Concise Total Synthesis and Stereochemical Revision of all (–)-Trigonoliimines

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Supporting Information

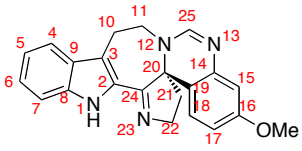
General Procedures. All reactions were performed in oven-dried or flame-dried round-bottomed flasks. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Where necessary (so noted), solutions were deoxygenated by argon purging for a minimum of 10 min. Flash column chromatography was performed as described by Still et al. using silica gel (60-Å pore size, 40–63 μm, 4-6% H_2O content, Zeochem).[1] Analytical thin–layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to an ethanolic phosphomolybdic acid (PMA), an acidic solution of *p*-anisaldehyde (Anis), an aqueous solution of ceric ammonium molybdate (CAM), an aqueous solution of potassium permanganate ($KMnO_4$) or an ethanolic solution of ninhydrin followed by heating (<1 min) on a hot plate (~250 °C). Organic solutions were concentrated at 29–33 °C on rotary evaporators capable of achieving a minimum pressure of ~2 torr.

Materials. Commercial reagents and solvents were used as received with the following exceptions: dichloromethane, tetrahydrofuran, acetonitrile, toluene, methanol, and dimethylformamide were purchased from J.T. Baker (Cycletainer™) and were purified by the method of Grubbs et al. under positive argon pressure.[2] 6-Methoxyindole was purchased from Chem-Impex International, Inc.. All other solvents and chemicals were purchased from Sigma–Aldrich.

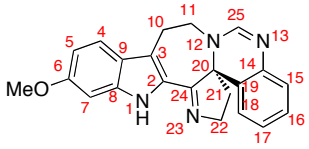
Instrumentation. Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance spectra were recorded with Varian inverse probe 500 INOVA, Varian 500 INOVA and Bruker 400 AVANCE spectrometers. Proton nuclear magnetic resonance (^{1}H NMR) spectra are reported in parts per million on the δ scale and are referenced from the residual protium in the NMR solvent ($CDCl_3$: δ 7.24 ($CHCl_3$), CD_3OD: δ 3.31 (CHD_2OD), $CD_3OD/CDCl_3$ = 1/3: δ 3.31 (CHD_2OD), DMSO-d_6: δ 2.50 (DMSO-d_5)). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, app = apparent, br = broad), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra are reported in parts per million on the δ scale and are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.23, CD_3OD: δ 49.15, $CD_3OD/CDCl_3$ = 1/3: δ 49.15, DMSO-d_6: δ 39.51). Data is reported as follows: chemical shift or chemical shift (assignment). Infrared data (IR) were obtained with a Perkin-Elmer 2000 FTIR and are reported as follows: [frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad)]. Optical Rotations were recorded on a Jasco P-1010 Polarimeter (chloroform, Aldrich, Chromasolv Plus 99.9%; methanol, Aldrich, Chromasolv Plus 99.9%) and specific rotations are reported as follows: [wavelength of light, temperature (°C), specific rotation, concentration in grams/100 mL of solution, solvent]. Chiral HPLC analysis was performed on an Agilent Technologies 1100 Series system. Preparative HPLC was performed on a Waters system with the 1525 Binary HPLC Pump, 2489 UV/Vis Detector, 3100 Mass Detector, System Fluidics Organizer, and 2767 Sample Manager components. The structures of (–)-**3**, (–)-**20**, and (–)-**28** were obtained at the X-ray crystallography laboratory of the Department of Chemistry, Massachusetts Institute of Technology, with the assistance of Mr. Justin Kim. We are grateful to Dr. Li Li for obtaining the mass spectrometric data at the Department of Chemistry's Instrumentation Facility, Massachusetts Institute of Technology. High-resolution mass spectrometric data (HRMS) were recorded on a Bruker APEXIV 4.7 t FT-ICR-MS spectrometer using electrospray ionization (ESI) source or direct analysis in real time (DART) ionization source.

[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

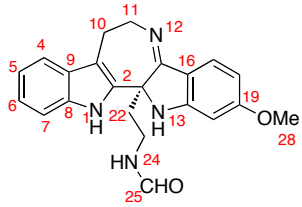
Positional Numbering System. In assigning the ^{1}H and ^{13}C NMR data of all intermediates en route to our total synthesis of (–)-**1**, (–)-**2**, (–)-**3**, and (–)-**4**, we have employed a uniform numbering system consistent with that of the final targets.



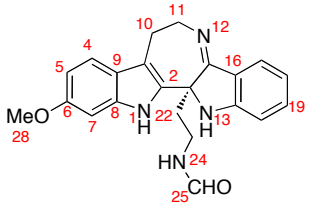
(–)-trigonoliimine A (**1**)



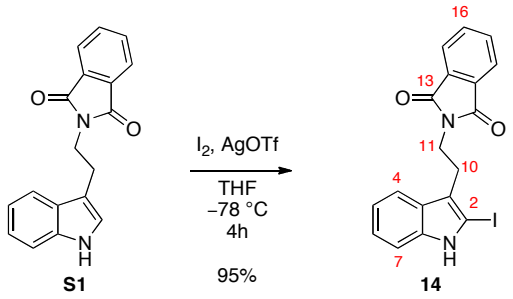
(–)-trigonoliimine B (**2**)



(–)-trigonoliimine C (**3**)



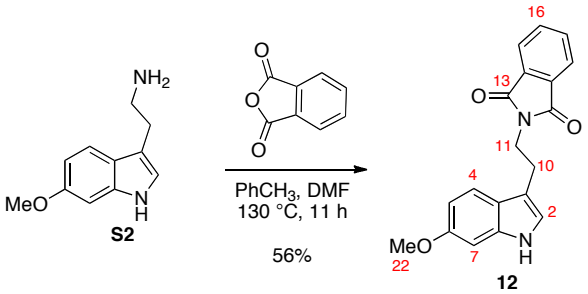
(–)-isotrigonoliimine C (**4**)



2-(2-(2-Iodo-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (14):

Iodine (1.9 g, 7.6 mmol, 1.1 equiv) was added as a solid in one portion to a solution of tryptamine **S1** (2.0 g, 6.9 mmol, 1 equiv) in anhydrous tetrahydrofuran (34 mL) at −78 °C. After 4 min, silver trifluoromethanesulfonate (AgOTf, 1.9 g, 7.6 mmol, 1.1 equiv) was added as a solid in one portion to the reaction mixture to form a yellow precipitate. After 4 h, sodium bicarbonate (1.3 g, 15 mmol, 2.2 equiv) was added as a solid in one portion, and the reaction mixture was allowed to warm to 23 °C. After 30 min, the resulting slurry was filtered through a plug of celite, and washed with ethyl acetate (200 mL). The resulting filtrate was quenched with a mixture of saturated aqueous sodium thiosulfate solution and saturated aqueous sodium bicarbonate solution (1:1, 200 mL), and the layers were separated. The aqueous layer was extracted with ethyl acetate (200 mL), and the combined organic layers were dried over anhydrous sodium sulfate, and were concentrated under reduced pressure. The sample of the crude residue was purified by flash column chromatography (silica gel: diam. 7 cm, ht. 10 cm; eluent: 33% ethyl acetate in hexanes) to afford iodide **14** (2.7 g, 95%) as a pale yellow solid.

^{1}H NMR (500.4 MHz, $CDCl_3$, 21 °C):	δ 7.99 (br-s, 1H, N_1**H**), 7.79 (dd, *J* = 5.5, 3.0 Hz, 2H, C_{15}**H**, C_{18}**H**), 7.67 (dd, *J* = 5.3, 3.0 Hz, 2H, C_{16}**H**, C_{17}**H**), 7.62 (d, *J* = 7.9 Hz, 1H, C_4**H**), 7.26 (d, *J* = 8.0 Hz, 1H, C_7**H**), 7.09 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H, C_6**H**), 7.04 (app-td, *J* = 7.5, 0.9 Hz, 1H, C_5**H**), 3.91 (app-t, *J* = 7.5 Hz, 2H, C_{11}**H**$_2$), 3.06 (app-t, *J* = 7.5 Hz, 2H, C_{10}**H**$_2$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C):	δ 168.5, 139.0, 134.1, 132.4, 127.7, 123.4 122.6, 120.3, 118.8, 118.1, 110.6, 78.5, 37.9, 26.3.
FTIR (neat) cm^{-1}:	3351 (s), 3058 (w), 2944 (w), 1770 (m), 1705 (s), 1397 (s), 1103 (m), 717 (s).
HRMS (DART) (*m*/*z*):	calc'd for $C_{18}H_{12}IN_2O_2$, $[M–H]^-$: 414.9949 found: 414.9945.
TLC (33% ethyl acetate in hexanes) R*f*:	0.50 (CAM, UV).

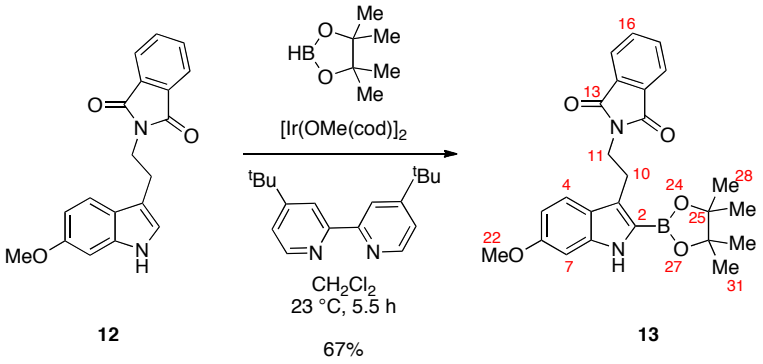


2-(2-(6-Methoxy-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (12):

A suspension of 6-methoxytryptamine[3] (**S2**, 2.00 g, 10.5 mmol, 1 equiv) in anhydrous dimethylformamide (DMF, 8.0 mL) at 23 °C was stirred vigorously under an argon atmosphere to result in a homogeneous solution. A portion of anhydrous toluene (105 mL) and additional anhydrous dimethylformamide (1.0 mL) was added to the homogenous solution of tryptamine derivative **S2** in DMF. Phthalic anhydride (1.70 g, 11.6 mmol, 1.10 equiv) was added as a solid in one portion, the reaction flask was equipped with a Dean-Stark trap, and the reaction set-up was sealed under an atmosphere of argon and heated to 130 °C. After 11 h, the reaction mixture was allowed to cool to 23 °C and concentrated under reduced pressure to afford a black solid residue. This solid was purified by flash column chromatography (silica gel: diam. 5 cm, ht. 12 cm; eluent: 2.5% acetone in dichloromethane) to afford the indole **12** (1.9 g, 56%) as a yellow solid.

^{1}H NMR (500.4 MHz, $CDCl_3$, 21 °C):	δ 7.86 (br-s, 1H, N_1**H**), 7.81 (dd, *J* = 5.5, 3.0 Hz, 2H, C_{15}**H**, C_{18}**H**), 7.68 (dd, *J* = 5.5, 3.0 Hz, 2H, C_{16}**H**, C_{17}**H**), 7.57 (d, *J* = 8.6 Hz, 1H, C_4**H**), 6.96 (d, *J* = 2.3 Hz, 1H, C_2**H**), 6.81 (d, *J* = 1.9 Hz, 1H, C_7**H**), 6.77 (dd, *J* = 8.6, 2.2 Hz, 1H, C_5**H**), 3.97 (app-t, *J* = 7.8 Hz, 2H, C_{11}**H₂**), 3.81 (s, 3H, O**Me**), 3.09 (app-t, *J* = 7.7 Hz, 2H, C_{10}**H₂**).
^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C):	δ 168.6 (**C**$_{13}$, **C**$_{20}$), 156.8 (**C**$_6$), 137.1 (**C**$_8$), 134.1 (**C**$_{16}$, **C**$_{17}$), 132.4 (**C**$_{14}$, **C**$_{19}$), 123.4 (**C**$_{15}$, **C**$_{18}$), 122.0 (**C**$_9$), 120.9 (**C**$_2$), 119.7 (**C**$_4$), 112.6 (**C**$_3$), 109.7 (**C**$_5$), 94.8 (**C**$_7$), 55.9 (**C**$_{22}$), 38.7 (**C**$_{11}$), 24.7 (**C**$_{10}$).
FTIR (neat) cm^{-1}:	3391 (br-m), 1766 (w), 1706 (s), 1629 (w), 1397 (s), 1161 (w), 990 (w), 713 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{19}H_{17}N_2O_3$, $[M+H]^+$: 321.1234 found: 321.1231.
TLC (5% acetone in dichloromethane) R*f*:	0.63 (CAM, UV).

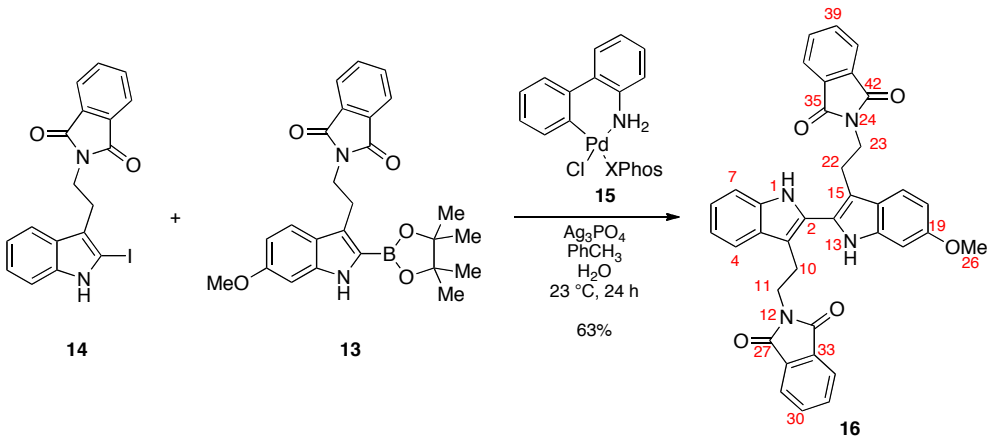
[3] 6-Methoxytryptamine (**S2**) can be purchased from commercial sources. Additionally, it can be prepared from 6-methoxyindole: Woodward, R. B.; Bader, F. E.; Bickel, H.; Frey, A. J.; Kierstead, R. W. *Tetrahedron* **1958**, *2*, 1–57.



2-(2-(6-Methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (13):

Pinacol borane (873 μL, 5.84 mmol, 2.20 equiv) was added to a solution of indole **12** (850 mg, 2.65 mmol, 1 equiv), (1,5-cyclooctadiene)(methoxy)iridium(I) dimer (87.9 mg, 133 μmol, 5.00 mol%) and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (71.2 mg, 265 μmol, 10.0 mol%) in degassed (purged with an argon stream) and anhydrous tetrahydrofuran (27.0 mL) sealed under an argon atmosphere at 23 °C. After 2.5 h, (1,5-cyclooctadiene)(methoxy)iridium(I) dimer (87.9 mg, 133 μmol, 5.00 mol%) was added at once to the reaction mixture and the contents resealed under an argon atmosphere. After 3 h, the resulting red homogeneous reaction mixture was purged with an air stream. After 10 min, silica gel (14 g) was added to the reaction mixture, and it was concentrated under reduced pressure. The resulting crude residue adsorbed onto silica gel was purified by flash column chromatography (silica gel: diam. 5 cm, ht. 10 cm; eluent: 20% ethyl acetate in hexane) to afford pinacol ester **13** (799 mg, 67.4%) as a yellow solid.

^{1}H NMR (500.4 MHz, $CDCl_3$, 21 °C):	δ 8.25 (br-s, 1H, N_1**H**), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H, C_{15}**H**, C_{18}**H**), 7.63 (dd, *J* = 5.5, 3.1 Hz, 2H, C_{16}**H**, C_{17}**H**), 7.58 (d, *J* = 8.6 Hz, 1H, C_4**H**), 6.73 (d, *J* = 1.8 Hz, 1H, C_7**H**), 6.71 (dd, *J* = 8.7, 2.2 Hz, 1H, C_5**H**), 3.96 (app-t, *J* = 7.2 Hz, 2H, C_{11}**H$_2$**), 3.79 (s, 3H, O**Me**), 3.33 (app-t, *J* = 7.2 Hz, 2H, C_{10}**H$_2$**), 1.27 (s, 12H, C_{28}**H$_3$** –C_{31}**H$_3$**).
^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C):	δ 168.4 (**C**$_{13}$, **C**$_{20}$), 158.0 (**C**$_6$), 139.1 (**C**$_8$), 133.8 (**C**$_{16}$, **C**$_{17}$), 132.5 (**C**$_{14}$, **C**$_{19}$), 125.5 (**C**$_2$), 123.2 (**C**$_{15}$, **C**$_{18}$), 123.0 (**C**$_9$), 120.5 (**C**$_4$), 110.4 (**C**$_3$), 110.4 (**C**$_5$), 94.0 (**C**$_7$), 83.9 (**C**$_{25}$, **C**$_{26}$), 55.7 (**C**$_{22}$), 39.4 (**C**$_{11}$), 24.9 (**C**$_{28}$–**C**$_{31}$), 24.7 (**C**$_{10}$).
FTIR (neat) cm^{-1}:	3391 (br-s), 2978 (s), 2937 (s), 2252(w), 1771 (s), 1712 (s), 1549 (s), 1268 (s), 1142 (s), 911 (s), 732 (s).
HRMS (DART) (*m*/*z*):	calc'd for $C_{25}H_{28}BN_2O_5$, $[M+H]^+$: 447.2186, found: 447.2118.
TLC (50% hexanes in ethyl acetate), R*f*:	0.73 (CAM, UV).



2,2'-((6-Methoxy-1*H*,1'*H*-[2,2'-biindole]-3,3'-diyl)bis(ethane-2,1-diyl))bis(isoindoline-1,3-dione) (16):

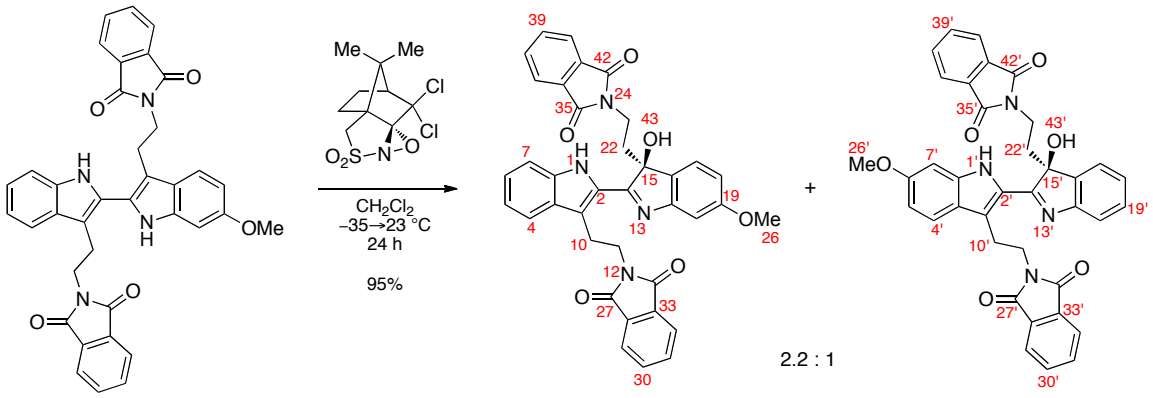
Degassed (purged with an argon stream) water (1.9 mL) was slowly added via syringe to a solution of pinacol ester **13** (0.300 g, 0.672 mmol, 1 equiv), iodide **14** (336 mg, 0.807 mmol, 1.20 equiv), palladium precatalyst[4] (**15**, 106 mg, 0.134 mmol, 20.0 mol%), and silver phosphate (574 mg, 1.34 mmol, 2.00 equiv) in degassed (purged with an argon stream) toluene (9.6 mL) at 23 °C, and the resulting solution was sealed under an argon atmosphere in the dark. After 24 h, brine (80 mL) was added to the reaction mixture and the heterogeneous mixture was extracted with dichloromethane (5 × 80 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered and were concentrated under reduced pressure. The resulting crude residue was adsorbed onto silica gel (15 g) for loading, and was purified by flash column chromatography (silica gel: diam. 5 cm, ht. 8 cm; eluent: 1% acetone in dichloromethane) to afford dimeric indole **16** (256 mg, 63.0%) as a bright yellow solid. Structural assignment of **16** utilized additional information from gCOSY, HSQC and HMBC. Dimeric indole **16** was prone to air oxidation and therefore was immediately moved to the next step.

^{1}H NMR (500.4 MHz, DMSO-d_6, 21 °C): δ 10.98 (br-s, 1H, N_1**H**), 10.83 (br-s, 1H, N_{13}**H**), 7.70–7.64 (m, 8H, C_{37}**H**–C_{40}**H**, C_{29}**H**–C_{32}**H**), 7.60 (d, J = 7.9 Hz, 1H, C_7**H**), 7.48 (d, J = 8.6 Hz, 1H, C_{17}**H**), 7.30 (dt, J = 8.1, 0.8 Hz, 1H, C_4**H**), 7.10 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H, C_6**H**), 7.01 (ddd, J = 7.9, 7.0, 1.0 Hz, 1H, C_5**H**), 6.77 (d, J = 2.2 Hz, 1H, C_{20}**H**), 6.69 (dd, J = 8.6, 2.3 Hz, 1H, C_{18}**H**), 3.79 (s, 3H, O**Me**), 3.77–3.73 (m, 4H, C_{11}**H$_2$**, C_{23}**H$_2$**), 3.01 (t, J = 7.5 Hz, 2H, C_{10}**H$_2$**), 2.97 (t, J = 7.7 Hz, 2H, C_{22}**H$_2$**).

^{13}C NMR (125.8 MHz, DMSO-d_6, 21 °C): δ 167.6 (**C**$_{27}$, **C**$_{34}$), 167.6 (**C**$_{35}$, **C**$_{42}$), 155.9 (**C**$_{19}$), 137.1 (**C**$_{21}$), 136.2 (**C**$_8$), 134.0 (**C**$_{30}$, **C**$_{31}$), 134.0 (**C**$_{38}$, **C**$_{39}$), 131.4 (**C**$_{28}$, **C**$_{33}$), 131.4 (**C**$_{36}$, **C**$_{41}$), 127.7 (**C**$_3$), 127.7 (**C**$_9$), 126.1 (**C**$_{15}$), 122.7 (**C**$_{29}$, **C**$_{32}$), 122.7 (**C**$_{37}$, **C**$_{40}$), 122.0 (**C**$_{16}$), 121.5 (**C**$_6$), 118.9 (**C**$_{17}$), 118.7 (**C**$_5$), 118.2 (**C**$_7$), 111.3 (**C**$_4$), 110.2 (**C**$_{14}$), 109.9 (**C**$_2$), 109.1 (**C**$_{18}$),

[4] Palladium precatalyst **15** was prepared according to the following procedure: Kinzel, T.; Zhang, Y.; Buchwald, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 14073–14075.

	94.3 (**C**$_{20}$), 55.2 (**C**$_{26}$), 37.8 (**C**$_{11}$), 37.8 (**C**$_{23}$), 23.6 (**C**$_{22}$), 23.5 (**C**$_{10}$).
FTIR (neat) cm^{-1}:	3365 (br-w), 1766 (m), 1703 (s), 1398 (s), 1352 (m), 714 (s).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{37}H_{28}N_4NaO_5$, $[M+Na]^+$: 631.1952, found: 631.1949.
TLC (1% acetone in dichloromethane), R*f*:	0.18 (CAM, UV).



16 (+)-**17** (+)-**18**

(*S*)-2,2'-((3'-Hydroxy-6'-methoxy-1*H*,3'*H*-[2,2'-biindole]-3,3'-diyl)bis(ethane-2,1-diyl))bis(isoindoline-1,3-dione) (17) and (*S*)-2,2'-((3'-hydroxy-6-methoxy-1*H*,3'*H*-[2,2'-biindole]-3,3'-diyl)bis(ethane-2,1-diyl))bis(isoindoline-1,3-dione) (18):

A solution of (+)-(8,8-dichlorocamphorylsulfonyl)oxaziridine (198 mg, 0.645 mmol, 2.00 equiv) in degassed (purged with an argon stream) and anhydrous dichloromethane (16 mL) at –35 °C was cannula transferred to a solution of dimeric indole **16** (196 mg, 0.323 mmol, 1 equiv) in degassed (purged with an argon stream) and anhydrous dichloromethane (32 mL) at –35 °C under an atmosphere of argon. The reaction mixture was allowed to gently warm to 23 °C. After 24 h, the reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel: diam. 2.5 cm, ht. 13 cm; eluent: 6% acetone in dichloromethane) to afford hydroxyindolenines (+)-**17** and (+)-**18** (2.2:1, **17**:**18**, 191 mg, 94.6%) as a yellow foam. Structural assignment of (+)-**17** utilized additional information from gCOSY, HSQC and HMBC.

(*S*)-2,2'-((3'-Hydroxy-6'-methoxy-1*H*,3'*H*-[2,2'-biindole]-3,3'-diyl)bis(ethane-2,1-diyl))bis(isoindoline-1,3-dione) (17)

^{1}H NMR (500.4 MHz, $CDCl_3$, 21 °C): δ 9.35 (s, 1H, N_1**H**), 7.75 (dd, *J* = 5.4, 3.1 Hz, 2H, C_{29}**H**, C_{32}**H**), 7.67 (dd, *J* = 5.4, 3.0 Hz, 2H, C_{30}**H**, C_{31}**H**), 7.53 (dd, *J* = 5.4, 3.1 Hz, 2H, C_{37}**H**, C_{40}**H**), 7.45 (dd, *J* = 5.5, 3.0 Hz, 2H, C_{38}**H**, C_{39}**H**), 7.35 (d, *J* = 8.1 Hz, 1H, C_{17}**H**), 7.25 (d, *J* = 6.3 Hz, 1H, C_7**H**), 6.82 (app-t, *J* = 7.6 Hz, 1H, C_6**H**), 6.68–6.64 (m, 2H, C_4**H**, C_5**H**), 6.50 (d, *J* = 2.2 Hz, 1H, C_{20}**H**), 6.44 (dd, *J* = 8.1, 2.3 Hz, 1H, C_{18}**H**), 4.29 (s, 1H, O_{43}**H**), 4.14 (ddd, *J* = 13.8, 8.7, 5.3 Hz, 1H, C_{11}**H**), 4.05 (dt, *J* = 13.5, 0.9 Hz, 1H, C_{11}**H**), 3.66 (s, 3H, O**Me**), 3.59–3.50 (m, 2H, C_{10}**H**, C_{23}**H**), 3.44–3.37 (m, 1H, C_{10}**H**), 3.30 (dt, *J* = 14.2, 5.9 Hz, 1H, C_{23}**H**), 2.70 (ddd, *J* = 14.5, 8.7, 6.0 Hz, 1H, C_{22}**H**), 2.09 (dt, *J* = 14.2, 5.6 Hz, 1H, C_{22}**H**).

^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C): 175.0 (**C**$_{14}$), 168.7 (**C**$_{27}$, **C**$_{34}$), 167.9 (**C**$_{35}$, **C**$_{42}$), 161.5 (**C**$_{19}$), 154.9 (**C**$_{21}$), 137.4 (**C**$_8$), 133.9 (**C**$_{30}$, **C**$_{31}$), 133.6 (**C**$_{38}$, **C**$_{39}$), 132.5 (**C**$_{28}$, **C**$_{33}$), 132.1 (**C**$_{36}$, **C**$_{41}$), 130.2 (**C**$_{16}$), 127.9 (**C**$_9$), 127.5 (**C**$_2$), 124.8 (**C**$_6$), 123.2 (**C**$_{29}$, **C**$_{32}$), 123.0 (**C**$_{17}$), 122.9 (**C**$_{37}$, **C**$_{40}$), 119.8 (**C**$_4$), 119.6

(**C**$_3$), 119.4 (**C**$_7$), 112.2 (**C**$_5$), 111.3 (**C**$_{18}$), 106.9 (**C**$_{20}$), 85.5 (**C**$_{15}$), 55.4 (**C**$_{26}$), 39.1 (**C**$_{11}$), 34.6 (**C**$_{22}$), 33.5 (**C**$_{23}$), 24.5 (**C**$_{10}$).

FTIR (neat) cm^{-1}: 3363 (br-s), 2939 (w), 2361 (w), 1771 (m), 1710 (s), 1617 (s), 1547 (m), 1397 (s), 1147 (m), 1021 (w), 718 (s).

HRMS (DART) (*m*/*z*): calc'd for $C_{37}H_{29}N_4O_6$, $[M+H]^+$: 625.2082, found: 625.2059.

$[\alpha]_D^{24}$: +252 (*c* 0.08, $CHCl_3$).

TLC (5% acetone in dichloromethane), R*f*: 0.18 (CAM, UV)

(*S*)-2,2'-((3'-Hydroxy-6-methoxy-1*H*,3'*H*-[2,2'-biindole]-3,3'-diyl)bis(ethane-2,1-diyl))bis(isoindoline-1,3-dione) (18)

^{1}H NMR (500.4 MHz, $CDCl_3$, 21 °C): δ 9.23 (s, 1H, $N_{1'}$**H**), 7.77 (dd, *J* = 5.4, 3.0 Hz, 2H, $C_{29'}$**H**, $C_{32'}$**H**), 7.66 (dd, *J* = 5.4, 3.0 Hz, 2H, $C_{30'}$**H**, $C_{31'}$**H**), 7.52 (dd, *J* = 5.5, 3.1 Hz, 2H, $C_{37'}$**H**, $C_{40'}$**H**), 7.47 (d, *J* = 6.8 Hz, 1H, $C_{17'}$**H**), 7.44 (dd, *J* = 5.5, 3.0 Hz, 2H, $C_{38'}$**H**, $C_{39'}$**H**), 7.08 (d, *J* = 8.7 Hz, 1H, $C_{4'}$**H**), 6.92–6.83 (m, 3H, $C_{18'}$**H**, $C_{19'}$**H**, $C_{20'}$**H**), 6.32 (dd, *J* = 8.8, 2.2 Hz, 1H, $C_{5'}$**H**), 6.08 (d, *J* = 1.5 Hz, 1H, $C_{7'}$**H**), 4.49 (s, 1H, $O_{43'}$**H**), 4.17 (ddd, *J* = 13.8, 9.1, 5.0 Hz, 1H, $C_{11'}$**H**), 4.02 (dt, *J* = 13.5, 5.4 Hz, 1H, $C_{11'}$**H**), 3.58–3.45 (m, 2H, $C_{10'}$**H**, $C_{23'}$**H**), 3.53 (s, 3H, O**Me**), 3.34–3.27 (m, 2H, $C_{10'}$**H**, $C_{23'}$**H**), 2.68 (ddd, *J* = 14.4, 8.3, 6.2 Hz, 1H, $C_{22'}$**H**), 2.10 (dt, *J* = 14.0, 5.8 Hz, 1H, $C_{22'}$**H**).

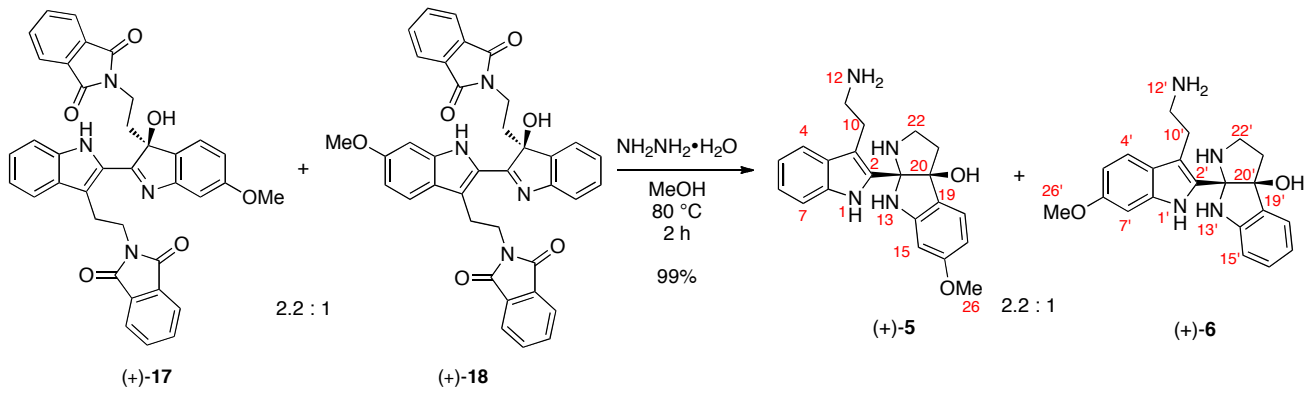
^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C): 173.6, 168.7, 167.9, 158.3, 153.3, 138.7, 138.1, 134.0, 133.5, 132.5, 132.1, 130.4, 126.6, 125.4, 123.2, 122.9, 122.6, 122.5, 120.5, 120.2, 120.2, 112.0, 93.5, 85.7, 55.1, 39.2, 34.5, 33.4, 24.6.

FTIR (neat) cm^{-1}: 3365 (br-w), 2932 (w), 2361 (w), 1771 (m), 1710 (s), 1626 (w), 1545 (m), 1396 (s), 1347 (m), 1240 (w), 717 (s).

HRMS (DART) (*m*/*z*): calc'd for $C_{37}H_{29}N_4O_6$, $[M+H]^+$: 625.2082, found: 625.2070.

$[\alpha]_D^{24}$: +121 (*c* 0.10, $CHCl_3$).

TLC (5% acetone in dichloromethane), R*f*: 0.18 (CAM, UV)



(3a*S*,8a*S*)-8a-(3-(2-Aminoethyl)-1*H*-indol-2-yl)-6-methoxy-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indol-3a-ol (5) and (3a*S*,8a*S*)-8a-(3-(2-aminoethyl)-6-methoxy-1*H*-indol-2-yl)-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indol-3a-ol (6):

Hydrazine monohydrate (252 μL, 5.09 mmol, 20.0 equiv) was added to a solution of hydroxyindolenines (+)-**17** and (+)-**18** (2.2:1, **17**:**18**, 163.0 mg, 0.2601 mmol, 1 equiv) in methanol (25 mL) at 23 °C and the reaction flask was equipped with a reflux condenser, was sealed under an atmosphere of argon and heated to 80 °C. After 2 h, the resulting yellow homogeneous solution was allowed to cool to 23 °C and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel: diam. 5 cm, ht. 12 cm; eluent: 9% methanol, 1% ammonium hydroxide in chloroform) to afford hydroxyaminals (+)-**5** and (+)-**6** (2.2:1, **5**:**6**, 94.2 mg, 99.4%) as a yellow solid mixture. Structural assignment of (+)-**5** utilized additional information from gCOSY, HSQC and HMBC.

(3a*S*,8a*S*)-8a-(3-(2-Aminoethyl)-1*H*-indol-2-yl)-6-methoxy-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indol-3a-ol (5)

^{1}H NMR (500.4 MHz, $CDCl_3$, 21 °C): δ 9.10 (s, 1H, N_1**H**), 7.43 (d, *J* = 7.2 Hz, 1H, C_4**H**), 7.33 (dt, *J* = 8.1, 0.8 Hz, 1H, C_7**H**), 7.16 (d, *J* = 8.2 Hz, 1H, C_{18}**H**), 7.13 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H, C_6**H**), 7.04 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H, C_5**H**), 6.34 (dd, *J* = 8.2, 2.2 Hz, 1H, C_{17}**H**), 6.16 (d, *J* = 2.2 Hz, 1H, C_{15}**H**), 3.79 (s, 3H, O**Me**), 3.12 (app-dd, *J* = 9.1, 5.8 Hz, 1H, C_{22}**H**), 2.97–2.91 (m, 3H, C_{10}**H**, C_{11}**H**, C_{22}**H**), 2.72 (app-t, *J* = 10.5 Hz, 1H, C_{11}**H**), 2.54 (t, *J* = 11.5 Hz, 1H, C_{10}**H**), 2.32–2.21 (m, 2H, C_{21}**H**$_2$).

^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C): δ 161.4 (**C**$_{16}$), 151.4 (**C**$_{14}$), 136.1 (**C**$_2$), 134.4 (**C**$_8$), 129.5 (**C**$_9$), 125.6 (**C**$_{18}$), 125.0 (**C**$_{19}$), 121.7 (**C**$_6$), 119.0 (**C**$_5$), 118.3 (**C**$_4$), 111.5 (**C**$_7$), 110.2 (**C**$_3$), 104.6 (**C**$_{17}$), 94.3 (**C**$_{15}$), 89.5 (**C**$_{20}$), 89.2 (**C**$_{24}$), 55.5 (**C**$_{26}$), 42.5 (**C**$_{22}$), 41.5 (**C**$_{21}$), 41.1 (**C**$_{11}$), 26.4 (**C**$_{10}$).

FTIR (neat) cm^{-1}: 3394 (br-m), 2961 (m), 2931 (m), 2853 (m), 1618 (s), 1500 (s), 1459 (s), 1334 (s), 1198 (s), 1159 (s), 1132 (m), 748 (s).

HRMS (DART) (*m*/*z*): calc'd for $C_{21}H_{25}N_4O_2$, $[M+H]^+$: 365.1972, found: 365.1987.

$[\alpha]_D^{24}$: +61.1 (*c* 0.17, $CHCl_3$).

TLC (18% methanol, 2% ammonium hydroxide in chloroform), R*f*: 0.19 (CAM, UV).

(3a*S*,8a*S*)-8a-(3-(2-Aminoethyl)-6-methoxy-1*H*-indol-2-yl)-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indol-3a-ol (6)

^{1}H NMR (500.4 MHz, $CDCl_3$, 21 °C): δ 9.00 (s, 1H, $N_{1'}$**H**), 7.28 (d, *J* = 8.8 Hz, 1H, $C_{4'}$**H**), 7.28 (dd, *J* = 6.9, 0.9 Hz, 1H, $C_{18'}$**H**), 7.13 (td, *J* = 7.7, 1.3 Hz, 1H, $C_{16'}$**H**), 6.84 (d, *J* = 2.2 Hz, 1H, $C_{7'}$**H**), 6.78 (td, *J* = 7.4, 0.8 Hz, 1H, $C_{17'}$**H**), 6.71 (dd, *J* = 8.6, 2.2 Hz, 1H, $C_{5'}$**H**), 6.61 (d, *J* = 7.9 Hz, 1H, $C_{15'}$**H**), 3.81 (s, 3H, O**Me**), 3.12 (app-t, *J* = 7.2 Hz, 1H, $C_{22'}$**H**), 2.98–2.86 (m, 3H, $C_{10'}$**H**, $C_{11'}$**H**, $C_{22'}$**H**), 2.68 (app-t, *J* = 10.5 Hz, 1H, $C_{11'}$**H**), 2.53–2.47 (m, 1H, $C_{10'}$**H**), 2.34–2.25 (m, 2H, $C_{21'}$**H**$_2$).

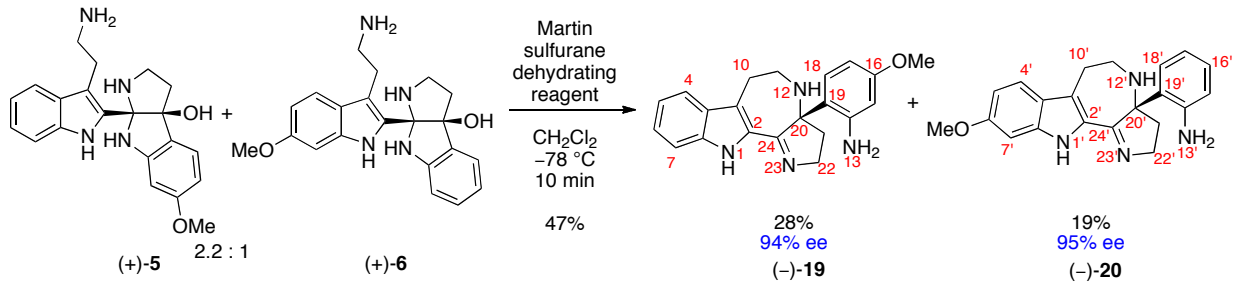
^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C): δ 156.5, 150.1, 135.1, 134.8, 132.7, 129.5, 125.3, 124.0, 119.5, 119.0, 110.1, 109.2, 108.4, 94.9, 89.8, 89.1, 55.9, 42.5, 41.6, 41.2, 26.5.

