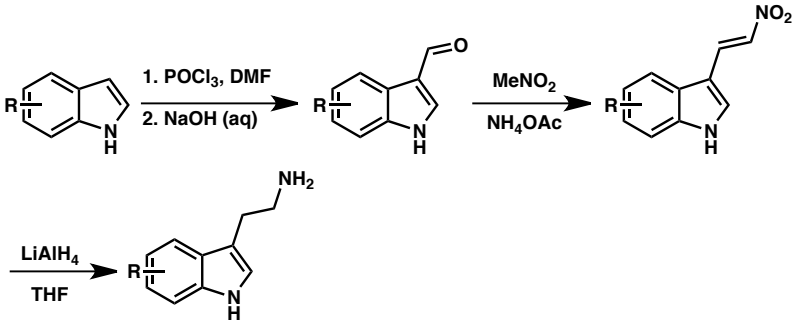
Supporting Information

I. General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Chiral anion phase-transfer (CAPT) pyrroloindolization reactions were performed in 2-dram (15 X 60 mm) vials equipped with a screw cap and stirred using a magnetic Teflon stir bar (1/2" X 5/16"), placed on the surface of a magnetic stir plate. Due to the heterogeneous nature of these reactions, it is important that fast and efficient stirring be maintained over the course of the reaction in order to obtain optimal results. Methyl *tert*-butyl ether (MTBE) was used as purchased from Fischer Scientific. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Merck silica gel 60 F254 TLC plates, and visualized under UV or by staining with ceric ammonium molybdate or $KMnO_4$. Column chromatography was performed on Merck Silica Gel 60 Å, 230 X 400 mesh. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker AV-600, AV-500, DRX-500, AVQ-400, AVB-400 and AV-300 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak ($CHCl_3$, δH = 7.26 ppm and δC = 77.0 ppm; DMSO, δH = 2.50 and δC = 39.5 ppm; CH_2Cl_2, δH = 5.32 and δC = 53.8 ppm). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, app t = apparent triplet, m = multiplet, br = broad resonance. Solvent abbreviations are reported as follows: MTBE = Methyl *tert*-butyl ether, EtOAc = ethyl acetate, hex = hexanes, DCM = dichloromethane, Et_2O = diethyl ether, MeOH = methanol, *i*PrOH = isopropanol, THF = tetrahydrofuran, DMF = N,N-dimethylformamide, Et_3N = triethylamine. Mass spectral data were obtained from the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley or by usage of an Agilent Time of Flight (Q-TOF) mass spectrometer in ESI mode. Enantiomeric excesses were measured on a Shimadzu VP Series Chiral HPLC using Chiralpak IA, IB, or IC columns. The syntheses of TRIP, H8-TRIP, TCYP, and STRIP, have been previously reported. **Caution:** Although we have not experienced any problems during the preparation and handling of the aryldiazounium tetrafluoroborates reported herein, appropriate safety precautions should be taken due to the explosive nature of diazonium salts, including the use of a blast shield. Racemic CAPT pyrroloindolinization products were synthesized utilizing racemic TRIP or under homogeneous conditions in the absence of phase-transfer catalyst with acetone as a solvent.

I. Experimental

*A. General procedure for synthesis of tryptamine derivatives **SI1**-**SI15***

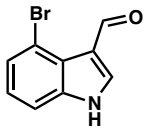


The synthesis of substituted tryptamines was adapted from the procedure of Dixon, *et al*.[2] To an oven-dried 250-mL round bottom flask was added dry DMF (20 mL) and a stir bar. The flask was cooled to 0 °C and $POCl_3$ (2.80 mL, 30 mmol, 1.5 equiv) was added dropwise. The solution was stirred for 15 min at this temperature before the addition of the

substituted indole (2.70 g, 20 mmol, 1.0 equiv) dissolved DMF (20 mL) over 15 min. The solution was subsequently heated at 38 °C for 1 hour, then cooled to rt at which point ice water (40 mL) was carefully added, followed by aqueous 1 N NaOH (20 mL), with vigorous stirring. Additional 1 N NaOH was added until the reaction mixture maintained a yellow color. The reaction was then heated at 170 °C and refluxed for 5 minutes before being allowed to cool to rt and stirred overnight. The mixture was then extracted with EtOAc (3 x 50 mL), and the combined organic layers were washed with water (2 x 75 mL), brine (2 x 70 mL), dried over magnesium sulfate, filtered, and concentrated to yield the aldehyde as a solid which required no further purification.

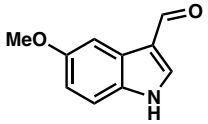
To an oven-dried 250-mL round bottom flask was added the crude aldehyde (14.6 mmol, 1.0 equiv), nitromethane (50 mL), and ammonium acetate (3.38 g, 43.9 mmol, 3.0 equiv). The reaction was then refluxed for 90 min with vigorous stirring. After this time, the reaction was concentrated to dryness *via* rotary evaporation and subsequently dissolved in EtOAc (60 mL). The organic layer was washed with water (50 mL), brine (50 mL), dried over magnesium sulfate, filtered and concentrated. The crude material was purified by flash column chromatography in 1:1 ethyl acetate/hexanes to afford the nitro alkene.

To an oven-dried 1-L round bottom flask containing a stir-bar was added solid LAH pellets (3.33 g, 87.84 mmol, 6.0 equiv) followed by dry THF (145 mL). The mixture was stirred in an ice bath to cool it to 0 °C. The nitro alkene (14.6 mmol, 1.0 equiv) was dissolved in THF (145 mL) and transferred to the cool LAH mixture *via* cannula over a period of 20 min. The mixture was allowed to slowly warm to rt and stir for 40 h. After this time, the reaction was cooled back to 0 °C before the slow addition of water (~15 mL) until the cessation of bubbles. Then the mixture was diluted with Et_2O (150 mL) followed by addition of saturated Rochelle's salt solution (200 mL). This mixture was then vigorously stirred for 24 hours. The layers were then separated and the aqueous layer was extracted with Et_2O (1 x 100 mL) and the collected organic layers extracted with 2 N HCl (3 x 75 mL). The aqueous layer was then cooled in an ice bath and basified with 3M KOH until pH ~ 10. This basic mixture was then extracted with Et_2O (3 x 75 mL), dried over magnesium sulfate, filtered, and concentrated to afford the pure tryptamine derivatives.



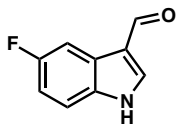
SI1

Following the first step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI1*** was isolated as a pale yellow solid in 52% yield whose NMR matched the published spectra.[13]



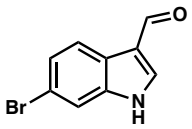
SI2

Following the first step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI2*** was isolated as a pale yellow solid in 79% yield whose NMR matched the published spectra.[14]



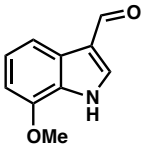
SI3

Following the first step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI3*** was isolated as a pale yellow solid in 73% yield whose NMR matched the published spectra.[2]



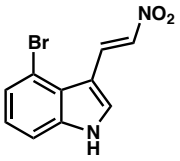
SI4

Following the first step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI4*** was isolated as a pale brown solid in 82% yield whose NMR matched the published spectra.[3]



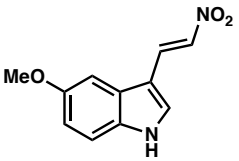
SI5

Following the first step of the general procedure for the synthesis of tryptamine derivatives (refluxed for 10 minutes), compound ***SI5*** was isolated as a pale yellow powder in 88% yield whose NMR matched the published spectra.[4]



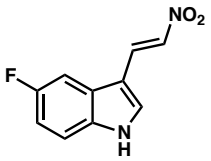
SI6

Following the second step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI6*** was isolated as a in 47% yield whose NMR matched the published spectra.[13]



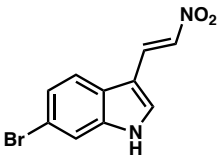
SI7

Following the second step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI7*** was isolated as a solid in 98% yield whose NMR matched the published spectra.[14]



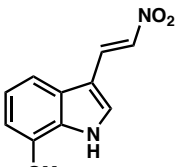
SI8

Following the second step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI8*** was isolated as a solid in 71% yield whose NMR matched the published spectra.[2]



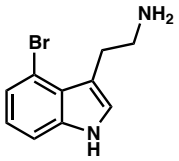
SI9

Following the second step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI9*** was isolated as a solid in 95% yield whose NMR matched the published spectra.[3]



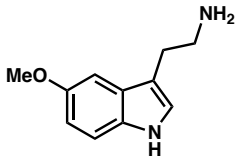
SI10

Following the second step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI10*** was isolated as a solid in 88% yield whose NMR matched the published spectra.[4]



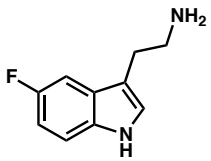
SI11

Following the third step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI11*** was isolated as a brown oil in 54% yield whose NMR matched the published spectra.[13]



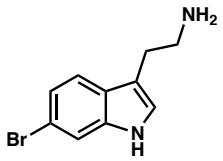
SI12

Following the third step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI12*** was isolated as a brown oil in 73% yield whose NMR matched the published spectra.[14]



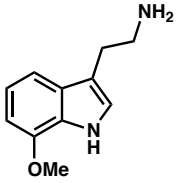
SI13

Following the third step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI13*** was isolated as a brown oil in 92% yield whose NMR matched the published spectra.[2]



SI14

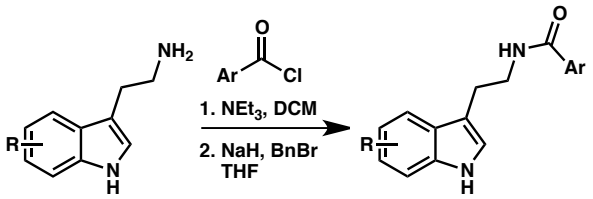
Following the third step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI14*** was isolated as a brown syrup in 77% yield whose NMR matched the published spectra.[3]



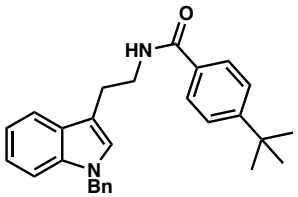
SI15

Following the third step of the general procedure for the synthesis of tryptamine derivatives, compound ***SI15*** was isolated as a brown oil in 73% yield whose NMR matched the published spectra.[4]

B. General amidation and benzylation procedures for for the synthesis of substrates ***SI17-SI27***

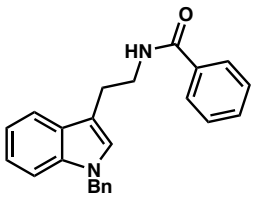


To an oven-dried 250 mL round bottom flask was added a stir-bar and the appropriate tryptamine (4.6 mmol, 1.0 equiv), Et_3N (1.3 mL, 9.2 mmol, 2.0 equiv), and dry DCM (20 mL). The solution was cooled to 0 °C before the dropwise addition of the 4-*t*-butylbenzoyl chloride (0.99 mL, 5.06 mmol, 1.1 equiv). The reaction was then stirred at room temperature for 3 h when TLC showed complete consumption of starting material. The reaction was then concentrated *via* rotary evaporation and the crude material was purified by flash column chromatography in 1:1 EtOAc/hex This material was then taken directly into the next step. The protected tryptamine (3.41 mmol, 1.0 equiv) was transferred to an oven-dried flask, dissolved in dry DMF (10 mL), and cooled to 0 °C. Sodium hydride (60 % dispersion in oil, 164 mg, 4.9 mmol, 1.2 equiv) was added slowly to the stirred solution. The reaction was then stirred at rt for 15 min before cooling back down to 0 °C, followed by dropwise addition of benzyl bromide (0.43 mL, 3.58 mmol, 1.05 equiv). The reaction was stirred cold for 5 minutes, before removal from the ice bath and stirring at rt for 16 hours. The reaction was quenched at 0 °C by the addition of aqueous ammonium chloride (10 mL) and water (10 mL). The mixture was extracted with EtOAc (3 x 25 mL) and the combined organic layers were washed with water (30 mL) and brine (30 mL), dried over magnesium sulfate, filtered, and concentrated. The crude reside was purified by flash column chromatography (1:4 to 1:1 EtOAc/hex) to afford pure product.



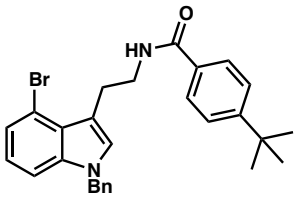
SI17

Following the general procedure for amidation and benzylation compound ***SI17*** was isolated as a white solid in 73% yield over two steps. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.32-7.20 (m, 5H), 7.15-7.09 (m, 3H), 7.00 (s, 1H), 6.29 (s, 1H), 5.27 (s, 2H), 3.79 (q, *J* = 6.3 Hz, 2H), 3.09 (t, *J* = 6.6 Hz, 2H), 1.33 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 154.8, 137.7, 136.9, 131.9, 128.9, 128.0, 127.7, 126.9, 126.76, 126.3, 125.5, 122.1, 119.4, 119.1, 112.4, 109.9, 50.0, 40.2, 35.0, 31.3, 25.4 ppm; HRMS (+ESI) calcd. for [$C_{28}H_{31}N_2O$] ([M+H$^+$]): 411.2431, found: 411.2425;



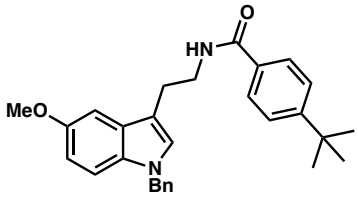
SI18

Following the general procedure for amidation (using benzoyl chloride) and benzylation compound ***SI18*** was isolated as a white solid in 70 % yield over two steps. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.64 (m, 3H), 7.48-7.44 (m, 1H), 7.37-7.34 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.28-7.25 (m, 3H), 7.21 (td, *J* = 7.6, 1.0 Hz, 1H), 7.15-7.09 (m, 3H), 6.99 (s, 1H), 6.30 (s, 1H), 5.27 (s, 2H), 3.79 (q, *J* = 6.3 Hz, 2H), 3.10 (t, *J* = 6.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 137.6, 136.9, 134.8, 131.4, 128.9, 128.6, 128.0, 127.7, 127.2, 126.9, 126.3, 122.2, 119.4, 119.1, 112.3, 109.9, 50.0, 40.3, 25.4; HRMS (+ESI) calcd. for [$C_{24}H_{23}N_2O$] ([M+H$^+$]): 355.1805, found: 355.1811.



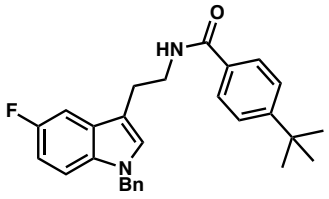
SI19

Following the general procedure for amidation (using benzoyl chloride) and benzylation compound ***SI19*** was isolated as a white solid in 54% yield over two steps. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.73-7.62 (m, 2H), 7.55-7.41 (m, 2H), 7.32 (m, 5H), 7.21-7.10 (m, 3H), 7.06 (t, *J* = 7.9 Hz, 1H), 5.27(s, 2H), 3.83 (dq, *J* = 21.9, 6.5 Hz, 2H), 3.39 (t, *J* = 6.8 Hz, 2H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 167.4, 155.2, 138.6, 137.7, 132.6, 129.3, 128.2, 127.3, 127.3, 127.1, 126.5, 125.9, 124.2, 123.1, 114.8, 113.5, 109.8, 50.6, 41.7, 35.3, 31.5, 26.5; HRMS (+ESI) calcd. for [$C_{24}H_{23}N_2O$] ([M+H$^+$]): 489.1536, found: 489.1542.



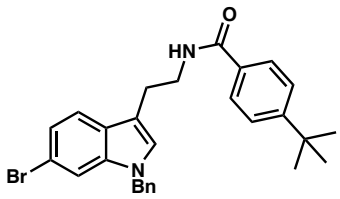
SI20

Following the general procedure for amidation (using benzoyl chloride) and benzylation, compound ***SI20*** was isolated as a white solid in 70% yield over two steps. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.66 – 7.53 (m, 2H), 7.46 – 7.35 (m, 2H), 7.34 – 7.21 (m, 3H), 7.16 (d, *J* = 8.9 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.06 (d, *J* = 2.4 Hz, 1H), 7.03 (s, 1H), 6.80 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.27 (t, *J* = 5.6 Hz, 1H), 5.25 (s, 2H), 3.74 (d, *J* = 14.3 Hz, 5H), 3.03 (t, *J* = 6.7 Hz, 2H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 167.3, 155.2, 154.5, 138.5, 132.5, 129.2, 128.9, 128.0, 128.0, 127.5, 127.3, 127.0, 125.9, 112.5, 112.4, 111.1, 101.1, 56.1, 50.6, 40.6, 35.3, 31.4, 25.8; HRMS (+ESI) calcd. for [$C_{29}H_{32}N_2O_2$] ([M+H$^+$]): 441.2537, found: 441.2540.



SI21

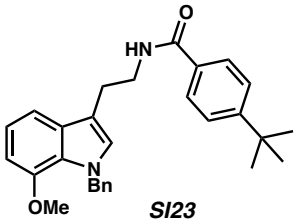
Following the general procedure for amidation and benzylation compound ***SI21*** was isolated as an off-white solid in 60% yield over two steps. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.48 (m, 2H), 7.45 – 7.33 (m, 2H), 7.33 – 7.22 (m, 5H), 7.17 (dd, *J* = 9.0, 4.3 Hz, 1H), 7.06 (dd, *J* = 6.4, 2.9 Hz, 2H), 6.23 (t, *J* = 5.6 Hz, 1H), 5.24 (s, 2H), 3.75 (q, *J* = 6.5 Hz, 2H), 3.02 (t, *J* = 6.8 Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 159.0, 157.2, 155.2, 137.6, 132.1, 128.3, 127.1, 127.0, 125.8, 112.5, 112.5, 110.9, 110.9, 110.7, 104.4, 104.2, 50.6, 40.3, 35.3, 31.5, 25.7; HRMS (+ESI) calcd. for [$C_{28}H_{30}N_2OF$] ([M+H$^+$]): 429.2337, found: 429.2338.



SI22

Following the general procedure for amidation and benzylation compound ***SI22*** was isolated as a white solid in 63% yield over two steps. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 1.7 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.24 (m, 3H), 7.21 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.06 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.95 (s, 1H), 6.28 – 6.12 (m, 1H), 5.21 (s, 2H), 3.75 (q, *J* = 6.5 Hz, 2H), 3.04 (t, *J* = 6.8 Hz, 2H), 1.32 (s, 9H); ^{13}C NMR (126 MHz,

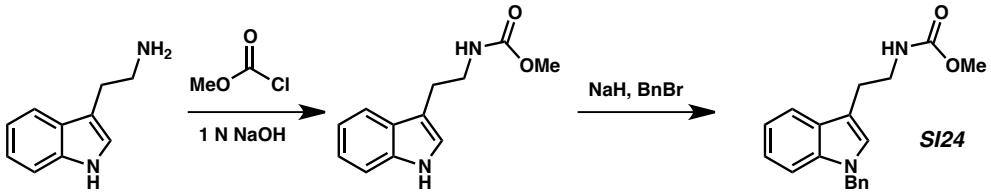
$CDCl_3$) δ 167.4, 154.9, 137.7, 137.1, 131.8, 129.0, 127.9, 126.9, 126.9, 126.8, 126.7, 125.6, 122.7, 120.5, 115.9, 112.9, 112.8, 50.0, 40.2, 35.0, 31.3, 25.4; HRMS (+ESI) calcd. for [$C_{28}H_{30}N_2OBr$] ([M+H^+]): 489.1536, found: 489.1535.



SI23

Following the general procedure for amidation and benzylation compound ***SI23*** was isolated as an off-white solid in 44% yield over two steps and was purified by recrystallization from hot EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 –7.49 (m, 2H), 7.46 – 7.33 (m, 2H), 7.33 – 7.20 (m, 4H), 7.12 (dd, *J* = 7.2, 2.2 Hz, 2H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.92 (s, 1H), 6.69 (d, *J* = 7.7 Hz, 1H), 6.21 (t, *J* = 5.3 Hz, 1H), 5.62 (s, 2H), 3.88 (s, 3H), 3.78 (q, *J* = 6.3 Hz, 2H), 3.06 (t, *J* = 6.6 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 154.7, 147.8, 139.8, 131.9, 130.2, 128.6, 127.3, 127.2, 126.8, 126.7, 126.6, 125.5, 119.9, 112.6, 111.9, 103.2, 55.5, 52.4, 40.0, 35.0, 31.3, 25.4; HRMS (+ESI) calcd. for [$C_{29}H_{32}N_2O_2$] ([M+H^+]): 441.2537, found: 441.2541.

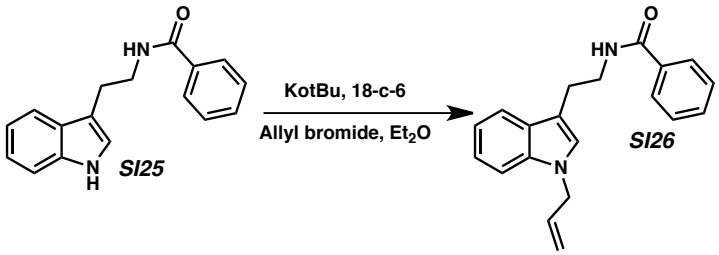
C. Synthesis of substrate ***SI24***



SI24

Moc-tryptamine was prepared in 90% yield following the procedure described by Skylar and Heathcock.[5] This carbamate was subsequently subjected to the general benzylation conditions and purified by flash chromatography (1:2 ethyl acetate/hexanes) to afford ***SI24*** as a colorless syrup (83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.20 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.17 – 7.08 (m, 3H), 6.97 (s, 1H), 5.29 (s, 2H), 4.79 (s, 1H), 3.67 (s, 3H), 3.53 (q, J = 6.6 Hz, 2H), 2.99 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 157.1, 137.6, 128.9, 127.7, 126.3, 119.3, 112.2, 109.9, 77.4, 77.4, 77.2, 76.9, 52.1, 50.0, 41.5, 25.9; HRMS (+ESI) calcd. for [$C_{19}H_{20}N_2O_2$] ([M+H^+]): 309.1958, found: 309.1961.

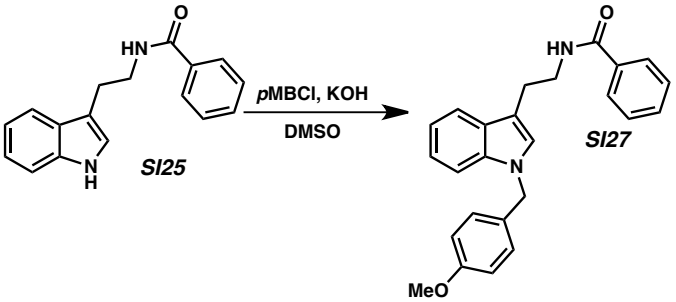
D. Synthesis of substrate ***SI26***



SI25 ***SI26***

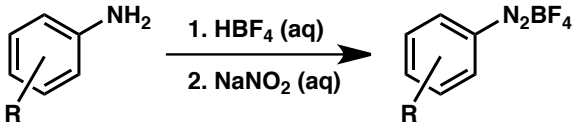
Tryptamine **SI25** (1.0 g, 3.8 mmol) was added to a mixture of 18-crown-6 (0.1 mg, 0.38 mmol), KO*t*Bu (508 mg, 4,5 mmol) in Et_2O (7.5 mL). The reaction mixture was cooled to 0 °C, at which time the allyl bromide (400 uL, 4.5 mmol) was added dropwise. The reaction was stireed at room temperature for 3 h, quenched with water, extracted in Et_2O and flashed in 1:1 EtOAc/hex to yield an orange powder. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.77 – 7.67 (m, 2H), 7.65 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.54 – 7.45 (m, 1H), 7.40 (tt, *J* = 6.6, 1.6 Hz, 2H), 7.36 – 7.28 (m, 1H), 7.21 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.10 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.00 (s, 1H), 6.46 (s, 1H), 6.00 (ddt, *J* = 17.1, 10.5, 5.4 Hz, 1H), 5.18 (dq, *J* = 10.2, 1.5 Hz, 1H), 5.06 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.70 (dt, *J* = 5.4, 1.7 Hz, 2H), 3.75 (td, *J* = 6.9, 5.6 Hz, 2H), 3.08 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 167.5, 137.1, 135.5, 134.3, 131.7, 128.9, 128.5, 127.3, 126.4, 122.2, 119.5, 119.4, 117.3, 112.5, 110.2, 49.1, 40.9, 25.8; HRMS (+ESI) calcd. for [$C_{20}H_{20}N_2O$] ([M+H^+]): 305.1648, found: 305.1653.

*E. Synthesis of substrate **SI27***



Tryptamine **SI25** (1.0 g, 3.8 mmol) and KOH (420 mg, 7.54 mmol) were strirred in DMSO (15 mL) for 1 hour. To the reaction mixture, *p*MBCl (1 mL, 7.54 mmol) was added dropwise. The reaction was stirred at rt overnight, quenched with water, extracted in EtOAc and flashed in 1:1 EtOAc/hex to yield an orange powder. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.77 – 7.57 (m, 3H), 7.55 – 7.44 (m, 1H), 7.44 –7.35 (m, 2H), 7.35 – 7.27 (m, 1H), 7.19 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.15 – 7.05 (m, 3H), 7.03 (s, 1H), 6.85 – 6.73 (m, 2H), 6.45 (s, 1H), 5.20 (s, 2H), 3.75 (d, *J* = 2.8 Hz, 5H), 3.08 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 167.5, 159.6, 137.2, 135.4, 131.7, 130.3, 128.9, 128.8, 128.7, 127.3, 126.7, 122.3, 119.5, 119.5, 114.5, 112.6, 110.3, 55.7, 49.9, 40.8, 25.8. HRMS (+ESI) calcd. for [$C_{25}H_{24}N_2O2$] ([M+H$^+$]): 385.1911, found: 385.1897.

F. Synthesis of aryldiazonium salts



The aniline (10mmol) was dissolved in a mixture of 50% (V/V) fluoroboric acid (3.5 mL) and water (4.0 mL). After cooling to 0° C, an aqueous solution of sodium nitrite (700 mg, 10.1 mmol, in 1.5 mL H_2O) was added in 0.25 mL portions. The mixture was stirred for 30 min and the thick precipitate was collected and dissolved in acetone. The diazonium tetrafluoroborate was then precipitated by the addition of Et_2O. The product was dried under high vacuum for several hours. Utilization of this procedure provided diazonium salts and yields comparable to those previously reported, and all spectral data that matched the data found in the literature; see the below references.

1. 4-Bromobenzenediazonium tetrafluoroborate, 4-fluorobenzenediazonium tetrafluoroborate, 4-*tert*-butylbenzenediazonium tetrafluoroborate, and 4-methoxycarbonylbenzenediazonium tetrafluoroborate.[6]

2. Benzenediazonium tetrafluoroborate, 4-methylcarbonylbenzenediazonium tetrafluoroborate, 4-methoxybenzenediazonium tetrafluoroborate, naphthalen-1-yl-diazonium tetrafluoroborate.[7]

3. 2-Chlorobenzenediazonium tetrafluoroborate.[8]

4. 2-Methylbenzenediazonium tetrafluoroborate, 3-methylbenzenediazonium tetrafluoroborate.[9]

5. 4-Trifluoromethylbenzenediazonium tetrafluoroborate.[10]

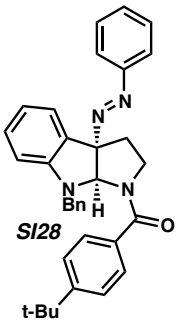
6. 3-Fluorobenzenediazonium tetrafluoroborate.[11]

7. 3-Bromo-4-methylbenzenediazonium tetrafluoroborate.[12]

G. General procedure for the phase-transfer diazenation reaction

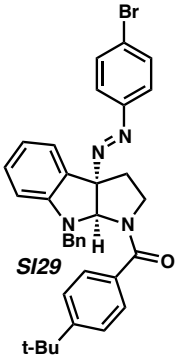
A suspension of the tryptamine (0.05 mmol), Na_3PO_4 (24 mg, 0.15 mmol, 3 equiv), and (*R*)-STRIP (1.8 mg, 0.0025 mmol, 5 mol%) in MTBE (0.5 mL) was stirred vigorously at rt for 15 minutes. To this suspension the aryldiazonium

salt (0.05 mmol, 1 equiv) was added rapidly in one portion. The reactions were stirred until TLC analysis indicated completion (1-12 h). The bright yellow reaction mixtures were filtered through cotton wool and the volatiles were removed by rotary evaporation. The crude product was dissolved in benzene and loaded onto a 1 cm column and eluted in 5:95 EtOAc:hex to yield yellow foams. The products were stable for several months at -20 °C neat, in protic solvents, or in pyridine. However, decomposition of some of the products occurred in halogenated solvents or aprotic polar solvents.



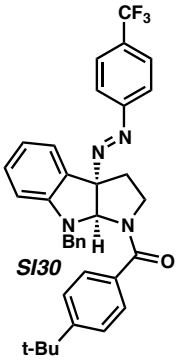
SI28

Following the general procedure for the diazenation, compound ***SI28*** was isolated in 99% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 7.69 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.45 (d, *J* = 5.9 Hz, 3H), 7.37 (t, *J* = 9.4 Hz, 4H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 2H), 7.21 (t, *J* = 7.0 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.81 (s, 1H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 7.8 Hz, 1H), 4.83 (s, 2H), 3.79 (t, *J* = 8.9 Hz, 1H), 3.58 (td, *J* = 11.5, 5.5 Hz, 1H), 2.59-2.47 (m, 2H), 1.30 (s, 9H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.1, 153.8, 151.8, 151.5, 139.5, 133.0, 131.1, 130.2, 129.1, 128.4, 127.5, 127.3, 127.0, 126.8, 125.12 125.1, 122.5, 117.5, 106.3, 88.7, 80.9, 49.9, 48.7, 36.6, 34.8, 31.0 ppm; HRMS (+ESI) calcd. for [$C_{34}H_{35}N_4O$] ([M+H$^+$]): 515.2805, found: 515.2797; HPLC (ChiralPak IB column) 98:02 (hex/*i*PrOH) 1mL/min; t_{major} (21.2 min), t_{minor} (26.7 min); 91% *ee.*



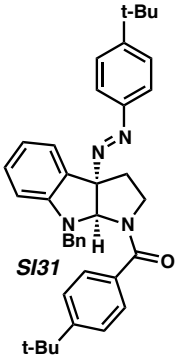
SI29

Following the general procedure for the diazenation, compound ***SI29*** was isolated in 82% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 7.63-7.59 (m, 4H), 7.42-7.33 (m, 6H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.15-7.12 (m, 1H), 6.82 (s, 1H), 6.71 (d, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 4.85 (s, 2H), 3.82 (dd, *J* = 10.6, 8.3 Hz, 1H), 3.61 (td, *J* = 11.5, 5.2 Hz, 1H), 2.60 (dd, *J* = 12.4, 5.1 Hz, 1H), 2.51 (td, *J* = 12.2, 7.8 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.1, 153.8, 151.5, 150.5, 139.4, 132.9, 132.3, 130.3, 128.4, 127.3, 127.0, 126.8, 126.5, 125.4, 125.2, 125.1, 124.2, 117.5, 106.4, 88.8, 80.7, 49.8, 48.7, 36.6, 34.8, 31.0 ppm; HRMS (+ESI) calcd. for [$C_{34}H_{34}N_4OBr$] ([M+H$^+$]): 593.1910, found: 593.1903; HPLC (ChiralPak IB column) 98:02 (hex/*i*PrOH) 1mL/min; t_{major} (12.1 min), t_{minor} (14.5 min); 88% *ee.*



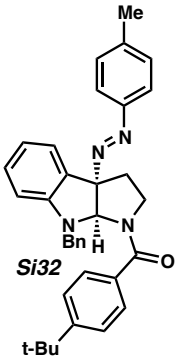
SI30

Following the general procedure for the diazenation, compound ***SI30*** was isolated in 88% yield. ^{1}H NMR (400 MHz; pyridine-d_5) δ 10.18 (s, 1H), 9.24 (s, 4H), 9.05-9.03 (m, 2H), 8.94 (t, J = 8.9 Hz, 3H), 8.80-8.66 (m, 6H), 8.34 (t, J = 7.3 Hz, 1H), 8.07 (d, J = 7.9 Hz, 1H), 6.55 (s, 2H), 5.30 (t, J = 8.9 Hz, 1H), 5.10 (td, J = 11.0, 4.7 Hz, 1H), 4.14 (dd, J = 12.3, 5.2 Hz, 1H), 4.02 (td, J = 12.0, 8.0 Hz, 1H), 2.73 (s, 9H); ^{13}C NMR (126 MHz, pyridine-d_5) δ 171.2, 154.8, 152.8, 151.2, 140.7, 136.7, 134.6, 133.0 (q, J = 32.1 Hz), 131.9, 129.8, 129.1, 128.5, 128.2, 127.8, 127.6, 126.6, 126.5, 124.7, 119.2, 108.2, 90.7, 81.9, 51.1, 49.8, 37.6, 35.8, 32.1; ^{19}F NMR (376 MHz, pyridine-d_5) δ -59.7 ppm; HRMS (+ESI) calcd. for [$C_{35}H_{34}N_4OF_3$] ([M+H$^+$]): 583.2679, found: 583.2668; HPLC (ChiralPak IB column) 98:02 (hex/*i*PrOH) 1mL/min; t_{major} (10.2 min), t_{minor} (13.3 min); 89% *ee.*



SI31

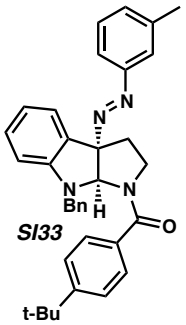
Following the general procedure for the diazenation, compound ***SI31*** was isolated in 53% yield. ^{1}H NMR (500 MHz; C_6D_6) δ 7.96 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 6.9 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.53 (d, J = 6.2 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.38-7.32 (m, 4H), 7.25 (t, J = 7.3 Hz, 2H), 6.92 (t, J = 7.4 Hz, 1H), 6.57 (d, J = 7.7 Hz, 1H), 5.16 (q, J = 21.3 Hz, 2H), 3.62-3.59 (m, 1H), 3.47-3.42 (m, 1H), 2.54-2.51 (m, 1H), 2.41 (q, J = 10.2 Hz, 1H), 1.36 (s, 9H), 1.35 (s, 9H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.0, 154.7, 153.7, 151.4, 149.6, 139.5, 133.0, 130.1, 128.3, 127.3, 127.0, 126.9, 126.7, 126.0, 125.1, 125.0, 122.2, 117.4, 106.2, 88.4, 80.9, 49.8, 48.7, 36.6, 34.9, 34.8, 31.0, 31.0; HRMS (+ESI) calcd. for [$C_{38}H_{43}N_4O$] ([M+H$^+$]): 571.3437, found: 571.3448; HPLC (ChiralPak IB column) 99:01 (hex/*i*PrOH) 1mL/min; t_{major} (13.6 min), t_{minor} (23.0 min); 93% *ee.*



Si32

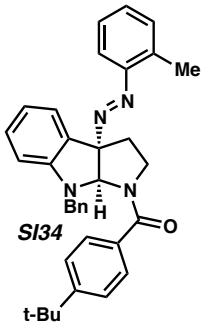
Following the general procedure for the diazenation, compound ***SI32*** was isolated in 66% yield. ^{1}H NMR (300 MHz; CD_2Cl_2) δ 7.63 (d, J = 8.4 Hz, 2H), 7.43-7.23 (m, 11H), 7.12 (t, J = 7.3 Hz, 2H), 6.83 (s, 1H), 6.70 (t, J = 7.3 Hz, 1H), 6.39 (d, J = 7.8 Hz, 1H), 4.86 (s, 2H), 3.85-3.77 (m, 1H), 3.66-3.59 (m, 1H), 2.58-2.51 (m, 2H), 2.41 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.0, 164.6, 153.7, 151.4, 149.8, 141.7, 139.4, 133.0, 130.1, 129.6, 128.3, 127.3, 127.0, 126.9, 126.7, 125.0, 122.5, 117.4, 106.2, 88.3, 80.9, 49.8, 48.7, 36.6, 34.7, 30.9, 21.2 ppm; HRMS (+ESI) calcd. for

$[C_{35}H_{37}N_4O]$ ($[M+H^+]$): 529.2962, found: 529.2980; HPLC (ChiralPak IB column) 98:02 (hex/*i*PrOH) 1mL/min; t_{major} (11.7 min), t_{minor} (14.5 min); 90% *ee.*



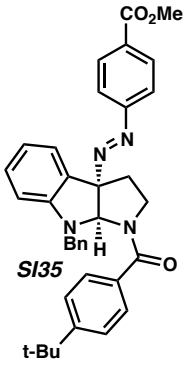
SI33

Following the general procedure for the diazenation, compound ***SI33*** was isolated in 91% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 7.51-7.50 (m, 2H), 7.40-7.32 (m, 7H), 7.28 (t, *J* = 7.4 Hz, 3H), 7.22 (d, *J* = 7.4 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.81 (s, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.39 (d, *J* = 7.9 Hz, 1H), 4.84 (s, 2H), 3.81 (dd, *J* = 10.5, 7.9 Hz, 1H), 3.60 (td, *J* = 11.4, 5.5 Hz, 1H), 2.60-2.49 (m, 2H), 2.41 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.5, 154.2, 152.3, 151.9, 139.9, 139.7, 133.5, 132.3, 130.7, 129.3, 128.9, 127.8, 127.4, 127.2, 125.6, 125.6, 123.2, 120.5, 117.9, 106.8, 89.1, 81.4, 50.3, 49.2, 37.0, 35.3, 31.5, 21.6 ppm; HRMS (+ESI) calcd. for $[C_{35}H_{37}N_4O]$ ($[M+H^+]$): 529.2967, found: 529.2979; HPLC (ChiralPak IB column) 98:02 (hex/*i*PrOH) 1mL/min; t_{major} (11.0 min), t_{minor} (14.1 min); 93% *ee.*



SI34

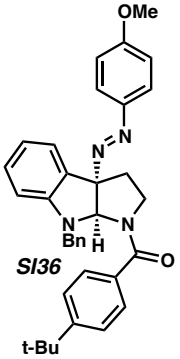
Following the general procedure for the diazenation, compound ***SI34*** was isolated in 87% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ; 7.41-7.28 (m, 11H), 7.22-7.19 (m, 2H), 7.12 (t, *J* = 7.8 Hz, 2H), 6.84 (s, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 4.88-4.81 (m, 2H), 3.82 (dd, *J* = 9.9, 7.9 Hz, 1H), 3.62 (td, *J* = 11.3, 5.8 Hz, 1H), 2.57-2.49 (m, 5H), 1.32 (s, 9H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.6, 154.2, 151.9, 150.3, 140.0, 137.9, 131.6, 131.4, 130.6, 128.9, 127.8, 127.7, 127.4, 127.3, 127.2, 126.8, 125.6, 118.3, 116.1, 107.0, 89.8, 82.0, 50.4, 48.7, 37.1, 35.3, 31.4, 30.1, 18.0 ppm; HRMS (+ESI) calcd. for $[C_{35}H_{37}N_4O]$ ($[M+H^+]$): 529.2962, found: 529.2980; HPLC (ChiralPak IB column) 98:02 (hex/*i*PrOH) 1mL/min; t_{major} (21.2 min), t_{minor} (26.7 min); 91% *ee.*



SI35

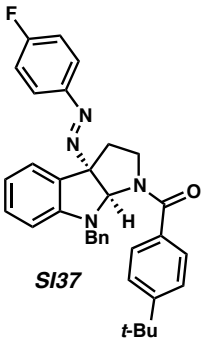
Following the general procedure for the diazenation, compound ***SI35*** was isolated in 77% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 8.16 (d, *J* = 7.8 Hz, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.45-7.26 (m, 10H), 7.17 (q, *J* = 6.5 Hz, 1H), 6.87 (s, 1H), 6.74 (t, *J* = 5.0 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 4.88 (s, 2H), 3.96 (s, 3H), 3.87 (t, *J* = 7.8 Hz, 1H), 3.68-3.63 (m, 1H), 2.67-2.53 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.0, 166.2, 164.6, 154.2, 153.7, 151.4, 139.3, 132.8, 132.1, 130.4, 130.3, 128.3, 127.3, 126.9, 126.8, 125.1, 122.4, 117.5, 106.4, 89.2, 80.6, 52.2, 49.8, 48.6, 36.5, 34.8, 30.9; HRMS

(+ESI) calcd. for [$C_{36}H_{37}N_4O_3$] ([M+H$^+$]): 573.2866, found: 573.2870; HPLC (ChiralPak IB column) 98:02 (hex/*i*PrOH) 1mL/min; t_{major} (23.8 min), t_{minor} (27.3 min); 87% *ee.*



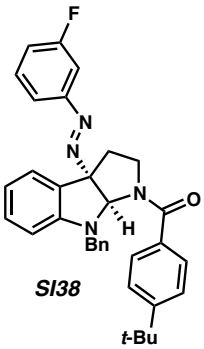
SI36

Following the general procedure for the diazenation, compound ***SI36*** was isolated in 63% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 7.72 (d, *J* = 8.9 Hz, 2H), 7.41-7.37 (m, 3H), 7.34-7.28 (m, 3H), 7.23 (d, *J* = 7.0 Hz, 4H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.80 (s, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 1H), 4.85 (s, 2H), 3.86 (s, 3H), 3.82-3.79 (m, 1H), 3.60 (td, *J* = 11.4, 5.4 Hz, 1H), 2.59-2.48 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.5, 162.6, 154.2, 151.9, 146.4, 140.0, 133.5, 130.5, 128.8, 127.8, 127.4, 127.2, 125.6, 125.5, 124.9, 117.9, 114.5, 106.7, 88.5, 81.5, 56.1, 50.3, 49.2, 37.2, 35.3, 31.5, 30.3 ppm; HRMS (+ESI) calcd. for [$C_{35}H_{37}N_4O_2$] ([M+H$^+$]): 545.2911, found: 545.2928; HPLC (ChiralPak IB column) 97:03 (hex/*i*PrOH) 1mL/min; t_{major} (18.3 min), t_{minor} (16.9 min); 94% *ee.*



SI37

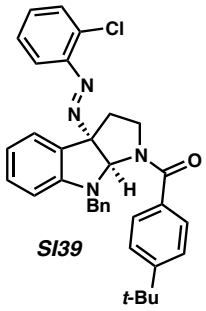
Following the general procedure for the diazenation, compound ***SI37*** was isolated in 79% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 7.83–7.75 (m, 2H), 7.48–7.12 (m, 13H), 6.86 (s, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 4.89 (s, 2H), 3.86 (dd, *J* = 11.1, 7.7 Hz, 1H), 3.65 (td, *J* = 11.6, 5.5 Hz, 1H), 2.60 (ddd, *J* = 36.1, 12.4, 6.6 Hz, 2H), 1.37 (s, 9H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.5, 165.9, 163.9, 154.2, 151.9, 148.8, 139.9, 133.4, 130.7, 128.9, 127.8, 127.4, 127.3, 125.5, 125.2, 125.1, 118.0, 116.4, 106.8, 89.0, 81.3, 50.3, 49.2, 37.1, 35.3, 31.5; HRMS (+ESI) calcd. for [$C_{34}H_{33}FN_4O$] ([M+H$^+$]): 533.2711, found: 533.2714; HPLC (ChiralPak IB column) 99:01 (hex/*i*PrOH) 1mL/min; t_{major} (16.6 min), t_{minor} (25.9 min); 93% *ee.*



SI38

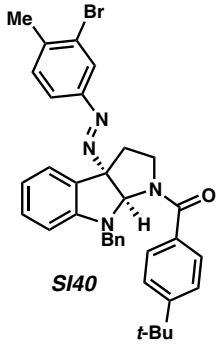
Following the general procedure for the diazenation, compound ***SI38*** was isolated in 95% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 7.59 (dt, *J* = 8.0, 1.3 Hz, 1H), 7.52–7.11 (m, 14H), 6.84 (s, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 7.9 Hz, 1H), 4.86 (s, 2H), 3.83 (dd, *J* = 11.2, 7.5 Hz, 1H), 3.62 (td, *J* = 11.6, 5.4 Hz, 1H), 2.62 (dd, *J* = 12.5, 5.4 Hz, 1H), 2.52 (td, *J* =

12.3, 7.7 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.5, 164.6, 162.7, 154.3, 153.7, 153.7, 151.9, 139.8, 133.4, 130.9, 128.9, 127.8, 127.5, 127.3, 127.0, 125.6, 120.7, 118.4, 118.2, 108.5, 106.9, 89.3, 81.1, 50.3, 49.1, 37.0, 35.3, 31.5; HRMS (+ESI) calcd. for [$C_{34}H_{33}FN_4O$] ([M+H$^+$]): 533.2711, found: 533.2713; HPLC (ChiralPak IB column) 99:01 (hex/*i*PrOH) 1mL/min; t_{major} (16.7 min), t_{minor} (23.1 min); 91% *ee.*



