Total Synthesis and Anti-Cancer Activity of All Known Communesin Alkaloids and Related Derivatives

Matthew M. Pompeo[†], Jaime H. Cheah,[‡] and Mohammad Movassaghi*[,†]

[†]*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

[‡]*The Koch Institute for Integrative Cancer Research, Massachusetts Institute of Technology, 500 Main Street, Cambridge, Massachusetts 02139*

Supporting Information

General Procedures. All reactions were performed in oven-dried or flame-dried round-bottom flasks fitted with rubber septa and were conducted under positive argon pressure using standard Schlenk techniques, unless noted otherwise. Cannulae or gas-tight syringes with stainless steel needles were used to transfer air- or moisture-sensitive liquids. Where necessary (so noted), solutions were degassed by sparging with argon for a minimum of 10 min. Flash column chromatography was performed as described by Still et al.[1] using granular silica gel (60-Å pore size, 40–63 μm, 4–6% H_2O content, Zeochem). Analytical thin layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) and irreversibly stained by treatment with an aqueous solution of ceric ammonium molybdate (CAM) or an aqueous solution of potassium permanganate ($KMnO_4$) followed by heating (~ 1 min) on a hot plate (~250 ºC). Organic solutions were concentrated at 30–35 °C on rotary evaporators capable of achieving a minimum pressure of ~10 Torr. Diazene photolysis was accomplished by irradiation in a Rayonet RMR-200 photochemical reactor (Southern New England Ultraviolet Company, Branford, CT, USA) equipped with 14 radially distributed (r = 12.7 cm) 25 W lamps.

Materials. Commercial reagents and solvents were used as received with the following exceptions: acetonitrile, dichloromethane, *N*,*N*-dimethylformamide, methanol, tetrahydrofuran, toluene, and triethylamine were purchased from EMD Millipore (ReCycler™) or Sigma-Aldrich (Pure-Pac™) and were purified by the method of Grubbs *et al.* under positive argon pressure.[2] Benzene, 1,2-dichloroethane, and *N*,*N*-diisopropylethylamine were dried by distillation over calcium hydride under an inert dinitrogen atmosphere. Deuterated solvents used for nuclear magnetic resonance (NMR) spectroscopy were purchased from Cambridge Isotope Laboratories, Inc. and were used as received with the exception of chloroform-*d*, which was stored over activated molecular sieves (Linde type 3Å, 1/16" pellets) and granular anhydrous potassium carbonate. Titanium(IV) ethoxide (containing 5–15% isopropanol) was purchased from Strem Chemicals Inc.; 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); (–)-diacetone-D-glucose was purchased from Chem-Impex International, Inc. and was further purified by flash chromatography on silica gel (eluent: 30% acetone in hexanes) or from Sigma-Aldrich and was used as received; hexafluoroisopropanol was purchased from Oakwood Products, Inc. and was stored under an argon atmosphere over activated 4 Å molecular sieves; tetra-*n*-butylammonium hydrogen sulfate, *tert*-butyl hypochlorite, and *N*-carbobenzoxy-2-nitrobenzenesulfonamide were purchased from TCI America; (*S*)-4-benzylthiazolidine-2-thione and tryptamine were purchased from AK Scientific, Inc.; calcium trifluoromethanesulfonate, cesium carbonate, lithium hydroxide monohydrate, thiophenol, and triphenylphosphine were purchased from Alfa Aesar. All other solvents and chemicals were purchased from Sigma-Aldrich.

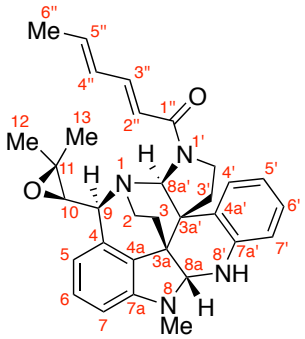
Instrumentation. Nuclear magnetic resonance (^1H, ^{13}C, and ^{19}F NMR) spectra were recorded with Bruker AVANCE NEO 600, Bruker AVANCE 600, Bruker AVANCE NEO 500, Varian inverse probe INOVA-500, Varian INOVA-500, JEOL ECZR 500, or Bruker AVANCE III 400 spectrometers and are reported in parts per million on the δ scale. Spectra were processed with

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

MestReNova 12.0.2 using the automatic phasing and third-order polynomial baseline correction capabilities. Splitting was determined using the automatic multiplet analysis function with manual intervention as necessary. Proton NMR spectra are referenced from the residual protium in the NMR solvent ($CHCl_3$: δ 7.26, CD_2HCN: δ 1.94, CD_2HOD: δ 3.31, DMSO-d_5: 2.50, C_6D_5H: δ 7.16).[3] Carbon-13 NMR spectra are referenced from the carbon resonances of the deuterated solvent ($CDCl_3$: δ 77.16, CD_3CN: δ 118.26, CD_3OD: δ 49.00, DMSO-d_6: 39.52, C_6D_6: δ 128.06).[3] Fluorine-19 NMR are referenced internally from the fluorine resonances of α,α,α-trifluorotoluene ($CF_3C_6H_5$ δ –63.72). Data are reported as follows: chemical shift (multiplicity [s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad, app = apparent], coupling constant(s) in Hertz, integration, assignment).

Infrared spectroscopic data were obtained with a Perkin-Elmer 2000 FTIR spectrometer or a Bruker ALPHA II FTIR spectrometer equipped with a diamond ATR sampling module and are reported as follows: frequency of absorption (cm^{-1}) [intensity of absorption (s = strong, m = medium, w = weak, br = broad)]. Optical rotations were measured on a Jasco P-1010 polarimeter with a sodium lamp and are reported as follows: $[\alpha]_\lambda^{T\ °C}$ (c = g/100 mL, solvent). Chiral HPLC analysis was performed on an Agilent Technologies 1100 Series instrument equipped with a diode array detector and columns with chiral stationary phases from Daicel Chemical Industries (CHIRALPAK® IA, Lot# IA00CE-PD046 and CHIRALCEL® OD-H, Lot# ODH0CE-KF021). Single crystal X-ray diffraction was carried out at the X-ray crystallography laboratory of the Department of Chemistry, Massachusetts Institute of Technology, with the assistance of Mr. Kyan A. D'Angelo, Dr. Charlene Tsay, and Dr. Peter Müller. We thank Dr. Mohanraja Kumar, Dr. Li Li, and Mr. Liam P. Kelly 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 an electrospray (ESI) (*m/z*) ionization source or a direct analysis in real time (DART) ionization source, on an Agilent 6510 QToF with a Dual ESI spray ionization source, or on a JEOL AccuTOF LC-plus 4G API-HRTOFMS equipped with an an IonSense DART ionization source.

Positional Numbering System. In assigning the ^1H and ^{13}C NMR data of all intermediates en route to the communesin alkaloids, we have employed a uniform numbering system illustrated below for (–)-communesin B (**4**).

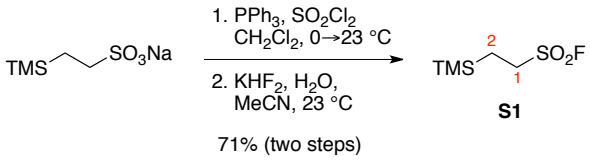


(–)-communesin B (**4**)

3. (a) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512. (b) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.

Cell Culture Information. Cells were grown in media supplemented with fetal bovine serum (FBS) and antibiotics (100 μg/mL penicillin and 100 U/mL streptomycin). Specifically, experiments were performed using the following cell lines and media compositions: HeLa (cervical adenocarcimona) and A549 (lung carcinoma) were grown in RPMI-1640 + 10% FBS; HCT 116 (colorectal carcinoma) was grown in DMEM + 10% FBS; DU 145 (prostate carcinoma) and MCF7 (breast adenocarcinoma) was grown in EMEM + 10% FBS. Cells were incubated at 37 °C in a 5% CO_2, 95% humidity atmosphere.

Cell Viability Assays. Cells were plated at 2000 cells/well into duplicate assay plates in 50 μL media into 384-well white, opaque, tissue-culture treated plates and allowed to adhere overnight at 37 °C/5% CO_2. Compounds were solubilized in DMSO as 1000x stocks and 100 nL was pin-transferred to cells (V&P pin tool mounted on Tecan Freedom Evo MCA96). Compounds were tested in 10-pt, 2-fold dilution with concentrations tested between 1 nM – 20 μM for most compounds, except where indicated. DMSO (32 wells of 384-wells) was used as vehicle control. After 72 hours of incubation at 37 °C/5% CO_2, 10 μL Cell Titer-Glo (Promega) was added to each well and plates were incubated at room temperature for 10 minutes before the luminescence was read on a Tecan M1000 plate reader. Cell Titer-Glo measures ATP levels of cells as a surrogate for cell viability. All compound-treated wells was normalized to the DMSO control averages and expressed as a % of DMSO viability. IC_{50} values were determined from the dose curves using Spotfire (Perkin Elmer).



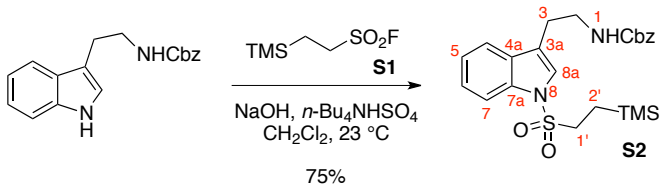
Sulfonyl Fluoride S1:

Sulfuryl chloride (4.60 mL, 56.7 mmol, 2.20 equiv) was added dropwise via syringe over 6 min to a solution of triphenylphosphine (13.5 g, 51.6 mmol, 2.00 equiv) in dichloromethane (20.6 mL) at 0 ºC. After stirring at this temperature for 10 min, a sample of sodium 2-(trimethylsilyl)ethanesulfonate (95 % purity, 5.60 g, 25.8 mmol, 1 equiv) was added as a solid in 12 portions over 6 min. After an additional 20 min at 0 ºC, the ice bath was removed and the resulting yellow suspension was allowed to stir vigorously at 23 ºC. After 24 h, the mixture was added dropwise via Pasteur pipette to a 500-mL round-bottom flask containing pentane (100 mL) with vigorous stirring over 15 min. After stirring for an additional 35 min, the suspension was diluted with pentane (100 mL) and was filtered through a 5.5-cm pad of silica gel, pre-packed with pentane in a 7.3-cm diameter column. The filter cake was washed with a solution of 5% diethyl ether in pentane (800 mL)[4] and the filtrate was concentrated under reduced pressure to yield crude 2-(trimethylsilyl)ethanesulfonyl chloride as a pale-yellow oil, which was used directly in the next step without further purification.[5]

Under an air atmosphere, a 50-mL polypropylene Falcon tube containing a solution of potassium bifluoride (4.03 g, 51.6 mmol, 2.00 equiv) in deionized water (12.0 mL) at 23 ºC was charged with a solution of crude 2-(trimethylsilyl)ethanesulfonyl chloride in HPLC-grade acetonitrile (10.0 mL). The transfer was quantitated with additional acetonitrile (2 × 3.0 mL). After vigorous stirring for 16 h, the layers were separated and the aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic extracts were washed successively with a 10% aqueous sodium chloride solution (2 × 50 mL) and a saturated aqueous sodium chloride solution (50 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 2→4% diethyl ether in pentane) to afford sulfonyl fluoride **S1** (3.38 g, 71.1%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	δ 3.34–3.24 (m, 2H, C1**H**$_2$), 1.23–1.13 (m, 2H, C2**H**$_2$), 0.10 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 48.1 (d, $J_{C,F}$ = 16.4 Hz, **C**1), 10.6 (**C**2), –2.0 (Si(**C**H$_3$)$_3$).
^{19}F NMR (470.9 MHz, $CDCl_3$, 20 °C):	δ 47.1 (s, SO_2**F**).
FTIR (thin film) cm^{-1}:	2958 (m), 2903 (w), 1399 (s), 1255 (s), 1206 (s), 1175 (w), 1125 (w), 1021 (w), 900 (m), 838 (s), 812 (s), 764 (s), 739 (m), 696 (m), 548 (s).
HRMS (DART) (*m/z*):	calc'd for $C_5H_{17}FNO_2SSi$ $[M+NH_4]^+$: 202.0728, found: 202.0723.
TLC (4% diethyl ether in pentane), R*f*:	0.41 ($KMnO_4$).

4. The filtrate was monitored by TLC (4% diethyl ether in pentane, $KMnO_4$) to ensure complete recovery of the sulfonyl chloride.
5. Procedure adapted from Han, X.; Civiello, R. L.; Fang, H.; Wu, D.; Gao, Q.; Chaturvedula, P. V.; Macor, J. E.; Dubowchik, G. M. *J. Org. Chem.* **2008**, *73*, 8502.

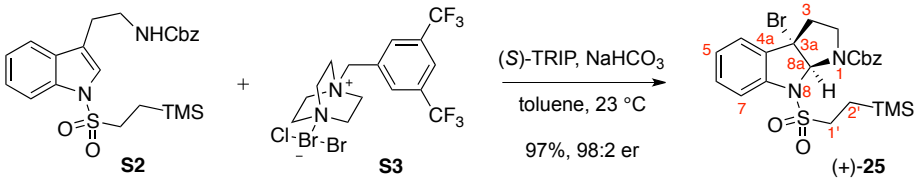


Tryptamine S2:

2-(Trimethylsilyl)ethanesulfonyl fluoride[6] (**S1**, 1.87 g, 10.2 mmol, 1.30 equiv) was added dropwise via syringe to a suspension of benzyl (2-(1*H*-indol-3-yl)ethyl)carbamate[7] (2.30 g, 7.81 mmol, 1 equiv), freshly crushed sodium hydroxide (937 mg, 23.4 mmol, 3.00 equiv), and tetra-*n*-butylammonium hydrogen sulfate (265 mg, 0.781 mmol, 0.100 equiv) in dichloromethane (31 mL) at 23 ºC. After vigorous stirring for 8 h, the suspension was cooled to 0 ºC and was acidified by portionwise addition of an aqueous hydrogen chloride solution (1 N, 31 mL). After warming to 23 ºC, the biphasic mixture was diluted with deionized water (30 mL) and the layers were separated. The aqueous phase was extracted with dichloromethane (3 × 30 mL) and the combined organic extracts were washed successively with water (2 × 100 mL) and a saturated aqueous sodium chloride solution (100 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 20%→25% ethyl acetate in hexanes) to afford tryptamine **S2** (2.69 g, 75.1%) as a colorless viscous oil. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	δ 7.88 (d, *J* = 8.2 Hz, 1H, C7**H**), 7.61 (d, *J* = 7.8 Hz, 1H, C4**H**), 7.40–7.29 (m, 7H, C5**H**, C6**H**, Ar_{Cbz}**H**), 7.28 (s, 1H, C8a**H**), 5.11 (s, 2H, N1CO_2C**H**$_2$Ph), 4.92 (br-t, *J* = 6.1 Hz, 1H, **H**N1CO_2CH_2Ph), 3.53 (app-q, *J* = 6.8 Hz, 2H, C2**H**), 3.20–3.10 (m, 2H, C1'**H**), 2.95 (t, *J* = 7.0 Hz, 2H, C3**H**), 0.94–0.80 (m, 2H, C2'**H**), –0.05 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 156.5 (N1**C**O_2CH_2Ph), 136.6 (Ar_{Cbz}), 135.6 (**C**7a), 130.5 (**C**4a), 128.7 (Ar_{Cbz}), 128.3 (Ar_{Cbz}), 128.2 (Ar_{Cbz}), 125.0 (**C**6), 124.1 (**C**8a), 123.2 (**C**5), 119.7 (**C**4), 118.4 (**C**3a), 113.3 (**C**7), 66.8 (N1CO_2**C**H_2Ph), 50.7 (**C**1'), 40.7 (**C**2), 25.7 (**C**3), 10.1 (**C**2'), –2.0 (Si(**C**H_3)$_3$).
FTIR (thin film) cm^{-1}:	3408 (br-w), 3341 (br-w), 2952 (w), 1702 (m), 1517 (m), 1448 (m), 1357 (m), 1249 (s), 1155 (s), 976 (m), 741 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{23}H_{30}N_2NaO_4SSi$ $[M+Na]^+$: 481.1588, found: 481.1588.
TLC (20% ethyl acetate in hexanes), R*f*:	0.28 (UV, CAM).

6. (a) When the corresponding sulfonyl chloride was used, the yield of sulfonamide **S2** was only 20%. (b) For a review of sulfur(VI) fluorides and their use in organic synthesis, see Dong, J.; Krasnova, L.; Finn, M. G.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2014**, *53*, 9430.
7. Kandukuri, S. R.; Schiffner, J. A.; Oestreich, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 1265.

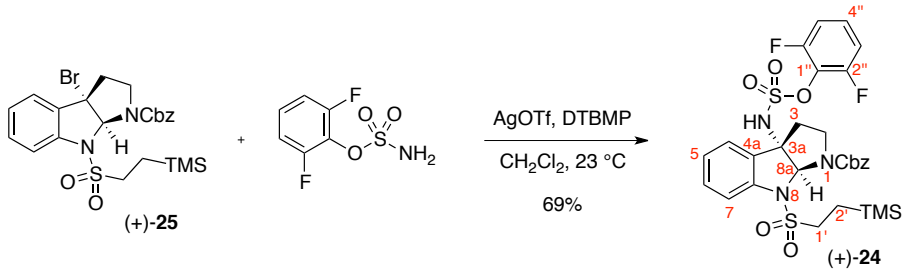


Bromocyclotryptamine (+)-25:

A sample of bromine salt **S3**[8] (5.63 g, 10.5 mmol, 1.30 equiv) was added to a suspension of tryptamine **S2** (3.72 g, 8.10 mmol, 1 equiv), *(S)*-3,3′-bis(2,4,6-triisopropylphenyl)-1,1′-binaphthyl-2,2′-diyl hydrogenphosphate[9] ((*S*)-TRIP, 610 mg, 0.810 mmol, 0.100 equiv), and crushed sodium hydrogen carbonate (2.72 g, 32.4 mmol, 4.00 equiv) in toluene (162 mL) at 23 ºC. After stirring for 24 h, the orange suspension was diluted with a saturated aqueous sodium thiosulfate solution (160 mL) and deionized water (320 mL) and was stirred vigorously for 15 min. The layers were separated and the aqueous layer was extracted with ethyl acetate (3 × 160 mL). The combined organic extracts were washed successively with an aqueous sodium thiosulfate solution (1 M, 320 mL) and a saturated aqueous sodium chloride solution (200 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: 14%→15% ethyl acetate in hexanes) to afford bromocyclotryptamine (+)-**25** (4.21 g, 96.6%, 98:2 er) as a white foam.[10] The enantiomeric ratio was determined by chiral HPLC analysis (CHIRALPAK® IA, 10% *i*PrOH in hexanes, 1.0 mL/min, 210 nm, t_R (major) = 10.3 min, t_R (minor) = 12.7 min). As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments also collected at elevated temperature.

^{1}H NMR (400 MHz, CD_3CN, 60 °C):	δ 7.52 (ddd, *J* = 7.7, 1.4, 0.6 Hz, 1H, C4**H**), 7.45–7.28 (m, 7H, C6**H**, C7**H**, Ar_{Cbz}**H**), 7.23 (ddd, *J* = 7.7, 7.1, 1.3 Hz, 1H, C5**H**), 6.34 (s, 1H, C8a**H**), 5.25–5.11 (m, 2H, N1CO_2C**H**$_2$Ph), 3.86–3.75 (m, 1H, C2**H**$_a$), 3.56 (td, *J* = 13.4, 4.7 Hz, 1H, C1'**H**$_a$), 3.35 (td, *J* = 13.5, 4.8 Hz, 1H, C1'**H**$_b$), 3.01–2.90 (m, 1H, C3**H**$_a$), 2.89–2.78 (m, 2H, C2**H**$_b$, C3**H**$_b$), 1.10 (m, 2H, C2'**H**$_2$), 0.04 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (100.6 MHz, CD_3CN, 60 °C):	δ 155.5 (N1**C**O_2CH_2Ph), 143.3 (**C**7a), 138.0 (Ar_{Cbz}), 134.7 (**C**4a), 131.8 (**C**6), 129.8 (Ar_{Cbz}), 129.4 (Ar_{Cbz}), 129.2 (Ar_{Cbz}), 126.6 (**C**5), 125.6 (**C**4), 118.9 (**C**7), 88.3 (**C**8a), 68.6 (N1CO_2**C**H_2Ph), 64.5 (**C**3a), 51.9 (**C**1'), 47.4 (**C**2), 42.0 (**C**3), 11.3 (**C**2'), –1.6 (Si(**C**H_3)$_3$).
FTIR (thin film) cm^{-1}:	2953 (w), 2896 (w), 1705 (s), 1601 (w), 1408 (s),1353 (s), 1251 (m), 1197 (m), 1148 (s), 844 (s), 753 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{23}H_{30}BrN_2O_4SSi$ $[M+H]^+$: 537.0873, found: 537.0878.
$[\alpha]_D^{23}$:	+198 (*c* = 0.37, CH_2Cl_2).
TLC (20% ethyl acetate in hexanes), R*f*:	0.36 (UV, CAM).

8. Xie, W.; Jiang, G.; Liu, H.; Hu, J.; Pan, X.; Zhang, H.; Wan, X.; Lai, Y.; Ma, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 12924.
9. Hoffmann, S.; Seayad, A. M.; List, B. *Angew. Chem., Int. Ed.* **2005**, *44*, 7424.
10. Further elution with 60% ethyl acetate in hexanes enables recovery of the (*S*)-TRIP catalyst.



Sulfamate ester (+)-24:

A sample of silver trifluoromethanesulfonate (2.72 g, 10.6 mmol, 2.00 equiv) was added to a solution of bromocyclotryptamine (+)-**25** (2.85 g, 5.30 mmol, 1 equiv), 2,6-difluorophenyl sulfamate[11] (2.22 g, 10.6 mmol, 2.00 equiv), and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 2.72 g, 13.2 mmol, 2.50 equiv) in dichloromethane (132 mL) at 23 ºC in the dark. After 1.5 h, the off-white milky suspension was diluted with ethyl acetate (265 mL) and was filtered through a pad of silica gel covered with a pad of Celite. The filter cake was washed with ethyl acetate (500 mL) and the colorless filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 50%→60% diethyl ether in hexanes) to yield a white foam, which was further purified by flash column chromatography on silica gel (eluent: 1%→4% acetonitrile in dichloromethane) to afford pure sulfamate ester (+)-**24** (2.42 g, 68.5%) as a white foam. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments also collected at elevated temperature.

^{1}H NMR (400 MHz, CD_3CN, 60 °C): δ 7.51 (dt, *J* = 7.7, 1.0 Hz, 1H, C4**H**), 7.44–7.28 (m, 8H, C6**H**, C7**H**, C4"**H**, Ar_{Cbz}**H**), 7.25–7.17 (m, 1H, C5**H**), 7.16–7.08 (m, 2H, C3"**H**), 6.98 (br-s, 1H, N**H**SO_3Ar), 6.55 (s, 1H, C8a**H**), 5.28–5.09 (m, 2H, N1CO_2C**H**$_2$Ph), 4.08–3.94 (m, 1H, C2**H**$_a$), 3.41 (br-t, *J* = 11.2 Hz, 1H, C1'**H**$_a$), 3.25 (td, *J* = 13.4, 4.5 Hz, 1H, C1'**H**$_b$), 2.94–2.78 (m, 2H, C2**H**$_b$, C3**H**$_a$), 2.57–2.44 (m, 1H, C3**H**$_b$), 1.18–0.97 (m, 2H, C2'**H**$_2$), 0.03 (s, 9H, Si(C**H**$_3$)$_3$).

^{13}C NMR (100.6 MHz, CD_3CN, 60 °C): δ 157.3 (dd, *J* = 252, 3.5 Hz, **C**2"), 155.7 (N1**C**O_2CH_2Ph), 144.7 (**C**7a), 138.0 (Ar_{Cbz}), 132.0 (**C**6), 131.1 (**C**4a), 129.74 (Ar_{Cbz}), 129.66 (t, *J* = 9.4 Hz, **C**4"), 129.3 (Ar_{Cbz}), 129.2 (Ar_{Cbz}), 127.9 (t, *J* = 15.7 Hz, **C**1"), 126.3 (**C**4), 125.7 (**C**5), 117.7 (**C**7), 114.2–113.9 (m, **C**3"), 84.1 (**C**8a), 74.1 (**C**3a), 68.6 (N1CO_2**C**H_2Ph), 51.3 (**C**1'), 46.2 (**C**2), 36.8 (**C**3), 11.1 (**C**2'), –1.6 (Si(**C**H_3)$_3$).

^{19}F NMR (376.4 MHz, CD_3CN, 25 °C): δ –126.2 (s, C_6H_3**F**$_2$).

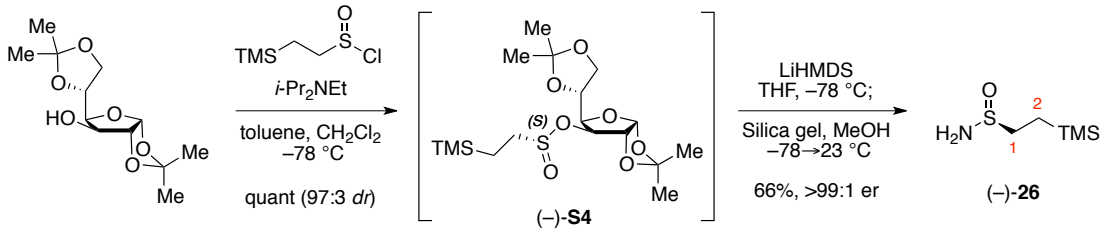
FTIR (thin film) cm^{-1}: 3161 (br-w), 2951 (w), 2896 (w), 1703 (m), 1682 (m), 1603 (m), 1479 (m), 1412 (m), 1345 (m), 1174 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{29}H_{33}F_2N_3NaO_7S_2Si$ [M+Na]$^+$: 688.1389, found: 688.1367.

11. Roizen, J. L.; Zalatan, D. L.; Du Bois, J. *Angew. Chem. Int. Ed.* **2013**, *52*, 11343.

$[\alpha]_D^{22}$: +84 (*c* = 0.33, CH_2Cl_2).

TLC (2% acetonitrile in dichloromethane), R*f*: 0.26 (UV, CAM).



(–)-(*S*)-2-(Trimethylsilyl)ethanesulfinamide (26):

A solution of freshly prepared (±)-2-(trimethylsilyl)ethanesulfinyl chloride[12] (11.8 g, 64.3 mmol, 1.25 equiv) in toluene (75 mL) was added dropwise from a pressure-equalizing addition funnel over 75 min[13] to a solution of (–)-diacetone-D-glucose[14] (13.4 g, 51.4 mmol, 1 equiv) and *N*,*N*-diisopropylethylamine (13.0 mL, 74.6 mmol, 1.45 equiv) in toluene (440 mL) and dichloromethane (70 mL) at –78 ºC. After 2 h, the viscous milky solution was diluted with a saturated aqueous ammonium chloride solution (500 mL) and deionized water (50 mL) and the mixture was allowed to stir in a 23 ºC water bath. After 75 min, the layers were separated and the aqueous layer was extracted with diethyl ether (3 × 300 mL). The combined organic extracts were washed successively with an aqueous hydrogen chloride solution (1 M, 500 mL), a saturated aqueous sodium bicarbonate solution (400 mL), and a saturated aqueous sodium chloride solution (400 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated to yield crude (S_S)-alkanesulfinate (–)-**S4** (21.8 g, quantitative yield, 97:3 dr)[15] as a light yellow viscous oil. This inseparable mixture of diastereomers was used directly in the next step without further purification.[16]

The sample of crude (S_S)-alkanesulfinate (–)-**S4** was azeotropically dried by concentration from benzene (3 × 100 mL). The flask was then charged with a stir bar, capped with a rubber septum, and placed under high vacuum (~0.1 Torr). After 25 min, the flask was refilled with argon and the residue was dissolved in tetrahydrofuran (206 mL). The rubber-septum was replaced with an oven-dried pressure-equalizing addition funnel and the resulting solution was cooled to –78 ºC. Subsequently, a solution of lithium bis(trimethylsilyl)amide (1.0 M in tetrahydrofuran, 54.0 mL, 54.0 mmol, 1.05 equiv) was added dropwise over 42 min, after which the addition funnel was rinsed with tetrahydrofuran (2.0 mL). After stirring at –78 ºC for an additional 90 min, methanol (83.0 mL, 2.06 mol, 40.0 equiv) and silica gel (51.4 g) were added sequentially and the suspension was allowed to stir in a 23 ºC water bath. After 1 h, the suspension was concentrated under reduced pressure and the resulting silica-adsorbed crude mixture was purified by flash column chromatography on silica gel (eluent: 10%→40% acetone in dichloromethane) to yield (–)-(*S*)-2-(trimethylsilyl)ethanesulfinamide[17] (**26**, 8.34 g, 98.1%, 88:12 er) as a light-yellow viscous oil, which solidified to an off-white waxy solid on concentration from *n*-heptane (3 × 30 mL) and

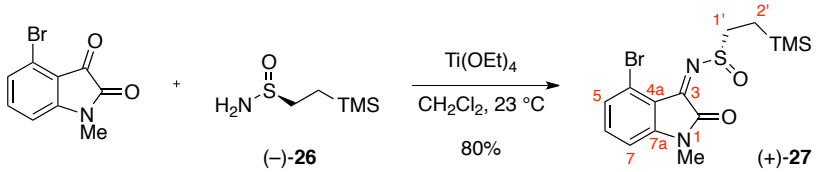
12. Prepared from *tert*-butyl 2-(trimethylsilyl)ethyl sulfoxide, according to Schwan, A. L.; Brillon, D.; Dufault, R. *Can. J. Chem.* **1994**, *72*, 325.
13. During this time, the internal temperature of the reaction mixture did not exceed –75 ºC.
14. For relevant studies on the use of (–)-diacetone-D-glucose (DAG) as a chiral controller for the preparation of chiral sulfoxides and sulfinamides, see: (a) Llera, J. M.; Fernández, I.; Alcudia, F. *Tetrahedron Lett.* **1991**, *32*, 7299. (b) Fernández, I.; Khiar, N.; Llera, J. M.; Alcudia, F. *J. Org. Chem.* **1992**, *57*, 6789. (c) Khiar, N.; Fernández, I.; Alcudia, F. *Tetrahedron Lett.* **1994**, *35*, 5719. (d) Fernández, I.; Valdivia, V.; Khiar, N. *J. Org. Chem.* **2008**, *73*, 745. (e) Chelouan, A.; Recio, R.; Alcudia, A.; Khiar, N.; Fernández, I. *Eur. J. Org. Chem.* **2014**, 6935.
15. The absolute configuration of alkanesulfinate (–)-**S4** at sulfur was inferred by comparison to literature precedent (see ref. 14).
16. For structural characterization, a sample of (–)-**S4** was purified by flash column chromatography on silica gel (eluent: 30→40% diethyl ether in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC, 97:3 dr): δ 5.90 (d, J = 3.6 Hz, 1H), 4.73 (d, J = 2.8 Hz, 1H), 4.62 (d, J = 3.6 Hz, 1H), 4.32–4.23 (m, 2H), 4.08 (dd, J = 8.5, 6.0 Hz, 1H), 4.00 (dd, J = 8.5, 5.1 Hz, 1H), 2.79–2.62 (m, 2H), 1.50 (s, 3H), 1.42 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H), 0.94–0.74 (m, 2H), 0.04 (s, 9H). δ ^{13}C NMR (150.9 MHz, $CDCl_3$, 20 ºC, 97:3 dr): δ 112.5, 109.3, 105.1, 83.8, 80.5, 79.0, 72.5, 66.8, 53.0, 26.9, 26.8, 26.4, 25.3, 7.6, –1.8. FTIR (thin film) cm^{-1}: 2987 (w), 2954 (w), 2896 (w), 1372 (m), 1250 (m), 1214 (m), 1161 (m), 1133 (m), 1072 (s), 1017 (s), 952 (m), 825 (s), 733 (m). HRMS (DART) (*m/z*): calc'd for $C_{17}H_{33}O_7SSi$ $[M+H]^+$: 409.1711, found: 409.1710. $[\alpha]_D^{23}$: –56 (c = 1.51, CH_2Cl_2).
17. The absolute configuration of sulfinamide (–)-**26** was inferred by comparison to literature precedent (see ref. 14) and by preparation of a derivative with a known stereochemical configuration as described later in this document.

standing for 7 h under high vacuum (~0.1 Torr).[18] The enantiomeric ratio was determined by chiral HPLC analysis of a 3 mg/mL solution of (–)-**26** in hexanes (CHIRALCEL® OD-H, 4% *i*PrOH in hexanes, 1.0 mL/min, 210 nm, t_R (minor) = 16.3 min, t_R (major) = 18.2 min).

To enrich the enantiomeric ratio, the product was transferred to a 100-mL round-bottom flask and was crushed with a Teflon rod. *n*-Heptane (30 mL) was added and the resulting suspension was sonicated for 1 h at 23 ºC under an atmosphere of argon. A stir bar and an additional portion of *n*-heptane (10 mL) were added and the suspension was stirred vigorously at 0 ºC for 30 min. The solid was then collected by filtration and was washed with cold (–20 ºC) *n*-heptane (35 mL). Drying under vacuum (~10 Torr) for 14 h provided (–)-**26** (5.60 g, 65.9%, >99:1 er) as a flocculent white solid. The enantiomeric ratio was determined by chiral HPLC analysis of a 3 mg/mL solution of (–)-**26** in hexanes (CHIRALCEL® OD-H, 4% *i*PrOH in hexanes, 1.0 mL/min, 210 nm, t_R (minor) = 16.6 min, t_R (major) = 18.2 min).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	δ 4.14 (s, 2H, N**H**$_2$), 2.78–2.56 (m, 2H, C1**H**$_2$), 0.96–0.79 (m, 2H, C2**H**$_2$), 0.04 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 52.9 (**C**1), 8.4 (**C**2), –1.8 (Si(**C**H$_3$)$_3$).
FTIR (thin film) cm^{-1}:	3222 (br-m), 2954 (m), 2897 (m), 2809 (w), 1653 (m), 1577 (m), 1419 (m), 1249 (m), 1162 (m), 1036 (br-m).
HRMS (DART) (*m/z*):	calc'd for $C_5H_{16}NOSSi$ $[M+H]^+$: 166.0716, found: 166.0719.
$[\alpha]_D^{23}$:	–22 (*c* = 1.47, CH_2Cl_2).
TLC (40% acetone in dichloromethane), R*f*:	0.38 (UV, CAM).

18. (–)-Diacetone-D-glucose (12.4 g, 92.6%) was also recovered as an amorphous white solid, which can be recycled without further purification.



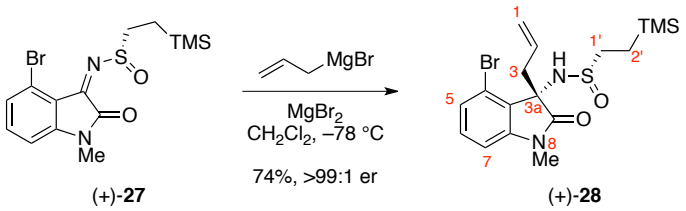
Alkanesulfinyl imine (+)-27:

Titanium ethoxide[19] (16.3 mL, 67.1 mmol, 2.20 equiv) was added via syringe to a stirred solution of (–)-(*S*)-2-(trimethylsilyl)ethanesulfinamide (**26**, 5.55 g, 33.6 mmol, 1.10 equiv) and 4-bromo-1-methylisatin[20] (7.33 g, 30.5 mmol, 1 equiv) in dichloromethane (61.0 mL) at 23 ºC. After 20 h, the reaction mixture was diluted with dichloromethane (61 mL) and deionized water (2.40 mL, 133 mmol, 4.40 equiv) was then added dropwise over 4 min with vigorous stirring. The resulting thick red slurry was diluted with an additional portion of dichloromethane (120 mL) and was stirred vigorously. After 10 min, oven-dried Celite (24 g) was added and the suspension was concentrated under reduced pressure. The Celite-adsorbed crude mixture was purified by flash column chromatography on silica gel (eluent: 5%→20% ethyl acetate in dichloromethane) to yield alkanesulfinyl imine (+)-**27** (9.47 g, 80.1%) as a dark orange solid. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	δ 7.34–7.27 (m, 2H, C5**H**, C6**H**), 6.83 (app-d, J = 7.2 Hz, 1H, C7**H**), 3.25 (s, 3H, N1C**H**$_3$), 3.06–2.96 (m, 1H, C1'**H**$_a$), 2.95–2.86 (m, 1H, C1'**H**$_b$), 1.19–1.06 (m, 2H, C2'**H**), 0.04 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 157.3 (**C**2), 155.3 (**C**3), 149.5 (**C**7a), 135.3 (**C**6), 129.1 (**C**5), 121.1 (**C**4), 117.7 (**C**4a), 108.3 (**C**7), 53.4 (**C**1'), 26.6 (N1**C**H$_3$), 9.3 (**C**2'), –1.6 (Si(**C**H$_3$)$_3$).
FTIR (thin film) cm^{-1}:	3080 (w), 2952 (m), 2894 (w), 1723 (s), 1596 (s), 1456 (m), 1355 (m), 1322 (m), 1249 (m), 1109 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{14}H_{20}BrN_2O_2SSi$ $[M+H]^+$: 387.0193, found: 387.0185.
$[\alpha]_D^{23}$:	+447 (c = 0.31, CH_2Cl_2).

TLC (10% ethyl acetate in dichloromethane), R*f*: 0.29 (UV, CAM).

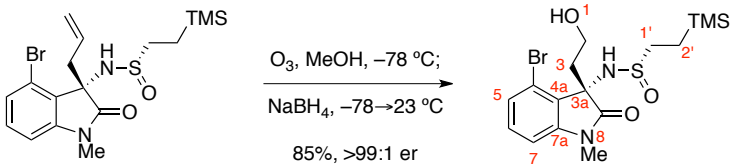
19. Strem Chemicals Inc. cat# 93-2209, containing 5-15% isopropanol, was dispensed assuming 85 w/w% purity.
20. Sin, N.; Venables, B. L.; Liu, X.; Huang, S.; Gao, Q.; Ng, A.; Dalterio, R.; Rajamani, R.; Meanwell, N. A. *J. Heterocyclic Chem.* **2009**, *46*, 432.



Allyl oxindole (+)-28:

A sample of alkanesulfinyl imine (+)-**27** (9.45 g, 24.4 mmol, 1 equiv) was azeotropically dried by concentration from benzene (3 × 80 mL). The flask was then charged with a stir bar, capped with a rubber septum, and placed under high vacuum (~0.1 Torr) for 14 h. A sample of magnesium bromide (8.98 g, 48.8 mmol, 2.00 equiv) and dichloromethane (160 mL) were added and the rubber septum was then replaced with an oven-dried pressure-equalizing addition funnel. The resulting dark orange suspension was cooled to –78 ºC and subsequently a solution of allylmagnesium bromide (1.28 M in diethyl ether, 19.8 mL, 25.3 mmol, 1.04 equiv) was added dropwise over 30 min. After stirring for an additional 45 min, the bright yellow suspension was diluted with a saturated aqueous ammonium chloride solution (160 mL) and deionized water (160 mL). The cold-bath was removed and the mixture was allowed to warm to 23 ºC with vigorous stirring. The layers were separated and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (300 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: 6→20% acetone in dichloromethane) to afford allyl oxindole (+)-**28** (7.76 g, 74.1%, >99:1 er) as a yellow solid. The enantiomeric ratio was determined by chiral HPLC analysis (CHIRALCEL® OD-H, 30% *i*-PrOH in hexanes, 0.7 mL/min, 220 nm, t_R (major) = 10.4 min, t_R (minor) = 6.6 min). Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	δ 7.22–7.15 (m, 2H, C5**H**, C6**H**), 6.82–6.75 (m, 1H, C7**H**), 5.23 (app-ddt, *J* = 17.1, 9.9, 7.3 Hz, 1H, C2**H**), 5.07 (app-dq, *J* = 17.0, 1.3 Hz, 1H, C1**H**$_a$), 4.91 (dd, *J* = 10.1, 1.8 Hz, 1H, C1**H**$_b$), 4.55 (s, 1H, N**H**), 3.21 (s, 3H, N8C**H**$_3$), 3.15 (dd, *J* = 12.9, 6.9 Hz, 1H, C3**H**$_a$), 2.81 (dd, *J* = 12.9, 7.7 Hz, 1H, C3**H**$_b$), 2.78–2.69 (m, 1H, C1'**H**$_a$), 2.69–2.58 (m, 1H, C1'**H**$_b$), 0.92–0.81 (m, 2H, C2'**H**), 0.02 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 174.5 (**C**8a), 145.1 (**C**7a), 131.1 (**C**6), 129.4 (**C**2), 127.28 (**C**4a), 127.25 (**C**5), 120.7 (**C**1), 119.9 (**C**4), 107.8 (**C**7), 66.6 (**C**3a), 53.3 (**C**1'), 39.9 (**C**3), 26.6 (N8**C**H$_3$), 8.6 (**C**2'), –1.7 (Si(C**H**$_3$)$_3$).
FTIR (thin film) cm^{-1}:	3249 (m), 2954 (m), 1716 (s), 1602 (s), 1583 (m), 1456 (m), 1343 (m), 1292 (m), 1074 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{17}H_{26}BrN_2O_2SSi$ $[M+H]^+$: 429.0662, found: 429.0675.
$[\alpha]_D^{23}$:	+15 (*c* = 0.29, CH_2Cl_2).
TLC (10% acetone in dichloromethane), R*f*:	0.27 (UV, CAM, $KMnO_4$).

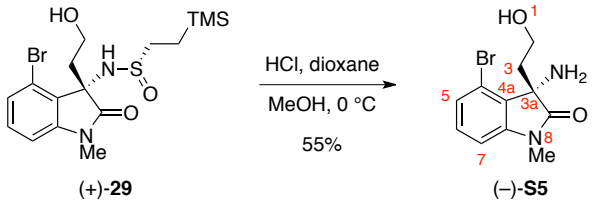


Alcohol (+)-29:

Ozone-enriched dioxygen was bubbled through a solution of allyl oxindole (+)-**28** (6.94 g, 16.2 mmol, 1 equiv) in methanol (81 mL) at –78 ºC. After 1.5 h, ozone bubbling was suspended and the solution was sparged with dinitrogen for 40 min. A sample of sodium borohydride[21] (2.12 g, 56.0 mmol, 3.46 equiv) was then added in 16 portions over 16 min. The cold bath was removed and the mixture was allowed to warm to 23 ºC. After 1 h, the solution was concentrated under reduced pressure and the resulting slurry was diluted with a saturated aqueous ammonium chloride solution (80 mL) and deionized water (80 mL). The mixture was extracted with ethyl acetate (3 × 100 mL) and the combined organic extracts were washed with a saturated aqueous sodium chloride solution (200 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 20%→40% acetone in dichloromethane) to afford alcohol (+)-**29** (5.94 g, 84.7%, >99:1 er) as an off-white foam. The enantiomeric ratio was determined by chiral HPLC analysis (CHIRALCEL® OD-H, 30% *i*-PrOH in hexanes, 0.7 mL/min, 220 nm, t_R (major) = 12.7 min, t_R (minor) = 7.7 min). Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	δ 7.23–7.17 (m, 2H, C5**H**, C6**H**), 6.86–6.79 (m, 1H, C7**H**), 4.76 (s, 1H, N**H**), 3.75–3.63 (m, 1H, C2**H**$_a$), 3.46 (app-dtd, J = 11.6, 7.8, 4.5 Hz, 1H, C2**H**$_b$), 3.22 (s, 3H, N8C**H**$_3$), 2.79–2.68 (m, 1H, C1'**H**$_a$), 2.68–2.56 (m, 2H, C1'**H**$_b$, C3**H**$_a$) 2.37 (dt, J = 14.2, 4.8 Hz, 1H, C3**H**$_b$), 2.18 (dd, J = 7.4, 4.2 Hz, 1H, O1**H**), 0.91–0.79 (m, 2H, C2'**H**$_2$), 0.02 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 175.7 (**C**8a), 145.0 (**C**7a), 131.3 (**C**6), 127.7 (**C**4a), 127.4 (**C**5), 119.9 (**C**4), 108.1 (**C**7), 65.4 (**C**3a), 58.2 (**C**2), 53.2 (**C**1'), 38.3 (**C**3), 26.9 (N8**C**H$_3$), 8.7 (**C**2'), –1.7 (Si(**C**H$_3$)$_3$).
FTIR (thin film) cm^{-1}:	3403 (br-m), 3242 (br-m), 2953 (m), 2893 (m), 1721 (s), 1605 (s), 1458 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{16}H_{26}BrN_2O_3SSi$ $[M+H]^+$: 433.0611, found: 433.0615.
$[\alpha]_D^{23}$:	+9 (c = 0.29, CH_2Cl_2).
TLC (30% acetone in dichloromethane), R*f*:	0.24 (UV, CAM).

21. (a) Sigma-Aldrich, cat# 452874 (granular, 10–40 mesh, 98%). (b) When powdered sodium borohydride (5 equiv, Sigma-Aldrich cat# 452882) was used, the intermediate aldehyde was often also observed, necessitating the addition of further reducing agent.



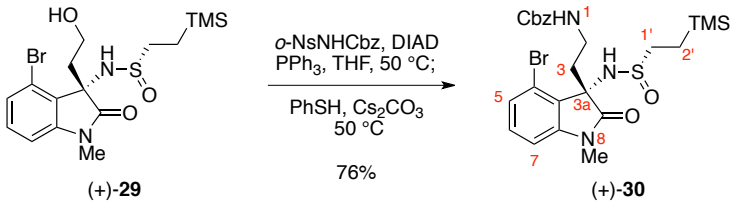
(+)-**29** (–)-**S5**

Amino alcohol (–)-S5:

A solution of hydrogen chloride in 1,4-dioxane (4.0 M, 58.0 µL, 232 µmol, 2.01 equiv) was added dropwise via syringe to a solution of alcohol (+)-**29** (50.0 mg, 115 µmol, 1 equiv) in methanol (2.30 mL) at 0 ºC. After 1 h, a saturated aqueous sodium bicarbonate solution (23 mL) and an aqueous sodium hydroxide solution (1 M, 1 mL) were added and the mixture was extracted with ethyl acetate (8 × 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: 3%→5% methanol in dichloromethane) to afford amino alcohol (–)-**S5** (18.1 mg, 55.1%) as a colorless film. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	δ 7.22–7.13 (m, 2H, C5**H**, C6**H**), 6.88–6.65 (m, 1H, C7**H**), 3.71 (app-dt, *J* = 11.6, 5.2 Hz, 1H, C2**H**$_a$), 3.50 (ddd, *J* = 11.6, 8.4, 4.4 Hz, 1H, C2**H**$_b$), 3.19 (s, 3H, N8C**H**$_3$), 2.46 (ddd, *J* = 14.2, 8.4, 4.7 Hz, 1H, C3**H**$_a$), 2.32 (ddd, *J* = 14.3, 5.7, 4.4 Hz, 1H, C3**H**$_b$), 2.04 (br-s, 3H, C2O**H**, C3aN**H**$_2$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 179.1 (**C**8a), 145.2 (**C**7a), 130.6 (**C**6), 129.9 (**C**4a), 127.2 (**C**5), 119.0 (**C**4), 107.7 (**C**7), 62.0 (**C**3a), 58.9 (**C**2), 39.2 (**C**3), 26.6 (N8**C**H$_3$).
FTIR (thin film) cm^{-1}:	3357 (br-m), 3284 (br-m), 2924 (w), 2883 (w), 1720 (s), 1605 (s), 1581 (m), 1456 (s), 1366 (m), 1288 (m), 1189 (w), 1101 (m), 1055 (m), 763 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{11}H_{14}BrN_2O_2$ $[M+H]^+$: 285.0233, found: 285.0222.
$[\alpha]_D^{23}$:	–10 (*c* = 0.91, CH_2Cl_2). [22]
TLC (3% methanol in dichloromethane), R*f*:	0.27 (UV, CAM).

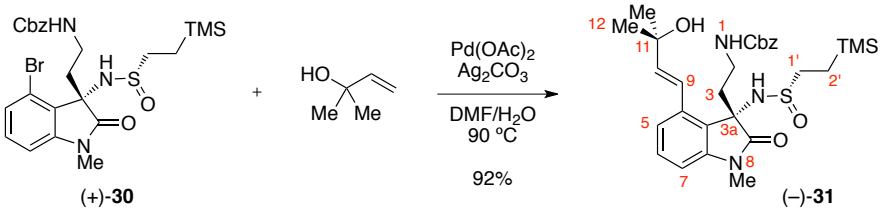
22. The same optical rotation was observed when (–)-**S5** was prepared from the (*S*$_s$)-*tert*-butanesulfinamide analogue (compound (+)-**44** in Lathrop, S. P.; Pompeo, M.; Chang, W.-T. T.; Movassaghi, M. *J. Am. Chem. Soc.* **2016**, *138*, 7763), which confirms the absolute stereochemical configuration of (*S*)-2-(trimethylsilyl)ethanesulfinamide (–)-**26**. A representative procedure is as follows: A solution of hydrogen chloride in 1,4-dioxane (4.0 M, 81.0 µL, 324 µmol, 1.99 equiv) was added dropwise via syringe to a solution of the (*S*$_s$)-*tert*-butane sulfinamide derivative (63.3 mg, 163 µmol, 1 equiv) in methanol (3.30 mL) at 23 ºC. After 3.2 h, a saturated aqueous sodium bicarbonate solution (15 mL) and deionized water (5 mL) were added and the mixture was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with a saturated sodium chloride solution (20 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 40%→50% acetone in dichloromethane) to afford amino alcohol (–)-**S5** (16.7 mg, 35.9%) as a colorless film. $[\alpha]_D^{23}$ = –10 (c = 0.83, CH_2Cl_2).



Carbamate (+)-30:

Diisopropyl azodicarboxylate (DIAD, 3.10 mL, 15.7 mmol, 1.15 equiv) was added dropwise via syringe to a solution of alcohol (+)-**29** (5.93 g, 13.7 mmol, 1 equiv), triphenylphosphine (4.13 g, 15.7 mmol, 1.15 equiv), and *N*-carbobenzoxy-2-nitrobenzenesulfonamide (5.29 g, 13.4 mmol, 1.15 equiv) in tetrahydrofuran (91 mL) at 23 ºC. The flask was fitted with a reflux condenser and was immersed in a preheated oil bath at 50 ºC. After stirring for 1 h, the mixture was cooled to 23 ºC and samples of cesium carbonate (17.8 g, 54.7 mmol, 4.00 equiv) and thiophenol (2.81 mL, 27.4 mmol, 2.00 equiv) were added. The flask was immersed in a preheated oil bath at 50 ºC and the mixture was stirred vigorously for 1.5 h. The bright yellow suspension was then cooled to 23 ºC, was diluted with deionized water (360 mL) and a saturated aqueous sodium chloride solution (90 mL), and was extracted with diethyl ether (3 × 230 mL). The combined organic extracts were washed successively with an aqueous sodium hydroxide solution (0.1 M, 350 mL) and a saturated aqueous sodium chloride solution (350 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 10%→20% isopropanol in hexanes) to afford carbamate (+)-**30** (5.90 g, 76.1%) as a white foam. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	δ 7.37–7.27 (m, 5H, Ar_{Cbz}**H**), 7.23–7.13 (m, 2H, C5**H**, C6**H**), 6.81–6.73 (m, 1H, C7**H**), 5.01 (d, *J* = 12.2 Hz, 1H, N1CO_2C**H**$_a$Ph), 4.96 (d, *J* =12.3 Hz, 1H, N1CO_2C**H**$_b$Ph), 4.77–4.63 (m, 1H, N1**H**), 4.63–4.47 (m, 1H, N**H**SOAlk) 3.16 (s, 3H, N8C**H**$_3$), 3.12–2.93 (m, 2H, C2**H**$_2$), 2.76–2.66 (m, 1H, C1'**H**$_a$), 2.66–2.57 (m, 1H, C1'**H**$_b$), 2.56–2.39 (m, 2H, C3**H**$_2$), 0.91–0.78 (m, 2H, C2'**H**$_2$), 0.02 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 174.6 (**C**8a), 155.9 (N1**C**O_2CH_2Ar), 144.9 (**C**7a), 136.5 (Ar_{Cbz}), 131.4 (**C**6), 128.6 (Ar_{Cbz}), 128.29 (Ar_{Cbz}), 128.26 (Ar_{Cbz}), 127.5 (**C**5), 127.2 (**C**4a), 120.0 (**C**4), 108.1 (**C**7), 66.7 (N1CO_2**C**H_2Ar), 65.4 (**C**3a), 53.3 (**C**1'), 36.1 (**C**2), 35.5 (**C**3), 26.8 (N8**C**H_3), 8.6 (**C**2'), –1.7 (Si(**C**H_3)$_3$).
FTIR (thin film) cm^{-1}:	3396 (s), 3246 (s), 3032 (m), 2952 (s), 2890 (s), 1724 (br-s), 1604 (s), 1520 (s), 1457 (s), 1251 (s).
HRMS (DART) (*m/z*):	calc'd for $C_{24}H_{33}BrN_3O_4SSi$ $[M+H]^+$: 566.1139, found: 566.1148.
$[\alpha]_D^{23}$:	+25 (*c* = 0.33, CH_2Cl_2).
TLC (15% isopropanol in hexanes), R*f*:	0.19 (UV, CAM).



Allylic alcohol (–)-31:

A pressure vessel was charged sequentially with carbamate (+)-**30** (5.89 g, 10.4 mmol, 1 equiv), silver(I) carbonate (5.73 g, 20.8 mmol, 2.00 equiv), palladium(II) acetate (350 mg, 1.56 mmol, 0.150 equiv), 1,1-dimethylallyl alcohol (21.7 mL, 208 mmol, 20.0 equiv), *N,N*-dimethylformamide (52 mL), and deionized water (52 mL). The resulting suspension was then degassed by vigorously sparging with argon for 15 min. The vessel was sealed with a Teflon screwcap and was immersed in a preheated oil bath at 90 ºC. After vigorous stirring for 2 h, the black suspension was cooled to 23 ºC and was diluted with diethyl ether (100 mL). The mixture was filtered through a pad of Celite and the filter cake was washed with diethyl ether (400 mL). The filtrate was washed with a saturated aqueous sodium chloride solution (450 mL) and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 180 mL) and the combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 250 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 30→80% acetonitrile in dichloromethane) to afford allylic alcohol (–)-**31** (5.43 g, 91.5%) as a pale-yellow foam. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 7.37–7.27 (m, 6H, C6**H**, Ar_{Cbz}**H**), 7.23 (d, *J* = 8.0 Hz, 1H, C5**H**), 7.12 (d, *J* = 15.9 Hz, 1H, C9**H**), 6.71 (d, *J* = 7.7 Hz, 1H, C7**H**), 6.36 (d, *J* = 15.9 Hz, 1H, C10**H**), 5.00 (d, *J* = 12.2 Hz, 1H, N1CO_2C**H**$_a$Ar), 4.97 (d, *J* = 12.2 Hz, 1H, N1CO_2C**H**$_b$Ar), 4.64 (br-t, *J* = 5.8 Hz, 1H, N1**H**), 4.35 (s, 1H, N**H**SOAlk), 3.35 (s, 1H, O**H**), 3.17 (s, 3H, N8C**H**$_3$), 2.98–2.86 (m, 1H, C2**H**$_a$), 2.78–2.69 (m, 1H, C2**H**$_b$), 2.68–2.54 (m, 3H, C3**H**$_a$, C1'**H**$_2$), 2.42–2.32 (m, 1H, C3**H**$_b$), 1.44 (s, 3H, C12**H**$_3$), 1.41 (s, 3H, C12**H**$_3$), 0.86–0.73 (m, 2H, C2'**H**$_2$), 0.00 (s, 9H, Si(C**H**$_3$)$_3$).

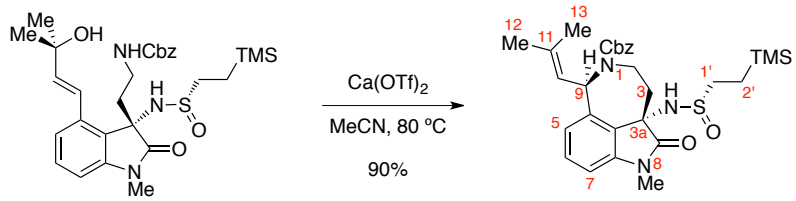
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C): δ 176.4 (**C**8a), 156.1 (N1**C**O_2CH_2Ar), 143.7 (**C**7a), 142.4 (**C**10), 136.6 (**C**4), 136.4 (Ar_{Cbz}), 130.4 (**C**6), 128.6 (Ar_{Cbz}), 128.23 (Ar_{Cbz}), 128.21 (Ar_{Cbz}), 123.5 (**C**4a), 122.3 (**C**9), 120.8 (**C**5), 107.5 (**C**7), 70.9 (**C**11), 66.7 (N1CO_2**C**H_2Ar), 63.9 (**C**3a), 53.0 (**C**1'), 36.9 (**C**3), 36.4 (**C**2), 29.7 (**C**12), 29.6 (**C**12), 26.7 (N8**C**H_3), 9.3 (**C**2'), –1.8 (Si(**C**H_3)$_3$).

FTIR (thin film) cm^{-1}: 3319 (br-m), 3066 (w), 2969 (m), 1714 (br-s), 1590 (m), 1532 (br-m), 1465 (m), 1368 (m), 1251(s).

HRMS (ESI) (*m/z*): calc'd for $C_{29}H_{41}N_3NaO_5SSi$ [M+Na]$^+$: 594.2428, found: 594.2422.

$[\alpha]_D^{23}$: –53 (*c* = 0.6, CH_2Cl_2).

TLC (50% acetonitrile in dichloromethane), R*f*: 0.33 (UV, CAM).



(–)-**31** (–)-**32**

Tricyclic oxindole (–)-32:

A sample of calcium trifluoromethanesulfonate (3.10 g, 9.18 mmol, 1.15 equiv) was added to a solution of allylic alcohol (–)-**31** (4.56 g, 7.98 mmol, 1 equiv) in acetonitrile (160 mL) at 23 ºC. The reaction flask was fitted with a reflux condenser and was immersed in a preheated oil bath at 80 ºC. After stirring for 36 h, the homogeneous yellow solution was cooled to 23 ºC and was concentrated under reduced pressure. The residue was diluted with a saturated aqueous sodium bicarbonate solution (160 mL) and deionized water (40 mL) and the mixture was extracted with ethyl acetate (3 × 100 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (200 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: 18→30% acetonitrile in dichloromethane) to afford tricyclic oxindole (–)-**32** (3.97 g, 89.9%) as a white foam. As a result of slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments collected at elevated temperature.

^{1}H NMR (400 MHz, DMSO-d_6, 100 °C):[23] δ 7.40–7.17 (m, 6H, Ar_{Cbz}**H**$_5$, C$_6$**H**), 6.88 (app-d, J = 7.8 Hz, 2H, C5**H**, C7**H**), 6.19 (br-s, 1H, N**H**), 5.88 (br-d, J = 8.6 Hz, 1H, C9**H**), 5.77 (br-s, 1H, C10**H**), 5.02 (d, J = 12.6 Hz, 1H, N1CO$_2$C**H**$_a$Ph), 4.98 (d, J = 12.6 Hz, 1H, N1CO$_2$C**H**$_b$Ph), 3.88 (ddd, J = 14.6, 7.7, 3.9 Hz, 1H, C2**H**$_a$), 3.68 (br-s, 1H, C2**H**$_b$), 3.12 (s, 3H, N8C**H**$_3$), 2.71–2.59 (m, 1H, C1'**H**$_a$), 2.59–2.50 (m, 1H, C1'**H**$_b$), 2.33–2.18 (m, 1H, C3**H**$_a$), 1.80 (s, 3H, C12/13**H**$_3$), 1.68 (s, 3H, C12/13**H**$_3$), 1.59 (ddd, J = 14.5, 7.6, 4.8 Hz, 1H, C3**H**$_b$), 0.77–0.65 (m, 2H, C2'**H**$_2$), 0.00 (s, 9H, Si(C**H**$_3$)$_3$).

^{13}C NMR (100.6 MHz, DMSO-d_6, 90 °C):[23] δ 175.7 (**C**8a), 154.2 (N1**C**O$_2$CH$_2$Ph), 143.2 (**C**7a), 136.3 (2C, **C**4, Ar_{Cbz}), 134.2 (**C**11), 128.6 (**C**6), 127.5 (Ar_{Cbz}), 127.0 (Ar_{Cbz}), 126.9 (Ar_{Cbz}), 124.9 (**C**4a), 121.2 (**C**10), 119.9 (**C**$_5$), 106.8 (**C**$_7$), 65.6 (N$_1$CO$_2$**C**H$_2$Ph), 61.8 (**C**$_{3a}$), 57.1 (**C**9), 50.9 (**C**1'), 39.8 (**C**2), 31.4 (**C**3), 25.5 (N8**C**H$_3$), 24.7 (**C**12/13), 17.5 (**C**12/13), 8.5 (**C**2'), –2.5 (Si(**C**H$_3$)$_3$).

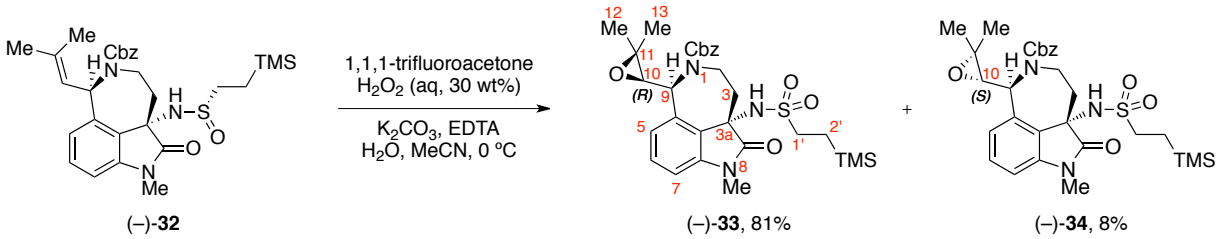
FTIR (thin film) cm^{-1}: 3229 (br-w), 2953 (m), 1706 (s), 1610 (m), 1599 (m), 1468 (m), 1418 (m), 1251 (m), 1050 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{29}H_{40}N_3O_4SSi$ $[M+H]^+$: 554.2503, found: 554.2497.

23. Acquisition of NMR spectra in DMSO-d_6 at 90 °C resulted in simplification of the spectra by convergence of the signals derived from various conformational isomers. However, we observed gradual sample decomposition during extended acquisition time.

$[\alpha]_D^{23}$: –64 (*c* = 0.22, CH_2Cl_2).

TLC (20% acetonitrile in dichloromethane), R*f*: 0.23 (UV, CAM).



(10*R*)-Tricyclic epoxide (–)-33:[24]

An aqueous potassium carbonate[25] solution (1.50 M in 4.00×10^{-4} M aqueous EDTA,[26] 4.50 mL) and an aqueous hydrogen peroxide solution[27] (30 wt%, 3.40 mL, 30.0 mmol, 10.0 equiv) were added successively to a solution of tricyclic oxindole (–)-**32** (1.66 g, 3.00 mmol, 1 equiv) and 1,1,1-trifluoroacetone (282 µL, 3.00 mmol, 1.00 equiv) in acetonitrile (4.50 mL) at 0 ºC. After vigorous stirring at 0 ºC for 7 h, an aqueous sodium thiosulfate solution (1 M, 90 mL) was added and the mixture was allowed to warm to 23 ºC. The resulting suspension was extracted with ethyl acetate (3 × 90 mL) and the combined organic extracts were washed with a saturated aqueous sodium chloride solution (180 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: 38%→45% ethyl acetate in hexanes) to afford (10*R*)-tricyclic epoxide (–)-**33** (1.43 g, 81.1%) as a white foam and the C10-epimer (–)-**34** (140 mg, 7.95%) as a light yellow film. As a result of slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments collected at elevated temperature.

(10*R*)-Tricyclic epoxide (–)-33:

^{1}H NMR (400 MHz, DMSO-d_6, 130 °C):[28] δ 7.37–7.22 (m, 6H, C6**H**, Ar_{Cbz}**H**), 7.02 (br-s, 1H, N**H**), 6.93–6.85 (m, 2H, C5**H**, C7**H**), 5.09 (d, J = 12.5 Hz, 1H, N1CO_2C**H**$_a$Ph), 5.02 (d, J = 12.5 Hz, 1H, N1CO_2C**H**$_b$Ph), 4.96 (br-d, J = 8.3 Hz, 1H, C9**H**), 3.91 (ddd, J = 14.9, 7.6, 4.3 Hz, 1H, C2**H**$_a$), 3.85–3.67 (br-m, 1H, C2**H**$_b$), 3.64–3.50 (br-m, 1H, C10**H**), 3.13 (s, 3H, N8C**H**$_3$), 2.88–2.78 (m, 1H, C1'**H**$_a$), 2.68–2.56 (m, 1H, C1'**H**$_b$), 2.34 (app-dt, J = 14.3, 4.9 Hz, 1H, C3**H**$_a$), 1.62 (ddd, J = 14.6, 7.5, 5.3 Hz, 1H, C3**H**$_b$), 1.41 (s, 3H, C12/13**H**$_3$), 1.35 (s, 3H, C12/13**H**$_3$), 0.90–0.77 (m, 2H, C2'**H**), –0.02 (s, 9H, Si(C**H**$_3$)$_3$).

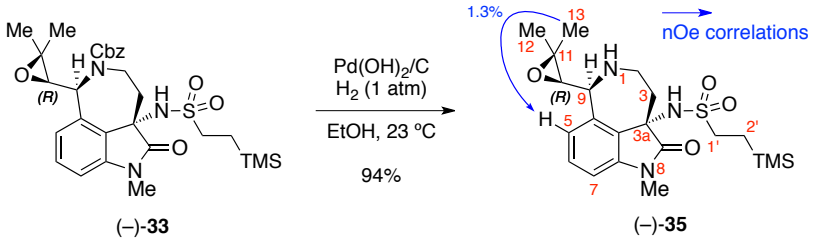
^{13}C NMR (100.6 MHz, DMSO-d_6, 130 °C): δ 174.5 (**C**8a), 154.5 (N1**C**O_2CH_2Ph), 143.3 (**C**7a), 136.6 (**C**4), 136.0 (Ar_{Cbz}), 128.6 (**C**6), 127.4 (Ar_{Cbz}), 126.8 (Ar_{Cbz}), 126.7 (Ar_{Cbz}), 124.9 (**C**4a), 118.8 (**C**5), 107.1 (**C**7), 65.9 (N1CO_2**C**H_2Ph), 61.2 (2C: **C**10, **C**3a),

24. All glassware used for the epoxidation reaction was carefully washed to remove trace metals, which may catalyze the decomposition of H_2O_2. Round-bottom flasks, Erlenmeyer flasks, and graduated cylinders used to prepare any component of the reaction mixture were washed successively with concentrated aqueous nitric acid, a saturated aqueous Na_4EDTA solution, and acetone (three times each), rinsing with deionized water between each component.
25. Sigma-Aldrich, cat# 367877, 99.995% trace metal basis.
26. Sigma-Aldrich, cat# 431788, 99.995% trace metal basis.
27. Sigma-Aldrich, cat# 216763, 30 wt% in H_2O with inhibitor (ACS reagent grade).
28. Acquisition of NMR spectra in DMSO-d_6 at 130 °C resulted in simplification of the spectra by convergence of the signals derived from various conformational isomers. However, we observed gradual sample decomposition with heating during extended acquisition time.

	59.1 (**C**9), 58.1 (**C**11), 49.1 (**C**1'), 43.8 (br-s, **C**2), 32.0 (**C**3), 25.5 (N8**C**H_3), 23.6 (**C**12/13), 18.0 (**C**12/13), 8.9 (**C**2'), –2.9 (Si(**C**H_3)$_3$).
FTIR (thin film) cm^{-1}:	3218 (br-m), 2957 (m), 2899 (m), 1717 (s), 1702 (s), 1601 (m), 1467 (s), 1420 (s), 1368 (m), 1327 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{29}H_{39}N_3NaO_6SSi$ $[M+Na]^+$: 608.2221, found: 608.2217.
$[\alpha]_D^{23}$:	–87 (*c* = 0.22, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.32 (UV, CAM).

(10*S*)-Tricyclic epoxide (–)-34:

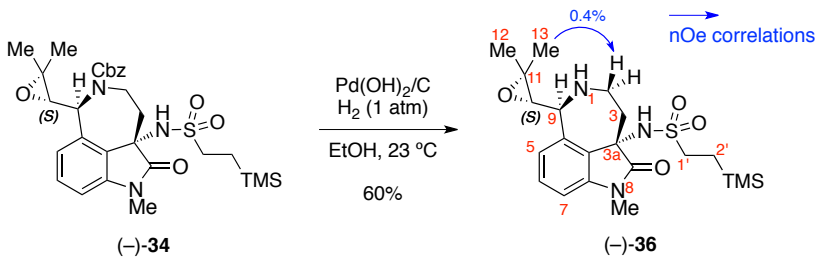
^{1}H NMR (400 MHz, CD_3CN, 70 °C):	δ 7.44–7.15 (m, 7H), 6.97–6.83 (m, 1H), 5.75 (br-s, 1H), 5.08 (d, *J* = 12.2 Hz, 1H), 5.00 (d, *J* = 12.6 Hz, 1H), 4.75 (br-s, 1H), 4.02 (br-s, 1H), 3.84 (ddd, *J* = 14.4, 9.4, 2.8 Hz, 2H), 3.15 (s, 3H), 2.77 (td, *J* = 13.5, 4.7 Hz, 1H), 2.45 (td, *J* = 13.6, 4.2 Hz, 1H), 2.18 (br-d, *J* = 14.2 Hz, 1H), 1.68 (ddd, *J* = 14.5, 9.8, 4.9 Hz, 1H), 1.45 (s, 3H), 1.33 (s, 3H), 0.85 (td, *J* = 13.6, 4.6 Hz, 1H), 0.74 (td, *J* = 13.7, 4.2 Hz, 1H), –0.03 (s, 9H).
^{13}C NMR (100.6 MHz, CD_3CN, 70 °C):	δ 177.5, 156.9, 146.3, 140.6, 138.4, 131.2, 129.9, 129.4 (2C), 126.3, 121.3, 109.6, 68.5, 63.9, 63.0 (br), 61.5, 60.1, 52.5, 48.1 (br), 34.3, 27.7, 25.5, 20.4, 11.0, –1.5.
FTIR (thin film) cm^{-1}:	3208 (br-w), 2956 (w), 2900 (w), 1709 (s), 1606 (m), 1474 (m), 1416 (m), 1367 (m), 1323 (s), 1251 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{29}H_{40}N_3O_6SSi$ $[M+H]^+$: 586.2402, found: 586.2403.
$[\alpha]_D^{23}$:	–70 (*c* = 0.83, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.44 (UV, CAM).



(10*R*)-Tetracyclic amine (–)-35:

A sample of palladium(II) hydroxide on carbon (15.7 wt% on wet support, 12.0 mg, 13.4 μmol, 0.0785 equiv) was added to a solution of (10*R*)-tricyclic epoxide (–)-**33** (100 mg, 171 μmol, 1 equiv) in anhydrous ethanol (200 proof, 3.40 mL) at 23 ºC. The resulting suspension was sparged with dihydrogen for 5 min by discharge of a balloon equipped with a needle extending into the reaction mixture. After stirring for 2 h under an atmosphere of dihydrogen, the suspension was sparged with dinitrogen for 5 min and was diluted with ethyl acetate (7 mL). The mixture was then filtered through a plug of Celite and the filter cake was washed with ethyl acetate (15 mL). The colorless filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: 40→50% acetone in dichloromethane) to afford (10*R*)-tetracyclic amine (–)-**35** (72.4 mg, 93.9%) as a white foam. As a result of slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments also collected at elevated temperature.

^{1}H NMR (400 MHz, C_6D_6, 70 °C):	δ 7.07 (t, *J* = 7.9 Hz, 1H, C6**H**), 6.68 (d, *J* = 7.9 Hz, 1H, C5**H**), 6.41 (d, *J* = 7.8 Hz, 1H, C7**H**), 4.22 (d, *J* = 8.7 Hz, 1H, C9**H**), 3.06–2.95 (m, 3H, C2**H**$_a$, C1'**H**$_2$), 2.92 (s, 3H, N8C**H**$_3$), 2.87 (d, *J* = 8.8 Hz, 1H, C10**H**), 2.83 (app-dt, *J* = 14.3, 6.0 Hz, 1H, C2**H**$_b$), 2.14 (app-dt, *J* = 14.1, 6.2 Hz, 1H, C3**H**$_a$), 1.36 (app-dt, *J* = 14.1, 5.9 Hz, 1H, C3**H**$_b$), 1.25 (s, 3H, C12/13**H**$_3$), 1.24 (s, 3H, C12/13**H**$_3$), 1.17–1.10 (m, 2H, C2'**H**$_2$), –0.09 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (100.6 MHz, C_6D_6, 70 °C):	δ 175.3 (**C**8a), 144.3 (**C**7a), 138.7 (**C**4), 129.6 (**C**6), 128.8 (**C**4a), 119.5 (**C**5), 107.4 (**C**7), 65.4 (**C**10), 63.2 (**C**3a), 60.2 (**C**11), 59.5 (**C**9), 52.1 (**C**1'), 42.3 (**C**2), 36.2 (**C**3), 26.4 (N8**C**H$_3$), 24.9 (**C**12/13), 19.4 (**C**12/13), 10.9 (**C**2'), –2.0 (Si(**C**H$_3$)$_3$).
FTIR (thin film) cm^{-1}:	3228 (br-w), 2955 (m), 1721 (s), 1606 (m), 1470 (m), 1327 (s), 1251 (m), 1148 (m).
HRMS (DART) (*m/z*):	calc'd for $C_{21}H_{34}N_3O_4SSi$ $[M+H]^+$: 452.2034, found: 452.2036.
$[\alpha]_D^{23}$:	–66 (*c* = 0.49, CH_2Cl_2).
TLC (50% acetone in dichloromethane), R*f*:	0.35 (UV, CAM).



(–)-**34** (–)-**36**

(10*S*)-Tetracyclic amine (–)-36:

A sample of palladium(II) hydroxide on carbon (15.7 wt% on wet support, 3.2 mg, 3.6 μmol, 0.080 equiv) was added to a solution of (10*S*)-tricyclic epoxide (–)-**34** (26.6 mg, 45.4 μmol, 1 equiv) in anhydrous ethanol (200 proof, 900 μL) at 23 ºC. The resulting suspension was sparged with dihydrogen for 5 min by discharge of a balloon equipped with a needle extending into the reaction mixture. After stirring for 2 h under an atmosphere of dihydrogen, the suspension was sparged with dinitrogen for 5 min and was diluted with ethyl acetate (3 mL). The mixture was then filtered through a plug of Celite and the filter cake was washed with ethyl acetate (10 mL). The colorless filtrate was concentrated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (eluent: 50% acetone in dichloromethane) to afford (10*S*)-tetracyclic amine (–)-**36** (12.3 mg, 60.1%) as a colorless film. Crystals suitable for X-ray diffraction were obtained by layer diffusion of *n*-heptane into a solution of (–)-**36** in dichloromethane at 0 ºC. The thermal ellipsoid representation of (–)-**36** is depicted later in this document. As a result of slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments also collected at elevated temperature.

^{1}H NMR (400 MHz, C_6D_6, 60 °C): δ 7.28 (app-dt, *J* = 7.9, 0.9 Hz, 1H, C5**H**), 7.08 (t, *J* = 7.9 Hz, 1H, C6**H**), 6.38 (d, *J* = 7.8 Hz, 1H, C7**H**), 6.28 (br-s, 1H, N**H**SO_2), 4.18 (d, *J* = 9.2 Hz, 1H, C9**H**), 3.52 (ddd, *J* = 14.5, 11.6, 2.7 Hz, 1H, C2**H**$_a$), 3.02 (ddd, *J* = 14.9, 4.2, 3.3 Hz, 1H, C2**H**$_b$), 2.95 (app-td, *J* = 13.3, 4.8 Hz, 1H, C1'**H**$_a$), 2.92 (s, 3H, N8C**H**$_3$), 2.84 (d, *J* = 9.2 Hz, 1H, C10**H**), 2.60 (app-td, *J* = 13.4, 4.0 Hz, 1H, C1'**H**$_b$), 2.21 (app-dt, *J* = 14.3, 2.9 Hz, 1H, C3**H**$_a$), 1.34 (s, 3H, C13**H**$_3$), 1.23 (s, 3H, C12**H**$_3$), 1.17 (ddd, *J* = 14.4, 11.7, 4.2 Hz, 1H, C3**H**$_b$), 1.01 (app-td, *J* = 13.8, 4.7 Hz, 1H, C2'**H**$_a$), 0.92 (app-td, *J* = 13.7, 4.0 Hz, 1H, C2'**H**$_b$), –0.12 (s, 9H, Si(C**H**$_3$)$_3$).

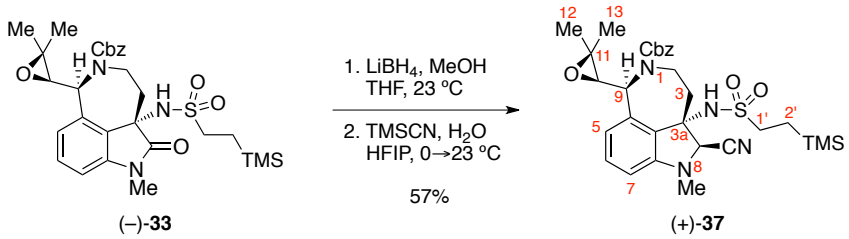
^{13}C NMR (100.6 MHz, C_6D_6, 60 °C): δ 177.2 (**C**8a), 145.1 (**C**7a), 144.0 (**C**4), 129.9 (**C**6), 126.6 (**C**4a), 119.0 (**C**5), 107.6 (**C**7), 64.5 (**C**10), 63.3 (**C**3a), 58.5 (2C, **C**11, **C**9), 51.7 (**C**1'), 46.8 (**C**2), 35.7 (**C**3), 26.7 (N8**C**H$_3$), 25.1 (**C**12), 19.4 (**C**13), 10.1 (**C**2'), –2.1 (Si(**C**H$_3$)$_3$).

FTIR (thin film) cm^{-1}: 3209 (br-m), 2954 (m), 1714 (s), 1605 (s), 1471 (m), 1422 (m), 1367 (m), 1327 (s), 1252 (m), 1151 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{21}H_{34}N_3O_4SSi$ $[M+H]^+$: 452.2034,
found: 452.2032.

$[\alpha]_D^{24}$: –67 (*c* = 0.62, CH_2Cl_2).

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



Aminonitrile (+)-37:

A solution of lithium borohydride (2.0 M in tetrahydrofuran, 3.8 mL, 7.6 mmol, 15 equiv) was added dropwise via syringe over 2 min to a solution of oxindole (–)-**33** (293 mg, 0.500 mmol, 1 equiv) in tetrahydrofuran (6.70 mL) at 23 ºC. Methanol (1.21 mL, 30.0 mmol, 60.0 equiv) was then added dropwise over 3 h by syringe pump and the resulting white suspension was allowed to stir vigorously at 23 ºC. After 17 h, the mixture was cooled to 0 ºC and was diluted with a saturated aqueous ammonium chloride solution (50 mL) and water (20 mL). After vigorous stirring at 23 ºC for 10 min, the mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (60 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to provide the crude hemiaminal as a white foam, which was used directly in the next step without further purification.

CAUTION! Trimethylsilyl cyanide is very toxic and should only be used with great caution.[29]

Trimethylsilyl cyanide (375 µL, 3.00 mmol, 6.00 equiv) was added dropwise over 2 min to a solution of the crude hemiaminal and water (81.0 µL, 4.50 mmol, 9.00 equiv) in hexafluoroisopropanol (HFIP, 3.30 mL) at 0 ºC. After 10 min, the reaction flask was sealed under an argon atmosphere with a Teflon-lined glass stopper and the ice bath was removed. After 20 h, the solution was cooled to 0 ºC and was diluted with an aqueous sodium hydroxide solution (0.5 M, 20 mL). After warming to 23 ºC, the mixture was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (40 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 20→24% ethyl acetate in hexanes) to afford aminonitrile (+)-**37** (171 mg, 57.3%) as a white foam. As a result of slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

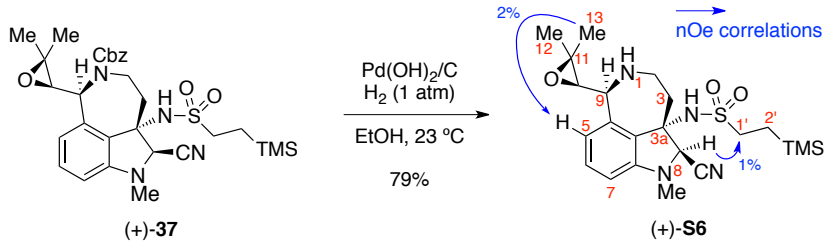
^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 7.58–7.06 (m, 6H), 6.71 (br-d, J = 7.0 Hz, 1H), 6.68 (d, J = 7.9 Hz, 1H), 5.40–4.82 (m, 5H), 4.16 (app br-s, 1H), 3.94–3.77 (m, 1H), 3.40 (app br-s, 1H), 3.07–2.97 (m, 1H), 2.95 (s, 3H), 2.90 (ddd, J = 14.0, 10.4, 7.5 Hz, 1H), 2.86–2.78 (m, 1H), 2.58 (ddd, J = 15.0, 9.9, 5.8 Hz, 1H), 1.41 (s, 3H), 1.37 (s, 3H), 1.01–0.90 (m, 2H), 0.05 (s, 9H).

^{1}H NMR (125.8 MHz, CD_3CN, 70 °C): δ 157.3, 153.1, 139.8, 138.4, 132.5, 129.8, 129.2, 129.0, 127.7, 119.2, 117.0, 109.7, 68.6 (2C), 68.5, 64.3, 61.2, 61.0, 53.1, 44.6, 35.8, 34.0, 25.1, 20.2, 11.4, –1.5.

FTIR (thin film) cm^{-1}: 3248 (br-w), 2956 (w), 1694 (m), 1596 (m), 1453 (m), 1419 (s), 1324 (s), 1250 (s), 1143 (s), 1119 (s), 991 (m), 840 (s), 744 (s), 697 (s), 540 (m).

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

HRMS (DART) (*m/z*):	calc'd for $C_{30}H_{41}N_4O_5SSi$ $[M+H]^+$: 597.2561, found: 597.2560.
$[\alpha]_D^{24}$:	+60 (*c* = 0.98, CH_2Cl_2).
TLC (22% ethyl acetate in hexanes), R*f*:	0.17 (UV, CAM).



(+)-**37** (+)-**S6**

Azepane (+)-S6:

A sample of palladium(II) hydroxide on carbon (15.7 wt% on wet support, 2.0 mg, 1.7 μmol, 0.10 equiv) was added to a solution of aminonitrile (+)-**37** (10 mg, 16.8 μmol, 1 equiv) in anhydrous ethanol (200 proof, 0.84 mL) at 23 ºC. The resulting black suspension was sparged with dihydrogen for 5 min by discharge of a balloon equipped with a needle extending into the reaction mixture. After stirring for 2 h under an atmosphere of dihydrogen, the suspension was sparged with argon for 5 min and was diluted with ethyl acetate (5 mL). The mixture was then filtered through a plug of Celite and the filter cake was washed with ethyl acetate (15 mL). The colorless filtrate was concentrated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (eluent: 40→45% ethyl acetate in hexanes) to afford azepane (+)-**S6** (6.2 mg, 79.4%) as a colorless oil. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 7.20 (t, *J* = 7.8 Hz, 1H, C6**H**), 6.53 (d, *J* = 7.8 Hz, 1H, C7**H**), 6.50 (app-dt, *J* = 7.7, 0.7 Hz, 1H, C5**H**), 5.33 (s, 3H, C8a**H**), 3.86 (d, *J* = 9.9 Hz, 1H, C_9**H**), 3.60 (ddd, *J* = 13.3, 7.4, 2.2 Hz, 1H, C2$\mathbf{H}_a$), 3.39 (ddd, *J* = 13.3, 10.5, 7.1 Hz, 1H, C2$\mathbf{H}_b$), 3.02 (d, *J* = 9.4 Hz, 1H, C10**H**), 2.92 (s, 3H, N8C$\mathbf{H}_3$), 2.91–2.83 (m, 2H, C1'$\mathbf{H}_2$), 2.75 (ddd, *J* = 14.3, 7.1, 2.1 Hz, 1H, C3$\mathbf{H}_a$), 2.48 (ddd, *J* = 14.2, 10.5, 7.3 Hz, 1H, C3$\mathbf{H}_b$), 1.49 (s, 3H, C13$\mathbf{H}_3$), 1.41 (s, 3H, C12$\mathbf{H}_3$), 1.07–0.96 (m, 1H, C2'$\mathbf{H}_a$), 0.92–0.79 (m, 1H, C2'$\mathbf{H}_b$), –0.02 (s, 9H, Si(C$\mathbf{H}_3$)$_3$)

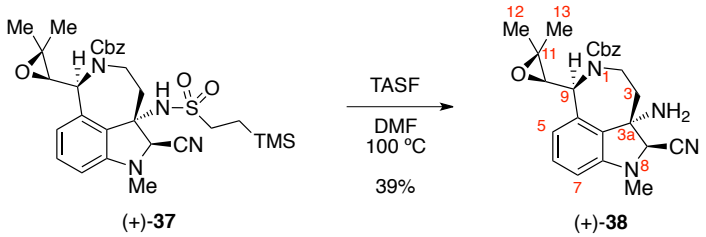
^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ 150.8 (**C**7a), 139.2 (**C**4), 130.7 (**C**6), 129.5 (**C**4a), 117.9 (**C**5), 115.5 (**C**N), 107.9 (**C**7), 67.2 (**C**3a), 64.9 (**C**10), 64.7 (**C**8a), 60.6 (**C**11), 59.4 (**C**9), 52.2 (**C**1'), 40.8 (**C**2), 36.4 (**C**3), 33.1 (N8**C**H_3), 25.0 (**C**12), 20.0 (**C**13), 10.5 (**C**2'), –1.9 (Si(**C**H_3)$_3$).

FTIR (thin film) cm^{-1}: 3248 (br-w), 2955 (m), 1595 (m), 1451 (m), 1329 (s), 1251 (s), 1143 (s), 968 (w), 905 (m), 843 (s).

HRMS (ESI) (*m/z*): calc'd for $C_{22}H_{35}N_4O_3SSi$ $[M+H]^+$: 463.2194, found: 463.2195.

$[\alpha]_D^{24}$: +141 (*c* = 0.31, CH_2Cl_2).

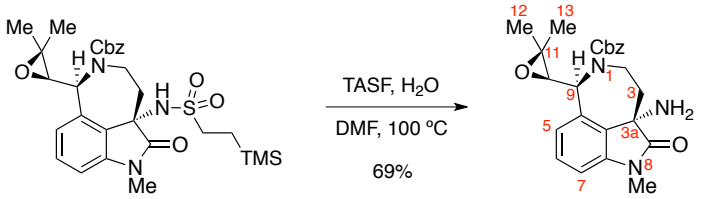
TLC (40% ethyl acetate in hexanes), R*f*: 0.15 (UV, CAM).



Benzylic aminonitrile (+)-38:

A sample of aminonitrile (+)-**37** (45.0 mg, 75.4 μmol, 1 equiv) contained in a 5-mL Schlenk flask (Kjeldahl shape) was azeotropically dried by concentration from anhydrous benzene (3 × 1 mL). After drying under high vacuum for 2.5 h, the flask was refilled with argon and was charged with a sample of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 83.1 mg, 302 μmol, 4.00 equiv). The mixture was dissolved in *N*,*N*-dimethylformamide (1.00 mL) and the resulting homogeneous solution was stirred at 23 ºC for 10 min. The flask was then sealed and was immersed in a preheated oil bath at 100 ºC. After stirring at this temperature for 9 h, the light-brown solution was cooled to 23 ºC and was diluted with a saturated aqueous sodium chloride solution (20 mL) and water (5 mL) and the yellow suspension was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 20 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 50→65% ethyl acetate in hexanes) to afford benzylic aminonitrile (+)-**38** (12.8 mg, 39.2%) as a pale-yellow film. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments also collected at elevated temperature.

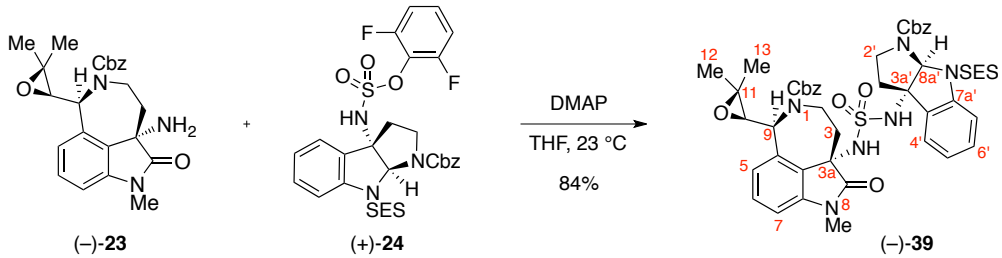
^{1}H NMR (400 MHz, CD_3CN, 70 °C):	δ 7.40–7.22 (br-m, 5H, Ar_{Cbz}**H**), 7.20 (t, *J* = 7.8 Hz, 1H, C6**H**), 6.67 (d, *J* = 7.3 Hz, 1H, C5**H**), 6.60 (d, *J* = 7.9 Hz, 1H, C7**H**), 5.10 (d, *J* = 12.6 Hz, 1H, N1CO_2C**H**$_a$Ph), 5.08 (d, *J* = 12.6 Hz, 1H, N1CO_2C**H**$_b$Ph), 4.94 (d, *J* = 8.8 Hz, 1H, C9**H**), 4.29 (s, 1H, C8a**H**), 4.06 (ddd, *J* = 14.8, 10.5, 4.6 Hz, 1H, C2**H**$_a$), 3.92–3.81 (m, 1H, C2**H**$_b$), 3.60–3.40 (br-m, 1H, C10**H**), 2.91 (s, 3H, N8C**H**$_3$), 2.47 (ddd, *J* = 14.1, 10.3, 5.6 Hz, 1H, C3**H**$_a$), 2.21 (ddd, *J* = 14.1, 4.8, 3.7 Hz, 1H, C3**H**$_b$), 1.37 (s, 3H, C12/13**H**$_3$), 1.33 (s, 3H, C12/13**H**$_3$).
^{13}C NMR (100.6 MHz, CD_3CN, 70 °C):	δ 157.4 (N1**C**O_2CH_2Ph), 151.8 (**C**7a), 139.0 (**C**4), 138.7 (Ar_{Cbz}), 132.2 (**C**4a), 131.1 (**C**6), 129.8 (Ar_{Cbz}), 129.2 (Ar_{Cbz}), 129.0 (Ar_{Cbz}), 118.8 (**C**5), 117.6 (**C**N), 109.2 (**C**7), 72.9 (**C**8a), 68.3 (N1CO_2**C**H_2Ph), 65.2 (**C**3a), 64.0 (**C**10), 61.7 (**C**9), 60.7 (**C**11), 45.4 (**C**2), 36.9 (**C**3), 34.1 (N8**C**H_3), 25.2 (**C**12/13), 19.9 (**C**12/13).
FTIR (thin film) cm^{-1}:	3371 (br-w), 3309 (br-w), 2960 (w), 1698 (s), 1597 (m), 1465 (m), 1419 (m), 1329 (m), 1259 (m), 747 (m).
HRMS (DART) (*m/z*):	calc'd for $C_{25}H_{29}N_4O_3$ $[M+H]^+$: 433.2234, found: 433.2239.
$[\alpha]_D^{23}$:	+65 (*c* = 0.55, CH_2Cl_2).
TLC (60% ethyl acetate in hexanes), R*f*:	0.13 (UV, CAM).



Benzylic amine (–)-23:

A sample of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 3.99 g, 14.5 mmol, 3.20 equiv) was added as a solid to a pressure flask containing a solution of tricyclic epoxide (–)-**33** (2.65 g, 4.52 mmol, 1 equiv) and deionized water (82.0 µL, 4.52 mmol, 1.00 equiv) in *N*,*N*-dimethylformamide (30.0 mL) at 23 ºC. The reaction vessel was sealed with a Teflon screwcap under an argon atmosphere and was immersed in a preheated oil bath at 100 ºC. After 19 h, the reaction mixture was cooled to 23 ºC, was diluted with a saturated aqueous sodium chloride solution (300 mL) and deionized water (50 mL) and was extracted with diethyl ether (5 × 200 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (3 × 400 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: 40% ethyl acetate, 4% triethylamine, 56% hexanes → 44% ethyl acetate, 4% triethylamine, 52% hexanes) to afford benzylic amine (–)-**23** (1.31 g, 68.7%) as a light-yellow foam. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments also collected at elevated temperature.

^{1}H NMR (400 MHz, DMSO-d_6, 130 °C):	δ 7.35–7.19 (m, 6H, C6**H**, Ar$_{Cbz}$**H**), 6.93–6.82 (m, 2H, C5**H**, C7**H**), 5.09–4.95 (m, 3H, N1CO$_2$C**H**$_2$Ph, C9**H**), 3.94 (ddd, *J* = 14.4, 8.8, 3.9 Hz, 1H, C2**H**$_a$), 3.83 (app-dt, *J* = 14.5, 5.0 Hz, 1H, C2**H**$_b$), 3.66 (d, *J* = 8.6 Hz, 1H, C10**H**), 3.13 (s, 3H, N8C**H**$_3$), 1.96 (ddd, *J* = 14.1, 5.2, 3.9 Hz, 1H, C3**H**$_a$), 1.85 (br-s, 2H, C3aN**H**$_2$), 1.54 (ddd, *J* = 13.9, 8.7, 4.8 Hz, 1H, C3**H**$_b$), 1.40 (s, 3H, C12/13**H**$_3$), 1.27 (s, 3H, C12/13**H**$_3$).
^{13}C NMR (100.6 MHz, DMSO-d_6, 130 °C):	δ 178.5 (**C**8a), 154.5 (N1**C**O$_2$CH$_2$Ph), 142.6 (**C**7a), 136.7 (**C**4), 136.1 (Ar$_{Cbz}$), 128.6 (**C**4a), 127.7 (**C**6), 127.3 (Ar$_{Cbz}$), 126.8 (Ar$_{Cbz}$), 126.7 (Ar$_{Cbz}$), 118.6 (**C**5), 106.7 (**C**7), 65.6 (N1CO$_2$**C**H$_2$Ph), 60.9 (**C**10), 59.3 (**C**9), 58.6 (**C**3a), 57.7 (**C**11), 44.7 (**C**2), 32.2 (**C**3), 25.1 (N8**C**H$_3$), 23.6 (**C**12/13), 17.8 (**C**12/13).
FTIR (thin film) cm^{-1}:	3360 (w), 3288 (w), 2962 (m), 1710 (s), 1608 (s), 1473 (s), 1417 (m), 1368 (m), 1301 (m), 1260 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{24}H_{28}N_3O_4$ [M+H]$^+$: 422.2074, found: 422.2079.
$[\alpha]_D^{23}$:	–111 (*c* = 1.14, CH_2Cl_2).
TLC (60% ethyl acetate in hexanes), R*f*:	0.20 (UV, CAM).



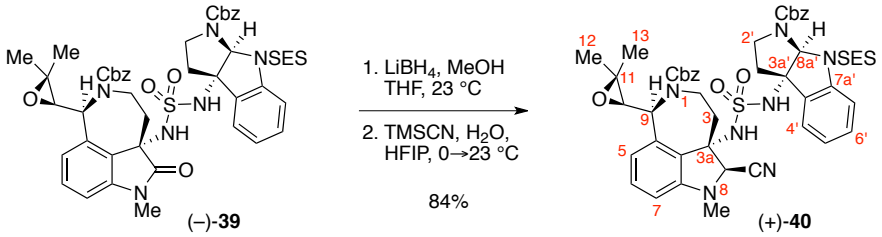
(–)-**23** (+)-**24** (–)-**39**

Sulfamide (–)-39:

A sample of 4-(dimethylamino)pyridine (DMAP, 386 mg, 3.16 mmol, 1.10 equiv) was added to a solution of benzylic amine (–)-**23** (1.21 g, 2.88 mmol, 1 equiv) and sulfamate ester (+)-**24** (2.87 g, 4.31 mmol, 1.50 equiv) in tetrahydrofuran (11.5 mL) at 23 ºC. After 24 h, the homogeneous solution was diluted with a saturated aqueous ammonium sulfate solution (80 mL) and deionized water (20 mL) and the resulting mixture was extracted with ethyl acetate (3 × 100 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (200 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 45%→50% ethyl acetate in hexanes) to afford sulfamide (–)-**39** (2.32 g, 84.3%) as a white foam. 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):[30]	δ 7.59–7.24 (m, 6H), 7.13–6.99 (m, 6H), 6.94 (t, *J* = 7.8 Hz, 2H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.55 (s, 1H), 6.50–6.20 (m, 2H), 5.16 (d, *J* = 12.2 Hz, 1H), 5.08 (d, *J* = 12.1 Hz, 1H), 4.97 (br-s, 3H), 3.77 (br-s, 1H), 3.69–3.46 (m, 2H), 3.38–3.21 (m, 1H), 3.15 (s, 3H), 2.52 (td, *J* = 11.6, 5.4 Hz, 1H), 2.33–1.80 (m, 3H), 1.61–0.99 (m, 10H), –0.10 (s, 9H).
^{13}C NMR (100.6 MHz, C_6D_6, 70 °C):[30]	δ 176.6, 156.2 (br), 155.0, 144.9, 143.6, 137.6, 137.0, 132.1, 130.1, 129.7 (br), 128.8 (2C), 128.6, 128.5 (2C), 127.9, 125.3, 124.5, 120.8, 117.2, 108.1, 83.3, 73.1, 67.8, 67.7, 62.9 (br), 59.1 (br), 51.5, 45.6, 36.5, 32.9, 26.8, 24.9, 19.4, 10.6, –2.0.
FTIR (thin film) cm^{-1}:	3415 (br-w), 3222 (br-w), 2956 (w), 1707 (s), 1602 (m), 1465 (m), 1412 (m), 1346 (m), 1317 (m), 1253 (m), 1198 (m), 1150 (m), 1102 (m), 753 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{47}H_{57}N_6O_{10}S_2Si$ $[M+H]^+$: 957.3341, found: 957.3353.
$[\alpha]_D^{23}$:	–37 (*c* = 0.37, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.30 (UV, CAM).

30. Atropisomerism causes significant signal broadening and not all ^{1}H and ^{13}C resonances were observed. All expected signals were observed in the product of the next step of our synthesis, aminonitrile sulfamide (+)-**40**.



Aminonitrile sulfamide (+)-40:

A solution of lithium borohydride (2.0 M in tetrahydrofuran, 15 mL, 30 mmol, 15 equiv) was added over 5 min to a solution of sulfamide (–)-**39** (1.91 g, 2.00 mmol, 1 equiv) in tetrahydrofuran (27.0 mL) at 23 ºC. Methanol (4.85 mL, 120 mmol, 60.0 equiv) was then added dropwise by syringe pump over 3.5 h and the resulting white suspension was allowed to stir vigorously at 23 ºC. After 17 h, the mixture was cooled to 0 ºC and was diluted with a saturated aqueous ammonium chloride solution (200 mL) and deionized water (50 mL). After vigorous stirring at 23 ºC for 10 min, the mixture was extracted with ethyl acetate (3 × 150 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (200 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to provide the crude hemiaminal as a white foam, which was used directly in the next step without further purification.

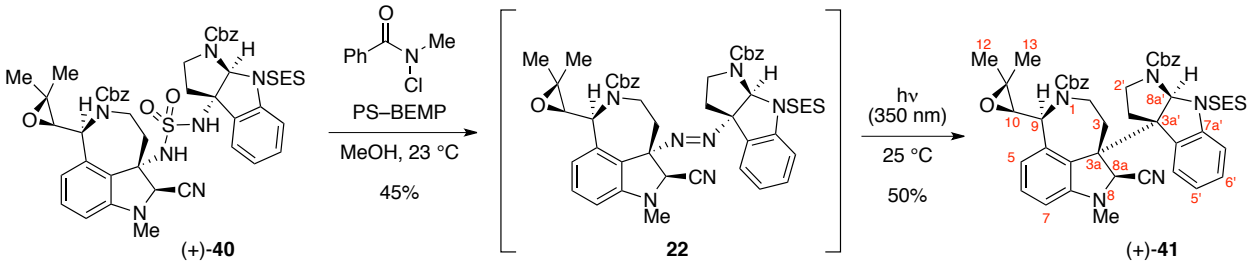
CAUTION! Trimethylsilyl cyanide is very toxic and should only be used with great caution.[29] Trimethylsilyl cyanide (1.50 mL, 12.0 mmol, 6.00 equiv) was added dropwise to a solution of the crude hemiaminal and deionized water (324 µL, 18.0 mmol, 9.00 equiv) in hexafluoroisopropanol (HFIP, 13.3 mL) at 0 ºC. After 5 min, the reaction flask was sealed under an argon atmosphere with a Teflon-lined glass stopper and the ice-bath was removed. After 20 h, the solution was cooled to 0 ºC and was diluted with an aqueous sodium hydroxide solution (0.1 M, 133 mL) and a saturated aqueous sodium chloride solution (133 mL). After warming to 23 ºC, the mixture was extracted with dichloromethane (3 × 130 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: 16% ethyl acetate, 42% hexanes, 42% dichloromethane → 20% ethyl acetate, 40% hexanes, 40% dichloromethane) to afford aminonitrile sulfamide (+)-**40** (1.62 g, 83.6%) as a white foam. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

^{1}H NMR (500 MHz, C_6D_6, 70 °C): δ 7.49 (d, *J* = 8.2 Hz, 1H), 7.35 (br-d, *J* = 5.7 Hz, 1H), 7.26 (d, *J* = 7.3 Hz, 2H), 7.23–7.16 (br-m, 2H), 7.15–6.98 (m, 8H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.85–6.59 (br-m, 1H), 6.50 (br-s, 1H), 6.26 (d, *J* = 7.9 Hz, 1H), 5.36 (br-s, 1H), 5.20 (s, 1H), 5.09 (s, 2H), 5.04 (s, 2H), 4.96–3.99 (br-m, 2H), 3.82–3.52 (m, 3H), 3.43 (td, *J* = 14.1, 13.6, 4.6 Hz, 1H), 3.32–2.75 (br-m, 2H), 2.74–2.42 (m, 6H), 2.25–2.14 (m, 1H), 1.38–1.09 (m, 5H), 1.02 (s, 3H), –0.07 (s, 9H).

^{13}C NMR (100.6 MHz, C_6D_6, 70 °C): δ 157.4, 154.9, 152.1, 143.8, 138.8, 137.3, 137.0, 131.9 (br), 131.4, 130.5, 128.8, 128.7, 128.4, 128.3, 128.2, 127.9 (br), 127.2, 125.0, 124.9 (br), 118.4 (br), 118.2, 115.6, 108.7, 83.4, 72.6, 68.2, 67.8, 67.6, 66.6, 63.4, 59.8, 59.4 (br), 50.9, 45.3, 41.1 (br), 36.5 (br), 33.6 (br), 33.0, 24.4, 19.9, 10.6, –1.9.

FTIR (thin film) cm^{-1}:	3246 (br-w), 2956 (w), 2896 (w), 1708 (m), 1600 (m), 1414 (m), 1357 (m), 1252 (m), 1149 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{48}H_{57}N_7NaO_9S_2Si$ $[M+Na]^+$: 990.3321, found: 990.3312.
$[\alpha]_D^{24}$:	+69 (*c* = 0.47, CH_2Cl_2).

TLC (19% ethyl acetate, 41% hexanes, 41% dichloromethane), R*f*: 0.29 (UV, CAM).



Heterodimer (+)-41:

N-Chloro-*N*-methylbenzamide[31] (672 mg, 3.96 mmol, 6.00 equiv) and resin-bound 2-*tert*-butyl-imino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2-diazaphosphorine (PS–BEMP, 3.62 g, 2.19 mmol/g on 200-400 mesh polystyrene resin, 7.92 mmol, 12.0 equiv) were added in rapid succession to a solution of aminonitrile sulfamide (+)-**40** (639 mg, 660 μmol, 1 equiv) in methanol (66.0 mL) at 23 ºC in the dark. After 15 min, the suspension was filtered through a pad of Celite, and the filter cake was washed sequentially with dichloromethane (70 mL) and ethyl acetate (70 mL). The light yellow filtrate was concentrated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (eluent: 6% ethyl acetate, 47% hexanes, 47% dichloromethane → 10% ethyl acetate, 45% hexanes, 45% dichloromethane) to afford unsymmetrical diazene **22** (270 mg, 45.3%) as a light yellow foam,[32] which was used directly in the next step without further purification.

A solution of diazene **22** (268 mg, 297 μmol, 1 equiv) in dichloromethane (20 mL) was concentrated under reduced pressure in a 500-mL round-bottom flask to provide a thin film of the diazene coating the flask. The flask was evacuated and backfilled with argon (three cycles) and was then irradiated in a Rayonet photoreactor equipped with 14 radially distributed (r = 12.7 cm) 25 W lamps (λ = 350 nm) at 25 ºC. After irradiating for 3 h, the lamps were turned off and the resulting residue was purified by flash column chromatography on silica gel (eluent: 10% ethyl acetate, 60% hexanes, 30% dichloromethane → 10% ethyl acetate, 45% hexanes, 45% dichloromethane) to afford heterodimer (+)-**41** (129 mg, 49.6%) as an off-white film. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments also collected at elevated temperature.

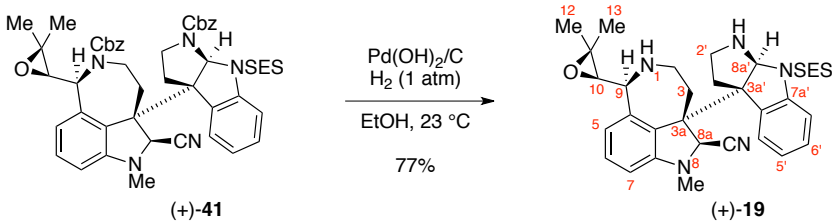
^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 7.56–7.45 (br-m, 1H, C4'**H**), 7.43–7.18 (m, 13H, C6**H**, C6'**H**, C7'**H**, Ar_{Cbz}**H**), 7.10 (br-t, *J* = 7.4 Hz, 1H, C5'**H**), 6.65 (app-dt, *J* = 7.8, 0.9 Hz, 1H, C7**H**), 6.59 (app-dt, *J* = 7.9, 1.0 Hz, 1H, C5**H**), 5.61 (s, 1H, C8a'**H**), 5.43 (d, *J* = 8.7 Hz, 1H, C9**H**), 5.36–4.97 (br-m, 2H, N1CO_2C**H**$_2$), 4.92 (d, *J* = 12.6 Hz, 1H, N1'CO_2C**H**$_a$), 4.89 (d, *J* = 12.6 Hz, 1H, N1'CO_2C**H**$_b$), 4.06 (dddd, *J* = 14.4, 3.8, 2.6, 1.0 Hz, 1H, C2**H**$_a$), 3.79 (s, 1H, C8a**H**), 3.50–3.38 (br-m, 1H, C2'**H**$_a$), 3.36 (ddd, *J* = 14.6, 12.6, 2.3 Hz, 1H, C2**H**$_b$),

31. The reagent was prepared as follows using a procedure adapted from Lengyel, I.; Cesare, V.; Stephani, R. *Synth. Commun.* **1998**, *28*, 1891: *tert*-Butyl hypochlorite (3.68 mL, 32.5 mmol, 1.30 equiv) was added dropwise via syringe to a stirred solution of *N*-methylbenzamide (3.38 g, 25.0 mmol, 1 equiv) in dichloromethane (50.0 mL) at 0 ºC in the dark. After 10 min, the ice-bath was removed and the pale-yellow solution was allowed to stir at 23 ºC in the dark. After 67 h, the solution was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 15→20% diethyl ether in pentane) to yield *N*-chloro-*N*-methylbenzamide (3.97 g, 93.5%) as a pale-yellow oil. Spectral data were consistent with those reported in Lathrop, S. P.; Pompeo, M.; Chang, W.-T. T.; Movassaghi, M. *J. Am. Chem. Soc.* **2016**, *138*, 7763.

32. As a result of the sensitivity of this intermediate, its slow conformational equilibrium at ambient temperature, and its instability at elevated temperatures, diazene **22** was used immediately in the next step. The measured HRMS was consistent with the desired product; HRMS (ESI) (*m/z*): calc'd for $C_{48}H_{55}N_7NaO_7SSi$ $[M+Na]^+$: 924.3545, found: 924.3542.

	3.22–3.09 (m, 2H, N8'$SO_2C\mathbf{H}_2$), 3.09–2.90 (br-m, 1H, C3$\mathbf{H}_a$), 2.86 (d, *J* = 8.7 Hz, 1H, C10**H**), 2.74 (s, 3H, N8C$\mathbf{H}_3$), 2.44–2.24 (br-m, 1H, C2'$\mathbf{H}_b$), 2.12 (app-dt, *J* = 15.5, 2.5 Hz, 1H, C3$\mathbf{H}_b$), 1.89–1.62, (br-m, 2H, C3'$\mathbf{H}_2$), 1.56 (br-s, 3H, C12/13$\mathbf{H}_3$), 1.38 (s, 3H, C12/13$\mathbf{H}_3$), 1.10–0.99 (m, 1H, N8'$SO_2CH_2C\mathbf{H}_a$), 0.93 (app-td, *J* = 13.6, 5.0 Hz, 1H, N8'$SO_2CH_2C\mathbf{H}_b$), –0.01 (s, 9H, $Si(C\mathbf{H}_3)_3$).
^{13}C NMR (125.8 MHz, CD_3CN, 70 °C):	δ 156.8 (N1'$\mathbf{C}O_2$), 155.3 (N1'$\mathbf{C}O_2$), 154.0 (**C**7a), 145.0 (**C**7a'), 138.7 (**C**4), 138.4 (Ar_{Cbz}), 138.0 (Ar_{Cbz}), 132.0 (**C**6), 131.4 (**C**4a'), 130.9 (**C**6'), 130.3 (**C**4'), 129.9 (Ar_{Cbz}), 129.7 (Ar_{Cbz}), 129.6 (Ar_{Cbz}), 129.2 (Ar_{Cbz}), 129.1 (Ar_{Cbz}), 126.3 (**C**4a), 126.0 (Ar_{Cbz}), 124.8 (**C**5'), 120.1 (**C**5), 117.7 (**C**N), 116.1 (**C**7'), 109.5 (**C**7), 82.1 (**C**8a'), 70.7 (**C**8a), 68.4 (N1'$CO_2\mathbf{C}H_2$), 68.1 (N1'$CO_2\mathbf{C}H_2$), 67.1 (**C**10), 67.0 (**C**3a'), 62.2 (**C**11), 59.3 (**C**9), 58.8 (**C**3a), 52.7 (N8'$SO_2\mathbf{C}H_2$), 45.7 (**C**2'), 43.0 (**C**2), 36.1 (**C**3'), 35.1 (br, **C**3), 34.9 (N8'$\mathbf{C}H_3$), 24.9 (**C**12/13), 20.0 (**C**12/13), 10.9 (N8'$SO_2CH_2\mathbf{C}H_2$), –1.6 ($Si(\mathbf{C}H_3)_3$).
FTIR (thin film) cm^{-1}:	3064 (w), 2956 (w), 2893 (w), 1700 (s), 1599 (w), 1413 (m), 1353 (m), 1113 (s), 860 (m), 732 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{48}H_{56}N_5O_7SSi$ $[M+H]^+$: 874.3664, found: 874.3661.
$[\alpha]_D^{23}$:	+214 (*c* = 0.70, CH_2Cl_2).

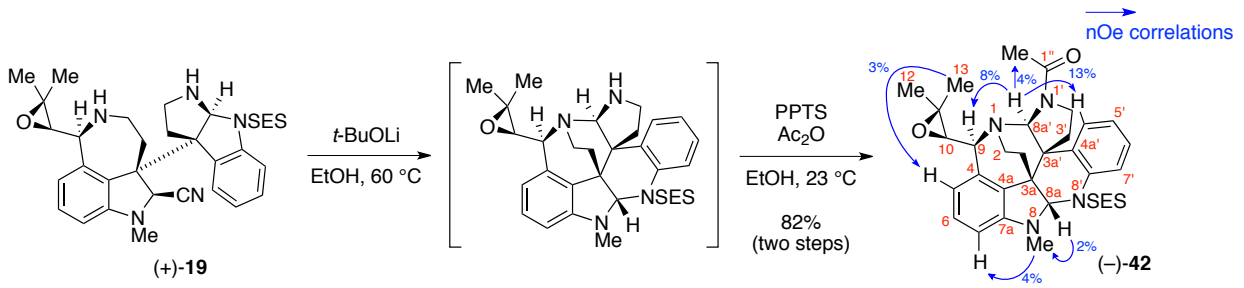
TLC (10% ethyl acetate, 60% hexanes, 30% dichloromethane), R*f*: 0.13 (UV, CAM).



Heterodimeric diamine (+)-19:

A sample of palladium(II) hydroxide on carbon (15.7 wt% on wet support, 79.1 mg, 88.5 μmol, 0.600 equiv) was added to a solution of heterodimer (+)-**41** (129 mg, 148 μmol, 1 equiv) in anhydrous ethanol (200 proof, 5.90 mL) at 23 ºC. The resulting suspension was sparged with dihydrogen for 5 min by discharge of a balloon equipped with a needle extending into the reaction mixture. After stirring for 6 h under an atmosphere of dihydrogen, the suspension was sparged with argon for 5 min, was diluted with ethanol (6 mL), and was filtered through a pad of Celite. The filter cake was washed with ethanol (60 mL) and the colorless filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 40→60% acetonitrile in dichloromethane) to afford heterodimeric diamine (+)-**19** (68.9 mg, 77.1%) as a white film. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, CD_3OD, 20 °C):	δ 7.47 (d, *J* = 7.6 Hz, 1H, C4'**H**), 7.38–7.30 (m, 3H, C6**H**, C6'**H**, C7'**H**), 7.09 (ddd, *J* = 8.2, 6.2, 2.3 Hz, 1H, C5'**H**), 6.79 (d, *J* = 7.7 Hz, 1H, C5**H**), 6.70 (d, *J* = 7.9 Hz, 1H, C7**H**), 5.65 (s, 1H, C8a'**H**), 4.15–4.09 (m, 2H, C8a**H**, C9**H**), 3.42–3.32 (m, 2H, N8'$SO_2C\mathbf{H}_2$), 3.18 (d, *J* = 8.1 Hz, 1H, C10**H**), 3.16–3.02 (m, 2H, C2**H**$_2$), 2.84 (s, 3H, N8C**H**$_3$), 2.82–2.78 (m, 1H, C2'**H**$_a$), 2.74–2.64 (m, 1H, C3**H**$_a$), 2.54 (dd, *J* = 10.9, 3.9 Hz, 1H, C3'**H**$_a$), 2.23 (app-td, *J* = 11.5, 3.9 Hz, 1H, C2'**H**$_b$), 2.17–2.04 (m, 2H, C3**H**$_b$, C3'**H**$_b$), 1.49 (s, 3H, C12/13**H**$_3$), 1.33 (s, 3H, C12/13**H**$_3$), 1.14 (ddd, *J* = 13.9, 10.9, 6.6 Hz, 1H, N8'$SO_2CH_2C\mathbf{H}_a$), 1.01 (ddd, *J* = 13.9, 11.2, 6.7 Hz, 1H, N8'$SO_2CH_2C\mathbf{H}_b$), 0.01 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, CD_3OD, 20 °C):	δ 153.2 (**C**7a), 144.9 (**C**7a'), 136.3 (**C**4), 132.0 (**C**6), 131.9 (**C**4a'), 130.8 (**C**6'), 128.5 (**C**4a), 127.5 (**C**4'), 123.9 (**C**5'), 117.7 (**C**5), 117.2 (**C**N), 113.7 (**C**7'), 109.3 (**C**7), 85.6 (**C**8a'), 67.9 (**C**8a), 67.2 (**C**10), 66.5 (**C**3a'), 60.2 (**C**11), 58.2 (**C**3a), 57.1 (**C**9), 51.6 (N8'$SO_2\mathbf{C}H_2$), 46.9 (**C**2'), 43.9 (**C**2), 39.0 (**C**3'), 34.3 (**C**3), 32.8 (N8**C**H$_3$), 24.9 (**C**12/13), 19.9 (**C**12/13), 10.3 (N8'$SO_2CH_2\mathbf{C}H_2$), –2.1 (Si(**C**H$_3$)$_3$).
FTIR (thin film) cm^{-1}:	3346 (br-w), 2955 (m), 2878 (w), 2227 (w), 1588 (m), 1476 (m), 1459 (m), 1347 (m), 1250 (m), 1149 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{32}H_{44}N_5O_3SSi$ $[M+H]^+$: 606.2929, found: 606.2929.
$[\alpha]_D^{23}$:	+262 (*c* = 0.13, CH_2Cl_2).
TLC (50% acetonitrile in dichloromethane), R*f*:	0.36 (UV, CAM).



