Supporting Information

Total Synthesis of Pentacyclic (−)-Ambiguine P Using Sequential Indole Functionalizations

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Table of Contents

1. General Considerations

1) Reagents and Solvents

Unless stated otherwise, reactions were performed in oven-dried glassware sealed with rubber septa under a nitrogen atmosphere and were stirred with Teflon®-coated magnetic stir bars. Liquid reagents and solvents were transferred by syringe using standard Schlenk techniques. Reagents were purchased from Sigma-Aldrich, Acros Organics, Chem-Impex, Fisher Scientific, or Alfa Aesar. Tetrahydrofuran (THF), toluene, acetonitrile (MeCN), methanol (MeOH), NEt_3 were dried by passage over a column of activated alumina; dichloromethane (DCM) was distilled over calcium hydride. All other solvents and reagents were used as received unless otherwise noted. Where stated, solutions were degassed using three cycles of freeze/pump/thaw (freezing the solution contained within a Schlenk flask in liquid nitrogen, opening the flask to vacuum for 5 min, then allowing the solution to thaw under vacuum).

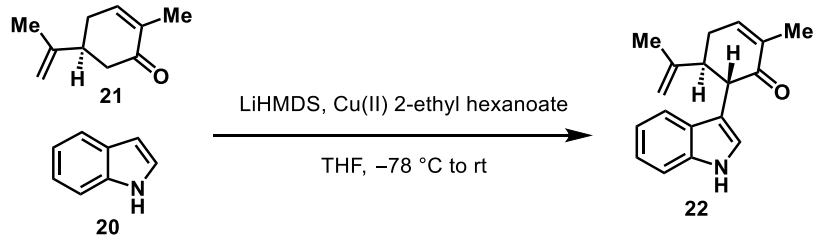
2) Reaction Monitoring/Purification

Reactions were monitored using a combination of thin layer chromatography (TLC) using SiliCycle silica gel 60 F-254 precoated plates (0.25 mm) and LC/MS. TLC plates were visualized by UV irradiation, anisaldehyde, cerium ammonium molybdenate (CAM), potassium permanganate, or iodine stain. LC/MS analysis was performed on a Shimadzu LCMS-2020 (UFLC) equipped with the LC20AD solvent delivery system, a SPD-20AV prominence UV/Vis detector (SPD-M20A Photo Diode Array), and a Thermo Scientific Hypersil GOLD HPLC column (5 μm particle size, 4.6 × 50 mm). Purifications were performed with a Yamazen® Smart S4 Flash EPCLC W-Prep 2XY (dual channel) automated flash chromatography system on prefilled, premium, universal columns using ACS grade solvents and gradients were determined by inputting R_f values and using the corresponding Yamazen® generated conditions.

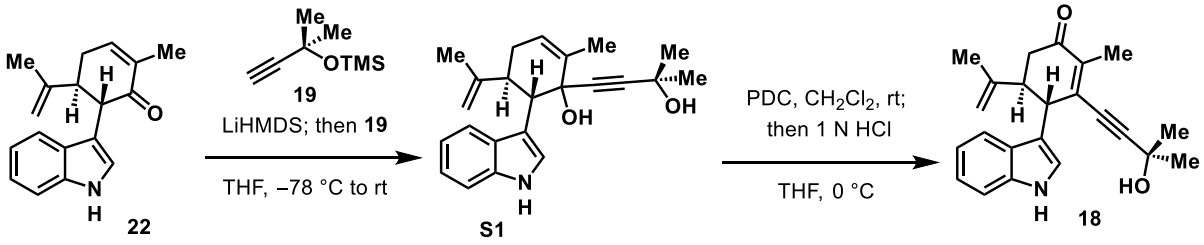
3) Instrumentation

Optical rotation was recorded on a Perkin Elmer Polarimeter 241 at the D line (1.0 dm path length), c = mg/mL, in $CHCl_3$ unless otherwise stated. ^1H and ^{13}C NMR experiments were performed on Bruker spectrometers operating at 300, 400, 500, 600, 700, or 900 MHz for ^1H and 75, 100, 125, 150, 176, or 226 MHz for ^{13}C experiments. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal ($CDCl_3$ δ = 7.26 for ^1H NMR and δ = 77.16 for ^{13}C NMR; $(CD_3)CO$ δ = 2.05 for ^1H NMR and δ = 29.84 for ^{13}C NMR; $(CD_3)SO$ δ = 2.50 for ^1H NMR and δ = 39.52 for ^{13}C NMR; C_6D_6 δ = 7.16 for ^1H NMR and δ = 128.06 for ^{13}C NMR; CD_3OD δ = 3.31 for ^1H NMR and δ = 49.00 for ^{13}C NMR). Data are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), dt (doublet of triplet), ddq (doublet of doublets of quartets), m (multiplet), bs (broad singlet). IR spectra were recorded on a Bruker ALPHA Platinum ATR FT-IR spectrometer. Samples were loaded onto the diamond surface either in their solid form or as a solution in DCM (allowing DCM to dry thoroughly). Low and high-resolution mass spectral data were obtained from the University of California, Berkeley Mass Spectral Facility, on a VG 70-Se Micromass spectrometer for FAB, and a VG Prospec Micromass spectrometer for EI.

2. Experimental Procedures and Characterization Data



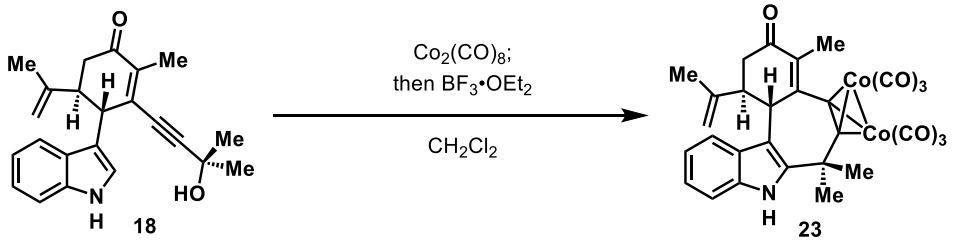
(5S,6S)-6-(1H-indol-3-yl)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-one (22): (Adapted from Baran et al.)[1] An oven-dried 2 L round-bottomed flask was charged with indole (**20**) (22.7 g, 194 mmol, 2.00 equiv) followed by (*S*)-carvone (**21**) (15 mL, 97 mmol, 1.0 equiv). To this mixture was added THF (484 mL) and the resulting solution was cooled in a dry ice/acetone bath to –78 °C. The reaction mixture was held at –78 °C while LHMDS (1.0 M in THF, 300 mL, 300 mmol, 3.1 equiv) was added via cannula transfer dropwise over 30 min. The resulting brownish solution was stirred at –78 °C for 1 h after which the flask was opened to the atmosphere and Cu(II) 2-ethylhexanoate (50.9 g, 145 mmol, 1.5 equiv) was added as a solid through a plastic funnel. The reaction mixture was quickly resealed with the septum and allowed to warm to room temperature overnight. The reaction mixture was quenched with ammonium chloride (sat. aq.) (500 mL) and the aqueous layer was extracted with ethyl acetate (3 x 500 mL). The organic layer was washed with brine (1 x 300 mL), dried over sodium sulfate, and the solvent was removed in vacuo. The crude product was purified via SiO_2 column chromatography eluting with 4:1 hexanes/ethyl acetate to afford pure product as an off-white solid (10.7 g, 40.2 mmol, 41.0%). Analytical data was identical in all aspects to that which was previously reported.[1]



Allylic alcohol S1: To a solution of alkyne **19** (10.2 mL, 52.5 mmol, 2.1 equiv) in THF (130 mL) at –78 °C was added LHMDS (1.0 M in THF, 54 mL, 54 mmol, 2.2 equiv) dropwise over 10 min. This solution was allowed to stir at –78 °C for 1 h after which indole-carvone adduct **22** (6.6 g, 25 mmol, 1.0 equiv) was added as a solution in THF (15 mL) dropwise over 5 min. The reaction mixture was immediately taken out of the –78 °C bath and allowed to warm to room temperature. The reaction mixture was then quenched with ammonium chloride (sat. aq.) (200 mL) and the aqueous layer was extracted with ethyl acetate (3 x 100 mL). The organic layers were combined and washed with brine (200 mL), dried over sodium sulfate, and the solvent was removed in vacuo. The yellowish-red crude

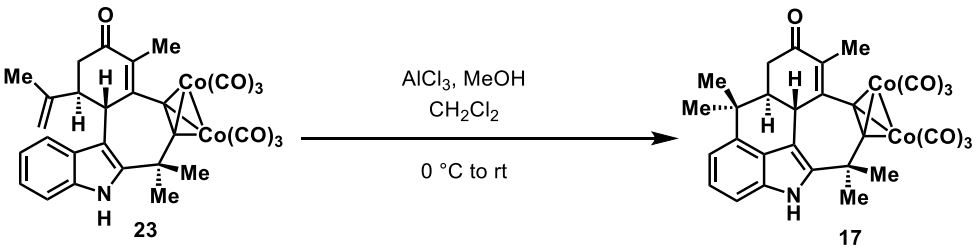
reaction mixture was used immediately in the next step.

Tricycle 18: The crude product from the previous step (**S1**) was dissolved in DCM (250 mL) and PDC (14.1 g, 37.5 mmol, 1.5 equiv) was added. The reaction mixture was allowed to stir at room temperature overnight. The reaction mixture was then filtered through a plug of Celite® eluting with DCM and to the filtrate was added 2N HCl/MeOH (50 mL). After complete removal of the TMS group as indicated by TLC analysis (approx. 10 min), the reaction mixture was quenched with sodium bicarbonate (sat. aq.) (200 mL) and the aqueous layer was washed with ethyl acetate (3 x 100 mL). The combined organic layers were washed with brine and dried over sodium sulfate. The solvent was removed in vacuo and the crude product was purified using SiO_2 column chromatography eluting with 2:1 hexanes/ethyl acetate then 1:1 hexanes/ethyl acetate to yield the product as a yellow foam (3.8 g, 11 mmol, 44% over 2 steps). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 4.75 - 4.64 (m, 2H), 4.12 (dd, *J* = 7.9, 2.2 Hz, 1H), 3.17 (td, *J* = 9.0, 4.5 Hz, 1H), 2.68 - 2.57 (m, 2H), 2.01 (d, *J* = 1.9 Hz, 3H), 1.72 (s, 3H), 1.17 (s, 3H), 1.13 (s, 3H). **^{13}C NMR**; (150 MHz, $CDCl_3$) δ 198.4, 145.4, 139.5, 138.1, 136.4, 127.5, 122.8, 122.3, 119.6, 119.2, 116.0, 113.1, 111.6, 109.0, 81.2, 65.5, 47.7, 41.9, 41.8, 30.7, 30.7, 20.4, 14.3. **IR** (thin film) 3324, 3260, 2979, 2850, 2220, 1640, 1456, 1340, 1167, 891, 739 cm^{-1}..**HRMS** (ESI) *m/z* calc'd for $C_{23}H_{26}O_2N$ $[M+H]^+$: 348.1958. Found 348.1960. $[\alpha]_D$ = +151 (c 7.5 x 10^{-3}, $CHCl_3$).

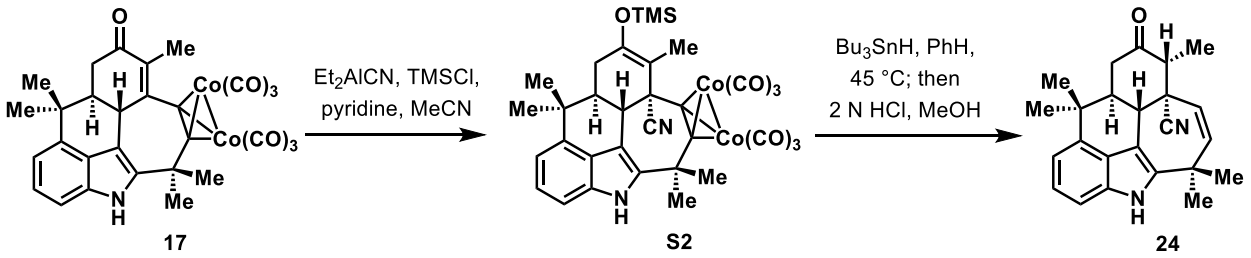


Cobalt-complexed tetracycle 23: A 1 L flask was charged with propargylic alcohol **18** (2.0 g, 5.9 mmol, 1.0 equiv). To this flask was added DCM (60 mL) followed by $Co_2(CO)_8$ (2.4 g, 7.0 mmol, 1.2 equiv). The reaction mixture was allowed to stir at room temperature for 5 h. To this reaction mixture was added $BF_3 \cdot OEt_2$ (0.72 mL, 5.9 mmol, 1.0 equiv). After stirring for 5 min, the reaction mixture was quenched with sodium bicarbonate (100 mL) and the aqueous layers were extracted with ethyl acetate (3 x 75 mL). The combined organic layers were washed with brine (sat. aq.) (100 mL), dried over sodium sulfate, and the solvent was removed in vacuo. The crude reaction mixture was purified using SiO_2 gel column chromatography eluting with hexanes then 2:1 hexanes/ethyl acetate. The product was isolated as a dark red solid (3.2 g, 5.2 mmol, 88%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.09 (dt, *J* = 19.6, 7.4 Hz, 2H), 4.82 (d, *J* = 13.3 Hz, 2H), 4.44 (s, 1H), 3.88 (d, *J* = 6.2 Hz, 1H), 3.23 (dd, *J* = 15.9, 5.1 Hz, 1H), 2.77 (dd, *J* = 15.8, 7.4 Hz, 1H), 2.00 (s, 3H), 1.96 (s, 3H), 1.80 (s, 3H), 1.77 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.5, 198.3, 198.1, 154.1, 146.4, 141.6, 138.0, 134.4, 126.9, 121.4, 120.4, 120.1, 112.3, 112.0, 111.4, 110.8, 85.2, 44.7, 42.3, 42.2, 39.7, 30.4, 29.6, 21.7, 12.6. **IR** (thin film) 3306, 2974, 2090, 2052, 2012, 1645, 1568, 1437, 1323, 898 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for

$C_{29}H_{24}O_7NCo$ $[M+H]^+$: 616.0211. Found 616.0222. We attempted to obtain optical rotations, however, at the wavelength we had access to (Na lamp, 584 nm), the transmittance was too low to obtain accurate rotations.

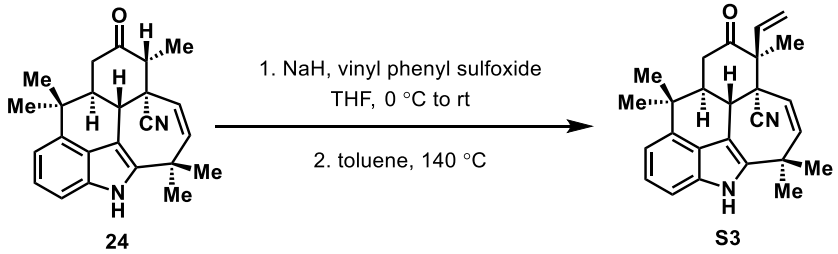


Cobalt-complexed pentacycle 17: A flame-dried 500 mL round-bottomed flask was brought into a glovebox and charged with $AlCl_3$ (3.0 g, 23 mmol, 15 equiv). The flask was fitted with a rubber septum and brought out of the glovebox. Freshly distilled DCM (150 mL) was added to the flask and the mixture was placed under a stream of N_2. The mixture was cooled to 0 °C and tetracycle **23** (0.923 g, 1.50 mmol, 1.0 equiv) was added as a solid immediately followed by the addition of MeOH (0.79 mL, 23 mmol, 15 equiv) via syringe. The reaction mixture was removed from the ice bath and allowed to warm to room temperature. After stirring for 3 h at room temperature, the reaction mixture was quenched by pouring into ice water (100 mL) and the aqueous layer was extracted with DCM (3 x 100 mL). The organic layers were combined, washed with brine (200 mL), dried over sodium sulfate, and the solvent was removed in vacuo. The crude product was subjected to the next reaction without purification.



Silyl enol ether S2: Crude cobalt-complexed pentacycle **17** was dissolved in MeCN (15 mL) in a round-bottomed flask. To this solution was added Et_2AlCN (1.0 M in toluene, 4.4 mL, 4.4 mmol, 3.0 equiv) via syringe over 1 min. After 30 min of stirring at room temperature, TMSCl (0.89 mL, 6.9 mmol, 4.8 equiv) followed by pyridine (0.89 mL, 11 mmol, 7.6 equiv) was added via syringe. After another 30 minutes of stirring at room temperature, the reaction mixture was quenched by pouring into ice and sodium bicarbonate (sat. aq.) (50 mL). The organic layer was washed with brine (2 x 50 mL) and the combined aqueous layers were extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over sodium sulfate and the solvent was removed in vacuo. The crude brown foam was immediately subjected to the next reaction without purification.

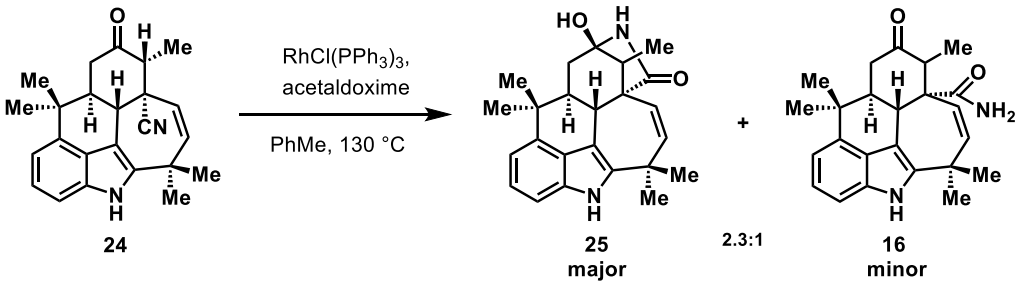
Nitrile ketone 24: Crude **S2** was dissolved in benzene (15 mL) and the solution was placed in an oil bath pre-heated to 45 °C. $SnBu_3H$ (2.1 mL, 7.3 mmol, 5.0 equiv) was added in four equal portions every half hour totaling 2.5 h reaction time at 45 °C. After this time, the solvent was removed in vacuo and the crude product was filtered through a SiO_2 plug eluting with hexanes (500 mL). The SiO_2 plug was then washed with ethyl acetate (500 mL) and the solvent was removed in vacuo. The crude reaction mixture was dissolved in ethyl acetate (100 mL) and a 2N HCl/MeOH (50 mL) mixture was added. Following complete desilylation (as indicated by TLC), the mixture was quenched with sodium bicarbonate (sat. aq.) (100 mL) and the aqueous layer was extracted with ethyl acetate (3 x 50 mL). The organic layer was washed with brine (100 mL), dried over sodium sulfate, and concentrated in vacuo. The crude reaction mixture was purified using SiO_2 column chromatography eluting with 2:1 hexanes/ethyl acetate to yield the desired product as a white-yellow solid (0.26 g, 0.72 mmol, 49% over 3 steps). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.15 (d, *J* = 4.1 Hz, 2H), 7.01 (t, *J* = 4.0 Hz, 1H), 5.80 (d, *J* = 12.1 Hz, 1H), 5.68 (d, *J* = 12.1 Hz, 1H), 3.51 (d, *J* = 11.1 Hz, 1H), 2.82 (dd, *J* = 13.2, 3.2 Hz, 1H), 2.71 (q, *J* = 6.6 Hz, 1H), 2.47 (t, *J* = 13.5 Hz, 1H), 2.29 (ddd, *J* = 14.1, 11.0, 3.2 Hz, 1H), 1.67 (s, 3H), 1.54 (s, 3H), 1.46 (s, 3H), 1.41 (d, *J* = 6.6 Hz, 3H), 1.18 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.3, 143.1, 139.2, 135.9, 133.4, 127.6, 125.8, 122.9, 119.1, 113.2, 108.0, 106.4, 52.0, 49.9, 48.5, 44.0, 41.8, 38.2, 37.9, 33.3, 28.2, 24.6, 24.3, 10.3. **IR** (thin film) 3393, 2955, 2866, 2365, 1719, 1450, 1327, 776 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for $C_{24}H_{26}N_2O$ $[M+H]^+$: 358.2040 found = 358.2046. $[\alpha]_D$ – 81.9 (c 4.7 x 10^{-3}, $CHCl_3$)



24 S3

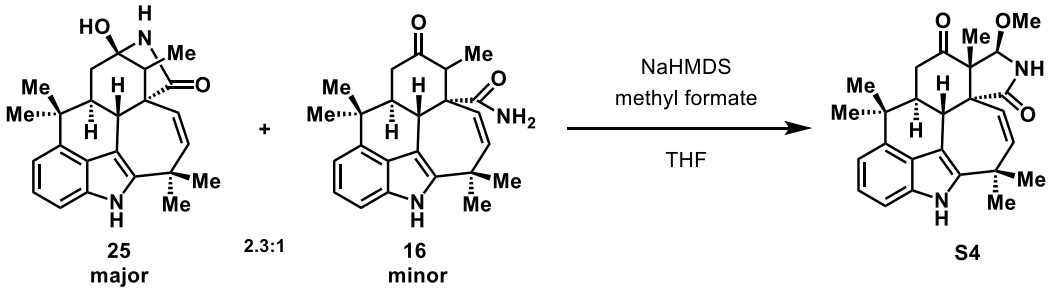
α-Functionalized nitrile ketone S3: To a 100 mL round-bottomed flask was added **24** (270 mg, 0.75 mmol, 1.0 equiv), phenyl vinyl sulfoxide (0.20 mL, 1.5 mmol, 2.0 equiv), and THF (20 mL). The resulting solution was cooled to 0 °C, then NaH (60% dispersion in mineral oil, 120 mg, 3.0 mmol, 5.0 equiv) was added. The ice bath was removed, and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was quenched with water (5 mL), and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with water (10 mL) followed by brine (10 mL), dried over magnesium sulfate, and concentrated in vacuo. The resulting crude compound was dissolved in toluene (20 mL) in a 10–20 mL microwave vial. The reaction mixture was stirred for 4 h at 140 °C, then cooled to room temperature and concentrated in vacuo. The product was purified by column chromatography eluting with 1:1 DCM: toluene to give an orange solid, which was recrystallized from DCM and hexanes to afford the vinylated product as a single diastereomer in 58% yield (168 mg, 58%). mp >260°C. See X-ray crystal structure data below · **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (br s, 1H), 7.17 – 7.13 (m, 2H), 7.03 – 6.99 (m, 1H), 6.30 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.81 (d, *J* = 12.4, 1H), 5.62 (d, *J* = 12.4 Hz, 1H), 5.47 (d, *J* =

10.8 Hz, 1H), 5.35 (d, *J* = 17.2 Hz, 1H), 3.74 (d, *J* = 11.3 Hz, 1H), 2.75 (dd, *J* = 13.7, 13.7 Hz, 1H), 2.69 (dd, *J* = 13.6, 4.0 Hz, 1H), 2.35 (ddd, *J* = 14.3, 11.3, 4.0 Hz, 1H), 1.64 (s, 3H), 1.58 (s, 3H), 1.52 (s, 3H), 1.45 (s, 3H), 1.19 (s, 3H). **^{13}C NMR** (150 MHz, CDCl3) δ 206.9, 143.7, 139.3, 136.2, 136.0, 133.5, 126.0, 124.2, 122.9, 120.6, 119.7, 113.1, 108.0, 106.3, 57.9, 51.8, 48.1, 39.9, 38.6, 38.4, 37.9, 33.1, 28.1, 24.6, 24.3, 18.5. **IR** (ATIR) 3355, 2966, 2237, 1713, 1469, 1328, 928, 773 cm−1 . **HRMS** (ESI) m/z calc'd for $C_{26}H_{28}ON_2{}^{39}K$ $[M+K]^+$ 428.1833, found 428.1840. $[\alpha]_D$ –63.8 (c 5.0 x 10–3 , $CHCl_3$)

