Supporting Information

One-Carbon Insertion and Polarity Inversion Enabled a Pyrrole Strategy to the Total Syntheses of Pyridine-Containing *Lycopodium* Alkaloids: Complanadine A and Lycodine

Donghui Ma,[†] Brandon S. Martin,[†] Katelyn S. Gallagher, Takeru Saito, and Mingji Dai[*]

Department of Chemistry and Center for Cancer Research, Purdue University,
West Lafayette, Indiana 47907, United States

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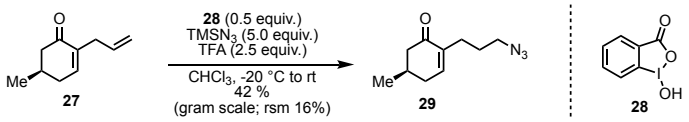
1. General Information

All reactions sensitive to air or moisture were conducted under argon atmosphere in dry and freshly distilled solvents under anhydrous conditions, unless otherwise noted. Anhydrous tetrahydrofuran (THF), dichloromethane (DCM), Dimethylformamide (DMF) and toluene were purified by passing the pre-degassed solvents through activated alumina columns. All other solvents and reagents were used as obtained from commercial sources (Aldrich, TCI, Alfa Aeser, Acros) without further purification unless otherwise noted. Room temperature (r.t.) is around 23 ^{o}C. Flash column chromatography was performed using silica gel (230-400 mesh). Thin layer chromatography (TLC) was performed using glass-backed silica plates (Silicycle). NMR spectra were recorded on a Bruker AV-500 spectrometer at room temperature (^{1}H at 500 MHz, and ^{13}C at 125 MHz). Chemical shifts (δ) were given in ppm with reference to the solvent signal [^{1}H NMR: $CDCl_3$ (7.26), CD_3OD (3.31); ^{13}C NMR: $CDCl_3$ (77.16), CD_3OD (49.00)]. ^{1}H NMR data were reported as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin (p) = quintuplet, m = multiplet, br = broad), coupling constant (Hz), and integration. ^{13}C NMR data were reported in terms of chemical shift and multiplicity. High-resolution mass measurements for compound characterization were carried out using a Waters SYNAPT G2-Si system with QuanTof analyzer or an Agilent 6550 QTOF system. IR data were recorded on a Thermo Nicolet iS50 FT-IR.

2. Experimental Procedures



Synthesis of **29**: A modified reaction condition reported by Xu et al. was used.[1] To a sealable 250 mL round-bottom flask equipped with a stir bar were added known cyclohexenone **27**[2] (1.16 g, 7.73 mmol) and benziodoxole **28** (1.02 g, 3.86 mmol, 0.5 equiv). After this flask was evacuated and backfilled with argon three times, anhydrous $CHCl_3$ (77 mL) was added via syringe. The reaction mixture was then cooled to -20 °C, and $TMSN_3$ (5.4 mL, 38.7 mmol, 5.0 equiv) was added to the reaction followed by addition of trifluoroacetic acid (1.5 mL, 19.3 mmol, 2.5 equiv). After that, the reaction mixture was degassed for three times with argon and warmed up to room temperature slowly and kept stirring for 17 h. The reaction mixture was cooled to 0 °C and saturated $NaHCO_3$ aqueous solution (30 mL) was added to quench the reaction and remove any residual hydrazoic acid. Additional hexanes (200 mL) were added as well. The reaction mixture was extracted with hexanes (3 × 100 mL). The combined organic phase was washed with brine (200 mL), dried over Na_2SO_4, filtered and concentrated. The resulting residue was purified by flash chromatography on silica gel using EtOAc in hexanes (0%~16%) as eluent to give the desired enone-azide **29** (626 mg, 42%) as a light-yellow oil and some recovered **27** (190 mg, 16%) as a light-yellow oil.

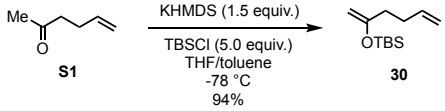
^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.74 – 6.69 (m, 1H), 3.25 (t, *J* = 6.8 Hz, 2H), 2.53 – 2.46 (m, 1H), 2.41 (dt, *J* = 18.4, 5.2 Hz, 1H), 2.25 (t, *J* = 7.6 Hz, 2H), 2.22 – 2.14 (m, 1H), 2.14 – 1.99 (m, 2H), 1.74 – 1.66 (m, 2H), 1.05 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 199.6, 145.4, 138.3, 51.1, 46.7, 34.5, 30.8, 28.0, 27.0, 21.3.

HRMS (ESI): *m/z* Calc. for $C_{10}H_{15}N_3ONa^+$ $[M+Na]^+$: 216.1107, found: 216.1108.

IR (film): 2955, 2872, 2096, 1672, 1382, 1254 cm^{-1}.

$[\alpha]_D^{26}$ = – 53.6 (*c* = 0.25, $CHCl_3$).