FTIR (neat) cm^{-1}: 3359 (br-m), 2927 (s), 1691 (w), 1610 (s), 1464 (s), 1205 (s), 751 (s).

HRMS (DART) (*m*/*z*): calc'd for $C_{21}H_{25}N_4O_2$, $[M+H]^+$: 365.1972, found: 365.1978.

$[\alpha]_D^{22}$: +34.6 (*c* 0.17, $CHCl_3$).

TLC (18% methanol, 2% ammonium hydroxide in chloroform), R*f*: 0.09 (CAM, UV).



(S)-2-(3,3a,4,5,6,11-Hexahydro-2H-pyrrolo[3',2':2,3]azepino[4,5-b]indol-3a-yl)-5-methoxyaniline (19) and (*S*)-2-(9-methoxy-3,3a,4,5,6,11-hexahydro-2*H*-pyrrolo[3',2':2,3]azepino[4,5-*b*]indol-3a-yl)aniline (20):

A solution of aminals (+)-**5** and (+)-**6** (2.2:1, **5**:**6**, 91.2 mg, 0.250 mmol, 1 equiv) in anhydrous dichloromethane (8 mL) at –78 °C under an atmosphere of argon was cannula transferred to a solution of bis[α,α-bis(trifluoromethyl)benzenemethanolato]diphenylsulfur (Martin sulfurane dehydrating reagent, 202 mg, 0.300 mmol, 1.20 equiv) in anhydrous dichloromethane (5 mL) at –78 °C under an atmosphere of argon. After 10 min, saturated aqueous sodium bicarbonate solution (20 mL) was added to the reaction mixture and the resulting mixture was diluted with dichloromethane (5 mL), and the layers were separated. The aqueous layer was extracted with dichloromethane (2 × 20 mL), and the combined organic layers were dried over anhydrous sodium sulfate, and were concentrated under reduced pressure. The sample of the crude residue was purified by flash column chromatography (silica gel: diam. 2.5 cm, ht. 18 cm; eluent: 0.9% methanol, 0.1 % ammonium hydroxide in chloroform to 2.3% methanol, 0.3 % ammonium hydroxide in chloroform) to afford pentacycle (–)-**19** (24.2 mg, 27.9%) and pentacycle (–)-**20** (16.4 mg, 18.9%) as pale yellow solids. Structural assignment of (–)-**19** and (–)-**20** utilized additional information from gCOSY, HSQC and HMBC.

Pentacycle (–)-**19** was found to be 94% ee by chiral HPLC analysis [Chiralcel OD-H 0.5 mL/min; 100% hexanes to 20% hexanes in isopropanol over 80 min; t_R(major) = 65.1 min, t_R(minor) = 41.8 min]. Pentacycle (–)-**20** was found to be 95% ee by chiral HPLC analysis [Chiralcel OD-H 0.5 mL/min; 100% hexanes to 20% hexanes in isopropanol over 80 min; t_R(major) = 54.5 min min, t_R(minor) = 43.8 min]. Crystal of (–)-**20** was obtained by slow evaporation of saturated solution of (–)-**20** in chloroform.

(S)-2-(3,3a,4,5,6,11-Hexahydro-2H-pyrrolo[3',2':2,3]azepino[4,5-b]indol-3a-yl)-5-methoxyaniline (19)

^{1}H NMR (500.4 MHz, $CDCl_3$, 21 °C): δ 9.54 (s, 1H, N_1**H**), 7.48 (d, *J* = 8.0 Hz, 1H, C_4**H**), 7.35 (dt, *J* = 8.2, 0.8 Hz, 1H, C_7**H**), 7.24 (app-td, *J* = 7.6, 1.1 Hz, 1H, C_6**H**), 7.06 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H, C_5**H**), 6.57 (d, *J* = 8.6 Hz, 1H, C_{18}**H**), 6.21 (d, *J* = 2.6 Hz, 1H, C_{15}**H**), 5.99 (dd, *J* = 8.5, 2.6 Hz, 1H, C_{17}**H**), 5.25 (s, 2H, N_{13}**H$_2$**), 4.01 (dd, *J* = 15.4, 7.7 Hz, 1H, C_{22}**H**), 3.67 (s, 3H, O**Me**), 3.45 (ddd, *J* = 15.5, 10.2, 5.5 Hz, 1H, C_{22}**H**), 3.22–3.10 (m, 2H, C_{11}**H$_2$**), 3.03–2.91 (m, 2H, C_{10}**H$_2$**), 2.75 (dd, *J* = 12.1, 5.7 Hz, 1H, C_{21}**H**), 1.93 (ddd, *J* = 12.1, 10.5, 7.8 Hz, 1H, C_{21}**H**).

^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C): δ 174.4 (**C**$_{24}$), 160.2 (**C**$_{16}$), 147.7 (**C**$_{14}$), 137.3 (**C**$_8$), 129.6 (**C**$_2$), 129.1 (**C**$_{18}$), 128.4 (**C**$_9$), 124.9 (**C**$_6$), 120.0

(**C**$_5$), 119.8 (**C**$_4$), 118.7 (**C**$_3$), 114.9 (**C**$_{19}$), 111.6 (**C**$_7$), 102.5 (**C**$_{17}$), 102.4 (**C**$_{15}$), 75.6 (**C**$_{20}$), 56.0 (**C**$_{22}$), 55.2 (**C**$_{26}$), 42.1 (**C**$_{11}$), 40.9 (**C**$_{21}$), 28.4 (**C**$_{10}$).

FTIR (neat) cm^{-1}: 3286 (br-s), 2924 (s), 1599 (s), 1509 (m), 1450 (m), 1331 (m), 1211 (s), 748 (s).

HRMS (ESI) (*m*/*z*): calc'd for $C_{21}H_{23}N_4O$, $[M+H]^+$: 347.1866, found: 347.1852.

$[\alpha]_D^{24}$: –96.2 (*c* 0.15, $CHCl_3$).

TLC (9% methanol, 1% ammonium hydroxide in chloroform), R*f*: 0.41 (CAM, UV).

(*S*)-2-(9-Methoxy-3,3a,4,5,6,11-hexahydro-2*H*-pyrrolo[3',2':2,3]azepino[4,5-*b*]indol-3a-yl)aniline (20)

^{1}H NMR (500.4 MHz, $CDCl_3$, 21 °C): δ 9.46 (s, 1H, $N_{1'}$**H**), 7.33 (d, *J* = 8.7 Hz, 1H, $C_{4'}$**H**), 7.02 (app-td, *J* = 7.6, 1.5 Hz, 1H, $C_{16'}$**H**), 6.78 (d, *J* = 2.1 Hz, 1H, $C_{7'}$**H**), 6.72 (dd, *J* = 8.7, 2.2 Hz, 1H, $C_{5'}$**H**), 6.69 (dd, *J* = 7.7, 1.3 Hz, 1H, $C_{18'}$**H**), 6.64 (dd, *J* = 7.9, 1.1 Hz, 1H, $C_{15'}$**H**), 6.44 (td, *J* = 7.5, 1.2 Hz, 1H, $C_{17'}$**H**), 3.99 (dd, *J* = 15.2, 7.7 Hz, 1H, $C_{22'}$**H**), 3.82 (s, 3H, O**Me**), 3.44 (ddd, *J* = 15.5, 10.3, 5.5 Hz, 1H, $C_{22'}$**H**), 3.18 (dt, 1H, *J* = 14.4, 5.0 Hz, 1H, $C_{11'}$**H**), 3.09 (ddd, *J* = 14.3, 9.6, 4.7 Hz, 1H, $C_{11'}$**H**), 2.99–2.92 (m, 1H, $C_{10'}$**H**), 2.86 (dt, *J* = 16.8, 4.7 Hz, 1H, $C_{10'}$**H**), 2.77 (dd, *J* = 12.2, 5.6, Hz, 1H, $C_{21'}$**H**), 1.94 (ddd, *J* = 12.1, 10.5, 7.8 Hz, 1H, $C_{21'}$**H**),

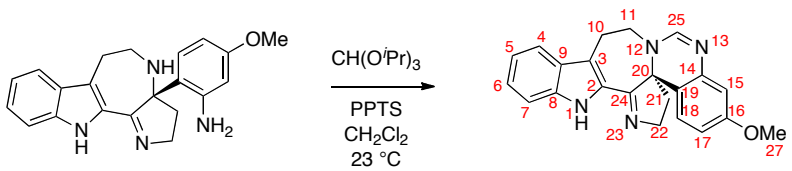
^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C): δ 173.9 (**C**$_{24'}$), 158.6 (**C**$_{6'}$), 146.4 (**C**$_{14'}$), 138.2 (**C**$_{8'}$), 128.9 (**C**$_{2'}$), 128.7 (**C**$_{16'}$), 128.2 (**C**$_{18'}$), 122.8 (**C**$_{9'}$), 122.3 (**C**$_{19'}$), 120.8 (**C**$_{4'}$), 118.7 (**C**$_{3'}$), 117.5 (**C**$_{17'}$), 116.7 (**C**$_{15'}$), 110.5 (**C**$_{5'}$), 94.0 (**C**$_{7'}$), 76.0 (**C**$_{20'}$), 56.1 (**C**$_{22'}$), 55.8 (**C**$_{26'}$), 42.2 (**C**$_{11'}$), 40.7 (**C**$_{21'}$), 28.4 (**C**$_{10'}$).

FTIR (neat) cm^{-1}: 3284 (br-m), 2924 (br-m), 1596 (s), 1495 (w), 1454 (w), 1273 (m), 752 (s).

HRMS (DART) (*m*/*z*): calc'd for $C_{21}H_{23}N_4O$, $[M+H]^+$: 347.1866, found: 347.1876.

$[\alpha]_D^{25}$: –176 (*c* 0.15, $CHCl_3$).

TLC (9% methanol, 1% ammonium hydroxide in chloroform), R*f*: 0.34 (CAM, UV).



(–)-Trigonoliimine A (1):

Anhydrous dichloromethane (4 mL) was added via syringe to a flask charged with pentacycle (–)-**19** (14.0 mg, 40.4 μmol, 1 equiv) and pyridinium *p*-toluenesulfonate (PPTS, 31.0 mg, 0.121 mmol, 3.00 equiv) at 23 °C under an atmosphere of argon to form a bright yellow solution. After 2 min, triisopropyl orthoformate (93.0 μL, 0.404 mmol, 10.0 equiv) was added to the reaction mixture. After 1h, saturated aqueous sodium bicarbonate solution (6 mL) was added to the reaction mixture and the resulting mixture was diluted with dichloromethane (2 mL), and the layers were separated. The aqueous layer was extracted with dichloromethane (2 × 6 mL), and the combined organic layers were dried over anhydrous sodium sulfate, and were concentrated under reduced pressure. The sample of the crude residue was purified by flash column chromatography (silica gel: diam. 2 cm, ht. 12 cm; eluent: 1.8% methanol, 0.2 % ammonium hydroxide in chloroform to 4.5% methanol, 0.5 % ammonium hydroxide in chloroform) to afford (–)-trigonoliimine A (**1**, 11.8 mg, 81.9%) as a pale yellow solid.

^{1}H NMR (500.4 MHz, DMSO-d_6, 21 °C): δ 11.50 (s, 1H, N_1**H**), 7.47 (s, 1H, C_{25}**H**), 7.45 (d, J = 7.9 Hz, 1H, C_4**H**), 7.34 (d, J = 8.2 Hz, 1H, C_7**H**), 7.16 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H, C_6**H**), 7.00 (app-t, J = 7.9 Hz, 1H, C_5**H**), 6.56–6.55 (m, 3H, C_{15}**H**, C_{17}**H**, C_{18}**H**), 4.11 (dd, J = 16.1, 8.1 Hz, 1H, C_{22}**H**), 4.01 (dt, J = 14.3, 3.3 Hz, 1H, C_{11}**H**), 3.74 (app-t, J = 12.1 Hz, 1H, C_{11}**H**), 3.66 (s, 3H, O**Me**), 3.55 (ddd, J = 16.1, 9.9, 6.1 Hz, 1H, C_{22}**H**), 3.07 (app-d, J = 17.1 Hz, 1H, C_{10}**H**), 2.96 (ddd, J = 16.9, 12.1, 4.3 Hz, 1H, C_{10}**H**), 2.19–2.13 (m, 1H, C_{21}**H**), 2.06 (dd, J = 12.0, 5.8 Hz, 1H, C_{21}**H**).

^{1}H NMR (500.4 MHz, $CDCl_3$/CD_3OD (3:1), 21 °C): δ 7.43 (d, J = 8.0 Hz, 1H, C_4**H**), 7.34 (d, J = 8.3 Hz, 1H, C_7**H**), 7.32 (s, 1H, C_{25}**H**), 7.20 (ddd, J = 8.2, 7.1, 1.1 Hz, 1H, C_6**H**), 7.03 (ddd, J = 8.0, 7.1, 0.9 Hz, 1H, C_5**H**), 6.65 (d, J = 2.0 Hz, 1H, C_{15}**H**), 6.57–6.53 (m, 2H, C_{17}**H**, C_{18}**H**), 4.13 (dd, J = 16.1, 8.1 Hz, 1H, C_{22}**H**), 3.92 (dt, J = 14.5, 3.5 Hz, 1H, C_{11}**H**), 3.84 (ddd, J = 14.3, 11.0, 3.1 Hz, 1H, C_{11}**H**), 3.70 (s, 3H, O**Me**), 3.65 (ddd, J = 16.1, 10.2, 5.9 Hz, 1H, C_{22}**H**), 3.19–3.08 (m, 2H, C_{10}**H₂**), 2.27 (dd, J = 12.3, 5.8 Hz, 1H, C_{21}**H**), 2.16 (ddd, J = 12.1, 10.3, 8.3 Hz, 1H, C_{21}**H**).

^{13}C NMR (125.8 MHz, DMSO-d_6, 21 °C): δ 166.5 (**C**$_{24}$), 159.6 (**C**$_{16}$), 150.2 (**C**$_{25}$), 143.1 (**C**$_{14}$), 136.5 (**C**$_8$), 128.0 (**C**$_2$), 127.1 (**C**$_9$), 123.4 (**C**$_6$), 123.2 (**C**$_{18}$), 119.2 (**C**$_5$), 119.1 (**C**$_4$), 115.6 (**C**$_3$), 115.0 (**C**$_{19}$),

111.6 (**C**$_7$), 110.2 (**C**$_{17}$), 109.3 (**C**$_{15}$), 76.5 (**C**$_{20}$), 56.2 (**C**$_{22}$), 55.0 (**C**$_{27}$), 46.6 (**C**$_{11}$), 40.6 (**C**$_{21}$), 29.2 (**C**$_{10}$).

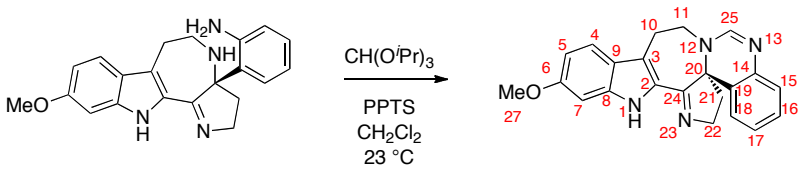
^{13}C NMR (125.8 MHz, $CDCl_3/CD_3OD$ (3:1), 21 °C): δ 168.2 (**C**$_{24}$), 160.7 (**C**$_{16}$), 150.5 (**C**$_{25}$), 142.0 (**C**$_{14}$), 137.4 (**C**$_8$), 127.9 (**C**$_9$), 127.2 (**C**$_2$), 125.0 (**C**$_6$), 123.9 (**C**$_{18}$), 120.2 (**C**$_5$), 119.6 (**C**$_4$), 118.1 (**C**$_3$), 114.5 (**C**$_{19}$), 112.1 (**C**$_7$), 112.0 (**C**$_{17}$), 109.4 (**C**$_{15}$), 77.5 (**C**$_{20}$), 56.6 (**C**$_{22}$), 55.6 (**C**$_{27}$), 48.5 (**C**$_{11}$), 41.1 (**C**$_{21}$), 30.1 (**C**$_{10}$).

FTIR (neat) cm^{-1}: 3406 (br-s), 1594 (s), 1488 (m), 1394 (w), 1251 (w), 1126 (w), 730 (s).

HRMS (ESI) (*m*/*z*): calc'd for $C_{22}H_{21}N_4O$, $[M+H]^+$: 357.1710, found: 357.1702.

$[\alpha]_D^{24}$: –294 (*c* 0.24, $CHCl_3$).

TLC (9% methanol, 1% ammonium hydroxide in chloroform), R*f*: 0.38 (CAM, UV).



(–)-Trigonoliimine B (2):

Anhydrous dichloromethane (4.3 mL) was added via syringe to a flask charged with pentacycle (–)-**20** (16.4 mg, 47.3 μmol, 1 equiv) and pyridinium *p*-toluenesulfonate (PPTS, 33.3 mg, 0.130 mmol, 3.00 equiv) at 23 °C under an atmosphere of argon to form a bright yellow solution. After 2 min, triisopropyl orthoformate (99.5 μL, 0.433 mmol, 10.0 equiv) was added to the reaction mixture. After 1h, saturated aqueous sodium bicarbonate solution (6 mL) was added to the reaction mixture and the resulting mixture was diluted with dichloromethane (2 mL), and the layers were separated. The aqueous layer was extracted with dichloromethane (2 × 6 mL), and the combined organic layers were dried over anhydrous sodium sulfate, and were concentrated under reduced pressure. The sample of the crude residue was purified by flash column chromatography (silica gel: diam. 2 cm, ht. 11.5 cm; eluent: 2.6% methanol, 0.3 % ammonium hydroxide in chloroform) to afford (–)-trigonoliimine B (**2**, 15.9 mg, 94.3%) as a pale yellow solid. Structural assignment of (–)-**2** utilized additional information from gCOSY, HSQC and HMBC.

^{1}H NMR (500.4 MHz, $CDCl_3/CD_3OD$ (3:1), 21 °C): δ 7.33 (s, 1H, C_{25}**H**), 7.28 (dd, *J* = 8.7, 0.4 Hz, 1H, C_4**H**), 7.18 (td, *J* = 7.6, 1.4 Hz, 1H, C_{16}**H**), 7.10 (dd, *J* = 7.9, 1.2 Hz, 1H, C_{15}**H**), 6.99 (td, *J* = 7.6, 1.3 Hz, 1H, C_{17}**H**), 6.80 (d, *J* = 2.1 Hz, 1H, C_7**H**), 6.68 (dd, *J* = 8.7, 2.2 Hz, 1H, C_5**H**), 6.66 (dd, *J* = 7.8, 1.4 Hz, 1H, C_{18}**H**), 4.11 (dd, *J* = 16.0, 8.1 Hz, 1H, C_{22}**H**), 3.92–3.81 (m, 2H, C_{11}**H₂**), 3.78 (s, 3H, O**Me**), 3.63 (ddd, *J* = 16.0, 10.2, 5.9 Hz, 1H, C_{22}**H**), 3.12 (td, *J* = 17.3, 2.7 Hz, 1H, C_{10}**H**), 3.09–3.02 (m, 1H, C_{10}**H**), 2.28 (dd, *J* = 12.2, 5.7 Hz, 1H, C_{21}**H**), 2.15 (ddd, *J* = 12.2, 10.3, 8.3 Hz, 1H, C_{21}**H**).

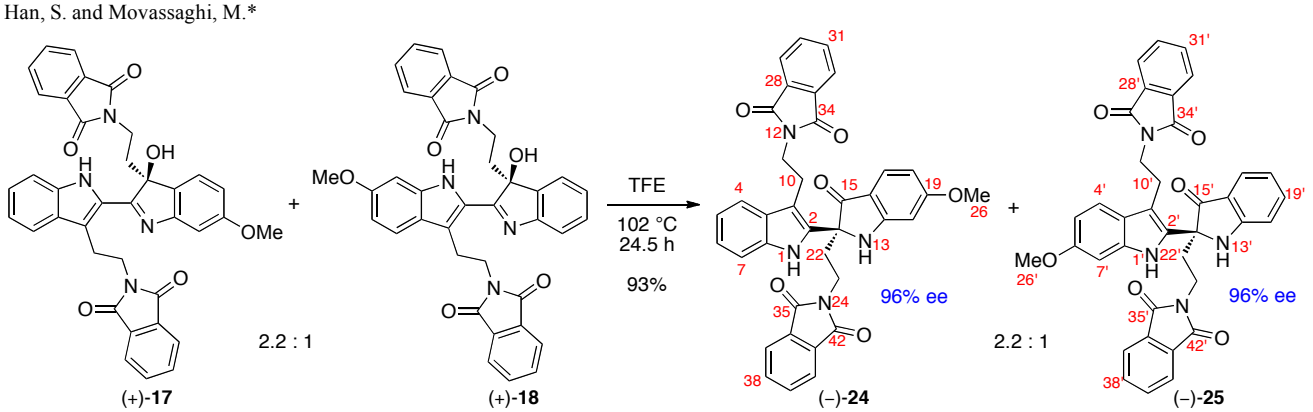
^{13}C NMR (125.8 MHz, $CDCl_3/CD_3OD$ (3:1), 21 °C): δ 167.7 (**C**$_{24}$), 158.8 (**C**$_6$), 150.2 (**C**$_{25}$), 140.7 (**C**$_{14}$), 138.6 (**C**$_8$), 129.5 (**C**$_{16}$), 126.3 (**C**$_2$), 126.0 (**C**$_{17}$), 124.7 (**C**$_{15}$), 122.9 (**C**$_{18}$), 122.5 (**C**$_9$), 122.1 (**C**$_{19}$), 120.5 (**C**$_4$), 118.9 (**C**$_3$), 111.2 (**C**$_5$), 94.5 (**C**$_7$), 77.6 (**C**$_{20}$), 56.4 (**C**$_{22}$), 55.8 (**C**$_{27}$), 48.7 (**C**$_{11}$), 41.0 (**C**$_{21}$), 30.2 (**C**$_{10}$).

FTIR (neat) cm^{-1}: 3406 (br-s), 1609 (s), 1590 (s), 1560 (m), 1478 (w), 1275 (w), 1164 (w), 754 (s).

HRMS (DART) (*m*/*z*): calc'd for $C_{22}H_{21}N_4O$, $[M+H]^+$: 357.1710, found: 357.1715.

$[\alpha]_D^{24}$: –352 (*c* 0.32, $CHCl_3$).

TLC (9% methanol, 1% ammonium hydroxide in chloroform), R*f*: 0.15 (CAM, UV).



(*S*)-2-(2-(2-(3-(2-(1,3-Dioxoisoindolin-2-yl)ethyl)-1*H*-indol-2-yl)-6-methoxy-3-oxoindolin-2-yl)ethyl)isoindoline-1,3-dione (24) and (*S*)-2-(2-(2-(2-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-3-oxoindolin-2-yl)-6-methoxy-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (25):

Trifluoroethanol (TFE, 15 mL) was added via syringe to a pressure vessel charged with hydroxyindolenines (+)-**17** and (+)-**18** (2.2:1, **17**:**18**, 150 mg, 0.239 mmol, 1 equiv). Tightly sealed reaction vessel was heated to 102 °C. After 24.5 h, the homogeneous orange reaction mixture was allowed to cool to 23 °C and was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel: diam. 2.5 cm, ht. 12 cm; eluent: 3.3% acetone in dichloromethane) to afford indoxyls (–)-**24** and (–)-**25** as a yellow solid mixture (2.2:1, **24**:**25**, 140 mg, 93.3%). Structural assignment of (–)-**24** and (–)-**25** utilized additional information from gCOSY, HSQC and HMBC.

The indoxyls (–)-**24** and (–)-**25** could be separated at this stage by preparative HPLC [Waters X-Bridge preparative HPLC column, C18, 5 μm, 19 × 250 mm; 20.0 mL/min; 40% water in acetonitrile; t_R(**25**) = 8.5 min, t_R(**24**) = 9.5 min], but a more practical separation was possible after the next step. Indoxyl (–)-**24** was found to be 96% ee by chiral HPLC analysis [Chiralpak IC 0.7 mL/min; 45% hexanes in isopropanol; t_R(major) = 24 min min, t_R(minor) = 55 min]. Indoxyl (–)-**25** was found to be 96% ee by chiral HPLC analysis [Chiralpak IC 0.7 mL/min; 45% hexanes in isopropanol; t_R(major) = 29.5 min min, t_R(minor) = 35.5 min].

(*S*)-2-(2-(2-(3-(2-(1,3-Dioxoisoindolin-2-yl)ethyl)-1*H*-indol-2-yl)-6-methoxy-3-oxoindolin-2-yl)ethyl)isoindoline-1,3-dione (24)

^{1}H NMR (500.4 MHz, $CDCl_3$, 21 °C): δ 9.10 (s, 1H, N_1**H**), 7.87 (dd, *J* = 5.4, 3.0 Hz, 2H, C_{37}**H**, C_{40}**H**), 7.73 (dd, *J* = 5.4, 3.0 Hz, 2H, C_{38}**H**, C_{39}**H**), 7.61 (dd, *J* = 5.5, 3.0 Hz, 2H, C_{29}**H**, C_{32}**H**), 7.52 (dd, *J* = 5.5, 3.0 Hz, 2H, C_{30}**H**, C_{31}**H**), 7.49 (d, *J* = 7.9 Hz, 1H, C_4**H**), 7.42 (d, *J* = 8.7 Hz, 1H, C_{17}**H**), 7.22 (d, *J* = 8.1 Hz, 1H, C_7**H**), 7.05 (app-t, *J* = 8.1 Hz, 1H, C_6**H**), 6.97 (app-t, *J* = 7.9 Hz, 1H, C_5**H**), 6.78 (s, 1H, N_{13}**H**), 6.64 (d, *J* = 2.1 Hz, 1H, C_{20}**H**), 6.34 (dd, *J* = 8.7, 2.1 Hz, 1H, C_{18}**H**), 3.91–3.73 (m, 4H, C_{11}**H$_2$**, C_{23}**H$_2$**), 3.87 (s, 3H, O**Me**), 3.11 (t, *J* = 8.7 Hz, 2H, C_{10}**H$_2$**), 2.70–2.64 (m, 1H, C_{22}**H**), 2.41–2.36 (m, 1H, C_{22}**H**).

^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C): δ 198.2 (**C**$_{15}$), 168.8 (**C**$_{35}$, **C**$_{42}$), 168.7 (**C**$_{19}$), 168.3 (**C**$_{27}$, **C**$_{34}$), 163.4 (**C**$_{21}$), 135.5 (**C**$_8$), 134.3 (**C**$_{38}$, **C**$_{39}$), 134.0 (**C**$_{30}$, **C**$_{31}$), 132.4 (**C**$_{36}$, **C**$_{41}$), 131.7 (**C**$_{28}$, **C**$_{33}$), 131.1 (**C**$_2$), 128.6 (**C**$_9$), 126.8 (**C**$_{17}$), 123.5 (**C**$_{37}$, **C**$_{40}$), 123.2 (**C**$_{29}$,

C$_{32}$), 122.5 (**C**$_6$), 119.8 (**C**$_5$), 118.1 (**C**$_4$), 111.9 (**C**$_{16}$), 111.2 (**C**$_7$), 109.9 (**C**$_{18}$), 108.7 (**C**$_3$), 94.8 (**C**$_{20}$), 68.2 (**C**$_{14}$), 55.9 (**C**$_{26}$), 39.0 (**C**$_{11}$), 37.0 (**C**$_{22}$), 33.7 (**C**$_{23}$), 24.4 (**C**$_{10}$).

FTIR (neat) cm^{-1}: 1768 (w), 1701 (s), 1609 (s), 1457 (w), 1394 (m), 1286 (w), 716 (s).

HRMS (DART) (*m*/*z*): calc'd for $C_{37}H_{27}N_4O_6$, $[M–H]^-$: 623.1936, found: 623.1936.

$[\alpha]_D^{24}$: –27.7 (*c* 0.26, $CHCl_3$).

TLC (5% acetone in dichloromethane), R*f*: 0.34 (CAM, UV).

(*S*)-2-(2-(2-(2-(2-(1,3-Dioxoisoindolin-2-yl)ethyl)-3-oxoindolin-2-yl)-6-methoxy-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (25)

^{1}H NMR (500.4 MHz, $CDCl_3$, 21 °C): δ 8.89 (s, 1H, $N_{1'}$**H**), 7.87 (dd, *J* = 5.4, 3.0 Hz, 2H, $C_{37'}$**H**, $C_{40'}$**H**), 7.72 (dd, *J* = 5.4, 3.0 Hz, 2H, $C_{38'}$**H**, $C_{39'}$**H**), 7.60 (dd, *J* = 5.5, 2.9 Hz, 2H, $C_{29'}$**H**, $C_{32'}$**H**), 7.52 (dd, *J* = 5.5, 3.2 Hz, 2H, $C_{30'}$**H**, $C_{31'}$**H**), 7.52 (d, *J* = 9.1 Hz, 1H, $C_{17'}$**H**), 7.48 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H, $C_{19'}$**H**), 7.32 (d, *J* = 8.6 Hz, 1H, $C_{4'}$**H**), 7.20 (d, *J* = 8.3 Hz, 1H, $C_{20'}$**H**), 6.76 (app-t, *J* = 7.8 Hz, 1H, $C_{18'}$**H**), 6.70 (d, *J* = 2.0 Hz, 1H, $C_{7'}$**H**), 6.70 (s, 1H, $N_{13'}$**H**), 6.61 (dd, *J* = 8.6, 2.3 Hz, 1H, $C_{5'}$**H**), 3.89–3.71 (m, 4H, $C_{11'}$**H$_2$**, $C_{23'}$**H$_2$**), 3.78 (s, 3H, O**Me**), 3.11–3.03 (m, 2H, $C_{10'}$**H$_2$**), 2.71–2.66 (m, 1H, $C_{22'}$**H**), 2.37–2.32 (m, 1H, $C_{22'}$**H**).

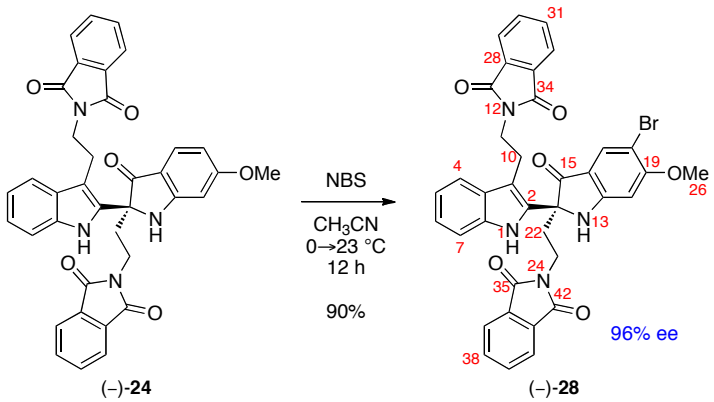
^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C): δ 200.9 (**C**$_{15'}$), 168.7 (**C**$_{35'}$, **C**$_{42'}$), 168.3 (**C**$_{27'}$, **C**$_{34'}$), 161.0 (**C**$_{21'}$), 156.9 (**C**$_{6'}$), 138.4 (**C**$_{19'}$), 136.3 (**C**$_{8'}$), 134.2 (**C**$_{38'}$, **C**$_{39'}$), 133.9 (**C**$_{30'}$, **C**$_{31'}$), 132.4 (**C**$_{36'}$, **C**$_{41'}$), 131.7 (**C**$_{28'}$, **C**$_{33'}$), 128.8 (**C**$_{2'}$), 125.4 (**C**$_{17'}$), 123.5 (**C**$_{37'}$, **C**$_{40'}$), 123.1 (**C**$_{29'}$, **C**$_{32'}$), 123.0 (**C**$_{9'}$), 119.2 (**C**$_{18'}$), 118.9 (**C**$_{4'}$), 118.5 (**C**$_{16'}$), 113.1 (**C**$_{20'}$), 110.0 (**C**$_{5'}$), 109.2 (**C**$_{3'}$), 94.5 (**C**$_{7'}$), 67.8 (**C**$_{14'}$), 55.8 (**C**$_{26'}$), 39.0 (**C**$_{11'}$), 36.7 (**C**$_{22'}$), 33.8 (**C**$_{23'}$), 24.3 (**C**$_{10'}$).

FTIR (neat) cm^{-1}: 1769 (m), 1705 (s) 1615 (m), 1467 (w), 1396 (m), 716 (m).

HRMS (DART) (*m*/*z*): calc'd for $C_{37}H_{27}N_4O_6$, $[M–H]^-$: 623.1936, found: 623.1938.

$[\alpha]_D^{24}$: –23.2 (*c* 0.20, $CHCl_3$).

TLC (5% acetone in dichloromethane), R*f*: 0.34 (CAM, UV).



(*S*)-2-(2-(2-(5-Bromo-2-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-6-methoxy-3-oxoindolin-2-yl)-1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione (28):

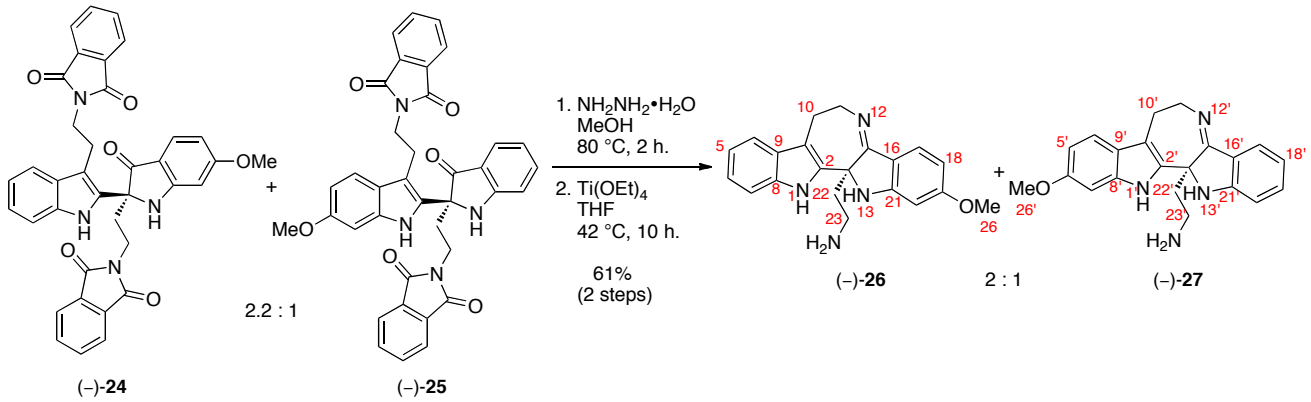
N-Bromosuccinimide (NBS, 2.4 mg, 0.013 mmol, 1.2 equiv) was added as a solid in one portion to a solution of indoxyl (–)-**24** (7.2 mg, 0.011 mmol, 1 equiv) in anhydrous acetonitrile (1.1 mL) at 0 °C and the reaction mixture was allowed to warm to 23°C. After 12 h, saturated aqueous sodium thiosulfate solution and saturated aqueous sodium bicarbonate solution (1:1, 3 mL) was added to the reaction mixture, the solution was diluted with dichloromethane (3 mL), and the layers were separated. The aqueous layer was extracted with dichloromethane (2 × 3 mL), and the combined organic layers were dried over anhydrous sodium sulfate and were concentrated under reduced pressure. The sample of the crude residue was purified by flash column chromatography (silica gel: diam. 1.5 cm, ht. 8 cm; eluent: 2.5% acetone in dichloromethane) to afford brominated indoxyl (–)-**28** (7.3 mg, 90%) as a yellow solid.

Brominated indoxyl (–)-**28** was found to be 96% ee by chiral HPLC analysis [Chiralpak IC 0.7 mL/min; 45% hexanes in isopropanol; t_R(major) = 20.7 min, t_R(minor) = 30 min]. Crystal of brominated indoxyl (–)-**28** was obtained by slow evaporation of a hexanes–dichloromethane (1:1, 0.5 mL) solution of (–)-**28** (7.2 mg).

^{1}H NMR (500.4 MHz, $CDCl_3$, 21 °C): δ 8.95 (s, 1H, N_1**H**), 7.87 (dd, *J* = 5.5, 3.0 Hz, 2H, C_{37}**H**, C_{40}**H**), 7.75 (dd, *J* = 5.4, 3.0 Hz, 2H, C_{38}**H**, C_{39}**H**), 7.61 (s, 1H, C_{17}**H**), 7.60 (dd, *J* = 5.6, 2.9 Hz, 2H, C_{29}**H**, C_{32}**H**), 7.52 (dd, *J* = 5.4, 3.1 Hz, 2H, C_{30}**H**, C_{31}**H**), 7.47 (d, *J* = 8.0 Hz, 1H, C_4**H**), 7.21 (app-dt, *J* = 8.1, 0.8 Hz, 1H, C_7**H**), 7.05 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H, C_6**H**), 6.97 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H, C_5**H**), 6.83 (s, 1H, N_{13}**H**), 6.75 (s, 1H, C_{20}**H**), 4.00 (s, 3H, O**Me**), 3.90–3.83 (m, 3H, C_{11}**H**, C_{23}**H$_2$**), 3.77–3.70 (ddd, *J* = 13.8, 10.4, 7.2 Hz, 1H, C_{11}**H**), 3.07 (ddd, *J* = 10.8, 6.4, 4.1 Hz, 2H, C_{10}**H$_2$**), 2.67 (dt, *J* = 14.6, 7.3 Hz, C_{22}**H**), 2.38 (dt, *J* = 14.5, 6.4 Hz, C_{22}**H**).

^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C): δ 197.1 (**C**$_{15}$), 168.8 (**C**$_{35}$, **C**$_{42}$), 168.3 (**C**$_{27}$, **C**$_{34}$), 163.9 (**C**$_{19}$), 162.1 (**C**$_{21}$), 135.6 (**C**$_8$), 134.4 (**C**$_{38}$, **C**$_{39}$), 134.0 (**C**$_{30}$, **C**$_{31}$), 132.4 (**C**$_{36}$, **C**$_{41}$), 131.6 (**C**$_{28}$, **C**$_{33}$), 130.4 (**C**$_2$), 129.5 (**C**$_{17}$), 128.5 (**C**$_9$), 123.5 (**C**$_{37}$, **C**$_{40}$), 123.2 (**C**$_{29}$, **C**$_{32}$), 122.7 (**C**$_6$), 119.9 (**C**$_5$), 118.2 (**C**$_4$), 112.4 (**C**$_{16}$), 111.3 (**C**$_7$), 108.9 (**C**$_3$), 103.8 (**C**$_{18}$), 94.9 (**C**$_{20}$), 68.5

	(**C**$_{14}$), 56.9 (**C**$_{26}$), 38.9 (**C**$_{11}$), 36.9 (**C**$_{22}$), 33.6 (**C**$_{23}$), 24.4 (**C**$_{10}$).
FTIR (neat) cm^{-1}:	3378 (br-m), 1770 (m), 1708 (s), 1609 (s), 1457 (m), 1397 (s), 1211 (m), 1034 (w), 717 (s).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{37}H_{28}BrN_4O_6$, $[M+H]^+$: 703.1187, found: 703.1187.
$[\alpha]_D^{24}$:	–56.2 (*c* 0.15, $CHCl_3$).
TLC (5% acetone in dichloromethane), R*f*:	0.5 (CAM, UV).