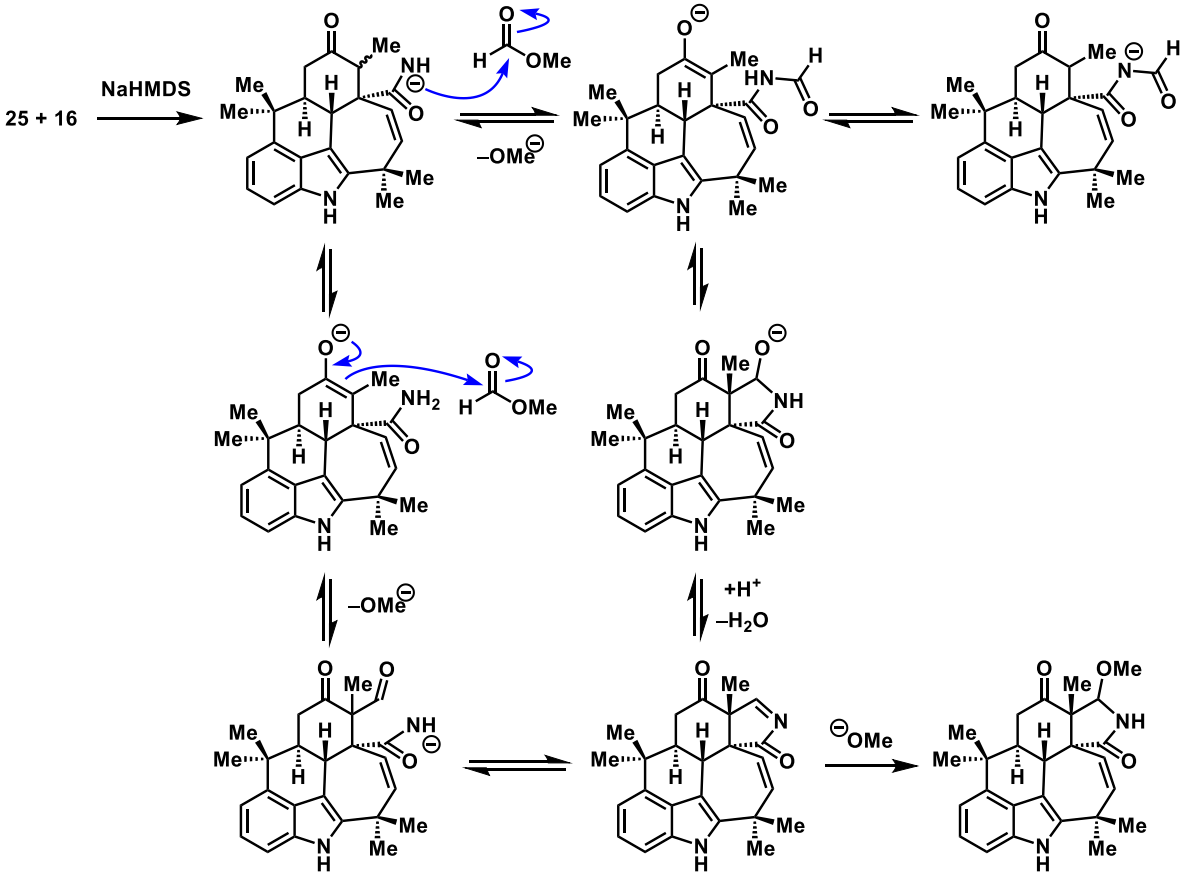


Amide 16 and aminal 25: Ketone **24** (260 mg, 0.72 mmol, 1.0 equiv) was added to a 25-mL round-bottomed flask. Toluene (2 mL) was added followed by acetaldoxime (freeze-pump-thawed (3x), 1.1 mL, 18 mmol, 25 equiv) via syringe. Wilkinson's catalyst, $RhCl(PPh_3)_3$ (0.14 mmol, 13 mg, 0.20 equiv), was added to the mixture and a reflux condenser flushed with N_2, was fitted on the flask. The setup was sealed with a septum with a N_2 inlet. The reaction mixture was placed in an oil bath preheated to130 °C and heated at reflux for 2.5 h at this temperature. After 2.5 h, the reaction flask was taken out of the oil bath and allowed to cool down to room temperature. The mixture was quenched with water (10 mL) and diluted with ethyl acetate (20 mL). The aqueous layer was extracted with ethyl acetate (3 x 20 mL) and the combined organic layers were washed with brine (20 mL) and dried over sodium sulfate. The crude mixture was concentrated in vacuo and purified using SiO_2 gel column chromatography on a Yamazen® automatic purification system using a gradient of 50% hexanes/ethyl acetate to 5% hexanes/ethyl acetate. The product was isolated as a slight orange foam to glassy solid as a mixture of constitutional isomers (150 mg, 0.41 mmol, 57% (NMR yield of combined **25** and **16**), 66% brsm). Both **16** and **25** are typically collected and subjected to the next step along with triphenylphosphine oxide the presence of which does not affect the efficiency of the subsequent steps. **Amide of lower polarity (16): R_f**: 0.5 (1:2 hexanes:EtOAc). **^{1}H NMR** (600 MHz, CD_3OD) δ 9.96 (s, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 5.72 (d, *J* = 13.2 Hz, 1H), 5.58 (d, *J* = 13.3 Hz, 1H), 3.21 (d, *J* = 11.3 Hz, 1H), 2.12 – 2.10 (m, 2H), 1.88 (td, *J* = 11.9, 5.5 Hz, 1H), 1.79 (t, *J* = 12.2 Hz, 1H), 1.67 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.20 (d, *J* = 6.8 Hz, 3H), 1.14 (s, 3H). **^{13}C NMR** (151 MHz, CD_3OD) δ 176.5, 144.2, 141.5, 138.2, 135.6, 127.2, 123.1, 122.3, 112.3, 108.4, 107.3, 87.8, 59.1, 55.0, 49.8, 42.8, 39.8, 38.0, 37.7, 32.9, 31.1, 25.3, 25.2, 10.4. **IR** (thin film) 3287, 2963, 2927, 1693, 1660, 1450, 1362, 1306, 1263, 1121, 1053, 1022, 735 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for $C_{24}H_{28}O_2N_2Na$ $[M+Na]^+$: 399.2043. Found 399.2049. $[\alpha]_D$ –83.3 (c 1.5 $x10^{-3}$, $CHCl_3$). **Aminal of higher polarity (25)**: **R_f**: 0.3 (1:2 hexanes:EtOAc). **^{1}H NMR** (600 MHz, 10% $(CD_3)_2CO$ in CD_3OD) δ7.05 (d, *J* = 7.9 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.02 (d, *J* = 13.0 Hz, 1H), 5.79 (d, *J* = 12.9 Hz, 1H), 3.64 (d, *J* = 11.2 Hz, 1H), 3.15 (ddd, *J* = 13.2, 11.1, 3.8 Hz, 1H), 2.70 – 2.67 (m, 2H),

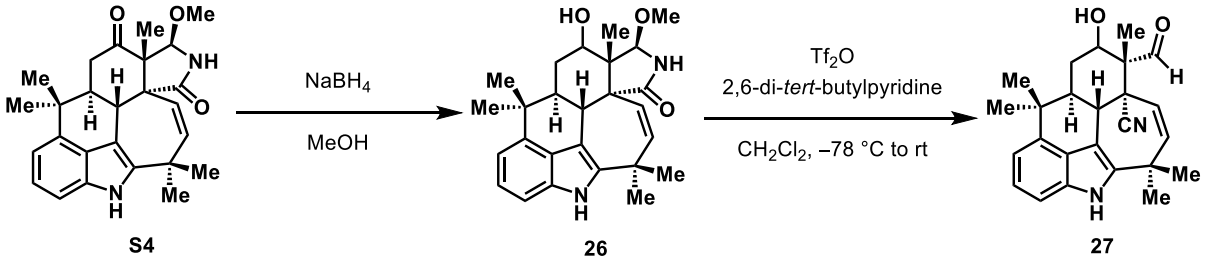
2.51-2.46 (m, 1H), 1.67 (s, 3H), 1.43 (s, 3H), 1.42 (s, 3H), 1.19 (d, J = 6.6 Hz, 3H), 1.18 (s, 3H), 1.03 (s, 3H). **^{13}C NMR** (151 MHz, 10% $(CD_3)_2CO$ in CD_3OD) δ 212.2, 175.6, 142.4, 141.0, 137.5, 135.4, 131.7, 127.3, 122.8, 112.5, 108.6, 107.4, 60.0, 52.9, 49.0, 46.9, 45.1, 42.4, 40.1, 38.3, 34.4, 30.0, 27.7, 24.4, 24.2, 10.1. **IR** (thin film) 3353, 2964, 2871, 2487, 1693, 1448, 1384, 1288, 1207, 746 cm^{-1}. $[\alpha]_D$ –26.7 (1.2 x10^{-3}, $CHCl_3$).



Hemiaminal ether S4: Mixture of **16** and **25** (330 mg, 0.87 mmol, 1.0 equiv) was dissolved in THF (8.7 mL) in a round-bottomed flask. To the solution was added NaHMDS (2.0 M in THF, 2.2 mL, 4.3 mmol, 5.0 equiv) at room temperature. After 10 min, methyl formate (2.6 mL, 43 mmol, 50 equiv) was added via syringe and the reaction mixture was allowed to stir for 10 min at room temperature. The reaction mixture was quenched with ammonium chloride (sat. aq.) (20 mL) and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine (50 mL) and dried over sodium sulfate. The crude mixture was concentrated in vacuo and purified using SiO_2 gel column chromatography eluting with 2:1 hexanes/ethyl acetate then 1:1 hexanes/ethyl acetate to give the product as white solid (196 mg, 4.69 mmol, 54%). **^{1}H NMR** (400 MHz, $(CD_3)_2CO$) δ 9.79 (s, 1H), 7.82 (s, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 7.2 Hz, 1H), 6.10 (d, J = 13.1 Hz, 1H), 5.60 (d, J = 13.1 Hz, 1H), 5.15 (s, 1H), 3.66 (d, J = 11.1 Hz, 1H), 3.38 (s, 3H), 2.88-2.76 (m, 4H), 2.59 (dd, J = 14.1, 3.0 Hz, 1H), 1.95 - 1.88 (m, 1H), 1.45 (s, 3H), 1.41 (s, 3H), 1.08 (s, 3H). **^{13}C NMR** (101 MHz, $(CD_3)_2CO$) δ 211.4, 175.3, 141.1, 139.4, 136.9, 134.9, 127.8, 127.4, 122.0, 112.3, 108.3, 105.8, 87.2, 60.6, 56.3, 55.4, 46.3, 40.1, 39.4, 38.3, 38.0, 32.8, 28.9, 25.3, 24.6, 15.1. **IR** (thin film) 3401, 3365, 2964, 2931, 1708, 1452, 1364, 1086, 1052, 735 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for $C_{26}H_{31}O_3N_2$ $[M+H]^+$: 419.2329. Found 419.2336. $[\alpha]_D$ –20.8 (c 2.6 x 10^{-3}, $CHCl_3$).



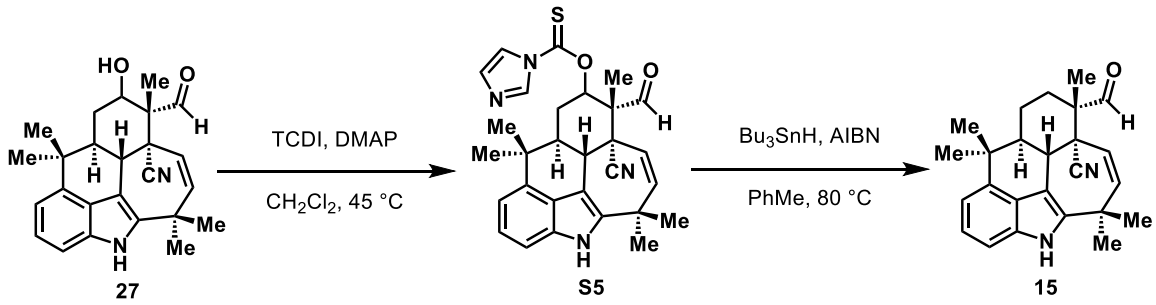
Scheme S1. Possible mechanism for the amide-directed C12 functionalization



Hydroxy hemiaminal ether 26: Hemiaminal ether **S4** (53.6 mg, 0.128 mmol, 1.0 equiv) was dissolved in MeOH (3 mL) in a round-bottomed flask and $NaBH_4$ (24.2 mg, 0.640 mmol, 5.0 equiv) was added all at once. After 1 h, the mixture was quenched with H_2O (10 mL) and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (10 mL) and dried over sodium sulfate. The crude mixture was concentrated in vacuo and isolated as an off-white solid. The crude product was taken forward to the next step without further purification.

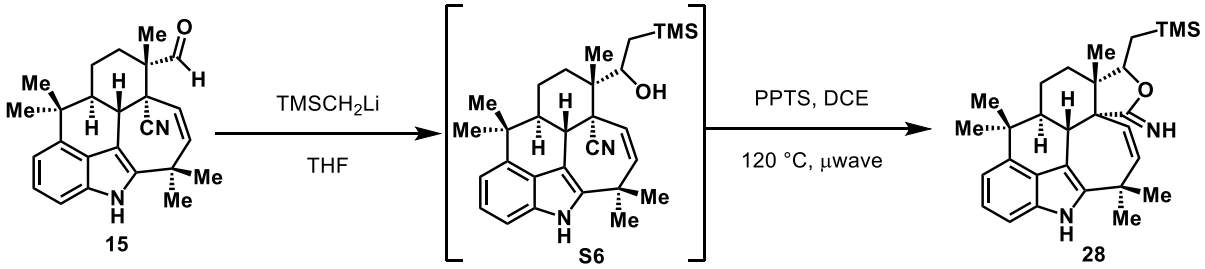
β-Hydroxy aldehyde 27: To the round-bottomed flask containing crude alcohol **26** was added DCM (13 mL). The starting material does not fully dissolve and results in an off-white suspension. To this mixture, di-*tert*-butylpyridine

(0.043 mL, 0.19 mmol, 1.5 equiv) was added via syringe and the reaction mixture was cooled to –78 °C. Tf_2O (0.11 mL, 0.64 mmol, 5.0 equiv) was added via syringe and the mixture was allowed to stir at –78 °C for 2.5 h at which time the reaction mixture was quenched with water (13 mL) at –78 °C. After stirring at –78 °C for 30 seconds, the flask was removed from the –78 °C bath and allowed to warm fully to room temperature. To the reaction mixture was added sodium bicarbonate (sat. aq.) (20 mL) and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine (300 mL) and dried over sodium sulfate. The crude mixture was concentrated in vacuo and purified using SiO_2 gel column chromatography on a Yamazen® automatic purification system. Pure aldehyde **27** was isolated as a white solid (26 mg, 0.066 mmol, 51% over 2 steps). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.81 (s, 1H), 7.15 (d, *J* = 5.5 Hz, 2H), 7.02 (dd, *J* = 5.6, 2.5 Hz, 1H), 5.75 (d, *J* = 12.3 Hz, 1H), 5.50 (d, *J* = 12.3 Hz, 1H), 4.59 (dd, *J* = 11.6, 4.5 Hz, 1H), 3.28 (d, *J* = 11.4 Hz, 1H), 2.21 (dt, *J* = 12.7, 4.1 Hz, 1H), 2.14 - 2.10 (m, 1H), 2.01 (bs, 1H), 1.68 (q, *J* = 12.5 Hz, 1H), 1.61 (s, 3H), 1.51 (s, 3H), 1.48 (s, 3H), 1.33 (s, 3H), 1.15 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 204.1, 144.0, 140.0 135.7, 133.6, 126.0, 122.9, 122.8, 119.8, 113.0, 107.9, 105.7, 69.1, 56.1, 46.1, 45.4, 38.7, 38.2, 37.5, 32.9, 29.3, 28.1, 24.9, 24.6, 8.5. **IR** (thin film) 3408, 2966, 2930, 2867, 1727, 1471, 1450, 1333, 1084, 753 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for C25H29O2N2 $[M+H]^+$: 389.2224. Found 389.2229. $[\alpha]_D$ –165 (c 3.8 x 10^{-3}, $CHCl_3$).

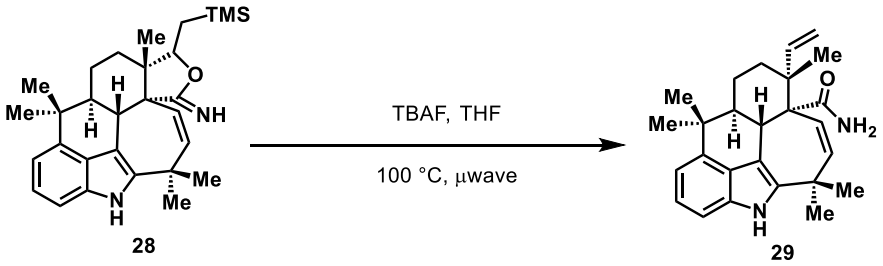


Thiocarbamate S5: Alcohol **27** (160 mg, 0.412 mmol, 1.0 equiv), DMAP (10 mg, 0.082 mmol, 0.2 equiv), in an oven-dried microwave vial were brought into a glovebox. TCDI (88 mg, 0.49 mmol, 1.0 equiv) and DCM (4 mL) were added and the vial was sealed. The reaction vessel was then removed from the glovebox and placed in an oil bath preheated to 45 °C and allowed to stir for 20 h. Once the vial had cooled to room temperature, the reaction mixture was concentrated in vacuo and immediately subjected to SiO_2 gel column chromatography on a Yamazen® automatic purification system. Pure thiocarbamate **S5** was isolated as a white solid (160 mg, 0.32 mmol, 79%, 91% brsm). **^{1}H NMR** 183 (700 MHz, $(CD_3)_2CO$) δ 10.14 (br s, 1H), 10.04 (s, 1H), 8.36 (s, 1H), 7.74 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.05 (s, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.48 (dd, *J* = 11.5, 4.6 Hz, 1H), 5.94 (d, *J* = 12.3 Hz, 1H), 5.58 (d, *J* = 12.3 Hz, 1H), 3.58 (d, *J* = 11.1 Hz, 1H), 2.76 - 2.73 (m, 1H), 2.19 (ddd, *J* = 13.9, 11.1, 3.1 Hz, 1H), 2.14 - 2.10 (m, 1H), 1.66 (s, 3H), 1.65 (s, 3H), 1.56 (s, 3H), 1.54 (s, 3H), 1.20 (s, 3H). **^{13}C NMR** (176 MHz, $(CD_3)_2CO$) δ 201.9, 184.3, 145.6, 140.1, 137.6, 137.3, 135.0, 131.9, 126.6, 123.1, 122.6, 119.9, 119.1, 113.1, 108.9, 105.2, 81.9, 56.3, 47.4, 47.1, 39.6, 39.2, 38.3, 32.5, 27.8, 25.6, 25.1, 24.8, 10.5. **IR** (thin film) 3370, 2966, 2934, 1789, 1731, 1470, 1388, 1330, 1286, 1229 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for $C_{29}H_{31}O_2N_4S$ $[M+H]^+$:499.2162. Found 499.2152. $[\alpha]_D$ –73 (c 3.75 x10^{-3}, $CHCl_3$).

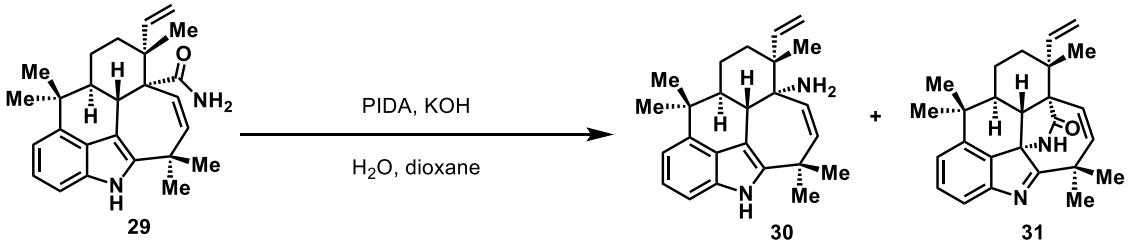
Deoxygenated aldehyde 15: Thiocarbamate **S4** (160 mg, 0.32 mmol, 1.0 equiv) and AIBN (21 mg, 0.13 mmol, 0.4 equiv) were added as solids to an oven-dried round-bottomed flask. A N_2 inlet was placed in the septum and the flask was evacuated and backfilled with N_2 three times. Toluene (9 mL) was added via syringe, followed by $SnBu_3H$ (0.13 mL, 0.49 mmol, 1.5 equiv) and the reaction vessel was placed in an oil bath preheated to 80 °C. After 30 min at this temperature, the reaction mixture was allowed to cool to room temperature and the contents were concentrated in vacuo. The crude reaction mixture was immediately subjected to SiO_2 gel column chromatography on a Yamazen® automatic purification system. Aldehyde **15** was isolated as a white solid (66 mg, 55%). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.83 (s, 1H), 7.16 - 7.13 (m, 2H), 7.01 (dd, *J* = 6.4, 1.7 Hz, 1H), 5.71 (d, *J* = 12.5 Hz, 1H), 5.38 (d, *J* = 12.3 Hz, 1H), 3.31 (d, *J* = 11.0 Hz, 1H), 2.25 - 2.21 (m, 1H), 2.08 - 2.01 (m, 2H), 1.71 - 1.65 (m, 1H), 1.63-1.60 (m, 4H), 1.50 (s, 3H), 1.47 (s, 3H), 1.34 (s, 3H), 1.14 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 204.0, 143.7, 140.4, 135.6, 133.6, 126.0, 124.1, 122.7, 120.3, 112.8, 107.7, 106.5, 51.5, 47.5, 45.5, 38.7, 38.5, 37.4, 32.8, 29.6, 28.2, 24.9, 24.6, 19.5, 14.2. **IR** (thin film): 3369, 2964, 2929, 2868, 2251, 1725, 1451, 1169, 908, 731 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for $C_{25}H_{29}ON_2$ $[M+H]^+$, 373.2274. Found 373.2278. $[\alpha]_D$ –141 (c 2.4 x10^{-3}, DCM).



Acetimidate 28: To a solution of **15** (11 mg, 0.031 mmol, 1.0 equiv) in THF (0.6 mL) was added $TMSCH_2Li$ (1.0 M solution in pentane, 0.31 mL, 0.31 mmol, 10 equiv). The solution was allowed to stir for 1 h at which time it was quenched with the addition of ammonium chloride (sat. aq.) (5 mL). The aqueous layer was extracted with ethyl acetate (3 x 5 mL) and the combined organic layers were washed with brine (5 mL), dried over sodium sulfate, and concentrated in vacuo to give a yellow foam likely consisting of **S6**. The crude mixture was transferred to a microwave vial as a solution in DCE (1 mL). PPTS (39 mg, 0.16 mmol, 5.0 equiv) was added and the vial was sealed. The vial was heated to 120 °C in the microwave for 30 min. Once the vial had cooled to room temperature, the solution was poured into H_2O (5 mL) and the aqueous layer was extracted with DCM (3 x10 mL). The combined organic layers were washed with brine (5 mL), dried over sodium sulfate, and concentrated in vacuo to yield the crude mixture of **28** as a yellow oil. The crude product was directly subjected to the next reaction without further purification.

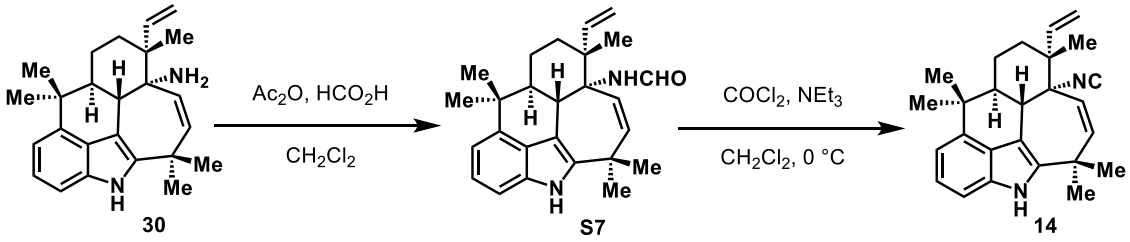


Amide 29: To a crude reaction mixture containing **28** in a microwave vial was added TBAF (1 M THF, 0.3 mL, 0.31 mmol, 10 equiv) and the vial was sealed. The resulting yellowish-brown solution was then heated to 100 °C in the microwave for 1 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate (5 mL) and washed with H_2O (5 mL). The aqueous layer was extracted with ethyl acetate (3 x 5 mL) and the combined organic layers were washed with brine (5 mL), dried over sodium sulfate and concentrated in vacuo to yield the crude reaction product. The crude product was purified using SiO_2 gel column chromatography on a Yamazen® automatic purification system. Amide **29** was isolated as a glassy, off-white solid (6.3 mg, 0.016 mmol, 52% over 3 steps). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.11 – 7.02 (m, 2H), 6.96 (d, *J* = 7.1 Hz, 1H), 6.16 (s, 1H), 5.98 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.84 (d, *J* = 13.1 Hz, 1H), 5.57 (d, *J* = 13.1 Hz, 1H), 5.27 (s, 1H), 5.17 (d, *J* = 17.4 Hz, 1H), 5.11 (d, *J* = 10.9 Hz, 1H), 3.36 (d, *J* = 11.3 Hz, 1H), 3.13 (ddd, *J* = 12.1, 3.6 Hz, 1H), 2.53 (ddd, *J* = 13.5, 4.4 Hz, 1H), 1.94 (dd, *J* = 13.1, 3.7 Hz, 1H), 1.62 (ddd, *J* = 13.4, 9.4 Hz, 1H), 1.48 (s, 3H), 1.47 (s, 3H), 1.38 – 1.34 (m, 1H), 1.31 (s, 6H), 1.01 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 175.2, 146.2, 141.9, 140.2, 134.9, 133.8, 131.3, 126.7, 122.2, 1133, 112.2, 109.2, 107.2, 56.4, 43.5, 43.2, 38.9, 38.8, 37.3, 34.6, 33.8, 27.8, 24.3, 21.2, 19.3. **IR** (thin film) 3361, 3310, 3185, 2992, 1589, 1561, 1463, 1435 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for $C_{26}H_{32}ON_2Na$ $[M+Na]^+$: 411.2407. Found 411.2409. $[\alpha]_D$ –196 (c 17.6 x10^{-3}, DCM).



