Concise Synthesis of (–)-Hodgkinsine, (–)-Calycosidine, (–)-Hodgkinsine B, (–)-Quadrigemine C, and (–)-Psycholeine via Convergent and Directed Modular Assembly of Cyclotryptamines

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Supporting Information

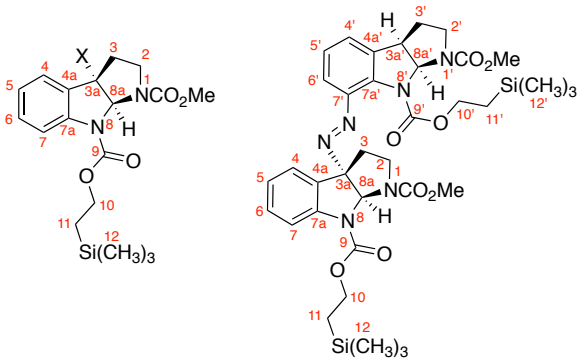
General Procedures. All reactions were performed in oven-dried or flame-dried round-bottom flasks, unless noted otherwise. The flasks were fitted with rubber septa, and reactions were conducted under a positive pressure of argon. Cannulae or gas-tight syringes with stainless steel needles were used to transfer air- or moisture-sensitive liquids. Where necessary (so noted), solutions were deoxygenated by sparging with nitrogen for a minimum of 5 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) or non-activated alumina (80–325 mesh, chromatographic grade). 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) or basic alumina 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 29–35 °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.

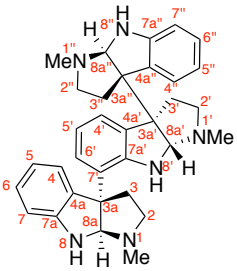
Materials. Commercial reagents and solvents were used as received with the following exceptions: dichloromethane, acetonitrile, tetrahydrofuran, methanol, pyridine, toluene, and triethylamine were purchased from J. T. Baker (Cycletainer™) and were purified by the method of Grubbs *et al.* under positive argon pressure.[2] Benzene and 1,2-dichloroethane were dried by distillation over calcium hydride under an inert nitrogen atmosphere and used directly. Silver bis(trifluoromethanesulfonyl)imide, palladium on carbon, and dichloro(pentamethylcyclopentadienyl) iridium (III) dimer were purchased from Strem Chemicals; 2,6-di-*tert*-butyl-4-methylpyridine was purchased from Matrix Scientific and was further purified by flash column chromatography on silica gel (eluent: hexanes); tetra-*n*-butylammonium hydrogen sulfate and 2-methyl-2-phenylpropionic acid were purchased from TCI America; tryptamine was purchased from AK Scientific, Inc. All other solvents and chemicals were purchased from Sigma–Aldrich, Alfa Aesar, Acros Organics, or Combi-Blocks Inc.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian inverse probe 500 INOVA spectrometer, or a Bruker AVANCE III 400 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 7.26, CD_2HCN: 1.94, C_6D_5H: 7.16, CD_3SOCD_2H: 2.50).[3] 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 (^{13}C NMR) spectra were recorded with a Varian 500 INOVA spectrometer, or a Bruker AVANCE III 400 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 77.16, CD_3CN: 118.26, C_6D_6: 128.06, DMSO-d_6: 39.52). Data are reported as 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 α,α,α-trifluorotoluene ($C_6H_5CF_3$ δ –63.72). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q =

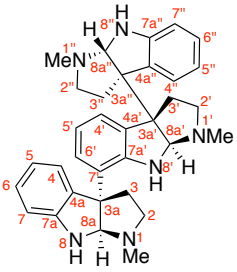
quartet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Infrared data were obtained with a Perkin-Elmer 2000 FTIR and are reported as follows: [frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad), assignment]. We thank Dr. 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 or direct analysis in real time (DART) ionization source.

Positional Numbering System. In assigning the ^{1}H and ^{13}C NMR data of all intermediates en route to (–)-hodgkinsine B (**3**), (−)-hodgkinsine (**4**), (–)-calycosidine (**5**), (–)-quadrigemine C (**7**), and (–)-psycholeine (**8**), we have employed a uniform numbering system.

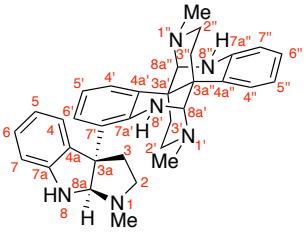




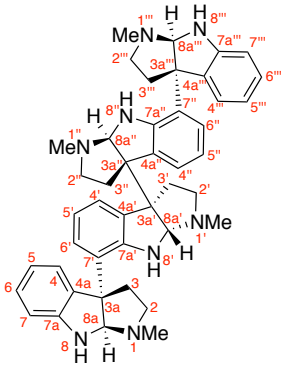
(–)-hodgkinsine B (**3**)



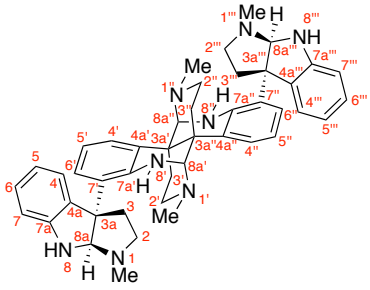
(–)-hodgkinsine (**4**)



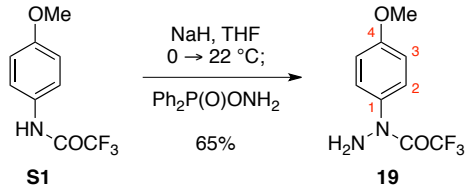
(–)-calycosidine (**5**)



(–)-quadrigemine C (**7**)



(–)-psycholeine (**8**)



2,2,2-Trifluoro-*N*-(4-methoxyphenyl)acetohydrazide (19):

Anilide **S1** (140 mg, 0.639 mmol, 1 equiv) was azeotropically dried by concentration from anhydrous benzene (3 × 2 mL) and the residue was dissolved in tetrahydrofuran (6.4 mL). The resulting solution was cooled to 0 °C and a sample of sodium hydride (60% in mineral oil, 30.7 mg, 0.767 mmol, 1.20 equiv) was added in one portion. The ice-water bath was removed and after 30 min, a sample of *O*-(diphenylphosphinyl)hydroxylamine (179 mg, 0.767 mmol, 1.20 equiv) was added in one portion. After 1 h, the reaction mixture was diluted with ethyl acetate (10 mL), was washed with a saturated aqueous sodium bicarbonate–water solution (10:1 v/v, 10 mL), and the aqueous layer was extracted with ethyl acetate (3 × 5 mL). The combined organic extracts 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: 7→20% ethyl acetate in hexanes) to afford hydrazide **19** (96.9 mg, 64.8%) as a tan solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, 1.7:1 mixture of atropisomers, *denotes minor atropisomer): δ 7.32 (d, J = 9.0 Hz, 2H, C_2**H***), 7.23 (d, J = 8.6 Hz, 2H, C_2**H**), 6.92 (app-dd, J = 6.3, 8.8 Hz, 4H, C_3**H**, C_3**H***), 4.70 (br-s, 2H, N**H**$_2$), 4.39 (s, 2H, N**H**$_2$*), 3.82 (s, 3H, OC**H**$_3$), 3.80 (s, 3H, OC**H**$_3$*).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, 1.7:1 mixture of atropisomers, *denotes minor atropisomer): δ 160.3 (**C**$_4$), 159.0 (**C**$_4$*), 158.0 (q, J = 34.8 Hz, **C**$COCF_3$*), 155.9 (q, J = 36.6 Hz, **C**OCF_3), 135.0 (**C**$_1$*), 131.9 (**C**$_1$), 128.7 (**C**$_2$), 125.1 (**C**$_2$*), 117.0 (q, J = 286.2 Hz, CO**C**F_3*), 116.5 (q, J = 286.3 Hz, CO**C**F_3), 114.7 (**C**$_3$*), 114.5 (**C**$_3$), 55.6 (2C, O**C**H_3, O**C**H_3*).

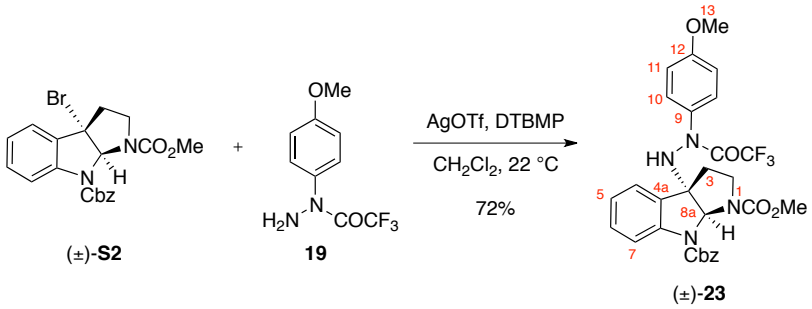
^{19}F NMR (282 MHz, $CDCl_3$, 25 °C, 1.5:1 mixture of atropisomers, *denotes minor atropisomer): δ –68.0 (s, COC**F**$_3$), –70.3 (s, COC**F**$_3$*).

FTIR (thin film) cm^{-1}: 3361 (m), 2966 (w), 2844 (w), 1701 (s), 1608 (m), 1512 (s), 1304 (m).

HRMS (DART) (*m/z*): calc'd for $C_9H_{10}F_3N_2O_2$ $[M+H]^+$: 235.0689, found: 235.0688.

TLC (50% ethyl acetate in hexanes), R*f*: 0.52 (UV, CAM).

M.p.: 67–69°C (CH_2Cl_2).



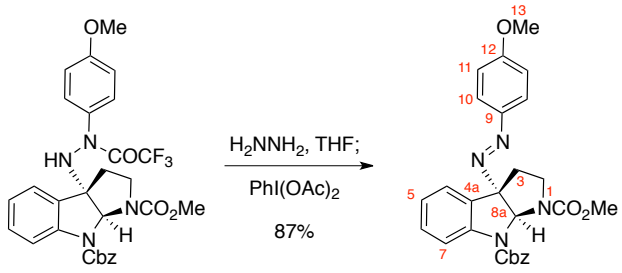
Trifluoroacetohydrazine (±)-23:

A sample of silver trifluoromethanesulfonate (61.7 mg, 240 μmol, 2.00 equiv) was added to a solution of bromocyclotryptamine (±)-**S2** (51.3 mg, 120 μmol, 1 equiv), hydrazide **19** (36.5 mg, 156 μmol, 1.30 equiv), and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 61.6 mg, 300 μmol, 2.50 equiv) in dichloromethane (1.2 mL) at 22 °C. After 1 h, the off-white suspension was diluted with dichloromethane (5 mL), was washed with a mixture of saturated aqueous sodium bicarbonate solution and saturated aqueous sodium thiosulfate solution (1:1 v/v, 10 mL), and the aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic extracts 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%→20% ethyl acetate in hexanes) to yield the trifluoroacetohydrazine (±)-**23** (50.8 mg, 72.4%) as a white solid. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, 13.5:1 mixture of atropisomers, *denotes minor atropisomer):
δ 7.78 (d, J = 8.3 Hz, 1H, C_7**H**), 7.40–7.27 (m, 6H, C_6**H**, Ph_{Cbz}-**H**), 7.22 (d, J = 7.6 Hz, 1H, C_4**H**), 7.03 (t, J = 7.4 Hz, 1H, C_5**H**), 6.70 (app-s, 4H, C_{10}**H**, C_{11}**H**), 6.41 (s, 1H, N**H**), 5.78 (s, 1H, C_{8a}**H**), 5.14 (d, J = 12.4 Hz, 1H, $Ph_{Cbz}C$**H**$_a$), 5.00 (d, J = 12.3 Hz, 1H, $Ph_{Cbz}C$**H**$_b$), 3.94–3.84 (m, 1H, C_2**H**$_a$), 3.74 (s, 3H, O**CH**$_3$*) 3.70 (s, 3H, O**CH**$_3$), 3.26 (br-s, 3H, NCO_2**CH**$_3$), 2.79 (td, J = 5.1, 11.8 Hz, 1H, C_2**H**$_b$), 2.23 (dd, J = 5.2, 12.0 Hz, 1H, C_3**H**$_a$), 2.16 (td, J = 7.7, 12.1 Hz, 1H, C_3**H**$_b$).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C):
δ 160.0 (**C**$_{12}$), 156.8 (q, J = 36.0 Hz, **C**OCF_3), 155.2 (NCO_2CH_3), 153.0 (N**C**=O_{Cbz}), 143.8 (**C**$_{7a}$), 135.9 (Ph_{Cbz}-*i*-**C**), 130.7 (**C**$_9$), 130.4 (**C**$_{4a}$), 128.6 (2C, **C**$_{10}$, **C**$_6$ or Ph_{Cbz}), 128.4 (**C**$_6$ or Ph_{Cbz}), 128.3 (**C**$_6$ or Ph_{Cbz}), 128.2 (**C**$_6$ or Ph_{Cbz}), 127.0 (**C**$_{3a}$), 124.4 (**C**$_4$), 123.9 (**C**$_5$), 116.4 (**C**$_7$), 116.3 (q, J = 286 Hz, CO**C**F_3), 114.1 (**C**$_{11}$), 80.0 (**C**$_{8a}$), 67.6 (Ph_{Cbz}**C**H_2), 55.5 (O**C**H_3), 52.5 (NCO_2**C**H_3), 44.5 (**C**$_2$), 36.8 (**C**$_3$).

^{19}F NMR (282 MHz, $CDCl_3$, 25 °C, 13.5:1 mixture of atropisomers, *denotes minor atropisomer):	δ –67.6 (s, COC**F**$_3$), –69.3 (s, COC**F**$_3$*).
FTIR (thin film) cm^{-1}:	3359 (s), 2958 (w), 1700 (s), 1606 (w), 1511 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{29}H_{27}F_3N_4NaO_6$ $[M+Na]^+$: 607.1775, found: 607.1792.
TLC (30% ethyl acetate in hexanes), R*f*:	0.15 (UV, CAM).
M.p.:	168–170°C (CH_2Cl_2).



(±)-**23** (±)-**25**

Diazine (±)-25:

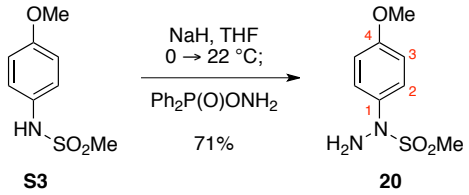
The trifluoroacetohydrazine (±)-**23** (36.5 mg, 62.4 μmol, 1 equiv) was dissolved in a solution of hydrazine (1.0 M in tetrahydrofuran, 1.25 mL, 1.25 mmol, 20.0 equiv) at 23 °C. After 19 h, the reaction mixture was washed with a saturated aqueous ammonium chloride solution and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude hydrazine was dissolved in tetrahydrofuran (0.6 mL) at 23 °C and a sample of (diacetoxyiodo)benzene (40.3 mg, 0.125 mmol, 2.50 equiv) was added in one portion. After 3 h, the reaction mixture was concentrated under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel (eluent: 10→18% ethyl acetate in hexanes) to afford diazene (±)-**25** (26.4 mg, 87.0%) as a bright yellow amorphous gum. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.80 (d, *J* = 8.1 Hz, 1H, C_7**H**), 7.69–7.63 (m, 2H, C_{10}**H**), 7.46 (br-dd, *J* = 1.6, 7.9 Hz, 2H, Ph_{Cbz}-*o*-**H**), 7.40–7.28 (m, 5H, C_4**H**, C_6**H**, Ph_{Cbz}-*m*-**H**, Ph_{Cbz}-*p*-**H**), 7.08 (td, *J* = 1.1, 7.5 Hz, C_5**H**), 6.95–6.89 (m, 2H, C_{10}**H**$_2$), 6.88 (s, 1H, C_{8a}**H**), 5.36 (d, *J* = 12.2 Hz, 1H, $Ph_{Cbz}C$**H**$_a$), 5.29 (d, *J* = 12.3 Hz, 1H, $Ph_{Cbz}C$**H**$_b$), 4.06 (dd, *J* = 8.0, 11.2 Hz, 1H, C_2**H**$_a$), 3.85 (s, 3H, O**CH**$_3$), 3.55 (s, 3H, NCO_2C**H**$_3$), 3.12 (td, *J* = 5.4, 11.8 Hz, C_2**H**$_b$), 2.53 (dd, *J* = 5.3, 12.4 Hz, 1H, C_3**H**$_a$), 2.44 (td, *J* = 7.8, 12.3 Hz, 1H, C_3**H**$_b$).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 162.3 (**C**$_{12}$), 155.4 (NCO_2CH_3), 153.5 (N**C**=O_{Cbz}), 145.8 (**C**$_9$), 143.2 (**C**$_{7a}$), 136.3 (Ph_{Cbz}-*i*-**C**), 130.1 (2C, **C**$_{4a}$ and **C**$_4$, **C**$_6$ or Ph_{Cbz}-*p*-**C**), 128.7 (**C**$_4$, **C**$_6$ or Ph_{Cbz}-*p*-**C**), 128.4 (Ph_{Cbz}-*m*-**C**), 128.3 (Ph_{Cbz}-*o*-**C**), 124.8 (**C**$_4$, **C**$_6$ or Ph_{Cbz}-*p*-**C**), 124.7 (**C**$_{10}$), 123.9 (**C**$_5$), 116.6 (**C**$_7$), 114.1 (**C**$_{11}$), 88.3 (br-s, **C**$_{3a}$), 78.9 (**C**$_{8a}$), 67.7 (Ph_{Cbz}**C**H_2), 55.7 (O**C**H_3), 52.7 (NCO_2**C**H_3), 45.8 (**C**$_2$), 35.9 (**C**$_3$).

FTIR (thin film) cm^{-1}: 2949 (m), 2890 (w), 1702 (s), 1601 (s), 1508 (m).

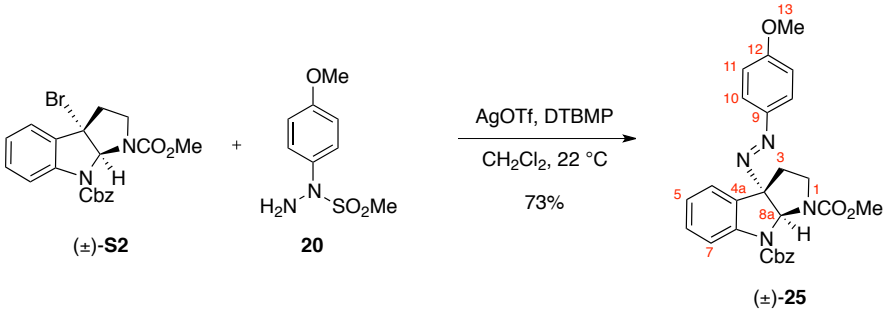
HRMS (DART) (*m/z*):	calc'd for $C_{27}H_{27}N_4O_5$ $[M+H]^+$: 487.1976, found: 487.1963.
TLC (30% ethyl acetate in hexanes), R*f*:	0.29 (UV, CAM).



***N*-(4-Methoxyphenyl)methanesulfonohydrazide (20):**

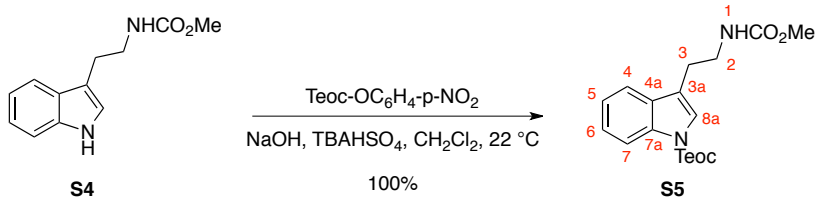
Anilide **S3** (50.2 mg, 0.249 mmol, 1 equiv) was azeotropically dried by concentration from anhydrous benzene (3 × 0.1 mL) and the residue was dissolved in tetrahydrofuran (2.5 mL). The solution was cooled to 0 °C and a sample of sodium hydride (60% in mineral oil, 12.0 mg, 0.299 mmol, 1.20 equiv) was added in one portion. The ice-water bath was removed and after 30 min, a sample of *O*-(diphenylphosphinyl)hydroxylamine (69.7 mg, 0.299 mmol, 1.20 equiv) was added in one portion. After 1 h, the reaction mixture was diluted with ethyl acetate (3 mL), was washed with saturated aqueous sodium bicarbonate–water solution (10:1 v/v, 5 mL), and the aqueous layer was extracted with ethyl acetate (3 × 3 mL). The combined organic extracts 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→40% ethyl acetate in hexanes) to afford hydrazine **20** (38.3 mg, 71.1%) as a tan solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):	δ 7.39–7.32 (m, 2H, C_2**H**), 6.94–6.88 (m, 2H, C_3**H**), 4.35 (s, 2H, N**H**$_2$), 3.81 (s, 3H, OC**H**$_3$), 3.03 (s, 3H, SO_2C**H**$_3$).
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):	δ 159.0 (**C**$_4$), 134.9 (**C**$_1$), 126.7 (**C**$_2$), 114.5 (**C**$_3$), 55.5 (O**C**H$_3$), 35.0 (SO_2**C**H$_3$).
FTIR (thin film) cm^{-1}:	3425 (s), 2091 (w), 1635 (s), 1508 (m), 1328 (m).
HRMS (DART) (*m/z*):	calc'd for $C_8H_{13}N_2O_3S$ $[M+H]^+$: 217.0641, found: 217.0642.
TLC (50% ethyl acetate in hexanes), R*f*:	0.26 (UV, CAM).
M.p.:	116–118 °C (decomp).



Diazine (±)-25:

A sample of silver trifluoromethanesulfonate (20.0 mg, 78.0 μmol, 2.00 equiv) was added to a solution of bromocyclotryptamine (±)-**S2** (16.8 mg, 39.0 μmol, 1 equiv), hydrazide **20** (12.8 mg, 59.0 μmol, 1.50 equiv), and DTBMP (20.1 mg, 98.0 μmol, 2.50 equiv) in dichloromethane (0.4 mL) at 22 °C. After 40 min, the off-white suspension was filtered through a pad of Celite. The filter cake was washed with ethyl acetate (5 mL) and the filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 20%→30% ethyl acetate in hexanes) to yield the diazene (±)-**25** (13.9 mg, 73.3%) as a bright yellow amorphous gum. Please see our alternative procedure for synthesis of diazene (±)-**25** and its full characterization data on page **S8**.

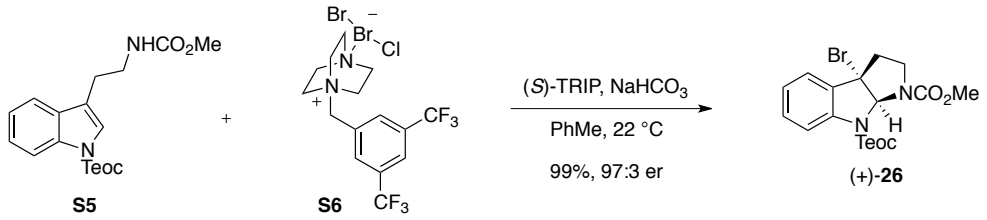


S4 **S5**

Tryptamine S5:

To a solution of 4-nitrophenyl (2-(trimethylsilyl)ethyl) carbonate[4] (7.17 g, 25.3 mmol, 1.50 equiv) in dichloromethane (170 mL) at 22 ºC under an air atmosphere were sequentially added tryptamine methyl carbamate **S4** (3.68 g, 16.9 mmol, 1 equiv), tetra-*n*-butylammonium hydrogen sulfate (570 mg, 1.69 mmol, 10.0 mol%), and powdered sodium hydroxide (2.02 g, 50.6 mmol, 3.00 equiv). After 13 h, the bright orange suspension was washed with an aqueous solution of sodium hydroxide (1N, 3 × 50 mL). The organic extract 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: 5%→20% ethyl acetate in hexanes) to afford tryptamine **S5** (6.10 g, 99.6%) as white solid. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):	δ 8.18 (d, *J* = 7.5 Hz, 1H, C_7**H**), 7.54 (d, *J* = 7.6 Hz, 1H, C_4**H**), 7.44 (s, 1H, C_{8a}**H**), 7.34 (app-t, *J* = 7.4 Hz, 1H, C_6**H**), 7.25 (app-t, *J* = 7.3 Hz, 1H, C_5**H**), 4.76 (br-s, 1H, N**H**), 4.58–4.37 (m, 2H, C_{10}**H**$_2$), 3.66 (s, 3H, $NHCO_2C$**H**$_3$), 3.51 (dd, *J* = 6.1, 12.4 Hz, 2H, C_2**H**$_2$), 2.91 (t, *J* = 6.7 Hz, 2H, C_3**H**$_2$), 1.32–1.14 (m, 2H, C_{11}**H**$_2$), 0.11 (s, 9H, (C_{12}**H**$_3$)$_3$).
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):	δ 157.1 ($NHCO_2CH_3$), 151.1 (**C**$_9$), 135.7 (**C**$_{7a}$), 130.4 (**C**$_{4a}$), 124.8 (**C**$_6$), 122.9 (2C, **C**$_5$, **C**$_{8a}$) 119.0 (**C**$_4$), 118.2 (**C**$_{3a}$), 115.5 (**C**$_7$), 65.7 (**C**$_{10}$), 52.2 ($NHCO_2$**C**H_3), 40.6 (**C**$_2$), 25.7 (**C**$_3$), 17.9 (**C**$_{11}$), 1.40 (**C**$_{12}$).
FTIR (thin film) cm^{-1}:	3356 (m), 2955 (s), 1734 (s), 1526 (m), 936 (w).
HRMS (DART) (*m/z*):	calc'd for $C_{18}H_{27}N_2O_4Si$ $[M+H]^+$: 363.1735, found: 363.1758.
TLC (30% ethyl acetate in hexanes), R*f*:	0.32 (UV, CAM).
M.p.:	68–70 °C (CH_2Cl_2).

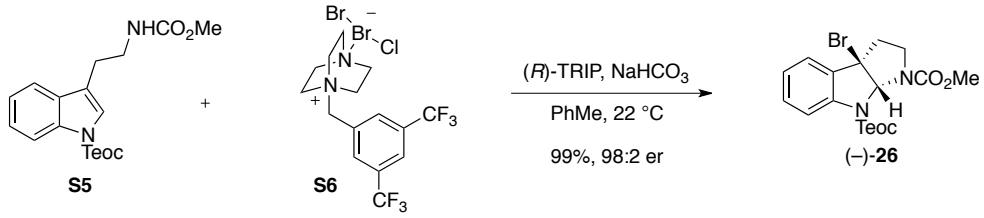


Bromocyclotryptamine (+)-26:

A sample of bromine salt **S6**[5] (2.88 g, 5.38 mmol, 1.30 equiv) was added to a suspension of tryptamine **S5** (1.50g, 4.14 mmol, 1 equiv), (*S*)-3,3′-Bis(2,4,6-triisopropyl-phenyl)-1,1′-binaphthyl-2,2′-diyl hydrogenphosphate[6] ((*S*)-TRIP, 309 mg, 410 μmol, 10.0 mol%), and sodium hydrogen carbonate (1.39 g, 16.6 mmol, 4.00 equiv) in toluene (83 mL) at 22 °C. After stirring for 24 h, the yellow suspension was diluted with a saturated aqueous sodium thiosulfate solution (20 mL) and was stirred vigorously for 10 min. The biphasic mixture was further diluted with deionized water (20 mL) and was then extracted with dichloromethane (3 × 40 mL). The combined organic extracts 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→15% acetone in hexanes) to afford bromocyclotryptamine (+)-**26** (1.81 g, 99.1%, 97:3 er) as a colorless amorphous gum.[7] The enantiomeric ratio was determined by chiral HPLC analysis (Chiralpak IA, 5% *i*PrOH / 95% hexanes, 1.0 mL/min, 254 nm, t_R (major) = 7.71 min, t_R (minor) = 11.2 min). Structural assignments were made using additional information from gCOSY, gHSQC and gHMBC experiments.

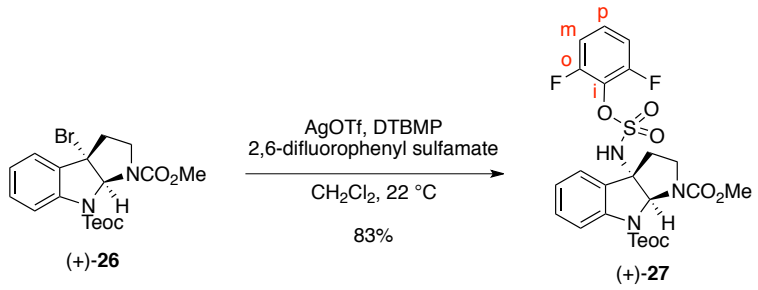
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):	δ 7.69 (d, *J* = 8.1 Hz, 1H, C_7**H**), 7.37 (dd, *J* = 0.8, 7.6 Hz, 1H, C_4**H**), 7.30 (td, *J* = 1.3, 7.9 Hz, 1H, C_6**H**), 7.10 (td, *J* = 1.0, 7.6 Hz, 1H, C_5**H**), 6.42 (s, 1H, C_{8a}**H**), 4.45–4.28 (m, 2H, C_{10}**H**$_2$), 3.81–3.74 (m, 1H, C_2**H**$_a$), 3.72 (s, 3H, $NHCO_2C$**H**$_3$), 2.92–2.80 (m, 2H, C_2**H**$_b$, C_3**H**$_a$), 2.80–2.69 (m, 1H, C_3**H**$_b$), 1.21–1.08 (m, 2H, C_{11}**H**$_2$), 0.06 (s, 9H, (C_{12}**H**$_3$)$_3$).
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):	δ 154.7 (NCO_2CH_3), 153.5 (**C**$_9$), 141.7 (**C**$_{7a}$), 132.3 (**C**$_{4a}$), 130.7 (**C**$_6$), 124.5 (**C**$_5$), 123.9 (**C**$_4$), 117.3 (**C**$_7$), 84.1 (**C**$_{8a}$), 64.9 (**C**$_{10}$), 62.1 (**C**$_{3a}$), 52.9 (NCO_2**C**H_3), 46.3 (**C**$_2$), 41.3 (**C**$_3$), 17.8 (**C**$_{11}$), –1.4 (**C**$_{12}$).
FTIR (thin film) cm^{-1}:	2954 (m), 2896 (w), 1717 (s), 1604 (w), 1402 (m).
HRMS (DART) (*m/z*):	calc'd for $C_{18}H_{26}BrN_2O_4Si$ $[M+H]^+$: 441.0840, found: 441.0848.
$[\alpha]_D^{24}$:	+183 (*c* = 0.58, CH_2Cl_2).

TLC (20% acetone in hexanes), R*f*: 0.43 (UV, CAM).



Bromocyclotryptamine (–)-26:

A sample of bromine salt **S6**[5] (2.88 g, 5.38 mmol, 1.30 equiv) was added to a suspension of tryptamine **S5** (1.50 g, 4.14 mmol, 1 equiv), (*R*)-TRIP[6] (309 mg, 410 μmol, 10.0 mol%), and sodium hydrogen carbonate (1.39 g, 16.6 mmol, 4.00 equiv) in toluene (83 mL) at 22 °C. After stirring for 24 h, the yellow suspension was diluted with a saturated aqueous sodium thiosulfate solution (20 mL) and was stirred vigorously for 10 min. The biphasic mixture was further diluted with deionized water (20 mL) and was then extracted with dichloromethane (3 × 40 mL). The combined organic extracts 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 bromocyclotryptamine (1.80 g, 98.5 %, 98:2 er) as a colorless amorphous gum.[7] The enantiomeric ratio was determined by chiral HPLC analysis (Chiralpak IA, 5% *i*PrOH / 95% hexanes, 1.0 mL/min, 254 nm, t_R (major) = 11.1 min, t_R (minor) = 7.63 min). For full characterization data for bromocyclotryptamine (–)-**26** ($[\alpha]_D^{24}$ = –182 (*c* = 0.63, CH_2Cl_2)) see previous procedure in this document.



Sulfamate ester (+)-27:

A sample of silver trifluoromethanesulfonate (139 mg, 540 μmol, 2.00 equiv) was added to a solution of bromocyclotryptamine (+)-**26** (119 mg, 270 μmol, 1 equiv), 2,6-difluorophenyl sulfamate[8] (82.7 mg, 405 μmol, 1.50 equiv), and DTBMP (139 mg, 675 μmol, 2.50 equiv) in dichloromethane (2.7 mL) at 22 °C. After 1 h, the off-white suspension was filtered through a pad of Celite. The filter cake was washed with ethyl acetate (5 mL) and the filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 10%→25% ethyl acetate in hexanes) to afford sulfamate ester (+)-**27** (128 mg, 83.2%) as a colorless amorphous gum. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.76 (d, J = 8.0 Hz, 1H, C_7**H**), 7.43 (d, J = 7.5 Hz, 1H, C_4**H**), 7.36 (app-t, J = 7.8 Hz, 1H, C_6**H**), 7.25–7.15 (m, 1H, C_p**H**), 7.11 (app-t, J = 7.5 Hz, 1H, C_5**H**), 6.98 (t, J = 8.1 Hz, 2H, C_m**H**), 6.52 (s, 1H, C_{8a}**H**), 5.77 (br-s, 1H, N**H**), 4.35–4.20 (m, 2H, C_{10}**H**$_2$), 3.90 (dd, J = 7.9, 10.6 Hz, 1H, C_2**H**$_a$), 3.68 (s, 3H, $NHCO_2C$**H**$_3$), 2.96 (dt, J = 7.6, 11.7 Hz, 1H, C_3**H**$_a$), 2.89–2.77 (m, 1H, C_2**H**$_b$), 2.49 (dd, J = 4.1, 11.8 Hz, 1H, C_3**H**$_b$), 1.07 (t, J = 8.8 Hz, 2H, C_{11}**H**$_2$), 0.03 (s, 9H, (C_{12}**H**$_3$)$_3$).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 156.1 (dd, J = 3.4, 253.7 Hz, **C**$_o$), 155.1 (NCO_2CH_3), 153.6 (**C**$_9$), 143.0 (**C**$_{7a}$), 131.2 (**C**$_6$), 129.5 (**C**$_{4a}$), 127.8 (t, J = 9.3 Hz, **C**$_p$), 126.9 (t, J = 15.6 Hz, **C**$_i$), 124.3 (**C**$_5$), 123.9 (**C**$_4$), 117.2 (**C**$_7$), 112.7 (dd, J = 4.6, 17.7 Hz, **C**$_m$), 79.8 (**C**$_{8a}$), 72.0 (**C**$_{3a}$), 64.8 (**C**$_{10}$), 52.9 (NCO_2**C**H_3), 45.3 (**C**$_2$), 34.2 (**C**$_2$), 17.8 (**C**$_{11}$), –1.5 (**C**$_{12}$).

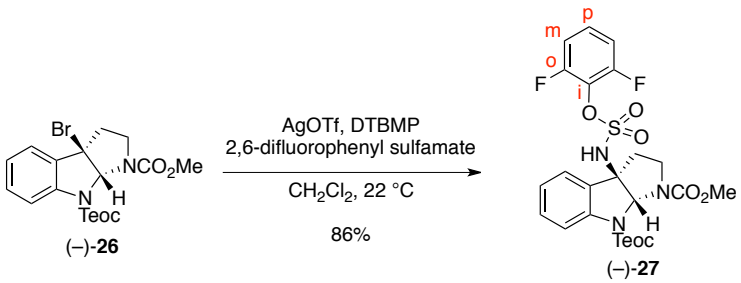
^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ –125.0 (C_6H_3**F**$_2$).

FTIR (thin film) cm^{-1}: 3173 (br-m), 2956 (m), 1683 (s), 1606 (m), 1098 (w).

HRMS (DART) (*m/z*): calc'd for $C_{24}H_{30}F_2N_3O_7SSi$ $[M+H]^+$: 570.1536, found: 570.1557.

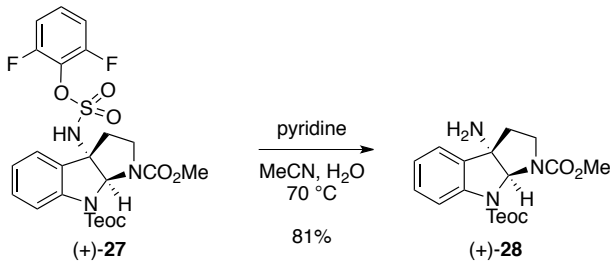
$[\alpha]_D^{24}$: +56 (*c* = 0.59, CH_2Cl_2).

TLC (30% ethyl acetate in hexanes), R*f*: 0.26 (UV, CAM).



Sulfamate ester (–)-27:

A sample of silver trifluoromethanesulfonate (334 mg, 1.30 mmol, 2.00 equiv) was added to a solution of bromocyclotryptamine (–)-**26** (287 mg, 650 μmol, 1 equiv), 2,6-difluorophenyl sulfamate[8] (199 mg, 975 μmol, 1.50 equiv), and DTBMP (334 mg, 1.63 mmol, 2.50 equiv) in dichloromethane (6.5 mL) at 22 °C. After 1 h, the off-white suspension was filtered through a pad of Celite. The filter cake was washed with ethyl acetate (15 mL) and the filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 10%→30% ethyl acetate in hexanes) to afford sulfamate ester (–)-**27** (320 mg, 86.4%) as a colorless amorphous gum. For full characterization data for sulfamate ester (–)-**27** ($[\alpha]_D^{24} = -55$ (*c* = 0.55, CH_2Cl_2)) see previous procedure in this document.



Amine (+)-28:

Pyridine (1.63 mL, 20.2 mmol, 20.0 equiv) was added to a solution of sulfamate ester (+)-**27** (576 mg, 1.01 mmol, 1 equiv) in a mixture of acetonitrile–water (2:1, 10 mL), via syringe at 22 °C. The reaction flask was fitted with a reflux condenser and heated to 70 ºC. After 23 h, the reaction mixture was allowed to cool to 22 °C. The mixture was diluted with dichloromethane (10 mL) and was washed with a saturated aqueous sodium bicarbonate solution (10 mL). The aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic extracts 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: 1→6% methanol in dichloromethane) to afford amine (+)-**28** (308 mg, 80.8%) as a colorless oil. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.73 (d, *J* = 8.1 Hz, 1H, C_7**H**), 7.35–7.27 (m, 2H, C_4**H**, C_6**H**), 7.12–7.05 (m, 1H, C_5**H**), 5.91 (s, 1H, C_{8a}**H**), 4.42–4.25 (m, 2H, C_{10}**H**$_2$), 3.91–3.80 (m, 1H, C_2**H**$_a$), 3.72 (s, 3H, $NHCO_2C$**H**$_3$), 2.90 (td, *J* = 5.5, 11.8 Hz, 1H, C_2**H**$_b$), 2.30 (dd, *J* = 5.4, 12.3 Hz, 1H, C_3**H**$_a$), 2.12 (td, *J* = 8.0, 12.2 Hz, 1H, C_3**H**$_b$), 1.73 (br-s, 2H, N**H**$_2$), 1.19–1.06 (m, 2H, C_{11}**H**$_2$), 0.06 (s, 9H, (C_{12}**H**$_3$)$_3$).

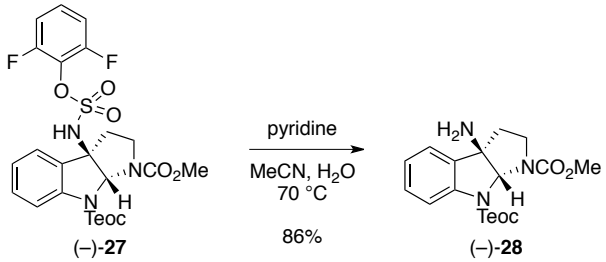
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 155.4 (N**C**O_2CH_3), 154.0 (**C**$_9$), 142.2 (**C**$_{7a}$), 134.2 (**C**$_{4a}$), 129.7 (**C**$_6$), 124.0 (**C**$_5$), 123.3 (**C**$_4$), 116.6 (**C**$_7$), 83.5 (**C**$_{8a}$), 69.3 (**C**$_{3a}$), 64.5 (**C**$_{10}$), 52.7 (NCO_2**C**H_3), 45.8 (**C**$_2$), 39.0 (**C**$_3$), 17.9 (**C**$_{11}$), –1.4 (**C**$_{12}$).

FTIR (thin film) cm^{-1}: 3370 (w), 2954 (m), 1701 (s), 1604 (w), 1405 (m).

HRMS (DART) (*m/z*): calc'd for $C_{18}H_{28}N_3O_4Si$ $[M+H]^+$: 378.1844, found: 378.1860.

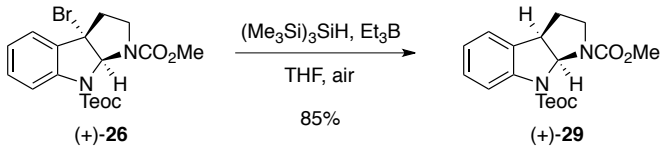
$[\alpha]_D^{24}$: +107 (*c* = 0.53, CH_2Cl_2).

TLC (6% methanol in dichloromethane), R*f*: 0.39 (UV, CAM).



Amine (–)-28:

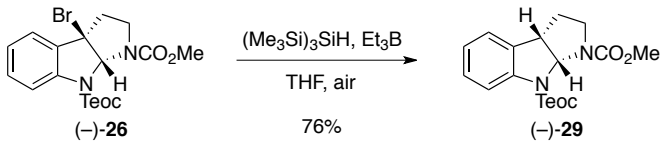
Pyridine (909 μL, 11.2 mmol, 20.0 equiv) was added to a solution of sulfamate ester (–)-**27** (320 mg, 562 μmol, 1 equiv) in a mixture of acetonitrile–water (2:1, 5.6 mL), via syringe at 22 °C. The reaction flask was fitted with a reflux condenser and heated to 70 ºC. After 24 h, the reaction mixture was allowed to cool to 22 °C. The mixture was diluted with dichloromethane (10 mL) and was washed with a saturated aqueous sodium bicarbonate solution (10 mL). The aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic extracts 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: 1→6% methanol in dichloromethane) to afford the amine (–)-**28** (182 mg, 85.8%) as a colorless oil. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments. For full characterization data for amine (–)-**28** ($[\alpha]_D^{24} = -106$ (*c* = 0.56, CH_2Cl_2)) see previous procedure in this document.



Cyclotryptamine (+)-29:

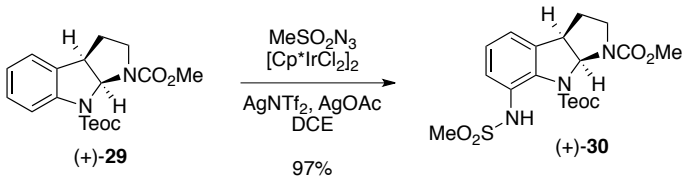
Triethylborane (1.0 M in THF, 210 µL, 210 µmol, 0.10 equiv) was slowly added via syringe to a solution of bromocyclotryptamine (+)-**26** (905 mg, 2.05 mmol, 1 equiv) and tris(trimethylsilyl)silane (1.90 mL, 6.15 mmol, 3.00 equiv) in tetrahydrofuran (21 mL) at 22 ºC under an air atmosphere. After 3 h, the reaction mixture was washed with a saturated aqueous sodium bicarbonate solution (20 mL), and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic extracts 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: 0→8% acetone in hexanes) to afford cyclotryptamine (+)-**29** (634 mg, 85.3%) as a colorless amorphous gum. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):	δ 7.69 (d, *J* = 8.0 Hz, 1H, C_7**H**), 7.21 (app-t, *J* = 7.8 Hz, 1H, C_6**H**), 7.15 (d, *J* = 7.4 Hz, 1H, C_4**H**), 7.01 (td, *J* = 0.7, 7.4 Hz, 1H, C_5**H**), 6.42 (d, 1H, C_{8a}**H**), 4.40–4.24 (m, 2H, C_{10}**H**$_2$), 4.00 (t, *J* = 7.3 Hz, 1H, C_{3a}**H**), 3.91–3.81 (m, 1H, C_2**H**$_a$), 3.72 (s, 3H, $NHCO_2C$**H**$_3$), 2.90 (td, *J* = 5.6, 11.6 Hz, 1H, C_2**H**$_b$), 2.21–2.09 (m, 1H, C_3**H**$_a$), 2.05 (dd, *J* = 5.5, 12.3 Hz, 1H, C_3**H**$_b$), 1.19–1.04 (m, 2H, C_{11}**H**$_2$), 0.05 (s, 9H, (C_{12}**H**$_3$)$_3$).
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):	δ 155.3 (N**C**O_2CH_3), 153.8 (**C**$_9$), 142.6 (**C**$_{7a}$), 131.7 (**C**$_{4a}$), 128.3 (**C**$_6$), 124.0 (**C**$_4$), 123.5 (**C**$_5$), 116.1 (**C**$_7$), 76.5 (**C**$_{8a}$), 64.3 (**C**$_{10}$), 52.7 (NCO_2**C**H_3), 45.4 (br, **C**$_{3a}$), 45.0 (**C**$_2$), 31.6 (**C**$_3$), 17.9 (**C**$_{11}$), –1.4 (**C**$_{12}$).
FTIR (thin film) cm^{-1}:	2952 (m), 2895 (w), 1699 (s), 1603 (w), 1401 (s), 1305 (m).
HRMS (DART) (*m/z*):	calc'd for $C_{18}H_{27}N_2O_4Si$ $[M+H]^+$: 363.1735, found: 363.1740.
$[\alpha]_D^{24}$:	+113 (*c* = 0.87, CH_2Cl_2).
TLC (20% acetone in hexanes), R*f*:	0.38 (UV, CAM).



Cyclotryptamine (–)-29:

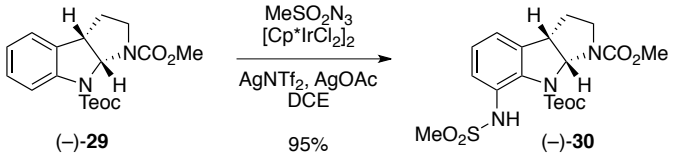
Triethylborane (1.0 M in THF, 320 μL, 320 μmol, 0.10 equiv) was slowly added via syringe to a solution of bromocyclotryptamine (–)-**26** (1.39 g, 3.16 mmol, 1 equiv) and tris(trimethylsilyl)silane (2.92 mL, 9.48 mmol, 3.00 equiv) in tetrahydrofuran (32 mL) at 22 ºC under an air atmosphere. After 3 h, the reaction mixture was washed with a saturated aqueous sodium bicarbonate solution (30 mL), and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic extracts 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: 0→8% acetone in hexanes) to afford cyclotryptamine (–)-**29** (866 mg, 75.6%) as a colorless amorphous gum. For full characterization data for cyclotryptamine (–)-**29** ($[\alpha]_D^{24} = -110$ (*c* = 0.52, CH_2Cl_2)) see previous procedure in this document.



Cyclotryptamine sulfonamide (+)-30:

To a suspension of cyclotryptamine (+)-**29** (96.6 mg, 266 μmol, 1 equiv), dichloro(pentamethylcyclopentadienyl)iridium (III) dimer ($[Cp^*IrCl_2]_2$, 17.0 mg, 21.3 μmol, 8.00 mol%), silver bis(trifluoromethanesulfonyl)imide (33.0 mg, 85.1 μmol, 0.320 equiv) and silver acetate (26.7 mg, 160 μmol, 0.600 equiv) in dichloroethane (0.27 mL) was added methanesulfonyl azide[9] (48.3 mg, 399 μmol, 1.50 equiv) via syringe. The reaction flask was sealed with a glass stopper and the reaction was allowed to stir for 20 h. The reaction mixture was filtered through a pad of Celite and the filter cake was rinsed with ethyl acetate (10 mL). The filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 20→40% ethyl acetate in hexanes) to afford cyclotryptamine sulfonamide (+)-**30** (117 mg, 96.5%) as a pale yellow amorphous gum. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

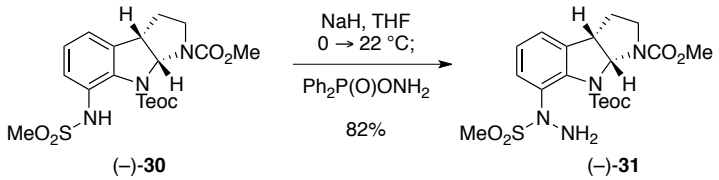
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):	δ 9.08 (s, 1H, N**H**SO_2CH_3), 7.42 (d, *J* = 8.0 Hz, 1H, C_6**H**), 7.20 (app-t, *J* = 7.8 Hz, 1H, C_5**H**), 7.10 (app-dt, *J* = 1.1, 7.5 Hz, 1H, C_4**H**), 6.32 (d, *J* = 5.7 Hz, 1H, C_{8a}**H**), 4.46–4.27 (m, 2H, C_{10}**H**$_2$), 4.06 (app-br-s, 1H, C_{3a}**H**), 3.65 (app-s, 4H, NCO_2C**H**$_3$, C_2**H**$_a$), 2.79 (app-dd, *J* = 9.6, 18.6 Hz, 1H, C_2**H**$_b$), 2.68 (s, 3H, $NHSO_2C$**H**$_3$), 2.26–2.14 (m, 2H, C_3**H**$_2$), 1.23–1.03 (m, 2H, C_{11}**H**$_2$), 0.05 (s, 9H, (C_{12}**H**$_3$)$_3$).
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):	δ 155.8 (**C**$_9$), 154.8 (N**C**O_2CH_3), 135.5 (**C**$_{4a}$), 135.4 (**C**$_{7a}$), 127.1 (2C, **C**$_7$, **C**$_5$), 125.8 (**C**$_6$), 121.6 (**C**$_4$), 77.8 (**C**$_{8a}$), 66.3 (**C**$_{10}$), 52.6 (NCO_2**C**H_3), 46.0 (**C**$_{3a}$), 45.2 (**C**$_2$), 38.7 ($NHSO_2$**C**H_3), 28.7 (**C**$_3$), 17.9 (**C**$_{11}$), –1.5 (**C**$_{12}$).
FTIR (thin film) cm^{-1}:	3163 (w), 2955 (m), 1711 (s), 1680 (s), 1160 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{19}H_{29}N_3NaO_6SSi$ $[M+Na]^+$: 478.1439, found 478.1430.
$[\alpha]_D^{24}$:	+226 (*c* = 0.61, CH_2Cl_2).
TLC (20% acetone in hexanes), R*f*:	0.20 (UV, CAM).



(–)-**29** (–)-**30**

Cyclotryptamine sulfonamide (–)-30:

To a suspension of cyclotryptamine (–)-**29** (278 mg, 767 μmol, 1 equiv), dichloro(pentamethylcyclopentadienyl)iridium (III) dimer ($[Cp^*IrCl_2]_2$, 48.9 mg, 61.4 μmol, 8.00 mol%), silver bis(trifluoromethanesulfonyl)imide (95.1 mg, 245 μmol, 0.320 equiv) and silver acetate (76.8 mg, 460 μmol, 0.600 equiv) in dichloroethane (0.77 mL) was added methanesulfonyl azide[9] (139 mg, 1.15 mmol, 1.50 equiv) via syringe. The reaction flask was sealed with a glass stopper and the reaction was allowed to stir for 20 h. The reaction mixture was filtered through a pad of Celite and the filter cake was rinsed with ethyl acetate (15 mL). The filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 20→40% ethyl acetate in hexanes) to afford cyclotryptamine sulfonamide (–)-**30** (331 mg, 94.7%) as a pale yellow amorphous gum. For full characterization data for cyclotryptamine sulfonamide (–)-**30** ($[\alpha]_D^{24} = –207$ (c = 0.68, CH_2Cl_2)) see previous procedure in this document.



Hydrazidocyclotryptamine (–)-31:

Cyclotryptamine sulfonamide (–)-**30** (2.02 g, 4.43 mmol, 1 equiv) was azeotropically dried by concentration from anhydrous benzene (3 × 5 mL) and the residue was dissolved in tetrahydrofuran (44 mL). The solution was cooled to 0 °C and a sample of sodium hydride (60% in mineral oil, 230 mg, 5.76 mmol, 1.30 equiv) was added in one portion. The ice-water bath was removed and after 30 min, a sample of *O*-(diphenylphosphinyl)hydroxylamine (1.34 g, 5.76 mmol, 1.30 equiv) was added in one portion. After 1 h, the reaction mixture was diluted with ethyl acetate (30 mL), was washed with a mixture of saturated aqueous sodium bicarbonate and water (10:1 v/v, 25 mL), and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts 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 hydrazidocyclotryptamine (–)-**31** (1.70 g, 81.5%) as an orange amorphous gum.[10] Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.31 (app-p, J = 3.7 Hz, 1H, C_5**H**), 7.20–7.14 (m, 2H, C_4**H**, C_6**H**), 6.27 (br-d, J = 5.7 Hz, 1H, C_{8a}**H**), 4.50 (br-s, 2H, N**H**$_2$), 4.29 (t, J = 8.9 Hz, 2H, C_{10}**H**$_2$), 4.02 (t, J = 6.0 Hz, 1H, C_{3a}**H**), 3.66 (s, 3H, NCO_2C**H**$_3$), 3.55 (br-s, 1H, C_2**H**$_a$), 3.04 (s, 3H, SO_2C**H**$_3$), 2.79 (td, J = 6.1, 11.0 Hz, 1H, C_2**H**$_b$), 2.21–2.01 (m, 2H, C_3**H**$_2$), 1.22–1.02 (m, 2H, C_{11}**H**$_2$), 0.03 (s, 9H, (C_{12}**H**$_3$)$_3$).

