H), 7.49 (m, 1H), 8.16 (brs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 51.8, 112.8, 113.2, 115.2, 122.2, 124.0, 125.4, 126.8, 126.9, 127.8, 128.3, 128.5, 128.8, 129.6, 135.0, 141.6, 142.5. IR (neat): 3514, 3329, 3130, 3025, 2872, 1459, 1419, 1268, 1224, 1101, 1044, 1032, 887, 794, 695 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{22}H_{19}BrNO^+$ ($[M+H]^+$): 392.0645, found: 392.0648. $[\alpha]_D^{24}$ –17.5 (c = 1.0, $CHCl_3$, > 99% ee). HPLC (Daicel Chiralcel® OD-H, hexane/i-PrOH = 70/30, flow rate = 0.8 mL/min, λ = 220 nm) t_R = 14.7 min (minor), t_R = 22.6 min (major).

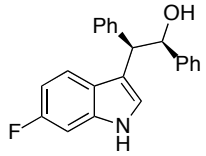
(1*R*,2*R*)-2-(5-Nitro-3-indolyl)-1,2-diphenylethanol (Table 2, entry 6)



According to the general procedure with 98.1 mg *cis*-stilbene oxide and 97.3 mg 5-nitroindole, the product was isolated as a yellow solid (m.p. = 68–73 °C). Reaction time = 45 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.25 (dd, J = 7.1, 8.9 Hz, 1H), 4.08 (dd, J = 7.1, 7.1 Hz, 1H), 5.00 (d, J = 8.9 Hz, 1H), 5.68 (s, 1H), 6.13 (dd, J = 1.4, 7.1 Hz, 1H), 6.62 (d, J = 8.7 Hz, 1H), 7.10-7.26 (m, 7H), 7.10-7.42 (m, 3H), 7.81-7.83 (m, 1H), 8.09 (dd, J = 2.3, 8.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 55.3, 61.7, 86.7, 94.4, 107.4, 120.9, 126.3, 126.8, 127.8, 128.2, 128.3, 128.6, 129.4, 130.7, 139.0, 140.3, 153.8. IR (neat): 3364, 3030, 2917, 1612, 1492, 1452, 1314, 1263, 1167, 1127, 1072, 1033, 1010, 937, 908, 844, 751 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{22}H_{19}N_2O_3^+$ ($[M+H]^+$): 359.1390, found: 359.1391. $[\alpha]_D^{24}$ –168.8 (c = 0.5, $CHCl_3$, 99% ee). HPLC (Daicel Chiralcel® OD-

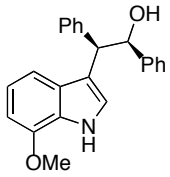
H, hexane/*i*-PrOH = 80/20, flow rate = 0.8 mL/min, λ = 220 nm) t_R = 27.6 min (minor), t_R = 33.1 min (major).

(1*R*,2*R*)-2-(6-Fluoro-3-indolyl)-1,2-diphenylethanol (Table 2, entry 7)



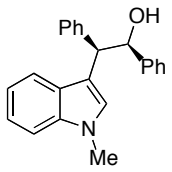
According to the general procedure with 98.1 mg *cis*-stilbene oxide and 81.1 mg 6-fluoroindole, the product was isolated as a white solid (m.p. = 160–162 °C). Reaction time = 20 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.43 (d, *J* = 2.9 Hz, 1H), 4.56 (dd, *J* = 0.7, 7.7 Hz, 1H), 5.32 (dd, *J* = 2.9, 7.7 Hz, 1H), 6.77 (ddd, *J* = 2.3, 7.7, 9.3 Hz, 1H), 7,01 (dd, *J* = 2.3, 9.3 Hz, 1H), 7.08-7.24 (m, 10H), 7.28 (dd, *J* = 5.3, 8.7 Hz, 1H), 7.33 (d, *J* = 2.4 Hz, 1H), 8.13 (brs, 1H). ^{13}C NMR ($CDCl_3$ + 1 drop DMSO-d_6, 100 MHz): δ = 52.1, 77.7, 97.6 (d, *J* = 25.5 Hz), 107.9 (d, *J* = 24.5 Hz), 115.3, 120.1 (d, *J* = 10.0 Hz), 123.3, 124.5, 126.4, 127.0, 127.4, 128.0, 128.2, 128.9, 136.5 (d, *J* = 12.3 Hz), 142.2, 143.1, 160.0 (d, *J* = 237.0 Hz). IR (neat): 3598, 3424, 3345, 3026, 2869, 1625, 1493, 1452, 1345, 1304, 1241, 1218, 1119, 1033, 1022, 947, 760, 695 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{22}H_{19}FNO^+$ ([M+H]$^+$): 332.1445, found: 332.1441. $[\alpha]_D^{24}$ –70.8 (*c* = 1.1, $CHCl_3$, 98% ee). HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 80/20, flow rate = 0.8 mL/min, λ = 220 nm) t_R = 14.5 min (major), t_R = 19.3 min (minor).

(1*R*,2*R*)-2-(7-Methoxy-3-indolyl)-1,2-diphenylethanol (Table 2, entry 8)



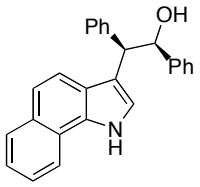
According to the general procedure with 98.1 mg *cis*-stilbene oxide and 78.4 μL 7-methoxyindole, the product was isolated as a white solid (m.p. = 125–128 °C). Reaction time = 41 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.51 (d, *J* = 2.8 Hz, 1H), 3.94 (s, 3H), 4.57 (d, *J* = 8.0 Hz, 1H), 5.35 (dd, *J* = 2.8, 8.0 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 7.06-7.25 (m, 11H), 7.33 (dd, *J* = 0.7, 2.9 Hz, 1H), 8.39 (brs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.5, 55.6, 77.9, 102.3, 112.4, 115.9, 120.3, 122.3, 126.5, 127.1, 127.2, 127.6, 128.2, 128.3, 128.9, 129.1, 142.0, 142.7, 146.3. IR (neat): 3491, 3266, 3059, 3025, 3001, 2887, 2836, 1625, 1577, 1499, 1451, 1421, 1371, 1260, 1235, 1109, 1052, 1039, 1025, 775, 694 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{23}H_{22}NO_2^+$ ([M+H]$^+$): 344.1645, found: 344.1649. $[\alpha]_D^{24}$ –70.7 (*c* = 1.0, $CHCl_3$, 98% ee). HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 60/40, flow rate = 0.8 mL/min, λ = 220 nm) t_R = 26.1 min (major), t_R = 36.2 min (minor).

(1*R*,2*R*)-2-(1-Methyl-3-indolyl)-1,2-diphenylethanol (Table 2, entry 9)[6]



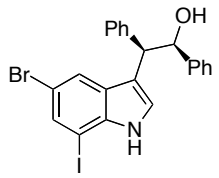
According to the general procedure with 98.1 mg *cis*-stilbene oxide and 74.5 μL *N*-methylindole, the product was isolated as a white solid (m.p. = 50–53 °C). Reaction time = 19 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.52 (d, *J* = 2.7 Hz, 1H), 3.81 (s, 3H), 4.58 (d, *J* = 8.2 Hz, 1H), 5.33 (dd, *J* =2.7, 8.2 Hz, 1H), 7.02-7.26 (m, 13H), 7.30 (dt, *J* = 1.0, 8.2 Hz, 1H), 7.46 (dt, *J* = 1.0, 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 33.1, 52.5, 77.9, 109.5, 114.0, 119.4, 119.8, 122.2, 126.5, 127.1, 127.4, 127.6, 128.2, 128.3, 128.4, 128.8, 137.4, 142.2, 142.7. IR (neat): 3541, 3408, 3058, 3027, 2883, 1614, 1601, 1584, 1543, 1473, 1423, 1373, 1329, 1235, 1189, 1154, 1041, 1030, 1013, 915, 800 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{23}H_{22}NO^+$ ($[M+H]^+$): 328.1696, found: 328.1696. $[\alpha]_D^{24}$ –66.5 (*c* = 1.0, $CHCl_3$, 96% ee). HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 80/20, flow rate = 0.8 mL/min, λ = 254 nm) t_R = 19.7 min (minor), t_R = 34.4 min (major).

(1*R*,2*R*)-2-(3-Benzo[*g*]indolyl)-1,2-diphenylethanol (Table 2, entry 10)



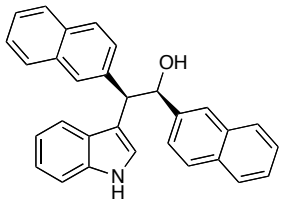
According to the general procedure with 98.1 mg *cis*-stilbene oxide and 100.3 mg benzo[*g*]indole, the product was isolated as a white solid (m.p. = 235–238 °C). Reaction time = 1 h. ^{1}H NMR ($CDCl_3$ + 1 drop DMSO-d_6, 400 MHz): δ = 2.25 (s, 1H), 4.60 (d, *J* = 8.0 Hz, 1H), 5.30 (dd, *J* = 2.9, 8.0 Hz, 1H), 6.99-7.20 (m, 10H), 7.30-7.46 (m, 5H), 7.80 (d, *J* = 8.1 Hz, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 10.38 (s, 1H). ^{13}C NMR ($CDCl_3$ + 1 drop DMSO-d_6, 100 MHz): δ = 52.1, 77.7, 116.7, 119.5, 119.7, 120.7, 121.3, 122.4, 123.5, 123.7, 125.2, 126.1, 127.0, 127.1, 127.9, 128.1, 128.5, 128.9, 130.3, 131.3, 142.7, 143.6. IR (neat): 3535, 3310, 3062, 3028, 2872, 1600, 1524, 1489, 1477, 1391, 1293, 1271, 1217, 1105, 1072, 1038, 1027, 953, 804, 749 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{26}H_{22}NO^+$ ($[M+H]^+$): 364.1696, found: 364.1699. $[\alpha]_D^{24}$ –152.4 (*c* = 0.5, MeOH, > 99% ee). HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 60/40, flow rate = 0.8 mL/min, λ = 220 nm) t_R = 41.9 min (minor), t_R = 53.8 min (major).

(1*R*,2*R*)-2-(5-Bromo-7-iodo-3-indolyl)-1,2-diphenylethanol (Table 2, entry 11)



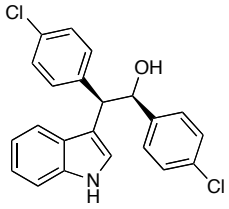
According to the general procedure with 98.1 mg *cis*-stilbene oxide and 193.2 mg 5-bromo-7-iodoindole, the product was isolated as a white solid (m.p. = 151–153 °C). Reaction time = 20 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.30 (d, *J* = 3.0 Hz, 1H), 4.51 (d, *J* = 6.9 Hz, 1H), 5.32 (dd, *J* = 3.0, 6.9 Hz, 1H), 7.12-7.25 (m, 10H), 7.41 (dd, *J* = 1.5, 2.5 Hz, 1H), 7.44 (d, *J* = 2.5 Hz, 1H), 7.59 (d, *J* = 1.5 Hz, 1H), 8.21 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 51.8, 77.7, 113.1, 116.7, 122.4, 124.6, 126.7, 127.8, 128.3, 128.6, 128.7, 129. 0, 132.7, 137.1, 141.4, 142.5. IR (neat): 3547, 3440, 3061, 3027, 1552, 1538, 1489, 1460, 1454, 1413, 1320, 1286, 1189, 1105, 1071, 1037, 985, 873, 866 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{22}H_{18}BrINO^{+}$ ($[M+H]^{+}$): 517.9611, found: 517.9615. $[\alpha]_D^{24}$ –70.2 (*c* = 1.0, MeOH, > 99% ee). HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 80/20, flow rate = 0.8 mL/min, λ = 220 nm) t_R = 16.8 min (major), t_R = 35.5 min (minor).

(1*R*,2*R*)-2-(1*H*-Indol-3-yl)-1,2-di(naphthalen-2-yl)ethanol (Scheme 1)[8]



According to the general procedure with 55.0 mg *cis*-2,3-di(naphthalen-2-yl)oxirane and 25.7 mg indole, the product was isolated as a white solid (m.p. = 198–201 °C). Reaction time = 24 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.65 (d, *J* = 2.8 Hz, 1H), 4.92 (d, *J* = 7.5 Hz, 1H), 5.65 (dd, *J* = 2.8, 7.5 Hz, 1H), 6.98-7.02 (m, 1H), 7.14-7.18 (m, 1H), 7.33-7.49 (m, 9H), 7.61-7.76 (m, 8H), 8.16 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 51.7, 77.5, 111.1, 115.0, 119.4, 119.7, 122.4, 122.8, 124.7, 125.4, 125.6, 125.7, 125.8, 125.8, 127.1, 127.2, 127.5, 127.5, 127.6, 127.8, 128.0, 128.0, 132.2, 132.8, 133.1, 133.3, 136.3, 136.6, 139.3, 139.9. IR (neat): 3540, 3415, 3051, 3029, 2887, 1679, 1618, 1455, 1395, 1242, 1222, 1069, 1034, 929, 812, 740, 689 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{30}H_{24}NO^{+}$ ($[M+H]^{+}$): 414.1852, found: 414.1835. $[\alpha]_D^{24}$ –159.7 (*c* = 1.0, MeOH, 96% ee). HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 35.2 min (minor), t_R = 46.8 min (major).

(1*R*,2*R*)-1,2-bis(4-Chlorophenyl)-2-(1*H*-indol-3-yl)ethanol (Scheme 1)

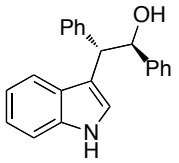


According to the general procedure with 60.0 mg *cis*-2,3-bis(4-chlorophenyl)oxirane and 31.8 mg indole, the product was isolated as a white solid (m.p. = 149–150 °C). Reaction time = 30 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.52 (d, *J* = 2.7 Hz, 1H), 4.50 (d, *J* = 8.1 Hz, 1H), 5.27 (dd, *J* = 2.7, 8.1 Hz, 1H), 7.04-7.08 (m, 3H), 7.10-7.16 (m, 4H), 7.18-7.22 (m, 3H), 7.32-7.33 (m, 1H), 7.37 (dt, *J* = 0.8, 8.0 Hz, 1H), 7.42 (dq, *J* = 0.8, 8.0 Hz, 1H), 8.20 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 51.6, 111.3, 114.6, 119.2, 119.9, 122.2, 122.6, 127.2, 128.1, 128.2, 128.4, 128.5, 129.9, 132.2, 133.2, 136.3, 139.8, 140.5. IR (neat): 3413, 3051, 2889, 1899, 1618, 1488, 1410, 1246, 1168, 1088, 1034, 1012, 855, 821, 741 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{22}H_{17}Cl_2NO^{+}$ ($[M^*]^{+}$): 382.0715, found: 382.0711. $[\alpha]_D^{24}$ –144.2 (*c* = 0.5, MeOH, 99% ee). HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 80/20, flow rate = 0.8 mL/min, λ = 220 nm) t_R = 22.6 min (minor), t_R = 26.7 min (major).

Procedure for the Kinetic Resolution of *trans*-Stilbene Oxide with Indole

A mixture of $Fe(ClO_4)_2{\cdot}6H_2O$ (18.1 mg, 0.05 mmol), Bolm's ligand **1** (19.7 mg, 0.06 mmol) and 4Å MS (50 mg) in distilled CH_2Cl_2 (0.5 mL) was stirred at room temperature for 0.5 h and then placed at the desired temperature (–20 °C). The indole (0.3 mmol) and the epoxide (0.6 mmol) were then subsequently added to the mixture. The reaction mixture was stirred at –20 °C for 42 hours and was then directly poured onto silica-gel column and eluted with CH_2Cl_2 to give the desired products. The unreacted *trans*-stilbene oxide was purified on silica-gel column and eluted with a mixture of hexanes and AcOEt (99:1). 85% of the unreacted epoxide was isolated and the enantiomeric ratio was determined by chiral HPLC analysis.

(1*R*,2*S*)-2-(1*H*-Indol-3-yl)-1,2-diphenylethanol (Scheme 2)[9]



According to the procedure for the kinetic resolution with 35.1 mg racemic *trans*-stilbene oxide and 117.7 mg indole at –20 °C, the product was isolated as a white solid (m.p. = 131–133 °C). Reaction time = 42 h. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.97 (brs, 1H), 4.63 (d, *J* = 6.6 Hz, 1H), 5.49 (d, *J* = 6.6 Hz, 1H), 6.97-7.01 (m, 1H), 7.11-7.15 (m, 1H), 7.20-7.34 (m, 13H), 7.98 (brs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 50.9, 76.6, 110.9, 116.8, 119.2, 119.4, 122.0, 122.5, 126.6, 126.8, 127.0, 127.4, 128.0, 128.3, 128.4, 135.9, 140.2,

142.8. IR (neat): 3530, 3306, 3025, 2888, 1590, 1460, 1422, 1337, 1324, 1132, 1088, 1018, 987, 740, 667. HRMS (ESI-TOF) calcd for $C_{22}H_{20}NO^+$ ($[M+H]^+$): 314.1539, found: 314.1517. $[\alpha]_D^{24}$ +0.265 (*c* = 1.0, $CHCl_3$, 54% ee). HPLC (Daicel Chiralpak® AD-H, hexane/*i*-PrOH = 70/30, flow rate = 0.7 mL/min, λ = 220 nm) t_R = 20.6 min (minor), t_R = 25.6 min (major).

The unreacted *trans*-stilbene oxide was purified on silica-gel column and eluted with a mixture of hexanes and AcOEt (99:1). 85% (61.2 mg) of the unreacted epoxide was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.41-7.33 (m, 10H), 3.87 (s, 2H). HPLC (Daicel Chiralcel® OD-H, hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, λ = 254 nm) t_R = 12.8 min (minor), t_R = 19.3 min (major).

Crystallization of $[FeBr_2 \cdot 1] \cdot (H_2O) \cdot 2THF$ Complex

Crystallization of **$[FeBr_2 \cdot 1] \cdot (H_2O) \cdot 2THF$** was carried out as follows: A mixture of $FeBr_2$ (5.0 mg, 23.2 μmol) and Bolm's ligand **1** (7.6 mg, 23.2 μmol) was dissolved in THF (0.25 mL). This solution was stirred at room temperature for 30 min and then cooled down to –18 °C. Crystals were obtained after 48 h.
CCDC 864123 ($[\mathbf{1} \cdot Fe \cdot 2THF \cdot H_2O]^{2+} \cdot 2Br^-$) 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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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 $Fe(OTf)_2 \cdot H_2O$ quantitatively. Thermogravimetric analysis confirmed the presence of one hydration water molecule. (M. Seredyuk, A. B. Gaspar, M. C. Muñoz, M. Verdaguer, F. Villain, P. Gütlich, *Eur. J. Inorg. Chem.* 2007, 4481.)
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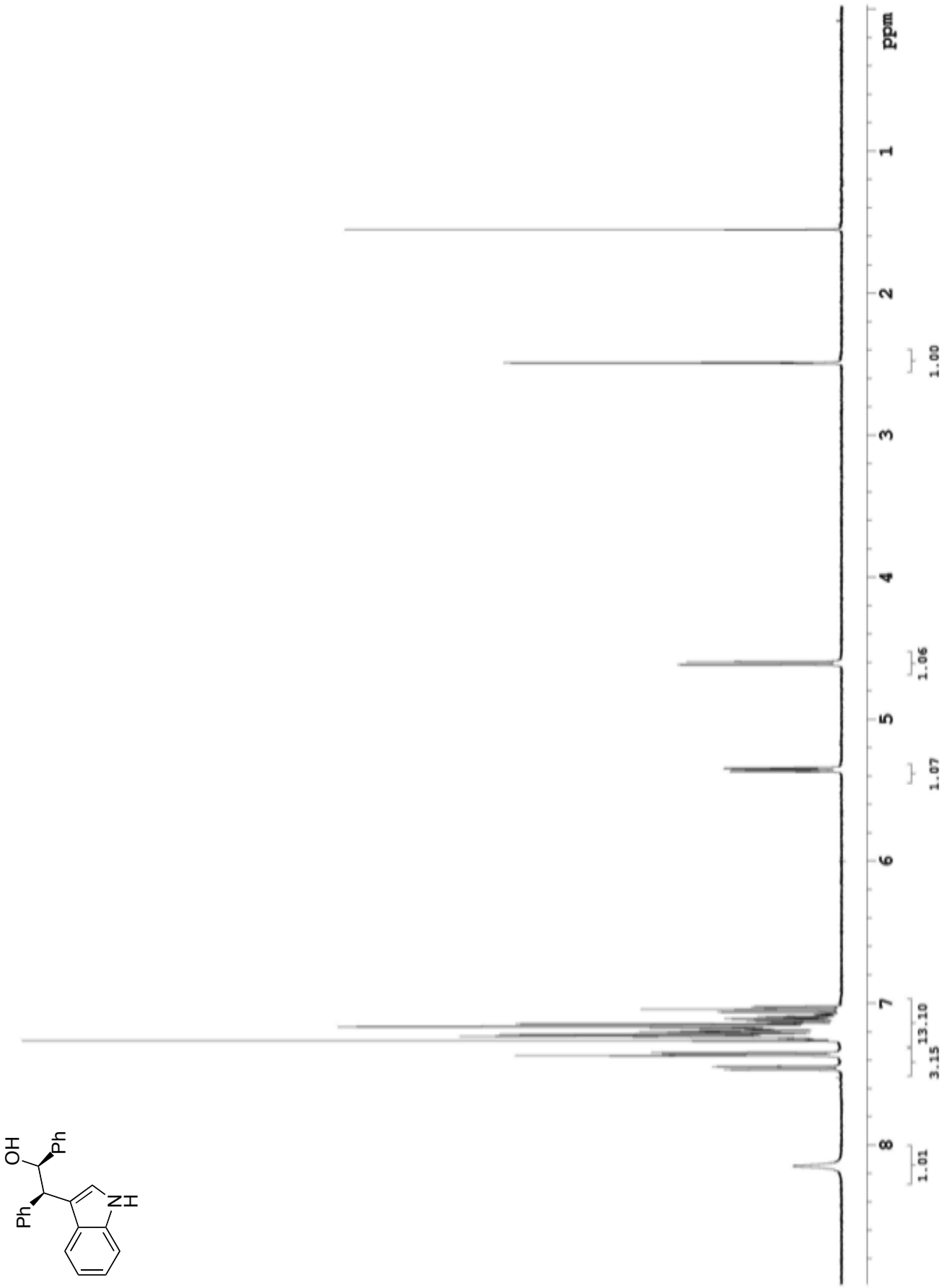

