SUPPORTING INFORMATION

Enantioselective Synthesis of Pyrroloindolines via Non-Covalent Stabilization of Indole Radical Cations and Applications to the Synthesis of Alkaloid Natural Products

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General Information

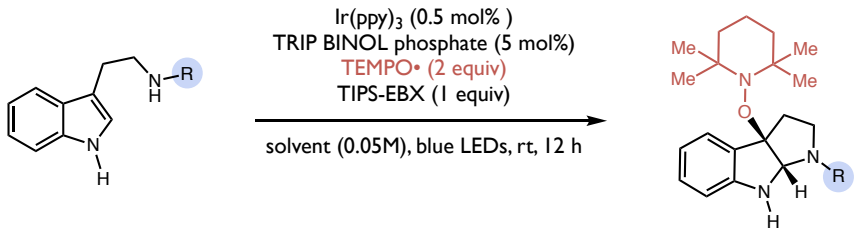
Materials:

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished by flash chromatography on Silicycle F60 silica gel or Sorbtech neutral alumina 32-63 μm according to the method of Still.[3] All reactions were carried out in well ventilated fume hoods. Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates or Sorbtech neutral alumina 250 μm. Visualization of the developed chromatogram was performed by irradiation with 254 nm UV light or treatment with a solution of ceric ammonium molybdate stain followed by heating. Yields refer to purified compounds unless otherwise noted.

Instrumentation:

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 (500 and 126 MHz for ^{1}H and ^{13}C, respectively) instrument, and are internally referenced to residual protio-solvent signals: $CDCl_3$ at δ 7.26 and 77.0 ppm, CD_3CN at δ 1.94 and 1.32 ppm, or CD_3OD at δ 3.31 and 49.0 ppm. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained at Princeton University mass spectrometry facility using an Agilent 6210 TOF LC/MS (Electrospray Ionization). The enantiomeric excess (ee) was determined using High Pressure Liquid Chromatography (HPLC) performed on an Agilent 1260 Infinity Series LC using commercial ChiralPak columns, notably ChiralPak AD-H (5 μm particle size, 4.6 mm vs. 250 mm), ChiralPak AS-H (5 μm particle size, 4.6 mm vs. 250 mm), and ChiralPak OD-H (5 μm particle size, 4.6 mm vs. 250 mm). Optical rotations were measured on a Jasco P-1010 polarimeter with $[\alpha]_D$ values reported in degrees; concentration (c) is in g/100 mL. Cyclic voltammograms were acquired on a CH Instruments 600E potentiostat. Stern-Volmer experiments were conducted on an Agilent Cary Eclipse Fluorescence Spectrophotometer.

Optimization of Enantioselective PCET Reaction:

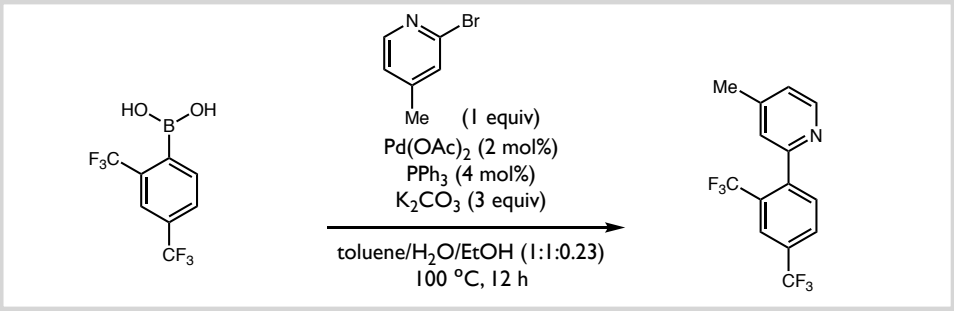


Entry	R	solvent	% yield	% ee
1	Cbz	THF	73	89
2[a]	Cbz	THF	85	89
3	Cbz	toluene	80	48
4	Cbz	dioxane	71	89
5	Cbz	MTBE	48	83
6	Cbz	DME	61	90
7	Cbz	CH_2Cl_2	77	52
8	CO_2Me	THF	61	73
9	Boc	THF	67	50
10	Ts	THF	64	42

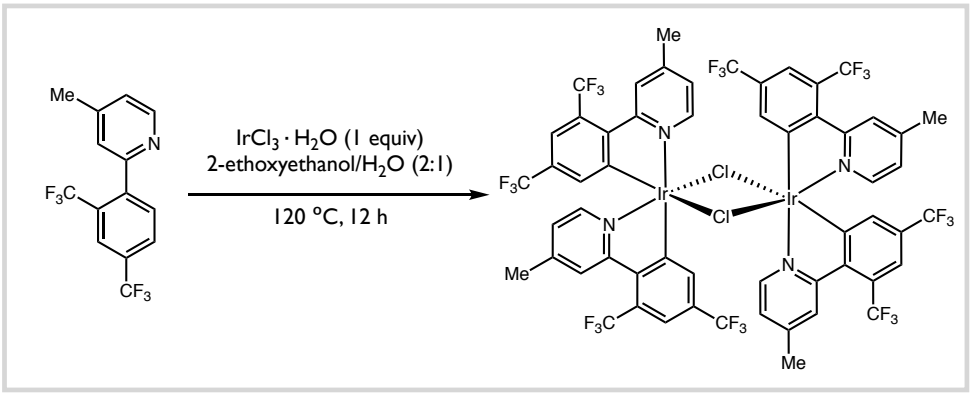
[a] with 1.2 equivalents of TIPS-EBX

Table S1: Evaluation of solvents and protecting groups in enantioselective PCET reaction.

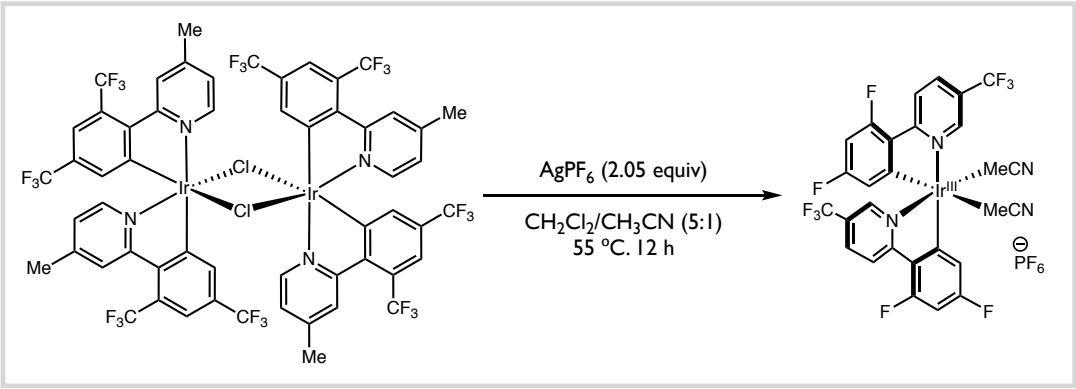
Synthesis of the Iridium photocatalyst:



2-bromo-4-methylpyridine (3 g, 17.44 mmol, 1 equiv.) and [2,4-bis(trifluoromethyl)phenyl] boronic acid (4.95 g, 19.18 mmol, 1.1 equiv.) were added to a 250-mL three-neck flask fitted with a condenser and stir bar. Palladium(II) acetate (0.078g, 0.349 mmol, 0.02 equiv.), triphenylphosphine (0.183 g, 0.698 mmol, 0.06 equiv.), and K_2CO_3 (7.23 g, 52.3 mmol, 3 equiv.) were then added and the flask was evacuated and backfilled with argon. A degassed 1:1:0.23 mixture of toluene/H_2O/EtOH was finally added to the flask via syringe and the reaction mixture was vigorously stirred at 100 °C for 12 hrs. After this time, the reaction was cooled to room temperature and the phases were separated. The aqueous layer was extracted with dichloromethane three times and the combined organic extracts were washed with brine, dried over $NaSO_4$, and concentrated *in vacuo* to give the crude product which was further purified by column chromatography on silica gel in ethyl acetate/hexanes to yield the product as a white solid (4.33 g, 81%). IR (neat): 2339, 1738, 1626, 1567, 1478, 1345, 1275, 1174, 1130, 1088, 1069, 1033, 1024, 911, 852, 833, 709, 667, cm^{-1}.; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 8.02 (s, 1H), 7.87 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 2.42 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.68, 150.13, 143.85, 136.93, 133.10, 132.79, 131.00, 130.74, 129.56, 128.58, 123.93, 123.49, 18.54. HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{10}F_6N$) requires *m/z* 306.07120, found *m/z* 306.07120 with a difference of 0.03 ppm.

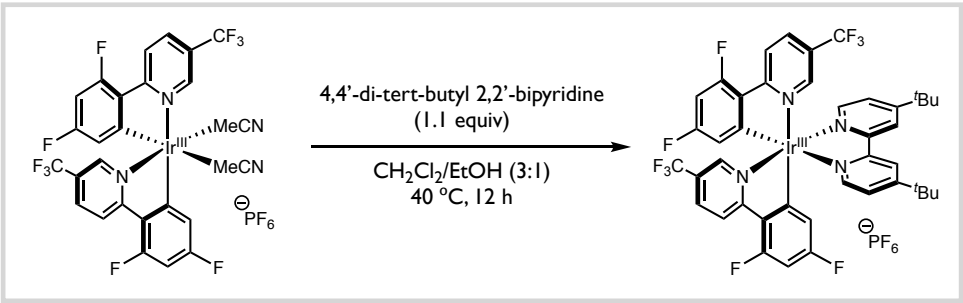


To a 250-mL three-neck flask equipped with condenser and stir bar were added iridium(III) chloride hydrate (1.5g, 4.74 mmol, 1 equiv.) and 2-[2,4-bis(trifluoromethyl)phenyl]-4-methylpyridine (2.96, 9.71 mmol, 2.05 equiv.). The flask was evacuated and backfilled with argon then degassed 2-ethoxyethanol and H_2O were added *via* syringe. The reaction mixture was vigorously stirred and allowed to stir at reflux (~120 °C) for 12 hrs. The reaction was then cooled to room temperature and filtered to give the crude product as a yellow solid which was then washed with water (400 mL), air dried for 1 hour, and then further dried in a vacuum oven until all residual solvent was removed. The product was carried on to the next step without further purification.



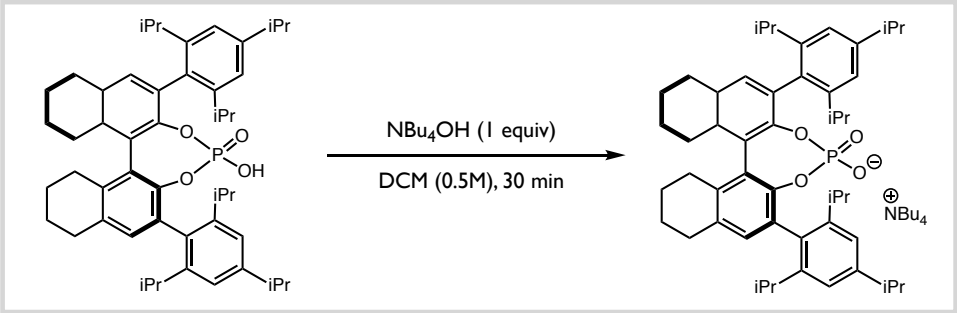
Silver(I) hexafluorophosphate (0.93g, 3.678mmol, 2.05 equiv.) and iridium dimer (3g, 1.794 mmol, 1 equiv.) was placed in a flame-dried 250-mL three-neck flask under a completely inert glovebox atmosphere (silver hexafluorophosphate is hygroscopic). The flask was fitted with a condenser and stir bar then sealed and removed from the glovebox. Degassed anhydrous acetonitrile (10 mL) and dichloromethane (50 mL) were then added *via* syringe. The reaction mixture was vigorously stirred at 55 °C for 12 hrs. The reaction was then cooled to room temperature and filtered to remove AgCl. The solid was washed with dichloromethane (100 mL) and the filtrate was concentrated to

give the crude product as a yellow solid. The solid was dissolved in warm dichloromethane then cooled down and pentanes were added to afford the product as yellow crystals which were carried through to the next step without further purification.



To a 250-mL three-neck flask fitted with a condenser and stir bar, the cationic iridium complex (2.8g, 2.96 mmol, 1 equiv.) and 4,4'-di-tert-butyl-2,2'-bipyridine (0.874g, 3.26 mmol, 1.1 equiv.) were added. The flask was evacuated and backfilled with argon then degassed dichloromethane (36 mL) and ethanol (12 mL) were added *via* syringe. The reaction mixture was vigorously stirred at 40 °C for 12 hours in which time it turned from clear yellow to turbid. The reaction was then cooled to room temperature and filtered. The solid was washed with dichloromethane (100 mL) and the filtrate was collected and concentrated to give the crude product as a yellow solid. The product was recrystallized by vapor diffusion in acetone/pentanes to yield bright yellow crystals which were then filtered and washed with pentanes to deliver pure product (3.04g, 85% yield). IR (neat): 2050, 1737, 1618, 1486, 1360, 1333, 1285, 1216, 1126, 1087, 835, cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.59 (s, 2H), 8.31 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.67 (s, 2H), 7.57 (d, *J* = 5.8 Hz, 2H), 7.50 (s, 2H), 7.46 (d, *J* = 5.9 Hz, 2H), 6.33 (s, 2H), 2.27 (s, 3H), 2.17 (s, 3H), 1.46 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.10, 160.59, 155.68, 153.65, 149.53, 148.51, 144.83, 139.76, 137.09, 130.60, 130.11, 125.80, 125.02, 123.39, 77.28, 77.23, 77.02, 76.77, 35.96, 30.97, 30.13, 22.36, 18.22, 14.09; HRMS (ESI) exact mass calculated for $[M]^+$ ($C_{46}H_{40}F_{12}IrN_4$) requires *m/z* 1067.26618, found *m/z* 1067.26671 with a difference of 0.5 ppm.

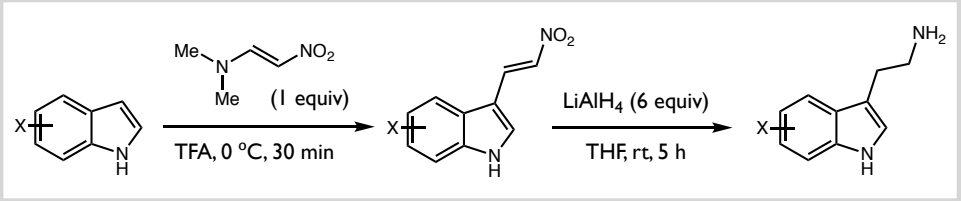
Synthesis of H8-TRIP BINOL Phosphate Base



H8-TRIP BINOL phosphoric acid was synthesized according to a previously reported method.[4]

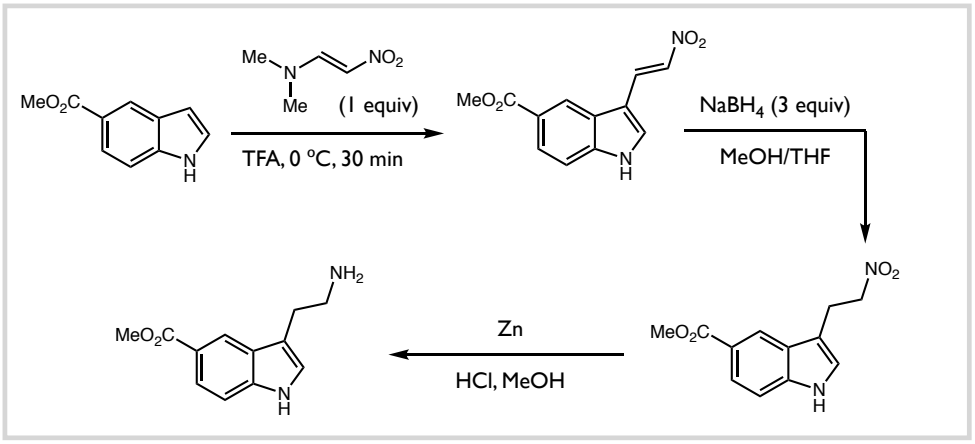
To a solution of (S)-H8-TRIP BINOL phosphoric acid (1 g, 1.328 mmol, 1 equiv) in CH_2Cl_2 (0.5 M) was added 1 M tetrabutylammonium hydroxide solution in MeOH (1.328 mL, 1.328 mmol, 1 equiv).[5] The resulting solution was allowed to stir at rt for 30 min then concentrated *in vacuo* to yield (S)-H8-TRIP BINOL phosphate (1.29 g, 1.297 mmol, 98% yield) as a slightly off-white solid.

General procedure for the synthesis of tryptamine derivatives (GP1):



4-Br, 5-Br, and 6-Br tryptamines were synthesized according to literature procedure and characterization data is consistent with reported data.[6]

5-Cl, 5-OMe, and 5-Me tryptamine hydrochloride salts are commercially available and were used as the free base.

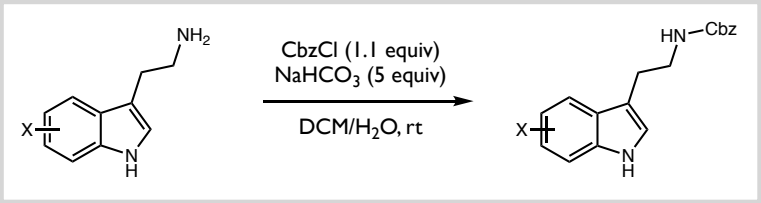


A 25-mL round bottom flask was charged with *N*,*N*-dimethyl-2-nitroethenamine (1.458 g, 12.56 mmol, 1.1 equiv) and methyl 1H-indole 5-carboxylate (2 g, 11.42 mmol, 1 equiv). To the resulting slurry was added trifluoroacetic acid (11.42 mL, 1 equiv) at room temperature. The reaction was allowed to stir at rt for 2 h then the reaction was slowly quenched with sat. aqueous $NaHCO_3$ solution. The aqueous mixture was extracted with EtOAc (3x) and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to yield the crude product as a bright yellow solid which was used without further purification.

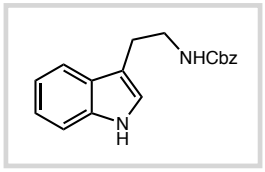
To a stirred slurry of $NaBH_4$ (3 equiv) in THF/MeOH (4:1) was slowly added the nitroalkene. The mixture was stirred overnight at room temperature then neutralized with 1 M HCl and extracted with ethyl acetate (3x). The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by column chromatography on silica gel using 5-15% EtOAc in hexanes to afford methyl 3-(2-nitroethyl)-1*H*-indole-5-carboxylate as a light yellow solid.

Methyl 3-(2-nitroethyl)-1*H*-indole-5-carboxylate: IR (thin film): 3335, 1693, 1677, 1551, 1430, 1284, 1247, 1113, 766, 747 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.30 (s, 1H), 7.94 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.14 (d, *J* = 2.3 Hz, 1H), 4.69 (t, *J* = 7.0 Hz, 2H), 3.95 (s, 3H), 3.52 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.10, 138.92, 126.45, 124.11, 124.05, 122.16, 121.24, 111.67, 111.28, 75.73, 52.14, 23.45. HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{12}H_{12}N_2NaO_4$) requires m/z 271.06948, found 271.06901 with a difference of 0.31 ppm.

General procedure for the Cbz protection of tryptamines (GP2):[7]

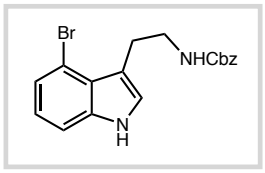


To a solution of tryptamine (1 equiv) in dichloromethane (0.1 M) was added a saturated aqueous solution of $NaHCO_3$ (5 equiv). The suspension was vigorously stirred and freshly distilled benzyl chloroformate (1.1 equiv) was added. The mixture was allowed to stir at rt for 2 h then the phases were separated and the aqueous phase extracted with dichloromethane (3x). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel using ethyl acetate and hexanes.



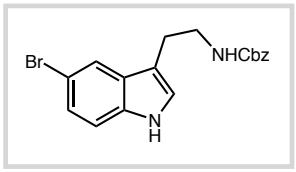
Benzyl (2-(1H-indol-3-yl)ethyl)carbamate

The title compound was synthesized according to general procedure **GP2** and purified on silica gel using a gradient of 10% ethyl acetate/hexanes to 30% ethyl acetate/hexanes to yield product as a white solid (92% by column chromatography, 79% by recrystallization). IR (neat): 3409, 3328, 3059, 2939, 1696, 1619, 1517, 1455, 1436, 1338, 1245, 1227, 1135, 1081, 1045, 1008, 741, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.29 (m, 6H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.01 (s, 1H), 5.10 (s, 2H), 4.82 (s, 1H), 3.55 (q, *J* = 6.5 Hz, 2H), 2.99 (t, *J* = 6.8 Hz, 2H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.37, 136.62, 136.36, 128.52, 128.14, 128.10, 127.26, 122.23, 122.06, 119.51, 118.77, 112.90, 111.20, 66.60, 41.25, 25.74.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{19}N_2O_2$) requires *m/z* 295.14411, found *m/z* 295.14388 with a difference of 0.75 ppm. Spectral data is in agreement with the reported literature values.[7]



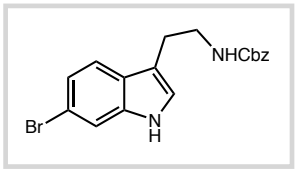
Benzyl (2-(4-bromo-1*H*-indol-3-yl)ethyl)carbamate

The title compound was synthesized according to general procedure **GP2** and purified on silica gel using a gradient of 20% ethyl acetate/hexanes to 30% ethyl acetate/hexanes to yield product as an off-white solid (72% yield). IR (thin film): 3419, 3309, 3063, 3034, 2940, 1694, 1517, 1424, 1334, 1243, 1184, 1137, 1041, 911, 773, 737, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.38 – 7.29 (m, 5H), 7.26 (t, *J* = 8.0 Hz, 2H), 7.04 – 6.87 (m, 2H), 5.10 (s, 2H), 4.98 – 4.56 (m, 0.85 H, major rotamer), 4.65 (s, 0.15 H, minor rotamer) 3.57 (q, *J* = 6.7 Hz, 2H), 3.20 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.61, 137.84, 136.72, 128.63, 128.21, 128.20, 125.38, 124.30, 124.05, 122.97, 114.25, 113.60, 110.79, 66.73, 42.61, 26.57; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{18}BrN_2O_2$) requires m/z 373.05462, found *m/z* 373.05496 with a difference of 0.92 ppm.



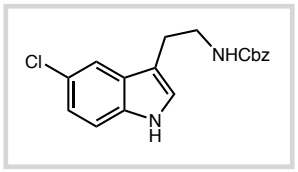
Benzyl (2-(5-bromo-1*H*-indol-3-yl)ethyl)carbamate

The title compound was synthesized according to general procedure **GP2** and purified on silica gel using a gradient of 20% ethyl acetate/hexanes to 30% ethyl acetate/hexanes to yield product as a white solid (84%). IR (thin film): 3422, 3319, 3033, 2940, 1698, 1519, 1456, 1250, 1137, 1094, 1043, 884, 795, 776, 746, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.71 (s, 1H), 7.39 – 7.29 (m, 5H), 7.28 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 5.10 (s, 2H), 4.81 (br s, 0.88 H, major rotamer), 4.58 (br s, 0.12 H, minor rotamer), 3.51 (q, *J* = 6.6 Hz, 2H), 2.93 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.48, 136.66, 135.06, 129.23, 128.67, 128.29, 128.27, 125.18, 123.41, 121.50, 112.92, 112.79, 66.83, 41.33, 25.70. HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{17}BrN_2O_2$) requires m/z 373.05462, found *m/z* 373.05436 with a difference of 0.69 ppm.



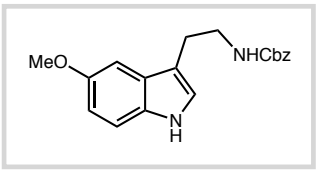
Benzyl (2-(6-bromo-1*H*-indol-3-yl)ethyl)carbamate

The title compound was synthesized according to general procedure **GP2** and purified on silica gel using a gradient of 20% ethyl acetate/hexanes to 30% ethyl acetate/hexanes to yield product as a light tan solid (92% yield). IR (thin film): 3420, 3319, 3033, 2940, 1696, 1518, 1455, 1333, 1244, 1136, 1048, 895, 802, 775, 741, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.49 (d, *J* = 1.7 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.40 – 7.29 (m, 5H), 7.20 (d, *J* = 8.3 Hz, 1H), 6.95 (s, 1H), 5.10 (s, 2H), 4.84 (s, 1H), 3.51 (q, *J* = 6.6 Hz, 2H), 2.94 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.52, 137.22, 136.63, 128.67, 128.28, 128.25, 126.35, 122.87, 122.75, 120.10, 115.83, 114.26, 113.19, 66.80, 41.40, 25.72. HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{18}BrN_2O_2$) requires *m/z* 373.05462, found *m/z* 373.05441 with a difference of 0.55 ppm.



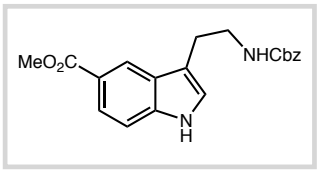
Benzyl (2-(5-chloro-1*H*-indol-3-yl)ethyl)carbamate

The title compound was synthesized according to general procedure **GP2** and purified on silica gel using a gradient of 20% ethyl acetate/hexanes to 30% ethyl acetate/hexanes to yield product as an off-white solid (91% yield). IR (thin film): 3422, 3319, 2939, 1696, 1517, 1458, 1243, 796, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.41 – 7.29 (m, 5H), 7.26 (d, *J* = 8.6 Hz, 1H), 7.14 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.99 (s, 1H), 5.11 (s, 2H), 4.85 (br s, 0.88 H, major rotamer), 4.63 (br s, 0.12 H, minor rotamer), 3.51 (q, *J* = 6.6 Hz, 2H), 2.92 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.51, 136.62, 134.78, 128.66, 128.53, 128.26, 128.24, 125.32, 123.60, 122.57, 118.34, 112.74, 112.36, 66.82, 41.33, 25.68; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{18}H_{18}ClN_2O_2$) requires *m/z* 329.10514, found *m/z* 329.10541 with a difference of 0.86 ppm.



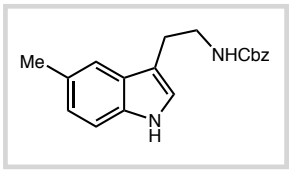
Benzyl (2-(5-methoxy-1*H*-indol-3-yl)ethyl)carbamate

The title compound was synthesized according to general procedure **GP2** and purified on silica gel using a gradient of 20% ethyl acetate/hexanes to 30% ethyl acetate/hexanes to yield product as a light brown oil (84% yield). IR (thin film): 3338, 2941, 1697, 1516, 1485, 1454, 1214, 1173, 1027, 796, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.46 – 7.32 (m, 5H), 7.26 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.98 – 6.85 (m, 2H), 5.17 (s, 2H), 5.11 – 5.02 (m, 0.85H, major rotamer), 4.85 (s, 0.15H, minor rotamer), 3.89 (s, 3H), 3.57 (q, *J* = 6.6 Hz, 2H), 2.97 (q, *J* = 13.5, 10.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.53, 153.97, 136.62, 131.60, 128.56, 128.14, 128.12, 127.67, 123.02, 112.38, 112.33, 112.09, 100.49, 66.66, 55.92, 41.32, 25.75; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{21}N_2O_3$) requires *m/z* 325.15467, found *m/z* 325.15517 with a difference of 1.55 ppm.



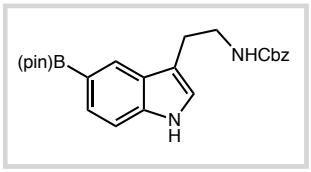
Methyl 3-(2-(((benzyloxy)carbonyl)amino)ethyl)-1*H*-indole-5-carboxylate

The title compound was synthesized according to general procedure **GP2** and purified on silica gel using a gradient of 20% ethyl acetate/hexanes to 30% ethyl acetate/hexanes to yield product as a white solid (89% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.90 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.39 – 7.27 (m, 6H), 5.10 (s, 2H), 4.89 (br s, 0.88 H, major rotamer), 4.65 (br s, 0.12 H, minor rotamer), 3.92 (s, 3H), 3.54 (q, *J* = 6.6 Hz, 2H), 2.99 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.30, 156.53, 139.07, 136.63, 128.63, 128.23, 128.19, 127.05, 123.65, 123.53, 121.79, 121.57, 114.39, 111.07, 66.79, 52.03, 41.36, 25.66. HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{20}H_{20}N_2NaO_4$) requires *m/z* 375.13208, found *m/z* 375.13181 with a difference of 0.79 ppm.



Benzyl (2-(5-methyl-1*H*-indol-3-yl)ethyl)carbamate

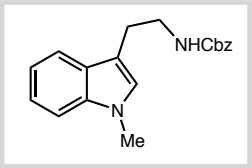
The title compound was synthesized according to general procedure **GP2** and purified on silica gel using a gradient of 10% ethyl acetate/hexanes to 30% ethyl acetate/hexanes to yield product as an off-white solid (93% yield). IR (thin film): 3405, 3329, 2925, 1695, 1514, 1454, 1243, 1226, 1133, 793, 735, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.31 – 7.19 (m, 6H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.94 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.85 (s, 1H), 5.02 (s, 2H), 4.76 (s, 0.85 H, major rotamer), 4.54 (s, 0.15 H, minor rotamer), 3.45 (q, *J* = 6.6 Hz, 2H), 2.86 (t, *J* = 6.8 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.50, 136.73, 134.82, 128.81, 128.63, 128.22, 128.20, 127.57, 123.89, 122.39, 118.50, 112.36, 111.01, 66.71, 41.36, 25.82, 21.63; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{20}H_{21}N_2O_2$) requires *m/z* 309.15976, found *m/z* 309.15974 with a difference of 0.04 ppm.



Benzyl (2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-3-yl)ethyl)carbamate

Preparation of the title compound was adapted from the synthesis of a similar compound.[8] A 50-mL round bottom flask was charged with benzyl (2-(5-bromo-1*H*-indol-3-yl)ethyl)carbamate (650 mg, 1.74 mmol, 1 equiv), XPhos Pd G3 (73.7 mg, 0.087 mmol, 0.05 equiv), XPhos (125 mg, 0.261 mmol, 0.15 equiv), bis(pinacolato)diboron (1.33 g, 5.22 mmol, 3 equiv), and tribasic potassium phosphate (1.11 g, 5.22 mmol, 3 equiv). The vessel was then evacuated and backfilled with argon three times. Degassed anhydrous DMSO (17.4 mL) was then added to the flask and the resulting mixture was stirred at 60 °C for 2 h. The resulting black solution was then allowed to cool to rt, diluted with ethyl acetate, and washed with sat. aqueous sodium bicarbonate solution. The aqueous layer was extracted with ethyl acetate (2x) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting crude residue was purified on silica gel using a gradient of 10% ethyl acetate/hexanes to 20% ethyl acetate/hexanes to yield product as a pale yellow solid (590 mg, 81% yield). IR (thin film): 3329, 2978, 1702, 1371, 1353, 1258, 1142,

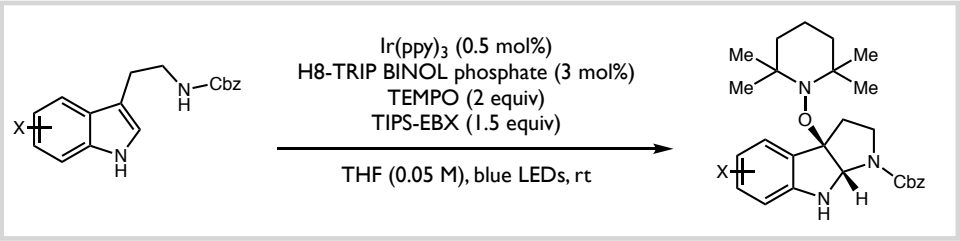
1098, 908, 737 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.66 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.38 – 7.27 (m, 6H), 6.95 (s, 1H), 5.09 (s, 2H), 4.88 (t, *J* = 6.1 Hz, 0.85H), 4.72 (s, 0.15H), 3.52 (q, *J* = 6.5 Hz, 2H), 2.97 (t, *J* = 6.8 Hz, 2H), 1.37 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.50, 138.59, 136.76, 128.61, 128.52, 128.22, 128.17, 127.07, 126.53, 122.29, 120.38, 113.51, 110.79, 83.62, 75.17, 66.71, 41.29, 25.02, 24.99; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{24}H_{30}BN_2O_4$) requires *m/z* 421.22931, found *m/z* 421.22912 with a difference of 0.46 ppm.



Benzyl (2-(1-methyl-1*H*-indol-3-yl)ethyl)carbamate

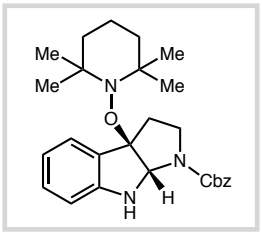
An acetone solution (0.33M) of *N'*-Cbz tryptamine **(1)** was cooled to 0 °C and powdered potassium hydroxide (5 equiv) was added to the solution. After 10 min, MeI (1.1 mmol) was added with vigorous stirring and the reaction was allowed to stir at room temperature for 30 min. After this time, the same amount of KOH and MeI were added again and the reaction was allowed to stir at room temperature overnight. Benzene was added and the mixture was filtered through Celite to remove all insoluble salts. The solution was concentrated *in vacuo* and purified on silica gel using 10-20% EtOAc/hexanes to yield the product as a clear oil in 89% yield.[9] IR (thin film): 3338, 3054, 2937, 1702, 1513, 1238, 1213, 1131, 733, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.29 (m, 6H), 7.25 – 7.21 (m, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.87 (s, 1H), 5.11 (s, 2H), 4.92 – 4.56 (m, 1H), 3.74 (s, 3H), 3.54 (q, *J* = 6.5 Hz, 2H), 2.98 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.46, 137.23, 136.76, 128.64, 128.27, 128.21, 127.79, 121.86, 119.04, 118.98, 111.36, 109.41, 66.70, 41.52, 32.77, 25.74; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{21}N_2O_3$) requires *m/z* 309.15976, found *m/z* 309.15935 with a difference of 1.3 ppm.

General procedure for the synthesis of TEMPO-functionalized pyrroloindoline products:



0.5 mmol batch reaction **(GP3)**: *N'*-Cbz tryptamine (147 mg, 0.5 mmol, 1.0 equiv), $Ir(ppy)_3$ (1.6 mg, 0.0025 mmol, 0.5 mol%), H-8 TRIP BINOL phosphate (15 mg, 0.015 mmol, 3 mol%), TEMPO (156 mg, 1 mmol, 2 equiv), TIPS-EBX iodonium (321 mg, 0.75 mmol, 1.5 equiv) were added to a 20-mL vial equipped with a magnetic stirbar. Anhydrous THF (10 mL) was then added and the reaction mixture was irradiated in a blue LED dish setup (see **Figure S2**) for 12h. After completion, the solvent was removed by rotary evaporation to give a crude residue that was further purified on silica gel in 2-5% EtOAc/hexanes with 1% added Et_3N.

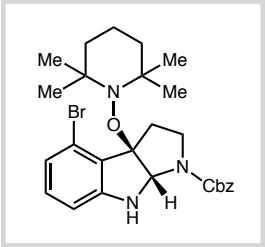
10mmol flow reaction **(GP4)***:* To a 250-mL round bottom flask was added *N*-Cbz tryptamine (2.94 g, 10 mmol, 1.0 equiv), $Ir(ppy)_3$ (33 mg, 0.05 mmol, 0.5 mol%), H-8 TRIP BINOL phosphate (301 mg, 0.3 mmol, 3 mol%), TEMPO (3.12 g, 20 mmol, 2 equiv) and TIPS-EBX iodonium (6.43 g, 15 mmol, 1.5 equiv) followed by addition of anhydrous THF (200 mL). The reaction was pumped through the irradiated reactor (see **Figure S1**) at room temperature (t_r = 7 min, 0.5 mmol/h). The solvent was then removed by rotary evaporation to give a crude residue that was further purified on silica gel in 2-5% EtOAc/hexanes with 1% added Et_3N.



Benzyl (3aS,8aR)-3a-((2,2,6,6-tetramethylpiperidin-1-yl)oxy) 3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (2)

Using **GP4**, the title compound was obtained as a white solid (3.63 g, 81% yield). The material was determined to be 93% ee by chiral HPLC analysis [ChiralPak AD-H, 10% IPA in hexanes, 1 mL/min, 250 nm, t_r (minor) = 9.1 min, t_r (major) = 10.2 min]. IR (thin

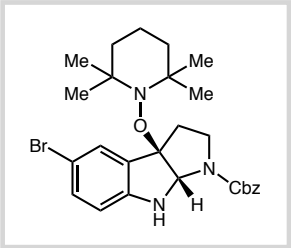
film): 3356, 2932, 1700, 1611, 1469, 1417, 1355, 1300, 1257, 1195, 1109, 743, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 7.47 – 7.28 (m, 5H), 7.10 (tdd, *J* = 6.4, 5.0, 1.2 Hz, 1H), 6.77 (td, *J* = 7.4, 3.4 Hz, 1H), 6.51 (dd, *J* = 24.5, 7.9 Hz, 1H), 6.00 (d, *J* = 38.8 Hz, 1H), 5.26 – 5.06 (m, 2H), 4.92 (s, 0.5H), 4.53 (s, 0.5H), 3.94 – 3.79 (m, 1H), 3.11 (dtd, *J* = 17.7, 11.3, 6.5 Hz, 1H), 2.67 (dtd, *J* = 26.7, 12.0, 8.7 Hz, 1H), 2.41 (dd, *J* = 12.5, 6.4 Hz, 1H), 1.55 – 1.14 (m, 6H), 1.08 (d, *J* = 3.2 Hz, 2H), 1.04 (s, 2H), 0.88 – 0.70 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 154.97, 154.24, 150.56, 150.35, 136.79, 136.63, 130.25, 130.14, 129.78, 129.73, 128.62, 128.48, 128.15, 128.10, 127.98, 127.79, 126.00, 125.90, 118.83, 118.59, 109.34, 109.26, 97.97, 96.87, 78.44, 77.74, 67.02, 66.83, 59.99, 59.27, 45.60, 45.36, 40.81, 40.42, 40.35, 40.12, 39.74, 33.01, 32.94, 32.62, 32.48, 20.59, 20.45, 20.41, 17.08; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{27}H_{35}N_3O_3$) requires *m/z* 450.27512, found *m/z* 450.27455 with a difference of 1.27 ppm; $[\alpha]_D^{21}$ = -139 (*c* = 1.00, $CHCl_3$).



Benzyl (3a*R*,8a*S*)-4-bromo-3a-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (3)

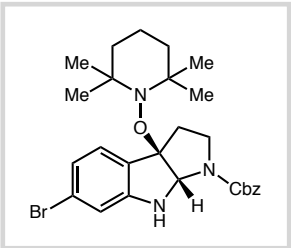
Using **GP3**, the title compound was obtained as a white foamy solid (208 mg, 79% yield). The desired product was found to be 90% ee by chiral HPLC analysis [ChiralPak AD-H, 10% IPA in hexanes, 1 mL/min, 250 nm, t_r (minor) = 8.8 min, t_r (major) = 10.8 min]. IR (thin film): 3346, 2932, 1694, 1601, 1452, 1415, 1352, 1297, 1255, 1215, 1181, 1115, 905, 754, 742, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 7.44 – 7.28 (m, 5H), 6.96 – 6.85 (m, 2H), 6.54 (dd, *J* = 31.2, 3.2 Hz, 1H), 6.42 (dd, *J* = 19.2, 7.6 Hz, 1H), 5.31 – 5.08 (m, 2H), 4.76 (dd, *J* = 179.8, 3.2 Hz, 1H), 3.98 – 3.81 (m, 1H), 3.30 – 3.15 (m, 1H), 2.84 – 2.59 (m, 2H), 1.54 – 1.23 (m, 6H), 1.16 (d, *J* = 5.4 Hz, 3H), 1.06 (d, *J* = 37.6 Hz, 6H), 0.39 (d, *J* = 11.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 155.23, 154.35, 151.31, 151.20, 136.92, 136.71, 131.10, 131.06, 130.18, 130.01, 128.71, 128.60, 128.26, 128.15, 128.11, 127.83, 123.15, 122.91, 119.62, 119.48, 107.98, 107.91, 98.92, 97.78, 76.20, 75.37, 67.13, 67.02, 60.19, 60.16, 59.54, 59.53, 45.18, 44.96, 40.67, 40.63, 40.56, 40.39, 39.07, 38.47, 33.65, 33.33, 32.30, 32.18, 21.26, 21.23, 20.77, 20.69, 17.14; HRMS (ESI)

exact mass calculated for $[M+H]^+$ ($C_{27}H_{35}BrN_3O_3$) requires *m/z* 528.18563, found *m/z* 528.18592 with a difference of 0.55 ppm; $[\alpha]_D^{21}$ = -239 (*c* = 0.5, $CHCl_3$).



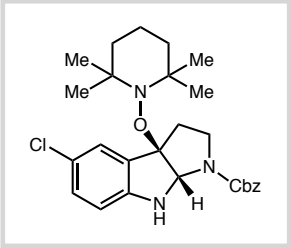
Benzyl (3a*R*,8a*S*)-5-bromo-3a-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (4)

Using **GP3**, the title compound was obtained as a white foamy solid (211 mg, 80% yield). the product was found to be 92% ee by chiral HPLC analysis [ChiralPak AD-H, 10% IPA in hexanes, 1 mL/min, 250 nm, t_r (minor) = 7.6 min, t_r (major) = 12.0 min]. IR (thin film): 3352, 2972, 2932, 1697, 1605, 1475, 1415, 1355, 1299, 1261, 1194, 1112, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 7.44 – 7.29 (m, 6H), 7.19 (ddd, *J* = 8.4, 3.5, 2.1 Hz, 1H), 6.39 (dd, *J* = 23.8, 8.4 Hz, 1H), 6.01 (dd, *J* = 36.0, 2.3 Hz, 1H), 5.24 – 5.08 (m, 2H), 4.74 (dd, *J* = 201.3, 2.3 Hz, 1H), 3.94 – 3.78 (m, 1H), 3.18 – 3.05 (m, 1H), 2.74 – 2.57 (m, 1H), 2.42 – 2.32 (m, 1H), 1.55 – 1.22 (m, 6H), 1.12 – 0.99 (m, 6H), 0.86 – 0.71 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 155.06, 154.23, 149.57, 149.36, 136.79, 136.62, 132.63, 132.57, 132.49, 129.02, 128.92, 128.78, 128.64, 128.37, 128.27, 128.19, 127.95, 110.79, 110.71, 110.38, 110.09, 97.71, 96.59, 78.81, 78.10, 67.25, 67.08, 60.23, 59.51, 45.64, 45.41, 40.89, 40.54, 40.47, 40.31, 39.94, 33.25, 33.18, 32.79, 32.65, 20.73, 20.64, 20.61, 17.17; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{27}H_{35}BrN_3O_3$) requires *m/z* 528.18563, *m/z* found 528.18494 with a difference of 1.31 ppm; $[\alpha]_D^{21}$ = -119 (*c* = 0.50, $CHCl_3$).



Benzyl (3a*R*,8a*S*)-6-bromo-3a-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (5)

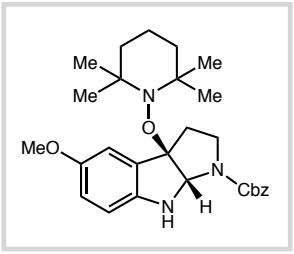
Using **GP3**, the title compound was obtained as a white foamy solid (171 mg, 65% yield). The desired product was found to be 87% ee by chiral HPLC analysis [ChiralPak AD-H, 10% IPA in hexanes, 1 mL/min, 250 nm, t_r (major) = 10.9 min, t_r (minor) = 12.3 min]. IR (thin film): 3354, 2973, 2932, 2873, 1697, 1604, 1481, 1449, 1415, 1353, 1311, 1298, 1240, 1195, 1110, 1044, 897, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 7.45 – 7.29 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.88 (ddd, *J* = 7.8, 5.3, 1.7 Hz, 1H), 6.64 (dd, *J* = 23.2, 1.7 Hz, 1H), 5.95 (dd, *J* = 33.1, 1.9 Hz, 1H), 5.25 – 5.07 (m, 2H), 4.82 (dd, *J* = 212.4, 1.9 Hz, 1H), 3.86 (dddd, *J* = 40.0, 10.5, 8.7, 1.3 Hz, 1H), 3.10 (dtd, *J* = 15.1, 11.3, 6.4 Hz, 1H), 2.64 (dtd, *J* = 26.4, 12.0, 8.7 Hz, 1H), 2.36 (dd, *J* = 12.4, 6.4 Hz, 1H), 1.55 – 1.22 (m, 7H), 1.09 – 1.00 (m, 6H), 0.83 – 0.73 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 155.04, 154.18, 151.90, 151.65, 136.76, 136.60, 129.14, 129.09, 128.78, 128.62, 128.38, 128.27, 128.18, 127.95, 127.41, 127.34, 123.72, 123.70, 121.68, 121.40, 112.19, 112.14, 97.33, 96.17, 78.91, 78.19, 67.25, 67.07, 60.18, 60.17, 59.47, 45.68, 45.46, 40.88, 40.50, 40.44, 40.23, 39.87, 33.33, 33.28, 32.70, 32.56, 20.71, 20.59, 20.56, 17.16; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{27}H_{35}BrN_3O_3$) requires *m/z* 528.18563, found *m/z* 528.18581 with a difference of 0.34 ppm; $[\alpha]_D^{21}$ = -234 (*c* = 0.50, $CHCl_3$).



Benzyl (3a*R*,8a*S*)-5-chloro-3a-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (6)

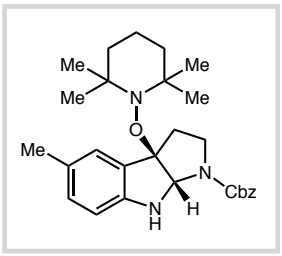
Using **GP3**, the title compound was obtained as a white foamy solid (178 mg, 77% yield). The desired product was found to be 92% ee by chiral HPLC analysis [ChiralPak AD-H, 10% IPA in hexanes, 1 mL/min, 250 nm, t_r (minor) = 7.5 min, t_r (major) = 10.9 min]. IR (thin film): 3353, 2932, 1695, 1479, 1415, 1354, 1260, 1194, 755, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 7.44 – 7.29 (m, 5H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.06 (ddd, *J* = 8.4, 3.7, 2.2 Hz, 1H), 6.43 (dd, *J* = 23.4, 8.4 Hz, 1H), 6.02 (dd, *J* = 36.8, 2.2 Hz, 1H), 5.24 – 5.07 (m, 2H), 4.74 (dd, *J* = 199.2, 2.3 Hz, 1H), 3.95 – 3.78 (m, 1H), 3.17 – 3.05 (m, 1H), 2.74 – 2.59 (m, 1H), 2.38 (dd, *J* = 12.6, 6.6 Hz, 1H), 1.57 – 1.23 (m, 7H), 1.10 – 1.01 (m, 6H), 0.85 – 0.70 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 154.99, 154.18, 149.11, 148.90, 136.75,

136.58, 132.04, 131.95, 129.78, 129.71, 128.72, 128.58, 128.31, 128.21, 128.13, 127.90, 126.09, 125.99, 123.43, 123.16, 110.22, 110.14, 97.70, 96.58, 78.88, 78.18, 67.19, 67.02, 60.17, 60.16, 59.45, 45.60, 45.36, 40.83, 40.49, 40.42, 40.25, 39.87, 33.19, 33.13, 32.73, 32.59, 20.68, 20.68, 20.59, 20.55, 17.12; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{27}H_{35}ClN_3O_3$) requires *m/z* 464.29077, found *m/z* 464.29163 with a difference of 1.87 ppm; $[\alpha]_D^{21}$ = -127 (*c* = 1.00, $CHCl_3$).



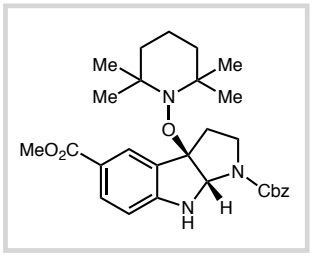
Benzyl (3a*R*,8a*S*)-5-methoxy-3a-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (7)

Using **GP3**, the title compound was obtained as a white foamy solid (149 mg, 62% yield). The desired product was found to be 88% ee by chiral HPLC analysis [ChiralPak AD-H, 10% IPA in hexanes, 1 mL/min, 250 nm, t_r (minor) =12.1 min, t_r (major) = 17.2 min]. IR (thin film): 3357, 2933, 1698, 1493, 1415, 1353, 1191, 1033, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 7.46 – 7.27 (m, 5H), 6.93 (t, *J* = 3.0 Hz, 1H), 6.75 – 6.69 (m, 1H), 6.48 (dd, *J* = 23.5, 8.5 Hz, 1H), 6.06 (d, *J* = 43.9 Hz, 1H), 5.28 – 5.05 (m, 2H), 4.49 (d, *J* = 168.3 Hz, 1H), 3.94 – 3.80 (m, 1H), 3.78 (s, 3H), 3.20 – 3.07 (m, 1H), 2.72 – 2.57 (m, 1H), 2.39 (dd, *J* = 12.2, 6.2 Hz, 1H), 1.55 – 1.23 (m, 7H), 1.09 (d, *J* = 3.9 Hz, 3H), 1.04 (s, 3H), 0.90 – 0.64 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 154.98, 154.34, 153.81, 153.70, 144.59, 144.38, 136.92, 136.74, 132.07, 131.89, 128.67, 128.55, 128.19, 128.15, 128.05, 127.89, 116.01, 115.91, 111.48, 111.44, 110.63, 110.52, 98.35, 97.27, 79.05, 78.35, 67.08, 66.91, 60.12, 60.11, 59.37, 56.19, 56.17, 45.57, 45.32, 40.96, 40.54, 40.46, 40.24, 39.82, 33.11, 33.03, 32.83, 32.66, 20.71, 20.69, 20.51, 20.48, 17.15; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{28}H_{38}N_3O_4$) requires *m/z* 480.28569, found *m/z* 480.28513 with a difference of 1.15 ppm; $[\alpha]_D^{21}$ = -104 (*c* = 1.00, $CHCl_3$).



Benzyl (3a*R*,8a*S*)-5-methyl-3a-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (8)

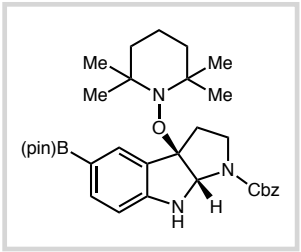
Using **GP3**, the title compound was obtained as a white foamy solid (182 mg, 79% yield). The desired product was found to be 91% ee by chiral HPLC analysis [ChiralPak AD-H, 10% IPA in hexanes, 1 mL/min, 250 nm, t_r (minor) = 7.4 min, t_r (major) = 10.2 min]. ^{1}H NMR (500 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 7.44 – 7.27 (m, 5H), 7.12 (s, 1H), 6.95 – 6.88 (m, 1H), 6.43 (dd, *J* = 23.8, 7.9 Hz, 1H), 6.05 (dd, *J* = 38.7, 2.7 Hz, 1H), 5.27 – 5.06 (m, 2H), 4.59 (dd, *J* = 182.9, 2.8 Hz, 1H), 3.94 – 3.77 (m, 1H), 3.18 – 3.05 (m, 1H), 2.73 – 2.58 (m, 1H), 2.43 – 2.33 (m, 1H), 2.29 (s, 3H), 1.63 – 1.19 (m, 7H), 1.09 (d, *J* = 3.7 Hz, 3H), 1.03 (s, 3H), 0.84 (d, *J* = 31.5 Hz, 3H), 0.70 (d, *J* = 8.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 155.05, 154.38, 148.34, 148.14, 136.96, 136.80, 130.98, 130.84, 130.43, 130.37, 128.70, 128.57, 128.42, 128.21, 128.19, 128.17, 128.06, 127.89, 126.28, 126.18, 109.54, 109.43, 98.13, 97.03, 78.58, 77.87, 67.08, 66.90, 60.09, 60.08, 59.34, 45.63, 45.39, 40.94, 40.57, 40.50, 40.16, 39.79, 33.07, 33.00, 32.93, 32.76, 21.10, 20.72, 20.70, 20.54, 20.51, 17.20; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{28}H_{38}N_3O_3$) requires *m/z* 464.29077, found *m/z* 464.29084 with a difference of 0.16 ppm; $[\alpha]_D^{21}$ = -121 (*c* = 1.00, $CHCl_3$).



1-benzyl 5-methyl (3a*R*,8a*S*)-3a-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1,5(2*H*)-dicarboxylate (9)

Using **GP3**, the title compound was obtained as a white foamy solid (162 mg, 64% yield). The desired product was found to be 92% ee by chiral HPLC analysis [ChiralPak AD-H, 10% IPA in hexanes, 1 mL/min, 280 nm, t_r (minor) = 11.6 min, t_r (major) = 20.6

min]. ^{1}H NMR (500 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 8.03 (t, *J* = 2.2 Hz, 1H), 7.87 (ddd, *J* = 8.4, 4.2, 1.7 Hz, 1H), 7.49 – 7.31 (m, 5H), 6.48 (dd, *J* = 23.1, 8.4 Hz, 1H), 6.09 (dd, *J* = 33.0, 1.6 Hz, 1H), 5.38 (s, 0.6H), 5.27 – 5.09 (m, 2H), 4.94 (s, 0.4H), 3.97 – 3.84 (m, 1H), 3.89 (s, 3H), 3.19 – 3.06 (m, 1H), 2.80 – 2.64 (m, 1H), 2.53 – 2.41 (m, 1H), 1.59 – 1.23 (m, 7H), 1.11 (d, *J* = 2.6 Hz, 3H), 1.06 (s, 3H), 0.88 – 0.74 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 167.45, 167.38, 155.11, 154.46, 154.23, 154.16, 136.72, 136.54, 132.80, 132.77, 129.92, 129.86, 128.81, 128.64, 128.43, 128.29, 128.22, 128.20, 128.15, 127.95, 120.32, 120.01, 107.72, 107.70, 97.18, 96.04, 78.64, 77.92, 67.31, 67.14, 60.20, 59.53, 51.84, 51.81, 45.65, 45.44, 40.83, 40.52, 40.45, 40.31, 39.91, 33.14, 33.07, 32.82, 32.67, 20.74, 20.73, 20.65, 20.62, 17.15; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{29}H_{38}N_3O_5$) requires *m/z* 508.27926, found *m/z* 508.28090 with a difference of 0.59 ppm; $[\alpha]_D^{21}$ = -142 (*c* = 1.00, $CHCl_3$).

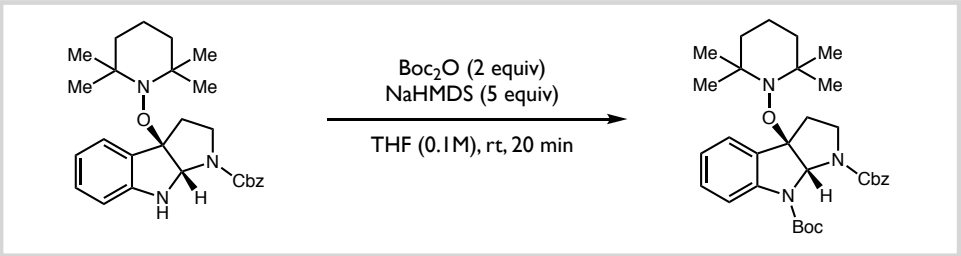


Benzyl (3a*R*,8a*S*)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (10)

Using **GP3**, the title compound was obtained as a white foamy solid (169 mg, 59% yield). The desired product was found to be 88% ee by chiral HPLC analysis [ChiralPak AD-H, 10% IPA in hexanes, 1 mL/min, 250 nm, t_r (major) = 9.7 min, t_r (minor) = 11.0 min]. IR (thin film): 3358, 2977, 2932, 1697, 1611, 1350, 1194, 1145, 753 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 7.78 (s, 1H), 7.60 (dd, *J* = 7.9, 5.1 Hz, 1H), 7.48 – 7.30 (m, 5H), 6.49 (dd, *J* = 22.4, 7.9 Hz, 1H), 6.17 (d, *J* = 29.0 Hz, 1H), 5.34 – 5.08 (m, 2.6H), 4.73 (s, 0.4H), 3.87 (dt, *J* = 38.5, 9.9 Hz, 1H), 3.22 – 3.06 (m, 1H), 2.80 – 2.63 (m, 1H), 2.55 – 2.44 (m, 1H), 1.50 – 1.25 (m, 21H), 1.09 (d, 7H), 0.90 (d, *J* = 30.4 Hz, 4H), 0.67 (d, *J* = 13.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 153.15, 152.91, 137.28, 136.74, 132.41, 132.34, 130.11, 130.06, 128.73, 128.59, 128.27, 128.15, 128.09, 127.86, 108.20, 108.14, 96.52, 83.41, 83.38, 77.68, 67.12, 66.96, 60.07, 59.39, 45.57, 45.36, 40.88, 40.60, 40.52, 40.16, 39.80, 33.12, 32.94, 32.89, 32.82, 25.21, 24.81, 20.71, 20.68, 20.56, 20.53, 17.20; HRMS (ESI) exact

mass calculated for $[M+H]^+$ ($C_{33}H_{47}BN_3NaO_5$) requires *m/z* 576.36053, found *m/z* 576.36016 with a difference of 0.64 ppm; $[\alpha]_D^{21}$ = -98 (*c* = 1.00, $CHCl_3$).

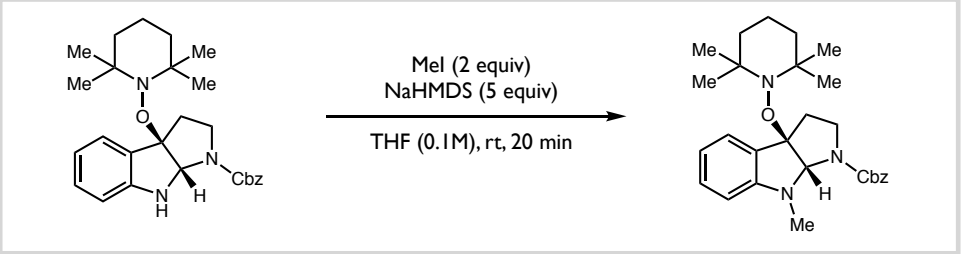
Protection of TEMPO-functionalized pyrroloindolines:



1-benzyl 8-(*tert*-butyl) (3a*R*,8a*R*)-3a-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (11)

To a solution of Boc_2O (2 equiv) and **2** (1 equiv) in THF (0.1M) was added NaHMDS (5 equiv) dropwise. Once addition is complete, the reaction was allowed to stir for 30 min then sat. $NaHCO_3$ solution was added and the mixture was extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography on silica gel using 2-5% EtOAc in hexanes to afford the desired product in 88% yield.

IR (thin film): 2975, 2932, 1705, 1604, 1480, 1407, 1364, 1341, 1312, 1290, 1253, 1236, 1193, 1151, 1092, 1079, 1022, 947, 735, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.45 – 7.31 (m, 5H), 7.31 – 7.27 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.88 (s, 1H), 5.17 (d, *J* = 10.8 Hz, 2H), 3.98 (dd, *J* = 11.5, 7.9 Hz, 1H), 2.84 (td, *J* = 13.0, 12.3, 5.1 Hz, 1H), 2.55 (dt, *J* = 12.2, 8.0 Hz, 1H), 2.30 (dd, *J* = 12.3, 5.2 Hz, 1H), 1.57 – 1.19 (m, 15H), 1.09 (s, 3H), 1.00 (s, 3H), 0.90 (s, 3H), 0.53 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.74, 144.19, 137.13, 133.36, 129.79, 128.51, 127.93, 127.88, 125.03, 123.43, 95.33, 81.50, 78.32, 66.95, 60.39, 59.53, 45.99, 40.91, 40.51, 33.07, 28.47, 20.73, 20.46, 17.15; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{32}H_{44}N_3O_5$) requires *m/z* 550.32755, *m/z* found 550.32818 with a difference of 1.14 ppm. $[\alpha]_D^{21}$ = -128 (*c* = 0.5, $CHCl_3$).

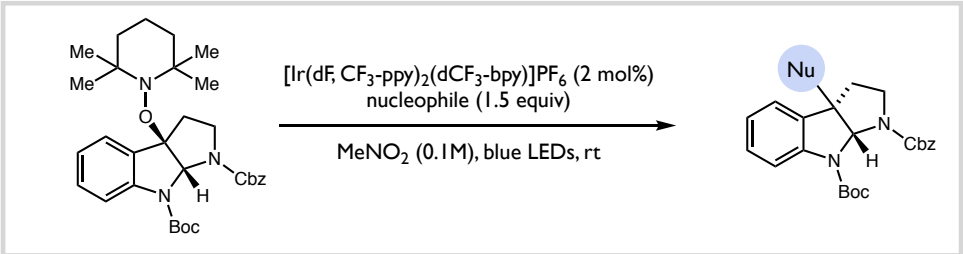


Benzyl (3a*R*,8a*S*)-8-methyl-3a-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (24)

To a solution of MeI (2 equiv) and **2** (1 equiv) in THF (0.1M) was added NaHMDS (5 equiv) dropwise. Once addition is complete, the reaction was allowed to stir for 30 min then sat. $NaHCO_3$ solution was added and the mixture was extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography on silica gel using 2-5% EtOAc in hexanes to afford the desired product in 93% yield.

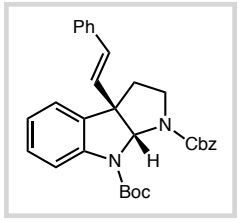
IR (thin film): 2931, 1702, 1609, 1411, 1360, 1195, 1094, 992, 939, 742, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 7.47 – 7.28 (m, 5H), 7.26 – 7.22 (m, 1H), 7.14 (tdd, *J* = 7.7, 6.2, 1.3 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.32 (dd, *J* = 21.3, 7.9 Hz, 1H), 6.16 (d, *J* = 37.2 Hz, 1H), 5.27 – 5.06 (m, 2H), 4.11 – 3.91 (m, 1H), 3.15 – 2.80 (m, 4H), 2.62 (dtd, *J* = 22.7, 12.1, 8.7 Hz, 1H), 2.36 – 2.25 (m, 1H), 1.55 – 1.18 (m, 6H), 1.09 (d, *J* = 3.8 Hz, 3H), 1.01 (d, *J* = 5.8 Hz, 3H), 0.84 (d, *J* = 14.8 Hz, 3H), 0.53 (d, *J* = 26.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, *ca.* 55:45 mixture of rotamers) δ 155.21, 154.50, 152.15, 151.95, 136.97, 136.69, 131.22, 131.15, 129.85, 129.82, 128.65, 128.59, 128.46, 128.25, 128.07, 127.92, 124.99, 124.92, 117.41, 117.24, 106.03, 105.94, 97.68, 96.59, 83.89, 82.97, 67.29, 66.98, 60.03, 59.98, 59.40, 45.27, 45.19, 41.50, 40.97, 40.94, 40.92, 40.54, 40.39, 33.64, 33.32, 33.29, 33.04, 33.02, 32.64, 20.79, 20.73, 20.50, 20.49, 17.17; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{28}H_{38}N_3O_3$) requires *m/z* 464.29077, *m/z* found 464.29044 with a difference of 0.70 ppm. $[\alpha]_D^{21}$ = -110 (*c* = 1.0, $CHCl_3$).

General procedure for mesolytic bond cleavage reaction (GP5):



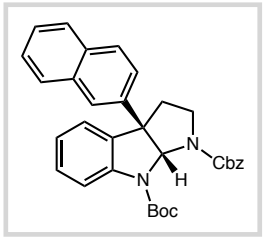
To a flame dried 2-dram vial equipped with stir bar was added **11** (0.25 mmol), nucleophile (0.375 mmol, 1.5 equiv), and [Ir(dF, CF_3-ppy)$_2$(dCF_3-bpy)]PF_6 (0.005 mmol, 0.02 equiv). The vial was evacuated and backfilled with argon three times then anhydrous degassed $MeNO_2$ (5 mL) was added. The reaction was sealed with parafilm

and irradiated at room temperature with 7 W blue LEDs for 12 h or until full conversion of starting material by TLC analysis (**See Figure S2**). The mixture was then concentrated *in vacuo* and the resulting residue was purified on silica gel by flash column chromatography.



1-benzyl 8-(*tert*-butyl) (3a*R*,8a*R*)-3a-((*E*)-styryl)-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (12)

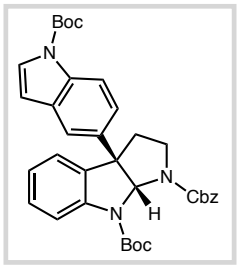
The crude material was purified on silica gel using 5% ethyl acetate in hexanes to give the desired product as a white solid (81mg, 65% yield) that was determined to be 94% ee by HPLC analysis (ChiralPak AS-H, 5% IPA in hexanes, 1 mL/min, 250nm, t_r (major) = 7.6 min, t_r (minor) = 10.5 min). IR (thin film): 1703, 1479, 1405, 1366, 1320, 1196, 1149, 1099, 747, 695 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 7.64 (d, *J* = 8.1 Hz, 1H), 7.40 – 7.18 (m, 12H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.52 (d, *J* = 16.1 Hz, 1H), 6.21 (d, *J* = 16.1 Hz, 1H), 6.16 (s, 1H), 5.13 (s, 2H), 3.88 – 3.72 (m, 1H), 2.96 – 2.79 (m, 1H), 2.40 – 2.24 (m, 2H), 1.47 (s, 9H); ^{13}C NMR (126 MHz, CD_3CN) δ 155.17, 153.30, 143.56, 138.30, 137.53, 134.86, 132.20, 130.78, 129.60, 129.52, 129.37, 128.77, 128.68, 128.48, 127.24, 125.20, 124.73, 82.14, 82.14, 67.31, 59.50, 47.14, 36.13, 28.41; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{31}H_{33}N_2O_4$) requires *m/z* 497.24349, found *m/z* 497.24319 with a difference of 0.59 ppm; $[\alpha]_D^{21}$ = -100 (*c* = 1.00, $CHCl_3$).