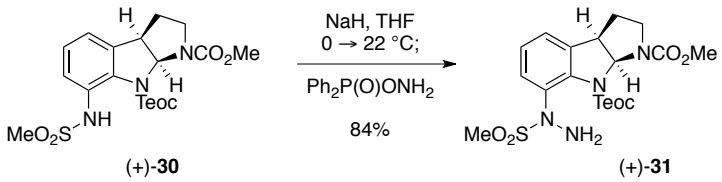
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 154.9 (**C**$_9$), 154.6 (N**C**O_2CH_3), 140.0 (**C**$_{7a}$), 136.7 (**C**$_{4a}$), 133.3 (**C**$_7$), 126.8 (**C**$_5$), 123.9 (2C, **C**$_4$, **C**$_6$), 78.1 (**C**$_{8a}$), 65.2 (**C**$_{10}$), 52.5 (NCO_2**C**H_3), 46.1 (br, **C**$_{3a}$), 44.8 (**C**$_2$), 37.7 (SO_2**C**H_3), 29.3 (**C**$_3$), 17.9 (**C**$_{11}$), –1.5 (**C**$_{12}$).

FTIR (thin film) cm^{-1}: 3366 (m), 2954 (m), 1700 (s), 1653 (w), 1559 (w), 1457 (s), 1337 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{19}H_{30}N_4NaO_6SSi$ $[M+Na]^+$: 493.1548, found 493.1519.

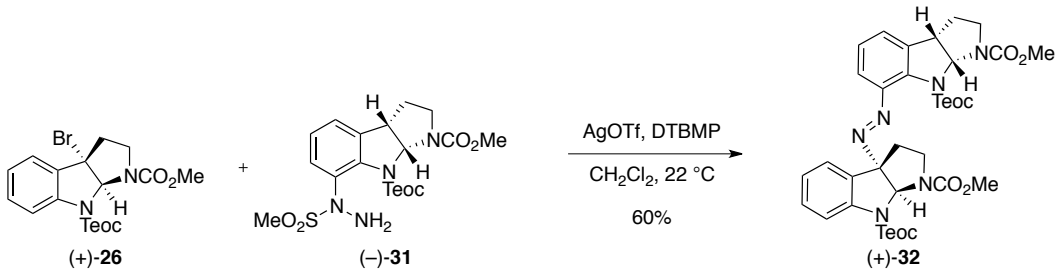
$[\alpha]_D^{24}$: –119 (*c* = 0.49, CH_2Cl_2).

TLC (50% ethyl acetate in hexanes), R*f*: 0.18 (UV, CAM).



Hydrazidocyclotryptamine (+)-31:

Cyclotryptamine sulfonamide (+)-**30** (106 mg, 233 μmol, 1 equiv) was azeotropically dried by concentration from anhydrous benzene (3 × 1 mL) and the residue was dissolved in tetrahydrofuran (2.3 mL). The solution was cooled to 0 °C and a sample of sodium hydride (60% in mineral oil, 12.1 mg, 303 μmol, 1.30 equiv) was added in one portion. The ice-water bath was removed and after 30 min, a sample of *O*-(diphenylphosphinyl)hydroxylamine (70.7 mg, 303 μmol, 1.30 equiv) was added in one portion. After 1 h, the reaction mixture was diluted with ethyl acetate (2 mL), washed with mixture of saturated aqueous sodium bicarbonate and water (10:1 v/v, 5 mL) and the aqueous layer was extracted with ethyl acetate (3 × 3 mL). The combined organic extracts 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 hydrazidocyclotryptamine (+)-**31** (91.8 mg, 83.7%) as an orange amorphous gum.[10] For full characterization data for hydrazidocyclotryptamine (+)-**31** ($[\alpha]_D^{24}$ = +132 (*c* = 0.50, CH_2Cl_2)) see previous procedure in this document.



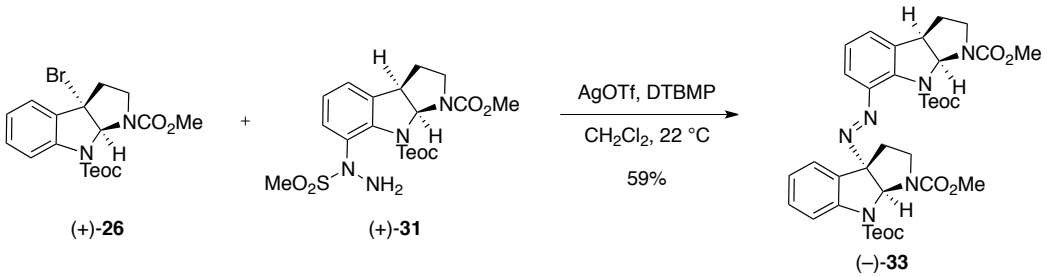
Diazene dimer (+)-32:

A sample of silver trifluoromethanesulfonate (827 mg, 3.22 mmol, 2.00 equiv) was added to a solution of bromocyclotryptamine (+)-**26** (711 mg, 1.61 mmol, 1 equiv), hydrazidocyclotryptamine (–)-**31** (983 mg, 2.09 mmol, 1.30 equiv), and DTBMP (828 mg, 4.03 mmol, 2.50 equiv) in dichloromethane (16 mL) at 22 °C. After 1 h, the off-white suspension was filtered through a pad of Celite. The filter cake was washed with ethyl acetate (25 mL) and the filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 20%→35% ethyl acetate in hexanes) to yield the diazene dimer (+)-**32** (725 mg, 60.0%) as a bright yellow amorphous gum. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.81 (d, J = 8.1 Hz, 1H, C_7**H**), 7.47 (d, J = 7.4 Hz, 1H, C_4**H**), 7.30 (app-td, J = 1.3, 7.9 Hz, 1H, C_6**H**), 7.25–7.19 (m, 2H, $C_{4'}$**H**, $C_{6'}$**H**) 7.16–7.10 (m, 1H, $C_{5'}$**H**), 7.07 (app-t, J = 7.3 Hz, 1H, C_5**H**), 6.87 (br-s, 1H, C_{8a}**H**), 6.37 (br-s, 1H, $C_{8a'}$**H**), 4.32 (ddd, J = 1.7, 5.4, 7.7 Hz, 2H, C_{10}**H**$_2$ or $C_{10'}$**H**$_2$), 4.12–4.03 (m, 4H, C_2**H**$_a$, $C_{3a'}$**H**, C_{10}**H**$_2$ or $C_{10'}$**H**$_2$), 3.79 (br-s, 3H, N_1CO_2C**H**$_3$ or $N_{1'}CO_2C$**H**$_3$), 3.75 (app-s, 4H, $C_{2'}$**H**$_a$, N_1CO_2C**H**$_3$ or $N_{1'}CO_2C$**H**$_3$), 3.09 (td, J = 5.3, 11.7 Hz, 1H, C_2**H**$_b$), 2.94 (td, J = 6.8, 10.9 Hz, 1H, $C_{2'}$**H**$_b$), 2.46 (dd, J = 11.8, 19.8 Hz, 1H, C_3**H**$_a$), 2.35 (dd, J = 4.8, 12.2 Hz, 1H, C_3**H**$_b$), 2.30–2.13 (m, 2H, $C_{3'}$**H**$_2$), 1.13 (dd, J = 6.9, 10.6 Hz, 2H, C_{11}**H**$_2$ or $C_{11'}$**H**$_2$), 0.86 (br-s, 2H, C_{11}**H**$_2$ or $C_{11'}$**H**$_2$), 0.04 (s, 9H, (C_{12}**H**$_3$)$_3$ or ($C_{12'}$**H**$_3$)$_3$), –0.05 (s, 9H, (C_{12}**H**$_3$)$_3$ or ($C_{12'}$**H**$_3$)$_3$).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 155.3 (2C, N_1**C**O_2CH_3, $N_{1'}$**C**O_2CH_3), 154.6 (**C**$_9$ or **C**$_{9'}$), 153.6 (**C**$_9$ or **C**$_{9'}$), 143.3 (**C**$_{7a}$), 141.5 (**C**$_{7'}$), 139.5 (**C**$_{7a'}$), 135.7 (**C**$_{4a'}$), 129.9 (**C**$_6$), 129.5 (**C**$_{4a}$), 125.8 (**C**$_4$), 125.6 (**C**$_{5'}$), 125.3 (**C**$_{4'}$), 123.5 (**C**$_5$), 117.2 (**C**$_{6'}$), 115.9 (**C**$_7$), 88.8 (**C**$_{3a}$), 79.0 (2C, **C**$_{8a}$, **C**$_{8a'}$), 64.6 (**C**$_{10}$ or **C**$_{10'}$), 64.3 (**C**$_{10}$ or **C**$_{10'}$), 52.8 (N_1CO_2**C**H_3 or $N_{1'}CO_2$**C**H_3), 52.6 (N_1CO_2**C**H_3 or

	$N_{1'}CO_2\mathbf{C}H_3$), 46.4 ($\mathbf{C}_{3a'}$), 45.8 ($\mathbf{C}_2$), 45.2 ($\mathbf{C}_{2'}$), 36.7 ($\mathbf{C}_3$), 29.4 ($\mathbf{C}_{3'}$), 17.9 ($\mathbf{C}_{11}$ or $\mathbf{C}_{11'}$), 17.7 ($\mathbf{C}_{11}$ or $\mathbf{C}_{11'}$), –1.5 (2C, $\mathbf{C}_{12}$, $\mathbf{C}_{12'}$).
FTIR (thin film) cm^{-1}:	2955 (m), 1701 (s), 1603 (w), 1448 (m), 1396 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{36}H_{50}N_6NaO_8Si_2$ $[M+Na]^+$: 773.3121, found 773.3104.
$[\alpha]_D^{24}$:	+361 (*c* = 0.61, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.33 (UV, CAM).



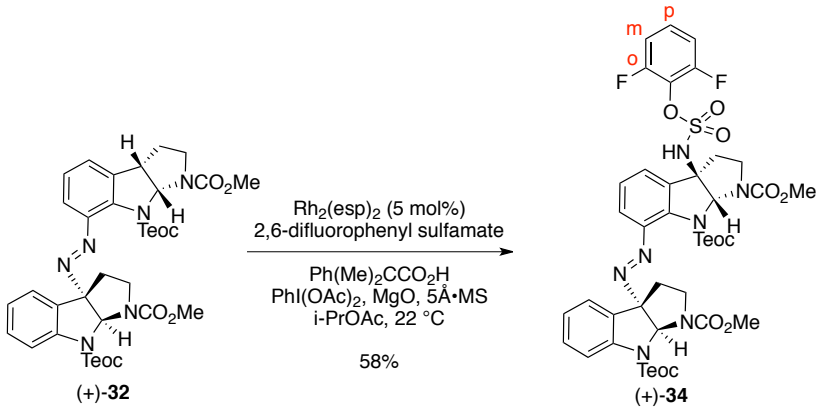
Diazene dimer (–)-33:

A sample of silver trifluoromethanesulfonate (673 mg, 2.62 mmol, 2.00 equiv) was added to a solution of bromocyclotryptamine (+)-**26** (578 mg, 1.31 mmol, 1 equiv), hydrazidocyclotryptamine (+)-**31** (802 mg, 1.70 mmol, 1.30 equiv), and DTBMP (674 mg, 3.28 mmol, 2.50 equiv) in dichloromethane (13 mL) at 22 °C. After 1 h, the off-white suspension was filtered through a pad of Celite. The filter cake was washed with ethyl acetate (20 mL) and the filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 25%→35% ethyl acetate in hexanes) to yield the diazene dimer (–)-**33** (582 mg, 59.2%) as a bright yellow amorphous gum. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.80 (d, J = 8.1 Hz, 1H, C_7**H**), 7.33–7.20 (m, 3H, C_6**H**, C_4**H**, $C_{4'}$**H**), 7.17 (d, J = 7.7 Hz, 1H, $C_{6'}$**H**), 7.15–7.08 (m, 1H, $C_{5'}$**H**), 7.03 (app-t, J = 7.5 Hz, 1H, C_5**H**), 6.89 (s, 1H, C_{8a}**H**), 6.41 (br-s, 1H, $C_{8a'}$**H**), 4.43–4.31 (m, 2H, C_{10}**H**$_2$ or $C_{10'}$**H**$_2$), 4.31–4.23 (m, 1H, C_{10}**H**$_a$ or $C_{10'}$**H**$_a$), 4.14–3.96 (m, 3H, C_2**H**$_a$, $C_{3a'}$**H**, C_{10}**H**$_b$ or $C_{10'}$**H**$_b$), 3.89–3.67 (m, 7H, $C_{2'}$**H**$_a$, N_1CO_2C**H**$_3$, $N_{1'}CO_2C$**H**$_3$), 3.10 (td, J = 5.2, 11.7 Hz, 1H, C_2**H**$_b$), 2.93 (td, J = 6.9, 10.8 Hz, 1H, $C_{2'}$**H**$_b$), 2.62–2.46 (m, 1H, C_3**H**$_a$), 2.37 (dd, J = 5.1, 12.6 Hz, 1H, C_3**H**$_b$), 2.28–2.13 (m, 2H, $C_{3'}$**H**$_2$), 1.15 (dd, J = 6.8, 10.8 Hz, 2H, C_{11}**H**$_2$ or $C_{11'}$**H**$_2$), 0.96 (br-s, 2H, C_{11}**H**$_2$ or $C_{11'}$**H**$_2$), 0.06 (s, 9H, (C_{12}**H**$_3$)$_3$ or ($C_{12'}$**H**$_3$)$_3$), –0.02 (s, 9H, (C_{12}**H**$_3$)$_3$ or ($C_{12'}$**H**$_3$)$_3$).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 155.4 (N_1**C**O_2CH_3 or $N_{1'}$**C**O_2CH_3), 155.3 (N_1**C**O_2CH_3 or $N_{1'}$**C**O_2CH_3), 154.9 (**C**$_9$ or **C**$_{9'}$), 153.8 (**C**$_9$ or **C**$_{9'}$), 143.5 (**C**$_{7a}$), 141.6 (**C**$_{7'}$), 139.7 (**C**$_{7a'}$), 135.7 (**C**$_{4a'}$), 130.0 (**C**$_6$), 129.2 (**C**$_{4a}$), 125.7 (**C**$_{5'}$), 125.4 (**C**$_4$ or **C**$_{4'}$), 125.3 (**C**$_4$ or **C**$_{4'}$), 123.5 (**C**$_5$), 117.1 (**C**$_{6'}$), 116.2 (**C**$_7$), 88.9 (**C**$_{3a}$), 79.6 (**C**$_{8a}$), 79.1 (**C**$_{8a'}$), 64.8 (**C**$_{10}$ or **C**$_{10'}$), 64.5 (**C**$_{10}$ or **C**$_{10'}$), 52.8 (N_1CO_2**C**H_3 or $N_{1'}CO_2$**C**H_3), 52.7 (N_1CO_2**C**H_3 or $N_{1'}CO_2$**C**H_3), 46.4 (**C**$_{3a'}$), 46.1 (**C**$_2$), 45.2 (**C**$_{2'}$), 35.9

	(**C**$_3$), 29.6 (**C**$_{3'}$), 17.9 (2C, **C**$_{11}$, **C**$_{11'}$), –1.4 (**C**$_{12}$ or **C**$_{12'}$), –1.5 (**C**$_{12}$ or **C**$_{12'}$).
FTIR (thin film) cm^{-1}:	2954 (m), 1707 (s), 1603 (w), 1397 (m), 1259 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{36}H_{50}N_6NaO_8Si_2$ $[M+Na]^+$: 773.3121, found 773.3115.
$[\alpha]_D^{24}$:	–86 (*c* = 0.61, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.32 (UV, CAM).

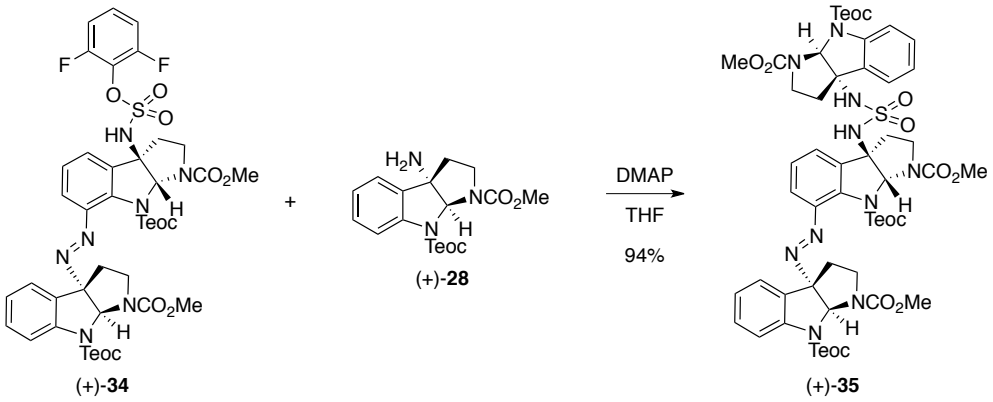


Diazene dimer sulfamate (+)-34:

A round-bottom flask equipped with a stir bar was charged with crushed 5Å molecular sieves (133 mg, 200 mg/mmol of (+)-**32**) and magnesium oxide (107 mg, 2.66 mmol, 4.00 equiv). The flask and its contents were flame-dried under reduced pressure for 5 min. The reaction vessel was allowed to cool to 22 °C and was then back filled with argon. Solid 2,6-difluorophenyl sulfamate[8] (177 mg, 866 μmol, 1.30 equiv), 2-methyl-2-phenylpropionic acid (54.7 mg, 333 μmol, 0.500 equiv), and $Rh_2(esp)_2$ (25.0 mg, 33.0 μmol, 5.00 mol%) were added sequentially. A solution of diazene dimer (+)-**32** (500 mg, 666 μmol, 1 equiv) in isopropyl acetate (1.33 mL) was added via syringe at 22 °C. The resulting mixture was allowed to stir for 5 min. A sample of (diacetoxyiodo)benzene (428 mg, 1.33 mmol, 2.00 equiv) was then added and the green suspension was allowed to stir vigorously at 22 °C. After 22 h, the reaction mixture was filtered through a pad of Celite and the filter cake was rinsed with ethyl acetate (5 mL). The filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 10→25% acetone in hexanes) to afford diazene dimer sulfamate (+)-**34** (371 mg, 58.1%) as a bright yellow amorphous gum. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.80 (d, J = 8.1 Hz, 1H, C_7**H**), 7.53–7.42 (m, 2H, C_4**H**, $C_{4'}$**H**), 7.38 (d, J = 7.8 Hz, 1H, $C_{6'}$**H**), 7.35–7.28 (m, 1H, C_6**H**), 7.25–7.14 (m, 2H, $C_{5'}$**H**, C_p**H**), 7.06 (app-t, J = 7.4 Hz, 1H, C_5**H**), 6.98 (t, J = 8.2 Hz, 2H, C_m**H**), 6.83 (s, 1H, C_{8a}**H**), 6.56 (br-s, 1H, $C_{8a'}$**H**), 5.74 (br-s, 1H, N**H**), 4.39–4.23 (m, 2H, C_{10}**H**$_2$ or $C_{10'}$**H**$_2$), 4.13–3.99 (m, 2H, C_2**H**$_a$, C_{10}**H**$_a$ or $C_{10'}$**H**$_a$), 3.89–3.80 (m, 1H, $C_{2'}$**H**$_a$), 3.77 (s, 3H, N_1CO_2C**H**$_3$ or $N_{1'}CO_2C$**H**$_3$), 3.73 (app-s, 4H, C_{10}**H**$_b$ or $C_{10'}$**H**$_b$, N_1CO_2C**H**$_3$ or $N_{1'}CO_2C$**H**$_3$), 3.08 (td, J = 5.0, 11.6 Hz, 1H, C_2**H**$_b$), 2.91 (br-d, J = 19.3 Hz, 2H, $C_{2'}$**H**$_b$, $C_{3'}$**H**$_a$) 2.58–2.41 (m, 2H, $C_{3'}$**H**$_b$, C_3**H**$_a$), 2.35 (dd, J = 4.2, 11.9 Hz, 1H, C_3**H**$_b$), 1.13 (dd, J = 6.7, 10.7 Hz, 2H, C_{11}**H**$_2$ or $C_{11'}$**H**$_2$), 0.84 (br-s, 2H,

	$C_{11}\mathbf{H}_2$ or $C_{11'}\mathbf{H}_2$), 0.03 (s, 9H, $(C_{12}\mathbf{H}_3)_3$ or $(C_{12'}\mathbf{H}_3)_3$), –0.02 (s, 9H, $(C_{12}\mathbf{H}_3)_3$ or $(C_{12'}\mathbf{H}_3)_3$).
^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):	δ 156.0 (dd, *J* = 3.3, 253.8 Hz, $\mathbf{C}_o$), 155.3 (2C, $N_1\mathbf{C}O_2CH_3$, $N_{1'}\mathbf{C}O_2CH_3$), 154.2 ($\mathbf{C}_9$ or $\mathbf{C}_{9'}$), 153.6 ($\mathbf{C}_9$ or $\mathbf{C}_{9'}$), 143.3 ($\mathbf{C}_{7a}$), 141.7 ($\mathbf{C}_{7'}$), 140.0 ($\mathbf{C}_{7a'}$), 133.1 ($\mathbf{C}_{4a'}$), 129.9 ($\mathbf{C}_6$), 129.4 ($\mathbf{C}_{4a}$), 127.7 (t, *J* = 9.1 Hz, $\mathbf{C}_p$), 126.8 (t, *J* = 15.7 Hz, $\mathbf{C}_i$), 126.0 ($\mathbf{C}_{5'}$), 125.7 ($\mathbf{C}_4$), 125.6 ($\mathbf{C}_{4'}$), 123.5 ($\mathbf{C}_5$), 119.8 ($\mathbf{C}_{6'}$), 115.9 ($\mathbf{C}_7$), 112.6 (d, *J* = 22.0 Hz, $\mathbf{C}_m$), 89.0 ($\mathbf{C}_{3a}$), 81.6 ($\mathbf{C}_{8a'}$), 78.9 ($\mathbf{C}_{8a}$), 71.5 ($\mathbf{C}_{3a'}$), 65.0 ($\mathbf{C}_{10}$ or $\mathbf{C}_{10'}$), 64.4 ($\mathbf{C}_{10}$ or $\mathbf{C}_{10'}$), 52.8 ($N_1CO_2\mathbf{C}H_3$ or $N_{1'}CO_2\mathbf{C}H_3$), 52.7 ($N_1CO_2\mathbf{C}H_3$ or $N_{1'}CO_2\mathbf{C}H_3$), 45.8 ($\mathbf{C}_2$), 44.9 ($\mathbf{C}_{2'}$), 36.4 ($\mathbf{C}_3$), 33.6 ($\mathbf{C}_{3'}$), 17.8 ($\mathbf{C}_{11}$ or $\mathbf{C}_{11'}$), 17.5 ($\mathbf{C}_{11}$ or $\mathbf{C}_{11'}$), –1.5 ($\mathbf{C}_{12}$ or $\mathbf{C}_{12'}$), –1.6 ($\mathbf{C}_{12}$ or $\mathbf{C}_{12'}$).
^{19}F NMR (282 MHz, $CDCl_3$, 25 °C):	δ –124.4 (s, $C_6H_3\mathbf{F}_2$).
FTIR (thin film) cm^{-1}:	3171 (br-m), 2955 (s), 1717 (s), 1606 (m), 1302 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{42}H_{53}F_2N_7NaO_{11}SSi_2$ $[M+Na]^+$: 980.2923, found 980.2904.
$[\alpha]_D^{24}$:	+282 (*c* = 0.77, CH_2Cl_2).
TLC (20% acetone in hexanes), R*f*:	0.10 (UV, CAM).



Diazene dimer mixed sulfamide (+)-35:

A sample of 4-(dimethylamino)pyridine (98.6 mg, 807 μmol, 2.20 equiv) was added to a solution of diazene dimer sulfamate (+)-**34** (352 mg, 367 μmol, 1 equiv) and amine (+)-**28** (153 mg, 404 μmol, 1.10 equiv) in tetrahydrofuran (3.7 mL) at 22 ºC. After 24 h, the bright yellow solution was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 15%→70% ethyl acetate in hexanes) to afford diazene dimer mixed sulfamide (+)-**35** (416 mg, 94.0%) as a bright yellow amorphous gum. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

^{1}H NMR (400 MHz, C_6D_6, 70 °C): δ 8.17 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.24–7.18 (m, 2H), 7.15–7.10 (m, 3H), 7.03–6.95 (m, 2H), 6.90 (app-t, *J* = 7.3 Hz, 1H), 6.76 (s, 1H), 6.68 (s, 1H), 5.47 (s, 1H), 5.26 (s, 1H), 4.48–4.30 (m, 5H), 4.14 (td, *J* = 6.2, 10.7 Hz, 1H), 4.01–3.91 (m, 1H), 3.66 (app-s, 5H), 3.61 (s, 3H), 3.52 (s, 3H), 2.96 (td, *J* = 4.9, 11.5 Hz, 1H), 2.65–2.54 (m, 2H), 2.43 (app-dd, *J* = 11.9, 20.4 Hz, 1H), 2.19 (dd, *J* = 4.4, 12.2 Hz, 1H), 2.12–1.90 (m, 4H), 1.20–1.00 (m, 6H), 0.00 (s, 9H), –0.03 (app-s, 18H).

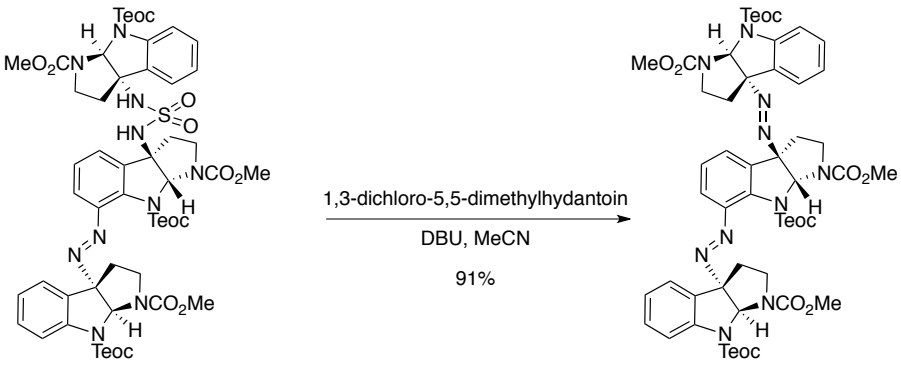
^{13}C NMR (100 MHz, C_6D_6, 70 °C): δ 155.7, 155.3, 155.2, 155.0, 154.3, 153.8, 144.4, 144.0, 142.6, 141.0, 134.5, 130.9, 130.4, 130.3, 130.2, 126.2, 125.8, 125.6, 124.7, 123.9, 123.6, 119.6, 117.5, 116.6, 89.9, 82.3, 80.2, 79.6, 71.4 (2C), 65.3, 64.8, 64.2, 52.4 (3C), 46.0, 45.1, 44.7, 37.2, 37.1, 36.7, 18.2 (2C), 18.1, –1.5 (3C).

FTIR (thin film) cm^{-1}: 3233 (m), 2955 (s), 1716 (s), 1604 (m), 1318 (w).

HRMS (ESI) (*m/z*): calc'd for $C_{54}H_{76}N_{10}NaO_{14}SSi_3$ $[M+Na]^+$: 1227.4463, found: 1227.4460.

$[\alpha]_D^{24}$: +264 (*c* = 0.67, CH_2Cl_2).

TLC (60% ethyl acetate in hexanes), R*f*: 0.25 (UV, CAM).



(+)-**35** (+)-**36**

Bis-diazene trimer (+)-36:

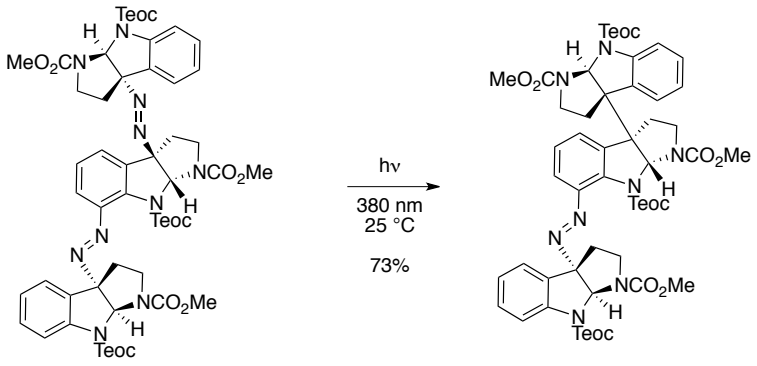
To a solution of diazene dimer mixed sulfamide (+)-**35** (302 mg, 251 μmol, 1 equiv) in acetonitrile (12.6 mL) at 22 °C was added via syringe 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 113 μL, 753 μmol, 3.00 equiv) followed immediately by 1,3-dichloro-5,5-dimethylhydantoin (124 mg, 628 μmol, 2.50 equiv) in a single portion. After 1 h, the mixture was diluted with dichloromethane (10 mL) and was washed with a saturated aqueous potassium carbonate–water solution (1:1, 10 mL). The aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic extracts 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 bis-diazene trimer (+)-**36** (260 mg, 90.9%) as a bright yellow amorphous gum. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

^{1}H NMR (400 MHz, CD_3CN, 50 °C): δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 7.1 Hz, 1H), 7.40–7.35 (m, 1H), 7.35–7.27 (m, 2H), 7.27–7.21 (m, 2H), 7.15–7.07 (m, 2H), 7.02 (app-td, *J* = 0.8, 7.5 Hz, 1H), 6.73 (s, 1H), 6.46 (s, 1H), 6.37 (s, 1H), 4.37–4.21 (m, 4H), 4.11–3.97 (m, 2H), 3.93–3.80 (m, 2H), 3.80–3.74 (m, 1H), 3.70 (app-s, 6H), 3.65 (s, 3H), 3.08–2.87 (m, 3H), 2.57 (dd, *J* = 5.3, 12.5 Hz, 1H), 2.53–2.38 (m, 3H), 2.36–2.18 (m, 2H), 1.16–1.02 (m, 4H), 0.91–0.73 (m, 2H), 0.07 (s, 9H), 0.05 (s, 9H), –0.01 (s, 9H).

^{13}C NMR (100 MHz, CD_3CN, 50 °C): δ 156.2, 156.1 (2C), 155.3, 154.5, 154.4, 144.6 (2C), 143.3, 140.9, 134.9, 131.2, 131.1, 131.0, 130.2, 127.6, 127.1, 126.8, 126.0, 124.7, 124.6, 120.3, 117.3, 116.9, 90.0, 89.7, 89.4, 81.8, 79.7, 79.6, 65.7, 65.2 (2C), 53.4, 53.3 (2C), 46.9, 46.7 (2C), 37.3, 36.1, 33.6, 18.7 (2C), 18.6, –1.1, –1.2 (2C).

FTIR (thin film) cm^{-1}: 2954 (m), 2896 (m), 1713 (s), 1603 (w), 1447 (m).

HRMS (ESI) (*m/z*):	calc'd for $C_{54}H_{74}N_{10}NaO_{12}Si_3$ $[M+Na]^+$: 1161.4688, found: 1161.4704.
$[\alpha]_D^{24}$:	+297 (*c* = 0.43, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.43 (UV, CAM).



(+)-**36** (+)-**37**

Mono-diazene trimer (+)-37:

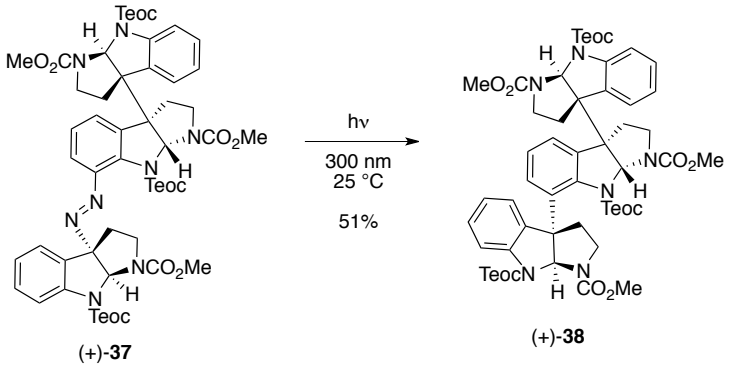
A solution of bis-diazene trimer (+)-**36** (397 mg, 348 μmol, 1 equiv) in dichloromethane (30 mL) was concentrated under reduced pressure in a 1 L round-bottom flask to provide a thin film of diazene coating the flask. The flask was backfilled with argon and irradiated in a Rayonet photoreactor equipped with 16 radially distributed (r=12.7 cm) 25 W lamps (λ=380 nm) at 25 ºC. After 15 h, the lamps were turned off and the resulting residue was purified by flash column chromatography on silica gel (eluent: 20→60% ethyl acetate in hexanes) to afford mono-diazene trimer (+)-**37** (282 mg, 72.9%) as a bright yellow amorphous gum. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

^{1}H NMR (400 MHz, CD_3CN, 60 °C): δ 7.75 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.32 (app-ddd, *J* = 1.3, 7.9, 8.8 Hz, 1H), 7.28–7.14 (m, 4H), 7.09 (app-td, *J* = 0.9, 7.5 Hz, 1H), 6.77 (app-t, *J* = 7.5 Hz, 1H), 6.66 (s, 1H), 6.40 (br-d, *J* = 6.6 Hz, 1H), 6.22 (s, 1H), 6.06 (s, 1H), 4.40–4.26 (m, 3H), 4.26–4.15 (m, 1H), 3.98 (ddd, *J* = 2.6, 6.0, 11.2 Hz, 1H), 3.88–3.72 (m, 3H), 3.68 (app-d, *J* = 1.9 Hz, 9H), 3.63–3.51 (m, 1H), 3.06–2.93 (m, 1H), 2.83–2.67 (m, 2H), 2.50–2.40 (m, 2H), 2.40–2.28 (m, 2H), 2.28–2.16 (m, 2H), 1.20–1.01 (m, 4H), 0.96–0.80 (m, 2H), 0.09 (s, 9H), 0.07 (s, 9H), 0.05 (s, 9H).

^{13}C NMR (100 MHz, CD_3CN, 60 °C):[11] δ 156.3, 155.9, 155.8, 154.6, 154.3, 154.2, 144.7, 144.5, 143.2, 140.7, 137.3, 132.2, 131.3, 131.1, 130.4, 127.0, 126.8, 125.3, 124.8, 124.7, 119.7, 117.3, 117.0, 90.1, 81.7, 79.9, 79.8, 65.8, 65.4, 65.2, 62.7, 61.8, 53.4 (2C), 53.3, 46.9 (2C), 46.5, 37.6, 35.2, 34.3, 18.9, 18.8, 18.5, –1.1 (3C).

FTIR (thin film) cm^{-1}: 2954 (m), 1717 (s), 1602 (w), 1448 (m), 1251 (m).

HRMS (ESI) (*m/z*):	calc'd for $C_{54}H_{74}N_8NaO_{12}Si_3$ $[M+Na]^+$: 1133.4626, found: 1133.4646.
$[\alpha]_D^{24}$:	+370 (*c* = 0.57, CH_2Cl_2).
TLC (70% ethyl acetate in hexanes), R*f*:	0.35 (UV, CAM).



Cyclotryptamine trimer (+)-38:

A solution of mono-diazene trimer (+)-**37** (52.9 mg, 47.6 μmol, 1 equiv) in dichloromethane (3 mL) was concentrated under reduced pressure in a 500-mL round-bottom flask to provide a thin film of diazene 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=300 nm) at 25 ºC. After 30 h, the lamps were turned off and the resulting residue was purified by flash column chromatography on silica gel (eluent: 18→35% ethyl acetate in hexanes) to afford cyclotryptamine trimer (+)-**38** (26.2 mg, 50.8%) as an off-white solid. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

^{1}H NMR (400 MHz, CD_3CN, 60 °C): δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.33–7.26 (m, 2H), 7.23–7.18 (m, 1H), 7.18–7.10 (m, 2H), 7.10–6.99 (app-br-s, 1H), 6.82 (app-t, *J* = 7.7 Hz, 1H), 6.73 (app-t, *J* = 7.8 Hz, 1H), 6.38 (s, 1H), 6.31 (br-s, 1H), 6.25 (s, 1H), 5.78 (s, 1H), 4.41–4.33 (m, 1H), 4.33–4.17 (m, 3H), 3.97 (app-t, *J* = 9.9 Hz, 1H), 3.80 (dd, *J* = 7.5, 11.1, 1H), 3.73–3.65 (m, 1H), 3.69 (s, 3H), 3.67 (s, 3H), 3.61 (s, 3H), 3.46–3.35 (m, 1H), 2.97–2.89 (m, 1H), 2.78–2.65 (m, 3H), 2.36–2.28 (m, 1H), 2.27–2.04 (m, 5H), 1.16–1.02 (m, 4H), 0.85–0.75 (m, 1H), 0.75–0.65 (m, 1H), 0.09 (s, 9H), 0.06 (s, 9H), 0.05 (s, 9H).

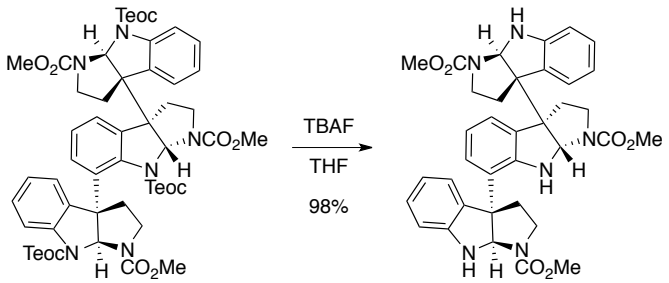
^{13}C NMR (100 MHz, CD_3CN, 60 °C): δ 156.4, 156.0, 155.6, 154.8, 154.7, 154.3, 144.3, 144.0, 142.5, 138.2, 136.6, 136.2, 132.3, 130.9, 130.2, 128.7, 127.6, 126.4, 125.5, 124.9, 124.1, 124.0, 117.1, 115.9, 86.2, 80.4, 80.1, 65.5, 65.4, 64.8, 62.2, 61.7, 61.2, 53.4 (2C), 53.1, 46.9, 46.2, 46.1, 35.7, 35.0 (2C), 19.0 (2C), 18.5, –1.1 (3C).

FTIR (thin film) cm^{-1}: 2954 (m), 2897 (w), 1716 (s), 1601 (w), 1400 (s).

HRMS (ESI) (*m/z*): calc'd for $C_{54}H_{74}N_6NaO_{12}Si_3$ $[M+Na]^+$: 1105.4565, found: 1105.4566.

$[\alpha]_D^{24}$: +129 (*c* = 0.50, CH_2Cl_2).

TLC (60% ethyl acetate in hexanes), R*f*: 0.26 (UV, CAM).



(+)-**38** (+)-**S9**

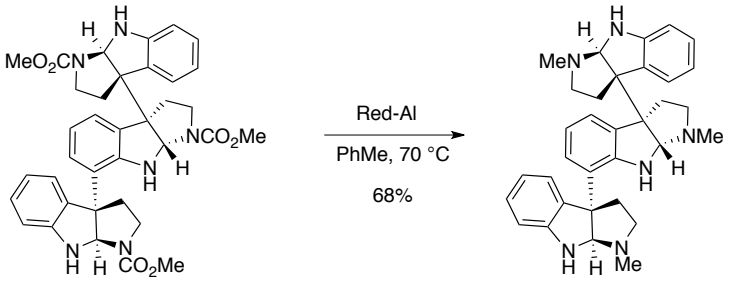
Cyclotryptamine trimer (+)-S9:

Tetrabutylammonium fluoride (1.0 M in tetrahydrofuran, 570 μL, 570 μmol, 15.0 equiv) was added to cyclotryptamine trimer (+)-**38** (41.2 mg, 38.0 μmol, 1 equiv) at 22 °C under an atmosphere of argon. After 1 h, the reaction mixture was diluted with ethyl acetate (5 mL) and washed with a saturated aqueous sodium carbonate solution (5 mL). The aqueous layer was extracted with dichloromethane (3 × 3 mL). The combined organic extracts were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting yellow-green residue was purified by flash column chromatography on silica gel (20→40% acetone in hexanes) to yield cyclotryptamine trimer (+)-**S9** (24.3 mg, 98.3%) as a pale yellow solid.

^{1}H NMR (400 MHz, CD_3CN, 25 °C):[12]	δ 7.31–7.05 (m, 1.5H), 7.05–6.93 (m, 2H), 6.90–6.78 (m, 1.5H), 6.78–6.57 (m, 4H), 6.57–6.31 (m, 2H), 6.10–5.64 (m, 1.5H), 5.57–5.31 (m, 2H), 5.28–5.04 (m, 2H), 4.98 (app-s, 0.5H), 3.78–3.59 (m, 9H), 3.59–3.37 (m, 4H), 3.02–2.89 (m, 1H), 2.89–2.71 (m, 1H), 2.66–2.44 (m, 3H), 2.44–2.19 (m, 3H).
^{13}C NMR (125 MHz, CD_3CN, 25 °C):	δ 155.8, 155.3, 155.1, 115.0, 154.7, 154.6, 151.3 (br), 149.4, 149.1, 131.8, 131.6, 130.4, 130.3, 129.9, 129.6, 129.5, 129.4, 129.3, 129.1, 129.0, 127.0, 126.9 (2C), 125.0, 124.2, 124.1, 123.9, 123.5 (br), 120.8, 120.7, 120.5, 120.4, 118.8, 118.7, 111.2, 110.9, 110.8, 110.5, 109.8 (2C), 109.6, 79.6, 79.5, 78.9, 78.8, 78.7, 78.6, 78.5, 77.9, 77.7, 77.1, 77.0, 76.9, 63.3, 63.2, 62.6, 62.5, 62.2, 62.1, 61.4, 61.3, 60.7, 60.6, 59.7, 59.6, 52.9 (2C), 52.7, 52.6, 64.3, 46.1, 46.0, 45.9, 45.6, 37.1 (2C), 37.0, 36.8, 36.6, 34.5, 34.1 (2C), 33.9, 33.1, 32.8 (2C).
FTIR (thin film) cm^{-1}:	3346 (br-m), 2956 (w), 1699 (s), 1456 (s), 1320 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{36}H_{39}N_6O_6$ $[M+H]^+$: 651.2926, found: 651.2922.
$[\alpha]_D^{24}$:	+111 (*c* = 0.52, CH_2Cl_2).

TLC (70% ethyl acetate in hexanes), R*f*: 0.20 (UV, CAM).

M.p.: 138–140 ºC (CH_2Cl_2).



(+)-**S9** (–)-hodgkinsine B (**3**)

(–)-Hodgkinsine B (3):

Cyclotryptamine trimer (+)-**S9** (47.3 mg, 72.7 μmol, 1 equiv) was azeotropically dried by concentration from anhydrous benzene (3 × 1 mL) and the residue was dissolved in toluene (3.6 mL). A solution of sodium bis(2-methoxyethoxy)aluminum hydride in toluene (Red-Al, 70% wt, 273 μL, 945 μmol, 13.5 equiv) was added via syringe at 22 °C. The reaction flask was fitted with a reflux condenser and was immersed in a pre-heated 70 ºC oil bath. After 1 h, the reaction mixture was allowed to cool to 22 °C and excess reducing reagent was quenched by the addition of a 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 (5 mL). The filtrate was concentrated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (eluent: 3.6% methanol, 0.4% ammonium hydroxide→9.0% methanol, 1.0% ammonium hydroxide in chloroform) to afford (–)-hodgkinsine B (**3**, 25.8 mg, 68.4%) as an off-white solid. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at –30 °C.

^{1}H NMR (400 MHz, $CDCl_3$, –30 °C, 1.5:1 mixture of atropisomers, *denotes minor atropisomer):
δ 7.36 (d, *J* = 7.5 Hz, 0.8H), 7.26–7.16 (m, 1.6H), 7.14–7.05 (m, 2H), 7.02–6.93 (m, 1H), 6.86–6.73 (m, 1.6H), 6.63 (app-d, *J* = 7.8 Hz, 0.6H), 6.60 (app-d, *J* = 9.0 Hz, 0.4H*), 6.56 (app-d, *J* = 7.8 Hz, 0.4H*), 6.48 (d, *J* = 7.7 Hz, 0.6H), 6.39 (t, *J* = 7.5 Hz, 0.4H*), 6.13 (t, *J* = 7.6 Hz, 0.6H), 5.82 (br-d, *J* = 7.6 Hz, 0.4H*), 5.63 (d, *J* = 7.4 Hz, 0.6H), 5.09–5.04 (m, 1.6H), 4.89 (br-s, 0.4H), 4.41 (d, *J* = 3.7 Hz, 0.6H), 4.32 (br-s, 0.4H), 4.24 (br-s, 0.4H), 4.13 (app br-d, *J* = 16.5 Hz, 1H), 3.84 (br-d, *J* = 3.8 Hz), 2.95 (t, *J* = 7.5 Hz, 0.6H), 2.91–2.62 (m, 3H), 2.61–2.21 (m, 13.2H), 2.46 (app-s), 2.42 (app-s), 2.34 (app-s), 2.32 (app-s) 2.19–2.01 (m, 3.2H), 1.93 (dd, *J* = 5.0, 12.1 Hz, 0.6H), 1.87–1.80 (m, 0.4H*).

^{13}C NMR (100 MHz, $CDCl_3$, –30 °C):[13] δ 152.0, 151.0, 150.9, 150.2, 149.5, 133.0, 132.1, 131.8, 131.6, 131.5, 128.2, 127.9, 127.7, 126.6, 125.3, 125.0, 124.7, 124.2, 122.5, 122.0, 121.8, 118.5, 118.2, 118.0, 115.6, 114.8, 109.2, 109.0,

	108.9, 107.8, 85.8, 85.4, 83.2, 82.7, 81.8, 63.2, 62.8, 62.7, 60.4, 60.3, 52.5, 52.3 (2C), 52.0, 51.8, 39.7, 38.7, 37.8, 37.6, 36.3, 35.7, 35.4, 35.3, 35.2.
FTIR (thin film) cm^{-1}:	3383 (br-s), 2933 (m), 2793 (w), 1653 (m), 1605 (s), 1487 (s), 1351 (w).
HRMS (DART) (*m/z*):	calc'd for $C_{33}H_{39}N_6$ $[M+H]^+$: 519.3231, found: 519.3230.
$[\alpha]_D^{24}$:	–88 (*c* = 0.21, CH_2Cl_2).[14]

TLC (9% methanol, 1% ammonium hydroxide in chloroform), R*f*: 0.22 (UV, CAM).

M.p.:	156–158 ºC (CH_2Cl_2).

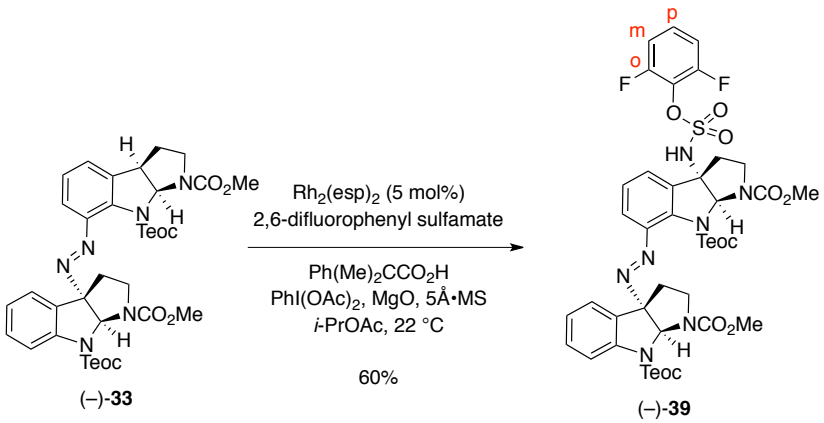
Table S1. Comparison of our ^{1}H NMR data for (–)-hodgkinsine B (3) with literature data ($CDCl_3$):

Overman′s Report[15] (–)-hodgkinsine B (**3**) ^{1}H NMR, 500 MHz $CDCl_3$, –30 ºC	**This Work** (–)-hodgkinsine B (**3**) ^{1}H NMR, 400 MHz $CDCl_3$, –30 ºC * denotes the minor isomer
7.37 (d, *J* = 7.8 Hz, 3H)	7.36 (d, *J* = 7.5 Hz, 0.8H)
7.23–7.16 (m, 8H)	7.26–7.16 (m, 1.6H)
7.13–7.06 (m, 10H)	7.14–7.05 (m, 2H)
6.99–6.95 (m, 6H)	7.02–6.93 (m, 1H)
6.83–6.78 (m, 8H)	6.86–6.73 (m, 1.6H)
6.64–6.55 (m, 9H)	6.63 (app-d, *J* = 7.8 Hz, 0.6H)
–	6.60 (app-d, *J* = 9.0 Hz, 0.4H*)
–	6.56 (app-d, *J* = 7.8 Hz, 0.4H*)
6.48 (d, *J* = 7.8 Hz, 3H)	6.48 (d, *J* = 7.7 Hz, 0.6H)
6.39 (t, *J* = 7.4 Hz, 2H)	6.39 (t, *J* = 7.5 Hz, 0.4H*)
6.13 (t, *J* = 7.6 Hz, 3H)	6.13 (t, *J* = 7.6 Hz, 0.6H)
5.84 (d, *J* = 7.4 Hz, 3H)	5.82 (br-d, *J* = 7.6 Hz, 0.4H*)
5.63 (d, *J* = 7.5 Hz, 3H)	5.63 (d, *J* = 7.4 Hz, 0.6H)
5.06–5.02 (m, 8H)	5.09–5.04 (m, 1.6H)
4.91 (br-s, 2H)	4.89 (br-s, 0.4H)
4.40 (d, *J* = 3.5 Hz, 3H)	4.41 (d, *J* = 3.7 Hz, 0.6H)
4.28 (s, 2H)	4.32 (br-s, 0.4H)
4.17–4.09 (m, 7H)	4.24 (br-s, 0.4H)
–	4.13 (app br-d, *J* = 16.5 Hz, N**H**, 1H)[16]
3.83 (s, 3H)	3.84 (br-d, *J* = 3.8 Hz, N**H**, 0.6H)
2.96 (t, *J* = 7.9 Hz, 3H)	2.95 (t, *J* = 7.5 Hz, 0.6H)
2.87–2.70 (m, 14H)	2.91–2.62 (m, 3H)
2.58–2.32 (m, 64H)	2.61–2.21 (m, 13.2H)
–	2.46 (app-s)
–	2.42 (app-s)
–	2.34 (app-s)
–	2.32 (app-s)
2.15–2.04 (m, 22H)	2.19–2.01 (m, 3.2H)
1.96–1.93 (m, 3H)	1.93 (dd, *J* = 5.0, 12.1 Hz, 0.6H)
1.84 (br-s, 2H)	1.87–1.80 (m, 0.4H*)
1.25–1.23 (m, 3H)	–[17]

Table S2. Comparison of our ^{13}C NMR data for (–)-hodgkinsine B (3) with literature data ($CDCl_3$):

Overman′s Report [15] (–)-hodgkinsine B (**3**) ^{13}C NMR, 125 MHz $CDCl_3$, –30 ºC	**This Work** (–)-hodgkinsine B (**3**) ^{13}C NMR, 100 MHz $CDCl_3$, –30 ºC	**Chemical Shift Difference** Δδ = δ (this work)–δ (Overman's Report)
152.3	152.0	–0.3
151.4	151.0	–0.4
151.2	150.9	–0.3
150.7	150.2	–0.5
149.9	149.5	–0.4
137.8	–	–[18]
133.5	133.0	–0.5
132.6	132.1	–0.5
132.5	131.8	–0.7
132.2	131.8	–0.6
132.1	131.6	–0.5
131.9	131.5	–0.4
130.2	–	–[18]
128.5	128.2	–0.3
128.3	127.9	–0.4
128.3	–	–[19]
128.0	127.7	–0.3
127.0	126.6	–0.3
125.6	125.3	–0.3
125.3	125.0	–0.3
125.1	124.7	–0.4
124.6	124.2	–0.4
122.9	122.5	–0.4
122.4	122.0	–0.4
–	121.8	–0.3[20]
118.9	118.5	–0.4
118.6	118.2	–0.4
118.3	118.0	–0.3
115.8	115.6	–0.2
115.2	114.8	–0.4
109.5	109.2	–0.3
109.3	108.9	–0.4
108.1	107.8	–0.3
86.2	85.8	–0.4
85.8	85.4	–0.4
83.6	83.2	–0.4

83.1	82.7	–0.4
82.2	81.8	–0.4
63.7	63.2	–0.5
63.6	63.2	–0.4
63.3	62.8	–0.5
63.0	62.7	–0.3
60.8	60.4	–0.4
60.7	60.3	–0.4
58.9	–	–[18]
52.9	52.5	–0.4
52.7	52.3	–0.4
52.6	52.3	–0.3
52.4	52.0	–0.4
52.1	51.8	–0.3
40.0	39.7	–0.3
39.2	38.7	–0.5
38.2	37.8	–0.4
38.0	37.6	–0.4
36.6	36.3	–0.3
36.1	35.7	–0.4
35.8	35.4	–0.4
35.7	35.3	–0.4
35.6	35.2	–0.4
21.6	–	–[21]
18.9	–	–[21]

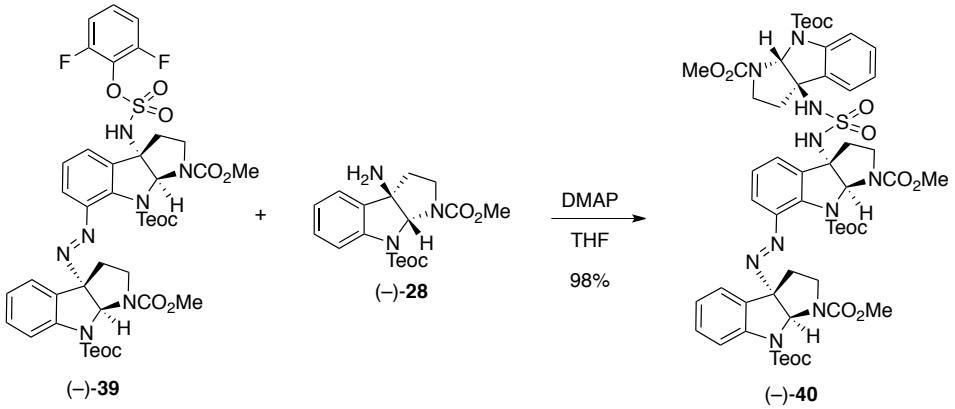


Diazene dimer sulfamate (–)-39:

A round-bottom flask equipped with a stir bar was charged with crushed 5Å molecular sieves (202 mg, 200 mg/mmol of (–)-**33**) and magnesium oxide (163 mg, 4.04 mmol, 4.00 equiv). The flask and its contents were flame-dried under vacuum for 5 min. The reaction vessel was allowed to cool to 22 °C and was then backfilled with argon. Solid 2,6-difluorophenyl sulfamate[8] (267 mg, 1.31 mmol, 1.30 equiv), 2-methyl-2-phenylpropionic acid (83.7 mg, 510 μmol, 0.500 equiv), and $Rh_2(esp)_2$ (38.7 mg, 51.0 μmol, 5.00 mol%) were added sequentially. A solution of diazene dimer (–)-**33** (757 mg, 1.01 mmol, 1 equiv) in isopropyl acetate (2.0 mL) was added via syringe at 22 °C and the mixture was allowed to stir for 5 min. A sample of (diacetoxyiodo)benzene (651 mg, 2.02 mmol, 2.00 equiv) was then added and the green suspension was allowed to stir vigorously at 22 °C. After 14 h, the reaction mixture was filtered through a pad of Celite and the filter cake was rinsed with ethyl acetate (7 mL). The filtrate was concentrated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (eluent: 5→20% acetone in hexanes) to afford diazene dimer sulfamate (–)-**39** (578 mg, 59.7%) as a bright yellow amorphous gum. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.77 (d, J = 8.1 Hz, 1H, C_7**H**), 7.48 (d J = 6.6 Hz, 1H, $C_{4'}$**H**), 7.33–7.27 (m, 2H, C_6**H**, $C_{6'}$**H**), 7.25–7.13 (m, 3H, $C_{4'}$**H**, $C_{5'}$**H**, C_p**H**), 7.01 (app-t, J = 7.2 Hz, 1H, C_5**H**), 6.96 (t, J = 8.1 Hz, 2H, C_m**H**), 6.85 (br-s, 1H, C_{8a}**H**), 6.58 (br-s, 1H, $C_{8a'}$**H**). 6.16 (br-s, 1H, N**H**), 4.39–4.27 (m, 2H, C_{10}**H**$_2$ or $C_{10'}$**H**$_2$), 4.27–4.19 (m, 1H, C_{10}**H**$_a$ or $C_{10'}$**H**$_a$), 4.13–3.96 (m, 2H, C_{10}**H**$_b$ or $C_{10'}$**H**$_b$, C_2**H**$_a$), 3.83–3.72 (m, 1H, $C_{2'}$**H**$_a$), 3.72 (app-s, 6H, N_1CO_2C**H**$_3$, $N_{1'}CO_2C$**H**$_3$), 3.07 (td, J = 5.2, 11.7 Hz, 1H, C_2**H**$_b$), 2.90 (br-s, 1H, $C_{3'}$**H**$_a$), 2.81 (br-s, 1H, $C_{2'}$**H**$_b$), 2.63–2.45 (m, 2H, C_3**H**$_a$, $C_{3'}$**H**$_b$), 2.35 (dd, J = 5.1, 12.5 Hz, 1H, C_3**H**$_b$), 1.17–1.07 (m, 2H, C_{11}**H**$_2$ or $C_{11'}$**H**$_2$), 1.03–0.80 (m, 2H, C_{11}**H**$_2$ or $C_{11'}$**H**$_2$), 0.05 (s, 9H, (C_{12}**H**$_3$)$_3$ or ($C_{12'}$**H**$_3$)$_3$), –0.03 (s, 9H, (C_{12}**H**$_3$)$_3$ or ($C_{12'}$**H**$_3$)$_3$).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):	δ 156.0 (dd, *J* = 3.3, 253.7 Hz, $\mathbf{C}_o$), 155.4 (2C, $N_1\mathbf{C}O_2CH_3$, $N_{1'}\mathbf{C}O_2CH_3$), 154.6 ($\mathbf{C}_9$ or $\mathbf{C}_{9'}$), 153.7 ($\mathbf{C}_9$ or $\mathbf{C}_{9'}$), 143.5 ($\mathbf{C}_{7a}$), 141.8 ($\mathbf{C}_{7'}$), 140.3 ($\mathbf{C}_{7a'}$), 133.1 ($\mathbf{C}_{4a'}$), 130.0 ($\mathbf{C}_6$), 129.0 ($\mathbf{C}_{4a}$), 127.8 (t, *J* = 9.2 Hz, $\mathbf{C}_p$), 126.9 (t, *J* = 15.6 Hz, $\mathbf{C}_i$), 126.2 ($\mathbf{C}_{5'}$), 125.5 ($\mathbf{C}_4$), 125.4 ($\mathbf{C}_{4'}$), 123.5 ($\mathbf{C}_5$), 119.7 ($\mathbf{C}_{6'}$), 116.3 ($\mathbf{C}_7$), 112.7 (dd, *J* = 4.4, 17.7 Hz, $\mathbf{C}_m$), 88.9 ($\mathbf{C}_{3a}$), 81.6 ($\mathbf{C}_{8a'}$), 79.7 ($\mathbf{C}_{8a}$), 71.6 ($\mathbf{C}_{3a'}$), 65.2 ($\mathbf{C}_{10}$ or $\mathbf{C}_{10'}$), 64.5 ($\mathbf{C}_{10}$ or $\mathbf{C}_{10'}$), 52.8 (2C, $N_1CO_2\mathbf{C}H_3$, $N_{1'}CO_2\mathbf{C}H_3$), 46.1 ($\mathbf{C}_2$), 45.0 ($\mathbf{C}_{2'}$), 35.6 ($\mathbf{C}_3$), 33.4 ($\mathbf{C}_{3'}$), 17.9 ($\mathbf{C}_{11}$ or $\mathbf{C}_{11'}$), 17.7 ($\mathbf{C}_{11}$ or $\mathbf{C}_{11'}$), –1.4 ($\mathbf{C}_{12}$ or $\mathbf{C}_{12'}$), –1.5 ($\mathbf{C}_{12}$ or $\mathbf{C}_{12'}$).
^{19}F NMR (282 MHz, $CDCl_3$, 25 °C):	δ –125.0 (s, $C_6H_3\mathbf{F}_2$).
FTIR (thin film) cm^{-1}:	3162 (s), 2955 (s), 1717 (s), 1457 (m), 862 (w), 733 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{42}H_{53}F_2N_7NaO_{11}SSi_2$ $[M+Na]^+$: 980.2923, found 980.2917.
$[\alpha]_D^{24}$:	–76 (*c* = 0.72, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.28 (UV, CAM).



