Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-*meso*-chimonanthine and related heterodimeric alkaloids.

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Supporting Information

General Procedures. All reactions were performed in oven-dried or flame-dried round-bottom flasks. The flasks were fitted with rubber septa, and reactions were conducted under a positive pressure of argon. Cannulae or gas-tight syringes with stainless steel needles were used to transfer air- or moisture-sensitive liquids. Where necessary (so noted), solutions were deoxygenated by sparging with argon for a minimum of 10 min. Flash column chromatography was performed as described by Still et al.[1] using granular silica gel (60-Å pore size, 40–63 μm, 4–6% H_2O content, Zeochem). 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). TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) and irreversibly stained by treatment with an aqueous solution of ceric ammonium molybdate (CAM) followed by heating (~ 1 min) on a hot plate (~ 250 ºC). Organic solutions were concentrated at 29–30 °C on rotary evaporators capable of achieving a minimum pressure of ~2 torr. The diazene photolysis was accomplished by irradiation in a Rayonet RMR-200 photochemical reactor (Southern New England Ultraviolet Company, Branford, CT, USA) equipped with 16 lamps.

Materials. Commercial reagents and solvents were used as received with the following exceptions: dichloromethane, acetonitrile, tetrahydrofuran, methanol, pyridine, toluene, and triethylamine were purchased from J. T. Baker (Cycletainer^{TM}) and were purified by the method of Grubbs *et al.* under positive argon pressure.[2] *N*,*N*′-diisopropylethylamine and benzene were dried by distillation over calcium hydride under an inert nitrogen atmosphere and used directly. L-tryptophan methyl ester hydrochloride was purchased from Chem-Impex International, Inc.; di-*tert*-butyl dicarbonate (Boc_2O) was purchased from Oakwood Chemicals, Inc.; trimethyltin hydroxide and sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al) were purchased from Strem Chemicals, Inc.; thiopyridine *N*-oxide and 2-methyl-2-phenylpropionic acid were purchased from TCI America; *N*,*N*,*N*′,*N*′-tetramethylchloroformamidinium hexafluorophosphate (TCFH) was purchased from AK Scientific, Inc. All other solvents and chemicals were purchased from Sigma–Aldrich.

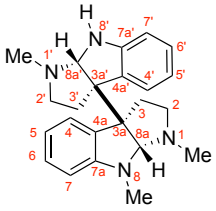
Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian inverse probe 500 INOVA spectrometer. Chemical shifts are recorded in parts per million on the δ scale and are referenced from the residual protium in the NMR solvent ($CHCl_3$: δ 7.24, $CDHCl_2$: 5.32, CD_2HCN: 1.94, CD_3SOCD_2H: 2.50, C_6D_5H: 7.16). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance spectra were recorded with a Varian 500 INOVA spectrometer and are recorded in parts per million on the δ scale and are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.23: CD_2Cl_2: 54.00 CD_3CN: 118.69, DMSO-d_6: 39.51, C_6D_6: 128.39). Data are reported as

[1] W. C. Still, M. Kahn, and A. Mitra . *J. Org. Chem.* 1978, **43**, 2923.

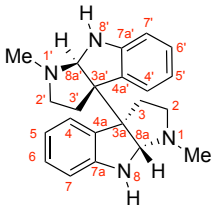
[2] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, and F. Timmers, *J. Organometallics* 1996, **15**, 1518.

follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hertz, assignment]. Fluorine-19 nuclear magnetic resonance spectra were recorded with a Varian 300 INOVA spectrometer and are recorded in parts per million on the δ scale and are referenced from the fluorine resonances of trifluoroacetic acid (CF_3CO_2H δ –76.55). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Infrared data 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), assignment]. We thank Dr. Li Li at the Massachusetts Institute of Technology Department of Chemistry instrumentation facility for obtaining mass spectroscopic data. High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics APEXIV 4.7 Tesla FT-ICR-MS using electrospray (ESI) (*m/z*) ionization source.

Positional Numbering System. In assigning the ^{1}H and ^{13}C NMR data of all intermediates en route to (−)-calycanthidine (**1**), *meso*-chimonanthine (**2**), *meso*-calycanthine (**36**), (–)- and (+)-N_1-desmethyl-*meso*-chimonanthine (**3**) we have employed a uniform numbering system.



(–)-calycanthidine (**1**)



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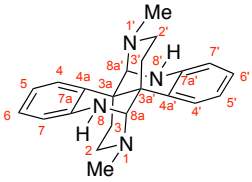
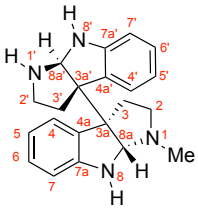


meso-calycanthine (**36**)



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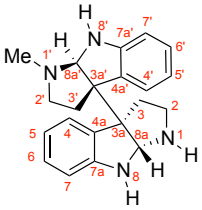
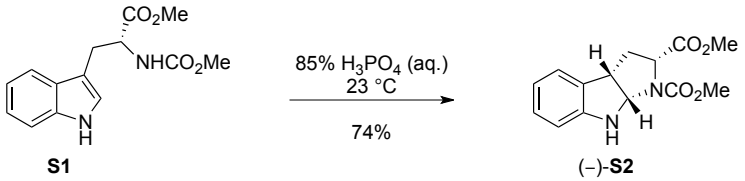


(+)-desmethyl-*meso*-chimonanthine (**3**)



N1-Carboxymethyl Hexahydropyrroloindole (–)-S2:

Aqueous phosphoric acid (85% w/v, 110 mL) was added to a flask containing indole **S1** (9.60 g, 36.3 mmol, 1 equiv) at 23 ºC. The resulting heterogeneous mixture was stirred vigorously. After 8 h, the homogenous solution was poured slowly into a vigorously stirred biphasic mixture of dichloromethane (200 mL) and a solution of potassium carbonate (480 g) and potassium hydroxide (160 g) in water (1 L) at 0 ºC. The pH of the mixture was maintained above 7 by the periodic addition of solid potassium carbonate (5 × 50 g). Once the addition was complete, the mixture was extracted with diethyl ether (3 × 300 mL). The combined organic layers were washed with brine (100 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 15→25% acetone in hexanes) to give N1-carboxymethyl hexahydropyrroloindole (–)-**S2**[3] (7.40 g, 73.7%) as a white solid. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

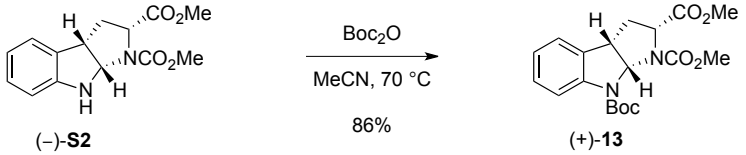
^{1}H NMR (500 MHz, C_6D_6, 20 °C): *Major Rotamer:* δ 6.91 (app-t, *J* = 7.7 Hz, 1H, C_6**H**), 6.78 (d, *J* = 7.5 Hz, 1H, C_4**H**), 6.60 (app-t, *J* = 7.4 Hz, 1H, C_5**H**), 6.33 (d, *J* = 7.7 Hz, 1H, C_7**H**), 5.44 (d, *J* = 6.7 Hz, 1H C_{8a}**H**), 5.39 (br-s, 1H, N_8**H**), 4.27 (d, *J* = 9.0 Hz, 1H, C_2**H**), 3.46 (s, 3H, N_1CO_2C**H**$_3$), 3.30–3.27 (m, 1H, C_{3a}**H**), 2.92 (s, 3H, CO_2C**H**$_3$), 2.30 (d, *J* = 13.1 Hz, 1H, C_3**H**$_a$), 1.92–1.84 (m, 1H, C_3**H**$_b$).

Minor Rotamer: δ 6.95 (app-t, *J* = 7.7 Hz, 1H, C_6**H**), 6.81 (d, *J* = 7.5 Hz, 1H, C_4**H**), 6.63 (app-t, *J* = 7.4 Hz, 1H, C_5**H**), 6.45 (d, *J* = 7.7 Hz, 1H, C_7**H**), 5.17 (d, *J* = 6.7 Hz, 1H C_{8a}**H**), 4.77 (br-s, 1H, N_8**H**), 4.61 (d, *J* = 9.0 Hz, 1H, C_2**H**), 3.49 (s, 3H, N_1CO_2C**H**$_3$), 3.30–3.27 (m, 1H, C_{3a}**H**), 2.93 (s, 3H, CO_2C**H**$_3$), 2.29 (d, *J* = 13.1 Hz, 1H, C_3**H**$_a$), 1.92–1.84 (m, 1H, C_3**H**$_b$).

^{13}C NMR (125.8 MHz, C_6D_6, 20 °C): *Major Rotamer:* δ 171.9 (**C**O_2CH_3), 155.6 (N_1**C**O_2CH_3), 151.3 (**C**$_{7a}$), 129.1 (**C**$_{4a}$), 128.9 (**C**$_6$), 124.5 (**C**$_4$), 118.8 (**C**$_5$), 109.7 (**C**$_7$), 78.1 (**C**$_{8a}$), 59.6

[3] Due to facile opening of cyclotryptophan (–)-**S2** to the corresponding tryptophan derivative this material was used in the next step immediately following purification..

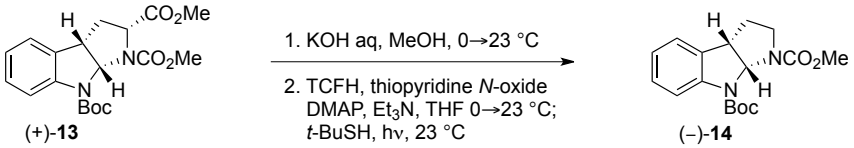
	(**C**$_2$), 52.7 (N_1CO_2**C**H_3), 52.0 (CO_2**C**H_3), 45.4 (**C**$_{3a}$), 34.9 (**C**$_3$). *Minor Rotamer:* δ 172.1 (**C**O_2CH_3), 154.8 (N_1**C**O_2CH_3), 150.8 (**C**$_{7a}$), 129.0 (**C**$_{4a}$), 128.7 (**C**$_6$), 124.6 (**C**$_4$), 119.2 (**C**$_5$) 109.6 (**C**$_7$), 77.3 (**C**$_{8a}$), 60.1 (**C**$_2$), 52.7 (N_1CO_2**C**H_3), 51.9 (CO_2**C**H_3), 46.7 (**C**$_{3a}$), 34.4 (**C**$_3$).
FTIR (thin film) cm^{-1}:	3383 (br-w), 2953 (m), 1755 (s), 1702 (s), 1611 (m), 1451 (s), 1382(s).
HRMS (ESI) (*m/z*):	calc'd for $C_{14}H_{17}N_2O_4$ $[M+H]^+$: 277.1183, found: 277.1179.
$[\alpha]_D^{24}$:	–232 (*c* = 1.52, CH_2Cl_2).
TLC (25% acetone in hexanes), R*f*:	0.38 (UV, CAM).



C2-Carboxymethyl Hexahydropyrroloindole (+)-13:

Di-*tert*-butyl dicarbonate (7.70 g, 35.2 mmol, 3.00 equiv) was added to a solution of N1-carboxymethyl hexahydropyrroloindole (–)-**S2** (3.10 g, 11.7 mmol, 1 equiv) in acetonitrile (50 mL) at 23 °C. The reaction flask was fitted with a reflux condenser and heated to 70 ºC. After 8 h, another portion of di-*tert*-butyl dicarbonate (7.70 g, 35.2 mmol, 3.00 equiv) was added and the solution was continued to stir at 70 ºC. After 15 h, the homogenous solution was allowed to cool to 23 °C and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 10→20% acetone in hexanes) to give C2-carboxymethyl hexahydropyrroloindole (+)-**13** (3.80 g, 86.3%) as a white foam. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

^{1}H NMR (500 MHz, CD_3CN, 20 °C):	δ 7.52 (d, *J* = 8.0 Hz, 1H, C_7**H**), 7.19–7.14 (m, 2H, C_4**H**, C_6**H**), 6.98 (app-t, *J* = 7.5 Hz, 1H, C_5**H**), 6.32 (d, *J* = 6.5 Hz, 1H, C_{8a}**H**), 4.54 (d, *J* = 8.7 Hz, 1H, C_2**H**), 4.01 (app-t, *J* = 6.6 Hz, 1H, C_{3a}**H**), 3.66 (s, 3H, N_1CO_2C**H**$_3$), 3.14 (s, 3H, CO_2C**H**$_3$), 2.58 (ddd, *J* = 7.0, 8.7, 13.2 Hz, 1H, C_3**H**$_a$), 2.53 (ddd, *J* = 1.7, 1.8, 13.2 Hz, 1H, C_3**H**$_b$), 1.55 (s, 9H, N_8CO_2C(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, CD_3CN, 20 ºC):	δ 173.1 (**C**O_2CH_3), 156.2 (N_1**C**O_2CH_3), 153.6 (N_8**C**$O_2C(CH_3)_3$), 144.4 (C_{7a}), 133.6 (C_{4a}), 129.4 (C_6), 125.4 (C_4), 124.4 (C_5), 117.9 (C_7), 82.3 (N_8CO_2**C**$(CH_3)_3$), 76.7, (C_{8a}), 60.7 (C_2), 53.5 (N_1CO_2**C**H_3), 52.3 (CO_2**C**H_3), 46.2 (C_{3a}), 34.3 (C_3), 28.9 (N_8CO_2C(**C**H_3)$_3$).
FTIR (thin film) cm^{-1}:	2979 (m), 1705 (s), 1605 (w), 1482 (s), 1447 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{19}H_{25}N_2O_6$ $[M+H]^+$: 377.1707, found: 377.1713.
$[\alpha]_D^{24}$:	+2.4 (*c* = 1.7, CH_2Cl_2).
TLC (33% acetone in hexanes), R*f*:	0.47 (UV, CAM).



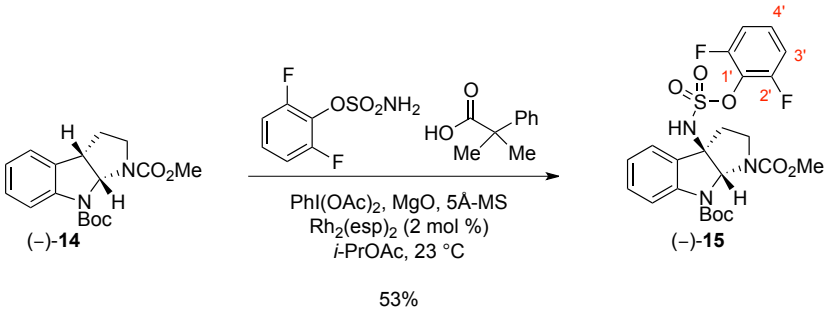
N8-Carboxy-*tert*-Butyl Hexahydropyrroloindole (–)-14:

An aqueous solution of potassium hydroxide (5 N, 55 mL) was added to a solution of C2-carboxymethyl hexahydropyrroloindole (+)-**13** (3.20 g, 8.50 mmol, 1 equiv) in methanol (110 mL) at 0 ºC in an ice bath. After 10 min, the ice bath was removed and the mixture was allowed to warm to 23 °C. After 2 h, the resulting solution was cooled to 0 ºC in an ice bath and adjusted to pH ~ 2 by the dropwise addition of an aqueous solution of hydrochloric acid (12 N, 25 mL). The mixture was allowed to warm to 23 °C and extracted with dichloromethane (3 × 150 mL). The combined organic layers were washed with brine (50 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to afford the crude carboxylic acid as a white foam.

Thiopyridine *N*-oxide (1.73 g, 13.6 mmol, 1.60 equiv), 4-(dimethylamino)pyridine (104 mg, 850 μmol, 0.10 equiv), and *N*,*N*,*N*′,*N*′-tetramethylchloroformamidinium hexafluorophosphate (TCFH, 3.19 g, 12.8 mmol, 1.50 equiv) were sequentially added to a solution of the crude carboxylic acid in tetrahydrofuran (85 mL) cooled to 0 ºC in an ice bath. The reaction flask was removed from the ice bath, covered in aluminum foil and triethylamine (4.75 mL, 34.0 mmol, 4.00 equiv) was added while the reaction mixture was still cold. After 1.5 h, *tert*-butylthiol (4.80 mL, 42.5 mmol, 5.00 equiv) was added via syringe and the aluminum foil was removed from the flask. The resulting suspension was irradiated with a flood lamp (500 W). After 2 h, the lamp was shut off and the tetrahydrofuran was removed under reduced pressure. The resulting residue was diluted with dichloromethane (200 mL) and was washed with aqueous saturated sodium bicarbonate solution (50 mL). The aqueous layer was extracted with dichloromethane (2 × 100 mL). The combined organic extracts were washed with brine (50 mL), were dried over anhydrous sodium sulfate, were filtered and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 5→10% acetone in hexanes) to afford N8-carboxy-*tert*-butyl hexahydropyrroloindole (–)-**14** (2.33 g, 86.1%, overall from (+)-**13**) as a clear viscous oil. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

^{1}H NMR (500 MHz, CD_3CN, 20 °C): δ 7.61 (d, *J* = 8.1 Hz, 1H, $C_7\mathbf{H}$), 7.23 (d, *J* = 7.4 Hz, 1H, $C_4\mathbf{H}$), 7.19 (app-t, *J* = 7.5 Hz, 1H, $C_6\mathbf{H}$), 7.03 (app-t, *J* = 7.5 Hz, 1H, $C_5\mathbf{H}$), 6.31 (d, *J* = 6.9 Hz, 1H, $C_{8a}\mathbf{H}$), 4.01 (app-t, *J* = 7.2 Hz, 1H, $C_{3a}\mathbf{H}$), 3.75 (dd, *J* = 7.7, 11.1 Hz, 1H, $C_2\mathbf{H}_a$) 3.64 (s, 3H, $N_1CO_2C\mathbf{H}_3$), 2.76 (app-dt, *J* = 5.6, 11.6 Hz, 1H, $C_2\mathbf{H}_b$), 2.15 (app-tt, *J* = 7.7, 12.0 Hz, 1H, $C_3\mathbf{H}_a$), 2.05 (dd, *J* = 5.6, 6.9 Hz, 1H, $C_3\mathbf{H}_b$), 1.53 (s, 9H, $N_8CO_2C(C\mathbf{H}_3)_3$).

^{13}C NMR (125.8 MHz, CD_3CN, 20 °C):	δ 156.5 ($N_1\mathbf{C}O_2CH_3$), 153.8 ($N_8\mathbf{C}O_2C(CH_3)_3$), 144.2 ($\mathbf{C}_{7a}$), 133.9 ($\mathbf{C}_{4a}$), 129.2 ($\mathbf{C}_6$), 125.5 ($\mathbf{C}_4$), 124.6 ($\mathbf{C}_5$), 117.1 ($\mathbf{C}_7$), 82.3 ($N_8CO_2\mathbf{C}(CH_3)_3$), 78.1 ($\mathbf{C}_{8a}$), 53.3 ($N_1CO_2\mathbf{C}H_3$), 46.6 ($\mathbf{C}_{3a}$), 46.3 ($\mathbf{C}_2$), 32.0 ($\mathbf{C}_3$), 28.9 ($N_8CO_2C(\mathbf{C}H_3)_3$).
FTIR (thin film) cm^{-1}:	2977 (m), 1704 (s), 1604 (w), 1483 (s), 1446 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{17}H_{23}N_2O_4$ $[M+H]^+$: 319.1652, found: 319.1672.
$[\alpha]_D^{24}$:	–127 (*c* = 1.37, CH_2Cl_2).
TLC (33% acetone in hexanes), R*f*:	0.42 (UV, CAM).



Hexahydropyrroloindole Sulfamate Ester (–)-15:

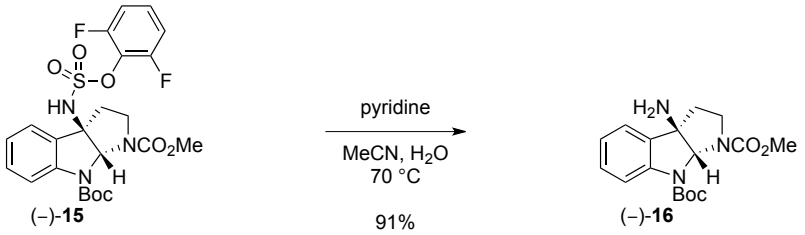
A round bottom flask was charged with 5Å molecular sieves (296 mg, 200 mg/mmol of **14**), magnesium oxide (239 mg, 5.92 mmol, 4.00 equiv) and flame-dried under vacuum for 5 min. The reaction vessel was allowed to cool to 23 °C and back filled with argon. Solid 2,6-difluorophenyl sulfamate[4] (402 mg, 1.92 mmol, 1.30 equiv), 2-methyl-2-phenylpropionic acid (122 mg, 0.740 mmol, 0.500 equiv), and $Rh_2(esp)_2$ (23.0 mg, 300 μmol, 0.0200 equiv) were added sequentially. A solution of N8-carboxy-*tert*-butyl hexahydropyrroloindole (–)-**14** (470 mg, 1.48 mmol, 1 equiv) in isopropyl acetate (3.0 mL) was added via syringe at 23 °C and the mixture was allowed to stir. After 5 min, (diacetoxyiodo)benzene (953 mg, 1.92 mmol, 2.00 equiv) was added and the green heterogeneous mixture was agitated by vigorous stirring at 23 °C. After 14 h, the reaction mixture was filtered through a pad of Celite and the filter cake was rinsed with ethyl acetate (40 mL). The filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: gradient, 15→33% ethyl acetate in hexanes) to afford the hexahydropyrroloindole sulfamate ester (–)-**15** (413 mg, 53.1%) as a white solid. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

^{1}H NMR (500 MHz, CD_3CN, 20 °C): δ 7.68 (d, J = 8.1 Hz, 1H, C_7**H**), 7.47 (d, J = 7.7 Hz, 1H, C_4**H**), 7.39–7.32 (m, 2H, C_6**H**, $C_{4'}$**H**), 7.16–7.11 (m, 3H, C_5**H**, $C_{3'}$**H**), 7.06 (br-s, 1H, C_{3a}N**H**), 6.50 (s, 1H, C_{8a}**H**), 3.85 (dd, J = 6.9, 10.3 Hz, 1H, C_2**H**$_a$) 3.66 (s, 3H, N_1CO_2C**H**$_3$), 2.77–2.65 (m, 2H, C_2**H**$_b$, C_3**H**$_a$), 2.47 (dd, J = 4.3, 11.4 Hz, 1H, C_3**H**$_b$), 1.50 (s, 9H, $N_8CO_2C(C$**H**$_3)_3$).

^{13}C NMR (125.8 MHz, CD_3CN, 20 °C): δ 157.2 (dd, J = 3.5, 251.8 Hz, **C**$_{2'}$), 156.2 (N_1**C**O_2CH_3), 153.5 (N_8**C**$O_2C(CH_3)_3$), 144.9 (**C**$_{7a}$), 131.8 (**C**$_6$), 130.8 (**C**$_{4a}$), 129.2 (app-t, J = 9.4 Hz, **C**$_{4'}$), 127.8 (t, J = 15.8 Hz, **C**$_{1'}$), 125.9 (**C**$_4$), 125.1 (**C**$_5$), 118.1 (**C**$_7$), 114.1 (dd, J = 4.0, 18.4 Hz, **C**$_{3'}$), 82.7 (N_8CO_2**C**$(CH_3)_3$), 81.1, (**C**$_{8a}$), 72.8 (**C**$_{3a}$), 53.6 (N_1CO_2**C**H_3), 46.2 (**C**$_2$), 36.6 (**C**$_3$), 28.8 ($N_8CO_2C($**C**$H_3)_3$).

[4] J. L. Roizen, D. N. Zalatan and J. Du Bois, *Angew. Chem. Int. Ed.*, 2013, *Early View*, DOI: 10.1002/anie.201304238.

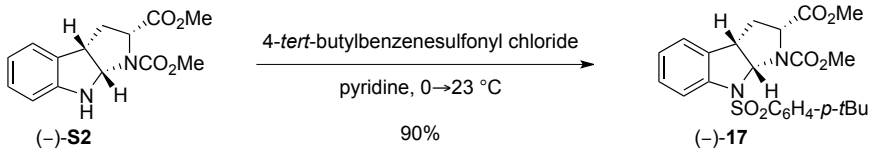
^{19}F NMR (282 MHz, $CDCl_3$, 20 °C):	δ –124.8 (t, J = 6.6 Hz, 2F, $C_6H_3\mathbf{F}_2$).
FTIR (thin film) cm^{-1}:	3168 (br-m), 2981 (w), 1712 (s), 1680 (s), 1606 (w), 1481 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{23}H_{26}F_2N_3O_7S$ $[M+H]^+$: 526.1454, found: 526.1465.
$[\alpha]_D^{24}$:	–82 (c = 1.04, CH_2Cl_2).
TLC (33% ethyl acetate in hexanes), R*f*:	0.26 (UV, CAM).



C3a-Aminohexahydropyrroloindole (–)-16:

Pyridine (613 μL, 7.61 mmol, 20.0 equiv) was added to a solution of hexahydropyrroloindole sulfamate ester (–)-**15** (200 mg, 381 μmol, 1 equiv) in a mixture of acetonitrile–water (2:1, 4.50 mL), via syringe at 23 °C. The reaction flask was fitted with a reflux condenser and heated to 70 ºC. After 24 h, the resulting yellow solution was allowed to cool to 23 °C. The mixture was diluted with dichloromethane (50 mL) and was washed with a saturated aqueous sodium bicarbonate solution (20 mL). The aqueous layer was extracted with dichloromethane (2 × 30 mL). The combined organic extracts were washed with brine (20 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: gradient, 1→5% methanol in dichloromethane) to afford the C3a-aminohexahydropyrroloindole (–)-**16** (115 mg, 90.5%) as a yellow oil. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

^{1}H NMR (500 MHz, CD_3CN, 20 °C):	δ 7.63 (d, *J* = 8.1 Hz, 1H, C_7**H**), 7.34 (d, *J* = 7.5 Hz, 1H, C_4**H**), 7.26 (app-t, *J* = 7.5 Hz, 1H, C_6**H**), 7.07 (app-t, *J* = 7.5 Hz, 1H, C_5**H**), 5.77 (s, 1H, C_{8a}**H**), 3.73 (dd, *J* = 7.9, 11.1 Hz, 1H, C_2**H**$_a$) 3.64 (s, 3H, N_1CO_2C**H**$_3$), 2.75 (app-dt, *J* = 5.6, 11.7 Hz, 1H, C_2**H**$_b$), 2.22 (dd *J* =7.9, 11.1 Hz, 1H, C_3**H**$_a$), 2.09 (app-dt, *J* = 8.1, 12.2 Hz, 1H, C_3**H**$_b$), 1.92 (br-s, 2H, N**H**$_2$)1.54 (s, 9H, $N_8CO_2C(C$**H**$_3)_3$).
^{13}C NMR (125.8 MHz, CD_3CN 20 °C):	δ 156.5 (N_1**C**O_2CH_3), 154.0 (N_8**C**$O_2C(CH_3)_3$), 143.9 (**C**$_{7a}$), 136.9 (**C**$_{4a}$), 130.3 (**C**$_6$), 124.8 (2C, **C**$_4$, **C**$_5$), 117.5 (**C**$_7$), 84.6 (**C**$_{8a}$), 82.3 (N_8CO_2**C**$(CH_3)_3$), 70.3 (**C**$_{3a}$), 53.3 (N_1CO_2**C**H_3), 47.0 (**C**$_2$), 39.4 (**C**$_3$), 28.9 ($N_8CO_2C($**C**$H_3)_3$).
FTIR (thin film) cm^{-1}:	3369 (br-w), 3302 (br-w), 2977 (w), 1702 (s), 1603 (w), 1480 (m), 1447 (m), 1393 (m), 1200 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{17}H_{24}N_3O_4$ $[M+H]^+$: 334.1761, found: 334.1783.
$[\alpha]_D^{24}$:	–119 (*c* = 1.55, CH_2Cl_2).
TLC (50% acetone in hexanes), R*f*:	0.15 (UV, CAM).



C2-Carboxymethyl Hexahydropyrroloindole (–)-17:

A solution of 4-*tert*-butylbenzenesulfonyl chloride (3.50 g, 15.1 mmol, 2.00 equiv) in pyridine (3 mL) was added dropwise via syringe to a solution of hexahydropyrroloindole (–)-**S2** (2.00 g, 7.57 mmol, 1 equiv) in pyridine (20 mL) at 0 ºC in an ice bath. After 15 min, the ice bath was removed and allowed to warm to 23 °C. After 4 h, the solution was concentrated under reduced pressure. The resulting residue was diluted with ethyl acetate (250 mL) and washed sequentially with an aqueous solution of hydrochloric acid (1 N, 2 × 25 mL), saturated aqueous solution of sodium bicarbonate (25 mL), and brine (50 mL). The organic layer was separated, was dried over anhydrous sodium sulfate, was filtered, and was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 15→25% acetone in hexanes) to give C2-carboxymethyl hexahydropyrroloindole (–)-**17** (3.20 g, 89.5%) as a white solid.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

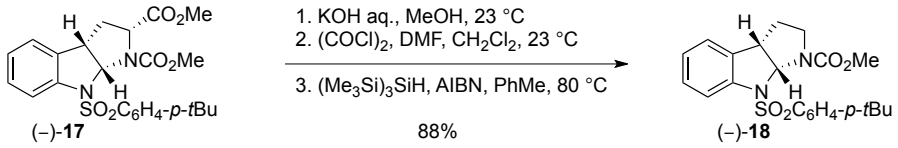
^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 7.66 (d, J = 8.6 Hz, 2H, N_8SO_2Ar-*o*-**H**), 7.50 (d, J = 8.6 Hz, 2H, N_8SO_2Ar-*m*-**H**), 7.38 (d, J = 8.1 Hz, 1H, C_7**H**), 7.23 (app-t, J = 7.2 Hz, 1H, C_6**H**), 7.10 (d, J = 7.4 Hz, 1H, C_4**H**), 7.07 (app-t, J = 7.2 Hz, 1H, C_5**H**), 6.29 (d, J = 6.5 Hz, 1H C_{8a}**H**), 4.54 (d, J = 9.0 Hz, 1H, C_2**H**), 3.71 (app-t, J = 6.9 Hz, 1H, C_{3a}**H**), 3.60 (s, 3H, N_1CO_2C**H**$_3$), 3.16 (s, 3H, CO_2C**H**$_3$), 2.61–2.49 (m, 2H, C_3**H**), 1.30 (s, 9H, $C(C$**H**$_3)_3$).

^{13}C NMR (125.8 MHz, CD_3CN, 70 °C): δ 173.2 (**C**O_2CH_3) 158.9 (N_8SO_2Ar-*p*-**C**), 156.5 (N_1**C**O_2CH_3), 144.3 (**C**$_{7a}$), 138.5 (N_8SO_2Ar-*ipso*-**C**), 135.8 (**C**$_{4a}$), 130.2 (**C**$_6$), 128.6 (N_8SO_2Ar-*o*-**C**), 127.7 (N_8SO_2Ar-*m*-**C**), 126.9 (**C**$_4$), 126.3 (**C**$_5$), 119.8 (**C**$_7$), 82.5 (**C**$_{8a}$), 60.9 (**C**$_2$), 53.8 (NCO_2**C**H_3), 53.1 (CO_2**C**H_3), 47.4 (**C**$_{3a}$), 36.6 (**C**$(CH_3)_3$), 35.1 (**C**$_3$), 32.1 ($C($**C**$H_3)_3$).

FTIR (thin film) cm^{-1}: 2956 (w), 1711 (s), 1595 (w), 1447 (m), 1384 (m), 1360 (m), 1169 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{24}H_{29}N_2O_6S$ $[M+H]^+$: 473.1741, found: 473.1740.

$[\alpha]_D^{24}$:	–71 (*c* = 0.44, CH_2Cl_2).
TLC (33% acetone in hexanes), R*f*:	0.33 (UV, CAM).



N8-*tert*-Butylbenzenesulfonyl Hexahydropyrroloindole (–)-18:

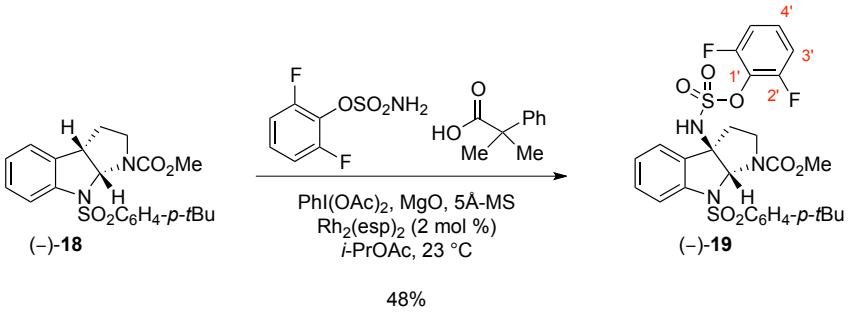
An aqueous solution of potassium hydroxide (5 N, 30 mL) was added to a solution of C2-carboxymethyl hexahydropyrroloindole (–)-**17** (3.10 g, 6.56 mmol, 1.00 equiv) in methanol (60 mL) at 23 °C. After 40 min, the resulting solution was cooled to 0 ºC in an ice bath and adjusted to pH ~ 2 by the dropwise addition of an aqueous solution of hydrochloric acid (12 N, 15 mL). The mixture was allowed to warm to 23 °C and was extracted with dichloromethane (3 × 150 mL). The combined organic layers were washed with brine (50 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to afford the crude carboxylic acid as a white foam. The crude carboxylic acid was concentrated from benzene (15 mL) under reduced pressure to remove residual methanol.

Oxalyl chloride (1.60 mL, 18.9 mmol, 3.00 equiv) and dimethylformamide (48.0 μL, 630 μmol, 0.100 equiv) were added sequentially via syringe to a solution of the crude carboxylic acid in dichloromethane (65 mL) at 23 °C. After 1 h, the solution was concentrated under reduce pressure. The resulting residue was concentrated from benzene (2 × 20 mL) to remove the remaining oxalyl chloride. The crude acid chloride was dissolved in toluene (120 mL) and argon was bubbled through the solution for 10 min. Tristrimethylsilylsilane (2.90 mL, 9.45 mmol, 1.50 equiv) and azobisisobutyronitrile (AIBN, 103 mg, 630 μmol, 0.10 equiv) were added to the solution at 23 ºC. The flask was fitted with a reflux condenser and heated to 80 ºC. After 45 min, an additional portion of tristrimethylsilylsilane (2.90 mL, 9.45 mmol, 1.50 equiv) and AIBN (103 mg, 630 μmol, 0.10 equiv) were added. After a further 1.5 h, another portion of AIBN (103 mg, 630 μmol, 0.10 equiv) was added. After an additional 1.5 h the reaction mixture was allowed to cool to 23 °C and was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 15→20% acetone in hexanes) to give N8-*tert*-butylbenzenesulfonyl hexahydropyrroloindole (–)-**18** (2.40 g, 88.3%, overall from (–)-**17**) as a white foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 7.65 (d, J = 8.6 Hz, 2H, N_8SO_2Ar-*o*-**H**), 7.50–7.49 (m, 3H, N_8SO_2Ar-*m*-**H**, C_7**H**), 7.25 (app-t, J = 8.0 Hz, 1H, C_6**H**), 7.16 (d, J = 7.4 Hz, 1H, C_4**H**), 7.10 (app-t, J = 7.4 Hz, 1H, C_5**H**), 6.25 (d, J = 6.7 Hz, 1H, C_{8a}**H**), 3.74–3.70 (m, 2H, C_{3a}**H**, C_2**H**$_a$), 3.67 (s, 3H, N_1CO_2C**H**$_3$), 2.77 (app-dt, J = 5.7, 11.5 Hz, 1H, C_2**H**$_b$), 2.15 (app-ddt, J = 7.9, 11.6, 12.6 Hz, 1H, C_3**H**$_a$), 2.00 (dd, J = 5.5, 12.2 Hz, 1H, C_3**H**$_b$), 1.30 (s, 9H, $C(C$**H**$_3)_3$).

^{13}C NMR (125.8 MHz, CD_3CN, 70 °C):	δ 159.1 (N_8SO_2Ar-*p*-**C**), 156.6 (N_1**C**O_2CH_3), 143.9 (C_{7a}), 137.9 (N_8SO_2Ar-*ipso*-**C**), 136.0 (C_{4a}), 130.0 (C_6), 128.8 (N_8SO_2Ar-*o*-**C**), 127.8 (N_8SO_2Ar-*m*-**C**), 127.1 (C_4), 126.3 (C_5), 118.9 (C_7), 82.0 (C_{8a}), 53.7 (N_1CO_2**C**H_3), 47.8 (C_{3a}), 46.5 (C_2), 36.6 (**C**$(CH_3)_3$), 32.2 (C_3), 32.1 (**C**$(CH_3)_3$).
FTIR (thin film) cm^{-1}:	2961 (m), 1709 (s), 1447 (m), 1385 (m), 1360 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{22}H_{27}N_2O_4S$ $[M+H]^+$: 415.1686, found: 415.1676 .
$[\alpha]_D^{24}$:	–198 (*c* = 0.19, CH_2Cl_2).
TLC (33% acetone in hexanes), R*f*:	0.34 (UV, CAM).

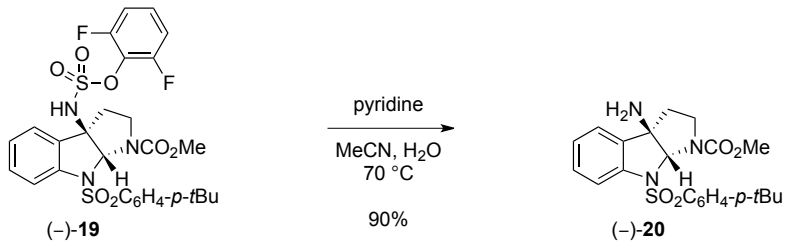


Hexahydropyrroloindole Sulfamate Ester (–)-19:

A round bottom flask was charged with 5Å molecular sieves (482 mg, 200 mg/mmol of **18**), magnesium oxide (388 mg, 9.64 mmol, 4.00 equiv), and flame-dried under vacuum for 5 min. The reaction vessel was allowed to cool to 23 °C and back filled with argon. Solid 2,6-difluorophenyl sulfamate[4] (656 mg, 3.14 mmol, 1.30 equiv), 2-methyl-2-phenylpropionic acid (198 mg, 1.21 mmol, 0.500 equiv), and $Rh_2(esp)_2$ (3.7 mg, 48 μmol, 0.020 equiv) were added sequentially and the mixture was sealed under argon. A solution of N8-*tert*-butylbenzenesulfonyl hexahydropyrroloindole (–)-**18** (1.00 g, 2.41 mmol, 1 equiv) in isopropyl acetate (5.0 mL) was added via syringe at 23 °C and the mixture was allowed to stir. After 5 min, (diacetoxyiodo)benzene (1.55 g, 4.82 mmol, 2.00 equiv) was added and the resulting green heterogeneous mixture was agitated by vigorous stirring at 23 °C. After 14 h, the mixture was filtered through a pad of Celite and the filter cake was rinsed with ethyl acetate (50 mL). The filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: gradient, 15→20% acetone in hexanes) to afford a mixture of the desired sulfamate ester (–)-**19** along with minor amounts of regioisomeric amination products. The mixture was triturated with dichloromethane in hexanes (33% v/v, 20 mL) and the resulting suspension was filtered over a sintered glass funnel and rinsed with cold dichloromethane in hexanes (33% v/v, 10 mL) to afford pure hexahydropyrroloindole sulfamate ester (–)-**19** (0.578 g, 38.5%) as a white solid. The filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: gradient, 20→33% ethyl acetate in hexanes) to afford a second portion of pure hexahydropyrroloindole sulfamate ester (–)-**19** (140 mg, 9.3%) as a white solid. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 7.71 (d, J = 8.1Hz, 1H, C_7**H**), 7.57 (br-s, 2H, N_8SO_2Ar-*o*-**H**), 7.43 (app-t, J = 7.6 Hz, 1H, C_6**H**), 7.37–7.34 (m, C_4**H**, N_8SO_2Ar-*m*-**H**), 7.26-7.20 (m, C_5**H**, $C_{4'}$**H**), 7.01 (app-t, J = 7.8 Hz, 2H, $C_{3'}$**H**), 6.20 (s, 1H, C_{8a}**H**), 3.94 (s, 1H, C_{3a}N**H**), 3.86 (dd, J = 8.0, 11.1, 1H, C_2**H**$_a$), 3.72 (s, 3H, N_1CO_2C**H**$_3$), 2.99 (app-dt, J = 8.1, 12.1Hz, 1H, C_2**H**$_a$), 2.76 (br-s, 1H, C_2**H**$_b$), 2.43 (dd, J = 4.9, 12.4 Hz, 1H C_3**H**$_b$), 1.18 (s, 9H, C(C**H**$_3$)$_3$).

^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 157.9 (N_8SO_2Ar-*p*-**C**), 156.1 (dd, *J* = 3.4, 253.7 Hz, $\mathbf{C}_{2'}$), 155.0 ($N_1\mathbf{C}O_2CH_3$), 142.7 ($\mathbf{C}_{7a}$), 135.1 (N_8SO_2Ar-*ipso*-**C**), 131.9 ($\mathbf{C}_{4a}$), 131.6 ($\mathbf{C}_6$), 128.1 (app-t, *J* = 9.3 Hz, $\mathbf{C}_{1'}$), 127.7 ($\mathbf{C}_{4'}$), 127.1 (N_8SO_2Ar-*o*-**C**), 126.8 (N_8SO_2Ar-*m*-**C**), 126.7 ($\mathbf{C}_5$), 124.3 ($\mathbf{C}_4$), 119.7 ($\mathbf{C}_7$), 112.9 (dd, *J* = 3.9, 18.4 Hz, $\mathbf{C}_{3'}$), 82.6 ($\mathbf{C}_{8a}$), 72.6 ($\mathbf{C}_{3a}$), 53.1 ($N_1CO_2\mathbf{C}H_3$), 45.2 ($\mathbf{C}_2$), 35.4 ($\mathbf{C}(CH_3)_3$), 32.7 ($\mathbf{C}_3$), 31.0 ($C(\mathbf{C}H_3)_3$).
^{19}F NMR (282 MHz, $CDCl_3$, 20 °C):	δ –124.9 (t, *J* = 6.6 Hz, 2F, $C_6H_3\mathbf{F}_2$).
FTIR (thin film) cm^{-1}:	2964 (m), 1689 (m), 1498 (m), 1390 (m), 1176 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{28}H_{30}F_2N_3O_7S_2$ $[M+H]^+$: 622.1488, found: 622.1499.
$[\alpha]_D^{24}$:	–46 (*c* = 0.35, CH_2Cl_2).
TLC (33% acetone in hexanes), R*f*:	0.26 (UV, CAM).