(–)-*N*8'-(Trimethylsilyl)ethanesulfonyl communesin A (42):

A sample of lithium *tert*-butoxide (25.0 mg, 312 μmol, 10.0 equiv) was added to a solution of heterodimer (+)-**19** (18.9 mg, 31.2 μmol, 1 equiv) in anhydrous ethanol (200 proof, 820 μL) at 23 ºC. The flask was sealed with a Teflon-lined glass stopper under an argon atmosphere and was immersed in a preheated oil bath at 60 ºC. After 22 h, the reaction mixture was cooled to 23 ºC and samples of pyridinium *p*-toluenesulfonate (PPTS, 62.8 mg, 250 μmol, 8.00 equiv) and acetic anhydride (12.0 μL, 125 μmol, 4.00 equiv) were added sequentially. After 40 min, a saturated aqueous sodium bicarbonate solution (10 mL) and deionized water (4 mL) were added and the resulting mixture was extracted with ethyl acetate (3 × 8 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 30% acetone in hexanes) to afford (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin A (**42**, 15.9 mg, 82.0%) as a white solid. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of (–)-**42** in 15% water in methanol at –20 ºC. The thermal ellipsoid representation of (–)-**42** is depicted later in this document. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, 5.9:1 mixture of atropisomers, *denotes minor atropisomer):

δ 7.56 (dd, *J* = 8.0, 1.3 Hz, 1H, C7'**H**), 7.41 (dd, *J* = 8.0, 1.3 Hz, 1H, C7'**H***), 7.20 (app-td, *J* = 7.9, 1.5 Hz, 2H, C6'**H**, C6'**H***), 7.06 (app-td, *J* = 7.6, 1.3 Hz, 2H, C5'**H**, C5'**H***), 6.91 (t, *J* = 7.8 Hz, 1H, C6**H**), 6.89 (t, *J* = 7.8 Hz, 1H, C6**H***), 6.84 (dd, *J* = 7.9, 1.5 Hz, 1H, C4'**H**), 6.78 (dd, *J* = 7.9, 1.4 Hz, 1H, C4'**H***), 6.14 (d, *J* = 7.9 Hz, 1H, C5**H***), 6.10 (d, *J* = 7.6 Hz, 1H, C5**H**), 5.98 (d, *J* = 7.6 Hz, 1H, C7**H**), 5.94 (d, *J* = 7.6 Hz, 1H, C7**H***), 5.71 (s, 1H, C8a**H**), 5.63 (s, 1H, C8a**H***), 5.43 (app-s, 1H, C8a'H*), 5.04 (d, *J* = 1.5 Hz, 1H, C8a'**H**), 4.49 (d, *J* = 9.0 Hz, 1H, C9**H***), 4.09 (d, *J* = 9.2 Hz, 1H, C9**H**), 3.93 (app-dd, *J* = 11.5, 9.1 Hz, 1H, C2'$\mathbf{H}_a$), 3.75 (app-t, *J* = 9.3 Hz, 1H, C2'$\mathbf{H}_a$*), 3.55 (app-dd, *J* = 16.0, 10.2 Hz, 1H, C2$\mathbf{H}_a$*), 3.49 (app-dd, *J* = 15.9, 9.8 Hz, 1H, C2$\mathbf{H}_a$), 3.40–3.29 (m, 3H, C2$\mathbf{H}_b$, C2$\mathbf{H}_b$*, N8'SO_2C$\mathbf{H}_a$*), 3.25 (app-td, *J* = 13.4, 5.0 Hz, 3H, N8'SO_2C$\mathbf{H}_a$, N8'SO_2C$\mathbf{H}_b$*, C2'$\mathbf{H}_b$*), 3.17 (app-td, *J* = 13.4, 4.9 Hz, 1H, N8'SO_2C$\mathbf{H}_b$), 3.14–3.04 (m, 1H, C2'$\mathbf{H}_b$) 3.07–2.96 (m, 1H, C3'$\mathbf{H}_a$*), 2.91 (s, 3H, N8C$\mathbf{H}_3$), 2.87 (s, 3H, N8C$\mathbf{H}_3$*), 2.85–2.75 (m, 1H, C3'$\mathbf{H}_a$) 2.84 (d, *J* = 9.0 Hz, 1H, C10**H**), 2.77 (d, *J* = 8.7 Hz, 1H, C10**H***), 2.55–2.43 (m, 2H, C3$\mathbf{H}_a$, C3$\mathbf{H}_a$*), 2.32–2.25 (m, 2H, C3$\mathbf{H}_b$, C3$\mathbf{H}_b$*), 2.32 (s, 3H, C2''$\mathbf{H}_3$), 2.11 (dd, *J* = 13.1, 7.5 Hz, 1H, C3'$\mathbf{H}_b$*), 2.09 (s,

3H, C2"**H**$_3$*), 1.93 (dd, *J* = 13.1, 6.4 Hz, 1H, C3'**H**$_b$), 1.57 (s, 3H, C13**H**$_3$*), 1.53 (s, 3H, C13**H**$_3$), 1.38 (s, 3H, C12**H**$_3$), 1.36 (s, 3H, C12**H**$_3$*), 1.31–1.13 (m, 4H, N8'SO$_2$CH$_2$C**H**$_2$, N8'SO$_2$CH$_2$C**H**$_2$*), 0.10 (s, 9H, Si(C**H**$_3$)$_3$*), 0.06 (s, 9H, Si(C**H**$_3$)$_3$).

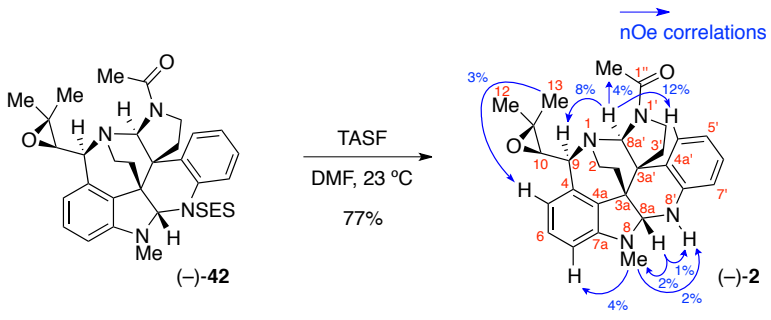
^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C, 5.9:1 mixture of atropisomers, *denotes minor atropisomer):
δ 171.8 (**C**1"), 170.5 (**C**1"*), 149.9 (**C**7a), 149.5 (**C**7a*), 139.2 (**C**4a'*), 139.0 (**C**4*), 138.3 (**C**4a'), 137.2 (**C**4), 136.1 (2C, **C**7a'*, **C**7a'), 131.2 (2C, **C**4a, **C**4a*), 129.4 (**C**6), 129.2 (**C**6*), 127.1 (**C**6'), 127.7 (**C**6'*), 126.8 (**C**5'*), 126.4 (**C**5'), 125.4 (**C**7'*), 124.9 (**C**7'), 124.3 (**C**4'*), 123.9 (**C**4'), 114.6 (**C**5*), 113.9 (**C**5), 102.6 (**C**7), 102.3 (**C**7*), 85.3 (**C**8a*), 84.7 (**C**8a), 80.0 (**C**8a'), 78.2 (**C**8a'*), 65.5 (**C**9), 65.2 (**C**9*), 63.9 (2C, **C**10, **C**10*), 59.9 (2C, **C**11, **C**11*), 54.2 (2C, **C**3a, **C**3a*), 52.5 (2C, **C**3a', N8'SO$_2$**C**H$_2$*), 51.8 (N8'SO$_2$**C**H$_2$), 50.3 (**C**3a'*), 45.9 (**C**2'*), 44.2 (**C**2'), 38.0 (**C**3*), 37.9 (**C**2*), 37.7 (**C**3), 36.6 (**C**2), 33.3 (**C**3'*), 31.7 (**C**3'), 31.0 (N8**C**H$_3$*), 30.9 (N8**C**H$_3$), 24.9 (**C**12), 24.8 (**C**12*), 23.1 (**C**2"*), 22.8 (**C**2"), 20.6 (**C**13), 20.5 (**C**13*), 10.8 (N8'SO$_2$CH$_2$**C**H$_2$*), 10.7 (N8'SO$_2$CH$_2$**C**H$_2$), –1.7 (Si(**C**H$_3$)$_3$*), –1.8 (Si(**C**H$_3$)$_3$).

FTIR (thin film) cm^{-1}: 3055 (w), 2954 (m), 2928 (m), 2880 (m), 1651 (s), 1598 (m), 1487 (m), 1454 (m), 1400 (s), 1341 (s), 1281 (m), 1250 (m), 1207 (m), 1155 (s), 1081 (m), 1054 (m), 859 (m), 843 (m), 740 (m), 568 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{33}H_{45}N_4O_4SSi$ $[M+H]^+$: 621.2925,
found: 621.2916.

$[\alpha]_D^{24}$: –144 (*c* = 0.81, CH_2Cl_2).

TLC (30% acetone in hexanes), R*f*: 0.13 (UV, CAM).



(–)-Communesin A (2):

A degassed solution of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 24.3 mg, 88.0 μmol, 4.00 equiv) in *N*,*N*-dimethylformamide (235 μL) was added to a degassed solution of (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin A (**42**, 13.6 mg, 22.0 μmol, 1 equiv) in *N*,*N*-dimethylformamide (500 μL) at 23 ºC. After 2.7 h, a saturated aqueous sodium chloride solution (10 mL) and deionized water (5 mL) were added and the mixture was extracted with ethyl acetate (3 × 8 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 40% acetone in hexanes) to afford (–)-communesin A (**2**, 7.74 mg, 77.0%) as a white solid. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (600 MHz, $CDCl_3$, 20 °C, 11:1 mixture of atropisomers, *denotes minor atropisomer):

δ 7.01 (app-td, *J* = 7.4, 1.9 Hz, 2H, C6'**H**, C6'**H***), 6.88 (t, *J* = 7.7 Hz, 2H, C6**H**, C6**H***), 6.74–6.66 (m, 5H, C4'**H**, C5'**H**, C5'**H***, C7'**H**, C7'**H***), 6.63 (d, *J* = 7.4 Hz, 1H, C4'**H***), 6.10 (d, *J* = 7.4 Hz, 1H, C5**H***), 6.06 (d, *J* = 7.7 Hz, 1H, C5**H**), 5.95 (d, *J* = 7.7 Hz, 1H, C7**H**), 5.91 (d, *J* = 7.4 Hz, 1H, C$_7$**H***), 5.41 (app-s, 1H, C8a'**H***), 5.02 (d, *J* = 1.5 Hz, 1H, C8a'**H**), 4.69 (s, 1H, C8a**H**), 4.67 (s, 1H, C8a**H***), 4.59 (br-s, 1H, N8'**H**), 4.53–4.47 (m, 1H, C9**H***), 4.08 (d, *J* = 9.1 Hz, 1H, C9**H**), 3.89 (app-dd, *J* = 11.8, 8.4 Hz, 1H, C2'**H**$_a$), 3.77–3.66 (m, 1H, C2'**H**$_a$*), 3.60–3.51 (m, 1H, C2**H**$_a$*), 3.47 (app-dd, *J* = 15.7, 9.6 Hz, 1H, C2**H**$_a$), 3.36 (app-dt, *J* = 16.3, 8.8 Hz, 2H, C2**H**$_b$, C2**H**$_b$*), 3.13 (app-q, *J* = 9.9 Hz, 1H, C2'**H**$_b$*), 3.01 (app-td, *J* = 11.6, 7.2 Hz, 1H, C2'**H**$_b$), 2.97–2.90 (m, 1H, C3'**H**$_a$*), 2.87 (d, *J* = 8.9 Hz, 1H, C10**H**), 2.84 (s, 3H, N8C**H**$_3$), 2.82 (s, 3H, N8C**H**$_3$*), 2.80 (d, *J* = 8.5 Hz, 1H, C10**H***), 2.78–2.70 (m, 1H, C3'**H**$_a$), 2.37 (app-dd, *J* = 12.5, 7.7 Hz, 2H, C3**H**$_a$, C3**H**$_a$*), 2.33 (s, 3H, C2"**H**$_3$), 2.28 (app-dt, *J* = 13.0, 9.3 Hz, 2H, C3**H**$_b$, C3**H**$_b$*), 2.09 (s, 3H, C2"**H**$_3$*), 2.07–2.02 (m, 1H, C3'**H**$_b$*), 1.97 (app-dd, *J* = 13.3, 7.1 Hz, 1H, C3'**H**$_b$), 1.58 (s, 3H, C13**H**$_3$*), 1.53 (s, 3H, C13**H**$_3$), 1.38 (s, 3H, C12**H**$_3$), 1.37 (s, 3H, C12**H**$_3$*).

^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, 11:1 mixture of atropisomers, *denotes minor atropisomer):	δ 172.1 (**C**1''), 150.7 (**C**7a), 150.6 (**C**7a*), 142.8 (**C**7a'), 137.0 (**C**4), 132.6 (**C**4a'), 132.4 (**C**4a), 129.0 (**C**6), 127.6 (**C**6'), 127.4 (**C**6'*), 123.6 (**C**4'*), 123.4 (**C**4'), 121.0 (**C**5'*), 120.7 (**C**5'), 117.3 (**C**7'*), 117.1 (**C**7'), 114.0 (**C**5*), 113.4 (**C**5), 102.0 (**C**7), 101.6 (**C**7*), 83.0 (**C**8a*), 82.6 (**C**8a), 79.8 (**C**8a'), 77.9 (**C**8a'*), 65.5 (**C**9), 64.2 (**C**10), 59.9 (**C**11), 52.1 (**C**3a'), 51.6 (**C**3a), 46.1 (**C**2'*), 44.2 (**C**2'), 38.2 (**C**3), 36.5 (**C**2), 32.7 (**C**3'*), 31.0 (**C**3'), 29.9 (N8**C**H_3*), 29.8 (N8**C**H_3), 24.9 (**C**12), 24.8 (**C**12*), 23.2 (**C**2''*), 22.8 (**C**2''), 20.6 (**C**13), 20.5 (**C**13*).
FTIR (thin film) cm^{-1}:	3320 (br-w), 3052 (w), 2961 (m), 2926 (m), 2880 (m), 1638 (s), 1605 (s), 1595 (s), 1493 (s), 1402 (s), 1347 (m), 1254 (m), 1083 (m), 1007 (m), 738 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{28}H_{33}N_4O_2$ $[M+H]^+$: 457.2598, found: 457.2590.
$[\alpha]_D^{24}$:	–165 (*c* = 0.39, $CHCl_3$).[33]
TLC (40% acetone in hexanes), R*f*:	0.19 (UV, CAM)

33. (a) Literature value: $[\alpha]_D^{22}$ = –58 (*c* = 0.14, $CHCl_3$), see Numata, A.; Takahashi, C.; Ito, Y.; Takada, T.; Kawai, K.; Usami, Y.; Matsumura, E.; Imachi, M.; Ito, T.; Hasegawa, T. *Tetrahedron Lett.* **1993**, *34*, 2355. (b) Literature value: $[\alpha]_D^{20}$ = –174 (*c* =1.34, $CHCl_3$), see Hayashi, H.; Matsumoto, H.; Akiyama, K. *Biosci. Biotechnol. Biochem.* **2004**, *68*, 753. (c) Literature value: $[\alpha]_D^{30}$ = –163.5 (*c* = 0.14, $CHCl_3$), see Zuo, Z.; Ma, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 12008.

Table S1. Comparison of our ^{1}H NMR data for (–)-communesin A (2) with literature data ($CDCl_3$, major atropisomer):

Assignment	**Numata's Isolation Report**[34,35] (–)-Communesin A (**2**) ^{1}H NMR, 300 MHz, $CDCl_3$	**Hayashi's Isolation Report**[36,37] (–)-Communesin A (**2**) ^{1}H NMR, $CDCl_3$	**Ma's Report**[38] (–)-Communesin A (**2**) ^{1}H NMR, 400 MHz, $CDCl_3$	**This Work** (–)-Communesin A (**2**) ^{1}H NMR, 600 MHz, $CDCl_3$
C2	3.47 (dd, *J* = 16.0, 9.0 Hz, 1H) 3.35 (dt, *J* = 16.0, 9.2 Hz, 1H)	3.32 (dd, *J* = 15.5, 9.5 Hz, 1H) 3.18 (dt, *J* = 16.0, 9.2 Hz, 1H)	3.47 (dd, *J* = 16.0, 9.2 Hz, 1H) 3.36 (dt, *J* = 16.0, 9.2 Hz, 1H)	3.47 (app-dd, *J* = 15.7, 9.6 Hz, 1H) 3.36 (app-dt, *J* = 16.3, 8.8 Hz, 1H)
C3	2.35 (m, 1H) 2.26 (dd, *J* = 12.4, 9.2 Hz, 1H)	2.27 (dd, *J* = 12.5 9.5 Hz, 1H) 2.12 (ddd, *J* = 12.5, 9.5,8.5 Hz, 1H)	2.39–2.25 (m, 2H)	2.37 (app-dd, *J* = 12.5, 7.7 Hz, 1H) 2.28 (app-dt, *J* = 13.0, 9.3 Hz, 1H)
C3a	–	–	–	–
C4a	–	–	–	–
C4	–	–	–	–
C5	6.07 (d, *J* = 7.8 Hz, 1H)	6.03 (d, *J* = 7.5 Hz, 1H)	6.06 (d, *J* = 7.6 Hz, 1H)	6.06 (d, *J* = 7.7 Hz, 1H)
C6	6.89 (t, *J* = 7.8 Hz, 1H)	6.79 (t, *J* = 7.5 Hz, 1H)	6.88 (t, *J* = 7.6 Hz, 1H)	6.88 (t, *J* = 7.7 Hz, 1H)
C7	5.95 (d, *J* = 7.8 Hz, 1H)	5.93 (d, *J* = 7.5 Hz, 1H)	5.95 (d, *J* = 7.6 Hz, 1H)	5.95 (d, *J* = 7.7 Hz, 1H)
C7a	–	–	–	–
N8CH_3	2.85 (s, 3H)	2.79 (s, 3H)	2.84 (s, 3H)	2.84 (s, 3H)
C8a	4.70 (s, 1H)	4.63 (d, *J* = 1.0 Hz, 1H)	4.69 (s, 1H)	4.69 (s, 1H)
C9	4.08 (d, *J* = 9.0 Hz, 1H)	4.13 (d, *J* = 9.0 Hz, 1H)	4.08 (d, *J* = 9.2 Hz, 1H)	4.08 (d, *J* = 9.1 Hz, 1H)
C10	2.87 (d, *J* = 9.0 Hz, 1H)	2.89 (d, *J* = 9.0 Hz, 1H)	2.86 (d, *J* = 9.6 Hz, 1H)	2.87 (d, *J* = 8.9 Hz, 1H)
C11	–	–	–	–
C12	1.39 (s, 3H)	1.31 (s, 3H)	1.38 (s, 3H)	1.38 (s, 3H)
C13	1.54 (s, 3H)	1.48 (s, 3H)	1.53 (s, 3H)	1.53 (s, 3H)
C2'	3.89 (dd, *J* = 12.0, 8.8 Hz, 1H) 3.01 (td, *J* = 12.0, 7.2 Hz, 1H)	3.67 (dt, *J* = 15.0, 7.0 Hz, 1H) 2.70 (m, 1H)	3.89 (dd, *J* = 12.0, 8.8 Hz, 1H) 3.01 (td, *J* = 11.6, 8.0 Hz, 1H)	3.89 (app-dd, *J* = 11.8, 8.4 Hz, 1H) 3.01 (app-td, *J* = 11.6, 7.2 Hz, 1H)
C3'	2.74 (td, *J* = 12.0, 8.8 Hz, 1H) 1.98 (td, *J* = 12.0, 7.2 Hz, 1H)	2.67 (m, 1H) 1.72 (dt, *J* = 12.5, 6.0 Hz, 1H)	2.78–2.70 (m, 1H) 1.97 (dd, *J* = 12.8, 7.2 Hz, 1H)	2.78–2.70 (m, 1H) 1.97 (app-dd, *J* = 13.3, 7.1 Hz, 1H)

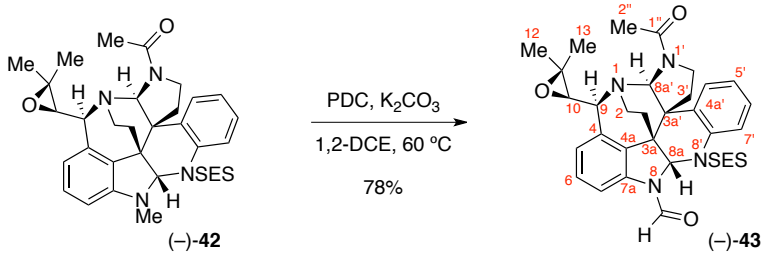
34. Numata, A.; Takahashi, C.; Ito, Y.; Takada, T.; Kawai, K.; Usami, Y.; Matsumura, E.; Imachi, M.; Ito, T.; Hasegawa, T. *Tetrahedron Lett.* **1993**, *34*, 2355.
35. The reference points for the residual protium and carbon resonances of the NMR solvent were not listed.
36. Hayashi, H.; Matsumoto, H.; Akiyama, K. *Biosci. Biotechnol. Biochem.* **2004**, *68*, 753.
37. Resonance frequencies and reference points for the residual protium and carbon resonances of the NMR solvent were not listed.
38. Zuo, Z.; Ma, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 12008.

C3a'	–	–	–	–
C4a'	–	–	–	–
C4'	6.70 (d, *J* = 2.8 Hz, 1H)	6.73 (dd, *J* = 7.5, 1.5 Hz, 1H)	6.73–6.67 (m, 3H)	6.74–6.66 (m, 3H)
C5'	6.71 (d, *J* = 7.5 Hz, 1H)	6.61 (td, *J* = 7.5, 1.5 Hz, 1H)	6.73–6.67 (m, 3H)	6.74–6.66 (m, 3H)
C6'	7.01 (td, *J* = 7.5, 2.8 Hz, 1H)	6.94 (td, *J* = 7.5, 1.5 Hz, 1H)	7.01 (td, *J* = 7.6, 1.6 Hz, 1H)	7.01 (app-td, *J* = 7.4, 1.9 Hz, 1H)
C7'	6.69 (d, *J* = 7.5 Hz, 1H)	6.80 (dd, *J* = 7.5, 1.5 Hz, 1H)	6.73–6.67 (m, 3H)	6.74–6.66 (m, 3H)
C7a'	–	–	–	–
C8a'	5.03 (s, 1H)	5.11 (s, 1H)	5.02 (s, 1H)	5.02 (d, *J* = 1.5 Hz, 1H)
C1"	–	–	–	–
C2"	2.34 (s, 3H)	2.23 (s, 3H)	2.33 (s, 3H)	2.33 (s, 3H)
N8'H	4.62 (br-s, 1H)	6.51 (d, 1.0 Hz)	–	4.59 (br-s, 1H)

Table S2. Comparison of our ^{13}C NMR data for (–)-communesin A (2) with literature data ($CDCl_3$, major atropisomer):

Assignment	**Numata's Isolation Report**[34,35] (–)-Communesin A (**2**) ^{13}C NMR, 75.4 MHz, $CDCl_3$	**Hayashi's Isolation Report**[36,37] (–)-Communesin A (**2**) ^{13}C NMR, $CDCl_3$	**Ma's Report**[38] (–)-Communesin A (**2**) ^{13}C NMR, 100 MHz, $CDCl_3$	**This Work** (–)-Communesin A (**2**) ^{13}C NMR, 150.9 MHz, $CDCl_3$	**Chemical Shift Difference** $\Delta\delta$ = δ (this work) – δ (Numata's report)
C2	36.03	35.7	36.3	36.45	**0.42**[39]
C3	38.03	37.8	38.0	38.19	0.16
C3a	51.42	50.7	51.4	51.59	0.17
C4a	132.23	132.5	132.3	132.40	0.17
C4	136.78	137.0	136.8	136.96	0.18
C5	113.19	112.7	113.2	113.36	0.17
C6	128.89	128.2	128.9	129.04	0.15
C7	101.81	101.3	101.8	101.97	0.16
C7a	150.55	150.6	150.6	150.71	0.16
N8$\mathbf{C}H_3$	29.63	29.6	29.6	29.78	0.15
C8a	82.44	81.4	82.5	82.62	0.18
C9	65.38	64.5	65.4	65.54	0.16
C10	64.01	63.1	64.0	64.16	0.15
C11	59.79	59.2	59.8	59.90	0.11
C12	24.80	24.5	24.8	24.94	0.14
C13	20.50	20.1	20.5	20.64	0.14
C2'	44.08	43.5	44.1	44.21	0.13
C3'	30.81	30.4	30.8	30.97	0.16
C3a'	51.92	51.4	52.0	52.10	0.18
C4a'	132.38	132.1	132.4	132.56	0.18
C4'	123.21	123.3	123.2	123.38	0.17
C5'	120.54	118.7	120.6	120.71	0.17
C6'	127.43	126.9	127.4	127.56	0.13
C7'	116.97	116.5	117.0	117.10	0.13
C7a'	142.69	144.1	142.7	142.80	0.11
C8a'	79.65	78.4	79.7	79.79	0.14
C1"	170.02	170.9	172.1	172.12	**2.10**[39]
C2"	22.65	22.2	22.6	22.80	0.15

39. Similar chemical shift discrepancies for the C2 and C1" resonances were noted by Ma and Zuo in their total synthesis report (ref. 38).



Heptacyclic formamide (–)-43:

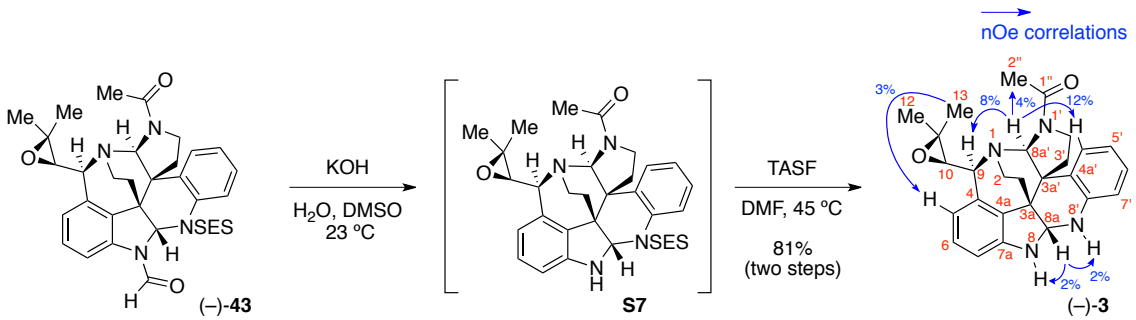
Samples of crushed potassium carbonate (123 mg, 891 μmol, 40.0 equiv) and pyridinium dichromate (PDC, 83.8 mg, 223 μmol, 10.0 equiv) were added sequentially to a solution of (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin A (**42**, 13.8 mg, 22.3 μmol, 1 equiv) in 1,2-dichloroethane (1.50 mL) at 23 ºC. The flask was sealed with a Teflon-lined glass stopper under an argon atmosphere and was immersed in a preheated oil bath at 60 ºC. After stirring for 8 h, the brown suspension was cooled to 23 ºC, was diluted with dichloromethane (5 mL), and was filtered through a pad of silica gel covered with a pad of Celite. The filter cake was washed with acetone–dichloromethane (1:1, 70 mL) and the filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 20% isopropanol in hexanes) to afford heptacyclic formamide (–)-**43** (11.0 mg, 77.6%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$, 20 °C, 23:9.6*:2.0:1.0 mixture of atropisomers, *denotes minor atropisomer): δ 8.83 (s, 1H), 8.81* (s, 1H), 7.25–7.15 (m, 2H), 7.12–7.00 (m, 2H), 6.81 (dd, *J* = 11.3, 7.4 Hz, 1H), 6.75 (app-t, *J* = 7.3 Hz, 1H), 6.64* (d, *J* = 8.1 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.43 (s, 1H), 6.38* (s, 1H), 5.41* (s, 1H), 5.01 (s, 1H), 4.59* (d, *J* = 8.1 Hz, 1H), 4.18 (d, *J* = 8.9 Hz, 1H), 4.11 (td, *J* = 13.8, 3.9 Hz, 1H), 3.95 (dd, *J* = 12.3, 8.7 Hz, 1H), 3.77* (app-t, *J* = 9.4 Hz, 1H), 3.59–3.45 (m, 2H), 3.44–3.35 (m, 1H), 3.30–3.21* (m, 1H), 3.10 (app-td, *J* = 11.4, 7.4 Hz, 1H), 3.06–2.97* (m, 1H), 2.88–2.81 (m, 1H), 2.79 (d, *J* = 8.9 Hz, 1H), 2.71* (d, *J* = 8.5 Hz, 1H), 2.67 (dd, *J* = 14.1, 8.2 Hz, 1H), 2.44* (dd, *J* = 14.1, 7.3 Hz, 1H), 2.32 (s, 3H), 2.37–2.25 (m, 2H), 2.10* (s, 3H), 1.57* (s, 3H), 1.54 (s, 3H), 1.37 (s, 3H), 1.35* (s, 3H), 1.31–1.15 (m, 2H), 0.16 (s, 9H).

^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, mixture of atropisomers):[40] δ 171.5, 170.7, 159.3, 141.2, 140.2, 139.9, 139.6, 139.2, 138.8, 135.6 (2C), 134.4, 134.2, 129.5, 129.3, 128.1, 127.9, 127.3, 127.2, 127.1, 126.6, 124.2, 123.8, 122.6, 122.1, 107.1, 106.7, 79.9, 78.5, 78.1, 76.9, 76.6, 65.2, 65.0, 63.8, 59.9, 59.8, 54.8, 54.6, 52.8, 52.7, 52.3, 50.0, 46.0, 44.3, 37.8, 37.1, 36.8, 36.4, 32.5, 30.9, 24.8 (2C), 23.1, 22.9, 20.6, 20.4, 10.9, 10.8, –1.5, –1.7, –1.8, (2C).

40. More than the expected 33 ^{13}C resonances were observed due to the presence of multiple atropisomers. All observed resonances are listed.

FTIR (thin film) cm^{-1}:	2954 (w), 2895 (w), 1682 (s), 1651 (s), 1592 (m), 1486 (m), 1468 (m), 1400 (m), 1342 (s), 1250 (m), 1072 (m), 893 (m), 842 (m), 701 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{33}H_{43}N_4O_5SSi$ $[M+H]^+$: 635.2718, found: 635.2715.
$[\alpha]_D^{23}$:	–56 (*c* = 0.49, CH_2Cl_2).
TLC (20% isopropanol in hexanes), R*f*:	0.21 (UV, CAM).



(–)-Communesin E (3):

An aqueous potassium hydroxide solution (0.5 M, 172 μL, 86.0 μmol, 5.00 equiv) was added rapidly to a solution of heptacyclic formamide (–)-**43** (10.9 mg, 17.2 μmol, 1 equiv) in dimethyl sulfoxide (1.72 mL) and deionized water (172 μL) at 23 ºC. After 25 min, the light-yellow homogeneous solution was diluted with a saturated aqueous sodium chloride solution (20 mL) and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 20 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 40% acetone in hexanes) to afford sulfonamide **S7** as a colorless film, contaminated with a trace amount of (–)-**3**. This mixture was used directly in the next step without further purification.

A degassed solution of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 19.0 mg, 68.8 μmol, 4.00 equiv) in *N*,*N*-dimethylformamide (175 μL) was added to a degassed solution of sulfonamide **S7** (1 equiv) in *N*,*N*-dimethylformamide (400 μL) at 23 ºC. The flask was then immersed in a preheated oil bath at 45 ºC. After 2 h, the solution was cooled to 23 ºC and a saturated aqueous sodium chloride solution (10 mL) and deionized water (5 mL) were added and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 50→60% ethyl acetate in dichloromethane) to afford (–)-communesin E (**3**, 6.14 mg, 80.9% over two steps) as an off-white film. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 21 °C, 11:1 mixture of atropisomers, *denotes minor atropisomer):

δ 7.02 (ddd, *J* = 7.6, 6.4, 2.7 Hz, 2H, C6'**H**, C6'**H***), 6.85 (app-t, *J* = 7.6 Hz, 1H, C6**H**), 6.84 (app-t, *J* = 7.6 Hz, 1H, C6**H***), 6.75–6.66 (m, 5H, C4'**H**, C5'**H**, C5'**H***, C7'**H**, C7'**H***), 6.64 (d, *J* = 7.5 Hz, 1H, C4'**H***), 6.22 (d, *J* = 7.6 Hz, 1H, C7**H**), 6.21 (d, *J* = 7.9 Hz, 1H, C5**H***), 6.19 (d, *J* = 7.1 Hz, 1H, C7**H***), 6.17 (d, *J* = 7.6 Hz, 1H, C5**H**), 5.41 (s, 1H, C8a'**H***), 5.03 (d, *J* = 1.8 Hz, 1H, C8a'**H**), 5.01 (s, 1H, C8a**H**), 4.52 (d, *J* = 8.5 Hz, 1H, C9**H***), 4.28 (br-s, 1H, N8**H**/N8'**H**), 4.20 (br-s, 1H, N8**H**/N8'**H**), 4.09 (d, *J* = 9.2 Hz, 1H, C9**H**), 3.89 (app-dd, *J* = 11.9, 8.2 Hz, 1H, C2'$\mathbf{H}_a$), 3.76–3.67 (m, 1H, C2'$\mathbf{H}_a$*), 3.60–3.50 (m, 1H, C2$\mathbf{H}_a$*), 3.50–3.42 (m, 1H, C2$\mathbf{H}_a$), 3.36 (app-dt, *J* = 15.9, 8.9 Hz, 2H, C2$\mathbf{H}_b$, C2$\mathbf{H}_b$*), 3.19–3.08 (m, 1H, C2'$\mathbf{H}_b$*), 3.03 (app-td, *J* = 11.6, 7.3 Hz, 1H, C2'$\mathbf{H}_b$), 2.98–2.89 (m, 1H, C3'$\mathbf{H}_a$*), 2.86 (d, *J* = 9.2 Hz, 1H, C10**H**), 2.80 (d, *J* = 8.9 Hz, 1H, C10**H***), 2.74 (ddd, *J* = 13.4, 11.6, 8.9 Hz, 1H, C3'$\mathbf{H}_a$), 2.42–2.34 (m, 1H,

C3**H**$_a$), 2.34 (s, 3H, C2"**H**$_3$), 2.33–2.25 (m, 1H, C3**H**$_b$), 2.08 (s, 3H, C2"**H**$_3$*), 2.02 (app-dd, J = 12.8, 7.6 Hz, 1H, C3'**H**$_b$*), 1.94 (app-dd, J = 13.1, 6.7 Hz, 1H, C3'**H**$_b$), 1.58 (s, 3H, C13**H**$_3$*), 1.53 (s, 3H, C13**H**$_3$), 1.39 (s, 3H, C12**H**$_3$), 1.37 (s, 3H, C12**H**$_3$*).

^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, 11:1 mixture of atropisomers, *denotes minor atropisomer):
δ 172.2 (**C**1"), 171.5 (**C**1"*), 149.8 (**C**7a), 142.7 (**C**7a'*), 142.6 (**C**7a'), 137.6 (**C**4), 133.0 (**C**4a), 131.9 (**C**4a'), 128.8 (**C**6), 128.7 (**C**6*), 127.5 (**C**6'), 127.3 (**C**6'*), 123.6 (**C**4'*), 123.3 (**C**4'), 120.9 (**C**5'*), 120.5 (**C**5'), 117.3 (**C**7'*), 117.0 (**C**7'), 116.1 (**C**5*), 115.5 (**C**5), 106.3 (**C**7), 106.0 (**C**7*), 80.0 (**C**8a'), 78.1 (**C**8a'*), 77.2 (**C**8a), 65.6 (**C**9), 65.2 (**C**9*), 64.1 (**C**10), 59.9 (**C**11), 52.5 (**C**3a), 52.0 (**C**3a'), 46.1 (**C**2'*), 44.2 (**C**2'), 38.3 (**C**3), 37.9 (**C**2*), 36.3 (**C**2), 32.6 (**C**3'*), 30.9 (**C**3'), 25.0 (**C**12), 24.9 (**C**12*), 23.2 (**C**2"*), 22.8 (**C**2"), 20.6 (**C**13), 20.5 (**C**13*).

FTIR (thin film) cm^{-1}: 3341 (br-m), 3051 (w), 3028 (w), 2962 (m), 2926 (m), 2879 (m), 1631 (s), 1605 (s), 1481 (m), 1460 (m), 1403 (s), 1348 (m), 1250 (m), 1166 (m), 1084 (m), 1062 (m), 1015 (m), 747 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{27}H_{31}N_4O_2$ $[M+H]^+$: 443.2442,
found: 443.2439.

$[\alpha]_D^{23}$: –191 (c = 0.31, $CHCl_3$).[41]

TLC (50% ethyl acetate in dichloromethane), R*f*: 0.11 (UV, CAM).

41. Literature value: $[\alpha]_D^{20}$ = –156 (c =0.11, $CHCl_3$), see Hayashi, H.; Matsumoto, H.; Akiyama, K. *Biosci. Biotechnol. Biochem.* **2004**, *68*, 753.

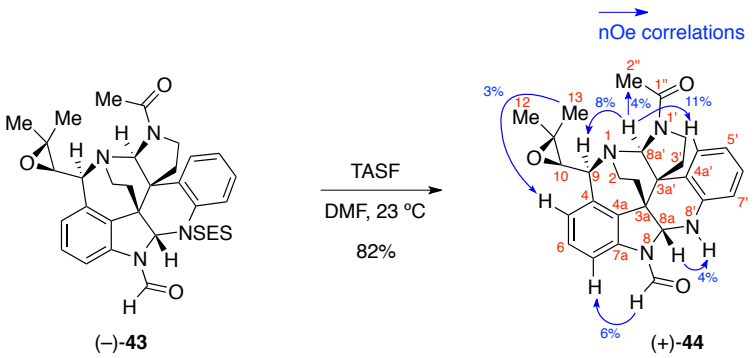
Table S3. Comparison of our ^{1}H NMR data for (–)-communesin E (3) with literature data ($CDCl_3$, major atropisomer):

Assignment	**Hayashi's Isolation Report**[36,37] (–)-Communesin E (**3**) ^{1}H NMR, $CDCl_3$	**This Work** (–)-Communesin E (**3**) ^{1}H NMR, 500 MHz, $CDCl_3$
C2	3.46 (ddd, *J* = 15.9, 8.9, 1.8 Hz, 1H) 3.36 (dt, *J* = 15.9, 9.2 Hz, 1H)	3.50–3.42 (m, 1H) 3.36 (app-dt, *J* = 15.9, 8.9 Hz, 1H)
C3	2.37 (ddd, *J* = 12.8, 9.2, 1.8 Hz, 1H) 2.30 (ddd, *J* = 12.8, 9.2, 8.9 Hz, 1H)	2.42–2.34 (m, 1H) 2.33–2.25 (m, 1H)
C3a	–	–
C4a	–	–
C4	–	–
C5	6.17 (d, *J* = 7.6 Hz, 1H)	6.17 (d, *J* = 7.6 Hz, 1H)
C6	6.85 (d, *J* = 7.6 Hz, 1H)	6.85 (d, *J* = 7.6 Hz, 1H)
C7	6.22 (d, *J* = 7.6 Hz, 1H)	6.22 (d, *J* = 7.6 Hz, 1H)
C7a	–	–
C8a	5.02 (s, 1H)	5.01 (s, 1H)
C9	4.10 (d, *J* = 9.1 Hz, 1H)	4.09 (d, *J* = 9.2 Hz, 1H)
C10	2.87 (d, *J* = 9.1 Hz, 1H)	2.86 (d, *J* = 9.2 Hz, 1H)
C11	–	–
C12	1.39 (s, 3H)	1.39 (s, 3H)
C13	1.54 (s, 3H)	1.53 (s, 3H)
C2'	3.90 (dd, *J* = 11.6, 8.6 Hz, 1H) 3.03 (td, *J* = 11.6, 7.3 Hz, 1H)	3.89 (app-dd, *J* = 11.9, 8.2 Hz, 1H) 3.03 (app-td, *J* = 11.6, 7.3 Hz, 1H)
C3'	2.74 (ddd, *J* = 13.4, 11.6, 8.6 Hz, 1H) 1.95 (dd, *J* = 13.4, 7.3 Hz, 1H)	2.74 (ddd, *J* = 13.4, 11.6, 8.9 Hz, 1H) 1.94 (app-dd, *J* = 13.1, 6.7 Hz, 1H)
C3a'	–	–
C4a'	–	–
C4'	6.71 (m, 3H)	6.75–6.66 (m, 3H)
C5'	6.71 (m, 3H)	6.75–6.66 (m, 3H)
C6'	7.02 (ddd, *J* = 7.9, 6.7, 2.1 Hz, 1H)	7.02 (ddd, *J* = 7.6, 6.4, 2.7 Hz, 1H)
C7'	6.71 (m, 3H)	6.75–6.66 (m, 3H)
C7a'	–	–
C8a'	5.04 (s, 1H)	5.03 (d, *J* = 1.8 Hz, 1H)
C1"	–	–
C2"	2.35 (s, 3H)	2.34 (s, 3H)
N8H / N8'H	–	4.28 (br-s, 1H)
N8H / N8'H	–	4.20 (br-s, 1H)

Table S4. Comparison of our ^{13}C NMR data for (–)-communesin E (3) with literature data ($CDCl_3$, major atropisomer):

Assignment	**Hayashi's Isolation Report**[36,37] (–)-Communesin E (**3**) ^{13}C NMR, $CDCl_3$	**This Work** (–)-Communesin E (**3**) ^{13}C NMR, 150.9 MHz, $CDCl_3$	**Chemical Shift Difference** $\Delta\delta = \delta$ (this work) – δ (Hayashi report)
C2	36.2	36.3	0.1
C3	38.1	38.3	0.2
C3a	51.8	**52.5**	**0.7**[42]
C4a	132.8	133.0	0.2
C4	137.4	137.6	0.2
C5	115.2	115.4	0.2
C6	128.7	128.8	0.1
C7	106.1	106.3	0.2
C7a	149.6	149.8	0.2
C8a	77.0	77.2	0.2
C9	65.4	65.6	0.2
C10	64.0	64.1	0.1
C11	59.8	59.9	0.1
C12	24.8	25.0	0.2
C13	20.5	20.6	0.1
C2'	44.1	44.2	0.1
C3'	30.7	30.9	0.2
C3a'	52.8	**52.0**	**–0.8**[42]
C4a'	131.6	131.9	0.3
C4'	123.1	123.3	0.2
C5'	120.3	120.5	0.2
C6'	127.3	127.5	0.2
C7'	116.9	117.1	0.2
C7a'	142.5	142.6	0.1
C8a'	79.8	80.0	0.2
C1"	172.1	172.2	0.1
C2"	22.7	22.8	0.1

42. Our revised assignment of C3a and C3a' resonances is supported by key gHMBC correlations (^1H,^{13}C) in ppm: (6.75–6.66, 52.00), (3.89,52.00), (6.17,52.54), and (3.46,52.54).

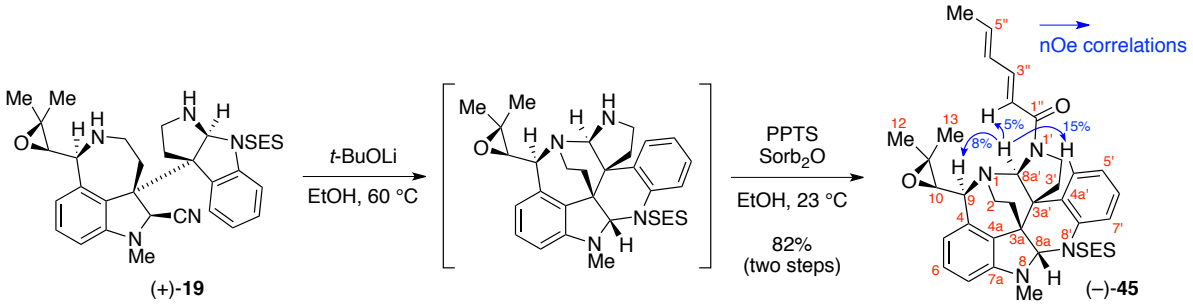


(+)-*N*8-Formyl communesin E (44):

A solution of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 16.7 mg, 60.5 μmol, 4.00 equiv) in *N*,*N*-dimethylformamide (200 μL) was added to a solution of heptacyclic formamide (–)-**43** (9.60 mg, 15.1 μmol, 1 equiv) in *N*,*N*-dimethylformamide (300 μL) at 23 ºC. After 2 h, a saturated aqueous sodium chloride solution (10 mL) and deionized water (5 mL) were added and the mixture was extracted with ethyl acetate (3 × 8 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 40%→50% acetone in hexanes) to afford (+)-*N*8-formyl communesin E (**44**, 5.83 mg, 81.9%) as a white solid. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, 48 : 8.9* : 1** mixture of atropisomers, * and ** denote minor atropisomers): δ 8.91 (d, *J* = 0.8 Hz, 1H, N8C**H**O), 8.89 (s, 1H, N8C**H**O*), 8.70 (s, 1H, N8C**H**O**), 7.09–6.99 (m, 4H, C6**H**, C6**H***, C6'**H**, C6'**H***), 6.81 (d, *J* = 7.9 Hz, 1H, C7**H**), 6.76 (d, *J* = 8.1 Hz, 1H, C7**H***), 6.74 (td, *J* = 7.5, 1.4 Hz, 2H, C5'**H**, C5'**H***), 6.72–6.67 (m, 3H, C4'**H**, C7'**H**, C7'**H***), 6.63 (d, *J* = 7.6 Hz, 1H, C4'**H***), 6.62 (d, *J* = 8.1 Hz, 1H, C5**H***), 6.59 (d, *J* = 7.8 Hz, 1H, C5**H**), 5.55 (app-t, *J* = 1.4 Hz, 1H, C8a**H**), 5.52 (d, *J* = 2.3 Hz, 1H, C8a**H***), 5.43 (d, *J* = 2.0 Hz, 1H, C8a**H****), 5.42–5.36 (m, 2H, C8a'**H***, N8'**H**), 5.05 (s, 1H, C8a'**H****), 5.02 (d, *J* = 1.7 Hz, 1H, C8a'**H**), 4.61–4.52 (m, 1H, C9**H***), 4.16 (d, *J* = 8.9 Hz, 1H, C9**H**), 3.91 (app-dd, *J* = 11.9, 8.4 Hz, 1H, C2'**H**$_a$), 3.72 (app-t, *J* = 8.9 Hz, 1H, C2'**H**$_a$*), 3.57–3.51 (m, 1H, C2**H**$_a$*), 3.48 (app-dd, *J* = 15.9, 9.6 Hz, 1H, C2**H**$_a$), 3.44–3.34 (m, 2H, C2**H**$_b$, C2**H**$_b$*), 3.14 (app-td, *J* = 10.8, 7.5 Hz, 1H, C2'**H**$_b$*), 3.00 (app-td, *J* = 11.6, 7.2 Hz, 1H, C2'**H**$_b$), 2.98–2.90 (m 1H, C3'**H**$_a$*), 2.84 (d, *J* = 8.9 Hz, 1H, C10**H**), 2.80–2.70 (m, 2H, C10**H***, C3'**H**$_a$), 2.52–2.45 (m, 1H, C3**H**$_a$*), 2.49 (ddd, *J* = 13.3, 8.7, 2.0 Hz, 1H, C3**H**$_a$), 2.36–2.25 (m, 2H, C3**H**$_b$, C3**H**$_b$*), 2.33 (s, 3H, C2"**H**$_3$), 2.12 (dd, *J* = 13.4, 7.0 Hz, 1H, C3'**H**$_b$*), 2.10 (s, 3H, C2"**H**$_3$*), 2.06 (dd, *J* = 13.4, 6.8 Hz, 1H, C3'**H**$_b$), 1.58 (br-s, 3H, C13**H**$_3$*), 1.55 (s, 3H, C13**H**$_3$), 1.40 (s, 3H, C12**H**$_3$), 1.38 (s, 3H, C12**H**$_3$*).

^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, 48 : 8.9* : 1 mixture of atropisomers, * denotes minor atropisomer):	δ 171.9 (**C**1''), 170.9 (**C**1''*), 158.2 (2C, N8**C**HO*, N8**C**HO), 141.7 (**C**7a'*), 141.5 (**C**7a'), 140.5 (**C**7a), 140.3 (**C**7a*), 139.4 (**C**4), 135.2 (**C**4a), 135.0 (**C**4a*), 131.6 (**C**4a'*), 131.2 (**C**4a'), 129.1 (**C**6), 128.9 (**C**6*), 128.0 (**C**6'), 127.8 (**C**6'*), 123.4 (**C**4'*), 123.2 (**C**4'), 122.5 (**C**5*), 121.9 (**C**5), 121.4 (**C**5'*), 121.1 (**C**5'), 117.4 (2C, **C**7'*, **C**7'), 106.5 (**C**7), 106.1 (**C**7*), 79.3 (**C**8a'), 77.8 (**C**8a*), 77.5 (**C**8a'*), 77.4 (**C**8a), 65.3 (**C**9), 64.9 (**C**9*), 63.9 (2C, **C**10, **C**10*), 60.0 (**C**11), 59.9 (**C**11*), 51.9 (**C**3a'), 50.9 (**C**3a), 50.8 (**C**3a*), 49.6 (**C**3a'*), 45.9 (**C**2'*), 44.1 (**C**2'), 38.0 (**C**3*), 37.8 (**C**3), 37.6 (**C**2*), 36.3 (**C**2), 32.5 (**C**3'*), 30.8 (**C**3'), 24.9 (**C**12), 24.8 (**C**12*), 23.1 (**C**2''*), 22.8 (**C**2''), 20.6 (**C**13), 20.4 (**C**13*).
FTIR (thin film) cm^{-1}:	3292 (br-w), 3056 (w), 2978 (w), 2959 (w), 2926 (w), 2876 (w), 1662 (s), 1640 (s), 1585 (m), 1495 (m), 1466 (m), 1415 (s), 1346 (m), 1254 (m), 750 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{28}H_{31}N_4O_3$ $[M+H]^+$: 471.2391, found: 471.2392.
$[\alpha]_D^{23}$:	+60 (*c* = 0.29, $CHCl_3$).
TLC (40% acetone in hexanes), R*f*:	0.11 (UV, CAM).



(–)-*N*8'-(Trimethylsilyl)ethanesulfonyl communesin B (45):

A sample of lithium *tert*-butoxide (21.5 mg, 268 μmol, 10.0 equiv) was added to a solution of heterodimer (+)-**19** (16.3 mg, 26.8 μmol, 1 equiv) in anhydrous ethanol (200 proof, 700 μL) at 23 ºC. The flask was sealed with a Teflon-lined glass stopper under an argon atmosphere and was immersed in a preheated oil bath at 60 ºC. After 20 h, the reaction mixture was cooled to 23 ºC and samples of pyridinium *p*-toluenesulfonate (PPTS, 54.0 mg, 215 μmol, 8.00 equiv) and sorbic anhydride[43] (22.1 mg, 107 μmol, 4.00 equiv) were added sequentially. After 30 min, a saturated aqueous sodium bicarbonate solution (10 mL) and deionized water (10 mL) were added and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 35%→40% ethyl acetate in hexanes) to afford (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin B (**45**, 14.8 mg, 82.1%) as a white solid. Crystals suitable for X-ray diffraction were obtained by slow evaporation a solution of (–)-**45** in ethanol at 0 ºC. The thermal ellipsoid representation of (–)-**45** is depicted later in this document. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (600 MHz, $CDCl_3$, 20 °C, 6.8:1 mixture of atropisomers, *denotes minor atropisomer):
δ 7.57 (dd, *J* = 8.0, 1.2 Hz, 1H, C7'**H**), 7.41 (d, *J* = 8.0 Hz, 1H, C7'**H***), 7.32 (dd, *J* = 15.1, 10.5 Hz, 2H, C3"**H**, C3"**H***), 7.17 (app-td, *J* = 7.7, 1.4 Hz, 2H, C6'**H**, C6'**H***), 7.02 (app-td, *J* = 7.6, 1.3 Hz, 2H, C5'**H**, C5'**H***), 6.91 (t, *J* = 7.7 Hz, 1H, C6**H**), 6.90 (t, *J* = 7.4 Hz, 1H, C6**H***), 6.80 (dd, *J* = 7.9, 1.4 Hz, 1H, C4'**H**), 6.77 (app-d, *J* = 7.8 Hz, 1H, C4'**H***), 6.48 (d, *J* = 15.1 Hz, 1H, C2"**H**), 6.24–6.09 (m, 6H, C4"**H**, C4"**H***, C5"**H**, C5"**H***, C5**H**, C5**H***), 6.08 (d, *J* = 16.2 Hz, 1H, C2"**H***), 5.98 (d, *J* = 7.8 Hz, 1H, C7**H**), 5.94 (d, *J* = 7.7 Hz, 1H, C7**H***), 5.73 (s, 1H, C8a**H**), 5.65 (s, 1H, C8a**H***), 5.54 (app-s, 1H, C8a'**H***), 5.13 (app-s, 1H, C8a'**H**), 4.58–4.50 (m, 1H, C9**H***), 4.18

43. The reagent was prepared as follows: oxalyl chloride (2.18 mL, 25 mmol, 1 equiv) was added dropwise to a solution of sorbic acid (5.61 g, 50 mmol, 2.00 equiv), triethylamine (6.97 mL, 50 mmol, 2.00 equiv), and *N*,*N*-dimethylformamide (19.0 μL, 250 μmol, 0.0100 equiv) in dichloromethane (250 mL) at 0 ºC, during which time gentle gas evolution was noted. After 20 min, the ice bath was removed and the solution was allowed to stir at 23 ºC. After 6 h, the mixture was diluted with a saturated aqueous ammonium chloride solution (200 mL) and deionized water (100 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (2 × 100 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (250 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: 60→80% dichloromethane in pentane) to afford sorbic anhydride (4.41 g, 85.4%) as a pale-yellow oil, which solidified on standing to an off-white waxy solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.43–7.30 (m, 2H), 6.32–6.17 (m, 4H), 5.81 (d, *J* = 15.2 Hz, 2H), 1.89 (d, *J* = 5.1 Hz, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$): 163.0, 148.9, 142.4, 129.8, 117.8, 19.0. Spectral data were in agreement with those previously reported in the literature: Honda, T.; Namiki, H.; Kudoh, M.; Nagase, H.; Mizutani, H. *Heterocycles* **2003**, *59*, 169.

(d, *J* = 9.0 Hz, 1H, C9**H**), 3.92 (app-dd, *J* = 12.2, 8.5 Hz, 2H, C2'**H**$_a$, C2'**H**$_a$*), 3.61–3.54 (m, 1H, C2**H**$_a$*), 3.50 (app-dd, *J* = 16.0, 9.6 Hz, 1H, C2**H**$_a$), 3.41 (app-dt, *J* = 16.2, 8.6 Hz, 2H, C2**H**$_b$, C$_2$**H**$_b$*), 3.33–3.24 (m, 1H, C2'**H**$_b$*), 3.23 (app-td, *J* = 13.5, 4.6 Hz, 2H, N8'SO$_2$C**H**$_a$, N8'SO$_2$C**H**$_a$*), 3.19–3.10 (m, 3H, C2'**H**$_b$, N8'SO$_2$C**H**$_b$, N8'SO$_2$C**H**$_b$*), 3.08–2.98 (m, 1H, C3'**H**$_a$*), 2.93 (s, 3H, N8C**H**$_3$), 2.88 (d, *J* = 9.0 Hz, 1H, C10**H**), 2.87 (s, 3H, N8C**H**$_3$*), 2.81 (app-td, *J* = 12.0, 8.6 Hz, 2H, C10**H***, C3'**H**$_a$), 2.56–2.44 (m, 2H, C3**H**$_a$, C3**H**$_a$*), 2.30 (app-dt, *J* = 13.1, 9.2 Hz, 2H, C3**H**$_b$, C3**H**$_b$*), 2.12 (app-dd, *J* = 13.3, 7.5 Hz, 1H, C3'**H**$_b$*), 1.93 (app-dd, *J* = 13.0, 7.2 Hz, 1H, C3'**H**$_b$), 1.85 (d, *J* = 6.4 Hz, 3H, C6"**H**$_3$), 1.83 (d, *J* = 6.8 Hz, 3H, C6"**H**$_3$*), 1.64 (s, 3H, C12/13**H**$_3$), 1.60 (s, 3H, C12/13**H**$_3$*), 1.41 (s, 3H, C12/13**H**$_3$), 1.35 (s, 3H, C12/13**H**$_3$*), 1.32–1.20 (m, 2H, N8'SO$_2$CH$_2$C**H**$_2$*), 1.23 (td, *J* = 13.8, 4.4 Hz, 1H, N8'SO$_2$CH$_2$C**H**$_a$), 1.16 (td, *J* = 13.7, 4.5 Hz, 1H, N8'SO$_2$CH$_2$C**H**$_b$), 0.10 (s, 9H, Si(C**H**$_3$)$_3$*), 0.06 (s, 9H, Si(C**H**$_3$)$_3$).

^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, 6.8:1 mixture of atropisomers, *denotes minor atropisomer):

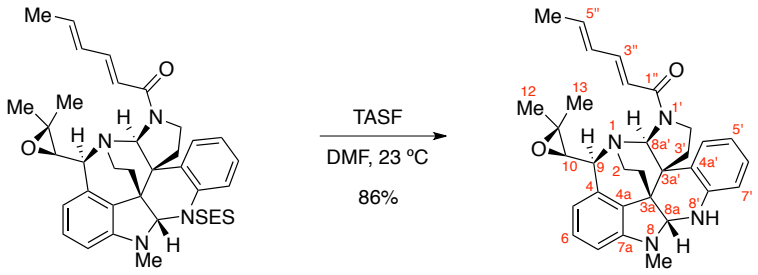
δ 168.2 (**C**1"), 166.5 (**C**1"*), 149.9 (**C**7a), 149.5 (**C**7a*), 143.3 (**C**3"*), 142.3 (**C**3"), 139.0 (2C, **C**4*, **C**4a'*), 138.4 (**C**5"*), 138.1 (**C**4a'), 137.7 (**C**5"), 137.0 (**C**4), 136.0 (2C, **C**7a', **C**7a'*), 131.2 (2C, **C**4a, **C**4a*), 130.7 (**C**4"), 130.3 (**C**4"*), 129.4 (**C**6), 129.2 (**C**6*), 127.9 (**C**6'), 127.7 (**C**6'*), 126.8 (**C**5'*), 126.3 (**C**5'), 125.2 (**C**7'*), 124.6 (**C**7'), 124.4 (**C**4'*), 124.2 (**C**4'), 120.9 (**C**2"), 119.6 (**C**2"*), 114.6 (**C**5*), 113.8 (**C**5), 102.6 (**C**7), 102.3 (**C**7*), 85.2 (**C**8a*), 84.7 (**C**8a), 79.3 (**C**8a'), 78.6 (**C**8a'*), 65.7 (**C**9), 65.3 (**C**9*), 64.0 (**C**10*), 63.9 (**C**10), 59.9 (2C, **C**11*, **C**11), 54.2 (**C**3a), 54.1 (**C**3a*), 52.7 (**C**3a'), 52.4 (N8'SO$_2$**C**H$_2$*), 51.7 (N8'SO$_2$**C**H$_2$), 50.1 (**C**3a'*), 45.2 (**C**2'*), 44.2 (**C**2'), 38.1 (**C**2*), 37.9 (**C**3*), 37.5 (**C**3), 36.3 (**C**2), 33.3 (**C**3'*), 31.4 (**C**3'), 31.0 (N8**C**H$_3$*), 30.9 (N8**C**H$_3$), 25.0 (**C**12/13), 24.9 (**C**12/13*), 20.7 (**C**12/13), 20.6 (**C**12/13*), 18.9 (**C**6"), 18.8 (**C**6"*), 10.8 (N8'SO$_2$CH$_2$**C**H$_2$*), 10.7 (N8'SO$_2$CH$_2$**C**H$_2$), –1.7 (Si(**C**H$_3$)$_3$*), –1.8 (Si(**C**H$_3$)$_3$).

FTIR (thin film) cm^{-1}: 3055 (w), 2956 (m), 1706 (w), 1654 (m), 1627 (m), 1599 (s), 1487 (m), 1391 (s), 1338 (s), 1284 (m), 1250 (m), 1156 (s), 1052 (m), 1000 (m), 859 (m), 760 (m), 564 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{37}H_{49}N_4O_4SSi$ $[M+H]^+$: 673.3238, found: 673.3216.

$[\alpha]_D^{22}$: –60 (*c* = 0.74, CH_2Cl_2).

TLC (40% ethyl acetate in hexanes), R*f*: 0.23 (UV, CAM).



(–)-**45** (–)-**4**

(–)-Communesin B (4):

A solution of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 23.3 mg, 84.6 μmol, 4.00 equiv) in *N*,*N*-dimethylformamide (200 μL) was added to a solution of (–)-*N*8′-(trimethylsilyl)ethanesulfonyl communesin B (**45**, 14.2 mg, 21.2 μmol, 1 equiv) in *N*,*N*-dimethylformamide (500 μL) at 23 ºC. After 2 h, a saturated aqueous sodium chloride solution (10 mL) and deionized water (5 mL) were added and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 30% acetone in hexanes) to afford (–)-communesin B (**4**, 9.27 mg, 86.2%) as a white solid. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, 11:1 mixture of atropisomers, *denotes minor atropisomer):

δ 7.31 (dd, *J* = 15.1, 10.6 Hz, 1H, C3"**H**), 6.98 (ddd, *J* = 7.7, 5.9, 3.0 Hz, 1H, C6'**H**), 6.88 (t, *J* = 7.7 Hz, 1H, C6**H**), 6.74–6.59 (m, 3H, C4'**H**, C5'**H**, C7'**H**), 6.54 (d, *J* = 15.1 Hz, 1H, C2"**H**), 6.19 (ddd, *J* = 14.9, 10.7, 1.6 Hz, 1H, C4"**H**), 6.14–6.04 (m, 2H, C5**H,** C5"**H**), 5.95 (d, *J* = 7.8 Hz, 1H, C7**H**), 5.54 (s, 1H, C8a'**H***), 5.10 (d, *J* = 1.5 Hz, 1H, C8a'**H**), 4.70 (s, 1H, C8a**H**), 4.62 (br-s, 1H, N8'**H**), 4.17 (d, *J* = 9.0 Hz, 1H, C9**H**), 3.87 (app-dd, *J* = 12.1, 8.3 Hz, 1H, C2'$\mathbf{H}_a$), 3.53–3.36 (m, 2H, C2$\mathbf{H}_2$), 3.07 (app-td, *J* = 11.8, 7.0 Hz, 1H, C2'$\mathbf{H}_b$), 2.90 (d, *J* = 9.0 Hz, 1H, C10**H**), 2.85 (s, 3H, N8C$\mathbf{H}_3$), 2.72 (app-td, *J* = 12.4, 8.4 Hz, 1H, C3'$\mathbf{H}_a$), 2.37 (ddd, *J* = 13.0, 8.5, 2.2 Hz, 1H, C3$\mathbf{H}_a$), 2.28 (app-dt, *J* = 12.9, 9.2 Hz, 1H, C3$\mathbf{H}_b$), 1.99 (dd, *J* = 13.1, 6.9 Hz, 1H, C3'$\mathbf{H}_b$), 1.85 (dd, *J* = 6.6, 1.3 Hz, 3H, C6"$\mathbf{H}_3$), 1.65 (s, 3H, C13$\mathbf{H}_3$), 1.42 (s, 3H, C12$\mathbf{H}_3$), 1.37 (s, 3H, C12$\mathbf{H}_3$*).

^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, 11:1 mixture of atropisomers, *denotes minor atropisomer):

δ 168.5 (**C**1"), 150.6 (**C**7a), 142.7 (**C**7a'), 141.9 (**C**3"), 137.3 (**C**5"), 136.7 (**C**4), 132.4 (2C, **C**4a, **C**4a'), 130.8 (**C**4"), 129.0 (**C**6), 127.5 (**C**6'), 123.5 (**C**4'), 121.4 (**C**2"), 120.7 (**C**5'), 116.9 (**C**7'), 113.4 (**C**5), 102.0 (**C**7), 82.5 (**C**8a), 79.1 (**C**8a'), 65.7 (**C**9), 64.1 (**C**10), 59.9 (**C**11), 52.3 (**C**3a'), 51.5 (**C**3a), 44.3 (**C**2'), 38.0 (**C**3), 36.2 (**C**2), 30.6 (**C**3'), 29.7 (N8**C**H_3), 25.0 (**C**12), 24.9 (**C**12*), 20.7 (**C**13), 18.9 (**C**6"), 18.8 (**C**6"*).

FTIR (thin film) cm^{-1}:	3319 (br-w), 3052 (w), 2960 (m), 2926 (m), 2877 (m), 1652 (m), 1625 (m), 1594 (s), 1493 (m), 1474 (m), 1389 (s), 1152 (m), 1000 (s), 737 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{32}H_{37}N_4O_2$ $[M+H]^+$: 509.2911, found: 509.2906.
$[\alpha]_D^{23}$:	–64 (*c* = 0.46, $CHCl_3$).[44]
TLC (30% acetone in hexanes), R*f*:	0.20 (UV, CAM).

44. (a) Literature value: $[\alpha]_D^{22}$ = +8.7 (*c* = 0.23, $CHCl_3$), see Numata, A.; Takahashi, C.; Ito, Y.; Takada, T.; Kawai, K.; Usami, Y.; Matsumura, E.; Imachi, M.; Ito, T.; Hasegawa, T. *Tetrahedron Lett.* **1993**, *34*, 2355. (b) Literature value: $[\alpha]_D$ = –58 (*c* = 0.10, MeOH), see Jadulco, R.; Edrada, R. A.; Ebel, R.; Berg, A.; Schaumann, K.; Wray, V.; Steube, K.; Proksch, P. *J. Nat. Prod.* **2004**, *67*, 78. (c) Literature value: $[\alpha]_D^{20}$ = –74.9 (*c* =1.50, $CHCl_3$), see Hayashi, H.; Matsumoto, H.; Akiyama, K. *Biosci. Biotechnol. Biochem.* **2004**, *68*, 753. (d) Literature value: $[\alpha]_D^{30}$ = –51.3 (*c* = 0.30, $CHCl_3$), see Zuo, Z.; Ma, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 12008.

Table S5. Comparison of our ^{1}H NMR data for (–)-communesin B (4) with literature data ($CDCl_3$, major atropisomer):

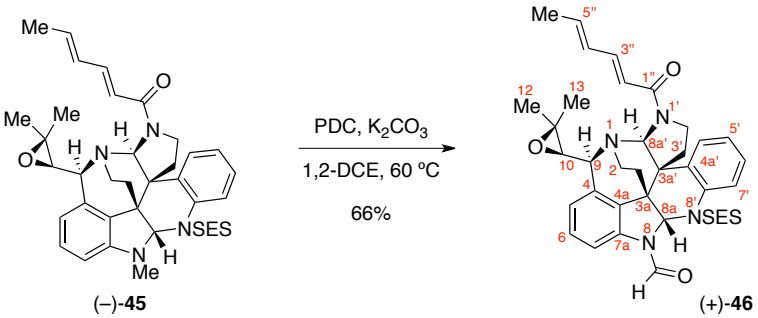
Assignment	Numata's Isolation Report[45,46] (–)-Communesin B (**4**) ^{1}H NMR, 300 MHz, $CDCl_3$	Hayashi's Isolation Report[47,48] (–)-Communesin B (**4**) ^{1}H NMR, $CDCl_3$	Ma's Report[49] (–)-Communesin B (**4**) ^{1}H NMR, 400 MHz, $CDCl_3$	This Work (–)-Communesin B (**4**) ^{1}H NMR, 500 MHz, $CDCl_3$
C2	3.48 (dd, *J* = 16.0, 9.2 Hz, 1H) 3.40 (dt, *J* = 16.0, 8.5 Hz, 1H)	3.47 (ddt, *J* = 15.9, 9.0, 1.0 Hz, 1H) 3.41 (ddd, *J* = 15.9, 9.8, 8.0 Hz, 1H)	3.51–3.38 (m, 2H)	3.53–3.36 (m, 2H)
C3	2.34 (ddd, *J* = 12.8, 9.2, 8.5 Hz, 1H) 2.25 (dd, *J* = 12.8, 8.5 Hz, 1H)	2.37 (ddd, *J* = 12.8, 8.0, 1.0 Hz, 1H) 2.28 (dt, *J* = 12.8, 9.0 Hz, 1H)	2.39–2.33 (m, 1H) 2.31–2.24 (m, 1H)	2.37 (ddd, *J* = 13.0, 8.5, 2.2 Hz, 1H) 2.28 (app-dt, *J* = 12.9, 9.2 Hz, 1H)
C3a	–	–	–	–
C4a	–	–	–	–
C4	–	–	–	–
C5	6.08 (d, *J* = 7.8 Hz, 1H)	6.08 (d, *J* = 7.6 Hz, 1H)	6.14–6.08 (m, 2H)	6.14–6.04 (m, 2H)
C6	6.87 (t, *J* = 7.8 Hz, 1H)	6.88 (t, *J* = 7.6 Hz, 1H)	6.89 (t, *J* = 7.5 Hz, 1H)	6.88 (t, *J* = 7.7 Hz, 1H)
C7	5.95 (d, *J* = 7.8 Hz, 1H)	5.95 (d, *J* = 7.6 Hz, 1H)	5.95 (d, *J* = 8.0 Hz, 1H)	5.95 (d, *J* = 7.8 Hz, 1H)
C7a	–	–	–	
N8CH_3	2.85 (s, 3H)	2.85 (s, 3H)	2.85 (s, 3H)	2.85 (s, 3H)
C8a	4.70 (s, 1H)	4.70 (s, 1H)	4.70 (s, 1H)	4.70 (s, 1H)
C9	4.18 (d, *J* = 9.0 Hz, 1H)	4.18 (d, *J* = 9.0 Hz, 1H)	4.18 (d, *J* = 9.0 Hz, 1H)	4.17 (d, *J* = 9.0 Hz, 1H)
C10	2.90 (d, *J* = 9.0 Hz, 1H)	2.90 (d, *J* = 9.0 Hz, 1H)	2.90 (d, *J* = 9.0 Hz, 1H)	2.90 (d, *J* = 9.0 Hz, 1H)
C11	–	–	–	–
C12	1.42 (s, 3H)	1.42 (s, 3H)	1.42 (s, 3H)	1.42 (s, 3H)
C13	1.65 (s, 3H)	1.65 (s, 3H)	1.65 (s, 3H)	1.65 (s, 3H)
C2'	3.87 (dd, *J* = 12.5, 8.4 Hz, 1H) 3.07 (td, *J* = 12.5, 7.0 Hz, 1H)	3.87 (dd, *J* = 11.9, 8.5 Hz, 1H) 3.07 (dt, *J* = 11.9, 7.0 Hz, 1H)	3.88 (dd, *J* = 12.0, 9.0 Hz, 1H) 3.07 (td, *J* = 11.5, 7.0 Hz, 1H)	3.87 (dd, *J* = 12.1, 8.3 Hz, 1H) 3.07 (app-td, *J* = 11.8, 7.0 Hz, 1H)
C3'	2.71 (td, *J* = 12.5, 8.4 Hz, 1H) 2.00 (dd, *J* = 12.5, 7.0 Hz, 1H)	2.72 (ddd, *J* = 13.1, 11.9, 8.5 Hz, 1H) 2.00 (dd, *J* = 13.1, 7.0 Hz, 1H)	2.76–2.68 (m, 1H) 2.00 (dd, *J* = 13.2, 6.8 Hz, 1H)	2.72 (app-td, *J* = 12.4, 8.4 Hz, 1H) 1.99 (dd, *J* = 13.1, 6.9 Hz, 1H)
C3a'	–	–	–	–

45. Numata, A.; Takahashi, C.; Ito, Y.; Takada, T.; Kawai, K.; Usami, Y.; Matsumura, E.; Imachi, M.; Ito, T.; Hasegawa, T. *Tetrahedron Lett.* **1993**, *34*, 2355.
46. The reference points for the residual protium and carbon resonances of the NMR solvent were not listed.
47. Hayashi, H.; Matsumoto, H.; Akiyama, K. *Biosci. Biotechnol. Biochem.* **2004**, *68*, 753.
48. Resonance frequencies and reference points for the residual protium and carbon resonances of the NMR solvent were not listed.
49. Zuo, Z.; Ma, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 12008.

C4a'	–	–	–	–
C4'	6.66 (d, J = 3.5 Hz, 1H)	6.65 (m, 3H)	6.68–6.66 (m, 3H)	6.74–6.59 (m, 3H)
C5'	6.67 (d, *J* = 7.8 Hz, 1H)	6.65 (m, 3H)	6.68–6.66 (m, 3H)	6.74–6.59 (m, 3H)
C6'	6.98 (ddd, *J* = 7.8, 5.2, 3.5 Hz, 1H)	6.98 (ddd, *J* = 7.6, 5.8, 3.3 Hz, 1H)	7.00–6.97 (m, 1H)	6.98 (ddd, *J* = 7.7, 5.9, 3.0 Hz, 1H)
C7'	6.66 (d, *J* = 5.2 Hz, 1H)	6.65 (m, 3H)	6.68–6.66 (m, 3H)	6.74–6.59 (m, 3H)
C7a'	–	–	–	–
C8a'	5.11 (s, 1H)	5.10 (s, 1H)	5.11 (s, 1H)	5.10 (d, *J* = 1.5 Hz, 1H)
C1"	–	–	–	–
C2"	6.55 (d, *J* = 15.2 Hz, 1H)	6.55 (d, *J* = 15.0 Hz, 1H)	6.55 (d, *J* = 15.0 Hz, 1H)	6.54 (d, *J* = 15.1 Hz, 1H)
C3"	7.32 (dd, *J* = 15.2, 10.1 Hz, 1H)	7.32 (dd, *J* = 15.0, 10.4 Hz, 1H)	7.31 (dd, *J* = 15.5, 10.5 Hz, 1H)	7.31 (dd, *J* = 15.1, 10.6 Hz, 1H)
C4"	6.18 (dd, *J* = 15.5, 10.1 Hz, 1H)	6.19 (dd, *J* = 15.0, 10.4 Hz, 1H)	6.19 (dd, *J* = 15.0, 9.0 Hz, 1H)	6.19 (ddd, *J* = 14.9, 10.7, 1.6 Hz, 1H)
C5"	6.12 (dd, *J* = 15.5, 5.8 Hz, 1H)	6.12 (dq, *J* = 15.0, 6.7 Hz, 1H)	6.14–6.08 (m, 2H)	6.14–6.04 (m, 2H)
C6"	1.85 (d, *J* = 5.8 Hz, 1H)	1.85 (d, *J* = 6.7 Hz, 1H)	1.85 (d, *J* = 6.4 Hz, 1H)	1.85 (dd, *J* = 6.6, 1.3 Hz, 3H)
N8'H	4.60 (br-s, 1H)	4.62 (br-s, 1H)	–	4.62 (br-s, 1H)

Table S6. Comparison of our ^{13}C NMR data for (–)-communesin B (4) with literature data ($CDCl_3$, major atropisomer):

Assignment	**Numata's Isolation Report**[45,46] (–)-Communesin B (**4**) ^{13}C NMR, 75.4 MHz, $CDCl_3$	**Hayashi's Isolation Report**[47,48] (–)-Communesin B (**4**) ^{1}H NMR, $CDCl_3$	**Ma's Report**[49] (–)-Communesin B (**4**) ^{13}C NMR, 100 MHz, $CDCl_3$	**This Work** (–)-Communesin B (**4**) ^{13}C NMR, 150.9 MHz, $CDCl_3$	**Chemical Shift Difference** $\Delta\delta = \delta$ (this work) – δ (Numata's report)
C2	36.03	35.9	36.0	36.16	0.13
C3	37.82	37.7	37.8	37.96	0.14
C3a	51.40	51.3	51.4	51.52	0.12
C4a	132.35	132.1	132.2	132.45	0.10
C4	136.57	136.4	136.6	136.69	0.12
C5	113.23	113.1	113.2	113.35	0.12
C6	128.87	128.8	128.9	128.98	0.11
C7	101.85	101.7	101.9	101.97	0.12
C7a	150.53	150.4	150.5	150.62	0.09
N8$\mathbf{C}H_3$	29.60	29.5	29.6	29.74	0.14
C8a	82.39	82.3	82.4	82.52	0.13
C9	65.55	65.4	65.6	65.67	0.12
C10	63.95	63.8	64.0	64.07	0.12
C11	59.75	59.7	59.8	59.87	0.12
C12	24.89	24.8	24.9	25.02	0.13
C13	20.54	20.5	20.5	20.68	0.14
C2'	44.21	44.1	44.2	44.33	0.12
C3'	30.46	30.3	30.5	30.58	0.12
C3a'	52.14	52.0	52.1	52.26	0.12
C4a'	132.32	132.2	132.2	132.36	0.04
C4'	123.41	123.3	123.4	123.55	0.14
C5'	120.52	120.4	120.5	120.65	0.13
C6'	127.38	127.3	127.4	127.49	0.11
C7'	116.82	116.7	116.8	116.93	0.11
C7a'	142.65	142.5	142.7	142.75	0.10
C8a'	79.00	78.9	79.0	79.11	0.11
C1"	168.43	168.3	168.4	168.52	0.09
C2"	121.27	121.1	121.3	121.39	0.12
C3"	141.83	141.7	141.8	141.93	0.10
C4"	130.72	130.6	130.7	130.84	0.12
C5"	137.13	137.1	137.2	137.26	0.13
C6"	18.71	18.7	18.7	18.85	0.14



(+)-*N*8'-(Trimethylsilyl)ethanesulfonyl communesin D (46):

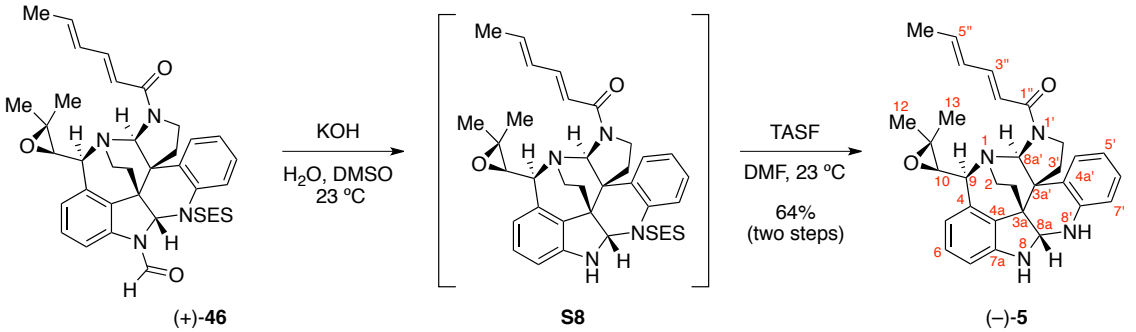
Samples of crushed potassium carbonate (161 mg, 1.17 mmol, 40.0 equiv) and pyridinium dichromate (PDC, 87.7 mg, 233 μmol, 8.00 equiv) were added sequentially to a solution of (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin B (**45**, 19.6 mg, 29.1 μmol, 1 equiv) in 1,2-dichloroethane (1.90 mL) at 23 ºC. The flask was sealed with a Teflon-lined glass stopper under an atmosphere of argon and was immersed in a preheated oil bath at 60 ºC. After stirring for 7 h, the brown suspension was cooled to 23 ºC, was diluted with dichloromethane (5 mL), and was filtered through a pad of silica gel covered with a pad of Celite. The filter cake was washed with acetone–hexanes (1:1, 65 mL) and the colorless filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 40% ethyl acetate in hexanes) to afford (+)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin D (**46**, 13.2 mg, 66.0%) as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, mixture of atropisomers, *denotes minor atropisomers):[50] δ 8.87* (s, 1H), 8.83* (s, 1H), 8.82 (s, 1H), 8.81* (s, 1H), 7.33 (dd, *J* = 15.1, 10.1 Hz, 1H), 7.23–7.13 (m, 2H), 7.11–7.00 (m, 2H), 6.88–6.72 (m, 2H), 6.68–6.59 (m, 1H), 6.51–6.36 (m, 2H), 6.25–6.04 (m, 2H), 5.54* (s, 1H), 5.51* (s. 1H), 5.28* (s, 1H), 5.18* (s, 1H), 5.15* (s, 1H), 5.09 (s, 1H), 4.63* (d, *J* = 6.6 Hz, 1H), 4.27 (d, *J* = 8.2 Hz, 1H), 4.12 (td, *J* = 13.7, 3.7 Hz, 1H), 3.98–3.83 (m, 1H), 3.60–3.35 (m, 3H), 3.30* (q, *J* = 10.1 Hz, 1H), 3.23* (dd, *J* = 10.2, 7.6 Hz, 1H), 3.14 (td, *J* = 12.0, 7.3 Hz, 1H), 3.03* (dt, *J* = 12.7, 9.5 Hz, 1H), 2.82 (d, *J* = 9.0 Hz, 1H), 2.80–2.75* (m, 1H), 2.72* (d, *J* = 8.7 Hz, 1H), 2.71–2.63 (m, 1H), 2.48–2.40* (m, 1H), 2.39–2.24 (m, 2H), 1.85 (d, *J* = 5.6 Hz, 3H), 1.84* (d, *J* = 6.1 Hz, 3H), 1.65 (s, 3H), 1.58* (s, 3H), 1.41 (s, 3H), 1.34* (s, 3H), 1.32–1.13 (m, 2H), 0.15 (s, 9H), 0.08* (s, 9H*).

^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, mixture of atropisomers):[51] δ 168.0, 166.5, 160.6, 159.3, 143.3, 142.7, 142.6, 142.4, 140.2, 139.9, 139.4, 139.2, 138.6, 138.4, 137.8, 135.6, 135.5, 134.5, 134.3, 130.7, 130.4, 129.5, 129.4, 129.2, 128.5, 128.0, 127.9, 127.3, 127.1 (2C), 126.4, 124.7, 124.4, 124.2, 124.0, 123.7, 122.7, 122.1, 120.9, 120.7, 119.6, 114.5, 107.1, 106.6, 79.1, 78.5, 77.4, 76.9, 76.6, 65.4, 65.1, 63.9, 63.7, 59.8, 59.7, 54.8, 54.6, 52.9, 52.7, 52.5, 49.8, 45.2, 44.4, 37.8, 37.1,

50. The reported integrals are an approximation due to the presence of multiple conformers and significant atropisomerism.
51. More than the expected 37 ^{13}C resonances were observed due to the presence of multiple atropisomers. All observed resonances are listed.

	36.7, 36.1, 32.5, 31.0, 30.6, 29.8, 24.9 (2C), 24.8, 20.7, 20.6 (2C), 18.8, 18.7, 10.9, 10.8, –1.7, –1.8.
FTIR (thin film) cm^{-1}:	2956 (m), 2899 (m), 1685 (s), 1656 (s), 1629 (s), 1595 (s), 1486 (s), 1469 (s), 1390 (s), 1343 (s), 1295 (m), 1251 (m), 1158 (s), 1093 (m), 1002 (m), 898 (m), 860 (s).
HRMS (ESI) (*m/z*):	calc'd for $C_{37}H_{47}N_4O_5SSi$ $[M+H]^+$: 687.3031, found: 687.3029.
$[\alpha]_D^{24}$:	+30 (*c* = 0.66, CH_2Cl_2).
TLC (50% ethyl acetate in hexanes), R*f*:	0.26 (UV, CAM).



(–)-Communesin C (5):

An aqueous potassium hydroxide solution (0.5 M, 175 µL, 87.3 µmol, 5.00 equiv) was added rapidly to a solution of (+)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin D (**46**, 12.0 mg, 17.5 µmol, 1 equiv) in dimethyl sulfoxide (1.75 mL) and deionized water (175 µL) at 23 ºC. After 21 min, the light-orange homogeneous solution was diluted with a saturated aqueous sodium chloride solution (20 mL) and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 20 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was filtered through a plug of silica gel (eluent: ethyl acetate) to afford crude sulfonamide **S8** as a pale-yellow solid, which was used directly in the next step without further purification.

A degassed solution of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 19.3 mg, 70.0 µmol, 4.00 equiv) in *N*,*N*-dimethylformamide (180 µL) was added to a degassed solution of crude sulfonamide **S8** (1 equiv) in *N*,*N*-dimethylformamide (400 µL) at 23 ºC. After 2 h, an additional portion of TASF (9.6 mg, 35 µmol, 2.0 equiv) in *N*,*N*-dimethylformamide (90 µL) was added. After 1 h, a saturated aqueous sodium chloride solution (10 mL) and deionized water (5 mL) were added and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 30%→40% acetone in hexanes) to afford (–)-communesin C (**5**, 5.53 mg, 63.8% over two steps) as a white solid. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, DMSO-d_6, 20 °C, 11:1 mixture of atropisomers, major atropisomer):
δ 7.07 (dd, *J* = 15.2, 9.7 Hz, 1H), 6.92 (ddd, *J* = 7.8, 6.2, 2.6 Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.61–6.55 (m, 2H), 6.53 (d, *J* = 15.1 Hz, 1H), 6.21–6.12 (m, 2H), 6.11 (d, *J* = 7.5 Hz, 1H), 6.05 (d, *J* = 7.6 Hz, 1H), 6.03 (d, *J* = 1.5 Hz, 1H), 5.85 (d, *J* = 1.4 Hz, 1H), 5.14 (d, *J* = 1.4 Hz, 1H), 4.84 (s, 1H), 4.19 (d, *J* = 9.0 Hz, 1H), 3.72 (dd, *J* = 11.2, 7.7 Hz, 1H), 3.30 (dd, *J* = 15.5, 9.8 Hz, 1H), 3.19 (dt, *J* = 15.4, 8.6 Hz, 1H), 2.90 (d, *J* = 9.2 Hz, 1H), 2.79 (td, *J* = 11.3, 6.6 Hz, 1H), 2.70 (td, *J* = 12.3, 8.1 Hz, 1H), 2.28 (td, *J* = 8.9, 4.2 Hz, 1H), 2.10 (dt, *J* = 12.8, 9.8 Hz, 1H), 1.82 (d, *J* = 5.3 Hz, 3H), 1.73–1.64 (m, 1H), 1.58 (s, 3H), 1.33 (s, 3H).

^{1}H NMR (600 MHz, $CDCl_3$, 20 °C, 15:1 mixture of atropisomers, *denotes minor atropisomer):
δ 7.32 (dd, *J* = 15.1, 10.8 Hz, 2H, C3"**H**, C3"**H***), 6.99 (ddd, *J* = 7.6, 5.4, 3.6 Hz, 2H, C6'**H**, C6'**H***), 6.85 (app-t, *J* = 7.7 Hz, 1H, C6**H**), 6.70–6.64 (m, 6H, C4'**H**, C4'**H***,

C5'**H**, C5'**H***, C7'**H**, C7'**H***), 6.57 (d, *J* = 14.8 Hz, 1H, C2"**H**), 6.25–6.15 (m, 6H, C5**H**, C5**H***, C7**H**, C7**H***, C4"**H**, C5"**H***), 6.14–6.04 (m, 3H, C2"**H***, C4"**H***, C5"**H**), 5.50 (s, 1H, C8a'**H***), 5.12 (s, 1H, C8a'**H**), 5.01 (s, 1H, C8a**H**), 4.57–4.51 (m, 1H, C9**H***), 4.28 (br-s, 1H, N8**H**/N8'**H**), 4.19 (br-s, 1H, N8**H**/N8'**H**), 4.18 (d, *J* = 9.1 Hz, 1H, C9**H**), 3.88 (app-dd, *J* = 12.3, 8.2 Hz, 1H, C2'$\mathbf{H}_a$), 3.83 (app-t, *J* = 9.2 Hz, 1H, C2'$\mathbf{H}_a$*), 3.57–3.49 (m, 1H, C2$\mathbf{H}_a$*), 3.50–3.38 (m, 2H, C2$\mathbf{H}_2$), 3.42–3.33 (m, 1H, C2$\mathbf{H}_b$*), 3.22–3.15 (m, 1H, C2'$\mathbf{H}_b$*), 3.09 (app-td, *J* = 12.0, 7.2 Hz, 1H, C2'$\mathbf{H}_b$), 2.97–2.91 (m, 1H, C3'$\mathbf{H}_a$*), 2.89 (d, *J* = 9.1 Hz, 1H, C10**H**), 2.80 (d, *J* = 8.7 Hz, 1H, C10**H***), 2.72 (app-td, *J* = 12.9, 8.7 Hz, 1H, C3'$\mathbf{H}_a$), 2.41–2.35 (m, 2H, C3$\mathbf{H}_a$, C3$\mathbf{H}_a$*), 2.29 (app-dt, *J* = 13.0, 9.3 Hz, 2H, C3$\mathbf{H}_b$, C3$\mathbf{H}_b$*), 2.03 (app-dd, *J* = 13.4, 6.8 Hz, 1H, C3'$\mathbf{H}_b$*), 1.97 (app-dd, *J* = 12.8, 6.7 Hz, 1H, C3'$\mathbf{H}_b$), 1.85 (d, *J* = 6.8 Hz, 3H, C6"$\mathbf{H}_3$), 1.83 (d, *J* = 6.6 Hz, 3H, C6"$\mathbf{H}_3$*), 1.65 (s, 3H, C13$\mathbf{H}_3$), 1.62 (s, 3H, C13$\mathbf{H}_3$*), 1.42 (s, 3H, C12$\mathbf{H}_3$), 1.37 (s, 3H, C12$\mathbf{H}_3$*).

^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, 15:1 mixture of atropisomers, *denotes minor atropisomer):

δ 168.6 (**C**1"), 149.8 (**C**7a), 142.9 (**C**3"*), 142.6 (**C**7a'), 142.0 (**C**3"), 137.4 (**C**4), 137.3 (**C**5"), 137.2 (**C**5"*), 133.0 (**C**4a), 131.7 (**C**4a'), 130.9 (2C, **C**4", **C**4"*), 128.8 (**C**6), 127.4 (2C, **C**6', **C**6'*), 123.8 (**C**4'*), 123.5 (**C**4'), 121.4 (**C**2"), 120.5 (**C**5'), 120.0 (**C**2"*), 117.2 (**C**7'*), 116.9 (**C**7'), 116.1 (**C**5*), 115.4 (**C**5), 106.3 (**C**7), 105.9 (**C**7*), 79.3 (**C**8a'), 78.4 (**C**8a'*), 77.1 (**C**8a), 65.7 (**C**9), 65.2 (**C**9*), 64.3 (**C**10*), 64.1 (**C**10), 59.9 (**C**11), 52.5 (**C**3a), 52.2 (**C**3a'), 45.3 (**C**2'*), 44.4 (**C**2'), 38.7 (**C**3*), 38.0 (**C**3), 37.8 (**C**2*), 36.0 (**C**2), 32.5 (**C**3'*), 30.5 (**C**3'), 25.0 (**C**12), 24.9 (**C**12*), 20.6 (2C, **C**13, **C**13*), 18.8 (2C, **C**6", **C**6"*).

FTIR (thin film) cm^{-1}: 3342 (br-m), 3054 (w), 3022 (w), 2963 (m), 2927 (m), 2878 (m), 1651 (s), 1624 (s), 1596 (s), 1482 (m), 1461 (m), 1400 (s), 1338 (m), 1250 (m), 1165 (m), 1062 (m), 1002 (m), 748 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{31}H_{35}N_4O_2$ $[M+H]^+$: 495.2755, found: 495.2760.

$[\alpha]_D^{23}$: –108 (*c* = 0.28, MeOH).[52]

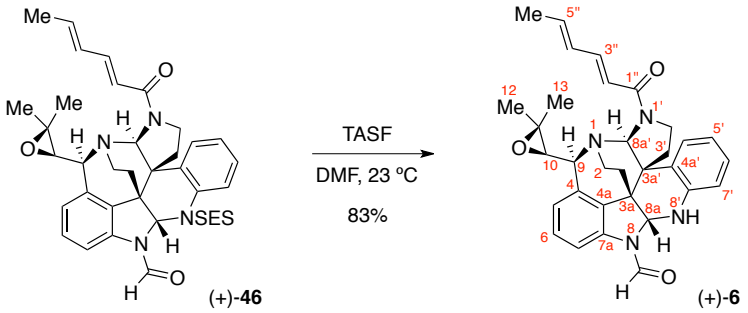
TLC (40% acetone in hexanes), R*f*: 0.26 (UV, CAM).

52. Literature value: $[\alpha]_D$ = –30 (*c* = 0.038, MeOH), see Jadulco, R.; Edrada, R. U.; Ebel, R.; Berg, A.; Schaumann, K.; Wray, V.; Steube, K.; Proksch, P. *J. Nat. Prod.* **2004,** *67,* 78.

Table S7. Comparison of our ^{1}H NMR data for (–)-communesin C (5) with literature data (DMSO-d_6, major atropisomer):

Assignment	**Proksch Isolation Report**[53,54] (–)-Communesin C (**5**) ^{1}H NMR, 500 MHz, DMSO-d_6	**This Work** (–)-Communesin C (**5**) ^{1}H NMR, 500 MHz, DMSO-$d6$
C2	_ [55]	3.30 (dd, J = 15.5, 9.8 Hz, 1H) 3.19 (dt, J = 15.4, 8.6 Hz, 1H)
C3	2.27 (m, 1H) 2.09 (m, 1H)	2.28 (td, J = 8.9, 4.2 Hz, 1H) 2.10 (dt, J = 12.8, 9.8 Hz, 1H)
C3a	–	–
C4a	–	–
C4	–	–
C5	6.10 (d, J = 7.7 Hz, 1H)	6.11 (d, J = 7.5 Hz, 1H)
C6	6.74 (dd, J = 8.2, 7.7 Hz, 1H)	6.74 (t, J = 7.6 Hz, 1H)
C7	6.03 (d, J = 8.2 Hz, 1H)	6.05 (d, J = 7.6 Hz, 1H)
C7a	–	–
C8a	4.83 (s, 1H)	4.84 (s, 1H)
C9	4.18 (d, J = 9.2 Hz, 1H)	4.19 (d, J = 9.0 Hz, 1H)
C10	2.88 (d, J = 9.2 Hz, 1H)	2.90 (d, J = 9.2 Hz, 1H)
C11	–	–
C12	1.55 (s, 3H)	1.58 (s, 3H)
C13	1.32 (s, 3H)	1.33 (s, 3H)
C2'	3.73 (m, 1H) 2.78 (m, 2H)	3.72 (dd, J = 11.2, 7.7 Hz, 1H) 2.79 (td, J = 11.3, 6.6 Hz, 1H)
C3'	2.78 (m, 2H) 1.78 (m, 1H)	2.70 (td, J = 12.3, 8.1 Hz, 1H) 1.73–1.64 (m, 1H)
C3a'	–	–
C4a'	–	–
C4'	6.57 (br-m, 2H)	6.61–6.55 (m, 2H)
C5'	6.57 (br-m, 2H)	6.61–6.55 (m, 2H)
C6'	6.90 (m, 1H)	6.92 (ddd, J = 7.8, 6.2, 2.6 Hz, 1H)
C7'	6.79 (br-d, J = 7.7 Hz, 1H)	6.70 (d, J = 7.9 Hz, 1H)
C7a'	–	–
C8a'	5.12 (s, 1H)	5.14 (d, J = 1.4 Hz, 1H)
C1"	–	–
C2"	6.53 (d, J = 15.1 Hz, 1H)	6.53 (d, J = 15.1 Hz, 1H)
C3"	7.07 (dd, J = 15.1, 10.1 Hz, 1H)	7.07 (dd, J = 15.2, 9.7 Hz, 1H),
C4"	6.16 (m, 2H)	6.21–6.12 (m, 2H)
C5"	6.16 (m, 2H)	6.21–6.12 (m, 2H)
C6"	1.81 (d, J = 5.4 Hz, 3H)	1.82 (d, J = 5.3 Hz, 3H)
N8H / N8'H	–	6.03 (d, J = 1.5 Hz, 1H)
N8H / N8'H	–	5.85 (d, J = 1.4 Hz, 1H)

53. Jadulco, R.; Edrada, R. A.; Ebel, R.; Berg, A.; Schaumann, K.; Wray, V.; Steube, K.; Proksch, P. *J. Nat. Prod.* **2004**, *67*, 78.
54. No ^{13}C-NMR spectroscopic data were tabulated for the natural sample of (–)-**5** in the isolation report. Based on analysis of the ^{1}H-NMR, gCOSY, and HRMS data, the authors state: "It was therefore clear that the new derivative [communesin C] is the *N*-demethyl derivative of [communesin B]."
55. These resonances were reported as concealed by the residual water signal.



(+)-Communesin D (6):

A solution of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 11.9 mg, 43.1 μmol, 4.00 equiv) in *N*,*N*-dimethylformamide (120 μL) was added to a solution of (+)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin D (**46**, 7.40 mg, 10.8 μmol, 1 equiv) in *N*,*N*-dimethylformamide (260 μL) at 23 ºC. After 2 h, a saturated aqueous sodium chloride solution (5 mL) and deionized water (3 mL) were added and the mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 10 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 40%→50% acetone in hexanes) to afford (+)-communesin D (**6**, 4.66 mg, 82.8%) as a white solid. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, 40 : 7.3* : 1** mixture of atropisomers, * and ** denote minor atropisomers): δ 8.92 (d, *J* = 0.9 Hz, 1H, N8C**H**O), 8.89 (s, 1H, N8C**H**O*), 8.70 (s, 1H, N8C**H**O**), 7.33 (dd, *J* = 15.1, 10.1 Hz, 1H, C3"**H**), 7.04 (app-t, *J* = 7.8 Hz, 1H, C6**H**), 7.03–6.99 (m, 2H, C6'**H**, C6'**H***), 6.81 (d, *J* = 7.9 Hz, 1H, C7**H**), 6.77 (d, *J* = 7.9 Hz, 1H, C7**H***), 6.73–6.67 (m, 3H, C5'**H**, C7'**H**, C7'**H***), 6.66 (dd, *J* = 7.7, 1.5 Hz, 1H, C4'**H**), 6.61 (d, *J* = 7.8 Hz, 1H, C5**H**), 6.49 (d, *J* = 15.1 Hz, 1H, C2"**H**), 6.24–6.04 (m, 4H, C2"**H***, C4"**H**, C4"**H***, C5"**H**), 5.57–5.54 (m, 1H, C8a**H**), 5.53 (s, C8a**H***), 5.50 (s, 1H, C8a'**H***), 5.43 (s, 1H, C8a**H****), 5.40–5.38 (m, 1H, N8'**H***), 5.37 (d, *J* = 2.0 Hz, 1H, N8'**H**), 5.13 (s, 1H, C8a'**H****), 5.10 (s, 1H, C8a'**H**), 4.68–4.57 (m, 1H, C9**H***), 4.26 (d, *J* = 8.8 Hz, 1H, C9**H**), 3.89 (app-dd, *J* = 12.1, 8.3 Hz, 2H, C2'$\mathbf{H}_a$, C2'$\mathbf{H}_a$*), 3.59–3.39 (m, 2H, C2$\mathbf{H}_2$), 3.19 (app-q, *J* = 9.2, 1H, C2'$\mathbf{H}_b$*), 3.06 (app-td, *J* = 11.9, 6.9 Hz, 1H, C2'$\mathbf{H}_b$), 2.96 (app-q, *J* = 11.1 Hz, 1H, C3'$\mathbf{H}_a$*), 2.88 (d, *J* = 8.9 Hz, 1H, C10**H**), 2.80–2.74 (m, 1H, C10**H***), 2.73 (app-td, *J* = 12.5, 8.5 Hz, 1H, C3'$\mathbf{H}_a$), 2.49 (d, *J* = 13.4, 8.0, 2.7 Hz, 1H, C3$\mathbf{H}_a$), 2.29 (app-dt, *J* = 13.2, 9.3 Hz, 1H, C3$\mathbf{H}_b$), 2.14 (app-dd, *J* = 13.4, 7.3 Hz, 1H, C3'$\mathbf{H}_b$*), 2.08 (app-dd, *J* = 13.1, 6.9 Hz, 1H, C3'$\mathbf{H}_b$), 1.85 (d, *J* = 6.1 Hz, 3H, C6"**H**), 1.84 (d, *J* = 6.2 Hz, 3H, C6"**H***), 1.66 (s, 3H, C13$\mathbf{H}_3$), 1.60 (s, 3H, C13$\mathbf{H}_3$*), 1.44 (s, 3H, C12$\mathbf{H}_3$), 1.37 (s, 3H, C12$\mathbf{H}_3$*).

^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, 40 : 7.3* : 1 mixture of atropisomers, * denotes minor observed atropisomer):	δ 168.4 (**C**1"), 166.9 (**C**1"*), 158.2 (N8**C**HO), 143.3 (**C**3"*), 142.3 (**C**3"), 141.6 (**C**7a'*), 141.5 (**C**7a'), 140.5 (**C**7a), 140.3 (**C**7a*), 139.2 (**C**4), 138.5 (**C**5"*), 137.7 (**C**5"), 135.3 (**C**4a), 135.0 (**C**4a*), 131.6 (**C**4a'*), 131.0 (**C**4a'), 130.7 (**C**4"), 130.3 (**C**4"*), 129.1 (**C**6), 129.0 (**C**6*), 128.0 (**C**6'), 127.8 (**C**6'*), 123.6 (**C**4'*), 123.4 (**C**4'), 122.5 (**C**5*), 121.9 (**C**5), 121.4 (**C**5'*), 121.1 (**C**5'), 121.0 (**C**2"), 119.6 (**C**2"*), 117.4 (**C**7'*), 117.2 (**C**7'), 106.5 (**C**7), 106.1 (**C**7*), 78.7 (**C**8a'), 77.9 (**C**8a'*), 77.8 (**C**8a*), 77.4 (**C**8a), 65.4 (**C**9), 65.0 (**C**9*), 64.0 (**C**10*), 63.8 (**C**10), 59.9 (**C**11), 52.1 (**C**3a'), 50.9 (**C**3a), 50.8 (**C**3a*), 49.5 (**C**3a'*), 45.1 (**C**2'*), 44.2 (**C**2'), 37.7 (**C**3), 36.0 (**C**2), 32.4 (**C**3'*), 30.4 (**C**3'), 25.0 (**C**12), 24.9 (**C**12*), 20.7 (**C**13), 20.5 (**C**13*), 18.9 (**C**6"), 18.8 (**C**6"*).
FTIR (thin film) cm^{-1}:	3378 (br-w), 2961 (w), 2934 (w), 2881 (w), 1651 (s), 1626 (m), 1605 (m), 1590 (m), 1488 (m), 1472 (m), 1403 (m), 1306 (m), 1170 (m), 996 (m), 752 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{32}H_{35}N_4O_3$ $[M+H]^+$: 523.2704, found: 523.2702.
$[\alpha]_D^{23}$:	+151 (*c* = 0.23, $CHCl_3$).[56]
TLC (40% acetone in hexanes), R*f*:	0.24 (UV, CAM).

56. Literature value: $[\alpha]_D^{20}$ = +150 (*c* = 0.14, $CHCl_3$), see Hayashi, H.; Matsumoto, H.; Akiyama, K. *Biosci. Biotechnol. Biochem.* **2004**, *68*, 753.

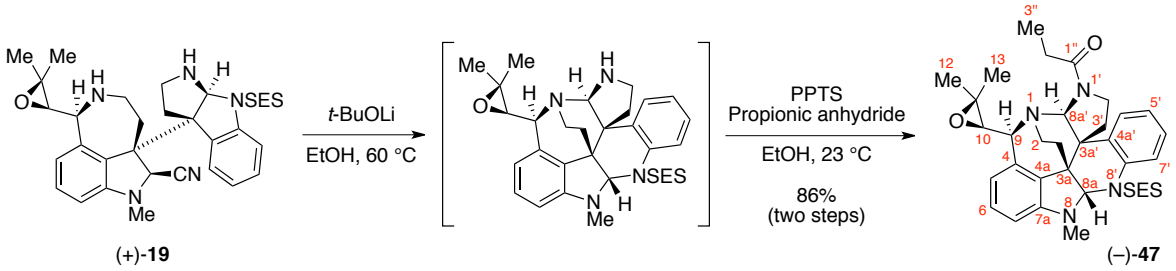
Table S8. Comparison of our ^{1}H NMR data for (+)-communesin D (6) with literature data ($CDCl_3$, major atropisomer):

Assignment	**Hayashi's Isolation Report**[57,58] (+)-Communesin D (**6**) ^{1}H NMR, $CDCl_3$	**This Work** (+)-Communesin D (**6**) ^{1}H NMR, 500 MHz, $CDCl_3$
C2	3.47 (m, 1H) 3.43 (m, 1H)	3.59–3.39 (m, 2H)
C3	2.50 (ddd, *J* = 13.0, 8.0, 2.5 Hz, 1H) 2.30 (dt, *J* = 13.0, 9.0 Hz, 1H)	2.49 (ddd, *J* = 13.4, 8.0, 2.7 Hz, 1H) 2.29 (app-dt, *J* = 13.2, 9.3 Hz, 1H)
C3a	–	–
C4a	–	–
C4	–	–
C5	6.62 (d, *J* = 8.0 Hz, 1H)	6.61 (d, *J* = 7.8 Hz, 1H)
C6	7.04 (t, *J* = 8.0 Hz, 1H)	7.04 (app-t, *J* = 7.8 Hz, 1H)
C7	6.81 (d, *J* = 8.0 Hz, 1H)	6.81 (d, *J* = 7.9 Hz, 1H)
C7a	–	–
N8C**H**O	8.91 (d, *J* = 0.5 Hz, 1H)	8.92 (d, *J* = 0.9 Hz, 1H)
C8a	5.55 (br-d, *J* = 1.0 Hz, 1H)	5.57–5.54 (m, 1H)
C9	4.26 (d, *J* = 9.0 Hz, 1H)	4.26 (d, *J* = 8.8 Hz, 1H)
C10	2.88 (d, *J* = 9.0 Hz, 1H)	2.88 (d, *J* = 8.9 Hz, 1H)
C11	–	–
C12	1.43 (s, 3H)	1.44 (s, 3H)
C13	1.67 (s, 3H)	1.66 (s, 3H)
C2'	3.89 (dd, *J* = 12.0, 8.5 Hz, 1H) 3.06 (dt, *J* = 12.0, 7.0 Hz, 1H)	3.89 (app-dd, *J* = 12.1, 8.3 Hz, 1H) 3.06 (app-td, *J* = 11.9, 6.9 Hz, 1H)
C3'	2.73 (ddd, *J* = 13.0, 8.0, 2.5 Hz, 1H) 2.09 (dd, *J* = 12.5, 7.0 Hz, 1H)	2.73 (app-td, *J* = 12.5, 8.5 Hz, 1H) 2.08 (app-dd, *J* = 13.1, 6.9 Hz, 1H)
C3a'	–	–
C4a'	–	–
C4'	6.69 (dd, *J* = 6.5, 2.0 Hz, 1H)	6.66 (dd, *J* = 7.7, 1.5 Hz, 1H)
C5'	6.70 (td, *J* = 6.5, 2.0 Hz, 1H)	6.73–6.67 (m, 2H)
C6'	7.01 (td, *J* = 6.5, 2.0 Hz, 1H)	7.03–6.99 (m, 1H)
C7'	6.65 (dd, *J* = 6.5, 2.0 Hz, 1H)	6.73–6.67 (m, 2H)
C7a'	–	–
C8a'	5.10 (s, 1H)	5.10 (s, 1H)
C1"	–	–
C2"	6.49 (d, *J* = 15.0 Hz, 1H)	6.49 (d, *J* = 15.1 Hz, 1H)
C3"	7.34 (dd, *J* = 15.0, 10.5 Hz)	7.33 (dd, *J* = 15.1, 10.1 Hz, 1H)
C4"	6.19 (dd, *J* = 16.0, 10.5 Hz, 1H)	6.24–6.04 (m, 2H)
C5"	6.14 (dq, *J* = 16.0, 6.0 Hz, 1H)	6.24–6.04 (m, 2H)
C6"	1.86 (d, *J* = 6.0 Hz, 3H)	1.85 (d, *J* = 6.1 Hz, 3H)
N8'H	5.37 (d, *J* = 1.5 Hz, 1H)	5.40–5.38 (m, 1H)

57. Hayashi, H.; Matsumoto, H.; Akiyama, K. *Biosci. Biotechnol. Biochem.* **2004**, *68*, 753.
58. Resonance frequencies and reference points for the residual protium and carbon resonances of the NMR solvent were not listed.

Table S9. Comparison of our ^{13}C NMR data for (+)-communesin D (6) with literature data ($CDCl_3$, major atropisomer):

Assignment	**Hayashi's Isolation Report**[57,58] (+)-Communesin D (**6**) ^{13}C NMR, $CDCl_3$	**This Work** (+)-Communesin D (**6**) ^{13}C NMR, 150.9 MHz, $CDCl_3$	**Chemical Shift Difference** $\Delta\delta = \delta$ (this work) – δ (Hayashi's report)
C2	35.8	36.0	0.2
C3	37.5	37.7	0.2
C3a	50.7	50.9	0.2
C4a	135.1	135.3	0.2
C4	139.0	139.2	0.2
C5	121.8	121.9	0.1
C6	128.9	129.0	0.2
C7	106.3	106.5	0.2
C7a	140.3	140.5	0.2
N8**C**HO	158.0	158.2	0.2
C8a	77.2	77.4	0.2
C9	65.2	65.4	0.2
C10	63.6	63.8	0.2
C11	59.8	59.9	0.1
C12	24.8	25.0	0.2
C13	20.5	20.7	0.2
C2'	44.0	44.2	0.2
C3'	30.2	30.4	0.2
C3a'	51.9	52.1	0.2
C4a'	130.8	131.0	0.2
C4'	123.2	123.4	0.2
C5'	120.9	121.1	0.2
C6'	127.8	128.0	0.2
C7'	117.0	117.2	0.2
C7a'	141.3	141.5	0.2
C8a'	78.4	78.7	0.3
C1"	168.2	168.4	0.2
C2"	120.8	121.1	0.3
C3"	142.1	142.3	0.2
C4"	130.5	130.7	0.2
C5"	137.5	137.7	0.2
C6"	18.7	18.9	0.2



(+)-**19** (–)-**47**

(–)-*N*8'-(Trimethylsilyl)ethanesulfonyl communesin G (47):

A sample of lithium *tert*-butoxide (14.4 mg, 180 μmol, 10.0 equiv) was added to a solution of heterodimer (+)-**19** (10.9 mg, 18.0 μmol, 1 equiv) in anhydrous ethanol (200 proof, 475 μL) at 23 ºC. The flask was sealed with a Teflon-lined glass stopper under an argon atmosphere and was immersed in a preheated oil bath at 60 ºC. After 21 h, the reaction mixture was cooled to 23 ºC and samples of pyridinium *p*-toluenesulfonate (PPTS, 36.3 mg, 144 μmol, 8.00 equiv) and propionic anhydride (9.5 μL, 74 μmol, 4.1 equiv) were added sequentially. The resulting viscous suspension was diluted with anhydrous ethanol (200 proof, 500 μL). After 30 min, a saturated aqueous sodium bicarbonate solution (8 mL) and deionized water (8 mL) were added and the resulting mixture was extracted with ethyl acetate (3 × 8 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (12 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 50% ethyl acetate in hexanes) to afford (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin G (**47**, 9.80 mg, 85.5%) as a white solid. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, 4.6:1 mixture of atropisomers, *denotes minor atropisomer):

δ 7.56 (dd, *J* = 7.9, 1.2 Hz, 1H, C7'**H**), 7.41 (d, *J* = 8.0, 1H, C7'**H***), 7.19 (app-td, *J* = 7.9, 1.5 Hz, 1H, C6'**H**), 7.18 (app-t, *J* = 7.8 Hz, 1H, C6'**H***), 7.05 (app-td, *J* = 7.6, 1.3 Hz, 1H, C5'**H**), 7.04 (app-t, *J* = 7.6 Hz, 1H, C5'**H***), 6.91 (t, *J* = 7.7 Hz, 2H, C6**H**, C6**H***), 6.81 (dd, *J* = 7.8, 1.5 Hz, 1H, C4'**H**), 6.73 (d, *J* = 7.6 Hz, 1H, C4'**H***), 6.14 (d, *J* = 8.1 Hz, 1H, C5**H***), 6.10 (d, *J* = 7.6 Hz, 1H, C5**H**), 5.97 (d, *J* = 7.8 Hz, 1H, C7**H**), 5.94 (d, *J* = 7.8 Hz, 1H, C7**H***), 5.71 (s, 1H, C8a**H**), 5.63 (s, 1H, C8a**H***), 5.43 (s, 1H, C8a'**H***), 5.07 (s, 1H, C8a'**H**), 4.51 (d, *J* = 8.9 Hz, 1H, C9**H***), 4.10 (d, *J* = 9.0 Hz, 1H, C9**H**), 3.94 (app-dd, *J* = 11.2, 8.8 Hz, 1H, C2'$\mathbf{H}_a$), 3.72 (app-t, *J* = 9.3 Hz, 1H, C2'$\mathbf{H}_a$*), 3.56 (app-dd, *J* = 15.6, 9.9 Hz, 1H, C2$\mathbf{H}_a$*), 3.48 (app-dd, *J* = 16.1, 10.0 Hz, 2H, C2$\mathbf{H}_a$, C2$\mathbf{H}_b$*), 3.41–3.29 (m, 2H, C2$\mathbf{H}_b$, N8'$SO_2C\mathbf{H}_a$*), 3.28–3.20 (m, 1H, N8'$SO_2C\mathbf{H}_b$*), 3.24 (app-td, *J* = 13.4, 5.0 Hz, 1H, N8'$SO_2C\mathbf{H}_a$), 3.22–3.15 (m, 1H, C2'$\mathbf{H}_b$*), 3.16 (app-td, *J* = 13.3, 4.7 Hz, 1H, N8'$SO_2C\mathbf{H}_b$), 3.10 (app-td, *J* = 11.4, 7.6 Hz, 1H, C2'$\mathbf{H}_b$), 3.05–2.96 (m, 1H, C3'$\mathbf{H}_a$*), 2.92 (s, 3H, N8C$\mathbf{H}_3$), 2.91–2.75 (m, 7H, N8C$\mathbf{H}_3$*, C10**H**, C10**H***, C3'$\mathbf{H}_a$, C2"$\mathbf{H}_a$), 2.55–2.44 (m, 2H, C3$\mathbf{H}_a$, $C_3\mathbf{H}_a$*), 2.39 (app-dq, *J* = 14.6, 7.4 Hz, 1H, C2"$\mathbf{H}_b$), 2.34–2.24 (m, 4H, C3$\mathbf{H}_b$, C3$\mathbf{H}_b$*, C2"$\mathbf{H}_2$*), 2.11 (app-dd, *J* = 13.4, 7.4 Hz, 1H, C3'$\mathbf{H}_b$*), 1.91 (app-dd, *J* = 13.2, 6.6 Hz, 1H, C3'$\mathbf{H}_b$), 1.58 (s, 3H, C13$\mathbf{H}_3$*), 1.53 (s, 3H,

C13**H**$_3$), 1.38 (s, 3H, C12**H**$_3$), 1.35 (s, 3H, C12**H**$_3$*), 1.30–1.19 (m, 5H, C3"**H**$_3$, N8'SO$_2$CH$_2$C**H**$_2$), 1.19–1.13 (m, 5H, C3"**H**$_3$*, N8'SO$_2$CH$_2$C**H**$_2$*), 0.10 (s, 9H, Si(C**H**$_3$)$_3$*), 0.06 (s, 9H, Si(C**H**$_3$)$_3$).