1-benzyl 8-(*tert*-butyl) (3a*R*,8a*R*)-3a-(naphthalen-2-yl)-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (13)

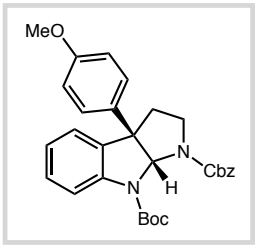
The crude material was purified on silica gel using 2-5% ethyl acetate in hexanes to give the desired product as a white solid (64mg, 49% yield) that was determined to be

94% ee by HPLC analysis (ChiralPak AD-H, 10% IPA in hexanes, 1 mL/min, 250nm, t_r (minor) = 10.4 min, t_r (major) = 11.6 min). IR (thin film): 1705, 1479, 1408, 1367, 1341, 1318, 1196, 1154, 751 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 7.86 – 7.76 (m, 3H), 7.73 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.41 – 7.24 (m, 8H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.47 (s, 1H), 5.14 (s, 2H), 3.93 (dd, *J* = 11.1, 6.9 Hz, 1H), 2.97 (td, *J* = 10.9, 6.1 Hz, 1H), 2.76 – 2.59 (m, 2H), 1.50 (s, 9H); ^{13}C NMR (126 MHz, CD_3CN) δ 155.17, 153.18, 143.05, 141.35, 138.26, 136.68, 134.12, 133.22, 129.68, 129.54, 129.36, 128.82, 128.78, 128.49, 128.37, 127.51, 127.16, 125.03, 124.92, 83.38, 82.39, 67.38, 61.09, 47.23, 36.43, 28.44; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{33}H_{33}N_2O_4$) requires *m/z* 521.24349, found *m/z* 521.24348 with a difference of 0.01 ppm; $[\alpha]_D^{21}$ = -196 (*c* = 1.00, $CHCl_3$).



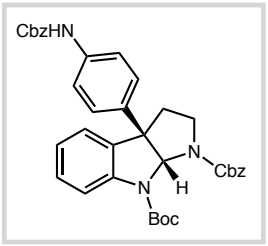
1-benzyl 8-(*tert*-butyl) (3a*R*,8a*R*)-3a-(1-(*tert*-butoxycarbonyl)-1*H*-indol-5-yl)-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (14)

The crude material was purified on silica gel using 5-10% ethyl acetate in hexanes to give the desired product as a white solid (79 mg, 52% yield) that determined to be 94% ee by HPLC analysis (ChiralPak AD-H, 20% IPA in hexanes, 1 mL/min, 250nm, t_r (minor) = 13.1 min, t_r (major) = 15.8 min). IR (thin film): 1706, 1407, 1368, 1338, 1254, 1196, 1162, 1144, 751 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 8.03 (d, *J* = 8.7 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 3.7 Hz, 1H), 7.45 (d, *J* = 1.9 Hz, 1H), 7.38 – 7.16 (m, 8H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.53 (d, *J* = 3.7 Hz, 1H), 6.38 (s, 1H), 5.13 (s, 2H), 3.95 – 3.85 (m, 1H), 2.93 (td, *J* = 10.8, 6.3 Hz, 1H), 2.68 – 2.56 (m, 2H), 1.61 (s, 9H), 1.48 (s, 9H); ^{13}C NMR (126 MHz, CD_3CN) δ 155.13, 153.16, 150.39, 142.92, 138.42, 138.25, 137.20, 134.93, 131.69, 129.34, 129.33, 128.74, 128.46, 127.79, 124.91, 124.81, 122.84, 118.75, 116.23, 107.91, 84.77, 83.78, 82.29, 67.32, 60.83, 47.25, 36.59, 28.42, 28.22; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{36}H_{40}N_3O_6$) requires *m/z* 610.29117, found *m/z* 610.29063 with a difference of 0.88 ppm; $[\alpha]_D^{21}$ = -151 (*c* = 1.00, $CHCl_3$).



1-benzyl 8-(*tert*-butyl) (3a*R*,8a*R*)-3a-(4-methoxyphenyl)-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (15)

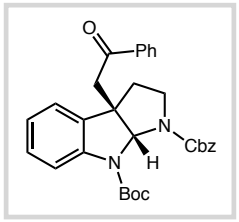
The crude material was purified on silica gel using 5-10% ethyl acetate in hexanes to give the desired product as a white solid (90 mg, 72% yield) that was determined to be 93% ee by HPLC analysis (ChiralPak AD-H, 5% IPA in hexanes, 1 mL/min, 250nm, t_r (minor) = 13.7 min, t_r (major) = 21.9 min). IR (thin film): 1704, 1407, 1367, 1316, 1252, 1182, 1148, 749, 697 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.28 (m, 5H), 7.26 (td, *J* = 7.7, 1.4 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.18 – 7.10 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.90 – 6.76 (m, 2H), 6.29 (s, 1H), 5.13 (s, 2H), 3.90 – 3.81 (m, 1H), 3.73 (s, 3H), 2.90 (td, *J* = 11.2, 5.5 Hz, 1H), 2.64 – 2.45 (m, 2H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, CD_3CN) δ 159.63, 155.13, 153.15, 142.86, 138.28, 137.13, 135.96, 129.36, 129.35, 128.77, 128.50, 127.68, 124.84, 124.79, 115.02, 83.53, 82.29, 67.32, 60.26, 55.85, 47.24, 36.48, 28.43; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{30}H_{33}N_2O_5$) requires *m/z* 501.23840, found *m/z* 501.23827 with a difference of 0.26 ppm; $[\alpha]_D^{21}$ = -159 (*c* = 1.00, $CHCl_3$).



1-benzyl 8-(*tert*-butyl) (3a*R*,8a*R*)-3a-(4-(((benzyloxy)carbonyl)amino)phenyl)-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (16)

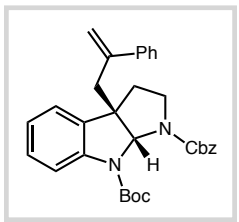
The crude material was purified on silica gel using 10-30% ethyl acetate in hexanes to give the desired product as a white solid (90 mg, 72% yield) that was determined to be 94% ee by HPLC analysis (ChiralPak AS-H, 5% IPA in hexanes, 1 mL/min, 250nm, t_r (major) = 7.6 min, t_r (minor) = 10.5 min). IR (thin film): 3314, 2976, 1704, 1531, 1479, 1409, 1368, 1322, 1217, 1150, 745 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 7.84 (s, 1H),

7.63 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.29 (m, 12H), 7.26 (td, *J* = 7.9, 1.4 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.30 (s, 1H), 5.14 (s, 4H), 3.87 (dd, *J* = 10.9, 7.4 Hz, 1H), 2.90 (td, *J* = 11.3, 5.6 Hz, 1H), 2.63 – 2.46 (m, 2H), 1.48 (s, 9H). ^{13}C NMR (126 MHz, CD_3CN) δ 155.15, 154.48, 153.13, 142.91, 138.78, 138.47, 138.25, 137.83, 136.85, 129.47, 129.41, 129.36, 128.99, 128.79, 128.77, 128.48, 127.12, 124.86, 119.77, 83.49, 82.33, 67.35, 67.17, 60.41, 47.22, 36.54, 28.42. HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{37}H_{38}N_3O_6$) requires *m/z* 620.27552, found *m/z* 620.27526 with a difference of 0.40 ppm; $[\alpha]_D^{21}$ = -77 (*c* = 1.00, $CHCl_3$).



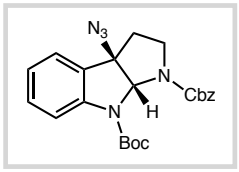
1-benzyl 8-(*tert*-butyl) (3a*R*,8a*R*)-3a-(2-oxo-2-phenylethyl)-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (17)

The crude material was purified on silica gel using 20-30% ethyl acetate in hexanes to give the desired product as a colorless oil (102 mg, 80% yield) that was determined to be 93% ee by HPLC analysis (ChiralPak AD-H, 20% IPA in hexanes, 1 mL/min, 250nm, t_r (minor) = 8.0 min, t_r (major) = 9.2 min). IR (thin film): 2977, 1693, 1407, 1366, 1321, 1198, 1154, 749, 692 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) δ 7.92 – 7.82 (m, 2H), 7.64 – 7.53 (m, 2H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.41 – 7.25 (m, 6H), 7.19 (td, *J* = 7.8, 1.3 Hz, 1H), 7.00 (td, *J* = 7.5, 1.1 Hz, 1H), 6.34 (s, 1H), 5.23 – 5.04 (m, 2H), 3.88 – 3.76 (m, 1H), 3.58 (dd, *J* = 63.8, 17.5 Hz, 2H), 2.85 – 2.72 (m, 1H), 2.28 – 2.19 (m, 2H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, CD_3CN) δ 198.72, 153.45, 143.97, 138.35, 138.07, 135.96, 134.21, 129.56, 129.34, 129.15, 128.92, 128.74, 128.52, 124.36, 124.18, 81.89, 81.41, 67.34, 54.75, 46.11, 45.85, 37.67, 28.50; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{31}H_{33}N_2O_5$) requires *m/z* 513.23706, found *m/z* 513.23752 with a difference of 1.72 ppm; $[\alpha]_D^{21}$ = -146 (*c* = 1.00, $CHCl_3$).



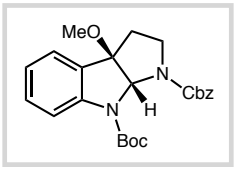
1-benzyl 8-(*tert*-butyl) (3a*S*,8a*R*)-3a-(2-phenylallyl)-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (18)

The crude material was purified on silica gel using 5-10% ethyl acetate in hexanes to give the desired product as a white solid (89 mg, 70% yield) that was determined to be 94% ee by HPLC analysis (ChiralPak AD-H, 5% IPA in hexanes, 1 mL/min, 280nm, t_r (minor) = 7.3 min, t_r (major) = 7.8 min). IR (thin film): 1704, 1480, 1407, 1367, 1316, 1162, 1149, 749, 699 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 7.48 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.27 (m, 5H), 7.18 (s, 5H), 7.12 – 7.05 (m, 2H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.00 (s, 1H), 5.21 – 4.94 (m, 4H), 3.64 (dd, *J* = 10.4, 7.4 Hz, 1H), 3.07 (d, *J* = 13.8 Hz, 1H), 2.89 (d, *J* = 13.9 Hz, 1H), 2.67 (td, *J* = 11.0, 6.4 Hz, 1H), 2.03 – 1.95 (m, 2H), 1.48 (s, 9H); ^{13}C NMR (126 MHz, CD_3CN) δ 155.08, 153.01, 146.40, 143.53, 142.66, 138.34, 135.57, 129.34, 129.05, 128.95, 128.72, 128.41, 128.19, 127.23, 124.74, 123.92, 118.08, 81.71, 80.62, 67.15, 57.76, 46.78, 43.22, 36.44, 28.44; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{32}H_{35}N_2O_4$) requires *m/z* 511.25914, found *m/z* 511.25864 with a difference of 0.97 ppm; $[\alpha]_D^{21}$ = -76 (*c* = 1.00, $CHCl_3$).



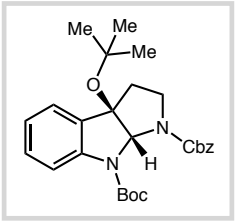
1-benzyl 8-(*tert*-butyl) (3a*R*,8a*R*)-3a-azido-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (19)

The crude material was purified on silica gel using 5-10% ethyl acetate in hexanes to give the desired product as a colorless oil (105 mg, 92% yield) that was determined to be 94% ee by HPLC analysis (ChiralPak AD-H, 10% IPA in hexanes, 1 mL/min, 250nm, t_r (minor) = 6.5 min, t_r (major) = 8.3 min). IR (thin film): 2978, 2100, 1709, 1479, 1407, 1368, 1313, 1152, 753 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.40 – 7.33 (m, 4H), 7.33 – 7.27 (m, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.13 (s, 1H), 5.13 (s, 2H), 3.82 (dd, *J* = 11.2, 8.3 Hz, 1H), 2.87 (td, *J* = 11.6, 5.5 Hz, 1H), 2.49 (dd, *J* = 12.4, 5.5 Hz, 1H), 2.31 (td, *J* = 12.2, 8.3 Hz, 1H), 1.50 (s, 9H); ^{13}C NMR (126 MHz, CD_3CN) δ 155.01, 152.89, 144.13, 138.06, 131.90, 129.44, 129.38, 128.84, 128.52, 125.00, 124.91, 82.82, 81.73, 75.88, 67.53, 46.82, 35.04, 28.37; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{23}H_{25}N_5NaO_4$) requires *m/z* 458.18045, found *m/z* 458.17930 with a difference of 1.32 ppm; $[\alpha]_D^{21}$ = -84 (*c* = 1.00, $CHCl_3$).



Benzyl 8-(*tert*-butyl) (3a*R*,8a*R*)-3a-methoxy-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (20)

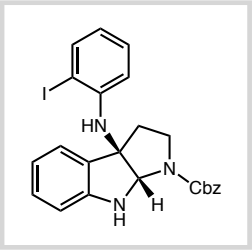
The crude material was purified on silica gel using 5-10% ethyl acetate in hexanes to give the desired product as a white solid (95 mg, 90% yield) that was determined to be 93% ee by HPLC analysis (ChiralPak AD-H, 10% IPA in hexanes, 1 mL/min, 250nm, t_r (minor) = 6.3 min, t_r (major) = 8.1 min). IR (thin film): 1705, 1479, 1406, 1367, 1342, 1310, 1192, 1148, 1091, 1076, 753 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 7.69 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.28 (m, 7H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.12 (s, 1H), 5.14 (s, 2H), 3.83 (dd, *J* = 11.3, 8.0 Hz, 1H), 2.81 (td, *J* = 11.7, 5.7 Hz, 1H), 2.41 – 2.23 (m, 2H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, CD_3CN) δ 155.33, 153.06, 145.09, 138.18, 131.35, 129.88, 129.37, 128.80, 128.49, 125.52, 124.57, 91.79, 82.45, 79.44, 67.45, 52.91, 46.42, 36.57, 28.42; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{24}H_{28}N_2NaO_5$) requires *m/z* 447.18959, found *m/z* 447.18866 with a difference of 0.90 ppm; $[\alpha]_D^{21}$ = -68 (*c* = 1.00, $CHCl_3$).



1-benzyl 8-(*tert*-butyl) (3a*R*,8a*R*)-3a-(*tert*-butoxy)-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (21)

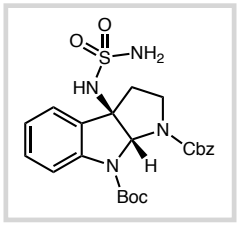
The crude material was purified on silica gel using 2-5% ethyl acetate in hexanes to give the desired product as a white solid (54 mg, 46% yield) that was determined to be 91% ee by HPLC analysis (ChiralPak AD-H, 1% IPA in hexanes, 1 mL/min, 280nm, t_r (minor) = 10.3 min, t_r (major) = 13.9 min). IR (thin film): 2976, 1709, 1479, 1407, 1367, 1341, 1309, 1192, 1152, 1097, 1074, 754 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.27 (m, 6H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.20 (s, 1H), 5.26 – 5.07 (m, 2H), 3.81 – 3.74 (m, 1H), 2.66 – 2.50 (m, 1H), 2.40 – 2.24 (m, 2H), 1.49 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, CD_3CN) δ 155.44, 153.34, 144.56, 138.26, 133.05, 130.95, 129.38, 128.82, 126.86, 124.17, 82.34, 80.81, 77.13, 70.79, 67.47, 45.16, 41.43, 30.72, 28.40; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{27}H_{34}N_2NaO_5$) requires *m/z*

489.23654, found *m/z* 489.23609 with a difference of 0.20 ppm; $[\alpha]_D^{21}$ = -50 (*c* = 0.50, $CHCl_3$).



Benzyl (3a*R*,8a*S*)-3a-((2-iodophenyl)amino)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (22)

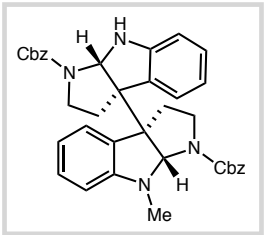
The crude material was purified on silica gel using 5-10% ethyl acetate in hexanes to give the desired product as a white solid (82 mg, 64% yield) that was determined to be 93% ee by HPLC analysis (ChiralPak AS-H, 10% IPA in hexanes, 1 mL/min, 250nm, t_r (major) = 16.6 min, t_r (minor) = 28.4 min). IR (thin film): 3384, 2955, 1696, 1415, 1351, 1318, 1198, 745, 697 cm^{-1}; ^1H NMR (*ca.* 1:1 mixture of rotamers, 500 MHz, $CDCl_3$) δ 7.69 – 7.61 (m, 1H), 7.42 – 7.29 (m, 5H), 7.20 – 7.11 (m, 2H), 6.99 (q, *J* = 7.7 Hz, 1H), 6.77 (td, *J* = 7.4, 3.4 Hz, 1H), 6.63 (dd, *J* = 27.5, 7.9 Hz, 1H), 6.45 – 6.32 (m, 2H), 5.71 (dd, *J* = 35.9, 2.3 Hz, 1H), 5.28 – 5.11 (m, 2.5H), 4.74 (s, 0.5H), 4.65 (d, *J* = 14.6 Hz, 1H), 3.95 – 3.77 (m, 1H), 3.41 – 3.29 (m, 1H), 2.66 – 2.56 (m, 1H), 2.44 – 2.34 (m, 1H); ^{13}C NMR (*ca.* 1:1 mixture of rotamers, 126 MHz, $CDCl_3$) δ 155.42, 154.57, 148.99, 148.82, 144.49, 144.45, 139.49, 139.38, 136.50, 136.45, 130.01, 129.95, 129.30, 129.27, 128.99, 128.82, 128.68, 128.43, 128.29, 128.11, 123.50, 123.40, 119.91, 119.81, 119.58, 113.68, 113.38, 109.78, 109.65, 87.79, 87.67, 78.34, 77.60, 73.82, 72.64, 67.47, 67.28, 44.72, 44.51, 39.31, 38.77; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{24}H_{23}IN_3O_2$) requires *m/z* 512.08295, found *m/z* 512.08206 with a difference of 1.73 ppm; $[\alpha]_D^{21}$ = -207 (*c* = 0.50, $CHCl_3$).



1-benzyl 8-(*tert*-butyl) (3a*R*,8a*R*)-3a-(sulfamoylamino)-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (23)

The reaction was performed according to **GP5** with 6 equivalents of sulfamide (144 mg, 1.5 mmol). The crude material was purified on silica gel using 30-50% ethyl acetate in hexanes to give the desired product as a white solid (87 mg, 71% yield) that was determined to be 93% ee by HPLC analysis (ChiralPak OD-H, 25% IPA in hexanes, 1 mL/min, 250nm, t_r (minor) = 9.9 min, t_r (major) = 16.8 min). IR (thin film): 3259, 2979, 1698, 1481, 1412, 1367, 1332, 1152, 1096, 750, 697 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 7.65 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.29 (m, 6H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.48 (s, 1H), 5.98 (s, 1H), 5.11 (d, *J* = 34.1 Hz, 4H), 3.83 (dd, *J* = 11.3, 7.8 Hz, 1H), 2.72 (td, *J* = 11.7, 5.2 Hz, 1H), 2.52 (td, *J* = 12.2, 7.9 Hz, 1H), 2.34 (dd, *J* = 12.3, 5.2 Hz, 1H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, CD_3CN) δ 155.23, 153.42, 144.48, 138.14, 131.09, 130.96, 129.37, 128.81, 128.49, 125.49, 124.49, 82.34, 80.77, 71.55, 67.52, 45.52, 37.28, 28.45; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{23}H_{28}N_4NaO_6S$) requires *m/z* 511.16273, found *m/z* 511.16293 with a difference of 1.54 ppm; $[\alpha]_D^{21}$ = -55 (*c* = 1.00, $CHCl_3$).

Synthesis of pyrroloindoline natural products:

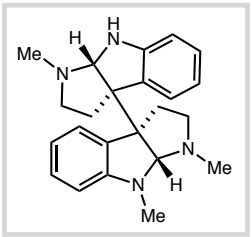


Dibenzyl (3a*S*,3'a*S*,8a*S*,8'a*S*)-8-methyl-2,2',3,3',8,8a,8',8'a-octahydro-1*H*,1'*H*-[3a,3'a-bipyrrolo[2,3-*b*]indole]-1,1'-dicarboxylate (heterodimer **26**)

To a flame dried 100-mL round bottom flask equipped with stir bar was added **24** (927 mg, 2 mmol, 1 equiv), *N'*-Cbz tryptamine **1** (882 mg, 3 mmol, 1.5 equiv), and [Ir(dCF$_3$, Me-ppy)$_2$(dtbbpy)]PF_6 (48.6 mg, 0.04 mmol, 0.02 equiv). The reaction vessel was evacuated and backfilled with argon three times then anhydrous degassed CH_2Cl_2 (40 mL) was added. The reaction mixture was then cooled to -40 °C in an acetonitrile/dry ice bath and degassed trifluoroacetic acid (0.153 mL, 2 mmol, 1 equiv) was added at low temperature. After addition, the reaction was irradiated in one of two possible set ups (see **Figures S3 & S4**): (1) in a cryocool bath with 7 W blue LEDs at -40 °C or (2) in an acetonitrile/dry ice bath with three 34W Kessil H150 blue lamps for 18 h or until complete conversion of starting material by TLC analysis at which point the reaction is deep magenta in color. Be careful to stop the reaction as soon as it reaches full conversion as product decomposition can occur under the reaction conditions. Upon

completion, the reaction was immediately quenched with sat. aqueous $NaHCO_3$ and the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield a bright red-orange residue. This crude material was purified by column chromatography on silica gel using 5-15% ethyl acetate in hexanes with 1% added Et_3N to yield the desired product as a 13:1 mixture of diastereomers (849 mg, 1.41 mmol, 71% yield, white solid) which were carried through to the next step without separation. The diastereomeric ratio was determined by ^1H NMR analysis of the crude reaction mixture. The dr is retained following the above purification protocol. If desired, the diastereomers can be separated by preparative TLC on silica gel using 2% ethyl acetate in chloroform.

The desired product was determined to be 97% ee by HPLC analysis (ChiralPak AD-H, 25% IPA in hexanes, 1 mL/min, 250nm, t_r (minor) = 12.6 min, t_r (major) = 14.0 min). IR (thin film): 3377, 2954, 2884, 1694, 1411, 1352, 1200, 1100, 746, 697 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 7.51 – 7.19 (m, 11H), 7.19 – 7.04 (m, 3H), 6.72 (p, *J* = 14.7, 7.4 Hz, 1H), 6.69 – 6.56 (m, 2H), 6.39 (d, *J* = 7.8 Hz, 1H), 5.51 – 5.25 (m, 1H), 5.18 – 4.92 (m, 5H), 4.79 (dd, *J* = 57.7, 44.7 Hz, 1H), 3.90 – 3.71 (m, 1H), 3.68 – 3.52 (m, 1H), 2.96 – 2.73 (m, 4H), 2.72 – 2.43 (m, 3H), 2.28 – 2.03 (m, 2H); ^{13}C NMR (126 MHz, CD_3CN) δ 155.75, 155.71, 155.04, 154.80, 154.18, 152.91, 151.78, 151.66, 138.14, 138.06, 137.90, 130.23, 130.09, 130.05, 130.03, 129.98, 129.74, 129.59, 129.57, 129.47, 129.40, 129.37, 128.86, 128.78, 128.77, 128.65, 128.40, 128.25, 125.84, 125.75, 125.67, 125.59, 125.54, 125.44, 125.37, 125.10, 124.84, 119.34, 118.11, 118.02, 110.26, 110.10, 106.75, 84.71, 84.27, 84.25, 79.70, 79.63, 79.02, 67.32, 67.24, 67.16, 63.10, 63.04, 62.53, 62.34, 61.83, 61.43, 61.27, 60.86, 46.17, 46.14, 46.05, 45.91, 34.56, 34.22, 34.18, 32.89, 32.76, 32.53; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{37}H_{37}N_4O_4$) requires *m/z* 601.28094, found *m/z* 601.28211 with a difference of 1.96 ppm; $[\alpha]_D^{21}$ = -198 (*c* = 1.00, $CHCl_3$).



(–)-calycanthidine (27)

To a 250 mL flame dried two-neck round bottomed flask was added heterodimer **26** (849 mg, 1.41 mmol, 1 equiv). The compound was then azeotropically dried from

anhydrous benzene (200mL) and the resulting residue was dissolved in anhydrous toluene (144mL). The reaction was equipped with a stir bar and reflux condenser then Red Al ® (70 wt% solution in toluene, 6.13 mL, 21.2 mmol, 15 equiv) was slowly added at room temperature. Following addition, the reaction was heated to reflux for 1 h. After completion, the solution was allowed to cool to rt then it was slowly quenched by sat. aqueous Na_2SO_4 solution until effervescence subsided and the resulting mixture was allowed to stir for 10 min. Solid Na_2SO_4 was then added and the mixture was stirred for another 10 min. The mixture was then poured through a plug of Celite washing thoroughly with CH_2Cl_2. The resulting solution was concentrated *in vacuo* to yield a light pink residue. Purification by flash column chromatography on silica gel using 1-4% aq. NH_4OH solution in acetonitrile yielded (–)-calycanthidine **(27)** as a white solid (404 mg, 1.12 mmol, 80% yield).

IR (thin film): 3315, 2932, 2791, 1603, 1488, 1251, 1155, 1024 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.99 (app-t, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.53 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 6.28 (d, *J* = 7.9 Hz, 1H), 4.47 (s, 1H), 4.38 (s, 1H), 3.00 (s, 3H), 2.68 – 2.42 (m, 8H), 2.40 (s, 3H), 2.35 (s, 3H), 2.04 – 1.91 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.14, 151.11, 133.64, 133.06, 128.28, 128.03, 124.58, 123.82, 118.42, 116.90, 109.17, 106.05, 92.25, 85.34, 63.66, 63.12, 52.83, 52.79, 38.11, 37.20, 35.94, 35.65, 35.54; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{23}H_{29}N_4$) requires *m/z* 361.23868, found *m/z* 361.23907 with a difference of 1.11 ppm; $[\alpha]_D^{21}$ = -115 (*c* = 1.00, $CHCl_3$).[10-13]

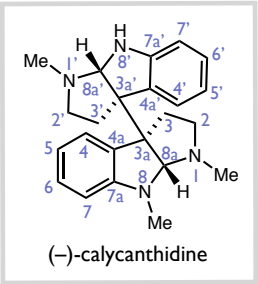
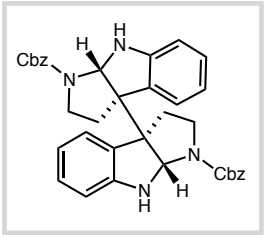


Table S2: Comparison of ^{1}H NMR data for (–)-calycanthidine:

Assignment	Overman's Report[11] (–)-calycanthidine (500 MHz, $CDCl_3$, 50 °C)	Takayama's Report[12] (–)-calycanthidine (500 MHz, $CDCl_3$, 50 °C)	Movassaghi's Report[13] (–)-calycanthidine (500 MHz, $CDCl_3$, 50 °C)	This Work (–)-calycanthidine (500 MHz, $CDCl_3$, 50 °C)
N1′-C**H**$_3$	2.41 (s, 3H)	2.38 (s, 3H)	2.38 (s, 3H)	2.40 (s, 3H)
N1-C**H**$_3$	2.36 (s, 3H)	2.33 (s, 3H)	2.33 (s, 3H)	2.35 (s, 3H)
C2′	2.68–2.42 (m, 2H)	2.65–2.40 (m, 2H)	2.65–2.40 (m, 2H)	2.68–2.42 (m, 2H)
C2	2.68–2.42 (m, 2H)	2.65–2.40 (m, 2H)	2.65–2.40 (m, 2H)	2.68–2.42 (m, 2H)
C3′	2.68–2.42 (m, 1H), 2.00–1.86 (m, 1H)	2.65–2.40 (m, 1H), 2.05-1.95 (m, 1H)	2.65–2.40 (m, 1H), 2.01–1.93 (m, 1H)	2.68–2.42 (m, 1H), 2.04–1.91 (m, 1H)
C3	2.68–2.42 (m, 1H), 2.00–1.86 (m, 1H)	2.65–2.40 (m, 1H), 2.05-1.95 (m, 1H)	2.65–2.40 (m, 1H), 2.01–1.93 (m, 1H)	2.68–2.42 (m, 1H), 2.04–1.91 (m, 1H)
C3a	–	–	–	–
C3a′	–	–	–	–
C4′	7.10 (d, *J* = 7.3 Hz, 1H)	7.07 (d, *J* = 7.3 Hz, 1H)	7.06 (d, *J* = 7.4 Hz, 1H)	7.08 (d, *J* = 7.5 Hz, 1H)
C4	7.05 (d, *J* = 7.2 Hz, 1H)	7.02 (d, *J* = 7.3 Hz, 1H)	7.00 (d, *J* = 5.8 Hz, 1H)	7.03 (d, *J* = 7.2 Hz, 1H)
C4a′	–	–	–	–
C4a	–	–	–	–
C5′	6.55 (t, *J* = 7.4 Hz, 1H)	6.52 (dd, *J* = 7.3, 7.3 Hz, 1H)	6.51 (app-t, *J* = 7.2 Hz, 1H)	6.53 (t, *J* = 7.3 Hz, 1H)
C5	6.58 (t, *J* = 7.4 Hz, 1H)	6.59 (dd, *J* = 7.3, 7.3 Hz, 1H	6.58 (app-t, *J* = 7.5 Hz, 1H)	6.60 (t, *J* = 6.9 Hz, 1H)
C6′	7.01 (dd, *J* = 7.5, 7.7 Hz, 1H)	6.98 (dd, *J* = 7.3, 7.6 Hz, 1H)	6.98 (app-t, *J* = 7.7 Hz, 1H)	6.99 (app-t, *J* = 7.8 Hz, 1H)
C6	6.94 (dd, *J* = 7.5, 7.5 Hz, 1H)	6.92 (dd, *J* = 7.3, 7.6 Hz, 1H)	6.92 (app-t, *J* = 7.5 Hz, 1H)	6.93 (t, *J* = 7.4 Hz, 1H)
C7′	6.30 (d, *J* = 7.8 Hz, 1H)	6.27 (d, *J* = 7.6 Hz, 1H)	6.27 (d, *J* = 7.7 Hz, 1H)	6.28 (d, *J* = 7.9 Hz, 1H)
C7	6.50 (d, *J* =7.8 Hz, 1H)	6.48 (d, *J* = 7.6 Hz, 1H)	6.48 (d, *J* = 8.0 Hz, 1H)	6.49 (d, *J* = 7.9 Hz, 1H)
C7a′	–	–	–	–
C7a	–	–	–	–
N8′-CH_3	3.01 (s, 3H)	2.98 (s, 3H)	2.98 (s, 3H)	3.00 (s, 3H)
N8-**H**	–	–	–	–
C8a′	4.40 (s, 1H)	4.38 (s, 1H)	4.37 (s, 1H)	4.38 (s, 1H)
C8a	4.48 (s, 1H)	4.42 (s, 1H)	4.47 (s, 1H)	4.47 (s, 1H)

Table S3: Comparison of ^{13}C NMR data for (–)-calycanthidine:

Assignment	**Overman's Report[11]** (–)-calycanthidine (500 MHz, $CDCl_3$, 50 °C)	**Takayama's Report[12]** (–)-calycanthidine (500 MHz, $CDCl_3$, 50 °C)	**Movassaghi's Report[13]** (–)-calycanthidine (500 MHz, $CDCl_3$, 50 °C)	**This Work** (–)-calycanthidine (500 MHz, $CDCl_3$, 50 °C)
N1′-**C**H_3	37.9	37.9	38.2	38.1
N1-**C**H_3	37.0	37.0	37.3	37.2
C2′	52.6	52.6	52.9	52.8
C2	52.6	52.6	52.9	52.8
C3′	35.7	35.7	35.7	35.9
C3	35.7	35.7	35.6	35.7
C3a	62.9	62.8	63.2	63.1
C3a′	63.5	63.2	63.8	63.7
C4′	123.6	123.6	124.0	123.8
C4	124.4	124.4	124.7	124.6
C4a′	132.9	132.7	133.1	133.1
C4a	133.4	133.3	133.6	133.6
C5′	116.7	116.7	117.1	116.9
C5	118.2	118.2	118.6	118.4
C6′	128.1	128.1	128.4	128.3
C6	127.8	127.9	128.2	128.0
C7′	105.8	105.9	106.2	106.1
C7	108.9	109.0	109.3	109.1
C7a′	152.9	152.8	153.2	153.1
C7a	151.0	150.8	151.2	151.1
N8′-**C**H_3	35.4	35.4	35.6	35.5
N8-H	–	–	–	–
C8a′	92.1	91.8	92.4	92.3
C8a	85.1	85.0	85.5	85.3

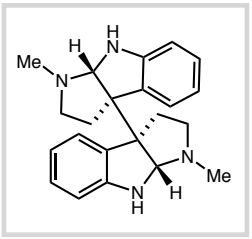


(-)-dibenzyl (3a*S*,3'a*S*,8a*S*,8'a*S*)-2,2',3,3',8,8a,8',8'a-octahydro-1*H*,1'*H*-[3a,3'a-bipyrrolo[2,3-*b*]indole]-1,1'-dicarboxylate (homodimer 28)

To a flame dried vial equipped with stir bar was added **2** (112 mg, 0.25 mmol, 1 equiv), *N'*-Cbz tryptamine **1** (88 mg, 0.3 mmol, 1.2 equiv), and [Ir(dCF$_3$, Me-ppy)$_2$(dtbbpy)]PF$_6$ (6.1 mg, 0.005 mmol, 0.02 equiv). The reaction vessel was evacuated and backfilled with argon three times then anhydrous degassed THF (2.5 mL) was added. The reaction mixture was then cooled to -40 °C in an acetonitrile/dry ice bath and degassed trifluoroacetic acid (0.057 mL, 0.75 mmol, 3 equiv) was added at low temperature. After addition, the reaction was irradiated with 7 W blue LEDs in a -40 °C cryocool bath (see **Figure S3**) for 36 h or until complete conversion of starting material by TLC analysis. Upon completion, the reaction was quenched with sat. aqueous NaHCO$_3$ and the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. This residue was purified by column chromatography on silica gel using 5-20% ethyl acetate in hexanes with 1% added Et_3N to yield the desired product as a 3:1 mixture of diastereomers as determined by ^{1}H NMR analysis (79 mg, 0.135 mmol, 54% yield).
To a vial containing this purified 3:1 mixture of diastereomers was added [Ir(dCF$_3$, Me-ppy)$_2$(dtbbpy)]PF$_6$ (3.3 mg, 0.0027 mmol, 0.02 equiv) and THF (1.35 mL). The reaction vial was equipped with a septa and cap and a large-gauged needle was pierced into the septa to expose the reaction to air. The reaction mixture was then irradiated with 7 W blue LEDs at -40 °C for 24 h or until the product composition reached >20:1 dr by ^{1}H NMR analysis. Upon completion, the reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography using 5-20% ethyl acetate in hexanes with 1% added Et_3N to yield the product as a single diastereomer in 69% yield.

IR (thin film): 3369, 2955, 1687, 1414, 1352, 1199, 1105, 744, 696 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) δ 7.41 – 7.20 (m, 13H), 7.11 (q, *J* = 8.4 Hz, 2H), 6.74 (td, *J* = 7.4, 3.7 Hz, 2H), 6.66 – 6.58 (m, 2H), 5.36 (dd, *J* = 83.4, 15.5 Hz, 2H), 5.17 – 4.89 (m, 4H), 4.80 (dd, *J* = 39.7, 15.6 Hz, 2H), 3.59 (ddd, *J* = 10.4, 7.9, 5.4 Hz, 2H), 2.83 – 2.69 (m, 2H), 2.66 – 2.53 (m, 2H), 2.26 – 2.18 (m, 2H); ^{13}C NMR (126 MHz, CD_3CN) δ 155.06, 154.19,

151.89, 151.85, 151.77, 151.73, 138.16, 138.13, 137.94, 130.09, 129.49, 129.41, 129.38, 128.87, 128.82, 128.66, 128.40, 126.19, 126.08, 125.98, 119.30, 118.30, 110.19, 110.16, 110.05, 110.01, 79.54, 78.85, 67.24, 62.89, 62.73, 61.64, 61.47, 46.12, 45.97, 32.74, 32.70, 32.65, 32.60; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{36}H_{35}N_4O_4$) requires *m/z* 587.26529, found *m/z* 587.26451 with a difference of 1.32 ppm; $[\alpha]_D^{21}$ = -168 (*c* = 1.00, $CHCl_3$).



(-)-chimonanthine

To a flame dried round bottomed flask was added homodimer **28** (55 mg, 0.094 mmol, 1 equiv). The compound was then azeotropically dried from anhydrous benzene (15 mL) and the resulting residue was dissolved in anhydrous toluene (10 mL). The reaction was equipped with a stir bar and reflux condenser then Red Al ® (70 wt% solution in toluene, 0.271 mL, 0.94 mmol, 10 equiv) was slowly added at room temperature. Following addition, the reaction was heated to reflux for 30 min. After completion, the solution was allowed to cool to rt then it was slowly quenched by sat. aqueous Na_2SO_4 solution until effervescence subsided and the resulting mixture was allowed to stir for 10 min. Solid Na_2SO_4 was then added and the mixture was stirred for another 10 min. The mixture was then poured through a plug of Celite washing thoroughly with CH_2Cl_2. The resulting solution was concentrated *in vacuo*. Purification by flash column chromatography on silica gel using 2-5% aq. NH_4OH solution in acetonitrile yielded (–)-chimonanthine **(29)** as a white solid (25.7 mg, 0.074 mmol, 79% yield).

IR (thin film): 3308, 2932, 1605, 1485, 1467, 1246, 734; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.4 Hz, 2H), 6.97 (t, 2H), 6.65 (t, 2H), 6.52 (d, *J* = 7.8 Hz, 2H), 4.38 (s, 3H), 4.18 (s, 2H), 2.74 – 2.44 (m, 6H), 2.32 (s, 6H), 2.18 – 1.95 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.94, 133.55, 128.15, 124.54, 118.67, 109.30, 85.40, 63.66, 52.82, 37.26, 35.87; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{22}H_{27}N_4$) requires *m/z* 347.22303, found *m/z* 347.22318 with a difference of 0.45 ppm; $[\alpha]_D^{21}$ = -139 (*c* = 1.00, $CHCl_3$).[14-17]

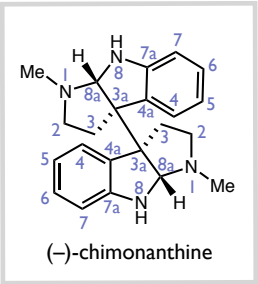
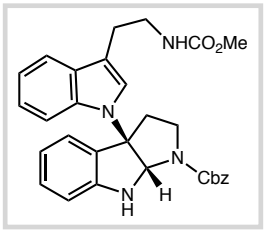


Table S4: Comparison of our ^{1}H NMR data for (–)-chimonanthine:

Assignment	Verotta's Report[15] (+)-chimonanthine (200 MHz, $CDCl_3$)	Movassaghi's Report[16] (+)-chimonanthine (500 MHz, $CDCl_3$, 50 °C)	This Work (–)-chimonanthine (500 MHz, $CDCl_3$, 50 °C)
C2	2.50 (m, 4H)	2.57 (m, 2H)	2.63-2.44 (m, 4H)
C3	2.50 (m, 2H), 2.07 (dt, *J* = 12.0, 6.4 Hz, 2H)	2.57 (m, 2H), 2.05 (app dd, *J* = 10.5, 5.0 Hz, 2H)	2.63-2.44 (m, 2H), 2.13-1.99 (m, 2H)
C3a	–	–	–
C4	7.20, (d, *J* = 7.4 Hz, 2H)	7.19 (d, J = 7.5 Hz, 2H)	6.52 (d, *J* = 7.3 Hz, 2H)
C4a	–	–	–
C5	6.67 (t, J = 7.3 Hz, 2H)	6.66 (t, J = 7.3, 2H)	6.65 (t, *J* = 7.3 Hz, 2H)
C6	7.00 (t, J = 7.6 Hz, 2H)	6.98 (t, J = 7.3 Hz, 2H)	6.99 (t, *J* = 7.3 Hz, 2H)
C7	6.55, (d, J = 7.7 Hz, 2H)	6.53 (d, J = 7.5 Hz, 2H)	6.52 (d, *J* = 7.3 Hz, 2H)
C7a	–	–	–
N8-**H**	–	4.23 (s, 2H)	4.18 (br s, 2H)
C8a	4.35 (br s, 2H)	4.40 (br s, 2H)	4.38 (br s, 2H)
N1-CH_3	2.31 (s, 6H)	2.33 (s, 6H)	2.32 (s, 6H)

Table S5: Comparison of our ^{13}C NMR data for (–)-chimonanthine:

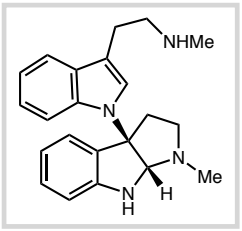
Assignment	Tokuyama's Report[17] (+)-chimonanthine (25.05 MHz, $CDCl_3$)	Movassaghi's Report[16] (+)-chimonanthine (125.8 MHz, $CDCl_3$, 50 °C)	This Work (–)-chimonanthine (125.8 MHz, $CDCl_3$, 50 °C)
C2	52.7	52.9	52.8
C3	36.5	36.1	35.9
C3a	63.2	63.8	63.7
C4	124.4	124.6	124.5
C4a	133.1	133.8	133.6
C5	118.7	118.8	118.7
C6	128.1	128.2	128.2
C7	109.4	109.4	109.3
C7a	150.6	151.1	150.9
N8-**H**	–	–	–
C8a	85.2	85.5	85.4
N1-CH_3	37.2	37.4	37.3



Benzyl (3a*R*,8a*S*)-3a-(3-(2-((methoxycarbonyl)amino)ethyl)-1*H*-indol-1-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate

Preparation of the title compound was adapted from the synthesis of a related compound.[18] To a flask was added aniline **22** (82 mg, 0.16 mmol, 1 equiv), alkyne **30** (73 mg, 0.392 mmol, 2.5 equiv), Na_2CO_3 (42 mg, 0.392 mmol, 2.5 equiv), LiCl (6.0 mg, 0.141 mmol, 0.9 equiv) and $Pd(OAc)_2$ (7.1mg, .031 mmol, 0.2 equiv). The vessel was evacuated and backfilled with argon three times before degassed anhydrous DMF (3.14 mL) was added and the resulting suspension was sparged with argon for 15 minutes. The reaction was heated to 100 °C for 30 min then allowed to cool, diluted with CH_2Cl_2 and concentrated *in vacuo*. The resulting residue was dissolved in ethyl acetate and washed with 2M HCl. The layers were separated and the aqueous layer was extracted with EtOAc (5x). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated to give a residue that was purified by column chromatography on silica gel with 2-10% EtOAc/CH_2Cl_2 to yield the desired product as a white foam in 83% yield.

IR (thin film): 3347, 1697, 1456, 1417, 1352, 1256, 1196, 745 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (t, *J* = 8.0 Hz, 1H), 7.41 – 7.31 (m, 6H), 7.25 – 7.19 (m, 2H), 7.19 – 7.09 (m, 2H), 6.95 (d, *J* = 5.6 Hz, 1H), 6.84 (q, *J* = 7.8 Hz, 1H), 6.71 (dd, *J* = 33.6, 7.9 Hz, 1H), 5.94 (d, *J* = 30.0 Hz, 1H), 5.28 – 5.11 (m, 2H), 4.75 (d, *J* = 38.4 Hz, 1H), 4.16 – 3.93 (m, 1H), 3.65 (s, 3H), 3.53 – 3.22 (m, 4H), 2.88 (t, *J* = 6.9 Hz, 2H), 2.71 – 2.56 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.16, 154.99, 154.16, 149.40, 149.18, 136.31, 135.39, 135.29, 130.88, 130.80, 129.90, 129.85, 128.87, 128.71, 128.51, 128.37, 128.20, 128.15, 126.90, 126.66, 125.09, 124.90, 124.33, 124.30, 122.15, 121.50, 119.86, 119.73, 119.60, 119.57, 119.45, 112.20, 112.06, 110.67, 110.50, 79.55, 78.94, 77.41, 77.16, 76.91, 75.86, 74.66, 67.60, 67.38, 52.16, 45.77, 45.58, 41.45, 35.83, 35.65, 25.87; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{30}H_{31}N_4O_4$) requires *m/z* 511.23399, found *m/z* 511.23416 with a difference of 0.35 ppm; $[\alpha]_D^{21}$ = -165 (*c* = 1.00, $CHCl_3$).



(–)-psychotriasine (31)

To a 25 mL flame dried round bottomed flask was added benzyl (3a*R*,8a*S*)-3a-(3-(2-((methoxycarbonyl)amino)ethyl)-1*H*-indol-1-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (66.5 mg, 0.13 mmol, 1 equiv). The compound was then azeotropically dried from anhydrous benzene (20 mL) and the resulting residue was dissolved in anhydrous toluene (13.5 mL). The reaction was equipped with a stir bar and reflux condenser then Red Al ® (70 wt% solution in toluene, 0.375 mL, 1.3 mmol, 10 equiv) was slowly added at room temperature. Following addition, the reaction was heated to reflux for 30 min. After completion, the solution was allowed to cool to rt then it was slowly quenched by sat. aqueous Na_2SO_4 solution until effervescence subsided and the resulting mixture was allowed to stir for 10 min. Solid Na_2SO_4 was then added and the mixture was stirred for another 10 min. The mixture was then poured through a plug of Celite washing thoroughly with CH_2Cl_2. The resulting solution was concentrated *in vacuo*. Purification by flash column chromatography on silica gel using 1% aq. NH_4OH solution in acetonitrile yielded (–)-psychotriasine **(31)** as a white solid (38.2 mg, 0.111 mmol, 85% yield).

IR (thin film): 3382, 2928, 1608, 1486, 1459, 742 cm^{-1}; ^1H NMR (500 MHz, CD_3OD) δ 7.53 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.41 (s, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.07 (td, *J* = 7.7, 1.2 Hz, 1H), 7.01 – 6.90 (m, 2H), 6.86 (dd, *J* = 7.5, 0.7 Hz), 6.70 (d, *J* = 7.8 Hz, 1H), 6.58 (td, *J* = 7.4, 1.0 Hz, 1H), 5.23 (s, 1H), 3.27 – 3.18 (m, 1H), 3.02 – 2.93 (m, 3H), 2.92 – 2.85 (m, 2H), 2.66 – 2.57 (m, 1H), 2.52 – 2.45 (m, 4H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, CD_3OD) δ 152.56, 137.76, 131.46, 130.84, 130.65, 125.08, 124.71, 122.44, 120.16, 119.69, 119.54, 113.00, 112.93, 110.11, 87.08, 77.48, 52.86, 52.15, 39.99, 36.34, 35.85, 25.75. HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{22}H_{27}N_4$) requires *m/z* 347.22303, found *m/z* 347.22250 with a difference of 1.50 ppm. $[\alpha]_D^{21}$ = -97 (*c* = 0.33, MeOH).[19,20]

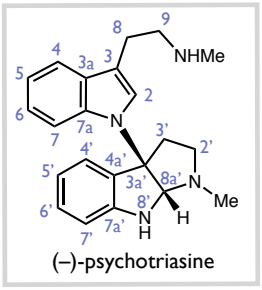


Table S6: Comparison of ^{1}H NMR data for (–)-psychotriasine:

Assignment	Hao's Report[20] (+)-psychotriasine (500 MHz, CD_3OD)	This Work (–)-psychotriasine (500 MHz, CD_3OD)
N′-C**H**$_3$	2.39 (s, 3H)	2.42 (s, 3H)
N-C**H**$_3$	2.44 (s, 3H)	2.47 (s, 3H)
C2′	2.96-2.93 (m, 1H), 2.57-2.54 (m, 1H)	3.01-2.97 (m, 1H), 2.64-2.58 (m, 1H)
C2	7.38 (s, 1H)	7.41 (s, 1H)
C3′	3.30-3.28 (m, 1H), 2.49-2.46 (m, 1H)	3.26-3.19 (m, 1H), 2.51-2.48 (m, 1H)
C3	–	–
C3a	–	–
C3a′	–	–
C4′	7.12 (dd, *J* = 7.8, 1.0 Hz)	7.13 (d, *J* = 8.1 Hz, 1H)
C4	6.85 (dd, *J* = 7.8, 1.0 Hz)	6.86 (dd, *J* = 7.5, 0.7 Hz)
C4a′	–	–
C5′	6.94 (dt, *J* = 7.8, 1.0 Hz)	6.96-6.91 (m, 1H)
C5	6.97 (dt, *J* = 7.8, 1.0 Hz)	6.98 (td, *J* = 7.8, 1.2 Hz)
C6′	6.56 (dt, *J* = 7.8, 1.0 Hz)	6.58 (td, *J* = 7.4, 1.0 Hz, 1H)
C6	7.04 (dt, *J* = 7.8, 1.0 Hz)	7.07 (td, *J* = 7.7, 1.2 Hz, 1H)
C7′	6.68 (dd, *J* = 7.8, 1.0 Hz)	6.70 (d, *J* = 7.8 Hz, 1H)
C7	7.52 (dd, *J* = 7.8, 1.0 Hz)	7.53 (dt, *J* = 8.1, 1.0 Hz)
C7a′	–	–
C7a	–	–
N8′-**H**	–	–
C8	2.94-2.91 (m, 2H)	2.98-2.94 (m, 2H)
C8a′	5.20 (s)	5.23 (s, 1H)
C9	2.88-2.85 (m, 2H)	2.91-2.85 (m, 1H)

Table S7: Comparison of ^{13}C NMR data for (–)-psychotriasine:

Assignment	Hao's Report (+)-psychotriasine (500 MHz, CD_3OD)	This Work (–)-psychotriasine (500 MHz, CD_3OD)
N′-$\mathbf{C}H_3$	35.7	35.9
N-$\mathbf{C}H_3$	36.3	36.3
C2′	52.0	52.2
C2	125.0	125.1
C3′	39.9	40.0
C3	112.7	112.9
C3a	130.4	130.8
C3a′	79.4	77.5
C4′	112.2	113.0
C4	124.7	124.7
C4a′	131.3	131.5
C5′	122.4	122.5
C5	120.1	120.2
C6′	119.6	119.5
C6	130.7	130.7
C7′	110.0	110.1
C7	120.1	119.7
C7a′	152.5	152.6
C7a	137.7	137.8
N8′-H	–	–
C8	25.6	25.8
C8a′	87.0	87.1
C9	52.0	52.9

Photochemical Flow Reactor Design:

The flow reactor was built using a glass condenser wrapped with 1/16" i.d. PFA tubing (IDEX Health and Science 1514L). Inside of the condenser were placed two LED strips and outside of the condenser was wrapped a blue LED "jacket" with four LED strips (470nm, SuperBrightLEDs, NFLS-X3-blue, 3.3W per 3.28 ft LED strip). Total light output was 20W. The apparatus was cooled by water flowing through the condenser and a small fan blowing over the system.

Figure S1: Flow photoreactor photos. Upper left/center: Blue LED "jacket".
Upper right: PFA tubing around condenser.
Lower right: Overall flow set up.

Photoredox Batch Reaction Design:

Photoredox reactions at room temperature were run in a blue LED dish setup with two blue LED strips (470nm, SuperBrightLEDs, NFLS-X3-blue, 3.3W per 3.28 ft LED strip) wrapped inside of a crystallizing dish. The set up was cooled by a small fan (Holmes HCF0611A-BM).

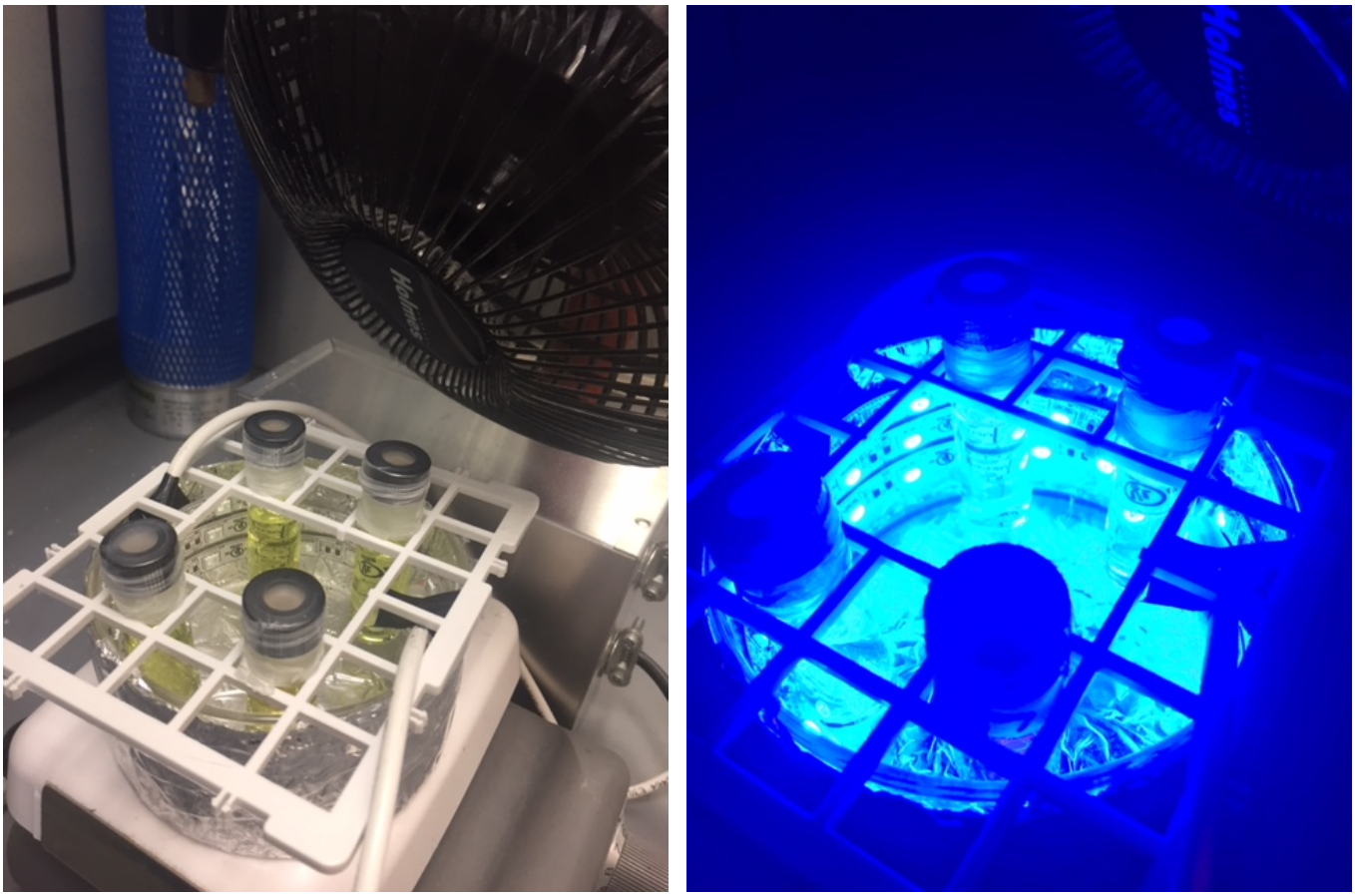


Figure S2: Blue LED dish set up.

The photoredox reactions run at low temperature can be set up in one of two ways:

(1) In a -40 °C Cryocool bath for optimum temperature control:
For this protocol, a submersible blue LED apparatus was made from a 2L beaker fused to a 300mL tall form beaker with an open bottom allowing the reaction to be effectively cooled. Two blue LED strips were wrapped around the outside of the inner beaker. The reaction was placed in the center of the inner beaker, approximately 2 cm from the light source.

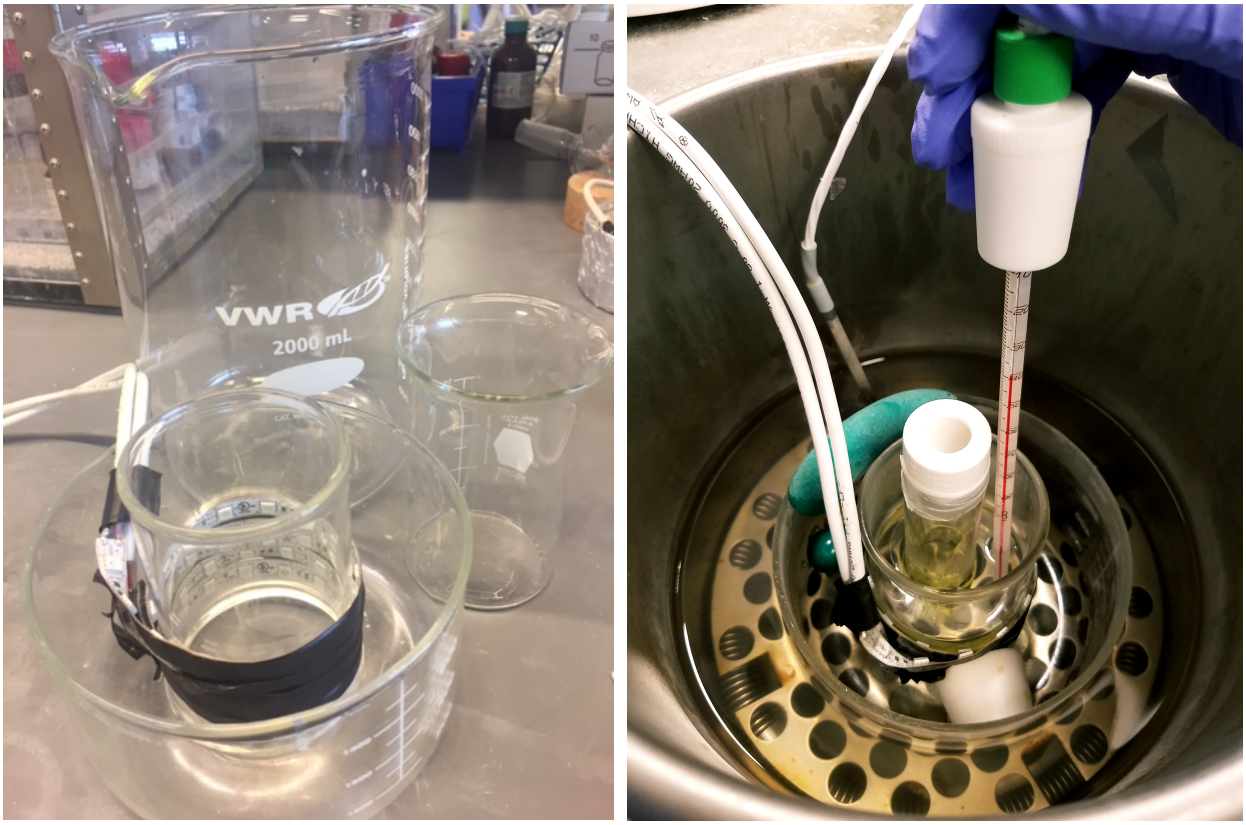


Figure S3: Low temperature cryocool set up.

(2) In an acetonitrile/dry ice bath irradiated with three 34W Kessil lamps:
A large dewar was filled with an acetonitrile/ dry ice mixture to maintain a temperature of -40 °C or lower.

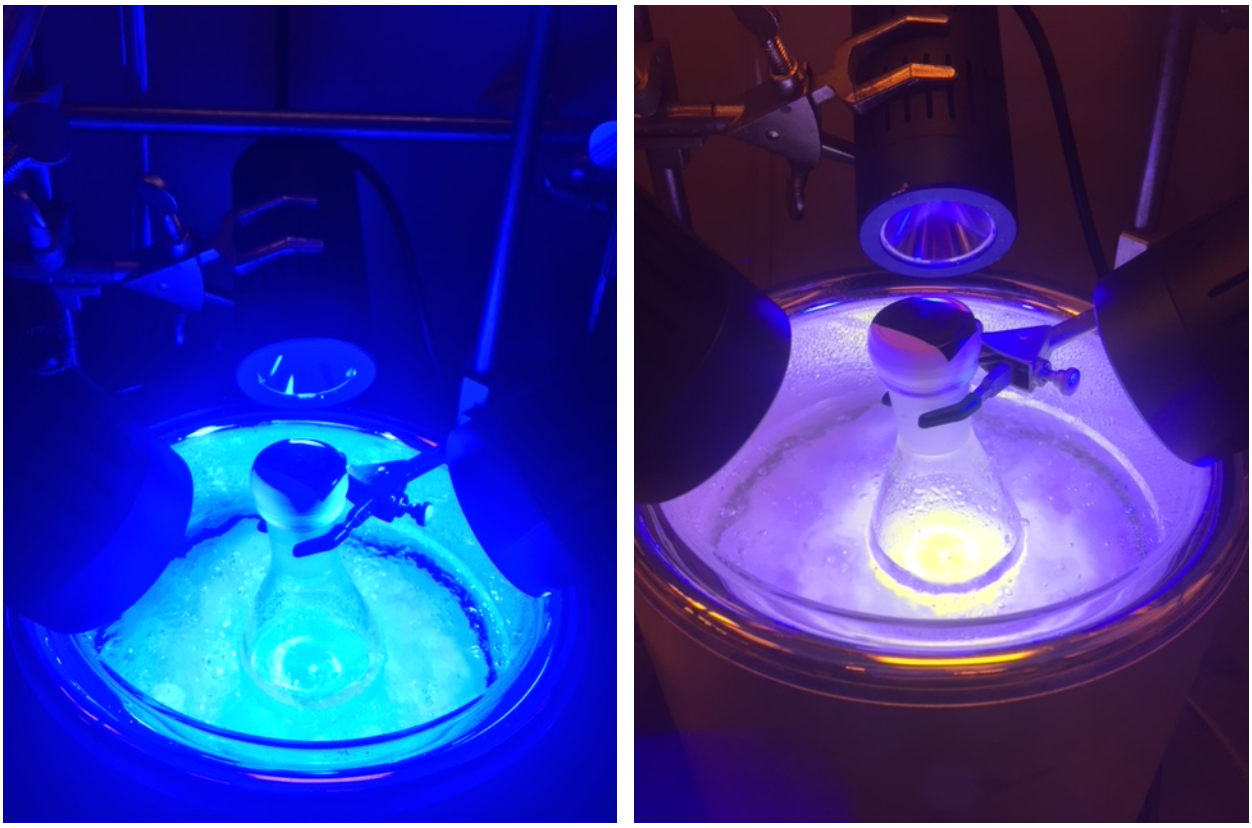
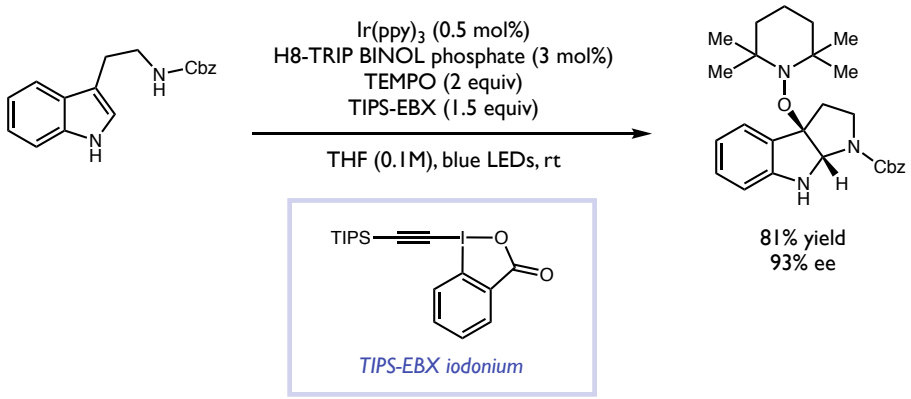


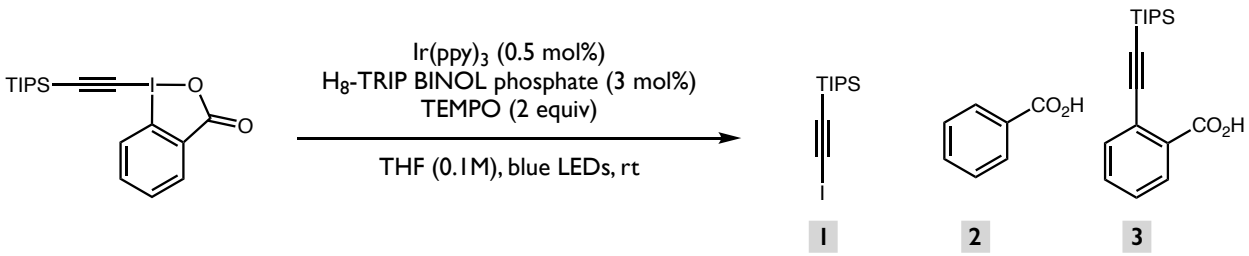
Figure S4: Acetonitrile/ dry ice bath set up for low temperature reactions. Picture on the right is filtered by blue-blocking lenses.