C3a-Aminohexahydropyrroloindole (–)-20:

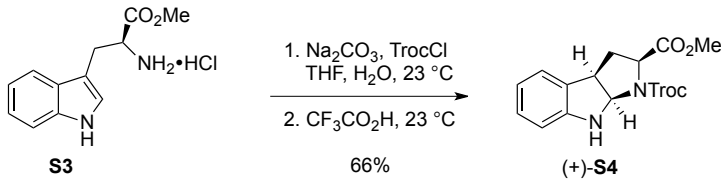
Pyridine (130 μL, 1.61 mmol, 20.0 equiv) was added to a solution of hexahydropyrroloindole sulfamate ester (–)-**19** (50.0 mg, 80.0 μmol, 1 equiv) in a mixture of acetonitrile–water (2:1, 900 μL) via syringe at 23 °C. The reaction flask was fitted with a reflux condenser and heated to 70 ºC. After 24 h, the resulting yellow solution was allowed to cool to 23 °C. The mixture was diluted with dichloromethane (25 mL) and was washed with a saturated aqueous sodium bicarbonate solution (10 mL). The aqueous layer was extracted with dichloromethane (2 × 15 mL). The combined organic extracts were washed with brine (10 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: gradient, 2→5% methanol in dichloromethane) to afford the C3a-aminohexahydropyrroloindole (–)-**20** (31.0 mg, 90.2%) as a yellow oil.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 70 °C):	δ 7.75 (d, J = 8.5 Hz, 2H, N_8SO_2Ar-*o*-**H**), 7.55–7.53 (m, 3H, N_8SO_2Ar-*m*-**H**, C_7**H**), 7.34–7.29 (m, 2H, C_6**H**, C_4**H**), 7.17 (app-t, J = 7.5 Hz, 1H, C_5**H**), 5.71 (s, 1H, C_{8a}**H**), 3.76 (app-t, J = 9.5 Hz, 1H, C_2**H**$_a$), 3.67 (s, 3H, N_1CO_2C**H**$_3$), 2.80 (app-dt, J = 6.0, 11.1 Hz, 1H, C_2**H**$_b$) 2.14 (dd, J = 6.0, 12.5 Hz, 1H, C_3**H**$_a$), 2.07 (app-dt, J = 8.0, 11.0 Hz, 1H, C_3**H**$_b$), 1.43 (br-s, 2H, N**H**$_2$) 1.30 (s, 9H, C(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, CD_3CN, 70 °C):	δ 159.3 (N_8SO_2Ar-*p*-**C**), 156.8 (N_1**C**O_2CH_3), 143.4 (**C**$_{7a}$), 138.3 (**C**$_{4a}$), 137.9 (N_8SO_2Ar-*ipso*-**C**), 131.1 (**C**$_6$), 129.0 (N_8SO_2Ar-*o*-**C**), 127.9 (N_8SO_2Ar-*m*-**C**), 127.0 (**C**$_5$), 125.6 (**C**$_4$), 118.6 (**C**$_7$), 88.5 (**C**$_{8a}$), 71.9 (**C**$_{3a}$), 53.7 (N_1CO_2**C**H_3), 47.4 (**C**$_2$), 40.5 (**C**$_3$), 36.7 (**C**$(CH_3)_3$), 32.0 (C(**C**H_3)$_3$).
FTIR (thin film) cm^{-1}:	3380 (br-w), 3316 (br-w), 2962 (m), 1710 (s), 1595 (w), 1448 (m), 1385 (m), 1197 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{22}H_{27}N_3NaO_4S$ $[M+Na]^+$: 452.1614, found: 452.1633.

$[\alpha]_D^{24}$: –175 (*c* = 1.66, CH_2Cl_2).

TLC (50% acetone in hexanes), R*f*: 0.24 (UV, CAM).



S3 66% (+)-**S4**

N1-Carboxytrichloroethyl Hexahydropyrroloindole (+)-S4:

Sodium carbonate (8.30 g, 78.5 mmol, 2.00 equiv) was added in one portion as a solid to a solution of L-tryptophan methyl ester hydrochloride (**S3**) (10.0 g, 39.3 mmol, 1 equiv) in tetrahydrofuran–water (1:1, 400 mL) at 23 °C. After 10 min, 2,2,2-trichloroethyl chloroformate (7.00 mL, 51.0 mmol, 1.30 equiv) was added via syringe. After 1 h, tetrahydrofuran was removed under reduced pressure, and the resulting aqueous suspension was extracted with dichloromethane (3 × 300 mL). The combined organic extracts were washed with brine (100 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to afford 2,2,2-trichloroethoxycarbonylated L-tryptophan methyl ester. The resulting tryptophan derivative was dissolved in trifluoroacetic acid (200 mL) and stirred at 23 °C. After 40 h, the homogenous solution was poured slowly into a vigorously stirred biphasic mixture of dichloromethane (200 mL) and aqueous sodium carbonate solution (10% w/v, 600 mL). The pH of the mixture was maintained above 7 by the periodic addition of solid sodium carbonate (5 × 50 g). Once the addition was complete, the mixture was extracted with dichloromethane (3 × 400 mL) and the combined organic layers were washed sequentially with water (100 mL) and brine (100 mL). The organic layer was separated, was dried over anhydrous sodium sulfate, was filtered, and was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 15→25% acetone in hexanes) to give N1-carboxytrichloroethyl hexahydropyrroloindole (+)-**S4**[5] (10.2 g, 65.9%) as a clear viscous oil. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

^{1}H NMR (500 MHz, C_6D_6, 20 °C):

Major Rotamer: δ 6.89 (app-t, J = 7.5 Hz, 1H, C_6**H**), 6.79–6.75 (m, 1H, C_4**H**), 6.61 (app-t, J = 7.4 Hz, 1H, C_5**H**), 6.25 (d, J = 7.7 Hz, 1H, C_7**H**), 5.33 (d, J = 6.6 Hz, 1H, C_{8a}**H**), 5.17 (br-s, 1H, N_8**H**), 4.65 (d, J = 11.9 Hz, 1H, N_1CO_2C**H**$_a$H$_b$CCl$_3$) 4.56–4.52 (m, 1H, $N_1CO_2CH_a$**H**$_b$CCl$_3$), 4.38 (d, J = 8.7 Hz, 1H, C_2**H**), 3.21 (app-t, J = 7.1 Hz, 1H, C_{3a}**H**), 2.92 (s, 3H, CO_2C**H**$_3$), 2.27 (d, J = 13.2 Hz, 1H, C_3**H**$_a$), 1.83–1.74 (m, 1H, C_3**H**$_b$).

Minor Rotamer: δ 6.94 (app-t, J = 7.5 Hz, 1H, C_6**H**), 6.79–6.75 (m, 1H, C_4**H**), 6.64 (app-t, J = 7.4 Hz, 1H, C_5**H**), 6.49 (d, J = 7.7 Hz, 1H, C_7**H**), 5.31 (d, J =

[5] Due to facile opening of cyclotryptophan **S4** to the corresponding tryptophan derivative this material was used in the next step immediately following purification.

6.6 Hz, 1H, $C_{8a}\mathbf{H}$), 4.99 (br-s, 1H, $N_8\mathbf{H}$), 4.65 (d, *J* = 11.9 Hz, 1H, $N_1CO_2C\mathbf{H}_aH_bCCl_3$) 4.56–4.52 (m, 1H $N_1CO_2CH_a\mathbf{H}_bCCl_3$), 4.50 (d, *J* = 8.7 Hz, 1H, $C_2\mathbf{H}$), 3.29 (app-t, *J* = 7.1 Hz, 1H, $C_{3a}\mathbf{H}$), 2.89 (s, 3H, $CO_2C\mathbf{H}_3$), 2.28 (d, *J* = 13.2 Hz, 1H, $C_3\mathbf{H}_a$), 1.83–1.74 (m, 1H, $C_3\mathbf{H}_b$).

^{13}C NMR (125.8 MHz, C_6D_6, 20 °C): *Major Rotamer:* δ 171.5 ($\mathbf{C}O_2CH_3$), 153.2 ($N_1\mathbf{C}O_2CH_2CCl_3$), 150.9 ($\mathbf{C}_{7a}$), 129.1 ($\mathbf{C}_6$), 128.7 ($\mathbf{C}_{4a}$), 124.5 ($\mathbf{C}_4$), 119.2 ($\mathbf{C}_5$), 109.7 ($\mathbf{C}_7$), 96.3 ($N_1CO_2CH_2\mathbf{C}Cl_3$), 78.3 ($\mathbf{C}_{8a}$), 75.2 ($N_1CO_2\mathbf{C}H_2CCl_3$), 59.7 ($\mathbf{C}_2$), 52.1 ($CO_2\mathbf{C}H_3$), 45.6 ($\mathbf{C}_{3a}$), 34.8 ($\mathbf{C}_3$).

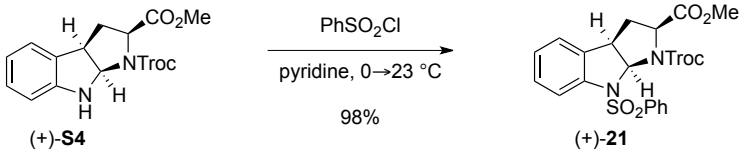
Minor Rotamer: δ 171.2 ($\mathbf{C}O_2CH_3$), 152.4 ($N_1\mathbf{C}O_2CH_2CCl_3$), 150.6 ($\mathbf{C}_{7a}$), 129.3 ($\mathbf{C}_6$), 128.9 ($\mathbf{C}_{4a}$), 124.7 ($\mathbf{C}_4$), 119.8 ($\mathbf{C}_5$), 109.5 ($\mathbf{C}_7$), 96.5 ($N_1CO_2CH_2\mathbf{C}Cl_3$), 77.7 ($\mathbf{C}_{8a}$), 75.2 ($N_1CO_2\mathbf{C}H_2CCl_3$), 60.2 ($\mathbf{C}_2$), 52.1 ($CO_2\mathbf{C}H_3$), 46.6 ($\mathbf{C}_{3a}$), 34.1 ($\mathbf{C}_3$).

FTIR (thin film) cm^{-1}: 3384 (br-w), 2951 (w), 1718 (s), 1610 (w), 1414 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{15}H_{16}Cl_3N_2O_4$ $[M+H]^+$: 393.0170, found: 393.0180.

$[\alpha]_D^{24}$: +168 (*c* = 0.58, CH_2Cl_2).

TLC (33% acetone in hexanes), R*f*: 0.34 (UV, CAM).



(+)-**S4** (+)-**21**

C2-Carboxymethyl Hexahydropyrroloindole (+)-21:

Benzenesulfonyl chloride (6.10 mL, 47.8 mmol, 2.00 equiv) was added dropwise via syringe to a solution of N1-carboxytrichloroethyl hexahydropyrroloindole (+)-**S4** (9.40 g, 23.9 mmol, 1 equiv) in pyridine (40 mL) at 0 ºC in an ice bath. After 15 min, the ice bath was removed and allowed to warm to 23 °C. After 15 h, the solution was concentrated under reduced pressure. The resulting residue was diluted with ethyl acetate (750 mL) and washed sequentially with an aqueous solution of hydrochloric acid (1 N, 2 × 50 mL), saturated aqueous solution of sodium bicarbonate (50 mL), and brine (100 mL). The organic layer was separated, was dried over anhydrous sodium sulfate, was filtered, and was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 25→50% ethyl acetate in hexanes) to give C2-carboxymethyl hexahydropyrroloindole (+)-**21** (12.5 g, 97.9%) as a white foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

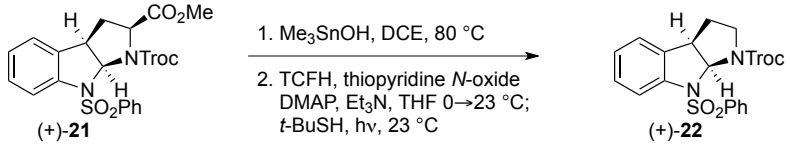
^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 7.72 (d, J = 8.3 Hz, 2H, N_8SO_2Ph-*o*-**H**), 7.57 (t, J = 7.8 Hz, 1H, N_8SO_2Ph-*p*-**H**), 7.45–7.40 (m, 3H, C_7**H**, N_8SO_2Ph-*m*-**H**), 7.25 (app-t, J = 8.3 Hz, 1H, C_6**H**), 7.09 (m, 2H, C_4**H**, C_5**H**), 6.38 (d, J = 6.4 Hz, 1H, C_{8a}**H**), 4.86 (d, J = 12.1 Hz, 1H, $N_1CO_2C\mathbf{H}_aH_bCCl_3$) 4.71 (d, J = 10.5 Hz, 1H, $N_1CO_2CH_a\mathbf{H}_bCCl_3$), 4.64 (d, J = 9.1 Hz, 1H, C_2**H**), 3.70 (app-t, J = 7.0 Hz, 1H, C_{3a}**H**), 3.15 (s, 3H, $CO_2C\mathbf{H}_3$), 2.61 (ddd, J = 7.5, 9.1, 13.4 Hz, 1H, $C_3\mathbf{H}_a$), 2.52 (d, J = 13.4 Hz, 1H, $C_3\mathbf{H}_b$).

^{13}C NMR (125.8 MHz, CD_3CN, 70 °C): δ 172.7 (**C**O_2CH_3), 154.0[6] (N_1**C**$O_2CH_2CCl_3$), 144.1 ($\mathbf{C}_{7a}$), 140.8 (N_8SO_2Ph-*ipso*-**C**), 135.9 ($\mathbf{C}_{4a}$), 135.0 (N_8SO_2Ph-*p*-**C**), 130.8 (N_8SO_2Ph-*m*-**C**), 130.4 ($\mathbf{C}_6$), 128.9 (N_8SO_2Ph-*o*-**C**), 127.3 ($\mathbf{C}_5$), 126.4 ($\mathbf{C}_4$), 120.0 ($\mathbf{C}_7$), 97.3 ($N_1CO_2CH_2\mathbf{C}Cl_3$), 82.9 ($\mathbf{C}_{8a}$), 76.7 ($N_1CO_2\mathbf{C}H_2CCl_3$), 61.1 ($\mathbf{C}_2$), 53.2 ($CO_2\mathbf{C}H_3$), 47.1 ($\mathbf{C}_{3a}$), 35.2 ($\mathbf{C}_3$).

FTIR (thin film) cm^{-1}: 2952 (w), 1731 (s), 1404 (m), 1357 (m), 1170 (m).

[6] Not observed directly in simple ^{13}C NMR. Assigned based on HMBC correlation to $NCO_2CH_a\mathbf{H}_bCCl_3$.

HRMS (ESI) (*m/z*):	calc'd for $C_{21}H_{20}Cl_3N_2O_6S$ $[M+H]^+$: 533.0102, found: 533.0107.
$[\alpha]_D^{24}$:	+93 (*c* = 0.41, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.47 (UV, CAM).



N8-Benzenesulfonyl Hexahydropyrroloindole (+)-22:

Trimethyltin hydroxide[7] (9.50 g, 52.5 mmol, 8.00 equiv) was added to a solution of C2-carboxymethyl hexahydropyrroloindole (+)-**21** (3.50 g, 6.55 mmol, 1 equiv) in dichloroethane (65 mL) at 23 °C. The reaction flask was fitted with a reflux condenser and heated to 80 ºC. After 48 h, the heterogeneous mixture was allowed to cool to 23 °C and was concentrated under reduced pressure. The resulting residue was diluted with ethyl acetate (600 mL) and was washed with aqueous hydrochloric acid solution (1 N, 3 × 100 mL), brine (50 mL), the organic layer was separated, was dried over anhydrous sodium sulfate, was filtered and was concentrated under reduced pressure. The resulting residue was filtered through a pad of silica gel (eluent: 5% methanol in dichloromethane→5% acetic acid in dichloromethane) to remove excess trimethyltin hydroxide. The filtrate was concentrated under reduced pressure to provide the crude carboxylic acid.

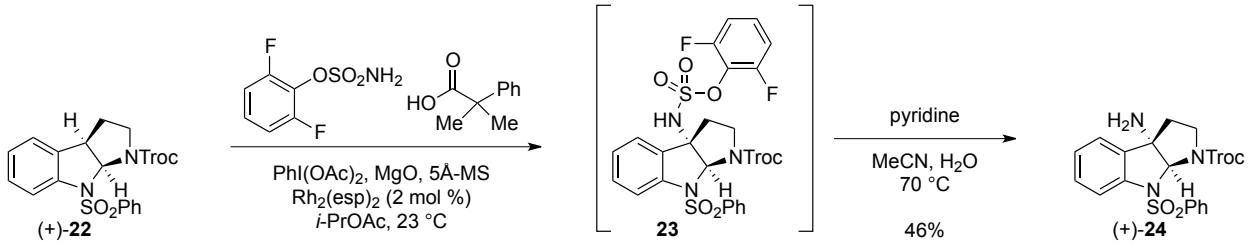
Thiopyridine *N*-oxide (1.33 g, 10.5 mmol, 1.60 equiv), 4-(dimethylamino)pyridine (80.0 mg, 650 μmol, 0.100 equiv), and *N*,*N*,*N*′,*N*′-tetramethylchloroformamidinium hexafluorophosphate (TCFH, 2.75 g, 9.81 mmol, 1.50 equiv) were sequentially added to a solution of the crude carboxylic acid in tetrahydrofuran (65 mL) at 0 ºC in an ice bath. The reaction flask was removed from the ice bath, covered in aluminum foil, and triethylamine (3.65 mL, 26.2 mmol, 4.00 equiv) was added while the reaction mixture was still cold. After 1.5 h, *tert*-butylthiol (3.70 mL, 32.7 mmol, 5.00 equiv) was added via syringe and the aluminum foil was removed from the flask. The resulting suspension was irradiated with a flood lamp (500 W). After 2 h, the lamp was turned off and the tetrahydrofuran was removed under reduced pressure. The resulting residue was diluted with dichloromethane (200 mL) and was washed with aqueous saturated sodium bicarbonate solution (50 mL). The aqueous layer was extracted with dichloromethane (2 × 100 mL). The combined organic extracts were washed with brine (50 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: gradient, 10→33% ethyl acetate in hexanes) to give N8-benzenesulfonyl hexahydropyrroloindole (+)-**22** (2.47 g, 79.3%, overall from (+)-**21**) as a white foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 7.74 (d, *J* = 7.8 Hz, 2H, N_8SO_2Ph-*o*-**H**), 7.59 (t, *J* = 7.5 Hz, 1H, N_8SO_2Ph-*p*-**H**) 7.52 (d, *J* = 8.1 Hz, 1H, C_7**H**) 7.45 (t, *J* = 7.3 Hz, 2H, N_8SO_2Ph-*m*-**H**),

[7] All operations involving trimethyltin hydroxide were carried out in a well-ventilated fume hood. This includes but is not limited to: measuring out the reagent, execution of the transformation, work-up of the reaction mixture, and concentration of the crude reaction mixture.

	7.27 (app-t, J = 7.3 Hz, 1H, $C_6\mathbf{H}$), 7.18–7.12 (m, 2H, $C_4\mathbf{H}$, $C_5\mathbf{H}$), 6.34 (d, J = 6.7 Hz, 1H, $C_{8a}\mathbf{H}$), 4.90–4.82 (m, 2H, $N_1CO_2C\mathbf{H}_2CCl_3$), 3.85 (dd, J = 8.3, 10.6 Hz, 1H, $C_2\mathbf{H}_a$), 3.73 (app-t, J = 7.1 Hz, 1H, $C_{3a}\mathbf{H}$), 2.85 (app-dt, J = 5.7, 11.4 Hz, 1H, $C_2\mathbf{H}_b$), 2.23–2.14 (m, 1H, $C_3\mathbf{H}_a$), 2.04 (dd, J = 5.6, 12.7 Hz, 1H, $C_3\mathbf{H}_b$).
^{13}C NMR (125.8 MHz, CD_3CN, 70 °C):	δ 154.3 ($N_1\mathbf{C}O_2CH_2CCl_3$), 143.7 ($\mathbf{C}_{7a}$), 140.4 ($N_8SO_2$Ph-*ipso*-**C**), 135.8 ($\mathbf{C}_{4a}$), 135.1 (NSO_2Ph-*p*-**C**), 130.9 (N_8SO_2Ph-*m*-**C**), 130.2 ($\mathbf{C}_6$), 129.0 (N_8SO_2Ph-*o*-**C**), 127.3 ($\mathbf{C}_5$), 126.4 ($\mathbf{C}_4$), 119.0 ($\mathbf{C}_7$), 97.7 ($N_1CO_2CH_2\mathbf{C}Cl_3$), 82.1 ($\mathbf{C}_{8a}$), 76.6 ($N_1CO_2\mathbf{C}H_2CCl_3$), 47.6 ($\mathbf{C}_{3a}$), 46.9 ($\mathbf{C}_2$), 37.3 ($\mathbf{C}_3$).
FTIR (thin film) cm^{-1}:	2952 (w), 1728 (s), 1407 (m), 1358 (m), 1173 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{19}H_{18}Cl_3N_2O_4S$ $[M+H]^+$: 475.0047, found: 475.0051.
$[\alpha]_D^{24}$:	+183 (*c* = 0.43, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.58 (UV, CAM).



C3a-Aminohexahydropyrroloindole (+)-24:

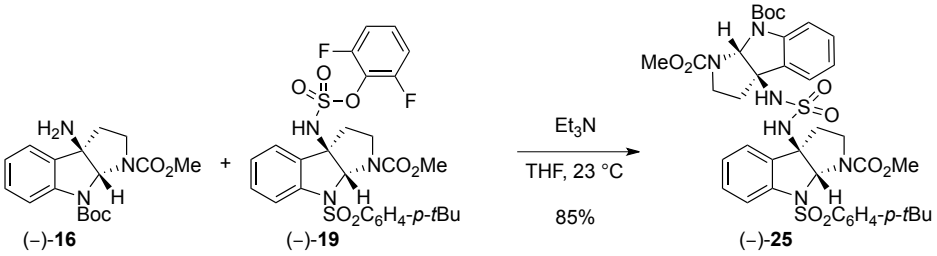
A round bottom flask was charged with 5Å molecular sieves (210 mg, 200 mg/mmol of **22**), magnesium oxide (169 mg, 4.20 mmol, 4.00 equiv) and flame-dried under vacuum. The reaction vessel was allowed to cool to 23 °C and back filled with argon. Solid 2,6-difluorophenyl sulfamate[4] (287 mg, 1.37 mmol, 1.30 equiv), 2-methyl-2-phenylpropionic acid (86.0 mg, 526 μmol, 0.500 equiv), and $Rh_2(esp)_2$ (16.0 mg, 21.0 μmol, 0.0200 equiv) were added sequentially. A solution of N8-benzenesulfonyl hexahydropyrroloindole (+)-**22** (500 mg, 1.05 mmol, 1 equiv) in isopropyl acetate (2.0 mL) was added at 23 °C and the mixture was allowed to stir. After 5 min, (diacetoxyiodo)benzene (676 mg, 2.10 mmol, 2.00 equiv) was added and the green heterogeneous mixture was vigorously agitated with stirring at 23 °C. After 24 h, the reaction mixture was filtered through a pad of Celite and the filter cake was rinsed with ethyl acetate (40 mL). The filtrate was concentrated under reduced pressure. The residue was diluted with dichloromethane (50 mL) and washed with a saturated solution of sodium thiosulfate (10 mL). The aqueous layer was then extracted with dichloromethane (2 × 30 mL). The combined organic extracts were washed with brine (25 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure.

The resulting crude aryl sulfamate ester **23** was dissolved in a mixture of acetonitrile–water (2:1, 21 mL). Pyridine (1.70 mL, 21.0 mmol, 20.0 equiv) was added via syringe at 23 °C. The reaction flask was fitted with a reflux condenser and heated to 70 ºC. After 24 h, the resulting dark brown solution was allowed to cool to 23 °C. The mixture was diluted with dichloromethane (50 mL) and was washed with a saturated aqueous solution of sodium bicarbonate (20 mL). The aqueous layer was extracted with dichloromethane (2 × 30 mL). The combined organic extracts were washed with brine (25 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: gradient, 15→ 33% acetone in hexane) to afford the C3a-aminohexahydropyrroloindole (+)-**24** (235 mg, 45.7%, overall from (+)-**22**) as an orange foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 7.86 (d, J = 7.9 Hz, 2H, N_8SO_2Ph-*o*-**H**), 7.61 (t, J = 7.8 Hz, 1H, N_8SO_2Ph-*p*-**H**) 7.55 (d, J = 8.1 Hz, 1H, C_7**H**), 7.49 (t, J = 7.4 Hz, 2H, N_8SO_2Ph-*m*-**H**), 7.35–7.31 (m, 2H, C_6**H**, C_4**H**), 7.18 (app-t, J = 7.5 Hz, 1H, C_5**H**), 5.82 (s, 1H, C_{8a}**H**), 4.88 (br-s, 1H, N_1CO_2C**H**$_a$H$_b$$CCl_3$), 4.81 (d, J = 10.9 Hz, 1H,

	$N_1CO_2CH_a\mathbf{H}_bCCl_3$), 3.90 (app-t, J = 9.5 Hz, 1H, $C_2\mathbf{H}_a$), 2.91 (app-dt, J = 6.0, 11.1 Hz, 1H, $C_2\mathbf{H}_b$), 2.19 (dd, J = 6.0, 12.5 Hz, 1H, $C_3\mathbf{H}_a$), 2.11 (app-dt, J = 8.0, 11.4 Hz, 1H, $C_3\mathbf{H}_b$) 1.47 (br-s, 2H, $N\mathbf{H}_2$).
^{13}C NMR (125.8 MHz, CD_3CN, 70 °C):	δ 154.6 ($N_1\mathbf{C}O_2CH_2CCl_3$), 143.2 ($\mathbf{C}_{7a}$), 140.5 ($N_8SO_2$Ph-*ipso*-**C**), 137.9 ($\mathbf{C}_{4a}$), 135.3 (N_8SO_2Ph-*p*-**C**), 131.3 ($\mathbf{C}_6$), 131.0 (N_8SO_2Ph-*m*-**C**), 129.2 (N_8SO_2Ph-*o*-**C**), 127.2 ($\mathbf{C}_5$), 125.8 ($\mathbf{C}_4$), 118.3 ($\mathbf{C}_7$), 97.7 ($N_1\mathbf{C}O_2CH_2\mathbf{C}Cl_3$), 88.5 ($\mathbf{C}_{8a}$), 76.6 ($N_1CO_2\mathbf{C}H_2CCl_3$), 71.8 ($\mathbf{C}_{3a}$), 47.8 ($\mathbf{C}_2$), 40.8 ($\mathbf{C}_3$).
FTIR (thin film) cm^{-1}:	2953 (w), 1733 (s), 1407 (m), 1361 (m), 1171 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{19}H_{19}Cl_3N_3O_4S$ $[M+H]^+$: 490.0156, found: 490.0139.
$[\alpha]_D^{24}$:	+164 (*c* = 0.48, CH_2Cl_2).
TLC (33% acetone in hexanes), R*f*:	0.16 (UV, CAM).



Mixed Sulfamide (–)-25:

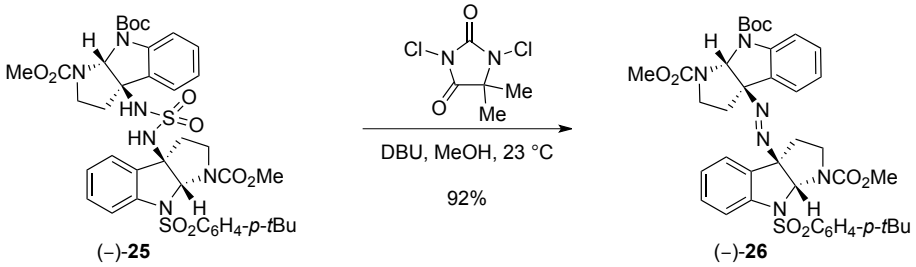
Triethylamine (82.0 μL, 587 μmol, 2.20 equiv) was added via syringe to a solution of C3a-aminohexahydropyrroloindole (–)-**16** (89.0 mg, 267 μmol, 1 equiv) and hexahydropyrroloindole sulfamate ester (–)-**19** (200 mg, 320 μmol, 1.20 equiv) in tetrahydrofuran (2.00 mL) at 23 °C. After 24 h, the clear solution was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 33% ethyl acetate in hexanes then 25% acetone in hexanes) to afford the mixed sulfamide (–)-**25** (187 mg, 84.9%) as a white solid.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, C_6D_6, 70 °C): δ 8.05 (d, J = 8.2Hz, 1H, $C_{7'}$**H**), 7.94 (br-s, 2H, N_8SO_2Ar-*o*-**H**), 7.74 (d, J = 8.1Hz, 1H, C_7**H**), 7.14 (d, J = 8.5 Hz, 2H, N_8SO_2Ar-*m*-**H**), 7.08–7.00 (m, 2H, C_6**H**, $C_{6'}$**H**), 6.95 (d, J = 5.6 Hz, 1H, $C_{4'}$**H**), 6.91 (s, 1H, C_{8a}**H**), 6.73 (app-t, J = 7.5 Hz, 1H, C_5**H**), 6.66 (d, J = 6.6 Hz, 1H, C_4**H**), 6.61 (s, 1H, $C_{8a'}$**H**), 6.53 (br-s, 1H, $C_{5'}$**H**), 5.15 (br-s, 1H, SO_2N**H**), 3.84 (br-s, 1H, SO_2N**H**), 3.80–3.67 (m, 2H, C_2**H**$_a$, $C_{2'}$**H**$_a$), 3.51 (s, 3H, N_1CO_2C**H**$_3$), 3.44 (s, 3H, $N_{1'}CO_2C$**H**$_3$), 2.66–2.54 (m, 3H, C_2**H**$_b$, $C_{2'}$**H**$_b$, C_3**H**$_a$), 2.14–2.07 (m, 2H, $C_{3'}$**H**$_a$ $C_{3'}$**H**$_b$), 1.79 (d, J = 7.1Hz, 1H, C_3**H**$_b$), 1.58 (s, 9H, $N_{1'}CO_2C(CH_3)_3$), 1.04 (s, 9H, $C(CH_3)_3$).

^{13}C NMR (125.8 MHz, C_6D_6, 70 °C): δ 157.5 (N_8SO_2Ar-*p*-**C**), 155.7 ($N_{1'}$**C**O_2CH_3), 155.5 (N_1**C**O_2CH_3), 153.3 ($N_{8'}$**C**$O_2C(CH_3)_3$), 145.5 (**C**$_{7a'}$), 143.3 (**C**$_{7a}$), 138.2 (N_8SO_2Ar-*ipso*-**C**), 132.8 (**C**$_{4a}$), 130.9 (**C**$_6$), 130.8 (**C**$_6$), 129.5 (**C**$_{4a'}$), 128.0 (N_8SO_2Ar-*o*-**C**), 126.7 (N_8SO_2Ar-*m*-**C**), 125.3 (**C**$_5$), 124.8 (**C**$_4$), 124.5 (**C**$_{4'}$), 123.5 (**C**$_{5'}$), 118.4 (**C**$_7$), 117.5 (**C**$_{7'}$), 82.5 (**C**$_{8a}$), 82.0 ($N_{8'}CO_2$**C**$(CH_3)_3$), 81.6 (**C**$_{8a'}$), 72.9 (**C**$_{3a}$), 72.0 (**C**$_{3a}$), 52.9 ($N_{1'}CO_2$**C**H_3), 52.6 (N_1CO_2**C**H_3), 45.4 (**C**$_2$), 45.2 (**C**$_{2'}$), 37.8 (**C**$_{3'}$), 37.3 (**C**$_3$), 35.4 (**C**$(CH_3)_3$), 31.3 (C(**C**$H_3)_3$), 28.8 ($N_{8'}CO_2C$(**C**$H_3)_3$).

FTIR (thin film) cm^{-1}:	3242 (br-m), 2960 (m), 1713 (s), 1480 (m), 1448 (m), 1392 (m), 1167 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{39}H_{48}N_6NaO_{10}S_2$ $[M+Na]^+$: 847.2766, found: 847.2767.
$[\alpha]_D^{24}$:	–111 (*c* = 0.66, CH_2Cl_2).
TLC (33% acetone in hexanes), R*f*:	0.25 (UV, CAM).



Unsymmetrical Diazene (–)-26:

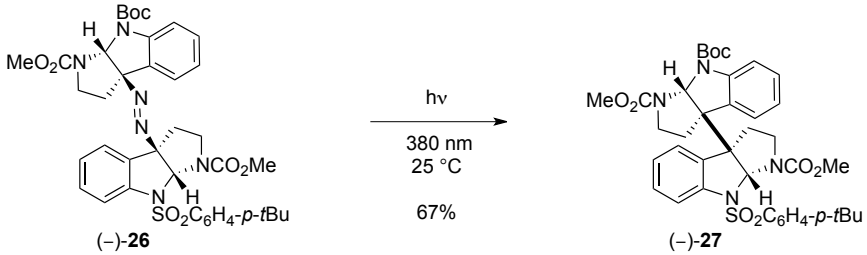
1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 152 μL, 1.02 mmol, 5.00 equiv), was added via syringe to a solution of mixed sulfamide (–)-**25** (169 mg, 205 μmol, 1 equiv) in methanol (15.0 mL) at 23 °C. After 5 min, a solution of 1,3-dichloro-5,5-dimethylhydantoin (101 mg, 513 μmol, 2.50 equiv) in methanol (5.00 mL) was added via syringe over 1 min at 23 °C. After 30 min, the clear solution was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 10→20% acetone in hexanes) to afford unsymmetrical diazene (–)-**26** (143 mg, 91.9%) as a white foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 50 °C): δ 7.72 (d, *J* = 8.5 Hz, 2H, N_8SO_2Ar-*o*-**H**), 7.68 (d, *J* = 8.2 Hz, 1H, $C_{7'}$**H**), 7.50 (d, *J* = 8.2 Hz, 1H, C_7**H**), 7.46 (d, *J* = 8.5 Hz, 2H, N_8SO_2Ar-*m*-**H**), 7.35–7.29 (m, 2H, C_6**H**, $C_{6'}$**H**), 7.13–6.97 (m, 4H, C_4**H**, $C_{4'}$**H**, C_5**H**, $C_{5'}$**H**), 6.64 (s, 1H, C_{8a}**H**), 6.51 (s, 1H, $C_{8a'}$**H**), 3.92–3.85 (m, 2H, C_2**H**$_a$, $C_{2'}$**H**$_a$), 3.69 (s, 3H, $N_{1'}CO_2C$**H**$_3$), 3.66 (s, 3H, N_1CO_2C**H**$_3$), 3.00–2.90 (m, 2H, C_2**H**$_b$, $C_{2'}$**H**$_b$), 2.28 (app-t, *J* = 5.1 Hz, 1H, $C_{3'}$**H**$_a$), 2.26 (app-t, *J* = 5.1 Hz, 1H, C_3**H**$_a$), 2.18 (app-dt, *J* = 8.0, 11.9 Hz, 1H, C_3**H**$_b$), 2.10 (app-dt, *J* = 8.2, 12.3 Hz, 1H, $C_{3'}$**H**$_b$), 1.54 (s, 9H, $N_{1'}CO_2C(CH_3)_3$), 1.26 (s, 9H, $C(CH_3)_3$).

^{13}C NMR (125.8 MHz, CD_3CN, 50 °C): δ 159.0 ($N_{8'}SO_2Ar$-*p*-**C**), 156.6 ($N_{1'}$**C**O_2CH_3), 156.2 (N_1**C**O_2CH_3), 153.8 ($N_{8'}$**C**$O_2C(CH_3)_3$), 145.3 ($C_{7a'}$), 144.0 (C_{7a}), 137.5 (N_8SO_2Ar-*ipso*-**C**), 131.9 (C_6), 131.7 ($C_{6'}$), 131.4 (C_{4a}), 130.6 ($C_{4a'}$), 129.0 (N_8SO_2Ar-*o*-**C**), 127.7 (N_8SO_2Ar-*m*-**C**), 127.0 (C_4), 126.4 (C_5), 126.3 ($C_{4'}$), 125.1 ($C_{5'}$), 118.2 ($C_{7'}$), 117.4 (C_7), 90.6 (C_{3a}), 89.9 ($C_{3a'}$), 83.2 ($N_{8'}CO_2$**C**$(CH_3)_3$), 83.0 (C_{8a}), 80.0 ($C_{8a'}$), 53.8 (N_1CO_2**C**H_3), 53.7 ($N_{1'}CO_2$**C**H_3), 47.1 ($C_{2'}$), 46.9 (C_2), 37.3 (C_3), 36.5 (**C**$(CH_3)_3$), 35.9 ($C_{3'}$), 31.9 ($C($**C**$H_3)_3$), 29.2 ($N_{8'}CO_2C($**C**$H_3)_3$).

FTIR (thin film) cm^{-1}:	2960 (m), 1712 (s), 1597 (w), 1447 (m), 1391 (s), 1171 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{39}H_{46}N_6NaO_8S$ $[M+Na]^+$: 781.2990, found: 781.2997.
$[\alpha]_D^{24}$:	–226 (*c* = 1.03, CH_2Cl_2).
TLC (33% acetone in hexanes), R*f*:	0.50 (UV, CAM).



Heterodimer (–)-27:

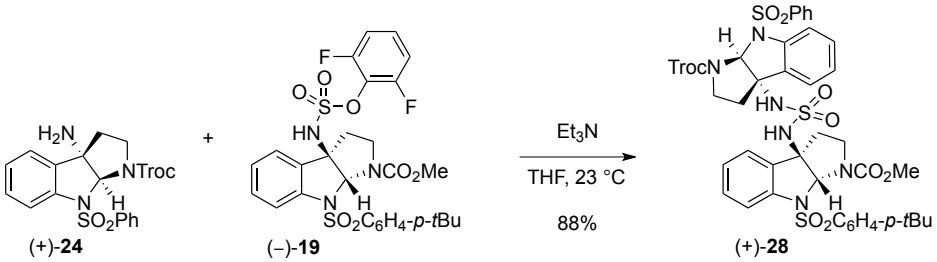
A solution of unsymmetrical diazene (–)-**26** (132 mg, 174 μmol, 1 equiv) in dichloromethane (30 mL) was concentrated under reduced pressure in a 100 mL round bottom flask to provide a thin film of diazene (–)-**26** coating the flask. The flask was back filled with argon and irradiated in a Rayonet photoreactor equipped with 16 radially distributed (r=12.7 cm) 25 W lamps (λ=380 nm) at 25 ºC. After 12 h, the lamps were turned off and the resulting residue was purified by flash column chromatography on silica gel (eluent: 10→20% acetone in hexanes) to afford the heterodimer (–)-**27** (85.0 mg, 66.8%) as a white foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 75 °C): δ 7.85 (d, *J* = 8.5 Hz, 2H, N_8SO_2Ar-*o*-**H**), 7.62 (d, *J* = 8.5 Hz, 2H, N_8SO_2Ar-*m*-**H**), 7.58 (d, *J* = 8.2Hz, 1H, $C_{7'}$**H**), 7.44 (d, *J* = 8.2Hz, 1H, C_7**H**), 7.25–7.13 (m, 4H, C_6**H**, $C_{6'}$**H**, C_4**H**, $C_{4'}$**H**), 6.97 (app-t, *J* = 7.7 Hz, 1H, C_5**H**), 6.88 (app-t, *J* = 7.6 Hz, 1H, $C_{5'}$**H**), 6.35 (s, 1H, C_{8a}**H**), 6.24 (s, 1H, $C_{8a'}$**H**), 3.87 (dd, *J* = 7.6, 11.5 Hz, 1H, C_2**H**$_a$), 3.76 (dd, *J* = 7.6, 10.9 Hz, 1H, $C_{2'}$**H**$_a$), 3.66 (s, 3H, $N_{1'}CO_2C$**H**$_3$), 3.53 (s, 3H, N_1CO_2C**H**$_3$), 2.70–2.62 (m, 2H, C_2**H**$_b$, $C_{2'}$**H**$_b$), 2.25 (app-dt, *J* = 7.7, 12.2 Hz, 1H, C_3**H**$_a$), 2.13 (dd, *J* = 7.7, 12.0 Hz, 1H, $C_{3'}$**H**$_a$), 2.08–2.01 (m, 2H, C_3**H**$_b$, $C_{3'}$**H**$_b$), 1.60 (s, 9H, $N_{1'}CO_2C(C$**H**$_3)_3$), 1.36 (s, 9H, $C(C$**H**$_3)_3$).

^{13}C NMR (125.8 MHz, CD_3CN, 70 °C): δ 159.1 ($N_{8'}SO_2Ar$-*p*-**C**), 156.6 ($N_{1'}$**C**O_2CH_3), 156.1 (N_1**C**O_2CH_3), 153.7 ($N_{8'}$**C**$O_2C(CH_3)_3$), 145.3 ($C_{7a'}$), 144.8 (C_{7a}), 140.1 (N_8SO_2Ar-*ipso*-**C**), 133.4 ($C_{4a'}$), 133.1 (C_{4a}), 131.0 (C_6), 130.7 ($C_{6'}$), 128.1 (N_8SO_2Ar-*m*-**C**), 128.0 (N_8SO_2Ar-*o*-**C**), 126.2 (C_4), 125.9 ($C_{4'}$), 125.1 (C_5), 124.9 ($C_{5'}$), 117.8 ($C_{7'}$), 115.6 (C_7), 83.5 ($N_{8'}CO_2$**C**$(CH_3)_3$), 83.3 (C_{8a}), 81.1 ($C_{8a'}$), 64.2 (C_{3a}), 63.2 ($C_{3a'}$), 54.0 (N_1CO_2**C**H_3), 53.9 ($N_{1'}CO_2$**C**H_3), 46.9 (C_2), 46.6 ($C_{2'}$), 37.5 (C_3),

	36.7 (**C**$(CH_3)_3$), 35.6 (**C**$_{3'}$), 32.1 (C(**C**$H_3)_3$), 29.5 ($N_{8'}CO_2C$(**C**$H_3)_3$).
FTIR (thin film) cm^{-1}:	2957 (w), 1711 (s), 1596 (w), 1479 (m), 1391 (w), 1366 (w), 1166 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{39}H_{46}N_4NaO_8S$ $[M+Na]^+$: 753.2929, found: 753.2927.
$[\alpha]_D^{24}$:	–162 (*c* = 0.13, CH_2Cl_2).
TLC (33% acetone in hexanes), R*f*:	0.37 (UV, CAM).