^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, 4.6:1 mixture of atropisomers, *denotes minor atropisomer):

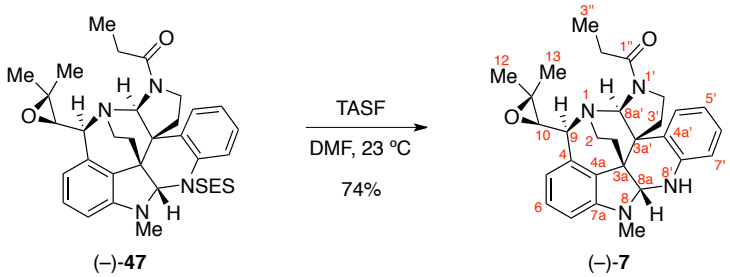
δ 175.0 (**C**1"), 173.6 (**C**1"*), 150.0 (**C**7a), 149.5 (**C**7a*), 139.3 (**C**4a'*), 138.4 (**C**4a'), 137.4 (**C**4), 136.2 (**C**7a'*), 136.1 (**C**7a'), 131.3 (**C**4a), 129.4 (**C**6), 129.2 (**C**6*), 127.9 (**C**6'), 127.7 (**C**6'*), 126.7 (**C**5'*), 126.4 (**C**5'), 125.4 (**C**7'*), 124.8 (**C**7'), 124.3 (**C**4'*), 124.0 (**C**4'), 114.6 (**C**5*), 113.9 (**C**5), 102.6 (**C**7), 102.3 (**C**7*), 85.3 (**C**8a*), 84.8 (**C**8a), 79.4 (**C**8a'), 78.4 (**C**8a'*), 65.4 (**C**9), 65.2 (**C**9*), 64.0 (**C**10*), 63.9 (**C**10), 59.8 (2C, **C**11, **C**11*), 54.2 (2C, **C**3a, **C**3a*), 52.6 (**C**3a'), 52.5 (N8'SO$_2$**C**H$_2$*), 51.8 (N8'SO$_2$**C**H$_2$), 50.2 (**C**3a'*), 45.1 (**C**2'*), 44.3 (**C**2'), 38.0 (2C, **C**3*, **C**2*), 37.8 (**C**3), 36.6 (**C**2), 33.3 (**C**3'*), 31.6 (**C**3'), 31.0 (N8**C**H$_3$*), 30.9 (N8**C**H$_3$), 28.2 (**C**2"*), 27.8 (**C**2"), 24.9 (2C, **C**12, **C**12*), 20.6 (2C, **C**13*, **C**13), 10.8 (N8'SO$_2$CH$_2$**C**H$_2$*), 10.7 (N8'SO$_2$CH$_2$**C**H$_2$), 9.3 (**C**3"), 8.7 (**C**3"*), –1.7 (Si(**C**H$_3$)$_3$*), –1.8 (Si(**C**H$_3$)$_3$).

FTIR (thin film) cm^{-1}: 3055 (w), 2955 (m), 2879 (w), 1650 (m), 1599 (s), 1487 (m), 1408 (m), 1341 (m), 1250 (m), 1157 (m), 1056 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{34}H_{47}N_4O_4SSi$ $[M+H]^+$: 635.3082, found: 635.3085.

$[\alpha]_D^{22}$: –129 (*c* = 0.49, CH_2Cl_2).

TLC (50% ethyl acetate in hexanes), R*f*: 0.19 (UV, CAM).



(–)-Communesin G (7):

A solution of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 12.7 mg, 46.0 μmol, 4.00 equiv) in *N*,*N*-dimethylformamide (180 μL) was added to a suspension of (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin G (**47**, 7.30 mg, 11.5 μmol, 1 equiv) in *N*,*N*-dimethylformamide (200 μL) at 23 °C. After 4 h, a saturated aqueous sodium chloride solution (5 mL) and deionized water (3 mL) were added and the mixture was extracted with ethyl acetate (3 × 8 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 30% acetone in hexanes) to afford (–)-communesin G (**7**, 3.99 mg, 73.8%) as a white solid. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, 8.7:1 mixture of atropisomers, *denotes minor atropisomer):

δ 7.00 (app-td, *J* = 7.6, 1.6 Hz, 2H, C6'**H**, C6'**H***), 6.88 (t, *J* = 7.7 Hz, 2H, C6**H**, C6**H***), 6.73–6.64 (m, 5H, C4'**H**, C5'**H**, C5'**H***, C7'**H**, C7'**H***), 6.60 (d, *J* = 7.0 Hz, 1H, C4'**H***), 6.09 (d, *J* = 7.2 Hz, 1H, C5**H***), 6.06 (d, *J* = 7.6 Hz, 1H, C5**H**), 5.95 (d, *J* = 7.8 Hz, 1H, C7**H**), 5.91 (d, *J* = 7.8 Hz, 1H, C7**H***), 5.30 (app-s, 1H, C8a'**H***), 5.05 (d, *J* = 1.4 Hz, 1H, C8a'**H**), 4.69 (s, 1H, C8a**H**), 4.67 (s, 1H, C8a**H***), 4.58 (br-s, 1H, N8'**H**), 4.50 (d, *J* = 8.5 Hz, 1H, C9**H***), 4.10 (d, *J* = 9.2 Hz, 1H, C9**H**), 3.89 (app-dd, *J* = 11.9, 8.4 Hz, 1H, C2'$\mathbf{H}_a$), 3.70–3.63 (m, 1H, C2'$\mathbf{H}_a$*), 3.54 (app-dd, *J* = 15.4, 9.2 Hz, 1H, C2$\mathbf{H}_a$*), 3.45 (app-dd, *J* = 15.7, 9.5 Hz, 1H, C2$\mathbf{H}_a$), 3.41–3.30 (m, 2H, C2$\mathbf{H}_b$, C2$\mathbf{H}_b$*), 3.12–3.06 (m, 1H, C2'$\mathbf{H}_b$*), 3.02 (app-td, *J* = 11.6, 7.3 Hz, 1H, C2'$\mathbf{H}_b$), 2.96–2.83 (m, 3H, C10**H**, C3'$\mathbf{H}_a$*, C2"$\mathbf{H}_a$), 2.84 (s, 3H, N8C$\mathbf{H}_3$), 2.82 (s, 3H, N8C$\mathbf{H}_3$*), 2.80 (d, *J* = 9.2 Hz, 1H, C10**H***), 2.73 (app-td, *J* = 12.3, 11.3, 8.6 Hz, 1H, C3'$\mathbf{H}_a$), 2.46–2.32 (m, 3H, C3$\mathbf{H}_a$, C3$\mathbf{H}_a$*, C2"$\mathbf{H}_b$), 2.32–2.22 (m, 3H, C3$\mathbf{H}_b$, C3$\mathbf{H}_b$*, C2"$\mathbf{H}_b$*), 2.03 (app-dd, *J* = 13.0, 7.2 Hz, 1H, C3'$\mathbf{H}_b$*), 1.96 (app-dd, *J* = 13.3, 6.7 Hz, 1H, C3'$\mathbf{H}_b$), 1.59 (s, 3H, C13$\mathbf{H}_3$*), 1.54 (s, 3H, C13$\mathbf{H}_3$), 1.38 (s, 3H, C12$\mathbf{H}_3$), 1.36 (s, 3H, C12$\mathbf{H}_3$*), 1.22 (t, *J* = 7.4 Hz, 3H, C3"$\mathbf{H}_3$), 1.16 (t, *J* = 7.3 Hz, 3H, C3"$\mathbf{H}_3$*).

^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, 8.7:1 mixture of atropisomers, *denotes minor atropisomer):

δ 175.3 (**C**1"), 150.7 (**C**7a), 150.6 (**C**7a*), 142.9 (**C**7a'*), 142.8 (**C**7a'), 137.1 (**C**4), 132.7 (**C**4a'), 132.4 (**C**4a), 132.2 (**C**4a*), 129.0 (**C**6), 128.8 (**C**6*), 127.5 (**C**6'),

	127.3 (**C**6'*), 123.6 (**C**4'*), 123.4 (**C**4'), 121.0 (**C**5'*), 120.7 (**C**5'), 117.2 (**C**7'*), 117.1 (**C**7'), 114.0 (**C**5*), 113.4 (**C**5), 101.9 (**C**7), 101.5 (**C**7*), 83.1 (**C**8a*), 82.7 (**C**8a), 79.1 (**C**8a'), 78.1 (**C**8a'*), 65.4 (**C**9), 65.1 (**C**9*), 64.2 (**C**10*), 64.1 (**C**10), 59.8 (**C**11), 52.1 (**C**3a'), 51.6 (**C**3a), 49.8 (**C**3a'*), 45.2 (**C**2'*), 44.3 (**C**2'), 38.5 (**C**3*), 38.2 (**C**3), 37.8 (**C**2*), 36.5 (**C**2), 32.6 (**C**3'*), 30.8 (**C**3'), 29.9 (N8**C**H_3*), 29.8 (N8**C**H_3), 28.3 (**C**2"*), 27.8 (**C**2"), 24.9 (2C, **C**12, **C**12*), 20.6 (2C, **C**13*, **C**13), 9.4 (**C**3"), 8.7 (**C**3"*).
FTIR (thin film) cm^{-1}:	3321 (br-m), 3052 (w), 2963 (m), 2921 (m), 2880 (m), 1641 (m), 1596 (m), 1494 (m), 1409 (m), 1280 (m), 1086 (m), 739 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{29}H_{35}N_4O_2$ $[M+H]^+$: 471.2755, found: 471.2754.
$[\alpha]_D^{23}$:	–163 (*c* = 0.20, MeOH).[59]
TLC (30% acetone in hexanes), R*f*:	0.16 (UV, CAM).

59. Literature value: $[\alpha]_D^{25}$ = –157 (*c* = 0.021, MeOH), see Dalsgaard, P. W.; Blunt, J. W.; Munro, M. H. G.; Frisvad, J. C.; Christophersen, C. *J. Nat. Prod.* **2005**, *68*, 258.

Table S10. Comparison of our ^{1}H NMR data for (–)-communesin G (7) with literature data ($CDCl_3$, major atropisomer):

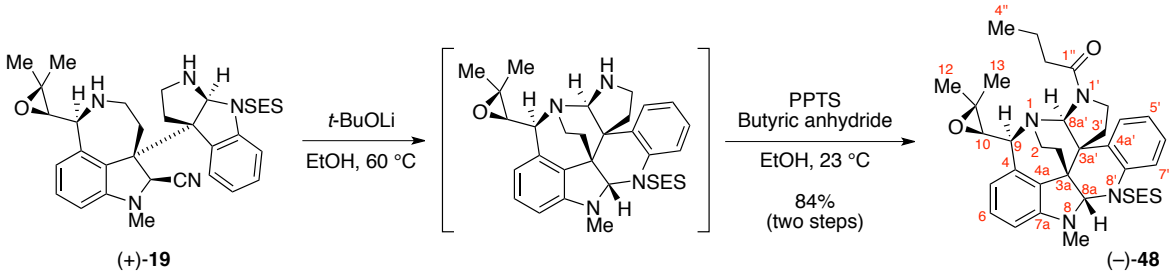
Assignment	**Christophersen's Isolation Report**[60,61] (–)-Communesin G (**7**) ^{1}H NMR, 500 MHz, $CDCl_3$	**This Work** (–)-Communesin G (**7**) ^{1}H NMR, 500 MHz, $CDCl_3$
C2	3.44 (m, 1H) 3.35 (m, 1H)	3.45 (app-dd, *J* = 15.7, 9.5 Hz, 1H) 3.41–3.30 (m, 1H)
C3	2.35 (m, 1H) 2.27 (m, 1H)	2.46–2.32 (m, 2H) 2.32–2.22 (m, 2H)
C3a	–	–
C4a	–	–
C4	–	–
C5	6.06 (d, *J* = 7.5 Hz, 1H)	6.06 (d, *J* = 7.6 Hz, 1H)
C6	6.87 (t, *J* = 7.5 Hz, 1H)	6.88 (t, *J* = 7.7 Hz, 1H)
C7	5.95 (d, *J* = 7.5 Hz, 1H)	5.95 (d, *J* = 7.8 Hz, 1H)
C7a	–	–
N8C**H**$_3$	2.82 (s, 3H)	2.84 (s, 3H)
C8a	4.69 (s, 1H)	4.69 (s, 1H)
C9	4.10 (d, *J* = 9.5 Hz, 1H)	4.10 (d, *J* = 9.2 Hz, 1H)
C10	2.85 (m, 1H)	2.96–2.83 (m, 2H)
C11	–	–
C12	1.37 (s, 3H)	1.38 (s, 3H)
C13	1.54 (s, 3H)	1.54 (s, 3H)
C2'	3.88 (dd, *J* = 12.0, 8.8 Hz, 1H) 3.01 (ddd, *J* = 12.0, 11.7, 6.5 Hz, 1H)	3.89 (app-dd, *J* = 11.9, 8.4 Hz, 1H) 3.02 (app-td, *J* = 11.6, 7.3 Hz, 1H)
C3'	2.73 (ddd, *J* = 13.0, 11.7, 8.8 Hz, 1H) 1.95 (dd, *J* = 13.0, 6.5 Hz, 1H)	2.73 (app-td, *J* = 12.3, 11.3, 8.6 Hz, 1H) 1.96 (app-dd, *J* = 13.3, 6.7 Hz, 1H)
C3a'	–	–
C4a'	–	–
C4'	6.66 (m, 1H)	6.73–6.64 (m, 3H)
C5'	6.68 (m, 1H)	6.73–6.64 (m, 3H)
C6'	6.99 (td, *J* = 8.0, 1.5 Hz, 1H)	7.00 (app-td, *J* = 7.6, 1.6 Hz, 1H)
C7'	6.69 (m, 1H)	6.73–6.64 (m, 3H)
C7a'	–	–
C8a'	5.05 (s, 1H)	5.05 (d, *J* = 1.4 Hz, 1H)
C1"	–	–
C2"	2.88 (m, 1H) 2.42 (m, 1H)	2.96–2.83 (m, 2H) 2.46–2.32 (m, 2H)
C3"	1.22 (t, *J* = 7.5 Hz, 3H)	1.22 (t, *J* = 7.4 Hz, 3H)
N8'H	–	4.58 (br-s, 1H)

60. Dalsgaard, P. W.; Blunt, J. W.; Munro, M. H. G.; Frisvad, J. C.; Christophersen, C. *J. Nat. Prod.* **2005**, *68*, 258.
61. Proton NMR spectra were referenced from the residual protium in the NMR solvent ($CHCl_3$: δ 7.25).

Table S11. Comparison of our ^{13}C NMR data for (–)-communesin G (7) with literature data ($CDCl_3$, major atropisomer):

Assignment	Christophersen's Isolation Report[60,62] (–)-Communesin G (**7**) ^{13}C NMR, 75 MHz $CDCl_3$	This Work (–)-Communesin G (**7**) ^{13}C NMR, 150.9 MHz, $CDCl_3$	Chemical Shift Difference $\Delta\delta = \delta$ (this work) – δ (Christophersen report)
C2	36.3	36.5	0.2
C3	38.0	38.2	0.2
C3a	51.7	51.6	**–0.1**[63]
C4a	132.4	132.4	0.0
C4	136.7	137.1	0.4
C5	113.2	113.4	0.2
C6	128.8	129.0	0.2
C7	101.7	101.9	0.2
C7a	150.5	150.7	0.2
N8**C**H_3	29.6	29.8	0.2
C8a	82.5	82.7	0.2
C9	65.1	65.4	0.3
C10	64.0	64.2	0.2
C11	59.7	59.8	0.1
C12	24.6	24.9	0.3
C13	20.4	20.6	0.2
C2'	44.1	44.3	0.2
C3'	30.5	30.8	0.3
C3a'	51.4	52.1	**0.7**[63]
C4a'	132.5	132.7	0.2
C4'	123.3	123.4	0.1
C5'	117.0	120.7	**3.7**[64]
C6'	127.4	127.5	0.1
C7'	120.6	117.1	**–3.5**[64]
C7a'	142.6	142.8	0.2
C8a'	78.9	79.1	0.2
C1"	175.3	175.3	0.0
C2"	27.6	27.8	0.2
C3"	9.2	9.4	0.2

62. Carbon-13 NMR spectra are referenced from the carbon resonances of the deuterated solvent ($CDCl_3$: δ 77.01)
63. Our revised assignment of C3a and C3a' resonances is supported by key gHMBC correlations (^1H,^{13}C) in ppm: (6.06,51.6), (3.45,51.6), (6.73,52.1), and (3.89,52.1).
64. Our revised assignment of C5' and C7' resonances is supported by a key 4-bond gHMBC correlation (^1H,^{13}C) in ppm: (4.69,117.1).



(–)-*N*8'-(Trimethylsilyl)ethanesulfonyl communesin H (48):

A sample of lithium *tert*-butoxide (21.6 mg, 270 µmol, 10.0 equiv) was added to a solution of heterodimer (+)-**19** (16.3 mg, 27.0 µmol, 1 equiv) in anhydrous ethanol (200 proof, 710 µL) at 23 ºC. The flask was sealed with a Teflon-lined glass stopper under an argon atmosphere and was immersed in a preheated oil bath at 60 ºC. After 23 h, the reaction mixture was cooled to 23 ºC and samples of pyridinium *p*-toluenesulfonate (PPTS, 54.2 mg, 216 µmol, 8.00 equiv) and butyric anhydride (18.0 µL, 108 µmol, 4.00 equiv) were added sequentially. After 40 min, a saturated aqueous sodium bicarbonate solution (10 mL) and deionized water (10 mL) were added and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 45→50% ethyl acetate in hexanes) to afford (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin H (**48**, 14.6 mg, 83.7%) as a white solid. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, 5.9:1 mixture of atropisomers, *denotes minor atropisomer):

δ 7.57 (dd, *J* = 8.0, 1.1 Hz, 1H, C7'**H**), 7.41 (d, *J* = 8.1, 1H, C7'**H***), 7.20–7.16 (m, 1H, C6'**H***), 7.19 (app-td, *J* = 7.8, 1.4 Hz, 1H, C6'**H**), 7.06–7.01 (m, 1H, C5'**H***), 7.05 (dd, *J* = 8.2, 6.9 Hz, 1H, C5'**H**), 6.91 (t, *J* = 7.7 Hz, 1H, C6**H**), 6.89 (t, *J* = 7.8 Hz, 1H, C6**H***), 6.81 (dd, *J* = 7.9, 1.3 Hz, 1H, C4'**H**), 6.75 (d, *J* = 7.9 Hz, 1H, C4'**H***), 6.14 (d, *J* = 8.1 Hz, 1H, C5**H***), 6.10 (d, *J* = 7.6 Hz, 1H, C5**H**), 5.98 (d, *J* = 7.8 Hz, 1H, C7**H**), 5.93 (d, *J* = 7.9 Hz, 1H, C7**H***), 5.71 (s, 1H, C8a**H**), 5.63 (s, 1H, C8a**H***), 5.44 (s, 1H, C8a'**H***), 5.06 (s, 1H, C8a'**H**), 4.51 (d, *J* = 8.4 Hz, 1H, C9**H***), 4.11 (d, *J* = 9.0 Hz, 1H, C9**H**), 3.93 (app-dd, *J* = 12.1, 8.4 Hz, 1H, C2'$\mathbf{H}_a$), 3.74 (app-t, *J* = 9.6 Hz, 1H, C2'$\mathbf{H}_a$*), 3.56 (app-dd, *J* = 15.7, 10.1 Hz, 1H, C2$\mathbf{H}_a$*), 3.48 (app-dd, *J* = 16.1, 9.5 Hz, 1H, C2$\mathbf{H}_a$), 3.36–3.20 (m, 2H, N8'$SO_2C\mathbf{H}_2$*), 3.35 (app-dt, *J* = 15.9, 8.8 Hz, 2H, C2$\mathbf{H}_b$, C2$\mathbf{H}_b$*), 3.24 (app-td, *J* = 13.4, 4.8 Hz, 1H, N8'$SO_2C\mathbf{H}_a$), 3.23–3.19 (m, 1H, C2'$\mathbf{H}_b$*), 3.16 (app-td, *J* = 13.4, 4.8 Hz, 1H, N8'$SO_2C\mathbf{H}_b$), 3.08 (app-td, *J* = 11.4, 7.2 Hz, 1H, C2'$\mathbf{H}_b$), 3.05–2.96 (m, 1H, C3'$\mathbf{H}_a$*), 2.92 (s, 3H, N8C$\mathbf{H}_3$), 2.87 (s, 3H, N8C$\mathbf{H}_3$*), 2.86–2.75 (m, 5H, C10**H**, C10**H***, C3'$\mathbf{H}_a$, C2"$\mathbf{H}_a$, C2"$\mathbf{H}_a$*), 2.48 (app-dd, *J* = 13.0, 8.2 Hz, 2H, C3$\mathbf{H}_a$, C3$\mathbf{H}_a$*), 2.38–2.21 (m, 4H, C3$\mathbf{H}_b$, C3$\mathbf{H}_b$*, C2"$\mathbf{H}_b$, C2"$\mathbf{H}_b$*), 2.10 (app-dd, *J* = 13.3, 7.3 Hz, 1H, C3'$\mathbf{H}_b$*), 1.90 (app-dd, *J* = 13.2, 6.8 Hz, 1H, C3'$\mathbf{H}_b$), 1.84–1.68 (m, 4H, C3"$\mathbf{H}_2$, C3"$\mathbf{H}_2$*),

1.58 (s, 3H, C13**H**$_3$*), 1.55 (s, 3H, C13**H**$_3$), 1.38 (s, 3H, C12**H**$_3$), 1.35 (s, 3H, C12**H**$_3$*), 1.33–1.13 (m, 4H, N8'SO$_2$CH$_2$C**H**$_2$, N8'SO$_2$CH$_2$C**H**$_2$*), 1.01 (t, J = 7.4 Hz, 3H, C4"**H**$_3$), 0.95 (t, J = 7.5 Hz, 3H, C4"**H**$_3$*), 0.10 (s, 9H, Si(C**H**$_3$)$_3$*), 0.06 (s, 9H, Si(C**H**$_3$)$_3$).

^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, 5.9:1 mixture of atropisomers, *denotes minor atropisomer):

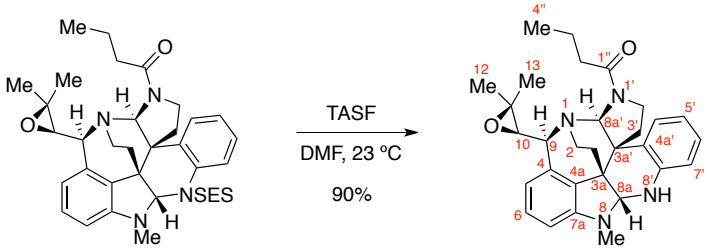
δ 174.3 (**C**1"), 173.0 (**C**1"*), 150.0 (**C**7a), 149.5 (**C**7a*), 139.3 (**C**4a'*), 138.4 (**C**4a'), 137.3 (**C**4), 136.2 (**C**7a'*), 136.1 (**C**7a'), 131.3 (2C, **C**4a, **C**4a*), 129.4 (**C**6), 129.2 (**C**6*), 127.9 (**C**6'), 127.7 (**C**6'*), 126.7 (**C**5'*), 126.4 (**C**5'), 125.4 (**C**7'*), 124.8 (**C**7'), 124.3 (**C**4'*), 124.0 (**C**4'), 114.7 (**C**5*), 113.9 (**C**5), 102.6 (**C**7), 102.3 (**C**7*), 85.3 (**C**8a*), 84.8 (**C**8a), 79.4 (**C**8a'), 78.3 (**C**8a'*), 65.4 (**C**9), 65.2 (**C**9*), 64.0 (**C**10*), 63.9 (**C**10), 59.8 (2C, **C**11, **C**11*), 54.2 (2C, **C**3a, **C**3a*), 52.6 (**C**3a'), 52.5 (N8'SO$_2$**C**H$_2$*), 51.8 (N8'SO$_2$**C**H$_2$), 50.1 (**C**3a'*), 45.2 (**C**2'*), 44.1 (**C**2'), 38.1 (**C**3*), 38.0 (**C**2*), 37.8 (**C**3), 37.1 (**C**2"*), 36.8 (**C**2"), 36.6 (**C**2), 33.3 (**C**3'*), 31.5 (**C**3'), 31.0 (N8**C**H$_3$*), 30.9 (N8**C**H$_3$), 24.9 (2C, **C**12, **C**12*), 20.6 (**C**13*), 20.5 (**C**13), 18.4 (**C**3"), 18.1 (**C**3"*), 14.3 (**C**4"), 14.2 (**C**4"*), 10.8 (N8'SO$_2$CH$_2$**C**H$_2$*), 10.7 (N8'SO$_2$CH$_2$**C**H$_2$), –1.7 (Si(**C**H$_3$)$_3$*), –1.8 (Si(**C**H$_3$)$_3$).

FTIR (thin film) cm^{-1}: 3055 (w), 2958 (m), 2875 (w), 1649 (m), 1599 (m), 1487 (m), 1408 (m), 1341 (m), 1251 (m), 1156 (m), 1053 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{35}H_{49}N_4O_4SSi$ $[M+H]^+$: 649.3238,
found: 649.3244.

$[\alpha]_D^{22}$: –128 (c = 0.73, CH_2Cl_2).

TLC (50% ethyl acetate in hexanes), R*f*: 0.35 (UV, CAM).



(–)-**48** (–)-**8**

(–)-Communesin H (8):

A degassed solution of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 19.0 mg, 69.0 μmol, 4.00 equiv) in *N*,*N*-dimethylformamide (175 μL) was added to a degassed solution of (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin H (**48**, 11.2 mg, 17.3 μmol, 1 equiv) in *N*,*N*-dimethylformamide (400 μL) at 23 ºC. After 2 h, a saturated aqueous sodium chloride solution (10 mL) and deionized water (5 mL) were added and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 30% acetone in hexanes) to afford (–)-communesin H (**8**, 7.51 mg, 89.8%) as a white solid. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, 12:1 mixture of atropisomers, *denotes minor atropisomer):
δ 7.00 (app-td, *J* = 7.5, 1.5 Hz, 2H, C6'**H**, C6'**H***), 6.88 (t, *J* = 7.7 Hz, 1H, C6**H**), 6.85 (t, *J* = 7.6 Hz, 1H, C6**H***), 6.73–6.63 (m, 5H, C4'**H**, C5'**H**, C5'**H***, C7'**H**, C7'**H***), 6.60 (d, *J* = 6.9 Hz, 1H, C4'**H***), 6.09 (d, *J* = 7.3 Hz, 1H, C5**H***), 6.07 (d, *J* = 7.8 Hz, 1H, C5**H**), 5.95 (d, *J* = 7.8 Hz, 1H, C7**H**), 5.90 (d, *J* = 7.6 Hz, 1H, C7**H***), 5.40 (app-s, 1H, C8a'**H***), 5.04 (d, *J* = 1.4 Hz, 1H, C8a'**H**), 4.69 (s, 1H, C8a**H**), 4.67 (s, 1H, C8a**H***), 4.59 (br-s, 1H, N8'**H**), 4.50 (d, *J* = 8.2 Hz, 1H, C9**H***), 4.10 (d, *J* = 9.0 Hz, 1H, C9**H**), 3.88 (app-dd, *J* = 11.6, 8.9 Hz, 1H, C2'$\mathbf{H}_a$), 3.69 (app-t, *J* = 9.2 Hz, 1H, C2'$\mathbf{H}_a$*), 3.54 (app-dd, *J* = 15.8, 9.2 Hz, 1H, C2$\mathbf{H}_a$*), 3.46 (app-dd, *J* = 15.8, 9.5 Hz, 1H, C2$\mathbf{H}_a$), 3.35 (app-dt, *J* = 16.2, 8.7 Hz, 2H, C2$\mathbf{H}_b$, C2$\mathbf{H}_b$*), 3.15–3.07 (m, 1H, C2'$\mathbf{H}_b$*), 3.00 (app-td, *J* = 11.6, 7.2 Hz, 1H, C2'$\mathbf{H}_b$), 2.96–2.88 (m, 1H, C3'$\mathbf{H}_a$*), 2.89–2.81 (m, 8H, N8C$\mathbf{H}_3$, N8C$\mathbf{H}_3$*, C10**H**, C2"$\mathbf{H}_a$), 2.79 (d, *J* = 8.9 Hz, 1H, C10**H***), 2.77–2.66 (m, 1H, C3'$\mathbf{H}_a$), 2.40–2.31 (m, 3H, C3$\mathbf{H}_a$, C3$\mathbf{H}_a$*, C2"$\mathbf{H}_b$), 2.31–2.22 (m, 4H, C3$\mathbf{H}_b$, C3$\mathbf{H}_b$*, C2"$\mathbf{H}_2$*), 2.03 (app-dd, *J* = 13.2, 7.1 Hz, 1H, C3'$\mathbf{H}_b$*), 1.96 (app-dd, *J* = 13.1, 7.0 Hz, 1H, C3'$\mathbf{H}_b$), 1.85–1.67 (m, 4H, C3"$\mathbf{H}_2$, C3"$\mathbf{H}_2$*), 1.58 (s, 3H, C13$\mathbf{H}_3$*), 1.55 (s, 3H, C13$\mathbf{H}_3$), 1.39 (s, 3H, C12$\mathbf{H}_3$), 1.36 (s, 3H, C12$\mathbf{H}_3$*), 1.01 (t, *J* = 7.4 Hz, 3H, C4"$\mathbf{H}_3$), 0.96 (t, *J* = 7.5 Hz, 3H, C4"$\mathbf{H}_3$*).

^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, 12:1 mixture of atropisomers, *denotes minor atropisomer):
δ 174.6 (**C**1"), 173.2 (**C**1"*), 150.8 (**C**7a), 150.6 (**C**7a*),

	143.0 (**C**7a'*), 142.9 (**C**7a'), 137.2 (**C**4), 133.3 (**C**4a'*), 132.8 (**C**4a'), 132.5 (**C**4a), 132.3 (**C**4a*), 129.0 (**C**6), 128.8 (**C**6*), 127.5 (**C**6'), 127.3 (**C**6'*), 123.7 (**C**4'*), 123.4 (**C**4'), 121.0 (**C**5'*), 120.7 (**C**5'), 117.2 (**C**7'*), 117.1 (**C**7'), 114.1 (**C**5*), 113.4 (**C**5), 102.0 (**C**7), 101.6 (**C**7*), 83.2 (**C**8a*), 82.8 (**C**8a), 79.2 (**C**8a'), 78.1 (**C**8a'*), 65.5 (**C**9), 65.2 (**C**9*), 64.3 (**C**10*), 64.2 (**C**10), 59.8 (**C**11), 52.2 (**C**3a'), 51.7 (**C**3a), 51.6 (**C**3a*), 49.8 (**C**3a'*), 45.4 (**C**2'*), 44.2 (**C**2'), 38.7 (**C**3*), 38.3 (**C**3), 37.9 (**C**2*), 37.2 (**C**2"*), 36.8 (**C**2"), 36.5 (**C**2), 32.7 (**C**3'*), 30.8 (**C**3'), 29.9 (N8**C**H_3*), 29.8 (N8**C**H_3), 25.0 (**C**12), 24.9 (**C**12*), 20.6 (2C, **C**13, **C**13*), 18.6 (**C**3"), 18.1 (**C**3"'*), 14.3 (**C**4"), 14.2 (**C**4"'*).
FTIR (thin film) cm^{-1}:	3321 (br-m), 3052 (w), 2961 (m), 2930 (m), 2876 (m), 1639 (m), 1596 (m), 1494 (m), 1427 (m), 1408 (m), 1339 (m), 1265 (m), 1090 (m), 1003 (w), 739 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{30}H_{37}N_4O_2$ $[M+H]^+$: 485.2911, found: 485.2913.
$[\alpha]_D^{23}$:	–168 (*c* = 0.38, MeOH).[65]
TLC (30% acetone in hexanes), R*f*:	0.19 (UV, CAM).

65. Literature value: $[\alpha]_D^{25}$ = –167 (*c* = 0.024, MeOH), see Dalsgaard, P. W.; Blunt, J. W.; Munro, M. H. G.; Frisvad, J. C.; Christophersen, C. *J. Nat. Prod.* **2005**, *68*, 258.

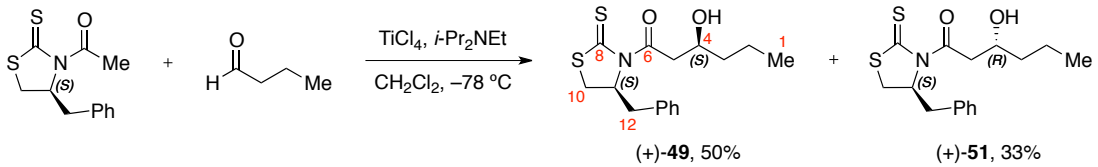
Table S12. Comparison of our ^{1}H NMR data for (–)-communesin H (8) with literature data ($CDCl_3$, major atropisomer):

Assignment	**Christophersen's Isolation Report**[60,61] (–)-Communesin H (**8**) ^{1}H NMR, 500 MHz, $CDCl_3$	**This Work** (–)-Communesin H (**8**) ^{1}H NMR, 500 MHz, $CDCl_3$
C2	3.44 (m, 1H) 3.36 (m, 1H)	3.46 (app-dd, *J* = 15.8, 9.5 Hz, 1H) 3.35 (app-dt, *J* = 16.2, 8.7 Hz, 2H)
C3	2.35 (m, 1H) 2.27 (m, 1H)	2.40–2.31 (m, 3H) 2.31–2.22 (m, 4H)
C3a	–	–
C4a	–	–
C4	–	–
C5	6.07 (d, *J* = 7.7 Hz, 1H)	6.07 (d, *J* = 7.8 Hz, 1H)
C6	6.89 (t, *J* = 7.7 Hz, 1H)	6.88 (t, *J* = 7.7 Hz, 1H)
C7	5.95 (d, *J* = 7.7 Hz, 1H)	5.95 (d, *J* = 7.8 Hz, 1H)
C7a	–	–
N8C**H**$_3$	2.84 (s, 3H)	2.89–2.81 (m, 8H)
C8a	4.69 (s, 1H)	4.69 (s, 1H)
C9	4.10 (d, *J* = 9.0 Hz, 1H)	4.10 (d, *J* = 9.0 Hz, 1H)
C10	2.86 (m, 1H)	2.89–2.81 (m, 8H)
C11	–	–
C12	1.39 (s, 3H)	1.39 (s, 3H)
C13	1.54 (s, 3H)	1.55 (s, 3H)
C2'	3.88 (dd, *J* = 11.8, 8.6 Hz, 1H) 3.00 (ddd, *J* = 11.8, 11.5, 7.4 Hz, 1H)	3.88 (app-dd, *J* = 11.6, 8.9 Hz, 1H) 3.00 (app-td, *J* = 11.6, 7.2 Hz, 1H)
C3'	2.72 (ddd, *J* = 13.2, 11.5, 8.6 Hz, 1H) 1.96 (dd, *J* = 13.2, 7.4 Hz, 1H)	2.77–2.66 (m, 1H) 1.96 (app-dd, *J* = 13.1, 7.0 Hz, 1H)
C3a'	–	–
C4a'	–	–
C4'	6.66 (m, 1H)	6.73–6.63 (m, 5H)
C5'	6.68 (m, 1H)	6.73–6.63 (m, 5H)
C6'	6.99 (td, *J* = 7.5, 1.5 Hz, 1H)	7.00 (app-td, *J* = 7.5, 1.5 Hz, 2H)
C7'	6.70 (m, 1H)	6.73–6.63 (m, 5H)
C7a'	–	–
C8a'	5.04 (s, 1H)	5.04 (d, *J* = 1.4 Hz, 1H)
C1"	–	–
C2"	2.84 (m, 1H) 2.35 (m, 1H)	2.89–2.81 (m, 8H) 2.40–2.31 (m, 3H)
C3"	1.75 (m, 2H)	1.85–1.67 (m, 4H)
C4"	1.00 (t, *J* = 7.4 Hz, 3H)	1.01 (t, *J* = 7.4 Hz, 3H)
N8'H	–	4.59 (br-s, 1H)

Table S13. Comparison of our ^{13}C NMR data for (–)-communesin H (8) with literature data ($CDCl_3$, major atropisomer):

Assignment	Christophersen's Isolation Report[60,62] (–)-Communesin H (**8**) ^{13}C NMR, 75 MHz $CDCl_3$	This Work (–)-Communesin H (**8**) ^{13}C NMR, 150.9 MHz, $CDCl_3$	Chemical Shift Difference $\Delta\delta = \delta$ (this work) – δ (Christophersen report)
C2	36.3	36.5	0.2
C3	38.1	38.3	0.2
C3a	51.9	51.7	**–0.2**[66]
C4a	132.3	132.5	0.2
C4	136.9	137.2	0.3
C5	113.2	113.4	0.2
C6	128.8	129.0	0.2
C7	101.7	102.0	0.3
C7a	150.5	150.8	0.3
N8$\mathbf{C}H_3$	29.6	29.8	0.2
C8a	82.4	82.8	0.4
C9	65.2	65.5	0.3
C10	63.9	64.2	0.3
C11	59.6	59.8	0.2
C12	24.8	25.0	0.2
C13	20.4	20.6	0.2
C2'	44.0	44.2	0.2
C3'	30.8	30.8	0.0
C3a'	51.4	52.2	**0.8**[66]
C4a'	132.4	132.8	0.4
C4'	123.2	123.4	0.2
C5'	116.9	120.7	**3.8**[67]
C6'	127.3	127.5	0.2
C7'	120.5	117.1	**–3.4**[67]
C7a'	142.6	142.9	0.3
C8a'	78.9	79.2	0.3
C1"	174.5	174.6	0.1
C2"	36.6	36.8	0.2
C3"	18.4	18.6	0.2
C4"	14.2	14.3	0.1

66. Our revised assignment of C3a and C3a' resonances is supported by key gHMBC correlations (^1H,^{13}C) in ppm: (6.07,51.7), (3.46,51.7), (6.73,52.2), and (3.88,52.2).
67. Our revised assignment of C5' and C7' resonances is supported by a key 4-bond gHMBC correlation (^1H,^{13}C) in ppm: (4.69,117.1).



Aldol adducts (+)-49 and (+)-51:

A sample of (*S*)-1-(4-benzyl-2-thioxothiazolidin-3-yl)ethan-1-one[68] (648 mg, 2.58 mmol, 1 equiv) was azeotropically dried by concentration from anhydrous benzene (2 × 5 mL). The residue was dissolved in dichloromethane (8.0 mL) and the resulting bright-yellow solution was cooled to –78 ºC. A freshly-prepared solution of titanium(IV) chloride (489 mg, 2.58 mmol, 1.00 equiv) in dichloromethane (2.0 mL) was then added dropwise over 4 min. The transfer was quantitated with additional dichloromethane (1.0 mL). After stirring at –78 ºC for 10 min, *N*,*N*-diisopropylethylamine (898 µL, 5.15 mmol, 2.00 equiv) was added dropwise via syringe over 4 min to the resulting bright-orange viscous suspension causing an immediate color change to dark burgundy. After 1 h, a solution of butyraldehyde (697 µL, 7.73 mmol, 3.00 equiv) in dichloromethane (4.0 mL) was added dropwise via syringe over 3 min and the transfer was quantitated with additional dichloromethane (1.0 mL). After 45 min, the resulting homogeneous burgundy-orange solution was diluted with a saturated aqueous ammonium chloride solution (20 mL) and deionized water (20 mL). The cooling bath was removed and the mixture was allowed to warm to 23 ºC. The layers were separated and the aqueous layer was extracted with dichloromethane (2 × 25 mL). The combined organic extracts were washed sequentially with an aqueous sodium bisulfite solution (1 M, 3 × 40 mL) and a saturated aqueous sodium chloride solution (40 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 30%→40% diethyl ether in hexanes) to afford impure aldol adducts (+)-**49** (more polar) and (+)-**51** (less polar) as viscous yellow oils. Each sample was independently subjected to a second chromatographic purification on silica gel (eluent: 0%→2% diethyl ether in dichloromethane) to afford pure (11*S*,4*S*)-adduct (+)-**49** (420 mg, 50.3%) as a bright-yellow viscous oil and pure (11*S*,4*R*)-adduct (+)-**51** (278 mg, 33.4%) as a bright-yellow solid.[69] Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments.

(11*S*,4*S*)-Aldol adduct (+)-49:

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 7.38–7.31 (m, 2H, Ph-*m*-**H**), 7.31–7.26 (m, 3H, Ph-*o*-**H**, Ph-*p*-**H**), 5.40 (app-ddd, *J* = 10.8, 7.1, 4.0 Hz, 1H, C11**H**), 4.21–4.12 (m, 1H, C4**H**), 3.64 (dd, *J* = 17.8, 2.4 Hz, 1H, C5$\mathbf{H}_a$), 3.40 (ddd, *J* = 11.6, 7.2, 1.0 Hz, 1H, C10$\mathbf{H}_a$), 3.22 (dd, *J* = 13.2, 4.0 Hz, 1H, C12$\mathbf{H}_a$), 3.13 (dd, *J* = 17.8, 9.5 Hz, 1H, C5$\mathbf{H}_b$), 3.05 (dd, *J* = 13.2, 10.5 Hz, 1H, C12$\mathbf{H}_b$), 2.89 (d, *J* = 11.6 Hz, 1H, C10$\mathbf{H}_b$), 2.77 (d, 1H, *J* = 3.9 Hz, C4O**H**), 1.64–1.54 (m, 1H, C3$\mathbf{H}_a$), 1.54–1.34 (m, 3H, C2$\mathbf{H}_2$, C3$\mathbf{H}_b$), 0.95 (t, *J* = 6.9 Hz, 3H, C1$\mathbf{H}_3$).

^{13}C NMR (125.8 MHz, $CDCl_3$, 24 °C): δ 201.5 (**C**8), 173.4 (**C**6), 136.5 (Ph-*ipso*-**C**), 129.5 (Ph-*o*-**C**), 129.0 (Ph-*m*-**C**), 127.4 (Ph-*p*-**C**), 68.4 (**C**11), 67.7 (**C**4), 46.0 (**C**5), 38.6 (**C**3), 36.9 (**C**12), 32.2 (**C**10), 18.9 (**C**2), 14.1 (**C**1).

68. Kitir, B.; Baldry, M.; Ingmer, H.; Olsen, C. A. *Tetrahedron* **2014**, *70*, 7721.
69. The relative stereochemical configuration of aldol adducts (+)-**49** and (+)-**51** were determined by polarimetric analysis of the corresponding carboxylic acids after hydrolysis, as described later in this document.

FTIR (thin film) cm^{-1}: 3448 (br-w), 2957 (m), 2930 (m), 1691 (s), 1455 (m), 1342 (s), 1267 (s), 1192 (m), 1138 (s), 1044 (s).

HRMS (ESI) (*m/z*): calc'd for $C_{16}H_{21}NNaO_2S_2$ $[M+Na]^+$: 346.0906, found: 346.0914.

$[\alpha]_D^{23}$: +234 (*c* = 0.89, CH_2Cl_2).

TLC (40% diethyl ether in hexanes), R*f*: 0.16 (UV, CAM).

(11*S*,4*R*)-Aldol adduct (+)-51:

^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.38–7.32 (m, 2H, Ph-*m*-**H**), 7.31–7.26 (m, 3H, Ph-*o*-**H**, Ph-*p*-**H**), 5.41 (app-ddd, *J* = 10.8, 7.1, 4.0 Hz, 1H, C11**H**), 4.07 (dddd, *J* = 9.9, 7.4, 4.3, 2.5 Hz, 1H, C4**H**), 3.46 (dd, *J* = 17.5, 9.4 Hz, 1H, C5$\mathbf{H}_a$), 3.40 (dd, *J* = 11.6, 7.2 Hz, 1H, C10$\mathbf{H}_a$), 3.33 (dd, *J* = 17.5, 2.6 Hz, 1H, C5$\mathbf{H}_b$), 3.22 (dd, *J* = 13.2, 4.0 Hz, 1H, C12$\mathbf{H}_a$), 3.13 (br-s, 1H, C4O**H**), 3.04 (dd, *J* = 13.2, 10.4 Hz, 1H, C12$\mathbf{H}_b$), 2.91 (d, *J* = 11.6 Hz, 1H, C10$\mathbf{H}_b$), 1.64–1.53 (m, 1H, C3$\mathbf{H}_a$), 1.53–1.34 (m, 3H, C2$\mathbf{H}_2$, C3$\mathbf{H}_b$), 0.94 (t, *J* = 6.9 Hz, 3H, C1$\mathbf{H}_3$).

^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): δ 201.6 (**C**8), 174.0 (**C**6), 136.5 (Ph-*ipso*-**C**), 129.5 (Ph-*o*-**C**), 129.1 (Ph-*m*-**C**), 127.4 (Ph-*p*-**C**), 68.3 (2C, **C**4, **C**11), 45.6 (**C**5), 38.9 (**C**3), 36.9 (**C**12), 32.1 (**C**10), 18.8 (**C**2), 14.1 (**C**1).

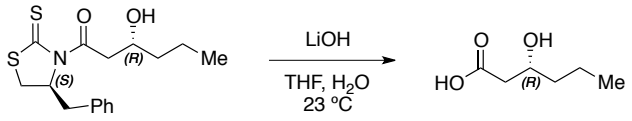
FTIR (thin film) cm^{-1}: 3435 (br-w), 2957 (m), 2930 (m), 1693 (m), 1454 (w), 1342 (s), 1293 (m), 1259 (s), 1164 (s), 1138 (s), 1041 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{16}H_{21}NNaO_2S_2$ $[M+Na]^+$: 346.0906, found: 346.0901.

$[\alpha]_D^{23}$: +160 (*c* = 0.81, CH_2Cl_2).

TLC (40% diethyl ether in hexanes), R*f*: 0.28 (UV, CAM).

Determination of the Relative Stereochemistry of Aldol Adducts (+)-49 and (+)-51:



(+)-**51** 77% (–)-**S9**

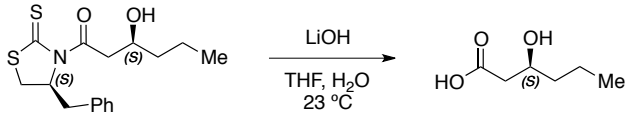
(–)-(3*R*)-Hydroxyhexanoic acid (S9):

An aqueous lithium hydroxide solution (1.0 M, 1.8 mL, 1.8 mmol, 4.0 equiv) was added to a bright-yellow solution of (11*S*,4*R*)-aldol adduct (+)-**51** (143 mg, 0.440 mmol, 1 equiv) in tetrahydrofuran (2.20 mL) at 23 ºC. After 30 min, the resulting off-white turbid solution was concentrated under reduced pressure to remove tetrahydrofuran. The aqueous suspension was diluted with deionized water (10 mL) and was washed with ethyl acetate (4 × 10 mL) to remove residual (*S*)-4-benzylthiazolidine-2-thione. The aqueous layer was acidified to pH ~ 1 by adding an aqueous hydrogen chloride solution (1 M, 3 mL) and was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to yield (–)-(3*R*)-hydroxyhexanoic acid (**S9**, 44.0 mg, 76.6%) as a colorless viscous oil. Spectral data were in agreement with those previously reported in the literature.[68]

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 7.62 (br-s, 1H), 4.05 (tdd, *J* = 7.9, 4.5, 3.1 Hz, 1H), 2.55 (dd, *J* = 16.5, 3.2 Hz, 1H), 2.46 (dd, *J* = 16.5, 9.1 Hz, 1H), 1.60–1.28 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 178.0, 68.0, 41.3, 38.6, 18.8, 14.0.

$[\alpha]_D^{23}$: –28 (*c* = 2.20, $CHCl_3$).[70]



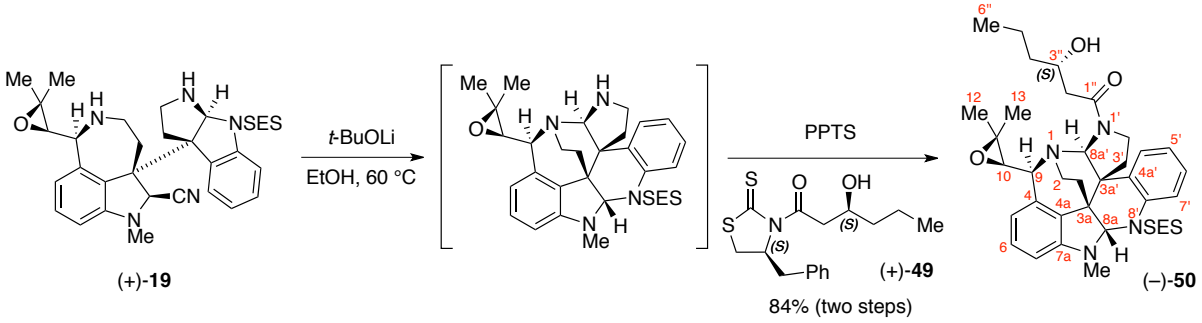
(+)-**49** 77% (+)-**S9**

(+)-(3*S*)-Hydroxyhexanoic acid (S9):

An aqueous lithium hydroxide solution (1.0 M, 1.7 mL, 1.7 mmol, 4.0 equiv) was added to a bright-yellow solution of (11*S*,4*S*)-aldol adduct (+)-**49** (138 mg, 0.430 mmol, 1 equiv) in tetrahydrofuran (1.50 mL) at 23 ºC. After 30 min, the resulting off-white turbid solution was concentrated under reduced pressure to remove tetrahydrofuran. The aqueous suspension was diluted with deionized water (10 mL) and was washed with ethyl acetate (4 × 10 mL) to remove residual (*S*)-4-benzylthiazolidine-2-thione. The aqueous layer was acidified to pH ~ 1 by adding an aqueous hydrogen chloride solution (1 M, 3 mL) and was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to yield (+)-(3*S*)-hydroxyhexanoic acid (**S9**, 43.6 mg, 77.2%) as a colorless semi-solid. Spectral data for (+)-(3*S*)-**S9** were identical to those obtained for (–)-(3*R*)-**S9** as described above.

$[\alpha]_D^{23}$: +25 (*c* = 2.18, $CHCl_3$).[71]

70. Literature value: $[\alpha]_D^{25}$ = –27.3 (*c* =2.1, $CHCl_3$), see Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127.
71. Literature value: $[\alpha]_D$ = +27 (*c* =1.2, $CHCl_3$), see Hsiao, C.-N.; Liu, L.; Miller, M. J. *J. Org. Chem.* **1987**, *52*, 2201.



(–)-*N*8'-(Trimethylsilyl)ethanesulfonyl (C3"*S*)-communesin I (50):

A sample of lithium *tert*-butoxide (11.5 mg, 143 μmol, 10.0 equiv) was added to a solution of heterodimer (+)-**19** (8.67 mg, 14.3 μmol, 1 equiv) in anhydrous ethanol (200 proof, 380 μL) at 23 ºC. The flask was sealed with a Teflon-lined glass stopper under an argon atmosphere and was immersed in a preheated oil bath at 60 ºC. After 18.5 h, the reaction mixture was cooled to 23 ºC and a sample of pyridinium *p*-toluenesulfonate (PPTS, 28.8 mg, 114 μmol, 8.00 equiv) was added as a solid followed by a solution of (11*S*,4*S*)-aldol adduct (+)-**49** (253 mg, 782 μmol, 54.7 equiv) in dichloromethane (500 μL). The transfer was quantitated with additional dichloromethane (300 μL). After 50 min, the solution was diluted with a saturated aqueous sodium bicarbonate solution (5 mL) and deionized water (5 mL) and the resulting mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (10 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 20%→30% acetone in hexanes) to afford (–)-*N*8'-(trimethylsilyl)ethanesulfonyl (C3"*S*)-communesin I (**50**, 8.27 mg, 83.5%) as a white solid. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (600 MHz, $CDCl_3$, 20 °C, 15:1 mixture of atropisomers, *denotes minor atropisomer): δ 7.54 (dd, *J* = 8.0, 1.2 Hz, 1H, C7'**H**), 7.42 (d, *J* = 8.5 Hz, 1H, C7'**H***), 7.20 (app-td, *J* = 7.7, 1.4 Hz, 2H, C6'**H**, C6'**H***), 7.07 (app-td, *J* = 7.6, 1.2 Hz, 2H, C5'**H**, C5'**H***), 6.91 (app-t, *J* = 7.7 Hz, 2H, C6**H**, C6**H***), 6.84 (dd, *J* = 7.7, 1.4 Hz, 1H, C4'**H**), 6.74–6.70 (m, 1H, C4'**H***), 6.15 (d, *J* = 7.6 Hz, 1H, C5**H***), 6.10 (d, *J* = 7.7 Hz, 1H, C5**H**), 5.98 (d, *J* = 7.8 Hz, 1H, C7**H**), 5.96 (d, *J* = 7.0 Hz, 1H, C7**H***), 5.71 (s, 1H, C8a**H**), 5.64 (s, 1H, C8a**H***), 5.50 (br-s, 1H, C8a'**H***), 5.08 (d, *J* = 1.6 Hz, 1H, C8a'**H**), 4.20–4.15 (m, 1H, C3"**H**), 4.06 (d, *J* = 9.1 Hz, 1H, C9**H**), 4.01 (br-s, 1H, C3"O**H**), 3.94 (app-dd, *J* = 11.7, 9.0 Hz, 1H, C2'$\mathbf{H}_a$), 3.47 (app-dd, *J* = 15.9, 9.7 Hz, 1H, C2$\mathbf{H}_a$), 3.33 (app-dt, *J* = 16.5, 8.8 Hz, 1H, C2$\mathbf{H}_b$), 3.25 (app-td, *J* = 13.5, 4.7 Hz, 1H, N8'$SO_2C\mathbf{H}_a$), 3.22–3.11 (m, 2H, C2"$\mathbf{H}_a$, N8'$SO_2C\mathbf{H}_b$), 3.08 (app-td, *J* = 11.6, 7.3 Hz, 1H, C2'$\mathbf{H}_b$), 2.92 (s, 3H, N8C$\mathbf{H}_3$), 2.87 (s, 3H, N8C$\mathbf{H}_3$*), 2.84 (d, *J* = 9.1 Hz, 1H, C10**H**), 2.83–2.77 (m, 1H, C3'$\mathbf{H}_a$), 2.49 (app-dd, *J* = 13.0, 8.7 Hz, 1H, C3$\mathbf{H}_a$), 2.36 (app-dd, *J* = 16.4, 9.8 Hz, 1H, C2"$\mathbf{H}_b$), 2.29 (app-dt, *J* = 13.1, 9.4 Hz, 1H, C3$\mathbf{H}_b$), 1.95 (app-dd, *J* = 13.1, 7.2 Hz, 1H, C3'$\mathbf{H}_b$), 1.61–1.41 (m, 7H, C13$\mathbf{H}_3$, C4"$\mathbf{H}_2$, C5"$\mathbf{H}_2$), 1.38 (s, 3H, C12$\mathbf{H}_3$), 1.30–1.15 (m, 2H,

N8'$SO_2CH_2C\mathbf{H}_2$), 0.96 (t, J = 7.0 Hz, 3H, C6"$\mathbf{H}_3$), 0.92 (t, J = 7.3 Hz, 3H, C6"$\mathbf{H}_3$*), 0.11 (s, 9H, Si($C\mathbf{H}_3$)$_3$*), 0.07 (s, 9H, Si($C\mathbf{H}_3$)$_3$).

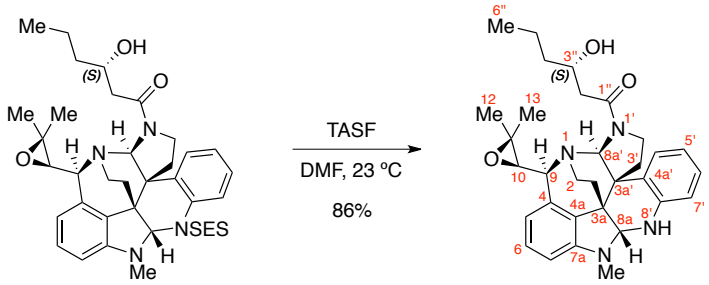
^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C, 15:1 mixture of atropisomers, *denotes minor atropisomer): δ 174.1 (**C**1"), 149.9 (**C**7a), 138.2 (**C**4a'), 136.9 (**C**4), 136.0 (**C**7a'), 131.2 (**C**4a), 129.5 (**C**6), 128.0 (**C**6'), 126.5 (**C**5'), 124.9 (**C**7'), 124.0 (**C**4'), 113.9 (**C**5), 102.7 (**C**7), 84.7 (**C**8a), 79.5 (**C**8a'), 68.1 (**C**3"), 65.6 (**C**9), 63.8 (**C**10), 60.0 (**C**11), 54.2 (**C**3a), 52.5 (**C**3a'), 52.0 (N8'$SO_2\mathbf{C}H_2$), 44.0 (**C**2'), 41.3 (**C**2"), 38.9 (**C**4"), 37.7 (**C**3), 36.5 (**C**2), 31.5 (**C**3'), 31.0 (N8$\mathbf{C}H_3$), 25.0 (**C**12), 20.5 (**C**13), 18.9 (**C**5"*), 18.8 (**C**5"), 14.3 (**C**6"), 14.2 (**C**6"*), 10.8 (N8'$SO_2CH_2\mathbf{C}H_2$*), 10.7 (N8'$SO_2CH_2\mathbf{C}H_2$), –1.7 (Si($\mathbf{C}H_3$)$_3$*), –1.8 (Si($\mathbf{C}H_3$)$_3$).

FTIR (thin film) cm^{-1}: 3438 (br-m), 2957 (s), 1630 (s), 1600 (s), 1487 (s), 1455 (s), 1340 (s), 1251 (s), 1156 (s), 1053 (m), 859 (m), 844 (m), 740 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{37}H_{53}N_4O_5SSi$ $[M+H]^+$: 693.3500, found: 693.3503

$[\alpha]_D^{23}$: –100 (*c* = 0.41, CH_2Cl_2).

TLC (30% acetone in hexanes), R*f*: 0.27 (UV, CAM).



(–)-**50** (–)-**9**

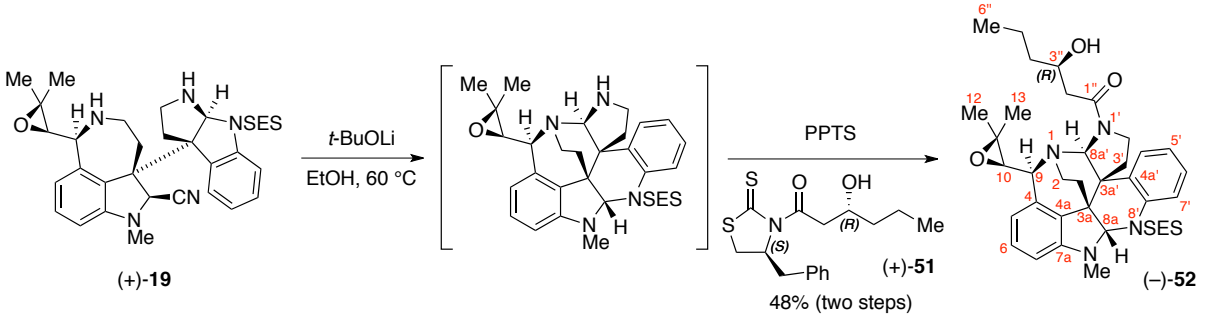
(–)-(C3"*S*)-Communesin I (9):

A degassed solution of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 12.3 mg, 44.6 μmol, 4.00 equiv) in *N*,*N*-dimethylformamide (100 μL) was added to a degassed solution of (–)-*N*8'-(trimethylsilyl)ethanesulfonyl (C3"*S*)-communesin I (**50**, 7.73 mg, 11.2 μmol, 1 equiv) in *N*,*N*-dimethylformamide (300 μL) at 23 °C. After 2.2 h, a saturated aqueous sodium chloride solution (10 mL) and deionized water (5 mL) were added and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 50%→60% ethyl acetate in hexanes) to afford (–)-(C3"*S*)-Communesin I (**9**, 5.08 mg, 86.1%) as a white solid. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, 34:1 mixture of atropisomers, *denotes minor atropisomer):
δ 7.01 (app-td, *J* = 7.6, 1.5 Hz, 1H, C6'**H**), 6.89 (t, *J* = 7.8 Hz, 1H, C6**H**), 6.86 (t, *J* = 7.9 Hz, 1H, C6**H***), 6.72 (app-td, *J* = 7.4, 1.2 Hz, 1H, C5'**H**), 6.70–6.64 (m, 1H, C7'**H**, C4'**H**), 6.60 (d, *J* = 6.6 Hz, 1H, C4'**H***), 6.09 (d, *J* = 7.7 Hz, 1H, C5**H***), 6.06 (d, *J* = 7.6 Hz, 1H, C5**H**), 5.95 (d, *J* = 7.6 Hz, 1H, C7**H**), 5.91 (d, *J* = 8.1 Hz, 1H, C7**H***), 5.41 (app-s, 1H, C8a'**H***), 5.04 (app-s, 1H, C8a'**H**), 4.70 (s, 1H, C8a**H**), 4.67 (s, 1H, C8a**H***), 4.59 (br-s, 1H, N8'**H**), 4.46 (d, *J* = 8.7 Hz, 1H, C9**H***), 4.22–4.12 (m, 1H, C3"**H**), 4.19 (d, *J* = 2.0 Hz, 1H, C3"O**H**), 4.05 (d, *J* = 9.2 Hz, 1H, C9**H**), 3.89 (app-dd, *J* = 11.8, 8.3 Hz, 1H, C2'$\mathbf{H}_a$), 3.45 (app-ddt, *J* = 16.1, 9.6, 1.6 Hz, 1H, C2$\mathbf{H}_a$), 3.34 (app-dt, *J* = 15.9, 8.8 Hz, 1H, C2$\mathbf{H}_b$), 3.21 (dd, *J* = 16.4, 2.2 Hz, 1H, C2"$\mathbf{H}_a$) 3.00 (app-td, *J* = 11.7, 7.2 Hz, 1H, C2'$\mathbf{H}_b$), 2.87 (d, *J* = 9.2 Hz, 1H, C10**H**), 2.84 (s, 3H, N8C$\mathbf{H}_3$), 2.81 (s, 3H, N8C$\mathbf{H}_3$*), 2.80 (d, *J* = 8.8 Hz, 1H, C10**H***), 2.72 (ddd, *J* = 13.3, 11.6, 8.7 Hz, 1H, C3'$\mathbf{H}_a$), 2.40–2.31 (m, 2H, C3$\mathbf{H}_a$, C2"$\mathbf{H}_b$), 2.27 (app-dt, *J* = 13.0, 9.4 Hz, 1H, C3$\mathbf{H}_b$), 1.99 (app-dd, *J* = 13.3, 6.7 Hz, 1H, C3'$\mathbf{H}_b$), 1.59–1.43 (m, 10H, C13$\mathbf{H}_3$, C13$\mathbf{H}_3$*, C4"$\mathbf{H}_2$, C5"$\mathbf{H}_2$), 1.39 (s, 3H, C12$\mathbf{H}_3$), 1.36 (s, 3H, C12$\mathbf{H}_3$*), 0.96 (t, *J* = 7.1 Hz, 3H, C6"$\mathbf{H}_3$).

^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C, 34:1 mixture of atropisomers, *denotes minor atropisomer):
δ 174.5 (**C**1"), 150.7 (**C**7a), 142.7 (**C**7a'), 136.6 (**C**4),

	132.3 (2C, **C**4a, **C**4a'), 129.1 (**C**6), 127.6 (**C**6'), 123.4 (**C**4'), 120.9 (**C**5'), 117.1 (**C**7'), 113.4 (**C**5), 102.1 (**C**7), 82.6 (**C**8a), 79.2 (**C**8a'), 68.1 (**C**3"), 65.6 (**C**9), 64.1 (**C**10), 60.0 (**C**11), 52.1 (**C**3a'), 51.6 (**C**3a), 44.1 (**C**2'), 41.1 (**C**2"), 38.8 (**C**4"), 38.1 (**C**3), 36.4 (**C**2), 30.7 (**C**3'), 29.8 (N8**C**H_3), 25.0 (**C**12), 20.5 (**C**13), 18.8 (**C**5"), 14.3 (**C**6").
FTIR (thin film) cm^{-1}:	3429 (br-w), 3330 (br-w), 3052 (w), 2957 (m), 2925 (m), 2873 (m), 1620 (s), 1606 (s), 1596 (s), 1493 (m), 1427 (s), 1338 (m), 1279 (m), 1004 (m), 908 (m), 740 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{32}H_{41}N_4O_3$ $[M+H]^+$: 529.3173, found: 529.3155.
$[\alpha]_D^{23}$:	–147 (*c* = 0.25, MeOH).
TLC (60% ethyl acetate in hexanes), R*f*:	0.15 (UV, CAM).



(+)-**19** (+)-**51** (–)-**52**

(–)-*N*8'-(Trimethylsilyl)ethanesulfonyl communesin I (52):

A sample of lithium *tert*-butoxide (12.8 mg, 0.160 mmol, 10.0 equiv) was added to a solution of heterodimer (+)-**19** (9.67 mg, 16.0 μmol, 1 equiv) in anhydrous ethanol (200 proof, 400 μL). The flask was sealed with a Teflon-lined glass stopper under an argon atmosphere and was immersed in a preheated oil bath at 60 ºC. After 16 h, the reaction mixture was cooled to 23 ºC and samples of pyridinium *p*-toluenesulfonate (PPTS, 34.1 mg, 136 μmol, 8.50 equiv) and (11*S*,4*R*)-aldol adduct (+)-**51** (77.7 mg, 0.240 mmol, 15.1 equiv) were added sequentially. After 23 min, an additional portion of (+)-**51** (79.4 mg, 0.246 mmol, 15.4 equiv) was added. After 47 min, a final portion of (+)-**51** (114 mg, 0.352 mmol, 22.1 equiv) was added. After 96 min, a saturated aqueous sodium bicarbonate solution (8 mL) was added and the resulting mixture 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 residue was purified by flash column chromatography on silica gel (eluent: 20%→30% acetone in hexanes) to afford (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin I (**52**, 5.27 mg, 47.7%) as a white solid. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective ROESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, 5.4:1 mixture of atropisomers, *denotes minor atropisomer): δ 7.56 (dd, *J* = 8.0, 1.2 Hz, 1H, C7'**H**), 7.40 (d, *J* = 7.9 Hz, 1H, C7'**H***), 7.21 (app-td, *J* = 7.8, 1.4 Hz, 2H, C6'**H**, C6'**H***), 7.07 (app-td, *J* = 7.6, 1.3 Hz, 2H, C5'**H**, C5'**H***), 6.91 (t, *J* = 7.8 Hz, 2H, C6**H**, C6**H***), 6.83 (dd, *J* = 7.8, 1.4 Hz, 1H, C4'**H**), 6.72 (d, *J* = 7.6 Hz, 1H, C4'**H***), 6.14 (d, *J* = 7.7 Hz, 1H, C5**H***), 6.09 (d, *J* = 7.7 Hz, 1H, C5**H**), 5.98 (d, *J* = 7.8 Hz, 1H, C7**H**), 5.94 (d, *J* = 7.7 Hz, 1H, C7**H***), 5.72 (s, 1H, C8a**H**), 5.63 (s, 1H, C8a**H***), 5.45 (s, 1H, C8a'**H***), 5.07 (s, 1H, C8a'**H**), 4.48 (d, *J* = 8.2 Hz, 1H, C9**H***), 4.20–4.14 (m, 1H, C3"**H***), 4.11 (d, *J* = 9.1 Hz, 1H, C9**H**), 4.09–4.03 (m, 1H, C3"**H**), 3.97 (app-dd, *J* = 12.0, 8.7 Hz, 1H, C2'$\mathbf{H}_a$), 3.70 (app-t, *J* = 9.4 Hz, 1H, C2'$\mathbf{H}_a$*), 3.48 (app-dd, *J* = 16.0, 9.6 Hz, 1H, C2$\mathbf{H}_a$), 3.41–3.31 (m, 1H, C2$\mathbf{H}_b$), 3.25 (app-td, *J* = 13.3, 4.9 Hz, 1H, N8'$SO_2C\mathbf{H}_a$), 3.17 (app-td, *J* = 13.4, 4.9 Hz, 1H, N8'$SO_2C\mathbf{H}_b$), 3.07 (app-td, *J* = 11.7, 7.3 Hz, 1H, C2'$\mathbf{H}_b$), 3.03–2.95 (m, 1H, C3'$\mathbf{H}_a$*), 2.92 (s, 3H, N8C$\mathbf{H}_3$), 2.88–2.74 (m, 3H, C10**H**, C3'$\mathbf{H}_a$, C2"$\mathbf{H}_a$), 2.87 (s, 3H, N8C$\mathbf{H}_3$*), 2.56–2.43 (m, 2H, C3$\mathbf{H}_a$, C2"$\mathbf{H}_b$), 2.36–2.24 (m, 1H, C3$\mathbf{H}_b$), 2.19–2.07 (m, 1H, C3'$\mathbf{H}_b$*), 1.94 (app-dd, *J* = 13.1, 7.2 Hz, 1H, C3'$\mathbf{H}_b$), 1.61–1.39 (m, 7H, C12/13$\mathbf{H}_3$, C4"$\mathbf{H}_2$, C5"$\mathbf{H}_2$), 1.38 (s, 3H, C12/13$\mathbf{H}_3$), 1.36 (s, 3H, C12/13$\mathbf{H}_3$*), 1.30–1.13 (m, 2H, N8'$SO_2CH_2C\mathbf{H}_2$),

0.95 (t, *J* = 6.9 Hz, 3H, C6"**H**$_3$), 0.92 (t, *J* = 6.9 Hz, 3H, C6"**H**$_3$*), 0.11 (s, 9H, Si(C**H**$_3$)$_3$*), 0.07 (s, 9H, Si(C**H**$_3$)$_3$).

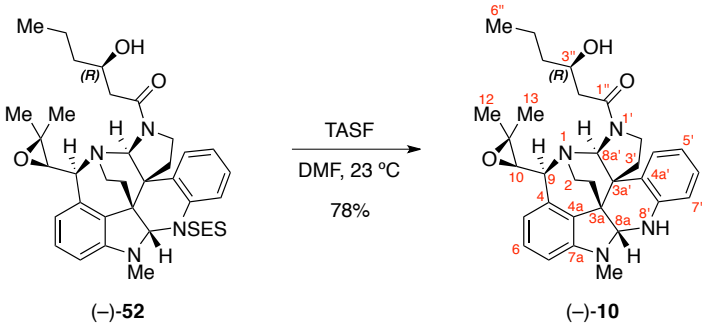
^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C, 5.4:1 mixture of atropisomers, *denotes minor atropisomer): δ 173.8 (**C**1"), 173.2 (**C**1"*), 149.9 (**C**7a), 149.5 (**C**7a*), 138.9 (**C**4a'*), 138.0 (**C**4a'), 136.6 (**C**4), 136.1 (**C**7a'), 136.0 (**C**7a'*), 131.1 (**C**4a), 129.5 (**C**6), 129.3 (**C**6*), 128.0 (**C**6'), 127.8 (**C**5'*), 126.4 (**C**5'), 125.5 (**C**7'*), 124.9 (**C**7'), 124.1 (**C**4'*), 123.9 (**C**4'), 114.6 (**C**5*), 113.8 (**C**5), 102.7 (**C**7), 102.4 (**C**7*), 85.2 (**C**8a*), 84.7 (**C**8a), 79.5 (**C**8a'), 78.2 (**C**8a'*), 69.0 (**C**3"), 67.6 (**C**3"*), 65.3 (2C, **C**9, **C**9*), 64.0 (**C**10), 60.5 (**C**11), 60.1 (**C**11*), 54.1 (2C, **C**3a, **C**3a*), 52.6 (**C**3a'), 51.9 (N8'SO_2**C**H_2), 50.1 (**C**3a'*), 45.2 (**C**2'*), 44.1 (**C**2'), 42.1 (**C**2"), 41.3 (**C**2"*), 39.5 (**C**4"), 38.7 (**C**4"*), 37.5 (**C**3), 36.3 (**C**2), 33.2 (**C**3'*), 31.5 (**C**3'), 31.0 (N8**C**H_3*), 30.9 (N8**C**H_3), 25.0 (**C**12/13), 24.8 (**C**12/13*), 20.6 (**C**12/13*), 20.5 (**C**12/13), 19.1 (**C**5"), 18.9 (**C**5"*), 14.3 (**C**6"), 14.2 (**C**6"*), 10.8 (N8'SO_2CH_2**C**H_2*), 10.7 (N8'SO_2CH_2**C**H_2), –1.7 (Si(**C**H_3)$_3$*), –1.8 (Si(**C**H_3)$_3$).

FTIR (thin film) cm^{-1}: 3474 (br-w), 2956 (s), 1636 (s), 1600 (s), 1489 (m), 1457 (m), 1338 (s), 1251 (m), 1157 (s), 1053 (m), 860 (m), 739 (m).

HRMS (ESI) (*m/z*): calc'd for $C_{37}H_{53}N_4O_5SSi$ $[M+H]^+$: 693.3500, found: 693.3482

$[\alpha]_D^{27}$: –111 (*c* = 0.27, CH_2Cl_2).

TLC (30% acetone in hexanes), R*f*: 0.25 (UV, CAM).



(–)-**52** (–)-**10**

(–)-Communesin I (10):[72]

A solution of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 8.3 mg, 0.030 mmol, 4.0 equiv) in *N*,*N*-dimethylformamide (50 µL) was added to a solution of (–)-*N*8'-(trimethylsilyl)-ethanesulfonyl communesin I (**52**, 5.2 mg, 7.5 µmol, 1 equiv) in *N*,*N*-dimethylformamide (200 µL) at 23 ºC. After 2 h, a saturated aqueous sodium chloride solution (5 mL) and deionized water (3 mL) were added and the mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (2 × 8 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: 50%→60% ethyl acetate in dichloromethane) to afford (–)-communesin I (**10**, 3.11 mg, 78.4%) as a colorless film. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, 11:1 mixture of atropisomers, *denotes minor atropisomer):
δ 7.01 (app-td, *J* = 7.6, 1.4 Hz, 2H, C6'**H**, C6'**H***), 6.88 (t, *J* = 7.7 Hz, 1H, C6**H**), 6.85 (t, *J* = 8.2 Hz, 1H, C6**H***), 6.72 (t, *J* = 7.4 Hz, 2H, C5'**H**, C5'**H***), 6.69 (d, *J* = 7.7 Hz, 2H, C7'**H**, C7'**H***), 6.68 (d, *J* = 6.7 Hz, 1H, C4'**H**), 6.58 (d, *J* = 7.5 Hz, 1H, C4'**H***), 6.09 (d, *J* = 7.6 Hz, 1H, C5**H***), 6.06 (d, *J* = 7.6 Hz, 1H, C5**H**), 5.95 (d, *J* = 7.7 Hz, 1H, C7**H**), 5.91 (d, *J* = 7.9 Hz, 1H, C7**H***), 5.41 (app-s, 1H, C8a'**H***), 5.05 (d, *J* = 1.5 Hz, 1H, C8a'**H**), 4.70 (s, 1H, C8a**H**), 4.67 (s, 1H, C8a**H***), 4.59 (br-s, 1H, N8'**H**), 4.47 (d, *J* = 9.1 Hz, 1H, C9**H***), 4.20–4.15 (m, 1H, C3"**H***), 4.14 (d, *J* = 5.9 Hz, 1H, C3"O**H**), 4.11 (d, *J* = 9.3 Hz, 1H, C9**H**), 4.09–4.02 (m, 1H, C3"**H**), 3.92 (app-dd, *J* = 12.0, 8.4 Hz, 1H, C2'$\mathbf{H}_a$), 3.64 (app-t, *J* = 9.1 Hz, 1H, C2'$\mathbf{H}_a$*), 3.55 (app-dd, *J* = 16.1, 8.9 Hz, 1H, C2$\mathbf{H}_a$*), 3.46 (app-dd, *J* = 15.9, 9.6 Hz, 1H, C2$\mathbf{H}_a$), 3.41–3.30 (m, 2H, C2$\mathbf{H}_b$, C2$\mathbf{H}_b$*), 3.13–3.06 (m, 1H, C2'$\mathbf{H}_b$*), 3.00 (app-td, *J* = 11.8, 7.2 Hz, 1H, C2'$\mathbf{H}_b$), 2.97–2.89 (m, 1H, C3'$\mathbf{H}_a$*), 2.87 (d, *J* = 9.1 Hz, 1H, C10**H**), 2.86–2.81 (m, 7H, N8C$\mathbf{H}_3$, N8C$\mathbf{H}_3$*, C2"$\mathbf{H}_a$), 2.80 (d, *J* = 9.1 Hz, 1H, C10**H***), 2.71 (app-td, *J* = 12.4, 8.6 Hz, 1H, C3'$\mathbf{H}_a$), 2.49 (app-dd, *J* = 14.5, 3.6 Hz, 1H, C2"$\mathbf{H}_b$), 2.37 (app-dd, *J* = 13.1, 6.9 Hz, 2H, C3$\mathbf{H}_a$, C3$\mathbf{H}_a$*), 2.29 (app-dt, *J* = 13.0, 9.3 Hz, 2H, C3$\mathbf{H}_b$, C3$\mathbf{H}_b$*), 2.08–2.03 (m, 1H, C3'$\mathbf{H}_b$*), 2.00 (app-dd, *J* = 13.3, 6.9 Hz, 1H, C3'$\mathbf{H}_b$), 1.64–1.50 (m, 9H, C13$\mathbf{H}_3$,

72. The structure of (–)-communesin I (**10**) with our revised C3"-confuguration is depicted.

C13**H**$_3$*, C4"**H**$_2$, C5"**H**$_a$), 1.49–1.40 (m, 1H, C5"**H**$_b$), 1.39 (s, 3H, C$_{12}$**H**$_3$), 1.37 (s, 3H, C12**H**$_3$*), 0.96 (t, J = 7.1 Hz, 3H, C6"**H**$_3$), 0.93 (t, J = 7.2 Hz, 3H, C6"**H**$_3$*).

^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C, 11:1 mixture of atropisomers, *denotes minor atropisomer): δ 174.1 (**C**1"), 150.7 (**C**7a), 142.8 (**C**7a'), 136.3 (**C**4), 132.3 (**C**4a), 132.2 (**C**4a'), 129.1 (**C**6), 128.9 (**C**6*), 127.7 (**C**6'), 127.5 (**C**6'*), 123.4 (**C**4'*), 123.3 (**C**4'), 121.2 (**C**5'*), 120.7 (**C**5'), 117.3 (**C**7'*), 117.2 (**C**7'), 113.3 (**C**5), 102.0 (**C**7), 101.6 (**C**7*), 83.0 (**C**8a*), 82.6 (**C**8a), 79.3 (**C**8a'), 77.9 (**C**8a'*), 69.2 (**C**3"), 67.6 (**C**3"*), 65.4 (**C**9), 65.2 (**C**9*), 64.2 (2C, **C**10, **C**10*), 60.5 (**C**11), 52.2 (**C**3a'), 51.5 (**C**3a), 45.3 (**C**2'*), 44.2 (**C**2'), 42.2 (**C**2"), 39.6 (**C**4"), 37.9 (**C**3), 36.2 (**C**2), 32.5 (**C**3'*), 30.8 (**C**3'), 29.8 (N8**C**H$_3$*), 29.7 (N8**C**H$_3$), 25.0 (**C**12), 24.9 (**C**12*), 20.6 (**C**13*), 20.5 (**C**13), 19.1 (**C**5"), 14.3 (**C**6"), 14.2 (**C**6"*).

FTIR (thin film) cm^{-1}: 3460 (br-w), 3325 (br-w), 3052 (w), 2957 (m), 2927 (m), 2872 (m), 1625 (s), 1606 (s), 1596 (s), 1493 (s), 1428 (s), 1338 (m), 1279 (m), 1002 (m), 908 (m), 737 (s).

HRMS (ESI) (*m/z*): calc'd for $C_{32}H_{41}N_4O_3$ $[M+H]^+$: 529.3173, found: 529.3167.

$[\alpha]_D^{23}$: –137 (c = 0.22, MeOH).[73]

TLC (50% ethyl acetate in dichloromethane), R*f*: 0.19 (UV, CAM).

73. Literature value: $[\alpha]_D^{20}$ = –59 (c = 0.1, MeOH), see Fan, Y.-Q.; Li, P.-H.; Chao, Y.-X.; Chen, H.; Du, N.; He, Q.-X.; Liu, K.-C. *Mar. Drugs.* **2015**, *13*, 6489.

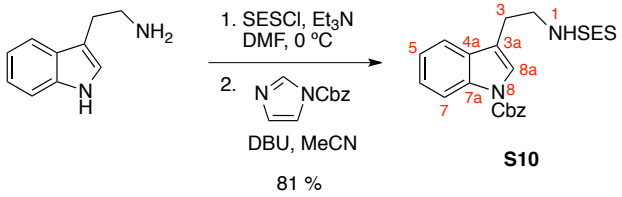
Table S14. Comparison of our ^{1}H NMR data for (–)-communesin I (10) with literature data ($CDCl_3$, major atropisomer):

Assignment	**Chen's Isolation Report**[74] (–)-Communesin I (**10**) ^{1}H NMR, 600 MHz, $CDCl_3$	**This Work** (–)-Communesin I (**10**) ^{1}H NMR, 600 MHz, $CDCl_3$
C2	3.46 (dd, *J* = 15.8, 9.5 Hz, 1H) 3.36 (dt, *J* = 15.8, 8.5 Hz, 1H)	3.46 (app-dd, *J* = 15.9, 9.6 Hz, 1H) 3.41–3.30 (m, 2H)
C3	2.37 (dd, *J* = 12.8, 8.5 Hz, 1H) 2.28 (dt, *J* = 12.8, 9.5 Hz, 1H)	2.37 (app-dd, *J* = 13.1, 6.9 Hz, 2H) 2.29 (app-dt, *J* = 13.0, 9.3 Hz, 2H)
C3a	–	–
C4a	–	–
C4	–	–
C5	6.05 (d, *J* = 7.7 Hz, 1H)	6.06 (d, *J* = 7.6 Hz, 1H)
C6	6.88 (t, *J* = 7.7 Hz, 1H)	6.88 (t, *J* = 7.7 Hz, 1H)
C7	5.95 (d, *J* = 7.7 Hz, 1H)	5.95 (d, *J* = 7.7 Hz, 1H)
C7a	–	–
N8C**H**$_3$	2.84 (s, 3H)	2.86–2.81 (m, 7H)
C8a	4.70 (s, 1H)	4.70 (s, 1H)
C9	4.11 (d, *J* = 9.0 Hz, 1H)	4.11 (d, *J* = 9.3 Hz, 1H)
C10	2.87 (d, *J* = 9.0 Hz, 1H)	2.87 (d, *J* = 9.1 Hz, 1H)
C11	–	–
C12	1.39 (s, 3H)	1.39 (s, 3H)
C13	1.57 (s, 3H)	1.64–1.50 (m, 9H)
C2'	3.92 (dd, *J* = 12.2, 8.7 Hz, 1H) 3.00 (dt, *J* = 12.2, 7.1 Hz, 1H)	3.92 (app-dd, *J* = 12.0, 8.4 Hz, 1H) 3.00 (app-td, *J* = 11.8, 7.2 Hz, 1H)
C3'	2.71 (dt, *J* = 12.2, 8.7 Hz, 1H) 2.00 (dd, *J* = 12.2, 7.1 Hz, 1H)	2.71 (app-td, *J* = 12.4, 8.6 Hz, 1H) 2.00 (app-dd, *J* = 13.3, 6.9 Hz, 1H)
C3a'	–	–
C4a'	–	–
C4'	6.68 (d, *J* = 7.6 Hz, 1H)	6.68 (d, *J* = 6.7 Hz, 1H)
C5'	6.71 (t, *J* = 7.6 Hz, 1H)	6.72 (t, *J* = 7.4 Hz, 2H)
C6'	7.01 (t, *J* = 7.6 Hz, 1H)	7.01 (app-td, *J* = 7.6, 1.4 Hz, 1H)
C7'	6.69 (d, *J* = 7.6 Hz, 1H)	6.69 (d, *J* = 7.7 Hz, 2H)
C7a'	–	–
C8a'	5.05 (s, 1H)	5.05 (d, *J* = 1.5 Hz, 1H)
C1"	–	–
C2"	2.82 (dd, *J* = 14.6, 3.4 Hz, 1H) 2.48 (dd, *J* = 14.6, 3.4 Hz, 1H)	2.86–2.81 (m, 7H) 2.49 (dd, *J* = 14.5, 3.6 Hz, 1H)
C3"	4.06 (br-s, 1H)	4.09–4.02 (m, 1H)
C3"O**H**	4.14 (br-s, 1H)	4.14 (d, *J* = 5.9 Hz, 1H)
C4"	1.60 (m, 1H), 1.53 (m, 1H)	1.64–1.50 (m, 9H)
C5"	1.54 (m, 1H), 1.44 (m, 1H)	1.64–1.50 (m, 9H), 1.49–1.40 (m, 1H)
C6"	0.96 (t, *J* = 7.0 Hz, 3H)	0.96 (t, *J* = 7.1 Hz, 3H)
N8'H	–	4.59 (br-s, 1H)

74. Fan, Y.-Q.; Li, P.-H.; Chao, Y.-X.; Chen, H.; Du, N.; He, Q.-X.; Liu, K.-C. *Mar. Drugs.* **2015**, *13*, 6489.

Table S15. Comparison of our ^{13}C NMR data for (–)-communesin I (10) with literature data ($CDCl_3$, major atropisomer):

Assignment	Chen's Isolation Report[74] (–)-Communesin I (**10**) ^{13}C NMR, 150 MHz $CDCl_3$	This Work (–)-Communesin I (**10**) ^{13}C NMR, 150.9 MHz, $CDCl_3$	Chemical Shift Difference $\Delta\delta = \delta$ (this work) – δ (Chen report)
C2	36.1	36.2	0.1
C3	37.7	37.9	0.2
C3a	51.3	51.5	0.2
C4a	132.1	132.3	0.2
C4	136.1	136.3	0.2
C5	113.1	113.3	0.2
C6	129.0	129.1	0.1
C7	101.9	102.0	0.1
C7a	150.5	150.7	0.2
N8$\mathbf{C}H_3$	29.6	29.7	0.1
C8a	82.4	82.6	0.2
C9	65.2	65.4	0.2
C10	64.1	64.2	0.1
C11	60.4	60.5	0.1
C12	24.9	25.0	0.1
C13	20.3	20.5	0.2
C2'	44.1	44.2	0.1
C3'	30.6	30.8	0.2
C3a'	52.1	52.2	0.1
C4a'	132.1	132.3	0.2
C4'	123.2	123.3	0.1
C5'	120.6	120.7	0.1
C6'	127.5	127.7	0.2
C7'	117.0	117.2	0.2
C7a'	142.6	142.8	0.2
C8a'	79.1	79.3	0.2
C1"	173.9	174.1	0.2
C2"	42.1	42.2	0.1
C3"	69.0	69.2	0.2
C4"	39.5	39.6	0.1
C5"	18.9	19.1	0.2
C6"	14.1	14.3	0.2



Tryptamine S10:

2-(Trimethylsilyl)ethanesulfonyl chloride (455 µL, 2.40 mmol, 1.20 equiv) was added dropwise via syringe over 15 min to a solution of tryptamine (320 mg, 2.00 mmol, 1 equiv) and triethylamine (1.00 mL, 7.20 mmol, 3.60 equiv) in *N*,*N*-dimethylformamide (4.00 mL) at 0 ºC. After 30 min, the suspension was diluted with a saturated aqueous ammonium sulfate solution (45 mL) and deionized water (15 mL). After warming to 23 ºC, the mixture was extracted with diethyl ether (3 × 40 mL) and the combined organic extracts were washed successively with an aqueous hydrogen chloride solution (1 N, 80 mL) and a saturated aqueous sodium chloride solution (80 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was dissolved in acetonitrile (6.00 mL) and samples of benzyl 1*H*-imidazole-1-carboxylate[75] (445 mg, 2.20 mmol, 1.10 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 75.0 µL, 0.500 mmol, 0.250 equiv) were then added. After stirring for 21 h at 23 ºC, the pale-beige solution was diluted with an aqueous hydrogen chloride solution (1 N, 10 mL) and deionized water (40 mL). The mixture was extracted with ethyl acetate (3 × 50 mL) and the combined organic extracts were washed with a saturated aqueous sodium chloride solution (100 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: 20%→25% ethyl acetate in hexanes) to afford tryptamine **S10** (747 mg, 81.5% over two steps) as white solid. Structural assignments were made using information from gCOSY, gHSQC, and gHMBC experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 21 °C): δ 8.19 (br-s, 1H, C7**H**), 7.55 (d, *J* = 7.6 Hz, 1H, C4**H**), 7.53–7.47 (m, 3H, C8a**H**, Ar_{Cbz}-*o*-**H**), 7.45–7.37 (m, 3H, Ar_{Cbz}-*m*-**H**, Ar_{Cbz}-*p*-**H**), 7.34 (app-t, *J* = 7.6 Hz, 1H, C6**H**), 7.27 (app-t, *J* = 7.1 Hz, 1H, C5**H**), 5.43 (s, 2H, N8$CO_2C\mathbf{H}_2$Ph), 4.66 (t, *J* = 6.3 Hz, 1H, N8**H**CO_2CH_2Ph), 3.43 (app-q, *J* = 6.9 Hz, 2H, C2$\mathbf{H}_2$), 2.97 (t, *J* = 7.1 Hz, 2H, C3$\mathbf{H}_2$), 2.89–2.83 (m, 2H, N1H$SO_2C\mathbf{H}_2$), 0.99–0.83 (m, 2H, N1H$SO_2CH_2C\mathbf{H}_2$), –0.01 (s, 9H, $Si(C\mathbf{H}_3)_3$).

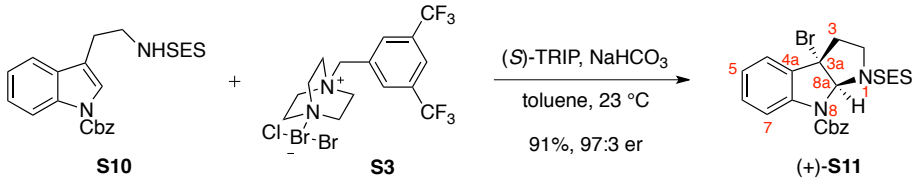
^{13}C NMR (125.8 MHz, $CDCl_3$, 21 °C): δ 150.7 (N8$\mathbf{C}O_2CH_2$Ph), 135.7 (**C**7a), 135.1 (Ar_{Cbz}-*ipso*-**C**), 130.0 (**C**4a), 128.8 (2C, Ar_{Cbz}-*m*-**C**, Ar_{Cbz}-*p*-**C**), 128.6 (Ar_{Cbz}-*o*-**C**), 125.1 (**C**6), 123.3 (**C**8a), 123.1 (**C**5), 118.9 (**C**4), 117.7 (**C**3a), 115.5 (**C**7), 68.8 (N8$CO_2\mathbf{C}H_2$Ph), 48.8 (N1$SO_2\mathbf{C}H_2$), 42.8 (**C**2), 26.4 (**C**3), 10.5 (N1$SO_2CH_2\mathbf{C}H_2$), –2.0 ($Si(\mathbf{C}H_3)_3$).

FTIR (thin film) cm^{-1}: 3239 (w), 2955 (w), 1739 (s), 1454 (m), 1394 (s), 1355 (s), 1317 (m), 1249 (s), 1212 (m), 860 (m), 742 (s).

HRMS (DART) (*m/z*): calc'd for $C_{23}H_{31}N_2O_4SSi$ $[M+H]^+$: 459.1768,
found: 459.1766.

TLC (20% ethyl acetate in hexanes), R*f*: 0.20 (UV, CAM).

75. Heller, S. T.; Schultz, E. E.; Sarpong, R. *Angew. Chem. Int. Ed.* **2012**, *51*, 8304.



Bromocyclotryptamine (+)-S11:

A sample of bromine salt **S3**[8] (437 mg, 817 μmol, 1.30 equiv) was added to a suspension of tryptamine **S10** (288 mg, 628 μmol, 1 equiv), *(S)*-3,3′-bis(2,4,6-triisopropyl-phenyl)-1,1′-binaphthyl-2,2′-diyl hydrogenphosphate ((*S*)-TRIP, 47.3 mg, 62.8 μmol, 0.100 equiv), and crushed sodium hydrogen carbonate (211 mg, 2.51 mmol, 4.00 equiv) in toluene (12.6 mL) at 23 ºC. After stirring for 23 h, the orange suspension was diluted with an aqueous sodium thiosulfate solution (1M, 50 mL) and was stirred vigorously for 5 min. The mixture was extracted with ethyl acetate (3 × 25 mL). The combined organic extracts were washed successively with an aqueous sodium thiosulfate solution (1 M, 75 mL) and a saturated aqueous sodium chloride solution (75 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 10% ethyl acetate in hexanes) to afford bromocyclotryptamine (+)-**S11** (307 mg, 90.9%, 97:3 er) as a sticky white foam.[10] The enantiomeric ratio was determined by chiral HPLC analysis (CHIRALPAK® IA, 15% *i*PrOH in hexanes, 1.0 mL/min, 220 nm, t_R (major) = 7.0 min, t_R (minor) = 9.3 min). As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments also collected at elevated temperature.

^{1}H NMR (500 MHz, CD_3CN, 60 °C): δ 7.69 (d, *J* = 8.2 Hz, 1H, C7**H**), 7.54–7.48 (m, 3H, C4**H**, Ar_{Cbz}-*o*-**H**), 7.45–7.39 (m, 2H, Ar_{Cbz}-*m*-**H**), 7.39–7.32 (m, 2H, C6**H**, Ar_{Cbz}-*p*-**H**), 7.19 (t, *J* = 7.6 Hz, 1H, C5**H**), 6.47 (s, 1H, C8a**H**), 5.41 (d, *J* = 12.2 Hz, 1H, N8CO_2C$\mathbf{H}_a$Ph), 5.29 (d, *J* = 12.2 Hz, 1H, N8CO_2C$\mathbf{H}_b$Ph), 3.86 (app-dd, *J* = 10.8, 7.2 Hz, 1H, C2$\mathbf{H}_a$), 3.14–2.99 (m, 2H, N1SO_2C$\mathbf{H}_2$), 2.93 (app-dd, *J* = 11.9, 4.3 Hz, 1H, C3$\mathbf{H}_a$), 2.85 (app-td, *J* = 10.9, 4.1 Hz, 1H, C2$\mathbf{H}_b$), 2.76 (app-td, *J* = 11.9, 7.5 Hz, 1H, C3$\mathbf{H}_b$), 1.01–0.78 (m, 2H, N1SO_2CH_2C$\mathbf{H}_2$), 0.01 (s, 9H, Si(C$\mathbf{H}_3$)$_3$).

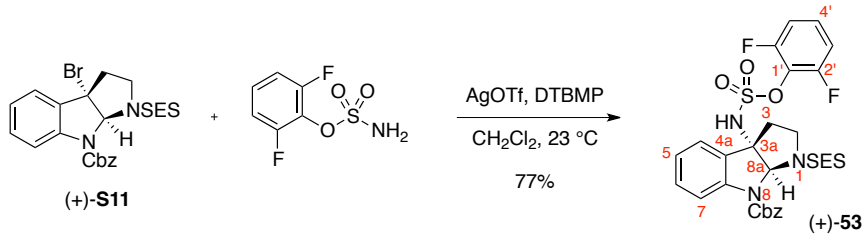
^{13}C NMR (125.8 MHz, CD_3CN, 60 °C): δ 154.2 (N8**C**O_2CH_2Ph), 142.2 (**C**7a), 137.2 (Ar_{Cbz}-*ipso*-**C**), 133.7 (**C**4a), 132.1 (**C**6), 129.9 (Ar_{Cbz}-*m*-**C**), 129.7 (2C, Ar_{Cbz}-*o*-**C**, Ar_{Cbz}-*p*-**C**), 126.1 (**C**5), 126.0 (**C**4), 117.6 (**C**7), 87.7 (**C**8a), 69.4 (N8CO_2**C**H_2Ph), 64.6 (**C**3a), 51.1 (N1SO_2**C**H_2), 50.1 (**C**2), 44.7 (**C**3), 11.3 (N1SO_2CH_2**C**H_2), –1.5 (Si(**C**H_3)$_3$).

FTIR (thin film) cm^{-1}: 2952 (w), 2896 (w), 1710 (s), 1481 (s), 1395 (s), 1326 (s), 1249 (s), 1140 (s), 1040 (m), 832 (s).

HRMS (DART) (*m/z*): calc'd for $C_{23}H_{30}BrN_2O_4SSi$ $[M+H]^+$: 537.0873, found: 537.0872.

$[\alpha]_D^{22}$: +77 (*c* = 1.43, CH_2Cl_2).

TLC (10% ethyl acetate in hexanes), R*f*: 0.25 (UV, CAM).



Sulfamate ester (+)-53:

A sample of silver trifluoromethanesulfonate (278 mg, 1.08 mmol, 2.00 equiv) was added to a solution of bromocyclotryptamine (+)-**S11** (291 mg, 0.542 mmol, 1 equiv), 2,6-difluorophenyl sulfamate[11] (227 mg, 1.08 mmol, 2.00 equiv), and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 278 mg, 1.35 mmol, 2.50 equiv) in dichloromethane (13.6 mL) at 23 ºC in the dark. After 1.5 h, the milky beige suspension was diluted with ethyl acetate (27 mL) and was filtered through a pad of pad of Celite. The filter cake was washed with ethyl acetate (136 mL) and the colorless filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 40%→50% diethyl ether in hexanes) to afford sulfamate ester (+)-**53** (278 mg, 77.0%) as a white foam. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature. Structural assignments were made using additional information from gCOSY, gHSQC, and gHMBC experiments also collected at elevated temperature.

^{1}H NMR (400 MHz, CD_3CN, 60 °C): δ 7.73 (br-d, *J* = 8.3 Hz, 1H, C7**H**), 7.53 (ddd, *J* = 7.7, 1.4, 0.6 Hz, 1H, C4**H**), 7.48–7.43 (m, 2H, Ar_{Cbz}-*o*-**H**), 7.43–7.38 (m, 1H, C6**H**), 7.38–7.27 (m, 4H, C4'**H**, Ar_{Cbz}-*m*-**H**, Ar_{Cbz}-*p*-**H**), 7.18 (app-td, *J* = 7.6, 1.1 Hz, 1H, C_5**H**), 7.13 (br-s, 1H, N**H**SO_3Ar), 7.11–7.04 (m, 2H, C3'**H**), 6.56 (s, 1H, C8a**H**), 5.37 (d, *J* = 12.3 Hz, 1H, N8CO_2C**H**$_a$Ph), 5.23 (d, *J* = 12.3 Hz, 1H, N8CO_2C**H**$_b$Ph), 3.93 (app-dd, *J* = 11.2, 7.5 Hz, 1H, C2**H**$_a$), 3.15–2.94 (m, 2H, N1SO_2C**H**$_2$), 2.87 (ddd, *J* = 12.2, 11.2, 4.6 Hz, 1H, C2**H**$_b$), 2.72 (app-td, *J* = 12.2, 7.5 Hz, 1H, C3**H**$_a$), 2.54 (app-dd, *J* = 12.2, 4.6 Hz, 1H, C3**H**$_b$), 0.99–0.79 (m, 2H, N1SO_2CH_2C**H**$_2$), 0.01 (s, 9H, Si(C**H**$_3$)$_3$).

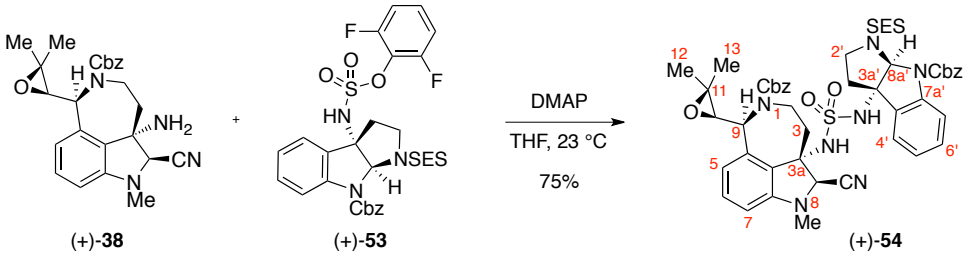
^{13}C NMR (100.6 MHz, CD_3CN, 60 °C): δ 157.0 (dd, *J* = 252, 3.7 Hz, **C**2'), 154.1 (N8**C**O_2CH_2Ph), 143.9 (**C**$_{7a}$), 137.2 (Ar_{Cbz}-*ipso*-**C**), 131.9 (**C**6), 130.3 (**C**4a), 129.6 (Ar_{Cbz}-*m*-**C**), 129.4 (t, *J* = 9.5 Hz, **C**4'), 129.4 (Ar_{Cbz}-*p*-**C**), 129.4 (Ar_{Cbz}-*o*-**C**), 127.6 (t, *J* = 15.8 Hz, **C**1'), 126.1 (**C**4), 125.3 (**C**5), 117.4 (**C**7), 114.0–113.6 (m, **C**3'), 82.7 (**C**8a), 74.0 (**C**3a), 68.8 (N8CO_2**C**H_2Ph), 50.7 (N1SO_2**C**H_2), 48.7 (**C**2), 38.8 (**C**3), 11.1 (N1SO_2CH_2**C**H_2), –1.8 (Si(**C**H_3)$_3$).

^{19}F NMR (376.4 MHz, CD_3CN, 25 °C): δ –126.2 (s, C_6H_3**F**$_2$).

FTIR (thin film) cm^{-1}: 3210 (br-w), 2952 (w), 2897 (w), 1710 (m), 1605 (m), 1480 (m), 1389 (m), 1324 (m), 1247 (m), 1138 (m), 1010 (s), 859 (s), 832 (s), 744 (s), 522 (s).

HRMS (DART) (*m/z*): calc'd for $C_{29}H_{34}F_2N_3O_7S_2Si$ $[M+H]^+$: 666.1570, found: 666.1562.

$[\alpha]_D^{23}$:	+52 (*c* = 0.51, CH_2Cl_2).
TLC (50% diethyl ether in hexanes), R*f*:	0.20 (UV, CAM).



(+)-**38** (+)-**53** (+)-**54**

Sulfamide (+)-54:

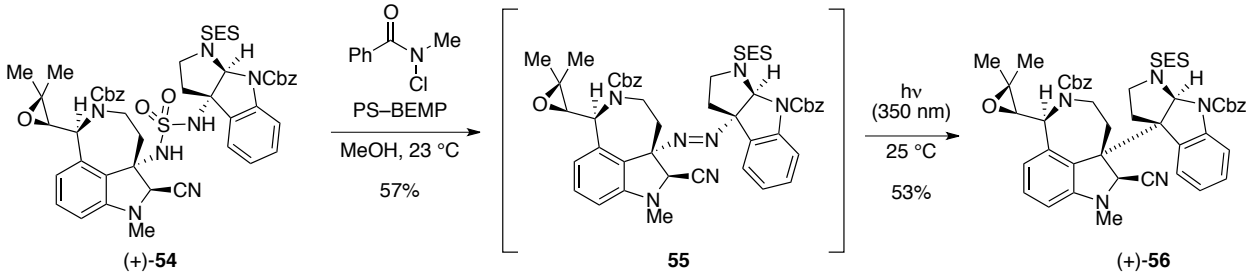
A 10-mL round-bottom flask was charged with samples of benzylic aminonitrile (+)-**38** (37.0 mg, 85.5 μmol, 1 equiv) and sulfamate ester (+)-**53** (102 mg, 154 μmol, 1.80 equiv) and the resulting mixture was azeotropically dried by concentration from anhydrous benzene (3 × 1.5 mL). The residue was dissolved in tetrahydrofuran (340 μL) and a sample of 4-(dimethylamino)pyridine (20.9 mg, 171 μmol, 2.00 equiv) was added as a solid at 23 ºC. After 23 h, the light-brown solution was diluted with a saturated aqueous ammonium sulfate solution (8 mL) and deionized water (4 mL) and the mixture was extracted with ethyl acetate (3 × 8 mL). The combined organic extracts were washed with a saturated aqueous sodium chloride solution (20 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 30%→40% ethyl acetate in hexanes) to afford sulfamide (+)-**54** (62.5 mg, 75.4%) as a white film. 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):[76]	δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.36 (dd, *J* = 7.3, 2.2 Hz, 3H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.19–7.15 (m, 3H), 7.15–7.03 (m, 6H), 7.03–6.95 (m, 1H), 6.95–6.78 (m, 2H), 6.45 (br-s, 1H), 6.20 (br-s, 1H), 5.36 (d, *J* = 9.3 Hz, 1H), 5.29 (d, *J* = 12.3 Hz, 1H), 5.18 (d, *J* = 12.3 Hz, 1H), 5.17–5.08 (m, 2H), 5.08–4.88 (br-m, 1H), 4.68 (br-s, 1H), 4.49 (s, 1H), 3.98 (dd, *J* = 11.6, 7.2 Hz, 1H), 3.56 (dd, *J* = 14.1, 6.3 Hz, 1H), 3.20 (dd, *J* = 13.3, 4.0 Hz, 1H), 3.09 (td, *J* = 13.6, 4.4 Hz, 1H), 2.88 (br-s, 1H), 2.71–2.24 (m, 6H), 2.11 (d, *J* = 8.3 Hz, 1H), 1.28 (s, 3H), 1.06–0.86 (m, 2H), 0.99 (s, 3H), –0.12 (s, 9H).
^{13}C NMR (100.6 MHz, C_6D_6, 70 °C):[77]	δ 157.7 (br), 153.9, 152.0, 143.3, 138.8, 137.2, 136.4, 131.4, 130.6, 128.9, 128.7 (2C), 128.5, 128.2, 127.9, 127.4 (br), 125.5, 124.2, 118.2, 116.6, 115.5, 108.6, 84.1, 73.1, 68.5, 68.3, 67.2, 66.9 (br), 63.4, 59.8, 59.0 (br), 50.8, 47.1, 41.5, 40.5 (br), 33.2 (br), 32.8, 24.3, 19.9, 10.8, –2.0.
FTIR (thin film) cm^{-1}:	3253 (br-w), 2955 (w), 2896 (w), 1708 (s), 1600 (m), 1484 (m), 1397 (m), 1327 (s), 1263 (s), 1250 (s), 1141 (s), 838 (m), 750 (m), 698 (m).
HRMS (ESI) (*m/z*):	calc'd for $C_{48}H_{57}N_7NaO_9S_2Si$ $[M+Na]^+$: 990.3321, found: 990.3337.

76. The reported integrals are an approximation due to the presence of multiple conformers and significant atropisomerism.
77. Atropisomerism causes significant signal broadening and not all ^{13}C resonances were observed. All expected ^{13}C signals were observed in the heterodimeric product isolated in the next step of our synthesis.

$[\alpha]_D^{23}$: +86 (*c* = 0.13, CH_2Cl_2).

TLC (40% ethyl acetate in hexanes), R*f*: 0.33 (UV, CAM).



Heterodimer (+)-56:

N-Chloro-*N*-methylbenzamide[31] (63.1 mg, 372 μmol, 6.00 equiv) and resin-bound 2-*tert*-butyl-imino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2-diazaphosphorine (PS–BEMP, 340 mg, 2.19 mmol/g on 200-400 mesh polystyrene resin, 744 μmol, 12.0 equiv) were added in rapid succession to a solution of sulfamide (+)-**54** (60.0 mg, 62.0 μmol, 1 equiv) in methanol (6.2 mL) at 23 ºC in the dark. After 15 min, the suspension was filtered through a pad of Celite, and the filter cake was washed sequentially with methanol (10 mL), dichloromethane (10 mL), and ethyl acetate (10 mL). The colorless filtrate was concentrated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (eluent: 6% ethyl acetate, 47% hexanes, 47% dichloromethane → 10% ethyl acetate, 45% hexanes, 45% dichloromethane) to afford diazene **55** (32.0 mg, 57.2%) as a light yellow foam,[78] which was used directly in the next step without further purification.

A solution of diazene **55** (32.0 mg, 35.5 μmol, 1 equiv) in dichloromethane (10 mL) was concentrated under reduced pressure in a 100-mL round bottom flask to provide a thin film of the diazene coating the flask. The flask was evacuated and backfilled with argon (three cycles) and was then irradiated in a Rayonet photoreactor equipped with 14 radially distributed (r = 12.7 cm) 25 W lamps (λ = 350 nm) at 25 ºC. After irradiating for 3 h, the lamps were turned off and the resulting residue was purified by flash column chromatography on silica gel (eluent: 8% ethyl acetate, 46% hexanes, 46% dichloromethane→10% ethyl acetate, 45% hexanes, 45% dichloromethane) to afford heterodimer (+)-**56** (16.4 mg, 52.8%) as a pale-yellow film. As a result of the slow conformational equilibration at ambient temperature, NMR spectra were collected at elevated temperature.

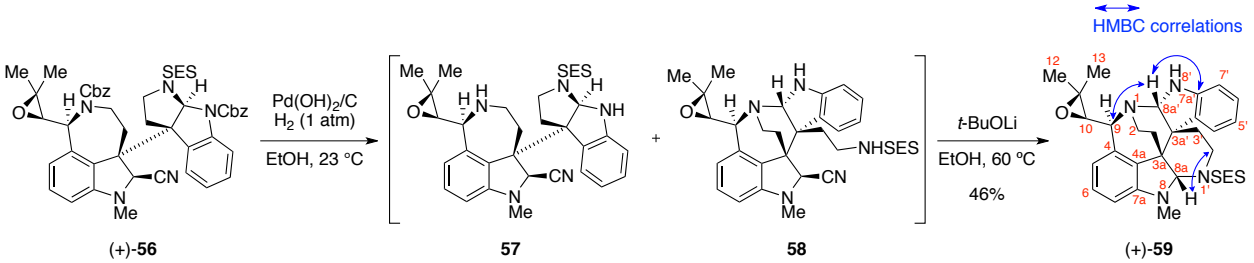
^{1}H NMR (400 MHz, CD_3CN, 70 °C):[76] δ 7.75 (d, *J* = 8.1 Hz, 1H), 7.56–7.48 (m, 4H), 7.48–7.35 (m, 7H), 7.34–7.27 (m, 2H), 7.15 (t, *J* = 6.8 Hz, 1H), 6.64 (dt, *J* = 7.9, 1.0 Hz, 1H), 6.36 (d, *J* = 7.3 Hz, 1H), 5.50 (s, 1H), 5.47 (d, *J* = 8.8 Hz, 1H), 5.36 (d, *J* = 12.1 Hz, 1H), 5.17 (d, *J* = 12.0 Hz, 2H), 4.05 (dt, *J* = 14.3, 2.7 Hz, 1H), 3.68 (s, 1H), 3.40–3.27 (m, 1H), 3.08–2.90 (m, 1H), 2.86 (d, *J* = 8.7 Hz, 1H), 2.67–2.55 (m, 2H), 2.45 (s, 3H), 2.44–2.33 (m, 1H), 2.04 (dt, *J* = 15.5, 2.2 Hz, 1H), 1.96 (s, 2H), 1.82 (br-s, 2H), 1.57 (s, 3H), 1.38 (s, 3H), 0.61–0.52 (m, 2H), –0.05 (s, 9H).

^{13}C NMR (100.6 MHz, CD_3CN, 70 °C): δ 156.9, 153.9, 153.8, 144.2, 139.2, 138.5, 137.4, 132.2, 132.1, 131.3, 130.5, 130.4, 130.0, 129.9, 129.7, 128.5, 126.5, 126.1, 125.7, 120.7, 118.1, 117.6, 109.5, 81.8, 70.8, 69.3, 68.6, 67.5, 67.2, 62.3, 59.5, 58.5, 50.1, 48.9, 43.0, 36.0, 34.3, 28.9, 24.9, 20.1, 11.3, –1.4.

78. As a result of the sensitivity of this intermediate, its slow conformational equilibrium at ambient temperature, and its instability at elevated temperatures, diazene **55** was used immediately in the next step.

FTIR (thin film) cm^{-1}:	2956 (w), 2893 (w), 1703 (s), 1585 (w), 1481 (m), 1403 (s), 1330 (s), 1141 (s), 1053 (m), 860 (m), 753 (s), 699 (s).
HRMS (DART) (*m/z*):	calc'd for $C_{48}H_{56}N_5O_7SSi$ $[M+H]^+$: 874.3664, found: 874.3678.
$[\alpha]_D^{23}$:	+128 (*c* = 0.82, CH_2Cl_2).

TLC (10% ethyl acetate, 45% hexanes, 45% dichloromethane), R*f*: 0.22 (UV, CAM).