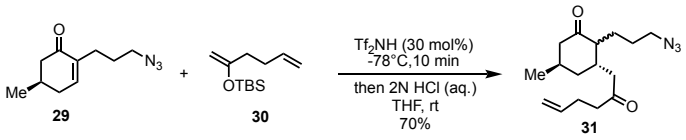
Synthesis of **30**[3]: A solution of KHMDS in THF (1 M, 45.0 mL, 45 mmol, 1.5 equiv.) was added to a solution of TBSCl (22.6 g, 150 mmol, 5.0 equiv.) in a mixture solvent of THF (75 mL) and toluene (60 mL) at -78 °C. To the resulting mixture was added dropwise a solution of allylacetone **S1** (2.94 g, 30 mmol) in toluene (15 mL) at -78°C over 30 min. After stirring at that temperature for 1.5 h, triethylamine (45 mL) was added followed by saturated $NaHCO_3$ aqueous solution (100 mL). The mixture was stirred at room temperature for 20 min and extracted with hexanes (3 × 200 mL). The organic layer was washed with water, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (column was pretreated with 5% trietylamine in hexanes) using hexanes as eluent to give the TBS silyl enol ether **30** (5.98 g, 94%) as a light-yellow oil. This silyl enol ether includes a little bit of inseparable impurities and was used for Mukaiyama-Michael reaction without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.83 (ddt, *J* = 16.9, 10.4, 6.6 Hz, 1H), 5.03 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.96 (ddd, *J* = 10.2, 2.1, 1.1 Hz, 1H), 4.04 (s, 2H), 2.24 (q, *J* = 6.9 Hz, 3H), 2.12 (dd, *J* = 8.7, 6.4 Hz, 2H), 0.93 (s, 6H), 0.17 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 159.0, 138.3, 114.7, 90.0, 36.2, 31.3, 25.8, 18.2, -4.5.

HRMS (ESI): *m/z* Calc. for $C_{12}H_{25}OSi^+$ $[M+H]^+$: 213.1669, found: 213.1666.

IR (film): 2956, 2930, 2858, 1640, 1473, 1254, 1003, 909, 835, 778, 698 cm^{-1}.



Synthesis of **31**: To a solution of enone-azide **29** (484.2 mg, 2.51 mmol), TBS silyl enol ether (2.13 g, 10.0 mmol, 4.0 eq.) in DCM (12.6 mL) under argon at -78 °C was added a solution of triflimide (Tf_2NH, 0.1 M in DCM; 30 mol%, 7.5 mL) dropwise. The reaction solution turned to yellow and was stirred at -78 °C for 10 min. 2 M HCl aqueous solution (12.6 mL) was added followed by THF (12.6 mL) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred at that temperature for 19 h. The reaction mixture was quenched with saturated $NaHCO_3$ aqueous solution (~26 mL), extracted with EtOAc (3 × 60 mL), washed with brine, dried over Na_2SO_4, filtered, and concentrate. The resulting residue was purified by flash chromatography on silica gel using hexanes/EtOAc (20:1~10:1~7:1) as eluent to give olefine-diketone **31** (511 mg, 70%, d.r. = 1:1) as a light-yellow oil.

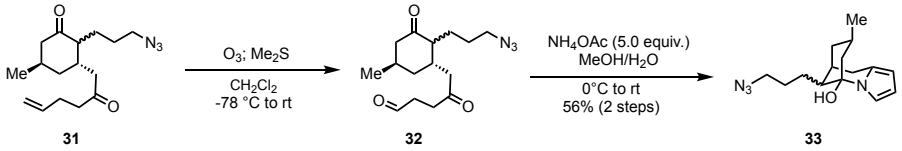
^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.86 – 5.70 (m, 1H), 5.08 – 4.90 (m, 2H), 3.35 – 3.17 (m, 2H), 2.90 – 2.41 (m, 4H), 2.41 – 2.22 (m, 4H), 2.18 – 1.94 (m, 3H), 1.80 – 1.65 (m, 2H), 1.65 – 1.06 (m, 4H), 1.04 – 0.95 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 213.8, 211.9, 208.6, 208.5, 136.9, 115.6, 54.5, 53.1, 51.6, 51.3, 50.5, 47.1, 46.9, 42.7, 42.6, 41.1, 38.4, 36.4, 35.1, 34.6, 31.0, 30.2, 27.9, 27.8, 27.7, 27.1, 26.8, 24.0, 22.4, 21.7.

HRMS (ESI): *m/z* Calc. for $C_{16}H_{25}N_3O_2Na^+$ $[M+Na]^+$: 314.1839, found: 314.1840.

IR (film): 2926, 2093, 1706, 1456, 1257, 914 cm^{-1}.

$[\alpha]_D^{25}$ = + 3.3 (*c* = 0.3, $CHCl_3$).



Synthesis of **32**: Through a stirred solution of **31** (293 mg, 1.0 mmol) in DCM (4 mL) at -78 °C was bubbled ozone gas (~10 min). After the color of the mixture changed to blue, oxygen gas was bubbled to this resulting solution for 10 min, followed by the addition of Me_2S (7.5 mL, 100 mmol, 100 equiv.) at -78 °C. The reaction was allowed to warm slowly to room temperature over 2 h and stirred at that temperature for 24 h. The reaction mixture was concentrated under reduced pressure to give crude aldehyde as yellow oil, and the resulting residue was purified by flash chromatography on silica gel using hexanes/EtOAc (4:1~3:1~2:1) as eluent to give aldehyde **32** (1:1 mixture) as a colorless oil. This aldehyde is not very stable and should be used immediately.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.81 – 9.73 (m, 1H), 3.35 – 3.18 (m, 2H), 2.90 – 1.95 (m, 11H), 1.82 – 1.65 (m, 2H), 1.66 – 1.07 (m, 4H), 1.05 – 0.96 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 213.7, 211.8, 207.2, 207.1, 200.31, 200.25, 54.4, 53.1, 51.6, 51.2, 50.4, 47.1, 46.5, 41.0, 38.3, 37.6, 36.5, 35.5, 35.4, 35.2, 34.5, 30.9, 30.2, 27.5, 27.1, 26.8, 23.9, 22.3, 21.6.