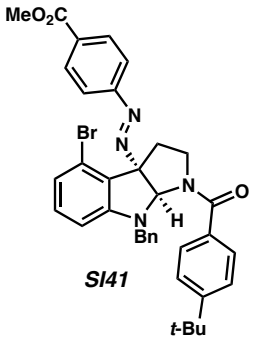
SI39

Following the general procedure for the diazenation, compound ***SI39*** was isolated in 87% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.43–7.13 (m, 13H), 6.88 (s, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 7.9 Hz, 1H), 5.32 (s, 1H), 4.85 (s, 2H), 3.87 – 3.79 (m, 1H), 3.63 (td, *J* = 11.2, 6.0 Hz, 1H), 2.61–2.51 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 165.3, 154.5, 152.2, 140.1, 134.9, 133.6, 132.5, 131.2, 129.1, 128.1, 128.0, 127.6, 127.5, 127.4, 126.9, 126.0, 125.9, 118.6, 118.3, 107.1, 90.2, 82.1, 50.6, 49.5, 37.3, 35.5, 31.7; HRMS (+ESI) calcd. For [$C_{34}H_{33}FN_4O$] ([M+H$^+$]): 549.2416, found: 549.2421; HPLC (ChiralPak IB column) 99:01 (hex/*i*PrOH) 1mL/min; t_{major} (22.3 min), t_{minor} (52.3 min); 91% *ee.*



SI40

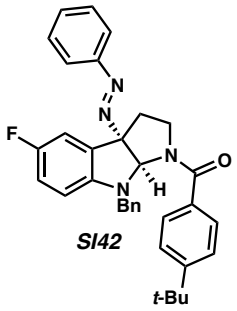
Following the general procedure for the diazenation, compound ***SI40*** was isolated in 93% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 7.88 (d, *J* = 2.1 Hz, 1H), 7.61 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.43 –7.08 (m, 12H), 6.79 (s, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 4.84 (s, 2H), 3.82 (dd, *J* = 11.1, 7.6 Hz, 1H), 3.60 (td, *J* = 11.5, 5.4 Hz, 1H), 2.55 (ddd, *J* = 36.2, 12.4, 6.6 Hz, 2H), 2.45 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 154.2, 151.9, 151.1, 141.6, 139.9, 133.4, 131.6, 130.7, 128.8, 127.8, 127.5, 127.1, 125.9, 125.7, 125.6, 125.6, 123.0, 118.0, 106.9, 100.5, 89.1, 81.2, 50.3, 49.2, 37.0, 35.3, 31.5, 23.2; HRMS (+ESI) calcd. for [$C_{30}H_{27}N_4O$] ([M+H$^+$]): 607.2067, found: 607.2071; HPLC (ChiralPak IB column) 99:01 (hex/*i*PrOH) 1mL/min; t_{major} (17.8 min), t_{minor} (27.8 min); 90% *ee.*



SI41

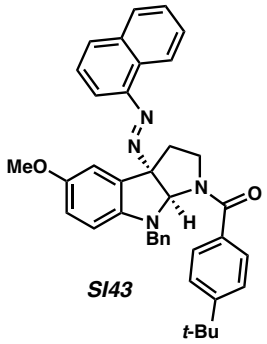
Following the general procedure for the diazenation, compound ***SI41*** was isolated in 39% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H) 7.50-7.09 (m, 9H), 7.01 (t, *J* = 8.1 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 6.48 (s, 1H), 6.38 (d, *J* = 8.1 Hz, 1H), 4.81 (s, 2H), 3.91 (app. s, 4H), 3.69 (m, 1H), 3.09 (dd, *J* = 13.0, 5.2 Hz, 1H),

2.91(td, J = 12.7, 8.4 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.2, 166.5, 154.6, 154.2, 153.8, 138.9, 132.9, 132.5, 132.0, 130.8, 130.7, 128.7, 127.6, 127.1, 125.8, 125.5, 122.7, 121.6, 105.7, 90.1, 81.5, 52.6, 49.9, 49.3, 35.1, 34.7, 31.2, 30.0; HRMS (+ESI) calcd. for [$C_{36}H_{35}N_4O_3Br$] ([M+H$^+$]): 651.1971, found: 651.1974; HPLC (ChiralPak IB column) 99:01 (hex/*i*PrOH) 1mL/min; t_{major} (23.3 min), t_{minor} (27.9 min); 89% *ee.*



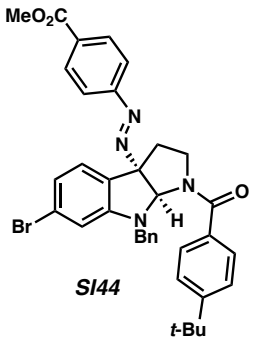
SI42

Following the general procedure for the diazenation, compound ***SI42*** was isolated in 80% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.72 (dd, J = 6.5, 3.0 Hz, 2H), 7.52 – 7.08 (m, 12H), 7.01 (d, J = 7.9 Hz, 1H), 6.90 – 6.72 (m, 2H), 6.28 (dd, J = 8.7, 4.0 Hz, 1H), 4.82 (s, 2H), 3.84 (t, J = 9.7 Hz, 1H), 3.63 (dt, J = 17.5, 7.8 Hz, 1H), 2.54 (dt, J = 13.1, 5.6 Hz, 2H), 1.32 (d, J = 2.7 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 165.1, 152.1, 148.3, 139.7, 131.7, 129.6, 128.7, 127.5, 127.3, 126.7, 125.7, 123.1, 117.2, 116.7, 116.5, 113.1, 112.9, 107.1, 88.7, 82.1, 51.0, 49.2, 37.2, 35.3, 31.5; HRMS (+ESI) calcd. for [$C_{34}H_{33}FN_4O$] ([M+H$^+$]): 533.2711, found: 533.2716; HPLC (ChiralPak IB column) 99:01 (hex/*i*PrOH) 1mL/min; t_{major} (46.4 min), t_{minor} (56.0 min); 86% *ee.*



SI43

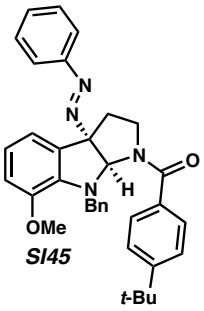
Following the general procedure for the diazenation, compound ***SI43*** was isolated in 67% yield. ^{1}H NMR (500 MHz, Pyridine-d_5) δ 8.92 (d, J = 7.9 Hz, 1H), 8.00 (dd, J = 23.6, 8.0 Hz, 3H), 7.73 (m, 5H), 7.56 – 7.47 (m, 4H), 7.42 (s, 1H), 7.37 (s, 1H), 7.31 (q, J = 6.7, 5.9 Hz, 3H), 6.94 (d, J = 8.8 Hz, 1H), 6.58 (d, J = 8.6 Hz, 1H), 5.22 (s, 2H), 3.91 (t, J = 9.4 Hz, 1H), 3.72 (m, 4H), 2.87 – 2.74 (m, 1H), 2.68 (d, J = 9.9 Hz, 1H), 1.28 (s, 9H);^{13}C NMR (126 MHz, Pyridine-d_5) δ 171.1, 154.5, 154.3, 147.7, 147.0, 140.8, 136.8, 135.8, 135.3, 134.6, 132.5, 131.8, 130.1, 129.7, 129.5, 129.4, 129.4, 129.1, 127.9, 127.7, 126.7, 126.4, 116.7, 113.5, 113.3, 108.7, 90.7, 83.1, 51.9, 49.8, 37.8, 35.6, 32.8, 30.3; HRMS (+ESI) calcd. for [$C_{39}H_{38}N_4O_2$] ([M+H$^+$]): 595.3068, found: 595.3059; HPLC (ChiralPak IB column) 99:01 (hex/*i*PrOH) 1mL/min; t_{major} (35.3 min), t_{minor} (53.6 min); 88% *ee.*



SI44

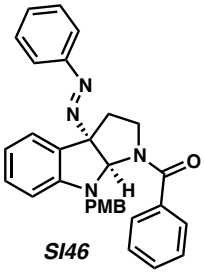
Following the general procedure for the diazenation, compound ***SI44*** was isolated in 52% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 8.16 (d, J = 8.1 Hz, 2H), 7.84 – 7.70 (m, 2H), 7.51 – 7.23 (m, 9H), 7.14 (d, J = 7.8 Hz, 1H), 6.87 (s, 2H), 6.65 –

6.49 (m, 1H), 5.09 (s, 2H), 4.84 (d, *J* = 5.7 Hz, 1H), 4.07 – 3.78 (m, 4H), 3.66 (s, 1H), 2.57 (ddd, *J* = 24.4, 12.4, 7.0 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 168.40, 166.15, 164.54, 130.43, 128.42, 127.26, 126.75, 122.36, 80.72, 53.89, 53.68, 53.46, 53.25, 53.03, 52.25, 49.47, 48.64, 34.75, 30.89; HRMS (+ESI) calcd. for [$C_{36}H_{35}BrN_4O_3$] ([M+H$^+$]): 459.2179, found: 459.2187; HPLC (ChiralPak IB column) 98:02 (hex/*i*PrOH) 1mL/min; t_{major} (36.1 min), t_{minor} (46.8 min); 92% *ee.*



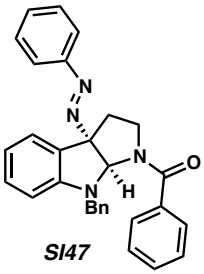
SI45

Following the general procedure for the diazenation, compound ***SI45*** was isolated in 99% yield. ^{1}H NMR (500 MHz, pyridine-d_5) δ 8.26 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.57 – 7.47 (m, 4H), 7.29 (m, 6H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.92 (s, 1H), 5.08 (s, 2H) 3.84 (d, *J* = 2.4 Hz, 5H), 2.65 (s, 2H), 1.28 (d, *J* = 2.8 Hz, 9H); ^{13}C NMR (126 MHz, Pyridine-d_5) δ 171.0, 166.9, 155.0, 154.7, 153.8, 139.8, 134.2, 133.4, 131.6, 129.6, 128.8, 128.1, 128.1, 127.9, 126.9, 126.3, 123.6, 121.4, 110.6, 89.8, 81.8, 50.4, 49.6, 37.4, 35.6, 31.8, 30.7; HRMS (+ESI) calcd. for [$C_{35}H_{36}N_4O_2$] ([M+H$^+$]): 545.2911, found: 545.2922; HPLC (ChiralPak IB column) 98:02 (hex/*i*PrOH) 1mL/min; t_{major} (88.1 min), t_{minor} (114.9 min); 96% *ee*.



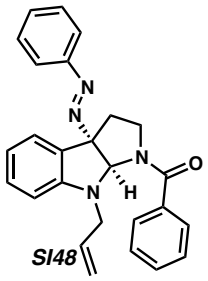
SI46

Following the general procedure for the diazenation, compound ***SI46*** was isolated in 58% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 7.87 – 7.62 (m, 2H), 7.62 – 7.09 (m, 12H), 6.89 – 6.80 (m, 3H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.9 Hz, 1H), 4.82 (d, *J* = 4.1 Hz, 2H), 3.78 (s, 4H), 3.61 (td, *J* = 11.5, 5.2 Hz, 1H), 2.71 – 2.46 (m, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.4, 165.1, 159.2, 152.2, 151.9, 136.5, 131.8, 131.5, 130.7, 129.5, 128.8, 127.9, 127.3, 125.6, 123.0, 118.0, 114.2, 107.0, 89.1, 81.1, 55.7, 49.8, 49.1, 37.1, 30.2; HRMS (+ESI) calcd. for [$C_{31}H_{28}N_4O2$] ([M+H$^+$]): 489.2285, found: 489.2287; HPLC (ChiralPak IB column) 98:02 (hex/*i*PrOH) 1mL/min; t_{major} (22.0 min), t_{minor} (18.2 min); 90% *ee.*



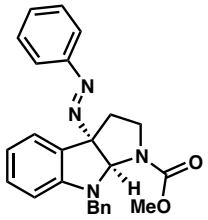
SI47

Following the general procedure for the diazenation, compound ***SI47*** was isolated in 85% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 7.71 (d, *J* = 5.7 Hz, 2H), 7.50-7.30 (m, 10H), 7.29 (t, *J* = 7.1 Hz, 2H), 7.23 (t, *J* = 6.9 Hz, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 6.83 (s, 1H), 6.70 (t, *J* = 7.0 Hz, 1H), 6.41 (d, *J* = 7.5 Hz, 1H), 4.86-4.84 (m, 2H), 3.77-3.73 (m, 1H), 3.62-3.56 (m, 1H), 2.62-2.50 (m, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.4, 165.1, 152.3, 151.9, 140.0, 136.5, 131.6, 130.7, 129.6, 129.5, 128.9, 128.7, 127.8, 127.4, 127.3, 125.6, 123.0, 118.0, 106.8, 89.1, 81.3, 50.3, 49.1, 37.1; HRMS (+ESI) calcd. for [$C_{30}H_{27}N_4O$] ([M+H$^+$]): 459.2179, found: 459.2187; HPLC (ChiralPak IB column) 98:02 (hex/*i*PrOH) 1mL/min; t_{major} (20.0 min), t_{minor} (17.3 min); 89% *ee.*



SI48

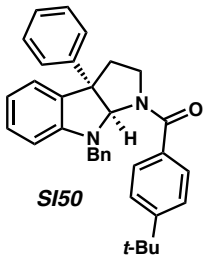
Following the general procedure for the diazenation, compound ***SI48*** was isolated in 98% yield. ^{1}H NMR (500 MHz; CD_2Cl_2) δ 7.73 (dd, *J* = 7.2, 2.4 Hz, 2H), 7.45 (ddt, *J* = 34.2, 13.5, 6.1 Hz, 8H), 7.18 (ddd, *J* = 20.0, 11.9, 7.3 Hz, 2H), 6.73 (s, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.9 Hz, 1H), 6.05 – 5.89 (m, 1H), 5.28 (dd, *J* = 17.2, 2.2 Hz, 1H), 5.14 (d, *J* = 10.2 Hz, 1H), 4.37 – 4.15 (m, 2H), 3.81 – 3.67 (m, 1H), 3.55 (td, *J* = 11.3, 6.1 Hz, 1H), 2.54 (qd, *J* = 11.7, 6.5 Hz, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.4, 165.1, 152.3, 136.6, 130.8, 129.5, 128.8, 128.5, 127.9, 127.8, 125.4, 123.0, 117.9, 115.9, 107.1, 89.0, 81.3, 66.2, 49.2, 42.2, 36.9, 30.2; HRMS (+ESI) calcd. for [$C_{30}H_{27}N_4O$] ([M+H$^+$]): 409.2023, found: 409.2027; HPLC (ChiralPak IB column) 99:01 (hex/*i*PrOH) 1mL/min; t_{major} (13.2 min), t_{minor} (14.9 min); 69% *ee*.



SI49

Following the general procedure for the diazenation, compound ***SI49*** was isolated in 85% yield. ^{1}H NMR (500 MHz; CD_2Cl_2): δ 7.72 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.66-7.11 (m, 15H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.92-6.77 (m, 2H), 6.41 (d, *J* = 7.5 Hz, 1H), 4.86-4.84 (m, 2H), 3.77-3.73 (m, 1H), 3.62-3.56 (m, 1H), 2.62-2.50 (m, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2): δ 170.4, 165.1, 152.3, 151.9, 140.0, 136.5, 131.6, 130.7, 129.6, 128.9, 128.71, 127.8, 127.4, 127.3, 125.6, 123.0, 118.0, 106.8, 89.1, 81.3, 50.3, 49.1, 37.1 ppm; HRMS (+ESI) calcd. for [$C_{25}H_{24}N_4O_2$] ([M+H$^+$]): 413.1972, found: 413.1976; HPLC (ChiralPak IB column) 99:01 (hexane/*i*PrOH) 1mL/min; t_{major} (9.0 min), t_{minor} (8.0 min); 73% *ee.*

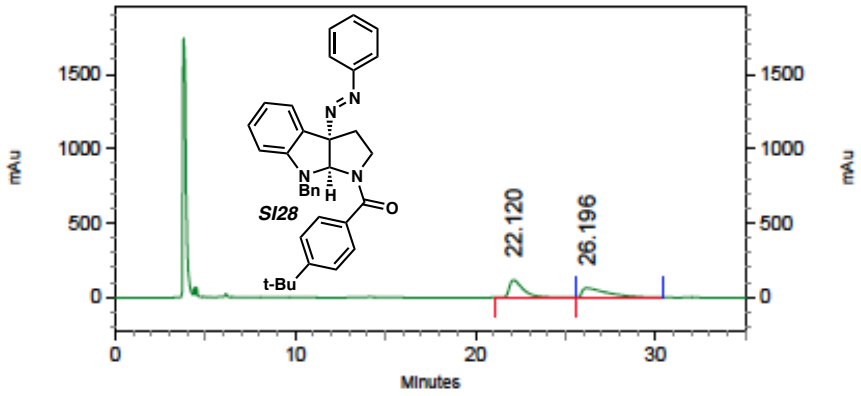
G. Procedure for photolysis reaction



SI50

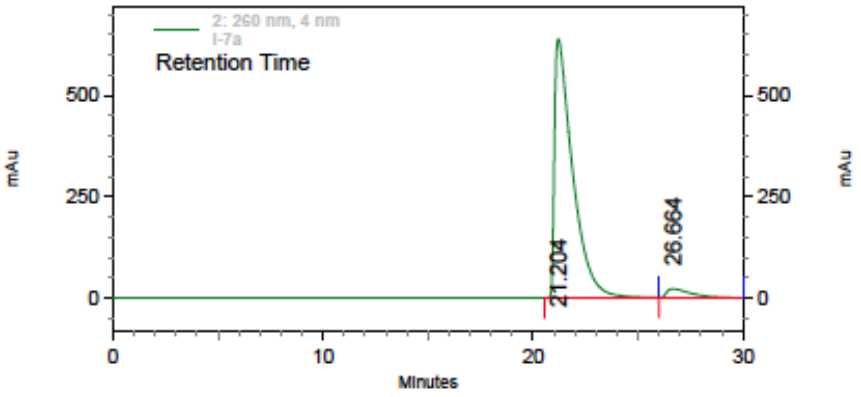
SI28 (xx mg, xx mmol) was dissolved cyclohexane (xx mL) in a 20 mL pyrex round-bottom flask, and sparged with nitrogen for 1 hour. The solvent was removed by rotary evaporation at elevated temperature (ca. 35 °C) to avoid freezing the cyclohexane. It is imperative that rapid rotation is maintained, as a widely-distributed, thin film is desired. The flask was backfilled with nitrogen and placed in a Rayonet photobox equiped with UVB spectrum bulbs for 12 h. NMR analysis using Toluene as an internal standard in CD_2Cl_2 indicated 78% conversion of starting material and 42% yield of the product. The product (***SI50***) was difficult to separate from the starting diazene in good yield. Extension of the reaction times, followed by preparatory TLC, allowed for isolation of the product in 36% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.49 – 7.24 (m, 14H), 7.09 (td, *J* = 7.6, 1.3 Hz, 1H), 7.06 – 6.99 (d, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.50 – 6.37 (m, 2H), 5.00 – 4.63 (m, 2H), 3.90 – 3.73 (m, 1H), 3.59 – 3.37 (m, 1H), 2.69 – 2.52 (m, 2H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 170.09, 153.72, 150.12, 145.05, 139.38, 133.08, 132.96, 129.47, 128.59, 128.51, 128.33, 127.37, 127.00, 126.75, 125.61, 125.04, 123.85, 117.61, 115.20, 106.39, 85.35, 59.42, 49.43, 38.40, 34.72, 30.91; HRMS (+ESI) calcd. for [$C_{34}H_{34}N_2O$] ([M+H$^+$]): 487.2744, found: 287.2750; HPLC (ChiralPak IB column) 99.5:0.05 (hex/*i*PrOH) 0.5mL/min; t_{major} (9.0 min), t_{minor} (8.0 min); 93% *ee*.

III. HPLC Traces



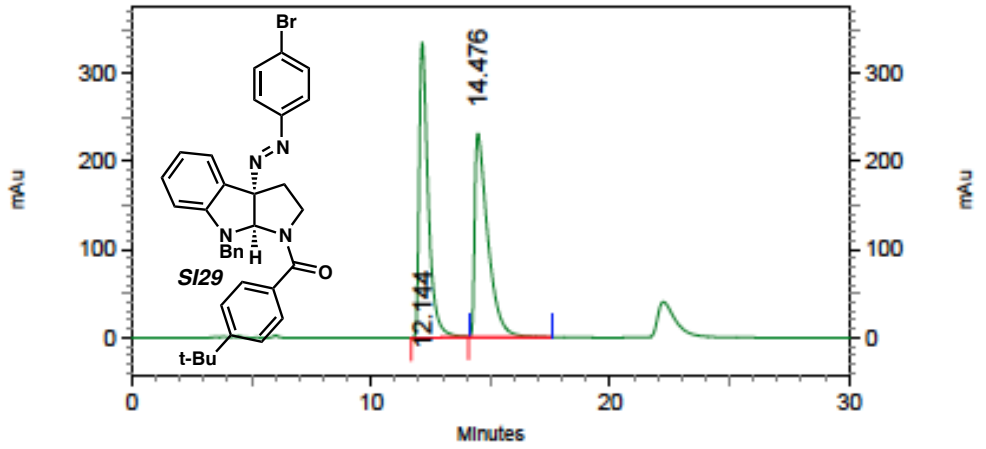
2: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
22.120	6316275	50.544	204
26.196	6180277	49.456	204



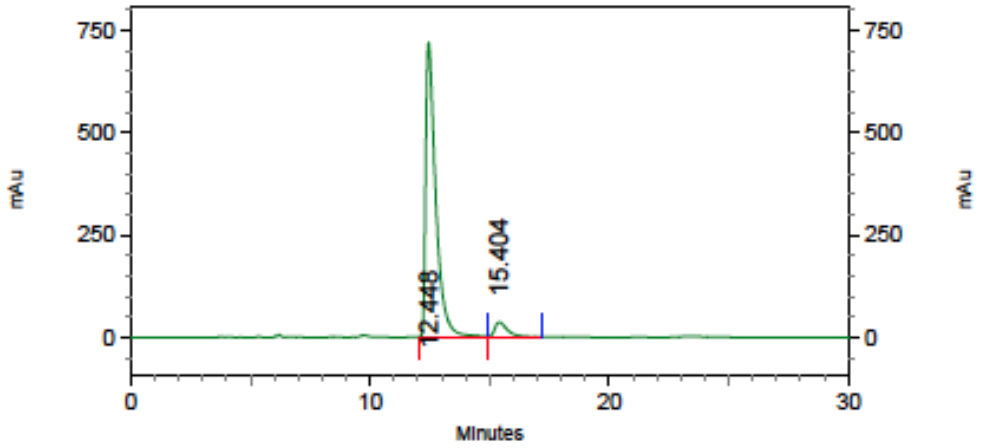
2: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
21.204	38505911	95.502	206
26.664	1813385	4.498	205



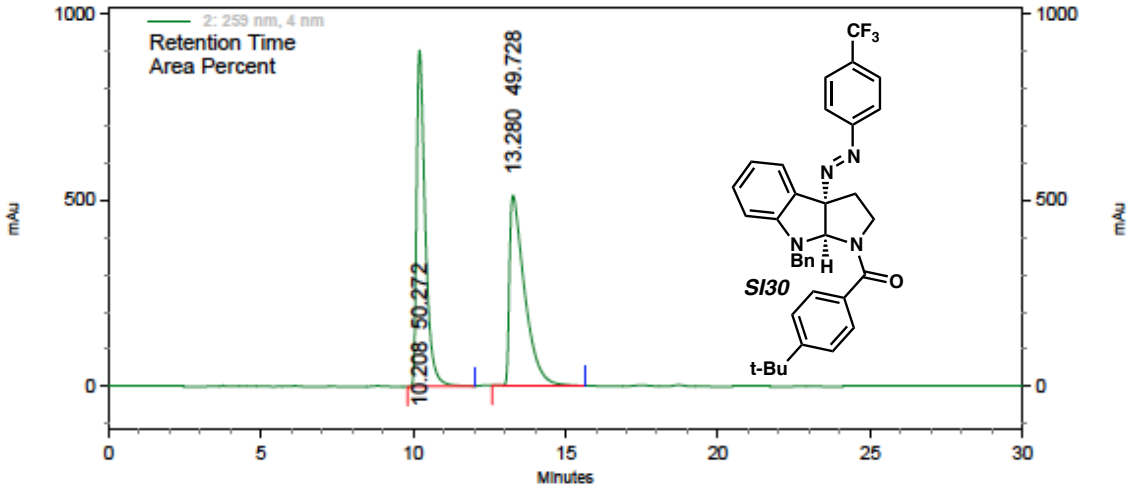
2: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
12.144	8807005	50.020	206
14.476	8799787	49.980	206



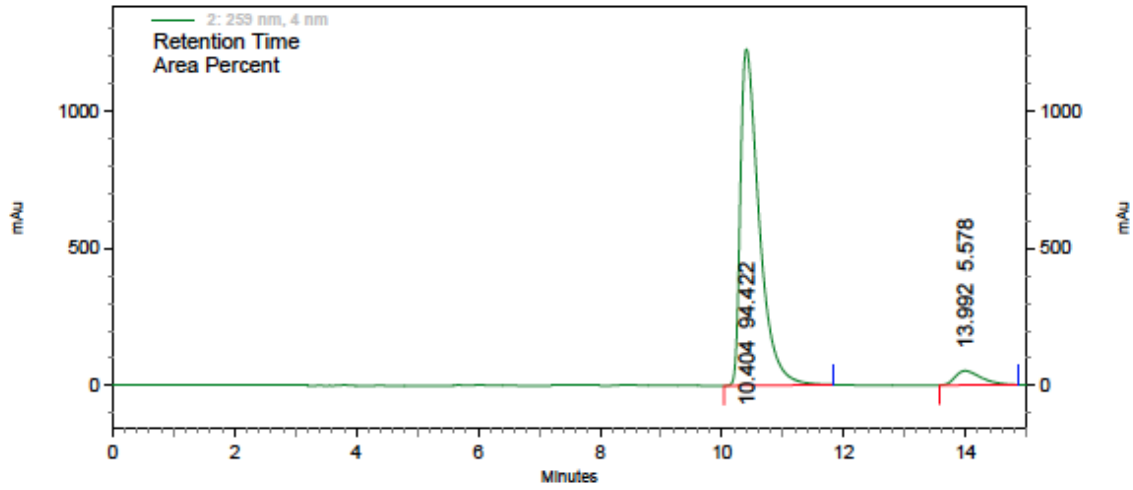
2: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
12.448	21091116	94.110	207
15.404	1320011	5.890	206



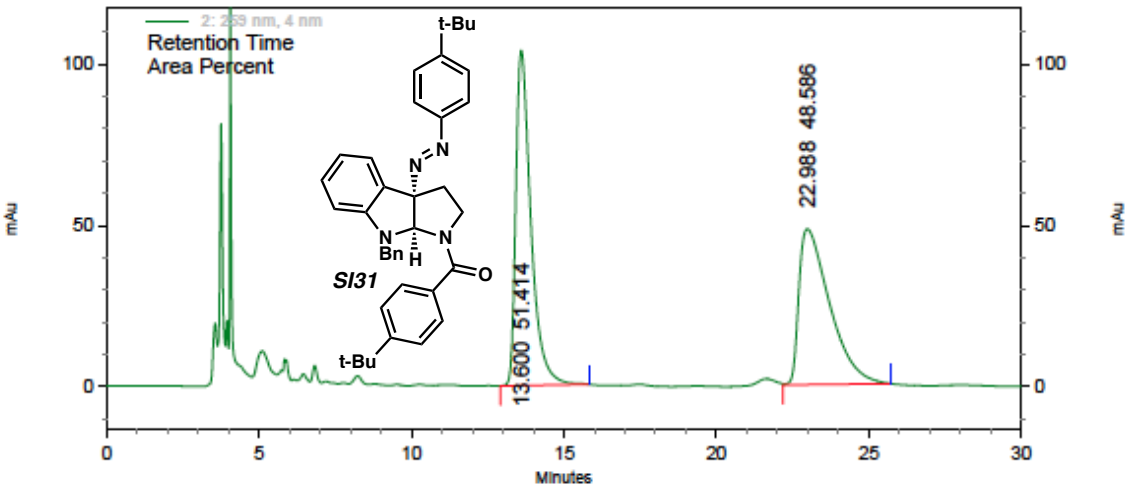
2: 259
nm, 4
nm
Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	10.208	17855081	50.272	207
2	13.280	17661687	49.728	207



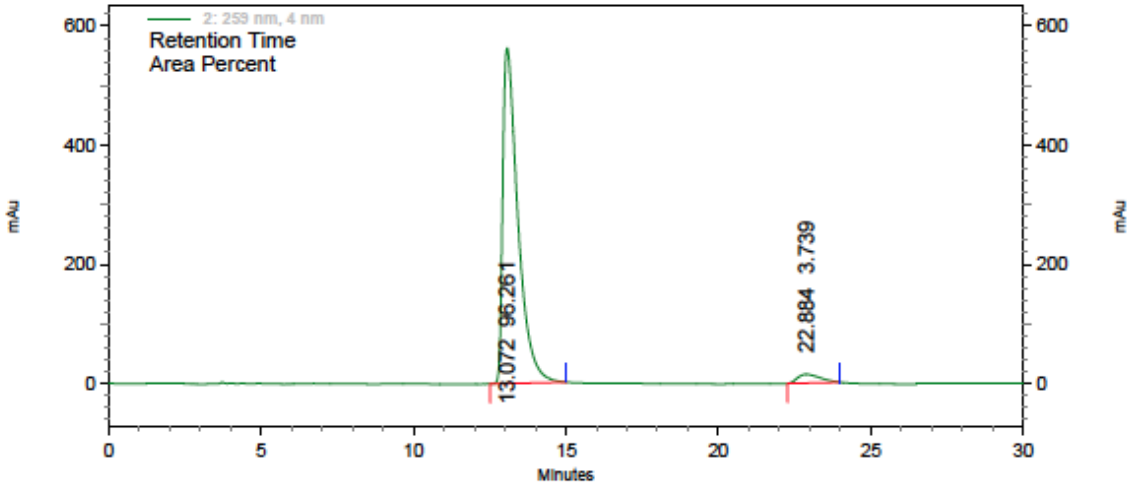
2: 259
nm, 4
nm
Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	10.404	26176166	94.422	209
2	13.992	1546483	5.578	206



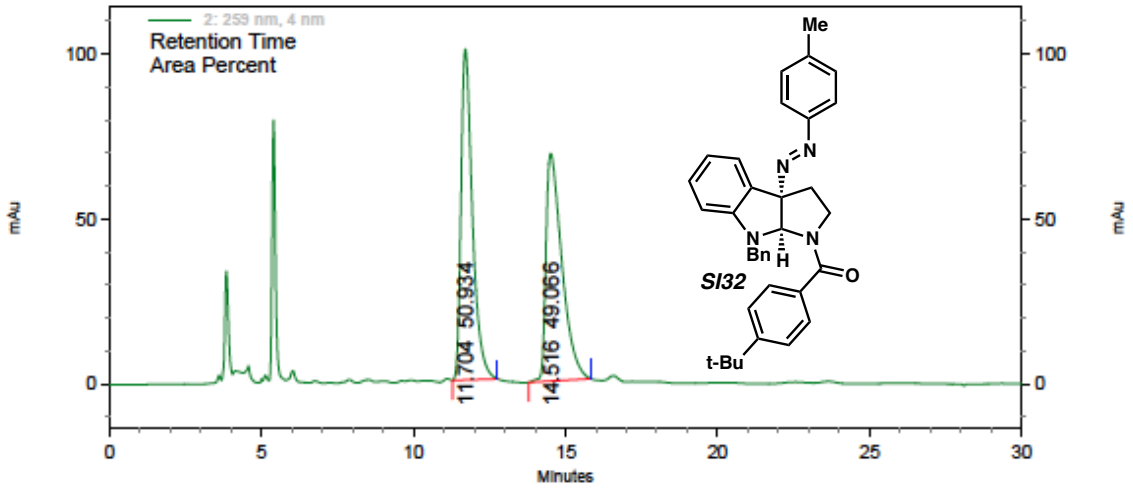
2: 259
nm, 4
nm
Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	13.600	3584506	51.414	205
2	22.988	3387369	48.586	205



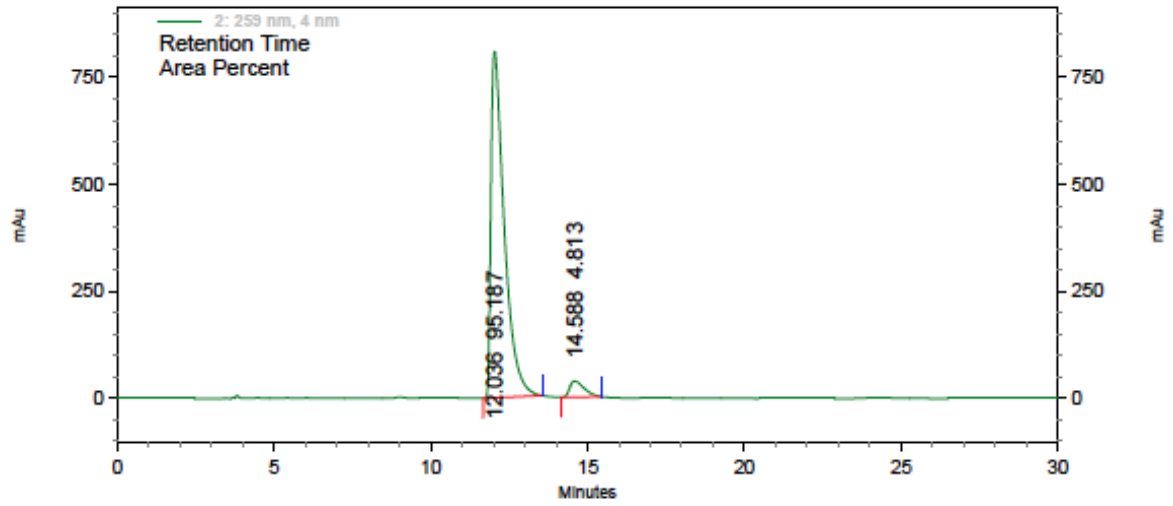
2: 259
nm, 4
nm
Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	13.072	19496513	96.261	206
2	22.884	757254	3.739	205



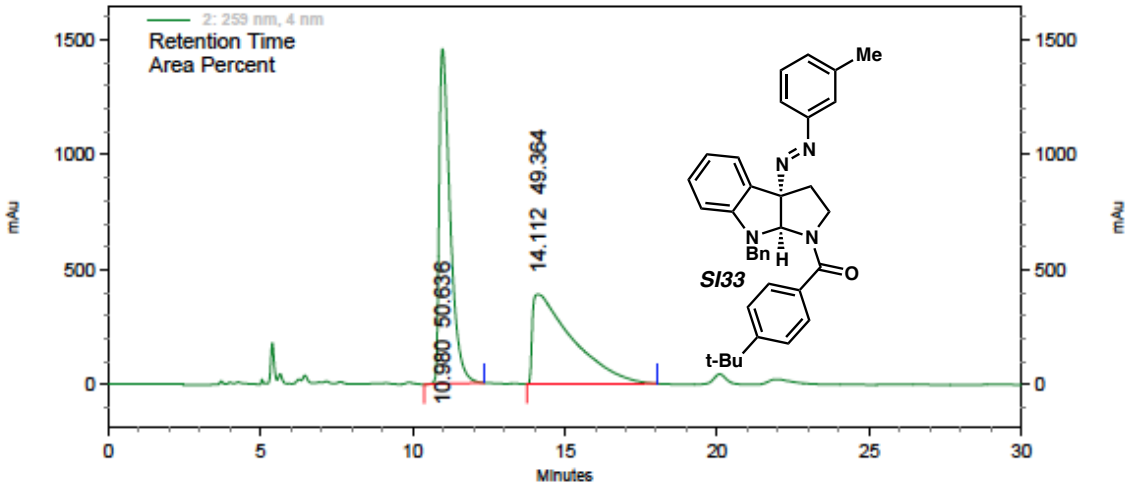
2: 259
nm, 4
nm
Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	11.704	2614780	50.934	206
2	14.516	2518871	49.066	206



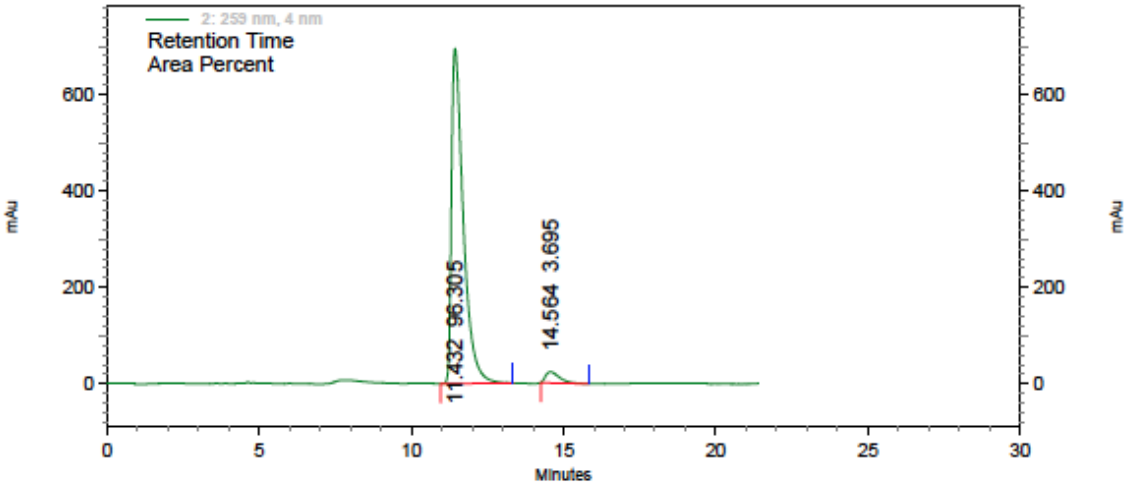
2: 259
nm, 4
nm
Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	12.036	23835140	95.187	207
2	14.588	1205244	4.813	206



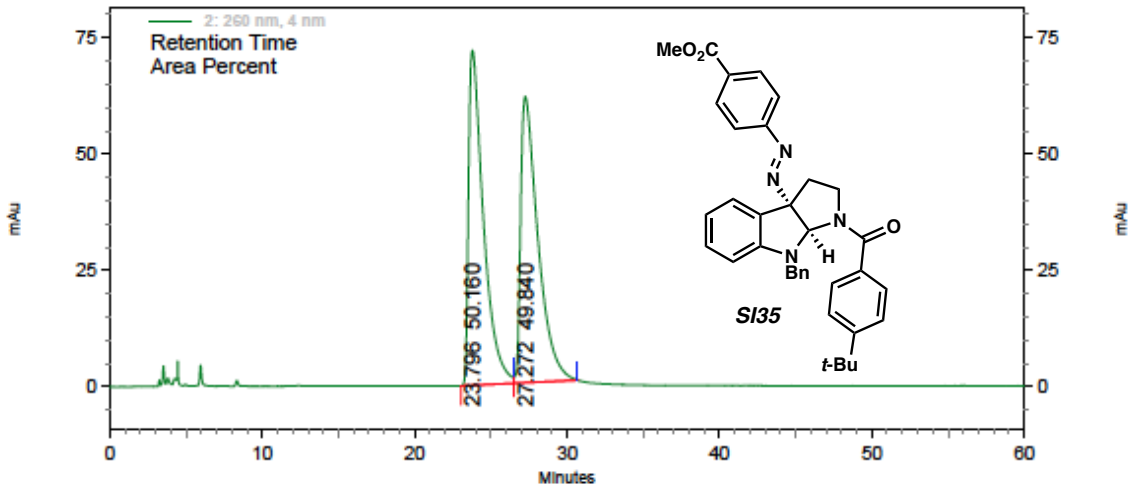
2: 259
nm, 4
nm
Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	10.980	36542873	50.636	208
2	14.112	35625010	49.364	207

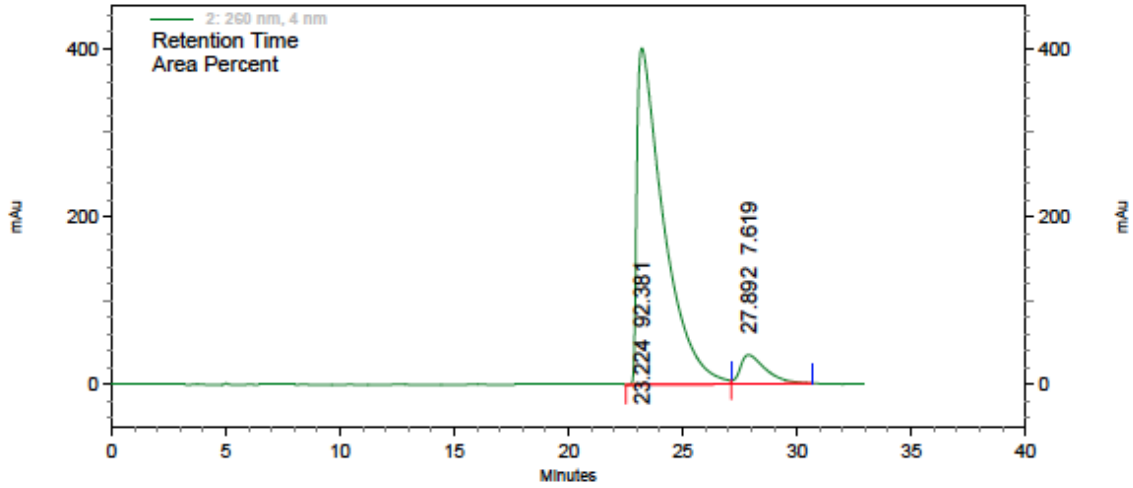


2: 259
nm, 4
nm
Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	11.432	18801723	96.305	207
2	14.564	721339	3.695	206

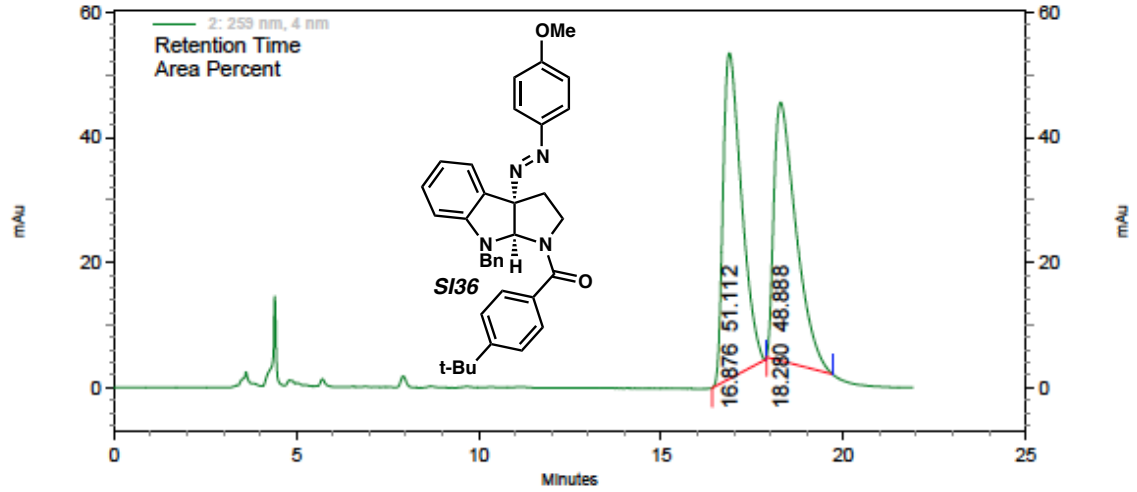


2: 260
nm, 4
nm



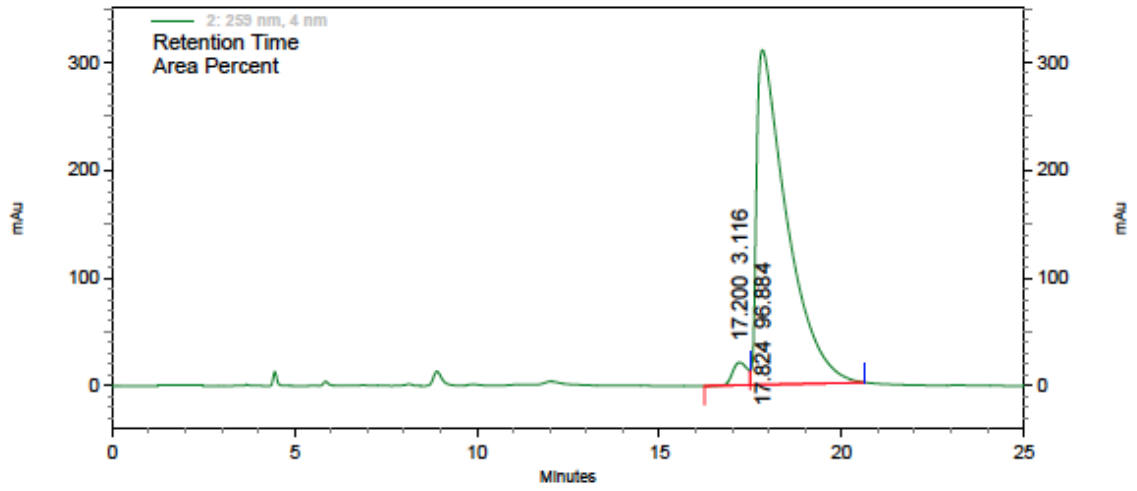
2: 260
nm, 4
nm
Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	23.224	32537856	92.381	207
2	27.892	2683649	7.619	206