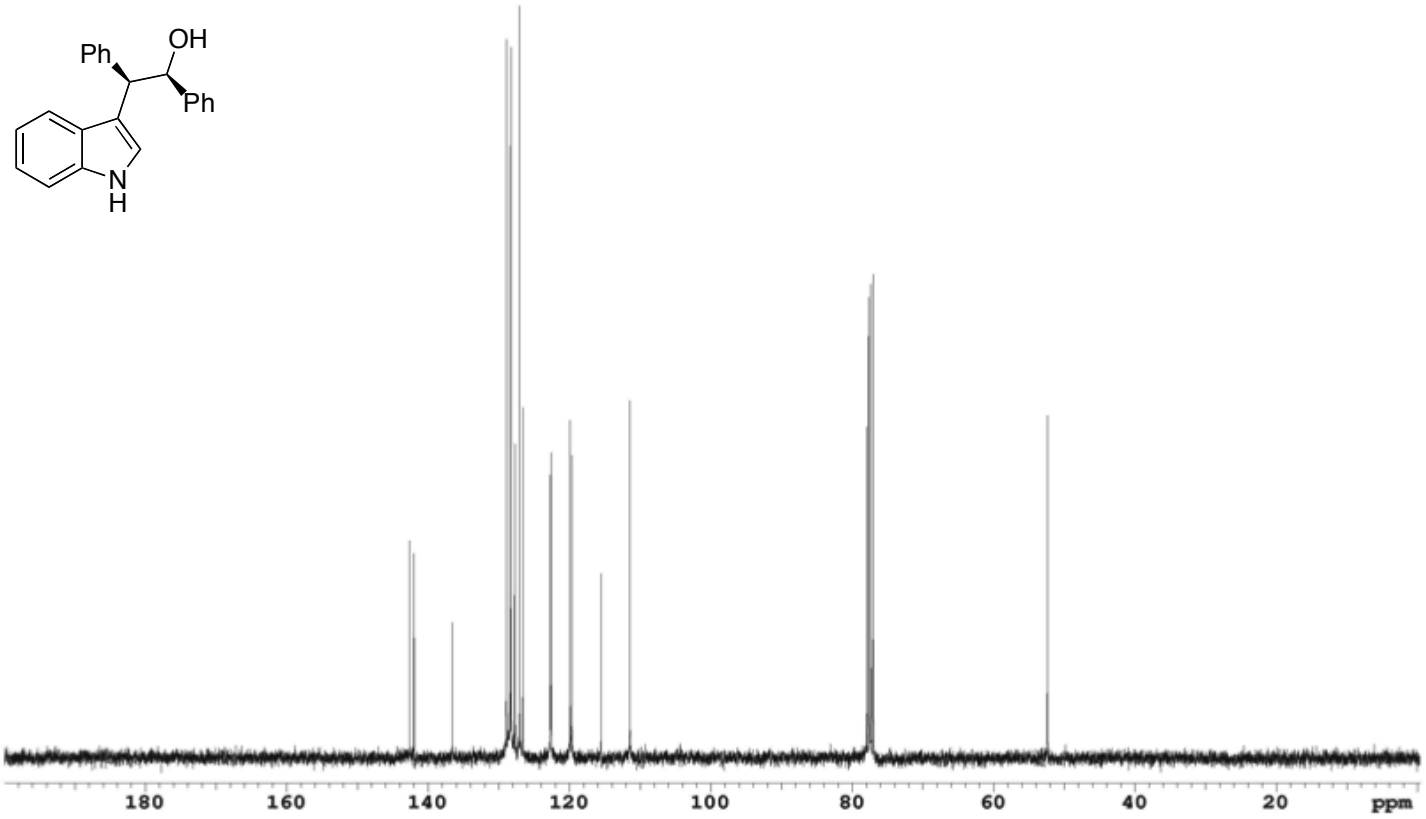

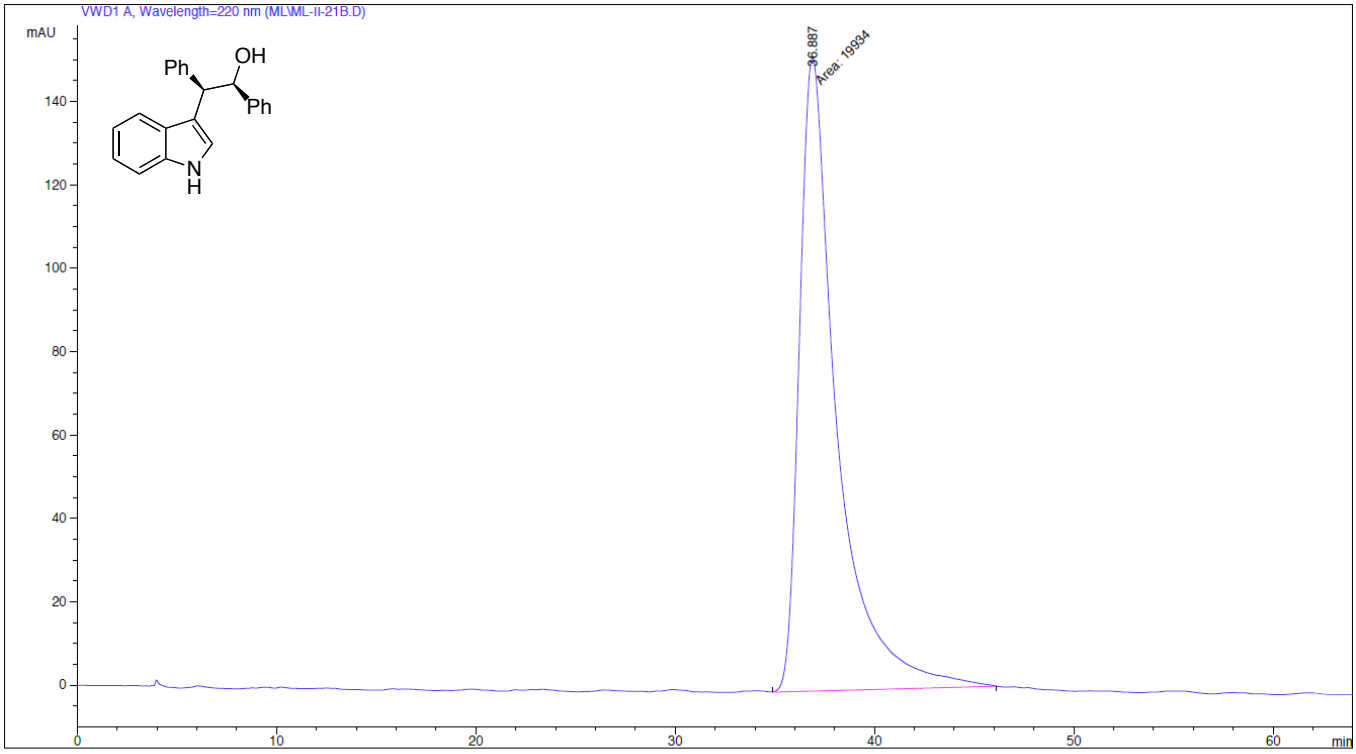

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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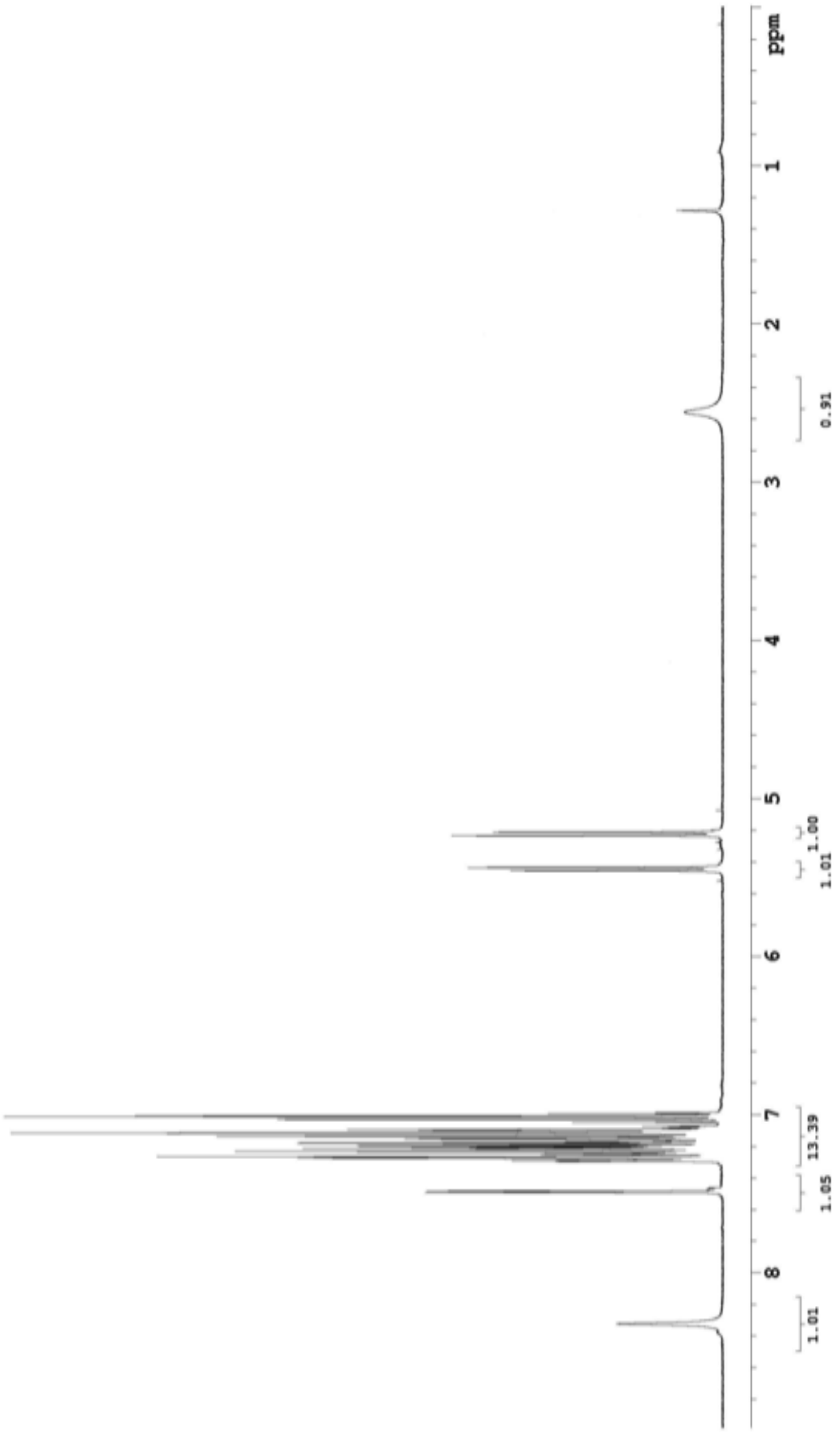
Totals :				1.99340e4	151.88126	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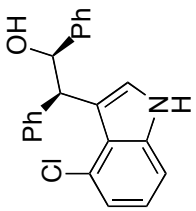
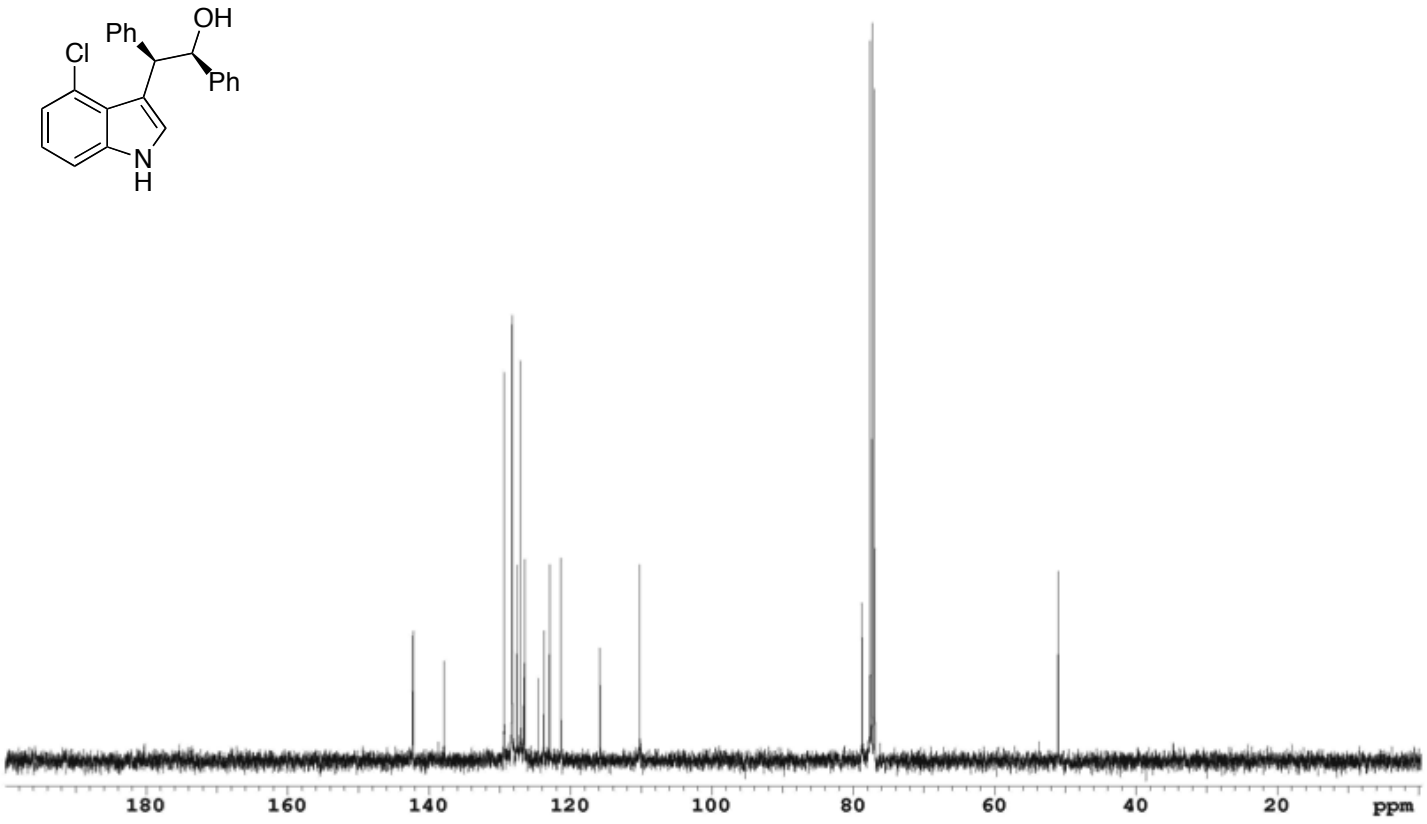
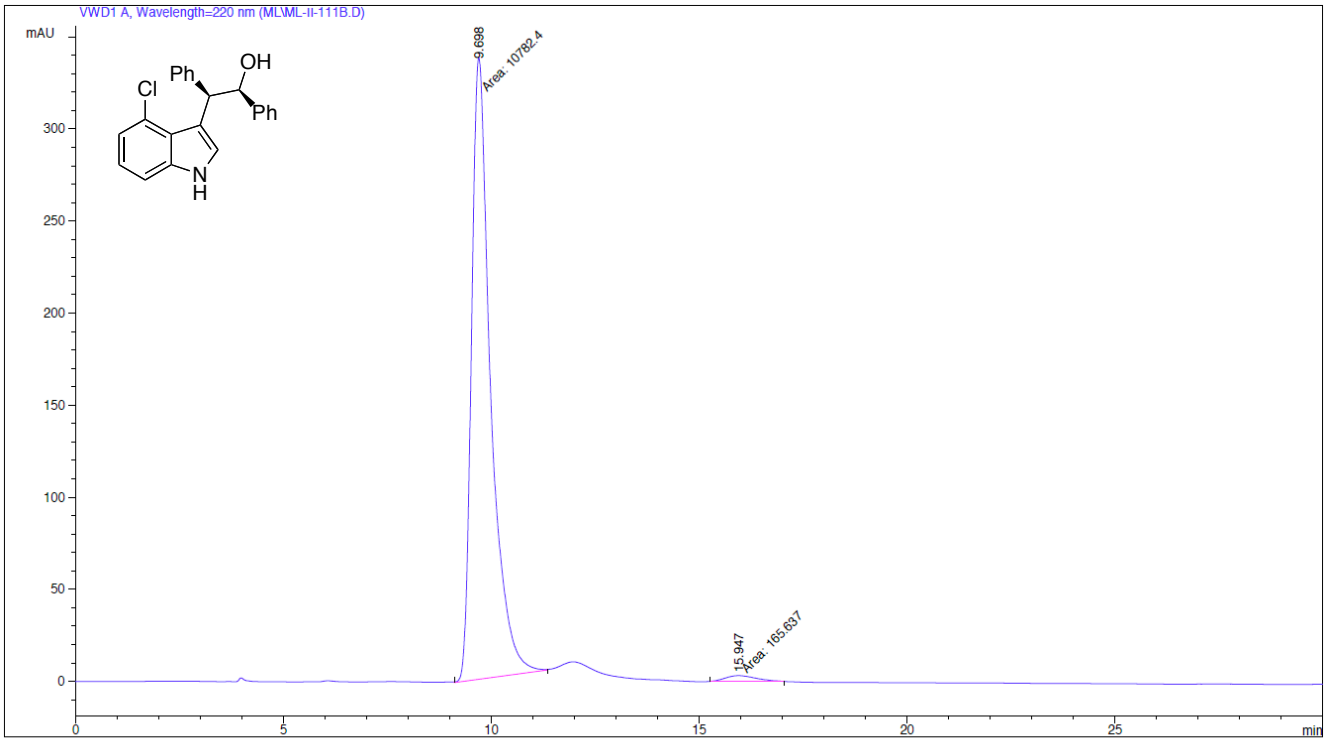
1
2
3
4
5
6
7
8
0.91
1.00
1.01
13.39
1.05
1.01