HRMS (ESI): *m/z* Calc. for $C_{15}H_{23}N_3O_3Na^+$ $[M+Na]^+$: 316.1632, found: 316.1631.

IR (film): 2955, 2096, 1708, 1257 cm^{-1}.

$[\alpha]_D^{25}$ = + 0.8 (*c* = 0.25, $CHCl_3$).

Synthesis of **33**: To a solution of the above aldehyde **32** in methanol (16 mL) was added a solution of NH_4OAc (397 mg, 5 mmol, 5 equiv.) in water (4 mL) under argon at 0°C, and the reaction mixture was degassed with argon for three times. The solution was stirred at 0°C for 7 h and stirred at room temperature for 12 h under argon. After most methanol was removed under reduced pressure, the resulting mixture was diluted with water, extracted with DCM (3 × 10 mL), dried with Na_2SO_4,

filtered and concentrated. The resulting residue was purified by flash chromatography on silica gel using hexanes/EtOAc (15:1~10:1) as eluent to give **33** (153 mg, 56%, d.r. = 1.2:1, two steps) as colorless oil.

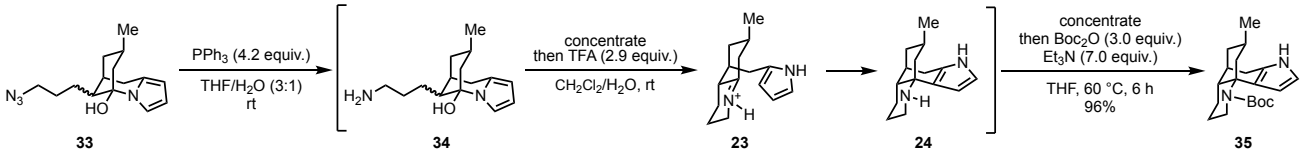
^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.92 – 6.74 (m, 1H), 6.22 – 6.12 (m, 1H), 5.72 – 5.83 (m, 1H), 3.42 – 3.24 (m, 2H), 3.12 – 2.94 (m, 1H), 2.79 – 2.29 (m, 3H), 1.95 – 1.55 (m, 6H), 1.55 – 1.22 (m, 3H), 1.17 – 0.92 (m, 1H), 0.86– 0.76 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 130.0, 129.4, 114.3, 114.1, 109.0, 108.7, 104.0, 103.8, 86.5, 85.4, 51.6, 49.2, 46.7, 46.0, 42.3, 42.1, 34.7, 32.5, 31.9, 30.7, 27.7, 27.0, 26.6, 24.5, 24.1, 22.7, 21.9, 21.7.

HRMS (ESI): *m/z* Calc. for $C_{15}H_{23}N_4O^+$ $[M+H]^+$: 275.1866, found: 275.1868.

IR (film): 3432, 2923, 2869, 2094, 1457, 1346, 1292, 1266, 1103, 1061, 709 cm^{-1}.

$[\alpha]_D^{24}$ = –52.5 (*c* = 0.6, $CHCl_3$).



One-pot procedure to the synthesis of **35**: To a solution of azide **33** (137 mg, 0.500 mmol) in THF/H_2O (3:1, 12.5 mL) at room temperature was added PPh_3 (550 mg, 2.1 mmol, 4.2 eq.) under argon. The reaction mixture was degassed with argon and stirred at room temperature for 24 h. The reaction mixture was concentrated to give crude amine **34** as a light-yellow oil and used directly in the next reaction without any other workup.

To a solution of the above crude amine **34** in DCM (25 mL) was added 2 drops of water (with 18G needle, ~ 30 μL) under argon at room temperature. After TFA (110 μL, 1.45 mmol, 2.9 equiv.) was added, the reaction was allowed to stir at room temperature for 2 days. The reaction mixture was concentrated to give the crude tetracyclic amine **24**, which was used in next reaction without any other workup.

To a solution of the above crude tetracyclic amine **24** and triethylamine (240 μL, 1.75 mmol, 3.5 equiv.) in THF (1 mL) was added a solution of Boc anhydride (164 mg, 0.750 mmol, 1.5 eq.) in THF (1 mL). The solution was heated at 60 °C for 6 h, at which point crude NMR indicated 50% conversion. After cooled to room temperature, triethylamine (240 mL, 1.75 mmol, 3.5 eq.) and a solution of Boc anhydride (164 mg, 750 mmol, 1.5 eq.) in THF (0.5 mL) were added into the reaction mixture. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel using hexanes/EtOAc (15:1~9:1) as eluent to give Boc-protected tetracyclic compound **35** (158 mg, 96%, one-pot) as an off-white foam.

For 1.385 g-scale of **33**, 95% yield of **35** was obtained.