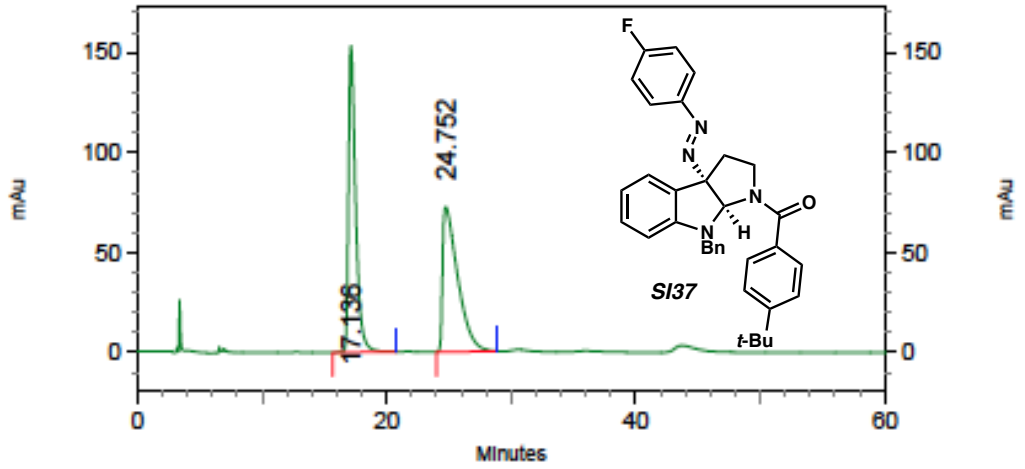
2: 259
nm, 4
nm
Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	16.876	1833504	51.112	206
2	18.280	1753709	48.888	206



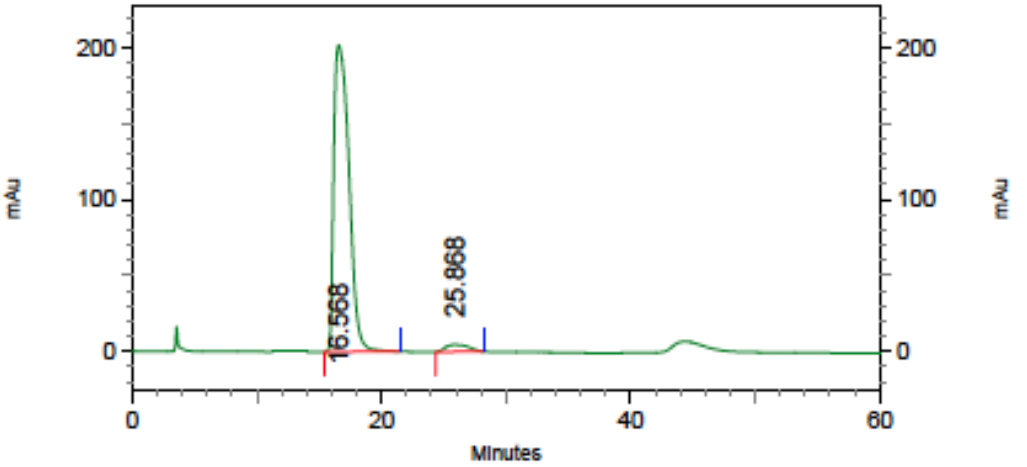
2: 259
nm, 4
nm
Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	17.200	578774	3.116	206
2	17.824	17993450	96.884	207



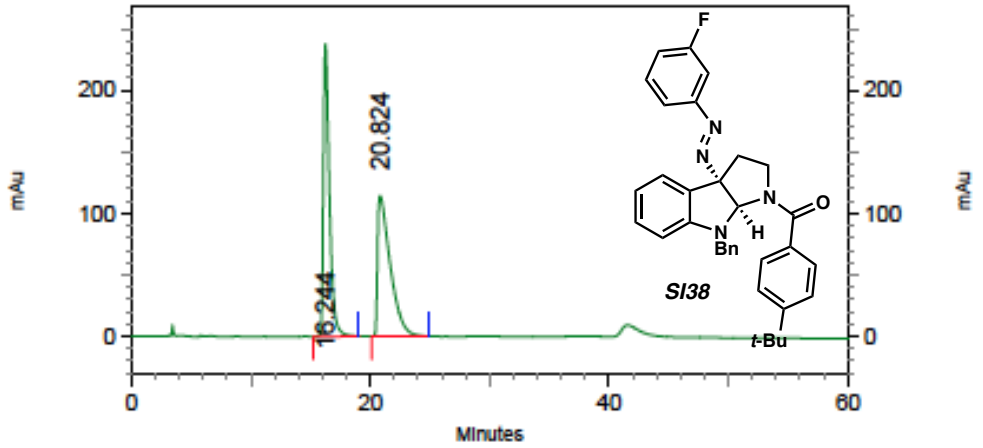
1: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
17.136	6184611	50.148	200
24.752	6148019	49.852	200



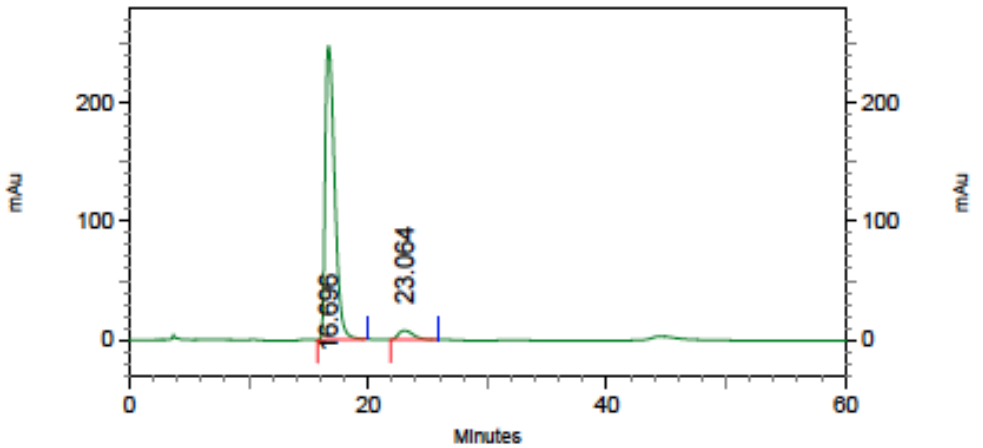
1: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
16.568	17162412	96.646	200
25.868	595653	3.354	205



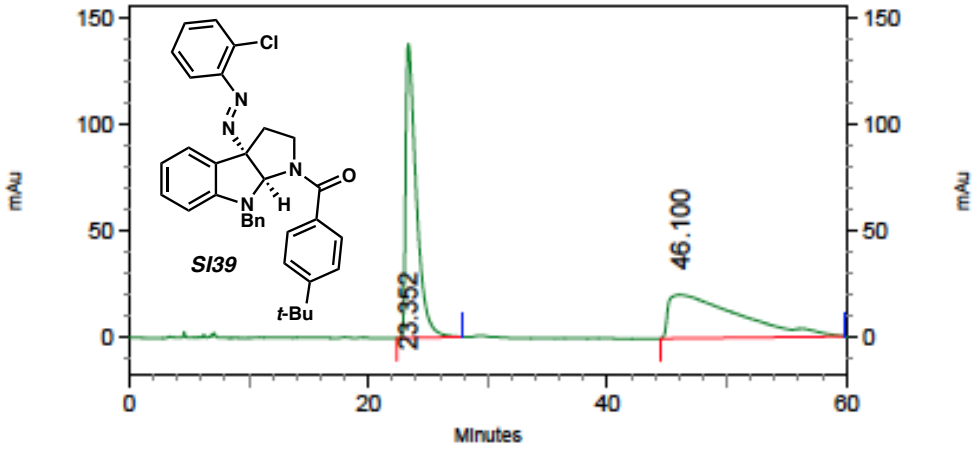
1: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
16.244	8402440	49.809	201
20.824	8466894	50.191	201



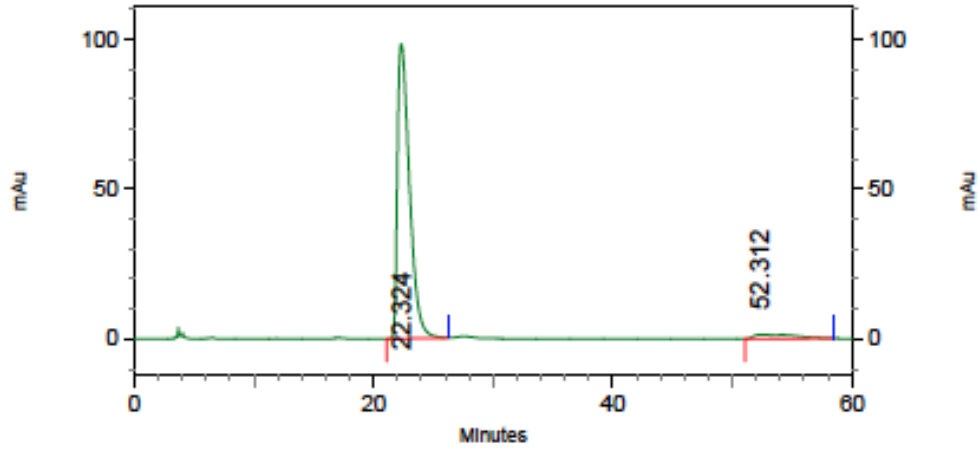
1: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
16.696	13653398	95.417	200
23.064	655849	4.583	200



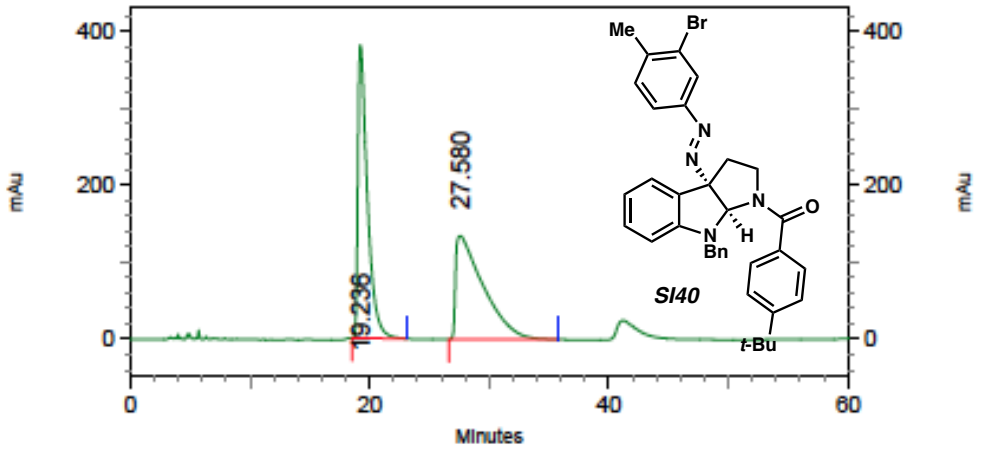
3: 288 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
23.352	8545996	50.401	201
46.100	8410104	49.599	201



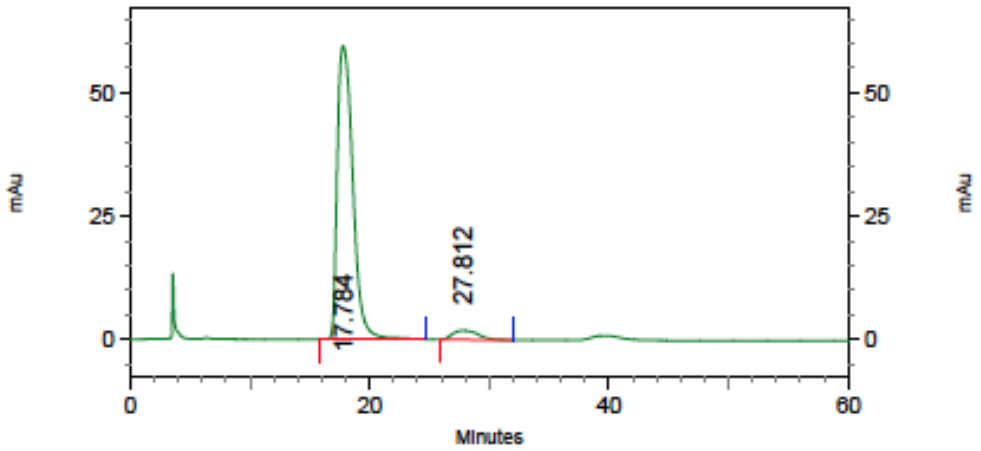
3: 288 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
22.324	6876351	95.530	201
52.312	321723	4.470	200



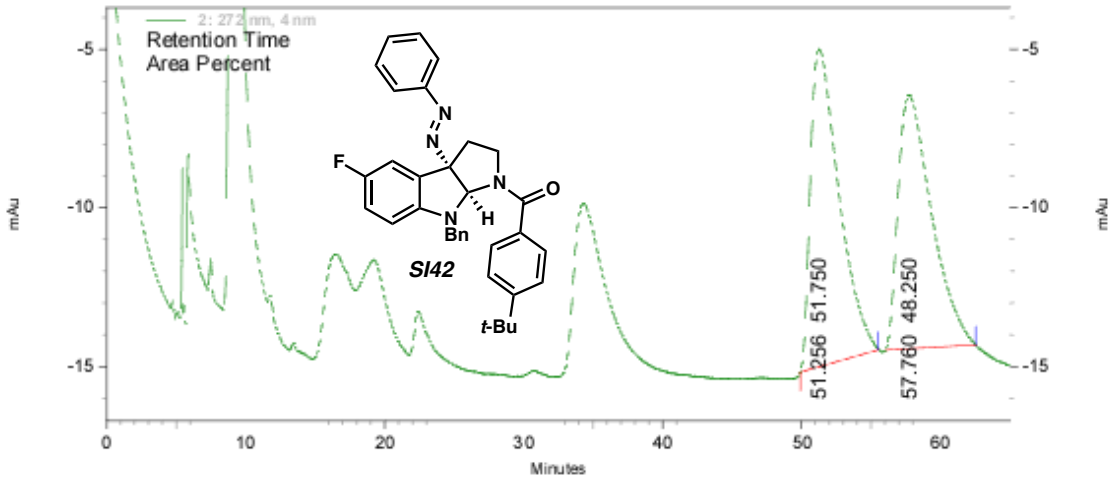
1: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
19.236	20944168	49.212	200
27.580	21614974	50.788	200



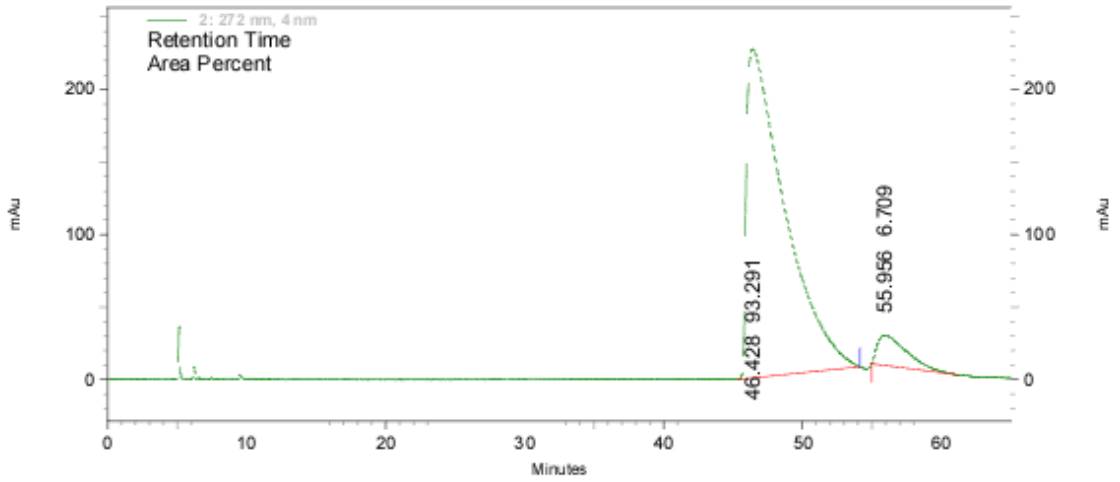
1: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
17.784	5355126	95.164	201
27.812	272149	4.836	206



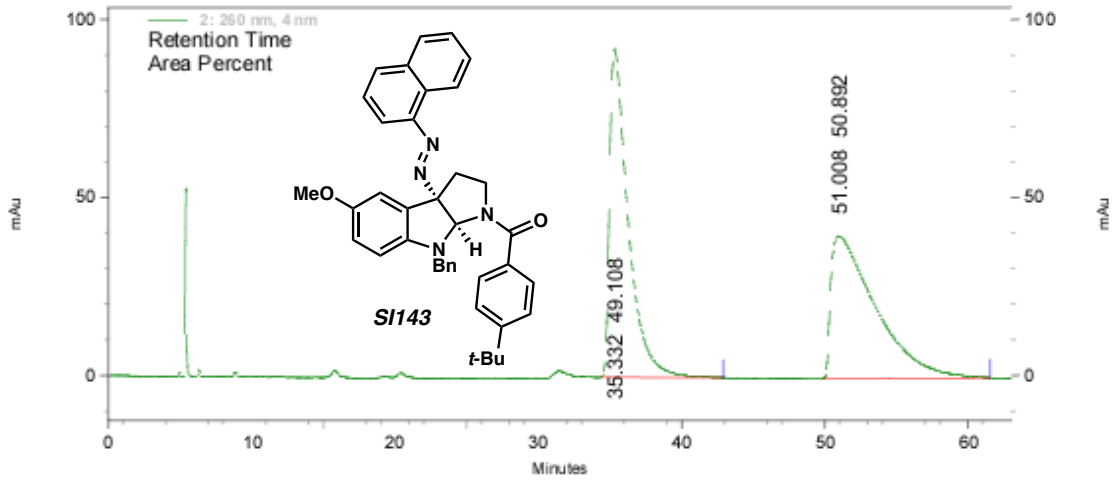
2: 272 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	51.256	51.750	202
2	57.760	48.250	202



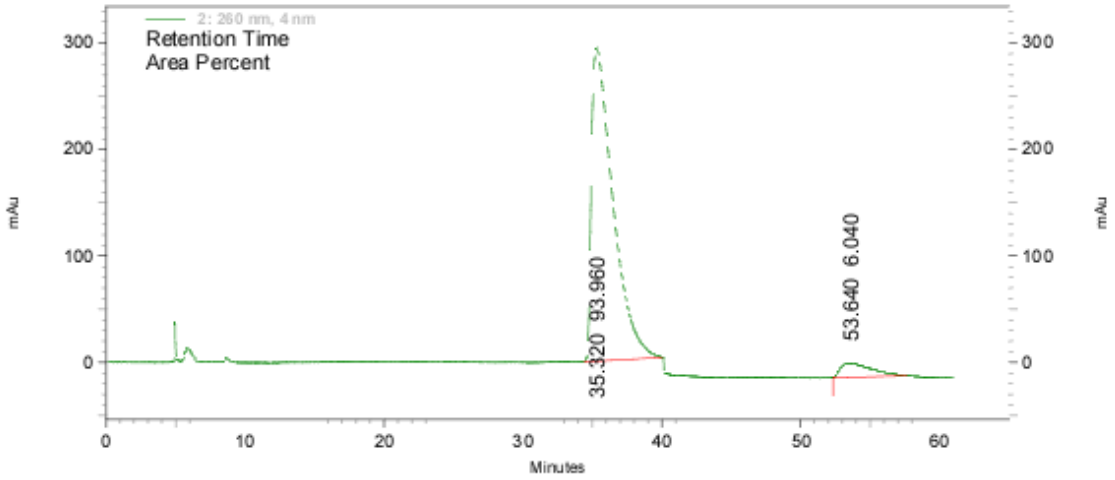
2: 272 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	46.428	93.291	249
2	55.956	6.709	203



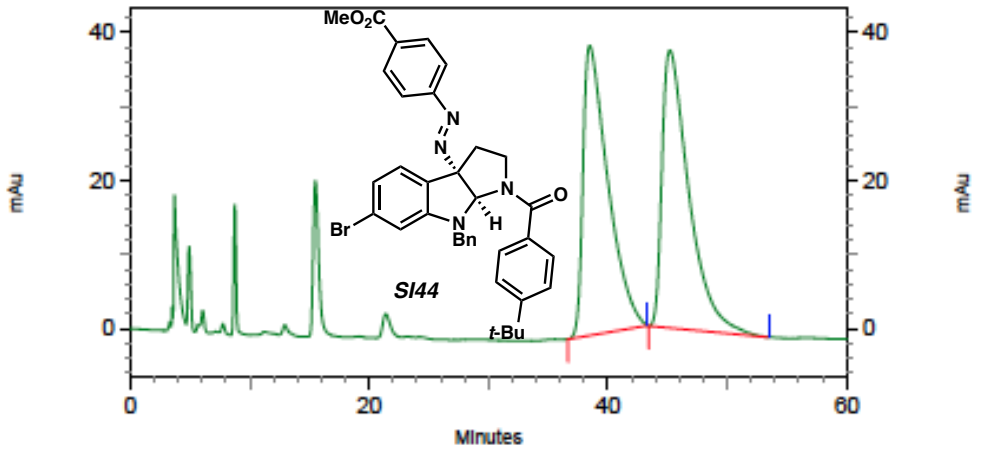
2: 260 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	35.332	49.108	243
2	51.008	50.892	213



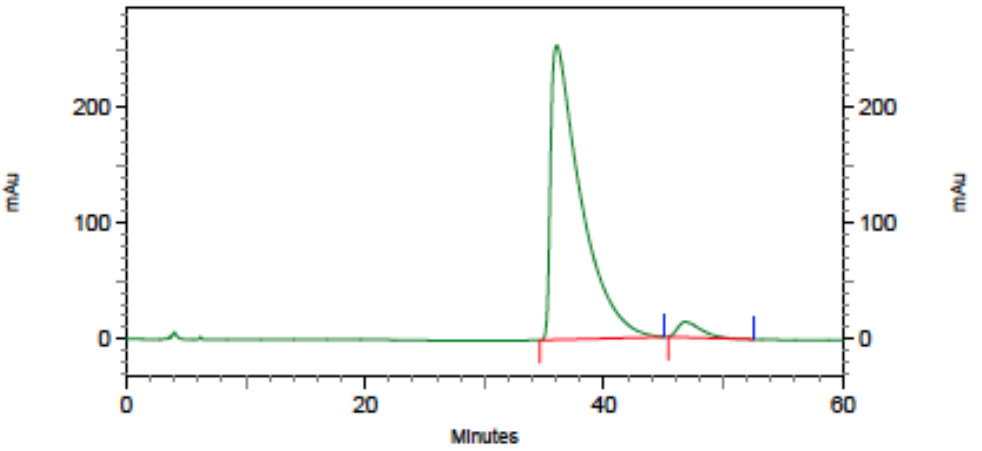
2: 260 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	35.320	93.960	199
2	53.640	6.040	212



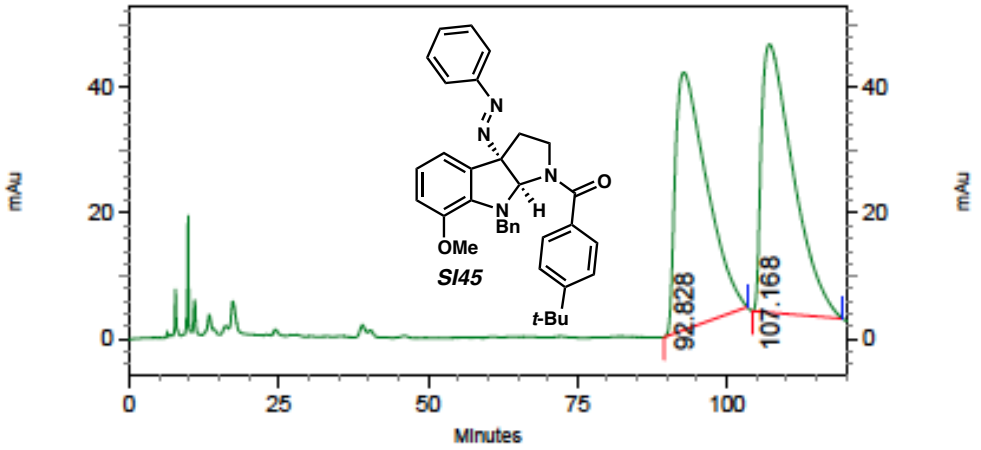
1: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
38.468	5670283	49.090	198
45.196	5880573	50.910	199



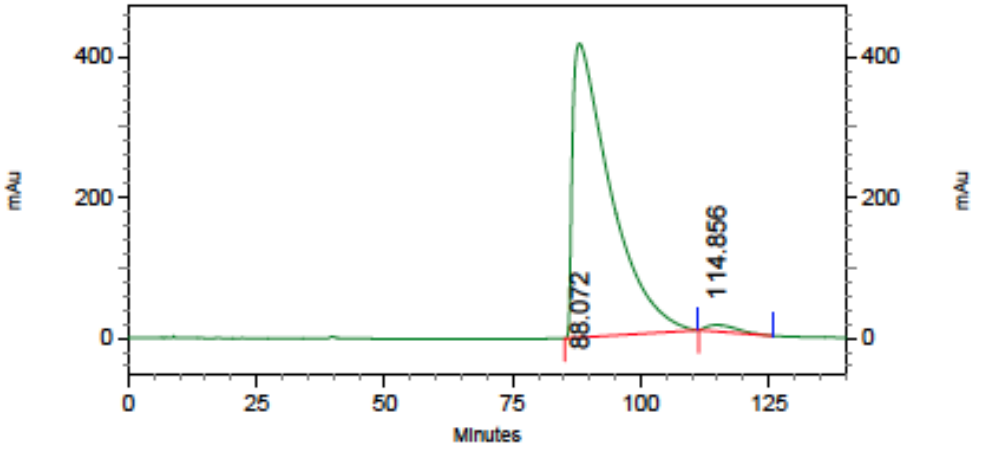
1: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
36.052	44456874	96.048	199
46.848	1829156	3.952	205



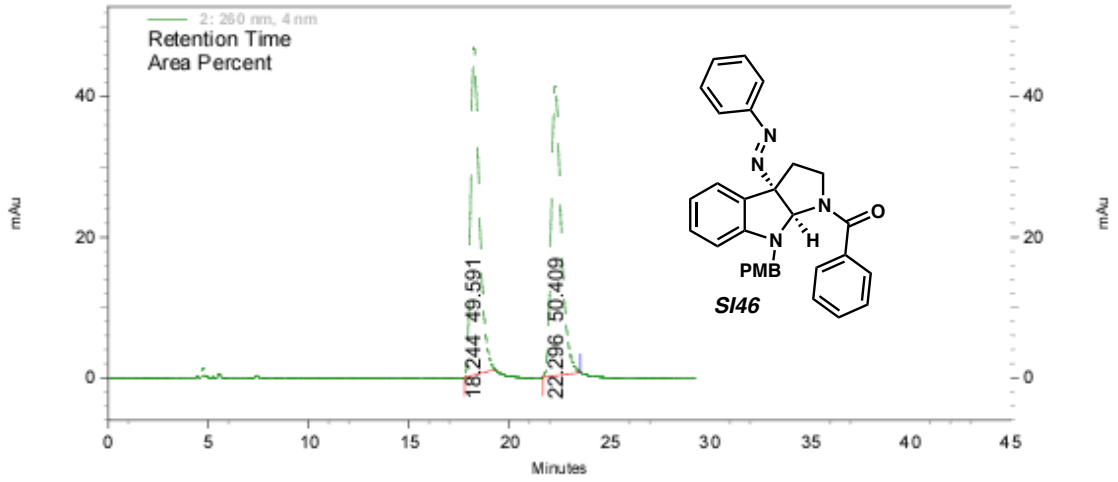
1: 259 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
92.828	14998304	48.685	197
107.168	15808275	51.315	197



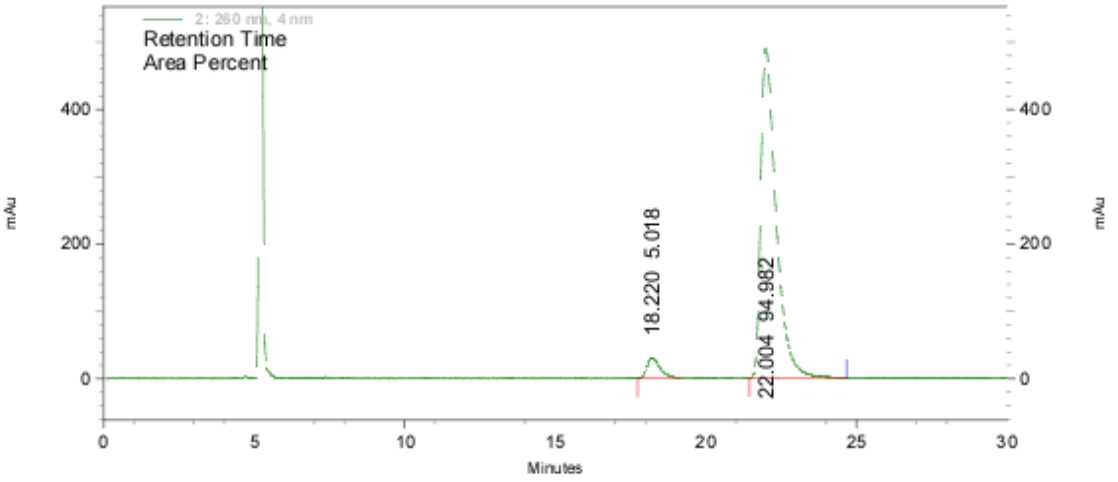
1: 259 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
88.072	216051561	98.245	197
114.856	3858445	1.755	196



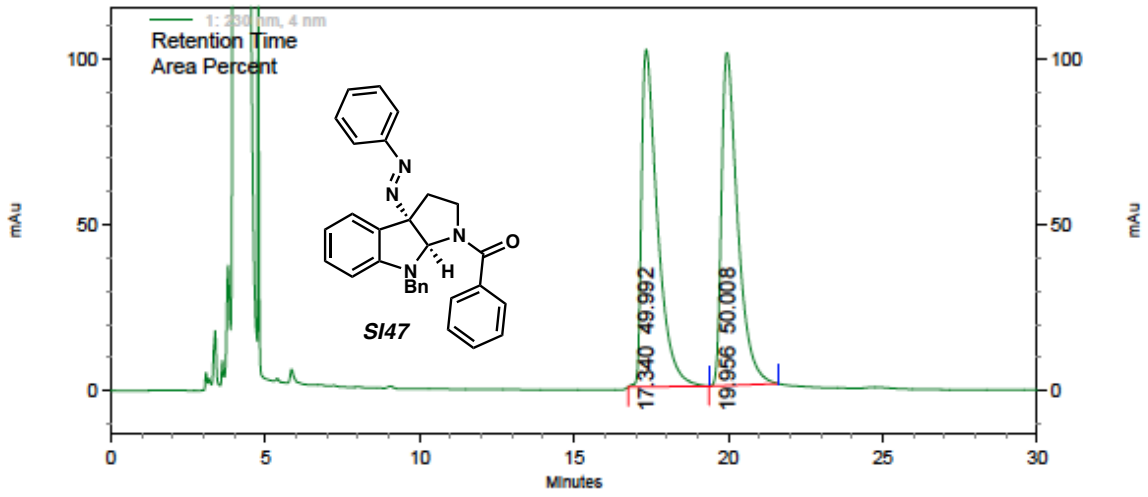
2: 260 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	18.244	49.591	203
2	22.296	50.409	203



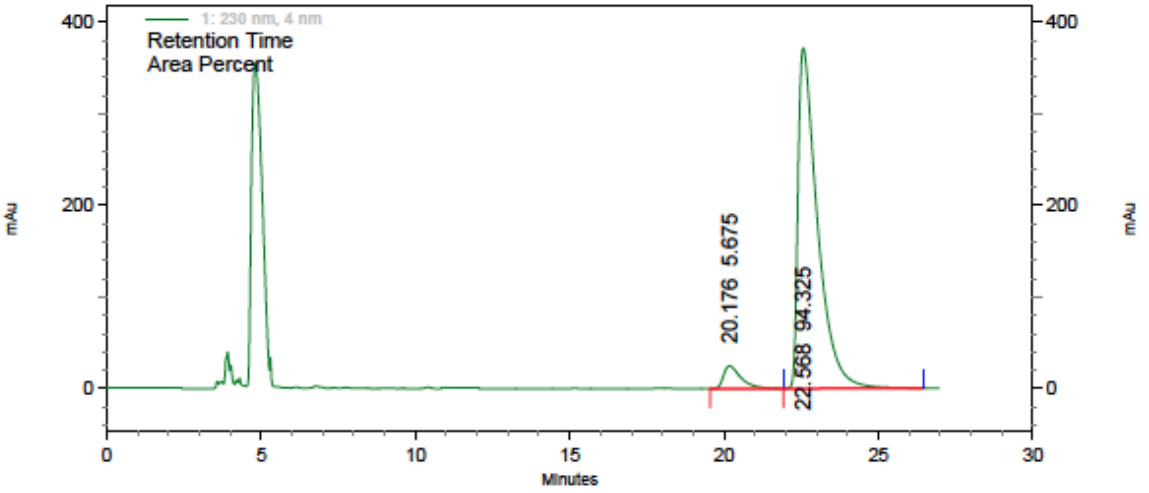
2: 260 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	18.220	5.018	204
2	22.004	94.982	198



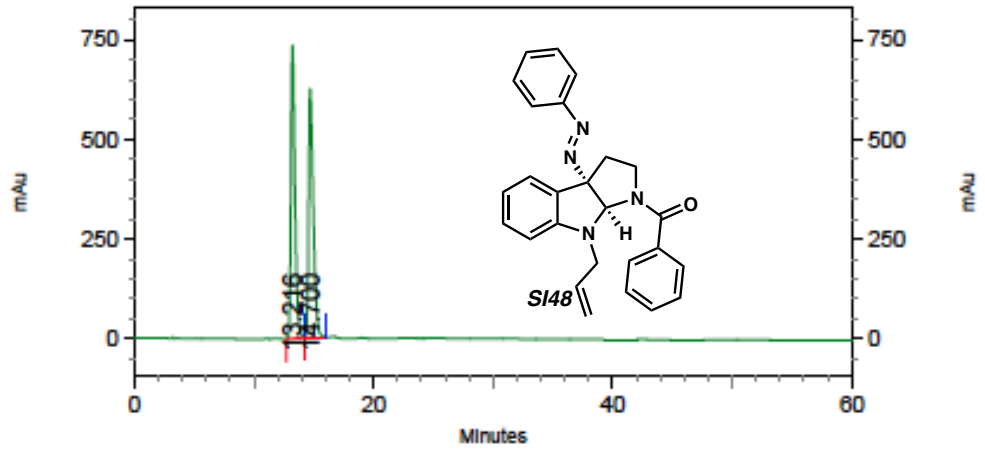
1: 230 nm, 4 nm Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	17.340	3666526	49.992	203
2	19.956	3667705	50.008	203



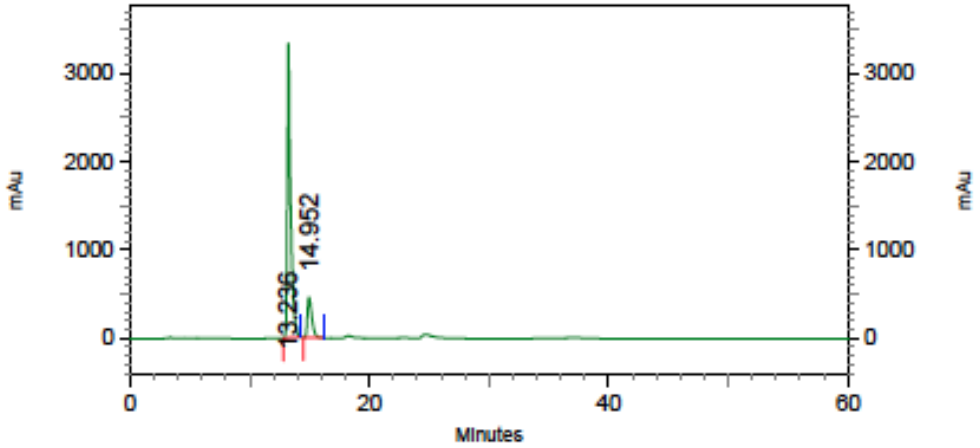
1: 230 nm, 4 nm Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	20.176	980710	5.675	205
2	22.568	16299679	94.325	197



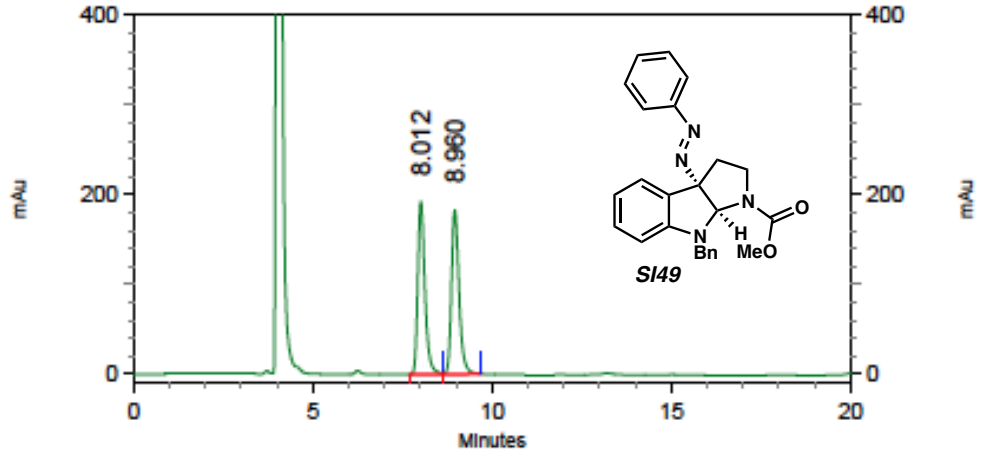
3: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
13.216	17196333	49.994	193
14.700	17200271	50.006	249



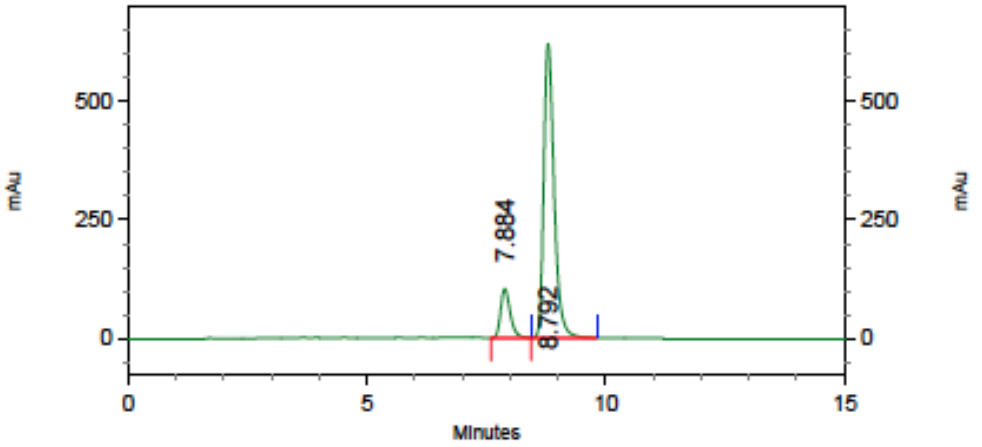
1: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
13.236	64271854	84.475	255
14.952	11811680	15.525	201



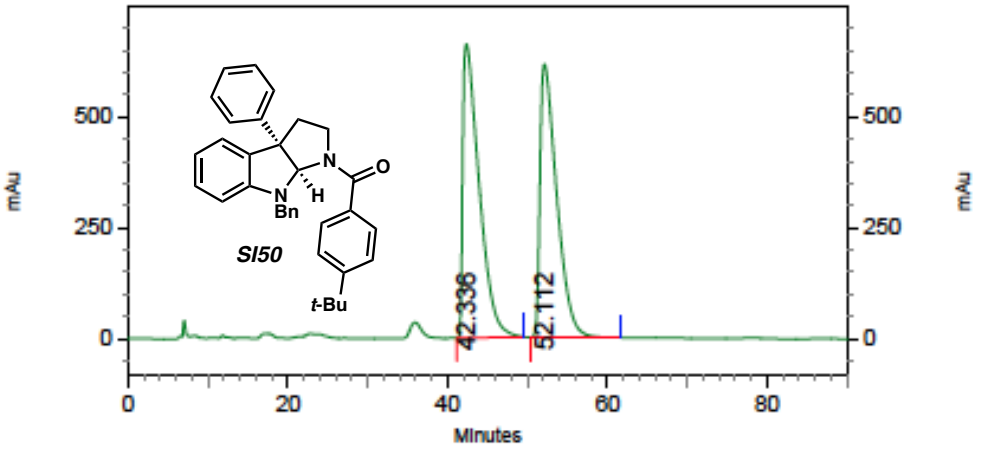
2: 260 nm, 4 nm Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	8.012	2668090	49.807	207
2	8.960	2688785	50.193	207



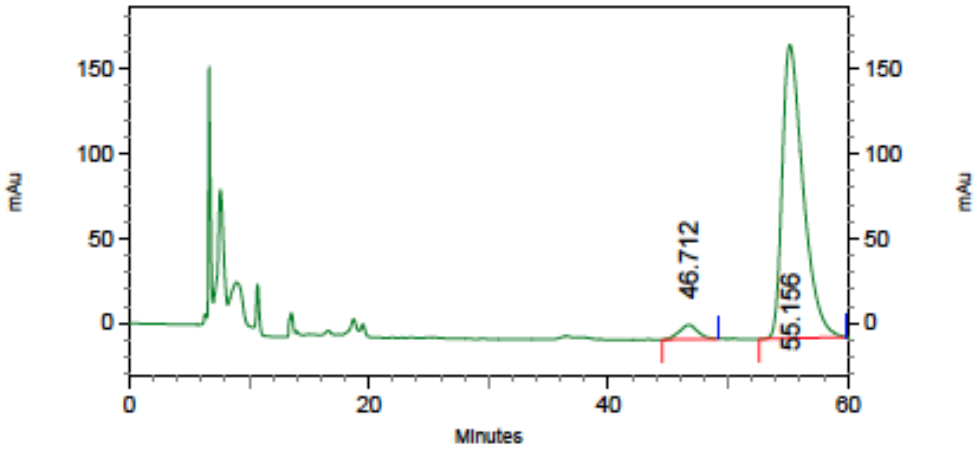
2: 260 nm, 4 nm Results

Pk #	Retention Time	Area	Area Percent	Lambda Max
1	7.884	1461730	13.546	207
2	8.792	9328984	86.454	207