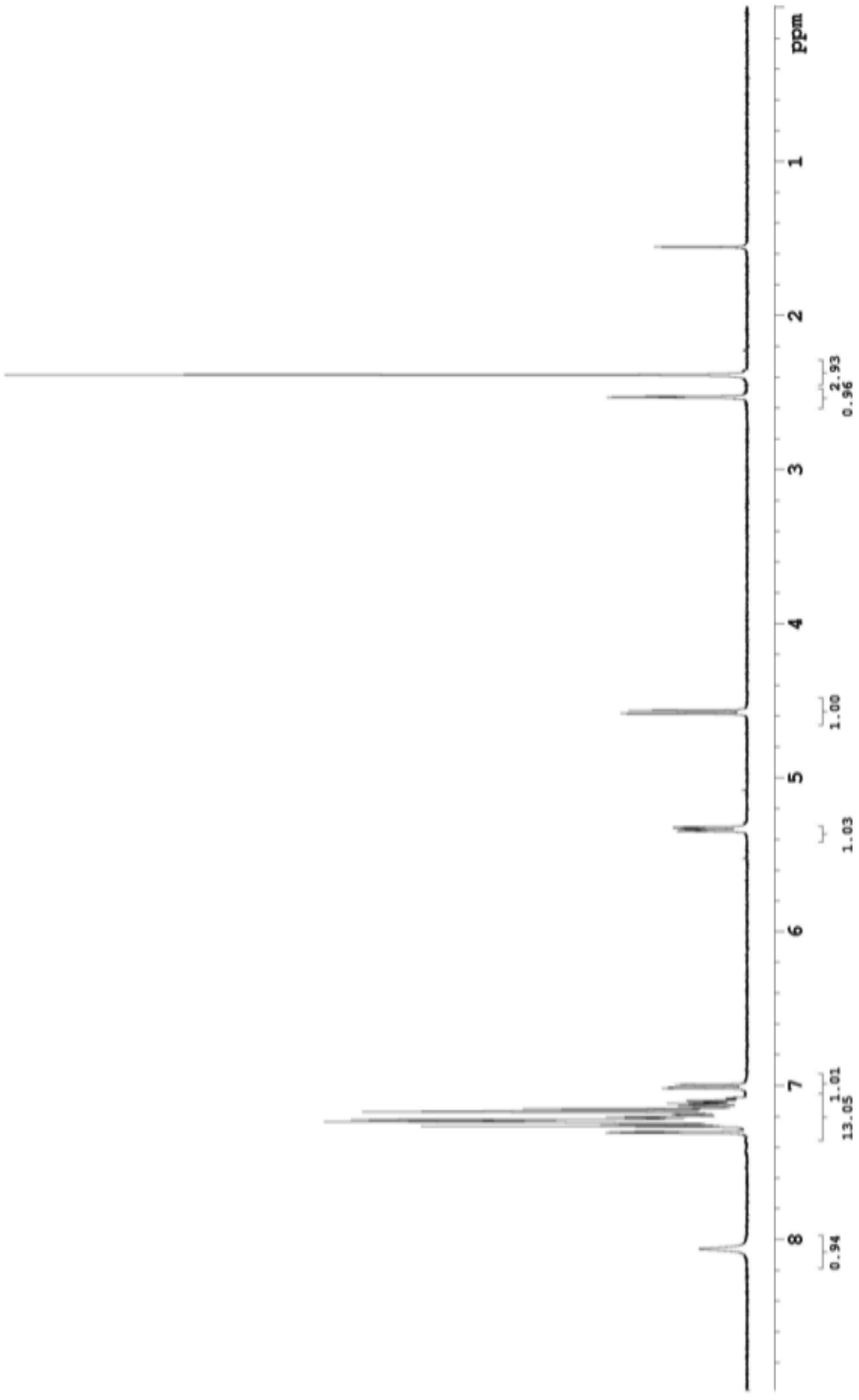

OH
Ph
Ph
N
H
Cl

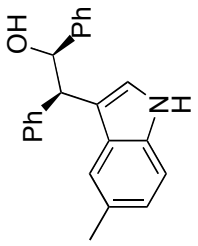


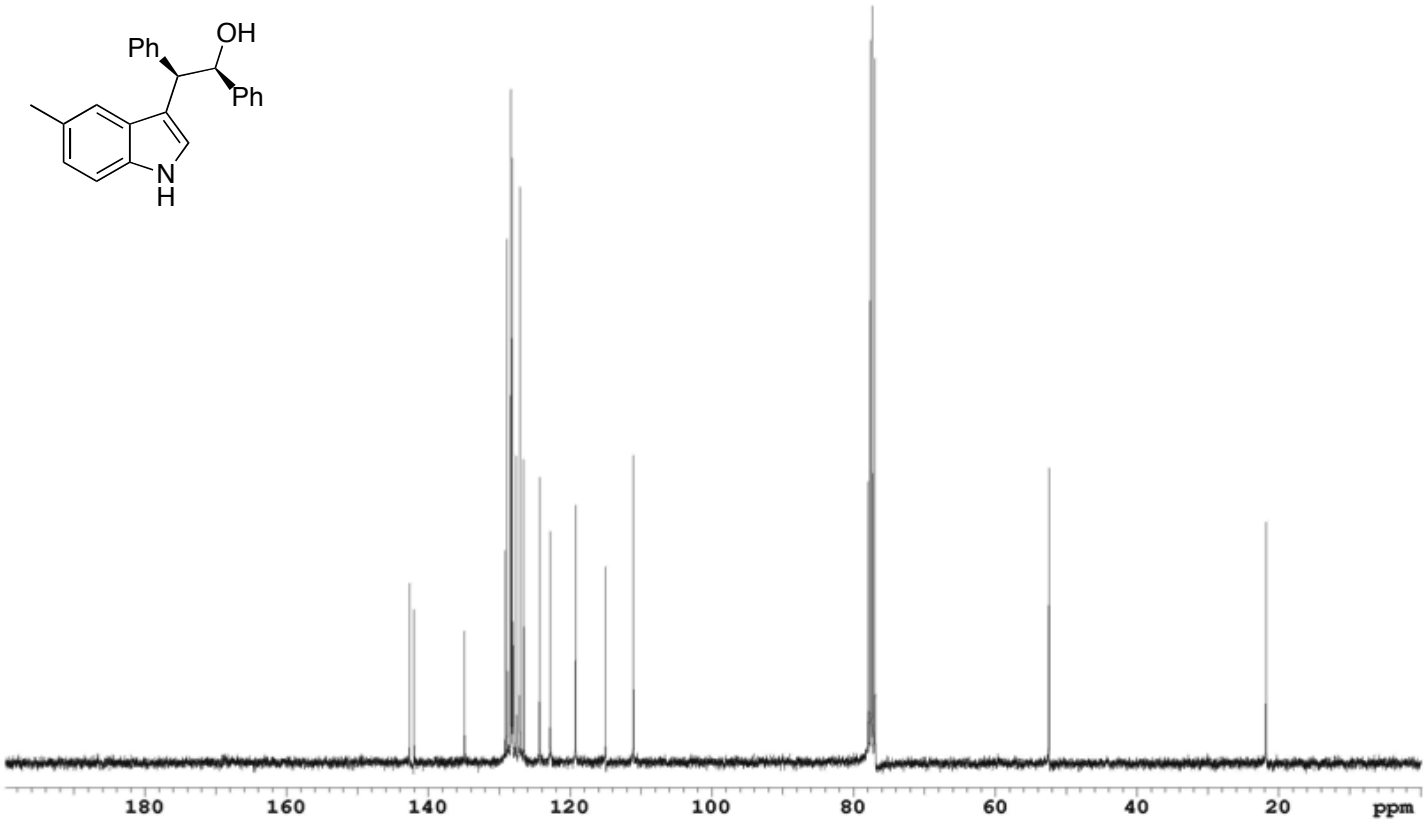


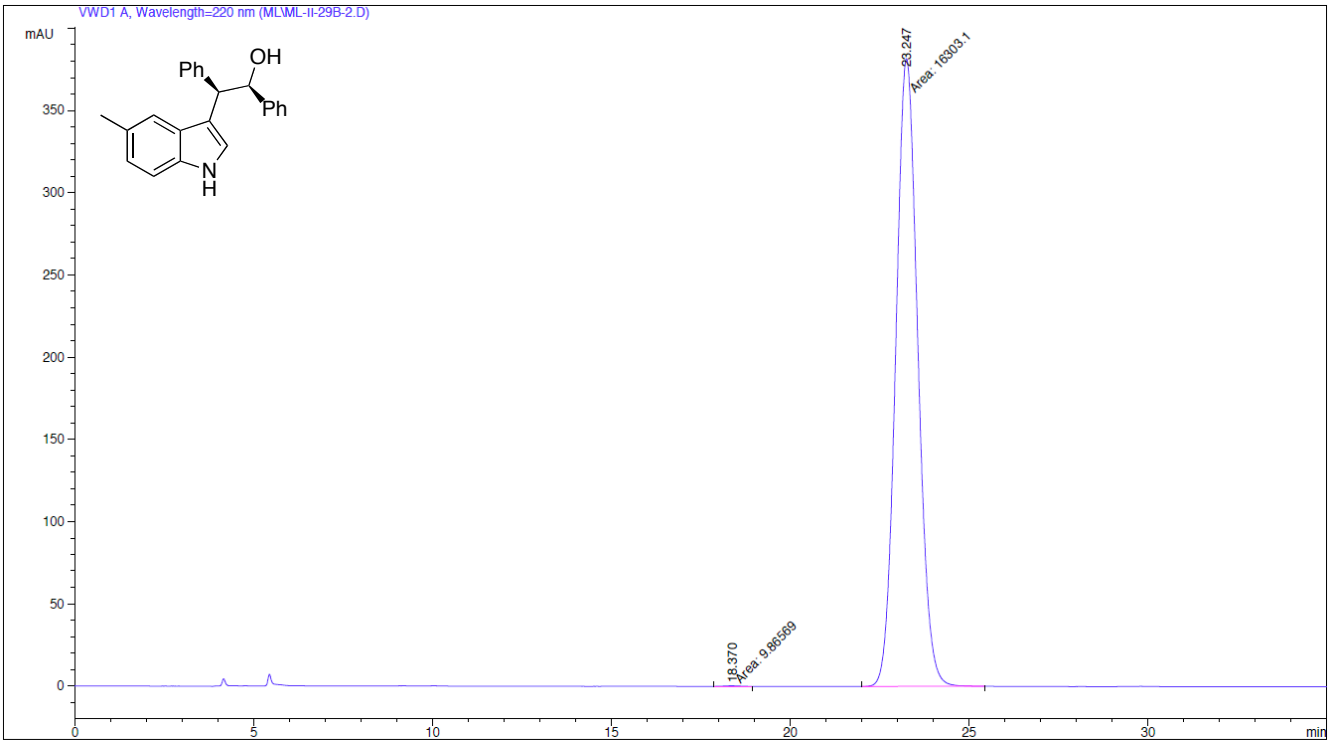
Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.698	MM	0.5324	1.07824e4	337.54364	98.4871
2	15.947	MM	0.8668	165.63678	3.18496	1.5129
Totals :				1.09481e4	340.72860	



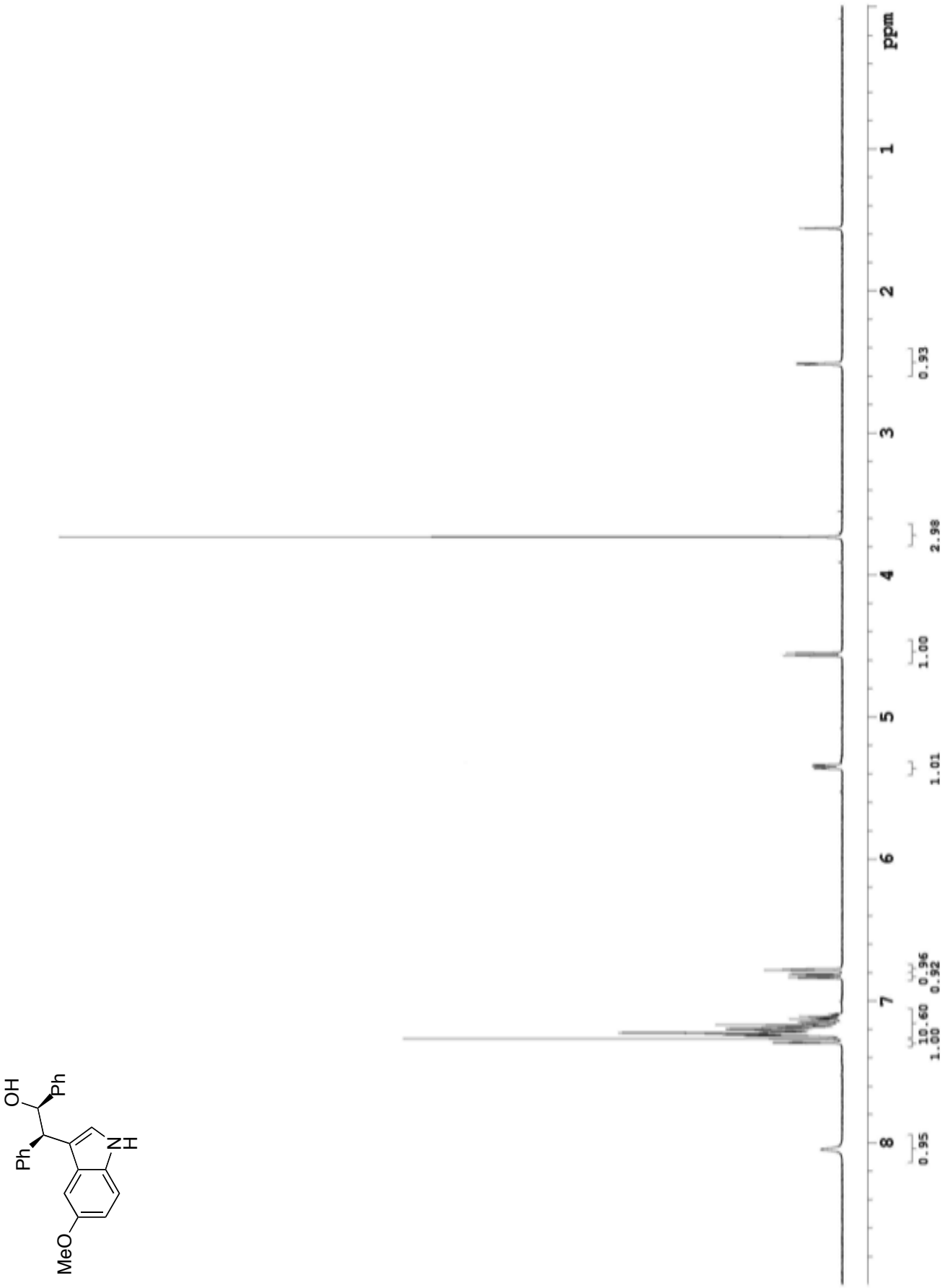


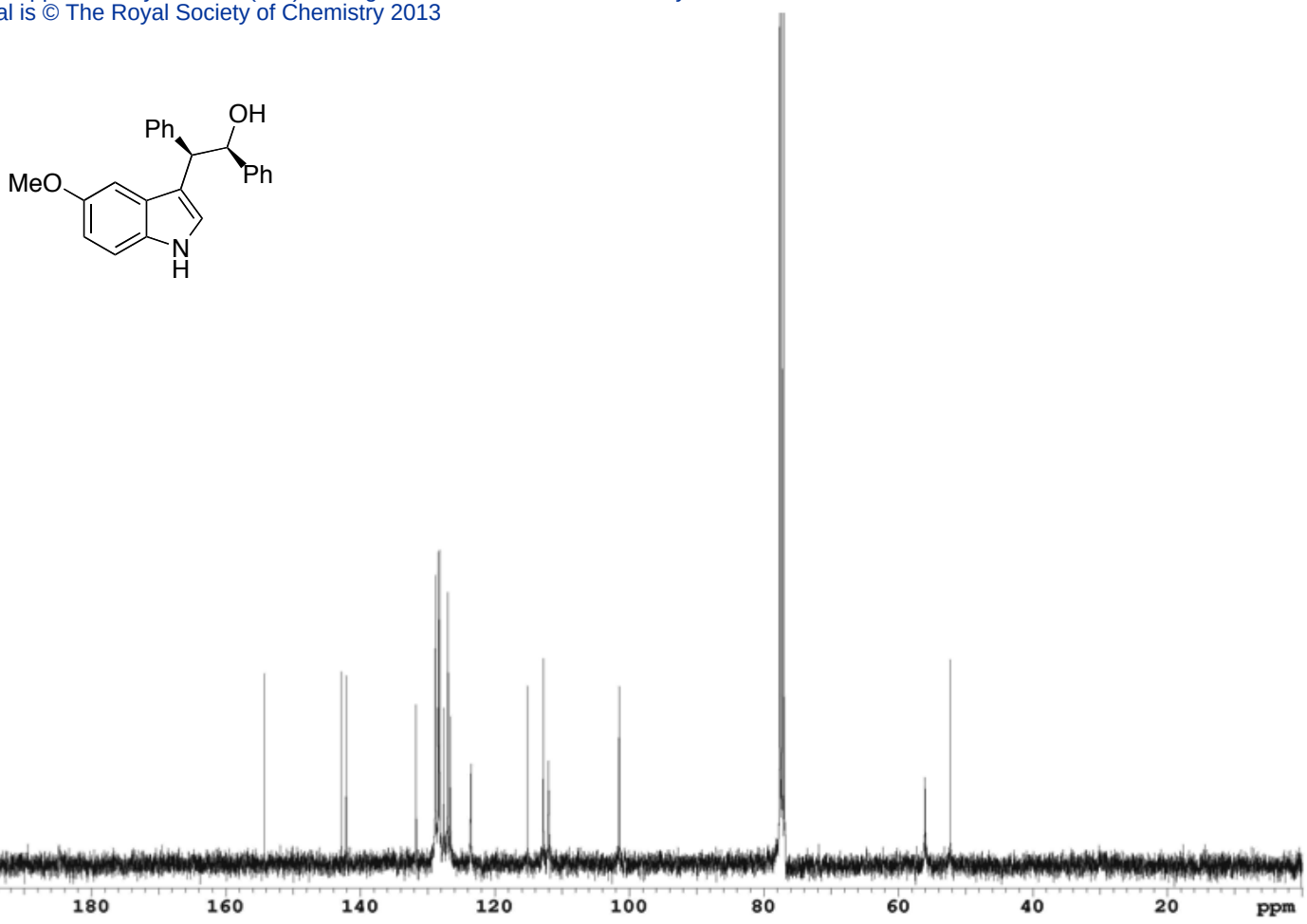


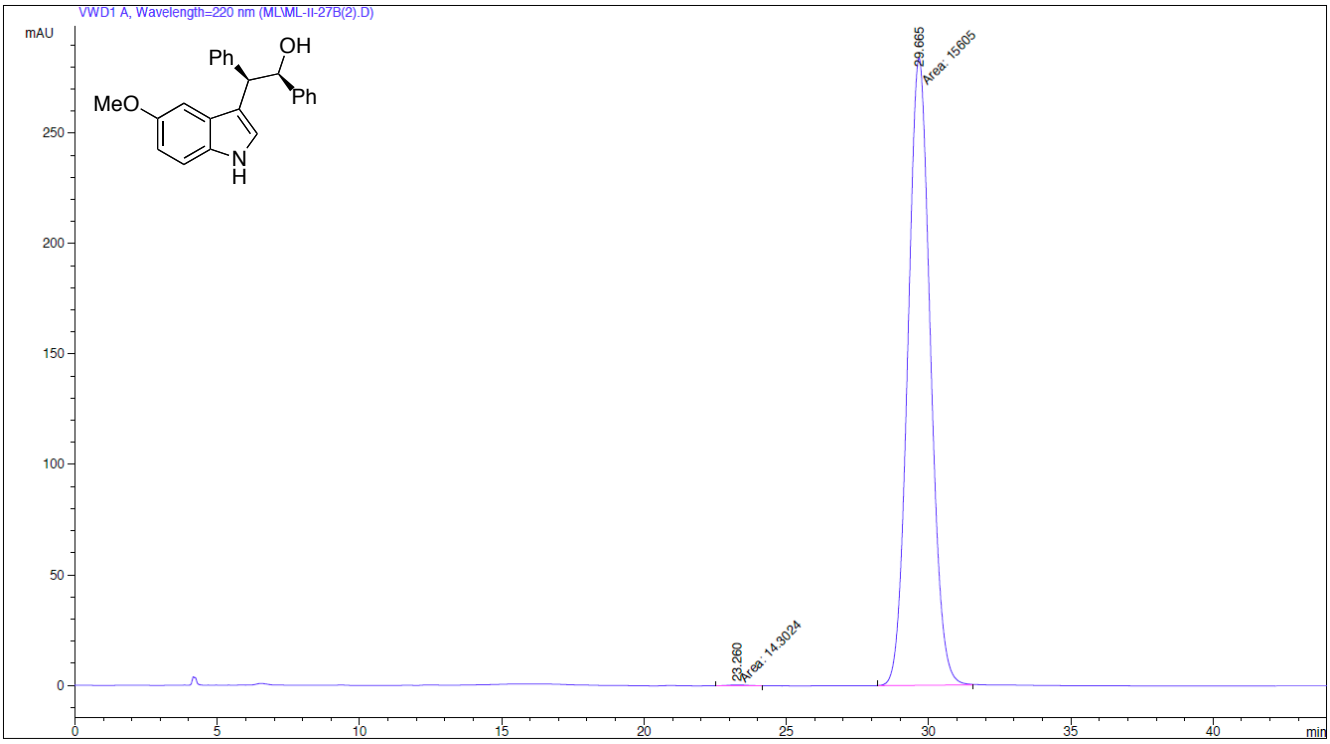


Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.370	MM	0.5433	9.86569	3.02664e-1	0.0605
2	23.247	MM	0.7118	1.63031e4	381.73770	99.9395
Totals :				1.63130e4	382.04037	