The proposed role of TIPS-EBX Iodonium



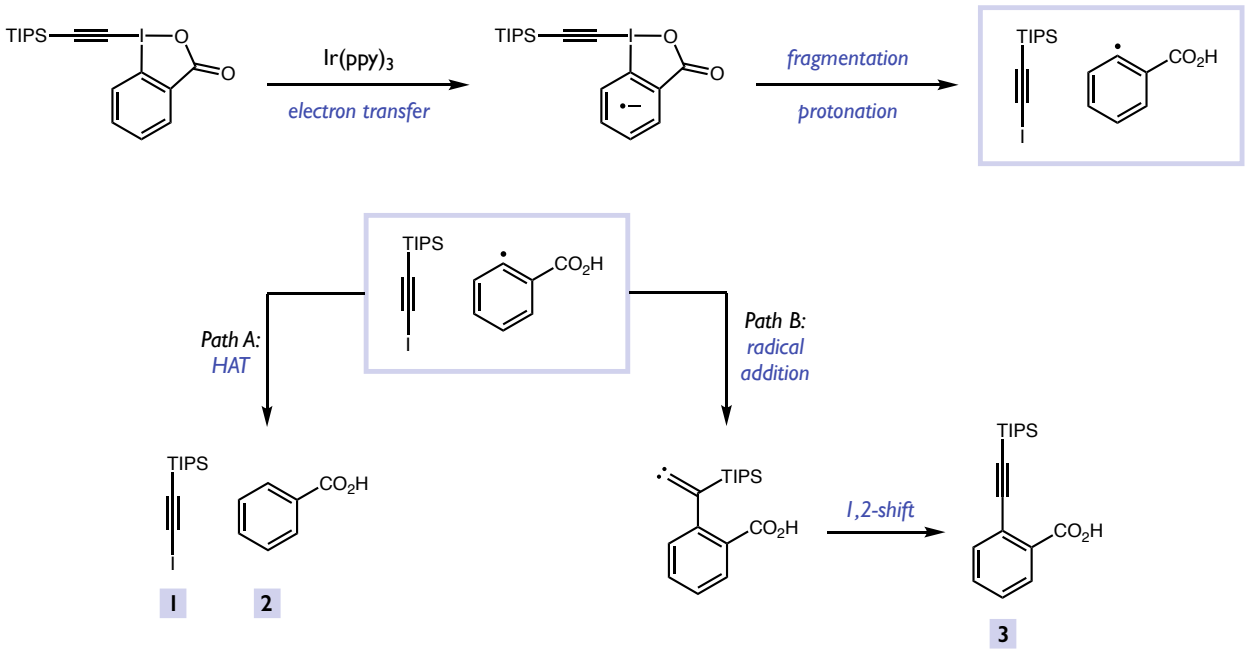
In the synthesis of TEMPOlated compound, TIPS-EBX Iodonium is proposed to act as a one electron oxidant turning $Ir^{III}(ppy)_3$ to $Ir^{IV}(ppy_3)$ which is competent to enter the catalytic cycle to initiate the PCET event. Stoichiometric amounts of the oxidant is used to turn over the catalytic cycle.

The observed side products of iodonium:



To get a better understanding of the mechanism of iodonium reactivity, we sought to isolate and identify the side products of TIPS-EBX iodonium. Using ^{1}H NMR, ^{13}C NMR and mass spectroscopy, compounds **1**, **2** and **3** were confirmed to be the major side products.

Proposed mechanism:

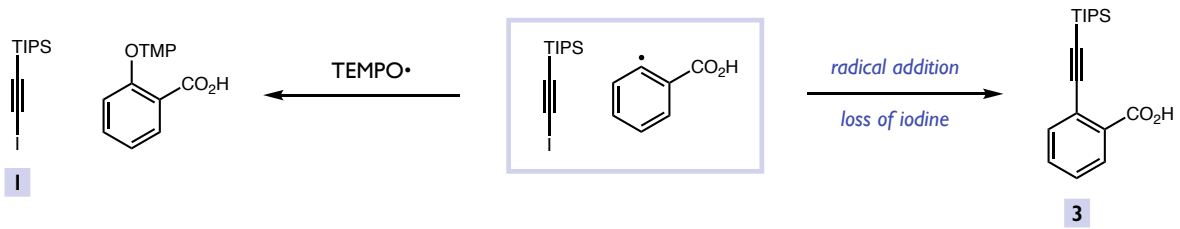


One electron reduction of the iodonium by $Ir(ppy)_3$ is proposed to trigger fragmentation followed by protonation of the benzoate to generate the alkynyl iodide **1** and aromatic carbon-centered radical. This highly reactive radical can readily undergo hydrogen atom transfer from TEMPO-H or the ethereal solvent (THF) to generate benzoic acid **2**. Alternatively, the radical can add to the acetylene iodide. A subsequent loss of iodine generates a carbene capable of 1,2- migration to deliver alkynylated benzoic acid **3**.

Support for the proposed mechanism:

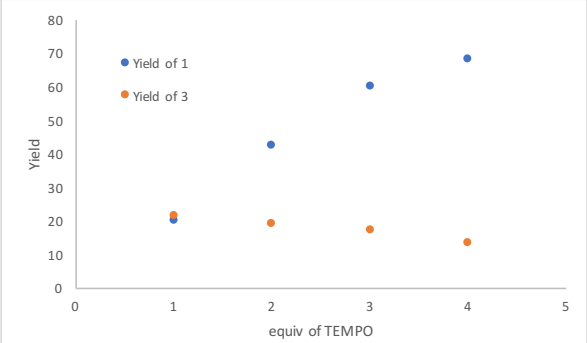
To probe this hypothesis, we tested the effect of TEMPO concentration on byproduct distribution. TEMPO is known to be an efficient radical scavenger and can therefore intercept any radicals that are generated in the reduction of iodonium. If the In support of our hypothesis, increasing concentrations of TEMPO led to an increase in the yield of alkynyl iodide **1**.

Furthermore, increasing TEMPO concetration resulted in decreasing yields of alkynylated benzoic acid. This is consistent with formation of this side product through radical addition to the iodide. Together these results support the proposed mechanism of EBX-iodonium fragmentation.



1 **3**

Affect of [TEMPO] on yield of byproducts



TEMPO (equiv)	% yield **1**	% yield **3**
1	20	21
2	42	19
3	60	17
4	68	13

Stern-Volmer Experiments

Stern-Volmer experiments were conducted on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer using the Cary Eclipse Scan Application. Stern-Volmer luminescence quenching experiments were run with freshly prepared solutions of 1.0×10^{-4} M $[Ir(ppy)_2(4,4'\text{-dtbbpy})](PF_6)$ in anhydrous THF at room temperature under an inert atmosphere. The solutions were irradiated at 360nm and luminescence was measured at 580 nm. The data summarized in the tables is the phosphorescence intensity measure three times for each sample. The data illustrated in the graphs is the average of three experiments.

Table S8: Luminescence quenching data for $Ir(ppy)_2(dtbbpy)PF_6$ and tryptamine. See Figure S5.

Experiment	Vial	1	2	3	Average	I_0/I	Tryptamine [M]
Run 1	0	897	892	908	899.0	1.00	0
	1	901	903	904	902.7	0.96	0.002
	2	891	889	890	890.0	0.97	0.004
	3	894	892	893	893.0	0.97	0.006
	4	880	880	891	883.7	0.98	0.008

Table S9: Luminescence quenching data for $Ir(ppy)_2(dtbbpy)PF_6$ and variable $NBu_4(OPh)_2PO_2$. See Figure S6.

Experiment	Vial	1	2	3	Average	I_0/I	base [M]
Run 1	0	865	867	882	871.3	1	0
	1	621	617	621	619.7	1.41	0.0005
	2	560	565	571	565.3	1.54	0.001
	3	551	534	544	543	1.60	0.0015
	4	518	520	519	519	1.68	0.002
Run 2	0	875	887	869	877	1	0
	1	620	625	616	620.3	1.41	0.0005
	2	566	575	567	569.3	1.54	0.001
	3	546	552	559	552.3	1.59	0.0015
	4	522	528	523	524.3	1.67	0.002
Run 3	0	884	898	905	895.7	1	0
	1	636	630	637	634.3	1.41	0.0005
	2	580	583	582	581.7	1.54	0.001
	3	557	559	554	556.7	1.61	0.0015
	4	530	531	537	532.7	1.68	0.002

Table S10: Luminescence quenching data for $Ir(ppy)_2(dtbbpy)PF_6$, 0.002M $NBu_4(OPh)_2PO_2$, and variable protiated tryptamine. See Fig S5.

Experiment	Vial	1	2	3	Average	I_0/I	tryptamine [M]
Run 1	0	523	515	514	517.3	1.00	0
	1	200	203	201	201.3	2.57	0.002
	2	136	138	137	137.0	3.78	0.004
	3	108	108	109	108.3	4.78	0.006
	4	91	90	90	90.3	5.73	0.008
Run 2	0	522	524	520	522.0	1	0
	1	223	225	226	224.7	2.32	0.002
	2	144	146	144	144.7	3.61	0.004
	3	112	115	114	113.7	4.59	0.006
	4	97	96	95	96.0	5.44	0.008
Run 3	0	524	535	539	532.7	1	0
	1	219	218	217	218	2.44	0.002
	2	148	147	150	148.3	3.59	0.004
	3	115	117	117	116.3	4.58	0.006
	4	95	94	95	94.7	5.63	0.008

Table S11: Luminescence quenching data for $Ir(ppy)_2(dtbbpy)PF_6$, 0.01M tryptamine, and variable $NBu_4(OPh)_2PO_2$. See Fig S6.

Experiment	Vial	1	2	3	Average	I_0/I	Base [M]
Run 1	0	855	869	868	864	1	0
	1	207	206	208	207	4.17	0.0005
	2	131	131	130	130.7	6.61	0.0010
	3	100	100	100	100	8.64	0.0015
	4	82	82	81	81.7	10.58	0.0020
Run 2	0	860	861	853	899.0	1	0
	1	203	202	201	902.7	4.25	0.0005
	2	130	129	130	890.0	6.62	0.0010
	3	100	101	100	100	8.55	0.0015
	4	81	81	82	81	10.55	0.0020
Run 3	0	876	873	872	873.7	1	0
	1	201	203	203	202.3	4.32	0.0005
	2	132	131	132	131.7	6.64	0.0010
	3	104	105	104	104.3	8.37	0.0015
	4	87	85	86	86	10.16	0.0020

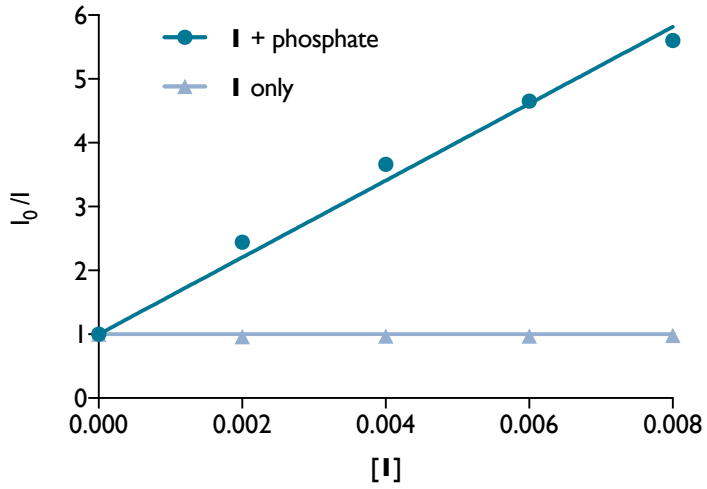


Figure S5: Luminescence quenching of $[Ir(ppy)_2(dtbbpy)]PF_6$ with varying concentrations of tryptamine in the presence (dark blue) and absence (light blue) of diphenyl phosphate.

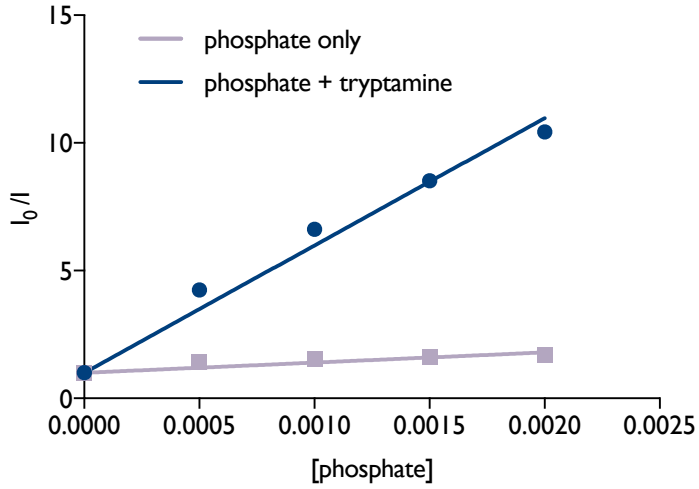


Figure S6: Luminescence quenching of $[Ir(ppy)_2(dtbbpy)]PF_6$ with varying concentrations of diphenyl phosphate in the presence (dark blue) and absence (light purple) of tryptamine.

Cyclic Voltammetry Experiments

Reduction potential of TIPS EBX iodonium in acetonitrile

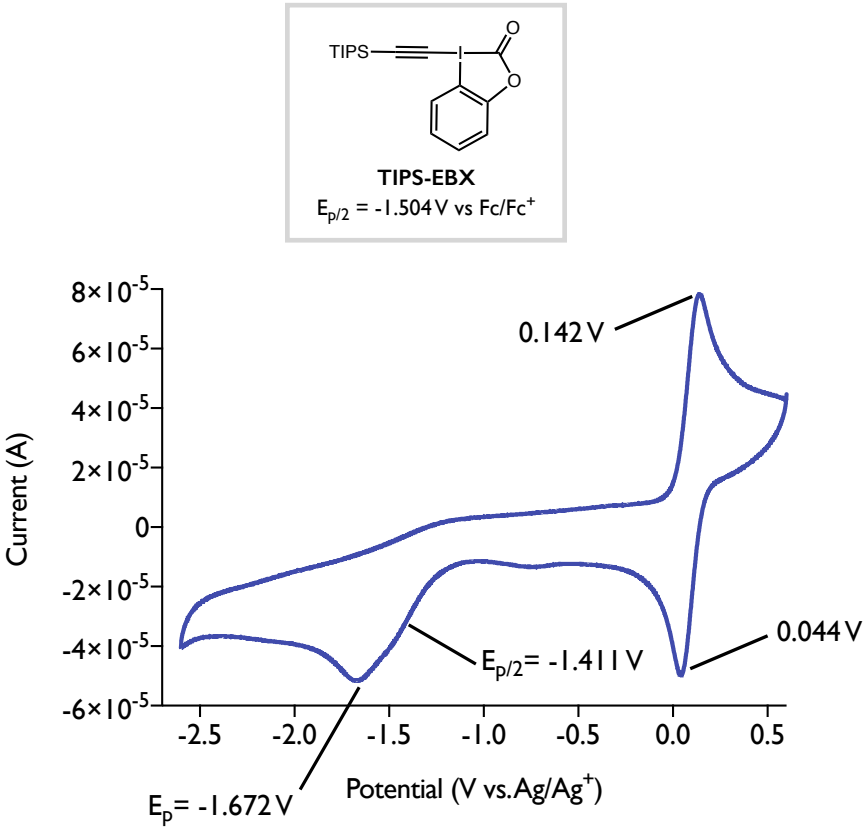


Figure S7: The cyclic voltammogram of TIPS-EBX iodonium and $FeCp_2^+$ vs Ag/Ag^+ in acetonitrile at 0.1V/s.

Conditions: 1mM of TIPS-EBX iodonium, 1mM $FeCp_2^+$ and 0.1M tetrabutylammonium hexafluorophosphate. A glassy working electrode and, Ag/Ag^+ reference electrode and platinum mesh counter electrode was used. The experiment was conducted in acetonitrile at 23 °C.

Reduction potential of *N'*-Cbz tryptamine **(1)** in THF

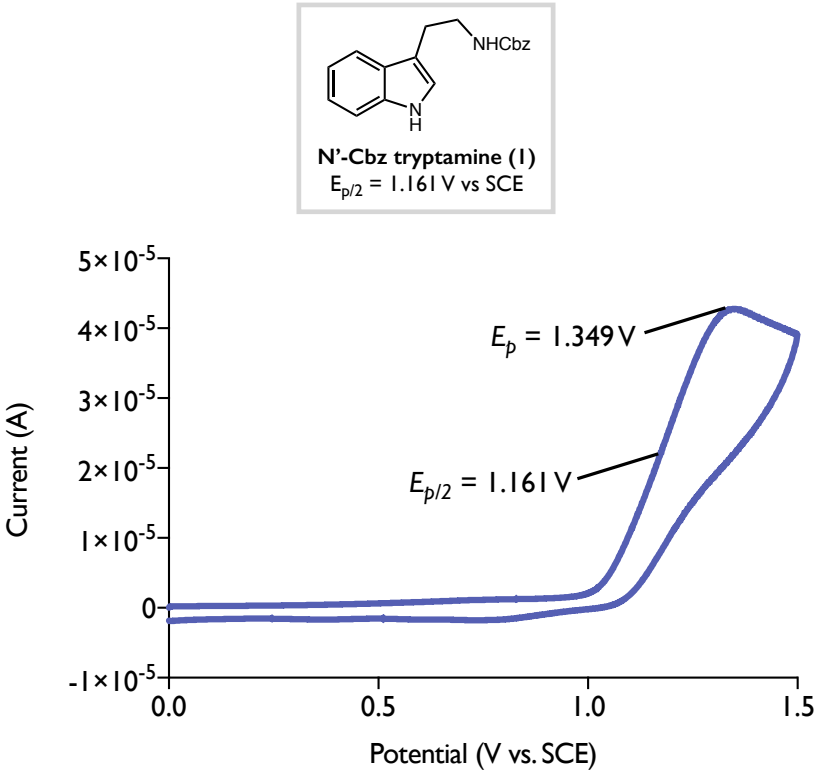
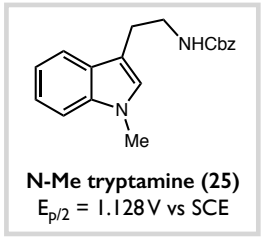


Figure S8: The cyclic voltammogram of *N'*-Cbz tryptamine **(1)** vs SCE in THF at 0.1V/s.

Conditions: 1mM of *N'*-Cbz tryptamine **(1)** and 0.1M tetrabutylammonium hexafluorophosphate. A glassy working electrode, SCE reference electrode and platinum mesh counter electrode was used. The experiment was conducted in THF at 23 °C.

Reduction potential of *N*-Me-*N'*-Cbz tryptamine **(25)** in THF



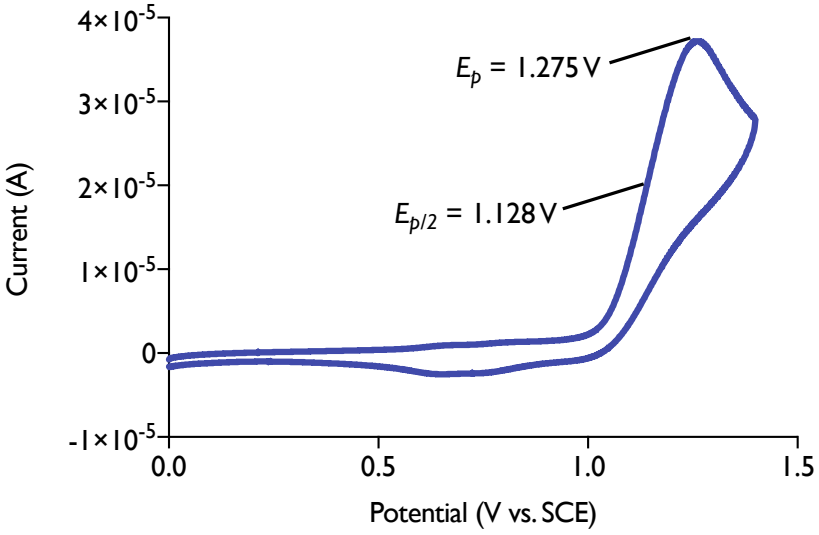


Figure S9: The cyclic voltammogram of *N*-Me-*N'*-Cbz tryptamine **(25)** and vs SCE in THF at 0.1V/s.

Conditions: 1mM of *N*-Me-*N'*-Cbz tryptamine **(25)** and 0.1M tetrabutylammonium hexafluorophosphate. A glassy working electrode, SCE reference electrode and platinum mesh counter electrode was used. The experiment was conducted in THF at 23 °C.

Upon oxidation, mesolytic cleavage of the TEMPO-substituted pyrroloindoline is apparent by liberation of TEMPO into solution:

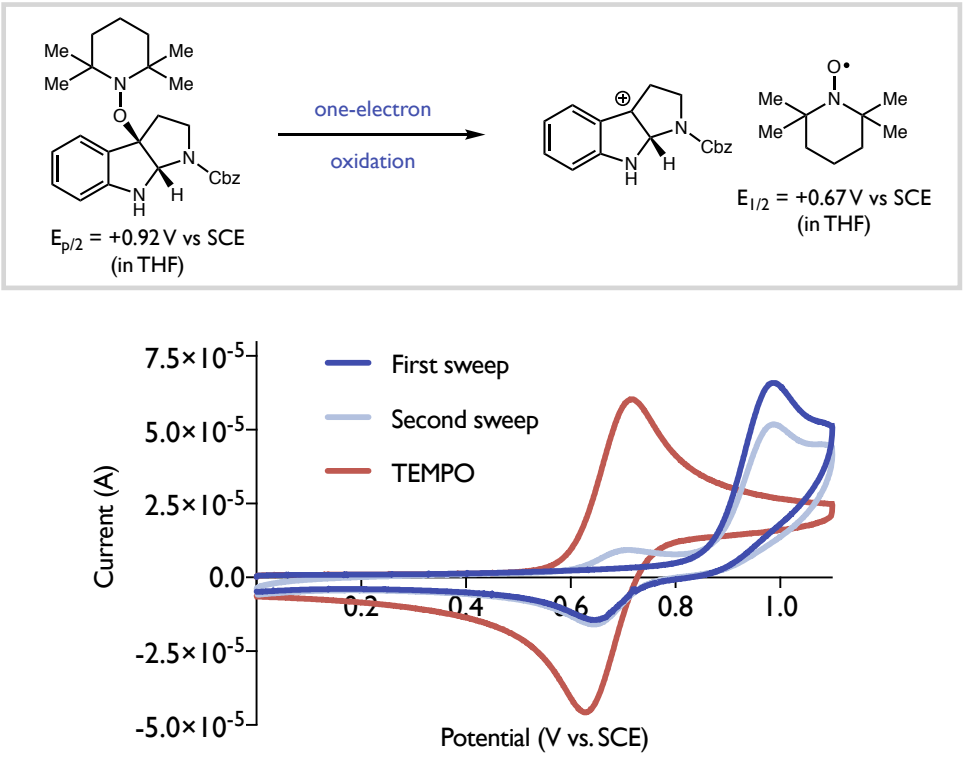


Figure S10: The cyclic voltammogram of **2** overlayed with TEMPO vs. SCE in THF at 0.1V/s.

Conditions: 1mM of TEMPO-functionalized pyrroloindoline **2** or 0.1mM TEMPO in 0.1M tetrabutylammonium hexafluorophosphate solution. A glassy working electrode, SCE reference electrode, and platinum mesh counter electrode were used. The experiments were conducted at 23 °C.

Mesolytic cleavage of the *N*-methylated TEMPO-functionalized pyrroloindoline:

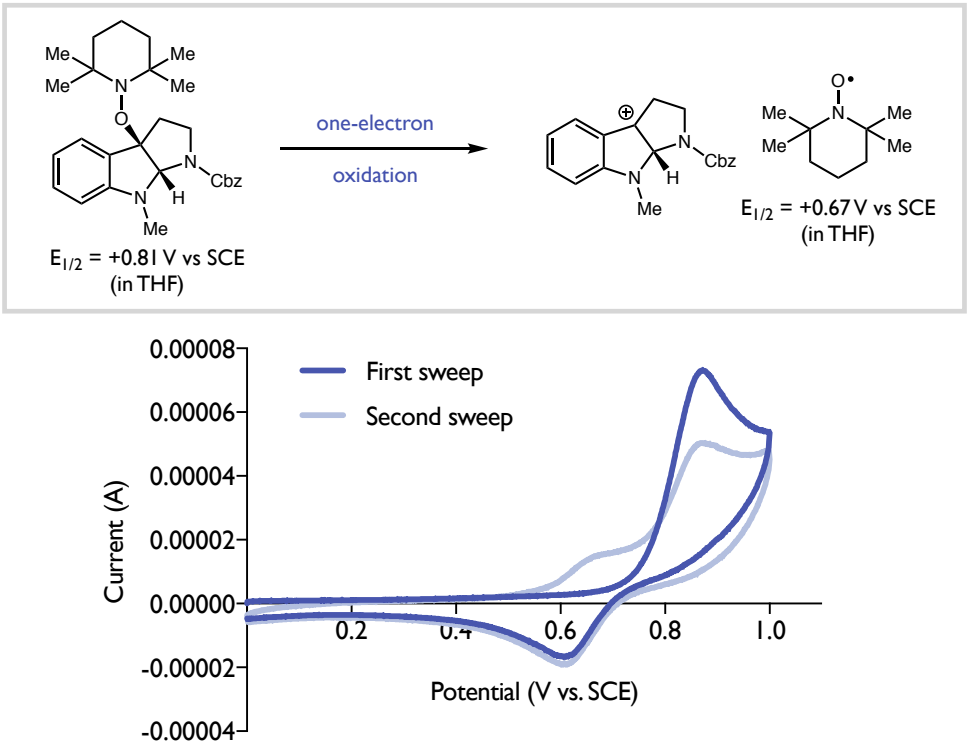
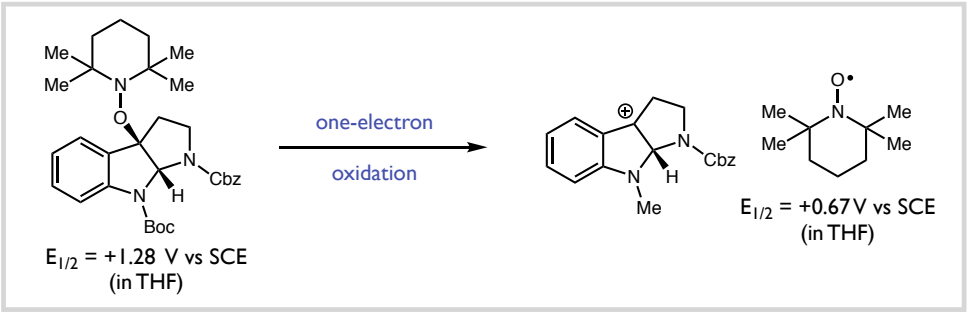


Figure S11: The cyclic voltammogram of *N*-methyl TEMPO-functionalized pyrroloindoline **24** vs SCE in THF at 0.1V/s.

Conditions: 1mM of *N*-methyl TEMPO derivative and 0.1M tetrabutylammonium hexafluorophosphate. A glassy working electrode, SCE reference electrode, and platinum mesh counter electrode was used. The experiment was conducted in THF at 23 °C.

Mesolytic cleavage of the *N*-Boc TEMPO-functionalized pyrroloindoline:



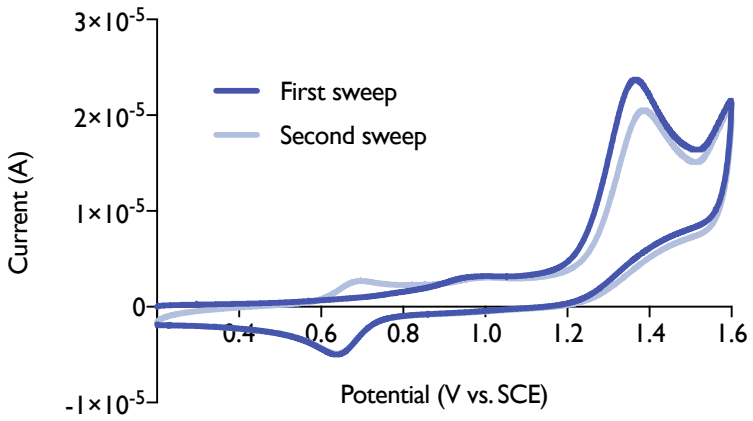


Figure S12: The cyclic voltammogram of *N*-Boc TEMPO-functionalized pyrroloindoline **11** vs SCE in THF at 0.1V/s.

Conditions: 1mM of *N*-Boc TEMPO derivative and 0.1M tetrabutylammonium hexafluorophosphate. A glassy working electrode, SCE reference electrode, and platinum mesh counter electrode was used. The experiment was conducted in THF at 23 °C.

Cyclic voltammogram of $Ir(ppy)_3$:

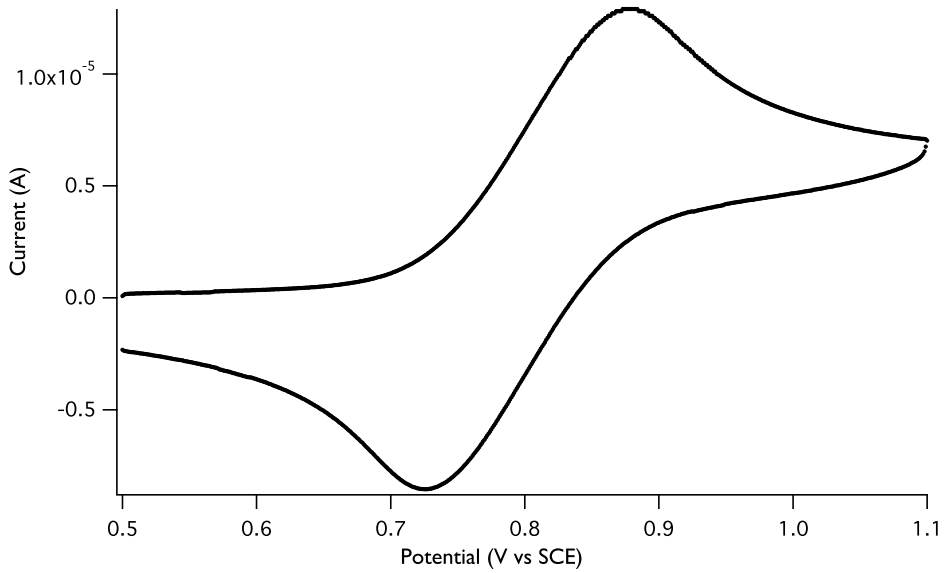


Figure S13: The cyclic voltammogram of $Ir(ppy)_3$ vs SCE in THF at 0.1V/s.

Conditions: 1mM of $Ir(ppy)_3$, and 0.1M tetrabutylammonium hexafluorophosphate. A glassy working electrode and, SCE reference electrode and platinum mesh counter electrode was used. The experiment was conducted in THF at 23 °C.

Cyclic voltammogram of $Ir(ppy)_3$ does not change upon addition of tryptamine **1**:

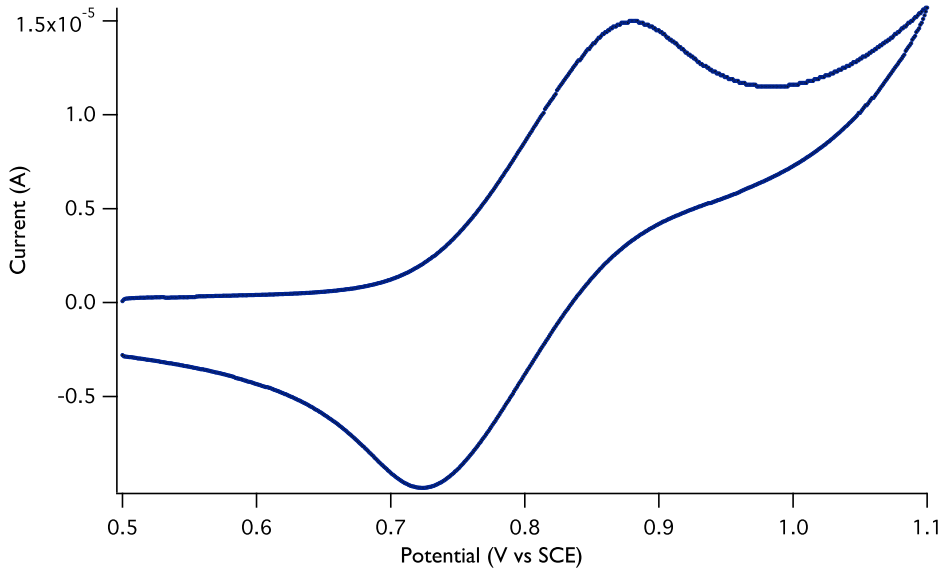


Figure S14: The cyclic voltammogram of a solution of **1** and $Ir(ppy)_3$ vs SCE in THF at 0.1V/s.

Conditions: 1mM of $Ir(ppy)_3$, 3mM of **1** and 0.1M tetrabutylammonium hexafluorophosphate. A glassy working electrode and, SCE reference electrode and platinum mesh counter electrode was used. The experiment was conducted in THF at 23 °C.

Cyclic voltammogram of $Ir(ppy)_3$ does not change upon addition of diphenyl phosphate base:

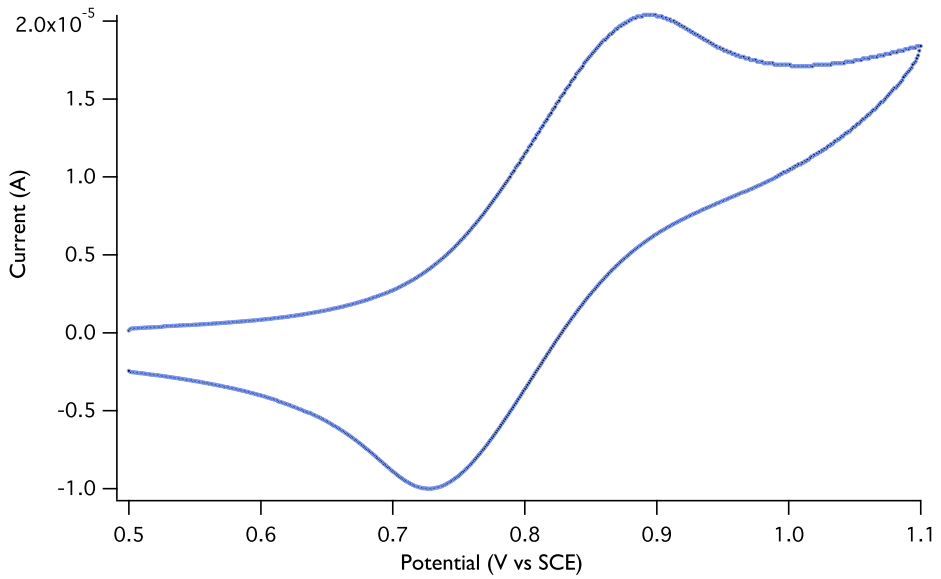


Figure S15: The cyclic voltammogram of a solution of $NBu_4(PhO)_2PO_2$ and $Ir(ppy)_3$ vs SCE in THF at 0.1V/s.

Conditions: 1mM of $Ir(ppy)_3$, 3mM of $NBu_4(PhO)_2PO_2$ and 0.1M tetrabutylammonium hexafluorophosphate. A glassy working electrode and, SCE reference electrode and platinum mesh counter electrode was used. The experiment was conducted in THF at 23 °C.

Addition of both **1** and diphenyl phosphate produces an irreversible catalytic peak:

In the presence of all the three components: **1**, diphenyl phosphate base, and $Ir(ppy)_3$, the return wave diminishes hence the $Ir^{III/IV}$ redox couple becomes irreversible and generates a catalytic peak. In this regime, the electrode initially oxidizes the $Ir(ppy)_3$ to its Ir^{IV} state. The tryptamine can then undergo oxidation by the ground state Ir^{IV} in the presence of base to generate the indole radical cation. The resulting Ir^{III} species will continue to cycle on the electrode in this process producing a catalytic current. This observation supports a PCET mechanism in which the base is necessary for one-electron oxidation of the tryptamine substrate.

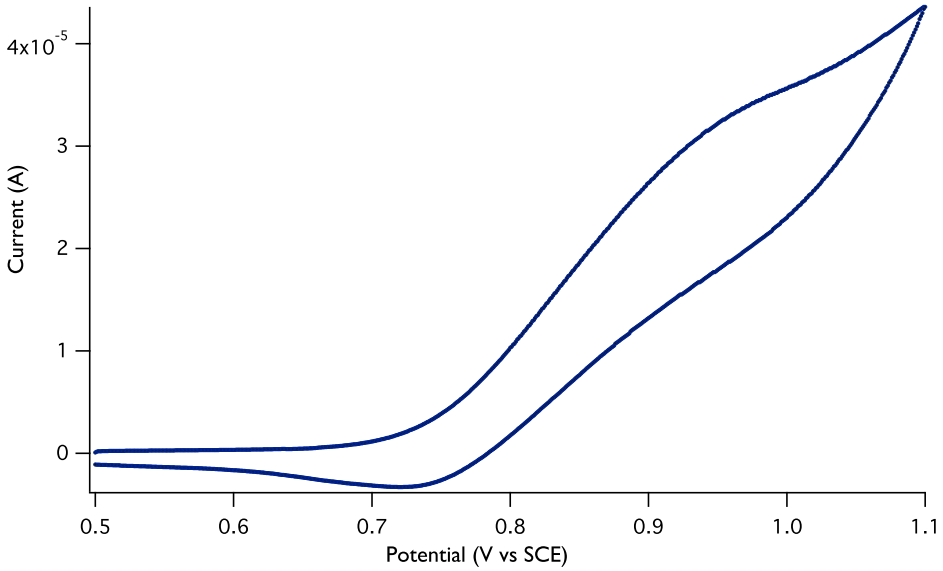


Figure S16: The cyclic voltammogram of a solution of N-Cbz tryptamine, $NBu_4(PhO)_2PO_2$ and $Ir(ppy)_3$ vs SCE in THF at 0.1V/s.

Conditions: 1mM of $Ir(ppy)_3$, 3mM of $NBu_4(PhO)_2PO_2$, 3mM of N-Cbz tryptamine and 0.1M tetrabutylammonium hexafluorophosphate. A glassy working electrode and, SCE reference electrode and platinum mesh counter electrode was used. The experiment was conducted in THF at 23 °C.

Mechanistic support for PCET oxidation of tryptamine:

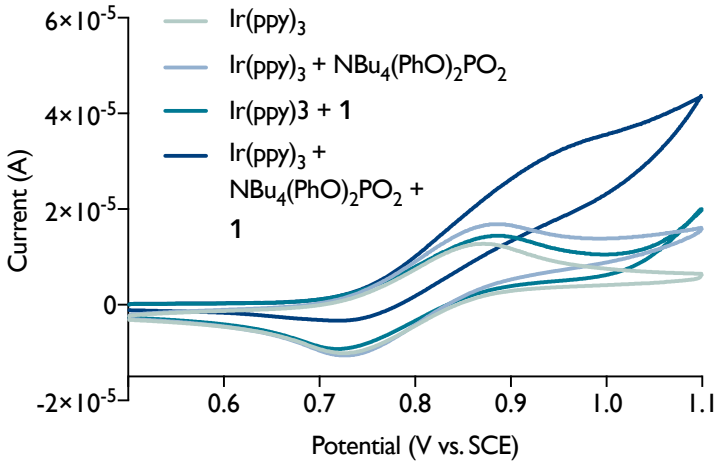


Figure S17: A superimposed cyclic voltammogram a solution of *N*-Cbz tryptamine, $NBu_4(PhO)_2PO_2$ and $Ir(ppy)_3$ vs SCE in THF at 0.1V/s. Each voltammogram obtained independently.

Conditions: 1mM of $Ir(ppy)_3$, 3mM of $NBu_4(PhO)_2PO_2$, 3mM of *N*-Cbz tryptamine and 0.1M tetrabutylammonium hexafluorophosphate. A glassy working electrode, SCE reference electrode and platinum mesh counter electrode was used. The experiment was conducted in THF at 23 °C.

Investigating the change in onset potential of tryptamine-phosphate complex:

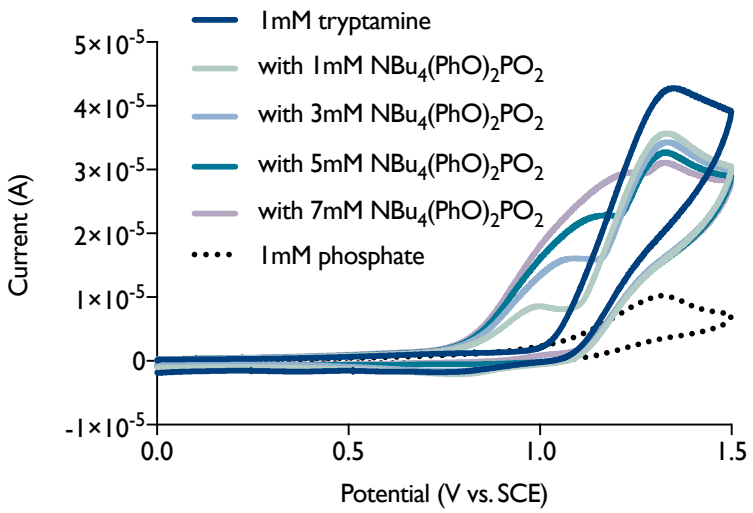
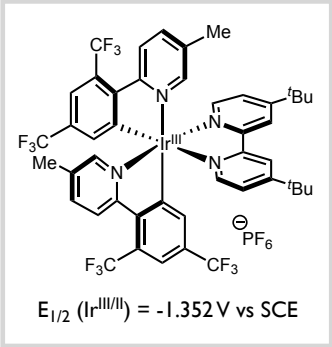


Figure S18: Cyclic voltammetry experiment to demonstrate early onset of tryptamine oxidation in the presence of phosphate base.

Conditions: 1mM of *N*-Cbz tryptamine, xmM of $NBu_4(PhO)_2PO_2$, and 0.1M tetrabutylammonium hexafluorophosphate. A glassy working electrode, SCE reference electrode and platinum mesh counter electrode was used. The experiment was conducted in THF at 23 °C with a scan rate of 0.1 V/s.

Determining the excited-state redox potential of [Ir(dCF$_3$, Me-ppy)$_2$(dtbbpy)]PF$_6$:



Ground state potentials were measured by cyclic voltammetry in MeCN with 0.1 M tetrabutylammonium hexafluorophosphate at room temperature using a 0.1 V/s scan rate with a negative initial direction. Excited state reduction potential was calculated using the Rehm-Weller equation:[21] $E^{o*}_{red} = E^{o}_{red} + E_{0\text{-}0}$ where E^{o*} denotes the excited state reduction potential, E^{o} the ground state reduction potential, and E0-0 the energy difference between the 0th vibration level of the ground state and that of the excited state. Due to the poor overlap between the absorption and emission spectra, E0-0 is approximated as the high-energy onset of phosphorescence where the emission intensity is 10% of the obtained at the maximum emission wavelength, using the "10% rule."[22] These estimations were corroborated by approximating the HOMO-LUMO gap as the difference between the onset of oxidation and the onset of reduction.[23] $E_{1/2}(Ir^{III}/Ir^{II})$ = -1.352 V vs. SCE; $E_{1/2}(*Ir^{III}/Ir^{II})$ = 1.22 V vs. SCE.

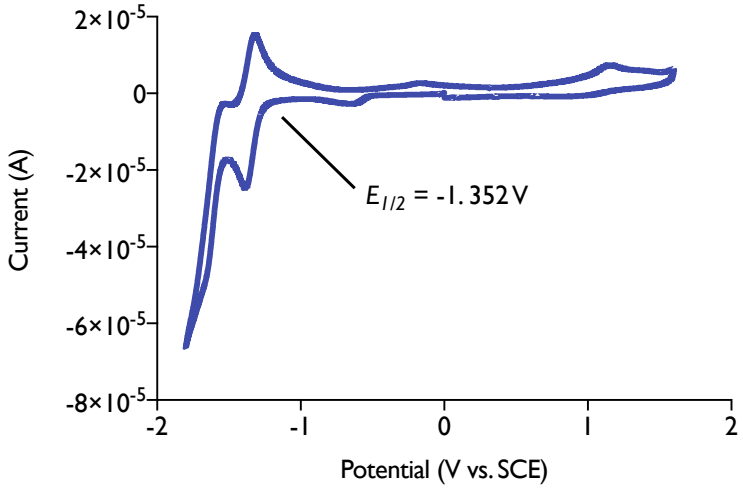


Figure S19: Cyclic voltammogram of [Ir(dCF$_3$, Me-ppy)$_2$(dtbbpy)]PF$_6$ in MeCN at 0.1 V/s.

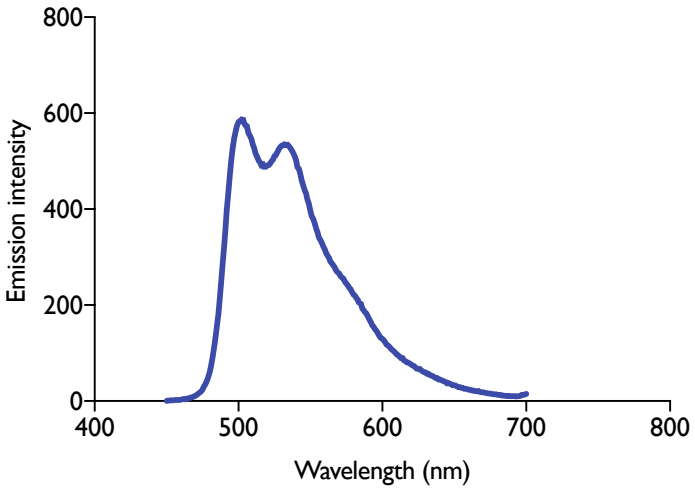


Figure S20: Phosphorescence emission spectra of $[Ir(dCF_3, Me\text{-}ppy)_2(dtbbpy)]PF_6$ in MeCN. Excitation wavelength = 380nm.

DFT Computations

All calculations used DFT methodology[24] as implemented in the Gaussian 16 series of computer programs.[25] We employed the unrestricted B3LYP functional[26] and 6-31+G(d,p) basis set.[27] Calculations were performed with the CPCM polarizable conductor calculation model for THF.[28]

We first evaluated the optimized geometry of the H-bonded indole radical cation complex with biphenyl phosphate. The input structure of the complex featured the proton bound to the phosphoric acid in a covalent O-H bond of 1.08 Å in length and an N-H distance of 2.19 Å. This structure then underwent geometry optimization and stationary points were subjected to normal mode analysis. Below are the Cartesian coordinates (Å) for both the input and output structures and the energies (Hartree) of the stationary point.

Input structure:

```
0 2
 C                -5.08474468    0.20723575   -0.70740261
 C                -3.72003059    0.25363794   -0.29153393
 C                -2.87473338    1.29242370   -0.60321858
 C                -3.42522248    2.35059463   -1.37981109
 C                -4.75662119    2.33606239   -1.80398159
 C                -5.60612819    1.26774323   -1.47573851
 C                -5.63065118   -1.00013057   -0.20116709
 C                -4.57907015   -1.66020230    0.51289049
 H                -1.84360036    1.30405394   -0.27336595
 H                -2.79035606    3.18377505   -1.64402493
 H                -5.13741654    3.15784084   -2.39186612
 H                -6.63554927    1.25899739   -1.80433215
 H                -6.63443318   -1.36952948   -0.31667225
 H                -4.61096784   -2.59992833    1.03425707
 N                -3.46779281   -0.92408230    0.45615730
 H                -1.50621506   -1.36983094    1.33069521
 O                -0.52134693   -1.55877229    1.74068484
 P                 0.80683953   -0.74011821    2.04237288
 O                 1.22246070   -0.32297134    3.50282103
 O                 0.70959685    0.62155976    0.91695791
 O                 2.19702666   -1.52120751    1.30619587
 C                 1.86140618    1.33233821    0.52656887
 C                 2.02590010    2.63038613    1.00879222
 C                 2.75979424    0.76407811   -0.39632350
 C                 3.10102911    3.40239914    0.56800873
 H                 1.30718219    3.01725566    1.71641785
 C                 3.83615296    1.56497488   -0.82453416
 C                 4.00755040    2.86659226   -0.35322840
 H                 3.23018174    4.40898285    0.94077287
 H                 4.55167479    1.14903666   -1.52054484
 H                 4.84803732    3.45493240   -0.69440861
 C                 2.27735333   -1.70154736   -0.08774608
 C                 2.12585686   -2.99338687   -0.59029331
 C                 2.58332546   -0.61187218   -0.92471802
 C                 2.29293029   -3.23116735   -1.95470394
 H                 1.89357190   -3.79298789    0.09777981
 C                 2.74639940   -0.87933264   -2.29795217
 C                 2.60509511   -2.16894988   -2.81032199
 H                 2.17982197   -4.23313781   -2.34482795
 H                 2.96976939   -0.05893421   -2.96617795
 H                 2.73021680   -2.34265585   -3.87011829
```