Vinyl amine 30 and Hofmann side product 31: Amide **29** (79 mg, 0.21 mmol, 1.0 equiv) was dissolved in 1,4-dioxane (4.1 mL) and H_2O (4.1 mL) was added. To this solution was added crushed KOH (402 mg, 7.18 mmol, 35 equiv) and the suspension was allowed to stir for 5 min at room temperature. At this time, PIDA (79 mg, 0.25 mmol, 1.2 equiv) was added and the solution turned light yellow. The suspension was allowed to stir at room temperature for 20 h at which time it was quenched with sodium bicarbonate (sat. aq.) (5 mL) and sodium thiosulfate (sat. aq.) (5 mL). After stirring for 5 min at room temperature, the mixture was diluted with ethyl acetate (10 mL) and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over sodium sulfate, and concentrated in vacuo to yield the crude reaction product. The crude product

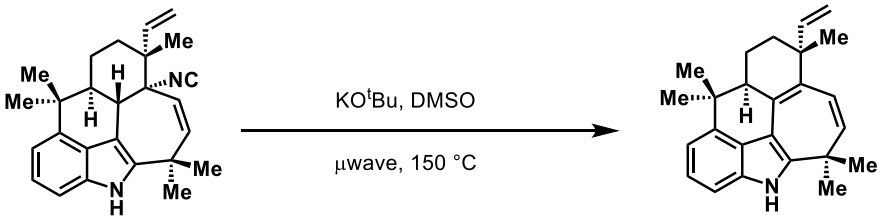
was purified using SiO_2 gel preparatory thin-layer chromatography eluting with a mixture of 10% acetone and 1% NH_4OH in DCM to yield the desired product (**30**, 29.0 mg, 0.0804 mmol, 39%) as well as Hofmann side product **31** (9.1 mg, 0.028 mmol, 14%). **Amine product (30): ^{1}H NMR** (700 MHz, CD_3OD) δ 7.06 (d, *J* = 7.9 Hz, 1H), 6.99 (dd, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.20 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.93 (d, *J* = 13.1 Hz, 1H), 5.42 (d, *J* = 13.0 Hz, 1H), 5.19 - 5.15 (m, 2H), 3.41 (d, *J* = 11.4 Hz, 1H), 2.10 - 2.05 (m, 1H), 1.93 - 1.87 (m, 2H), 1.71 - 1.65 (m, 1H), 1.51 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H), 1.38 - 1.35 (m, 1H), 1.29 (s, 3H), 1.06 (s, 3H). **^{13}C NMR** (176 MHz, CD_3OD) δ 146.5, 142.0, 139.5, 137.0, 135.8, 134.8, 127.8, 122.8, 186 114.2, 112.4, 108.3, 107.1, 59.6, 46.3, 44.3, 41.1, 39.5, 38.0, 34.1, 32.9, 30.1, 25.1, 25.0, 22.3, 20.2. **IR** (thin film) 3500, 2963, 2926, 2854, 1467, 1449, 914, 744 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for $C_{25}H_{33}N_2$ $[M+H]^+$: 361.2638. Found 361.2643. $[\alpha]_D$ –73.5 (MeOH). **Hofmann side product (31):** In a 4 mL vial, compound **31** (9 mg) was dissolved in a minimal amount of DCM (~0.5 mL). A layer of hexanes (~0.2 mL) was carefully added on top of the DCM solution. The mixture was lightly capped and allowed to crystallize in a freezer with minimal agitation. mp 118-122°C. See X-ray crystal structure data below. **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.7 Hz, 1H), 7.27 (m, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.07 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.62 (d, *J* = 13.3 Hz, 1H), 5.45 (d, *J* = 13.3 Hz, 1H), 5.21 (d, *J* = 11.0 Hz, 1H), 5.17 – 5.14 (m, 2H), 2.35 (dd, *J* = 11.0, 1.6 Hz, 1H), 2.26 (ddd, *J* = 13.8, 10.9, 3.1 Hz, 1H), 1.91 (td, *J* = 13.4, 3.7 Hz, 1H), 1.84 (dq, *J* = 13.4, 3.4 Hz, 1H), 1.56 (m, 1H), 1.54 (s, 3H), 1.50 (dd, *J* = 13.1, 3.2 Hz, 1H), 1.47 (s, 3H) 1.46 (s, 3H), 1.13 (s, 3H), 0.94 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 192.9, 178.0, 155.5, 146.9, 144.6, 138.4, 131.5, 130.8, 128.1, 122.9, 117.3, 113.4, 70.0, 55.8, 47.6, 43.3, 42.6, 41.5, 38.1, 37.2, 31.7, 31.5, 27.3, 26.3, 20.3, 20.2. **IR** (thin film) 3223, 2966, 2927, 2854, 1697. **HRMS** (ESI) *m/z* calc'd for $C_{26}H_{31}ON_2$ $[M+H]^+$: 387.2431. Found 387.2437. $[\alpha]_D$ –216 (c 1.8 x10^{-3}, DCM).



Formamide S7: To amine **30** (12 mg, 1.0 equiv) in a round-bottomed flask was added DCM (1 mL) followed by Ac_2O (56 µL, 0.59 mmol, 18 equiv) and formic acid (25 µL, 0.66 mmol, 20 equiv). This solution was allowed to stir at room temperature for 14 h. The solution was quenched with sodium bicarbonate (10 mL) and diluted with DCM (10 mL). The aqueous layer was extracted with DCM (3 x 10 mL) and the combined organic layers were washed with brine (10 mL), dried over sodium sulfate, then concentrated in vacuo. The crude product was purified using SiO_2 gel preparatory thin-layer chromatography eluting with a mixture of 2:1 hexanes/ethyl acetate to give the desired product (**S7**) as a white solid (13 mg, 0.033 mmol, 99%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 11.1 Hz, 1H), 7.95 (s, 1H), 7.18 - 7.04 (m, 2H), 6.97 (dd, *J* = 5.7, 2.6 Hz, 1H), 5.96 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.89 (d, *J* = 12.9 Hz, 1H), 5.82 (d, *J* = 11.7 Hz, 1H), 5.60 (d, *J* = 12.6 Hz, 1H), 5.27 (d, *J* = 10.8 Hz, 1H), 5.23 (d, *J* = 17.5 Hz,

1H), 3.49 (d, *J* = 10.1 Hz, 1H), 1.92 - 1.88 (m, 1H), 1.81 - 1.77 (m, 1H), 1.72 - 1.64 (m, 2H), 1.50 - 1.47 (m, 1H), 1.47 (s, 3H) 1.40 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H), 1.11 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 166.5, 143.7, 141.5, 140.5, 135.8, 133.6, 129.0, 126.5, 122.3, 116.1, 112.4, 107.6, 106.0, 60.9, 45.5, 44.2, 39.6, 38.2, 37.5, 33.2, 33.0, 28.0, 24.6, 24.5, 20.6, 19.8. **IR** (thin film) 3297, 2965, 2926, 2868, 1669, 1453, 1337, 761, 739 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for $C_{26}H_{32}ON_2Na$ $[M+Na]^+$: 411.2407. Found 411.2399. $[\alpha]_D$ –121 (c 3.5 x10^{-3}, $CHCl_3$)

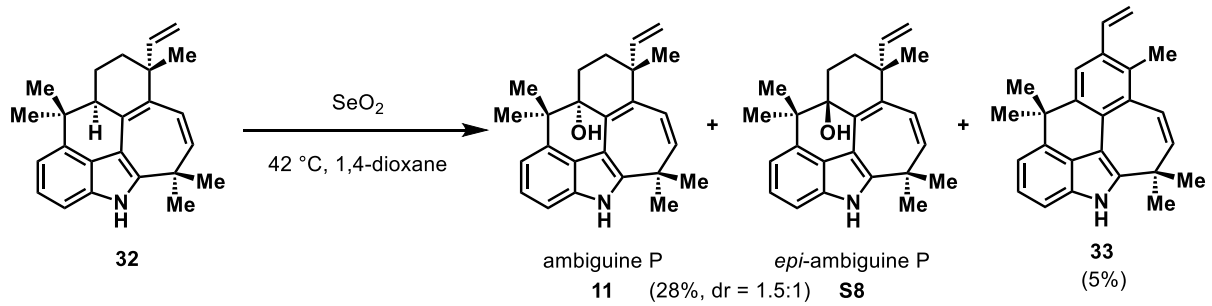
Isonitrile (14): Crude formamide **S5** (6.8 mg, 0.018 mmol, 1.0 equiv) was dissolved in DCM (1 mL) and the reaction mixture was cooled to 0 °C. NEt_3 (49 µL, 0.035 mmol, 20 equiv) was added followed by phosgene (20% in toluene, 46 µL, 0.088 mmol, 5.0 equiv). After stirring for 10 min at 0 °C, the reaction mixture was quenched with sodium bicarbonate (5 mL) and diluted with DCM (5 mL). The aqueous layer was extracted with DCM (3 x 10 mL) and the combined organic layers were washed with brine (10 mL), dried over sodium sulfate, and concentrated in vacuo. The crude product was purified using SiO_2 gel preparatory thin-layer chromatography eluting with a mixture of 2:1 hexanes/ethyl acetate to yield the desired product (**14**) as an off-white solid (6.3 mg, 0.017 mmol, 97%). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.12 (d, *J* = 4.0 Hz, 1H), 7.00 - 6.98 (m, 1H), 6.23 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.67 (d, *J* = 12.6 Hz, 1H), 5.61 (d, *J* = 12.6 Hz, 1H), 5.28 (d, *J* = 10.9 Hz, 1H), 5.24 (d, *J* = 17.5 Hz, 1H), 3.37 (dt, *J* = 11.1, 3.3 Hz, 1H), 2.08 - 2.03 (m, 1H), 2.02 - 1.98 (m, 1H), 1.91 - 1.89 (m, 1H), 1.68 - 1.62 (m, 1H), 1.59 (s, 3H), 1.47 (s, 3H), 1.46 (s, 3H), 1.29 (s, 3H), 1.24 - 1.20 (m, 1H), 1.14 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 156.2, 143.8, 142.4, 140.9, 135.2, 133.6, 127.0, 126.6, 122.3, 115.2, 112.5, 107.5, 106.6, 67.6, 45.8, 43.2, 39.4, 38.3, 37.3, 33.7, 32.9, 27.9, 25.1, 24.6, 20.6, 17.7. **IR** (thin film) 3344, 2923, 2854, 2124, 1719, 1636, 1454, 730 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for $C_{25}H_{30}N_2$ $[M–HNC+H]^+$: 344.2373. Found 344.2372. $[\alpha]_D$ –181 (c 3.5 x10^{-3}, DCM).



14 32

Deoxy-ambiguine P (32): Isonitrile **14** (3.5 mg, 0.0094 mmol, 1.0 equiv) and KO^{t}Bu (11 mg, 0.094 mmol) were placed in a 1 mL microwave vial with DMSO (0.5 mL), and subjected to microwave irradiation at 150 °C. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate (5 mL) and washed with H_2O (3 x 5 mL). The aqueous layer was extracted with ethyl acetate (2 x 5 mL) and the combined organic layers were washed with brine (5 mL), dried over sodium sulfate and concentrated in vacuo. The crude product was purified using SiO_2 gel preparatory thin-layer chromatography eluting with a mixture of 2:1 hexanes/ethyl acetate to yield the pure product as an off-white solid (2.5 mg, 0.0073 mmol, 77%). **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.16 - 7.13 (m, 2H), 7.03 (dd, *J* = 5.3, 2.6 Hz, 1H), 5.93 (dd, *J* = 11.4, 1.0 Hz, 1H), 5.86 (dd, *J* = 17.5, 10.6 Hz, 1H), 5.34 (dd, *J* = 11.4, 1.0 Hz, 1H), 5.09 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.03 (dd, *J* = 10.6, 1.4 Hz, 1H), 2.89 (dd, *J* = 11.2, 7.0 Hz, 1H),

2.00 - 1.96 (m, 1H), 1.95 - 1.89 (m, 1H), 1.73 - 1.69 (m, 1H), 1.66 - 1.63 (m, 1H), 1.65 (s, 3H) 1.54 (s, 3H), 1.41 (s, 3H), 1.04 (s, 3H), 1.00 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 149.2, 140.8, 138.1, 134.8, 132.9, 130.1, 129.4, 128.2, 125.5, 122.7, 113.4, 110.9, 110.3, 108.1, 46.7, 40.3, 39.6, 36.8, 35.3, 26.9, 25.7, 25.0, 23.7, 23.6, 19.8. **IR** (thin film): 3419, 3003, 2923, 2330, 1570, 1470, 909, 748 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for $C_{25}H_{30}N_2$ $[M+H]^+$: 344.2373. Found 344.2372. $[\alpha]_D$ –15.5 (c 2.0 x 10^{-3} DCM).



Ambiguine P (11): Deoxy ambiguine P **32** (0.013 mmol, 4.4 mg, 1.0 equiv) was dissolved in 1,4-dioxane (0.05 M, 0.26 mL) and SeO_2 (0.026 mmol, 2.8 mg, 2.0 equiv) was added. The 4-mL vial was placed in a pre-heated aluminum heating block at 42 °C and allowed to stir at this temperature for 10 h. The vial was removed from the aluminum heating block and allowed to cool to room temperature. The crude mixture was quenched with saturated sodium thiosulfate solution, and the aqueous layer was extracted with ethyl acetate (3 x 2 mL). The combined organic layers were washed with brine (2 mL), dried over sodium sulfate then concentrated in vacuo. The crude product was purified using Al_3O_2 preparatory thin-layer chromatography eluting multiple times with 2:1 hexanes/DCM until separation of the diastereomers was observed. Isolation of the bands gave ambiguine P (**11**) (0.8 mg, 0.002 mmol, 17%) and epi-ambiguine P (**S7**, 0.5 mg, 0.001 mmol, 11%) as white solids. Over-oxidation side product **33** (0.2 mg, 5 x 10^{-4} mmol, 5%) and starting material (**32**) (0.5 mg, 0.001, 11%) were also isolated from this mixture. **Ambiguine P (11): ^{1}H NMR** (900 MHz, CD_3OD) δ 7.16 (d, *J* = 7.9 Hz, 1H), 7.07 (dd, *J* = 8.0, 7.1 Hz, 1H), 6.95 (d, *J* = 7.1 Hz, 1H), 5.93 (d, *J* = 11.4 Hz, 1H), 5.89 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.40 (d, *J* = 11.4 Hz, 1H), 5.11 (dd, *J* = 10.6, 1.8 Hz, 1H), 4.93 (dd, *J* = 17.4, 1.8 Hz, 1H), 2.17 – 2.13 (m, 1H), 1.96 (ddd, *J* = 14.3, 13.2, 2.7 Hz, 1H), 1.79 (ddd, *J* = 13.4, 4.0, 2.7 Hz, 1H), 1.68 (s, 3H), 1.60 (dt, *J* = 13.2, 3.5 Hz, 1H), 1.53 (s, 3H), 1.23 (s, 3H), 1.02 (s, 3H), 1.00 (s, 3H). **^{13}C NMR** (226 MHz, CD_3OD) δ 146.9, 142.1, 139.2, 134.9, 133.9, 133.5, 133.2, 128.6, 125.6, 123.5, 114.8, 114.6, 109.6, 108.8, 77.2, 45.9, 42.5, 36.7, 34.0, 29.2, 28.9, 27.5, 27.1, 26.4, 18.6. **IR** (thin film): 3331, 2966, 2349, 1458, 1318, 1032, 916, 751 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for $C_{25}H_{30}ON$ $[M+H]^+$: 360.2322. Found 360.2319. $[\alpha]_D$ –48 (c 4.5 x 10^{-4}, MeOH) All spectroscopic data matches that for the natural product (**11**) as reported by Orjala et. al.[2] ***epi*-ambiguine P (S8): ^{1}H NMR** (900 MHz, CD_3OD) δ 7.16 (d, *J* = 7.9 Hz, 1H), 7.07 (dd, *J* = 8.0, 7.2 Hz, 1H), 6.96 (d, *J* = 7.1 Hz, 1H), 5.89 (d, *J* = 11.4 Hz, 1H), 5.87 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.34 (d, *J* = 11.4 Hz, 1H), 5.11 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.00 (dd, *J* = 10.7, 1.4 Hz, 1H), 2.31 (td, *J* = 14.2, 3.3 Hz, 1H), 2.05 (td, *J* = 13.9, 3.2 Hz, 1H), 1.91 (dt, *J* = 13.7, 3.4 Hz, 1H), 1.66 (s, 3H), 1.56 (s, 3H), 1.49 (dt, *J* = 13.2, 3.4 Hz, 1H), 1.39 (s, 3H), 1.04 (s, 3H), 1.02 (s, 3H). **^{13}C NMR** (226 MHz, CD_3OD) δ 150.0, 141.9, 139.0, 135.3, 135.0, 133.0, 131.9, 128.6, 125.6,

123.5, 114.9, 111.4, 109.6, 108.7, 77.0, 45.7, 41.5, 36.7, 34.1, 29.0, 27.6, 27.4, 26.5, 23.0, 18.5. IR (thin film) 3206, 2966, 2359, 1576, 1485, 902, 693 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for $C_{25}H_{30}ON$ $[M+H]^+$: 360.2322. Found 360.2318. $[\alpha]_D$ +6.7 (c 3.0 x 10^{-4}, MeOH). **Aromatized product (33): ^{1}H NMR** (900 MHz, CD_3OD) δ 7.61 (s, 1H), 7.15 – 7.10 (m, 3H), 7.02 (d, *J* = 6.9 Hz, 1H), 6.64 (d, *J* = 12.5 Hz, 1H), 5.65 (d, *J* = 12.5 Hz, 1H), 5.59 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.27 (dd, *J* = 10.9, 1.5 Hz, 1H), 2.37 (s, 3H), 1.66 (s, 6H), 1.48 (s, 6H). **^{13}C NMR** (226 MHz, CD_3OD) δ 143.4, 140.5, 139.0, 137.7, 136.4, 135.1, 134.8, 132.9, 131.5, 130.0, 126.8, 126.3, 125.7, 124.1, 115.3, 114.6, 108.4, 107.7, 40.6, 38.2, 35.1, 30.5, 16.1. **IR** (thin film) 3432, 2963, 2923, 2858, 2349, 1570, 1457, 1125, 905, 752 cm^{-1}. **HRMS** (ESI) *m/z* calc'd for $C_{25}H_{26}N$ $[M+H]^+$: 340.2060. Found 340.2058.

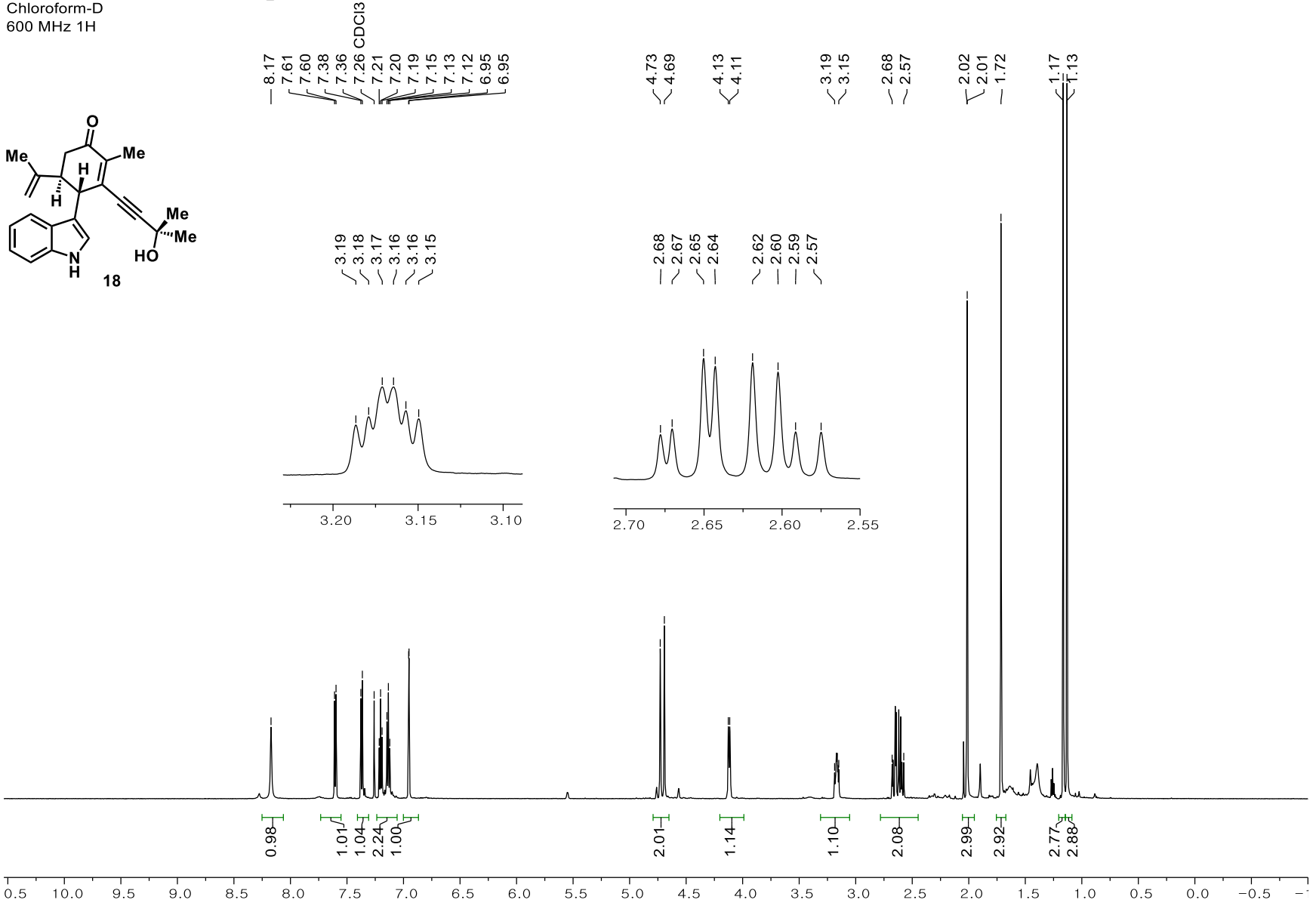
3. References

1. Baran, P.S.; Richter, J.M. Direct Coupling of Indoles with Carbonyl Compounds: Short, Enantioselective, Gram-Scale Synthetic Entry into the Hapalindole and Fischerindole Alkaloid Families *J. Am. Chem. Soc.* **2004**, *126*, 7450.