(–)-**24** (–)-**25**

(*S*)-2-(2-Methoxy-7,12,12b,13-tetrahydro-6*H*-azepino[3,2-*b*:4,5-*b*′]diindol-12b-yl)ethanamine (26) and (*S*)-2-(10-methoxy-7,12,12b,13-tetrahydro-6*H*-azepino[3,2-*b*:4,5-*b*′]diindol-12b-yl)ethanamine (27):

Hydrazine monohydrate (81.0 μL, 1.64 mmol, 10.0 equiv) was added via syringe to a solution of indoxyls (–)-**24** and (–)-**25** (2.2:1, **24**:**25**, 103 mg, 0.164 mmol, 1 equiv) in methanol (16 mL) under an atmosphere of argon at 23 °C, and the reaction flask was equipped with a reflux condenser, and the reaction set-up was sealed under an atmosphere of argon and heated to 80 °C. After 2 h, the pale yellow homogeneous reaction mixture was allowed to cool to 23 °C and the volatiles were removed under reduced pressure to result in a pale yellow solid. A solution of titanium ethoxide (153 μL, 0.656 mmol, 4.00 equiv) in anhydrous tetrahydrofuran (16 mL) was added via syringe to the yellow solid under an atmosphere of argon, and the resulting mixture was warmed to 42 °C. After 10 h, the reaction mixture was concentrated under reduced pressure, the crude residue adsorbed onto silica gel (6 g) was dry loaded and purified by flash column chromatography (silica gel: diam. 3 cm, ht. 9 cm; eluent: 6% methanol, 0.6% ammonium hydroxide in chloroform) to afford imines (–)-**26** and (–)-**27** (2:1, **26**:**27**, 34.6 mg, 60.9%, 2 steps) as a yellow solid mixture. Structural assignment of (–)-**26** utilized additional information from gCOSY, HSQC and HMBC.

(*S*)-2-(2-Methoxy-7,12,12b,13-tetrahydro-6*H*-azepino[3,2-*b*:4,5-*b*′]diindol-12b-yl)ethanamine (26)

^{1}H NMR (500.4 MHz, CD_3OD, 21 °C): δ 7.46 (d, J = 8.6 Hz, 1H, C_{17}**H**), 7.43 (dt, J = 7.8, 1.0 Hz, 1H, C_4**H**), 7.32 (dt, J = 8.1, 0.9 Hz, 1H, C_7**H**), 7.09 (ddd, J = 8.2, 7.0, 1. Hz, 1H, C_6**H**), 6.99 (ddd, J = 7.9, 7.0, 1.0 Hz, 1H, C_5**H**), 6.34 (dd, J = 8.5, 2.3 Hz, 1H, C_{18}**H**), 6.32 (d, J = 2.1 Hz, 1H, C_{20}**H**), 4.31 (br-s, 1H, C_{11}**H**), 3.93 (br-s, 1H, C_{11}**H**), 3.80 (s, 3H, O**Me**), 3.12 (app-d, J = 16.4 Hz, 1H, C_{10}**H**), 2.95 (app-dt, J = 14.9, 3.4 Hz, 1H, C_{10}**H**), 2.81–2.69 (m, 2H, C_{23}**H**$_2$), 2.65–2.59 (m, 1H, C_{22}**H**), 2.40–2.34 (m, 1H, C_{22}**H**).

^{1}H NMR (500.4 MHz, CD_3OD, 21 °C)[5]: δ 7.59 (app-d, J = 9.4 Hz, 1H, C_{17}**H**), 7.47 (dt, J = 7.9, 0.9 Hz, 1H, C_4**H**), 7.41 (dt, J = 8.2, 0.8 Hz, 1H, C_7**H**), 7.16 (ddd, J = 8.2, 7.1, 1.1 Hz, 1H, C_6**H**), 7.04 (ddd, J = 8.0, 7.1, 0.9 Hz, 1H, C_5**H**), 6.46 (app-s, 1H, C_{20}**H**), 6.45 (dd, J = 8.7, 2.2 Hz, 1H, C_{18}**H**), 4.46 (td, J = 13.5, 2.9

[5] 2 equivalent of acetic acid-d_4 was added, which resulted in sharpening of peaks: See attached copies of spectra.

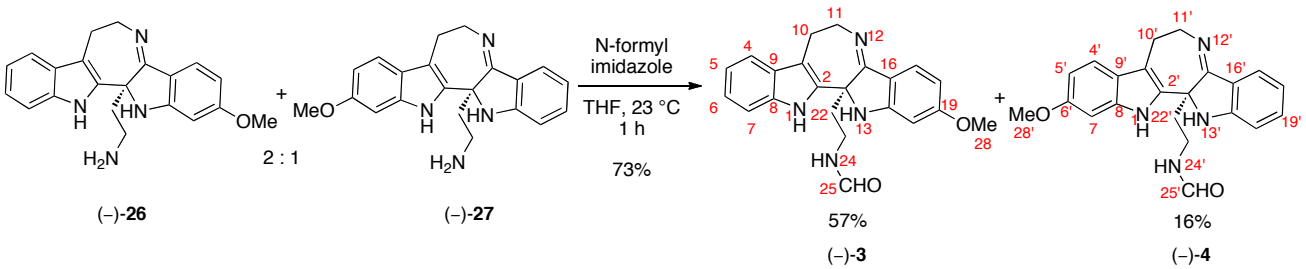
	Hz 1H, C_{11}**H**), 4.02 (dt, *J* = 13.7, 3.6 Hz 1H, C_{11}**H**), 3.88 (s, 3H, O**Me**), 3.24 (dt, *J* = 16.8, 3.0 Hz, 1H, C_{10}**H**), 3.15–3.11 (m, 1H, C_{10}**H**), 3.09–3.03 (m, 1H, C_{23}**H**), 2.93–2.88 (m, 1H, C_{23}**H**), 2.79–2.75 (m, 2H, C_{22}**H**).
^{13}C NMR (125.8 MHz, CD_3OD, 21 °C)[5]:	δ 176.9 (**C**$_{15}$), 170.8 (**C**$_{19}$), 162.7 (**C**$_{21}$), 137.4 (**C**$_{8}$), 129.5 (**C**$_{9}$), 128.1 (**C**$_{2}$), 126.8 (**C**$_{17}$), 123.9 (**C**$_{6}$), 120.6 (**C**$_{5}$), 119.1 (**C**$_{4}$), 112.5 (**C**$_{16}$), 112.3 (**C**$_{18}$), 112.3 (**C**$_{7}$), 111.3 (**C**$_{3}$), 94.7 (**C**$_{20}$), 69.8 (**C**$_{14}$), 56.7 (**C**$_{26}$), 46.0 (**C**$_{11}$), 39.1 (**C**$_{22}$), 36.9 (**C**$_{23}$), 25.1 (**C**$_{10}$).
FTIR (neat) cm^{-1}:	3180 (br-m), 2927 (m), 1612 (s), 1460 (m), 1303 (m), 1206 (m), 1165 (m), 741 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{21}H_{23}N_4O$, $[M+H]^+$: 347.1866,
	found: 347.1856.
$[\alpha]_D^{24}$:	–179 (*c* 0.21, CD_3OD).

TLC (18% methanol, 2% ammonium hydroxide in chloroform), R*f*: 0.36 (CAM, UV).

(*S*)-2-(10-Methoxy-7,12,12b,13-tetrahydro-6*H*-azepino[3,2-*b*:4,5-*b*′]diindol-12b-yl)ethanamine (27)

^{1}H NMR (500.4 MHz, CD_3OD, 21 °C):	δ 7.61 (dd, *J* = 7.3, 0.6 Hz, 1H, $C_{17'}$**H**), 7.36 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H, $C_{19'}$**H**), 7.32 (d, *J* = 8.6 Hz, 1H, $C_{4'}$**H**), 6.90 (d, *J* = 2.1 Hz, 1H, $C_{7'}$**H**), 6.87 (d, *J* = 8.2 Hz, 1H, $C_{20'}$**H**), 6.79 (app-td, *J* = 8.0, 0.8 Hz, 1H, $C_{18'}$**H**), 6.69 (dd, *J* = 8.7, 2.2 Hz, 1H, $C_{5'}$**H**), 4.38 (app-td, *J* = 13.1, 2.6 Hz, 1H, $C_{11'}$**H**), 4.07 (app-dt, *J* = 12.4, 3.5 Hz, 1H, $C_{11'}$**H**), 3.81 (s, 3H, O**Me**), 3.14 (app-dt, *J* = 16.8, 3.3 Hz, 1H, $C_{10'}$**H**), 3.07–2.93 (m, 3H, $C_{10'}$**H,** $C_{23'}$**H**$_2$), 2.76 (ddd, *J* = 13.7, 12.1, 5.2 Hz, 1H, $C_{22'}$**H**), 2.63 (ddd, *J* = 13.5, 12.3, 4.5 Hz, 1H, $C_{22'}$**H**).
^{13}C NMR (100.6 MHz, CD_3OD, 21 °C)[5]:	δ 177.4, 158.4, 157.6, 138.1, 136.4, 129.1, 124.5, 124.1, 123.5, 120.4, 119.7, 112.7, 111.2, 110.4, 95.4, 67.9, 56.1, 48.0, 39.1, 37.3, 24.4.
FTIR (neat) cm^{-1}:	3271 (br-m), 2924 (m), 1647 (w), 1612 (s), 1465 (s), 1318 (m), 1252 (w), 1159 (m), 1030 (w), 750 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{21}H_{23}N_4O$, $[M+H]^+$: 347.1866,
	found: 347.1876.
$[\alpha]_D^{24}$:	–194 (*c* 0.07, $CHCl_3$).

TLC (18% methanol, 2% ammonium hydroxide in chloroform), R*f*: 0.42 (CAM, UV).



(–)-Trigonoliimine C (3) and (–)-Isotrigonoliimine C (4):

Freshly prepared *N*-formyl imidazole[6] solution (0.0574 M solution in tetrahydrofuran, 1.80 mL, 0.105 mmol, 1.05 equiv) was added dropwise via syringe to a flask containing a mixture of amines (–)-**26** and (–)-**27** (2:1, **26**:**27**, 34.6 mg, 99.9 μmol, 1 equiv) at 23 °C and placed under an argon atmosphere. After 40 min, additional *N*-formyl imidazole[6] solution (0.0574 M solution in tetrahydrofuran, 200 μL, 11.7 μmol, 0.117 equiv) was slowly added to the reaction mixture. After 20 min, saturated aqueous sodium bicarbonate solution (14 mL) was added to the reaction mixture and the resulting mixture was diluted with dichloromethane (14 mL), and the layers were separated. The aqueous layer was extracted with dichloromethane (2 × 14 mL), and the combined organic layers were dried over anhydrous sodium sulfate, and were concentrated under reduced pressure. The sample of the crude residue was purified by flash column chromatography (silica gel: diam. 2.5 cm, ht. 9.5 cm; eluent: 2.2% methanol, 0.2 % ammonium hydroxide in chloroform) to afford (–)-trigonoliimine C (**3**, 21.3 mg, 57.0%) and (–)-isotrigonoliimine C (**4**, 5.8 mg, 15.5%) as yellow solids. Crystal of (–)-trigonoliimine C (**3**) was obtained by slow evaporation of a methanol (0.5 mL) solution of (–)-**3** (5.0 mg). Structural assignment of (–)-**4** utilized additional information from gCOSY, HSQC and HMBC.

(–)-Trigonoliimine C (3)

^{1}H NMR (500.4 MHz, DMSO-d_6, 21 °C): δ 10.79 (s, 1H, N_1**H**), 8.00 (app-s, 1H, N_{24}**H**), 7.93 (d, J = 1.7 Hz, 1H, C_{25}**H**), 7.40 (d, J = 7.8 Hz, 1H, C_4**H**), 7.34 (d, J = 7.8 Hz, 1H, C_7**H**), 7.31 (d, J = 8.2 Hz, 1H, C_{17}**H**), 7.07 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H, C_6**H**), 6.97 (br-s, 1H, N_{13}**H**), 6.96 (app-t, J = 7.9 Hz, 1H, C_5**H**), 6.24 (d, J = 2.2 Hz, 1H, C_{20}**H**), 6.23 (dd, J = 10.4, 2.2 Hz, 1H, C_{18}**H**), 4.22 (app-dt, J = 13.8, 2.3 Hz, 1H, C_{11}**H**), 3.99 (app-dt, J = 11.8, 3.4 Hz, 1H, C_{11}**H**), 3.75 (s, 3H, O**Me**), 3.17–3.08 (m, 2H, C_{23}**H**$_2$), 3.05 (app-dt, J = 17.1, 3.2 Hz, 1H, C_{10}**H**), 2.80 (ddd, J = 16.7, 13.7, 3.2 Hz, 1H, C_{10}**H**), 2.54–2.48 (m, 1H, C_{22}**H**), 2.33–2.27 (m, 1H, C_{22}**H**).

^{1}H NMR (500.4 MHz, CD_3OD, 21 °C): δ 7.96 (s, 1H, C_{25}**H**), 7.50 (app-d, J = 9.3 Hz, 1H, C_{17}**H**), 7.43 (dt, J = 7.9, 0.9 Hz, 1H, C_4**H**), 7.33 (dt, J = 8.1, 0.8 Hz, 1H, C_7**H**), 7.10 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H, C_6**H**), 7.00 (ddd, J = 7.9, 7.0, 0.9 Hz, 1H, C_5**H**), 6.36 (d, J = 2.4 Hz, 1H, C_{17}**H**), 6.36 (dd, J = 6.8, 2.2 Hz, 1H, C_{18}**H**),

[6] *N*-Formyl imidazole was prepared according to the following procedure: Staab, H. A.; Polenski, B. *Liebigs Ann. Chem.* **1962**, *655*, 95–102.

4.42 (app-td, J = 14.3, 2.7 Hz, 1H, C_{11}**H**), 4.01 (dt, J = 12.4, 3.5 Hz, 1H, C_{11}**H**), 3.82 (s, 3H, O**Me**), 3.30–3.28 (m, 2H, C_{23}**H**$_2$), 3.15 (dt, J = 16.7, 3.1 Hz, 1H, C_{10}**H**), 2.99 (ddd, J = 16.8, 13.5, 3.4 Hz, 1H, C_{10}**H**), 2.75 (ddd, J = 14.1, 10.2, 6.5 Hz, 1H, C_{22}**H**), 2.40 (ddd, J = 14.0, 8.9, 6.9 Hz, 1H, C_{22}**H**).

^{13}C NMR (125.8 MHz, DMSO-d_6, 21 °C): δ 170.0 (**C**$_{15}$), 164.2 (**C**$_{19}$), 161.0 (**C**$_{25}$), 156.6 (**C**$_{21}$), 134.8 (**C**$_8$), 131.9 (**C**$_2$), 127.9 (**C**$_9$), 123.4 (**C**$_{17}$), 121.3 (**C**$_6$), 118.4 (**C**$_5$), 117.7 (**C**$_4$), 116.5 (**C**$_{16}$), 110.8 (**C**$_7$), 108.7 (**C**$_3$), 105.3 (**C**$_{18}$), 93.8 (**C**$_{20}$), 66.3 (**C**$_{14}$), 55.2 (**C**$_{28}$), 46.6 (**C**$_{11}$), 39.5 (**C**$_{22}$), 33.6 (**C**$_{23}$), 23.3 (**C**$_{10}$).

^{13}C NMR (125.8 MHz, $CDCl_3$/CD_3OD (3:1), 21 °C): δ174.1 (**C**$_{15}$), 166.1 (**C**$_{19}$), 162.9 (**C**$_{25}$), 158.3 (**C**$_{21}$), 135.7 (**C**$_8$), 130.8 (**C**$_2$), 128.7 (**C**$_9$), 124.9 (**C**$_{17}$), 122.5 (**C**$_6$), 119.5 (**C**$_5$), 118.3 (**C**$_4$), 116.2 (**C**$_{16}$), 111.2 (**C**$_7$), 110.2 (**C**$_3$), 108.1 (**C**$_{18}$), 95.1 (**C**$_{20}$), 67.6 (**C**$_{14}$), 55.8 (**C**$_{28}$), 47.2 (**C**$_{11}$), 39.8 (**C**$_{22}$), 34.6 (**C**$_{23}$), 24.0 (**C**$_{10}$).

^{13}C NMR (125.8 MHz, CD_3OD, 21 °C): δ 175.6 (**C**$_{15}$), 167.3 (**C**$_{19}$), 164.0 (**C**$_{25}$), 159.6 (**C**$_{21}$), 137.1 (**C**$_8$), 132.3 (**C**$_2$), 130.0 (**C**$_9$), 125.6 (**C**$_{17}$), 123.1 (**C**$_6$), 120.1 (**C**$_5$), 119.0 (**C**$_4$), 117.4 (**C**$_{16}$), 111.9 (**C**$_7$), 110.6 (**C**$_3$), 108.7 (**C**$_{18}$), 95.9 (**C**$_{20}$), 68.7 (**C**$_{14}$), 56.1 (**C**$_{28}$), 48.1 (**C**$_{11}$), 40.8 (**C**$_{22}$), 35.3 (**C**$_{23}$), 24.7 (**C**$_{10}$).

FTIR (neat) cm^{-1}: 3305 (br-w), 1732 (w), 1640 (s), 1610 (s), 1458 (m), 1376 (m), 1329 (m), 1300 (m), 1223 (w), 1029 (w), 735 (s).

HRMS (ESI) (m/z): calc'd for $C_{22}H_{23}N_4O_2$, $[M+H]^+$: 375.1816, found: 375.1818.

$[\alpha]_D^{24}$: –147 (c 0.12, $CHCl_3$).

TLC (18% methanol, 2% ammonium hydroxide in chloroform), Rf: 0.52 (CAM, UV).

(–)-Isotrigonoliimine C (4):

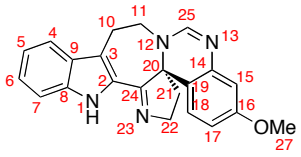
^{1}H NMR (500.4 MHz, CD_3OD, 21 °C): δ 7.95 (s, 1H, $C_{25'}$**H**), 7.59 (d, J = 7.8 Hz, 1H, $C_{17'}$**H**), 7.31 (app-dt, J = 9.5, 1.2 Hz, 1H, $C_{19'}$**H**), 7.30 (d, J = 8.7 Hz, 1H, $C_{4'}$**H**), 6.87 (d, J = 2.1 Hz, 1H, $C_{7'}$**H**), 6.84 (d, J = 8.1 Hz, 1H, $C_{20'}$**H**), 6.77 (app-t, J = 7.1 Hz, 1H, $C_{18'}$**H**), 6.67 (dd, J = 8.6, 2. 2 Hz, 1H, $C_{5'}$**H**), 4.43 (app-td, J = 14.7, 2.8 Hz, 1H, $C_{11'}$**H**), 4.06 (app-dt, J = 12.1, 3.5 Hz, 1H, $C_{11'}$**H**), 3.81 (s, 3H, O**Me**), 3.29–3.22 (m, 2H, $C_{23'}$**H**$_2$), 3.11 (app-dt, J = 16.5, 3.1 Hz, 1H, $C_{10'}$**H**), 2.96 (ddd, J = 16.8, 13.7, 3.4 Hz, 1H, $C_{10'}$**H**), 2.71 (ddd, J = 14.0, 10.5, 5.7 Hz, 1H, $C_{22'}$**H**), 2.39 (ddd, J = 14.0, 10.1, 5.8 Hz, 1H, $C_{22'}$**H**).

^{13}C NMR (125.8 MHz, CD_3OD, 21 °C): δ 176.6 (**C**$_{15'}$), 164.0 (**C**$_{25'}$), 158.1 (**C**$_{6'}$), 157.6 (**C**$_{21'}$), 137.8 (**C**$_{8'}$), 135.5 (**C**$_{19'}$), 130.8 (**C**$_{2'}$), 124.8 (**C**$_{16'}$), 124.3

	(**C**$_{9'}$), 124.2 (**C**$_{17'}$), 120.2 (**C**$_{18'}$), 119.5 (**C**$_{4'}$), 112.6 (**C**$_{20'}$), 110.6 (**C**$_{3'}$), 110.1 (**C**$_{5'}$), 95.4 (**C**$_{7'}$), 68.0 (**C**$_{14'}$), 56.1 (**C**$_{28'}$), 48.6 (**C**$_{11'}$), 40.7 (**C**$_{22'}$), 35.4 (**C**$_{23'}$), 24.4 (**C**$_{10'}$).
FTIR (neat) cm^{-1}:	3278 (br-m), 2923 (br-m), 2361 (w), 1647 (s), 1613 (s), 1467 (m), 1316 (m), 1156 (m), 1027 (w), 745 (m).
HRMS (DART) (*m*/*z*):	calc'd for $C_{22}H_{21}N_4O_2$, $[M–H]^-$: 373.1670, found: 373.1684.
$[\alpha]_D^{24}$:	–220 (*c* 0.10, CH_3OH).

TLC (18% methanol, 2% ammonium hydroxide in chloroform), R*f*: 0.50 (CAM, UV).

Table S1. Comparison of our ^{1}H NMR data for (–)-trigonoliimine A (1) with literature data:



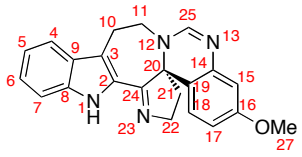
(–)-trigonoliimine A (**1**)

Assignment	**Hao's Report**[7] ^{1}H NMR, 500 MHz, DMSO-d_6	**This Work**[8] ^{1}H NMR, 500.4 MHz, DMSO-d_6, 21 °C
N1	11.50 (s, 1H)	11.5 (s, 1H)
C4	7.44 (d, J = 7.5 Hz, 1H)	7.45 (d, J = 7.9 Hz, 1H)
C5	6.99 (t, J = 7.5 Hz, 1H)	7.00 (app-t, J = 7.9 Hz, 1H)
C6	7.15 (t, J = 7.5 Hz, 1H)	7.16 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H)
C7	7.32 (d, J = 7.5 Hz, 1H)	7.34 (d, J = 8.2 Hz, 1H)
C10α	3.06 (m, 1H)	3.07 (d, J = 17.1 Hz, 1H)
C10β	2.95 (m, 1H)	2.96 (ddd, J = 16.9, 12.1, 4.3 Hz, 1H)
C11α	4.00 (br-d, J = 14.5 Hz, 1H)	4.01 (dt, J = 14.3, 3.3 Hz, 1H)
C11β	3.74 (t, J = 12.5 Hz, 1H)	3.74 (app-t, J = 12.1 Hz, 1H)
C15	6.55 (overlapped, 1H)	6.56 (overlapped, 1H)
C17	6.54 (overlapped, 1H)	6.56 (overlapped, 1H)
C18	6.53 (overlapped, 1H)	6.55 (overlapped, 1H)
C21α	2.05 (m, 1H)	2.06 (dd, J = 12.0, 5.8 Hz, 1H)
C21β	2.14 (m, 1H)	2.19–2.13 (m, 1H)
C22α	3.55 (m, 1H)	3.55 (ddd, J = 16.1, 9.9, 6.1 Hz, 1H)
C22β	4.10 (m, 1H)	4.11 (dd, J = 16.1, 8.1 Hz, 1H)
C25	7.48 (s, 1H)	7.47 (s, 1H)
C27	3.65 (s, 3H)	3.66 (s, 3H)

[7] The reference points for the residual protium and carbon resonances of the NMR solvent were not listed. Tan, C. J.; Di, Y. T.; Wang, Y. H.; Zhang, Y.; Si, Y. K.; Zhang, Q.; Gao, S.; Hu, X. J.; Fang, X.; Li, S. F.; Hao, X. J. *Org. Lett.* **2010**, *12*, 2370–2373.

[8] In this report, the NMR spectra are referenced from the residual protium resonance, DMSO-d_6: δ 2.50 (DMSO-d_5), and carbon resonance, DMSO-d_6: δ 39.51.

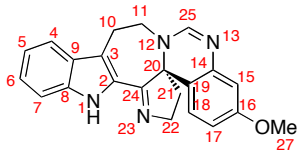
Table S2. Comparison of our ^{13}C NMR data for (–)-trigonoliimine A (1) with literature data:



(–)-trigonoliimine A (**1**)

Assignment	**Hao's Report**[7] ^{13}C NMR, 100 MHz, DMSO-d_6	**This Work**[8] ^{13}C NMR, 125.8 MHz, DMSO-d_6, 21 °C
C2	127.9	128.0
C3	115.6	115.6
C4	119.1	119.1
C5	119.1	119.2
C6	123.4	123.4
C7	111.7	111.6
C8	136.5	136.5
C9	127.1	127.1
C10	29.1	29.2
C11	46.6	46.6
C14	143.0	143.1
C15	109.2	109.3
C16	159.6	159.6
C17	110.3	110.2
C18	123.2	123.2
C19	115.0	115.0
C20	76.5	76.5
C21	40.6	40.6
C22	56.2	56.2
C24	166.4	166.5
C25	150.2	150.2
C27	55.1	55.0

Table S3. Comparison of our ^{13}C NMR data for (–)-trigonoliimine A (1) with literature data:

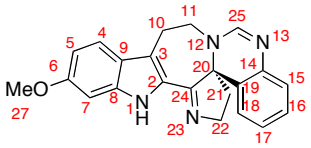


(–)-trigonoliimine A (**1**)

Assignment	**Hao's Report**[7] ^{13}C NMR, 100 MHz, $CDCl_3/CD_3OD$ (3:1)	**This Work**[9] ^{13}C NMR, 125.8 MHz, $CDCl_3/CD_3OD$ (3:1), 21 °C	**Chemical Shift Difference** Δδ δ (Hao's Report) - δ (This Report)
C2	126.5	127.2	–0.7
C3	117.4	118.1	–0.7
C4	119.0	119.6	–0.6
C5	119.6	120.2	-0.6
C6	124.3	125.0	–0.7
C7	111.4	112.1	–0.7
C8	136.8	137.4	–0.6
C9	127.2	127.9	–0.7
C10	29.4	30.1	–0.7
C11	47.9	48.5	–0.6
C14	141.0	142.0	–1.0
C15	108.6	109.4	–0.8
C16	160.1	160.7	–0.6
C17	111.4	112.0	–0.6
C18	123.2	123.9	–0.7
C19	113.7	114.5	–0.8
C20	77.2	77.5	–0.3
C21	40.4	41.1	–0.7
C22	56.0	56.6	–0.6
C24	167.4	168.2	–0.8
C25	149.9	150.5	–0.6
C27	55.0	55.6	–0.6

[9] In this report, the NMR spectra are referenced from the residual protium resonance, CD_3OD: δ 3.31 (CHD_2OD), and carbon resonance, CD_3OD: δ 49.15.

Table S4. Comparison of our ^{13}C NMR data for (–)-trigonoliimine B (2) with literature data:



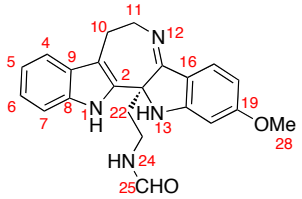
(–)-trigonoliimine B (**2**)

Assignment	**Hao's Report**[10] ^{13}C NMR, 100 MHz, $CDCl_3/CD_3OD$ (3:1)	**This Work**[9] ^{13}C NMR, 125.8 MHz, $CDCl_3/CD_3OD$ (3:1), 21 °C	**Chemical Shift Difference** Δδ δ (Hao's Report) - δ (This Report)
C2	125.1	126.3	–1.2
C3	117.7	118.9	–1.2
C4	119.3	120.5	–1.2
C5	110.0	111.2	–1.2
C6	157.6	158.8	–1.2
C7	93.4	94.5	–1.1
C8	137.4	138.6	–1.2
C9[11]	121.0	122.5	–1.5
C10	29.0	30.2	–1.2
C11	47.5	48.7	–1.2
C14	139.6	140.7	–1.1
C15	123.4	124.7	–1.3
C16	128.2	129.5	–1.3
C17	124.8	126.0	–1.2
C18	121.8	122.9	–1.1
C19[11]	121.3	122.1	–0.8
C20	76.5	77.6	–1.1
C21	39.8	41.0	–1.2
C22	55.2	56.4	–1.2
C24	166.6	167.7	–1.1
C25	149.0	150.2	–1.2
C27	54.6	55.8	–1.2

[10] The provided copy of the NMR spectra in the Supporting Information of the report indicates referencing of the residual carbon resonance of $CDCl_3$ at δ 76.51. Tan, C. J.; Di, Y. T.; Wang, Y. H.; Zhang, Y.; Si, Y. K.; Zhang, Q.; Gao, S.; Hu, X. J.; Fang, X.; Li, S. F.; Hao, X. J. *Org. Lett.* **2010**, *12*, 2370–2373.

[11] Our assignment of these resonances is supported by key HMBC signals (^{1}H, ^{13}C) in ppm: (2.28 (C_{21}**H**), 122.1 (**C**$_{19}$)), (6.68 (C_5**H**), 122.5 (**C**$_9$)), (6.80 (C_7**H**),122.5 (**C**$_9$)).

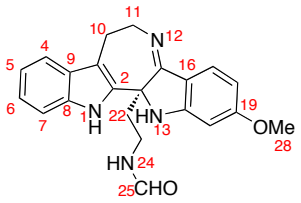
Table S5. Comparison of our ^{1}H NMR data for (–)-trigonoliimine C (3) with literature data:



(–)-trigonoliimine C (**3**)

Assignment	**Hao's Report**[7] ^{1}H NMR, 500 MHz, DMSO-d_6	**This Work**[8] ^{1}H NMR, 500.4 MHz, DMSO-d_6, 21 °C
N1	10.64 (s, 1H)	10.79 (s, 1H)
C4	7.41 (d, J = 7.5 Hz, 1H)	7.40 (d, J = 7.8 Hz, 1H)
C5	6.98 (t, J = 7.5 Hz, 1H)	6.96 (app-t, J = 7.9 Hz, 1H)
C6	7.08 (t, J = 7.5 Hz, 1H)	7.07 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H)
C7	7.36 (d, J = 7.5 Hz, 1H)	7.34 (d, J = 7.8 Hz, 1H)
C10α	3.05 (br-d, J = 11.0 Hz, 1H)	3.05 (app-dt, J = 17.1, 3.2 Hz, 1H)
C10β	2.80 (t, J = 11.0 Hz, 1H)	2.80 (ddd, J = 16.7, 13.7, 3.2 Hz, 1H)
C11α	4.24 (t, J = 12.0 Hz, 1H)	4.22 (app-dt, J = 13.8, 2.3 Hz, 1H)
C11β	3.99 (br-d, J = 12.0 Hz, 1H)	3.99 (app-dt, J = 11.8, 3.4 Hz, 1H)
N13	6.83 (br-s, 1H)	6.97 (br-s, 1H)
C17	7.34 (d, J = 8.0 Hz, 1H)	7.31 (d, J = 8.2 Hz, 1H)
C18	6.26 (dd, J = 8.0, 2.5 Hz, 1H)	6.23 (dd, J = 10.4, 2.2 Hz, 1H)
C20	6.27 (d, J = 2.5 Hz, 1H)	6.24 (d, J = 2.2 Hz, 1H)
C22α	2.29 (m, 1H)	2.54–2.48 (m, 1H)
C22β	2.51 (m, 1H)	2.33–2.27 (m, 1H)
C23	3.14 (m, 2H)	3.17–3.08 (m, 2H)
N24	7.99 (br-s, 1H)	8.00 (app-s, 1H)
C25	7.93 (s, 1H)	7.93 (d, J = 1.7 Hz, 1H)
C28	3.77 (s, 3H)	3.75 (s, 3H)

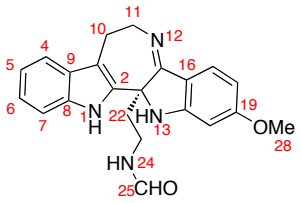
Table S6. Comparison of our ^{13}C NMR data for (–)-trigonoliimine C (3) with literature data:



(–)-trigonoliimine C (**3**)

Assignment	**Hao's Report**[7] ^{13}C NMR, 100 MHz, DMSO-d_6	**This Work**[8] ^{13}C NMR, 125.8 MHz, DMSO-d_6, 21 °C
C2	131.8	131.9
C3	108.8	108.7
C4	117.8	117.7
C5	118.6	118.4
C6	121.6	121.3
C7	110.9	110.8
C8	134.8	134.8
C9	127.9	127.9
C10	23.3	23.3
C11	46.5	46.6
C14	66.4	66.3
C15	170.3	170.0
C16	116.4	116.5
C17	123.6	123.4
C18	105.7	105.3
C19	164.3	164.2
C20	94.0	93.8
C21	156.8	156.6
C22	39.5	39.5
C23	33.6	33.6
C25	161.1	161.0
C28	55.3	55.2

Table S7. Comparison of our ^{13}C NMR data for (–)-trigonoliimine C (3) with literature data:

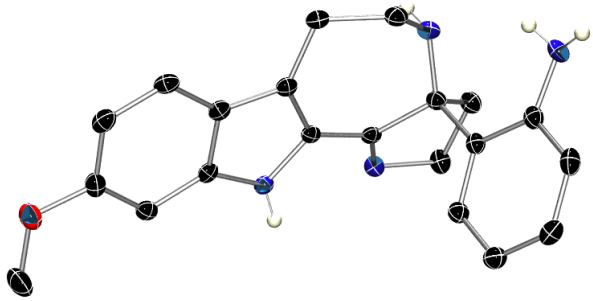


(–)-trigonoliimine C (**3**)

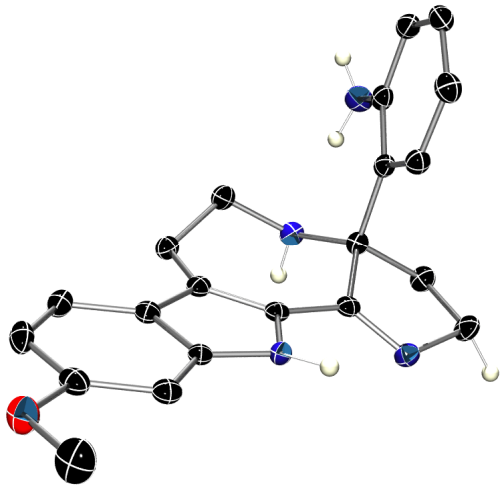
Assignment	**Hao's Report**[7] ^{13}C NMR, 100 MHz, $CDCl_3/CD_3OD$ (3:1)	**This Work**[9] ^{13}C NMR, 125.8 MHz, $CDCl_3/CD_3OD$ (3:1), 21 °C	**Chemical Shift Difference** Δδ δ (Hao's Report) - δ (This Report)
C2	131.4	130.8	0.6
C3	110.3	110.2	0.1
C4	118.5	118.3	0.2
C5	119.7	119.5	0.2
C6	122.7	122.5	0.2
C7	111.5	111.2	0.3
C8	136.3	135.7	0.6
C9	129.2	128.7	0.5
C10	24.3	24.0	0.3
C11	47.5	47.2	0.3
C14	68.1	67.6	0.5
C15	174.9	174.1	0.2
C16	116.5	116.2	0.3
C17	125.2	124.9	0.3
C18	108.4	108.1	0.3
C19	166.8	166.1	0.7
C20	95.3	95.1	0.2
C21	159.0	158.3	0.7
C22	40.2	39.8	0.2
C23	34.9	34.6	0.3
C25	163.4	162.9	0.5
C28	55.8	55.8	0.0

Crystal Structure of Pentacycle (–)-20

View 1:



View 2:



View 3:

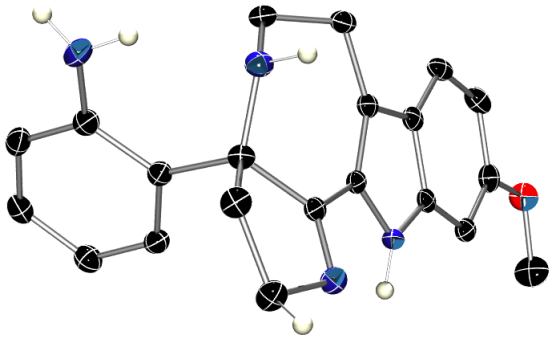


Table S8. Crystal data and structure refinement for **(–)-20**.

Identification code	x8_11097	
Empirical formula	C43 H45 Cl3 N8 O2	
Formula weight	812.22	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 15.1283(4) Å	a= 90°.
	b = 15.9902(4) Å	b= 90°.
	c = 16.2625(4) Å	g= 90°.
Volume	3933.97(17) $Å^3$	
Z	4	
Density (calculated)	1.371 Mg/m^3	
Absorption coefficient	2.502 mm^{-1}	
F(000)	1704	
Crystal size	0.20 x 0.20 x 0.15 mm^3	
Theta range for data collection	3.88 to 66.58°.	
Index ranges	-18<=h<=17, -18<=k<=19, -19<=l<=19	
Reflections collected	51159	
Independent reflections	6942 [R(int) = 0.0314]	
Completeness to theta = 66.58°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7053 and 0.6345	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6942 / 8 / 531	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0823	
R indices (all data)	R1 = 0.0306, wR2 = 0.0824	
Absolute structure parameter	0.008(8)	
Largest diff. peak and hole	0.595 and -0.385 $e.Å^{-3}$	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(–)-20**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1A)	-3689(1)	3882(1)	9534(1)	15(1)
C(2A)	-3677(1)	3141(1)	9086(1)	16(1)
C(3A)	-4491(1)	3011(1)	8731(1)	16(1)
C(4A)	-5892(1)	3958(1)	8758(1)	20(1)
C(5A)	-6195(1)	4713(1)	9030(1)	24(1)
C(6A)	-5666(1)	5235(1)	9530(1)	22(1)
C(7A)	-4813(1)	5011(1)	9748(1)	19(1)
C(8A)	-4502(1)	4241(1)	9448(1)	16(1)
C(9A)	-5025(1)	3710(1)	8961(1)	17(1)
C(10A)	-4831(1)	2273(1)	8250(1)	21(1)
C(11A)	-4165(1)	1832(1)	7700(1)	22(1)
N(12A)	-3378(1)	1486(1)	8103(1)	22(1)
N(13A)	-2246(2)	1315(1)	6737(1)	40(1)
C(14A)	-2196(1)	2176(1)	6809(1)	27(1)
C(15A)	-1931(2)	2652(2)	6135(1)	35(1)
C(16A)	-1823(1)	3500(1)	6190(1)	33(1)
C(17A)	-1960(1)	3906(1)	6936(1)	29(1)
C(18A)	-2237(1)	3438(1)	7609(1)	20(1)
C(19A)	-2374(1)	2580(1)	7561(1)	19(1)
C(20A)	-2662(1)	2074(1)	8318(1)	17(1)
C(21A)	-1867(1)	1592(1)	8681(1)	20(1)
C(22A)	-1491(1)	2206(1)	9308(1)	21(1)
N(23A)	-2252(1)	2720(1)	9583(1)	18(1)
C(24A)	-2866(1)	2655(1)	9043(1)	16(1)
O(25A)	-6074(1)	5960(1)	9776(1)	31(1)
C(26A)	-5562(2)	6543(1)	10226(1)	35(1)
N(1B)	2900(1)	1460(1)	8783(1)	15(1)
C(2B)	3380(1)	723(1)	8724(1)	14(1)
C(3B)	3655(1)	604(1)	7926(1)	16(1)
C(4B)	3387(1)	1536(1)	6643(1)	18(1)
C(5B)	2993(1)	2266(1)	6391(1)	21(1)
C(6B)	2548(1)	2787(1)	6954(1)	20(1)

C(7B)	2468(1)	2579(1)	7774(1)	17(1)
C(8B)	2863(1)	1826(1)	8026(1)	15(1)
C(9B)	3322(1)	1300(1)	7472(1)	16(1)
C(10B)	4149(1)	-111(1)	7544(1)	18(1)
C(11B)	4794(1)	-565(1)	8101(1)	19(1)
N(12B)	4421(1)	-956(1)	8840(1)	19(1)
N(13B)	6073(1)	-1137(1)	9567(1)	23(1)
C(14B)	5939(1)	-311(1)	9799(1)	18(1)
C(15B)	6670(1)	161(1)	10049(1)	22(1)
C(16B)	6581(1)	966(1)	10346(1)	22(1)
C(17B)	5751(1)	1329(1)	10395(1)	22(1)
C(18B)	5022(1)	877(1)	10123(1)	18(1)
C(19B)	5092(1)	63(1)	9816(1)	16(1)
C(20B)	4256(1)	-415(1)	9553(1)	17(1)
C(21B)	3892(1)	-937(1)	10276(1)	20(1)
C(22B)	3285(1)	-317(1)	10712(1)	21(1)
N(23B)	2949(1)	239(1)	10058(1)	18(1)
C(24B)	3482(1)	199(1)	9450(1)	15(1)
O(25B)	2214(1)	3504(1)	6606(1)	25(1)
C(26B)	1812(2)	4099(1)	7141(1)	32(1)
C(1S)	565(1)	1315(1)	7530(1)	29(1)
Cl(1S)	-47(1)	437(1)	7202(1)	44(1)
Cl(2S)	69(1)	2242(1)	7185(1)	40(1)
Cl(3S)	649(1)	1313(1)	8611(1)	32(1)

Table S10. Bond lengths [Å] and angles [°] for **(–)-20**.