Diazene dimer mixed sulfamide (–)-40:

A sample of 4-(dimethylamino)pyridine (109 mg, 891 μmol, 2.20 equiv) was added to a solution of diazene dimer sulfamate (–)-**39** (388 mg, 405 μmol, 1 equiv) and amine (–)-**28** (168 mg, 446 μmol, 1.10 equiv) in tetrahydrofuran (4.10 mL) at 22 ºC. After 24 h, the bright yellow solution was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 20%→70% ethyl acetate in hexanes) to afford diazene dimer mixed sulfamide (–)-**40** (480 mg, 98.3%) as a bright yellow amorphous gum. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

^{1}H NMR (400 MHz, C_6D_6, 70 °C): δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.31 (dd, *J* = 1.1, 8.0 Hz, 1H), 7.20 (s, 1H), 7.19–7.12 (m, 5H), 6.96 (app-t, *J* = 7.7 Hz, 1H), 6.91 (td, *J* = 0.9, 7.5 Hz, 1H), 6.86 (td, *J* = 0.9, 7.5 Hz, 1H), 6.81 (s, 1H), 6.69 (s, 1H), 5.38 (br-s, 1H), 5.25 (br-s, 1H), 4.49 (td, *J* = 6.2, 10.9 Hz, 1H), 4.45–4.32 (m, 4H), 4.23 (td, *J* = 6.4, 10.8 Hz, 1H), 3.98 (dd, *J* = 7.9, 11.2 Hz, 1H), 3.70–3.60 (m, 5H), 3.58 (s, 3H), 3.53 (s, 3H), 2.98 (td, *J* = 5.3, 11.7 Hz, 1H), 2.66–2.45 (m, 3H), 2.19 (dd, *J* = 5.2, 12.5 Hz, 1H), 2.11–1.90 (m, 4H), 1.19–0.98 (m, 6H), –0.01 (app-d, *J* = 2.9 Hz, 18H), –0.03 (s, 9H).

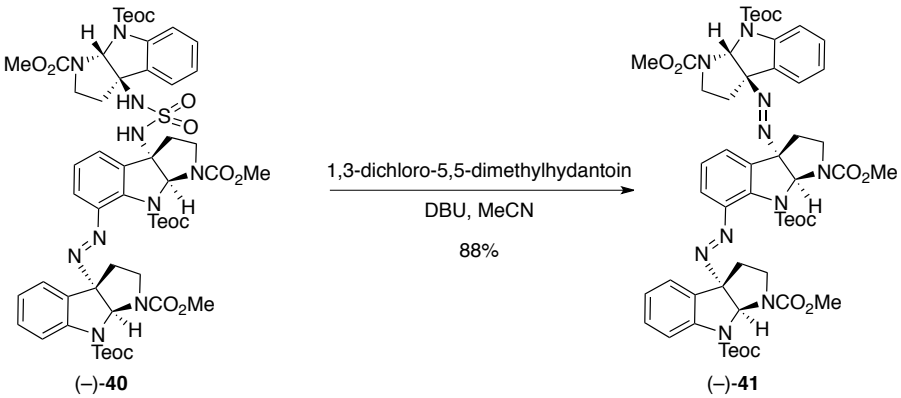
^{13}C NMR (100 MHz, C_6D_6, 70 °C): δ 156.0, 155.3, 155.2, 154.9, 154.4, 153.9, 144.6, 144.1, 142.8, 141.1, 134.6, 130.9, 130.5, 130.3, 130.0, 126.1, 125.8, 125.3, 124.6, 123.9, 123.6, 119.4, 117.6, 116.8, 89.9, 82.2, 80.2 (2C), 71.4, 71.3, 65.5, 64.8, 64.3, 52.4 (3C), 46.1, 45.0, 44.7, 37.2, 36.7, 36.2, 18.2 (2C), 18.1, –1.5 (3C).

FTIR (thin film) cm^{-1}: 3228 (m), 2955 (m), 2896 (w), 1715 (s), 1402 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{54}H_{76}N_{10}NaO_{14}SSi_3$ $[M+Na]^+$: 1227.4463, found: 1227.4462.

$[\alpha]_D^{24}$: –83 (*c* = 0.64, CH_2Cl_2).

TLC (60% ethyl acetate in hexanes), R*f*: 0.28 (UV, CAM).



(–)-**40** (–)-**41**

Bis-diazene trimer (–)-41:

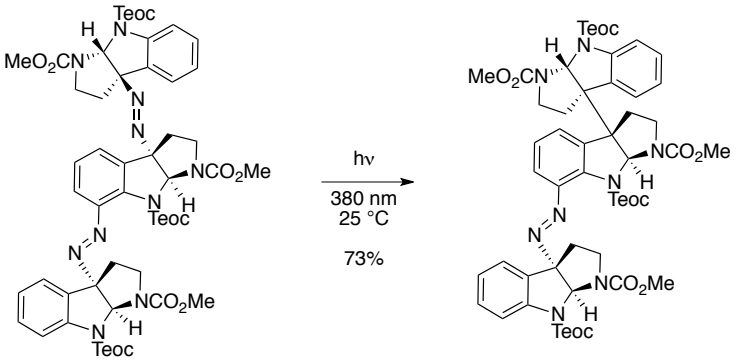
To a solution of diazene dimer mixed sulfamide (–)-**40** (480 mg, 398 μmol, 1 equiv) in acetonitrile (20.0 mL) at 22 °C was added via syringe 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 178 μL, 1.19 mmol, 3.00 equiv) followed immediately by 1,3-dichloro-5,5-dimethylhydantoin (196 mg, 995 μmol, 2.50 equiv) in a single portion. After 1 h, the mixture was diluted with dichloromethane (20 mL) and was washed with a saturated aqueous potassium carbonate–water solution (1:1, 30 mL). The aqueous layer was extracted with dichloromethane (3 × 30 mL). The combined organic extracts 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→50% ethyl acetate in hexanes) to afford bis-diazene trimer (–)-**41** (397 mg, 87.5%) as a bright yellow amorphous gum. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

^{1}H NMR (400 MHz, CD_3CN, 50 °C): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.42–7.19 (m, 6H), 7.12 (app-t, *J* = 6.4 Hz, 1H), 7.08 (app-t, *J* = 7.5 Hz, 1H), 7.02 (app-t, *J* = 7.4 Hz, 1H), 6.73 (s, 1H), 6.46 (s, 1H), 6.39 (s, 1H), 4.38-4.20 (m, 4H), 4.20–4.08 (m, 1H), 4.01 (br-dd, *J* = 7.4, 10.3 Hz, 1H), 3.93–3.76 (m, 3H), 3.69 (app-s, 6H), 3.65 (s, 3H), 3.08–2.89 (m, 2H), 2.57 (dd, *J* = 5.1, 12.5 Hz, 1H), 2.53–2.38 (m, 3H), 2.37–2.20 (m, 2H), 1.17–1.03 (m, 4H), 0.90–0.67 (m, 2H), 0.07 (app-s, 18H), –0.03 (s, 9H).

^{13}C NMR (100 MHz, CD_3CN, 50 °C): δ 156.2, 156.0 (2C), 155.3, 154.4, 154.3, 144.6, 144.5, 143.1, 141.3, 134.8, 131.2, 131.1, 130.6, 130.1, 127.7, 127.1, 126.6, 125.9, 124.6, 124.5, 119.8, 117.2, 117.0, 90.2, 89.6, 89.3, 81.8, 79.7, 79.6, 65.7, 65.2, 65.1, 53.3 (2C), 53.2, 46.9, 46.6 (2C), 36.9, 36.0, 33.6, 18.6 (3C), –1.2 (2C), –1.3.

FTIR (thin film) cm^{-1}: 2954 (m), 2896 (w), 1713 (s), 1603 (w), 1401 (m), 1252 (w).

HRMS (ESI) (*m/z*):	calc'd for $C_{54}H_{74}N_{10}NaO_{12}Si_3$ $[M+Na]^+$: 1161.4688, found: 1161.4673.
$[\alpha]_D^{24}$:	–86 (*c* = 0.61, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.23 (UV, CAM).



(–)-**41** (–)-**S7**

Mono-diazene trimer (–)-S7:

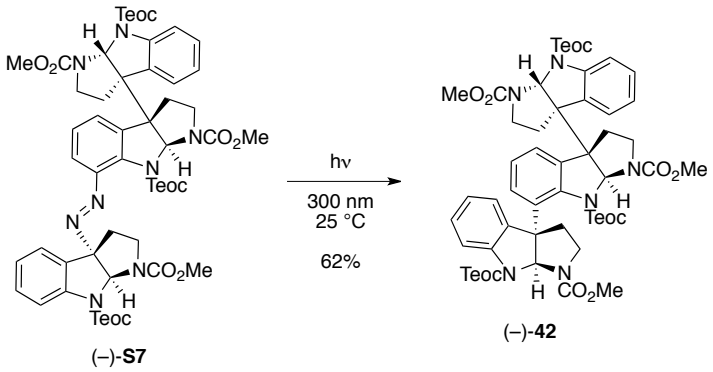
A solution of bis-diazene trimer (–)-**41** (397 mg, 348 μmol, 1 equiv) in dichloromethane (30 mL) was concentrated under reduced pressure in a 1 L round-bottom flask to provide a thin film of diazene coating the flask. The flask was backfilled with argon and irradiated in a Rayonet photoreactor equipped with 16 radially distributed (r=12.7 cm) 25 W lamps (λ=380 nm) at 25 ºC. After 15 h, the lamps were turned off and the resulting residue was purified by flash column chromatography on silica gel (eluent: 20→60% ethyl acetate in hexanes) to afford mono-diazene trimer **(–)-S7** (282 mg, 72.9%) as a bright yellow amorphous gum. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

^{1}H NMR (400 MHz, CD_3CN, 60 °C): δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H, 7.38–7.27 (m, 2H), 7.27–7.15 (m, 4H), 7.06 (app-t, *J* = 7.5 Hz, 1H), 6.77 (app-t, *J* = 7.8 Hz, 1H), 6.69 (s, 1H), 6.41 (br-d, *J* = 5.8 Hz, 1H), 6.23 (s, 1H), 6.08 (s, 1H), 4.39–4.28 (m, 3H), 4.21 (td, *J* = 7.0, 10.5 Hz, 1H), 3.99 (dd, *J* = 7.8, 11.1 Hz, 1H), 3.94–3.85 (m, 1H), 3.82 (dd, *J* = 7.7, 11.0 Hz, 1H), 3.75 (dd, *J* = 7.9, 10.9 Hz, 1H), 3.72–3.62 (m, 10H), 3.01 (td, *J* = 5.6, 11.6 Hz, 1H), 2.75 (app-dtd, *J* = 5.5, 11.5, 14.1 Hz, 2H), 2.47 (td, *J* = 7.8, 12.1 Hz, 1H), 2.35 (app-ddd, *J* = 7.0, 12.2, 13.5 Hz, 3H), 2.28–2.16 (m, 2H), 1.18–1.04 (m, 4H), 0.94–0.81 (m, 2H), 0.10 (s, 9H), 0.07 (s, 9H), 0.06 (s, 9H).

^{13}C NMR (100 MHz, CD_3CN, 60 °C): δ 156.4, 155.9, 155.8, 154.6, 154.4, 154.3, 144.8, 144.5, 143.0, 141.2, 137.3, 132.2, 131.1, 130.8, 130.4, 127.0, 126.9 (2C), 125.3, 124.8, 124.6, 119.2, 117.3, 117.1, 90.2, 81.7, 80.3, 79.9, 65.8, 65.4, 65.3, 62.7, 61.8, 53.4 (2C), 53.3, 47.1, 46.9, 46.5, 37.2, 36.2, 34.2, 18.9, 18.8, 18.6, –1.1 (3C).

FTIR (thin film) cm^{-1}: 2954 (m), 2896 (w), 1717 (s), 1448 (m), 1400 (m).

HRMS (ESI) (*m/z*):	calc'd for $C_{54}H_{74}N_8NaO_{12}Si_3$ $[M+Na]^+$: 1133.4626, found: 1133.4601.
$[\alpha]_D^{24}$:	–162 (*c* = 0.54, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.19 (UV, CAM).



Cyclotryptamine trimer (–)-42:

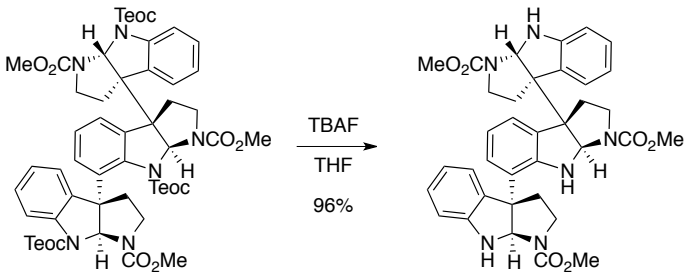
A solution of mono-diazene trimer (–)-**S7** (141 mg, 127 μmol, 1 equiv) in dichloromethane (15 mL) was concentrated under reduced pressure in a 2 L round-bottom flask to provide a thin film of diazene coating the flask. The flask was back filled with argon and irradiated in a Rayonet photoreactor equipped with 16 radially distributed (r=12.7 cm) 25 W lamps (λ=300 nm) at 25 ºC. After 15 h, the lamps were turned off and the resulting residue was purified by flash column chromatography on silica gel (eluent: 30→40% ethyl acetate in hexanes) to afford cyclotryptamine trimer (–)-**42** (84.9 mg, 61.7%) as an off-white solid. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

^{1}H NMR (400 MHz, CD_3CN, 60 °C): δ 7.74 (d, *J* = 8.0 Hz, 1H, 7.70 (d, *J* = 8.1 Hz, 1H), 7.29 (app-dd, *J* = 7.2, 14.2 Hz, 2H), 7.22 (app-t, *J* = 7.8 Hz, 1H), 7.13–7.00 (m, 2H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.69 (s, 1H), 6.48 (d, *J* = 7.9 Hz, 1H), 6.40 (br-d, *J* = 5.8 Hz, 1H), 6.36 (s, 1H), 6.04 (s, 1H), 4.50–4.34 (m, 2H), 4.33–4.22 (m, 2H), 3.94 (td, *J* = 6.0, 11.4 Hz, 1H), 3.80 (dd, *J* = 7.4, 11.1 Hz, 1H), 3.76–3.59 (m, 3H), 3.69 (s, 3H), 3.67 (s, 3H), 3.62 (s, 3H), 2.95 (td, *J* = 8.3, 11.8 Hz, 1H), 2.79–2.36 (m, 3H), 2.35–2.15 (m, 3H), 2.09 (td, *J* = 8.5, 11.9 Hz, 1H), 1.98–1.91 (m, 1H), 1.25–1.06 (m, 4H), 1.04–0.81 (m, 2H), 0.12 (s, 9H), 0.08 (s, 9H), 0.06 (s, 9H).

^{13}C NMR (100 MHz, CD_3CN, 60 °C): δ 156.2, 156.0, 155.8, 155.0 (2C), 154.4, 144.5, 144.4, 142.7, 139.5, 138.2, 134.8, 133.0, 132.3, 130.4, 129.8, 127.4, 125.5, 125.4, 125.3, 125.0, 124.3, 117.6, 117.2, 83.0, 80.7, 80.2, 66.1, 65.4, 65.0, 61.7 (2C), 61.5, 53.4, 53.2, 53.1, 46.9 (2C), 46.1, 35.7, 34.3, 33.4, 19.0 (2C), 18.7, –1.0 (2C), –1.1.

FTIR (thin film) cm^{-1}: 2954 (m), 2896 (w), 1716 (s), 1447 (w), 1400 (m).

HRMS (ESI) (*m/z*):	calc'd for $C_{54}H_{74}N_6NaO_{12}Si_3$ $[M+Na]^+$: 1105.4565, found: 1105.4539.
$[\alpha]_D^{24}$:	–35 (*c* = 0.57, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.28 (UV, CAM).
M.p.:	108–110 °C (CH_2Cl_2).



(–)-**42** (+)-**S8**

Cyclotryptamine trimer (+)-S8:

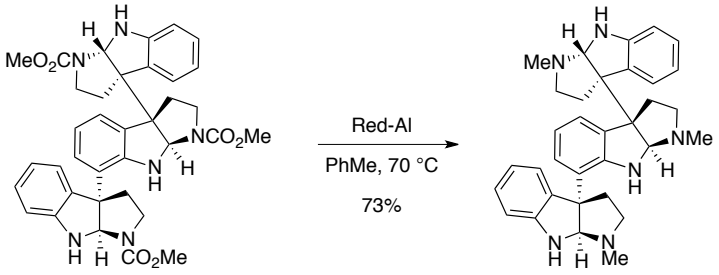
Tetrabutylammonium fluoride (1M in tetrahydrofuran, 1.80 mL, 1.80 mmol, 15.0 equiv) was added to cyclotryptamine trimer (–)-**42** (130 mg, 120 μmol) at 22 °C under an atmosphere of argon. After 1 h, the reaction mixture was diluted with ethyl acetate (2 mL) and washed with a saturated aqueous sodium carbonate solution (3 × 3 mL). The aqueous layer was extracted with dichloromethane (3 × 3 mL). The combined organic extracts were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting yellow-green residue was purified by flash column chromatography on silica gel (eluent: 20→40% acetone in hexanes) to yield cyclotryptamine trimer (+)-**S8** (75.1 mg, 96.2%) as a pale yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6, 90 °C):[22] δ 7.11 (d, J = 7.7 Hz, 1H), 7.00 (app-td, J = 0.9, 7.6 Hz, 1H), 6.95 (d, J = 7.3 Hz, 1H), 6.86 (app-t, J = 7.5 Hz, 1H), 6.77 (d, J = 6.9 Hz, 1H), 6.70–6.59 (m, 3H), 6.42 (d, J = 7.8 Hz, 1H), 6.27 (app-t, J = 7.3 Hz, 1H), 6.22–6.13 (m, 2H), 5.89 (s, 1H), 5.54 (s, 1H), 5.30 (s, 1H), 5.27 (s, 1H), 5.17 (s, 1H), 3.75–3.68 (m, 4H), 3.65 (s, 3H), 3.63 (s, 3H), 3.61–3.54 (m, 2H), 3.01–2.92 (m, 1H), 2.88 (td, J = 7.4, 10.3 Hz, 1H), 2.78 (td, J = 6.1, 10.9 Hz, 1H), 2.62–2.52 (m, 1H), 2.42 (br-ddd, J = 2.0, 6.7, 8.0 Hz, 1H), 2.33–2.20 (m, 3H), 2.07 (dd, J = 5.9, 12.5 Hz, 1H).

^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ 7.25–7.10 (m, 1H), 7.03 (br-t, J = 8.2 Hz, 1H), 6.99–6.90 (m, 1H), 6.90–6.81 (m, 1H), 6.81–6.71 (m, 2H), 6.71–6.57 (m, 2H), 6.48–6.31 (m, 1H), 6.30–6.00 (m, 2H), 5.99–5.70 (m, 1H), 5.63–5.37 (m, 1H), 5.32–5.23 (m, 1H), 5.23–5.11 (m, 2H), 5.11–5.00 (m, 1H), 3.77 (app-d, J = 8.0 Hz, 2H), 3.74–3.49 (m, 10H), 2.99–2.80 (m, 2H), 2.80–2.66 (m, 1H), 2.65–2.37 (m, 2H), 2.37–2.22 (m, 3H), 2.17–2.02 (m, 1H).

^{13}C NMR (100 MHz, CD_3CN, 25 °C):[23] δ 155.9, 155.8, 155.7, 155.3, 155.1, 154.9, 151.0, 150.8, 150.8, 149.4, 149.0, 148.9, 148.8, 131.1, 131.0, 130.7, 130.6, 129.6 (2C), 129.4, 129.3, 129.2, 129.1, 127.2, 127.1, 126.9, 124.9, 124.7, 123.7, 123.6, 121.0, 120.6, 120.5, 119.3, 119.2, 118.7,

	110.6, 110.3, 109.6, 109.5, 109.4, 109.3, 80.5, 80.3, 79.9, 79.6, 78.5, 78.0, 77.7, 77.3, 63.3, 62.5, 62.3, 62.2, 61.4, 60.7, 59.6, 52.9, 52.8, 52.7, 46.3, 46.2, 46.0, 45.9, 45.8, 37.1, 36.9, 36.6, 34.5, 34.2, 33.3, 33.2.
FTIR (thin film) cm^{-1}:	3335 (br-m), 2955 (m), 1700 (s), 1608 (m), 1457 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{36}H_{39}N_6O_6$ $[M+H]^+$: 651.2926, found: 651.2916.
$[\alpha]_D^{24}$:	+187 (*c* = 0.54, CH_2Cl_2).
TLC (70% ethyl acetate in hexanes), R*f*:	0.10 (UV, CAM).
M.p.:	153–155 °C (CH_2Cl_2).



(+)-**S8** (–)-hodgkinsine (**4**)

(–)-Hodgkinsine (4):

Cyclotryptamine trimer (+)-**S8** (49.9 mg, 76.7 μmol, 1 equiv) was azeotropically dried from anhydrous benzene (3 × 1 mL) and the residue was dissolved in toluene (3.8 mL). A solution of sodium bis(2-methoxyethoxy)aluminum hydride in toluene (Red-Al, 70% wt, 300 mL, 1.04 mmol, 13.5 equiv) was added via syringe at 22 °C. The reaction flask was fitted with a reflux condenser and was immerse in a pre-heated 70 ºC oil bath. After 1 h, the reaction mixture was allowed to cool to 22 °C, and the excess reducing reagent was quenched by the addition of a saturated aqueous sodium sulfate solution (100 μL). The resulting heterogeneous mixture was stirred for 5 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 ethyl acetate (15 mL). The filtrate was concentrated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (eluent: 3.6% methanol, 0.4% ammonium hydroxide→7.2% methanol, 0.5% ammonium hydroxide in chloroform) to afford (–)-hodgkinsine (**4**, 28.9 mg, 72.6%) as a white solid. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at –30 °C.

^{1}H NMR (400 MHz, $CDCl_3$, –30 °C): δ 7.36 (d, *J* = 7.5 Hz, 1H), 7.22 (app-d, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.14–7.03 (m, 4H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.85–6.75 (m, 3H), 6.74–6.58 (m, 3H), 6.50 (d, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 6.17 (app-dt, *J* = 15.1, 7.5 Hz, 2H), 5.54 (d, *J* = 7.4 Hz, 1H), 5.42 (br-d, *J* = 6.1 Hz, 1H), 5.07 (br-s, 2H), 4.94 (d, *J* = 3.9 Hz, 1H), 4.50 (s, 1H), 4.27 (br-s, 2H), 4.10 (s, 1H), 4.04 (d, *J* = 4.0 Hz, 1H), 3.74 (d, *J* = 3.7 Hz, 1H), 3.13–2.96 (m, 4H), 2.95–2.80 (m, 4H), 2.63–2.24 (m, 28H), 2.14–1.96 (m, 4H), 1.93–1.80 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, –30 °C): δ 152.2, 151.1, 150.9, 150.8, 149.5, 132.7, 132.3, 132.2, 131.7, 131.6, 128.3, 127.9, 127.6, 126.7, 126.6, 126.2, 125.2, 124.3, 124.1, 122.5, 122.1, 118.6, 118.4, 118.2, 117.5, 116.9, 115.3, 109.2, 109.1, 108.5, 108.3, 87.1, 86.7, 82.8, 82.4, 82.2, 82.0, 63.6, 63.3, 63.0, 62.9, 60.4, 60.2, 52.5, 52.2, 51.9, 38.7, 38.3, 38.0, 36.9, 36.1, 35.6, 35.3 (2C), 34.9.

FTIR (thin film) cm^{-1}: 3379 (br-m), 2936 (s), 1605 (m), 1486 (s), 1350 (w).

HRMS (DART) (*m/z*): calc'd for $C_{33}H_{39}N_6$ $[M+H]^+$: 519.3231, found: 519.3254.

$[\alpha]_D^{24}$: – 39 (*c* = 0.38, $CHCl_3$).[24]

TLC (9% methanol, 1% ammonium hydroxide in chloroform), R*f*: 0.10 (UV, CAM).

M.p.: 124–126 °C (CH_2Cl_2).[25]

Table S3. Comparison of our ^{1}H NMR data for (–)-hodgkinsine (4) with literature data:

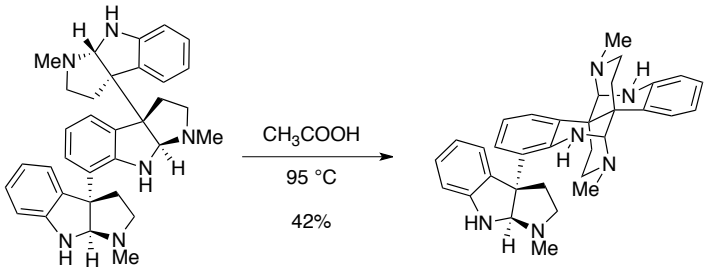
Assignment	**Verotta's Isolation Report**[26,27] (–)-hodgkinsine (**4**) ^{1}H NMR, 600 MHz $CDCl_3$, –30 ºC *denotes minor conformer	**This Work** (–)-hodgkinsine (**4**) ^{1}H NMR, 400 MHz $CDCl_3$, –30 ºC
C4"	7.37* (d, *J* = 7.9 Hz, 1H)	7.36 (d, *J* = 7.5 Hz, 1H)
C4'	7.23 (d, *J* = 7.7 Hz, 1H)	7.22 (app-d, *J* = 7.2 Hz, 2H)
C4	7.22 (d, *J* = 7.8 Hz, 1H)	–
C4	7.17* (d, *J* = 7.8 Hz, 1H)	7.18 (d, *J* = 7.4Hz, 1H)
C6'	7.13 (d, *J* = 7.9 Hz, 1H)	7.14–7.03 (m, 4H)
C6"	7.11* (t, *J* = 7.3 Hz, 1H)	–
C6	7.10 (t, *J* = 7.3 Hz, 1H)	–
C6	7.08* (t, *J* = 7.3 Hz, 1H)	–
C6'	6.98* (d, *J* = 7.9 Hz, 1H)	6.96 (d, *J* = 7.8 Hz, 1H)
C6"	6.89 (t, *J* = 7.3 Hz, 1H)	6.89 (t, *J* = 7.6 Hz, 1H)
C5	6.84 (t, *J* = 7.2 Hz, 1H)	6.85–6.75 (m, 3H)
C5"	6.81* (t, *J* = 7.3 Hz, 1H)	–
C5	6.79* (t, *J* = 7.2 Hz, 1H)	–
C5'	6.70 (t, *J* = 7.4 Hz, 1H)	6.74–6.58 (m, 3H)
C7	6.65 (d, *J* = 7.7 Hz, 1H)	–
C7	6.62* (d, *J* = 7.7 Hz, 1H)	–
C7"	6.51 (d, *J* = 7.9 Hz, 1H)	6.50 (d, *J* = 7.8 Hz, 1H)
C7"	6.46* (d, *J* = 7.9 Hz, 1H)	6.44 (d, *J* = 7.8 Hz, 1H)
C5"	6.20 (t, *J* = 7.3 Hz, 1H)	6.17 (app-dt, *J* = 15.1, 7.5 Hz, 2H)
C5'	6.16* (t, *J* = 7.4 Hz, 1H)	
C4'	5.57* (d, *J* = 7.7 Hz, 1H)	5.54 (d, *J* = 7.4 Hz, 1H)
C4"	5.44 (d, *J* = 7.9 Hz, 1H)	5.42 (br-d, *J* = 6.1 Hz, 1H)
C8a'	5.08 (br-s, *J* = 6.7 Hz, 1H)	5.07 (br-s, 2H)
C8a"	5.08* (br-s, 1H)	–
C8a"	5.08 (br-s, 1H)	–
C8a	4.97 (br-s, *J* = 4.8 Hz, 1H)	4.94 (d, *J* = 3.9 Hz, 1H)
C8a	4.52* (br-s, *J* = 6.5 Hz, 1H)	4.50 (s, 1H)
N-H	4.25 (br-s, *J* = 5.0 Hz, 1H)	4.27 (br-s, 2H)
C8a'	4.23* (br-s, *J* = 6.7 Hz, 1H)	–
N-H	4.20 (br-s, 1H)	–
N-H	4.15* (br-s, 1H)	4.10 (s, 1H)
N-H	4.12 (br-s, *J* = 6.5 Hz, 1H)	–
N-H	4.04* (br-s, *J* = 5.7 Hz, 1H)	4.04 (d, *J* = 4.0 Hz, 1H)
N-H	3.72* (br-s, *J* = 5.0 Hz, 1H)	3.74 (d, *J* = 3.7 Hz, 1H)
C3"β	3.04 (dd, *J* = 12.6 Hz, 1H)	3.13–2.96 (m, 4H)
C3"β	3.01* (dd, *J* = 11.0 Hz, 1H)	–
C2"β	3.01* (m, 1H)	–

C2'β	2.92* (m, 1H)	2.95–2.80 (m, 4H)
C2"β	2.89 (m, 1H)	–
C2β	2.86 (m, 1H)	–
C2β	2.86* (m, 1H)	–
C2'β	2.86 (m, 1H)	–
C3'β	2.59* (m, *J* = 11.4 Hz, 1H)	2.63–2.24 (m, 28H)
C2"α	2.56* (m, 1H)	–
C3'β	2.53 (m, *J* = 12.6 Hz, 1H)	–
C2"α	2.51 (m, 1H)	–
N–CH_3	2.46* (s, 3H)	–
N–CH_3	2.45 (s, 3H)	–
C3β	2.44* (m, 1H)	–
C3β	2.43 (m, 1H)	–
N–CH_3	2.42 (s, 3H)	–
N–CH_3	2.38 (s, 3H)	–
C2α	2.37 (m, 1H)	–
C2α	2.36* (m, 1H)	–
C2'α	2.36 (m, 1H)	–
C2'α	2.32* (m, 1H)	–
N–CH_3	2.31* (s, 3H)	–
N–CH_3	2.20* (s, 3H)	–
C3α	2.13 (m, 1H)	2.14–1.96 (m, 4H)
C3α	2.11* (m, 1H)	–
C3'α	2.07* (dd, *J* = 12.6, 5.5 Hz, 1H)	–
C3'α	2.01 (dd, *J* = 12.6, 5.5 Hz, 1H)	–
C3"α	1.91* (dd, *J* = 12.6, 5.5 Hz, 1H)	1.93–1.80 (m, 2H)
C3"α	1.87 (dd, *J* = 12.6, 5.5 Hz, 1H)	–

Table S4. Comparison of our ^{13}C NMR data for (–)-hodgkinsine (4) with literature data:

Assignment	Verotta's Isolation Report[26,27] (–)-hodgkinsine (**4**) ^{13}C NMR, 200 MHz $CDCl_3$, –30 ºC *denotes minor conformer	This Work (–)-hodgkinsine (**4**) ^{13}C NMR, 125 MHz $CDCl_3$, –30 ºC	Chemical Shift Difference Δδ = δ (this work)–δ (Verotta Report)
C7a"	152.1*	152.2	0.1
C7a"	151.1	151.1	0
C7a'	150.8	150.9	0.1
C7a	150.8	150.8	0
C7a	150.8*	-	N/A
C7a'	149.5*	149.5	0
C4a"	132.7*	132.7	0
C4a'	132.3	132.3	0
C4a'	132.3*	132.2	–0.1
C4a"	131.7	131.7	0
C4a	131.7	131.6	–0.1
C4a	131.6*	-	N/A
C6	127.9	128.3	0.4
C6"	127.9*	127.9	0
C6	127.8*	-	N/A
C6"	127.4	127.6	0.2
C4	126.4	126.7	0.3
C4	126.3*	126.6	0.3
C6'	126.0	126.2	0.2
C6'	125.0*	125.2	0.2
C4"	124.2	124.3	0.1
C4"	124.0*	124.1	0.1
C4'	122.4*	122.5	0.1
C4'	121.9	122.1	0.2
C5	118.5	118.6	0.1
C5	118.2*	118.4	0.2
C5"	118.2*	118.2	0
C5"	117.5	117.5	0
C5'	116.8	116.9	0.1
C5'	115.3*	115.3	0
C7	109.0*	109.2	0.2
C7	109.0	109.1	0.1
C7"	108.4*	108.5	0.1
C7"	108.1	108.3	0.2
C8a	87.0*	87.1	0.1
C8a	86.4	86.7	0.3

C8a'	82.6*	82.8	0.2
C8a''	82.3*	82.4	0.1
C8a''	82.3	82.2	–0.1
C8a'	81.7	82.0	0.3
C3a	63.0*	63.6	0.6
C3a'	63.0	63.3	0.3
C3a'	62.9*	63.0	0.1
C3a	62.8	62.9	0.1
C3a''	60.3*	60.4	0.1
C3a''	60.0	60.2	0.2
C2''	52.2*	52.5	0.3
C2	51.9*	52.2	0.3
C2''	51.9	51.9	0
C2'	51.9	-	N/A
C2'	51.7*	-	N/A
C3''	38.4*	38.7	0.3
C3''	38.0	38.3	0.3
C3	37.6	38.0	0.4
C3'	37.6*	-	N/A
C3'	36.7	36.9	0.2
C3	35.7*	36.1	0.4
N–CH_3	35.2	35.6	0.4
N–CH_3	35.1	35.3	0.2
N–CH_3	35.0	35.3	0.3
N–CH_3	34.9	34.9	0
N–CH_3	34.9*	-	N/A
N–CH_3	34.9*	-	N/A
C2	5.17[28]	-	N/A
C7'	nd	-	N/A
C7'	nd	-	N/A



(–)-hodgkinsine (**4**) (–)-calycosidine (**5**)

(–)-Calycosidine (5):

A solution of (–)-hodgkinsine (**4**, 10.5 mg, 20.2 μmol, 1 equiv) in aqueous acetic acid (0.1 M, 1 mL) contained in a pressure tube was sparged with argon for 5 min. The pressure tube was sealed and was immersed in a pre-heated 95 ºC oil bath. After 36 h, the mixture was allowed to cool to 22 °C and was partitioned between dichloromethane (3 mL) and an aqueous sodium hydroxide solution (1 N, 2 mL). The layers were separated, and the aqueous layer was extracted with dichloromethane (2 × 3 mL). The combined organic layers were washed with a saturated aqueous sodium bicarbonate solution (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 alumina (eluent: 100% ethyl acetate→10% methanol in dichloromethane) followed by flash column chromatography on silica (eluent: 2.7% methanol, 0.3% ammonium hydroxide→5.4% methanol, 0.6% ammonium hydroxide in chloroform) to afford (–)-calycosidine (**5**, 4.4 mg, 42 %) as a tan amorphous gum.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):	δ 7.25 (d, *J* = 7.0 Hz, 1H), 7.20 (d, *J* = 7.1 Hz, 1H), 7.11–7.06 (m, 2H), 7.03 (td, *J* = 1.4, 7.6 Hz, 1H), 6.87–6.79 (m, 2H), 6.77–6.67 (m, 3H), 6.56 (dd, *J* = 1.2, 8.0 Hz, 1H), 5.57 (s, 1H), 4.83 (d, *J* = 3.8 Hz, 1H, N**H**), 4.30 (s, 1H), 4.20 (d, *J* = 3.4 Hz, 1H), 3.14–2.78 (m, 1H, N**H**), 2.67–2.57 (m, 1H), 2.50–2.38 (m, 1H), 2.34 (s, 3H), 2.31–2.28 (m, 1H), 2.27 (s, 3H), 2.24–2.20 (m, 1H), 2.23 (s, 3H), 2.20–2.08 (m, 3H), 1.98–1.74 (m, 3H), 1.32–1.20 (m, 1H), 1.03 (dd, *J* = 3.1, 11.6 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 25 °C):	δ 148.1, 147.3, 144.5, 133.4, 128.8, 128.2, 126.9 (2C), 124.8, 124.5, 123.7, 120.2, 120.0, 119.8, 117.6, 117.4, 112.2, 110.4, 88.3, 74.6, 71.0, 59.9, 47.8, 46.2 (2C), 43.2, 42.2, 38.3, 38.2, 36.4 (2C), 33.4, 33.1.
FTIR (thin film) cm^{-1}:	2924 (s), 2853 (m), 1653 (w), 1607 (s), 1487 (s), 1374 (w), 1265 (m).
HRMS (DART) (*m/z*):	calc'd for $C_{33}H_{39}N_6$ $[M+H]^+$: 519.3231, found: 519.3249.

$[\alpha]_D^{24}$: –7 (*c* = 0.11, $CHCl_3$).[29]

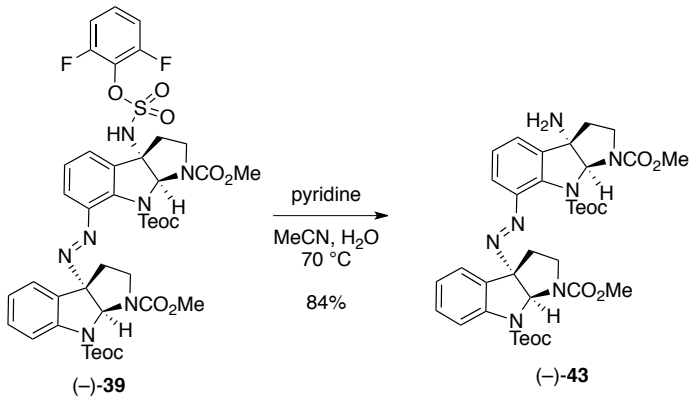
TLC (Al_2O_3, 1% methanol in dichloromethane), R*f*: 0.33 (UV, CAM).

Table S5. Comparison of our ^{1}H NMR data for (–)-calycosidine (5) with literature data:

Kunesch's Isolation Report[29] (–)-calycosidine (**5**) ^{1}H NMR, 400 MHz $CDCl_3$	**This Work** (–)-calycosidine (**5**) ^{1}H NMR, 400 MHz $CDCl_3$, 25 ºC
7.25 (d, *J* = 9 Hz, 1H)	7.25 (d, *J* = 7.0 Hz, 1H)
7.20 (d, *J* = 9 Hz, 1H)	7.20 (d, *J* = 7.1 Hz, 1H)
7.09 (d, *J* = 9 Hz, 1H)	7.11–7.06 (m, 2H)
7.08 (t, *J* = 9 Hz, 1H)	
7.03 (t, *J* = 9 Hz, 1H)	7.03 (td, *J* = 1.4, 7.6 Hz, 1H)
6.84 (t, *J* = 9 Hz, 1H)	6.87–6.79 (m, 2H)
6.82 (t, *J* = 9Hz, 1H)	
6.74 (t, *J* = 9 Hz, 1H)	6.77–6.67 (m, 3H)
6.73 (t, *J* = 9 Hz, 1H)	
6.70 (d, *J* = 9Hz, 1H)	
6.58 (d, *J* = 9Hz, 1H)	6.56 (dd, *J* = 1.2, 8.0 Hz, 1H)
5.57 (s, 1H)	5.57 (s, 1H)
–	4.83 (d, *J* = 3.8 Hz, 1H, N**H**)[30]
4.36 (s, 1H)	4.30 (s, 1H)
4.17 (s, 1H)	4.20 (d, *J* = 3.4 Hz, 1H)
–	3.14–2.78 (m, 1H, N**H**)[30]
2.63 (m, 2H)	2.67–2.57 (m, 1H)
2.45 (m, 2H)	2.50–2.38 (m, 1H)
2.33 (s, 3H)	2.34 (s, 3H)
2.25 (s, 3H)	2.31–2.28 (m, 1H)
–	2.27 (s, 3H)
2.23 (s, 3H)	2.24–2.20 (m, 1H)
–	2.23 (s, 3H)
2.17 (s, 3H)	2.20–2.08 (m, 3H)
1.88 (m, 3H)	1.98–1.74 (m, 3H)
1.25 (dd, *J* = 3, 12 Hz, 1H)	1.32–1.20 (m, 1H)
1.03 (dd, *J* = 3, 12 Hz, 1H)	1.03 (dd, *J* = 3.1, 11.6 Hz, 1H)

Table S6. Comparison of our ^{13}C NMR data for (–)-calycosidine (5) with literature data ($CDCl_3$):

Assignment[29]	**Kunesch's Isolation Report**[29] (–)-calycosidine (**5**) ^{13}C NMR, 100 MHz $CDCl_3$	**This Work** (–)-calycosidine (**5**) ^{13}C NMR, 100 MHz $CDCl_3$, 25 ºC	**Chemical Shift Difference** $\Delta\delta = \delta$ (this work)– δ (Kunesch Report)
C7a/C7a'/C7a"	148.1	148.1	0
C7a/C7a'/C7a"	147.3	147.3	0
C7a/C7a'/C7a"	144.5	144.5	0
C4a/C4a'/C4a"	133.3	133.4	0.1
C4a/C4a'/C4a"	128.7	128.8	0.1
–	128.1	128.2	0.1
–	126.8	126.9	0.1
–	–	126.9	N/A[31]
C4a/C4a'/C4a"	124.7	124.8	0.1
–	124.4	124.5	0.1
–	123.6	123.7	0.1
–	120.1	120.2	0.1
–	119.9	120.0	0.1
–	118.9	119.8	0.9
–	117.5	117.6	0.1
–	117.4	117.4	0
C7/C7'/C7"	112.2	112.2	0
C7/C7'/C7"	110.4	110.4	0
C8a/C8a'/C8a"	88.2	88.3	0.1
C8a/C8a'/C8a"	74.5	74.6	0.1
C8a/C8a'/C8a"	70.9	71.0	0.1
C3a/C3a'/C3a"	58.9	59.9	0.1
C2/C2'/C2"	47.7[32]	47.8	0.1
C2/C2'/C2"	46.2	46.2	0
–	46.1	46.2	0.1
N1-**C**H_3/ N1'-**C**H_3/ N1"-**C**H_3	43.2	43.2	0
N1-**C**H_3/ N1'-**C**H_3/ N1"-**C**H_3	42.1	42.2	0.1
C3/C3'/C3"	38.2	38.3	0.1
C3/C3'/C3"	38.1	38.2	0.1
–	37.5	36.4	–1.1
N1-**C**H_3/ N1'-**C**H_3/ N1"-**C**H_3	36.4	36.4	0
C3a/C3a'/C3a"	33.4	33.4	0
C3a/C3a'/C3a"	33.1	33.1	0



(–)-**39** (–)-**43**

Diazene dimer amine (–)-43:

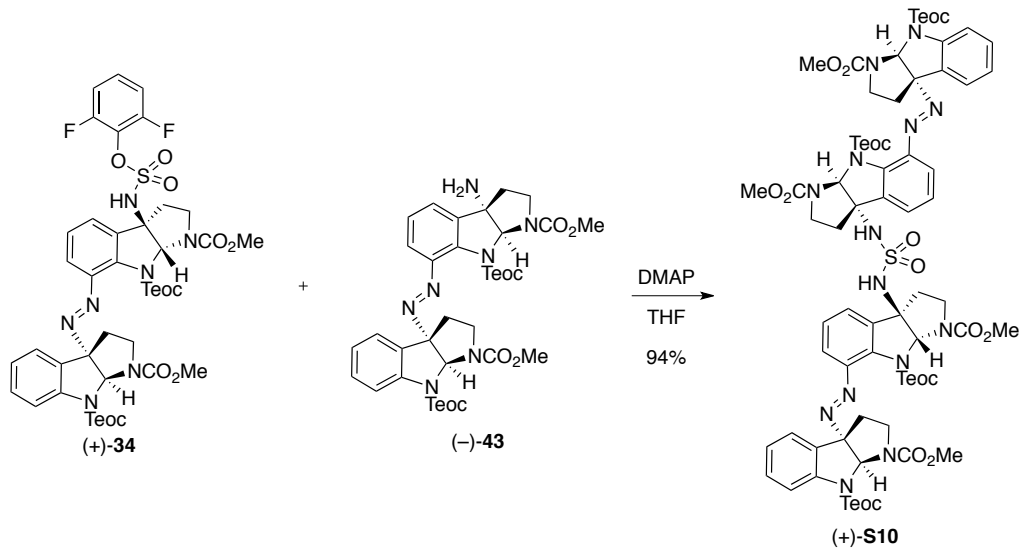
Pyridine (645 μL, 7.98 mmol, 20.0 equiv) was added to a solution of diazene dimer sulfamate (–)-**39** (382 mg, 399 μmol, 1 equiv) in a mixture of acetonitrile–water (2:1, 4 mL) via syringe at 22 °C. The reaction flask was fitted with a reflux condenser and was immersed in a pre-heated 70 ºC oil bath. After 24 h, the reaction mixture was allowed to cool to 22 °C. The mixture was diluted with dichloromethane (50 mL) and was washed with a saturated aqueous sodium bicarbonate solution (50 mL). The aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic extracts 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: 1→6% methanol in dichloromethane) to afford the diazene dimer amine (–)-**43** (257 mg, 84.1%) as a bright yellow oil. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.80 (d, *J* = 8.1 Hz, 1H, C_7**H**), 7.37 (app-dd, *J* = 1.3, 7.3 Hz, 1H, $C_{4'}$**H**), 7.33–7.27 (m, 1H, C_6**H**), 7.27–7.22 (m, 2H, C_4**H**, $C_{6'}$**H**), 7.20–7.14 (m, 1H, $C_{5'}$**H**), 7.02 (app-td, *J* = 0.8, 7.5 Hz, 1H, C_5**H**), 6.89 (s, 1H, C_{8a}**H**), 5.90 (br-s, 1H, $C_{8a'}$**H**), 4.43–4.23 (m, 3H, C_{10}**H**$_2$ or $C_{10'}$**H**$_2$, C_{10}**H**$_a$ or $C_{10'}$**H**$_a$), 4.16–3.98 (m, 2H, C_2**H**$_a$, C_{10}**H**$_a$ or $C_{10'}$**H**$_a$), 3.81–3.73 (m, 1H, $C_{2'}$**H**$_a$), 3.75 (app-s, 6H, N_1CO_2C**H**$_3$, $N_{1'}CO_2C$**H**$_3$), 3.11 (td, *J* = 5.3, 11.8 Hz, 1H, C_2**H**$_b$), 2.89 (td, *J* = 5.4, 11.6 Hz, 1H, $C_{2'}$**H**$_b$), 2.56 (td, *J* = 8.0, 12.3 Hz, 1H, C_3**H**$_a$), 2.39 (dd, *J* = 2.6, 5.0 Hz, 1H, $C_{3'}$**H**$_a$), 2.36 (dd, *J* = 2.9, 5.0 Hz, 1H, C_3**H**$_b$), 2.21 (td, *J* = 8.2, 12.2 Hz, 1H, $C_{3'}$**H**$_b$), 1.70 (br-s, 2H, N**H**$_2$), 1.15 (dd, *J* = 7.0, 10.6 Hz, 2H, C_{11}**H**$_2$ or $C_{11'}$**H**$_2$), 0.97 (br-s, 2H, C_{11}**H**$_2$ or $C_{11'}$**H**$_2$), 0.06 (s, 9H, (C_{12}**H**$_3$)$_3$ or ($C_{12'}$**H**$_3$)$_3$), 0.00 (s, 9H, (C_{12}**H**$_3$)$_3$ or ($C_{12'}$**H**$_3$)$_3$).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 155.4 (2C, (N_1**C**O_2CH_3, $N_{1'}$**C**O_2CH_3), 155.0 (**C**$_9$ or **C**$_{9'}$), 153.8 (**C**$_9$ or **C**$_{9'}$), 143.5 (**C**$_{7a}$), 141.8 (**C**$_{7'}$), 139.3 (**C**$_{7a'}$), 137.6 (**C**$_{4a'}$), 130.0 (**C**$_6$), 129.1 (**C**$_{4a}$), 126.1 (**C**$_{5'}$), 125.4 (**C**$_4$), 124.8 (**C**$_{4'}$), 123.5 (**C**$_5$),

	118.5 ($\mathbf{C}_{6'}$), 116.2 ($\mathbf{C}_{7}$), 89.0 ($\mathbf{C}_{3a}$), 85.5 ($\mathbf{C}_{8a'}$), 79.6 ($\mathbf{C}_{8a}$), 69.6 ($\mathbf{C}_{3a'}$), 64.9 ($\mathbf{C}_{10}$ or $\mathbf{C}_{10'}$), 64.5 ($\mathbf{C}_{10}$ or $\mathbf{C}_{10'}$), 52.8 ($N_1CO_2\mathbf{C}H_3$ or $N_{1'}CO_2\mathbf{C}H_3$), 52.7 ($N_1CO_2\mathbf{C}H_3$ or $N_{1'}CO_2\mathbf{C}H_3$), 46.1 ($\mathbf{C}_{2}$), 45.7 ($\mathbf{C}_{2'}$), 36.9 (br, $\mathbf{C}_{3}$), 35.8 ($\mathbf{C}_{3}$), 17.9 ($\mathbf{C}_{11}$ or $\mathbf{C}_{11}$), 17.8 ($\mathbf{C}_{11}$ or $\mathbf{C}_{11}$), –1.4 (2C, $\mathbf{C}_{12}$, $\mathbf{C}_{12'}$).
FTIR (thin film) cm^{-1}:	3378 (w), 2954 (m), 1706 (s), 1603 (w), 1252 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{36}H_{51}N_7NaO_8Si_2$ $[M+Na]^+$: 788.3230, found 788.3219.
$[\alpha]_D^{24}$:	–104 (*c* = 0.69, CH_2Cl_2).