1: 220 nm, 4 nm Results

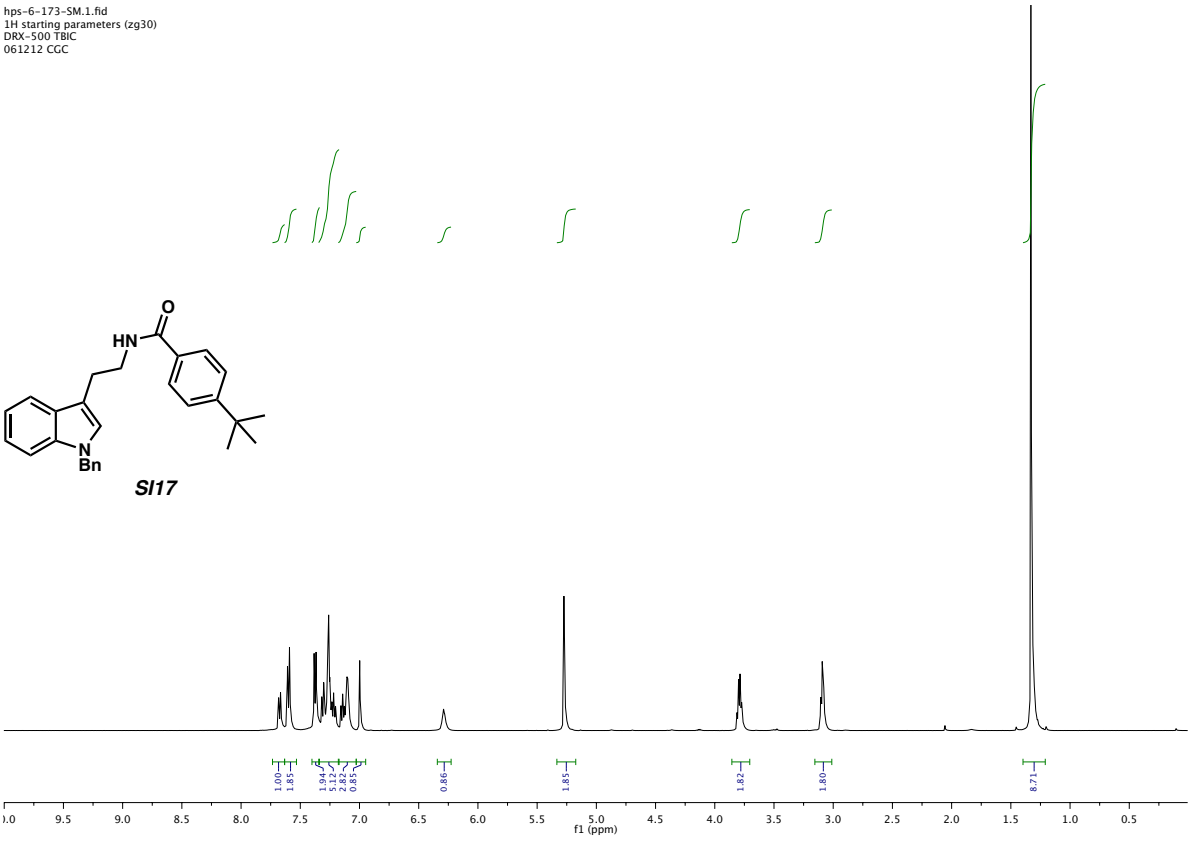
Retention Time	Area	Area Percent	Lambda Max
42.336	94401467	51.184	200
52.112	90033468	48.816	200

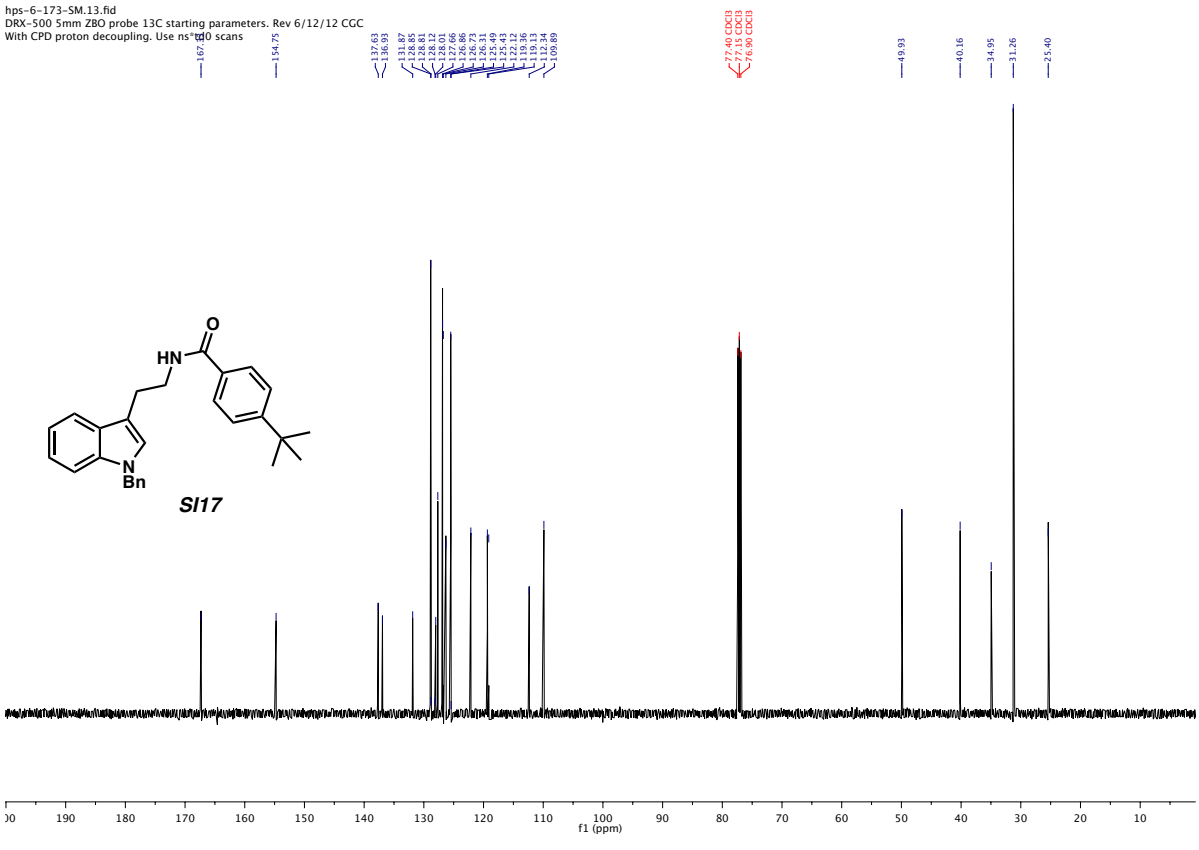


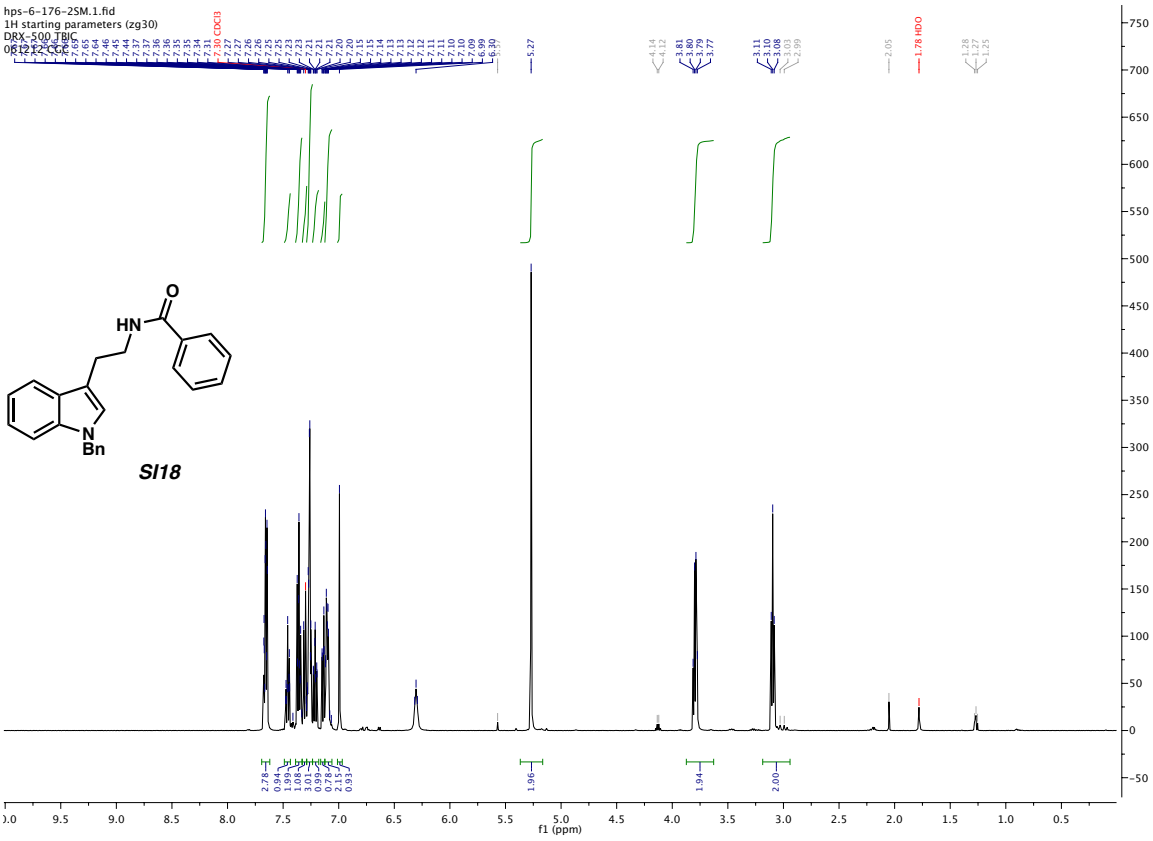
1: 220 nm, 4 nm Results

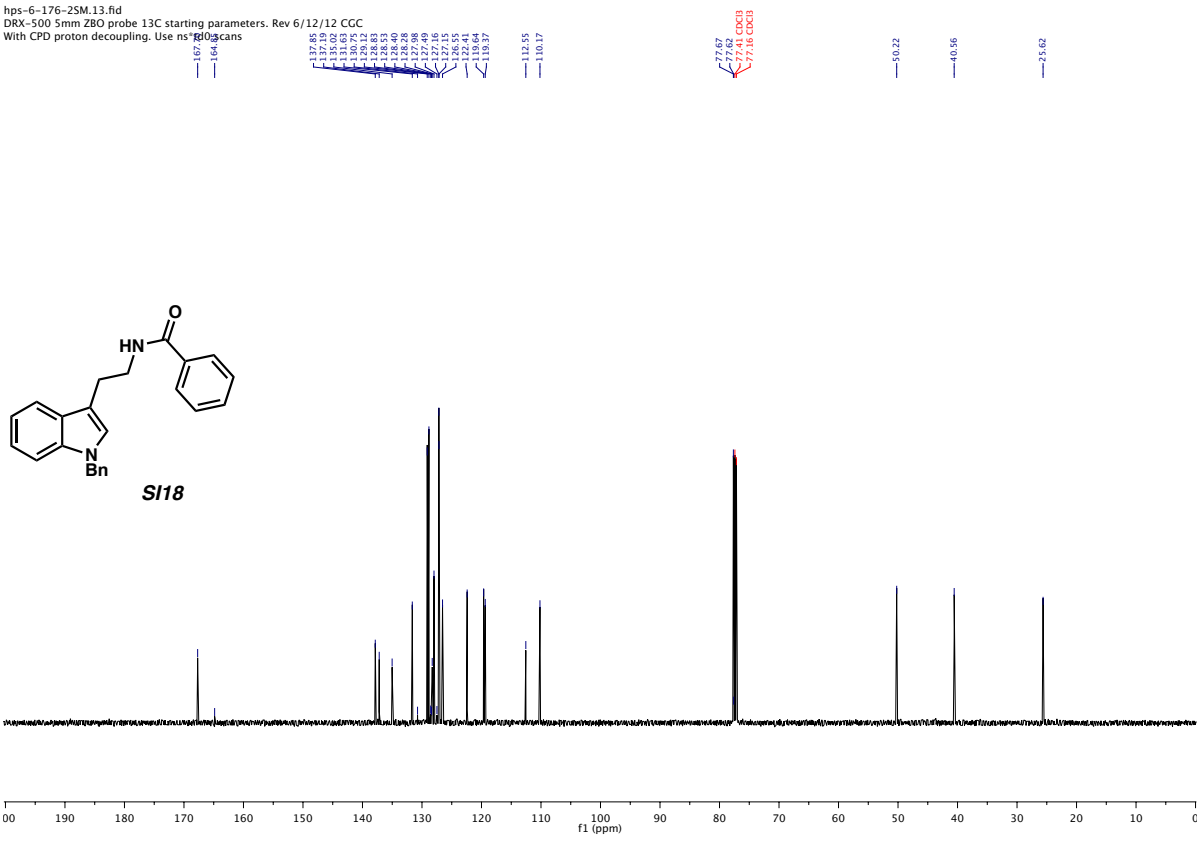
Retention Time	Area	Area Percent	Lambda Max
46.712	908713	4.151	653
55.156	20983573	95.849	200

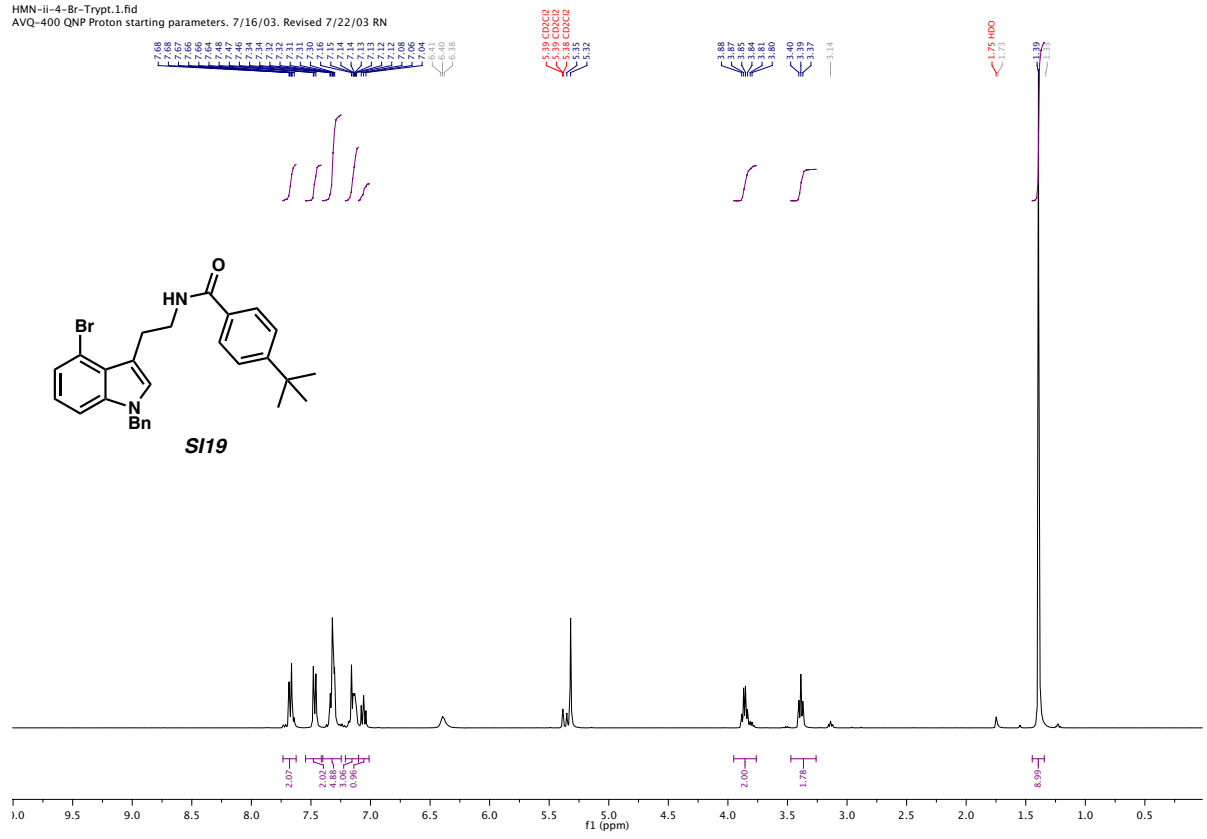
IV. NMR Spectra

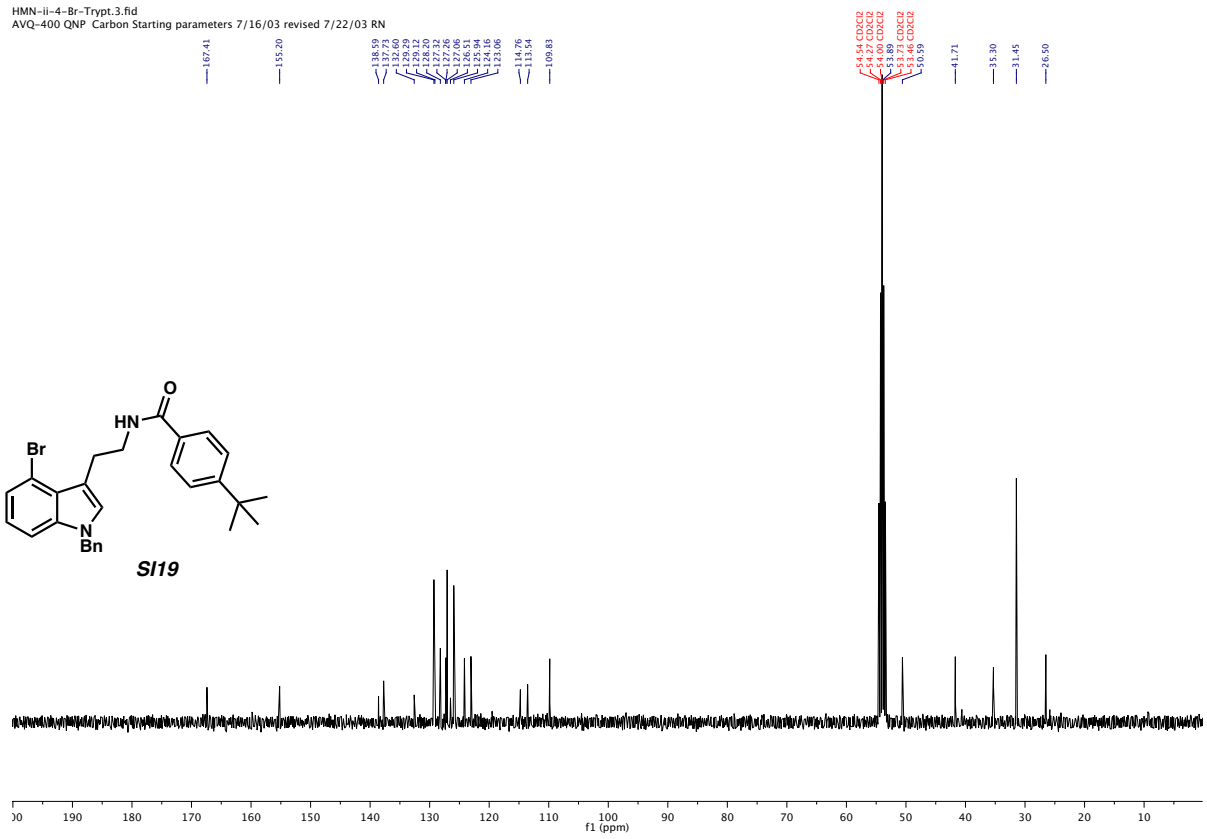

hps-6-173-SM.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
HN
O
N
Bn
SI17
1.00
1.85
1.94
5.12
2.82
0.85
0.86
1.85
1.82
1.80
8.71
f1 (ppm)

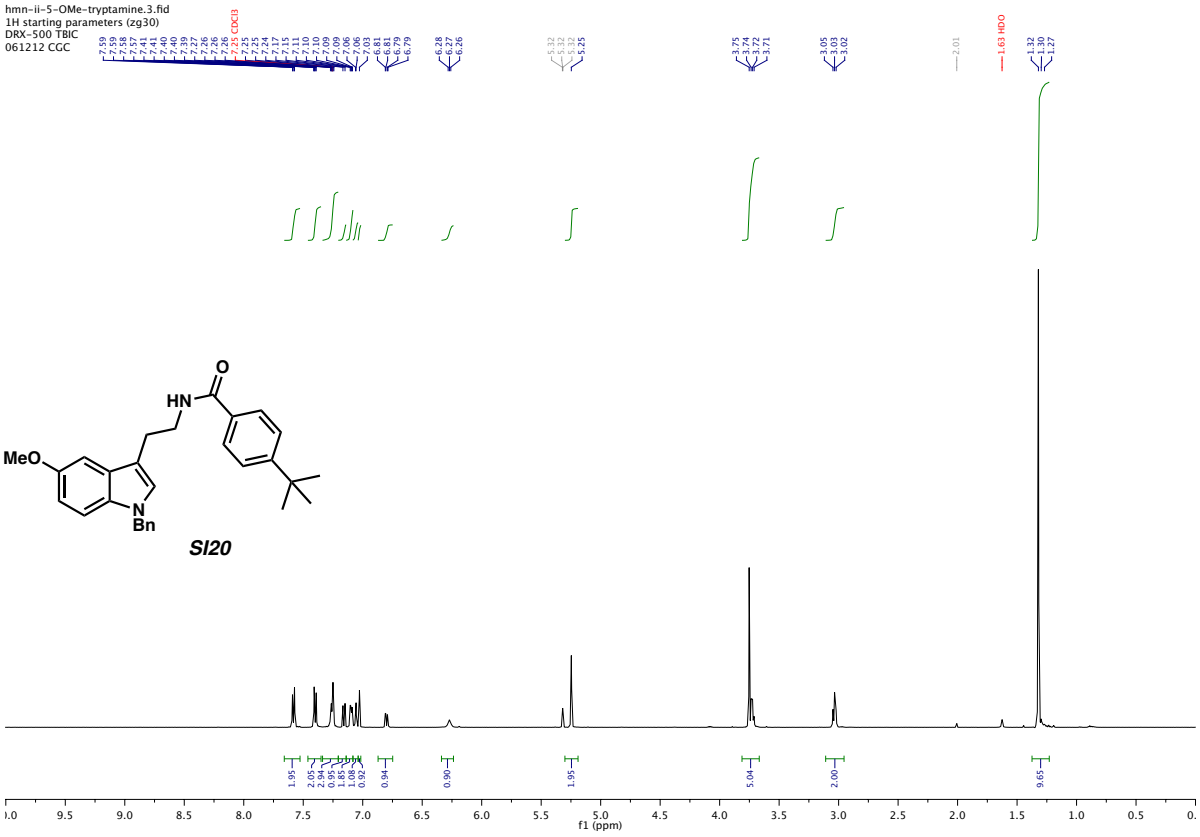

hps-6-173-SM.13.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*40 scans
167.63
154.75
137.63
136.65
131.87
128.87
128.81
128.12
126.61
127.66
126.86
126.73
126.51
125.49
125.43
125.22
119.36
119.13
112.34
109.89
77.40 CDCl3
77.15 CDCl3
76.90 CDCl3
49.93
40.16
34.95
31.26
25.40
HN
O
N
Bn
SI17
f1 (ppm)

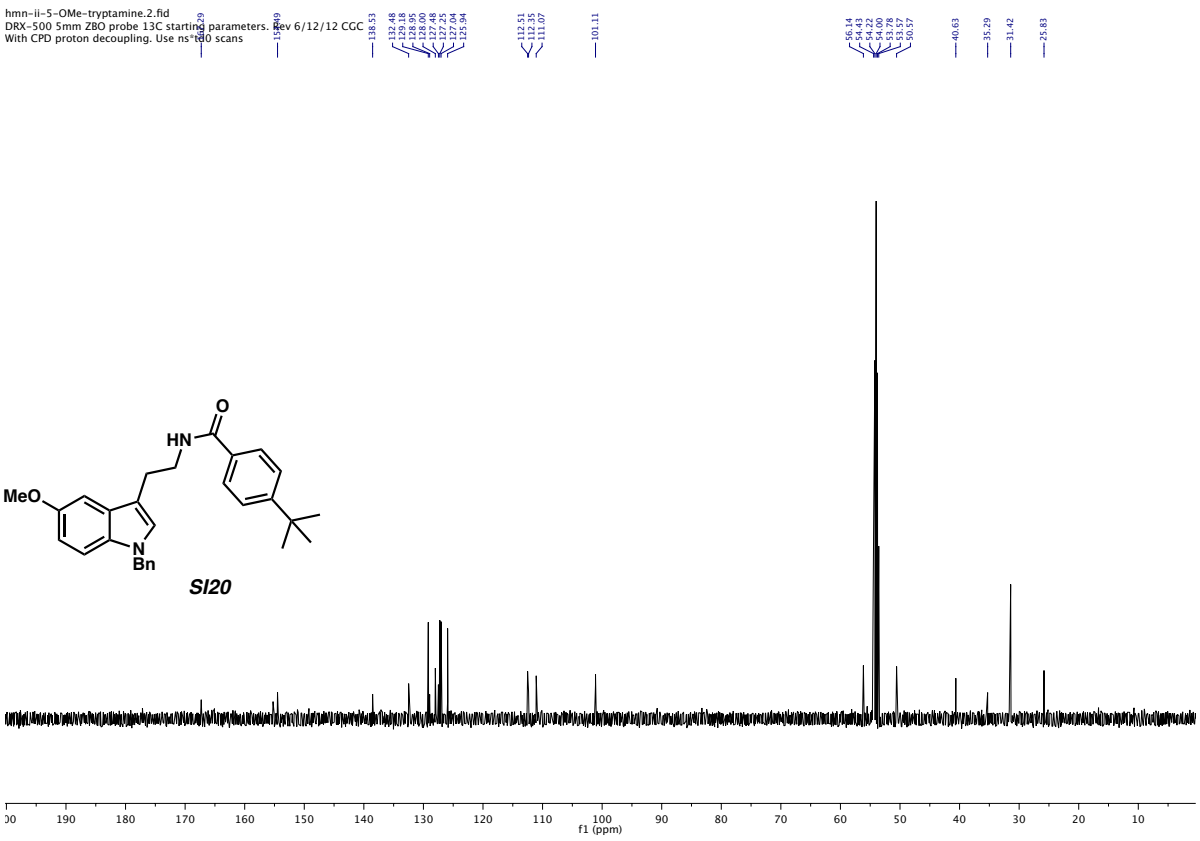

hps-6-176-2SM.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
HN
O
N
Bn
SI18
f1 (ppm)

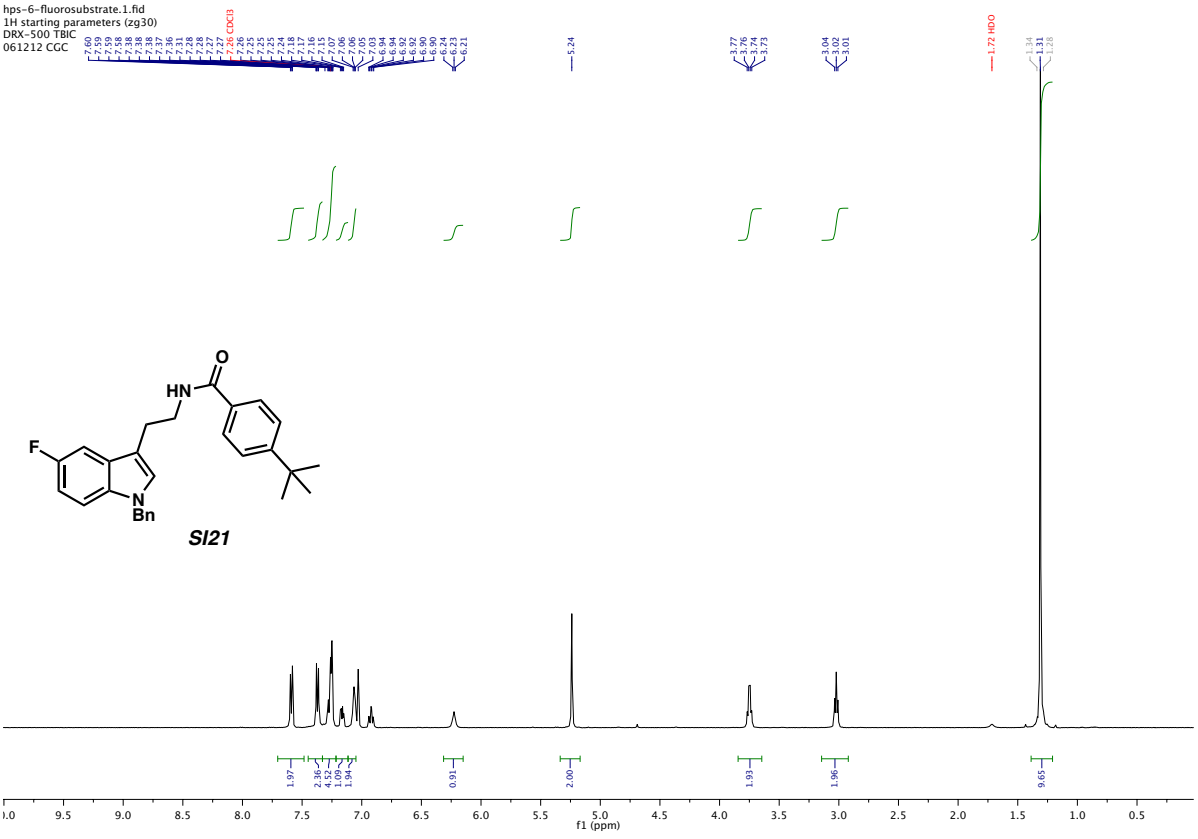

hps-6-176-2SM.13.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*80 scans
HN
O
N
Bn
SI18
f1 (ppm)


HMN-ii-4-Br-Trypt.1.fid
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
Br
HN
O
N
Bn
SI19
f1 (ppm)


HMN-ii-4-Br-Trypt.3.fid
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN
Br
HN
O
N
Bn
SI19
f1 (ppm)

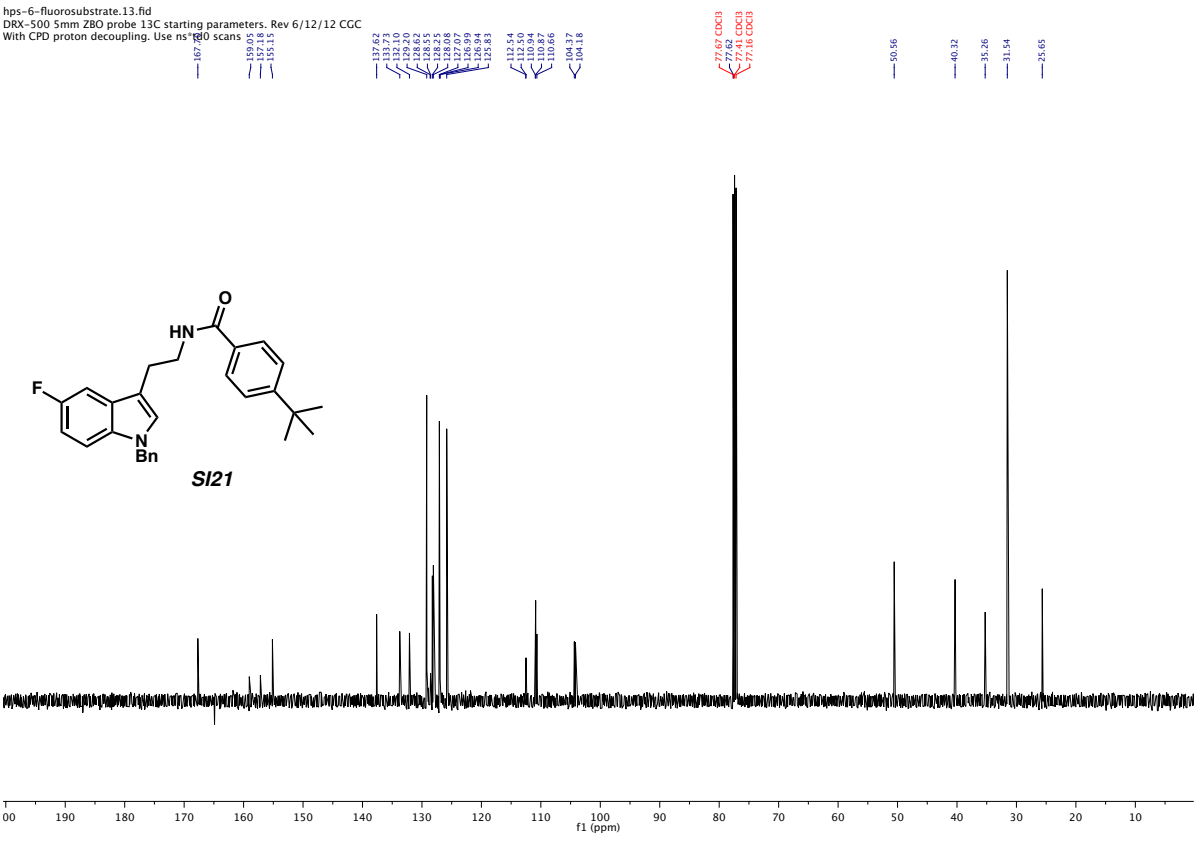

hmn-ii-5-OMe-tryptamine.3.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
MeO
HN
O
N
Bn
SI20
f1 (ppm)


hmn-ii-5-OMe-tryptamine.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns 1200 scans
MeO
HN
O
N
Bn
SI20
f1 (ppm)


hps-6-fluorosubstrate.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
CDCl3
5.24
1.72 HDO
f1 (ppm)

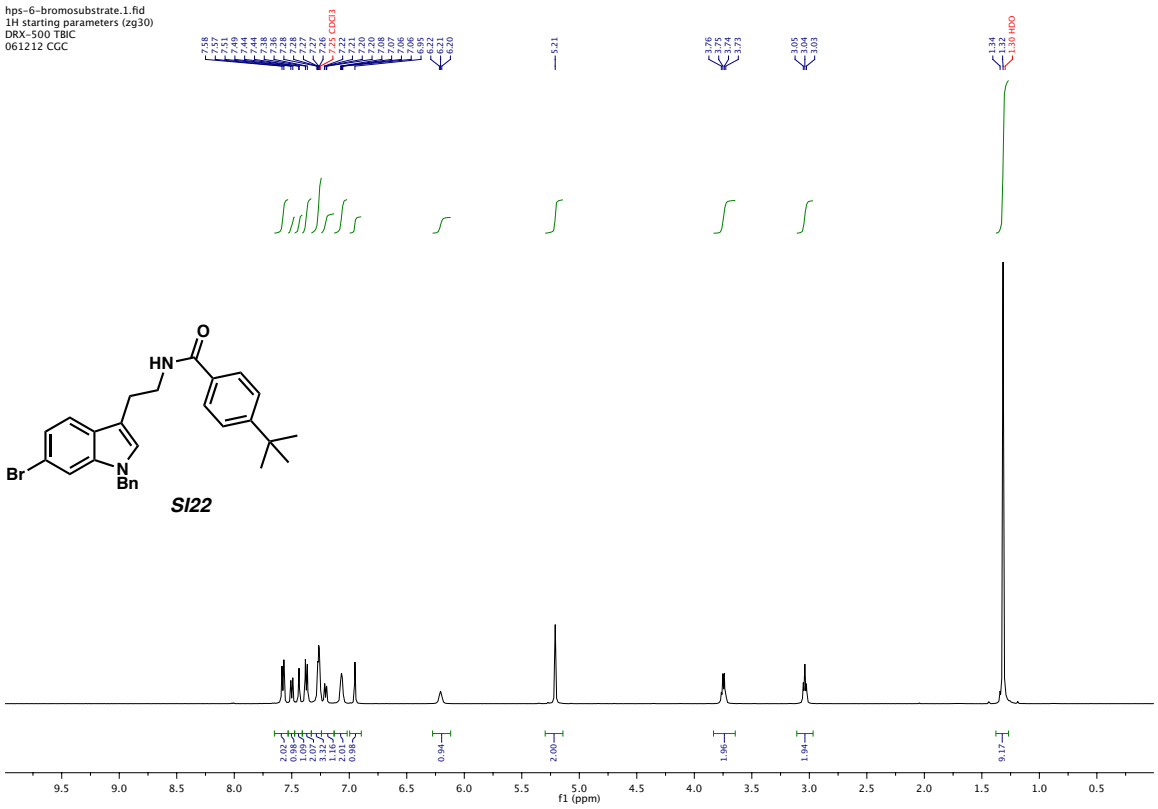
O
HN
F
N
Bn

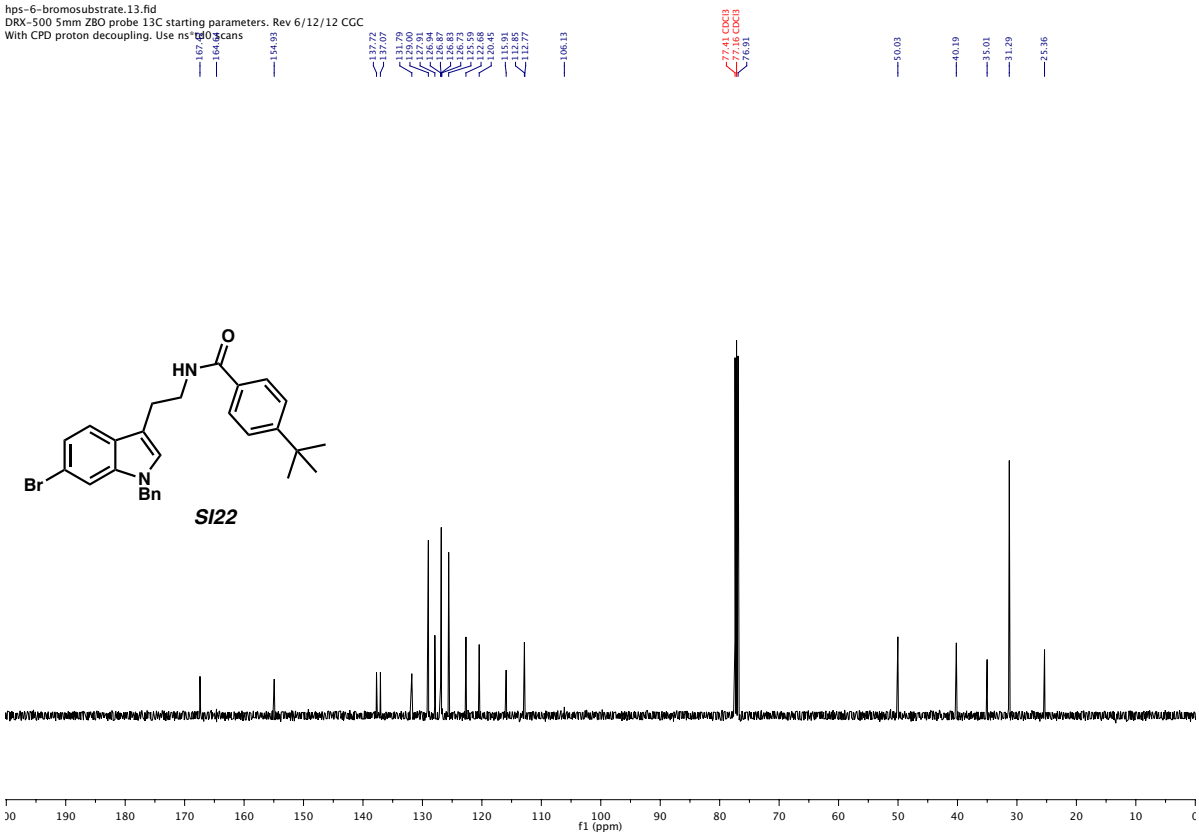
SI21

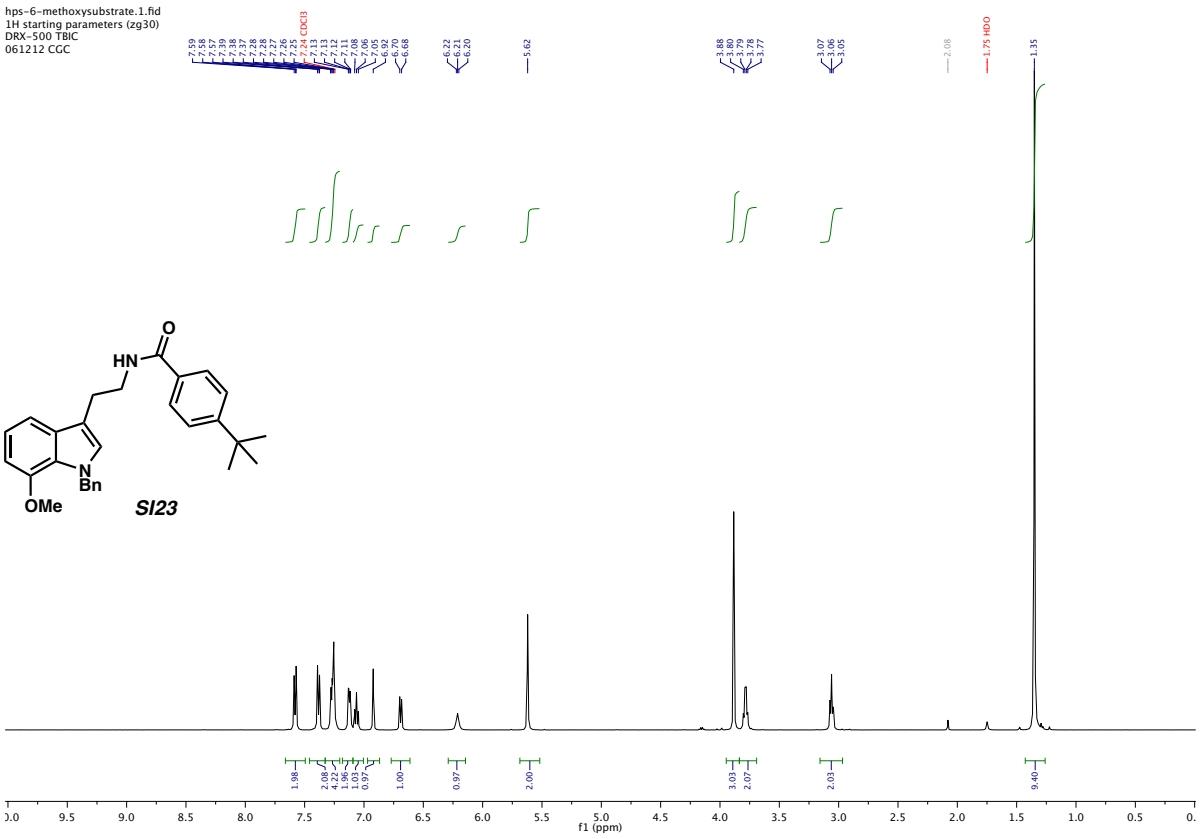

hps-6-fluorosubstrate.13.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*** 0 scans
CDCl3
f1 (ppm)