N(1A)-C(8A)	1.365(2)	C(19B)-C(20B)	1.539(2)
N(1A)-C(2A)	1.392(2)	C(20B)-C(24B)	1.537(2)
C(2A)-C(3A)	1.375(2)	C(20B)-C(21B)	1.544(2)
C(2A)-C(24A)	1.454(2)	C(21B)-C(22B)	1.527(2)
C(3A)-C(9A)	1.429(2)	C(22B)-N(23B)	1.476(2)
C(3A)-C(10A)	1.507(2)	N(23B)-C(24B)	1.278(2)
C(4A)-C(5A)	1.365(3)	O(25B)-C(26B)	1.425(2)
C(4A)-C(9A)	1.409(2)	C(1S)-Cl(2S)	1.754(2)
C(5A)-C(6A)	1.413(3)	C(1S)-Cl(3S)	1.7622(19)
C(6A)-O(25A)	1.373(2)	C(1S)-Cl(1S)	1.765(2)
C(6A)-C(7A)	1.385(3)		
C(7A)-C(8A)	1.405(3)	C(8A)-N(1A)-C(2A)	108.40(14)
C(8A)-C(9A)	1.406(2)	C(3A)-C(2A)-N(1A)	109.68(15)
C(10A)-C(11A)	1.521(3)	C(3A)-C(2A)-C(24A)	130.91(16)
C(11A)-N(12A)	1.466(2)	N(1A)-C(2A)-C(24A)	119.39(15)
N(12A)-C(20A)	1.476(2)	C(2A)-C(3A)-C(9A)	106.19(15)
N(13A)-C(14A)	1.383(3)	C(2A)-C(3A)-C(10A)	129.87(16)
C(14A)-C(15A)	1.394(3)	C(9A)-C(3A)-C(10A)	123.77(15)
C(14A)-C(19A)	1.409(3)	C(5A)-C(4A)-C(9A)	119.03(17)
C(15A)-C(16A)	1.369(3)	C(4A)-C(5A)-C(6A)	121.27(16)
C(16A)-C(17A)	1.391(3)	O(25A)-C(6A)-C(7A)	124.20(17)
C(17A)-C(18A)	1.390(3)	O(25A)-C(6A)-C(5A)	114.34(16)
C(18A)-C(19A)	1.391(3)	C(7A)-C(6A)-C(5A)	121.45(17)
C(19A)-C(20A)	1.537(2)	C(6A)-C(7A)-C(8A)	116.73(17)
C(20A)-C(24A)	1.533(2)	N(1A)-C(8A)-C(7A)	129.40(16)
C(20A)-C(21A)	1.545(2)	N(1A)-C(8A)-C(9A)	108.15(15)
C(21A)-C(22A)	1.525(2)	C(7A)-C(8A)-C(9A)	122.42(16)
C(22A)-N(23A)	1.483(2)	C(8A)-C(9A)-C(4A)	119.08(16)
N(23A)-C(24A)	1.283(2)	C(8A)-C(9A)-C(3A)	107.54(14)
O(25A)-C(26A)	1.415(3)	C(4A)-C(9A)-C(3A)	133.26(17)
N(1B)-C(8B)	1.365(2)	C(3A)-C(10A)-C(11A)	116.29(15)
N(1B)-C(2B)	1.388(2)	N(12A)-C(11A)-C(10A)	116.73(15)
C(2B)-C(3B)	1.377(2)	C(11A)-N(12A)-C(20A)	117.49(14)
C(2B)-C(24B)	1.455(2)	N(13A)-C(14A)-C(15A)	119.54(19)
C(3B)-C(9B)	1.427(2)	N(13A)-C(14A)-C(19A)	121.24(18)
C(3B)-C(10B)	1.501(2)	C(15A)-C(14A)-C(19A)	119.16(18)
C(4B)-C(5B)	1.374(3)	C(16A)-C(15A)-C(14A)	121.6(2)
C(4B)-C(9B)	1.404(2)	C(15A)-C(16A)-C(17A)	120.11(19)
C(5B)-C(6B)	1.409(3)	C(18A)-C(17A)-C(16A)	118.73(18)
C(6B)-O(25B)	1.375(2)	C(17A)-C(18A)-C(19A)	122.10(18)
C(6B)-C(7B)	1.379(3)	C(18A)-C(19A)-C(14A)	118.24(17)
C(7B)-C(8B)	1.407(2)	C(18A)-C(19A)-C(20A)	121.13(16)
C(8B)-C(9B)	1.413(2)	C(14A)-C(19A)-C(20A)	120.55(16)
C(10B)-C(11B)	1.516(2)	N(12A)-C(20A)-C(24A)	114.87(15)
C(11B)-N(12B)	1.467(2)	N(12A)-C(20A)-C(19A)	110.68(14)
N(12B)-C(20B)	1.467(2)	C(24A)-C(20A)-C(19A)	110.76(13)
N(13B)-C(14B)	1.389(2)	N(12A)-C(20A)-C(21A)	110.18(13)
C(14B)-C(15B)	1.399(3)	C(24A)-C(20A)-C(21A)	99.48(13)
C(14B)-C(19B)	1.413(2)	C(19A)-C(20A)-C(21A)	110.34(15)
C(15B)-C(16B)	1.382(3)	C(22A)-C(21A)-C(20A)	103.05(13)
C(16B)-C(17B)	1.385(3)	N(23A)-C(22A)-C(21A)	105.56(14)
C(17B)-C(18B)	1.391(3)	C(24A)-N(23A)-C(22A)	108.14(14)
C(18B)-C(19B)	1.397(2)	N(23A)-C(24A)-C(2A)	122.37(15)

N(23A)-C(24A)-C(20A)	115.45(15)	N(13B)-C(14B)-C(15B)	118.42(16)
C(2A)-C(24A)-C(20A)	122.06(15)	N(13B)-C(14B)-C(19B)	122.73(16)
C(6A)-O(25A)-C(26A)	117.49(15)	C(15B)-C(14B)-C(19B)	118.83(16)
C(8B)-N(1B)-C(2B)	108.80(14)	C(16B)-C(15B)-C(14B)	121.81(17)
C(3B)-C(2B)-N(1B)	109.94(15)	C(15B)-C(16B)-C(17B)	119.88(17)
C(3B)-C(2B)-C(24B)	130.73(15)	C(16B)-C(17B)-C(18B)	118.87(16)
N(1B)-C(2B)-C(24B)	119.27(15)	C(17B)-C(18B)-C(19B)	122.50(16)
C(2B)-C(3B)-C(9B)	105.82(14)	C(18B)-C(19B)-C(14B)	118.02(16)
C(2B)-C(3B)-C(10B)	130.28(15)	C(18B)-C(19B)-C(20B)	119.95(15)
C(9B)-C(3B)-C(10B)	123.80(15)	C(14B)-C(19B)-C(20B)	121.95(15)
C(5B)-C(4B)-C(9B)	118.96(16)	N(12B)-C(20B)-C(24B)	114.79(14)
C(4B)-C(5B)-C(6B)	121.06(16)	N(12B)-C(20B)-C(19B)	111.88(14)
O(25B)-C(6B)-C(7B)	124.46(17)	C(24B)-C(20B)-C(19B)	109.85(13)
O(25B)-C(6B)-C(5B)	113.64(16)	N(12B)-C(20B)-C(21B)	110.10(13)
C(7B)-C(6B)-C(5B)	121.90(16)	C(24B)-C(20B)-C(21B)	99.03(13)
C(6B)-C(7B)-C(8B)	116.72(16)	C(19B)-C(20B)-C(21B)	110.49(14)
N(1B)-C(8B)-C(7B)	130.28(16)	C(22B)-C(21B)-C(20B)	102.53(13)
N(1B)-C(8B)-C(9B)	107.50(14)	N(23B)-C(22B)-C(21B)	105.28(14)
C(7B)-C(8B)-C(9B)	122.22(15)	C(24B)-N(23B)-C(22B)	108.11(14)
C(4B)-C(9B)-C(8B)	119.11(16)	N(23B)-C(24B)-C(2B)	122.13(15)
C(4B)-C(9B)-C(3B)	132.93(16)	N(23B)-C(24B)-C(20B)	115.34(15)
C(8B)-C(9B)-C(3B)	107.94(14)	C(2B)-C(24B)-C(20B)	122.49(14)
C(3B)-C(10B)-C(11B)	116.00(14)	C(6B)-O(25B)-C(26B)	117.54(15)
N(12B)-C(11B)-C(10B)	116.47(14)	Cl(2S)-C(1S)-Cl(3S)	110.59(12)
C(20B)-N(12B)-C(11B)	117.55(13)	Cl(2S)-C(1S)-Cl(1S)	110.58(11)
		Cl(3S)-C(1S)-Cl(1S)	109.71(11

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **(–)-20**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1A)	12(1)	18(1)	16(1)	-1(1)	-3(1)	-2(1)
C(2A)	18(1)	15(1)	13(1)	2(1)	0(1)	-3(1)
C(3A)	18(1)	16(1)	14(1)	3(1)	-1(1)	-5(1)
C(4A)	14(1)	30(1)	17(1)	3(1)	0(1)	-4(1)
C(5A)	14(1)	37(1)	21(1)	4(1)	0(1)	3(1)
C(6A)	20(1)	28(1)	19(1)	1(1)	4(1)	5(1)
C(7A)	18(1)	24(1)	16(1)	0(1)	2(1)	-1(1)
C(8A)	15(1)	18(1)	13(1)	3(1)	2(1)	-2(1)
C(9A)	14(1)	23(1)	14(1)	4(1)	1(1)	-5(1)
C(10A)	20(1)	20(1)	24(1)	1(1)	-5(1)	-8(1)
C(11A)	26(1)	20(1)	21(1)	-3(1)	-6(1)	-8(1)
N(12A)	28(1)	16(1)	22(1)	0(1)	-4(1)	-5(1)
N(13A)	66(1)	32(1)	21(1)	-12(1)	6(1)	-1(1)
C(14A)	31(1)	29(1)	20(1)	1(1)	-4(1)	-1(1)
C(15A)	38(1)	47(1)	19(1)	1(1)	2(1)	2(1)
C(16A)	25(1)	46(1)	27(1)	17(1)	4(1)	4(1)
C(17A)	23(1)	26(1)	39(1)	11(1)	2(1)	0(1)
C(18A)	15(1)	21(1)	26(1)	1(1)	-1(1)	2(1)
C(19A)	18(1)	22(1)	18(1)	2(1)	-3(1)	0(1)
C(20A)	22(1)	14(1)	16(1)	-2(1)	-2(1)	-1(1)
C(21A)	25(1)	17(1)	19(1)	2(1)	1(1)	3(1)
C(22A)	20(1)	22(1)	20(1)	0(1)	-3(1)	6(1)
N(23A)	18(1)	18(1)	18(1)	-1(1)	-3(1)	2(1)
C(24A)	19(1)	14(1)	15(1)	3(1)	-1(1)	-3(1)
O(25A)	25(1)	35(1)	33(1)	-7(1)	0(1)	12(1)
C(26A)	33(1)	30(1)	42(1)	-8(1)	5(1)	9(1)
N(1B)	14(1)	18(1)	13(1)	-2(1)	1(1)	0(1)
C(2B)	12(1)	15(1)	17(1)	-3(1)	-1(1)	-2(1)
C(3B)	13(1)	16(1)	18(1)	-2(1)	-1(1)	-4(1)
C(4B)	21(1)	18(1)	17(1)	-3(1)	2(1)	-6(1)
C(5B)	27(1)	21(1)	15(1)	3(1)	-1(1)	-7(1)
C(6B)	18(1)	19(1)	23(1)	4(1)	-4(1)	-3(1)
C(7B)	15(1)	16(1)	21(1)	-2(1)	-1(1)	-2(1)

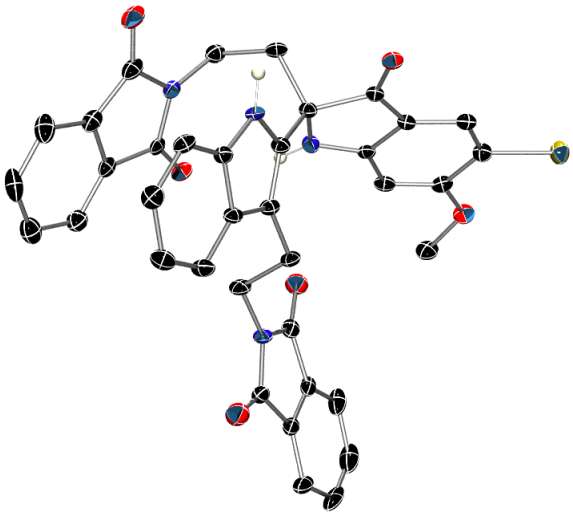
C(8B)	12(1)	18(1)	15(1)	0(1)	-1(1)	-5(1)
C(9B)	14(1)	17(1)	18(1)	-1(1)	-1(1)	-5(1)
C(10B)	19(1)	18(1)	17(1)	-4(1)	2(1)	-2(1)
C(11B)	20(1)	20(1)	18(1)	-4(1)	3(1)	2(1)
N(12B)	20(1)	15(1)	21(1)	-3(1)	1(1)	-1(1)
N(13B)	21(1)	21(1)	28(1)	-2(1)	-1(1)	8(1)
C(14B)	20(1)	20(1)	15(1)	4(1)	1(1)	2(1)
C(15B)	17(1)	30(1)	18(1)	4(1)	0(1)	4(1)
C(16B)	22(1)	26(1)	18(1)	2(1)	-3(1)	-6(1)
C(17B)	26(1)	19(1)	21(1)	-1(1)	-2(1)	-1(1)
C(18B)	18(1)	19(1)	18(1)	-1(1)	1(1)	2(1)
C(19B)	16(1)	18(1)	14(1)	2(1)	1(1)	1(1)
C(20B)	19(1)	14(1)	17(1)	1(1)	1(1)	0(1)
C(21B)	22(1)	17(1)	21(1)	4(1)	2(1)	-1(1)
C(22B)	21(1)	23(1)	20(1)	6(1)	4(1)	0(1)
N(23B)	17(1)	18(1)	19(1)	2(1)	2(1)	-1(1)
C(24B)	13(1)	15(1)	18(1)	-4(1)	-1(1)	-3(1)
O(25B)	31(1)	20(1)	25(1)	6(1)	0(1)	2(1)
C(26B)	42(1)	21(1)	35(1)	7(1)	1(1)	8(1)
C(1S)	26(1)	38(1)	23(1)	1(1)	3(1)	-5(1)
Cl(1S)	41(1)	48(1)	42(1)	-12(1)	13(1)	-18(1)
Cl(2S)	34(1)	46(1)	39(1)	19(1)	-5(1)	-3(1)
Cl(3S)	29(1)	44(1)	22(1)	6(1)	0(1)	4(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **(–)-20**.

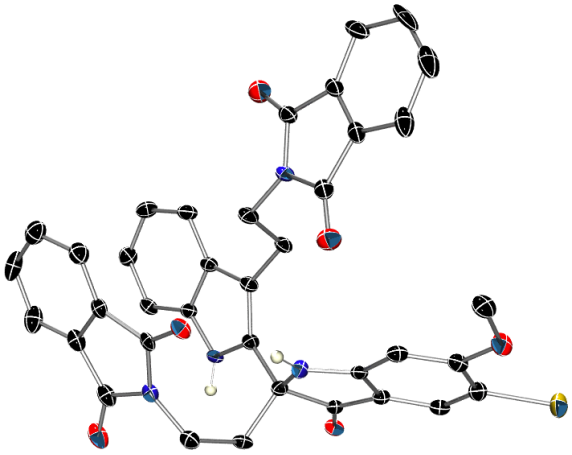
	x	y	z	U(eq)
H(1NA)	-3244(12)	4108(13)	9752(13)	18
H(4A)	-6260	3605	8436	24
H(5A)	-6772	4891	8881	29
H(7A)	-4456	5361	10083	23
H(10A)	-5328	2465	7902	26
H(10B)	-5070	1859	8644	26
H(11A)	-4473	1370	7413	27
H(11B)	-3966	2233	7274	27
H(4NA)	-3526(15)	1211(13)	8575(11)	26
H(2NA)	-2638(16)	1080(16)	7054(16)	47
H(3NA)	-2164(19)	1116(16)	6267(12)	47
H(15A)	-1821	2381	5625	42
H(16A)	-1655	3812	5718	39
H(17A)	-1865	4491	6985	35
H(18A)	-2336	3714	8118	25
H(21A)	-2061	1067	8949	24
H(21B)	-1427	1459	8250	24
H(22A)	-1227	1902	9779	25
H(22B)	-1031	2561	9054	25
H(26A)	-5340	6278	10728	52
H(26B)	-5930	7025	10372	52
H(26C)	-5063	6730	9889	52
H(1NB)	2759(14)	1665(12)	9255(10)	18
H(4B)	3698	1195	6262	22
H(5B)	3021	2423	5828	25
H(7B)	2160	2928	8150	21
H(10C)	4480	104	7063	22
H(10D)	3713	-522	7337	22
H(11C)	5091	-1006	7774	23
H(11D)	5254	-163	8275	23
H(4NB)	3943(12)	-1225(13)	8696(13)	22
H(2NB)	5619(13)	-1355(14)	9316(14)	28
H(3NB)	6590(12)	-1240(15)	9383(14)	28
H(15B)	7243	-79	10014	26
H(16B)	7088	1271	10517	26
H(17B)	5681	1877	10611	26
H(18B)	4455	1130	10147	22
H(21C)	3559	-1430	10076	24
H(21D)	4374	-1128	10643	24
H(22C)	2791	-612	10987	25
H(22D)	3616	7	11130	25
H(26D)	1295	3846	7406	49
H(26E)	1627	4589	6823	49
H(26F)	2237	4271	7563	49
H(1S)	1174	1279	7292	35

Crystal Structure of Bromoindoxyl (–)-28

View 1:



View 2:



View 3:

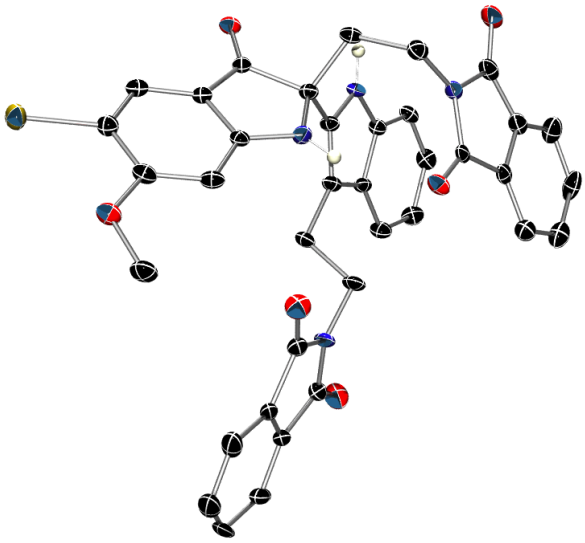


Table S13. Crystal data and structure refinement for (–)-**28**.

Identification code	x8_11013	
Empirical formula	C37.50 H28 Br Cl N4 O6	
Formula weight	746.00	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2	
Unit cell dimensions	a = 41.6761(19) Å	a= 90°.
	b = 7.7113(3) Å	b= 90°.
	c = 10.0688(5) Å	g = 90°.
Volume	3235.9(3) $Å^3$	
Z	4	
Density (calculated)	1.531 Mg/m^3	
Absorption coefficient	1.409 mm^{-1}	
F(000)	1524	
Crystal size	0.15 x 0.15 x 0.05 mm^3	
Theta range for data collection	1.95 to 30.32°.	
Index ranges	-57<=h<=59, -10<=k<=10, -14<=l<=14	
Reflections collected	61869	
Independent reflections	9654 [R(int) = 0.0571]	
Completeness to theta = 30.32°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9329 and 0.8164	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9654 / 0 / 448	
Goodness-of-fit on F^2	1.181	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.0877	
R indices (all data)	R1 = 0.0564, wR2 = 0.0899	
Absolute structure parameter	0.021(7)	
Largest diff. peak and hole	0.338 and -0.686 $e.Å^{-3}$	

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (–)-**28**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	8246(1)	-6823(1)	4487(1)	27(1)
O(1)	9328(1)	-4385(3)	7788(2)	19(1)
O(2)	7977(1)	738(3)	8040(2)	28(1)
O(3)	7878(1)	468(3)	12547(2)	31(1)
O(4)	8848(1)	2822(3)	8671(2)	21(1)
O(5)	9913(1)	1992(3)	9474(3)	30(1)
O(6)	7936(1)	-3445(3)	4962(2)	24(1)
N(1)	9392(1)	-1424(3)	10231(2)	15(1)
N(2)	8810(1)	-810(3)	7483(2)	17(1)
N(3)	9384(1)	2103(3)	8817(2)	17(1)
N(4)	8007(1)	624(3)	10322(3)	18(1)
C(1)	7801(1)	467(4)	11395(3)	21(1)
C(2)	7472(1)	321(4)	10793(3)	22(1)
C(3)	7177(1)	77(4)	11397(4)	33(1)
C(4)	6912(1)	-91(4)	10537(6)	44(1)
C(5)	6945(1)	-11(5)	9195(5)	42(1)
C(6)	7241(1)	237(4)	8590(4)	32(1)
C(7)	7505(1)	390(3)	9436(4)	22(1)
C(8)	7849(1)	600(4)	9106(3)	21(1)
C(9)	8354(1)	719(4)	10443(4)	22(1)
C(10)	8501(1)	-1089(4)	10288(3)	18(1)
C(11)	8859(1)	-1113(3)	10473(3)	17(1)
C(12)	9007(1)	-894(4)	11739(3)	16(1)
C(13)	8891(1)	-474(4)	13012(3)	22(1)
C(14)	9108(1)	-217(4)	14029(3)	23(1)
C(15)	9440(1)	-386(4)	13801(3)	22(1)
C(16)	9561(1)	-847(4)	12581(3)	18(1)
C(17)	9341(1)	-1069(4)	11549(3)	16(1)
C(18)	9102(1)	-1386(3)	9564(3)	16(1)
C(19)	9104(1)	-1492(4)	8064(3)	16(1)
C(20)	9107(1)	-3400(4)	7569(3)	15(1)
C(21)	8818(1)	-3620(4)	6793(3)	16(1)
C(22)	8701(1)	-5052(4)	6092(3)	19(1)
C(23)	8411(1)	-4923(4)	5465(3)	20(1)
C(24)	8228(1)	-3386(4)	5549(3)	19(1)
C(25)	8345(1)	-1924(4)	6197(3)	19(1)
C(26)	8646(1)	-2066(4)	6813(3)	15(1)
C(27)	7725(1)	-1982(5)	5155(3)	27(1)
C(28)	9403(1)	-634(4)	7459(3)	17(1)
C(29)	9416(1)	1348(4)	7502(3)	21(1)
C(30)	9100(1)	2835(3)	9275(3)	16(1)
C(31)	9174(1)	3577(3)	10596(3)	18(1)
C(32)	8978(1)	4401(4)	11490(3)	25(1)
C(33)	9109(1)	4899(4)	12687(3)	29(1)
C(34)	9431(1)	4592(4)	12970(4)	32(1)
C(35)	9628(1)	3787(4)	12057(4)	30(1)
C(36)	9495(1)	3281(4)	10862(3)	22(1)
C(37)	9637(1)	2402(4)	9695(3)	22(1)
Cl(1S)	10048(1)	3137(1)	5419(1)	29(1)
C(1S)	10000	5000	6421(4)	22(1)

Table S15. Bond lengths [Å] and angles [°] for (–)-**28**.

Br(1)-C(23)	1.895(3)	C(36)-C(37)	1.480(4)
O(1)-C(20)	1.213(3)	Cl(1S)-C(1S)	1.767(3)
O(2)-C(8)	1.202(4)	C(1S)-Cl(1S)#1	1.767(3)
O(3)-C(1)	1.204(4)		
O(4)-C(30)	1.215(3)	C(24)-O(6)-C(27)	117.6(2)
O(5)-C(37)	1.214(3)	C(17)-N(1)-C(18)	109.2(2)
O(6)-C(24)	1.355(3)	C(26)-N(2)-C(19)	111.3(2)
O(6)-C(27)	1.443(4)	C(30)-N(3)-C(37)	111.4(2)
N(1)-C(17)	1.371(4)	C(30)-N(3)-C(29)	122.8(2)
N(1)-C(18)	1.383(3)	C(37)-N(3)-C(29)	125.3(2)
N(2)-C(26)	1.363(4)	C(1)-N(4)-C(8)	113.1(2)
N(2)-C(19)	1.453(3)	C(1)-N(4)-C(9)	123.8(3)
N(3)-C(30)	1.390(3)	C(8)-N(4)-C(9)	123.1(3)
N(3)-C(37)	1.393(4)	O(3)-C(1)-N(4)	125.8(3)
N(3)-C(29)	1.453(4)	O(3)-C(1)-C(2)	129.3(3)
N(4)-C(1)	1.386(4)	N(4)-C(1)-C(2)	104.9(3)
N(4)-C(8)	1.390(4)	C(7)-C(2)-C(3)	122.0(3)
N(4)-C(9)	1.454(3)	C(7)-C(2)-C(1)	108.0(2)
C(1)-C(2)	1.503(4)	C(3)-C(2)-C(1)	130.0(3)
C(2)-C(7)	1.374(5)	C(2)-C(3)-C(4)	116.0(4)
C(2)-C(3)	1.384(4)	C(5)-C(4)-C(3)	121.8(3)
C(3)-C(4)	1.410(6)	C(4)-C(5)-C(6)	122.1(4)
C(4)-C(5)	1.360(7)	C(5)-C(6)-C(7)	116.3(4)
C(5)-C(6)	1.390(5)	C(2)-C(7)-C(6)	121.8(3)
C(6)-C(7)	1.394(4)	C(2)-C(7)-C(8)	108.8(3)
C(7)-C(8)	1.483(4)	C(6)-C(7)-C(8)	129.4(3)
C(9)-C(10)	1.531(4)	O(2)-C(8)-N(4)	125.2(3)
C(10)-C(11)	1.501(3)	O(2)-C(8)-C(7)	129.6(3)
C(11)-C(18)	1.383(4)	N(4)-C(8)-C(7)	105.2(3)
C(11)-C(12)	1.426(4)	N(4)-C(9)-C(10)	110.1(2)
C(12)-C(13)	1.407(4)	C(11)-C(10)-C(9)	113.3(2)
C(12)-C(17)	1.410(4)	C(18)-C(11)-C(12)	106.9(2)
C(13)-C(14)	1.380(4)	C(18)-C(11)-C(10)	130.4(3)
C(14)-C(15)	1.411(4)	C(12)-C(11)-C(10)	122.6(3)
C(15)-C(16)	1.373(4)	C(13)-C(12)-C(17)	118.9(3)
C(16)-C(17)	1.397(4)	C(13)-C(12)-C(11)	133.9(3)
C(18)-C(19)	1.513(4)	C(17)-C(12)-C(11)	107.1(2)
C(19)-C(28)	1.539(4)	C(14)-C(13)-C(12)	119.0(3)
C(19)-C(20)	1.553(4)	C(13)-C(14)-C(15)	120.6(3)
C(20)-C(21)	1.448(4)	C(16)-C(15)-C(14)	121.9(3)
C(21)-C(26)	1.395(4)	C(15)-C(16)-C(17)	117.2(3)
C(21)-C(22)	1.398(4)	N(1)-C(17)-C(16)	129.9(3)
C(22)-C(23)	1.368(4)	N(1)-C(17)-C(12)	107.7(2)
C(23)-C(24)	1.412(4)	C(16)-C(17)-C(12)	122.4(3)
C(24)-C(25)	1.392(4)	N(1)-C(18)-C(11)	108.9(3)
C(25)-C(26)	1.404(4)	N(1)-C(18)-C(19)	118.8(2)
C(28)-C(29)	1.530(4)	C(11)-C(18)-C(19)	132.2(2)
C(30)-C(31)	1.480(4)	N(2)-C(19)-C(18)	112.3(2)
C(31)-C(32)	1.371(4)	N(2)-C(19)-C(28)	111.6(2)
C(31)-C(36)	1.384(4)	C(18)-C(19)-C(28)	112.0(2)
C(32)-C(33)	1.377(5)	N(2)-C(19)-C(20)	102.8(2)
C(33)-C(34)	1.391(5)	C(18)-C(19)-C(20)	111.8(2)
C(34)-C(35)	1.381(5)	C(28)-C(19)-C(20)	105.8(2)
C(35)-C(36)	1.381(4)	O(1)-C(20)-C(21)	131.1(3)

O(1)-C(20)-C(19)	122.8(2)
C(21)-C(20)-C(19)	106.0(2)
C(26)-C(21)-C(22)	120.6(3)
C(26)-C(21)-C(20)	108.6(2)
C(22)-C(21)-C(20)	130.9(3)
C(23)-C(22)-C(21)	118.9(3)
C(22)-C(23)-C(24)	120.7(3)
C(22)-C(23)-Br(1)	120.3(2)
C(24)-C(23)-Br(1)	118.9(2)
O(6)-C(24)-C(25)	123.2(2)
O(6)-C(24)-C(23)	115.6(3)
C(25)-C(24)-C(23)	121.2(2)
C(24)-C(25)-C(26)	117.3(3)
N(2)-C(26)-C(21)	111.1(2)
N(2)-C(26)-C(25)	127.7(3)
C(21)-C(26)-C(25)	121.2(3)
C(29)-C(28)-C(19)	116.5(2)
N(3)-C(29)-C(28)	115.0(2)
O(4)-C(30)-N(3)	124.6(3)
O(4)-C(30)-C(31)	129.3(2)
N(3)-C(30)-C(31)	106.1(2)
C(32)-C(31)-C(36)	121.6(3)
C(32)-C(31)-C(30)	130.2(3)
C(36)-C(31)-C(30)	108.1(2)
C(31)-C(32)-C(33)	118.0(3)
C(32)-C(33)-C(34)	120.8(3)
C(35)-C(34)-C(33)	121.0(3)
C(34)-C(35)-C(36)	117.9(3)
C(35)-C(36)-C(31)	120.7(3)
C(35)-C(36)-C(37)	131.4(3)
C(31)-C(36)-C(37)	107.9(3)
O(5)-C(37)-N(3)	123.8(3)
O(5)-C(37)-C(36)	130.0(3)
N(3)-C(37)-C(36)	106.2(2)
Cl(1S)-C(1S)-Cl(1S)#1	110.3(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,z

Table S16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (–)-**28**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

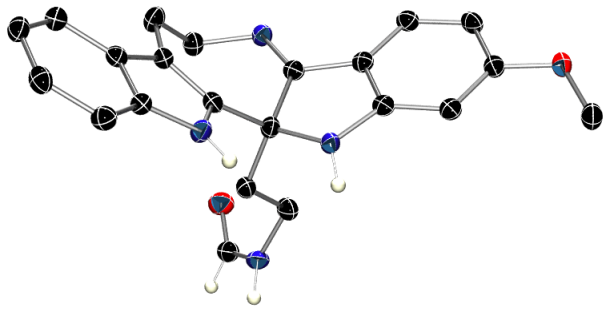
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	24(1)	26(1)	31(1)	-6(1)	-7(1)	-1(1)
O(1)	15(1)	21(1)	20(1)	4(1)	1(1)	2(1)
O(2)	31(1)	30(1)	22(1)	2(1)	2(1)	0(1)
O(3)	36(1)	36(1)	22(1)	0(1)	3(1)	-8(1)
O(4)	13(1)	26(1)	24(1)	4(1)	-4(1)	-1(1)
O(5)	14(1)	24(1)	51(1)	2(1)	-5(1)	1(1)
O(6)	15(1)	29(1)	29(1)	-1(1)	-6(1)	2(1)
N(1)	10(1)	21(1)	14(1)	1(1)	2(1)	0(1)
N(2)	14(1)	18(1)	20(1)	-3(1)	-3(1)	3(1)
N(3)	14(1)	14(1)	22(1)	2(1)	-2(1)	0(1)
N(4)	10(1)	24(1)	22(1)	-2(1)	2(1)	1(1)
C(1)	20(1)	17(1)	27(2)	-1(1)	6(1)	-2(1)
C(2)	14(1)	16(1)	36(2)	-6(1)	4(1)	0(1)
C(3)	20(2)	20(2)	60(2)	-6(2)	18(2)	-1(1)
C(4)	9(1)	23(2)	101(4)	-9(2)	11(2)	-2(1)
C(5)	17(2)	28(2)	82(3)	-15(2)	-10(2)	3(1)
C(6)	22(2)	22(2)	51(2)	-7(2)	-13(2)	2(1)
C(7)	12(1)	15(1)	38(2)	-6(1)	-1(1)	2(1)
C(8)	17(1)	18(1)	27(2)	-2(1)	-1(1)	3(1)
C(9)	9(1)	29(1)	26(1)	-2(1)	1(1)	2(1)
C(10)	11(1)	23(1)	21(2)	0(1)	1(1)	-1(1)
C(11)	12(1)	19(1)	20(1)	2(1)	1(1)	1(1)
C(12)	13(1)	15(1)	20(1)	2(1)	3(1)	3(1)
C(13)	18(1)	28(2)	18(1)	1(1)	4(1)	0(1)
C(14)	26(2)	28(2)	13(1)	2(1)	2(1)	3(1)
C(15)	24(2)	27(2)	16(1)	2(1)	-4(1)	-2(1)
C(16)	13(1)	20(1)	21(1)	6(1)	-1(1)	-1(1)
C(17)	15(1)	18(1)	15(1)	1(1)	1(1)	0(1)
C(18)	11(1)	19(1)	18(1)	0(1)	-1(1)	3(1)
C(19)	13(1)	20(1)	15(1)	-2(1)	0(1)	1(1)
C(20)	14(1)	17(1)	13(1)	0(1)	2(1)	1(1)
C(21)	14(1)	18(1)	14(1)	0(1)	1(1)	2(1)
C(22)	17(1)	21(1)	19(1)	3(1)	3(1)	3(1)
C(23)	18(1)	22(1)	20(1)	0(1)	-2(1)	0(1)
C(24)	15(1)	26(1)	17(1)	4(1)	-2(1)	0(1)
C(25)	15(1)	25(1)	16(1)	2(1)	0(1)	4(1)
C(26)	13(1)	20(1)	13(1)	0(1)	3(1)	-1(1)
C(27)	16(1)	31(2)	34(2)	2(2)	-2(1)	4(1)
C(28)	14(1)	24(2)	14(1)	6(1)	3(1)	2(1)
C(29)	19(1)	20(1)	23(2)	3(1)	2(1)	0(1)
C(30)	13(1)	9(1)	25(2)	3(1)	0(1)	-1(1)
C(31)	18(1)	11(1)	24(1)	4(1)	-3(1)	-1(1)
C(32)	21(1)	23(2)	30(2)	-1(1)	0(1)	0(1)
C(33)	41(2)	21(2)	25(2)	0(1)	0(1)	0(1)
C(34)	45(2)	19(2)	32(2)	-7(1)	-17(2)	3(2)
C(35)	28(2)	23(2)	38(2)	-4(1)	-14(1)	2(1)
C(36)	17(1)	18(1)	30(2)	4(1)	-5(1)	0(1)
C(37)	15(1)	20(1)	33(2)	5(1)	-5(1)	0(1)
Cl(1S)	32(1)	28(1)	28(1)	2(1)	7(1)	3(1)
C(1S)	17(2)	29(2)	21(2)	0	0	4(2)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for (–)-**28**.

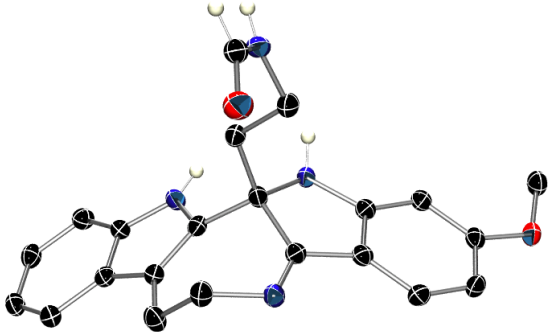
	x	y	z	U(eq)
H(1)	9580	-1642	9868	18
H(2)	8747	274	7555	21
H(3)	7155	27	12335	40
H(4)	6705	-264	10906	53
H(5)	6760	-129	8654	51
H(6)	7263	298	7652	38
H(9A)	8412	1202	11322	26
H(9B)	8441	1500	9750	26
H(10A)	8402	-1878	10947	22
H(10B)	8450	-1538	9392	22
H(13)	8667	-369	13169	26
H(14)	9033	76	14891	27
H(15)	9585	-175	14511	27
H(16)	9785	-1009	12445	22
H(22)	8821	-6098	6052	23
H(25)	8226	-873	6223	22
H(27A)	7687	-1812	6106	40
H(27B)	7520	-2203	4707	40
H(27C)	7824	-938	4781	40
H(28A)	9594	-1087	7929	21
H(28B)	9420	-1004	6520	21
H(29A)	9622	1731	7114	25
H(29B)	9242	1809	6933	25
H(32)	8760	4622	11290	30
H(33)	8978	5459	13328	35
H(34)	9516	4941	13803	38
H(35)	9849	3589	12245	36
H(1S)	10190	5144	6998	26
H(2S)	9810	4856	6998	26

Crystal Structure of (–)-Trigonoliimine C (3)

View 1:



View 2:



View 3:

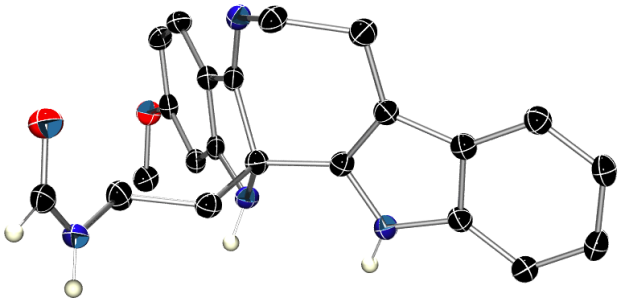


Table S18. Crystal data and structure refinement for (–)-Trigonoliimine C (**3**).