(+)-*N*1'-(Trimethylsilyl)ethanesulfonyl *iso*-communesin (59):

A sample of palladium(II) hydroxide on carbon (15.7 wt% on wet support, 3.2 mg, 3.6 μmol, 0.60 equiv) was added to a solution of heterodimer (+)-**56** (5.3 mg, 6.0 μmol, 1 equiv) in anhydrous ethanol (200 proof, 400 μL) at 23 ºC. The resulting suspension was sparged with dihydrogen for 7 min by discharge of a balloon equipped with a needle extending into the reaction mixture. After vigorous stirring for 3.5 h under an atmosphere of dihydrogen, the suspension was sparged with dinitrogen for 5 min and was then diluted with ethyl acetate (6 mL) and filtered through a plug of Celite. The filter cake was washed with ethyl acetate (8 mL) and the colorless filtrate was concentrated under reduced pressure. The resulting residue was filtered through a plug of silica gel (eluent: ethyl acetate) and the filtrate was concentrated under reduced pressure to yield a mixture of heterodimeric diamine **57** (major) and hexacyclic aminonitrile **58** (minor), which was used directly in the next step without further purification.[79]

The crude mixture of **57** and **58** was dissolved in dichloromethane (1 mL) and transferred to a pressure tube equipped with a magnetic stir bar. The transfer was quantitated with additional dichloromethane (2 × 1 mL) and the resulting solution was concentrated under reduced pressure. The tube was refilled with argon and was then charged with a solution of lithium *tert*-butoxide in anhydrous ethanol (0.20 M, 0.60 mL, 0.12 mmol, 20 equiv). The tube was sealed under an argon atmosphere with a Teflon screwcap and was immersed in a pre-heated oil bath at 60 ºC. After stirring at this temperature for 45 h, the homogeneous orange solution was cooled to 23 ºC and was diluted with a saturated aqueous sodium bicarbonate solution (5 mL). The mixture was extracted with ethyl acetate (3 × 5 mL) and the combined organic extracts were washed with a saturated aqueous sodium chloride solution (10 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting orange residue was purified by flash column chromatography on silica gel (eluent: 30%→40% ethyl acetate in hexanes) to afford (+)-*N*1'-(trimethylsilyl)ethanesulfonyl *iso*-communesin (**59**, 1.62 mg, 46.3%) as a white film. Structural assignments were made using additional information from gCOSY, gHSQC, gHMBC, and 1D selective NOESY experiments.

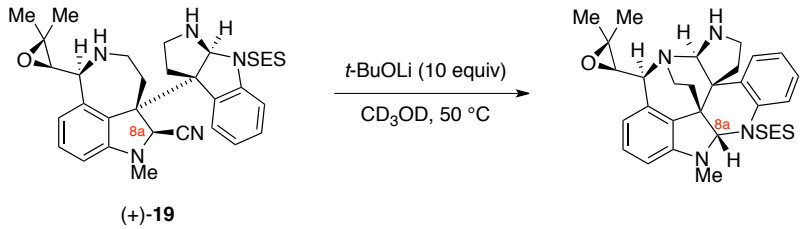
^{1}H NMR (600 MHz, CD_3OD, 25 °C): δ 7.19 (d, *J* = 7.8 Hz, 1H, C4'**H**), 6.89 (t, *J* = 7.8 Hz, 1H, C6**H**), 6.78 (td, *J* = 7.5, 1.3 Hz, 1H, C6'**H**), 6.44 (d, *J* = 7.8 Hz, 1H, C7'**H**), 6.42 (d, *J* = 7.8 Hz, 1H, C7**H**), 6.18 (td, *J* = 7.5, 1.3 Hz, 1H, C5'**H**), 6.05 (d, *J* = 8.0 Hz, 1H, C5**H**), 4.88 (s, 1H, C8a**H**), 4.39 (s, 1H, C8a'**H**), 3.75 (dt, *J* = 15.0, 3.0 Hz, 1H, C2'$\mathbf{H}_a$), 3.69 (d, *J* = 9.5 Hz, 1H, C9**H**), 3.57–3.49 (m, 2H, C2$\mathbf{H}_a$, C2'$\mathbf{H}_b$), 3.26–3.13 (m, 3H, C2$\mathbf{H}_b$, N1'$SO_2C\mathbf{H}_2$), 3.09 (d, *J* = 9.3 Hz, 1H, C10**H**), 2.88 (s, 3H, N8C$\mathbf{H}_3$), 2.48 (dt, *J* = 13.5, 9.5 Hz, 1H, C3$\mathbf{H}_a$), 2.09 (td, *J* = 13.1, 3.6 Hz, 1H, C3'$\mathbf{H}_a$), 2.00–1.94 (m, 1H, C3$\mathbf{H}_b$), 1.40 (s, 3H, C12$\mathbf{H}_3$), 1.37 (dt, *J* = 13.5,

79. While **57** and **58** can be separated via flash chromatography on silica gel, the mixture was used directly in the next step since **57** rapidly converts to **58** upon treatment with ethanolic lithium *tert*-butoxide at 23 ºC in the subsequent step. See later in this document for *in situ* monitoring of the rearrangement of pure **57** to (+)-**59** by ^{1}H NMR spectroscopy.

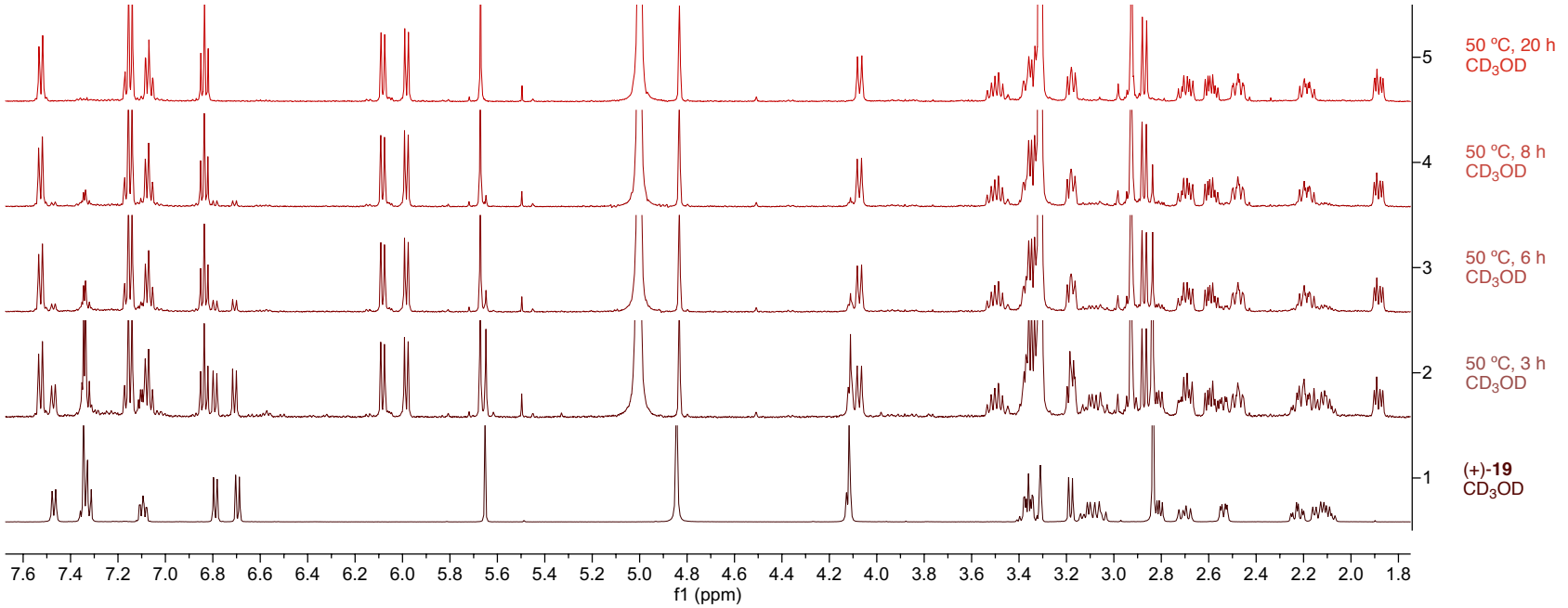
	2.4 Hz, 1H, C3'**H**$_b$), 1.21 (s, 3H, C13**H**$_3$), 1.16–1.10 (m, 2H, N1'SO$_2$CH$_2$C**H**$_2$), 0.13 (s, 9H, Si(CH$_3$)$_3$).
^{13}C NMR (150.9 MHz, CD_3OD, 25 °C):	δ 150.5 (2C, **C**7a, **C**7a'), 137.6 (**C**4), 132.9 (**C**4a'), 132.5 (**C**4a), 129.8 (**C**6), 129.2 (**C**6'), 126.2 (**C**4'), 118.3 (**C**5'), 117.6 (**C**5), 108.5 (**C**7'), 108.1 (**C**7), 83.8 (**C**8a'), 82.9 (**C**8a), 65.0 (**C**10), 62.2 (**C**11), 59.6 (**C**9), 56.3 (**C**3a'), 50.5 (N1'SO$_2$**C**H$_2$), 43.4 (**C**3a), 41.0 (**C**2), 39.4 (**C**2'), 35.3 (**C**3), 33.2 (N8**C**H$_3$), 31.1 (**C**3'), 24.9 (**C**12), 19.6 (**C**13), 11.6 (N1'SO$_2$CH$_2$**C**H$_2$), –2.0 (Si(**C**H$_3$)$_3$).
FTIR (thin film) cm^{-1}:	3354 (br-w), 2954 (m), 2925 (m), 2867 (w), 1605 (m), 1468 (s), 1341 (m), 1324 (m), 1144 (s), 1029 (s), 860 (s), 833 (s), 742 (s), 600 (m).
HRMS (DART) (*m/z*):	calc'd for $C_{31}H_{43}N_4O_3SSi$ $[M+H]^+$: 579.2820, found: 579.2823.
$[\alpha]_D^{22}$:	+94 (*c* = 0.08, MeOH).
TLC (40% ethyl acetate in hexanes), R*f*:	0.22 (UV, CAM).

In Situ ^{1}H NMR Monitoring of the Conversion of Heterodimeric Diamine (+)-19 to the Epoxide-bearing Communesin Core:

Treatment of diamine (+)-**19** with lithium *tert*-butoxide (10 equiv) in methanol-d_4 provided clean and complete conversion to the desired heptacyclic structure within 20 h at 50° C as observed by in situ ^{1}H NMR spectroscopy. Trace1: ^{1}H NMR (500 MHz, 20 ºC, CD_3OD) of pure diamine (+)-**19** for reference. Trace2–5: monitoring of the conversion of diamine (+)-**19** to the epoxide-bearing communesin core. We observe D-incorporation at C8a (~16%) and at the acidic alpha-methylene of the sulfonyl group (84% -SO_2CD_2-, 16% -SO_2CDH-) of the product.

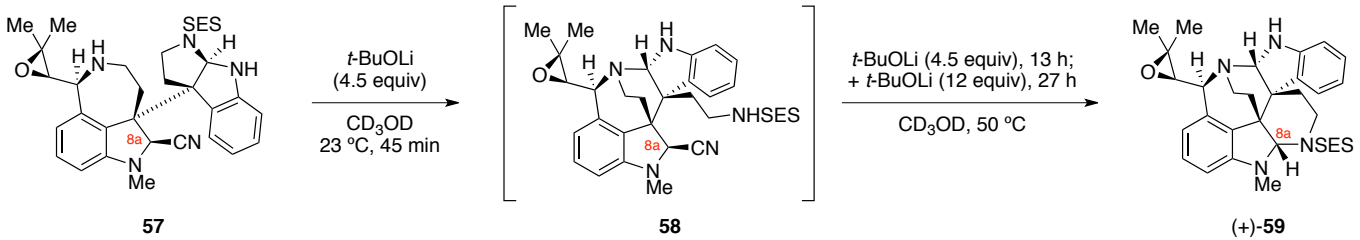


(+)-**19**

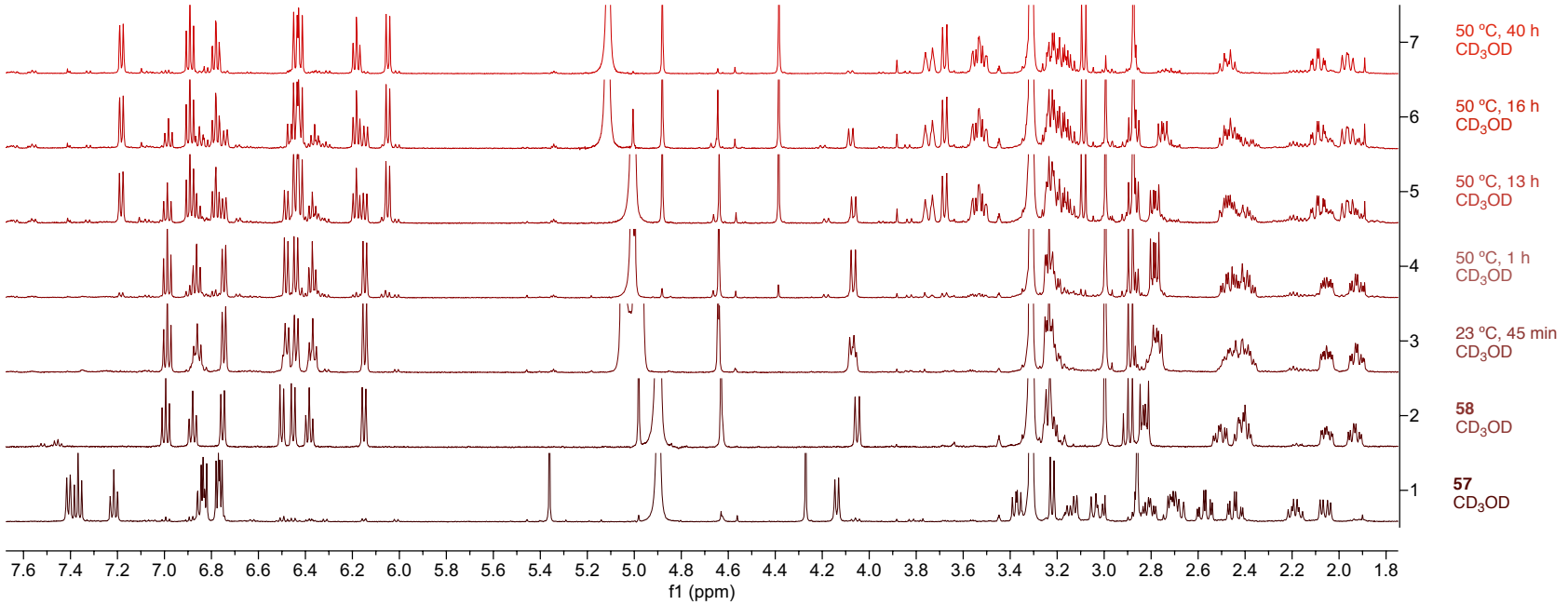


In Situ ^{1}H NMR Monitoring of the Conversion of Diamine 57 to Heptacycle (+)-59:

Treatment of diamine **57** with lithium *tert*-butoxide in methanol-d_4 provided clean and complete conversion to the desired heptacyclic structure (+)-**59** within 40 h at 50° C as observed by in situ ^{1}H NMR spectroscopy. Trace1: ^{1}H NMR (500 MHz, 20 ºC, CD_3OD) of pure heterodimer **57** for reference. Trace2: ^{1}H NMR (500 MHz, 20 ºC, CD_3OD) of pure hexacyclic aminonitrile **58** for reference**.** Trace 3: ^{1}H NMR (500 MHz, 20 ºC, CD_3OD) of **57** with *t*-BuOLi (4.5 equiv) at 23 ºC for 45 min, which produced quantitative conversion to **58**. Trace4–7: monitoring of the conversion of hexacyclic aminonitrile **58** to the *iso*-communesin core (+)-**59**. We observe D-incorporation at C8a (~17%) of the product.



57 **58** (+)-**59**



Crystal Structure of (10*S*)-Tetracyclic Amine (–)-36:

Structural parameters for (10*S*)-Tetracyclic Amine (–)-**36** are freely available from the Cambridge Crystallographic Data Center (CCDC 1937970).

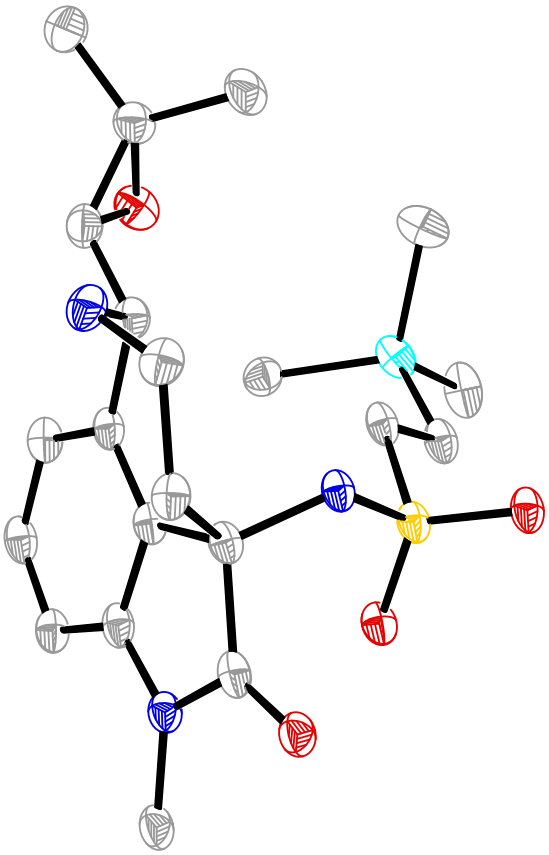


Table S16. Crystal data and structure refinement for (10*S*)-Tetracyclic Amine (–)-**36**.

Identification code	5-19_10	
Empirical formula	C21 H33 N3 O4.25 S Si	
Formula weight	455.65	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 13.949(3) Å	a= 90°.
	b = 9.712(2) Å	b= 110.621(4)°.
	c = 19.552(5) Å	g = 90°.
Volume	2479.1(10) $Å^3$	
Z	4	
Density (calculated)	1.221 Mg/m^3	
Absorption coefficient	0.210 mm^{-1}	
F(000)	976	
Crystal size	0.200 x 0.120 x 0.002 mm^3	
Theta range for data collection	1.565 to 25.025°.	
Index ranges	-16<=h<=16, -11<=k<=11, -23<=l<=23	
Reflections collected	95005	
Independent reflections	8749 [R(int) = 0.1056]	
Completeness to theta = 25.025°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.5839	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8749 / 229 / 610	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0503, wR2 = 0.1051	
R indices (all data)	R1 = 0.0844, wR2 = 0.1208	
Absolute structure parameter	-0.01(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.471 and -0.374 e.$Å^{-3}$	

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for (10*S*)-Tetracyclic Amine (–)-**36**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1X)	4001(1)	4910(2)	7283(1)	50(1)
O(1X)	5022(3)	3520(4)	9139(2)	51(1)
N(1X)	3577(4)	8774(5)	8825(3)	49(1)
O(2X)	1381(3)	9217(5)	7073(3)	68(2)
C(2X)	4577(4)	8107(6)	9043(4)	50(2)
O(3X)	4826(3)	4926(5)	7008(2)	64(1)
C(3AX)	4038(4)	5612(6)	8645(3)	44(2)
C(3X)	4654(4)	6591(6)	9259(3)	47(2)
O(4X)	3611(3)	3637(4)	7420(2)	62(1)
C(4AX)	2895(4)	5798(6)	8465(3)	45(2)
C(4X)	2298(4)	6952(6)	8229(3)	50(2)
C(5X)	1271(4)	6852(6)	8160(4)	57(2)
C(6X)	897(4)	5644(7)	8363(4)	64(2)
C(7AX)	2517(4)	4621(6)	8674(3)	46(2)
C(7X)	1505(4)	4521(6)	8635(4)	55(2)
N(8X)	3300(3)	3643(5)	8951(3)	46(1)
C(8AX)	4193(4)	4118(6)	8936(3)	46(2)
C(9X)	2811(4)	8281(6)	8133(3)	51(2)
C(10X)	2045(4)	9414(6)	7815(4)	56(2)
C(11X)	2074(5)	10387(7)	7254(4)	59(2)
C(12X)	1530(5)	11747(7)	7183(4)	67(2)
C(13X)	2902(5)	10370(7)	6938(4)	71(2)
C(14X)	3145(4)	2253(6)	9177(4)	54(2)
N(15X)	4389(3)	5821(5)	8026(3)	47(1)
C(21X)	2998(4)	5895(7)	6676(3)	52(2)
C(22X)	2558(4)	5291(7)	5912(3)	56(2)
Si(1X)	1675(5)	6518(7)	5271(4)	55(2)
C(23X)	630(10)	6945(18)	5611(7)	89(5)
C(24X)	2484(11)	8045(12)	5250(7)	85(5)
C(25X)	1109(17)	5770(30)	4340(8)	58(5)
Si(1Z)	1364(8)	6179(12)	5286(7)	67(3)
C(23Z)	312(13)	5600(30)	5598(12)	102(8)
C(24Z)	1450(20)	8077(17)	5350(12)	103(7)
C(25Z)	1140(30)	5560(50)	4341(12)	84(10)
S(1Y)	7349(1)	5191(2)	8631(1)	49(1)
Si(1Y)	7938(1)	5830(2)	6577(1)	68(1)
O(1Y)	8052(3)	3735(4)	10425(2)	57(1)
O(2Y)	7006(3)	1366(5)	6462(3)	72(2)
O(3Y)	6639(3)	6269(4)	8617(2)	55(1)
O(4Y)	8395(2)	5336(4)	9112(2)	55(1)
N(1Y)	6394(4)	262(6)	8083(3)	62(2)
C(2Y)	6031(4)	975(7)	8615(4)	60(2)
C(3AY)	7532(4)	2640(6)	9209(3)	45(2)
C(3Y)	6830(4)	1501(6)	9317(3)	51(2)
C(4Y)	8026(4)	1445(6)	8181(3)	48(2)
C(4AY)	8242(4)	2087(6)	8848(3)	45(2)
C(5Y)	8852(5)	1016(6)	7998(4)	58(2)
C(6Y)	9858(5)	1189(7)	8499(4)	60(2)
C(7AY)	9247(4)	2193(6)	9348(4)	52(2)
C(7Y)	10058(4)	1731(6)	9177(4)	55(2)

N(8Y)	9244(3)	2779(5)	10002(3)	50(2)
C(8AY)	8285(4)	3128(6)	9958(4)	54(2)
C(9Y)	6914(4)	1159(7)	7714(3)	54(2)
C(10Y)	6795(5)	492(7)	6990(4)	65(2)
C(11Y)	5988(5)	765(8)	6303(4)	67(2)
C(12Y)	5711(6)	-306(9)	5714(4)	92(3)
C(13Y)	5154(5)	1816(8)	6223(4)	76(2)
C(14Y)	10166(4)	3154(7)	10606(4)	63(2)
N(15Y)	6874(3)	3779(5)	8814(3)	44(1)
C(21Y)	7349(4)	4948(6)	7741(3)	52(2)
C(22Y)	7776(5)	6196(7)	7466(4)	61(2)
C(23Y)	6657(5)	5500(10)	5882(4)	95(3)
C(24Y)	8516(6)	7396(9)	6328(5)	91(3)
C(25Y)	8800(6)	4309(8)	6688(4)	71(2)
O(1W)	4978(7)	8264(11)	7103(7)	88(3)

Table S18. Bond lengths [Å] and angles [°] for (10*S*)-Tetracyclic Amine (–)-**36**.

S(1X)-O(4X)	1.414(5)
S(1X)-O(3X)	1.431(4)
S(1X)-N(15X)	1.623(5)
S(1X)-C(21X)	1.764(6)
O(1X)-C(8AX)	1.227(6)
N(1X)-C(2X)	1.460(7)
N(1X)-C(9X)	1.478(8)
N(1X)-H(1X)	0.86(3)
O(2X)-C(10X)	1.433(7)
O(2X)-C(11X)	1.452(7)
C(2X)-C(3X)	1.525(8)
C(2X)-H(2X1)	0.9900
C(2X)-H(2X2)	0.9900
C(3AX)-N(15X)	1.471(7)
C(3AX)-C(4AX)	1.518(7)
C(3AX)-C(3X)	1.535(8)
C(3AX)-C(8AX)	1.546(8)
C(3X)-H(3X1)	0.9900
C(3X)-H(3X2)	0.9900
C(4AX)-C(4X)	1.375(8)
C(4AX)-C(7AX)	1.379(8)
C(4X)-C(5X)	1.394(8)
C(4X)-C(9X)	1.519(8)
C(5X)-C(6X)	1.397(9)
C(5X)-H(5X)	0.9500
C(6X)-C(7X)	1.369(8)
C(6X)-H(6X)	0.9500
C(7AX)-C(7X)	1.391(7)
C(7AX)-N(8X)	1.405(7)
C(7X)-H(7X)	0.9500
N(8X)-C(8AX)	1.338(7)
N(8X)-C(14X)	1.460(7)
C(9X)-C(10X)	1.507(8)
C(9X)-H(9X)	1.0000
C(10X)-C(11X)	1.459(9)
C(10X)-H(10X)	1.0000
C(11X)-C(13X)	1.489(9)
C(11X)-C(12X)	1.506(9)
C(12X)-H(12A)	0.9800
C(12X)-H(12B)	0.9800
C(12X)-H(12C)	0.9800
C(13X)-H(13A)	0.9800
C(13X)-H(13B)	0.9800
C(13X)-H(13C)	0.9800
C(14X)-H(14A)	0.9800
C(14X)-H(14B)	0.9800
C(14X)-H(14C)	0.9800
N(15X)-H(15X)	0.85(3)
C(21X)-C(22X)	1.518(8)
C(21X)-H(21A)	0.9900
C(21X)-H(21B)	0.9900
C(22X)-Si(1X)	1.850(9)
C(22X)-Si(1Z)	1.892(12)
C(22X)-H(22A)	0.9900
C(22X)-H(22B)	0.9900
C(22X)-H(22E)	0.9900
C(22X)-H(22F)	0.9900
Si(1X)-C(23X)	1.850(12)
Si(1X)-C(25X)	1.859(12)
Si(1X)-C(24X)	1.872(12)
C(23X)-H(23A)	0.9800
C(23X)-H(23B)	0.9800
C(23X)-H(23C)	0.9800
C(24X)-H(24A)	0.9800
C(24X)-H(24B)	0.9800
C(24X)-H(24C)	0.9800
C(25X)-H(25A)	0.9800
C(25X)-H(25B)	0.9800
C(25X)-H(25C)	0.9800
Si(1Z)-C(24Z)	1.849(16)
Si(1Z)-C(25Z)	1.863(17)
Si(1Z)-C(23Z)	1.865(15)
C(23Z)-H(23D)	0.9800

C(23Z)-H(23E)	0.9800	C(14Y)-H(14D)	0.9800
C(23Z)-H(23F)	0.9800	C(14Y)-H(14E)	0.9800
C(24Z)-H(24D)	0.9800	C(14Y)-H(14F)	0.9800
C(24Z)-H(24E)	0.9800	N(15Y)-H(15Y)	0.87(3)
C(24Z)-H(24F)	0.9800	C(21Y)-C(22Y)	1.529(8)
C(25Z)-H(25D)	0.9800	C(21Y)-H(21C)	0.9900
C(25Z)-H(25E)	0.9800	C(21Y)-H(21D)	0.9900
C(25Z)-H(25F)	0.9800	C(22Y)-H(22C)	0.9900
S(1Y)-O(3Y)	1.434(4)	C(22Y)-H(22D)	0.9900
S(1Y)-O(4Y)	1.437(4)	C(23Y)-H(23G)	0.9800
S(1Y)-N(15Y)	1.617(5)	C(23Y)-H(23H)	0.9800
S(1Y)-C(21Y)	1.757(6)	C(23Y)-H(23I)	0.9800
Si(1Y)-C(23Y)	1.852(7)	C(24Y)-H(24G)	0.9800
Si(1Y)-C(22Y)	1.864(7)	C(24Y)-H(24H)	0.9800
Si(1Y)-C(24Y)	1.865(8)	C(24Y)-H(24I)	0.9800
Si(1Y)-C(25Y)	1.868(7)	C(25Y)-H(25G)	0.9800
O(1Y)-C(8AY)	1.223(7)	C(25Y)-H(25H)	0.9800
O(2Y)-C(10Y)	1.446(8)	C(25Y)-H(25I)	0.9800
O(2Y)-C(11Y)	1.464(8)		
N(1Y)-C(9Y)	1.476(8)	O(4X)-S(1X)-O(3X)	119.7(3)
N(1Y)-C(2Y)	1.479(8)	O(4X)-S(1X)-N(15X)	109.7(3)
N(1Y)-H(1Y)	0.88(3)	O(3X)-S(1X)-N(15X)	105.8(2)
C(2Y)-C(3Y)	1.520(8)	O(4X)-S(1X)-C(21X)	109.5(3)
C(2Y)-H(2Y1)	0.9900	O(3X)-S(1X)-C(21X)	107.1(3)
C(2Y)-H(2Y2)	0.9900	N(15X)-S(1X)-C(21X)	104.0(3)
C(3AY)-N(15Y)	1.470(7)	C(2X)-N(1X)-C(9X)	115.6(4)
C(3AY)-C(4AY)	1.503(8)	C(2X)-N(1X)-H(1X)	105(4)
C(3AY)-C(3Y)	1.541(8)	C(9X)-N(1X)-H(1X)	113(4)
C(3AY)-C(8AY)	1.545(9)	C(10X)-O(2X)-C(11X)	60.8(4)
C(3Y)-H(3Y1)	0.9900	N(1X)-C(2X)-C(3X)	118.4(5)
C(3Y)-H(3Y2)	0.9900	N(1X)-C(2X)-H(2X1)	107.7
C(4Y)-C(4AY)	1.381(8)	C(3X)-C(2X)-H(2X1)	107.7
C(4Y)-C(5Y)	1.386(8)	N(1X)-C(2X)-H(2X2)	107.7
C(4Y)-C(9Y)	1.523(8)	C(3X)-C(2X)-H(2X2)	107.7
C(4AY)-C(7AY)	1.403(8)	H(2X1)-C(2X)-H(2X2)	107.1
C(5Y)-C(6Y)	1.410(9)	N(15X)-C(3AX)-C(4AX)	114.8(5)
C(5Y)-H(5Y)	0.9500	N(15X)-C(3AX)-C(3X)	107.5(4)
C(6Y)-C(7Y)	1.360(9)	C(4AX)-C(3AX)-C(3X)	111.1(4)
C(6Y)-H(6Y)	0.9500	N(15X)-C(3AX)-C(8AX)	112.9(4)
C(7AY)-C(7Y)	1.363(8)	C(4AX)-C(3AX)-C(8AX)	101.3(4)
C(7AY)-N(8Y)	1.401(8)	C(3X)-C(3AX)-C(8AX)	109.0(5)
C(7Y)-H(7Y)	0.9500	C(2X)-C(3X)-C(3AX)	114.6(5)
N(8Y)-C(8AY)	1.352(7)	C(2X)-C(3X)-H(3X1)	108.6
N(8Y)-C(14Y)	1.453(8)	C(3AX)-C(3X)-H(3X1)	108.6
C(9Y)-C(10Y)	1.511(9)	C(2X)-C(3X)-H(3X2)	108.6
C(9Y)-H(9Y)	1.0000	C(3AX)-C(3X)-H(3X2)	108.6
C(10Y)-C(11Y)	1.442(9)	H(3X1)-C(3X)-H(3X2)	107.6
C(10Y)-H(10Y)	1.0000	C(4X)-C(4AX)-C(7AX)	121.7(5)
C(11Y)-C(12Y)	1.497(10)	C(4X)-C(4AX)-C(3AX)	129.6(5)
C(11Y)-C(13Y)	1.514(9)	C(7AX)-C(4AX)-C(3AX)	108.2(5)
C(12Y)-H(12D)	0.9800	C(4AX)-C(4X)-C(5X)	117.1(5)
C(12Y)-H(12E)	0.9800	C(4AX)-C(4X)-C(9X)	118.6(5)
C(12Y)-H(12F)	0.9800	C(5X)-C(4X)-C(9X)	124.0(5)
C(13Y)-H(13D)	0.9800	C(4X)-C(5X)-C(6X)	120.3(6)
C(13Y)-H(13E)	0.9800	C(4X)-C(5X)-H(5X)	119.8
C(13Y)-H(13F)	0.9800	C(6X)-C(5X)-H(5X)	119.8

C(7X)-C(6X)-C(5X)	122.5(5)	S(1X)-C(21X)-H(21A)	108.8
C(7X)-C(6X)-H(6X)	118.8	C(22X)-C(21X)-H(21B)	108.8
C(5X)-C(6X)-H(6X)	118.8	S(1X)-C(21X)-H(21B)	108.8
C(4AX)-C(7AX)-C(7X)	121.9(5)	H(21A)-C(21X)-H(21B)	107.7
C(4AX)-C(7AX)-N(8X)	110.4(4)	C(21X)-C(22X)-Si(1X)	111.1(5)
C(7X)-C(7AX)-N(8X)	127.6(5)	C(21X)-C(22X)-Si(1Z)	114.8(5)
C(6X)-C(7X)-C(7AX)	116.3(6)	C(21X)-C(22X)-H(22A)	109.4
C(6X)-C(7X)-H(7X)	121.8	Si(1X)-C(22X)-H(22A)	109.4
C(7AX)-C(7X)-H(7X)	121.8	C(21X)-C(22X)-H(22B)	109.4
C(8AX)-N(8X)-C(7AX)	111.2(5)	Si(1X)-C(22X)-H(22B)	109.4
C(8AX)-N(8X)-C(14X)	124.3(5)	H(22A)-C(22X)-H(22B)	108.0
C(7AX)-N(8X)-C(14X)	124.4(4)	C(21X)-C(22X)-H(22E)	108.6
O(1X)-C(8AX)-N(8X)	127.5(5)	Si(1Z)-C(22X)-H(22E)	108.6
O(1X)-C(8AX)-C(3AX)	123.8(5)	C(21X)-C(22X)-H(22F)	108.6
N(8X)-C(8AX)-C(3AX)	108.7(5)	Si(1Z)-C(22X)-H(22F)	108.6
N(1X)-C(9X)-C(10X)	108.6(5)	H(22E)-C(22X)-H(22F)	107.5
N(1X)-C(9X)-C(4X)	112.5(5)	C(22X)-Si(1X)-C(23X)	108.7(6)
C(10X)-C(9X)-C(4X)	112.1(5)	C(22X)-Si(1X)-C(25X)	111.2(9)
N(1X)-C(9X)-H(9X)	107.8	C(23X)-Si(1X)-C(25X)	108.8(9)
C(10X)-C(9X)-H(9X)	107.8	C(22X)-Si(1X)-C(24X)	105.2(5)
C(4X)-C(9X)-H(9X)	107.8	C(23X)-Si(1X)-C(24X)	112.8(8)
O(2X)-C(10X)-C(11X)	60.3(4)	C(25X)-Si(1X)-C(24X)	110.0(9)
O(2X)-C(10X)-C(9X)	115.6(5)	Si(1X)-C(23X)-H(23A)	109.5
C(11X)-C(10X)-C(9X)	125.5(6)	Si(1X)-C(23X)-H(23B)	109.5
O(2X)-C(10X)-H(10X)	114.6	H(23A)-C(23X)-H(23B)	109.5
C(11X)-C(10X)-H(10X)	114.6	Si(1X)-C(23X)-H(23C)	109.5
C(9X)-C(10X)-H(10X)	114.6	H(23A)-C(23X)-H(23C)	109.5
O(2X)-C(11X)-C(10X)	59.0(4)	H(23B)-C(23X)-H(23C)	109.5
O(2X)-C(11X)-C(13X)	115.9(5)	Si(1X)-C(24X)-H(24A)	109.5
C(10X)-C(11X)-C(13X)	122.3(6)	Si(1X)-C(24X)-H(24B)	109.5
O(2X)-C(11X)-C(12X)	113.1(5)	H(24A)-C(24X)-H(24B)	109.5
C(10X)-C(11X)-C(12X)	119.4(6)	Si(1X)-C(24X)-H(24C)	109.5
C(13X)-C(11X)-C(12X)	114.3(6)	H(24A)-C(24X)-H(24C)	109.5
C(11X)-C(12X)-H(12A)	109.5	H(24B)-C(24X)-H(24C)	109.5
C(11X)-C(12X)-H(12B)	109.5	Si(1X)-C(25X)-H(25A)	109.5
H(12A)-C(12X)-H(12B)	109.5	Si(1X)-C(25X)-H(25B)	109.5
C(11X)-C(12X)-H(12C)	109.5	H(25A)-C(25X)-H(25B)	109.5
H(12A)-C(12X)-H(12C)	109.5	Si(1X)-C(25X)-H(25C)	109.5
H(12B)-C(12X)-H(12C)	109.5	H(25A)-C(25X)-H(25C)	109.5
C(11X)-C(13X)-H(13A)	109.5	H(25B)-C(25X)-H(25C)	109.5
C(11X)-C(13X)-H(13B)	109.5	C(24Z)-Si(1Z)-C(25Z)	112.0(15)
H(13A)-C(13X)-H(13B)	109.5	C(24Z)-Si(1Z)-C(23Z)	108.7(12)
C(11X)-C(13X)-H(13C)	109.5	C(25Z)-Si(1Z)-C(23Z)	110.5(15)
H(13A)-C(13X)-H(13C)	109.5	C(24Z)-Si(1Z)-C(22X)	112.8(9)
H(13B)-C(13X)-H(13C)	109.5	C(25Z)-Si(1Z)-C(22X)	107.2(15)
N(8X)-C(14X)-H(14A)	109.5	C(23Z)-Si(1Z)-C(22X)	105.3(9)
N(8X)-C(14X)-H(14B)	109.5	Si(1Z)-C(23Z)-H(23D)	109.5
H(14A)-C(14X)-H(14B)	109.5	Si(1Z)-C(23Z)-H(23E)	109.5
N(8X)-C(14X)-H(14C)	109.5	H(23D)-C(23Z)-H(23E)	109.5
H(14A)-C(14X)-H(14C)	109.5	Si(1Z)-C(23Z)-H(23F)	109.5
H(14B)-C(14X)-H(14C)	109.5	H(23D)-C(23Z)-H(23F)	109.5
C(3AX)-N(15X)-S(1X)	124.0(4)	H(23E)-C(23Z)-H(23F)	109.5
C(3AX)-N(15X)-H(15X)	119(4)	Si(1Z)-C(24Z)-H(24D)	109.5
S(1X)-N(15X)-H(15X)	108(4)	Si(1Z)-C(24Z)-H(24E)	109.5
C(22X)-C(21X)-S(1X)	113.7(4)	H(24D)-C(24Z)-H(24E)	109.5
C(22X)-C(21X)-H(21A)	108.8	Si(1Z)-C(24Z)-H(24F)	109.5

H(24D)-C(24Z)-H(24F)	109.5	N(8Y)-C(7AY)-C(4AY)	110.0(5)
H(24E)-C(24Z)-H(24F)	109.5	C(6Y)-C(7Y)-C(7AY)	117.6(6)
Si(1Z)-C(25Z)-H(25D)	109.5	C(6Y)-C(7Y)-H(7Y)	121.2
Si(1Z)-C(25Z)-H(25E)	109.5	C(7AY)-C(7Y)-H(7Y)	121.2
H(25D)-C(25Z)-H(25E)	109.5	C(8AY)-N(8Y)-C(7AY)	111.4(5)
Si(1Z)-C(25Z)-H(25F)	109.5	C(8AY)-N(8Y)-C(14Y)	124.2(6)
H(25D)-C(25Z)-H(25F)	109.5	C(7AY)-N(8Y)-C(14Y)	123.8(5)
H(25E)-C(25Z)-H(25F)	109.5	O(1Y)-C(8AY)-N(8Y)	126.1(6)
O(3Y)-S(1Y)-O(4Y)	118.4(3)	O(1Y)-C(8AY)-C(3AY)	125.7(5)
O(3Y)-S(1Y)-N(15Y)	106.9(2)	N(8Y)-C(8AY)-C(3AY)	108.1(5)
O(4Y)-S(1Y)-N(15Y)	109.8(2)	N(1Y)-C(9Y)-C(10Y)	107.1(5)
O(3Y)-S(1Y)-C(21Y)	108.6(3)	N(1Y)-C(9Y)-C(4Y)	112.7(5)
O(4Y)-S(1Y)-C(21Y)	107.8(3)	C(10Y)-C(9Y)-C(4Y)	113.1(5)
N(15Y)-S(1Y)-C(21Y)	104.4(3)	N(1Y)-C(9Y)-H(9Y)	107.9
C(23Y)-Si(1Y)-C(22Y)	108.3(3)	C(10Y)-C(9Y)-H(9Y)	107.9
C(23Y)-Si(1Y)-C(24Y)	110.1(4)	C(4Y)-C(9Y)-H(9Y)	107.9
C(22Y)-Si(1Y)-C(24Y)	107.0(4)	C(11Y)-C(10Y)-O(2Y)	60.9(4)
C(23Y)-Si(1Y)-C(25Y)	111.3(4)	C(11Y)-C(10Y)-C(9Y)	125.9(6)
C(22Y)-Si(1Y)-C(25Y)	109.1(3)	O(2Y)-C(10Y)-C(9Y)	115.7(6)
C(24Y)-Si(1Y)-C(25Y)	110.8(3)	C(11Y)-C(10Y)-H(10Y)	114.3
C(10Y)-O(2Y)-C(11Y)	59.4(4)	O(2Y)-C(10Y)-H(10Y)	114.3
C(9Y)-N(1Y)-C(2Y)	114.7(5)	C(9Y)-C(10Y)-H(10Y)	114.3
C(9Y)-N(1Y)-H(1Y)	115(5)	C(10Y)-C(11Y)-O(2Y)	59.7(4)
C(2Y)-N(1Y)-H(1Y)	110(5)	C(10Y)-C(11Y)-C(12Y)	119.7(6)
N(1Y)-C(2Y)-C(3Y)	117.9(5)	O(2Y)-C(11Y)-C(12Y)	114.1(6)
N(1Y)-C(2Y)-H(2Y1)	107.8	C(10Y)-C(11Y)-C(13Y)	122.6(6)
C(3Y)-C(2Y)-H(2Y1)	107.8	O(2Y)-C(11Y)-C(13Y)	113.9(6)
N(1Y)-C(2Y)-H(2Y2)	107.8	C(12Y)-C(11Y)-C(13Y)	114.1(6)
C(3Y)-C(2Y)-H(2Y2)	107.8	C(11Y)-C(12Y)-H(12D)	109.5
H(2Y1)-C(2Y)-H(2Y2)	107.2	C(11Y)-C(12Y)-H(12E)	109.5
N(15Y)-C(3AY)-C(4AY)	114.5(5)	H(12D)-C(12Y)-H(12E)	109.5
N(15Y)-C(3AY)-C(3Y)	107.6(4)	C(11Y)-C(12Y)-H(12F)	109.5
C(4AY)-C(3AY)-C(3Y)	111.3(5)	H(12D)-C(12Y)-H(12F)	109.5
N(15Y)-C(3AY)-C(8AY)	110.9(5)	H(12E)-C(12Y)-H(12F)	109.5
C(4AY)-C(3AY)-C(8AY)	102.3(4)	C(11Y)-C(13Y)-H(13D)	109.5
C(3Y)-C(3AY)-C(8AY)	110.1(5)	C(11Y)-C(13Y)-H(13E)	109.5
C(2Y)-C(3Y)-C(3AY)	114.6(5)	H(13D)-C(13Y)-H(13E)	109.5
C(2Y)-C(3Y)-H(3Y1)	108.6	C(11Y)-C(13Y)-H(13F)	109.5
C(3AY)-C(3Y)-H(3Y1)	108.6	H(13D)-C(13Y)-H(13F)	109.5
C(2Y)-C(3Y)-H(3Y2)	108.6	H(13E)-C(13Y)-H(13F)	109.5
C(3AY)-C(3Y)-H(3Y2)	108.6	N(8Y)-C(14Y)-H(14D)	109.5
H(3Y1)-C(3Y)-H(3Y2)	107.6	N(8Y)-C(14Y)-H(14E)	109.5
C(4AY)-C(4Y)-C(5Y)	117.1(5)	H(14D)-C(14Y)-H(14E)	109.5
C(4AY)-C(4Y)-C(9Y)	119.1(5)	N(8Y)-C(14Y)-H(14F)	109.5
C(5Y)-C(4Y)-C(9Y)	123.7(6)	H(14D)-C(14Y)-H(14F)	109.5
C(4Y)-C(4AY)-C(7AY)	121.6(5)	H(14E)-C(14Y)-H(14F)	109.5
C(4Y)-C(4AY)-C(3AY)	130.1(5)	C(3AY)-N(15Y)-S(1Y)	121.7(3)
C(7AY)-C(4AY)-C(3AY)	108.0(5)	C(3AY)-N(15Y)-H(15Y)	117(4)
C(4Y)-C(5Y)-C(6Y)	119.9(6)	S(1Y)-N(15Y)-H(15Y)	110(4)
C(4Y)-C(5Y)-H(5Y)	120.0	C(22Y)-C(21Y)-S(1Y)	112.3(5)
C(6Y)-C(5Y)-H(5Y)	120.0	C(22Y)-C(21Y)-H(21C)	109.2
C(7Y)-C(6Y)-C(5Y)	122.4(6)	S(1Y)-C(21Y)-H(21C)	109.2
C(7Y)-C(6Y)-H(6Y)	118.8	C(22Y)-C(21Y)-H(21D)	109.2
C(5Y)-C(6Y)-H(6Y)	118.8	S(1Y)-C(21Y)-H(21D)	109.2
C(7Y)-C(7AY)-N(8Y)	128.9(6)	H(21C)-C(21Y)-H(21D)	107.9
C(7Y)-C(7AY)-C(4AY)	121.1(6)	C(21Y)-C(22Y)-Si(1Y)	111.6(5)

C(21Y)-C(22Y)-H(22C)	109.3
Si(1Y)-C(22Y)-H(22C)	109.3
C(21Y)-C(22Y)-H(22D)	109.3
Si(1Y)-C(22Y)-H(22D)	109.3
H(22C)-C(22Y)-H(22D)	108.0
Si(1Y)-C(23Y)-H(23G)	109.5
Si(1Y)-C(23Y)-H(23H)	109.5
H(23G)-C(23Y)-H(23H)	109.5
Si(1Y)-C(23Y)-H(23I)	109.5
H(23G)-C(23Y)-H(23I)	109.5
H(23H)-C(23Y)-H(23I)	109.5
Si(1Y)-C(24Y)-H(24G)	109.5
Si(1Y)-C(24Y)-H(24H)	109.5
H(24G)-C(24Y)-H(24H)	109.5
Si(1Y)-C(24Y)-H(24I)	109.5
H(24G)-C(24Y)-H(24I)	109.5
H(24H)-C(24Y)-H(24I)	109.5
Si(1Y)-C(25Y)-H(25G)	109.5
Si(1Y)-C(25Y)-H(25H)	109.5
H(25G)-C(25Y)-H(25H)	109.5
Si(1Y)-C(25Y)-H(25I)	109.5
H(25G)-C(25Y)-H(25I)	109.5
H(25H)-C(25Y)-H(25I)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S19. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (10*S*)-Tetracyclic Amine (–)-**36**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1X)	41(1)	46(1)	64(1)	-4(1)	21(1)	7(1)
O(1X)	32(2)	50(3)	74(3)	4(2)	22(2)	5(2)
N(1X)	47(3)	41(3)	62(3)	-5(3)	24(3)	2(2)
O(2X)	55(3)	53(3)	85(3)	-2(3)	10(2)	3(2)
C(2X)	39(3)	50(4)	68(4)	-12(3)	27(3)	-7(3)
O(3X)	48(2)	73(3)	76(3)	-15(3)	30(2)	10(2)
C(3AX)	29(3)	47(4)	60(4)	-4(3)	19(2)	1(2)
C(3X)	35(3)	49(4)	60(4)	-5(3)	20(3)	-4(3)
O(4X)	83(3)	36(2)	67(3)	-4(2)	25(2)	-1(2)
C(4AX)	34(3)	40(3)	63(4)	-12(3)	19(3)	4(2)
C(4X)	41(3)	43(3)	67(4)	-14(3)	21(3)	1(3)
C(5X)	40(3)	41(4)	85(5)	-6(3)	18(3)	4(3)
C(6X)	29(3)	58(4)	107(5)	-23(4)	25(3)	1(3)
C(7AX)	33(3)	46(4)	58(4)	-14(3)	14(3)	-2(2)
C(7X)	38(3)	40(3)	88(5)	-9(3)	22(3)	-4(3)
N(8X)	33(2)	40(3)	66(3)	-4(2)	18(2)	0(2)
C(8AX)	40(3)	46(4)	54(4)	-5(3)	19(3)	2(3)
C(9X)	48(3)	42(4)	66(4)	-7(3)	22(3)	9(3)
C(10X)	49(4)	47(4)	73(5)	-7(3)	24(3)	2(3)
C(11X)	57(4)	43(4)	74(4)	-10(3)	18(3)	2(3)
C(12X)	63(4)	46(4)	91(5)	5(4)	26(4)	6(3)
C(13X)	89(5)	48(4)	89(5)	-2(4)	48(4)	11(4)
C(14X)	43(3)	42(4)	75(4)	-1(3)	18(3)	-3(3)
N(15X)	33(2)	48(3)	64(3)	-2(2)	22(2)	2(2)
C(21X)	43(3)	53(4)	64(4)	-3(3)	25(3)	9(3)
C(22X)	57(3)	49(4)	69(4)	-4(3)	29(3)	2(3)
Si(1X)	65(3)	51(3)	52(2)	2(2)	24(2)	9(2)
C(23X)	82(8)	113(12)	68(8)	-10(8)	23(7)	34(8)
C(24X)	117(11)	68(8)	53(7)	3(6)	9(7)	-19(7)
C(25X)	52(9)	58(9)	65(8)	-9(8)	21(7)	8(7)
Si(1Z)	63(5)	78(6)	66(4)	7(4)	31(4)	0(4)
C(23Z)	73(11)	160(20)	86(13)	-10(15)	44(10)	0(13)
C(24Z)	131(17)	91(10)	79(13)	-3(10)	27(12)	17(12)

C(25Z)	100(20)	90(20)	63(11)	12(12)	32(13)	15(18)
S(1Y)	33(1)	43(1)	74(1)	6(1)	22(1)	1(1)
Si(1Y)	56(1)	78(2)	74(2)	25(1)	27(1)	5(1)
O(1Y)	48(2)	54(3)	68(3)	1(2)	20(2)	11(2)
O(2Y)	60(3)	93(4)	72(3)	5(3)	33(2)	9(3)
O(3Y)	38(2)	49(3)	84(3)	4(2)	30(2)	6(2)
O(4Y)	30(2)	47(2)	87(3)	7(2)	20(2)	-5(2)
N(1Y)	65(3)	48(3)	78(4)	-2(3)	31(3)	-9(3)
C(2Y)	51(4)	55(4)	81(5)	0(4)	34(3)	-12(3)
C(3AY)	35(3)	47(4)	60(4)	8(3)	25(3)	5(2)
C(3Y)	50(3)	44(4)	69(4)	6(3)	33(3)	-4(3)
C(4Y)	46(3)	38(3)	67(4)	10(3)	27(3)	5(3)
C(4AY)	35(3)	41(3)	66(4)	9(3)	26(3)	1(2)
C(5Y)	58(4)	50(4)	79(5)	9(3)	39(3)	3(3)
C(6Y)	48(4)	51(4)	91(5)	15(4)	38(3)	11(3)
C(7AY)	43(3)	39(3)	80(5)	10(3)	27(3)	2(3)
C(7Y)	40(3)	45(4)	86(5)	6(3)	27(3)	1(3)
N(8Y)	37(3)	44(3)	69(4)	2(3)	17(2)	3(2)
C(8AY)	47(4)	45(4)	75(5)	12(3)	27(3)	10(3)
C(9Y)	54(4)	49(4)	64(4)	5(3)	27(3)	2(3)
C(10Y)	67(4)	53(4)	77(5)	0(4)	26(4)	8(3)
C(11Y)	55(4)	79(5)	69(5)	-6(4)	26(3)	9(4)
C(12Y)	93(6)	85(6)	91(6)	-23(5)	23(5)	18(5)
C(13Y)	57(4)	92(6)	80(5)	-4(4)	27(4)	24(4)
C(14Y)	44(4)	52(4)	86(5)	2(4)	14(3)	11(3)
N(15Y)	32(2)	42(3)	64(3)	8(2)	23(2)	3(2)
C(21Y)	40(3)	47(4)	77(4)	17(3)	29(3)	6(3)
C(22Y)	47(3)	55(4)	88(5)	14(4)	33(3)	8(3)
C(23Y)	70(5)	122(8)	83(5)	16(5)	15(4)	-4(5)
C(24Y)	96(6)	81(6)	124(7)	38(5)	73(5)	19(5)
C(25Y)	82(5)	72(5)	61(4)	-4(4)	28(4)	5(4)
O(1W)	64(6)	78(7)	125(9)	2(7)	35(6)	4(5)

Table S20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for (10*S*)-Tetracyclic Amine (–)-**36**.

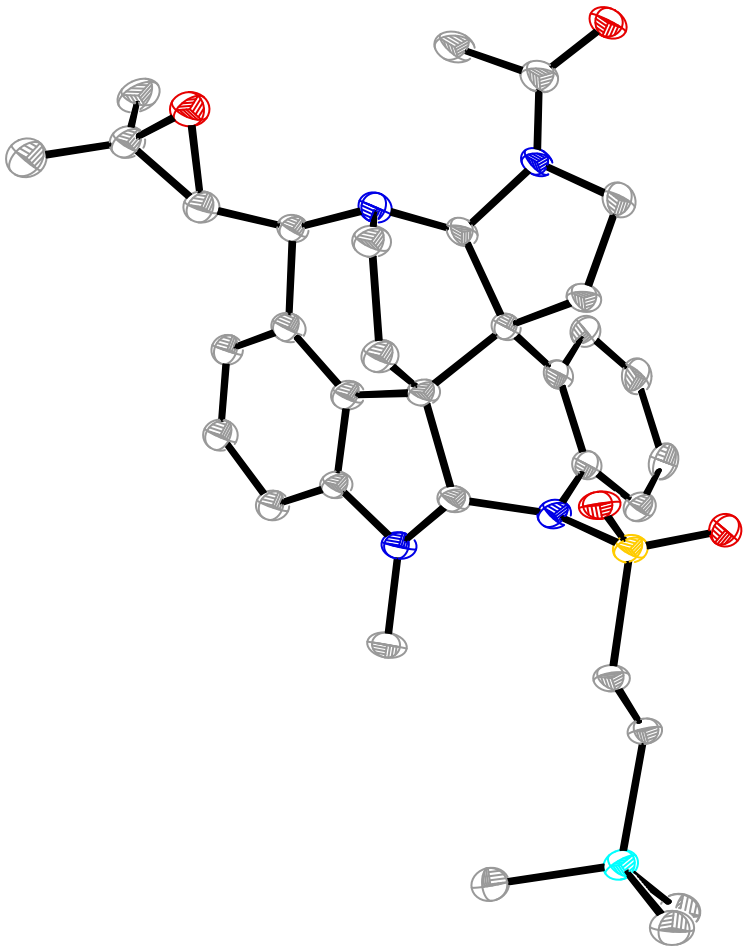
	x	y	z	U(eq)
H(1X)	3380(50)	8680(70)	9190(20)	59
H(2X1)	5050	8629	9461	60
H(2X2)	4834	8202	8633	60
H(3X1)	4414	6483	9675	56
H(3X2)	5383	6313	9428	56
H(5X)	824	7609	7975	68
H(6X)	194	5601	8310	77
H(7X)	1249	3717	8789	67
H(9X)	3175	8096	7784	62
H(10X)	1698	9767	8149	67
H(12A)	1229	12000	6665	101
H(12B)	2020	12457	7447	101
H(12C)	986	11671	7389	101
H(13A)	3167	9431	6957	106

H(13B)	3457	10984	7222	106
H(13C)	2627	10683	6430	106
H(14A)	3761	1701	9249	81
H(14B)	2560	1828	8798	81
H(14C)	3011	2296	9636	81
H(15X)	5010(20)	6050(60)	8110(30)	57
H(21A)	2443	5978	6879	62
H(21B)	3256	6833	6643	62
H(22A)	2185	4430	5927	68
H(22B)	3123	5059	5737	68
H(22E)	2396	4308	5953	68
H(22F)	3089	5331	5685	68
H(23A)	157	7596	5275	133
H(23B)	259	6103	5641	133
H(23C)	919	7363	6097	133
H(24A)	2059	8742	4917	127
H(24B)	2780	8435	5742	127
H(24C)	3035	7759	5080	127
H(25A)	645	6436	4012	87
H(25B)	1657	5532	4156	87
H(25C)	725	4931	4362	87
H(23D)	257	4591	5567	154
H(23E)	461	5886	6106	154
H(23F)	-337	6009	5287	154
H(24D)	1570	8363	5854	154
H(24E)	2022	8392	5207	154
H(24F)	812	8484	5023	154
H(25D)	1098	4548	4330	125
H(25E)	497	5941	4006	125
H(25F)	1707	5850	4190	125
H(1Y)	6740(50)	-490(50)	8290(30)	74
H(2Y1)	5574	335	8750	71
H(2Y2)	5608	1769	8363	71
H(3Y1)	7261	716	9572	62
H(3Y2)	6474	1859	9638	62
H(5Y)	8742	605	7535	70
H(6Y)	10416	917	8359	72
H(7Y)	10738	1785	9519	67
H(9Y)	6543	2060	7610	65
H(10Y)	7095	-453	7032	79
H(12D)	6296	-920	5787	138
H(12E)	5529	144	5236	138
H(12F)	5125	-842	5732	138
H(13D)	4607	1395	6356	114
H(13E)	4875	2134	5715	114
H(13F)	5441	2601	6545	114
H(14D)	10490	3948	10466	95
H(14E)	10643	2375	10725	95
H(14F)	9988	3390	11033	95
H(15Y)	6340(30)	3960(60)	8930(30)	53
H(21C)	7767	4128	7734	63
H(21D)	6640	4771	7407	63
H(22C)	8447	6453	7833	73
H(22D)	7305	6986	7406	73
H(23G)	6475	4530	5902	142
H(23H)	6670	5712	5395	142

H(23I)	6148	6085	5981	142
H(24G)	8468	7332	5817	137
H(24H)	9237	7465	6644	137
H(24I)	8146	8215	6393	137
H(25G)	8408	3461	6664	106
H(25H)	9359	4362	7162	106
H(25I)	9085	4305	6296	106

Crystal Structure of (–)-*N*8'-(Trimethylsilyl)ethanesulfonyl communesin A (42):[80]

Structural parameters for (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin A (**42**) are freely available from the Cambridge Crystallographic Data Center (CCDC 1937971).



The data deposited at Cambridge Crystallographic Data Center (CCDC 1937971) includes the methanol molecule present in the lattice. The methanol molecule is disordered and has consequently been refined in two positions. The major position (~80%) is well resolved, but the minor position (~20%) is not as resolved since it contributes to a fraction of the diffraction data. As a result, the hydrogen atoms of this methanol molecule in the minor position are difficult to place and checkCIF may interpret them as too close to other atoms and results in the corresponding alerts. These alerts have been explained in the additional comments associated with the deposited data file. The disorder of the solvent methanol molecule has no impact on the alkaloid structure depicted above.

80. Solvent molecules (methanol) omitted for clarity.

Table S21. Crystal data and structure refinement for (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin A (**42**).

Identification code	5-68-12	
Empirical formula	C34 H48 N4 O5 S Si	
Formula weight	652.91	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 7.9317(5) Å	α= 90°.
	b = 15.4939(11) Å	β= 92.123(4)°.
	c = 13.8939(11) Å	γ = 90°.
Volume	1706.3(2) $Å^3$	
Z	2	
Density (calculated)	1.271 Mg/m^3	
Absorption coefficient	1.552 mm^{-1}	
F(000)	700	
Crystal size	0.391 x 0.033 x 0.022 mm^3	
Theta range for data collection	3.183 to 68.231°.	
Index ranges	-9<=h<=9, -18<=k<=15, -16<=l<=16	
Reflections collected	22916	
Independent reflections	5423 [R(int) = 0.0794]	
Completeness to theta = 67.679°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7543 and 0.5696	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5423 / 3 / 437	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0665, wR2 = 0.1736	
R indices (all data)	R1 = 0.0794, wR2 = 0.1861	
Absolute structure parameter	0.061(16)	
Extinction coefficient	0.0050(10)	
Largest diff. peak and hole	0.539 and -0.688 e.$Å^{-3}$	

Table S22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin A (**42**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	10083(2)	5338(1)	7881(1)	43(1)
Si(1)	12162(2)	7697(1)	9423(2)	48(1)
O(1)	2873(6)	4707(4)	3156(4)	54(1)
O(2)	3550(6)	1961(3)	6332(4)	54(1)
O(3)	10628(5)	5037(3)	6959(4)	46(1)
O(4)	10145(5)	4765(3)	8681(4)	46(1)
N(1)	4284(6)	4475(4)	5130(4)	42(1)
C(2)	5984(8)	4568(5)	4733(6)	48(2)
C(3)	7060(7)	5298(5)	5229(5)	47(2)
C(3A)	6331(7)	5507(4)	6210(5)	40(2)
C(4)	3355(7)	5994(5)	5484(5)	42(2)
C(4A)	4821(7)	6089(5)	6058(5)	42(2)
C(5)	2156(8)	6652(5)	5445(5)	45(2)
C(6)	2449(8)	7412(5)	5927(6)	50(2)
C(7)	3957(8)	7557(5)	6473(6)	48(2)
C(7A)	5107(7)	6881(5)	6527(5)	42(2)
N(8)	6657(6)	6873(4)	7029(5)	46(2)
C(8)	7578(8)	7642(5)	7316(6)	53(2)
C(8A)	7569(7)	6077(4)	6833(5)	42(2)
C(9)	3086(7)	5170(4)	4891(5)	41(2)
C(10)	3133(8)	5409(5)	3842(5)	49(2)
C(11)	1675(8)	5400(6)	3141(5)	51(2)
C(12)	1742(11)	5980(7)	2288(7)	67(2)
C(13)	-86(8)	5170(6)	3432(6)	60(2)
N(1X)	4519(6)	3322(4)	6304(5)	44(1)
C(2X)	6136(8)	3087(5)	6768(6)	49(2)
C(3X)	7199(7)	3911(4)	6727(6)	42(2)
C(3AX)	5869(7)	4648(4)	6723(5)	38(1)
C(4AX)	5541(7)	4839(4)	7788(5)	39(2)
C(4X)	4196(7)	4495(5)	8296(5)	46(2)
C(5X)	4129(8)	4634(5)	9284(6)	51(2)
C(6X)	5367(8)	5100(5)	9776(6)	51(2)
C(7X)	6702(7)	5437(5)	9272(5)	46(2)
C(7AX)	6765(7)	5312(5)	8300(5)	42(1)
C(8AX)	4337(8)	4256(4)	6151(5)	42(2)
N(8X)	8112(6)	5680(4)	7745(4)	41(1)
C(1XX)	3320(8)	2733(6)	6134(6)	52(2)
C(2XX)	1684(9)	3040(6)	5647(7)	65(2)
C(20)	11272(7)	6287(5)	8167(5)	44(2)
C(21)	10960(8)	6666(5)	9147(5)	45(2)
C(22)	11866(11)	7965(6)	10703(6)	65(2)
C(23)	11327(11)	8578(6)	8637(7)	67(2)
C(24)	14428(9)	7525(6)	9223(7)	60(2)
O(30A)	3556(18)	1440(9)	8188(8)	120(5)
C(30A)	2552(17)	2083(11)	8550(9)	84(4)
O(30B)	4420(30)	-433(17)	7837(17)	51(7)
C(30B)	4130(50)	440(30)	7820(30)	100(20)

Table S23. Bond lengths [Å] and angles [°] for (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin A (**42**).

S(1)-O(4)	1.421(5)
S(1)-O(3)	1.444(5)
S(1)-N(8X)	1.655(5)
S(1)-C(20)	1.785(7)
Si(1)-C(24)	1.848(8)
Si(1)-C(22)	1.849(9)
Si(1)-C(23)	1.855(9)
Si(1)-C(21)	1.892(7)
O(1)-C(11)	1.433(9)
O(1)-C(10)	1.455(9)
O(2)-C(1XX)	1.239(10)
N(1)-C(8AX)	1.458(9)
N(1)-C(9)	1.465(8)
N(1)-C(2)	1.482(9)
C(2)-C(3)	1.562(10)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(3A)	1.535(10)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(3A)-C(4A)	1.509(8)
C(3A)-C(8A)	1.559(8)
C(3A)-C(3AX)	1.560(9)
C(4)-C(5)	1.394(10)
C(4)-C(4A)	1.394(8)
C(4)-C(9)	1.529(10)
C(4A)-C(7A)	1.403(10)
C(5)-C(6)	1.370(11)
C(5)-H(5)	0.9500
C(6)-C(7)	1.410(8)
C(6)-H(6)	0.9500
C(7)-C(7A)	1.389(10)
C(7)-H(7)	0.9500
C(7A)-N(8)	1.391(7)
N(8)-C(8)	1.446(9)
N(8)-C(8A)	1.459(9)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(8A)-N(8X)	1.459(9)
C(8A)-H(8A1)	1.0000
C(9)-C(10)	1.506(10)
C(9)-H(9)	1.0000
C(10)-C(11)	1.484(8)
C(10)-H(10)	1.0000
C(11)-C(12)	1.490(12)
C(11)-C(13)	1.512(10)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
N(1X)-C(1XX)	1.333(9)
N(1X)-C(2X)	1.460(7)
N(1X)-C(8AX)	1.468(9)
C(2X)-C(3X)	1.533(10)
C(2X)-H(2X1)	0.9900
C(2X)-H(2X2)	0.9900
C(3X)-C(3AX)	1.555(9)
C(3X)-H(3X1)	0.9900
C(3X)-H(3X2)	0.9900
C(3AX)-C(4AX)	1.539(9)
C(3AX)-C(8AX)	1.552(8)
C(4AX)-C(7AX)	1.392(9)
C(4AX)-C(4X)	1.406(9)
C(4X)-C(5X)	1.392(10)
C(4X)-H(4X)	0.9500
C(5X)-C(6X)	1.380(10)
C(5X)-H(5X)	0.9500
C(6X)-C(7X)	1.392(10)
C(6X)-H(6X)	0.9500
C(7X)-C(7AX)	1.367(10)
C(7X)-H(7X)	0.9500
C(7AX)-N(8X)	1.457(9)
C(8AX)-H(8AX)	1.0000
C(1XX)-C(2XX)	1.517(9)
C(2XX)-H(2X3)	0.9800
C(2XX)-H(2X4)	0.9800
C(2XX)-H(2X5)	0.9800
C(20)-C(21)	1.511(10)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
O(30A)-C(30A)	1.382(18)
O(30A)-H(30A)	0.8400
C(30A)-H(30B)	0.9800
C(30A)-H(30C)	0.9800
C(30A)-H(30D)	0.9800
O(30B)-C(30B)	1.37(3)
O(30B)-H(30E)	0.8400
C(30B)-H(30F)	0.9800
C(30B)-H(30G)	0.9800
C(30B)-H(30H)	0.9800
O(4)-S(1)-O(3)	119.3(3)
O(4)-S(1)-N(8X)	107.1(3)
O(3)-S(1)-N(8X)	108.4(3)
O(4)-S(1)-C(20)	109.7(3)

O(3)-S(1)-C(20)	106.9(3)	H(8B)-C(8)-H(8C)	109.5
N(8X)-S(1)-C(20)	104.5(3)	N(8X)-C(8A)-N(8)	109.1(6)
C(24)-Si(1)-C(22)	109.6(4)	N(8X)-C(8A)-C(3A)	113.7(5)
C(24)-Si(1)-C(23)	110.2(4)	N(8)-C(8A)-C(3A)	106.0(4)
C(22)-Si(1)-C(23)	110.2(5)	N(8X)-C(8A)-H(8A1)	109.3
C(24)-Si(1)-C(21)	109.5(4)	N(8)-C(8A)-H(8A1)	109.3
C(22)-Si(1)-C(21)	107.7(4)	C(3A)-C(8A)-H(8A1)	109.3
C(23)-Si(1)-C(21)	109.6(3)	N(1)-C(9)-C(10)	111.1(6)
C(11)-O(1)-C(10)	61.8(4)	N(1)-C(9)-C(4)	114.5(5)
C(8AX)-N(1)-C(9)	112.7(5)	C(10)-C(9)-C(4)	107.9(6)
C(8AX)-N(1)-C(2)	113.0(5)	N(1)-C(9)-H(9)	107.7
C(9)-N(1)-C(2)	115.8(5)	C(10)-C(9)-H(9)	107.7
N(1)-C(2)-C(3)	113.3(6)	C(4)-C(9)-H(9)	107.7
N(1)-C(2)-H(2A)	108.9	O(1)-C(10)-C(11)	58.3(5)
C(3)-C(2)-H(2A)	108.9	O(1)-C(10)-C(9)	116.2(6)
N(1)-C(2)-H(2B)	108.9	C(11)-C(10)-C(9)	125.9(6)
C(3)-C(2)-H(2B)	108.9	O(1)-C(10)-H(10)	114.6
H(2A)-C(2)-H(2B)	107.7	C(11)-C(10)-H(10)	114.6
C(3A)-C(3)-C(2)	109.1(6)	C(9)-C(10)-H(10)	114.6
C(3A)-C(3)-H(3A)	109.9	O(1)-C(11)-C(10)	59.8(4)
C(2)-C(3)-H(3A)	109.9	O(1)-C(11)-C(12)	114.9(7)
C(3A)-C(3)-H(3B)	109.9	C(10)-C(11)-C(12)	117.8(7)
C(2)-C(3)-H(3B)	109.9	O(1)-C(11)-C(13)	116.0(7)
H(3A)-C(3)-H(3B)	108.3	C(10)-C(11)-C(13)	122.1(7)
C(4A)-C(3A)-C(3)	109.0(5)	C(12)-C(11)-C(13)	114.6(6)
C(4A)-C(3A)-C(8A)	102.6(5)	C(11)-C(12)-H(12A)	109.5
C(3)-C(3A)-C(8A)	111.3(5)	C(11)-C(12)-H(12B)	109.5
C(4A)-C(3A)-C(3AX)	112.0(5)	H(12A)-C(12)-H(12B)	109.5
C(3)-C(3A)-C(3AX)	109.2(6)	C(11)-C(12)-H(12C)	109.5
C(8A)-C(3A)-C(3AX)	112.6(5)	H(12A)-C(12)-H(12C)	109.5
C(5)-C(4)-C(4A)	119.8(7)	H(12B)-C(12)-H(12C)	109.5
C(5)-C(4)-C(9)	120.6(5)	C(11)-C(13)-H(13A)	109.5
C(4A)-C(4)-C(9)	119.6(6)	C(11)-C(13)-H(13B)	109.5
C(4)-C(4A)-C(7A)	118.4(6)	H(13A)-C(13)-H(13B)	109.5
C(4)-C(4A)-C(3A)	131.1(6)	C(11)-C(13)-H(13C)	109.5
C(7A)-C(4A)-C(3A)	110.1(5)	H(13A)-C(13)-H(13C)	109.5
C(6)-C(5)-C(4)	120.5(5)	H(13B)-C(13)-H(13C)	109.5
C(6)-C(5)-H(5)	119.8	C(1XX)-N(1X)-C(2X)	121.1(6)
C(4)-C(5)-H(5)	119.8	C(1XX)-N(1X)-C(8AX)	125.7(5)
C(5)-C(6)-C(7)	121.6(7)	C(2X)-N(1X)-C(8AX)	112.9(5)
C(5)-C(6)-H(6)	119.2	N(1X)-C(2X)-C(3X)	104.5(6)
C(7)-C(6)-H(6)	119.2	N(1X)-C(2X)-H(2X1)	110.8
C(7A)-C(7)-C(6)	116.8(7)	C(3X)-C(2X)-H(2X1)	110.8
C(7A)-C(7)-H(7)	121.6	N(1X)-C(2X)-H(2X2)	110.8
C(6)-C(7)-H(7)	121.6	C(3X)-C(2X)-H(2X2)	110.8
C(7)-C(7A)-N(8)	126.9(6)	H(2X1)-C(2X)-H(2X2)	108.9
C(7)-C(7A)-C(4A)	122.6(5)	C(2X)-C(3X)-C(3AX)	103.8(5)
N(8)-C(7A)-C(4A)	110.4(6)	C(2X)-C(3X)-H(3X1)	111.0
C(7A)-N(8)-C(8)	124.0(6)	C(3AX)-C(3X)-H(3X1)	111.0
C(7A)-N(8)-C(8A)	110.4(5)	C(2X)-C(3X)-H(3X2)	111.0
C(8)-N(8)-C(8A)	119.9(5)	C(3AX)-C(3X)-H(3X2)	111.0
N(8)-C(8)-H(8A)	109.5	H(3X1)-C(3X)-H(3X2)	109.0
N(8)-C(8)-H(8B)	109.5	C(4AX)-C(3AX)-C(8AX)	114.2(5)
H(8A)-C(8)-H(8B)	109.5	C(4AX)-C(3AX)-C(3X)	106.0(5)
N(8)-C(8)-H(8C)	109.5	C(8AX)-C(3AX)-C(3X)	103.4(5)
H(8A)-C(8)-H(8C)	109.5	C(4AX)-C(3AX)-C(3A)	109.1(5)

C(8AX)-C(3AX)-C(3A)	107.1(5)
C(3X)-C(3AX)-C(3A)	117.2(5)
C(7AX)-C(4AX)-C(4X)	118.0(6)
C(7AX)-C(4AX)-C(3AX)	117.0(5)
C(4X)-C(4AX)-C(3AX)	124.7(6)
C(5X)-C(4X)-C(4AX)	119.6(6)
C(5X)-C(4X)-H(4X)	120.2
C(4AX)-C(4X)-H(4X)	120.2
C(6X)-C(5X)-C(4X)	121.1(7)
C(6X)-C(5X)-H(5X)	119.4
C(4X)-C(5X)-H(5X)	119.4
C(5X)-C(6X)-C(7X)	119.2(7)
C(5X)-C(6X)-H(6X)	120.4
C(7X)-C(6X)-H(6X)	120.4
C(7AX)-C(7X)-C(6X)	120.0(6)
C(7AX)-C(7X)-H(7X)	120.0
C(6X)-C(7X)-H(7X)	120.0
C(7X)-C(7AX)-C(4AX)	122.0(6)
C(7X)-C(7AX)-N(8X)	121.5(6)
C(4AX)-C(7AX)-N(8X)	116.5(6)
N(1)-C(8AX)-N(1X)	111.7(6)
N(1)-C(8AX)-C(3AX)	113.6(5)
N(1X)-C(8AX)-C(3AX)	104.0(5)
N(1)-C(8AX)-H(8AX)	109.1
N(1X)-C(8AX)-H(8AX)	109.1
C(3AX)-C(8AX)-H(8AX)	109.1
C(7AX)-N(8X)-C(8A)	115.2(4)
C(7AX)-N(8X)-S(1)	121.5(4)
C(8A)-N(8X)-S(1)	118.8(4)
O(2)-C(1XX)-N(1X)	121.5(6)
O(2)-C(1XX)-C(2XX)	121.2(7)
N(1X)-C(1XX)-C(2XX)	117.2(7)
C(1XX)-C(2XX)-H(2X3)	109.5
C(1XX)-C(2XX)-H(2X4)	109.5
H(2X3)-C(2XX)-H(2X4)	109.5
C(1XX)-C(2XX)-H(2X5)	109.5
H(2X3)-C(2XX)-H(2X5)	109.5
H(2X4)-C(2XX)-H(2X5)	109.5
C(21)-C(20)-S(1)	114.7(5)
C(21)-C(20)-H(20A)	108.6
S(1)-C(20)-H(20A)	108.6
C(21)-C(20)-H(20B)	108.6
S(1)-C(20)-H(20B)	108.6
H(20A)-C(20)-H(20B)	107.6
C(20)-C(21)-Si(1)	114.4(5)
C(20)-C(21)-H(21A)	108.7
Si(1)-C(21)-H(21A)	108.7
C(20)-C(21)-H(21B)	108.7
Si(1)-C(21)-H(21B)	108.7
H(21A)-C(21)-H(21B)	107.6
Si(1)-C(22)-H(22A)	109.5
Si(1)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
Si(1)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
Si(1)-C(23)-H(23A)	109.5
Si(1)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
Si(1)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
Si(1)-C(24)-H(24A)	109.5
Si(1)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
Si(1)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(30A)-O(30A)-H(30A)	109.5
O(30A)-C(30A)-H(30B)	109.5
O(30A)-C(30A)-H(30C)	109.5
H(30B)-C(30A)-H(30C)	109.5
O(30A)-C(30A)-H(30D)	109.5
H(30B)-C(30A)-H(30D)	109.5
H(30C)-C(30A)-H(30D)	109.5
C(30B)-O(30B)-H(30E)	109.5
O(30B)-C(30B)-H(30F)	109.5
O(30B)-C(30B)-H(30G)	109.5
H(30F)-C(30B)-H(30G)	109.5
O(30B)-C(30B)-H(30H)	109.5
H(30F)-C(30B)-H(30H)	109.5
H(30G)-C(30B)-H(30H)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S24. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin A (**42**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	24(1)	31(1)	72(1)	-1(1)	-18(1)	-1(1)
Si(1)	38(1)	36(1)	67(1)	-2(1)	-20(1)	-1(1)
O(1)	53(3)	40(3)	65(3)	-6(3)	-16(2)	5(2)

O(2)	48(3)	30(3)	84(3)	0(3)	-18(2)	-4(2)
O(3)	34(2)	33(3)	70(3)	-15(2)	-16(2)	0(2)
O(4)	28(2)	37(3)	73(3)	8(2)	-16(2)	-2(2)
N(1)	29(2)	29(3)	67(3)	2(3)	-17(2)	2(2)
C(2)	34(3)	35(4)	72(4)	-5(3)	-18(3)	2(3)
C(3)	33(3)	38(4)	69(4)	-1(4)	-18(3)	1(3)
C(3A)	28(2)	28(4)	61(4)	-5(3)	-19(2)	2(2)
C(4)	26(3)	31(4)	68(4)	1(3)	-12(3)	1(3)
C(4A)	26(3)	34(4)	64(4)	-1(3)	-16(3)	1(3)
C(5)	33(3)	34(4)	66(4)	3(3)	-21(3)	4(3)
C(6)	32(3)	40(4)	75(5)	2(4)	-18(3)	3(3)
C(7)	35(3)	35(4)	73(4)	2(3)	-21(3)	2(3)
C(7A)	30(3)	31(4)	63(4)	0(3)	-19(3)	-1(3)
N(8)	31(3)	25(3)	82(4)	-3(3)	-23(2)	3(2)
C(8)	41(3)	27(4)	89(5)	-4(4)	-19(3)	-6(3)
C(8A)	28(3)	25(4)	72(4)	2(3)	-20(3)	-2(2)
C(9)	34(3)	27(4)	60(4)	2(3)	-19(3)	-1(3)
C(10)	41(3)	35(4)	68(4)	-2(4)	-23(3)	3(3)
C(11)	45(3)	41(4)	65(4)	0(4)	-26(3)	-2(3)
C(12)	62(4)	58(6)	78(5)	5(5)	-27(4)	-6(4)
C(13)	42(3)	66(6)	71(5)	-9(4)	-24(3)	-7(4)
N(1X)	34(3)	22(3)	76(4)	2(3)	-21(2)	0(2)
C(2X)	35(3)	35(4)	76(5)	6(4)	-17(3)	2(3)
C(3X)	32(3)	27(4)	68(4)	-2(3)	-15(3)	-2(3)
C(3AX)	28(3)	24(3)	61(4)	3(3)	-18(2)	0(2)
C(4AX)	23(2)	26(4)	67(4)	4(3)	-13(2)	3(2)
C(4X)	25(3)	42(4)	69(4)	10(3)	-17(3)	-4(3)
C(5X)	30(3)	48(5)	74(5)	12(4)	-12(3)	5(3)
C(6X)	36(3)	53(5)	62(4)	5(4)	-15(3)	9(3)
C(7X)	30(3)	39(4)	68(4)	1(4)	-18(3)	-1(3)
C(7AX)	28(2)	29(3)	67(4)	5(3)	-17(2)	1(3)
C(8AX)	31(3)	24(4)	69(4)	4(3)	-18(3)	0(2)
N(8X)	24(2)	37(3)	61(3)	2(3)	-12(2)	-5(2)
C(1XX)	41(3)	36(4)	78(5)	-1(4)	-15(3)	-4(3)
C(2XX)	42(4)	38(4)	111(7)	-1(5)	-34(4)	-8(3)
C(20)	29(3)	27(4)	75(4)	-5(3)	-18(3)	-1(3)
C(21)	35(3)	30(4)	68(4)	-4(3)	-20(3)	-4(3)
C(22)	70(5)	46(5)	79(5)	-3(4)	-16(4)	-8(4)
C(23)	68(5)	42(5)	87(6)	4(4)	-35(4)	-7(4)
C(24)	54(4)	41(5)	83(5)	-7(4)	-15(4)	-5(4)
O(30A)	148(11)	105(10)	105(7)	34(8)	-15(7)	49(8)
C(30A)	85(8)	93(12)	72(7)	20(7)	-17(6)	-18(8)
O(30B)	55(13)	40(16)	57(14)	2(11)	-10(10)	-15(11)
C(30B)	42(18)	170(70)	80(30)	40(40)	18(17)	-40(30)

Table S25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin A (**42**).

	x	y	z	U(eq)
H(2A)	5860	4693	4035	57
H(2B)	6594	4013	4809	57

H(3A)	8247	5106	5318	56
H(3B)	7038	5820	4819	56
H(5)	1130	6574	5081	54
H(6)	1615	7852	5894	60
H(7)	4177	8091	6788	58
H(8A)	8508	7733	6882	79
H(8B)	8031	7573	7977	79
H(8C)	6817	8140	7283	79
H(8A1)	8582	6215	6454	51
H(9)	1928	4950	5013	49
H(10)	4053	5820	3682	58
H(12A)	2918	6130	2174	100
H(12B)	1102	6508	2409	100
H(12C)	1250	5685	1720	100
H(13A)	-723	4928	2877	91
H(13B)	-657	5689	3657	91
H(13C)	-22	4742	3952	91
H(2X1)	6674	2610	6417	59
H(2X2)	5988	2906	7443	59
H(3X1)	7857	3926	6135	51
H(3X2)	7984	3955	7296	51
H(4X)	3338	4170	7967	55
H(5X)	3216	4403	9625	61
H(6X)	5309	5191	10450	61
H(7X)	7570	5753	9604	55
H(8AX)	3272	4456	6443	50
H(2X3)	1903	3238	4994	97
H(2X4)	1221	3517	6018	97
H(2X5)	872	2563	5616	97
H(20A)	12487	6149	8134	53
H(20B)	11005	6731	7672	53
H(21A)	11273	6232	9645	54
H(21B)	9738	6784	9190	54
H(22A)	12400	8521	10853	98
H(22B)	12384	7515	11112	98
H(22C)	10658	7999	10821	98
H(23A)	10175	8720	8815	100
H(23B)	11319	8390	7964	100
H(23C)	12045	9089	8719	100
H(24A)	14560	7254	8593	90
H(24B)	14910	7149	9728	90
H(24C)	15015	8082	9240	90
H(30A)	3561	1480	7585	180
H(30B)	3268	2533	8846	125
H(30C)	1824	1839	9035	125
H(30D)	1852	2334	8025	125
H(30E)	4421	-621	7270	76
H(30F)	3521	607	8397	145
H(30G)	3447	592	7244	145
H(30H)	5207	749	7819	145

Crystal Structure of (–)-*N*8'-(Trimethylsilyl)ethanesulfonyl communesin B (45):

Structural parameters for (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin B (**45**) are freely available from the Cambridge Crystallographic Data Center (CCDC 1937972).

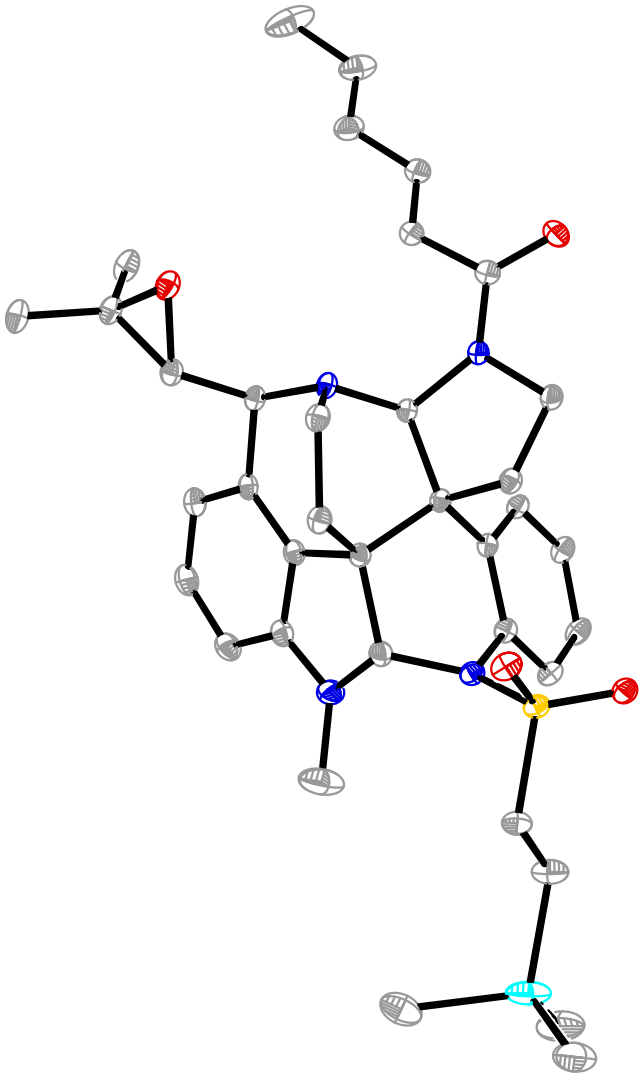


Table S26. Crystal data and structure refinement for (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin B (**45**).

Identification code	3-264_7_sq	
Empirical formula	C37 H48 N4 O4 S Si	
Formula weight	672.94	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.86180(10) Å	α= 90°.
	b = 17.7249(3) Å	β= 90°.
	c = 27.6554(5) Å	γ = 90°.
Volume	3853.77(11) $Å^3$	
Z	4	
Density (calculated)	1.160 Mg/m^3	
Absorption coefficient	1.371 mm^{-1}	
F(000)	1440	
Crystal size	0.250 x 0.035 x 0.025 mm^3	
Theta range for data collection	2.961 to 77.367°.	
Index ranges	-9<=h<=9, -22<=k<=22, -34<=l<=35	
Reflections collected	134233	
Independent reflections	8171 [R(int) = 0.0599]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7543 and 0.6759	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8171 / 504 / 462	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0827	
R indices (all data)	R1 = 0.0332, wR2 = 0.0843	
Absolute structure parameter	0.007(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.274 and -0.261 e.$Å^{-3}$	

Table S27. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin B (**45**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	1285(1)	6297(1)	3988(1)	22(1)
Si(1)	-531(1)	5293(1)	5400(1)	49(1)
O(1)	8057(2)	4859(1)	1732(1)	28(1)
O(2)	7464(2)	8209(1)	2311(1)	39(1)
O(3)	618(2)	6134(1)	3516(1)	28(1)
O(4)	1355(2)	7064(1)	4150(1)	25(1)
N(1)	6753(2)	5801(1)	2514(1)	21(1)
C(2)	5025(3)	5563(1)	2389(1)	24(1)
C(3)	4009(3)	5230(1)	2817(1)	24(1)
C(3A)	4855(3)	5473(1)	3293(1)	21(1)
C(4)	7837(3)	4850(1)	3111(1)	23(1)
C(4A)	6418(3)	4985(1)	3394(1)	22(1)
C(5)	9109(3)	4366(1)	3288(1)	29(1)
C(6)	8910(3)	4014(1)	3731(1)	33(1)
C(7)	7449(3)	4117(1)	4010(1)	32(1)
C(7A)	6219(3)	4607(1)	3836(1)	26(1)
N(8)	4670(3)	4783(1)	4043(1)	34(1)
C(8)	3907(4)	4393(2)	4437(1)	61(1)
C(8A)	3700(3)	5295(1)	3739(1)	25(1)
C(9)	8007(3)	5206(1)	2615(1)	22(1)
C(10)	7895(3)	4603(1)	2225(1)	25(1)
C(11)	9310(3)	4333(1)	1921(1)	27(1)
C(12)	9181(3)	3553(1)	1706(1)	35(1)
C(13)	11081(3)	4640(2)	1958(1)	35(1)
N(1X)	6524(2)	7148(1)	2670(1)	23(1)
C(1X)	5018(3)	7530(1)	2865(1)	25(1)
C(2X)	3961(3)	6885(1)	3071(1)	22(1)
C(3AX)	5347(2)	6328(1)	3264(1)	20(1)
C(4AX)	5813(2)	6615(1)	3764(1)	20(1)
C(4X)	7191(3)	7078(1)	3866(1)	23(1)
C(5X)	7439(3)	7363(1)	4331(1)	27(1)
C(6X)	6320(3)	7178(1)	4700(1)	28(1)
C(7X)	4921(3)	6718(1)	4603(1)	25(1)
C(7AX)	4672(3)	6450(1)	4138(1)	22(1)
C(8AX)	6795(3)	6394(1)	2881(1)	20(1)
N(8X)	3256(2)	5968(1)	4025(1)	23(1)
C(1XX)	7660(3)	7532(1)	2398(1)	28(1)
C(2XX)	9099(3)	7093(1)	2195(1)	29(1)
C(3XX)	10538(3)	7422(1)	2052(1)	32(1)
C(4XX)	11934(3)	7039(2)	1815(1)	37(1)
C(5XX)	13340(4)	7385(2)	1666(1)	45(1)
C(6XX)	14755(4)	7005(3)	1395(1)	72(1)
C(20)	99(3)	5740(1)	4405(1)	28(1)
C(21)	573(4)	5885(2)	4929(1)	38(1)
C(22A)	-103(17)	4226(7)	5238(4)	53(2)
C(23A)	-2800(30)	5384(13)	5363(9)	58(3)
C(24A)	407(16)	5489(12)	5974(3)	62(3)
C(22B)	160(40)	4401(14)	5381(15)	103(8)
C(23B)	-2950(30)	5480(20)	5406(12)	62(7)
C(24B)	120(20)	5873(19)	6013(6)	67(5)

Table S28. Bond lengths [Å] and angles [°] for (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin B (**45**).

S(1)-O(4)	1.4328(15)
S(1)-O(3)	1.4358(16)
S(1)-N(8X)	1.6584(18)
S(1)-C(20)	1.782(2)
Si(1)-C(22B)	1.67(2)
Si(1)-C(24A)	1.784(8)
Si(1)-C(23A)	1.80(2)
Si(1)-C(21)	1.884(3)
Si(1)-C(23B)	1.93(2)
Si(1)-C(22A)	1.972(12)
Si(1)-C(24B)	2.05(3)
O(1)-C(10)	1.442(3)
O(1)-C(11)	1.453(3)
O(2)-C(1XX)	1.234(3)
N(1)-C(8AX)	1.461(2)
N(1)-C(2)	1.464(3)
N(1)-C(9)	1.470(3)
C(2)-C(3)	1.544(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(3A)	1.538(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(3A)-C(4A)	1.528(3)
C(3A)-C(8A)	1.562(3)
C(3A)-C(3AX)	1.567(3)
C(4)-C(4A)	1.382(3)
C(4)-C(5)	1.406(3)
C(4)-C(9)	1.517(3)
C(4A)-C(7A)	1.402(3)
C(5)-C(6)	1.384(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.396(4)
C(6)-H(6)	0.9500
C(7)-C(7A)	1.386(3)
C(7)-H(7)	0.9500
C(7A)-N(8)	1.382(3)
N(8)-C(8)	1.422(3)
N(8)-C(8A)	1.455(3)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(8A)-N(8X)	1.472(3)
C(8A)-H(8A1)	1.0000
C(9)-C(10)	1.520(3)
C(9)-H(9)	1.0000
C(10)-C(11)	1.474(3)
C(10)-H(10)	1.0000
C(11)-C(13)	1.499(3)
C(11)-C(12)	1.508(3)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
N(1X)-C(1XX)	1.350(3)
N(1X)-C(1X)	1.467(3)
N(1X)-C(8AX)	1.474(2)
C(1X)-C(2X)	1.523(3)
C(1X)-H(1X1)	0.9900
C(1X)-H(1X2)	0.9900
C(2X)-C(3AX)	1.565(3)
C(2X)-H(2X1)	0.9900
C(2X)-H(2X2)	0.9900
C(3AX)-C(4AX)	1.519(3)
C(3AX)-C(8AX)	1.558(3)
C(4AX)-C(4X)	1.387(3)
C(4AX)-C(7AX)	1.400(3)
C(4X)-C(5X)	1.395(3)
C(4X)-H(4X)	0.9500
C(5X)-C(6X)	1.387(3)
C(5X)-H(5X)	0.9500
C(6X)-C(7X)	1.396(3)
C(6X)-H(6X)	0.9500
C(7X)-C(7AX)	1.384(3)
C(7X)-H(7X)	0.9500
C(7AX)-N(8X)	1.439(3)
C(8AX)-H(8AX)	1.0000
C(1XX)-C(2XX)	1.483(3)
C(2XX)-C(3XX)	1.333(3)
C(2XX)-H(2XX)	0.9500
C(3XX)-C(4XX)	1.447(3)
C(3XX)-H(3XX)	0.9500
C(4XX)-C(5XX)	1.330(4)
C(4XX)-H(4XX)	0.9500
C(5XX)-C(6XX)	1.500(4)
C(5XX)-H(5XX)	0.9500
C(6XX)-H(6X1)	0.9800
C(6XX)-H(6X2)	0.9800
C(6XX)-H(6X3)	0.9800
C(20)-C(21)	1.518(3)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22A)-H(22A)	0.9800
C(22A)-H(22B)	0.9800
C(22A)-H(22C)	0.9800
C(23A)-H(23A)	0.9800
C(23A)-H(23B)	0.9800
C(23A)-H(23C)	0.9800
C(24A)-H(24A)	0.9800
C(24A)-H(24B)	0.9800
C(24A)-H(24C)	0.9800
C(22B)-H(22D)	0.9800
C(22B)-H(22E)	0.9800
C(22B)-H(22F)	0.9800

C(23B)-H(23D)	0.9800
C(23B)-H(23E)	0.9800
C(23B)-H(23F)	0.9800
C(24B)-H(24D)	0.9800
C(24B)-H(24E)	0.9800
C(24B)-H(24F)	0.9800
O(4)-S(1)-O(3)	119.31(9)
O(4)-S(1)-N(8X)	106.18(9)
O(3)-S(1)-N(8X)	109.03(9)
O(4)-S(1)-C(20)	110.09(10)
O(3)-S(1)-C(20)	106.61(10)
N(8X)-S(1)-C(20)	104.73(10)
C(24A)-Si(1)-C(23A)	116.3(10)
C(22B)-Si(1)-C(21)	110.8(9)
C(24A)-Si(1)-C(21)	108.4(4)
C(23A)-Si(1)-C(21)	111.6(7)
C(22B)-Si(1)-C(23B)	118.7(19)
C(21)-Si(1)-C(23B)	111.5(10)
C(24A)-Si(1)-C(22A)	108.6(7)
C(23A)-Si(1)-C(22A)	104.1(9)
C(21)-Si(1)-C(22A)	107.3(4)
C(22B)-Si(1)-C(24B)	114.8(12)
C(21)-Si(1)-C(24B)	100.2(4)
C(23B)-Si(1)-C(24B)	98.9(15)
C(10)-O(1)-C(11)	61.22(13)
C(8AX)-N(1)-C(2)	113.07(15)
C(8AX)-N(1)-C(9)	111.72(15)
C(2)-N(1)-C(9)	117.41(16)
N(1)-C(2)-C(3)	114.14(16)
N(1)-C(2)-H(2A)	108.7
C(3)-C(2)-H(2A)	108.7
N(1)-C(2)-H(2B)	108.7
C(3)-C(2)-H(2B)	108.7
H(2A)-C(2)-H(2B)	107.6
C(3A)-C(3)-C(2)	109.00(16)
C(3A)-C(3)-H(3A)	109.9
C(2)-C(3)-H(3A)	109.9
C(3A)-C(3)-H(3B)	109.9
C(2)-C(3)-H(3B)	109.9
H(3A)-C(3)-H(3B)	108.3
C(4A)-C(3A)-C(3)	110.21(16)
C(4A)-C(3A)-C(8A)	102.14(16)
C(3)-C(3A)-C(8A)	111.57(17)
C(4A)-C(3A)-C(3AX)	111.04(16)
C(3)-C(3A)-C(3AX)	109.42(16)
C(8A)-C(3A)-C(3AX)	112.29(16)
C(4A)-C(4)-C(5)	118.8(2)
C(4A)-C(4)-C(9)	120.74(18)
C(5)-C(4)-C(9)	120.40(19)
C(4)-C(4A)-C(7A)	120.03(19)
C(4)-C(4A)-C(3A)	130.05(18)
C(7A)-C(4A)-C(3A)	109.81(18)
C(6)-C(5)-C(4)	120.2(2)
C(6)-C(5)-H(5)	119.9
C(4)-C(5)-H(5)	119.9
C(5)-C(6)-C(7)	121.6(2)
C(5)-C(6)-H(6)	119.2
C(7)-C(6)-H(6)	119.2
C(7A)-C(7)-C(6)	117.5(2)
C(7A)-C(7)-H(7)	121.2
C(6)-C(7)-H(7)	121.2
N(8)-C(7A)-C(7)	127.7(2)
N(8)-C(7A)-C(4A)	110.64(19)
C(7)-C(7A)-C(4A)	121.7(2)
C(7A)-N(8)-C(8)	125.4(2)
C(7A)-N(8)-C(8A)	111.26(18)
C(8)-N(8)-C(8A)	121.7(2)
N(8)-C(8)-H(8A)	109.5
N(8)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
N(8)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
N(8)-C(8A)-N(8X)	108.57(17)
N(8)-C(8A)-C(3A)	106.09(18)
N(8X)-C(8A)-C(3A)	113.50(16)
N(8)-C(8A)-H(8A1)	109.5
N(8X)-C(8A)-H(8A1)	109.5
C(3A)-C(8A)-H(8A1)	109.5
N(1)-C(9)-C(4)	114.20(17)
N(1)-C(9)-C(10)	109.37(16)
C(4)-C(9)-C(10)	110.20(17)
N(1)-C(9)-H(9)	107.6
C(4)-C(9)-H(9)	107.6
C(10)-C(9)-H(9)	107.6
O(1)-C(10)-C(11)	59.77(14)
O(1)-C(10)-C(9)	116.38(17)
C(11)-C(10)-C(9)	126.13(19)
O(1)-C(10)-H(10)	114.3
C(11)-C(10)-H(10)	114.3
C(9)-C(10)-H(10)	114.3
O(1)-C(11)-C(10)	59.00(13)
O(1)-C(11)-C(13)	114.91(19)
C(10)-C(11)-C(13)	122.87(19)
O(1)-C(11)-C(12)	113.69(18)
C(10)-C(11)-C(12)	118.2(2)
C(13)-C(11)-C(12)	115.01(19)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(1XX)-N(1X)-C(1X)	120.37(17)
C(1XX)-N(1X)-C(8AX)	125.58(17)

C(1X)-N(1X)-C(8AX)	112.87(16)	C(5XX)-C(4XX)-H(4XX)	118.2
N(1X)-C(1X)-C(2X)	103.38(16)	C(3XX)-C(4XX)-H(4XX)	118.2
N(1X)-C(1X)-H(1X1)	111.1	C(4XX)-C(5XX)-C(6XX)	124.4(3)
C(2X)-C(1X)-H(1X1)	111.1	C(4XX)-C(5XX)-H(5XX)	117.8
N(1X)-C(1X)-H(1X2)	111.1	C(6XX)-C(5XX)-H(5XX)	117.8
C(2X)-C(1X)-H(1X2)	111.1	C(5XX)-C(6XX)-H(6X1)	109.5
H(1X1)-C(1X)-H(1X2)	109.1	C(5XX)-C(6XX)-H(6X2)	109.5
C(1X)-C(2X)-C(3AX)	102.74(16)	H(6X1)-C(6XX)-H(6X2)	109.5
C(1X)-C(2X)-H(2X1)	111.2	C(5XX)-C(6XX)-H(6X3)	109.5
C(3AX)-C(2X)-H(2X1)	111.2	H(6X1)-C(6XX)-H(6X3)	109.5
C(1X)-C(2X)-H(2X2)	111.2	H(6X2)-C(6XX)-H(6X3)	109.5
C(3AX)-C(2X)-H(2X2)	111.2	C(21)-C(20)-S(1)	113.34(16)
H(2X1)-C(2X)-H(2X2)	109.1	C(21)-C(20)-H(20A)	108.9
C(4AX)-C(3AX)-C(8AX)	114.65(16)	S(1)-C(20)-H(20A)	108.9
C(4AX)-C(3AX)-C(2X)	105.51(15)	C(21)-C(20)-H(20B)	108.9
C(8AX)-C(3AX)-C(2X)	103.30(15)	S(1)-C(20)-H(20B)	108.9
C(4AX)-C(3AX)-C(3A)	109.65(16)	H(20A)-C(20)-H(20B)	107.7
C(8AX)-C(3AX)-C(3A)	106.72(15)	C(20)-C(21)-Si(1)	116.93(17)
C(2X)-C(3AX)-C(3A)	117.17(16)	C(20)-C(21)-H(21A)	108.1
C(4X)-C(4AX)-C(7AX)	118.31(18)	Si(1)-C(21)-H(21A)	108.1
C(4X)-C(4AX)-C(3AX)	124.83(18)	C(20)-C(21)-H(21B)	108.1
C(7AX)-C(4AX)-C(3AX)	116.62(17)	Si(1)-C(21)-H(21B)	108.1
C(4AX)-C(4X)-C(5X)	120.66(19)	H(21A)-C(21)-H(21B)	107.3
C(4AX)-C(4X)-H(4X)	119.7	Si(1)-C(22A)-H(22A)	109.5
C(5X)-C(4X)-H(4X)	119.7	Si(1)-C(22A)-H(22B)	109.5
C(6X)-C(5X)-C(4X)	120.3(2)	H(22A)-C(22A)-H(22B)	109.5
C(6X)-C(5X)-H(5X)	119.9	Si(1)-C(22A)-H(22C)	109.5
C(4X)-C(5X)-H(5X)	119.9	H(22A)-C(22A)-H(22C)	109.5
C(5X)-C(6X)-C(7X)	119.79(19)	H(22B)-C(22A)-H(22C)	109.5
C(5X)-C(6X)-H(6X)	120.1	Si(1)-C(23A)-H(23A)	109.5
C(7X)-C(6X)-H(6X)	120.1	Si(1)-C(23A)-H(23B)	109.5
C(7AX)-C(7X)-C(6X)	119.4(2)	H(23A)-C(23A)-H(23B)	109.5
C(7AX)-C(7X)-H(7X)	120.3	Si(1)-C(23A)-H(23C)	109.5
C(6X)-C(7X)-H(7X)	120.3	H(23A)-C(23A)-H(23C)	109.5
C(7X)-C(7AX)-C(4AX)	121.59(19)	H(23B)-C(23A)-H(23C)	109.5
C(7X)-C(7AX)-N(8X)	121.03(19)	Si(1)-C(24A)-H(24A)	109.5
C(4AX)-C(7AX)-N(8X)	117.35(17)	Si(1)-C(24A)-H(24B)	109.5
N(1)-C(8AX)-N(1X)	111.88(16)	H(24A)-C(24A)-H(24B)	109.5
N(1)-C(8AX)-C(3AX)	113.68(16)	Si(1)-C(24A)-H(24C)	109.5
N(1X)-C(8AX)-C(3AX)	103.40(15)	H(24A)-C(24A)-H(24C)	109.5
N(1)-C(8AX)-H(8AX)	109.2	H(24B)-C(24A)-H(24C)	109.5
N(1X)-C(8AX)-H(8AX)	109.2	Si(1)-C(22B)-H(22D)	109.5
C(3AX)-C(8AX)-H(8AX)	109.2	Si(1)-C(22B)-H(22E)	109.5
C(7AX)-N(8X)-C(8A)	114.49(17)	H(22D)-C(22B)-H(22E)	109.5
C(7AX)-N(8X)-S(1)	121.83(14)	Si(1)-C(22B)-H(22F)	109.5
C(8A)-N(8X)-S(1)	118.24(14)	H(22D)-C(22B)-H(22F)	109.5
O(2)-C(1XX)-N(1X)	121.1(2)	H(22E)-C(22B)-H(22F)	109.5
O(2)-C(1XX)-C(2XX)	122.0(2)	Si(1)-C(23B)-H(23D)	109.5
N(1X)-C(1XX)-C(2XX)	116.83(19)	Si(1)-C(23B)-H(23E)	109.5
C(3XX)-C(2XX)-C(1XX)	122.1(2)	H(23D)-C(23B)-H(23E)	109.5
C(3XX)-C(2XX)-H(2XX)	119.0	Si(1)-C(23B)-H(23F)	109.5
C(1XX)-C(2XX)-H(2XX)	119.0	H(23D)-C(23B)-H(23F)	109.5
C(2XX)-C(3XX)-C(4XX)	124.9(2)	H(23E)-C(23B)-H(23F)	109.5
C(2XX)-C(3XX)-H(3XX)	117.5	Si(1)-C(24B)-H(24D)	109.5
C(4XX)-C(3XX)-H(3XX)	117.5	Si(1)-C(24B)-H(24E)	109.5
C(5XX)-C(4XX)-C(3XX)	123.7(3)	H(24D)-C(24B)-H(24E)	109.5

Si(1)-C(24B)-H(24F)	109.5
H(24D)-C(24B)-H(24F)	109.5
H(24E)-C(24B)-H(24F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S29. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin B (**45**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

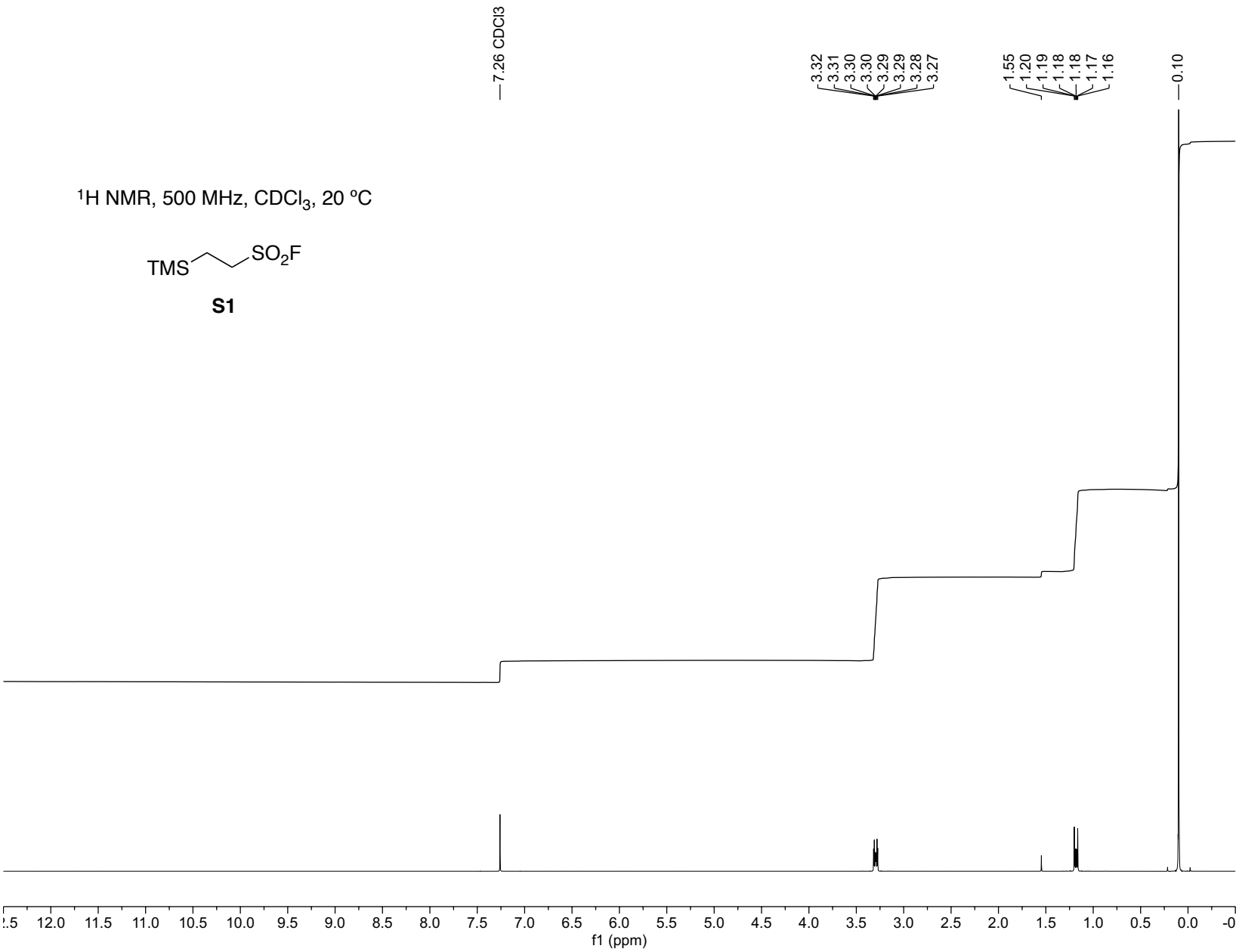
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	18(1)	27(1)	21(1)	-1(1)	0(1)	-2(1)
Si(1)	34(1)	75(1)	38(1)	28(1)	4(1)	-6(1)
O(1)	31(1)	31(1)	24(1)	-6(1)	-3(1)	6(1)
O(2)	44(1)	26(1)	46(1)	10(1)	14(1)	6(1)
O(3)	23(1)	38(1)	25(1)	-4(1)	-2(1)	-2(1)
O(4)	21(1)	28(1)	26(1)	-1(1)	1(1)	1(1)
N(1)	22(1)	21(1)	21(1)	-5(1)	-2(1)	2(1)
C(2)	25(1)	26(1)	21(1)	-5(1)	-5(1)	1(1)
C(3)	23(1)	24(1)	25(1)	-5(1)	-4(1)	-2(1)
C(3A)	22(1)	20(1)	22(1)	-2(1)	-1(1)	-1(1)
C(4)	25(1)	18(1)	24(1)	-5(1)	-3(1)	0(1)
C(4A)	24(1)	19(1)	24(1)	-3(1)	-4(1)	-1(1)
C(5)	28(1)	24(1)	35(1)	-3(1)	-4(1)	3(1)
C(6)	34(1)	24(1)	40(1)	0(1)	-8(1)	6(1)
C(7)	38(1)	27(1)	31(1)	5(1)	-6(1)	1(1)
C(7A)	30(1)	22(1)	28(1)	-2(1)	-3(1)	-1(1)
N(8)	39(1)	32(1)	32(1)	11(1)	8(1)	10(1)
C(8)	45(2)	74(2)	64(2)	40(2)	9(2)	3(2)
C(8A)	28(1)	22(1)	25(1)	-2(1)	0(1)	-1(1)
C(9)	21(1)	21(1)	24(1)	-5(1)	-1(1)	1(1)
C(10)	25(1)	24(1)	26(1)	-4(1)	-1(1)	0(1)
C(11)	26(1)	28(1)	26(1)	-8(1)	-2(1)	3(1)
C(12)	38(1)	31(1)	34(1)	-13(1)	-2(1)	5(1)
C(13)	26(1)	40(1)	39(1)	-16(1)	0(1)	1(1)
N(1X)	25(1)	20(1)	24(1)	0(1)	2(1)	4(1)
C(1X)	27(1)	23(1)	25(1)	0(1)	2(1)	6(1)
C(2X)	21(1)	23(1)	22(1)	-2(1)	-2(1)	4(1)
C(3AX)	20(1)	20(1)	19(1)	-2(1)	-2(1)	1(1)
C(4AX)	20(1)	20(1)	21(1)	-2(1)	-2(1)	2(1)
C(4X)	22(1)	25(1)	23(1)	-4(1)	1(1)	0(1)
C(5X)	22(1)	31(1)	28(1)	-8(1)	-1(1)	0(1)
C(6X)	24(1)	37(1)	23(1)	-9(1)	-3(1)	1(1)
C(7X)	22(1)	32(1)	21(1)	-3(1)	1(1)	2(1)
C(7AX)	18(1)	24(1)	23(1)	-2(1)	-2(1)	1(1)
C(8AX)	21(1)	19(1)	21(1)	-2(1)	0(1)	1(1)
N(8X)	20(1)	26(1)	23(1)	-1(1)	0(1)	-1(1)
C(1XX)	31(1)	26(1)	26(1)	2(1)	2(1)	1(1)
C(2XX)	34(1)	26(1)	28(1)	2(1)	6(1)	3(1)
C(3XX)	37(1)	30(1)	28(1)	4(1)	4(1)	4(1)
C(4XX)	38(1)	44(1)	28(1)	6(1)	3(1)	9(1)
C(5XX)	37(1)	69(2)	30(1)	10(1)	2(1)	4(1)

C(6XX)	42(2)	138(4)	36(2)	10(2)	8(1)	22(2)
C(20)	24(1)	32(1)	29(1)	4(1)	3(1)	-5(1)
C(21)	37(1)	50(2)	28(1)	6(1)	2(1)	-11(1)
C(22A)	60(4)	54(4)	45(4)	22(3)	-10(3)	-6(3)
C(23A)	56(7)	62(5)	57(6)	15(4)	14(5)	-11(5)
C(24A)	70(5)	92(8)	23(2)	4(4)	-1(3)	-24(5)
C(22B)	117(16)	61(8)	130(19)	43(9)	57(14)	15(10)
C(23B)	22(5)	111(18)	53(10)	39(11)	4(5)	3(7)
C(24B)	51(7)	110(13)	40(5)	31(7)	-3(5)	-32(8)

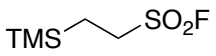
Table S30. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for (–)-*N*8'-(trimethylsilyl)ethanesulfonyl communesin B (**45**).

	x	y	z	U(eq)
H(2A)	5090	5180	2129	29
H(2B)	4398	6004	2259	29
H(3A)	2821	5415	2807	29
H(3B)	3990	4673	2794	29
H(5)	10109	4281	3103	34
H(6)	9789	3695	3848	39
H(7)	7302	3861	4309	38
H(8A)	3124	4009	4312	91
H(8B)	3278	4751	4639	91
H(8C)	4794	4149	4631	91
H(8A1)	2636	5040	3627	30
H(9)	9163	5439	2594	27
H(10)	6971	4224	2277	30
H(12A)	7981	3413	1673	52
H(12B)	9754	3191	1919	52
H(12C)	9725	3548	1387	52
H(13A)	11604	4650	1637	53
H(13B)	11755	4318	2173	53
H(13C)	11041	5153	2090	53
H(1X1)	4391	7800	2608	30
H(1X2)	5338	7893	3121	30
H(2X1)	3256	6646	2817	26
H(2X2)	3212	7062	3335	26
H(4X)	7974	7202	3616	28
H(5X)	8378	7685	4395	32
H(6X)	6505	7364	5018	34
H(7X)	4146	6589	4853	30
H(8AX)	7920	6383	3049	24
H(2XX)	8991	6561	2165	35
H(3XX)	10657	7948	2110	38
H(4XX)	11841	6510	1764	44
H(5XX)	13456	7907	1735	54
H(6X1)	14508	6465	1365	108
H(6X2)	15825	7074	1571	108
H(6X3)	14855	7229	1072	108
H(20A)	-1127	5846	4361	34
H(20B)	287	5200	4331	34
H(21A)	339	6422	5002	46