Output information:

```
 E(UB3LYP) =  -1468.31454034
Zero-point correction=                           0.307356 (Hartree/Particle)
Thermal correction to Energy=                    0.328186
Thermal correction to Enthalpy=                  0.329130
Thermal correction to Gibbs Free Energy=         0.252803
Sum of electronic and zero-point Energies=          -1468.007185
Sum of electronic and thermal Energies=             -1467.986355
Sum of electronic and thermal Enthalpies=           -1467.985411
Sum of electronic and thermal Free Energies=        -1468.061737

             Symbolic Z-matrix:
             Charge =  0 Multiplicity = 2
             C                    -5.08474   0.20724  -0.7074
             C                    -3.72003   0.25364  -0.29153
             C                    -2.87473   1.29242  -0.60322
             C                    -3.42522   2.35059  -1.37981
             C                    -4.75662   2.33606  -1.80398
             C                    -5.60613   1.26774  -1.47574
             C                    -5.63065  -1.00013  -0.20117
             C                    -4.57907  -1.6602    0.51289
             H                    -1.8436    1.30405  -0.27337
             H                    -2.79036   3.18378  -1.64402
             H                    -5.13742   3.15784  -2.39187
             H                    -6.63555   1.259    -1.80433
             H                    -6.63443  -1.36953  -0.31667
             H                    -4.61097  -2.59993   1.03426
             N                    -3.46779  -0.92408   0.45616
             H                    -1.50622  -1.36983   1.3307
             O                    -0.52135  -1.55877   1.74068
             P                     0.80684  -0.74012   2.04237
             O                     1.22246  -0.32297   3.50282
             O                     0.7096    0.62156   0.91696
             O                     2.19703  -1.52121   1.3062
             C                     1.86141   1.33234   0.52657
             C                     2.0259    2.63039   1.00879
             C                     2.75979   0.76408  -0.39632
             C                     3.10103   3.4024    0.56801
             H                     1.30718   3.01726   1.71642
             C                     3.83615   1.56497  -0.82453
             C                     4.00755   2.86659  -0.35323
             H                     3.23018   4.40898   0.94077
             H                     4.55167   1.14904  -1.52054
             H                     4.84804   3.45493  -0.69441
             C                     2.27735  -1.70155  -0.08775
             C                     2.12586  -2.99339  -0.59029
             C                     2.58333  -0.61187  -0.92472
             C                     2.29293  -3.23117  -1.9547
             H                     1.89357  -3.79299   0.09778
             C                     2.7464   -0.87933  -2.29795
             C                     2.6051   -2.16895  -2.81032
             H                     2.17982  -4.23314  -2.34483
             H                     2.96977  -0.05893  -2.96618
             H                     2.73022  -2.34266  -3.87012
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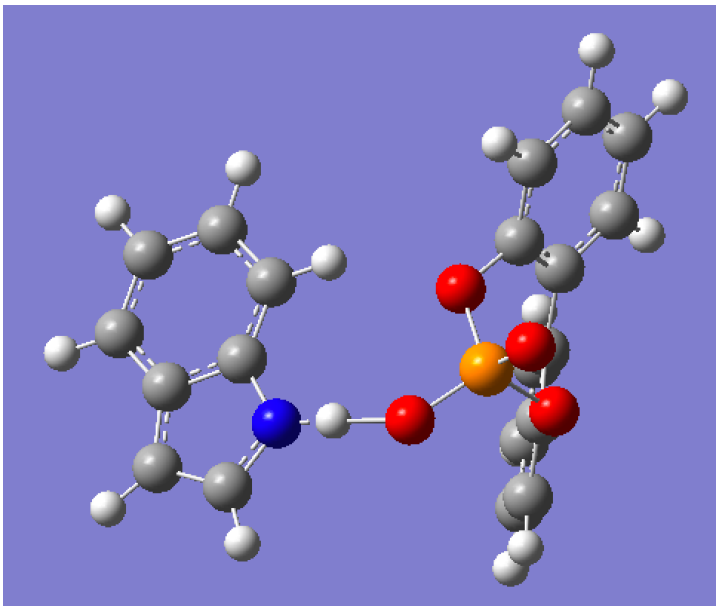
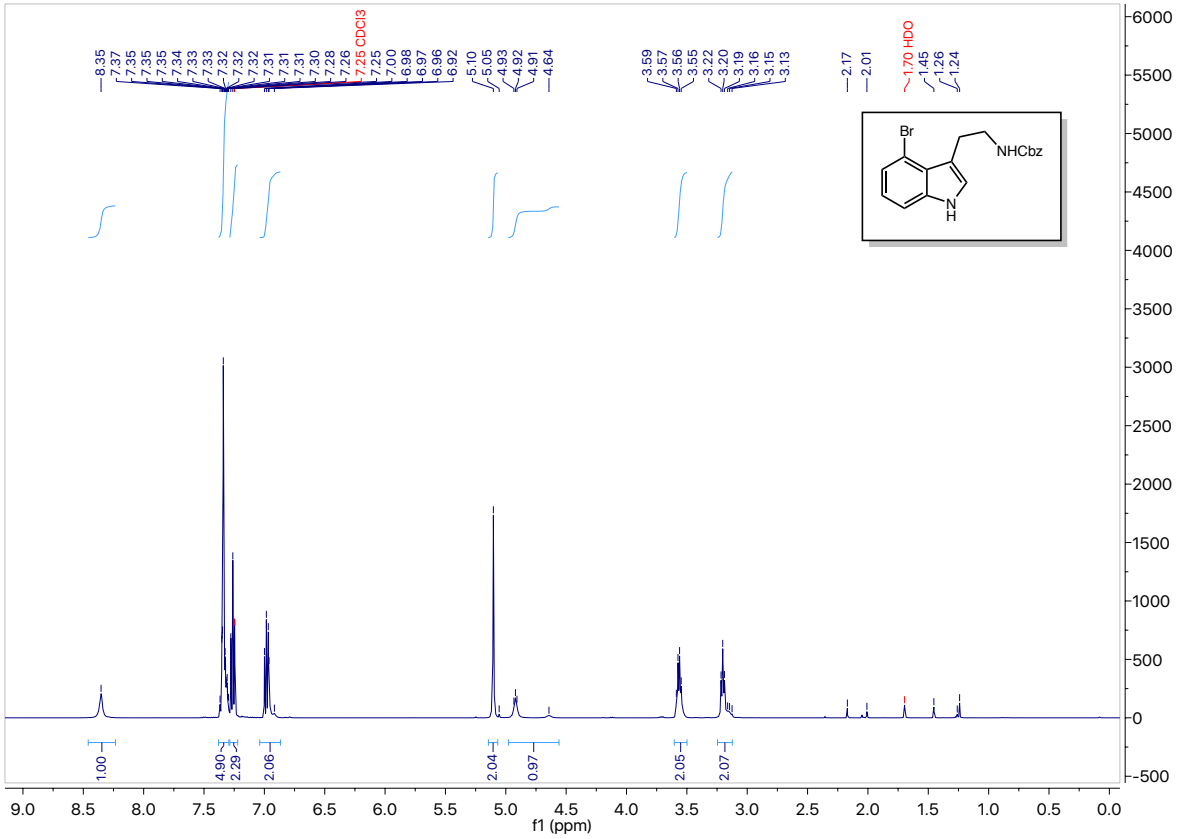


Figure S21: Optimized geometry of oxidized indole-biphenyl phosphate complex using UB3LYP/6-31G+(d,p). Bond distance (N-H) = 1.075 Å; bond distance (O-H) = 1.527 Å.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7.31
7.30
7.28
7.26
7.25 CDCl3
7.25
7.00
6.98
6.97
6.96
6.92
5.10
5.05
4.93
4.92
4.91
4.64
3.59
3.57
3.56
3.55
3.22
3.20
3.19
3.16
3.15
3.13
2.17
2.01
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1.45
1.26
1.24
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N
H
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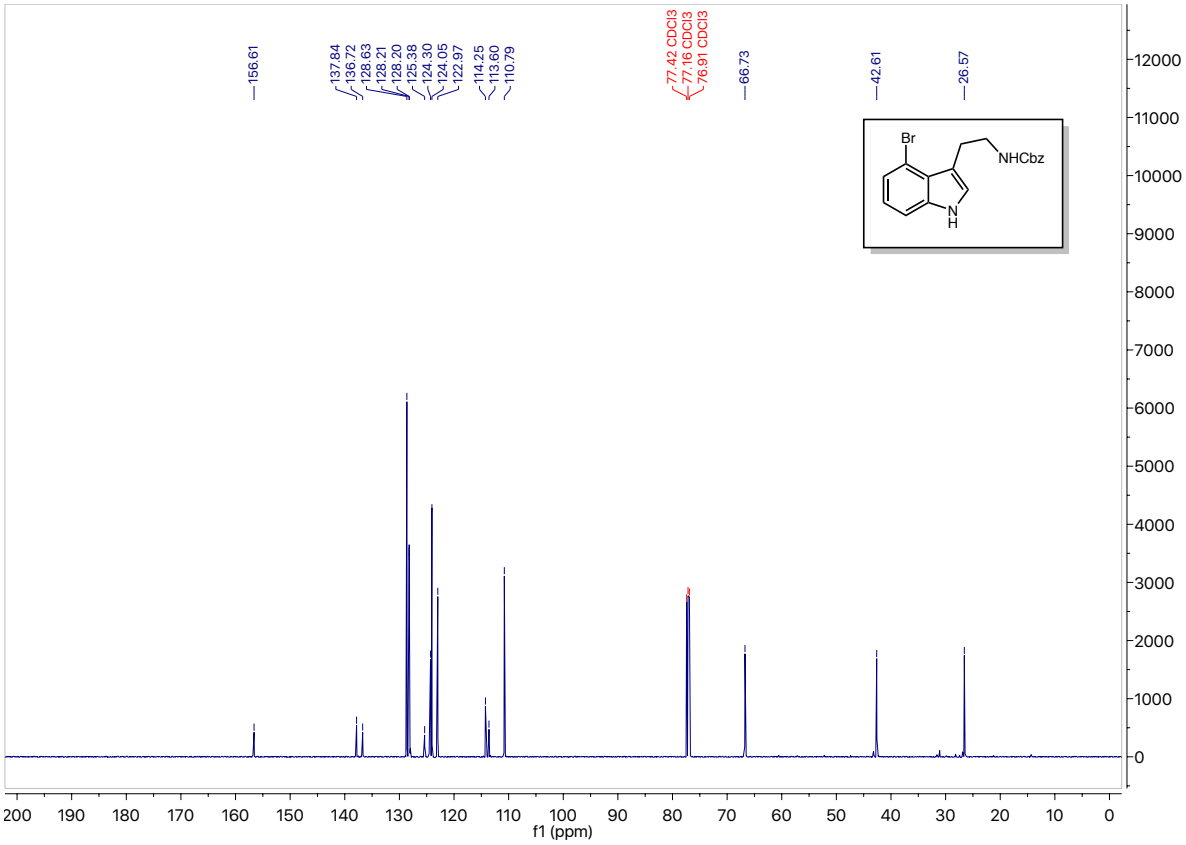
2.07
f1 (ppm)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110.79
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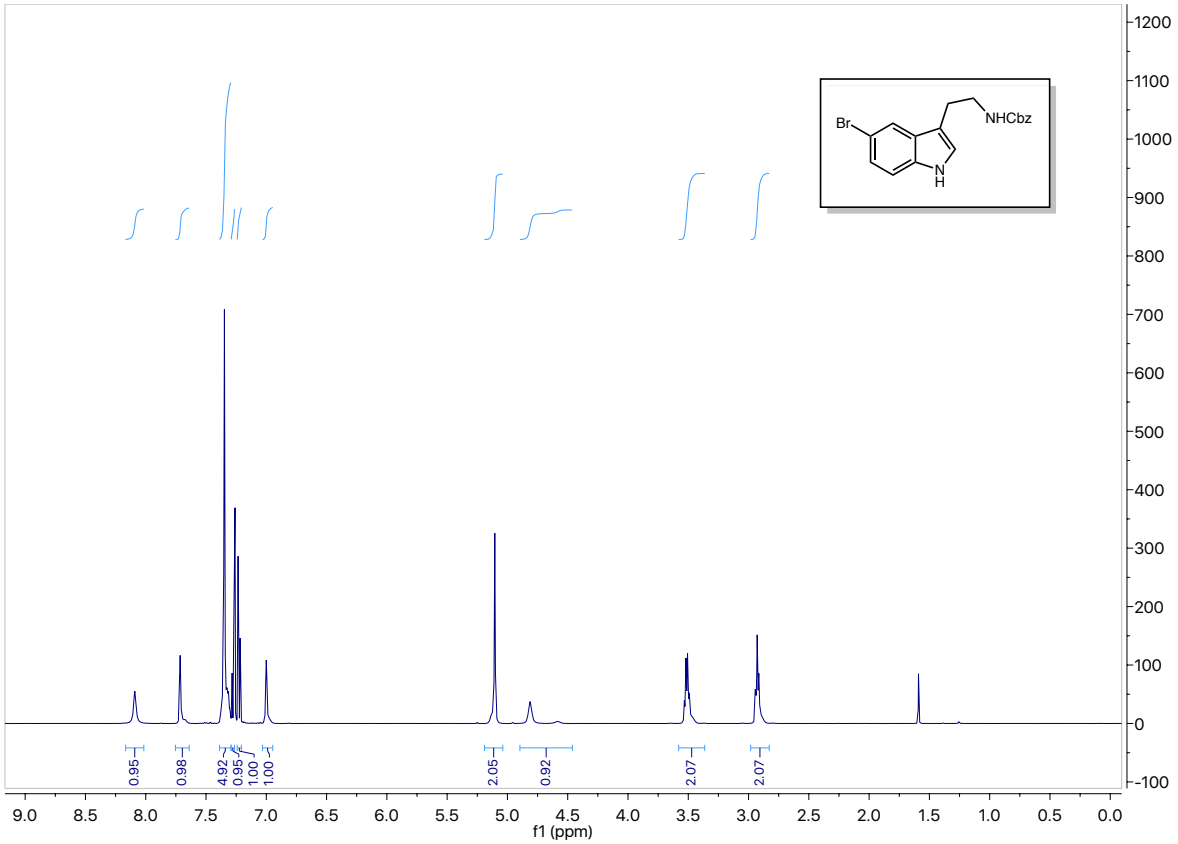
N
H
f1 (ppm)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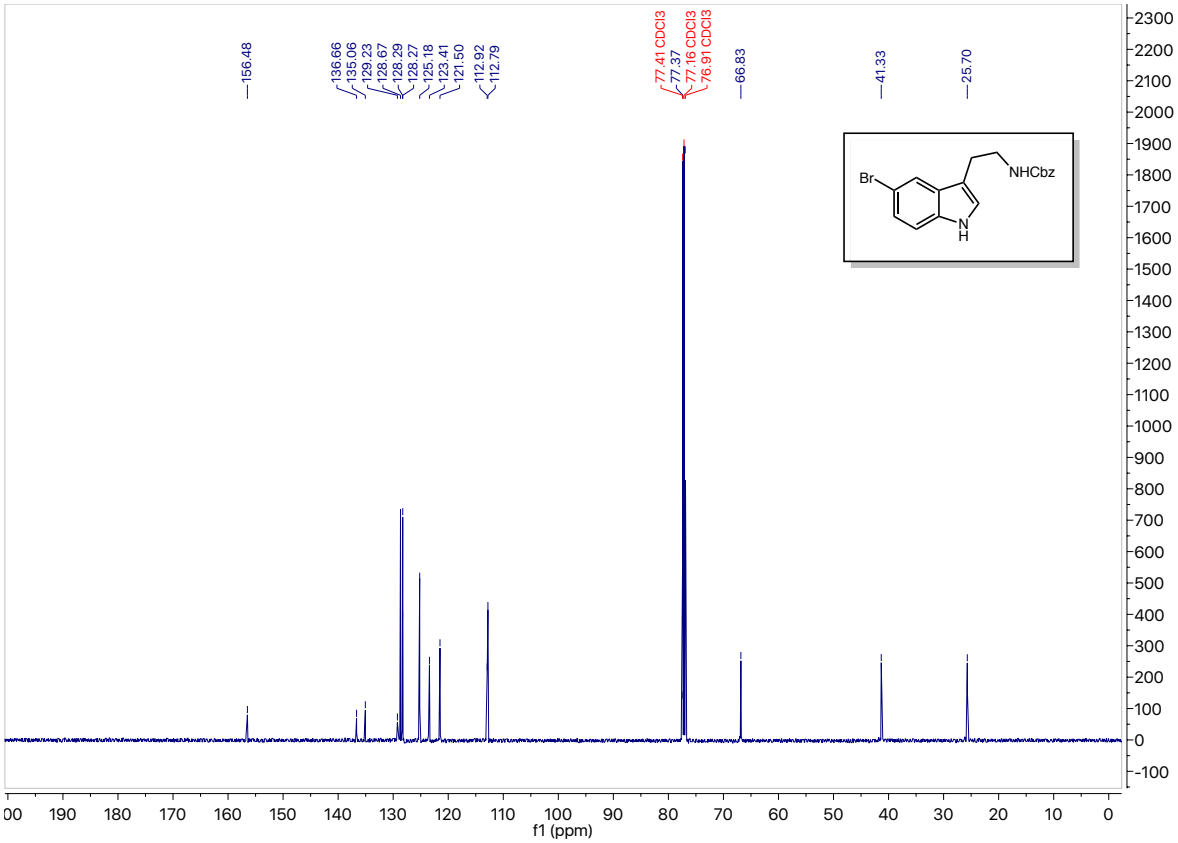
f1 (ppm)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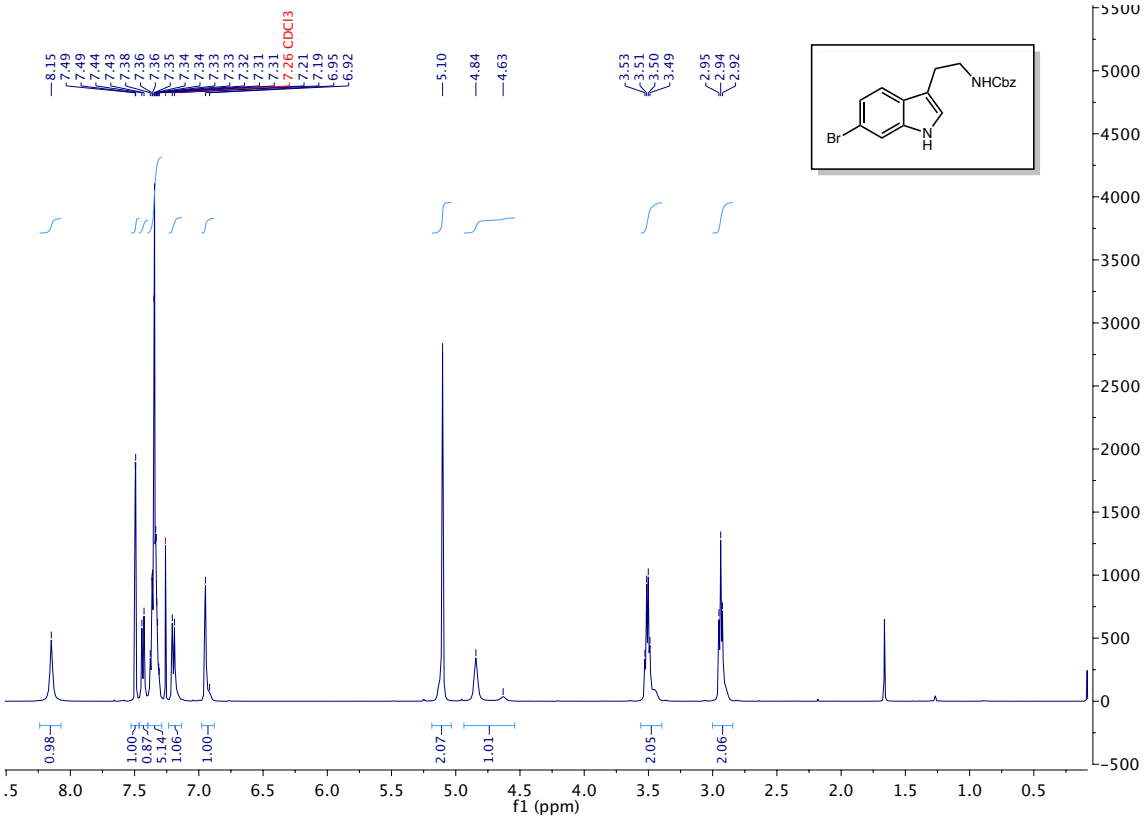
25.70
Br
NHCbz
N
H
f1 (ppm)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7.31
7.26 CDCl3
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4.63
3.53
3.51
3.50
3.49
2.95
2.94
2.92
NHCbz
Br
N
H
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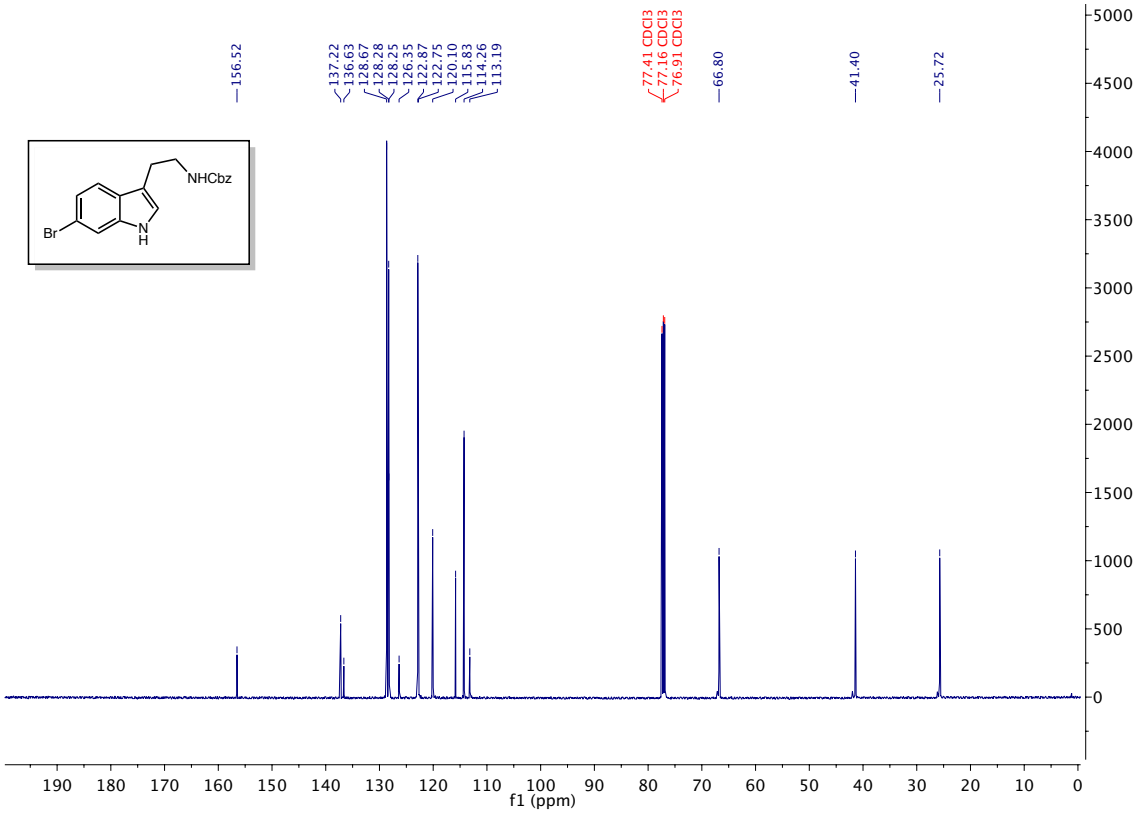
5.14
1.06
1.00
2.07
1.01
2.05
2.06
f1 (ppm)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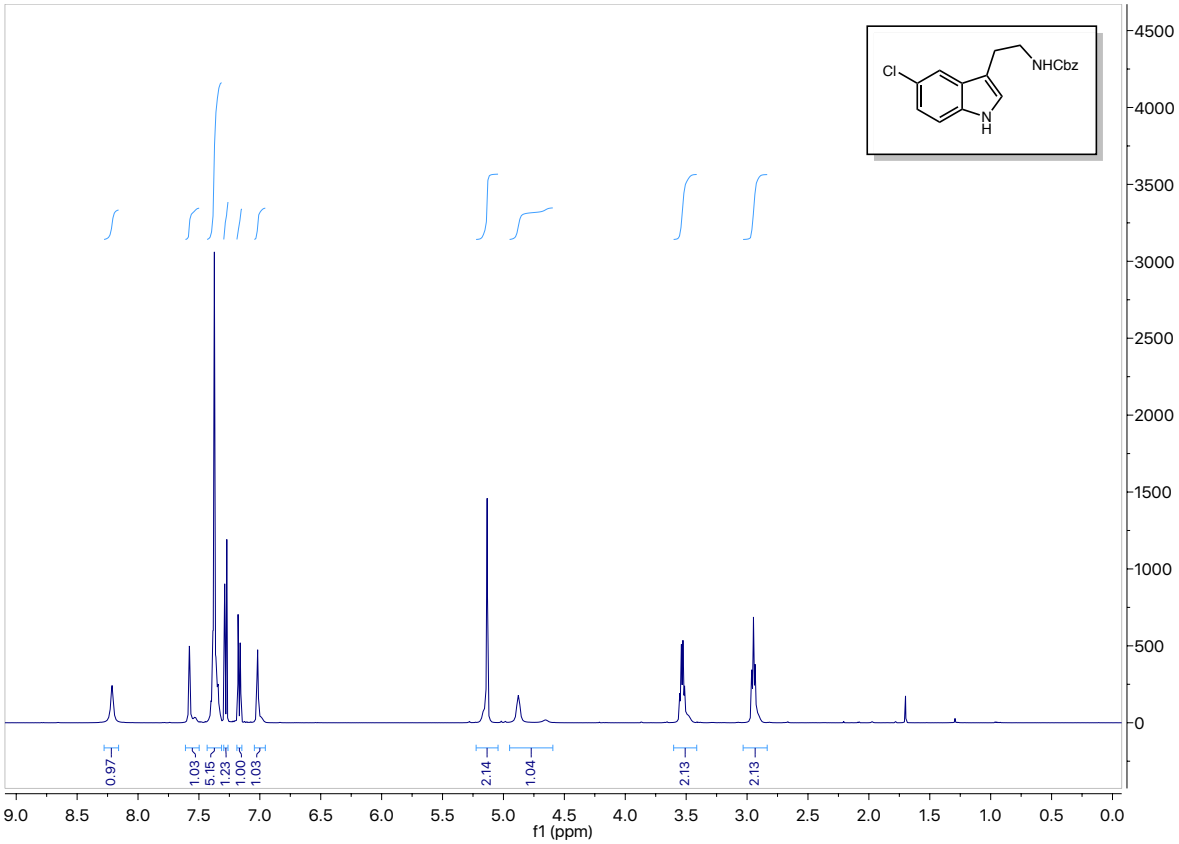
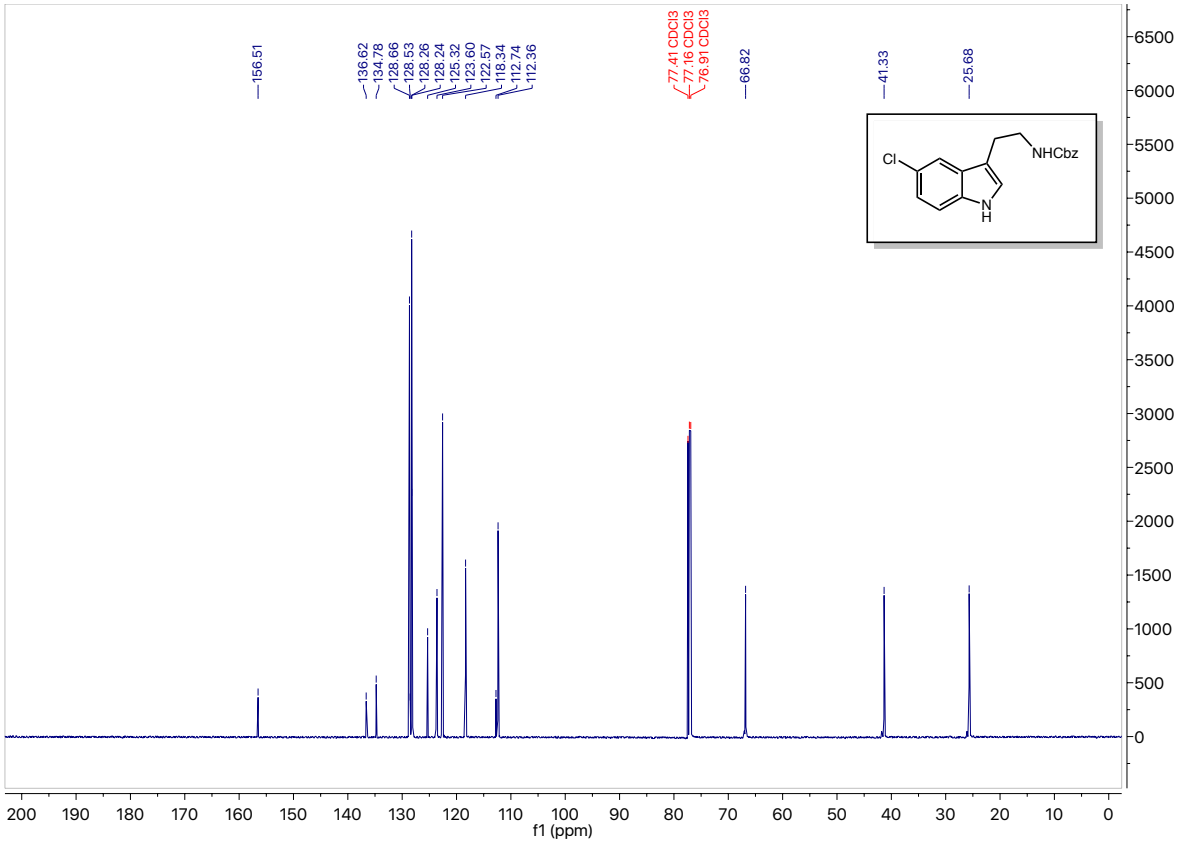
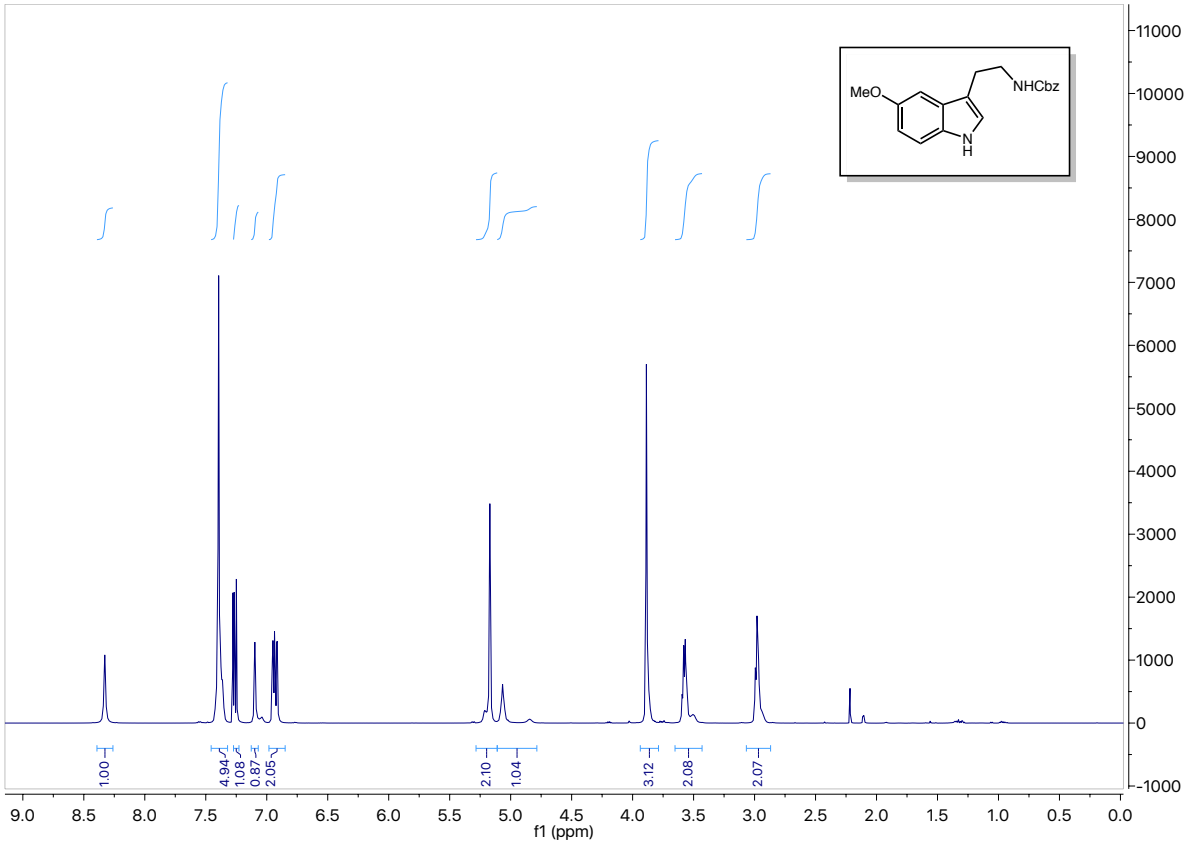
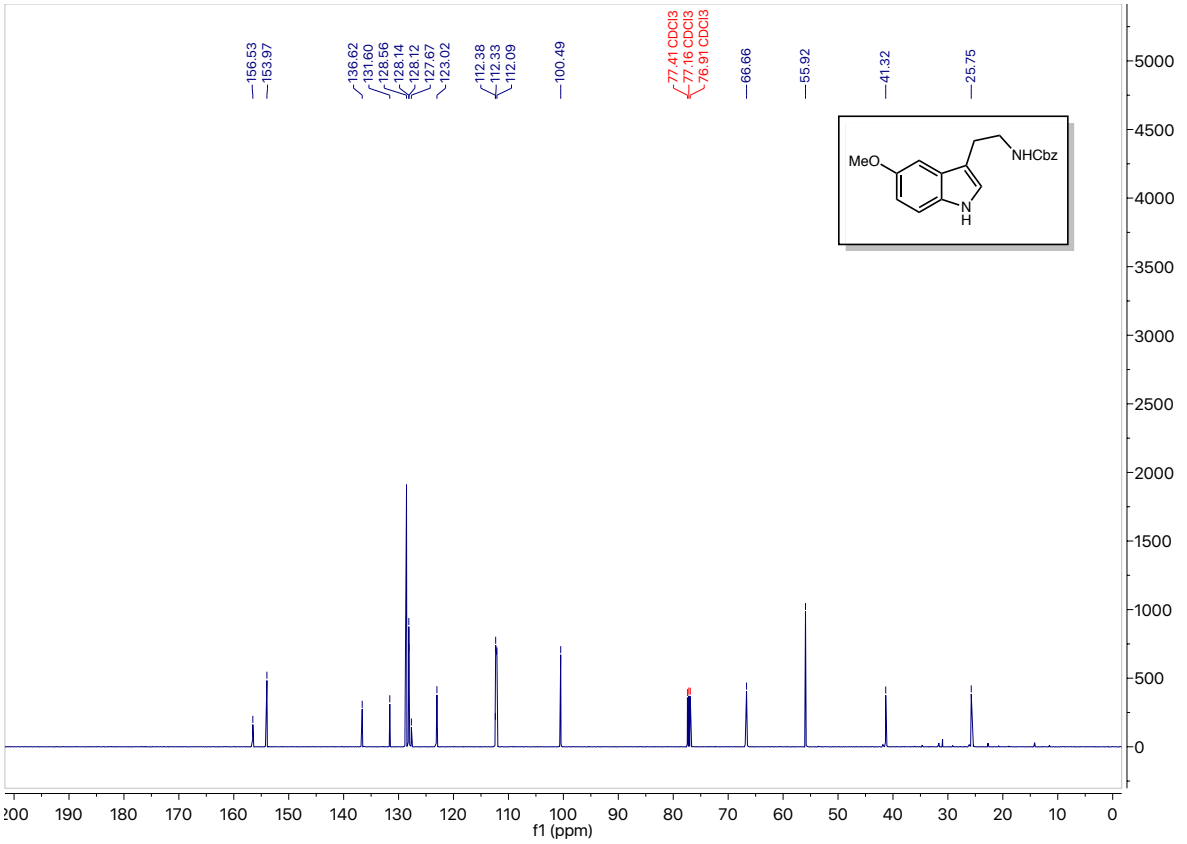
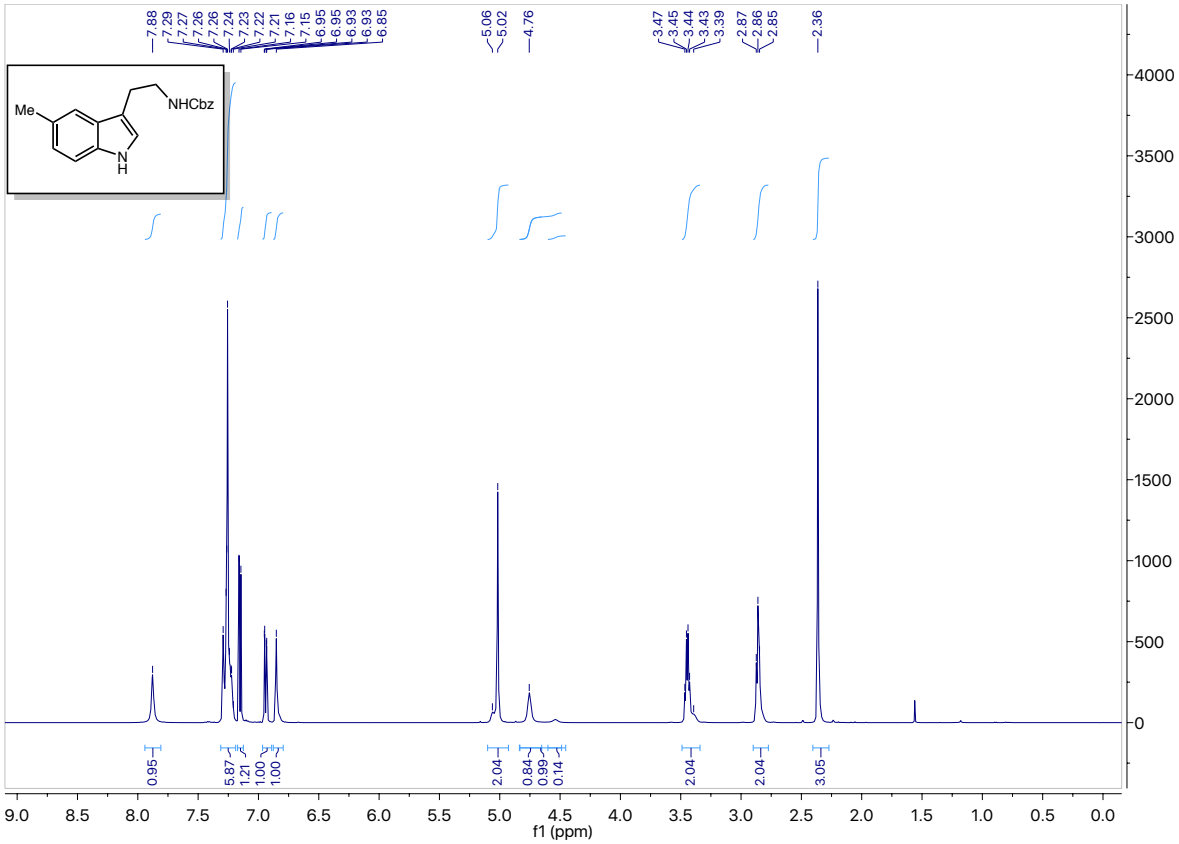
137.22
136.63
128.67
128.28
128.25
126.35
122.87
122.75
120.10
115.83
114.26
113.19
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.80
41.40
25.72
NHCbz
Br
N
H
f1 (ppm)

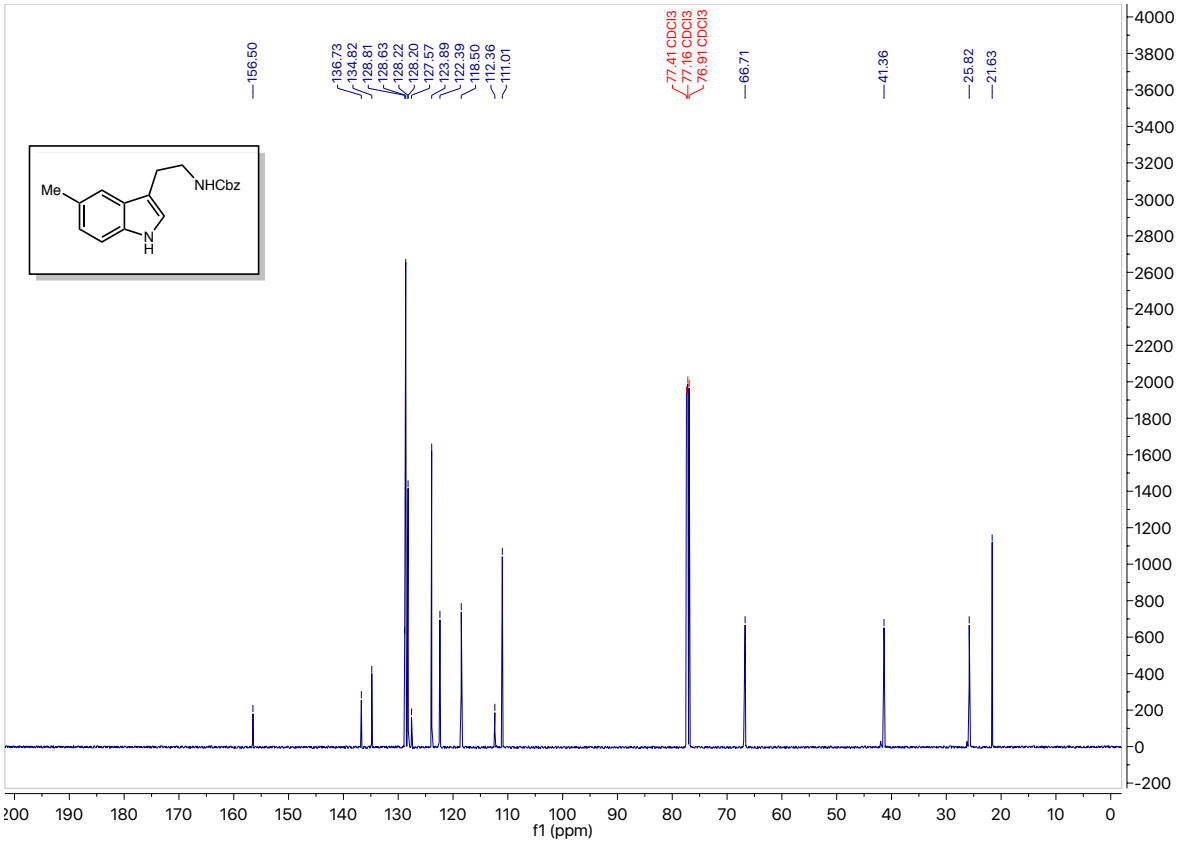

Cl
NHCbz
N
H
0.97
1.03
5.15
1.23
1.00
1.03
2.14
1.04
2.13
2.13
f1 (ppm)

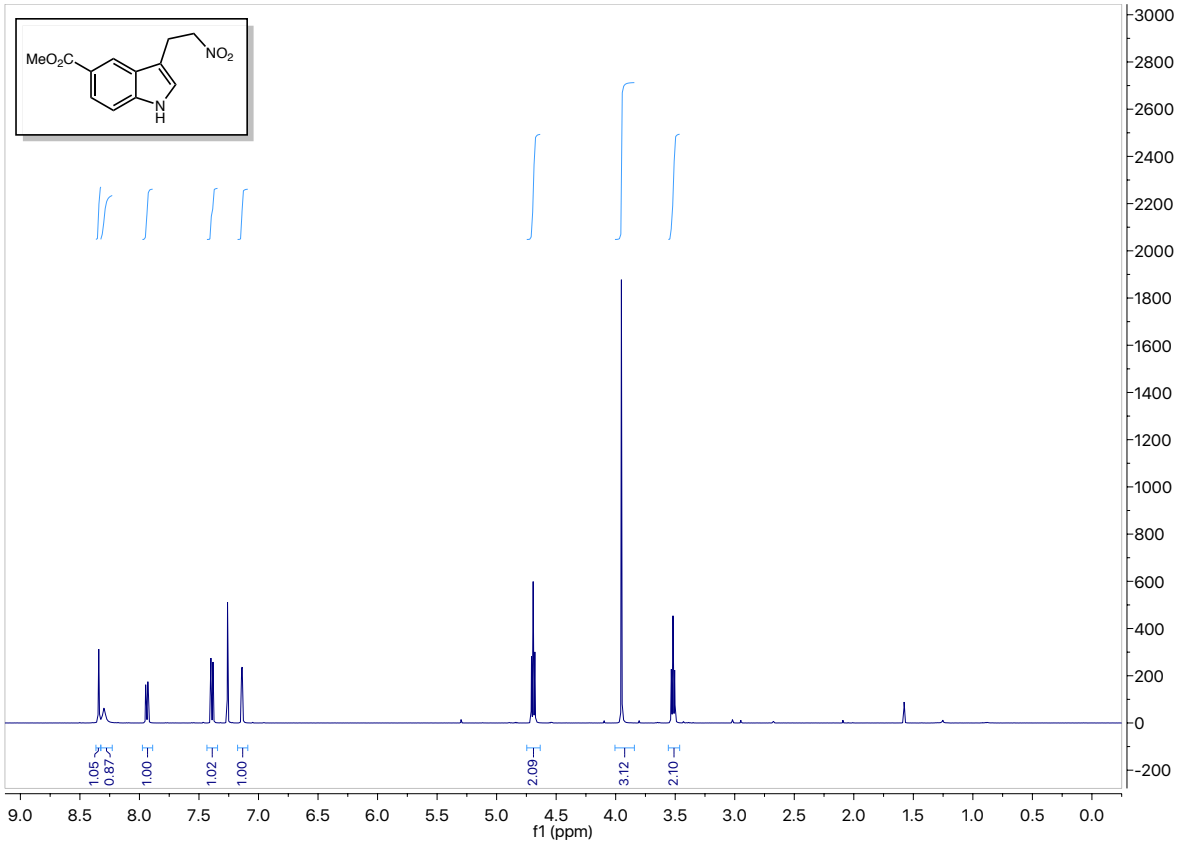

156.51
136.62
134.78
128.66
128.53
128.26
128.24
125.32
123.60
122.57
118.34
112.74
112.36
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.82
41.33
25.68
Cl
NHCbz
N
H
f1 (ppm)

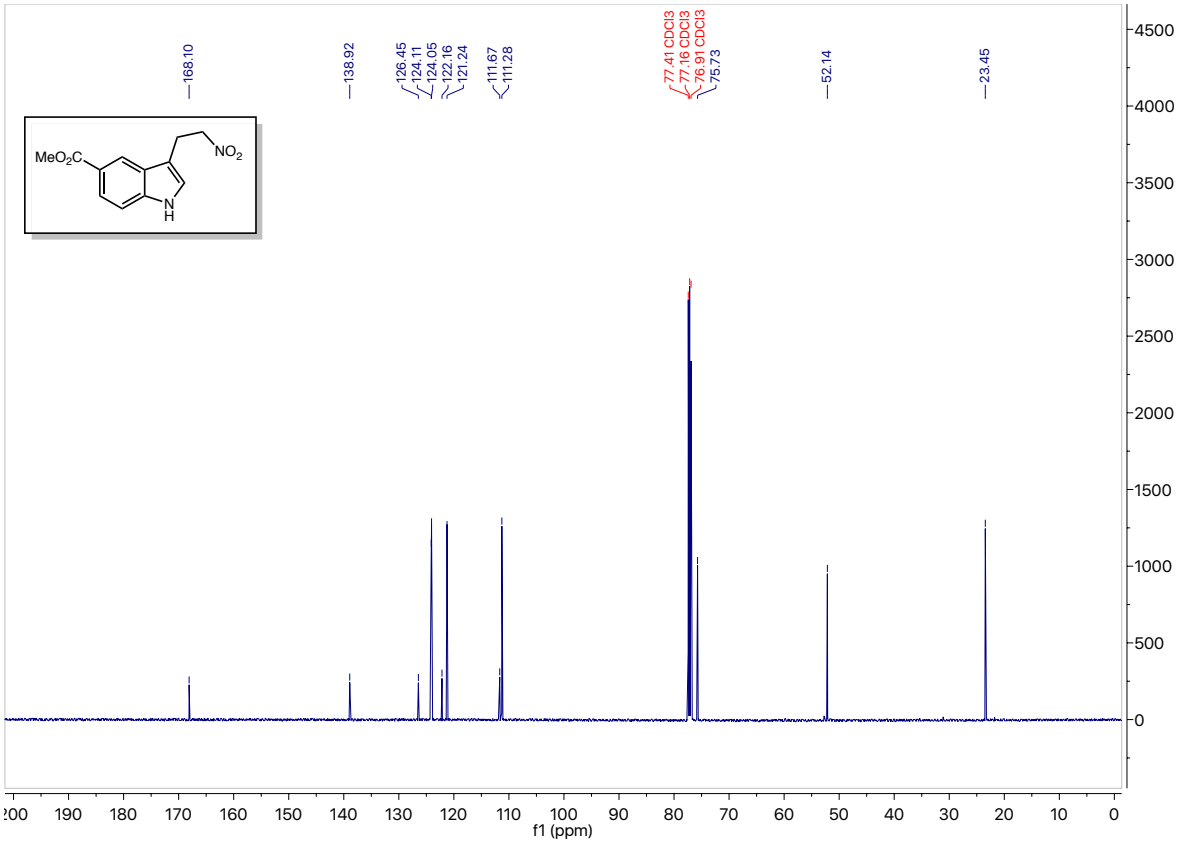

MeO
NHCbz
N
H
1.00
4.94
1.08
0.87
2.05
2.10
1.04
3.12
2.08
2.07
f1 (ppm)

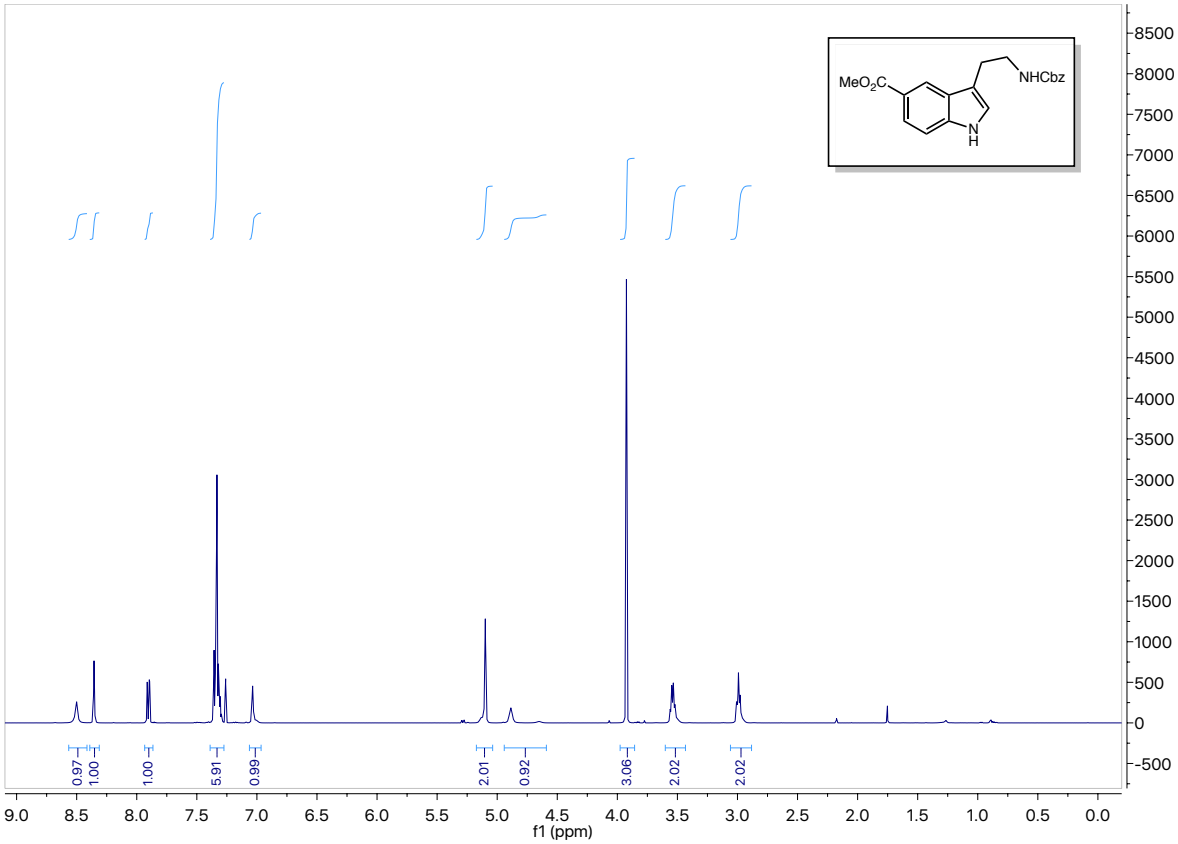

156.53
153.97
136.62
131.60
128.56
128.14
128.12
127.67
123.02
112.38
112.33
112.09
100.49
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.66
55.92
41.32
25.75
MeO
NHCbz
N
H
f1 (ppm)

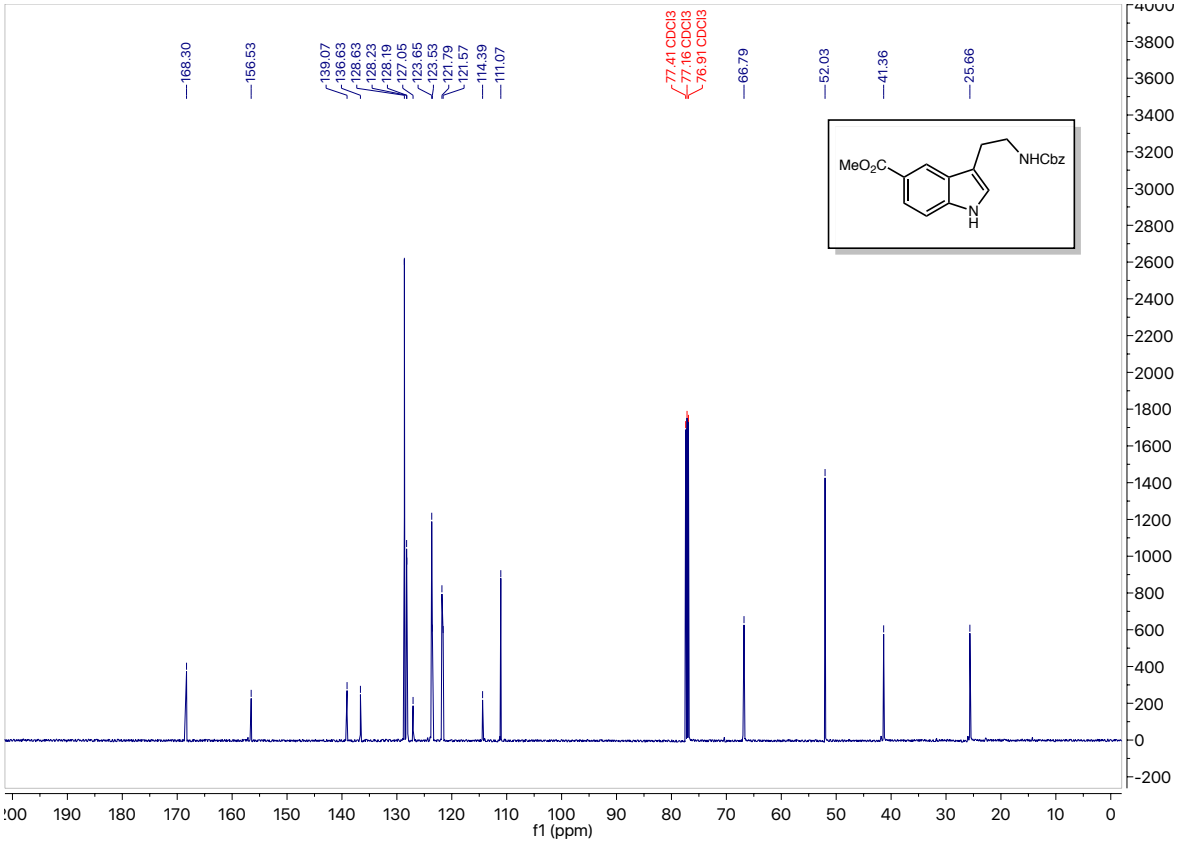