Mixed Sulfamide (+)-28:

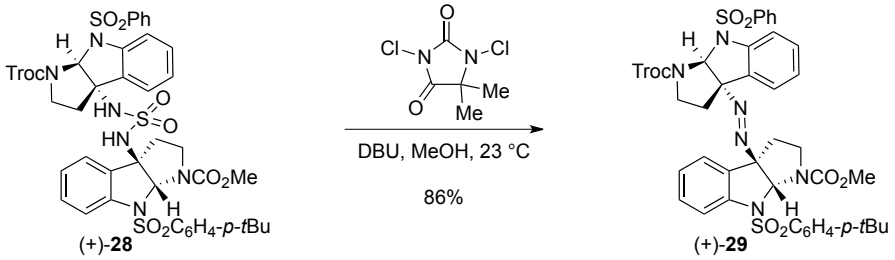
Triethylamine (206 μL, 1.47 mmol, 2.20 equiv) was added via syringe to a solution of C3a-aminohexahydropyrroloindole (+)-**24** (328 mg, 670 μmol, 1 equiv) and hexahydropyrroloindole sulfamate ester (–)-**19** (500 mg, 804 μmol, 1.20 equiv) in tetrahydrofuran (3.50 mL) at 23 °C. After 24 h, the clear solution was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 20→33% acetone in hexanes) to afford the mixed sulfamide (+)-**28** (581 mg, 88.3%) as a white solid.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, C_6D_6, 70 °C): δ 8.04 (br-s, 2H, $N_{8'}SO_2$Ph-*o*-**H**), 7.96 (d, *J* = 7.7 Hz, 2H, N_8SO_2Ar-*o*-**H**), 7.66–7.63 (m, 2H, C_7**H** $C_{7'}$**H**) 7.31 (d, *J* = 7.5 Hz, 1H, C_4**H**) 7.24 (d, *J* = 7.1 Hz, 1H, $C_{4'}$**H**), 7.20 (d, *J* = 7.6 Hz, 2H, N_8SO_2Ar-*m*-**H**), 7.09–7.05 (m, 2H, C_6**H**, $C_{6'}$**H**), 7.04–7.00 (m, 3H, $N_{8'}SO_2$Ph-*p*-**H**, $N_{8'}SO_2$Ph-*m*-**H**), 6.95–6.90 (m, 2H, C_5**H**, $C_{5'}$**H**), 6.84 (s, 1H, C_{8a}**H**), 6.74 (br-s, 1H, $C_{8a'}$**H**), 4.96 (br-s, 2H, SO_2N**H**$_2$), 4.74 (br-s, 1H, $N_{1'}CO_2C$**H**$_a$H$_b$CCl$_3$), 4.53 (d, *J* = 11.6 Hz, 1H, $N_{1'}CO_2CH_a$**H**$_b$CCl$_3$), 3.83 (app-t, *J* = 10.6 Hz, 1H, C_2**H**$_a$), 3.74 (app-t, *J* = 8.8 Hz, 1H, $C_{2'}$**H**$_a$), 3.41 (s, 3H, N_1CO_2C**H**$_3$), 2.66–2.56 (m, 2H, C_2**H**$_b$, $C_{2'}$**H**$_b$), 2.54–2.45 (m, 2H, C_3**H**$_a$, $C_{3'}$**H**$_a$), 2.06 (m, 2H, C_3**H**$_b$, $C_{3'}$**H**$_b$), 1.07 (s, 9H, C(C**H**$_3$)$_3$).

^{13}C NMR (125.8 MHz, C_6D_6, 70 °C): δ 157.5 ($N_{8'}SO_2$Ar-*p*-**C**), 155.4 (N_1**C**O$_2$CH$_3$), 153.3 ($N_{1'}$**C**O$_2$CH$_2$CCl$_3$), 143.5 (**C**$_{7a'}$), 143.3 (**C**$_{7a}$), 140.8 ($N_{8'}SO_2$Ph-*ipso*-**C**), 138.7 (N_8SO_2Ar-*ipso*-**C**), 133.6 ($N_{8'}SO_2$Ph-*p*-**C**), 132.5 (**C**$_{4a'}$) 132.1 (**C**$_{4a}$), 131.0 (2C, **C**$_6$, **C**$_{6'}$), 129.5 ($N_{8'}SO_2$Ph-*m*-**C**), 128.3 (N_8SO_2Ar-*o*-**C**) 128.0 ($N_{8'}SO_2$Ph-*o*-**C**), 126.7 (N_8SO_2Ar-*m*-**C**), 125.7 (**C**$_4$), 125.6 (**C**$_{4'}$), 125.5 (2C, **C**$_5$, **C**$_{5'}$), 117.8 (**C**$_{7'}$), 117.3 (**C**$_{7'}$), 95.6 ($N_{1'}CO_2CH_2$**C**Cl$_3$), 83.6 (**C**$_{8a}$), 83.5 (**C**$_{8a'}$), 75.9 ($N_{1'}CO_2$**C**H$_2$CCl$_3$), 73.2 (2C,

	C$_{3a}$, **C**$_{3a'}$), 52.9 (N_1CO_2**C**H_3), 45.8 (**C**$_2$), 45.7 (**C**$_{2'}$), 37.4 (**C**$_3$), 36.6 (**C**$_{3'}$), 35.4 (**C**$(CH_3)_3$), 31.3 ($C($**C**$H_3)_3$).
FTIR (thin film) cm^{-1}:	2959 (w), 1717 (m), 1600 (w), 1448 (m), 1400 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{41}H_{47}Cl_3N_7O_{10}S_3$ $[M+NH_4]^+$: 998.1607, found: 998.1611.
$[\alpha]_D^{24}$:	+19 (*c* = 0.32, CH_2Cl_2).
TLC (33% acetone in hexanes), R*f*:	0.18 (UV, CAM).



Unsymmetrical Diazene (+)-29:

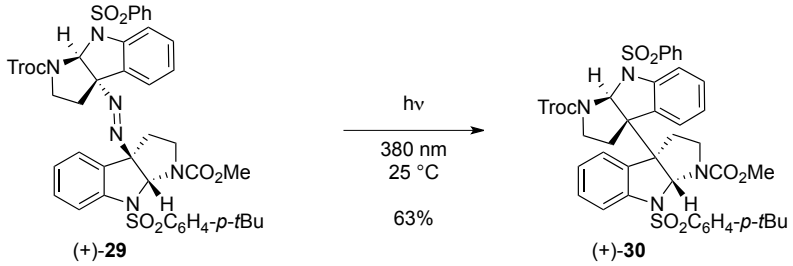
1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 152 μL, 1.02 mmol, 5.00 equiv) was added via syringe to a solution of mixed sulfamide (+)-**28** (200 mg, 203 μmol, 1 equiv) in methanol (15.0 mL) at 23 °C. After 5 min, a solution of 1,3-dichloro-5,5-dimethylhydantoin (100 mg, 507 μmol, 2.50 equiv) in methanol (5 mL) was added via syringe over 1 min. After 30 min, the clear solution was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 17→25% acetone in hexanes) to afford the unsymmetrical diazene (+)-**29** (159 mg, 85.5%) as a white foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 7.82–7.79 (m, 4H, $N_{8'}SO_2$Ph-*o*-**H**, N_8SO_2Ar-*o*-**H**), 7.62 (d, *J* = 8.3 Hz, 1H, $C_{7'}$**H**) 7.55–7.49 (m, 4H, $N_{8'}SO_2$Ph-*p*-**H**, N_8SO_2Ar-*m*-**H**, C_7**H**), 7.41–7.36 (m, 4H, $N_{8'}SO_2$Ph-*m*-**H**, C_6**H**, $C_{6'}$**H**), 7.20–7.16 (m, 2H, C_5**H**, $C_{4'}$**H**), 7.11–7.05 (m, 2H, $C_{5'}$**H**, C_4**H**), 6.71 (s, 1H, $C_{8a'}$**H**), 6.55 (s, 1H, C_{8a}**H**), 4.92 (d, *J* = 10.8, 1H, $N_{1'}CO_2C$**H**$_a$H$_b$CCl$_3$), 4.80 (d, *J* = 12.1 Hz, 1H, $N_{1'}CO_2CH_a$**H**$_b$CCl$_3$), 4.01 (dd, *J* = 7.9, 11.7 Hz, 1H, $C_{2'}$**H**$_a$), 3.83 (dd, *J* = 8.0, 11.4 Hz, 1H, C_2**H**$_a$), 3.65 (s, 3H, N_1CO_2C**H**$_3$), 3.05 (app-dt, *J* = 5.5, 11.8 Hz, 1H, $C_{2'}$**H**$_b$) 2.94 (app-dt, *J* = 5.7, 12.7 Hz, 1H, C_2**H**$_b$), 2.21 (dd, *J* = 5.3, 12.7 Hz, 1H, $C_{3'}H_a$), 2.12 (dd, *J* = 5.6, 12.7 Hz, 1H, C_3**H**$_a$), 2.01–1.89 (m, 2H, C_3**H**$_b$, $C_{3'}$**H**$_b$), 1.28 (s, 9H, C(C**H**$_3$)$_3$).

^{13}C NMR (125.8 MHz, CD_3CN, 70 °C): δ 159.3 ($N_{8'}SO_2$Ar-*p*-**C**), 156.4 (N_1**C**O$_2$CH$_3$), 154.3 ($N_{1'}$**C**O$_2$CH$_2$CCl$_3$), 144.3 (**C**$_{7a}$), 144.1 (**C**$_{7a'}$), 140.1 ($N_{8'}SO_2$Ph-*ipso*-**C**), 138.3 (N_8SO_2Ar-*ipso*-**C**), 135.4 ($N_{8'}SO_2$Ph-*p*-**C**), 132.4 (**C**$_{6'}$), 132.1 (**C**$_6$), 131.2 (**C**$_{4a'}$), 131.1 (**C**$_{4a}$), 131.0 ($N_{8'}SO_2$Ph-*m*-**C**), 129.1 (N_8SO_2Ar-*o*-**C**), 129.0 ($N_{8'}SO_2$Ph-*o*-**C**), 128.1 (N_8SO_2Ar-*m*-**C**), 127.3 (**C**$_{4'}$), 127.0 (**C**$_4$), 126.9 (**C**$_{5'}$), 126.5 (**C**$_5$), 117.5 (**C**$_{7'}$), 117.2 (**C**$_{7'}$), 97.5 ($N_{1'}CO_2CH_2$**C**Cl$_3$), 90.9 (2C, **C**$_{3a}$, **C**$_{3a'}$), 83.2 (**C**$_{8a}$), 82.7 (**C**$_{8a'}$), 76.8 ($N_{1'}CO_2$**C**H$_2$CCl$_3$), 54.0

	($N_1CO_2\mathbf{C}H_3$), 47.4 ($\mathbf{C}_{2'}$), 47.1 ($\mathbf{C}_2$), 38.7 ($\mathbf{C}_{3'}$), 37.8 ($\mathbf{C}_3$), 36.7 ($\mathbf{C}(CH_3)_3$), 32.1 ($C(\mathbf{C}H_3)_3$).
FTIR (thin film) cm^{-1}:	2958 (w), 1718 (s), 1597 (w), 1447 (m), 1366 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{41}H_{45}Cl_3N_7O_8S_2$ $[M+NH_4]^+$: 932.1831, found: 932.1853.
$[\alpha]_D^{24}$:	+13 (*c* = 0.38, CH_2Cl_2).
TLC (33% acetone in hexanes), R*f*:	0.29 (UV, CAM).



Heterodimer (+)-30:

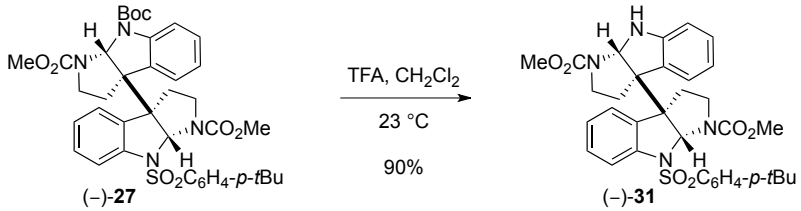
A solution of unsymmetrical diazene (+)-**29** (159 mg, 174 μmol, 1 equiv) in dichloromethane (30 mL) was concentrated under reduced pressure in a 250 mL round bottom flask to provide a thin film of diazene (+)-**29** coating the flask. The flask was back filled with argon and irradiated in a Rayonet photoreactor equipped with 16 radially distributed (r=12.7 cm) 25 W lamps (λ_{max}=380 nm) at 25 ºC. After 7 h, the thin film was purified by flash column chromatography on silica gel (eluent: 17→50% ethyl acetate in hexanes) to afford the heterodimer (+)-**30** (98 mg, 63.4%) as a white foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, DMSO-d_6, 100 °C): δ 7.92 (d, J = 7.6 Hz, 2H, $N_{8'}SO_2Ph$-*o*-**H**), 7.73 (d, J = 8.4 Hz, 2H, N_8SO_2Ar-*o*-**H**), 7.67 (t, J = 7.3Hz, 1H, $N_{8'}SO_2Ph$-*p*-**H**), 7.60–7.57 (m, 4H, N_8SO_2Ar-*m*-**H**, $N_{8'}SO_2Ph$-*m*-**H**), 7.40–7.37 (m, 2H, C_7**H**, $C_{7'}$**H**), 7.34–7.28 (m, 2H, C_6**H**, $C_{6'}$**H**), 7.20 (br-s, 1H, $C_{4'}$**H**), 7.07 (app-t, J = 7.5 Hz, 1H, C_5**H**), 6.98 (app-t, J = 7.4 Hz, 1H, $C_{5'}$**H**), 6.80 (br-s, 1H, C_4**H**), 6.47 (s, 1H, $C_{8a'}$**H**), 6.28 (s, 1H, C_{8a}**H**), 4.82 (d, J = 11.9, 1H, $N_{1'}CO_2C$**H**$_a$H$_b$CCl$_3$), 4.71 (d, J = 11.9 Hz, 1H, $N_{1'}CO_2CH_a$**H**$_b$CCl$_3$), 3.82 (dd, J = 7.3, 11.7 Hz, 1H, $C_{2'}$**H**$_a$), 3.72 (dd, J = 7.6, 11.5 Hz, 1H, C_2**H**$_a$), 3.50 (s, 3H, N_1CO_2C**H**$_3$), 2.67–2.60 (m, 2H, C_2**H**$_b$, $C_{2'}$**H**$_b$), 2.05–1.99 (m, 2H, C_3**H**, $C_{3'}$**H**$_a$), 1.89 (dd, J = 12.5, 19.9 Hz, 1H, $C_{3'}$**H**$_b$), 1.77 (app-dt, J = 7.9, 11.7 Hz, 1H, C_3**H**$_b$), 1.31 (s, 9H, C(C**H**$_3$)$_3$).

^{13}C NMR (125.8 MHz, DMSO-d_6, 100 °C): δ 156.0 ($N_{8'}SO_2Ar$-*p*-**C**), 153.0 (N_1**C**O_2CH_3), 151.2 ($N_{1'}$**C**$O_2CH_2CCl_3$), 142.3 (**C**$_{7a}$), 141.9 (**C**$_{7a'}$), 139.8 ($N_{8'}SO_2Ph$-*ipso*-**C**), 137.1 (N_8SO_2Ar-*ipso*-**C**), 132.8 ($N_{8'}SO_2Ph$-*p*-**C**), 130.0 (**C**$_{4a}$), 129.6 (**C**$_{4a'}$), 129.1 (**C**$_{6/6'}$), 128.8 ($N_{8'}SO_2Ph$-*m*-**C**), 125.7 $N_{8'}SO_2Ph$-*o*-**C**), 125.5 (N_8SO_2Ar-*o*/*m*-**C**), 123.7 (2C, **C**$_4$, **C**$_{4'}$), 123.4 (2C, **C**$_5$, **C**$_{5'}$), 113.7 (**C**$_7$), 113.4 (**C**$_{7'}$), 95.1 ($N_{1'}CO_2CH_2$**C**Cl$_3$), 79.8 (2C, **C**$_{8a}$, **C**$_{8a'}$), 73.9

	($N_{1'}CO_2\mathbf{C}H_2CCl_3$), 61.3 (2C, $\mathbf{C}_{3a}$, $\mathbf{C}_{3a'}$), 51.8 ($N_1CO_2\mathbf{C}H_3$), 44.8 ($\mathbf{C}_{2'}$), 44.4 ($\mathbf{C}_2$), 35.0 ($\mathbf{C}_{3'}$), 34.5 ($\mathbf{C}_3$), 34.3 ($\mathbf{C}(CH_3)_3$), 31.2 ($C(\mathbf{C}H_3)_3$).
FTIR (thin film) cm^{-1}:	2957(w), 1716 (s), 1595 (w), 1447 (m), 1167 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{41}H_{41}Cl_3N_4NaO_8S_2$ $[M+Na]^+$: 909.1324, found: 909.1313.
$[\alpha]_D^{24}$:	+23 (*c* = 0.49, CH_2Cl_2).
TLC (33% ethyl acetate in hexanes), R*f*:	0.29 (UV, CAM).



N8'-H Heterodimer (–)-31:

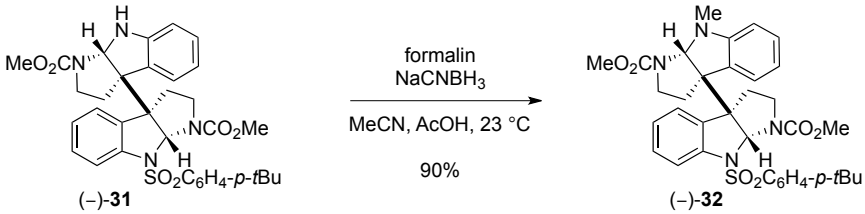
Trifluoroacetic acid (400 μL) was added via syringe to a solution of heterodimer (–)-**27** (67.0 mg, 91.8 μmol, 1 equiv) in dichloromethane (1.60 mL) at 23 °C. After 45 min, the orange solution was diluted with dichloromethane (25 mL) and washed with aqueous saturated sodium bicarbonate solution (2 × 15 mL). The combined aqueous washes were extracted with dichloromethane (2 × 20 mL). The combined organic extracts were washed with brine (15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 20→25% acetone in hexanes) to afford the N8'-H heterodimer (–)-**31** (52.0 mg, 89.6%) as a white foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 7.84 (d, *J* = 8.3Hz, 2H, N_8SO_2Ar-*o*-**H**), 7.64 (d, *J* = 8.3Hz, 2H, N_8SO_2Ar-*m*-**H**), 7.53 (d, *J* = 8.3Hz, 1H, C_7**H**), 7.46 (d, *J* = 7.7 Hz, 1H, C_4**H**), 7.27 (app-t, *J* = 7.9 Hz, 1H, C_6**H**), 7.06–7.02 (m, 3H, $C_{6'}$**H**, C_5**H**, $C_{4'}$**H**), 6.61 (app-t, *J* = 7.5 Hz, 1H, $C_{5'}$**H**), 6.55 (d, *J* = 7.7 Hz, 1H, $C_{7'}$**H**), 5.96 (s, 1H, C_{8a}**H**), 4.85 (br-s, 1H, $N_{8'}$**H**), 4.79 (s, 1H, $C_{8a'}$**H**), 3.88 (dd, *J* = 7.9, 11.1 Hz, 1H, C_2**H**$_a$), 3.61 (s, 3H, $N_{1'}CO_2C$**H**$_3$), 3.54 (app-t, *J* = 8.4 Hz, 1H, $C_{2'}$**H**$_a$), 3.47 (s, 3H, N_1CO_2C**H**$_3$), 2.80–2.67 (m, 2H, C_2**H**$_b$, $C_{2'}$**H**$_b$), 2.46 (app-dt, *J* = 7.9, 12.1 Hz, 1H, C_3**H**$_a$), 2.35 (dd, *J* = 11.2, 20.3 Hz, 1H, $C_{3'}$**H**$_a$), 2.12 (dd, *J* = 6.0, 12.5 Hz, 1H, $C_{3'}$**H**$_b$), 2.07 (dd, *J* = 5.4, 12.5 Hz, 1H, C_3**H**$_b$), 1.37 (s, 9H, C(C**H**$_3$)$_3$).

^{13}C NMR (125.8 MHz, CD_3CN, 70 °C): δ 159.2 ($N_{8'}SO_2Ar$-*p*-**C**), 156.1 (2C, $N_{1'}$**C**O_2CH_3, N_1**C**O_2CH_3), 152.3 (**C**$_{7a'}$), 144.7 (**C**$_{7a}$), 139.3 (N_8SO_2Ar-*ipso*-**C**), 133.7 (**C**$_{4a}$), 131.0 (**C**$_5$, **C**$_6$), 130.3 (**C**$_{4a'}$), 128.5 (N_8SO_2Ar-*o*-**C**), 128.1 (N_8SO_2Ar-*m*-**C**), 127.0 (**C**$_4$), 126.1 (**C**$_{6'}$), 125.3 (**C**$_{4'}$), 120.3 (**C**$_{5'}$), 115.5 (**C**$_7$), 111.2 (**C**$_{7'}$), 83.2 (**C**$_{8a}$), 80.3 (**C**$_{8a'}$), 64.3 (2C, **C**$_{3a}$, **C**$_{3a'}$), 53.8 (N_1CO_2**C**H_3), 53.6 ($N_{1'}CO_2$**C**H_3), 46.5 (2C, **C**$_2$, **C**$_{2'}$), 37.6 (**C**$_3$), 36.8 (**C**(CH$_3$)$_3$), 34.5 (**C**$_{3'}$), 32.2 (C(**C**H$_3$)$_3$).

FTIR (thin film) cm^{-1}:	3550 (br-m), 2956 (w), 1706 (s), 1595 (w), 1448 (s), 1384 (m), 1175 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{34}H_{39}N_4O_6S$ $[M+H]^+$: 631.2585, found: 631.2588.
$[\alpha]_D^{24}$:	–283 (*c* = 0.53, CH_2Cl_2).
TLC (33% ethyl acetate in hexanes), R*f*:	0.30 (UV, CAM).



N8'-Methyl Heterodimer (–)-32:

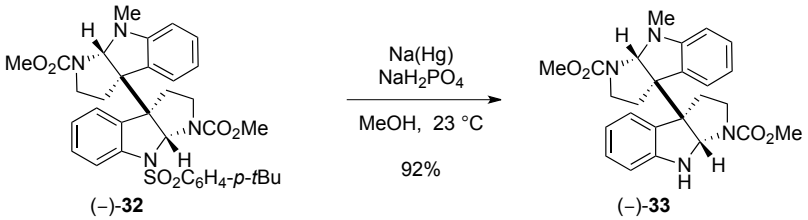
Formalin (37% wt, 1.26 mL, 16.76 mmol, 235 equiv) and sodium cyanoborohydride in tetrahydrofuran (1.0 M, 214 μL, 214 μmol, 3.00 equiv) were added sequentially via syringe to a solution of N8'-H heterodimer (–)-**31** (45.0 mg, 71.3 μmol, 1 equiv) in acetonitrile–acetic acid (10:1, 3.85 mL) at 23 °C. After 30 min, another portion of sodium cyanoborohydride (1.0 M in tetrahydrofuran, 71.0 μL, 71.0 μmol, 1.00 equiv) was added via syringe. After an additional 30 min, a saturated aqueous sodium bicarbonate solution (10 mL) was added and the resulting mixture was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with brine (15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 15→20% acetone in hexanes) to afford the N8'-methyl heterodimer (–)-**32** (41.0 mg, 89.6%) as a white foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 7.83 (d, J = 8.3 Hz, 2H, N_8SO_2Ar-*o*-**H**), 7.61 (d, J = 8.3Hz, 2H, N_8SO_2Ar-*m*-**H**), 7.43 (d, J = 8.3 Hz, 1H, C_7**H**), 7.36 (d, J = 7.7 Hz, 1H, C_4**H**), 7.25 (app-t, J = 7.9 Hz, 1H, C_6**H**), 7.08 (app-t, J = 7.7 Hz, 1H, $C_{6'}$**H**), 7.04–6.97 (m, 2H, C_5**H**, $C_{4'}$**H**), 6.50 (app-t, J = 7.5 Hz, 1H, $C_{5'}$**H**), 6.35 (d, J = 8.0 Hz, 1H, $C_{7'}$**H**), 6.05 (s, 1H, C_{8a}**H**), 5.16 (s, 1H, $C_{8a'}$**H**), 3.87 (dd, J = 8.0, 11.2 Hz, 1H, C_2**H**$_a$), 3.77 (dd, J = 8.5, 10.4 Hz, 1H, $C_{2'}$**H**$_a$), 3.60 (s, 3H, $N_{1'}CO_2C$**H**$_3$), 3.45 (s, 3H, N_1CO_2C**H**$_3$), 2.83 (s, 3H, $N_{1'}C$**H**$_3$), 2.77–2.65 (m, 2H, C_2**H**$_b$, $C_{2'}$**H**$_b$), 2.43 (app dt, J = 8.0, 12.0 Hz, 1H, C_3**H**$_a$), 2.24 (app-dt, J = 8.0, 11.7 Hz, 1H, $C_{3'}$**H**$_a$), 2.11 (dd, J = 5.4, 12.5 Hz, 1H, C_3**H**$_b$), 2.05 (dd, J = 5.6, 12.3Hz, 1H, $C_{3'}$**H**$_b$), 1.35 (s, 9H, C(C**H**$_3$)$_3$).

^{13}C NMR (125.8 MHz, CD_3CN, 70 °C): δ 159.0 ($N_{8'}SO_2Ar$-*p*-**C**), 156.9 ($N_{1'}$**C**O_2CH_3), 156.1 (N_1**C**O_2CH_3), 153.7 (**C**$_{7a'}$), 144.7 (**C**$_{7a}$), 139.9 (N_8SO_2Ar-*ipso*-**C**), 133.8 (**C**$_{4a}$), 131.1 (**C**$_{6'}$), 130.8 (2C**,** **C**$_6$, **C**$_{4a'}$), 128.2 (N_8SO_2Ar-*o*-**C**), 128.1 (N_8SO_2Ar-*m*-**C**), 126.6 (**C**$_4$), 125.6 (**C**$_{4'}$), 125.2 (**C**$_5$,), 118.9 (**C**$_{5'}$), 115.7 (**C**$_7$), 107.5 (**C**$_{7'}$), 85.6

	(**C**$_{8a'}$), 83.3 (**C**$_{8a}$), 64.4 (**C**$_{3a}$), 63.6 (**C**$_{3a'}$), 53.8 ($N_1CO_2\mathbf{C}H_3$), 53.6 ($N_{1'}CO_2\mathbf{C}H_3$), 46.6 (2C, **C**$_2$, **C**$_{2'}$), 37.2 (**C**$_3$), 36.7 ($\mathbf{C}(CH_3)_3$), 36.0 (**C**$_{3'}$), 33.0 ($N_{1'}\mathbf{C}H_3$), 32.1 ($C(\mathbf{C}H_3)_3$).
FTIR (thin film) cm^{-1}:	2956 (w), 1708 (s), 1605 (w), 1446 (m), 1385 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{35}H_{41}N_4O_6S$ $[M+H]^+$: 645.2741, found: 645.2728.
$[\alpha]_D^{24}$:	–321 (*c* = 0.17, CH_2Cl_2).
TLC (25% acetone in hexanes), R*f*:	0.18 (UV, CAM).



(–)-N1,N1'-Carboxymethyl Calycanthidine (33):

Sodium amalgam (5%-Na, 469 mg, 1.02 mmol, 20.0 equiv)[8] was added to a suspension of sodium phosphate monobasic monohydrate (154 mg, 1.12 mmol, 22.0 equiv) and N8'-methyl heterodimer (–)-**32** (33.0 mg, 51.2 μmol, 1 equiv) in methanol at 23 °C. After 1 h, another portion of sodium phosphate monobasic monohydrate (154 mg, 1.12 mmol, 22.0 equiv) and sodium amalgam (5%-Na, 469 mg, 1.02 mmol, 20.0 equiv) were added sequentially. After an additional 1 h, the reaction mixture was diluted with ethyl acetate (20 mL) and was washed with a 5% aqueous sodium bicarbonate solution (10 mL). The aqueous phase was separated and extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with brine (10 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: gradient, 15→20% acetone in hexanes) to afford (–)-N1,N1′-carboxymethyl calycanthidine (**33**, 21.0 mg, 91.8%) as a white foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

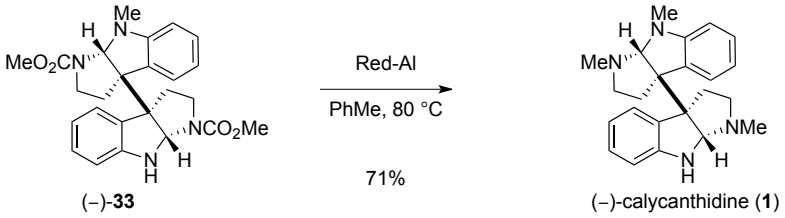
^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 7.27–7.23 (m, 2H, C_4**H**, $C_{4'}$**H**), 7.13 (app-t, J = 7.5 Hz, 1H, $C_{6'}$**H**), 7.08 (app-t, J = 7.7 Hz, 1H, C_6**H**), 6.71 (app-t, J = 7.4 Hz, 1H, C_5**H**), 6.65 (app-t, J = 7.5 Hz, 1H, $C_{5'}$**H**), 6.61 (d, J = 7.7 Hz, 1H, C_7**H**), 6.40 (d, J = 8.0 Hz, 1H, $C_{7'}$**H**), 5.30 (br-s, 1H, N_8**H**), 5.10 (s, 1H, $C_{8a'}$**H**), 4.85 (s, 1H, C_{8a}**H**), 3.82–3.73 (m, 1H, $C_{2'}$**H**$_a$), 3.63–3.57 (m, 1H, C_2**H**$_a$), 3.61 (s, 3H, N_1CO_2C**H**$_3$), 3.57 (s, 3H, $N_{1'}CO_2C$**H**$_3$), 2.90 (s, 3H, $N_{8'}C$**H**$_3$), 2.81 (app-dt, J = 6.1, 10.7 Hz, 1H, C_2**H**$_b$), 2.71 (app-dt, J = 5.8, 11.2 Hz, 1H, $C_{2'}$**H**$_b$), 2.62–2.46 (m, 2H, C_3**H**$_a$, $C_{3'}$**H**$_a$), 2.21 (dd, J = 6.1, 12.5 Hz, 1H, C_3**H**$_b$), 2.12 (dd, J = 5.6, 12.3 Hz, 1H, $C_{3'}$**H**$_b$).

^{13}C NMR (125.8 MHz, CD_3CN, 70 °C): δ 157.0 ($N_{1'}$**C**O_2CH_3), 153.9 (**C**$_{7a'}$), 152.7 (**C**$_{7a}$), 131.3, (**C**$_{4a'}$) 131.0 ($C_{6'}$), 130.9 (**C**$_{4a}$), 130.8 (**C**$_6$), 126.5 (**C**$_4$), 126.2 (**C**$_{4'}$), 120.1 (**C**$_5$), 118.8 (**C**$_{5'}$), 111.0 (**C**$_7$), 107.5 (**C**$_{7'}$), 85.8 ($C_{8a'}$), 80.4 (**C**$_{8a}$), 63.0

[8] The reagent was prepared according to R. N. McDonald and C. E. Reineke *Org. Synth.*1988, **6**, 461.

	(**C**$_{3a'}$), 53.5 (2C, $N_1CO_2\mathbf{C}H_3$, $N_{1'}CO_2\mathbf{C}H_3$), 46.8 (2C, **C**$_2$, **C**$_{2'}$), 35.4 (**C**$_{3'}$), 34.0 (**C**$_3$), 33.5 ($N_{8'}\mathbf{C}H_3$).[9]
FTIR (thin film) cm^{-1}:	3363 (br-w), 2953 (w), 2881 (w), 1698 (s), 1605 (m), 1449 (s), 1383 (s), 1202 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{25}H_{29}N_4O_4$ $[M+H]^+$: 499.2183, found: 449.2172.
$[\alpha]_D^{24}$:	–509 (*c* = 0.78, CH_2Cl_2).
TLC (25% acetone in hexanes), R*f*:	0.30 (UV, CAM).

[9] The **C**$_{3a}$, and $N_1\mathbf{C}O_2CH_3$ were not observed, due to signal broadening, even at 70 °C. All expected ^{13}C signals were observed in the following compound.



(–)-**33** (–)-calycanthidine (**1**)

(–)-Calycanthidine (1):

(–)-N1,N1′-Carboxymethyl calycanthidine (**33**, 15.4 mg, 34.3 μmol, 1 equiv) was azeotropically dried from anhydrous benzene (2 × 5 mL) and the residue was dissolved in toluene (3.5 mL). A solution of sodium bis(2-methoxyethoxy)aluminum hydride in toluene (Red-Al, 70% wt, 149 μL, 515 μmol, 15.0 equiv) was added via syringe at 23 °C. The reaction flask was fitted with a reflux condenser and heated to 80 ºC. After 1 h, the reaction mixture was allowed to cool to 23 °C and excess reducing reagent was quenched by the addition of saturated aqueous sodium sulfate solution (100 μL). The resulting heterogeneous mixture was stirred for 10 min and then solid anhydrous sodium sulfate was added. The mixture was filtered through a plug of Celite and the filter cake was rinsed with dichloromethane (15 mL). The filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 10% methanol→10% methanol saturated with ammonium hydroxide in chloroform) to afford (–)-calycanthidine (**1**, 8.7 mg, 70.9%) as a white solid.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 7.06 (d, *J* = 7.4 Hz, 1H, $C_{4'}$**H**), 7.00 (d, *J* = 5.8 Hz, 1H, C_4**H**), 6.98 (app-t, *J* = 7.7 Hz, 1H, $C_{6'}$**H**), 6.92 (app-t, *J* = 7.5 Hz, 1H, C_6**H**), 6.58 (app-t, *J* = 7.5 Hz, 1H, C_5**H**), 6.51 (app-t, *J* = 7.2 Hz, 1H, $C_{5'}$**H**), 6.48 (d, *J* = 8.0 Hz, 1H, C_7**H**), 6.27 (d, *J* = 7.7 Hz, 1H, $C_{7'}$**H**), 4.47 (s, 1H, C_{8a}**H**), 4.37 (s, 1H, $C_{8a'}$**H**), 2.98 (s, 3H, $N_{8'}C$**H**$_3$), 2.65–3.41 (m, 6H, C_2**H**$_a$, $C_{2'}$**H**$_a$, C_2**H**$_b$, $C_{2'}$**H**$_b$, C_3**H**$_a$, $C_{3'}$**H**$_a$), 2.38 (s, 3H, $N_{1'}C$**H**$_3$), 2.33 (s, 3H, N_1C**H**$_3$), 2.01–1.93 (m, 2H, C_3**H**$_b$, $C_{3'}$**H**$_b$).

^{13}C NMR (125.8 MHz, $CDCl_3$, 50 °C): δ 153.2 (**C**$_{7a'}$), 151.2 (**C**$_{7a}$), 133.6, (**C**$_{4a}$), 133.1 (**C**$_{4a}$), 128.4 (C$_{6'}$), 128.2 (**C**$_6$), 124.7 (**C**$_4$), 124.0 (**C**$_{4'}$), 118.6 (**C**$_5$), 117.1 (**C**$_{5'}$), 109.3 (**C**$_7$), 106.2 (**C**$_{7'}$), 92.4 (C$_{8a'}$), 85.5 (**C**$_{8a}$), 63.8 (**C**$_{3a}$), 63.2 (**C**$_{3a'}$), 52.9 (2C, **C**$_2$, **C**$_{2'}$), 38.2 ($N_{1'}$**C**H$_3$), 37.3 (N_1**C**H$_3$), 35.7 (**C**$_{3'}$), 35.6 (**C**$_3$), 35.6 ($N_{8'}$**C**H$_3$).

^{1}H NMR (500 MHz, DMSO-d_6, 100 °C):	δ 7.04 (d, J = 7.6 Hz, 1H, $C_{4'}$**H**), 6.94 (d, J = 7.2 Hz, 1H, C_4**H**), 6.89 (app-t, J = 7.4 Hz, 1H, $C_{6'}$**H**), 6.80 (app-t, J = 7.2 Hz, 1H, C_6**H**), 6.45–6.40 (m, 2H, C_5**H**, $C_{5'}$**H**), 6.38 (d, J = 7.6 Hz, 1H, C_7**H**), 6.26 (d, J = 7.8 Hz, 1H, $C_{7'}$**H**), 5.90 (br-s, 1H, N_8**H**), 4.54 (s, 1H, C_{8a}**H**), 4.44 (s, 1H, $C_{8a'}$**H**), 2.93 (s, 3H, $N_{8'}C$**H**$_3$), 2.65–2.57 (m, 2H, C_2**H**$_a$, $C_{2'}$**H**$_a$), 2.43–2.33 (m, 4H, C_2**H**$_b$, $C_{2'}$**H**$_b$, C_3**H**$_a$, $C_{3'}$**H**$_a$), 2.36 (s, 3H, $N_{1'}C$**H**$_3$), 2.30 (s, 3H, N_1C**H**$_3$), 1.91–1.82 (m, 2H, C_3**H**$_b$, $C_{3'}$**H**$_b$).
^{13}C NMR (125.8 MHz, DMSO-d_6, 100 °C):	δ 152.3 (**C**$_{7a'}$), 151.2 (**C**$_{7a}$), 132.4, (2C, **C**$_{4a}$, **C**$_{4a'}$) 127.1 ($C_{6'}$), 126.7 (**C**$_6$), 123.1 (**C**$_4$), 122.7 (**C**$_{4'}$), 116.0 (**C**$_5$), 115.8 (**C**$_{5'}$), 107.3 (**C**$_7$), 105.0 (**C**$_{7'}$), 91.1 ($C_{8a'}$), 84.1 (**C**$_{8a}$), 62.1 (**C**$_{3a'}$), 62.0 (**C**$_{3a}$), 51.3 (**C**$_{2'}$), 51.2 (**C**$_2$), 36.9 ($N_{1'}$**C**H$_3$), 35.7 (N_1**C**H$_3$), 34.9 (**C**$_{3/3'}$), 34.6 (**C**$_{3/3'}$) 34.5 ($N_{8'}$**C**H$_3$).
FTIR (thin film) cm^{-1}:	3385 (br-w), 2929 (w), 2789 (w), 1603 (m), 1488 (w), 1249 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{23}H_{29}N_4$ $[M+H]^+$: 361.2387, found: 361.2397.
$[\alpha]_D^{24}$:	–278 (*c* = 0.28, MeOH).[10]

TLC (10% methanol in chloroform saturated ammonium hydroxide), R*f*: 0.55 (UV, CAM).

[10] Literature value: $[\alpha]^{24}_D$ = – 285.1 (*c* 1.992, MeOH), see G. Barger, A. Jacob, J. Madinaveitia *Trav. Chim.* 1938, **57**, 548. Literature value: $[\alpha]^{27}_D$ = – 301 (*c* 0.97, MeOH), see E. A. Peterson, PhD Dissertation, University of California, Irvine, 2005.

Table S1. Comparison of our ^{1}H NMR data for (–)-calycanthidine (1) with literature data ($CDCl_3$):

Assignment	Overman's Report[11] (–)-calycanthidine ^{1}H NMR, 500 MHz $CDCl_3$, 50 ºC	Takayama's Report[12] (–)-calycanthidine ^{1}H NMR, 500 MHz $CDCl_3$ 50 ºC	This Work (–)-calycanthidine ^{1}H NMR, 500 MHz $CDCl_3$ 50 ºC
N1′-C**H**$_3$	2.41 (s, 3H)	2.38 (s, 3H)	2.38 (s, 3H)
N1-C**H**$_3$	2.36 (s, 3H)	2.33 (s, 3H)	2.33 (s,3H)
C2′	2.68–2.42 (m, 2H)	2.65–2.40 (m, 2H)	2.65–2.40 (m, 2H)
C2	2.68–2.42 (m, 2H)	2.65–2.40 (m, 2H)	2.65–2.40 (m, 2H)
C3′	2.68–2.42 (m, 2H)	2.65–2.40 (m, 2H)	2.65–2.40 (m, 2H)
C3	2.68–2.42 (m, 2H)	2.65–2.40 (m, 2H)	2.65–2.40 (m, 2H)
C3a	–	–	–
C3a′	–	–	–
C4′	7.10 (d, *J* = 7.3Hz, 1H)	7.07 (d, *J* = 7.3Hz, 1H)	7.06 (d, *J* = 7.4 Hz, 1H)
C4	7.05 (d, *J* = 7.2Hz, 1H)	7.02 (d, *J* = 7.3, 1H)	7.00 (d, *J* = 5.8 Hz, 1H)
C4a′	–	–	–
C4a	–	–	–
C5′	6.55 (t, *J* = 7.4 Hz, 1H)	6.52 (dd, *J* = 7.3, 7.3Hz, 1H)	6.51 (app-t, *J* = 7.2Hz, 1H)
C5	6.58 (t, *J* = 7.4 Hz, 1H)	6.59 (dd, *J* = 7.3, 7.3Hz, 1H)	6.58 (app-t, *J* = 7.5 Hz, 1H)
C6′	7.01 (dd, *J* = 7.5, 7.7 Hz, 1H)	6.98 (dd, *J* = 7.3, 7.6 Hz, 1H)	6.98 (app-t, *J* = 7.7 Hz, 1H)
C6	6.94 (dd, *J* = 7.5, 7.5 Hz, 1H)	6.92 (dd, *J* = 7.3, 7.6 Hz, 1H)	6.92 (app-t, *J* = 7.5 Hz, 1H)
C7′	6.30 (d, *J* = 7.8 Hz, 1H)	6.27 (d, *J* = 7.6 Hz, 1H)	6.27 (d, *J* = 7.7 Hz, 1H)
C7	6.50 (d, *J* =7.8 Hz, 1H)	6.48 (d, *J* = 7.6 Hz, 1H)	6.48 (d, *J* = 8.0 Hz, 1H)
C7a′	–	–	–
C7a	–	–	–
N8′-CH_3	3.01 (s, 3H)	2.98 (s, 1H)	2.98 (s, 1H)
N8-**H**	–	–	–
C8a′	4.40 (s, 1H)	4.38 (s, 1H)	4.37 (s, 1H)
C8a	4.48 (s, 1H)	4.42 (s, 1H)	4.47 (s, 1H)

[11] E. A. Peterson,. PhD. Dissertation, University of California, Irvine, 2005.
[12] H. Takayama, Y. Matsuda, K. Maubuchi, A. Ishida, M. Kitajima, and N. Aimi, *Tetrahedron*, 2004, **60**, 893.