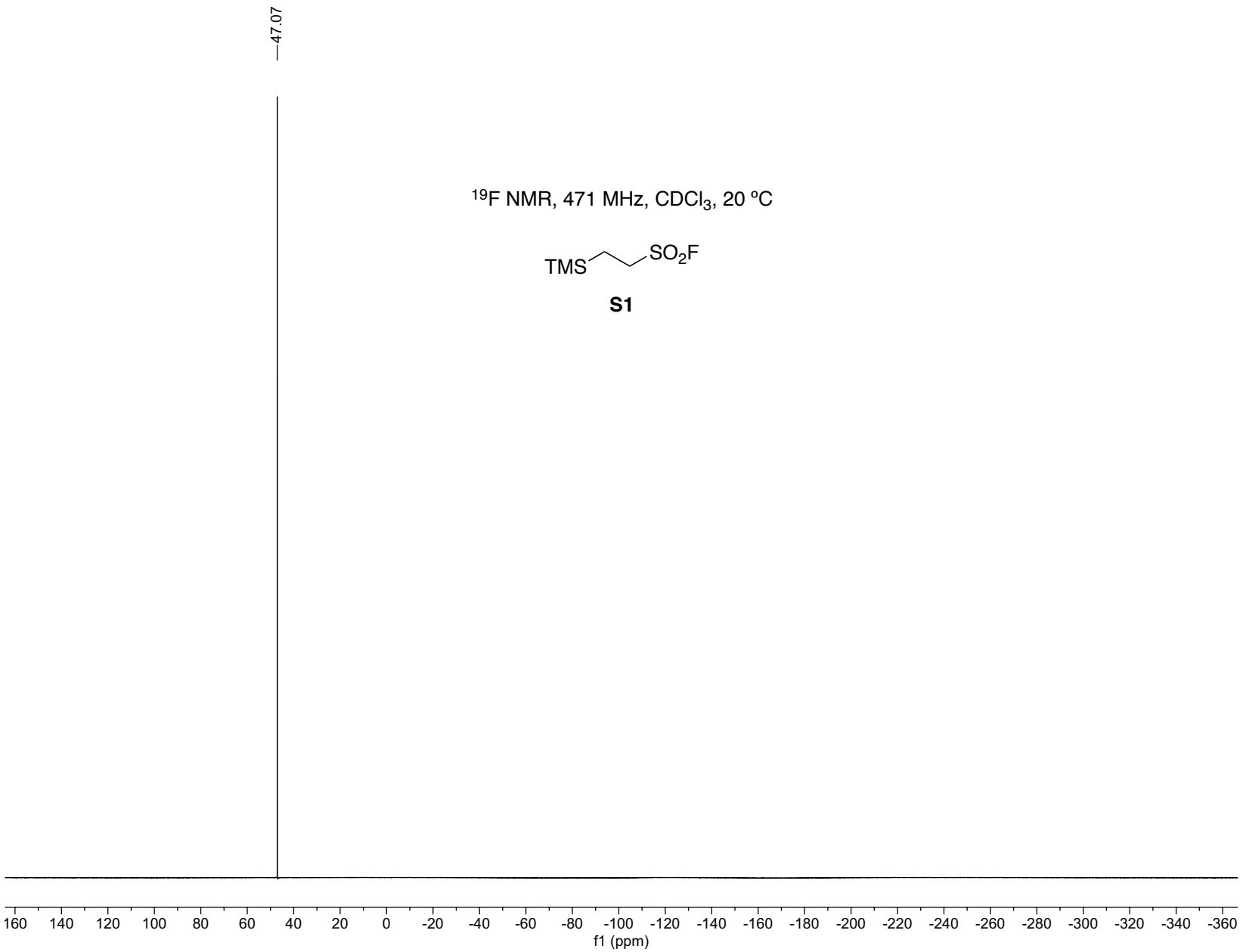
H(21B)	1814	5807	4964	46
H(22A)	1097	4108	5296	79
H(22B)	-375	4139	4897	79
H(22C)	-818	3903	5441	79
H(23A)	-3331	5108	5631	87
H(23B)	-3201	5176	5055	87
H(23C)	-3116	5918	5384	87
H(24A)	489	6036	6019	93
H(24B)	1547	5266	5988	93
H(24C)	-300	5272	6231	93
H(22D)	-184	4169	5075	154
H(22E)	-334	4117	5651	154
H(22F)	1403	4394	5407	154
H(23D)	-3403	5413	5079	93
H(23E)	-3166	5992	5518	93
H(23F)	-3499	5117	5625	93
H(24D)	-417	5635	6294	101
H(24E)	-273	6397	5986	101
H(24F)	1358	5866	6052	101


7.26 CDCl3
3.32
3.31
3.30
3.30
3.29
3.29
3.28
3.27
1.55
1.20
1.19
1.18
1.18
1.17
1.16
0.10
^{1}H NMR, 500 MHz, $CDCl_3$, 20 °C
TMS
SO_2F
S1
f1 (ppm)

^{13}C NMR, 126 MHz, $CDCl_3$, 20 ºC

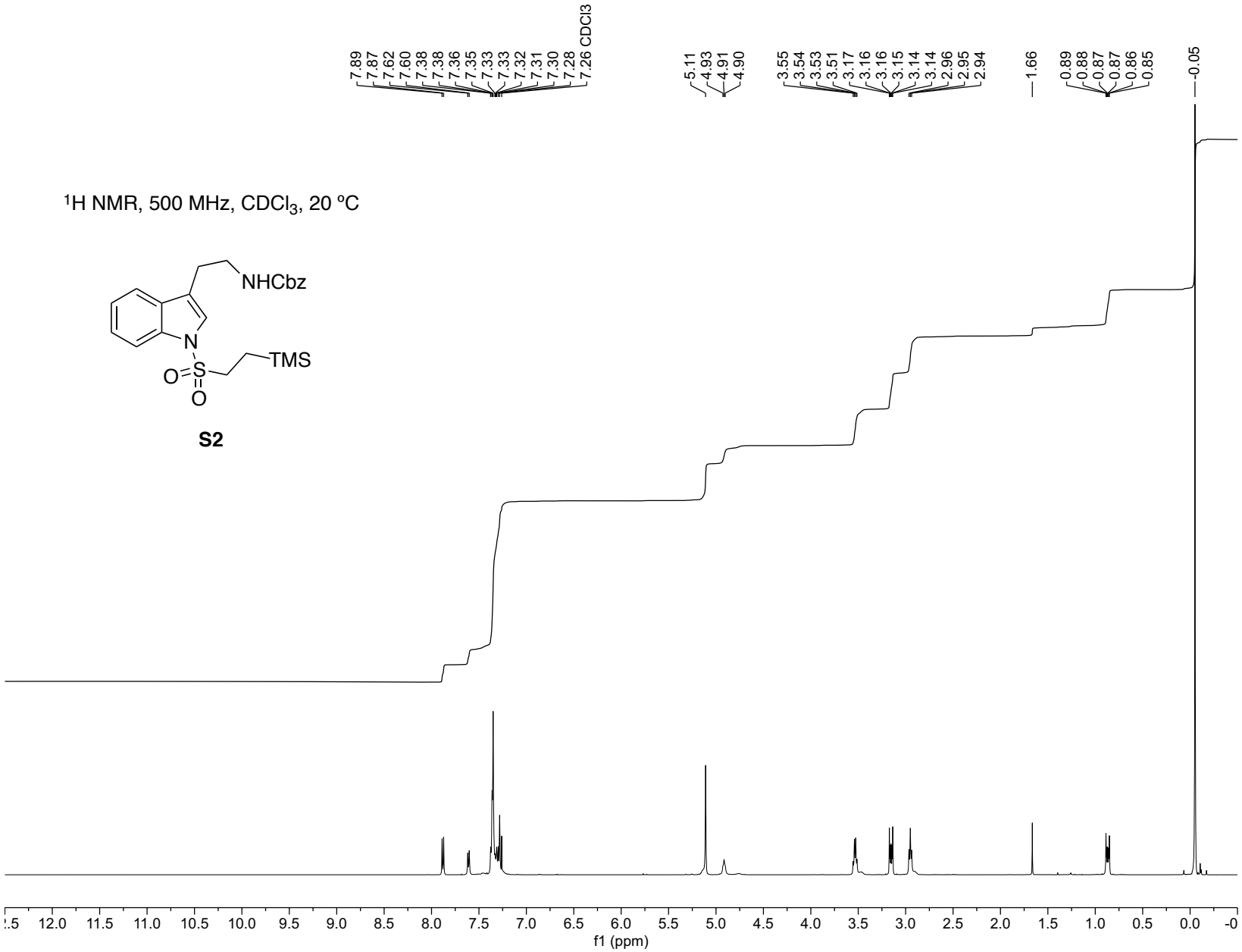


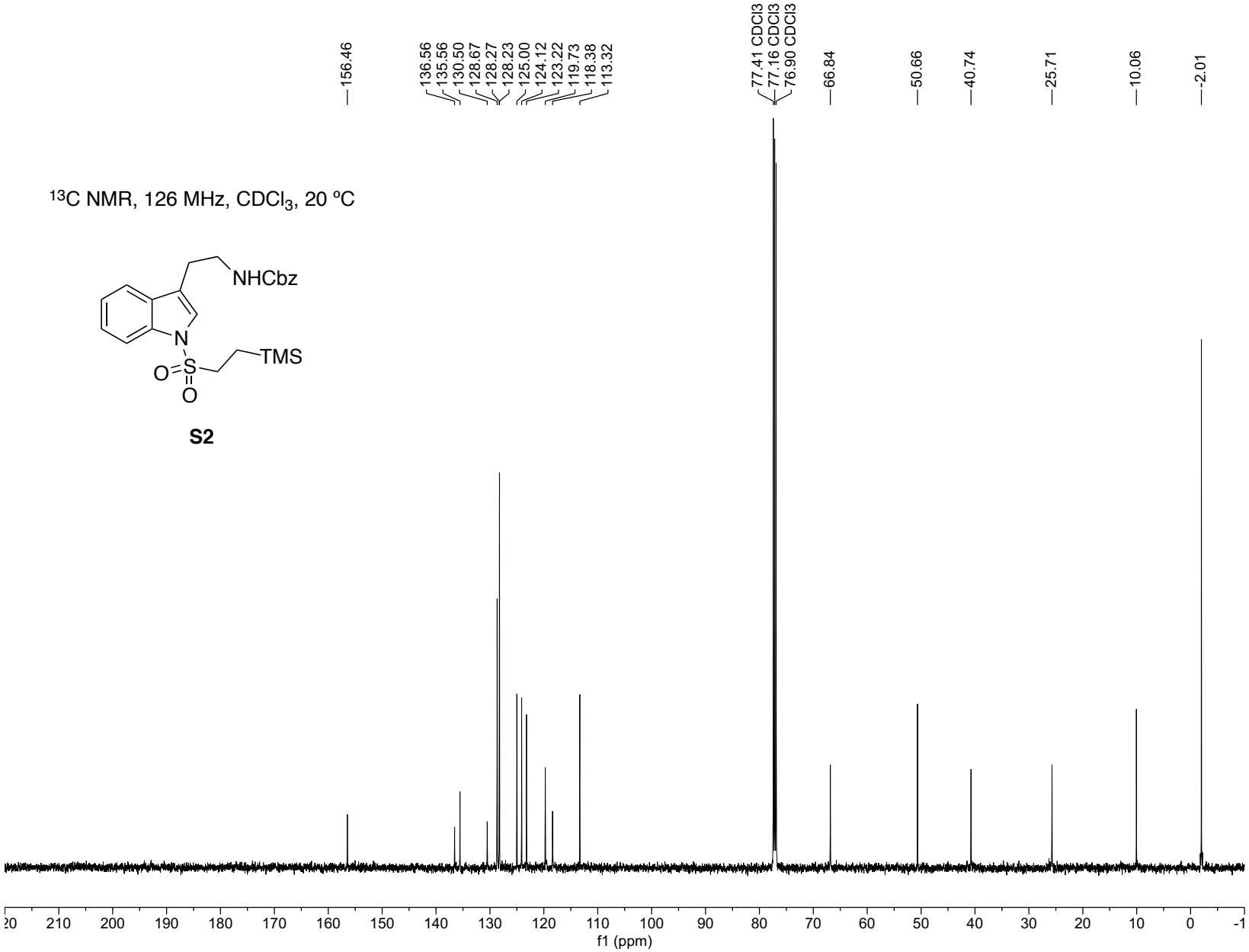
S1

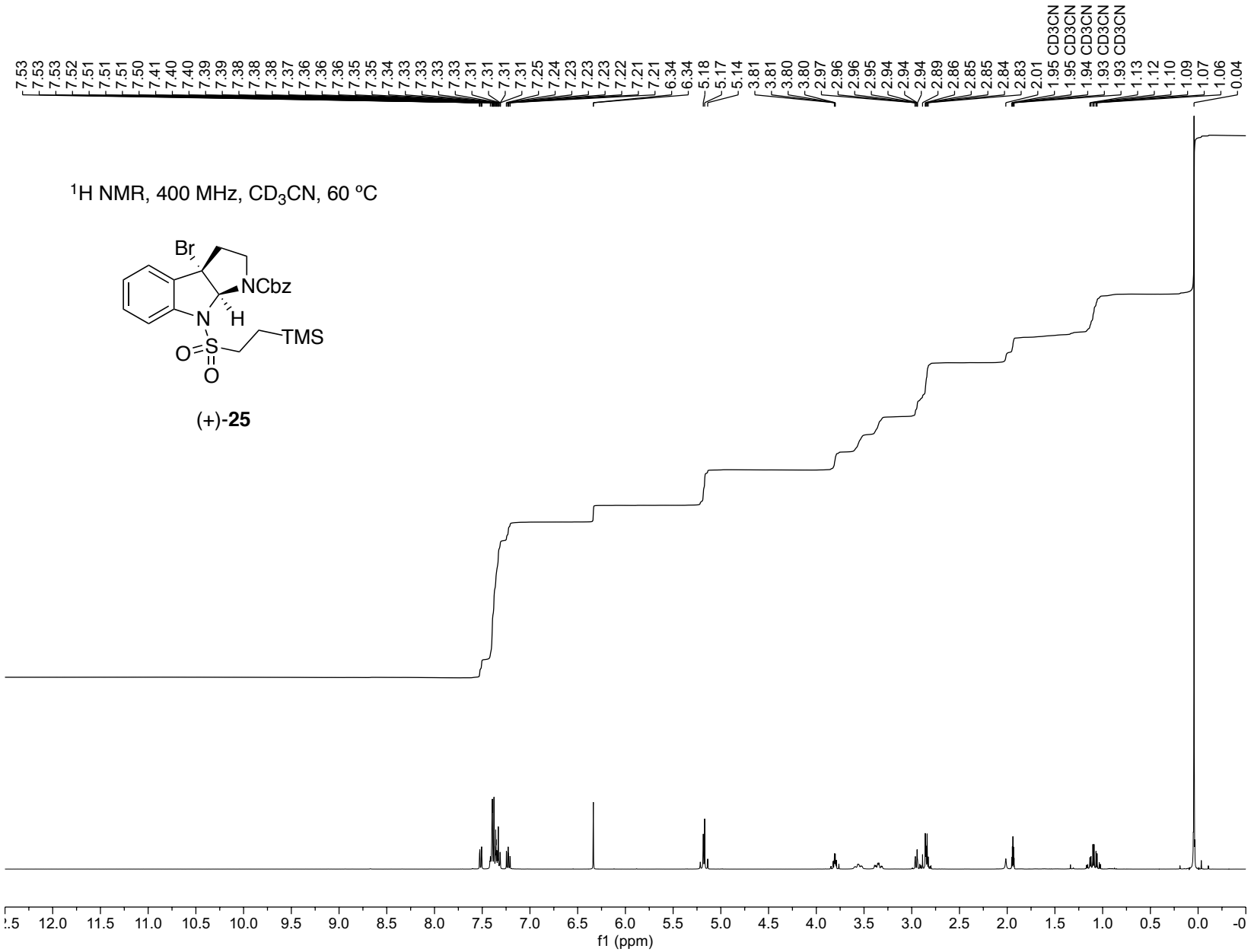


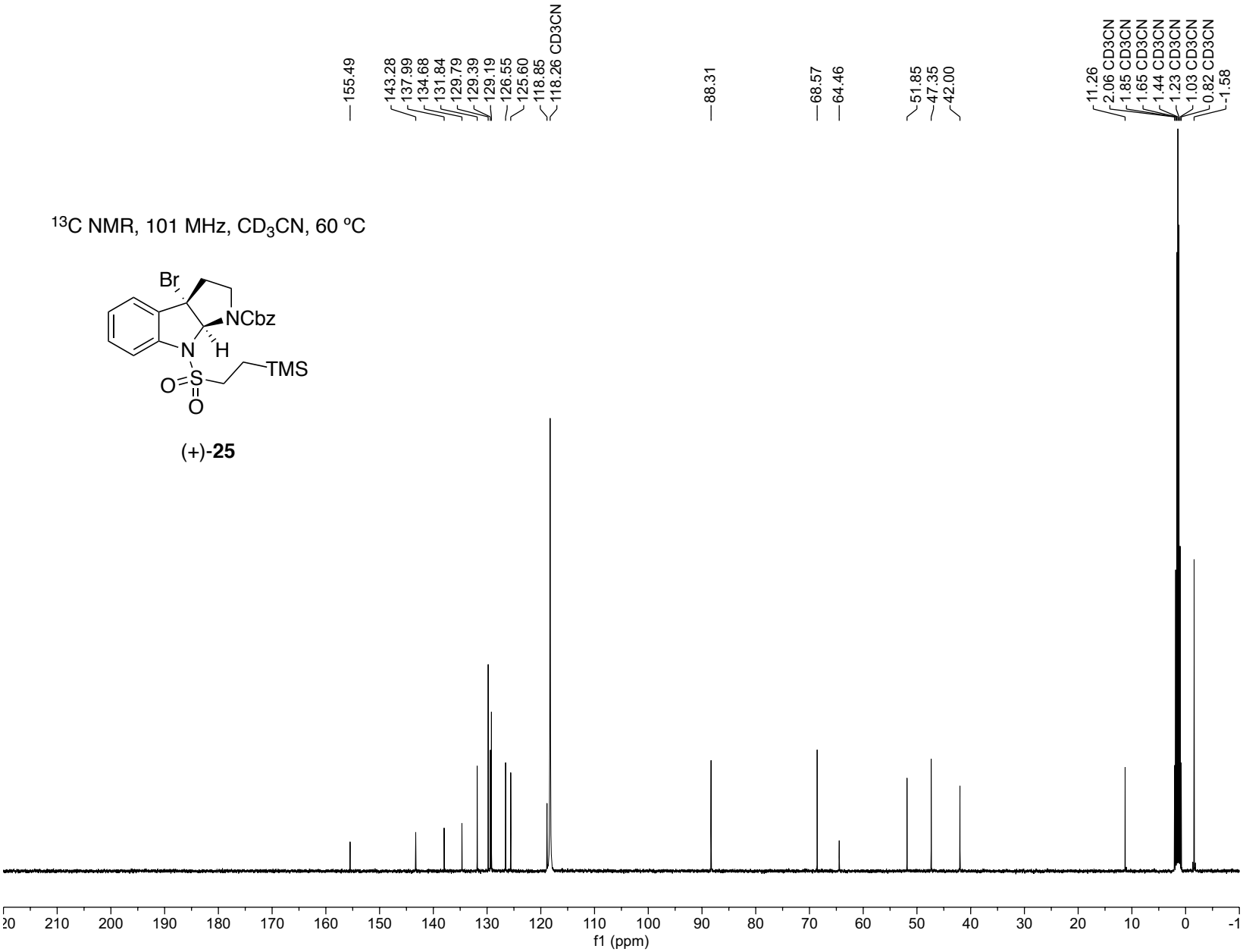
^{19}F NMR, 471 MHz, $CDCl_3$, 20 ºC

S1

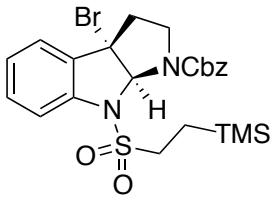

7.89
7.87
7.62
7.60
7.38
7.38
7.36
7.35
7.33
7.33
7.32
7.31
7.30
7.28
7.26 CDCl3
5.11
4.93
4.91
4.90
3.55
3.54
3.53
3.51
3.17
3.16
3.16
3.15
3.14
3.14
2.96
2.95
2.94
1.66
0.89
0.88
0.87
0.87
0.86
0.85
-0.05
1H NMR, 500 MHz, CDCl3, 20 ºC
NHCbz
N
O
S
O
TMS
S2
f1 (ppm)


156.46
136.56
135.56
130.50
128.67
128.27
128.23
125.00
124.12
123.22
119.73
118.38
113.32
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
66.84
50.66
40.74
25.71
10.06
-2.01
13C NMR, 126 MHz, CDCl3, 20 ºC
NHCbz
N
TMS
O
S
O
S2
f1 (ppm)


7.53 7.53 7.53 7.52 7.51 7.51 7.51 7.50 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.33 7.31 7.31 7.31 7.31 7.25 7.24 7.23 7.23 7.23 7.22 7.21 6.34 6.34 5.18 5.17 5.14 3.81 3.81 3.80 3.80 2.97 2.96 2.96 2.95 2.94 2.94 2.94 2.89 2.86 2.85 2.85 2.84 2.83 2.01 1.95 CD3CN 1.95 CD3CN 1.94 CD3CN 1.93 CD3CN 1.93 CD3CN 1.13 1.12 1.10 1.09 1.07 1.06 0.04
1H NMR, 400 MHz, CD3CN, 60 ºC
Br
NCbz
N
H
TMS
O
S
O
(+)-25
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
f1 (ppm)

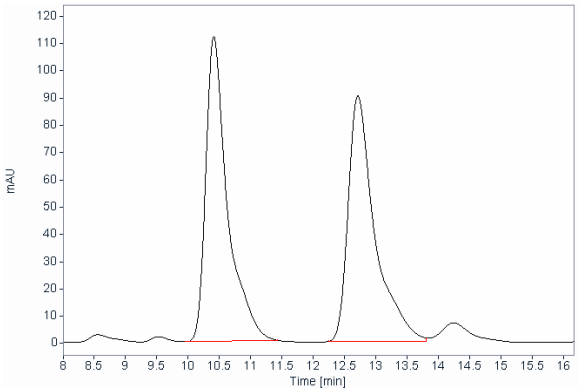

155.49
143.28
137.99
134.68
131.84
129.79
129.39
129.19
126.55
125.60
118.85
118.26 CD3CN
88.31
68.57
64.46
51.85
47.35
42.00
11.26
2.06 CD3CN
1.85 CD3CN
1.65 CD3CN
1.44 CD3CN
1.23 CD3CN
1.03 CD3CN
0.82 CD3CN
-1.58
13C NMR, 101 MHz, CD3CN, 60 ºC
Br
NCbz
N
H
TMS
O
S
O
(+)-25
f1 (ppm)

racemate



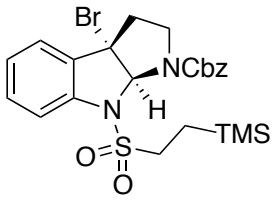
(±)-**25**

HPLC conditions:
CHIRALPAK® IA, Lot# IA00CE-PD046
10% *i*-PrOH in hexanes
1.0 mL/min
λ = 210 nm



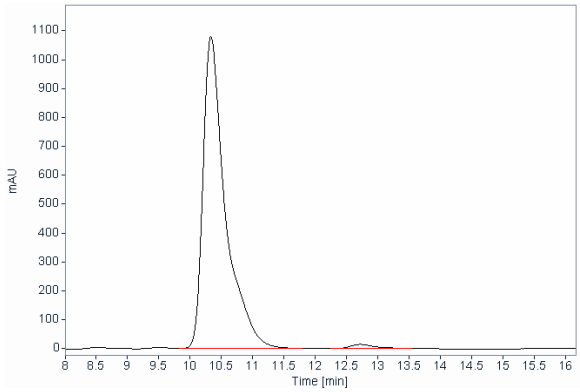
Signal: DAD1 C, Sig=210,8 Ref=360,100

Ret. Time (min)	Area%
10.403	50.3953
12.705	49.6047



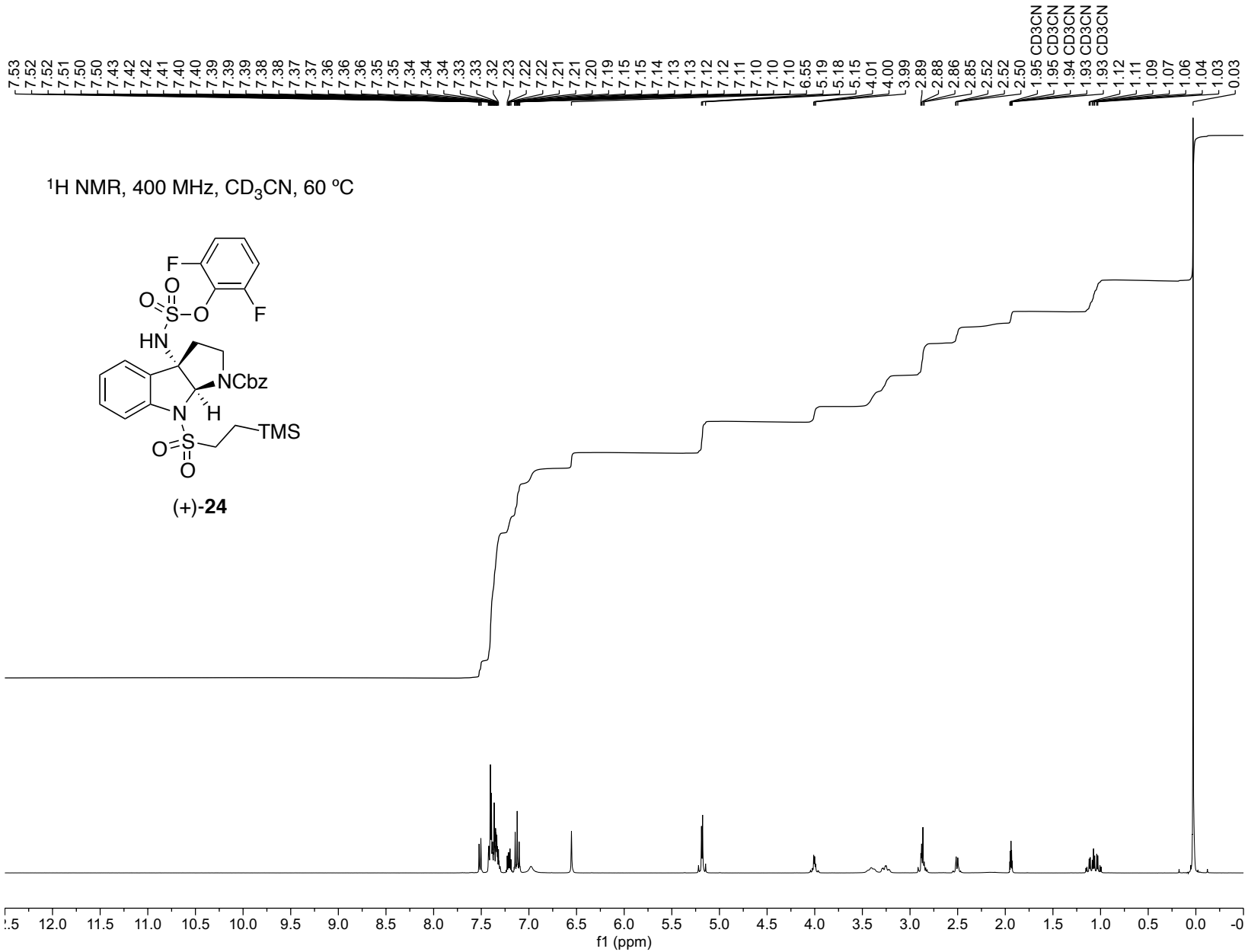
(+)-**25**

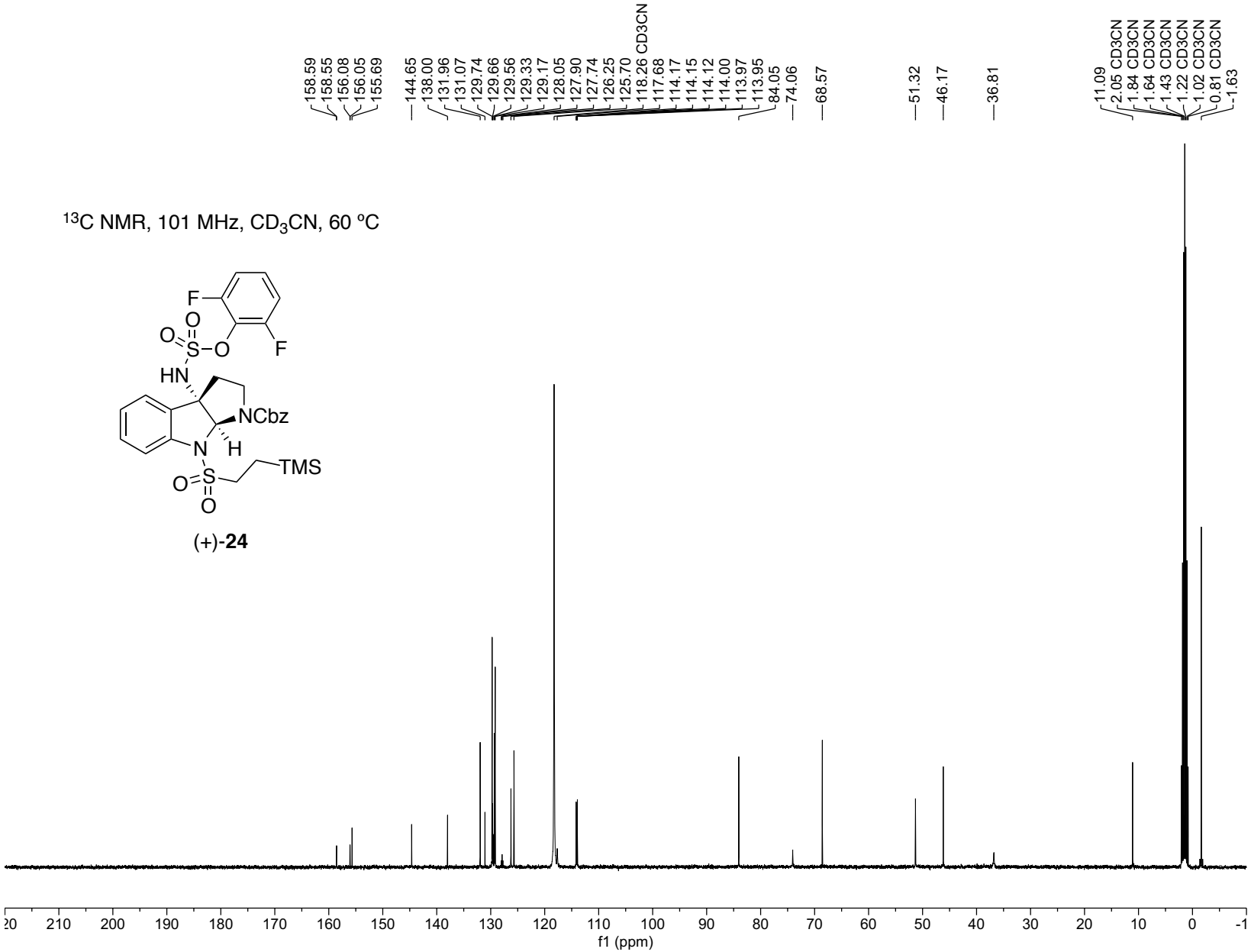
HPLC conditions:
CHIRALPAK® IA, Lot# IA00CE-PD046
10% *i*-PrOH in hexanes
1.0 mL/min
λ = 210 nm



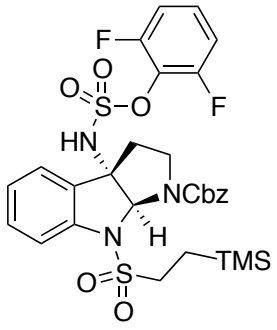
Signal: DAD1 C, Sig=210,8 Ref=360,100

Ret. Time (min)	Area%
10.324	98.4645
12.711	1.5355

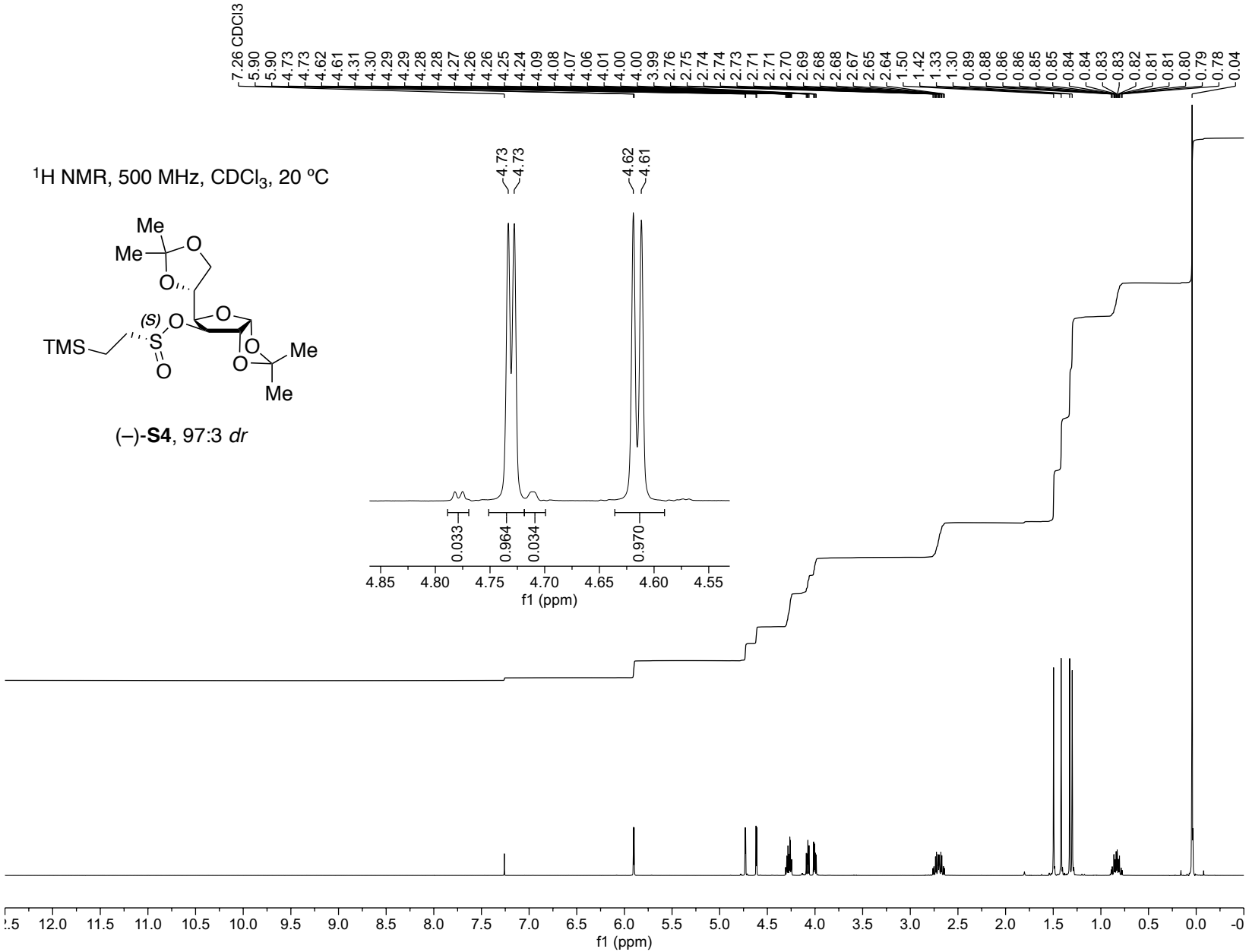

7.53 7.52 7.52 7.51 7.50 7.50 7.43 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.23 7.22 7.22 7.21 7.21 7.20 7.19 7.15 7.15 7.14 7.13 7.13 7.12 7.12 7.11 7.10 7.10 7.10 6.55 5.19 5.18 5.15 4.01 4.00 3.99 2.89 2.88 2.86 2.85 2.52 2.52 2.50 1.95 CD3CN 1.95 CD3CN 1.94 CD3CN 1.93 CD3CN 1.93 CD3CN 1.12 1.11 1.09 1.07 1.06 1.04 1.03 0.03
1H NMR, 400 MHz, CD3CN, 60 ºC
F
O
O
S
O
F
HN
NCbz
N
H
TMS
O
S
O
(+)-24
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
f1 (ppm)

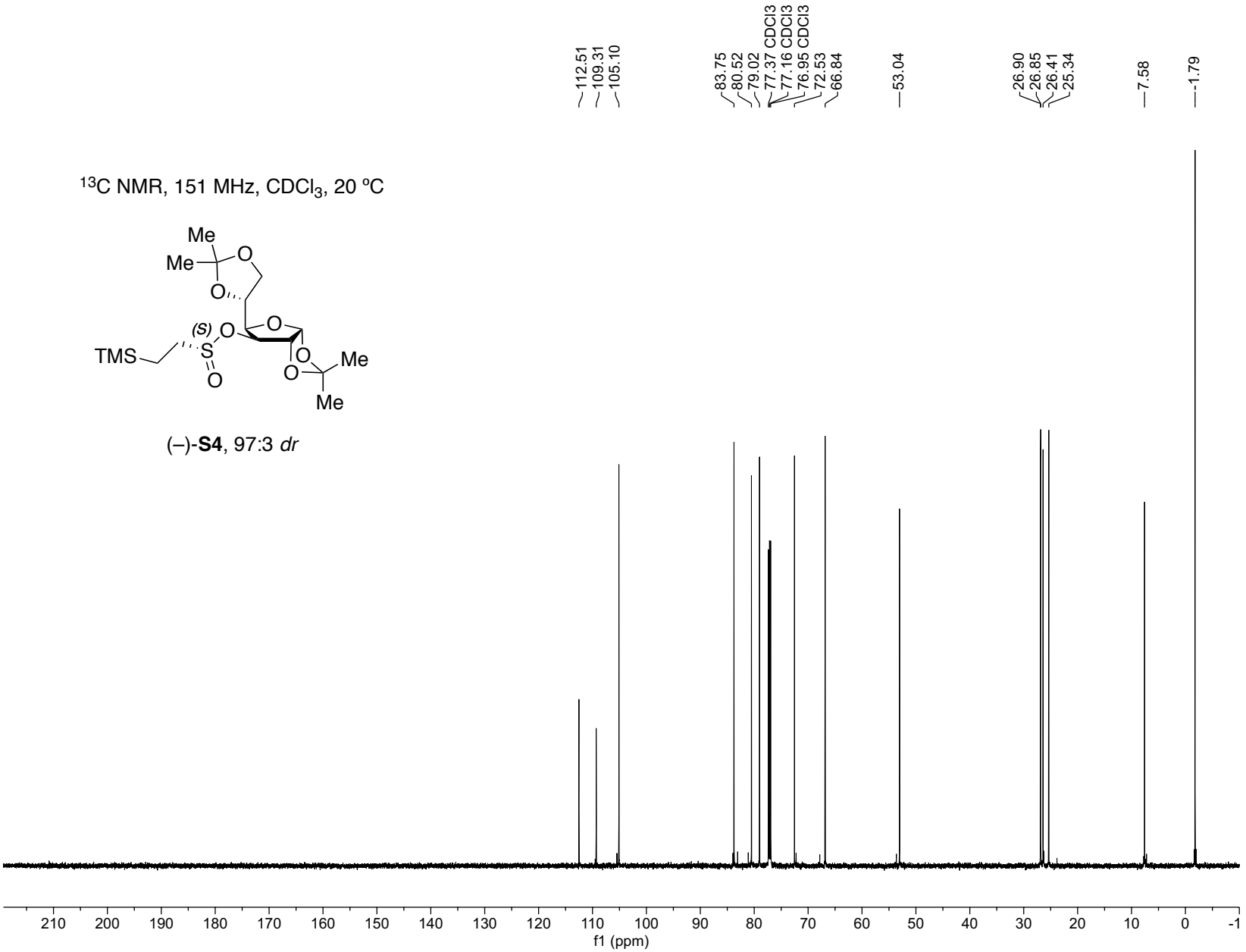

158.59
158.55
156.08
156.05
155.69
144.65
138.00
131.96
131.07
129.74
129.66
129.56
129.33
129.17
128.05
127.90
127.74
126.25
125.70
118.26 CD3CN
117.68
114.17
114.15
114.12
114.00
113.97
113.95
84.05
74.06
68.57
51.32
46.17
36.81
11.09
2.05 CD3CN
1.84 CD3CN
1.64 CD3CN
1.43 CD3CN
1.22 CD3CN
1.02 CD3CN
0.81 CD3CN
-1.63
13C NMR, 101 MHz, CD3CN, 60 ºC
F
O
O
S
O
F
HN
NCbz
N
H
TMS
O
S
O
(+)-24
f1 (ppm)

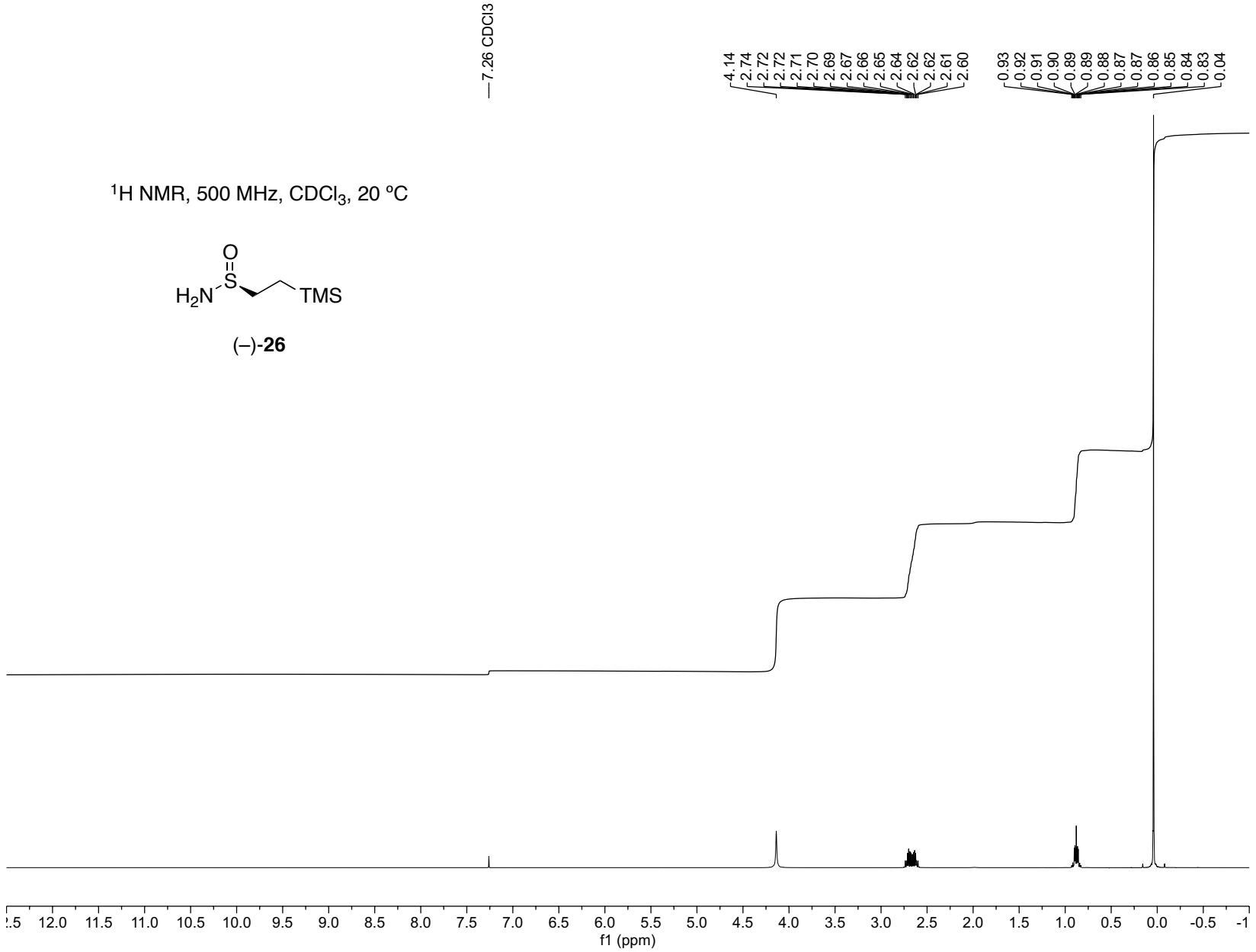
^{19}F NMR, 376 MHz, CD_3CN, 25ºC



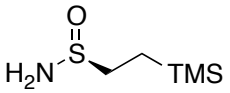
(+)-**24**


7.26 CDCl3
5.90 5.90 4.73 4.73 4.62 4.61 4.31 4.30 4.29 4.29 4.28 4.28 4.27 4.26 4.26 4.25 4.24 4.09 4.08 4.07 4.06 4.01 4.00 4.00 3.99 2.76 2.75 2.74 2.74 2.73 2.71 2.71 2.70 2.69 2.68 2.68 2.67 2.65 2.64 1.50 1.42 1.33 1.30 0.89 0.88 0.86 0.86 0.85 0.85 0.84 0.84 0.83 0.83 0.82 0.81 0.81 0.80 0.79 0.78 0.04
1H NMR, 500 MHz, CDCl3, 20 ºC
Me
Me
O
O
(S)
O
O
TMS
S
O
O
O
Me
Me
(–)-S4, 97:3 dr
4.73
4.73
4.62
4.61
0.033
0.964
0.034
0.970
4.85 4.80 4.75 4.70 4.65 4.60 4.55
f1 (ppm)
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
f1 (ppm)


112.51
109.31
105.10
83.75
80.52
79.02
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
72.53
66.84
53.04
26.90
26.85
26.41
25.34
7.58
-1.79
13C NMR, 151 MHz, CDCl3, 20 ºC
Me
Me
O
O
(S)
O
O
TMS
S
O
O
O
Me
Me
(–)-S4, 97:3 dr
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

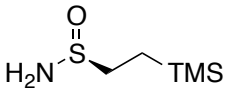

7.26 CDCl3
4.14
2.74
2.72
2.72
2.71
2.70
2.69
2.67
2.66
2.65
2.64
2.62
2.62
2.61
2.60
0.93
0.92
0.91
0.90
0.89
0.89
0.88
0.87
0.87
0.86
0.85
0.84
0.83
0.04
1H NMR, 500 MHz, CDCl3, 20 ºC
O
S
H2N
TMS
(–)-26
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

^{13}C NMR, 126 MHz, $CDCl_3$, 20 °C



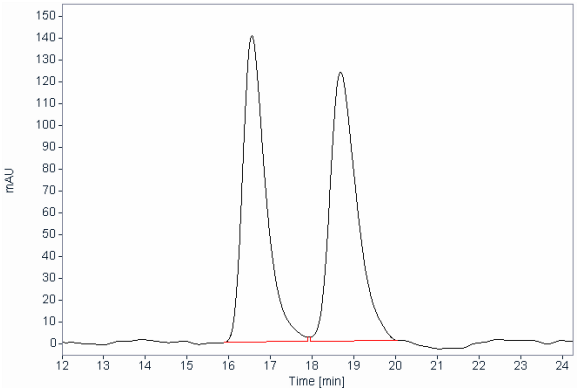
(–)-**26**

racemate



(±)-**26**

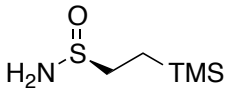
HPLC conditions:
CHIRALPAK® OD-H, Lot# ODH0CE-KF021
4% *i*-PrOH in hexanes
1.0 mL/min
λ = 210 nm



Signal: DAD1 C, Sig=210,8 Ref=360,100

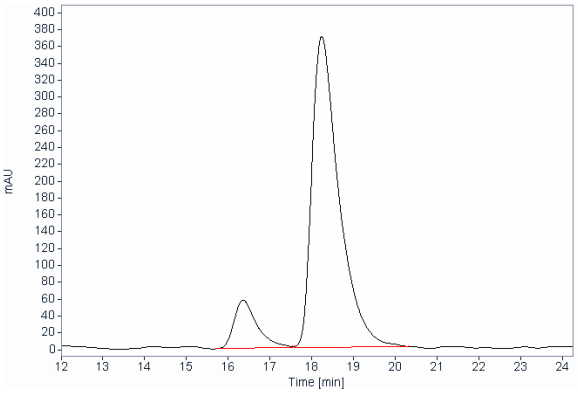
Ret. Time (min)	Area%
16.541	49.5636
18.669	50.4364

After flash chromatography:



(–)-**26**

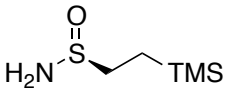
HPLC conditions:
CHIRALPAK® OD-H, Lot# ODH0CE-KF021
4% *i*-PrOH in hexanes
1.0 mL/min
λ = 210 nm



Signal: DAD1 C, Sig=210,8 Ref=360,100

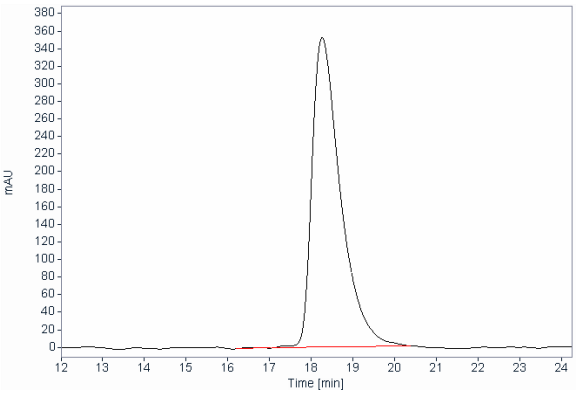
Ret. Time (min)	Area%
16.343	11.8066
18.226	88.1934

After heptane trituration:



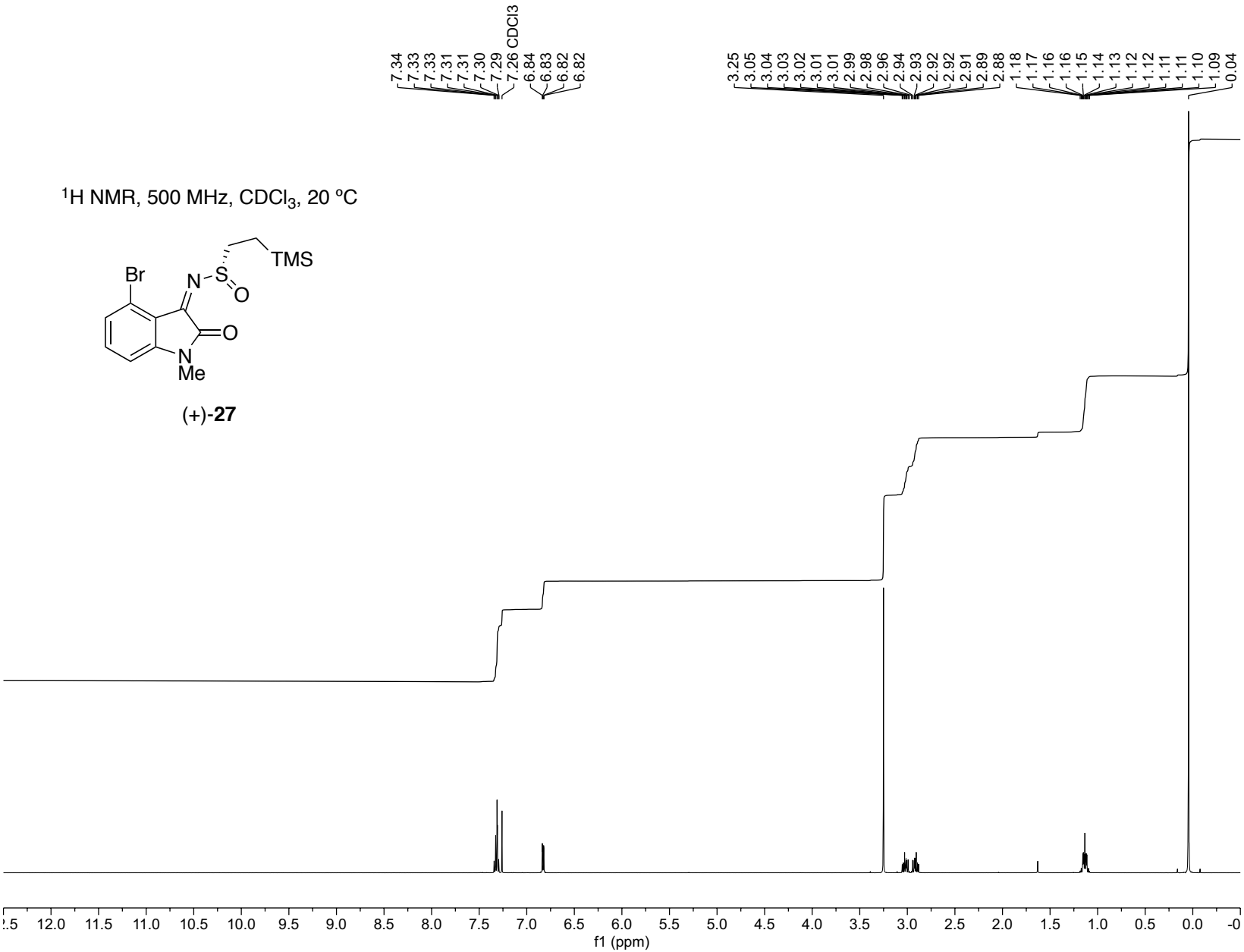
(–)-**26**

HPLC conditions:
CHIRALPAK® OD-H, Lot# ODH0CE-KF021
4% *i*-PrOH in hexanes
1.0 mL/min
λ = 210 nm

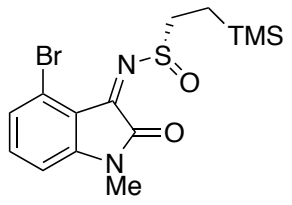


Signal: DAD1 C, Sig=210,8 Ref=360,100

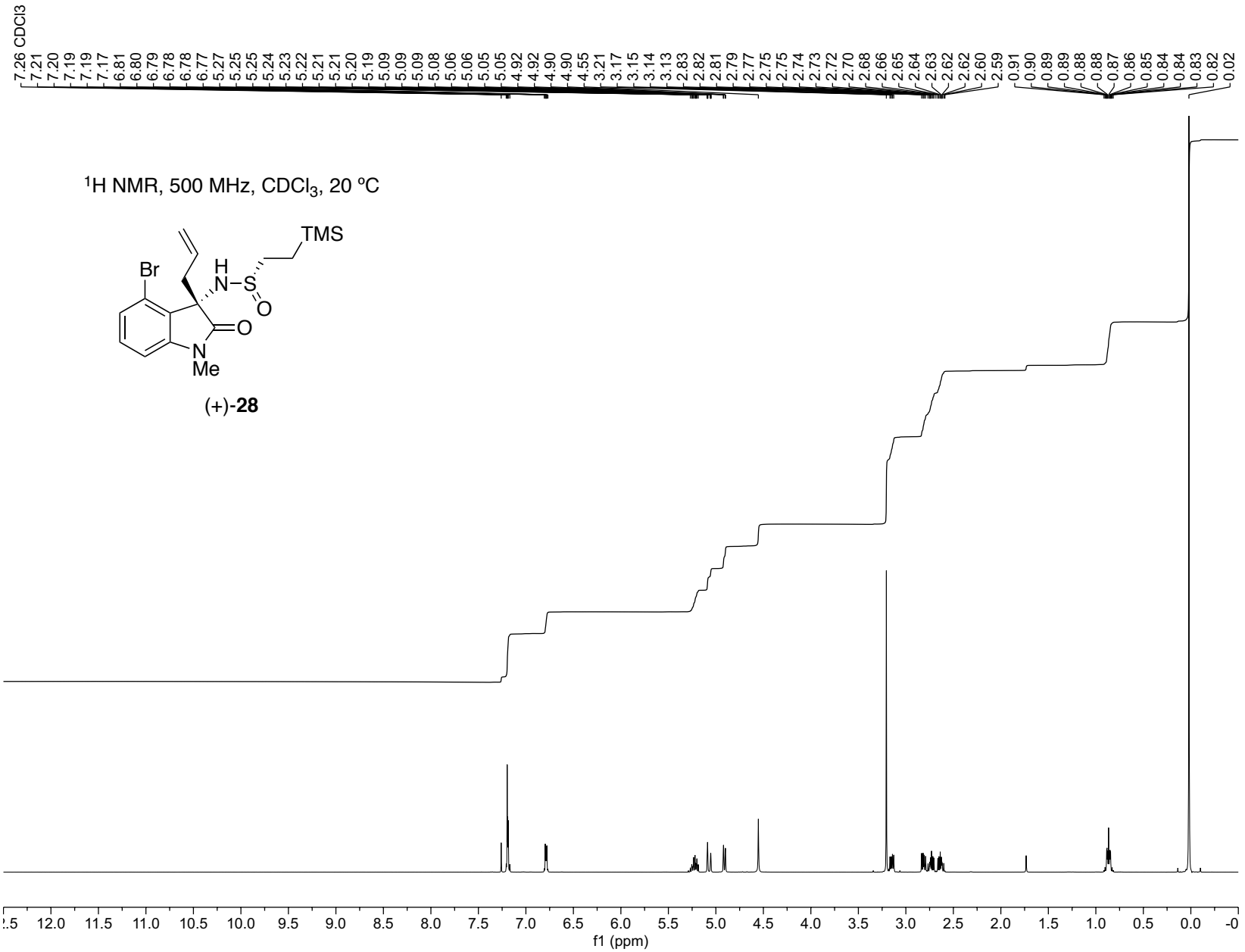
Ret. Time (min)	Area%
16.518	0.2878
18.248	99.7122

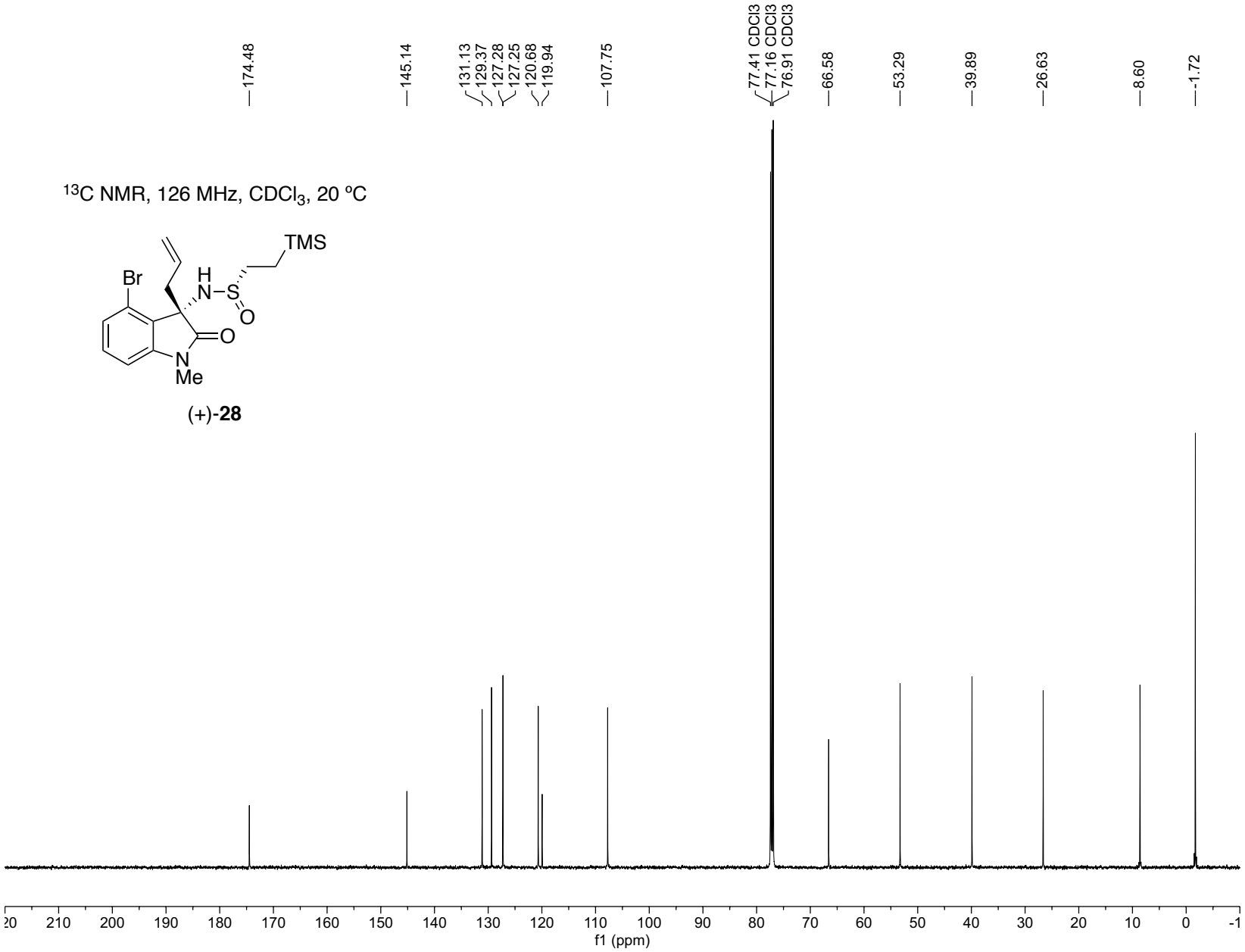

7.34
7.33
7.33
7.31
7.31
7.30
7.29
7.26 CDCl3
6.84
6.83
6.82
6.82
3.25
3.05
3.04
3.03
3.02
3.01
3.01
2.99
2.98
2.96
2.94
2.93
2.92
2.92
2.91
2.89
2.88
1.18
1.17
1.16
1.16
1.15
1.14
1.13
1.12
1.12
1.11
1.11
1.10
1.09
0.04
1H NMR, 500 MHz, CDCl3, 20 ºC
Br
N
S
O
TMS
O
N
Me
(+)-27
f1 (ppm)

^{13}C NMR, 126 MHz, $CDCl_3$, 20 ºC



(+)-**27**

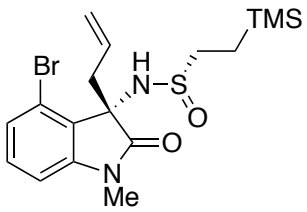

7.26 CDCl3
7.21 7.20 7.19 7.19 7.17 6.81 6.80 6.79 6.78 6.78 6.77 5.27 5.25 5.25 5.24 5.23 5.22 5.21 5.21 5.20 5.19 5.09 5.09 5.09 5.08 5.06 5.06 5.05 5.05 4.92 4.92 4.90 4.90 4.55 3.21 3.17 3.15 3.14 3.13 2.83 2.82 2.81 2.79 2.77 2.75 2.75 2.74 2.73 2.72 2.70 2.68 2.66 2.65 2.64 2.63 2.62 2.62 2.60 2.59 0.91 0.90 0.89 0.89 0.88 0.88 0.87 0.86 0.85 0.84 0.84 0.83 0.82 0.02
1H NMR, 500 MHz, CDCl3, 20 ºC
TMS
Br
H
N
S
O
O
N
Me
(+)-28
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
f1 (ppm)



^{13}C NMR, 126 MHz, $CDCl_3$, 20 ºC

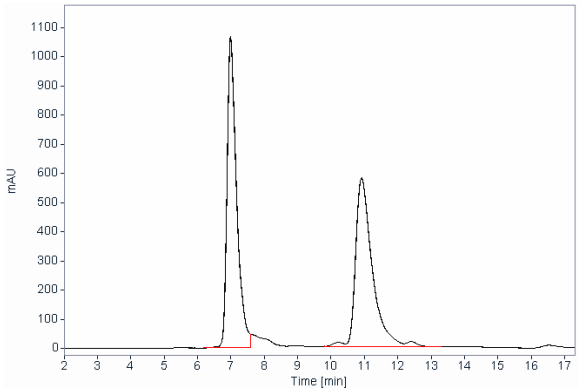
(+)-**28**

racemate



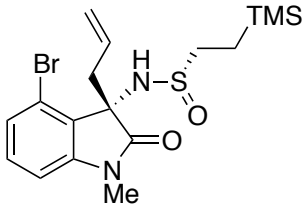
(±)-**28**

HPLC conditions:
CHIRALPAK® OD-H, Lot# ODH0CE-KF021
30% *i*-PrOH in hexanes
0.7 mL/min
λ = 220 nm



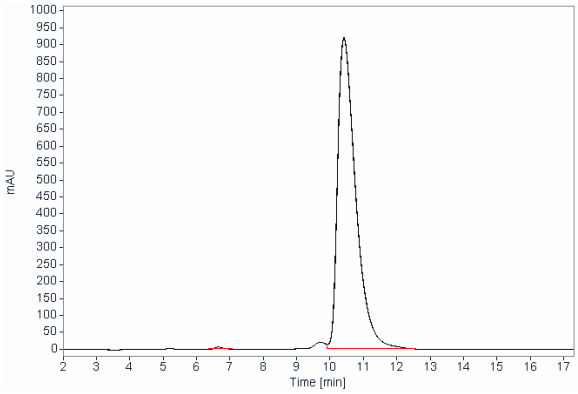
Signal: DAD1 B, Sig=220,16 Ref=360,100

Ret. Time (min)	Area%
6.976	50.6693
10.909	49.3307



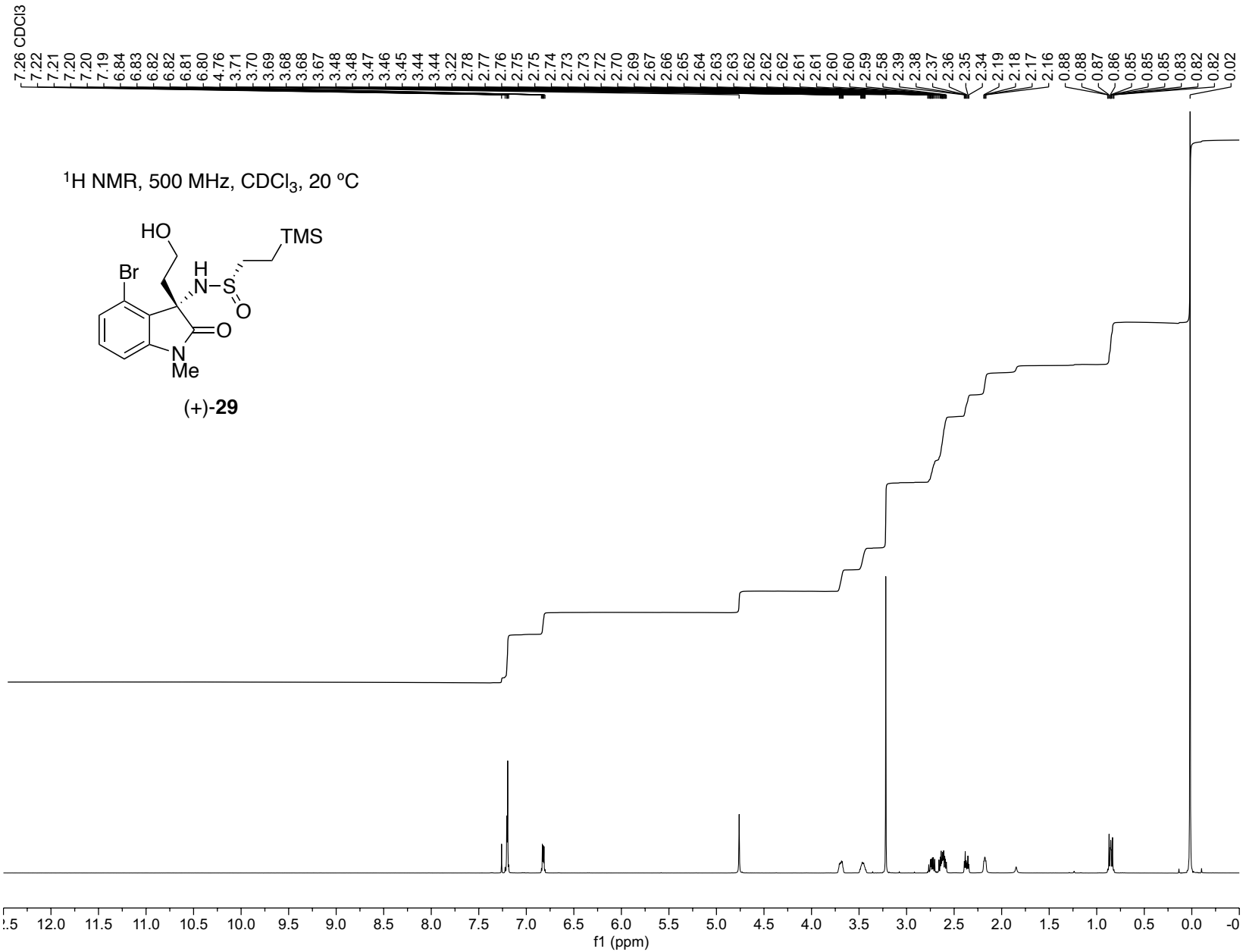
(+)-**28**

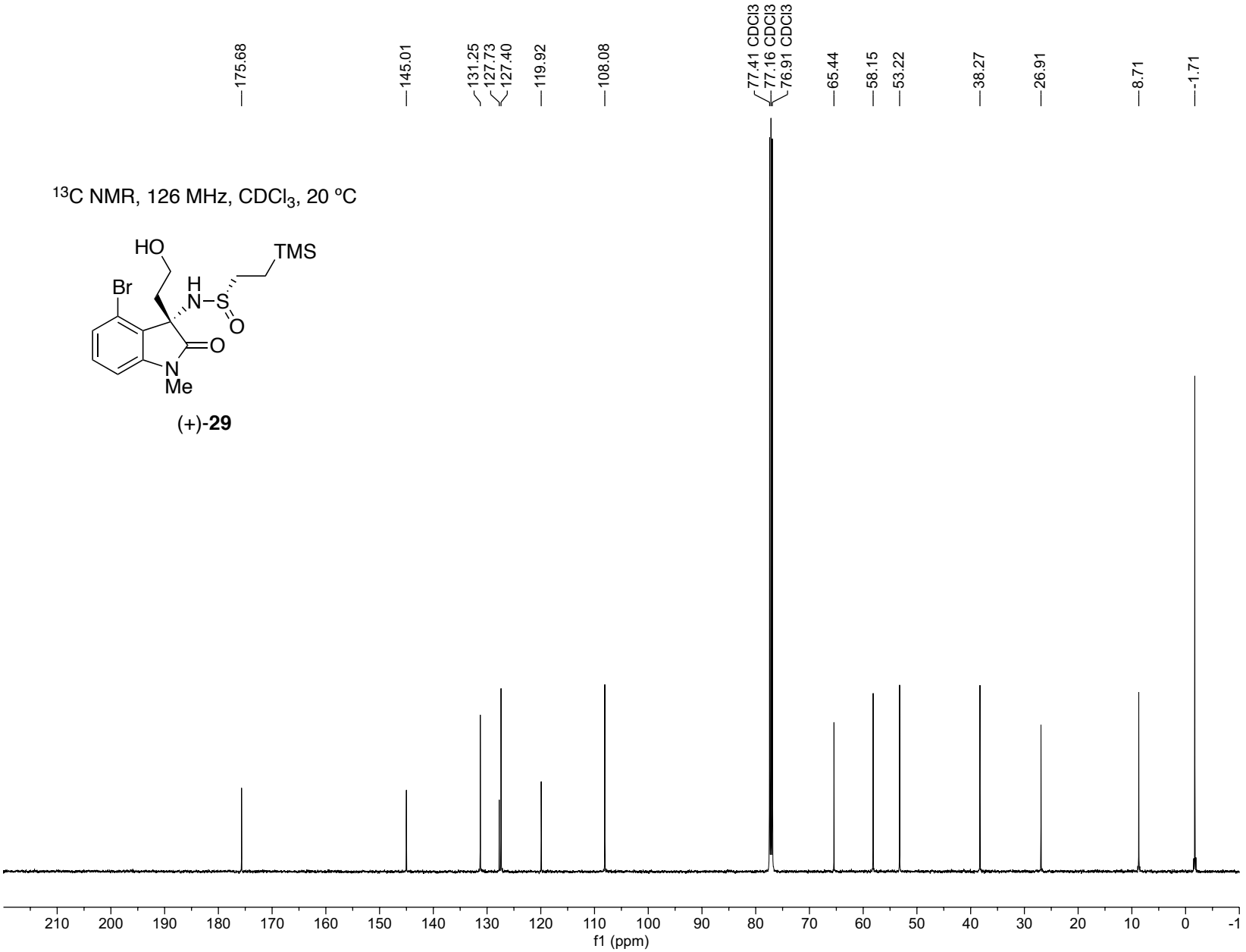
HPLC conditions:
CHIRALPAK® OD-H, Lot# ODH0CE-KF021
30% *i*-PrOH in hexanes
0.7 mL/min
λ = 220 nm



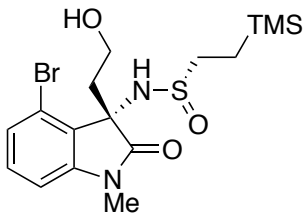
Signal: DAD1 B, Sig=220,16 Ref=360,100

Ret. Time (min)	Area%
6.638	0.2943
10.406	99.7057


7.26 CDCl3
7.22 7.21 7.20 7.20 7.19 6.84 6.83 6.82 6.82 6.81 6.80 4.76 3.71 3.70 3.69 3.68 3.68 3.67 3.48 3.48 3.47 3.46 3.45 3.44 3.44 3.22 2.78 2.77 2.76 2.75 2.75 2.74 2.73 2.73 2.72 2.70 2.69 2.67 2.66 2.65 2.64 2.63 2.63 2.62 2.62 2.62 2.61 2.61 2.60 2.60 2.59 2.58 2.39 2.38 2.37 2.36 2.35 2.34 2.19 2.18 2.17 2.16 0.88 0.88 0.87 0.86 0.85 0.85 0.85 0.83 0.82 0.82 0.02
1H NMR, 500 MHz, CDCl3, 20 °C
HO
TMS
Br
H
N–S
O
O
N
Me
(+)-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
f1 (ppm)

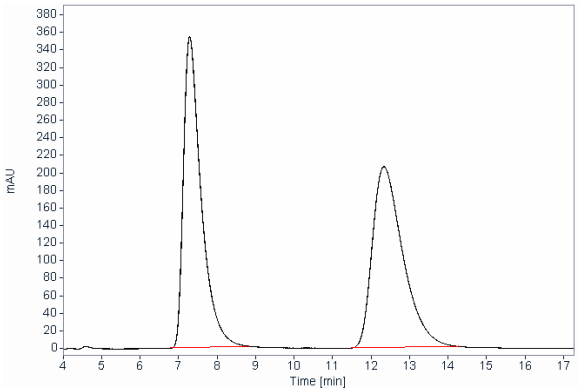

175.68
145.01
131.25
127.73
127.40
119.92
108.08
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
65.44
58.15
53.22
38.27
26.91
8.71
-1.71
^{13}C NMR, 126 MHz, $CDCl_3$, 20 ºC
HO
TMS
Br
H
N
S
O
O
N
Me
(+)-29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

racemate



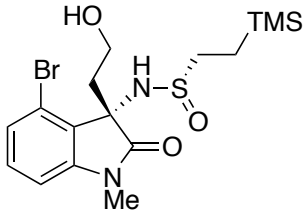
(±)-**29**

HPLC conditions:
CHIRALPAK® OD-H, Lot# ODH0CE-KF021
30% *i*-PrOH in hexanes
0.7 mL/min
λ = 220 nm



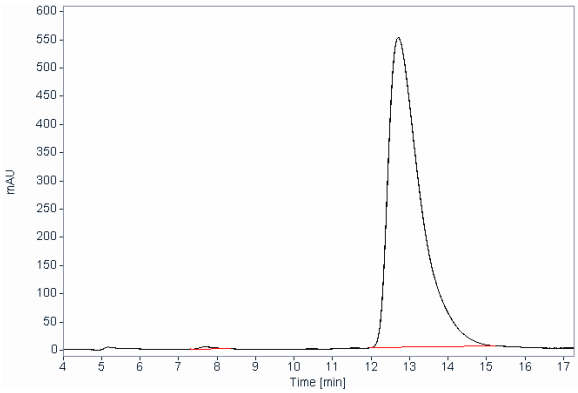
Signal: DAD1 B, Sig=220,16 Ref=360,100

Ret. Time (min)	Area%
7.278	49.9198
12.323	50.0802



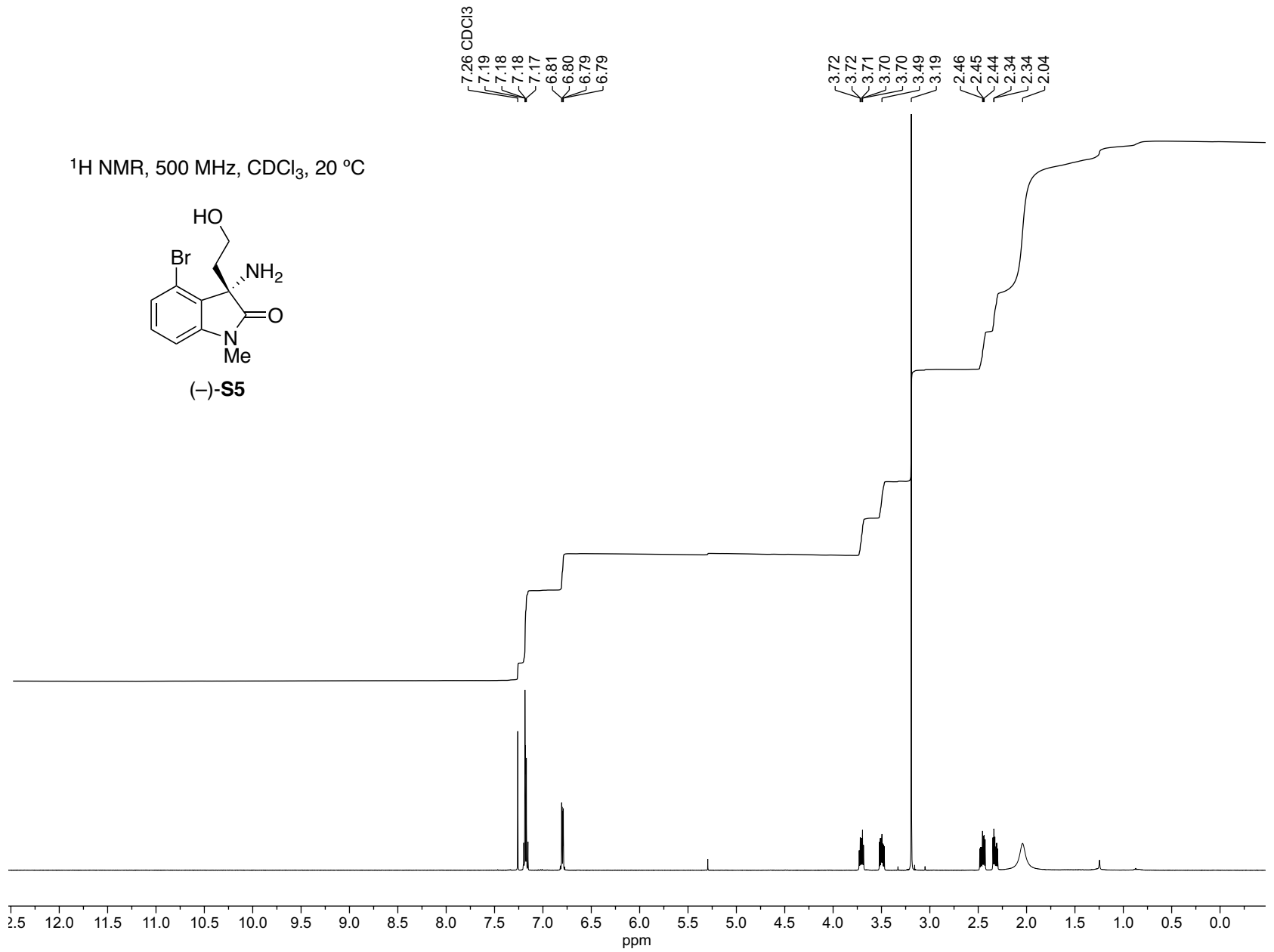
(+)-**29**

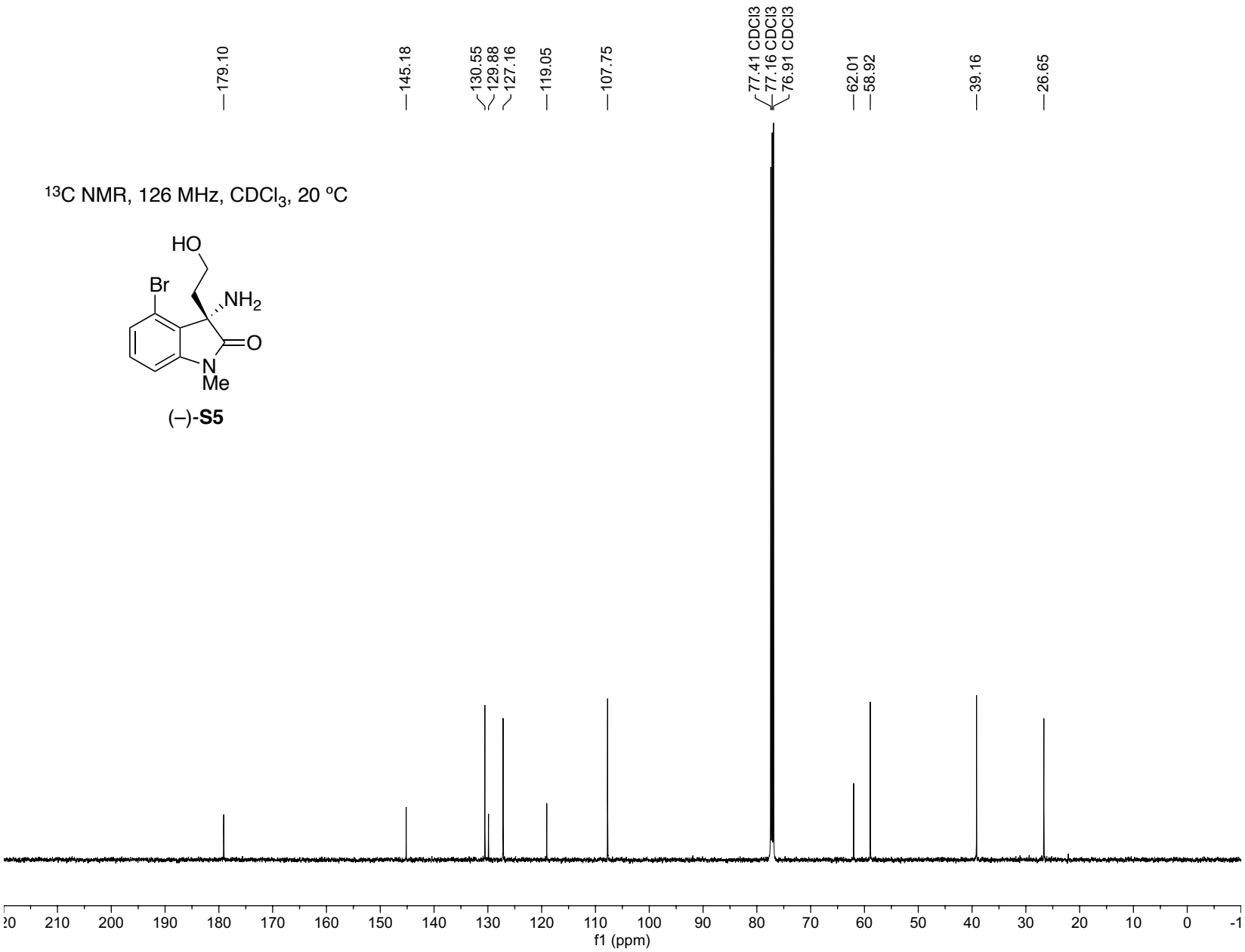
HPLC conditions:
CHIRALPAK® OD-H, Lot# ODH0CE-KF021
30% *i*-PrOH in hexanes
0.7 mL/min
λ = 220 nm

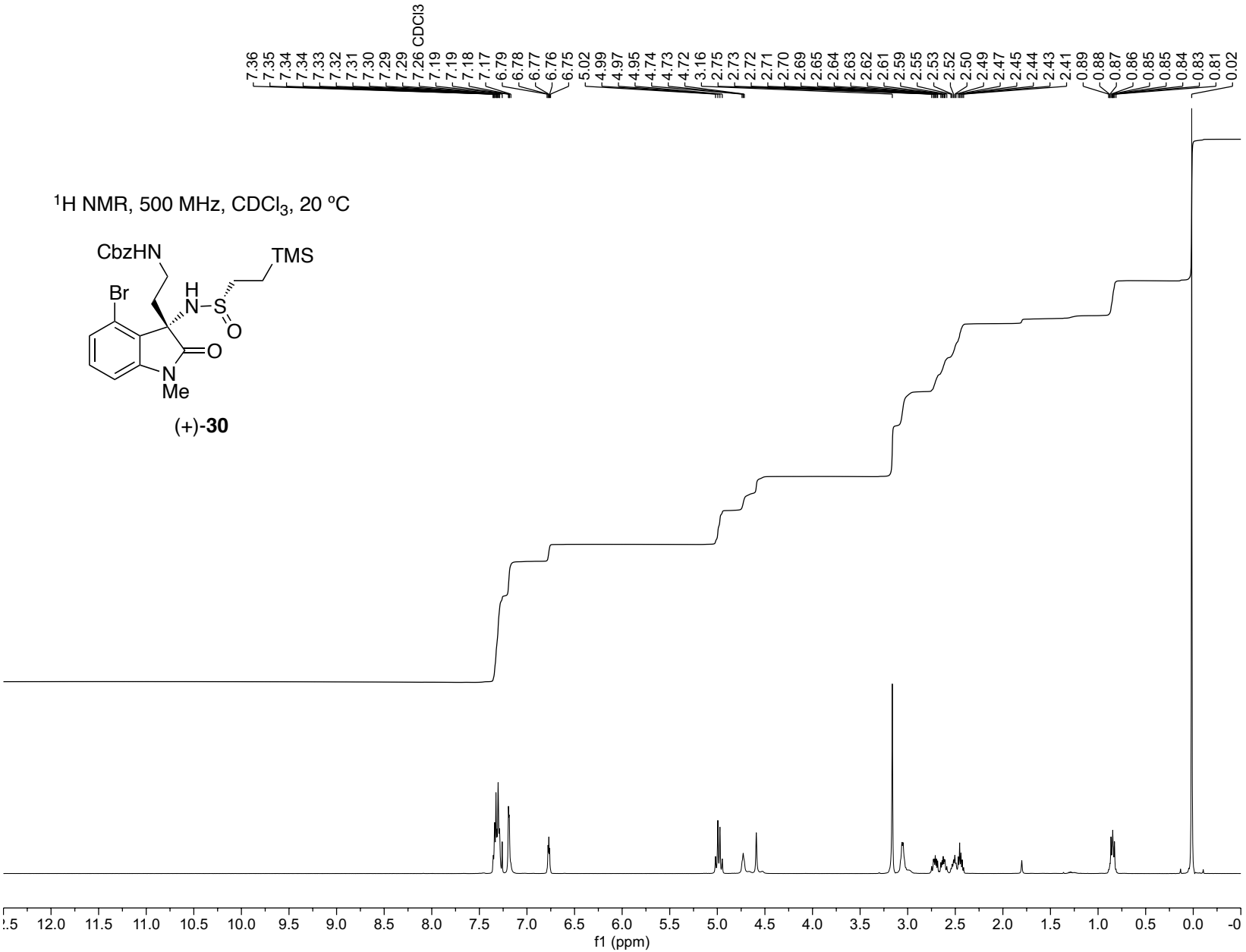


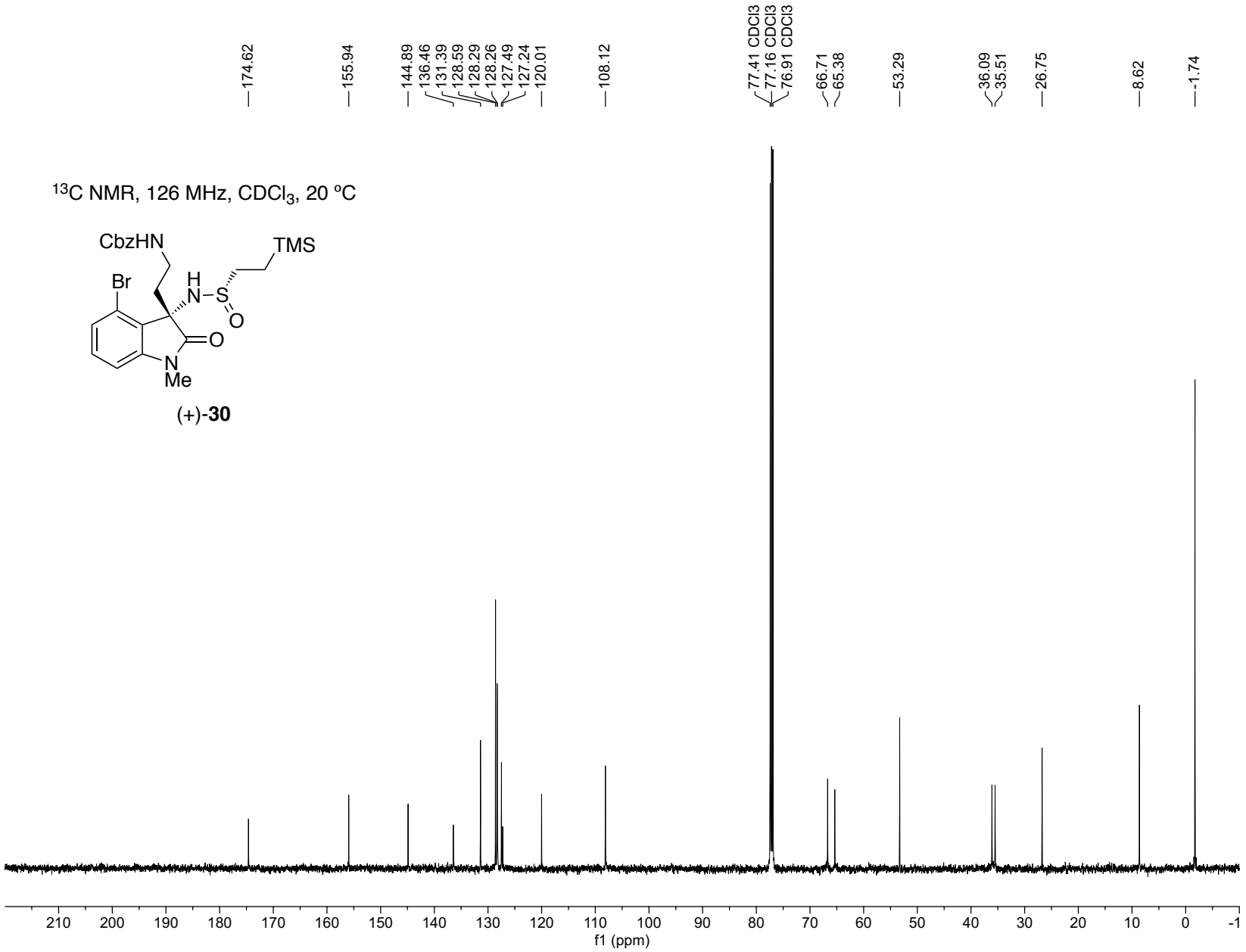
Signal: DAD1 B, Sig=220,16 Ref=360,100

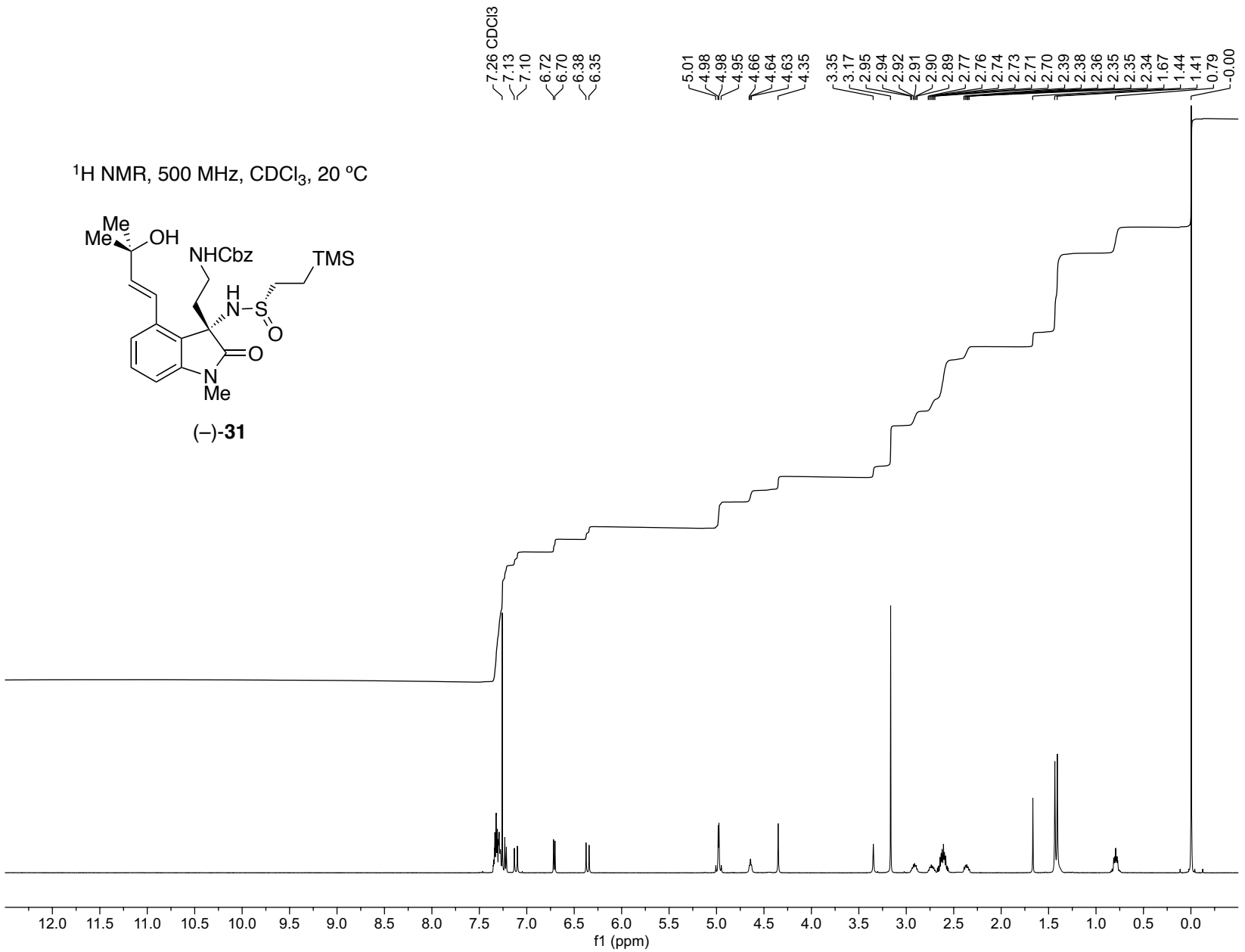
Ret. Time (min)	Area%
7.687	0.4002
12.697	99.5998

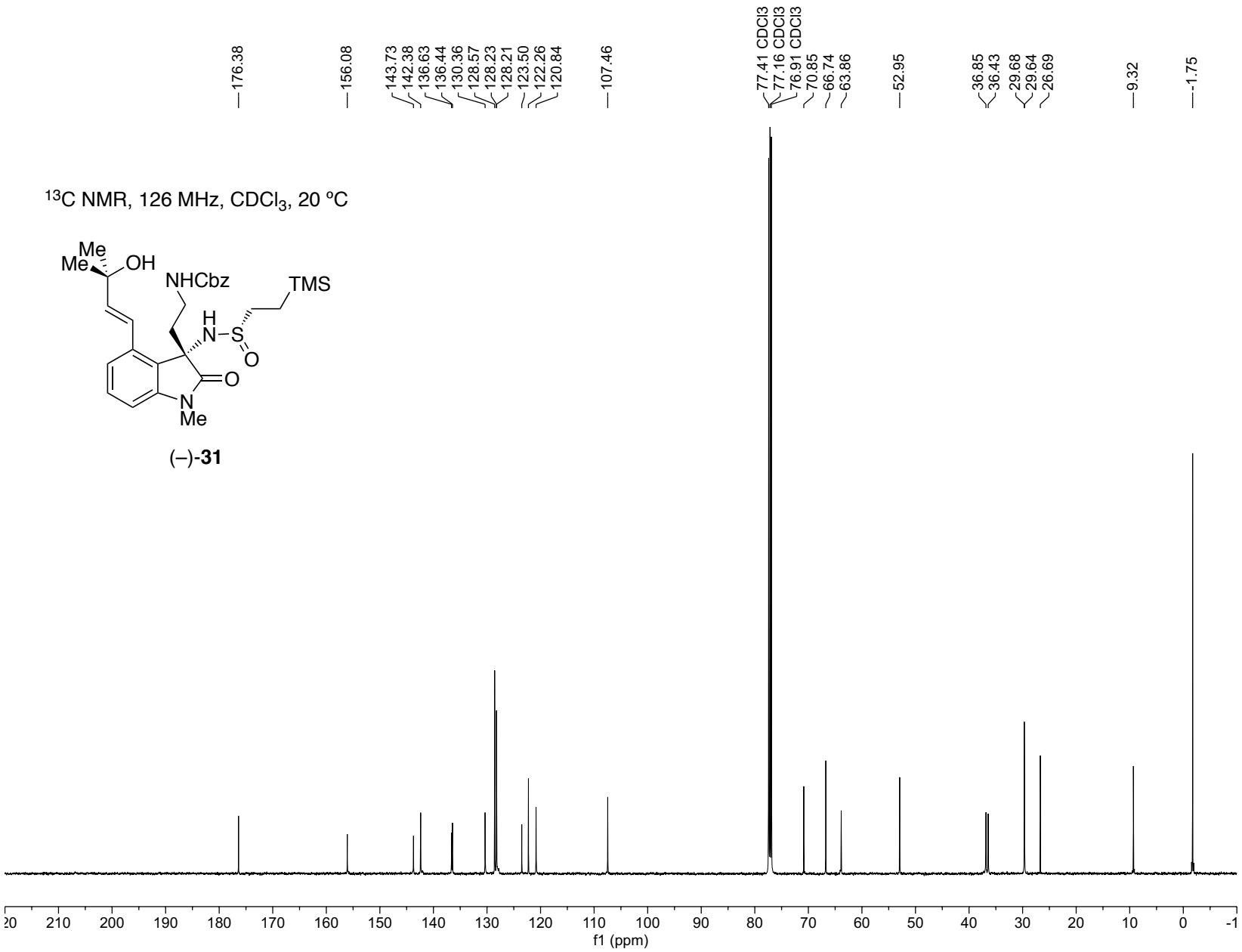

7.26 CDCl3
7.19
7.18
7.18
7.17
6.81
6.80
6.79
6.79
3.72
3.72
3.71
3.70
3.70
3.49
3.19
2.46
2.45
2.44
2.34
2.34
2.04
^{1}H NMR, 500 MHz, $CDCl_3$, 20 ºC
HO
Br
NH_2
O
N
Me
(–)-**S5**
ppm

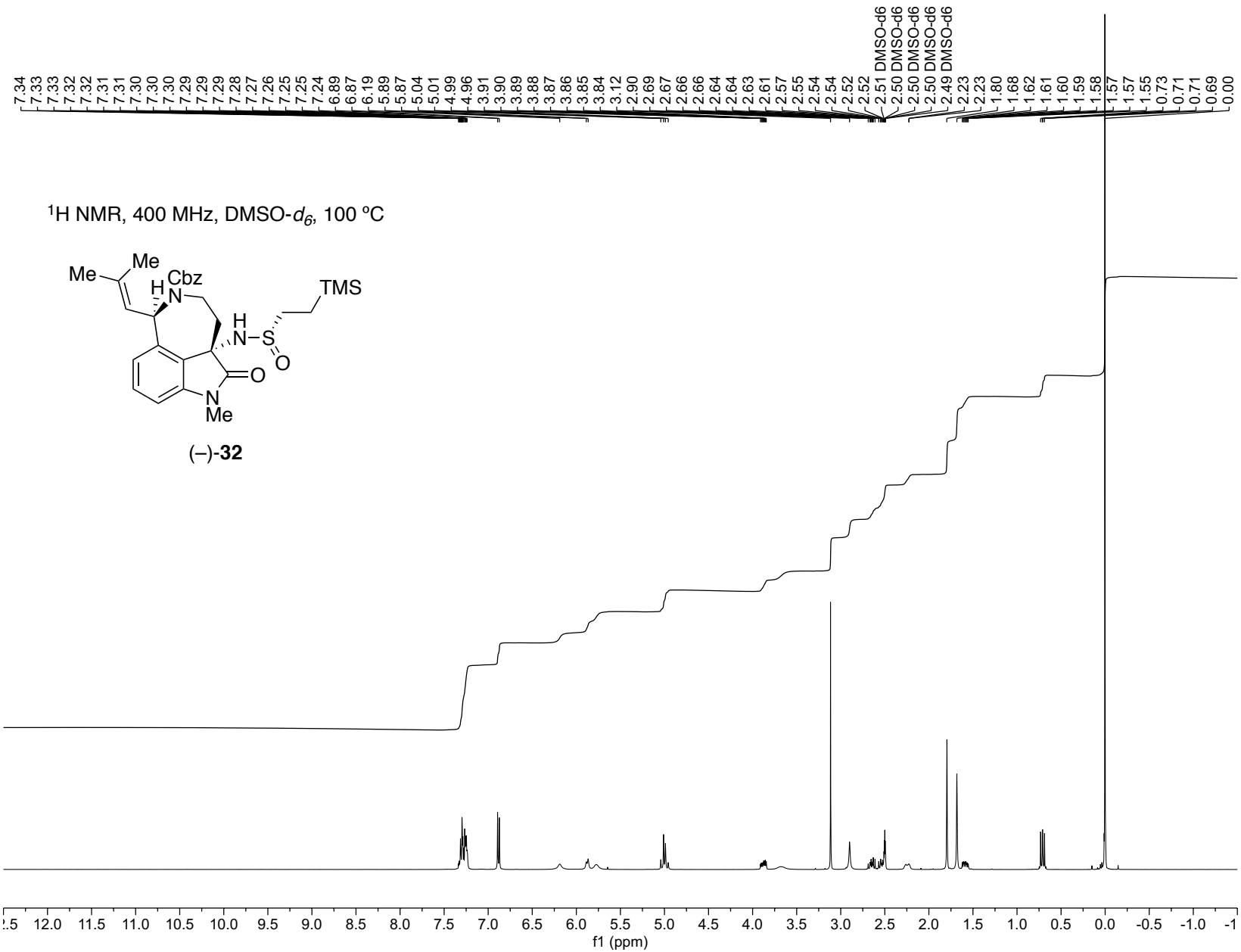

179.10
145.18
130.55
129.88
127.16
119.05
107.75
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
62.01
58.92
39.16
26.65
13C NMR, 126 MHz, CDCl3, 20 ºC
HO
Br
NH2
O
N
Me
(–)-S5
f1 (ppm)

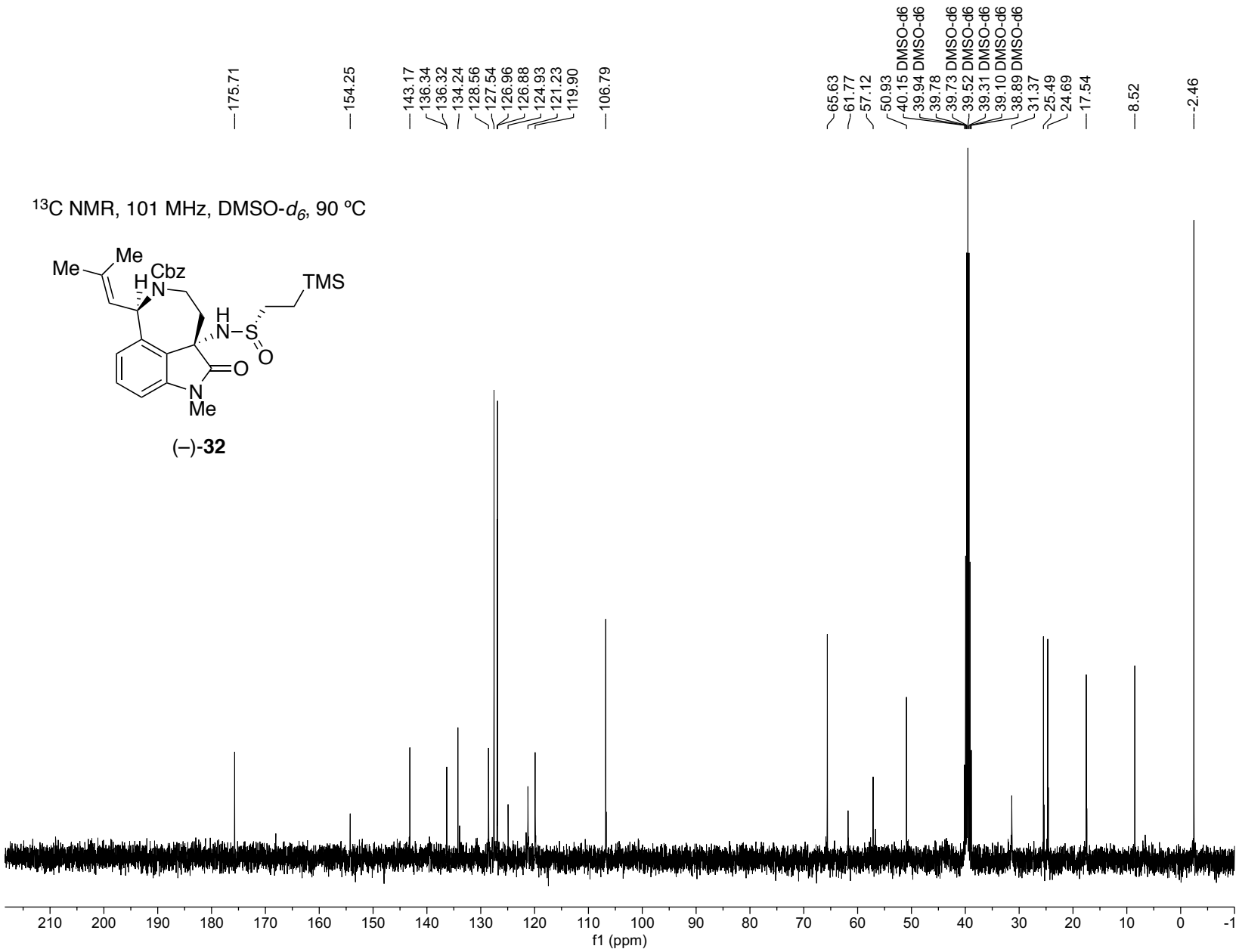

CDCl3
7.36 7.35 7.34 7.34 7.33 7.32 7.31 7.30 7.29 7.29 7.26 7.19 7.19 7.18 7.17 6.79 6.78 6.77 6.76 6.75
5.02 4.99 4.97 4.95 4.74 4.73 4.72 3.16 2.75 2.73 2.72 2.71 2.70 2.69 2.65 2.64 2.63 2.62 2.61 2.59 2.55 2.53 2.52 2.50 2.49 2.47 2.45 2.44 2.43 2.41
0.89 0.88 0.87 0.86 0.85 0.85 0.84 0.83 0.81 0.02
1H NMR, 500 MHz, CDCl3, 20 °C
CbzHN
TMS
Br
H
N–S
O
O
N
Me
(+)-30
f1 (ppm)

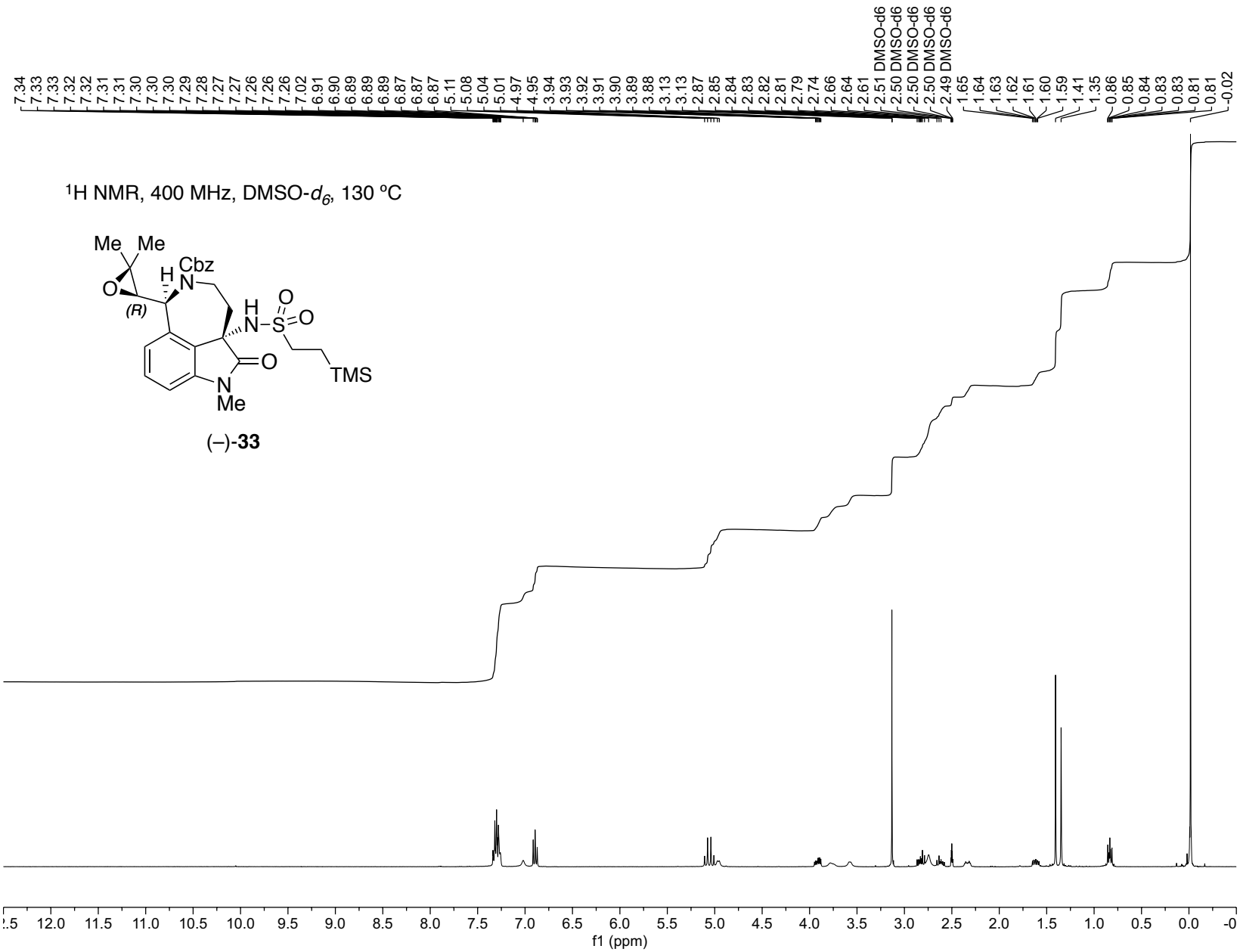

174.62
155.94
144.89
136.46
131.39
128.59
128.29
128.26
127.49
127.24
120.01
108.12
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.71
65.38
53.29
36.09
35.51
26.75
8.62
-1.74
13C NMR, 126 MHz, CDCl3, 20 ºC
CbzHN
TMS
Br
H
N
S
O
O
N
Me
(+)-30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.26 CDCl3
7.13
7.10
6.72
6.70
6.38
6.35
5.01
4.98
4.98
4.95
4.66
4.64
4.63
4.35
3.35
3.17
2.95
2.94
2.92
2.91
2.90
2.89
2.77
2.76
2.74
2.73
2.71
2.70
2.39
2.38
2.36
2.35
2.35
2.34
1.67
1.44
1.41
0.79
-0.00
1H NMR, 500 MHz, CDCl3, 20 ºC
Me
Me
OH
NHCbz
TMS
H
N
S
O
O
N
Me
(–)-31
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
f1 (ppm)


176.38
156.08
143.73
142.38
136.63
136.44
130.36
128.57
128.23
128.21
123.50
122.26
120.84
107.46
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
70.85
66.74
63.86
52.95
36.85
36.43
29.68
29.64
26.69
9.32
-1.75
13C NMR, 126 MHz, CDCl3, 20 °C
Me
Me
OH
NHCbz
TMS
H
N
S
O
O
N
Me
(–)-31
f1 (ppm)

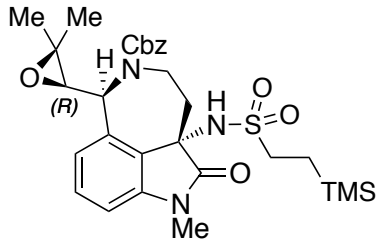

7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.28 7.27 7.26 7.25 7.25 7.24 6.89 6.87 6.19 5.89 5.87 5.04 5.01 4.99 4.96 3.91 3.90 3.89 3.88 3.87 3.86 3.85 3.84 3.12 2.90 2.69 2.67 2.66 2.66 2.64 2.64 2.63 2.61 2.57 2.55 2.54 2.54 2.52 2.52 2.51 DMSO-d6 2.50 DMSO-d6 2.50 DMSO-d6 2.50 DMSO-d6 2.49 DMSO-d6 2.23 2.23 1.80 1.68 1.62 1.61 1.60 1.59 1.58 1.57 1.57 1.55 0.73 0.71 0.71 0.69 0.00
1H NMR, 400 MHz, DMSO-d6, 100 ºC
Me
Me
H
Cbz
N
TMS
H
N–S
O
O
N
Me
(–)-32
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 -1.0 -1
f1 (ppm)


175.71
154.25
143.17
136.34
136.32
134.24
128.56
127.54
126.96
126.88
124.93
121.23
119.90
106.79
65.63
61.77
57.12
50.93
40.15 DMSO-d6
39.94 DMSO-d6
39.78
39.73 DMSO-d6
39.52 DMSO-d6
39.31 DMSO-d6
39.10 DMSO-d6
38.89 DMSO-d6
31.37
25.49
24.69
17.54
8.52
-2.46
13C NMR, 101 MHz, DMSO-d6, 90 ºC
Me
Me
H
Cbz
N
TMS
H
N
S
O
O
N
Me
(–)-32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