Identification code	d8_10127	
Empirical formula	C22 H22 N4 O2	
Formula weight	374.44	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.3013(2) Å	a = 90°.
	b = 7.5801(2) Å	b = 90°.
	c = 32.8941(8) Å	c = 90°.
Volume	1820.51(8) $Å^3$	
Z	4	
Density (calculated)	1.366 Mg/m^3	
Absorption coefficient	0.723 mm^{-1}	
F(000)	792	
Crystal size	0.20 x 0.20 x 0.10 mm^3	
Theta range for data collection	2.69 to 66.57°.	
Index ranges	-8<=h<=8, -9<=k<=9, -38<=l<=32	
Reflections collected	39871	
Independent reflections	3212 [R(int) = 0.0276]	
Completeness to theta = 66.57°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9312 and 0.8688	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3212 / 3 / 263	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0306, wR2 = 0.0798	
R indices (all data)	R1 = 0.0309, wR2 = 0.0802	
Absolute structure parameter	-0.1(2)	
Largest diff. peak and hole	0.220 and -0.160 $e.Å^{-3}$	

Table S19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (–)-trigonoliimine C (**3**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-2704(2)	-52(2)	807(1)	33(1)
O(2)	7869(2)	5273(2)	53(1)	24(1)
N(12)	527(2)	5010(2)	1153(1)	21(1)
N(24)	95(2)	-1317(2)	890(1)	23(1)
N(1)	4158(2)	2386(2)	2060(1)	21(1)
N(13)	4710(2)	2433(2)	1197(1)	19(1)
C(21)	4949(2)	3584(2)	870(1)	19(1)
C(18)	4935(2)	6092(2)	256(1)	22(1)
C(16)	3426(2)	4649(2)	813(1)	20(1)
C(4)	1632(2)	4764(2)	2807(1)	23(1)
C(15)	2034(2)	4175(2)	1110(1)	19(1)
C(5)	2563(2)	4394(2)	3163(1)	23(1)
C(6)	4080(2)	3251(2)	3168(1)	24(1)
C(19)	6457(2)	4993(2)	318(1)	20(1)
C(9)	2249(2)	3997(2)	2444(1)	20(1)
C(22)	1756(2)	840(2)	1315(1)	21(1)
C(7)	4743(2)	2507(2)	2813(1)	24(1)
C(3)	1637(2)	4083(2)	2030(1)	20(1)
C(25)	-1709(2)	-1336(2)	853(1)	25(1)
C(26)	9348(2)	4038(2)	56(1)	26(1)
C(23)	1213(2)	293(2)	886(1)	26(1)
C(11)	-762(2)	4527(2)	1478(1)	23(1)
C(8)	3827(2)	2911(2)	2452(1)	20(1)
C(10)	-48(2)	5067(2)	1894(1)	25(1)
C(2)	2848(2)	3099(2)	1806(1)	19(1)
C(14)	2822(2)	2596(2)	1357(1)	19(1)
C(17)	3427(2)	5922(2)	503(1)	22(1)
C(20)	6502(2)	3733(2)	624(1)	20(1)

Table S20. Bond lengths [Å] and angles [°] for (–)-trigonoliimine C (**3**).

O(1)-C(25)	1.224(2)	C(16)-C(15)	1.454(2)
O(2)-C(19)	1.3661(18)	C(4)-C(5)	1.382(2)
O(2)-C(26)	1.430(2)	C(4)-C(9)	1.405(2)
N(12)-C(15)	1.277(2)	C(15)-C(14)	1.558(2)
N(12)-C(11)	1.471(2)	C(5)-C(6)	1.406(2)
N(24)-C(25)	1.323(2)	C(6)-C(7)	1.383(2)
N(24)-C(23)	1.468(2)	C(19)-C(20)	1.390(2)
N(1)-C(8)	1.373(2)	C(9)-C(8)	1.416(2)
N(1)-C(2)	1.379(2)	C(9)-C(3)	1.433(2)
N(13)-C(21)	1.3961(19)	C(22)-C(23)	1.523(2)
N(13)-C(14)	1.4817(19)	C(22)-C(14)	1.549(2)
C(21)-C(16)	1.387(2)	C(7)-C(8)	1.397(2)
C(21)-C(20)	1.396(2)	C(3)-C(2)	1.372(2)
C(18)-C(17)	1.374(2)	C(3)-C(10)	1.507(2)
C(18)-C(19)	1.403(2)	C(11)-C(10)	1.520(2)
C(16)-C(17)	1.404(2)	C(2)-C(14)	1.525(2)
C(19)-O(2)-C(26)	117.64(12)	C(23)-C(22)-C(14)	116.69(13)
C(15)-N(12)-C(11)	120.59(13)	C(6)-C(7)-C(8)	117.38(15)
C(25)-N(24)-C(23)	124.21(15)	C(2)-C(3)-C(9)	106.49(13)
C(8)-N(1)-C(2)	109.50(13)	C(2)-C(3)-C(10)	129.47(14)
C(21)-N(13)-C(14)	109.80(12)	C(9)-C(3)-C(10)	124.03(13)
C(16)-C(21)-C(20)	121.74(14)	O(1)-C(25)-N(24)	126.39(17)
C(16)-C(21)-N(13)	111.55(14)	N(24)-C(23)-C(22)	111.30(13)
C(20)-C(21)-N(13)	126.70(14)	N(12)-C(11)-C(10)	111.57(13)
C(17)-C(18)-C(19)	119.63(14)	N(1)-C(8)-C(7)	130.72(15)
C(21)-C(16)-C(17)	119.84(14)	N(1)-C(8)-C(9)	106.98(13)
C(21)-C(16)-C(15)	109.04(13)	C(7)-C(8)-C(9)	122.29(14)
C(17)-C(16)-C(15)	131.12(15)	C(3)-C(10)-C(11)	114.48(13)
C(5)-C(4)-C(9)	118.63(15)	C(3)-C(2)-N(1)	109.58(13)
N(12)-C(15)-C(16)	123.68(14)	C(3)-C(2)-C(14)	130.38(14)
N(12)-C(15)-C(14)	129.83(14)	N(1)-C(2)-C(14)	119.77(14)
C(16)-C(15)-C(14)	106.42(13)	N(13)-C(14)-C(2)	110.76(12)
C(4)-C(5)-C(6)	121.50(14)	N(13)-C(14)-C(22)	111.29(12)
C(7)-C(6)-C(5)	121.14(14)	C(2)-C(14)-C(22)	107.98(12)
O(2)-C(19)-C(20)	123.48(14)	N(13)-C(14)-C(15)	102.81(12)
O(2)-C(19)-C(18)	114.45(13)	C(2)-C(14)-C(15)	108.62(12)
C(20)-C(19)-C(18)	122.07(14)	C(22)-C(14)-C(15)	115.31(12)
C(4)-C(9)-C(8)	118.96(14)	C(18)-C(17)-C(16)	119.58(14)
C(4)-C(9)-C(3)	133.59(15)	C(19)-C(20)-C(21)	117.14(15)
C(8)-C(9)-C(3)	107.43(13)		

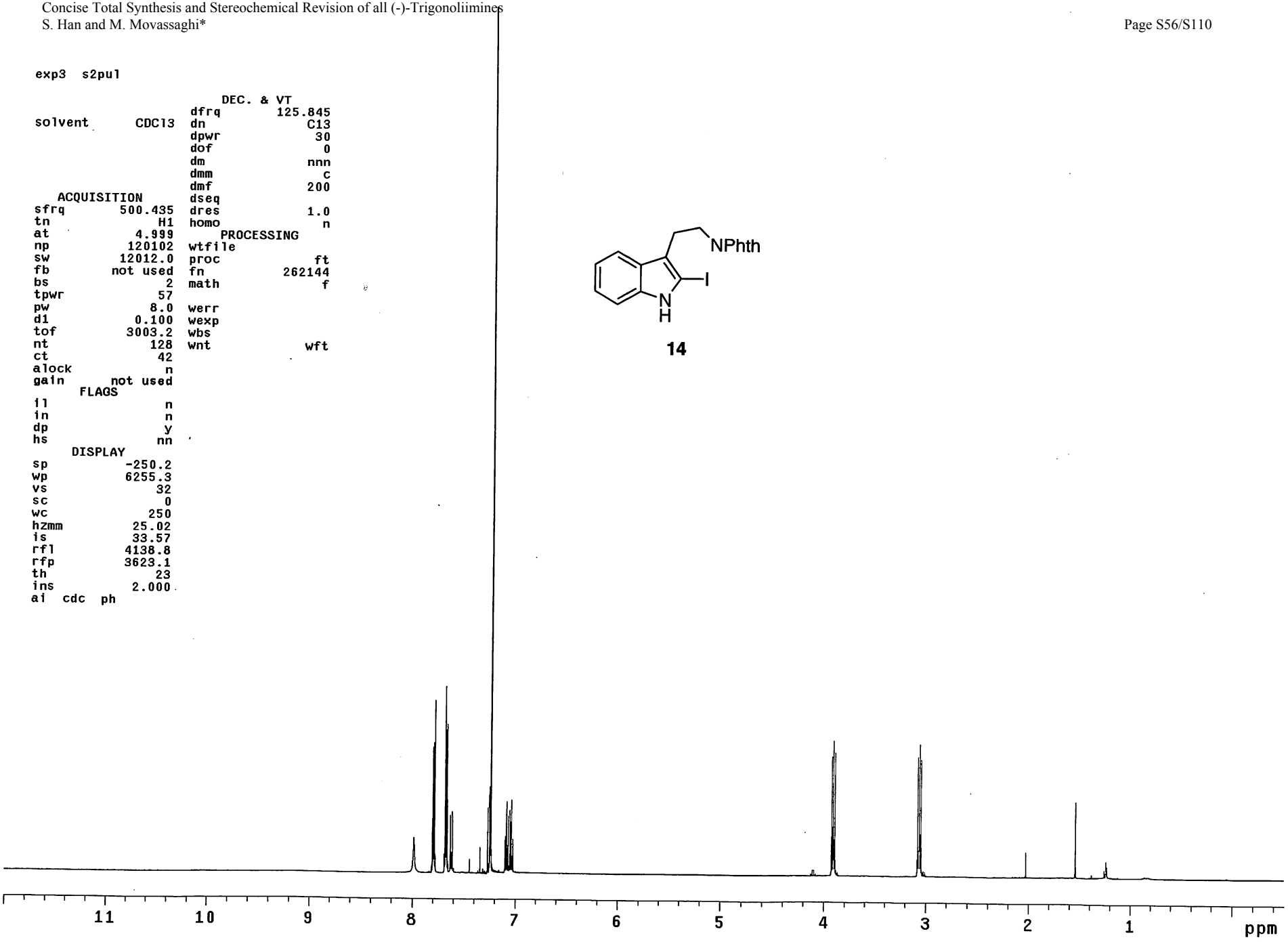
Symmetry transformations used to generate equivalent atoms:

Table S21. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (–)-trigonoliimine C (**3**). 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}
O(1)	39(1)	29(1)	30(1)	2(1)	-2(1)	6(1)
O(2)	25(1)	26(1)	20(1)	3(1)	5(1)	0(1)
N(12)	22(1)	22(1)	18(1)	1(1)	0(1)	2(1)
N(24)	33(1)	18(1)	20(1)	0(1)	-2(1)	4(1)
N(1)	23(1)	22(1)	17(1)	-1(1)	1(1)	4(1)
N(13)	22(1)	20(1)	16(1)	2(1)	2(1)	3(1)
C(21)	24(1)	19(1)	14(1)	-3(1)	-4(1)	-3(1)
C(18)	29(1)	21(1)	18(1)	4(1)	-1(1)	-1(1)
C(16)	22(1)	20(1)	18(1)	-2(1)	-2(1)	0(1)
C(4)	24(1)	23(1)	22(1)	0(1)	2(1)	0(1)
C(15)	24(1)	19(1)	15(1)	-1(1)	-3(1)	-1(1)
C(5)	26(1)	25(1)	19(1)	-3(1)	3(1)	-3(1)
C(6)	27(1)	28(1)	17(1)	1(1)	-2(1)	-5(1)
C(19)	24(1)	21(1)	16(1)	-3(1)	0(1)	-5(1)
C(9)	21(1)	18(1)	21(1)	0(1)	1(1)	-3(1)
C(22)	23(1)	21(1)	19(1)	2(1)	2(1)	1(1)
C(7)	25(1)	23(1)	23(1)	0(1)	-2(1)	1(1)
C(3)	22(1)	19(1)	18(1)	1(1)	2(1)	-1(1)
C(25)	34(1)	22(1)	17(1)	0(1)	-3(1)	1(1)
C(26)	25(1)	30(1)	22(1)	2(1)	5(1)	0(1)
C(23)	34(1)	24(1)	19(1)	1(1)	2(1)	-3(1)
C(11)	20(1)	27(1)	22(1)	3(1)	1(1)	3(1)
C(8)	23(1)	18(1)	19(1)	0(1)	2(1)	0(1)
C(10)	23(1)	31(1)	21(1)	0(1)	2(1)	7(1)
C(2)	20(1)	18(1)	18(1)	2(1)	0(1)	-3(1)
C(14)	21(1)	21(1)	16(1)	0(1)	2(1)	1(1)
C(17)	25(1)	20(1)	21(1)	2(1)	-1(1)	3(1)
C(20)	22(1)	20(1)	17(1)	-3(1)	-2(1)	-1(1)

Table S22. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for (–)-trigonoliimine C (**3**).

	x	y	z	U(eq)
H(24N)	550(30)	-2340(20)	952(6)	28
H(1N)	5110(20)	1760(20)	1977(5)	25
H(13N)	5170(20)	1380(20)	1173(6)	23
H(18)	4947	6947	45	27
H(4)	595	5521	2809	27
H(5)	2171	4925	3410	28
H(6)	4659	2985	3419	29
H(22A)	2515	-114	1433	25
H(22B)	628	926	1480	25
H(7)	5781	1751	2815	28
H(25)	-2290	-2457	863	29
H(26A)	9973	4086	319	39
H(26B)	10217	4334	-161	39
H(26C)	8869	2846	11	39
H(23A)	512	1259	756	31
H(23B)	2330	86	722	31
H(11A)	-964	3235	1474	27
H(11B)	-1954	5110	1428	27
H(10A)	234	6344	1889	30
H(10B)	-1030	4880	2097	30
H(17)	2391	6662	464	26
H(20)	7544	3003	665	24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pw 8.0
d1 0.100
tof 3003.2
nt 128
ct 42
alock n
gain not used
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in n
dp y
hs nn
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wp 6255.3
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sc 0
wc 250
hzmm 25.02
is 33.57
rfl 4138.8
rfp 3623.1
th 23
ins 2.000
ai cdc ph
DEC. & VT
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dn C13
dpwr 30
dof 0
dm nnn
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dmf 200
dseq
dres 1.0
homo n
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math f
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wexp
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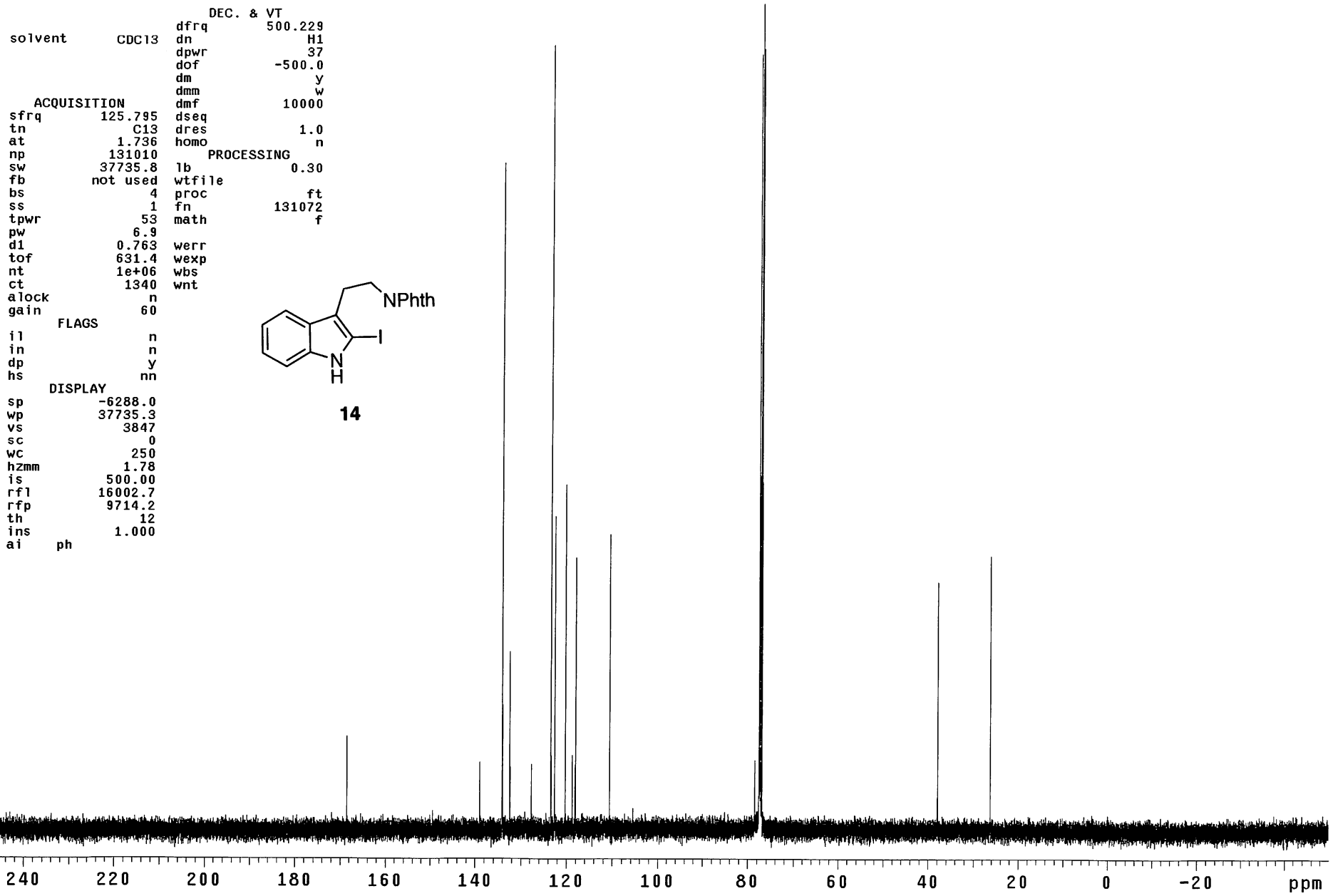
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solvent CDCl3
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sw 37735.8
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homo n
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wexp
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NPhth
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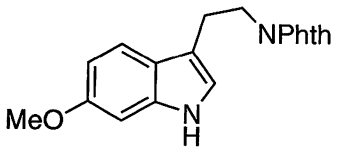
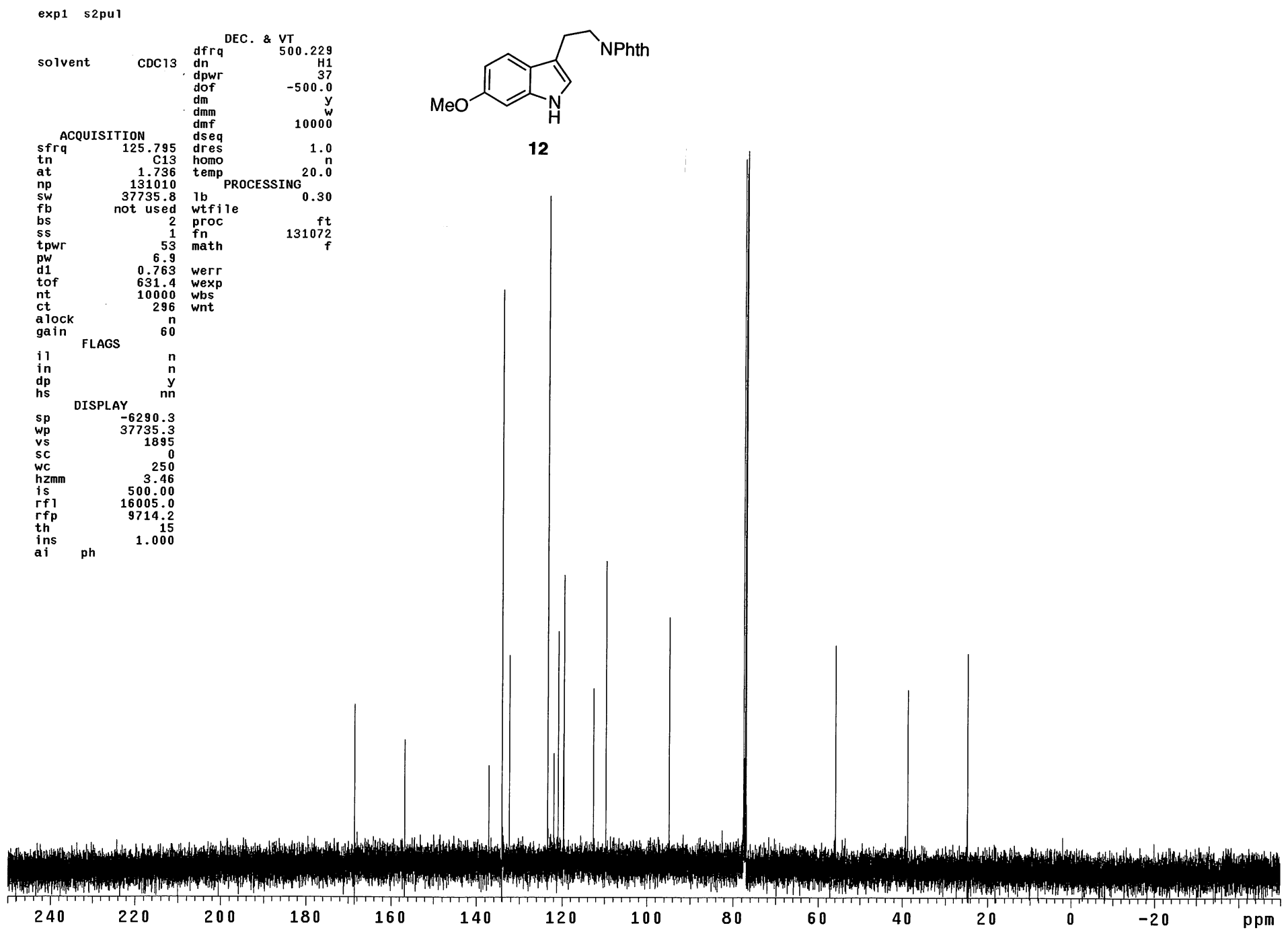
sfrq        500.435   dm              nnn
tn               H1   dmm               c
at            4.999   dmf             200
np           120102   dseq
sw         12012.0    dres            1.0
fb        not used    homo              n
bs               2        PROCESSING
tpwr            57   wtfile
pw             8.0    proc             ft
d1           0.100    fn           262144
tof         3003.2    math              f
nt              32
ct              14   werr
alock            n   wexp
gain      not used    wbs
      FLAGS          wnt             wft
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -250.2
wp          6255.3
vs              18
sc               0
wc             250
hzmm          4.24
is           33.57
rfl          4139.0
rfp          3623.1
th               7
ins          1.000
ai  cdc  ph
```

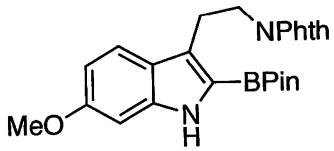


12

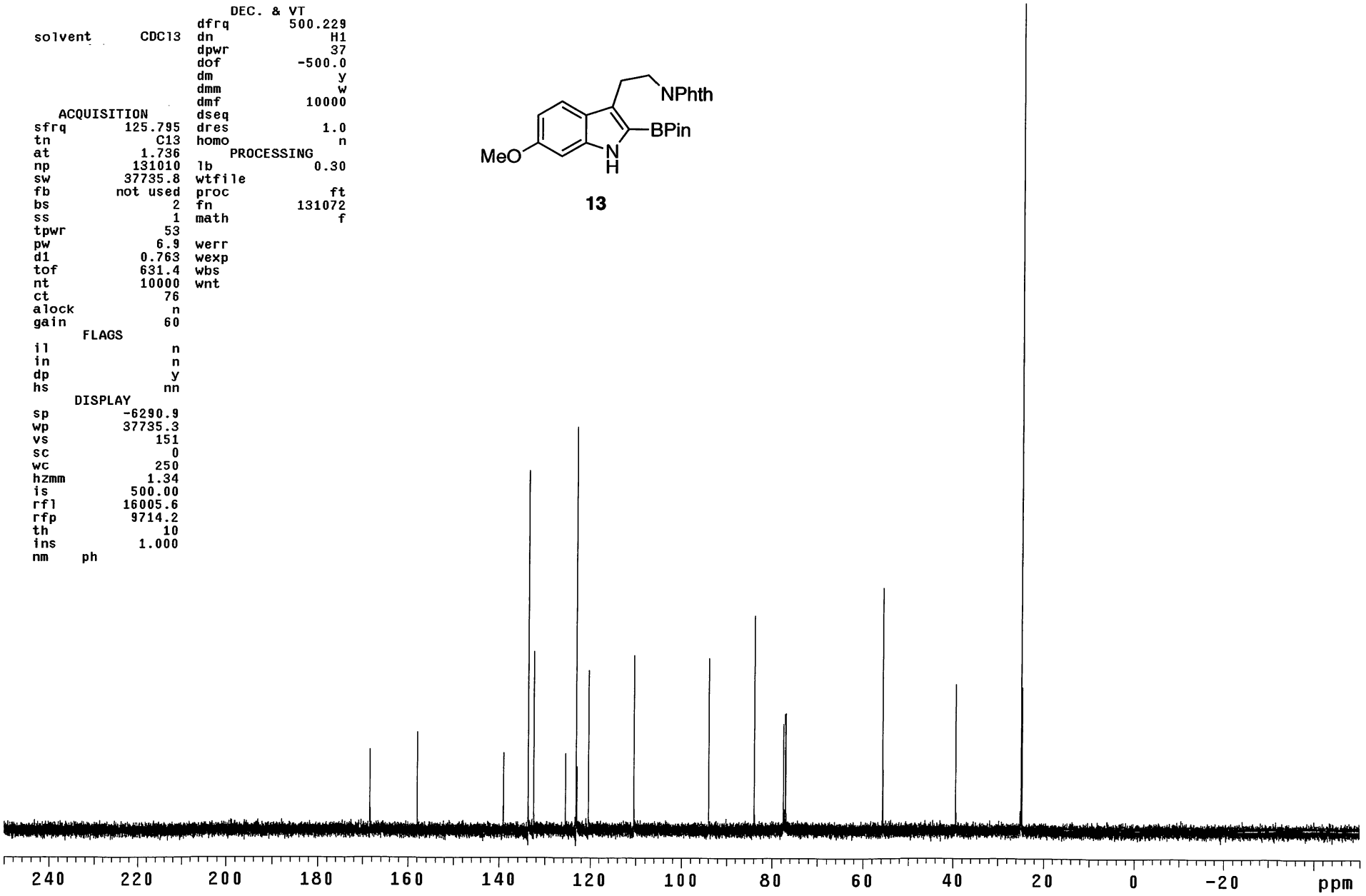

exp1 s2pul
solvent CDCl3
ACQUISITION
sfrq 125.795
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 2
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 10000
ct 296
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -6290.3
wp 37735.3
vs 1895
sc 0
wc 250
hzmm 3.46
is 500.00
rfl 16005.0
rfp 9714.2
th 15
ins 1.000
ai ph
DEC. & VT
dfrq 500.229
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 20.0
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
MeO
N
H
NPhth
12
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

exp2 s2pul

		DEC. & VT	
		dfrq	125.845
solvent	CDCl3	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	500.435	dm	nnn
tn	H1	dmm	c
at	4.999	dmf	200
np	120102	dseq	
sw	12012.0	dres	1.0
fb	not used	homo	n
bs	2	PROCESSING	
tpwr	57	wtfile	
pw	8.0	proc	ft
d1	0.100	fn	262144
tof	3003.2	math	f
nt	32		
ct	14	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	6255.3		
vs	23		
sc	0		
wc	250		
hzmm	1.12		
is	33.57		
rfl	4138.7		
rfp	3623.1		
th	7		
ins	100.000		
ai cdc ph			

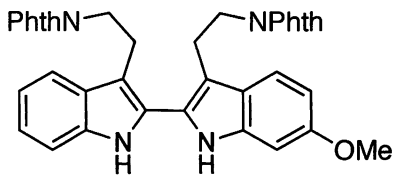


13

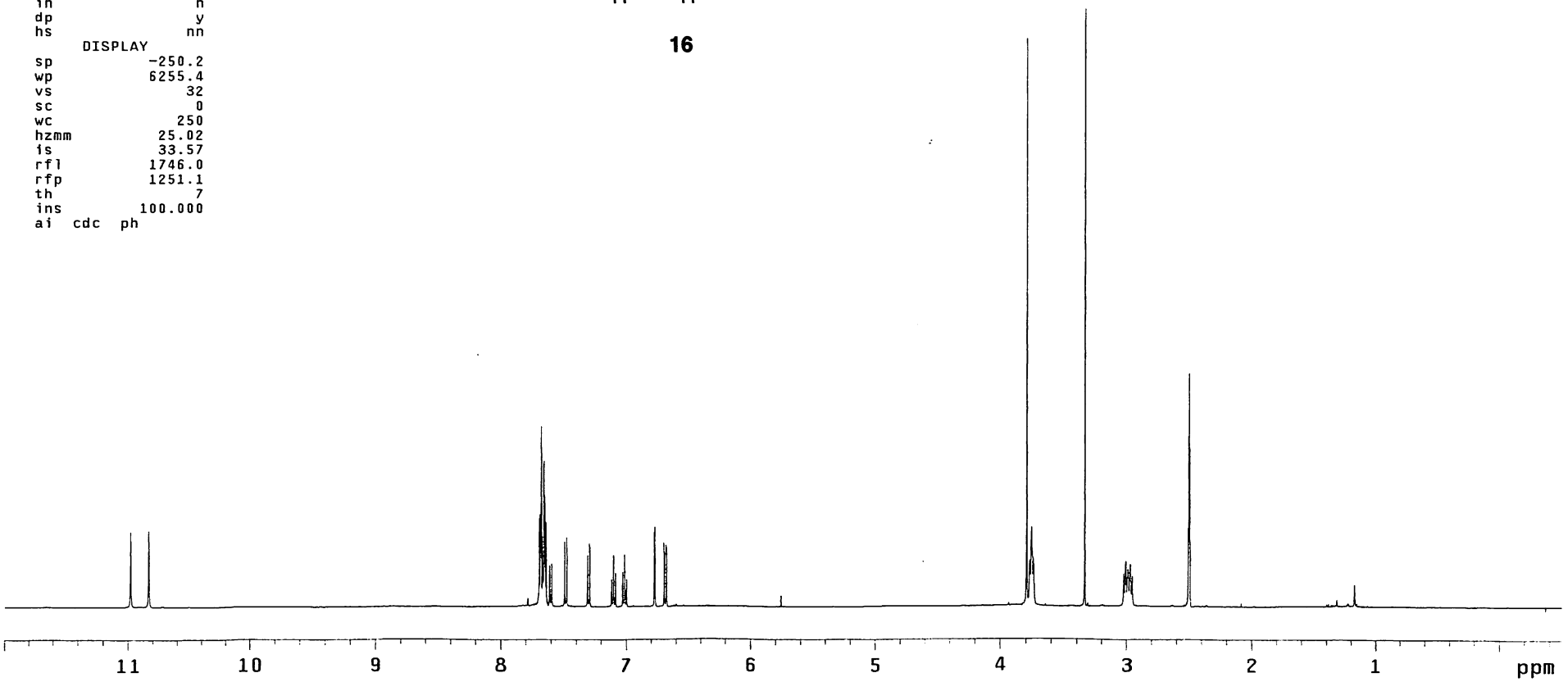

exp1 s2pul
solvent CDCl3
ACQUISITION
sfrq 125.795
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 2
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 10000
ct 76
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -6290.9
wp 37735.3
vs 151
sc 0
wc 250
hzmm 1.34
is 500.00
rfl 16005.6
rfp 9714.2
th 10
ins 1.000
nm ph
DEC. & VT
dfrq 500.229
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
NPhth
BPin
MeO
N
H
13
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

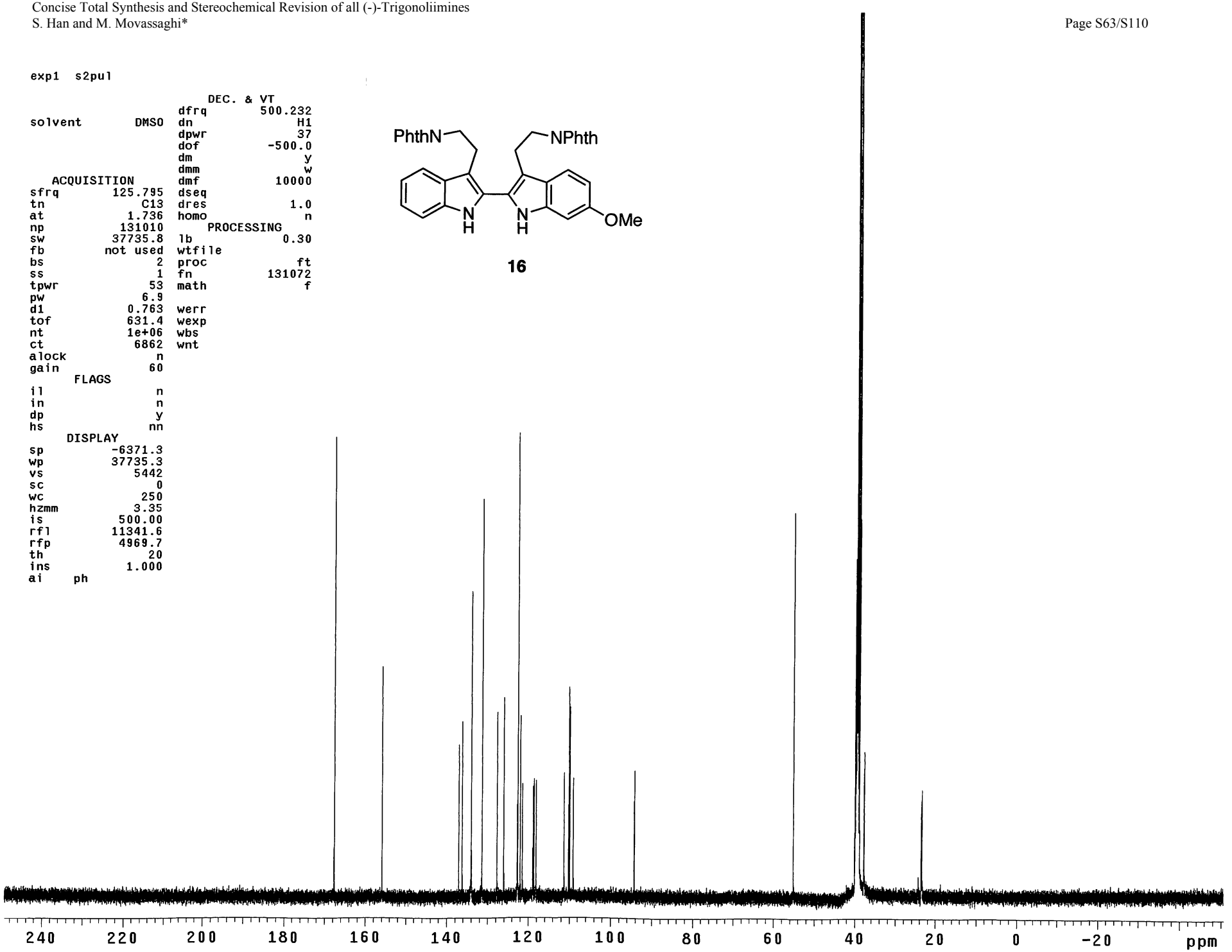
exp2 s2pul

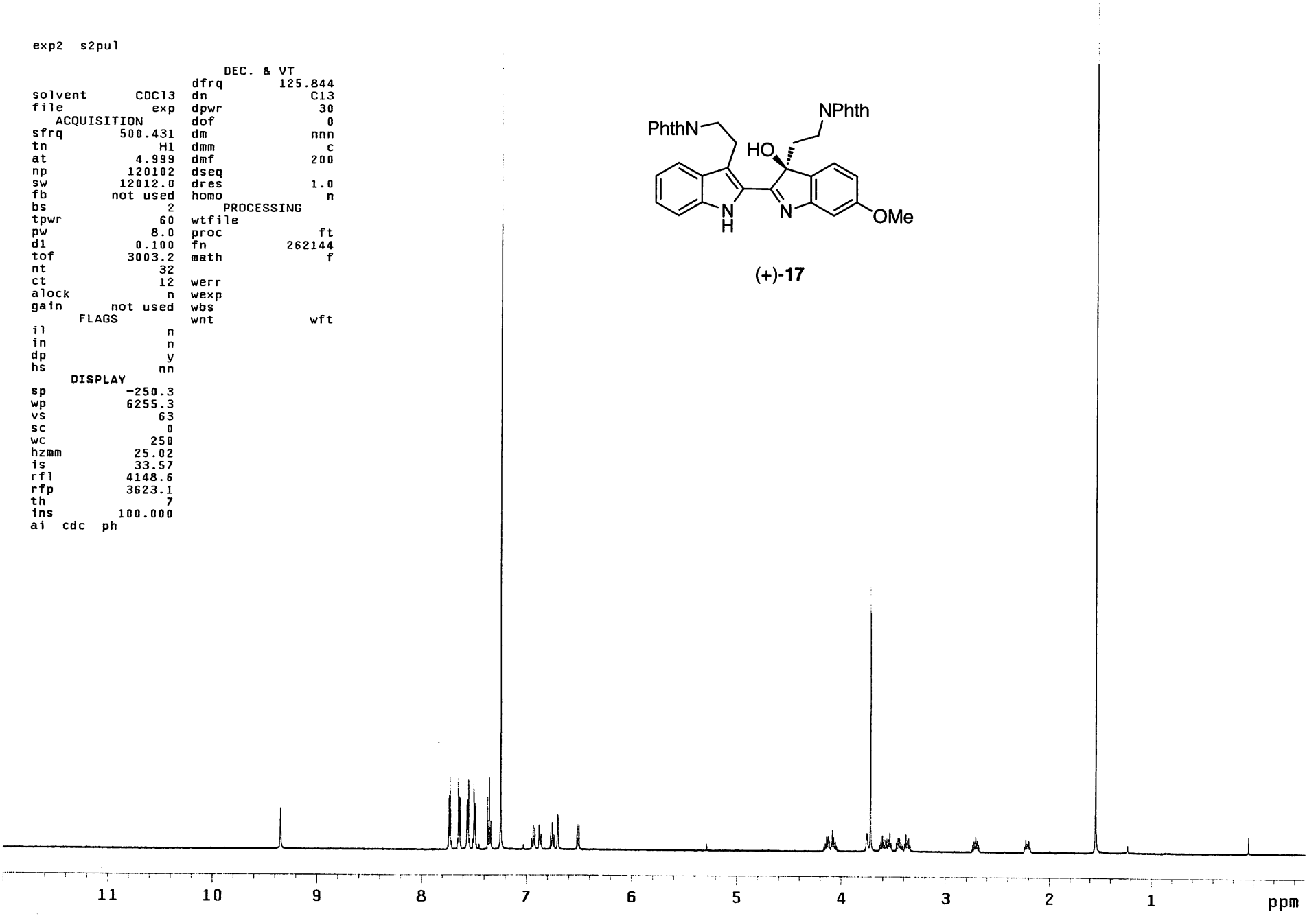
		DEC. & VT	
		dfrq	125.846
solvent	DMSO	dn	C13
		dpwr	30
		dof	0
sfrq	500.437	dm	nnn
tn	H1	dmm	c
at	4.999	dmf	200
np	120102	dseq	
sw	12012.0	dres	1.0
fb	not used	homo	n
bs	2	PROCESSING	
tpwr	57	wtfile	
pw	8.0	proc	ft
d1	0.100	fn	262144
tof	3003.2	math	f
nt	32		
ct	14	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	6255.4		
vs	32		
sc	0		
wc	250		
hzmm	25.02		
is	33.57		
rfl	1746.0		
rfp	1251.1		
th	7		
ins	100.000		
ai cdc ph			



16

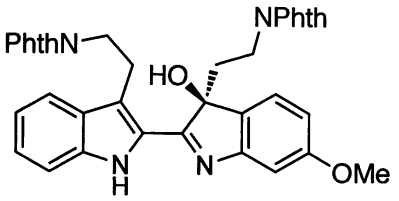



exp1 s2pul
DEC. & VT
dfrq 500.232
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
ACQUISITION
sfrq 125.795
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 2
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 1e+06
ct 6862
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -6371.3
wp 37735.3
vs 5442
sc 0
wc 250
hzmm 3.35
is 500.00
rfl 11341.6
rfp 4969.7
th 20
ins 1.000
ai ph
PhthN
NPhth
N
H
N
H
OMe
16
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

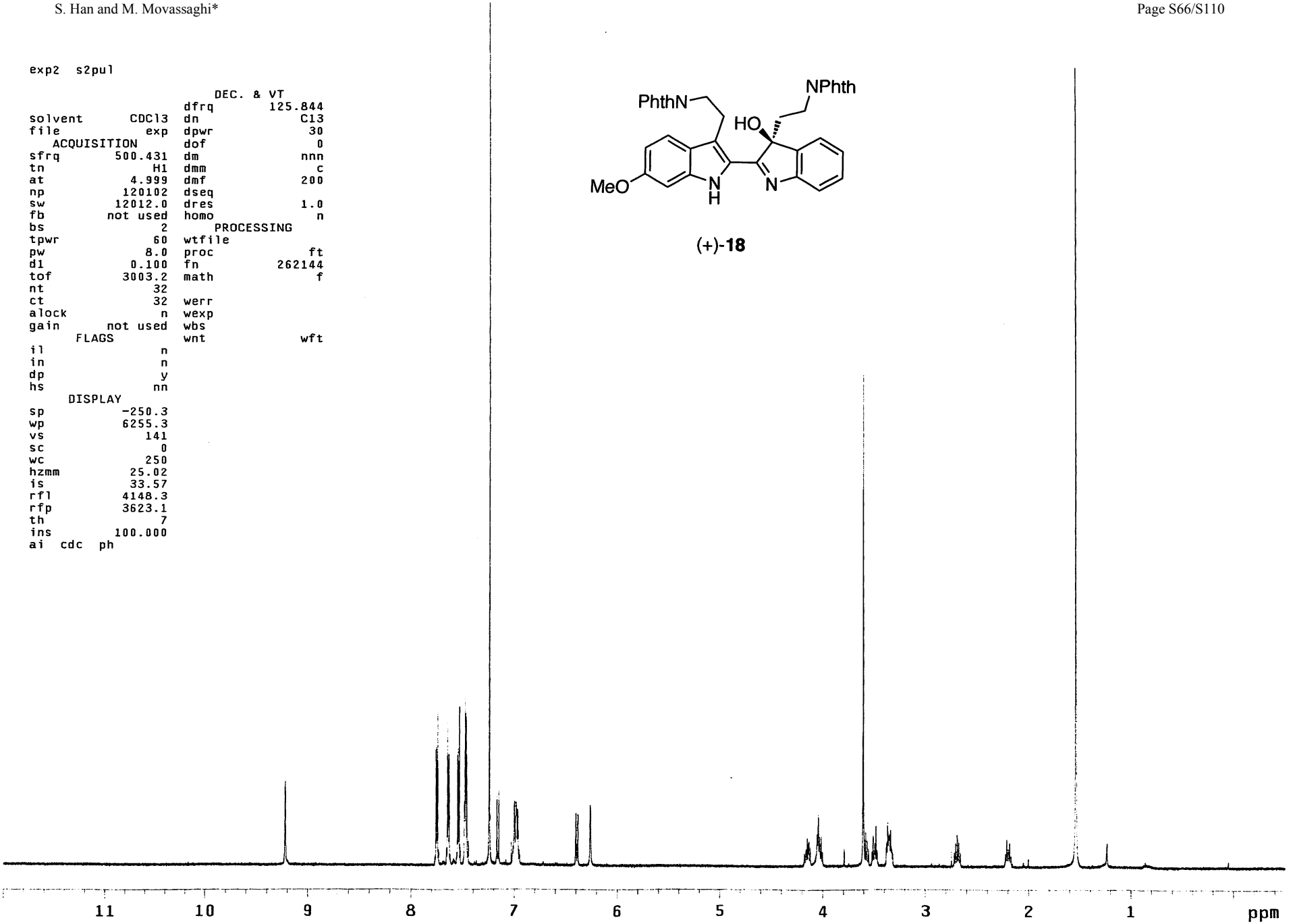

exp2 s2pul
DEC. & VT
solvent CDCl3
file exp
ACQUISITION
sfrq 500.431
tn H1
at 4.999
np 120102
sw 12012.0
fb not used
bs 2
tpwr 60
pw 8.0
d1 0.100
tof 3003.2
nt 32
ct 12
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 6255.3
vs 63
sc 0
wc 250
hzmm 25.02
is 33.57
rfl 4148.6
rfp 3623.1
th 7
ins 100.000
ai cdc ph
dfrq 125.844
dn C13
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
PhthN
NPhth
HO
N
H
N
OMe
(+)-17
11
10
9
8
7
6
5
4
3
2
1
ppm

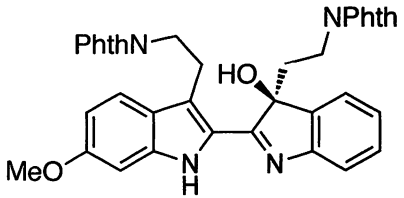
exp1 s2pul

		DEC. & VT	
solvent	CDCl3	dfrq	500.229
		dn	H1
		dpwr	37
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
ACQUISITION		dseq	
sfrq	125.795	dres	1.0
tn	C13	homo	n
at	1.736	PROCESSING	
np	131010	lb	0.30
sw	37735.8	wtfile	
fb	not used	proc	ft
bs	2	fn	131072
ss	1	math	f
tpwr	53		
pw	6.9	werr	
d1	0.763	wexp	
tof	631.4	wbs	
nt	1e+06	wnt	
ct	1162		
alock	n		
gain	60		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-6286.8		
wp	37735.3		
vs	168		
sc	0		
wc	250		
hzmm	1.56		
is	500.00		
rfl	16001.6		
rfp	9714.2		
th	18		
ins	1.000		
nm	ph		



(+)-**17**

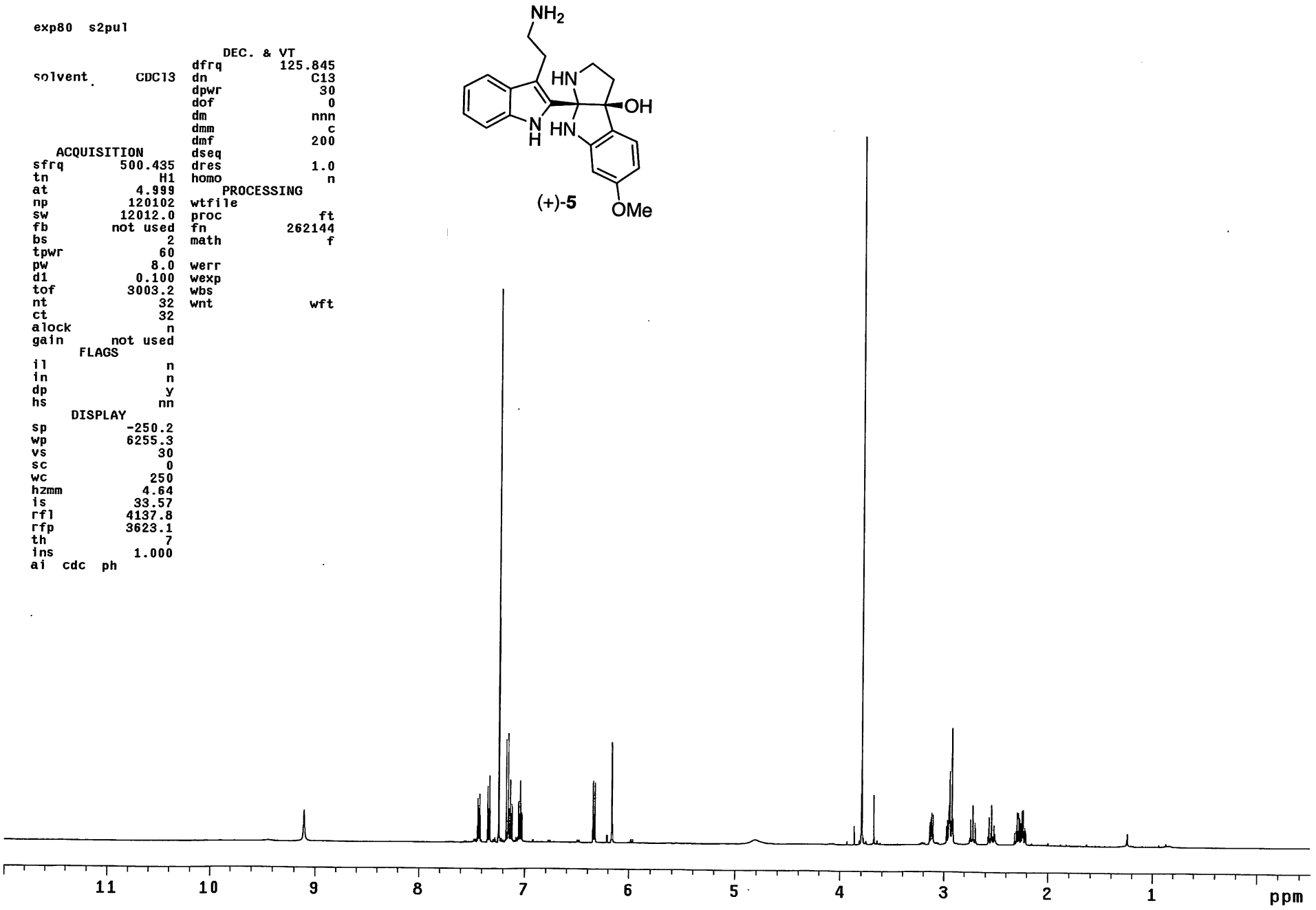

exp2 s2pul
DEC. & VT
solvent CDCl3
file exp
ACQUISITION
sfrq 500.431
tn H1
at 4.999
np 120102
sw 12012.0
fb not used
bs 2
tpwr 60
pw 8.0
d1 0.100
tof 3003.2
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 6255.3
vs 141
sc 0
wc 250
hzmm 25.02
is 33.57
rfl 4148.3
rfp 3623.1
th 7
ins 100.000
ai cdc ph
dfrq 125.844
dn C13
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
PhthN
NPhth
HO
MeO
N
H
N
(+)-18
11
10
9
8
7
6
5
4
3
2
1
ppm



(+)-**18**

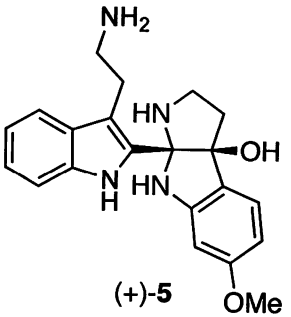
```
exp1  s2pul

