Concise Total Synthesis of (+)-Luteoalbusins A and B

Timothy C. Adams,[†] Joshua N. Payette,[†] 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, Cambridge, Massachusetts 02139*

Supporting Information

General Procedures. All reactions were performed in oven-dried or flame-dried round-bottom flasks. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Cannulae or gas-tight syringes with stainless steel needles were used to transfer air- or moisture-sensitive liquids. Where necessary, so noted, solutions were deoxygenated by sparging with argon for a minimum of 10 min. Flash column chromatography was performed as described by Still et al. using granular silica gel (60-Å pore size, 40–63 μm, 4–6% H_2O content, Zeochem).[1] Analytical thin layer chromatography (TLC) was performed using glass plates pre-coated (0.25 mm) with 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 an aqueous solution of ceric ammonium molybdate (CAM) followed by heating on a hot plate (~ 250 ºC). Organic solutions were concentrated at 29–30 °C on rotary evaporators capable of achieving a minimum pressure of ~2 torr. The benzenesulfonyl photodeprotection was accomplished by irradiation in a Rayonet RMR-200 photochemical reactor (Southern New England Ultraviolet Company, Branford, CT, USA) equipped with 16 lamps (RPR-3500, 24 W, λ_{max} = 350 nm, bandwidth ~ 20 nm).

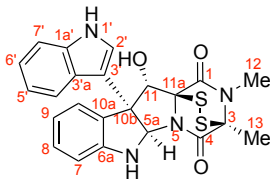
Materials. Commercial reagents and solvents were used as received with the following exceptions: dichloromethane, acetonitrile, tetrahydrofuran, methanol, pyridine, toluene, and triethylamine were purchased from J.T. Baker (Cycletainer™) and were purified by the method of Grubbs *et al*. under positive argon pressure.[2] Nitromethane and nitroethane (from Sigma–Aldrich) were purified by fractional distillation over calcium hydride and were stored over Linde 4Å molecular sieves in Schlenk flasks sealed with septa and teflon tape under argon atmosphere.[3] Bromine and silver hexafluoroantimonate(V) were purchased from Strem Chemicals, Inc.; *N*-Boc-L-sarcosine, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride, *N*-hydroxybenzotriazole, *tert*-butyldimethylsilyl trifluoromethanesulfonate, trifluoroacetic acid, 4-(dimethylamino)pyridine, silver nitrate were purchased from Chem-Impex; 1,4-dimethoxynaphthalene and trimethyltin hydroxide were purchased from Alfa Aesar; 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) was purchased from OChem Incorporation; triphenylmethanesulfenyl chloride and hafnium trifluoromethanesulfonate were purchased from TCI America, Inc. All other solvents and chemicals were purchased from Sigma–Aldrich. 1,4-Dimethoxynaphthalene was purified by crystallization from absolute ethanol.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian inverse probe 500 INOVA spectrometer, a Bruker Advance 400, or a Bruker Advance III 400 spectrometer, are reported in parts per million on the δ scale, and are referenced from the residual protium in the NMR solvent ($CHCl_3$: δ 7.26, $CHDCl_2$: δ 7.16, acetone-d_5: δ 2.05).[4] Data are reported as follows: chemical shift [multiplicity (br = broad, s = singlet, d = doublet, t = triplet, sp = septet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian 500 INOVA spectrometer, a Bruker Advance 400, or a Bruker Advance III 400 spectrometer, are reported in parts per million on the δ scale, and are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.23, CD_2Cl_2: δ 54.00, acetone-d_6: 29.84). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hertz, assignment]. Fluorine-19

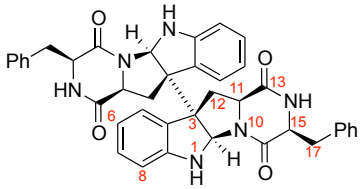
[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
[3] Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth–Heinemann: London, 2003.
[4] 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.

nuclear magnetic resonance spectra were recorded with a Bruker Advance III 400 spectrometer and are recorded in parts per million on the δ scale and are referenced from the fluorine resonances of trifluoroacetic acid (CF_3CO_2H: δ –76.55). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Infrared data (IR) were obtained with a Perkin-Elmer 2000 FTIR and are reported as follows: frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad). Optical rotations were measured on a Jasco-1010 polarimeter with a sodium lamp and are reported as follows: $[\alpha]_{\lambda}^{T\,^{\circ}C}$ (c = g/100 mL, solvent). We are grateful to Dr. Li Li and Deborah Bass for obtaining the mass spectrometric data at the Department of Chemistry's Instrumentation Facility, Massachusetts Institute of Technology. High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics APEXIV 4.7 Tesla FT-ICR-MS using an electrospray (ESI) ionization source.

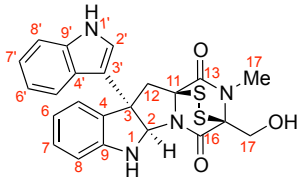
Positional Numbering System. At least three numbering systems for dimeric diketopiperazine alkaloids exist in the literature.[5] In assigning the ^{1}H and ^{13}C NMR data of all intermediates en route to our total syntheses of (+)-luteoalbusin A (**1**) and B (**2**), we wished to employ a uniform numbering scheme. For ease of direct comparison, particularly between early intermediates, non-thiolated diketopiperazines, and advanced compounds, the numbering system used by Barrow for (+)-WIN-64821 (using positional numbers 1–21) is optimal and used throughout this report. In key instances, the products are accompanied by the numbering system as shown below.



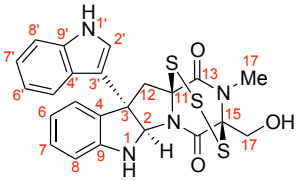
(+)-bionectin A
Kim's isolation report
Overman's reports



(+)-WIN-64821
Barrow's numbering for the simpler diketopiperazine framework



(+)-luteoalbusin A (**1**)
This document



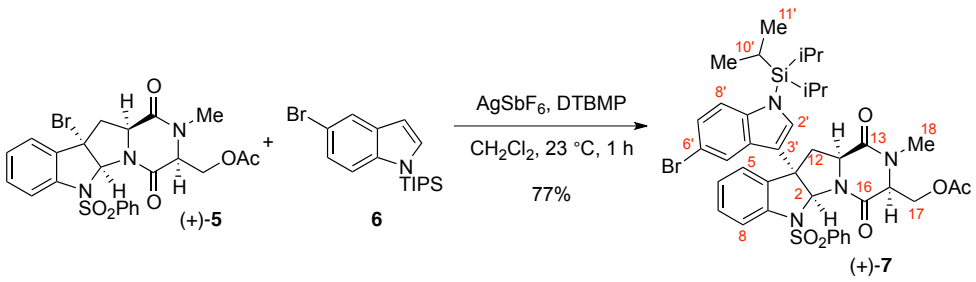
(+)-luteoalbusin B (**2**)
This document

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)

[5] (a) Von Hauser, D.; Weber, H. P.; Sigg, H. P. *Helv. Chim. Acta* **1970**, *53*, 1061. (b) Barrow, C. J.; Cai, P.; Snyder, J. K.; Sedlock, D. M.; Sun, H. H.; Cooper, R. *J. Org. Chem.* **1993**, *58*, 6016. (c) Springer, J. P.; Büchi, G.; Kobbe, B.; Demain, A. L.; Clardy, J. *Tetrahedron Lett.* **1977**, *28*, 2403. (d) Zheng, C.-J. ; Kim, C.-J. ; Bae, K. S. ; Kim, Y.-H. ; Kim, W.-G. *J. Nat. Prod.* **2006**, *69*, 1816. (e) DeLorbe, J. E. ; Jabri, S. Y. ; Mennen, S. M. ; Overman, L. E. ; Zhang, F.-L. *J. Am. Chem. Soc.* **2011**, *133*, 6549.

was grown in DMEM + 10% FBS; 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 16-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 were 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).



3-(Bromoindol-3-yl)-diketopiperazine (+)-7:

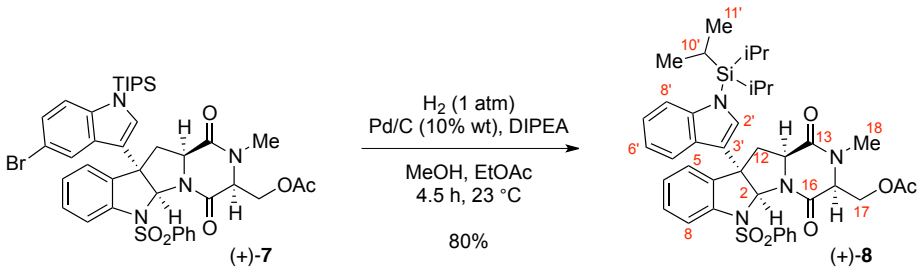
A round-bottom flask was charged with diketopiperazine (+)-**5** (500 mg, 912 μmol, 1 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 468 mg, 2.28 mmol, 2.50 equiv), and 5-bromo-1-triisopropylsilyl-1*H*-indole[6] (**6**, 1.28 g, 3.64 mmol, 4.00 equiv), and the mixture was dried azeotropically (concentration of a benzene solution, 2 × 20 mL) under reduced pressure and placed under an argon atmosphere. Anhydrous dichloromethane (10 mL) was introduced via syringe. Solid silver hexafluoroantimonate(V) (625 mg, 1.82 mmol, 2.00 equiv) was added in one portion to the solution at 23 °C and the flask was sealed under an argon atmosphere. After 1 h, the reaction mixture was diluted with dichloromethane (50 mL), was filtered through a Celite pad, and the solid was washed with dichloromethane (3 × 50 mL). The filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (eluent: gradient, 2 → 10% acetone in dichloromethane) to afford the bromoindolyl diketopiperazine (+)-**7** (573 mg, 76.6%) as a white solid. Structural assignments were made with additional information from gCOSY, HSQC, and HMBC data.

^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC): δ 7.97 (d, *J* = 8.5, 2H, SO_2Ph-*o*-**H**), 7.71 (d, *J* = 8.5, 1H, C_8**H**), 7.51 (*t*, *J* = 7.5, 1H, SO_2Ph-*p*-**H**), 7.36 (t, *J* = 7.5, 2H, SO_2Ph-*m*-**H**), 7.29-7.25 (m, 2H, C_7**H**, $C_{8'}$**H**), 7.13 (dd, *J* = 9.0, 2.0, 1H, $C_{7'}$**H**), 6.96 (app-t, *J* = 7.5, 1H, C_6**H**), 6.89 (s, 1H, $C_{2'}$**H**), 6.84 (d, *J* = 7.5, 1H, C_5**H**), 6.51, (d, *J* = 1.8, 1H, $C_{5'}$**H**), 6.27 (s, 1H, C_2**H**), 4.86 (dd, *J* = 12.5, 2.5, 1H, C_{17}**H**$_a$), 4.60 (dd, *J* = 12.5, 2.5, 1H, C_{17}**H**$_b$), 4.47 (dd, *J* = 10.5, 7.5, 1H, C_{15}**H**) 4.05 (app-*t*, *J* = 2.5, 1H, C_{15}**H**), 3.05 (dd, *J* = 14.5, 10.5, 1H, C_{12}**H**$_a$), 3.03 (s, 3H, C_{18}**H**), 2.80 (dd, *J* = 14.5, 10.5, 1H, C_{12}**H**$_b$), 1.96 (s, 3H, C**H**$_{3acetate}$), 1.56 (app-*sp*, *J* = 7.5, 3H, $C_{10'}$**H**), 1.07 (app-d, *J* = 18.0, 18H, C_{11}**H**).

^{13}C NMR (125 MHz, $CDCl_3$, 20 ºC): δ 170.9 (**C**=O$_{acetate}$), 168.5 (**C**$_{13}$), 166.0 (**C**$_{16}$), 141.3 (**C**$_{9'}$), 139.8 (**C**$_9$), 137.3 (SO_2Ph-*i*-**C**), 134.6 (**C**$_4$), 134.2 (SO_2Ph-*p*-**C**), 130.9 (**C**$_{2'}$), 130.3 (**C**$_{4'}$), 129.6 (**C**$_7$), 129.3 (SO_2Ph-*m*-**C**), 127.9 (SO_2Ph-*o*-**C**), 125.4 (**C**$_{7'}$), 124.7 (**C**$_6$), 124.1, (**C**$_5$), 121.8 (**C**$_{5'}$),

[6] 5-Bromo-1-triisopropylsilyl-1*H*-indole (**6**) was prepared in quantitative yield by silylation of commercially available 5-bromoindole using triisopropylsilyl chloride and sodium hydride in THF. For preparation and characterization, see: Brown, D. A.; Mishra, M.; Zhang, S.; Biswa, S.; Parrington, I.; Antonio, T.; Reith, M. E. A.; Dutta, A. K. *Bioorg. Med. Chem.* **2009**, *17*, 3923.

	116.1 ($\mathbf{C}_{8'}$), 115.74 ($\mathbf{C}_{8}$), 115.4 ($\mathbf{C}_{3'}$), 113.6 ($\mathbf{C}_{6'}$), 83.1, ($\mathbf{C}_{2}$), 61.1 ($\mathbf{C}_{11}$), 60.8 ($\mathbf{C}_{17}$), 59.1 ($\mathbf{C}_{15}$), 55.0 ($\mathbf{C}_{3}$), 38.5 ($\mathbf{C}_{12}$), 30.0 ($\mathbf{C}_{14}$), 20.9 ($\mathbf{C}H_{3\text{acetate}}$) 18.3 ($\mathbf{C}_{11'}$) 12.9 ($\mathbf{C}_{10'}$).
FTIR (thin film) cm^{-1}:	3069 (w), 2951 (m), 2869 (m), 1737 (s), 1677 (m), 1460 (m), 1385 (s).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{40}H_{48}BrN_4O_6SSi$ $[M+H]^+$: 819.2242, found: 819.2262.
$[\alpha]_D^{24}$:	+139.9 (*c* = 0.34, $CHCl_3$).
TLC (5% acetone in dichloromethane), R*f*:	0.26 (UV, CAM, $KMnO_4$).



3-(Indol-3-yl)-diketopiperazine (+)-8:

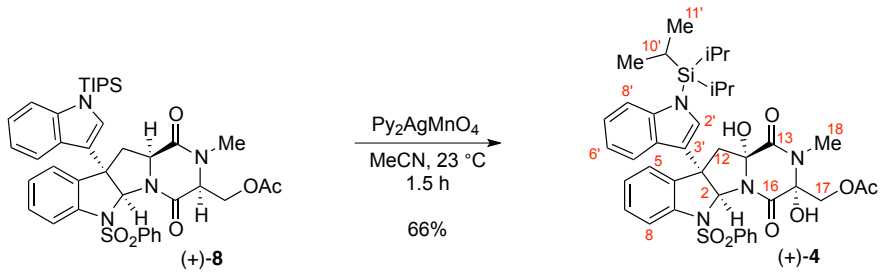
Palladium on activated charcoal (10% w/w, 488 mg) and *N*,*N*-diisopropylethylamine (DIPEA, 444 μL, 2.55 mmol, 1.10 equiv) were sequentially added to a mixture of bromoindolyl diketopiperazine (+)-**7** (1.90 g, 2.32 mmol, 1 equiv) in anhydrous methanol and ethyl acetate (3:2 v/v, 90 mL) under an atmosphere of argon. The flask was then sealed under an atmosphere of hydrogen after being purged with hydrogen gas for 10 min. The solution was vigorously stirred at room temperature for 4.5 h at 23 °C. The reaction mixture was diluted with ethyl acetate (100 mL), was filtered through a Celite pad, and the solid was washed with ethyl acetate (3 × 50 mL). The filtrate was concentrated under reduced pressure and the resulting orange residue was purified by flash column chromatography (eluent: gradient, 2 → 10% acetone in dichloromethane) to afford the C3-indolyl diketopiperazine (+)-**8** (1.38 g, 80.3%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC): δ 8.05 (d, *J* = 7.0, 2H, SO_2Ph-*o*-**H**), 7.82 (d, *J* = 8.5, 1H, C_8**H**), 7.57 (app-*t*, *J* = 7.0, 1H, SO_2Ph-*p*-**H**), 7.41–7.38 (m, 3H, $C_{8'}$**H**, SO_2Ph-*m*-**H**), 7.25 (t, *J* = 8.0, 1H, C_7**H**), 7.01 (t, *J* = 7.5, 1H, $C_{7'}$**H**), 6.97 (s, 1H, $C_{2'}$**H**), 6.93 (t, *J* = 7.5, 1H, C_6**H**), 6.76 (d, *J* = 7.5, 1H, C_5**H**), 6.56 (t, *J* = 7.5, 1H, $C_{6'}$**H**), 6.32 (s, 1H, C_2**H**), 6.02 (d, *J* = 8.5, 1H, $C_{5'}$**H**), 4.90 (dd, *J* = 11.5, 3.0, 1H, C_{17}**H**$_a$), 4.60 (dd, *J* = 11.5, 3.0, 1H, C_{17}**H**$_b$), 4.46 (dd, *J* = 10.5, 6.5, 1H, C_{15}**H**), 4.03 (app-t, *J* = 2.7, 1H, C_{11}**H**), 3.09 (dd, *J* = 14.0, 10.5, 1H, C_{12}**H**$_a$), 3.05 (s, 3H, C_{18}**H**), 2.69 (dd, *J* = 14.5, 10.0, 1H, C_{12}**H**$_b$), 2.04 (s, 3H, C**H**$_{3acetate}$), 1.61 (app-sp, *J* = 7.5, 3H, $C_{10'}$**H**), 1.07 (app-d, *J* = 18.0, 18H, $C_{11'}$**H**).

^{13}C NMR (125 MHz, $CDCl_3$, 20 ºC): δ 171.0 (**C**=O$_{acetate}$), 168.9 (**C**$_{13}$), 166.5 (**C**$_{16}$), 142.7 (**C**$_{9'}$), 139.7 (**C**$_9$), 137.0 (SO_2Ph-*i*-**C**), 135.0 (**C**$_4$), 133.7 (SO_2Ph-*p*-**C**), 129.4 (**C**$_{2'}$), 129.3 (SO_2Ph-*m*-**C**), 129.1 (SO_2Ph-*o*-**C**), 128.5 (**C**$_{4'}$), 128.3 (**C**$_7$), 124.6 (**C**$_{7'}$), 123.8 (**C**$_6$), 122.3 (**C**$_5$), 120.2 (**C**$_{5'}$), 119.3 (**C**$_{8'}$), 115.7 (**C**$_8$) 115.3 (**C**$_{3'}$), 114.6 (**C**$_{6'}$), 82.9 (**C**$_2$), 61.1 (**C**$_{11}$), 60.9 (**C**$_{17}$), 59.5 (**C**$_{15}$), 55.3 (**C**$_3$), 38.6 (**C**$_{12}$), 29.9 (**C**$_{17}$), 21.0 (**C**H$_{3acetate}$), 18.4 (**C**$_{11'}$), 13.0 (**C**$_{10'}$).