7.88
7.29
7.27
7.26
7.26
7.24
7.23
7.22
7.21
7.16
7.15
6.95
6.95
6.93
6.93
6.85
5.06
5.02
4.76
3.47
3.45
3.44
3.43
3.39
2.87
2.86
2.85
2.36
Me
NHCbz
N
H
0.95
5.87
1.21
1.00
1.00
2.04
0.84
0.99
0.14
2.04
2.04
3.05
f1 (ppm)


156.50
136.73
134.82
128.81
128.63
128.22
128.20
127.57
123.89
122.39
118.50
112.36
111.01
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.71
41.36
25.82
21.63
Me
NHCbz
N
H
f1 (ppm)


MeO2C
NO2
N
H
1.05
0.87
1.00
1.02
1.00
2.09
3.12
2.10
f1 (ppm)


168.10
138.92
126.45
124.11
124.05
122.16
121.24
111.67
111.28
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
75.73
52.14
23.45
MeO2C
NO2
N
H
f1 (ppm)


MeO2C
NHCbz
N
H
0.97
1.00
1.00
5.91
0.99
2.01
0.92
3.06
2.02
2.02
f1 (ppm)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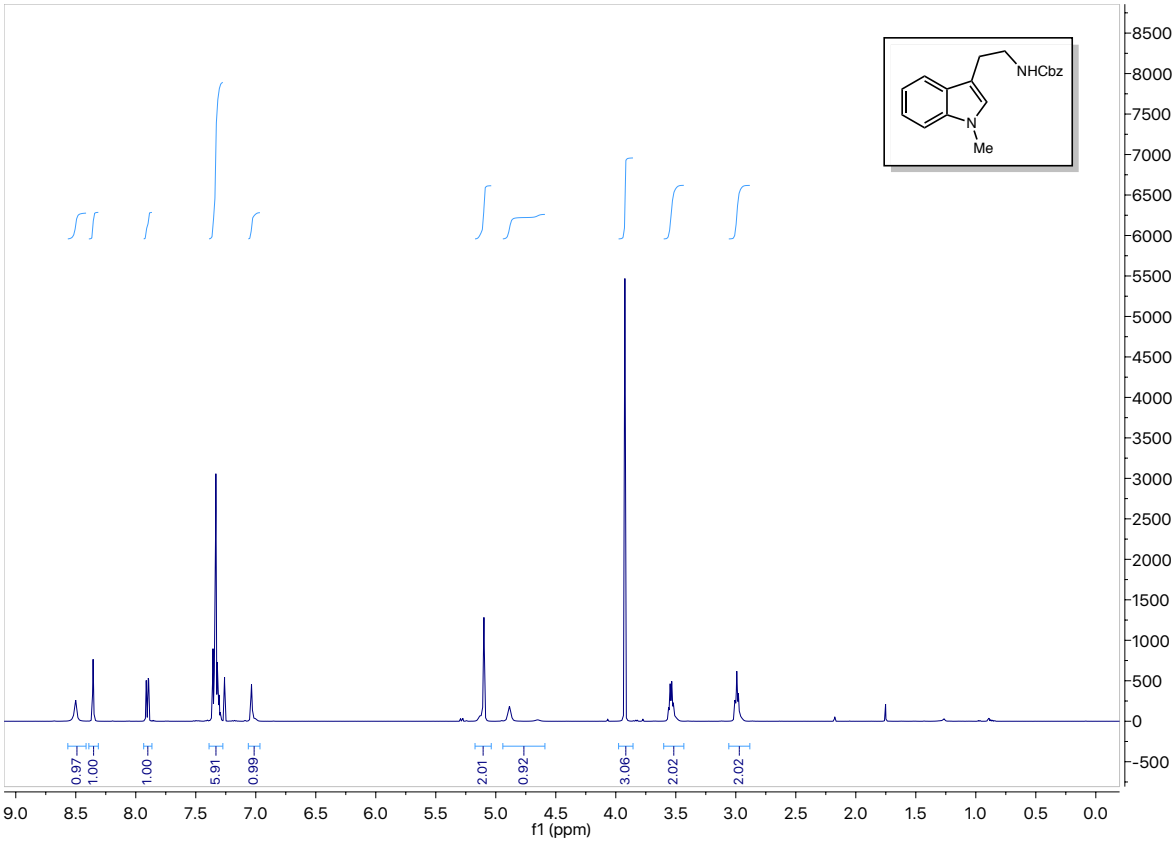
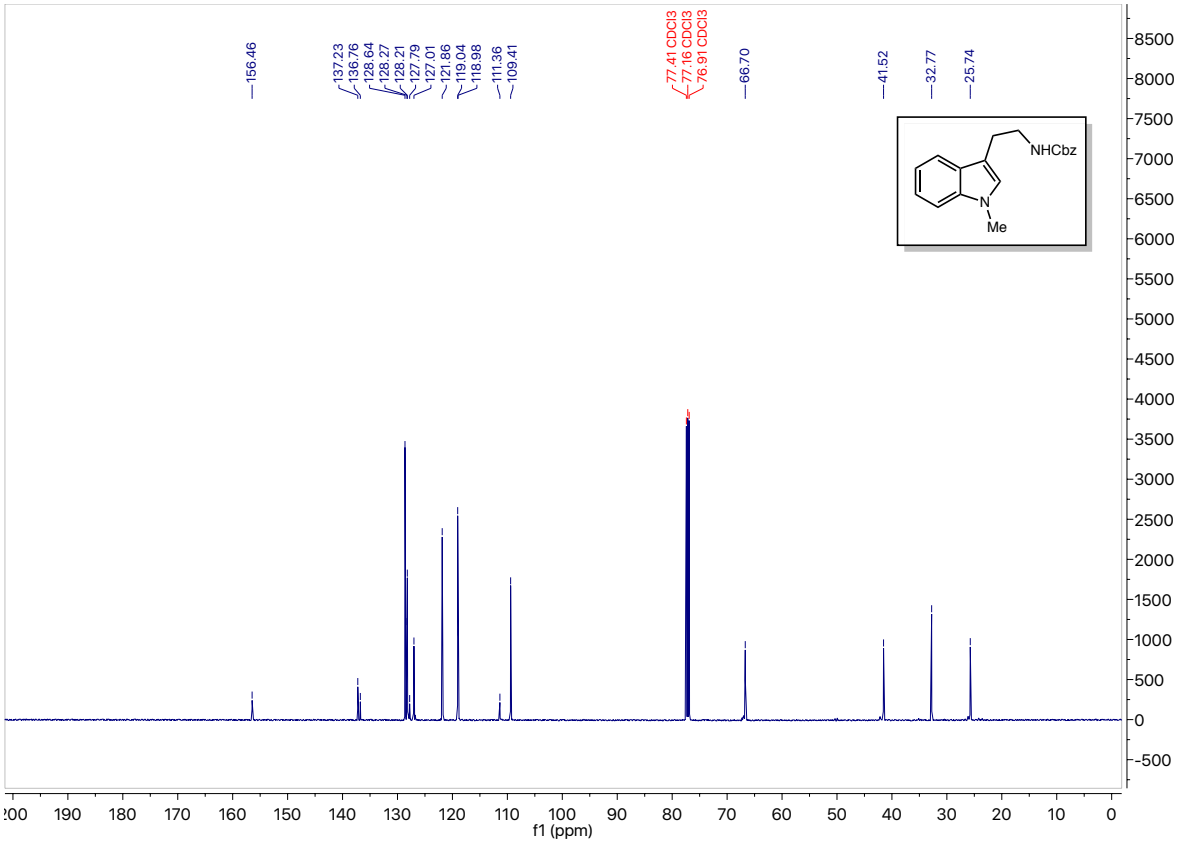
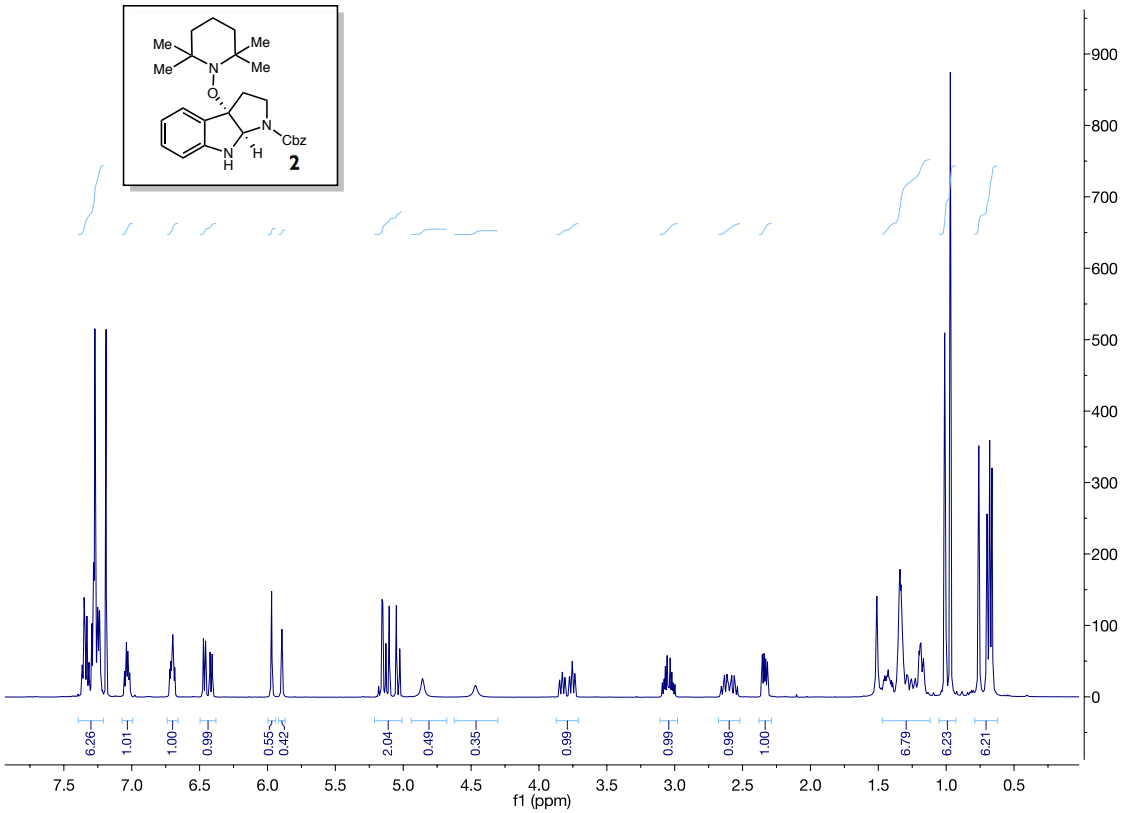
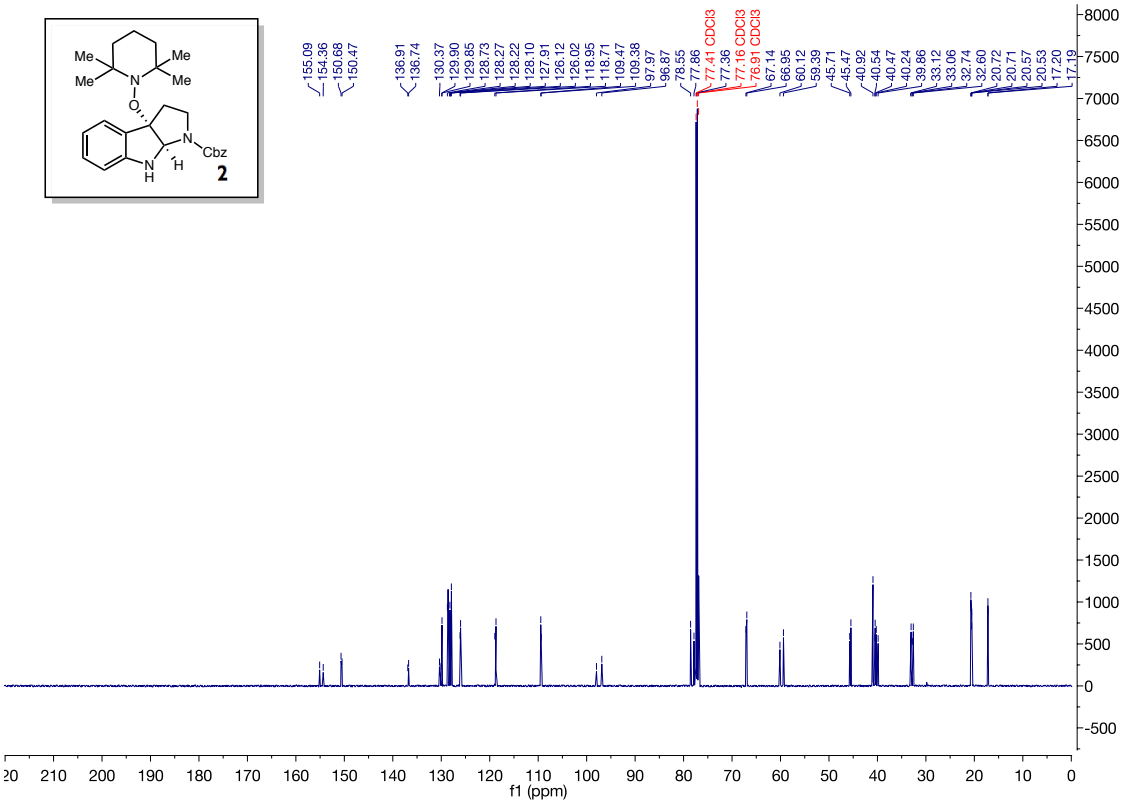
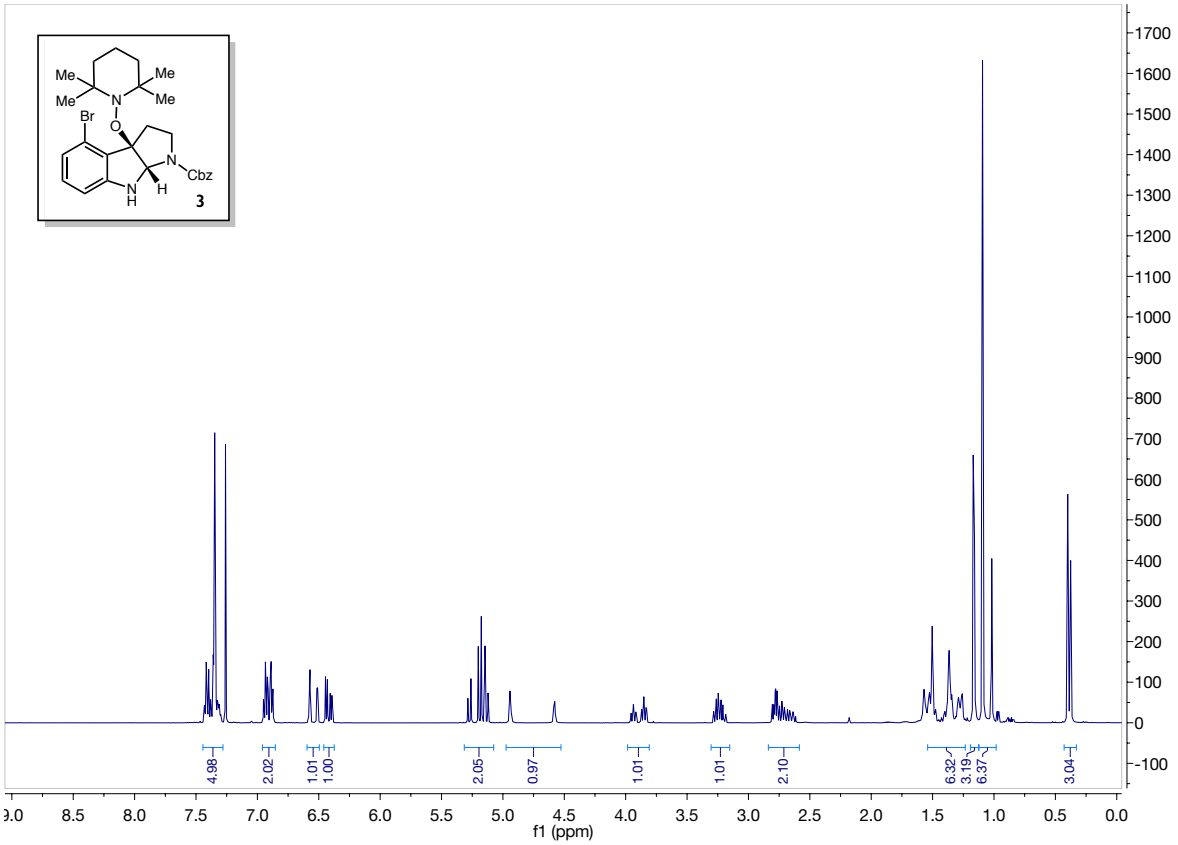
156.53
139.07
136.63
128.63
128.23
128.19
127.05
123.65
123.53
121.79
121.57
114.39
111.07
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.79
52.03
41.36
25.66
MeO2C
NHCbz
N
H
f1 (ppm)

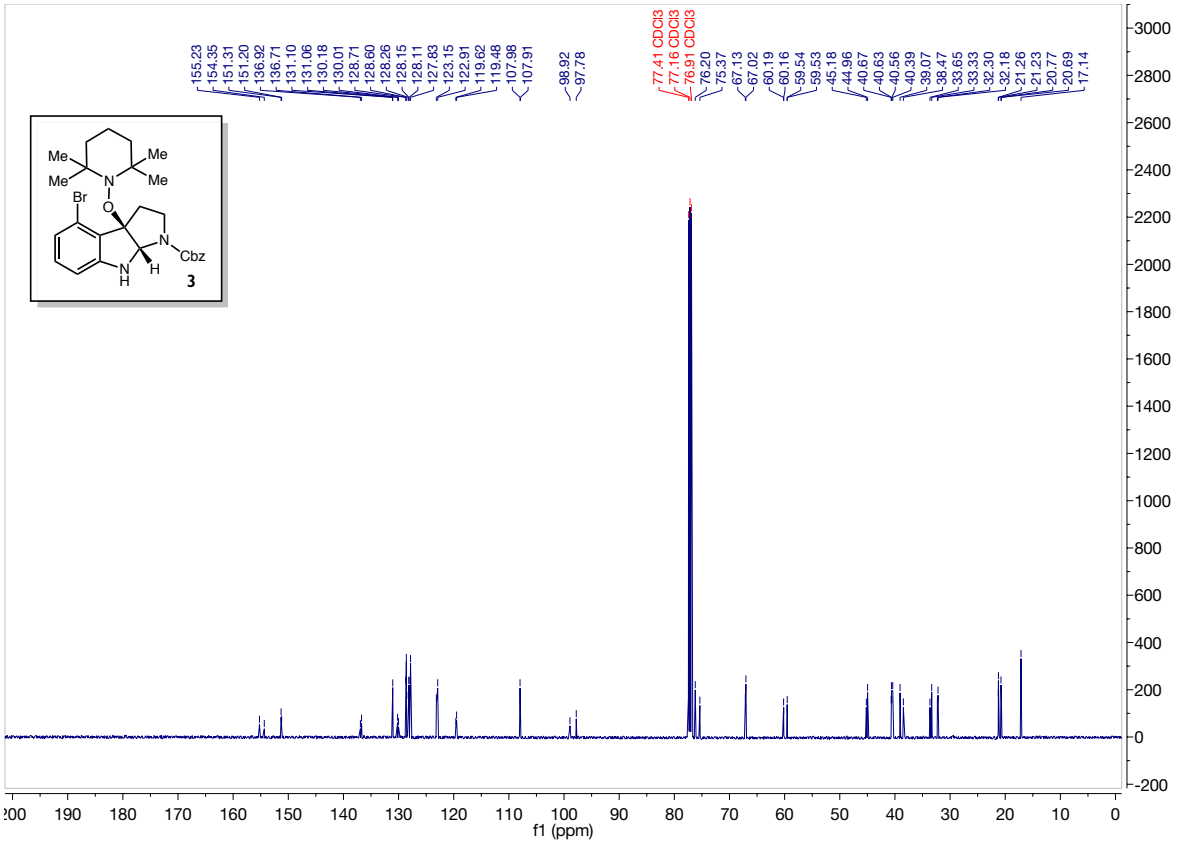

NHCbz
N
Me
0.97
1.00
1.00
5.91
0.99
2.01
0.92
3.06
2.02
2.02
f1 (ppm)

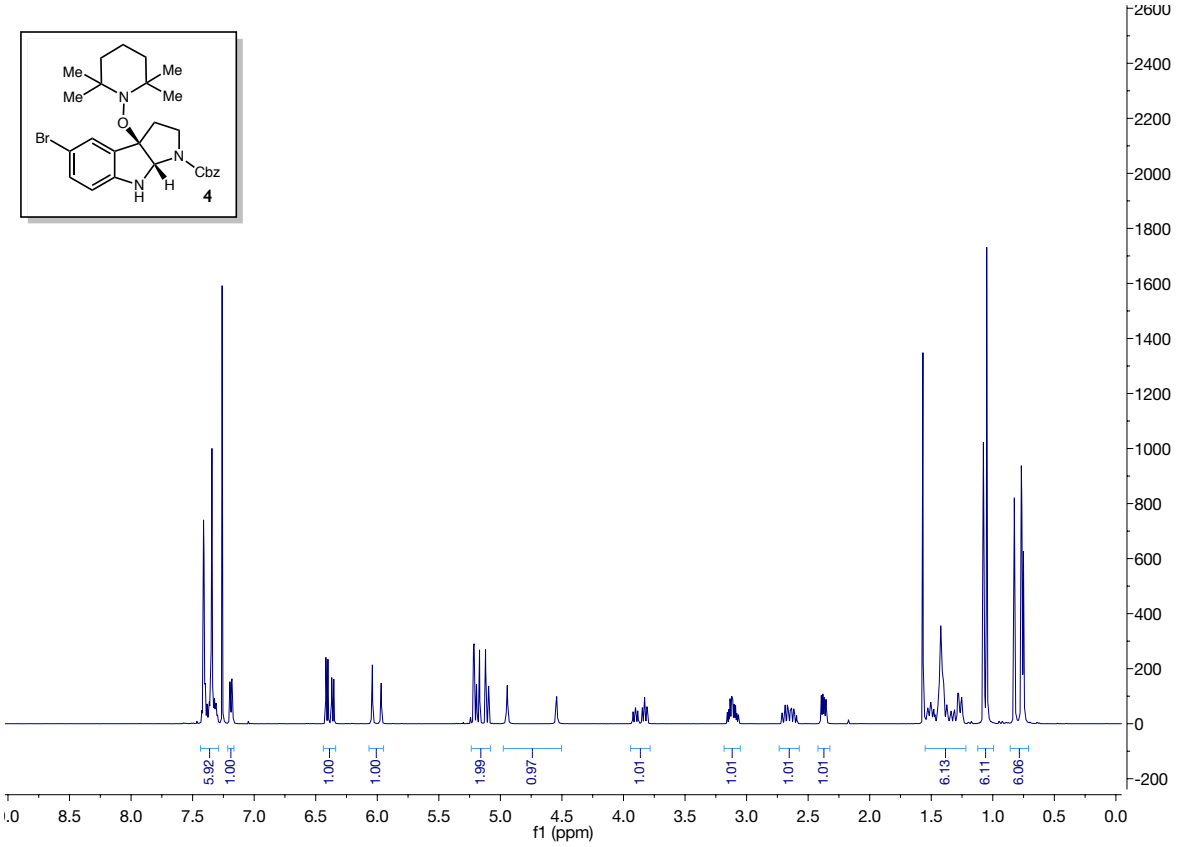

156.46
137.23
136.76
128.64
128.27
128.21
127.79
127.01
121.86
119.04
118.98
111.36
109.41
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.70
41.52
32.77
25.74
NHCbz
N
Me
f1 (ppm)

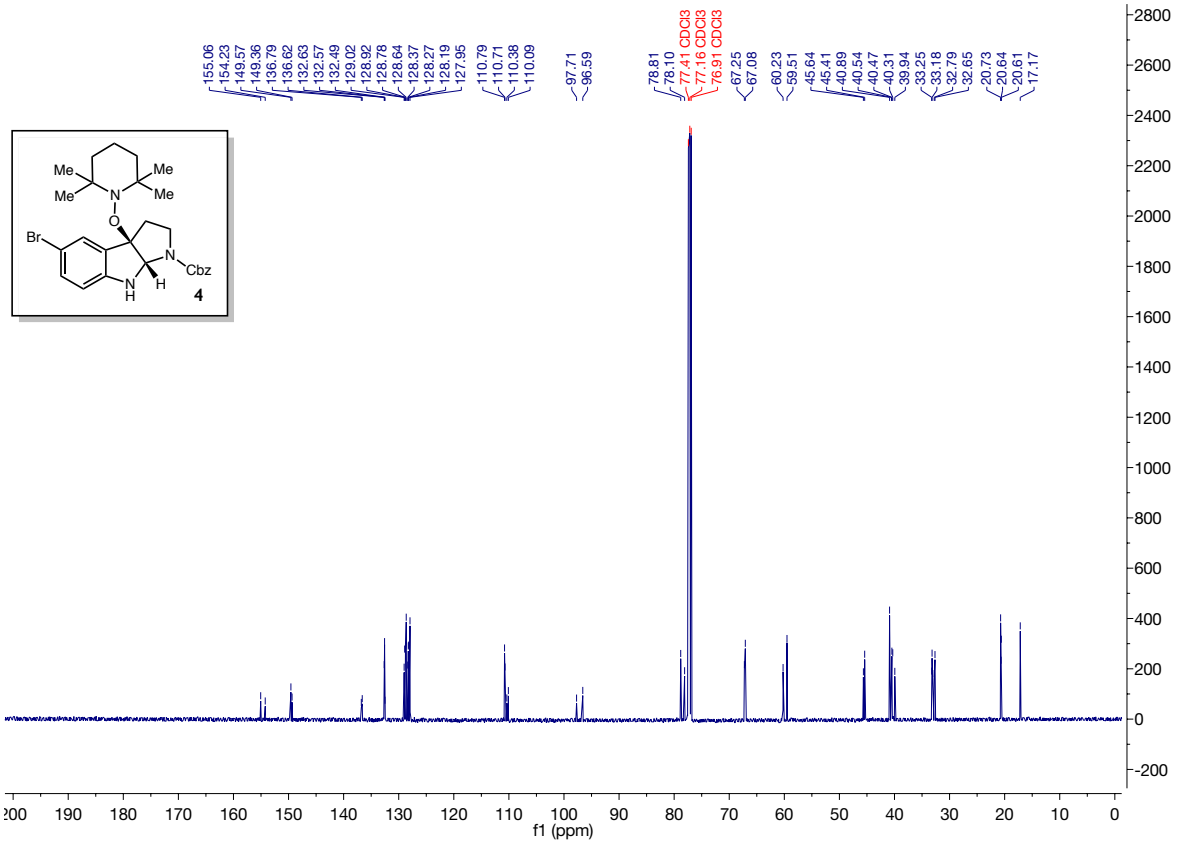

Me
Me
Me
Me
N
O
N
Cbz
H
N
H
2
6.26
1.01
1.00
0.99
0.55
0.42
2.04
0.49
0.35
0.99
0.99
0.98
1.00
6.79
6.23
6.21
f1 (ppm)

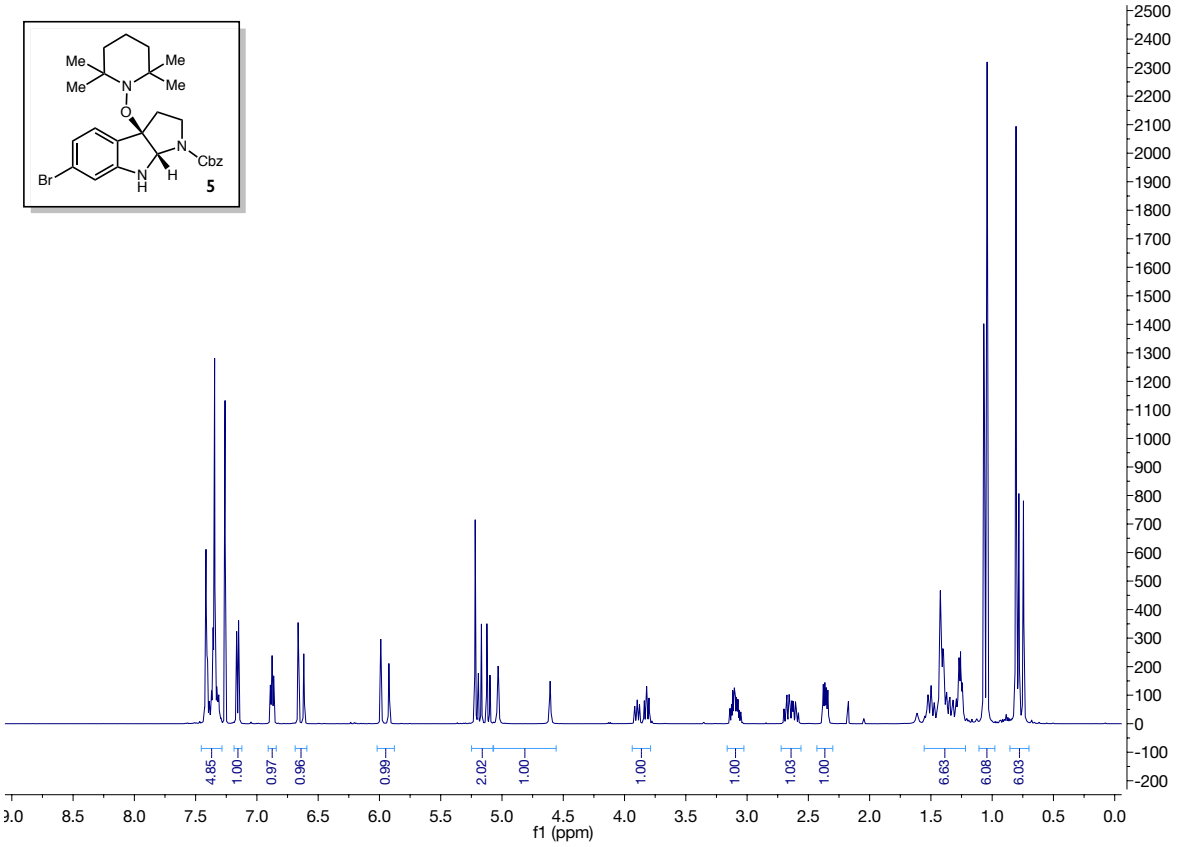

Me
Me
Me
Me
N
O
N
Cbz
H
N
H
2
155.09
154.36
150.88
150.47
136.91
136.74
130.37
129.90
129.85
128.73
128.27
128.22
128.10
127.91
126.12
126.02
118.95
118.71
109.47
109.38
97.97
96.87
78.55
77.86
77.41 CDCl3
77.36
77.16 CDCl3
76.91 CDCl3
67.14
66.95
60.12
59.39
45.71
45.47
40.92
40.54
40.47
40.24
39.86
33.12
33.06
32.74
32.60
20.72
20.71
20.57
20.53
17.20
17.19
f1 (ppm)

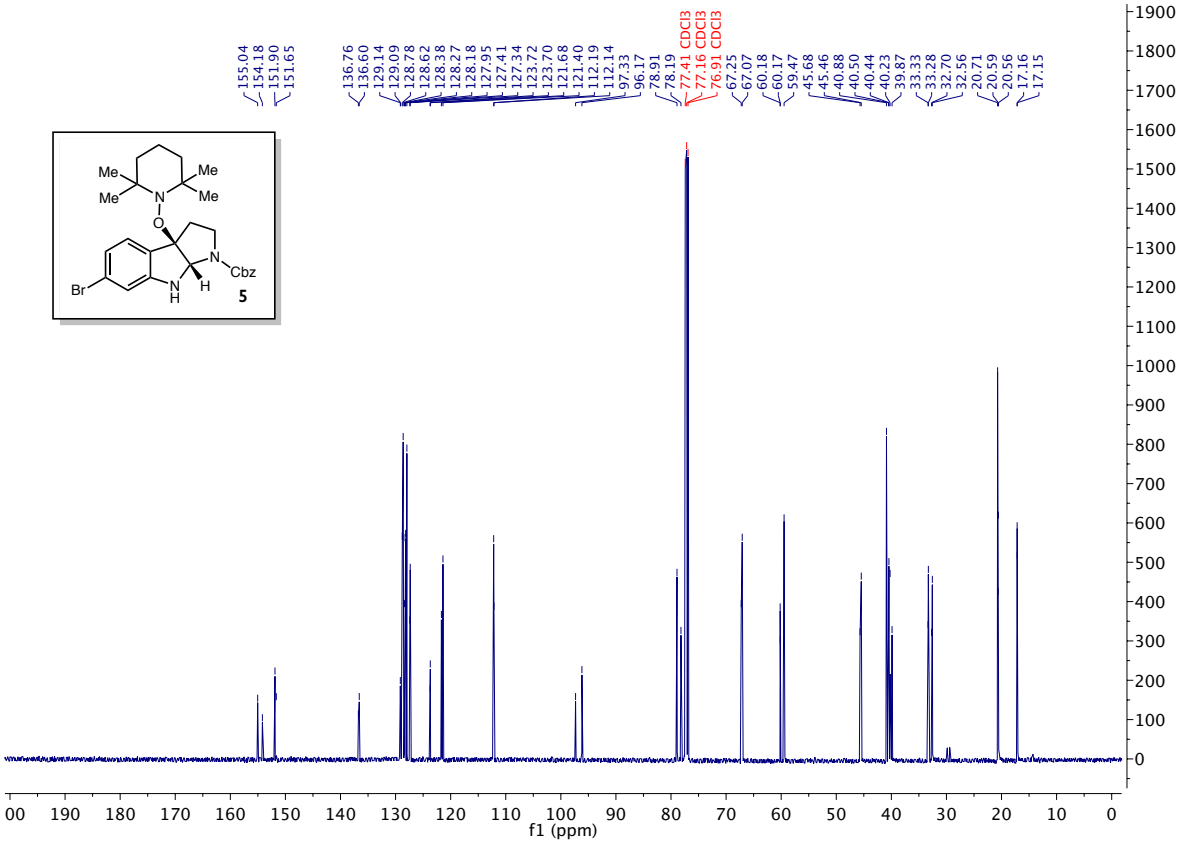

Me
Me
Me
Me
N
O
Br
N
Cbz
N
H
H
3
4.98
2.02
1.01
1.00
2.05
0.97
1.01
1.01
2.10
6.32
3.19
6.37
3.04
f1 (ppm)

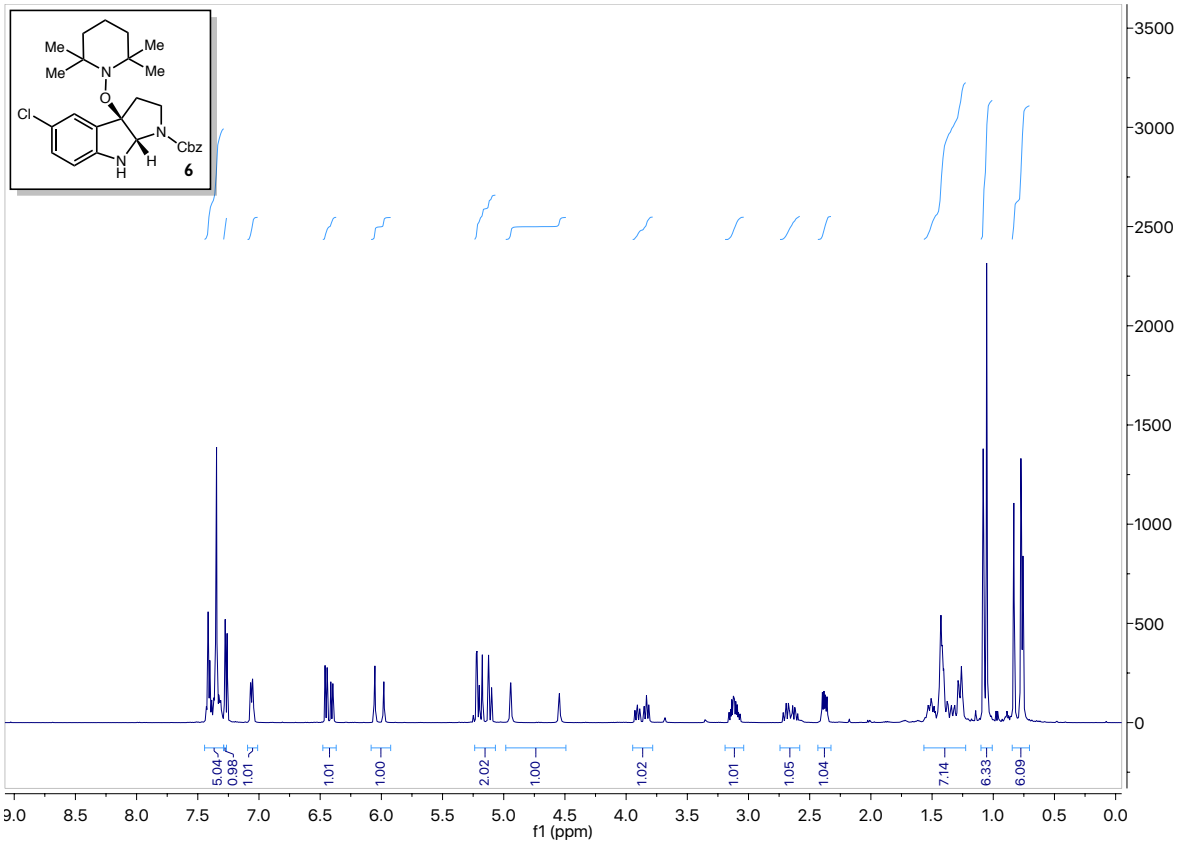

155.23
154.35
151.31
151.20
136.92
136.71
131.10
131.06
130.18
130.01
128.71
128.60
128.26
128.15
128.11
127.83
123.15
122.91
119.62
119.48
107.98
107.91
98.92
97.78
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
76.20
75.37
67.13
67.02
60.19
60.16
59.54
59.53
45.18
44.96
40.67
40.63
40.56
40.39
39.07
38.47
33.65
33.33
32.30
32.18
21.26
21.23
20.77
20.69
17.14
Me
Me
Me
Me
N
O
Br
N
Cbz
N
H
H
3
f1 (ppm)

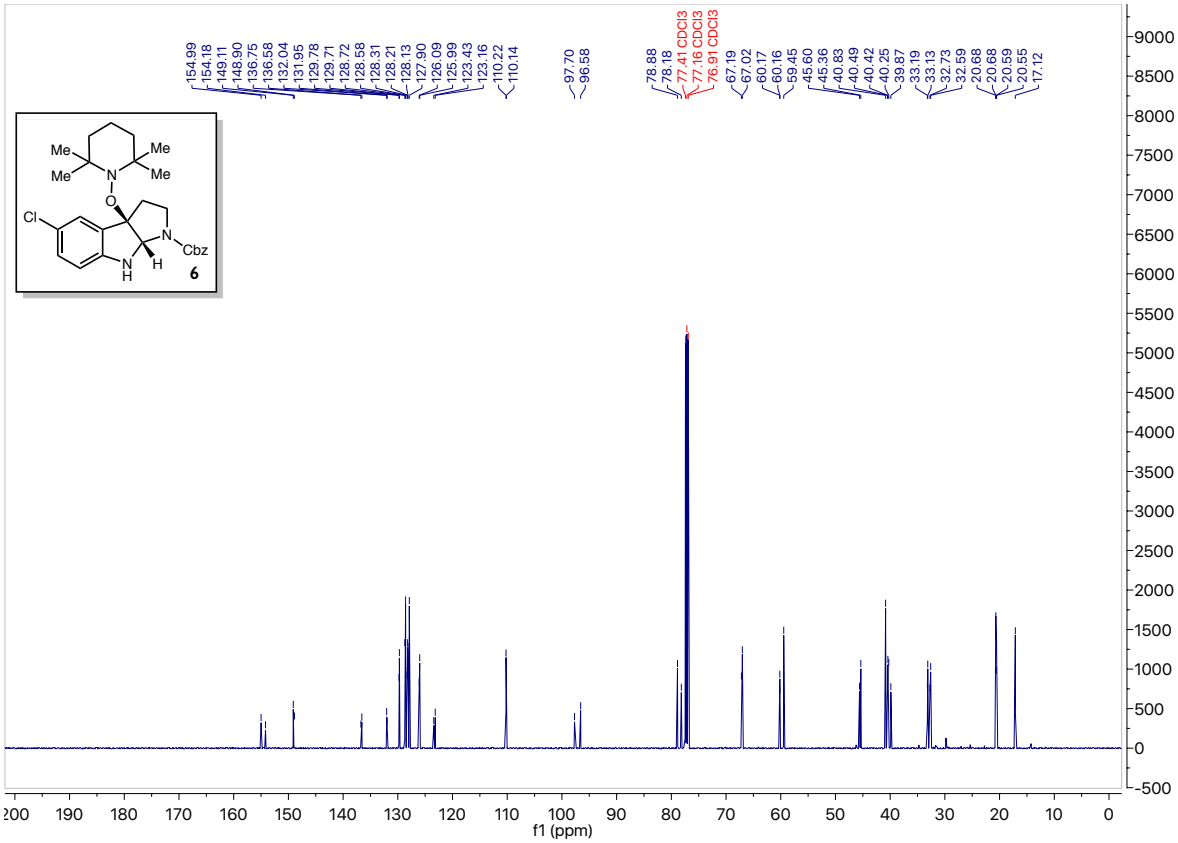

Me
Me
Me
Me
N
O
Br
N
Cbz
N
H
H
4
5.92
1.00
1.00
1.00
1.99
0.97
1.01
1.01
1.01
1.01
6.13
6.11
6.06
f1 (ppm)

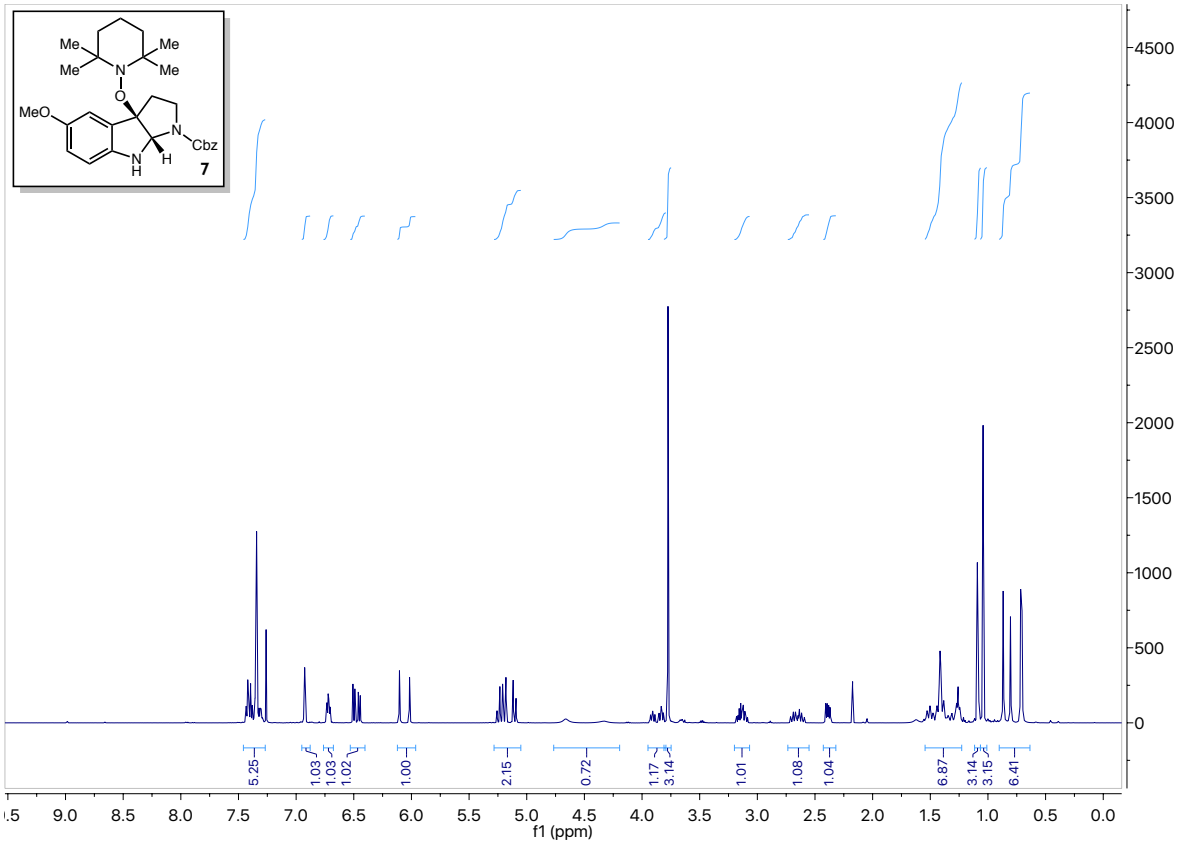

155.06
154.23
149.57
149.36
136.79
136.62
132.63
132.57
132.49
129.02
128.92
128.78
128.64
128.37
128.27
128.19
127.95
110.79
110.71
110.38
110.09
97.71
96.59
78.81
78.10
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.25
67.08
60.23
59.51
45.64
45.41
40.89
40.54
40.47
40.31
39.94
33.25
33.18
32.79
32.65
20.73
20.64
20.61
17.17
Me
Me
Me
Me
N
O
Br
N
Cbz
N
H
H
4
f1 (ppm)

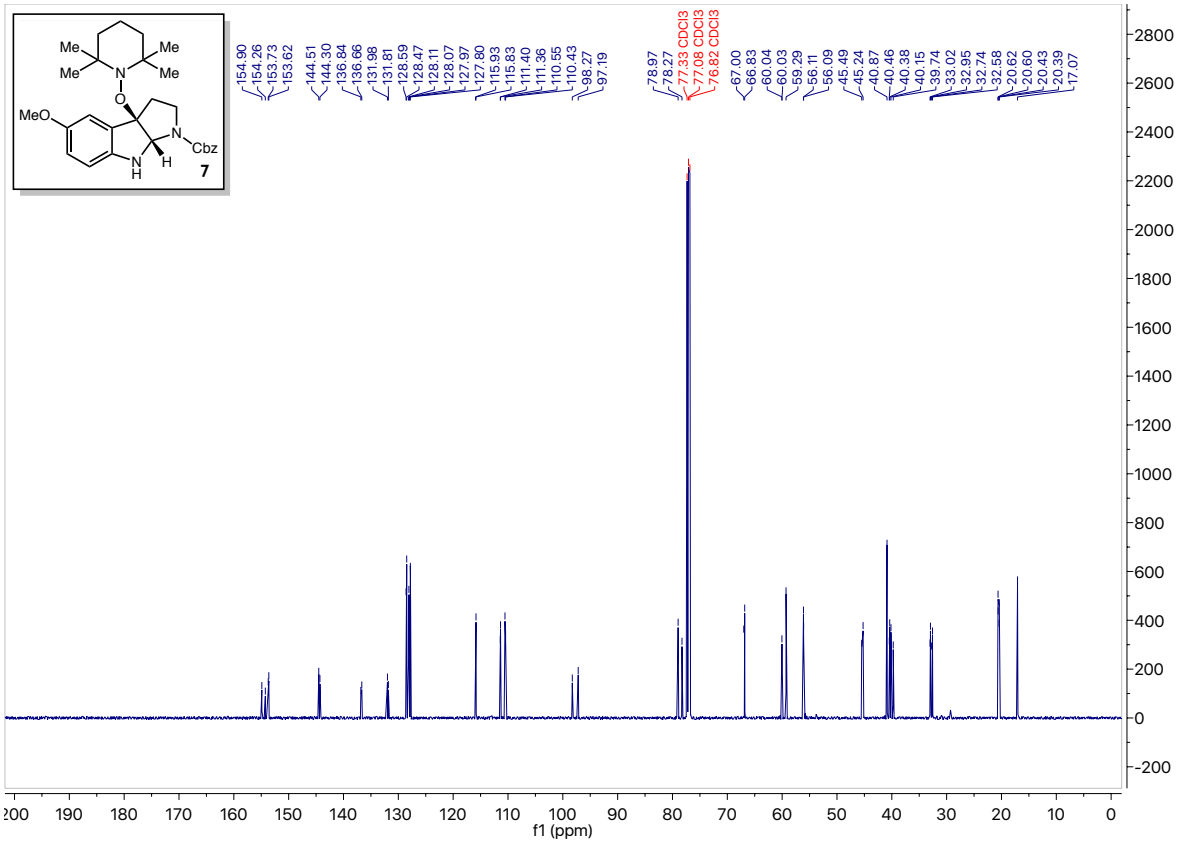

Me
Me
Me
Me
N
O
N
Cbz
Br
N
H
H
5
4.85
1.00
0.97
0.96
0.99
2.02
1.00
1.00
1.00
1.03
1.00
6.63
6.08
6.03
f1 (ppm)

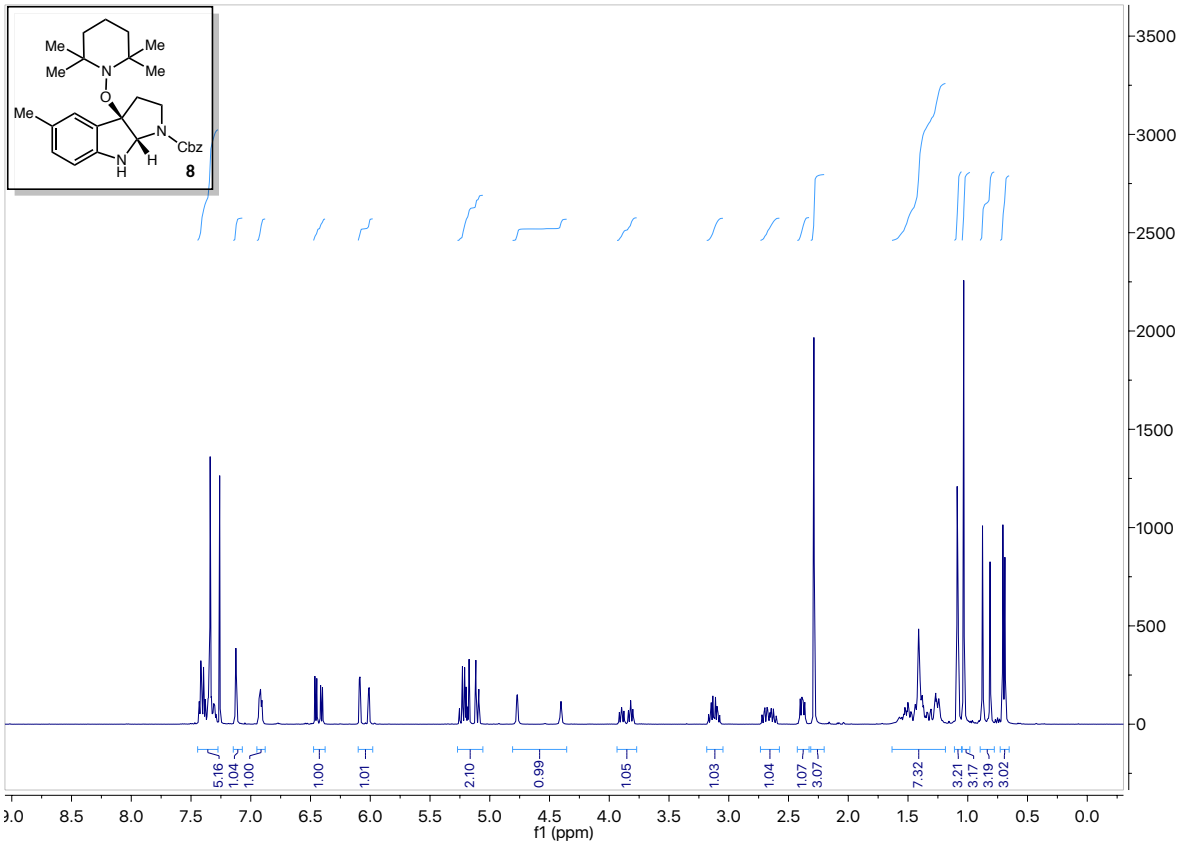

155.04
154.18
151.90
151.65
136.76
136.60
129.14
129.09
128.78
128.62
128.38
128.27
128.18
127.95
127.41
127.34
123.72
123.70
121.68
121.40
112.19
112.14
97.33
96.17
78.91
78.19
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.25
67.07
60.18
60.17
59.47
45.68
45.46
40.88
40.50
40.44
40.23
39.87
33.33
33.28
32.70
32.56
20.71
20.59
20.56
17.16
17.15
Me
Me
Me
Me
N
O
N
Cbz
Br
N
H
H
5
f1 (ppm)

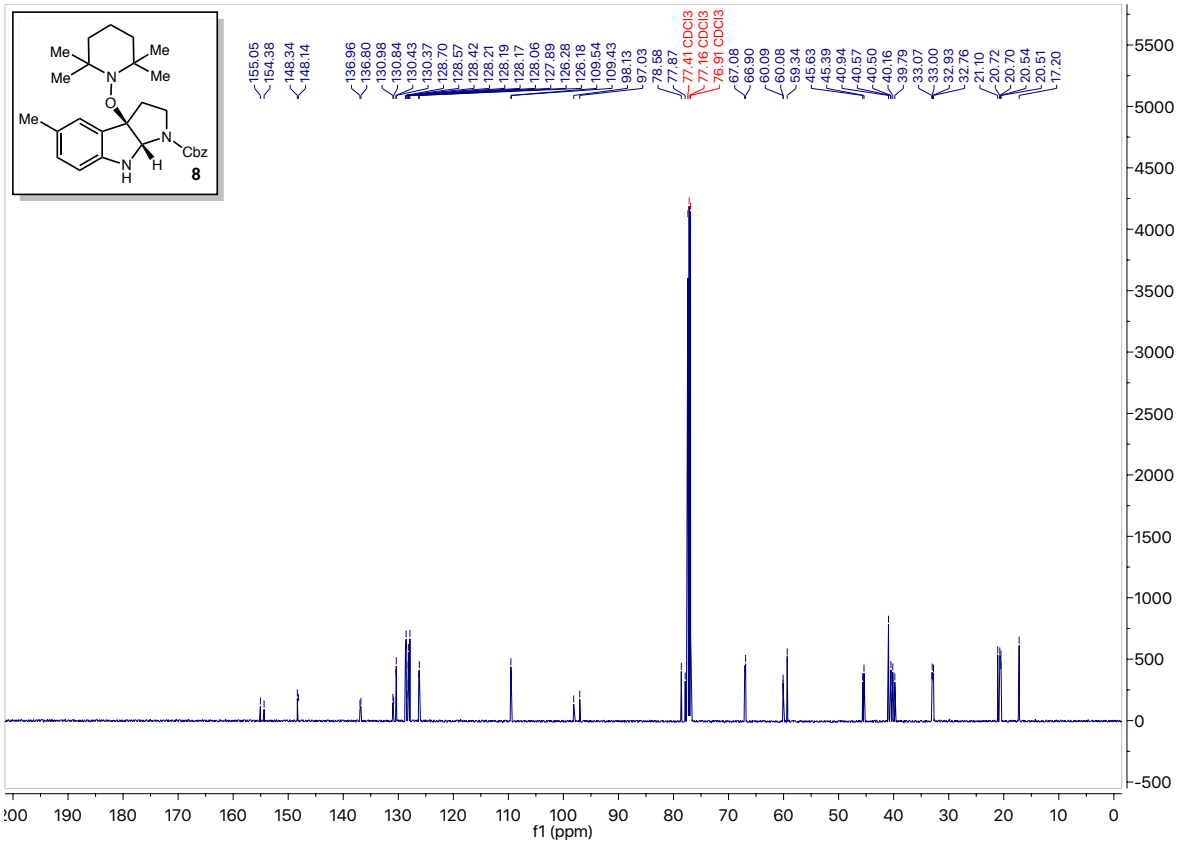

Me
Me
Me
Me
N
O
Cl
N
Cbz
N
H
H
6
5.04
0.98
1.01
1.01
1.00
2.02
1.00
1.02
1.01
1.05
1.04
7.14
6.33
6.09
f1 (ppm)

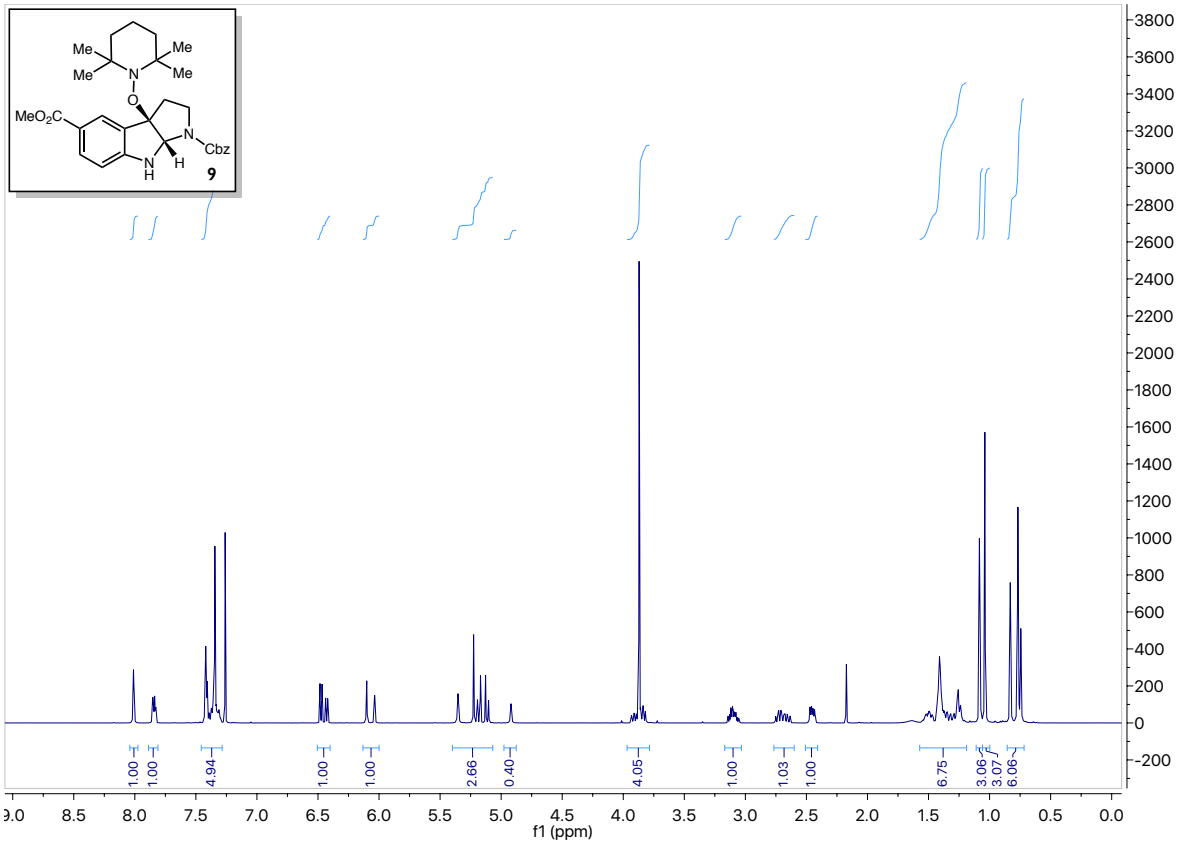

154.99
154.18
149.11
148.90
136.75
136.58
132.04
131.95
129.78
129.71
128.72
128.58
128.31
128.21
128.13
127.90
126.09
125.99
123.43
123.16
110.22
110.14
97.70
96.58
78.88
78.18
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.19
67.02
60.17
60.16
59.45
45.60
45.36
40.83
40.49
40.42
40.25
39.87
33.19
33.13
32.73
32.59
20.68
20.68
20.59
20.55
17.12
Me
Me
Me
Me
N
O
Cl
N
Cbz
N
H
H
6
f1 (ppm)

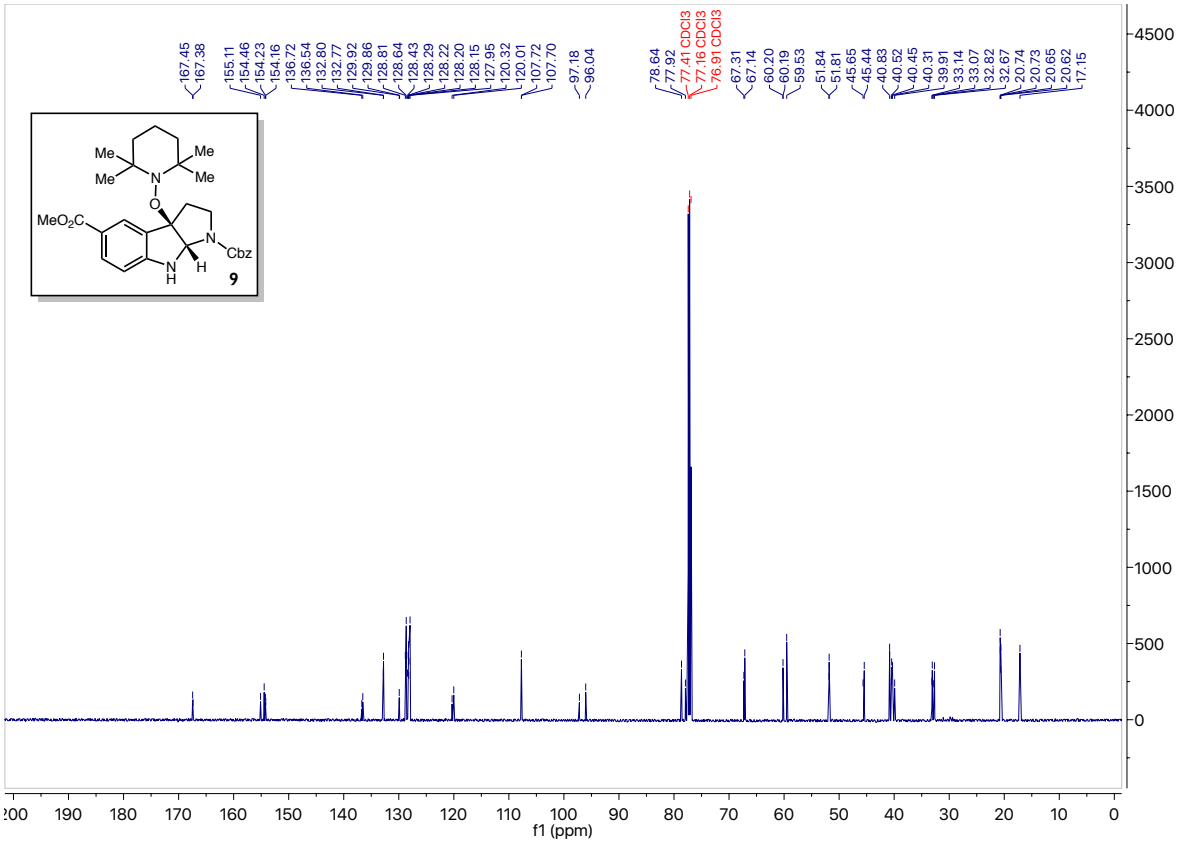

Me
Me
Me
Me
N
O
MeO
N
Cbz
N
H
H
7
5.25
1.03
1.03
1.02
1.00
2.15
0.72
1.17
3.14
1.01
1.08
1.04
6.87
3.14
3.15
6.41
f1 (ppm)

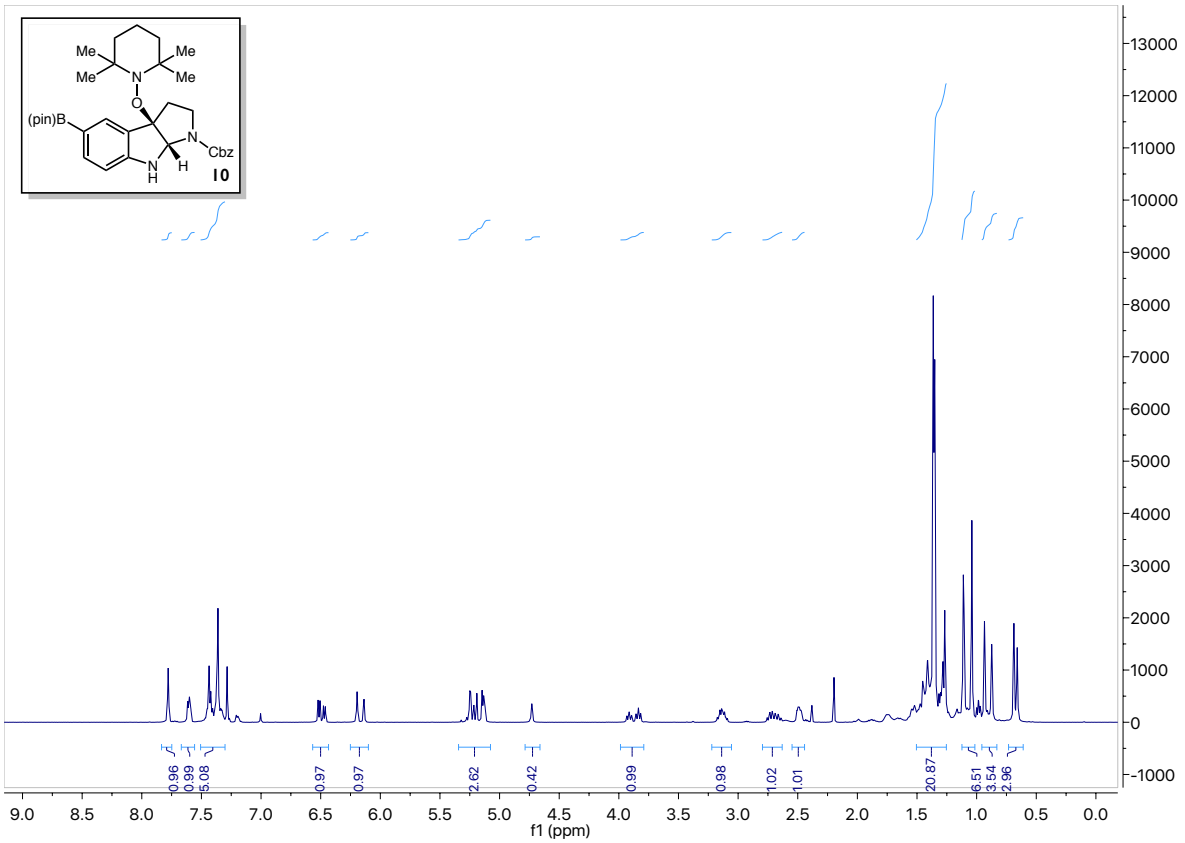

Me
Me
Me
Me
N
O
MeO
N
Cbz
N
H
H
7
154.90
154.26
153.73
153.62
144.51
144.30
136.84
136.66
131.98
131.81
128.59
128.47
128.11
128.07
127.97
127.80
115.93
115.83
111.40
111.36
110.55
110.43
98.27
97.19
78.97
78.27
77.33 CDCl3
77.08 CDCl3
76.82 CDCl3
67.00
66.83
60.04
60.03
59.29
56.11
56.09
45.49
45.24
40.87
40.46
40.38
40.15
39.74
33.02
32.95
32.74
32.58
20.62
20.60
20.43
20.39
17.07
f1 (ppm)

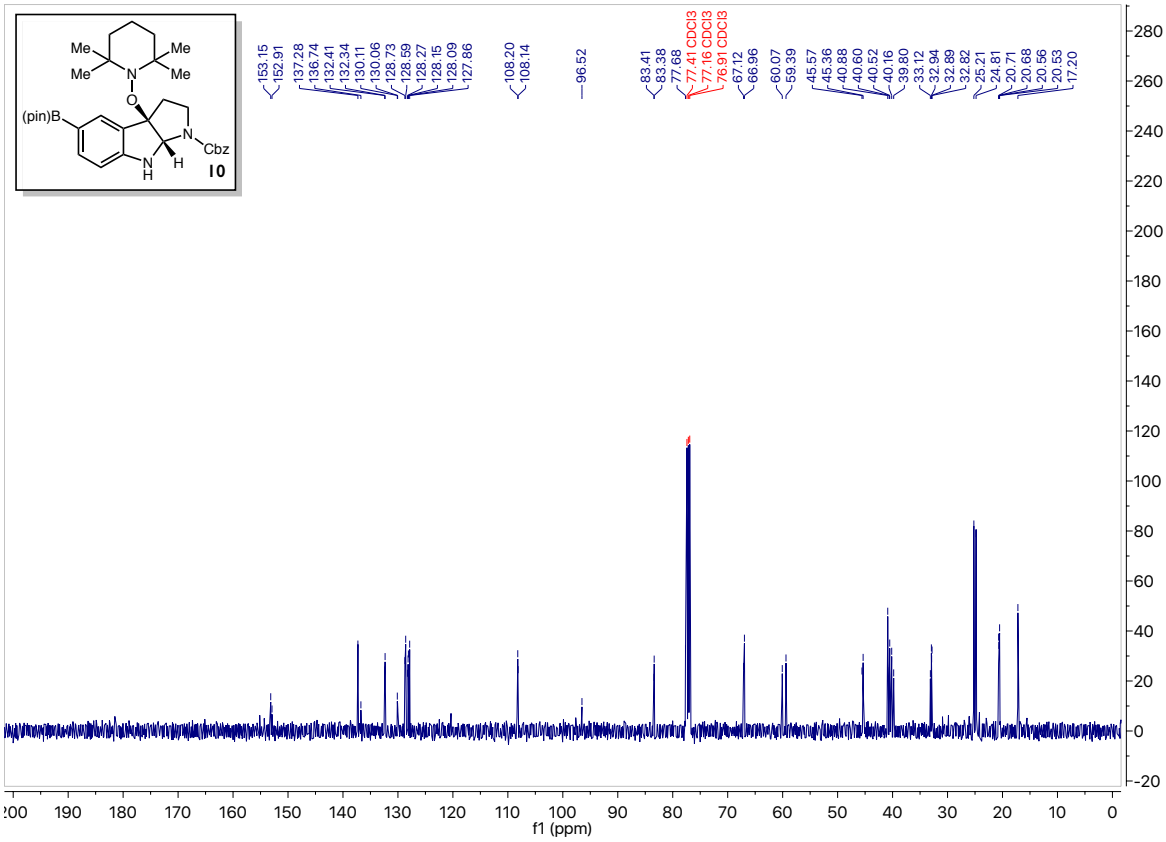

Me
Me
Me
Me
N
O
Me
N
Cbz
N
H
H
8
5.16
1.04
1.00
1.00
1.01
2.10
0.99
1.05
1.03
1.04
1.07
3.07
7.32
3.21
3.17
3.19
3.02
f1 (ppm)

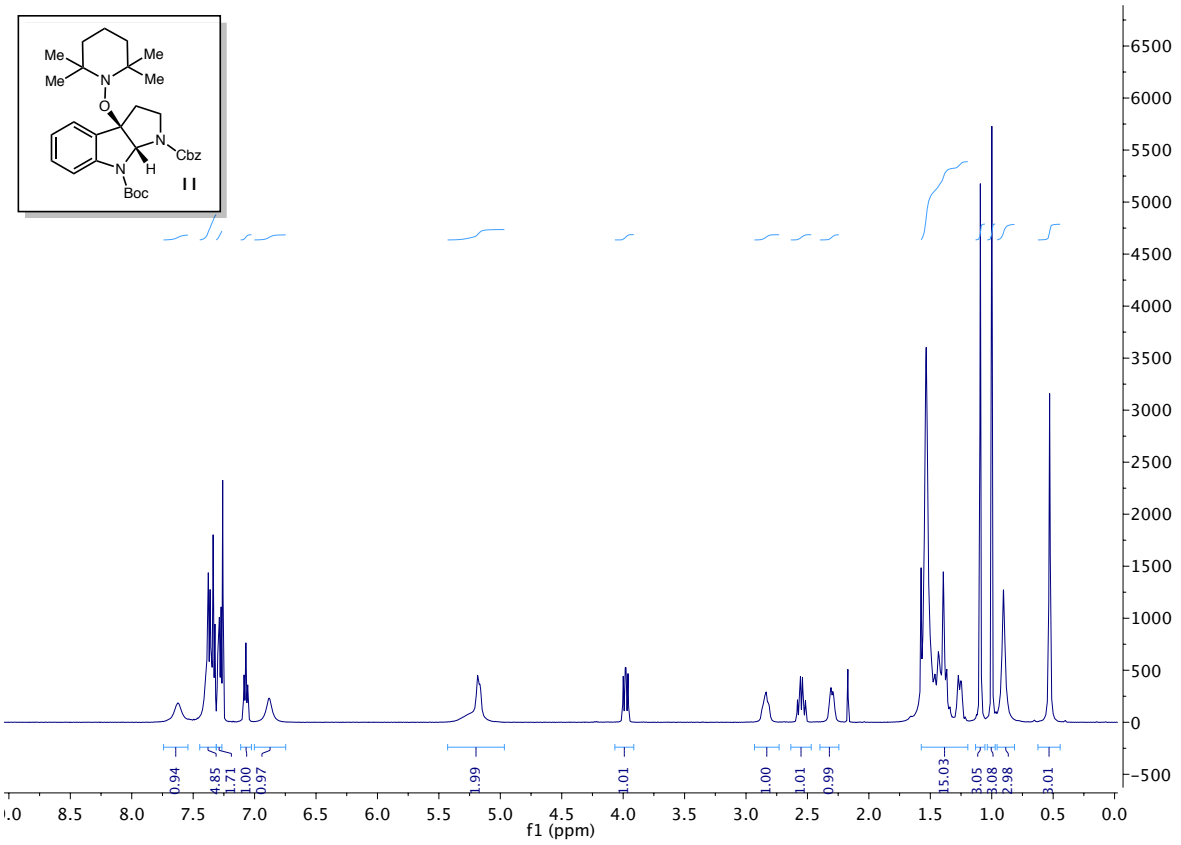

Me
Me
Me
Me
N
O
Me
N
Cbz
N
H
H
8
155.05
154.38
148.34
148.14
136.96
136.80
130.98
130.84
130.43
130.37
128.70
128.57
128.42
128.21
128.19
128.17
128.06
127.89
126.28
126.18
109.54
109.43
98.13
97.03
78.58
77.87
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.08
66.90
60.09
60.08
59.34
45.63
45.39
40.94
40.57
40.50
40.16
39.79
33.07
33.00
32.93
32.76
21.10
20.72
20.70
20.54
20.51
17.20
f1 (ppm)

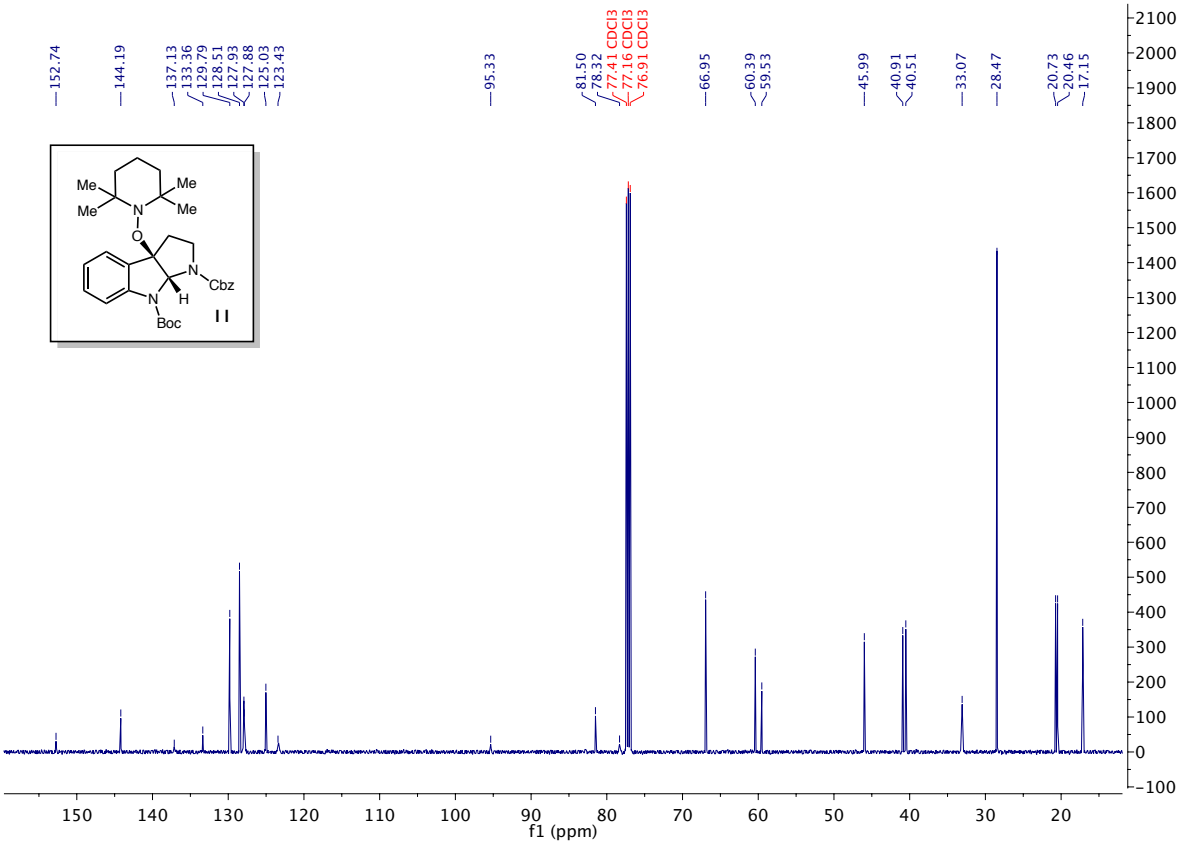

Me
Me
Me
Me
N
O
MeO2C
N
Cbz
N
H
H
9
1.00
1.00
4.94
1.00
1.00
2.66
0.40