TLC (6% methanol in dichloromethane), R*f*: 0.45 (UV, CAM).



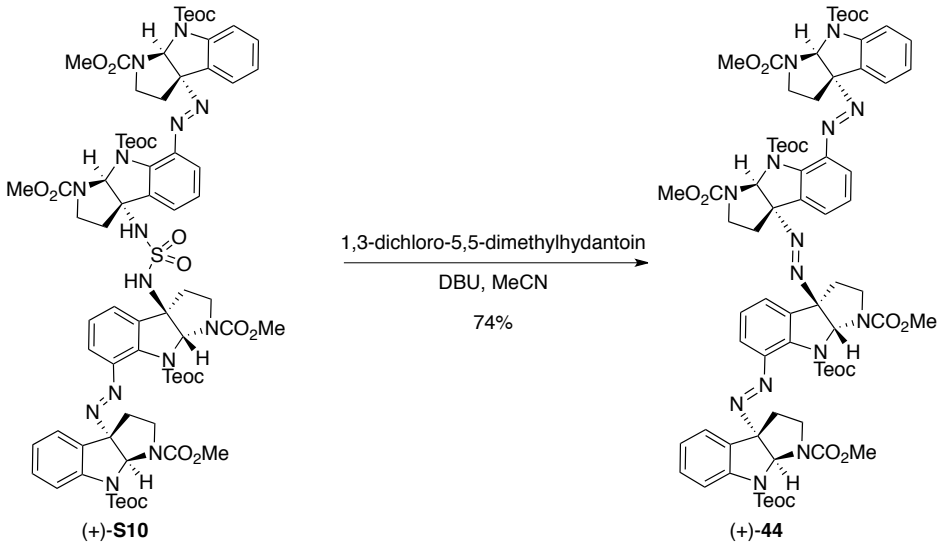
Diazene dimer mixed sulfamide (+)-S10:

A sample of 4-(dimethylamino)pyridine (137 mg, 1.12 mmol, 2.20 equiv) was added to a solution of diazene dimer sulfamate (+)-**34** (490 mg, 511 μmol, 1 equiv) and diazene amine (–)-**43** (430 mg, 562 μmol, 1.10 equiv) in tetrahydrofuran (5.10 mL) at 22 ºC. After 7 h, the bright yellow solution was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 30%→75% ethyl acetate in hexanes) to afford diazene dimer mixed sulfamide (+)-**S10** (766 mg, 94.0%) as a bright yellow amorphous gum. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

^{1}H NMR (400 MHz, C_6D_6, 70 °C): δ 8.19 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.22–7.14 (m, 6H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.99 (td, *J* = 7.5, 0.7 Hz, 1H), 6.93 (t, *J* = 7.8 Hz, 1H), 6.87 (td, *J* = 7.5, 5.6 Hz, 2H), 6.83 (s, 1H), 6.80 (s, 1H), 5.62 (br-s, 1H), 5.42 (br-s, 1H), 4.53–4.35 (m, 6H), 4.19 (app-dtd, *J* = 17.3, 10.9, 6.4 Hz, 2H), 4.00–3.90 (m, 2H), 3.68 (s, 3H), 3.65 (s, 3H), 3.62 (s, 3H), 3.59 (s, 3H), 3.55–3.40 (m, 2H), 2.96 (td, *J* = 11.7, 5.3 Hz, 2H), 2.58–2.44 (m, 2H), 2.39 (ddd, *J* = 15.5, 9.9, 6.1 Hz, 2H), 2.19 (ddd, *J* = 12.3, 4.9, 2.4 Hz, 2H), 1.86 (dd, *J* = 12.0, 4.9 Hz, 1H), 1.77 (dd, *J* = 12.0, 5.1 Hz, 1H), 1.65 (td, *J* = 11.9, 8.1 Hz, 1H), 1.54 (td, *J* = 11.9, 8.5 Hz, 1H), 1.24–0.94 (m, 8), 0.00 (s, 9H), –0.01 (s, 9H), –0.02 (s, 9H), –0.04 (s, 9H).

^{13}C NMR (100 MHz, C_6D_6, 70 °C): δ 156.4, 156.2, 155.3 (2C), 154.9, 154.8 (2C), 153.7, 144.5, 144.4, 142.7, 142.6, 141.0, 140.8, 135.0, 134.8, 130.3, 130.2 (2C), 130.0, 126.2, 126.0 (2C),

	125.8 (2C), 125.2, 123.6, 123.5, 119.5, 119.2, 116.8, 116.6, 89.9, 89.8, 81.8, 81.6, 79.8, 79.5, 71.1, 70.9, 65.7, 65.5, 64.4, 64.2, 52.4 (4C), 46.0 (2C), 44.6 (2C), 37.1, 36.7 (2C), 36.4, 18.2 (2C), 18.0, 17.9, –1.5 (4C).
FTIR (thin film) cm^{-1}:	3228 (w), 2954 (m), 1701 (s), 1457 (m), 838 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{72}H_{100}N_{14}NaO_{18}SSi_4$ $[M+Na]^+$: 1615.6030, found: 1615.6162.
$[\alpha]_D^{24}$:	+130 (*c* = 0.59, CH_2Cl_2).
TLC (70% ethyl acetate in hexanes), R*f*:	0.21 (UV, CAM).



(+)-**S10** (+)-**44**

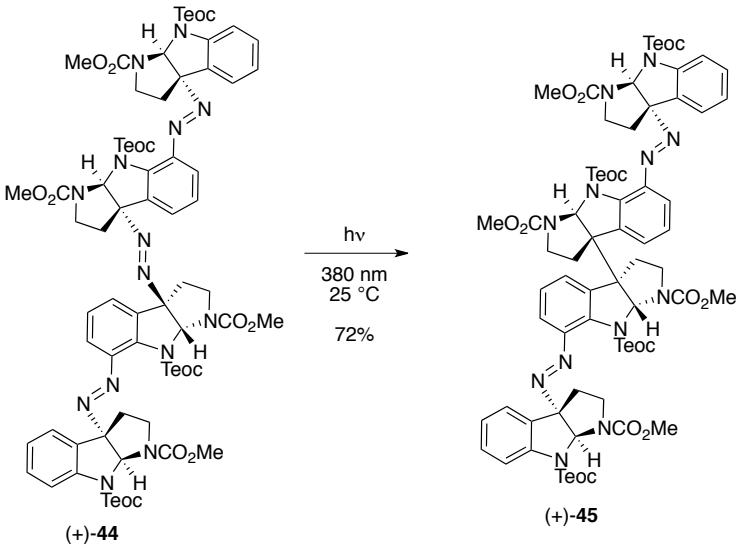
Tris-diazene tetramer (+)-44:

To a solution of diazene dimer mixed sulfamide (+)-**S10** (766 mg, 481 μmol, 1 equiv) in acetonitrile (24.1 mL) at 22 °C was added via syringe 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 215 μL, 1.44 mmol, 3.00 equiv) followed immediately by 1,3-dichloro-5,5-dimethylhydantoin (236 mg, 1.20 mmol, 2.50 equiv) in a single portion. After 1 h, the mixture was diluted with dichloromethane (10 mL) and was washed with a saturated aqueous potassium carbonate–water solution (1:1, 30 mL). The aqueous layer was extracted with dichloromethane (3 × 30 mL) and the combined organic extracts 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: 35→60% ethyl acetate in hexanes) to afford tris-diazene tetramer (+)-**44** (541 mg, 73.6%) as a bright yellow amorphous gum. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

^{1}H NMR (400 MHz, CD_3CN, 50 °C): δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.38–7.18 (m, 9H), 7.09 (app-dtd, *J* = 1.0, 7.5, 11.6 Hz, 2H), 6.74 (app-s, 2H), 6.32 (app-d, *J* = 1.7Hz, 1H), 6.30 (app-d, *J* = 2.2 Hz, 1H), 4.40–4.26 (m, 4H), 4.19–3.94 (m, 4H), 3.89–3.73 (m, 4H), 3.70 (s, 6H), 3.69 (s, 3H), 3.68 (s, 3H), 3.08–2.98 (m, 2H), 2.93 (td, *J* = 5.6, 11.4 Hz, 2H), 2.56–2.35 (m, 8H), 1.18–1.07 (m, 4H), 0.92–0.69 (m, 4H), 0.07 (s, 9H), 0.05 (s, 9H), 0.01 (s, 9H), –0.01(s, 9H).

^{13}C NMR (100 MHz, CD_3CN, 50 °C): δ 156.3, 156.2, 156.0 (2C), 155.3, 155.2, 154.5 (2C), 144.7, 144.6, 143.4, 143.2, 141.4, 141.0, 134.7 (2C), 131.1 (3C), 130.7, 127.7, 127.6, 127.1 (2C), 126.8, 126.7, 124.6 (2C), 120.3, 119.9, 117.1, 116.9, 90.3, 90.1, 89.5 (2C), 81.8, 81.7, 79.8, 79.7, 65.8, 65.7,

	65.2 (2C), 53.4 (2C), 53.3 (2C), 47.0, 46.9, 46.7 (2C), 37.4, 37.1, 33.7 (2C), 18.7 (4C), –1.1 (4C).
FTIR (thin film) cm^{-1}:	2954 (m), 2896 (w), 1717 (s), 1448 (w), 1395 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{72}H_{98}N_{14}NaO_{16}SSi_4$ $[M+Na]^+$: 1549.6255, found: 1549.6665.
$[\alpha]_D^{24}$:	+145 (*c* = 0.62, CH_2Cl_2).
TLC (60% ethyl acetate in hexanes), R*f*:	0.33 (UV, CAM).



(+)-**44** (+)-**45**

Bis-diazene tetramer (+)-45:

A solution of tris-diazene tetramer (+)-**44** (541 mg, 354 μmol, 1 equiv) in dichloromethane (30 mL) was concentrated under reduced pressure in a 2 L round-bottom flask to provide a thin film of diazene 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 24 h, the lamps were turned off and the resulting residue was purified by flash column chromatography on silica gel (eluent: 30→70% ethyl acetate in hexanes) to afford bis-diazene tetramer (+)-**45** (384 mg, 72.3%) as a bright yellow amorphous gum. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

^{1}H NMR (400 MHz, CD_3CN, 70 °C): δ 7.78 (app-t, *J* = 7.2 Hz, 2H), 7.49 (app-t, *J* = 6.8 Hz, 1H), 7.37–7.26 (m, 3H), 7.21–7.14 (m, 2H), 7.14–7.01 (m, 4H), 6.94 (br-s, 2H), 6.75 (dd, *J* = 6.5, 10.7 Hz, 2H), 6.22 (app-br-s, 2H), 4.41–4.26 (m, 4H), 4.13–3.93 (m, 4H), 3.93–3.78 (m, 2H), 3.78–3.65 (m, 14H), 3.09–2.94 (m, 2H), 2.80–2.66 (m, 2H), 2.57–2.34 (m, 4H), 2.26 (app-br-s, 4H), 1.20–1.06 (m, 4H), 1.01–0.79 (m, 4H), 0.13–0.01 (m, 36H).

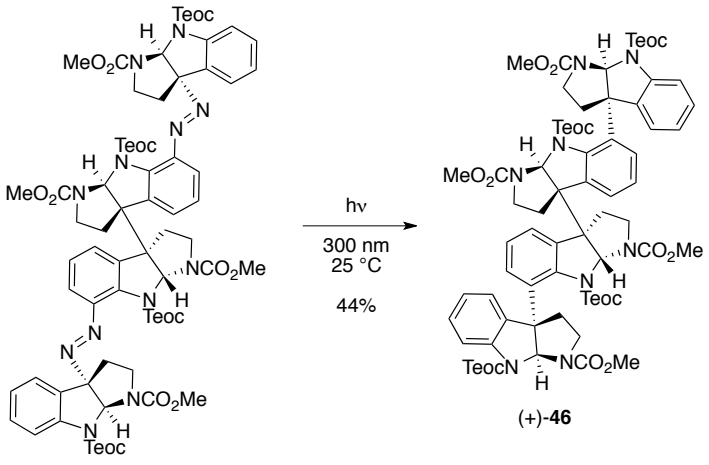
^{13}C NMR (100 MHz, CD_3CN, 70 °C): δ 156.5, 156.4, 155.9, 155.8, 154.9 (2C), 154.8 (2C), 145.0, 144.9, 143.4, 143.3, 141.3, 140.8, 136.9 (2C), 131.4, 131.3, 131.2, 131.0, 127.4, 127.3, 127.0 (2C), 126.9 (2C), 124.8, 124.7, 119.8, 119.4, 117.2 (2C), 90.4 (2C), 82.0, 81.9, 80.5, 80.0, 66.2 (2C), 65.4, 65.3, 62.3 (2C), 53.5 (2C), 53.5 (2C), 47.2, 47.1, 46.7 (2C), 37.8, 37.6, 34.7, 34.6, 19.1 (3C), 19.0, -0.8 (2C), –0.9 (2C).

FTIR (thin film) cm^{-1}: 2954 (m), 2896 (w), 1717 (s), 1457 (m), 1251 (w).

HRMS (ESI) (*m/z*): calc'd for $C_{72}H_{98}N_{12}NaO_{16}Si_4$ $[M+Na]^+$: 1521.6193, found: 1521.6283.

$[\alpha]_D^{24}$: +155 (*c* = 0.55, CH_2Cl_2).

TLC (50% ethyl acetate in hexanes), R*f*: 0.13 (UV, CAM).



(+)-**45** (+)-**46**

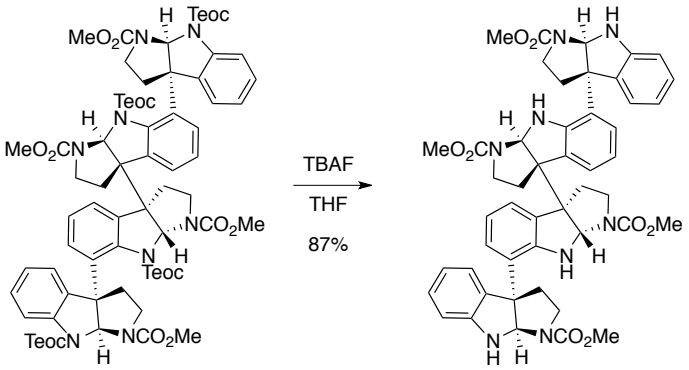
Tetramer (+)-46:

A solution of bis-diazene tetramer (+)-**45** (62.2 mg, 41.5 μmol, 1 equiv) in dichloromethane (5 mL) was concentrated under reduced pressure in a 500-mL round-bottom flask to provide a thin film of diazene coating the flask. The flask was backfilled with argon and irradiated in a Rayonet photoreactor equipped with 16 radially distributed (r=12.7 cm) 25 W lamps (λ=300 nm) at 25 ºC. After 18 h, the lamps were turned off and the resulting residue was purified by flash column chromatography on silica gel (eluent: 6→12% acetone in hexanes) to afford tetramer (+)-**46** (26.2 mg, 43.7%) as a bright yellow amorphous gum. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

^{1}H NMR (400 MHz, CD_3CN, 70 °C): δ 7.75 (app-d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.20 (app-br t, *J* = 7.8 Hz, 4H), 7.11–6.99 (m, 4H), 6.97–6.86 (m, 2H), 6.78 (s, 1H), 6.50 (d, *J* = 7.9 Hz, 1H), 6.44 (s, 1H), 6.33 (s, 1H), 6.27 (s, 1H), 4.43–4.34 (m, 1H), 4.34–4.24 (m, 3H), 4.20 (br-td, *J* = 5.3, 11.4 Hz, 1H), 4.08–3.89 (m, 4H), 3.84–3.75 (m, 1H), 3.73–3.63 (m, 1H), 3.69 (app-s, 6H), 3.66 (s, 3H), 3.64 (s, 3H), 3.60 (br-dd, *J* = 8.5, 10.3 Hz, 1H), 3.53 (br-dd, *J* = 8.3, 10.2 Hz, 1H), 3.06 (dt, *J* = 8.0, 11.7 Hz, 1H), 2.98 (dt, *J* = 6.8, 11.0 Hz, 1H), 2.87–2.74 (m, 2H), 2.69–2.54 (m, 2H), 2.25 (br-dd, *J* = 5.4, 12.5 Hz, 1H), 2.07–1.99 (m, 2H), 1.91–1.78 (m, 2H), 1.15–0.98 (m, 6H), 0.98–0.86 (m, 2H), 0.08 (app-d, *J* = 2.7 Hz, 18H), 0.06 (s, 9H), 0.02 (s, 9H).

^{13}C NMR (100 MHz, CD_3CN, 70 °C): δ 156.5, 156.3, 156.0, 155.9 (2C), 155.7, 155.1, 154.8, 144.5, 144.2, 142.7, 142.3, 139.4, 138.4, 138.2, 137.0, 136.4, 135.2, 133.1, 131.2, 129.9, 129.1, 128.3, 127.9, 126.6, 125.6, 125.4, 124.3 (2C), 124.1, 117.8, 116.2, 86.5, 83.0, 81.2, 81.1, 66.5,

	66.2, 65.2, 65.0, 61.8, 61.5, 61.1, 60.9, 53.5, 53.4, 53.3 (2C), 47.1, 46.5, 46.4 (2C), 35.0, 34.3 (2C), 33.9, 19.4, 19.3, 19.1, 19.0, –0.9, –1.0 (3C).
FTIR (thin film) cm^{-1}:	2954 (m), 2896 (w), 1717 (s), 1396 (m), 1043 (w).
HRMS (ESI) (*m/z*):	calc'd for $C_{72}H_{98}N_8NaO_{16}Si_4$ $[M+Na]^+$: 1465.6070, found: 1465.6112.
$[\alpha]_D^{24}$:	+95 (*c* = 0.28, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.31 (UV, CAM).
M.p.:	127–129 °C (CH_2Cl_2).



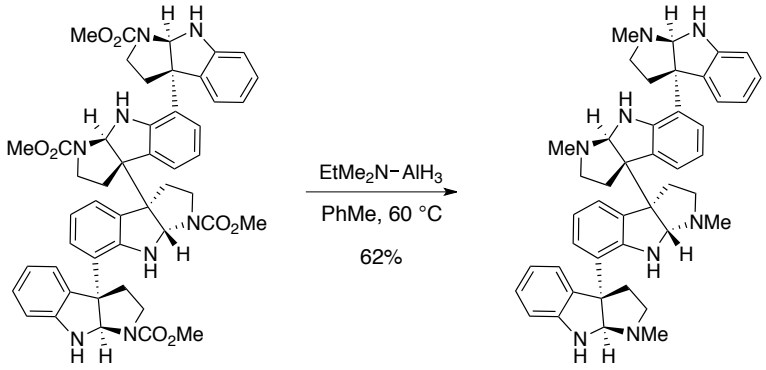
(+)-**46** (+)-**S11**

Tetramer (+)-S11:

Tetrabutylammonium fluoride (1.0 M in tetrahydrofuran, 1.30 mL, 1.30 mmol, 20.0 equiv) was added to tetramer (+)-**46** (94.0 mg, 65.1 μmol, 1 equiv) at 22 °C under an atmosphere of argon. After 1 h, the reaction mixture was diluted with ethyl acetate (2 mL) and washed with a saturated aqueous sodium carbonate solution (3 × 3 mL). The aqueous layer was extracted with dichloromethane (3 × 3 mL). The combined organic extracts were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting yellow-green residue was purified by flash column chromatography on silica gel (eluent: 20→35% acetone in hexanes) to yield tetramer (+)-**S11** (49.0 mg, 86.8%) as a pale yellow solid.

^{1}H NMR (400 MHz, CD_3CN, 25 °C):[33]	δ 7.30–6.96 (m, 5.5H), 6.96–6.73 (m, 2.5H), 6.73–6.47 (m, 5H), 6.38 (s, 1H), 6.23–5.74 (m, 2H), 5.74–5.38 (m, 2.5H), 5.31–5.05 (m, 2H), 5.05–4.87 (m, 1H), 4.76 (app-d, *J* = 22.2 Hz, 0.5H), 3.88–3.54 (m, 13H), 3.54–3.40 (m, 3H), 3.40–3.27 (m, 1H), 3.03–2.88 (m, 2H), 2.88–2.78 (m, 1H), 2.78–2.42 (m, 5H), 2.37–2.26 (m, 1H), 2.17–2.11 (m, 2H).
^{13}C NMR (100 MHz, CD_3CN, 25 °C):[34]	δ 155.8, 155.3, 155.1, 154.9, 154.7 (2C), 149.2, 148.9, 148.8, 131.1, 129.7, 129.1, 129.0, 126.8, 126.7, 126.3, 125.2, 124.6, 124.1, 124.0, 123.9, 123.5, 123.4, 123.2, 123.1, 121.3, 121.2, 120.6 (2C), 120.3, 119.6, 110.7, 110.5, 80.2, 79.7, 79.4, 79.3, 78.7, 77.9, 77.7, 77.3, 76.3, 76.1, 62.3, 62.2, 61.4, 61.2, 60.7, 60.6, 59.6, 59.5, 53.2, 52.9 (2C), 52.8, 52.6, 46.4, 46.2, 46.1, 46.0, 45.8, 45.6, 37.2, 36.5, 33.7, 32.2, 29.7.
FTIR (thin film) cm^{-1}:	3325 (m), 2955 (m), 2879 (w), 1700 (s), 1599 (w), 1457 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{48}H_{50}N_8NaO_8$ $[M+Na]^+$: 889.3644, found: 889.3668.

$[\alpha]_D^{24}$:	+ 290 (*c* = 0.58, CH_2Cl_2).
TLC (80% ethyl acetate in hexanes), R*f*:	0.20 (UV, CAM).
M.p.:	165 °C (decomp.).



(+)-**S11** (–)-quadrigemine C (**7**)

(–)-Quadrigemine C (7):

Tetramer (+)-**S11** (53.5 mg, 61.7 μmol, 1 equiv) was azeotropically dried by concentration from anhydrous benzene (3 × 1 mL) and the residue was dissolved in toluene (0.9 mL). A solution of alane *N*,*N*-dimethylethylamine complex in toluene (0.5 M, 2.22 mL, 1.11 mmol, 18.0 equiv) was added via syringe at 22 °C. The reaction flask was then sealed and immersed in a pre-heated 60 ºC oil bath. After 1 h, the reaction mixture was allowed to cool to 22 °C and excess reducing reagent was quenched by the addition of a saturated aqueous sodium sulfate solution (200 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 ethyl acetate (10 mL). The filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 3.6% methanol, 0.4% ammonium hydroxide→5.4% methanol, 0.6% ammonium hydroxide in chloroform) to afford (–)-quadrigemine C (**7**, 26.2 mg, 61.5%) as an off-white solid. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at –32 °C.

^{1}H NMR (400 MHz, $CDCl_3$, –32 °C, 2.2:1 mixture of atropisomers, *denotes minor atropisomer):[35] δ 7.26–7.03 (m, 5H), 6.96–6.89 (m, 1H), 6.89–6.75 (m, 2.3H), 6.70–6.52 (m, 3H), 6.20 (t, *J* = 7.6 Hz, 0.7H), 6.02 (t, *J* = 7.5 Hz, 0.3H*), 5.71 (d, *J* = 7.2 Hz, 0.7H), 5.56–5.27 (m, 1H), 5.16–4.74 (m, 2.5H), 4.55–4.02 (m, 3.5H), 3.14–2.66 (m, 6H), 2.66–1.69 (m), 2.49 (s), 2.44 (s), 2.41 (s), 2.38 (s), 2.33 (s), 2.27 (s).

^{13}C NMR (100 MHz, $CDCl_3$, –32 °C):[36] δ 151.0, 150.8, 150.4, 149.4, 149.1, 132.0, 131.8, 131.7, 127.9, 127.0, 126.8, 126.2, 125.9, 125.2, 124.5, 123.2, 122.5, 122.3, 122.0, 121.5, 118.5, 116.2, 115.3, 109.3, 109.0, 87.0, 86.5, 85.4, 81.9, 77.5, 77.4, 77.2, 76.8, 63.0, 62.7, 62.6, 62.4, 60.6, 60.3, 60.2, 52.6, 52.5, 52.4, 52.3, 51.8, 39.6, 39.1, 38.1, 37.0, 36.0, 35.4, 35.2 (2C).

FTIR (thin film) cm^{-1}:	2934 (m), 2793 (m), 1670 (s), 1606 (s), 1487 (s), 1352 (m), 1248 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{44}H_{51}N_8$ $[M+H]^+$: 691.4231, found: 691.4236.
$[\alpha]_D^{24}$:	–81 (*c* = 0.51, $CHCl_3$).[37]

TLC (9% methanol, 1% ammonium hydroxide in chloroform), R*f*: 0.24 (UV, CAM).

M.p.:	150–152 °C (CH_2Cl_2).

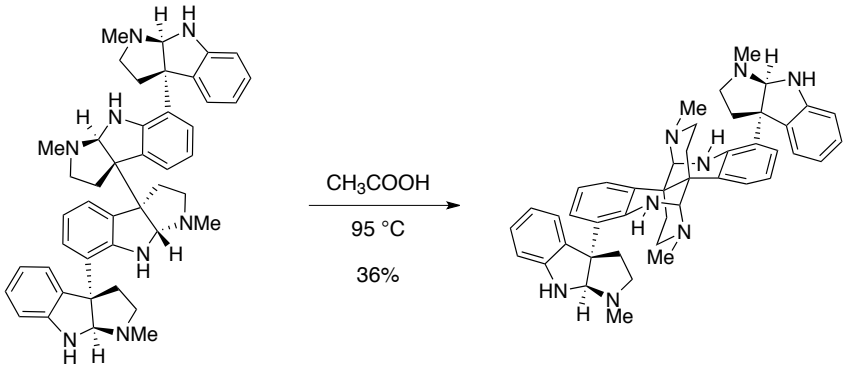
Table S7. Comparison of our ^{1}H NMR data for (–)-quadrigemine C (7) with literature data:

Poisson's Isolation Report[38,39] (–)-quadrigemine C (**7**) ^{1}H NMR $CDCl_3$	**This Work** (–)-quadrigemine C (**7**) ^{1}H NMR, 400 MHz $CDCl_3$, –30 ºC *denotes minor conformer
7.15–6.63 (m)	7.26–7.03 (m, 5H)
–	6.96–6.89 (m, 1H)
–	6.89–6.75 (m, 2.3H)
–	6.70–6.52 (m, 3H)
–	6.20 (t, J = 7.6 Hz, 0.7H)
–	6.02* (t, J = 7.5 Hz, 0.3H)
5.67 (m)	5.71 (d, J = 7.2 Hz, 0.7H)
5.07 (m)	5.56–5.27 (m, 1H)
4.65 (m)	5.16–4.74 (m, 2.5H)
4.23 (m)	4.55–4.02 (m, 3.5H)
–	3.14–2.66 (6H)
–	2.66–1.69 (m)
2.50 (m, 12H)	2.49 (s)
–	2.44 (s)
–	2.41 (s)
–	2.38 (s)
–	2.33 (s)
–	2.27 (s)

Table S8. Comparison of our ^{13}C NMR data for (–)-quadrigemine C (7) with literature data:

Poisson's Isolation Report[38,39] (–)-quadrigemine C (**7**) ^{13}C NMR, 20 MHz $CDCl_3$	**This Work** (–)-quadrigemine C (**7**) ^{13}C NMR, 125 MHz $CDCl_3$, –30 ºC	**Chemical Shift Difference** $\Delta\delta = \delta$ (this work)–δ (Poisson Report)
–	151.0	N/A
–	150.8	N/A
150.6	150.4	–0.2
–	149.4	N/A
–	149.1	N/A
132.2	132.0	–0.2
–	131.8	N/A
–	131.7	N/A
127.6	127.9	0.3
–	127.0	N/A
–	126.8	N/A
126.2	126.2	0
125.7	125.9	0.2
124.8	125.2	0.4
124.0	124.5	0.5
123.6	123.2	–0.4
–	122.5	N/A
–	122.3	N/A
122.2	122.0	–0.2
–	121.5	N/A
118.5	118.5	0
117.0		N/A
116.1	116.2	–0.1
115.6	115.3	–0.3
–	109.3	N/A
108.7	109.0	0.3
–	87.0	N/A
86.7	86.5	–0.2
85.8	85.4	–0.4
82.3	81.9	–0.4
–	77.5	N/A
–	77.4	N/A
–	77.2	N/A
–	76.8	N/A
–	63.0	N/A
–	62.7	N/A
62.6	62.6	0

–	62.4	N/A
60.6	60.6	0
–	60.3	N/A
–	60.2	N/A
53.2	52.6	-0.6
–	52.5	N/A
–	52.4	N/A
–	52.3	N/A
–	51.8	N/A
–	39.6	N/A
–	39.1	N/A
–	38.1	N/A
–	37.0	N/A
36.3	36.0	–0.3
–	35.4	N/A
35.2	35.2 (3C)	0



(–)-quadrigemine C (**7**) (–)-psycholeine (**8**)

(–)-Psycholeine (8):

A solution of (–)-quadrigemine C (**7**, 9.8 mg, 14.2 μmol, 1 equiv) in aqueous acetic acid (0.1 M, 700 μL) contained in a pressure tube was sparged with argon for 5 min. The pressure tube was sealed and was immersed in a pre-heated 95 ºC oil bath. After 36 h, the mixture was allowed to cool to 22 °C and partitioned between dichloromethane (3 mL) and aqueous solution of sodium hydroxide (1 N, 3 mL). The layers were separated, and the aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed with a saturated aqueous sodium bicarbonate solution (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: 1→3% methanol in dichloromethane saturated with ammonium hydroxide) to afford (–)-psycholeine (**8**, 3.5 mg, 36%) as a tan solid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.28–7.23 (m, 2H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.09–7.03 (m, 2H), 6.97 (app-td, *J* = 1.1, 7.8 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.73 (app-td, *J* = 1.8, 7.5 Hz, 2H), 6.69–6.64 (m, 2H), 6.57 (d, *J* = 7.8 Hz, 1H), 5.94 (s, 1H), 5.56 (s, 1H), 4.46 (s, 1H), 4.22 (s, 1H), 2.75–2.58 (m, 4H), 2.55–2.16 (m, 9H), 2.39 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.14 (s, 3H), 2.03–1.97 (m, 1H), 1.90–1.74 (m, 4H), 1.12 (app-d, *J* = 11.1 Hz, 1H), 1.05 (app-d, *J* = 12.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 149.4, 148.1, 147.3, 146.7, 133.4, 133.3, 128.7 (2C), 128.2, 127.7, 124.9, 124.8, 123.7, 123.2, 120.2 (3C), 120.1, 119.9, 119.6, 117.6, 117.3, 110.4, 109.8. 88.0, 87.6, 74.2, 72.1, 60.9, 59.9, 48.6, 47.7, 46.6, 46.0, 43.9, 43.0, 38.6, 38.1, 37.8, 37.6, 36.5, 36.3, 32.9, 32.5.

FTIR (thin film) cm^{-1}: 2920 (m), 1653 (w), 1609 (s), 1489 (s), 1312 (w), 1267 (m).

HRMS (DART) (*m/z*): calc'd for $C_{44}H_{51}N_8$ $[M+H]^+$: 691.4231, found: 691.4223.

$[\alpha]_D^{24}$: –155 (*c* = 0.14, EtOH).[40]

TLC (10% methanol in ammonia-saturated dichloromethane), R*f*: 0.27 (UV, CAM).

M.p.: 220 °C (decomp.).

Table S9. Comparison of our ^{1}H NMR data for (–)-psycholeine (8) with literature data ($CDCl_3$):

Sevenet's Isolation Report[41] (–)-psycholeine (**8**) ^{13}C NMR, 400 MHz $CDCl_3/CD_3OD$	**Lebsack's Ph.D. Dissertation**[42,43] (–)-psycholeine (**8**) ^{1}H NMR, 500 MHz $CDCl_3$, "rt"	**This Work** (–)-psycholeine (**8**) ^{1}H NMR, 400 MHz $CDCl_3$, 25 ºC
–	7.27–7.23 (m, 2H)	7.28–7.23 (m, 2H)
–	7.20 (d, *J* = 6.8 Hz, 1H)	7.20 (d, *J* = 7.2 Hz, 1H)
–	7.08–7.02 (m, 2H)	7.09–7.03 (m, 2H)
–	6.96 (app-t, *J* = 7.0 Hz, 1H)	6.97 (app-td, *J* = 1.1, 7.8 Hz, 1H)
–	6.91 (d, *J* = 7.6 Hz, 1H)	6.91 (d, *J* = 7.6 Hz, 1H)
–	6.85 (d, *J* = 7.5 Hz, 1H)	6.86 (d, *J* = 7.6 Hz, 1H)
–	6.80 (t, *J* = 7.0 Hz, 1H)	6.81 (t, *J* = 7.3 Hz, 1H)
–	6.73 (app-dt, *J* = 1.8, 7.4 Hz, 2H)	6.73 (app-dt, *J* = 1.8, 7.5 Hz, 2H)
–	6.68–6.65 (m, 2H)	6.69–6.64 (m, 2H)
–	6.56 (d, *J* = 7.7 Hz, 1H)	6.57 (s, 1H)
5.95 (s)	5.93 (s, 1H)	5.94 (s, 1H)
5.57 (s)	5.56 (s, 1H)	5.56 (s, 1H)
4.46 (s)	4.46 (s, 1H)	4.46 (s, 1H)
4.21 (s)	4.22 (s, 1H)	4.22 (s, 1H)
2.66 (m)	2.70–2.58 (m, 4H)	2.75–2.58 (m, 4H)
2.66 (m)	–	–
2.45 (m)	2.46–2.14 (m, 21H)	2.55–2.16 (m, 9H))
2.40 (s)	–	2.39 (s, 3H)
2.40 (s)	–	2.38 (s, 3H)
2.33 (s)	–	2.36 (s, 3H)
2.16 (s)	–	2.14 (s, 3H)
2.20 (m)	2.20–1.98 (m, 1H)	2.03–1.97 (m, 1H)
2.20 (m)	–	–
1.94 (m)	1.91–1.78 (m, 4H)	1.90–1.74 (m, 4H)
1.80 (m)	–	–
1.77 (m)	–	–
1.74 (m)	–	–
1.12 (d, *J* = 12Hz)	1.13 (app-dd, *J* = 9.8 Hz, 1H)	1.12 (app-d, *J* = 11.1 Hz, 1H)
1.04 (d, *J* = 12Hz)	1.06 (app-dd, *J* = 13.7 Hz, 1H)	1.05 (app-d, *J* = 12.4 Hz, 1H)

Table S10. Comparison of our ^{13}C NMR data for (–)-psycholeine (8) with literature data ($CDCl_3$):

Sevenet's Isolation Report (–)-psycholeine (**8**) ^{13}C NMR, 100 MHz $CDCl_3/CD_3OD$	**Lebsack's Ph.D. Dissertation**[42] (–)-psycholeine (**8**) ^{13}C NMR, 125 MHz $CDCl_3$, "rt"	**This Work** (–)-psycholeine (**8**) ^{13}C NMR, 100 MHz $CDCl_3$, 25 ºC	**Chemical Shift Difference** $\Delta\delta = \delta$ (this work)–δ (Lebsack's Dissertation)
–	149.5	149.4	–0.1
–	148.3	148.1	–0.2
–	147.4	147.3	–0.1
–	146.8	146.7	–0.1
133.80	133.6	133.4	–0.2
132.40	133.5	133.3	–0.3
129.00	128.9	128.7	–0.2
–	–	128.7	N/A[44]
–	128.2	128.2	0
–	127.8	127.7	–0.1
–	124.9	124.9	0
–	124.8	124.8	0
–	123.7	123.7	0
–	123.3	123.2	–0.1
–	120.3	120.2	–0.1
–	120.2	120.2	0
–	–	120.2	N/A[44]
–	–	120.1	N/A[44]
–	119.9	119.9	0
–	119.6	119.6	0
–	117.7	117.6	–0.1
–	117.4	117.3	–0.1
–	110.4	110.4	0
–	109.9	109.8	–0.1
88.51	88.1	88.0	–0.1
87.50	87.7	87.6	–0.1
74.00	74.4	74.2	–0.2
72.00	72.2	72.1	–0.1
60.65	61.1	60.9	–0.2
59.56	61.0	59.9	–0.1
48.05	48.8	48.6	–0.2
47.17	47.9	47.7	–0.2
46.30	46.7	46.6	–0.1
45.85	46.1	46.0	–0.1
43.69	43.9	43.9	0
42.61	43.1	43.0	–0.1

–	38.9	38.6	–0.3
38.05	38.6	38.1	–0.5
–	37.9	37.8	–0.1
37.50 (2C)	37.7	37.6	–0.1
36.08	36.8	36.5	–0.3
35.60	36.7	36.3	–0.4
32.80	33.0	32.9	–0.1
32.40	32.6	32.5	–0.1

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[10] This compound decomposes when stored as a solution in chloroform or dichloromethane.
[11] All expected ^{13}C signals were observed in the product of the next step of our synthesis, trimer (+)-**25**. One of the 48 carbon resonances for intermediate (+)-**24** is obscured (likely a second aromatic resonance at 126.8 ppm).
[12] The reported integrals for intermediate (+)-**26** are an approximation due to presence of multiple conformers and significant atropisomerism.
[13] Due to atropisomerism, we observe more than the expected 33 ^{13}C NMR signals.
[14] Literature value: $[\alpha]_D^{27} = -77.0$ (*c* 1, $CHCl_3$) and: $[\alpha]_D^{27} = -55.0$ (*c* 0.8, $CHCl_3$, 83% ee), see J. J. Kodanko, L. E. Overman *Angew. Chem. Int. Ed.* **2003**, *42*, 2528. Literature value: $[\alpha]_D^{25} = -69.5$ (*c* 1, $CHCl_3$), see R. H. Snell, R. L. Woodward, M. C. Willis *Angew. Chem. Int. Ed.* **2011**, *50*, 9116.
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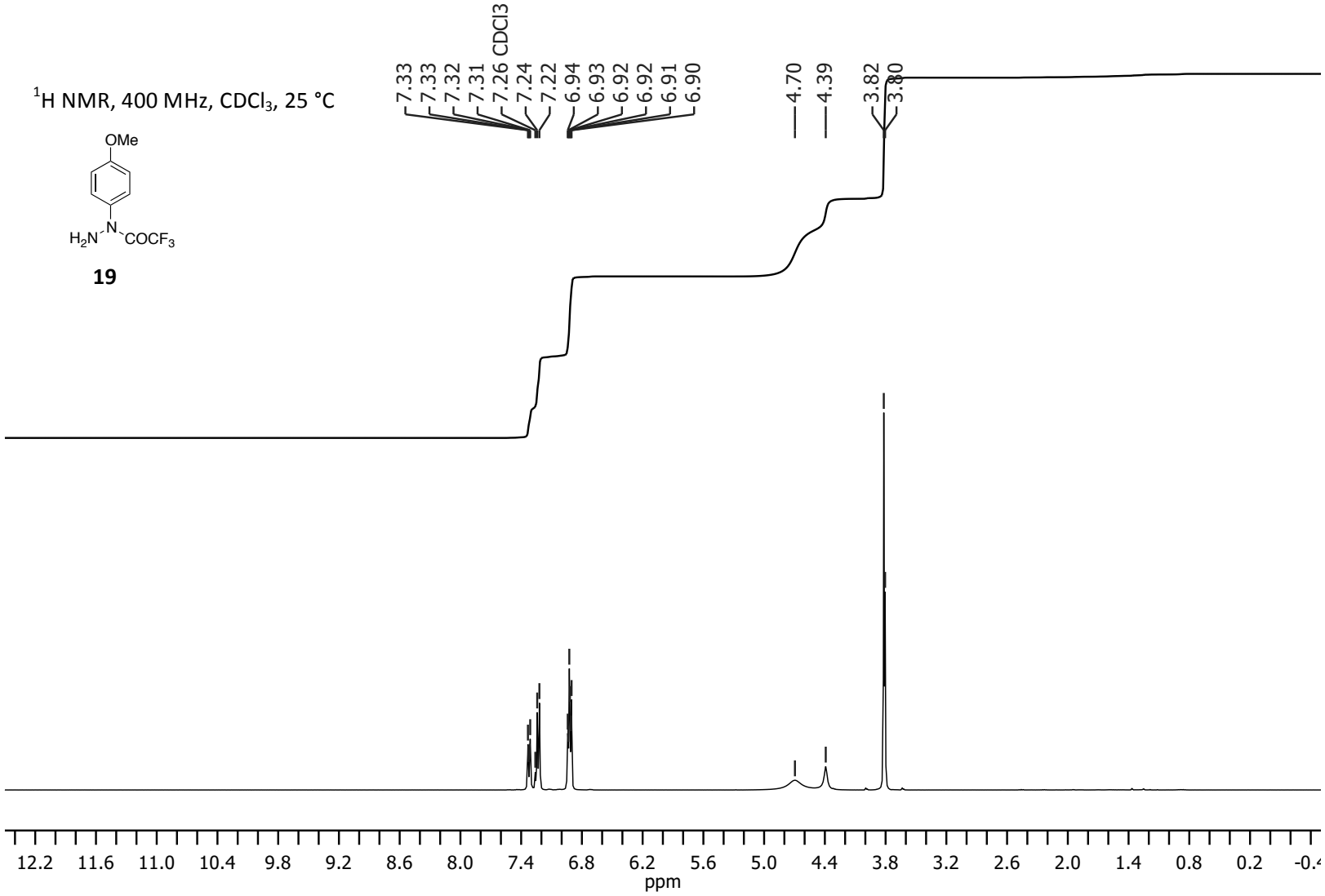
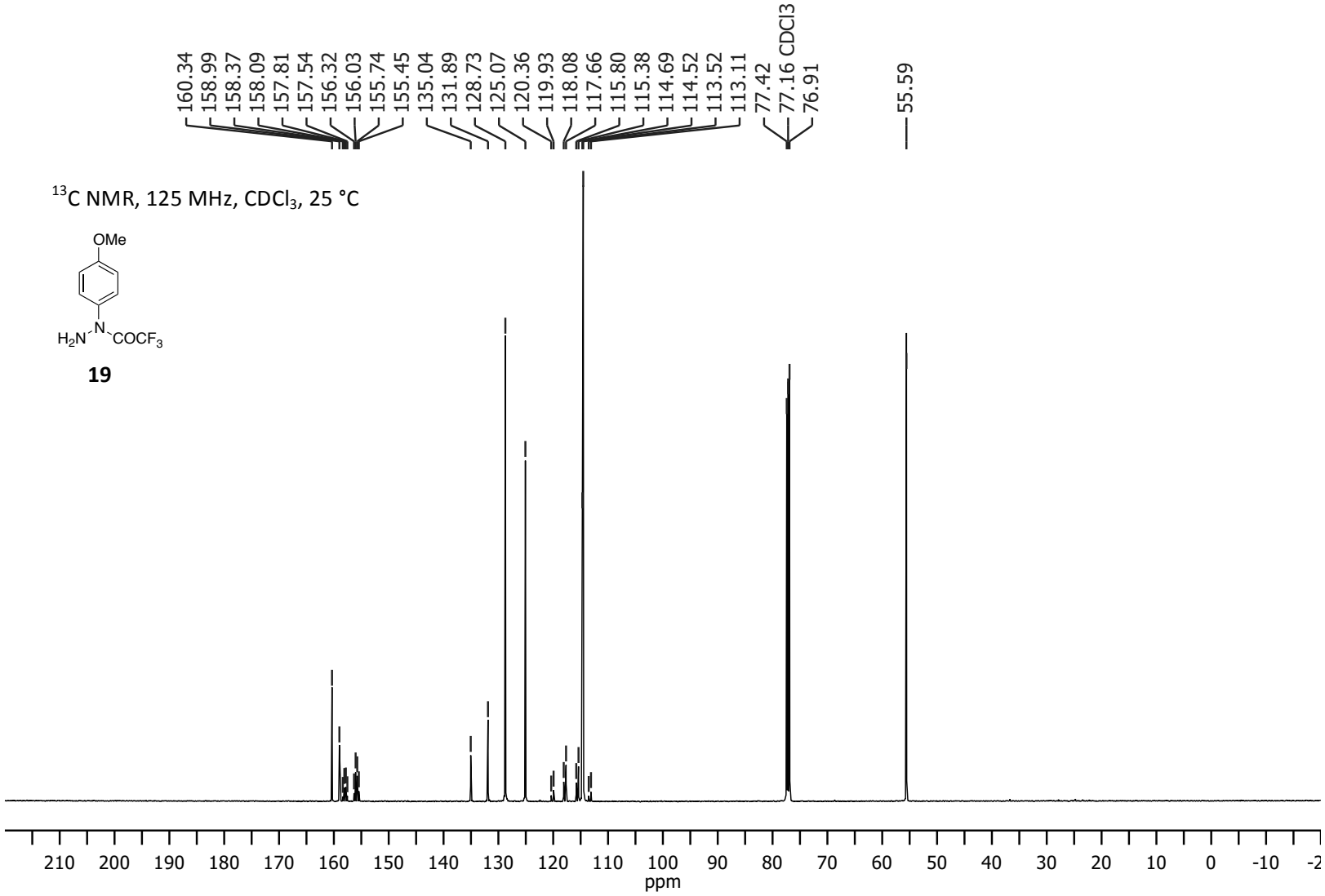
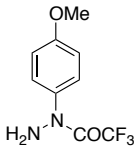
[16] Our assignment of these resonances is supported by key HSQC correlations.
[17] We do not observe any signal at 1.25–1.23 ppm in pure samples of (–)-hodgkinsine B (**3**).
[18] We do not observe signals at 137.8, 130.2 and 58.9 ppm in our data, which has an excellent signal-to-noise ratio.
[19] Similar to Overman's observation regarding the two overlapping signals at 128.3 ppm, we suspect the signal at 127.9 ppm also corresponds to two resonances. We only list one as observed.
[20] An unreported peak is observed at 122.1 ppm in the ^{13}C spectrum of (–)-hodgkinsine B in ref. 15, consistent with our observed data.
[21] We do not observe signals at 21.6 and 18.9 ppm in our data, which has an excellent signal-to-noise ratio. Notably, trimeric cyclotryptamines do not have ^{13}C signals below 30 ppm, see J. J. Kodanko; S. Hiebert; E. A. Peterson; L. Sung; L. E. Overman; V. de Moura Linck; G. C. Goerck; T. A. Amador; M. B. Leal; E. Elisabetsky *J. Org. Chem*. **2007**, *72*, 7909.
[22] Acquisition of NMR spectra in DMSO-d_6 at 90 °C resulted in simplification of the spectra by convergence of the signals for some of the atropisomers. However, we observed gradual sample decomposition with heating during extended acquisition time as previously noted, see: S. M. Canham; B. D. Hafensteiner; A. D. Lebsack; T. L. May-Dracka; S. Nam; B. A. Stearns; L. E. Overman *Tetrahedron* **2015**, *71*, 6424. Acquisition of NMR spectra at low temperature (–80°C to 0 °C) did not yield more informative NMR spectra.
[23] More than the expected 36 ^{13}C resonances were observed due to presence of multiple atropisomers. All observed resonances are listed.
[24] Literature value: $[\alpha]_D^{24} = -33.6$ (*c* 1, $CHCl_3$), see L. Verotta, T. Pilati, M. Tatò, E. Elisabetsky, T. A. Amador, D. S. Nunes *J. Nat. Prod.* **1998**, *61*, 392.
[25] Literature value: 128 °C, see L. Verotta, T. Pilati, M. Tatò, E. Elisabetsky, T. A. Amador, D. S. Nunes *J. Nat. Prod.* **1998**, *61*, 392.
[26] Verotta, L.; Pilati, T.; Tatò, M.; Elisabetsky, E.; Amador, T. A.; Nunes, D. S. *J. Nat. Prod.* **1998**, *61*, 392.
[27] Synthetic sample of (–)-hodgkinsine (**4**): While no spectroscopic data was tabulated for the synthetic sample in Kodanko, J. J.; Overman, L. E. *Angew. Chem. Int. Ed.* **2003**, *42*, 2528, the authors state that the "NMR spectra at rt and 234K were identical to those reported [Verotta isolation report] for natural hodgkinsine".
[28] This resonance is likely a typographical error as all C2 resonances are observed near 52 ppm in these systems.
[29] Literature value: $[\alpha]_D = -18$ (*c* 1, $CHCl_3$), see F. Libot, N. Kunesch, J. Poisson *Heterocycles* **1988**, *27*, 2381. Literature value: $[\alpha]_D = -18$ (*c* 1, $CHCl_3$), see F. Libot, C. Miet, N. Kunesch, J. Poisson *J. Nat. Prod.* **1987**, *50*, 468.
[30] Our assignment of these resonances is supported by HSQC correlations.
[31] The reported data only lists 31 of the 33 theoretical ^{13}C signals.

[32] The signal at 47.7 was omitted in the list of ^{13}C resonances provided for (–)-calycosidine in reference 29; however, it is in the assignment table of the same report.
[33] The reported integrals for intermediate (+)-**S11** are an approximation due to presence of multiple conformers and significant atropisomerism
[34] Due to atropisomerism, we observe more than the expected 48 ^{13}C NMR signals.
[35] The reported integrals for (–)-quadrigemine C (**7**) are an approximation due to presence of multiple conformers and significant atropisomerism.
[36] Due to atropisomerism, we observe more than the expected 44 ^{13}C NMR signals.
[37] Literature value: $[\alpha]_D = –69$ (*c* 1, $CHCl_3$), see F. Libot, C. Miet, N. Kunesch, J. Poisson *J. Nat. Prod.* **1987**, *50*, 468. Literature value: $[\alpha]_D^{20} = –64$ (*c* 1, $CHCl_3$), see L. Verotta, T. Pilati, M. Tatò, E. Elisabetsky, T. A. Amador, D. S. Nunes *J. Nat. Prod.* **1998**, *61*, 392.
[38] Libot, F.; Miet, C.; Kunesch, N.; Poisson, J.; *J. Nat. Prod.* **1987**, *50*, 468.
[39] Synthetic sample of (–)-quadrigemine C (**7**): While no spectroscopic data was tabulated for the synthetic sample in Lebsack, A.D.; Link, J. T.; Overman, L. E.; Stearns, B. A. *J. Am. Chem. Soc.* **2002**, *124*, 9008, the authors state that "spectral (^1H and ^{13}C NMR in $CDCl_3$ at rt and 241 K; IR) were indistinguishable from those of a sample of natural [quadrigemine C]".
[40] Literature value: $[\alpha]_D^{20} = –150$ (*c* 0.4, EtOH), see Guéritte-Voegelein, F.; Sévenet, T.; Pusset, J.; Adeline, M.-T.; Gillet, B.; Beloeil, J.-C.; Guénard, D.; Potier, P. *J. Nat. Prod.* **1992**, *55*, 923. Literature value: $[\alpha]_D^{28} = –150$ (*c* 0.1, EtOH), see Lebsack, A. D.; Link, J. T.; Overman, L. E.; Stearns, B. A. *J. Am. Chem. Soc.* **2002**, *124*, 9008.
[41] Guéritte-Voegelein, F.; Sévenet, T.; Pusset, J.; Adeline, M.-T.; Gillet, B.; Beloeil, J.-C.; Guénard, D.; Potier, P. *J. Nat. Prod.* **1992**, *55*, 923. All available data from is tabulated in Table S9.
[42] Lebsack, A. D. Ph.D. Dissertation, University of California, Irvine, 2002.
[43] For the original publication, see Lebsack, A. D.; Link, J. T.; Overman, L. E.; Stearns, B. A. *J. Am. Chem. Soc.* **2002**, *124*, 9008.
[44] The previously reported ^{13}C data for (–)-psycholeine (**8**) lists 41 of the 44 theoretical signals, whereas we are able to detect all the expected resonances.