Table S2. Comparison of ^{13}C NMR data of (–)-calycanthidine (1) with literature data ($CDCl_3$):

Assignment	**Overman′s Report**[11] (–)-calycanthidine ^{13}C NMR, 125.8 MHz $CDCl_3$, 50 ºC	**Takayama′s Report**[12] (–)-calycanthidine ^{13}C NMR, 125.8 MHz $CDCl_3$ 50 ºC	**This Work** (–)-calycanthidine ^{13}C NMR, 125.8 MHz $CDCl_3$ 50 ºC	**Chemical Shift Difference** Δδ = δ (this work) – δ (ref 11)	**Chemical Shift Difference** Δδ = δ (this work) – δ (ref 12)
N1′-**C**H$_3$	37.9	37.9	38.2	0.3	0.3
N1-**C**H$_3$	37.0	37.0	37.3	0.3	0.3
C2′	52.6	52.6	52.9	0.3	0.3
C2	52.6	52.6	52.9	0.3	0.3
C3′	35.7	35.7	35.7	0.0	0.0
C3	35.6	35.7	35.6	0.0	-0.1
C3a′	62.9	62.8	63.2	0.3	0.4
C3a	63.5	63.2	63.8	0.3	0.6
C4′	123.6	123.6	124.0	0.4	0.4
C4	124.4	124.4	124.7	0.3	0.3
C4a′	132.9	132.7	133.1	0.2	0.4
C4a	133.4	133.3	133.6	0.2	0.3
C5′	116.7	116.7	117.1	0.4	0.4
C5	118.2	118.2	118.6	0.4	0.4
C6′	128.1	128.1	128.4	0.3	0.3
C6	127.8	127.9	128.2	0.4	0.3
C7′	105.8	105.9	106.2	0.4	0.3
C7	108.9	109.0	109.3	0.4	0.3
C7a′	152.9	152.8	153.2	0.3	0.4
C7a	151.0	150.8	151.2	0.2	0.4
N8′-**C**H$_3$	35.4	35.4	35.6	0.2	0.2
N8-H	–	–	–	–	–
C8a′	92.1	91.8	92.4	0.3	0.6
C8a	85.1	85.0	85.5	0.4	0.5

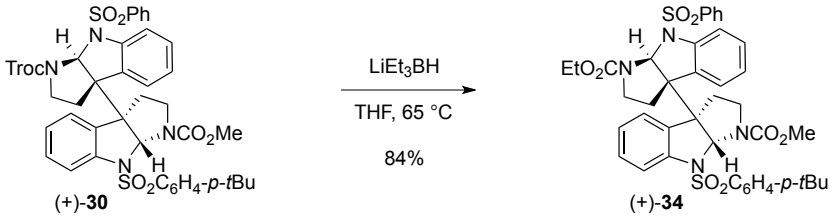
Table S3. Comparison of our ^{1}H NMR data for (–)-calycanthidine (1) with literature data (DMSO-d_6):

Assignment	Overman's Report[13] (–)-calycanthidine ^{1}H NMR, 500 MHz DMSO-d_6, 100 ºC	This Work (–)-calycanthidine ^{1}H NMR, 500 MHz DMSO-d_6, 100 ºC
N1′-C**H**$_3$	2.40 (m, 3H)	2.36 (s, 3H)
N1-C**H**$_3$	2.33 (s, 3H)	2.30 (s, 3H)
C2′	2.68–2.59 (m, 2H) 2.51–2.42 (m, 2H)	2.65–2.57 (m, 2H) 2.43–2.33 (m, 2H)
C2	2.68–2.59 (m, 2H) 2.51–2.42 (m, 2H)	2.65–2.57 (m, 2H) 2.43–2.33 (m, 2H)
C3′	2.40–2.36 (m, 1H) 2.00–1.86 (m, 2H)	2.43–2.33 (m, 2H) 1.91–1.82 (m, 2H)
C3	2.51–2.42 (m, 2H) 2.00–1.86 (m, 2H)	2.43–2.33 (m, 2H) 1.91–1.82 (m, 2H)
C3a	–	–
C3a′	–	–
C4′	7.08 (dd, J = 7.4, 0.8 Hz, 1H)	7.04 (d, J = 7.6 Hz, 1H)
C4	6.99 (d, J = 7.4 Hz, 1H)	6.94 (d, J = 7.2Hz, 1H)
C4a′	–	–
C4a	–	–
C5′	6.49–6.41 (m, 2H)	6.45–6.40 (m, 2H)
C5	6.49–6.41 (m, 2H)	6.45–6.40 (m, 2H)
C6′	6.92 (app-dt, J = 7.7, 1.2Hz, 1H)	6.89 (app-t, J = 7.4 Hz, 1H)
C6	6.84 (app-dt, J = 7.6, 1.2Hz, 1H)	6.80 (app-t, J = 7.2Hz, 1H)
C7′	6.28 (d, J = 7.8 Hz, 1H)	6.26 (d, J = 7.8 Hz, 1H)
C7	6.49 (d, J = 7.8 Hz, 1H)	6.38 (d, J = 7.6 Hz, 1H)[14]
C7a′	–	–
C7a	–	–
N8′-C**H**$_3$	2.96 (s, 3H)	2.93 (s, 3H)
N8-**H**	5.83 (s br, 1H)	5.90 (s br, 1H)
C8a′	4.45 (s, 1H)	4.44 (s, 1H)
C8a	4.55 (s, 1H)	4.54 (s, 1H)

[13] L. E. Overman and E. A. Peterson, *Tetrahedron* 2003, **59**, 6905.
[14] Our assignment of these resonances is supported by key gCOSY, HSCQ, and HMBC correlations.

Table S4. Comparison of ^{13}C NMR data of (–)-calycanthidine (1) with literature data (DMSO-d_6):

Assignment	Overman's Report[13] (–)-calycanthidine ^{13}C NMR, 125.8 MHz DMSO-d_6, 100 ºC	This Work (–)-calycanthidine ^{13}C NMR, 125.8 MHz DMSO-d_6, 100 ºC	Chemical Shift Difference $\Delta\delta = \delta$ (this work) – δ (ref 13)
N1′-**C**H$_3$	36.9	36.9	0.0
N1-**C**H$_3$	35.6	35.7	0.1
C2′	51.3	51.3	0.0
C2	51.2	51.2	0.0
C3′/3	34.9 or 34.6	34.9 or 34.6	0.0
C3a′	62.1	62.1	0.0
C3a	62.0	62.0	0.0
C4′	122.7	122.7	0.0
C4	123.1	123.1	0.0
C4a′	132.4	132.4	0.0
C4a	132.4	132.4	0.0
C5′	115.7	115.8	0.1
C5	115.9	116.0	0.1
C6′	127.0	127.1	0.1
C6	126.7	126.7	0.0
C7′	104.9	105.0	0.1
C7	107.2	107.3	0.1
C7a′	152.3	152.3	0.0
C7a	151.2	151.2	0.0
N8′-**C**H$_3$	34.4	34.5	0.1
N8-H	–	–	0.0
C8a′	91.1	91.1	0.0
C8a	84.0	84.1	0.1



N1'-Carboxyethyl Heterodimer (+)-34:

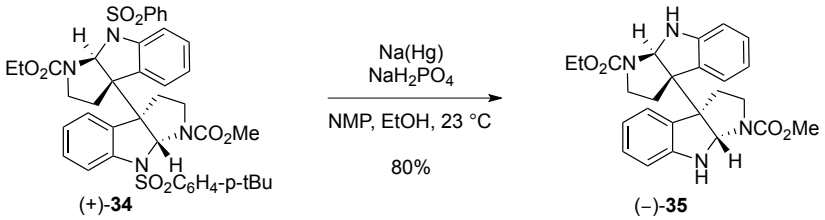
A solution of lithium triethylborohydride in tetrahydrofuran (1.0 M, 530 µL, 530 µmol, 10.0 equiv,) was added via syringe to a solution of heterodimer (+)-**30** (47.0 mg, 52.9 µmol, 1 equiv) in tetrahydrofuran (2.70 mL) at 23 °C. The reaction flask was fitted with a reflux condenser and heated to 65 ºC. After 11 h, another portion of lithium triethylborohydride (1.0 M in tetrahydrofuran, 265 µL, 265 µmol, 5.00 equiv,) was added and the mixture was stirred at 65 ºC. After 12 h, the yellow solution was allowed to cool to 23 °C and a saturated aqueous ammonium chloride solution (10 mL) was added. The resulting suspension was extracted with dichloromethane (3 × 15 mL). The combined organic extracts were washed with brine (10 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 10→25% acetone in hexanes) to afford the N1'-carboxyethyl heterodimer (+)-**34** (35 mg, 84.1%) as a white foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 7.88 (d, J = 7.5 Hz, 2H, $N_{8'}SO_2Ph$-*o*-**H**), 7.78 (d, J = 8.6 Hz, 2H, N_8SO_2Ar-*o*-**H**), 7.62 (t, J = 7.5 Hz, 1H, $N_{8'}SO_2Ph$-*p*-**H**), 7.57 (d, J = 8.8 Hz, 2H, N_8SO_2Ar-*m*-**H**), 7.52 (t, 2H, J = 8.0 Hz, $N_{8'}SO_2Ph$-*m*-**H**), 7.44–7.39 (m, 2H, $C_{7/7'}$**H**), 7.32–7.27 (m, 2H, $C_{6/6'}$**H**), 7.02–6.98 (m, 3H, $C_{5/5'}$**H**, $C_{4'}$**H**), 6.93 (br-s, 1H, C_4**H**), 6.44 (s, 1H, $C_{8a'}$**H**), 6.36 (s, 1H, C_{8a}**H**), 4.08 (app-dq, J = 7.1, 10.6 Hz, 1H, N1′CO_2C**H**$_a$H$_b$$CH_3$), 3.96 (app-dq, J = 7.1, 10.6 Hz, 1H, N1′CO_2CH_a**H**$_b$$CH_3$), 3.80–3.76 (m, 2H, $C_{2/2'}$**H**$_a$), 3.54 (s, 3H, N_1CO_2C**H**$_3$), 2.67–2.56 (m, 2H, $C_{2/2'}$**H**$_b$), 2.06 (dd, J = 5.1, 12.2 Hz, 1H, $C_{3'}$**H**$_a$), 2.02 (dd, J = 5.1, 12.3 Hz, 1H, C_3**H**$_a$), 1.94 –1.84 (m, 2H, $C_{3/3'}$**H**$_b$), 1.34 (s, 9H, C(C**H**$_3$)$_3$), 1.22 (t, J = 7.1 Hz, 3H, $N_{1'}$CO2CH_2C**H**$_3$).

^{13}C NMR (125.8 MHz, CD_3CN, 70 °C): δ 158.9 ($N_{8'}SO_2Ar$-*p*-**C**), 156.1 (N_1**C**O_2CH_3), 155.8 ($N_{1'}$**C**$O_2CH_2CH_3$), 145.2 (**C**$_{7a'}$), 145.0 (**C**$_{7a}$), 143.1 ($N_{8'}SO_2Ph$-*ipso*-**C**), 140.6 (N_8SO_2Ar-*ipso*-**C**), 134.9 ($N_{8'}SO_2Ph$-*p*-**C**), 132.8 (2C, **C**$_{4a}$, **C**$_{4a'}$), 131.4 (2C,

	C$_6$, **C**$_{6'}$), 131.1 (N$_{8'}$SO$_2$Ph-*m*-**C**), 128.2 (N$_{8'}$SO$_2$Ph-*o*-**C**), 128.1 (N$_8$SO$_2$Ar-*o*-**C**$_{/meta}$), 126.5 (**C**$_4$), 126.4 (C$_{4'}$), 125.6 (2C, **C**$_5$, **C**$_{5'}$), 116.2 (C$_7$/C$_{7'}$), 116.0 (C$_7$/C$_{7'}$), 82.6 (2C, **C**$_{8a}$, **C**$_{8a'}$), 64.2 (2C, **C**$_{3a}$, **C**$_{3a'}$), 63.5 (N$_{1'}$CO$_2$**C**H$_2$CH$_3$), 54.0 (N$_1$CO$_2$**C**H$_3$), 46.9 (2C, **C**$_2$, **C**$_{2'}$), 37.6 (**C**$_{3'}$), 37.5 (**C**$_3$), 36.7 (**C**(CH$_3$)$_3$), 32.1 (C(**C**H$_3$)$_3$), 15.6 (N$_{1'}$CO$_2$CH$_2$**C**H$_3$).
FTIR (thin film) cm^{-1}:	2957 (w), 1712 (s), 1595 (w), 1477 (m), 1350 (m).
HRMS (ESI) (*m/z*):	calc'd for C$_{41}$H$_{44}$N$_4$NaO$_8$S$_2$ [M+Na]$^+$: 807.2493, found: 807.2492.
$[\alpha]_D^{24}$:	+6.5 (*c* = 0.31, CH$_2$Cl$_2$).
TLC (33% ethyl acetate in hexanes), R*f*:	0.29 (UV, CAM).



(–)-N1-Carboxymethyl-N1'-Carboxyethyl *meso*-Chimonanthine (35):

Sodium amalgam (5%-Na, 58.0 mg, 128 μmol, 20.0 equiv)[8] was added to a suspension of sodium phosphate monobasic monohydrate (19.0 mg, 141.0 μmol, 22.0 equiv) and N1'-carboxyethyl heterodimer (+)-**34** (5.0 mg, 6.40 μmol, 1 equiv) in a mixture of ethanol-*N*-methylpyrrolidinone (2:1, 900 μL) at 23 °C. After 45 min, another portion of sodium phosphate monobasic monohydrate (19.0 mg, 141 μmol, 22.0 equiv) and sodium amalgam (5%-Na, 58.0 mg, 128 μmol, 20.0 equiv) were added. After an additional 1h, a final portion of sodium phosphate monobasic monohydrate (19.0 mg, 141 μmol, 22.0 equiv) and sodium amalgam (5%-Na, 58.0 mg, 128 μmol, 20.0 equiv) were added. After 1 h, the reaction mixture was diluted with ethyl acetate (10 mL) and was washed with 5% aqueous sodium bicarbonate solution (5 mL). The aqueous phase was separated and extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed with brine (5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 33→50% ethyl acetate in hexanes) to afford (–)-N1-carboxymethyl-N1'-carboxyethyl *meso*-chimonanthine (**35**, 2.3 mg, 80.1%) as a white solid.

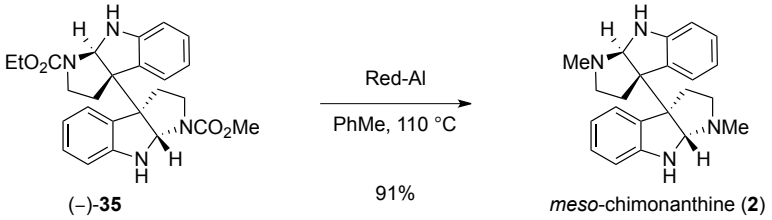
As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz CD_3CN, 75 °C): δ 7.05 (app-t, J = 7.4 Hz, 2H, $C_6\mathbf{H}$, $C_{6'}\mathbf{H}$), 6.69 (d, J = 7.4 Hz, 1H, C_4), 6.66 (d, J = 6.8 Hz, 1H, $C_{4'}$), 6.61–6.57 (m, 2H, $C_5\mathbf{H}$, $C_{5'}\mathbf{H}$), 6.53–6.49 (m, 2H, $C_7\mathbf{H}$, $C_{7'}\mathbf{H}$), 5.39 (s, 1H), 5.38 (s, 1H), 5.06 (br-s, 2H, $N_8\mathbf{H}$, $N_{8'}\mathbf{H}$), 4.13 (q, J = 6.7, 13.7 Hz, 2H, $N_{1'}CO_2C\mathbf{H}_2CH_3$), 3.71–3.65 (m, 5H, $C_2\mathbf{H}_a$, $C_{2'}\mathbf{H}_a$, $N_1CO_2C\mathbf{H}_3$) 2.92–2.84 (m, 2H, $C_2\mathbf{H}_b$, $C_{2'}\mathbf{H}_b$), 2.40–2.32 (m, 2H, $C_3\mathbf{H}_a$, $C_{3'}\mathbf{H}_a$), 2.31–2.25 (m, 2H, $C_3\mathbf{H}_b$, $C_{3'}\mathbf{H}_b$), 1.26 (t, J = 6.6 Hz, 3H, $N_{1'}CO_2CH_2C\mathbf{H}_3$).

^{13}C NMR (125.8 MHz, CD_3CN, 75 °C): δ 152.7 (2C, $\mathbf{C}_{7a}$, $\mathbf{C}_{7a'}$), 131.4 (2C, $\mathbf{C}_{4a}$, $\mathbf{C}_{4a'}$), 130.6 (2C, $\mathbf{C}_6$, $\mathbf{C}_{6'}$), 126.1 (2C, $\mathbf{C}_4$, $\mathbf{C}_{4'}$), 120.0 (2C, $\mathbf{C}_5$, $\mathbf{C}_{5'}$), 110.7 (2C, $\mathbf{C}_7$, $\mathbf{C}_{7'}$), 79.4 (2C, $\mathbf{C}_{8a}$, $\mathbf{C}_{8a'}$), 62.7 ($N_{1'}CO_2\mathbf{C}H_2CH_3$), 53.6 ($N_1CO_2\mathbf{C}H_3$), 46.9 (2C, $\mathbf{C}_2$, $\mathbf{C}_{2'}$), 35.6 (2C, $\mathbf{C}_3$, $\mathbf{C}_{3'}$), 15.9 ($N_{1'}CO_2CH_2\mathbf{C}H_3$).[15]

[15] The C_{3a}, $C_{3a'}$, and the carbonyl carbons of the carbamates were not observed, due to signal broadening even at 75 °C. All expected signals were observed in the following compound, *meso*-chimonanthine (**2**).

FTIR (thin film) cm^{-1}:	3360 (br-m), 2953 (w), 1693 (m), 1451 (w), 1381 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{25}H_{29}N_4O_4$ $[M+H]^+$: 449.2183: found: 449.2182.
$[\alpha]_D^{24}$:	–6.2 (*c* = 0.20, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.24 (UV, CAM).



(–)-**35** *meso*-chimonanthine (**2**)

***meso*-Chimonanthine (2):**

(–)-N1-Carboxymethyl-N1′-carboxyethyl *meso*-chimonanthine (**35**, 30.0 mg, 66.9 μmol, 1 equiv) was azeotropically dried from anhydrous benzene (2 × 5 mL) and the residue was dissolved in toluene (6.5 mL). Sodium bis(2-methoxyethoxy)aluminum hydride in toluene (Red-Al, 70% wt, 193 μL, 670 μmol, 10.0 equiv) was added via syringe at 23 °C. The reaction flask was fitted with a reflux condenser and heated to 110 ºC. After 1.5 h, the reaction mixture was allowed to cool to 23 °C. Excess reducing reagent was quenched by the addition of 10% methanol in chloroform saturated with ammonium hydroxide. The resulting mixture was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 10% methanol in chloroform saturated with ammonium hydroxide) to afford *meso*-chimonanthine (**2**, 21.0 mg, 90.5%) as a white solid.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3OD, 55 °C): δ 6.94 (app-t, J = 7.2 Hz, 2H, $C_6\mathbf{H}$, $C_{6'}\mathbf{H}$), 6.47 (br-s, 2H, $C_5\mathbf{H}$, $C_{5'}\mathbf{H}$), 6.45 (d, J = 7.8 Hz, $C_7\mathbf{H}$, $C_{7'}\mathbf{H}$), 4.54 (s, 2H, $C_{8a}\mathbf{H}$, $C_{8a'}\mathbf{H}$), 2.72 (ddd, J = 2.3, 6.1, 8.8 Hz, $C_2\mathbf{H}_a$, $C_{2'}\mathbf{H}_a$), 2.54–2.46 (m, 2H, $C_3\mathbf{H}_a$, $C_{3'}\mathbf{H}_a$), 2.41 (app-dt, J = 5.6, 8.9 Hz, 2H, $C_2\mathbf{H}_b$, $C_{2'}\mathbf{H}_b$), 2.34 (s, 6H, $N_1C\mathbf{H}_3$, $N_{1'}C\mathbf{H}_3$), 2.05 (ddd, J = 2.9, 5.2, 11.8 Hz, 2H, $C_3\mathbf{H}_b$, $C_{3'}\mathbf{H}_b$).[16]

^{13}C NMR (125.8 MHz, CD_3OD, 55°C): δ 153.7 (2C, $\mathbf{C}_{7a}$, $\mathbf{C}_{7a'}$), 134.3 (2C, $\mathbf{C}_{4a}$, $\mathbf{C}_{4a'}$), 129.2 (2C, $\mathbf{C}_6$, $\mathbf{C}_{6'}$), 125.5 (2C, $\mathbf{C}_4$, $\mathbf{C}_{4'}$), 118.8 (2C, $\mathbf{C}_5$, $\mathbf{C}_{5'}$), 109.7 (2C, $\mathbf{C}_7$, $\mathbf{C}_{7'}$), 84.7 (2C $\mathbf{C}_{8a}$, $\mathbf{C}_{8a'}$), 65.1 (2C, $\mathbf{C}_{3a}$, $\mathbf{C}_{3a'}$), 53.7 (2C, $\mathbf{C}_2$, $\mathbf{C}_{2'}$), 37.4 (2C, $\mathbf{C}_3$, $\mathbf{C}_{3'}$), 36.5 ($N_1\mathbf{C}H_3$, $N_{1'}\mathbf{C}H_3$).

^{1}H NMR (500 MHz, DMSO-d_6, 120 °C): δ 6.86 (app-t, J = 7.7 Hz, 2H, $C_6\mathbf{H}$, $C_{6'}\mathbf{H}$), 6.54 (br-s, 2H, $\mathbf{C}_4\mathbf{H}$, $C_{4'}\mathbf{H}$), 6.40–6.33 (m, 4H, $C_5\mathbf{H}$, $C_{5'}\mathbf{H}$, $C_7\mathbf{H}$, $C_{7'}\mathbf{H}$), 5.45 (s, 1H, $N_8\mathbf{H}$, $N_{8'}\mathbf{H}$), 4.58 (s, 2H, $C_{8a}\mathbf{H}$, $C_{8a'}\mathbf{H}$), 2.69 (ddd, J = 1.8, 6.8, 8.8 Hz, $C_2\mathbf{H}_a$, $C_{2'}\mathbf{H}_a$), 2.48–2.43 (m, 2H, $C_3\mathbf{H}_a$, $C_{3'}\mathbf{H}_a$), 2.35–2.32 (m, 2H,

[16] The $C_4\mathbf{H}$ and $C_{4a}\mathbf{H}$ were not observed, due to signal broadening even at 55 °C. All expected signals were observed in DMSO-d_6 at 120 °C.

	$C_2\mathbf{H}_b$, $C_{2'}\mathbf{H}_b$), 2.30 (s, 6H, $N_1C\mathbf{H}_3$, $N_{1'}C\mathbf{H}_3$), 1.88 (ddd, J = 1.8, 5.5, 11.6 Hz, 2H, $C_3\mathbf{H}_b$, $C_{3'}\mathbf{H}_b$).
^{13}C NMR (125.8 MHz, DMSO-d_6, 120°C):	δ 151.9 (2C, $\mathbf{C}_{7a}$, $\mathbf{C}_{7a'}$), 132.3 (2C, $\mathbf{C}_{4a}$, $\mathbf{C}_{4a'}$), 126.7 (2C, $\mathbf{C}_6$, $\mathbf{C}_{6'}$), 123.1 (2C, $\mathbf{C}_4$, $\mathbf{C}_{4'}$), 115.4 (2C, $\mathbf{C}_5$, $\mathbf{C}_{5'}$), 106.7 (2C, $\mathbf{C}_7$, $\mathbf{C}_{7'}$), 82.5 (2C $\mathbf{C}_{8a}$, $\mathbf{C}_{8a'}$), 62.6 (2C, $\mathbf{C}_{3a,}$ $\mathbf{C}_{3a'}$), 51.1 (2C, $\mathbf{C}_2$, $\mathbf{C}_{2'}$), 36.1 (2C, $\mathbf{C}_3$, $\mathbf{C}_{3'}$), 34.8 ($N_1\mathbf{C}H_3$, $N_{1'}\mathbf{C}H_3$).
FTIR (thin film) cm^{-1}:	3380 (w), 2929 (w), 1604 (m), 1485 (m), 1347 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{22}H_{27}N_4$ $[M+H]^+$: 347.223, found: 347.2232.

TLC (18% methanol, 2% ammonium hydroxide in chloroform), R*f*: 0.3 (UV, CAM).

Table S5. Comparison of our ^{1}H NMR data for *meso*-chimonanthine (2) with literature data (CD_3OD):

Assignment	Overman's Report[17] *meso*-chimonanthine ^{1}H NMR, 500 MHz CD_3OD	This Work *meso*-chimonanthine ^{1}H NMR, 500 MHz CD_3OD, 55 ºC
N1-C**H**3/N1′-C**H**3	2.30 (br-s, 6H)	2.34 (s, 6H)
C2/2′	2.49 (br-m, 4H)	2.72 (ddd, J = 2.3, 6.1, 8.8 Hz, 2H) 2.41 (app-dt, J = 5.6, 8.9 Hz, 2H)
C3/3′	2.02 (br-m, 4H)	2.54–2.46 (m, 2H) 2.05 (ddd, J = 2.9, 5.2, 11.8 Hz, 2H)
C3a/3a′	–	–
C4a/4a′	–	–
C4/4′	6.89 (br-s, 4H)	–[16]
C5/5′	6.39 (d, J = 7.7 Hz, 4H)	6.47 (br-s, 2H)
C6/6′	6.89 (br-s, 4H)	6.94 (app-t, J = 7.2 Hz, 2H)
C7/7′	6.39 (d, J = 7.7 Hz, 4H)	6.45 (d, J = 7.8 Hz, 2H)
C7a/7a′	–	–
N8/8′	4.38 (br-s, 2H)	–[18]
C8a/8a′	2.67 (br-s, 2H)	4.54 (br-s, 2H)[19]

[17] J. T. Link and L. E. Overman *J. Am. Chem. Soc.* 1996, **118**, 8166.
[18] The resonance for this proton is not observed due to rapid deuterium exchange in CD_3OD. However, all expected signals are observed in DMSO-d_6, see Table S7.
[19] Our assignment of these resonances is supported by key HSCQ and HMBC correlations.

Table S6. Comparison of ^{13}C NMR data of *meso*-chimonanthine (2) with literature data (CD_3OD):

Assignment	**Overman′s Report**[17] *meso*-chimonanthine ^{1}H NMR, 500 MHz CD_3OD	**This Work** *meso*-chimonanthine ^{1}H NMR, 500 MHz CD_3OD, 55 ºC	**Chemical Shift Difference** $\Delta\delta = \delta$ (this work) – δ (ref 17)
N1-C**H**3/N1′-C**H**3	–	36.5[19]	–
C2/2′	53.5	53.7	0.2
C3/3′	37.1	37.4	0.3
C3a/3a′	64.8	65.1	0.3
C4a/4a′	133.8	134.3	0.5
C4/4′	125.4	125.5	0.1
C5/5′	118.6	118.8	0.2
C6/6′	129.1	129.2	0.1
C7/7′	109.4	109.7	0.3
C7a/7a′	153.5	153.7	0.2
N8/8′	–	–	–
C8a/8a′	84.2	84.7	0.4

Table S7. Comparison of our ^{1}H NMR data for *meso*-chimonanthine (2) with literature data (DMSO-d_6):

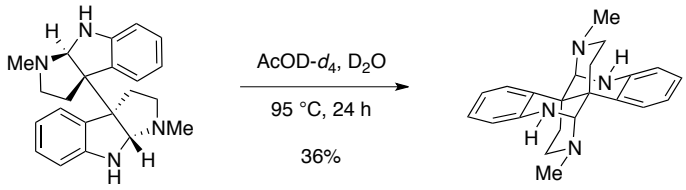
Assignment	Willis's Report[20] *meso*-chimonanthine ^{1}H NMR, 500 MHz DMSO-d_6, 120 ºC	This Work *meso*-chimonanthine ^{1}H NMR, 500 MHz DMSO-d_6, 120 ºC
N1-C**H**3/N1′-C**H**3	2.28 (s, 6H)	2.30 (s, 6H)
C2/2′	2.74–2.64 (m, 2H) 2.52–2.43 (m, 2H)	2.69 (ddd, J = 1.8, 6.8, 8.8 Hz, 2H) 2.35–2.31 (m, 2H)[21]
C3/3′	2.37–2.29 (m, 2H) 1.92–1.86 (m, 2H)	2.48–2.43 (m, 2H)[21] 1.88 (ddd, J = 1.8, 5.5, 11.6 Hz, 2H)
C3a/3a′	–	–
C4a/4a′	–	–
C4/4′	6.55 (br-s, 2H)	6.54 (br-s, 2H)
C5/5′	6.40–6.34 (m, 2H)	6.40–6.33 (m, 2H)
C6/6′	6.87 (dd, J = 7.6, 7.5 Hz, 2H)	6.86 (app-t, J = 7.7 Hz, 2H)
C7/7′	6.40–6.34 (m, 2H)	6.40–6.33 (m, 2H)
C7a/7a′	–	–
N8/8′	5.49 (br-s, 2H)	5.45 (br-s, 2H)
C8a/8a′	4.58 (s, 2H)	4.58 (s, 2H)

[20] R. H. Snell, R. L. Woodward, and M. C. Willis, *Angew. Chem., Int. Ed.* 2011, **50**, 9116.
[21] Our assignment of these resonances is supported by key gCOSY, HSCQ, and HMBC correlations.

Table S8. Comparison of ^{13}C NMR data of *meso*-chimonanthine (2) with literature data (DMSO-d_6):

Assignment	Willis's Report[20] *meso*-chimonanthine ^{1}H NMR, 500 MHz DMSO-d_6, 120 ºC	This Work *meso*-chimonanthine ^{1}H NMR, 500 MHz DMSO-d_6, 120 ºC	Chemical Shift Difference Δδ = δ (this work) – δ (ref 20)
N1-C**H**3/N1′-C**H**3	22.6[22]	34.8	12.2
C2/2′	52.2	51.1	–1.1
C3/3′	35.9	36.1	0.2
C3a/3a′	63.7	62.6	–1.1
C4a/4a′	133.5	132.3	–1.2
C4/4′	124.3	123.1	–1.2
C5/5′	116.7	115.4	–1.3
C6/6′	127.8	126.7	–1.1
C7/7′	107.8	106.7	–1.1
C7a/7a′	153.1	151.9	–1.2
N8/8′	–	–	–
C8a/8a′	83.6	82.5	–1.1

[22] The reported signal at 22.6 ppm is not visible in the ^{13}C NMR spectrum of *meso*-chimonanthine provided in ref 20; however, in the same spectrum an unreported peak is observed at ~35 ppm consistent with our observation.



meso-chimonanthine (**2**) *meso*-calycanthine (**36**)

***meso*-Calycanthine (36):**

A solution of *meso*-chimonanthine (**2**, 20.0 mg, 57.7 μmol, 1 equiv) in a mixture of acetic acid-d_4 (17 μL, 0.43 M) in deuterium oxide (700 μL) was placed in a standard NMR tube, capped with a plastic cap, sealed with Teflon tape, and heated to 95 ºC. After 24 h, the mixture was allowed to cool to 23 °C and partitioned between dichloromethane (10 mL) and saturated aqueous sodium bicarbonate solution (10 mL). The layers were separated, and the aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed with brine (5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 4.5% methanol, 0.5% ammonium hydroxide→9% methanol, 1% ammonium hydroxide in chloroform) to afford *meso*-calycanthine (**36**, 7.2 mg, 36.0 %) as a white solid. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C): δ 7.03–6.96 (m, 4H, $C_{6/6'}\mathbf{H}$, $\mathbf{C}_{4/4'}\mathbf{H}$), 6.66 (dt, J = 1.3, 7.4 Hz, 2H, $C_{5/5'}\mathbf{H}$), 6.57 (dd, J = 0.8, 7.9 Hz, 2H, $C_{7/7'}\mathbf{H}$), 4.94 (br-s, 2H, $N_{8/8'}\mathbf{H}$), 4.28 (d, J = 3.8 Hz, 2H, $C_{8a/8a'}\mathbf{H}$), 2.36 (dd, J = 2.1, 7.9 Hz, 2H, $C_{2/2'}\mathbf{H}_a$), 2.29 (s, 6H, $N_{1/1'}C\mathbf{H}_3$), 2.20–2.09 (m, 4H, $C_{2/2'}\mathbf{H}_b$, $C_{3/3'}\mathbf{H}_a$), 1.20–1.11 (m, 2H, $C_{3/3'}\mathbf{H}_b$).

^{13}C NMR (125.8 MHz, CD_2Cl_2, 20 °C): δ 145.3 (2C, $\mathbf{C}_{7a}$, $\mathbf{C}_{7a'}$), 127.0 (2C, $\mathbf{C}_{4/6}$, $\mathbf{C}_{4'/6'}$), 126.9 (2C, $\mathbf{C}_{4/6}$, $\mathbf{C}_{4'/6'}$), 125.0 (2C, $\mathbf{C}_{4a}$, $\mathbf{C}_{4a'}$), 117.5 (2C, $\mathbf{C}_5$, $\mathbf{C}_{5'}$), 112.4 (2C, $\mathbf{C}_7$, $\mathbf{C}_{7'}$), 71.2 (2C $\mathbf{C}_{8a}$, $\mathbf{C}_{8a'}$), 46.5 (2C, $\mathbf{C}_2$, $\mathbf{C}_{2'}$), 42.4 ($N_1\mathbf{C}H_3$, $N_{1'}\mathbf{C}H_3$), 37.3 (2C, $\mathbf{C}_{3a}$, $\mathbf{C}_{3a'}$), 34.6 (2C, $\mathbf{C}_3$, $\mathbf{C}_{3'}$).

FTIR (thin film) cm^{-1}: 3438 (w br), 2964 (w), 1608 (m), 1487 (m), 1304 (w).

HRMS (ESI) (*m/z*): calc'd for $C_{22}H_{27}N_4$ $[M+H]^+$: 347.2230, found: 347.2214.

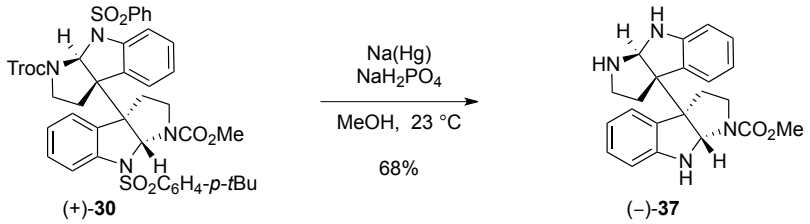
TLC (18% methanol, 2% ammonium hydroxide in chloroform), R*f*: 0.63 (UV, CAM).

Table S9. Comparison of ^{1}H NMR data of *meso*-calycanthine (36) with literature data:

Assignment	**Overman's Report**[17] *meso*-chimonanthine ^{1}H NMR, 500 MHz CD_2Cl_2	**This Work** *meso*-chimonanthine ^{1}H NMR, 500 MHz CD_2Cl_2, 20 ºC
N1-C**H**$_3$/N1′-C**H**$_3$	2.27 (s, 3H)	2.29 (s, 1H)
C2/2′	2.33 (m, 2H) 2.11 (m, 4H)	2.36 (dd, *J* = 2.1, 7.9 Hz, 2H) 2.20–2.09 (m, 4H)
C3/3′	2.11 (m, 4H) 1.14 (m, 2H)	2.20–2.09 (m, 4H) 1.20–1.11 (m, 2H)
C3a/3a′	–	–
C4a/4a′	–	–
C4/4′	6.97 (m, 4H)	7.03–6.96 (m, 4H)
C5/5′	6.63 (t, *J* = 7.5 Hz, 2H)	6.66 (app-dt, *J* = 1.3, 7.4 Hz, 2H)
C6/6′	6.97 (m, 4H)	7.03–6.96 (m, 4H)
C7/7′	6.54 (d, *J* = 7.9 Hz, 2H)	6.57 (dd, *J* = 0.8, 7.9 Hz, 2H)
C7a/7a′	–	–
N8/8′	4.91 (s, 2H)	4.94 (br-s, 2H)
C8a/8a′	4.25 (s, 2H)	4.28 (d, *J* = 3.8 Hz, 2H)

Table S10. Comparison of ^{13}C NMR data of *meso*-calycanthine (36) with literature data:

Assignment	**Overman's Report**[17] *meso*-chimonanthine ^{1}H NMR, 500 MHz CD_2Cl_2	**This Work** *meso*-chimonanthine ^{1}H NMR, 500 MHz CD_2Cl_2, 20 ºC	**Chemical Shift Difference** $\Delta\delta = \delta$ (this work) – δ (ref 17)
N1-C**H**$_3$/N1′-C**H**$_3$	42.2	42.4	0.2
C2/2′	46.3	46.3	0.0
C3/3′	34.4	34.6	0.2
C3a/3a′	37.2	37.3	0.1
C4a/4a′	124.9	125.0	0.1
C4/4′	126.9 or 126.7	127.0 or 126.9	0.0–0.3
C5/5′	117.4	117.5	0.1
C6/6′	126.9 or126.7	127.0 or 126.9	0.0–0.3
C7/7′	112.3	112.4	0.1
C7a/7a′	145.1	145.3	0.2
N8/8′	–	–	–
C8a/8a′	71.1	71.2	0.1



(–)-N1-Carboxymethyl Desmethyl-*meso*-Chimonanthine (37):

Sodium amalgam (5%-Na, 583 mg, 1.27 mmol, 25.0 equiv)[8] was added to a suspension of sodium phosphate monobasic monohydrate (196 mg, 1.43 mmol, 28.0 equiv) and heterodimer (+)-**30** (45.0 mg, 50.7 μmol, 1 equiv) in methanol at 23 °C. After 1 h, another portion of sodium phosphate monobasic monohydrate (84.0 mg, 612 μmol, 12.0 equiv) and sodium amalgam (5%-Na, 235 mg, 510 μmol, 10.0 equiv) were added sequentially. After an additional 1 h, the reaction mixture was diluted with ethyl acetate (20 mL) and washed with a 5% aqueous sodium bicarbonate solution (10 mL). The aqueous phase was separated and extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with brine (10 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 9% methanol, 1.0% ammonium hydroxide→18% methanol, 2.0% ammonium hydroxide in chloroform) to afford the heterodimer (–)-N1-carboxymethyl desmethyl-*meso*-chimonanthine (**37**, 13.0 mg, 67.7%) as a white solid.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 75 °C): δ 7.04 (app-t, J = 7.6 Hz, 1H, C_6**H**), 6.96 (app-t, J = 8.5 Hz, 1H, $C_{6'}$**H**), 6.77 (d, J = 13.1Hz, 1H, C_4**H**), 6.59 (app-t, J = 7.4 Hz, 1H, C_5**H**), 6.52–6.46 (m, 3H, $C_{5'}$**H**, C_7**H**, $C_{4'}$**H**), 6.44 (d, J = 7.8 Hz, 1H, $C_{7'}$**H**), 5.32 (s, 1H, C_{8a}**H**), 5.01 (br-s, 1H, N**H**), 4.92 (s, 1H, $C_{8a'}$**H**), 3.74–3.67 (m, 1H C_2**H**$_a$), 3.69 (s, 3H, N_1CO_2C**H**$_3$), 3.00 (dd, J = 6.9, 10.3Hz, 1H, $C_{2'}$**H**$_a$), 2.94 (app-dt, J = 6.3, 11.1 Hz, 1H, C_2**H**$_b$), 2.58 (app-dt, J = 5.3, 10.9 Hz, 1H, $C_{2'}$**H**$_b$), 2.47 (app-dt, J = 8.3, 12.1Hz, 1H, C_3**H**$_a$), 2.40–2.05 (br-s, 1H, $N_{1'}$**H**) 2.32 (dd, J = 6.2, 12.4 Hz, 1H, C_3**H**$_b$), 2.18 (app-dt, J = 6.7, 11.7 Hz, 1H, $C_{3'}$**H**$_a$), 2.07 (dd, J = 5.2, 11.8 Hz, 1H, $C_{3'}$**H**$_b$).

^{13}C NMR (125.8 MHz, CD_3CN, 75 °C): δ 155.6 ($N_1CO_2CH_3$), 154.1 (**C**$_{7a'}$), 152.7 (**C**$_{7a}$), 133.1 (**C**$_{4a'}$), 132.6 (**C**$_{4a}$), 130.3 (**C**$_6$), 129.9 (**C**$_{6'}$), 126.4 (**C**$_{4'}$), 126.1 (**C**$_4$), 119.8 (**C**$_5$), 119.2 (**C**$_{5'}$), 110.4 (**C**$_7$), 109.7 (**C**$_{7'}$), 81.9 (**C**$_{8a'}$), 79.8 (**C**$_{8a}$), 65.7

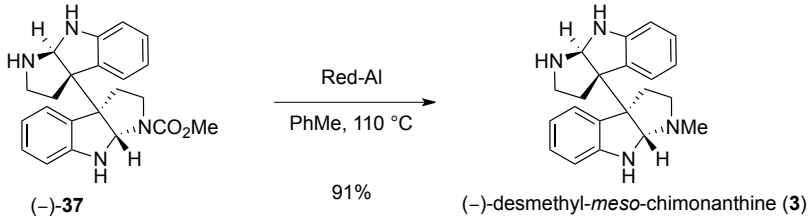
(2C, $\mathbf{C}_{3a}$, $\mathbf{C}_{3a'}$), 53.5 ($N_1CO_2\mathbf{C}H_3$), 47.2 ($\mathbf{C}_{2'}$), 46.8 ($\mathbf{C}_2$), 40.3 ($\mathbf{C}_{3'}$), 36.2 ($\mathbf{C}_3$).

FTIR (thin film) cm^{-1}: 3350 (br-m), 2954 (w), 1692 (s), 1606 (w), 1451 (m), 1385 (w).

HRMS (ESI) (*m/z*): calc'd for $C_{22}H_{25}N_4O_2$ $[M+H]^+$: 377.1972, found: 377.1976

$[\alpha]_D^{24}$: –223 (*c* = 0.32, CH_2Cl_2).

TLC (10% methanol in chloroform), R*f*: 0.18 (UV, CAM).