FTIR (thin film) cm^{-1}: 2950 (br-m), 1734 (s), 1675 (s), 1451 (s), 1385 (s), 1180 (s), 1150 (m).

HRMS (ESI) (*m*/*z*):	calc'd for $C_{40}H_{52}N_5O_6SSi$ $[M+NH_4]^+$: 758.3402, found: 758.3391.
$[\alpha]_D^{24}$:	+137.1 (*c* = 1.12, $CHCl_3$).
TLC (5% acetone in dichloromethane), R*f*:	0.34 (UV, CAM, $KMnO_4$).



3-(Indol-3-yl)-diketopiperazine diol (+)-4:

Bis(pyridine)silver permanganate[7] (3.77 g, 9.80 mmol, 5.00 equiv) was added as a solid to a solution of C3-indolyl diketopiperazine (+)-**8** (1.45 g, 1.96 mmol, 1 equiv) in acetonitrile (45 mL) at 23 °C. After 1.5 h, the dark purple solution was diluted with ethyl acetate (10 mL) and washed with aqueous sodium bisulfite solution (1 M, 20 mL). The resulting aqueous layer was extracted with ethyl acetate (2 × 20 mL) and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 5% acetone in dichloromethane) to afford diol (+)-**4** (1.00 g, 66.0%) as a white solid. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

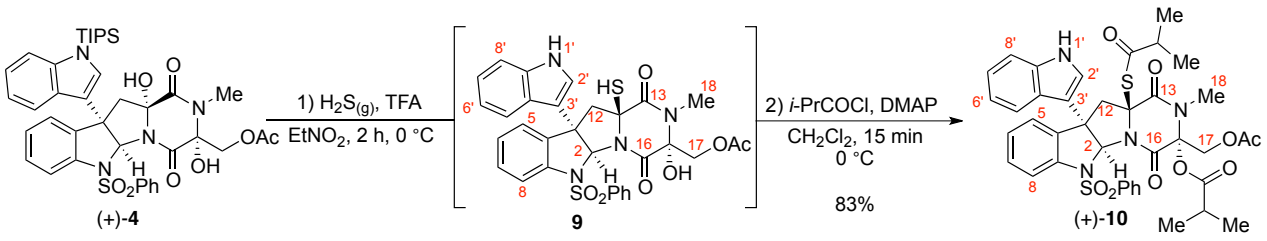
^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC): δ 7.94 (d, *J* = 7.8, 2H, SO_2Ph-*o*-**H**), 7.76 (d, *J* = 8.1, 1H, C_8**H**), 7.54 (t, *J* = 7.5, 1H, SO_2Ph-*p*-**H**), 7.42 (d, *J* = 8.4, 1H, $C_{8'}$**H**), 7.34 (t, *J* = 7.7, 2H, SO_2Ph-*m*-**H**), 7.29–7.25 (m, 1H, C_7**H**), 7.06 (t, *J* = 6.6, 1H, $C_{7'}$**H**), 7.03 (s, 1H, $C_{2'}$**H**), 6.98 (t, *J* = 7.5, 1H, C_6**H**), 6.85 (d, *J* = 7.5, 1H, C_5**H**), 6.65 (s, 1H, C_2**H**), 6.64–6.61 (m, 1H, $C_{6'}$**H**), 6.30 (br-d, *J* = 7.6, 1H, $C_{5'}$**H**), 4.91 (d, *J* = 11.6, 1H, C_{17}**H**$_a$), 4.48 (br-s, 1H, O**H**), 4.46 (br-s, 1H, O**H**), 4.16 (d, *J* = 11.7, 1H, C_{17}**H**$_b$), 3.18 (d, *J* = 14.7, 1H, C_{12}**H**$_a$), 3.11 (d, *J* = 14.8, 1H, C_{12}**H**$_b$), 3.04 (s, 3H, C_{17}**H**), 1.97 (s, 3H, C**H**$_{3acetate}$), 1.64–1.58 (m, 3H, $C_{10'}$**H**), 1.07 (app-d, *J* = 7.5, 18H, $C_{11'}$**H**).

^{13}C NMR (125 MHz, $CDCl_3$, 20 ºC): δ 170.4 (**C**=O$_{acetate}$), 168.3 (**C**$_{13}$), 167.0 (**C**$_{16}$), 142.6 (**C**$_{9'}$), 139.7 (**C**$_9$), 137.5 (**C**$_{4'}$), 136.4 (**C**$_4$), 133.7 (SO_2Ph-*p*-**C**), 131.0 (**C**$_6$), 129.4 (**C**$_{7'}$), 129.2 (SO_2Ph-*m*-**C**), 128.4 (SO_2Ph-*i*-**C**), 128.1 (SO_2Ph-*o*-**C**), 125.0 (**C**$_{2'}$), 124.6 (**C**$_5$), 122.3 (**C**$_{7'}$) 120.6 (**C**$_{6'}$), 119.4 (**C**$_{5'}$), 116.7 (**C**$_{3'}$), 115.9 (**C**$_8$), 114.6 (**C**$_{8'}$), 88.3 (**C**$_{11}$), 86.3 (**C**$_{15}$), 83.7 (**C**$_2$), 63.8 (**C**$_{17}$), 54.3 (**C**$_3$), 46.4 (**C**$_{12}$), 27.7 (**C**$_{18}$), 20.9 (**C**H$_{3acetate}$), 18.4 (**C**$_{11'}$), 13.0 (**C**$_{10'}$).

FTIR (thin film) cm^{-1}: 3374 (br-s), 2949 (s), 2869 (m), 1749 (m), 1697 (s), 1450 (m), 1375 (s), 1229 (m), 1170 (s).

[7] Firouzabadi, H.; Vessal, B.; Naderi, M. *Tetrahedron Lett.* **1982**, *23*, 1847.

HRMS (ESI) (*m*/*z*):	calc'd for $C_{40}H_{49}N_4O_8SSi$ $[M+H]^+$: 773.3035, found: 773.3016.
$[\alpha]_D^{24}$:	+9.0 (*c* = 0.91, $CHCl_3$).
TLC (10% acetone in dichloromethane), R*f*:	0.23 (UV, CAM).



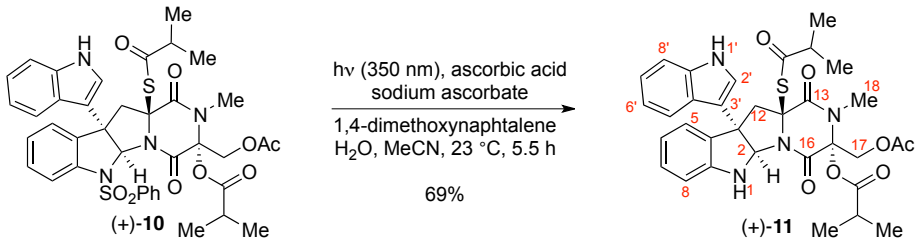
3-(Indol-3-yl)-diketopiperazine thioisobutyrate (+)-10:

A slow stream of hydrogen sulfide gas was introduced into a solution of diol (+)-**4** (859 mg, 1.11 mmol, 1 equiv) in anhydrous nitroethane (60 mL) at 0 °C, providing a saturated hydrogen sulfide solution. After 15 min, trifluoroacetic acid (30 mL) was added via syringe, and the slow introduction of hydrogen sulfide into the mixture was maintained for another 10 min. The reaction mixture was maintained under an atmosphere of hydrogen sulfide at 0 °C. After 2 h, the resulting mixture was concentrated under reduced pressure to afford the thiol **9** that was used in the next step without further purification. A solution of the thiol **9** in anhydrous dichloromethane (90 mL) was placed under an atmosphere of argon and cooled to 0 °C. Solid 4-dimethylaminopyridine (DMAP, 1.36 g, 11.1 mmol, 10.0 equiv) was added in one portion to the solution. The mixture was sealed under an atmosphere of argon and isobutyryl chloride (582 μL, 5.55 mmol, 5.00 equiv) was added via syringe. After 15 min, methanol (2 mL) was added to the reaction mixture. After 5 min, the reaction mixture was diluted with dichloromethane (90 mL) and warmed to 23 °C. The resulting mixture was sequentially washed with aqueous hydrogen chloride solution (1 N, 2 × 30 mL), water (2 × 30 mL), and saturated aqueous sodium chloride solution (30 mL). The organic layer was dried over anhydrous sodium sulfate, was filtered, and was concentrated under reduced pressure. The yellow residue was purified by flash column chromatography on silica gel (eluent: gradient, 15 → 30% acetone in hexanes) to afford the thioisobutyrate (+)-**10** (708 mg, 82.6%) as a colorless gel.

^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC): δ 7.90 (br-s, 1H, $N_{1'}$**H**), 7.77 (d, *J* = 8.2, 1H, C_8**H**), 7.57 (app-d, *J* = 8.0, 2H, SO_2Ph-*o*-**H**), 7.35–7.24 (m, 4H, $C_{6'}$**H**, C_7**H**, SO_2Ph-*p*-**H**, C_5**H**), 7.14 (app-d, *J* = 7.5, 1H, $C_{8'}$**H**), 7.10 (app-d, *J* = 7.6, 1H, $C_{5'}$**H**), 7.07–7.03 (m, 3**H**, SO_2Ph-*m*-**H**, C_6**H**), 6.77 (app-t, *J* = 7.8, 1H, $C_{7'}$**H**), 6.76 (s, 1H, C_2**H**), 6.41 (d, *J* = 2.3, 1H, $C_{2'}$**H**), 4.83 (d, *J* = 11.5, 1H, C_{17}**H**$_a$), 4.51 (d, *J* = 11.5, 1H, C_{17}**H**$_b$), 3.93 (d, *J* = 14.4, 1H, C_{12}**H**$_a$), 3.54 (d, *J* = 14.4, 1H, C_{12}**H**$_b$), 2.91 (s, 3H, C_{18}**H**), 2.66 (app-sp, *J* = 7.0, 1H, C**H**$_{isobutyrate}$), 2.20 (app-sp, *J* = 6.9, 1H, C**H**$_{thioisobutyrate}$), 2.17 (s, 3H, C**H**$_{3acetate}$), 1.24 (d, *J* = 7.1, 3H, C**H**$_{3isobutyrate}$), 1.23 (d, *J* = 6.9, 3H, C**H**$_{3isobutyrate}$), 0.95 (d, *J* = 7.0, 3H, C**H**$_{3thioisobutyrate}$), 0.84 (d, *J* = 6.9, 3H, C**H**$_{3thioisobutyrate}$).

^{13}C NMR (125 MHz, $CDCl_3$, 20 ºC): δ 200.2 (**C**=O$_{thioisobutyrate}$), 175.3 (**C**=O$_{isobutyrate}$), 170.0 (**C**=O$_{acetate}$), 166.2 (**C**$_{13}$), 161.1 (**C**$_{16}$), 142.6 (**C**$_9$), 138.0 (SO_2Ph-*i*-**C**), 137.1 (**C**$_{9'}$), 136.2 (**C**$_4$), 133.1 (SO_2Ph-*p*-**C**), 129.3 (**C**$_7$), 128.6 (SO_2Ph-*m*-**C**), 127.2 (SO_2Ph-*o*-**C**), 125.3 (**C**$_6$), 125.0 (**C**$_5$), 124.5 (**C**$_{4'}$), 123.4 (**C**$_{2'}$), 122.4 (**C**$_{7'}$), 120.1 (**C**$_{6'}$),

	119.6 ($\mathbf{C}_{5'}$), 116.9 ($\mathbf{C}_{8}$), 116.1 ($\mathbf{C}_{3'}$), 111.4 ($\mathbf{C}_{8'}$), 86.8 ($\mathbf{C}_{15}$), 84.6 ($\mathbf{C}_{2}$), 74.3 ($\mathbf{C}_{11}$), 63.4 ($\mathbf{C}_{17}$), 53.8 ($\mathbf{C}_{3}$), 44.0 ($\mathbf{C}_{12}$), 43.4 ($\mathbf{C}H_{\text{thioisobutyrate}}$), 33.9 ($\mathbf{C}H_{\text{isobutyrate}}$), 28.6 ($\mathbf{C}_{18}$), 21.3 ($\mathbf{C}H_{\text{3acetate}}$), 19.3 ($\mathbf{C}H_{\text{3isobutyrate}}$), 19.1 ($\mathbf{C}H_{\text{3isobutyrate}}$), 19.1 ($\mathbf{C}H_{\text{3thioisobutrate}}$), 18.5 ($\mathbf{C}H_{\text{3thiosisobutyrate}}$).
FTIR (thin film) cm^{-1}:	3398 (s), 2973 (m), 1745 (s), 1698 (s), 1461 (m), 1448 (m), 1369 (s), 1266 (w), 1220 (m), 1171 (m), 1092 (m), 1054 (m), 950 (m).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{39}H_{40}N_4NaO_9S_2$ $[M+Na]^+$: 795.2134, found: 795.2161.
$[\alpha]_D^{24}$:	+31 ($c = 0.45$, $CHCl_3$).
TLC (5% ethyl acetate in dichloromethane), R*f*:	0.26 (UV, CAM, $KMnO_4$).



3-(Indol-3-yl)-diketopiperazine amine (+)-11:

A solution of sulfonamide (+)-**10** (734 mg, 949 μmol, 1 equiv) in a water–acetonitrile (20% v/v, 100 mL) in a 250-mL Pyrex round-bottom flask was sequentially charged with L-ascorbic acid (1.67 g, 9.49 mmol, 10.0 equiv), sodium L-ascorbate (1.88 g, 9.49 mmol, 10.0 equiv), and 1,4-dimethoxynaphthalene (3.58 g, 19.0 mmol, 20.0 equiv). The resulting mixture was purged with argon for 15 min at 23 °C. The reaction mixture was irradiated with a Rayonet photoreactor equipped with 16 lamps emitting at 350 nm at 23 °C under an argon atmosphere with vigorous stirring. After 5.5 h, the lamps were turned off, and the reaction mixture was diluted with ethyl acetate (150 mL). The resulting solution was sequentially washed with saturated aqueous sodium bicarbonate solution (30 mL) and saturated aqueous sodium chloride solution (30 mL). The aqueous layer was extracted with ethyl acetate (2 × 40 mL). The combined organic layers 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: gradient, 5→20% acetone in hexanes) to afford the amine (+)-**11** (413 mg, 68.8%) as a tan solid.

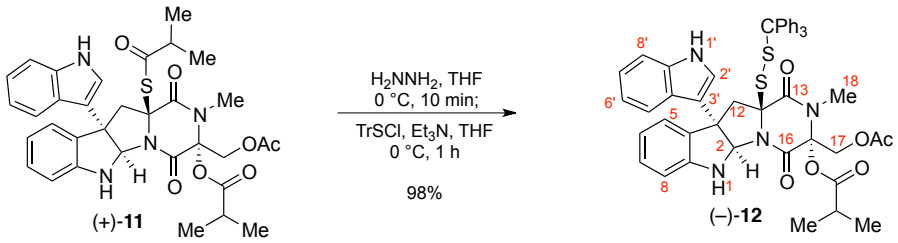
^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC):

δ 8.05 (br-s, 1H, $N_{1'}$**H**), 7.83 (d, *J* = 8.1, 1H, $C_{5'}$**H**), 7.33 (d, *J* = 8.1, 1H, $C_{8'}$**H**), 7.18–7.15 (m, 2H, $C_{7'}$**H**, C_5**H**), 7.11 (app-t, *J* = 7.4, 1H, C_7**H**), 7.04 (app-t, *J* = 7.2, 1H, $C_{6'}$**H**), 6.90 (d, *J* = 2.6, 1H, $C_{2'}$**H**), 6.73 (app-t, *J* = 7.5, 1H, C_6**H**), 6.68 (d, *J* = 7.8, 1H, C_8**H**), 6.09 (s, 1H, C_2**H**), 4.81 (d, *J* = 11.6, 1H, C_{17}**H**$_a$), 4.43 (d, *J* = 11.7, 1H, C_{17}**H**$_b$), 4.18 (d, *J* = 14.5, 1H, C_{12}**H**$_a$), 3.59 (d, *J* = 14.5, 1H, C_{12}**H**$_b$), 2.92 (s, 3H, C_{18}**H**), 2.63 (app-sp, *J* = 7.0 1H, C**H**$_{isobutyrate}$), 2.19 (app-sp, *J* = 6.9 1H, C**H**$_{thioisobutyrate}$), 2.14 (s, 3H, C**H**$_{3acetate}$), 1.22 (d, *J* = 7.1, 3H, C**H**$_{3isobutyrate}$), 1.20 (d, *J* = 7.0, 3H, C**H**$_{3isobutyrate}$), 0.95 (d, *J* = 7.0, 3H, C**H**$_{3thioisobutyrate}$), 0.86 (d, *J* = 6.9, 3H, C**H**$_{3thioisobutyrate}$).

^{13}C NMR (125 MHz, $CDCl_3$, 20 ºC):

δ 200.6 (**C**=O$_{thiosiobutyrate}$), 174.9 (**C**=O$_{isobutyrate}$), 169.9 (**C**=O$_{acetate}$), 166.0 (**C**$_{13}$), 162.1 (**C**$_{16}$), 149.0 (**C**$_9$), 137.4 (**C**$_{9'}$), 132.6 (**C**$_4$), 128.8 (**C**$_7$), 125.1 (**C**$_{4'}$), 124.5 (**C**$_5$), 122.9 (**C**$_{2'}$), 122.3 (**C**$_{7'}$), 120.3 (**C**$_{6'}$), 119.8 (**C**$_{5'}$), 119.5 (**C**$_6$), 117.6 (**C**$_{3'}$), 111.6 (**C**$_{8'}$), 109.6 (**C**$_8$), 86.5 (**C**$_{15}$), 83.4 (**C**$_2$), 73.3 (**C**$_{11}$), 63.1 (**C**$_{17}$), 54.1 (**C**$_3$), 43.4 (**C**$_{12}$), 43.3 (**C**H$_{thioisobutyrate}$), 33.9 (**C**H$_{isobutyrate}$), 28.5 (**C**$_{18}$), 21.3 (**C**H$_{3acetate}$), 19.3 (**C**H$_{3isobutyrate}$), 19.1 (**C**H$_{3isobutyrate}$), 18.9 (**C**H$_{3thioisobutryate}$), 18.5 (**C**H$_{3thioisobutyrate}$).