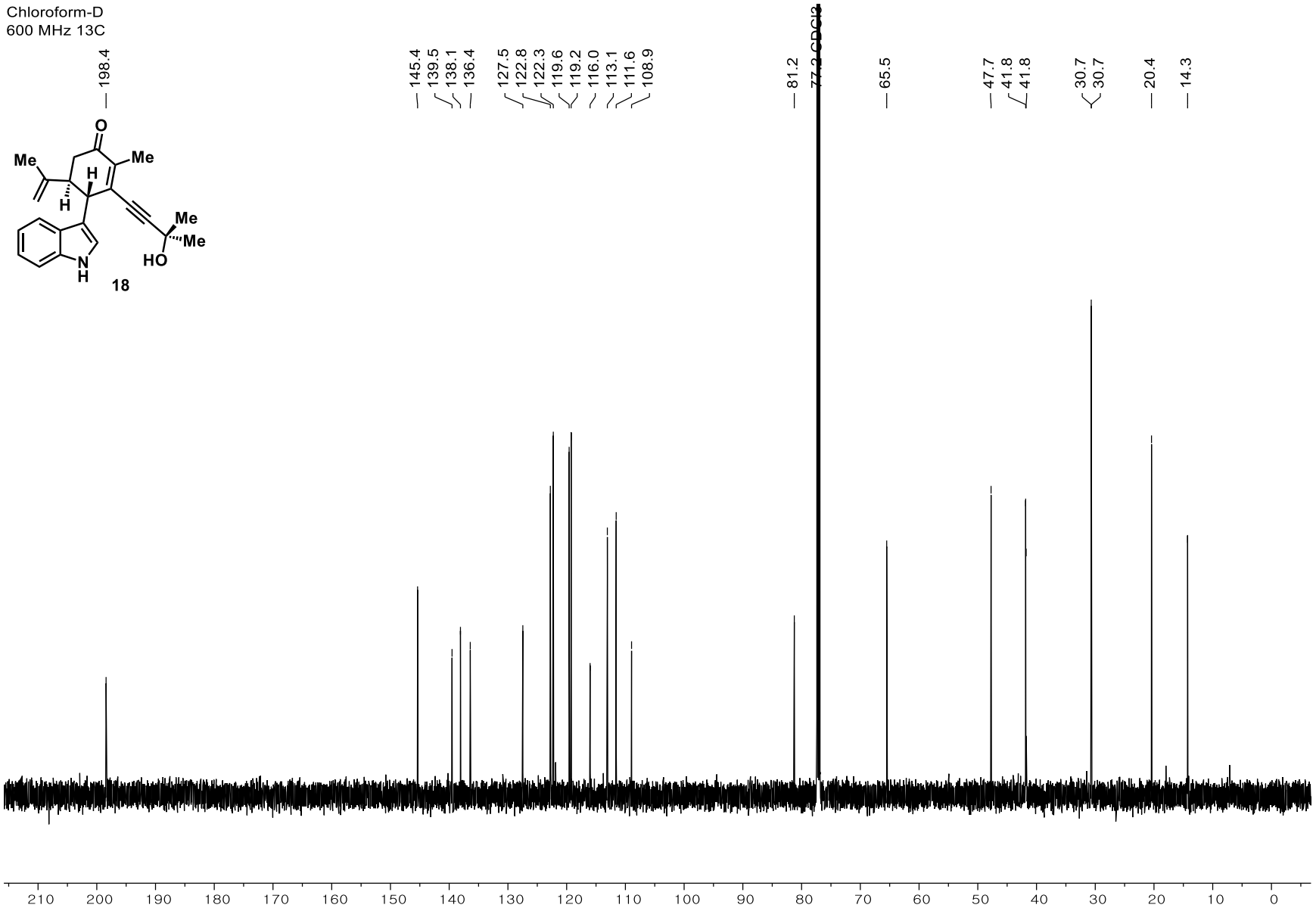
2. Mo, S.; Krunic, A.; Chlipala, G.; Orjala, J. Antimicrobial ambiguine isonitriles from the cyanobacterium *Fischerella ambigua. J. Nat. Prod.* **2009**, *72*, 894.

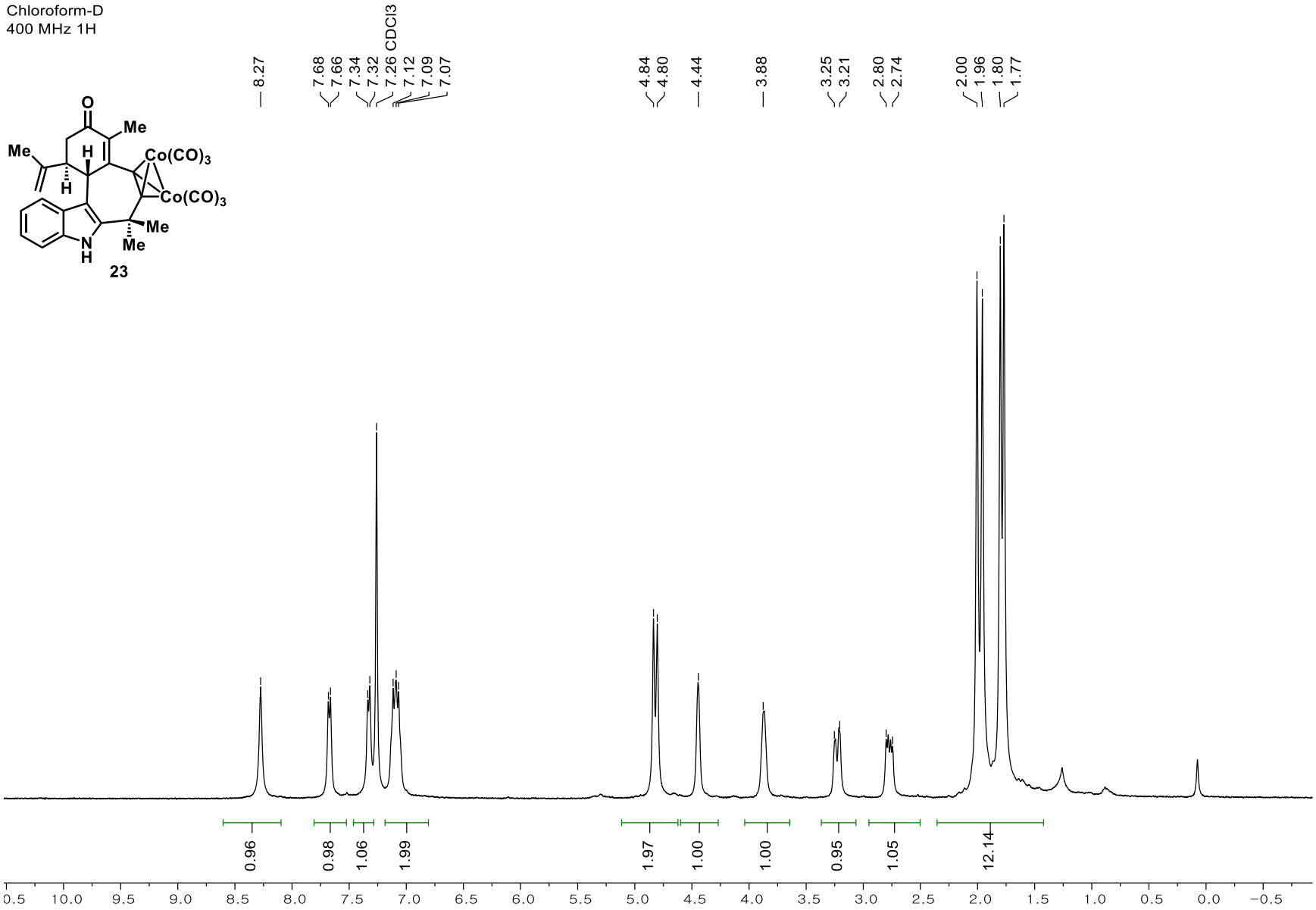
4. ^{1}H and ^{13}C NMR Spectra

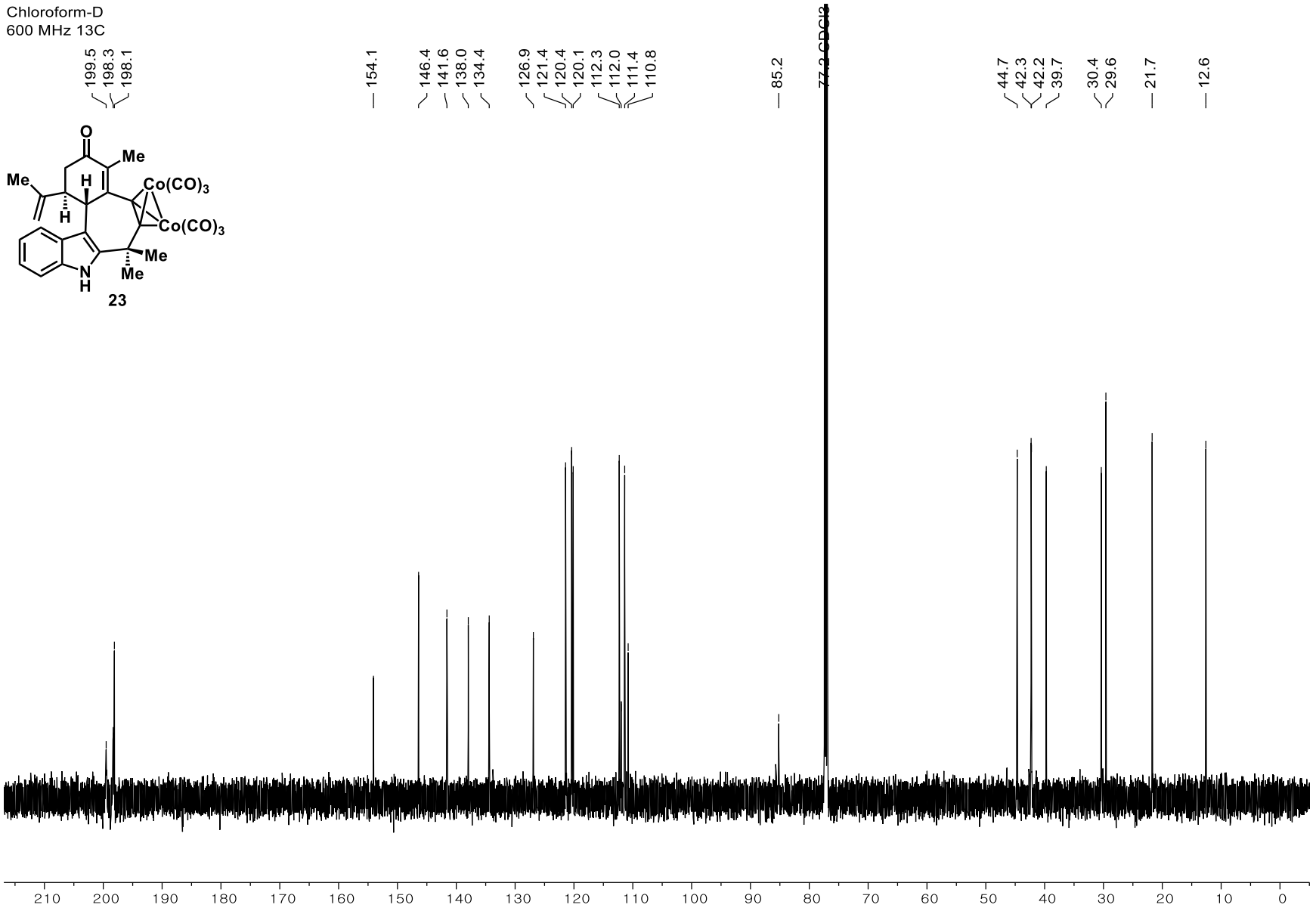
Chloroform-D
600 MHz 1H



18


Chloroform-D
600 MHz 13C
198.4
145.4
139.5
138.1
136.4
127.5
122.8
122.3
119.6
119.2
116.0
113.1
111.6
108.9
81.2
77.2 CDCl3
65.5
47.7
41.8
41.8
30.7
30.7
20.4
14.3
O
Me
Me
H
H
Me
Me
HO
N
H
18
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Chloroform-D
400 MHz 1H
8.27
7.68
7.66
7.34
7.32
7.26 CDCl3
7.12
7.09
7.07
4.84
4.80
4.44
3.88
3.25
3.21
2.80
2.74
2.00
1.96
1.80
1.77
O
Me
Me
H
Co(CO)3
H
Co(CO)3
Me
Me
N
H
23
0.96
0.98
1.06
1.99
1.97
1.00
1.00
0.95
1.05
12.14
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


Chloroform-D
600 MHz 13C
199.5
198.3
198.1
154.1
146.4
141.6
138.0
134.4
126.9
121.4
120.4
120.1
112.3
112.0
111.4
110.8
85.2
77.2 CDCl3
44.7
42.3
42.2
39.7
30.4
29.6
21.7
12.6
O
Me
Me
H
Co(CO)3
H
Co(CO)3
Me
N
H
Me
23
210
200
190
180
170
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150
140
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90
80
70
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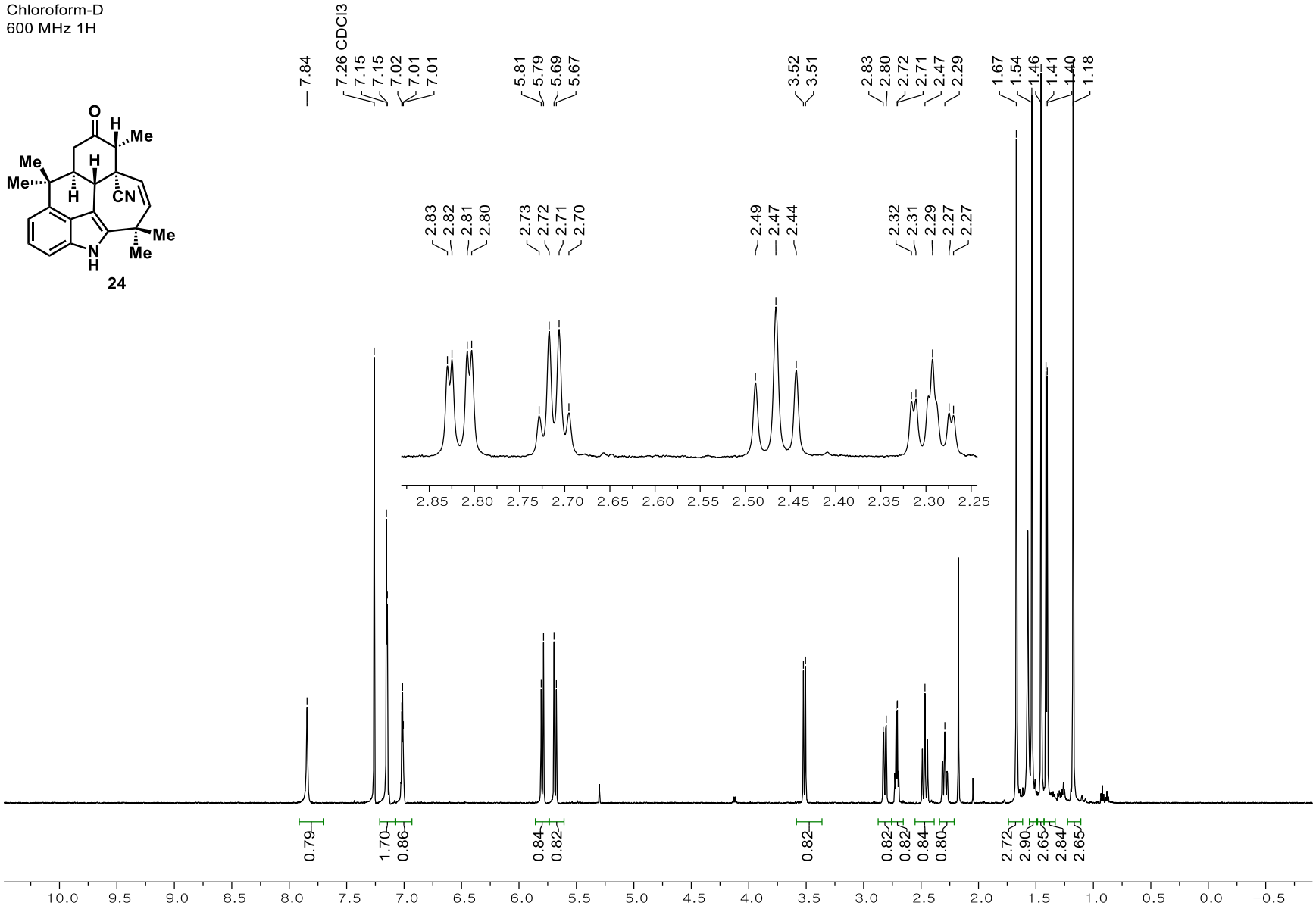
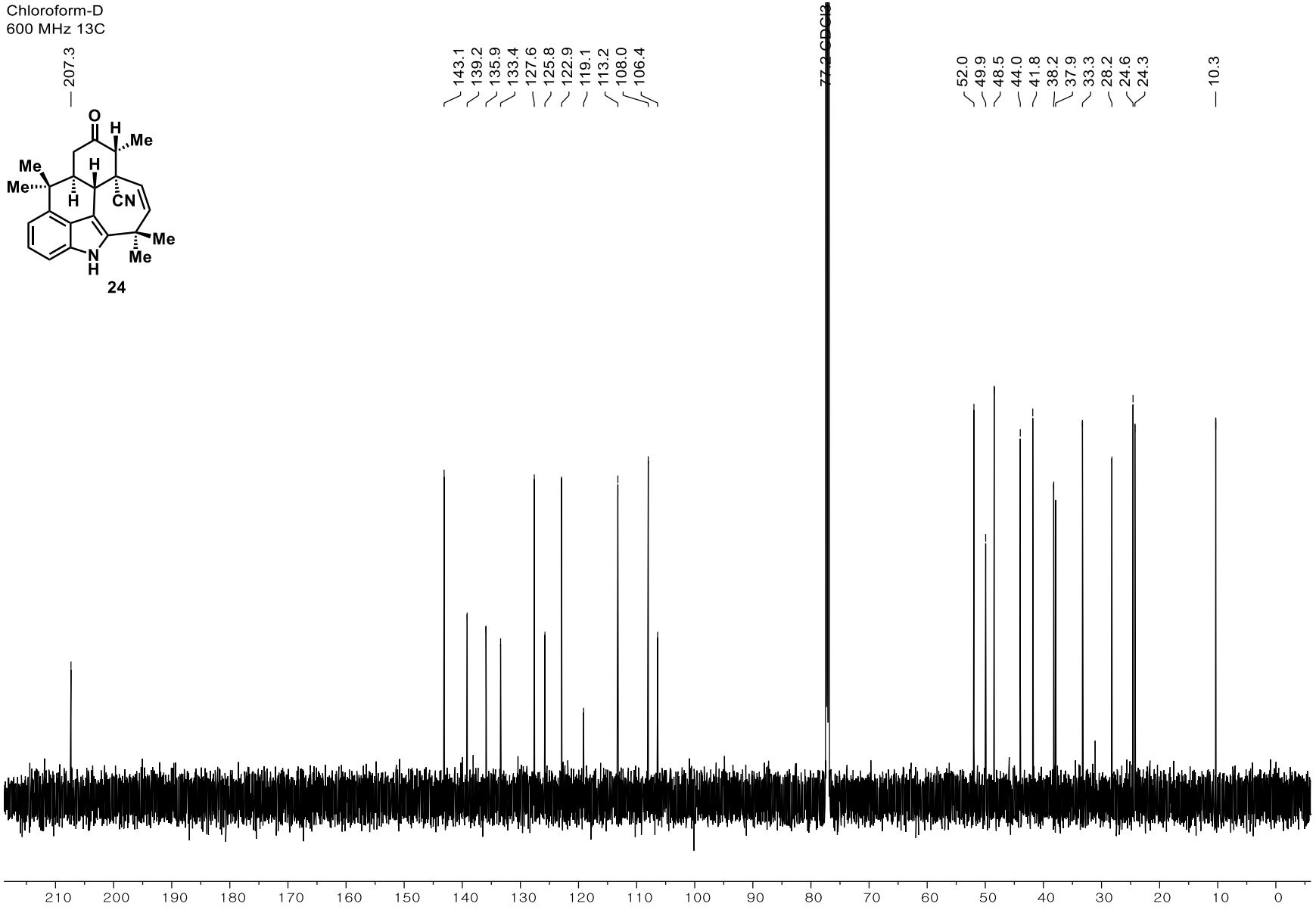
50
40
30
20
10
0


Chloroform-D
600 MHz 1H
24


Chloroform-D
600 MHz 13C
207.3
143.1
139.2
135.9
133.4
127.6
125.8
122.9
119.1
113.2
108.0
106.4
77.2 CDCl3
52.0
49.9
48.5
44.0
41.8
38.2
37.9
33.3
28.2
24.6
24.3
10.3
O
H
Me
Me
Me
H
H
CN
Me
Me
N
H
24
210
200
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10
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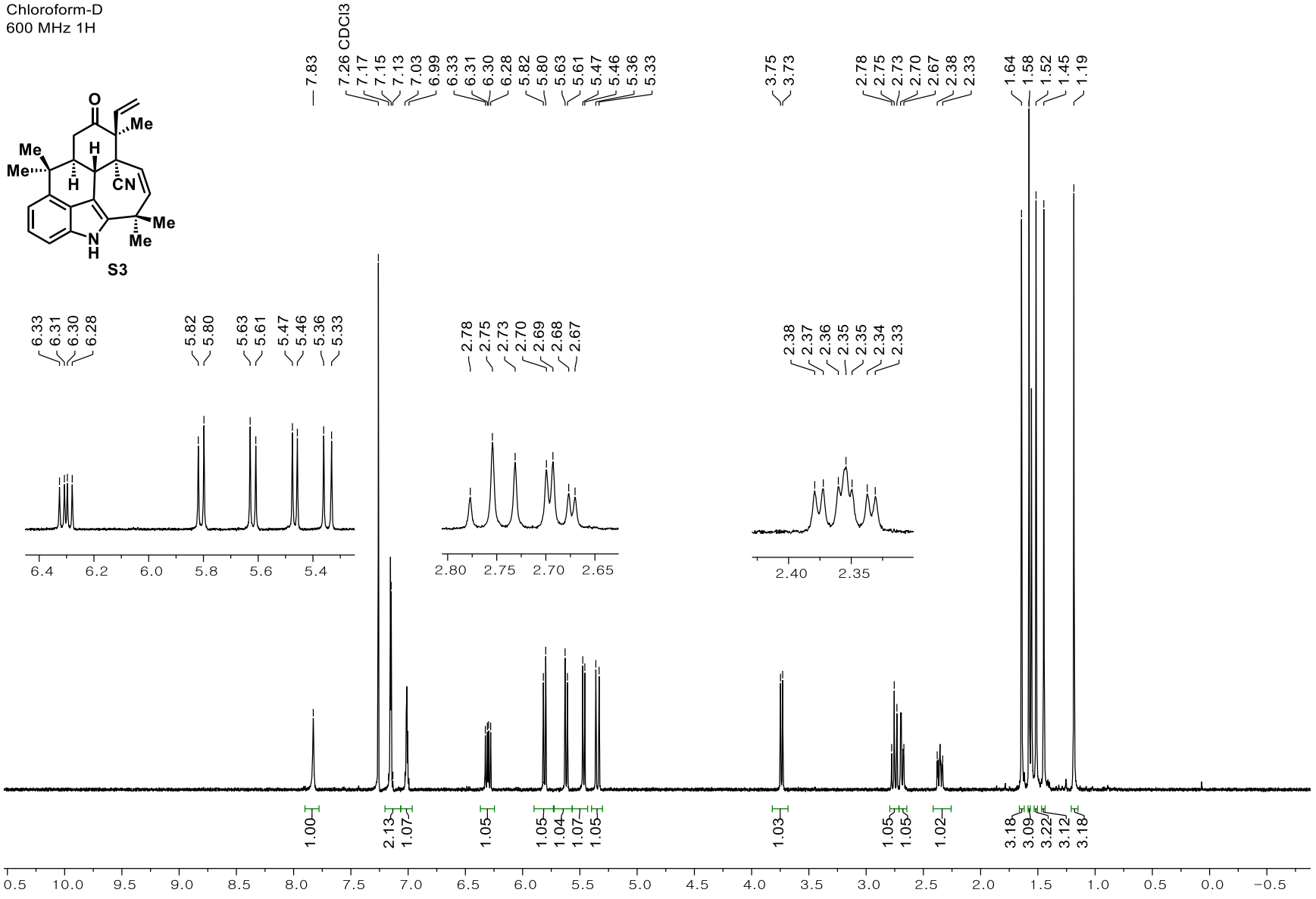
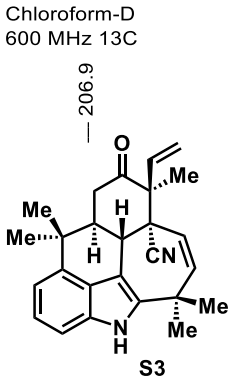