(–)-**37** (–)-desmethyl-*meso*-chimonanthine (**3**)

(–)-Desmethyl-*meso*-Chimonanthine (3):

(–)-N1-Carboxymethyl-N1′-desmethyl-*meso*-chimonanthine (**37**, 20.0 mg, 53.1 μmol, 1 equiv) was azeotropically dried from anhydrous benzene (2 × 5 mL) and the residue was dissolved in toluene (5.0 mL). A solution of sodium bis(2-methoxyethoxy)aluminum hydride in toluene (Red-Al, 70% wt, 153 μL, 530 μmol, 10.0 equiv) was added via syringe at 23 °C. The reaction flask was fitted with a reflux condenser and heated to 110 ºC. After 1.5 h, the reaction mixture was allowed to cool to 23 °C. Excess reducing reagent was quenched by the addition of 10% methanol in chloroform saturated with ammonium hydroxide and then concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: gradient, 10% methanol in chloroform→10% methanol in chloroform saturated with ammonium hydroxide) to afford (–)-desmethyl-*meso*-chimonanthine (**3**, 16.0 mg, 90.8%) as a white solid.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

Characterization in $CDCl_3$ at 50 °C[23]:

^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 7.04–6.91 (m, 2H, $C_6\mathbf{H}$, $C_{6'}\mathbf{H}$), 6.64–6.50 (m, 4H, $C_5\mathbf{H}$, $C_{5'}\mathbf{H}$, $C_4\mathbf{H}$, $C_{4'}\mathbf{H}$), 6.46 (app t, J = 7.1 Hz, 4H, $C_7\mathbf{H}$, $C_{7'}\mathbf{H}$), 5.02 (br-s, 1H, $C_{8a'}\mathbf{H}$), 4.57 (br-s, 1H, $C_{8a}\mathbf{H}$), 3.07 (dd, J = 6.7, 10.6 Hz, 1H, $C_{2'}\mathbf{H}_a$), 2.78 (ddd, J = 1.9, 6.6, 8.5 Hz, 1H, $C_2\mathbf{H}_a$), 2.72 (app-dt, J = 5.1, 11.1 Hz, 1H, $C_{2'}\mathbf{H}_b$), 2.52–2.39 (m, 2H, $C_2\mathbf{H}_b$, $C_3\mathbf{H}_a$), 2.37 (s, 3H, $N_1C\mathbf{H}_3$), 2.31 (app-dt, J = 6.9, 11.8 Hz, 1H, $C_{3'}\mathbf{H}_a$), 2.15 (dd, J = 5.1, 11.9 Hz, 2H, $C_{3'}\mathbf{H}_b$), 2.10–2.04 (m, 1H, $C_3\mathbf{H}_b$).

^{13}C NMR (125.8 MHz, $CDCl_3$, 50 °C): δ 152.0 (2C, $\mathbf{C}_{7a}$, $\mathbf{C}_{7a'}$), 133.4 ($\mathbf{C}_{4a}$), 132.2 ($\mathbf{C}_{4a'}$), 128.4 (2C, $\mathbf{C}_6$, $\mathbf{C}_{6'}$), 124.9 ($\mathbf{C}_{4/4'}$), 124.6 ($\mathbf{C}_{4/4'}$), 118.7 (2C, $\mathbf{C}_5$, $\mathbf{C}_{5'}$), 109.1 ($\mathbf{C}_{7/7'}$), 108.8 ($\mathbf{C}_{7/7'}$), 83.9 ($\mathbf{C}_{8a}$), 80.4 ($\mathbf{C}_{8a'}$), 64.7 ($C_{3a'}$), 64.0 (C_{3a}), 52.5 ($\mathbf{C}_2$), 45.8 ($\mathbf{C}_{2'}$), 38.7 ($\mathbf{C}_{3'}$), 37.1 ($\mathbf{C}_3$), 35.9 ($N_1\mathbf{C}H_3$).

Characterization in DMSO-d_6 at 50 °C[24]

[23] We found data collection in $CDCl_3$ at 50 °C provided optimal resolution for ^{13}C and ^{1}H NMR.
[24] ^{1}H and ^{13}C NMR were also obtained in DMSO-d_6 for comparison with other natural products synthesized in this report.

^{1}H NMR (500 MHz, DMSO-d_6, 100 °C): δ 6.90–6.84 (m, 2H, C_6**H**, $C_{6'}$**H**), 6.63 (br-s, 1H, C_4**H**), 6.45–6.30 (m, 5H, $C_{4'}$**H**, C_5**H**, $C_{5'}$**H**, C_7**H**, $C_{7'}$**H**), 5.52 (s, 1H, N_8**H**), 5.40 (s, 1H, $N_{8'}$**H**), 4.92 (s, 1H, $C_{8a'}$**H**), 4.51 (s, 1H, C_{8a}**H**), 2.97 (app-t, J = 9.1Hz, 1H, $C_{2'}$**H**$_a$), 2.69 (app-t, J = 7.6 Hz, 1H, C_2**H**$_a$), 2.45–2.25 (m, 4H, C_2**H**$_b$, $C_{2'}$**H**$_b$, C_3**H**$_a$, $C_{3'}$**H**$_a$), 2.29 (s, 3H, N_1C**H**$_3$), 1.98 (dd, J = 5.1, 12.1Hz, 1H, $C_{3'}$**H**$_b$), 1.90 (dd, J = 5.1, 11.5 Hz, 1H, C_3**H**$_b$).

^{13}C NMR (125.8 MHz, DMSO-d_6, 100 °C): δ 151.9 (2C, **C**$_{7a}$, **C**$_{7a'}$), 132.6 (**C**$_{4a}$), 131.4 (**C**$_{4a'}$) 126.8 (2C, **C**$_6$, **C**$_{6'}$), 123.2 (**C**$_4$), 123.6 (**C**$_{4'}$), 115.7 (2C, **C**$_5$, **C**$_{5'}$), 106.8 (**C**$_7$), 106.3 (**C**$_{7'}$), 82.6 (**C**$_{8a}$), 79.2 (**C**$_{8a'}$), 63.1 ($C_{3a'}$), 62.3 (C_{3a}), 51.2 (**C**$_2$), 44.2 (**C**$_{2'}$), 37.7 (**C**$_{3'}$), 36.4 (**C**$_3$). 35.0 (N_1**C**H$_3$).

Characterization in $CDCl_3$ at –40 °C[25]

^{1}H NMR (500 MHz, $CDCl_3$, –40 °C): *Major* R*otamer:* δ 7.35–7.28 (m, 1H, $C_{4'}$**H**), 7.09 (app-t, J = 7.6 Hz, 1H, $C_{6'}$**H**), 6.91 (app-t, J = 6.9 Hz, 1H, C_6**H**), 6.80 (app-t, J = 7.4 Hz, 1H, $C_{5'}$**H**), 6.51–6.43 (m, 2H, $C_{7/7'}$**H**), 6.30 (app-t, J = 7.2 Hz, 1H, C_5**H**), 5.71–5.63 (m, 1H, C_4**H**), 5.30 (br-s, 1H, C_{8a}**H**), 4.93 (br-s, 1H, $N_{1'}$**H**), 4.55 (br-s, 1H, N_8**H**), 4.29 (br-s, 1H, $C_{8a'}$**H**), 3.77 (br-s, 1H, $N_{8'}$**H**), 3.16–3.02 (m, 2H, $C_{2'}$**H**$_b$, $C_{2'}$**H**$_a$), 2.60–2.45 (m, 2H, $C_{3'}$**H**$_a$, $C_{3'}$**H**$_b$), 2.27 (s, 3H, N_1C**H**$_3$), 2.25–2.10 (m, 2H, C_2**H**$_a$, C_2**H**$_b$), 2.10–2.03 (m, 2H, C_3**H**$_a$, C_3**H**$_b$).

Minor Rotamer: δ 7.35–7.28 (m, 1H, C_4**H**), 7.09 (app-t, J = 7.6 Hz, 1H, $C_{6'}$**H**), 6.91 (app-t, J = 6.9 Hz, 1H, C_6**H**), 6.80 (app-t, J = 7.4 Hz, 1H, $C_{5'}$**H**), 6.51–6.43 (m, 2H, $C_{7/7'}$**H**), 6.28 (app-t, J = 7.2 Hz, 1H, C_5**H**), 5.71–5.63 (m, 1H, $C_{4'}$**H**), 5.30 (br-s, 1H, $C_{8a'}$**H**), 4.93 (br-s, 1H, $N_{1'}$**H**), 4.55 (br-s, 1H, $N_{8'}$**H**), 4.29 (br-s, 1H, C_{8a}**H**), 3.77 (br-s, 1H, N_8**H**), 3.16–3.02 (m, 2H, $C_{2'}$**H**$_b$, $C_{2'}$**H**$_a$), 2.87–2.69 (m, 2H, C_2**H**$_a$, C_2**H**$_b$), 2.60–2.45 (m, 2H, $C_{3'}$**H**$_a$, $C_{3'}$**H**$_b$), 2.43 (s, 3H, N_1C**H**$_3$), 2.10–2.03 (m, 2H, C_3**H**$_a$, C_3**H**$_b$).

^{13}C NMR (125.8 MHz, $CDCl_3$, –40 °C): *Major Rotamer:* δ 151.97 (**C**$_{7a'}$), 150.87 (**C**$_{7a}$), 132.95 (**C**$_{4a'}$), 130.91 (**C**$_{4a}$), 128.44 (**C**$_6$), 128.11 (**C**$_{6'}$), 124.80 (**C**$_4$), 124.18 (**C**$_{4'}$), 118.52 (**C**$_{5'}$), 117.94 (**C**$_5$), 109.21 (**C**$_{7'}$), 108.08 (**C**$_7$), 83.01 (**C**$_{8a}$),

[25] ^{1}H and ^{13}C NMR were obtained in $CDCl_3$ at –40 °C for comparison to the data provided in the isolation report, see V. Jannic, F. Guéritte, O. Laprévote, L. Serani, M.-T. Martin, T. Sévenet, and P. Potier, *J. Nat. Prod.* 1999, **62**, 838. However, we found ^{1}H and ^{13}C NMR data collected at –40 °C difficult to analyze and less informative than data collected at 50 °C; see footnote 23.

79.74 (**C**$_{8a'}$), 64.40 (C$_{3a}$), 63.05 (C$_{3a'}$), 52.09 (**C**$_2$), 45.62 (**C**$_{2'}$), 39.13 (**C**$_3$), 36.14 (**C**$_{3'}$), 35.56 (N$_1$**C**H$_3$).

Minor Rotamer: δ 151.20 (**C**$_{7a'}$), 151.07 (**C**$_{7a}$), 132.05 (**C**$_{4a/4a'}$), 131.87 (**C**$_{4a/4a'}$), 128.63 (**C**$_{6'}$), 127.98 (**C**$_6$), 124.49 (**C**$_4$), 124.36 (**C**$_{4'}$), 118.89 (**C**$_5$), 117.77 (**C**$_{5'}$), 109.21 (**C**$_7$), 108.08 (**C**$_{7'}$), 82.53 (**C**$_{8a}$), 79.88 (**C**$_{8a'}$), 63.88 (C$_{3a'}$), 63.62 (C$_{3a}$), 51.89 (**C**$_2$), 45.14 (**C**$_{2'}$), 38.12 (**C**$_{3'}$), 37.03 (**C**$_3$), 35.48 (N$_1$**C**H$_3$).

FTIR (thin film) cm^{-1}: 3377 (br-m), 2931 (w), 1604 (m), 1485 (m), 1247 (w).

HRMS (ESI) (*m/z*): calc'd for $C_{21}H_{25}N_4$ $[M+H]^+$: 333.2074, found: 333.2075.

$[\alpha]_D^{24}$: –1.8 (*c* = 0.21, EtOH).[26]
–13.7 (*c* = 0.20, CH_2Cl_2).

TLC (10% methanol in chloroform saturated with ammonium hydroxide), R*f*: 0.26 (UV, CAM).

[26] Literature value: $[\alpha]^{24}_D$ = + 0.5 (*c* 1, EtOH), see V. Jannic, F. Guéritte, O. Laprévote, L. Serani, M.-T. Martin, T. Sévenet, and P. Potier, *J. Nat. Prod.* 1999, **62**, 838.

Table S11. Comparison of our ^{1}H NMR data for (–)-desmethyl-*meso*-chimonanthine (3) with literature data ($CDCl_3$):

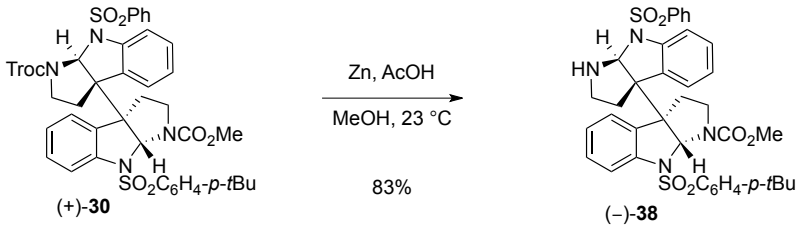
Assign-ment	Guéritte's Report[26] (+)-desmethyl-*meso*-chimonanthine ^{1}H NMR, 400 MHz $CDCl_3$, –40 ºC * denotes minor conformer	This Work (–)-desmethyl-*meso*-chimonanthine ^{1}H NMR, 500 MHz $CDCl_3$, –40 ºC * denotes minor conformer	Dalko's Report[27] (±)-desmethyl-*meso*-chimonanthine ^{1}H NMR, 300 MHz $CDCl_3$	This Work (–)-desmethyl-*meso*-chimonanthine ^{1}H NMR, 500 MHz $CDCl_3$, 50 ºC
N1′-**H**	5.02 (s, 1H) 5.02 (s, 1H)*	4.93 (s, 1H) 4.93 (s, 1H)*	–	–
N1-C**H**$_3$	2.32 (s, 3H) 2.47 (s, 3H)*	2.27 (s, 3H) 2.43 (s, 3H)*	2.30 (s, 3H)	2.37 (s, 3H)
C2′	3.18–2.73 (m, 2H) 3.18 (m, 2H)*	3.16–3.02 (m, 2H) 3.16–3.02 (m, 2H)*	3.02 (dd, *J* = 6.6, 10.5 Hz, 1H) 2.66–2.63 (m, 1H)	3.07 (dd, *J* =6.7, 10.6 Hz, 1H) 2.72 (app-dt, *J* = 5.1, 11.1 Hz, 1H)
C2	2.10 (m, 2H) 2.82–2.42 (m, 2H)*	2.25–2.10 (m, 2H) 2.87–2.69 (m, 2H)*	2.74–2.70 (m, 1H) 2.44–2.38 (m, 1H)	2.78 (ddd, *J* = 1.9, 6.6, 8.5 Hz, 1H) 2.52–2.39 (m, 2H)
C3′	2.60–2.40 (m, 2H) 2.10 (m)*	2.60–2.45 (m, 2H) 2.60–2.45 (m, 2H)*	2.30–2.20 (m, 2H) 2.10 (dd, *J* = 5.1, 11.7 Hz, 1H)	2.31 (app-dt, *J* = 6.9, 11.8 Hz, 1H) 2.15 (dd, *J* = 5.1, 11.9 Hz, 1H)
C3	2.10 (m) 2.10 (m)*	2.10–2.03 (m, 2H) 2.10–2.03 (m, 2H)*	2.30–2.20 (m, 2H) 2.01 (dd, *J* = 1.8, 10.0 Hz, 1H)	2.52–2.39 (m, 2H) 2.10–2.04 (m, 1H)
C3a	–	–	–	–
C3a′	–	–	–	–
C4′	7.28 (d, 1H) 5.62 (d, 1H)*	7.35–7.28 (m, 2H) 5.71–5.63 (m, 2H)*	6.60–6.42 (m, 3H)	6.64–6.50 (m, 4H)
C4	5.67 (d, 1H) 7.32 (d, 1H)*	5.71–5.63 (m, 2H) 7.35–7.28 (m, 2H)*	6.60–6.42 (m, 3H)	6.64–6.50 (m,4H)
C4a′	–	–	–	–
C4a	–	–	–	–
C5′	6.80 (t, 1H) 6.28 (t, 1H)*	6.80 (app-t, J = 7.4 Hz, 1H) 6.28 (app-t, J = 7.2 Hz, 1H)*	–	–
C5	6.30 (t, 1H) 6.82 (t, 1H)*	6.30 (app-t, J = 7.2 Hz, 1H) 6.80 (app-t, J = 7.4 Hz, 1H)*	–	–
C5/5′	–	–	6.60–6.42 (m, 3H) 6.98–6.88 (m, 3H)	6.64–6.50 (m,4H)
C6′	7.10 (t, 1H) 6.91 (t, 1H)*	7.09 (app-t, J = 7.6 Hz, 1H) 6.91 (app-t, J = 6.9 Hz, 1H)*	6.98–6.88 (m, 3H)	7.04–6.91 (m, 2H)
C6	6.91 (t, 1H) 7.10 (t, 1H)*	6.91 (app-t, J = 6.9 Hz, 1H) 7.09 (app-t, J = 7.6 Hz, 1H)*	6.98–6.88 (m, 3H)	7.04–6.91 (m, 2H)
C7′	6.46 (d, 1H) 6.49 (d, 1H)*	6.51–6.43 (m, 1H) 6.51–6.43 (m, 1H)*	6.41 (d, *J* = 7.9 Hz, 1H)	6.46 (app t, *J* = 7.1 Hz, 2H)

[27] C. Menozzi, P. I. Dalko, and J. Cossy, *Chem. Commun*. 2006, 4638.

C7	6.48 (d, 1H) 6.48 (d, 1H)*	6.51–6.43 (m, 1H) 6.51–6.43 (m, 1H)*	6.40 (d, J = 7.7 Hz, 1H)	6.46 (app t, J = 7.1 Hz, 2H)
C7a′	–	–	–	–
C7a	–	–	–	–
N8′-H	3.80 (s, 1H) 4.62 (s, 1H)*	3.77 (s, 1H) 4.55 (s, 1H)*	–	–
N8-**H**	4.64 (s, 1H) 3.80 (s, 1H)*	4.55 (s, 1H) 3.77 (s, 1H)*	–	–
C8a′	4.32 (s, 1H) 5.42 (s, 1H)	4.29 (s, 1H) 5.30 (s, 1H)*	4.97 (s, 1H)	5.02 (br-s, 1H)
C8a	5.42 (s, 1H) 4.32 (s, 1H)*	5.30 (s, 1H) 4.29 (s, 1H)*	4.46 (s, 1H)	4.57 (br-s, 1H)

Table S12. Comparison of ^{13}C NMR data of (–)-desmethyl-*meso*-chimonanthine (3) with literature data ($CDCl_3$):

Assign-ment	Guéritte′s Report[26] (–)-desmethyl-*meso*-chimonanthine ^{13}C NMR, 100 MHz $CDCl_3$, – 40 ºC *denotes minor conformer	This Work (–)-desmethyl-*meso*-chimonanthine ^{13}C NMR, 125 MHz $CDCl_3$, –40 ºC *denotes minor conformer	Chemical Shift Difference Δδ = δ (this work) – δ (ref 26)	Dalko′s Report[27] (±)-desmethyl-*meso*-chimonanthine ^{13}C NMR, 300 MHz $CDCl_3$	This Work (–)-desmethyl-*meso*-chimonanthine ^{13}C NMR, 125 MHz $CDCl_3$, 50 ºC	Chemical Shift Difference Δδ = δ (this work) – δ (ref 27)
N1′-H	–	–	–	–	–	–
N1-**C**H$_3$	35.12 35.12*	35.56 35.48*	0.44 0.36*	35.7	35.9	0.2
C2′	44.87 44.57*	45.62 45.14*	0.75 0.57*	45.6	45.8	0.2
C2	51.85 51.66*	52.09 51.89*	0.24 0.23*	52.2	52.5	0.3
C3′	35.73 37.59*	36.14 38.12*	0.41 0.53*	38.0	38.7	0.7
C3	38.06 36.37*	39.13 37.03*	1.07 0.66*	36.5	37.1	0.6
C3a′	62.85 63.63*	63.05 63.88*	0.2 0.25*	64.4	64.7	0.3
C3a	63.95 63.30*	64.40 63.62*	0.45 0.32*	63.6	64.0	0.4
C4′	123.91 124.25*	124.18 124.36*	0.27 0.11*	–	–	–
C4	124.43 124.06*	124.80 124.49*	0.37 0.43*	–	–	–
C4/4′	–	–	–	124.7, 124.3	124.9, 124.6	–0.1–0.6
C4a′	132.22 131.31*	132.95 131.87*	0.73 0.56	131.4	132.2	0.8
C4a	130.04 131.31*	130.91 131.87*	0.87 0.56	131.5	133.4	1.9
C5′	118.45 117.73*	118.52 117.77*	0.07 0.04	–	–	–
C5	117.97 118.83*	117.94 118.89*	–0.03 0.06	–	–	–
C5/5′	–	–	–	118.8, 118.3	118.7, 118.7	–0.1–0.4
C6′	128.19 128.65*	128.11 128.63*	–0.08 –0.02	128.1	128.4	0.3
C6	128.43 127.95*	128.44 127.98*	0.01 0.03	128.1	128.4	0.3
C7′	109.10 108.19*	109.21 108.08*	0.11 0.11	–	–	–
C7	108.19 109.10*	108.08 109.21*	–0.11 –0.11	–	–	–
C7/C7′	–	–	–	108.8, 108.4	109.1, 108.8	0–0.7
C7a′	151.75 151.04*	151.97 151.20*	0.22 0.16	151.6	152.0	0.4
C7a	150.30 151.51*	150.87 152.01*	0.57 0.5	151.6	152.0	0.4
N8′-**H**	–	–	–	–	–	–
N8–H	–	–	–	–	–	–
C8a′	79.30 82.36*	79.74 79.88*	0.44 –2.48	80.1	80.4	0.3
C8a	82.36 82.36*	83.01 82.53*	0.65 0.17	83.4	83.9	0.5



N1'-H Heterodimer (–)-38:

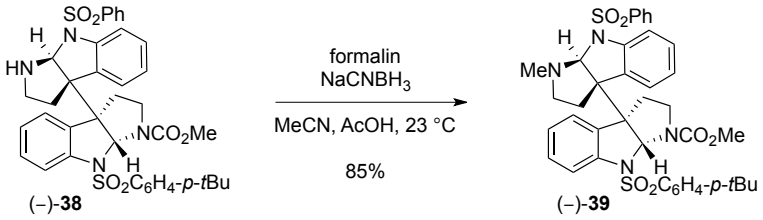
Activated zinc dust (106 mg, 1.62 mmol, 20.0 equiv) and acetic acid (185 μL, 3.24 mmol, 40 equiv) were added sequentially to a solution of heterodimer (+)-**30** (72 mg, 81.1 μmol, 1 equiv) in methanol (7.0 mL) at 23 °C. After 1.5 h, an aqueous solution of sodium hydroxide (1 N, 10 mL) was added and the resulting suspension was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with brine (10 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 30→50% ethyl acetate in hexanes) to afford the N1'-H heterodimer (–)-**38** (48.0 mg, 83.1%) as a white foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, DMSO-d_6, 80°C): δ 7.89 (d, J = 7.1 Hz, 2H, N_8SO_2Ar-*o*-**H**), 7.68 (d, J = 8.3 Hz, 2H, N_8SO_2Ar-*m*-**H**), 7.51 (t, J = 7.2 Hz, 1H, $N_{8'}SO_2Ph$-*p*-**H**), 7.35–7.10 (m, 9H, $N_{8'}SO_2Ph$-*m*-**H**, $N_{8'}SO_2Ph$-*o*-**H**, C_7**H**, $C_{7'}$**H**, $C_{6'}$**H**, $C_{4'}$**H**), 7.02 (app-t, J = 6.9 Hz, 1H, C_6**H**), 6.95 (br-s, 1H, $C_{5'}$**H**), 6.54 (br-s, 1H, C_{8a}**H**), 6.37 (br-s, 1H, C_5**H**), 6.01 (br-s, 1H, C_4**H**), 4.85 (br-s, 1H, $C_{8a'}$**H**), 3.92 (dd, J = 7.5, 11.4 Hz, 1H, C_2**H**$_a$), 3.66 (s, 3H, N_1CO_2C**H**$_3$), 3.16 (s, 1H, $N_{1'}$**H**), 3.11–3.03 (m, 1H, $C_{2'}$**H**$_a$), 2.70 (app-dt, J = 5.0, 11.8 Hz, 1H, C_2**H**$_b$), 2.61 (br-s, 1H, $C_{2'}$**H**$_b$), 2.43–2.31 (m, 1H, C_3**H**$_a$), 2.11–1.85 (m, 3H, C_3**H**$_b$, $C_{3'}$**H**$_a$, $C_{3'}$**H**$_b$), 1.29 (s, 9H, C(C**H**$_3$)$_3$).

^{13}C NMR (125.8 MHz, DMSO-d_6, 80 °C): δ 156.4 ($N_{8'}SO_2Ar$-*p*-**C**), 153.2 (N_1**C**O_2CH_3), 141.7 ($N_{8'}SO_2Ph$-*ipso*-**C**), 141.1 (**C**$_{7a}$), 138.0 (**C**$_{7a'}$), 136.1 (N_8SO_2Ar-*ipso*-**C**), 132.4 ($N_{8'}SO_2Ph$-*p*-**C**), 131.7 (**C**$_{4a'}$), 130.6 (**C**$_{4a}$), 128.9 (**C**$_6$), 128.7 ($N_{8'}SO_2Ph$-*m*-**C**), 128.5 (**C**$_{6'}$), 126.2 (N_8SO_2Ar-*o*-**C**), 126.0 (N_8SO_2Ar-*m*-**C**), 125.8 ($N_{8'}SO_2Ph$-*o*-**C**), 124.5 (**C**$_{4'}$), 123.8 (**C**$_4$), 122.8 (**C**$_5$), 122.5 (**C**$_{5'}$), 112.2 (**C**$_7$), 111.2 (**C**$_{7'}$), 84.2 (**C**$_{8a'}$), 80.0 (**C**$_{8a}$), 62.0 (**C**$_{3a}$), 60.8 (**C**$_{3a'}$), 52.0 (N_1CO_2**C**H_3), 44.2 (**C**$_2$), 43.2 (**C**$_{2'}$),

	37.2 (**C**$_{3'}$), 37.0 (**C**$_3$), 34.5 (**C**(CH$_3$)$_3$), 30.2 (C(**C**H$_3$)$_3$).
FTIR (thin film) cm^{-1}:	2956 (m), 1713 (s), 1595 (m), 1477 (m), 1447 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{38}H_{41}N_4O_6S_2$ $[M+H]^+$: 713.2462, found: 713.2470.
$[\alpha]_D^{24}$:	–13 (*c* = 0.65 CH_2Cl_2).
TLC (33% ethyl acetate in hexanes), R*f*:	0.13 (UV, CAM).



N1'-Methyl Heterodimer (–)-39:

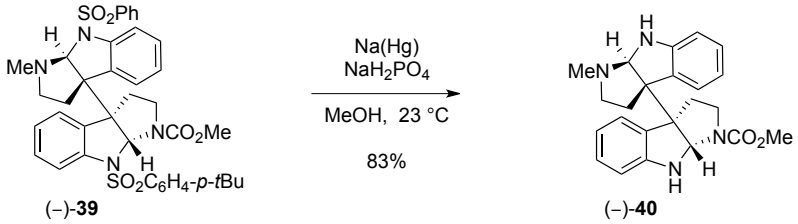
Formalin (37% wt, 1.28 mL, 16.8 mmol, 235 equiv) and sodium cyanoborohydride in tetrahydrofuran (1.0 M, 219 µL, 219 µmol, 3.00 equiv) were added sequentially via syringe to a solution of N1'-H heterodimer (–)-**38** (52.0 mg, 74.4 µmol, 1 equiv) in acetonitrile–acetic acid (10:1, 7.70 mL) at 23 °C. After 30 min, another portion of sodium cyanoborohydride (1.0 M in tetrahydrofuran, 146 µL, 146 µmol, 2.00 equiv) was added via syringe. After an additional 30 min, saturated aqueous sodium bicarbonate solution (10 mL) was added and the resulting mixture was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with brine (15 mL), were dried over anhydrous sodium sulfate, were filtered and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 25→50% ethyl acetate in hexanes) to afford the N1′-methyl heterodimer (–)-**39** (45.0 mg, 84.9%) as a white foam.

As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 7.88 (d, *J* = 8.7 Hz, 2H, N_8SO_2Ar-*o*-**H**), 7.64 (d, *J* = 8.3 Hz, 2H, N_8SO_2Ar-*m*-**H**), 7.56–7.47 (m, 3H, $N_{8'}SO_2Ph$-*p*-**H**, $N_{8'}SO_2Ph$-*o*-**H**), 7.45 (d, *J* = 8.0 Hz, 1H, C_7**H**), 7.38–7.32 (m, 2H, $N_{8'}SO_2Ph$-*m*-**H**), 7.29–7.15 (m, 4H, C_6**H**, $C_{6'}$**H**, $C_{4'}$**H**, $C_{7'}$**H**), 7.02 (app-t, *J* = 7.4 Hz, 1H, $C_{5'}$**H**), 6.59 (br-s, 1H, C_5**H**), 6.52 (s, 1H, C_{8a}**H**), 6.33 (br-s, 1H, C_4**H**), 5.20 (s, 1H, $C_{8a'}$**H**), 3.81 (dd, *J* = 7.7, 11.2 Hz, 1H, C_2**H**$_a$), 3.59 (s, 3H, N_1CO_2C**H**$_3$), 2.77–2.71 (m, 1H, $C_{2'}$**H**$_a$), 2.68 (app-dt, *J* = 5.3, 11.8 Hz, 1H, C_2**H**$_b$), 2.56 (s, 3H, $N_{1'}C$**H**$_3$), 2.40 (app-dt, *J* = 5.0, 10.2 Hz, 1H, $C_{2'}$**H**$_b$), 2.21–2.08 (m, 1H, C_3**H**$_a$), 1.98–1.84 (m, 3H, C_3**H**$_b$ $C_{3'}$**H**$_a$ $C_{3'}$**H**$_b$), 1.33 (s, 9H, C(C**H**$_3$)$_3$).

^{13}C NMR (125.8 MHz, CD_3CN, 70 °C): δ 159.1 (N_8SO_2Ar-*p*-**C**), 156.0 (N_1**C**O_2CH_3), 144.6 (2C **C**$_{7a}$, **C**$_{7a'}$), 141.3 ($N_{8'}SO_2Ph$-*ipso*-**C**), 139.7 (N_8SO_2Ar-*ipso*-**C**), 135.2 (**C**$_{4a'}$), 134.6 ($N_{8'}SO_2Ph$-*p*-**C**), 133.3 (**C**$_{4a}$), 131.2 (**C**$_6$), 131.0 ($N_{8'}SO_2Ph$-*m*-**C**), 130.6 (**C**$_{6'}$), 129.1 ($N_{8'}SO_2Ph$-*o*-**C**), 128.3 (N_8SO_2Ar-*o*-**C**, N_8SO_2Ar-*m*-**C**), 126.7 (2C, **C**$_4$, **C**$_{4'}$), 125.6 (**C**$_5$), 125.3 (**C**$_{5'}$), 115.8 (**C**$_7$), 115.5 (**C**$_{7'}$), 91.2

	(**C**$_{8a'}$), 82.7 (**C**$_{8a}$), 64.7 (**C**$_{3a'}$), 64.3 (**C**$_{3a}$), 54.0 (N$_1$CO$_2$**C**H$_3$), 53.3 (**C**$_{2'}$), 46.7 (**C**$_2$), 39.3 (**C**$_3$), 39.0 (**C**$_{3'}$), 38.8 (N$_{1'}$**C**H$_3$), 36.7 (**C**(CH$_3$)$_3$), 32.1 (C(**C**H$_3$)$_3$).
FTIR (thin film) cm^{-1}:	2956 (m) ,1713 (s), 1595 (m), 1477 (m), 1447 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{39}H_{43}N_4O_6S_2$ $[M+H]^+$: 727.2619, found: 727.2627.
$[\alpha]_D^{24}$:	–15 (*c* = 0.96, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.55 (UV, CAM).



(–)-N1-Carboxymethyl-*meso*-Chimonanthine (40):

Sodium amalgam (5%-Na, 443 mg, 963 μmol, 20.0 equiv)[8] was added to a suspension of sodium phosphate monobasic monohydrate (146 mg, 1.06 mmol, 22.0 equiv) and N1′-methyl heterodimer (–)-**39** (35.0 mg, 49.1 μmol, 1 equiv) in methanol at 23 °C. After 1 h, another portion of sodium phosphate monobasic monohydrate (146 mg, 1.06 mmol, 22.0 equiv) and sodium amalgam (5%-Na, 443 mg, 963 μmol, 20.0 equiv) were added sequentially. After an additional 1 h, sodium phosphate monobasic monohydrate (146 mg, 1.06 mmol, 22.0 equiv) and sodium amalgam (5%-Na, 443 mg, 0.963 mmol, 20.0 equiv) were added. After 1 h, the reaction mixture was diluted with ethyl acetate (20 mL) and was washed with 5% aqueous sodium bicarbonate solution (10 mL). The aqueous layer was separated and extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with brine (10 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: gradient, 5% methanol→9% methanol, 1.0% ammonium hydroxide in chloroform) to afford the heterodimer (–)-N1-carboxymethyl-*meso*-chimonanthine (**40**, 15.5 mg, 82.6%) as a white solid.

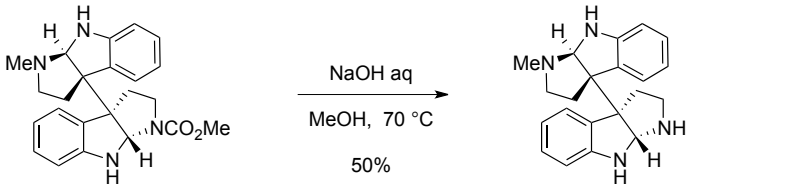
As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 75 °C): δ 7.02 (app-t, J = 7.5 Hz, 1H, C_6**H**), 6.98 (app-t, J = 7.5 Hz, 1H, $C_{6'}$**H**), 6.70–6.58 (m, 2H, C_4**H**, $C_{4'}$**H**), 6.57–6.47 (m, 3H, C_5**H**, $C_{5'}$**H**, C_7**H**), 6.45 (d, J = 8.0 Hz, 1H, $C_{7'}$**H**), 5.35 (br-s, 1H, C_{8a}**H**), 5.03 (br-s, 1H, N_8**H**), 4.56 (s, 2H, $C_{8a'}$**H**, $N_{8'}$**H**), 3.73–3.65 (m, 4H, C_2**H**$_a$, N_1CO_2C**H**$_3$), 2.91 (app-dt, J = 6.4, 10.9 Hz, 1H, C_2**H**$_b$), 2.76–2.67 (m, 1H, $C_{2'}$**H**$_a$), 2.52 (app-dt, J = 8.5, 11.8 Hz, 1H, C_3**H**$_a$), 2.43–2.36 (m, 2H, $C_{2'}$**H**$_b$, $C_{3'}$**H**$_a$), 2.34 (s, 3H, $N_{1'}$C**H**$_3$), 2.28 (dd, J = 6.3, 12.3 Hz, 1H, C_3**H**$_b$), 2.03–1.96 (m, 1H, $C_{3'}$**H**$_b$).

^{13}C NMR (125.8 MHz, CD_3CN, 75 °C): δ 156.7 (N_1**C**O_2CH_3), 154.2 (**C**$_{7a'}$), 152.8 (**C**$_{7a}$), 134.2 (**C**$_{4a'}$), 132.4 (**C**$_{4a'}$), 130.3 (**C**$_6$), 129.8 (**C**$_{6'}$), 126.2 (2C, **C**$_4$, **C**$_{4'}$), 119.8 (**C**$_5$), 119.3 (**C**$_{5'}$), 110.4 (**C**$_7$), 110.1 (**C**$_{7'}$), 85.3 (**C**$_{8a'}$), 79.7 (**C**$_{8a}$), 65.1 (2C, **C**$_{3a}$, **C**$_{3a'}$), 53.9 (**C**$_{2'}$), 53.5 (N_1CO_2**C**H_3), 46.8 (**C**$_2$), 38.6 (**C**$_{3'}$), 36.9 (**C**$_3$), 36.2 ($N_{1'}$**C**H_3).

FTIR (thin film) cm^{-1}:	3372 (br-m), 2955 (m), 1696 (s), 1606 (m), 1451 (s),1386 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{23}H_{27}N_4O_2$ $[M+H]^+$: 391.2129, found: 391.2132.
$[\alpha]_D^{24}$:	–202 (*c* = 0.95, CH_2Cl_2).

TLC (9% methanol, 1% ammonium hydroxide in chloroform), R*f*: 0.40 (UV, CAM).



(–)-**40** (+)-desmethyl-*meso*-chimonanthine (**3**)

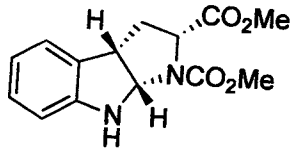
(+)-Desmethyl-*meso*-Chimonanthine (3):

An aqueous solution of sodium hydroxide (5 N, 1.5 mL) was added to solution of (–)-N1-carboxymethyl-*meso*-chimonanthine (**40**, 18.0 mg, 46.1 μmol, 1 equiv) in methanol (3 mL) in a sealed tube at 23 ºC. The reaction vessel was sealed and heated to 70 ºC. After 26 h, the brown mixture was allowed to cool to 23 °C and was extracted with dichloromethane (2 × 20 mL). The combined organic extracts were washed with brine (10 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 4.5% methanol, 0.5% ammonium hydroxide→18% methanol, 2.0% ammonium hydroxide in chloroform) to afford the (+)-desmethyl-*meso*-chimonanthine (**3**, 7.7 mg, 50.4%) as a white solid.

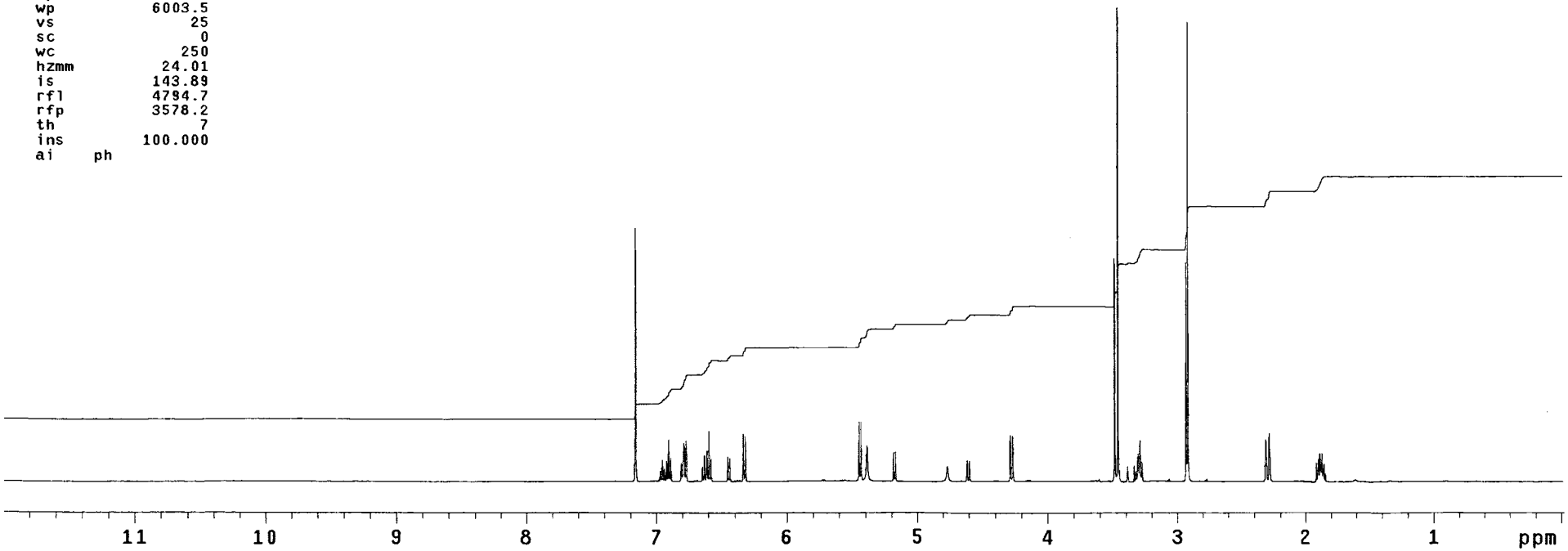
The corresponding enantiomer, (–)-desmethyl-*meso*-chimonanthine (**3**, 16 mg, 91%) was obtained by Red-Al reduction of (–)-N1-carboxymethyl desmethyl-*meso*-chimonanthine (**37**). For full characterization of compound **3**, see pages S67–S72.

$[\alpha]_D^{24}$: +2.7 (c = 0.13, EtOH).[26]
+13.7 (c = 0.13, CH_2Cl_2).