4.05
1.00
1.03
1.00
6.75
3.06
3.07
6.06
f1 (ppm)

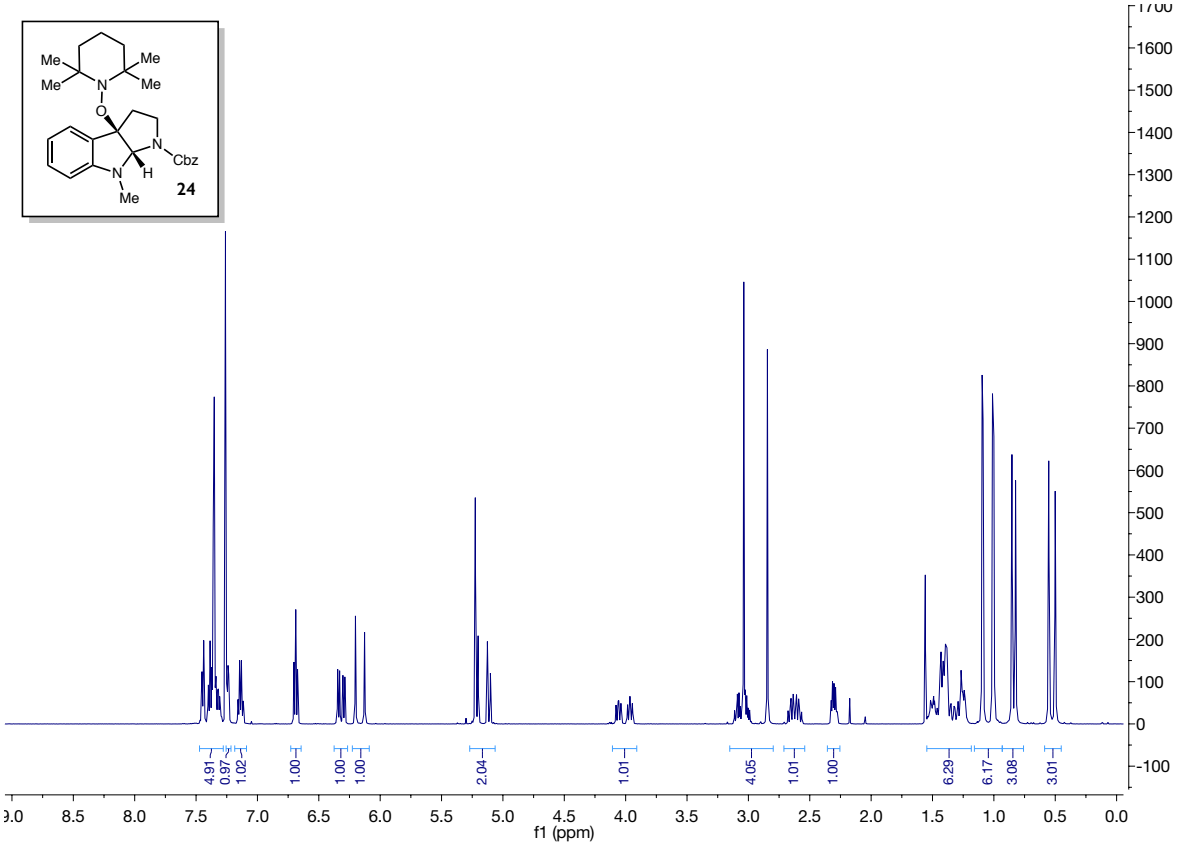

167.45
167.38
155.11
154.46
154.23
154.16
136.72
136.54
132.80
132.77
129.92
129.86
128.81
128.64
128.43
128.29
128.22
128.20
128.15
127.95
120.32
120.01
107.72
107.70
97.18
96.04
78.64
77.92
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.31
67.14
60.20
60.19
59.53
51.84
51.81
45.65
45.44
40.83
40.52
40.45
40.31
39.91
33.14
33.07
32.82
32.67
20.74
20.73
20.65
20.62
17.15
Me
Me
Me
Me
N
O
MeO2C
N
Cbz
N
H
H
9
f1 (ppm)

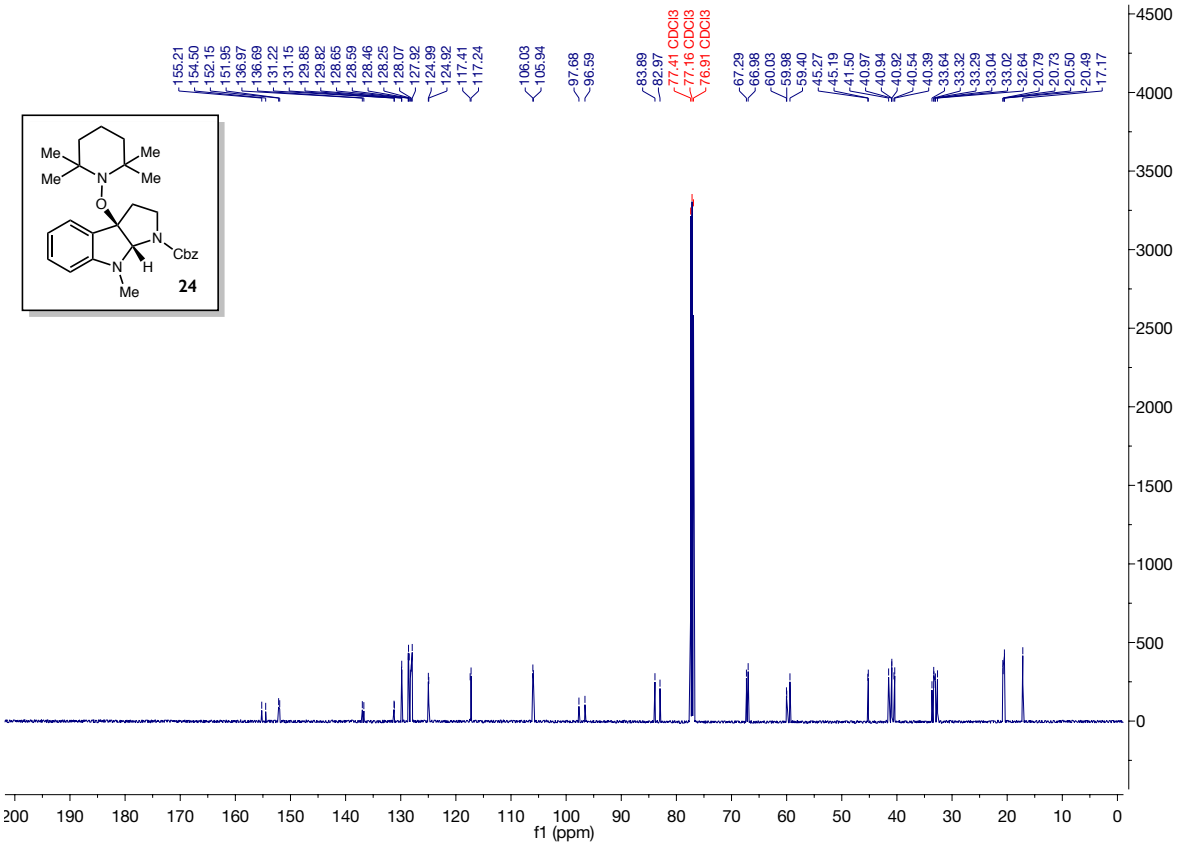

Me
Me
Me
Me
N
O
(pin)B
N
Cbz
N
H
H
10
0.96
0.99
5.08
0.97
0.97
2.62
0.42
0.99
0.98
1.02
1.01
20.87
6.51
3.54
2.96
f1 (ppm)

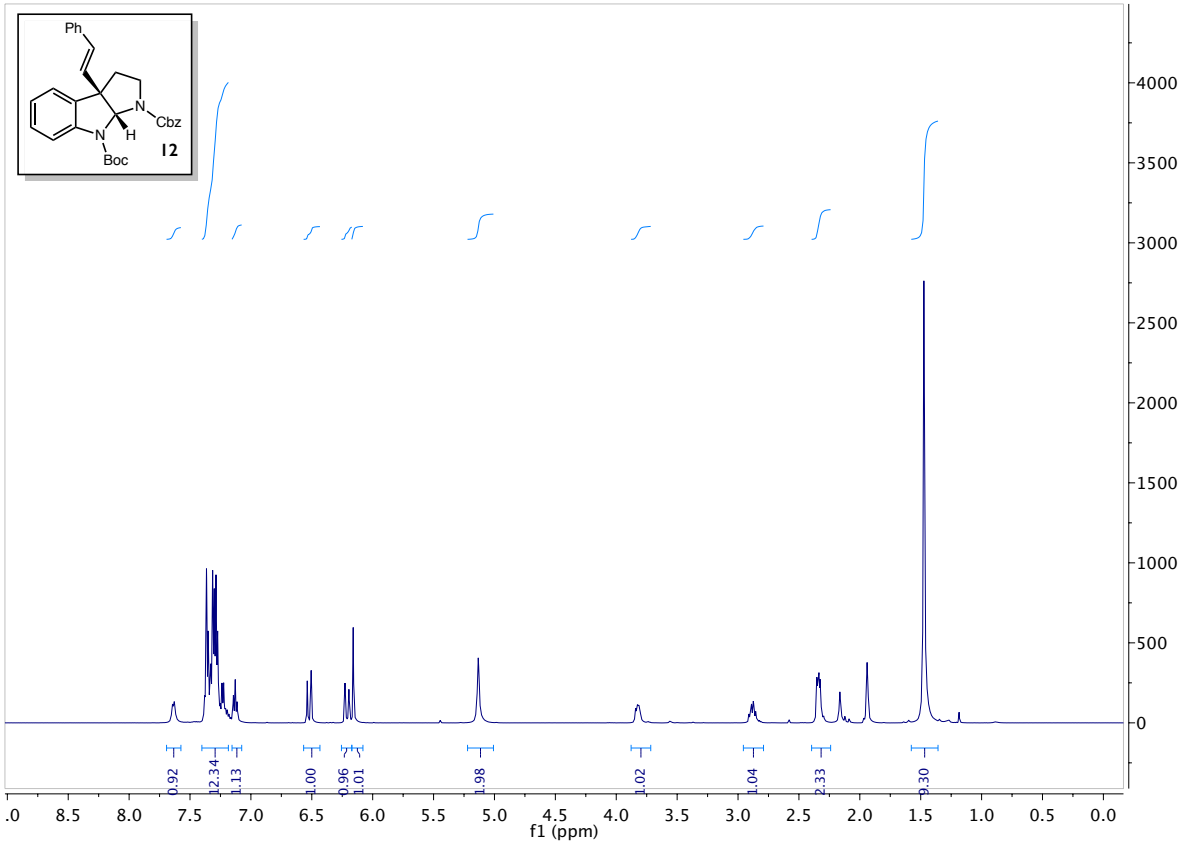

Me
Me
Me
Me
N
O
(pin)B
N
Cbz
N
H
H
10
153.15
152.91
137.28
136.74
132.41
132.34
130.11
130.06
128.73
128.59
128.27
128.15
128.09
127.86
108.20
108.14
96.52
83.41
83.38
77.68
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.12
66.96
60.07
59.39
45.57
45.36
40.88
40.60
40.52
40.16
39.80
33.12
32.94
32.89
32.62
25.21
24.81
20.71
20.68
20.56
20.53
17.20
f1 (ppm)

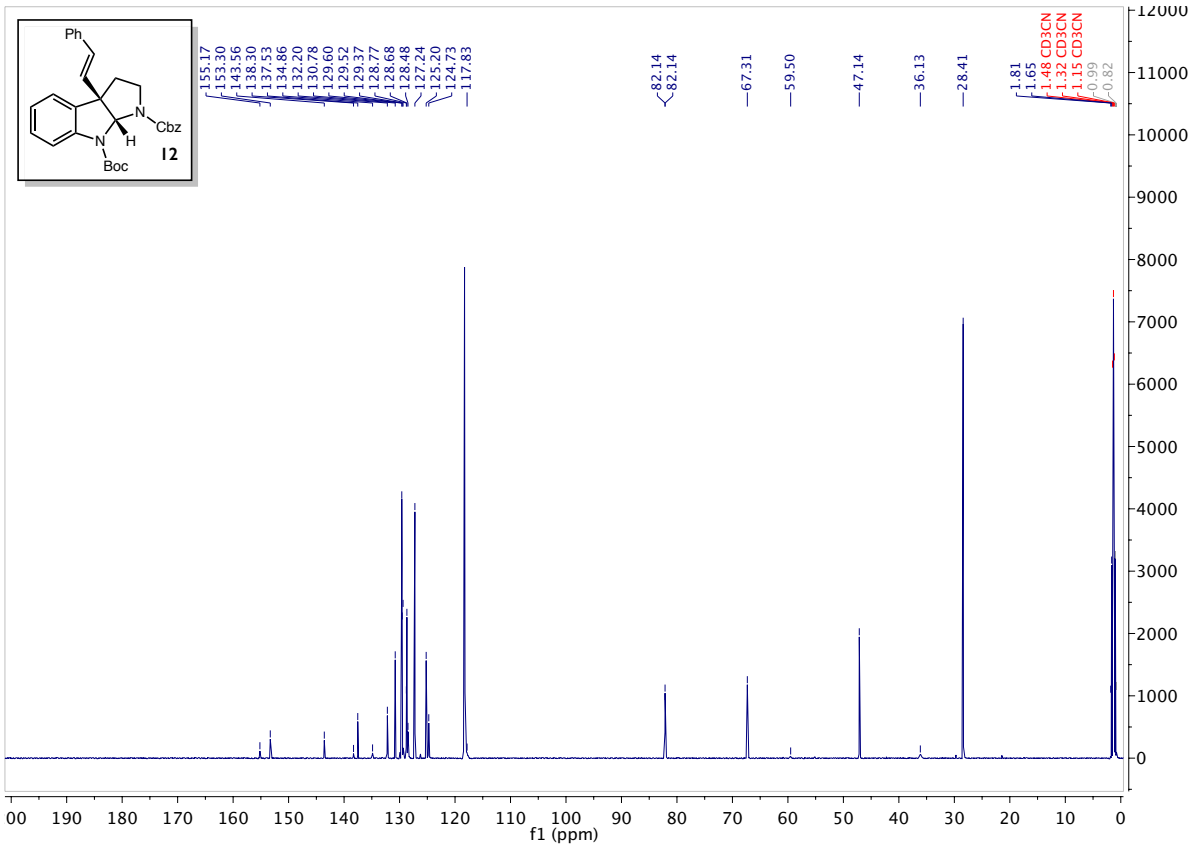

Me
Me
Me
Me
N
O
N
Cbz
N
H
Boc
II
0.94
4.85
1.71
1.00
0.97
1.99
1.01
1.00
1.01
0.99
15.03
3.05
3.08
2.98
3.01
f1 (ppm)

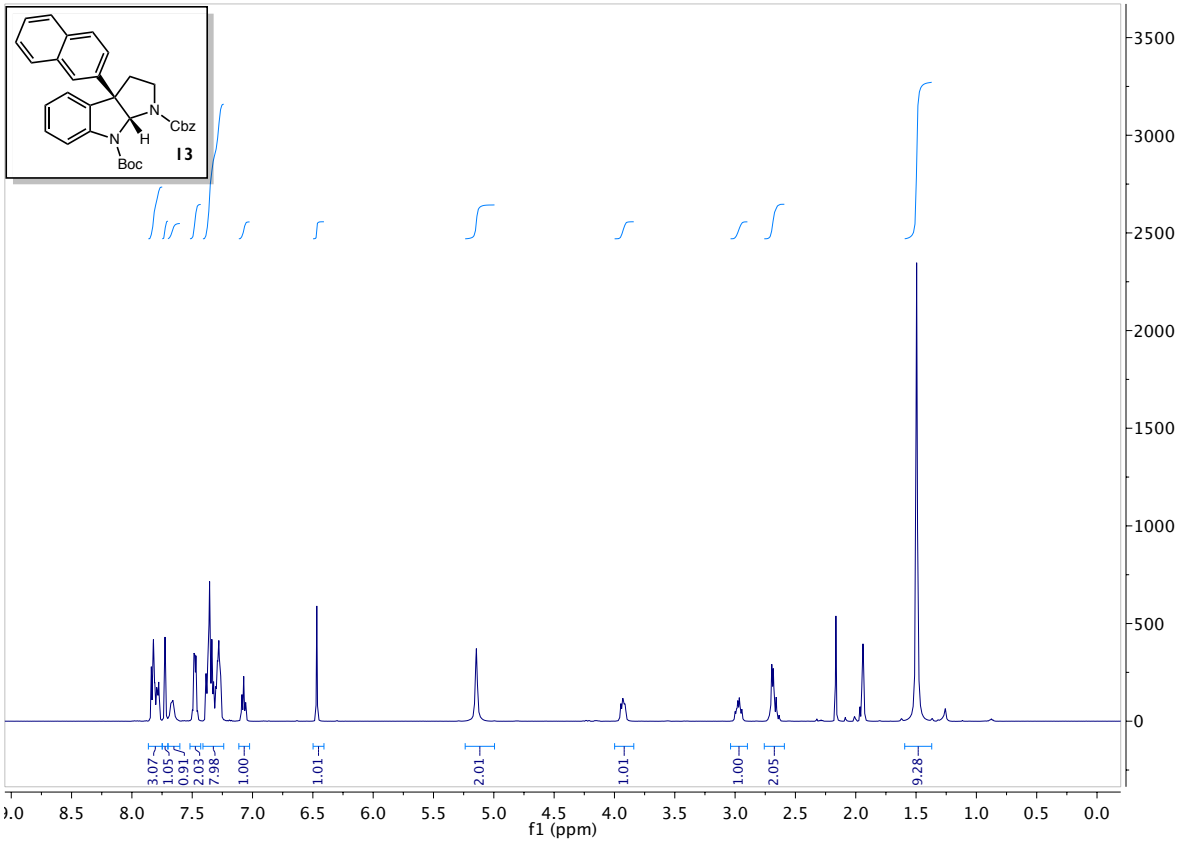

152.74
144.19
137.13
133.36
129.79
128.51
127.93
127.88
125.03
123.43
95.33
81.50
78.32
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.95
60.39
59.53
45.99
40.91
40.51
33.07
28.47
20.73
20.46
17.15
Me
Me
Me
Me
N
O
N
Cbz
N
H
Boc
II
f1 (ppm)

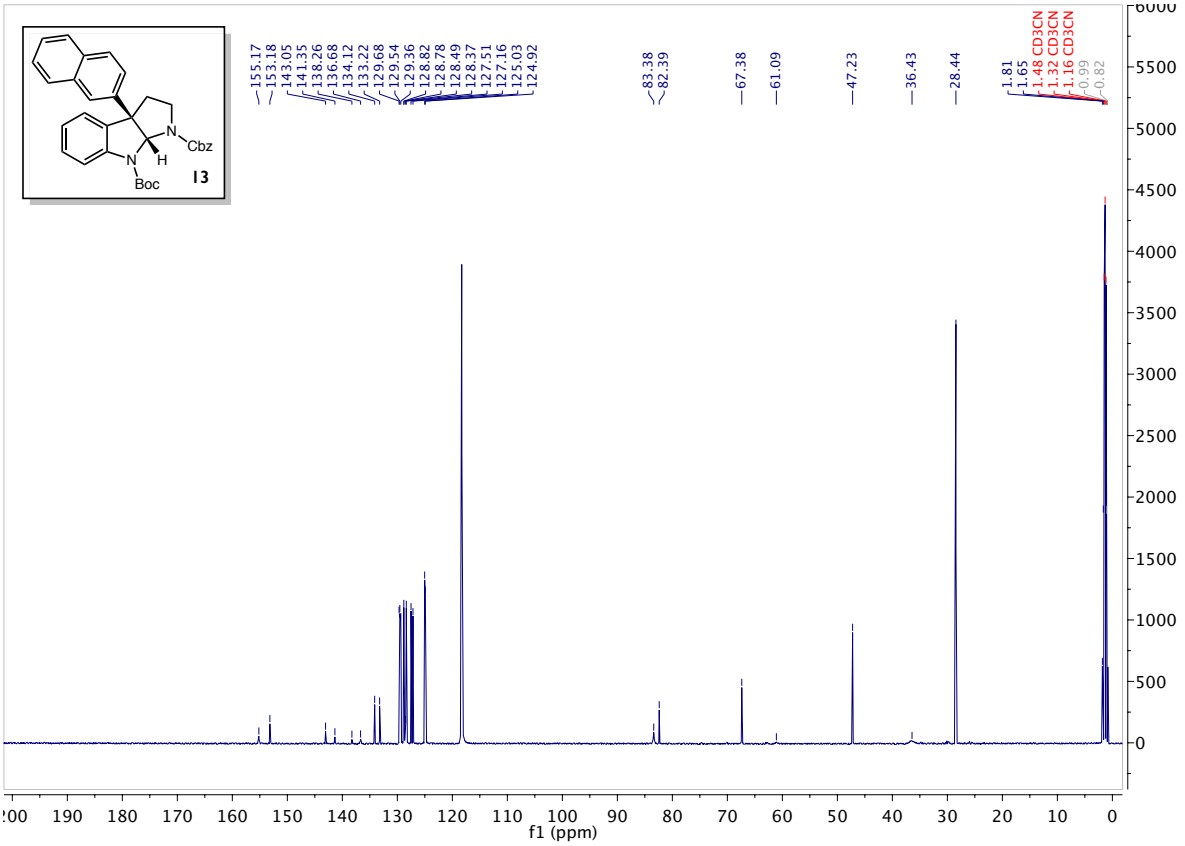

Me
Me
Me
Me
N
O
N
Cbz
N
H
Me
24
4.91
0.97
1.02
1.00
1.00
1.00
2.04
1.01
4.05
1.01
1.00
6.29
6.17
3.08
3.01
f1 (ppm)

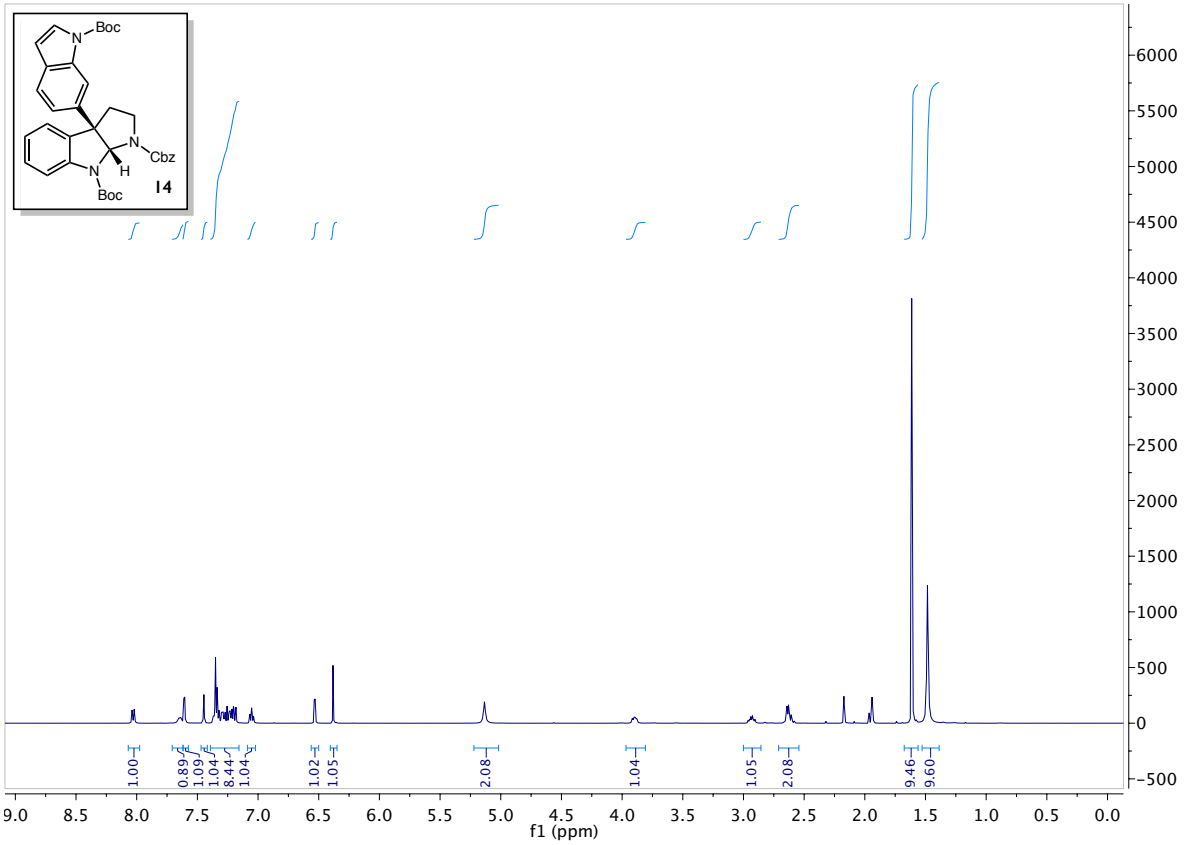

155.21
154.50
152.15
151.95
136.97
136.69
131.22
131.15
129.85
129.82
128.65
128.59
128.46
128.25
128.07
127.92
124.99
124.92
117.41
117.24
106.03
105.94
97.68
96.59
83.89
82.97
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.29
66.98
60.03
59.98
59.40
45.27
45.19
41.50
40.97
40.94
40.92
40.54
40.39
33.64
33.32
33.29
33.04
33.02
32.64
20.79
20.73
20.50
20.49
17.17
Me
Me
Me
Me
N
O
N
Cbz
N
H
Me
24
f1 (ppm)

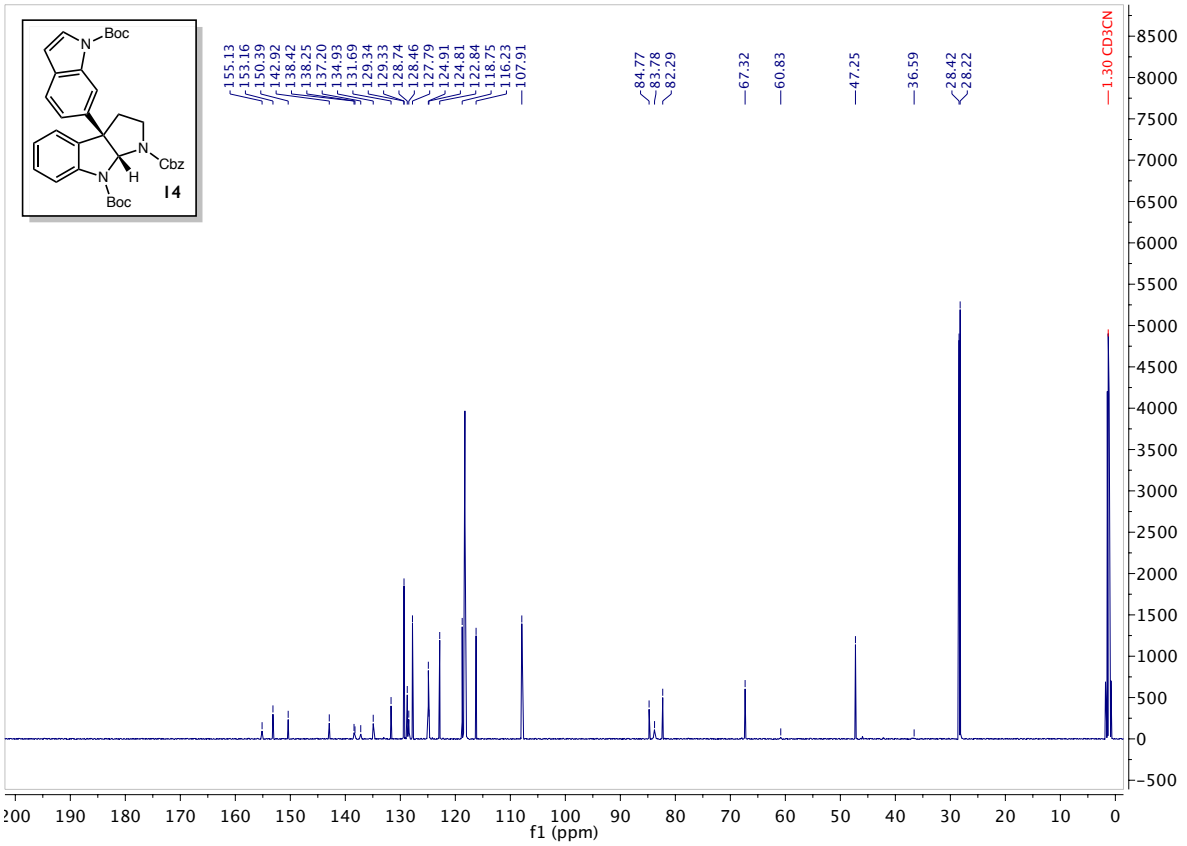

Ph
Cbz
N
H
N
Boc
I2
0.92
12.34
1.13
1.00
0.96
1.01
1.98
1.02
1.04
2.33
9.30
f1 (ppm)


Ph
Cbz
N
H
N
Boc
I2
155.17
153.30
143.56
138.30
137.53
134.86
132.20
130.78
129.60
129.52
129.37
128.77
128.68
128.48
127.24
125.20
124.73
117.83
82.14
82.14
67.31
59.50
47.14
36.13
28.41
1.81
1.65
1.48 CD3CN
1.32 CD3CN
1.15 CD3CN
0.99
0.82
f1 (ppm)


Cbz
N
H
N
Boc
13
3.07
1.05
0.91
2.03
7.98
1.00
1.01
2.01
1.01
1.00
2.05
9.28
f1 (ppm)


Cbz
N
H
N
Boc
13
155.17
153.18
143.05
141.35
138.26
136.68
134.12
133.22
129.68
129.54
129.36
128.82
128.78
128.49
128.37
127.51
127.16
125.03
124.92
83.38
82.39
67.38
61.09
47.23
36.43
28.44
1.81
1.65
1.48 CD3CN
1.32 CD3CN
1.16 CD3CN
0.99
0.82
f1 (ppm)


Boc
Cbz
H
Boc
14
1.00
0.89
1.09
1.04
8.44
1.04
1.02
1.05
2.08
1.04
1.05
2.08
9.46
9.60
f1 (ppm)


Boc
Cbz
H
Boc
14
155.13
153.16
150.39
142.92
138.42
138.25
137.20
134.93
131.69
129.34
129.33
128.74
128.46
127.79
124.91
124.81
122.84
118.75
116.23
107.91
84.77
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82.29
67.32
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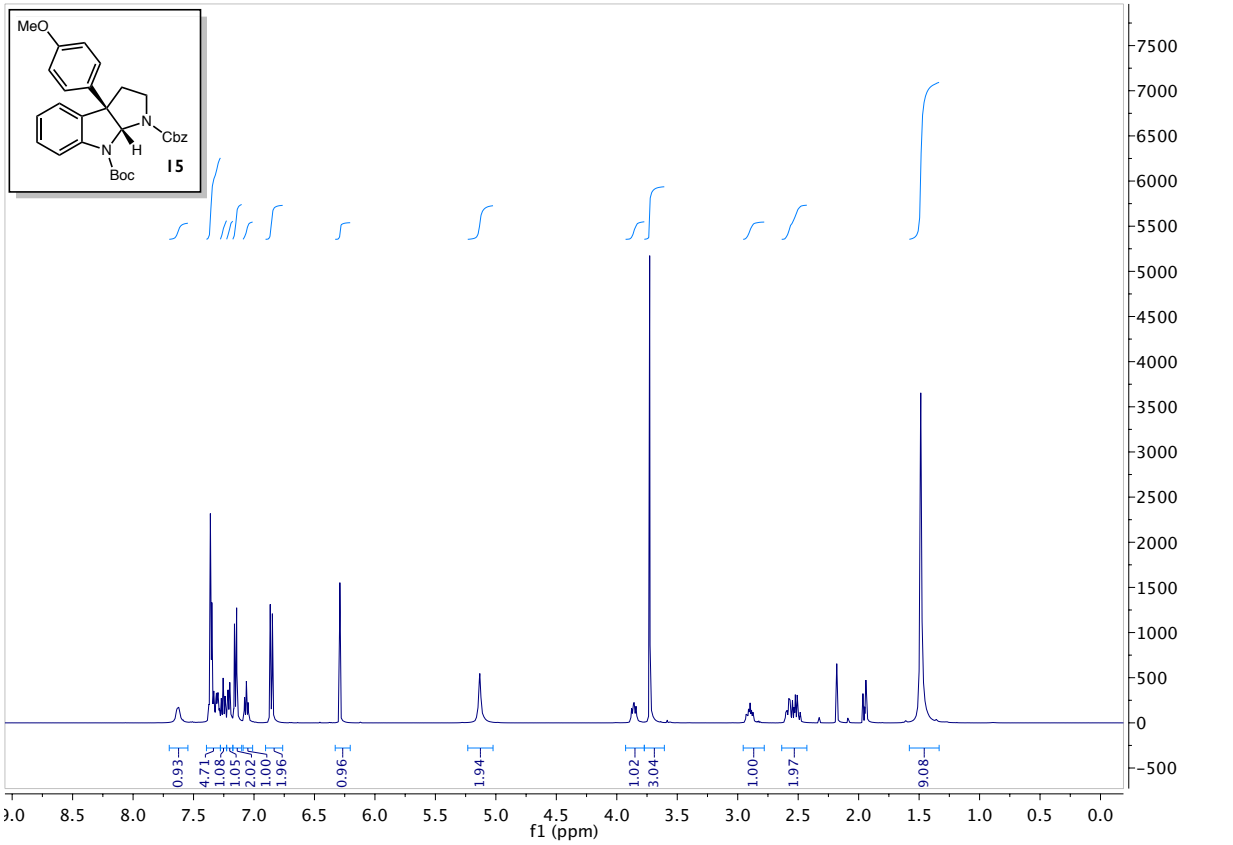
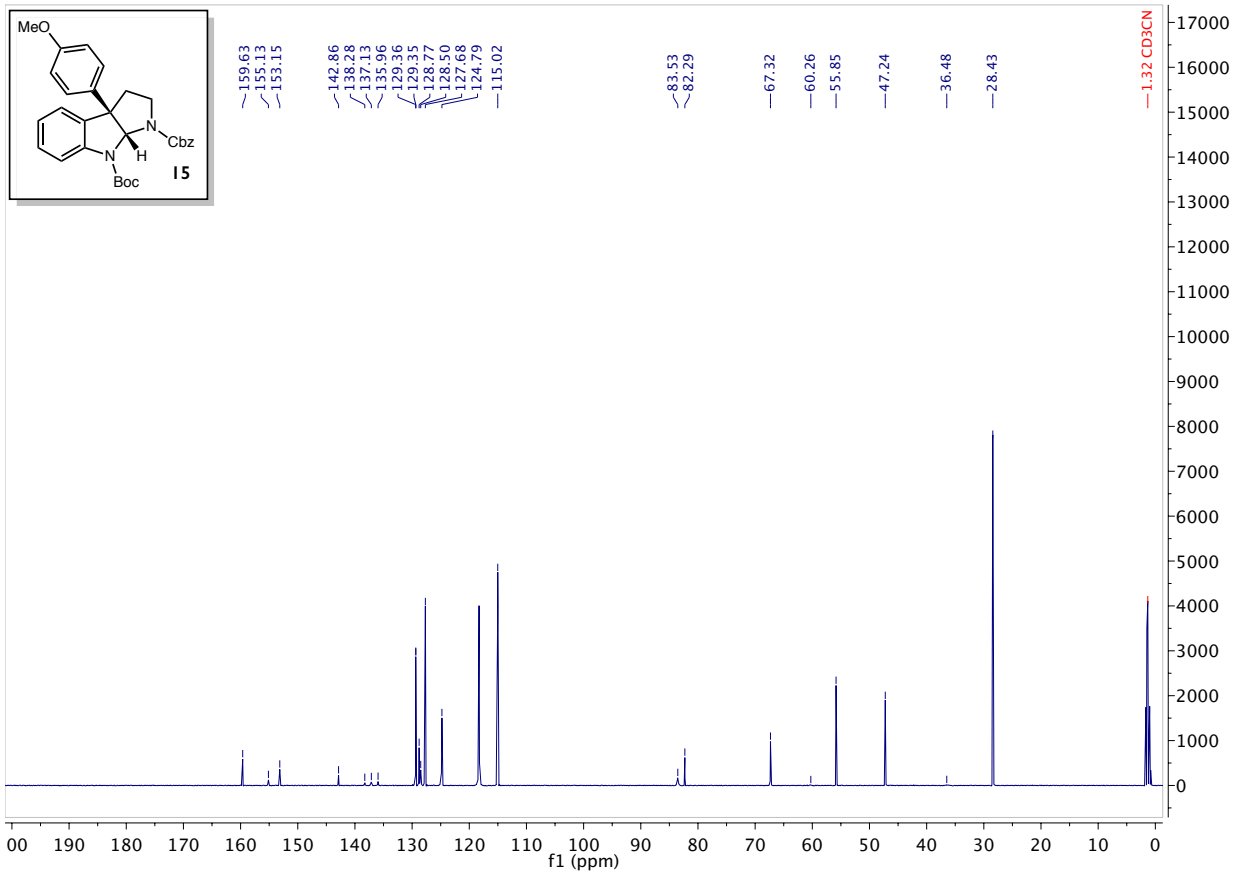
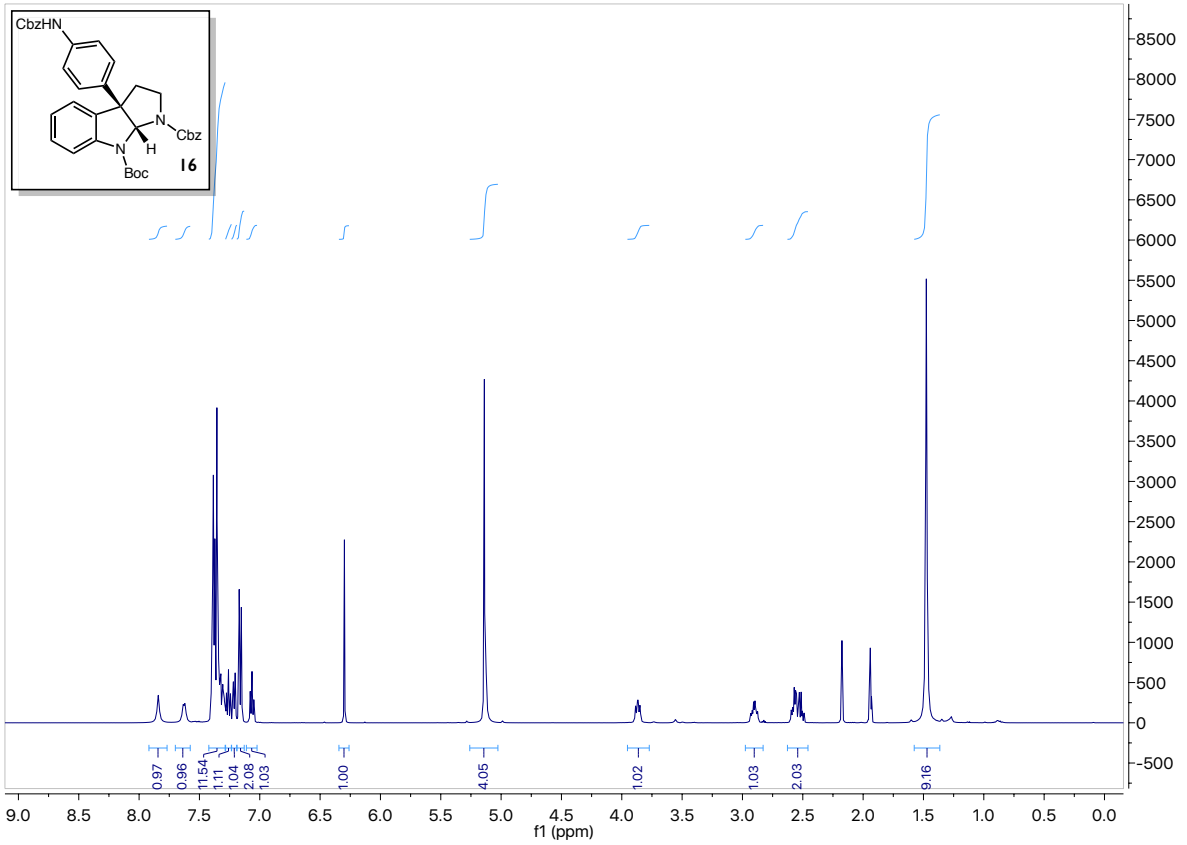
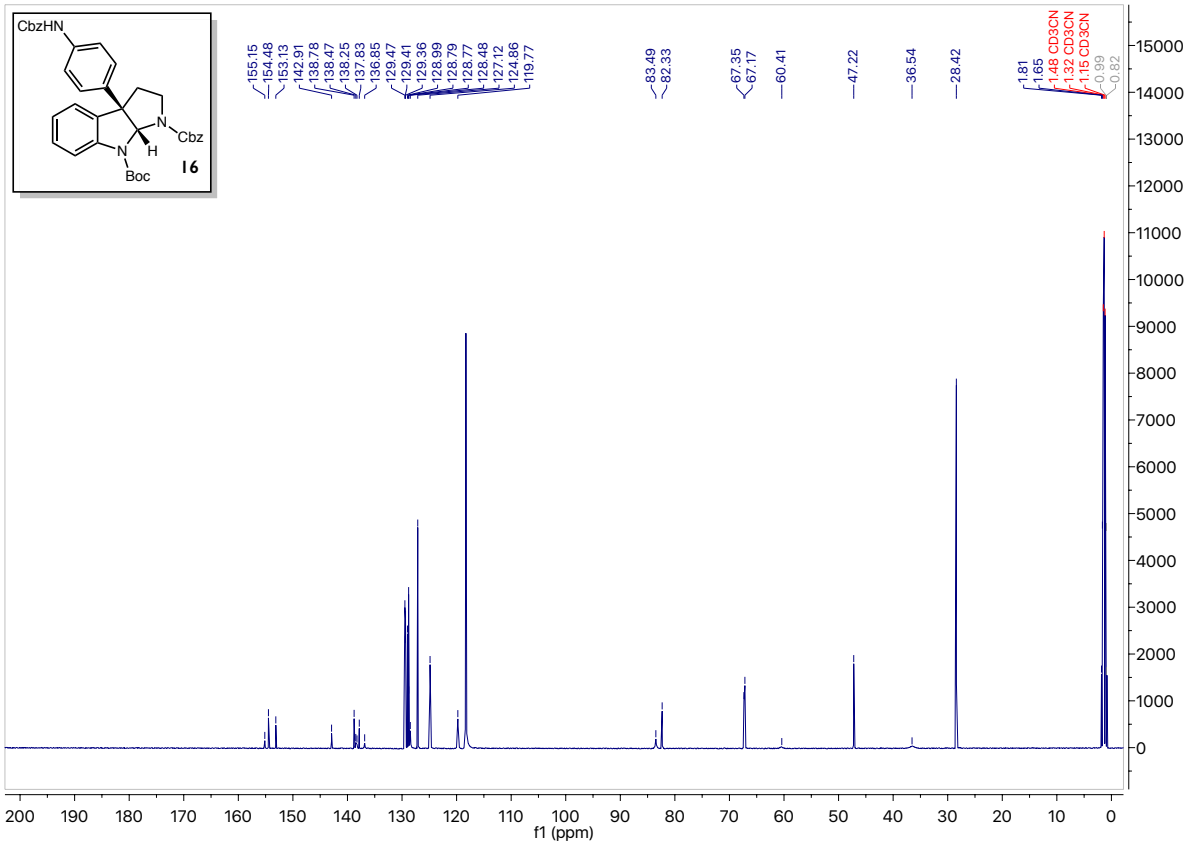
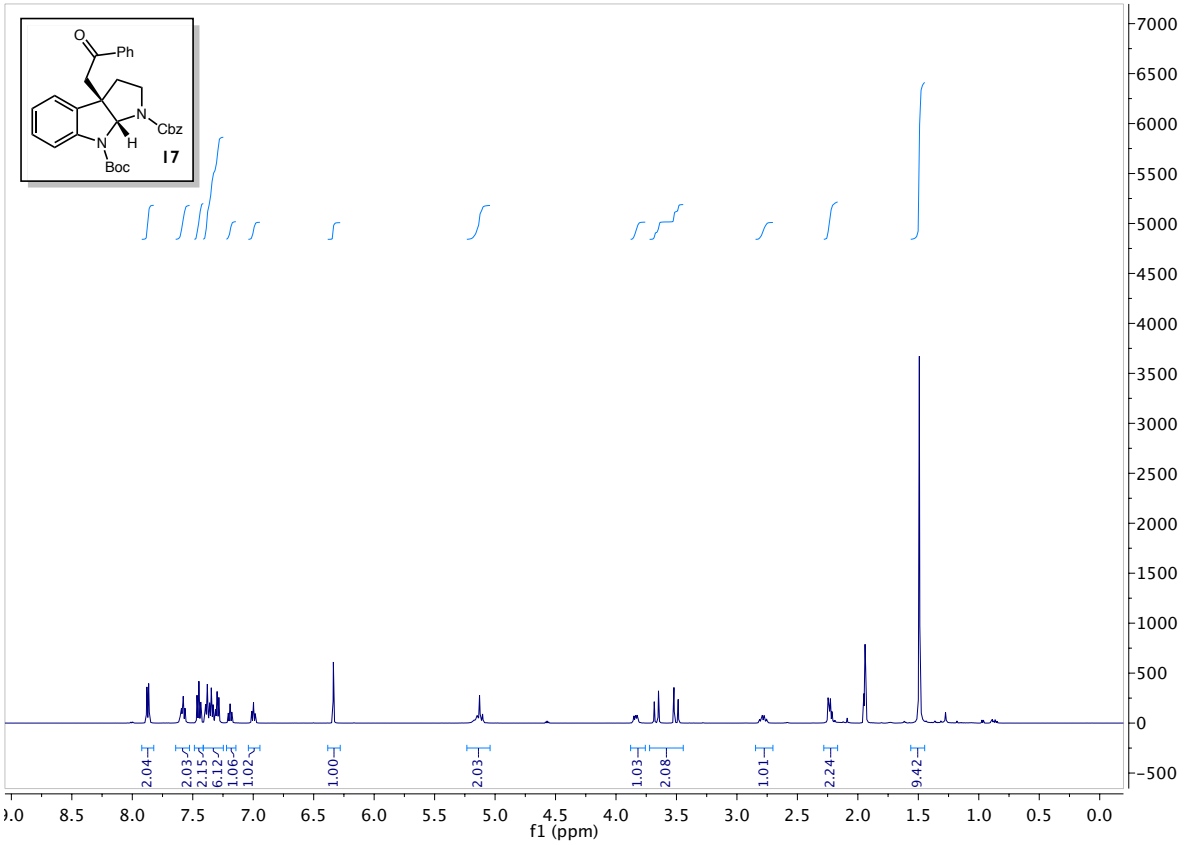
36.59
28.42
28.22
1.30 CD3CN
f1 (ppm)

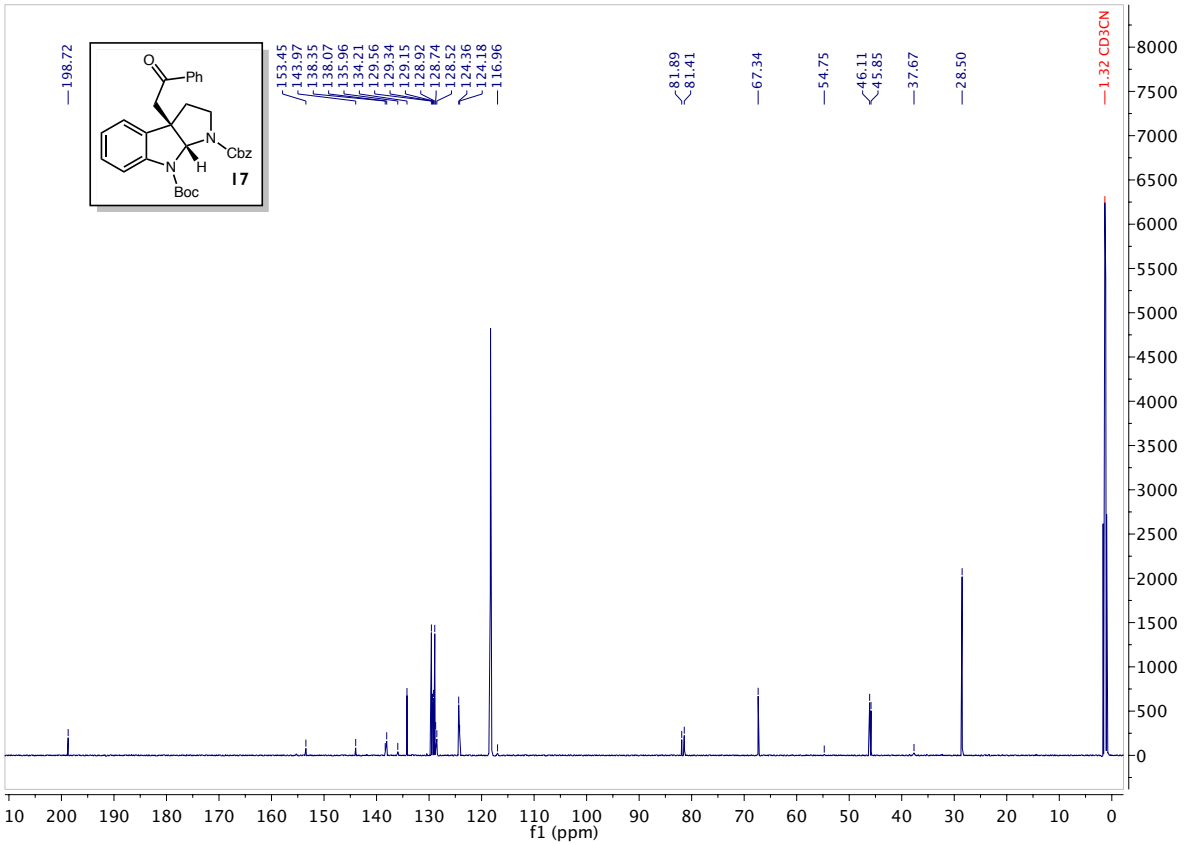

MeO
N
Cbz
H
N
Boc
15
0.93
4.71
1.08
1.05
2.02
1.00
1.96
0.96
1.94
1.02
3.04
1.00
1.97
9.08
f1 (ppm)

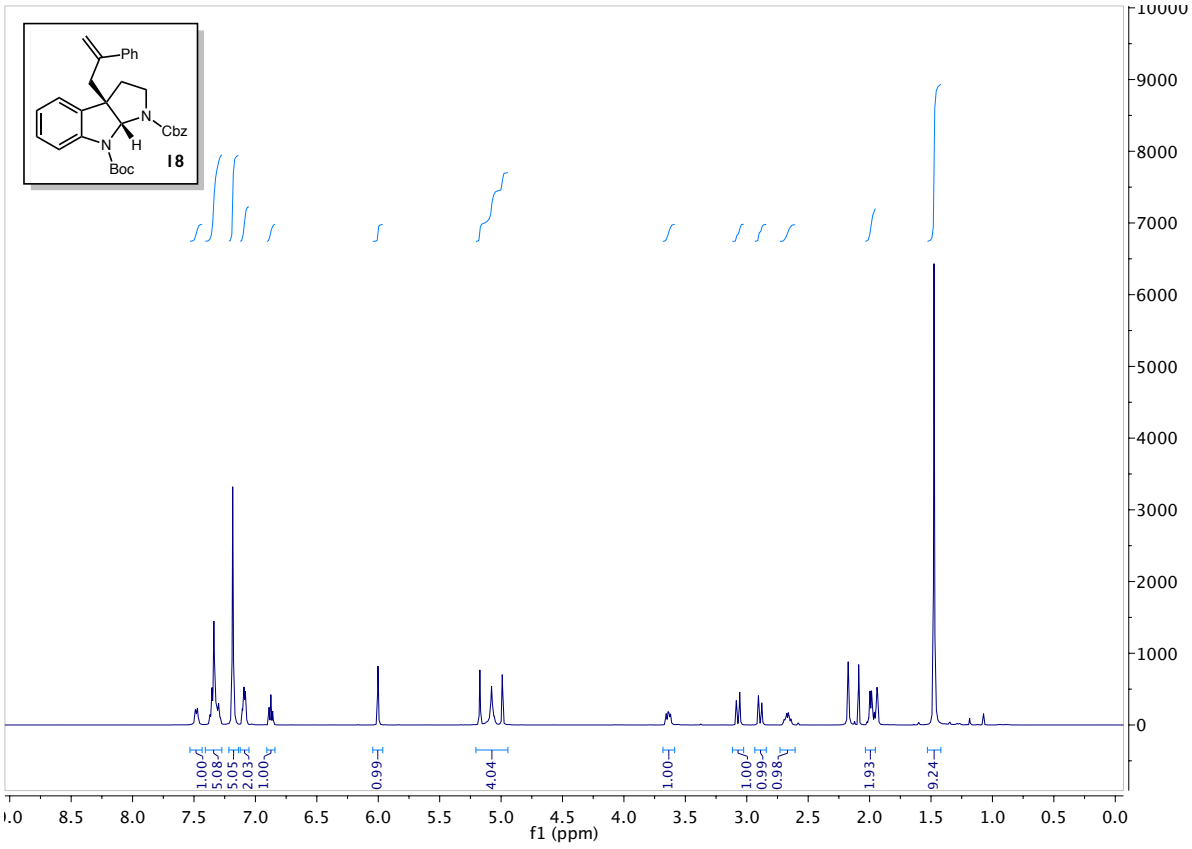

MeO
N
Cbz
H
N
Boc
15
159.63
155.13
153.15
142.86
138.28
137.13
135.96
129.36
129.35
128.77
128.50
127.68
124.79
115.02
83.53
82.29
67.32
60.26
55.85
47.24
36.48
28.43
1.32 CD3CN
f1 (ppm)

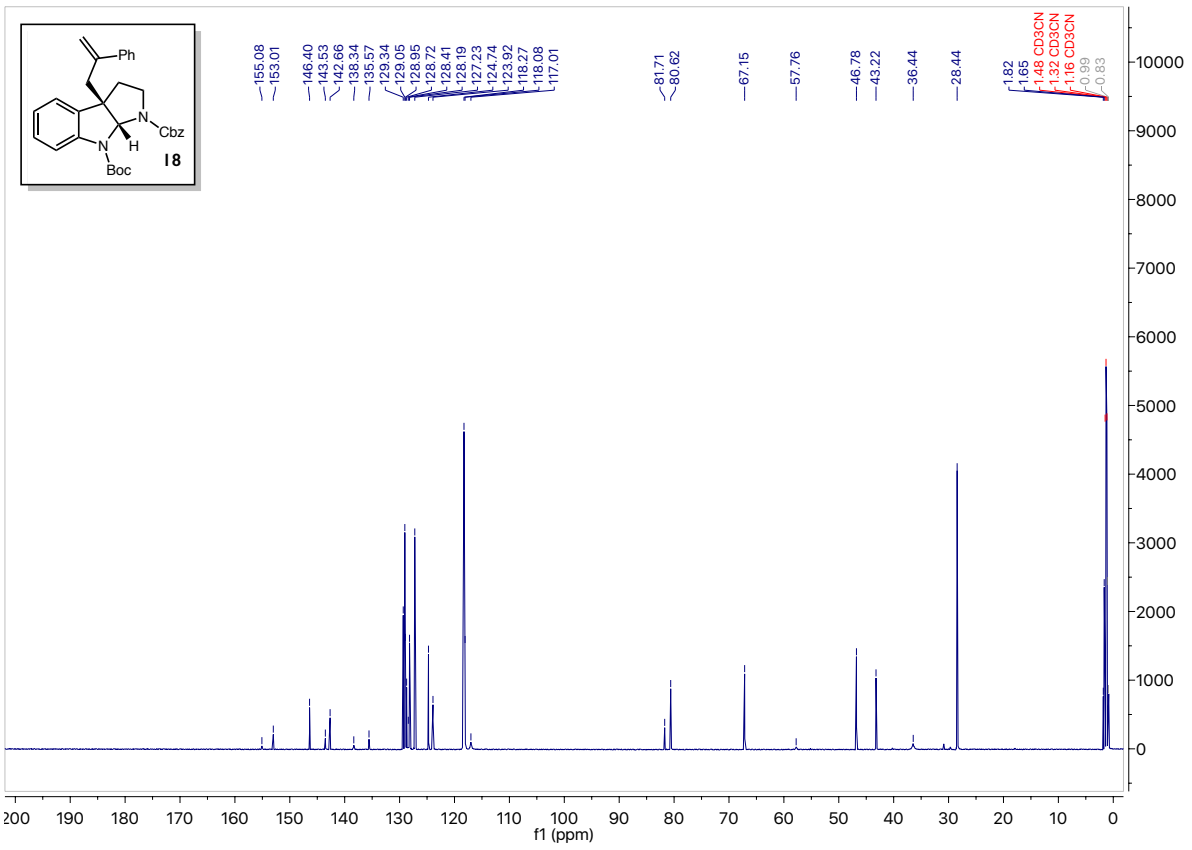

CbzHN
N
Cbz
N
H
Boc
16
0.97
0.96
11.54
1.11
1.04
2.08
1.03
1.00
4.05
1.02
1.03
2.03
9.16
f1 (ppm)

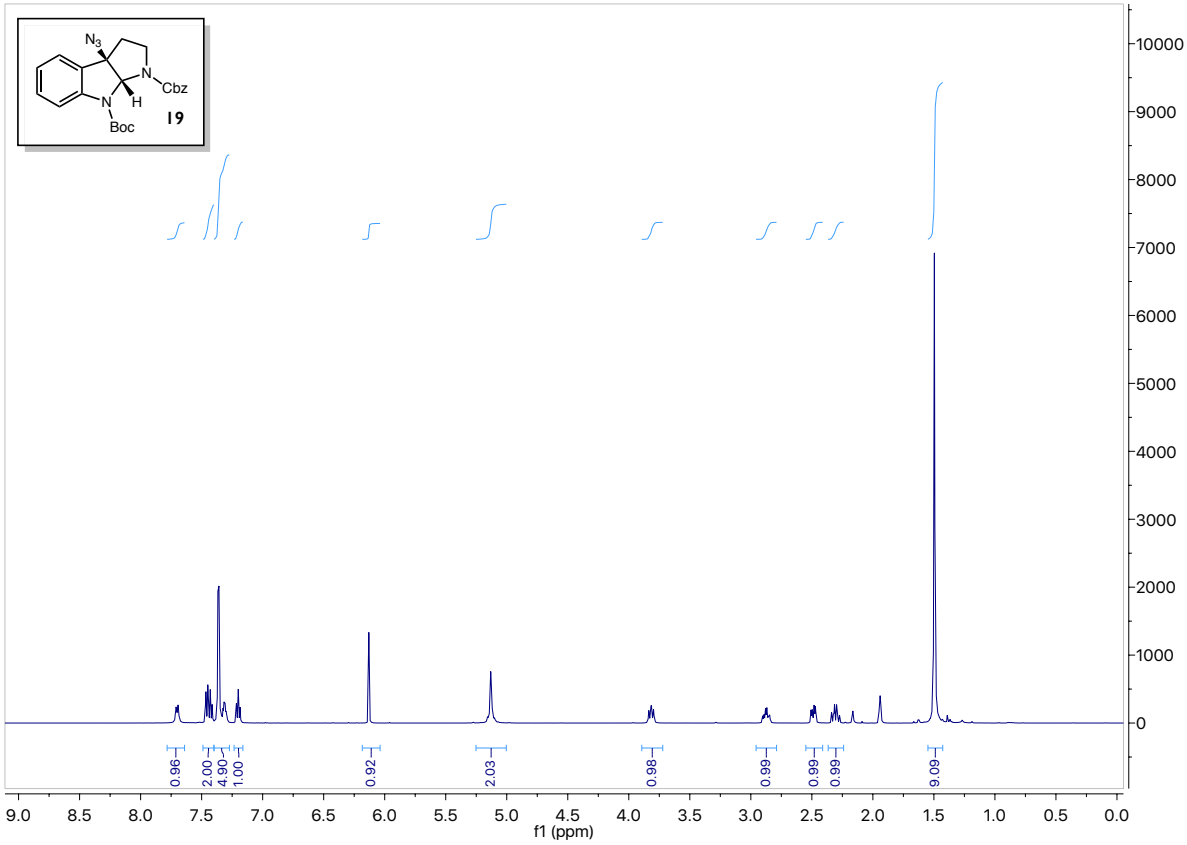

CbzHN
N
Cbz
N
H
Boc
16
155.15
154.48
153.13
142.91
138.78
138.47
138.25
137.83
136.85
129.47
129.41
129.36
128.99
128.79
128.77
128.48
127.12
124.86
119.77
83.49
82.33
67.35
67.17
60.41
47.22
36.54
28.42
1.81
1.65
1.48 CD3CN
1.32 CD3CN
1.15 CD3CN
0.99
0.82
f1 (ppm)

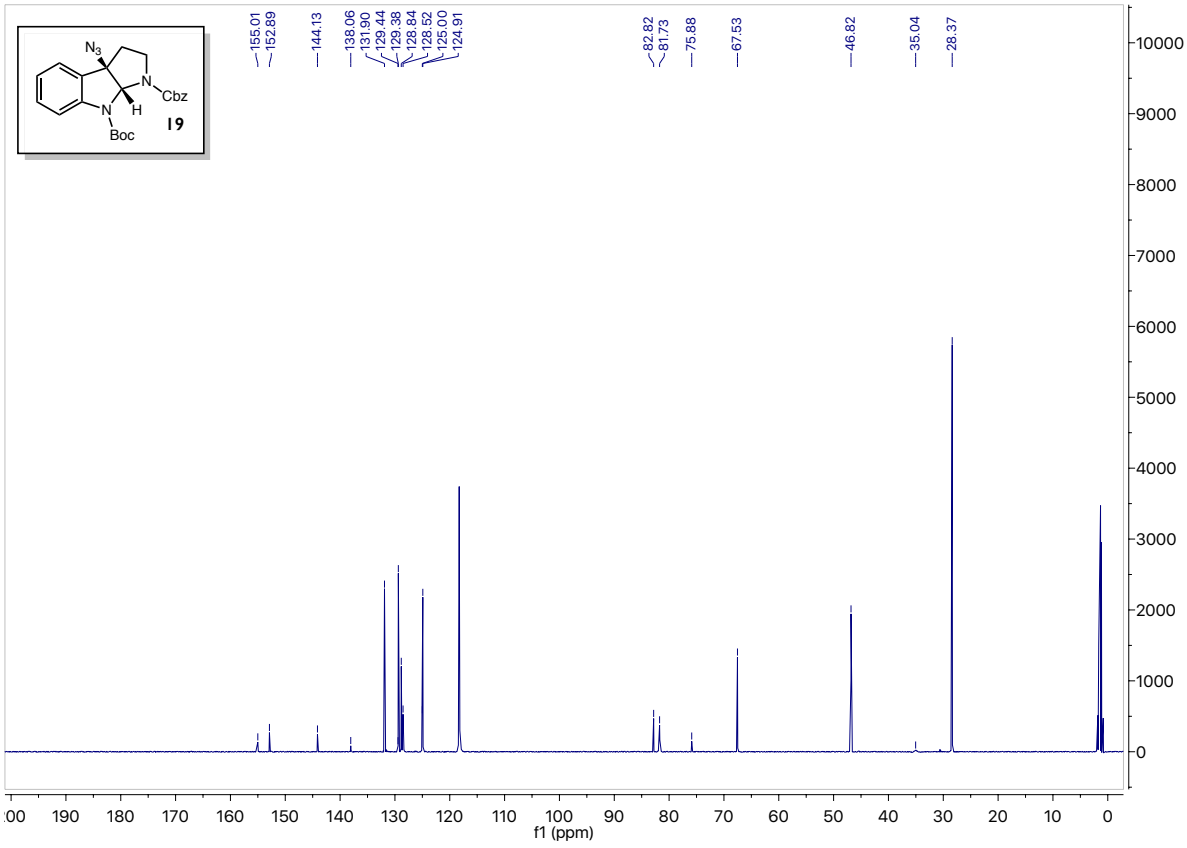

O
Ph
N
Cbz
H
N
Boc
17
2.04
2.03
2.15
6.12
1.06
1.02
1.00
2.03
1.03
2.08
1.01
2.24
9.42
f1 (ppm)

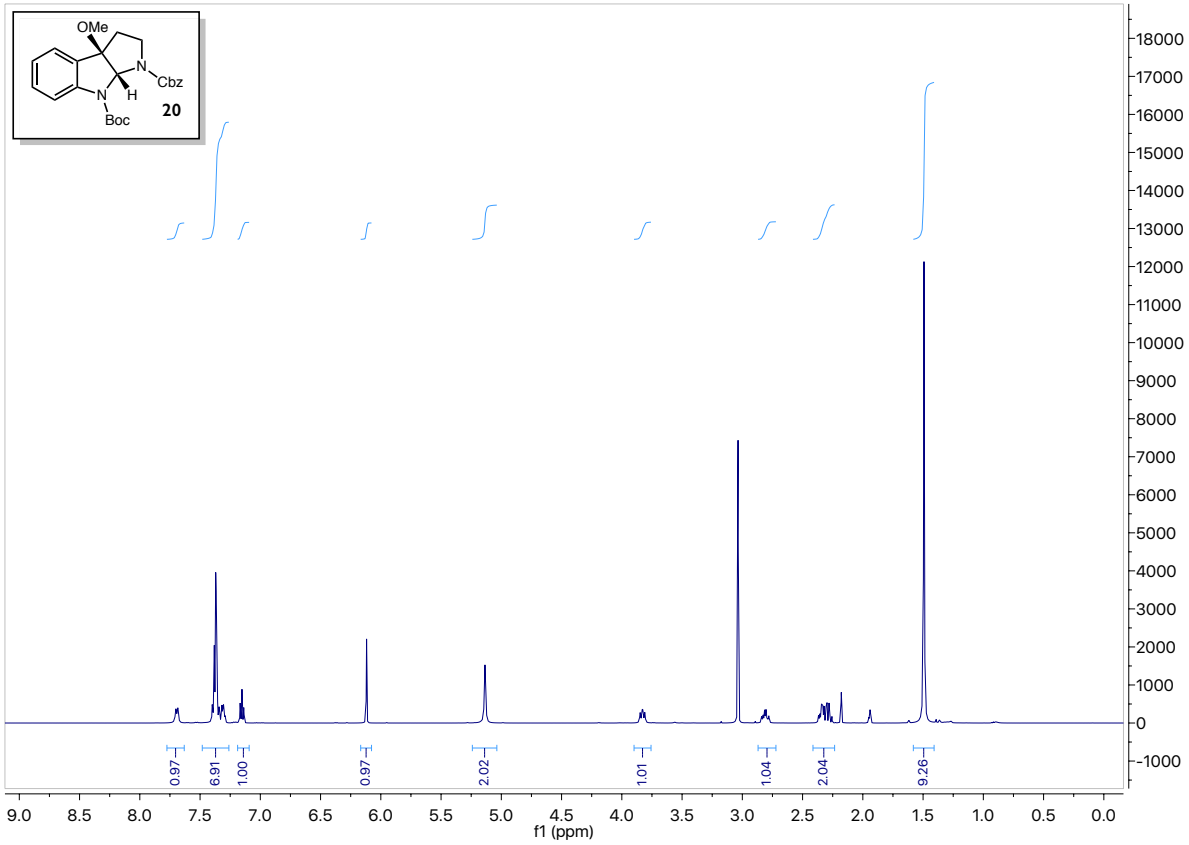

198.72
153.45
143.97
138.35
138.07
135.96
134.21
129.56
129.34
129.15
128.92
128.74
128.52
124.36
124.18
116.96
81.89
81.41
67.34
54.75
46.11
45.85
37.67
28.50
1.32 CD3CN
O
Ph
N
Cbz
H
N
Boc
17
f1 (ppm)

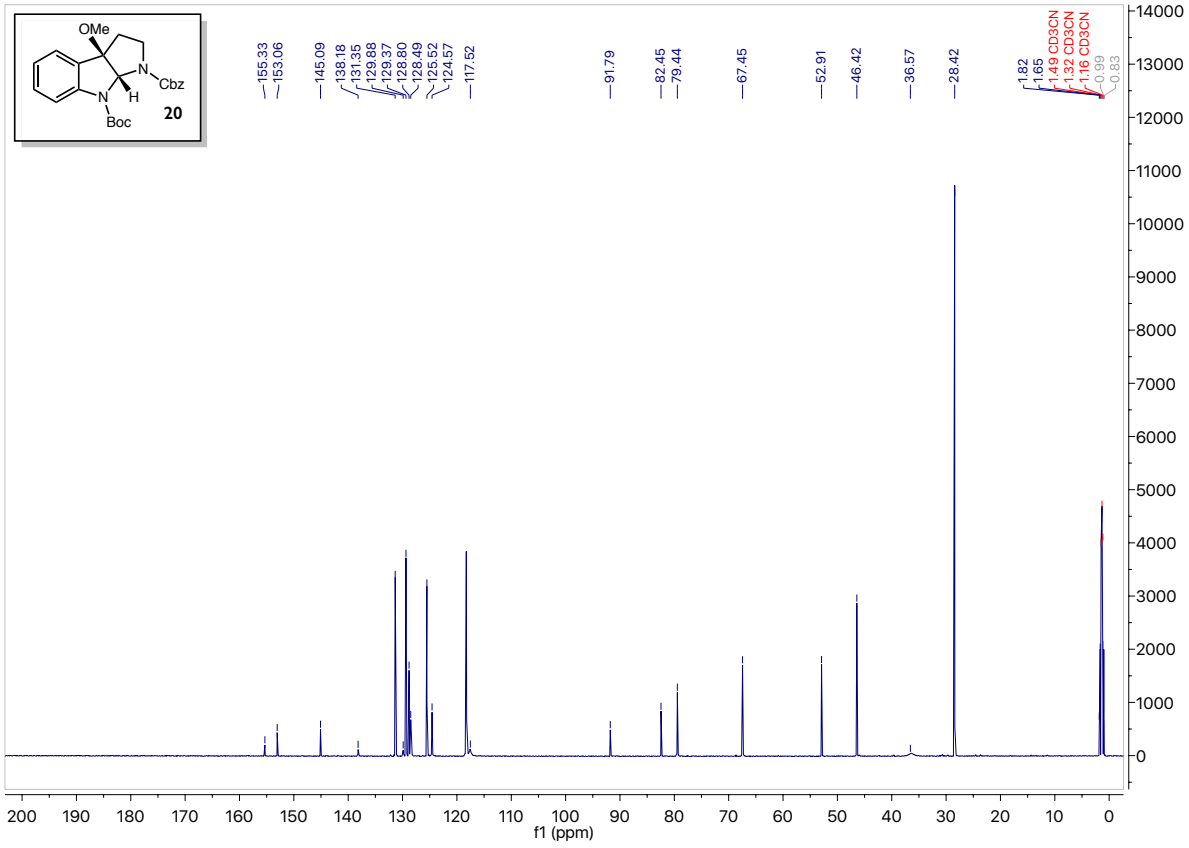

Ph
Cbz
N
H
Boc
18
1.00
5.08
5.05
2.03
1.00
0.99
4.04
1.00
1.00
0.99
0.98
1.93
9.24
f1 (ppm)

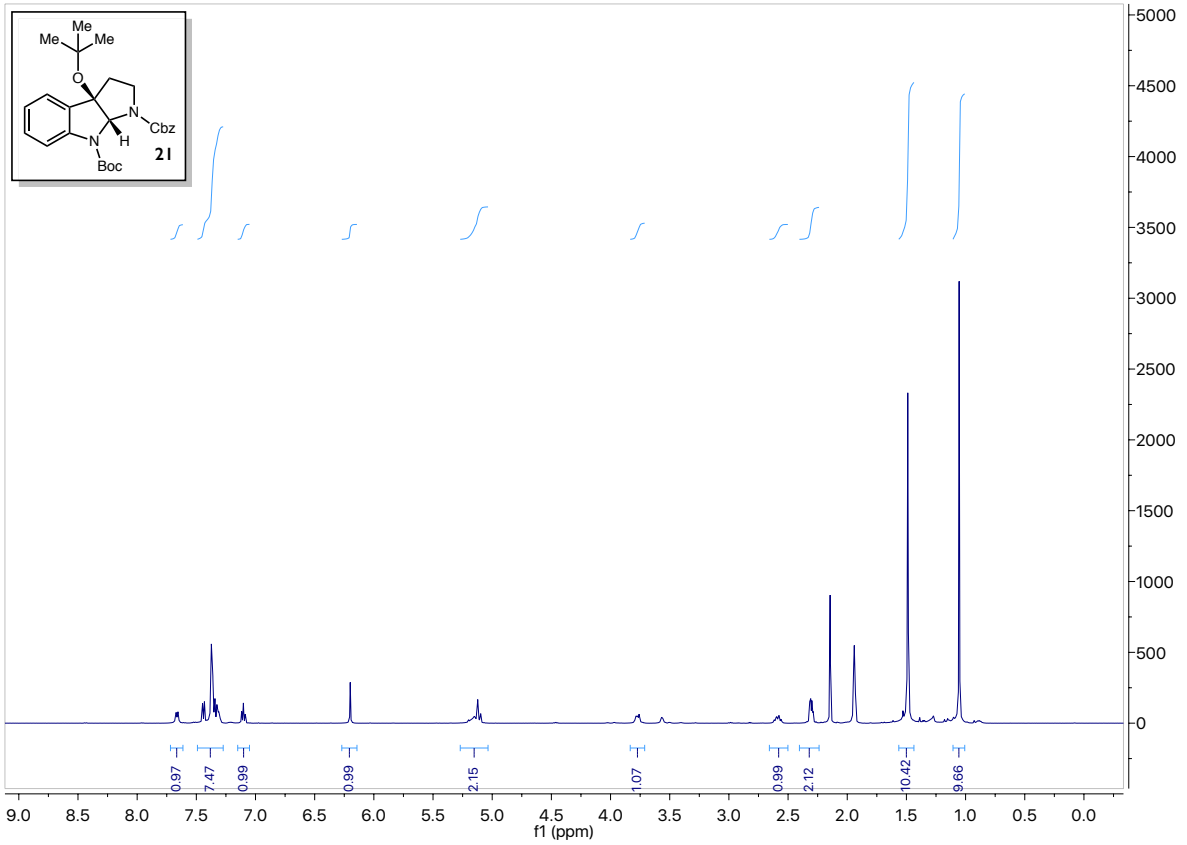

Ph
Cbz
N
H
Boc
18
155.08
153.01
146.40
143.53
142.66
138.34
135.57
129.34
129.05
128.95
128.72
128.41
128.19
127.23
124.74
123.92
118.27
118.08
117.01
81.71
80.62
67.15
57.76
46.78
43.22
36.44
28.44
1.82
1.65
1.48 CD3CN
1.32 CD3CN
1.16 CD3CN
0.99
0.83
f1 (ppm)

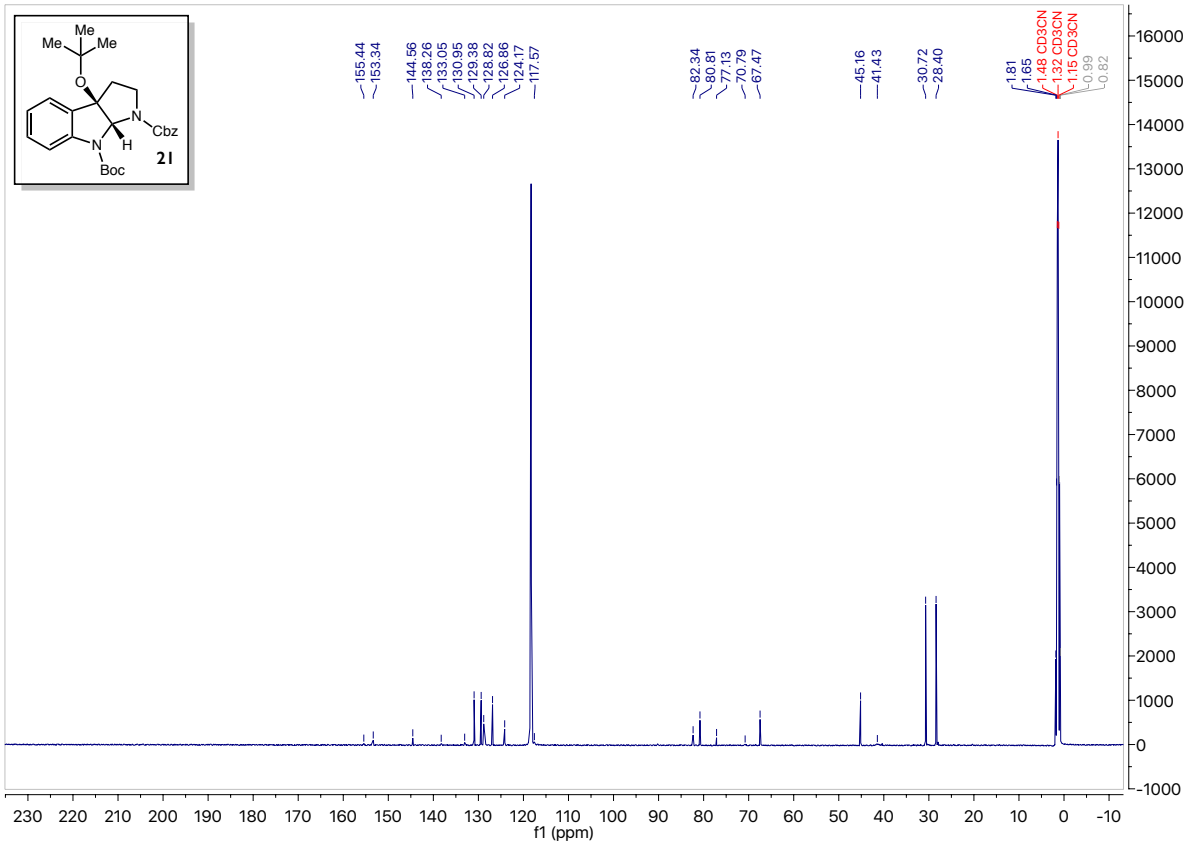

N3
N
Cbz
H
N
Boc
19
0.96
2.00
4.90
1.00
0.92
2.03
0.98
0.99
0.99
0.99
9.09
f1 (ppm)

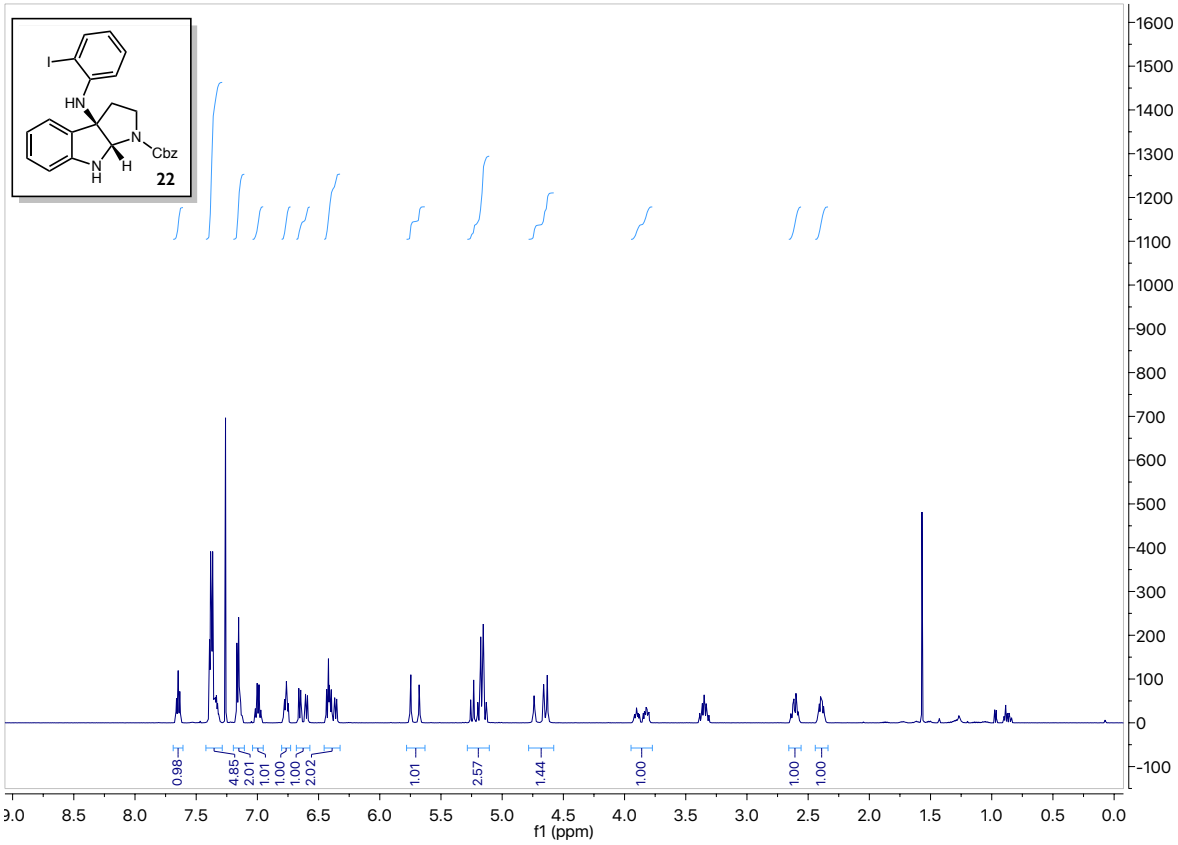

N3
N
Cbz
H
N
Boc
19
155.01
152.89
144.13
138.06
131.90
129.44
129.38
128.84
128.52
125.00
124.91
82.82
81.73
75.88
67.53
46.82
35.04
28.37
f1 (ppm)

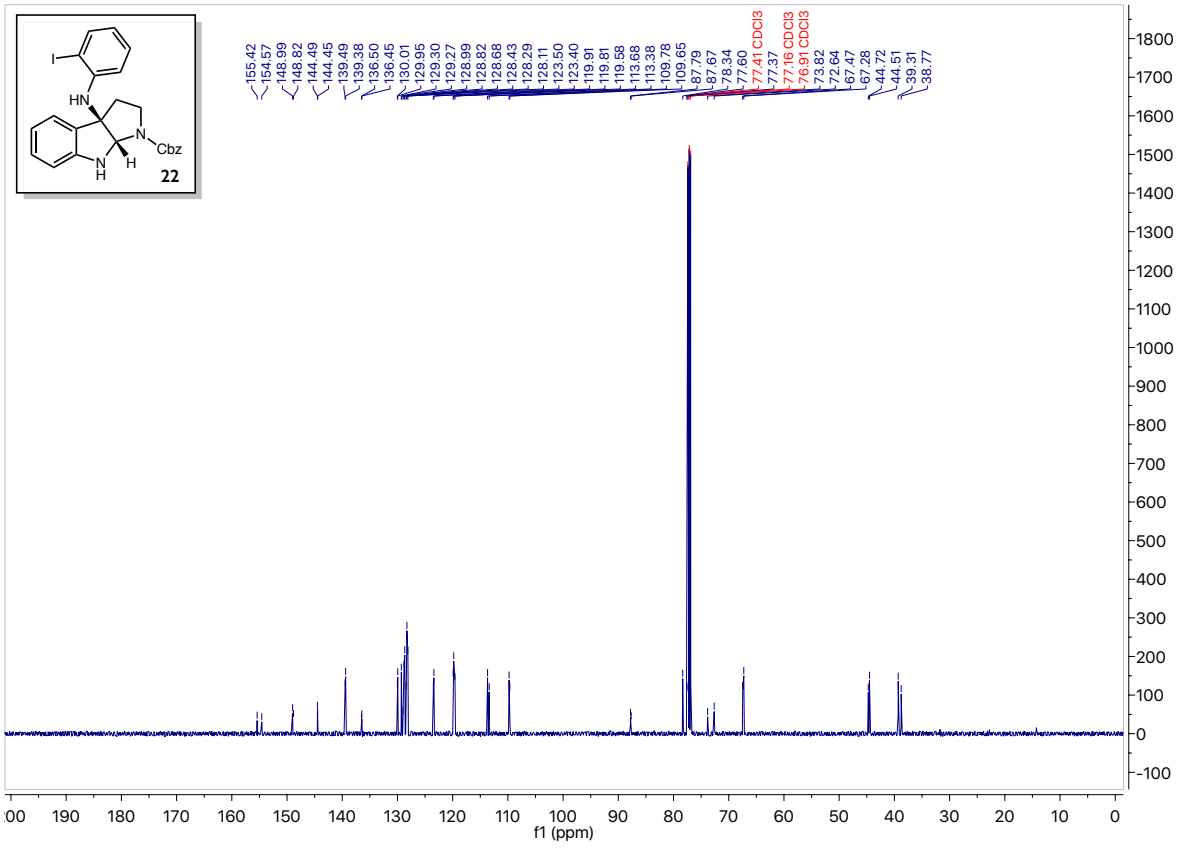

OMe
Cbz
N
H
N
Boc
20
0.97
6.91
1.00
0.97
2.02
1.01
1.04
2.04
9.26
f1 (ppm)

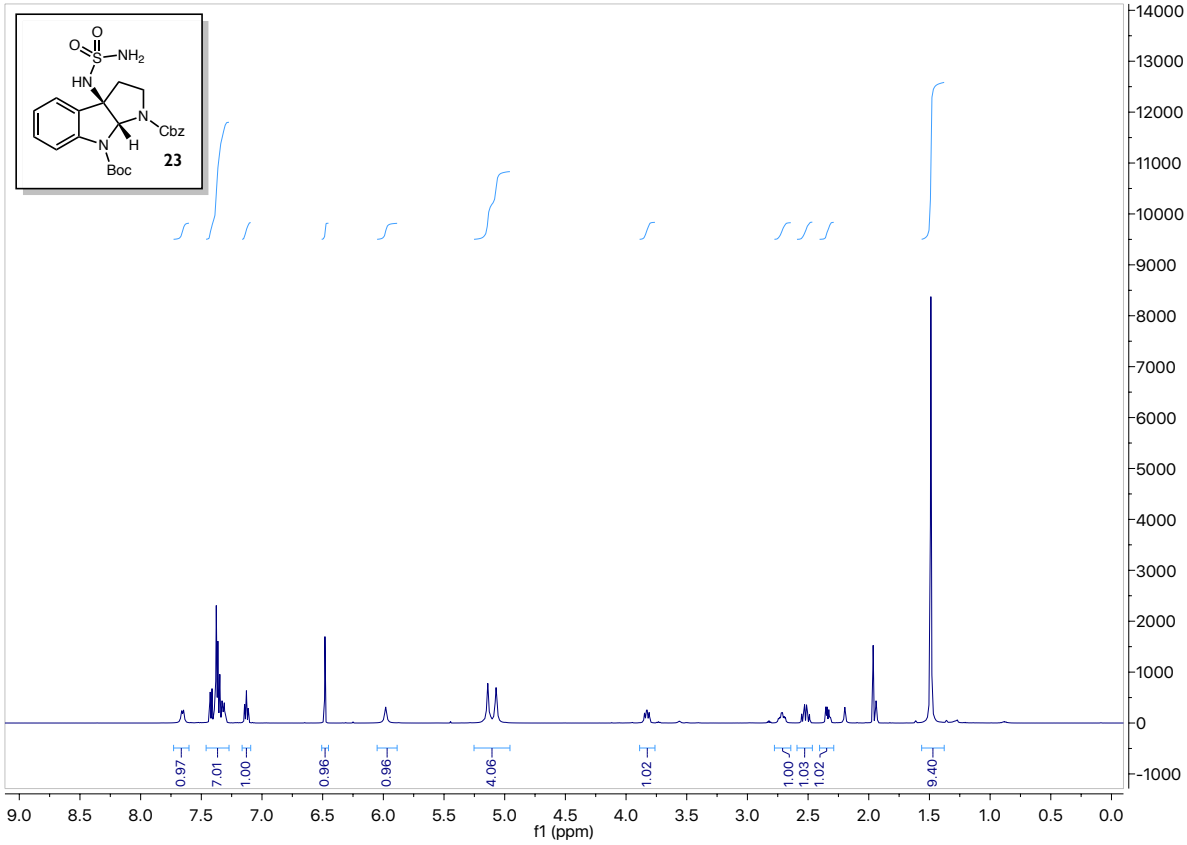

OMe
Cbz
N
H
N
Boc
20
155.33
153.06
145.09
138.18
131.35
129.88
129.37
128.80
128.49
125.52
124.57
117.52
91.79
82.45
79.44
67.45
52.91
46.42
36.57
28.42
1.82
1.65
1.49 CD3CN