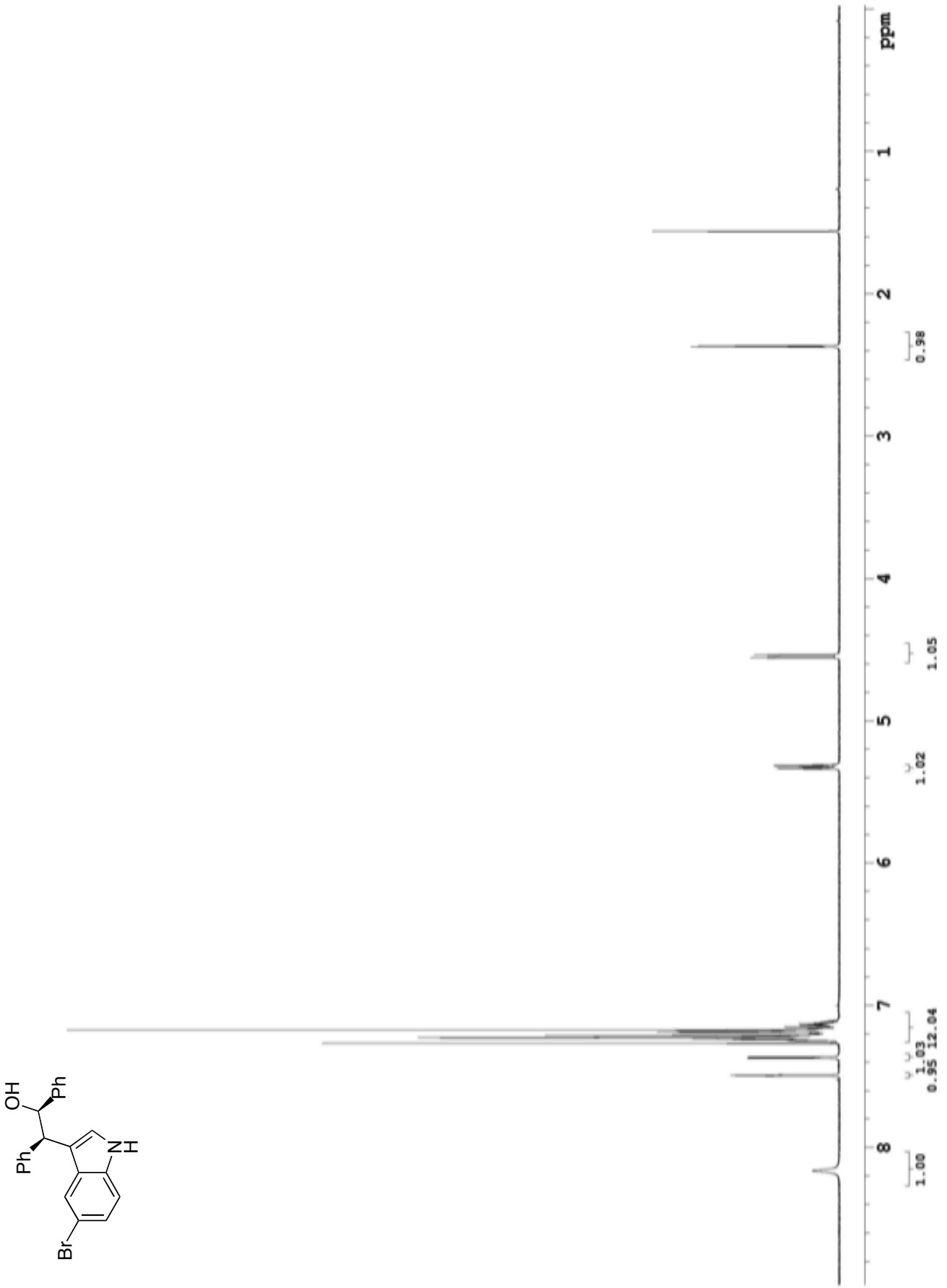


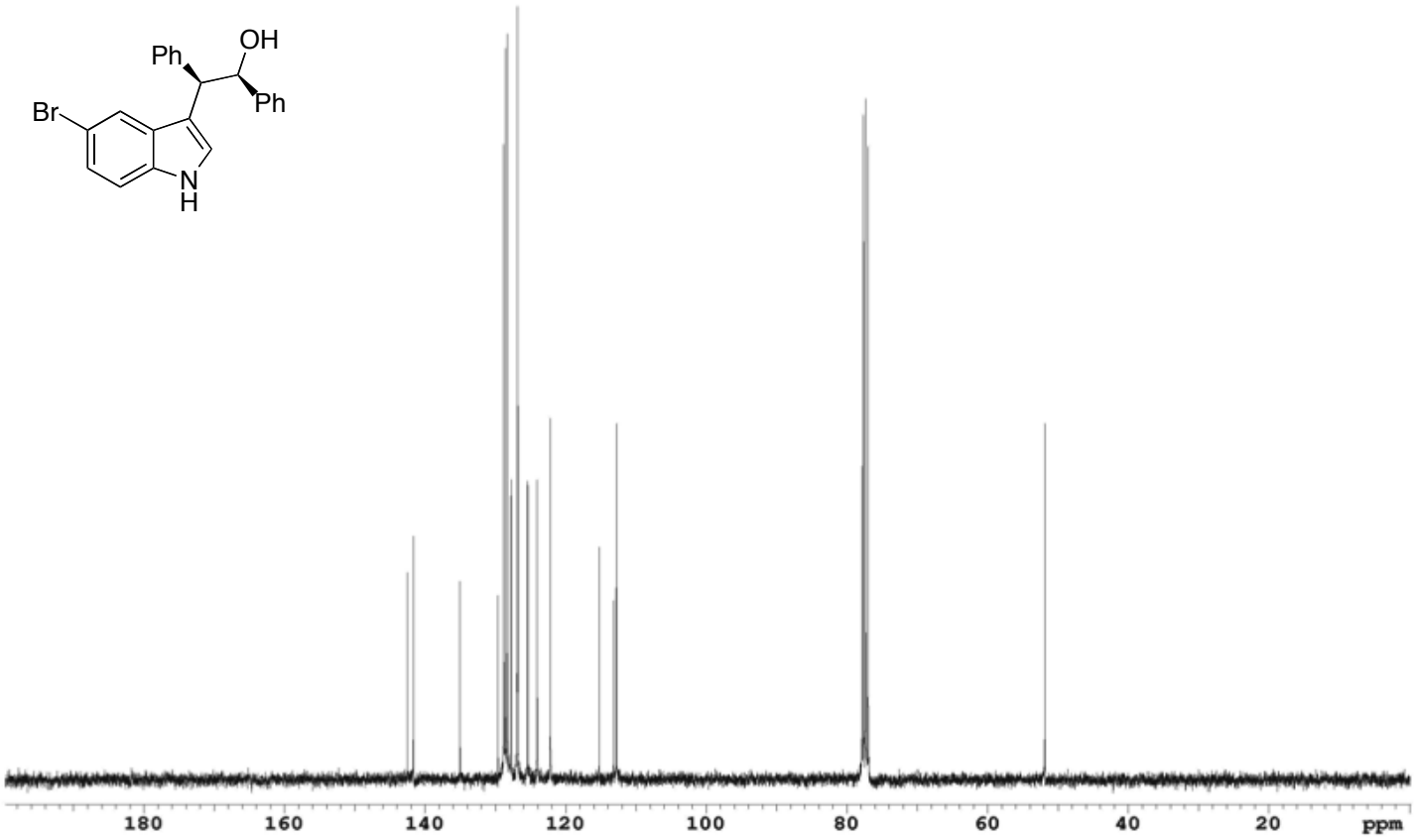


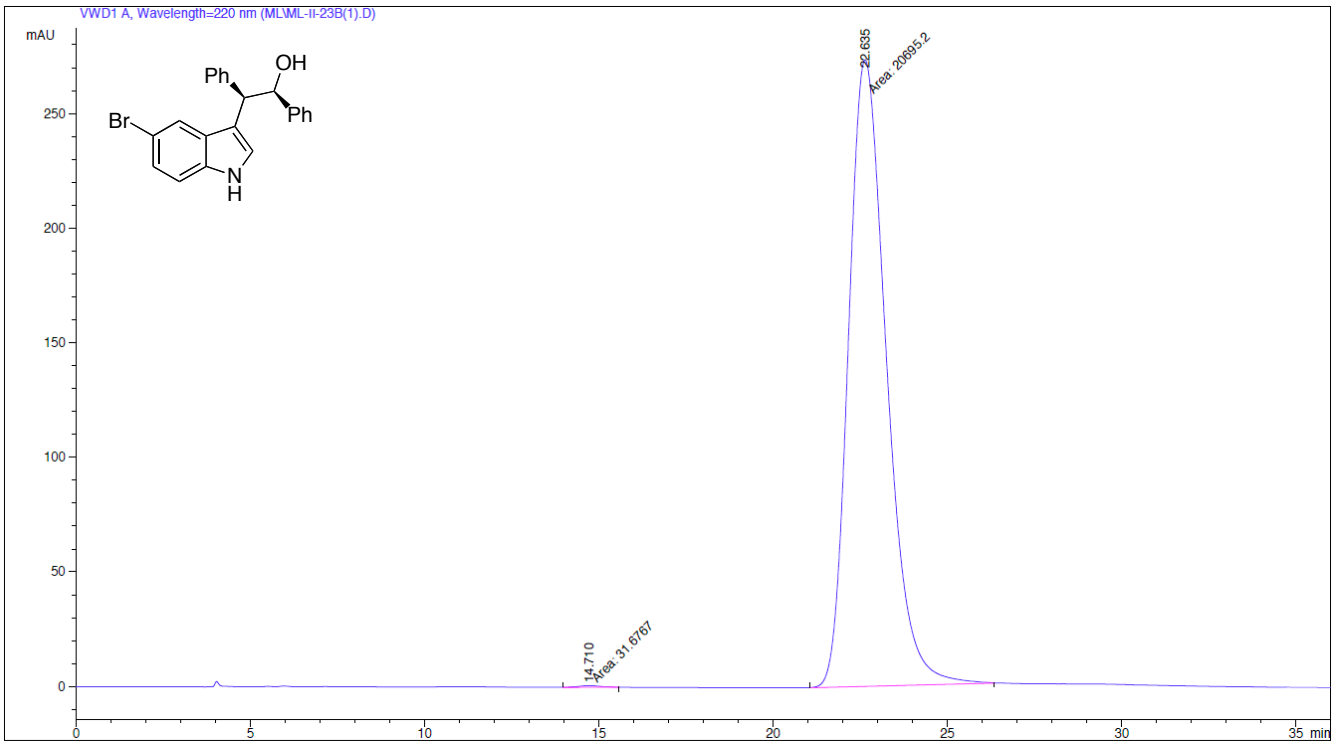


Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.260	MM	0.7377	14.30244	3.23110e-1	0.0916
2	29.665	MM	0.9156	1.56050e4	284.06409	99.9084
Totals :				1.56193e4	284.38720	







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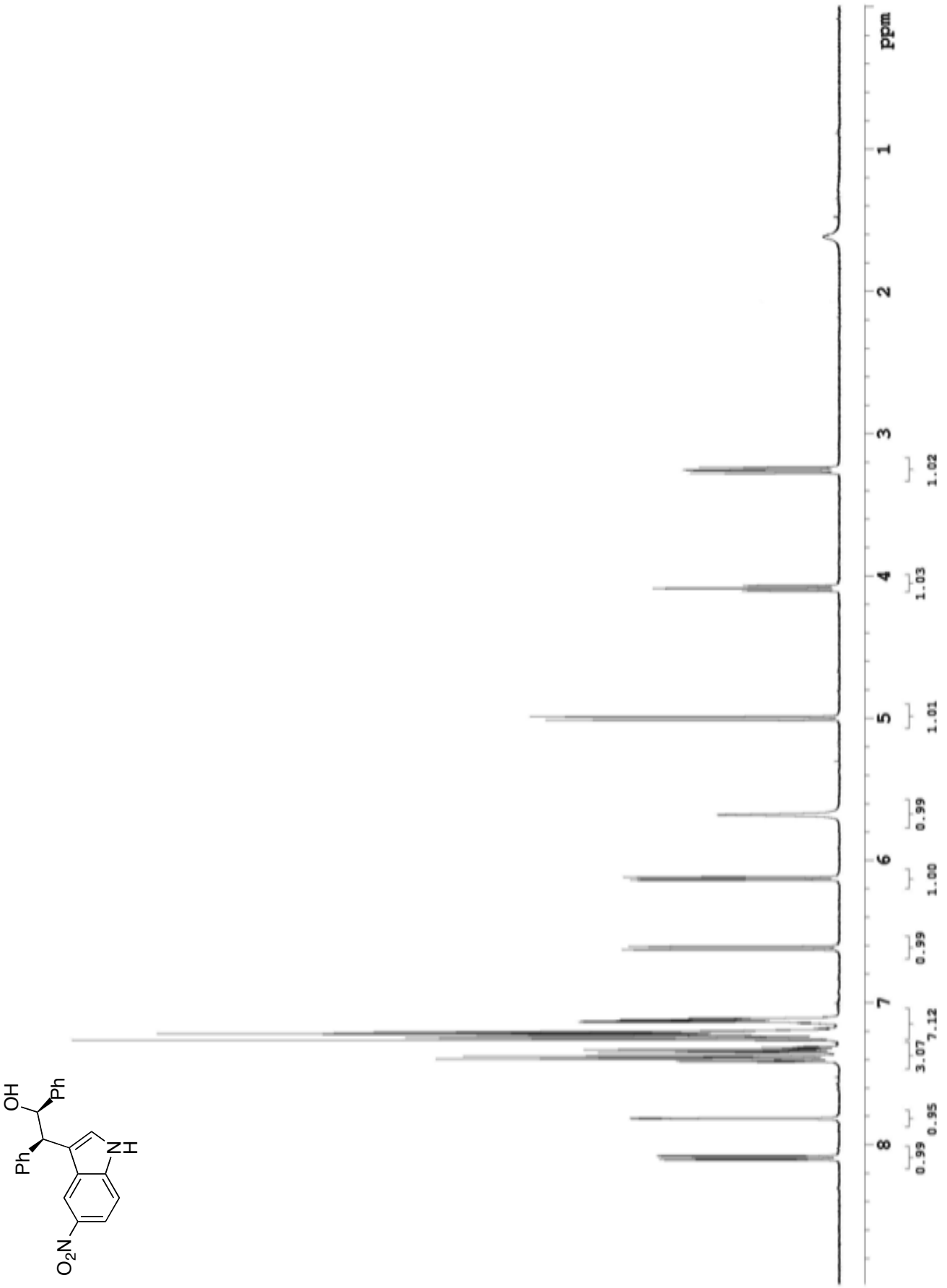
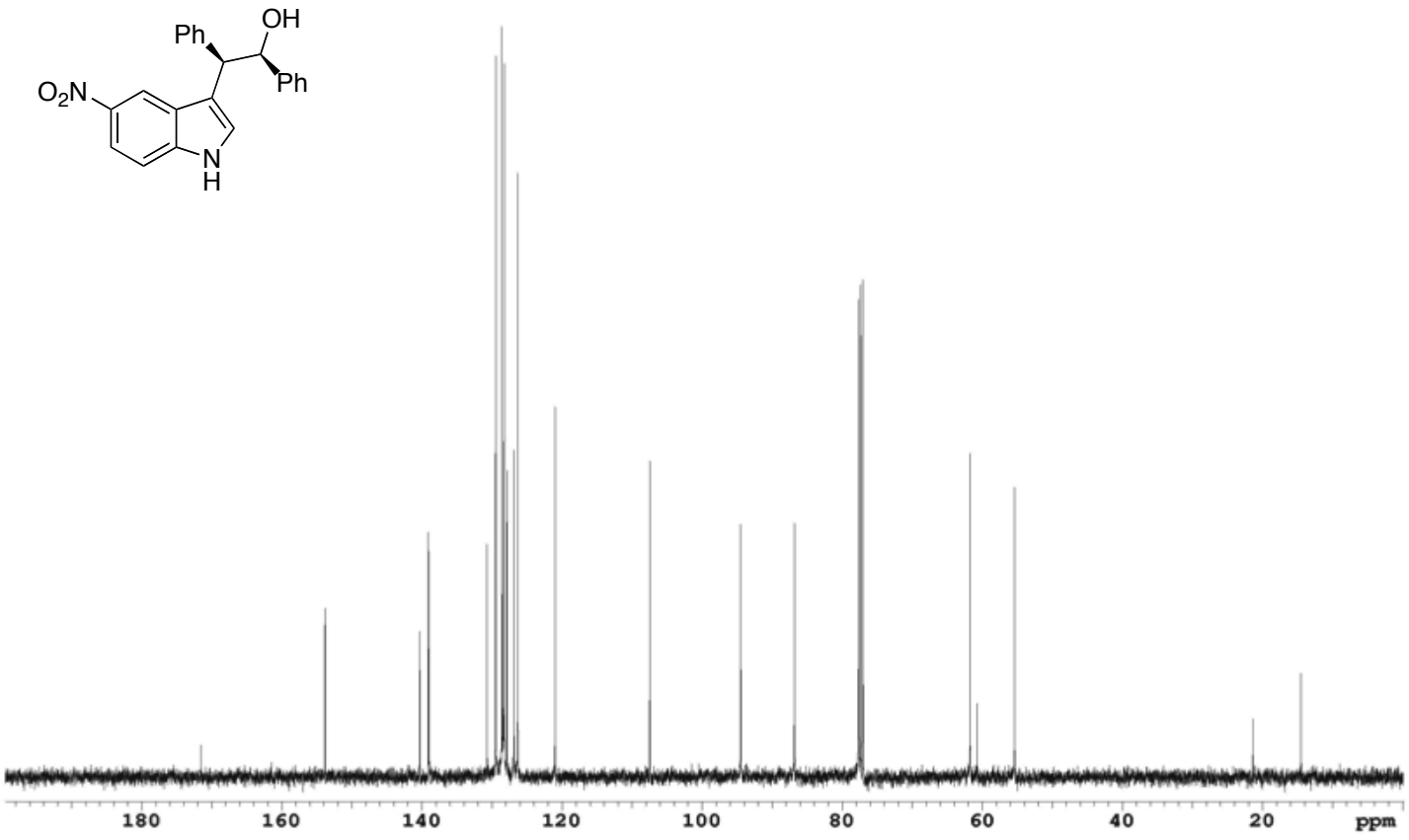
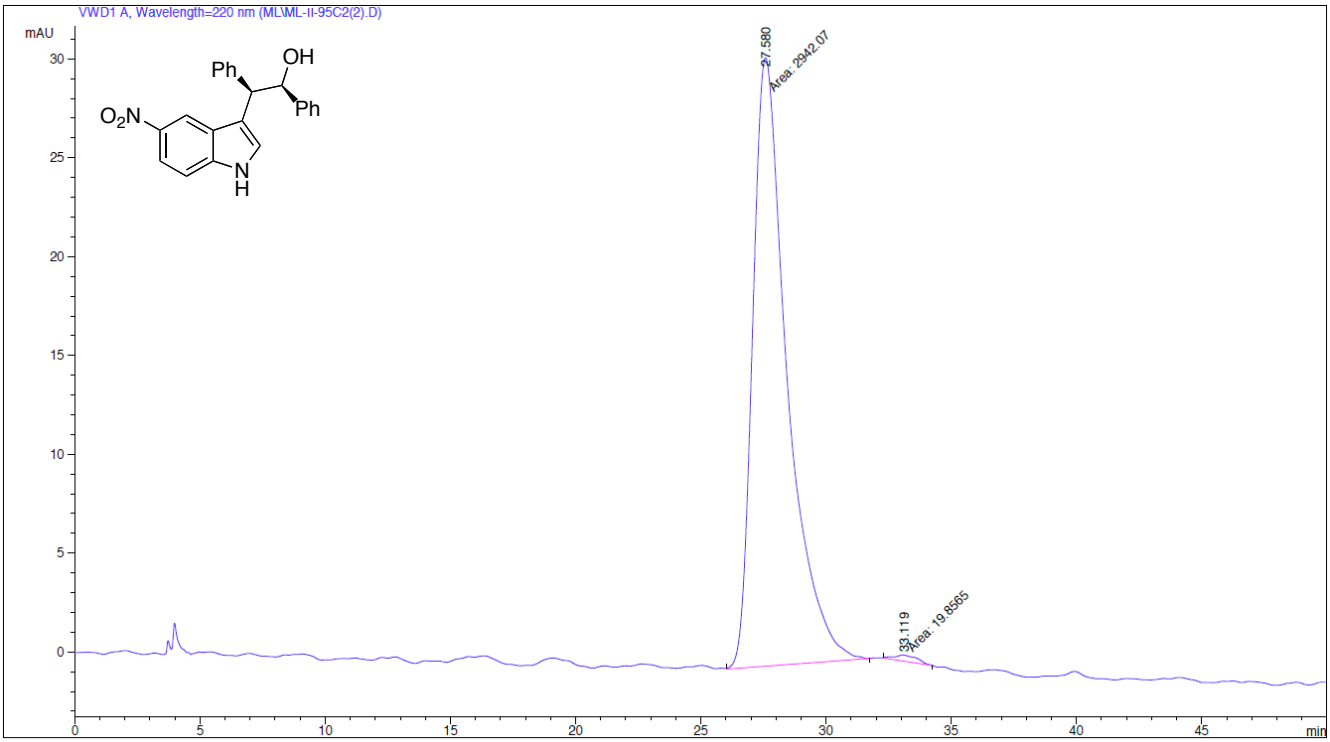
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.710	MM	0.7720	31.67671	6.83902e-1	0.1528
2	22.635	MM	1.2610	2.06952e4	273.52768	99.8472
Totals :				2.07269e4	274.21158	







Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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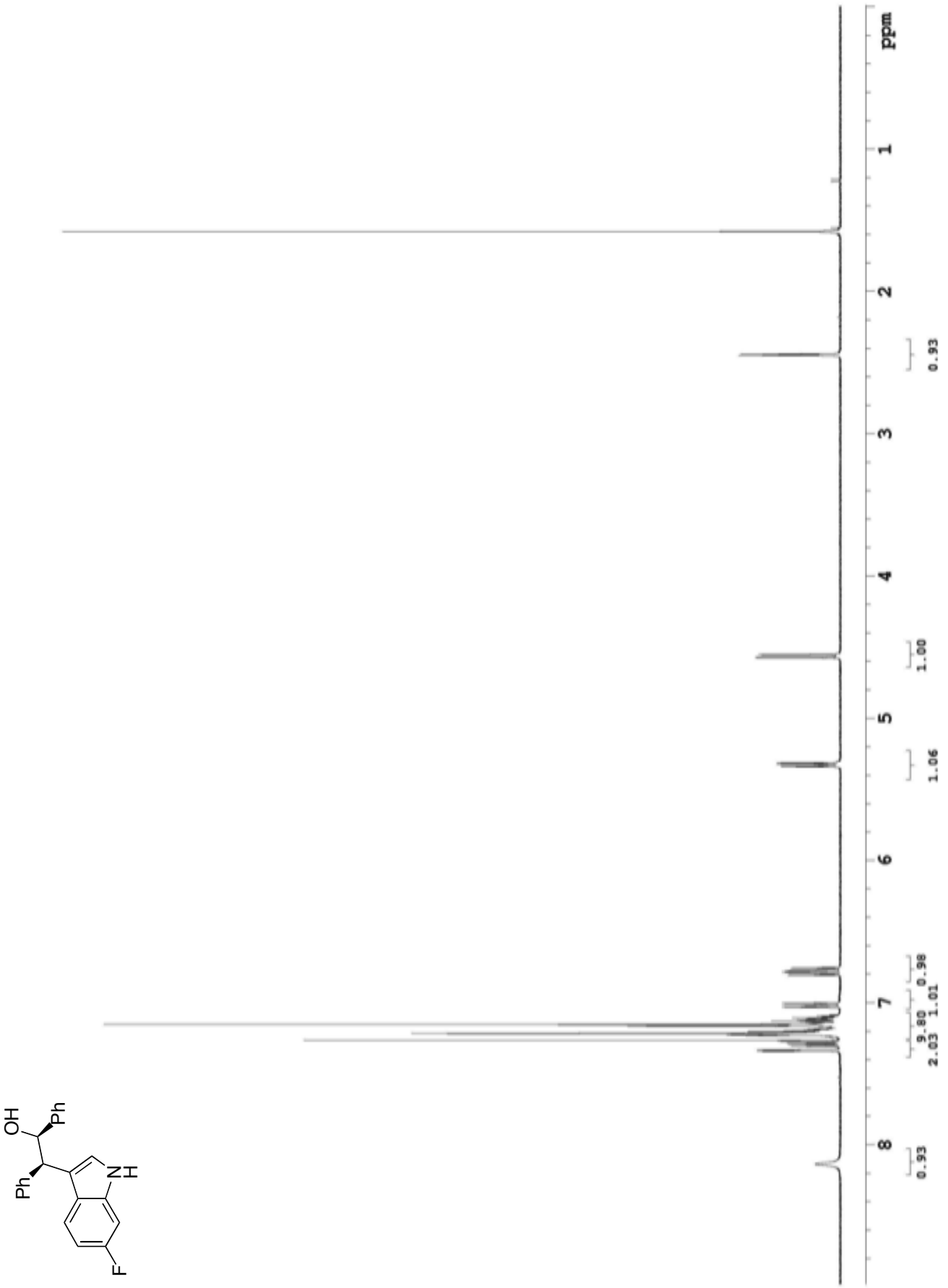
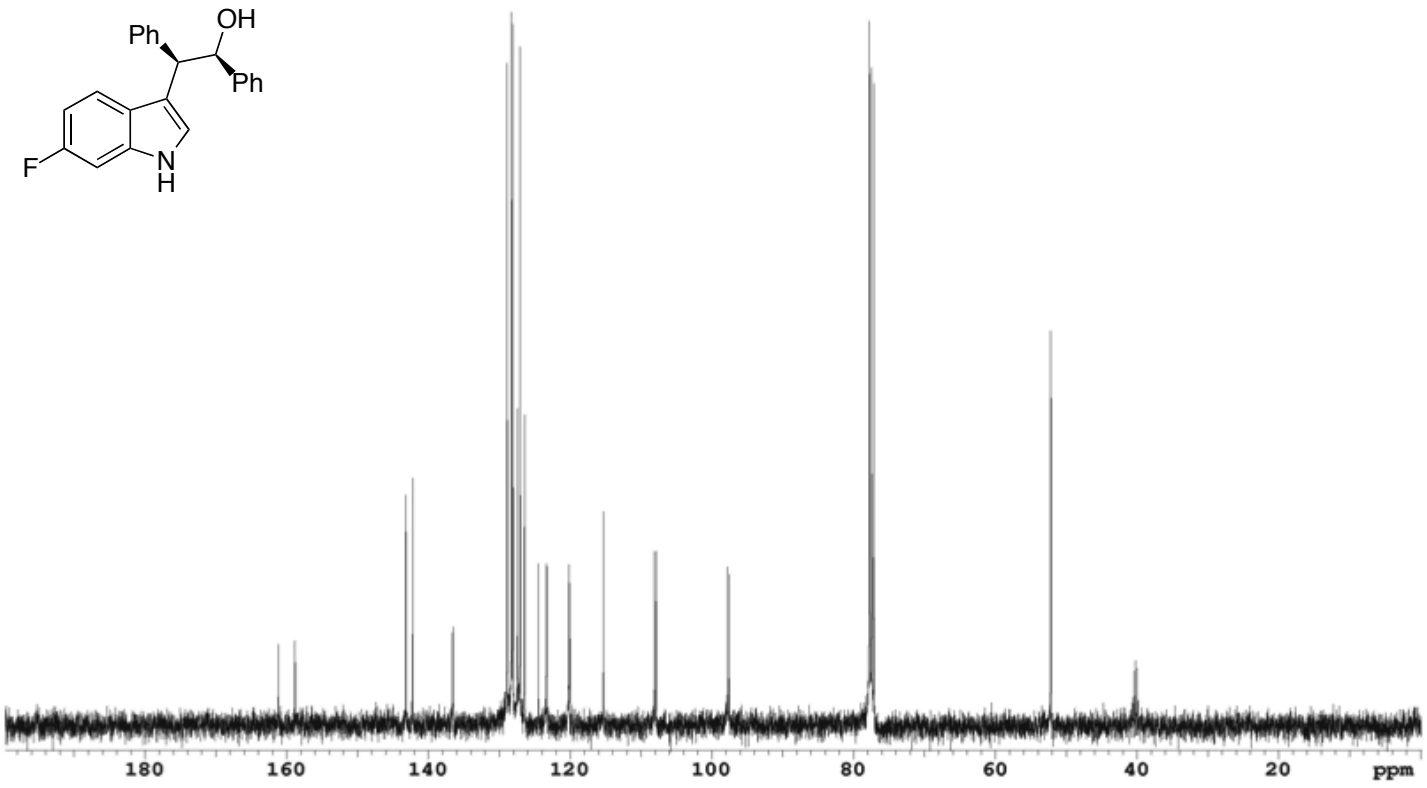
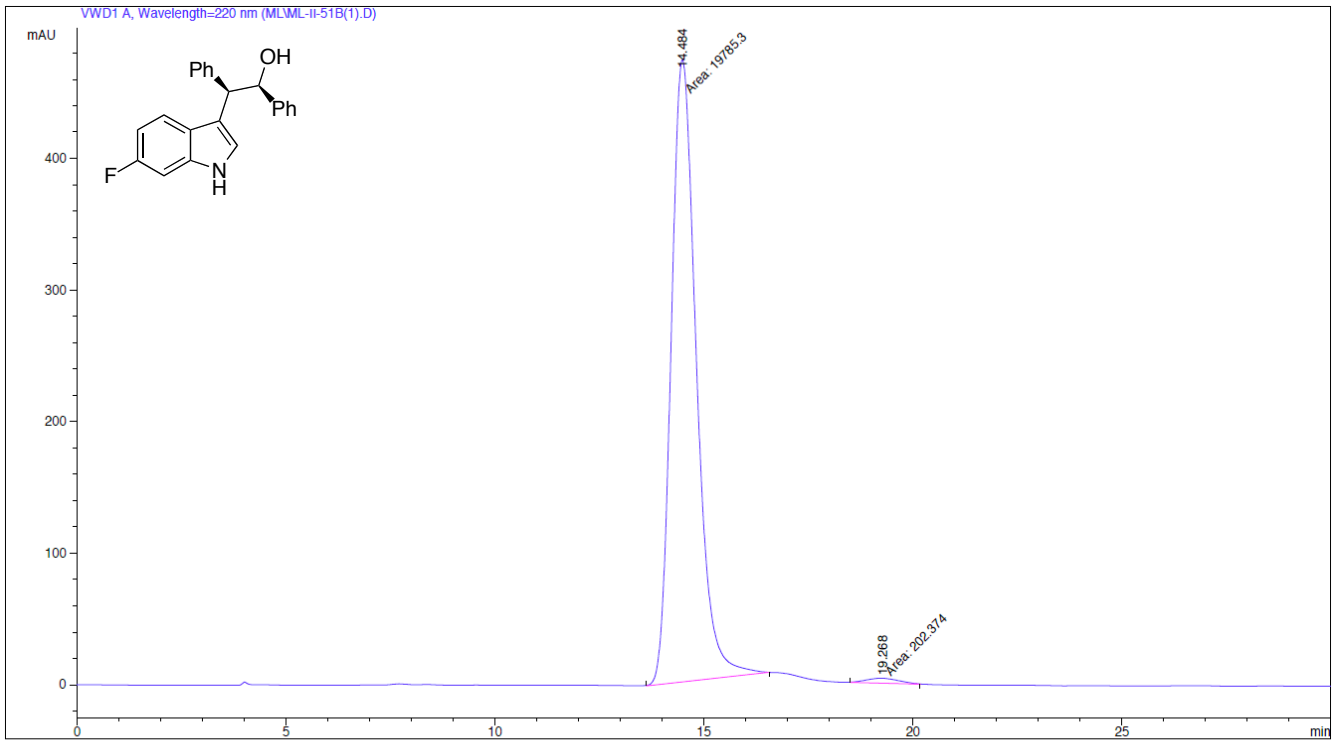
Totals :				2961.93146	31.07859	

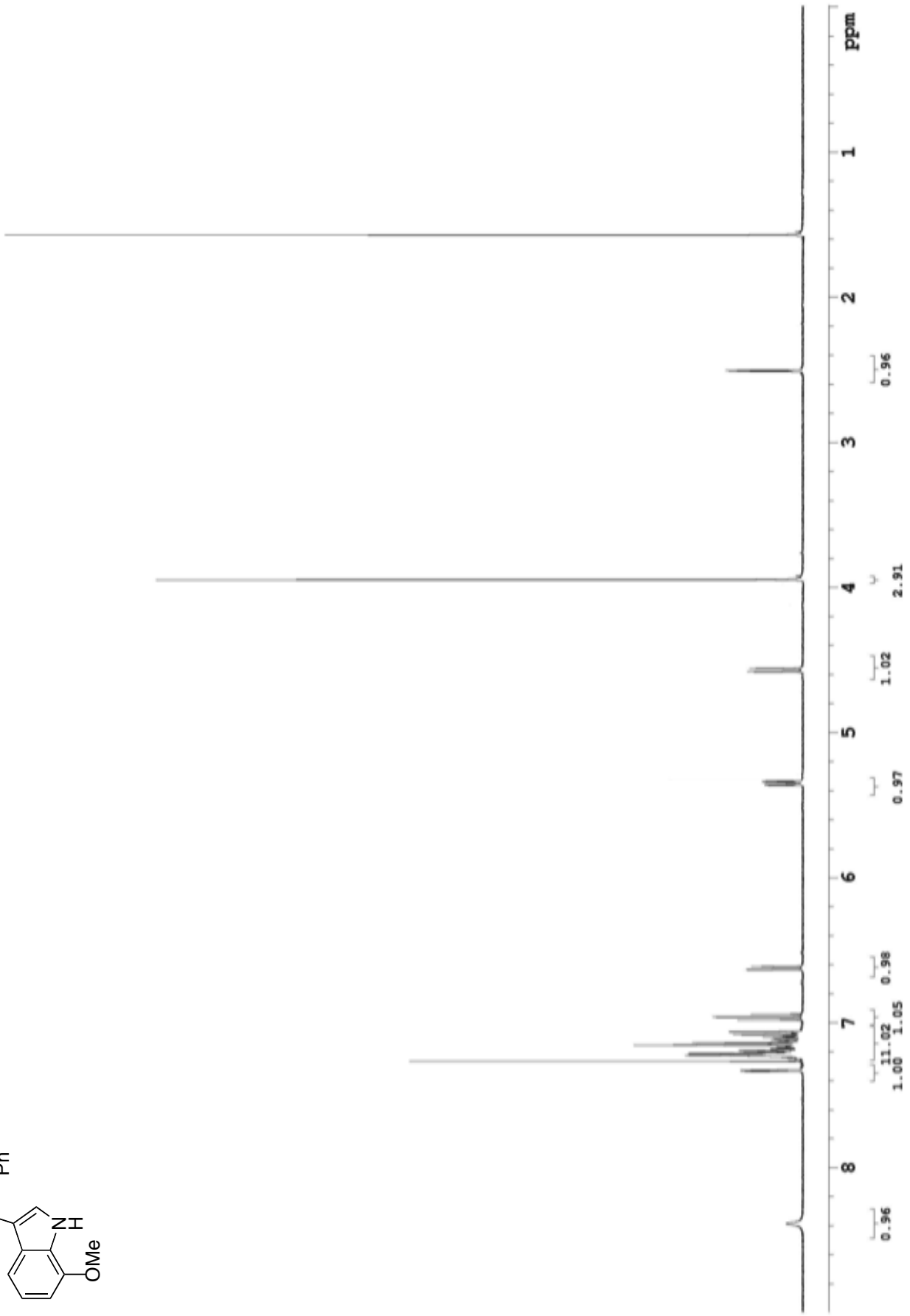


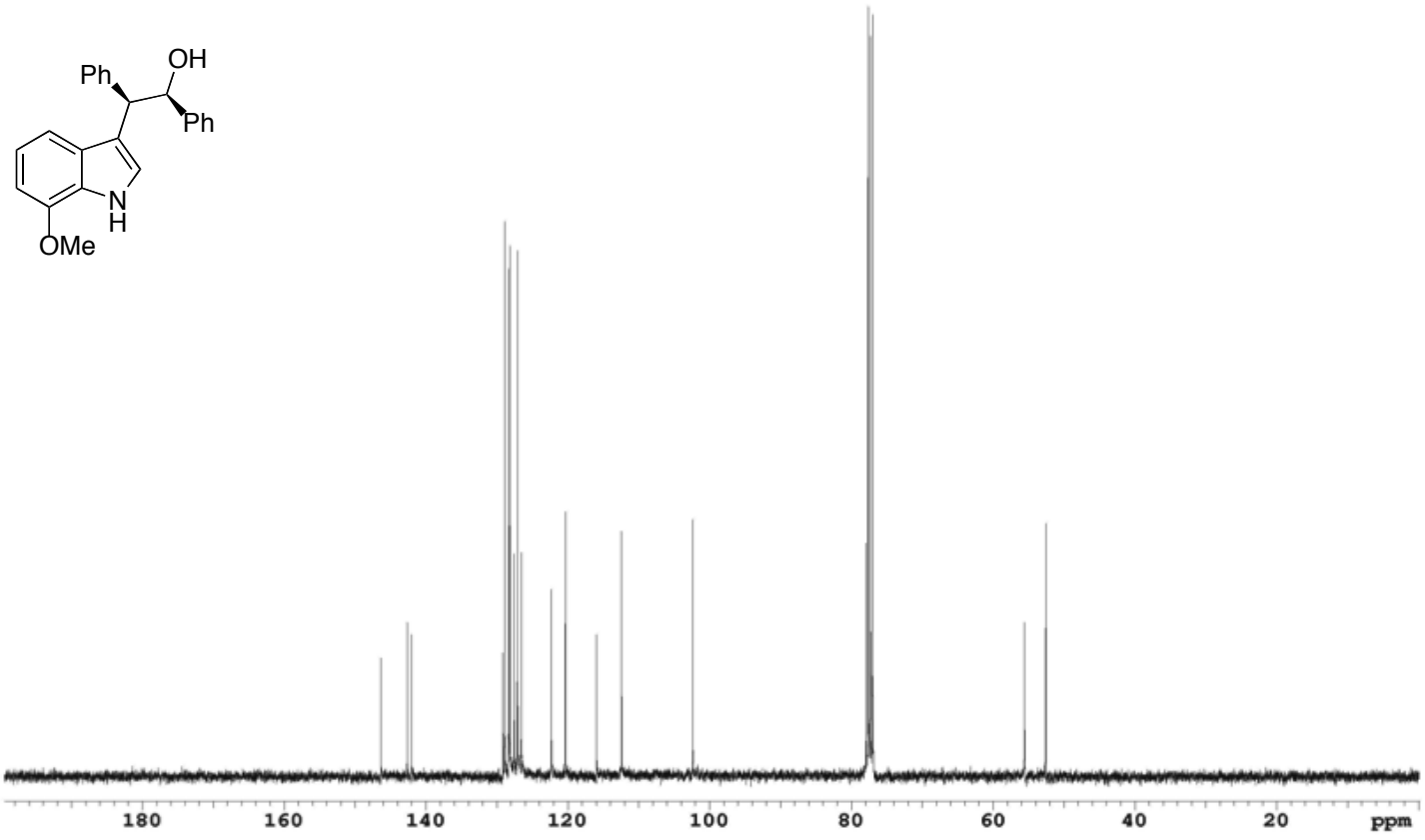


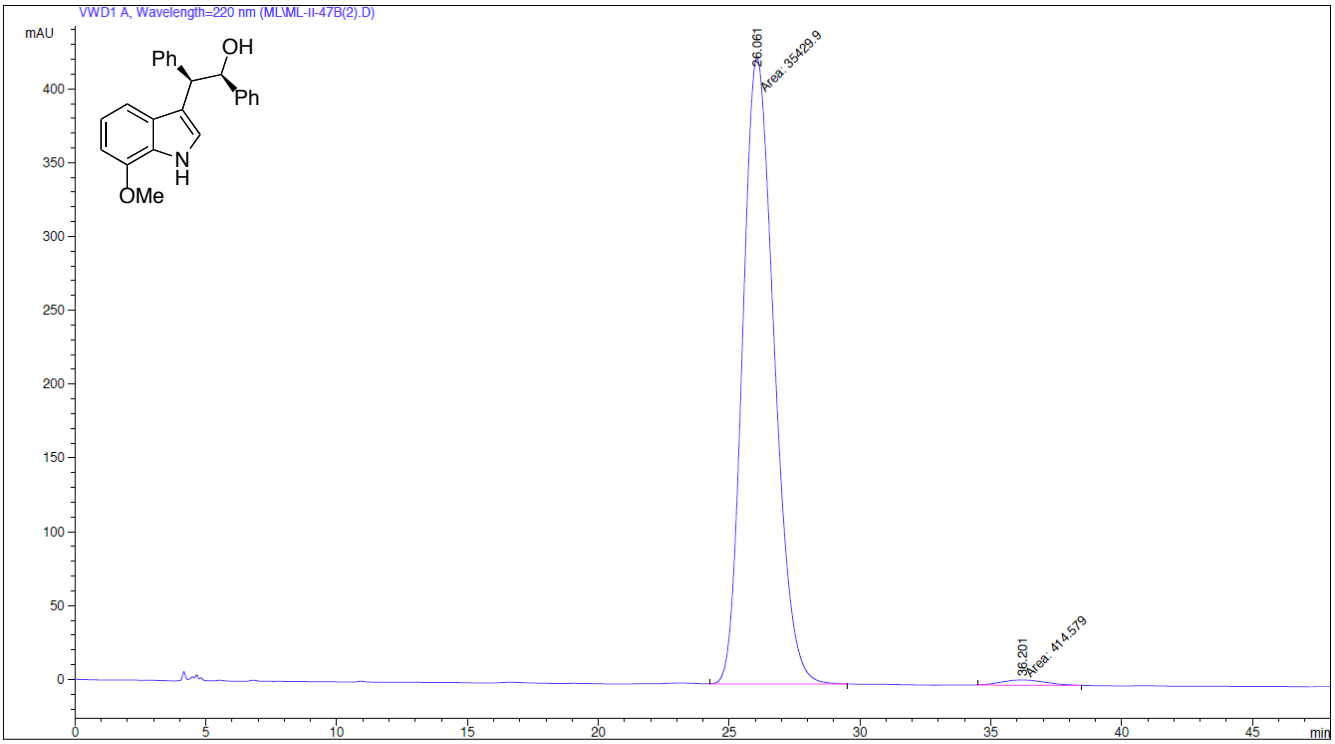


Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.484	MM	0.6974	1.97853e4	472.82312	98.9875
2	19.268	MM	0.8963	202.37360	3.76299	1.0125
Totals :				1.99876e4	476.58611	