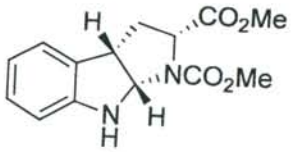
SAMPLE		DEC. & VT	
solvent	Benzene	dfrq	125.672
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
ACQUISITION		dseq	
sfrq	499.746	dres	1.0
tn	H1	homo	n
at	3.001	PROCESSING	
np	63050	wtfile	
sw	10504.2	proc	ft
fb	not used	fn	262144
bs	4	math	f
tpwr	56		
pw	8.6	werr	
d1	2.000	wexp	
tof	1519.5	wbs	
nt	16	wnt	wft
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-11.0		
wp	6003.5		
vs	25		
sc	0		
wc	250		
hzmm	24.01		
is	143.89		
rfl	4794.7		
rfp	3578.2		
th	7		
ins	100.000		
ai	ph		



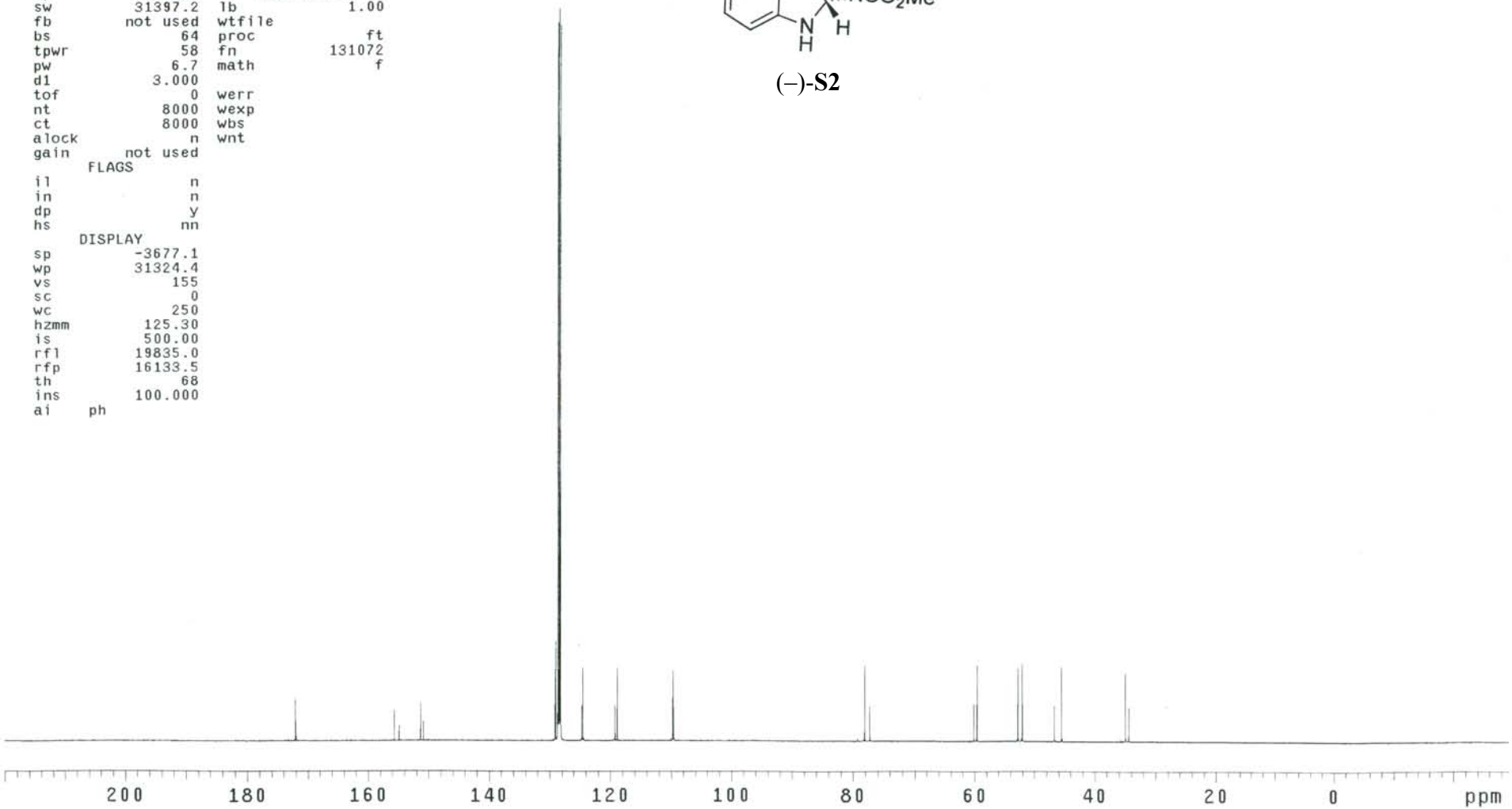
(–)-S2



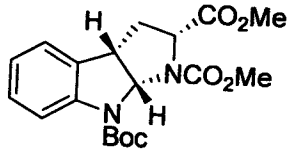
SAMPLE		DEC. & VT	
solvent	Benzene	dfrq	499.744
		dn	H1
		dpwr	34
		dof	0
		dm	yyy
		dmm	w
ACQUISITION		dmf	10000
sfrq	125.672	dseq	
tn	C13	dres	1.0
at	2.000	homo	n
np	125588	PROCESSING	
sw	31397.2	lb	1.00
fb	not used	wtfile	
bs	64	proc	ft
tpwr	58	fn	131072
pw	6.7	math	f
d1	3.000		
tof	0	werr	
nt	8000	wexp	
ct	8000	wbs	
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-3677.1		
wp	31324.4		
vs	155		
sc	0		
wc	250		
hzmm	125.30		
is	500.00		
rfl	19835.0		
rfp	16133.5		
th	68		
ins	100.000		
ai	ph		



(–)-**S2**

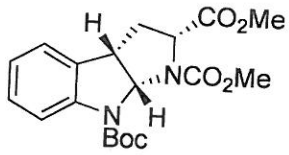


SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
		homo	n
ACQUISITION		PROCESSING	
sfrq	499.748	wtfile	
tn	H1	proc	ft
at	3.001	fn	262144
np	63050	math	f
sw	10504.2		
fb	not used		
bs	4	werr	
tpwr	56	wexp	
pw	8.6	wbs	
d1	2.000	wnt	wft
tof	1519.5		
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-503.6		
wp	6497.4		
vs	7		
sc	0		
wc	250		
hzmm	25.99		
is	201.44		
rfl	2218.8		
rfp	969.5		
th	7		
ins	100.000		
ai	ph		



(+)-**13**

SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	499.747
		dn	H1
		dpwr	34
		dof	0
		dm	yyy
		dmm	w
		dmf	10400
		dseq	
		dres	1.0
		homo	n
ACQUISITION		PROCESSING	
sfrq	125.673	lb	1.00
tn	C13	wtfile	
at	2.000	proc	ft
np	125588	fn	131072
sw	31397.2	math	f
fb	not used		
bs	64		
tpwr	59	werr	
pw	6.7	wexp	
d1	3.000	wbs	
tof	0	wnt	
nt	5000		
ct	4864		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-3598.5		
wp	31247.2		
vs	505		
sc	0		
wc	250		
hzmm	124.99		
is	500.00		
rfl	18538.1		
rfp	14914.7		
th	3		
ins	100.000		
ai	ph		



(+)-**13**

SAMPLE	
solvent	CD3CN

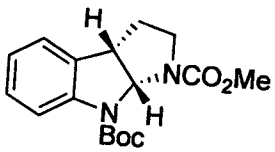
ACQUISITION	
sfrq	499.748
tn	H1
at	3.001
np	63050
sw	10504.2
fb	not used
bs	4
tpwr	56
pw	8.6
d1	2.000
tof	1519.5
nt	16
ct	16
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-509.6
wp	6503.4
vs	7
sc	0
wc	250
hzmm	26.01
is	158.18
rfl	2218.9
rfp	969.5
th	7
ins	100.000
ai	ph

DEC. & VT	
dfrq	125.673
dn	C13
dpwr	30
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n

PROCESSING	
wtfile	
proc	ft
fn	262144
math	f
werr	
wexp	
wbs	
wnt	wft

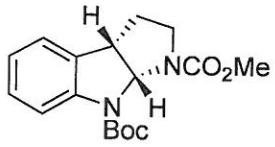


(–)-**14**

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE	
solvent	CD3CN
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	32
ss	1
tpwr	58
pw	6.9
d1	0.763
tof	631.4
nt	10000
ct	10000
alock	n
gain	not used
FLAGS	
il	n
in	n
dp	y
hs	nn
DISPLAY	
sp	-2559.1
wp	30200.3
vs	710
sc	0
wc	250
hzmm	120.80
is	500.00
rfl	21073.8
rfp	14929.2
th	20
ins	1.000
ai	ph

DEC. & VT	
dfrq	500.232
dn	H1
dpwr	39
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	



(–)-**14**

SAMPLE	
solvent	CD3CN

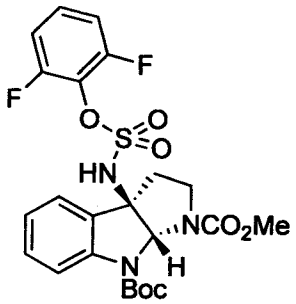
ACQUISITION	
sfrq	499.748
tn	H1
at	3.001
np	63050
sw	10504.2
fb	not used
bs	4
tpwr	56
pw	8.6
d1	2.000
tof	1519.5
nt	16
ct	12
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-500.4
wp	6494.3
vs	10
sc	0
wc	250
hzmm	25.98
is	132.51
rfl	2218.9
rfp	969.5
th	7
ins	100.000
ai	ph

DEC. & VT	
dfrq	125.673
dn	C13
dpwr	30
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n

PROCESSING	
wtfile	
proc	ft
fn	262144
math	f
werr	
wexp	
wbs	
wnt	wft



(–)-**15**

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE	
solvent	CD3CN

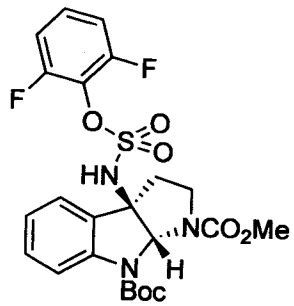
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	64
ss	1
tpwr	59
pw	6.9
d1	0.763
tof	631.4
nt	30000
ct	17216
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-2536.1
wp	30253.3
vs	161
sc	0
wc	250
hzmm	121.01
is	500.00
rfl	21075.0
rfp	14929.2
th	20
ins	1.000
ai	ph

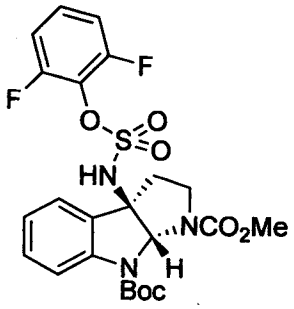
DEC. & VT	
dfrq	500.232
dn	H1
dpwr	38
dof	-500.0
dm	y
dmm	w
dmf	10700
dseq	
dres	1.0
homo	n

PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	

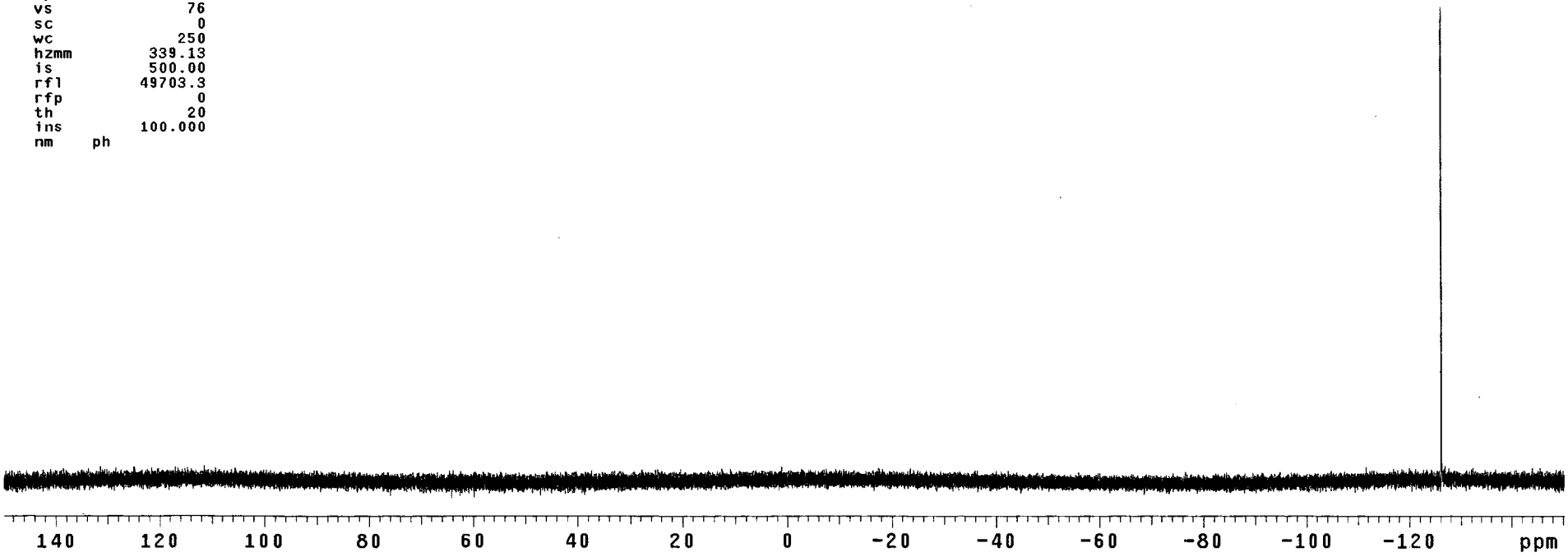


(–)-**15**

SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	300.109
		dn	H1
		dpwr	30
		dof	0
		dm	nnn
		dmm	c
ACQUISITION		dmf	200
sfrq	282.383	PROCESSING	
tn	F19	lb	0.30
at	0.300	wtfile	
np	59906	proc	ft
sw	100000.0	fn	262144
fb	55000		
bs	8	werr	
tpwr	56	wexp	
pw	11.0	wbs	
d1	4.000	wnt	
tof	29637.2		
nt	64		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-42485.9		
wp	84781.6		
vs	76		
sc	0		
wc	250		
hzmm	339.13		
is	500.00		
rfl	49703.3		
rfp	0		
th	20		
ins	100.000		
nm	ph		



(–)-**15**



SAMPLE	
solvent	CD3CN

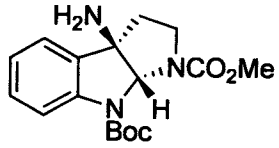
ACQUISITION	
sfrq	499.748
tn	H1
at	3.001
np	63050
sw	10504.2
fb	not used
bs	4
tpwr	56
pw	8.6
d1	2.000
tof	1519.5
nt	16
ct	16
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-518.7
wp	6521.7
vs	11
sc	0
wc	250
hzmm	26.09
is	113.83
rfl	2218.9
rfp	969.5
th	7
ins	100.000
ai	ph

DEC. & VT	
dfrq	125.673
dn	C13
dpwr	30
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n

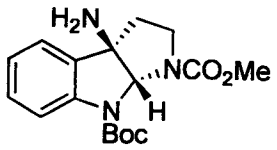
PROCESSING	
wtfile	
proc	ft
fn	262144
math	f
werr	
wexp	
wbs	
wnt	wft



(–)-**16**

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

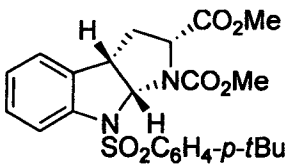
SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	500.232
		dn	H1
		dpwr	39
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
		homo	n
ACQUISITION		PROCESSING	
sfrq	125.795	lb	0.30
tn	C13	wtfile	
at	1.736	proc	ft
np	131010	fn	131072
sw	37735.8	math	f
fb	not used		
bs	32		
ss	1	werr	
tpwr	58	wexp	
pw	6.9	wbs	
d1	0.763	wnt	
tof	631.4		
nt	20000		
ct	6432		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2501.0		
wp	30188.2		
vs	361		
sc	0		
wc	250		
hzmm	120.75		
is	500.00		
rfl	21072.7		
rfp	14929.2		
th	20		
ins	1.000		
ai	ph		



(–)-16

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.748	temp	70.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	4		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-502.4		
wp	6497.4		
vs	12		
sc	0		
wc	250		
hzmm	25.99		
is	223.88		
rfl	2217.6		
rfp	969.5		
th	7		
ins	1.000		
ai	ph		



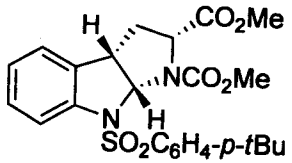
(–)-**17**

SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	500.232
		dn	H1
		dpwr	38
		dof	-500.0
		dm	y
		dmm	w
		dmf	10700
		dseq	
		dres	1.0
		homo	n
		temp	70.0
		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	16
ss	1
tpwr	59
pw	6.9
d1	0.763
tof	631.4
nt	10000
ct	2912
alock	n
gain	not used

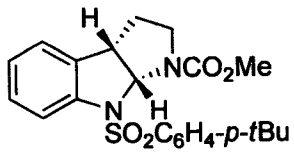
FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-2522.3
wp	30199.7
vs	333
sc	0
wc	250
hzmm	120.80
is	500.00
rfl	21013.4
rfp	14929.1
th	20
ins	1.000
ai	ph



(–)-17

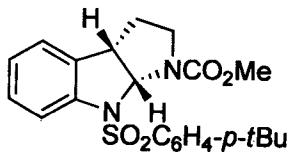
SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.748	temp	70.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	4		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-502.5		
wp	6497.4		
vs	10		
sc	0		
wc	250		
hzmm	25.99		
is	137.28		
rfl	2217.7		
rfp	969.5		
th	7		
ins	1.000		
ai	ph		



(–)-**18**

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	500.232
		dn	H1
		dpwr	38
		dof	-500.0
		dm	y
		dmm	w
		dmf	10700
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	125.795	temp	70.0
tn	C13	PROCESSING	
at	1.736	lb	0.30
np	131010	wtfile	
sw	37735.8	proc	ft
fb	not used	fn	131072
bs	16	math	f
ss	1		
tpwr	59	werr	
pw	6.9	wexp	
d1	0.763	wbs	
tof	631.4	wnt	
nt	10000		
ct	1856		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2553.4		
wp	30264.2		
vs	126		
sc	0		
wc	250		
hzmm	121.06		
is	500.00		
rfl	21012.2		
rfp	14929.1		
th	20		
ins	1.000		
ai ph			



(–)-**18**

SAMPLE	
solvent	CDCl3

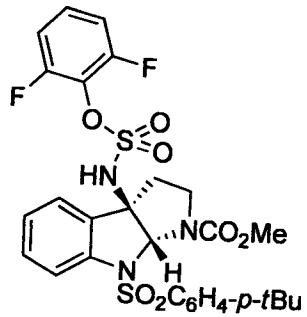
ACQUISITION	
sfrq	499.746
tn	H1
at	3.001
np	63050
sw	10504.2
fb	not used
bs	4
tpwr	56
pw	8.6
d1	2.000
tof	1519.5
nt	16
ct	16
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-508.0
wp	6494.3
vs	17
sc	0
wc	250
hzmm	25.98
is	268.59
rfl	4866.0
rfp	3618.1
th	7
ins	100.000
ai	ph

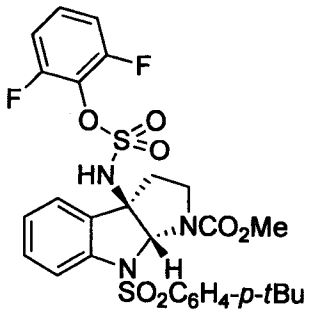
DEC. & VT	
dfrq	125.672
dn	C13
dpwr	30
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n

PROCESSING	
wtfile	
proc	ft
fn	262144
math	f
werr	
wexp	
wbs	
wnt	wft



(–)-**19**

SAMPLE		DEC. & VT	
solvent	CDCl3	dfrq	500.229
		dn	H1
		dpwr	38
		dof	-500.0
		dm	y
		dmm	w
		dmf	10700
		dseq	
		dres	1.0
		homo	n
ACQUISITION		PROCESSING	
sfrq	125.795	lb	0.30
tn	C13	wtfile	
at	1.736	proc	ft
np	131010	fn	131072
sw	37735.8	math	f
fb	not used		
bs	16		
ss	1	werr	
tpwr	59	wexp	
pw	6.9	wbs	
d1	0.763	wnt	
tof	631.4		
nt	20000		
ct	6512		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2549.9		
wp	30220.5		
vs	222		
sc	0		
wc	250		
hzmm	120.88		
is	500.00		
rfl	16005.0		
rfp	9714.2		
th	20		
ins	1.000		
ai	ph		



(–)-**19**

SAMPLE	
solvent	CDCl3

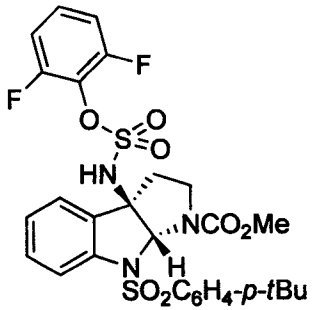
ACQUISITION	
sfrq	282.382
tn	F19
at	0.300
np	59906
sw	100000.0
fb	55000
bs	4
tpwr	56
pw	11.0
d1	4.000
tof	29637.2
nt	32
ct	16
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y

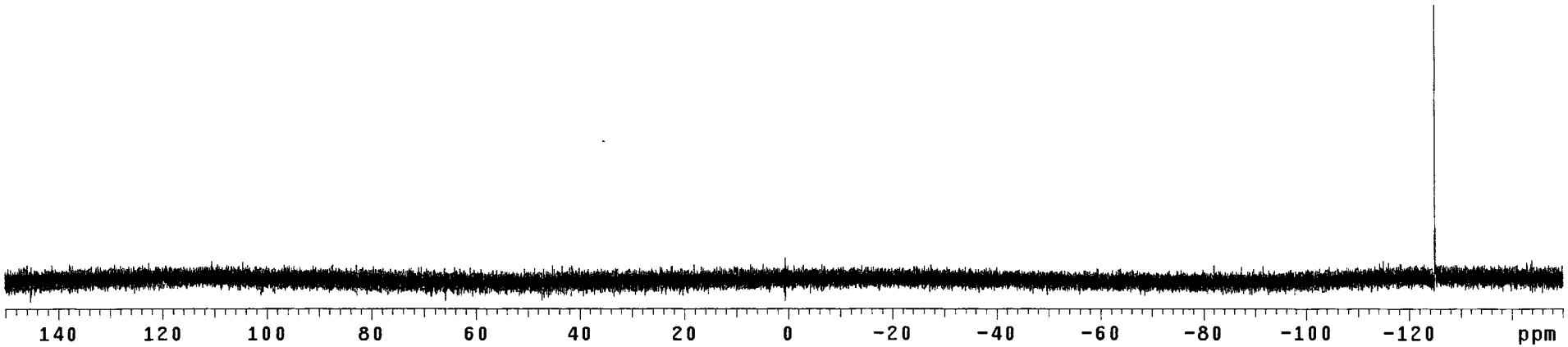
DISPLAY	
sp	-42384.3
wp	84781.6
vs	43
sc	0
wc	250
hzmm	339.13
is	500.00
rfl	49862.6
rfp	0
th	47
ins	100.000
nm	ph

DEC. & VT	
dfrq	300.107
dn	H1
dpwr	30
dof	0
dm	nnn
dmm	c
dmf	200

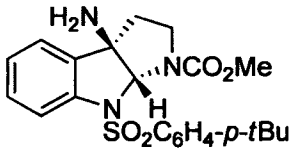
PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	262144
werr	
wexp	
wbs	
wnt	



(–)-**19**



SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.748	temp	70.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	4		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-509.2		
wp	6503.4		
vs	27		
sc	0		
wc	250		
hzmm	26.01		
is	115.71		
rfl	2218.5		
rfp	969.5		
th	7		
ins	100.000		
ai	ph		



(–)-**20**

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE	
solvent	CD3CN

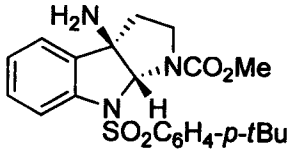
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	64
ss	1
tpwr	58
pw	6.9
d1	0.763
tof	631.4
nt	25000
ct	16896
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

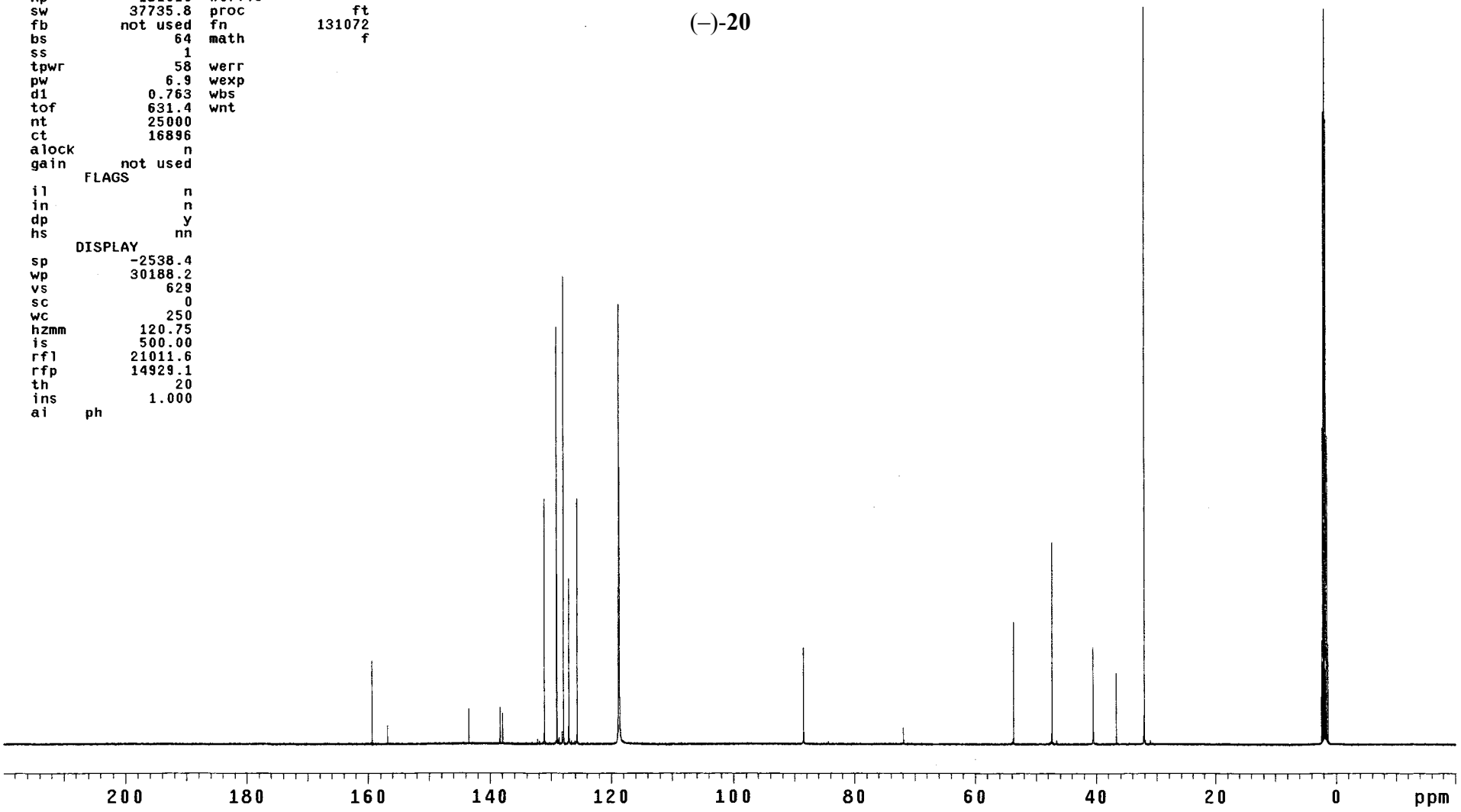
DISPLAY	
sp	-2538.4
wp	30188.2
vs	629
sc	0
wc	250
hzmm	120.75
is	500.00
rfl	21011.6
rfp	14929.1
th	20
ins	1.000
ai	ph

DEC. & VT	
dfrq	500.232
dn	H1
dpwr	39
dof	-500.0
dm	y
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
temp	70.0

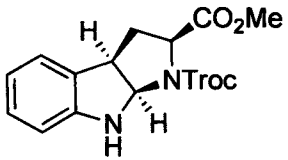
PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



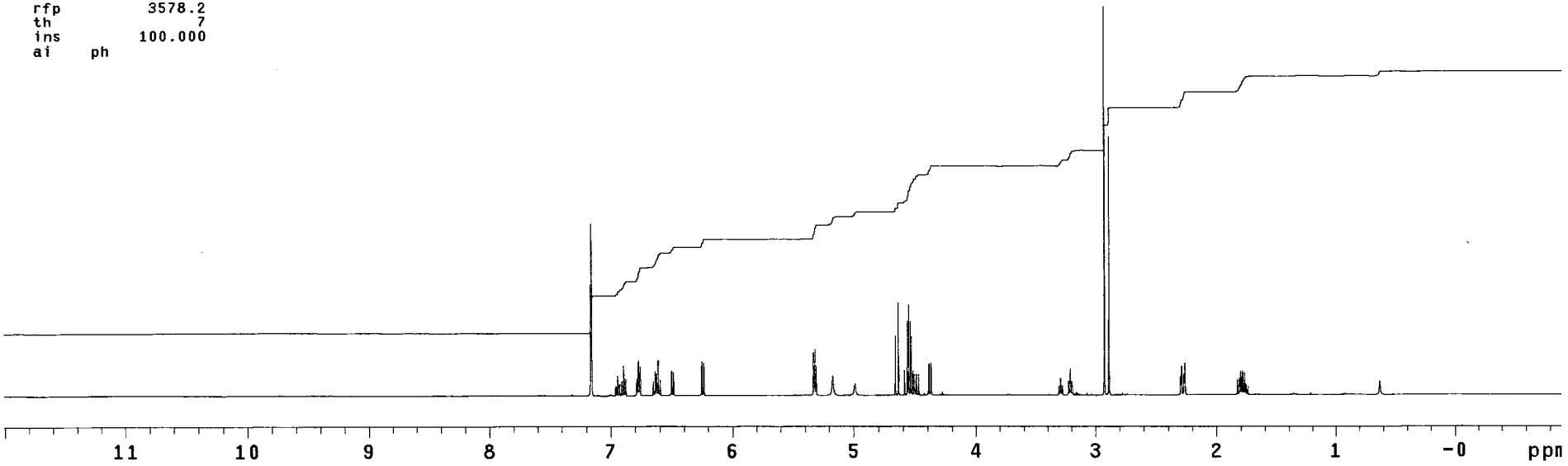
(–)-**20**



SAMPLE		DEC. & VT	
solvent	Benzene	dfrq	125.672
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
ACQUISITION		dmf	10000
sfrq	499.746	dseq	
tn	H1	dres	1.0
at	3.001	homo	n
np	63050	PROCESSING	
sw	10504.2	wtfile	
fb	not used	proc	ft
bs	4	fn	262144
tpwr	56	math	f
pw	8.6		
d1	2.000	werr	
tof	1519.5	wexp	
nt	16	wbs	
ct	16	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-501.3		
wp	6501.7		
vs	17		
sc	0		
wc	250		
hzmm	26.01		
is	141.88		
rfl	4794.8		
rfp	3578.2		
th	7		
ins	100.000		
ai	ph		

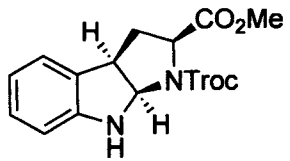


(+)-**S4**



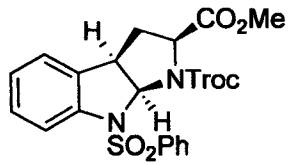
Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE		DEC. & VT	
solvent	Benzene	dfrq	500.229
		dn	H1
		dpwr	39
		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	32	proc	ft
ss	1	fn	131072
tpwr	58	math	f
pw	6.9		
d1	0.763	werr	
tof	631.4	wexp	
nt	10000	wbs	
ct	6496	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2528.7		
wp	30199.7		
vs	853		
sc	0		
wc	250		
hzmm	120.80		
is	500.00		
rfl	22374.0		
rfp	16149.2		
th	20		
ins	1.000		
ai	ph		



(+)-**S4**

SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.748	temp	70.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	4		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	32		
ct	12		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-510.2		
wp	6497.4		
vs	63		
sc	0		
wc	250		
hzmm	25.99		
is	206.92		
rfl	2217.2		
rfp	969.5		
th	7		
ins	1.000		
ai	ph		



(+)-**21**

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE	
solvent	CD3CN

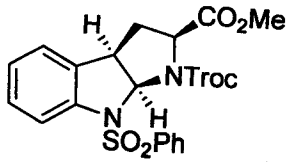
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	16
ss	1
tpwr	59
pw	6.9
d1	0.763
tof	631.4
nt	10000
ct	2384
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-2543.9
wp	30229.1
vs	232
sc	0
wc	250
hzmm	120.92
is	500.00
rfl	21012.0
rfp	14876.8
th	2
ins	1.000
ai	ph

DEC. & VT	
dfrq	500.232
dn	H1
dpwr	38
dof	-500.0
dm	y
dmm	w
dmf	10700
dseq	
dres	1.0
homo	n
temp	70.0

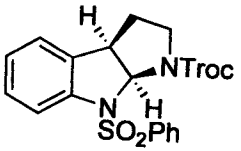
PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



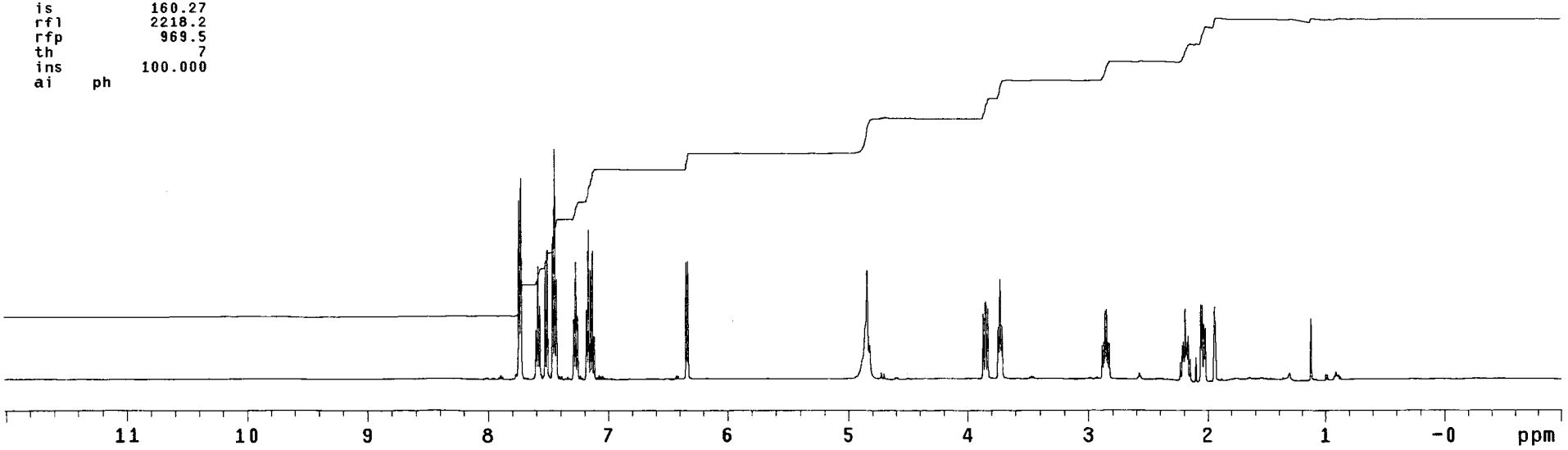
(+)-**21**

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

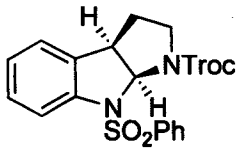
SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.748	temp	70.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	4		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-503.1		
wp	6505.7		
vs	55		
sc	0		
wc	250		
hzmm	26.02		
is	160.27		
rfl	2218.2		
rfp	969.5		
th	7		
ins	100.000		
ai	ph		



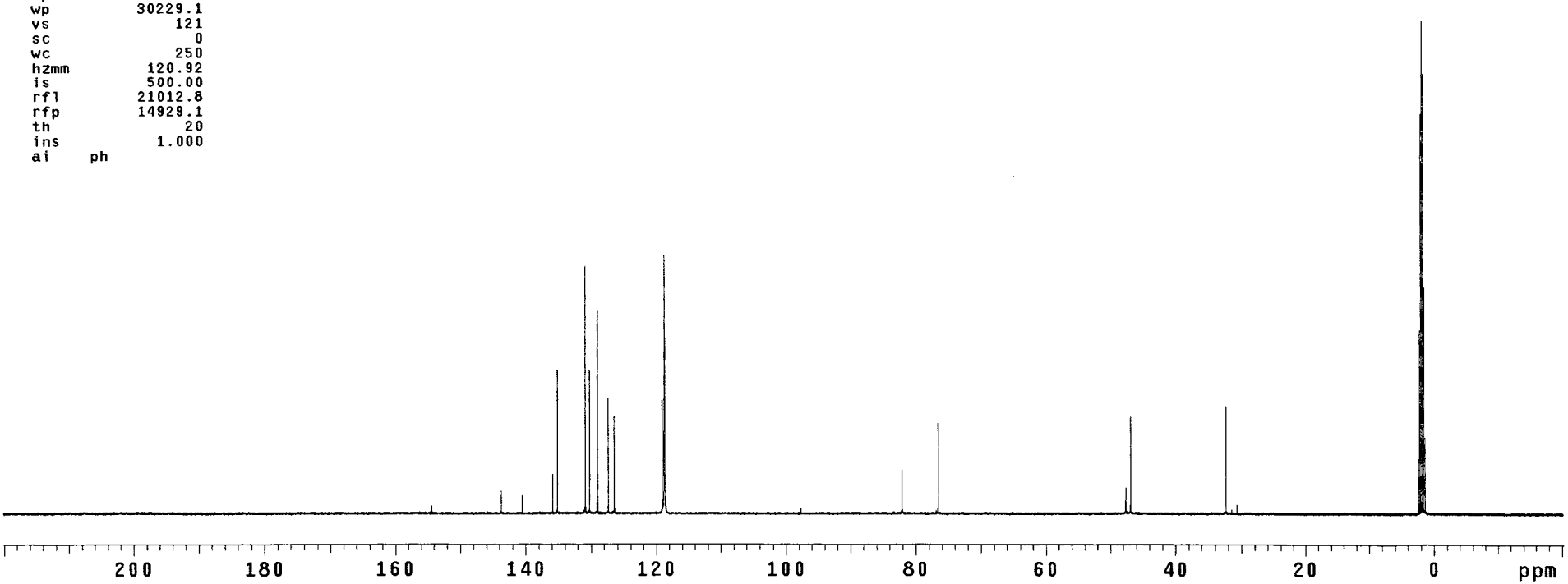
(+)-22



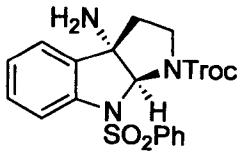
SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	500.232
		dn	H1
		dpwr	38
		dof	-500.0
		dm	y
		dmm	w
		dmf	10700
		dseq	
		dres	1.0
		homo	n
ACQUISITION		temp	70.0
sfrq	125.795	PROCESSING	
tn	C13	lb	0.30
at	1.736	wtfile	
np	131010	proc	ft
sw	37735.8	fn	131072
fb	not used	math	f
bs	16		
ss	1	werr	
tpwr	59	wexp	
pw	6.9	wbs	
d1	0.763	wnt	
tof	631.4		
nt	20000		
ct	3264		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2551.1		
wp	30229.1		
vs	121		
sc	0		
wc	250		
hzmm	120.92		
is	500.00		
rfl	21012.8		
rfp	14929.1		
th	20		
ins	1.000		
ai	ph		



(+)-**22**



SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.748	temp	70.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	4		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-518.1		
wp	6494.3		
vs	98		
sc	0		
wc	250		
hzmm	25.98		
is	186.52		
rfl	2218.3		
rfp	969.5		
th	7		
ins	100.000		
ai	ph		



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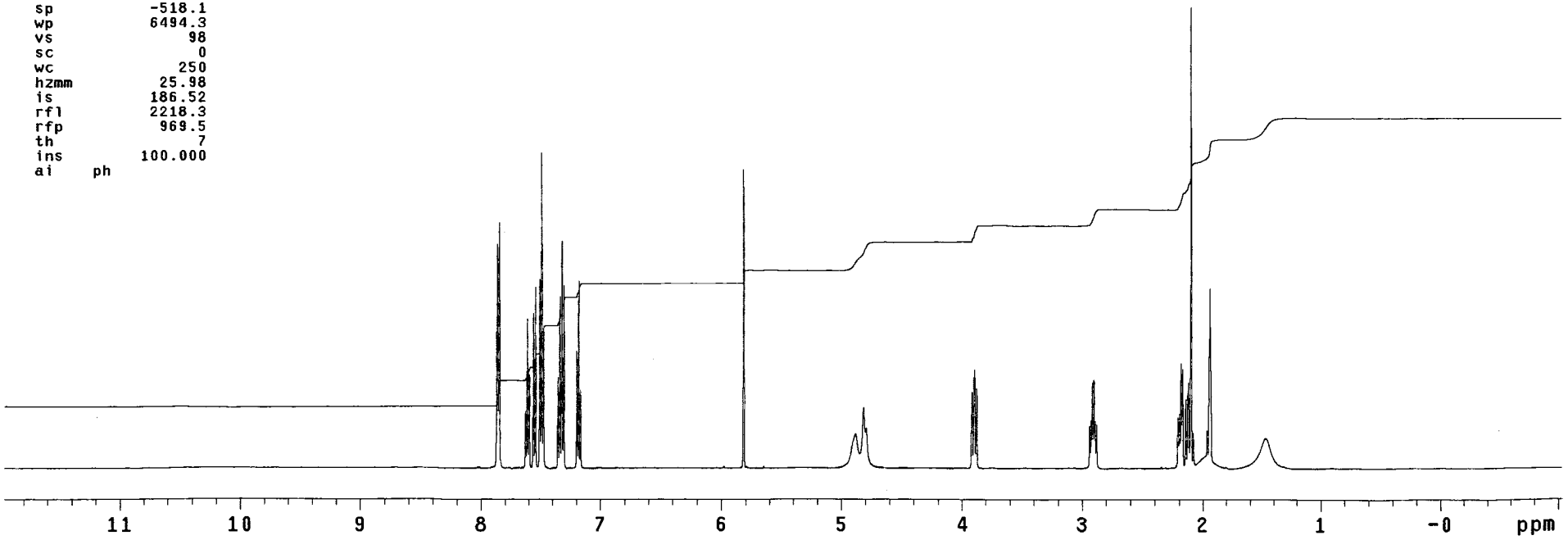
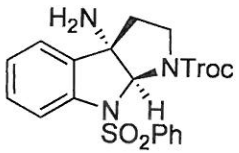


SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	500.232
		dn	H1
		dpwr	39
		dof	-500.0
		dm	y
		dmm	w
ACQUISITION		dmf	10000
sfrq	125.795	dseq	
tn	C13	dres	1.0
at	1.736	homo	n
np	131010	temp	70.0
sw	37735.8	PROCESSING	
fb	not used	lb	0.30
bs	64	wtfile	
ss	1	proc	ft
tpwr	58	fn	131072
pw	6.9	math	f
d1	0.763		
tof	631.4	werr	
nt	20000	wexp	
ct	19904	wbs	
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2556.0		
wp	30230.3		
vs	602		
sc	0		
wc	250		
hzmm	120.92		
is	500.00		
rfl	21011.4		
rfp	14930.9		
th	20		
ins	1.000		
ai	ph		



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SAMPLE	
solvent	Benzene

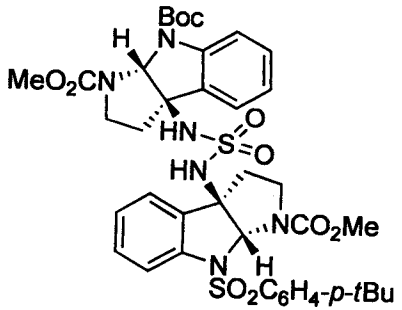
ACQUISITION	
sfrq	499.746
tn	H1
at	3.001
np	63050
sw	10504.2
fb	not used
bs	4
tpwr	56
pw	8.6
d1	2.000
tof	1519.5
nt	16
ct	16
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-502.9
wp	6494.3
vs	77
sc	0
wc	250
hzmm	25.98
is	167.69
rfl	4793.6
rfp	3578.2
th	7
ins	100.000
ai	ph

DEC. & VT	
dfrq	125.672
dn	C13
dpwr	30
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
temp	70.0

PROCESSING	
wtfile	
proc	ft
fn	262144
math	f
werr	
wexp	
wbs	
wnt	wft



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Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE	
solvent	Benzene

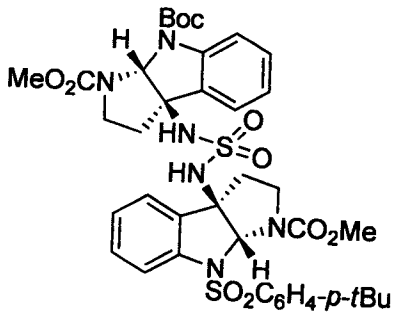
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	32
ss	1
tpwr	58
pw	6.9
d1	0.763
tof	631.4
nt	20000
ct	6560
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-2533.9
wp	30188.2
vs	1147
sc	0
wc	250
hzmm	120.75
is	500.00
rfl	22358.4
rfp	16149.2
th	20
ins	1.000
ai	ph

DEC. & VT	
dfrq	500.229
dn	H1
dpwr	39
dof	-500.0
dm	y
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
temp	70.0

PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



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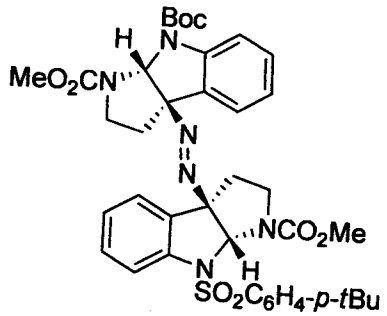
SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
		homo	n
ACQUISITION		temp	50.0
sfrq	499.748	PROCESSING	
tn	H1	wtfile	
at	3.001	proc	ft
np	63050	fn	262144
sw	10504.2	math	f
fb	not used		
bs	4		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-497.5		
wp	6505.0		
vs	32		
sc	0		
wc	250		
hzmm	26.02		
is	173.97		
rfl	2218.0		
rfp	969.5		
th	7		
ins	100.000		
ai ph			



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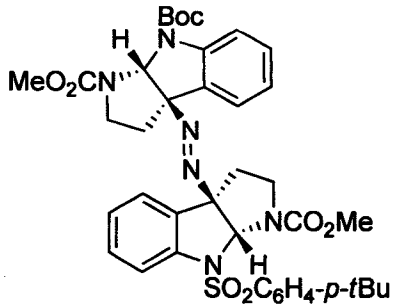
Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	500.232
		dn	H1
		dpwr	39
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	125.795	temp	50.0
tn	C13	PROCESSING	
at	1.736	lb	0.30
np	131010	wtfile	
sw	37735.8	proc	ft
fb	not used	fn	131072
bs	64	math	f
ss	1		
tpwr	58	werr	
pw	6.9	wexp	
d1	0.763	wbs	
tof	631.4	wnt	
nt	25000		
ct	20352		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2500.4		
wp	30175.6		
vs	251		
sc	0		
wc	250		
hzmm	120.70		
is	500.00		
rfl	21037.0		
rfp	14929.1		
th	20		
ins	1.000		
ai ph			



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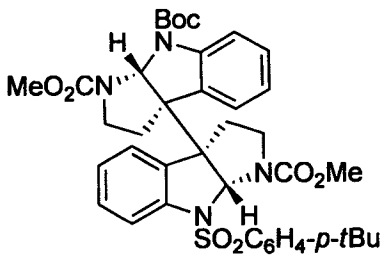
SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.748	temp	75.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	4		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-515.4		
wp	6522.5		
vs	70		
sc	0		
wc	250		
hzmm	26.09		
is	188.01		
rfl	2218.5		
rfp	969.5		
th	7		
ins	100.000		
ai	ph		



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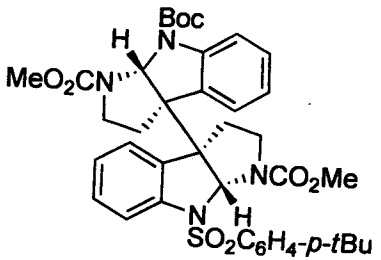
SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	500.232
		dn	H1
		dpwr	39
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
		homo	n
ACQUISITION		temp	70.0
sfrq	125.795	PROCESSING	
tn	C13	lb	0.30
at	1.736	wtfile	
np	131010	proc	ft
sw	37735.8	fb	not used
fn	131072	bs	64
math	f	ss	1
		tpwr	58
werr		pw	6.9
wexp		d1	0.763
wbs		tof	631.4
wnt		nt	25000
		ct	17728
		alock	n
		gain	not used
		FLAGS	
		il	n
		in	n
		dp	y
		hs	nn
		DISPLAY	
		sp	-2505.0
		wp	30143.9
		vs	840
		sc	0
		wc	250
		hzmm	120.58
		is	500.00
		rfl	21010.5
		rfp	14929.1
		th	20
		ins	1.000
		ai	ph



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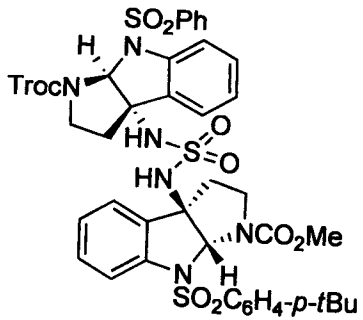
SAMPLE		DEC. & VT	
solvent	Benzene	dfrq	125.672
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.746	temp	70.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	4		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-512.5		
wp	6512.6		
vs	25		
sc	0		
wc	250		
hzmm	26.05		
is	156.68		
rfl	4793.9		
rfp	3578.2		
th	7		
ins	100.000		
ai	ph		



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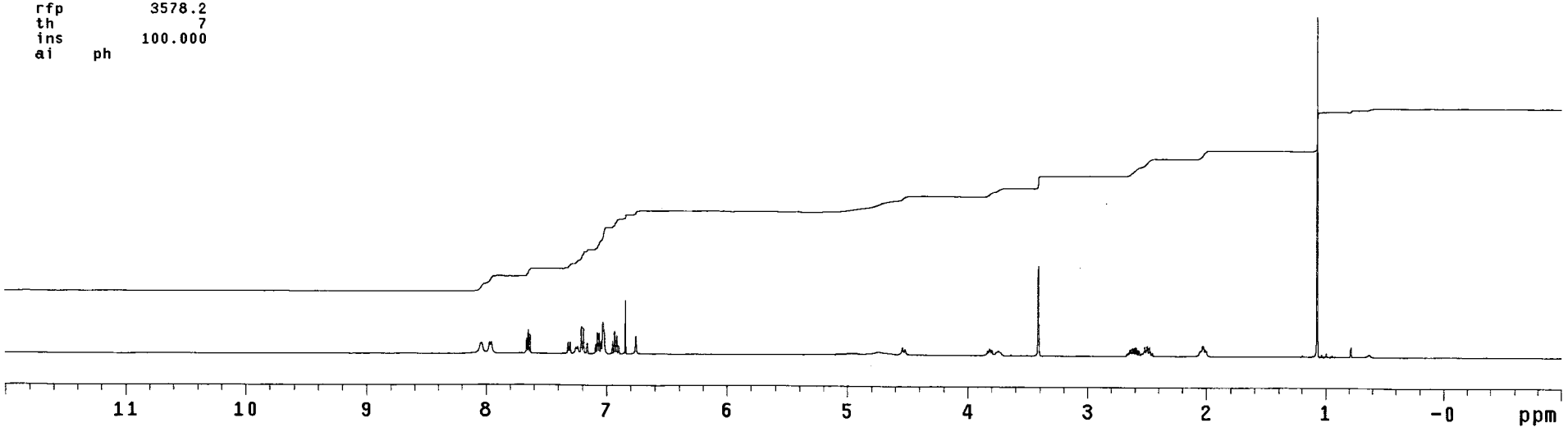


SAMPLE	
solvent	Benzene

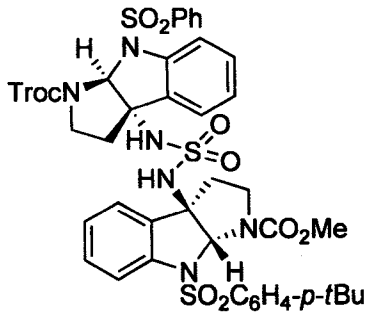
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	32
ss	1
tpwr	58
pw	6.9
d1	0.763
tof	631.4
nt	20000
ct	6784
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-2533.9
wp	30220.5
vs	560
sc	0
wc	250
hzmm	120.88
is	500.00
rfl	22358.4
rfp	16149.2
th	20
ins	1.000
ai	ph

DEC. & VT	
dfrq	500.229
dn	H1
dpwr	39
dof	-500.0
dm	y
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
temp	70.0

PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



(+)-**28**

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE	
solvent	CD3CN

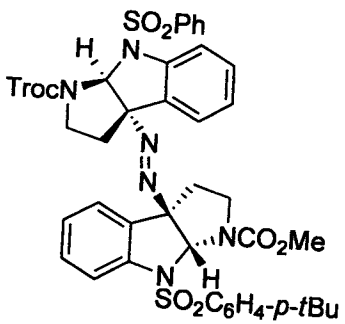
ACQUISITION	
sfrq	499.748
tn	H1
at	3.001
np	63050
sw	10504.2
fb	not used
bs	8
tpwr	56
pw	8.6
d1	2.000
tof	1519.5
nt	32
ct	16
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-499.2
wp	6485.1
vs	20
sc	0
wc	250
hzmm	25.94
is	164.51
rfl	2217.7
rfp	969.5
th	7
ins	100.000
ai	ph

DEC. & VT	
dfrq	125.673
dn	C13
dpwr	30
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
temp	70.0

PROCESSING	
wtfile	
proc	ft
fn	262144
math	f
werr	
wexp	
wbs	
wnt	wft



(+)-**29**

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE	
solvent	CD3CN

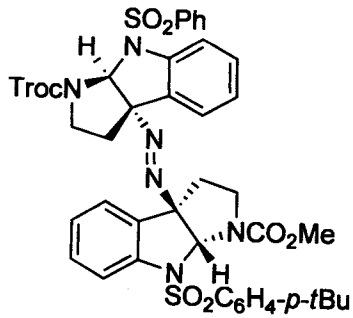
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	32
ss	1
tpwr	59
pw	6.9
d1	0.763
tof	631.4
nt	20000
ct	19200
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-2540.2
wp	30220.5
vs	290
sc	0
wc	250
hzmm	120.88
is	500.00
rfl	21013.4
rfp	14929.1
th	3
ins	1.000
ai	ph

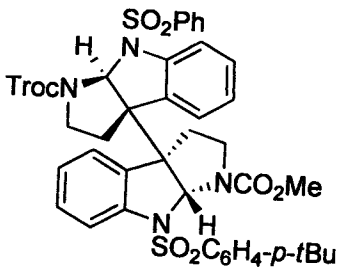
DEC. & VT	
dfrq	500.232
dn	H1
dpwr	38
dof	-500.0
dm	y
dmm	w
dmf	10700
dseq	
dres	1.0
homo	n
temp	70.0

PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



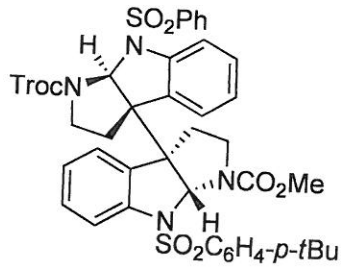
(+)-**29**

SAMPLE		DEC. & VT	
solvent	DMSO	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.748	temp	100.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	4		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-512.5		
wp	6505.0		
vs	46		
sc	0		
wc	250		
hzmm	26.02		
is	167.87		
rfl	2478.0		
rfp	1249.4		
th	7		
ins	100.000		
ai	ph		



(+)-**30**

SAMPLE		DEC. & VT	
solvent	DMSO	dfrq	500.232
		dn	H1
		dpwr	38
		dof	-500.0
		dm	y
		dmm	w
		dmf	10700
		dseq	
		dres	1.0
		homo	n
ACQUISITION		temp	100.0
sfrq	125.795	PROCESSING	
tn	C13	lb	0.30
at	1.736	wtfile	
np	131010	proc	ft
sw	37735.8	fn	131072
fb	not used	math	f
bs	32		
ss	1	werr	
tpwr	59	wexp	
pw	6.9	wbs	
d1	0.763	wnt	
tof	631.4		
nt	30000		
ct	17888		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2533.0		
wp	30211.8		
vs	1060		
sc	0		
wc	250		
hzmm	120.85		
is	500.00		
rfl	11414.2		
rfp	4969.7		
th	20		
ins	1.000		
ai	ph		



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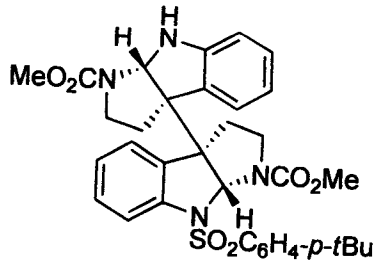
SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.748	temp	70.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	8		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	32		
ct	24		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-515.8		
wp	6500.6		
vs	55		
sc	0		
wc	250		
hzmm	26.00		
is	171.22		
rfl	2218.7		
rfp	969.5		
th	7		
ins	100.000		
ai ph			



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Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE	
solvent	CD3CN

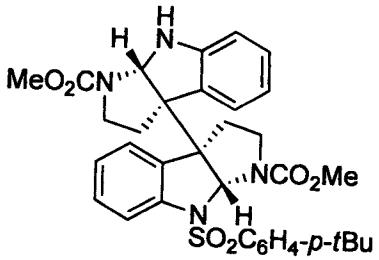
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	32
ss	1
tpwr	58
pw	6.9
d1	0.763
tof	631.4
nt	20000
ct	10528
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-2593.1
wp	30294.7
vs	193
sc	0
wc	250
hzmm	121.18
is	500.00
rfl	21011.1
rfp	14929.1
th	20
ins	1.000
ai	ph

DEC. & VT	
dfrq	500.232
dn	H1
dpwr	39
dof	-500.0
dm	y
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
temp	70.0

PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



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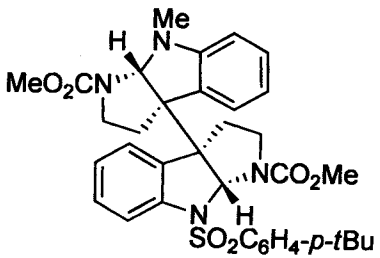
SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.748	temp	70.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	4		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-496.1		
wp	6490.7		
vs	75		
sc	0		
wc	250		
hzmm	25.96		
is	142.12		
rfl	2218.8		
rfp	969.5		
th	7		
ins	100.000		
ai	ph		



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SAMPLE	
solvent	CD3CN

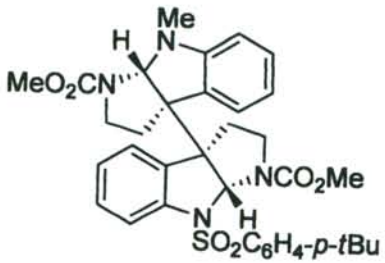
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	64
ss	1
tpwr	58
pw	6.9
d1	0.763
tof	631.4
nt	20000
ct	18880
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-2560.9
wp	30234.3
vs	801
sc	0
wc	250
hzmm	120.94
is	500.00
rfl	21010.5
rfp	14929.1
th	20
ins	1.000
ai	ph

DEC. & VT	
dfrq	500.232
dn	H1
dpwr	39
dof	-500.0
dm	y
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
temp	70.0

PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



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SAMPLE	
solvent	CD3CN

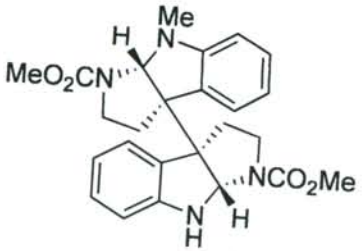
ACQUISITION	
sfrq	499.748
tn	H1
at	3.001
np	63050
sw	10504.2
fb	not used
bs	4
tpwr	56
pw	8.6
d1	2.000
tof	1519.5
nt	16
ct	16
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-498.0
wp	6492.9
vs	45
sc	0
wc	250
hzmm	25.97
is	152.95
rfl	2218.5
rfp	969.5
th	7
ins	100.000
ai	ph

DEC. & VT	
dfrq	125.673
dn	C13
dpwr	30
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
temp	70.0

PROCESSING	
wtfile	
proc	ft
fn	262144
math	f
werr	
wexp	
wbs	
wnt	wft



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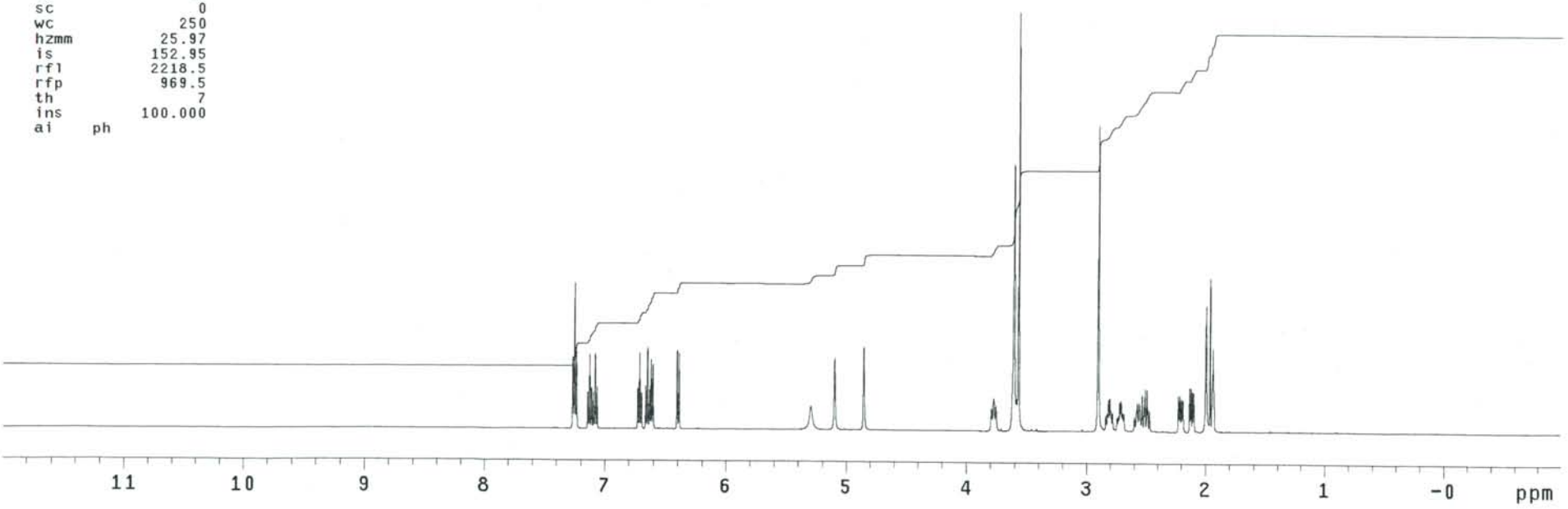
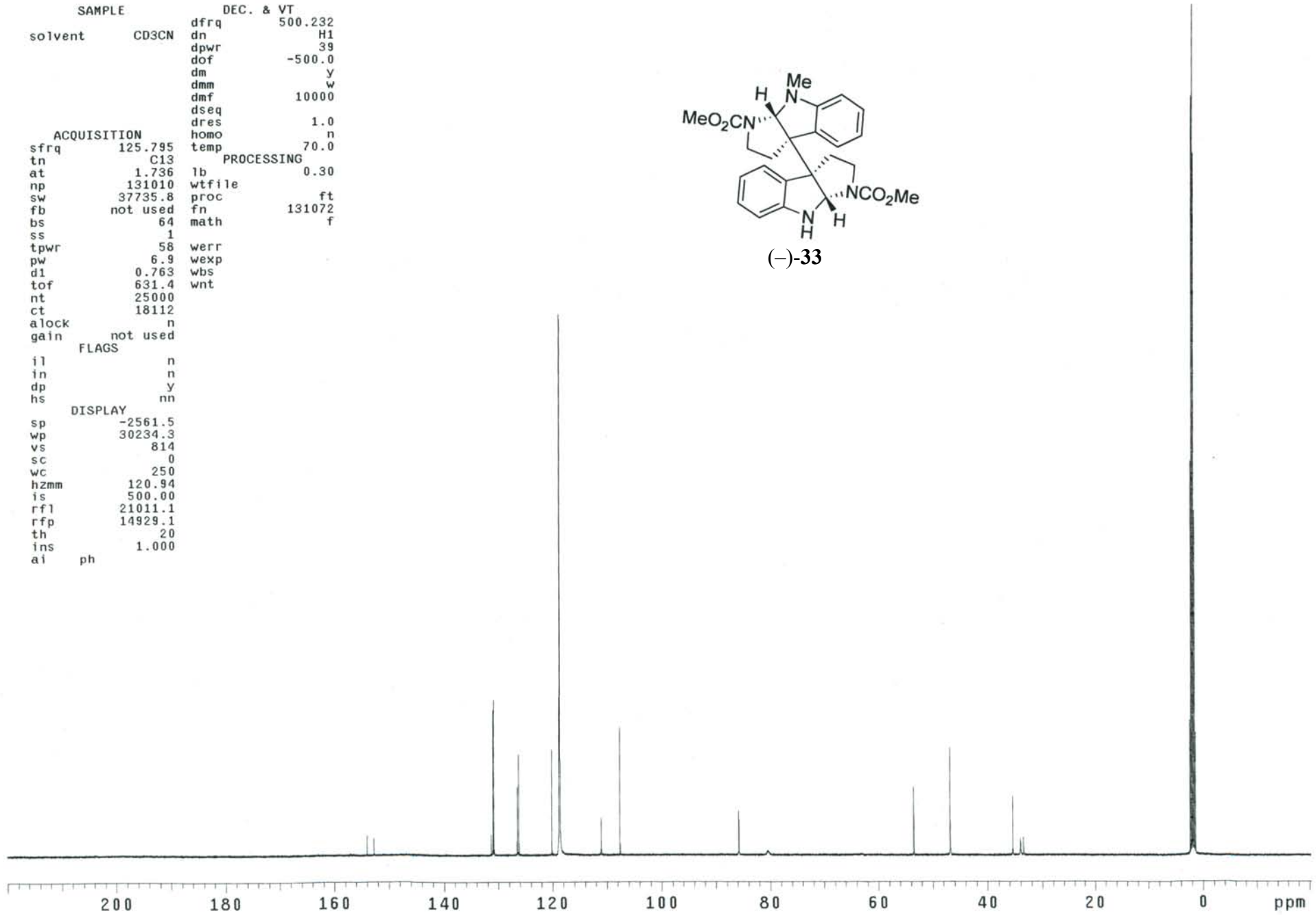
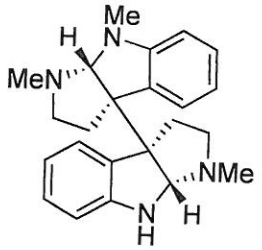


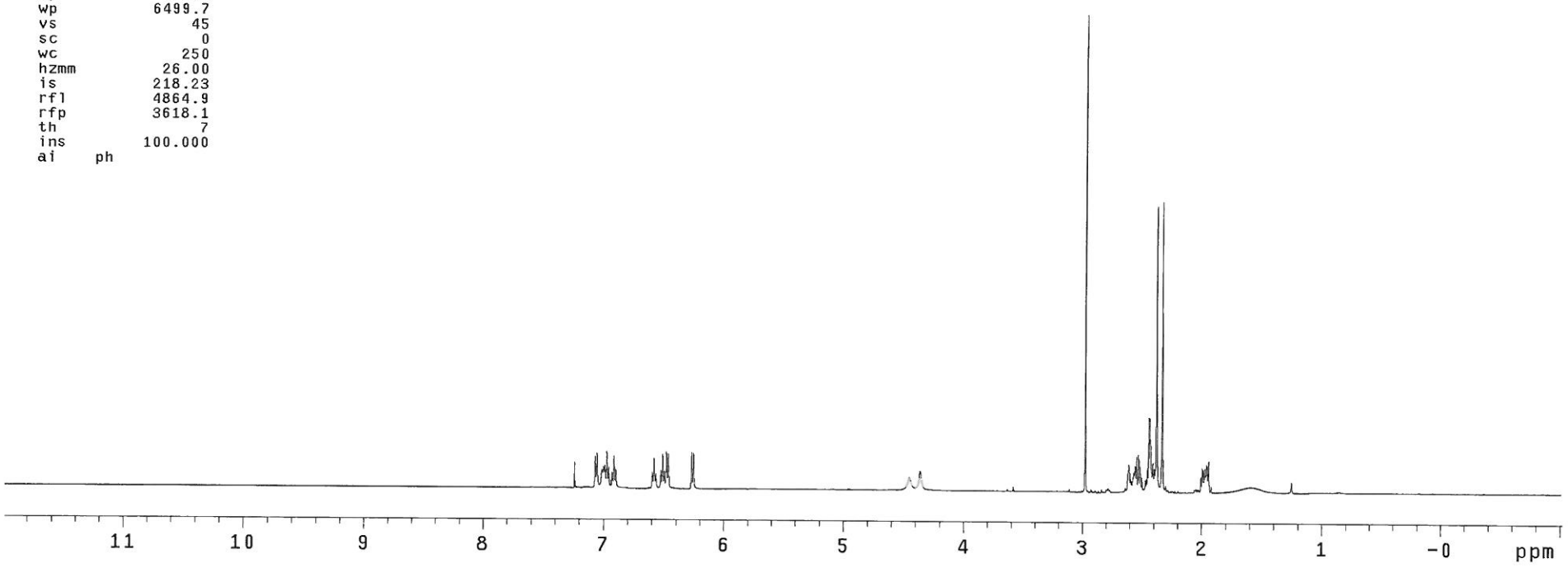

SAMPLE
solvent CD3CN
ACQUISITION
sfrq 125.795
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 64
ss 1
tpwr 58
pw 6.9
d1 0.763
tof 631.4
nt 25000
ct 18112
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2561.5
wp 30234.3
vs 814
sc 0
wc 250
hzmm 120.94
is 500.00
rfl 21011.1
rfp 14929.1
th 20
ins 1.000
ai ph
DEC. & VT
dfrq 500.232
dn H1
dpwr 39
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 70.0
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
N
H
MeO2CN
NCO2Me
N
H
H
200
180
160
140
120
100
80
60
40
20
0
ppm

(–)-**33**

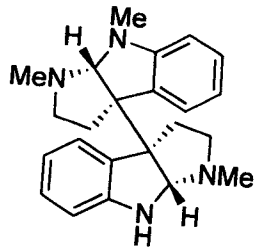
SAMPLE		DEC. & VT	
solvent	CDCl3	dfrq	125.672
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
ACQUISITION		dseq	
sfrq	499.746	dres	1.0
tn	H1	homo	n
at	3.001	temp	50.0
np	63050	PROCESSING	
sw	10504.2	wtfile	
fb	not used	proc	ft
bs	4	fn	262144
tpwr	56	math	f
pw	8.6		
d1	2.000	werr	
tof	1519.5	wexp	
nt	16	wbs	
ct	16	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-509.4		
wp	6499.7		
vs	45		
sc	0		
wc	250		
hzmm	26.00		
is	218.23		
rfl	4864.9		
rfp	3618.1		
th	7		
ins	100.000		
ai	ph		



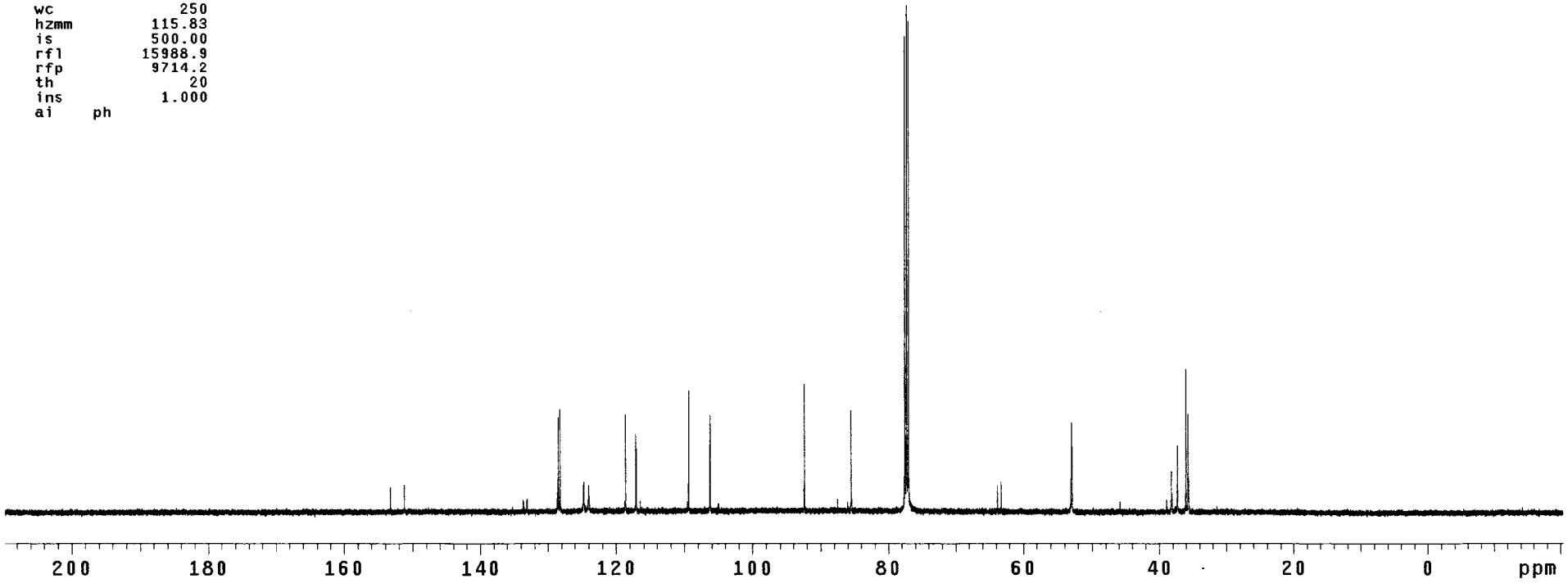
(–)-calycanthidine (**1**)



SAMPLE		DEC. & VT	
solvent	CDCl3	dfrq	500.229
		dn	H1
		dpwr	39
		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	temp	50.0
sw	37735.8	PROCESSING	
fb	not used	lb	0.30
bs	64	wtfile	
ss	1	proc	ft
tpwr	58	fn	131072
pw	6.9	math	f
d1	0.763		
tof	631.4	werr	
nt	25000	wexp	
ct	21696	wbs	
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2578.7		
wp	28957.7		
vs	2712		
sc	0		
wc	250		
hzmm	115.83		
is	500.00		
rfl	15988.9		
rfp	9714.2		
th	20		
ins	1.000		
ai	ph		

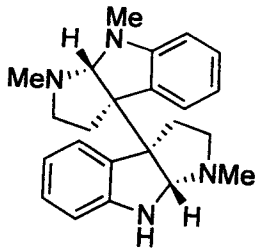


(–)-calycanthidine (**1**)

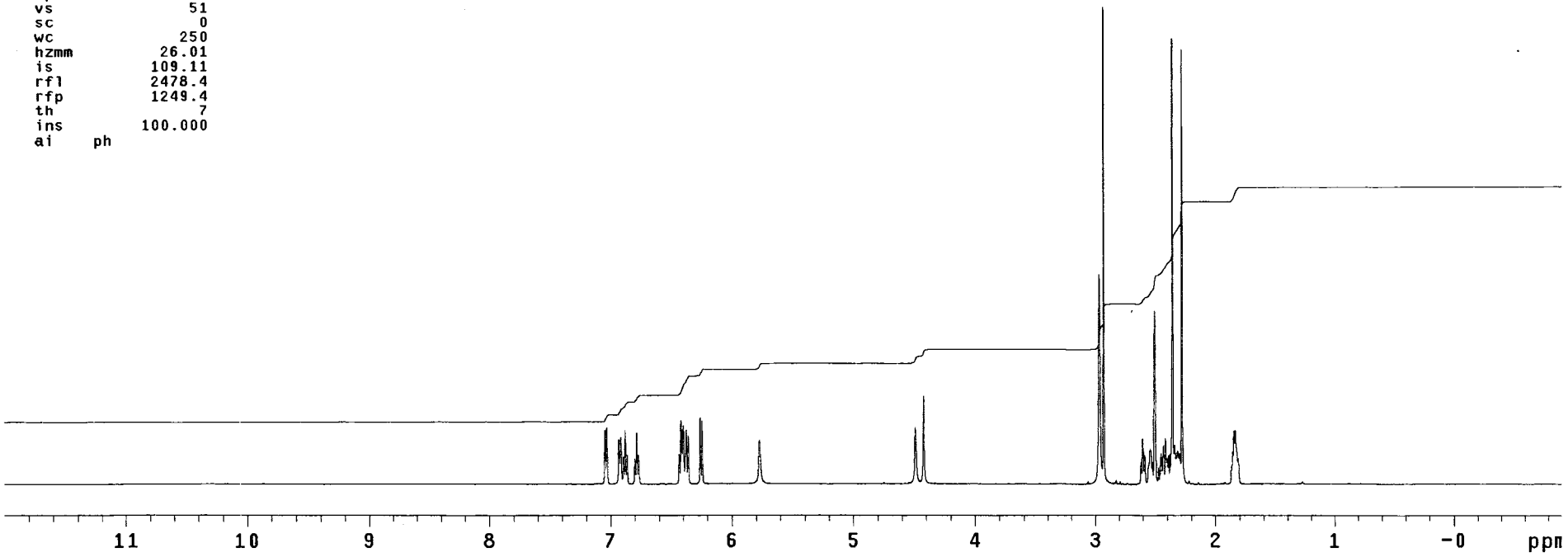


Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE		DEC. & VT	
solvent	DMSO	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
ACQUISITION		dmf	10000
sfrq	499.748	dseq	
tn	H1	dres	1.0
at	3.001	homo	n
np	63050	temp	100.0
sw	10504.2	PROCESSING	
fb	not used	wtfile	
bs	4	proc	ft
tpwr	56	fn	262144
pw	8.6	math	f
d1	2.000		
tof	1519.5	werr	
nt	16	wexp	
ct	16	wbs	
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-505.7		
wp	6501.7		
vs	51		
sc	0		
wc	250		
hzmm	26.01		
is	109.11		
rfl	2478.4		
rfp	1249.4		
th	7		
ins	100.000		
ai	ph		

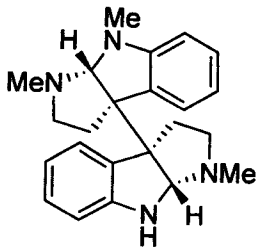


(–)-calycanthidine (**1**)

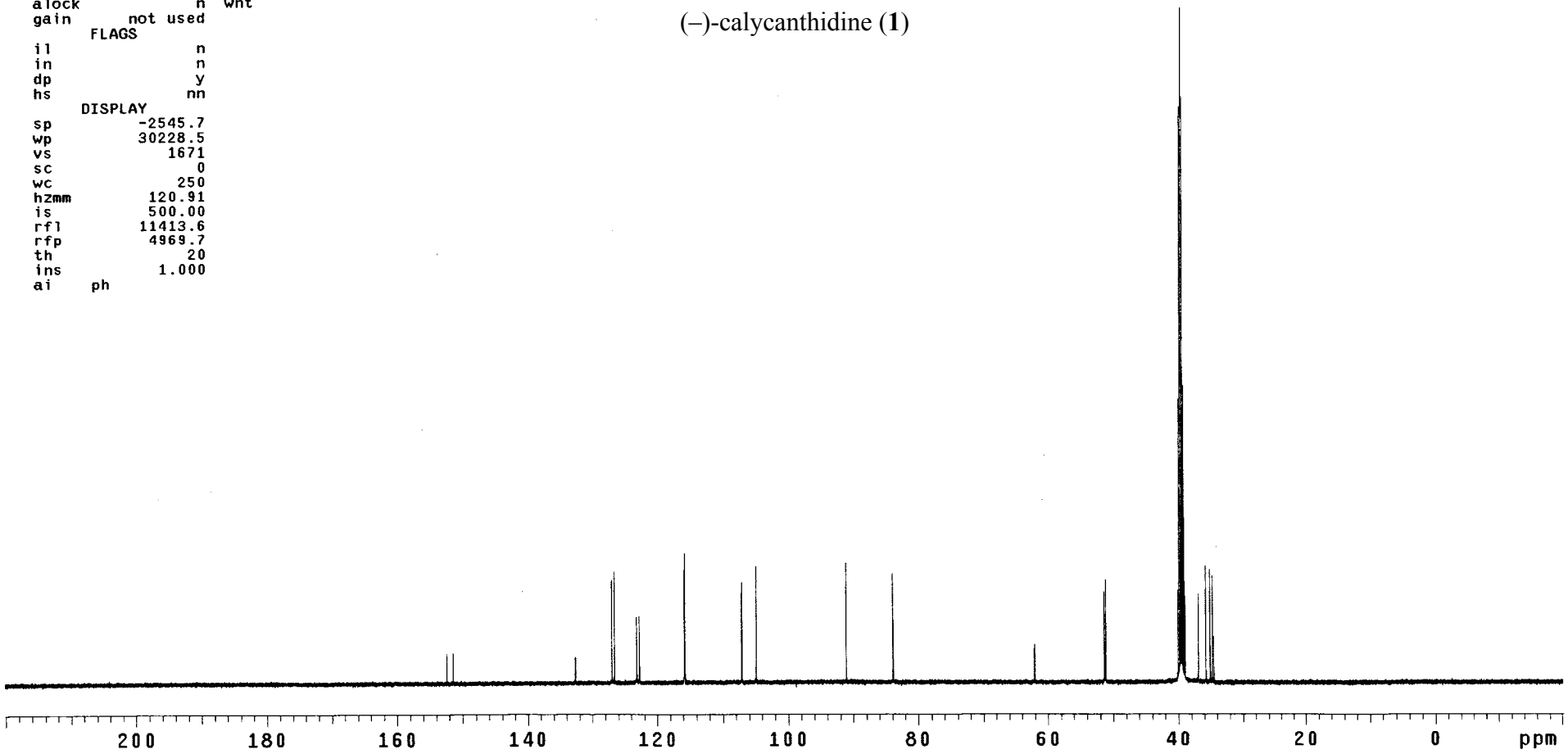


Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

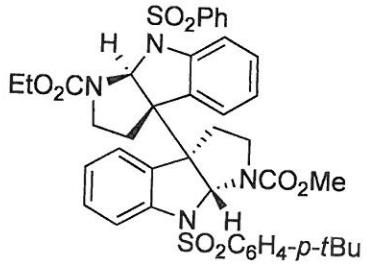
SAMPLE		DEC. & VT	
solvent	DMSO	dfrq	500.232
		dn	H1
		dpwr	39
		dof	-500.0
		dm	y
		dmm	w
ACQUISITION		dmf	10000
sfrq	125.795	dseq	
tn	C13	dres	1.0
at	1.736	homo	n
np	131010	temp	100.0
sw	37735.8	PROCESSING	
fb	not used	lb	0.30
bs	64	wtfile	
ss	1	proc	ft
tpwr	58	fn	131072
pw	6.9	math	f
d1	0.763		
tof	631.4	werr	
nt	20000	wexp	
ct	17280	wbs	
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2545.7		
wp	30228.5		
vs	1671		
sc	0		
wc	250		
hzmm	120.91		
is	500.00		
rfl	11413.6		
rfp	4969.7		
th	20		
ins	1.000		
ai	ph		



(–)-calycanthidine (**1**)



SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.748	temp	70.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	4		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-496.2		
wp	6482.3		
vs	29		
sc	0		
wc	250		
hzmm	25.93		
is	288.73		
rfl	2217.8		
rfp	969.5		
th	7		
ins	100.000		
ai ph			



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Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE	
solvent	CD3CN

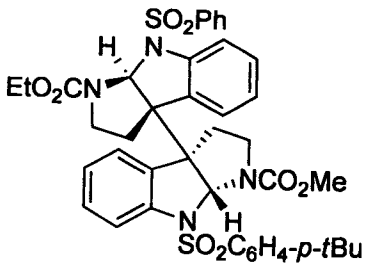
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	32
ss	1
tpwr	59
pw	6.9
d1	0.763
tof	631.4
nt	25000
ct	20992
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-2522.3
wp	30188.2
vs	2423
sc	0
wc	250
hzmm	120.75
is	500.00
rfl	21011.6
rfp	14929.1
th	20
ins	1.000
ai	ph

DEC. & VT	
dfrq	500.232
dn	H1
dpwr	38
dof	-500.0
dm	y
dmm	w
dmf	10700
dseq	
dres	1.0
homo	n
temp	70.0

PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



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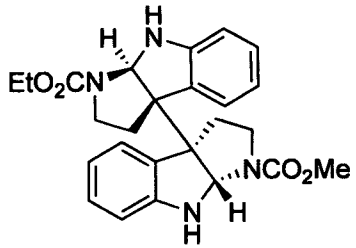
SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.748	temp	75.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	8		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	32		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-504.7		
wp	6500.6		
vs	234		
sc	0		
wc	250		
hzmm	26.00		
is	490.69		
rfl	2217.4		
rfp	969.5		
th	7		
ins	100.000		
ai	ph		



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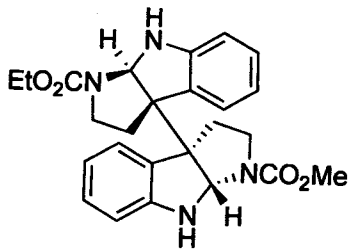
Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	500.232
		dn	H1
		dpwr	39
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
		homo	n
		temp	75.0
ACQUISITION		PROCESSING	
sfrq	125.795	lb	0.30
tn	C13	wtfile	
at	1.736	proc	ft
np	131010	fn	131072
sw	37735.8	math	f
fb	not used		
bs	64	werr	
ss	1	wexp	
tpwr	58	wbs	
pw	6.9	wnt	
d1	0.763		
tof	631.4		
nt	25000		
ct	17216		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2586.2		
wp	30223.3		
vs	892		
sc	0		
wc	250		
hzmm	120.89		
is	500.00		
rfl	21004.2		
rfp	14929.1		
th	20		
ins	1.000		
ai ph			