Chloroform-D
600 MHz 1H
S3

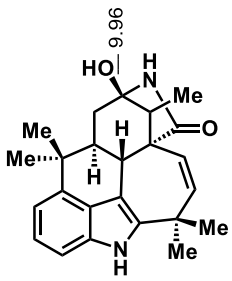
Chloroform-D
600 MHz 13C



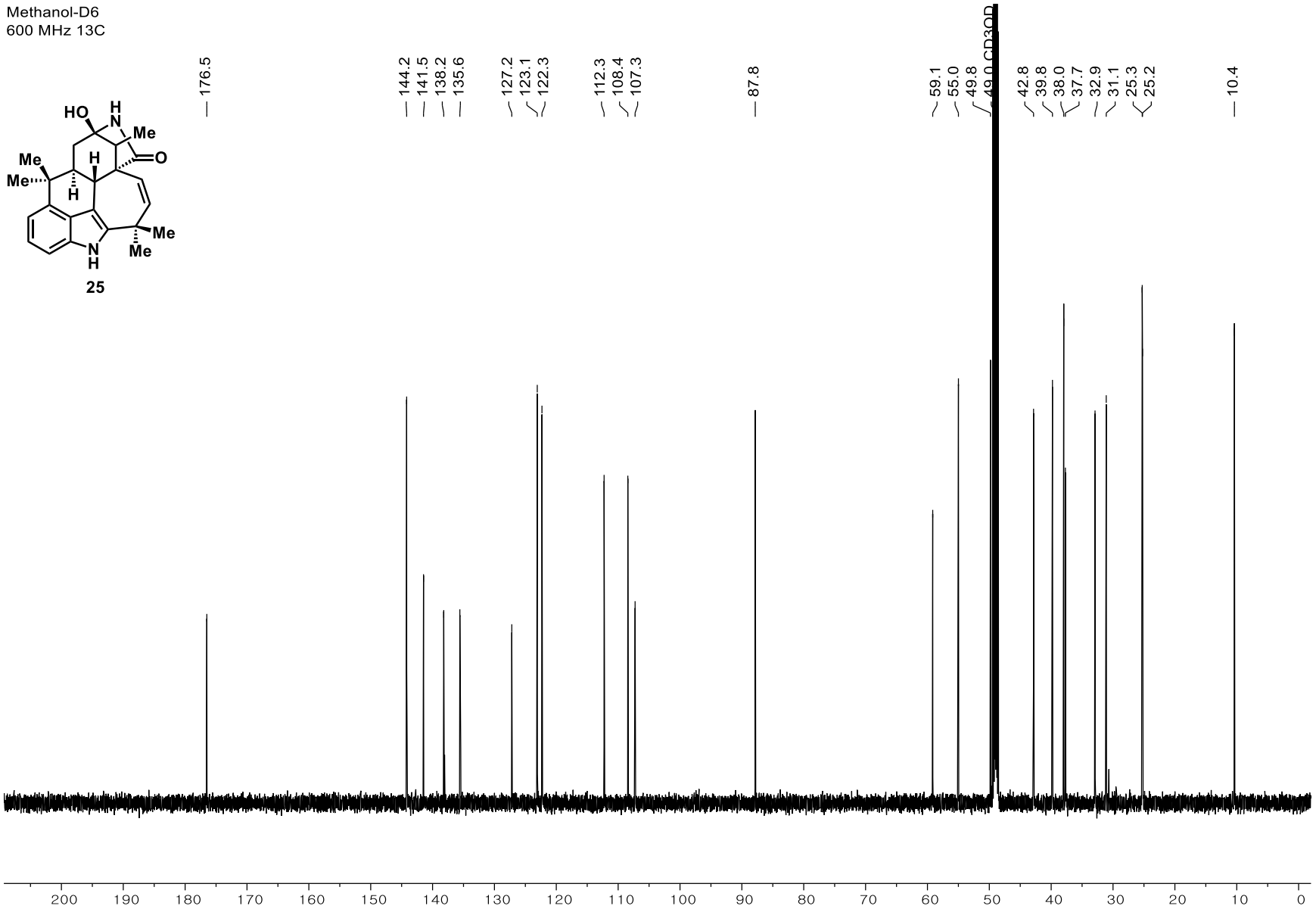
S3

206.9
143.7
139.3
136.2
136.0
133.5
126.0
124.2
122.9
120.6
119.7
113.1
108.0
106.3
77.2 CDCl3
57.9
51.8
48.1
39.9
38.6
38.4
37.9
33.1
28.1
24.6
24.3
18.5

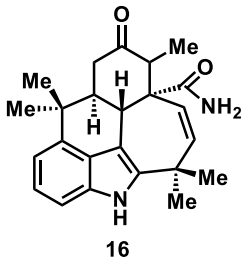
Methanol-D6
600 MHz 1H



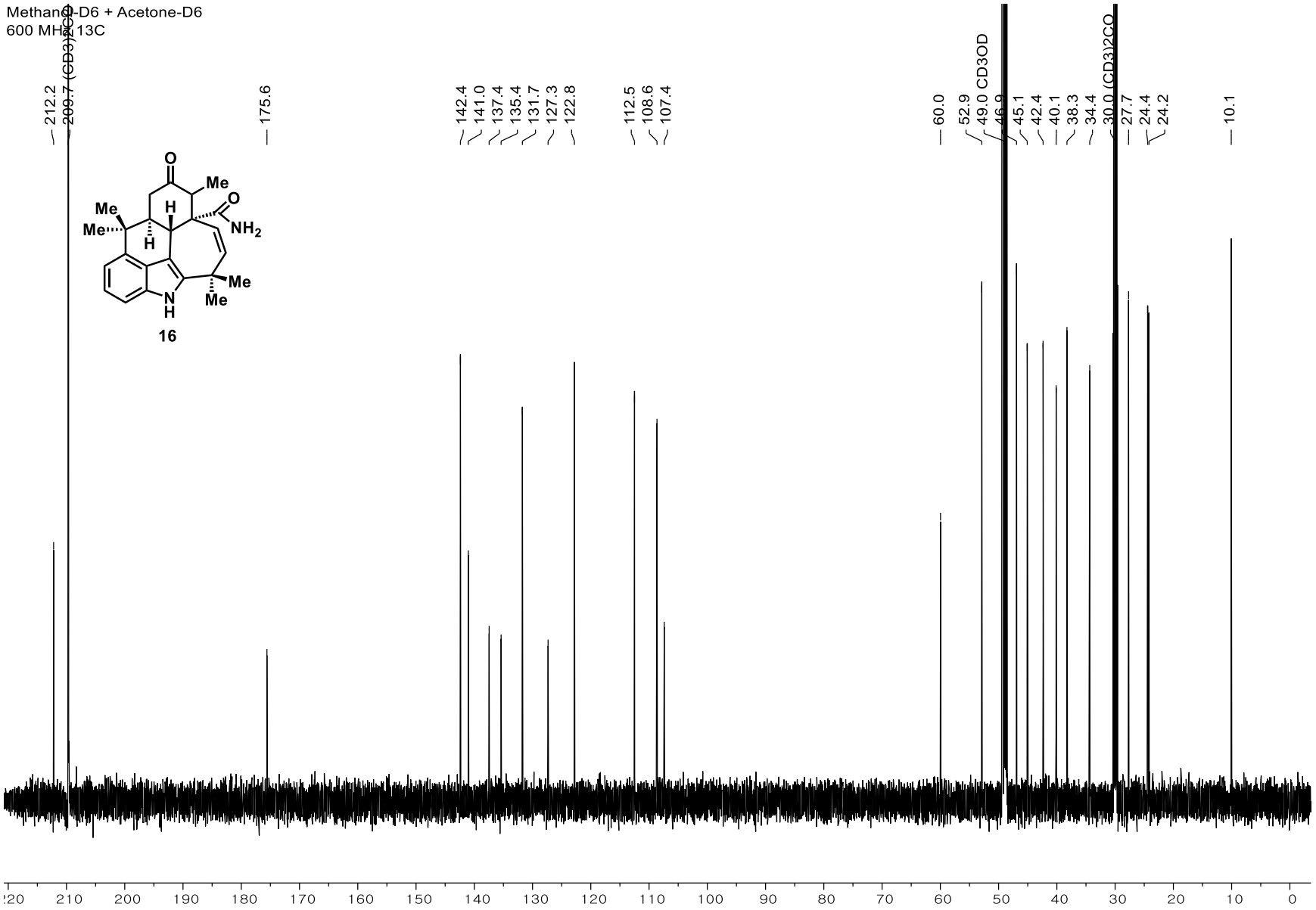
25


Methanol-D6
600 MHz 13C
176.5
144.2
141.5
138.2
135.6
127.2
123.1
122.3
112.3
108.4
107.3
87.8
59.1
55.0
49.8
49.0 CD3OD
42.8
39.8
38.0
37.7
32.9
31.1
25.3
25.2
10.4
HO
H
N
Me
O
Me
Me
H
H
Me
Me
N
H
25
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

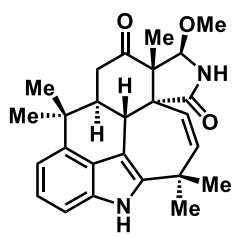
Methanol-D6 + Acetone-D6
600 MHz 1H



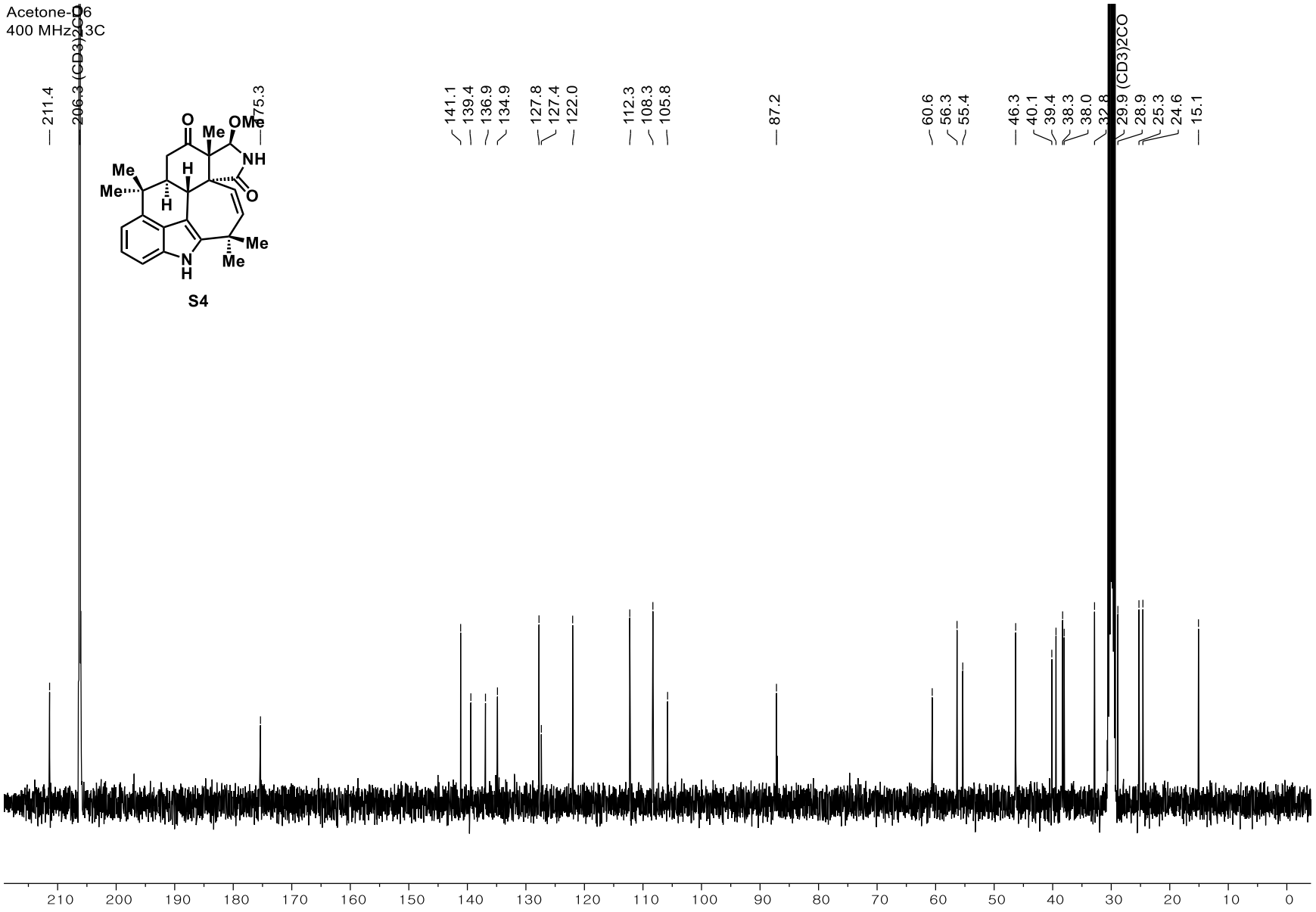
16


Methanol-D6 + Acetone-D6
600 MHz 13C
212.2
209.7 (CD3)2CO
175.6
142.4
141.0
137.4
135.4
131.7
127.3
122.8
112.5
108.6
107.4
60.0
52.9
49.0 CD3OD
46.9
45.1
42.4
40.1
38.3
34.4
30.0 (CD3)2CO
27.7
24.4
24.2
10.1
16

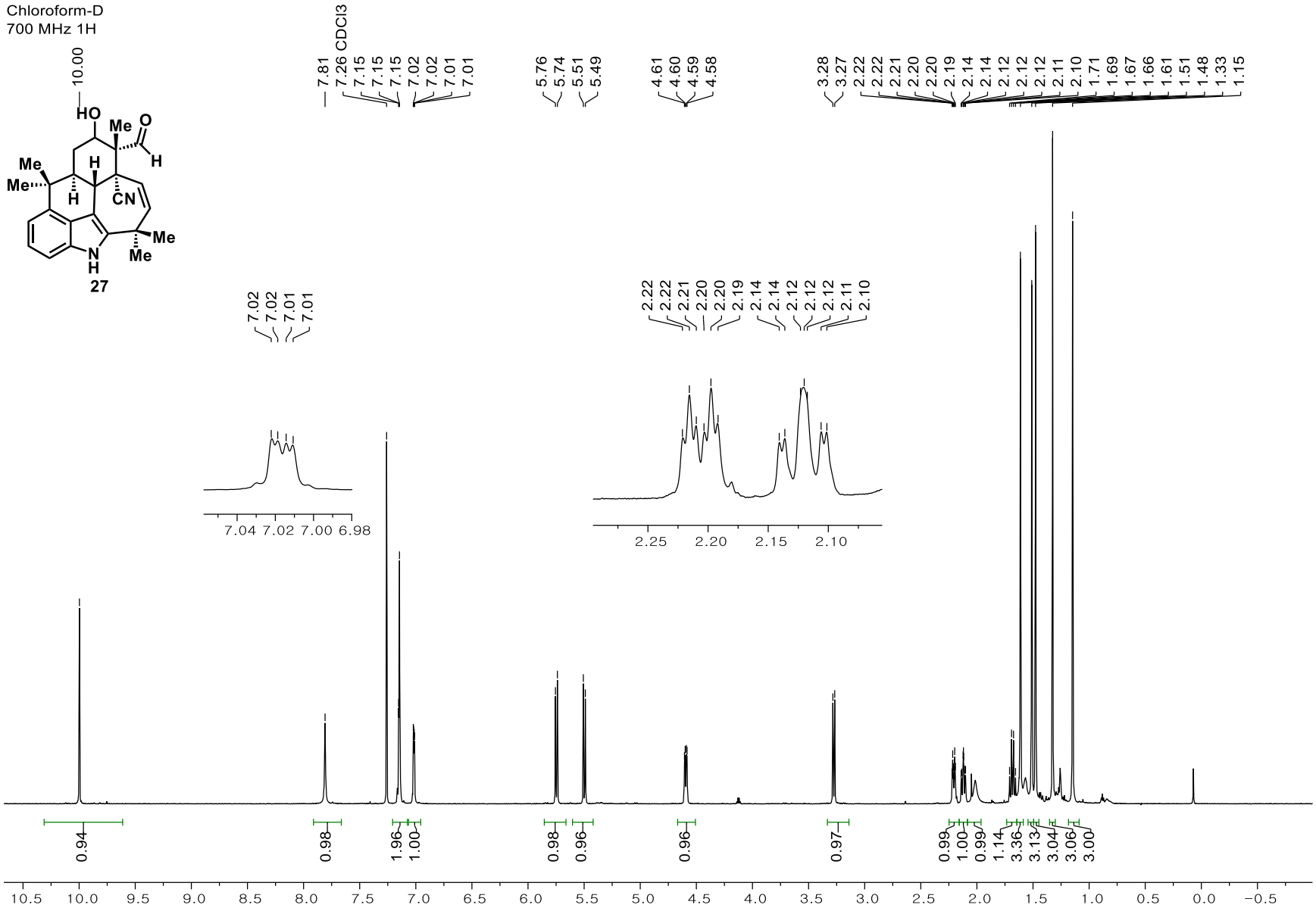
Acetone-D6
400 MHz 1H

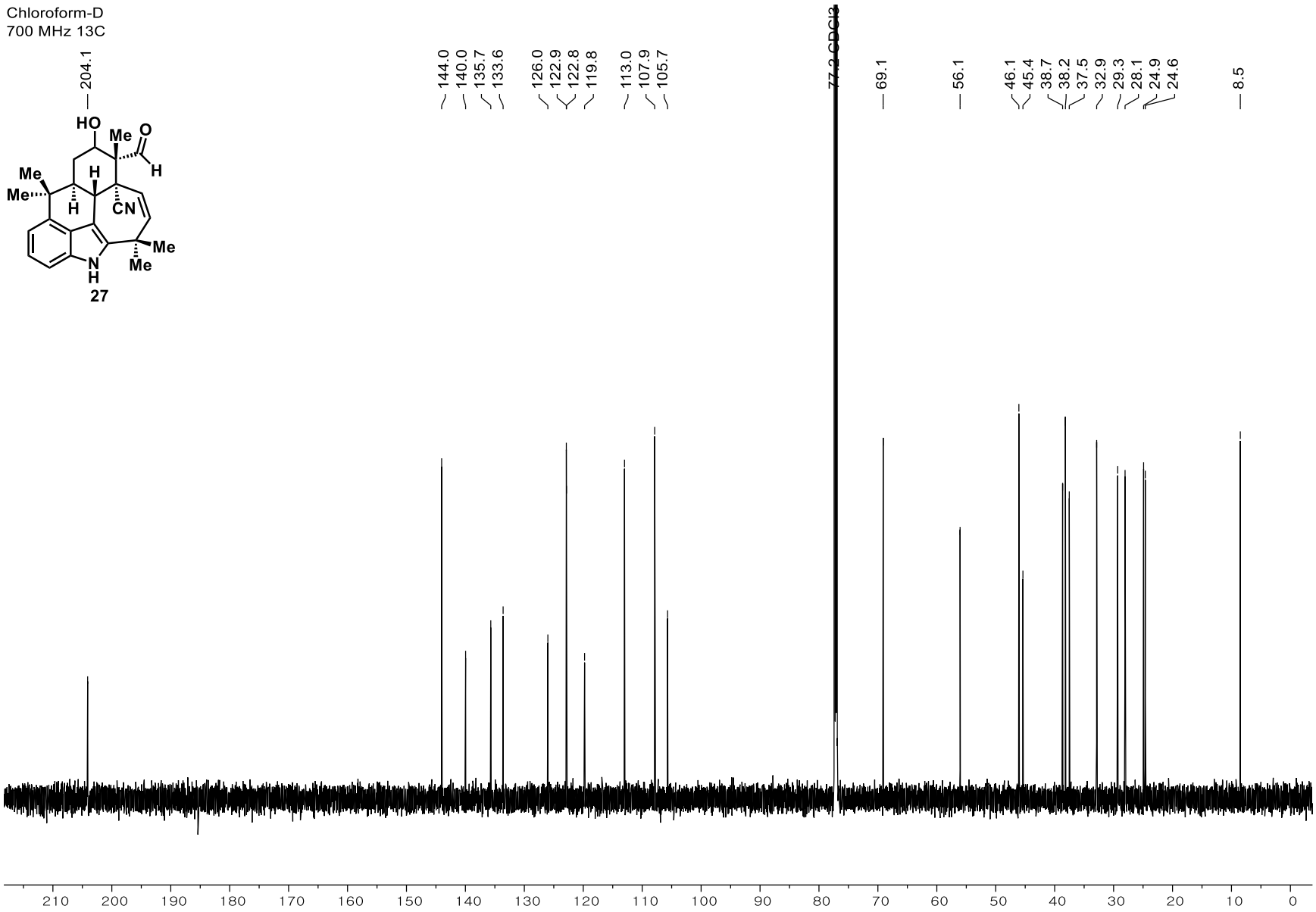


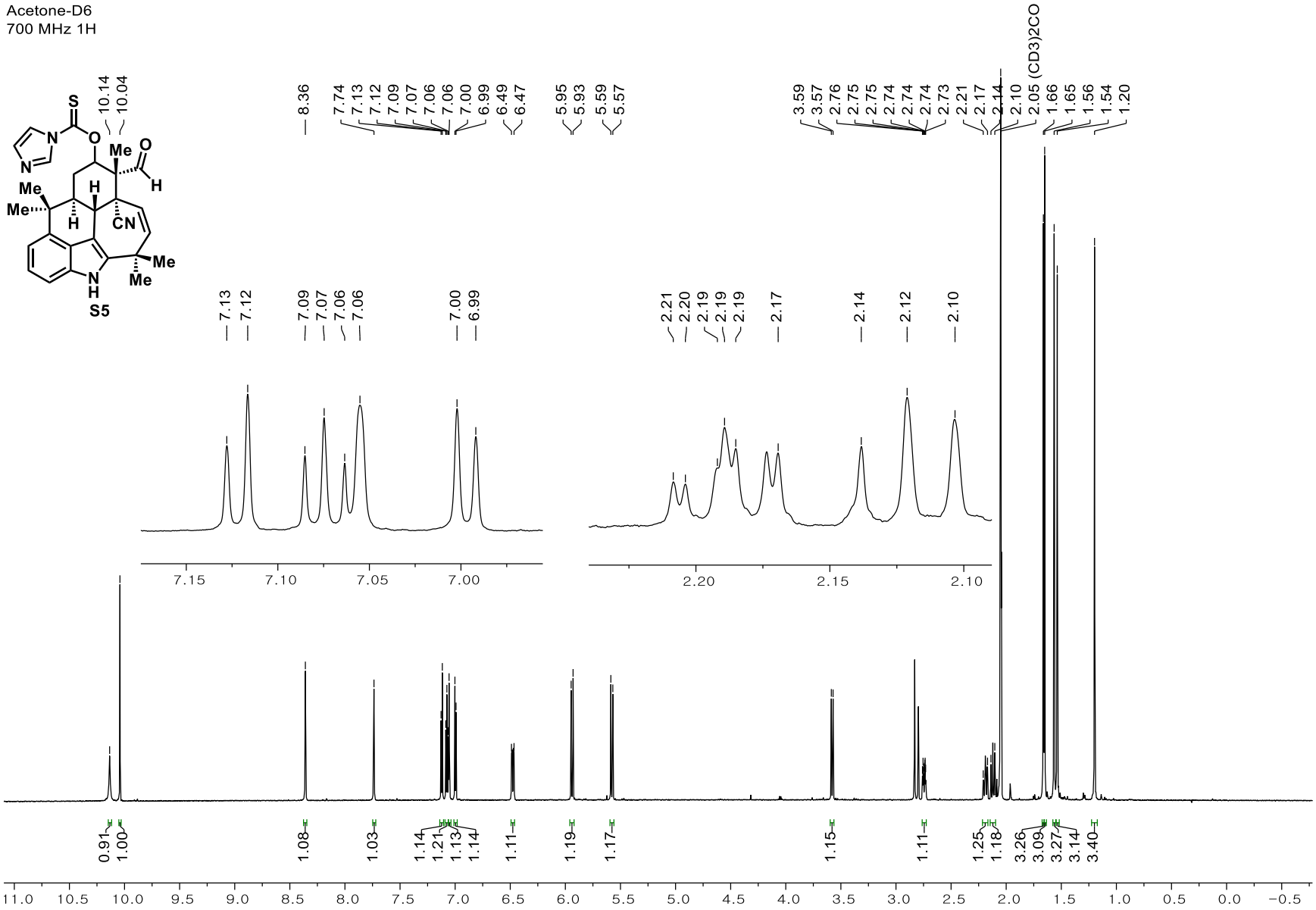
S4

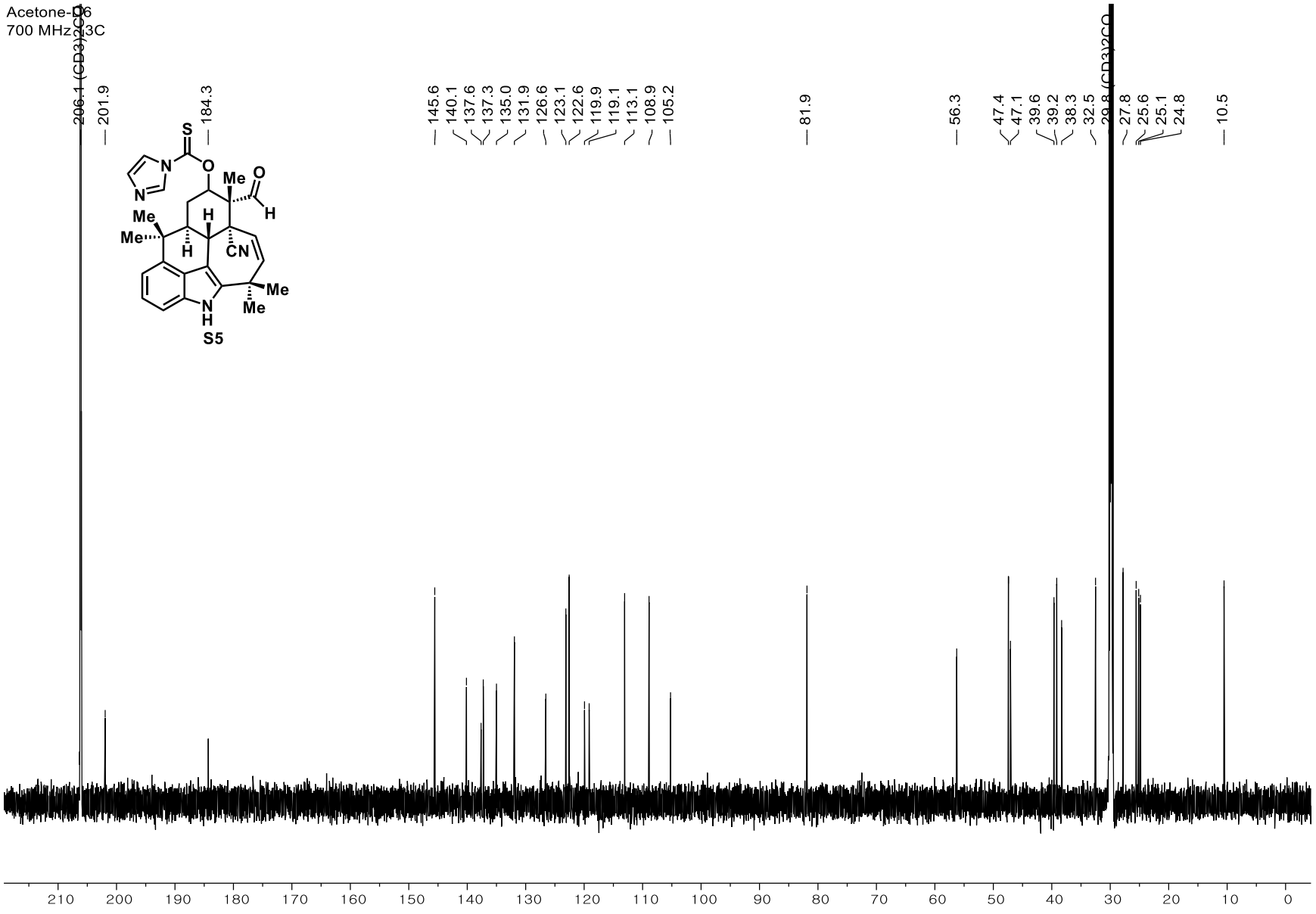

Acetone-D6
400 MHz, 13C
211.4
206.3 (CD3)2CO
175.3
141.1
139.4
136.9
134.9
127.8
127.4
122.0
112.3
108.3
105.8
87.2
60.6
56.3
55.4
46.3
40.1
39.4
38.3
38.0
32.8
29.9 (CD3)2CO
28.9
25.3
24.6
15.1
O
Me
OMe
NH
Me
Me
H
H
O
Me
Me
N
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