FTIR (thin film) cm^{-1}:	3385 (br-s), 2975 (m), 1748 (s), 1686 (s), 1484 (w), 1461 (m), 1379 (m), 1223 (m), 1067 (w), 747 (m).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{33}H_{36}N_4NaO_7S$ $[M+Na]^+$: 655.2202, found: 655.2183.
$[\alpha]_D^{24}$:	+26 (*c* = 0.085, $CHCl_3$).
TLC (50% ethyl acetate in hexanes), R*f*:	0.38 (UV, CAM).



Triphenylmethanedisulfide (–)-12:

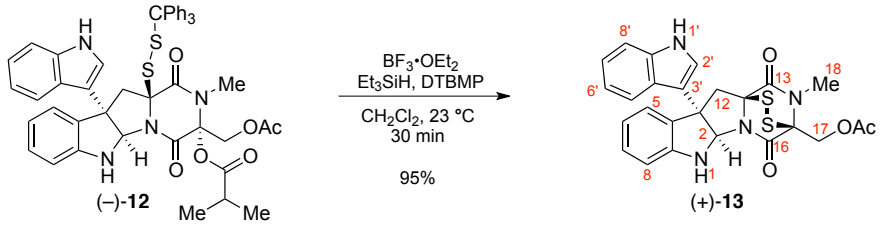
Anhydrous hydrazine (1 M in THF, 16.6 µL, 16.6 µmol, 1.05 equiv) was added via syringe to a solution of thioisobutyrate (+)-**11** (10.0 mg, 15.8 µmol, 1 equiv) in anhydrous tetrahydrofuran (0.5 mL) at 0 °C under an atmosphere of argon. After 10 min, triethylamine (22.0 µL, 158 µmol, 10.0 equiv) was added via syringe. Solid triphenylmethanesulfenyl chloride (24.6 mg, 79.0 µmol, 5.00 equiv) was then added in one portion at 0 ºC and the flask was sealed under an argon atmosphere. After 1 h, the solution was partitioned between saturated aqueous ammonium chloride (5 mL) and ethyl acetate (15 mL). The aqueous layer was extracted with ethyl acetate (2 × 10 mL), and the combined organic layers were washed with saturated aqueous sodium chloride solution (5 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: gradient, 10 → 40% ethyl acetate in hexanes) to afford triphenylmethanedisulfide (–)-**12** (13.0 mg, 98.2 %) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC): δ 7.95 (br-s, 1H, $N_{1'}$**H**), 7.82 (d, *J* = 8.0, 1H, $C_{5'}$**H**), 7.32 (d, *J* = 8.0, 1H, $C_{8'}$**H**), 7.27–7.23 (m, 9H, C(Ph-*o*-**H**)$_3$, C(Ph-*p*-**H**)$_3$), 7.22–7.19 (m, 2H, C_7**H**, $C_{7'}$**H**), 7.17–7.14 (m, 6H, C(Ph-*m*-**H**)$_3$), 7.06 (app-t, *J* = 7.5, 1H, $C_{6'}$**H**), 6.82 (d, *J* = 7.5, 1H, C_8**H**), 6.73–6.69 (m, 3H, $C_{2'}$**H,** C_6**H**, C_5**H**), 5.93 (s, 1H, C_2**H**), 4.93 (s, 1H, N_1**H**), 4.66 (d, *J* = 12.5, 1H, C_{17}**H**$_a$), 4.40 (d, *J* = 12.5, 1H, C_{17}**H**$_b$), 3.55 (d, *J* = 15.0, 1H, C_{12}**H**$_a$), 2.92 (d, *J* = 15.0, 1H, C_{12}**H**$_b$), 2.80 (s, 3H, C_{18}**H**), 2.61 (app-sp, *J* = 7.5, 1H, C**H**$_{isobutyrate}$), 1.98 (s, 3H, C**H**$_{3acetate}$), 1.20 (d, *J* = 7.0, 3H, C**H**$_{3isobutyrate}$), 1.18 (d, *J* = 7.0, 3H, C**H**$_{3isobutyrate}$).

^{13}C NMR (125 MHz, $CDCl_3$, 20 ºC): δ 175.0 (**C**=O$_{isobutyrate}$), 170.3 (**C**=O$_{acetate}$), 164.2 (**C**$_{13}$), 162.6 (**C**$_{16}$), 148.2 (**C**$_9$), 144.3 (C(Ph-*i*-**C**)$_3$), 137.4 (**C**$_{9'}$), 131.5 (**C**$_4$), 130.9 (C(Ph-*m*-**C**)$_3$), 128.8 (**C**$_7$), 127.7 (C(Ph-*o*-**C**)$_3$), 127.3 (C(Ph-*p*-**C**)$_3$), 125.4 (**C**$_{4'}$), 125.1 (**C**$_5$), 123.0 (**C**$_{2'}$), 122.5 (**C**$_{7'}$), 120.6 (**C**$_{6'}$), 120.0 (**C**$_{5'}$), 119.9 (**C**$_6$), 117.8 (**C**$_{3'}$), 111.5 (**C**$_{8'}$), 109.8 (**C**$_8$), 87.0 (**C**$_2$), 83.7 (**C**$_{15}$), 77.5 (**C**(Ph$_3$)), 73.2 (**C**$_{11}$), 62.9 (**C**$_{17}$), 53.8 (**C**$_3$), 46.8 (**C**$_{12}$), 33.9 (**C**H$_{isobutyrate}$), 28.3 (**C**$_{18}$), 21.2 (**C**H$_{3acetate}$), 19.0 (**C**H$_{3isobutyrate}$), 18.6 (**C**H$_{3isobutyrate}$).

FTIR (thin film) cm^{-1}: 3402 (br-m), 3056 (w), 2975 (w), 1747 (s), 1684 (s), 1609 (w), 1485 (w), 1459 (w), 1446 (w), 1377 (m), 1223 (m), 1067 (w).

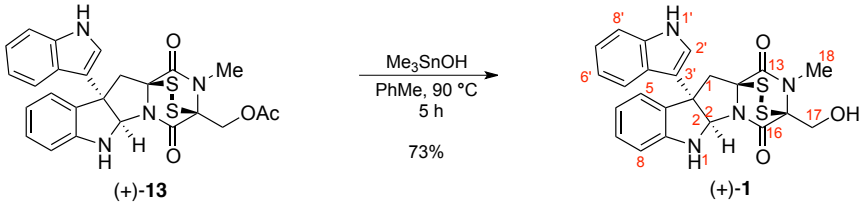
HRMS (ESI) (*m*/*z*):	calc'd for $C_{48}H_{44}N_4NaO_6S_2$ $[M+Na]^+$: 859.2600, found: 859.2569.
$[\alpha]_D^{24}$:	–50 (*c* = 0.38, $CHCl_3$).
TLC (50% ethyl acetate in hexanes), R*f*:	0.58 (UV, CAM).



(+)-Luteoalbusin A Acetate (13):

To a solution of triphenylmethanedisulfide (–)-**12** (21.0 mg, 25.1 μmol, 1 equiv) and 2,6-di-*tert*-butyl-4-methylpyridine (77.3 mg, 377 μmmol, 15.0 equiv) in dichloromethane (3 mL) at 23 °C under an argon atmosphere were sequentially added triethylsilane (39.9 μL, 251 μmol, 10.0 equiv) and borontrifluoride-etherate (30.9 μL, 251 μmol, 10.0 equiv) via syringe. After 30 min, a saturated aqueous ammonium chloride solution (2 mL) was added to the solution. The reaction mixture was diluted with ethyl acetate (15 mL) and washed with saturated aqueous ammonium chloride solution (5 mL). The aqueous layer was extracted with ethyl acetate (2 × 10 mL), and the combined organic layers 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: gradient, 25 → 50% ethyl acetate in hexanes) to afford (+)-luteoalbusin A acetate (**13**, 12.1 mg, 95.2%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC):	δ 8.07 (br-s, 1H, $N_{1'}$**H**), 7.51 (d, *J* = 7.5, 1H, $C_{5'}$**H**), 7.38 (d, *J* = 8.0, 1H, $C_{8'}$**H**), 7.24–7.18 (m, 3H, C_7**H**, $C_{7'}$**H**, C_5**H**), 7.10 (app-t, *J* = 8.5, 1H, C_6**H**), 6.96 (d, *J* = 2.6, 1H, $C_{2'}$**H**), 6.88 (app-t, *J* = 7.5, 1H, $C_{6'}$**H**), 6.75 (d, *J* = 7.5, 1H, C_8**H**), 5.99 (s, 1H, C_2**H**), 5.32 (s, 1H, N_1**H**), 4.99 (d, *J* = 13.5, 1H, C_{17}**H**$_a$), 4.71 (d, *J* = 13.5, 1H, C_{17}**H**$_b$), 4.15 (d, *J* = 15.0, 1H, C_{12}**H**$_a$), 3.14 (s, 3H, C_{18}**H**), 3.00 (d, *J* = 15.0, 1H, C_{12}**H**$_b$), 2.18 (s, 3H, C**H**$_{3acetate}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 ºC):	δ 169.9 (**C**=O$_{acetate}$), 166.1 (**C**$_{13}$), 161.4 (**C**$_{16}$), 148.2 (**C**$_9$), 137.5 (**C**$_{9'}$), 131.8 (**C**$_4$), 129.4 (**C**$_7$), 125.1 (**C**$_{4'}$), 124.2 (**C**$_5$), 122.9 (**C**$_{2'}$), 122.9 (**C**$_{7'}$), 120.4 (**C**$_{6'}$), 120.1 (**C**$_{5'}$), 119.6 (**C**$_6$), 116.5 (**C**$_{3'}$), 111.9 (**C**$_{8'}$), 110.3 (**C**$_8$), 83.3 (**C**$_2$), 75.1 (**C**$_{15}$), 74.5 (**C**$_{11}$), 60.1 (**C**$_{17}$), 55.7 (**C**$_3$), 43.8 (**C**$_{12}$), 28.4 (**C**$_{18}$), 20.9 (**C**H$_{3acetate}$).
FTIR (thin film) cm^{-1}:	3380 (br-s), 2921 (s), 2850 (m), 1750 (m), 1689 (s), 1459 (m), 1378 (m), 1224 (s), 1048 (m), 744 (m).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{25}H_{23}N_4O_4S_2$ $[M+H]^+$: 507.1155, found: 507.1146.
$[\alpha]_D^{24}$:	+42.0 (*c* = 0.095, $CHCl_3$).
TLC (50% ethyl acetate in hexanes), R*f*:	0.36 (UV, CAM).



(+)-Luteoalbusin A (1):

Solid trimethyltin hydroxide (3.9 mg, 22 μmol, 1.0 equiv) was added in one portion to a pressure tube reaction vessel containing a solution of (+)-luteoalbusin A acetate (**13**, 11.0 mg, 21.7 μmol, 1 equiv) in toluene (2.0 mL) under an argon atmosphere. The vessel was subsequently sealed under an argon atmosphere and was heated to 90 °C. After 5 h, the solution was cooled to 23 °C and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 50% ethyl acetate in hexanes) to afford (+)-luteoalbusin A (**1**, 7.4 mg, 73%) as a white solid.

^{1}H NMR (500 MHz, acetone-d_6, 20 ºC): δ 10.25 (br-s, 1H, $N_{1'}$**H**), 7.56 (d, J = 8.0, 1H, $C_{5'}$**H**), 7.43 (d, J = 8.0, 1H, $C_{8'}$**H**), 7.33 (d, J = 8.0, 1H, C_5**H**), 7.15 (d, J = 2.5, 1H, $C_{2'}$**H**), 7.12 (dd, J = 7.9, 7.6, 1H, C_7**H**), 7.12 (dd, J = 8.0, 7.5, 1H, $C_{7'}$**H**) 6.99 (dd, J = 8.0, 7.5, 1H, $C_{6'}$**H**), 6.79 (d, J = 8.0, 1H, C_8**H**), 6.78 (dd, J = 8.0, 7.5, 1H, C_6**H**), 6.22 (br-s, 1H, N_1**H**), 5.98 (d, J = 1.0, 1H, C_2**H**), 4.66 (dd, J = 7.5, 6.0, 1H, O**H**), 4.41 (d, J = 12.7, 1H, C_{17}**H**$_b$), 4.34 (d, J = 12.7, 1H, C_{17}**H**$_a$), 4.05 (d, J = 15.0, 1H, C_{12}**H**$_a$), 3.18 (s, 3H, C_{18}**H**), 3.10 (d, J = 15.0, 1H, C_{12}**H**$_b$).

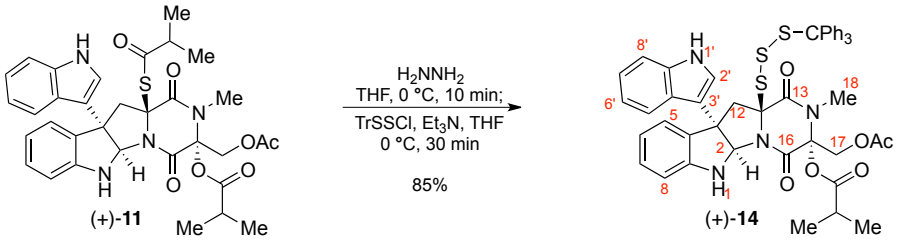
^{13}C NMR (125 MHz, acetone-d_6, 20 ºC): δ 166.9 (**C**$_{13}$), 163.1 (**C**$_{16}$), 149.5 (**C**$_9$), 138.5 (**C**$_{9'}$), 133.2 (**C**$_4$), 129.4 (**C**$_7$), 125.9 (**C**$_{4'}$), 124.8 (**C**$_5$), 123.8 (**C**$_{2'}$), 122.5 (**C**$_{7'}$), 120.0 (**C**$_{6'}$), 119.7 (**C**$_{5'}$), 119.6 (**C**$_6$), 117.3 (**C**$_{3'}$), 112.7 (**C**$_{8'}$), 110.4 (**C**$_8$), 83.9 (**C**$_2$), 77.9 (**C**$_{15}$), 74.9 (**C**$_{11}$), 60.6 (**C**$_{17}$), 56.3 (**C**$_3$), 44.4 (**C**$_{12}$), 27.6 (**C**$_{14}$).

FTIR (thin film) cm^{-1}: 3583 (w), 3396 (br-s), 2923 (w), 1751 (m), 1701 (s), 1481 (w), 1461 (w), 1345 (m), 1222 (s).

HRMS (ESI) (*m*/*z*): calc'd for $C_{23}H_{21}N_4O_3S_2$ [M+H]$^+$: 465.1050, found: 465.1045.

$[\alpha]_D^{24}$: +290 (c = 0.085, $CHCl_3$).

TLC (50% ethyl acetate in hexanes), R*f*: 0.36 (UV, CAM).



Triphenylmethanetrisulfide (+)-14:

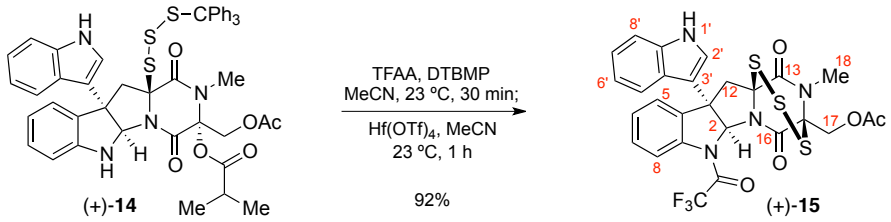
Anhydrous hydrazine (1 M in THF, 200 µL, 200 µmol, 1.05 equiv) was added via syringe to a solution of thioisobutyrate (+)-**11** (121 mg, 191 µmol, 1 equiv) in anhydrous tetrahydrofuran (5.5 mL) at 0 °C under an argon atmosphere. After 10 min, triethylamine (265 µL, 1.91 mmol, 10.0 equiv) was added via syringe. Solid chloro(triphenylmethyl)disulfane[8] (326 mg, 955 µmol, 5.00 equiv) was then added in one portion at 0 ºC and the flask was sealed under an argon atmosphere. After 30 min, the solution was partitioned between saturated aqueous ammonium chloride (5 mL) and ethyl acetate (25 mL). The aqueous layer was extracted with ethyl acetate (2 × 20 mL), and the combined organic layers were washed with 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: gradient, 20 → 35% ethyl acetate in hexanes) to afford triphenylmethanetrisulfide (+)-**14** (140 mg, 84.5 %) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC): δ 7.97 (br-s, 1H, $N_{1'}$**H**), 7.80 (d, *J* = 8.0, 1H, $C_{5'}$**H**), 7.31 (d, *J* = 8.5, 1H, C_8**H**), 7.27 (d, J = 6.5, 1H, C_5**H**), 7.22–7.21 (m, 9H, C(Ph-*o*-**H**)$_3$, C(Ph-*p*-**H**)$_3$), 7.17–7.13 (m, 2H, $C_{7'}$**H**, $C_{7'}$**H**), 7.06–6.99 (m, 7H, C_6H, C(Ph-*m*-**H**)$_3$), 6.81 (d, *J* = 2.5, 1H, $C_{2'}$**H**), 6.67 (d, *J* = 8.0, 1H, $C_{8'}$**H**), 6.16 (br-t, *J* = 7.5, 1H, $C_{6'}$**H**), 6.05 (s, 1H, C_2**H**), 4.94 (br-s, 1H, N_1**H**), 4.73 (d, *J* = 12.0, 1H, C_{17}**H**$_a$), 4.36 (d, *J* = 12.0, 1H, C_{17}**H**$_b$), 3.66 (d, *J* = 13.0, 1H, C_{12}**H**$_a$), 3.43 (d, *J* = 13.0, 1H, C_{12}**H**$_b$), 2.87 (s, 3H, C_{18}**H**), 2.62 (app-sp, *J* = 8.0, 1H, C**H**$_{isobutyrate}$), 1.85 (s, 3H, C**H**$_{3aceate}$), 1.21 (d, *J* = 7.0, 3H, C**H**$_{3isobutyrate}$), 1.19 (d, *J* = 7.0, 3H, C**H**$_{3isobutyrate}$).