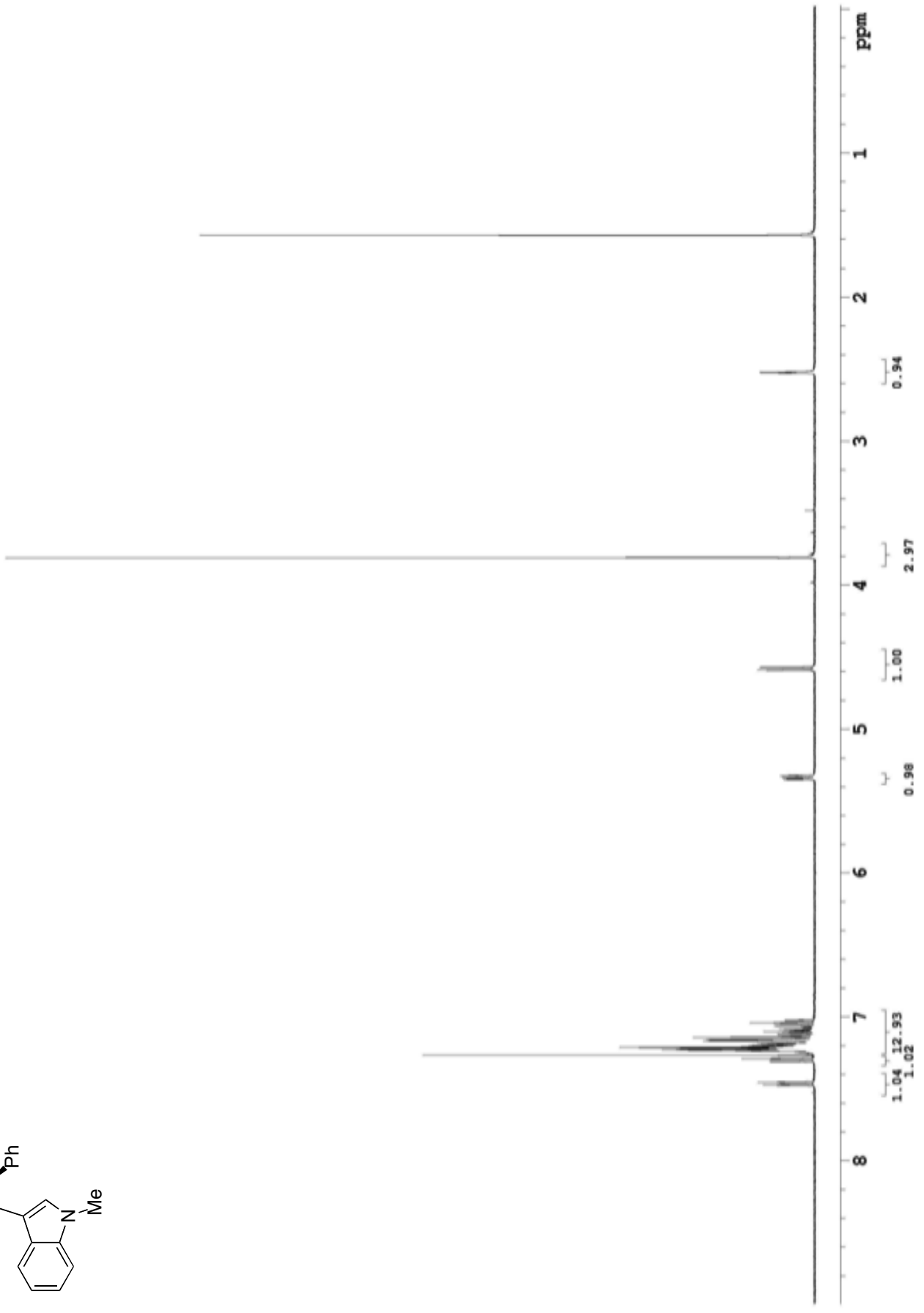


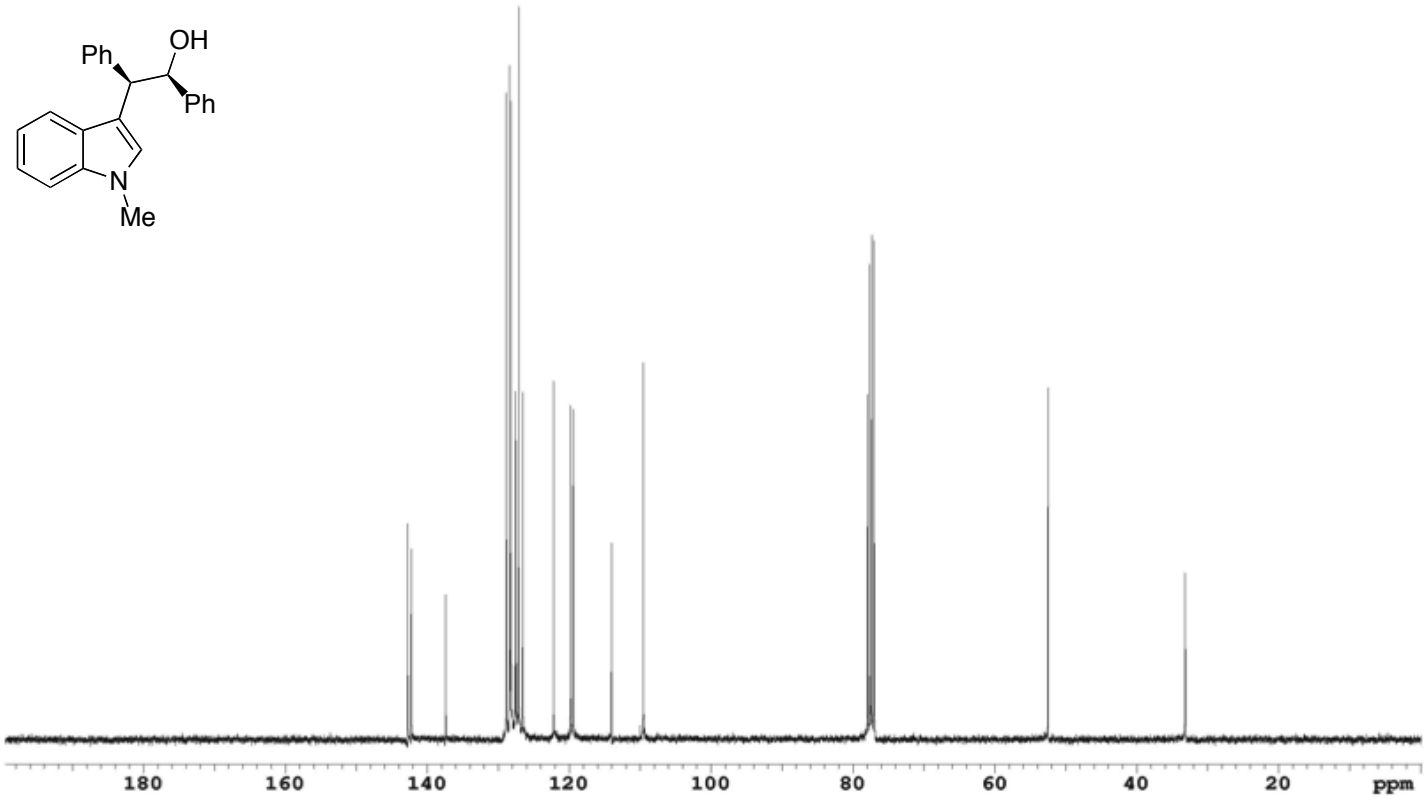


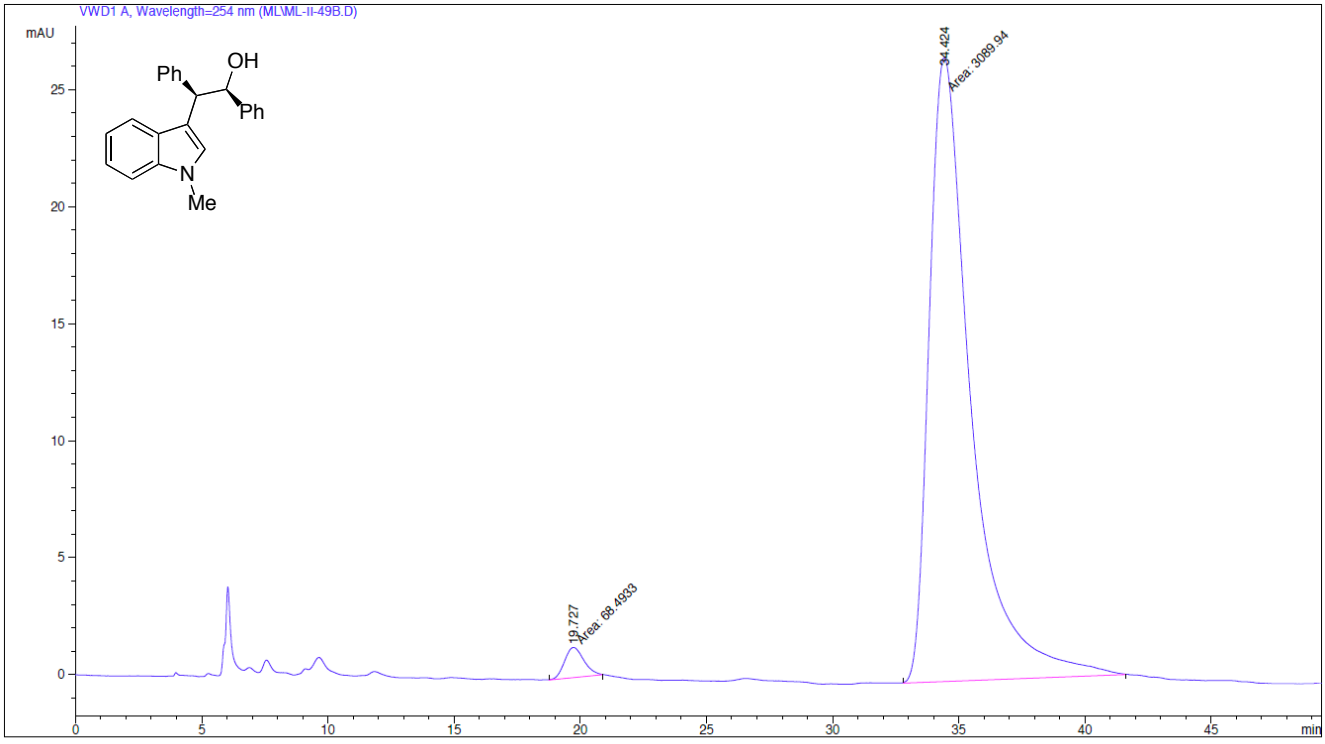


Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.061	MM	1.3927	3.54299e4	423.99191	98.8434
2	36.201	MM	1.9314	414.57886	3.57753	1.1566
Totals :				3.58445e4	427.56944	

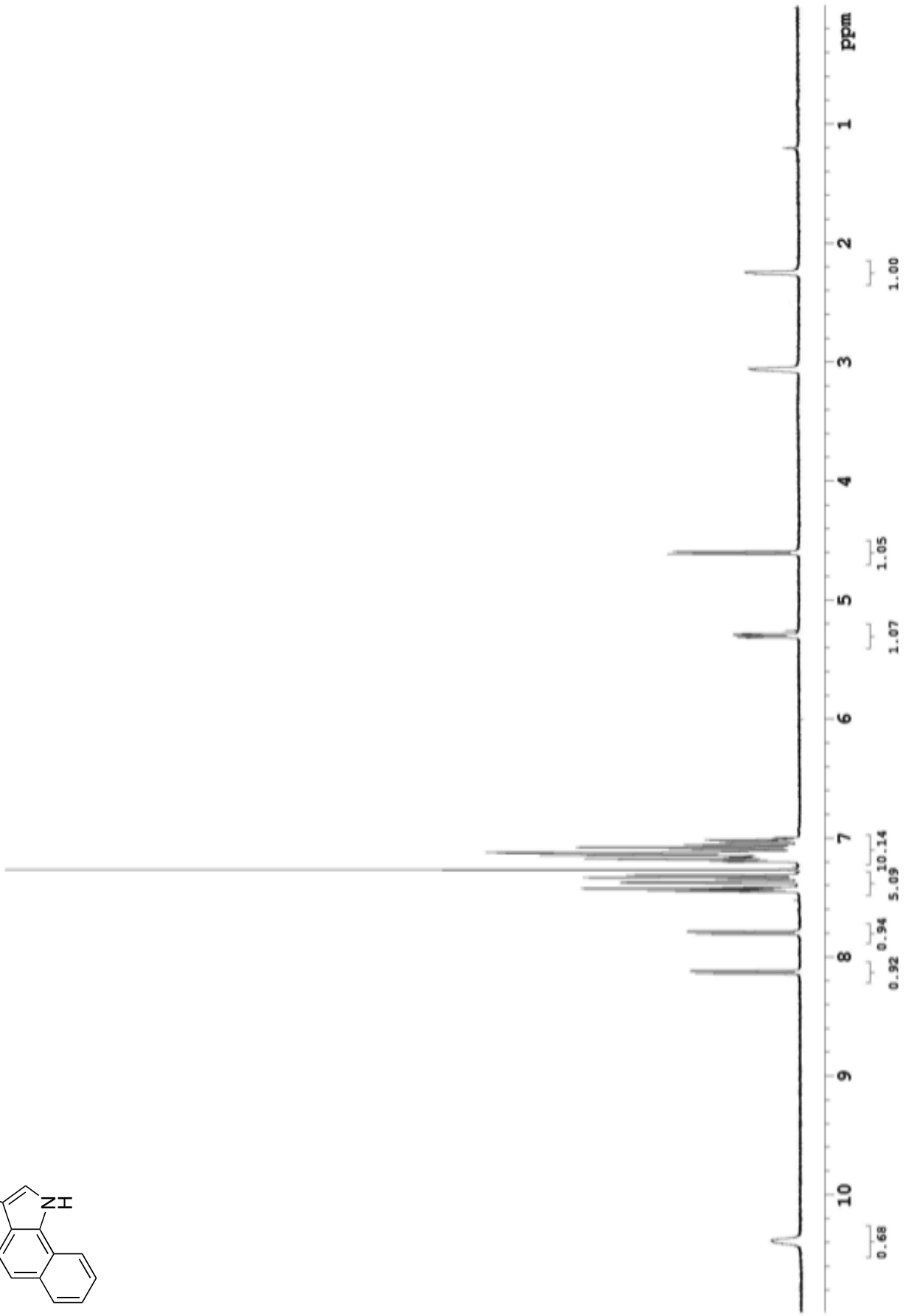


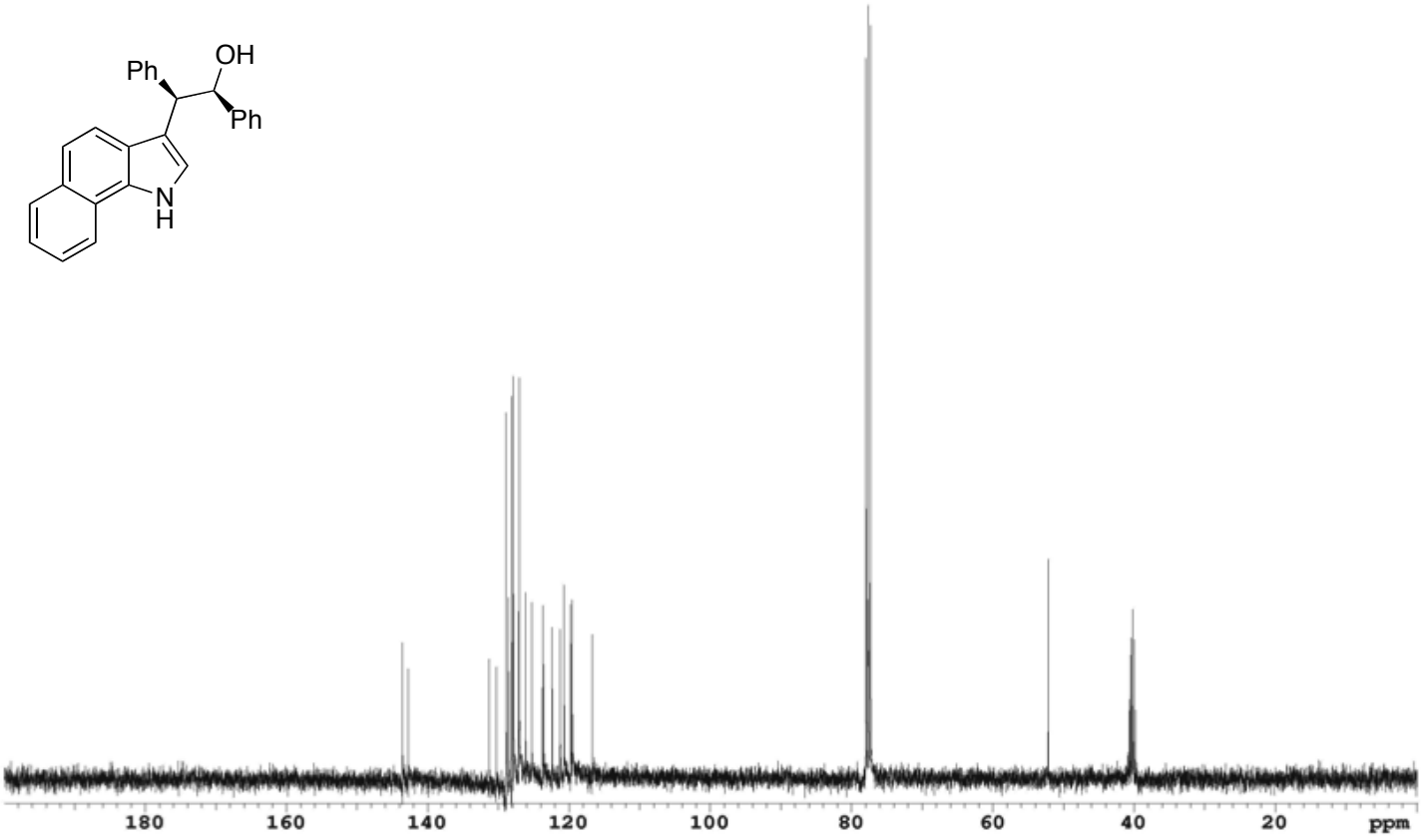


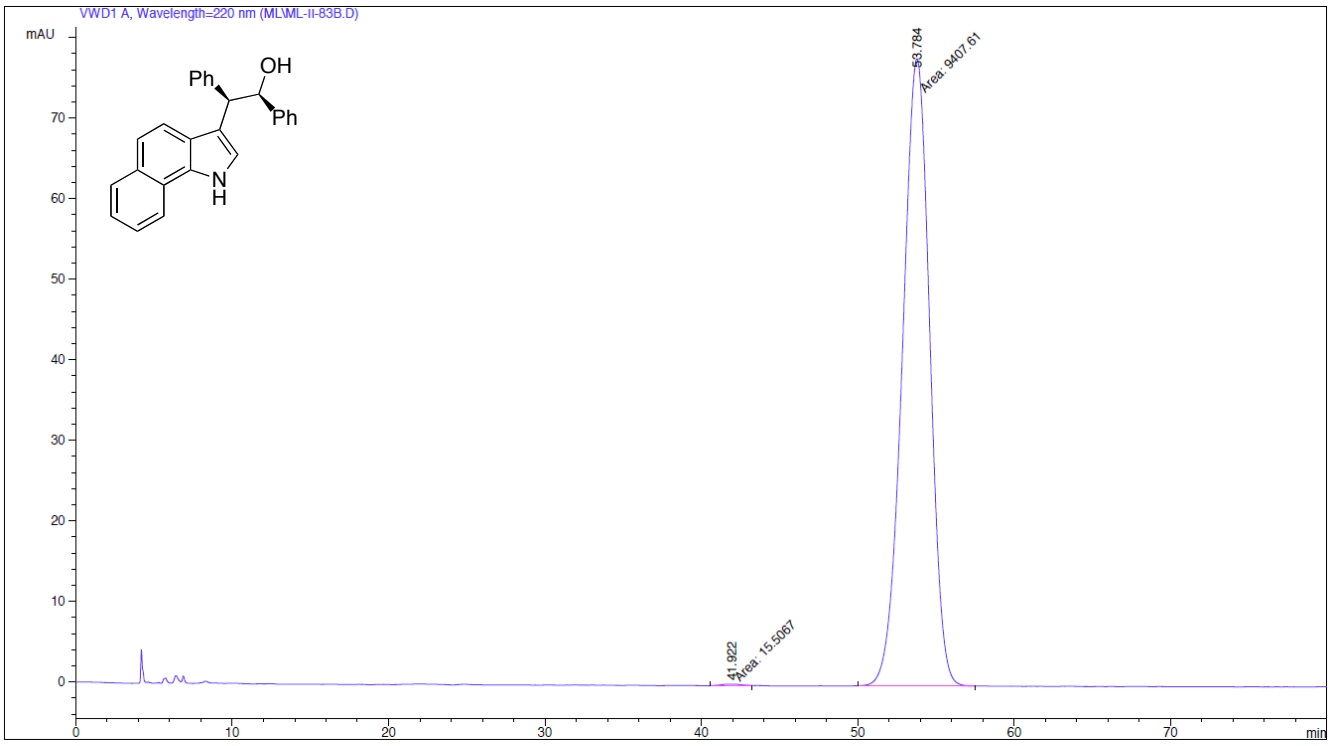


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.727	MM	0.8847	68.49332	1.29027	2.1686
2	34.424	MM	1.9315	3089.93921	26.66301	97.8314
Totals :				3158.43253	27.95328	

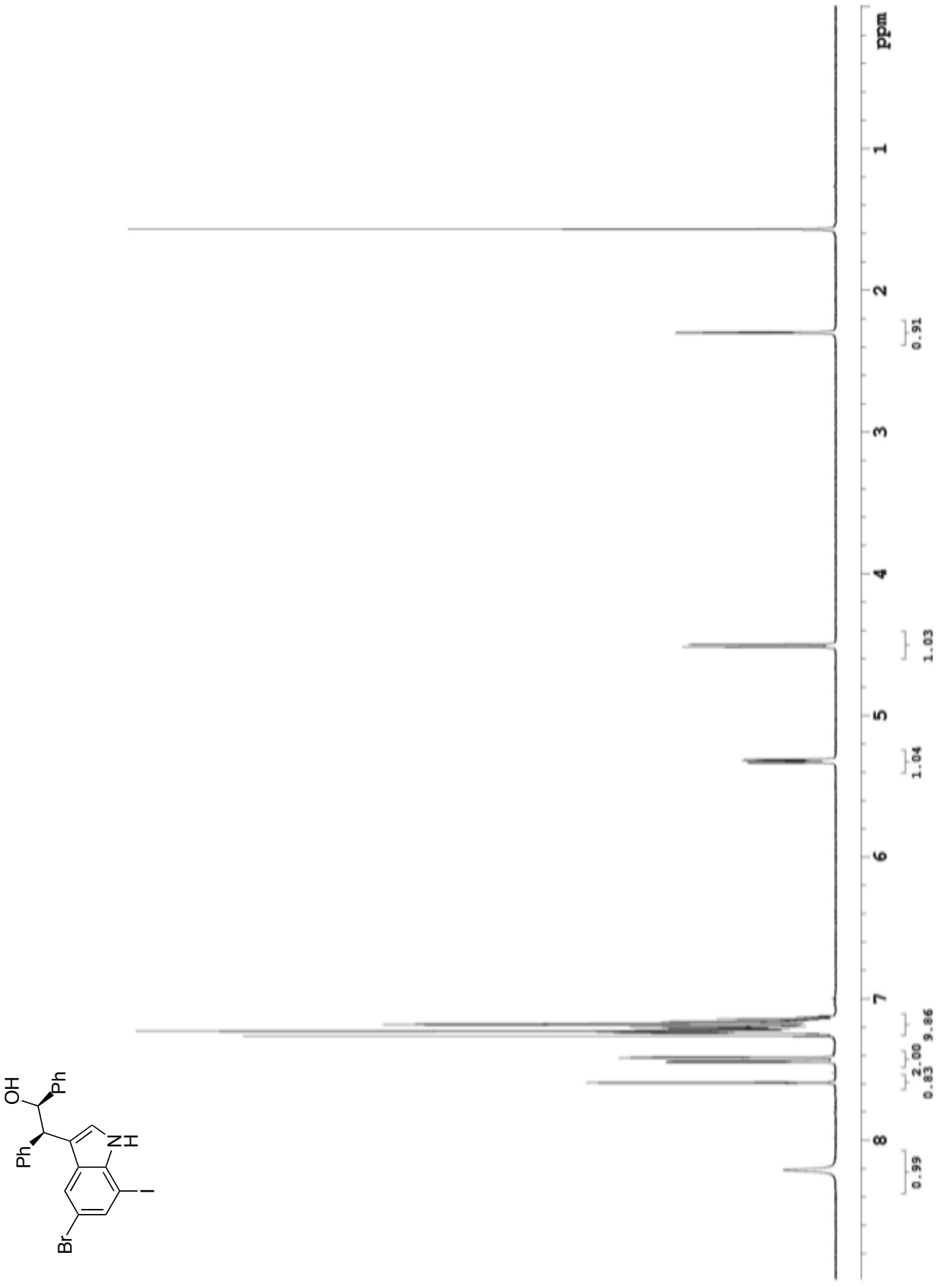






Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	41.922	MM	1.3514	15.50669	1.91244e-1	0.1646
2	53.784	MM	2.0151	9407.61230	77.80868	99.8354
Totals :				9423.11900	77.99992	