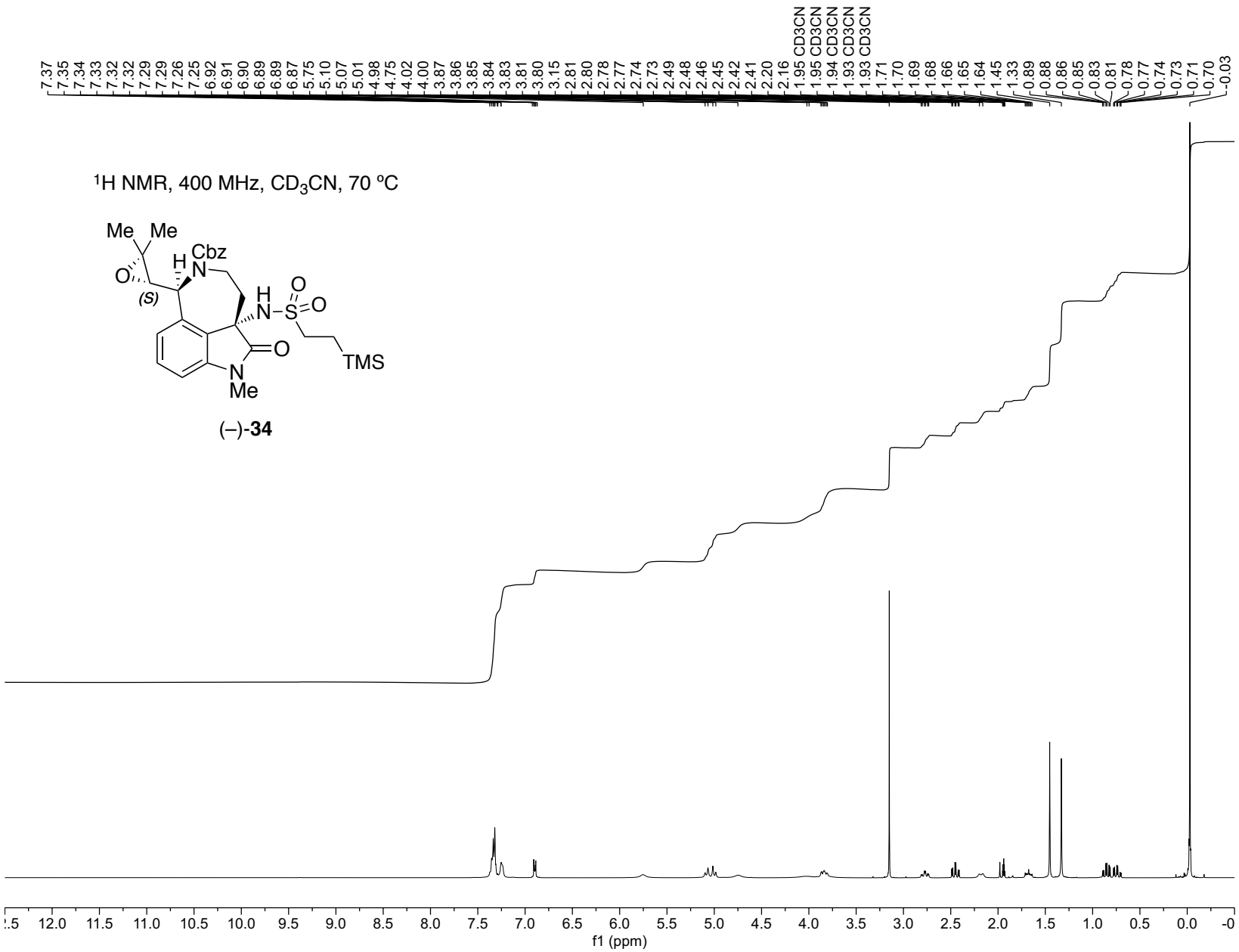

7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.28 7.27 7.27 7.26 7.26 7.26 7.02 6.91 6.90 6.89 6.89 6.89 6.87 6.87 6.87 5.11 5.08 5.04 5.01 4.97 4.95 3.94 3.93 3.92 3.91 3.90 3.89 3.88 3.13 3.13 2.87 2.85 2.84 2.83 2.82 2.81 2.79 2.74 2.66 2.64 2.61 2.51 DMSO-d6 2.50 DMSO-d6 2.50 DMSO-d6 2.50 DMSO-d6 2.49 DMSO-d6 1.65 1.64 1.63 1.62 1.61 1.60 1.59 1.41 1.35 0.86 0.85 0.84 0.83 0.83 0.81 0.81 -0.02
1H NMR, 400 MHz, DMSO-d6, 130 °C
Me Me
Cbz
H
N
O
(R)
H
N–S
O
O
O
TMS
N
Me
(–)-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
f1 (ppm)

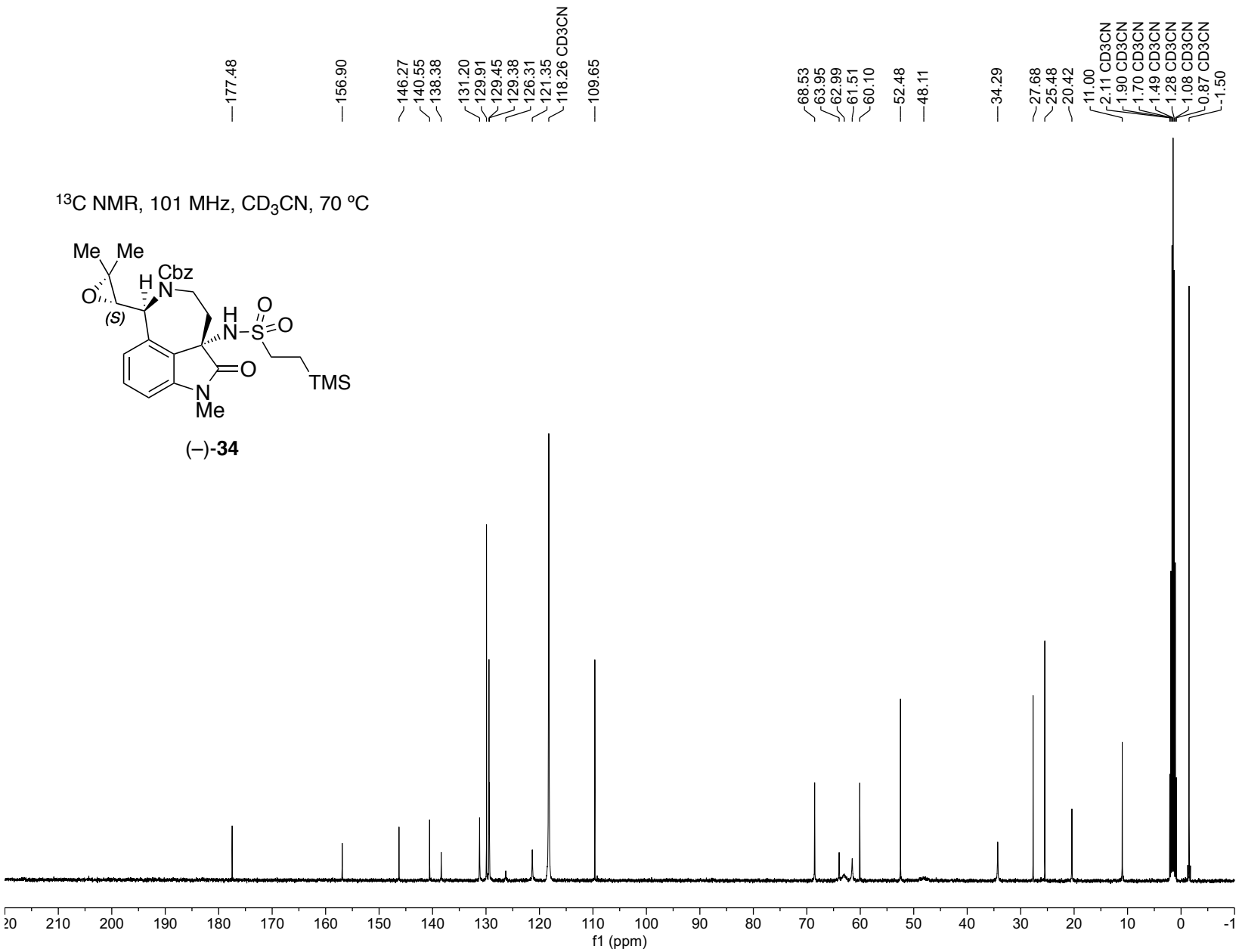
174.51
154.51
143.31
136.59
136.02
128.64
127.36
126.81
126.75
124.86
118.83
107.08
65.89
61.24
59.10
58.11
49.66
43.78
40.15 DMSO-d6
39.94 DMSO-d6
39.73 DMSO-d6
39.52 DMSO-d6
39.31 DMSO-d6
39.10 DMSO-d6
38.90 DMSO-d6
32.01
25.48
23.55
18.04
8.86
-2.93

^{13}C NMR, 101 MHz, DMSO-d_6, 130 °C

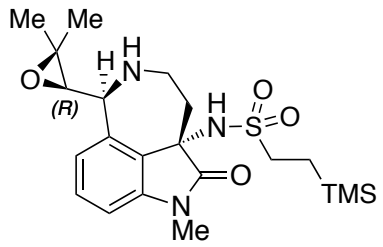


(–)-**33**


7.37 7.35 7.34 7.33 7.32 7.32 7.29 7.29 7.26 7.25 6.92 6.91 6.90 6.89 6.89 6.87 5.75 5.10 5.07 5.01 4.98 4.75 4.02 4.00 3.87 3.86 3.85 3.84 3.83 3.81 3.80 3.15 2.81 2.80 2.78 2.77 2.74 2.73 2.49 2.48 2.46 2.45 2.42 2.41 2.20 2.16 1.95 CD3CN 1.95 CD3CN 1.94 CD3CN 1.93 CD3CN 1.93 CD3CN 1.71 1.70 1.69 1.68 1.66 1.65 1.64 1.45 1.33 0.89 0.88 0.86 0.85 0.83 0.81 0.78 0.77 0.74 0.73 0.71 0.70 -0.03
1H NMR, 400 MHz, CD3CN, 70 °C
Me Me
H Cbz
N
O
(S)
H
N
S
O
O
O
TMS
N
Me
(–)-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
f1 (ppm)

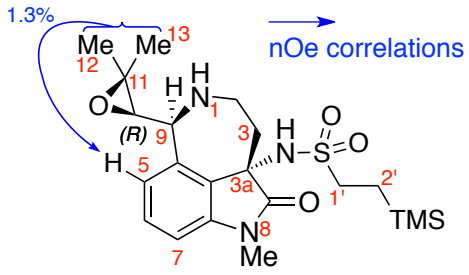

177.48
156.90
146.27
140.55
138.38
131.20
129.91
129.45
129.38
126.31
121.35
118.26 CD3CN
109.65
68.53
63.95
62.99
61.51
60.10
52.48
48.11
34.29
27.68
25.48
20.42
11.00
2.11 CD3CN
1.90 CD3CN
1.70 CD3CN
1.49 CD3CN
1.28 CD3CN
1.08 CD3CN
0.87 CD3CN
-1.50
13C NMR, 101 MHz, CD3CN, 70 °C
Me
Me
H
Cbz
N
O
(S)
H
N
S
O
O
O
TMS
N
Me
(–)-34
f1 (ppm)

^{1}H NMR, 400 MHz, C_6D_6, 70 ºC

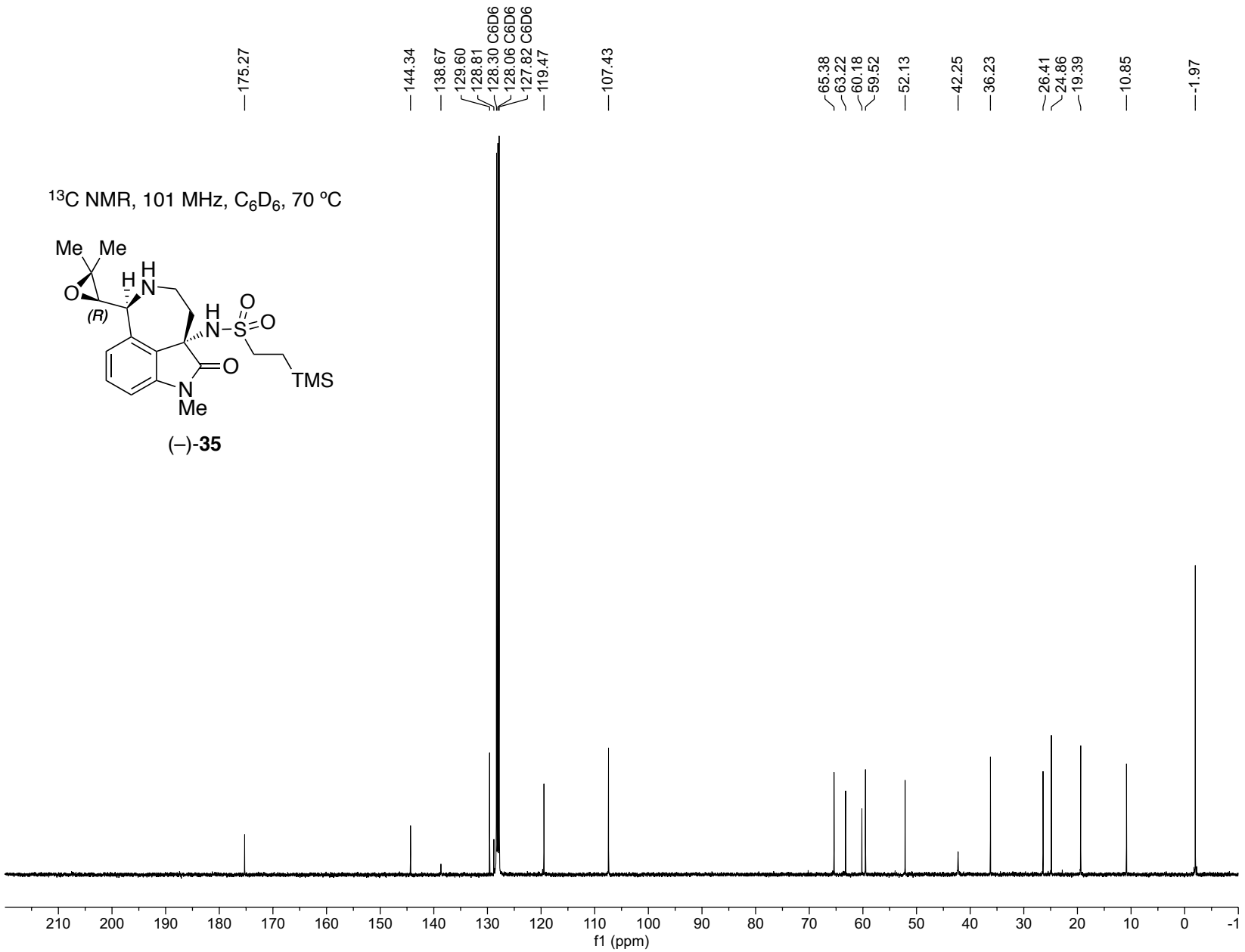


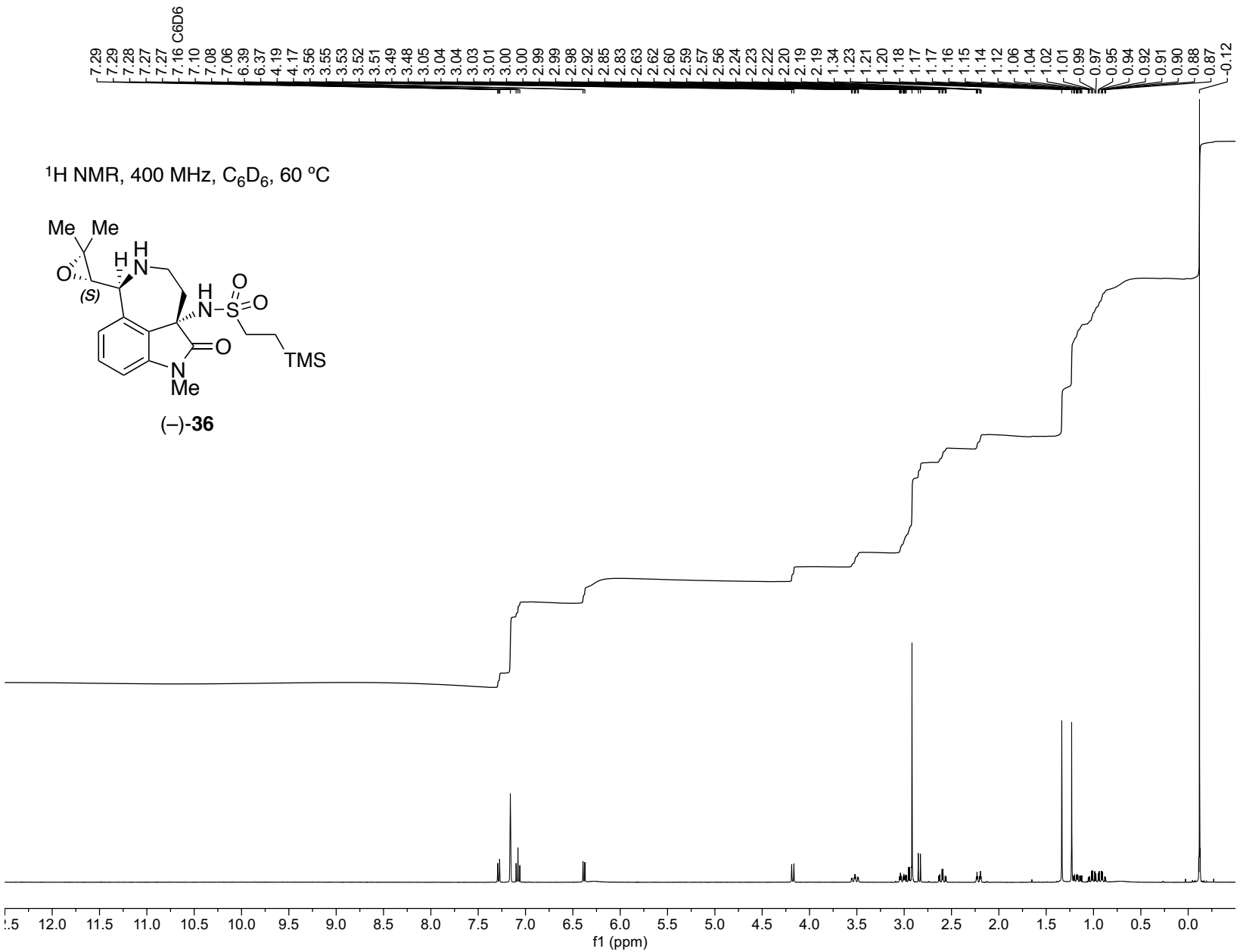
(–)-**35**

1D selective NOESY with
chemical shift selective filter (cssf)
mixing time = 500 ms
500 MHz, C_6D_6, 70 °C

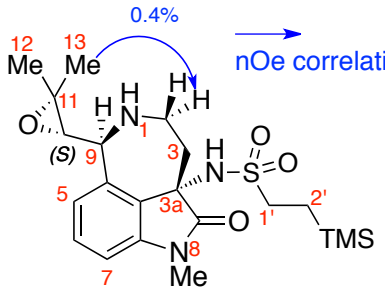


(–)-**35**

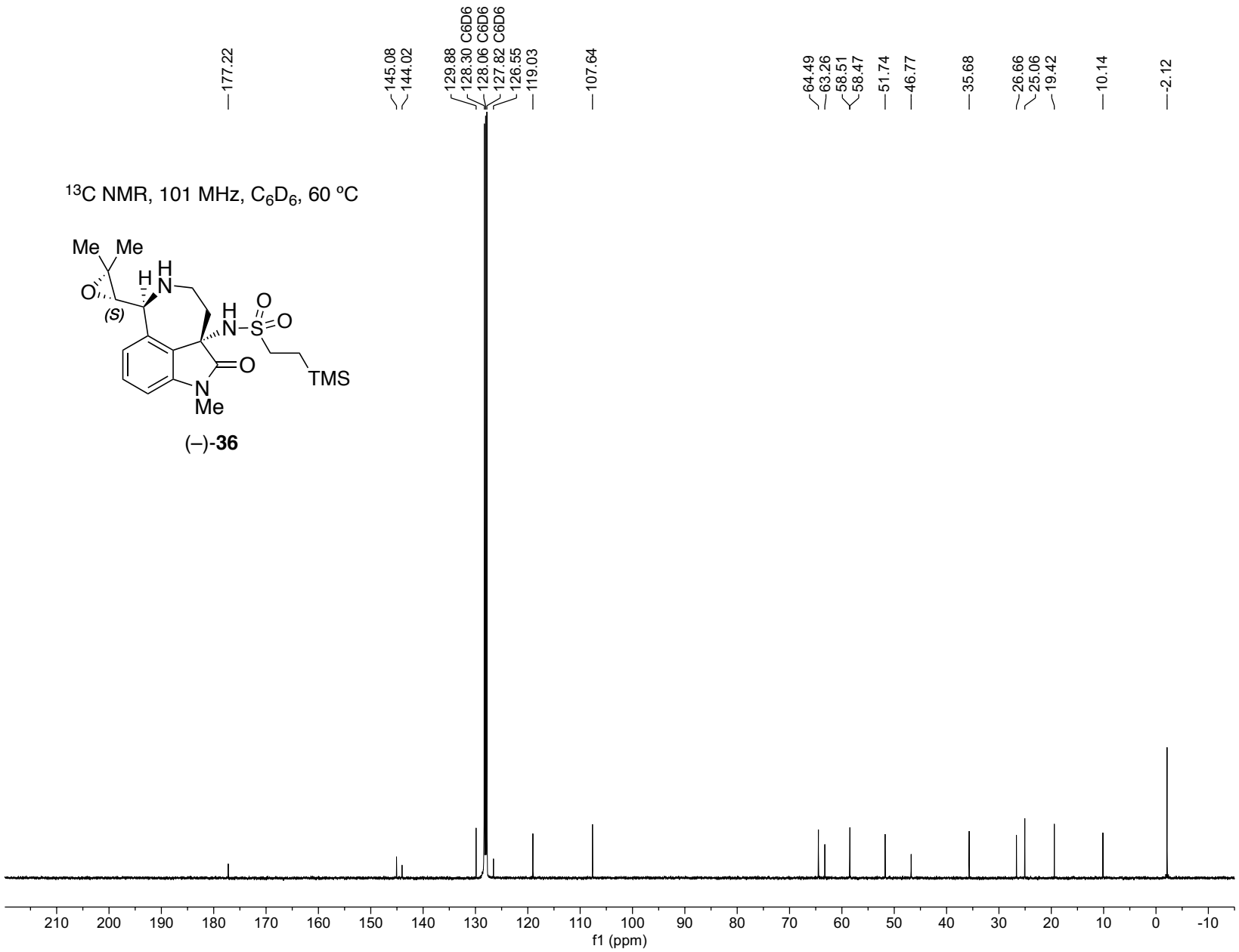

175.27
144.34
138.67
129.60
128.81
128.30 C6D6
128.06 C6D6
127.82 C6D6
119.47
107.43
65.38
63.22
60.18
59.52
52.13
42.25
36.23
26.41
24.86
19.39
10.85
-1.97
13C NMR, 101 MHz, C6D6, 70 ºC
Me
Me
H
N
O
(R)
H
N
S
O
O
O
TMS
N
Me
(–)-35
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

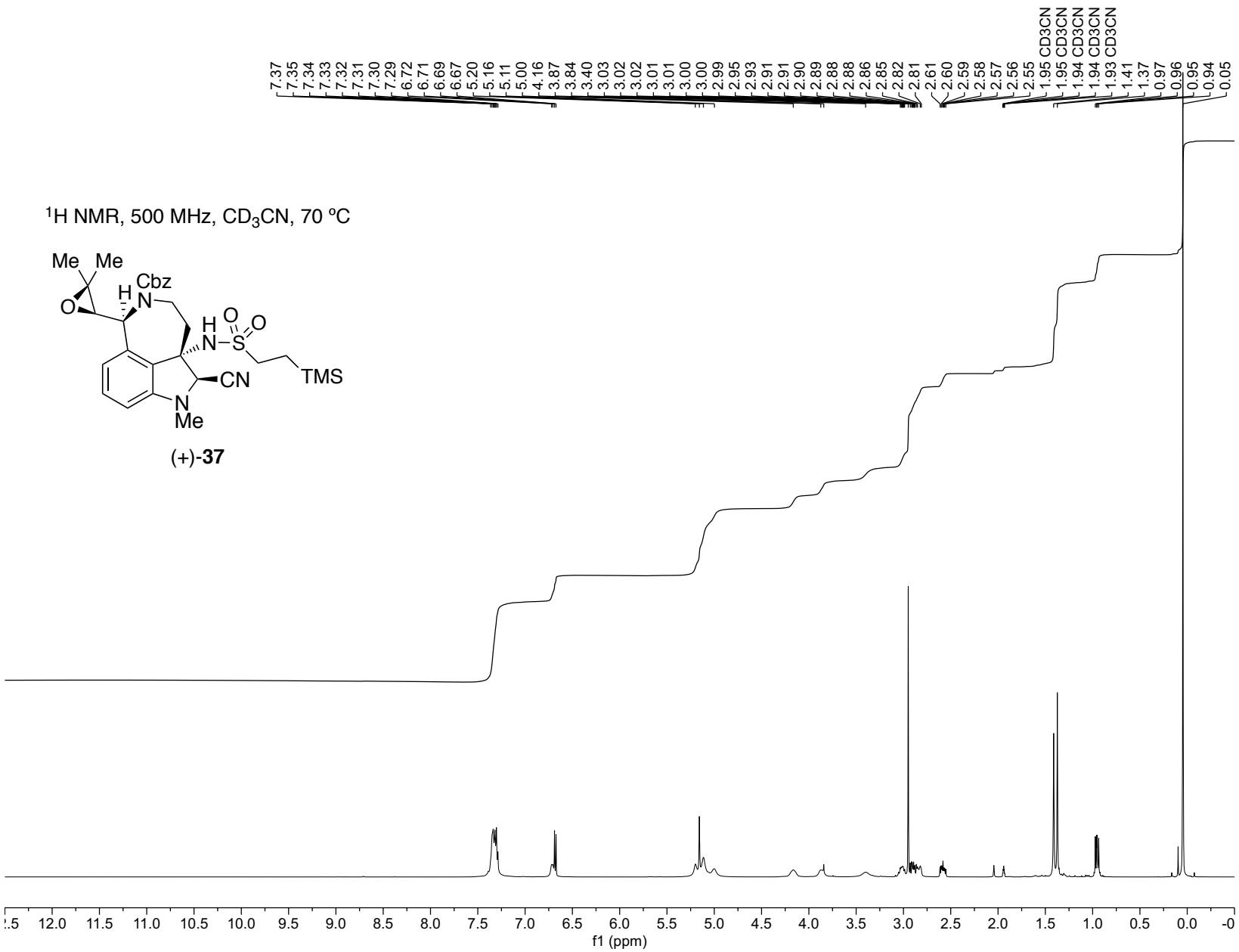

7.29 7.29 7.28 7.27 7.27 7.16 C6D6 7.10 7.08 7.06 6.39 6.37 4.19 4.17 3.56 3.55 3.53 3.52 3.51 3.49 3.48 3.05 3.04 3.04 3.03 3.01 3.00 3.00 2.99 2.99 2.98 2.92 2.85 2.83 2.63 2.62 2.60 2.59 2.57 2.56 2.24 2.23 2.22 2.20 2.19 2.19 1.34 1.23 1.21 1.20 1.18 1.17 1.17 1.16 1.15 1.14 1.12 1.06 1.04 1.02 1.01 0.99 0.97 0.95 0.94 0.92 0.91 0.90 0.88 0.87 -0.12
1H NMR, 400 MHz, C6D6, 60 °C
Me Me
H
N
O
(S)
H
N
O
S
O
O
TMS
N
Me
(–)-36
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
f1 (ppm)

1D selective NOESY with
chemical shift selective filter (cssf)
mixing time = 800 ms
500 MHz, C_6D_6, 60 °C



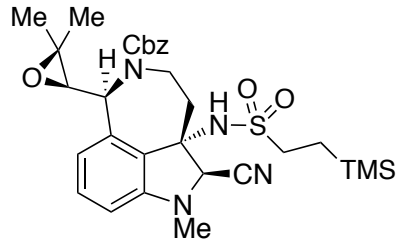
(–)-**36**


177.22
145.08
144.02
129.88
128.30 C6D6
128.06 C6D6
127.82 C6D6
126.55
119.03
107.64
64.49
63.26
58.51
58.47
51.74
46.77
35.68
26.66
25.06
19.42
10.14
-2.12
13C NMR, 101 MHz, C6D6, 60 °C
Me
Me
H
N
O
(S)
H
N
O
S
O
O
TMS
N
Me
(–)-36
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

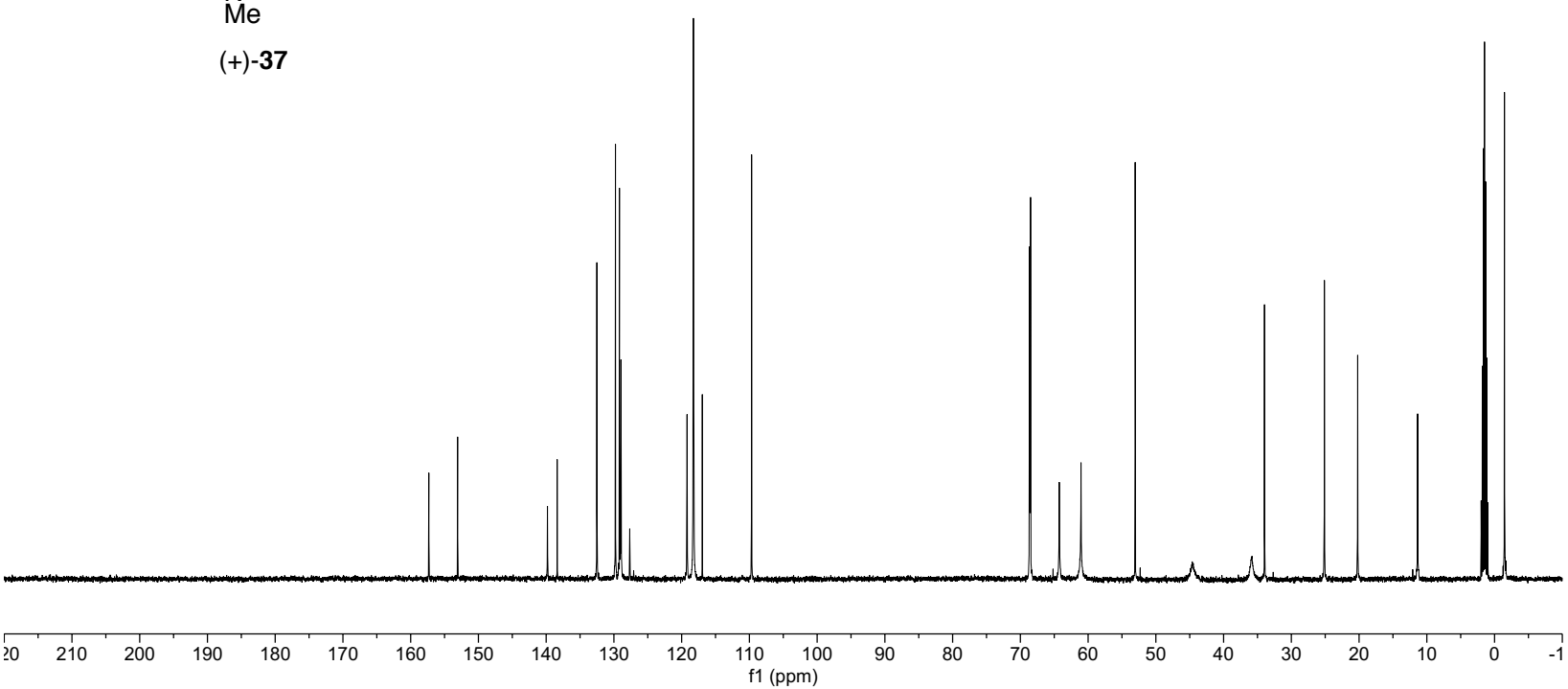

7.37
7.35
7.34
7.33
7.32
7.31
7.30
7.29
6.72
6.71
6.69
6.67
5.20
5.16
5.11
5.00
4.16
3.87
3.84
3.40
3.03
3.02
3.02
3.01
3.01
3.00
3.00
2.99
2.95
2.93
2.91
2.91
2.90
2.89
2.88
2.88
2.86
2.85
2.82
2.81
2.61
2.60
2.59
2.58
2.57
2.56
2.55
1.95 CD3CN
1.95 CD3CN
1.94 CD3CN
1.94 CD3CN
1.93 CD3CN
1.41
1.37
0.97
0.96
0.95
0.94
0.05
^{1}H NMR, 500 MHz, CD_3CN, 70 ºC
Me
Me
Cbz
H
N
O
H
N
O
S
O
CN
TMS
N
Me
(+)-**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
f1 (ppm)

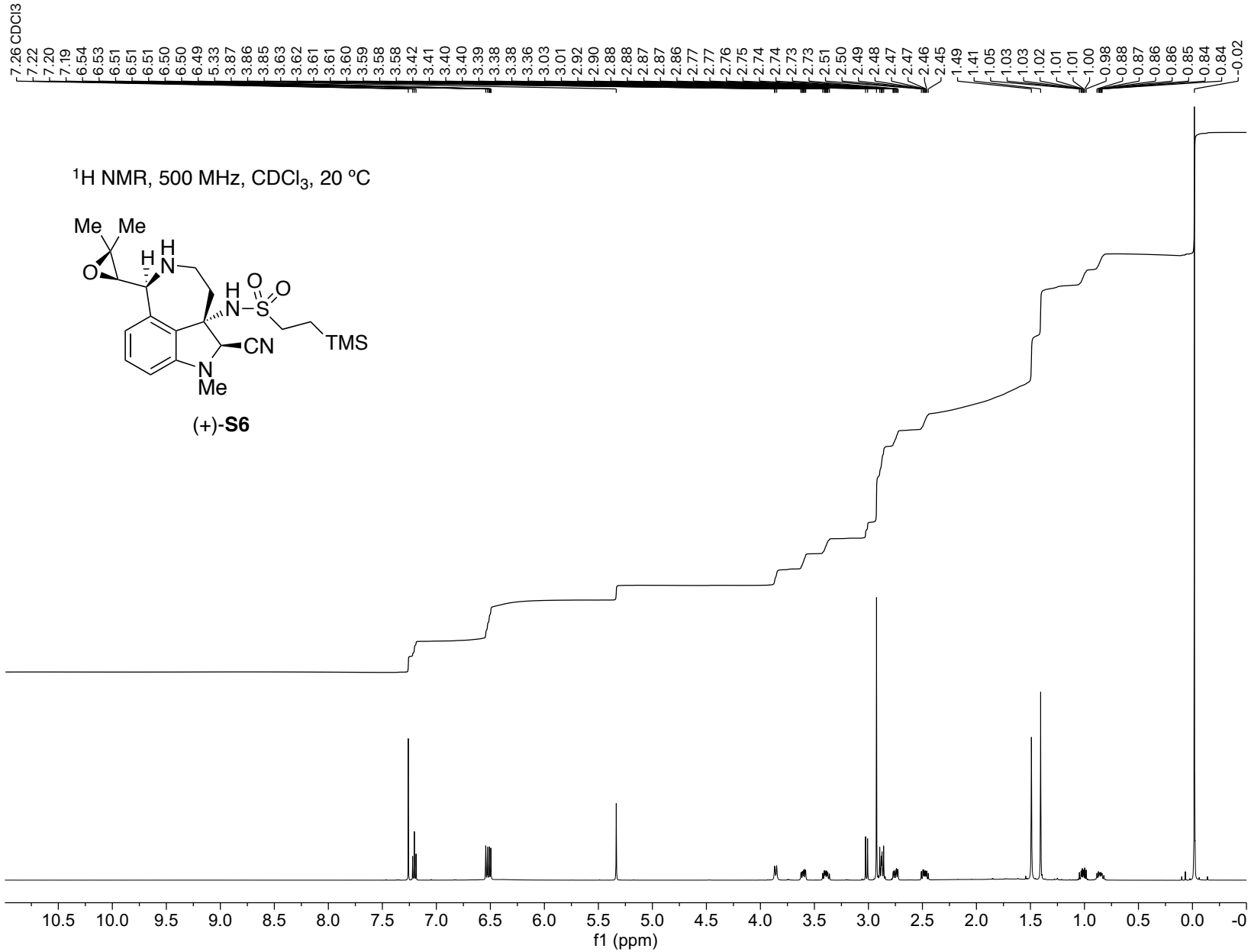
157.32
153.07
139.81
138.38
132.52
129.77
129.18
128.96
127.66
119.20
118.26 CD3CN
116.95
109.67
68.64
68.58
68.50
64.25
61.17
61.05
53.05
44.63
35.81
33.96
25.12
20.21
11.36
1.98 CD3CN
1.81 CD3CN
1.65 CD3CN
1.48 CD3CN
1.32 CD3CN
1.16 CD3CN
0.99 CD3CN
-1.46

^{13}C NMR, 126 MHz, CD_3CN, 70 °C

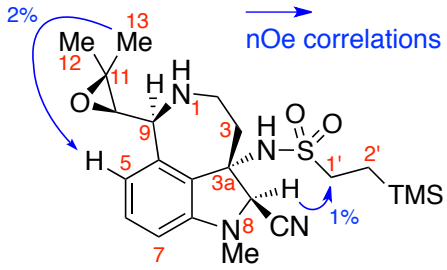


(+)-**37**

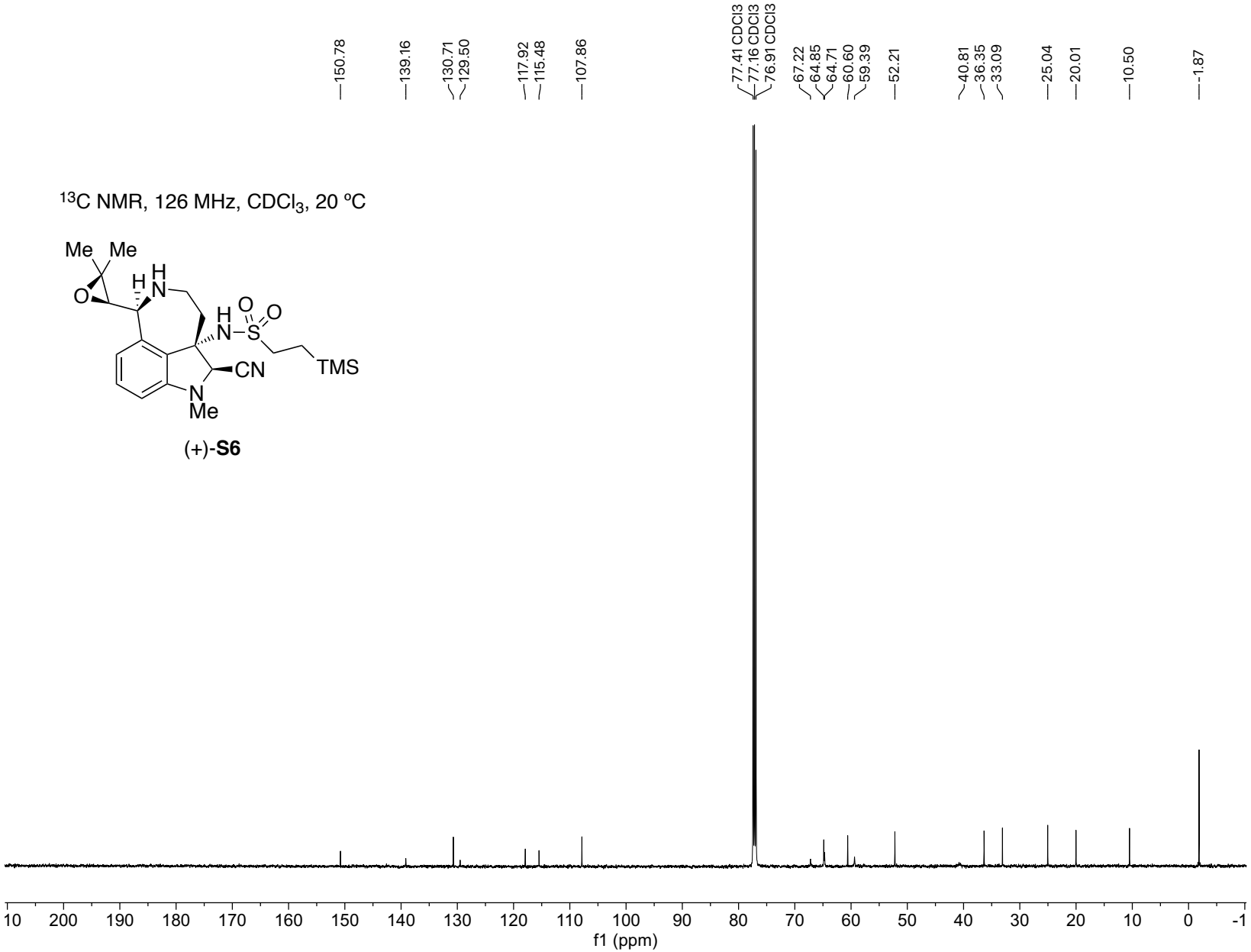


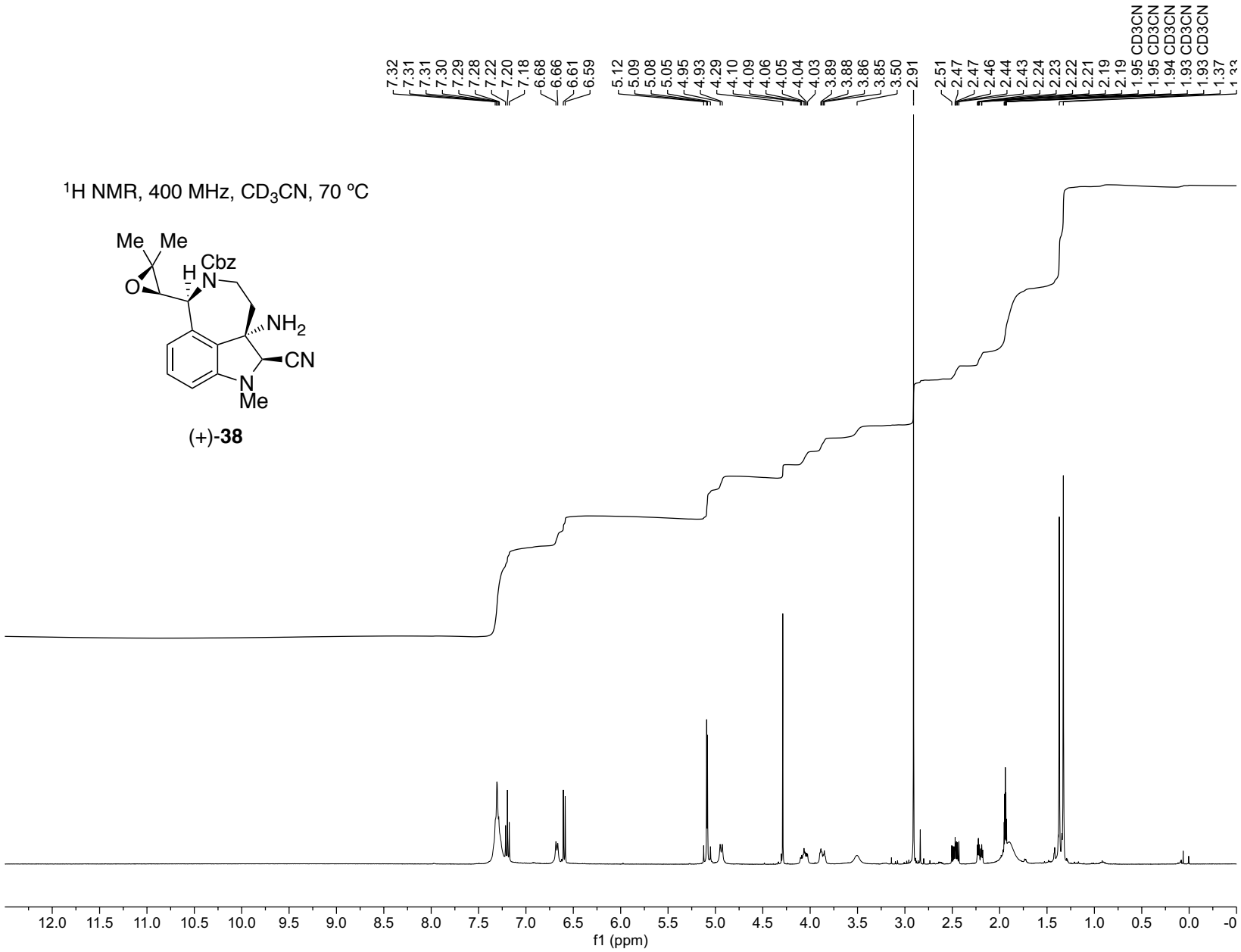

7.26 CDCl3
7.22 7.20 7.19 6.54 6.53 6.51 6.51 6.51 6.50 6.50 6.49 5.33 3.87 3.86 3.85 3.63 3.62 3.61 3.61 3.60 3.59 3.58 3.58 3.42 3.41 3.40 3.40 3.39 3.38 3.38 3.36 3.03 3.01 2.92 2.90 2.88 2.88 2.87 2.87 2.86 2.77 2.77 2.76 2.75 2.74 2.74 2.73 2.51 2.50 2.49 2.48 2.47 2.47 2.46 2.45 1.49 1.41 1.05 1.03 1.03 1.02 1.01 1.01 1.00 0.98 0.88 0.87 0.86 0.86 0.85 0.84 0.84 -0.02
^{1}H NMR, 500 MHz, $CDCl_3$, 20 °C
Me Me
H
N
O
H
N
O
O
S
CN
TMS
N
Me
(+)-**S6**
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
f1 (ppm)

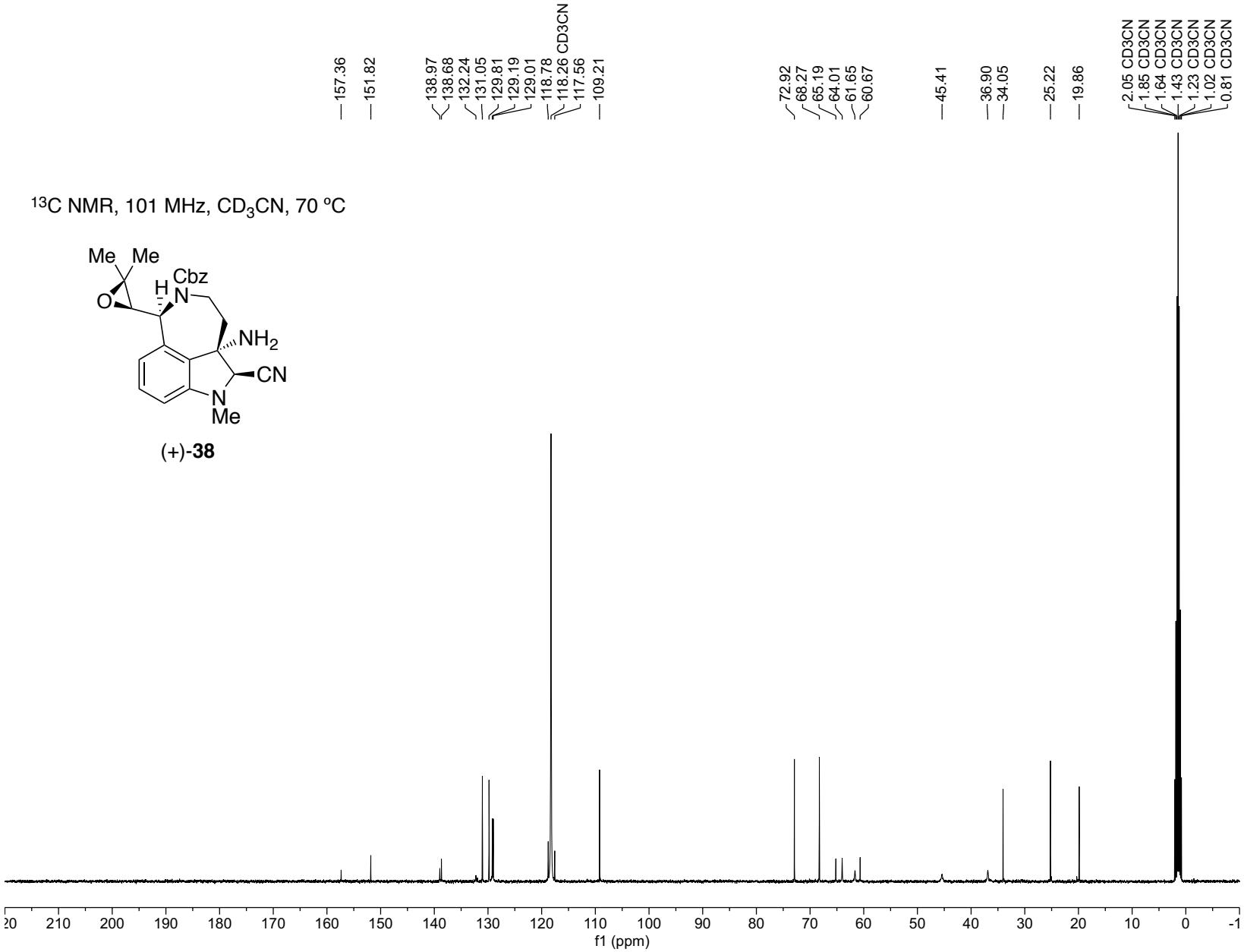
1D selective NOESY
mixing time = 500 ms
500 MHz, $CDCl_3$, 20 °C

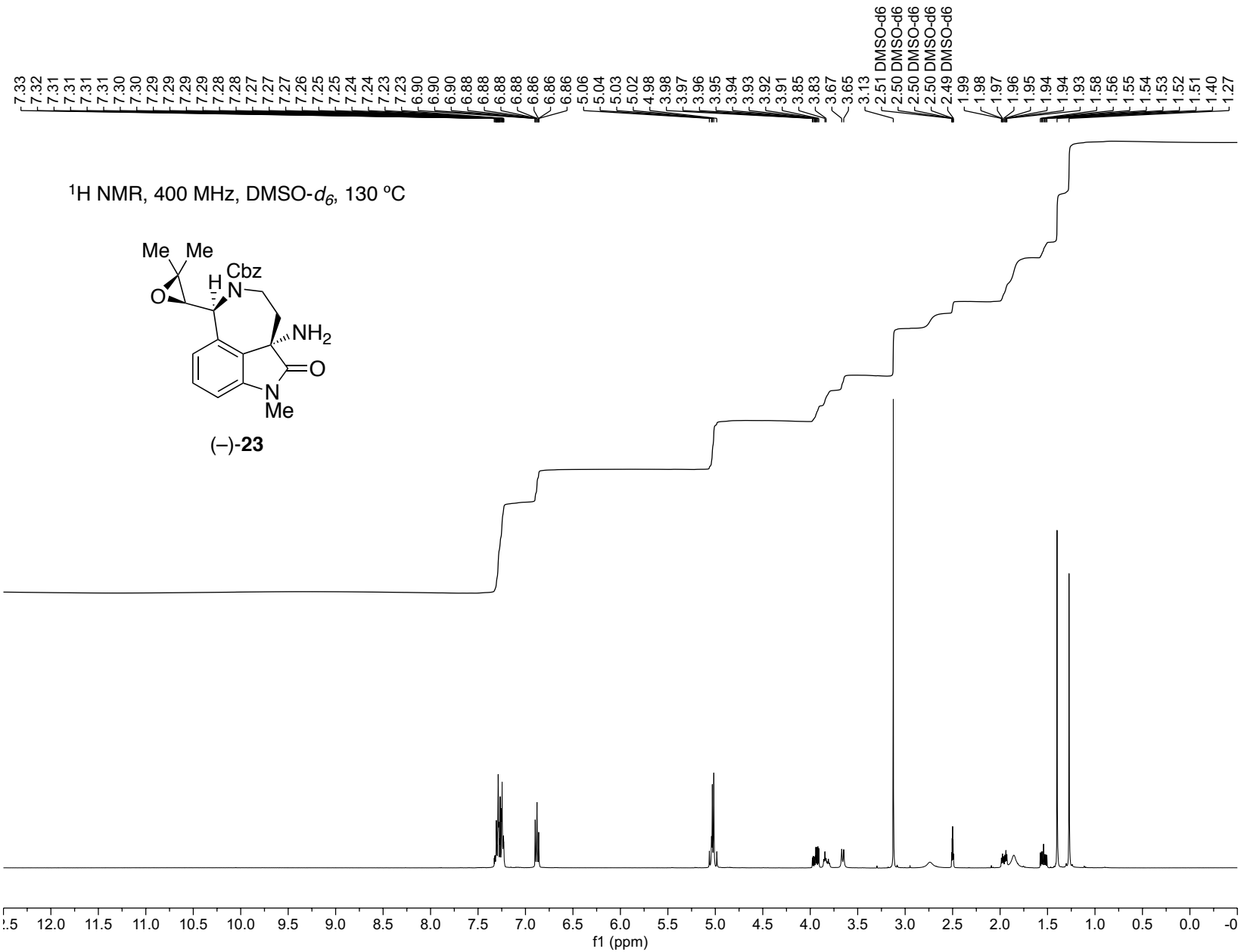


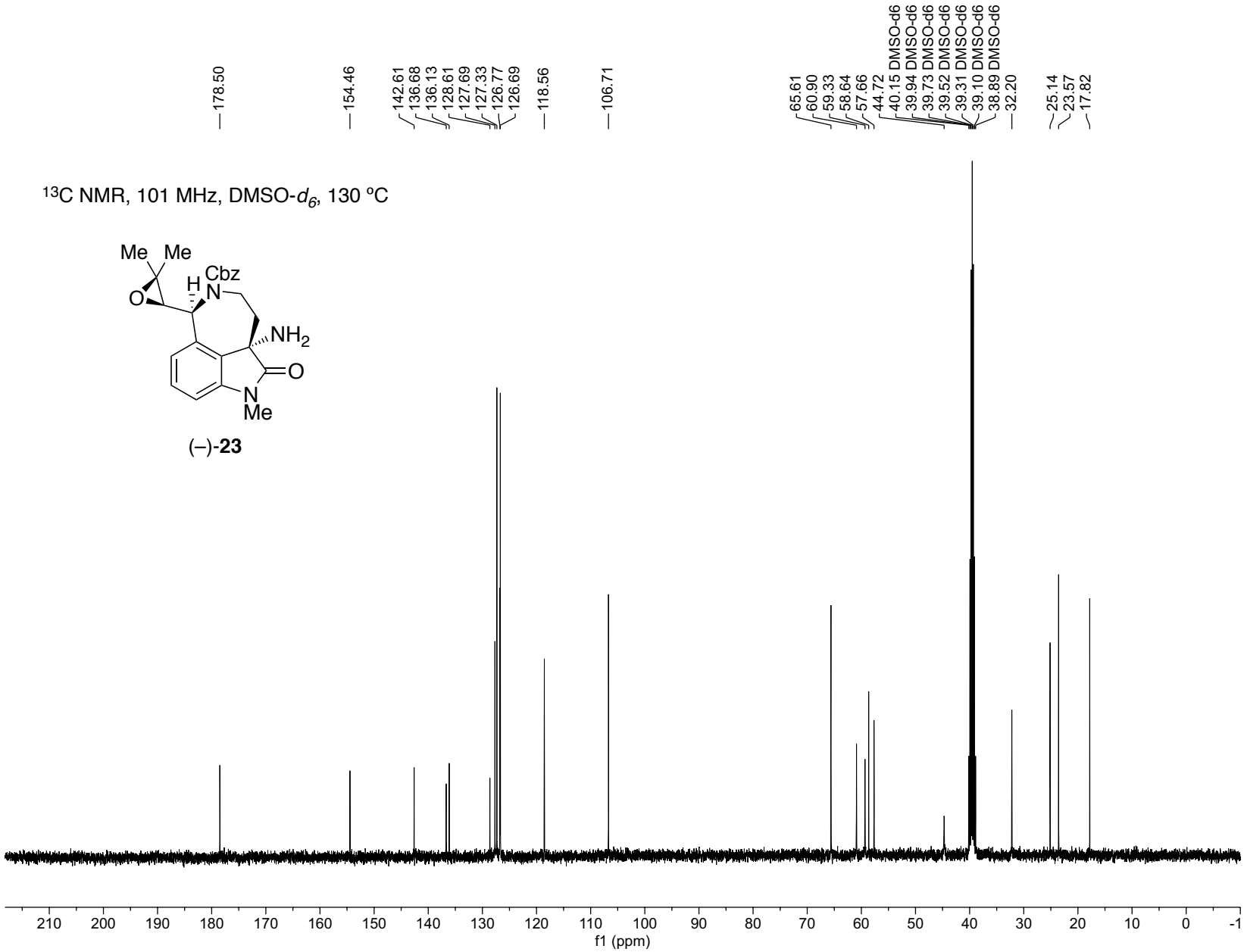
(+)-**S6**

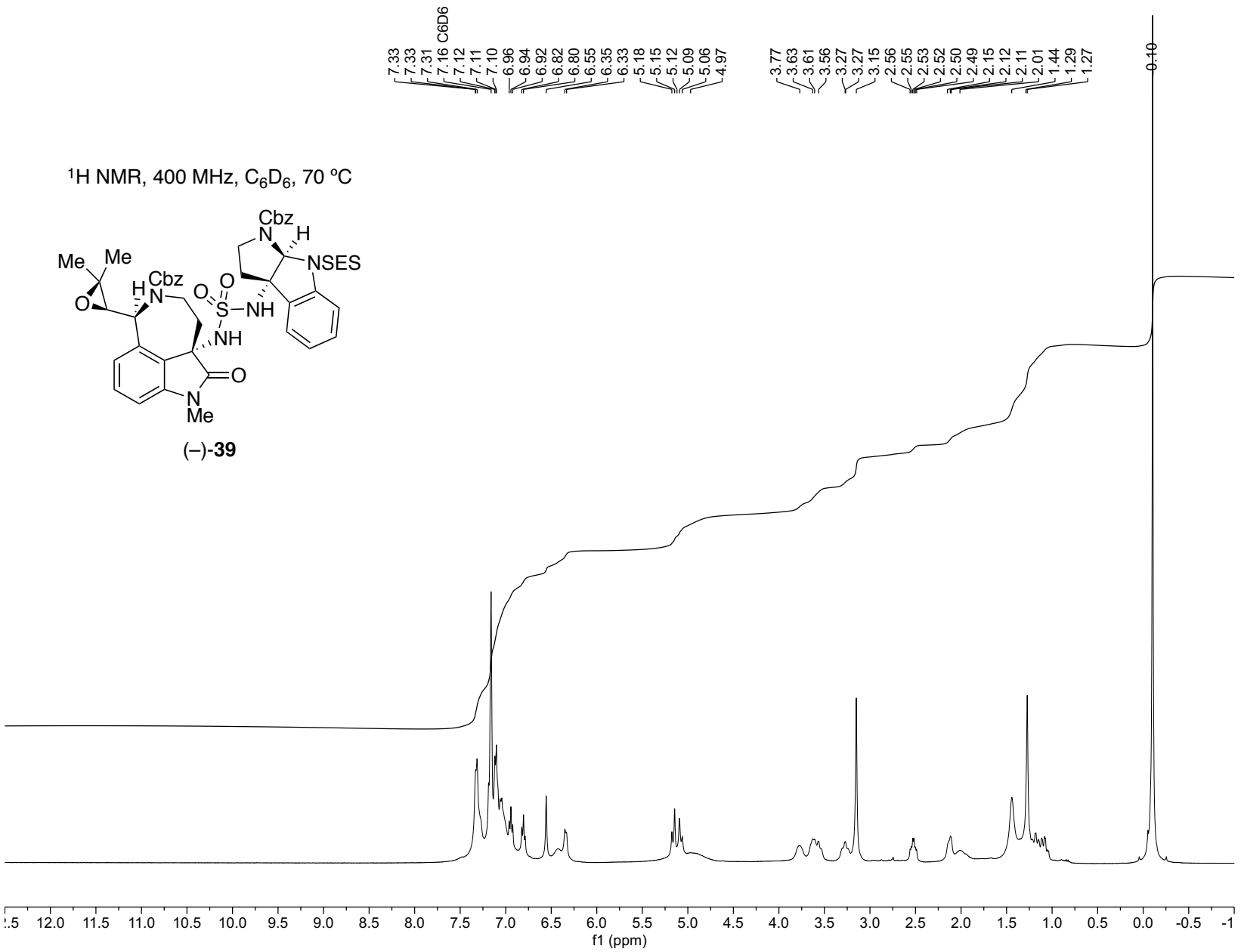

150.78
139.16
130.71
129.50
117.92
115.48
107.86
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.22
64.85
64.71
60.60
59.39
52.21
40.81
36.35
33.09
25.04
20.01
10.50
-1.87
13C NMR, 126 MHz, CDCl3, 20 ºC
Me
Me
O
H
N
H
N
O
O
S
CN
TMS
N
Me
(+)-S6
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

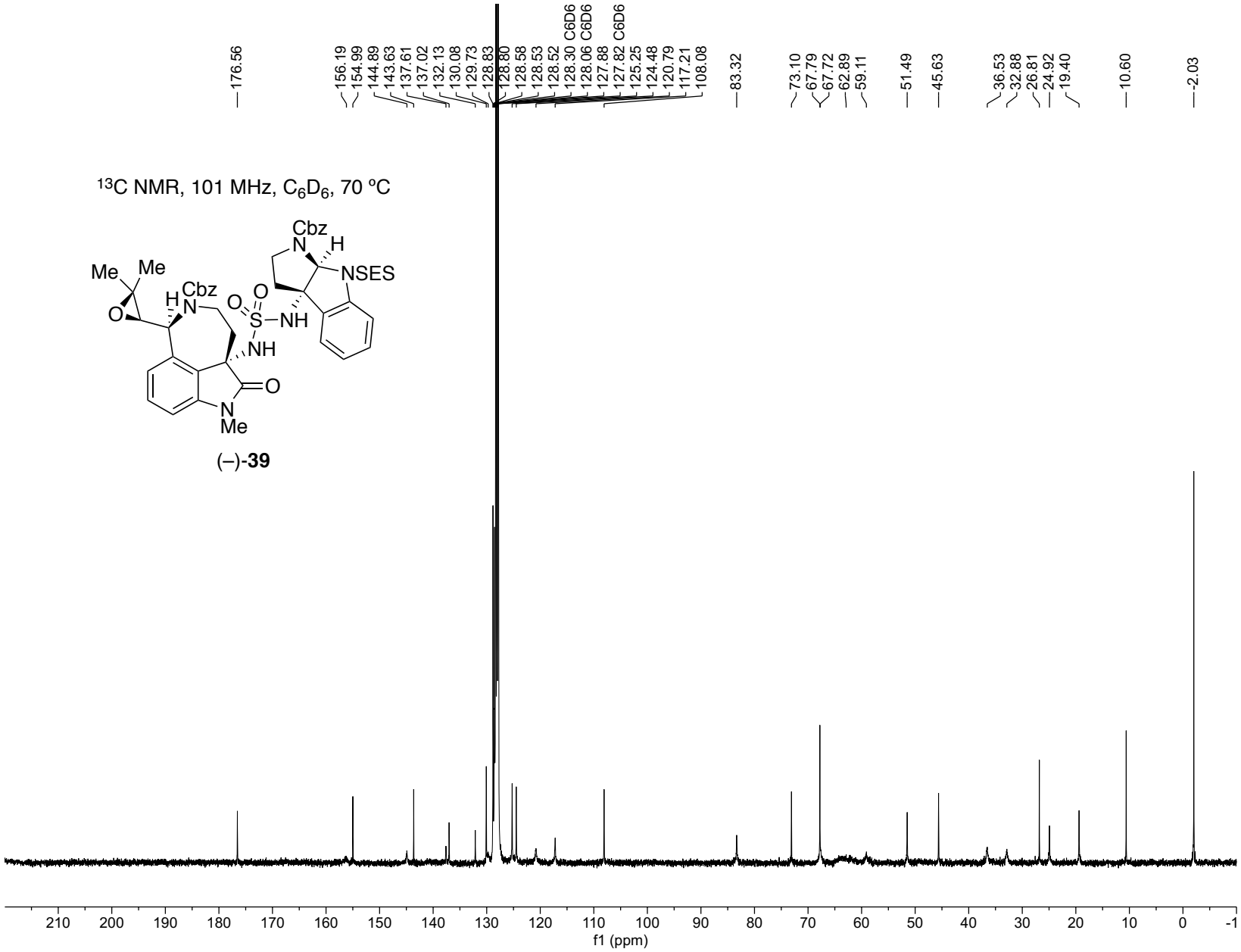

7.32
7.31
7.31
7.30
7.29
7.28
7.22
7.20
7.18
6.68
6.66
6.61
6.59
5.12
5.09
5.08
5.05
4.95
4.93
4.29
4.10
4.09
4.06
4.05
4.04
4.03
3.89
3.88
3.86
3.85
3.50
2.91
2.51
2.47
2.47
2.46
2.44
2.43
2.24
2.23
2.22
2.21
2.19
2.19
1.95 CD3CN
1.95 CD3CN
1.94 CD3CN
1.93 CD3CN
1.93 CD3CN
1.37
1H NMR, 400 MHz, CD3CN, 70 ºC
Me
Me
Cbz
H
N
O
NH2
CN
N
Me
(+)-38
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
f1 (ppm)


157.36
151.82
138.97
138.68
132.24
131.05
129.81
129.19
129.01
118.78
118.26 CD3CN
117.56
109.21
72.92
68.27
65.19
64.01
61.65
60.67
45.41
36.90
34.05
25.22
19.86
2.05 CD3CN
1.85 CD3CN
1.64 CD3CN
1.43 CD3CN
1.23 CD3CN
1.02 CD3CN
0.81 CD3CN
13C NMR, 101 MHz, CD3CN, 70 ºC
Me
Me
Cbz
H
N
O
NH2
CN
N
Me
(+)-38
f1 (ppm)

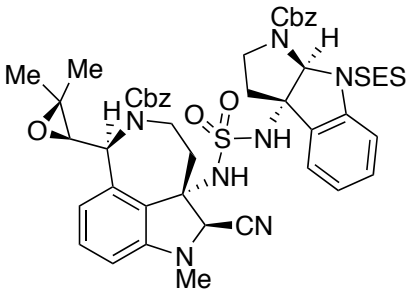

7.33 7.32 7.31 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.25 7.25 7.24 7.24 7.23 7.23 6.90 6.90 6.90 6.88 6.88 6.88 6.86 6.86 6.86
5.06 5.04 5.03 5.02 4.98 3.98 3.97 3.96 3.95 3.94 3.93 3.92 3.91 3.85 3.83 3.67 3.65
3.13 2.51 DMSO-d6 2.50 DMSO-d6 2.50 DMSO-d6 2.50 DMSO-d6 2.49 DMSO-d6
1.99 1.98 1.97 1.96 1.95 1.94 1.94 1.93 1.58 1.56 1.55 1.54 1.53 1.52 1.51 1.40 1.27
^{1}H NMR, 400 MHz, DMSO-d_6, 130 ºC
Me Me
Cbz
H N
O
NH$_2$
O
N
Me
(–)-**23**
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
f1 (ppm)


178.50
154.46
142.61
136.68
136.13
128.61
127.69
127.33
126.77
126.69
118.56
106.71
65.61
60.90
59.33
58.64
57.66
44.72
40.15 DMSO-d6
39.94 DMSO-d6
39.73 DMSO-d6
39.52 DMSO-d6
39.31 DMSO-d6
39.10 DMSO-d6
38.89 DMSO-d6
32.20
25.14
23.57
17.82
13C NMR, 101 MHz, DMSO-d6, 130 ºC
Me
Me
Cbz
H
N
O
NH2
O
N
Me
(–)-23
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

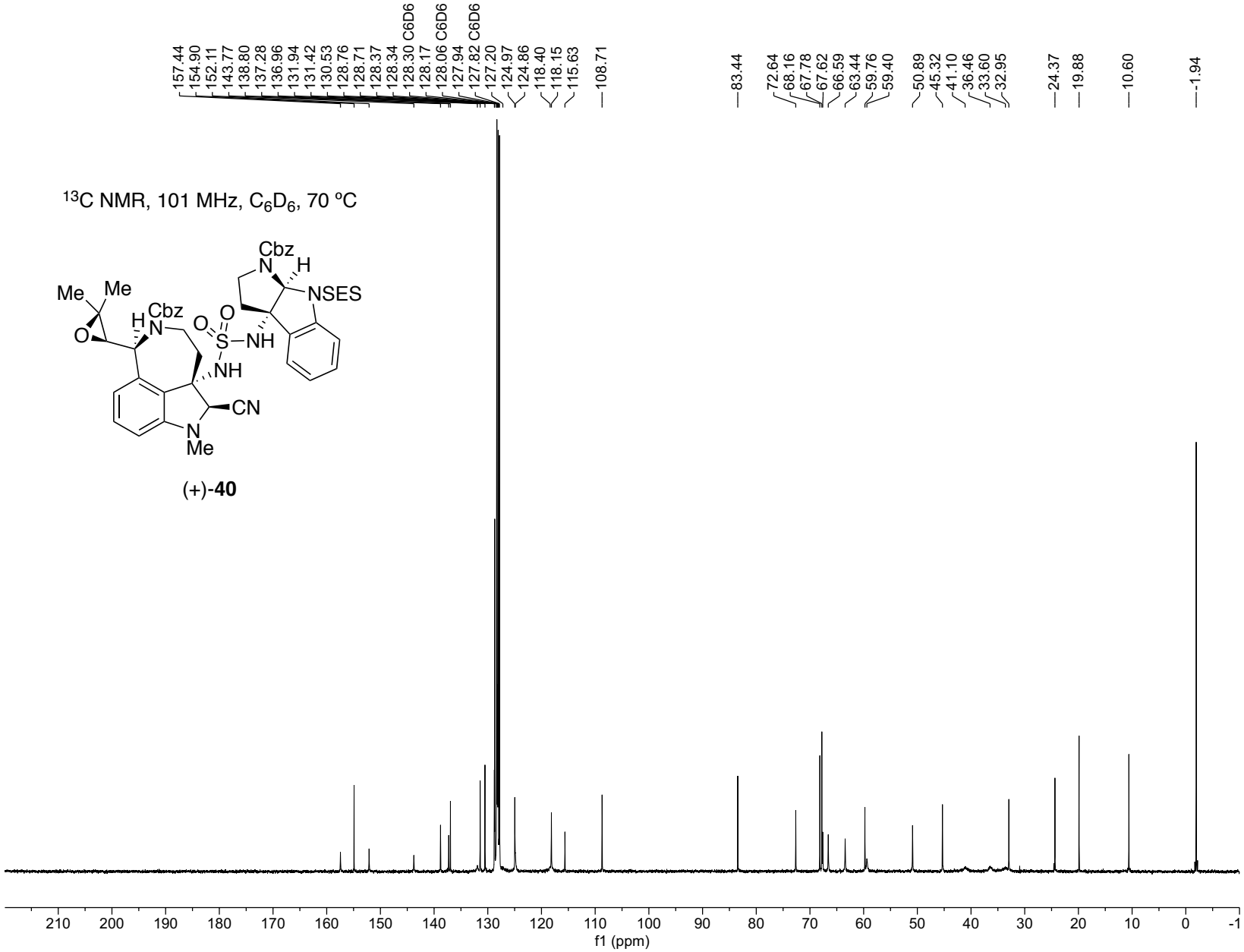

7.33
7.33
7.31
7.16 C6D6
7.12
7.11
7.10
6.96
6.94
6.92
6.82
6.80
6.55
6.35
6.33
5.18
5.15
5.12
5.09
5.06
4.97
3.77
3.63
3.61
3.56
3.27
3.27
3.15
2.56
2.55
2.53
2.52
2.50
2.49
2.15
2.12
2.11
2.01
1.44
1.29
1.27
0.10
1H NMR, 400 MHz, C6D6, 70 ºC
Me
Me
O
H
N
Cbz
O
O
S
NH
NH
O
N
Me
Cbz
N
H
NSES
(–)-39
f1 (ppm)

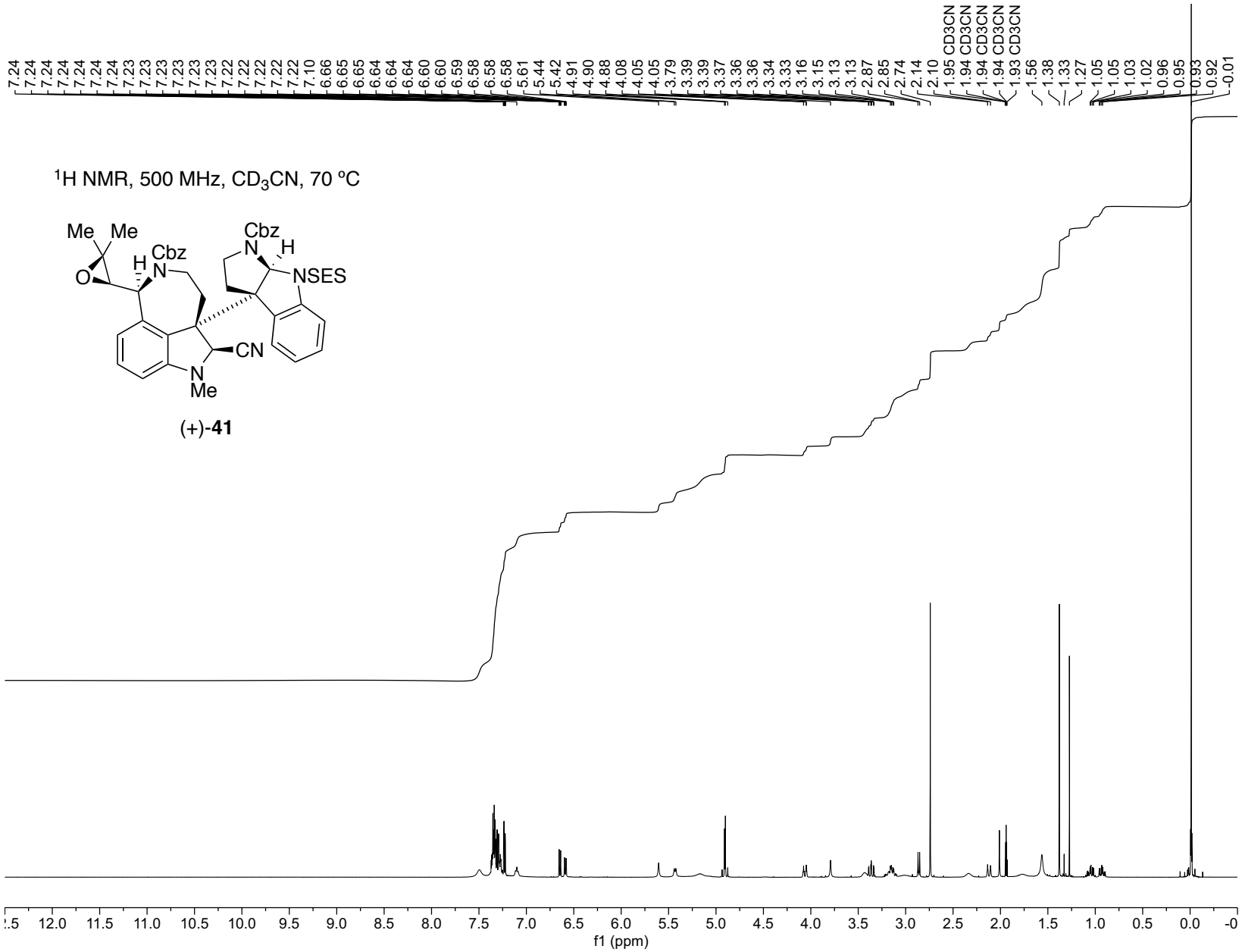

176.56
156.19
154.99
144.89
143.63
137.61
137.02
132.13
130.08
129.73
128.83
128.80
128.58
128.53
128.52
128.30 C6D6
128.06 C6D6
127.88
127.82 C6D6
125.25
124.48
120.79
117.21
108.08
83.32
73.10
67.79
67.72
62.89
59.11
51.49
45.63
36.53
32.88
26.81
24.92
19.40
10.60
-2.03
13C NMR, 101 MHz, C6D6, 70 ºC
Cbz
N
H
NSES
Me
Me
H
Cbz
N
O
O
O
S
NH
NH
O
N
Me
(–)-39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

^{1}H NMR, 500 MHz, C_6D_6, 70 °C

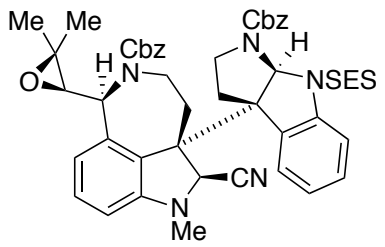


(+)-**40**

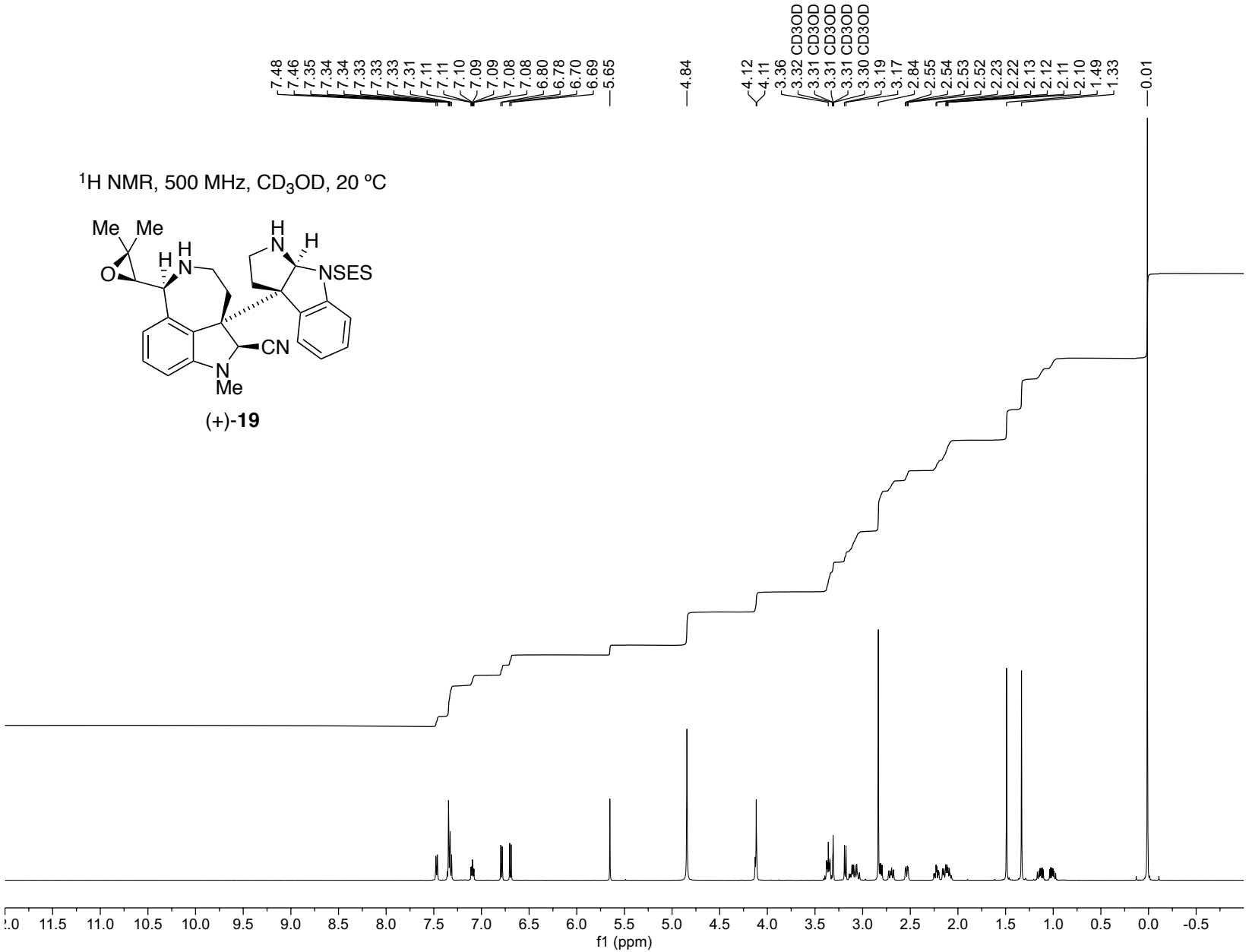

157.44
154.90
152.11
143.77
138.80
137.28
136.96
131.94
131.42
130.53
128.76
128.71
128.37
128.34
128.30 C6D6
128.17
128.06 C6D6
127.94
127.82 C6D6
127.20
124.97
124.86
118.40
118.15
115.63
108.71
83.44
72.64
68.16
67.78
67.62
66.59
63.44
59.76
59.40
50.89
45.32
41.10
36.46
33.60
32.95
24.37
19.88
10.60
-1.94
13C NMR, 101 MHz, C6D6, 70 ºC
Cbz
N
H
NSES
Me
Me
O
H
N
Cbz
O
O
S
NH
NH
CN
N
Me
(+)-40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.24 7.24 7.24 7.24 7.24 7.24 7.23 7.23 7.23 7.23 7.22 7.22 7.22 7.22 7.10 6.66 6.65 6.65 6.64 6.64 6.64 6.60 6.60 6.59 6.58 6.58 6.58 5.61 5.44 5.42 4.91 4.90 4.88 4.08 4.05 4.05 3.79 3.39 3.39 3.37 3.36 3.36 3.34 3.33 3.16 3.15 3.13 3.13 2.87 2.85 2.74 2.14 2.10
1.95 CD3CN 1.94 CD3CN 1.94 CD3CN 1.94 CD3CN 1.93 CD3CN
1.56 1.38 1.33 1.27 1.05 1.05 1.03 1.02 0.96 0.95 0.93 0.92 -0.01
1H NMR, 500 MHz, CD3CN, 70 ºC
Me Me
O
H
Cbz
N
Cbz
N
H
NSES
CN
N
Me
(+)-41
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
f1 (ppm)

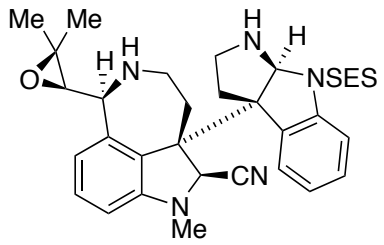
^{13}C NMR, 126 MHz, CD_3CN, 70 °C



(+)-**41**

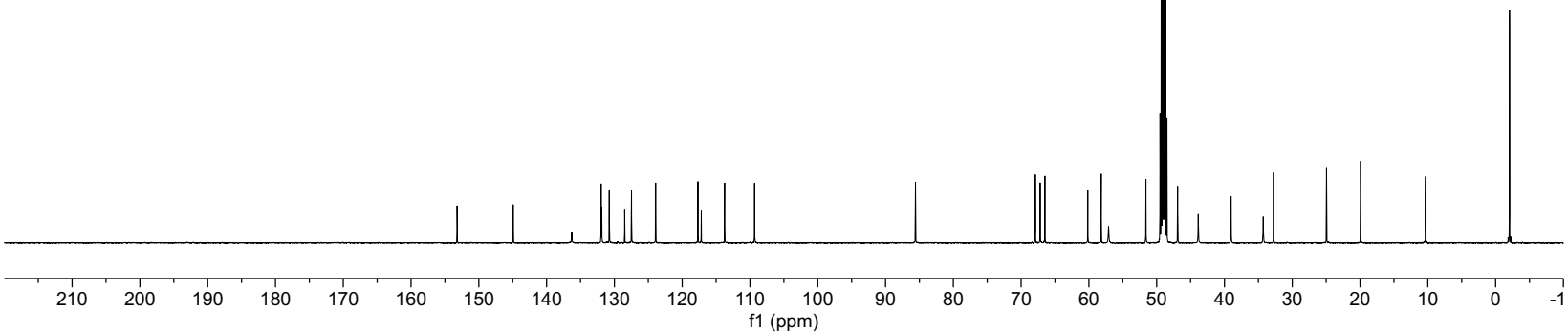

7.48
7.46
7.35
7.34
7.34
7.33
7.33
7.33
7.31
7.11
7.11
7.10
7.09
7.09
7.08
7.08
6.80
6.78
6.70
6.69
5.65
4.84
4.12
4.11
3.36
3.32 CD3OD
3.31 CD3OD
3.31 CD3OD
3.31 CD3OD
3.30 CD3OD
3.19
3.17
2.84
2.55
2.54
2.53
2.52
2.23
2.22
2.13
2.12
2.11
2.10
1.49
1.33
0.01
1H NMR, 500 MHz, CD3OD, 20 ºC
Me
Me
O
H
N
H
N
H
N
H
NSES
CN
N
Me
(+)-19
f1 (ppm)

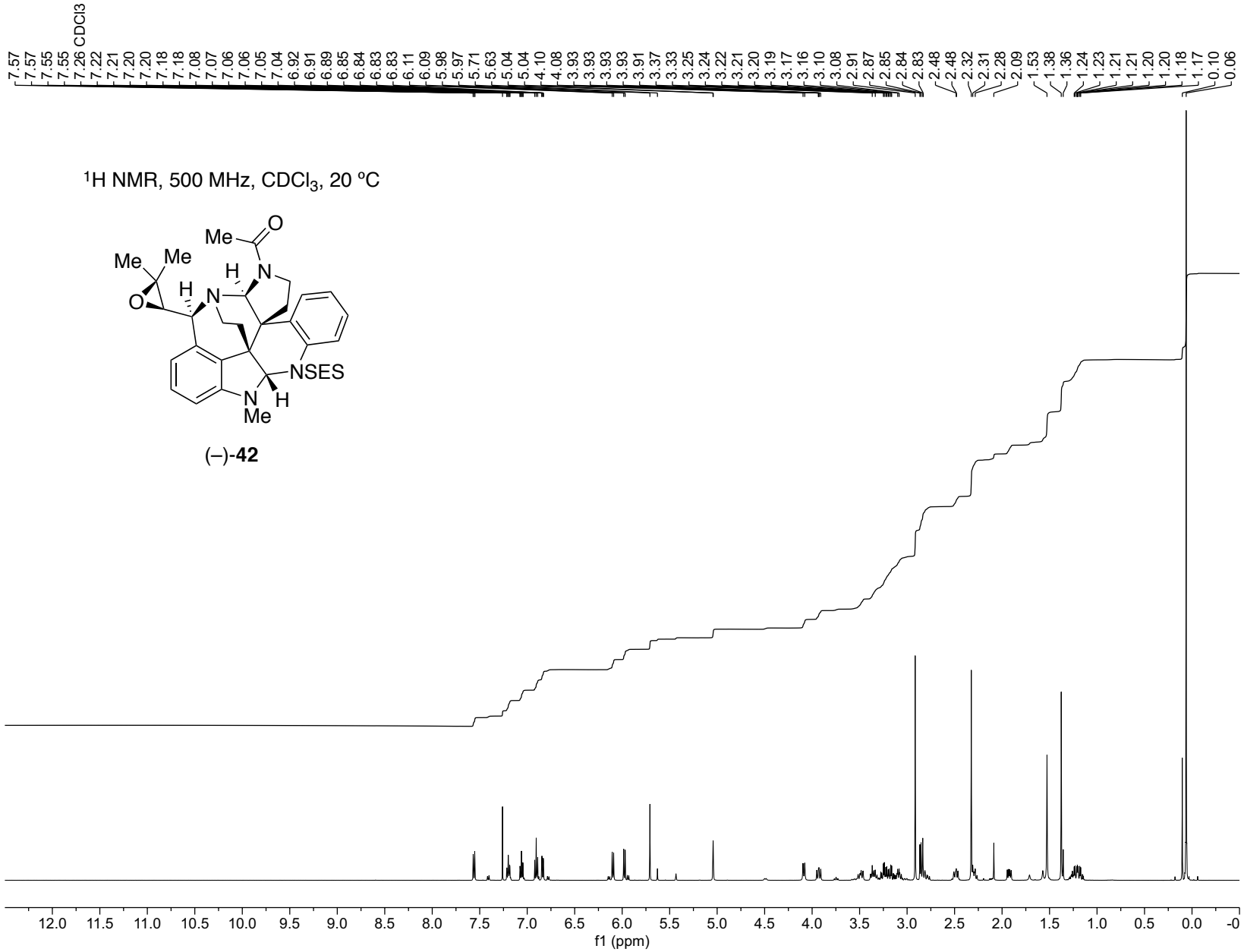
^{13}C NMR, 126 MHz, CD_3OD, 20 °C

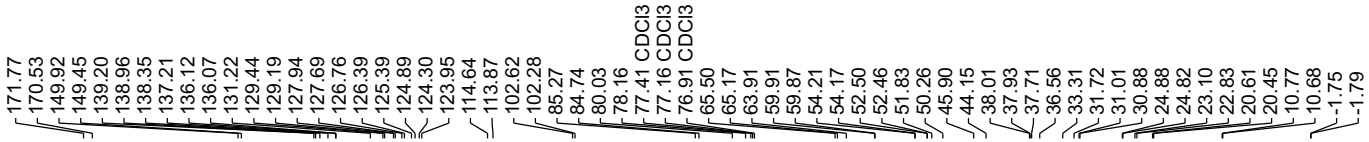


(+)-**19**

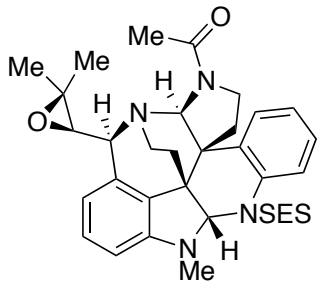
153.21
144.93
136.30
131.95
131.86
130.76
128.48
127.48
123.91
117.68
117.19
113.74
109.32
85.59
67.90
67.19
66.49
60.16
58.18
57.10
51.59
49.51 CD3OD
49.34 CD3OD
49.17 CD3OD
49.00 CD3OD
48.83 CD3OD
48.66 CD3OD
48.49 CD3OD
46.91
43.87
39.02
34.28
32.75
24.94
19.92
10.33
-2.05



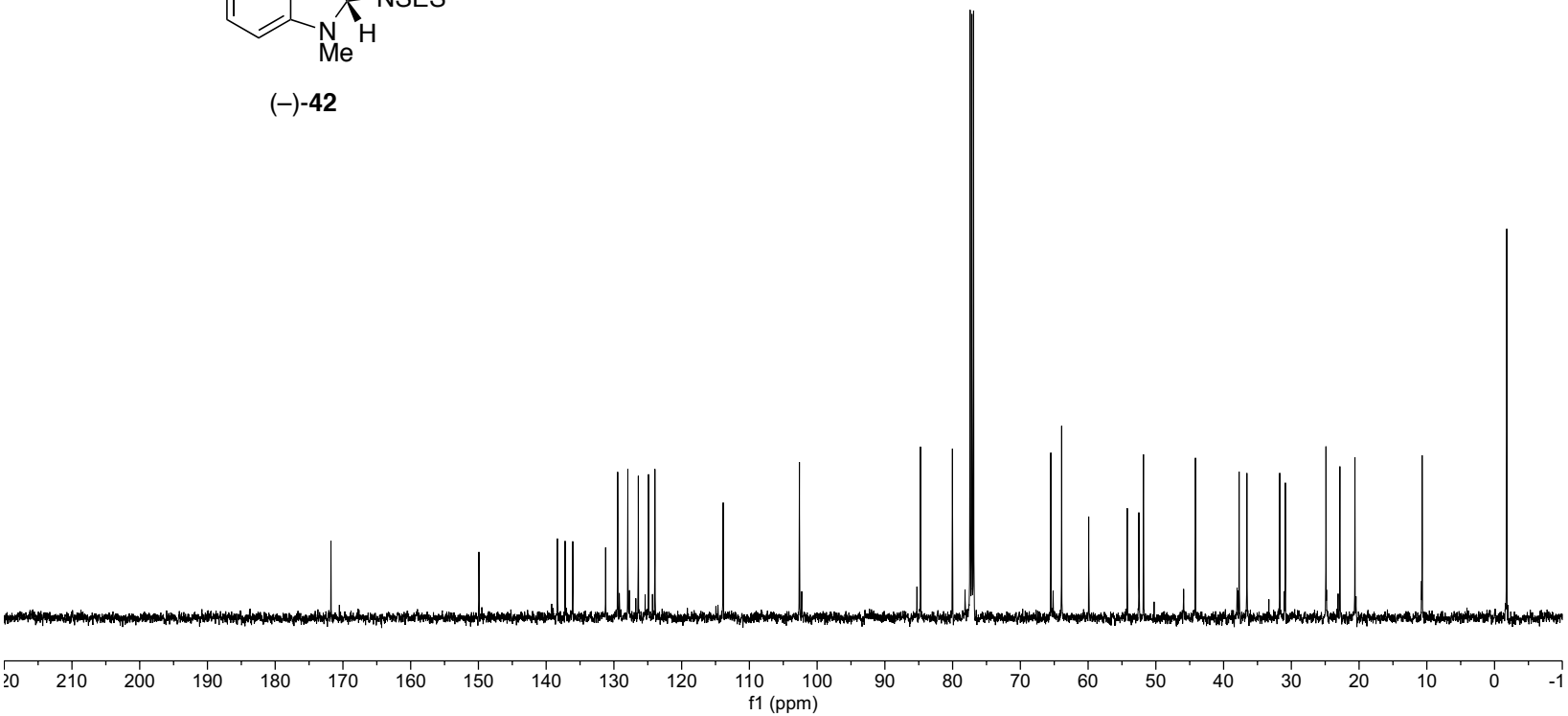

CDCl3
7.57 7.57 7.55 7.55 7.26 7.22 7.21 7.20 7.20 7.18 7.18 7.08 7.07 7.06 7.06 7.05 7.04 6.92 6.91 6.89 6.85 6.84 6.83 6.83 6.11 6.09 5.98 5.97 5.71 5.63 5.04 5.04 4.10 4.08 3.93 3.93 3.93 3.91 3.37 3.33 3.25 3.24 3.22 3.21 3.20 3.19 3.17 3.16 3.10 3.08 2.91 2.87 2.85 2.84 2.83 2.48 2.48 2.32 2.31 2.28 2.09 1.53 1.38 1.36 1.24 1.23 1.21 1.21 1.20 1.20 1.18 1.17 0.10 0.06
1H NMR, 500 MHz, CDCl3, 20 °C
Me
O
Me
Me
H
N
O
H
N
NSES
N
H
Me
(–)-42
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
f1 (ppm)

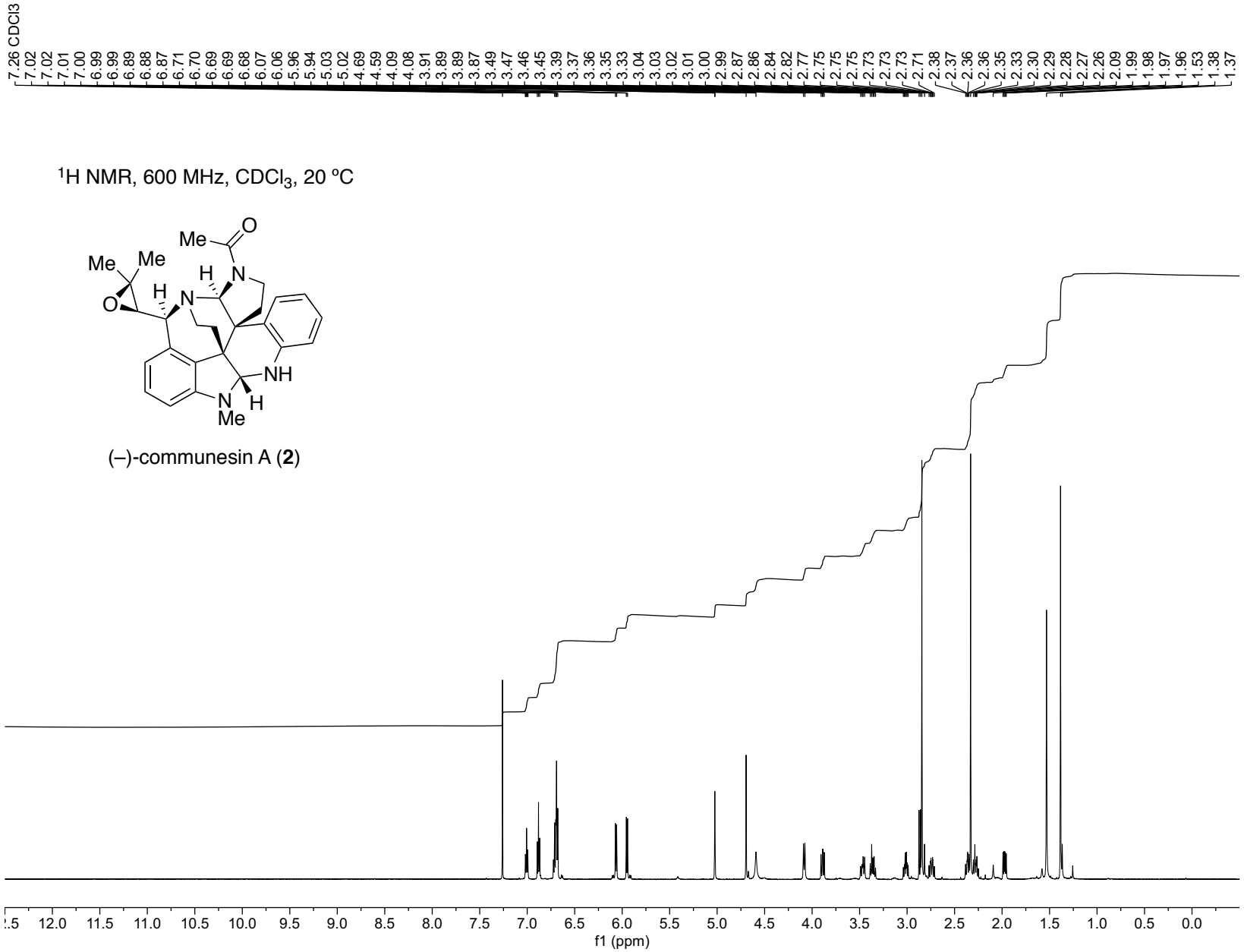


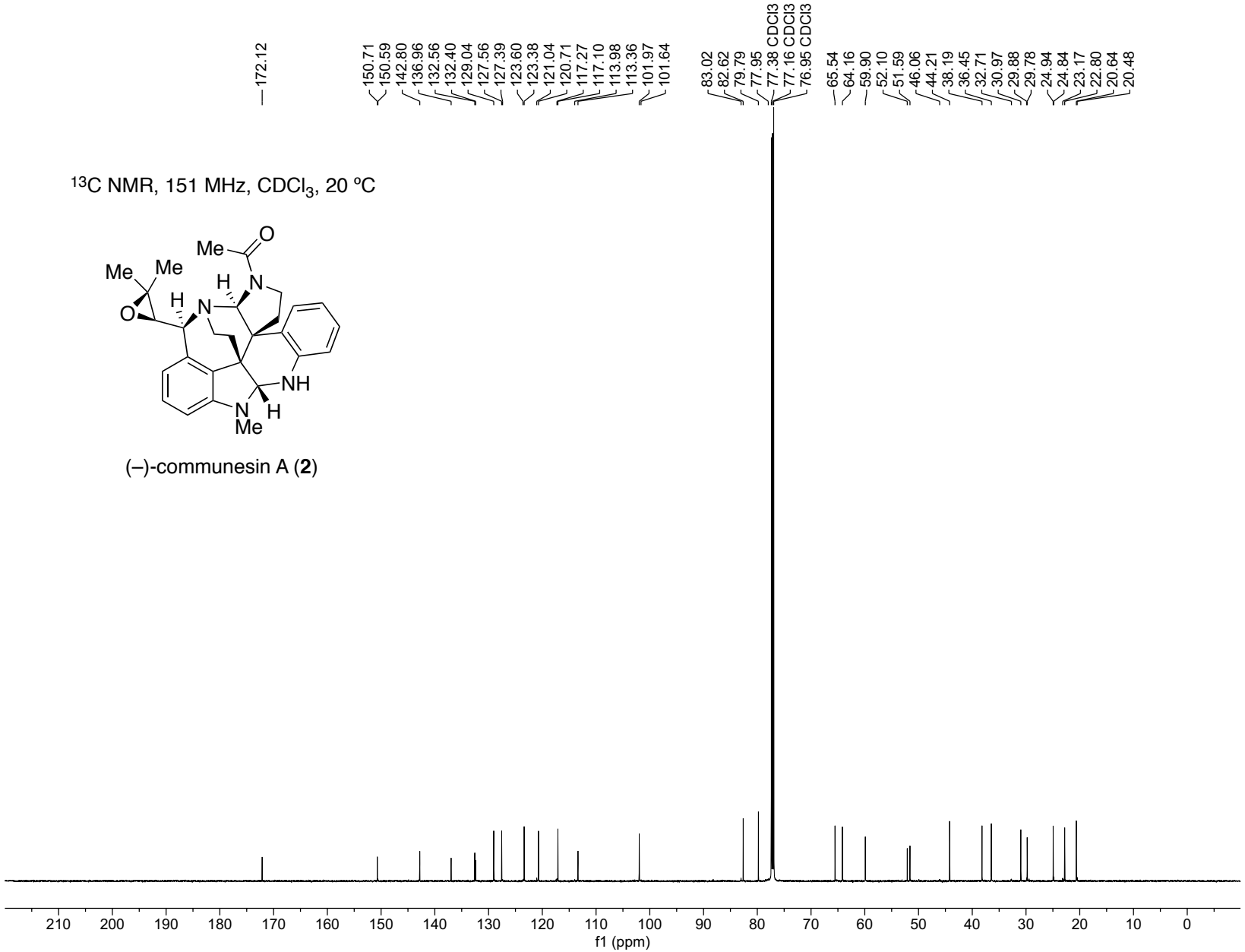
^{13}C NMR, 126 MHz, $CDCl_3$, 20 ºC



(–)-**42**

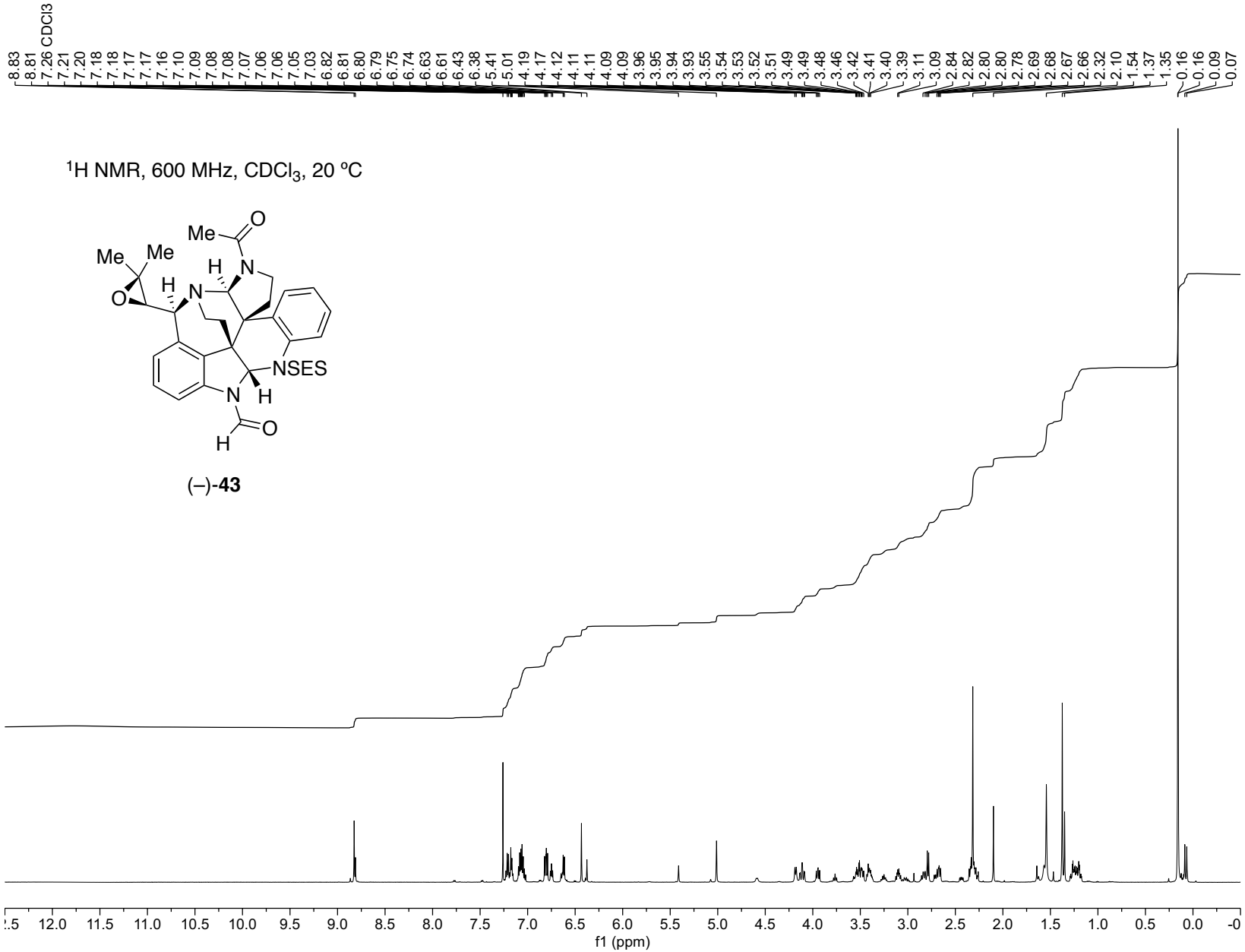


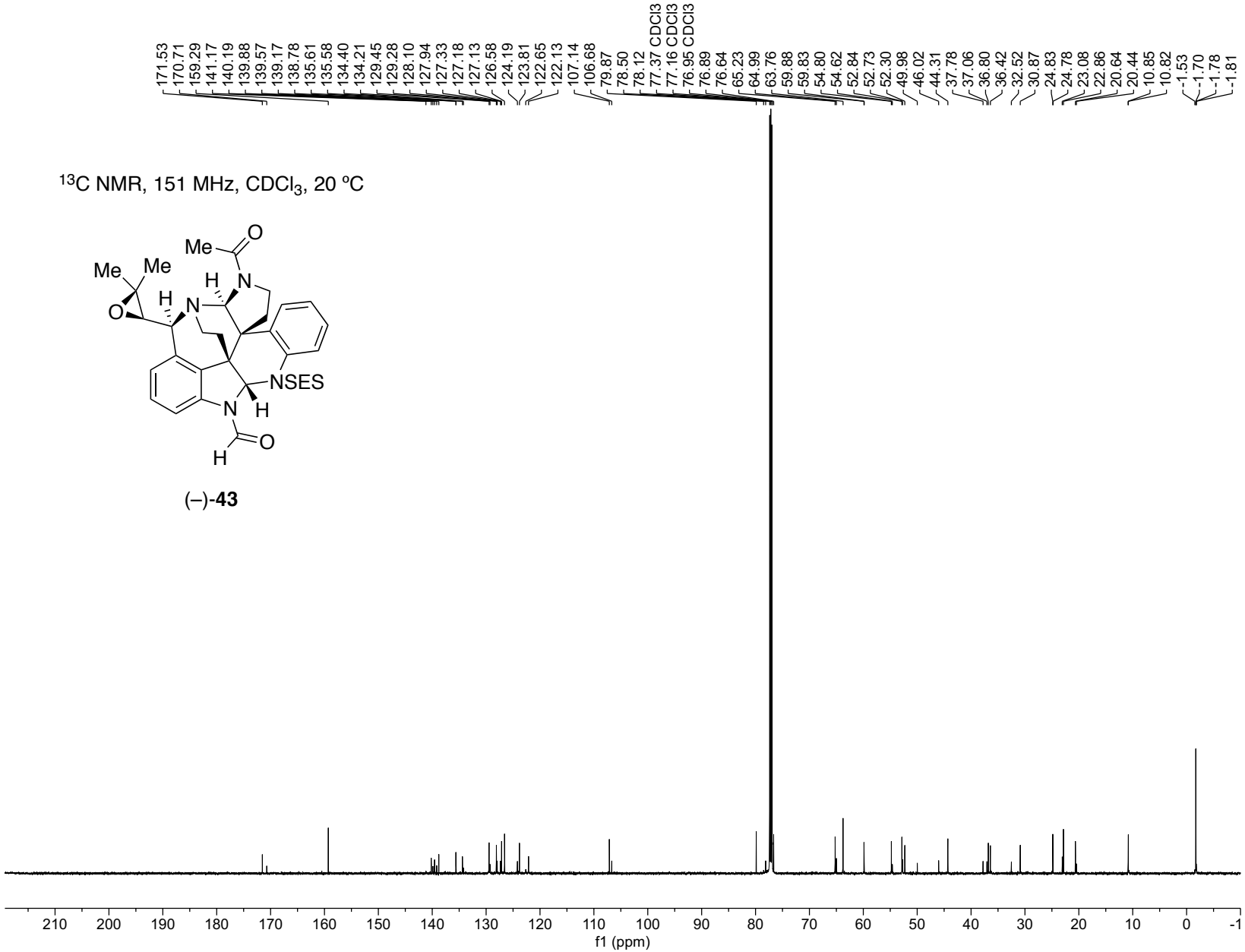

7.26 CDCl3
7.02 7.02 7.01 7.00 6.99 6.99 6.89 6.88 6.87 6.71 6.70 6.69 6.69 6.68 6.07 6.06 5.96 5.94 5.03 5.02 4.69 4.59 4.09 4.08 3.91 3.89 3.89 3.87 3.49 3.47 3.46 3.45 3.39 3.37 3.36 3.35 3.33 3.04 3.03 3.02 3.01 3.00 2.99 2.87 2.86 2.84 2.82 2.77 2.75 2.75 2.75 2.73 2.73 2.73 2.71 2.38 2.37 2.36 2.36 2.35 2.33 2.30 2.29 2.28 2.27 2.26 2.09 1.99 1.98 1.97 1.96 1.53 1.38 1.37
1H NMR, 600 MHz, CDCl3, 20 ºC
Me
O
Me
Me
H
N
O
H
N
NH
N
H
Me
(–)-communesin A (2)
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
f1 (ppm)



^{13}C NMR, 151 MHz, $CDCl_3$, 20 ºC

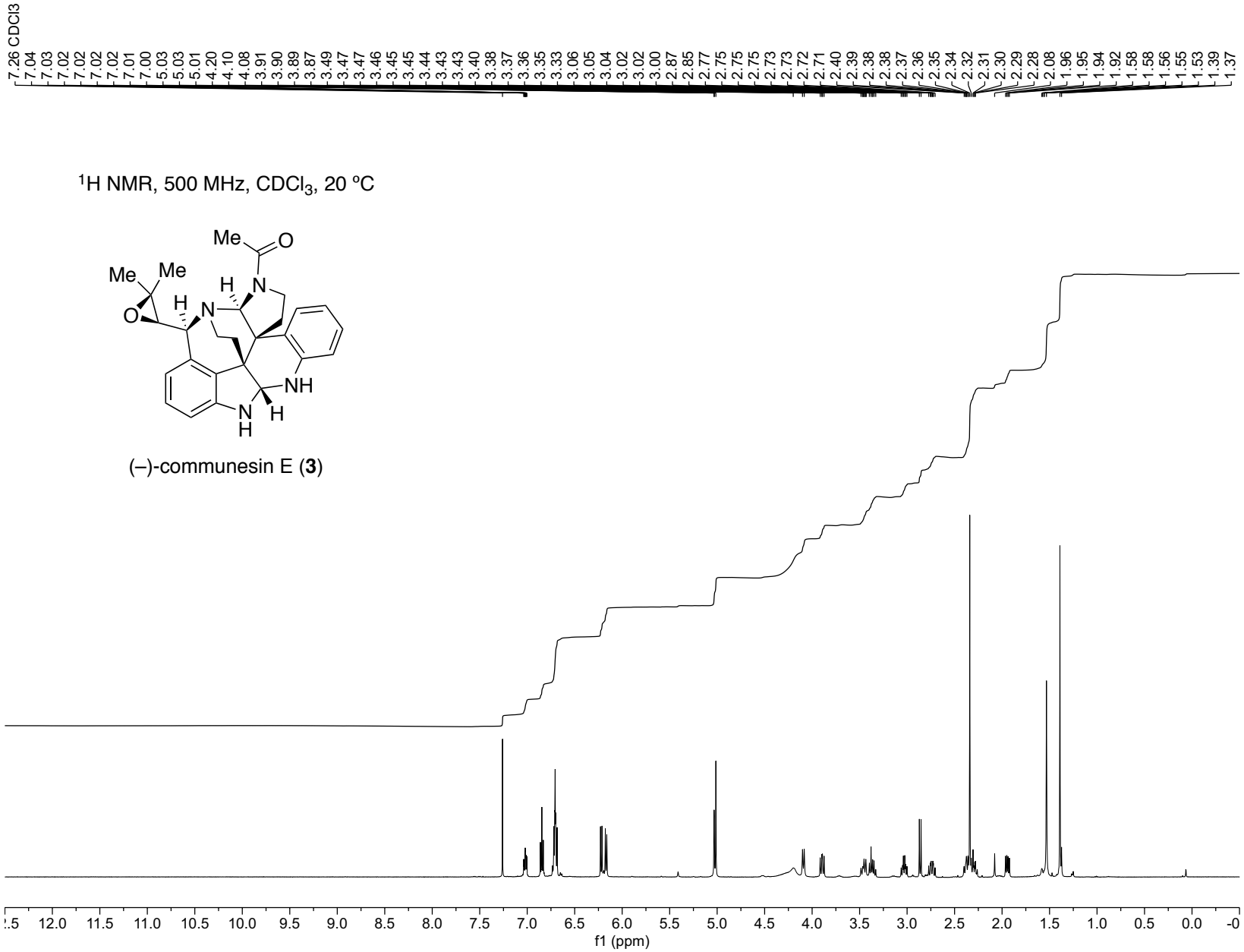
(–)-communesin A (**2**)