^{1}H NMR, 400 MHz, $CDCl_3$, 25 °C
OMe
H_2N
N
$COCF_3$
19
7.33
7.33
7.32
7.31
7.26 CDCl3
7.24
7.22
6.94
6.93
6.92
6.92
6.91
6.90
4.70
4.39
3.82
3.80
12.2
11.6
11.0
10.4
9.8
9.2
8.6
8.0
7.4
6.8
6.2
5.6
5.0
4.4
3.8
3.2
2.6
2.0
1.4
0.8
0.2
ppm

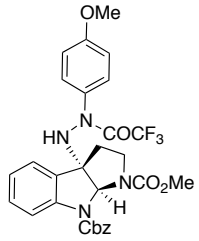

160.34
158.99
158.37
158.09
157.81
157.54
156.32
156.03
155.74
155.45
135.04
131.89
128.73
125.07
120.36
119.93
118.08
117.66
115.80
115.38
114.69
114.52
113.52
113.11
77.42
77.16 CDCl3
76.91
55.59
13C NMR, 125 MHz, CDCl3, 25 °C
OMe
H2N
N
COCF3
19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
ppm

^{19}F NMR, 282 MHz, $CDCl_3$, 25 °C

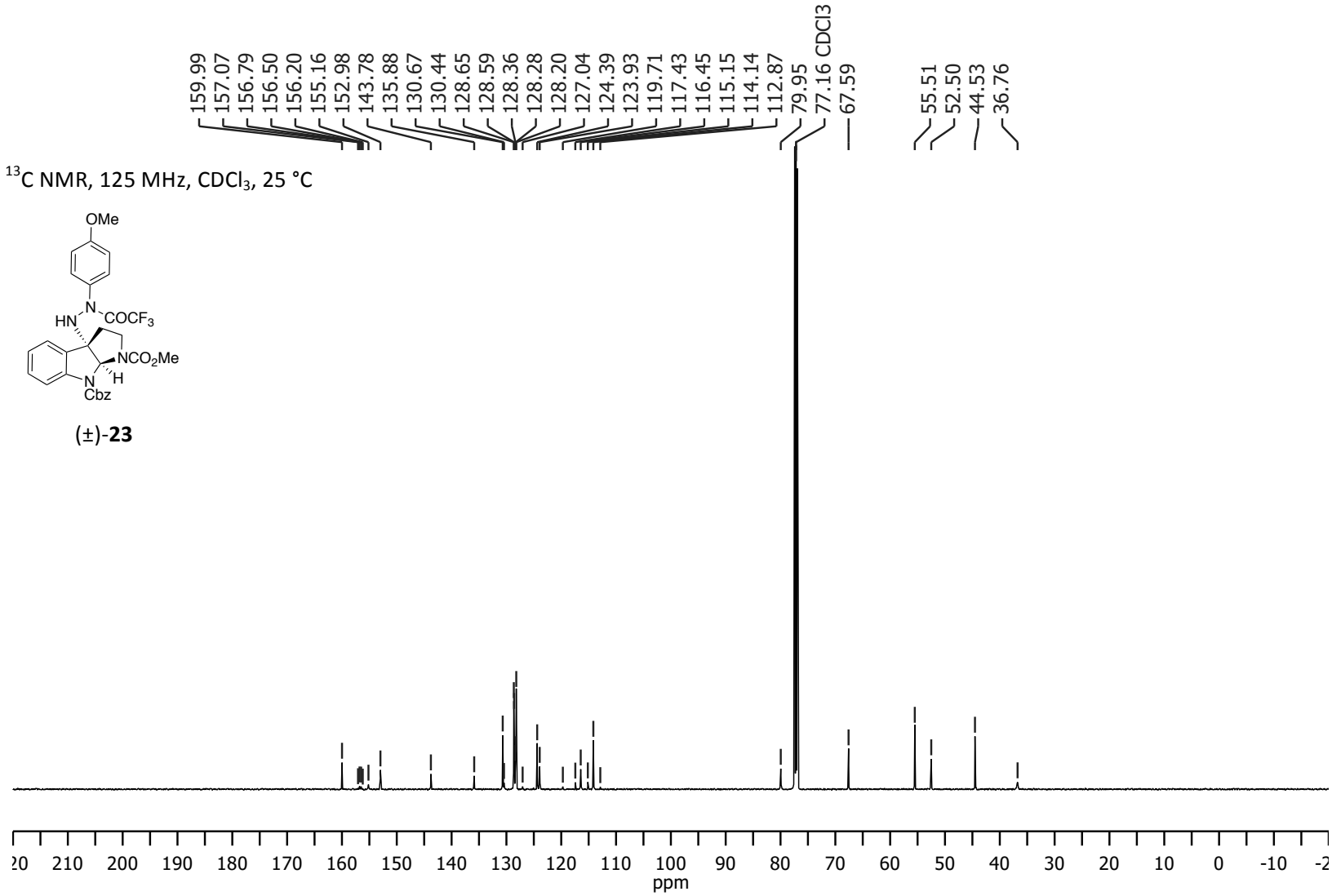


19

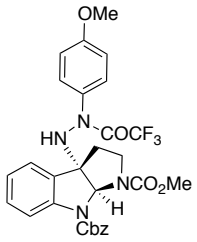
^{1}H NMR, 400 MHz, $CDCl_3$, 25 °C



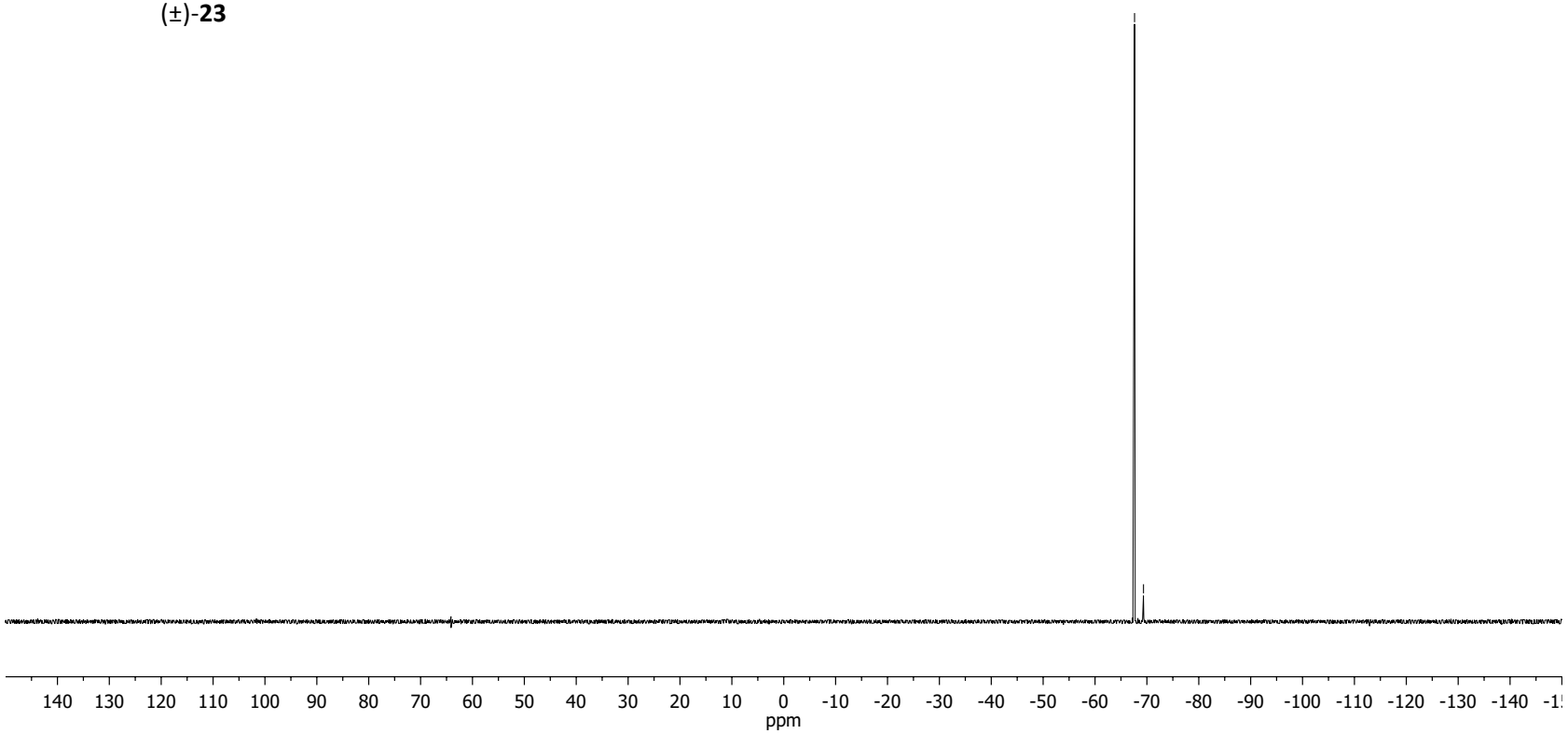
(±)-**23**

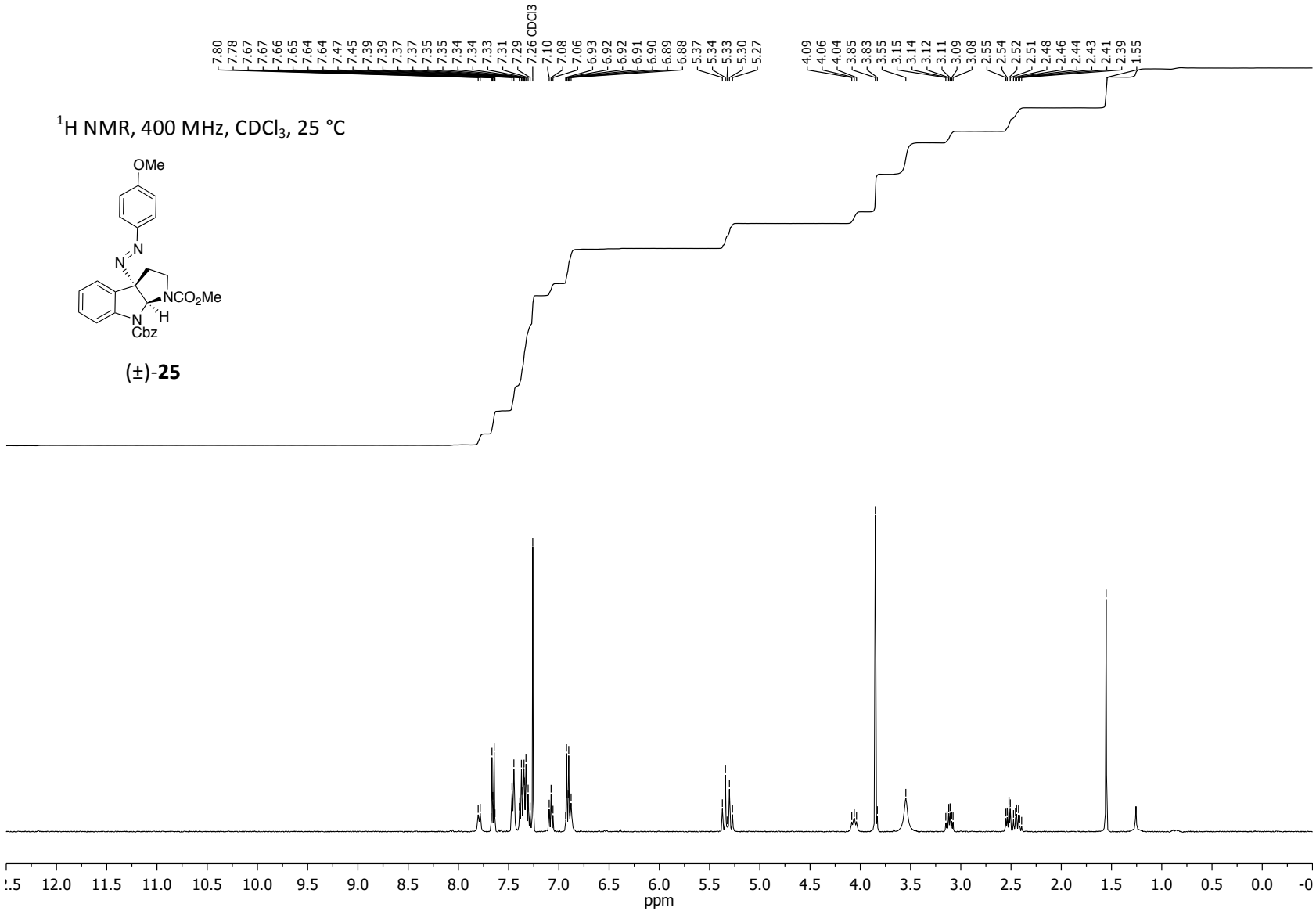

159.99
157.07
156.79
156.50
156.20
155.16
152.98
143.78
135.88
130.67
130.44
128.65
128.59
128.36
128.28
128.20
127.04
124.39
123.93
119.71
117.43
116.45
115.15
114.14
112.87
79.95
77.16 CDCl3
67.59
55.51
52.50
44.53
36.76
13C NMR, 125 MHz, CDCl3, 25 °C
OMe
N
HN
COCF3
NCO2Me
N
H
Cbz
(±)-23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

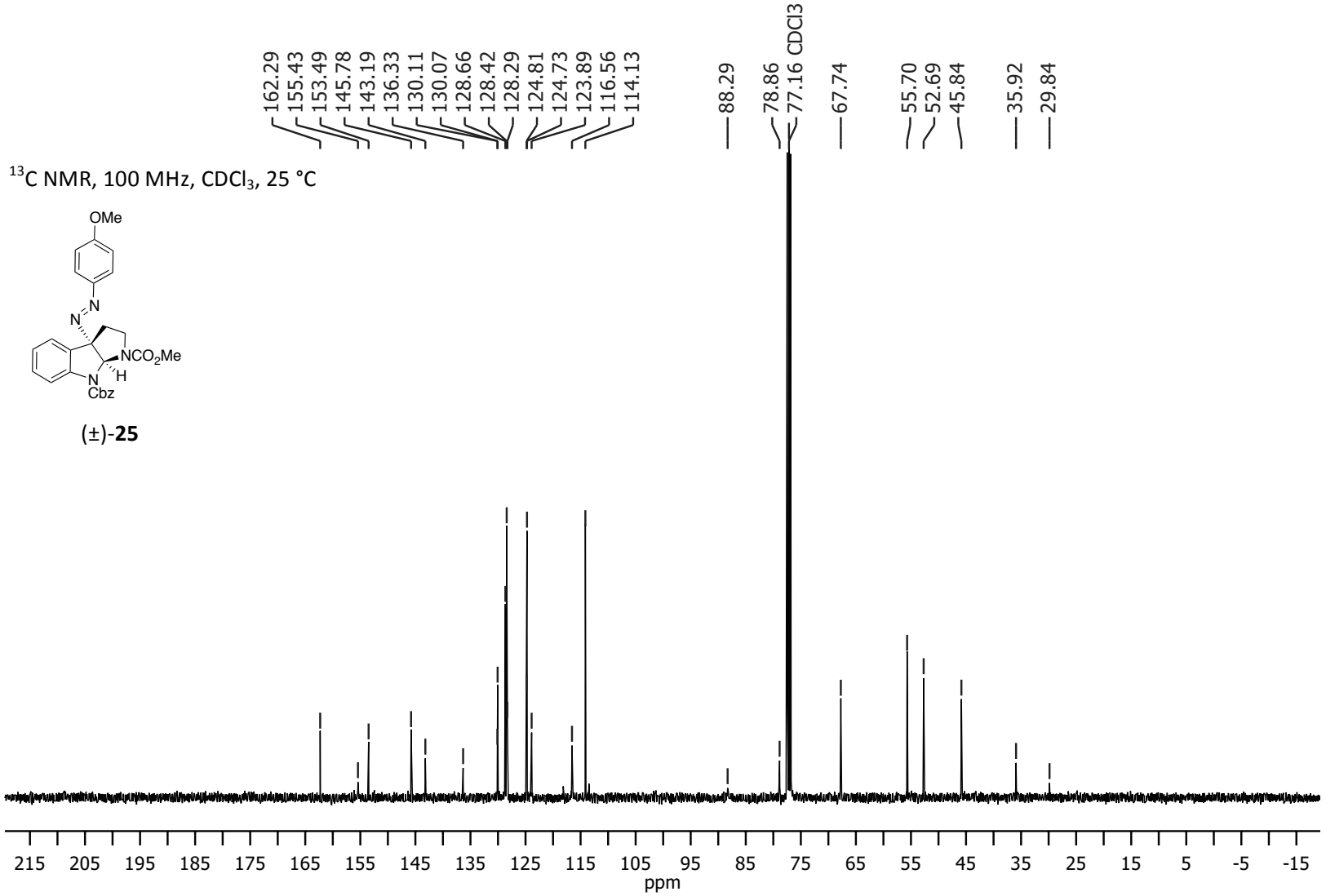
^{19}F NMR, 282 MHz, $CDCl_3$, 25 °C



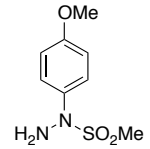
(±)-**23**




7.80
7.78
7.67
7.67
7.66
7.65
7.64
7.64
7.47
7.45
7.39
7.39
7.37
7.37
7.35
7.35
7.34
7.34
7.33
7.31
7.29
7.26 CDCl3
7.10
7.08
7.06
6.93
6.92
6.92
6.91
6.90
6.89
6.88
5.37
5.34
5.33
5.30
5.27
4.09
4.06
4.04
3.85
3.83
3.55
3.15
3.14
3.12
3.11
3.09
3.08
2.55
2.54
2.52
2.51
2.48
2.46
2.44
2.43
2.41
2.39
1.55
1H NMR, 400 MHz, CDCl3, 25 °C
OMe
N
N
NCO2Me
N
H
Cbz
(±)-25
ppm

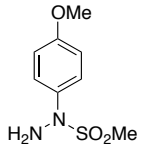

162.29
155.43
153.49
145.78
143.19
136.33
130.11
130.07
128.66
128.42
128.29
124.81
124.73
123.89
116.56
114.13
88.29
78.86
77.16 CDCl3
67.74
55.70
52.69
45.84
35.92
29.84
13C NMR, 100 MHz, CDCl3, 25 °C
OMe
N
N
NCO2Me
N
H
Cbz
(±)-25
215 205 195 185 175 165 155 145 135 125 115 105 95 85 75 65 55 45 35 25 15 5 -5 -15
ppm

^{1}H NMR, 400 MHz, $CDCl_3$, 25 °C



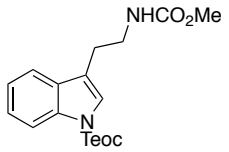
20

^{13}C NMR, 100 MHz, $CDCl_3$, 25 °C



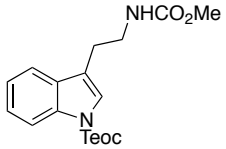
20

^{1}H NMR, 400 MHz, $CDCl_3$, 25 °C

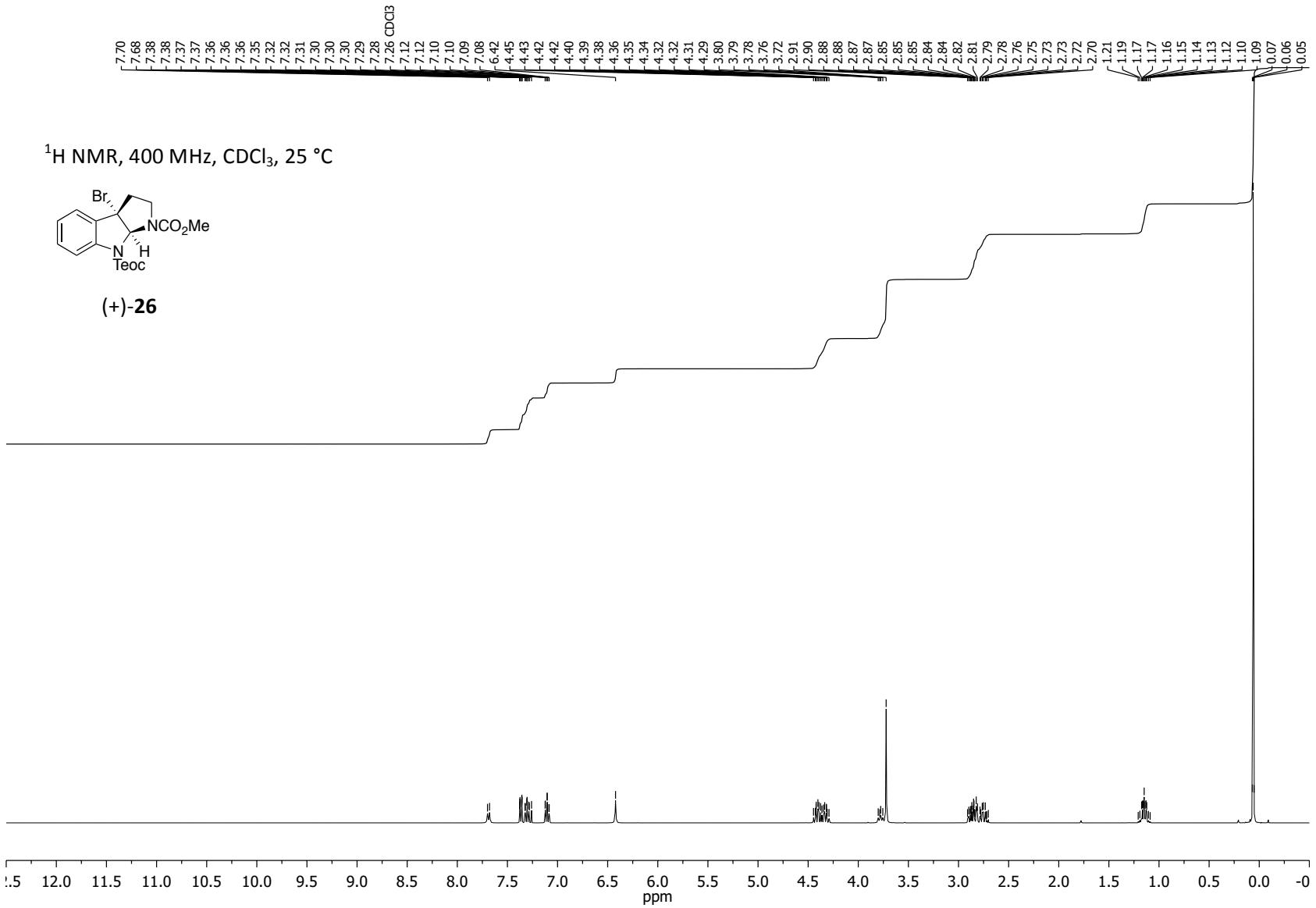


S5

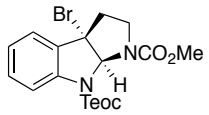
^{13}C NMR, 100 MHz, $CDCl_3$, 25 °C



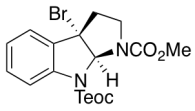
S5


CDCl3
7.70 7.68 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.32 7.32 7.31 7.30 7.30 7.30 7.29 7.28 7.26 7.12 7.12 7.10 7.10 7.09 7.08 6.42 4.45 4.43 4.42 4.42 4.40 4.39 4.38 4.36 4.35 4.34 4.32 4.32 4.31 4.29 3.80 3.79 3.78 3.76 3.72 2.91 2.90 2.88 2.88 2.87 2.87 2.85 2.85 2.85 2.84 2.84 2.82 2.81 2.79 2.78 2.76 2.75 2.73 2.73 2.72 2.70 1.21 1.19 1.17 1.17 1.16 1.15 1.14 1.13 1.12 1.10 1.09 0.07 0.06 0.05
^{1}H NMR, 400 MHz, $CDCl_3$, 25 °C
Br
NCO2Me
N
H
Teoc
(+)-26
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

^{13}C NMR, 100 MHz, $CDCl_3$, 25 °C



(+)-**26**



(±)-**26**

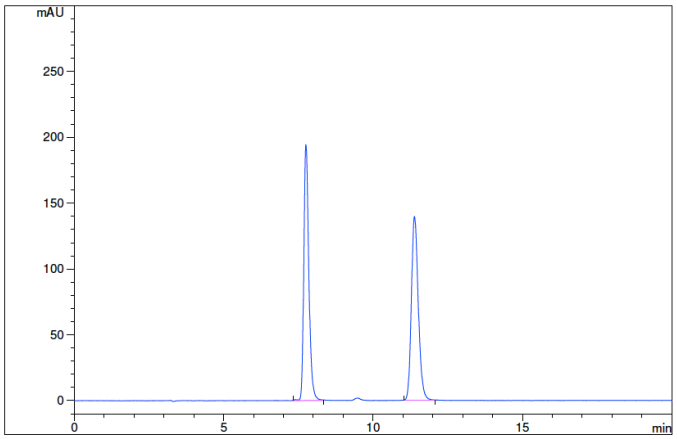
HPLC Conditions:

Chiralpak IA, column no. IA00CE-PD046

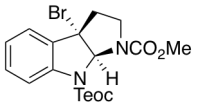
5% Isopropanol/ 95% Hexanes

1.0 mL/min

254 nm



#	Meas. Ret. Time	Area %
1	7.753	50.036
2	11.386	49.964



(+)-**26**

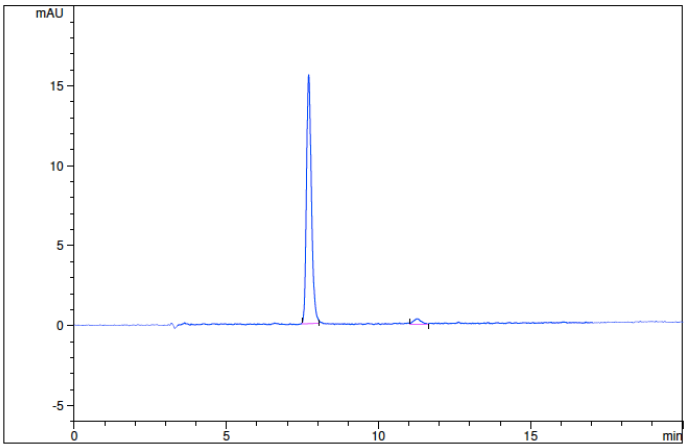
HPLC Conditions:

Chiralpak IA, column no. IA00CE-PD046

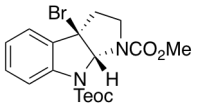
5% Isopropanol/ 95% Hexanes

1.0 mL/min

254 nm



#	Meas. Ret. Time	Area %
1	7.705	96.842
2	11.251	3.158



(–)-**26**

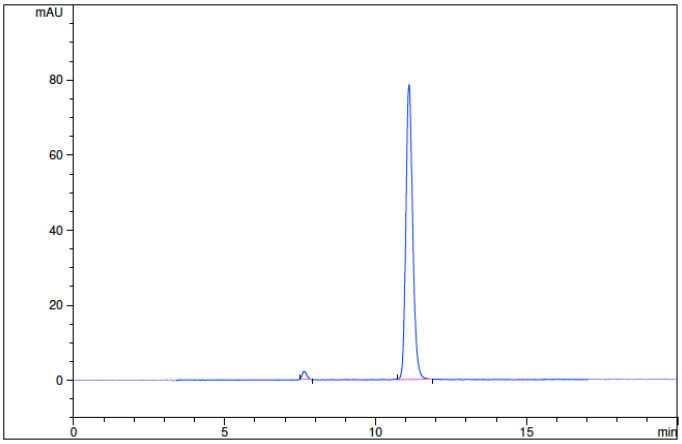
HPLC Conditions:

Chiralpak IA, column no. IA00CE-PD046

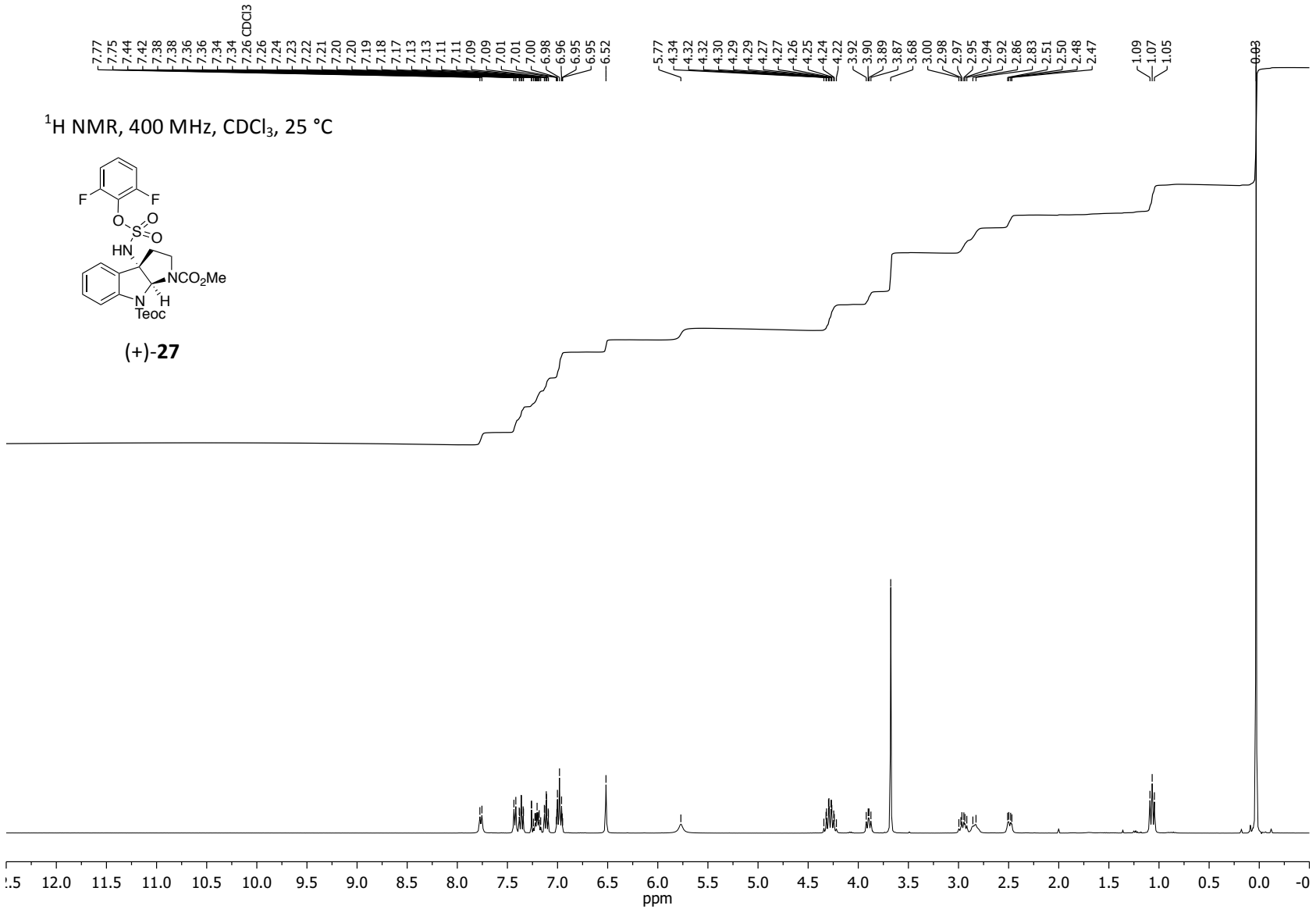
5% Isopropanol/ 95% Hexanes

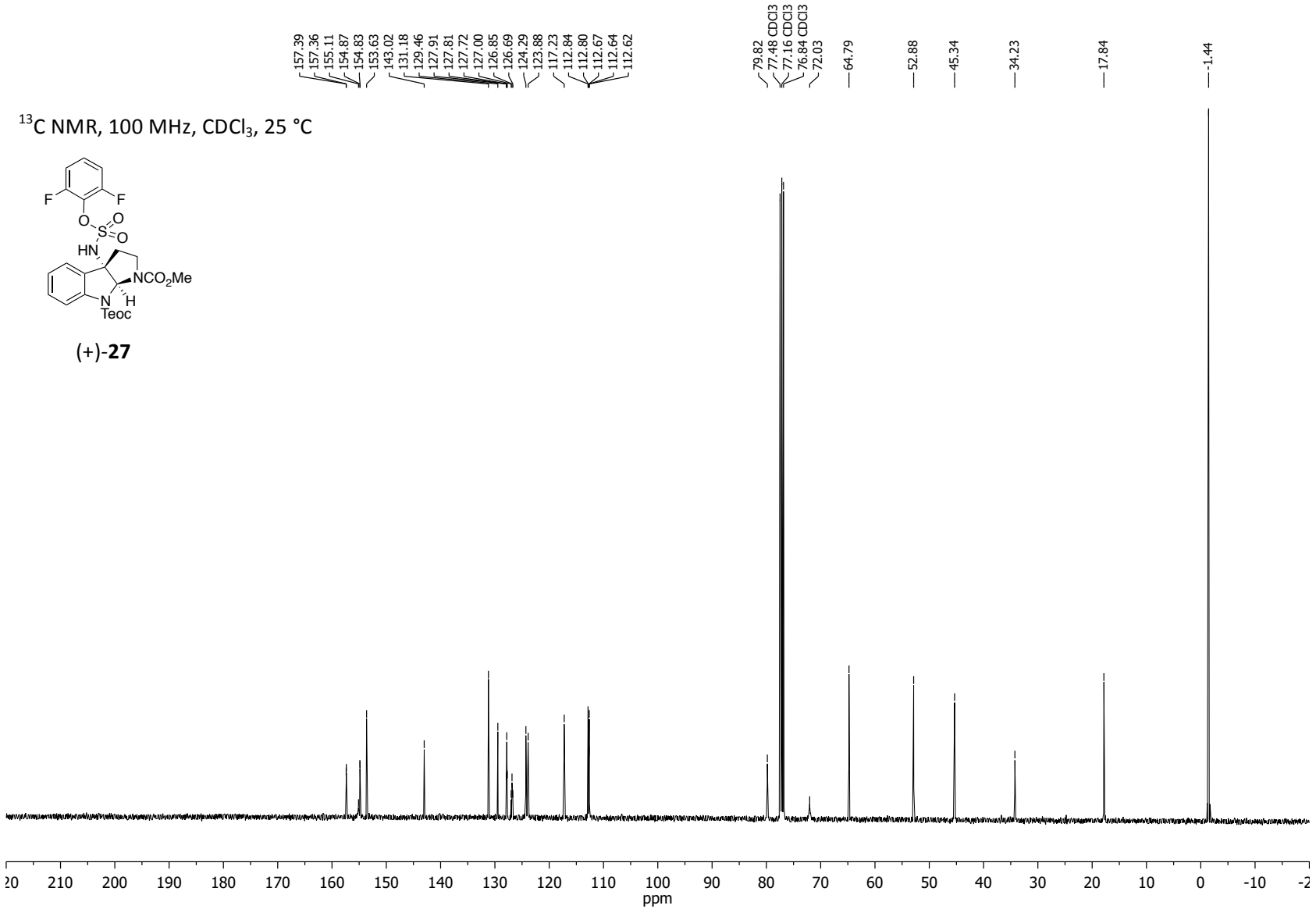
1.0 mL/min

254 nm

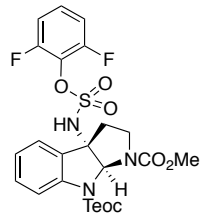


#	Meas. Ret. Time	Area %
1	7.635	1.857
2	11.106	98.143

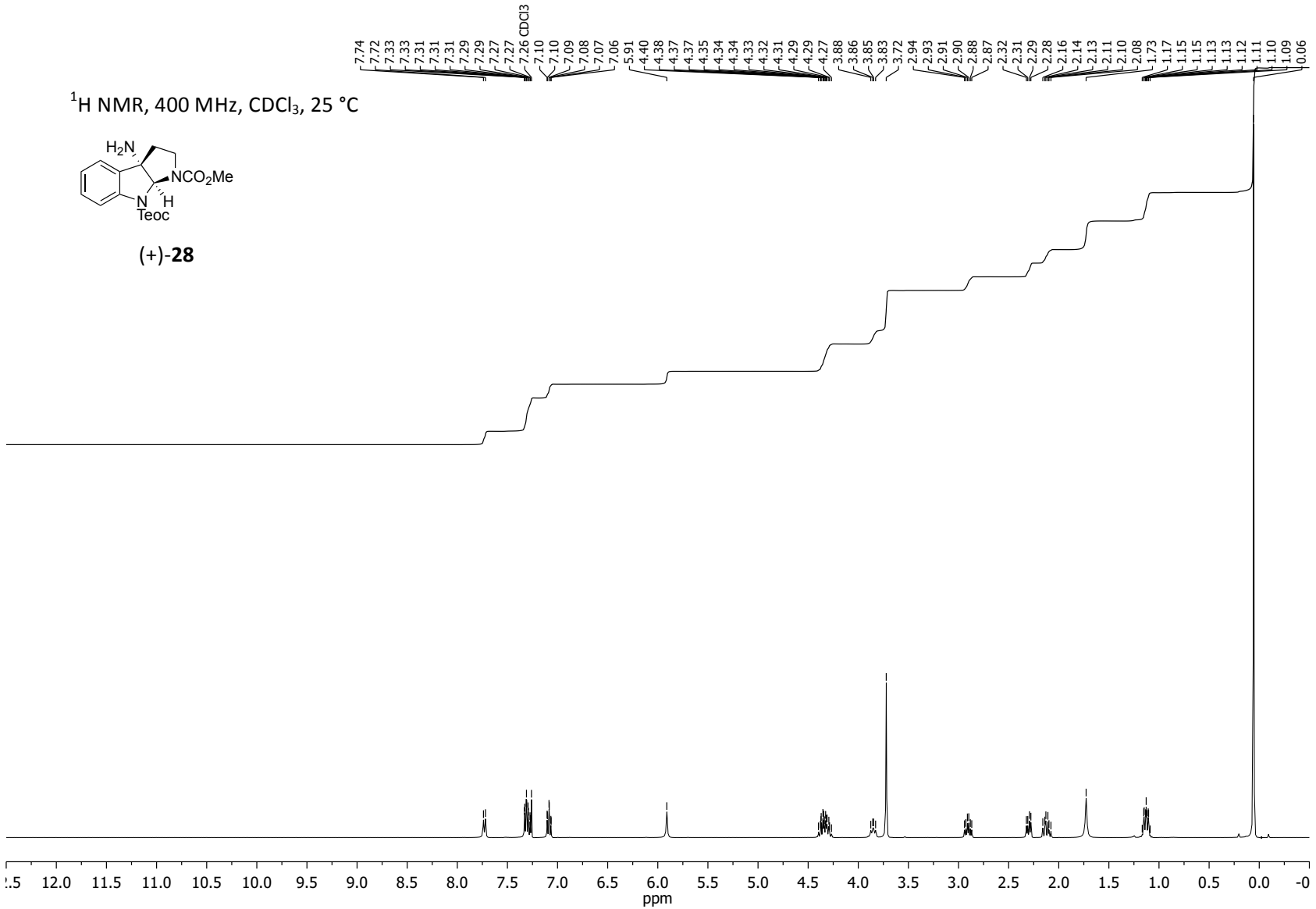

7.77
7.75
7.44
7.42
7.38
7.38
7.36
7.36
7.34
7.34
7.26 CDCl3
7.26
7.24
7.23
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.13
7.13
7.11
7.11
7.09
7.09
7.01
7.01
7.00
6.98
6.96
6.95
6.95
6.52
5.77
4.34
4.32
4.32
4.30
4.29
4.29
4.27
4.27
4.26
4.25
4.24
4.22
3.92
3.90
3.89
3.87
3.68
3.00
2.98
2.97
2.95
2.94
2.92
2.86
2.83
2.51
2.50
2.48
2.47
1.09
1.07
1.05
0.03
1H NMR, 400 MHz, CDCl3, 25 °C
F
F
O
S
O
O
HN
NCO2Me
N
H
Teoc
(+)-27
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

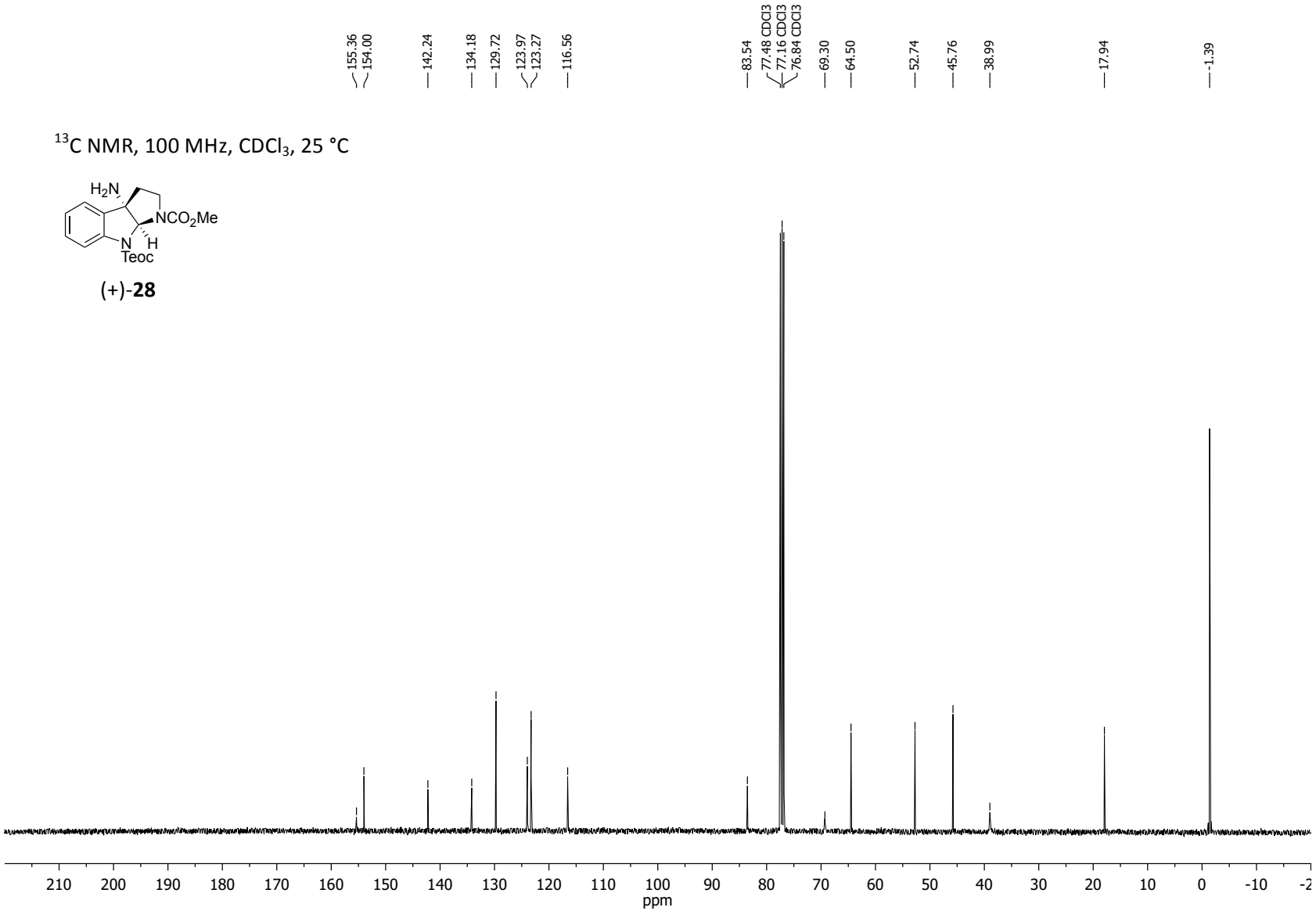

157.39
157.36
155.11
154.87
154.83
153.63
143.02
131.18
129.46
127.91
127.81
127.72
127.00
126.85
126.69
124.29
123.88
117.23
112.84
112.80
112.67
112.64
112.62
79.82
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
72.03
64.79
52.88
45.34
34.23
17.84
-1.44
13C NMR, 100 MHz, CDCl3, 25 °C
F
F
O
S
O
O
HN
NCO2Me
N
H
Teoc
(+)-27
ppm

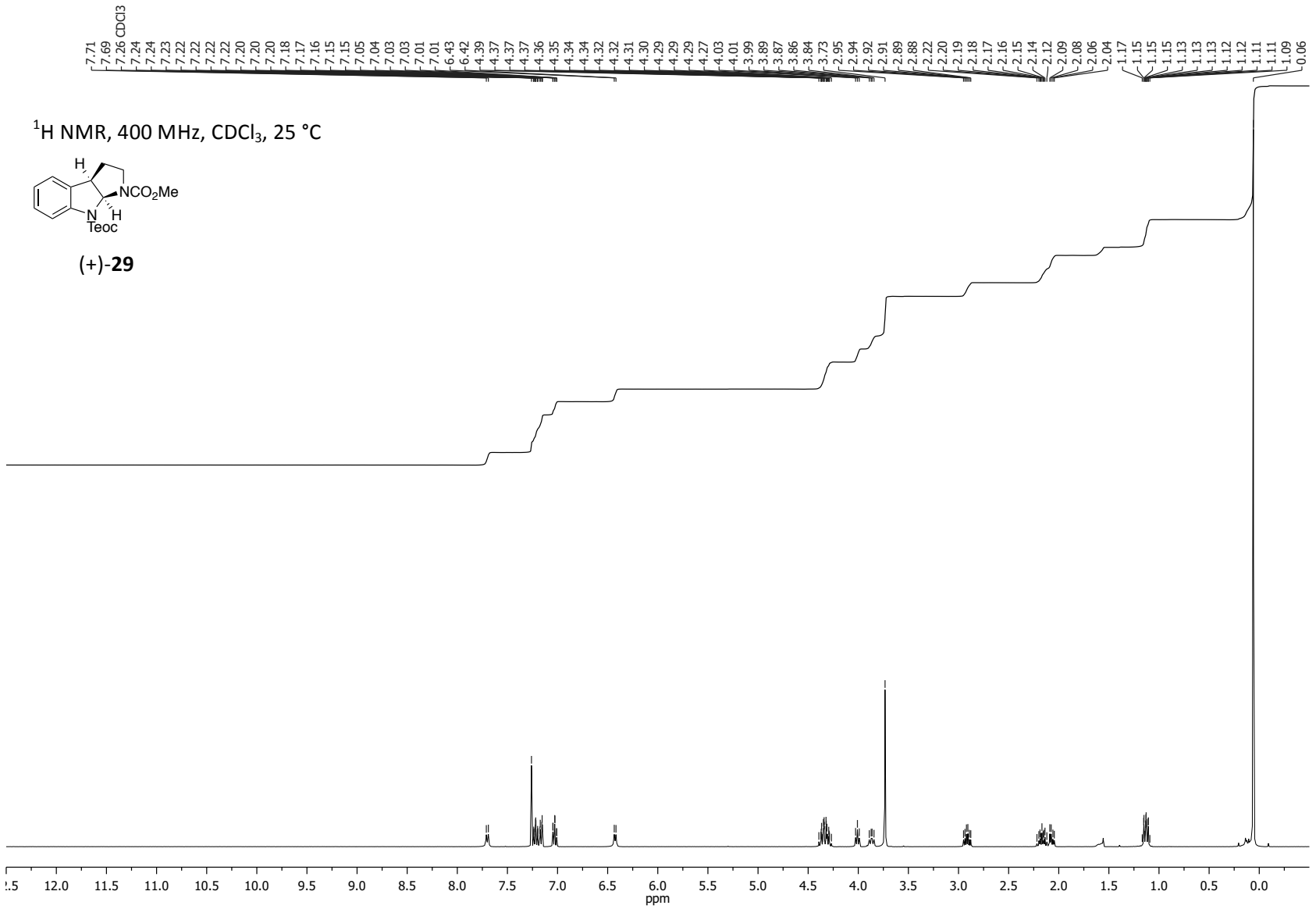
^{19}F NMR, 282 MHz, $CDCl_3$, 25 °C



(+)-**27**

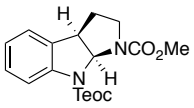

7.74
7.72
7.33
7.33
7.31
7.31
7.31
7.29
7.29
7.27
7.27
7.26
CDCl3
7.10
7.10
7.09
7.08
7.07
7.06
5.91
4.40
4.38
4.37
4.37
4.35
4.34
4.34
4.33
4.32
4.31
4.29
4.29
4.27
3.88
3.86
3.85
3.83
3.72
2.94
2.93
2.91
2.90
2.88
2.87
2.32
2.31
2.29
2.28
2.16
2.14
2.13
2.11
2.10
2.08
1.73
1.17
1.15
1.15
1.13
1.13
1.12
1.11
1.10
1.09
0.06
1H NMR, 400 MHz, CDCl3, 25 °C
H2N
NCO2Me
N
H
Teoc
(+)-28
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


155.36
154.00
142.24
134.18
129.72
123.97
123.27
116.56
83.54
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.30
64.50
52.74
45.76
38.99
17.94
-1.39
^{13}C NMR, 100 MHz, $CDCl_3$, 25 °C
H_2N
NCO_2Me
N H
Teoc
(+)-**28**
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
ppm

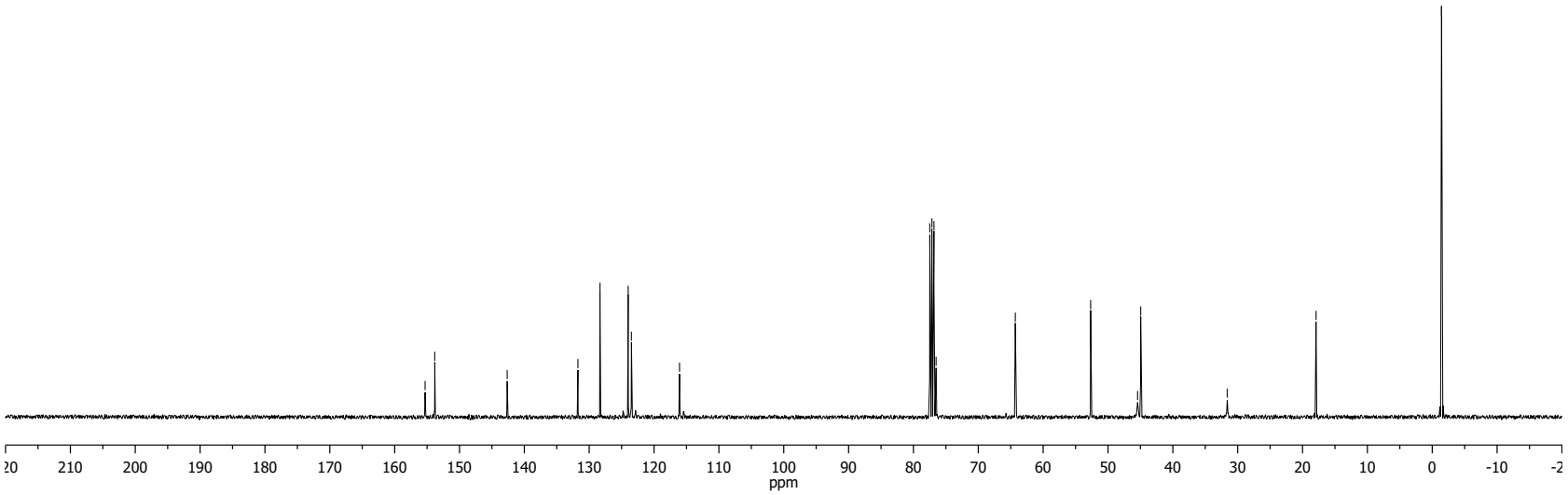

7.71 7.69 CDCl3 7.26 7.24 7.24 7.23 7.22 7.22 7.22 7.20 7.20 7.18 7.17 7.16 7.15 7.15 7.05 7.04 7.03 7.03 7.01 7.01 6.43 6.42 4.39 4.37 4.37 4.37 4.36 4.35 4.34 4.34 4.32 4.32 4.31 4.30 4.29 4.29 4.29 4.27 4.03 4.01 3.99 3.89 3.87 3.86 3.84 3.73 2.95 2.94 2.92 2.91 2.89 2.88 2.22 2.20 2.19 2.18 2.17 2.16 2.15 2.14 2.12 2.09 2.08 2.06 2.04 1.17 1.15 1.15 1.15 1.13 1.13 1.12 1.12 1.11 1.11 1.09 0.06
^{1}H NMR, 400 MHz, $CDCl_3$, 25 °C
H
NCO2Me
N H
Teoc
(+)-29
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