^{13}C NMR (125 MHz, $CDCl_3$, 20 ºC): δ 174.9 (**C**=O$_{isobutyrate}$), 170.1 (**C**=O$_{acetate}$), 165.1 (**C**$_{13}$), 162.5 (**C**$_{16}$), 148.5 (**C**$_9$), 143.6 (C(Ph-*i*-**C**)$_3$), 137.4 (**C**$_{9'}$), 131.8 (**C**$_4$), 130.7 (C(Ph-*m*-**C**)$_3$), 129.0 (**C**$_7$), 128.0 (C(Ph-*o*-**C**)$_3$), 127.4 (C(Ph-*p*-**C**)$_3$), 127.4 (**C**$_{4'}$), 125.1 (**C**$_5$), 123.0 (**C**$_{2'}$), 122.5 (**C**$_{7'}$), 120.6 (**C**$_{6'}$), 120.1 (**C**$_{5'}$), 119.8 (**C**$_6$), 118.4 (**C**$_{3'}$), 111.4 (**C**$_{8'}$), 109.3 (**C**$_8$), 86.8 (**C**$_{15}$), 84.2 (**C**$_2$), 74.5 (**C**(Ph$_3$)), 73.8 (**C**$_{11}$), 63.4 (**C**$_{17}$), 54.3 (**C**$_3$), 45.0 (**C**$_{12}$), 34.0 (**C**H$_{isobutyrate}$), 28.4 (**C**$_{18}$), 21.4 (**C**H$_{3acetate}$), 19.0 (**C**H$_{3isobutyrate}$), 18.6 (**C**H$_{3isobutyrate}$).

[8] Williams, C. R.; Britten, J. F.; Harpp, D. N. *J. Org. Chem.* **1994**, *59*, 806.

FTIR (thin film) cm^{-1}:	3411 (br-m), 3057 (w), 2973 (w), 1748 (s), 1684 (s), 1609 (w), 1485 (w), 1460 (w), 1442 (w), 1377 (m), 1222 (m), 1067 (w).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{48}H_{44}N_4NaO_6S_3$ $[M+Na]^+$: 891.2321, found: 891.2310.
$[\alpha]_D^{24}$:	+49.8 (*c* = 0.33, $CHCl_3$).
TLC (50% ethyl acetate in hexanes), R*f*:	0.46 (UV, CAM).



(+)-*N*-Trifluoracetyl Luteoalbusin B Acetate (15):

A schlenk flask was charged with triphenylmethanetrisulfide (+)-**14** (40.0 mg, 46.0 μmol, 1 equiv) and 2,6-di-*tert*-butyl-4-methylpyridine (47.2 mg, 230 μmol, 5.00 equiv), and the mixture was dried azeotropically (concentration of a benzene solution, 3 × 2 mL) under reduced pressure and placed under an argon atmosphere. Anhydrous acetonitrile (4 mL) and trifluoroacetic anhydride (TFAA, 19.2 μL, 138 μmol, 3.00 equiv) were added sequentially to the reaction mixture via syringe at 23 °C. After 30 min, the resulting reaction mixture was concentrated to dryness under reduced pressure and placed under an argon atmosphere. The residue was dried azeotropically by concentration of a benzene solution (2 mL) under reduced pressure and the residue was placed under an argon atmosphere. Anhydrous acetonitrile (6 mL) followed by a solution of hafnium trifluoromethanesulfonate (178 mg, 230 μmol, 5.00 equiv) in anhydrous acetonitrile (7.5 mL) were introduced to the reaction flask via cannula at 23 °C to produce a bright yellow solution. After 1 h, the solution was partitioned between saturated aqueous sodium bicarbonate solution (5 mL) and ethyl acetate (50 mL). The aqueous layer was extracted with ethyl acetate (2 × 15 mL), and the combined organic layers were washed with 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: gradient, 20 → 50% ethyl acetate in hexanes) to afford *N*-trifluoracetyl luteoalbusin B acetate (+)-**15** (26.8 mg, 91.8%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 20 °C; the product exists as a mixture (1:1.6) of epitrisulfide conformers). *major conformer:* δ 8.21 (br-s, 1H, $N_{1'}$**H**), 7.48 (t, *J* = 7.5, 1H, $C_{6'}$**H**), 7.39–7.34 (m, 3H, C_5**H**, C_8**H**, $C_{8'}$**H**), 7.30–7.20 (m, 3H, $C_{5'}$**H**, C_7**H**, $C_{7'}$**H**), 7.13–7.08 (m, C_6**H**), 6.87 (d, *J* = 2.4, 1H, $C_{2'}$**H**), 6.79 (s, 1H, C_2**H**), 4.80 (d, *J* = 12.4, 1H, C_{17}**H**$_a$), 4.39 (d, *J* = 12.4, 1H, C_{17}**H**$_b$), 3.89 (d, *J* = 14.7, 1H, C_{12}**H**$_a$), 3.27 (d, *J* = 14.7, 1H, C_{12}**H**$_b$), 3.20 (s, 3H, C_{18}**H**), 2.10 (s, 3H, C**H**$_{3acetate}$). *minor conformer:* δ 8.10 (br-s, 1H, $N_{1'}$**H**), 7.39–7.20 (m, 7H, $C_{6'}$**H**, C_5**H**, C_8**H**, $C_{8'}$**H**, $C_{5'}$**H**, C_7**H**, $C_{7'}$**H**), 7.13–7.08 (m, 2H, C_6**H**, C_2**H**) 6.93 (br-s, 1H, $C_{2'}$**H**), 4.91 (d, *J* = 12.2, 1H, C_{17}**H**$_a$), 4.45 (d, *J* = 12.2, 1H, C_{17}**H**$_b$), 3.80 (d, *J* = 14.7, 1H, C_{12}**H**$_a$), 3.20 (obscured, 1H, C_{12}**H**$_b$), 2.99 (s, 3H, C_{18}**H**), 2.12 (s, 3H, C**H**$_{3acetate}$).

^{13}C NMR (100 MHz, $CDCl_3$, 20 ºC; the product exists as a mixture (1:1.6) of epitrisulfide conformers):[9] δ 169.8, 168.8, 167.3, 163.7, 142.0, 137.4, 134.7, 130.7, 130.4, 129.7, 128.5, 128.2, 127.3, 127.0, 125.2, 124.7, 124.6, 123.3, 123.2, 123.1, 120.9, 119.4, 118.8, 118.4, 117.7, 114.9, 113.9, 113.6, 112.3, 112.2, 83.3, 82.2, 79.0, 78.5, 74.4, 74.2, 62.4, 61.6, 53.4, 47.7, 45.7, 29.5, 28.3, 21.0, 20.9.

^{19}F NMR (376 MHz, $CDCl_3$, 20 ºC; the product exists as a mixture (1:1.6) of epitrisulfide conformers). *major conformer:* δ –69.0 (s, C**F**$_3$). *minor conformer:* δ –69.0 (s, C**F**$_3$).

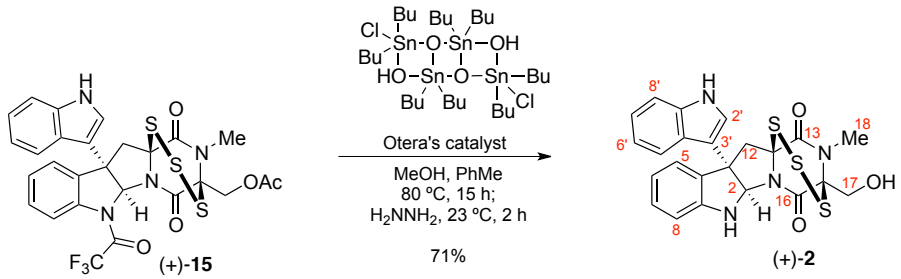
FTIR (thin film) cm^{-1}: 3398 (m), 1749 (m), 1695 (s), 1460 (m), 1342 (m), 1219 (s), 1153 (s), 1042 (m), 909 (m), 761 (s).

HRMS (ESI) (*m*/*z*): calc'd for $C_{27}H_{22}F_3N_4O_5S_3$ $[M+H]^+$: 635.0699, found: 635.0693.

$[\alpha]_D^{24}$: +203 (*c* = 0.22, $CHCl_3$).

TLC (33% acetone in hexanes), R*f*: 0.25 (UV, CAM).

[9] The additional presence of trifluoroacetamide atropisomers prevents assignment of all peaks in the ^{13}C NMR spectra for the two epitrisulfide conformers. The observed chemical shifts of the collective population of amide and epitrisulfide conformers are reported.



(+)-Luteoalbusin B (2):

Solid Otera's catalyst[10] (29.0 mg, 27.1 μmol, 0.500 equiv) was added in one portion to a pressure tube reaction vessel containing a solution of (+)-*N*-trifluoracetyl luteoalbusin B acetate (**15**, 34.5 mg, 54.4 μmol, 1 equiv) in toluene (7 mL) and methanol (1.05 mL) under an argon atmosphere. The vessel was subsequently sealed under an atmosphere of argon and was heated to 80 °C. After 15 h, the reaction mixture was allowed to cool to room temperature, followed by addition of anhydrous hydrazine (1 M in THF, 544 μL, 544 μmol, 10.0 equiv) via syringe under an argon atmosphere. After 2 h, saturated aqueous ammonium chloride (5 mL) was added to the reaction mixture, the layers were separated, and the aqueous layer was extracted with ethyl acetate (20 mL). The aqueous layer was further extracted with ethyl acetate (2 × 10 mL). The combined organic layers 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 (+)-luteoalbusin B (**2**, 20.9 mg) as a white solid. The ^{1}H NMR of this material was found to contain trace amounts of an impurity (<5%). An analytically pure sample was obtained by trituration whereby the sample of (+)-luteoalbusin B (**2**) was dissolved in a minimal amount of dichloromethane (0.5 mL) followed by slow dissolution by addition of hexanes (20 fold dilution, 10 mL) which caused the formation of a white precipitate. The resulting heterogenous solution was stirred at 40 °C for 14 h. The solution was allowed to cool to 23 °C, and the solvent was then removed via cannula. The white solid that remained was dried under reduced pressure to afford analytically pure (+)-luteoalbusin B (**2**, 19.3 mg, 71.2%).

^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C; the product exists as a mixture (4:1) of epitrisulfide conformers). *major conformer:* δ 8.23 (br-s, 1H, $N_{1'}$**H**), 7.48 (d, *J* = 8.1, 1H, $C_{5'}$**H**), 7.36 (d, *J* = 8.2, 1H, $C_{8'}$**H**), 7.22–7.12 (m, 3H, C_5**H**, C_7**H**, C_6**H**), 7.05–7.00 (m, 2H, $C_{2'}$**H**, $C_{7'}$**H**), 6.84–6.76 (m, 2H, C_6**H**, C_8**H**), 5.84 (s, 1H, C_2**H**), 4.24 (d, *J* = 12.7, 1H, C_{17}**H**$_a$), 4.02 (d, *J* = 12.6, 1H, C_{17}**H**$_b$), 3.76 (d, *J* = 14.6, 1H, C_{12}**H**$_a$), 3.24 (s, 3H, C_{18}**H**), 3.21 (d, *J* = 14.7, 1H, C_{12}**H**$_b$). *minor conformer:* δ 8.37 (br-s, 1H, $N_{1'}$**H**), 7.54 (d, *J* = 8.1, 1H, $C_{5'}$**H**), 7.37 (d, *J* = 7.8, 1H, $C_{8'}$**H**), 7.22–7.07 (m, 3H, C_5**H**, C_7**H**, C_6**H**), 7.05–7.00 (m, 2H, $C_{2'}$**H**, $C_{7'}$**H**), 6.74 (app-t, *J* = 7.5, 1H, C_6**H**), 6.70 (d, *J* = 8.2, 1H, C_8**H**), 6.15 (s, 1H, C_2**H**), 4.59 (d, *J* = 12.6, 1H, C_{17}**H**$_a$), 3.82 (d, *J* = 12.6, 1H, C_{17}**H**$_b$), 3.66 (d, *J* = 14.6, 1H, C_{12}**H**$_a$), 3.17 (obscured, 1H, C_{12}**H**$_b$), 3.06 (s, 3H, C_{18}**H**).

[10] Otera, J.; Dan-oh, N.; Nozaki, H. *J. Org. Chem.* **1991**, *56*, 5307.

^{13}C NMR (100 MHz, CD_2Cl_2, 20 ºC; the product exists as a mixture (4:1) of epitrisulfide conformers).	*major conformer:* δ 169.6 ($\mathbf{C}_{13}$), 166.1 ($\mathbf{C}_{16}$), 150.1 ($\mathbf{C}_{9}$), 137.7 ($\mathbf{C}_{9'}$), 131.6 ($\mathbf{C}_{4}$), 130.2 ($\mathbf{C}_{7}$), 125.5 ($\mathbf{C}_{4'}$), 125.1 ($\mathbf{C}_{5}$), 123.0 ($\mathbf{C}_{2'}$), 122.5 ($\mathbf{C}_{7'}$), 120.5 ($\mathbf{C}_{6'}$), 120.3 ($\mathbf{C}_{6}$), 120.1 ($\mathbf{C}_{5'}$), 117.2 ($\mathbf{C}_{3'}$), 112.1 ($\mathbf{C}_{8'}$), 110.7 ($\mathbf{C}_{8}$), 82.7 ($\mathbf{C}_{2}$), 79.6 ($\mathbf{C}_{11}$), 76.0 ($\mathbf{C}_{15}$), 63.0 ($\mathbf{C}_{17}$), 54.1 ($\mathbf{C}_{3}$), 50.0 ($\mathbf{C}_{12}$), 28.0 ($\mathbf{C}_{18}$). *minor conformer:* δ 168.6 ($\mathbf{C}_{13}$), 164.5 ($\mathbf{C}_{16}$), 148.7 ($\mathbf{C}_{9}$), 137.7 ($\mathbf{C}_{9'}$), 132.3 ($\mathbf{C}_{4}$), 129.4 ($\mathbf{C}_{7}$), 125.5 ($\mathbf{C}_{4'}$), 124.6 ($\mathbf{C}_{5}$), 123.0 ($\mathbf{C}_{2'}$), 122.5 ($\mathbf{C}_{7'}$), 120.5 ($\mathbf{C}_{6'}$), 120.3 ($\mathbf{C}_{6}$), 120.1 ($\mathbf{C}_{5'}$), 117.4 ($\mathbf{C}_{3'}$), 112.1 ($\mathbf{C}_{8'}$), 110.0 ($\mathbf{C}_{8}$), 84.5 ($\mathbf{C}_{2}$), 79.7 ($\mathbf{C}_{11}$), 75.3 ($\mathbf{C}_{15}$), 62.9 ($\mathbf{C}_{17}$), 54.5 ($\mathbf{C}_{3}$), 47.6 ($\mathbf{C}_{12}$), 29.1 ($\mathbf{C}_{18}$).
FTIR (thin film) cm^{-1}:	3403 (br-s), 3051 (m), 1662 (s), 1607 (m), 1458 (m), 1412 (m), 1353 (s), 1058 (s), 1013 (m), 732 (s).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{23}H_{21}N_4O_3S_3$ $[M+H]^+$: 497.0770, found: 497.0778.
$[\alpha]_D^{24}$:	+306 (*c* = 0.08, $CHCl_3$).
TLC (50% ethyl acetate in hexanes), R*f*:	0.41 (UV, CAM).

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

Assignment	**Wang's Report**[11] (+)-Luteoalbusin A ^{1}H NMR, 500 MHz, acetone-d_6, 20 °C	**This Work** (+)-Luteoalbusin A ^{1}H NMR, 500 MHz, acetone-d_6, 20 °C
N1	6.22 (s)	6.22 (s)
C2	5.98 (d, J = 1.0)	5.98 (d, J = 0.9)
C3	–	–
C4	–	–
C5	7.32 (d, J = 8.0)	7.33 (d, J = 8.0
C6	6.77 (dd, J = 8.0, 7.5)	6.78 (dd, J = 8.0, 7.5)
C7	7.11 (dd, J = 8.0, 7.5)	7.12 (dd, J = 7.9, 7.6)
C8	6.78 (d, J = 8.0)	6.79 (d, J = 8.0)
C9	–	–
N10	–	–
C11	–	–
C12	3.09 (d, J = 15.0), 4.06 (d, J = 15.0)	3.10 (d, J = 15.0), 4.05 (d, J = 15.0)
C13	–	–
C14	3.17 (s)	3.18 (s)
C15	–	–
C16	–	–
C17	4.34 (d, J = 12.7), 4.41 (d, J = 12.7)	4.34 (d, J = 12.8), 4.41 (d, J = 12.8)
OH	–	4.67 (dd, J = 7.5, 6.0)
N1'	10.27 (s)	10.25 (s)
C2'	7.13 (d, J = 2.5)	7.15 (d, J = 2.5)
C3'	–	–
C4'	–	–
C5'	7.55 (d, J = 8.0)	7.56 (d, J = 7.9)
C6'	6.99 (dd, J = 8.0, 7.5)	6.99 (dd, J = 8.0, 7.4)
C7'	7.11 (dd, J = 8.0, 7.5)	7.12 (dd, J = 8.0, 7.5)
C8'	7.42 (d, J = 8.0)	7.43 (d, J = 8.0)
C9'	–	–

[11] The specific value used for reference in the ^{1}H NMR spectra of (+)-Luteoalbusin A was not reported.

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

Assignment	**Wang's Report**[12] (+)-Luteoalbusin A ^{13}C NMR, 125 MHz, acetone-d_6, 20 °C	**This Work** (+)-Luteoalbusin A ^{13}C NMR, 125 MHz, acetone-d_6, 20 °C	**Δδ** δ (this work) – δ (Wang's report)
N1	–	–	–
C2	85.1	83.9	–1.2
C3	57.5	56.3	–1.2
C4	134.4	133.2	–1.2
C5	125.9	124.8	–1.1
C6	120.7	119.6	–1.1
C7	130.5	129.4	–1.1
C8	111.5	110.4	–1.1
C9	150.7	149.5	–1.2
N10	–	–	–
C11	76.0	74.9	–1.1
C12	45.5	44.4	–1.1
C13	168.1	166.9	–1.2
C14	28.7	27.6	–1.1
C15	79.1	77.9	–1.2
C16	164.2	163.1	–1.1
C17	61.7	60.6	–1.1
OH	–	–	–
N1'	–	–	–
C2'	124.9	123.8	–1.1
C3'	118.4	117.3	–1.1
C4'	127.1	125.9	–1.2
C5'	121.1	119.7	–1.4
C6'	121.1	120.0	–1.1
C7'	123.6	122.5	–1.1
C8'	113.8	112.7	–1.1
C9'	139.7	138.5	–1.2

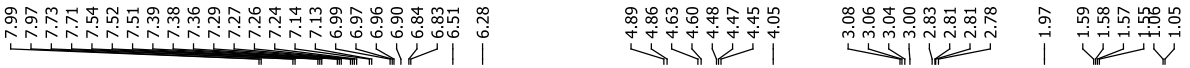
[12] The specific value used for reference in the ^{13}C NMR spectra of (+)-Luteoalbusin A was not reported.