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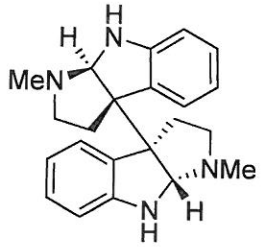
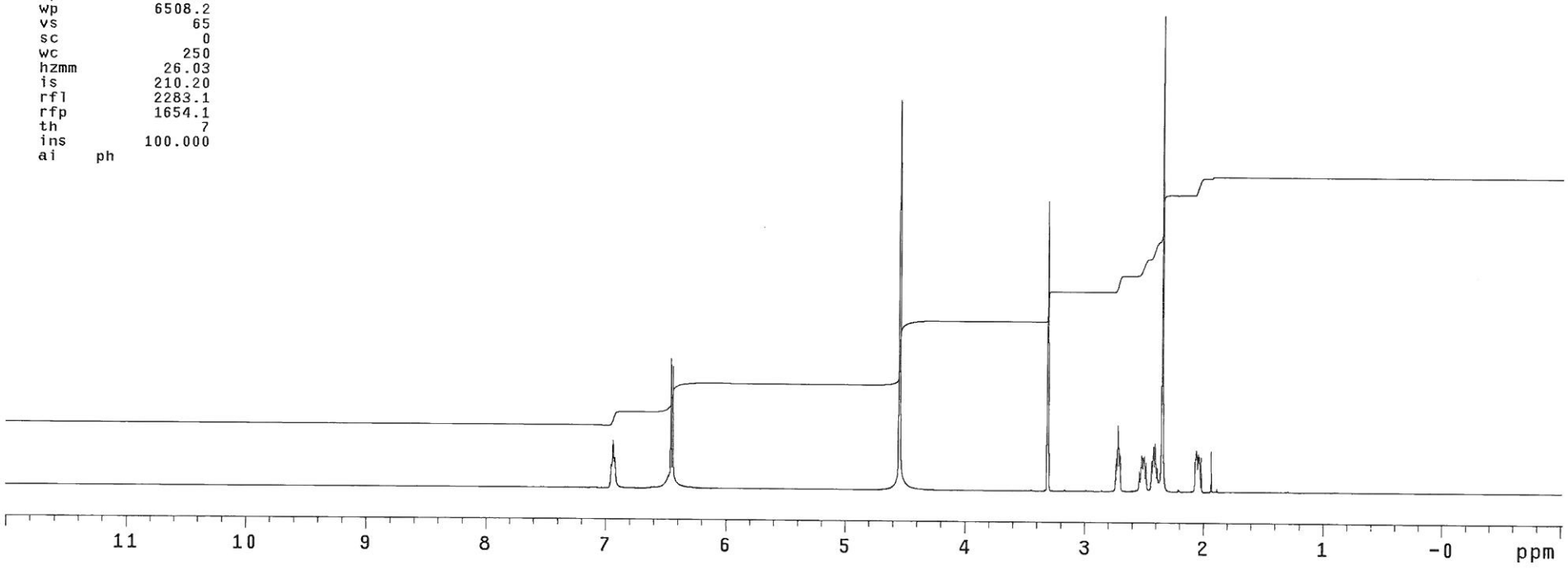
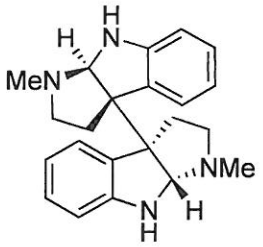
SAMPLE		DEC. & VT	
solvent	CD3OD	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
ACQUISITION		dseq	
sfrq	499.748	dres	1.0
tn	H1	homo	n
at	3.001	temp	55.0
np	63050	PROCESSING	
sw	10504.2	wtfile	
fb	not used	proc	ft
bs	4	fn	262144
tpwr	56	math	f
pw	8.6		
d1	2.000	werr	
tof	1519.5	wexp	
nt	16	wbs	
ct	16	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-508.9		
wp	6508.2		
vs	65		
sc	0		
wc	250		
hzmm	26.03		
is	210.20		
rfl	2283.1		
rfp	1654.1		
th	7		
ins	100.000		
ai	ph		



meso-chimonanthine (**2**)

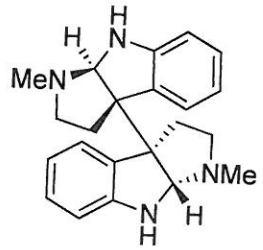


SAMPLE		DEC. & VT	
solvent	CD3OD	dfrq	500.231
		dn	H1
		dpwr	39
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
ACQUISITION		dseq	
sfrq	125.795	dres	1.0
tn	C13	homo	n
at	1.736	temp	55.0
np	131010	PROCESSING	
sw	37735.8	lb	0.30
fb	not used	wtfile	
bs	64	proc	ft
ss	1	fn	131072
tpwr	58	math	f
pw	6.9		
d1	0.763	werr	
tof	631.4	wexp	
nt	18000	wbs	
ct	16832	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2573.3		
wp	30249.8		
vs	2412		
sc	0		
wc	250		
hzmm	121.00		
is	500.00		
rfl	12298.8		
rfp	6182.5		
th	20		
ins	1.000		
ai	ph		



meso-chimonanthine (**2**)

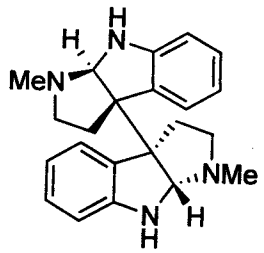
SAMPLE		DEC. & VT	
solvent	DMSO	dfrq	125.795
		dn	C13
		dpwr	39
		dof	0
		dm	nnn
		dmm	c
ACQUISITION		dmf	10000
sfrq	500.234	dseq	
tn	H1	dres	1.0
at	3.200	homo	n
np	64000	temp	120.0
sw	10000.0	PROCESSING	
fb	not used	wtfile	
bs	8	proc	ft
ss	1	fn	131072
tpwr	60	math	f
pw	9.0		
d1	1.800	werr	
tof	1498.2	wexp	
nt	32	wbs	
ct	32	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-498.0		
wp	6501.5		
vs	61		
sc	0		
wc	250		
hzmm	26.01		
is	203.12		
rfl	2243.7		
rfp	1250.6		
th	7		
ins	1.000		
ai	ph		



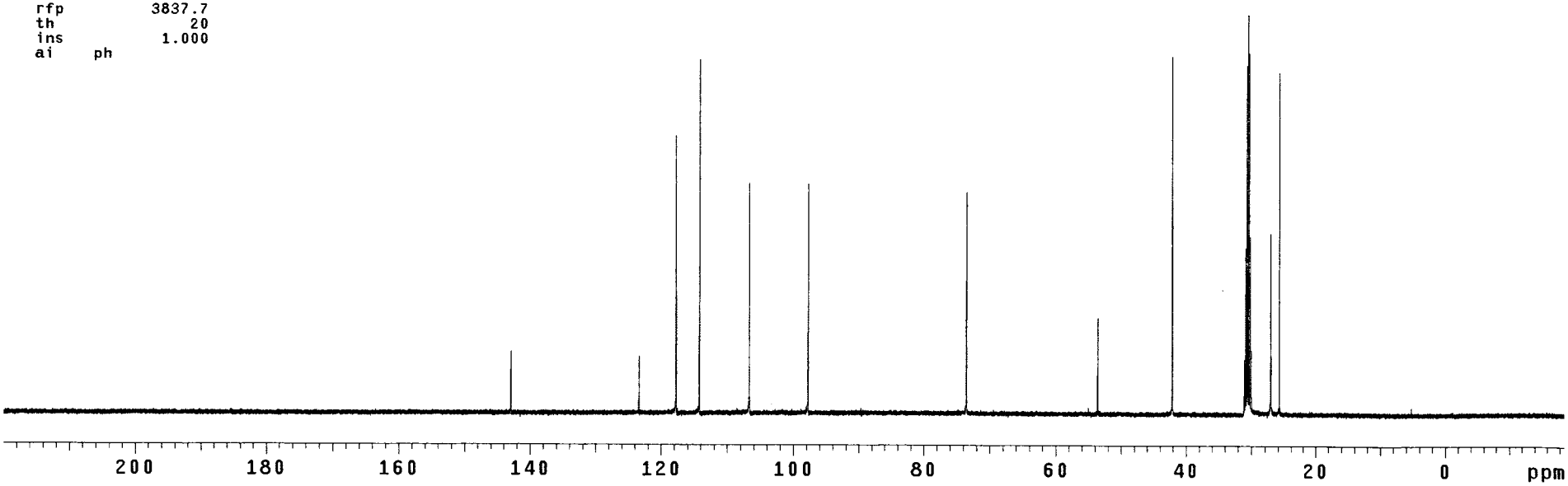
meso-chimonanthine (**2**)

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

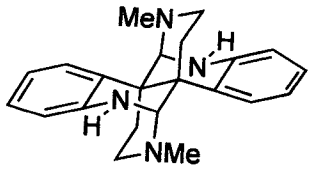
SAMPLE		DEC. & VT	
solvent	DMSO	dfrq	500.232
		dn	H1
		dpwr	40
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	125.795	temp	120.0
tn	C13	PROCESSING	
at	1.736	lb	0.30
np	131010	wtfile	
sw	37735.8	proc	ft
fb	not used	fn	131072
bs	32	math	f
ss	1		
tpwr	58	werr	
pw	6.9	wexp	
d1	0.763	wbs	
tof	631.4	wnt	
nt	25000		
ct	16192		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2508.8		
wp	30170.4		
vs	537		
sc	0		
wc	250		
hzmm	120.68		
is	500.00		
rfl	11428.0		
rfp	3837.7		
th	20		
ins	1.000		
ai	ph		



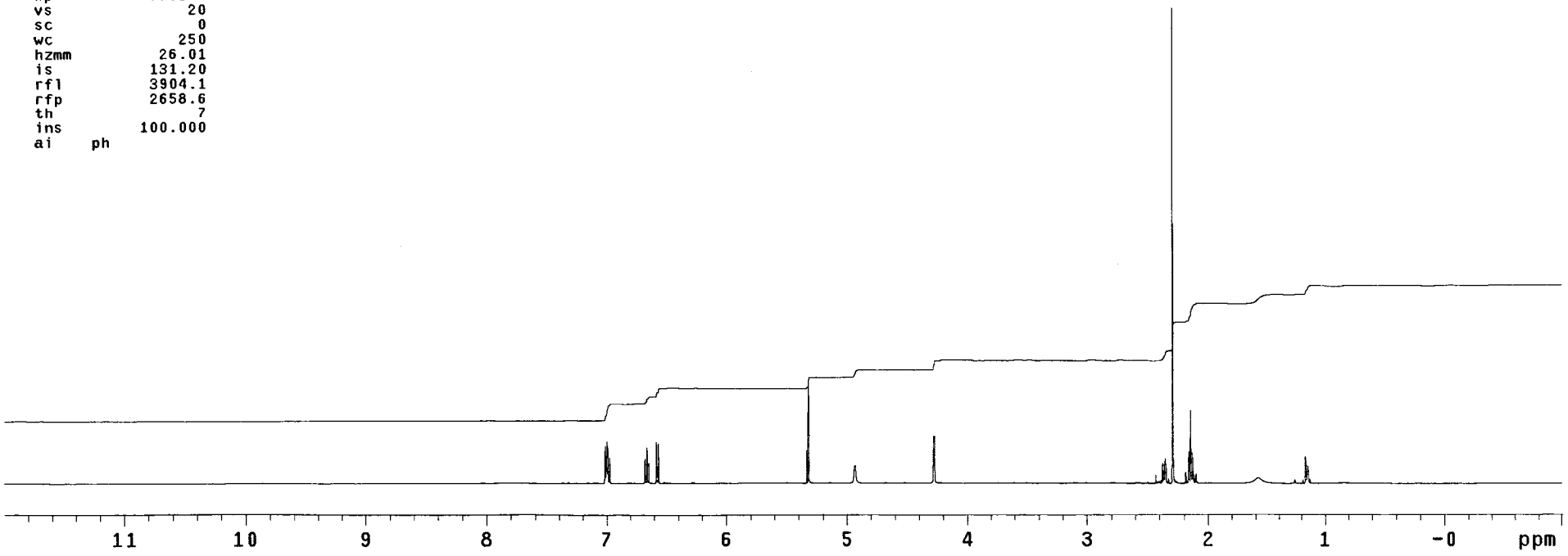
meso-chimonanthine (**2**)



SAMPLE		DEC. & VT	
solvent	CD2Cl2	dfrq	125.672
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
ACQUISITION		dmf	10000
sfrq	499.747	dseq	
tn	H1	dres	1.0
at	3.001	homo	n
np	63050	PROCESSING	
sw	10504.2	wtfile	
fb	not used	proc	ft
bs	4	fn	262144
tpwr	56	math	f
pw	8.6		
d1	2.000	werr	
tof	1519.5	wexp	
nt	16	wbs	
ct	8	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-506.0		
wp	6501.7		
vs	20		
sc	0		
wc	250		
hzmm	26.01		
is	131.20		
rfl	3904.1		
rfp	2658.6		
th	7		
ins	100.000		
ai	ph		

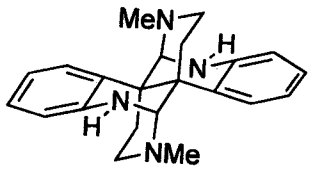


meso-calycanthine (**36**)



Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE		DEC. & VT	
solvent	CD2Cl2	dfrq	500.230
		dn	H1
		dpwr	39
		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	64	proc	ft
ss	1	fn	131072
tpwr	58	math	f
pw	6.9		
d1	0.763	werr	
tof	631.4	wexp	
nt	20000	wbs	
ct	13632	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2519.1		
wp	30170.4		
vs	2132		
sc	0		
wc	250		
hzmm	120.68		
is	500.00		
rfl	13036.2		
rfp	6792.2		
th	20		
ins	1.000		
ai	ph		



meso-calycanthine (**36**)

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE	
solvent	CD3CN

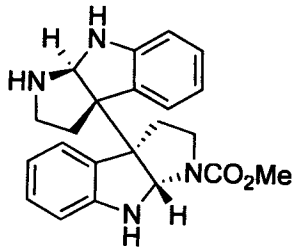
ACQUISITION	
sfrq	499.748
tn	H1
at	3.001
np	63050
sw	10504.2
fb	not used
bs	8
tpwr	56
pw	8.6
d1	2.000
tof	1519.5
nt	32
ct	24
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

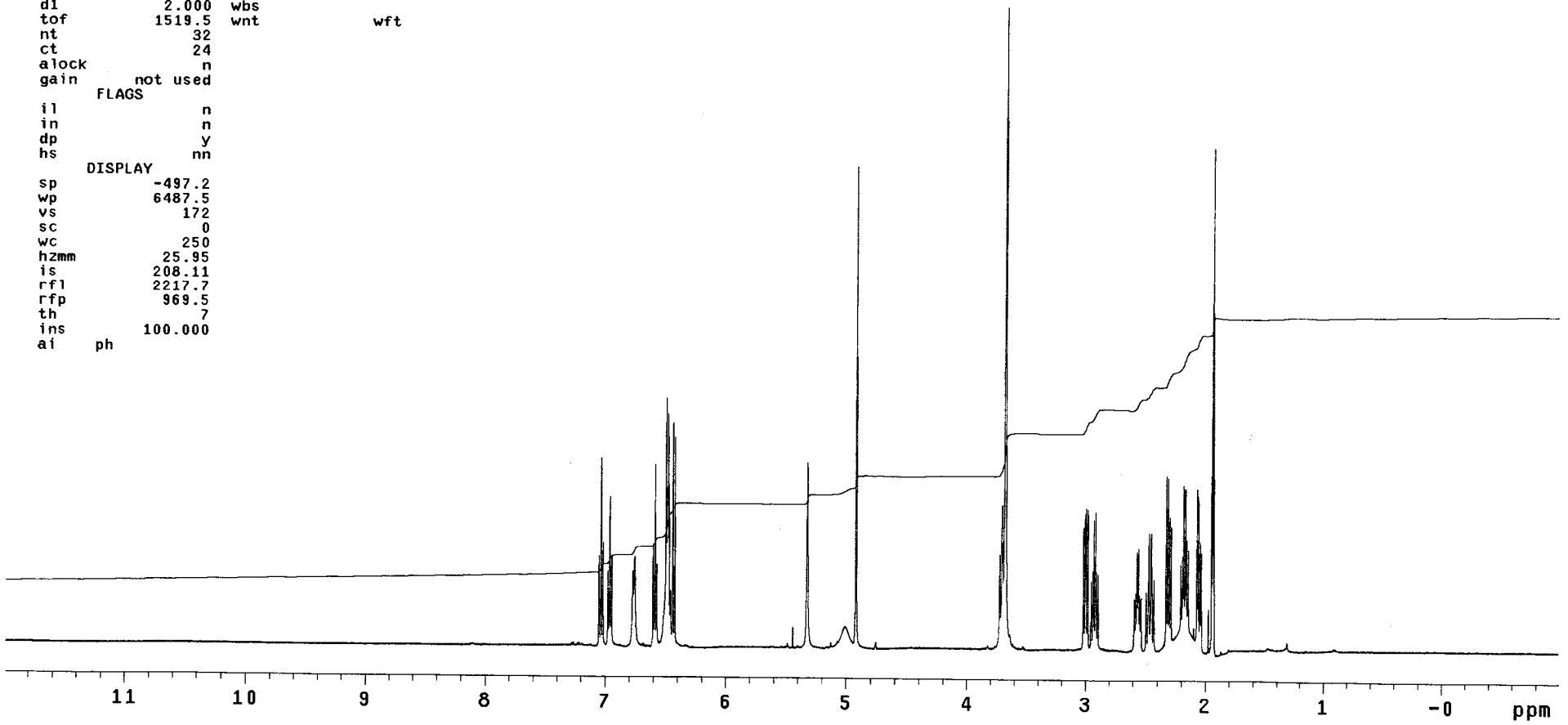
DISPLAY	
sp	-497.2
wp	6487.5
vs	172
sc	0
wc	250
hzmm	25.95
is	208.11
rfl	2217.7
rfp	969.5
th	7
ins	100.000
ai	ph

DEC. & VT	
dfrq	125.673
dn	C13
dpwr	30
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
temp	75.0

PROCESSING	
wtfile	
proc	ft
fn	262144
math	f
werr	
wexp	
wbs	
wnt	wft



(–)-37



Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE	
solvent	CD3CN

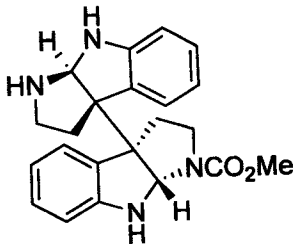
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	32
ss	1
tpwr	59
pw	6.9
d1	0.763
tof	631.4
nt	30000
ct	24608
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-2590.2
wp	30223.3
vs	749
sc	0
wc	250
hzmm	120.89
is	500.00
rfl	21008.2
rfp	14929.1
th	20
ins	1.000
ai	ph

DEC. & VT	
dfrq	500.232
dn	H1
dpwr	38
dof	-500.0
dm	y
dmm	w
dmf	10700
dseq	
dres	1.0
homo	n
temp	75.0

PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



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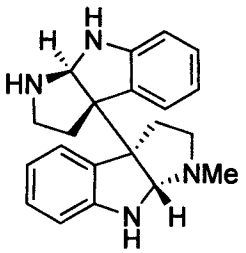
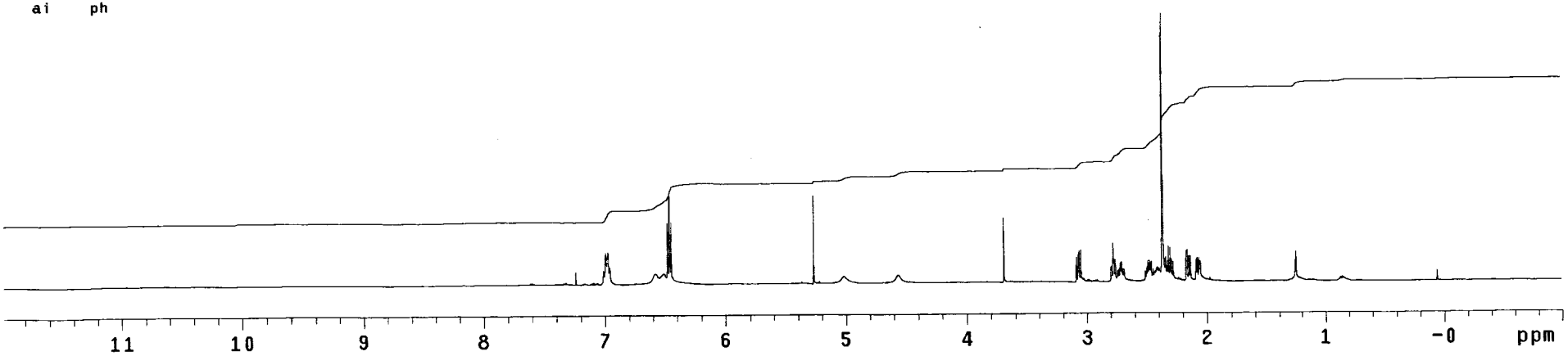
SAMPLE		DEC. & VT	
solvent	CDCl3	dfrq	125.672
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
		homo	n
ACQUISITION		temp	50.0
sfrq	499.746	PROCESSING	
tn	H1	wtfile	
at	3.001	proc	ft
np	63050	fn	262144
sw	10504.2	math	f
fb	not used		
bs	4	werr	
tpwr	56	wexp	
pw	8.6	wbs	
d1	2.000	wnt	wft
tof	1519.5		
nt	16		
ct	12		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-499.8		
wp	6485.7		
vs	29		
sc	0		
wc	250		
hzmm	25.94		
is	89.53		
rfl	4865.4		
rfp	3618.1		
th	7		
ins	100.000		
ai ph			



(–)-desmethyl-*meso*-chimonanthine (**3**)



Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE	
solvent	CDCl3

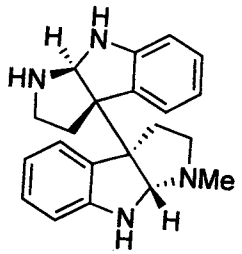
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	64
ss	1
tpwr	58
pw	6.9
d1	0.763
tof	631.4
nt	20000
ct	16896
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-2551.6
wp	30199.7
vs	7875
sc	0
wc	250
hzmm	120.80
is	500.00
rfl	15990.6
rfp	9714.2
th	20
ins	1.000
ai	ph

DEC. & VT	
dfrq	500.229
dn	H1
dpwr	39
dof	-500.0
dm	y
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
temp	50.0

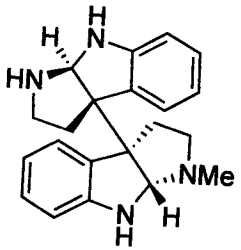
PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



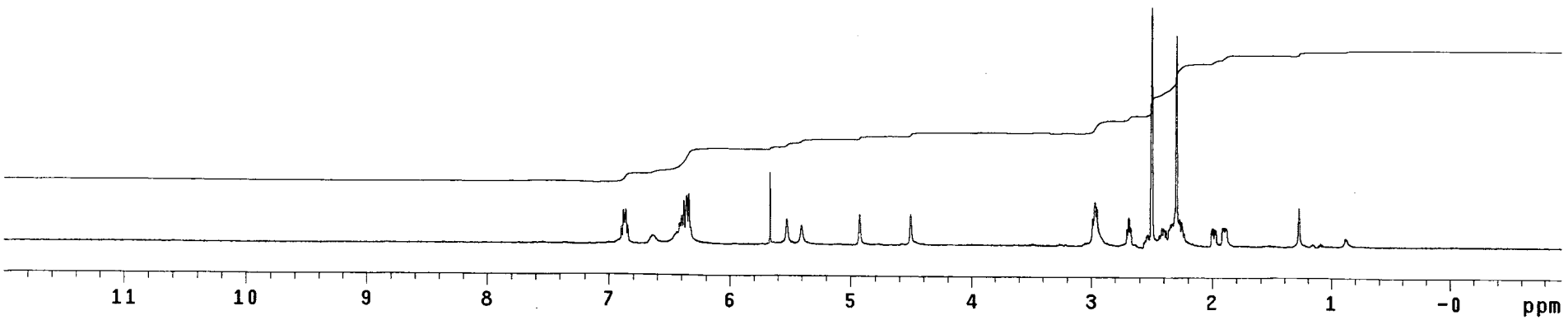
(–)-desmethyl-*meso*-chimonanthine (**3**)

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

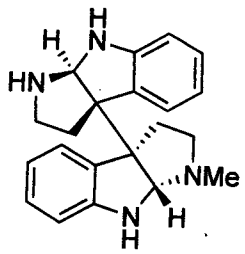
SAMPLE		DEC. & VT	
solvent	DMSO	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
		homo	n
ACQUISITION		temp	100.0
sfrq	499.748	PROCESSING	
tn	H1	wtfile	
at	3.001	proc	ft
np	63050	fn	262144
sw	10504.2	math	f
fb	not used		
bs	8	werr	
tpwr	56	wexp	
pw	8.6	wbs	
d1	2.000	wnt	wft
tof	1519.5		
nt	32		
ct	24		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-497.9		
wp	6493.7		
vs	60		
sc	0		
wc	250		
hzmm	25.97		
is	107.81		
rfl	2478.7		
rfp	1249.4		
th	7		
ins	100.000		
ai	ph		



(–)-desmethyl-*meso*-chimonanthine (**3**)



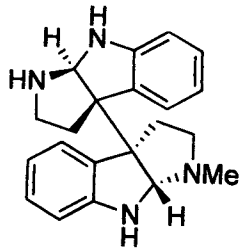
SAMPLE		DEC. & VT	
solvent	DMSO	dfrq	500.232
		dn	H1
		dpwr	39
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
		homo	n
ACQUISITION		temp	100.0
sfrq	125.795	PROCESSING	
tn	C13	lb	0.30
at	1.736	wtfile	
np	131010	proc	ft
sw	37735.8	fn	131072
fb	not used	math	f
bs	64		
ss	1	werr	
tpwr	58	wexp	
pw	6.9	wbs	
d1	0.763	wnt	
tof	631.4		
nt	25000		
ct	17600		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2573.9		
wp	30257.3		
vs	10088		
sc	0		
wc	250		
hzmm	121.03		
is	500.00		
rfl	11412.4		
rfp	4969.7		
th	20		
ins	1.000		
ai	ph		



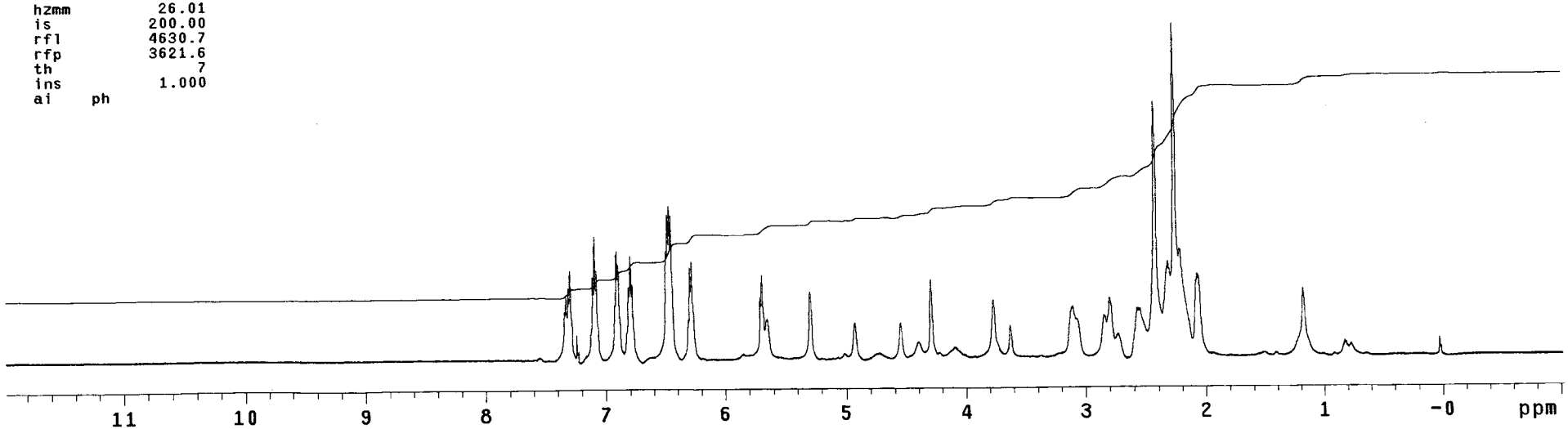
(–)-desmethyl-*meso*-chimonanthine (**3**)

Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE		DEC. & VT	
solvent	CDCl3	dfrq	125.794
		dn	C13
		dpwr	39
		dof	0
		dm	nnn
		dmm	c
		dmf	10000
		dseq	
		dres	1.0
		homo	n
ACQUISITION		temp	-40.0
sfrq	500.231	PROCESSING	
tn	H1	wtfile	
at	3.200	proc	ft
np	64000	fn	131072
sw	10000.0	math	f
fb	not used		
bs	4	werr	
ss	1	wexp	
tpwr	60	wbs	
pw	9.0	wnt	
d1	1.800		
tof	1498.2		
nt	16		
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-511.7		
wp	6503.3		
vs	307		
sc	0		
wc	250		
hzmm	26.01		
is	200.00		
rfl	4630.7		
rfp	3621.6		
th	7		
ins	1.000		
ai ph			



(–)-desmethyl-*meso*-chimonanthine (**3**)



Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE	
solvent	CDCl3

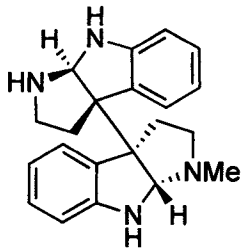
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	32
ss	1
tpwr	58
pw	6.9
d1	0.763
tof	631.4
nt	15000
ct	4256
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-2539.0
wp	30199.7
vs	2273
sc	0
wc	250
hzmm	120.80
is	500.00
rfl	16036.4
rfp	9714.9
th	20
ins	1.000
ai	ph

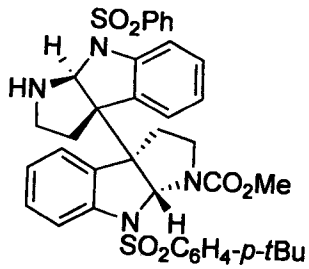
DEC. & VT	
dfrq	500.229
dn	H1
dpwr	39
dof	-500.0
dm	y
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
temp	-40.0

PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



(–)-desmethyl-*meso*-chimonanthine (**3**)

SAMPLE		DEC. & VT	
solvent	DMSO	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	499.748	temp	80.0
tn	H1	PROCESSING	
at	3.001	wtfile	
np	63050	proc	ft
sw	10504.2	fn	262144
fb	not used	math	f
bs	4		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	32		
ct	24		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-515.7		
wp	6508.8		
vs	66		
sc	0		
wc	250		
hzmm	26.04		
is	254.60		
rfl	2477.9		
rfp	1249.4		
th	7		
ins	100.000		
ai	ph		



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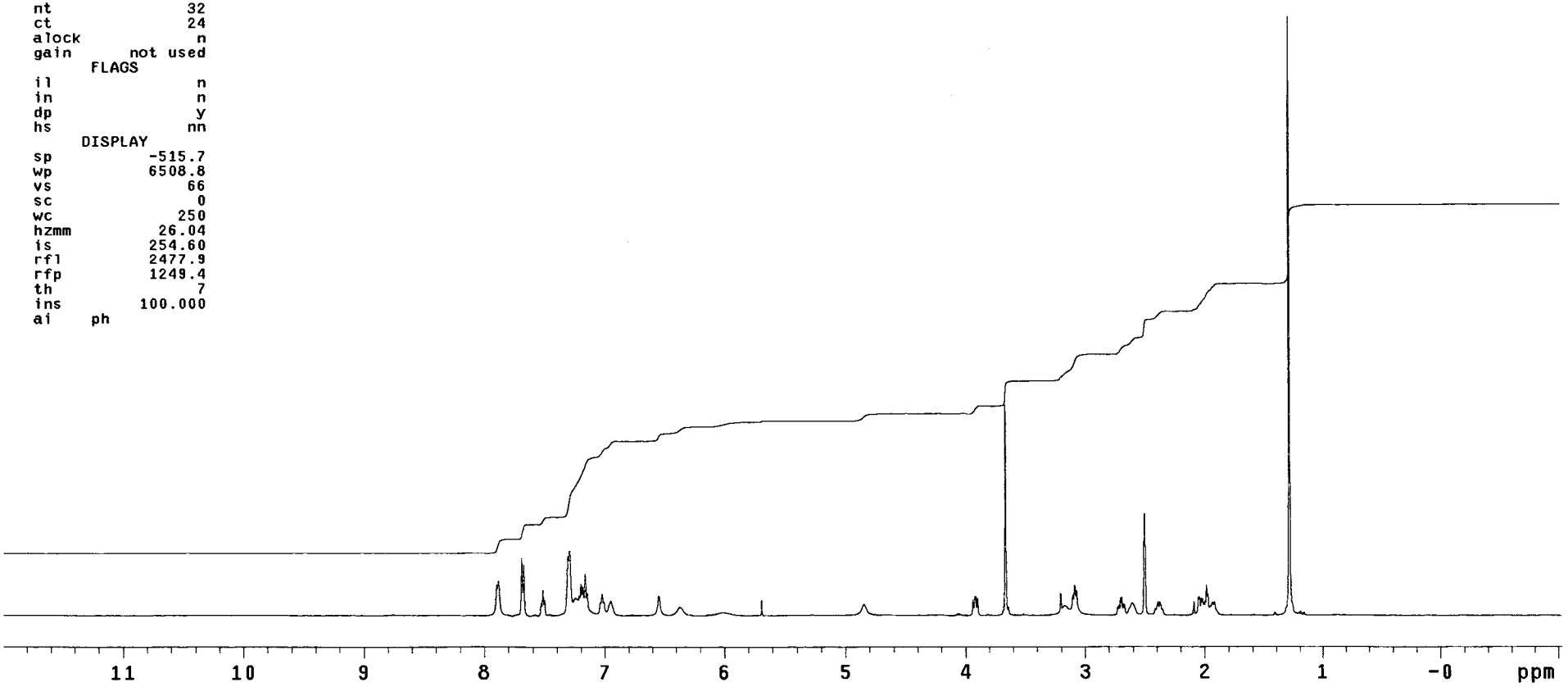
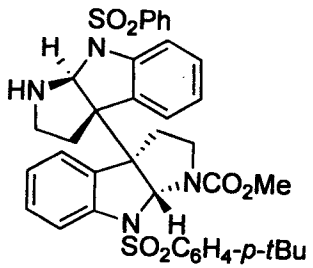


Application of diazene-directed fragment assembly to the enantioselective total synthesis and stereochemical assignment of (+)-desmethyl-meso-chimonanthine and related heterodimeric alkaloids.
Stephen P. Lathrop and Mohammad Movassaghi*

SAMPLE		DEC. & VT	
solvent	DMSO	dfrq	500.232
		dn	H1
		dpwr	39
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
ACQUISITION		homo	n
sfrq	125.795	temp	80.0
tn	C13	PROCESSING	
at	1.736	lb	0.30
np	131010	wtfile	
sw	37735.8	proc	ft
fb	not used	fn	131072
bs	64	math	f
ss	1		
tpwr	58	werr	
pw	6.9	wexp	
d1	0.763	wbs	
tof	631.4	wnt	
nt	25000		
ct	16448		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2554.9		
wp	30221.6		
vs	2340		
sc	0		
wc	250		
hzmm	120.89		
is	500.00		
rfl	11399.8		
rfp	4969.7		
th	20		
ins	1.000		
ai	ph		



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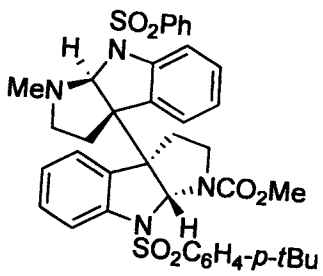
SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	125.673
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
		homo	n
ACQUISITION		temp	70.0
sfrq	499.748	PROCESSING	
tn	H1	wtfile	
at	3.001	proc	ft
np	63050	fn	262144
sw	10504.2	math	f
fb	not used		
bs	8		
tpwr	56	werr	
pw	8.6	wexp	
d1	2.000	wbs	
tof	1519.5	wnt	wft
nt	32		
ct	32		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-497.6		
wp	6490.0		
vs	24		
sc	0		
wc	250		
hzmm	25.96		
is	151.08		
rfl	2217.4		
rfp	969.5		
th	7		
ins	100.000		
ai	ph		



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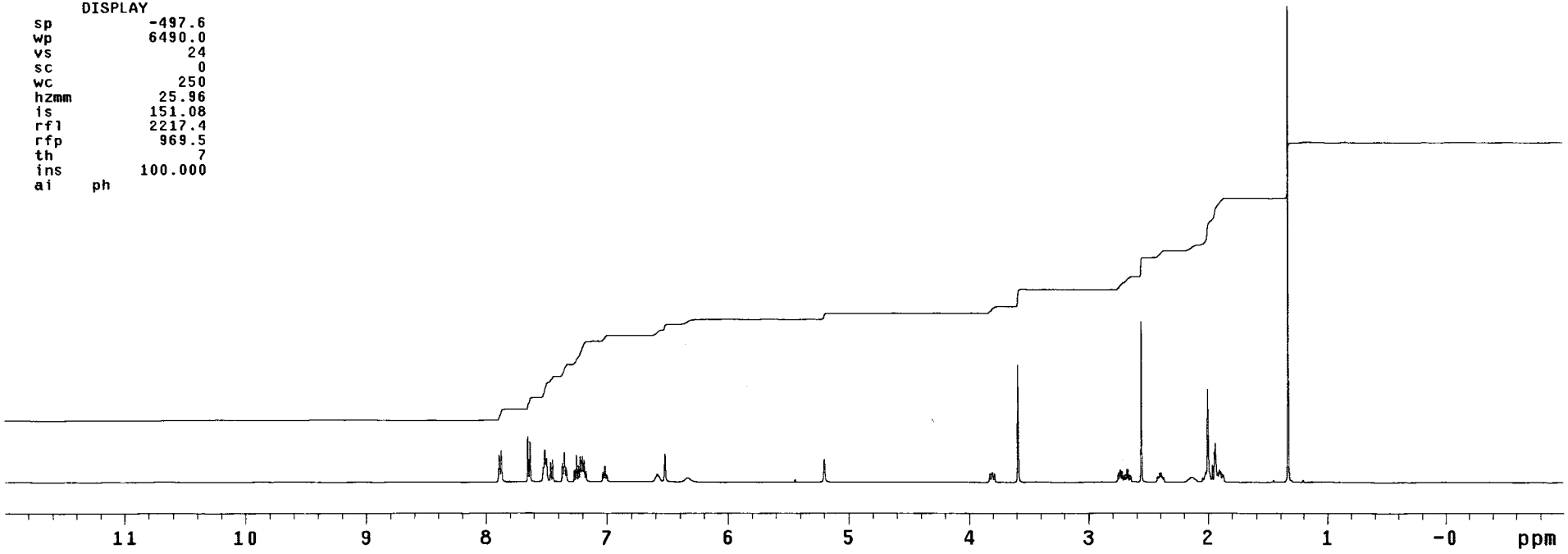
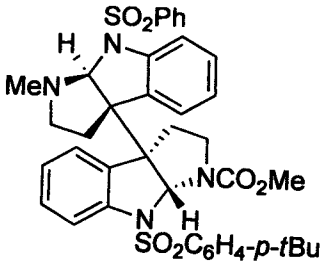


SAMPLE		DEC. & VT	
solvent	CD3CN	dfrq	500.232
		dn	H1
		dpwr	39
		dof	-500.0
		dm	y
		dmm	w
		dmf	10000
		dseq	
		dres	1.0
		homo	n
ACQUISITION		temp	70.0
sfrq	125.795	PROCESSING	
tn	C13	lb	0.30
at	1.736	wtfile	
np	131010	proc	ft
sw	37735.8	fn	131072
fb	not used	math	f
bs	64		
ss	1		
tpwr	58	werr	
pw	6.9	wexp	
d1	0.763	wbs	
tof	631.4	wnt	
nt	25000		
ct	18816		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-2510.8		
wp	30188.2		
vs	755		
sc	0		
wc	250		
hzmm	120.75		
is	500.00		
rfl	21011.6		
rfp	14929.1		
th	20		
ins	1.000		
ai ph			



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SAMPLE	
solvent	CD3CN

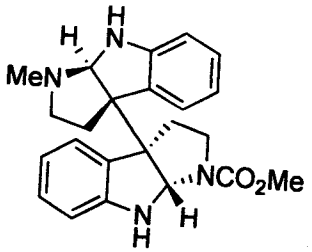
ACQUISITION	
sfrq	499.748
tn	H1
at	3.001
np	63050
sw	10504.2
fb	not used
bs	4
tpwr	56
pw	8.6
d1	2.000
tof	1519.5
nt	16
ct	16
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-508.0
wp	6508.8
vs	23
sc	0
wc	250
hzmm	26.04
is	72.74
rfl	2218.5
rfp	969.5
th	7
ins	100.000
ai	ph

DEC. & VT	
dfrq	125.673
dn	C13
dpwr	30
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
temp	75.0

PROCESSING	
wtfile	
proc	ft
fn	262144
math	f
werr	
wexp	
wbs	
wnt	wft



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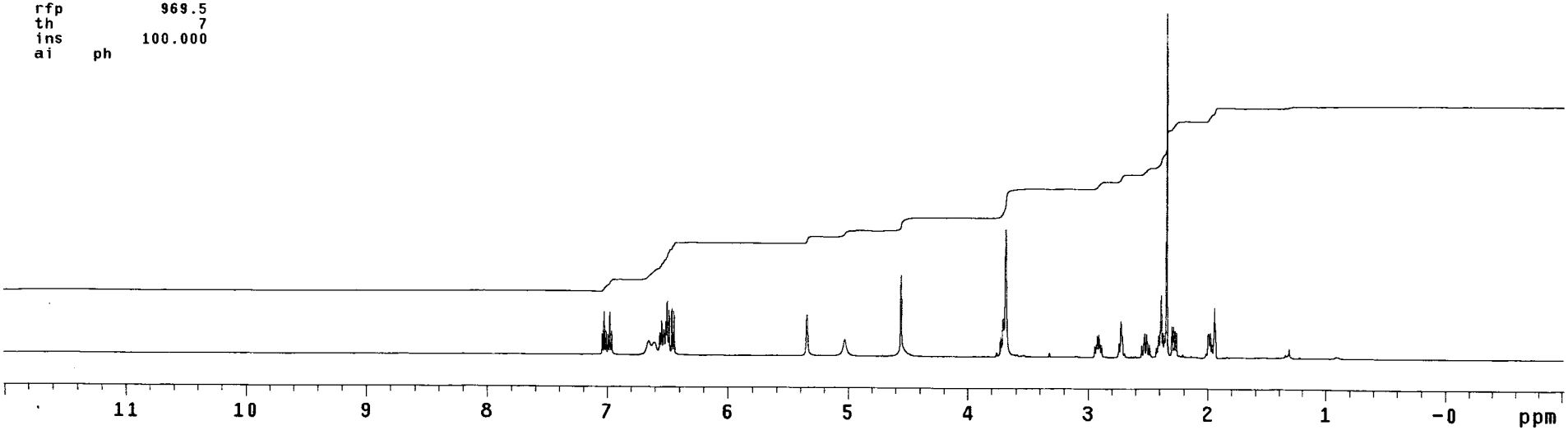


SAMPLE	
solvent	CD3CN

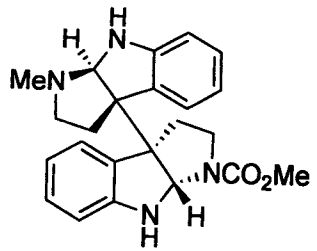
ACQUISITION	
sfrq	125.795
tn	C13
at	1.736
np	131010
sw	37735.8
fb	not used
bs	64
ss	1
tpwr	58
pw	6.9
d1	0.763
tof	631.4
nt	20000
ct	14912
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-2585.1
wp	30271.7
vs	1018
sc	0
wc	250
hzmm	121.09
is	500.00
rfl	21003.6
rfp	14929.1
th	20
ins	1.000
ai	ph

DEC. & VT	
dfrq	500.232
dn	H1
dpwr	39
dof	-500.0
dm	y
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
temp	75.0

PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



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