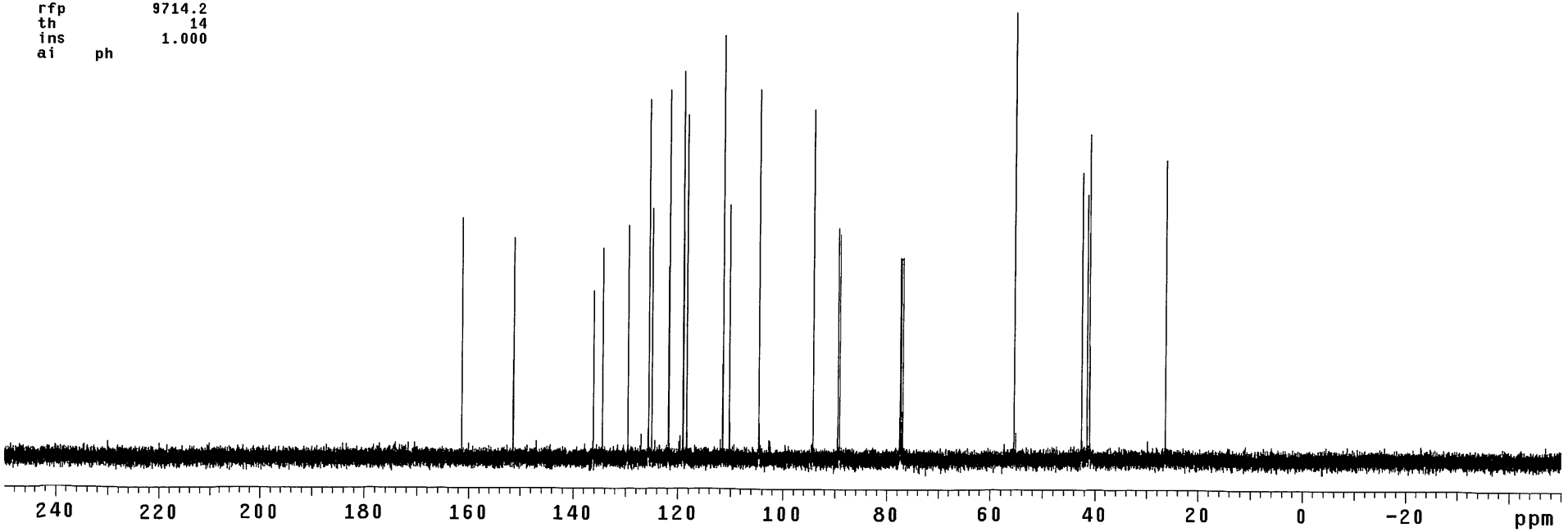
                                    DEC. & VT
                                dfrq        500.229
solvent       CDCl3             dn               H1
                                dpwr              37
                                dof           -500.0
                                dm                y
                                dmm               w
                                dmf           10000
   ACQUISITION                  dseq
sfrq         125.795            dres             1.0
tn               C13            homo              n
at             1.736                PROCESSING
np           131010             lb             0.30
sw          37735.8             wtfile
fb        not used              proc              ft
bs                2             fn           131072
ss                1             math              f
tpwr             53
pw              6.9             werr
d1            0.763             wexp
tof           631.4             wbs
nt           100000             wnt
ct            17052
alock             n
gain             60
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp         -6287.4
wp         37735.3
vs           16132
sc               0
wc             250
hzmm          2.34
is          500.00
rfl        16002.2
rfp         9714.2
th               20
ins           1.000
ai    ph
```


exp80 s2pul
solvent CDCl3
ACQUISITION
sfrq 500.435
tn H1
at 4.999
np 120102
sw 12012.0
fb not used
bs 2
tpwr 60
pw 8.0
d1 0.100
tof 3003.2
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 6255.3
vs 30
sc 0
wc 250
hzmm 4.64
is 33.57
rfl 4137.8
rfp 3623.1
th 7
ins 1.000
ai cdc ph
DEC. & VT
dfrq 125.845
dn C13
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
NH2
HN
OH
N
H
HN
(+)-5
OMe
11
10
9
8
7
6
5
4
3
2
1
ppm

exp1 s2pul

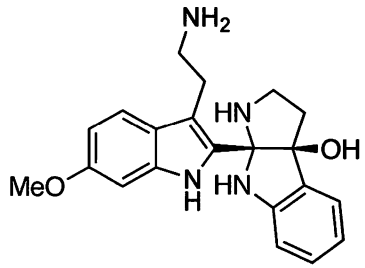
		DEC. & VT	
solvent	CDCl3	dfrq	500.229
		dn	H1
		dpwr	37
		dof	-500.0
		dm	y
		dmm	w
ACQUISITION		dmf	10000
sfrq	125.795	dseq	
tn	C13	dres	1.0
at	1.736	homo	n
np	131010	PROCESSING	
sw	37735.8	lb	0.30
fb	not used	wtfile	
bs	2	proc	ft
ss	1	fn	131072
tpwr	53	math	f
pw	6.9		
d1	0.763	werr	
tof	631.4	wexp	
nt	100000	wbs	
ct	86	wnt	
alock	n		
gain	60		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-6297.8		
wp	37735.3		
vs	626		
sc	0		
wc	250		
hzmm	2.79		
is	500.00		
rfl	16012.5		
rfp	9714.2		
th	14		
ins	1.000		
ai	ph		



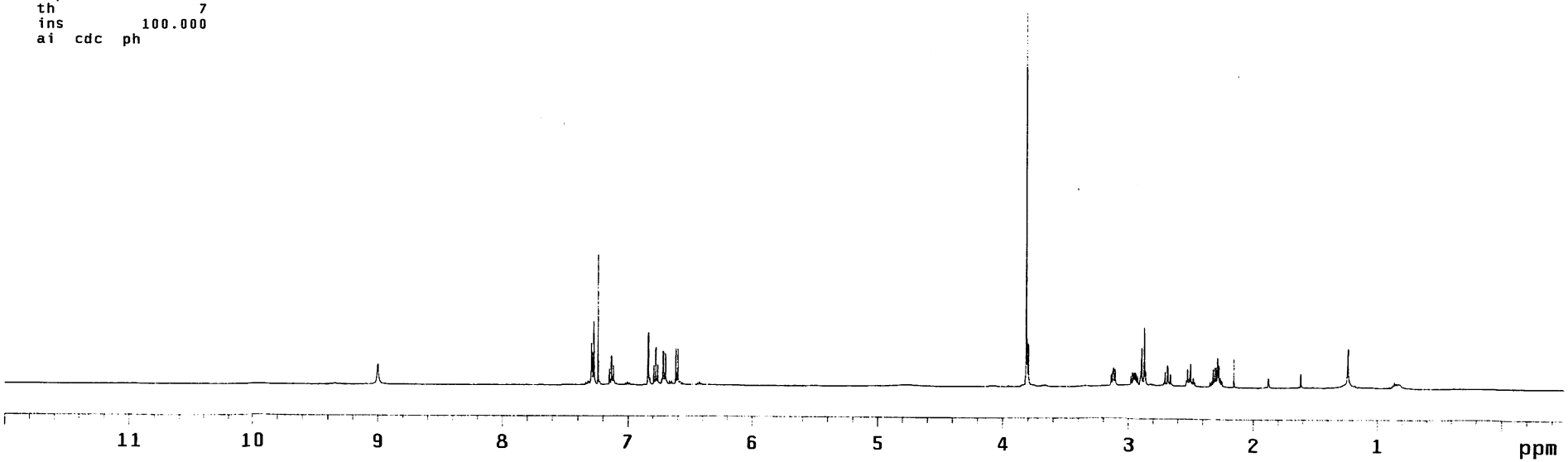


exp2 s2pul

		DEC. & VT	
		dfrq	125.844
solvent	CDCl3	dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	2	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	32	wbs	
ct	10	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.3		
wp	6255.3		
vs	20		
sc	0		
wc	250		
hzmm	25.02		
is	33.57		
rfl	4147.8		
rfp	3623.1		
th	7		
ins	100.000		
ai cdc ph			

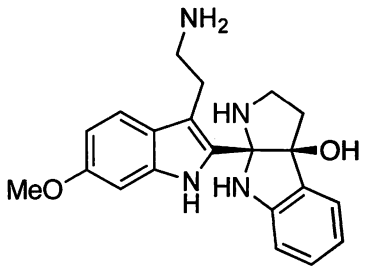


(+)-**6**

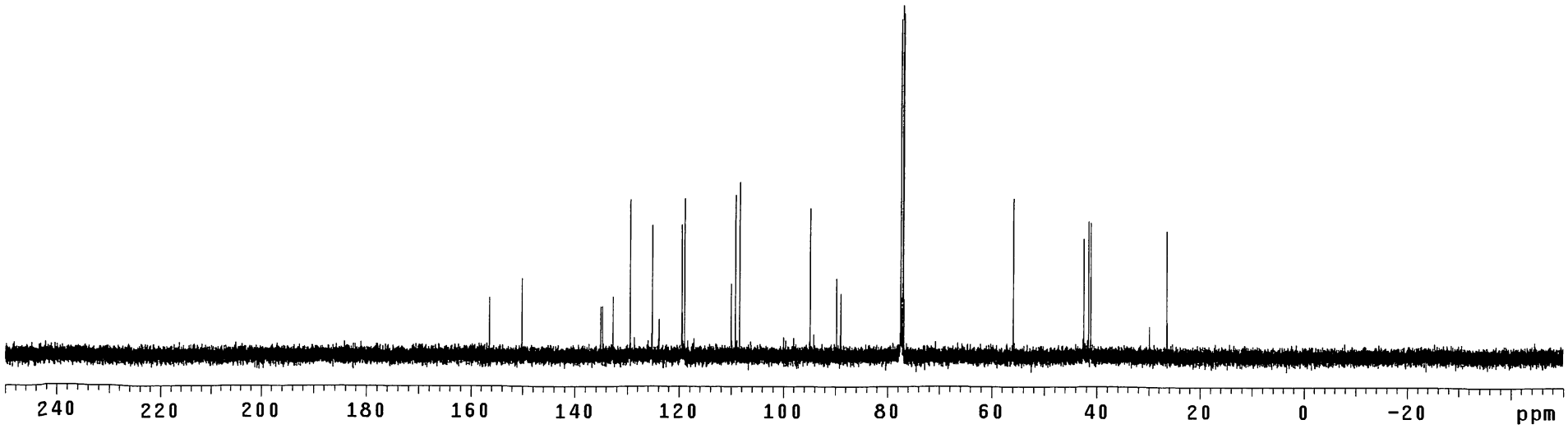


exp1 s2pul

		DEC. & VT	
		dfrq	500.229
solvent	CDCl3	dn	H1
		dpwr	37
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
ACQUISITION		dseq	
sfrq	125.795	dres	1.0
tn	C13	homo	n
at	1.736	PROCESSING	
np	131010	lb	0.30
sw	37735.8	wtfile	
fb	not used	proc	ft
bs	2	fn	131072
ss	1	math	f
tpwr	53		
pw	6.9	werr	
d1	0.763	wexp	
tof	631.4	wbs	
nt	10000	wnt	
ct	420		
alock	n		
gain	60		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-6289.1		
wp	37735.3		
vs	1242		
sc	0		
wc	250		
hzmm	2.45		
is	500.00		
rfl	16003.9		
rfp	9714.2		
th	15		
ins	1.000		
ai	ph		

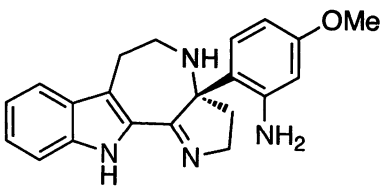


(+)-**6**



exp2 s2pul

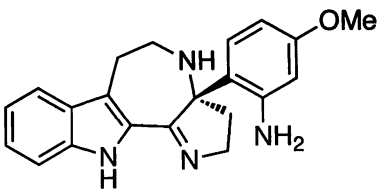
		DEC. & VT	
		dfrq	125.844
solvent	CDCl3	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	500.431	dm	nnn
tn	H1	dmm	c
at	4.999	dmf	200
np	120102	dseq	
sw	12012.0	dres	1.0
fb	not used	homo	n
bs	2	PROCESSING	
tpwr	60	wtfile	
pw	8.0	proc	ft
d1	0.100	fn	262144
tof	3003.2	math	f
nt	32		
ct	10	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.3		
wp	6255.3		
vs	29		
sc	0		
wc	250		
hzmm	25.02		
is	33.57		
rfl	4149.1		
rfp	3623.1		
th	7		
ins	100.000		
ai cdc ph			



(–)-**19**

exp1 s2pul

		DEC. & VT	
solvent	CDCl3	dfrq	500.229
		dn	H1
		dpwr	37
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
ACQUISITION		dseq	
sfrq	125.795	dres	1.0
tn	C13	homo	n
at	1.736	PROCESSING	
np	131010	lb	0.30
sw	37735.8	wtfile	
fb	not used	proc	ft
bs	2	fn	131072
ss	1	math	f
tpwr	53		
pw	6.9	werr	
d1	0.763	wexp	
tof	631.4	wbs	
nt	100000	wnt	
ct	2952		
alock	n		
gain	60		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-6286.8		
wp	37735.3		
vs	11673		
sc	0		
wc	250		
hzmm	2.79		
is	500.00		
rfl	16001.6		
rfp	9714.2		
th	10		
ins	1.000		
ai	ph		

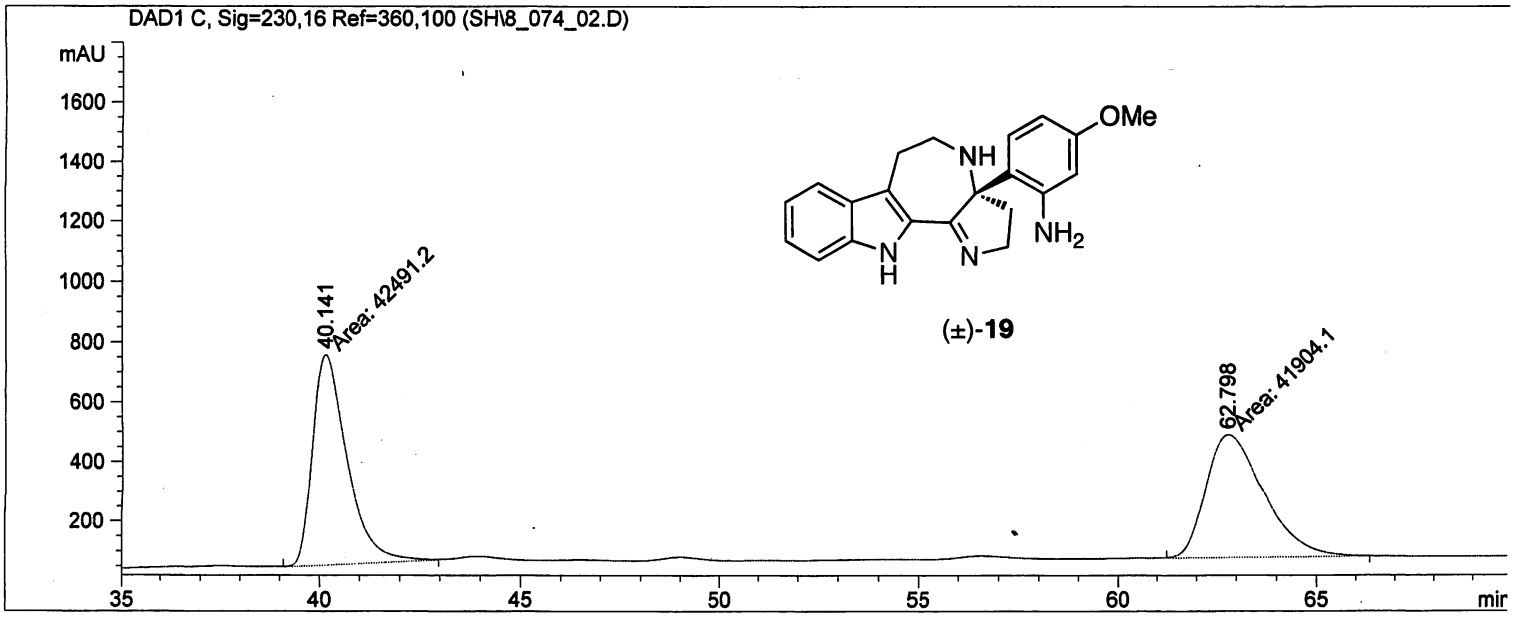


(–)-**19**

Chiralcell OD-H 0.5mL/min, 100% Hexane -> 80:20=iPrOH:H
x in 80 min

```
==========================================================================
Injection Date  :                                  Seq. Line :   6
Sample Name     :                                   Location : Vial 27
Acq. Operator   :                                        Inj :   1
                                                  Inj Volume : 0 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 10 µl
Acq. Method     :
Last changed    :
Analysis Method :
Last changed    :

==========================================================================
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=230,16 Ref=360,100

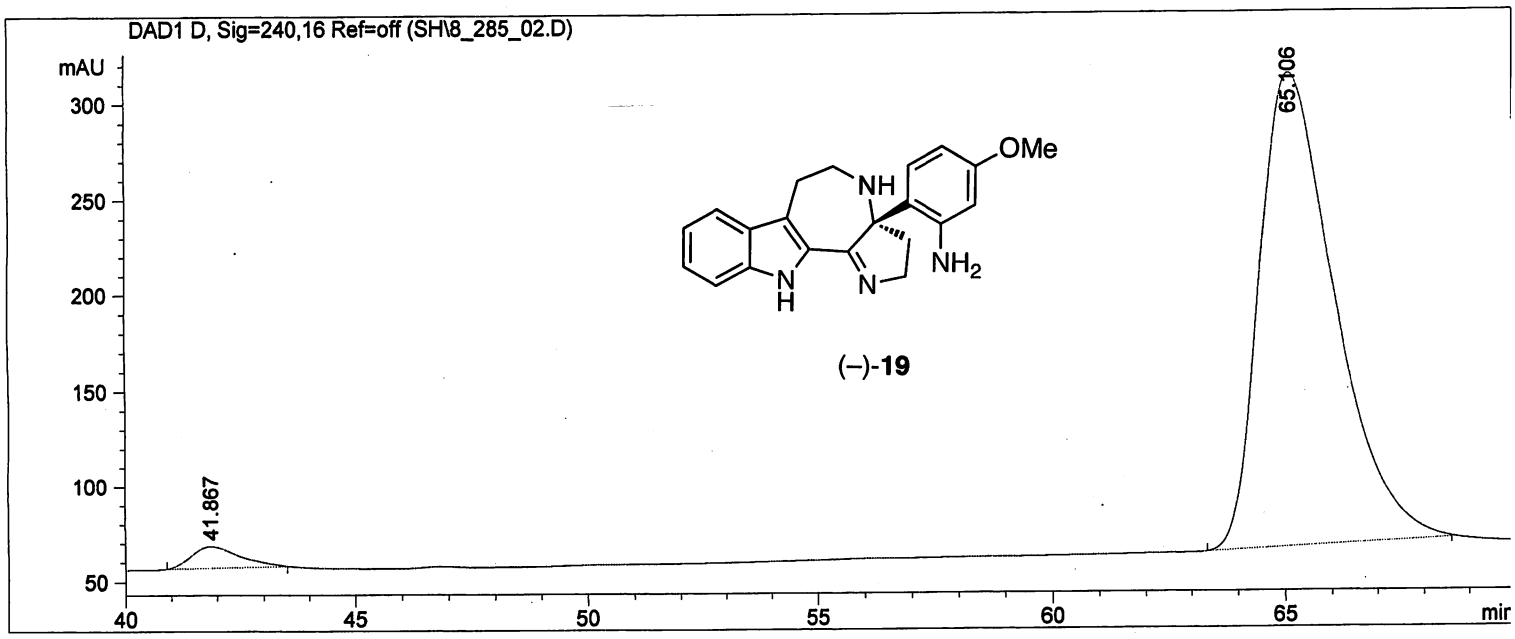
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  40.141 MM    1.0038 4.24912e4   705.52020  50.3479
   2  62.798 MM    1.6881 4.19041e4   413.71451  49.6521

Totals :                  8.43953e4  1119.23471

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

chiralpak OD-H 100%Hexanes to 80% IPrOH over 80 min

```
==========================================================================
Injection Date  :                                    Seq. Line :   1
Sample Name     :                                     Location : Vial 24
Acq. Operator   :                                         Inj :   1
                                                   Inj Volume : 0 µl
Different Inj Volume from Sequence !      Actual Inj Volume : 3 µl
Acq. Method     :
Last changed    :
Analysis Method :
Last changed    :
==========================================================================
```



(–)-**19**

```
==========================================================================
                          Area Percent Report
==========================================================================

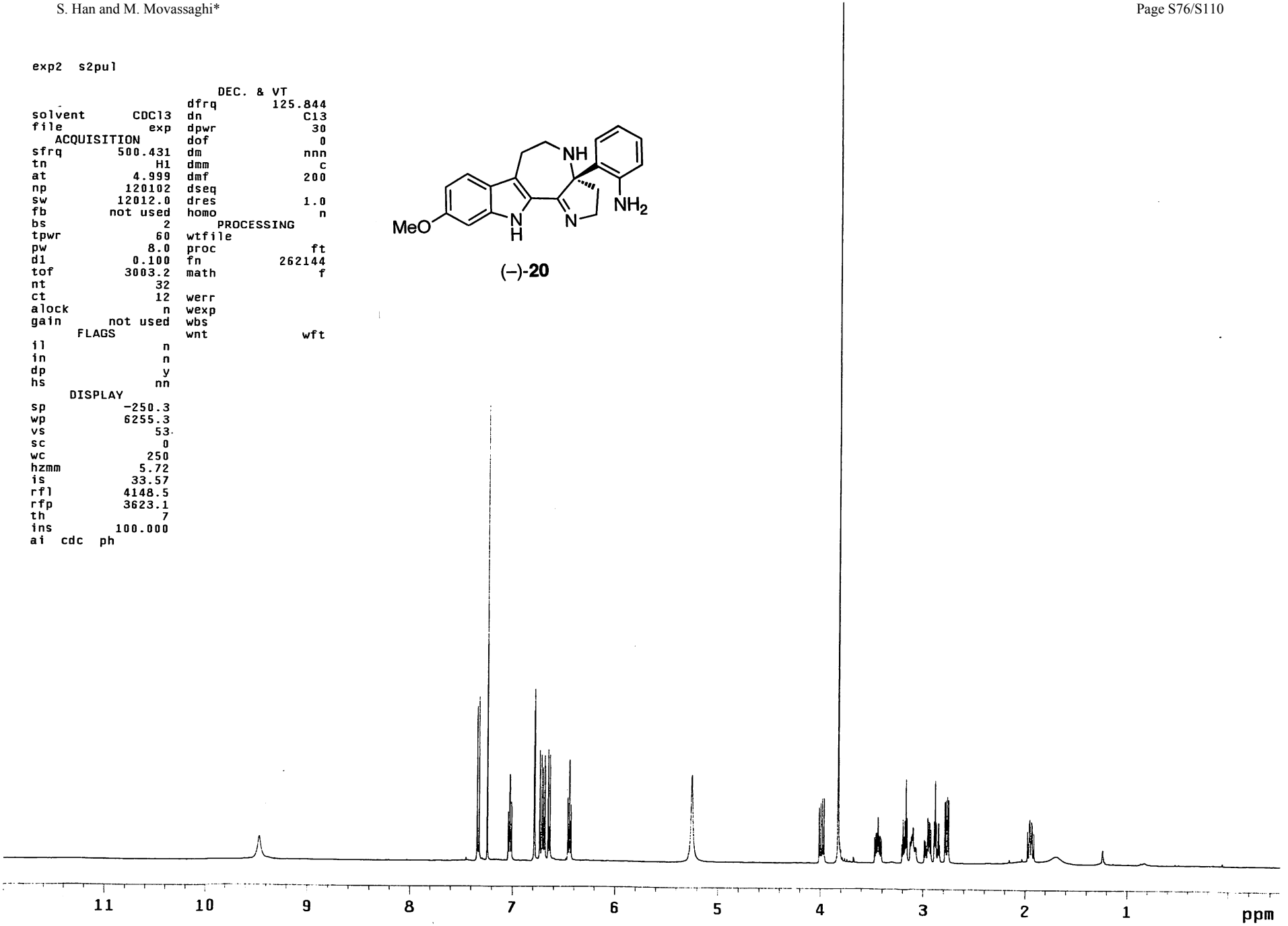
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

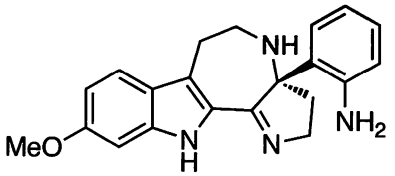

Signal 1: DAD1 D, Sig=240,16 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  41.867 BB    0.8883  854.34039   11.46530   3.0007
   2  65.106 BB    1.5928 2.76173e4   247.50766  96.9993

Totals :                  2.84717e4   258.97296

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```


exp2 s2pul
solvent CDCl3
file exp
ACQUISITION
sfrq 500.431
tn H1
at 4.999
np 120102
sw 12012.0
fb not used
bs 2
tpwr 60
pw 8.0
d1 0.100
tof 3003.2
nt 32
ct 12
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 6255.3
vs 53
sc 0
wc 250
hzmm 5.72
is 33.57
rfl 4148.5
rfp 3623.1
th 7
ins 100.000
ai cdc ph
DEC. & VT
dfrq 125.844
dn C13
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
NH
NH2
MeO
N
H
N
(–)-20
11
10
9
8
7
6
5
4
3
2
1
ppm



(–)-**20**

```
exp1  s2pul

solvent      CDCl3

   ACQUISITION
sfrq        125.795
tn              C13
at             1.736
np            131010
sw          37735.8
fb        not used
bs                2
ss                1
tpwr             53
pw              6.9
d1            0.763
tof           631.4
nt            10000
ct             1298
alock             n
gain             60
      FLAGS
il                n
in                n
dp                y
hs               nn
    DISPLAY
sp          -6289.7
wp          37735.3
vs             4012
sc                0
wc              250
hzmm           4.13
is           500.00
rfl         16004.5
rfp          9714.2
th                18
ins            1.000
ai    ph

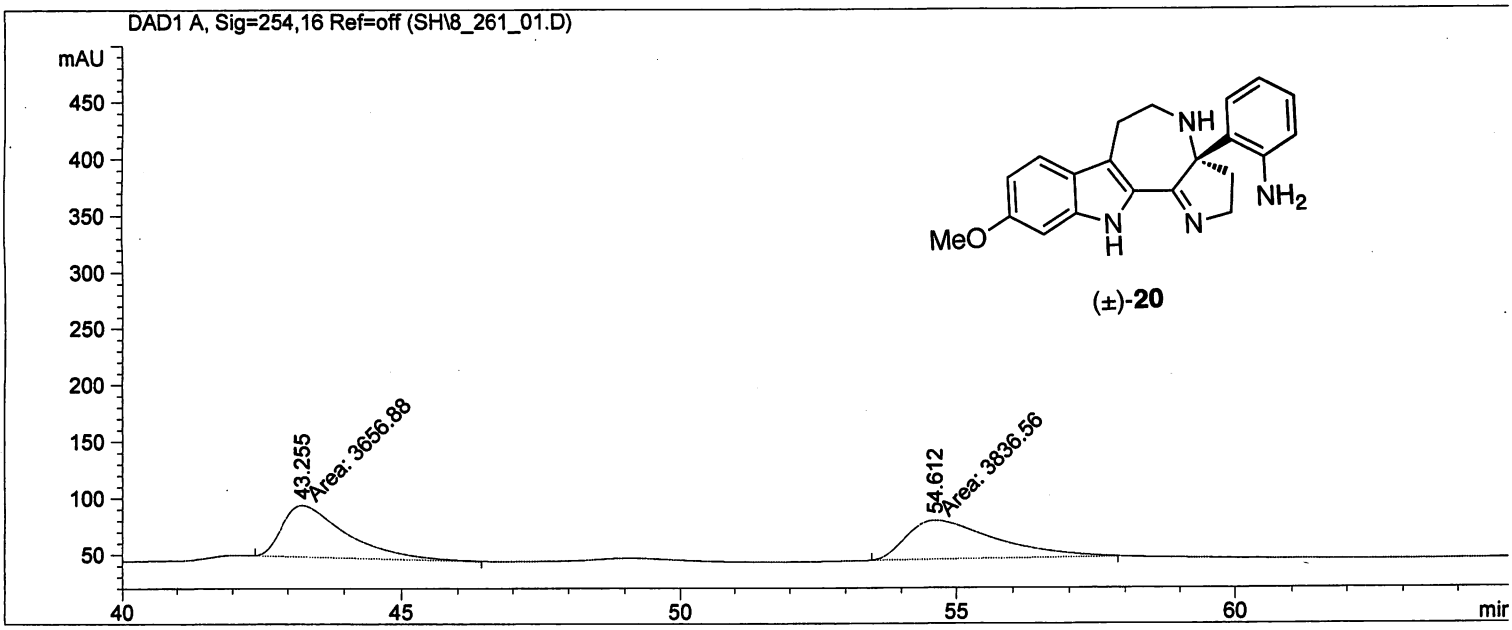
          DEC. & VT
dfrq        500.229
dn               H1
dpwr             37
dof          -500.0
dm                y
dmm               w
dmf           10000
dseq
dres            1.0
homo              n
     PROCESSING
lb              0.30
wtfile
proc              ft
fn           131072
math              f

werr
wexp
wbs
wnt
```

OD-H 100%Hexanes->80%IPA:20%Hxns over 80 min

```
==========================================================================
Injection Date  :                                  Seq. Line :   1
Sample Name     :                                   Location : Vial 23
Acq. Operator   :                                       Inj :   1
                                                 Inj Volume : 0 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 10 µl
Acq. Method     :
Last changed    :
Analysis Method :
Last changed    :