Table S3. Comparison of our ^{1}H NMR data for (+)-Luteoalbusin B (2) with literature:

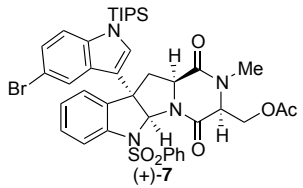
Assignment	**Wang's Report**[11] (+)-Luteoalbusin B ^{1}H NMR, 500 MHz, acetone-d_6, 20 °C	**This Work** (+)-Luteoalbusin B ^{1}H NMR, 400 MHz, acetone-d_6, 20 °C
N1	6.42 (s)	6.41 (s)
C2	5.85 (s)	5.85 (s)
C3	–	–
C4	–	–
C5	7.20 (d, J = 7.9)	7.22–7.20 (m)
C6	6.69 (dd, J = 7.5, 7.5)	6.71 (dd, J = 7.5, 7.5)
C7	7.14 (dd, J = 7.9, 7.5)	7.13–7.10 (m)
C8	6.80 (d, J = 7.9)	6.86 (d, J = 7.8)
C9	–	–
N10	–	–
C11	–	–
C12	3.23 (d, J = 14.6), 3.78 (d, J = 14.6)	3.23 (d, J = 14.5), 3.79 (d, J = 14.6)
C13	–	–
C14	3.27 (s)	3.28 (s)
C15	–	–
C16	–	–
C17	3.96 (d, J = 11.8), 4.31 (d, J = 11.8)	3.97 (dd, J = 6.9, 12.3), 4.32 (dd, J = 5.8, 12.2)
OH	–	4.44 (app-t, J = 6.3)
N1'	10.27 (s)	10.21 (s)
C2'	7.18 (d, J = 2.5)	7.20–7.17 (m)
C3'	–	–
C4'	–	–
C5'	7.51 (d, J = 7.5)	7.52 (d, J = 7.8)
C6'	6.94 (dd, J = 7.5, 7.5)	6.95 (dd, J = 7.8, 7.8)
C7'	7.10 (dd, J = 7.5, 7.5)	7.11–7.07 (m)
C8'	7.39 (d, J = 7.5)	7.40 (d, J = 8.1)
C9'	–	–

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

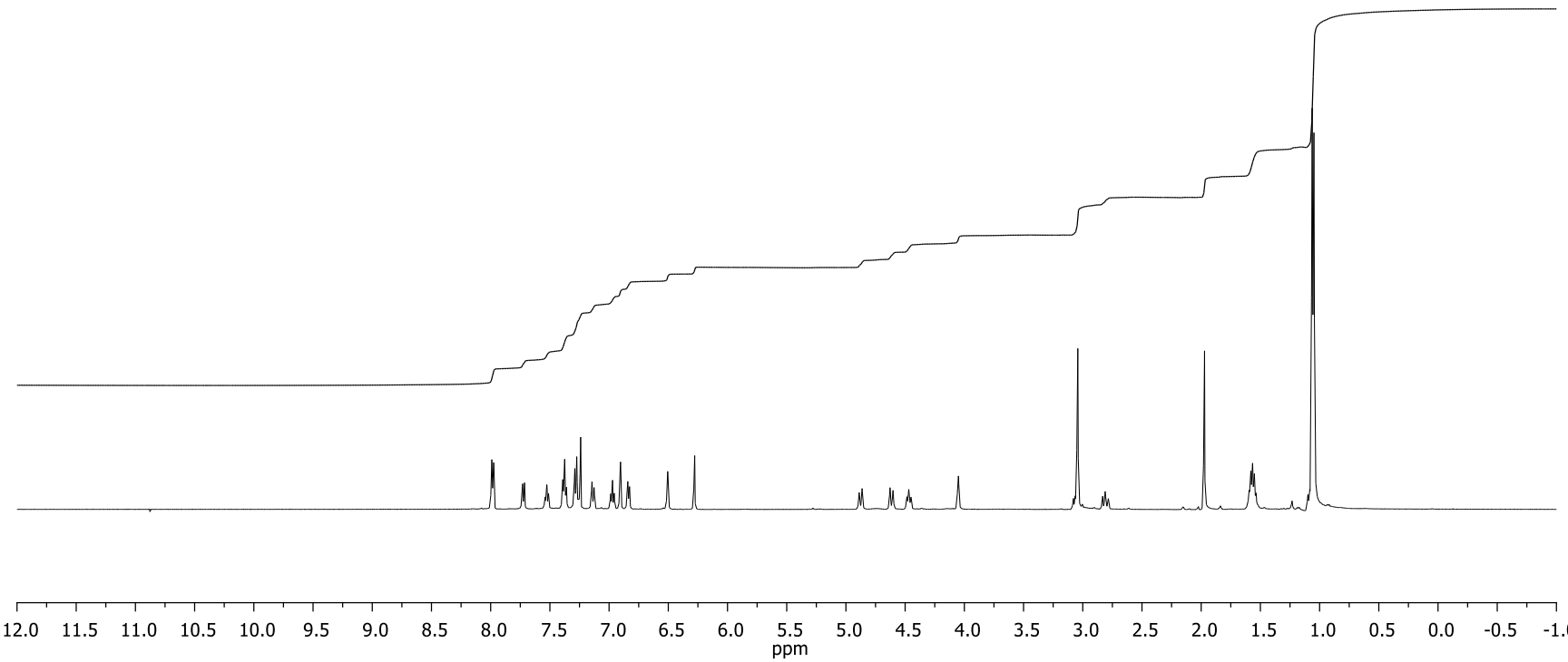
Assignment	**Wang's Report**[12] (+)-Luteoalbusin B ^{13}C NMR, 125 MHz, acetone-d_6, 20 °C	**This Work** (+)-Luteoalbusin B ^{13}C NMR, 100 MHz, acetone-d_6, 20 °C	**Δδ** δ (this work) – δ (Wang's report)
N1	–	–	–
C2	84.3	83.2	–1.1
C3	55.4	54.5	–0.9
C4	133.4	132.3	–1.1
C5	126.3	125.4	–0.9
C6	120.8	119.9	–0.9
C7	131.0	130.1	–0.9
C8	111.7	110.7	–1.0
C9	152.4	151.4	–1.0
N10	–	–	–
C11	81.2	80.2	–1.0
C12	51.6	50.6	–1.0
C13	170.7	169.7	–1.0
C14	28.7	27.8	–0.9
C15	78.0	77.0	–1.0
C16	166.1	165.1	–1.0
C17	63.1	62.1	–1.0
OH	–	–	–
N1'	–	–	–
C2'	125.9	124.9	–1.0
C3'	118.5	117.5	–1.0
C4'	126.9	126.1	–0.8
C5'	121.1	120.0	–1.1
C6'	121.1	120.2	–0.9
C7'	123.5	122.6	–0.9
C8'	113.7	112.7	–1.0
C9'	139.6	138.6	–1.0



^{1}H NMR, 500 MHz, $CDCl_3$, 20 ºC

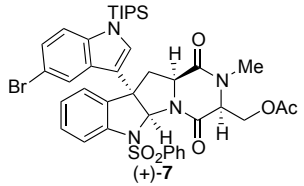


(+)-**7**

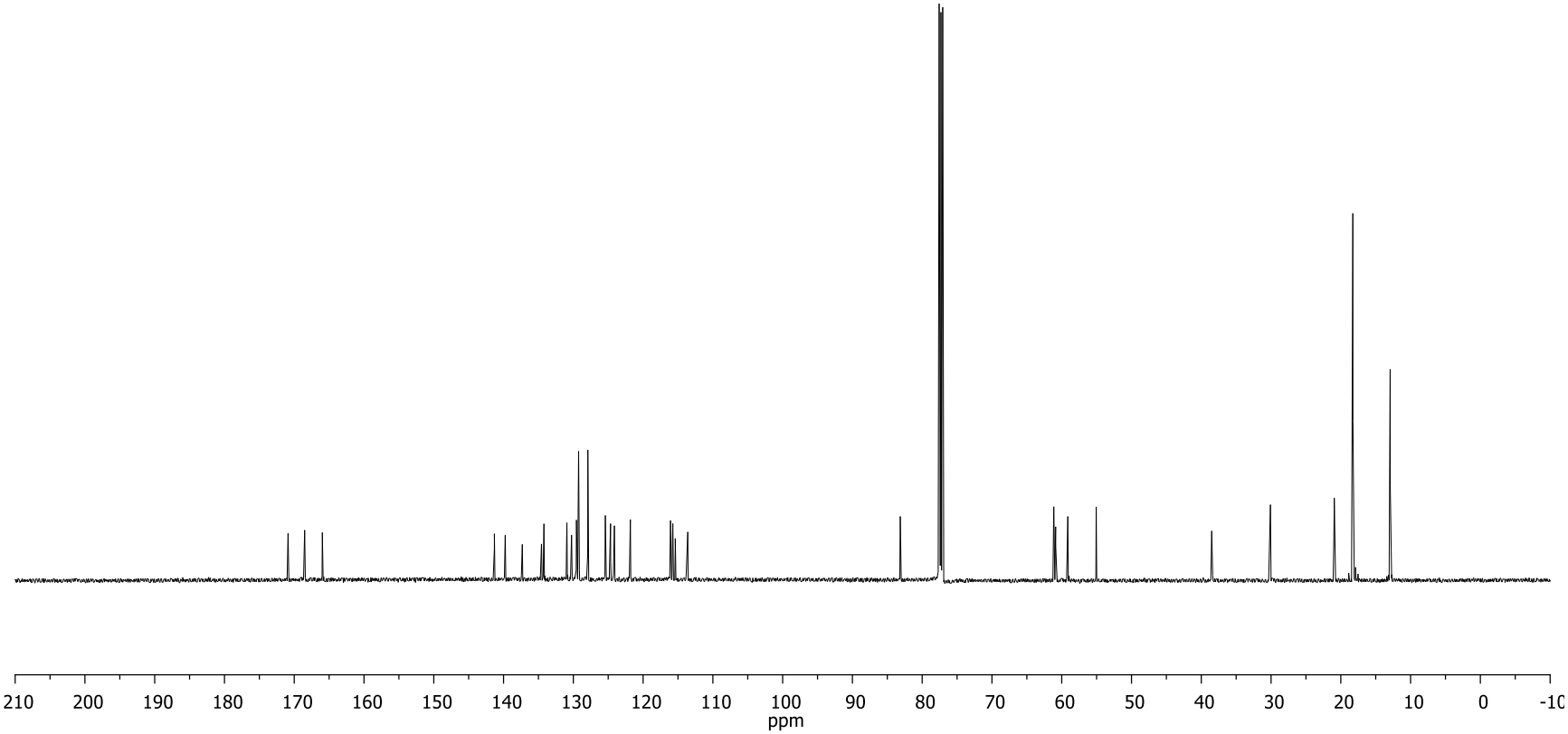


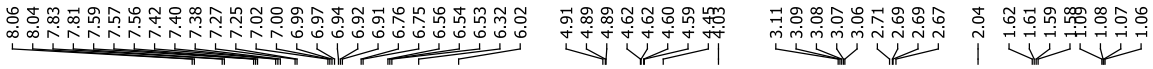
170.9
168.5
166.0
141.3
139.8
137.3
134.6
134.2
130.9
130.3
129.6
129.2
127.9
125.4
124.7
124.1
121.8
116.1
115.7
115.4
113.6
83.1
61.1
60.9
59.1
55.1
38.5
30.1
20.9
18.3
12.9

^{13}C NMR, 125 MHz, $CDCl_3$, 20 ºC

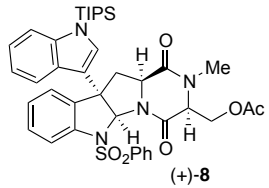


(+)-**7**

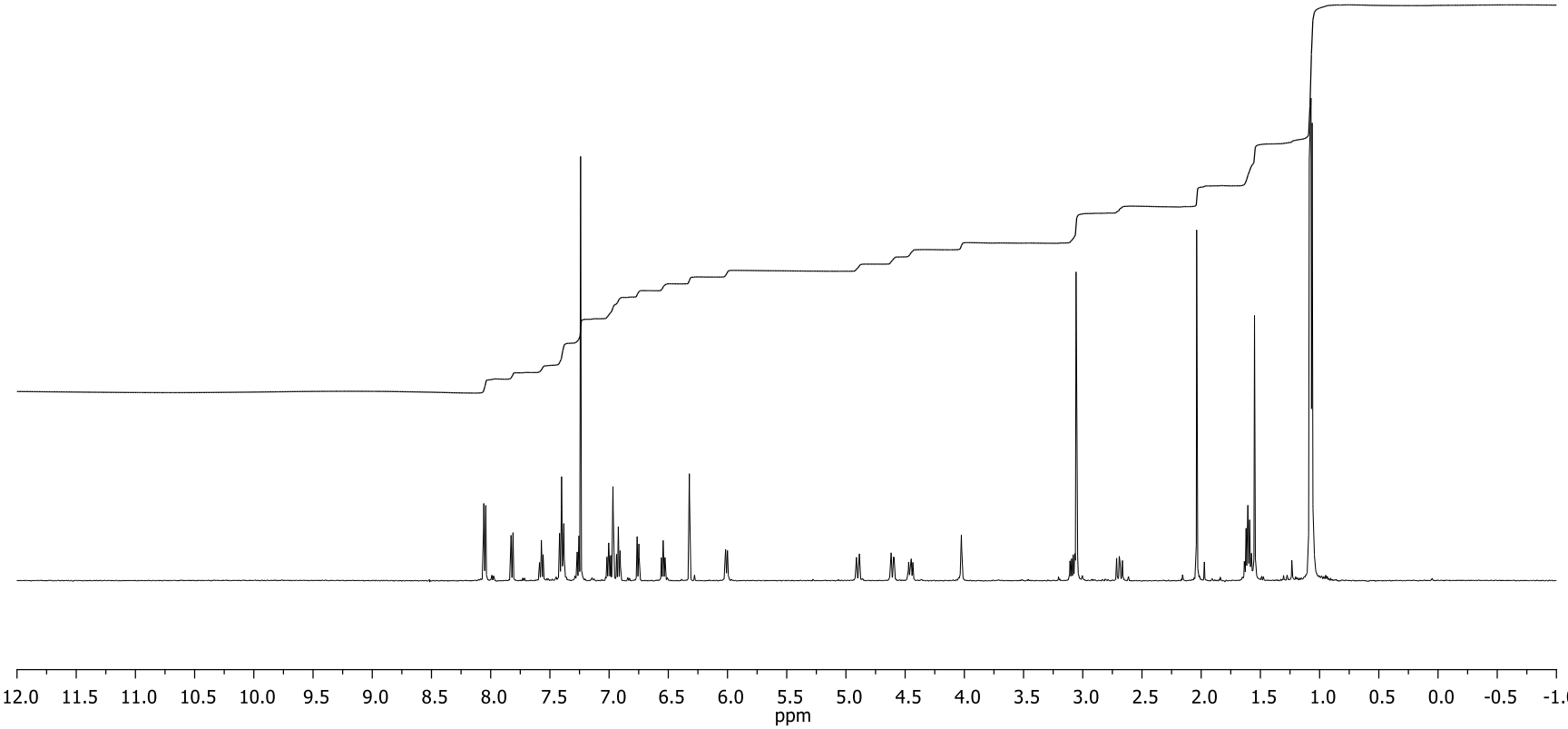




^{1}H NMR, 500 MHz, $CDCl_3$, 20 ºC

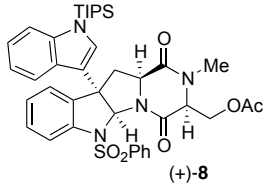


(+)-**8**

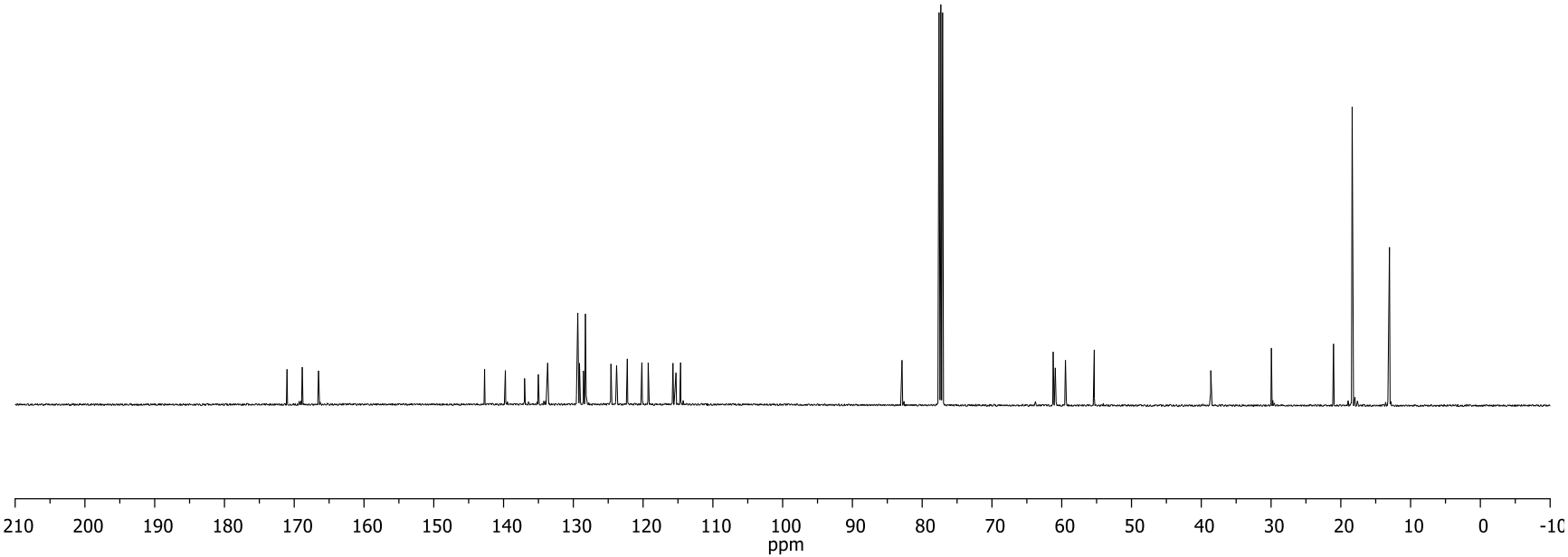


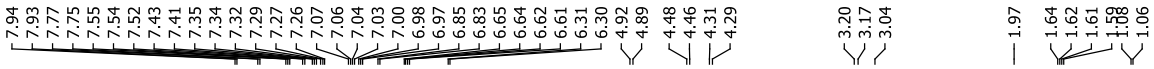
171.0
168.9
166.5
142.7
139.7
137.0
135.0
133.7
129.4
129.3
129.1
128.6
128.3
124.6
123.8
122.3
120.2
119.3
115.7
115.3
114.6
82.9
61.2
60.9
59.5
55.3
38.6
30.0
21.0
18.4
13.0