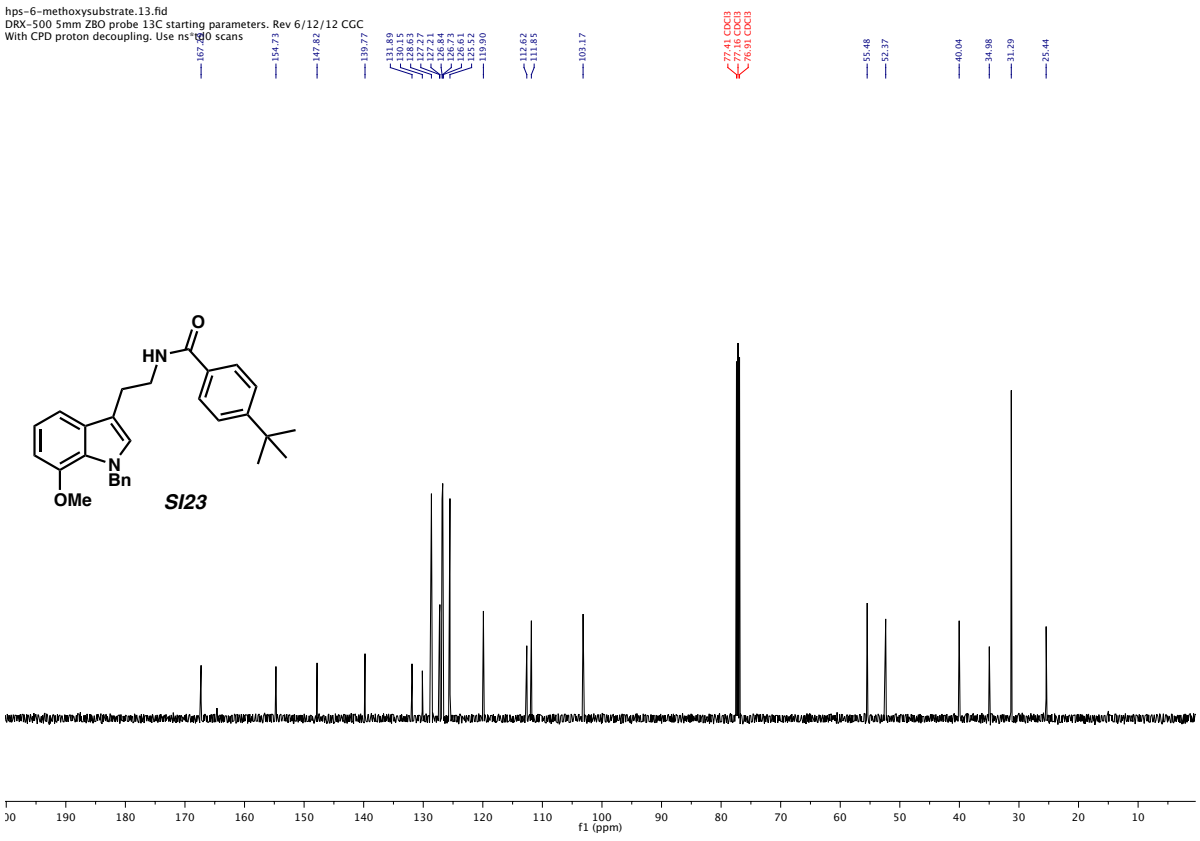
O
HN
F
N
Bn

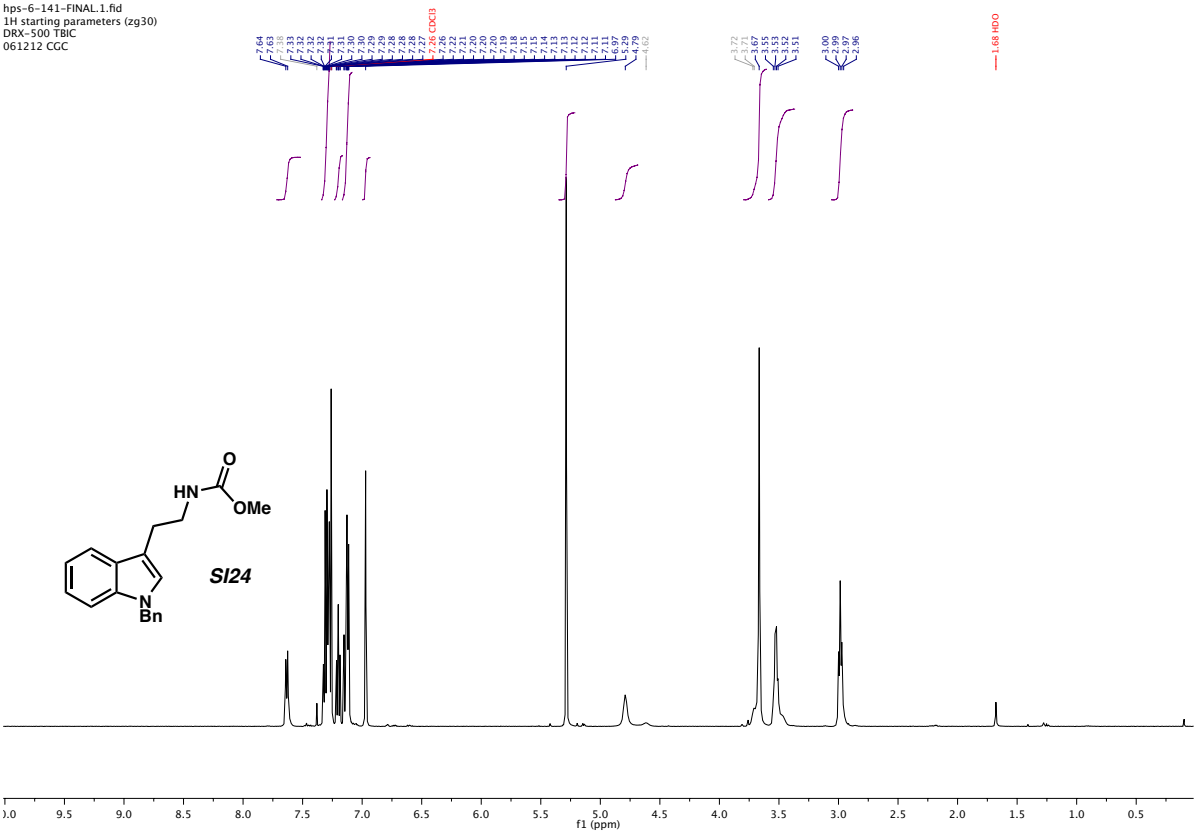
SI21

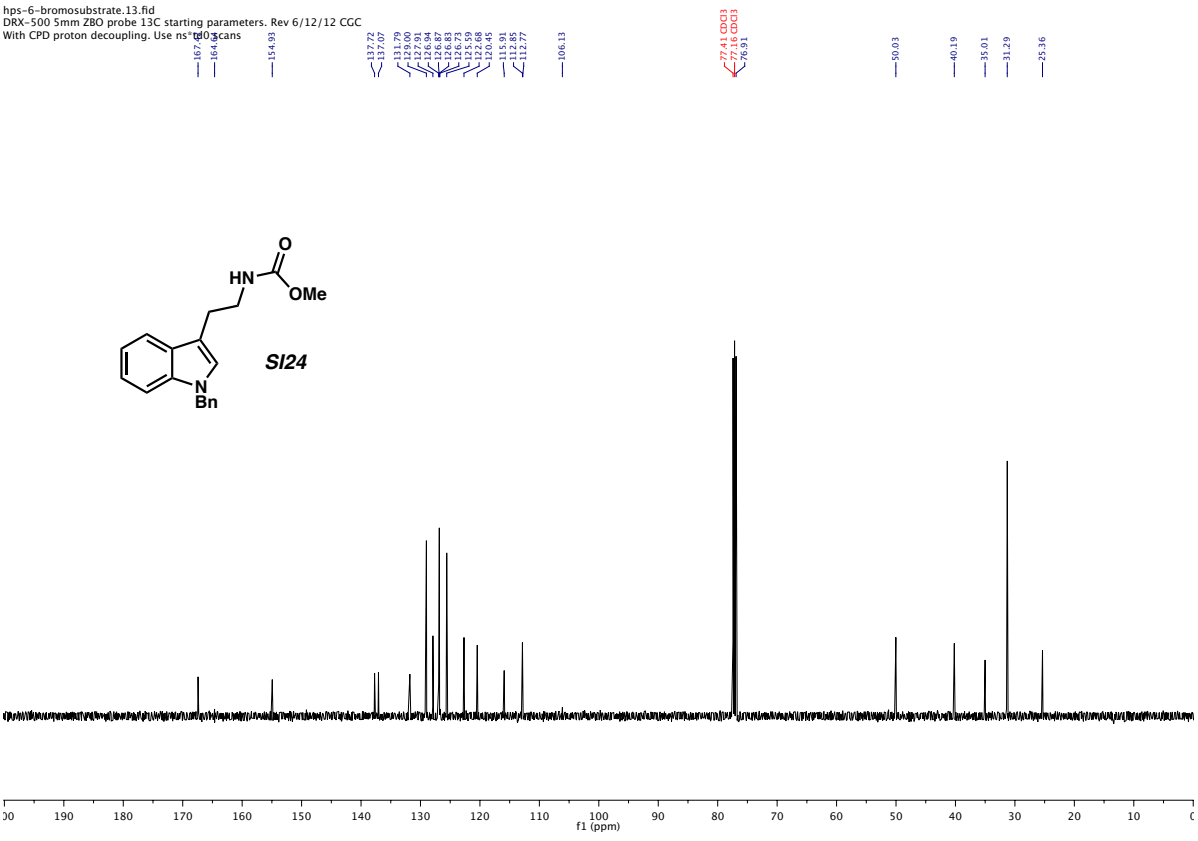

hps-6-bromosubstrate.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
CDCl3
HDO
HN
O
Br
N
Bn
SI22
f1 (ppm)

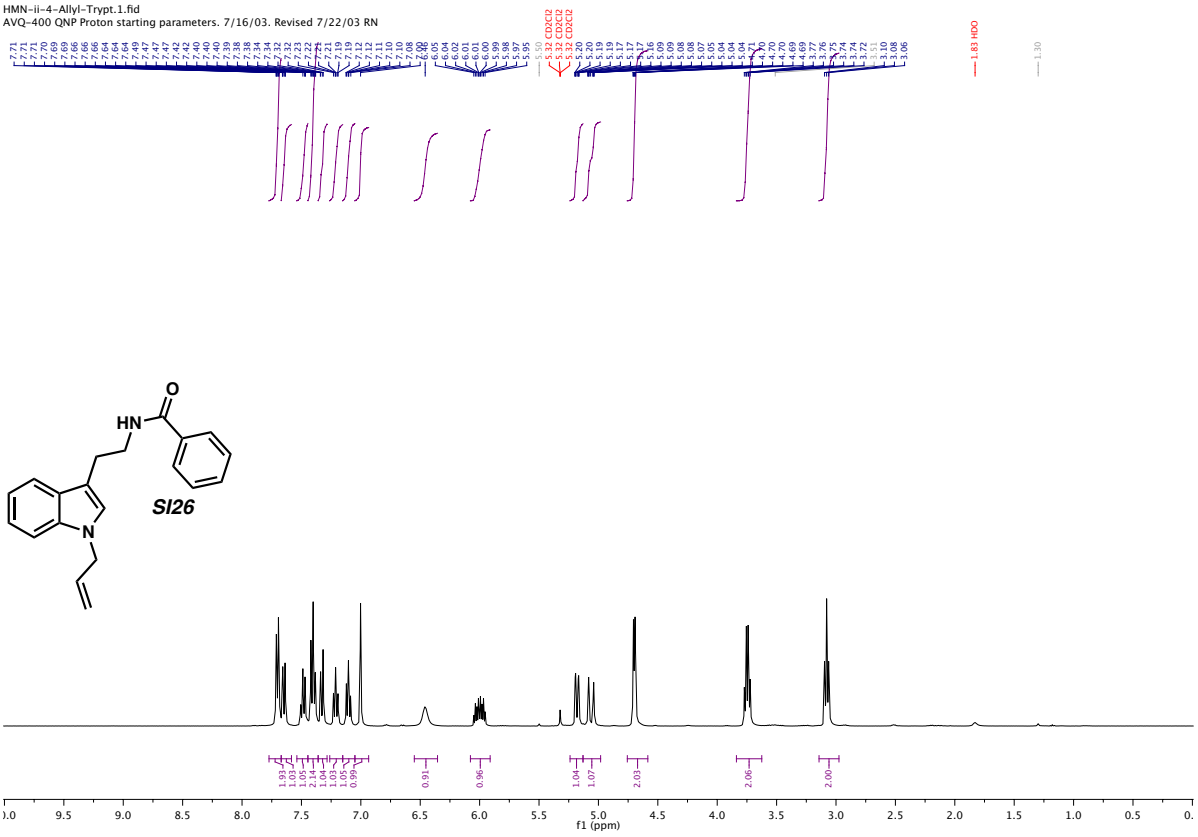

hps-6-bromosubstrate.13.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns = 603 scans
CDCl3
CDCl3
HN
O
Br
N
Bn
SI22
f1 (ppm)

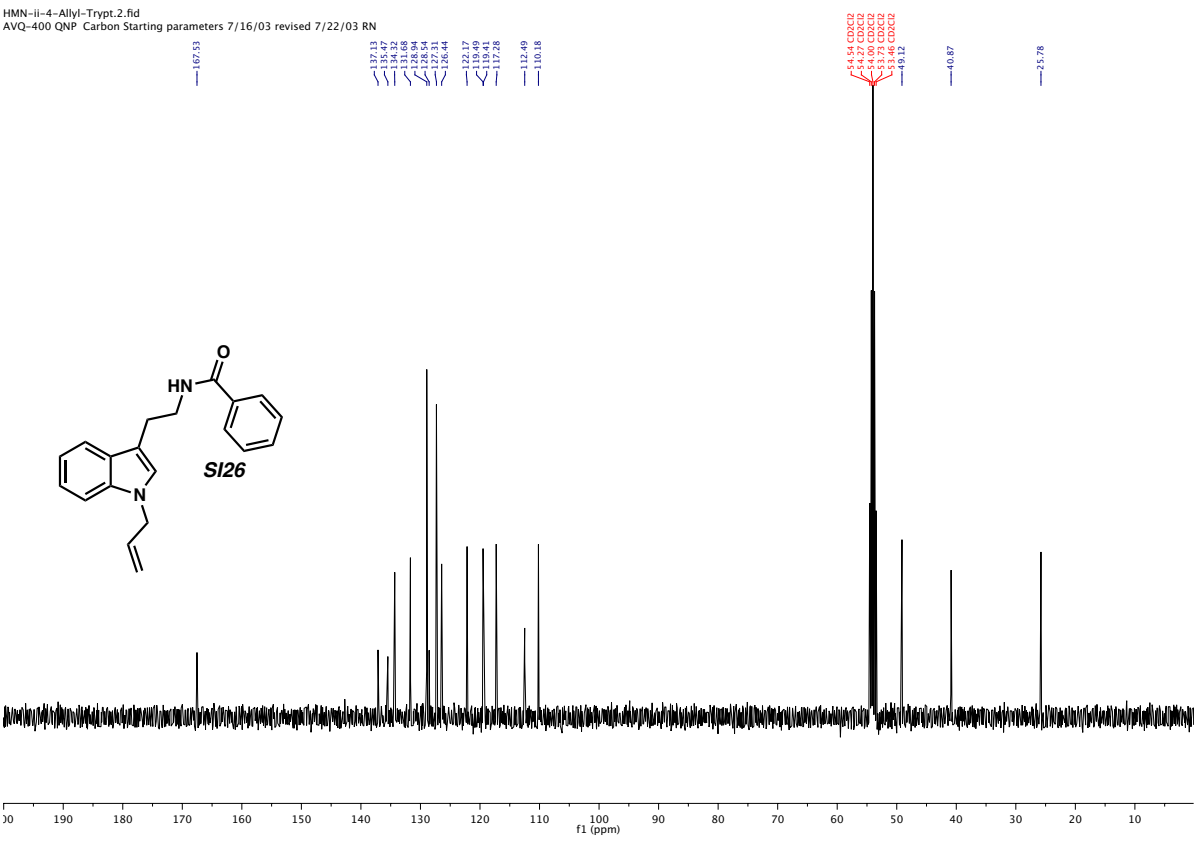

hps-6-methoxysubstrate.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
HN
O
N
Bn
OMe
SI23
f1 (ppm)

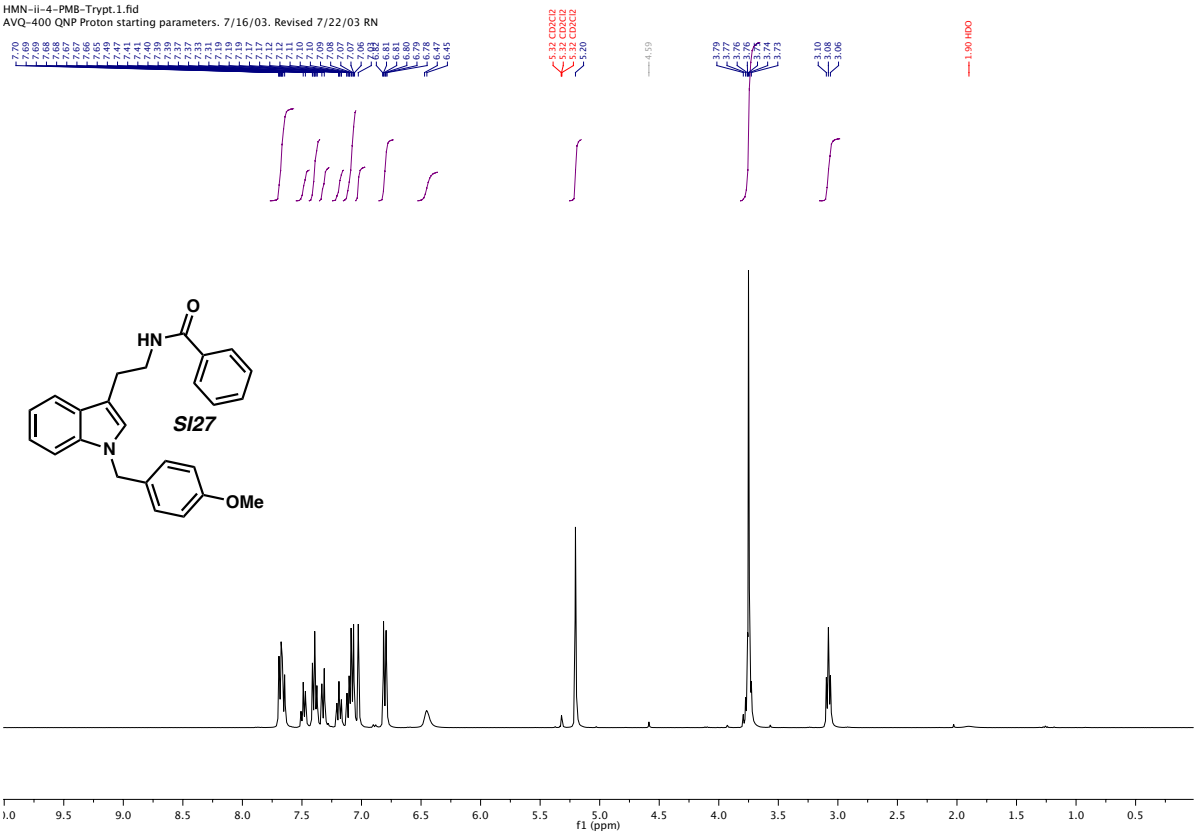

hps-6-methoxysubstrate.13.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*** 0 scans
HN
O
N
Bn
OMe
SI23
f1 (ppm)

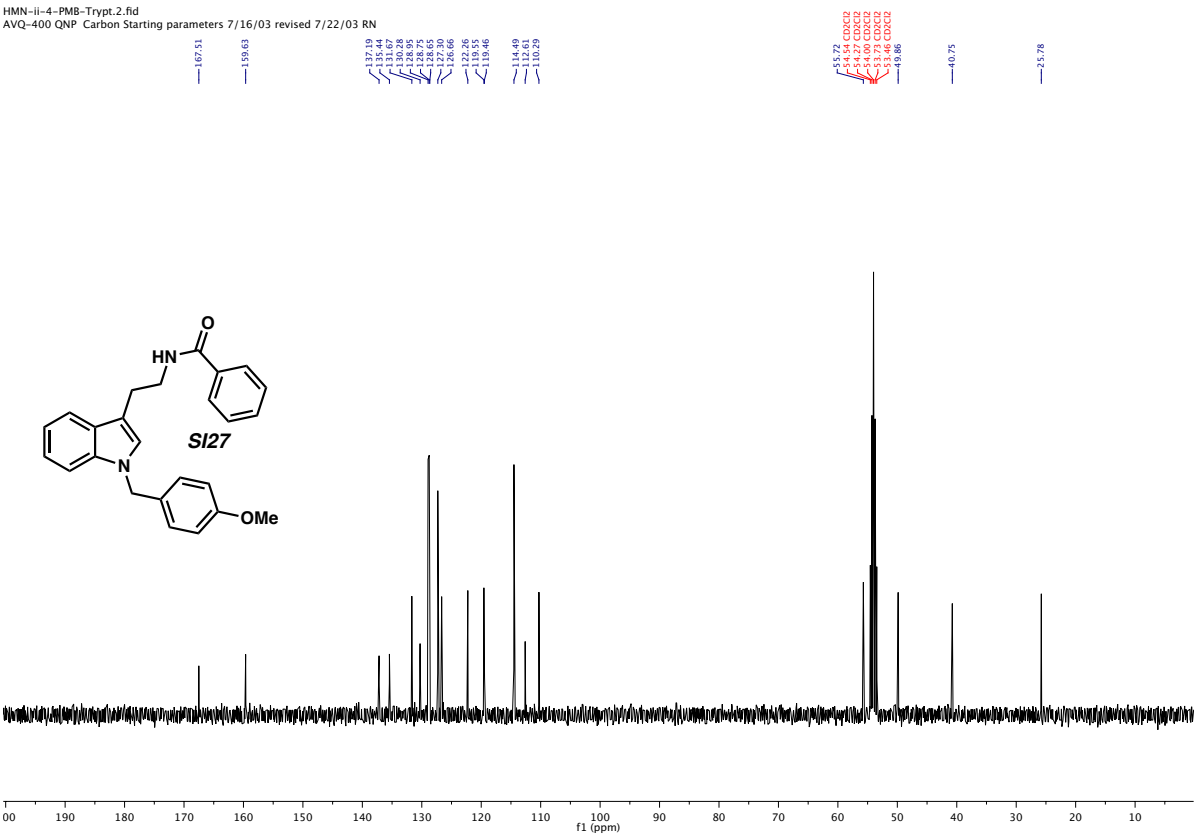

hps-6-141-FINAL.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
HN
O
OMe
N
Bn
SI24
f1 (ppm)


hps-6-bromosubstrate.13.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns=600 scans
HN
O
OMe
N
Bn
SI24
f1 (ppm)

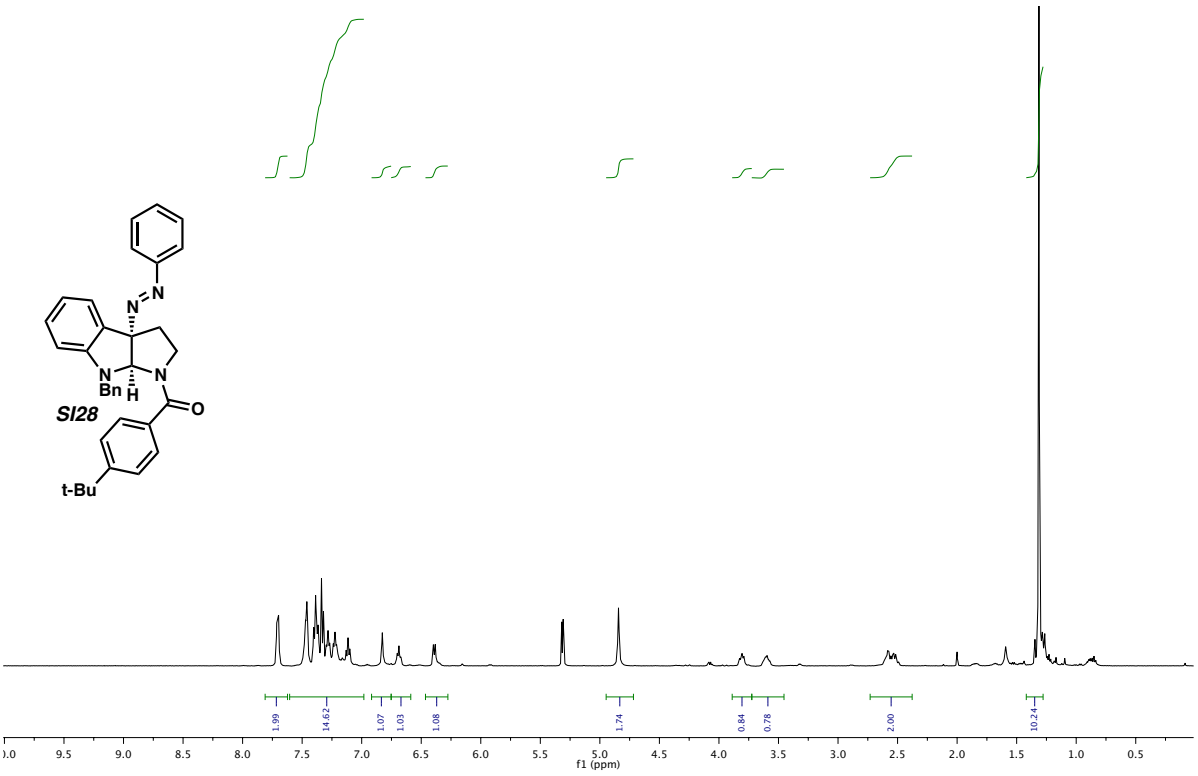

HMN-ii-4-Allyl-Trypt.1.fid
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
SI26
f1 (ppm)


HMN-ii-4-Allyl-Trypt.2.fid
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN
SI26
f1 (ppm)

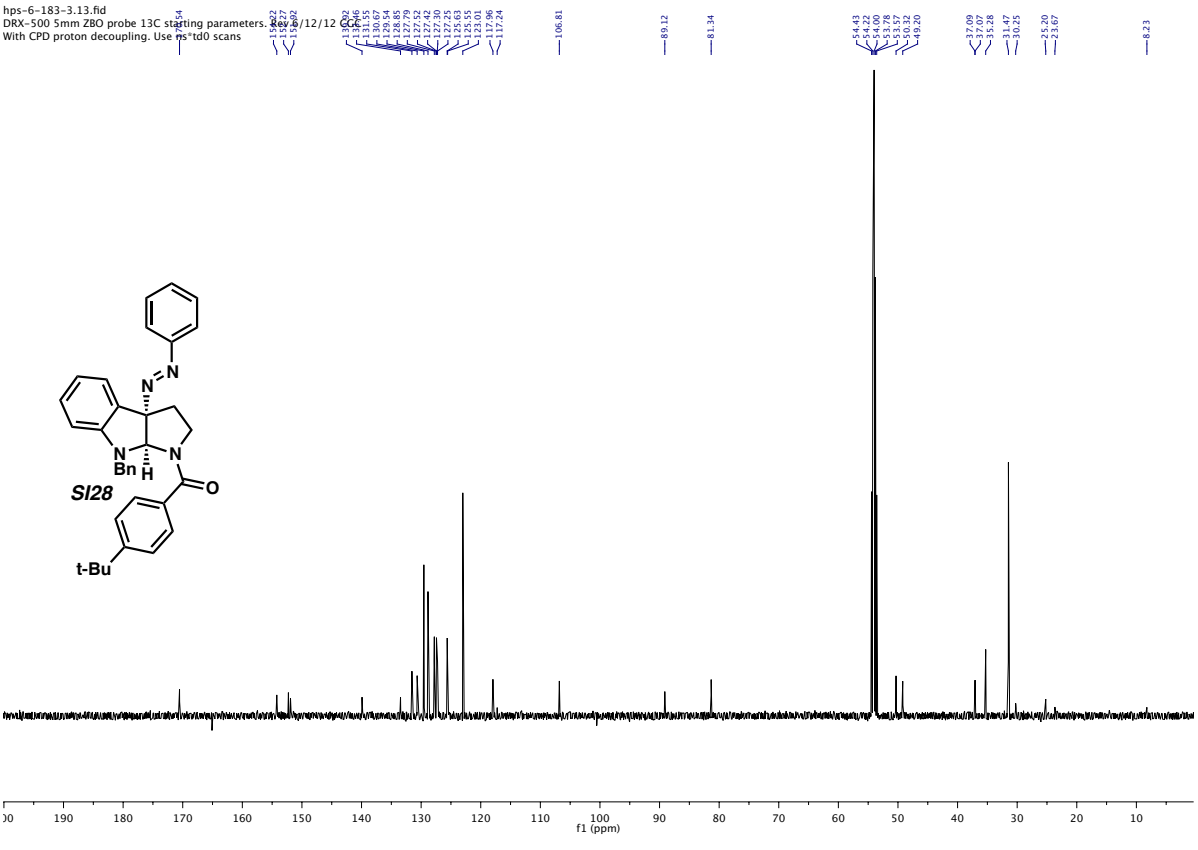

HMN-ii-4-PMB-Trypt.1.fid
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
HN
O
SI27
N
OMe
f1 (ppm)

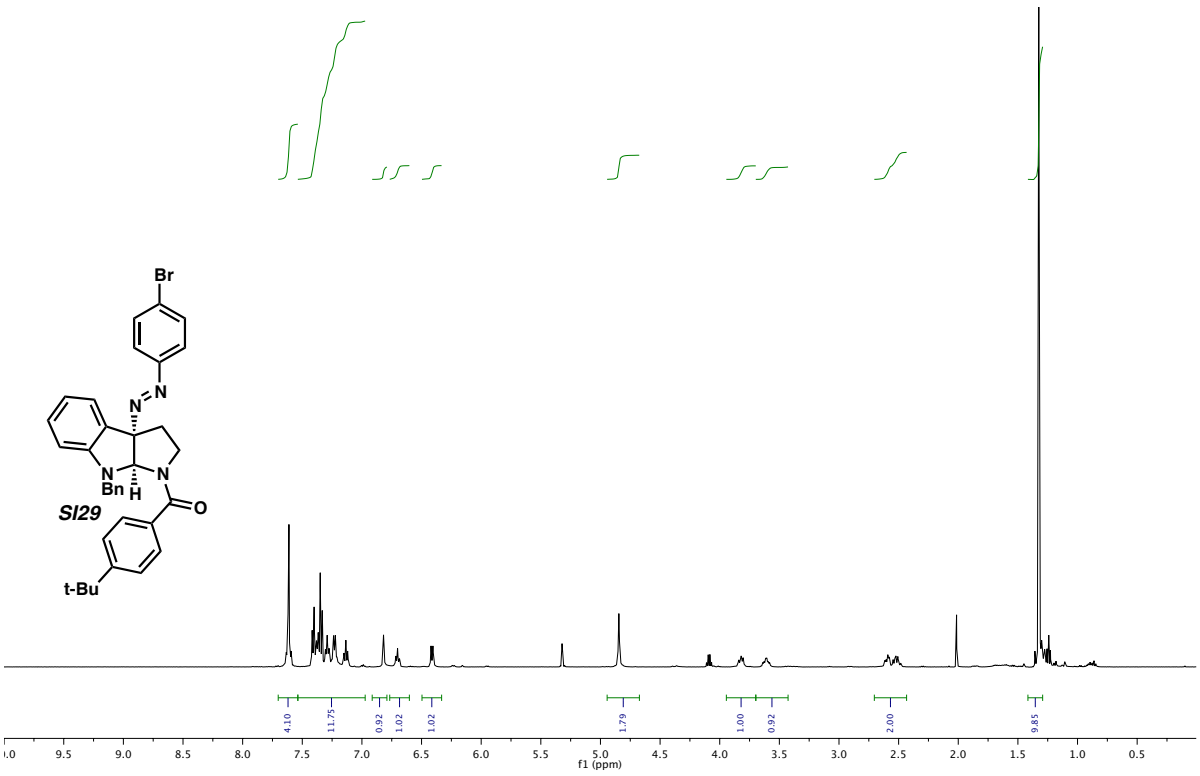

HMN-ii-4-PMB-Trypt.2.fid
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN
HN
O
SI27
N
OMe
f1 (ppm)

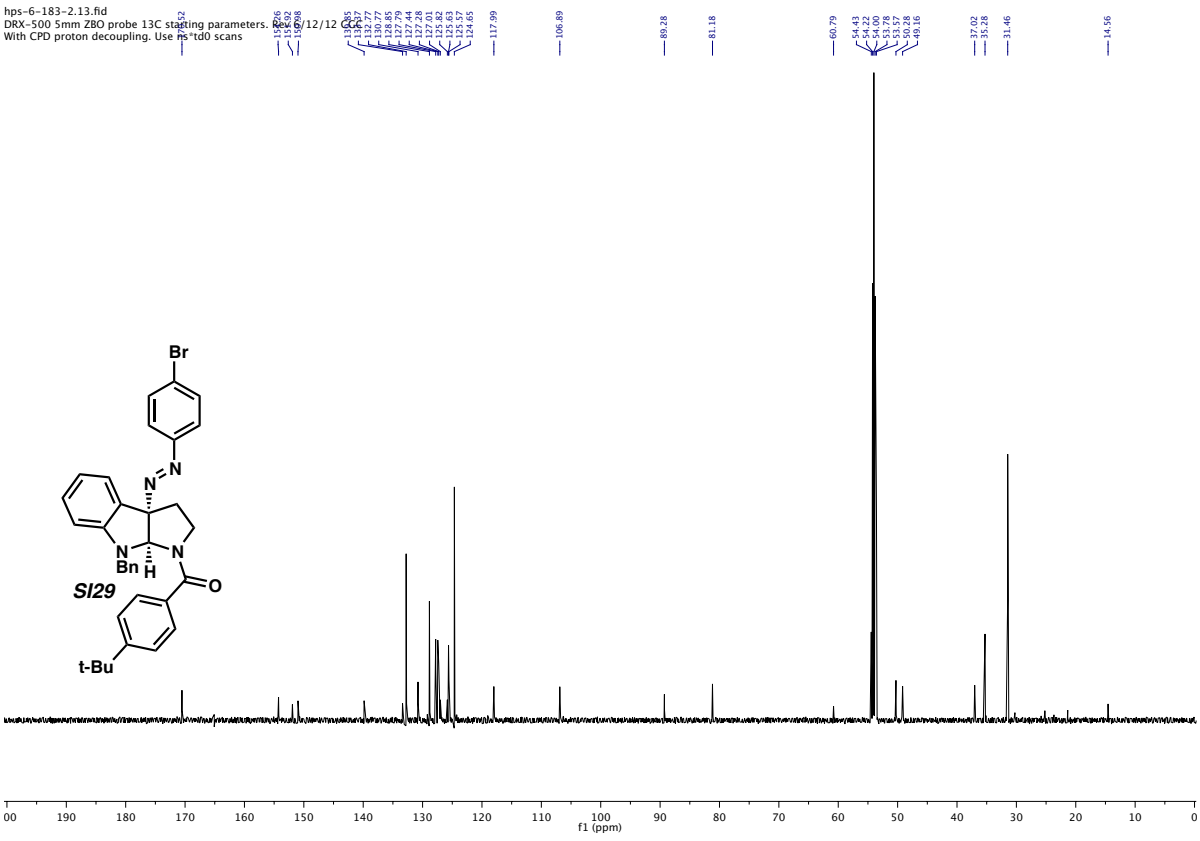
hps-6-183-3.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC



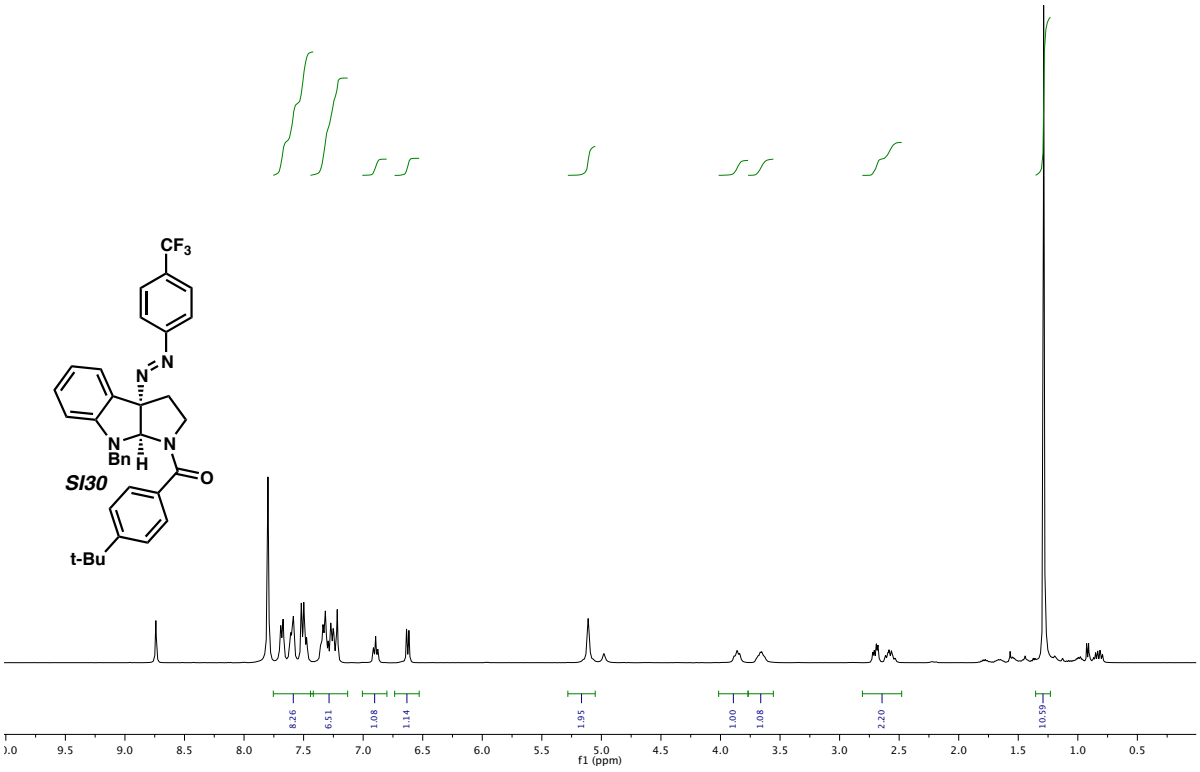
hps-6-183-3.13.fid
DRX-500 5mm ZBO probe 13C starting parameters 061212 CGC
With CPD proton decoupling. Use 3*td0 scans



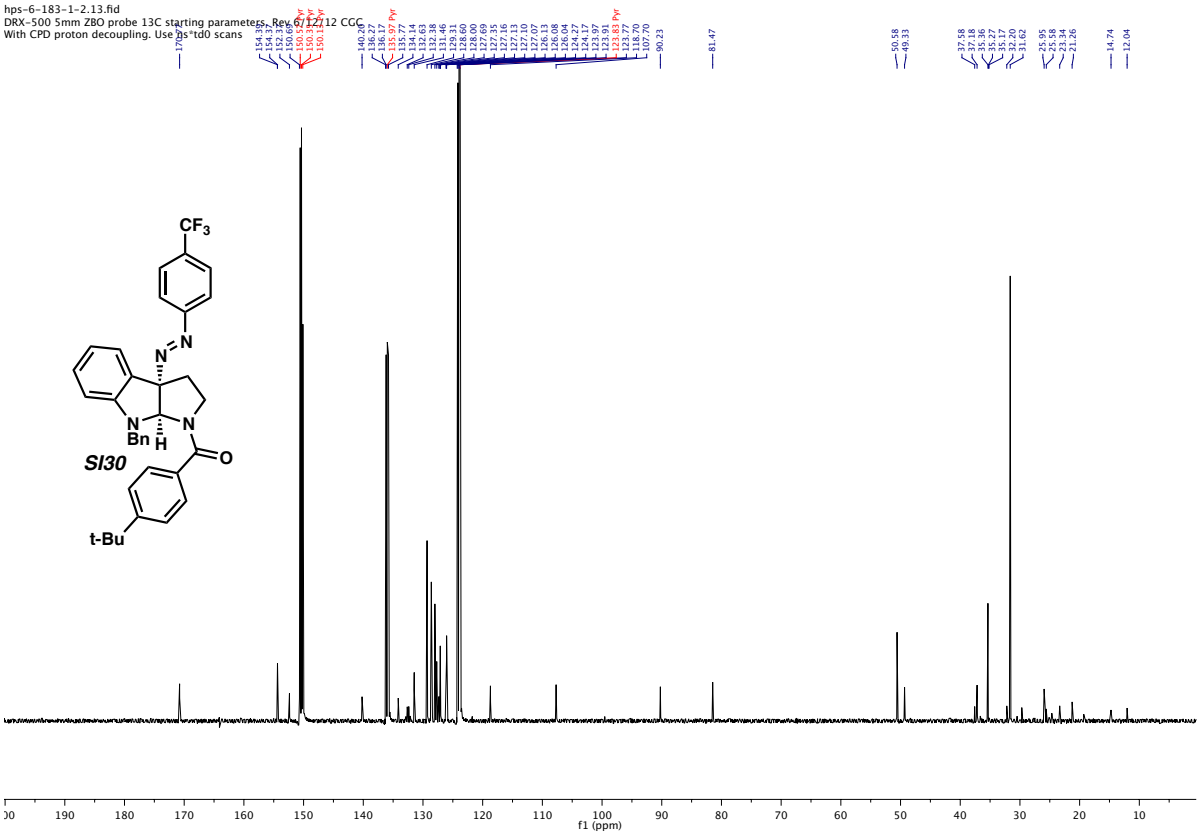

hps-6-183-2.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
Br
N
N
Bn
H
N
O
SI29
t-Bu
4.10
11.75
0.92
1.02
1.02
1.79
1.00
0.92
2.00
9.85
f1 (ppm)

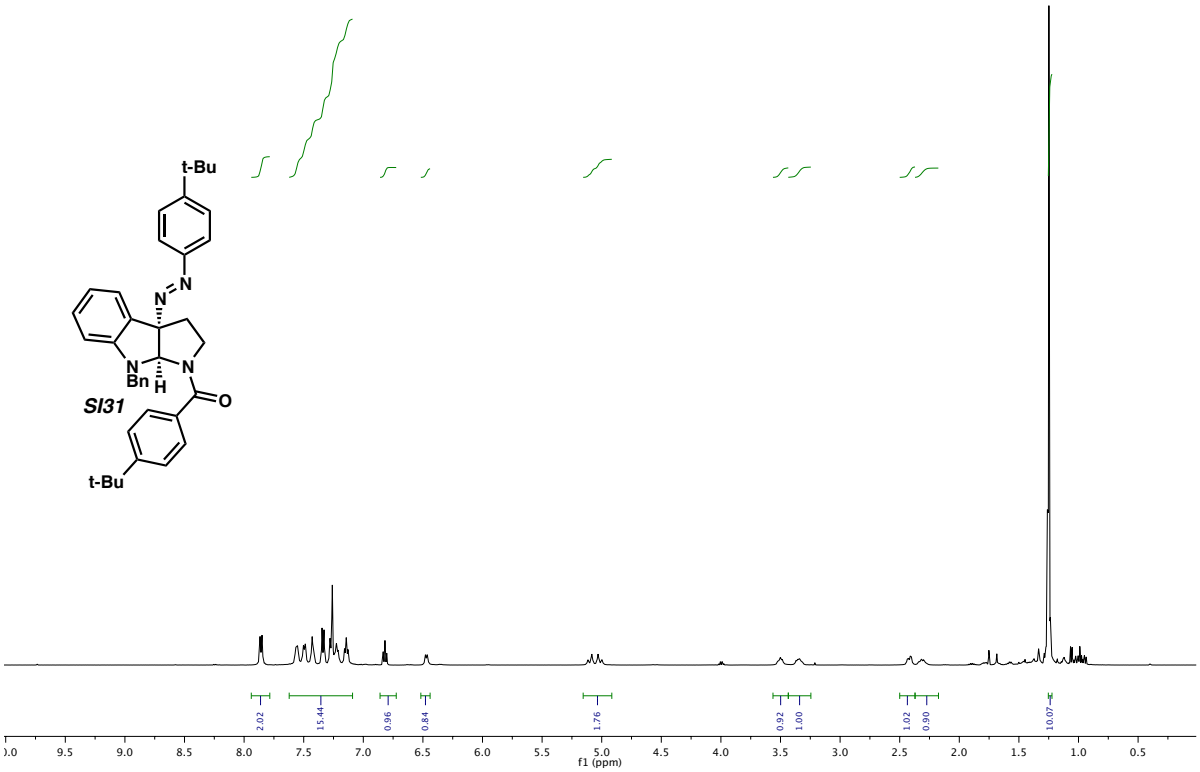

hps-6-183-2.13.fid
DRX-500 5mm ZBO probe 13C starting parameters. AS 061212 CGC
With CPD proton decoupling. Use ns *td0 scans
117.99
106.89
89.28
81.18
60.79
54.43
54.22
54.00
53.78
53.57
50.28
48.16
37.02
35.28
31.46
14.56
Br
N
N
Bn
H
N
O
SI29
t-Bu
f1 (ppm)

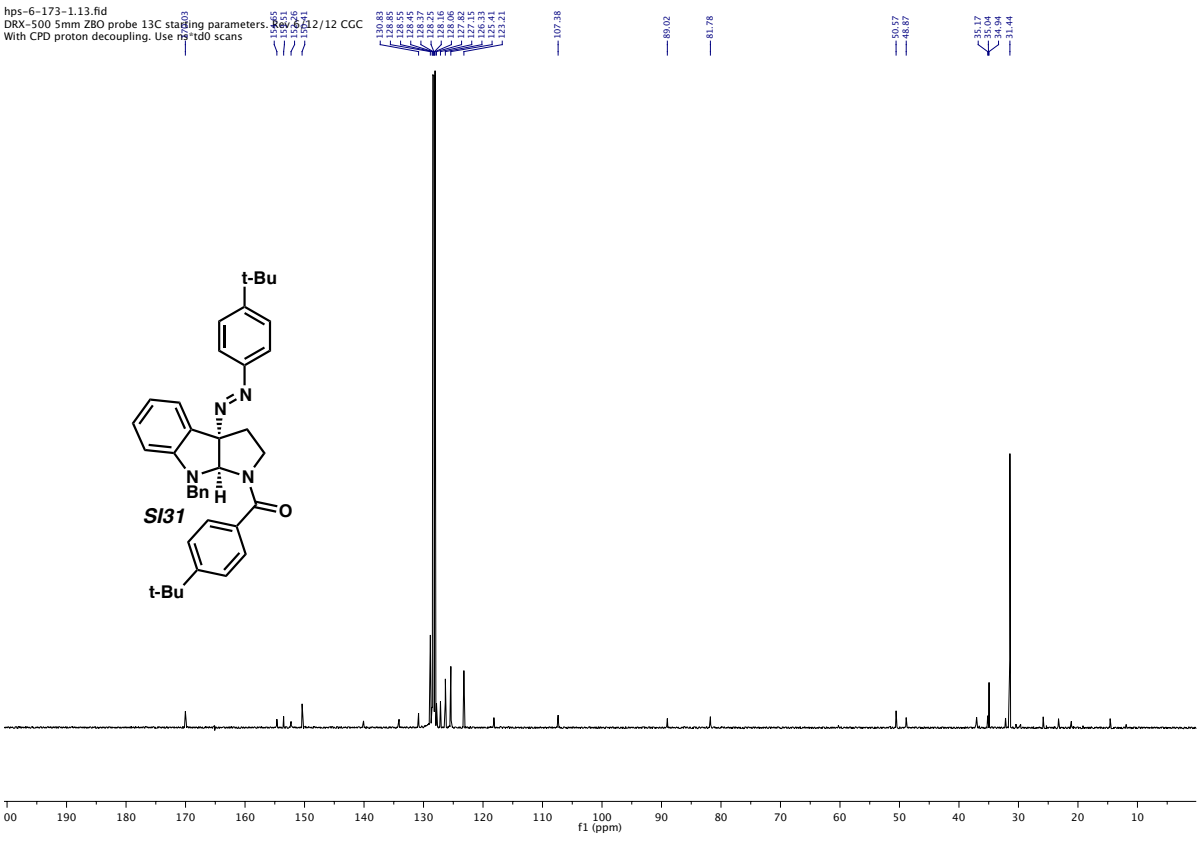
hps-6-183-1-2.1.fid
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN



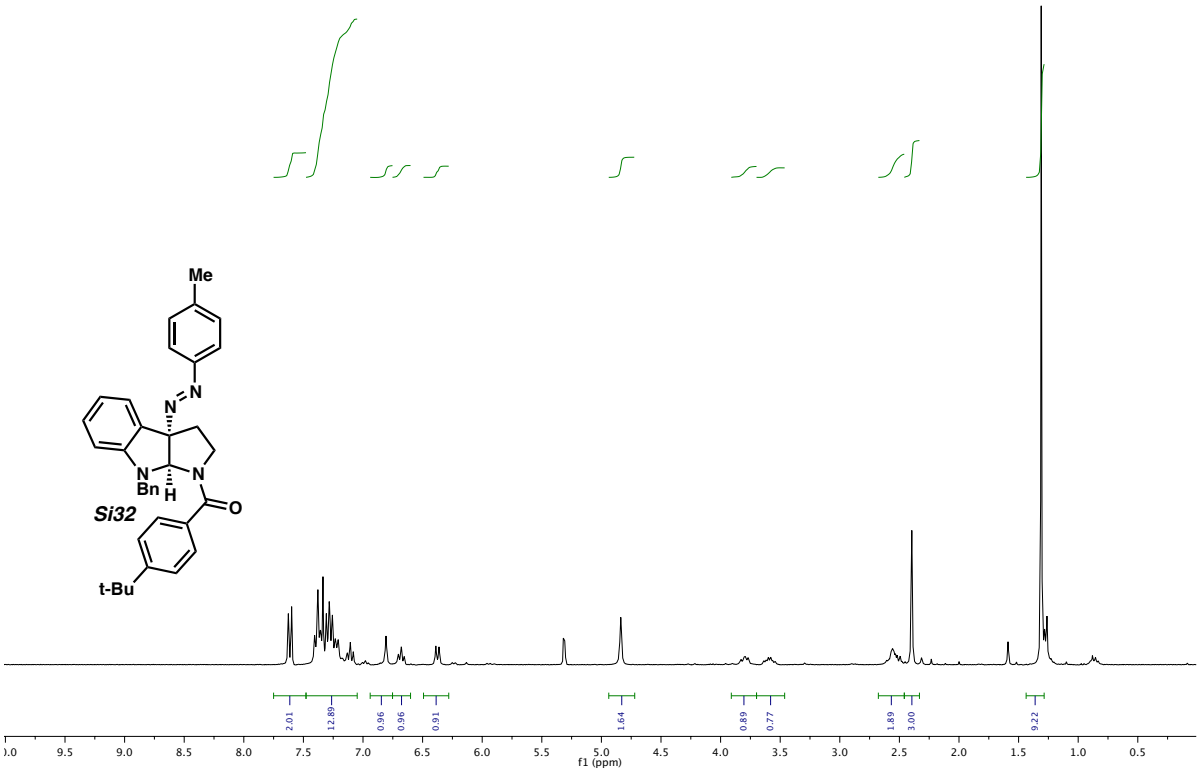
hps-6-183-1-2.13.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns *td0 scans



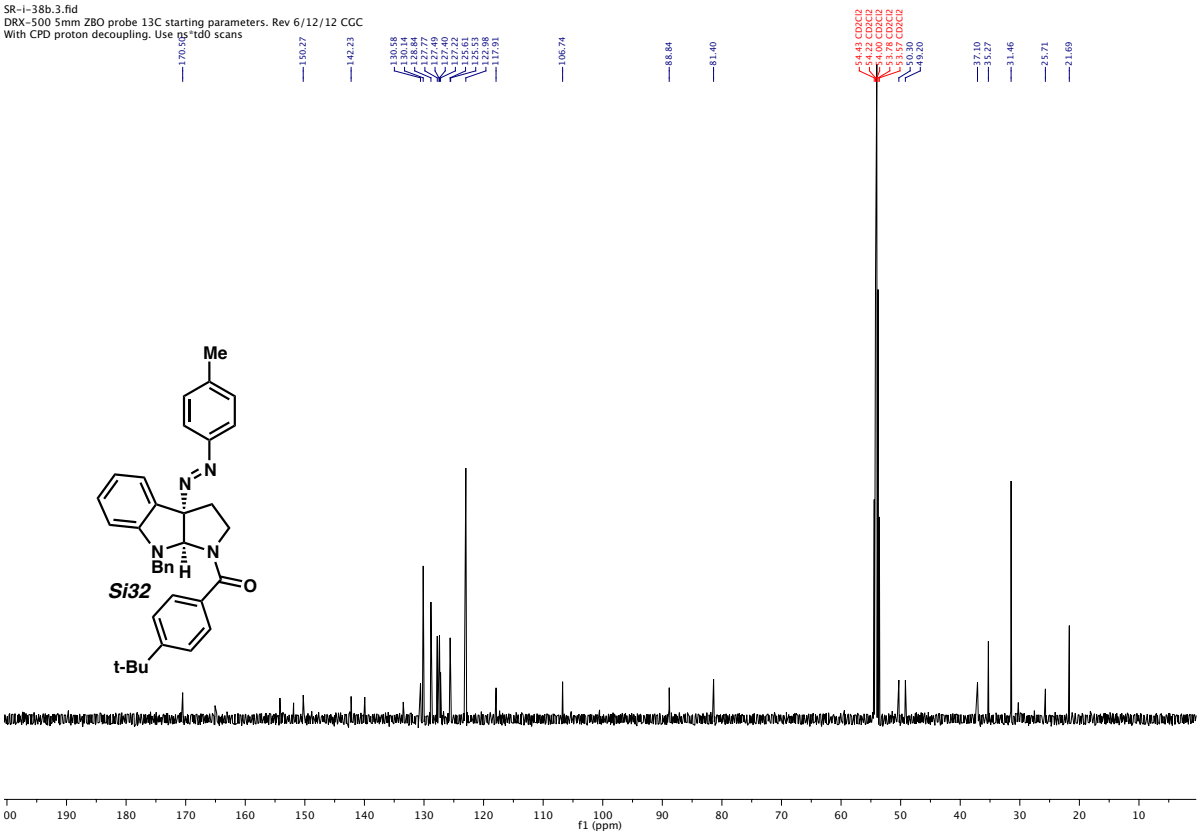

hps-6-173-1.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
t-Bu
N
N
N
Bn
H
N
O
SI31
t-Bu
2.02
15.44
0.96
0.84
1.76
0.92
1.00
1.02
0.90
10.07
f1 (ppm)

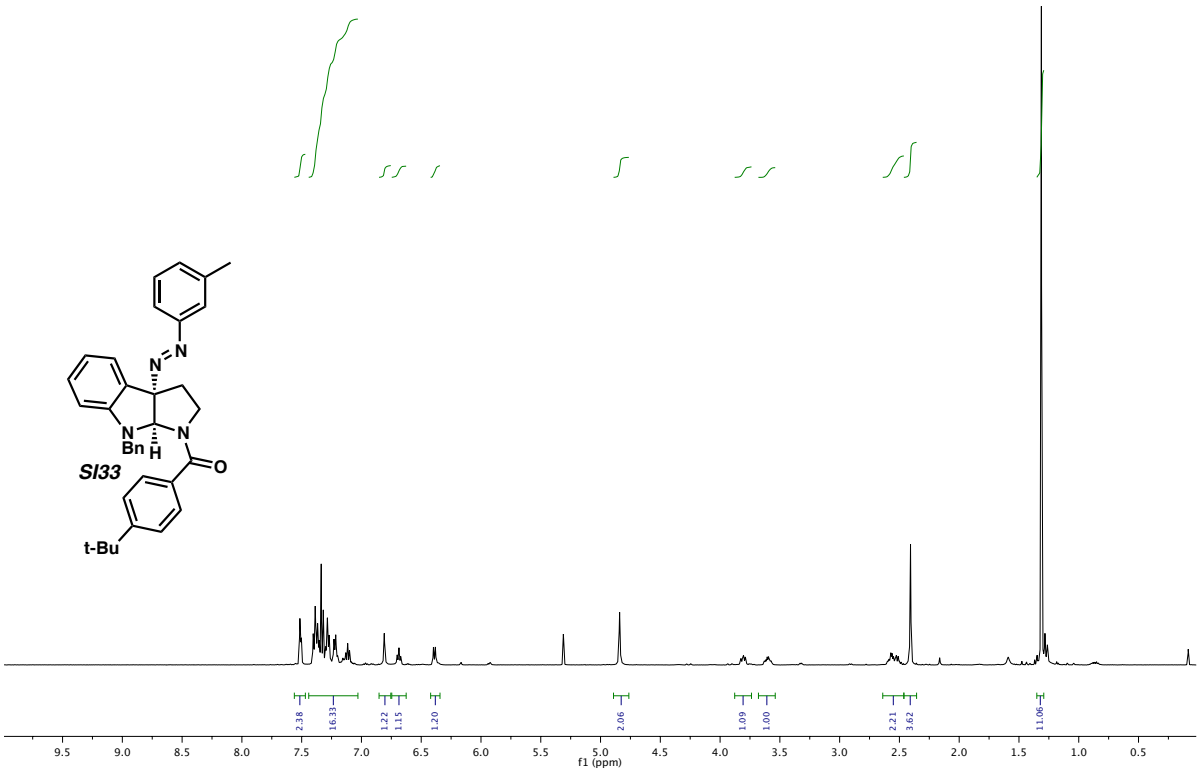

hps-6-173-1.13.fid
DRX-500 5mm ZBO probe 13C starting parameters 061212 CGC
With CPD proton decoupling. Use ns*td0 scans
77.03
130.83
128.85
128.55
128.45
128.37
128.25
128.16
128.06
127.82
127.15
126.33
125.41
123.21
107.38
89.02
81.78
50.57
48.87
35.17
35.04
34.94
31.44
t-Bu
N
N
N
Bn
H
N
O
SI31
t-Bu
f1 (ppm)

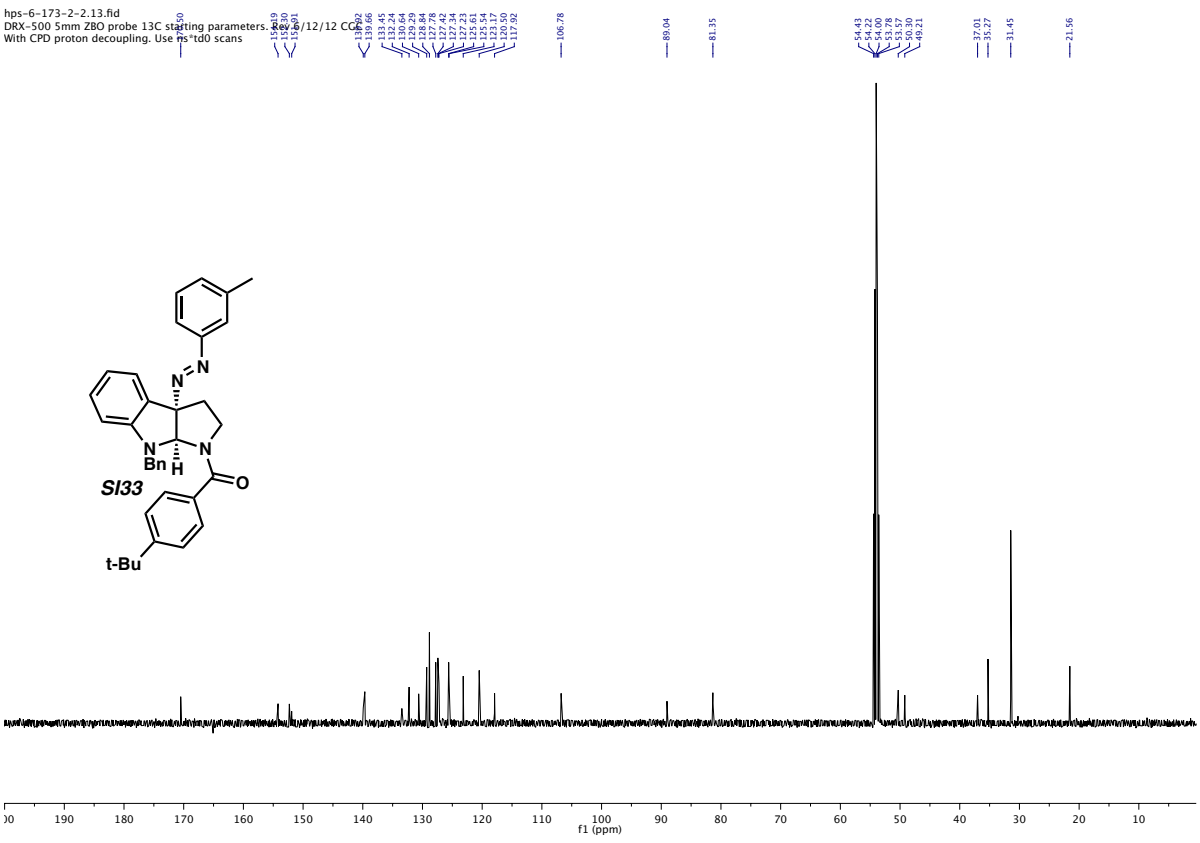
SR-i-38b.1.fid
AV-300 Dual C-H probe proton starting parameters 7/23/03 RN.

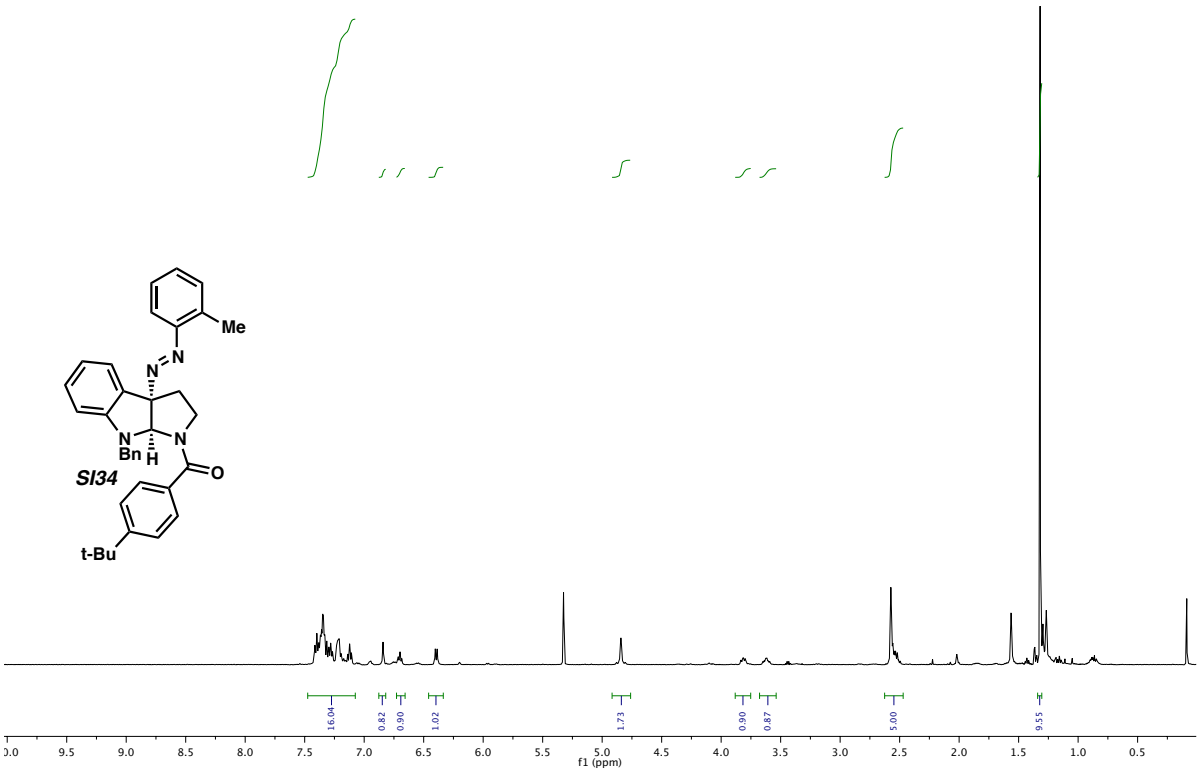


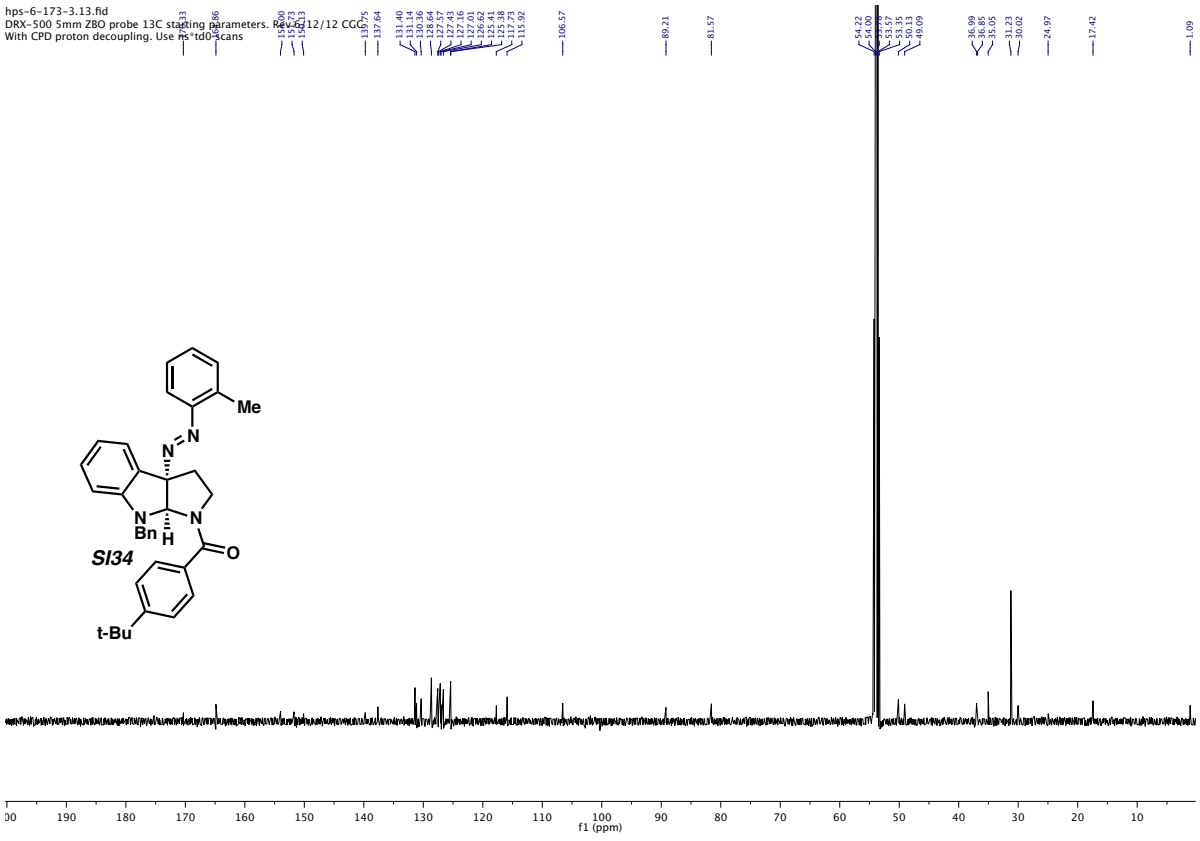
SR-i-38b.3.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans

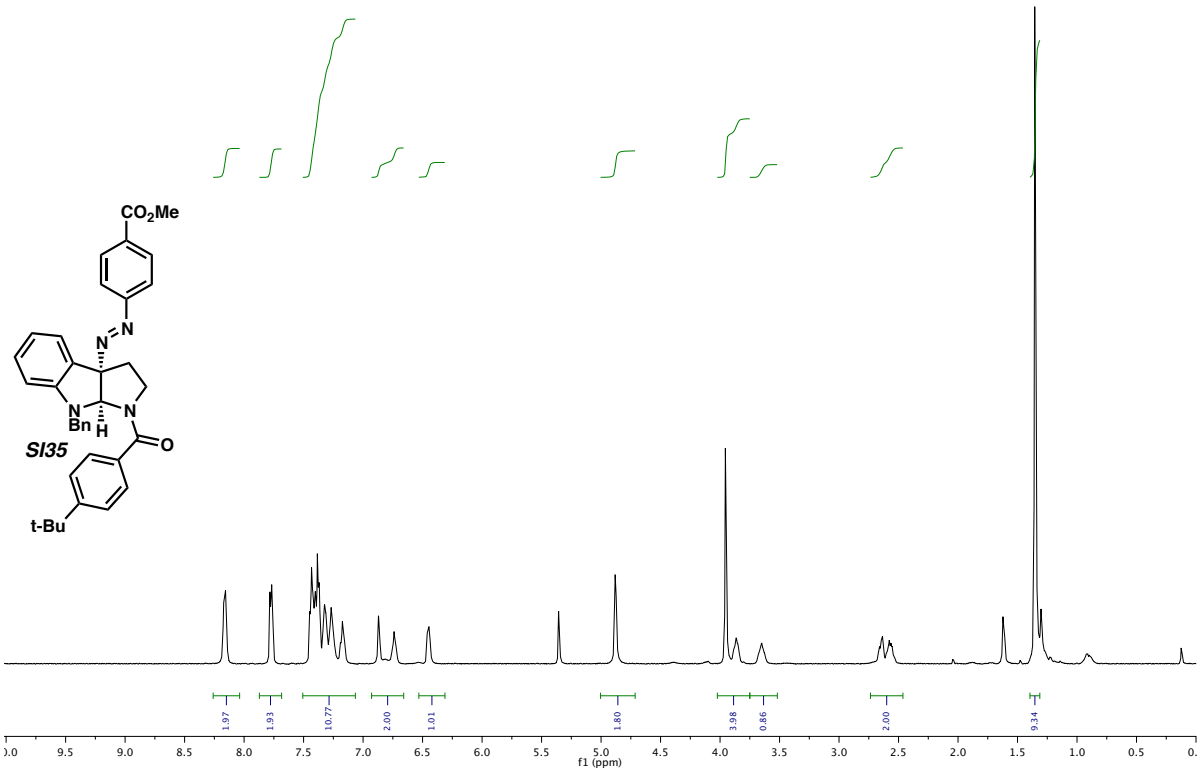


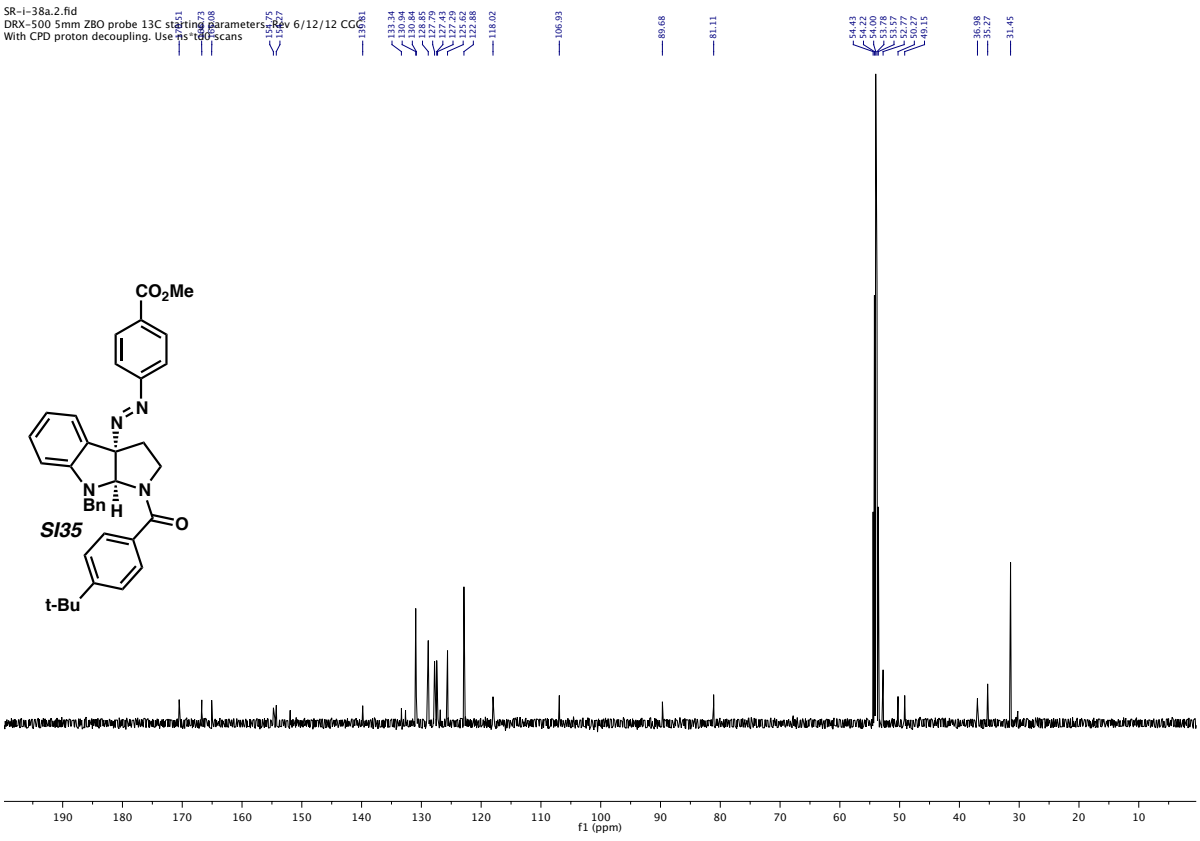

hps-6-173-2-2.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
N
N
Bn
H
N
O
SI33
t-Bu
2.38
16.33
1.22
1.15
1.20
2.06
1.09
1.00
2.21
3.62
11.06
f1 (ppm)

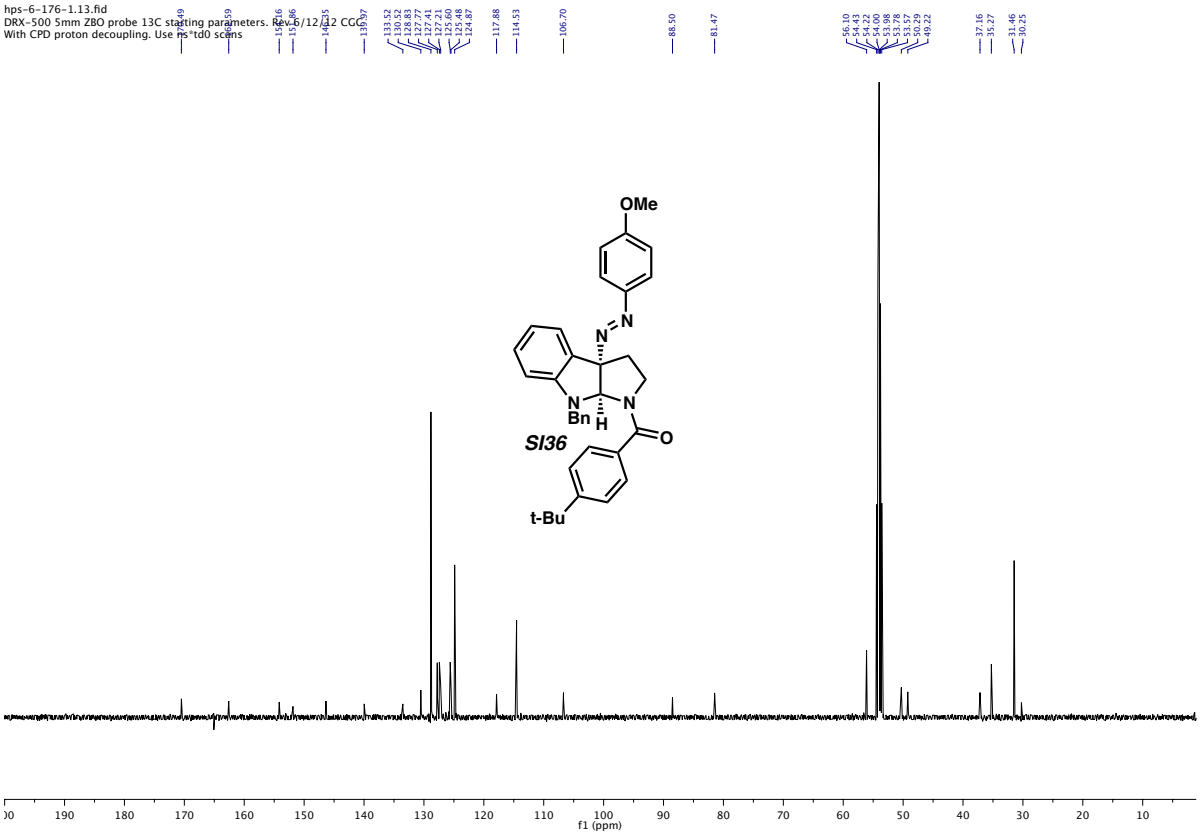

hps-6-173-2-2.13.fid
DRX-500 5mm ZBO probe 13C starting parameters, 6/12/12 CGC
With CPD proton decoupling. Use ns *td0 scans
106.78
89.04
81.35
54.43
54.22
54.00
53.78
53.57
50.30
49.21
37.01
35.27
31.45
21.56
N
N
Bn
H
N
O
SI33
t-Bu
f1 (ppm)

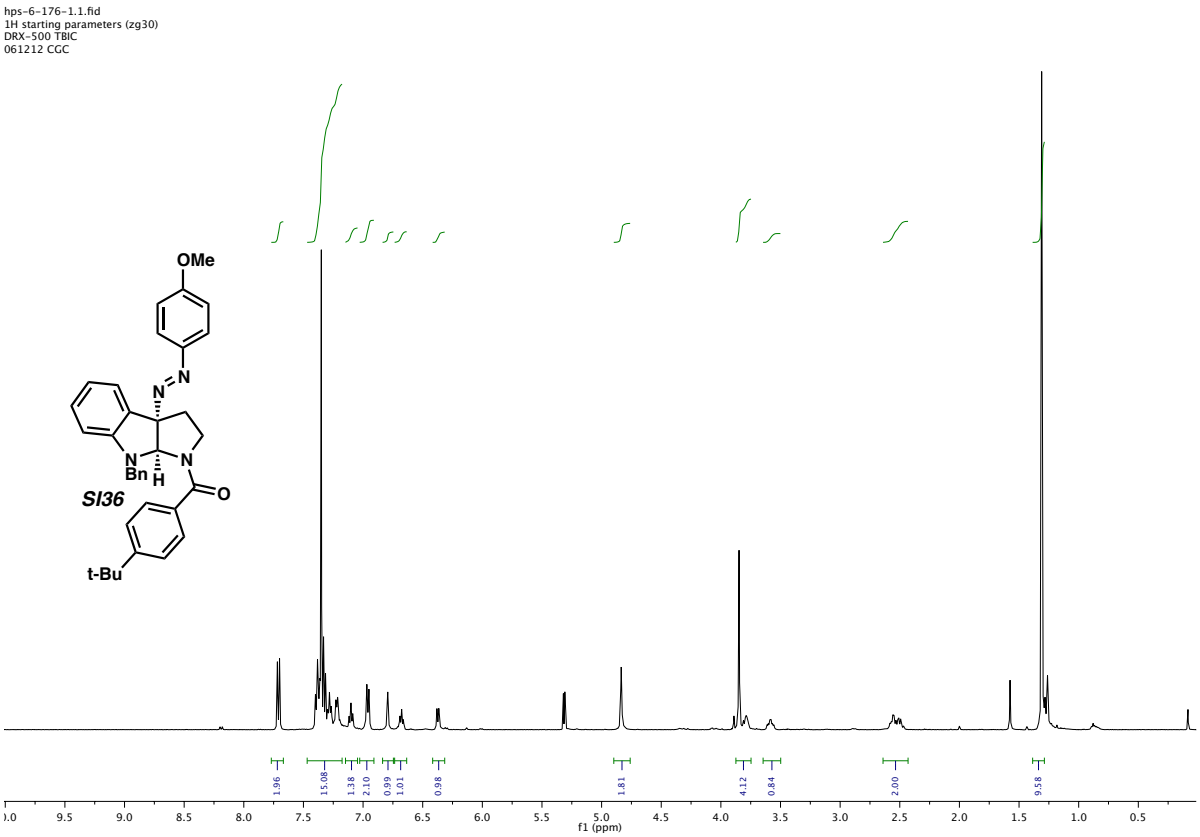

hps-6-173-3.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
Me
N
N
N
Bn
H
N
O
SI34
t-Bu
16.04
0.82
0.90
1.02
1.73
0.90
0.87
5.00
9.55
f1 (ppm)

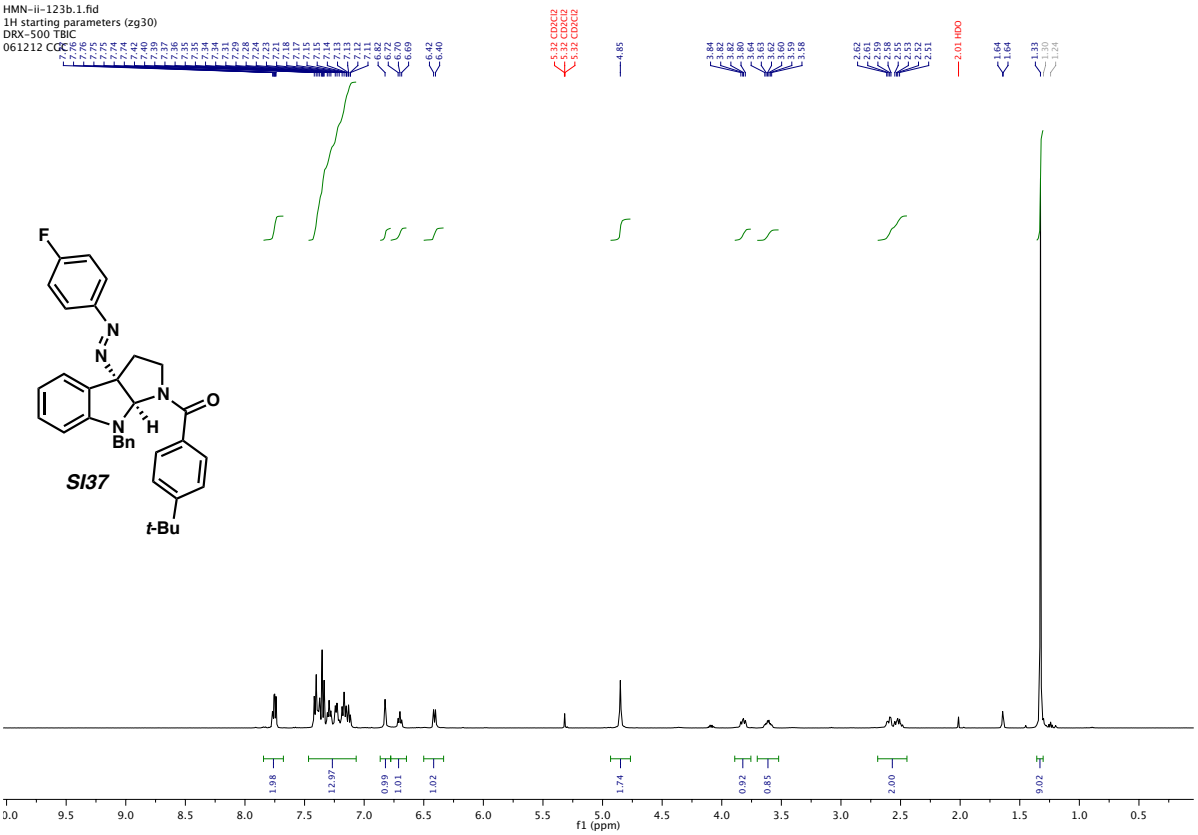

hps-6-173-3.13.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev. 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
Me
N
N
N
Bn
H
N
O
SI34
t-Bu
f1 (ppm)

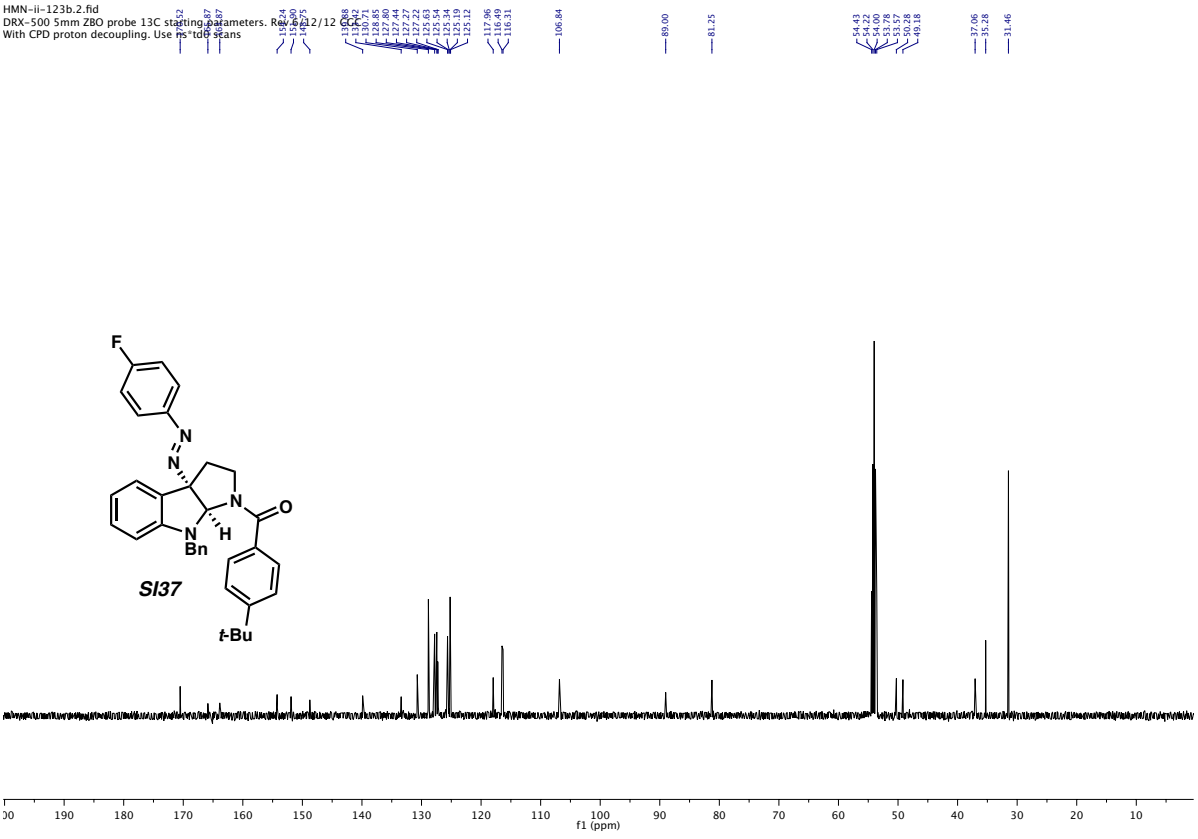

SR-i-38a.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
CO2Me
N
N
N
Bn
H
N
O
SI35
t-Bu
1.97
1.93
10.77
2.00
1.01
1.80
3.98
0.86
2.00
9.34
f1 (ppm)

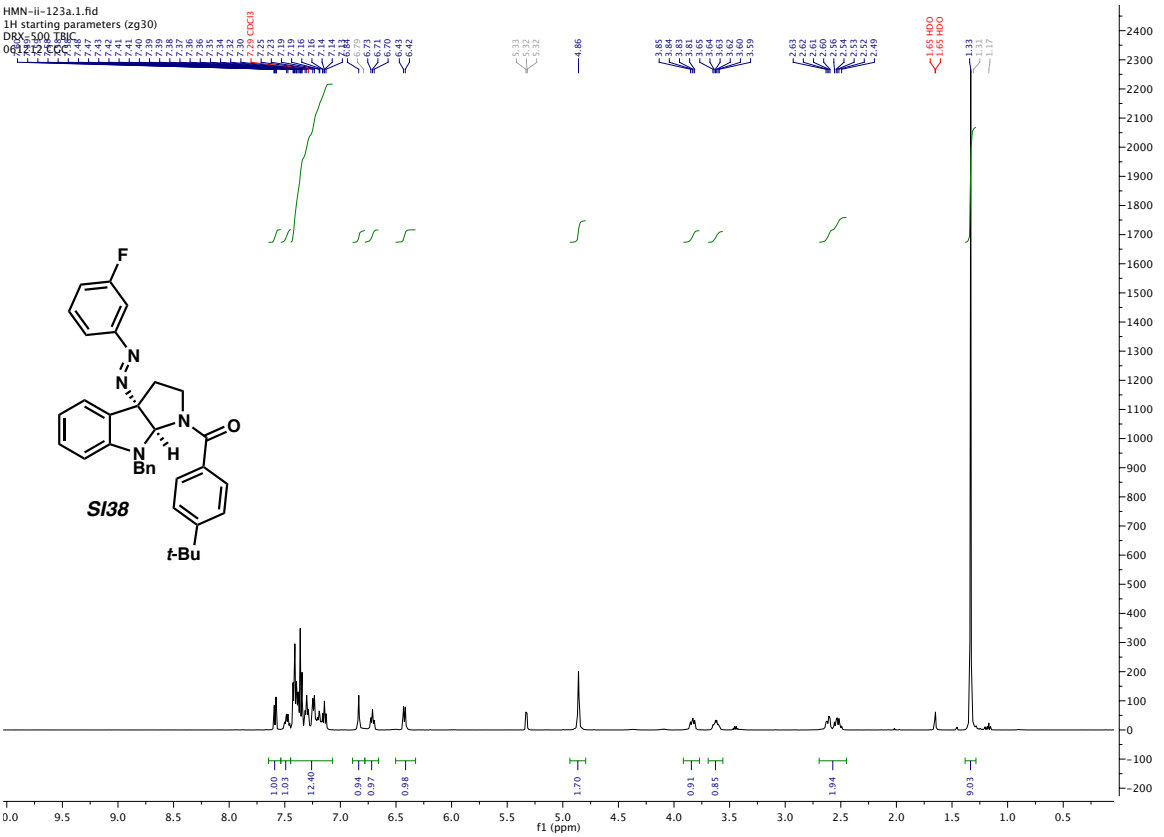

SR-i-38a.2.fid
DRX-500 5mm ZBO probe 13C starting parameters rev 6/12/12 CGC
With CPD proton decoupling. Use ns 100 scans
CO2Me
N
N
N
Bn
H
N
O
SI35
t-Bu
f1 (ppm)

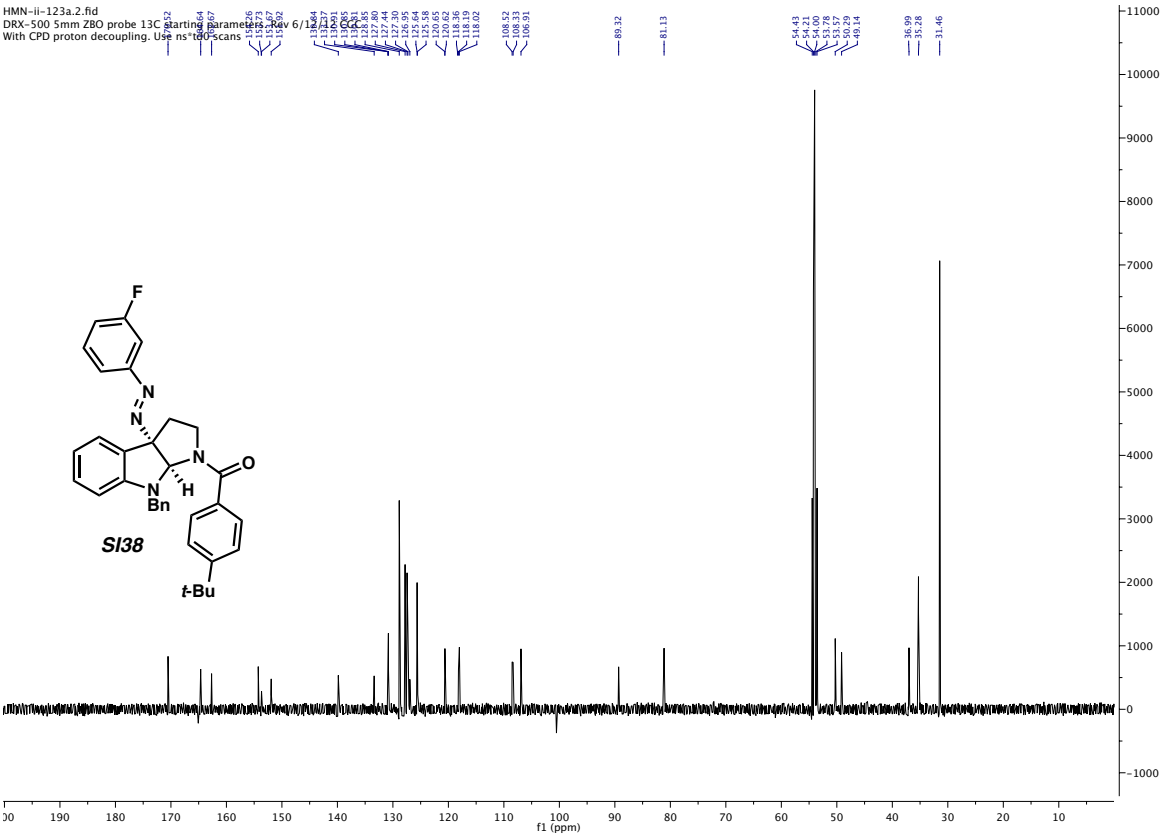

hps-6-176-1.13.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev. 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
OMe
N
N
N
Bn
H
N
O
SI36
t-Bu
f1 (ppm)