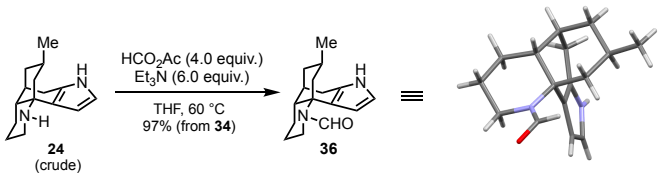
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.71 (s, 1H), 6.63 (s, 1H), 5.95 (s, 1H), 4.04 (d, *J* = 13.2 Hz, 1H), 3.09 – 2.99 (m, 1H), 2.84 (dd, *J* = 16.4, 7.1 Hz, 1H), 2.80 – 2.71 (m, 1H), 2.24 (d, *J* = 16.3 Hz, 1H), 2.11 – 2.02 (m, 1H), 1.69 (dt, *J* = 12.5, 3.5 Hz, 1H), 1.64 – 1.44 (m, 13H), 1.44 – 1.22 (m, 4H), 0.83 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.9, 126.7, 120.3, 116.2, 105.5, 76.9, 61.5, 46.9, 45.1, 44.1, 43.4, 35.8, 28.8, 27.3, 27.1, 25.9, 25.6, 22.6.

HRMS (ESI): *m/z* Calc. for $C_{20}H_{31}N_2O_2^+$ $[M+H]^+$: 331.2380, found: 331.2382.

IR (film): 3348, 2922, 1678, 1648, 1390, 1364, 1268, 1173, 1156, 1141, 1078, 720, 696 cm^{-1}.

$[\alpha]_D^{25}$ = + 53.2 (*c* = 0.25, $CHCl_3$).



Synthesis of **36**: Formic acid (320 μL, 8.00 mmol) was added dropwise to Ac_2O (760 μL, 8.00 mmol) under argon at room temperature. The reaction mixture was stirred for 2 h at 60 °C to give the acetic formic anhydride solution (7.3 M; 8.00 mmol HCO_2Ac in about 1.1 mL; not isolated)[4]. To a solution of the above crude tetracyclic amine **24** (288 mg, 0.200 mmol, 16% purity) in THF (0.8 mL) and triethylamine (170 μL, 1.2 mmol, 6 equiv.) was added the above freshly prepared HCO_2Ac (110 μL, 0.8 mmol, 4 equiv.) under argon. The reaction was stirred at 60 °C for 4 h. The reaction mixture was cooled to rt. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using EtOAc in hexanes (30%~50%) as eluent to give tetracyclic compound **36** (50.1 mg, 97%, 3 steps) as a white solid. The absolute configuration of **36** has been confirmed by X-ray crystallographic analysis.

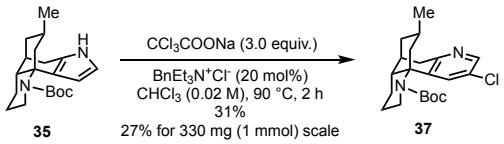
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.58 (s, 1H), 8.03 (s, 1H), 6.65 (t, *J* = 2.7 Hz, 1H), 5.81 (t, *J* = 2.7 Hz, 1H), 4.52 – 4.42 (m, 1H), 2.88 (dd, *J* = 16.5, 6.9 Hz, 1H), 2.64 – 2.52 (m, 1H), 2.31 (d, *J* = 16.5 Hz, 1H), 2.17 – 2.09 (m, 1H), 2.06 – 1.97 (m, 1H), 1.72 – 1.54 (m, 3H), 1.52 – 1.37 (m, 5H), 1.35 – 1.23 (m, 1H), 0.87 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.1, 126.9, 119.0, 117.0, 104.2, 59.8, 45.1, 45.1, 42.9, 37.4, 35.0, 26.8, 26.4, 25.6, 25.4, 22.4.

HRMS (ESI): *m/z* Calc. for $C_{16}H_{23}N_2O^+$ $[M+H]^+$: 259.1805, found: 259.1806.

IR (film): 3278, 2922, 1636, 1588, 1391, 1263, 1129, 735, 694 cm^{-1}.

$[\alpha]_D^{25}$ = + 57.3 (*c* = 0.3, $CHCl_3$).



Synthesis of **37**: A flame-dried microwave tube was charged with a stir bar, powdered sodium trichloroacetate (57.2 mg, 0.300 mmol, 3.0 equiv.) and Boc-protected tetracyclic compound **35** (33 mg, 0.100 mmol). A solution of $BnEt_3N^+Cl^-$ (4.6 mg, 20 μmol, 20 mol%) in anhydrous $CHCl_3$ (5.0 mL, *c* = 0.02 M) was added in one portion under argon when stirring. The reaction mixture was stirred for 10 min at room temperature and then heated at 90 °C for 2 h. The reaction was filtered through celite, washed with $CHCl_3$ (3 × 6 mL), and concentrated. The resulting residue was purified by flash chromatography on silica gel using acetone in hexanes (5%~15%) as eluent to give an impure 3-chloropyridine **37** as a black-red oil. The impure product was further purified by preparative thin layer chromatography (hexanes/acetone=20:1) to give the pure 3-chloropyridine **37** (11.5 mg, 31%) as a light-yellow oil.

For 330 mg-scale of **35**, the reaction yield was 27%.