^{13}C NMR, 125 MHz, $CDCl_3$, 20 ºC

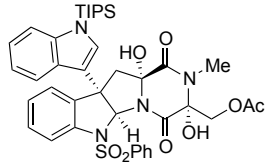


(+)-**8**

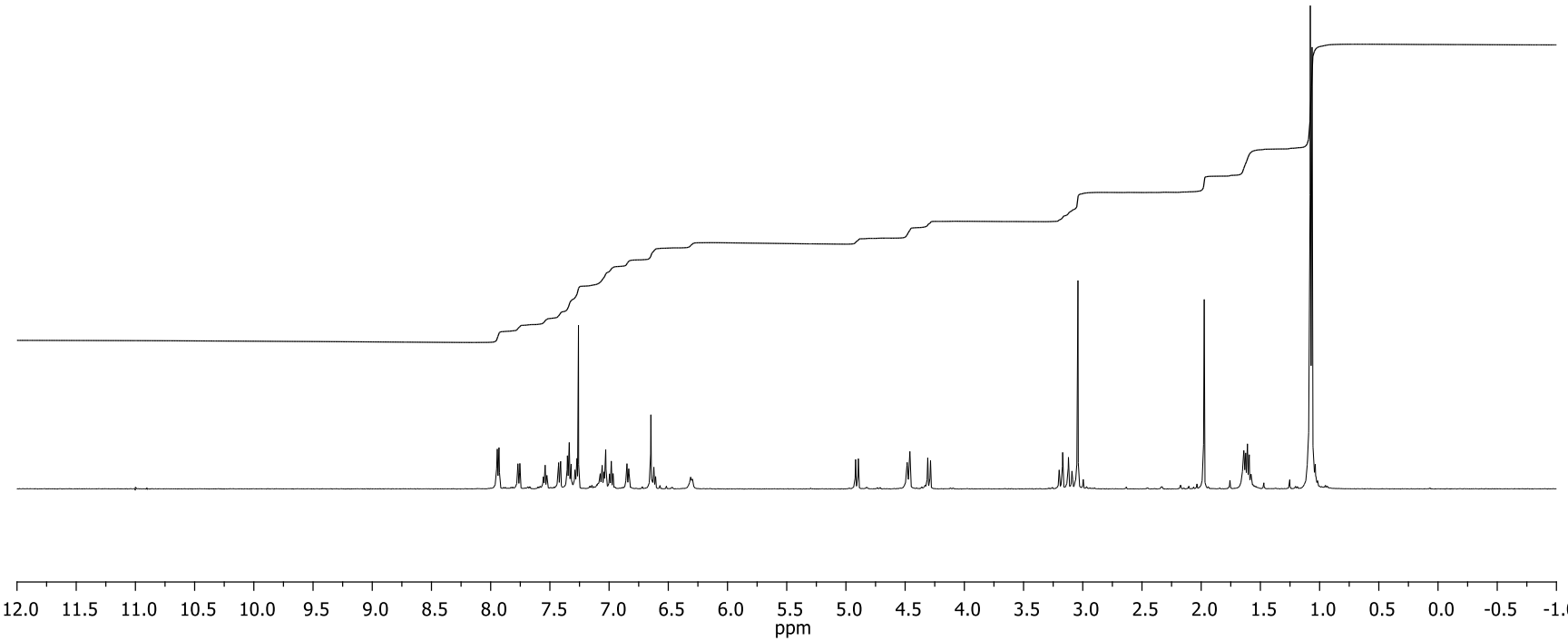




^{1}H NMR, 500 MHz, $CDCl_3$, 20 ºC

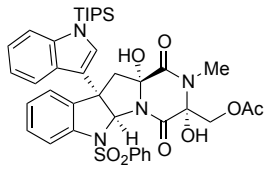


(+)-**4**

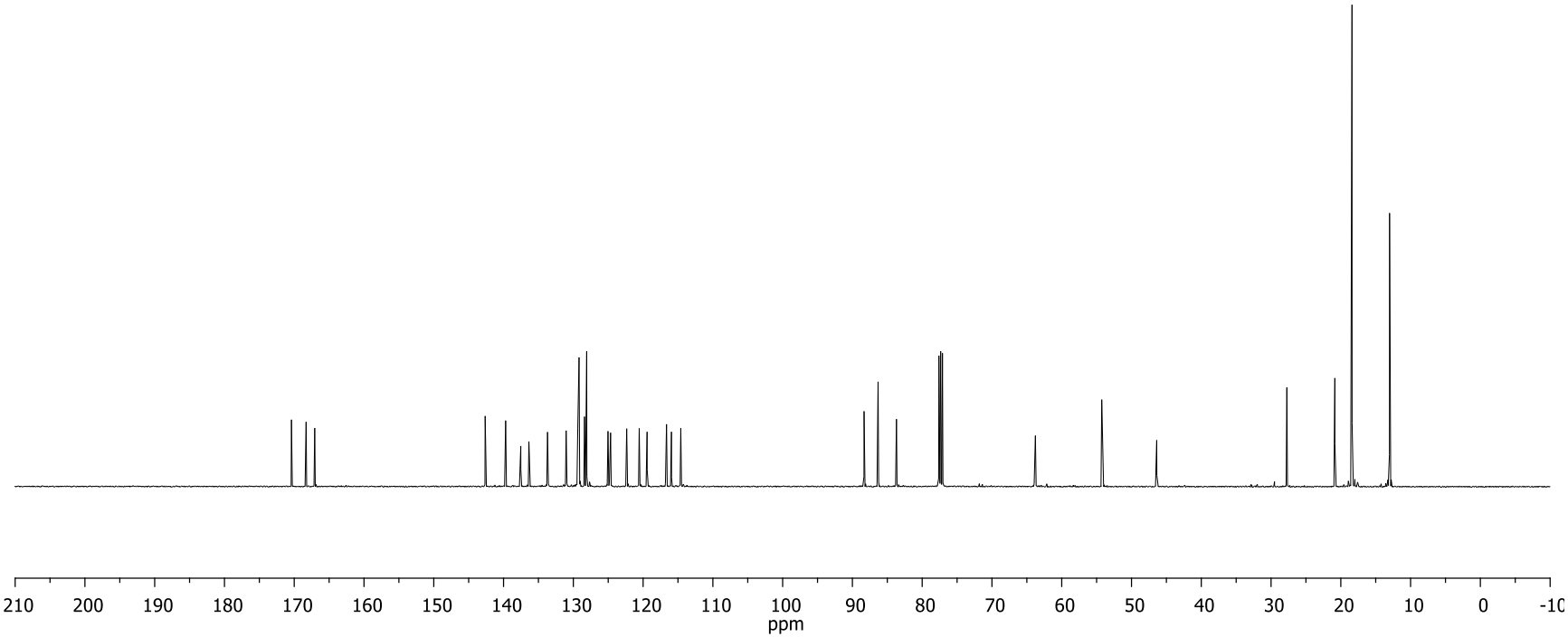


170.4
168.3
167.1
142.6
139.7
137.5
136.4
133.7
131.0
129.4
129.2
128.4
128.1
125.0
124.7
122.4
120.6
119.4
116.6
115.9
114.6
88.3
86.3
83.7
63.8
54.3
46.4
27.7
20.9
18.4
18.4
13.0

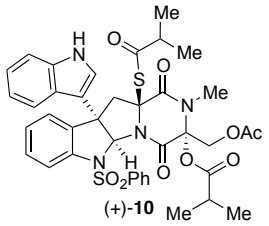
^{13}C NMR, 125 MHz, $CDCl_3$, 20 ºC

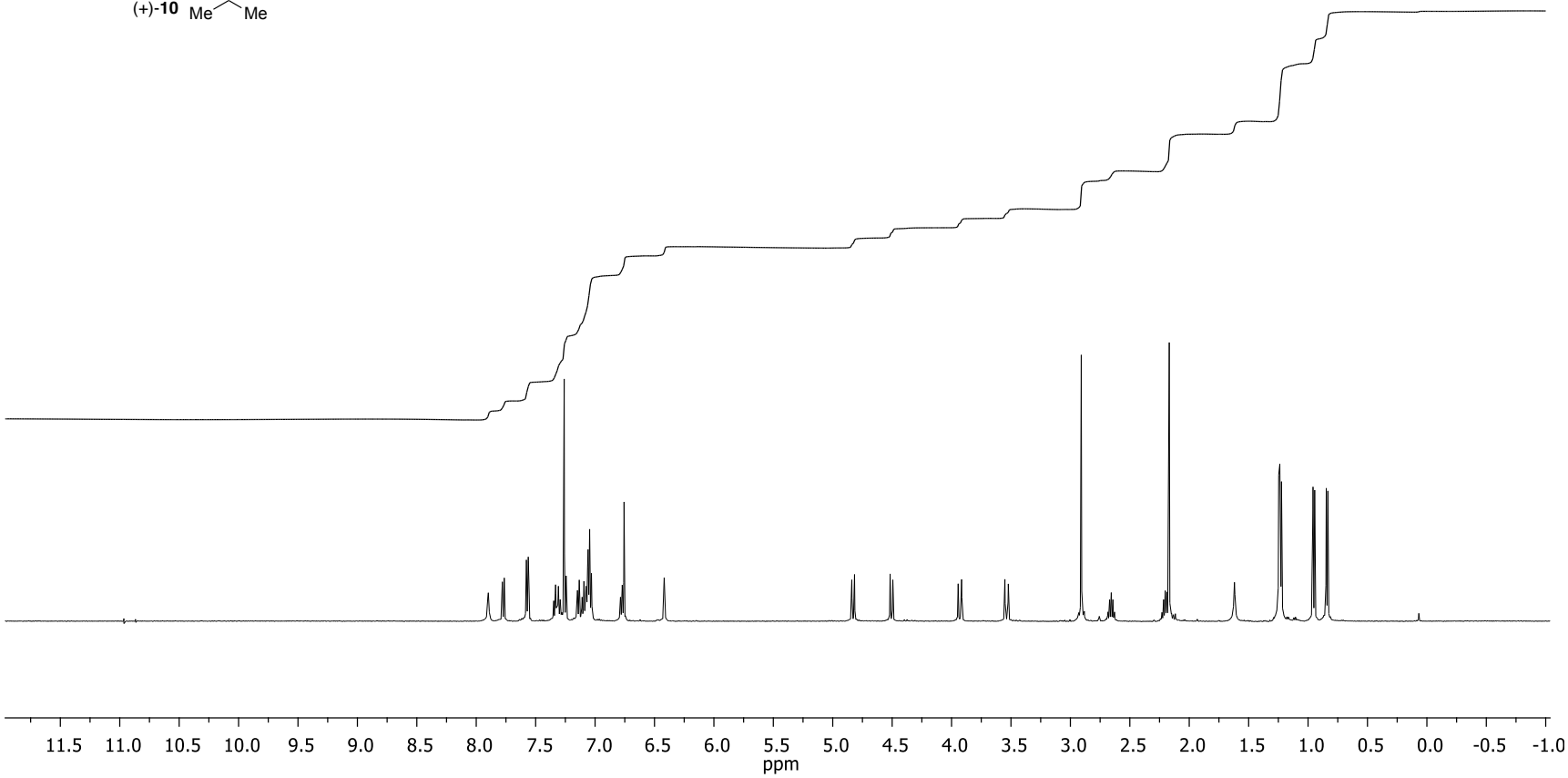


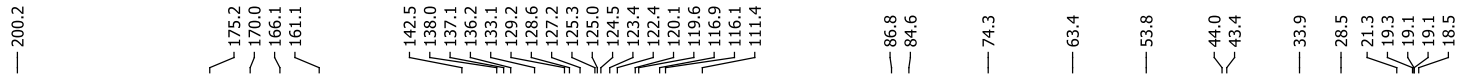
(+)-**4**



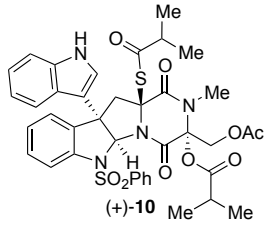
^{1}H NMR, 500 MHz, $CDCl_3$, 20 ºC

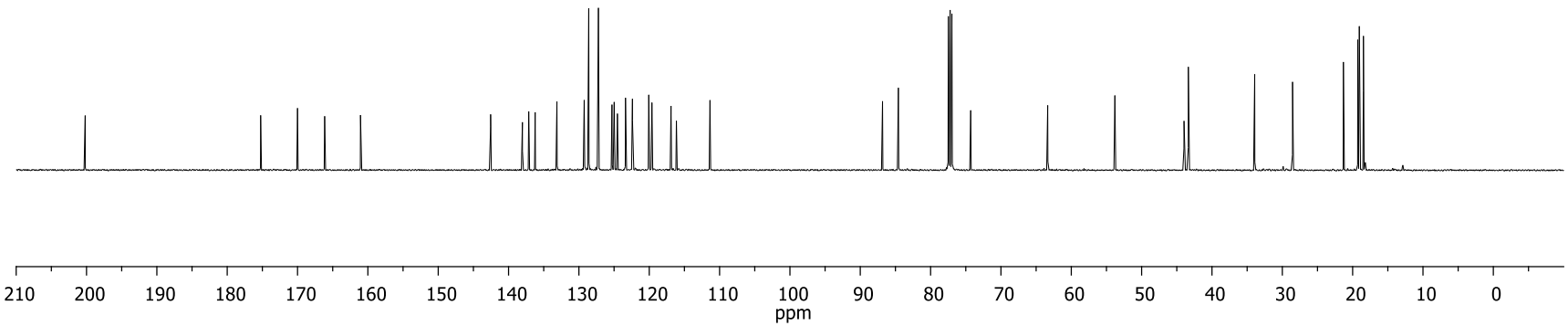




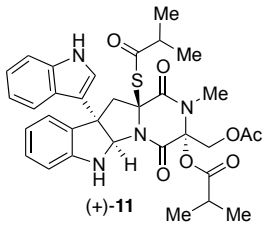


^{13}C NMR, 125 MHz, $CDCl_3$, 20 ºC



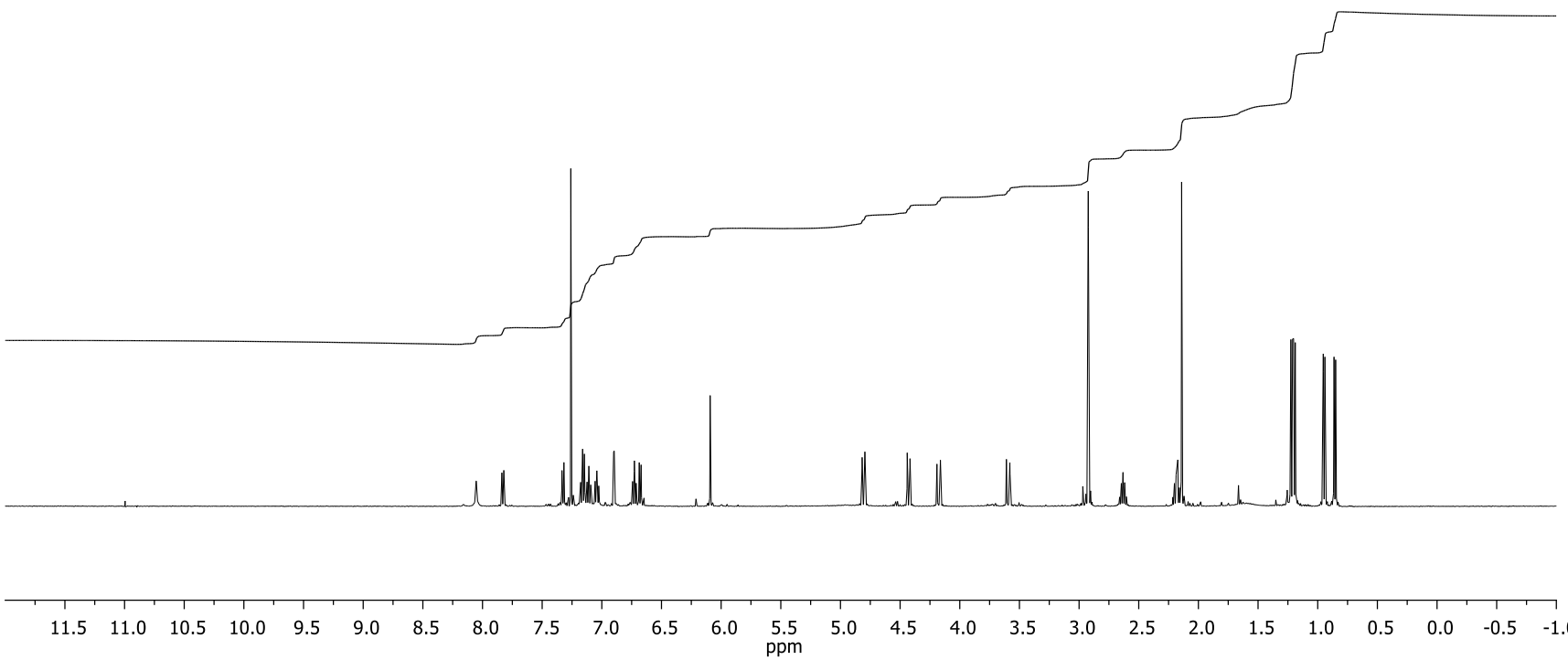


^{1}H NMR, 500 MHz, $CDCl_3$, 20 ºC



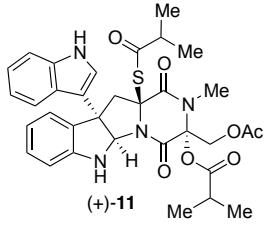
(+)-**11**

8.05 | 7.33 7.32 7.16 7.15 7.11 7.04 6.90 6.90 6.73 6.69 6.67 6.67 | 4.82 4.80 4.44 4.42 4.19 4.16 | 3.61 3.58 | 2.92 2.66 2.65 2.63 2.62 2.60 | 2.20 2.19 2.17 2.14 1.22 1.21 1.20 1.19 | 0.95 0.94 0.86 0.85