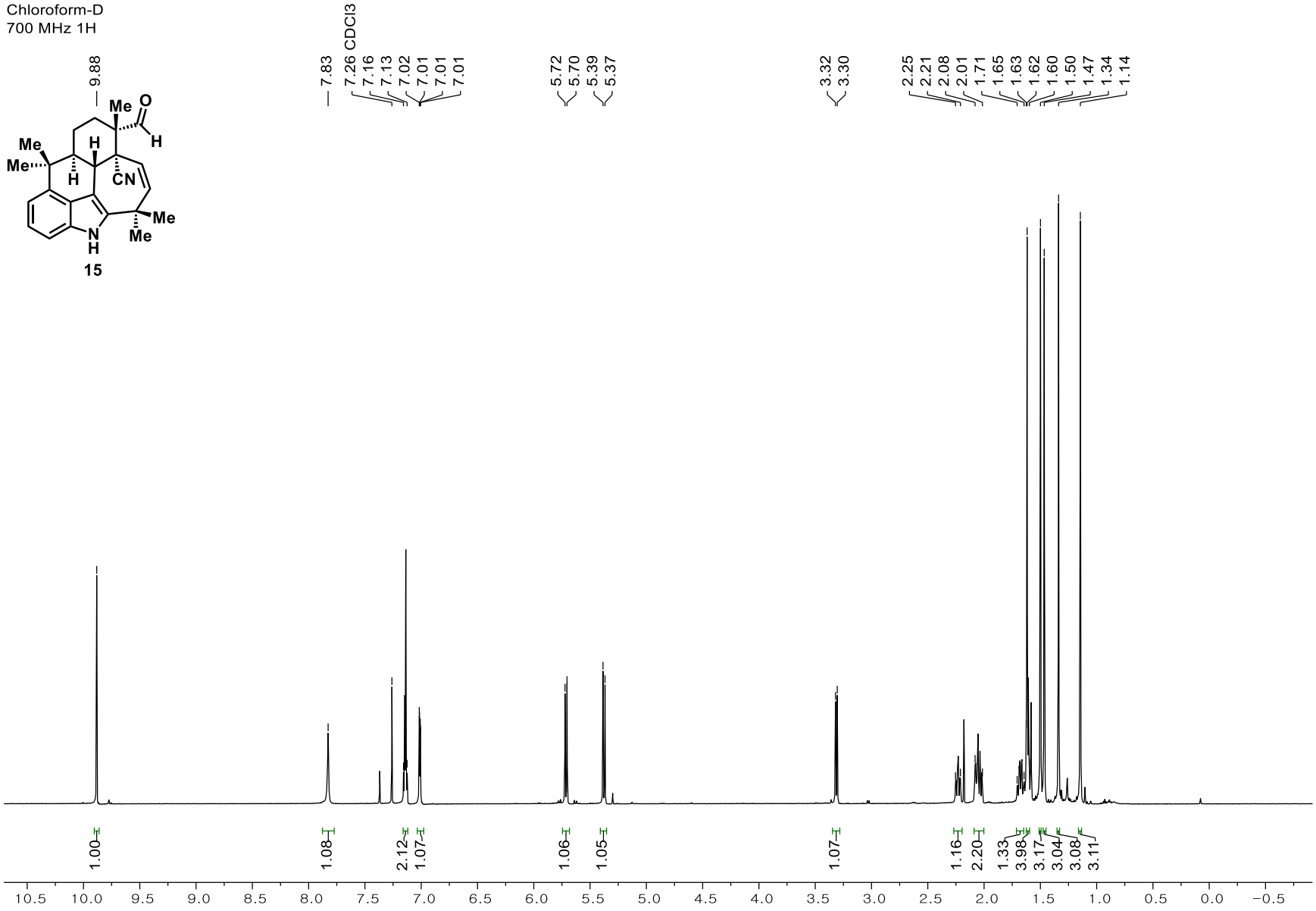
S4

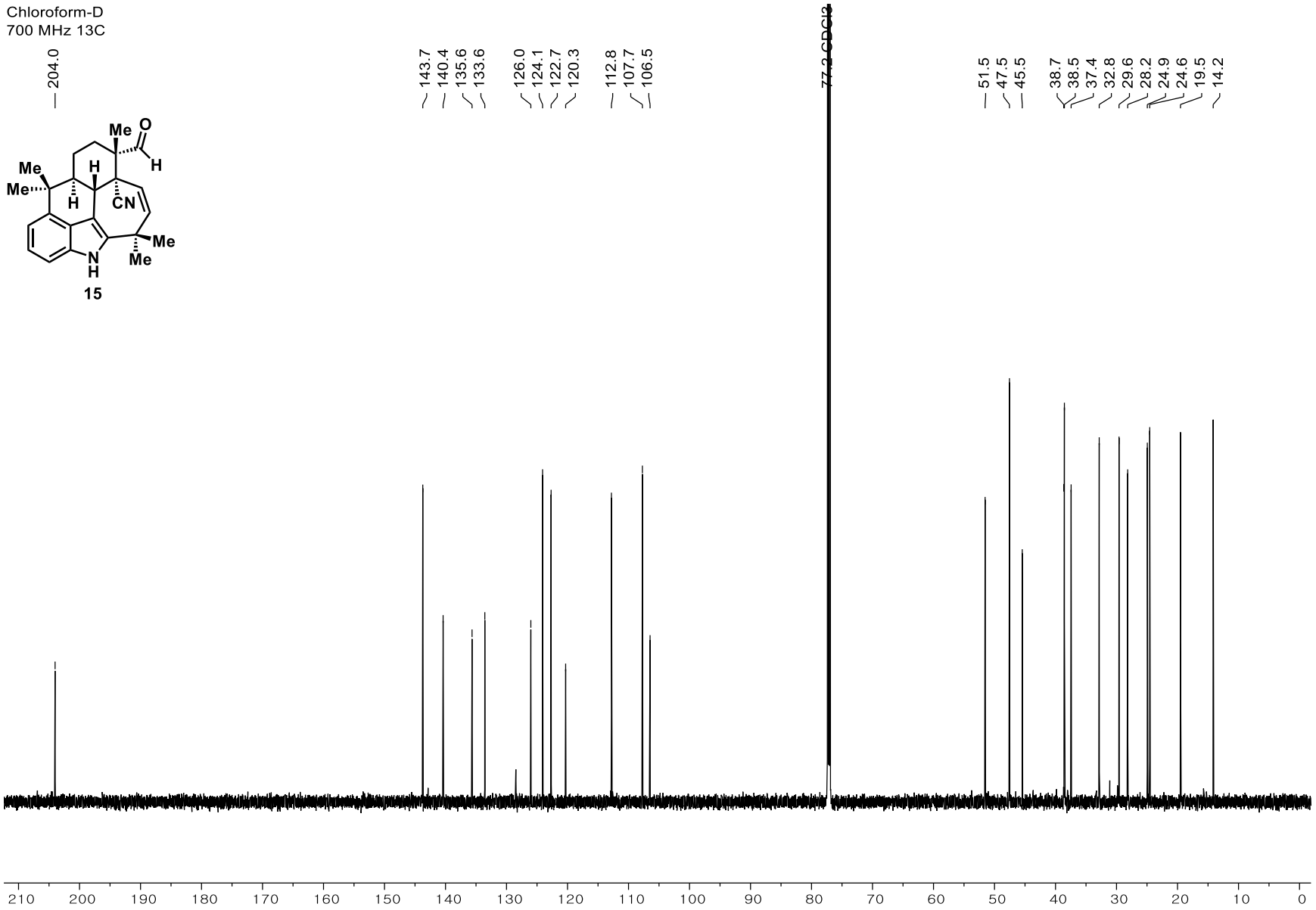

Chloroform-D
700 MHz 1H
10.00
7.81
7.26 CDCl3
7.15
7.15
7.15
7.02
7.02
7.01
7.01
5.76
5.74
5.51
5.49
4.61
4.60
4.59
4.58
3.28
3.27
2.22
2.22
2.21
2.20
2.20
2.19
2.14
2.14
2.12
2.12
2.12
2.11
2.10
1.71
1.69
1.67
1.66
1.61
1.51
1.48
1.33
1.15
HO
Me
O
H
Me
Me
H
H
CN
N
H
Me
Me
27
7.04 7.02 7.00 6.98
2.25 2.20 2.15 2.10
0.94
0.98
1.96
1.00
0.98
0.96
0.96
0.97
0.99
1.00
0.99
1.14
3.36
3.13
3.04
3.06
3.00
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


Chloroform-D
700 MHz 13C
204.1
144.0
140.0
135.7
133.6
126.0
122.9
122.8
119.8
113.0
107.9
105.7
77.2 CDCl3
69.1
56.1
46.1
45.4
38.7
38.2
37.5
32.9
29.3
28.1
24.9
24.6
8.5
HO
Me
O
H
Me
Me
H
H
CN
Me
N
H
Me
27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

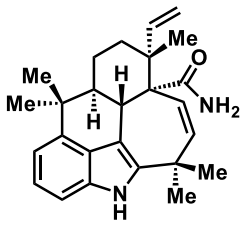

Acetone-D6
700 MHz 1H
S5
(CD3)2CO


Acetone-D6
700 MHz, 13C
206.1 (CD3)2CO
201.9
184.3
145.6
140.1
137.6
137.3
135.0
131.9
126.6
123.1
122.6
119.9
119.1
113.1
108.9
105.2
81.9
56.3
47.4
47.1
39.6
39.2
38.3
32.5
29.8 (CD3)2CO
27.8
25.6
25.1
24.8
10.5
S5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Chloroform-D
700 MHz 1H
9.88
7.83
7.26 CDCl3
7.16
7.13
7.02
7.01
7.01
7.01
5.72
5.70
5.39
5.37
3.32
3.30
2.25
2.21
2.08
2.01
1.71
1.65
1.63
1.62
1.60
1.50
1.47
1.34
1.14
Me
O
H
Me
Me
H
H
CN
Me
Me
N
H
15
1.00
1.08
2.12
1.07
1.06
1.05
1.07
1.16
2.20
1.33
3.98
3.17
3.04
3.08
3.11
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

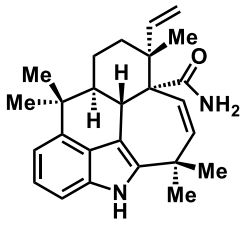

Chloroform-D
700 MHz 13C
204.0
143.7
140.4
135.6
133.6
126.0
124.1
122.7
120.3
112.8
107.7
106.5
77.2 CDCl3
51.5
47.5
45.5
38.7
38.5
37.4
32.8
29.6
28.2
24.9
24.6
19.5
14.2
Me
O
H
Me
Me
H
H
CN
Me
Me
N
H
15
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Chloroform-D
700 MHz 1H



29

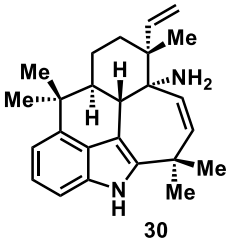
Chloroform-D
700 MHz 13C



29

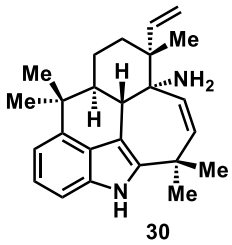
175.2
146.2
141.9
140.2
134.9
133.8
131.3
126.7
122.2
113.3
112.2
109.2
107.2
77.2 CDCl3
56.4
43.5
43.2
38.9
38.8
37.3
34.6
33.8
27.8
24.3
21.2
19.3

Methanol-D6
700 MHz 1H



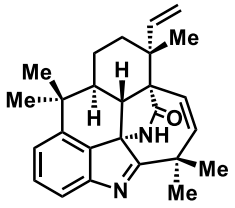
30

Methanol-D6
700 MHz 13C

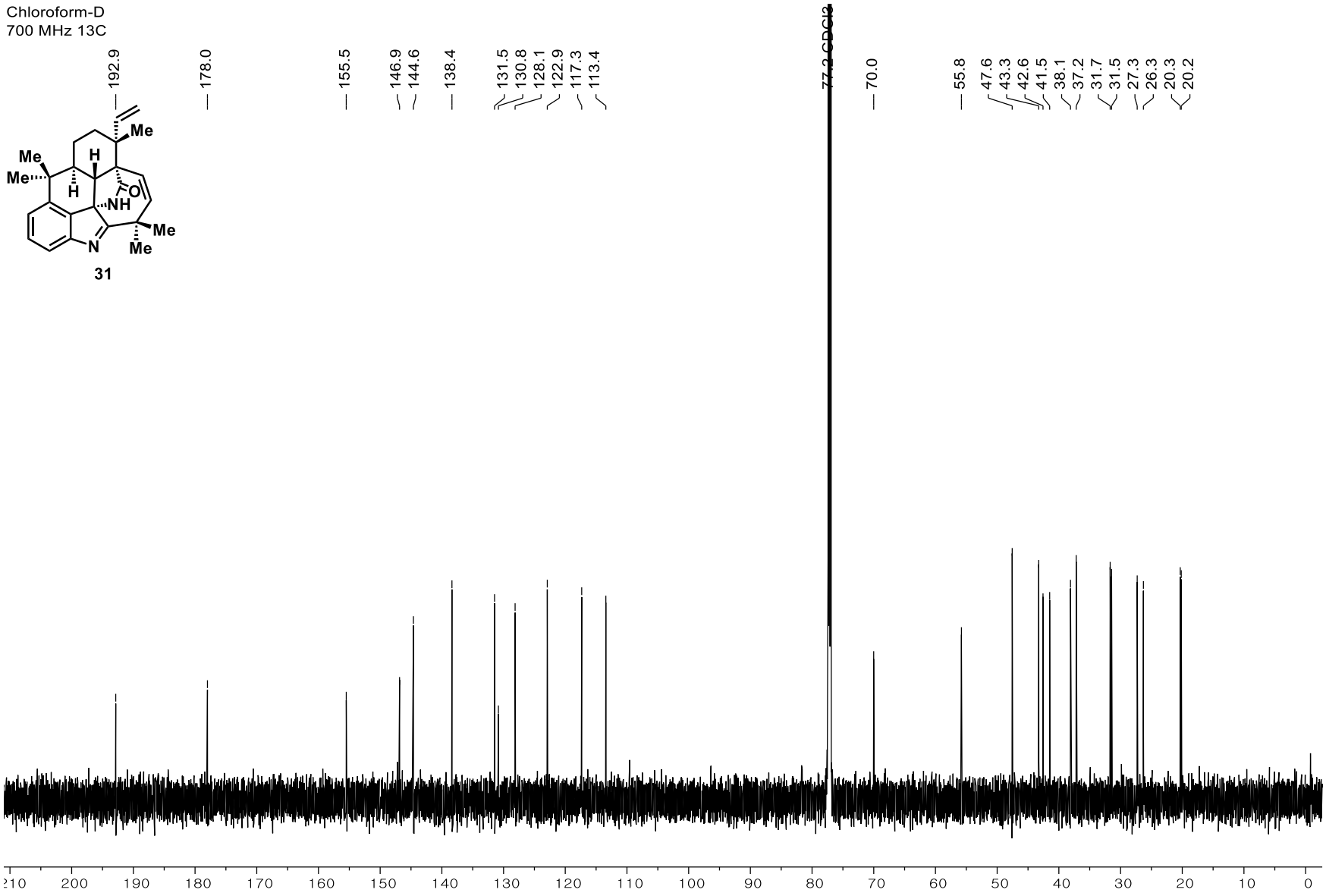


30

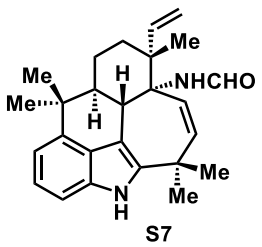
Chloroform-D
600 MHz 1H



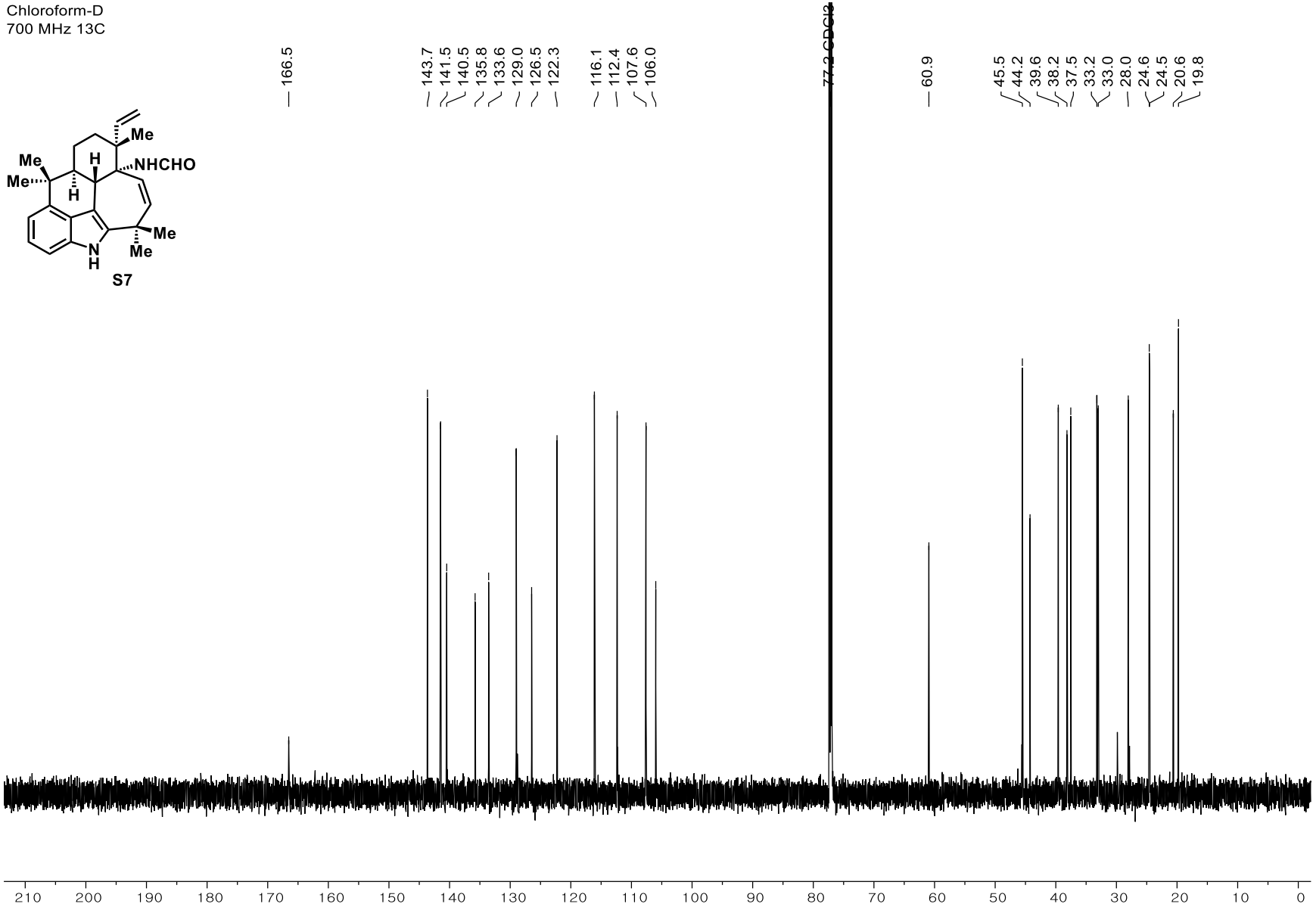
31

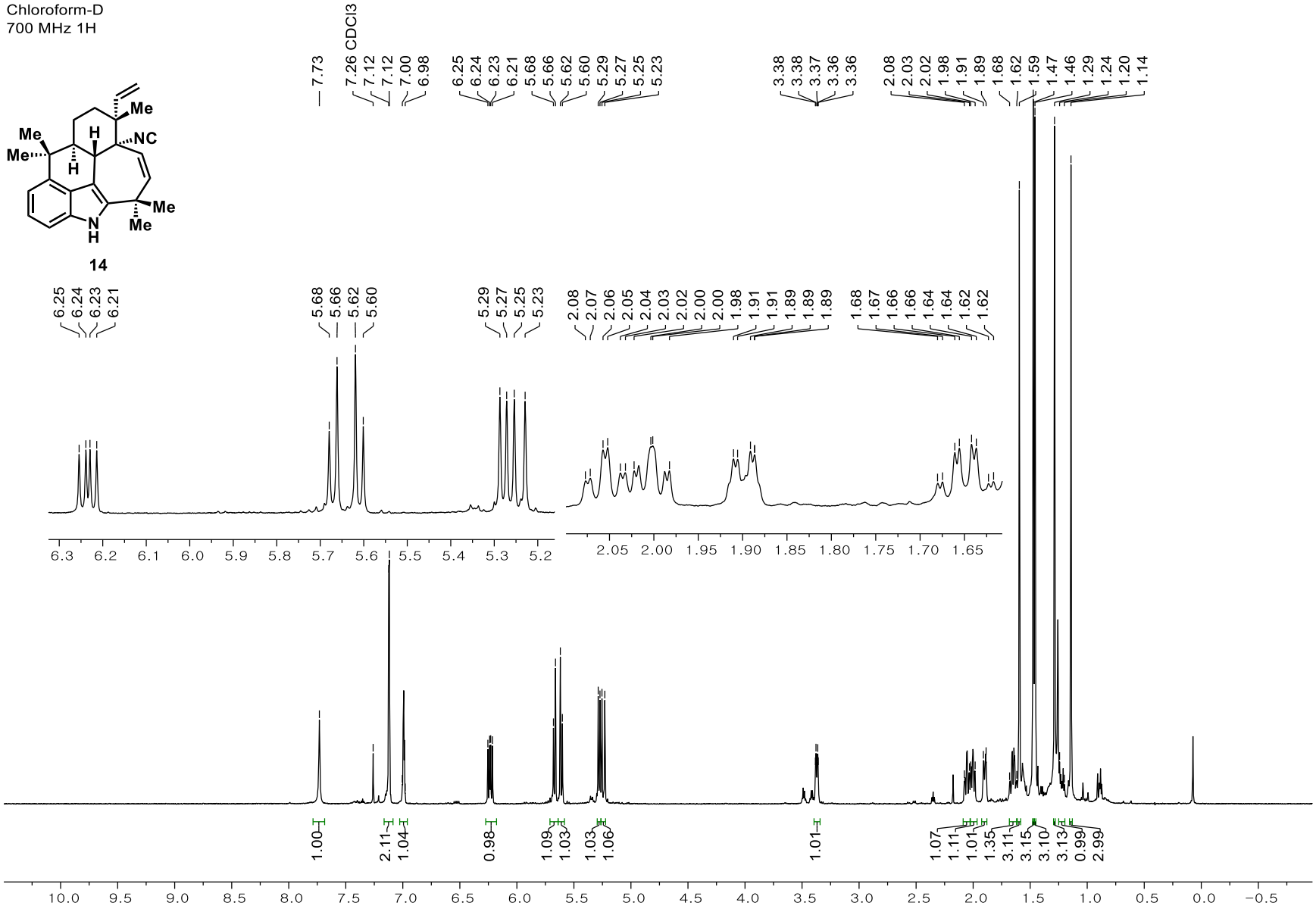

Chloroform-D
700 MHz 13C
192.9
178.0
155.5
146.9
144.6
138.4
131.5
130.8
128.1
122.9
117.3
113.4
77.2 CDCl3
70.0
55.8
47.6
43.3
42.6
41.5
38.1
37.2
31.7
31.5
27.3
26.3
20.3
20.2
Me
Me
Me
H
H
O
NH
N
Me
Me
31
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Chloroform-D
600 MHz 1H