==========================================================================
```



(±)-**20**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,16 Ref=off

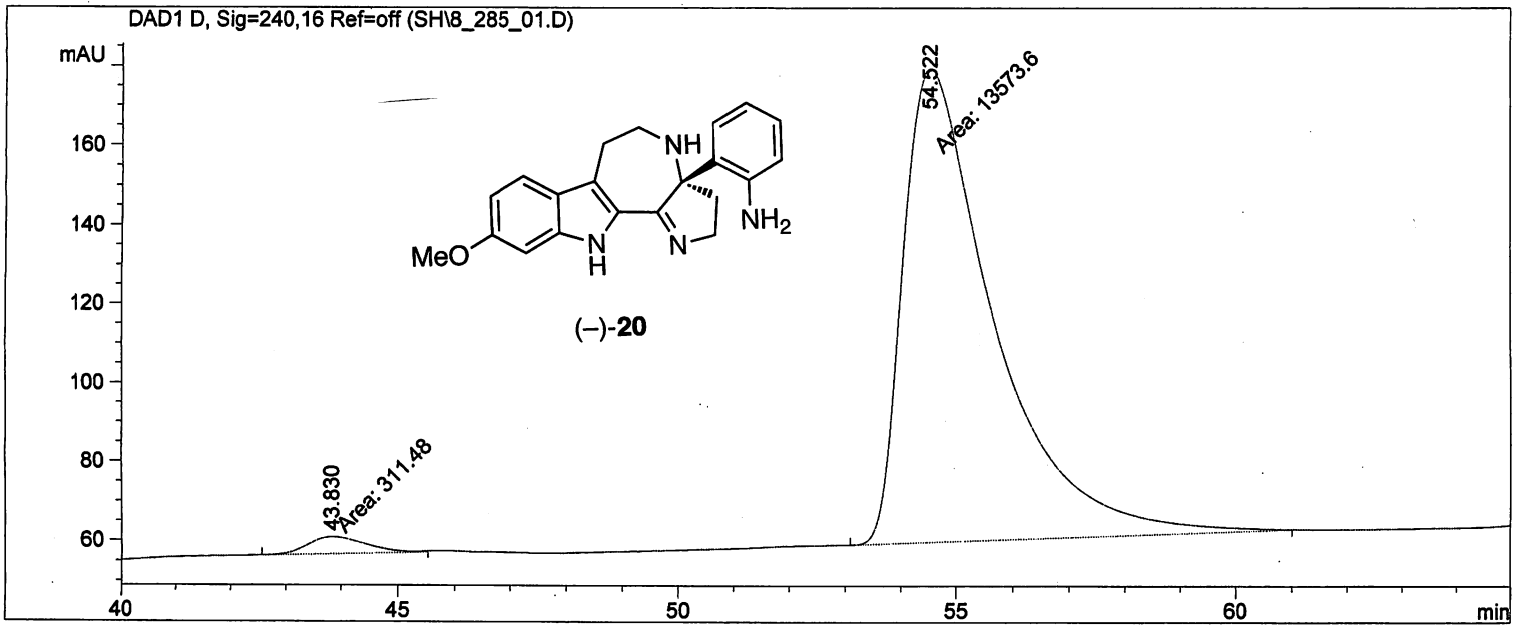
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  43.255 MM    1.3339 3656.88037   45.69140  48.8011
   2  54.612 MM    1.8544 3836.56177   34.48214  51.1989

Totals :                  7493.44214   80.17355

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

chiralpak OD-H 100%Hexanes to 80% IPrOH over 80 min

```
==========================================================================
Injection Date  :                                  Seq. Line :   1
Sample Name     :                                   Location : Vial 26
Acq. Operator   :                                        Inj :   1
                                                  Inj Volume : 0 µl
Different Inj Volume from Sequence !      Actual Inj Volume : 10 µl
Acq. Method     :
Last changed    :
Analysis Method :
Last changed    :
==========================================================================
```




```
==========================================================================
                          Area Percent Report
==========================================================================

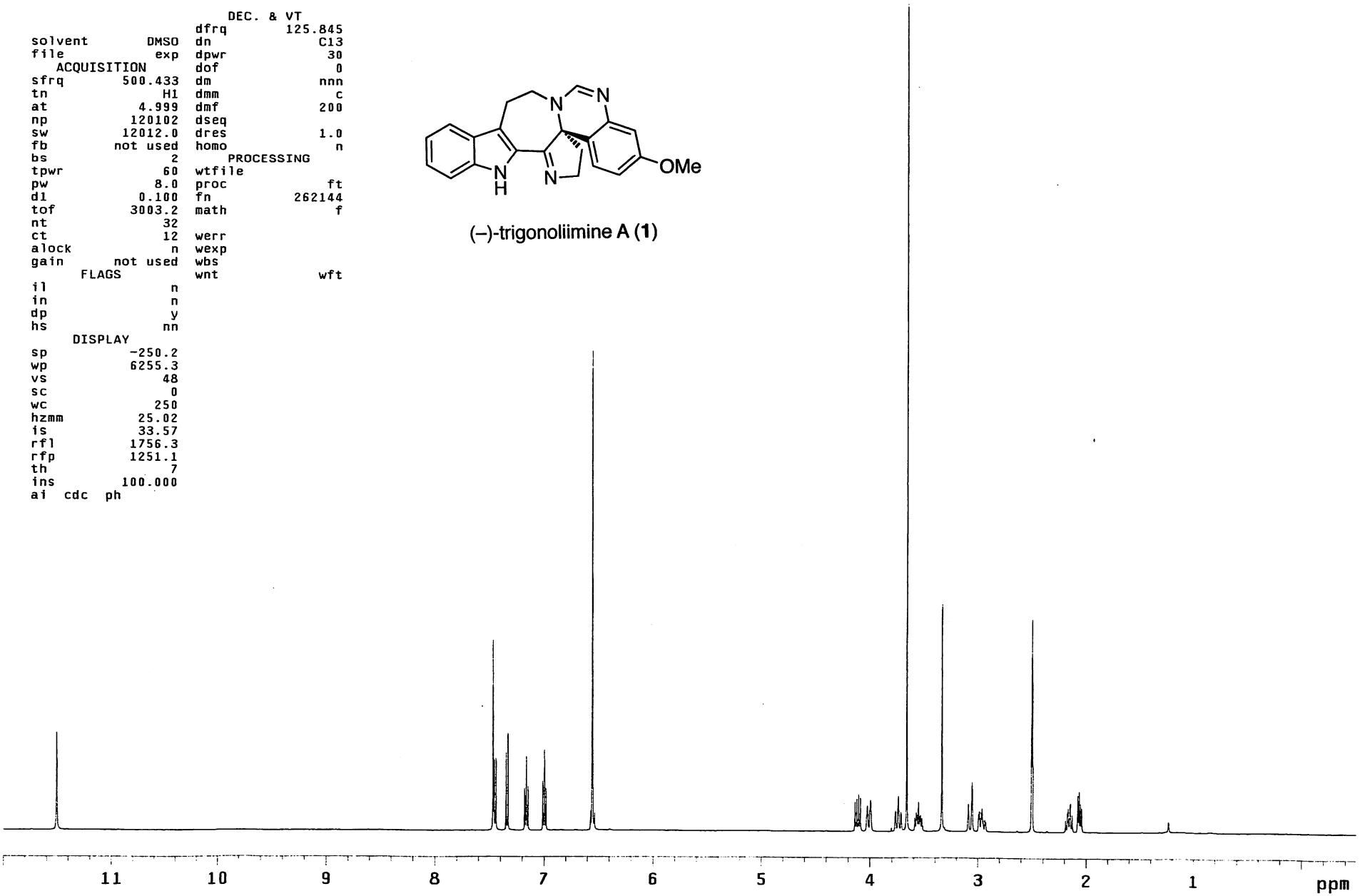
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=240,16 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  43.830 MM    1.2124  311.47989    4.28179   2.2433
   2  54.522 MM    1.8907 1.35736e4   119.65495  97.7567

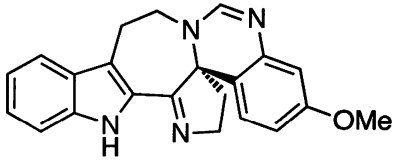
Totals :                  1.38851e4   123.93674

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```


exp2 s2pul
solvent DMSO
file exp
ACQUISITION
sfrq 500.433
tn H1
at 4.999
np 120102
sw 12012.0
fb not used
bs 2
tpwr 60
pw 8.0
d1 0.100
tof 3003.2
nt 32
ct 12
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 6255.3
vs 48
sc 0
wc 250
hzmm 25.02
is 33.57
rfl 1756.3
rfp 1251.1
th 7
ins 100.000
ai cdc ph
DEC. & VT
dfrq 125.845
dn C13
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
N
N
N
H
N
OMe
(–)-trigonoliimine A (1)
11
10
9
8
7
6
5
4
3
2
1
ppm

exp2 s2pul

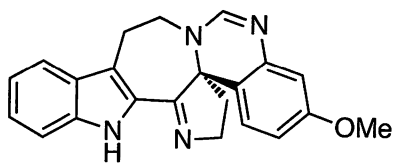
		DEC. & VT	
		dfrq	125.844
solvent	CD3OD	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	500.433	dm	nnn
tn	H1	dmm	c
at	4.999	dmf	200
np	120102	dseq	
sw	12012.0	dres	1.0
fb	not used	homo	n
bs	2	PROCESSING	
tpwr	60	wtfile	
pw	8.0	proc	ft
d1	0.100	fn	262144
tof	3003.2	math	f
nt	32		
ct	10	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	6255.3		
vs	50		
sc	0		
wc	250		
hzmm	25.02		
is	33.57		
rfl	2170.5		
rfp	1656.4		
th	7		
ins	100.000		
ai cdc ph			



(–)-trigonoliimine A (**1**)
($CDCl_3$:CD_3OD = 3:1)

```
exp1  s2pul

                          DEC. & VT
                      dfrq        500.232
solvent       DMSO    dn               H1
                      dpwr             37
                      dof          -500.0
                      dm                y
                      dmm               w
                      dmf           10000
   ACQUISITION        dseq
sfrq        125.795   dres             1.0
tn              C13   homo              n
at            1.736       PROCESSING
np           131010   lb             0.30
sw          37735.8   wtfile
fb        not used    proc             ft
bs                2   fn           131072
ss                1   math              f
tpwr             53
pw              6.9   werr
d1            0.763   wexp
tof           631.4   wbs
nt           100000   wnt
ct              832
alock             n
gain             18
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp          -6371.3
wp          37735.3
vs           635796
sc                0
wc              250
hzmm         150.94
is           500.00
rfl         11341.6
rfp          4969.7
th               20
ins           1.000
ai    ph
```

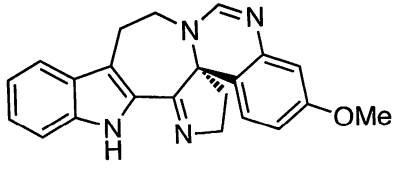


(–)-trigonoliimine A (**1**)

CDCl3/MeOD

exp1 s2pul

		DEC. & VT	
		dfrq	500.231
solvent	CD3OD	dn	H1
		dpwr	37
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
ACQUISITION		dseq	
sfrq	125.795	dres	1.0
tn	C13	homo	n
at	1.736	PROCESSING	
np	131010	lb	0.30
sw	37735.8	wtfile	
fb	not used	proc	ft
bs	2	fn	131072
ss	1	math	f
tpwr	53		
pw	6.9	werr	
d1	0.763	wexp	
tof	631.4	wbs	
nt	100000	wnt	
ct	914		
alock	n		
gain	60		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-6259.7		
wp	37735.3		
vs	3537		
sc	0		
wc	250		
hzmm	1.00		
is	500.00		
rfl	12442.5		
rfp	6182.2		
th	7		
ins	1.000		
ai ph			

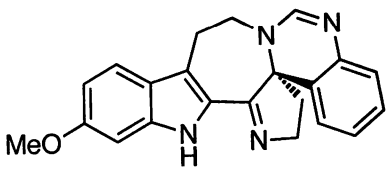


(–)-trigonoliimine A (**1**)
($CDCl_3$:CD_3OD = 3:1)

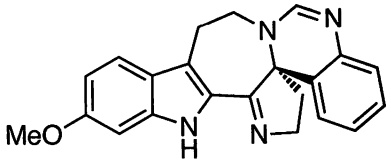
```
exp2  s2pul

                        DEC. & VT
                    dfrq        125.673
solvent       CD3OD dn              C13
file            exp dpwr             30
   ACQUISITION      dof               0
sfrq        499.748 dm              nnn
tn               H1 dmm               w
at            3.001 dmf           10000
np            63050 dseq
sw          10504.2 dres             1.0
fb        not used  homo              n
bs               2          DEC2
tpwr            56 dfrq2             0
pw             8.6 dn2
d1           2.000 dpwr2             1
tof         1519.5 dof2              0
nt              16 dm2               n
ct              10 dmm2              c
alock            n dmf2            200
gain      not used  dseq2
      FLAGS        dres2            1.0
il               n homo2             n
in               n          DEC3
dp               y dfrq3             0
hs              nn dn3
     DISPLAY       dpwr3            1
sp          -249.9 dof3              0
wp          6246.7 dm3               n
vs              34 dmm3              c
sc               0 dmf3            200
wc             250 dseq3
hzmm         24.99 dres3            1.0
is           33.57 homo3             n
rfl         2889.9      PROCESSING
rfp         1654.2 wtfile
th               7 proc              ft
ins        100.000 fn           262144
ai  cdc  ph        math              f

                   werr
                   wexp
                   wbs
                   wnt             wft
```



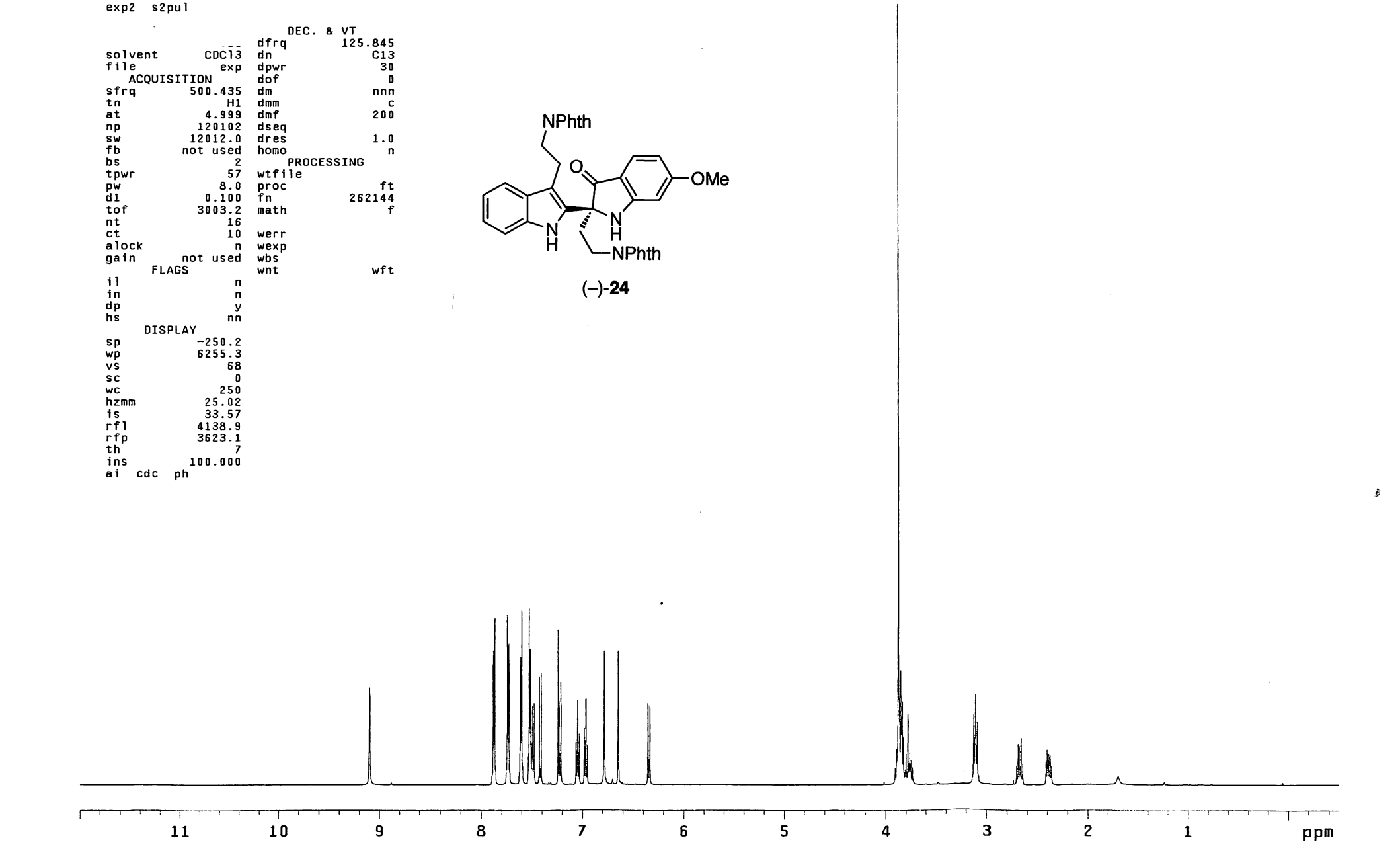
(–)-trigonoliimine B (**2**)
($CDCl_3$:CD_3OD = 3:1)



(–)-trigonoliimine B (**2**)
($CDCl_3$:CD_3OD = 3:1)

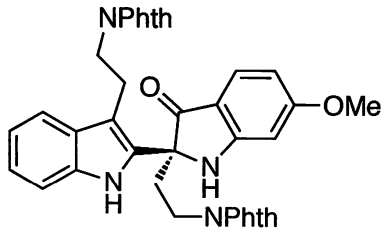
```
exp1  s2pul

                                    DEC. & VT
                                dfrq        500.229
solvent       CDCl3             dn               H1
                                dpwr              37
                                dof           -500.0
                                dm                y
                                dmm               w
                                dmf           10000
   ACQUISITION                  dseq
sfrq        125.795             dres             1.0
tn              C13             homo             n
at             1.736        PROCESSING
np          131010              lb             0.30
sw         37735.8              wtfile
fb        not used              proc             ft
bs                2              fn          131072
ss                1              math             f
tpwr             53
pw              6.9             werr
d1            0.763             wexp
tof           631.4             wbs
nt           100000             wnt
ct                0
alock             n
gain             60
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp         -6240.8
wp         37735.3
vs            3273
sc               0
wc             250
hzmm          1.78
is          500.00
rfl        12423.5
rfp         6182.2
th               16
ins           1.000
ai    ph
```

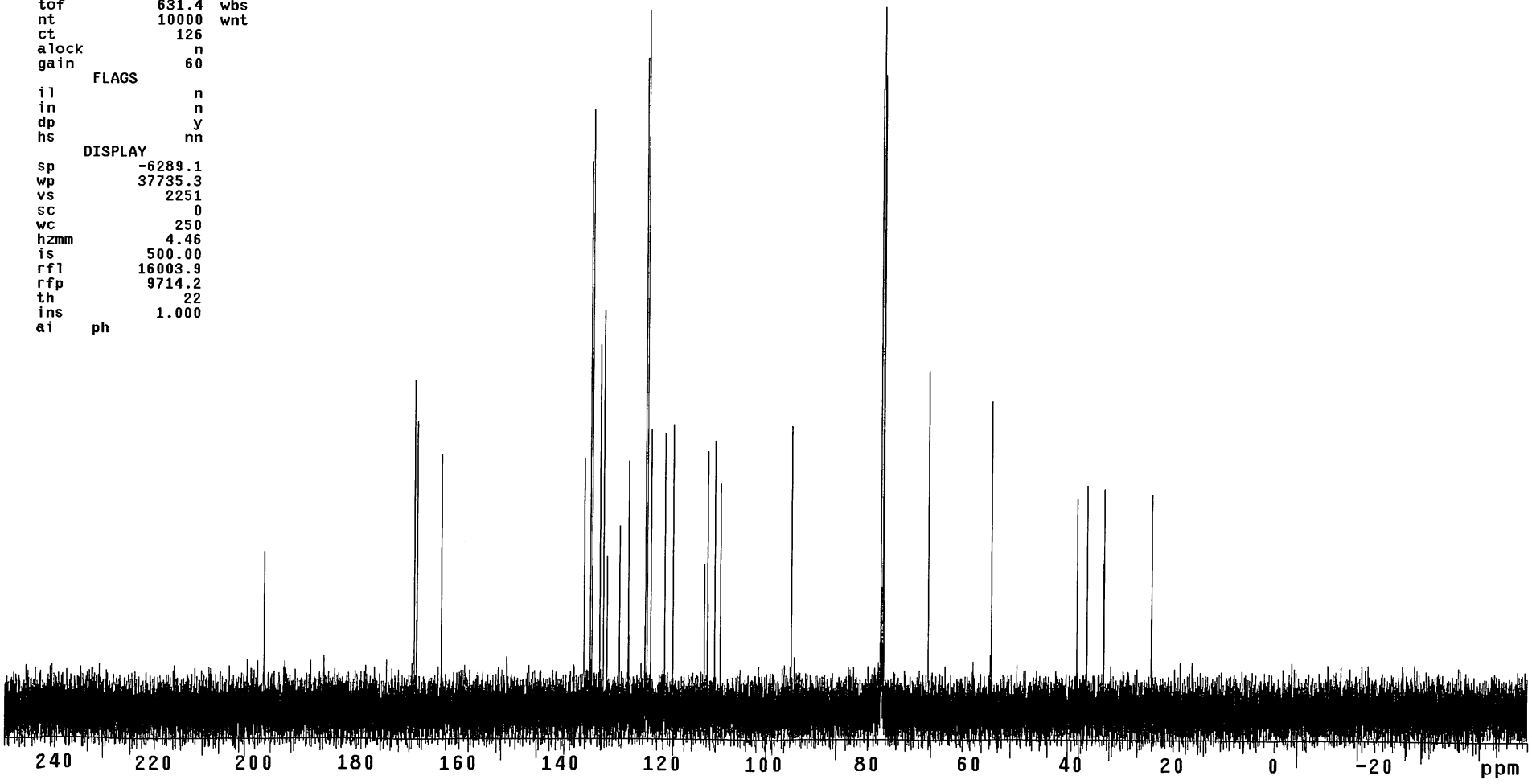

exp2 s2pul
solvent CDCl3
file exp
ACQUISITION
sfrq 500.435
tn H1
at 4.999
np 120102
sw 12012.0
fb not used
bs 2
tpwr 57
pw 8.0
d1 0.100
tof 3003.2
nt 16
ct 10
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 6255.3
vs 68
sc 0
wc 250
hzmm 25.02
is 33.57
rfl 4138.9
rfp 3623.1
th 7
ins 100.000
ai cdc ph
DEC. & VT
dfrq 125.845
dn C13
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
NPhth
O
OMe
N
H
N
H
NPhth
(–)-24
11
10
9
8
7
6
5
4
3
2
1
ppm

```
exp1  s2pul

                          DEC. & VT
                    dfrq        500.229
solvent      CDCl3  dn               H1
                    dpwr             37
                    dof          -500.0
                    dm                y
                    dmm               w
                    dmf           10000
   ACQUISITION      dseq
sfrq        125.795 dres             1.0
tn              C13 homo              n
at            1.736      PROCESSING
np           131010 lb             0.30
sw          37735.8 wtfile
fb        not used  proc             ft
bs                2 fn           131072
ss                1 math              f
tpwr             53
pw              6.9 werr
d1            0.763 wexp
tof           631.4 wbs
nt            10000 wnt
ct              126
alock             n
gain             60
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp         -6289.1
wp         37735.3
vs            2251
sc               0
wc             250
hzmm          4.46
is          500.00
rfl        16003.9
rfp         9714.2
th               22
ins           1.000
ai    ph
```



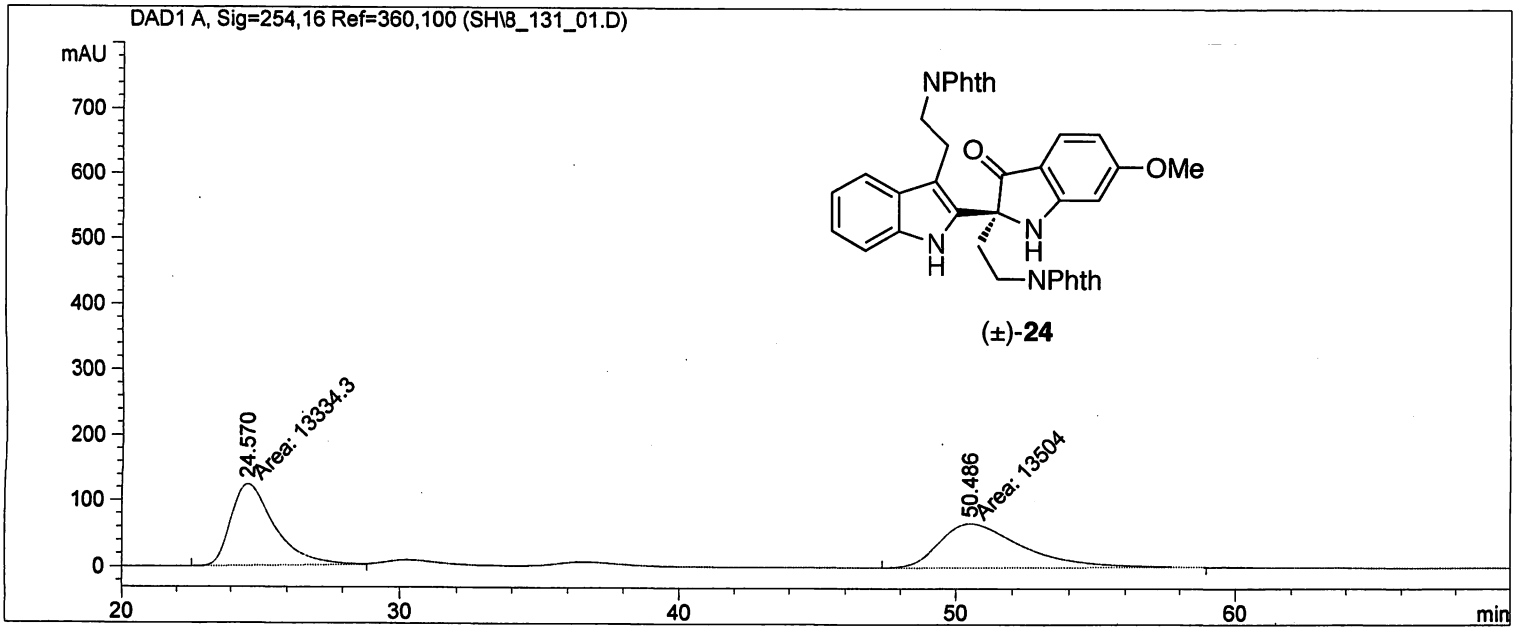
(–)-**24**



ChiralPak IC 0.7mL/min, 55:45=iPrOH:Hexane

```
==========================================================================
Injection Date  :                                  Seq. Line :   1
Sample Name     :                                   Location : Vial 23
Acq. Operator   :                                        Inj :   1
                                                  Inj Volume : 0 µl
Different Inj Volume from Sequence !      Actual Inj Volume : 10 µl
Acq. Method     :
Last changed    :
Analysis Method :
Last changed    :

==========================================================================
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,16 Ref=360,100

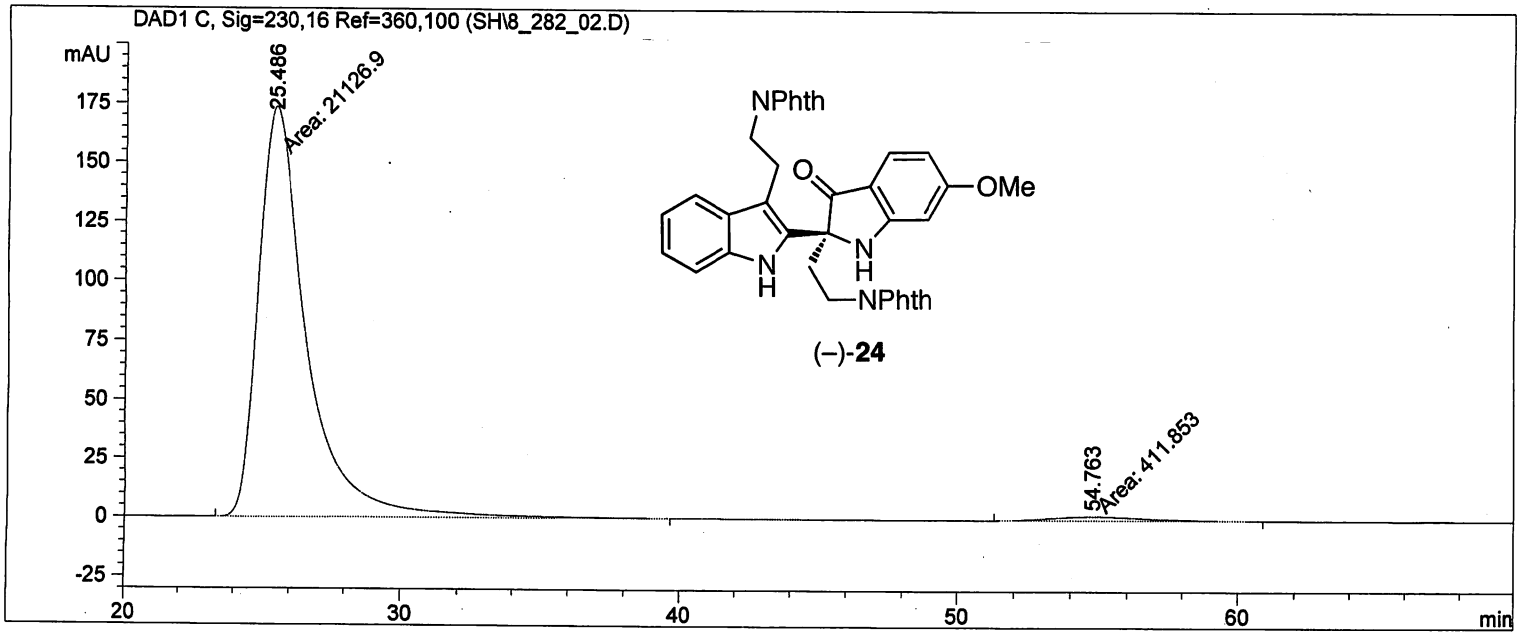
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.570 MM    1.7985 1.33343e4   123.56780  49.6839
   2  50.486 MM    3.4308 1.35040e4    65.60233  50.3161

Totals :                  2.68383e4   189.17013

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

chiralpak IC 45%Hexanes:55%IPA; 0.7 mL/min

```
==========================================================================
Injection Date  :                                  Seq. Line :   2
Sample Name     :                                   Location : Vial 25
Acq. Operator   :                                        Inj :   1
                                                  Inj Volume : 0 µl
Different Inj Volume from Sequence !      Actual Inj Volume : 10 µl
Acq. Method     :
Last changed    :
Analysis Method :
Last changed    :
==========================================================================
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=230,16 Ref=360,100

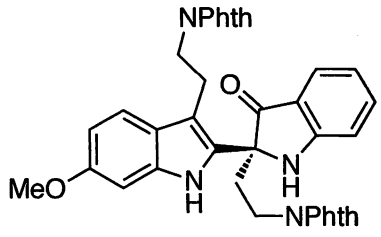
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  25.486 MM    2.0268 2.11269e4   173.72997  98.0878
   2  54.763 MM    4.0101  411.85291    1.71173   1.9122

Totals :                  2.15387e4   175.44169

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

```
exp2  s2pul

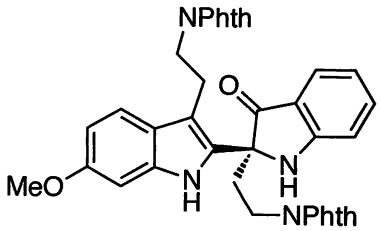
                          DEC. & VT
                      dfrq        125.845
solvent       CDCl3   dn              C13
file            exp   dpwr             30
   ACQUISITION        dof               0
sfrq        500.435   dm              nnn
tn               H1   dmm               c
at            4.999   dmf             200
np           120102   dseq
sw         12012.0    dres            1.0
fb        not used    homo              n
bs               2         PROCESSING
tpwr            57   wtfile
pw             8.0    proc             ft
d1           0.100    fn           262144
tof         3003.2    math              f
nt              16
ct              12    werr
alock            n    wexp
gain      not used    wbs
      FLAGS           wnt             wft
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -250.2
wp          6255.3
vs              84
sc               0
wc             250
hzmm         25.02
is           33.57
rfl         4138.8
rfp         3623.1
th               7
ins        100.000
ai  cdc  ph
```



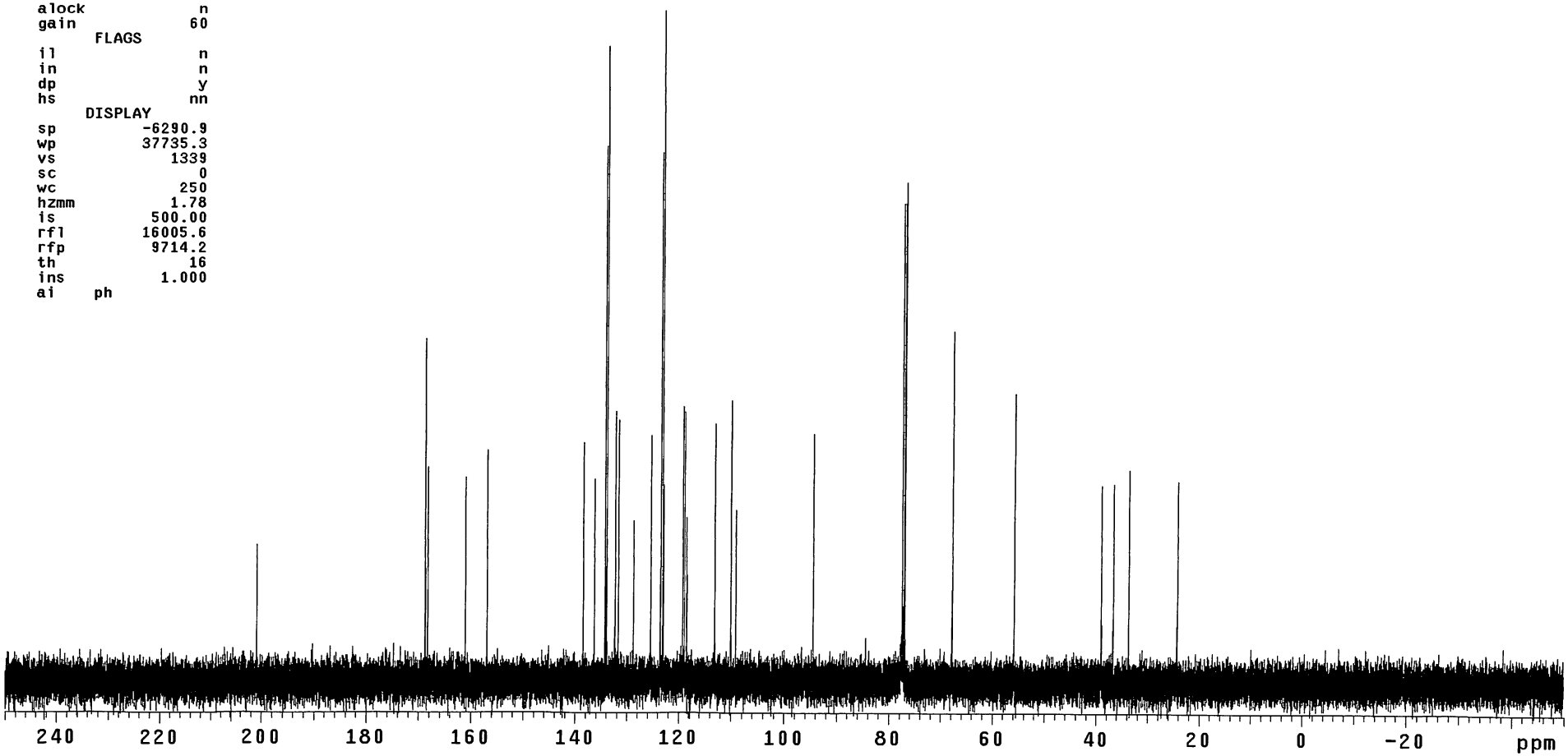
(–)-**25**

```
exp1  s2pul

                                    DEC. & VT
                                dfrq        500.229
solvent       CDCl3             dn               H1
                                dpwr              37
                                dof           -500.0
                                dm                y
                                dmm               w
                                dmf           10000
   ACQUISITION                  dseq
sfrq         125.795            dres             1.0
tn               C13            homo             n
at             1.736                PROCESSING
np           131010             lb             0.30
sw           37735.8            wtfile
fb         not used             proc             ft
bs                2             fn           131072
ss                1             math             f
tpwr             53
pw              6.9             werr
d1            0.763             wexp
tof           631.4             wbs
nt           100000             wnt
ct               92
alock             n
gain             60
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp          -6290.9
wp          37735.3
vs             1339
sc                0
wc              250
hzmm           1.78
is           500.00
rfl        16005.6
rfp         9714.2
th               16
ins           1.000
ai    ph
```