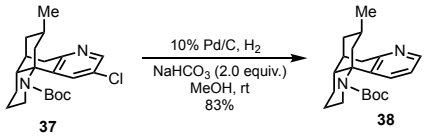
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.35 (d, *J* = 2.4 Hz, 1H), 7.53 (d, *J* = 2.4 Hz, 1H), 4.11 (dq, *J* = 13.6, 2.9 Hz, 1H), 3.16 (dd, *J* = 18.9, 7.3 Hz, 1H), 2.74 (ddd, *J* = 13.2, 3.9, 1.7 Hz, 1H), 2.66 (d, *J* = 18.9 Hz, 1H), 2.44 – 2.34 (m, 1H), 2.13 (dt, *J* = 6.8, 3.4 Hz, 1H), 1.89 – 1.80 (m, 2H), 1.72 (dp, *J* = 13.0, 2.1 Hz, 1H), 1,64 – 1,46 (m, 11H), 1.40 – 1.09 (m, 4H), 0.84 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.3, 156.2, 146.4, 137.4, 133.7, 130.0, 80.2, 64.0, 48.4, 44.4, 43.5, 43.0, 34.7, 34.3, 28.7, 27.8, 26.7, 25.7, 22.5.

HRMS (ESI): *m/z* Calc. for $C_{21}H_{30}ClN_2O_2^+$ $[M+H]^+$: 377.1990, found: 377.1990.

IR (film): 2924, 1698, 1679, 1455, 1435, 1365, 1268, 1251, 1156, 1115, 968 cm^{-1}.

$[\alpha]_D^{26}$ = + 102.0 (*c* = 0.3, $CHCl_3$).



Synthesis of **38**: To a solution of 3-chloropyridine **37** (102.4 mg, 272 mmol) in MeOH (6 mL) was added 10% Pd/C (102 mg) and $NaHCO_3$ (46 mg, 0.543 mmol, 2 equiv.). The mixture was degassed with H_2 for three times. After stirring at room temperature under H_2 for 36 h, the reaction mixture was filtered through celite, washed with MeOH and concentrated. The resulting residue was purified by preparative thin layer chromatography (hexanes/ethyl acetate=4:1) to afford pyridine **38** (77.1 mg, 83%) as a light-yellow oil.

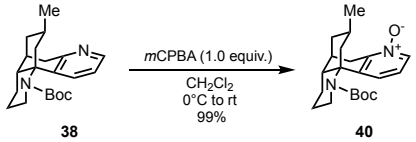
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.40 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.54 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.13 (dd, *J* = 7.9, 4.7 Hz, 1H), 4.10 (dq, *J* = 13.7, 3.0 Hz, 1H), 3.22 (dd, *J* = 18.9, 7.4 Hz, 1H), 2.75 (ddd, *J* = 13.2, 4.0, 1.8 Hz, 1H), 2.70 (d, *J* = 18.9 Hz, 1H), 2.43 – 2.33 (m, 1H), 2.13 (dq, *J* = 6.8, 3.3 Hz, 1H), 1.89 – 1.79 (m, 2H), 1.76 – 1.69 (m, 1H), 1.65 – 1.46 (m, 11H), 1.40 – 1.12 (m, 4H), 0.83 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 158.0, 156.4, 147.5, 135.9, 134.2, 122.1, 79.9, 64.1, 48.6, 44.3, 43.8, 43.2, 35.2, 34.5, 28.7, 27.8, 26.8, 25.9, 22.6.

HRMS (ESI): *m/z* Calc. for $C_{21}H_{31}N_2O_2^+$ $[M+H]^+$: 343.2380, found: 343.2380.

IR (film): 2923, 1698, 1675, 1455, 1437, 1425, 1389, 1365, 1269, 1252, 1155, 962 cm^{-1}.

$[\alpha]_D^{26}$ = + 97.7 (*c* = 0.75, $CHCl_3$).



Synthesis of **40**: To a solution of pyridine **38** (36.6 mg, 0.107 mmol) in DCM (2.0 mL) was added a solution of *m*CPBA (24.0 mg, 0.107, 77% purity) in DCM (1.0 mL) at 0 °C. After stirring at room temperature for 2 h, the reaction mixture was quenched with saturated Na_2SO_3 aqueous solution (1.0 mL), treated with 2 M Na_2CO_3 aqueous solution (1.0 mL), extracted with DCM (3 × 3 mL), dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by flash chromatography on silica gel using DCM/MeOH (19:1) as eluent to afford pyridine-*N*-oxide **40** (38.0 mg, 99%) as a light-yellow oil.

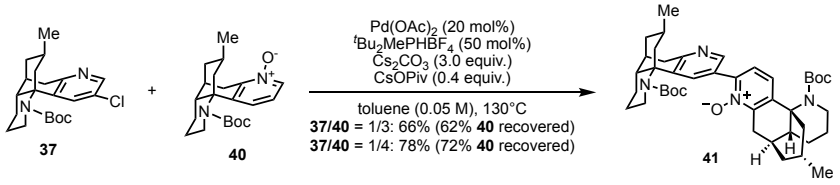
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.17 (dd, *J* = 6.2, 1.3 Hz, 1H), 7.20 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.15 (dd, *J* = 7.9, 6.3 Hz, 1H), 4.11 (dq, *J* = 13.7, 2.9 Hz, 1H), 3.01 (dd, *J* = 20.3, 7.5 Hz, 1H), 2.87 – 2.76 (m, 2H), 2.40 – 2.30 (m, 1H), 2.22 (dt, *J* = 6.7, 3.4 Hz, 1H), 1.90 – 1.77 (m, 2H), 1.70 (dp, *J* = 12.8, 2.1 Hz, 1H), 1.63 – 1.44 (m, 12H), 1.35 – 1.13 (m, 3H), 0.83 (d, *J* = 6.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.1, 149.4, 140.2, 137.3, 123.5, 123.1, 80.2, 63.6, 47.9, 44.5, 43.3, 42.6, 33.3, 28.7, 28.5, 27.6, 26.5, 25.5, 22.3.