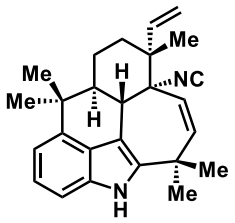


S7


Chloroform-D
700 MHz 13C
166.5
143.7
141.5
140.5
135.8
133.6
129.0
126.5
122.3
116.1
112.4
107.6
106.0
77.2 CDCl3
60.9
45.5
44.2
39.6
38.2
37.5
33.2
33.0
28.0
24.6
24.5
20.6
19.8
Me
Me
Me
H
H
NHCHO
Me
Me
N
H
S7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Chloroform-D
700 MHz 1H
Me
Me
Me
H
H
NC
Me
Me
N
H
14

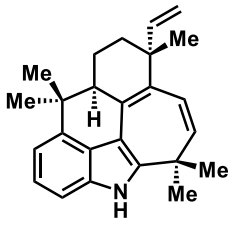
Chloroform-D
700 MHz 13C



14

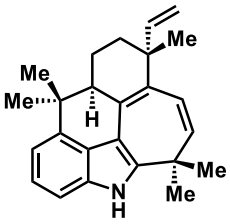
156.2
143.8
142.4
140.9
135.2
133.6
127.0
126.5
122.3
115.2
112.5
107.5
106.6
77.2 CDCl3
67.6
45.8
43.2
39.4
38.3
37.3
33.7
32.9
27.9
25.1
24.6
20.6
17.7

Chloroform-D
700 MHz 1H

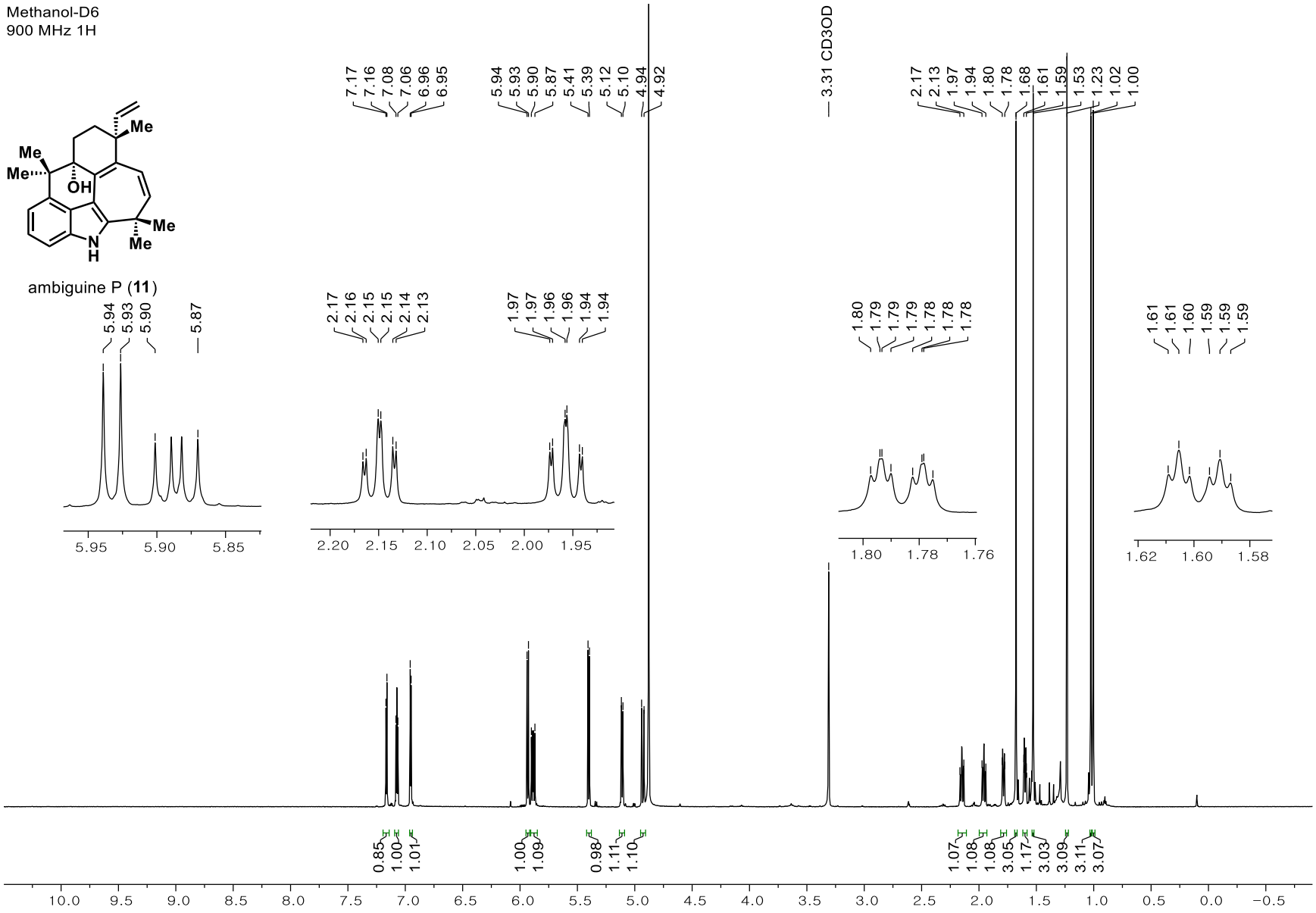


32

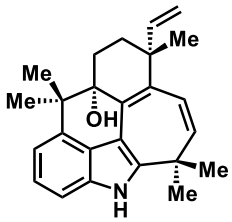
Chloroform-D
700 MHz 13C



32

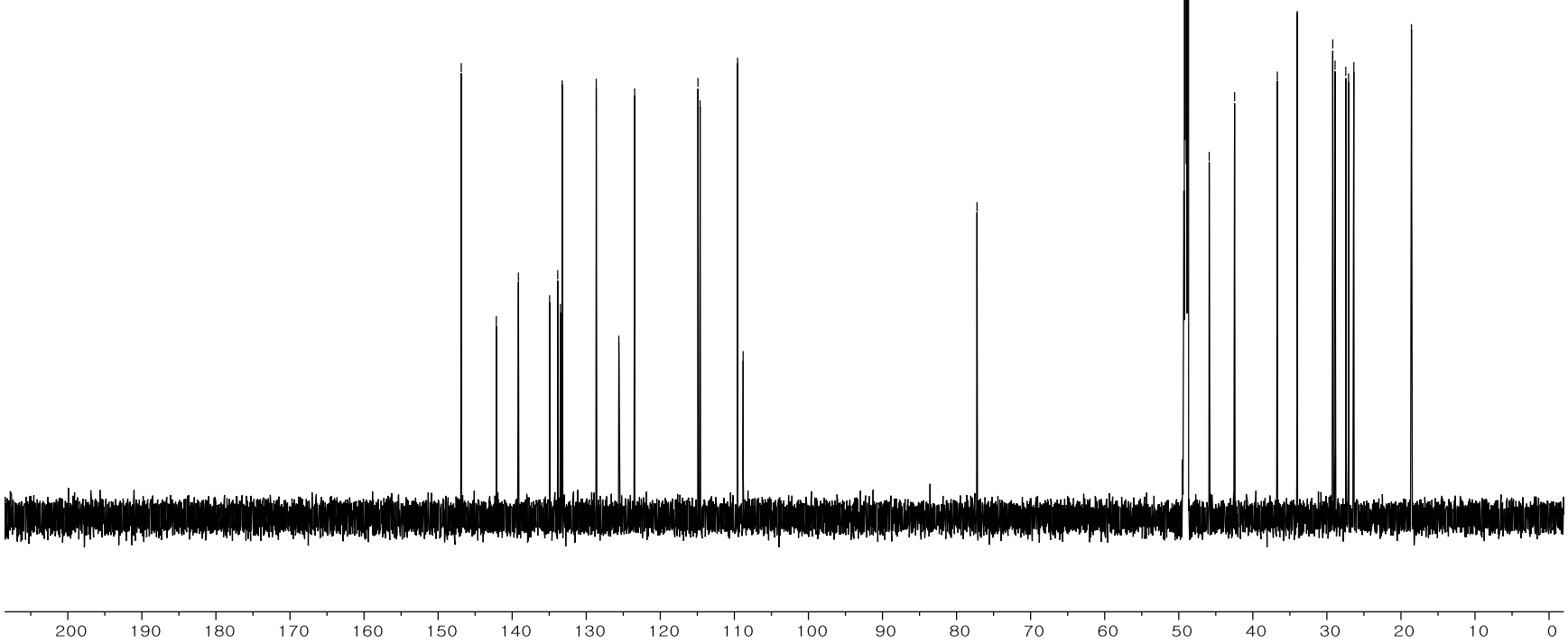

Methanol-D6
900 MHz 1H
ambiguine P (11)
— 3.31 CD3OD

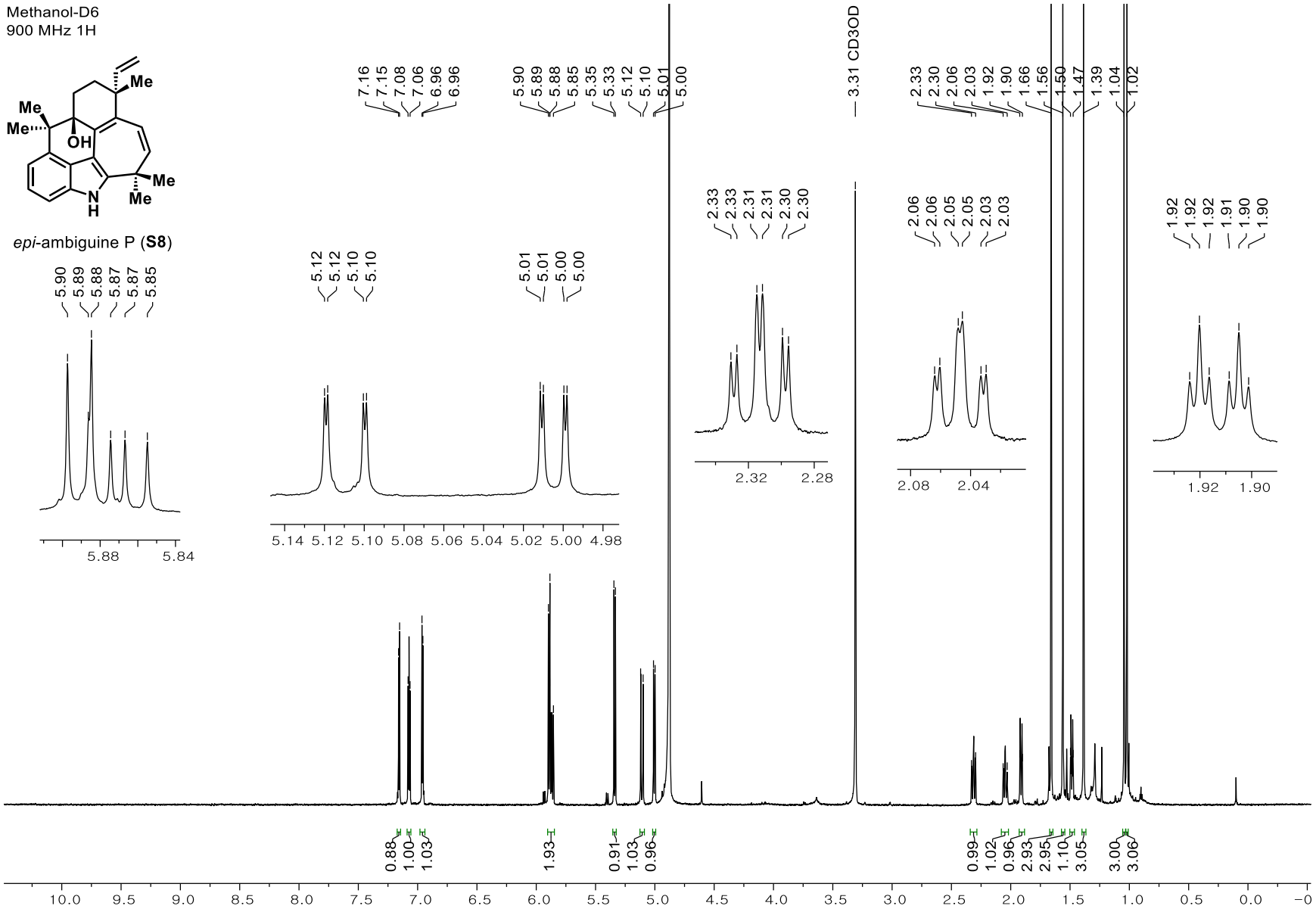
Methanol-D6
900 MHz 13C



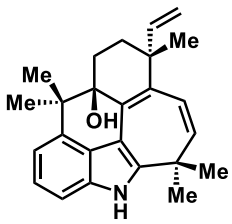
ambiguine P (**11**)

146.9
142.1
139.2
134.9
133.9
133.5
133.2
128.6
125.6
123.5
114.9
114.6
109.6
108.8
77.2
49.0 CD3OD
45.9
42.5
36.7
34.0
29.2
28.9
27.5
27.1
26.4
18.6



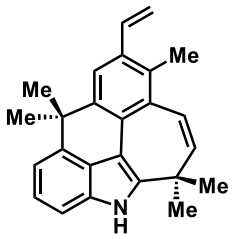

Methanol-D6
900 MHz 1H
Me
Me
Me
OH
Me
Me
N
H
epi-ambiguine P (S8)
7.16 7.15 7.08 7.06 6.96 6.96
5.90 5.89 5.88 5.85 5.35 5.33 5.12 5.10 5.01 5.00
3.31 CD3OD
2.33 2.30 2.06 2.03 1.92 1.90 1.66 1.56 1.50 1.47 1.39 1.04 1.02
0.88 1.00 1.03 1.93 0.91 1.03 0.96 0.99 1.02 0.96 2.93 2.95 1.10 3.05 3.00 3.06
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

Methanol-D6
900 MHz 13C



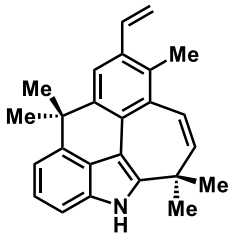
epi-ambiguine P (**S8**)

Methanol-D6
900 MHz 1H



33

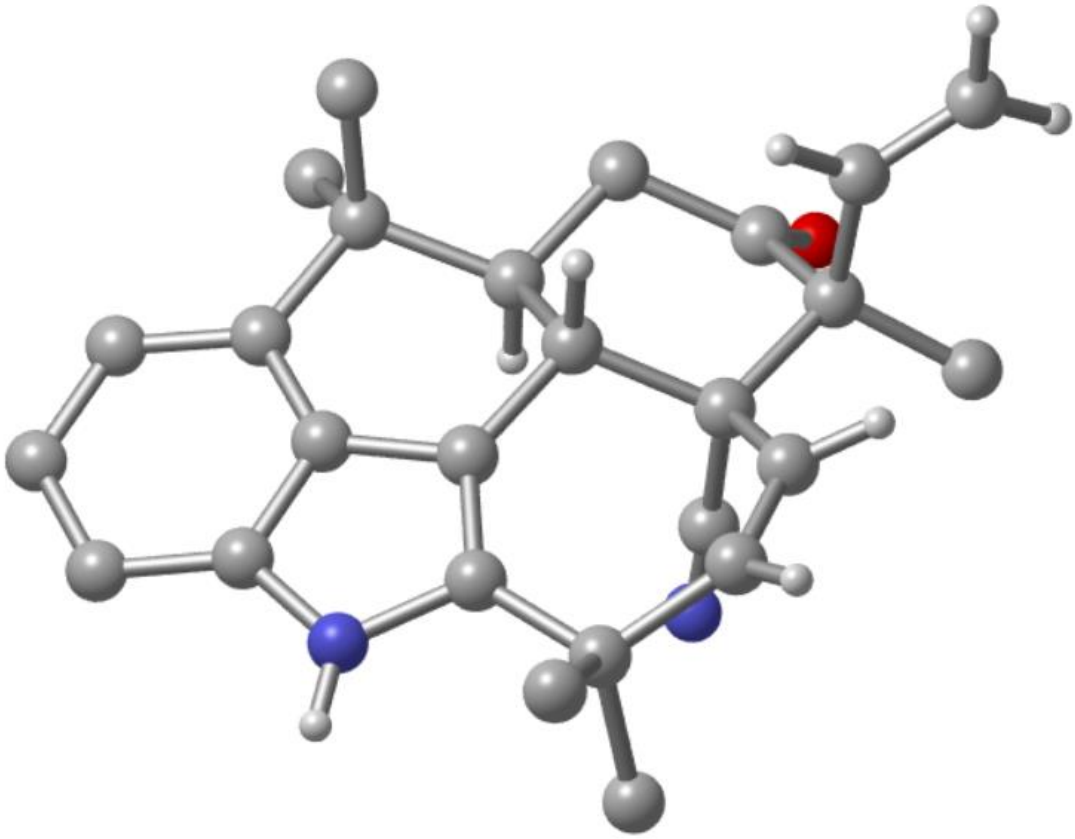
Methanol-D6
900 MHz 13C



33

5. X-Ray Crystallographic Data

*1) Nitrile Ketone (**S3**)*



A colorless needle 0.060 x 0.020 x 0.020 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using and scans. Crystal-to-detector distance was 60 mm and exposure time was 20 seconds per frame using a scan width of 2.0°. Data collection was 99.7% complete to 67.000° in . A total of 30752 reflections were collected covering the indices, -11<=*h*<=10, -15<=*k*<=15, -21<=*l*<=21. 3856 reflections were found to be symmetry independent, with an R_{int} of 0.0559. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be P 21 21 21 (No. 19). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom

using the appropriate HFIX command in SHELXL-2014. Absolute stereochemistry was unambiguously determined to be *R* at C1 and *S* at C2, C5 and C18, respectively.

Table 1. Crystal data and structure refinement for sarpong135.

X-ray ID	sarpong135	
Sample/notebook ID	MLH-B1-115	
Empirical formula	C26 H28 N2 O	
Formula weight	384.50	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.2170(3) Å	α= 90°.
	b = 12.9842(4) Å	β= 90°.
	c = 17.6732(6) Å	γ = 90°.
Volume	2115.05(12) $Å^3$	
Z	4	
Density (calculated)	1.208 Mg/m^3	
Absorption coefficient	0.568 mm^{-1}	
F(000)	824	
Crystal size	0.060 x 0.020 x 0.020 mm^3	
Theta range for data collection	4.225 to 68.345°.	
Index ranges	-11<=h<=10, -15<=k<=15, -21<=l<=21	
Reflections collected	30752	
Independent reflections	3856 [R(int) = 0.0559]	
Completeness to theta = 67.000°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.809	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3856 / 0 / 267	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.1002	
R indices (all data)	R1 = 0.0460, wR2 = 0.1044	
Absolute structure parameter	0.00(17)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.706 and -0.161 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for sarpong135. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6365(3)	5390(2)	4145(2)	26(1)
C(2)	7261(3)	6419(2)	4006(2)	28(1)
C(3)	8779(3)	6098(2)	3729(2)	31(1)
C(4)	8813(3)	5400(2)	3054(2)	34(1)
C(5)	8003(3)	4392(2)	3216(2)	26(1)
C(6)	8158(3)	3597(2)	2553(2)	29(1)
C(7)	7337(3)	2622(2)	2764(1)	26(1)
C(8)	7577(3)	1644(2)	2483(2)	31(1)
C(9)	6756(3)	804(2)	2734(2)	34(1)
C(10)	5665(3)	904(2)	3270(2)	33(1)
C(11)	5380(3)	1894(2)	3532(2)	28(1)
C(12)	6201(3)	2732(2)	3278(1)	25(1)
C(13)	5667(3)	3642(2)	3633(1)	24(1)
C(14)	4544(3)	3346(2)	4094(2)	29(1)
C(15)	3544(3)	3933(2)	4615(2)	34(1)
C(16)	3691(3)	5083(2)	4525(2)	36(1)
C(17)	4804(3)	5679(2)	4344(2)	31(1)
C(18)	6419(3)	4637(2)	3458(1)	24(1)
C(19)	7052(3)	4845(2)	4786(2)	27(1)
C(20)	7416(3)	7054(2)	4731(2)	36(1)
C(21)	6545(3)	7024(2)	3368(2)	35(1)
C(22)	6538(4)	8021(3)	3290(2)	51(1)
C(23)	7536(4)	4012(2)	1812(2)	41(1)
C(24)	9770(3)	3338(3)	2439(2)	44(1)
C(25)	1951(3)	3651(3)	4424(2)	46(1)
C(26)	3836(4)	3629(3)	5447(2)	43(1)
N(1)	4384(2)	2283(2)	4032(1)	30(1)
N(2)	7626(3)	4404(2)	5260(1)	35(1)
O(1)	9871(2)	6387(2)	4044(1)	41(1)

Table 3. Bond lengths [Å] and angles [°] for sarpong135.