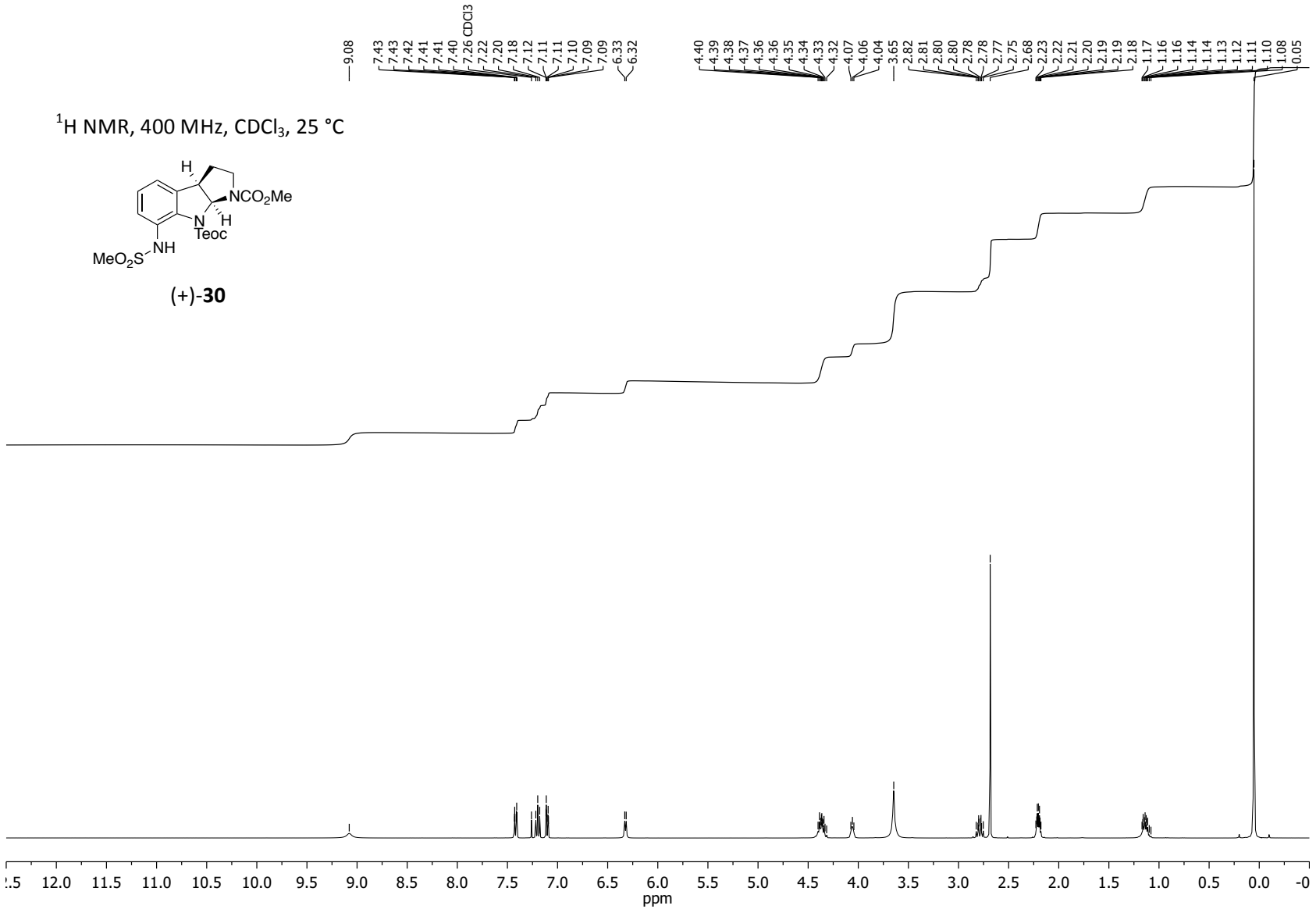
155.30
153.81
142.65
131.74
128.34
123.99
123.48
116.07
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.51
64.29
52.68
45.44
44.96
31.61
17.92
-1.43

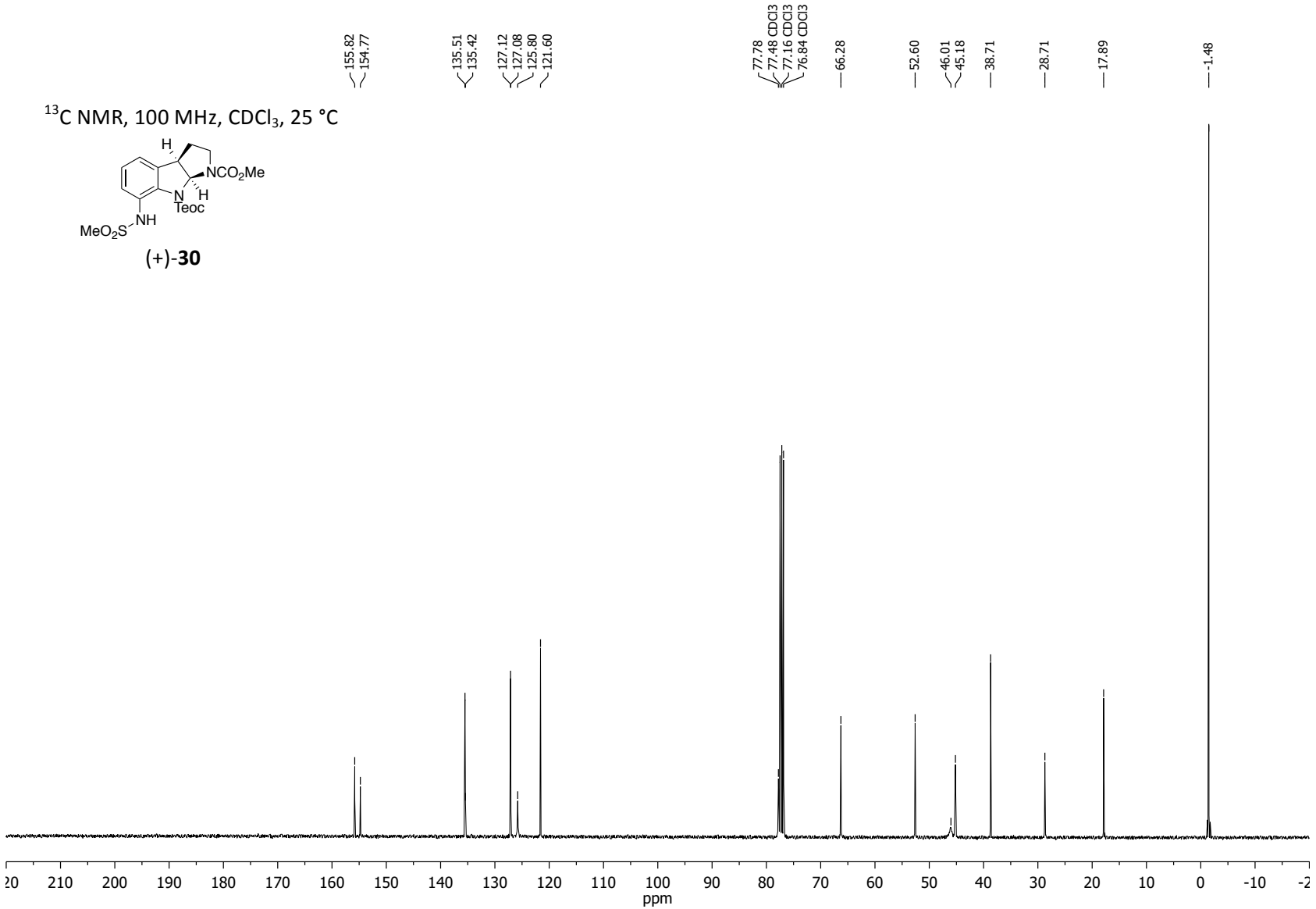
^{13}C NMR, 100 MHz, $CDCl_3$, 25 °C



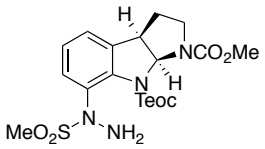
(+)-**29**




9.08
7.43
7.43
7.42
7.41
7.41
7.40
CDCl3
7.26
7.22
7.20
7.18
7.12
7.11
7.11
7.10
7.09
7.09
6.33
6.32
4.40
4.39
4.38
4.37
4.36
4.36
4.35
4.34
4.33
4.32
4.07
4.06
4.04
3.65
2.82
2.81
2.80
2.80
2.78
2.78
2.77
2.75
2.68
2.23
2.22
2.21
2.20
2.19
2.19
2.18
1.17
1.16
1.16
1.14
1.14
1.13
1.12
1.11
1.10
1.08
0.05
1H NMR, 400 MHz, CDCl3, 25 °C
H
NCO2Me
N
H
Teoc
NH
MeO2S
(+)-30
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

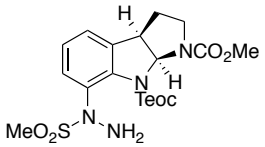

155.82
154.77
135.51
135.42
127.12
127.08
125.80
121.60
77.78
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
66.28
52.60
46.01
45.18
38.71
28.71
17.89
-1.48
13C NMR, 100 MHz, CDCl3, 25 °C
H
NCO2Me
N
H
Teoc
NH
MeO2S
(+)-30
ppm

^{1}H NMR, 400 MHz, $CDCl_3$, 25 °C

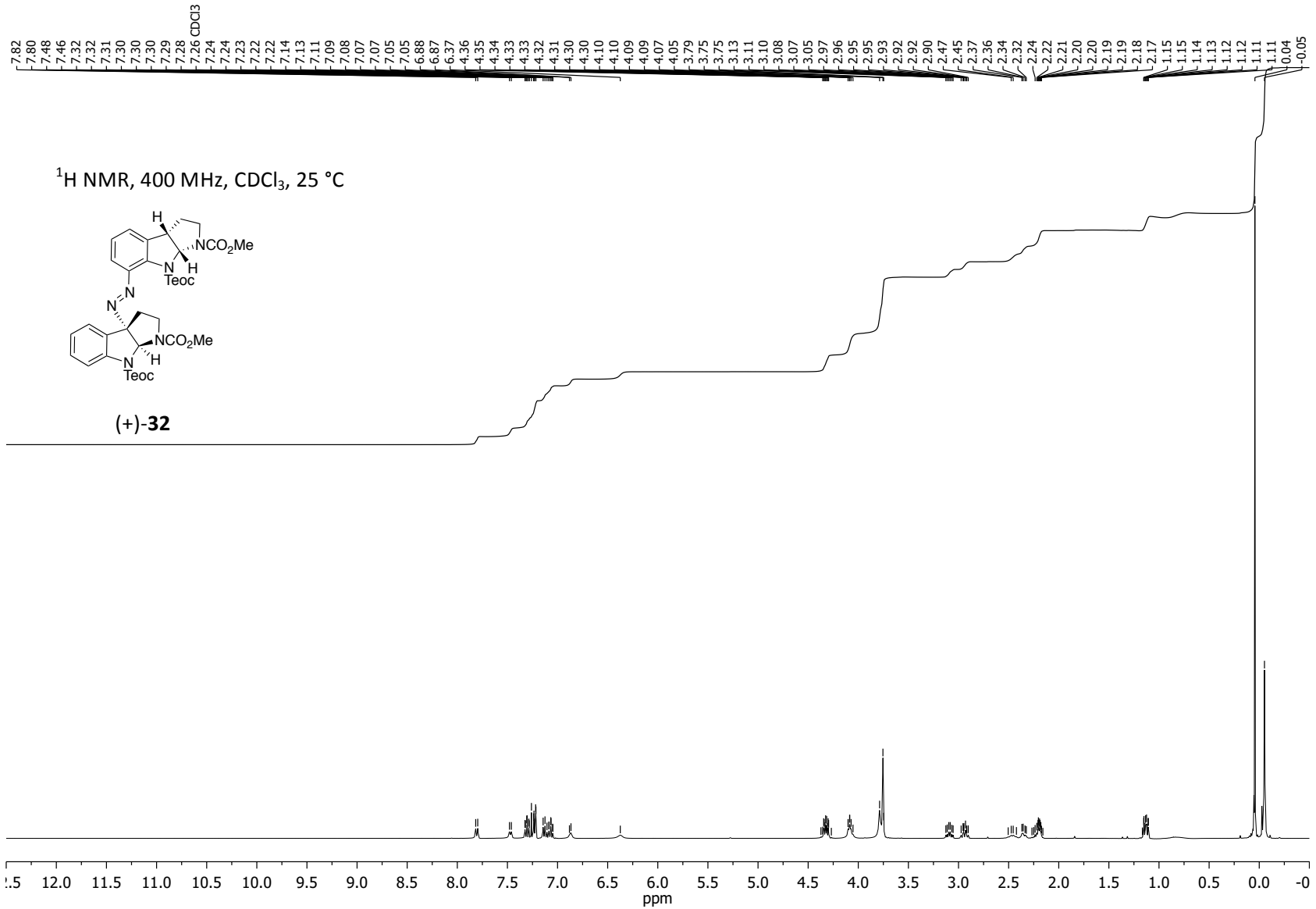


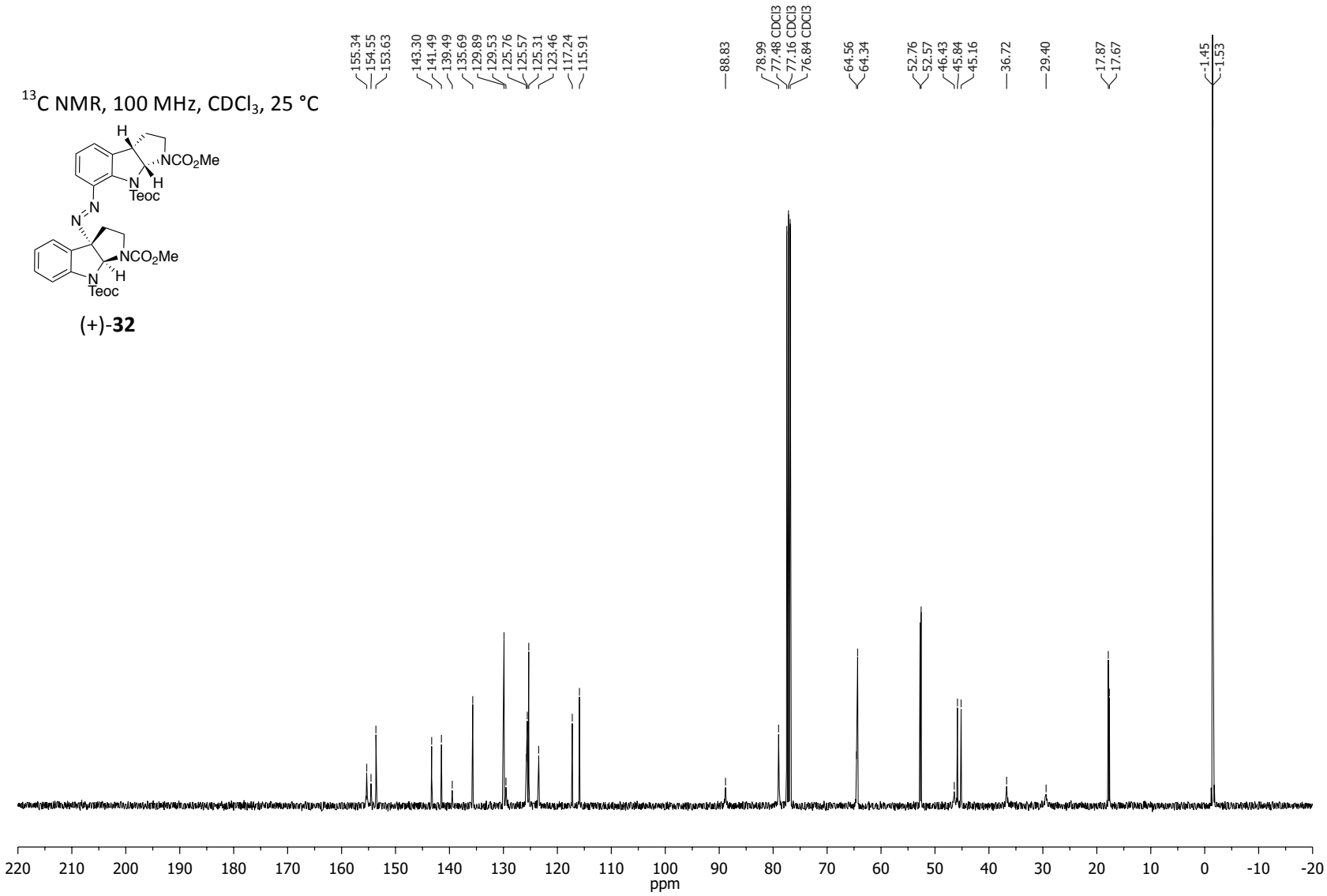
(+)-**31**

^{13}C NMR, 100 MHz, $CDCl_3$, 25 °C



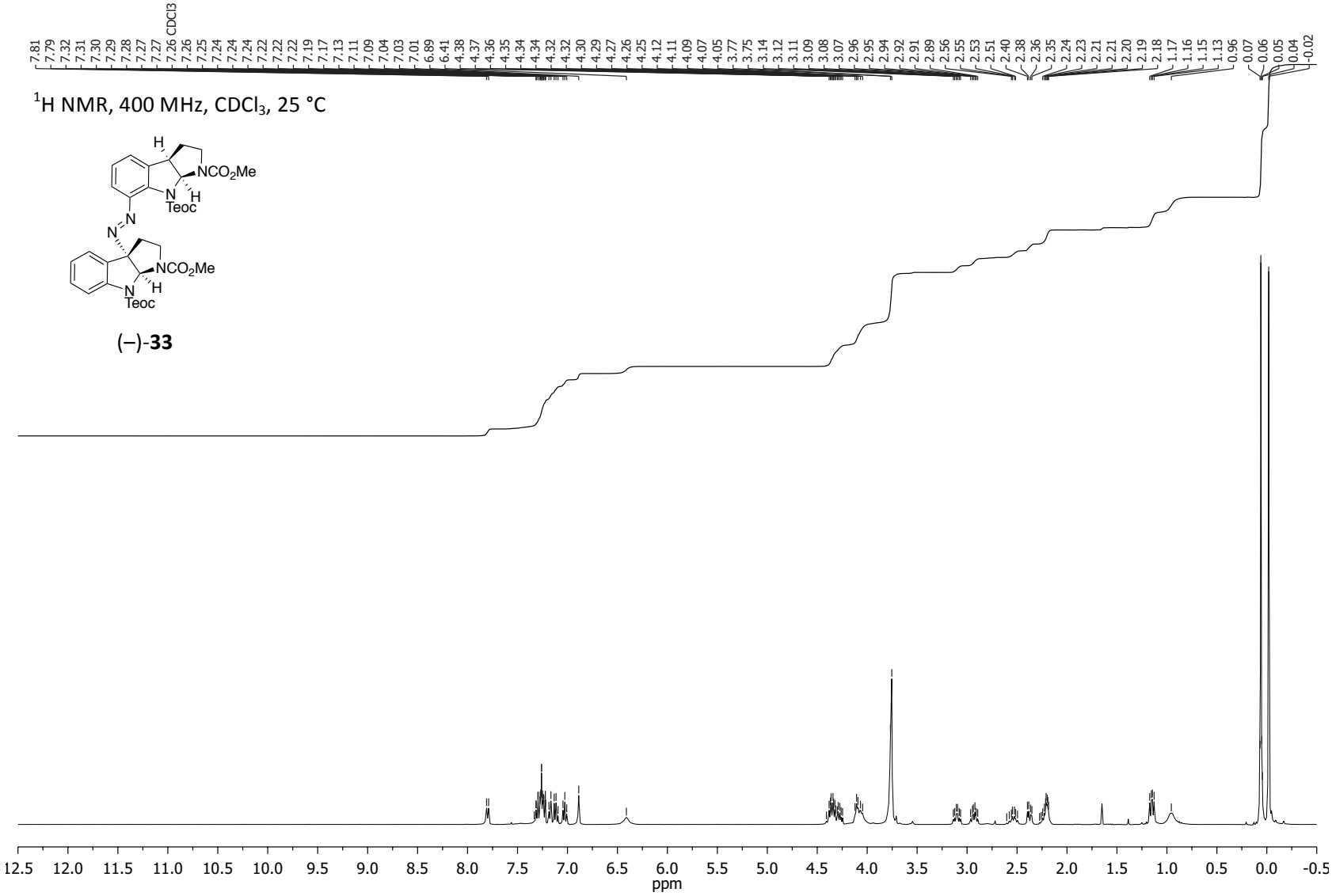
(+)-**31**


CDCl3
7.82 7.80 7.48 7.46 7.32 7.32 7.31 7.30 7.30 7.30 7.29 7.28 7.26 7.24 7.24 7.23 7.22 7.22 7.14 7.13 7.11 7.09 7.08 7.07 7.07 7.05 7.05 6.88 6.87 6.37 4.36 4.35 4.34 4.33 4.33 4.32 4.31 4.30 4.30 4.10 4.10 4.09 4.09 4.07 4.05 3.79 3.75 3.75 3.13 3.11 3.10 3.08 3.07 3.05 2.97 2.96 2.95 2.95 2.93 2.92 2.92 2.90 2.47 2.45 2.37 2.36 2.34 2.32 2.24 2.22 2.21 2.20 2.20 2.19 2.19 2.18 2.17 1.15 1.15 1.14 1.13 1.12 1.12 1.11 1.11 0.04 -0.05
1H NMR, 400 MHz, CDCl3, 25 °C
H
NCO2Me
N H
Teoc
N
N
NCO2Me
N H
Teoc
(+)-32
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

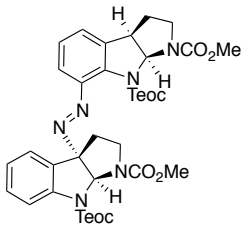


^{13}C NMR, 100 MHz, $CDCl_3$, 25 °C

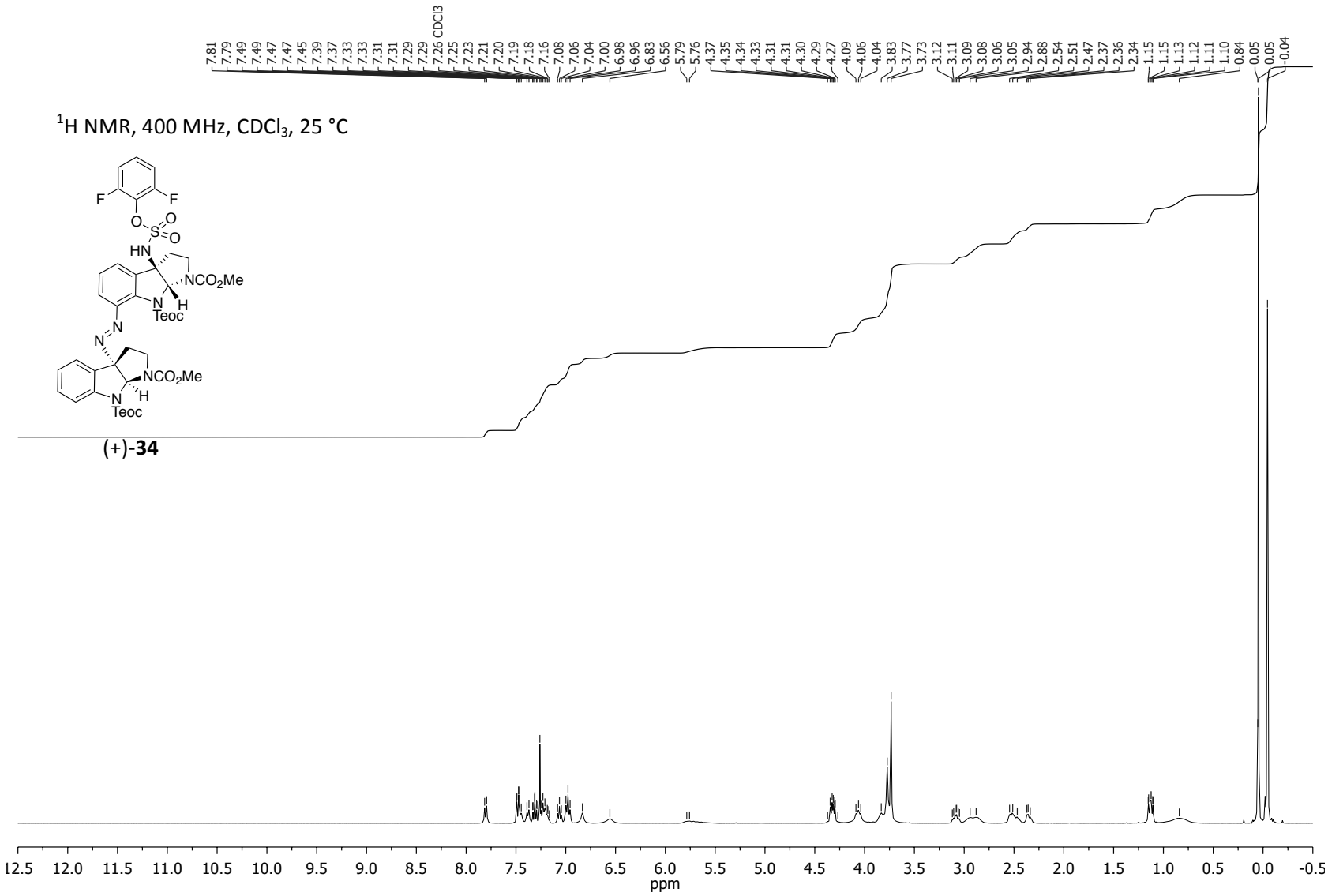
(+)-**32**


7.81 7.79 7.32 7.31 7.30 7.29 7.28 7.27 7.27 7.26 CDCl3 7.26 7.25 7.24 7.24 7.24 7.22 7.22 7.22 7.19 7.17 7.13 7.11 7.09 7.04 7.03 7.01 6.89 6.41 4.38 4.37 4.36 4.35 4.34 4.34 4.32 4.32 4.30 4.29 4.27 4.26 4.25 4.12 4.11 4.09 4.07 4.05 3.77 3.75 3.14 3.12 3.11 3.09 3.08 3.07 2.96 2.95 2.94 2.92 2.91 2.89 2.56 2.55 2.53 2.51 2.40 2.38 2.36 2.35 2.24 2.23 2.21 2.21 2.20 2.19 2.18 1.17 1.16 1.15 1.13 0.96 0.07 0.06 0.05 0.04 -0.02
1H NMR, 400 MHz, CDCl3, 25 °C
H
NCO2Me
N H
Teoc
N
N
NCO2Me
N H
Teoc
(–)-33
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

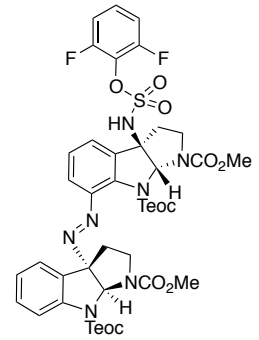
^{13}C NMR, 100 MHz, $CDCl_3$, 25 °C



(–)-**33**

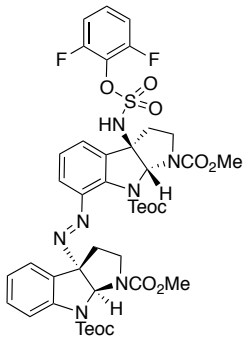

7.81 7.79 7.49 7.47 7.47 7.45 7.39 7.37 7.33 7.31 7.31 7.29 7.29 7.26 CDCl3 7.25 7.23 7.21 7.20 7.19 7.18 7.16 7.08 7.06 7.04 7.00 6.98 6.96 6.83 6.56 5.79 5.76 4.37 4.35 4.34 4.33 4.31 4.31 4.30 4.29 4.27 4.09 4.06 4.04 3.83 3.77 3.73 3.12 3.11 3.09 3.08 3.06 3.05 2.94 2.88 2.54 2.51 2.47 2.37 2.36 2.34 1.15 1.15 1.13 1.12 1.11 1.10 0.84 0.05 0.05 -0.04
1H NMR, 400 MHz, CDCl3, 25 °C
F
F
O
S
O
O
HN
NCO2Me
N
H
Teoc
N
N
NCO2Me
N
H
Teoc
(+)-34
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

^{13}C NMR, 100 MHz, $CDCl_3$, 25 °C

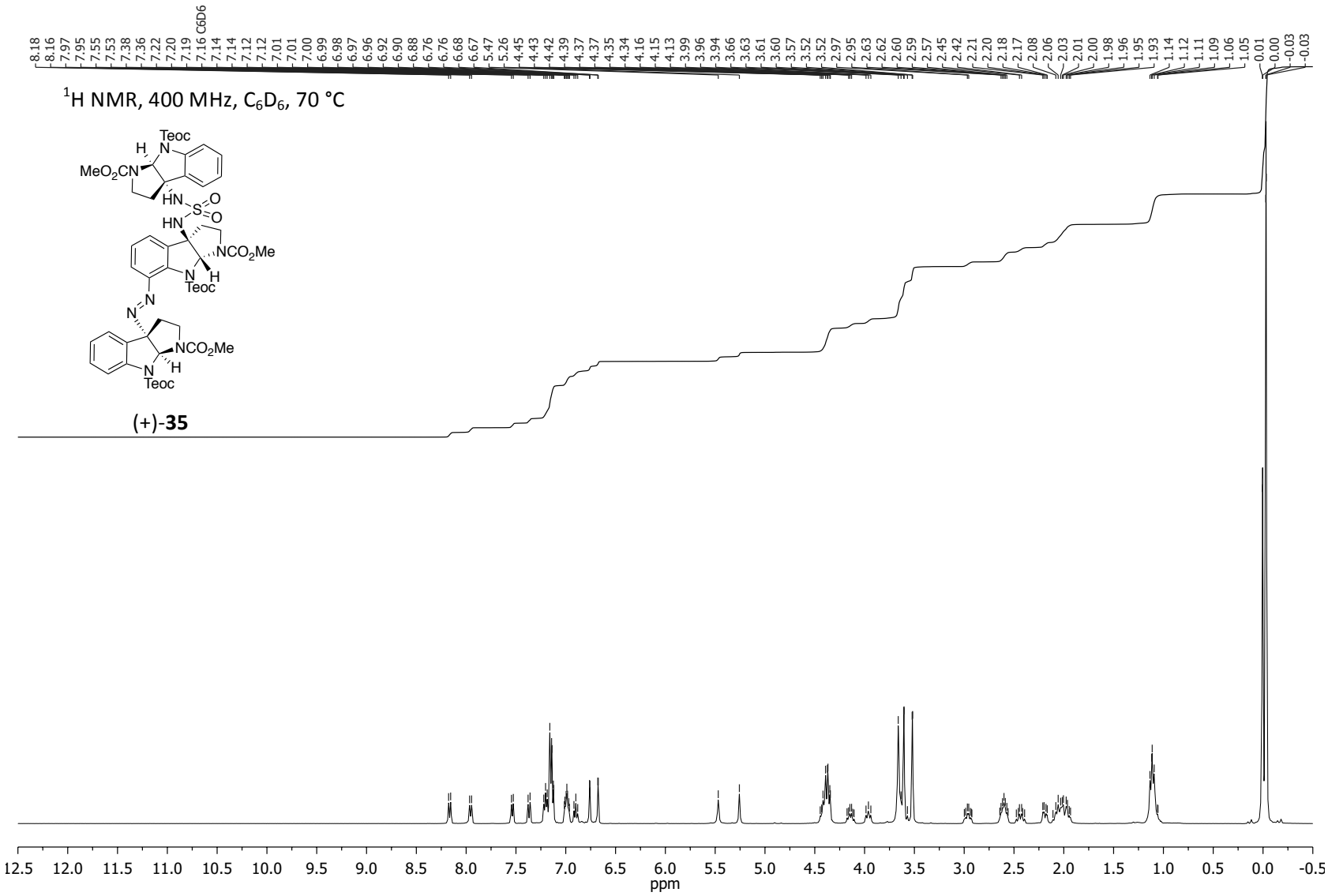


(+)-**34**

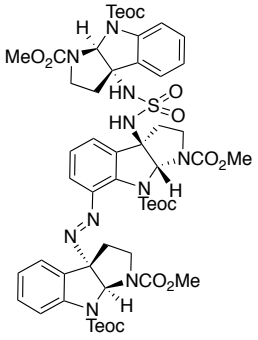
^{19}F NMR, 282 MHz, $CDCl_3$, 25 °C



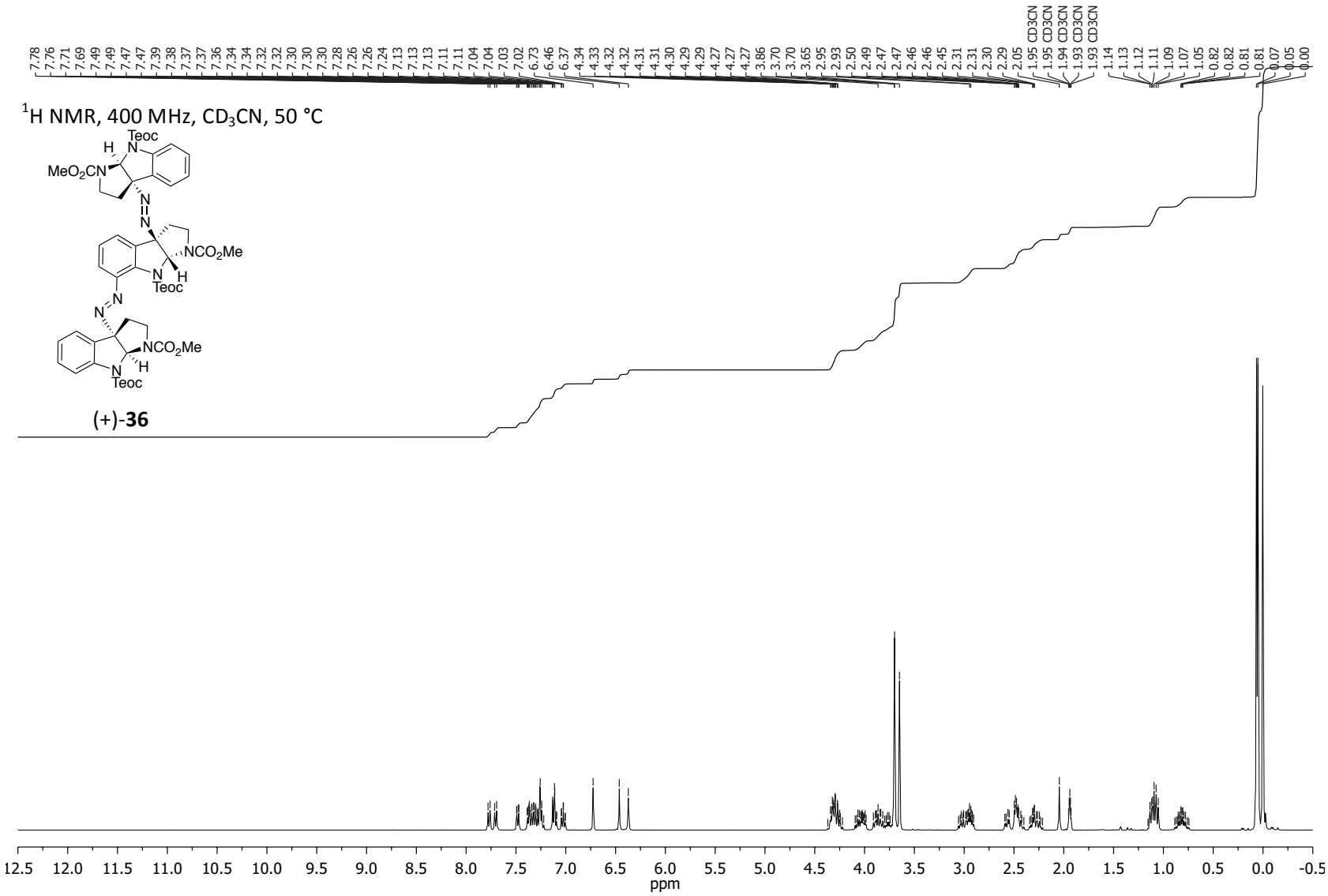
(+)-**34**


^{1}H NMR, 400 MHz, C_6D_6, 70 °C
(+)-35
ppm

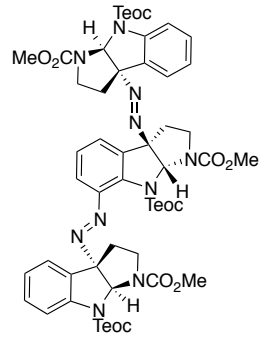
^{13}C NMR, 100 MHz, C_6D_6, 70 °C



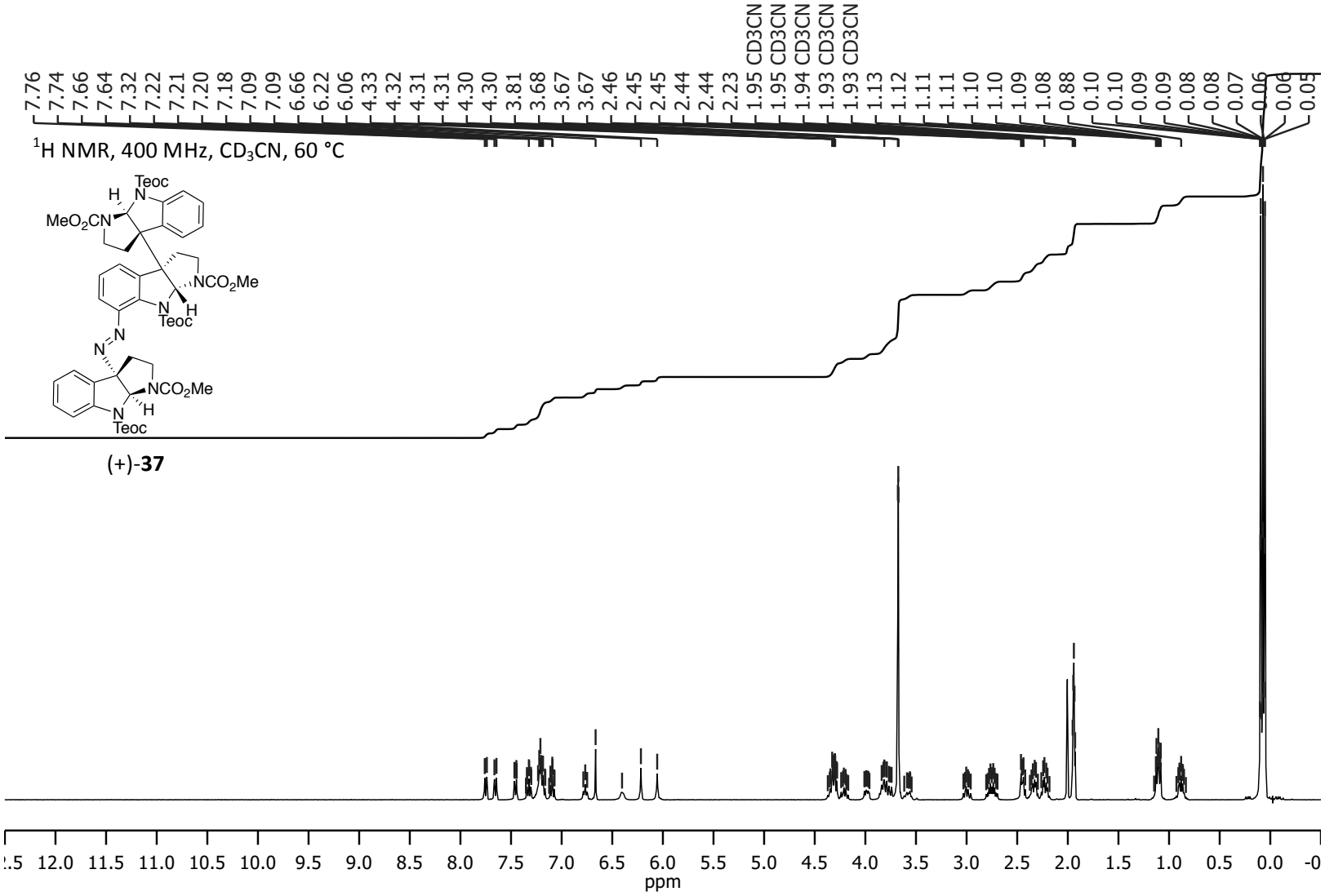
(+)-**35**


^{1}H NMR, 400 MHz, CD_3CN, 50 °C
(+)-36
ppm

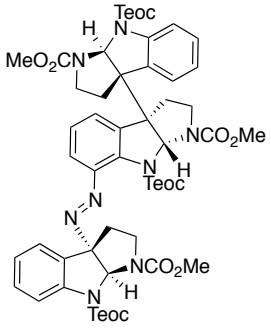
^{13}C NMR, 100 MHz, CD_3CN, 50 °C



(+)-**36**

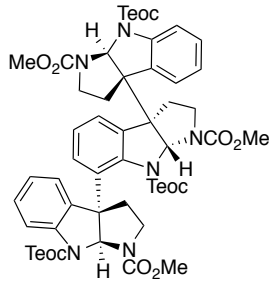

7.76 7.74 7.66 7.64 7.32 7.22 7.21 7.20 7.18 7.09 7.09 6.66 6.22 6.06 4.33 4.32 4.31 4.31 4.30 4.30 3.81 3.68 3.67 3.67 2.46 2.45 2.45 2.44 2.44 2.23 1.95 CD3CN 1.95 CD3CN 1.94 CD3CN 1.93 CD3CN 1.93 CD3CN 1.13 1.12 1.11 1.11 1.10 1.10 1.09 1.08 0.88 0.10 0.10 0.09 0.09 0.08 0.08 0.07 0.06 0.06 0.05
^{1}H NMR, 400 MHz, CD_3CN, 60 °C
Teoc
H
N
MeO2CN
NCO2Me
N
H
Teoc
N
N
NCO2Me
N
H
Teoc
(+)-37
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

^{13}C NMR, 100 MHz, CD_3CN, 60 °C

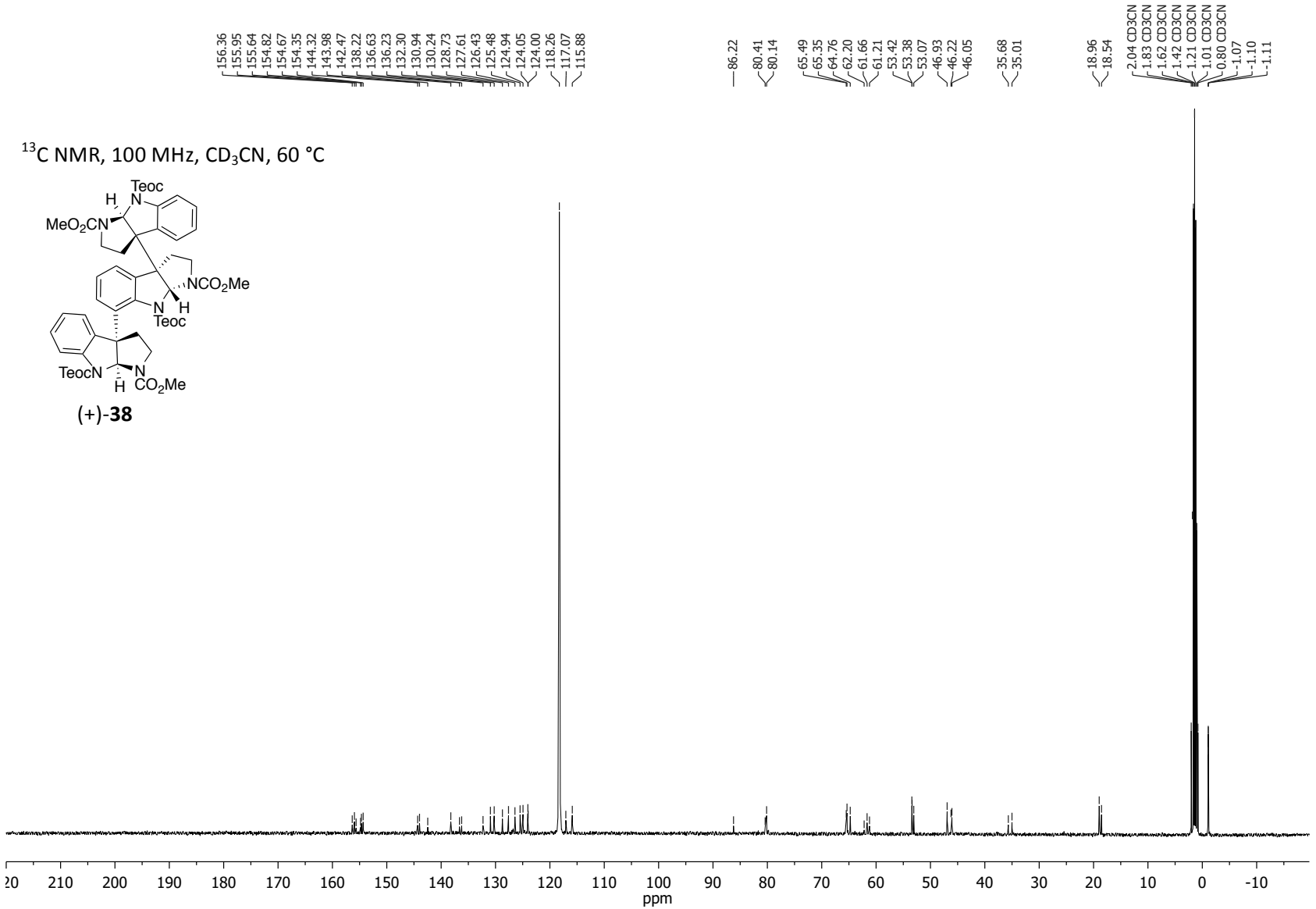


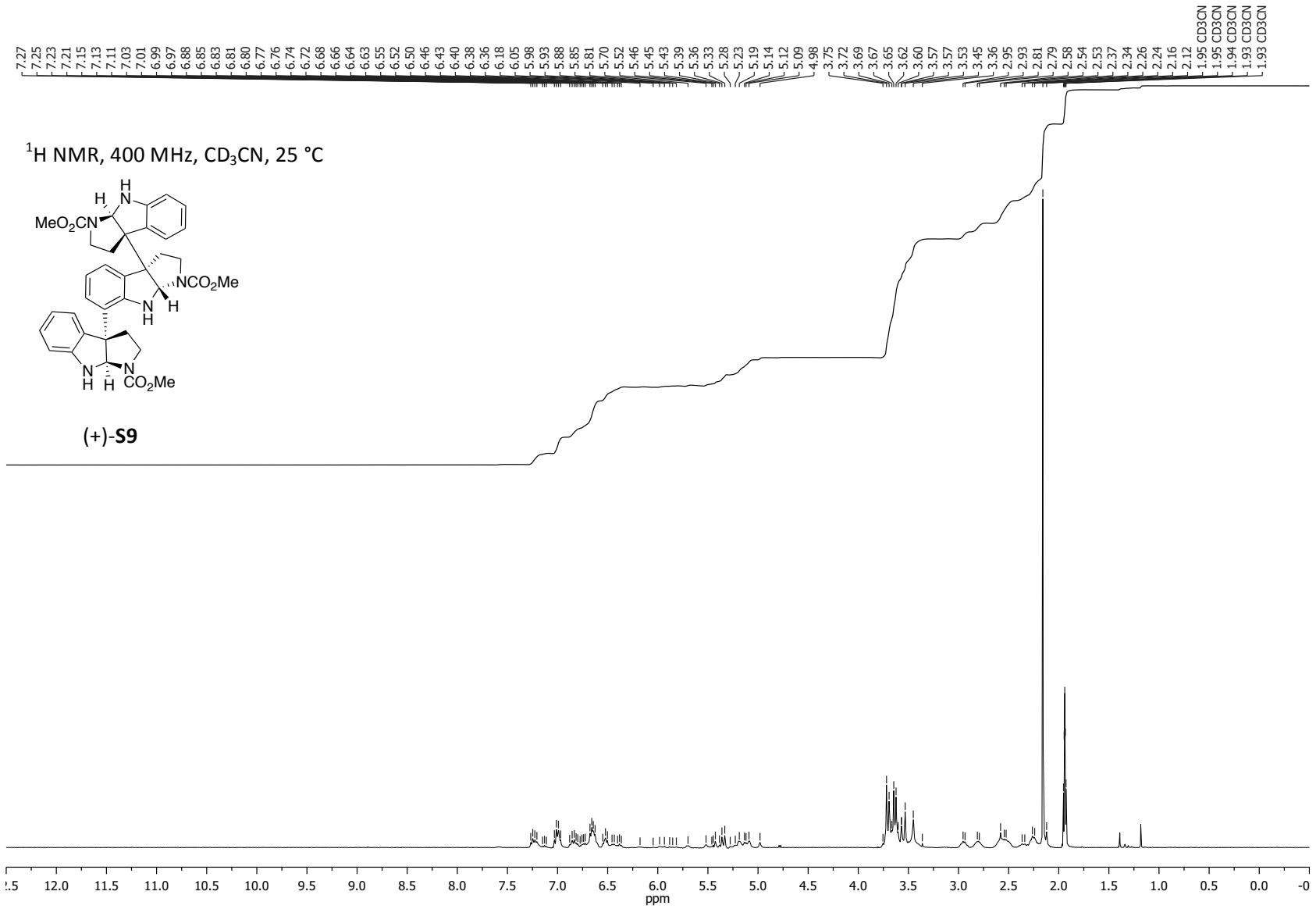
(+)-**37**

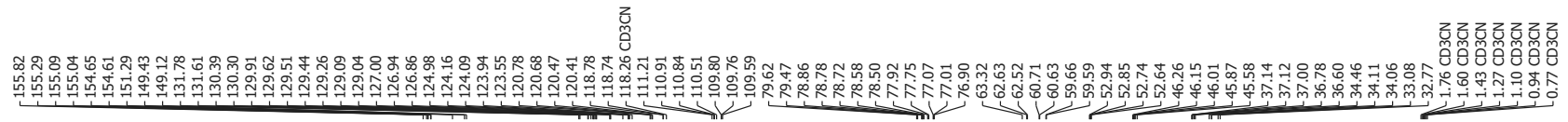
^{1}H NMR, 100 MHz, CD_3CN, 60 °C



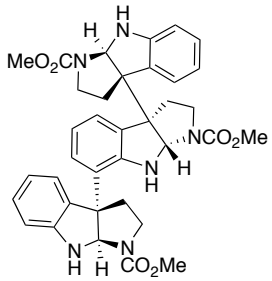
(+)-**38**


156.36
155.95
155.64
154.82
154.67
154.35
144.32
143.98
142.47
138.22
136.63
136.23
132.30
130.94
130.24
128.73
127.61
126.43
125.48
124.94
124.05
124.00
118.26
117.07
115.88
86.22
80.41
80.14
65.49
65.35
64.76
62.20
61.66
61.21
53.42
53.38
53.07
46.93
46.22
46.05
35.68
35.01
18.96
18.54
2.04 CD3CN
1.83 CD3CN
1.62 CD3CN
1.42 CD3CN
1.21 CD3CN
1.01 CD3CN
0.80 CD3CN
-1.07
-1.10
-1.11
^{13}C NMR, 100 MHz, CD_3CN, 60 °C
Teoc
H
N
MeO_2CN
NCO_2Me
N H
Teoc
TeocN
H
N
CO_2Me
(+)-38
ppm

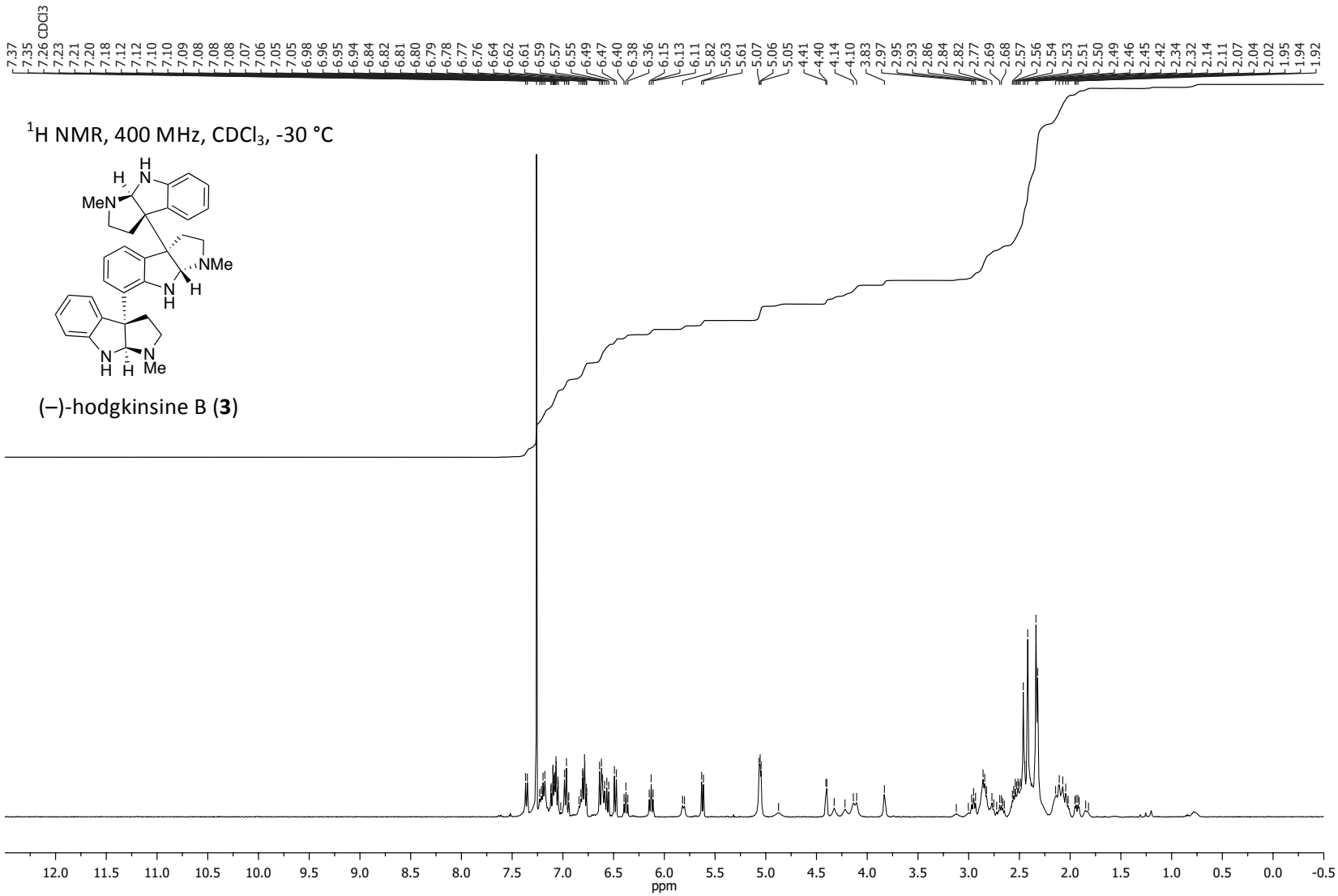

7.27 7.25 7.23 7.21 7.15 7.13 7.11 7.03 7.01 6.99 6.97 6.88 6.85 6.83 6.81 6.80 6.77 6.76 6.74 6.72 6.68 6.66 6.64 6.63 6.55 6.52 6.50 6.46 6.43 6.40 6.38 6.36 6.18 6.05 5.98 5.93 5.88 5.85 5.81 5.70 5.52 5.46 5.45 5.43 5.39 5.36 5.33 5.28 5.23 5.19 5.14 5.12 5.09 4.98 3.75 3.72 3.69 3.67 3.65 3.62 3.60 3.57 3.57 3.53 3.45 3.36 2.95 2.93 2.81 2.79 2.58 2.54 2.53 2.37 2.34 2.26 2.24 2.16 2.12 1.95 CD3CN 1.95 CD3CN 1.94 CD3CN 1.93 CD3CN 1.93 CD3CN
^{1}H NMR, 400 MHz, CD_3CN, 25 °C
MeO_2CN
NCO_2Me
CO_2Me
(+)-**S9**
ppm