HRMS (ESI): *m/z* Calc. for $C_{21}H_{31}N_2O_3^+$ $[M+H]^+$: 359.2329, found: 359.2328.

IR (film): 2926, 1698, 1675, 1430, 1389, 1365, 1250, 1154, 892 cm^{-1}.

$[\alpha]_D^{26}$ = + 73.4 (*c* = 0.5, $CHCl_3$).



Synthesis of **41** with **37**/**40** (1:3): 3-Chloropyridine **37** (4.0 mg, 10.6 μmol, 1.0 equiv.) and pyridine-*N*-oxide **40** (11.4 mg, 31.8 μmol, 3.0 equiv.) were added into a microwave tube. The mixture was azeotroped with toluene for three times (3 × 1 mL), transferred into the glovebox, and then combined with $Pd(OAc)_2$ (0.5 mg, 21.2 μmol, 20 mol%), *t*Bu_2MeP·HBF_4 (1.3 mg, 5.31 μmol, 50 mol%), CsOPiv (1.0 mg, 4.24 μmol, 0.4 equiv.) and cesium carbonate powder (Cs_2CO_3, 10.3 mg, 31.8 μmol, 3.0 equiv.). The tube was sealed with a rubber septum and removed from the glovebox. After toluene (0.22 ml, 0.05 M) was added, the resulting mixture was stirred at 130°C for 14 h (overnight) and cooled to room temperature. The dark resulting mixture was filtered by celite and concentrated. The residue was purified by preparative thin layer chromatography (DCM/acetone=2:1) to **41** (4.9 mg, 66%) as a white solid and the recycled pyridine-*N*-oxide **40** (7.1 mg, 62%) as a light-yellow oil.

Synthesis of **41** with **37**/**40** (1:4): 3-Chloropyridine **37** (10.0 mg, 26.5μmol, 1.0 equiv.) and pyridine-*N*-oxide **40** (38.0 mg, 106 μmol, 4.0 equiv.) were added into a microwave tube. The mixture was azeotroped with toluene for three times (3 × 1 mL), transferred into the glovebox, and then combined with $Pd(OAc)_2$ (1.2 mg, 5.31 μmol, 20 mol%), *t*Bu_2MeP·HBF_4 (3.3 mg, 13.3 μmol, 50 mol%), CsOPiv (2.5 mg, 10.6 μmol, 0.4 equiv.) and cesium carbonate powder (Cs_2CO_3, 26.0 mg, 80.0 μmol, 3.0 equiv.). The tube was sealed with a rubber septum and removed from the glovebox. After toluene (0.53 mL, 0.05 M) was added, the resulting mixture was stirred at 130°C for 17 h (overnight) and cooled to room temperature. The dark resulting mixture was filtered by celite and concentrated. The residue was purified by preparative thin layer chromatography (DCM/acetone=2:1) to afford **41** (14.5 mg, 78%) as a white solid and the recycled pyridine-*N*-oxide **40** (27.3 mg, 72%) as a light-yellow oil.

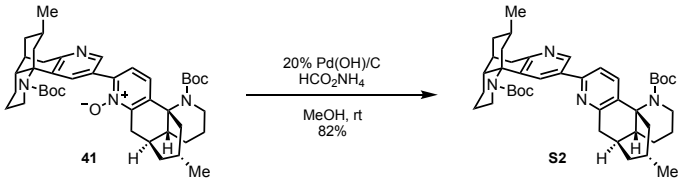
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.89 (d, *J* = 2.1 Hz, 1H), 8.08 (d, *J* = 2.1 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 4.15 (d, *J* = 14.5 Hz, 2H), 3.25 (dd, *J* = 19.1, 7.3 Hz, 1H), 3.03 (dd, *J* = 20.3, 7.5 Hz, 1H), 2.91 – 2.70 (m, 4H), 2.58 – 2.49 (m, 1H), 2.48 – 2.39 (m, 1H), 2.25 (dd, *J* = 7.1, 3.2 Hz, 1H), 2.17 (dd, *J* = 6.9, 3.4 Hz, 1H), 1.93 – 1.81 (m, 4H), 1.80 – 1.67 (m, 3H), 1.66 – 1.47 (m, 21H), 1.40 – 1.20 (m, 8H), 0.87 (d, *J* = 5.9 Hz, 3H), 0.84 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 158.8, 156.8, 156.2, 150.0, 147.8, 144.3, 139.1, 135.2, 134.9, 127.8, 124.1, 122.7, 80.2, 64.3, 63.7, 48.5, 47.9, 44.5, 44.4, 43.9, 43.2, 43.1, 42.7, 35.3, 34.5, 33.5, 29.0, 28.7, 27.8, 27.6, 26.7, 26.5, 25.8, 25.6, 22.5, 22.4.