C(1)-C(19)	1.478(4)	C(14)-N(1)	1.393(4)
C(1)-C(17)	1.528(4)	C(14)-C(15)	1.508(4)
C(1)-C(18)	1.560(4)	C(15)-C(16)	1.508(4)
C(1)-C(2)	1.590(4)	C(15)-C(26)	1.545(4)
C(2)-C(21)	1.524(4)	C(15)-C(25)	1.551(4)
C(2)-C(20)	1.530(4)	C(16)-C(17)	1.324(4)
C(2)-C(3)	1.540(4)	C(16)-H(16)	0.9500
C(3)-O(1)	1.210(4)	C(17)-H(17)	0.9500
C(3)-C(4)	1.498(4)	C(18)-H(18)	1.0000
C(4)-C(5)	1.533(4)	C(19)-N(2)	1.144(4)
C(4)-H(4A)	0.9900	C(20)-H(20A)	0.9800
C(4)-H(4B)	0.9900	C(20)-H(20B)	0.9800
C(5)-C(18)	1.555(4)	C(20)-H(20C)	0.9800
C(5)-C(6)	1.568(4)	C(21)-C(22)	1.302(4)
C(5)-H(5)	1.0000	C(21)-H(21)	0.9500
C(6)-C(7)	1.521(4)	C(22)-H(22A)	0.9500
C(6)-C(23)	1.528(4)	C(22)-H(22B)	0.9500
C(6)-C(24)	1.536(4)	C(23)-H(23A)	0.9800
C(7)-C(8)	1.381(4)	C(23)-H(23B)	0.9800
C(7)-C(12)	1.393(4)	C(23)-H(23C)	0.9800
C(8)-C(9)	1.399(4)	C(24)-H(24A)	0.9800
C(8)-H(8)	0.9500	C(24)-H(24B)	0.9800
C(9)-C(10)	1.389(4)	C(24)-H(24C)	0.9800
C(9)-H(9)	0.9500	C(25)-H(25A)	0.9800
C(10)-C(11)	1.391(4)	C(25)-H(25B)	0.9800
C(10)-H(10)	0.9500	C(25)-H(25C)	0.9800
C(11)-N(1)	1.371(4)	C(26)-H(26A)	0.9800
C(11)-C(12)	1.399(4)	C(26)-H(26B)	0.9800
C(12)-C(13)	1.425(4)	C(26)-H(26C)	0.9800
C(13)-C(14)	1.372(4)	N(1)-H(1)	0.8800
C(13)-C(18)	1.499(4)		

C(19)-C(1)-C(17)	110.2(2)
C(19)-C(1)-C(18)	106.5(2)
C(17)-C(1)-C(18)	111.3(2)
C(19)-C(1)-C(2)	107.4(2)
C(17)-C(1)-C(2)	108.5(2)
C(18)-C(1)-C(2)	112.9(2)
C(21)-C(2)-C(20)	112.4(2)
C(21)-C(2)-C(3)	107.3(2)
C(20)-C(2)-C(3)	109.1(2)
C(21)-C(2)-C(1)	108.8(2)
C(20)-C(2)-C(1)	111.8(2)
C(3)-C(2)-C(1)	107.1(2)
O(1)-C(3)-C(4)	122.5(3)
O(1)-C(3)-C(2)	121.7(2)
C(4)-C(3)-C(2)	115.9(2)
C(3)-C(4)-C(5)	110.9(2)
C(3)-C(4)-H(4A)	109.5
C(5)-C(4)-H(4A)	109.5
C(3)-C(4)-H(4B)	109.5
C(5)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	108.0
C(4)-C(5)-C(18)	109.5(2)
C(4)-C(5)-C(6)	112.3(2)
C(18)-C(5)-C(6)	115.2(2)
C(4)-C(5)-H(5)	106.4
C(18)-C(5)-H(5)	106.4
C(6)-C(5)-H(5)	106.4
C(7)-C(6)-C(23)	108.5(2)
C(7)-C(6)-C(24)	109.4(2)
C(23)-C(6)-C(24)	109.1(3)
C(7)-C(6)-C(5)	108.6(2)
C(23)-C(6)-C(5)	111.9(2)
C(24)-C(6)-C(5)	109.3(2)
C(8)-C(7)-C(12)	116.7(2)
C(8)-C(7)-C(6)	126.6(2)
C(12)-C(7)-C(6)	116.7(2)

C(7)-C(8)-C(9)	121.1(3)
C(7)-C(8)-H(8)	119.5
C(9)-C(8)-H(8)	119.5
C(10)-C(9)-C(8)	122.3(3)
C(10)-C(9)-H(9)	118.8
C(8)-C(9)-H(9)	118.8
C(9)-C(10)-C(11)	116.8(3)
C(9)-C(10)-H(10)	121.6
C(11)-C(10)-H(10)	121.6
N(1)-C(11)-C(10)	132.9(3)
N(1)-C(11)-C(12)	106.4(2)
C(10)-C(11)-C(12)	120.6(3)
C(7)-C(12)-C(11)	122.4(2)
C(7)-C(12)-C(13)	129.2(2)
C(11)-C(12)-C(13)	108.4(2)
C(14)-C(13)-C(12)	106.9(2)
C(14)-C(13)-C(18)	135.4(3)
C(12)-C(13)-C(18)	117.6(2)
C(13)-C(14)-N(1)	108.1(2)
C(13)-C(14)-C(15)	133.0(3)
N(1)-C(14)-C(15)	119.0(2)
C(16)-C(15)-C(14)	112.4(2)
C(16)-C(15)-C(26)	109.7(3)
C(14)-C(15)-C(26)	110.2(2)
C(16)-C(15)-C(25)	107.2(3)
C(14)-C(15)-C(25)	109.1(3)
C(26)-C(15)-C(25)	108.1(3)
C(17)-C(16)-C(15)	132.4(3)
C(17)-C(16)-H(16)	113.8
C(15)-C(16)-H(16)	113.8
C(16)-C(17)-C(1)	129.9(3)
C(16)-C(17)-H(17)	115.1
C(1)-C(17)-H(17)	115.1
C(13)-C(18)-C(5)	108.3(2)
C(13)-C(18)-C(1)	111.4(2)
C(5)-C(18)-C(1)	111.9(2)

C(13)-C(18)-H(18)	108.4
C(5)-C(18)-H(18)	108.4
C(1)-C(18)-H(18)	108.4
N(2)-C(19)-C(1)	176.9(3)
C(2)-C(20)-H(20A)	109.5
C(2)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(2)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-C(2)	126.4(3)
C(22)-C(21)-H(21)	116.8
C(2)-C(21)-H(21)	116.8
C(21)-C(22)-H(22A)	120.0
C(21)-C(22)-H(22B)	120.0
H(22A)-C(22)-H(22B)	120.0
C(6)-C(23)-H(23A)	109.5
C(6)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(6)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(6)-C(24)-H(24A)	109.5
C(6)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(6)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(15)-C(25)-H(25A)	109.5
C(15)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(15)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(15)-C(26)-H(26A)	109.5
C(15)-C(26)-H(26B)	109.5

H(26A)-C(26)-H(26B)	109.5
C(15)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(11)-N(1)-C(14)	110.2(2)
C(11)-N(1)-H(1)	124.9
C(14)-N(1)-H(1)	124.9

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for sarpong135. 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}
C(1)	31(1)	25(1)	21(1)	1(1)	2(1)	0(1)
C(2)	39(2)	23(1)	23(1)	1(1)	0(1)	-1(1)
C(3)	38(2)	28(2)	27(1)	6(1)	3(1)	-6(1)
C(4)	36(2)	34(2)	34(2)	0(1)	9(1)	-6(1)
C(5)	28(1)	27(1)	22(1)	1(1)	3(1)	-1(1)
C(6)	31(1)	32(1)	23(1)	-1(1)	3(1)	2(1)
C(7)	26(1)	30(1)	22(1)	-2(1)	-6(1)	1(1)
C(8)	31(1)	34(2)	28(1)	-4(1)	-3(1)	5(1)
C(9)	38(2)	29(2)	35(2)	-6(1)	-10(1)	3(1)
C(10)	36(2)	29(1)	33(2)	1(1)	-12(1)	-5(1)
C(11)	30(1)	32(2)	23(1)	1(1)	-7(1)	-3(1)
C(12)	28(1)	26(1)	21(1)	0(1)	-5(1)	0(1)
C(13)	26(1)	25(1)	21(1)	1(1)	-1(1)	1(1)
C(14)	30(1)	32(2)	25(1)	1(1)	-2(1)	-2(1)
C(15)	29(1)	40(2)	33(2)	2(1)	6(1)	-3(1)
C(16)	34(2)	42(2)	30(2)	-4(1)	5(1)	6(1)
C(17)	35(2)	31(2)	28(1)	-1(1)	3(1)	6(1)
C(18)	29(1)	24(1)	19(1)	2(1)	0(1)	0(1)
C(19)	34(2)	28(1)	20(1)	-3(1)	5(1)	-2(1)
C(20)	45(2)	33(2)	29(1)	-2(1)	-1(1)	-3(1)
C(21)	45(2)	28(2)	32(2)	3(1)	-5(1)	-5(1)

C(22)	57(2)	36(2)	59(2)	8(2)	-21(2)	2(2)
C(23)	63(2)	38(2)	22(1)	1(1)	2(2)	1(2)
C(24)	33(2)	42(2)	56(2)	-16(2)	11(2)	-3(1)
C(25)	31(2)	52(2)	55(2)	-3(2)	7(2)	-4(2)
C(26)	44(2)	53(2)	32(2)	6(2)	13(1)	-2(2)
N(1)	31(1)	31(1)	29(1)	6(1)	2(1)	-8(1)
N(2)	45(1)	35(1)	25(1)	1(1)	-1(1)	5(1)
O(1)	39(1)	44(1)	40(1)	-2(1)	0(1)	-10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for sarpong135.

	x	y	z	U(eq)
H(4A)	9833	5245	2920	41
H(4B)	8359	5752	2617	41
H(5)	8486	4076	3666	31
H(8)	8311	1541	2113	37
H(9)	6953	142	2529	41
H(10)	5139	325	3450	39
H(16)	2817	5451	4616	43
H(17)	4601	6397	4337	37
H(18)	5911	4970	3021	29
H(20A)	8004	7667	4627	54
H(20B)	7891	6636	5121	54
H(20C)	6454	7264	4908	54
H(21)	6055	6636	2991	42
H(22A)	7012	8444	3652	61
H(22B)	6058	8326	2870	61
H(23A)	7649	3493	1414	61
H(23B)	8056	4640	1668	61
H(23C)	6504	4169	1880	61
H(24A)	10166	3047	2906	65
H(24B)	10302	3967	2308	65

H(24C)	9869	2836	2028	65
H(25A)	1295	4034	4759	70
H(25B)	1804	2910	4498	70
H(25C)	1745	3831	3897	70
H(26A)	4845	3789	5576	64
H(26B)	3664	2889	5512	64
H(26C)	3183	4016	5780	64
H(1)	3737	1914	4278	36

*2) Hoffman side product (**31**)*

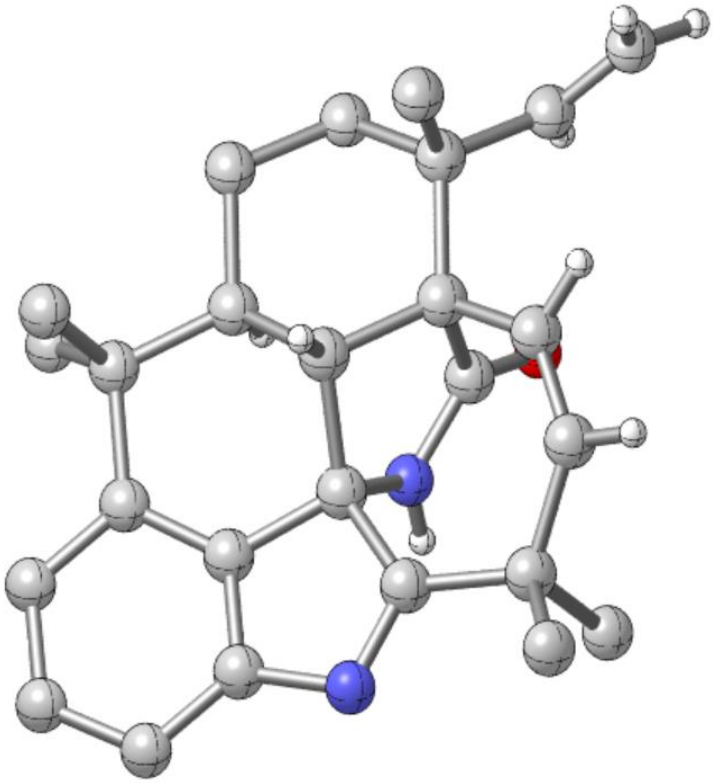


Table 1. Crystal data and structure refinement for hr001_sarpong.

Identification code	PIDAsidepdt	
Empirical formula	C27 H32 Cl2 N2 O	
Formula weight	471.44	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.92760(10) Å	α= 99.7130(10)°.
	b = 10.75250(10) Å	β= 104.8560(10)°.
	c = 12.95480(10) Å	γ = 110.2590(10)°.
Volume	1202.34(2) $Å^3$	
Z	2	
Density (calculated)	1.302 Mg/m^3	
Absorption coefficient	2.591 mm^{-1}	

F(000)	500
Crystal size	0.220 x 0.200 x 0.190 mm^3
Theta range for data collection	3.681 to 74.493°.
Index ranges	-12<=h<=12, -13<=k<=13, -16<=l<=16
Reflections collected	58641
Independent reflections	4913 [R(int) = 0.0411]
Completeness to theta = 74.000°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.83742
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4913 / 0 / 298
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0395, wR2 = 0.1062
R indices (all data)	R1 = 0.0397, wR2 = 0.1063
Extinction coefficient	n/a
Largest diff. peak and hole	0.413 and -0.501 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for hr001_sarpong. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-1072(2)	2198(2)	5225(1)	33(1)
C(2)	162(2)	3369(2)	5555(1)	26(1)
C(3)	1326(2)	4073(1)	6717(1)	23(1)
C(4)	766(2)	3410(2)	7580(1)	29(1)
C(5)	1536(2)	5594(2)	7012(1)	26(1)
C(6)	2783(2)	6455(2)	8127(1)	27(1)
C(7)	4314(2)	6456(1)	8095(1)	21(1)
C(8)	5706(2)	7540(1)	9104(1)	23(1)
C(9)	5939(2)	9005(2)	9015(1)	31(1)
C(10)	5441(2)	7411(2)	10210(1)	30(1)
C(11)	7139(2)	7310(1)	9118(1)	23(1)
C(12)	8596(2)	8154(2)	9919(1)	29(1)
C(13)	9804(2)	7756(2)	10046(1)	30(1)
C(14)	9607(2)	6462(2)	9428(1)	28(1)
C(15)	8192(2)	5657(1)	8629(1)	24(1)
C(16)	7035(2)	6137(1)	8415(1)	21(1)
C(17)	5629(2)	4992(1)	7561(1)	20(1)
C(18)	4209(2)	4937(1)	7857(1)	20(1)
C(19)	2890(2)	3995(1)	6764(1)	20(1)
C(20)	3621(2)	4528(1)	5917(1)	20(1)
C(21)	2641(2)	2474(1)	6527(1)	24(1)
C(22)	3591(2)	1852(1)	6519(1)	26(1)
C(23)	5281(2)	2365(1)	6723(1)	24(1)
C(24)	5514(2)	2292(2)	5578(1)	30(1)
C(25)	5886(2)	1390(2)	7241(1)	32(1)
C(26)	6199(2)	3821(1)	7491(1)	22(1)
C(27)	699(2)	1729(2)	2886(1)	35(1)
Cl(1)	1733(1)	687(1)	3041(1)	49(1)
Cl(2)	-1291(1)	740(1)	2375(1)	40(1)
N(1)	7631(1)	4235(1)	8024(1)	25(1)
N(2)	5147(1)	5112(1)	6419(1)	20(1)

O(1)	2957(1)	4395(1)	4931(1)	23(1)

Table 3. Bond lengths [Å] and angles [°] for hr001_sarpong.

C(1)-C(2)	1.323(2)
C(1)-H(1A)	0.9500
C(1)-H(1B)	0.9500
C(2)-C(3)	1.5146(19)
C(2)-H(2A)	0.9500
C(3)-C(5)	1.5408(19)
C(3)-C(4)	1.5421(18)
C(3)-C(19)	1.5706(18)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-C(6)	1.522(2)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7)	1.5301(19)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.5558(19)
C(7)-C(18)	1.5722(17)
C(7)-H(7)	1.0000
C(8)-C(11)	1.5226(19)
C(8)-C(9)	1.5397(18)
C(8)-C(10)	1.5410(18)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(16)	1.3797(19)
C(11)-C(12)	1.412(2)
C(12)-C(13)	1.389(2)
C(12)-H(12)	0.9500
C(13)-C(14)	1.404(2)

C(13)-H(13)	0.9500
C(14)-C(15)	1.380(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.4000(19)
C(15)-N(1)	1.4295(18)
C(16)-C(17)	1.4987(18)
C(17)-N(2)	1.4763(16)
C(17)-C(18)	1.5384(18)
C(17)-C(26)	1.5477(17)
C(18)-C(19)	1.5467(18)
C(18)-H(18)	1.0000
C(19)-C(21)	1.5298(17)
C(19)-C(20)	1.5467(17)
C(20)-O(1)	1.2369(16)
C(20)-N(2)	1.3454(18)
C(21)-C(22)	1.333(2)
C(21)-H(21)	0.9500
C(22)-C(23)	1.507(2)
C(22)-H(22)	0.9500
C(23)-C(26)	1.5139(19)
C(23)-C(25)	1.5414(19)
C(23)-C(24)	1.5520(19)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-N(1)	1.2850(19)
C(27)-Cl(2)	1.7632(17)
C(27)-Cl(1)	1.7653(17)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
N(2)-H(2)	0.84(2)

C(2)-C(1)-H(1A)	120.0

C(2)-C(1)-H(1B)	120.0
H(1A)-C(1)-H(1B)	120.0
C(1)-C(2)-C(3)	127.24(14)
C(1)-C(2)-H(2A)	116.4
C(3)-C(2)-H(2A)	116.4
C(2)-C(3)-C(5)	107.12(11)
C(2)-C(3)-C(4)	111.45(12)
C(5)-C(3)-C(4)	108.59(11)
C(2)-C(3)-C(19)	110.78(11)
C(5)-C(3)-C(19)	110.04(11)
C(4)-C(3)-C(19)	108.81(11)
C(3)-C(4)-H(4A)	109.5
C(3)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(3)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
C(6)-C(5)-C(3)	112.57(11)
C(6)-C(5)-H(5A)	109.1
C(3)-C(5)-H(5A)	109.1
C(6)-C(5)-H(5B)	109.1
C(3)-C(5)-H(5B)	109.1
H(5A)-C(5)-H(5B)	107.8
C(5)-C(6)-C(7)	109.84(11)
C(5)-C(6)-H(6A)	109.7
C(7)-C(6)-H(6A)	109.7
C(5)-C(6)-H(6B)	109.7
C(7)-C(6)-H(6B)	109.7
H(6A)-C(6)-H(6B)	108.2
C(6)-C(7)-C(8)	113.43(11)
C(6)-C(7)-C(18)	109.92(11)
C(8)-C(7)-C(18)	115.71(11)
C(6)-C(7)-H(7)	105.6
C(8)-C(7)-H(7)	105.6
C(18)-C(7)-H(7)	105.6
C(11)-C(8)-C(9)	109.59(12)

C(11)-C(8)-C(10)	108.09(11)
C(9)-C(8)-C(10)	108.84(11)
C(11)-C(8)-C(7)	110.13(11)
C(9)-C(8)-C(7)	109.41(11)
C(10)-C(8)-C(7)	110.75(12)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(16)-C(11)-C(12)	115.87(13)
C(16)-C(11)-C(8)	120.23(12)
C(12)-C(11)-C(8)	123.42(12)
C(13)-C(12)-C(11)	121.47(13)
C(13)-C(12)-H(12)	119.3
C(11)-C(12)-H(12)	119.3
C(12)-C(13)-C(14)	121.31(14)
C(12)-C(13)-H(13)	119.3
C(14)-C(13)-H(13)	119.3
C(15)-C(14)-C(13)	116.78(13)
C(15)-C(14)-H(14)	121.6
C(13)-C(14)-H(14)	121.6
C(14)-C(15)-C(16)	121.38(13)
C(14)-C(15)-N(1)	127.29(13)
C(16)-C(15)-N(1)	110.91(12)
C(11)-C(16)-C(15)	121.80(13)
C(11)-C(16)-C(17)	127.97(12)
C(15)-C(16)-C(17)	107.98(11)
N(2)-C(17)-C(16)	118.52(11)

N(2)-C(17)-C(18)	99.11(10)
C(16)-C(17)-C(18)	110.09(10)
N(2)-C(17)-C(26)	106.30(10)
C(16)-C(17)-C(26)	99.15(10)
C(18)-C(17)-C(26)	125.07(11)
C(17)-C(18)-C(19)	102.36(10)
C(17)-C(18)-C(7)	106.12(10)
C(19)-C(18)-C(7)	110.85(10)
C(17)-C(18)-H(18)	112.3
C(19)-C(18)-H(18)	112.3
C(7)-C(18)-H(18)	112.3
C(21)-C(19)-C(18)	113.68(11)
C(21)-C(19)-C(20)	104.82(10)
C(18)-C(19)-C(20)	99.20(10)
C(21)-C(19)-C(3)	108.06(11)
C(18)-C(19)-C(3)	113.10(10)
C(20)-C(19)-C(3)	117.73(11)
O(1)-C(20)-N(2)	124.53(12)
O(1)-C(20)-C(19)	127.26(12)
N(2)-C(20)-C(19)	108.12(11)
C(22)-C(21)-C(19)	132.43(13)
C(22)-C(21)-H(21)	113.8
C(19)-C(21)-H(21)	113.8
C(21)-C(22)-C(23)	133.82(13)
C(21)-C(22)-H(22)	113.1
C(23)-C(22)-H(22)	113.1
C(22)-C(23)-C(26)	113.79(11)
C(22)-C(23)-C(25)	109.00(12)
C(26)-C(23)-C(25)	108.29(12)
C(22)-C(23)-C(24)	107.87(12)
C(26)-C(23)-C(24)	109.80(11)
C(25)-C(23)-C(24)	107.95(11)
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5

H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(23)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
N(1)-C(26)-C(23)	120.53(12)
N(1)-C(26)-C(17)	113.69(12)
C(23)-C(26)-C(17)	124.98(12)
Cl(2)-C(27)-Cl(1)	112.08(9)
Cl(2)-C(27)-H(27A)	109.2
Cl(1)-C(27)-H(27A)	109.2
Cl(2)-C(27)-H(27B)	109.2
Cl(1)-C(27)-H(27B)	109.2
H(27A)-C(27)-H(27B)	107.9
C(26)-N(1)-C(15)	107.59(11)
C(20)-N(2)-C(17)	112.86(11)
C(20)-N(2)-H(2)	123.6(14)
C(17)-N(2)-H(2)	121.0(14)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for hr001_sarpong. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	31(1)	34(1)	30(1)	6(1)	11(1)	10(1)
C(2)	28(1)	31(1)	24(1)	8(1)	12(1)	14(1)
C(3)	26(1)	26(1)	21(1)	8(1)	11(1)	12(1)
C(4)	30(1)	36(1)	27(1)	12(1)	16(1)	14(1)
C(5)	30(1)	29(1)	25(1)	7(1)	9(1)	17(1)
C(6)	34(1)	27(1)	24(1)	4(1)	10(1)	18(1)
C(7)	31(1)	20(1)	17(1)	6(1)	9(1)	14(1)
C(8)	33(1)	21(1)	18(1)	4(1)	9(1)	14(1)
C(9)	41(1)	21(1)	31(1)	6(1)	12(1)	16(1)
C(10)	39(1)	33(1)	18(1)	5(1)	10(1)	17(1)
C(11)	32(1)	22(1)	17(1)	7(1)	9(1)	12(1)
C(12)	35(1)	26(1)	21(1)	3(1)	7(1)	11(1)
C(13)	30(1)	31(1)	22(1)	6(1)	5(1)	9(1)
C(14)	28(1)	33(1)	26(1)	11(1)	10(1)	14(1)
C(15)	31(1)	24(1)	21(1)	8(1)	12(1)	14(1)
C(16)	28(1)	21(1)	18(1)	8(1)	9(1)	11(1)
C(17)	28(1)	18(1)	17(1)	7(1)	10(1)	11(1)
C(18)	27(1)	20(1)	17(1)	7(1)	10(1)	12(1)
C(19)	26(1)	19(1)	18(1)	7(1)	11(1)	10(1)
C(20)	27(1)	16(1)	19(1)	6(1)	11(1)	10(1)
C(21)	29(1)	19(1)	25(1)	7(1)	13(1)	8(1)
C(22)	35(1)	17(1)	29(1)	7(1)	14(1)	10(1)
C(23)	33(1)	19(1)	24(1)	6(1)	13(1)	14(1)
C(24)	38(1)	27(1)	26(1)	4(1)	15(1)	15(1)
C(25)	45(1)	24(1)	33(1)	9(1)	15(1)	22(1)
C(26)	31(1)	20(1)	21(1)	8(1)	14(1)	14(1)
C(27)	38(1)	24(1)	37(1)	6(1)	13(1)	7(1)
Cl(1)	55(1)	50(1)	48(1)	18(1)	15(1)	30(1)
Cl(2)	38(1)	34(1)	38(1)	-2(1)	14(1)	7(1)
N(1)	30(1)	24(1)	26(1)	8(1)	12(1)	14(1)
N(2)	26(1)	21(1)	16(1)	7(1)	10(1)	10(1)

O(1)	27(1)	26(1)	17(1)	7(1)	9(1)	9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for hr001_sarpong.

	x	y	z	U(eq)
H(1A)	-1305	1704	5744	39
H(1B)	-1726	1850	4469	39
H(2A)	338	3818	5000	31
H(4A)	527	2419	7360	43
H(4B)	-152	3541	7614	43
H(4C)	1568	3848	8314	43
H(5A)	1795	6000	6421	32
H(5B)	560	5629	7034	32
H(6A)	2525	6066	8727	32
H(6B)	2859	7415	8290	32
H(7)	4449	6757	7425	26
H(9A)	6142	9107	8325	46
H(9B)	6808	9688	9655	46
H(9C)	5017	9151	9008	46
H(10A)	4632	7710	10275	45
H(10B)	6387	7994	10834	45
H(10C)	5135	6445	10223	45
H(12)	8752	9014	10381	34
H(13)	10784	8372	10562	36
H(14)	10409	6156	9553	34
H(18)	4139	4552	8503	24
H(21)	1609	1853	6352	29
H(22)	3096	875	6346	31
H(24A)	5064	2847	5206	44
H(24B)	5017	1329	5115	44
H(24C)	6609	2653	5691	44
H(25A)	6966	1674	7321	48
H(25B)	5301	440	6756	48
H(25C)	5773	1436	7974	48
H(27A)	982	2393	3616	42

H(27B)	981	2266	2366	42
H(2)	5770(20)	5300(20)	6072(17)	37(5)