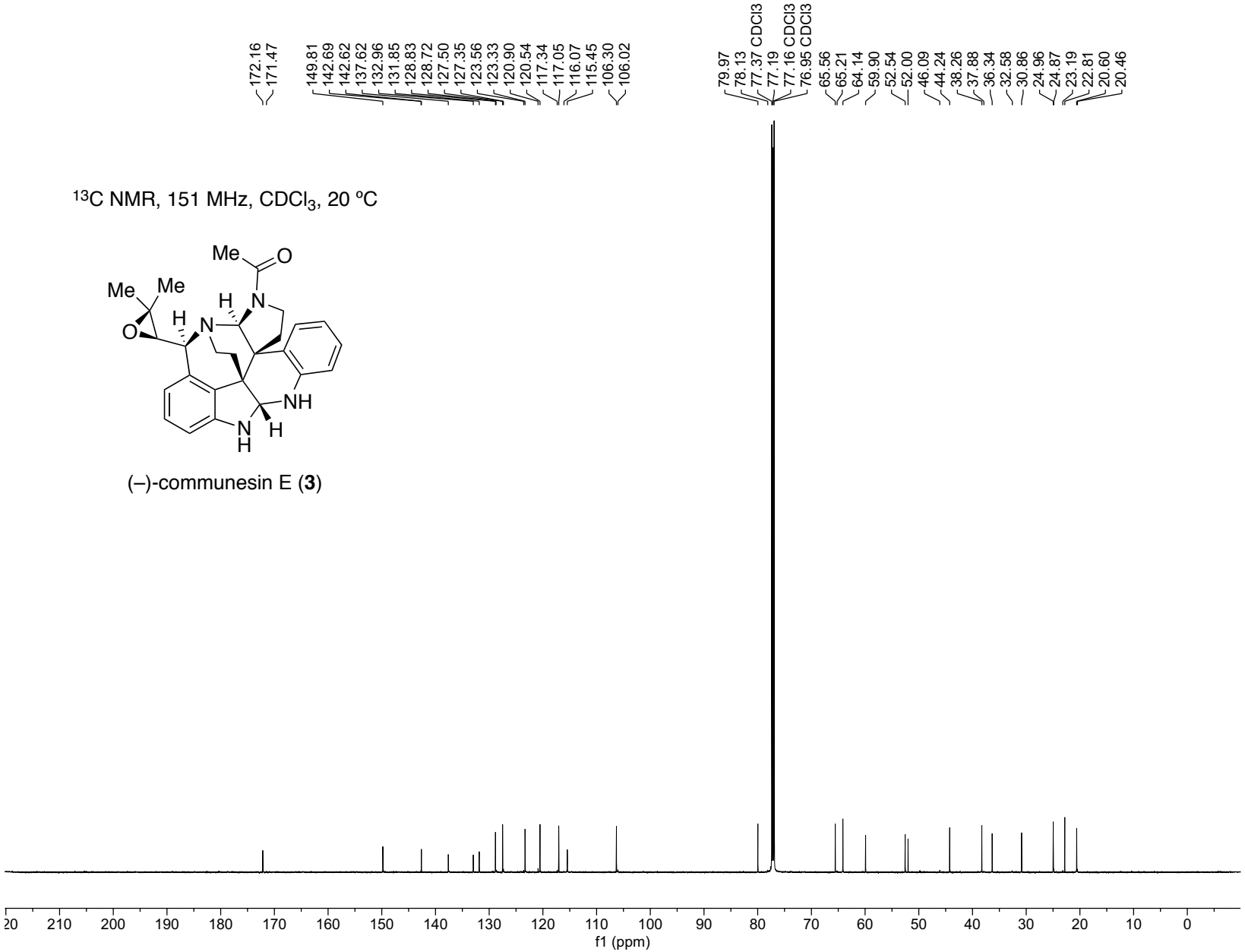

8.83 8.81 7.26 CDCl3 7.21 7.20 7.18 7.18 7.17 7.17 7.16 7.10 7.09 7.08 7.08 7.07 7.06 7.06 7.05 7.03 6.82 6.81 6.80 6.79 6.75 6.74 6.63 6.61 6.43 6.38 5.41 5.01 4.19 4.17 4.12 4.11 4.11 4.09 4.09 3.96 3.95 3.94 3.93 3.55 3.54 3.53 3.52 3.51 3.49 3.49 3.48 3.46 3.42 3.41 3.40 3.39 3.11 3.09 2.84 2.82 2.80 2.80 2.78 2.69 2.68 2.67 2.66 2.32 2.10 1.54 1.37 1.35 0.16 0.16 0.09 0.07
1H NMR, 600 MHz, CDCl3, 20 ºC
Me
O
Me
Me
H
N
H
N
O
NSES
N
H
O
H
(–)-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
f1 (ppm)



^{13}C NMR, 151 MHz, $CDCl_3$, 20 ºC

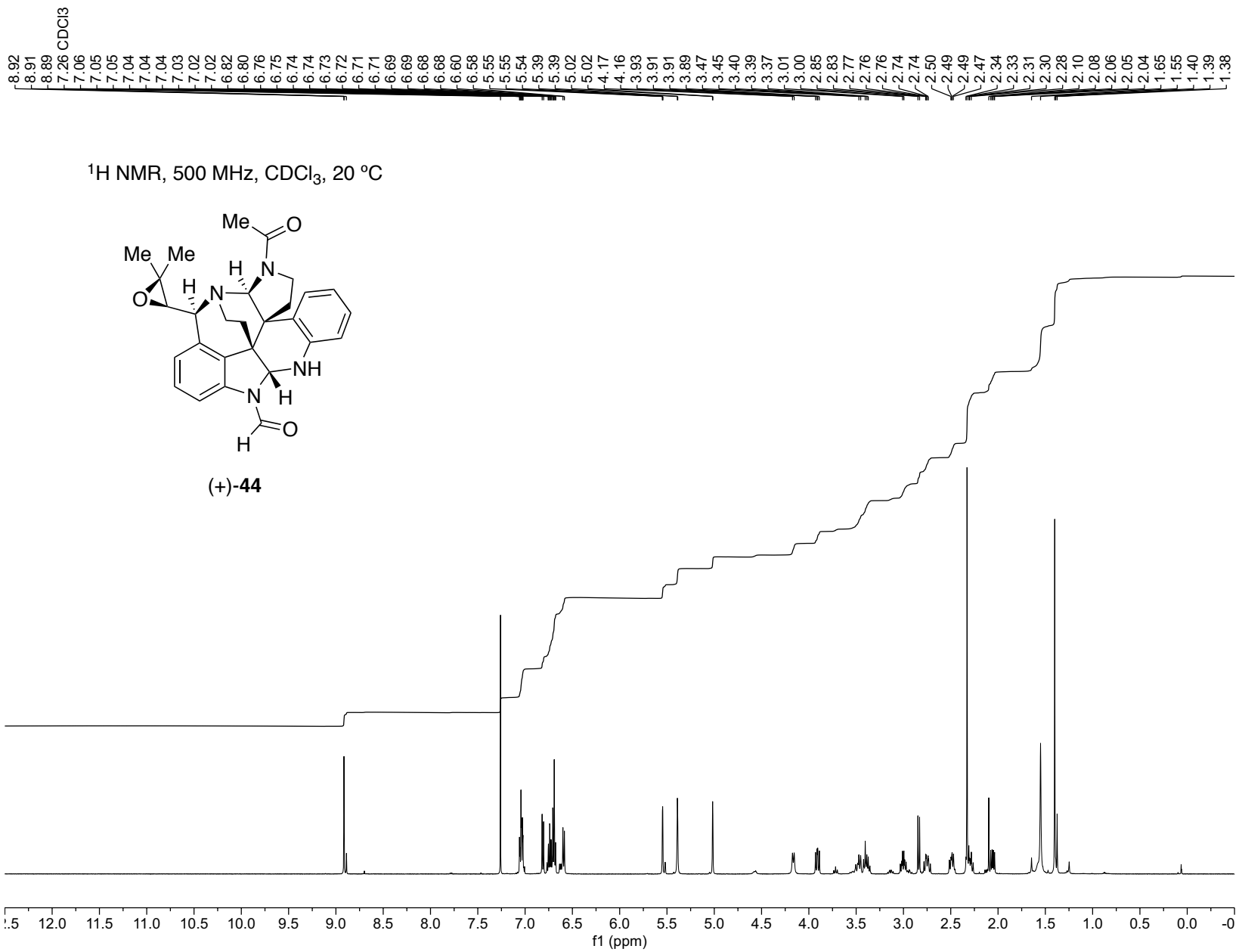
(–)-**43**

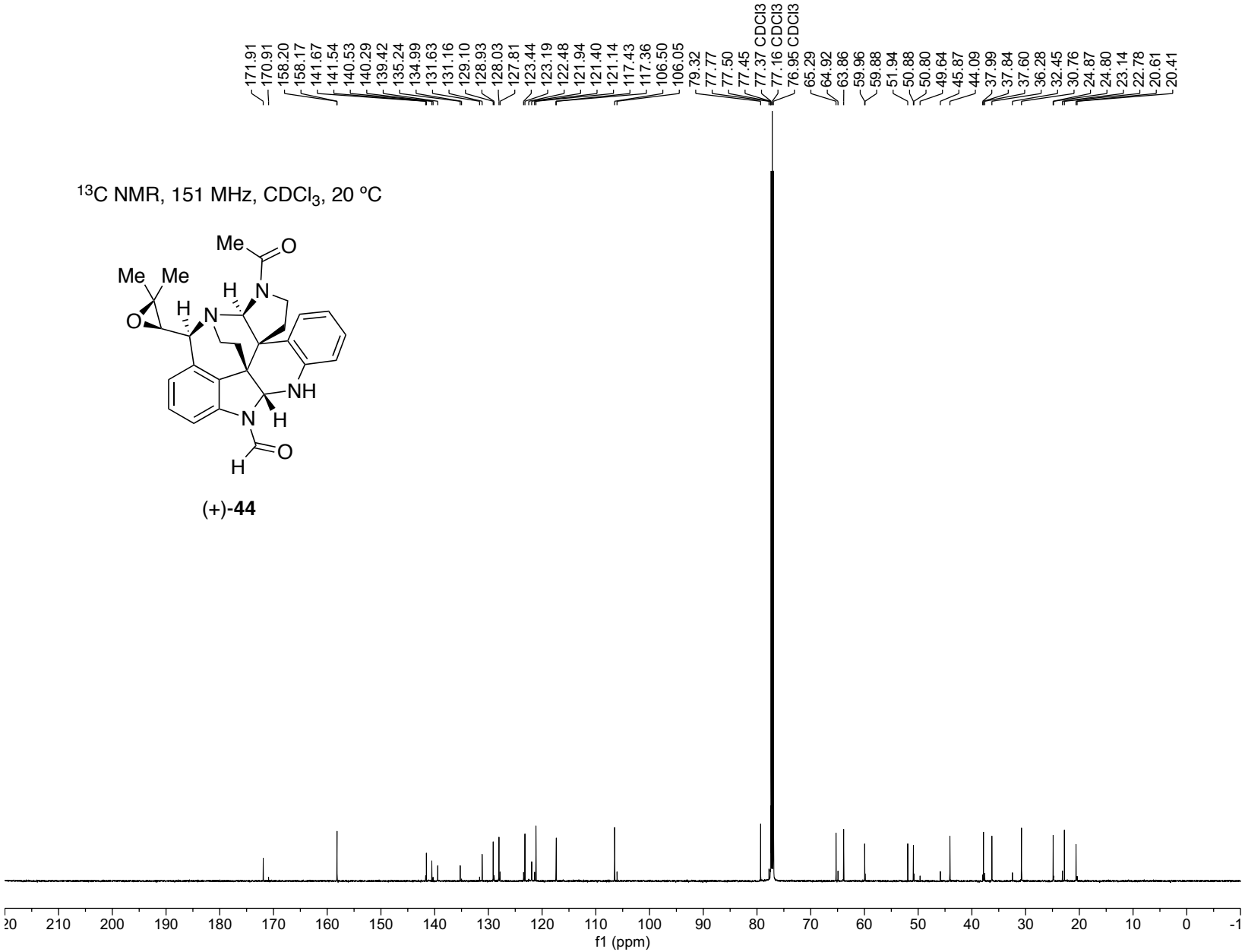

7.26 CDCl3
7.04 7.03 7.02 7.02 7.02 7.02 7.01 7.00 5.03 5.03 5.01 4.20 4.10 4.08 3.91 3.90 3.89 3.87 3.49 3.47 3.47 3.46 3.45 3.45 3.44 3.43 3.40 3.38 3.37 3.36 3.35 3.33 3.06 3.05 3.04 3.02 3.02 3.00 2.87 2.85 2.77 2.75 2.75 2.73 2.73 2.72 2.71 2.40 2.39 2.38 2.38 2.37 2.36 2.35 2.34 2.32 2.31 2.30 2.29 2.28 2.08 1.96 1.95 1.94 1.92 1.58 1.58 1.56 1.55 1.53 1.39 1.37
1H NMR, 500 MHz, CDCl3, 20 ºC
Me
O
Me
Me
H
N
O
H
N
NH
N
H
H
(–)-communesin E (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
f1 (ppm)

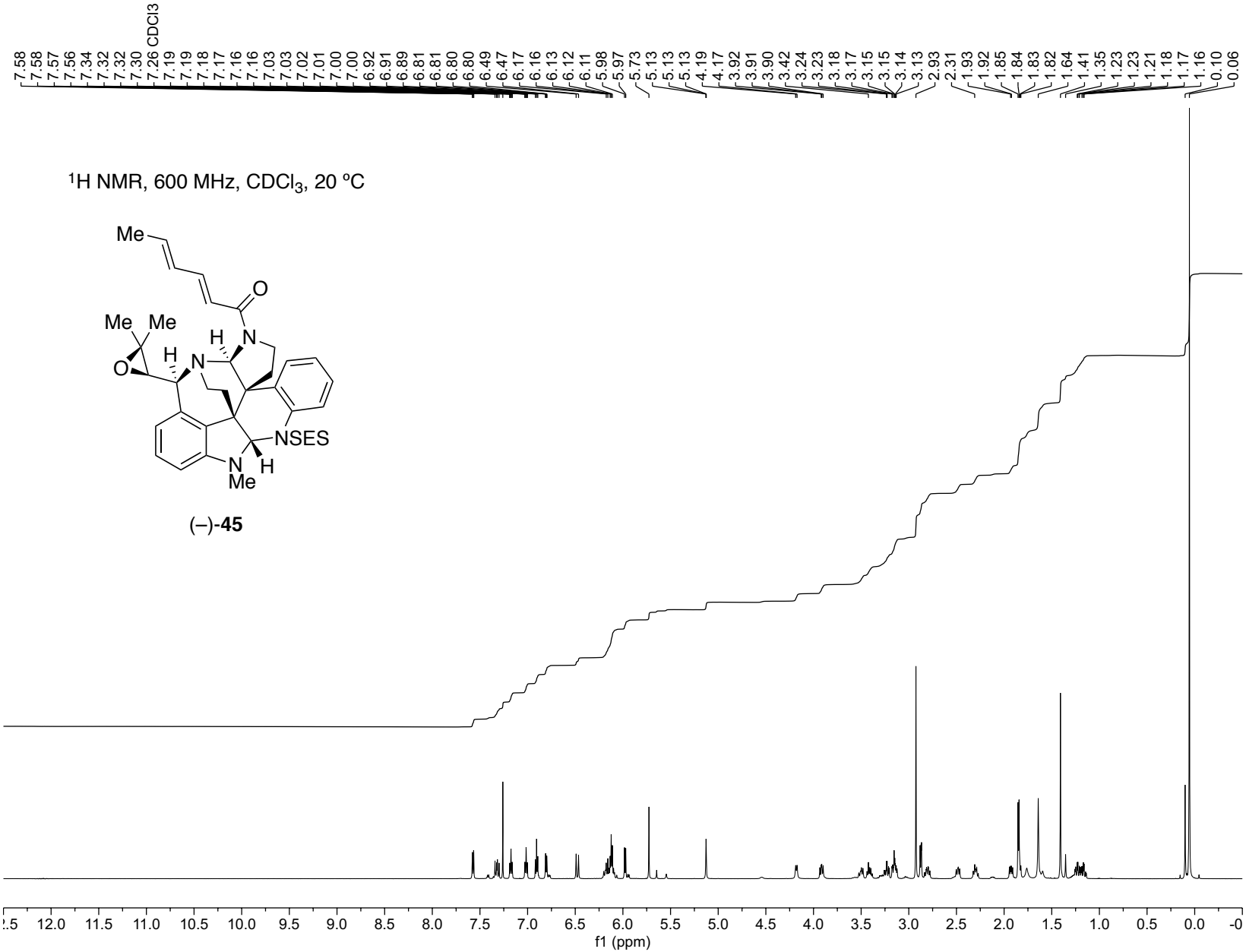


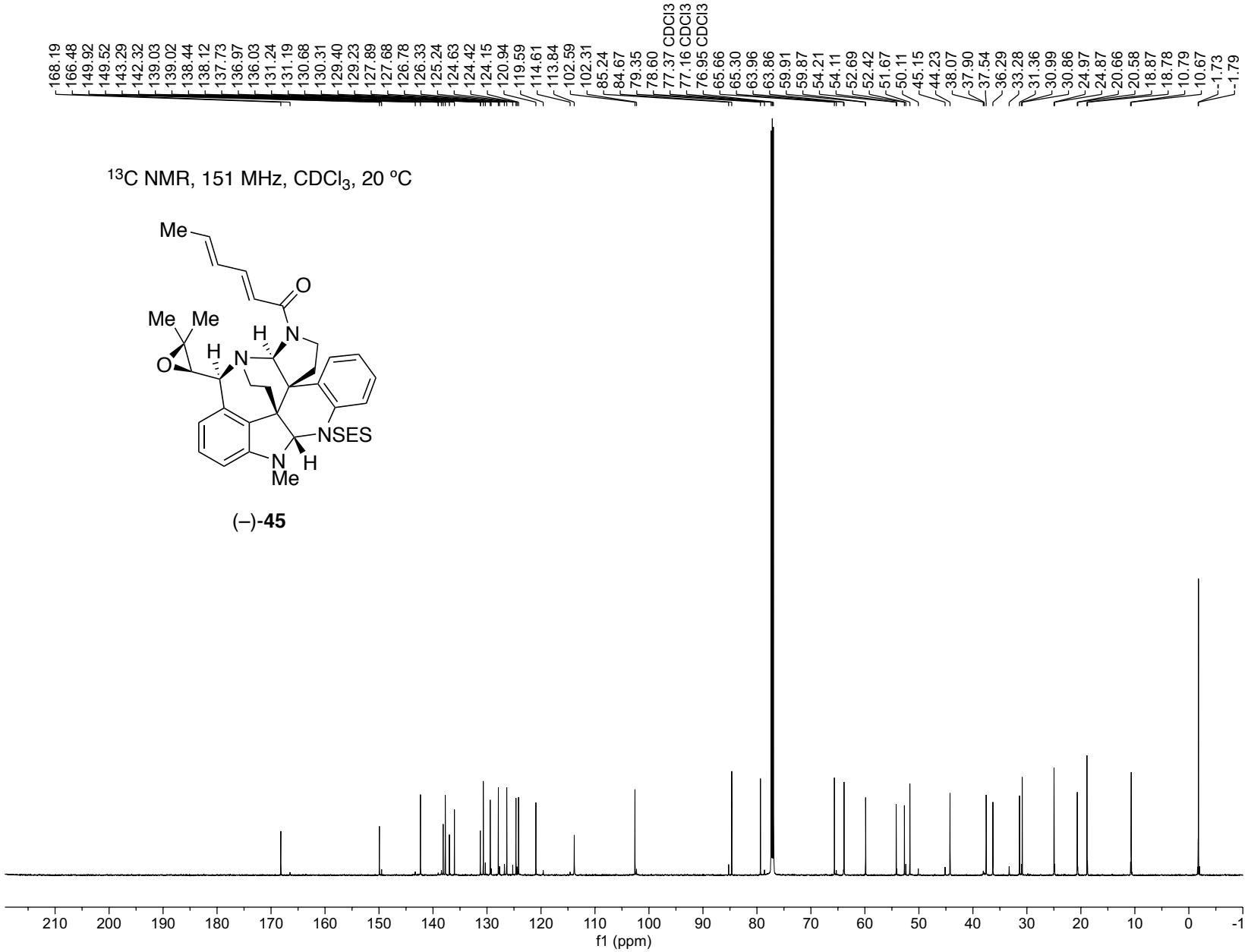
^{13}C NMR, 151 MHz, $CDCl_3$, 20 ºC

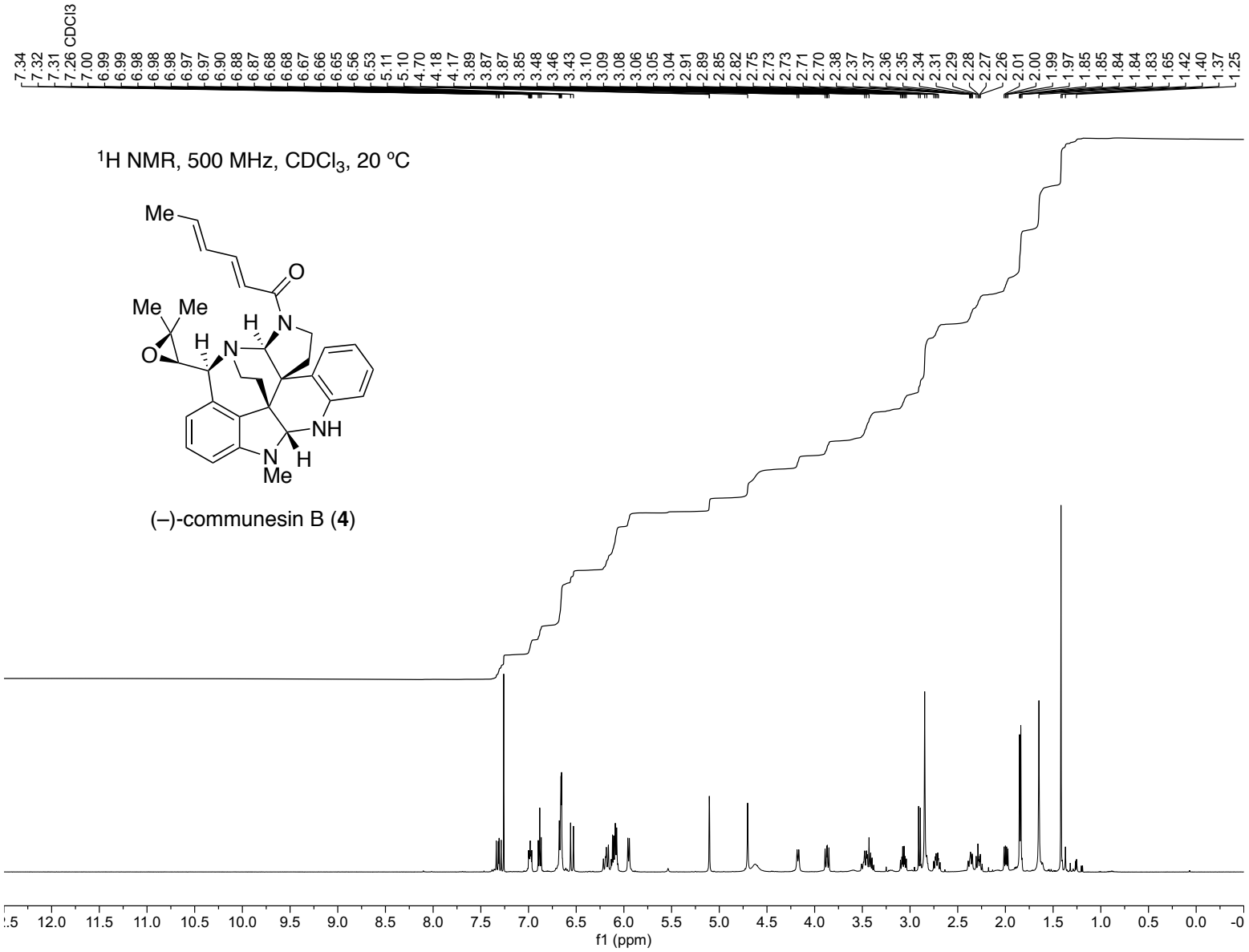
(–)-communesin E (**3**)

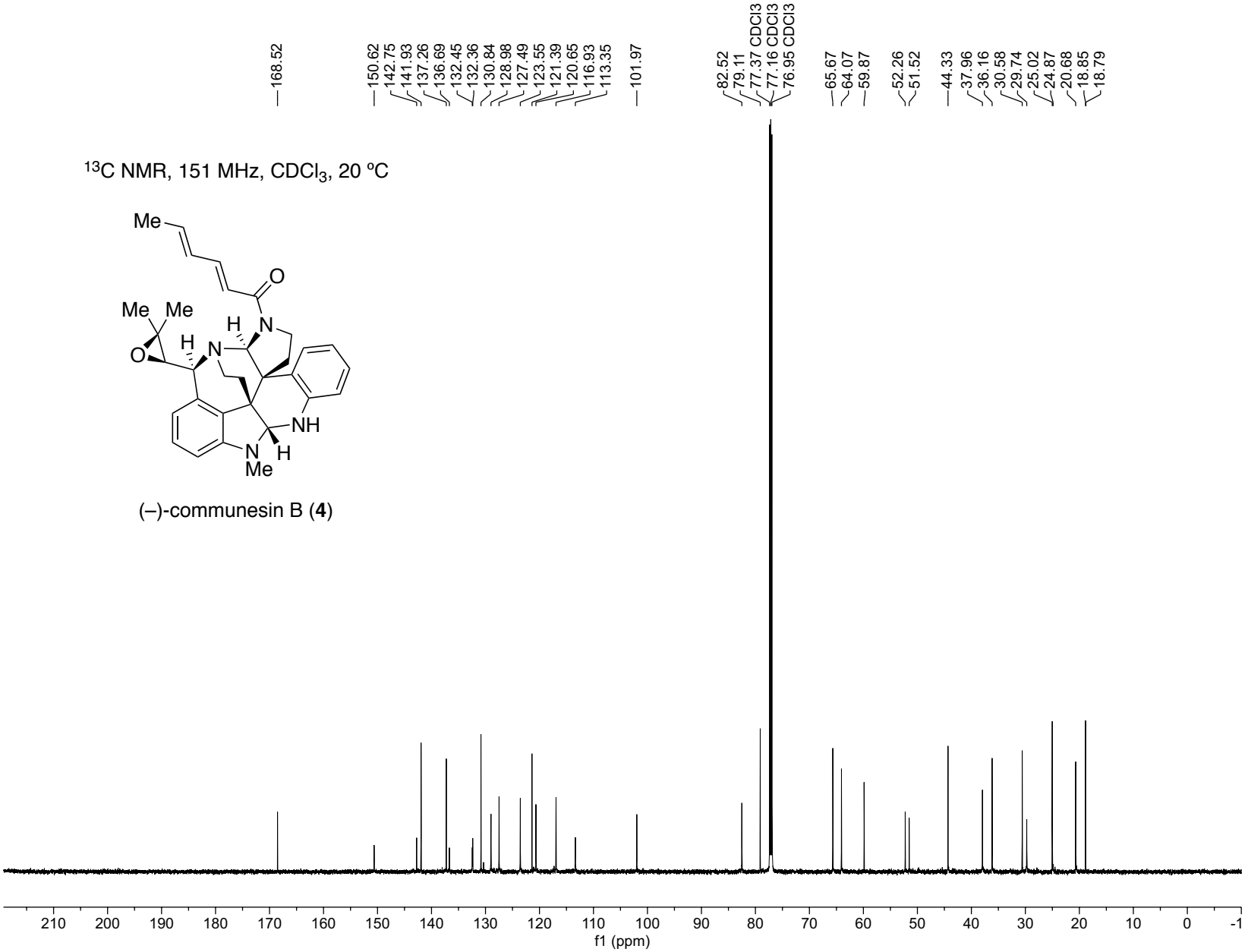

8.92
8.91
8.89
CDCl3
7.26
7.06
7.05
7.05
7.04
7.04
7.04
7.03
7.02
7.02
6.82
6.80
6.76
6.75
6.74
6.74
6.73
6.72
6.71
6.71
6.69
6.69
6.68
6.68
6.60
6.58
5.55
5.55
5.54
5.39
5.39
5.02
5.02
4.17
4.16
3.93
3.91
3.91
3.89
3.47
3.45
3.40
3.39
3.37
3.01
3.00
2.85
2.83
2.77
2.76
2.76
2.74
2.74
2.50
2.49
2.49
2.47
2.34
2.33
2.31
2.30
2.28
2.10
2.08
2.06
2.05
2.04
1.65
1.55
1.40
1.39
1.38
1H NMR, 500 MHz, CDCl3, 20 ºC
Me
O
Me
Me
H
N
O
H
N
NH
N
H
O
H
(+)-44
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
f1 (ppm)

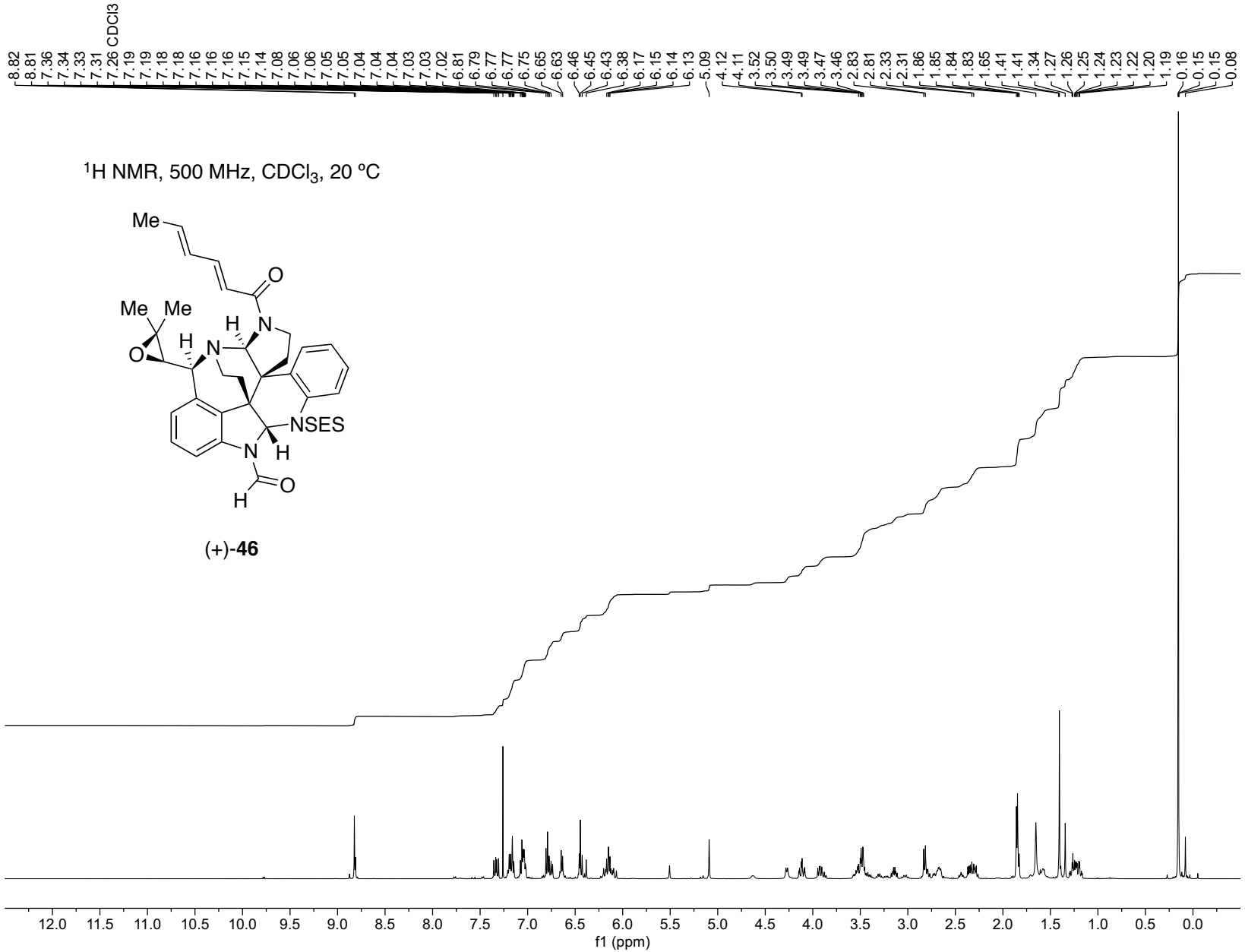

171.91
170.91
158.20
158.17
141.67
141.54
140.53
140.29
139.42
135.24
134.99
131.63
131.16
129.10
128.93
128.03
127.81
123.44
123.19
122.48
121.94
121.40
121.14
117.43
117.36
106.50
106.05
79.32
77.77
77.50
77.45
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
65.29
64.92
63.86
59.96
59.88
51.94
50.88
50.80
49.64
45.87
44.09
37.99
37.84
37.60
36.28
32.45
30.76
24.87
24.80
23.14
22.78
20.61
20.41
13C NMR, 151 MHz, CDCl3, 20 °C
Me
O
Me
Me
H
N
H
N
O
NH
N
H
O
H
(+)-44
f1 (ppm)

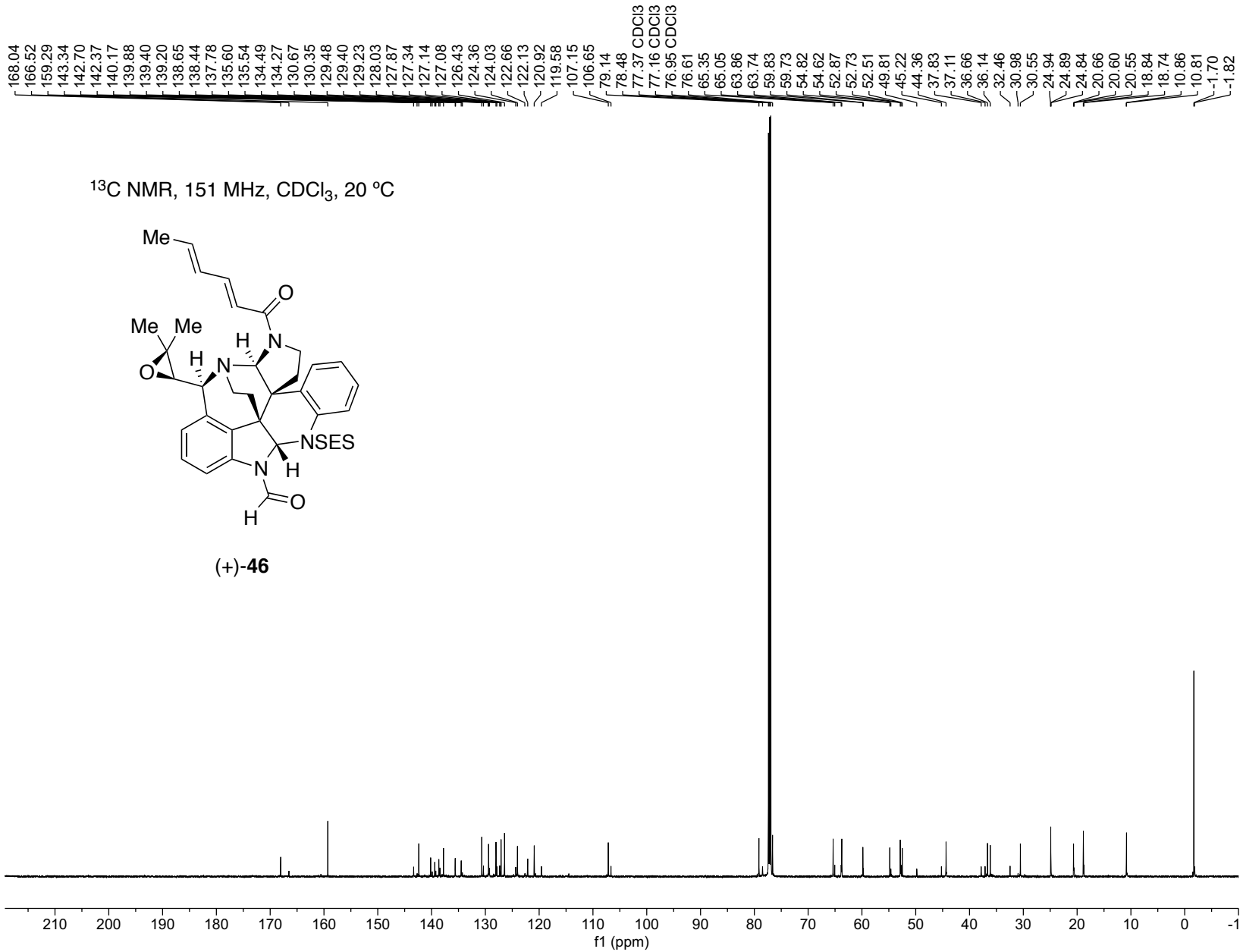

CDCl3
7.58 7.58 7.57 7.56 7.34 7.32 7.32 7.30 7.26 7.19 7.19 7.18 7.17 7.16 7.16 7.03 7.03 7.02 7.01 7.00 7.00 6.92 6.91 6.89 6.81 6.81 6.80 6.80 6.49 6.47 6.17 6.16 6.13 6.12 6.11 5.98 5.97 5.73 5.13 5.13 5.13 4.19 4.17 3.92 3.91 3.90 3.42 3.24 3.23 3.18 3.17 3.15 3.15 3.14 3.13 2.93 2.31 1.93 1.92 1.85 1.84 1.83 1.82 1.64 1.41 1.35 1.23 1.23 1.21 1.18 1.17 1.16 0.10 0.06
1H NMR, 600 MHz, CDCl3, 20 ºC
Me
O
Me Me
H
N
H
N
O
NSES
N H
Me
(–)-45
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
f1 (ppm)

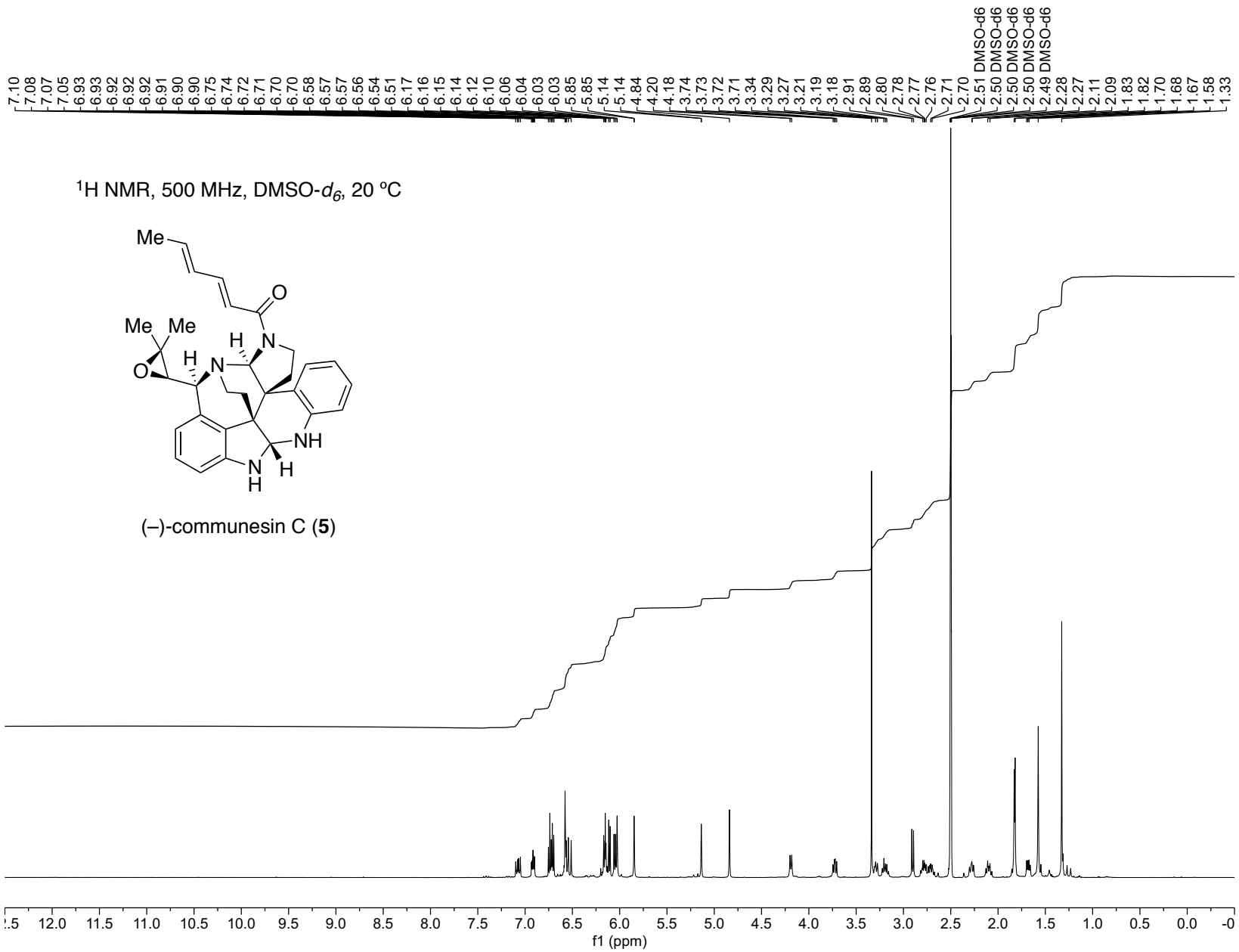

168.19
166.48
149.92
149.52
143.29
142.32
139.03
139.02
138.44
138.12
137.73
136.97
136.03
131.24
131.19
130.68
130.31
129.40
129.23
127.89
127.68
126.78
126.33
125.24
124.63
124.42
124.15
120.94
119.59
114.61
113.84
102.59
102.31
85.24
84.67
79.35
78.60
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
65.66
65.30
63.96
63.86
59.91
59.87
54.21
54.11
52.69
52.42
51.67
50.11
45.15
44.23
38.07
37.90
37.54
36.29
33.28
31.36
30.99
30.86
24.97
24.87
20.66
20.58
18.87
18.78
10.79
10.67
-1.73
-1.79
13C NMR, 151 MHz, CDCl3, 20 ºC
Me
O
Me Me
H
N
O
H
N
NSES
N
H
Me
(–)-45
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

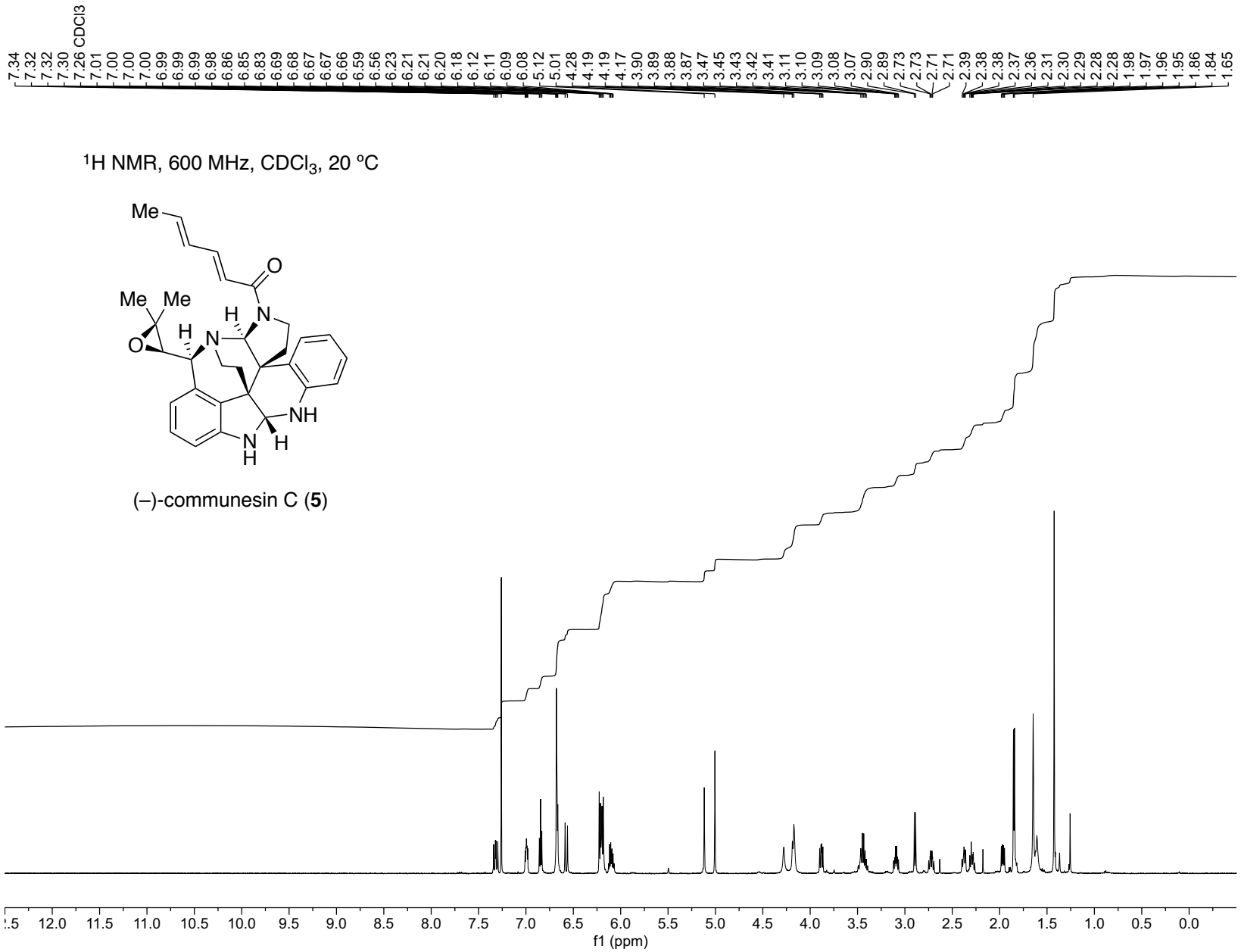

CDCl3
7.34 7.32 7.31 7.26 7.00 6.99 6.99 6.98 6.98 6.98 6.97 6.97 6.90 6.88 6.87 6.68 6.68 6.67 6.66 6.65 6.56 6.53 5.11 5.10 4.70 4.18 4.17 3.89 3.87 3.87 3.85 3.48 3.46 3.43 3.10 3.09 3.08 3.06 3.05 3.04 2.91 2.89 2.85 2.82 2.75 2.73 2.73 2.71 2.70 2.38 2.37 2.37 2.36 2.35 2.34 2.31 2.29 2.28 2.27 2.26 2.01 2.00 1.99 1.97 1.85 1.85 1.84 1.84 1.83 1.65 1.42 1.40 1.37 1.25
1H NMR, 500 MHz, CDCl3, 20 ºC
Me
O
Me Me
H N
O
H N
NH
N H
Me
(–)-communesin B (4)
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
f1 (ppm)

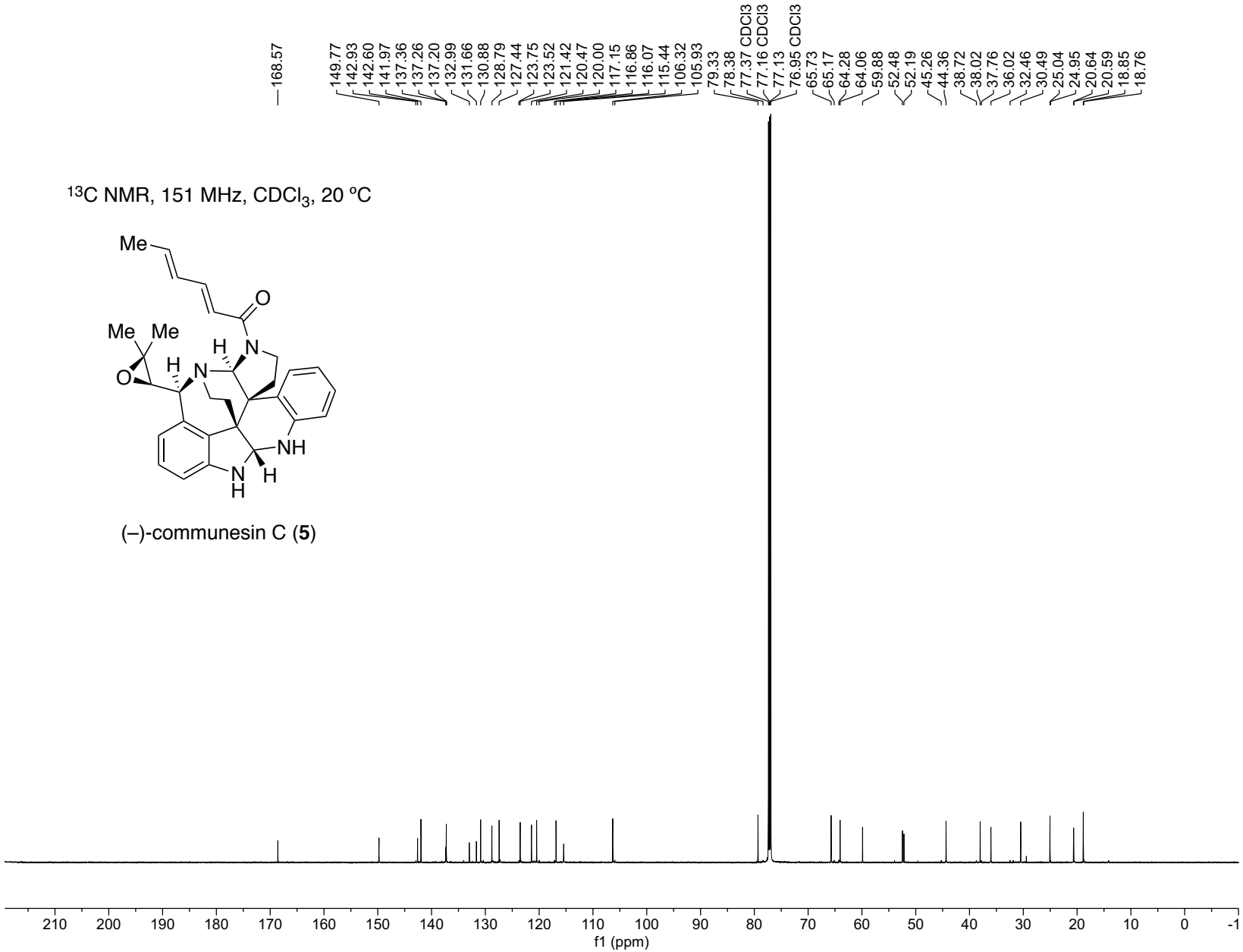

168.52
150.62
142.75
141.93
137.26
136.69
132.45
132.36
130.84
128.98
127.49
123.55
121.39
120.65
116.93
113.35
101.97
82.52
79.11
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
65.67
64.07
59.87
52.26
51.52
44.33
37.96
36.16
30.58
29.74
25.02
24.87
20.68
18.85
18.79
13C NMR, 151 MHz, CDCl3, 20 ºC
Me
O
Me Me
H
N
H
N
O
NH
N H
Me
(–)-communesin B (4)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

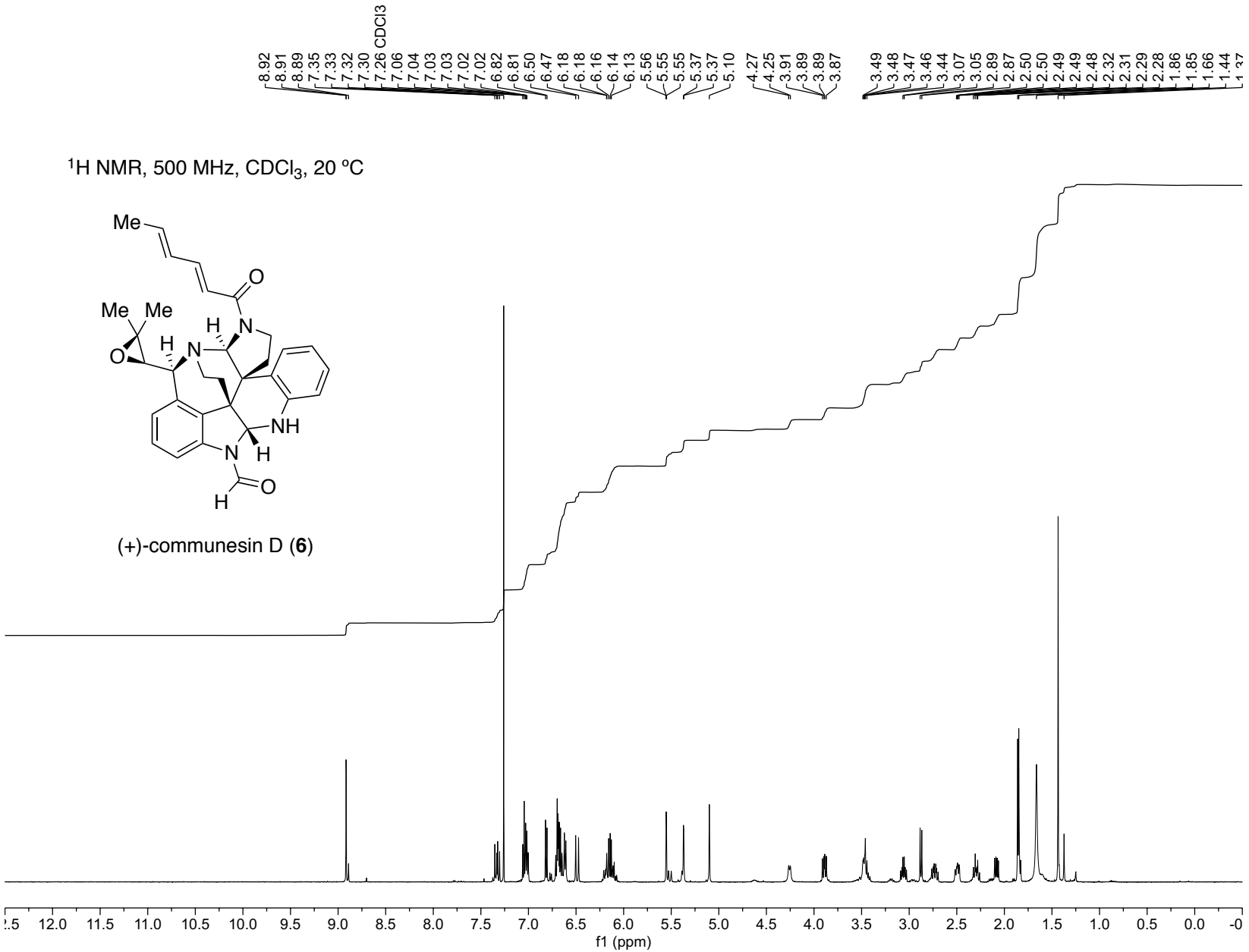

8.82 8.81 7.36 7.34 7.33 7.31 CDCl3 7.26 7.19 7.19 7.18 7.18 7.16 7.16 7.16 7.15 7.14 7.08 7.06 7.06 7.05 7.05 7.04 7.04 7.04 7.03 7.03 7.02 6.81 6.79 6.77 6.77 6.75 6.65 6.63 6.46 6.45 6.43 6.38 6.17 6.15 6.14 6.13 5.09 4.12 4.11 3.52 3.50 3.49 3.49 3.47 3.46 2.83 2.81 2.33 2.31 1.86 1.85 1.84 1.83 1.65 1.41 1.41 1.34 1.27 1.26 1.25 1.24 1.23 1.22 1.20 1.19 0.16 0.15 0.15 0.08
^{1}H NMR, 500 MHz, $CDCl_3$, 20 °C
Me
O
Me Me
H
N
H
N
O
NSES
N
H
O
H
(+)-46
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
f1 (ppm)

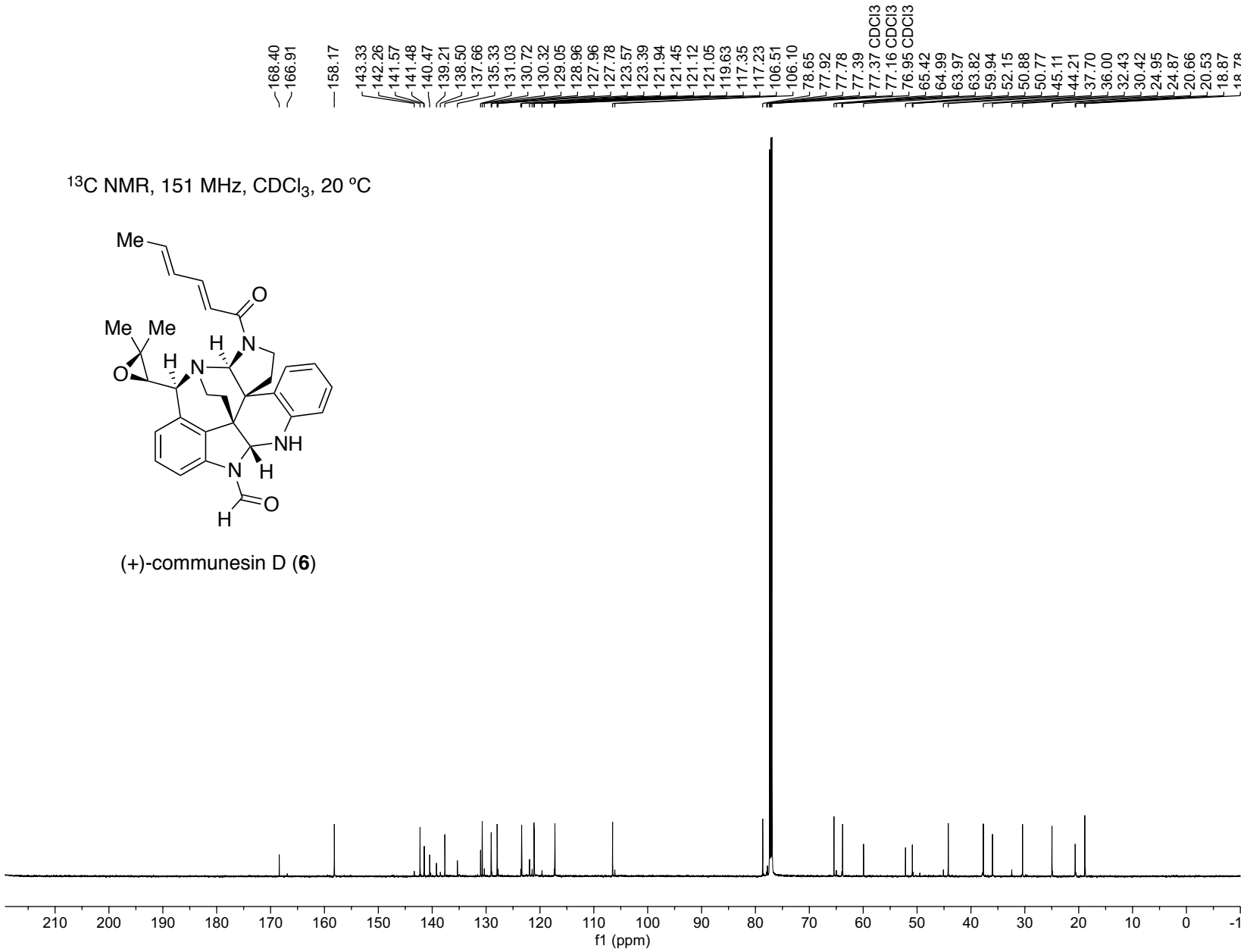

168.04
166.52
159.29
143.34
142.70
142.37
140.17
139.88
139.40
139.20
138.65
138.44
137.78
135.60
135.54
134.49
134.27
130.67
130.35
129.48
129.40
129.23
128.03
127.87
127.34
127.14
127.08
126.43
124.36
124.03
122.66
122.13
120.92
119.58
107.15
106.65
79.14
78.48
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
76.61
65.35
65.05
63.86
63.74
59.83
59.73
54.82
54.62
52.87
52.73
52.51
49.81
45.22
44.36
37.83
37.11
36.66
36.14
32.46
30.98
30.55
24.94
24.89
24.84
20.66
20.60
20.55
18.84
18.74
10.86
10.81
-1.70
-1.82
13C NMR, 151 MHz, CDCl3, 20 ºC
Me
O
Me Me
H
N
H
N
O
NSES
N
H
O
H
(+)-46
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.10 7.08 7.07 7.05 6.93 6.93 6.92 6.92 6.92 6.91 6.90 6.90 6.75 6.74 6.72 6.71 6.70 6.70 6.58 6.57 6.57 6.56 6.54 6.51 6.17 6.16 6.15 6.14 6.12 6.10 6.06 6.04 6.03 6.03 5.85 5.85 5.14 5.14 4.84 4.20 4.18 3.74 3.73 3.72 3.71 3.34 3.29 3.27 3.21 3.19 3.18 2.91 2.89 2.80 2.78 2.77 2.76 2.71 2.70 2.51 DMSO-d6 2.50 DMSO-d6 2.50 DMSO-d6 2.50 DMSO-d6 2.49 DMSO-d6 2.28 2.27 2.11 2.09 1.83 1.82 1.70 1.68 1.67 1.58 1.33
1H NMR, 500 MHz, DMSO-d6, 20 ºC
Me
O
Me Me
H
N
H
N
O
NH
N
H
H
(–)-communesin C (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
f1 (ppm)


7.34 7.32 7.32 7.30 CDCl3 7.26 7.01 7.00 7.00 7.00 6.99 6.99 6.99 6.98 6.86 6.85 6.83 6.69 6.68 6.67 6.67 6.66 6.59 6.56 6.23 6.21 6.21 6.20 6.18 6.12 6.11 6.09 6.08 5.12 5.01 4.28 4.19 4.19 4.17 3.90 3.89 3.88 3.87 3.47 3.45 3.43 3.42 3.41 3.11 3.10 3.09 3.08 3.07 2.90 2.89 2.73 2.73 2.71 2.71 2.39 2.38 2.38 2.37 2.36 2.31 2.30 2.29 2.28 2.28 1.98 1.97 1.96 1.95 1.86 1.84 1.65
1H NMR, 600 MHz, CDCl3, 20 ºC
Me
O
Me Me
H
N
H
N
O
NH
N
H
H
(–)-communesin C (5)
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
f1 (ppm)

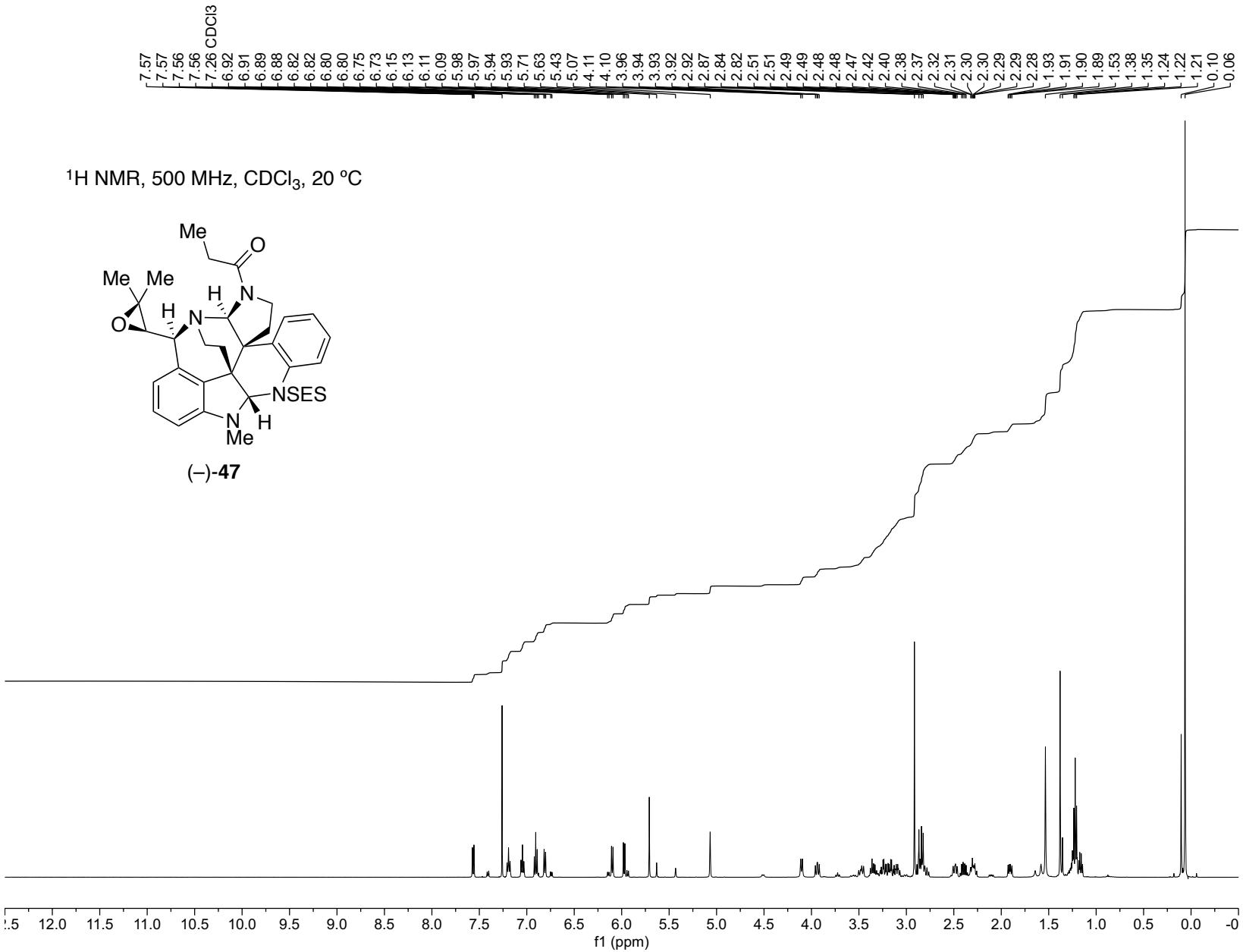

168.57
149.77
142.93
142.60
141.97
137.36
137.26
137.20
132.99
131.66
130.88
128.79
127.44
123.75
123.52
121.42
120.47
120.00
117.15
116.86
116.07
115.44
106.32
105.93
79.33
78.38
77.37 CDCl3
77.16 CDCl3
77.13
76.95 CDCl3
65.73
65.17
64.28
64.06
59.88
52.48
52.19
45.26
44.36
38.72
38.02
37.76
36.02
32.46
30.49
25.04
24.95
20.64
20.59
18.85
18.76
13C NMR, 151 MHz, CDCl3, 20 °C
Me
O
Me Me
H
N
O
H
N
NH
N
H
H
(–)-communesin C (5)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

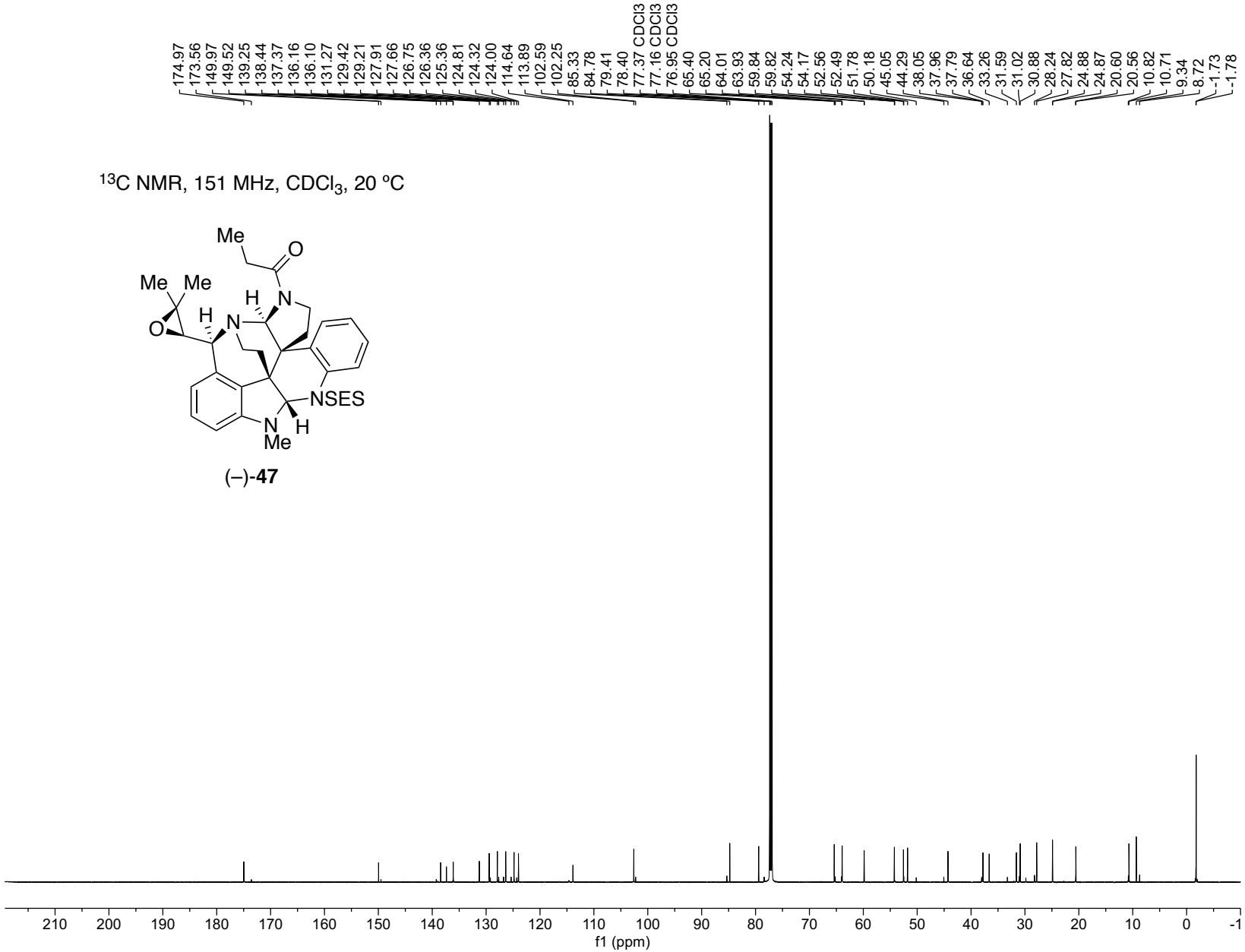

CDCl3
8.92
8.91
8.89
7.35
7.33
7.32
7.30
7.26
7.06
7.04
7.03
7.03
7.02
7.02
6.82
6.81
6.50
6.47
6.18
6.18
6.16
6.14
6.13
5.56
5.55
5.55
5.37
5.37
5.10
4.27
4.25
3.91
3.89
3.89
3.87
3.49
3.48
3.47
3.46
3.44
3.07
3.05
2.89
2.87
2.50
2.50
2.49
2.49
2.48
2.32
2.31
2.29
2.28
1.86
1.85
1.66
1.44
1H NMR, 500 MHz, CDCl3, 20 ºC
Me
O
Me Me
H
N
H
N
O
NH
N
H
O
H
(+)-communesin D (6)
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
f1 (ppm)

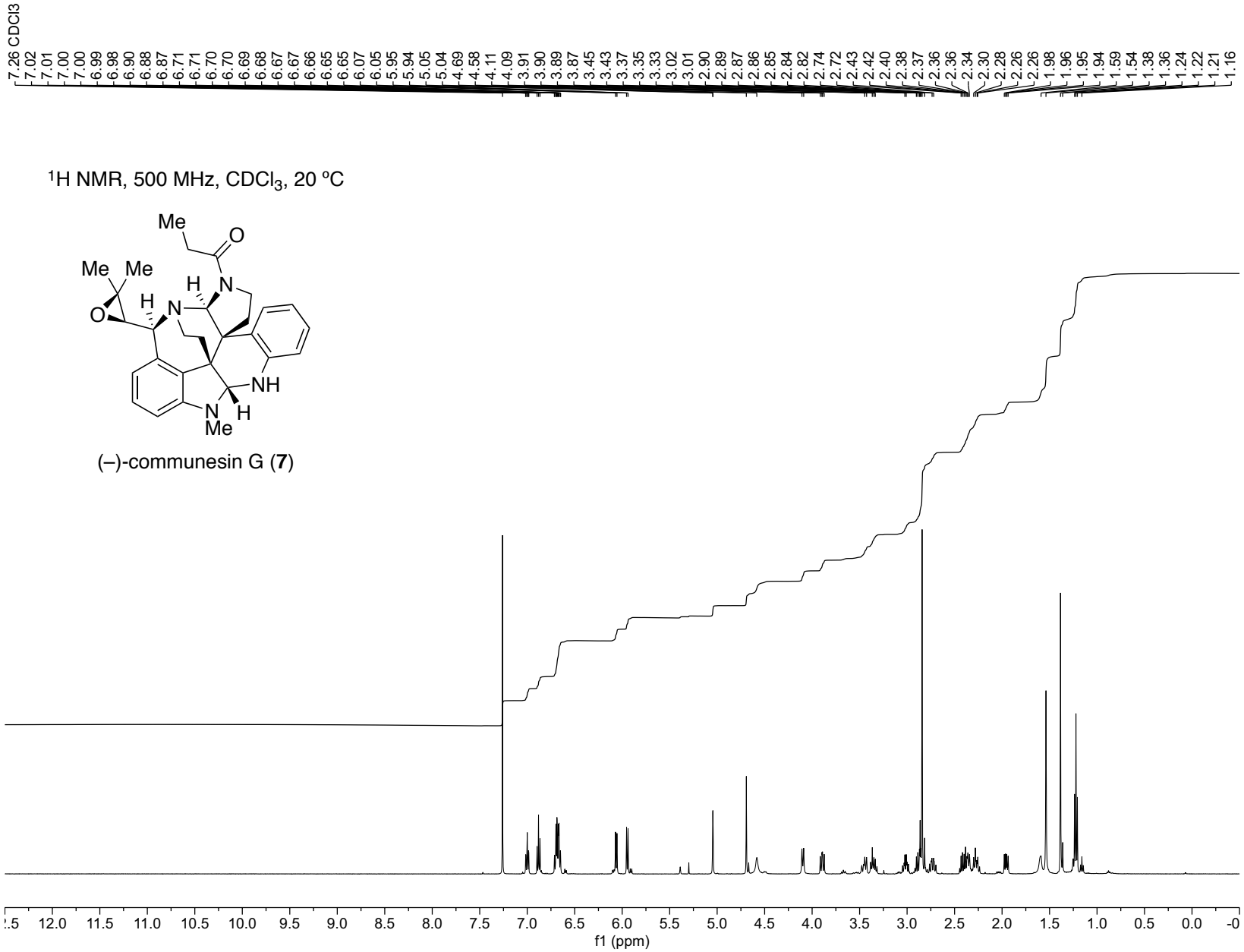


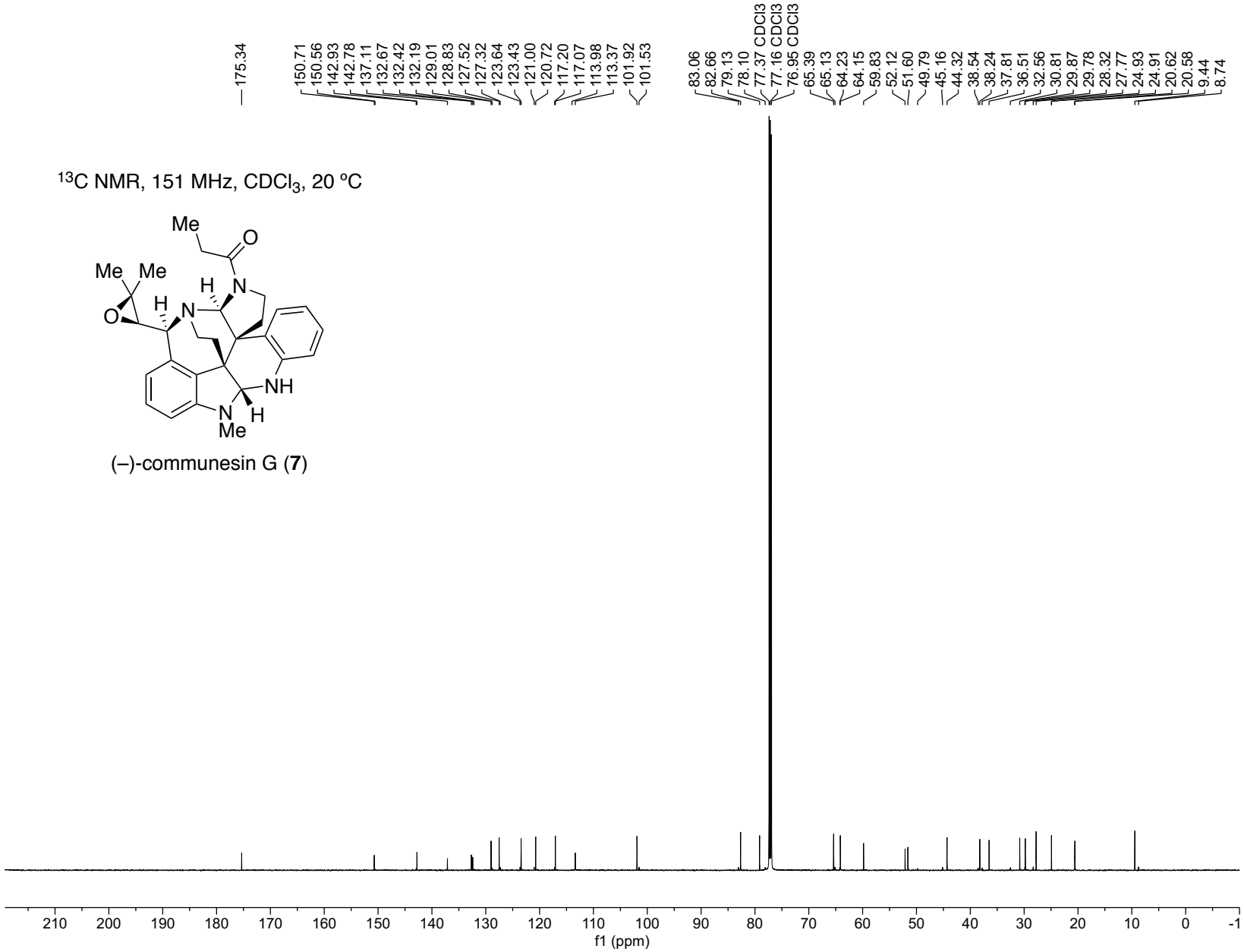
^{13}C NMR, 151 MHz, $CDCl_3$, 20 ºC

(+)-communesin D (**6**)


CDCl3
7.57 7.57 7.56 7.56 7.26 6.92 6.91 6.89 6.88 6.82 6.82 6.80 6.80 6.75 6.73 6.15 6.13 6.11 6.09 5.98 5.97 5.94 5.93 5.71 5.63 5.43 5.07 4.11 4.10 3.96 3.94 3.93 3.92 2.92 2.87 2.84 2.82 2.51 2.51 2.49 2.49 2.48 2.48 2.47 2.42 2.40 2.38 2.37 2.32 2.31 2.30 2.30 2.29 2.29 2.28 1.93 1.91 1.90 1.89 1.53 1.38 1.35 1.24 1.22 1.21 0.10 0.06
1H NMR, 500 MHz, CDCl3, 20 ºC
Me
O
Me Me
H
N
O
H
N
NSES
N
H
Me
(–)-47
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
f1 (ppm)

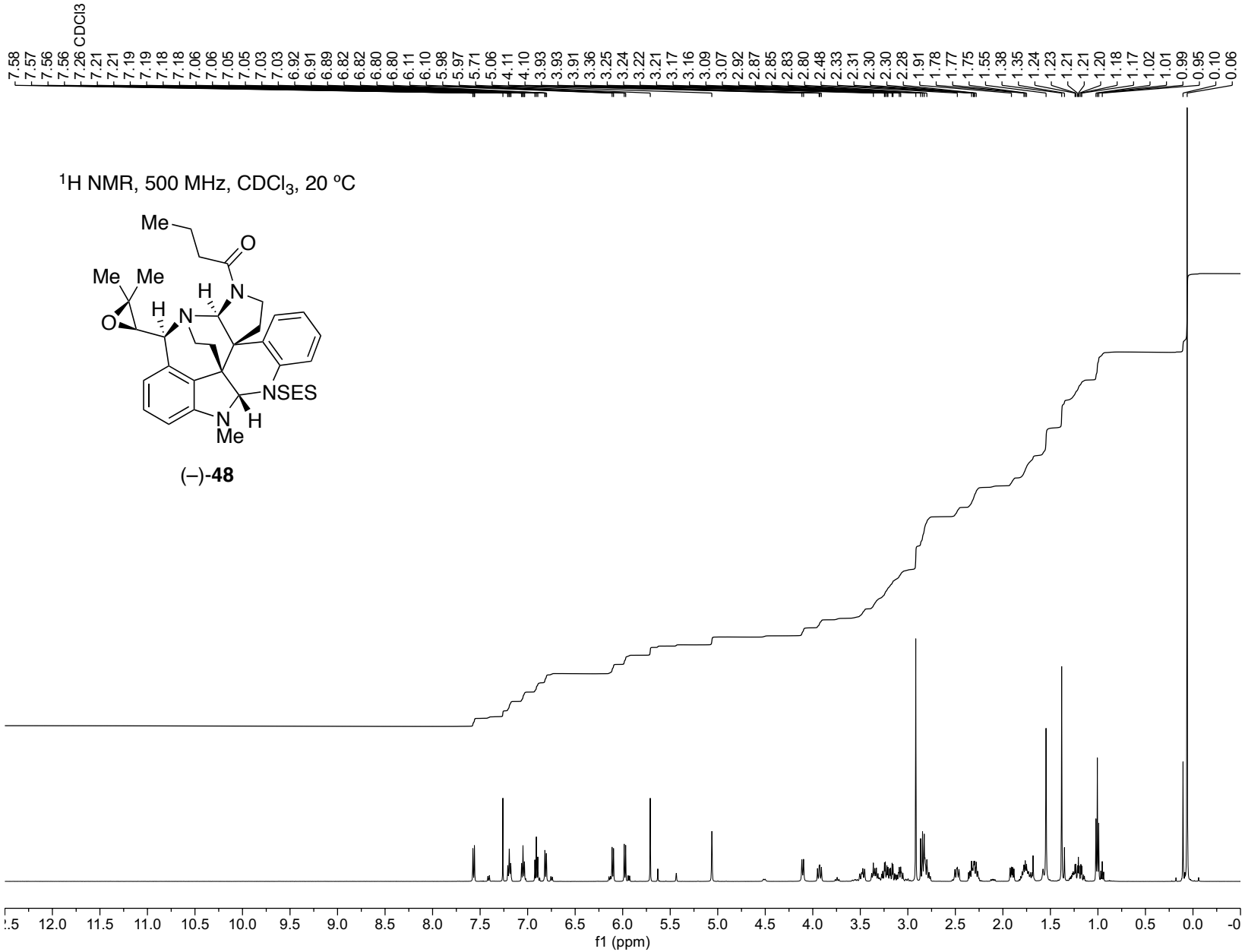

174.97
173.56
149.97
149.52
139.25
138.44
137.37
136.16
136.10
131.27
129.42
129.21
127.91
127.66
126.75
126.36
125.36
124.81
124.32
124.00
114.64
113.89
102.59
102.25
85.33
84.78
79.41
78.40
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
65.40
65.20
64.01
63.93
59.84
59.82
54.24
54.17
52.56
52.49
51.78
50.18
45.05
44.29
38.05
37.96
37.79
36.64
33.26
31.59
31.02
30.88
28.24
27.82
24.88
24.87
20.60
20.56
10.82
10.71
9.34
8.72
-1.73
-1.78
13C NMR, 151 MHz, CDCl3, 20 °C
Me
O
Me Me
H
N
H
N
O
NSES
N
H
Me
(–)-47
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

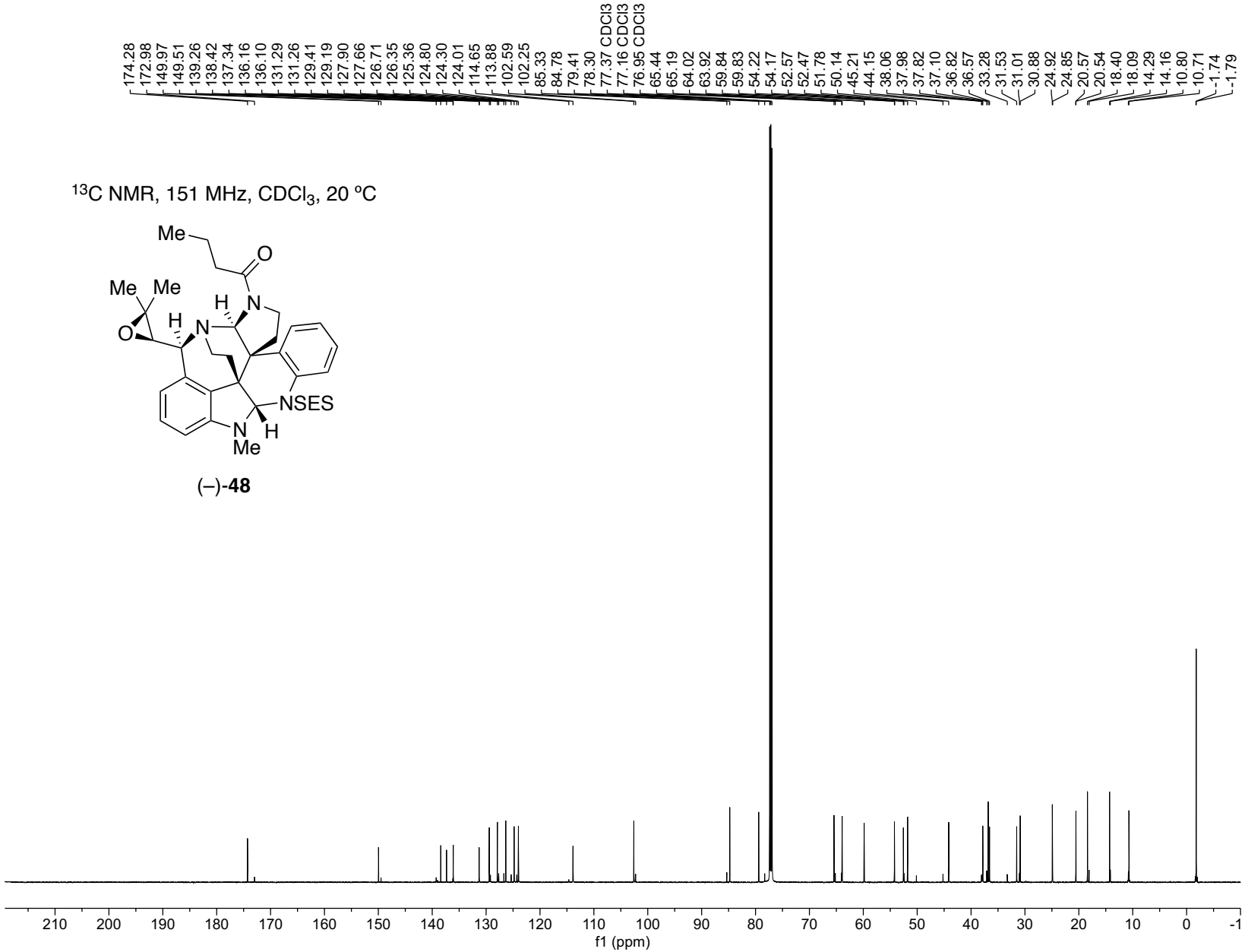

7.26 CDCl3
7.02 7.01 7.00 7.00 6.99 6.98 6.90 6.88 6.87 6.71 6.71 6.70 6.70 6.69 6.68 6.67 6.67 6.66 6.65 6.65 6.07 6.05 5.95 5.94 5.05 5.04 4.69 4.58 4.11 4.09 3.91 3.90 3.89 3.87 3.45 3.43 3.37 3.35 3.33 3.02 3.01 2.90 2.89 2.87 2.86 2.85 2.84 2.82 2.74 2.72 2.43 2.42 2.40 2.38 2.37 2.36 2.36 2.34 2.30 2.28 2.26 2.26 1.98 1.96 1.95 1.94 1.59 1.54 1.38 1.36 1.24 1.22 1.21 1.16
1H NMR, 500 MHz, CDCl3, 20 ºC
Me
O
Me Me
H
N
H
N
O
NH
N
H
Me
(–)-communesin G (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
f1 (ppm)



^{13}C NMR, 151 MHz, $CDCl_3$, 20 ºC

(–)-communesin G (**7**)

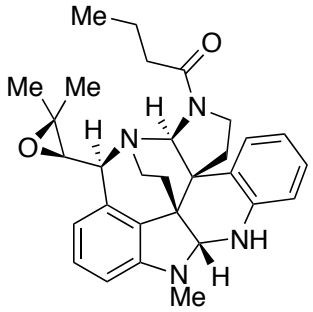

CDCl3
7.58 7.57 7.56 7.56 7.26 7.21 7.21 7.19 7.19 7.18 7.18 7.06 7.06 7.05 7.05 7.03 7.03 6.92 6.91 6.89 6.82 6.82 6.80 6.80 6.11 6.10 5.98 5.97 5.71 5.06 4.11 4.10 3.93 3.93 3.91 3.36 3.25 3.24 3.22 3.21 3.17 3.16 3.09 3.07 2.92 2.87 2.85 2.83 2.80 2.48 2.33 2.31 2.30 2.30 2.28 1.91 1.78 1.77 1.75 1.55 1.38 1.35 1.24 1.23 1.21 1.21 1.20 1.18 1.17 1.02 1.01 0.99 0.95 0.10 0.06
1H NMR, 500 MHz, CDCl3, 20 ºC
Me
O
Me Me
H N
O
H N
NSES
N H
Me
(–)-48
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
f1 (ppm)



^{13}C NMR, 151 MHz, $CDCl_3$, 20 °C

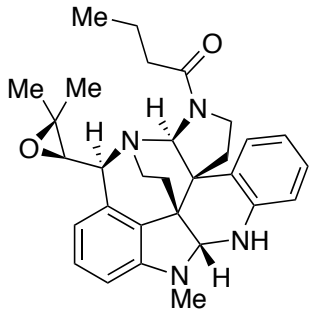
(–)-**48**

^{1}H NMR, 500 MHz, $CDCl_3$, 20 °C

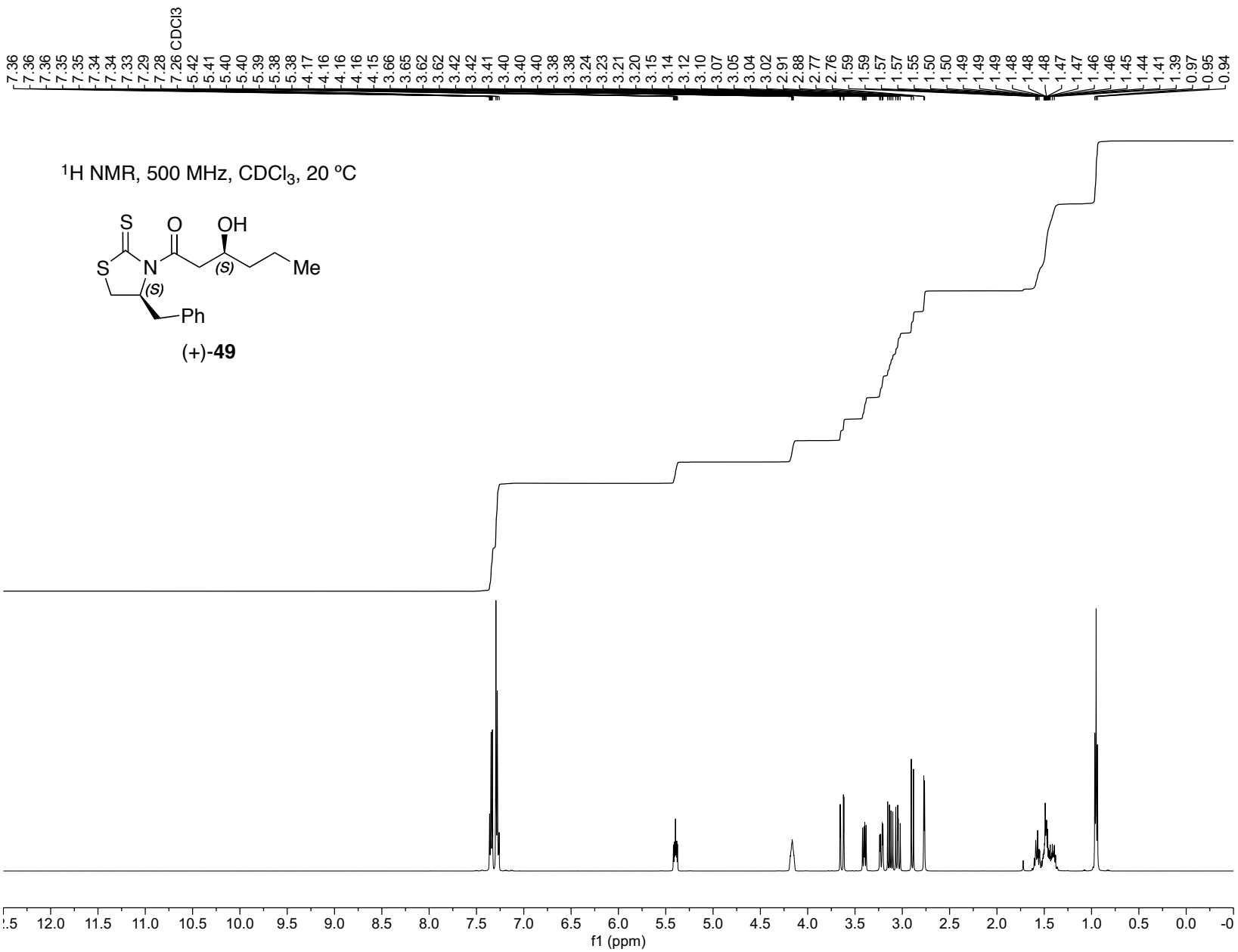


(–)-communesin H (**8**)

^{13}C NMR, 151 MHz, $CDCl_3$, 20 ºC

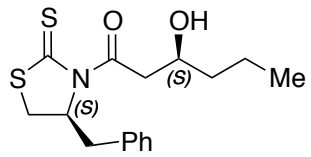


(–)-communesin H (**8**)

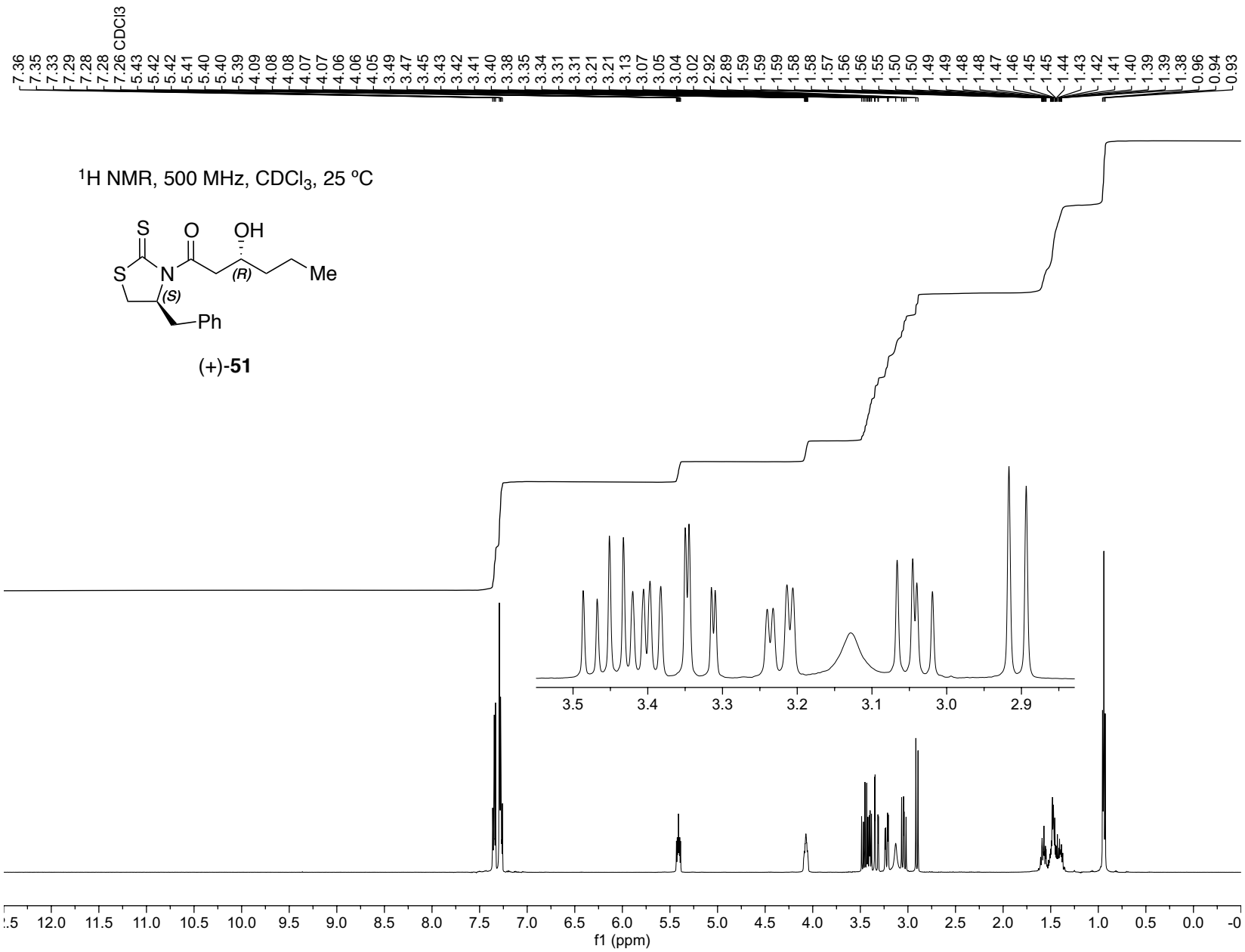

7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.29 7.28 CDCl3 7.26 5.42 5.41 5.40 5.40 5.39 5.38 5.38 4.17 4.16 4.16 4.15 3.66 3.65 3.62 3.62 3.42 3.42 3.41 3.40 3.40 3.40 3.38 3.38 3.24 3.23 3.21 3.20 3.15 3.14 3.12 3.10 3.07 3.05 3.04 3.02 2.91 2.88 2.77 2.76 1.59 1.59 1.57 1.57 1.55 1.50 1.50 1.49 1.49 1.49 1.48 1.48 1.48 1.47 1.47 1.46 1.46 1.45 1.44 1.41 1.39 0.97 0.95 0.94
1H NMR, 500 MHz, CDCl3, 20 °C
S
O
OH
S
N
(S)
(S)
Me
Ph
(+)-49
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
f1 (ppm)

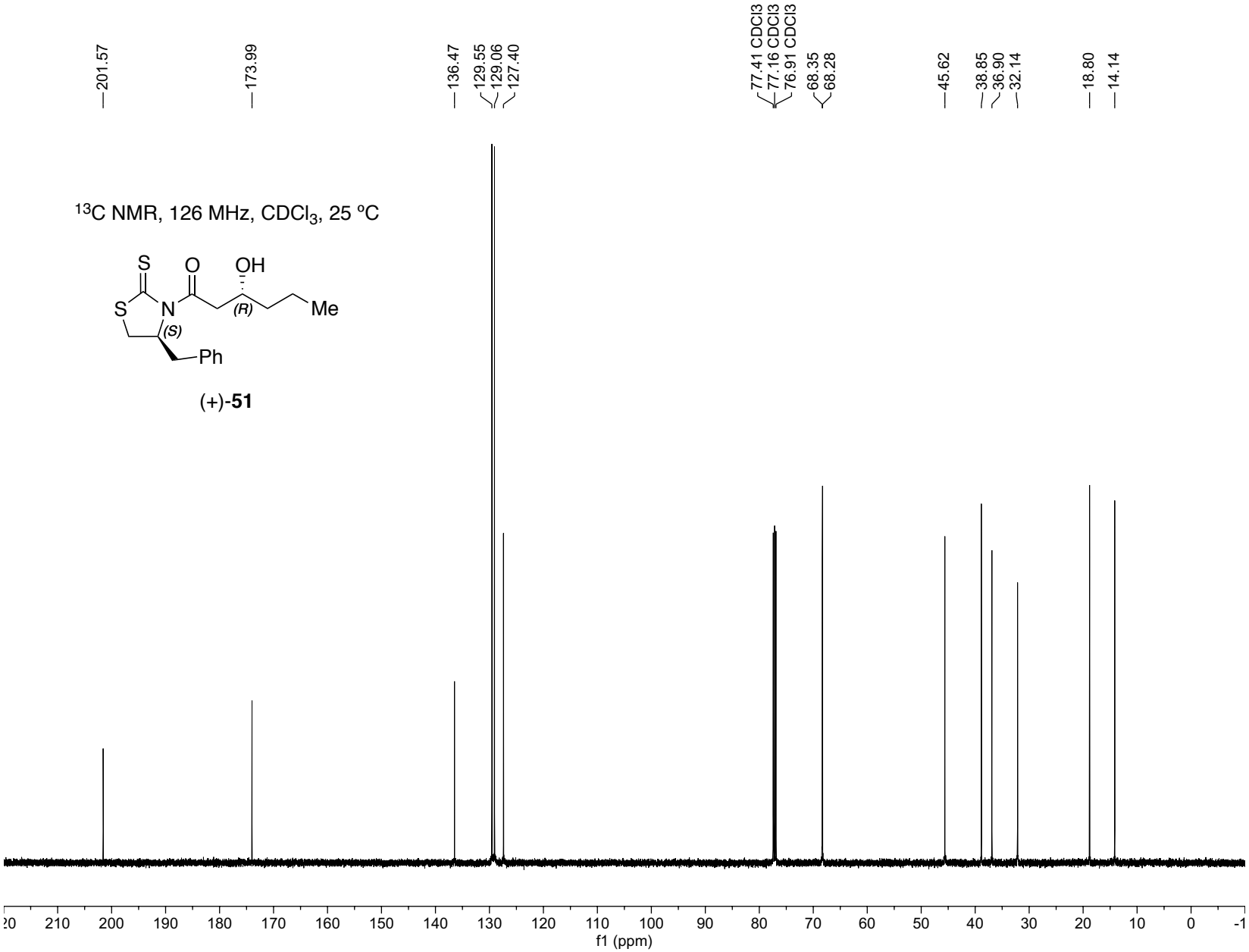
201.49
173.42
136.51
129.53
129.03
127.38
77.42 CDCl3
77.16 CDCl3
76.90 CDCl3
68.43
67.65
46.02
38.61
36.93
32.15
18.86
14.11

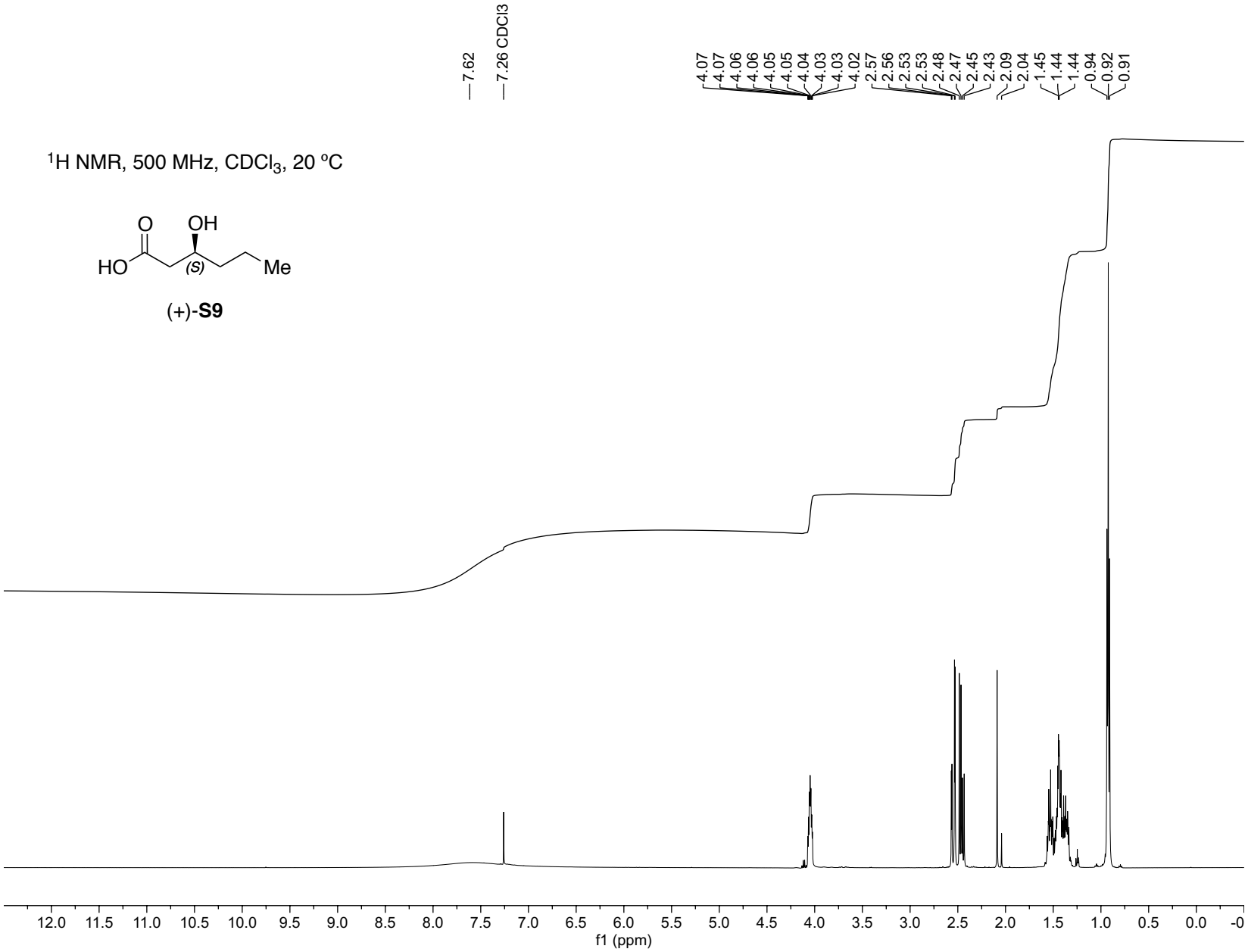
^{13}C NMR, 126 MHz, $CDCl_3$, 24 °C



(+)-**49**

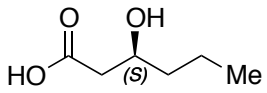

CDCl3
7.36 7.35 7.33 7.29 7.28 7.28 7.26 5.43 5.42 5.42 5.41 5.40 5.40 5.39 4.09 4.08 4.08 4.07 4.07 4.06 4.06 4.05 3.49 3.47 3.45 3.43 3.42 3.41 3.40 3.38 3.35 3.34 3.31 3.31 3.21 3.21 3.13 3.07 3.05 3.04 3.02 2.92 2.89 1.59 1.59 1.59 1.58 1.58 1.57 1.56 1.56 1.55 1.50 1.50 1.49 1.49 1.48 1.48 1.47 1.46 1.45 1.45 1.44 1.43 1.42 1.41 1.40 1.39 1.39 1.38 0.96 0.94 0.93
1H NMR, 500 MHz, CDCl3, 25 ºC
S
O
OH
S
N
(R)
Me
(S)
Ph
(+)-51
3.5 3.4 3.3 3.2 3.1 3.0 2.9
f1 (ppm)


201.57
173.99
136.47
129.55
129.06
127.40
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
68.35
68.28
45.62
38.85
36.90
32.14
18.80
14.14
13C NMR, 126 MHz, CDCl3, 25 ºC
S
O
OH
S
N
(R)
Me
(S)
Ph
(+)-51
f1 (ppm)

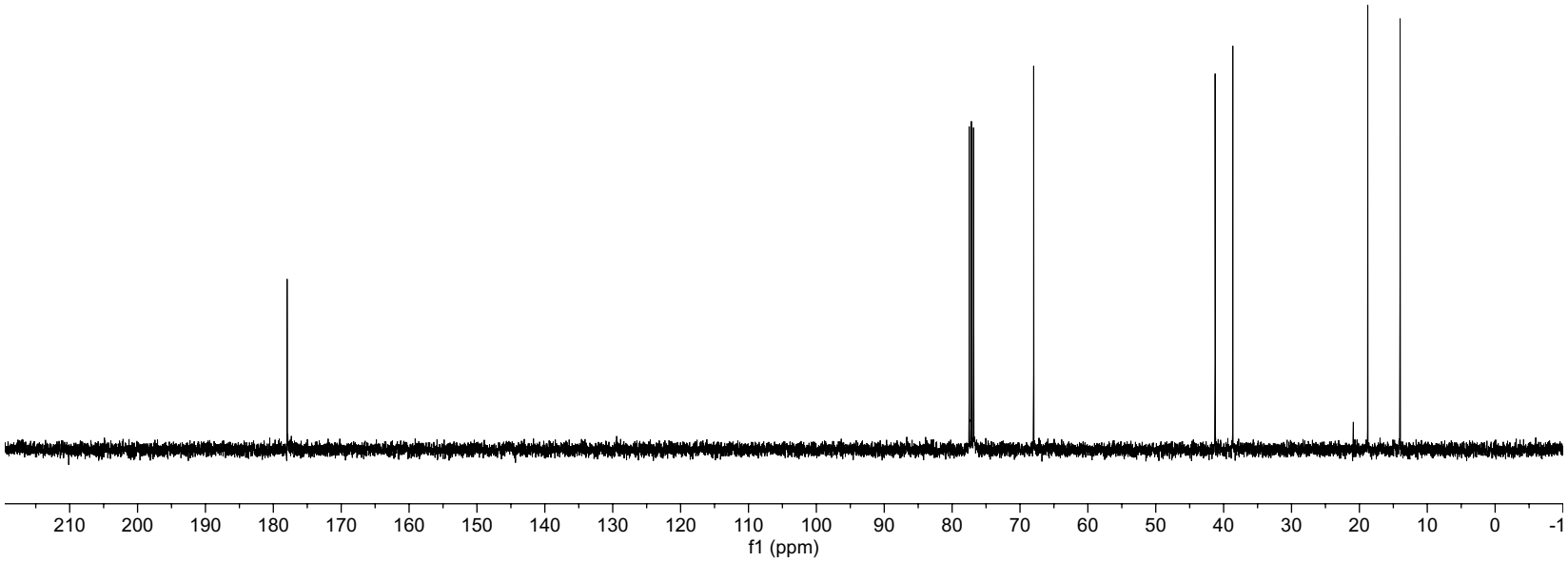

7.62
7.26 CDCl3
4.07
4.07
4.06
4.06
4.05
4.05
4.04
4.03
4.03
4.02
2.57
2.56
2.53
2.53
2.48
2.47
2.45
2.43
2.09
2.04
1.45
1.44
1.44
0.94
0.92
0.91
1H NMR, 500 MHz, CDCl3, 20 °C
O
OH
HO
(S)
Me
(+)-S9
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

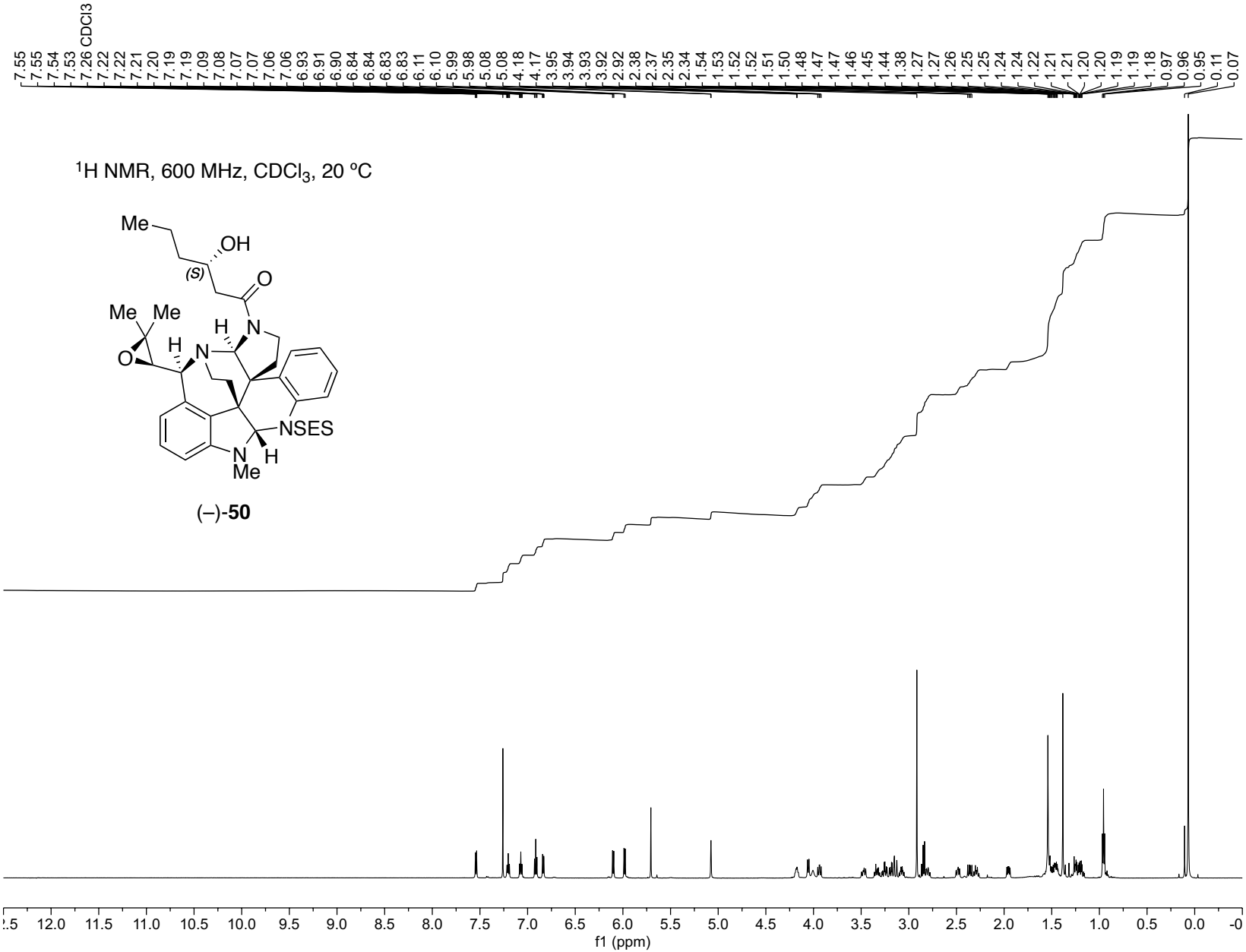
177.97
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.99
41.25
38.65
18.76
14.01