HRMS (ESI): *m/z* Calc. for $C_{42}H_{59}N_4O_5^+$ $[M+H]^+$: 699.4480, found: 699.4480.

IR (film): 2924, 1698, 1676, 1454, 1389, 1364, 1268, 1252, 1155, 1115, 735 cm^{-1}.

$[\alpha]_D^{25}$ = + 128.5 (*c* = 0.2, $CHCl_3$).



Synthesis of Boc-protected complanadine A (**S2**): To a 25 mL round-bottom flask was added **41** (7.7 mg, 11.0 μmol), ammonium formate (69 mg, 1.10 mmol, 100 equiv.), $Pd(OH)_2$/C (20% w/w, 50% wet, 46.2 mg) and methanol (8 mL). The mixture was degassed with argon for three times and stirred at room temperature for 6 h. The reaction was filtered through celite, washed with MeOH and concentrated. The resulting residue was purified by preparative thin layer chromatography (hexanes/acetone=2:1) to afford Boc-protected complanadine A (**S2**) (6.2 mg, 82%) as a white solid.

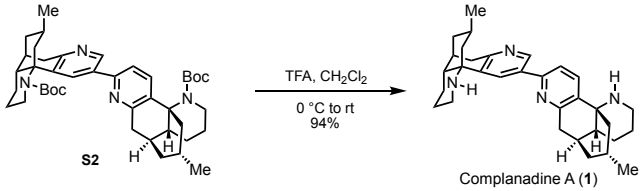
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.96 (d, *J* = 2.1 Hz, 1H), 8.19 (d, *J* = 2.1 Hz, 1H),7.59 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 4.15 (dd, *J* = 19.0, 15.5 Hz, 2H), 3.24 (ddd, *J* = 21.9, 19.0, 7.3 Hz, 2H), 2.92 (dd, *J* = 12.5, 2.0 Hz, 1H), 2.82 – 2.70 (m, 3H), 2.46 (qd, *J* = 13.4, 2.7 Hz, 2H), 2.16 (ddt, *J* = 13.9, 7.1, 3.3 Hz, 2H), 1.92 – 1.79 (m, 4H), 1.73 (t, *J* = 12.6 Hz, 2H), 1.66 – 1.47 (m, 22H), 1.45 – 1.19 (m, 8H), 0.83 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 158.5, 158.1, 156.7, 156.4, 152.6, 145.7, 135.8, 135.0, 134.9, 133.7, 132.8, 118.8, 80.1, 79.9, 64.24, 64.16, 48.6, 48.6, 44.3, 43.9, 43.8, 43.2, 43.1, 35.4, 35.0, 34.6, 34.5, 28.8, 28.8, 27.94, 27.89, 26.8, 26.7, 25.88, 25.85, 22.54, 22.49.

HRMS (ESI): *m/z* Calc. for $C_{42}H_{59}N_4O_4^+$ $[M+H]^+$: 683.4531, found: 683.4531.

IR (film): 2923, 1697, 1675, 1445, 1389, 1364, 1267, 1251, 1154, 735 cm^{-1}.

$[\alpha]_D^{25}$ = + 113.0 (*c* = 0.1, $CHCl_3$).



Synthesis of Complanadine A (**1**): To a solution of Boc-protected complanadine A (**S2**) (6.0 mg, 8.79 μmol) in DCM (0.6 mL) was added dropwise TFA (0.2 mL) at 0 °C and the resulting solution was stirred at room temperature for 1 h. The reaction solution was cooled to 0°C and adjusted the pH to 12 with 2 M NaOH aqueous solution and extracted with DCM (3 × 2 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated to yield crude complanadine A (**1**) (impure from ^{1}H NMR and major impurities include some grease). The resulting residue was further purified by flash chromatography on basic aluminum oxide using DCM/MeOH (19:0 ~ 19:1) as eluent to afford complanadine A (**1**) (4.0 mg, 94%) as a pale-yellow oil.

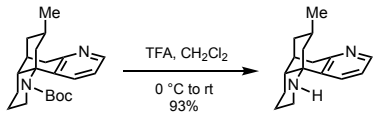
^{1}H NMR (500 MHz, CD_3OD) δ = 8.89 (d, *J* = 2.1 Hz, 1H), 8.45 (d, *J* = 2.1 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 3.23 (ddd, *J* = 19.2, 12.2, 7.2 Hz, 2H), 2.84 – 2.71 (m, 4H), 2.50 (tdd, *J* = 12.4, 9.5, 2.9 Hz, 2H), 2.17 (dq, *J* = 7.1, 3.7, 3.3 Hz, 2H), 1.84 (dp, *J* = 13.2, 2.1 Hz, 2H), 1.75 (ddt, *J* = 13.0, 10.0, 3.1 Hz, 2H), 1.70 – 1.64 (m, 1H), 1.64 – 1.55 (m, 6H), 1.52 (ddd, *J* = 12.0, 3.8, 1.7 Hz, 1H), 1.42 (tt, *J* = 12.5, 3.9 Hz, 2H), 1.38 – 1.16 (m, 8H), 0.83 (d, *J* = 6.3 Hz, 3H), 0.82 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (125 MHz, CD_3OD) δ = 160.5, 159.9, 153.7, 146.1, 137.7, 136.7, 135.9, 135.1, 133.7, 120.5, 57.9, 57.8, 51.7, 51.6, 44.9, 44.8, 44.7, 42.1, 36.2, 35.7, 34.9, 34.8, 27.7, 27.3, 27.1, 22.41, 22.38.