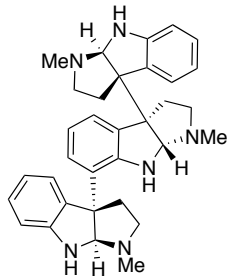
^{13}C NMR, 125 MHz, CD_3CN, 25°C



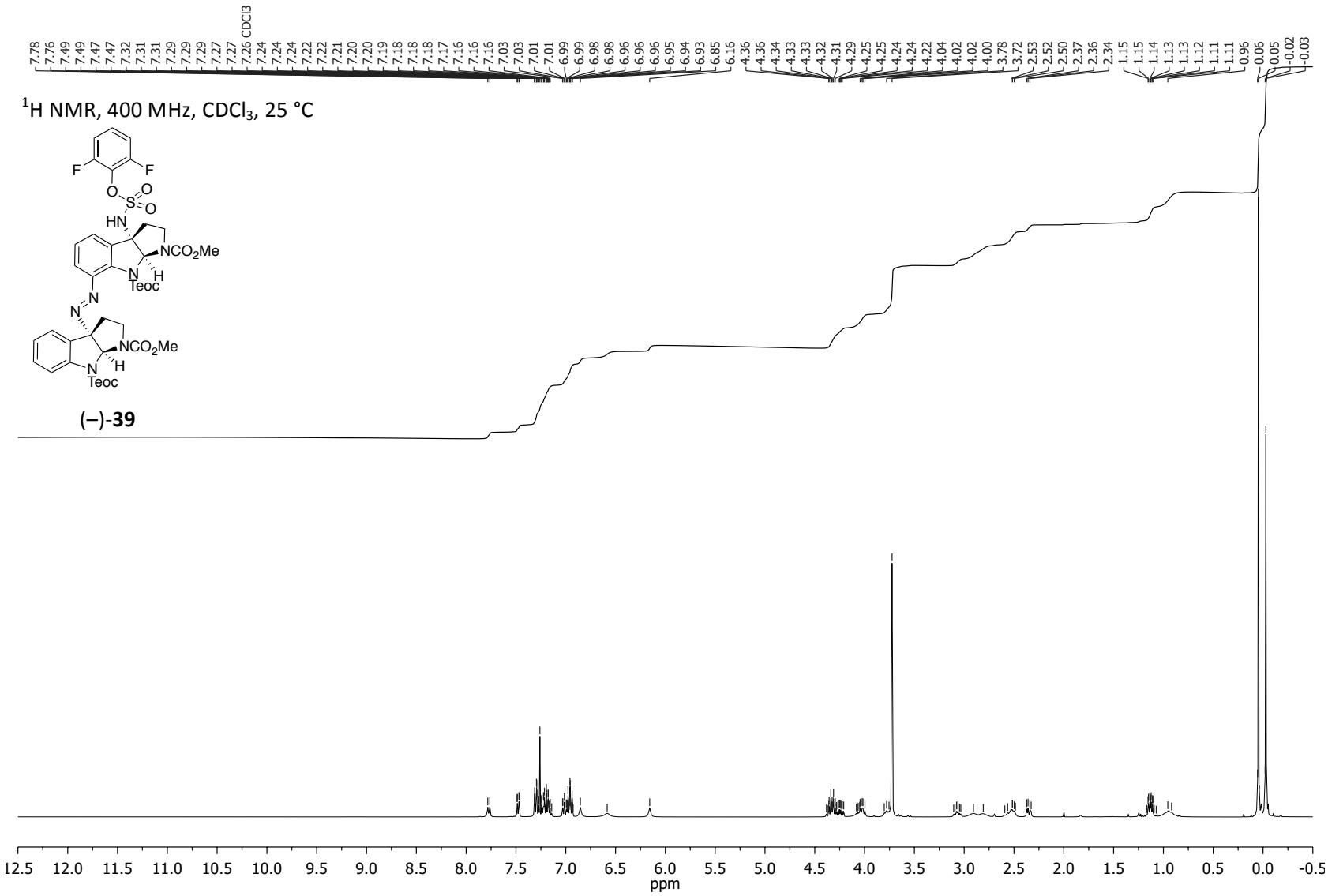
(+)-**S9**


7.37
7.35
CDCl3
7.26
7.23
7.21
7.20
7.18
7.12
7.12
7.10
7.10
7.09
7.08
7.08
7.08
7.07
7.06
7.05
7.05
6.98
6.96
6.95
6.94
6.84
6.82
6.81
6.80
6.79
6.78
6.77
6.76
6.64
6.62
6.61
6.59
6.57
6.55
6.49
6.47
6.40
6.38
6.36
6.15
6.13
6.11
5.82
5.63
5.61
5.07
5.06
5.05
4.41
4.40
4.14
4.10
3.83
2.97
2.95
2.93
2.86
2.84
2.82
2.77
2.69
2.68
2.57
2.56
2.54
2.53
2.51
2.50
2.49
2.46
2.45
2.42
2.34
2.32
2.14
2.11
2.07
2.04
2.02
1.95
1.94
1.92
1H NMR, 400 MHz, CDCl3, -30 °C
MeN
NMe
N H
H
N H H N Me
(–)-hodgkinsine B (3)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm

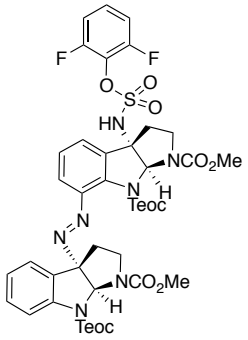
^{13}C NMR, 100 MHz, $CDCl_3$, -30 °C



(–)-hodgkinsine B (**3**)

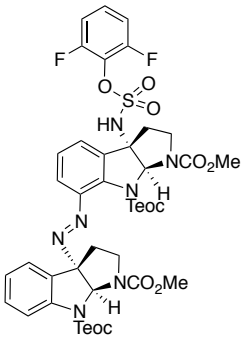

7.78 7.76 7.49 7.49 7.47 7.47 7.32 7.31 7.31 7.29 7.29 7.29 7.27 7.27 7.26 CDCl3 7.24 7.24 7.24 7.22 7.21 7.20 7.20 7.19 7.18 7.18 7.18 7.17 7.16 7.16 7.16 7.03 7.01 7.01 6.99 6.99 6.98 6.98 6.96 6.96 6.96 6.95 6.94 6.93 6.85 6.16 4.36 4.36 4.34 4.33 4.32 4.31 4.29 4.25 4.25 4.24 4.24 4.22 4.04 4.02 4.02 4.00 3.78 3.72 2.53 2.52 2.50 2.37 2.36 2.34 1.15 1.15 1.14 1.13 1.13 1.12 1.11 1.11 0.96 0.06 0.05 -0.02 -0.03
1H NMR, 400 MHz, CDCl3, 25 °C
F
F
O
S
O
O
HN
NCO2Me
N
H
Teoc
N
N
NCO2Me
N
H
Teoc
(–)-39
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

^{13}C NMR, 100 MHz, $CDCl_3$, 25 °C

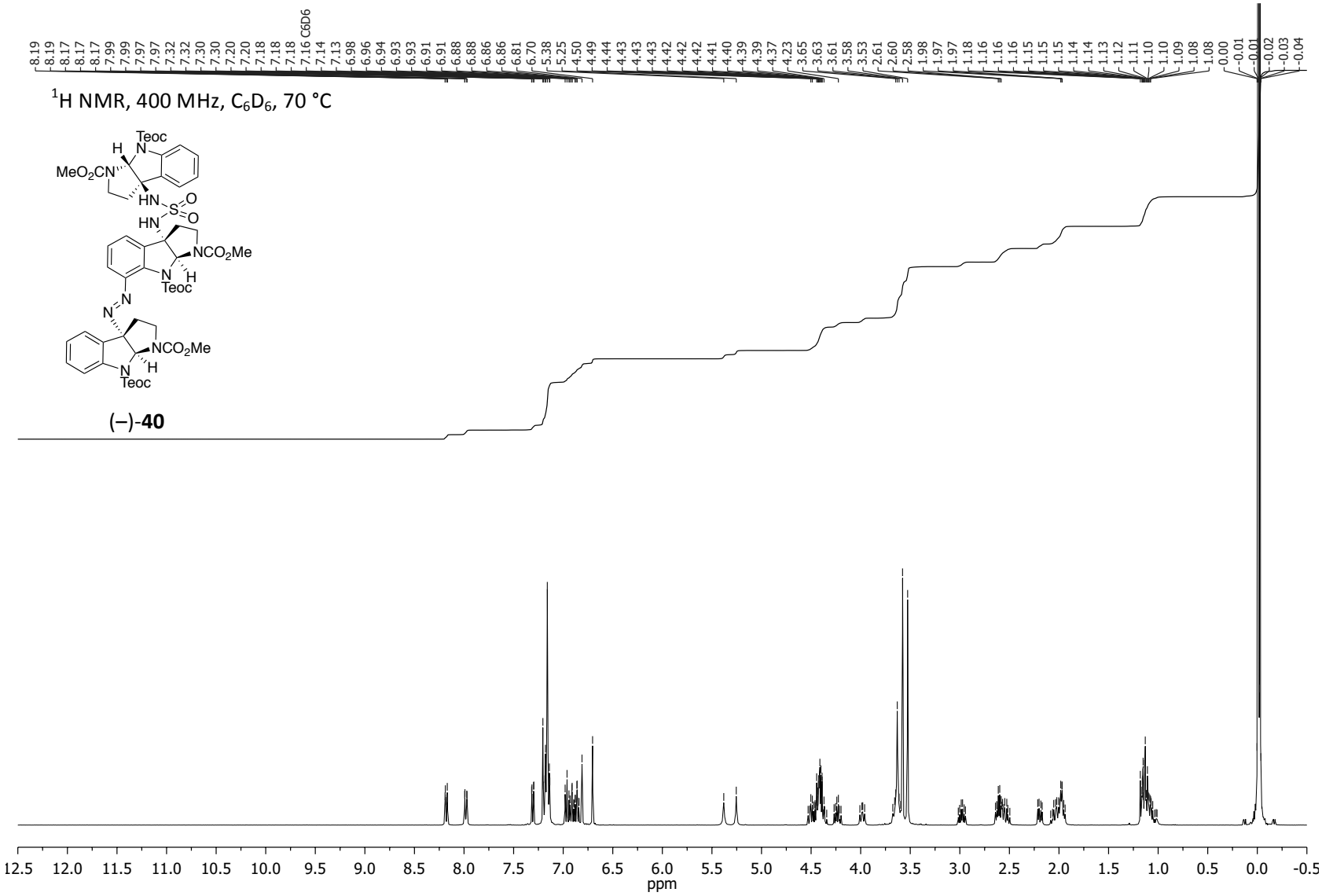


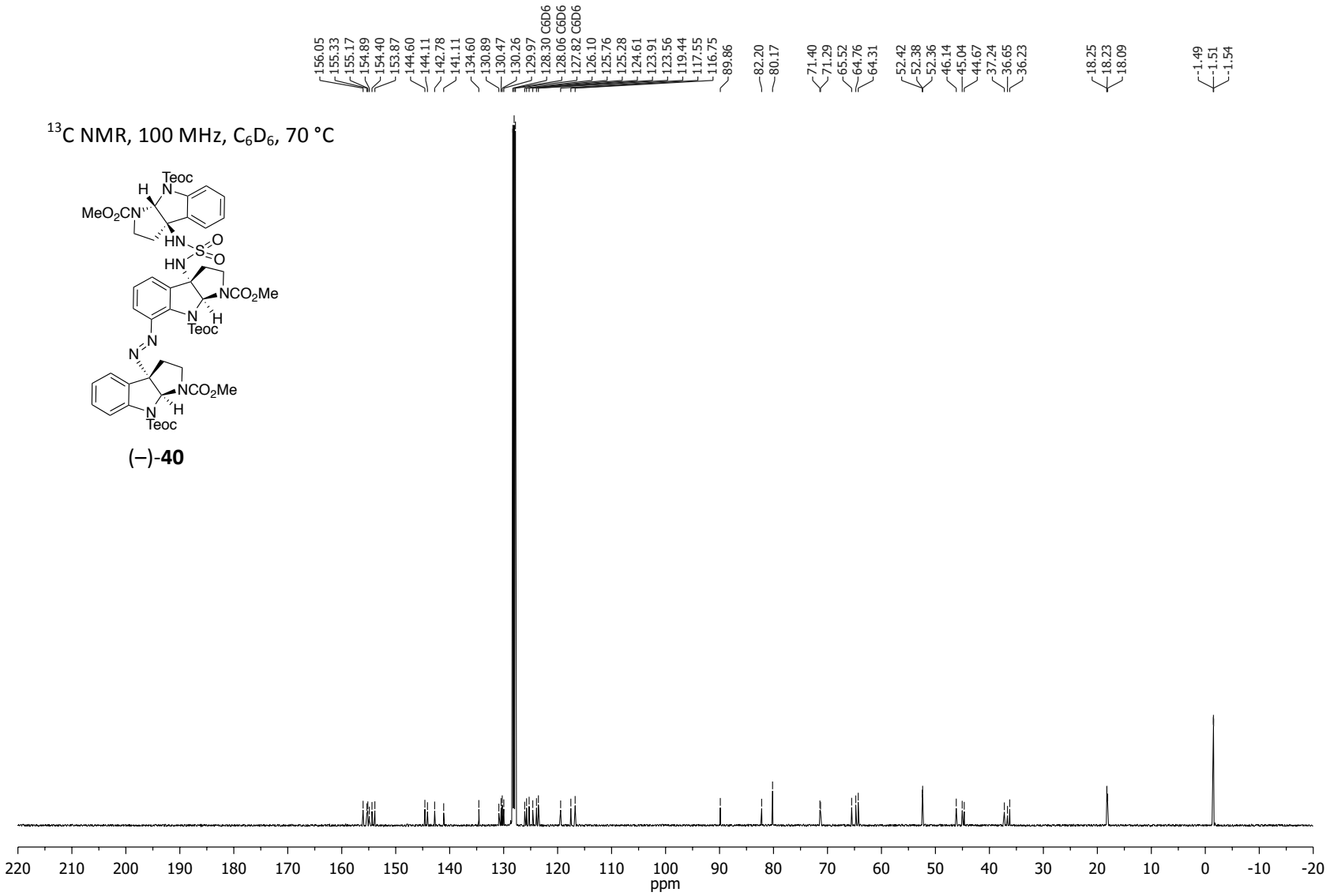
(–)-**39**

^{19}F NMR, 282 MHz, $CDCl_3$, 25 °C



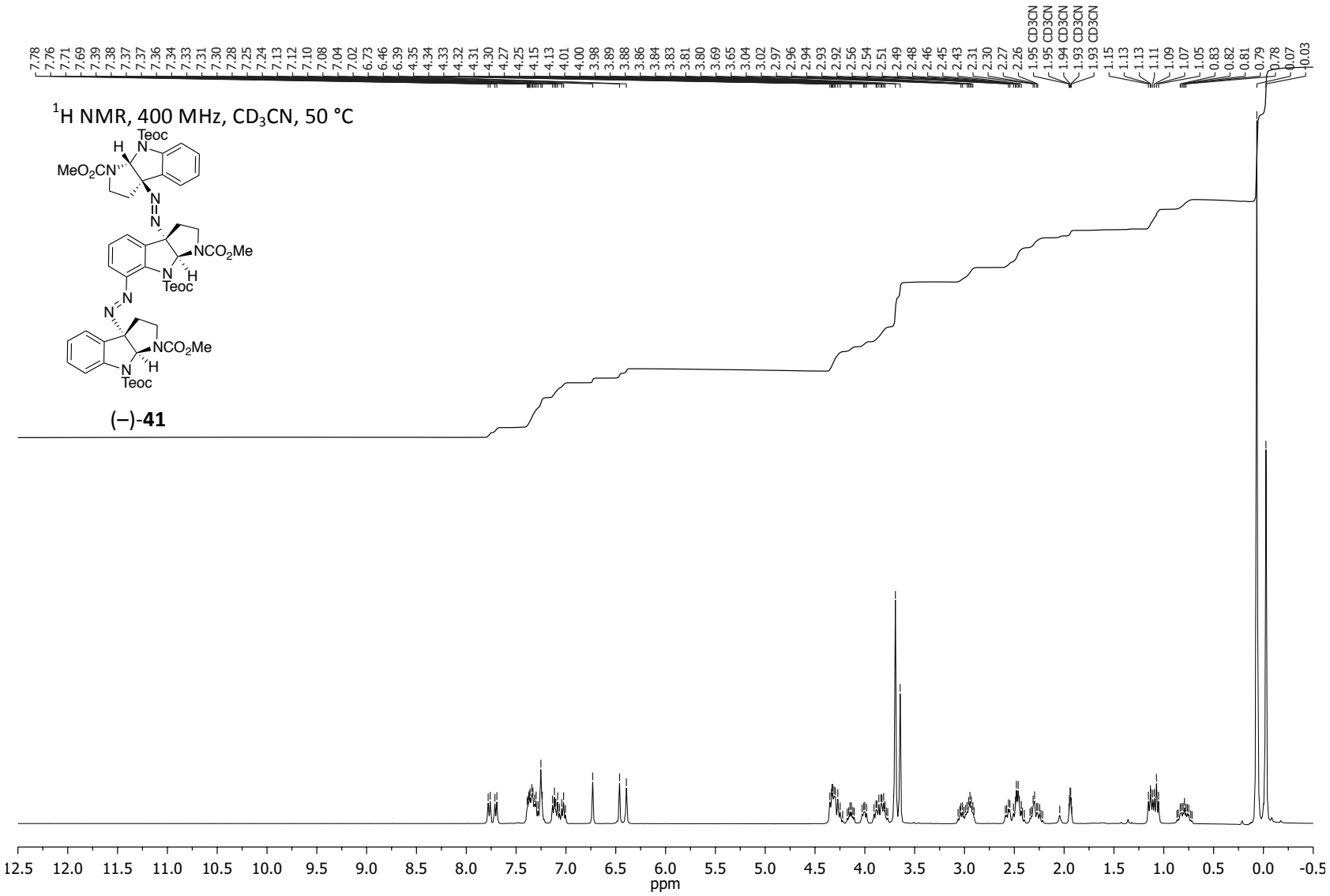
(–)-**39**


8.19 8.19 8.17 8.17 8.17 7.99 7.99 7.97 7.97 7.32 7.30 7.30 7.20 7.20 7.18 7.18 7.18 7.16 C6D6 7.14 7.13 6.98 6.96 6.94 6.93 6.93 6.91 6.91 6.88 6.88 6.86 6.86 6.81 6.70 5.38 5.25 4.50 4.49 4.44 4.43 4.43 4.43 4.42 4.42 4.42 4.41 4.40 4.39 4.37 4.23 3.65 3.63 3.61 3.58 3.53 2.61 2.60 2.58 1.98 1.97 1.97 1.18 1.16 1.16 1.15 1.15 1.15 1.14 1.14 1.13 1.12 1.11 1.10 1.10 1.09 1.08 1.08 0.00 -0.01 -0.01 -0.02 -0.03 -0.04
^{1}H NMR, 400 MHz, C_6D_6, 70 °C
Teoc
H
N
MeO2CN
HN
S
O
O
HN
NCO2Me
N
H
Teoc
N
N
NCO2Me
N
H
Teoc
(–)-40
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

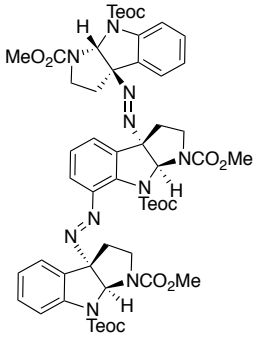


^{13}C NMR, 100 MHz, C_6D_6, 70 °C

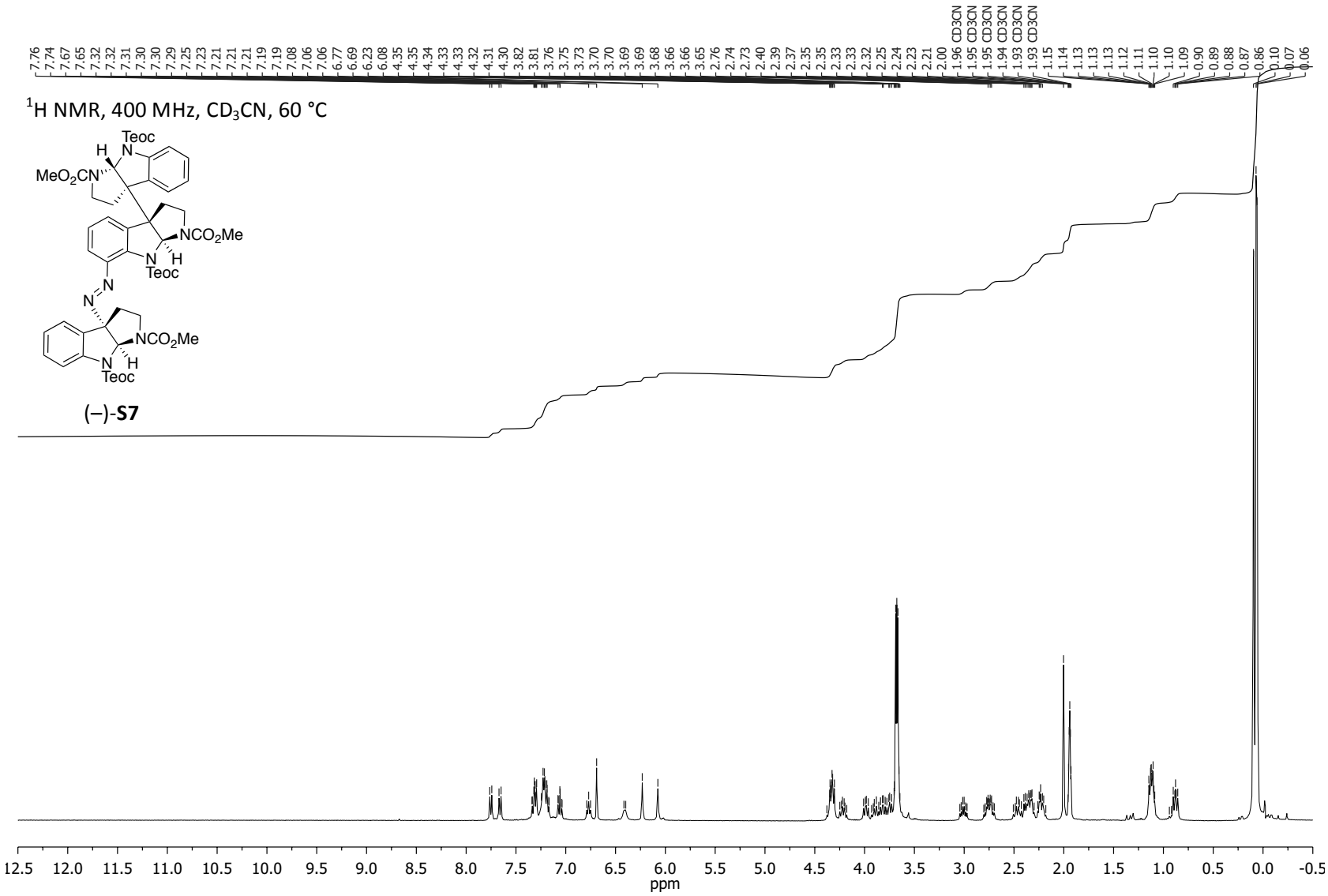
(–)-**40**


^{1}H NMR, 400 MHz, CD_3CN, 50 °C
(–)-41
ppm

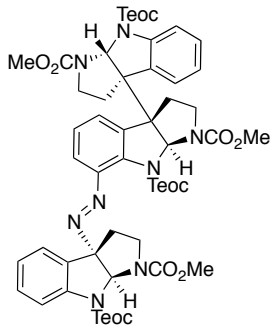
^{13}C NMR, 100 MHz, CD_3CN, 50 °C



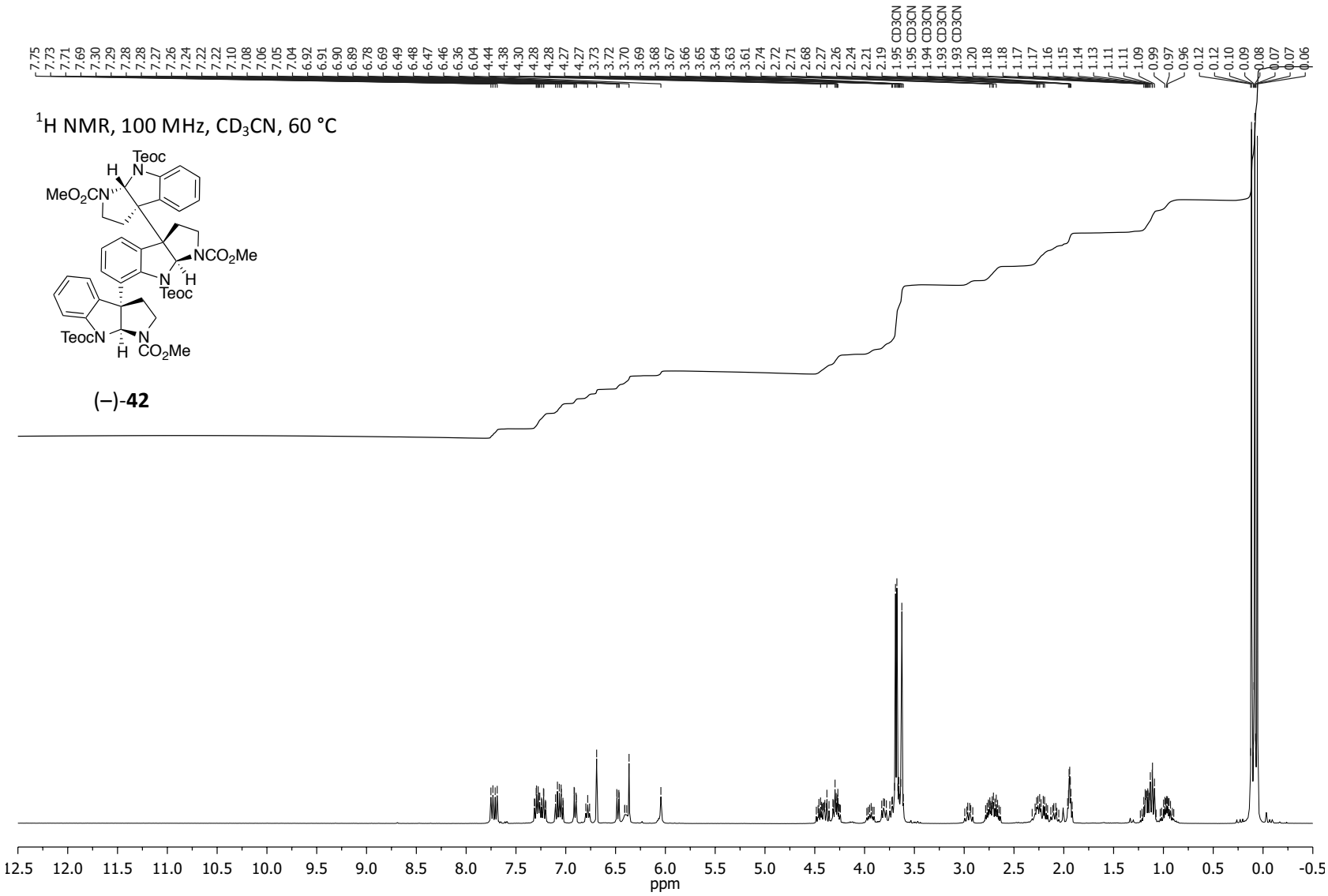
(–)-**41**

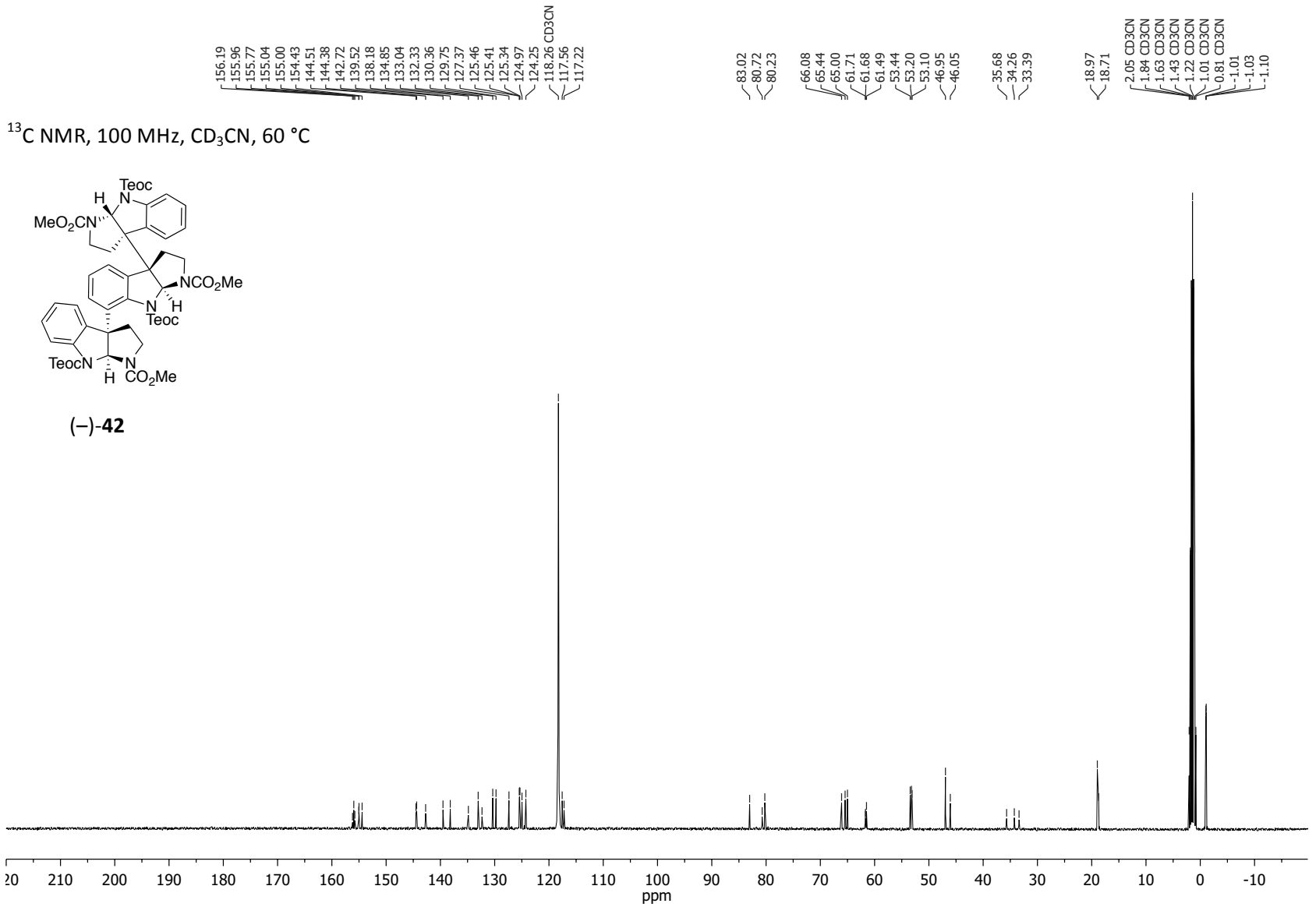

^{1}H NMR, 400 MHz, CD_3CN, 60 °C
Teoc
H N
MeO_2CN
NCO_2Me
N H
Teoc
N
N
NCO_2Me
N H
Teoc
(–)-**S7**
ppm

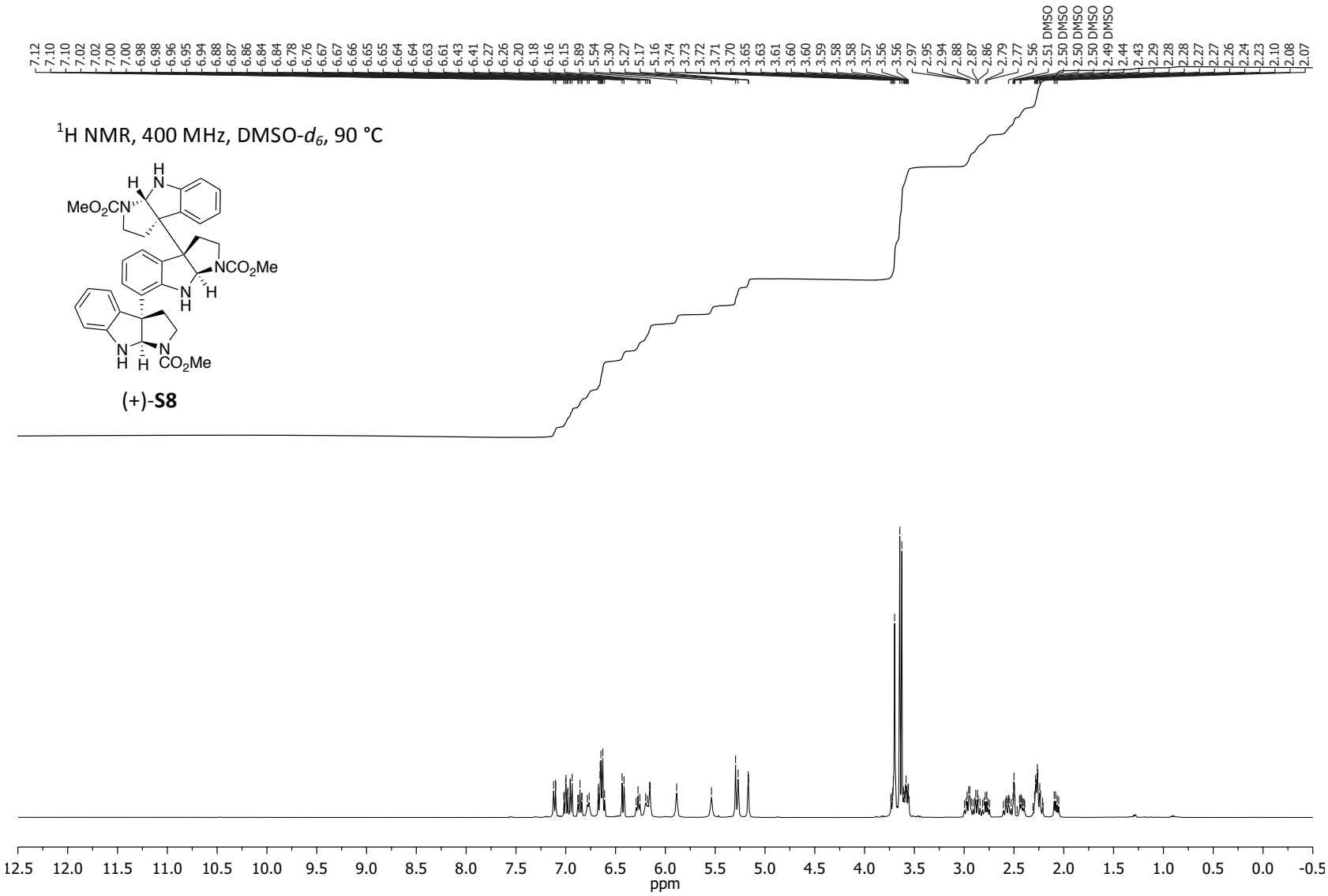
^{13}C NMR, 100 MHz, CD_3CN, 60 °C

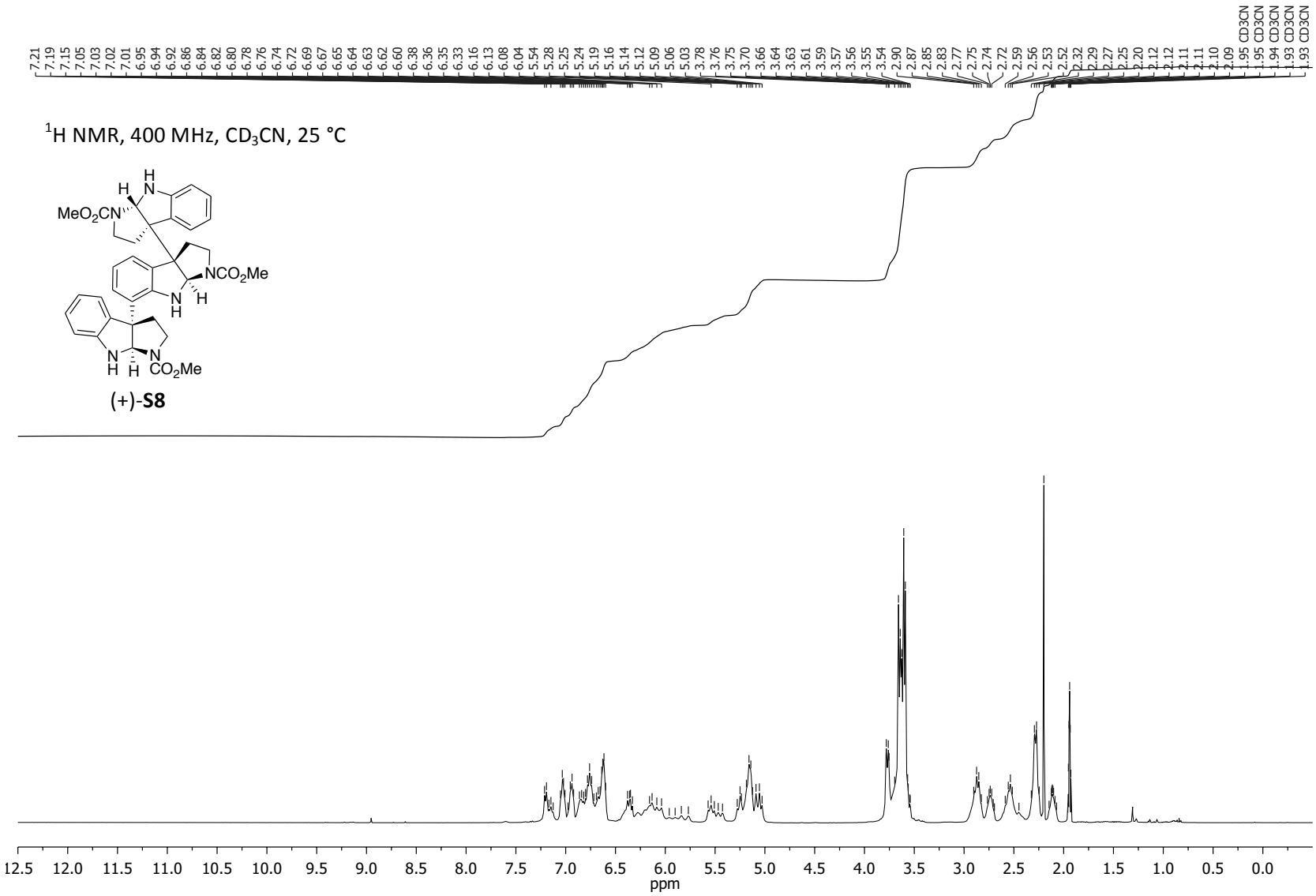


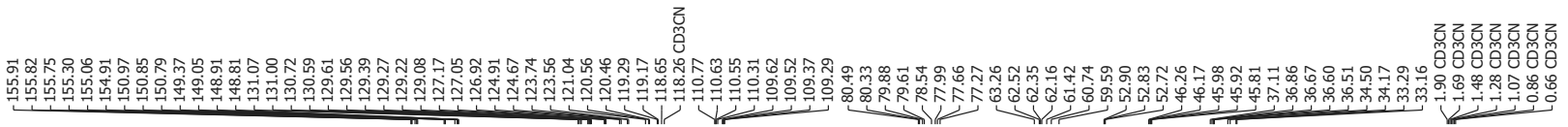
(–)-**S7**


^{1}H NMR, 100 MHz, CD_3CN, 60 °C
Teoc
H N
MeO_2CN
NCO_2Me
N H
Teoc
TeocN
N
H CO_2Me
(–)-42
ppm

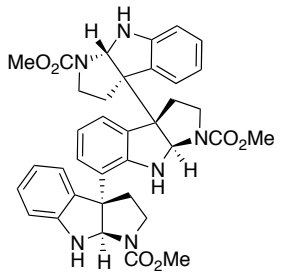

156.19
155.96
155.77
155.04
155.00
154.43
144.51
144.38
142.72
139.52
138.18
134.85
133.04
132.33
130.36
129.75
127.37
125.46
125.41
125.34
124.97
124.25
118.26 CD3CN
117.56
117.22
83.02
80.72
80.23
66.08
65.44
65.00
61.71
61.68
61.49
53.44
53.20
53.10
46.95
46.05
35.68
34.26
33.39
18.97
18.71
2.05 CD3CN
1.84 CD3CN
1.63 CD3CN
1.43 CD3CN
1.22 CD3CN
1.01 CD3CN
0.81 CD3CN
-1.01
-1.03
-1.10
^{13}C NMR, 100 MHz, CD_3CN, 60 °C
Teoc
H
N
MeO2CN
NCO2Me
N
H
Teoc
TeocN
N
H
CO2Me
(–)-42
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


7.12 7.10 7.10 7.02 7.02 7.00 7.00 6.98 6.98 6.96 6.95 6.94 6.88 6.87 6.86 6.84 6.84 6.78 6.76 6.67 6.67 6.66 6.65 6.65 6.64 6.64 6.63 6.61 6.43 6.41 6.27 6.26 6.20 6.18 6.16 6.15 5.89 5.54 5.30 5.27 5.17 5.16 3.74 3.73 3.72 3.71 3.70 3.65 3.63 3.61 3.60 3.60 3.59 3.58 3.58 3.57 3.56 3.56 2.97 2.95 2.94 2.88 2.87 2.86 2.79 2.77 2.56 2.51 DMSO 2.50 DMSO 2.50 DMSO 2.50 DMSO 2.49 DMSO 2.44 2.43 2.29 2.28 2.28 2.27 2.27 2.26 2.24 2.23 2.10 2.08 2.07
^{1}H NMR, 400 MHz, DMSO-d_6, 90 °C
(+)-**S8**
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


7.21 7.19 7.15 7.05 7.03 7.02 7.01 6.95 6.94 6.92 6.86 6.84 6.82 6.80 6.78 6.76 6.74 6.72 6.69 6.67 6.65 6.64 6.63 6.62 6.60 6.38 6.36 6.35 6.33 6.16 6.13 6.08 6.04 5.54 5.28 5.25 5.24 5.19 5.16 5.14 5.12 5.09 5.06 5.03 3.78 3.76 3.75 3.70 3.66 3.64 3.63 3.61 3.59 3.57 3.56 3.55 3.54 2.90 2.87 2.85 2.83 2.77 2.75 2.74 2.72 2.59 2.56 2.53 2.52 2.32 2.29 2.27 2.25 2.20 2.12 2.12 2.11 2.11 2.10 2.09 1.95 CD3CN 1.95 CD3CN 1.94 CD3CN 1.93 CD3CN 1.93 CD3CN
^{1}H NMR, 400 MHz, CD_3CN, 25 °C
MeO_2CN
NCO_2Me
CO_2Me
(+)-**S8**
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

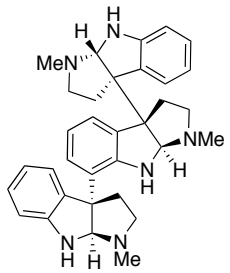


^{13}C NMR, 100 MHz, CD_3CN, 25 °C

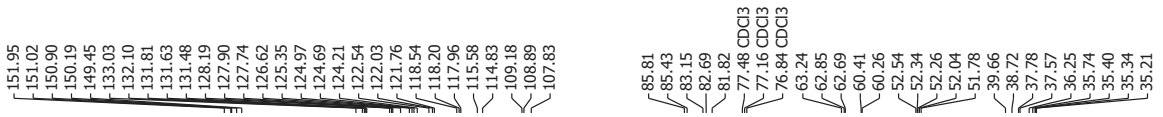


(+)-**S8**

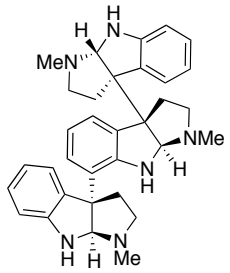
^{1}H NMR, 400 MHz, $CDCl_3$, –30 °C



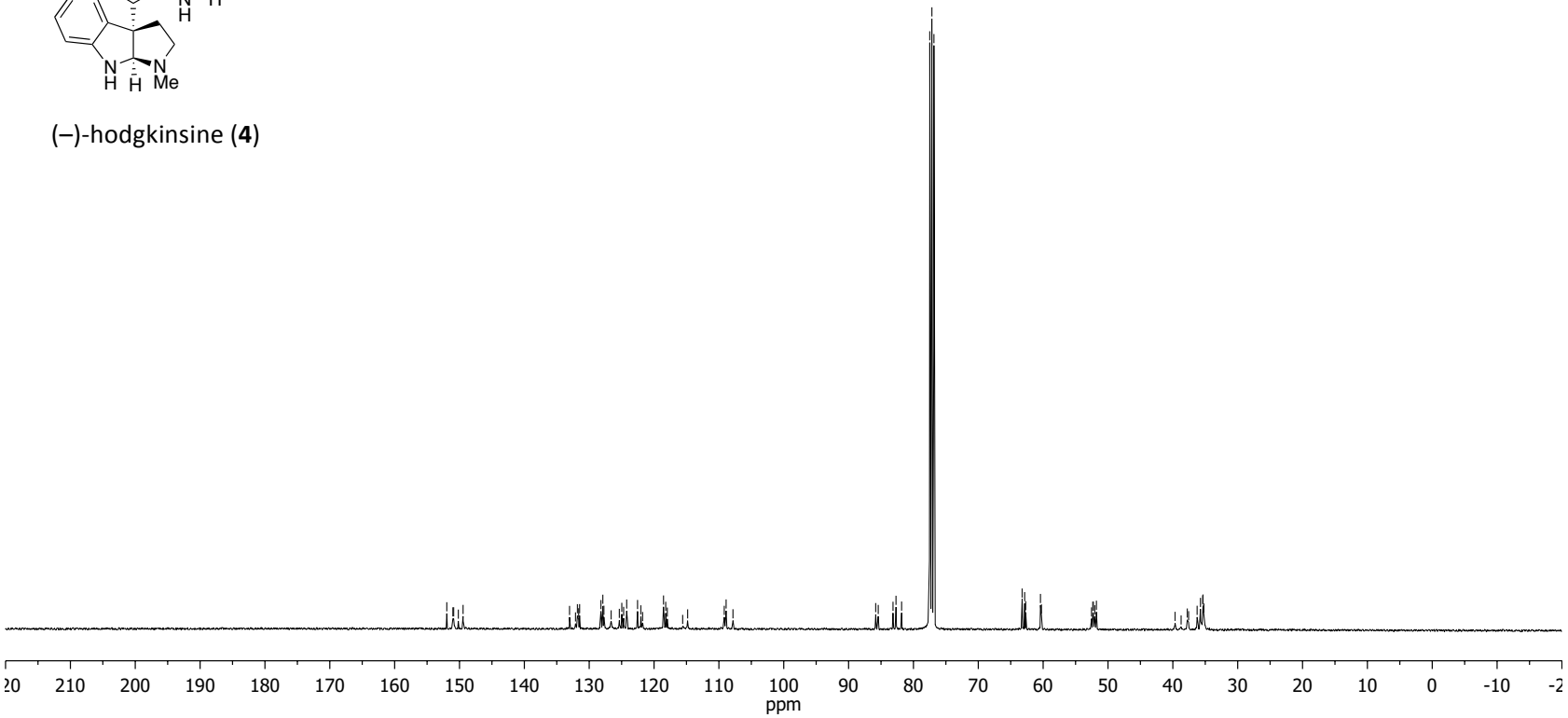
(–)-hodgkinsine (**4**)

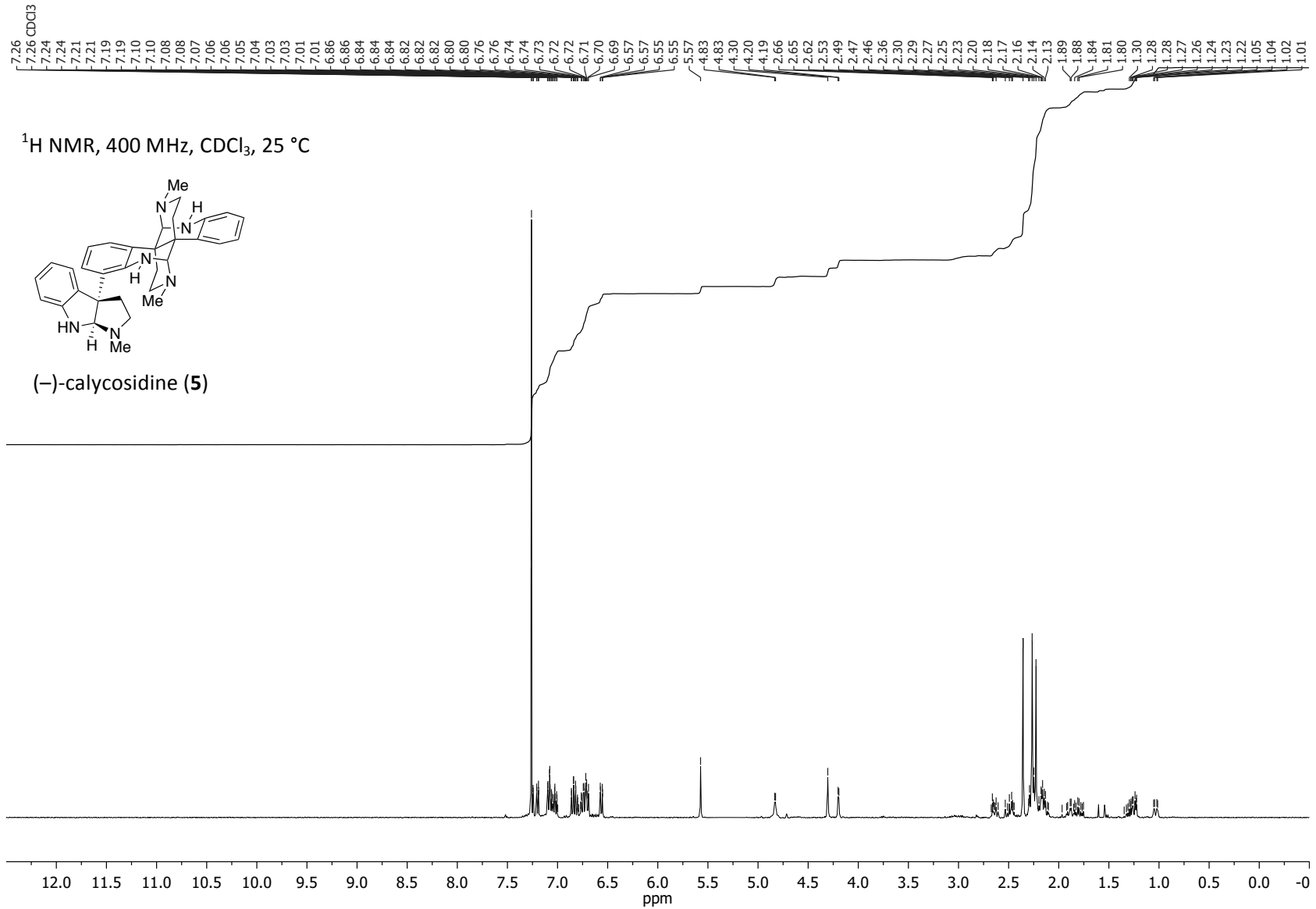


^{13}C NMR, 100 MHz, $CDCl_3$, –30 °C

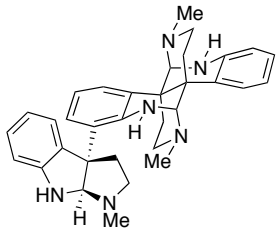


(–)-hodgkinsine (**4**)