OH
Ph
Ph
NH
I
Br
ppm
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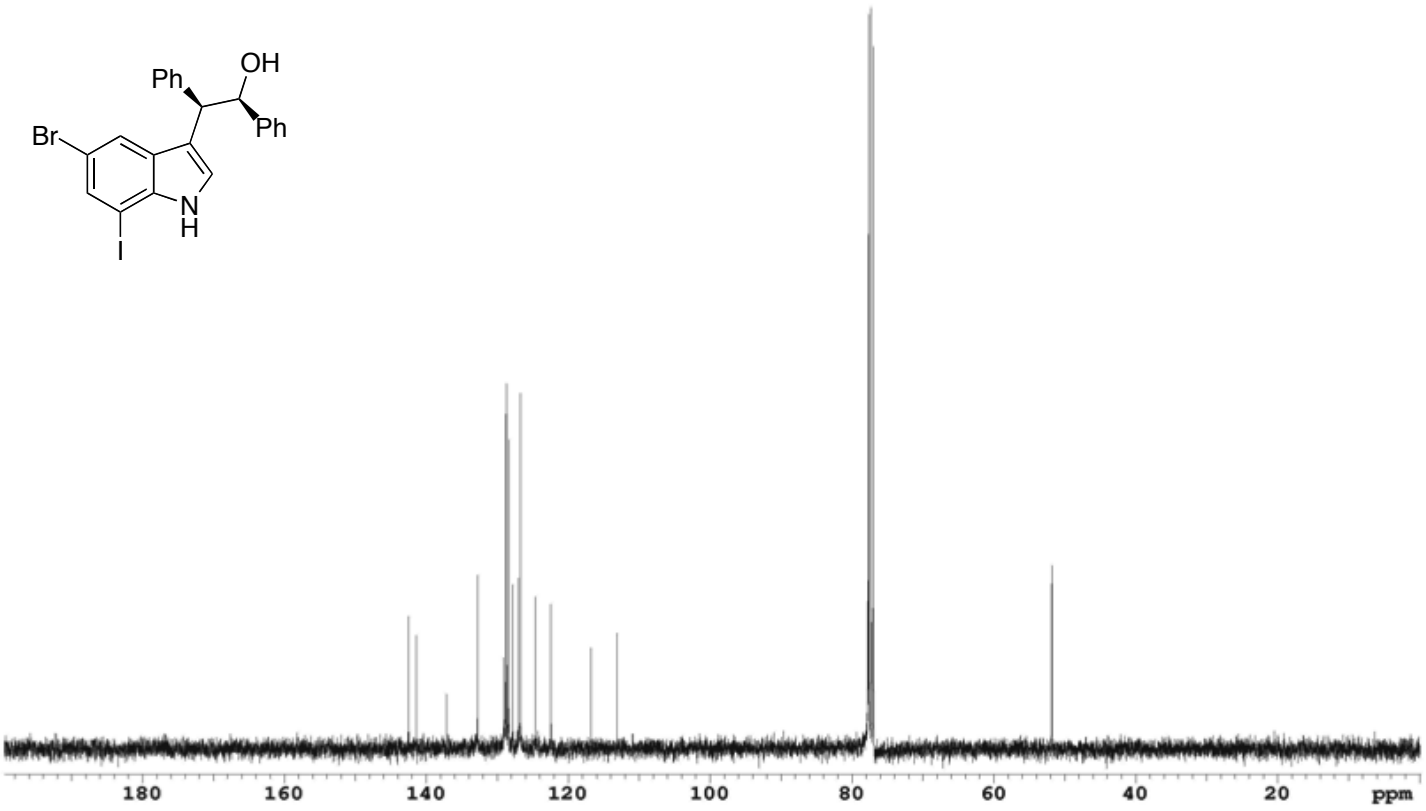
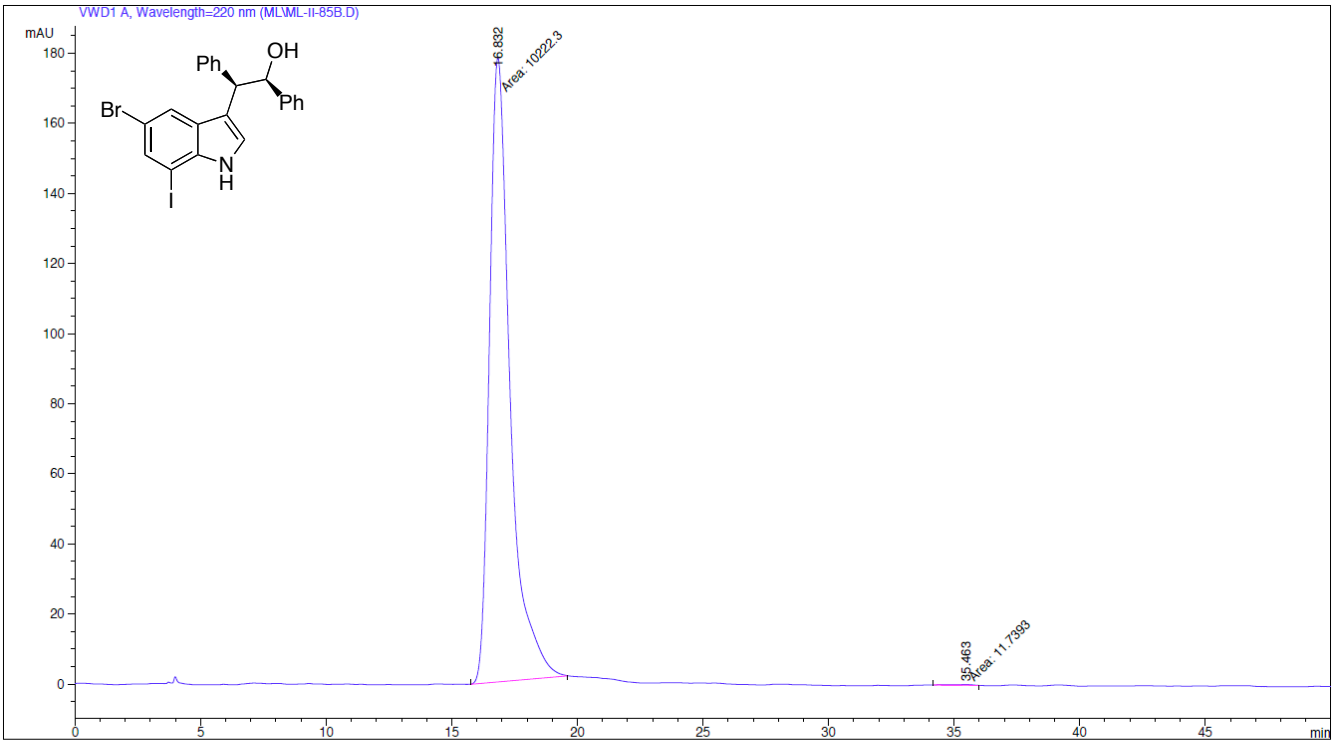
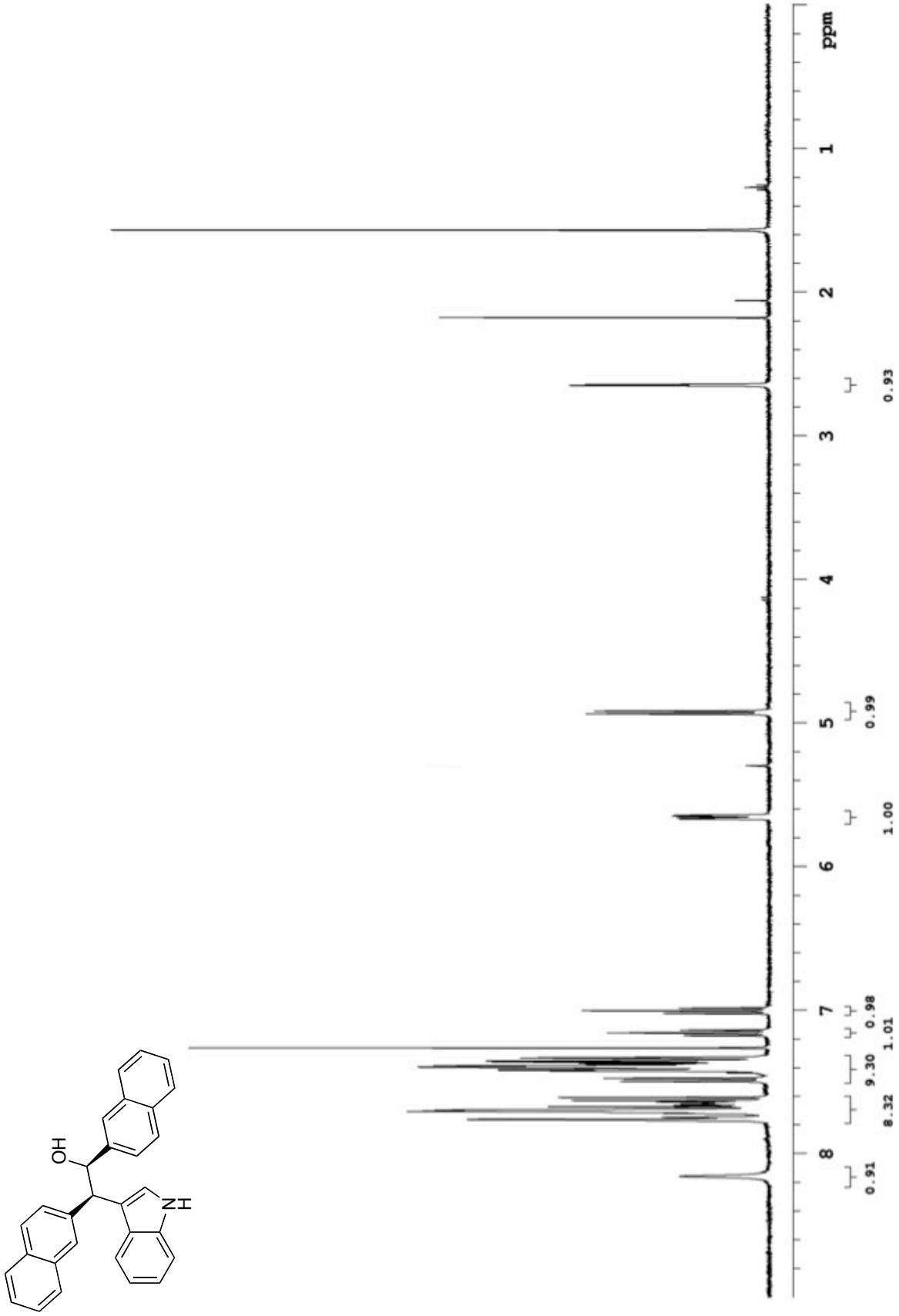
2
3
4
5
6
7
8
0.91
1.03
1.04
2.00
0.83
9.86
0.99

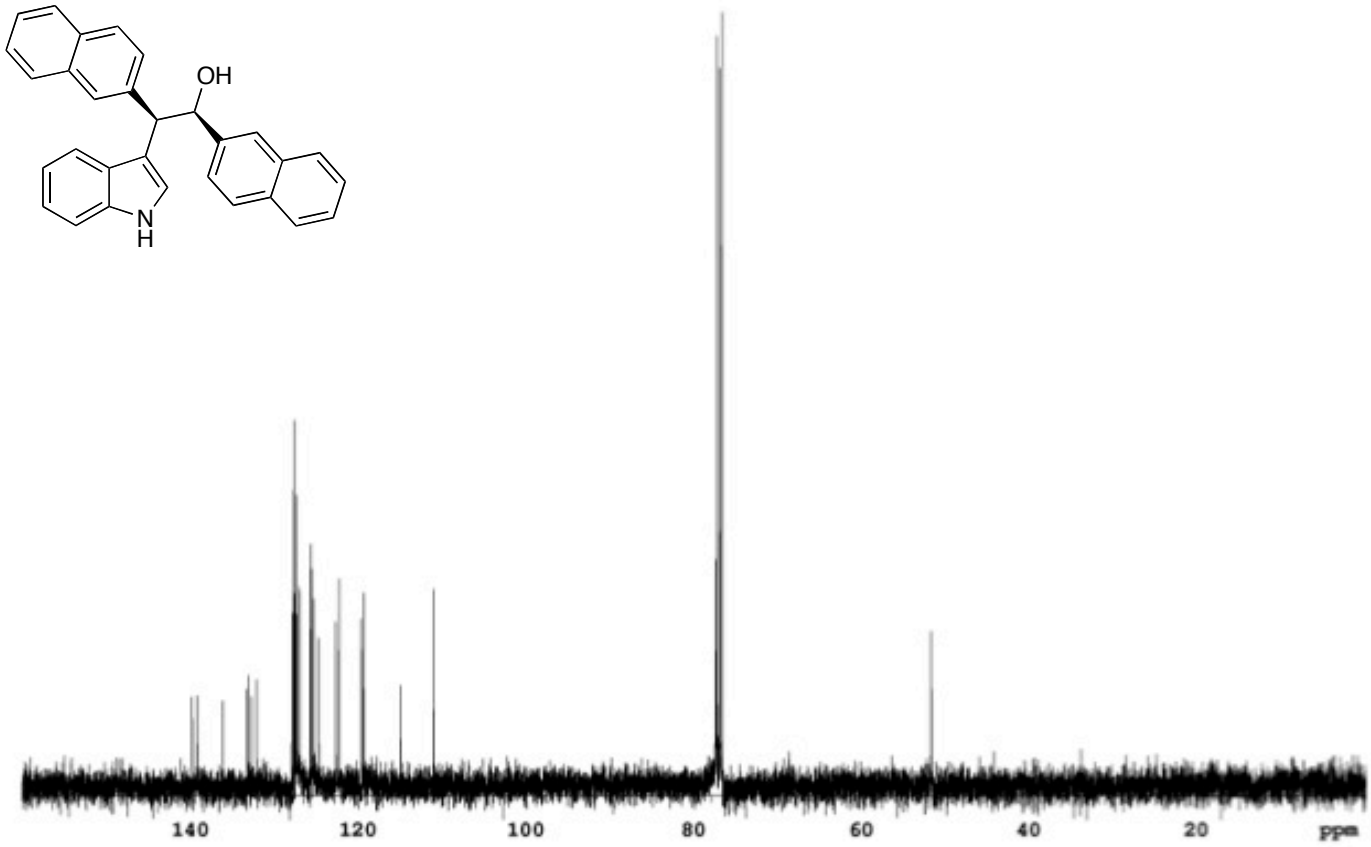


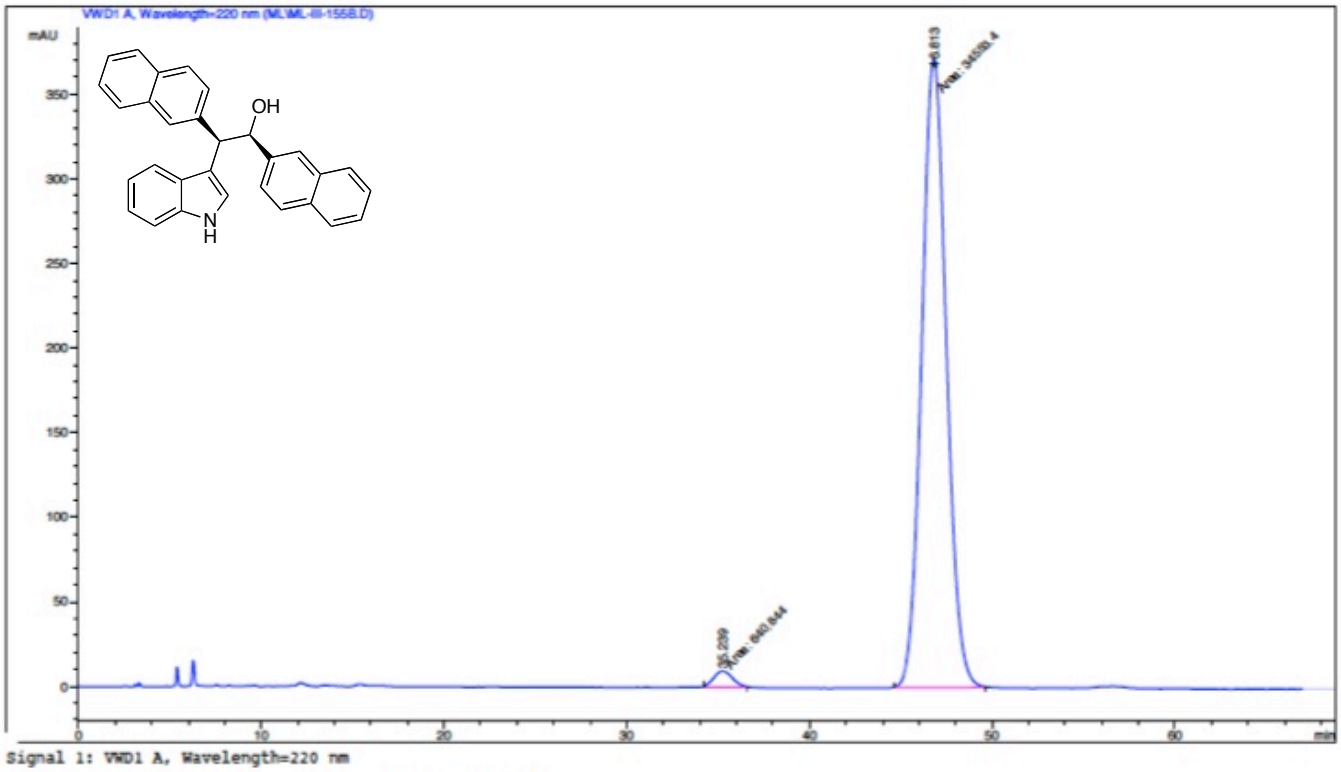


Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.832	MM	0.9568	1.02223e4	178.05617	99.8853
2	35.463	MM	0.8209	11.73933	2.38329e-1	0.1147
Totals :				1.02341e4	178.29450	