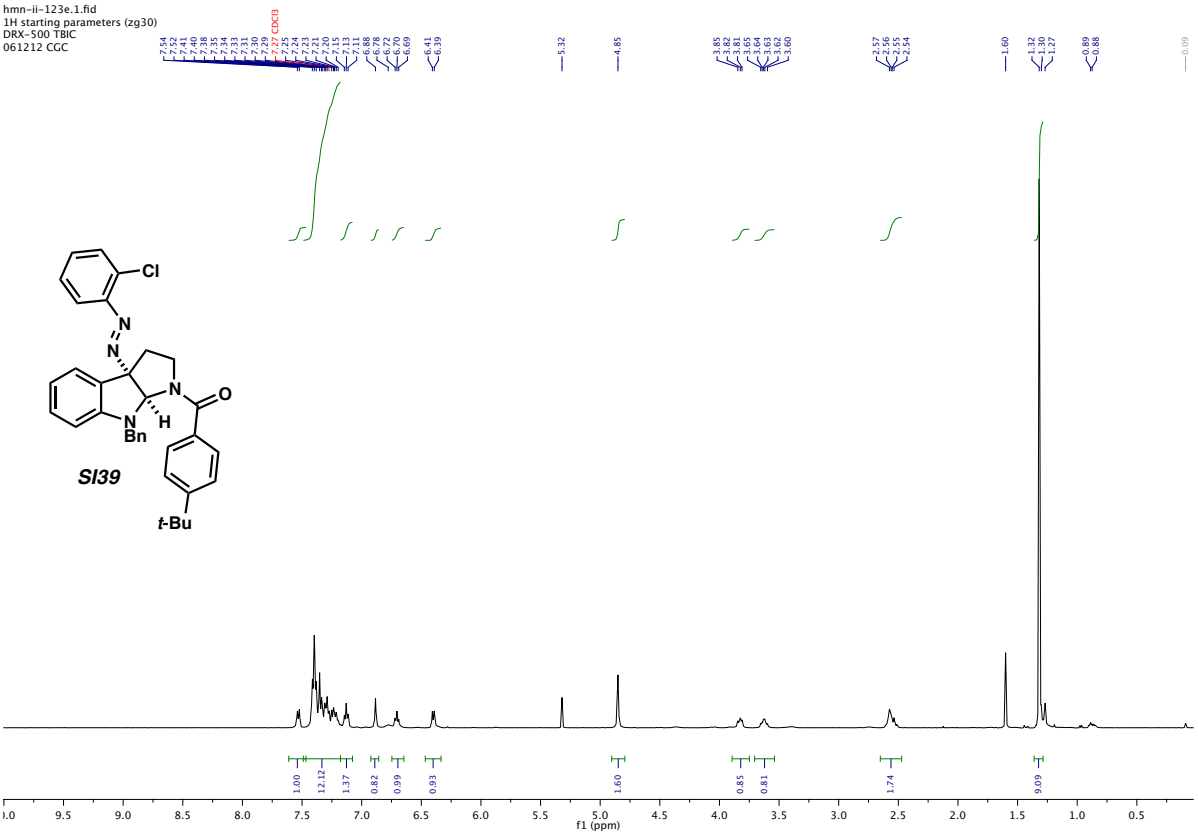

hps-6-176-1.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
OMe
N
N
N
Bn
H
N
O
SI36
t-Bu
1.96
15.08
1.38
2.10
0.99
1.01
0.98
1.81
4.12
0.84
2.00
9.58
f1 (ppm)

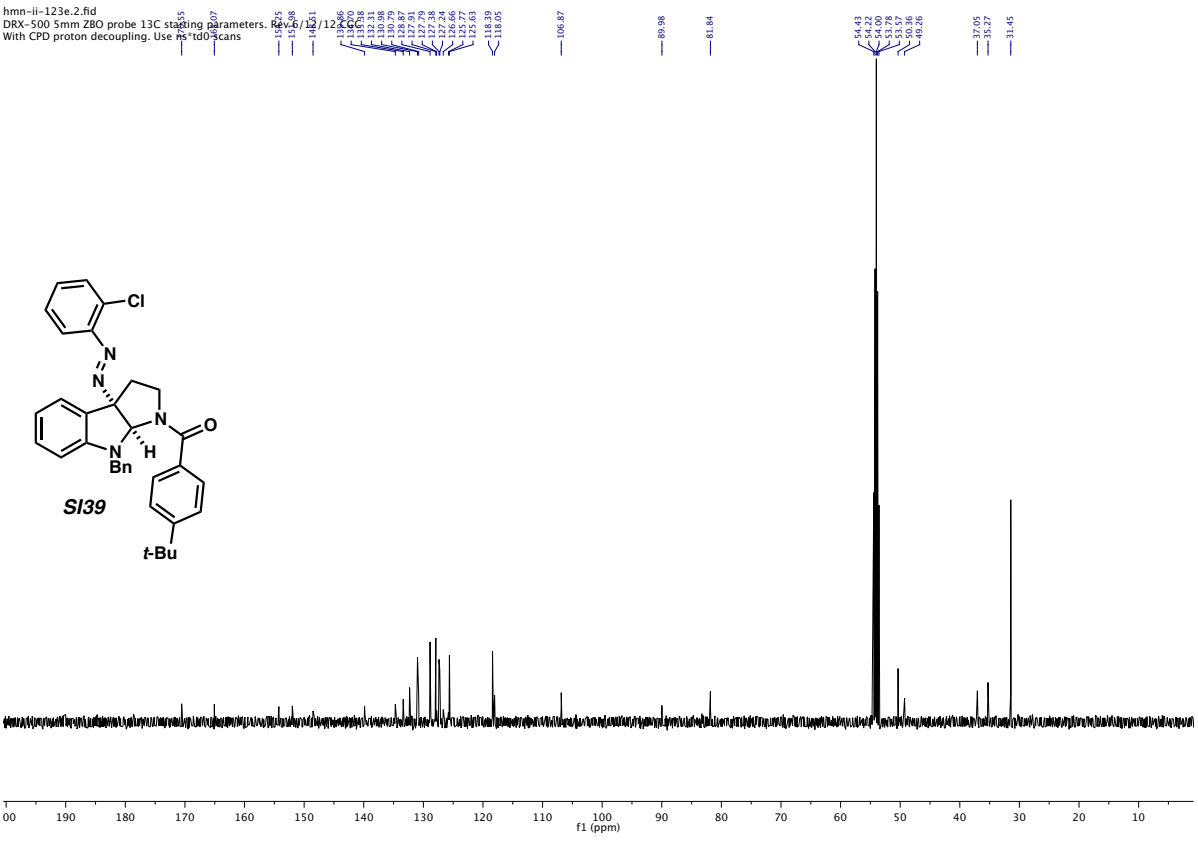

HMN-ii-123b.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CDCl3
F
N
N
N
O
N
H
Bn
SI37
t-Bu
f1 (ppm)

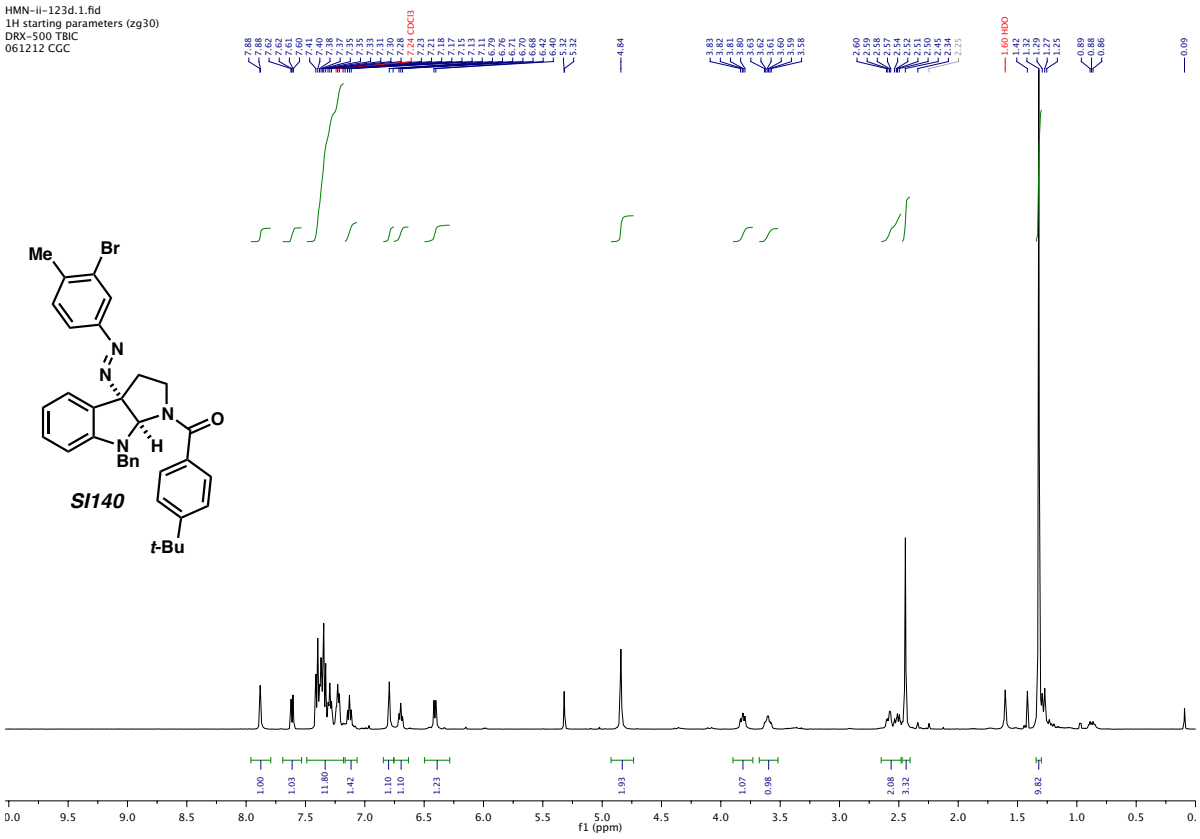

HMN-ii-123b.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Run 6E2/12 CDCl3
With CPD proton decoupling. Use ns*td0 scans
F
N
N
N
O
N
H
Bn
SI37
t-Bu
f1 (ppm)

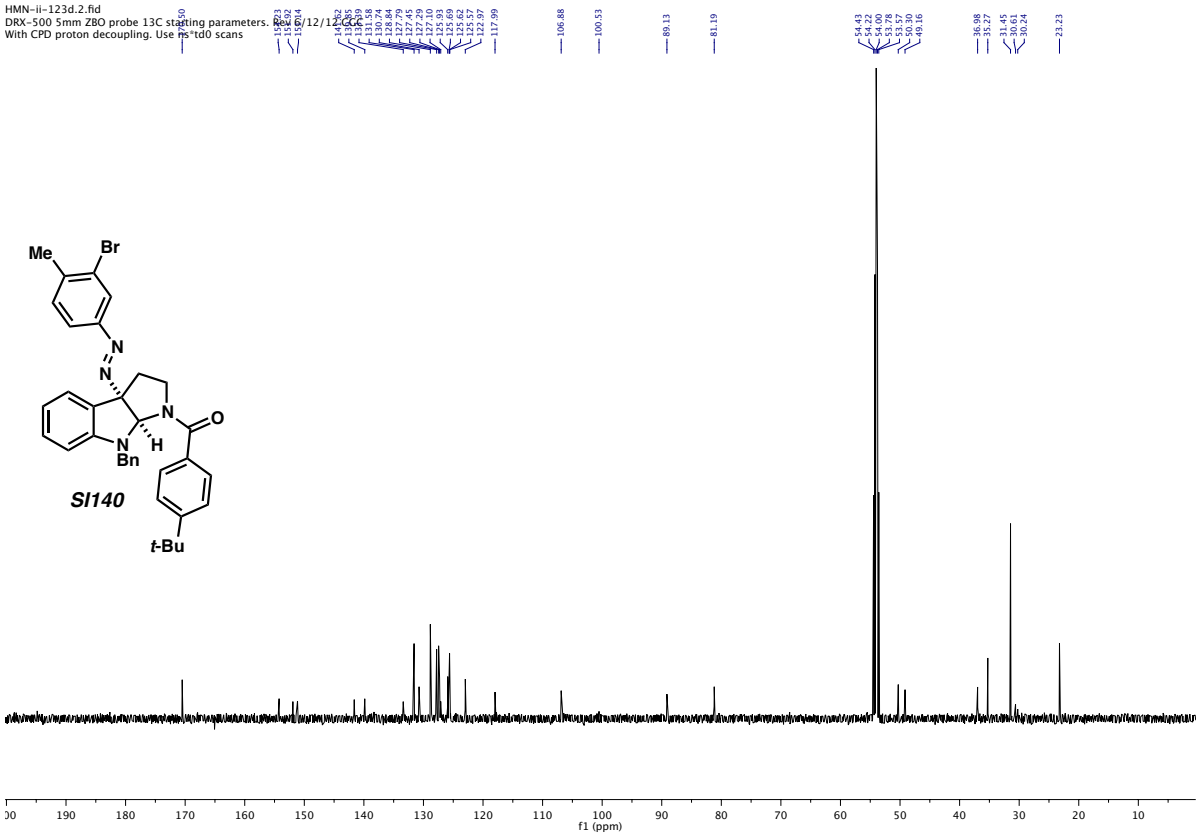

HMN-ii-123a.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
SI38
t-Bu
f1 (ppm)

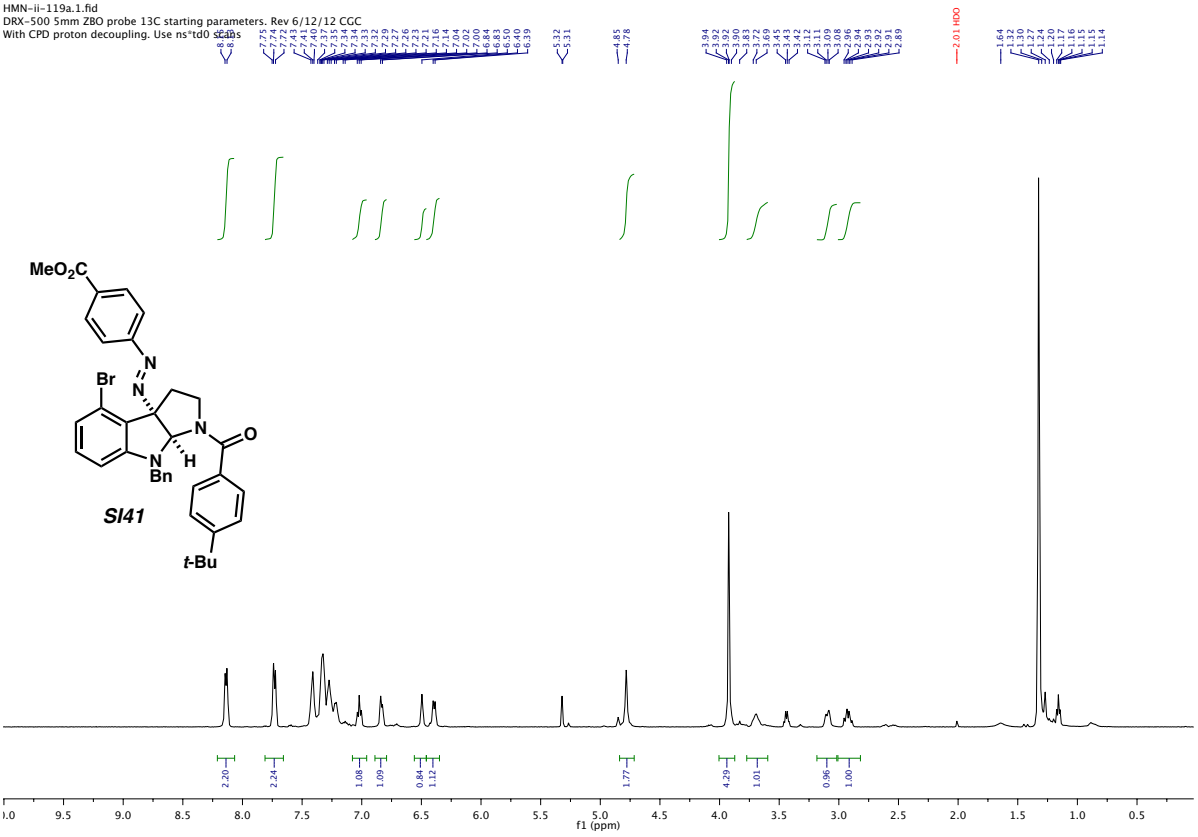

HMN-ii-123a.2.fid
DRX-500 5mm ZBO probe 13C starting parameters zgpg 6/1
With CPD proton decoupling. Use ns 100 scans
SI38
t-Bu
f1 (ppm)

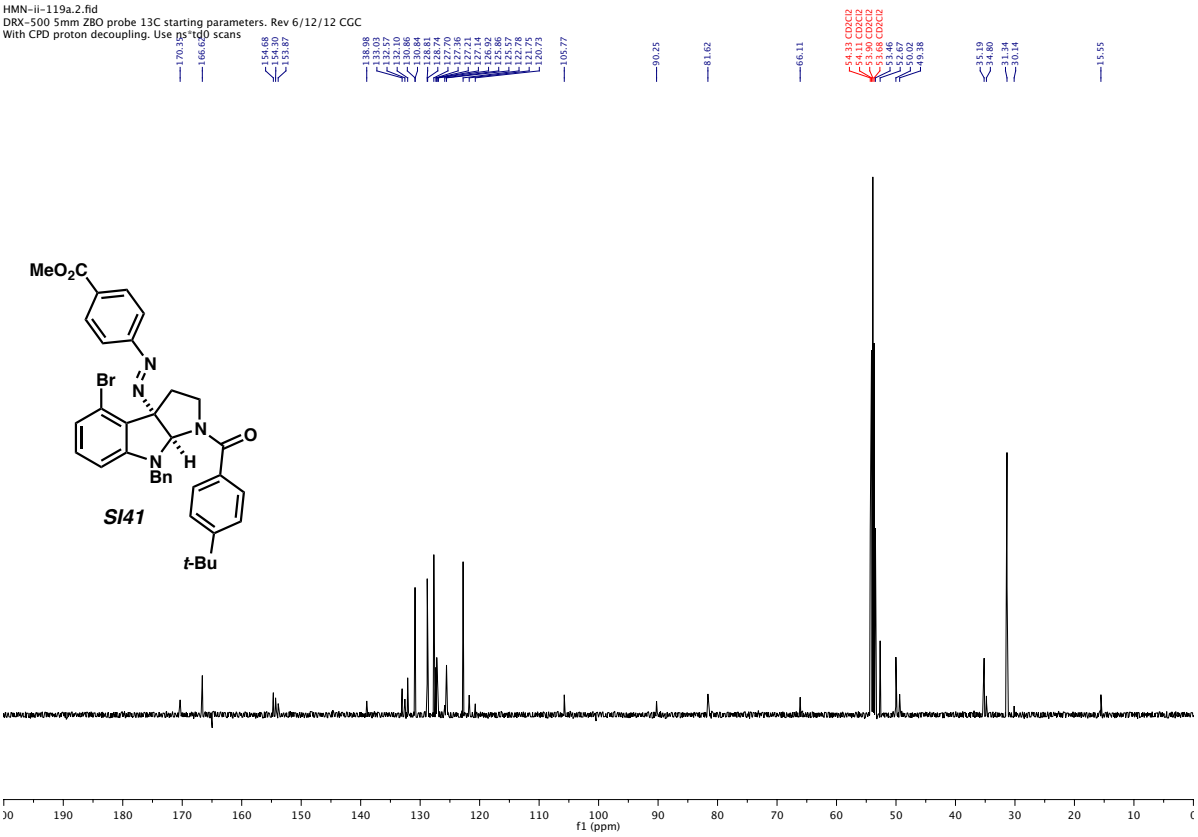

hmn-ii-123e.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
CDCl3
SI39
t-Bu
f1 (ppm)

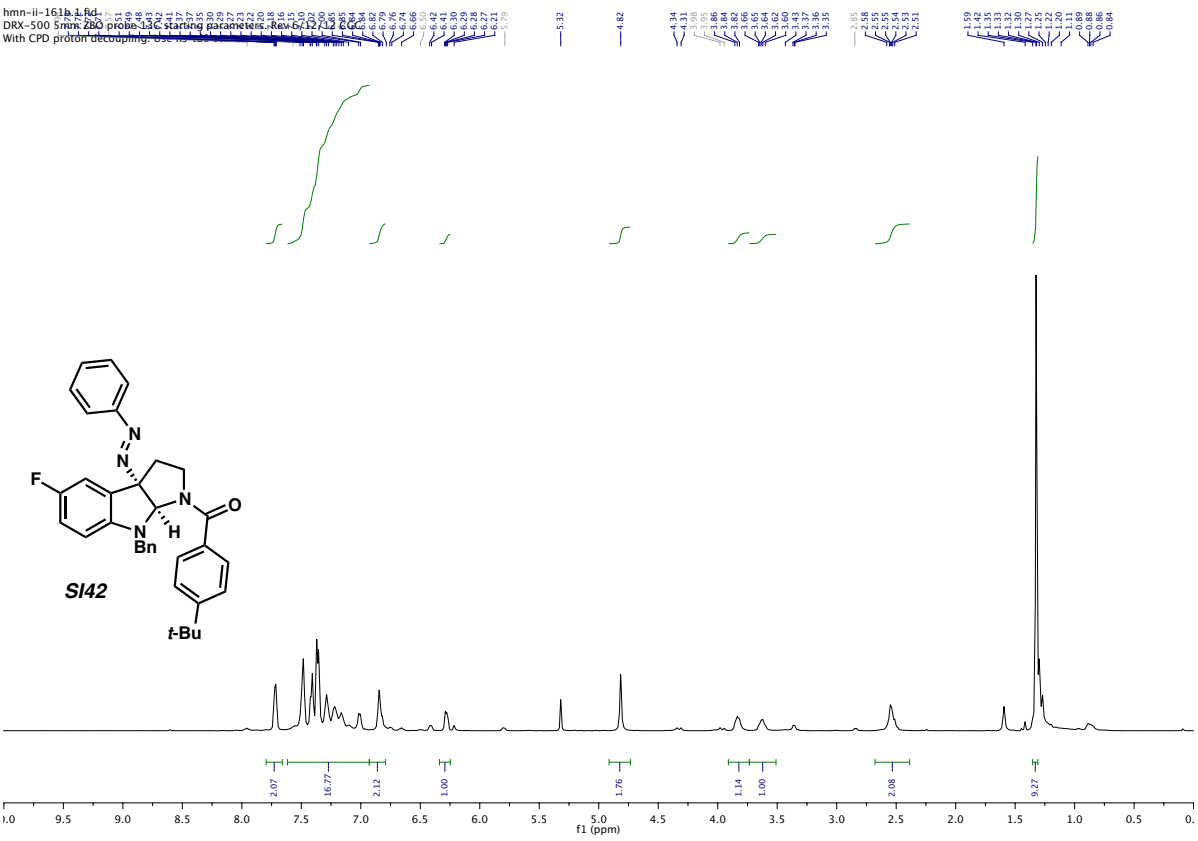

hmn-ii-123e.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. RS: 6/12/12 CGC
With CPD proton decoupling. Use ns*tdO scans
SI39
t-Bu
f1 (ppm)

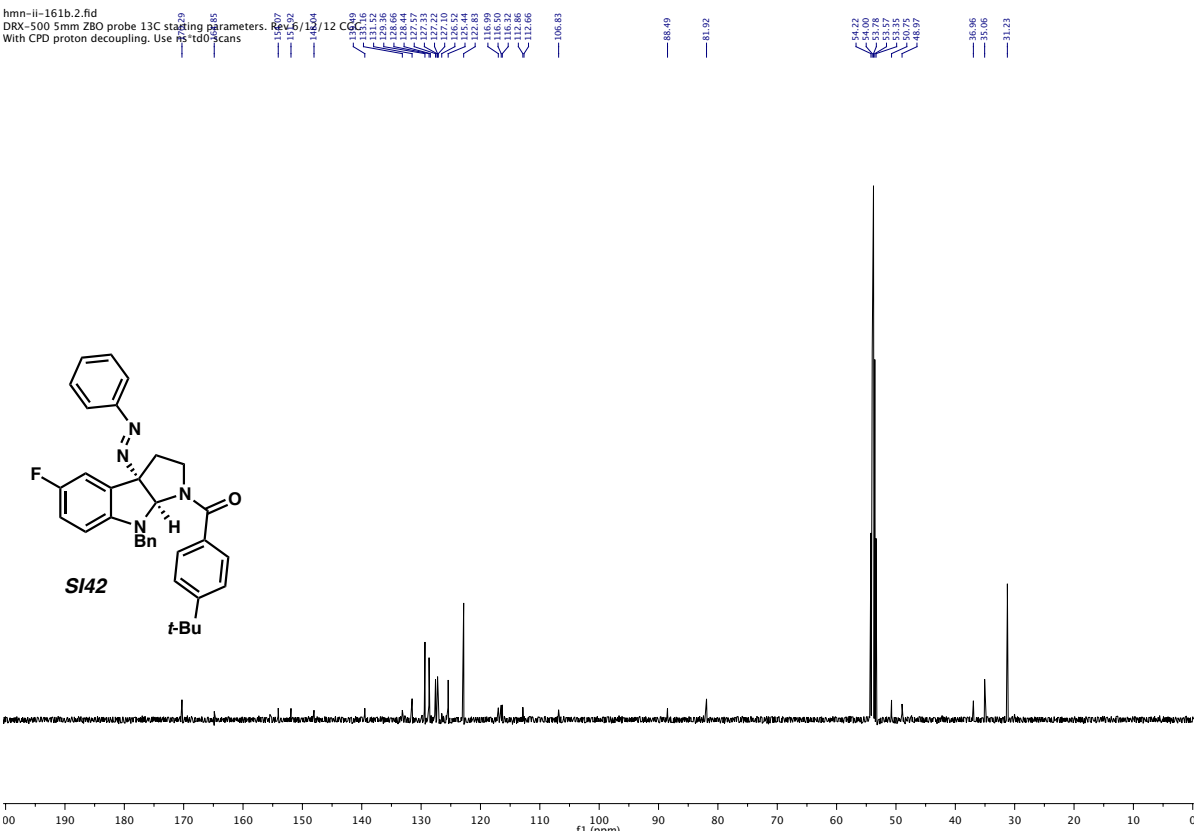

HMN-ii-123d.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
Me
Br
N
N
N
H
Bn
O
SI140
t-Bu
f1 (ppm)

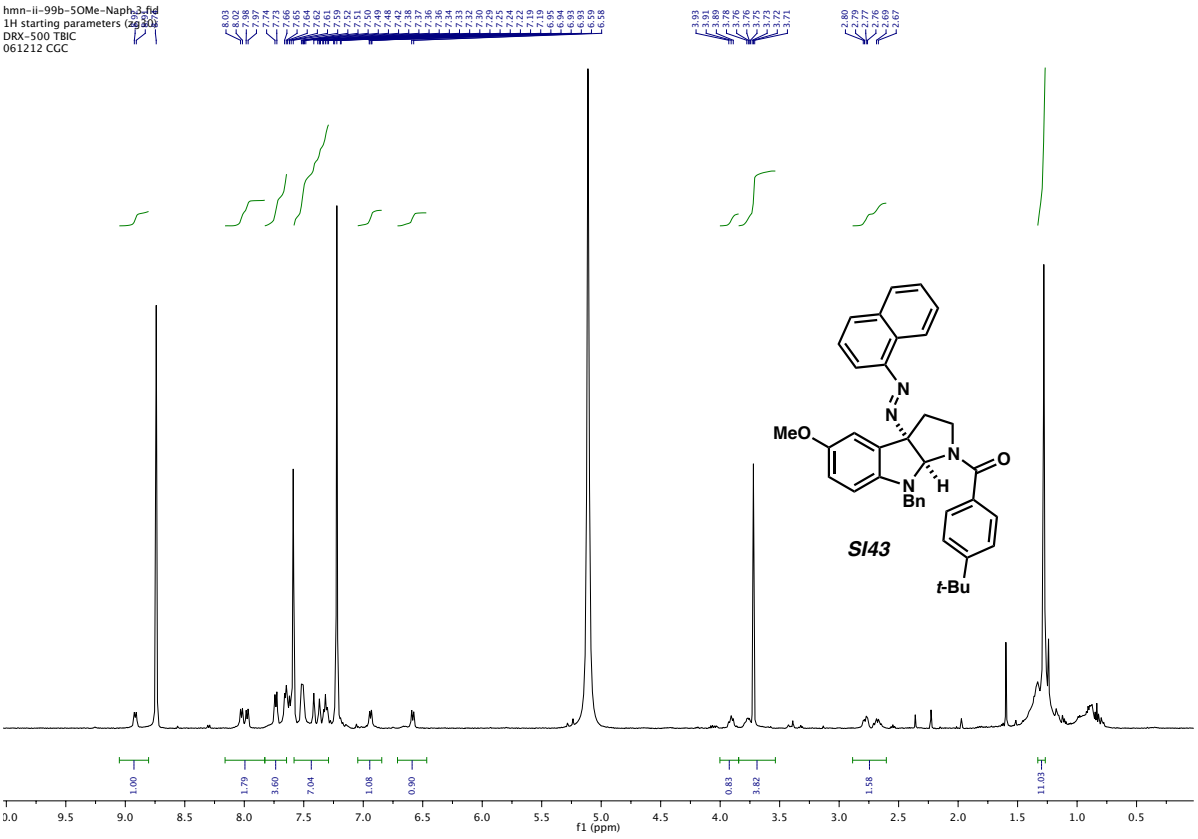

HMN-ii-123d.2.fid
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling. Use ns*td0 scans
Me
Br
N
N
N
H
Bn
O
SI140
t-Bu
f1 (ppm)

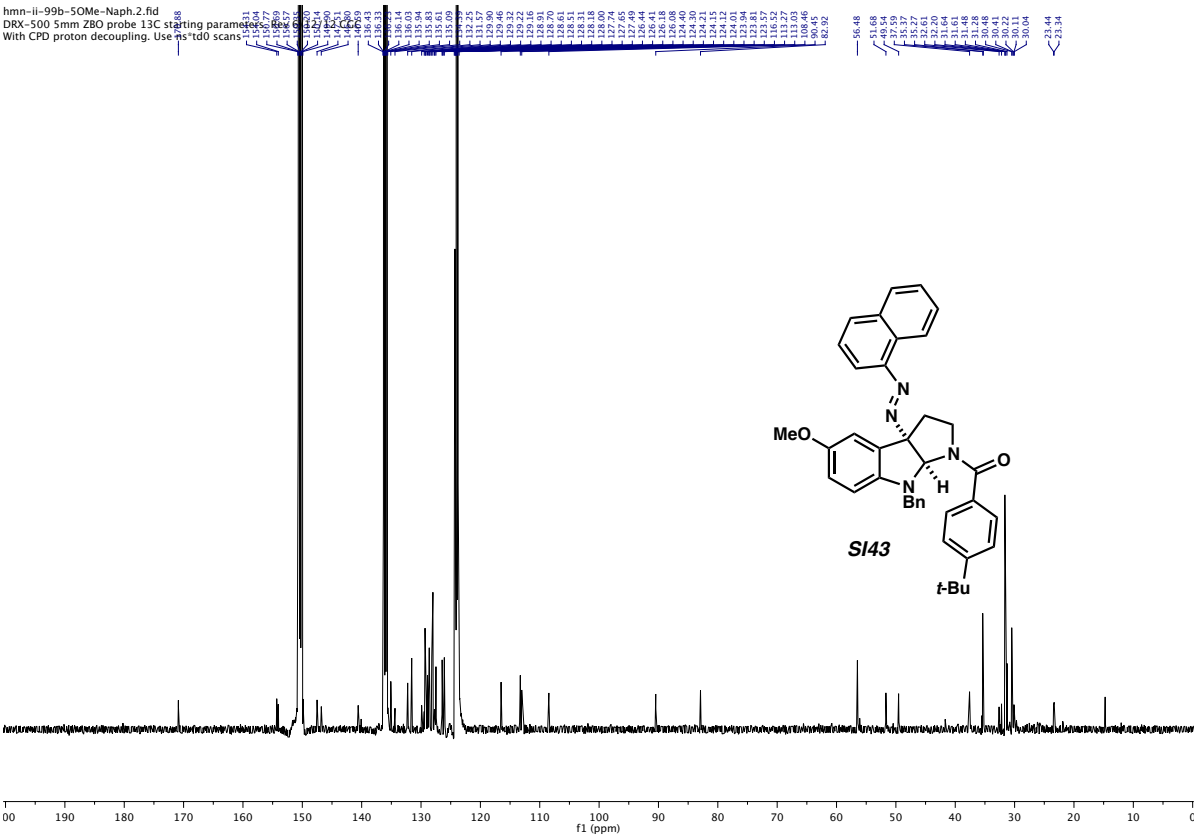

HMN-ii-119a.1.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
MeO2C
Br
N
N
N
O
N
H
Bn
t-Bu
SI41
f1 (ppm)

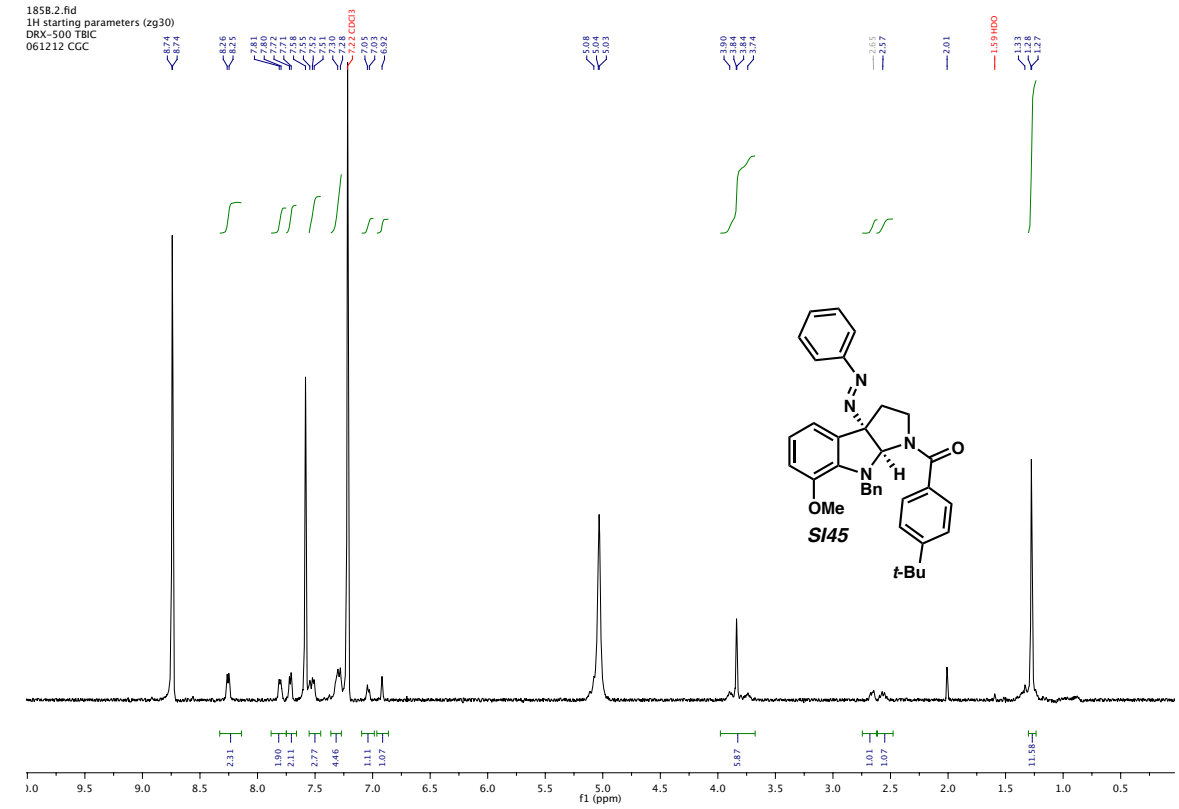

HMN-ii-119a.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
MeO2C
Br
N
N
N
O
N
H
Bn
t-Bu
SI41
f1 (ppm)

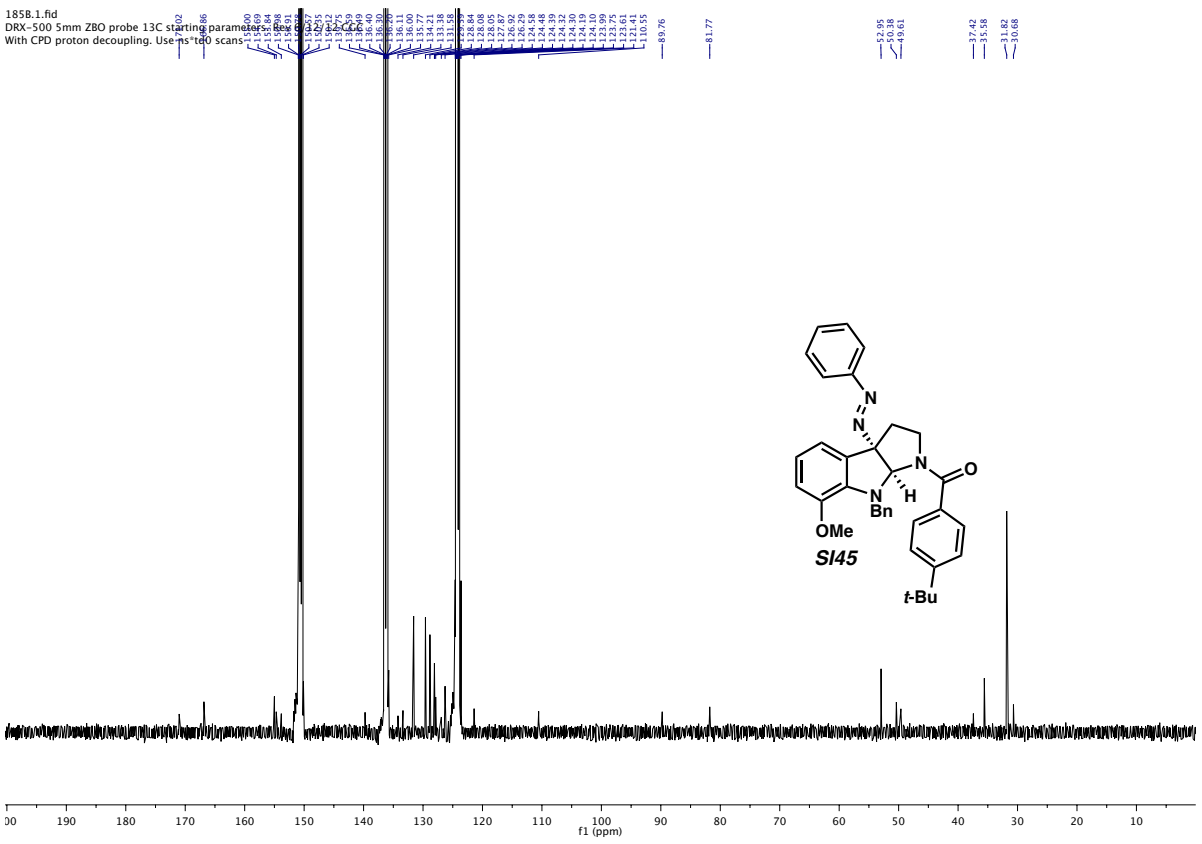

hmn-ii-161b.1.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev.6/12/12 CCL
With CPD proton decoupling. Use ns *td0 scans
N
N
F
N
O
N
H
Bn
SI42
t-Bu
2.07
16.77
2.12
1.00
1.76
1.14
1.00
2.08
9.27
f1 (ppm)

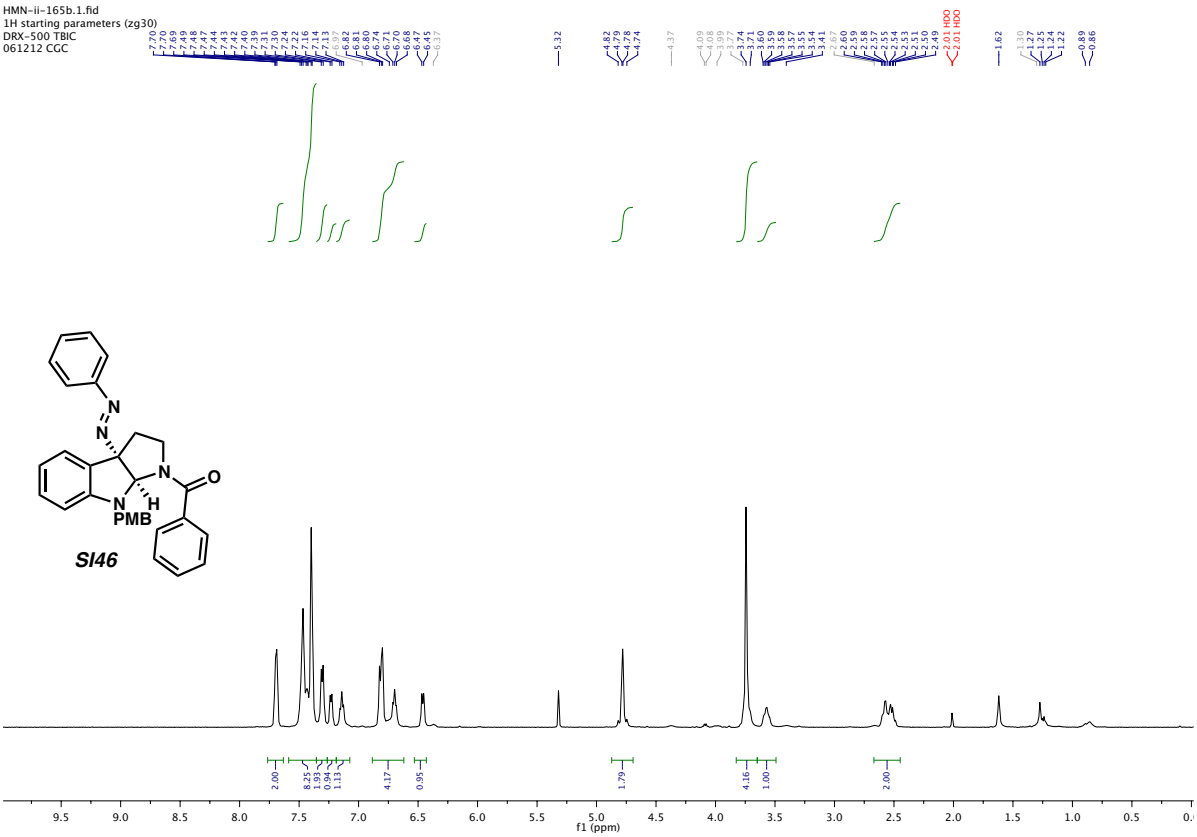

hmn-ii-161b.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev.6/12/12 CCL
With CPD proton decoupling. Use ns *td0 scans
N
N
F
N
O
N
H
Bn
SI42
t-Bu
f1 (ppm)