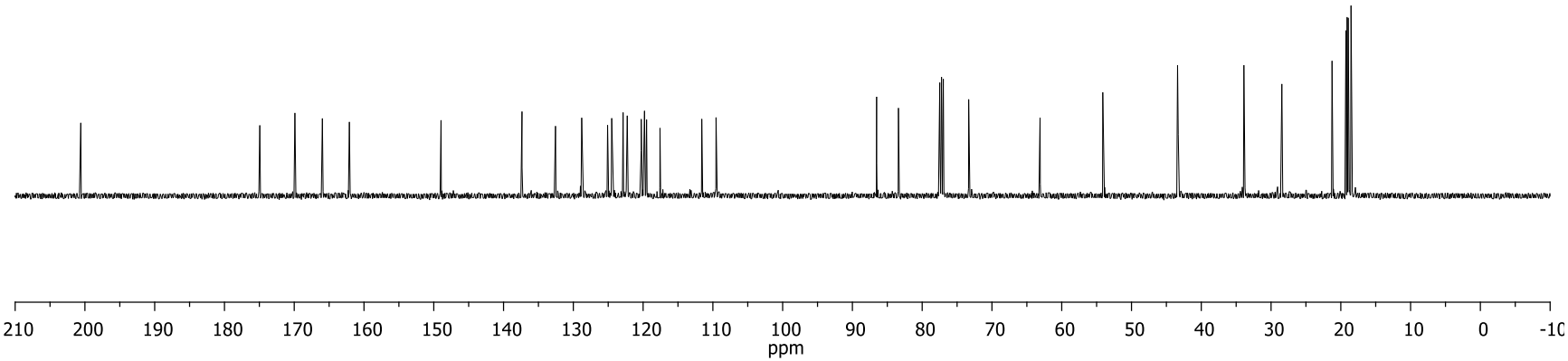


200.6 174.9 169.9 166.0 162.1 149.0 137.4 132.6 128.8 125.1 124.5 122.9 122.3 120.3 119.8 119.5 117.6 111.6 109.5 86.5 83.4 73.3 63.1 54.1 43.4 43.3 33.9 28.5 21.3 19.3 19.1 18.9 18.5

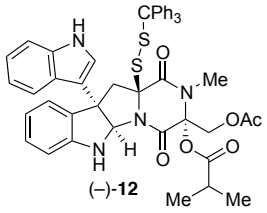
^{13}C NMR, 125 MHz, $CDCl_3$, 20 ºC



(+)-**11**

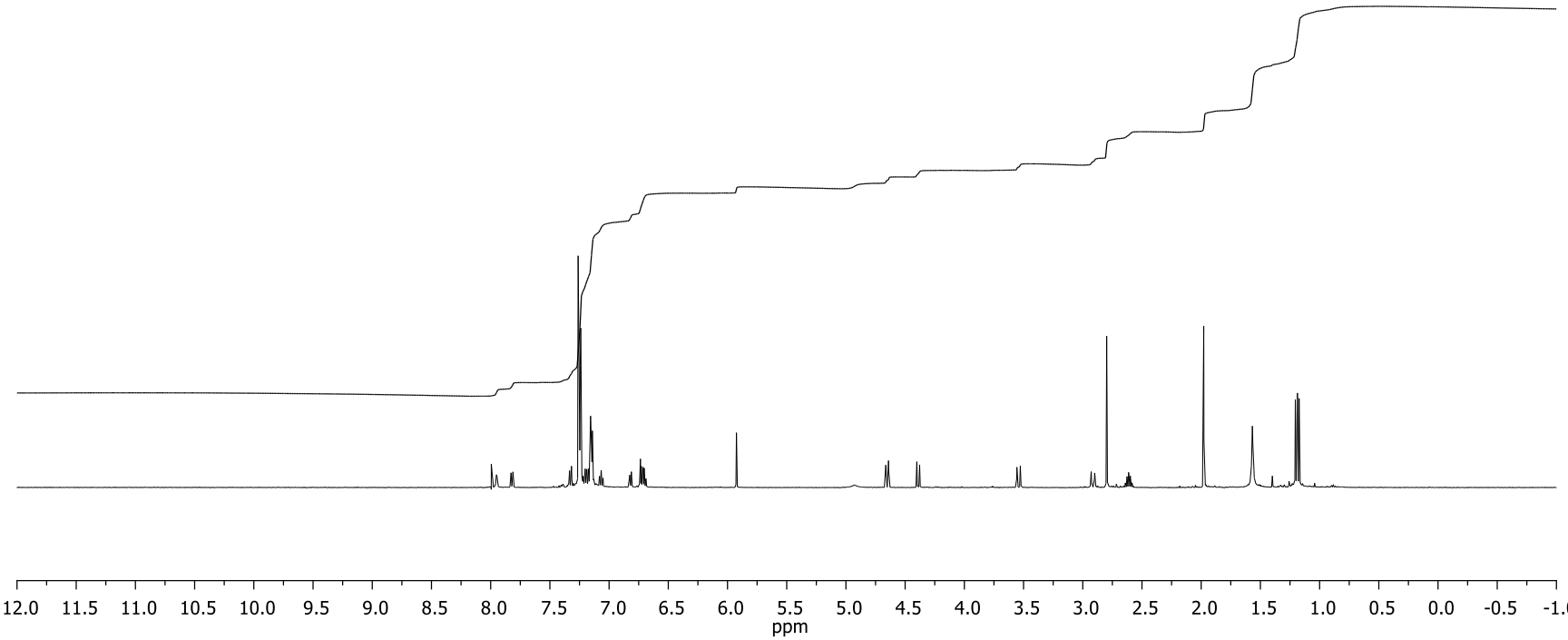


^{1}H NMR, 500 MHz, $CDCl_3$, 20 ºC



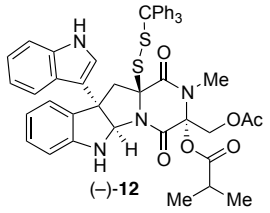
(–)-**12**

7.95 7.83 7.81 7.26 7.26 7.25 7.25 7.24 7.24 7.16 7.15 7.15 7.14 5.92 4.93 4.66 4.64 4.40 4.38 3.56 3.53 2.93 2.90 2.80 2.64 2.63 2.61 2.60 2.58 1.98 1.21 1.19 1.19 1.17

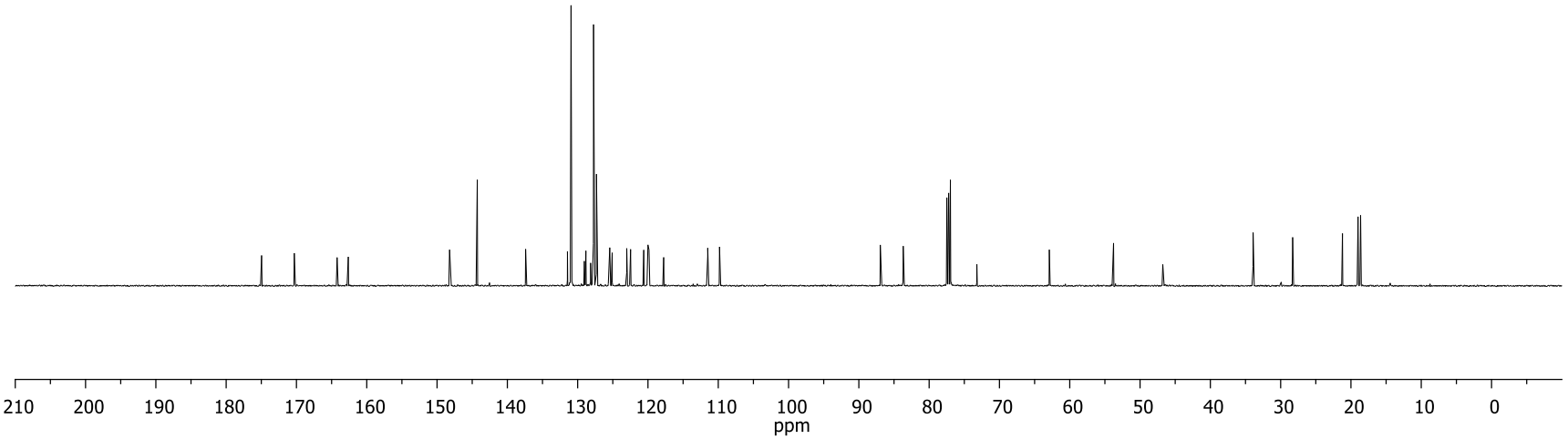


175.0 170.3 164.2 162.6 148.2 144.3 137.4 130.9 127.7 127.3 125.4 123.0 122.5 120.6 120.0 111.5 109.8 86.9 83.7 73.2 62.9 53.8 46.8 33.9 28.3 21.2 19.0 18.6

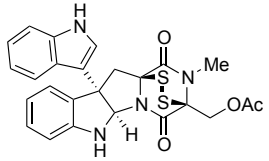
^{13}C NMR, 125 MHz, $CDCl_3$, 20 ºC



(–)-**12**

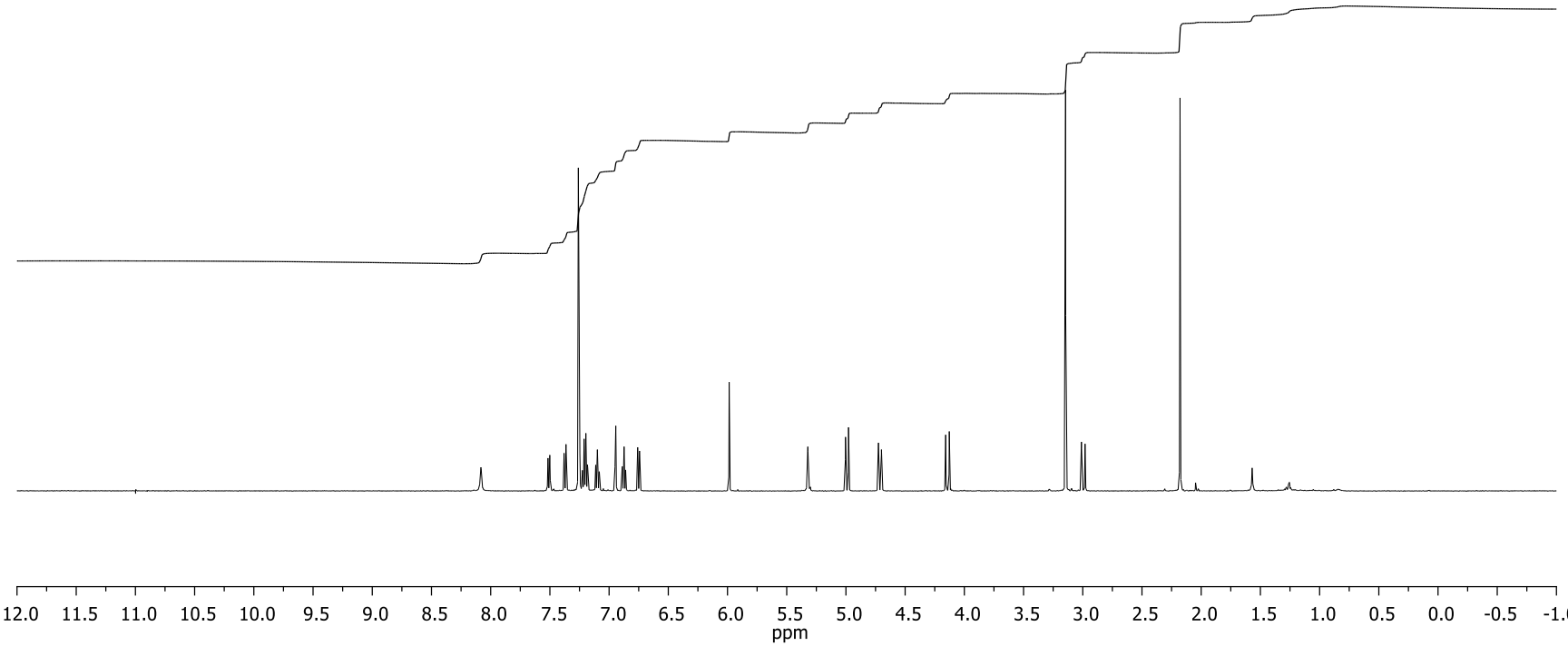


^{1}H NMR, 500 MHz, $CDCl_3$, 20 ºC

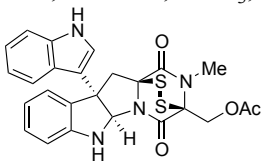


(+)-**13**

8.08, 7.38, 7.36, 7.25, 7.21, 7.20, 7.20, 7.10, 6.95, 6.94, 6.87, 6.76, 6.74, 5.99, 5.32, 5.00, 4.98, 4.73, 4.70, 4.16, 4.13, 3.15, 3.01, 2.98, 2.18

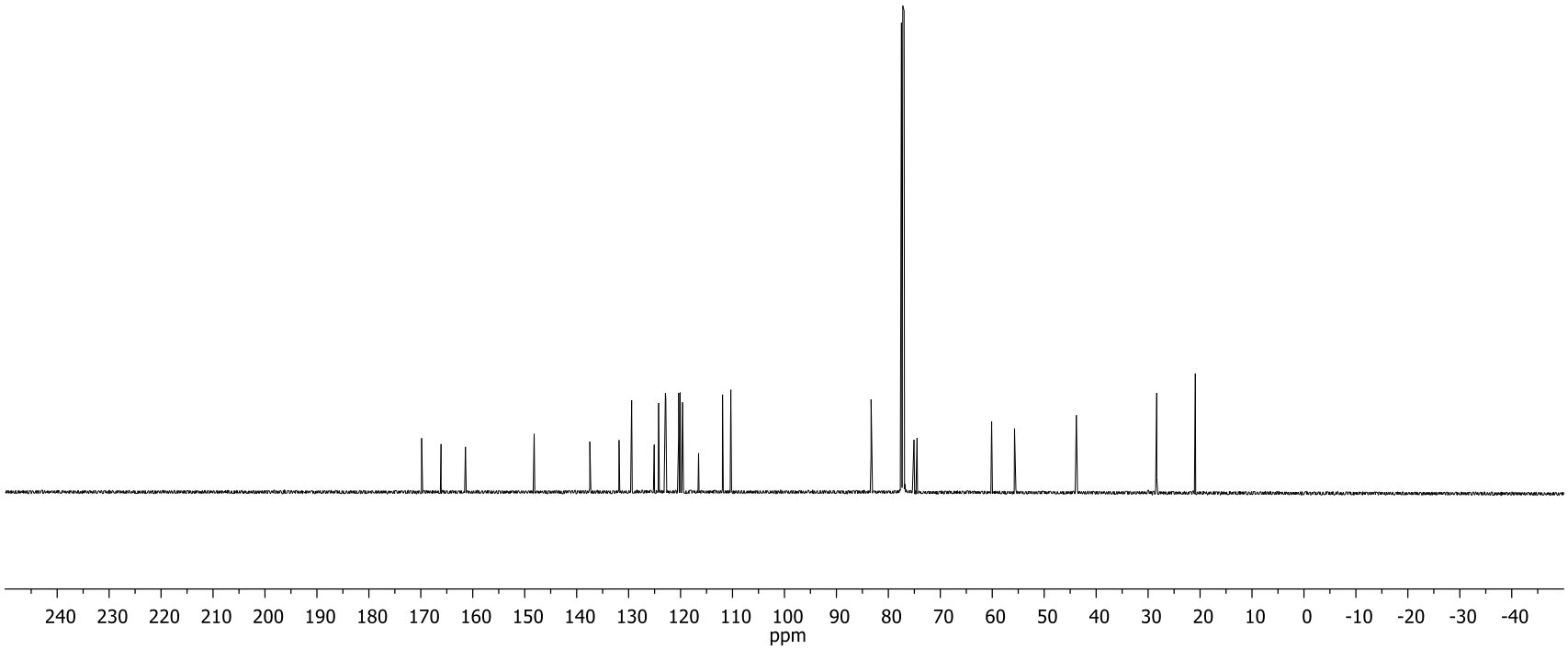


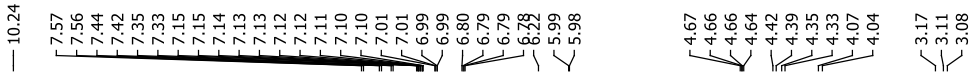
^{13}C NMR, 125 MHz, $CDCl_3$, 20 ºC



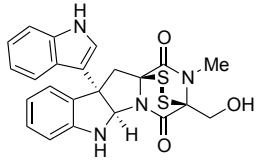
(+)-**13**

169.8
166.1
161.4
148.2
137.5
131.8
125.1
124.2
122.9
122.8
120.4
120.1
119.6
116.5
111.9
110.3
83.3
75.1
74.5
60.1
55.7
43.8
28.3
20.9