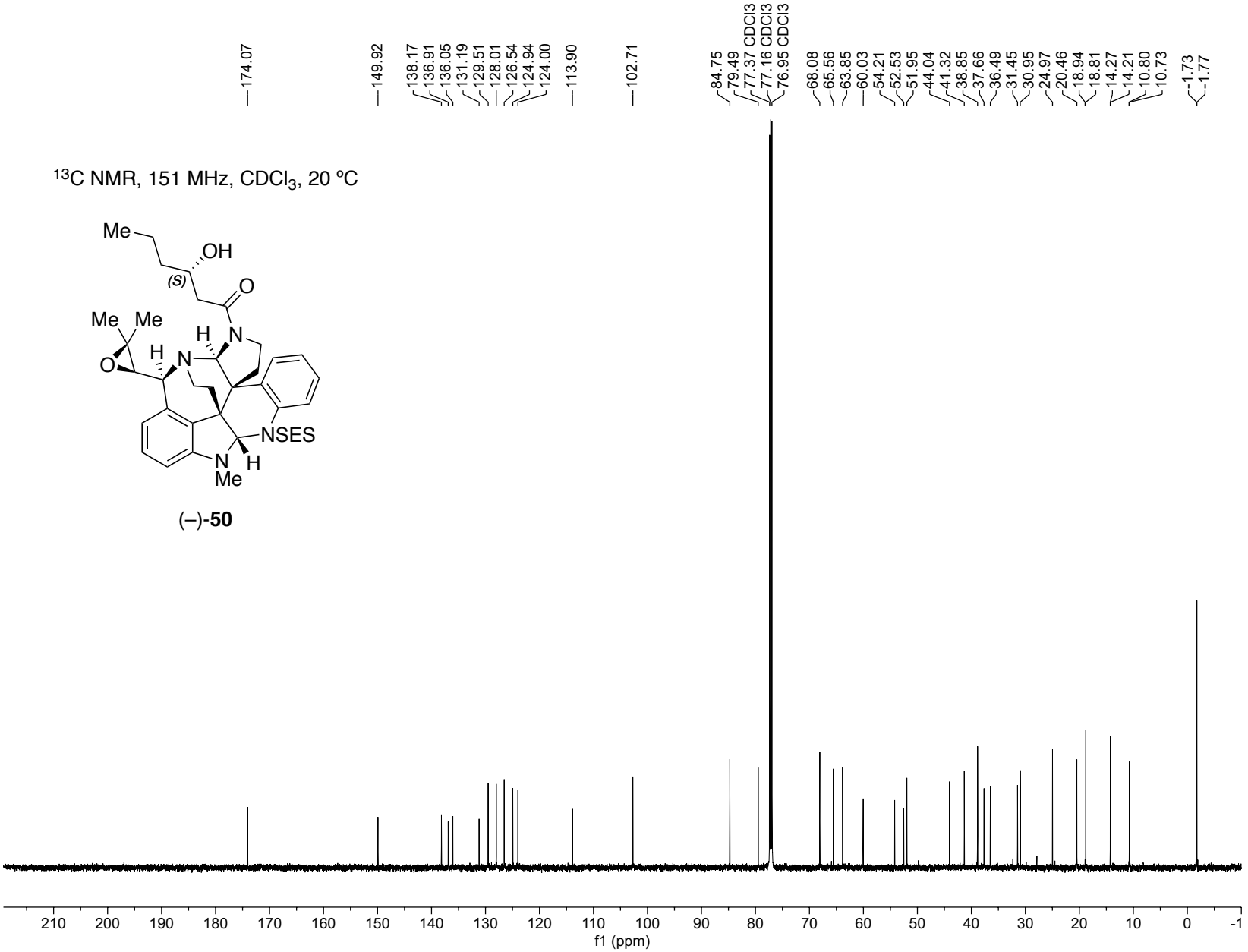
^{13}C NMR, 101 MHz, $CDCl_3$, 25 °C

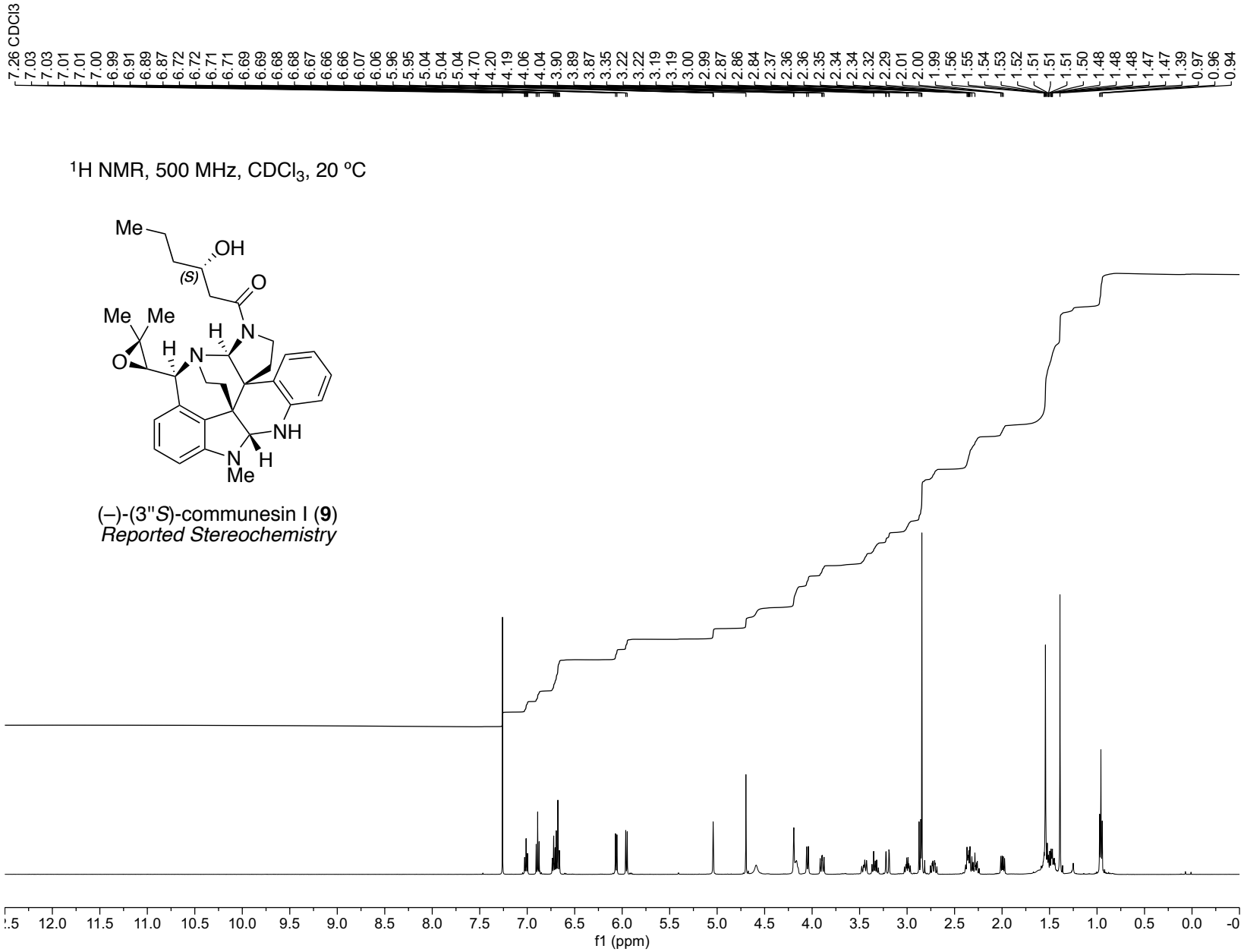


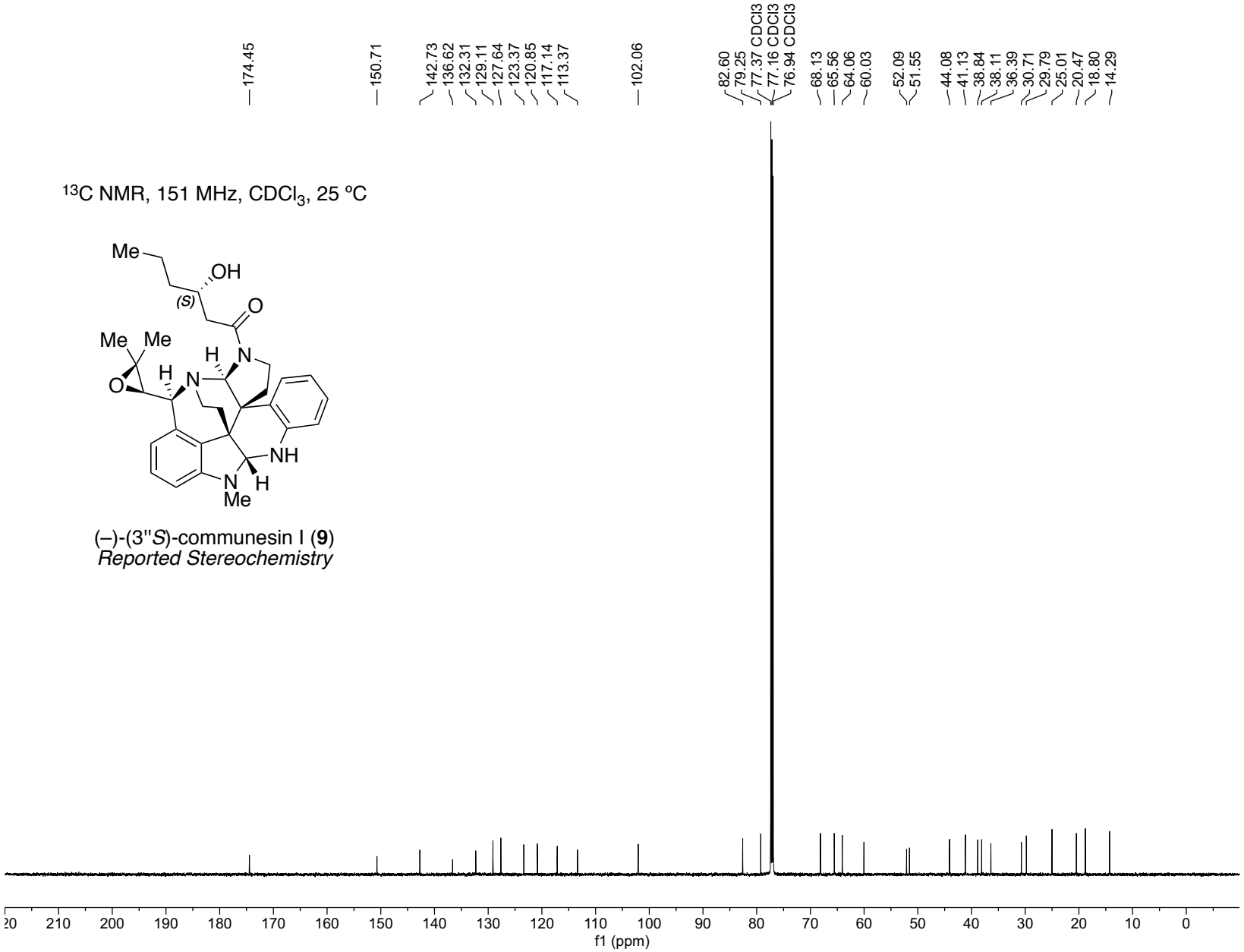
(+)-**S9**

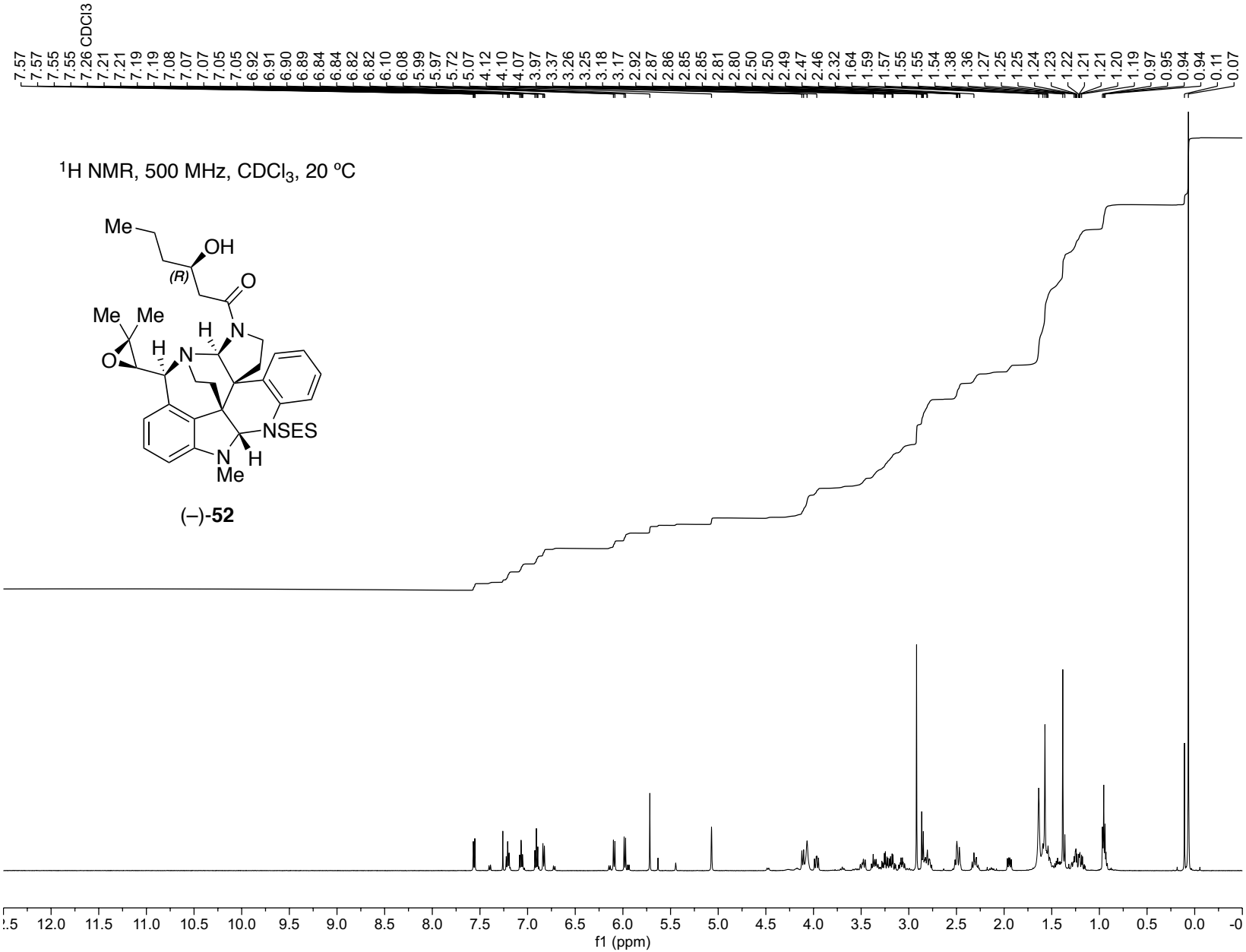


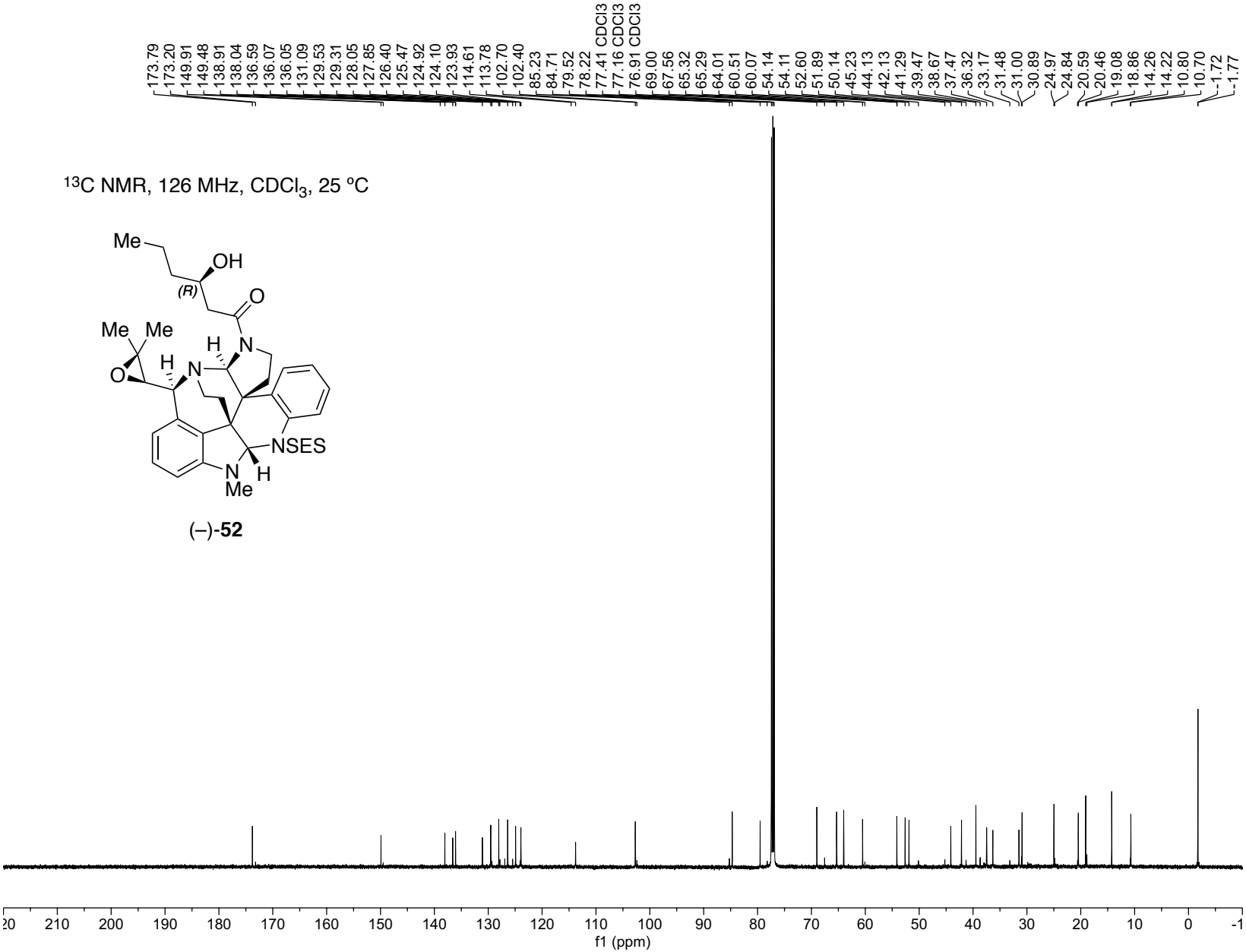

CDCl3
7.55 7.55 7.54 7.53 7.26 7.22 7.22 7.21 7.20 7.19 7.19 7.09 7.08 7.07 7.07 7.06 7.06 6.93 6.91 6.90 6.84 6.84 6.83 6.83 6.11 6.10 5.99 5.98 5.08 5.08 4.18 4.17 3.95 3.94 3.93 3.92 2.92 2.38 2.37 2.35 2.34 1.54 1.53 1.52 1.52 1.51 1.50 1.48 1.47 1.47 1.46 1.45 1.44 1.38 1.27 1.27 1.26 1.25 1.25 1.24 1.24 1.22 1.21 1.21 1.20 1.20 1.19 1.19 1.18 0.97 0.96 0.95 0.11 0.07
1H NMR, 600 MHz, CDCl3, 20 ºC
Me
OH
(S)
O
Me Me
H
N
O
H
N
NSES
N H
Me
(–)-50
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
f1 (ppm)

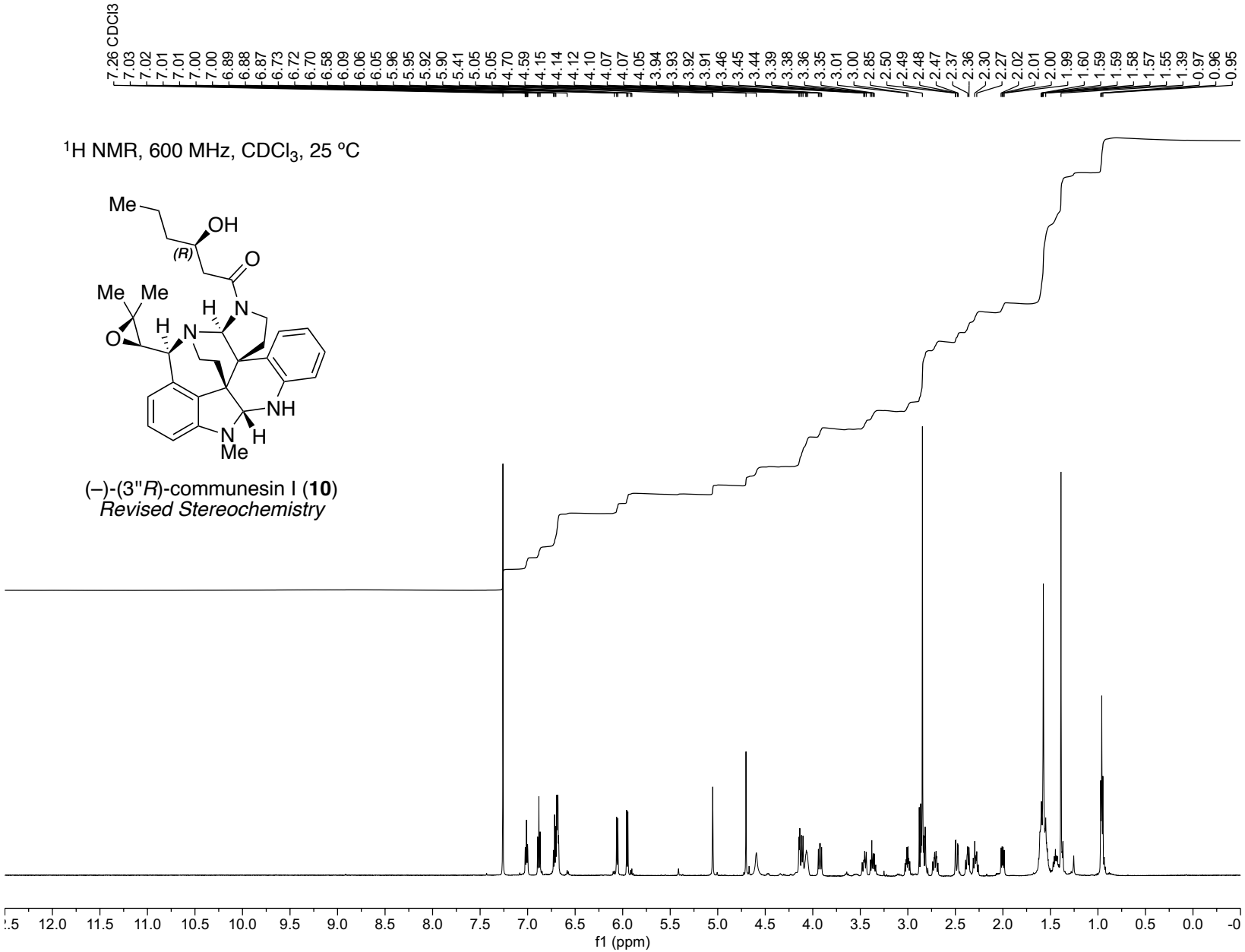

174.07
149.92
138.17
136.91
136.05
131.19
129.51
128.01
126.54
124.94
124.00
113.90
102.71
84.75
79.49
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
68.08
65.56
63.85
60.03
54.21
52.53
51.95
44.04
41.32
38.85
37.66
36.49
31.45
30.95
24.97
20.46
18.94
18.81
14.27
14.21
10.80
10.73
-1.73
-1.77
13C NMR, 151 MHz, CDCl3, 20 ºC
Me
OH
(S)
O
Me Me
H
N
O
H
N
NSES
N
H
Me
(–)-50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

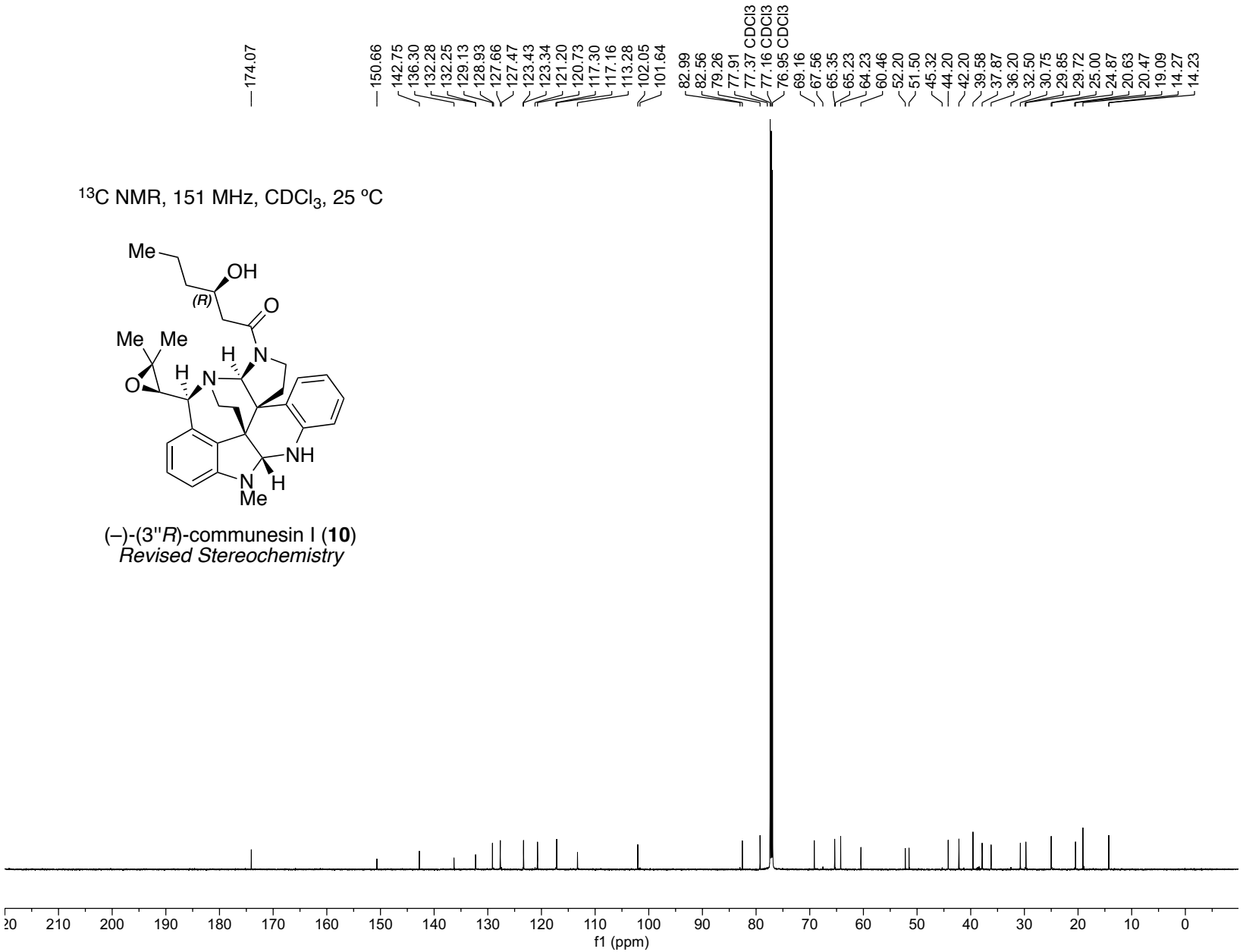

7.26 CDCl3
7.03 7.03 7.01 7.01 7.00 6.99 6.91 6.89 6.87 6.72 6.72 6.71 6.71 6.69 6.69 6.68 6.68 6.67 6.66 6.66 6.07 6.06 5.96 5.95 5.04 5.04 5.04 4.70 4.20 4.19 4.06 4.04 3.90 3.89 3.87 3.35 3.22 3.22 3.19 3.19 3.00 2.99 2.87 2.86 2.84 2.37 2.36 2.36 2.35 2.34 2.34 2.32 2.29 2.01 2.00 1.99 1.56 1.55 1.54 1.53 1.52 1.51 1.51 1.51 1.50 1.48 1.48 1.47 1.47 1.39 0.97 0.96 0.94
1H NMR, 500 MHz, CDCl3, 20 ºC
Me
OH
(S)
O
Me Me
H N
O
H N
NH
N H
Me
(–)-(3"S)-communesin I (9)
Reported Stereochemistry
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
f1 (ppm)


174.45
150.71
142.73
136.62
132.31
129.11
127.64
123.37
120.85
117.14
113.37
102.06
82.60
79.25
77.37 CDCl3
77.16 CDCl3
76.94 CDCl3
68.13
65.56
64.06
60.03
52.09
51.55
44.08
41.13
38.84
38.11
36.39
30.71
29.79
25.01
20.47
18.80
14.29
13C NMR, 151 MHz, CDCl3, 25 ºC
Me
OH
(S)
O
Me Me
H
N
O
H
N
NH
N H
Me
(–)-(3''S)-communesin I (9)
Reported Stereochemistry
f1 (ppm)


CDCl3
7.57 7.57 7.55 7.55 7.26 7.21 7.21 7.19 7.19 7.08 7.07 7.07 7.05 7.05 6.92 6.91 6.90 6.89 6.84 6.84 6.82 6.82 6.10 6.08 5.99 5.97 5.72 5.07 4.12 4.10 4.07 3.97 3.37 3.26 3.25 3.18 3.17 2.92 2.87 2.86 2.85 2.85 2.81 2.80 2.50 2.50 2.49 2.47 2.46 2.32 1.64 1.59 1.57 1.55 1.55 1.54 1.38 1.36 1.27 1.25 1.25 1.24 1.23 1.22 1.21 1.21 1.20 1.19 0.97 0.95 0.94 0.94 0.11 0.07
1H NMR, 500 MHz, CDCl3, 20 ºC
Me
OH
(R)
O
Me Me
H
N
O
H
N
NSES
N
H
Me
(–)-52
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
f1 (ppm)

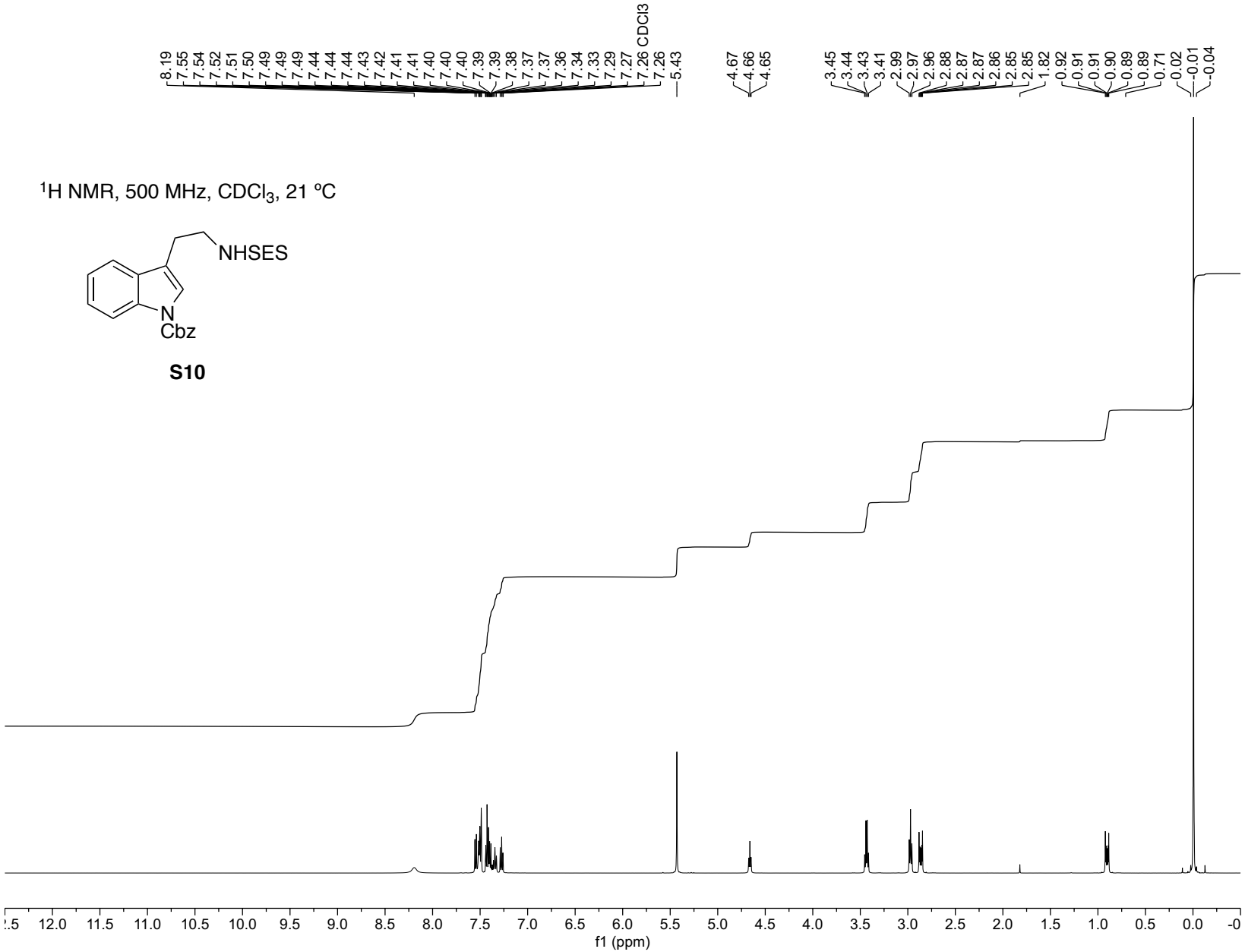

173.79
173.20
149.91
149.48
138.91
138.04
136.59
136.07
136.05
131.09
129.53
129.31
128.05
127.85
126.40
125.47
124.92
124.10
123.93
114.61
113.78
102.70
102.40
85.23
84.71
79.52
78.22
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
69.00
67.56
65.32
65.29
64.01
60.51
60.07
54.14
54.11
52.60
51.89
50.14
45.23
44.13
42.13
41.29
39.47
38.67
37.47
36.32
33.17
31.48
31.00
30.89
24.97
24.84
20.59
20.46
19.08
18.86
14.26
14.22
10.80
10.70
-1.72
-1.77
13C NMR, 126 MHz, CDCl3, 25 ºC
Me
OH
(R)
O
Me Me
H
N
H
N
O
NSES
N
H
Me
(–)-52
f1 (ppm)

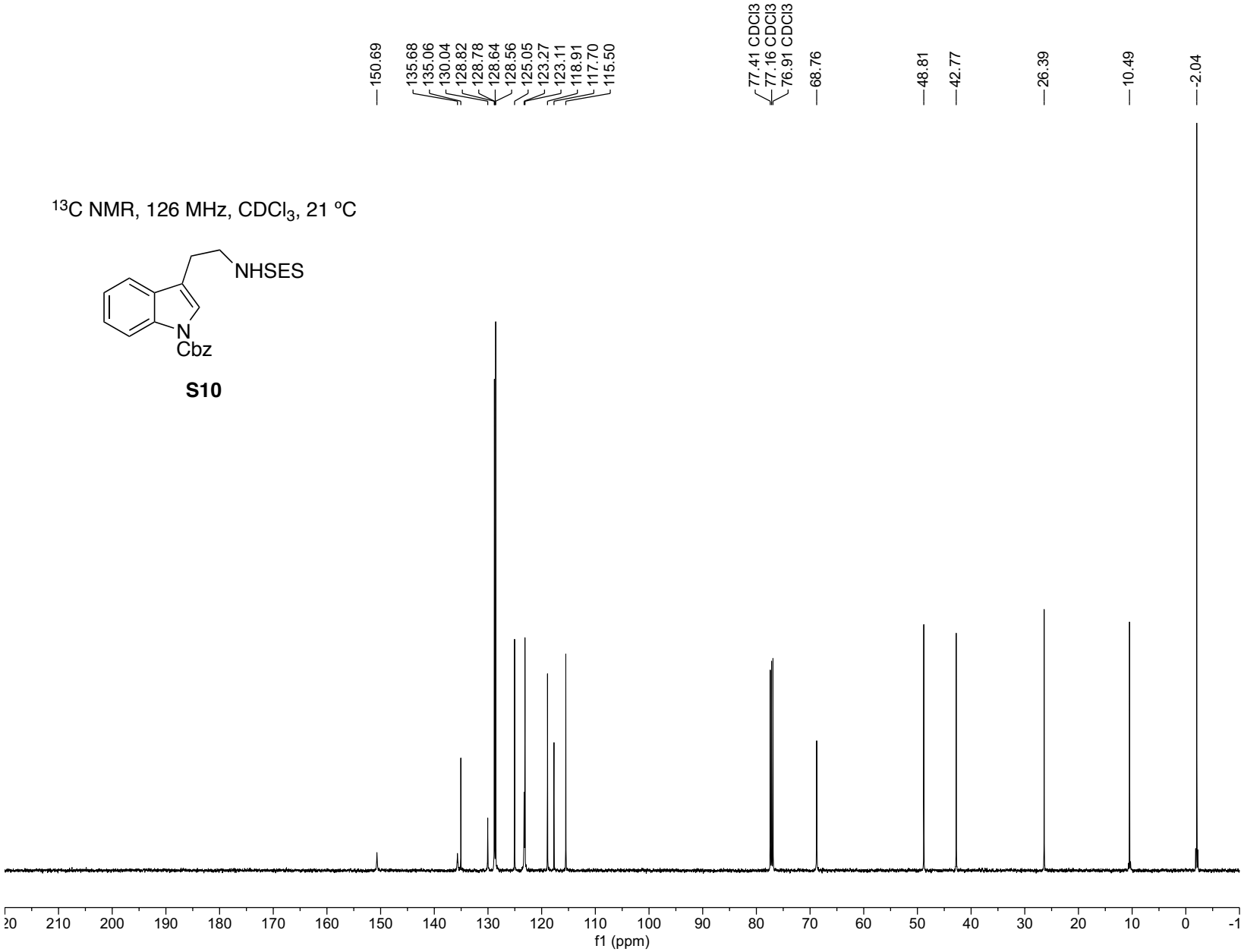

7.26 CDCl3
7.03 7.02 7.01 7.01 7.00 7.00 6.89 6.88 6.87 6.73 6.72 6.70 6.58 6.09 6.06 6.05 5.96 5.95 5.92 5.90 5.41 5.05 5.05 4.70 4.59 4.15 4.14 4.12 4.10 4.07 4.07 4.05 3.94 3.93 3.92 3.91 3.46 3.45 3.44 3.39 3.38 3.36 3.35 3.01 3.00 2.85 2.50 2.49 2.48 2.47 2.37 2.36 2.30 2.27 2.02 2.01 2.00 1.99 1.60 1.59 1.59 1.58 1.57 1.55 1.39 0.97 0.96 0.95
1H NMR, 600 MHz, CDCl3, 25 ºC
Me
OH
(R)
O
Me Me
H
N
O
H
N
NH
N
H
Me
(–)-(3"R)-communesin I (10)
Revised Stereochemistry
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
f1 (ppm)

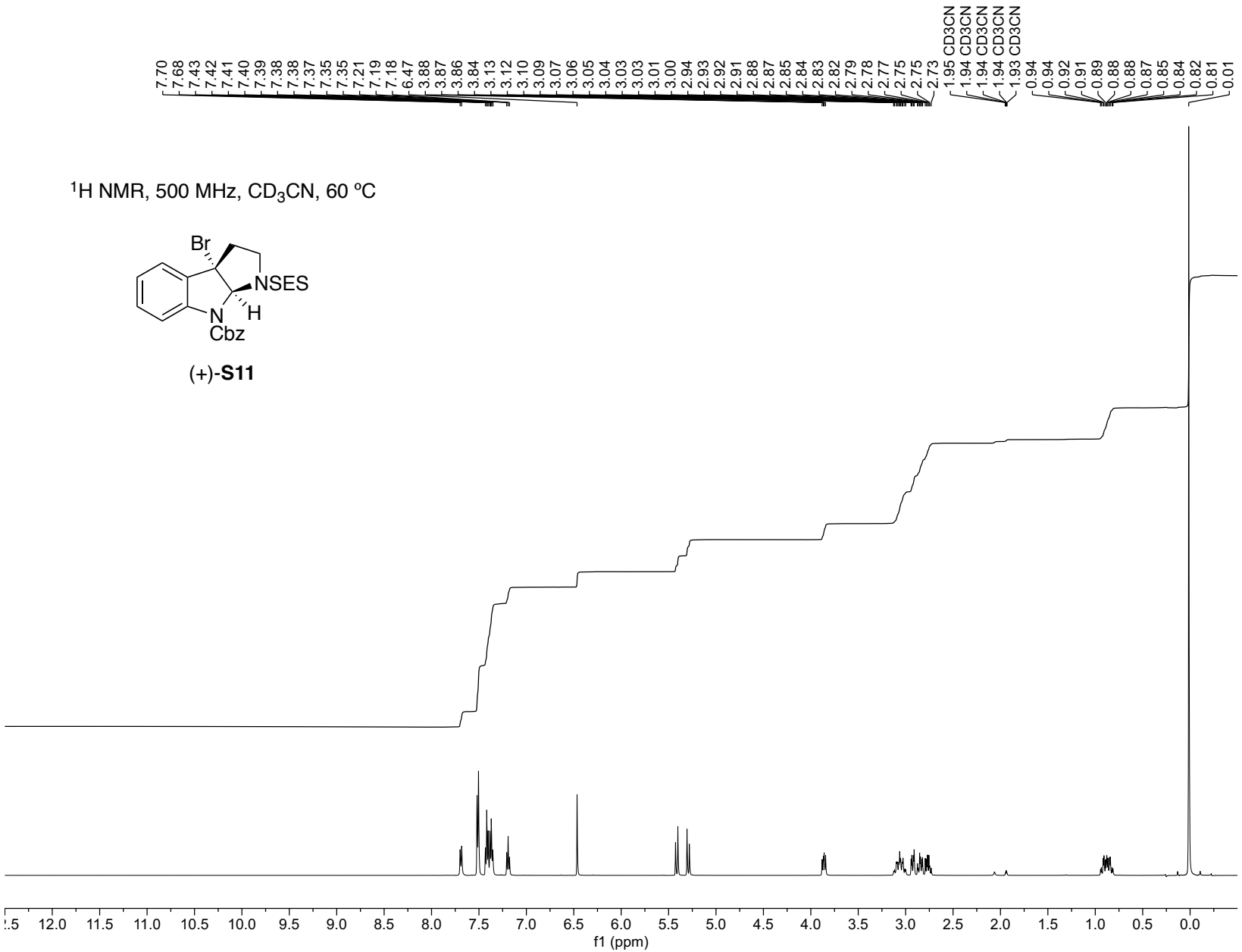


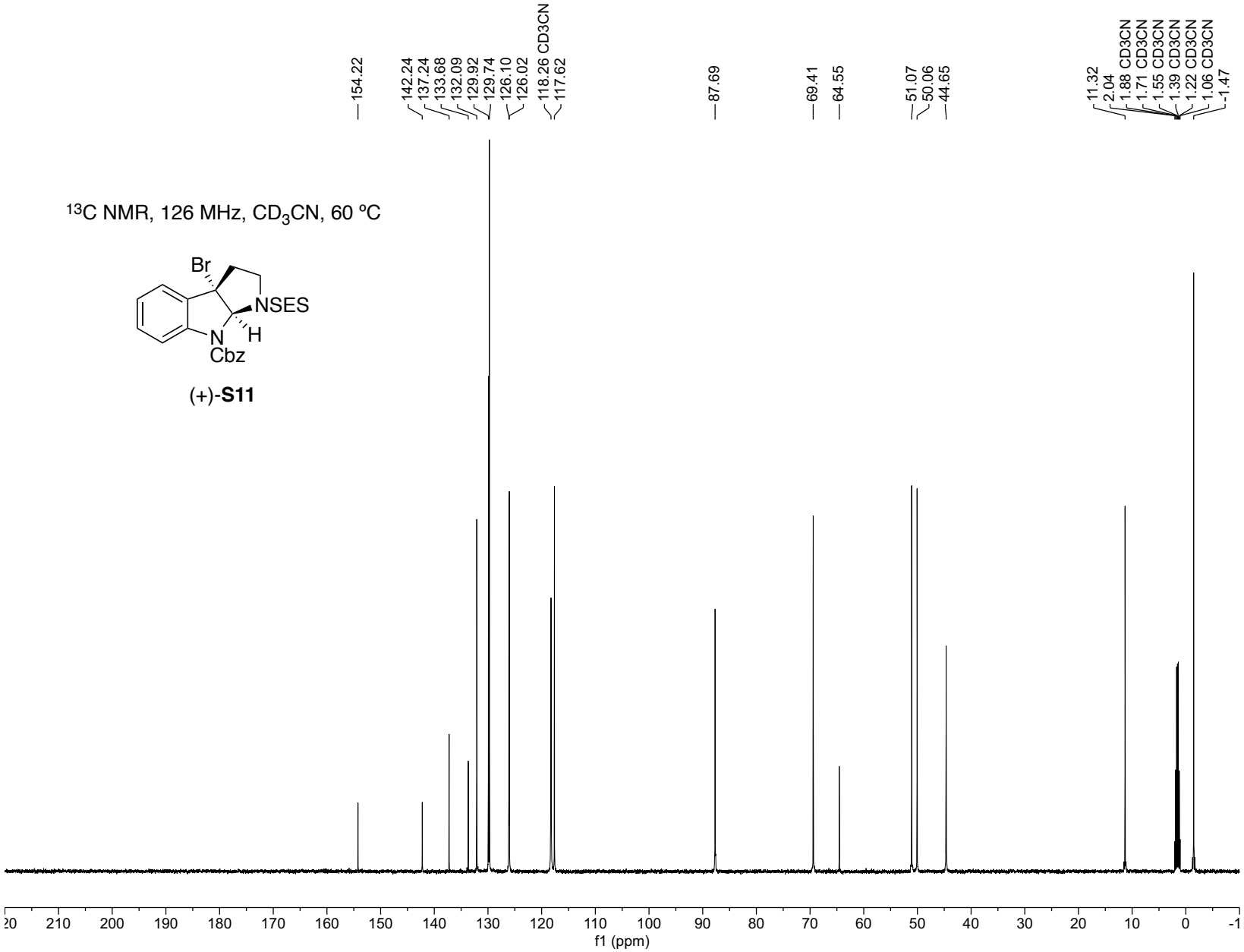
^{13}C NMR, 151 MHz, $CDCl_3$, 25 ºC

(–)-(3''*R*)-communesin I (**10**)
Revised Stereochemistry

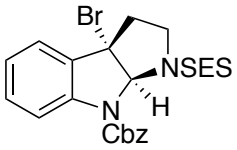

8.19
7.55
7.54
7.52
7.51
7.50
7.49
7.49
7.49
7.44
7.44
7.44
7.43
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.34
7.33
7.29
7.27
7.26 CDCl3
7.26
5.43
4.67
4.66
4.65
3.45
3.44
3.43
3.41
2.99
2.97
2.96
2.88
2.87
2.87
2.86
2.85
2.85
1.82
0.92
0.91
0.91
0.90
0.89
0.89
0.71
0.02
-0.01
-0.04
1H NMR, 500 MHz, CDCl3, 21 ºC
NHSES
N
Cbz
S10
f1 (ppm)


150.69
135.68
135.06
130.04
128.82
128.78
128.64
128.56
125.05
123.27
123.11
118.91
117.70
115.50
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
68.76
48.81
42.77
26.39
10.49
-2.04
13C NMR, 126 MHz, CDCl3, 21 ºC
NHSES
N
Cbz
S10
f1 (ppm)


7.70 7.68 7.43 7.42 7.41 7.40 7.39 7.38 7.38 7.37 7.35 7.35 7.21 7.19 7.18 6.47 3.88 3.87 3.86 3.84 3.13 3.12 3.10 3.09 3.07 3.06 3.05 3.04 3.03 3.03 3.01 3.00 2.94 2.93 2.92 2.91 2.88 2.87 2.85 2.84 2.83 2.82 2.79 2.78 2.77 2.75 2.75 2.73
1.95 CD3CN 1.94 CD3CN 1.94 CD3CN 1.94 CD3CN 1.93 CD3CN
0.94 0.94 0.92 0.91 0.89 0.88 0.88 0.87 0.85 0.84 0.82 0.81 0.01
^{1}H NMR, 500 MHz, CD_3CN, 60 ºC
Br
NSES
N
H
Cbz
(+)-**S11**
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
f1 (ppm)

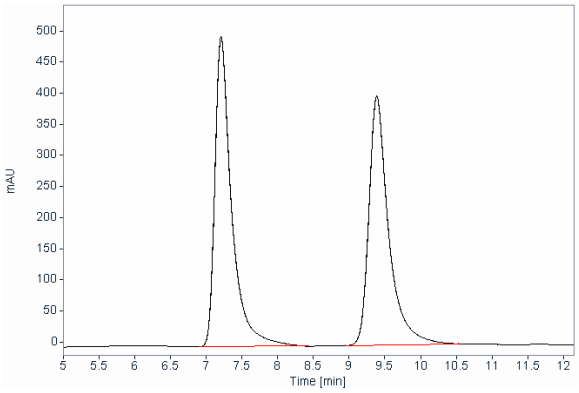

154.22
142.24
137.24
133.68
132.09
129.92
129.74
126.10
126.02
118.26 CD3CN
117.62
87.69
69.41
64.55
51.07
50.06
44.65
11.32
2.04
1.88 CD3CN
1.71 CD3CN
1.55 CD3CN
1.39 CD3CN
1.22 CD3CN
1.06 CD3CN
-1.47
13C NMR, 126 MHz, CD3CN, 60 ºC
Br
NSES
N
H
Cbz
(+)-S11
f1 (ppm)

racemate



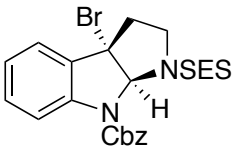
(±)-**S11**

HPLC conditions:
CHIRALPAK® IA, Lot# IA00CE-PD046
15% *i*-PrOH in hexanes
1.0 mL/min
λ = 220 nm



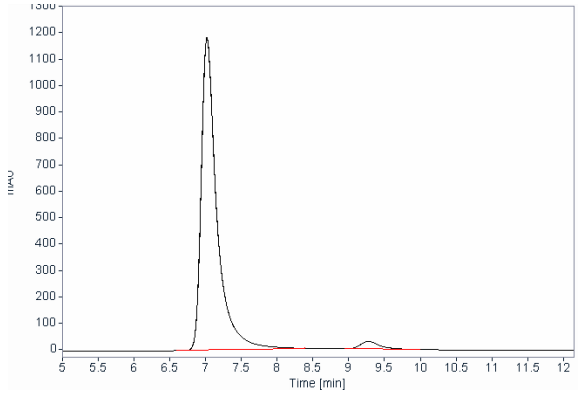
Signal: DAD1 B, Sig=220,16 Ref=360,100

Ret. Time (min)	Area%
7.204	51.3217
9.381	48.6783



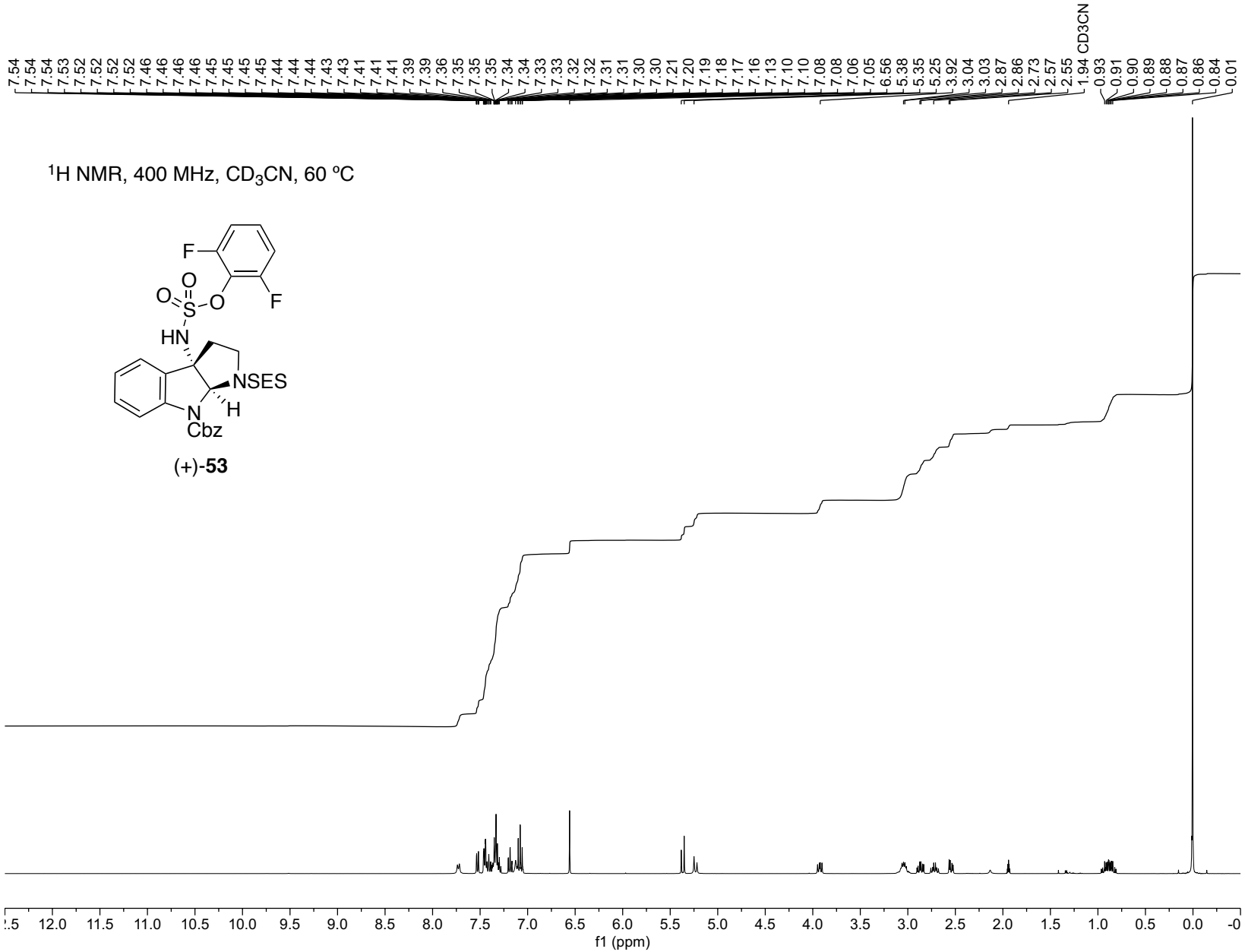
(+)-**S11**

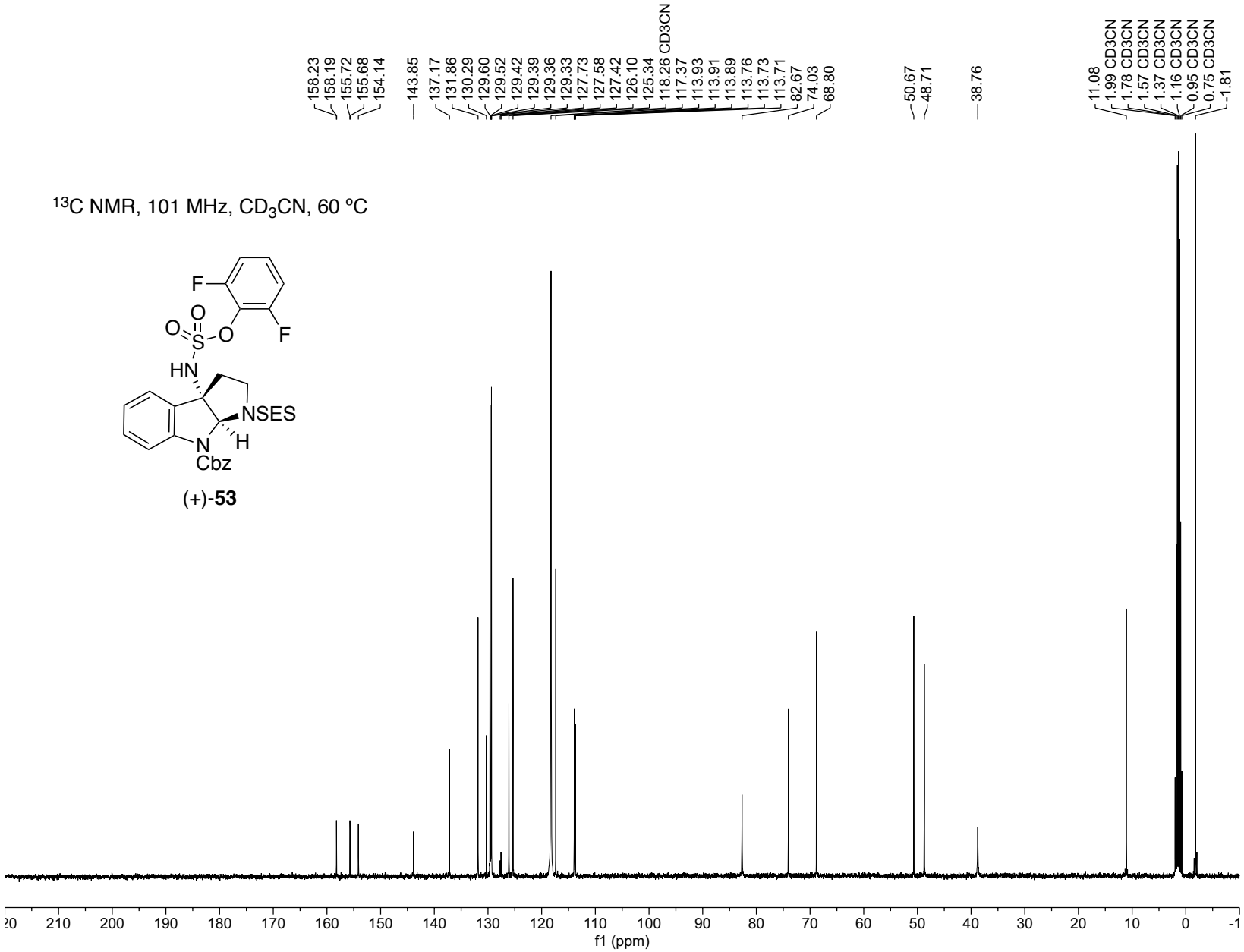
HPLC conditions:
CHIRALPAK® IA, Lot# IA00CE-PD046
15% *i*-PrOH in hexanes
1.0 mL/min
λ = 220 nm



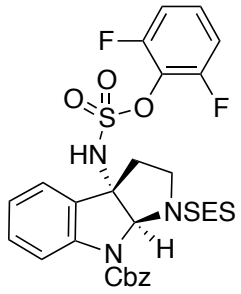
Signal: DAD1 B, Sig=220,16 Ref=360,100

Ret. Time (min)	Area%
7.016	97.0436
9.267	2.9564

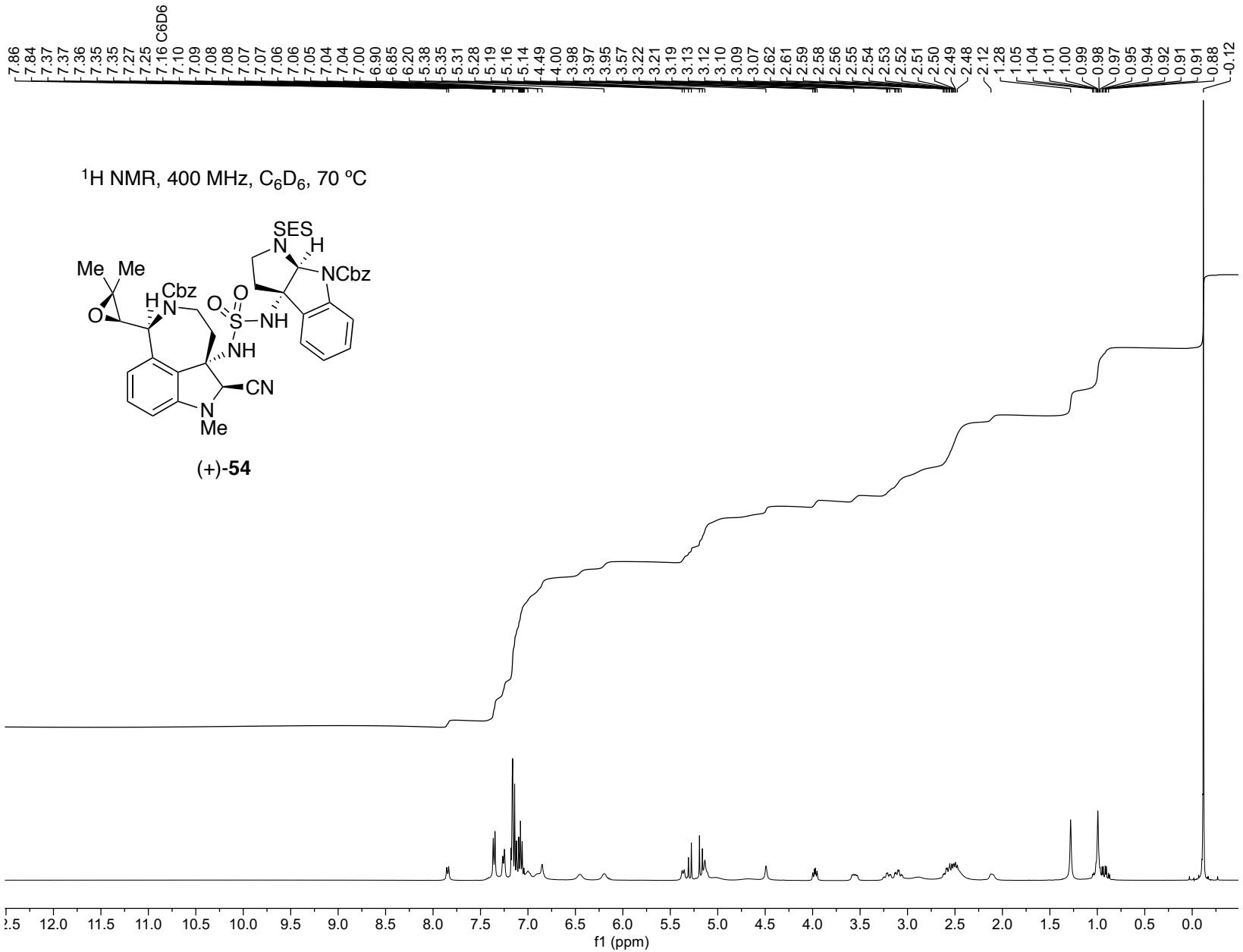

7.54 7.54 7.54 7.53 7.52 7.52 7.52 7.52 7.46 7.46 7.46 7.45 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.41 7.41 7.41 7.39 7.39 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.21 7.20 7.19 7.18 7.17 7.16 7.13 7.10 7.10 7.08 7.08 7.06 7.05 6.56 5.38 5.35 5.25 3.92 3.04 3.03 2.87 2.86 2.73 2.57 2.55 1.94 CD3CN 0.93 0.91 0.90 0.89 0.88 0.87 0.86 0.84 0.01
1H NMR, 400 MHz, CD3CN, 60 ºC
F
O
O
S
O
F
HN
NSES
N
H
Cbz
(+)-53
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
f1 (ppm)

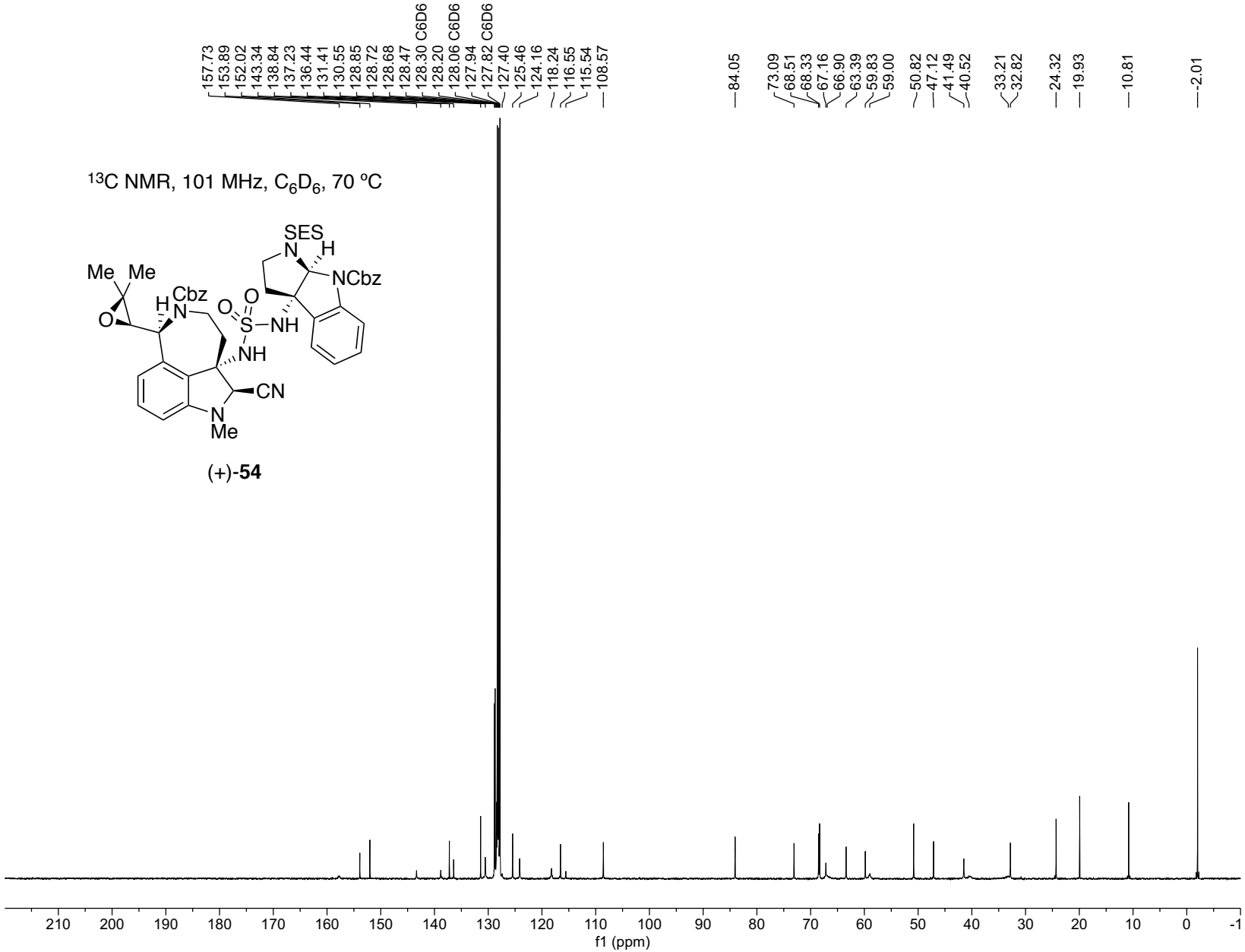

158.23
158.19
155.72
155.68
154.14
143.85
137.17
131.86
130.29
129.60
129.52
129.42
129.39
129.36
129.33
127.73
127.58
127.42
126.10
125.34
118.26 CD3CN
117.37
113.93
113.91
113.89
113.76
113.73
113.71
82.67
74.03
68.80
50.67
48.71
38.76
11.08
1.99 CD3CN
1.78 CD3CN
1.57 CD3CN
1.37 CD3CN
1.16 CD3CN
0.95 CD3CN
0.75 CD3CN
-1.81
13C NMR, 101 MHz, CD3CN, 60 ºC
F
O
O
S
O
F
HN
NSES
N
H
Cbz
(+)-53
f1 (ppm)

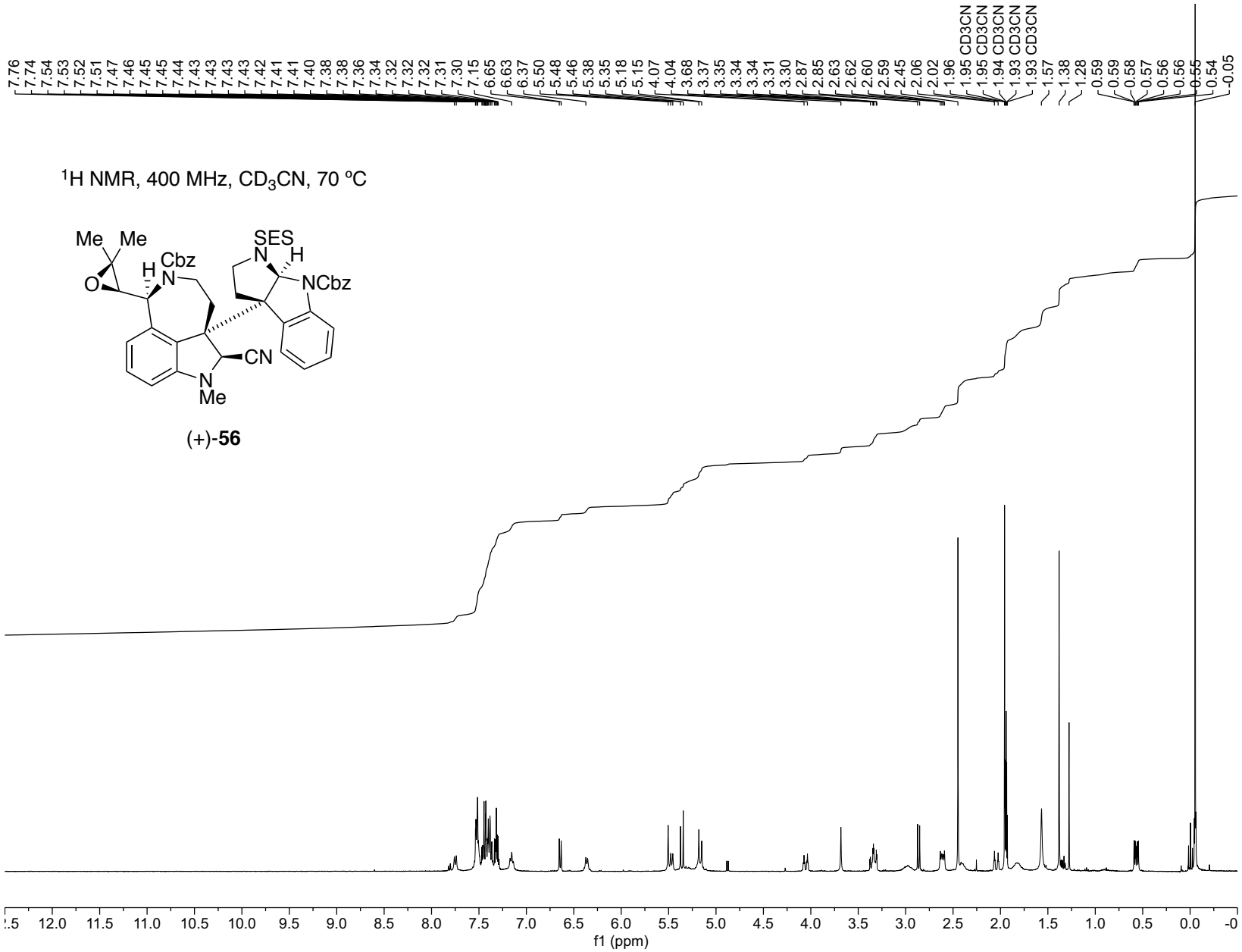
^{19}F NMR, 376 MHz, CD_3CN, 25 °C

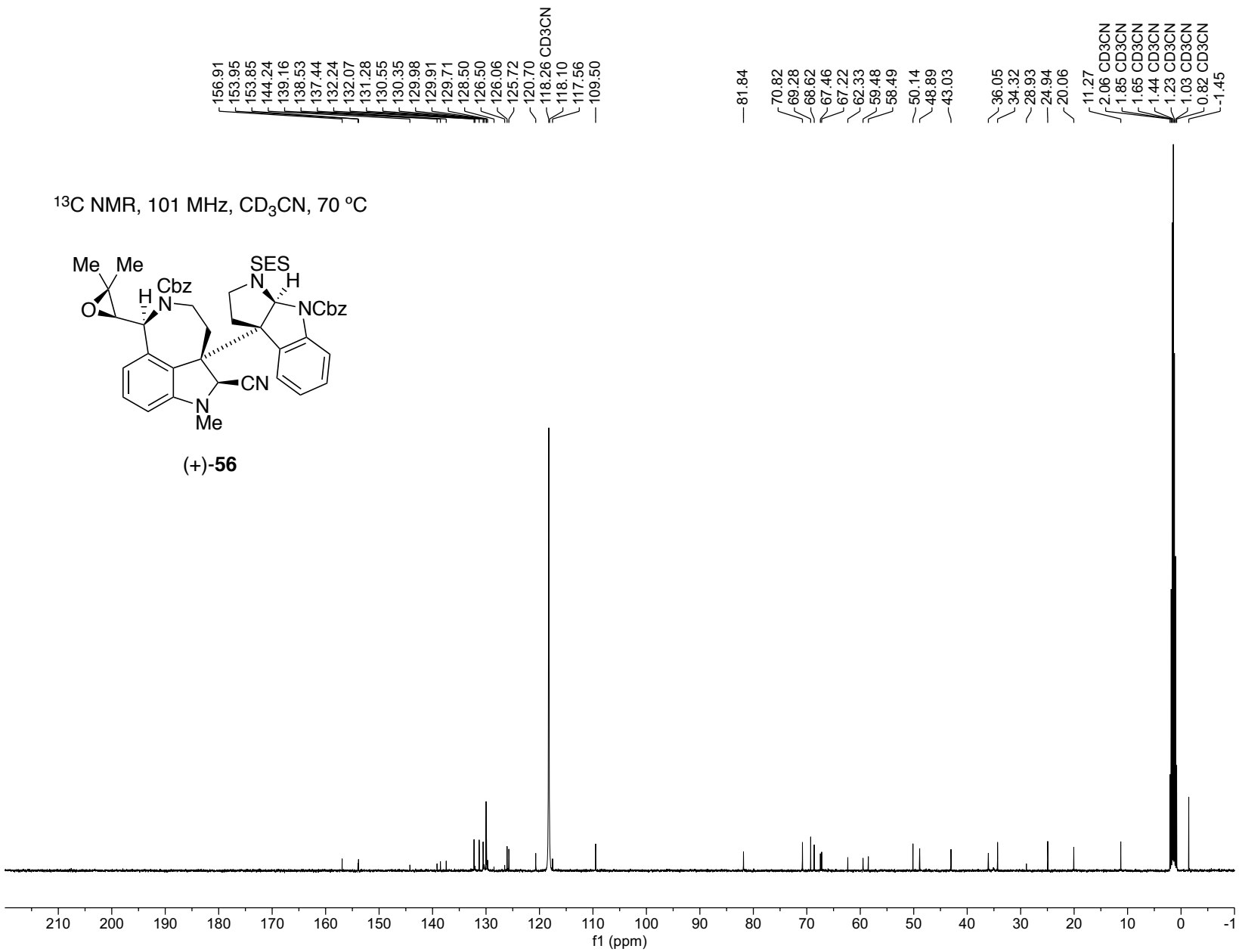


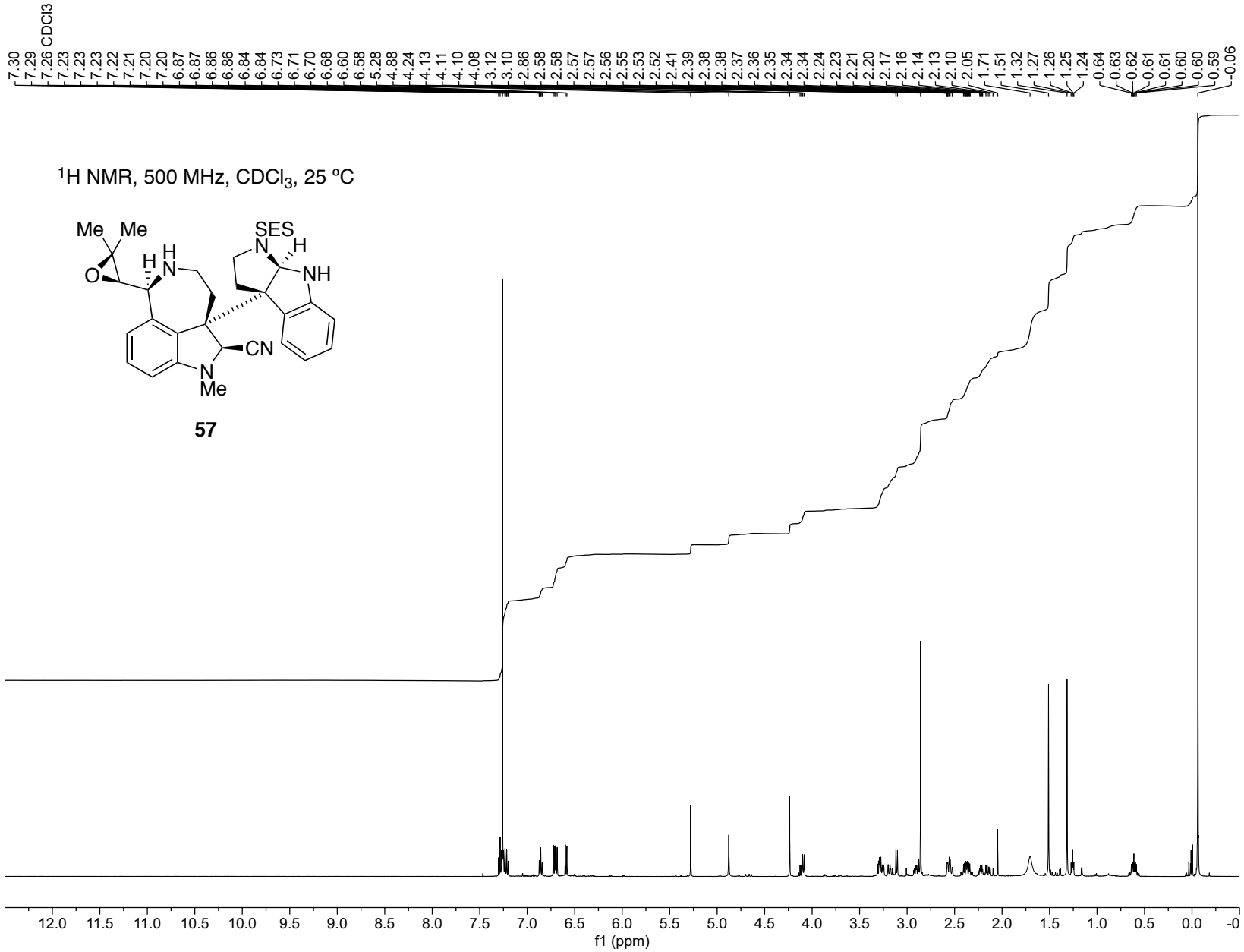
(+)-**53**

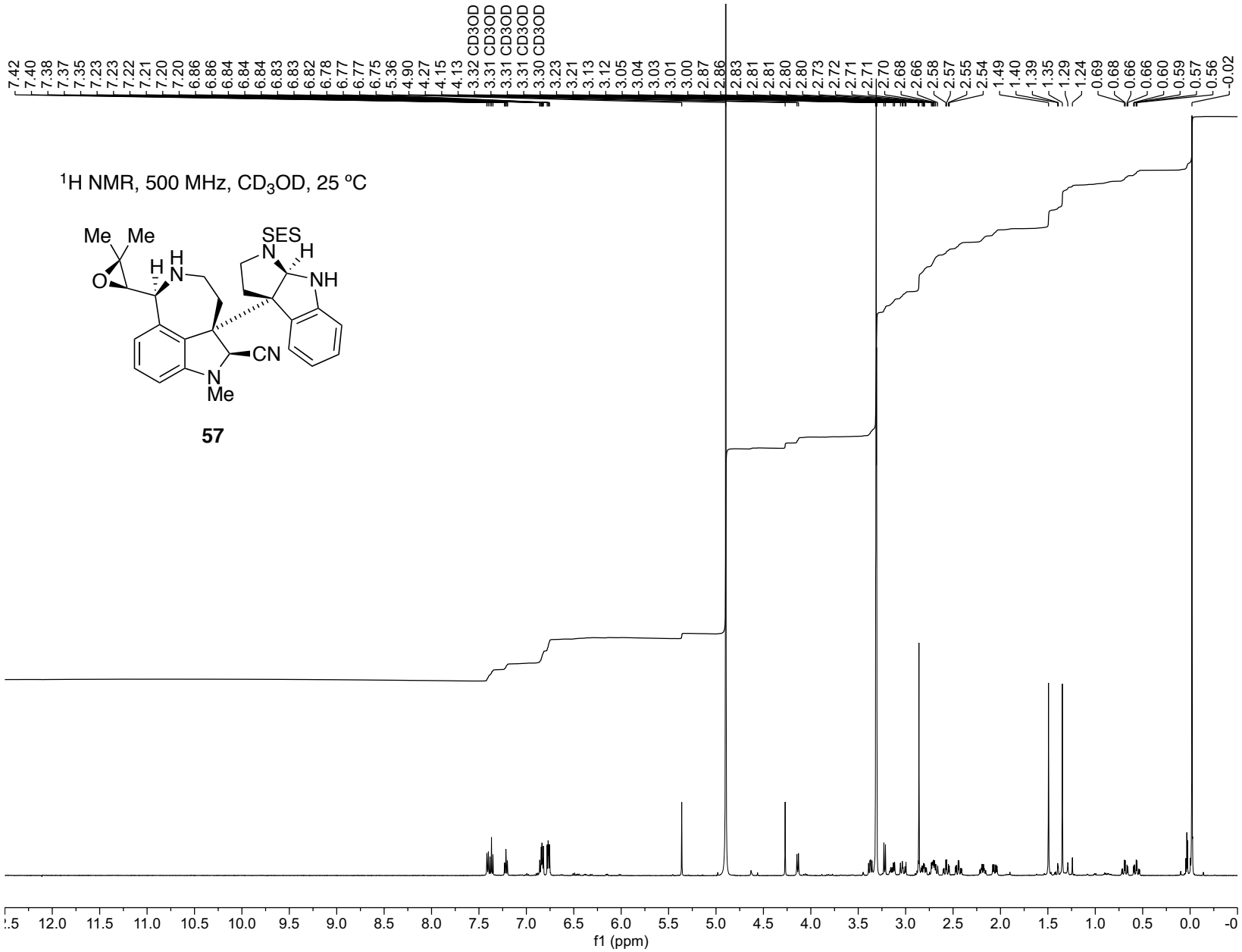

7.86 7.84 7.37 7.37 7.36 7.35 7.35 7.27 7.25 7.16 C6D6 7.10 7.09 7.08 7.08 7.07 7.07 7.06 7.06 7.05 7.04 7.04 7.00 6.90 6.85 6.20 5.38 5.35 5.31 5.28 5.19 5.16 5.14 4.49 4.00 3.98 3.97 3.95 3.57 3.22 3.21 3.19 3.13 3.12 3.10 3.09 3.07 2.62 2.61 2.59 2.58 2.56 2.55 2.54 2.53 2.52 2.51 2.50 2.49 2.48 2.12 1.28 1.05 1.04 1.01 1.00 0.99 0.98 0.97 0.95 0.94 0.92 0.91 0.91 0.88 -0.12
1H NMR, 400 MHz, C6D6, 70 ºC
SES
N H
NCbz
Me Me
Cbz
H N
O
O
O
S
NH
NH
CN
N
Me
(+)-54
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
f1 (ppm)

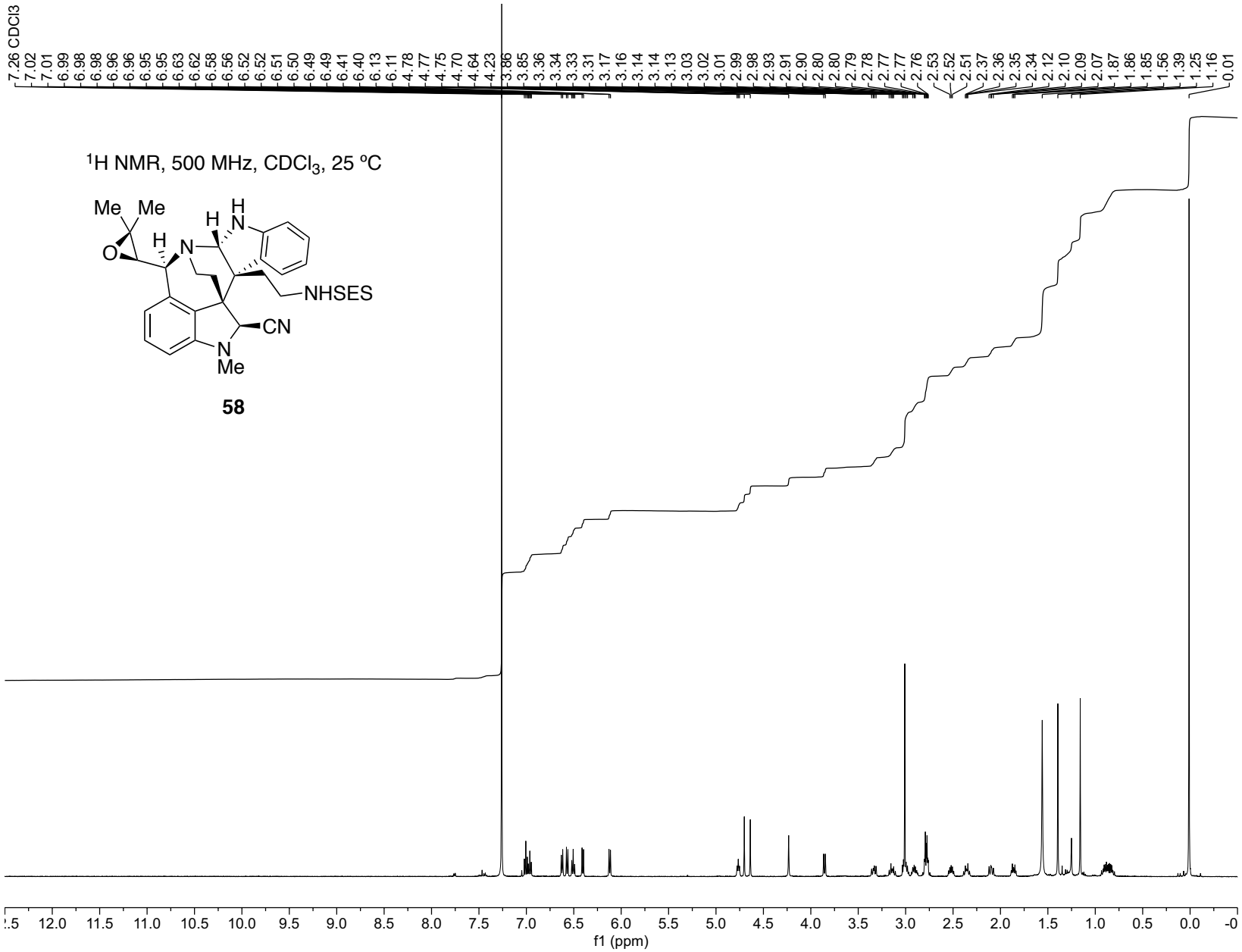

157.73
153.89
152.02
143.34
138.84
137.23
136.44
131.41
130.55
128.85
128.72
128.68
128.47
128.30 C6D6
128.20
128.06 C6D6
127.94
127.82 C6D6
127.40
125.46
124.16
118.24
116.55
115.54
108.57
84.05
73.09
68.51
68.33
67.16
66.90
63.39
59.83
59.00
50.82
47.12
41.49
40.52
33.21
32.82
24.32
19.93
10.81
-2.01
13C NMR, 101 MHz, C6D6, 70 ºC
SES
N
H
NCbz
Me
Me
Cbz
H
N
O
O
O
S
NH
NH
CN
N
Me
(+)-54
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

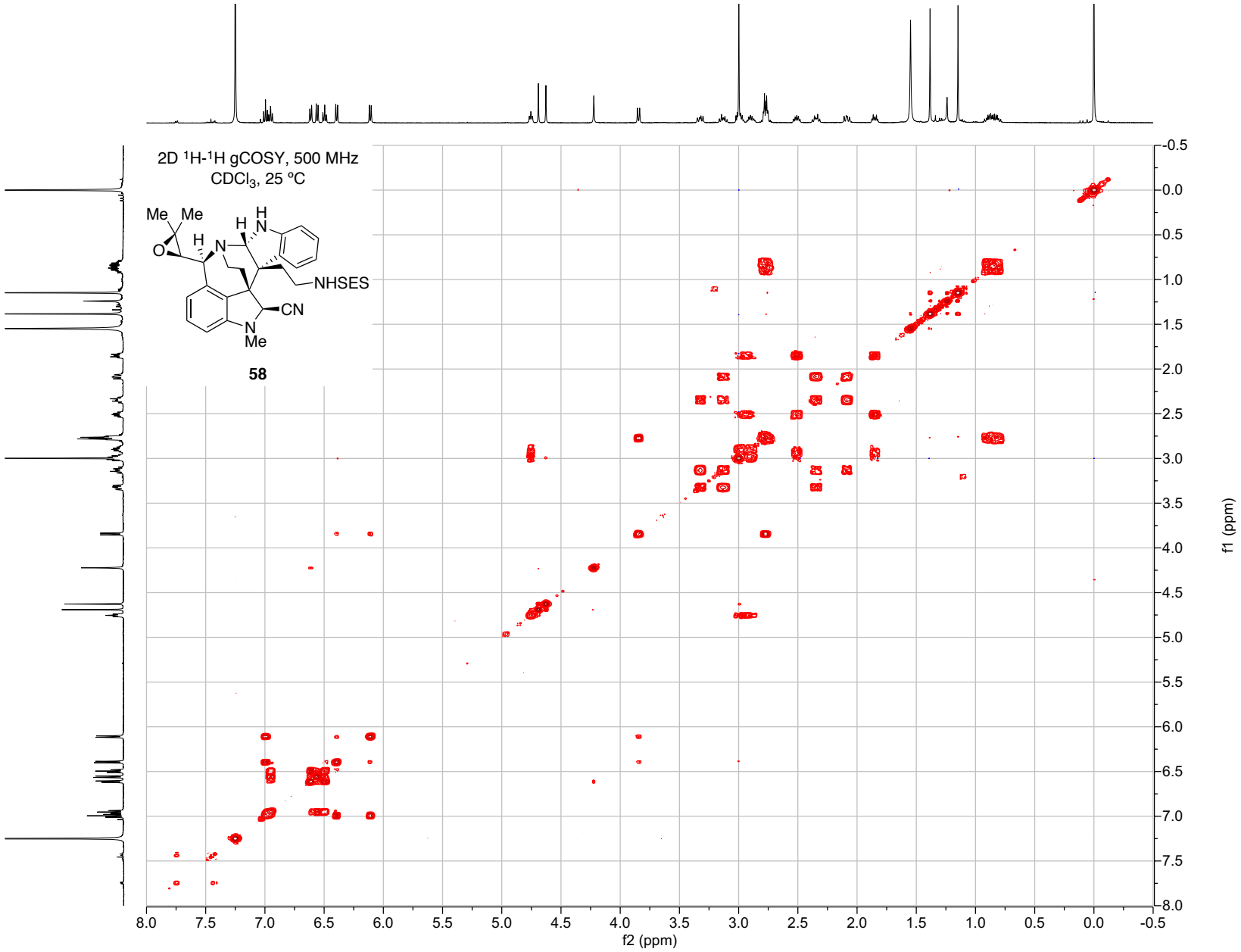

7.76 7.74 7.54 7.53 7.52 7.51 7.47 7.46 7.45 7.45 7.44 7.43 7.43 7.43 7.43 7.42 7.41 7.41 7.40 7.38 7.38 7.36 7.34 7.32 7.32 7.32 7.31 7.30 7.15 6.65 6.63 6.37 5.50 5.48 5.46 5.38 5.35 5.18 5.15 4.07 4.04 3.68 3.37 3.35 3.34 3.34 3.31 3.30 2.87 2.85 2.63 2.62 2.60 2.59 2.45 2.06 2.02 1.96 1.95 CD3CN 1.95 CD3CN 1.94 CD3CN 1.93 CD3CN 1.93 CD3CN 1.57 1.38 1.28 0.59 0.59 0.58 0.57 0.56 0.56 0.55 0.54 -0.05
1H NMR, 400 MHz, CD3CN, 70 ºC
Me Me
O
H Cbz
N
SES
N H
NCbz
CN
N
Me
(+)-56
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
f1 (ppm)

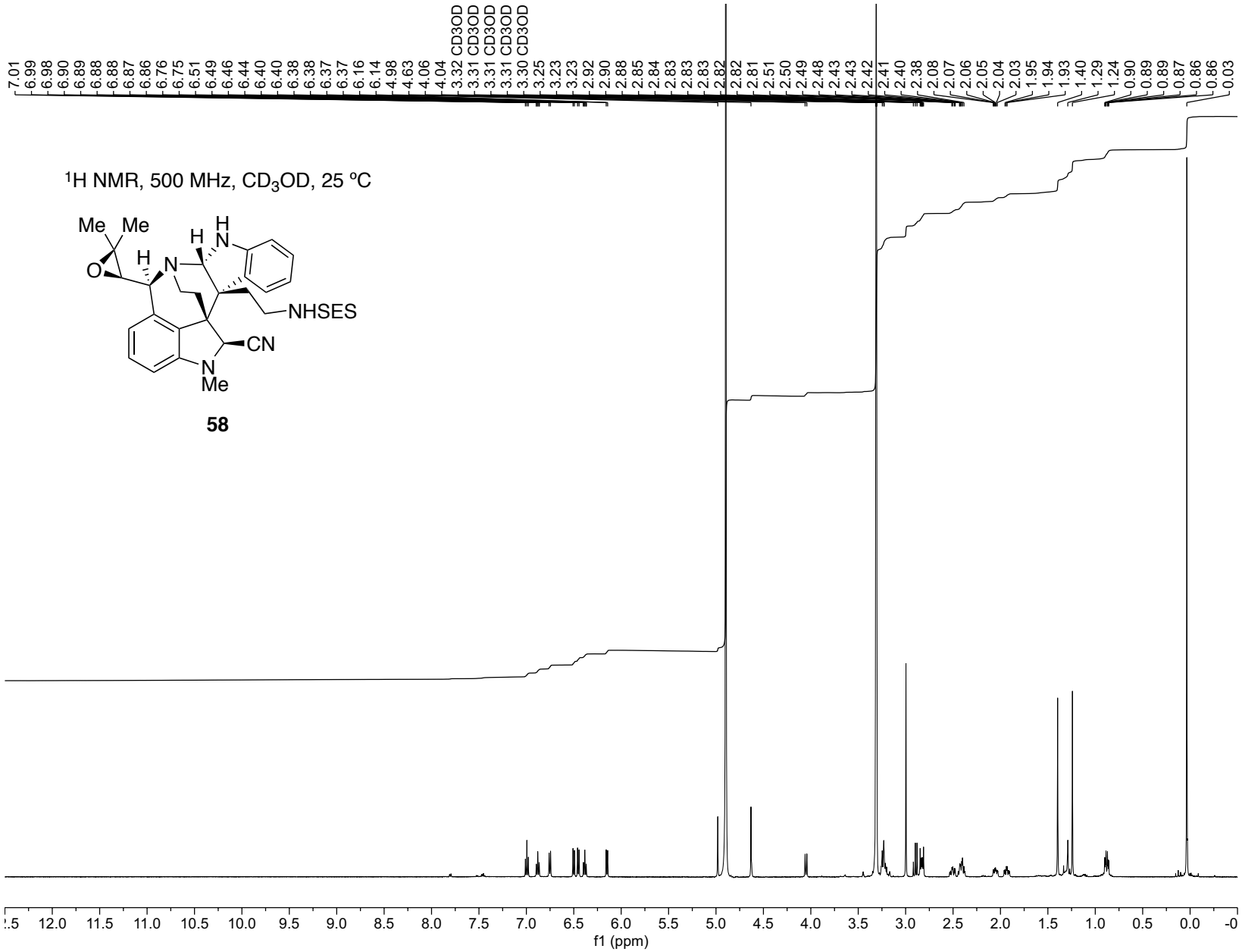

156.91
153.95
153.85
144.24
139.16
138.53
137.44
132.24
132.07
131.28
130.55
130.35
129.98
129.91
129.71
128.50
126.50
126.06
125.72
120.70
118.26 CD3CN
118.10
117.56
109.50
81.84
70.82
69.28
68.62
67.46
67.22
62.33
59.48
58.49
50.14
48.89
43.03
36.05
34.32
28.93
24.94
20.06
11.27
2.06 CD3CN
1.85 CD3CN
1.65 CD3CN
1.44 CD3CN
1.23 CD3CN
1.03 CD3CN
0.82 CD3CN
-1.45
13C NMR, 101 MHz, CD3CN, 70 °C
Me
Me
H
Cbz
N
O
SES
N
H
NCbz
CN
N
Me
(+)-56
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

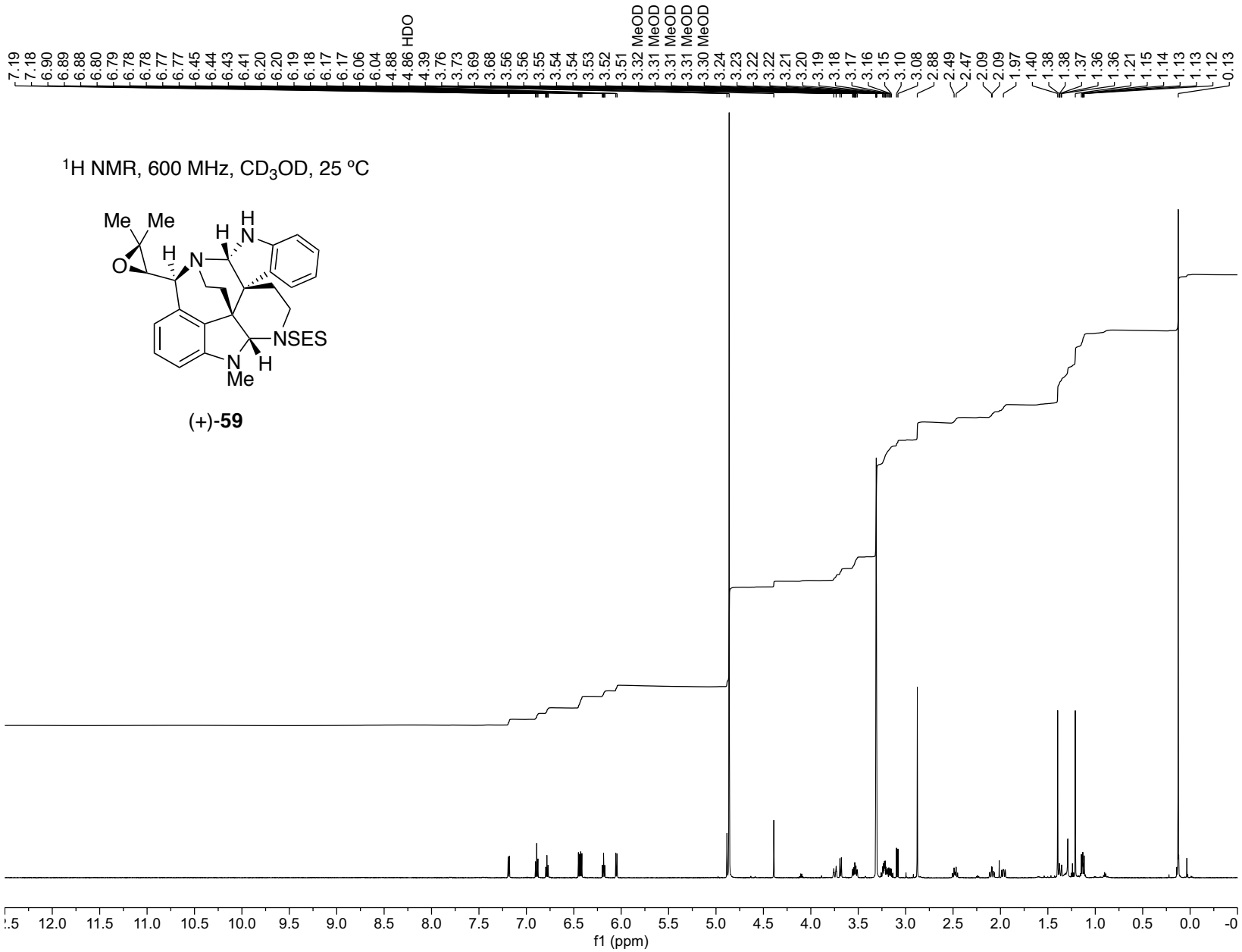

CDCl3
7.30 7.29 7.26 7.23 7.23 7.23 7.22 7.21 7.20 7.20 6.87 6.87 6.86 6.86 6.84 6.84 6.73 6.71 6.70 6.68 6.60 6.58 5.28 4.88 4.24 4.13 4.11 4.10 4.08 3.12 3.10 2.86 2.58 2.58 2.57 2.57 2.56 2.55 2.53 2.52 2.41 2.39 2.38 2.38 2.37 2.36 2.35 2.34 2.34 2.24 2.23 2.21 2.20 2.17 2.16 2.14 2.13 2.10 2.05 1.71 1.51 1.32 1.27 1.26 1.25 1.24 0.64 0.63 0.62 0.61 0.61 0.60 0.60 0.59 -0.06
1H NMR, 500 MHz, CDCl3, 25 ºC
Me Me
O
H
H
N
SES
N
H
NH
CN
N
Me
57
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
f1 (ppm)


7.42 7.40 7.38 7.37 7.35 7.23 7.23 7.22 7.21 7.20 7.20 6.86 6.86 6.84 6.84 6.84 6.83 6.83 6.82 6.78 6.77 6.77 6.75 5.36 4.90 4.27 4.15 4.13 3.32 CD3OD 3.31 CD3OD 3.31 CD3OD 3.31 CD3OD 3.30 CD3OD 3.23 3.21 3.13 3.12 3.05 3.04 3.03 3.01 3.00 2.87 2.86 2.83 2.81 2.81 2.80 2.80 2.73 2.72 2.71 2.71 2.70 2.68 2.66 2.58 2.57 2.55 2.54 1.49 1.40 1.39 1.35 1.29 1.24 0.69 0.68 0.66 0.66 0.60 0.59 0.57 0.56 -0.02
1H NMR, 500 MHz, CD3OD, 25 ºC
Me Me
H N
O
SES
N H
NH
CN
N
Me
57
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
f1 (ppm)

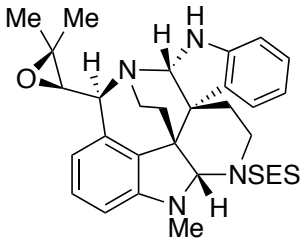

7.26 CDCl3
7.02 7.01 6.99 6.98 6.98 6.96 6.96 6.95 6.95 6.63 6.62 6.58 6.56 6.52 6.52 6.51 6.50 6.49 6.49 6.41 6.40 6.13 6.11 4.78 4.77 4.75 4.70 4.64 4.23 3.86 3.85 3.36 3.34 3.33 3.31 3.17 3.16 3.14 3.14 3.13 3.03 3.02 3.01 2.99 2.98 2.93 2.91 2.90 2.80 2.80 2.79 2.78 2.77 2.77 2.76 2.53 2.52 2.51 2.37 2.36 2.35 2.34 2.12 2.10 2.09 2.07 1.87 1.86 1.85 1.56 1.39 1.25 1.16 0.01
1H NMR, 500 MHz, CDCl3, 25 ºC
Me Me
H
N
H
N
O
NHSES
CN
N
Me
58
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
f1 (ppm)


2D ¹H-¹H gCOSY, 500 MHz
CDCl3, 25 °C
Me
Me
H
N
O
H
N
NHSES
CN
N
Me
58
f2 (ppm)
f1 (ppm)

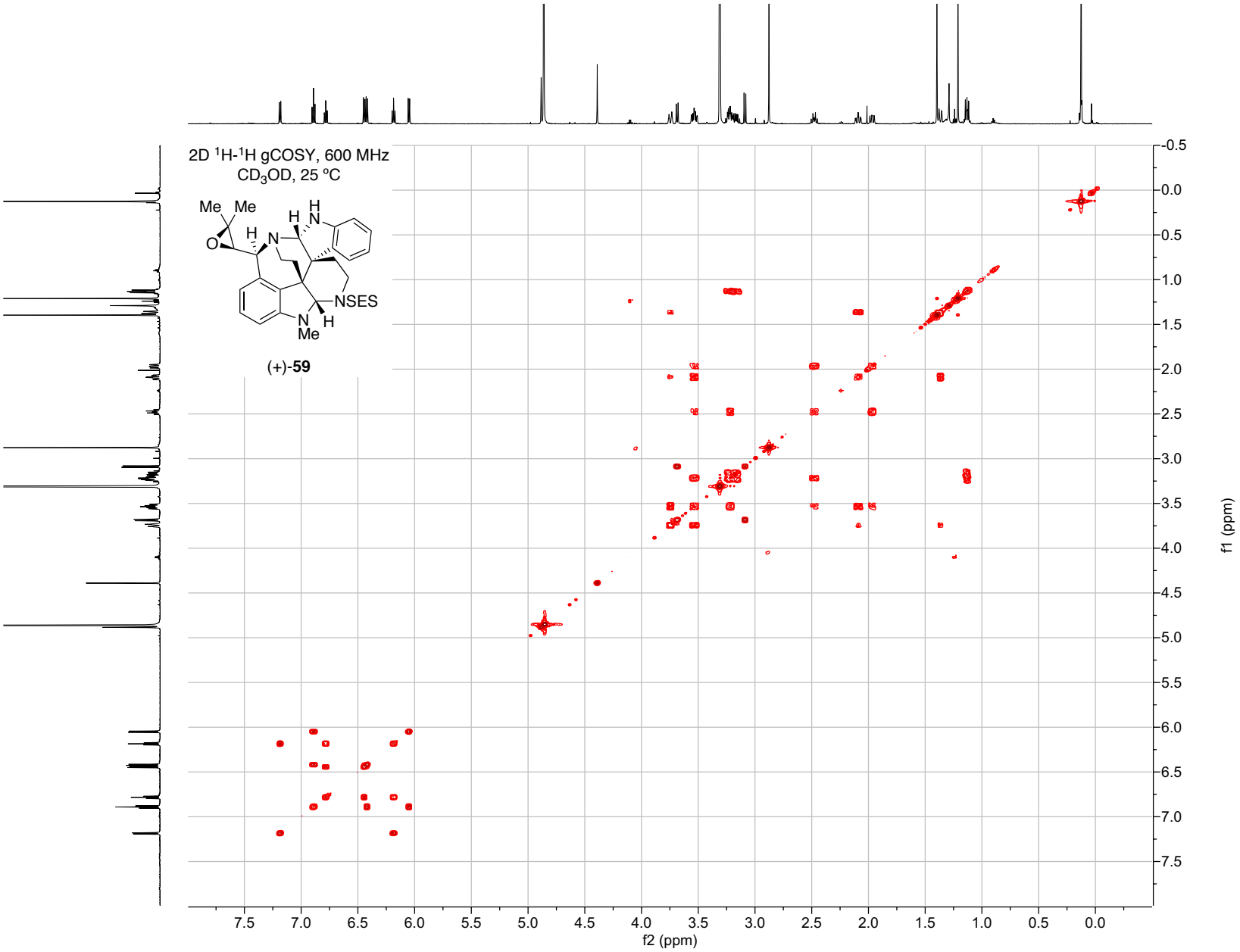

7.01 6.99 6.98 6.90 6.89 6.88 6.88 6.87 6.86 6.76 6.75 6.51 6.49 6.46 6.44 6.40 6.40 6.38 6.38 6.37 6.37 6.16 6.14 4.98 4.63 4.06 4.04 3.32 CD3OD 3.31 CD3OD 3.31 CD3OD 3.31 CD3OD 3.30 CD3OD 3.25 3.23 3.23 2.92 2.90 2.88 2.85 2.84 2.83 2.83 2.83 2.82 2.82 2.81 2.51 2.50 2.49 2.48 2.43 2.43 2.42 2.41 2.40 2.38 2.08 2.07 2.06 2.05 2.04 2.03 1.95 1.94 1.93 1.40 1.29 1.24 0.90 0.89 0.89 0.87 0.86 0.86 0.03
1H NMR, 500 MHz, CD3OD, 25 ºC
Me Me
H
N
H
N
O
NHSES
CN
N
Me
58
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
f1 (ppm)

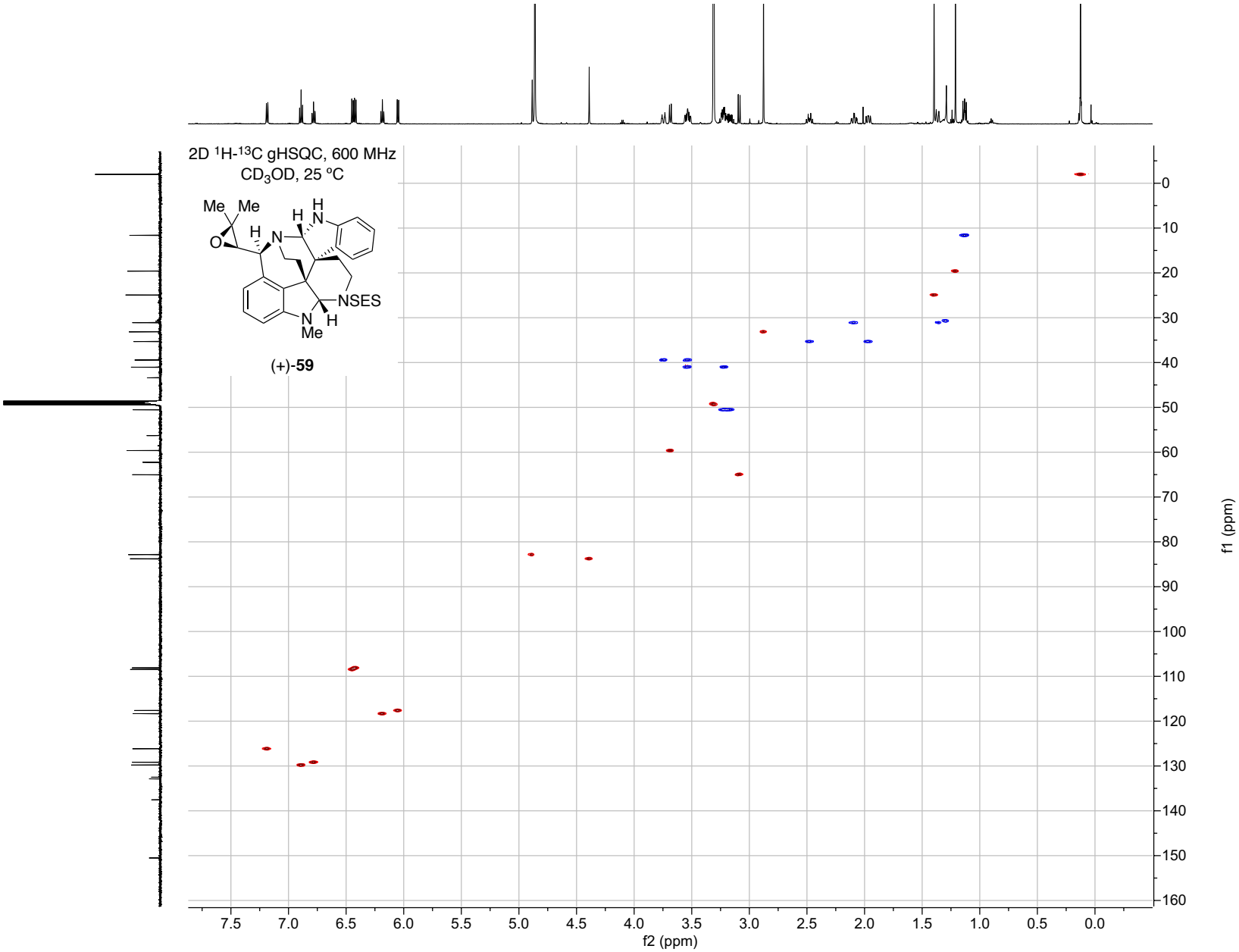

7.19 7.18 6.90 6.89 6.88 6.80 6.79 6.78 6.78 6.77 6.77 6.45 6.44 6.43 6.41 6.20 6.20 6.19 6.18 6.17 6.17 6.06 6.04 4.88 4.86 HDO 4.39 3.76 3.73 3.69 3.68 3.56 3.55 3.54 3.54 3.53 3.52 3.51 3.32 MeOD 3.31 MeOD 3.31 MeOD 3.31 MeOD 3.30 MeOD 3.24 3.23 3.22 3.22 3.21 3.20 3.19 3.18 3.17 3.16 3.15 3.10 3.08 2.88 2.49 2.47 2.09 2.09 1.97 1.40 1.38 1.38 1.37 1.36 1.36 1.21 1.15 1.14 1.13 1.13 1.12 0.13
1H NMR, 600 MHz, CD3OD, 25 ºC
Me Me
H
N
H
N
O
NSES
N
H
Me
(+)-59
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
f1 (ppm)

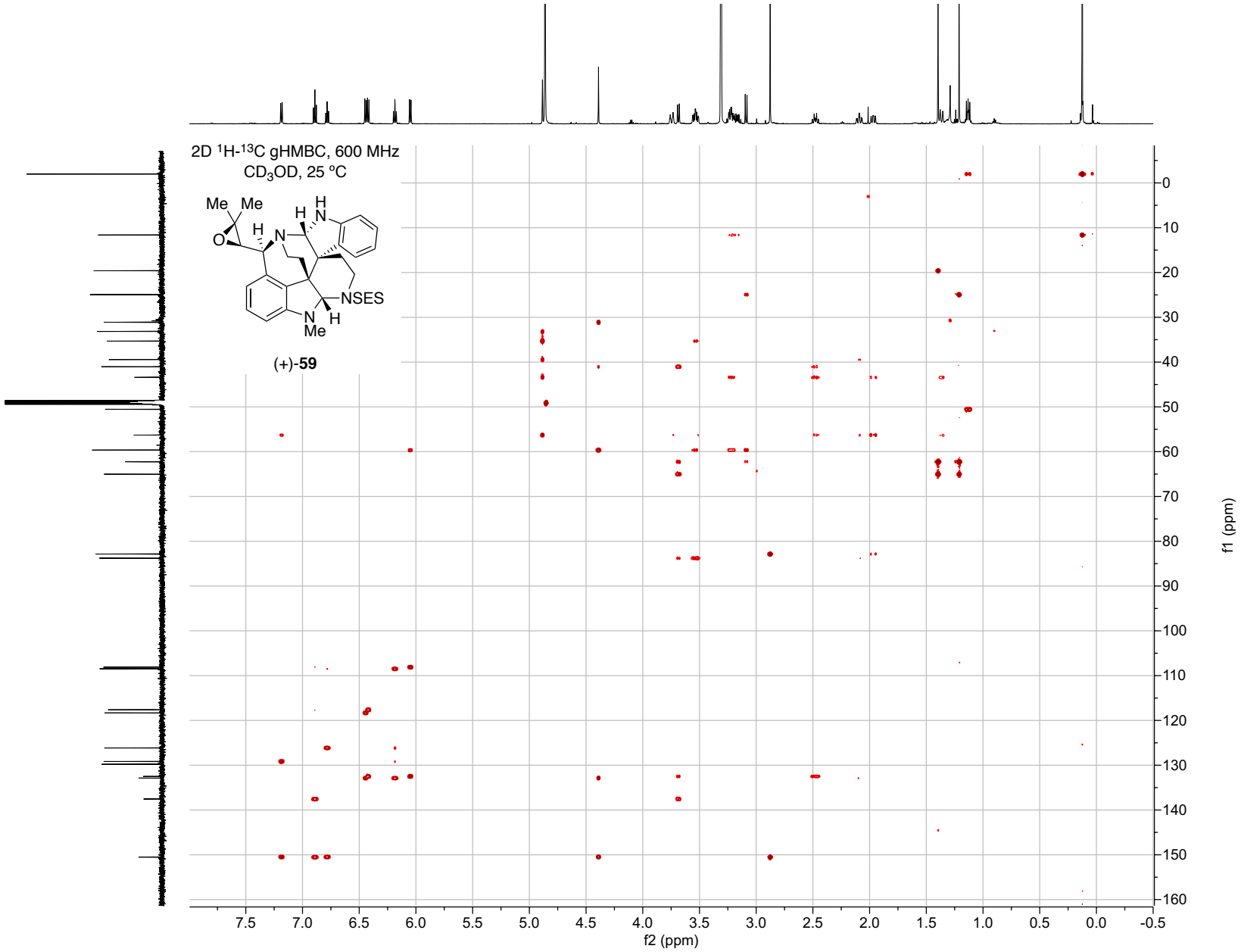
^{13}C NMR, 151 MHz, CD_3OD, 25 ºC



(+)-**59**


2D ^{1}H-^{1}H gCOSY, 600 MHz
CD_3OD, 25 °C
Me Me
H
N
O
H
N
H
N
NSES
N
H
Me
(+)-59
f2 (ppm)
f1 (ppm)


2D ^{1}H-^{13}C gHSQC, 600 MHz
CD_3OD, 25 °C
Me
Me
H
N
O
H
N
H
N
NSES
N
H
Me
(+)-59
f2 (ppm)
f1 (ppm)


2D ^{1}H-^{13}C gHMBC, 600 MHz
CD_3OD, 25 °C
Me Me
H
O
N
H N
H
NSES
N H
Me
(+)-59
f2 (ppm)
f1 (ppm)