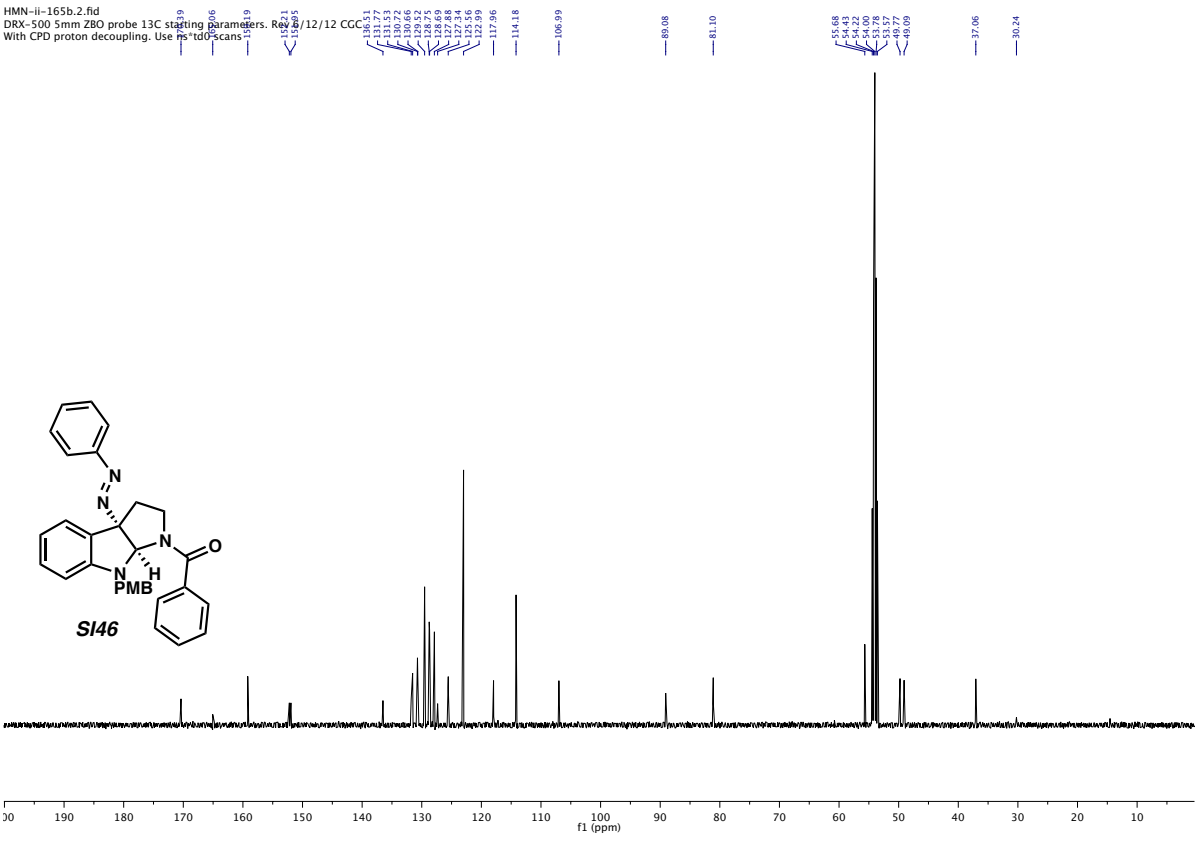

MeO
N
N
N
O
N
H
Bn
SI43
t-Bu
f1 (ppm)

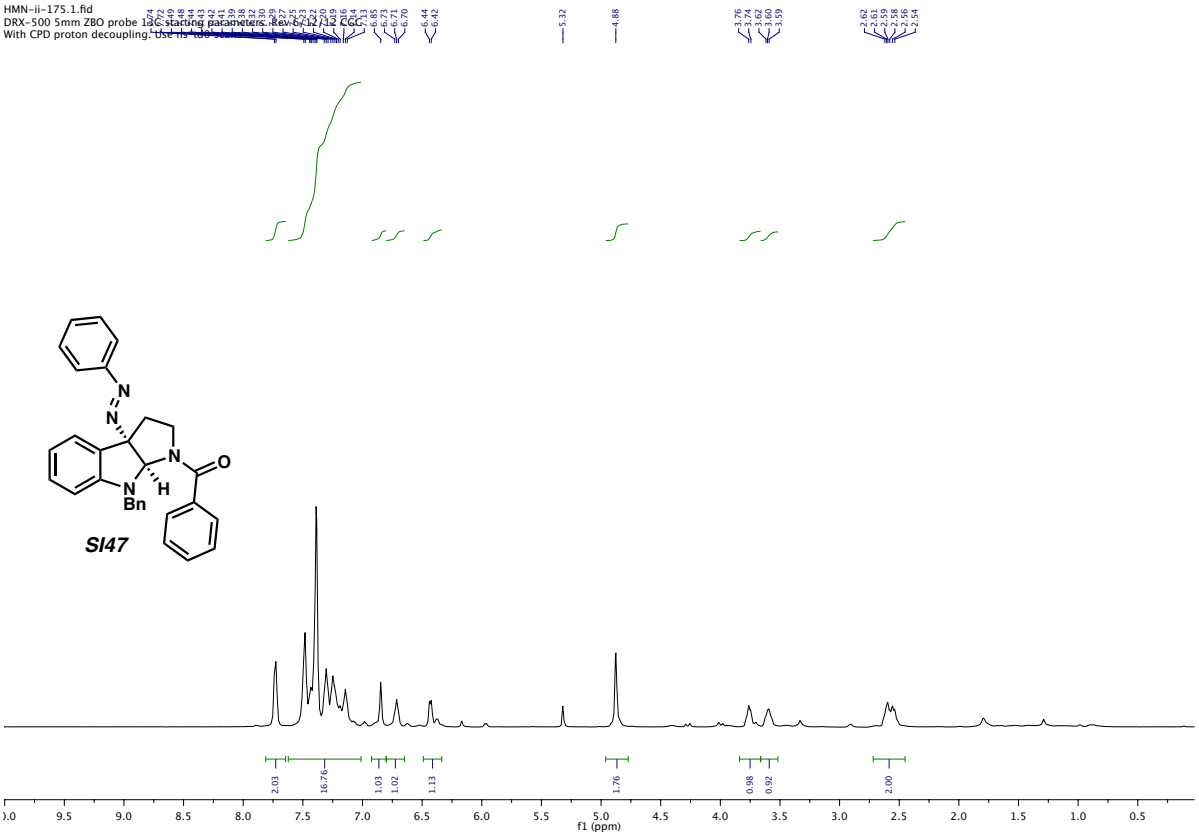

MeO
N
N
N
O
N
H
Bn
SI43
t-Bu
f1 (ppm)

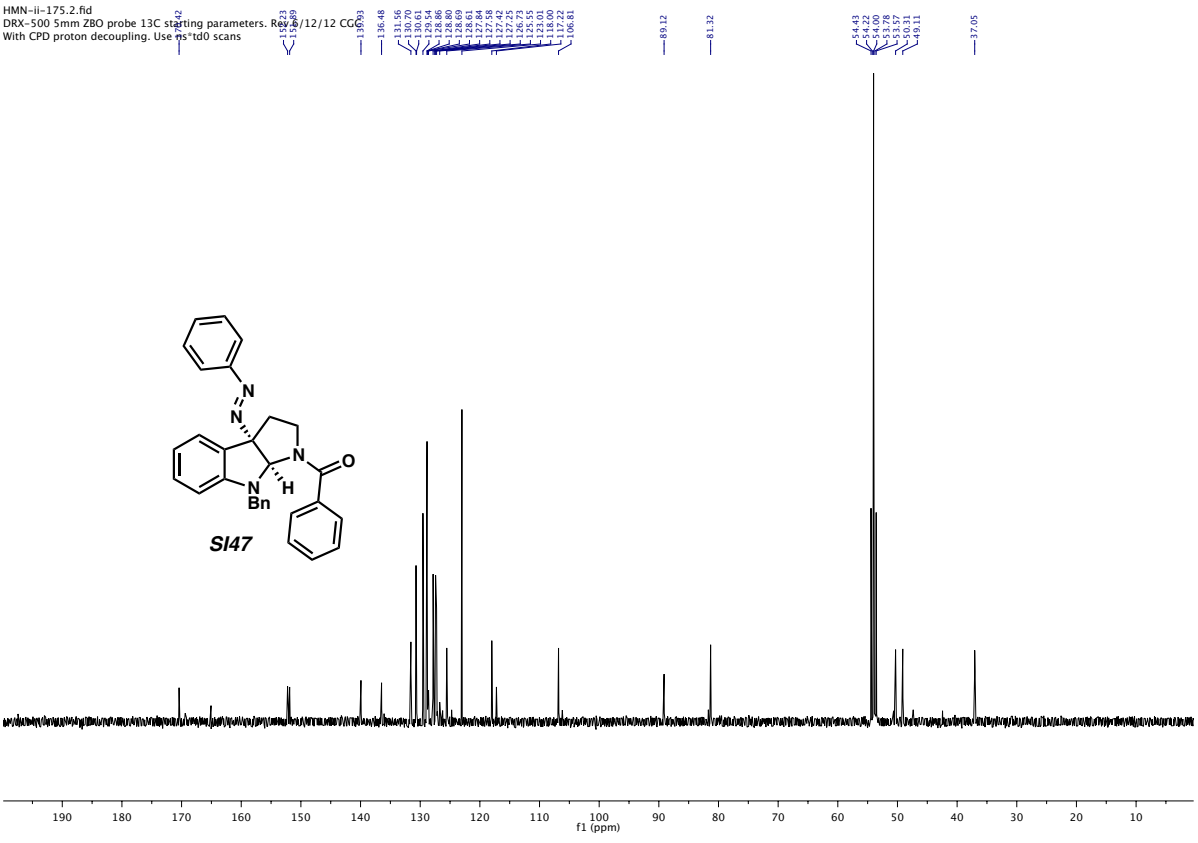

185B.2.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
f1 (ppm)
OMe
Bn
t-Bu
SI45


185B.1.fid
DRX-500 5mm ZBO probe 13C starting parameters Rev 6.0.2
With CPD proton decoupling. Use ns*te0 scans
f1 (ppm)
OMe
Bn
t-Bu
SI45

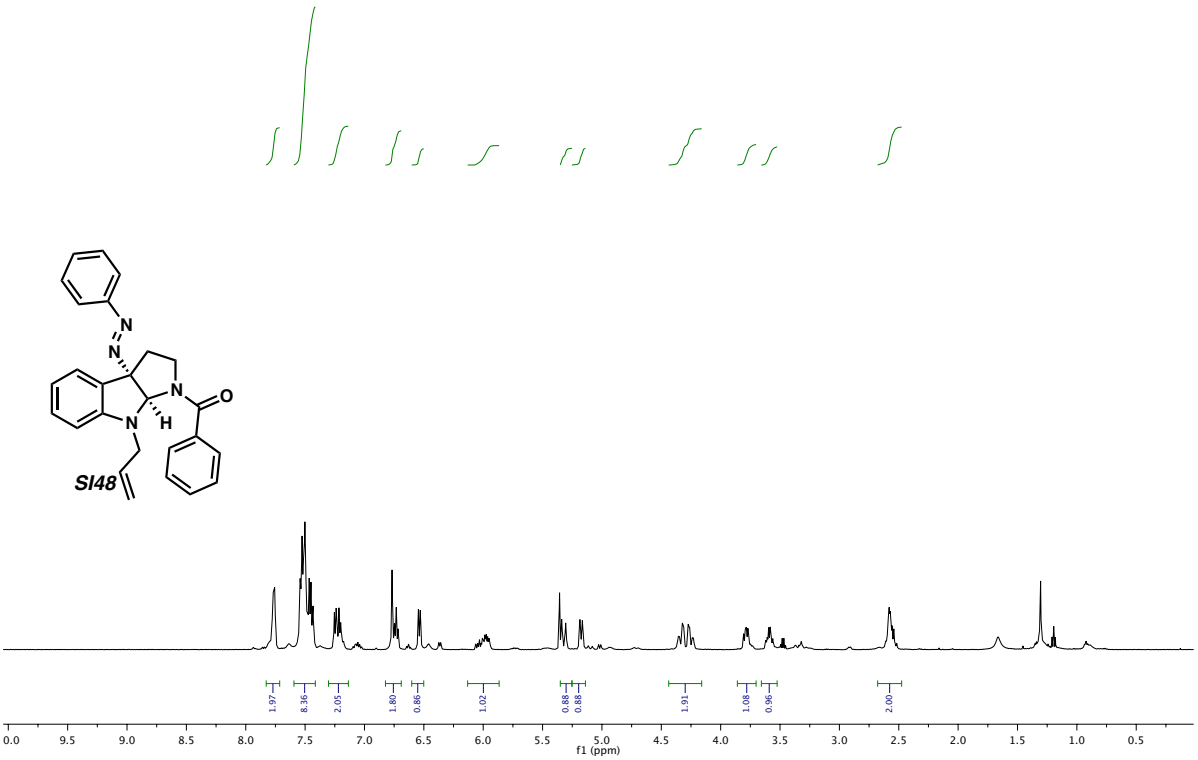

HMN-ii-165b.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
PMB
SI46
f1 (ppm)


HMN-ii-165b.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. R 061212 CGC
With CPD proton decoupling. Use ns *tdd scans
PMB
SI46
f1 (ppm)

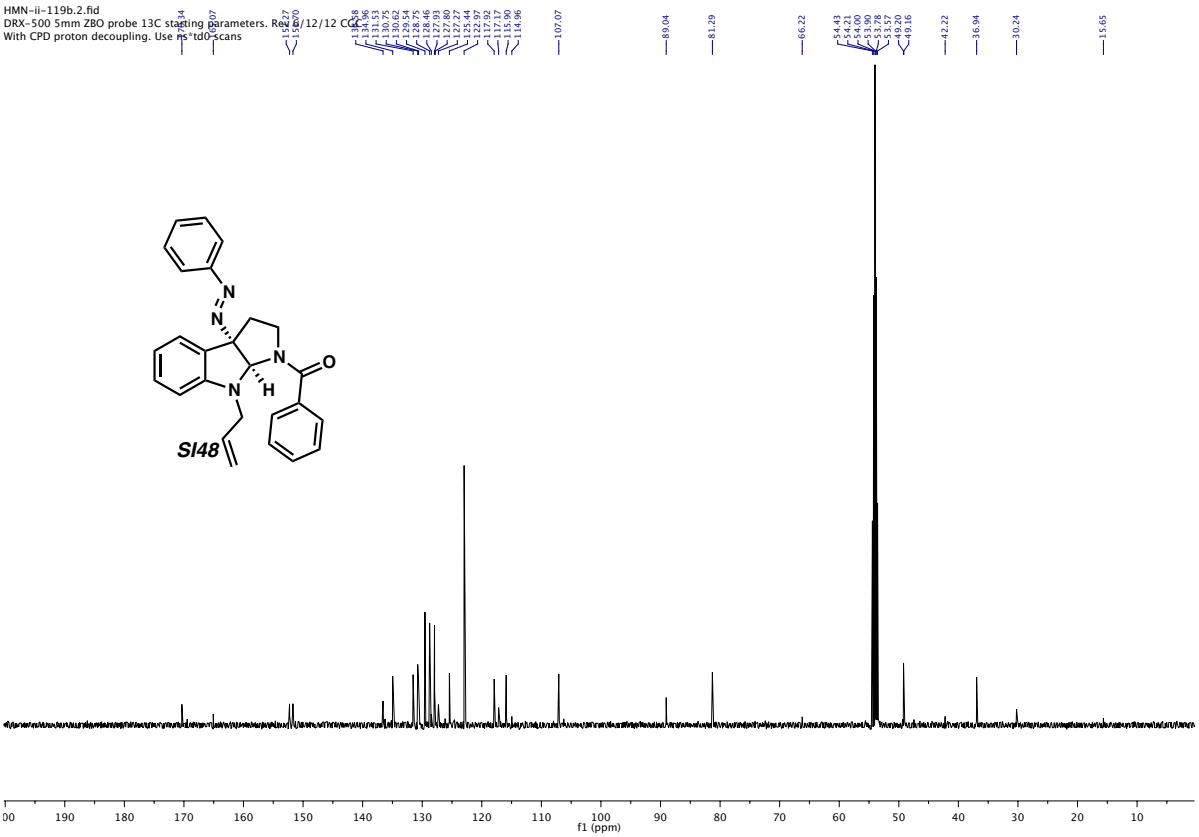

HMN-ii-175.1.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev. 7/12/12 CCG
With CPD proton decoupling. Use ns*td0 scans
5.32
4.88
3.76
3.74
3.62
3.60
3.59
2.62
2.61
2.59
2.58
2.56
2.54
6.44
6.42
6.71
6.70
6.85
6.83
7.13
2.03
16.76
1.03
1.02
1.13
1.76
0.98
0.92
2.00
f1 (ppm)
N
N
N
O
N
H
Bn
SI47

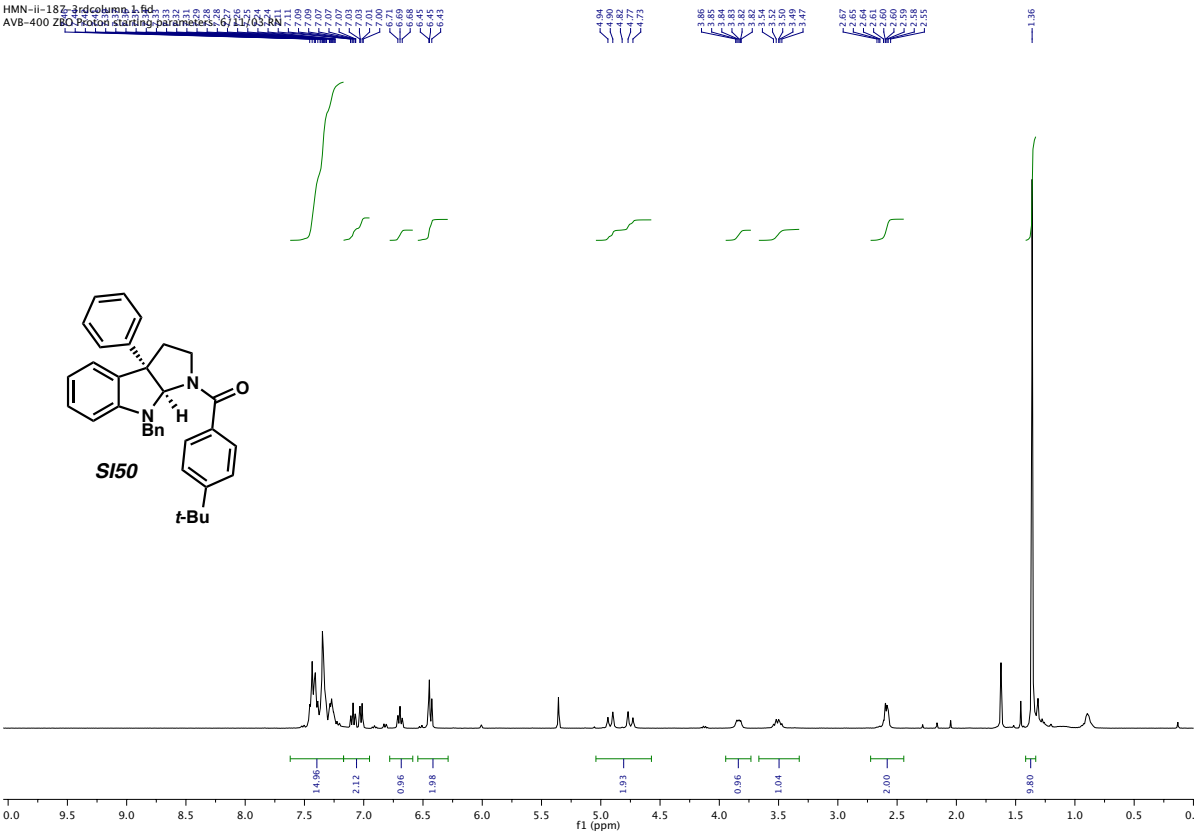

HMN-ii-175.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev. 7/12/12 CCG
With CPD proton decoupling. Use ns*td0 scans
152.23
150.89
136.48
131.56
130.70
130.61
128.86
128.80
128.69
127.84
127.58
127.42
127.25
126.73
125.55
121.01
118.00
117.22
106.81
89.12
81.32
54.43
54.22
54.00
53.78
53.57
50.31
49.11
37.05
f1 (ppm)
N
N
N
O
N
H
Bn
SI47

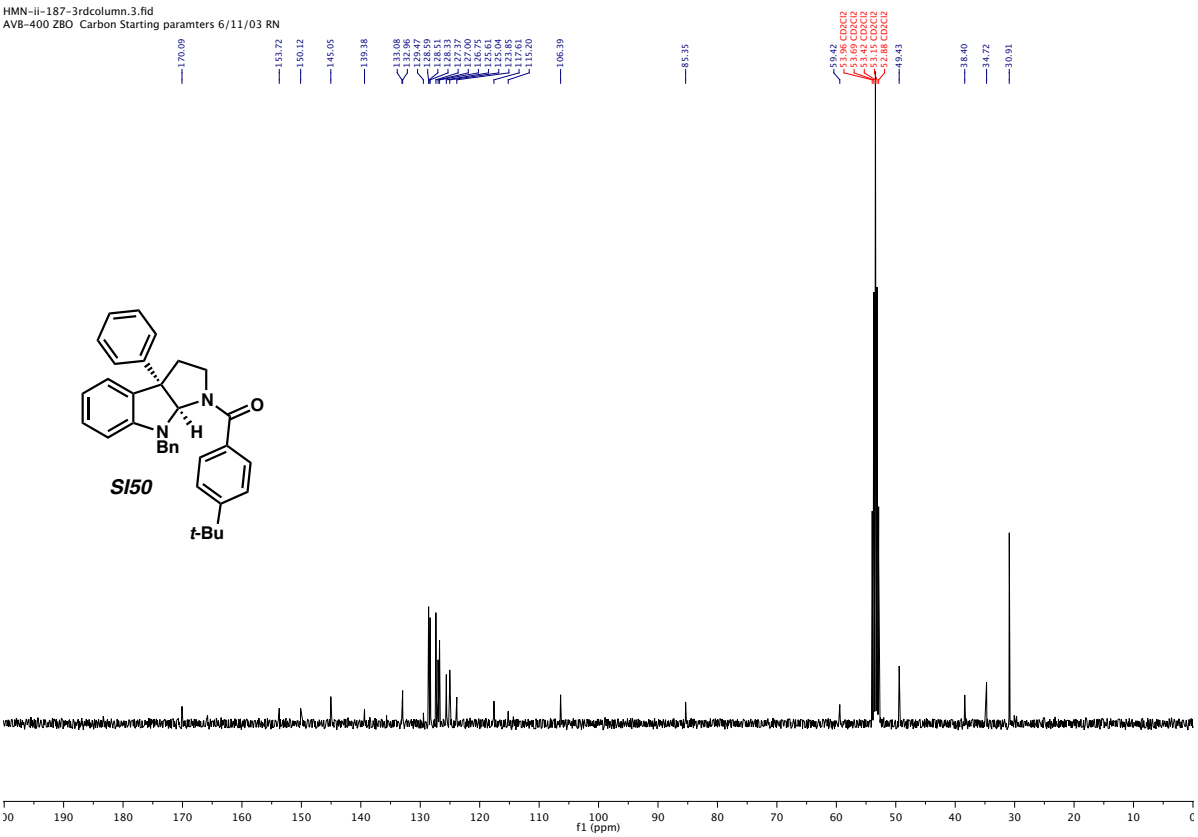
HMN-ii-119b.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC



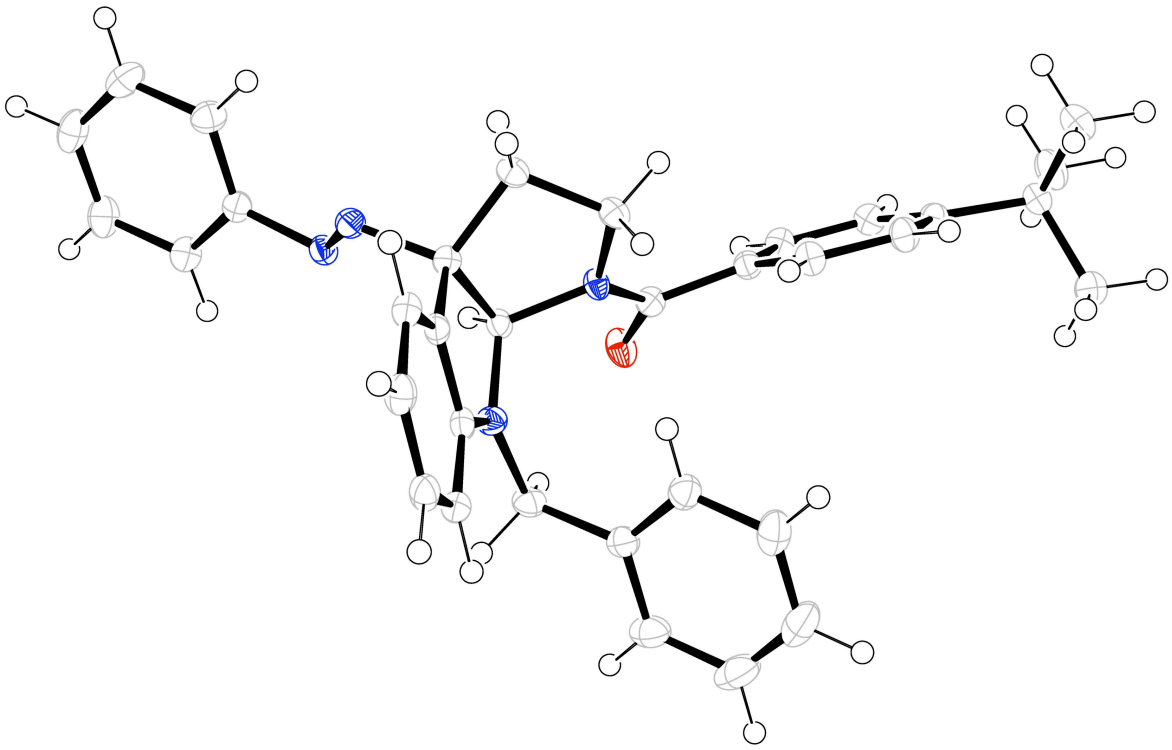
HMN-ii-119b.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev. 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans




HMN-ii-187-3rdcolumn.1.fid
AVB-400 ZBO Proton starting parameters 6/11/03 RN
SI50
t-Bu
f1 (ppm)


HMN-ii-187-3rdcolumn.3.fid
AVB-400 ZBO Carbon Starting paramters 6/11/03 RN
SI50
t-Bu
f1 (ppm)

V. X-Ray Data for SI28.



A yellow prism 0.120 x 0.060 x 0.030 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 1.0°. Data collection was 99.2% complete to 67.000° in θ. A total of 30604 reflections were collected covering the indices, -15<=*h*<=15, -6<=*k*<=7, -21<=*l*<=21. 4714 reflections were found to be symmetry independent, with an R_{int} of 0.0220. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21 (No. 4). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2013). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2013. Absolute stereochemistry

was unambiguously determined to be *S* at C1 and *R* at C8, respectively.

Table 1. Crystal data and structure refinement for toste81.

X-ray ID	toste81	
Sample/notebook ID	SR-1-6E	
Empirical formula	C34 H34 N4 O	
Formula weight	514.65	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 12.5207(8) Å	α= 90°.
	b = 6.2144(4) Å	β= 102.219(2)°.
	c = 18.0695(12) Å	γ = 90°.
Volume	1374.11(15) $Å^3$	
Z	2	
Density (calculated)	1.244 Mg/m^3	
Absorption coefficient	0.593 mm^{-1}	
F(000)	548	
Crystal size	0.120 x 0.060 x 0.030 mm^3	
Crystal color/habit	yellow prism	
Theta range for data collection	2.502 to 68.223°.	
Index ranges	-15<=h<=15, -6<=k<=7, -21<=l<=21	
Reflections collected	30604	
Independent reflections	4714 [R(int) = 0.0220]	
Completeness to theta = 67.000°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.894	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4714 / 1 / 355	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0256, wR2 = 0.0669	
R indices (all data)	R1 = 0.0258, wR2 = 0.0672	
Absolute structure parameter	0.09(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.163 and -0.167 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for toste81. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8725(1)	2000(3)	7873(1)	16(1)
C(2)	8742(1)	1202(3)	8671(1)	18(1)
C(3)	9260(1)	-543(3)	9059(1)	20(1)
C(4)	9162(1)	-876(3)	9808(1)	23(1)
C(5)	8560(1)	551(3)	10146(1)	23(1)
C(6)	8025(1)	2309(3)	9757(1)	21(1)
C(7)	8111(1)	2599(3)	9007(1)	18(1)
C(8)	7814(1)	3749(3)	7750(1)	17(1)
C(9)	7112(1)	410(3)	7121(1)	18(1)
C(10)	8352(1)	319(3)	7252(1)	19(1)
C(11)	11006(1)	5210(3)	7585(1)	19(1)
C(12)	11349(1)	7313(3)	7742(1)	24(1)
C(13)	12384(1)	7924(3)	7652(1)	28(1)
C(14)	13048(1)	6456(3)	7383(1)	28(1)
C(15)	12675(1)	4404(3)	7192(1)	29(1)
C(16)	11656(1)	3758(3)	7292(1)	24(1)
C(17)	6853(1)	5714(3)	8673(1)	22(1)
C(18)	5793(1)	4758(3)	8808(1)	22(1)
C(19)	5129(1)	6024(4)	9158(1)	30(1)
C(20)	4146(2)	5227(4)	9284(1)	39(1)
C(21)	3815(1)	3173(4)	9069(1)	37(1)
C(22)	4476(1)	1886(4)	8729(1)	31(1)
C(23)	5457(1)	2674(3)	8598(1)	24(1)
C(24)	6068(1)	3911(3)	6821(1)	19(1)
C(25)	5120(1)	2818(3)	6312(1)	18(1)
C(26)	4673(1)	868(3)	6481(1)	20(1)
C(27)	3711(1)	99(3)	6029(1)	21(1)
C(28)	3167(1)	1222(3)	5390(1)	18(1)
C(29)	3649(1)	3112(3)	5207(1)	21(1)
C(30)	4599(1)	3917(3)	5663(1)	20(1)
C(31)	2058(1)	405(3)	4946(1)	20(1)
C(32)	2133(1)	-1976(3)	4748(1)	28(1)
C(33)	1218(1)	668(3)	5448(1)	29(1)
C(34)	1661(2)	1661(3)	4210(1)	30(1)

N(1)	7635(1)	4173(2)	8503(1)	18(1)
N(2)	6891(1)	2700(2)	7226(1)	17(1)
N(3)	9839(1)	2688(2)	7820(1)	18(1)
N(4)	9937(1)	4645(2)	7699(1)	18(1)
O(1)	6077(1)	5889(2)	6878(1)	26(1)

Table 3. Bond lengths [Å] and angles [°] for toste81.

C(1)-N(3)	1.4815(19)	C(13)-H(13)	0.9500
C(1)-C(2)	1.521(2)	C(14)-C(15)	1.377(3)
C(1)-C(10)	1.532(2)	C(14)-H(14)	0.9500
C(1)-C(8)	1.557(2)	C(15)-C(16)	1.386(2)
C(2)-C(3)	1.377(2)	C(15)-H(15)	0.9500
C(2)-C(7)	1.396(2)	C(16)-H(16)	0.9500
C(3)-C(4)	1.400(2)	C(17)-N(1)	1.448(2)
C(3)-H(3)	0.9500	C(17)-C(18)	1.520(2)
C(4)-C(5)	1.386(2)	C(17)-H(17A)	0.9900
C(4)-H(4)	0.9500	C(17)-H(17B)	0.9900
C(5)-C(6)	1.392(2)	C(18)-C(23)	1.389(3)
C(5)-H(5)	0.9500	C(18)-C(19)	1.390(2)
C(6)-C(7)	1.394(2)	C(19)-C(20)	1.390(3)
C(6)-H(6)	0.9500	C(19)-H(19)	0.9500
C(7)-N(1)	1.382(2)	C(20)-C(21)	1.372(3)
C(8)-N(1)	1.450(2)	C(20)-H(20)	0.9500
C(8)-N(2)	1.4813(18)	C(21)-C(22)	1.385(3)
C(8)-H(8)	1.0000	C(21)-H(21)	0.9500
C(9)-N(2)	1.470(2)	C(22)-C(23)	1.388(2)
C(9)-C(10)	1.521(2)	C(22)-H(22)	0.9500
C(9)-H(9A)	0.9900	C(23)-H(23)	0.9500
C(9)-H(9B)	0.9900	C(24)-O(1)	1.233(2)
C(10)-H(10A)	0.9900	C(24)-N(2)	1.358(2)
C(10)-H(10B)	0.9900	C(24)-C(25)	1.502(2)
C(11)-C(12)	1.387(2)	C(25)-C(30)	1.393(2)
C(11)-C(16)	1.392(2)	C(25)-C(26)	1.395(2)
C(11)-N(4)	1.4407(19)	C(26)-C(27)	1.389(2)
C(12)-C(13)	1.392(2)	C(26)-H(26)	0.9500
C(12)-H(12)	0.9500	C(27)-C(28)	1.397(2)
C(13)-C(14)	1.390(3)	C(27)-H(27)	0.9500

C(28)-C(29)	1.392(2)	C(32)-H(32B)	0.9800
C(28)-C(31)	1.536(2)	C(32)-H(32C)	0.9800
C(29)-C(30)	1.390(2)	C(33)-H(33A)	0.9800
C(29)-H(29)	0.9500	C(33)-H(33B)	0.9800
C(30)-H(30)	0.9500	C(33)-H(33C)	0.9800
C(31)-C(32)	1.530(3)	C(34)-H(34A)	0.9800
C(31)-C(34)	1.532(2)	C(34)-H(34B)	0.9800
C(31)-C(33)	1.536(2)	C(34)-H(34C)	0.9800
C(32)-H(32A)	0.9800	N(3)-N(4)	1.246(2)

N(3)-C(1)-C(2)	109.30(11)	N(2)-C(8)-C(1)	103.47(12)
N(3)-C(1)-C(10)	107.16(12)	N(1)-C(8)-H(8)	111.1
C(2)-C(1)-C(10)	114.42(13)	N(2)-C(8)-H(8)	111.1
N(3)-C(1)-C(8)	117.46(13)	C(1)-C(8)-H(8)	111.1
C(2)-C(1)-C(8)	103.04(12)	N(2)-C(9)-C(10)	103.25(12)
C(10)-C(1)-C(8)	105.69(12)	N(2)-C(9)-H(9A)	111.1
C(3)-C(2)-C(7)	121.16(14)	C(10)-C(9)-H(9A)	111.1
C(3)-C(2)-C(1)	130.55(15)	N(2)-C(9)-H(9B)	111.1
C(7)-C(2)-C(1)	108.28(13)	C(10)-C(9)-H(9B)	111.1
C(2)-C(3)-C(4)	118.70(15)	H(9A)-C(9)-H(9B)	109.1
C(2)-C(3)-H(3)	120.7	C(9)-C(10)-C(1)	103.42(12)
C(4)-C(3)-H(3)	120.7	C(9)-C(10)-H(10A)	111.1
C(5)-C(4)-C(3)	119.90(16)	C(1)-C(10)-H(10A)	111.1
C(5)-C(4)-H(4)	120.0	C(9)-C(10)-H(10B)	111.1
C(3)-C(4)-H(4)	120.0	C(1)-C(10)-H(10B)	111.1
C(4)-C(5)-C(6)	121.86(14)	H(10A)-C(10)-H(10B)	109.0
C(4)-C(5)-H(5)	119.1	C(12)-C(11)-C(16)	120.53(15)
C(6)-C(5)-H(5)	119.1	C(12)-C(11)-N(4)	117.22(14)
C(5)-C(6)-C(7)	117.69(15)	C(16)-C(11)-N(4)	122.17(15)
C(5)-C(6)-H(6)	121.2	C(11)-C(12)-C(13)	119.28(16)
C(7)-C(6)-H(6)	121.2	C(11)-C(12)-H(12)	120.4
N(1)-C(7)-C(6)	128.33(15)	C(13)-C(12)-H(12)	120.4
N(1)-C(7)-C(2)	111.05(13)	C(14)-C(13)-C(12)	120.19(18)
C(6)-C(7)-C(2)	120.62(15)	C(14)-C(13)-H(13)	119.9
N(1)-C(8)-N(2)	115.22(12)	C(12)-C(13)-H(13)	119.9
N(1)-C(8)-C(1)	104.32(12)	C(15)-C(14)-C(13)	119.92(16)

C(15)-C(14)-H(14)	120.0	C(30)-C(25)-C(24)	117.51(15)
C(13)-C(14)-H(14)	120.0	C(26)-C(25)-C(24)	124.08(14)
C(14)-C(15)-C(16)	120.57(17)	C(27)-C(26)-C(25)	120.56(14)
C(14)-C(15)-H(15)	119.7	C(27)-C(26)-H(26)	119.7
C(16)-C(15)-H(15)	119.7	C(25)-C(26)-H(26)	119.7
C(15)-C(16)-C(11)	119.36(17)	C(26)-C(27)-C(28)	121.63(15)
C(15)-C(16)-H(16)	120.3	C(26)-C(27)-H(27)	119.2
C(11)-C(16)-H(16)	120.3	C(28)-C(27)-H(27)	119.2
N(1)-C(17)-C(18)	115.33(15)	C(29)-C(28)-C(27)	117.24(14)
N(1)-C(17)-H(17A)	108.4	C(29)-C(28)-C(31)	122.96(14)
C(18)-C(17)-H(17A)	108.4	C(27)-C(28)-C(31)	119.74(14)
N(1)-C(17)-H(17B)	108.4	C(30)-C(29)-C(28)	121.52(15)
C(18)-C(17)-H(17B)	108.4	C(30)-C(29)-H(29)	119.2
H(17A)-C(17)-H(17B)	107.5	C(28)-C(29)-H(29)	119.2
C(23)-C(18)-C(19)	118.42(16)	C(29)-C(30)-C(25)	120.78(15)
C(23)-C(18)-C(17)	123.04(15)	C(29)-C(30)-H(30)	119.6
C(19)-C(18)-C(17)	118.55(16)	C(25)-C(30)-H(30)	119.6
C(18)-C(19)-C(20)	120.6(2)	C(32)-C(31)-C(34)	108.28(14)
C(18)-C(19)-H(19)	119.7	C(32)-C(31)-C(28)	110.35(14)
C(20)-C(19)-H(19)	119.7	C(34)-C(31)-C(28)	112.12(13)
C(21)-C(20)-C(19)	120.61(18)	C(32)-C(31)-C(33)	108.98(15)
C(21)-C(20)-H(20)	119.7	C(34)-C(31)-C(33)	108.82(14)
C(19)-C(20)-H(20)	119.7	C(28)-C(31)-C(33)	108.24(13)
C(20)-C(21)-C(22)	119.37(17)	C(31)-C(32)-H(32A)	109.5
C(20)-C(21)-H(21)	120.3	C(31)-C(32)-H(32B)	109.5
C(22)-C(21)-H(21)	120.3	H(32A)-C(32)-H(32B)	109.5
C(21)-C(22)-C(23)	120.3(2)	C(31)-C(32)-H(32C)	109.5
C(21)-C(22)-H(22)	119.8	H(32A)-C(32)-H(32C)	109.5
C(23)-C(22)-H(22)	119.8	H(32B)-C(32)-H(32C)	109.5
C(22)-C(23)-C(18)	120.69(17)	C(31)-C(33)-H(33A)	109.5
C(22)-C(23)-H(23)	119.7	C(31)-C(33)-H(33B)	109.5
C(18)-C(23)-H(23)	119.7	H(33A)-C(33)-H(33B)	109.5
O(1)-C(24)-N(2)	120.99(14)	C(31)-C(33)-H(33C)	109.5
O(1)-C(24)-C(25)	119.60(14)	H(33A)-C(33)-H(33C)	109.5
N(2)-C(24)-C(25)	119.38(14)	H(33B)-C(33)-H(33C)	109.5
C(30)-C(25)-C(26)	118.17(14)	C(31)-C(34)-H(34A)	109.5

C(31)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(31)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(7)-N(1)-C(17)	123.03(13)
C(7)-N(1)-C(8)	110.99(13)
C(17)-N(1)-C(8)	124.44(13)
C(24)-N(2)-C(9)	127.54(13)
C(24)-N(2)-C(8)	120.05(13)
C(9)-N(2)-C(8)	111.48(12)
N(4)-N(3)-C(1)	114.91(13)
N(3)-N(4)-C(11)	113.03(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for toste81. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	17(1)	15(1)	18(1)	1(1)	4(1)	0(1)
C(2)	14(1)	21(1)	17(1)	-1(1)	2(1)	-4(1)
C(3)	16(1)	20(1)	23(1)	1(1)	3(1)	-1(1)
C(4)	19(1)	25(1)	22(1)	6(1)	1(1)	-2(1)
C(5)	19(1)	33(1)	16(1)	2(1)	2(1)	-5(1)
C(6)	17(1)	28(1)	19(1)	-3(1)	4(1)	-3(1)
C(7)	14(1)	18(1)	20(1)	-1(1)	2(1)	-4(1)
C(8)	16(1)	15(1)	19(1)	-2(1)	3(1)	-2(1)
C(9)	22(1)	13(1)	20(1)	0(1)	2(1)	0(1)
C(10)	23(1)	16(1)	18(1)	0(1)	3(1)	1(1)
C(11)	18(1)	21(1)	17(1)	3(1)	3(1)	0(1)
C(12)	22(1)	22(1)	26(1)	2(1)	4(1)	0(1)
C(13)	24(1)	25(1)	33(1)	7(1)	3(1)	-4(1)
C(14)	20(1)	37(1)	28(1)	13(1)	5(1)	-2(1)
C(15)	26(1)	35(1)	30(1)	5(1)	13(1)	5(1)
C(16)	26(1)	23(1)	24(1)	1(1)	9(1)	0(1)
C(17)	24(1)	17(1)	25(1)	-4(1)	5(1)	3(1)
C(18)	20(1)	26(1)	17(1)	1(1)	2(1)	4(1)
C(19)	30(1)	36(1)	24(1)	-3(1)	5(1)	10(1)
C(20)	29(1)	60(2)	31(1)	2(1)	11(1)	16(1)
C(21)	21(1)	60(2)	31(1)	12(1)	7(1)	3(1)
C(22)	23(1)	39(1)	30(1)	7(1)	2(1)	-4(1)
C(23)	21(1)	28(1)	24(1)	1(1)	4(1)	1(1)
C(24)	20(1)	15(1)	22(1)	1(1)	5(1)	0(1)
C(25)	17(1)	17(1)	20(1)	-1(1)	3(1)	1(1)
C(26)	21(1)	19(1)	20(1)	3(1)	2(1)	0(1)
C(27)	22(1)	18(1)	22(1)	2(1)	4(1)	-3(1)
C(28)	18(1)	18(1)	17(1)	-2(1)	4(1)	1(1)
C(29)	22(1)	20(1)	19(1)	3(1)	2(1)	2(1)

C(30)	21(1)	14(1)	25(1)	3(1)	5(1)	1(1)
C(31)	21(1)	19(1)	20(1)	-1(1)	2(1)	-2(1)
C(32)	31(1)	25(1)	27(1)	-5(1)	1(1)	-3(1)
C(33)	22(1)	36(1)	28(1)	-5(1)	3(1)	-2(1)
C(34)	30(1)	31(1)	25(1)	1(1)	-5(1)	-4(1)
N(1)	19(1)	18(1)	19(1)	-1(1)	4(1)	2(1)
N(2)	17(1)	14(1)	19(1)	-1(1)	1(1)	-2(1)
N(3)	19(1)	19(1)	18(1)	0(1)	5(1)	-1(1)
N(4)	19(1)	18(1)	17(1)	-1(1)	3(1)	-2(1)
O(1)	25(1)	14(1)	33(1)	0(1)	-3(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for toste81.

	x	y	z	U(eq)
H(3)	9676	-1503	8823	24
H(4)	9507	-2077	10085	27
H(5)	8511	322	10658	28
H(6)	7615	3277	9994	25
H(8)	8054	5079	7520	20
H(9A)	6769	-74	6603	22
H(9B)	6839	-493	7493	22
H(10A)	8606	696	6785	23
H(10B)	8628	-1130	7422	23
H(12)	10884	8326	7909	28
H(13)	12636	9347	7775	33
H(14)	13759	6869	7331	34
H(15)	13120	3422	6989	35
H(16)	11403	2337	7163	29
H(17A)	6675	6749	8248	26
H(17B)	7204	6533	9130	26
H(19)	5350	7446	9312	36
H(20)	3698	6112	9522	47
H(21)	3140	2639	9153	44
H(22)	4256	457	8584	38

H(23)	5904	1779	8364	29
H(26)	5030	60	6908	24
H(27)	3417	-1224	6158	25
H(29)	3320	3869	4760	25
H(30)	4897	5233	5532	24
H(32A)	1423	-2470	4460	42
H(32B)	2340	-2819	5215	42
H(32C)	2686	-2163	4442	42
H(33A)	1171	2187	5584	44
H(33B)	1445	-189	5910	44
H(33C)	501	173	5172	44
H(34A)	1559	3176	4328	46
H(34B)	965	1059	3936	46
H(34C)	2205	1550	3893	46

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