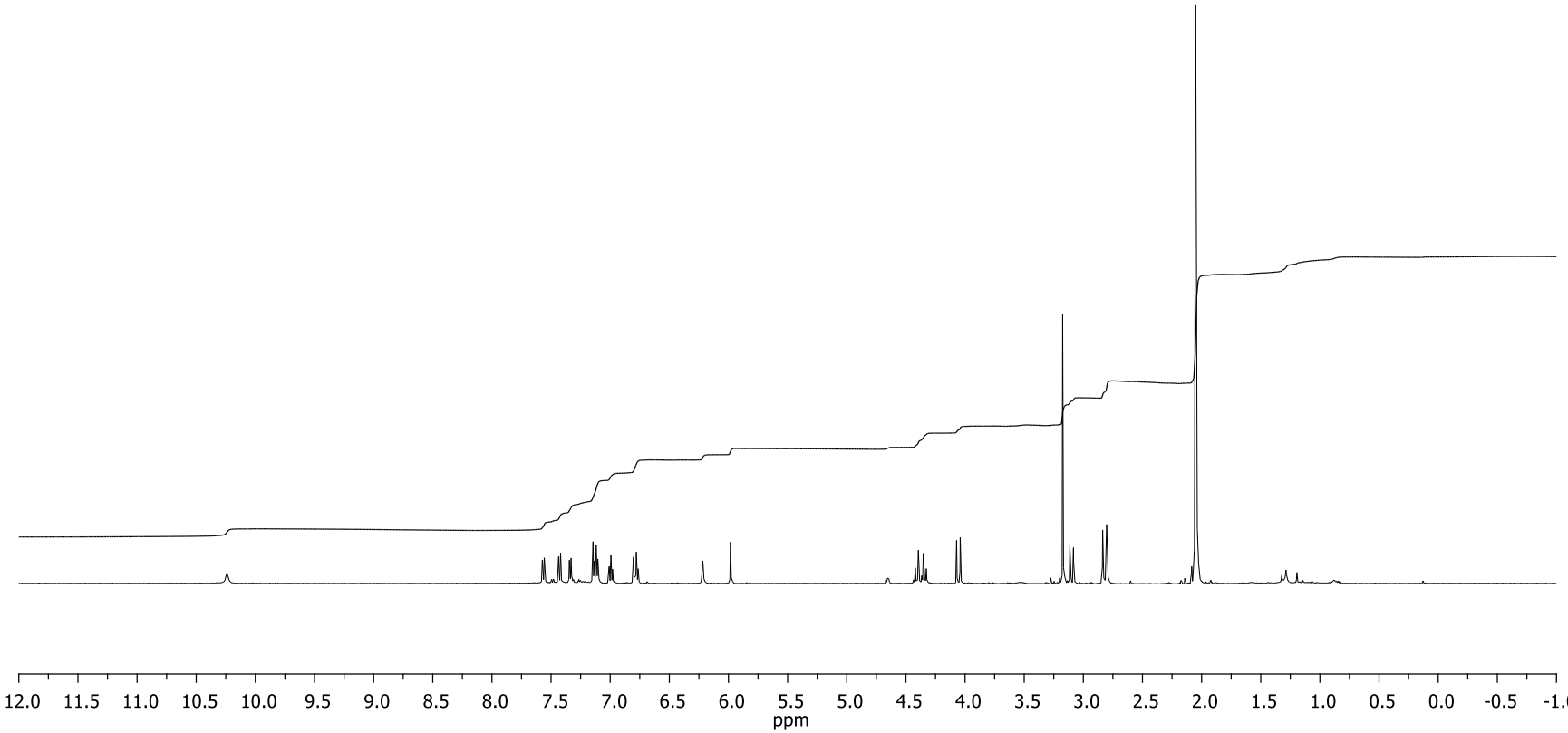




^{1}H NMR, 500 MHz, acetone-d_6, 20 ºC

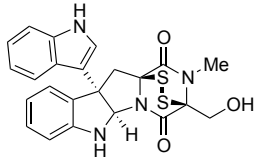


(+)-**1**

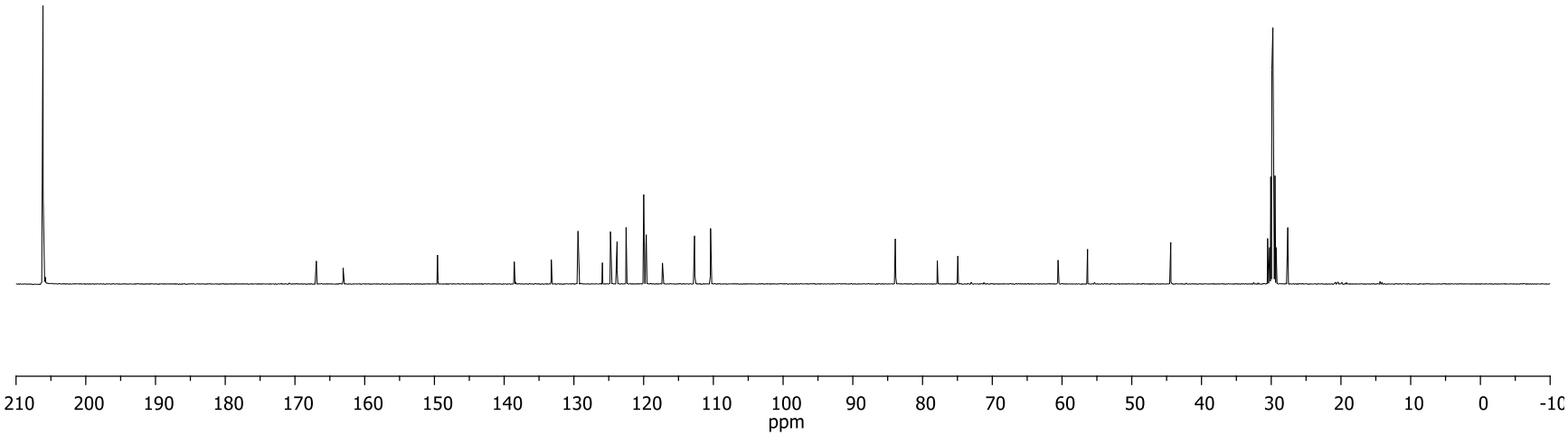


166.9
163.1
149.6
138.5
133.2
129.4
125.9
124.8
123.8
122.5
120.0
119.6
117.3
112.7
110.4
83.9
77.9
74.9
60.6
56.3
44.4
27.6

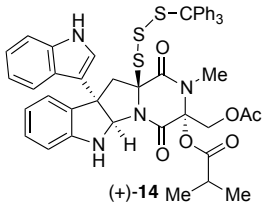
^{13}C NMR, 125 MHz, acetone-d_6, 20 ºC



(+)-**1**

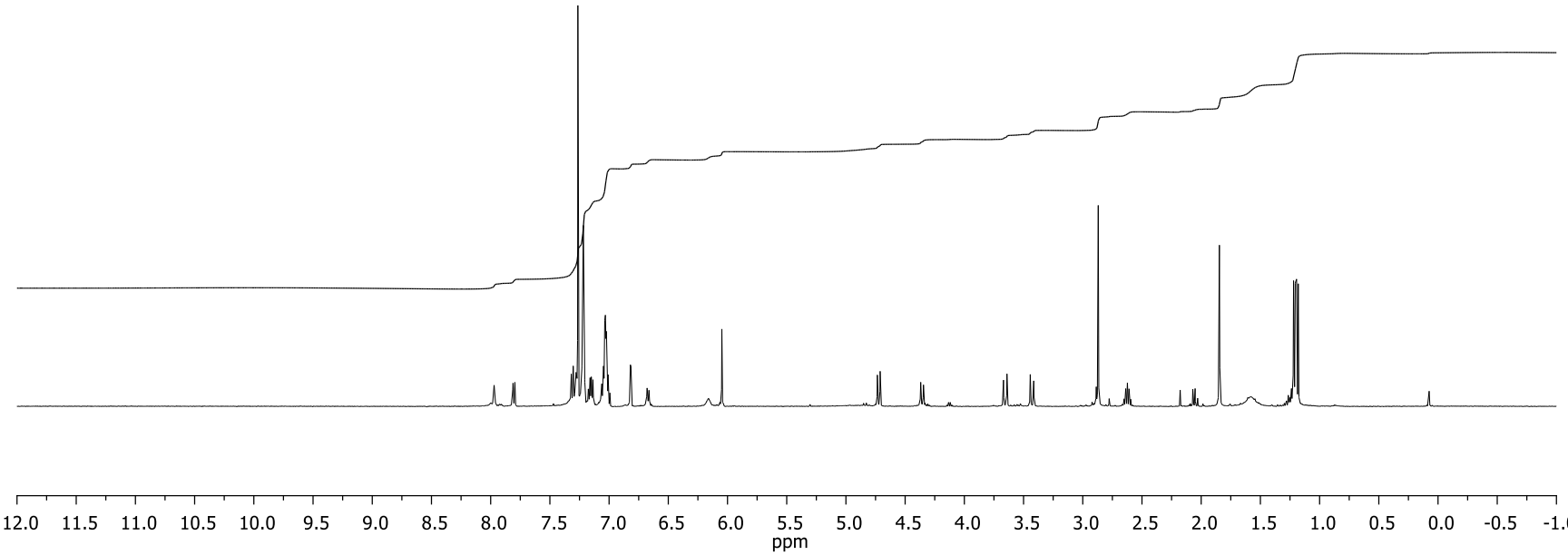


^{1}H NMR, 500 MHz, $CDCl_3$, 20 ºC



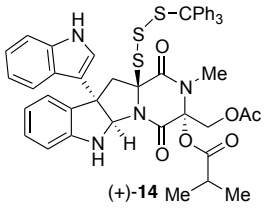
(+)-**14**

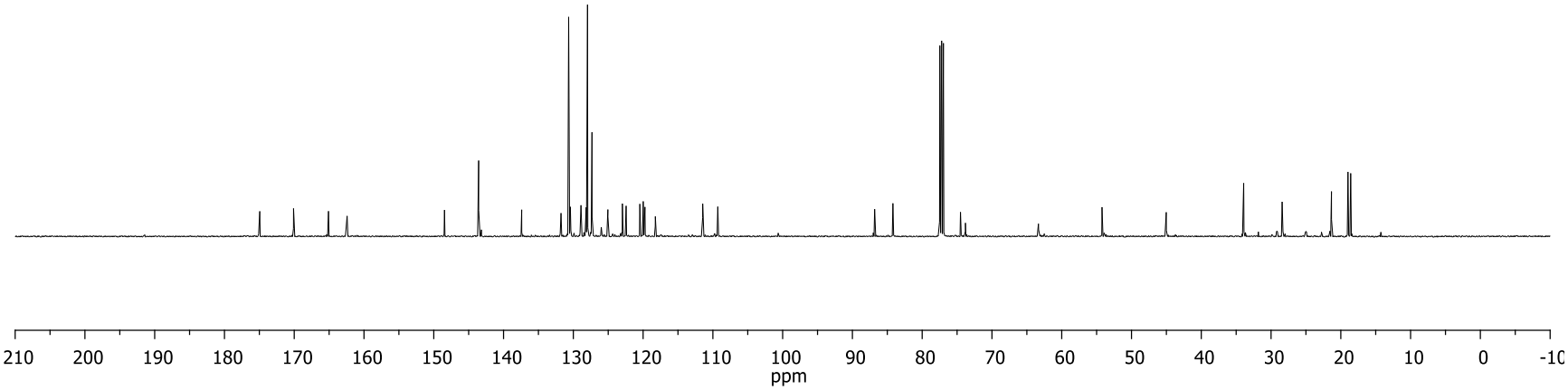
7.97 7.81 7.79 7.32 7.30 7.28 7.22 7.21 7.15 7.03 6.82 6.16 6.05 4.73 4.71 4.37 4.35 3.67 3.64 3.44 3.41 2.87 2.65 2.64 2.62 2.61 2.60 1.85 1.22 1.21 1.19 1.18



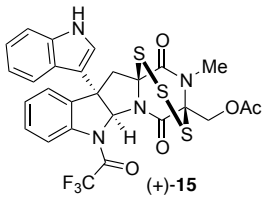
174.9
170.1
165.1
162.4
148.5
143.6
137.4
130.7
128.9
128.0
127.3
123.0
120.5
120.0
111.5
109.3
86.8
84.2
74.5
73.8
63.3
54.2
45.0
33.9
28.4
21.3
19.0
18.6

^{13}C NMR, 125 MHz, $CDCl_3$, 20 ºC



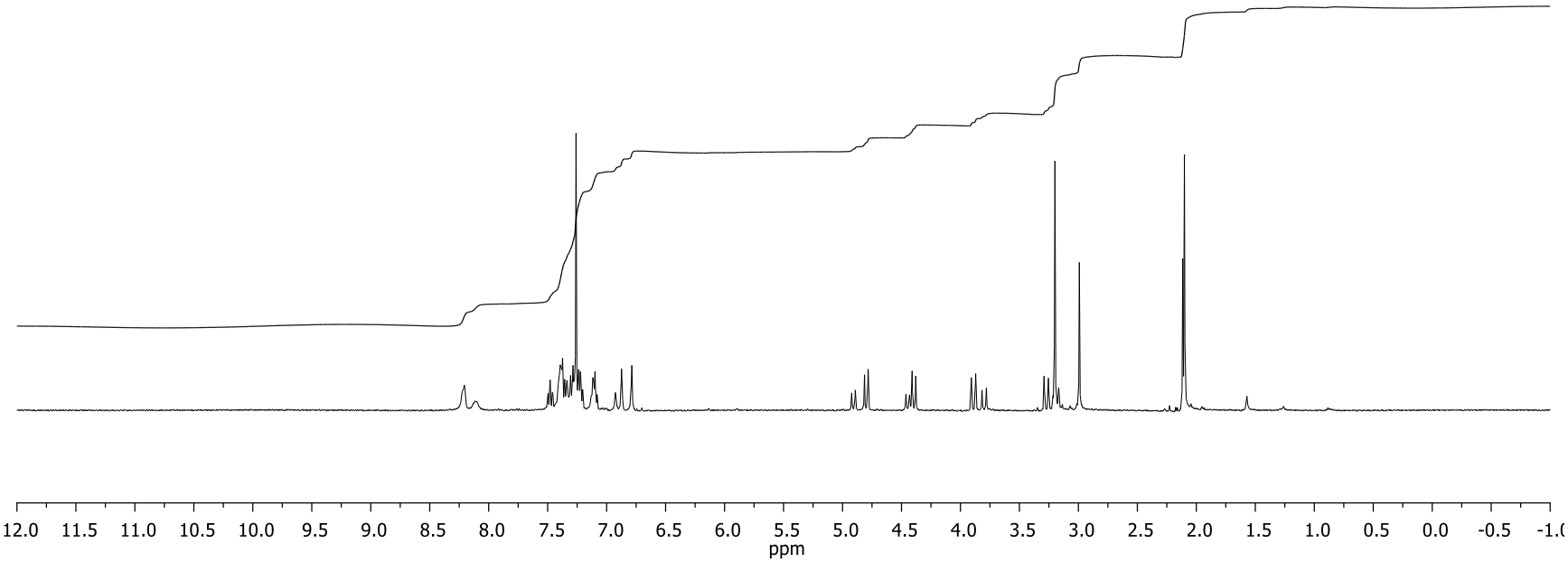


^{1}H NMR, 400 MHz, $CDCl_3$, 20 ºC

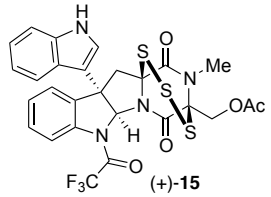


(+)-**15**

8.21 8.10 7.48 7.41 7.39 7.38 7.37 7.36 7.30 7.29 7.28 7.24 7.22 7.12 7.11 7.10 6.87 6.79 4.92 4.89 4.81 4.78 4.46 4.41 4.38 3.91 3.87 3.78 3.29 3.25 3.20 3.17 2.99 2.12 2.10

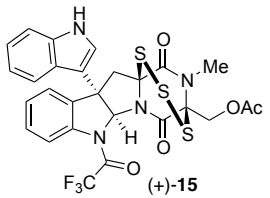


^{13}C NMR, 100 MHz, $CDCl_3$, 20 ºC



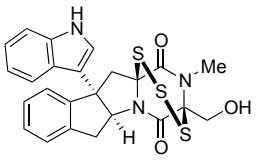
(+)-**15**

^{19}F NMR, 376 MHz, $CDCl_3$, 20 ºC

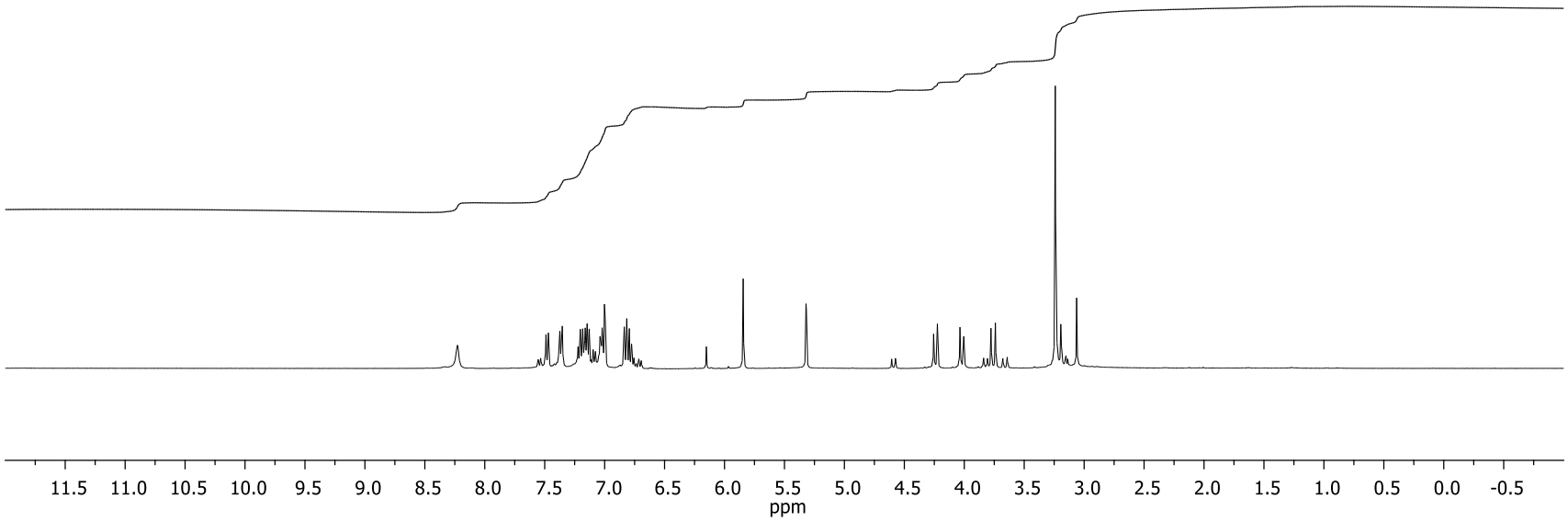


(+)-**15**

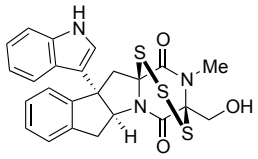
^{1}H NMR, 400 MHz, CD_2Cl_2, 20 ºC



(+)-**2**



^{13}C NMR, 100 MHz, CD_2Cl_2, 20 ºC



(+)-**2**