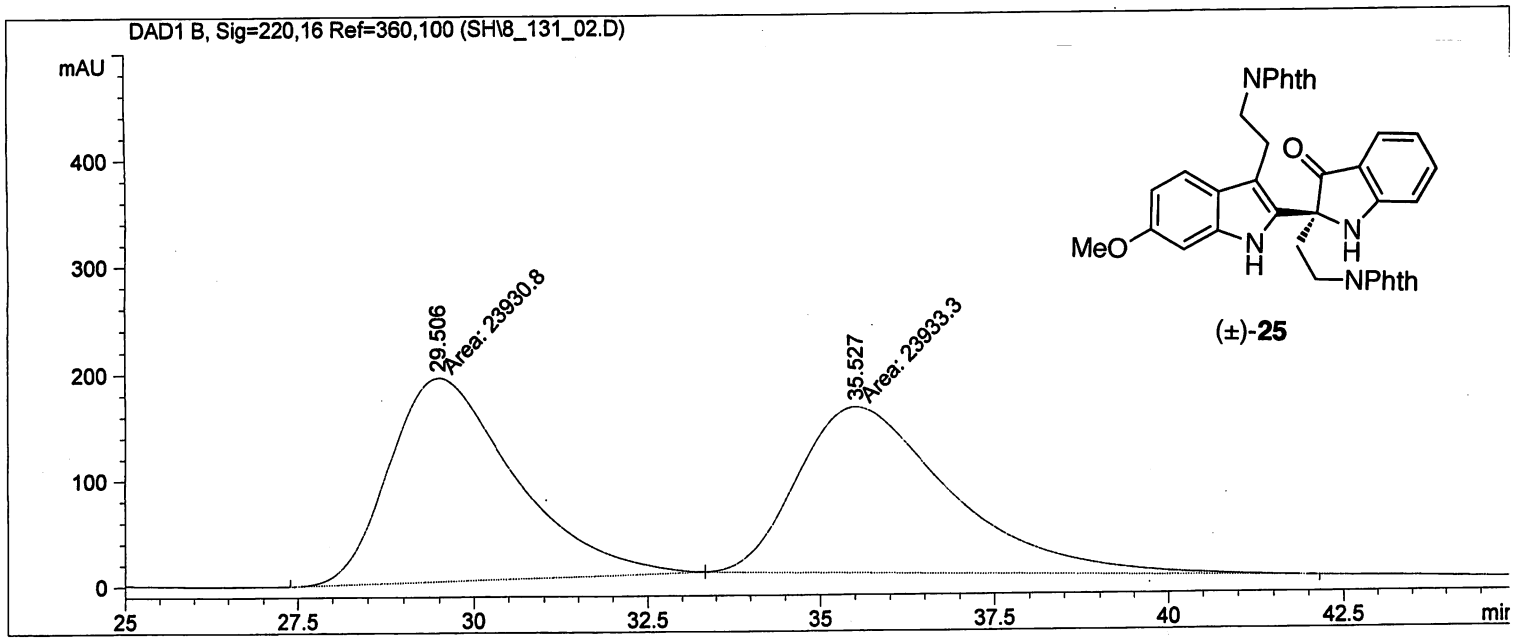


(–)-**25**



ChiralPak IC 0.7mL/min, 55:45=iPrOH:Hexane

```
==========================================================================
Injection Date  :                                    Seq. Line :   1
Sample Name     :                                     Location : Vial 27
Acq. Operator   :                                          Inj :   1
                                                   Inj Volume : 0 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 10 µl
Acq. Method     :
Last changed    :
Analysis Method :
Last changed    :
==========================================================================
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

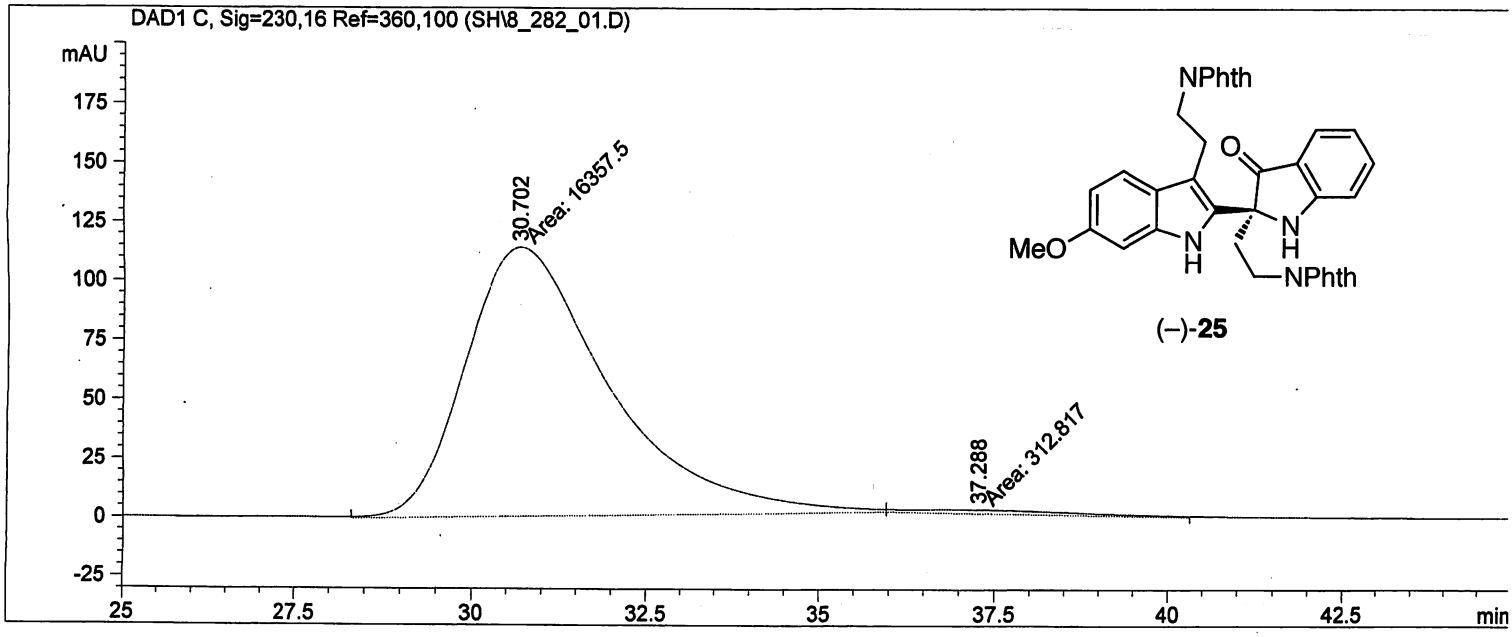
Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  29.506 MM    2.0782 2.39308e4   191.91936  49.9974
   2  35.527 MM    2.5518 2.39333e4   156.31505  50.0026

Totals :                  4.78641e4   348.23441

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

chiralpak IC 45%Hexanes:55%IPA; 0.7 mL/min

Injection Date	:	Seq. Line	: 1
Sample Name	:	Location	: Vial 24
Acq. Operator	:	Inj	: 1
		Inj Volume	: 0 µl
		Actual Inj Volume	: 10 µl
Acq. Method	:		
Last changed	:		
Analysis Method	:		
Last changed	:		



(–)-**25**

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=230,16 Ref=360,100

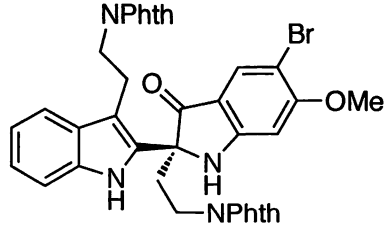
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.702	MM	2.3934	1.63575e4	113.90890	98.1235
2	37.288	MM	3.0133	312.81677	1.73019	1.8765
Totals :				1.66703e4	115.63909	

Results obtained with enhanced integrator!

*** End of Report ***

exp2 s2pul

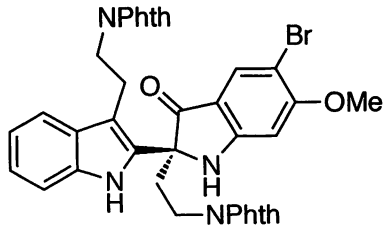
		DEC. & VT	
solvent	CDCl3	dfrq	125.845
file	exp	dn	C13
ACQUISITION		dpwr	30
sfrq	500.435	dof	0
tn	H1	dm	nnn
at	4.999	dmm	c
np	120102	dmf	200
sw	12012.0	dseq	
fb	not used	dres	1.0
bs	2	homo	n
tpwr	57	PROCESSING	
pw	8.0	wtfile	
d1	0.100	proc	ft
tof	3003.2	fn	262144
nt	32	math	f
ct	12		
alock	n	werr	
gain	not used	wexp	
FLAGS		wbs	
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	6255.3		
vs	40		
sc	0		
wc	250		
hzmm	25.02		
is	33.57		
rfl	4139.0		
rfp	3623.1		
th	7		
ins	100.000		
ai cdc ph			



(–)-**28**

exp1 s2pul

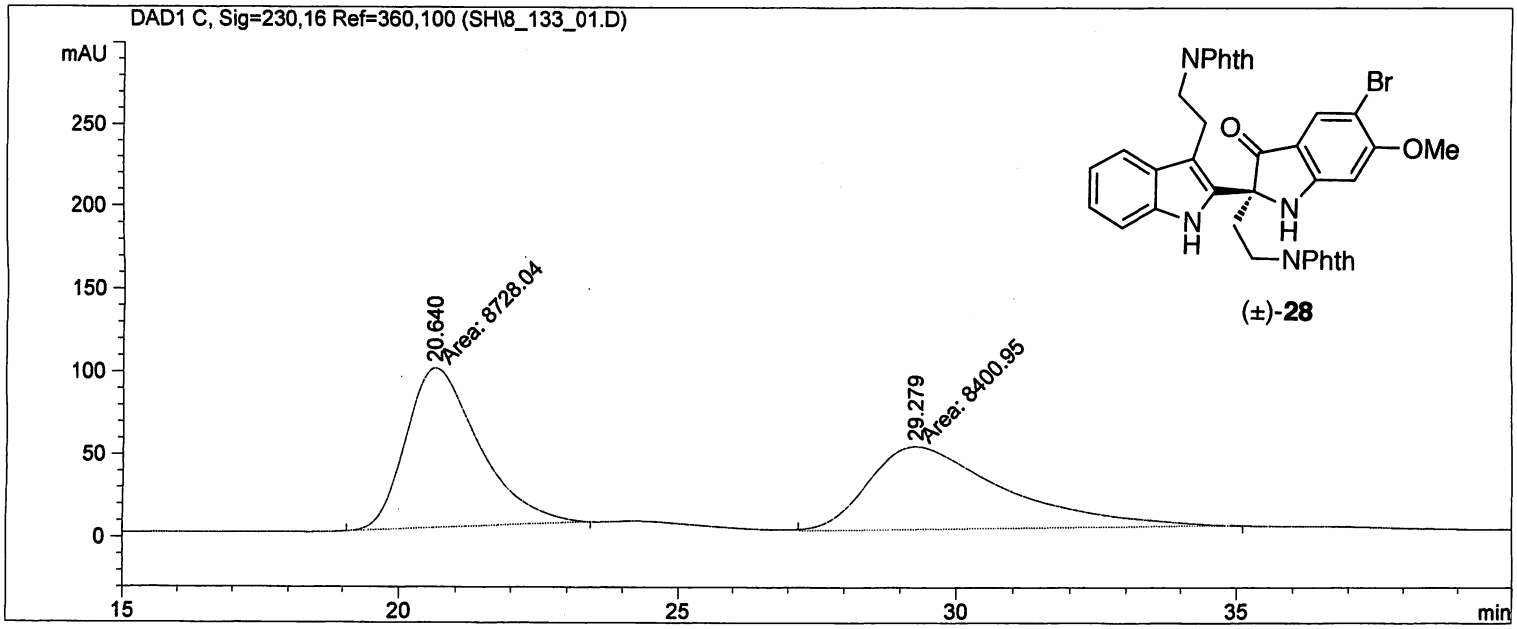
		DEC. & VT	
solvent	CDCl3	dfrq	500.229
		dn	H1
		dpwr	37
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
ACQUISITION		dseq	
sfrq	125.795	dres	1.0
tn	C13	homo	n
at	1.736	PROCESSING	
np	131010	lb	0.30
sw	37735.8	wtfile	
fb	not used	proc	ft
bs	2	fn	131072
ss	1	math	f
tpwr	53		
pw	6.9	werr	
d1	0.763	wexp	
tof	631.4	wbs	
nt	1e+06	wnt	
ct	2310		
alock	n		
gain	60		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-6286.8		
wp	37735.3		
vs	7611		
sc	0		
wc	250		
hzmm	1.00		
is	500.00		
rfl	16001.6		
rfp	9714.2		
th	20		
ins	1.000		
ai ph			



(–)-**28**

ChiralPak IC 0.7mL/min, 55:45=iPrOH:Hexane

```
==========================================================================
Injection Date  :                                  Seq. Line :   1
Sample Name     :                                   Location : Vial 23
Acq. Operator   :                                        Inj :   1
                                                  Inj Volume : 0 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 20 µl
Acq. Method     :
Last changed    :
Analysis Method :
Last changed    :
==========================================================================
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  20.640 MM    1.5072 8728.03906   96.51717  50.9548
   2  29.279 MM    2.8044 8400.94922   49.92635  49.0452

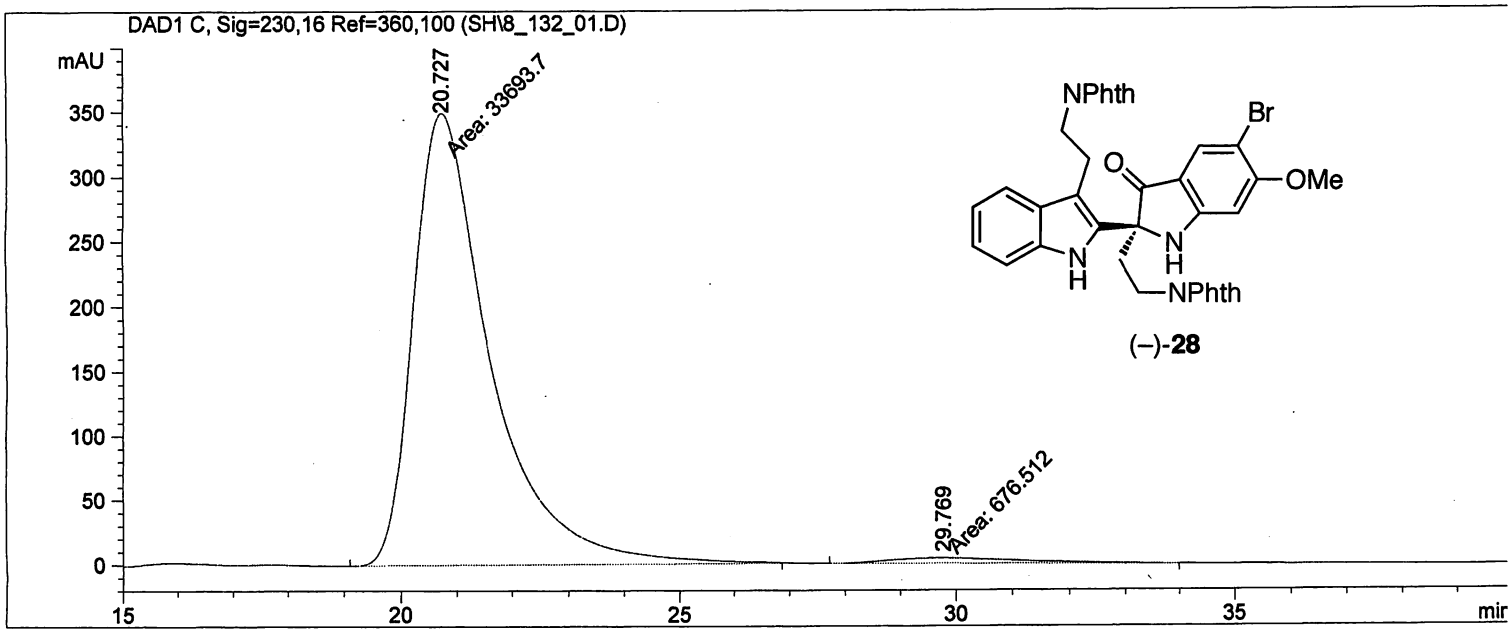
Totals :                  1.71290e4   146.44352

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

ChiralPak IC 0.7mL/min, 55:45=iPrOH:Hexane

```
==========================================================================
Injection Date  :                                    Seq. Line :   1
Sample Name     :                                     Location : Vial 27
Acq. Operator   :                                         Inj :   1
                                                  Inj Volume : 0 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 10 µl
Acq. Method     :
Last changed    :
Analysis Method :
Last changed    :

==========================================================================
```



(–)-**28**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=230,16 Ref=360,100

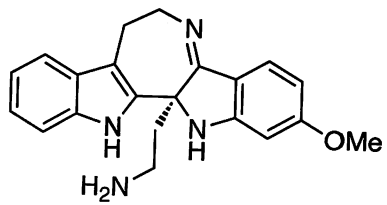
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  20.727 MM    1.6073 3.36937e4   349.37302  98.0317
   2  29.769 MM    2.7526  676.51196    4.09626   1.9683

Totals :                  3.43702e4   353.46927

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

```
exp1  s2pul

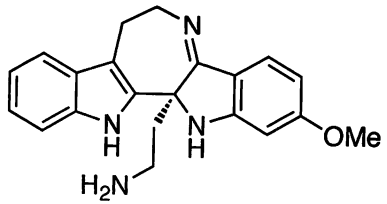
                          DEC. & VT
                      dfrq        125.846
solvent       CD3OD   dn              C13
                      dpwr             30
                      dof               0
                      dm              nnn
                      dmm               c
   ACQUISITION        dmf             200
sfrq        500.437   dseq
tn               H1   dres            1.0
at             4.999  homo              n
np           120102       PROCESSING
sw           12012.0  wtfile
fb         not used   proc             ft
bs                2   fn           262144
tpwr             57   math              f
pw              8.0
d1            0.100   werr
tof          3003.2   wexp
nt                32   wbs
ct                18   wnt             wft
alock              n
gain       not used
      FLAGS
il                 n
in                 n
dp                 y
hs                nn
     DISPLAY
sp           -250.2
wp           6255.4
vs               36
sc                0
wc              250
hzmm          25.02
is            33.57
rfl          2159.4
rfp          1656.4
th                7
ins         100.000
ai  cdc  ph
```



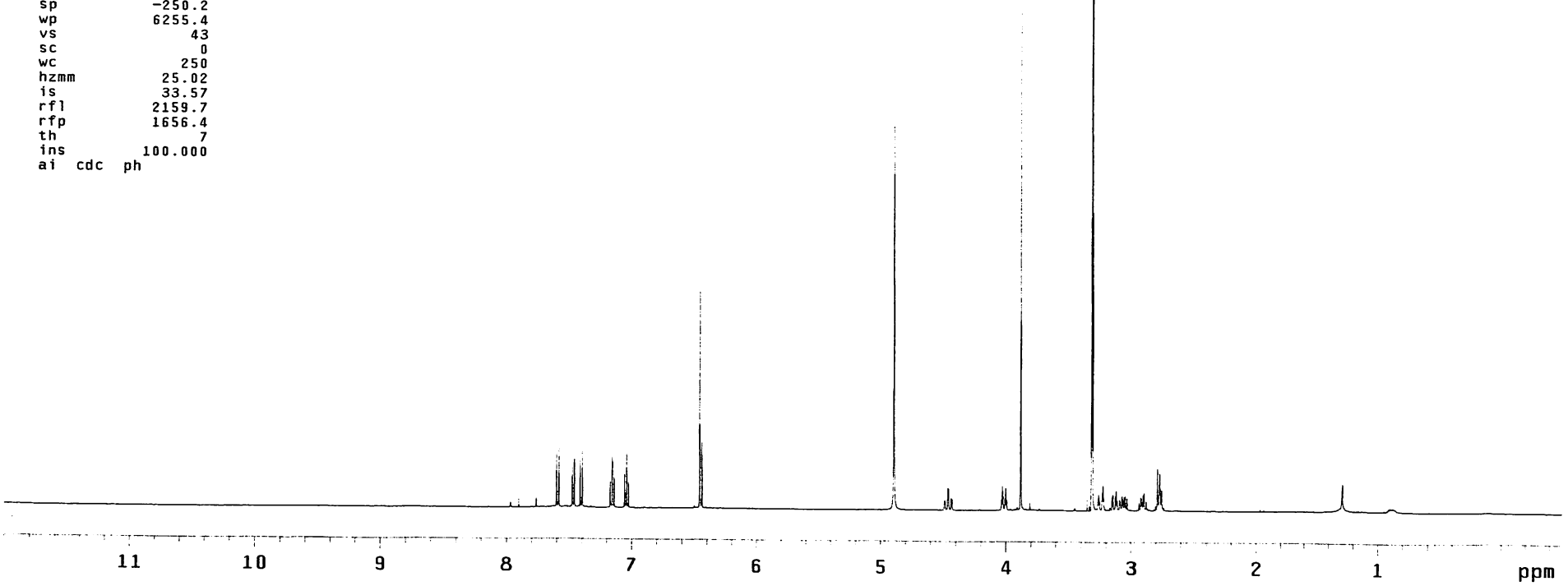
(–)-**26**

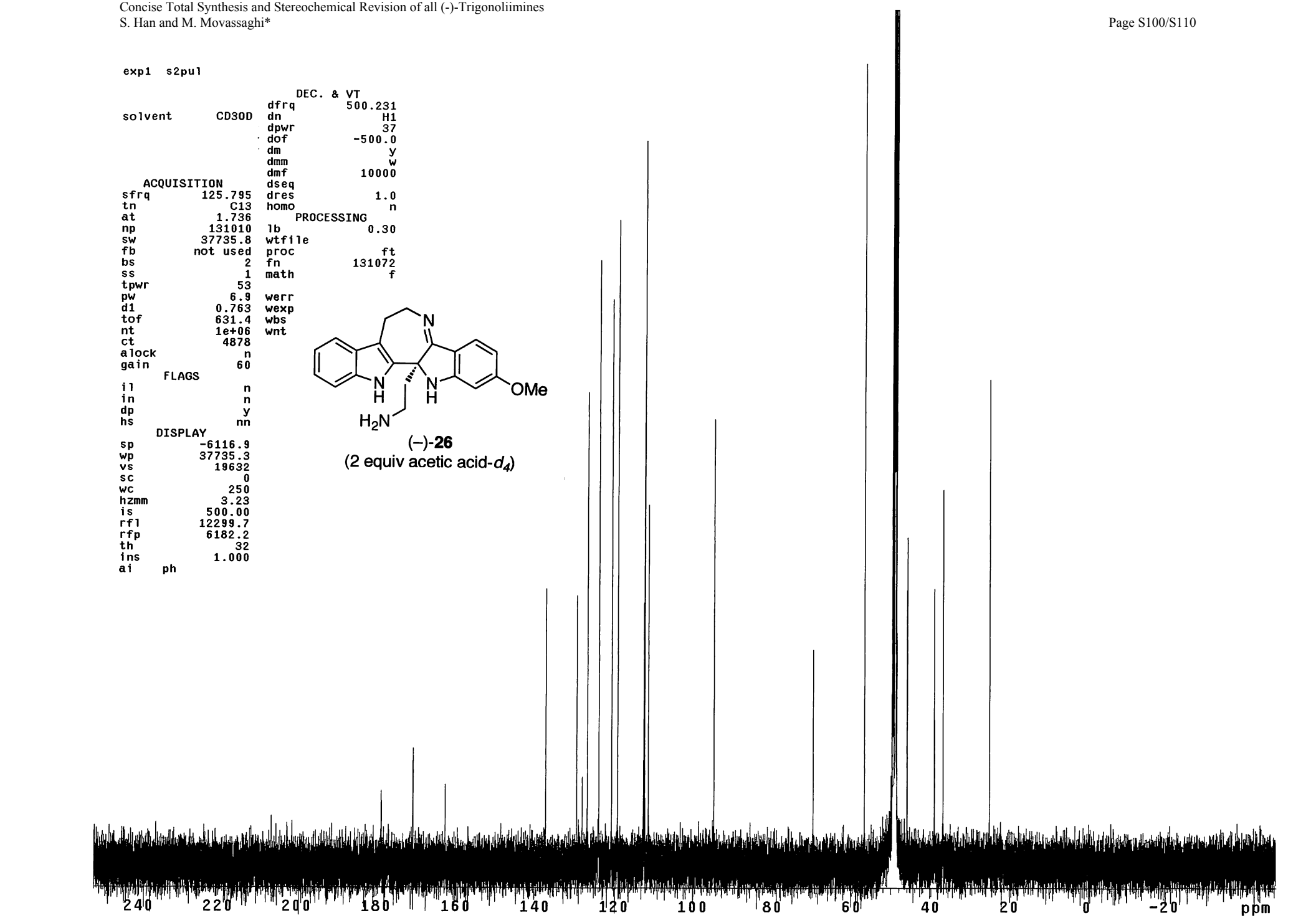
```
exp1  s2pul

                          DEC. & VT
                      dfrq        125.846
solvent       CD3OD   dn              C13
                      dpwr             30
                      dof               0
                      dm              nnn
                      dmm               c
   ACQUISITION        dmf             200
sfrq        500.437   dseq
tn               H1   dres            1.0
at            4.999   homo              n
np           120102       PROCESSING
sw         12012.0    wtfile
fb        not used    proc             ft
bs               2    fn           262144
tpwr            60    math              f
pw             8.0
d1           0.100    werr
tof         3003.2    wexp
nt              32    wbs
ct              10    wnt             wft
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -250.2
wp          6255.4
vs              43
sc               0
wc             250
hzmm         25.02
is           33.57
rfl        2159.7
rfp        1656.4
th               7
ins        100.000
ai  cdc  ph
```



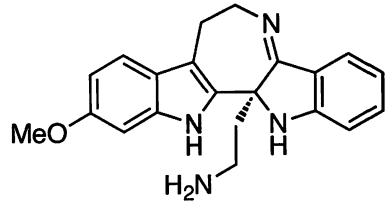
(–)-**26**
(2 equiv acetic acid-d_4)



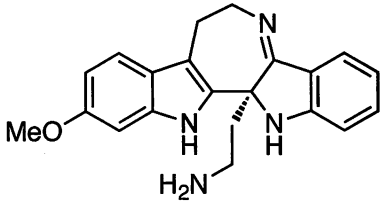

exp1 s2pul
solvent CD3OD
ACQUISITION
sfrq 125.795
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 2
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 1e+06
ct 4878
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -6116.9
wp 37735.3
vs 19632
sc 0
wc 250
hzmm 3.23
is 500.00
rfl 12299.7
rfp 6182.2
th 32
ins 1.000
ai ph
DEC. & VT
dfrq 500.231
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
N
N
H
N
H
OMe
H2N
(–)-26
(2 equiv acetic acid-d4)
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

```
exp1  s2pul

                        DEC. & VT
                    dfrq        125.846
solvent       CD3OD dn              C13
                    dpwr             30
                    dof               0
                    dm              nnn
                    dmm               c
   ACQUISITION      dmf             200
sfrq        500.437 dseq
tn               H1 dres            1.0
at            4.999 homo              n
np          120102      PROCESSING
sw          12012.0 wtfile
fb        not used  proc             ft
bs                2 fn           262144
tpwr             60 math              f
pw              8.0
d1            0.100 werr
tof          3003.2 wexp
nt                32 wbs
ct                24 wnt             wft
alock              n
gain       not used
      FLAGS
il                 n
in                 n
dp                 y
hs                nn
     DISPLAY
sp           -250.2
wp           6255.4
vs               37
sc                0
wc              250
hzmm          25.02
is            33.57
rfl          2159.8
rfp          1656.4
th                7
ins         100.000
ai  cdc  ph
```



(–)-**27**
(2 equiv acetic acid-d_4)



(–)-**27**
(2 equiv acetic acid-d_4)


```
Current Data Parameters
NAME
EXPNO
PROCNO                    1

F2 - Acquisition Parameters
Date_
Time
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG               zgpg30
TD                     65536
SOLVENT                CDC13
NS                      2820
DS                         2
SWH                23980.814 Hz
FIDRES              0.365918 Hz
AQ                  1.3664756 sec
RG                    14596.5
DW                   20.850 usec
DE                    6.00 usec
TE                   296.2 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                        1

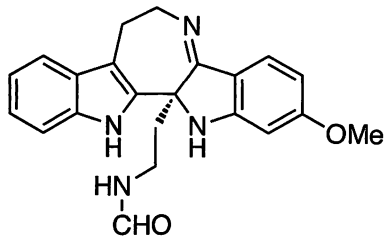
======== CHANNEL f1 ========
NUC1                     13C
P1                    8.75 usec
PL1                  -3.00 dB
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 14.52 dB
PL13                 18.00 dB
SFO2            400.1316005 MHz

F2 - Processing parameters
SI                     65536
SF              100.6126115 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                     1.40
```

```
exp1  s2pul

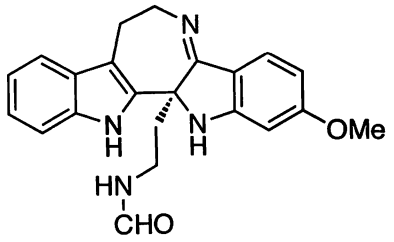
                          DEC. & VT
                      dfrq        125.846
solvent        DMSO   dn              C13
                      dpwr             30
                      dof               0
                      dm              nnn
                      dmm               c
   ACQUISITION        dmf             200
sfrq         500.437  dseq
tn                H1  dres            1.0
at             4.999  homo              n
np            120102       PROCESSING
sw           12012.0  wtfile
fb         not used   proc             ft
bs                2   fn           262144
tpwr             57   math              f
pw              8.0
d1            0.100   werr
tof          3003.2   wexp
nt                32   wbs
ct                12   wnt             wft
alock              n
gain       not used
      FLAGS
il                 n
in                 n
dp                 y
hs                nn
     DISPLAY
sp           -250.2
wp           6255.4
vs                54
sc                 0
wc               250
hzmm           25.02
is             33.57
rfl          1748.6
rfp          1251.1
th                 7
ins          100.000
ai  cdc  ph
```



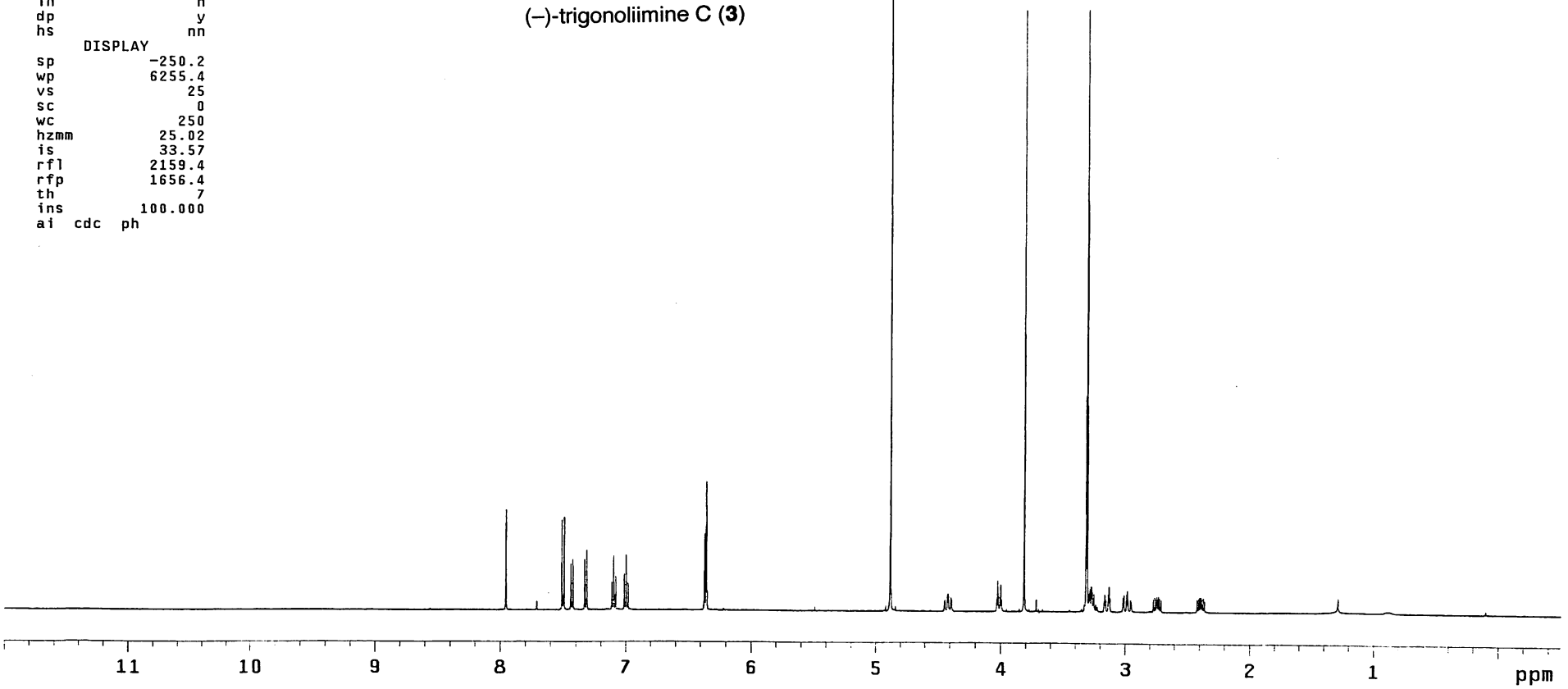
(–)-trigonoliimine C (**3**)

exp2 s2pul

		DEC. & VT	
solvent	CD3OD	dfrq	125.846
file	exp	dn	C13
ACQUISITION		dpwr	30
sfrq	500.437	dof	0
tn	H1	dm	nnn
at	4.999	dmm	c
np	120102	dmf	200
sw	12012.0	dseq	
fb	not used	dres	1.0
bs	2	homo	n
tpwr	57	PROCESSING	
pw	8.0	wtfile	
d1	0.100	proc	ft
tof	3003.2	fn	262144
nt	3	math	f
ct	3		
alock	n	werr	
gain	not used	wexp	
FLAGS		wbs	
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	6255.4		
vs	25		
sc	0		
wc	250		
hzmm	25.02		
is	33.57		
rfl	2159.4		
rfp	1656.4		
th	7		
ins	100.000		
ai cdc ph			



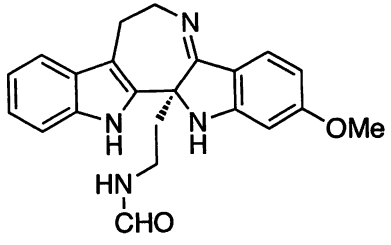
(–)-trigonoliimine C (**3**)



CDCl3/MeOD=3/1

exp2 s2pul

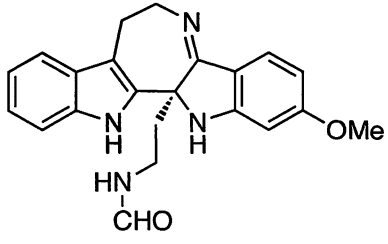
		DEC. & VT	
		dfrq	125.846
solvent	CD3OD	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	500.437	dm	nnn
tn	H1	dmm	c
at	4.999	dmf	200
np	120102	dseq	
sw	12012.0	dres	1.0
fb	not used	homo	n
bs	2	PROCESSING	
tpwr	57	wtfile	
pw	8.0	proc	ft
d1	0.100	fn	262144
tof	3003.2	math	f
nt	32		
ct	24	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	6255.4		
vs	56		
sc	0		
wc	250		
hzmm	25.02		
is	33.57		
rfl	2160.1		
rfp	1656.4		
th	7		
ins	100.000		
ai cdc ph			



(–)-trigonoliimine C (**3**)
($CDCl_3$:CD_3OD = 3:1)

```
exp1  s2pul

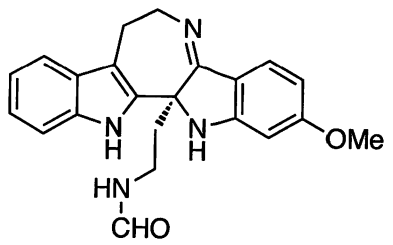
                          DEC. & VT
                      dfrq        500.232
solvent        DMSO   dn               H1
                      dpwr             37
                      dof          -500.0
                      dm                y
                      dmm               w
                      dmf           10000
   ACQUISITION        dseq
sfrq        125.795   dres             1.0
tn              C13   homo              n
at            1.736       PROCESSING
np           131010   lb             0.30
sw          37735.8   wtfile
fb        not used    proc             ft
bs                2   fn           131072
ss                1   math              f
tpwr             53
pw              6.9   werr
d1            0.763   wexp
tof           631.4   wbs
nt            1e+07   wnt
ct             4114
alock             n
gain             60
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp         -6371.3
wp         37735.3
vs           10973
sc               0
wc             250
hzmm          3.23
is          500.00
rfl        11341.6
rfp         4969.7
th               20
ins           1.000
ai    ph
```



(–)-trigonoliimine C (**3**)

```
exp1  s2pul

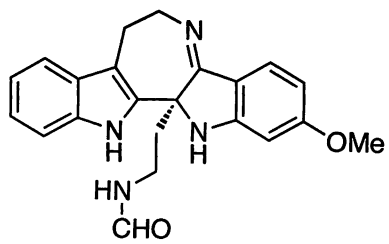
                          DEC. & VT
                      dfrq          500.231
solvent       CD3OD   dn                 H1
                      dpwr               37
                      dof            -500.0
                      dm                  y
                      dmm                 w
                      dmf            10000
                      dseq
   ACQUISITION        dres             1.0
sfrq          125.795 homo               n
tn                C13       PROCESSING
at              1.736 lb              0.30
np             131010 wtfile
sw           37735.8  proc              ft
fb         not used   fn            131072
bs                 2  math               f
ss                 1
tpwr              53  werr
pw               6.9  wexp
d1             0.763  wbs
tof            631.4  wnt
nt            100000
ct              3320
alock              n
gain              60
      FLAGS
il                 n
in                 n
dp                 y
hs                nn
     DISPLAY
sp           -6254.4
wp           37735.3
vs               684
sc                 0
wc               250
hzmm           27.97
is            500.00
rfl          12437.5
rfp           6182.5
th                12
ins            1.000
nm    ph
```



(–)-trigonoliimine C (**3**)
($CDCl_3$:CD_3OD = 3:1)

```
exp1  s2pul

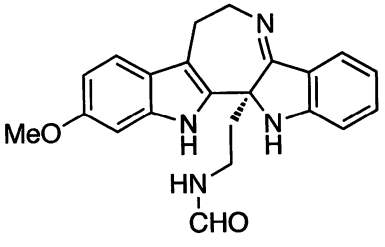
                                DEC. & VT
                          dfrq        500.231
solvent       CD3OD       dn               H1
                          dpwr              37
                          dof           -500.0
                          dm                y
                          dmm               w
                          dmf           10000
   ACQUISITION            dseq
sfrq          125.795     dres             1.0
tn                C13     homo              n
at              1.736         PROCESSING
np            131010      lb              0.30
sw           37735.8      wtfile
fb         not used       proc              ft
bs                2       fn            131072
ss                1       math              f
tpwr             53
pw              6.9       werr
d1            0.763       wexp
tof           631.4       wbs
nt            1e+06       wnt
ct             2794
alock             n
gain             60
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp          -6116.9
wp          37735.3
vs             9011
sc                0
wc              250
hzmm         150.94
is           500.00
rfl         12299.7
rfp          6182.2
th                17
ins            1.000
ai    ph
```



(–)-trigonoliimine C (**3**)

```
exp2  s2pul

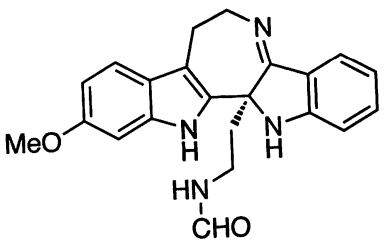
                        DEC. & VT
                    dfrq        125.844
solvent       CD3OD dn              C13
file            exp dpwr             30
   ACQUISITION      dof               0
sfrq        500.433 dm              nnn
tn               H1 dmm               c
at            4.999 dmf             200
np           120102 dseq
sw         12012.0  dres            1.0
fb        not used  homo              n
bs               2      PROCESSING
tpwr            60  wtfile
pw             8.0  proc             ft
d1           0.100  fn           262144
tof         3003.2  math              f
nt              32
ct              32  werr
alock            n  wexp
gain      not used  wbs
      FLAGS         wnt             wft
il               n
in               n
dp               y
hs              nn
    DISPLAY
sp          -250.2
wp          6255.3
vs              83
sc               0
wc             250
hzmm         25.02
is           33.57
rfl         2169.2
rfp         1656.4
th               7
ins        100.000
ai  cdc  ph
```



(–)-isotrigonoliimine C (**4**)

```
exp1  s2pul

                          DEC. & VT
                      dfrq        500.231
solvent       CD3OD   dn               H1
                      dpwr             37
                      dof          -500.0
                      dm                y
                      dmm               w
                      dmf           10000
   ACQUISITION        dseq
sfrq         125.795  dres             1.0
tn               C13  homo              n
at             1.736      PROCESSING
np           131010   lb             0.30
sw           37735.8  wtfile
fb         not used   proc             ft
bs                2   fn           131072
ss                1   math              f
tpwr             53
pw              6.9   werr
d1            0.763   wexp
tof           631.4   wbs
nt           100000   wnt
ct            18494
alock             n
gain             60
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp         -6115.8
wp         37735.3
vs           12803
sc               0
wc             250
hzmm          3.68
is          500.00
rfl         12298.6
rfp          6182.2
th               20
ins           1.000
ai    ph
```



(–)-isotrigonoliimine C (**4**)