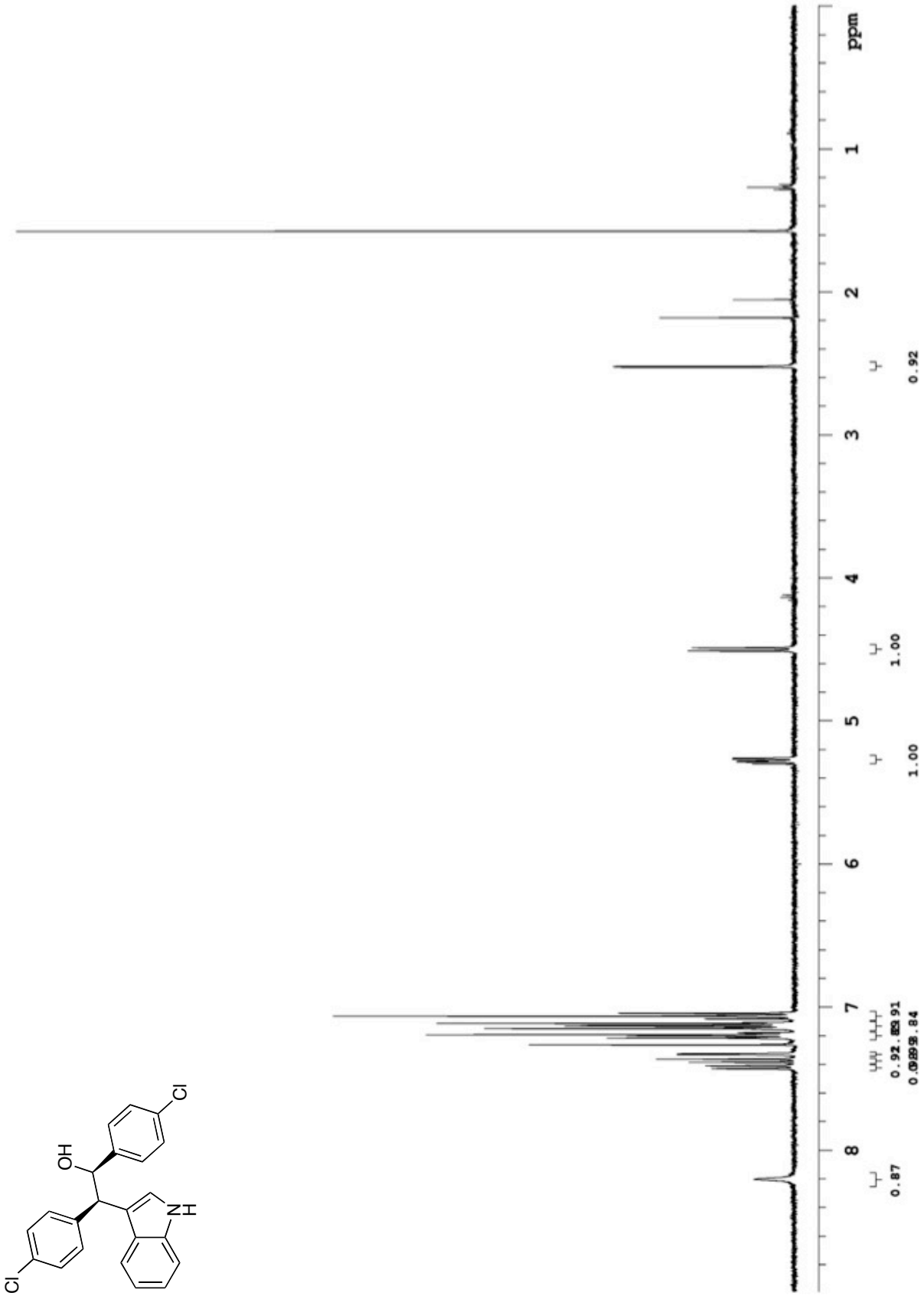


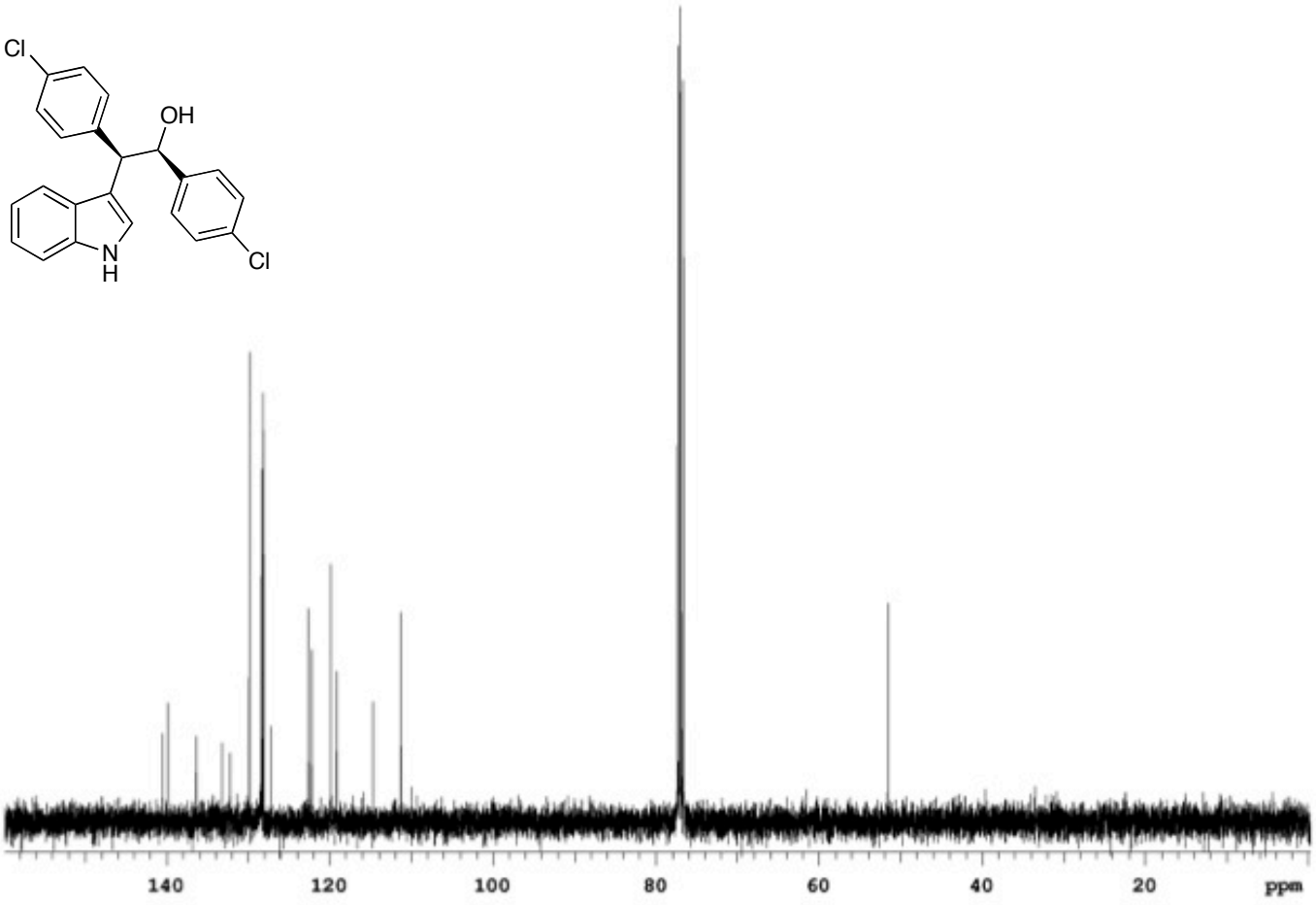


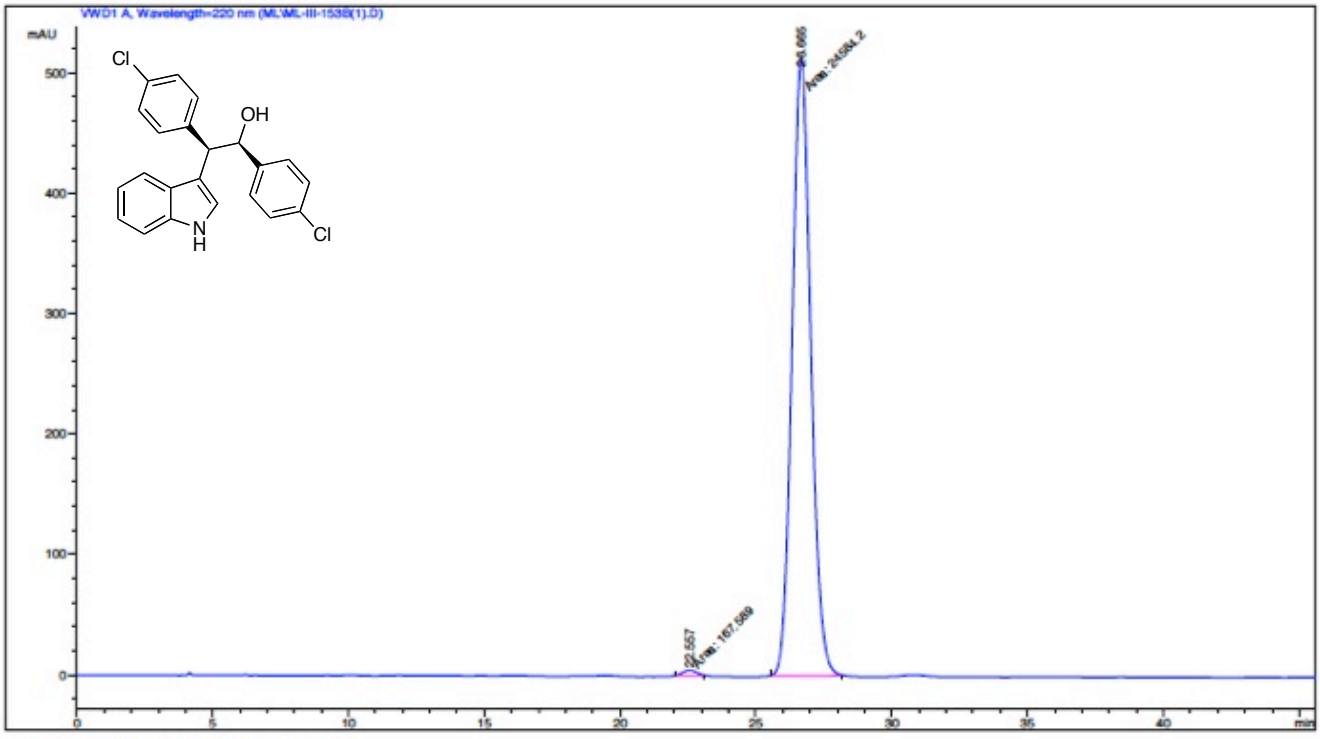


Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.239	MM	1.1556	640.84351	9.24266	1.8209
2	46.813	MM	1.5507	3.45534e4	371.38165	98.1791
Totals :				3.51943e4	380.62431	

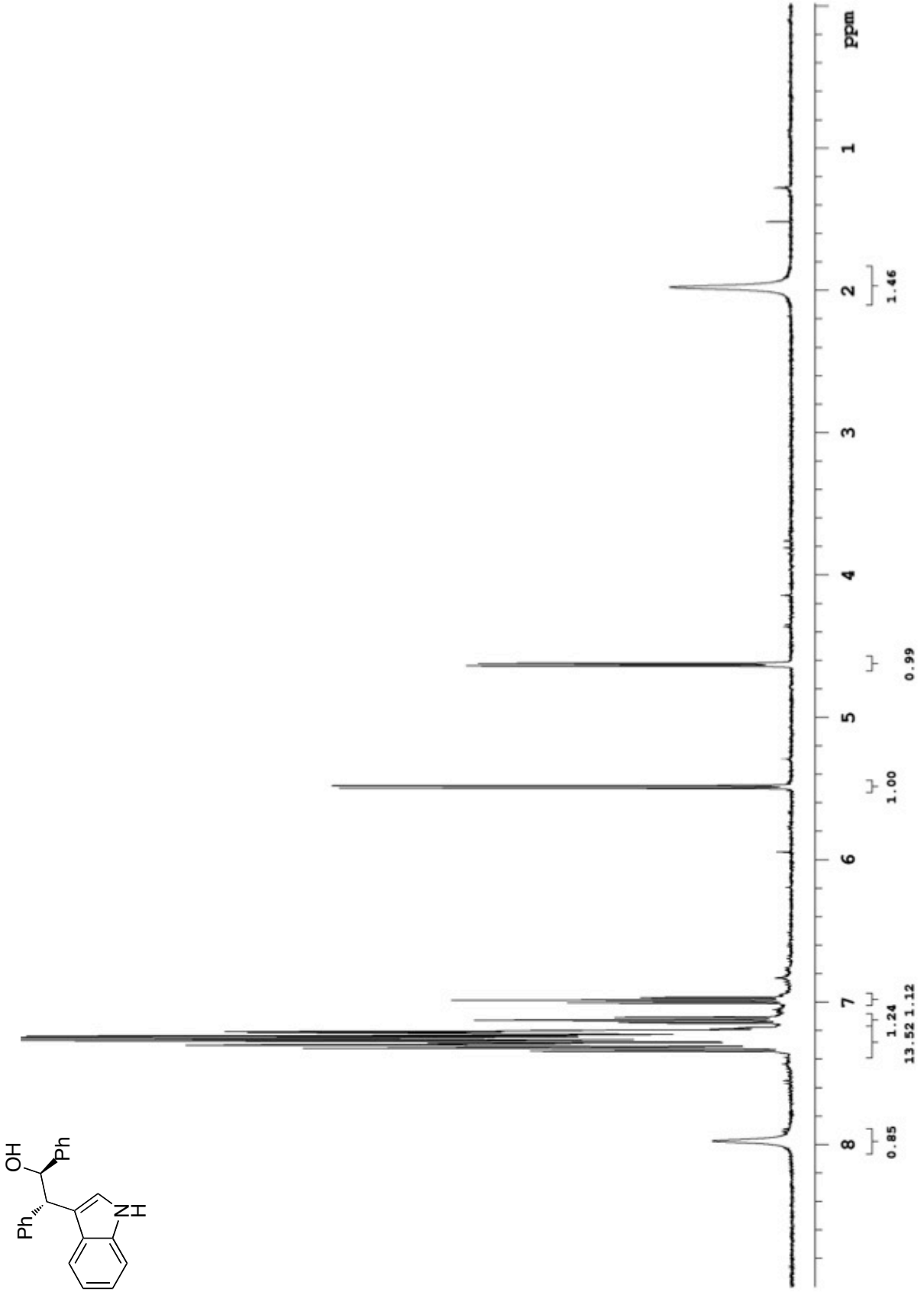


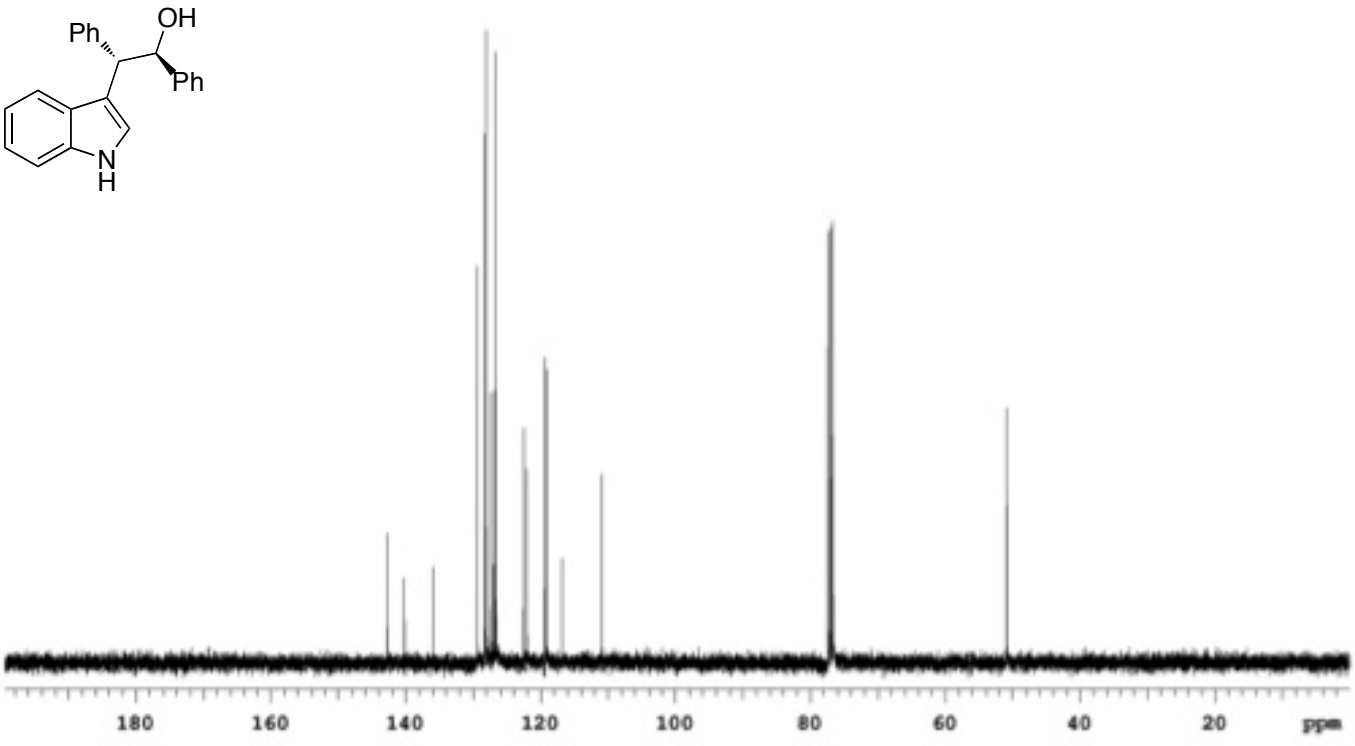


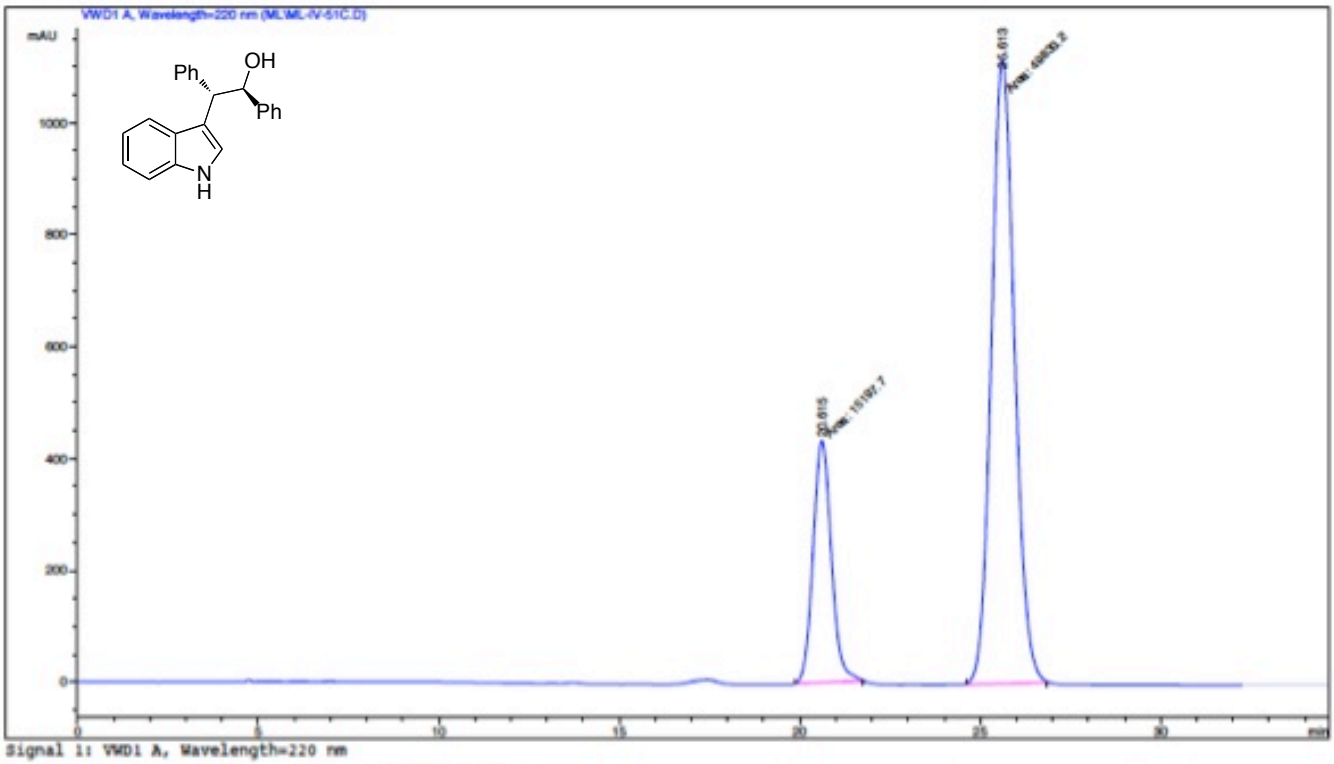


Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.557	MM	0.6205	167.58907	4.50122	0.6771
2	26.665	MM	0.7987	2.45842e4	513.02307	99.3229
Totals :				2.47518e4	517.52429	

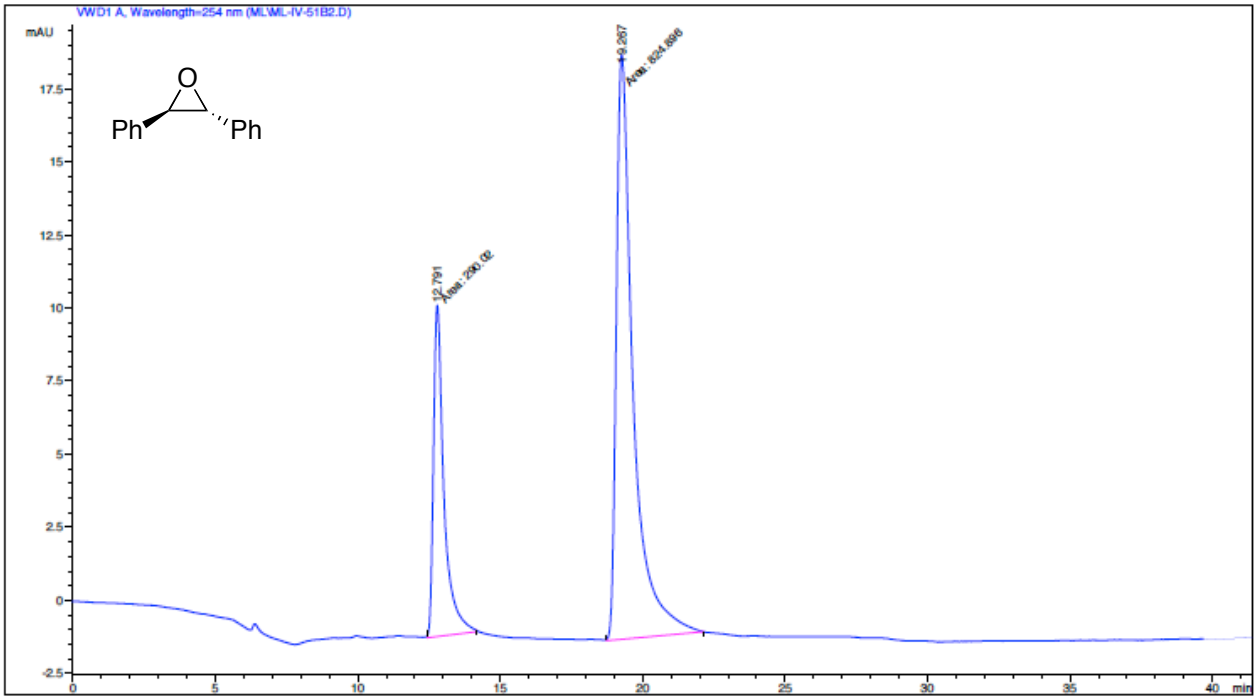

OH
Ph
Ph
NH
ppm
1
2
3
4
5
6
7
8
1.46
0.99
1.00
1.24
13.52
1.12
0.85





Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.615	MM	0.5857	1.51977e4	432.42847	23.3700
2	25.613	MM	0.7446	4.98332e4	1115.44226	76.6300
Totals :				6.50309e4	1547.87073	



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.791	MM	0.4266	290.01962	11.32957	26.0127
2	19.267	MM	0.6874	824.89642	20.00179	73.9873