1.32 CD3CN
1.16 CD3CN
0.99
0.83
f1 (ppm)

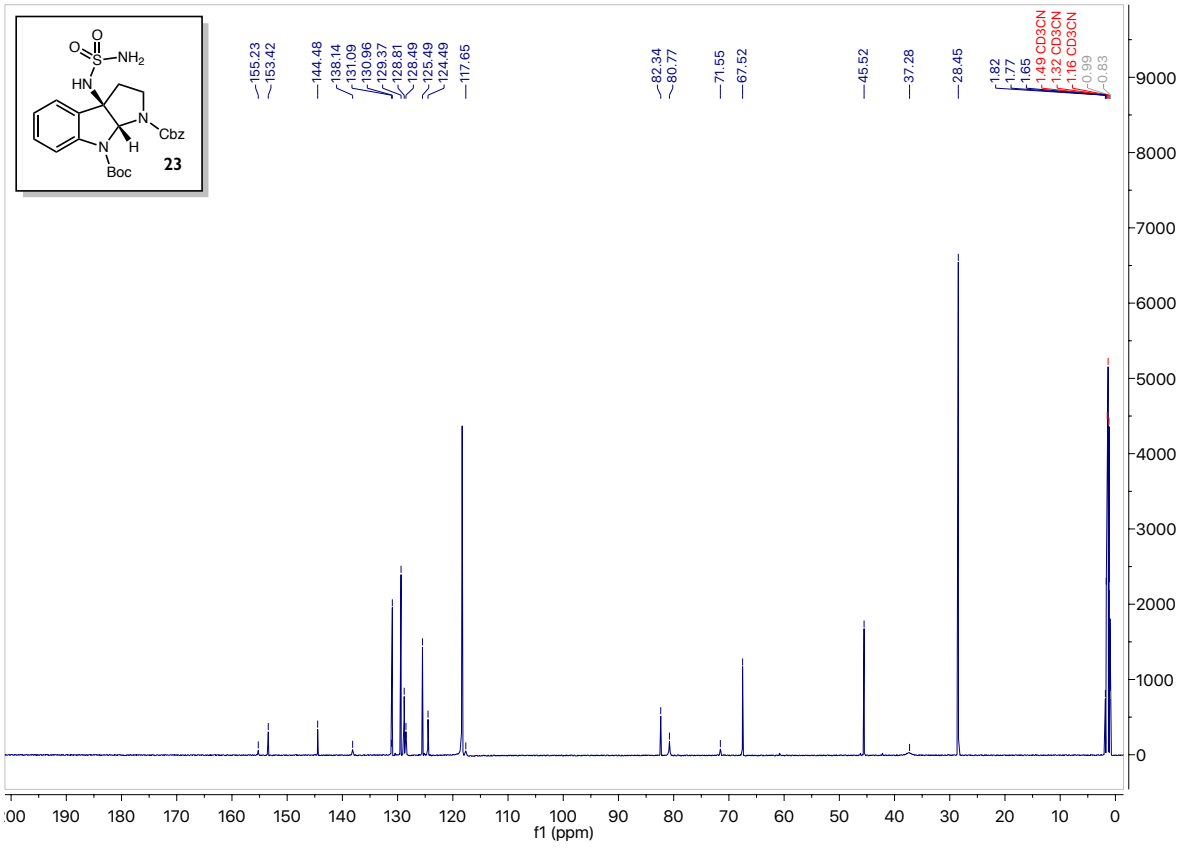

Me
Me
Me
O
N
Cbz
N
H
Boc
2l
0.97
7.47
0.99
0.99
2.15
1.07
0.99
2.12
10.42
9.66
f1 (ppm)

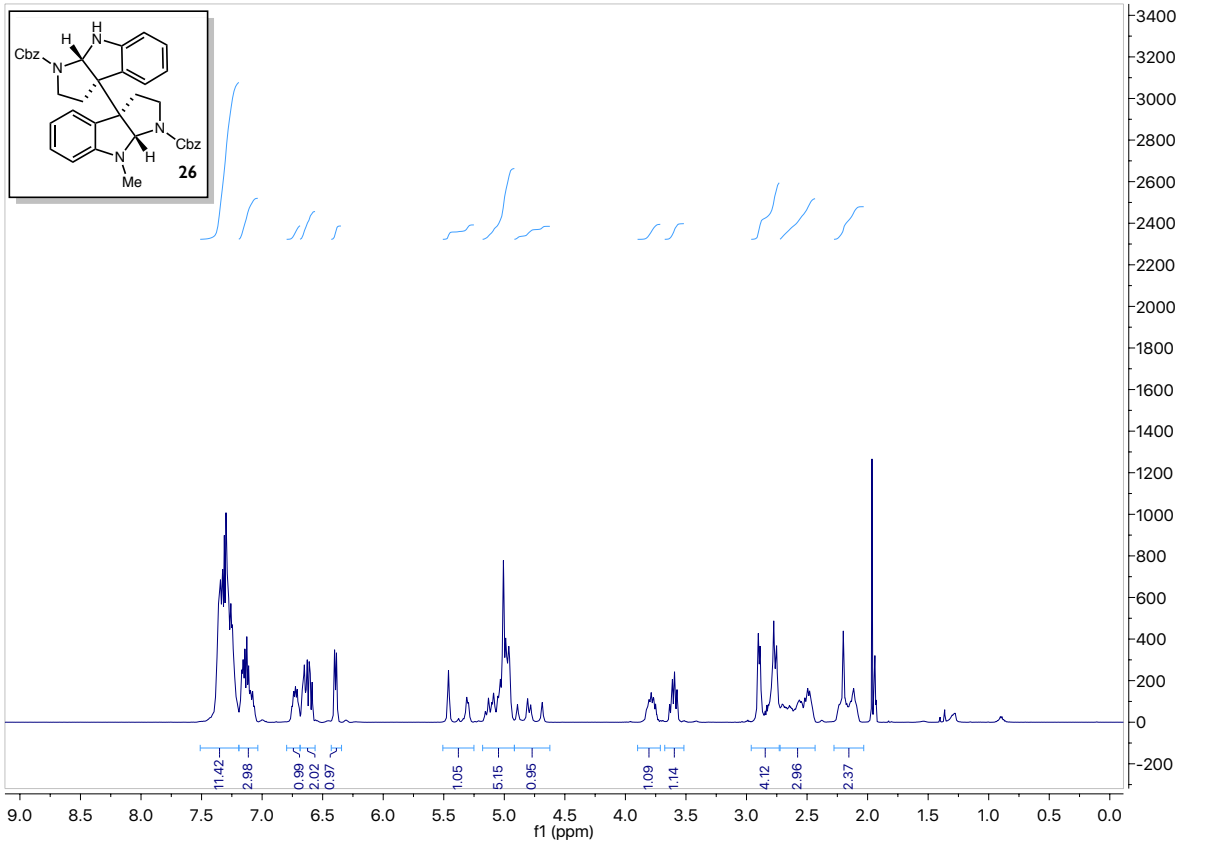

Me
Me
Me
O
N
Cbz
N
H
Boc
2l
155.44
153.34
144.56
138.26
133.05
130.95
129.38
128.82
126.86
124.17
117.57
82.34
80.81
77.13
70.79
67.47
45.16
41.43
30.72
28.40
1.81
1.65
1.48 CD3CN
1.32 CD3CN
1.15 CD3CN
0.99
0.82
f1 (ppm)

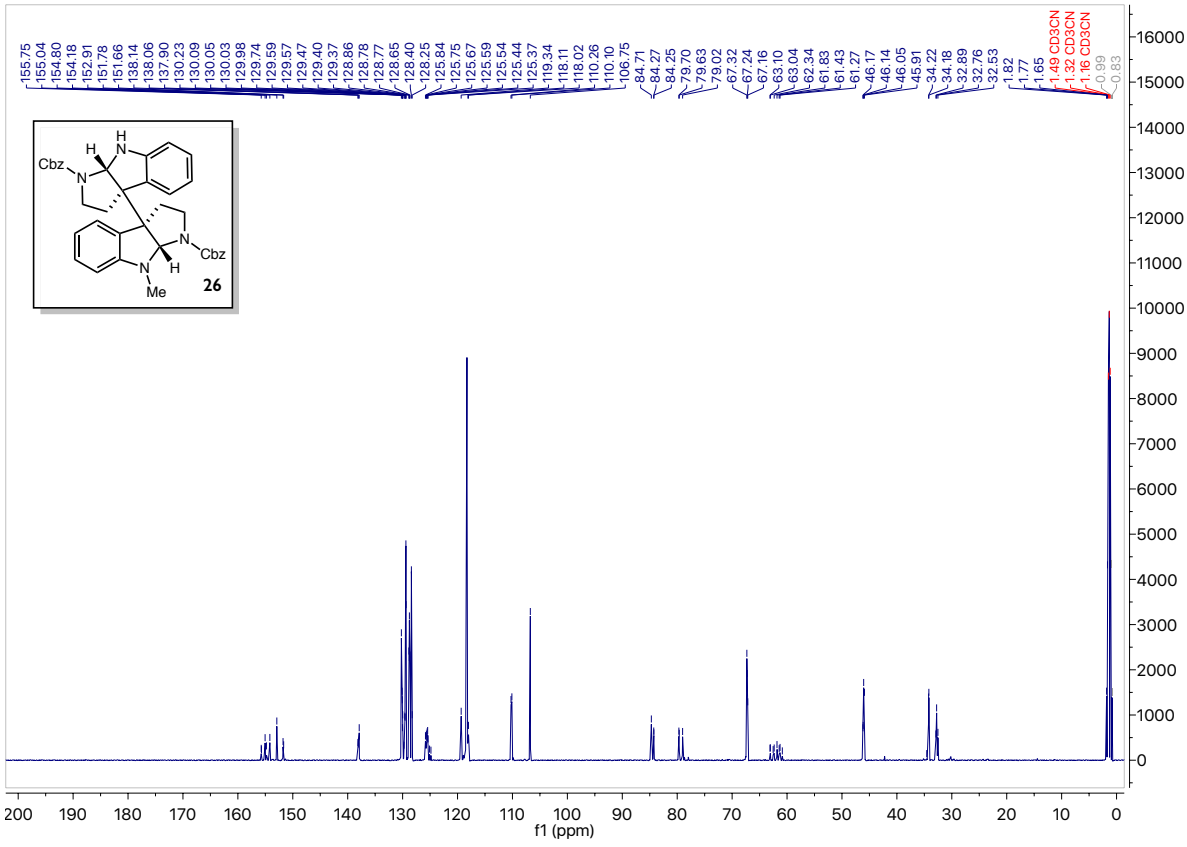

I
HN
N
Cbz
N
H
H
22
0.98
4.85
2.01
1.01
1.00
1.00
2.02
1.01
2.57
1.44
1.00
1.00
1.00
f1 (ppm)

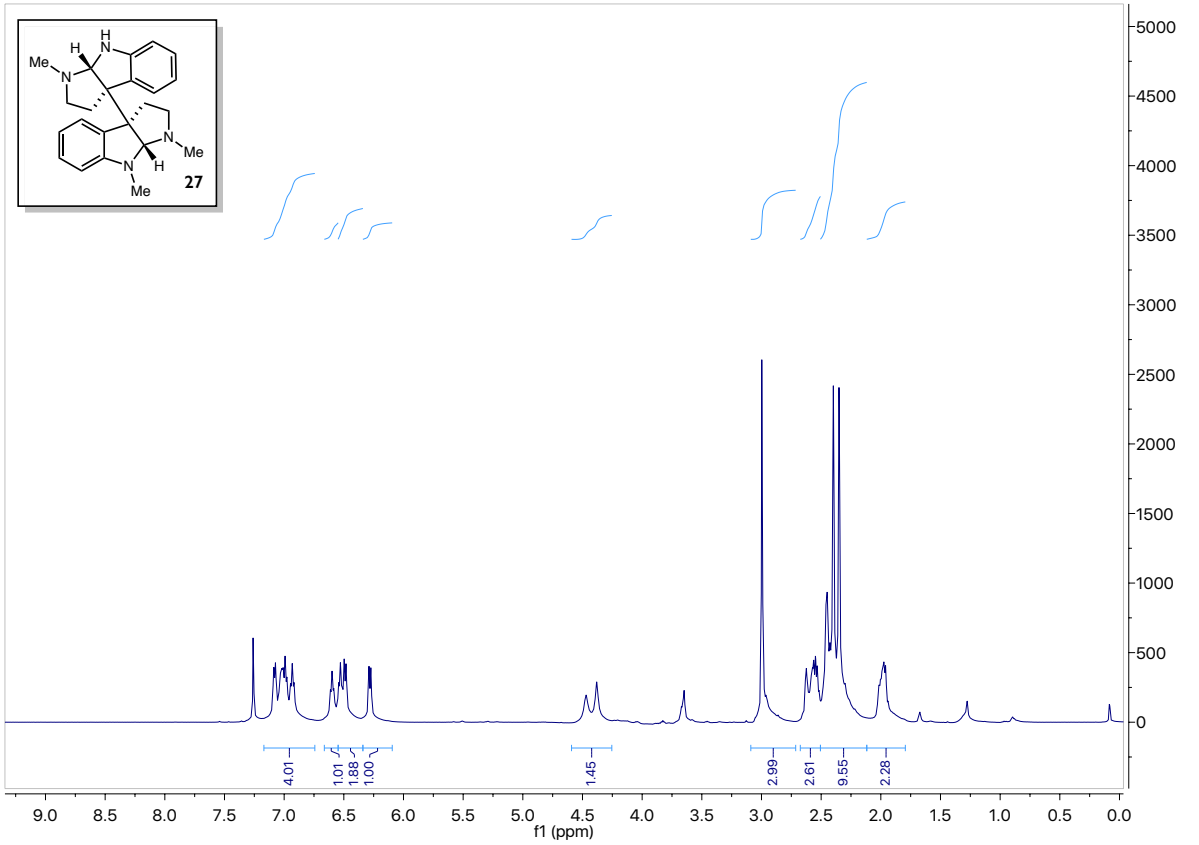

I
HN
N
Cbz
N
H
H
22
155.42
154.57
148.99
148.82
144.49
144.45
139.49
139.38
136.50
136.45
130.01
129.95
129.30
129.27
128.99
128.82
128.88
128.43
128.29
128.11
123.50
123.40
119.91
119.81
119.58
113.68
113.38
109.78
109.65
87.79
87.67
78.34
77.60
77.41 CDCl3
77.37
77.16 CDCl3
76.91 CDCl3
73.82
72.64
67.47
67.28
44.72
44.51
39.31
38.77
f1 (ppm)

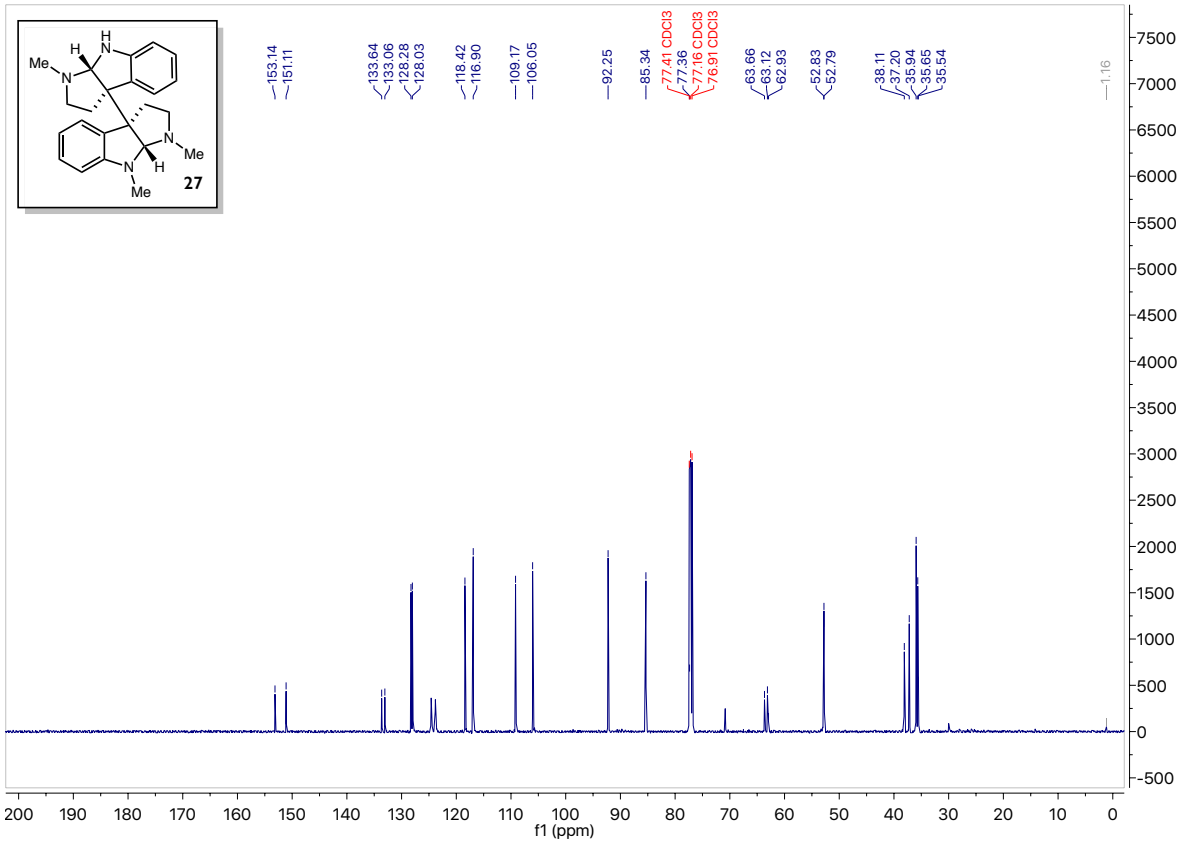

23
Boc
Cbz
0.97
7.01
1.00
0.96
0.96
4.06
1.02
1.00
1.03
1.02
9.40
f1 (ppm)

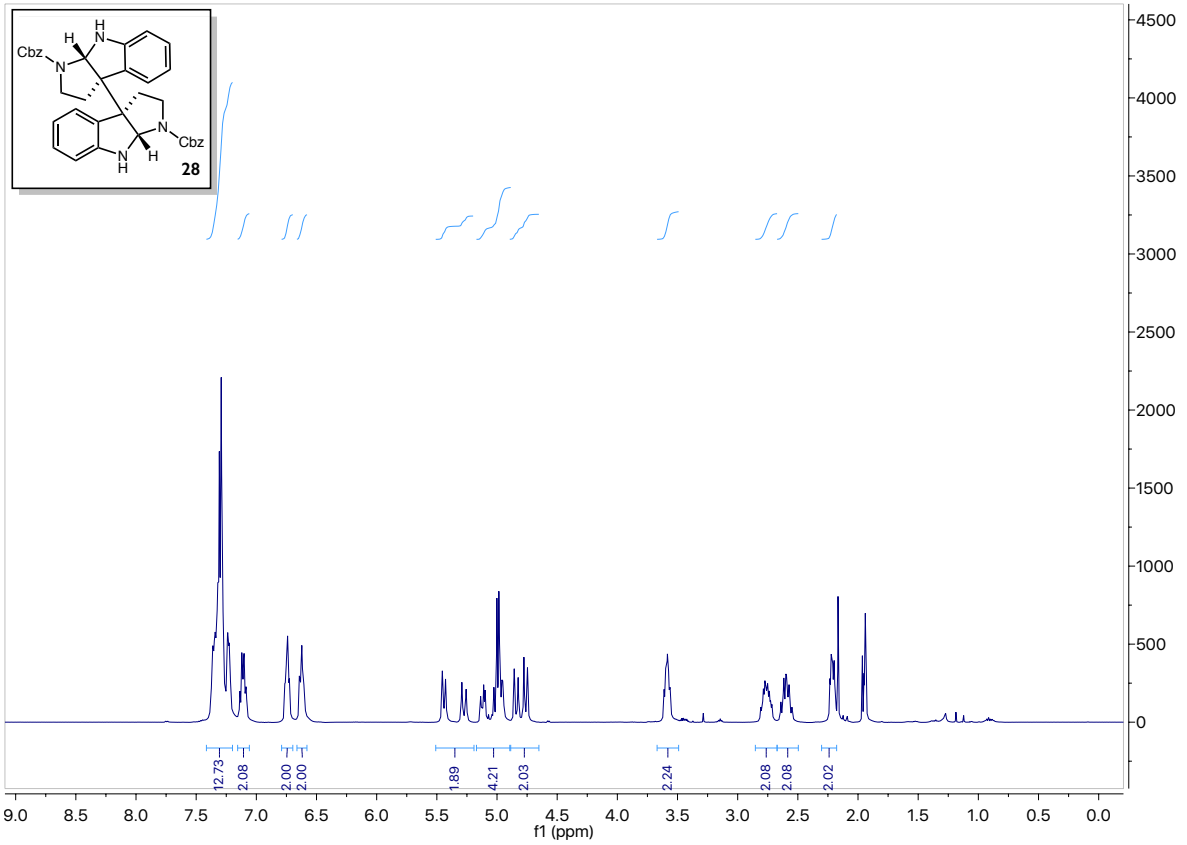

23
Boc
Cbz
155.23
153.42
144.48
138.14
131.09
130.96
129.37
128.81
128.49
125.49
124.49
117.65
82.34
80.77
71.55
67.52
45.52
37.28
28.45
1.82
1.77
1.65
1.49 CD3CN
1.32 CD3CN
1.16 CD3CN
0.99
0.83
f1 (ppm)

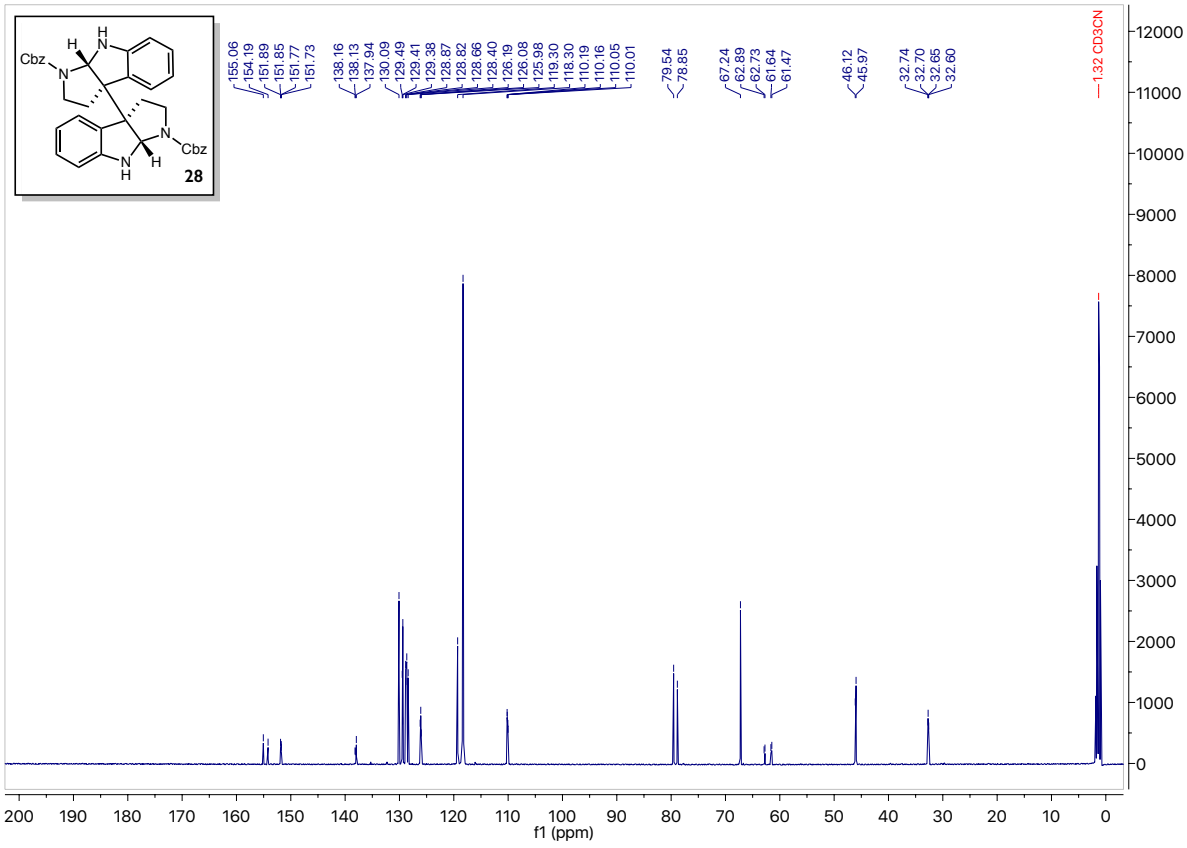

Cbz
Cbz
Me
26
11.42
2.98
0.99
2.02
0.97
1.05
5.15
0.95
1.09
1.14
4.12
2.96
2.37
f1 (ppm)


Cbz
Cbz
Me
26
f1 (ppm)


Me
H
N
N
Me
N
H
Me
27
4.01
1.01
1.88
1.00
1.45
2.99
2.61
9.55
2.28
f1 (ppm)


Me
H
N
N
Me
N
H
Me
27
153.14
151.11
133.64
133.06
128.28
128.03
118.42
116.90
109.17
106.05
92.25
85.34
77.41 CDCl3
77.36
77.16 CDCl3
76.91 CDCl3
63.66
63.12
62.93
52.83
52.79
38.11
37.20
35.94
35.65
35.54
1.16
f1 (ppm)


Cbz
Cbz
28
12.73
2.08
2.00
2.00
1.89
4.21
2.03
2.24
2.08
2.08
2.02
f1 (ppm)


Cbz
Cbz
28
155.06
154.19
151.89
151.85
151.77
151.73
138.16
138.13
137.94
130.09
129.49
129.41
129.38
128.87
128.82
128.66
128.40
126.19
126.08
125.98
119.30
118.30
110.19
110.16
110.05
110.01
79.54
78.85
67.24
62.89
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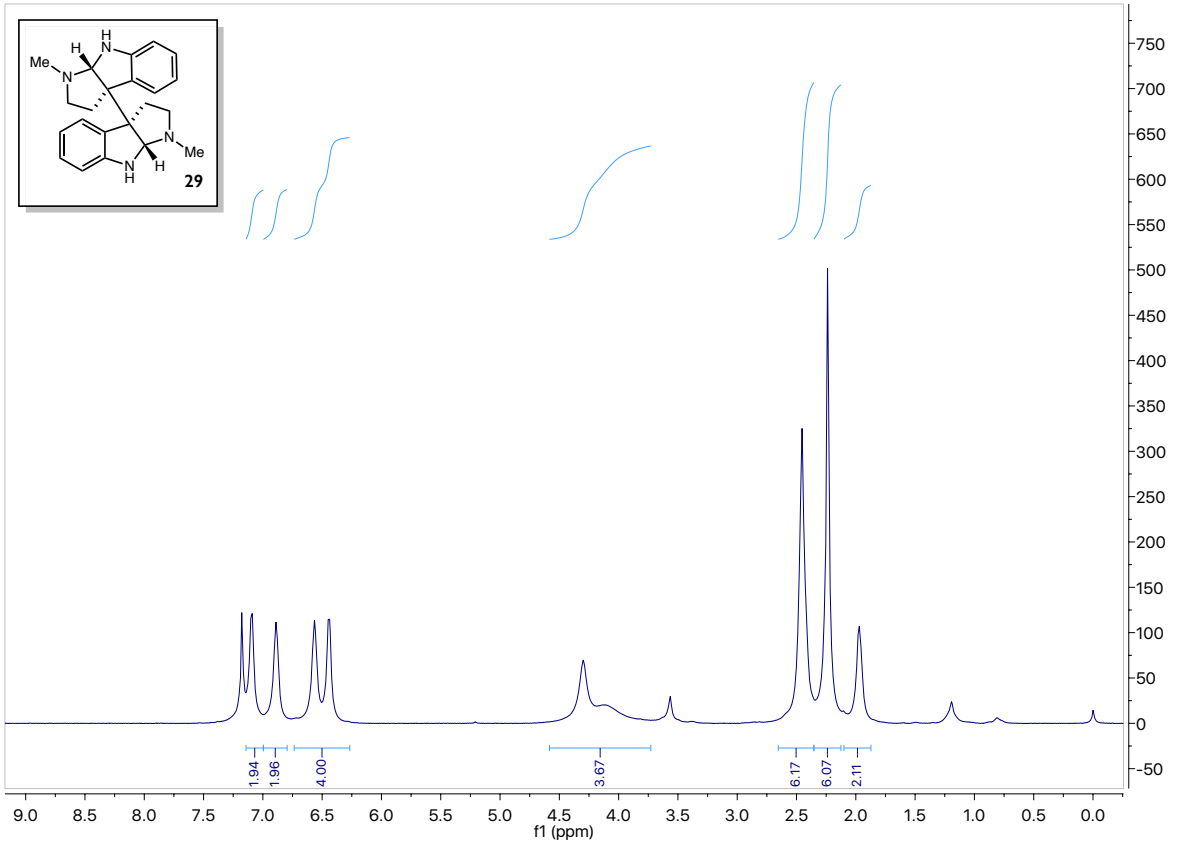
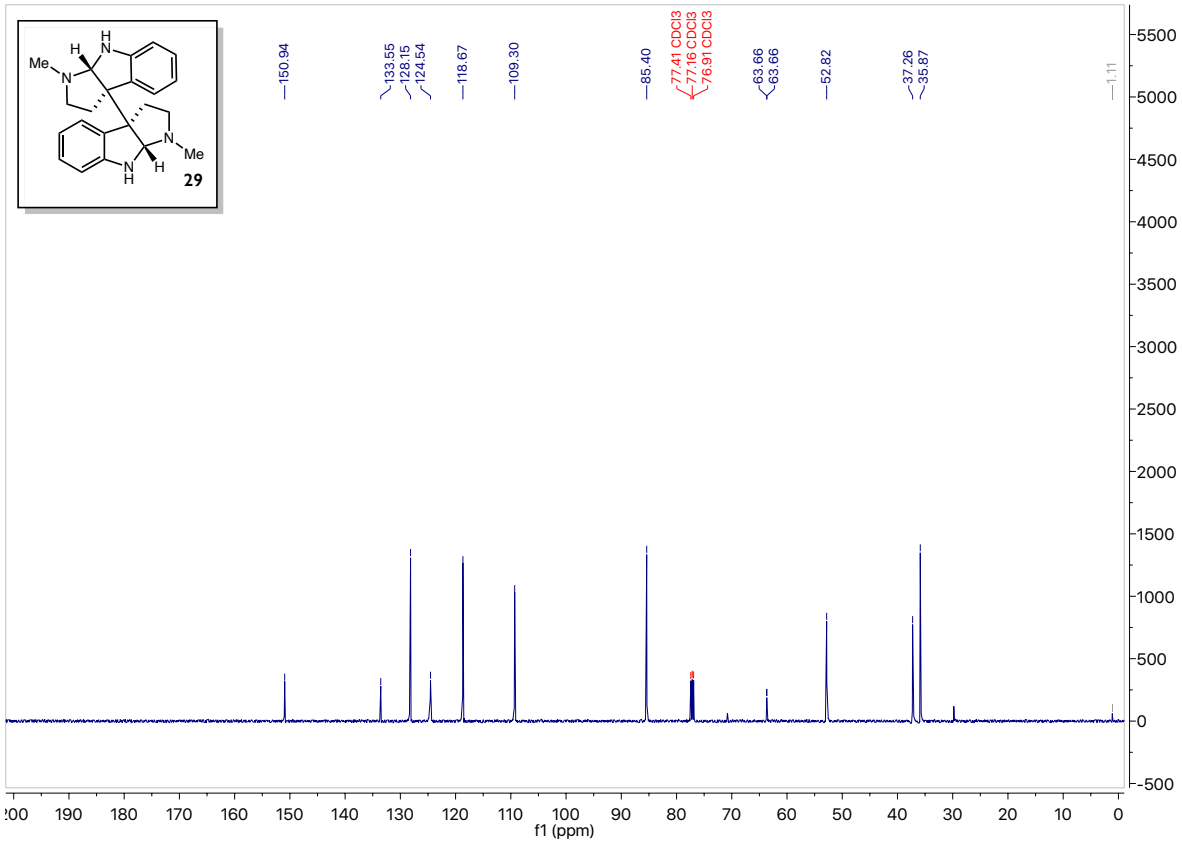
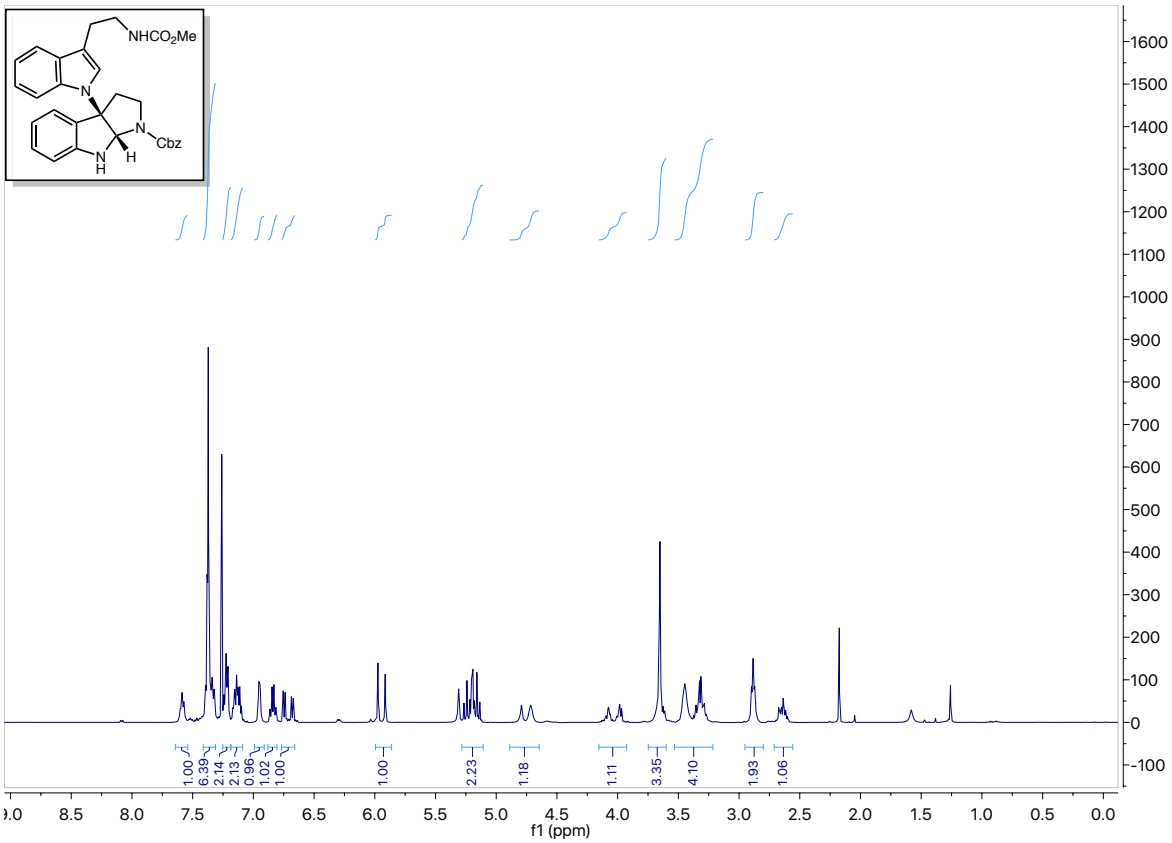
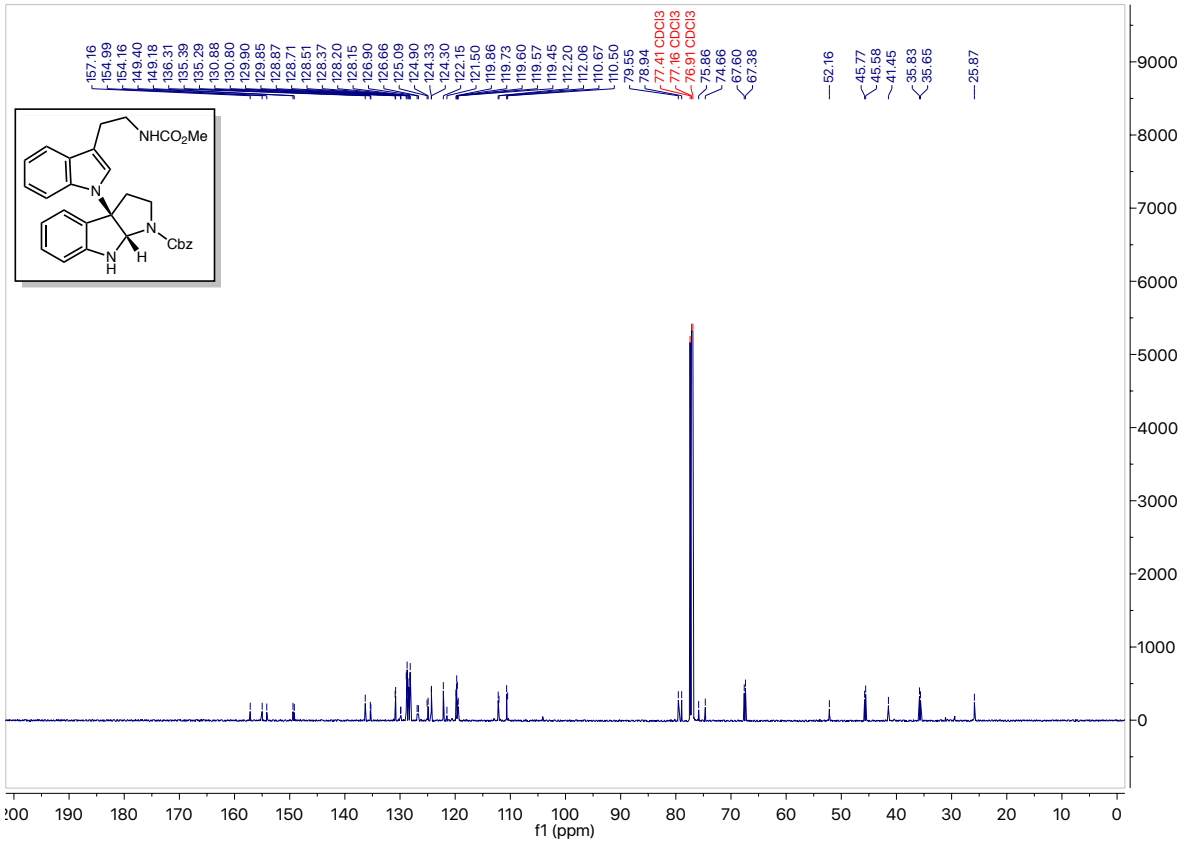
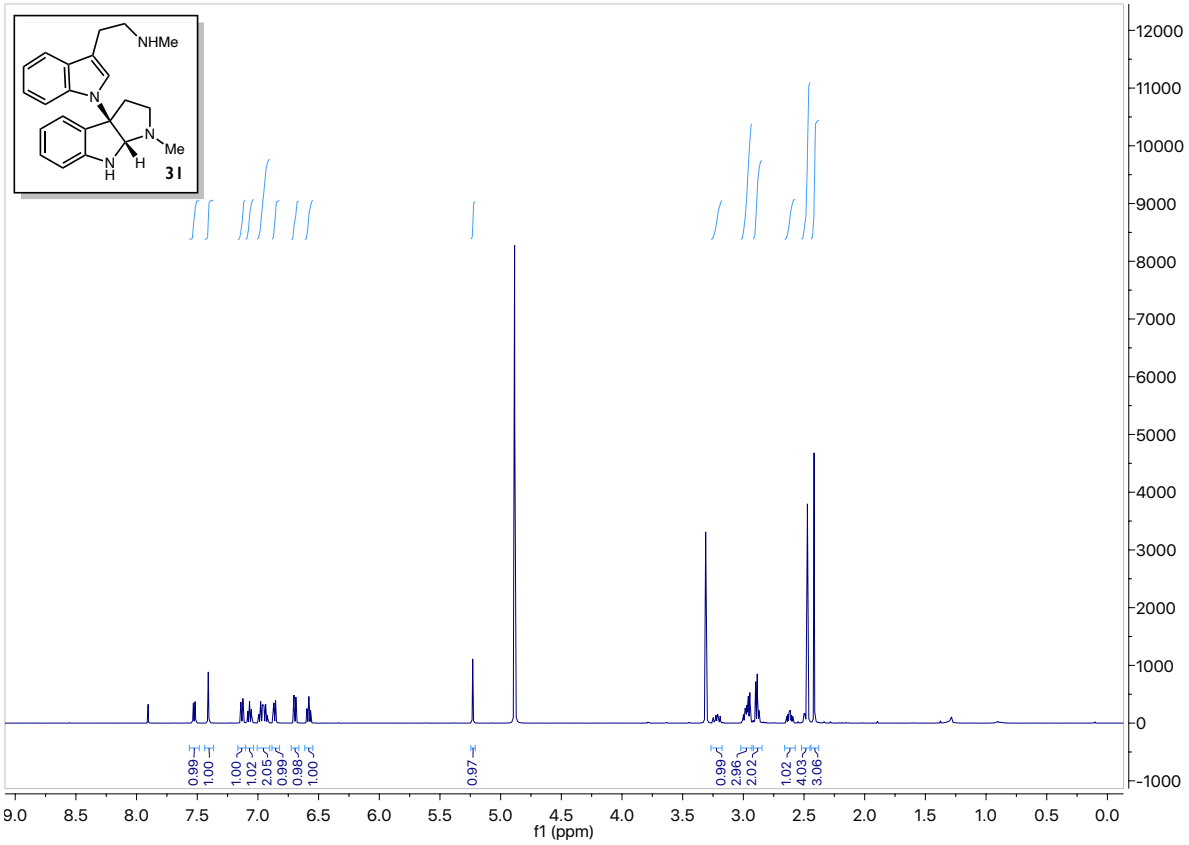
32.70
32.65
32.60
1.32 CD3CN
f1 (ppm)

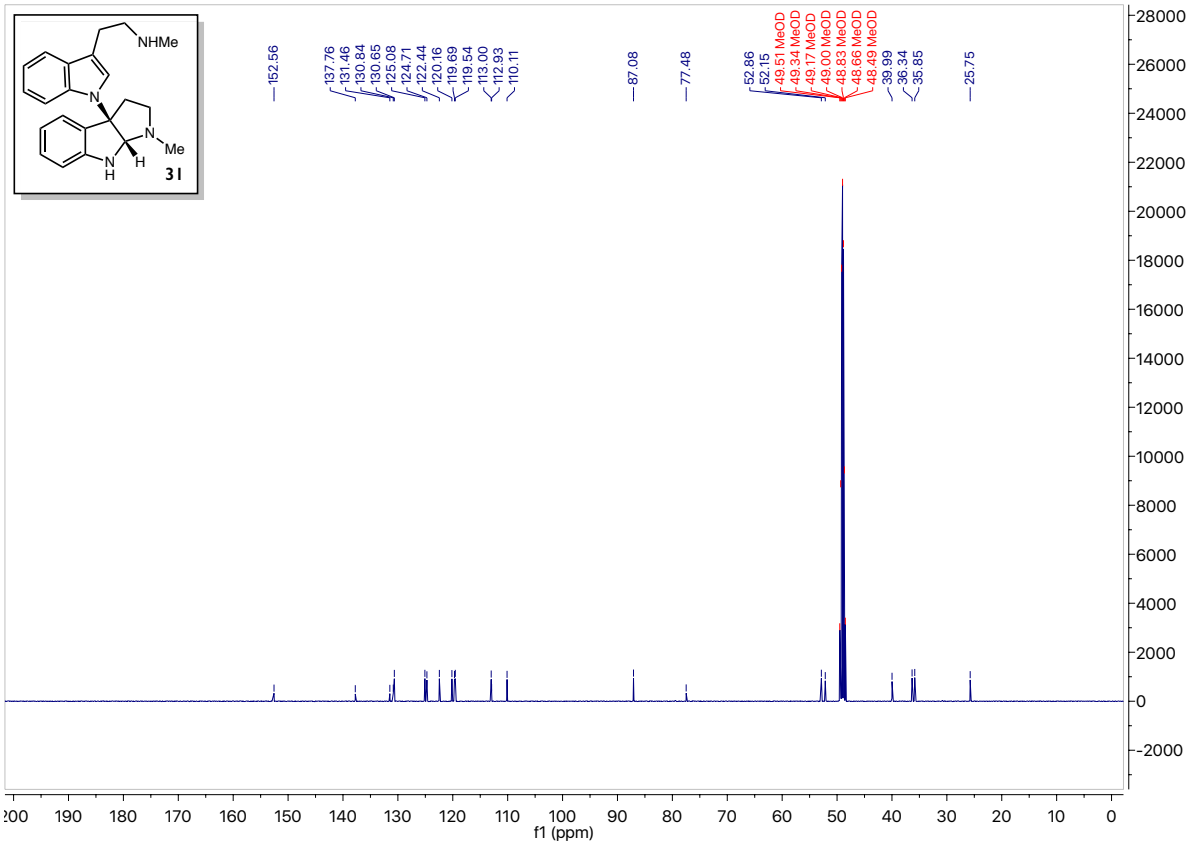

29
1.94
1.96
4.00
3.67
6.17
6.07
2.11
f1 (ppm)

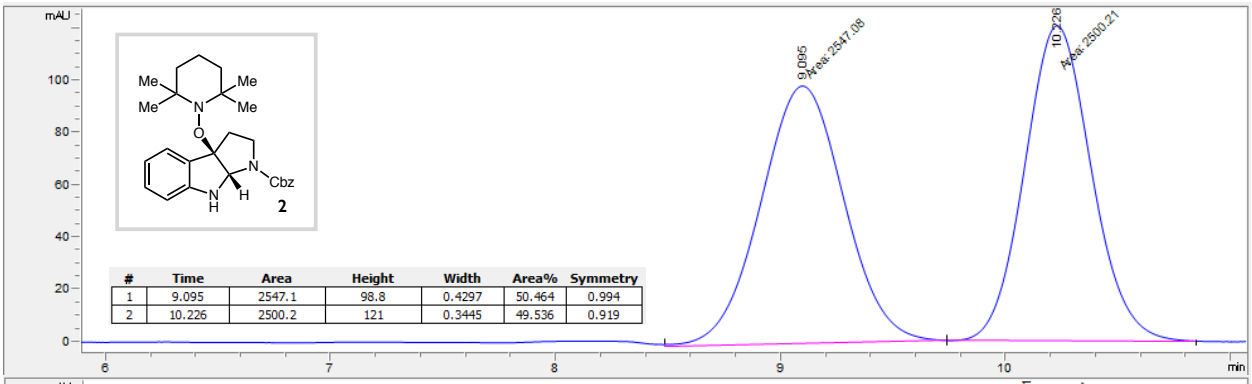

29
150.94
133.55
128.15
124.54
118.67
109.30
85.40
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
63.66
63.66
52.82
37.26
35.87
f1 (ppm)


NHCO2Me
N
N
Cbz
N
H
H
1.00
6.39
2.14
2.13
0.96
1.02
1.00
1.00
2.23
1.18
1.11
3.35
4.10
1.93
1.06
f1 (ppm)

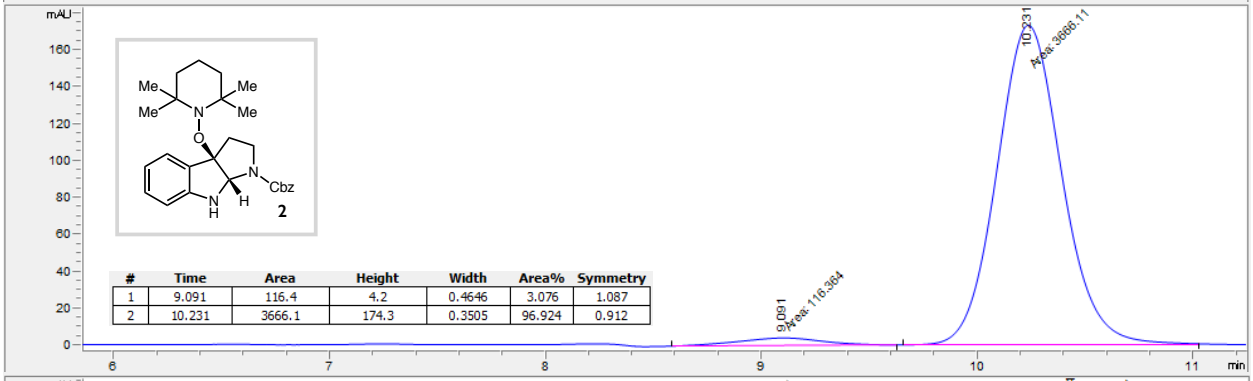

157.16
154.99
154.16
149.40
149.18
136.31
135.39
135.29
130.88
130.80
129.90
129.85
128.87
128.71
128.51
128.37
128.20
128.15
126.90
126.66
125.09
124.90
124.33
124.30
122.15
121.50
119.86
119.73
119.60
119.57
119.45
112.20
112.06
110.67
110.50
79.55
78.94
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
75.86
74.66
67.60
67.38
52.16
45.77
45.58
41.45
35.83
35.65
25.87
NHCO2Me
N
N
Cbz
N
H
H
f1 (ppm)


NHMe
N
N
Me
N
H
H
3 l
0.99
1.00
1.00
1.02
2.05
0.99
0.98
1.00
0.97
0.99
2.96
2.02
1.02
4.03
3.06
f1 (ppm)

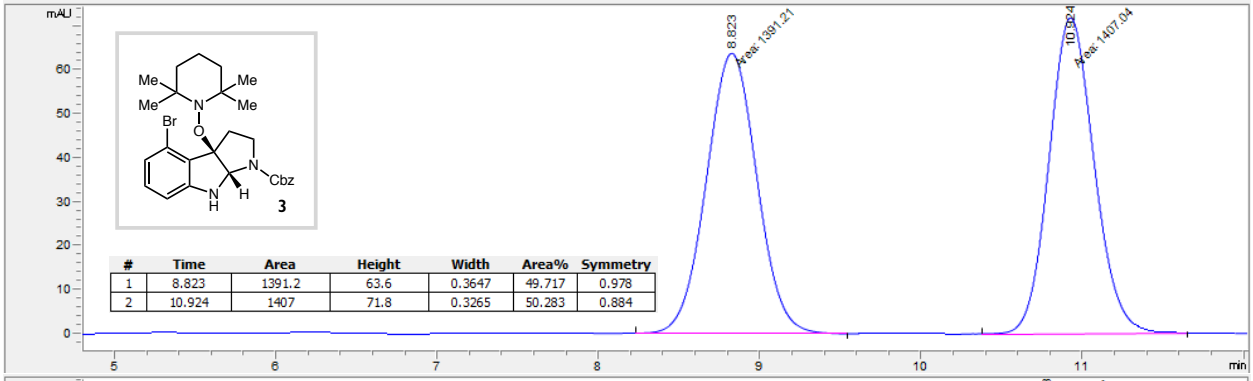

NHMe
N
N
Me
N
H
H
3 l
152.56
137.76
131.46
130.84
130.65
125.08
124.71
122.44
120.16
119.69
119.54
113.00
112.93
110.11
87.08
77.48
52.86
52.15
49.51 MeOD
49.34 MeOD
49.17 MeOD
49.00 MeOD
48.83 MeOD
48.66 MeOD
48.49 MeOD
39.99
36.34
35.85
25.75
f1 (ppm)



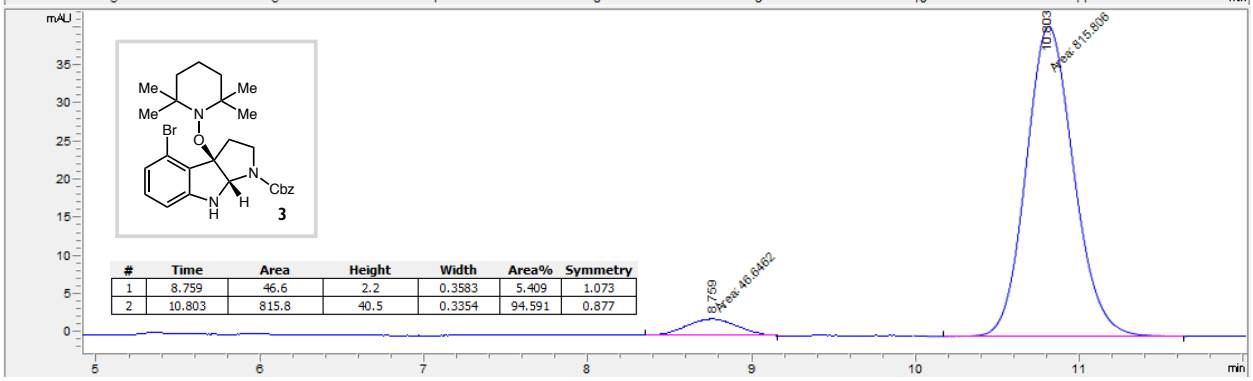
#	Time	Area	Height	Width	Area%	Symmetry
1	9.095	2547.1	98.8	0.4297	50.464	0.994
2	10.226	2500.2	121	0.3445	49.536	0.919



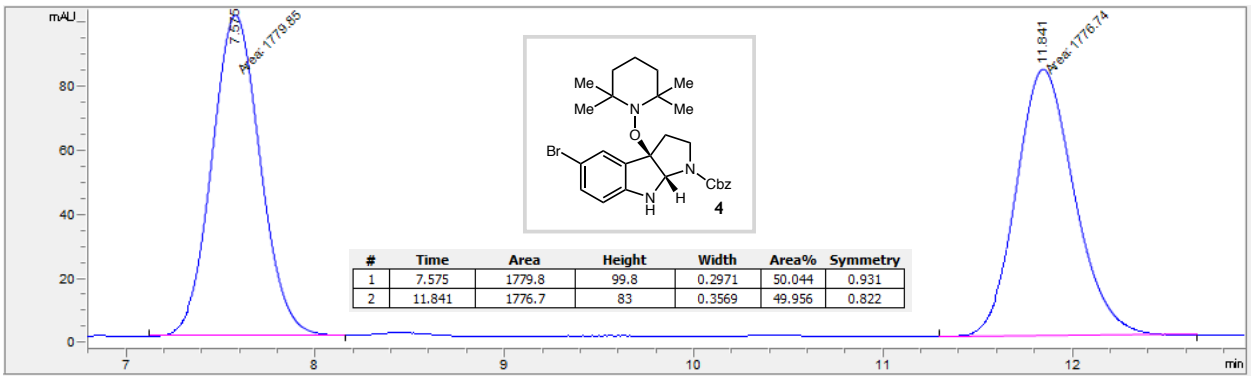
#	Time	Area	Height	Width	Area%	Symmetry
1	9.091	116.4	4.2	0.4646	3.076	1.087
2	10.231	3666.1	174.3	0.3505	96.924	0.912



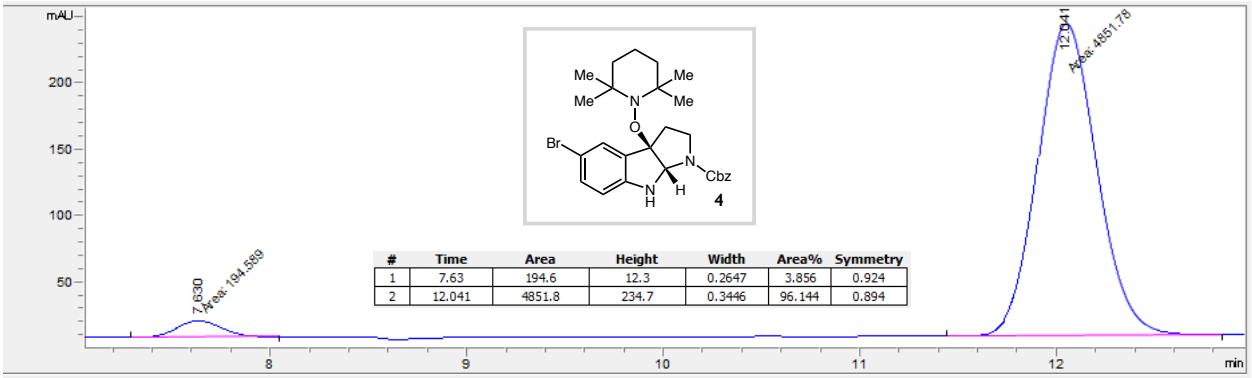
#	Time	Area	Height	Width	Area%	Symmetry
1	8.823	1391.2	63.6	0.3647	49.717	0.978
2	10.924	1407	71.8	0.3265	50.283	0.884



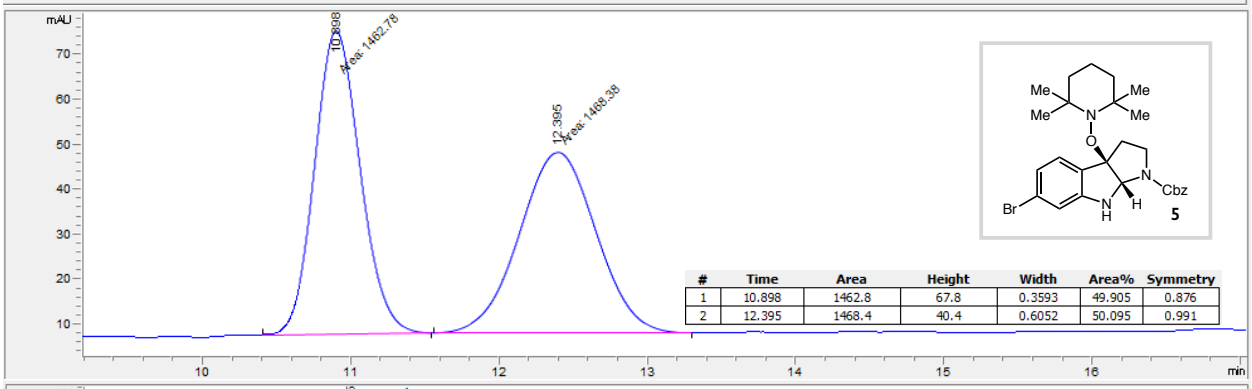
#	Time	Area	Height	Width	Area%	Symmetry
1	8.759	46.6	2.2	0.3583	5.409	1.073
2	10.803	815.8	40.5	0.3354	94.591	0.877



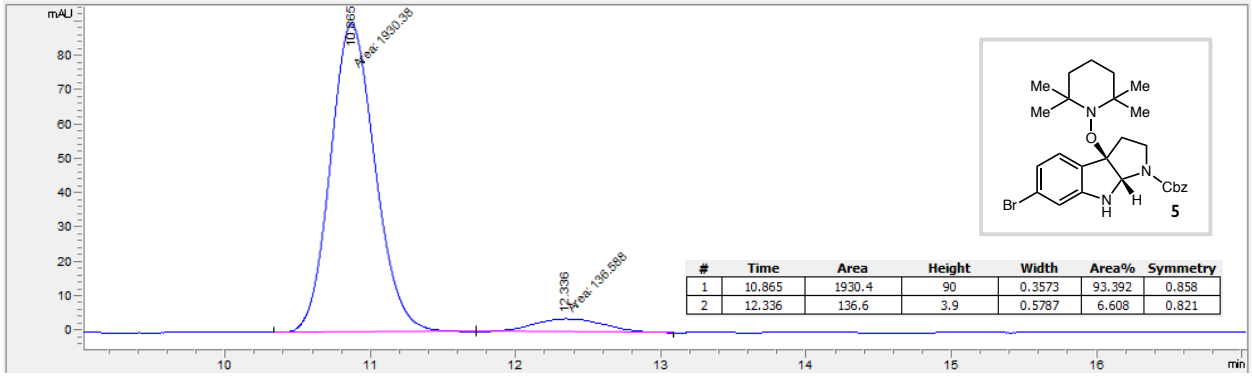
#	Time	Area	Height	Width	Area%	Symmetry
1	7.575	1779.8	99.8	0.2971	50.044	0.931
2	11.841	1776.7	83	0.3569	49.956	0.822



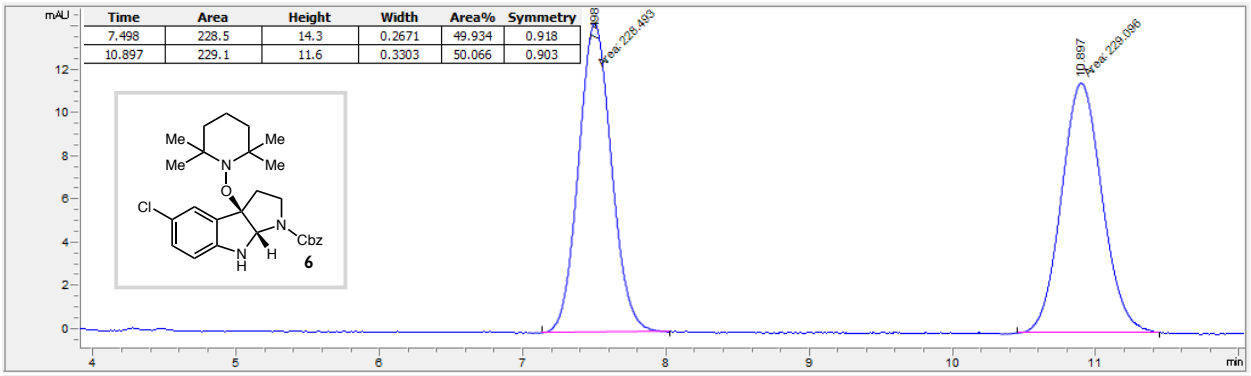
#	Time	Area	Height	Width	Area%	Symmetry
1	7.63	194.6	12.3	0.2647	3.856	0.924
2	12.041	4851.8	234.7	0.3446	96.144	0.894

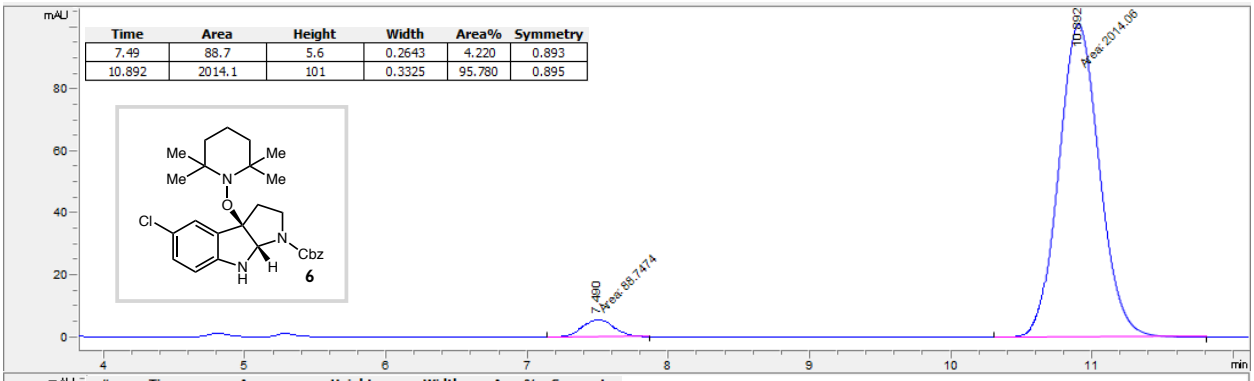


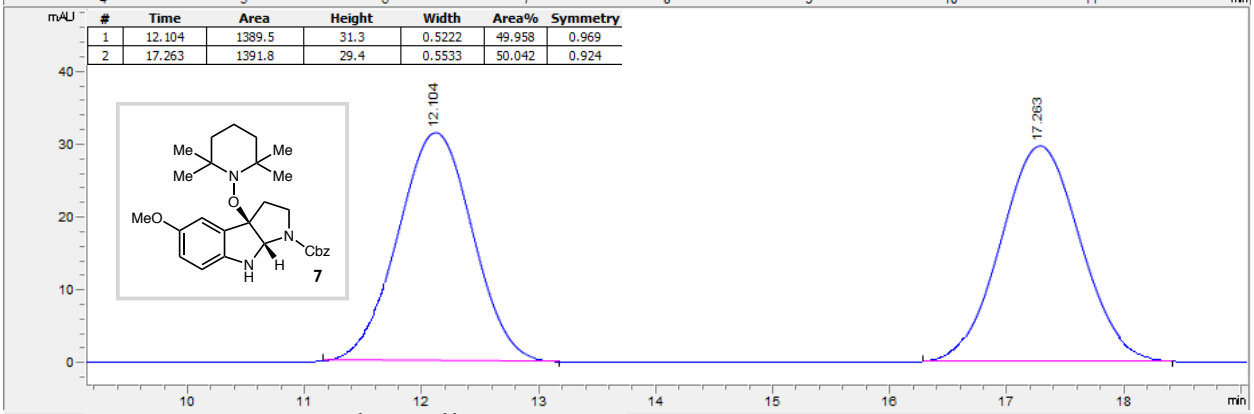
#	Time	Area	Height	Width	Area%	Symmetry
1	10.898	1462.8	67.8	0.3593	49.905	0.876
2	12.395	1468.4	40.4	0.6052	50.095	0.991

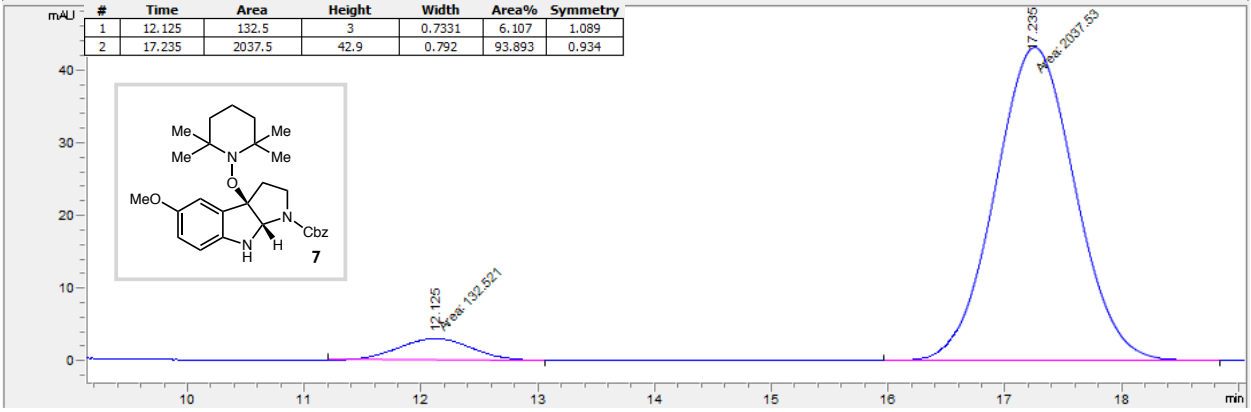


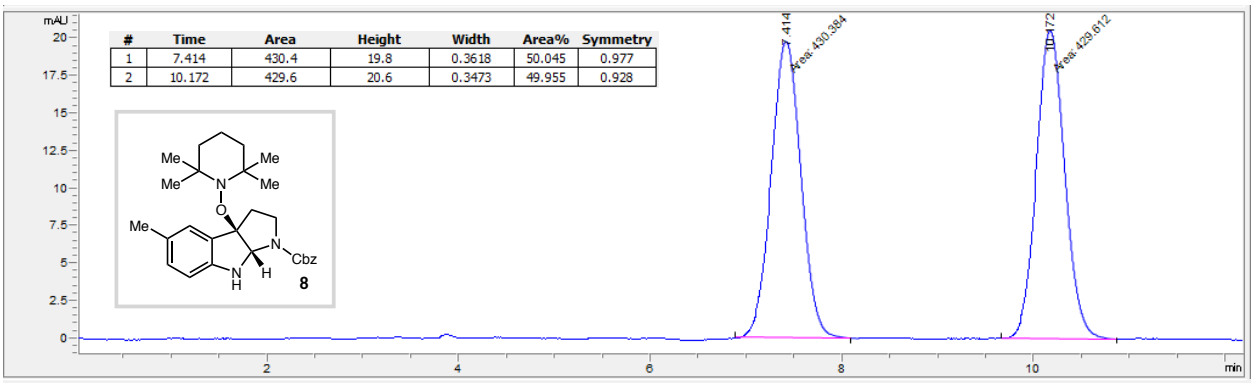
#	Time	Area	Height	Width	Area%	Symmetry
1	10.865	1930.4	90	0.3573	93.392	0.858
2	12.336	136.6	3.9	0.5787	6.608	0.821

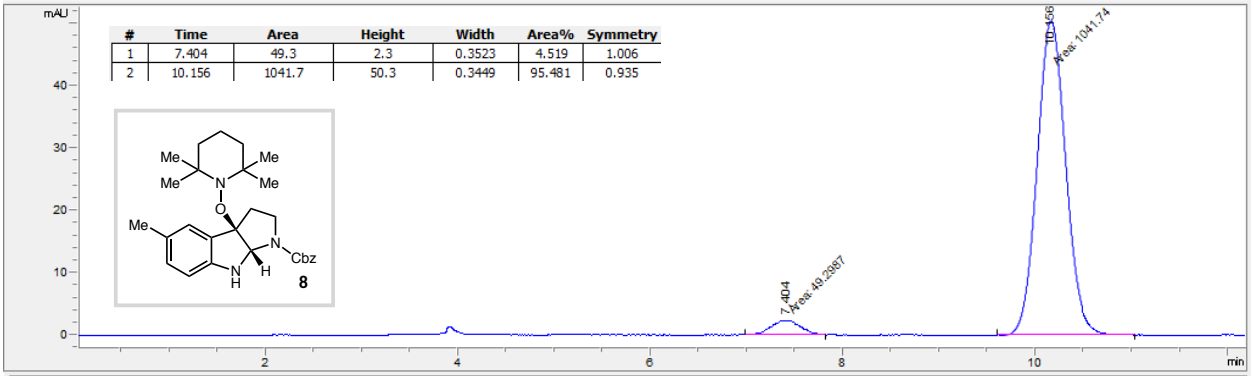

mAU
Time Area Height Width Area% Symmetry
7.498 228.5 14.3 0.2671 49.934 0.918
10.897 229.1 11.6 0.3303 50.066 0.903
7.498
Area: 228.493
10.897
Area: 229.096
Me Me Me Me N O Cl N Cbz H N H
6
min

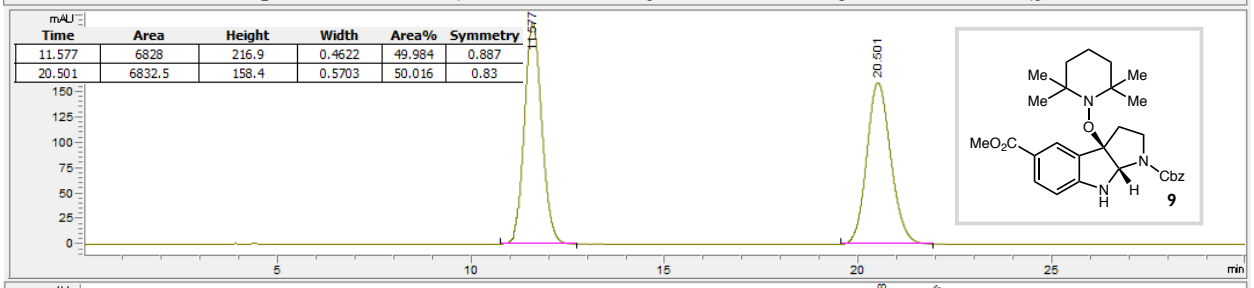

mAU
Time Area Height Width Area% Symmetry
7.49 88.7 5.6 0.2643 4.220 0.893
10.892 2014.1 101 0.3325 95.780 0.895
10.892
Area: 2014.06
7.490
Area: 88.7474
Me Me Me Me N O Cl N Cbz H N H
6
min

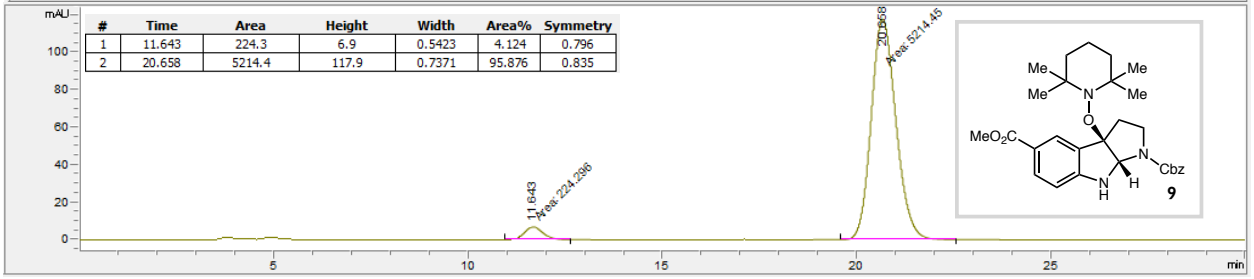

mAU
Time Area Height Width Area% Symmetry
1 12.104 1389.5 31.3 0.5222 49.958 0.969
2 17.263 1391.8 29.4 0.5533 50.042 0.924
12.104
17.263
Me Me Me Me N O MeO N Cbz H N H
7
min

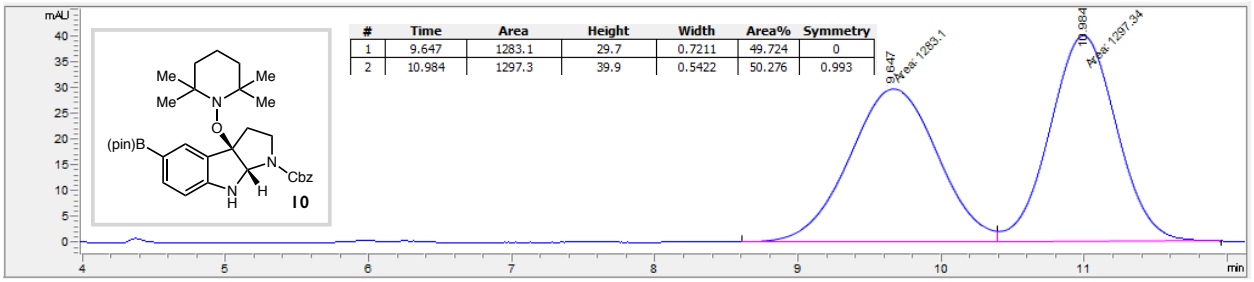

mAU
Time Area Height Width Area% Symmetry
1 12.125 132.5 3 0.7331 6.107 1.089