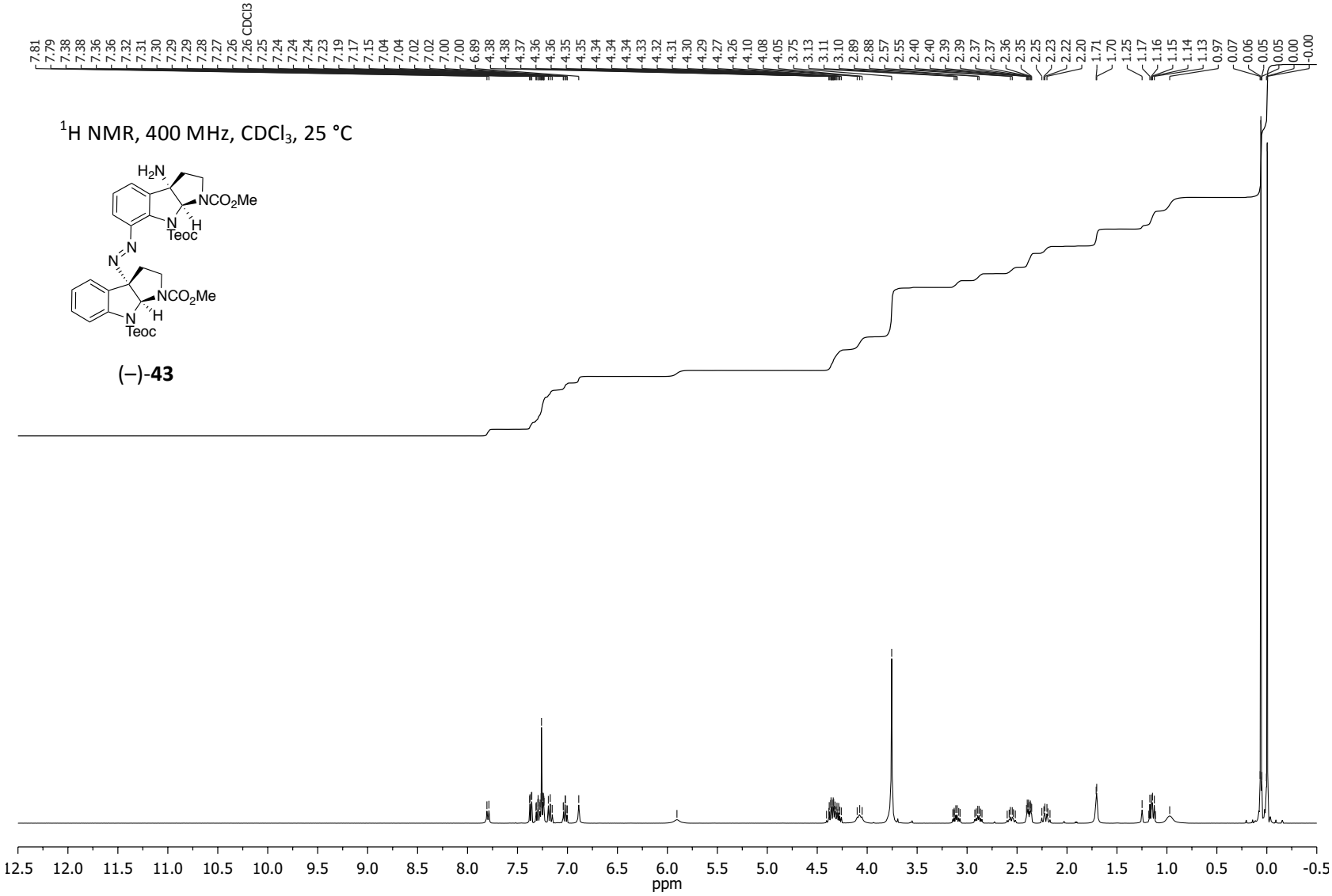



7.26 CDCl3
7.26 7.24 7.24 7.21 7.21 7.19 7.19 7.10 7.10 7.08 7.08 7.07 7.06 7.06 7.05 7.04 7.03 7.03 7.01 7.01 6.86 6.86 6.84 6.84 6.84 6.82 6.82 6.82 6.80 6.80 6.76 6.76 6.74 6.74 6.73 6.72 6.72 6.71 6.70 6.69 6.57 6.57 6.55 6.55 5.57 4.83 4.83 4.30 4.20 4.19 2.66 2.65 2.62 2.53 2.49 2.47 2.46 2.36 2.30 2.29 2.27 2.25 2.23 2.20 2.18 2.17 2.16 2.14 2.13 1.89 1.88 1.84 1.81 1.80 1.30 1.28 1.28 1.27 1.26 1.24 1.23 1.22 1.05 1.04 1.02 1.01
1H NMR, 400 MHz, CDCl3, 25 °C
Me
N
H
N
N
H
N
Me
HN
N
H
Me
(–)-calycosidine (5)
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
ppm

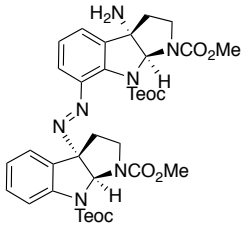
^{13}C NMR, 125 MHz, $CDCl_3$, 25 °C



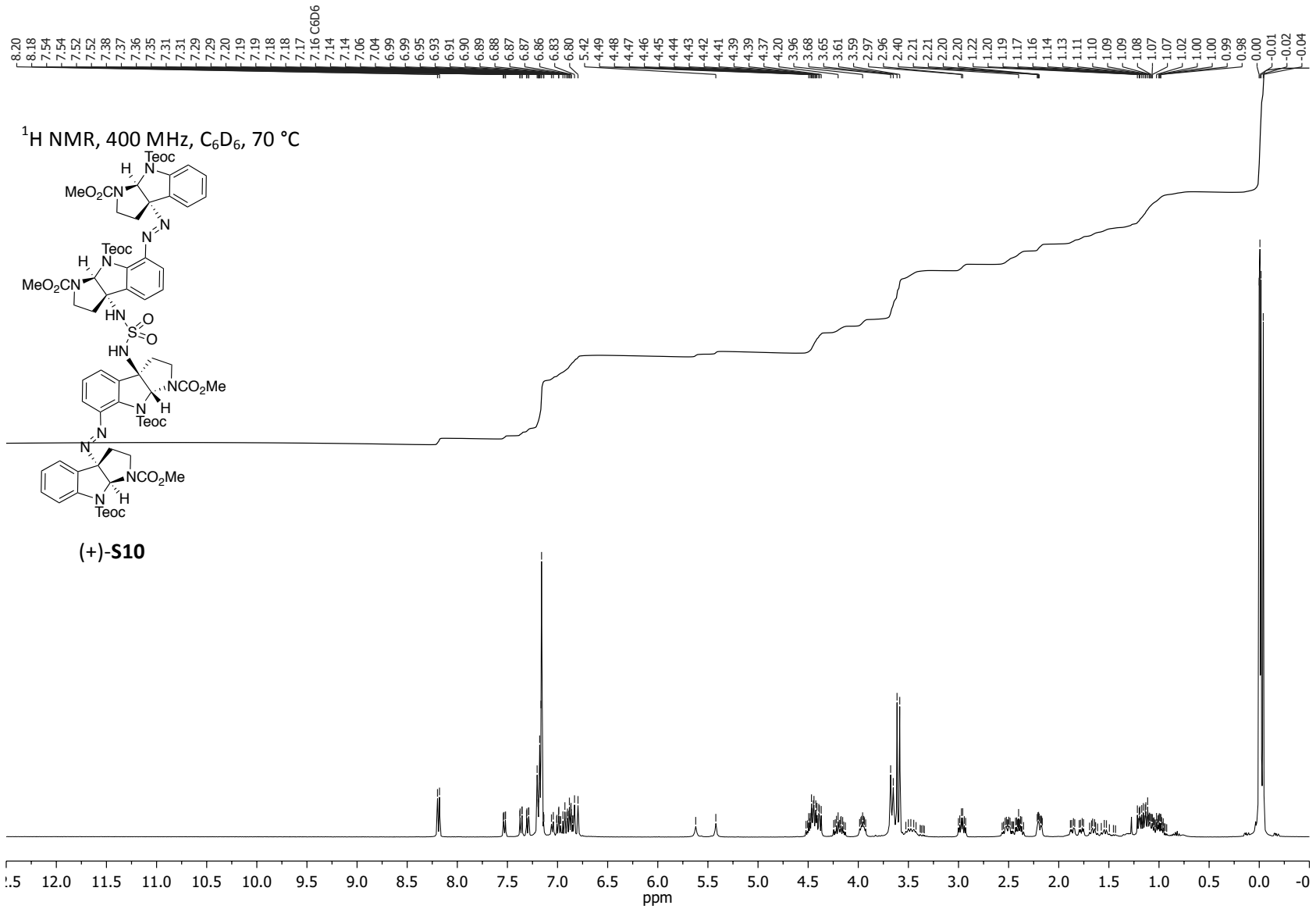
(–)-calycosidine (**5**)


7.81 7.79 7.38 7.38 7.36 7.36 7.32 7.31 7.30 7.29 7.29 7.28 7.27 7.26 7.26 CDCl3 7.25 7.24 7.24 7.24 7.23 7.19 7.17 7.15 7.04 7.04 7.02 7.02 7.00 7.00 6.89 4.38 4.38 4.37 4.36 4.36 4.35 4.35 4.34 4.34 4.34 4.33 4.32 4.31 4.30 4.29 4.27 4.26 4.10 4.08 4.05 3.75 3.13 3.11 3.10 2.89 2.88 2.57 2.55 2.40 2.40 2.39 2.39 2.37 2.37 2.36 2.35 2.25 2.23 2.22 2.20 1.71 1.70 1.25 1.17 1.16 1.15 1.14 1.13 0.97 0.07 0.06 0.05 0.05 0.00 -0.00
^{1}H NMR, 400 MHz, CDCl$_3$, 25 °C
H2N
NCO2Me
N
H
Teoc
N
N
NCO2Me
N
H
Teoc
(–)-43
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

^{13}C NMR, 100 MHz, $CDCl_3$, 25 °C

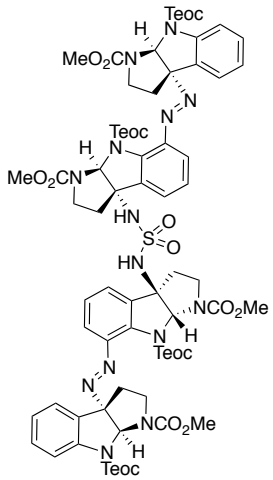


(–)-**43**

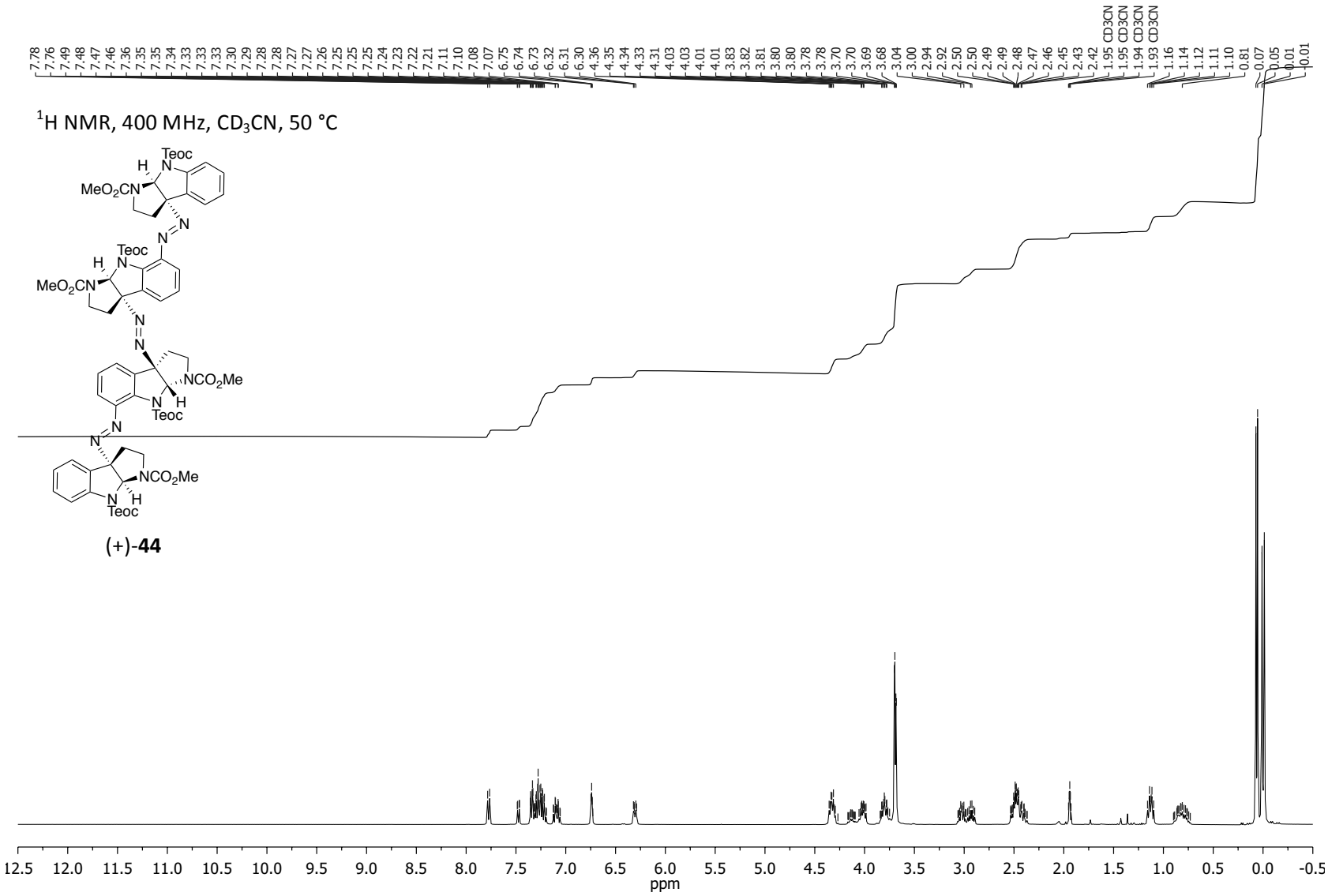

^{1}H NMR, 400 MHz, C_6D_6, 70 °C
(+)-**S10**
ppm

156.42
156.22
155.28
154.88
154.81
153.84
153.73
144.50
144.42
142.73
142.64
141.04
140.85
135.05
134.84
130.30
130.22
129.99
128.30 C6D6
128.06 C6D6
127.82 C6D6
126.16
125.97
125.84
125.76
125.23
123.59
123.55
119.53
119.24
116.78
116.62
89.85
89.80
81.82
81.63
79.79
79.54
71.06
70.86
65.66
65.49
64.35
64.21
52.38
46.02
45.98
44.60
37.13
36.69
36.36
18.25
18.20
18.02
17.94
-1.50

^{13}C NMR, 100 MHz, C_6D_6, 70 °C

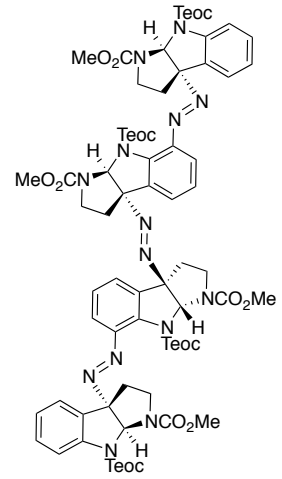


(+)-**S10**

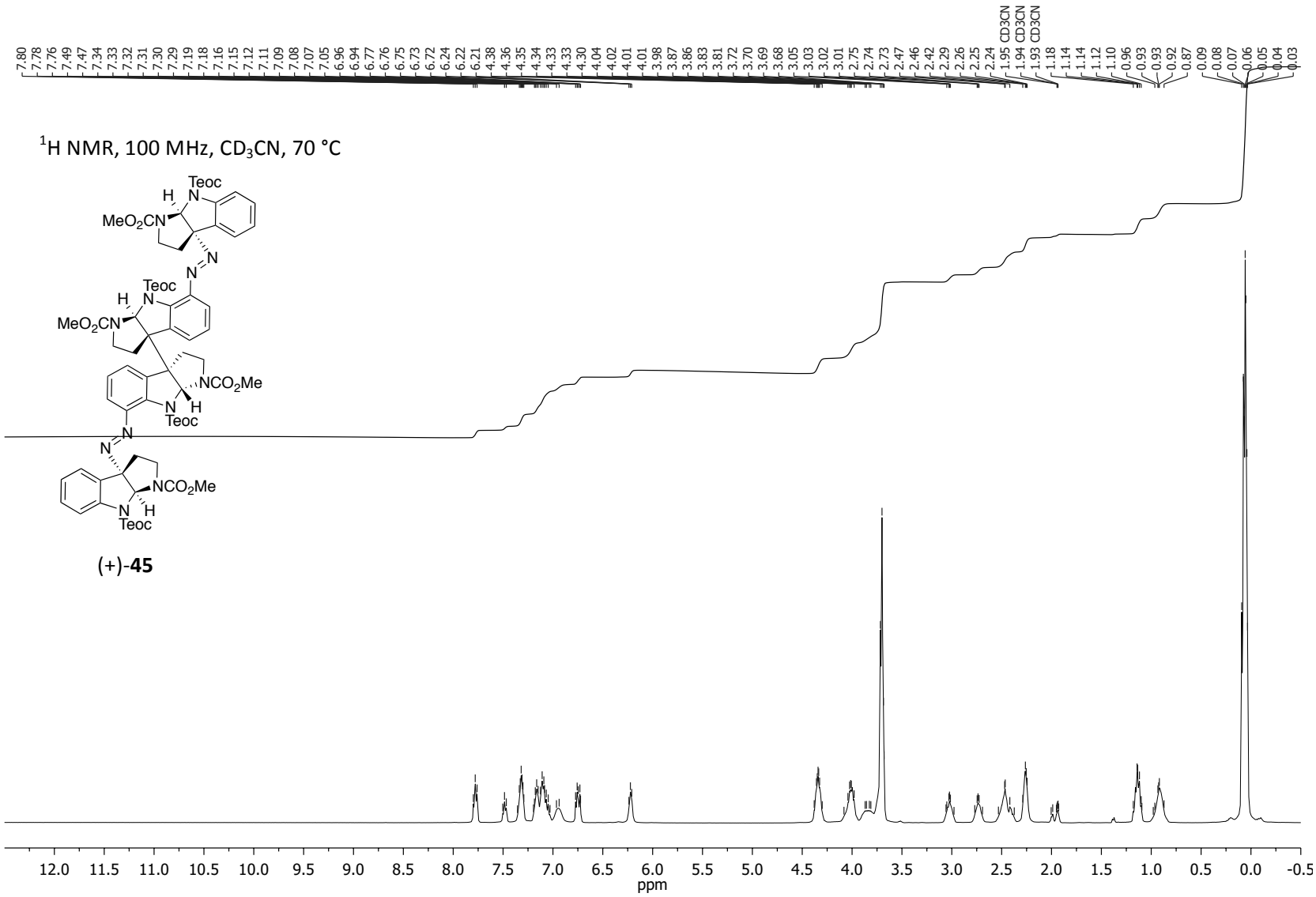

7.78 7.76 7.49 7.48 7.47 7.46 7.36 7.35 7.35 7.34 7.33 7.33 7.33 7.30 7.29 7.28 7.28 7.27 7.27 7.26 7.25 7.25 7.25 7.24 7.23 7.22 7.21 7.11 7.10 7.08 7.07 6.75 6.74 6.73 6.32 6.31 6.30 4.36 4.35 4.34 4.33 4.31 4.03 4.03 4.01 4.01 3.83 3.82 3.81 3.80 3.80 3.78 3.78 3.70 3.70 3.69 3.68 3.04 3.00 2.94 2.92 2.50 2.50 2.49 2.49 2.48 2.47 2.46 2.45 2.43 2.42 1.95 CD3CN 1.95 CD3CN 1.94 CD3CN 1.93 CD3CN 1.16 1.14 1.12 1.11 1.10 0.81 0.07 0.05 0.01 -0.01
^{1}H NMR, 400 MHz, CD_3CN, 50 °C
Teoc
H
N
MeO2CN
N
N
Teoc
H
N
MeO2CN
N
N
NCO2Me
N
H
Teoc
N
N
NCO2Me
N
H
Teoc
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

(+)-**44**

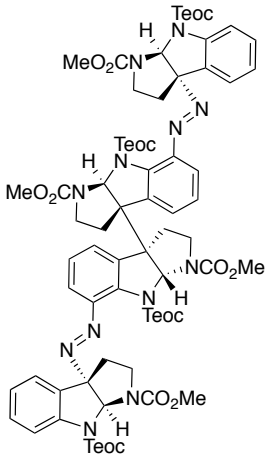
^{13}C NMR, 100 MHz, CD_3CN, 50 °C



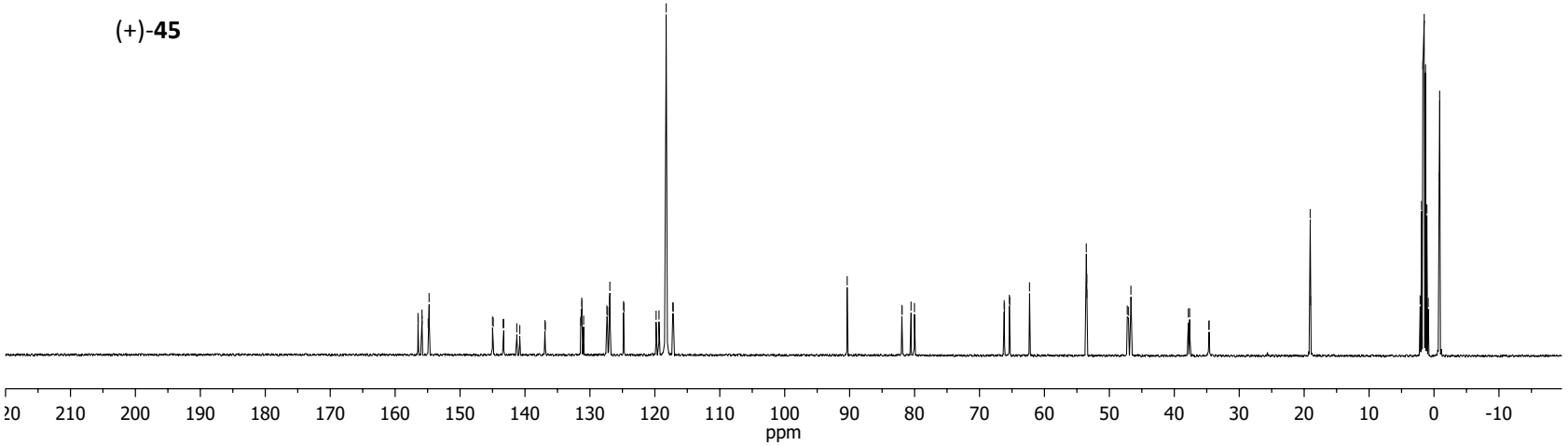
(+)-**44**

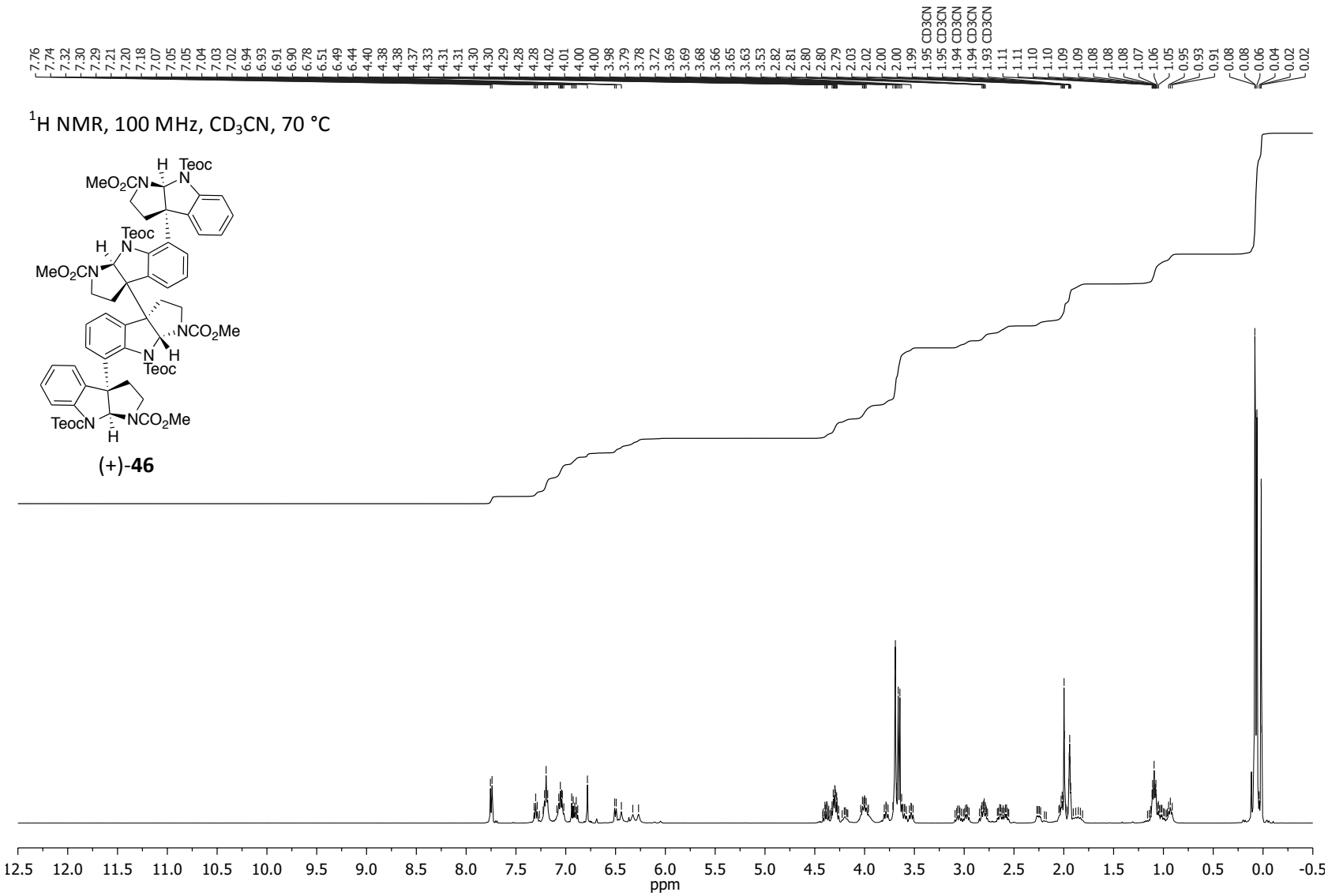

^{1}H NMR, 100 MHz, CD_3CN, 70 °C
Teoc
MeO_2CN
NCO_2Me
(+)-**45**
ppm

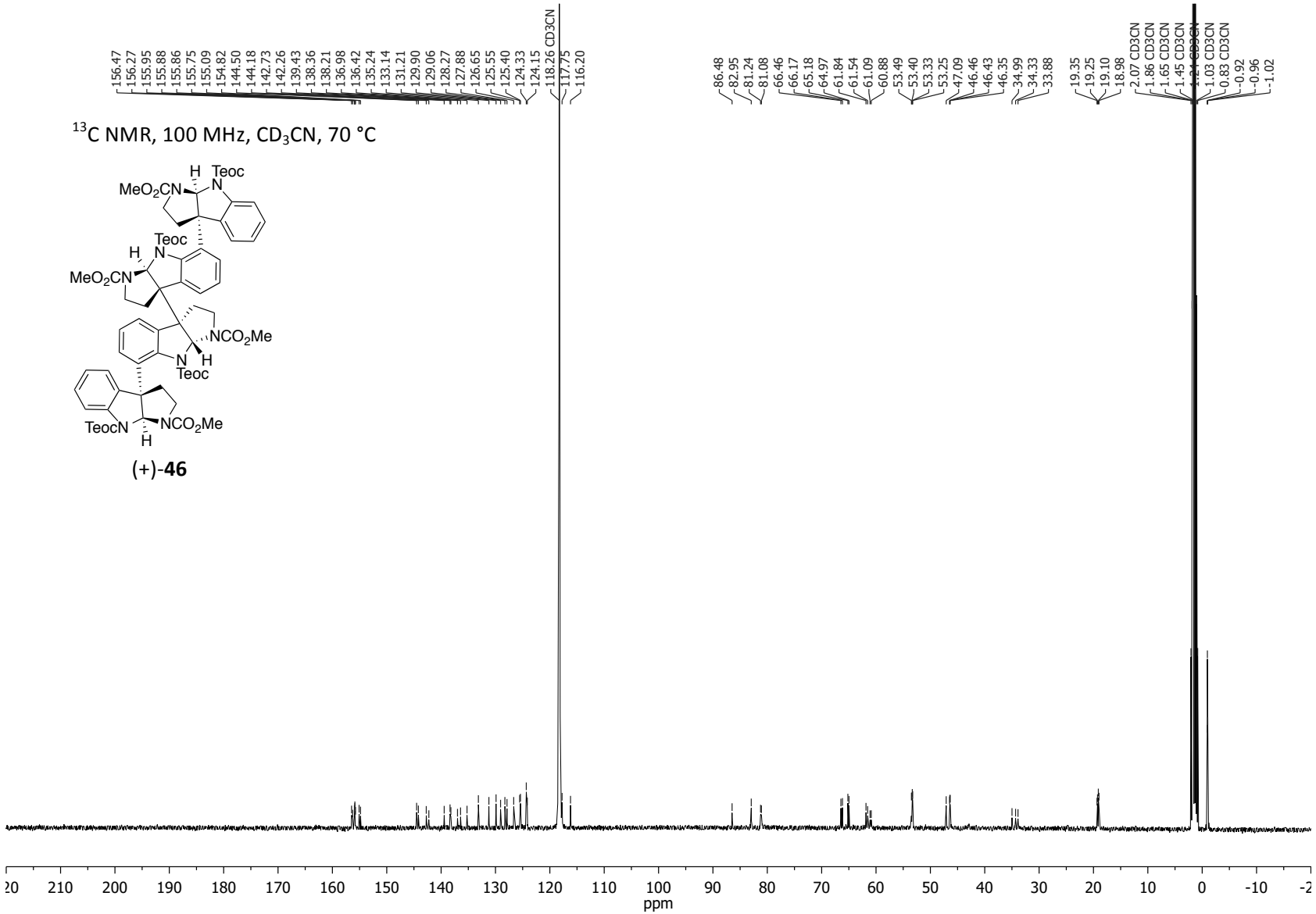
^{13}C NMR, 100 MHz, CD_3CN, 70 °C

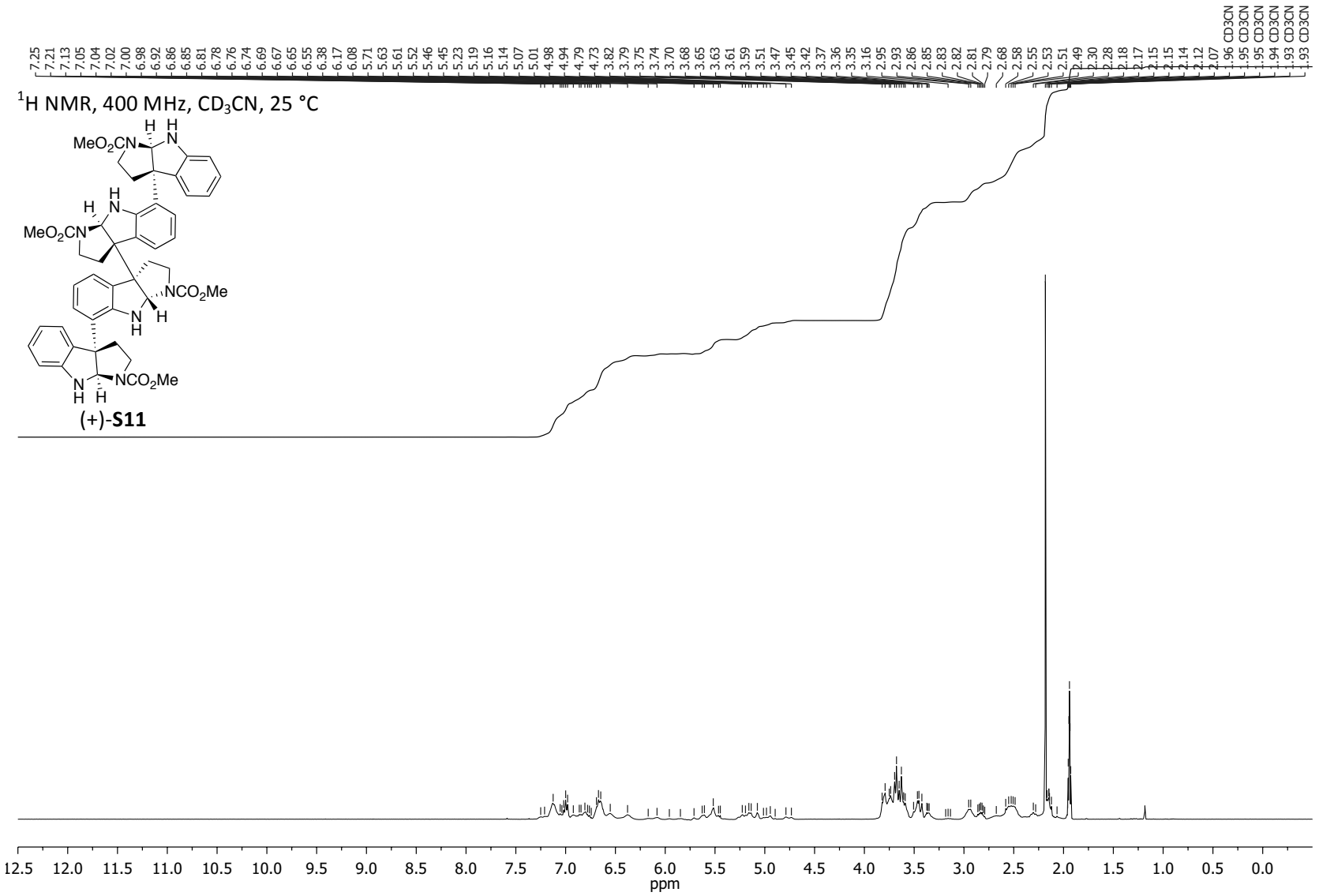


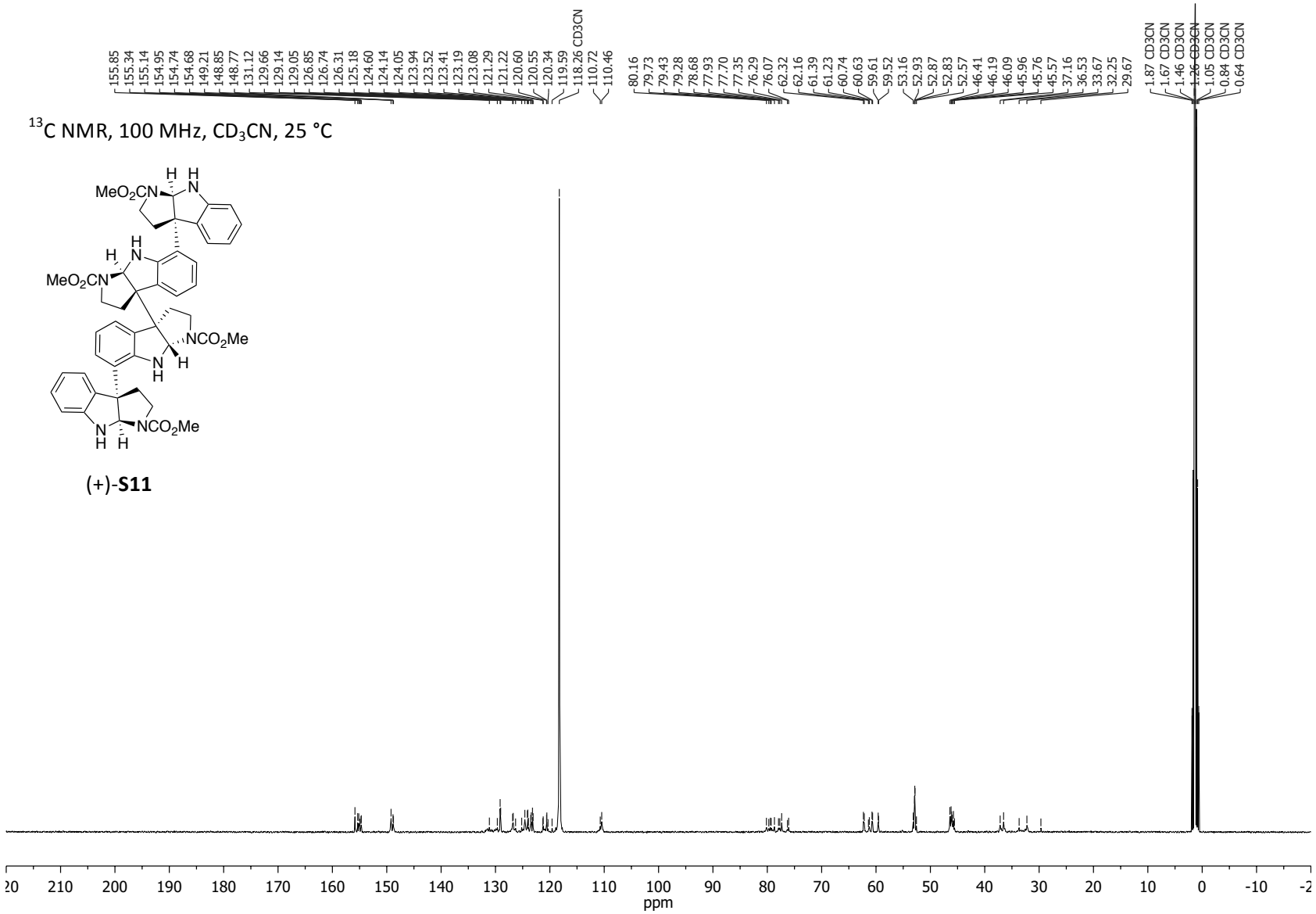
(+)-**45**

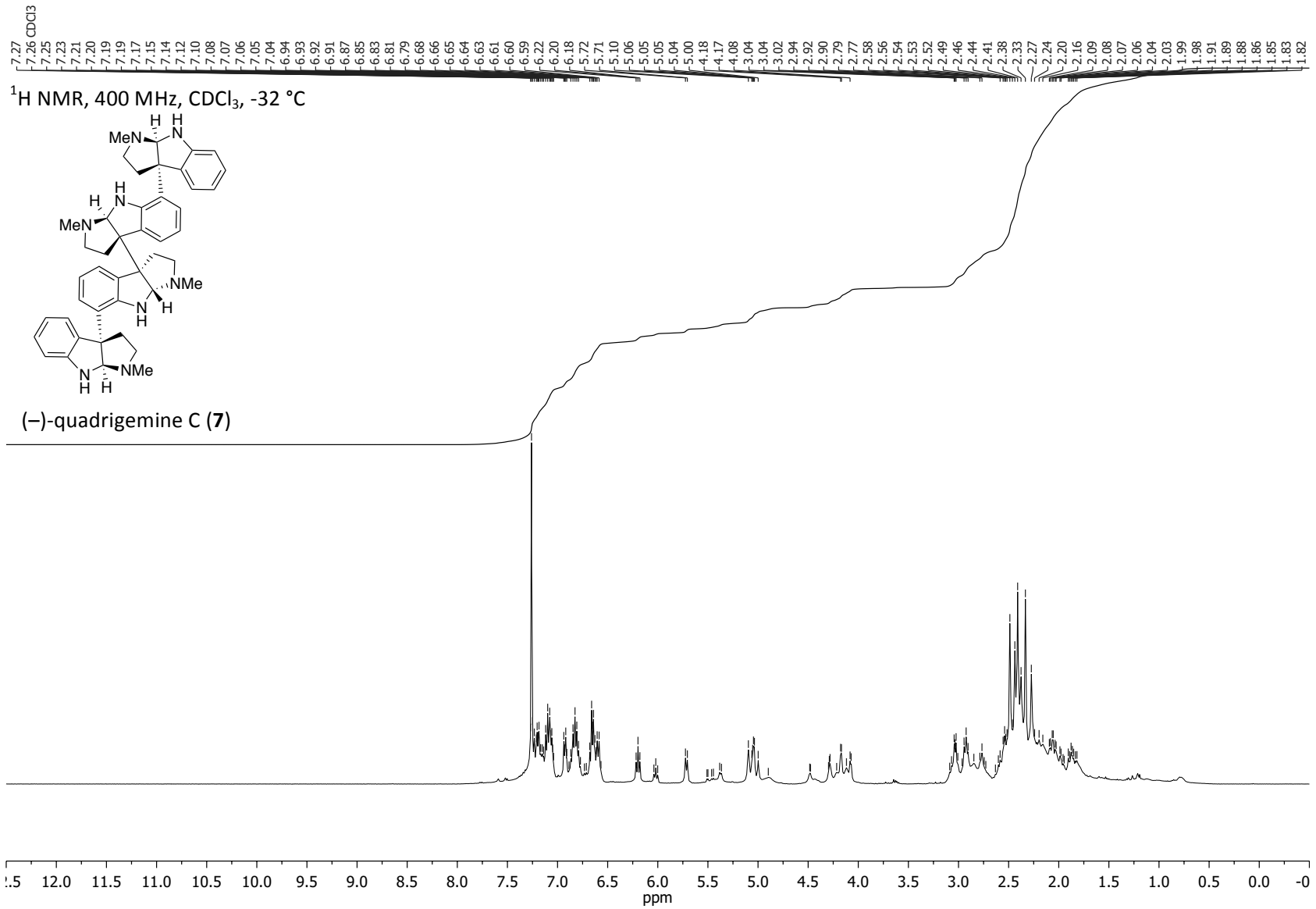


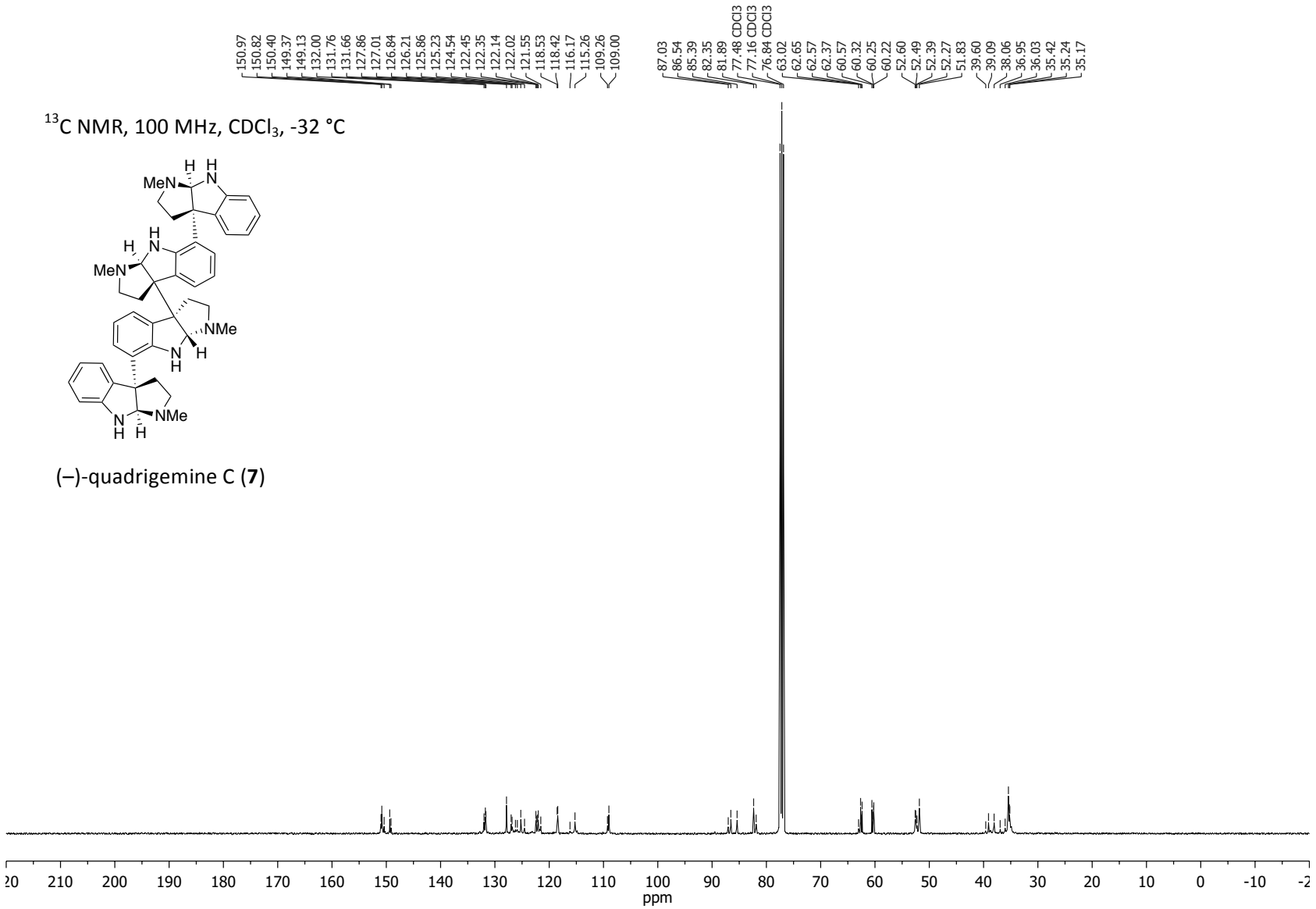

7.76 7.74 7.32 7.30 7.29 7.21 7.20 7.18 7.07 7.05 7.05 7.04 7.03 7.02 6.94 6.93 6.91 6.90 6.78 6.51 6.49 6.44 4.40 4.38 4.38 4.37 4.33 4.31 4.31 4.30 4.30 4.29 4.28 4.28 4.02 4.01 4.00 4.00 3.98 3.79 3.78 3.72 3.69 3.69 3.68 3.66 3.65 3.63 3.53 2.82 2.81 2.80 2.80 2.79 2.03 2.02 2.00 2.00 1.99 1.95 CD3CN 1.95 CD3CN 1.94 CD3CN 1.94 CD3CN 1.93 CD3CN 1.11 1.11 1.10 1.10 1.09 1.09 1.08 1.08 1.08 1.07 1.06 1.05 0.95 0.93 0.91 0.08 0.08 0.06 0.04 0.02 0.02
1H NMR, 100 MHz, CD3CN, 70 °C
H Teoc
MeO2CN
N
Teoc
H
N
MeO2CN
NCO2Me
N H
Teoc
TeocN
NCO2Me
H
(+)-46
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


156.47
156.27
155.95
155.88
155.86
155.75
155.09
154.82
144.50
144.18
142.73
142.26
139.43
138.36
138.21
136.98
136.42
135.24
133.14
131.21
129.90
129.06
128.27
127.88
126.65
125.55
125.40
124.33
124.15
118.26 CD3CN
117.75
116.20
86.48
82.95
81.24
81.08
66.46
66.17
65.18
64.97
61.84
61.54
61.09
60.88
53.49
53.40
53.33
53.25
47.09
46.46
46.43
46.35
34.99
34.33
33.88
19.35
19.25
19.10
18.98
2.07 CD3CN
1.86 CD3CN
1.65 CD3CN
1.45 CD3CN
1.24 CD3CN
1.03 CD3CN
0.83 CD3CN
-0.92
-0.96
-1.02
^{13}C NMR, 100 MHz, CD$_3$CN, 70 °C
MeO$_2$CN
H
Teoc
N
Teoc
H
N
MeO$_2$CN
NCO$_2$Me
N
H
Teoc
TeocN
NCO$_2$Me
H
(+)-46
ppm


^{1}H NMR, 400 MHz, CD_3CN, 25 °C
(+)-**S11**
ppm

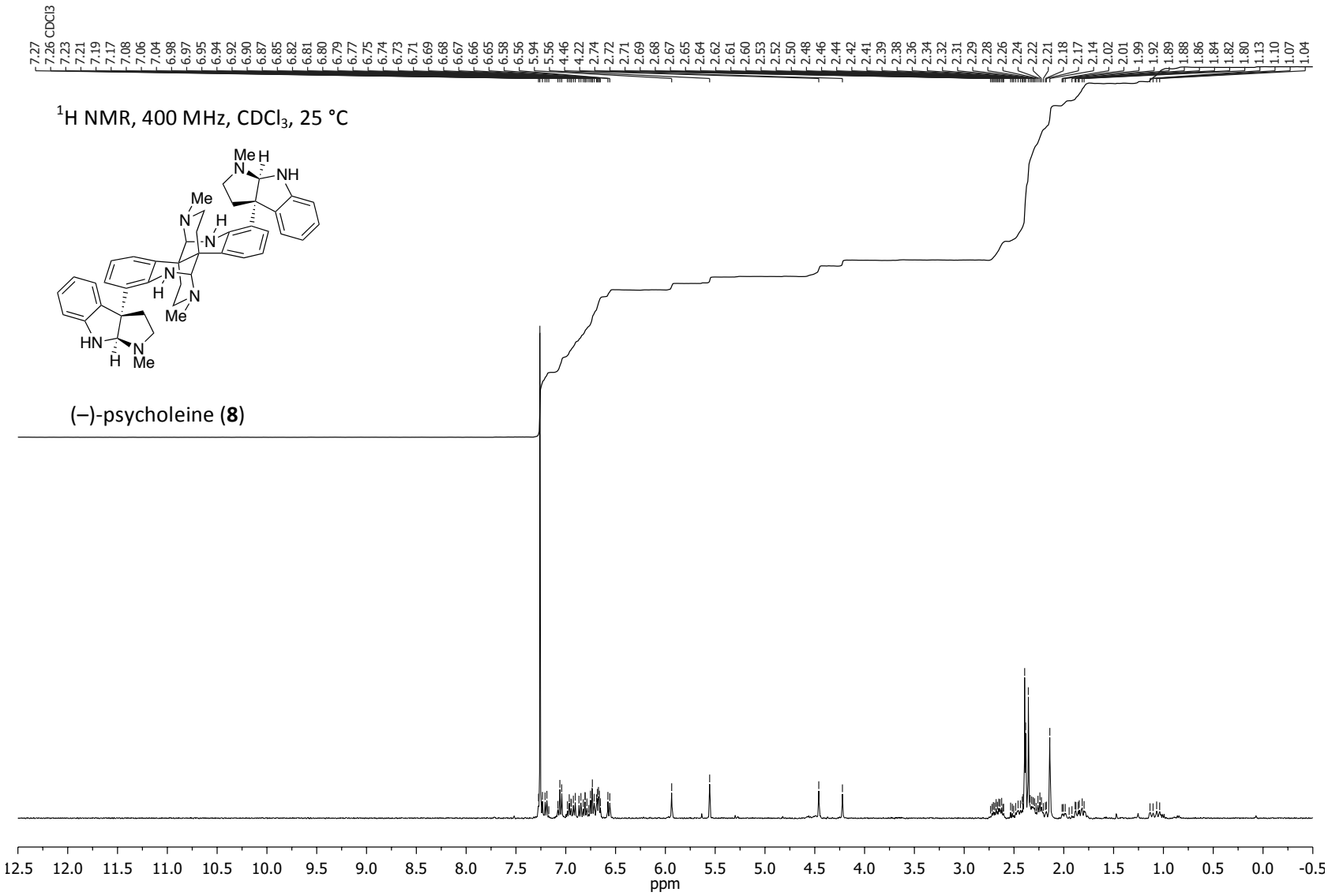

155.85
155.34
155.14
154.95
154.74
154.68
149.21
148.85
148.77
131.12
129.66
129.14
129.05
126.85
126.74
126.31
125.18
124.60
124.14
124.05
123.94
123.52
123.41
123.19
123.08
121.29
121.22
120.60
120.55
120.34
119.59
118.26 CD3CN
110.72
110.46
80.16
79.73
79.43
79.28
78.68
77.93
77.70
77.35
76.29
76.07
62.32
62.16
61.39
61.23
60.74
60.63
59.61
59.52
53.16
52.93
52.87
52.83
52.57
46.41
46.19
46.09
45.96
45.76
45.57
37.16
36.53
33.67
32.25
29.67
1.87 CD3CN
1.67 CD3CN
1.46 CD3CN
1.26 CD3CN
1.05 CD3CN
0.84 CD3CN
0.64 CD3CN
^{13}C NMR, 100 MHz, CD_3CN, 25 °C
MeO2CN
NCO2Me
(+)-**S11**
ppm

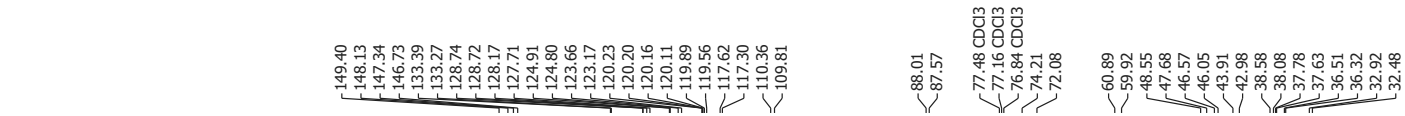

CDCl3
7.27 7.26 7.25 7.23 7.21 7.20 7.19 7.19 7.17 7.15 7.14 7.12 7.10 7.08 7.07 7.06 7.05 7.04 6.94 6.93 6.92 6.91 6.87 6.85 6.83 6.81 6.79 6.68 6.66 6.65 6.64 6.63 6.61 6.60 6.59 6.22 6.20 6.18 5.72 5.71 5.10 5.06 5.05 5.05 5.04 5.00 4.18 4.17 4.08 3.04 3.04 3.02 2.94 2.92 2.90 2.79 2.77 2.58 2.56 2.54 2.53 2.52 2.49 2.46 2.44 2.41 2.38 2.33 2.27 2.24 2.20 2.16 2.09 2.08 2.07 2.06 2.04 2.03 1.99 1.98 1.91 1.89 1.88 1.86 1.85 1.83 1.82
1H NMR, 400 MHz, CDCl3, -32 °C
MeN
NMe
NMe
(–)-quadrigemine C (7)
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm



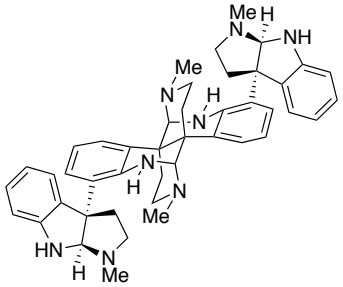
^{13}C NMR, 100 MHz, $CDCl_3$, -32 °C

(–)-quadrigemine C (**7**)


7.27 7.26 CDCl3 7.23 7.21 7.19 7.17 7.08 7.06 7.04 6.98 6.97 6.95 6.94 6.92 6.90 6.87 6.85 6.82 6.81 6.80 6.79 6.77 6.75 6.74 6.73 6.71 6.69 6.68 6.67 6.66 6.65 6.58 6.56 5.94 5.56 4.46 4.22 2.74 2.72 2.71 2.69 2.68 2.67 2.65 2.64 2.62 2.61 2.60 2.53 2.52 2.50 2.48 2.46 2.44 2.42 2.41 2.39 2.38 2.36 2.34 2.32 2.31 2.29 2.28 2.26 2.24 2.22 2.21 2.18 2.17 2.14 2.02 2.01 1.99 1.92 1.89 1.88 1.86 1.84 1.82 1.80 1.13 1.10 1.07 1.04
^{1}H NMR, 400 MHz, $CDCl_3$, 25 °C
(–)-psycholeine (8)
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm



^{13}C NMR, 100 MHz, $CDCl_3$, 25 °C



(–)-psycholeine (**8**)