2 17.235 2037.5 42.9 0.792 93.893 0.934
17.235
Area: 2037.53
12.125
Area: 132.521
Me Me Me Me N O MeO N Cbz H N H
7
min

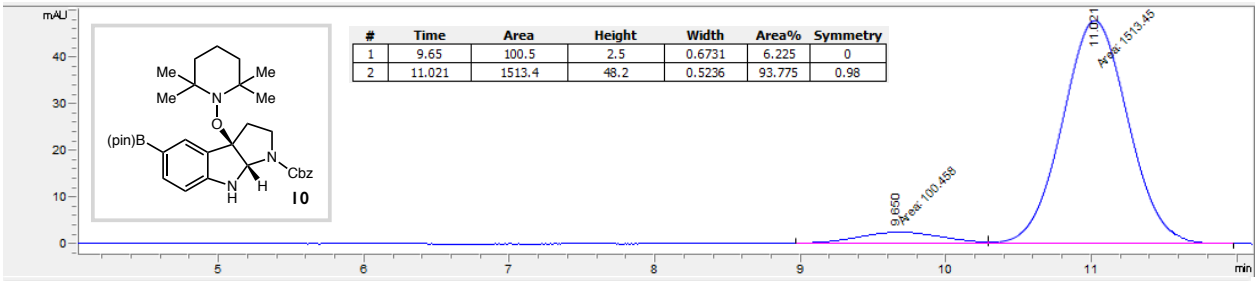

mAU
Time Area Height Width Area% Symmetry
1 7.414 430.4 19.8 0.3618 50.045 0.977
2 10.172 429.6 20.6 0.3473 49.955 0.928
7.414
Area: 430.384
10.172
Area: 429.612
Me Me Me Me Me N O N Cbz N H H
8
min


mAU
Time Area Height Width Area% Symmetry
1 7.404 49.3 2.3 0.3523 4.519 1.006
2 10.156 1041.7 50.3 0.3449 95.481 0.935
10.156
Area: 1041.74
7.404
Area: 49.2987
Me Me Me Me Me N O N Cbz N H H
8
min

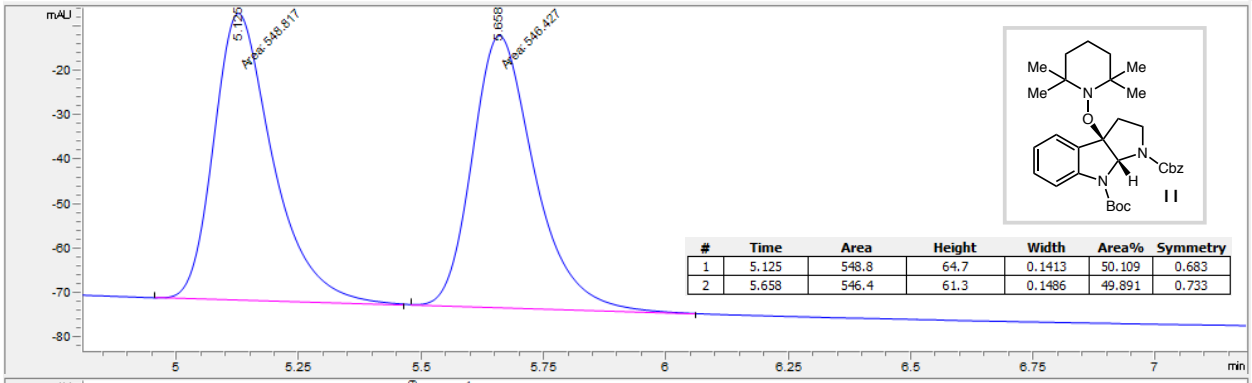

mAU
Time Area Height Width Area% Symmetry
11.577 6828 216.9 0.4622 49.984 0.887
20.501 6832.5 158.4 0.5703 50.016 0.83
11.577
20.501
Me Me Me Me MeO2C N O N Cbz N H H
9
min


mAU
Time Area Height Width Area% Symmetry
1 11.643 224.3 6.9 0.5423 4.124 0.796
2 20.658 5214.4 117.9 0.7371 95.876 0.835
20.658
Area: 5214.45
11.643
Area: 224.286
Me Me Me Me MeO2C N O N Cbz N H H
9
min

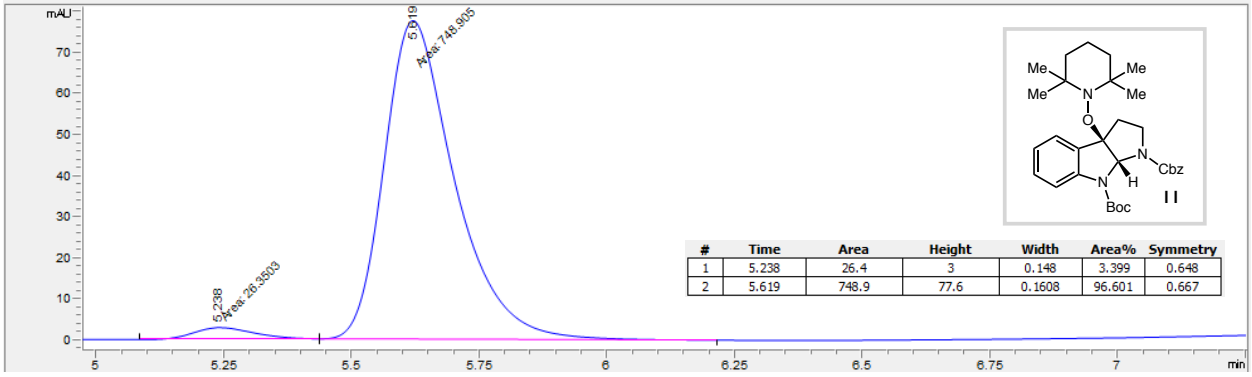

mAU
Time Area Height Width Area% Symmetry
1 9.647 1283.1 29.7 0.7211 49.724 0
2 10.984 1297.3 39.9 0.5422 50.276 0.993
9.647
Area: 1283.1
10.984
Area: 1297.34
Me Me Me Me (pin)B N O N Cbz N H H
10
min



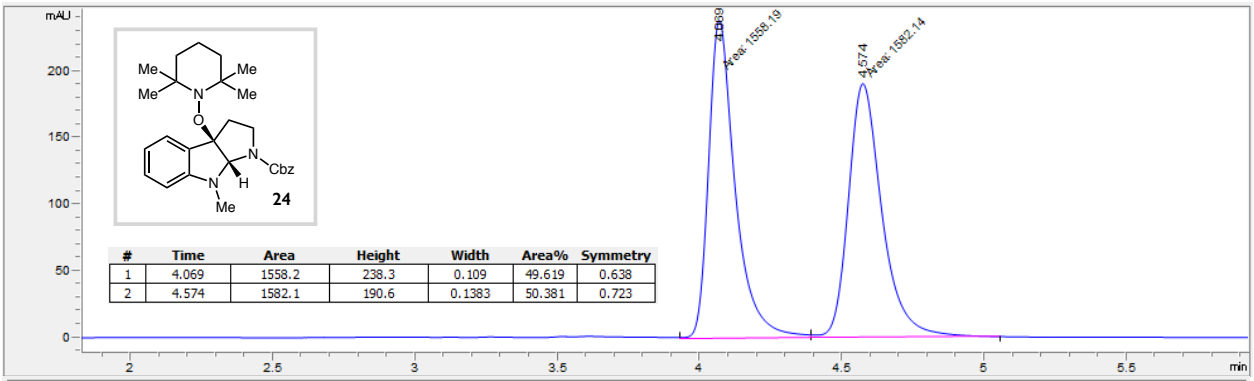
#	Time	Area	Height	Width	Area%	Symmetry
1	9.65	100.5	2.5	0.6731	6.225	0
2	11.021	1513.4	48.2	0.5236	93.775	0.98



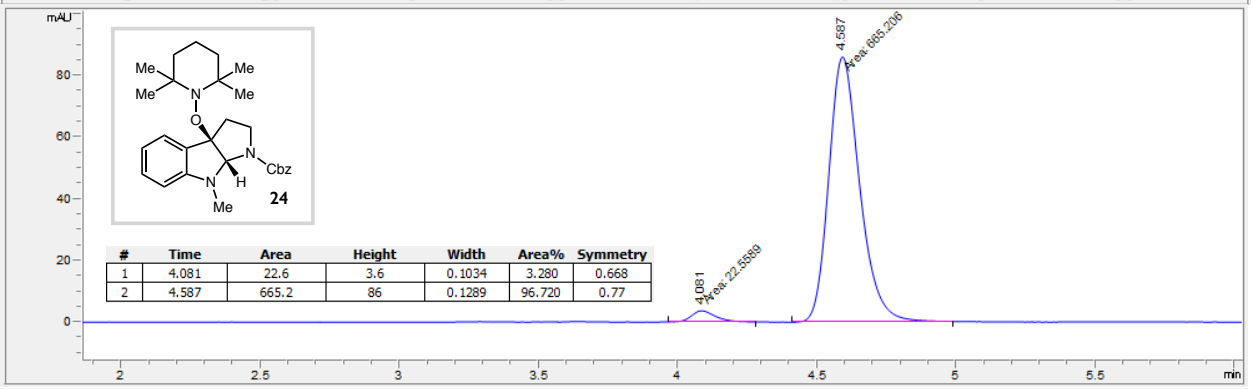
#	Time	Area	Height	Width	Area%	Symmetry
1	5.125	548.8	64.7	0.1413	50.109	0.683
2	5.658	546.4	61.3	0.1486	49.891	0.733



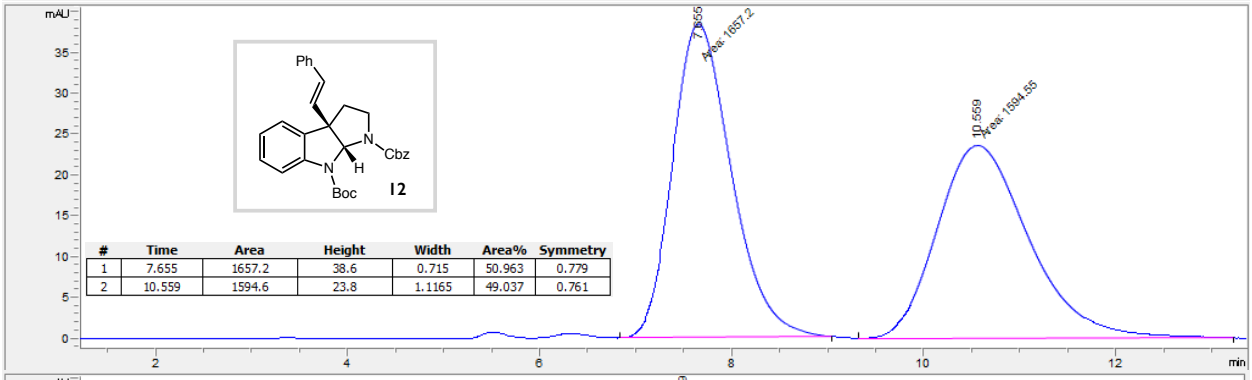
#	Time	Area	Height	Width	Area%	Symmetry
1	5.238	26.4	3	0.148	3.399	0.648
2	5.619	748.9	77.6	0.1608	96.601	0.667



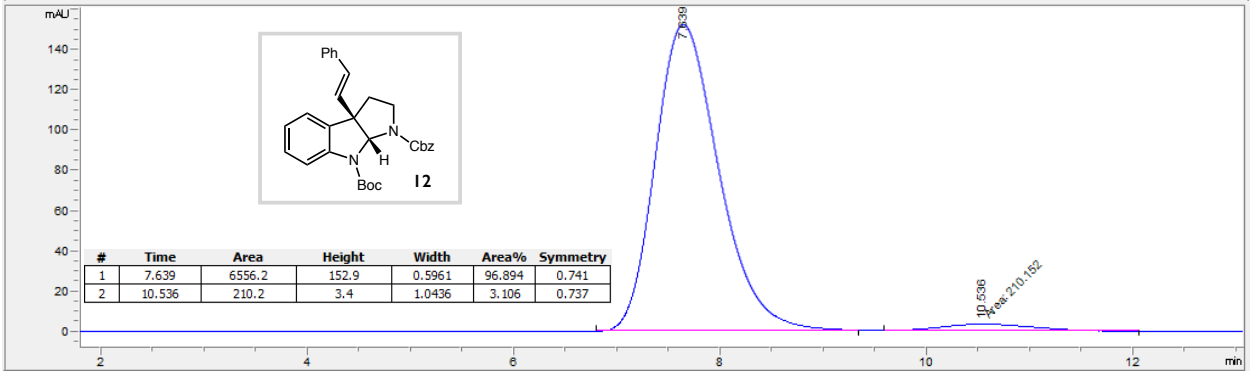
#	Time	Area	Height	Width	Area%	Symmetry
1	4.069	1558.2	238.3	0.109	49.619	0.638
2	4.574	1582.1	190.6	0.1383	50.381	0.723



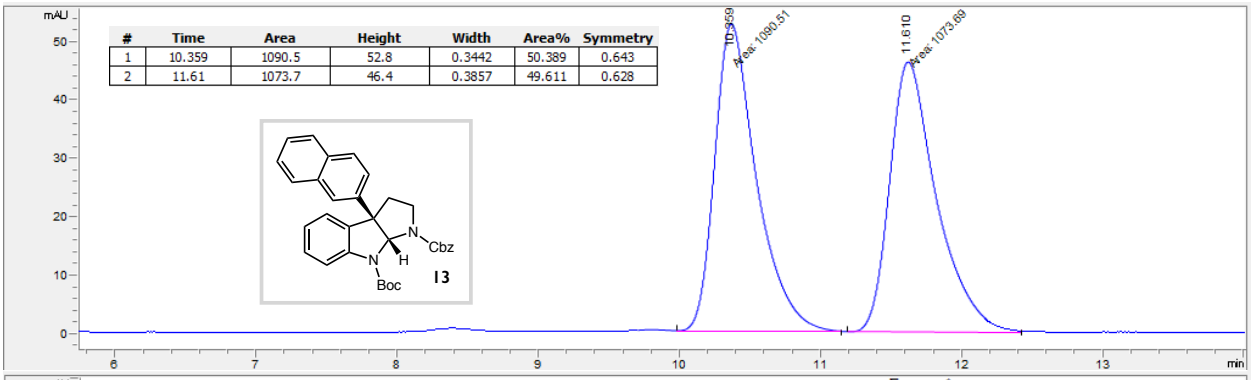
#	Time	Area	Height	Width	Area%	Symmetry
1	4.081	22.6	3.6	0.1034	3.280	0.668
2	4.587	665.2	86	0.1289	96.720	0.77



#	Time	Area	Height	Width	Area%	Symmetry
1	7.655	1657.2	38.6	0.715	50.963	0.779
2	10.559	1594.6	23.8	1.1165	49.037	0.761

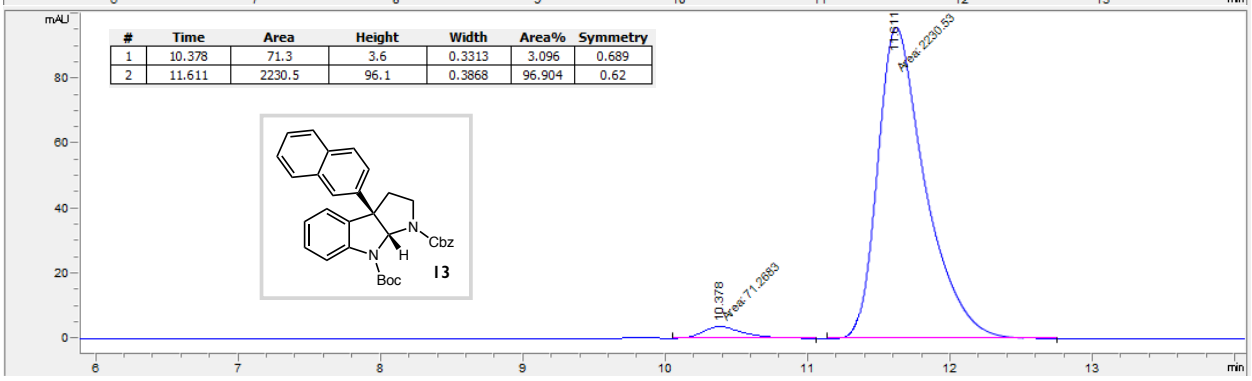


#	Time	Area	Height	Width	Area%	Symmetry
1	7.639	6556.2	152.9	0.5961	96.894	0.741
2	10.536	210.2	3.4	1.0436	3.106	0.737



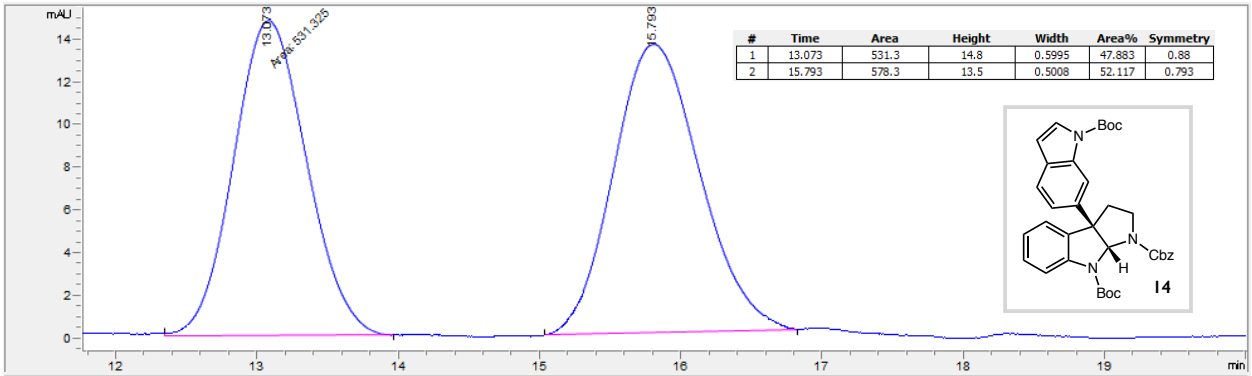
#	Time	Area	Height	Width	Area%	Symmetry
1	10.359	1090.5	52.8	0.3442	50.389	0.643
2	11.61	1073.7	46.4	0.3857	49.611	0.628

13



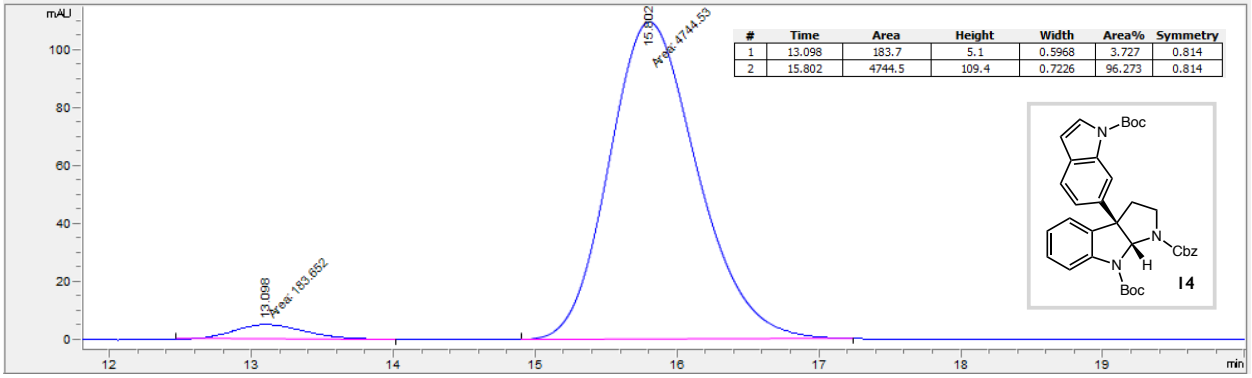
#	Time	Area	Height	Width	Area%	Symmetry
1	10.378	71.3	3.6	0.3313	3.096	0.689
2	11.611	2230.5	96.1	0.3868	96.904	0.62

13



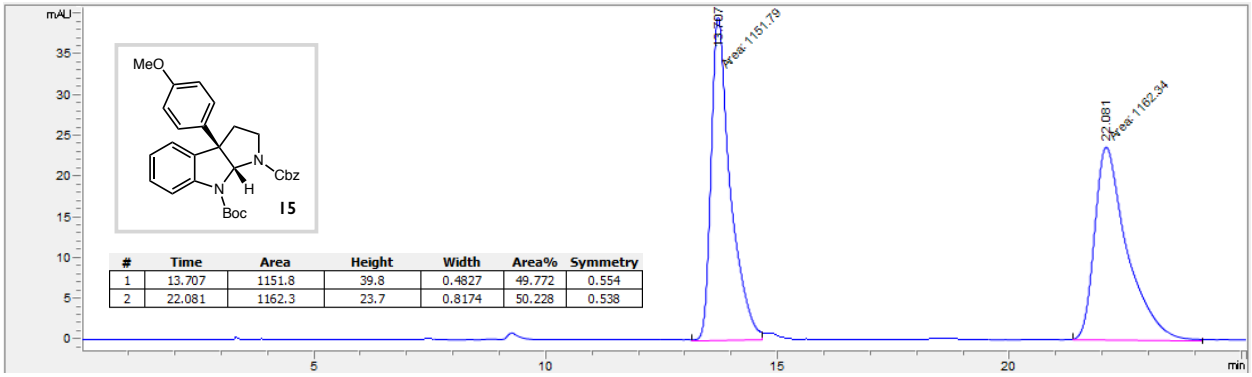
#	Time	Area	Height	Width	Area%	Symmetry
1	13.073	531.3	14.8	0.5995	47.883	0.88
2	15.793	578.3	13.5	0.5008	52.117	0.793

14

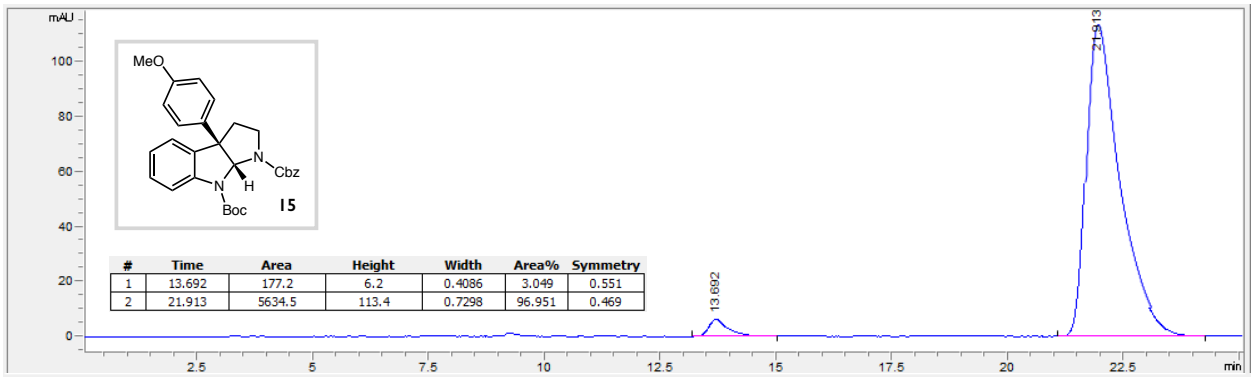


#	Time	Area	Height	Width	Area%	Symmetry
1	13.098	183.7	5.1	0.5968	3.727	0.814
2	15.802	4744.5	109.4	0.7226	96.273	0.814

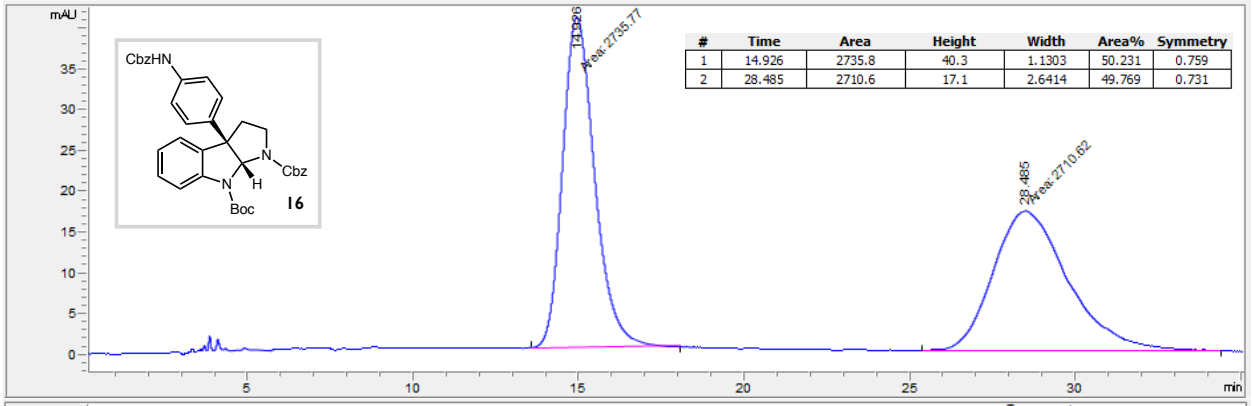
14



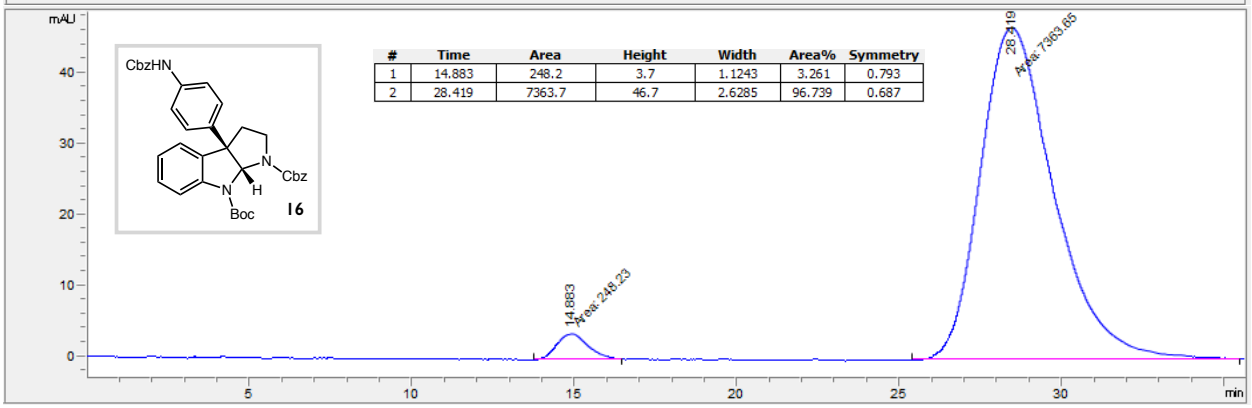
#	Time	Area	Height	Width	Area%	Symmetry
1	13.707	1151.8	39.8	0.4827	49.772	0.554
2	22.081	1162.3	23.7	0.8174	50.228	0.538



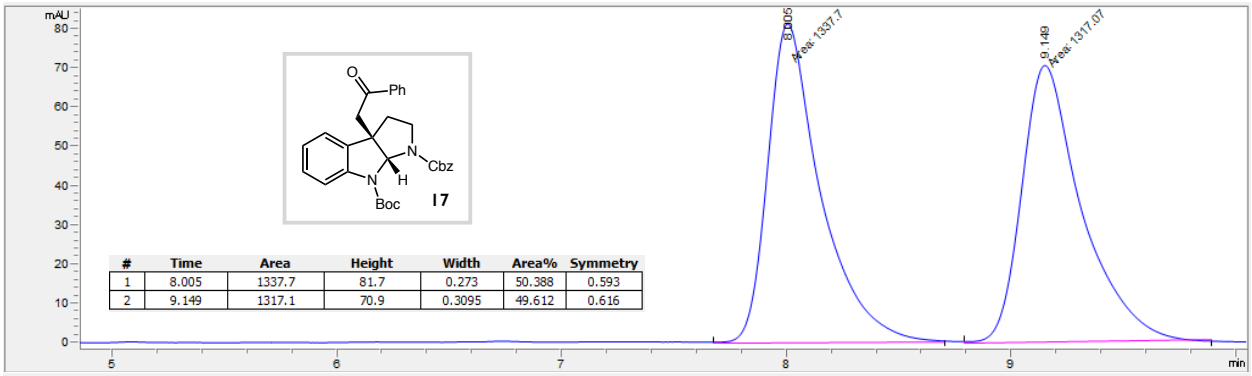
#	Time	Area	Height	Width	Area%	Symmetry
1	13.692	177.2	6.2	0.4086	3.049	0.551
2	21.913	5634.5	113.4	0.7298	96.951	0.469



#	Time	Area	Height	Width	Area%	Symmetry
1	14.926	2735.8	40.3	1.1303	50.231	0.759
2	28.485	2710.6	17.1	2.6414	49.769	0.731

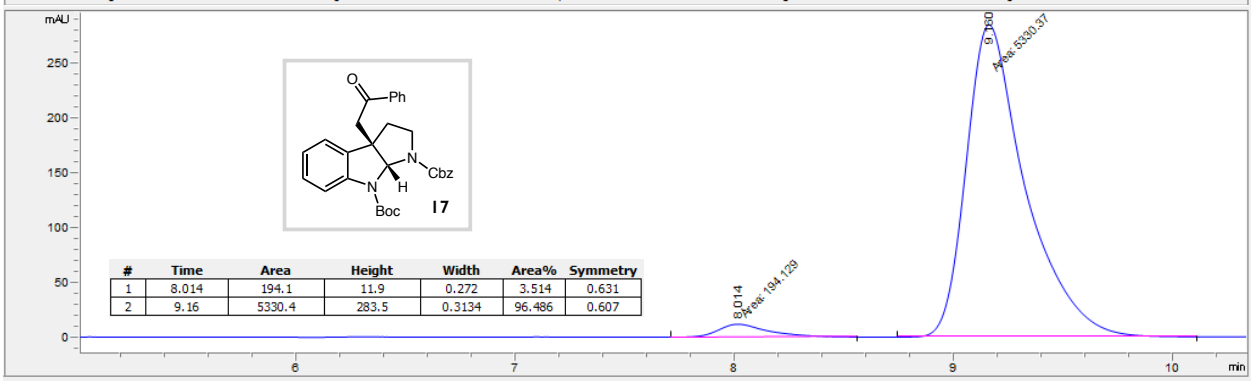


#	Time	Area	Height	Width	Area%	Symmetry
1	14.883	248.2	3.7	1.1243	3.261	0.793
2	28.419	7363.7	46.7	2.6285	96.739	0.687



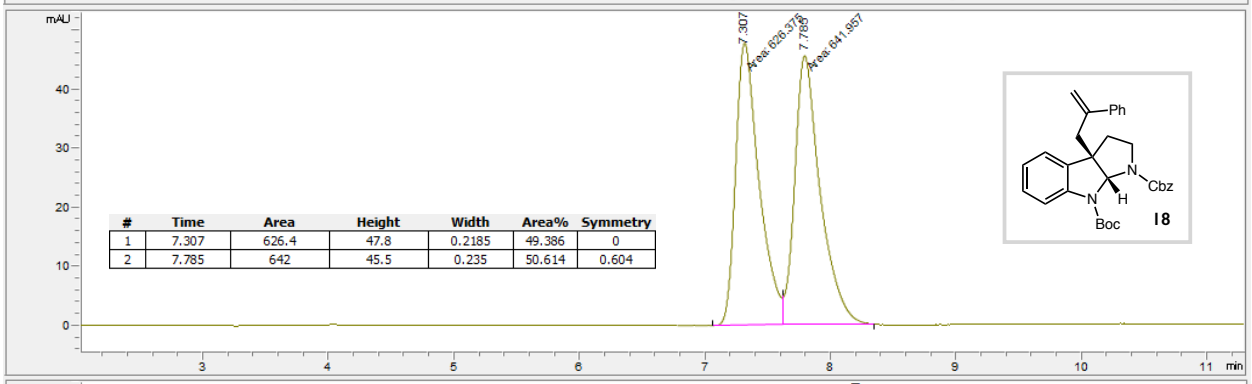
#	Time	Area	Height	Width	Area%	Symmetry
1	8.005	1337.7	81.7	0.273	50.388	0.593
2	9.149	1317.1	70.9	0.3095	49.612	0.616

17



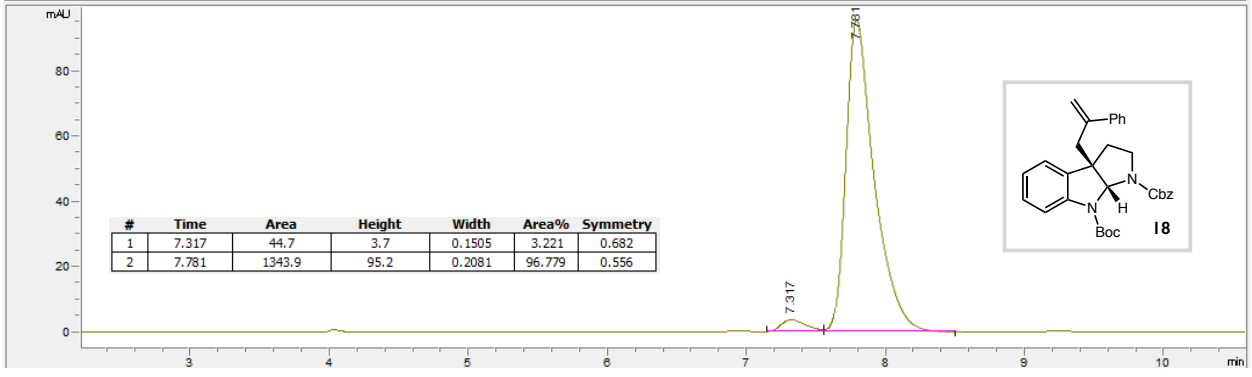
#	Time	Area	Height	Width	Area%	Symmetry
1	8.014	194.1	11.9	0.272	3.514	0.631
2	9.16	5330.4	283.5	0.3134	96.486	0.607

17



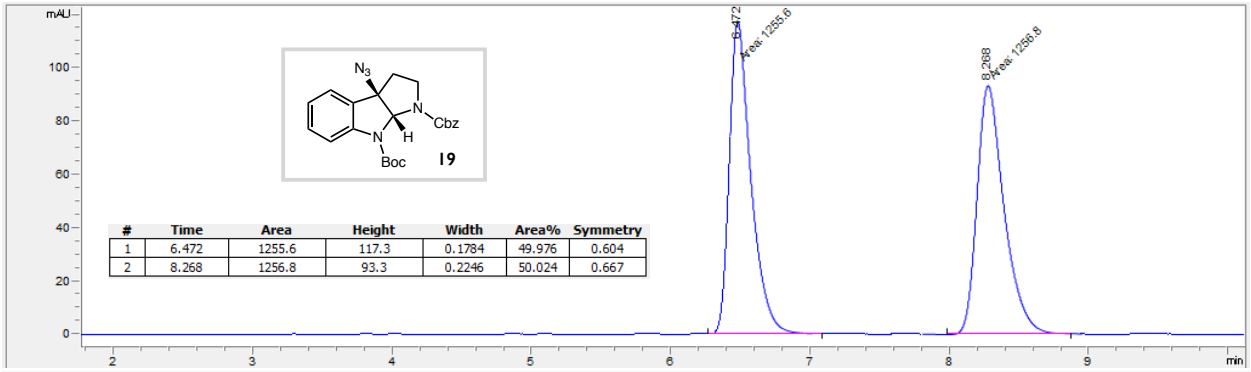
#	Time	Area	Height	Width	Area%	Symmetry
1	7.307	626.4	47.8	0.2185	49.386	0
2	7.785	642	45.5	0.235	50.614	0.604

18



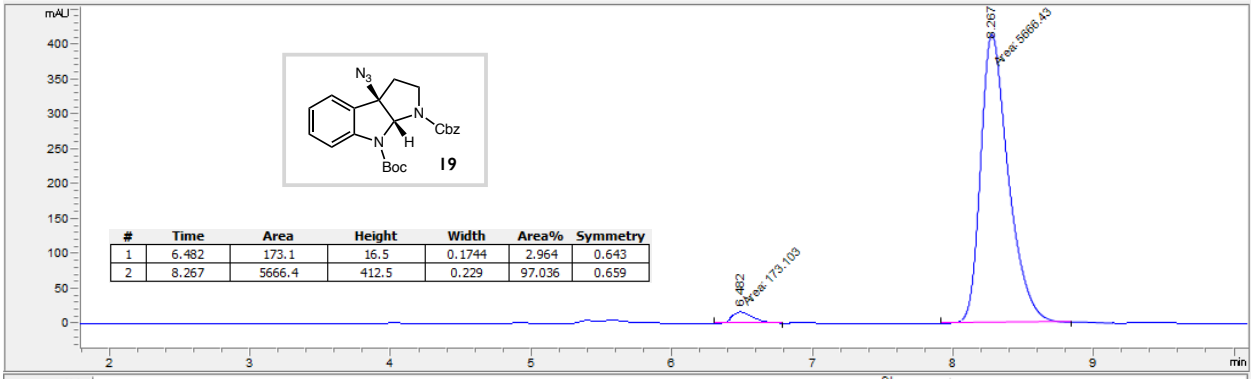
#	Time	Area	Height	Width	Area%	Symmetry
1	7.317	44.7	3.7	0.1505	3.221	0.682
2	7.781	1343.9	95.2	0.2081	96.779	0.556

18



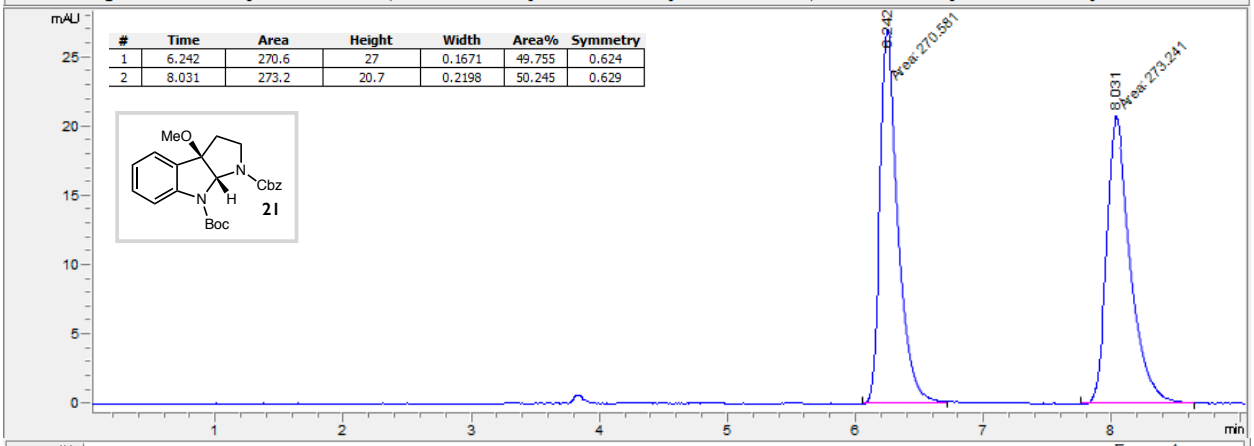
#	Time	Area	Height	Width	Area%	Symmetry
1	6.472	1255.6	117.3	0.1784	49.976	0.604
2	8.268	1256.8	93.3	0.2246	50.024	0.667

19



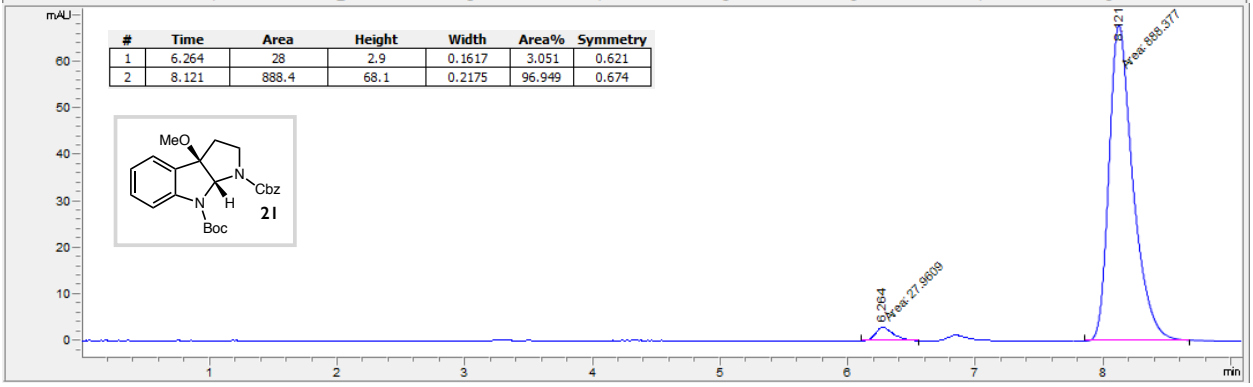
#	Time	Area	Height	Width	Area%	Symmetry
1	6.482	173.1	16.5	0.1744	2.964	0.643
2	8.267	5666.4	412.5	0.229	97.036	0.659

19



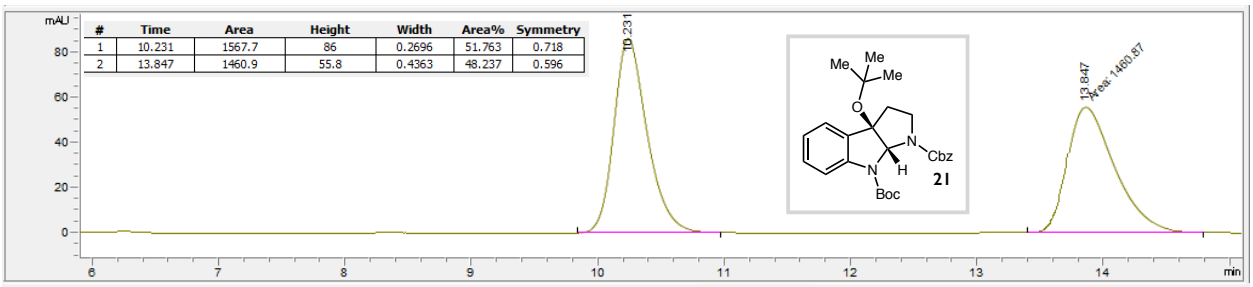
#	Time	Area	Height	Width	Area%	Symmetry
1	6.242	270.6	27	0.1671	49.755	0.624
2	8.031	273.2	20.7	0.2198	50.245	0.629

21

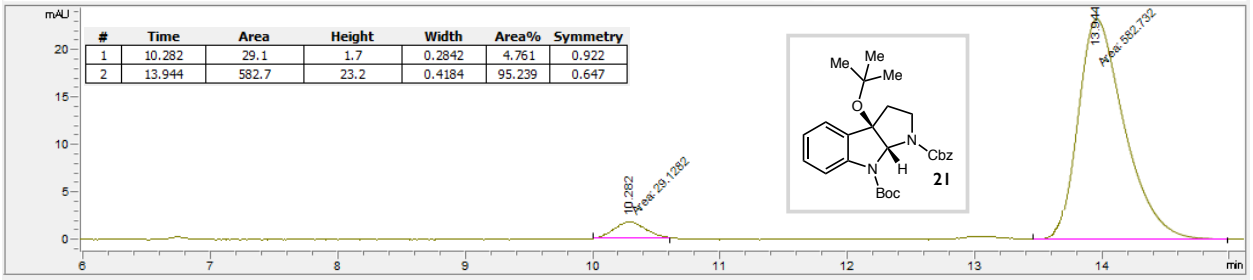


#	Time	Area	Height	Width	Area%	Symmetry
1	6.264	28	2.9	0.1617	3.051	0.621
2	8.121	888.4	68.1	0.2175	96.949	0.674

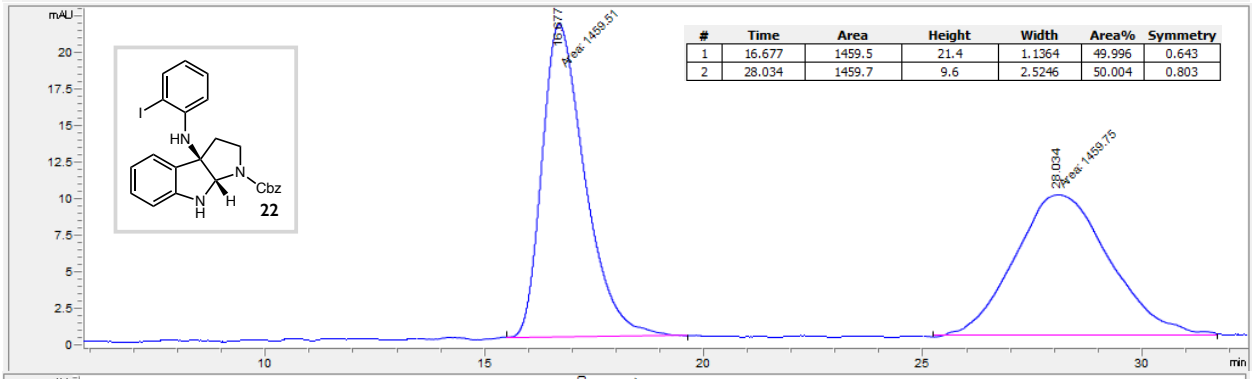
21



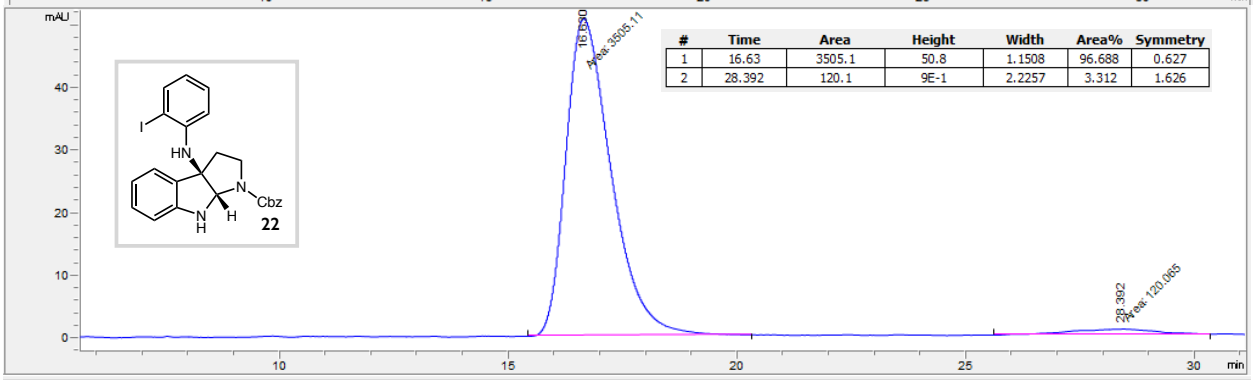
#	Time	Area	Height	Width	Area%	Symmetry
1	10.231	1567.7	86	0.2696	51.763	0.718
2	13.847	1460.9	55.8	0.4363	48.237	0.596



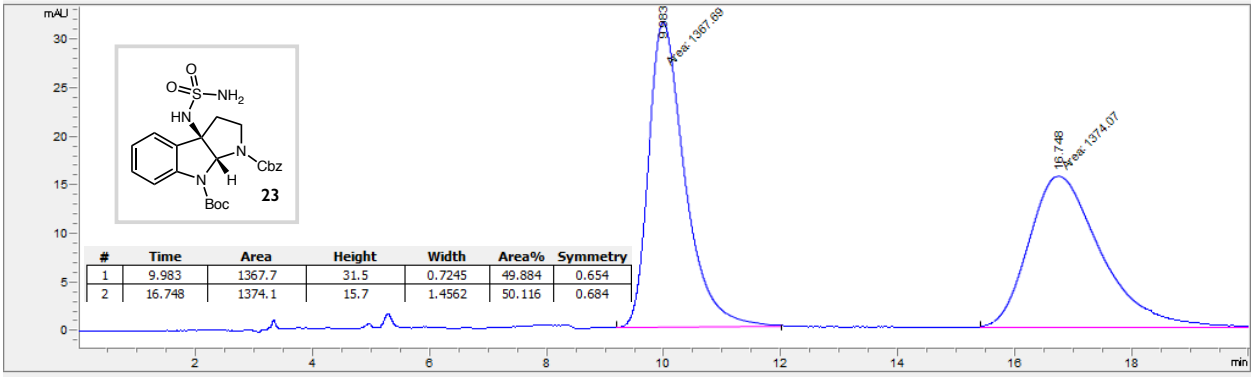
#	Time	Area	Height	Width	Area%	Symmetry
1	10.282	29.1	1.7	0.2842	4.761	0.922
2	13.944	582.7	23.2	0.4184	95.239	0.647



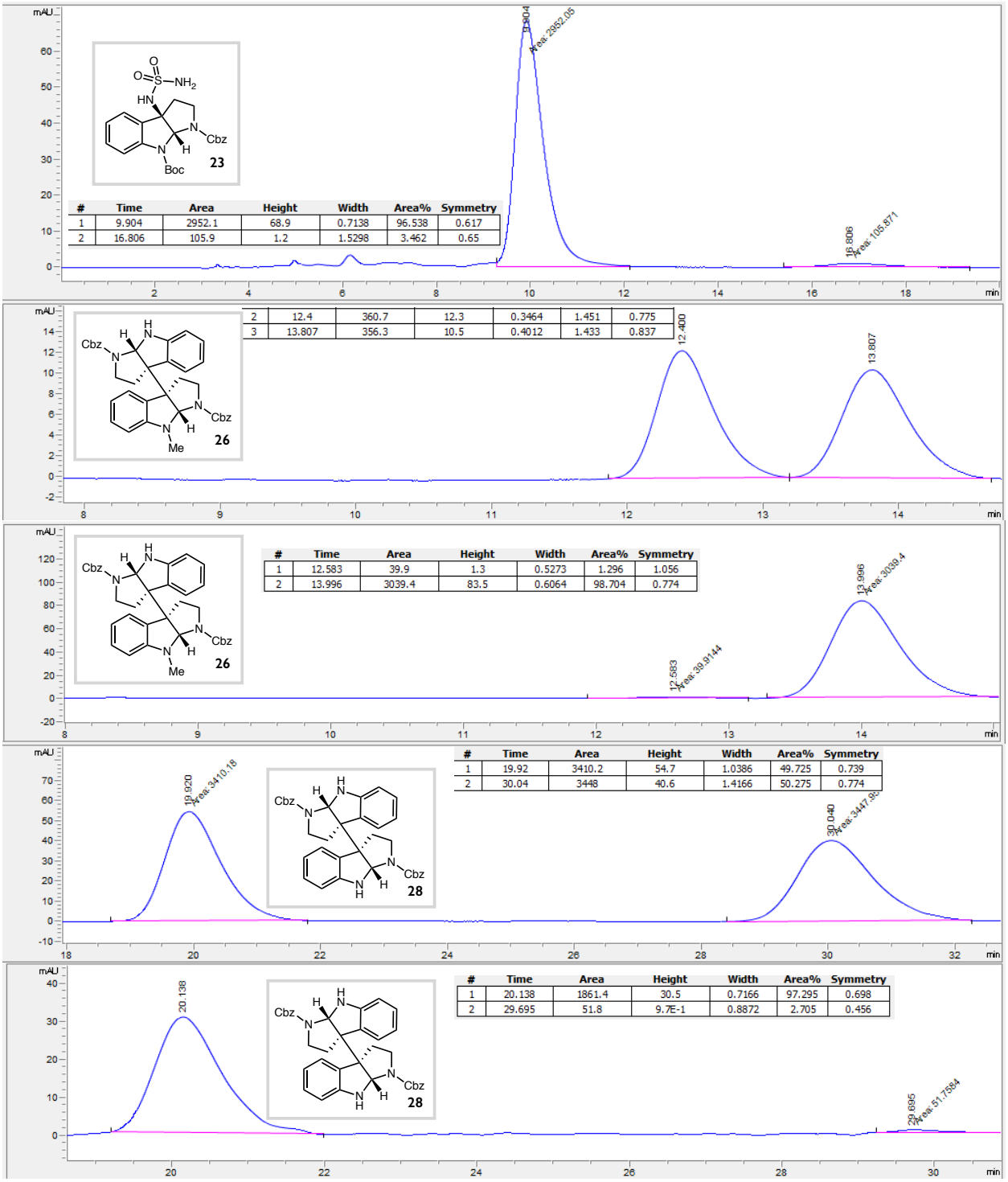
#	Time	Area	Height	Width	Area%	Symmetry
1	16.677	1459.5	21.4	1.1364	49.996	0.643
2	28.034	1459.7	9.6	2.5246	50.004	0.803



#	Time	Area	Height	Width	Area%	Symmetry
1	16.63	3505.1	50.8	1.1508	96.688	0.627
2	28.392	120.1	9E-1	2.2257	3.312	1.626



#	Time	Area	Height	Width	Area%	Symmetry
1	9.983	1367.7	31.5	0.7245	49.884	0.654
2	16.748	1374.1	15.7	1.4562	50.116	0.684



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