HRMS (ESI): *m/z* Calc. for $C_{32}H_{43}N_4^+$ $[M+H]^+$: 483.3482, found: 483.3481.

IR (film): 2921, 2853, 1452, 1376, 1259, 1142, 1099, 700 cm^{-1}.

$[\alpha]_D^{25}$ = – 24.0 (*c* = 0.1, MeOH).



38 Lycodine (**4**)

Synthesis of Lycodine (**4**): To a solution of pyridine **38** (5.0 mg, 14.6 μmol) in DCM (0.6 mL) was added dropwise TFA (0.2 mL) at 0 °C and the resulting solution was stirred at room temperature for 1 h. The reaction solution was cooled to 0°C and adjusted the pH to 12 with 2 M NaOH aqueous solution and extracted with DCM (3 × 2 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated to yield crude lycodine (**4**) (pure from ^{1}H NMR besides a little bit of grease). The resulting residue was further purified by flash chromatography on basic aluminum oxide using DCM/MeOH (19:0 ~ 19:1) as eluent to afford lycodine (**4**) (3.3 mg, 93%) as a white solid.

^{1}H NMR (500 MHz, CD_3OD) δ = 8.30 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.91 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.28 (dd, *J* = 7.9, 4.8 Hz, 1H), 3.15 (dd, *J* = 18.8, 7.2 Hz, 1H), 2.75 (ddt, *J* = 12.6, 4.1, 1.9 Hz, 1H), 2.68 (d, *J* = 18.8 Hz, 1H), 2.43 (td, *J* = 12.5, 3.0 Hz, 1H), 2.13 (dq, *J* = 6.9, 3.4 Hz, 1H), 1.81 (ddt, *J* = 13.2, 4.6, 2.2 Hz, 1H), 1.72 (dt, *J* = 12.9, 3.3 Hz, 1H), 1.65 (dt, *J* = 12.7, 3.9 Hz, 1H), 1.62 – 1.53 (m, 2H), 1.48 (ddd, *J* = 12.2, 4.1, 1.8 Hz, 1H), 1.44 – 1.35 (m, 1H), 1.35 – 1.26 (m, 2H), 1.22 – 1.10 (m, 2H), 0.81 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (125 MHz, CD_3OD) δ = 159.6, 147.4, 137.7, 135.4, 123.3, 57.7, 51.6, 44.8, 44.6, 42.0, 35.7, 34.8, 27.6, 27.2, 27.0, 22.4.

HRMS (ESI): *m/z* Calc. for $C_{16}H_{23}N_2^+$ $[M+H]^+$: 243.1856, found: 243.1856.

IR (film): 3297, 2921, 2852, 1574, 1436, 1377, 1129, 806, 735 cm^{-1}.

$[\alpha]_D^{25}$ = – 8.0 (*c* = 0.075, EtOH).

3. Natural Product NMR Data Comparison

Table S1. ^{1}H NMR Data Comparison of Natural (Kobayashi's[5]) and Synthetic (Sarpong's,[6] Siegel's,[7] Hirama/Tsukano's,[8a] and ours) Complanadine A (**1**) [CD_3OD (ppm, Hz, Amount of Proton)]

entry	**Kobayashi's**	**Sarpong's**	**Siegel's**	**Hirama/Tsukano's**	**Ours**
1	9.03 (1H, d, 2.1)	8.99 (s, 1H)	8.93 (s, 1H)	8.89 (d, 1.7 Hz, 1H)	8.89 (d, 2.1 Hz, 1H)
2	8.61 (1H, d, 2.1)	8.54 (s, 1H)	8.48 (s, 1H)	8.44 (d, 1.7 Hz, 1H)	8.45 (d, 2.1 Hz, 1H)
3	8.00 (1H, d, 8.2)	7.99 (d, 10.5, 1H)	8.00 (d, 8.0 Hz, 1H)	7.97 (d, 8.2 Hz, 1H)	7.98 (d, 8.2 Hz, 1H)
4	7.89 (1H, d, 8.2)	7.86 (d, 10.5, 1H)	7.77 (d, 8.0 Hz, 1H)	7.74 (d, 8.2 Hz, 1H)	7.74 (d, 8.2 Hz, 1H)
5	3.27 (1H, dd, 7.2, 19.2) 3.24 (1H, dd, 7.2, 19.2)	3.31 –3.21 (m, 2H)	3.20-3.30 (m, 2H)	3.28-3.13 (m, 2H)	3.23 (ddd, 19.2, 12.2, 7.2 Hz, 2H)
6	3.07 (1H, brd, 13.5) 3.05 (1H, brd, 13.5)	3.05 – 2.90 (m, 2H)	2.76-2.85 (m, 4H)	2.82-2.73 (m, 4H)	2.84 – 2.71 (m, 4H)
7	2.82 (1H, d, 19.2) 2.77 (1H, d, 19.2) 2.73 (2H, m)	2.89 – 2.62 (m, 4H)	2.48-2.57 (m, 2H)	2.54-2.47 (m, 2H)	2.50 (tdd, 12.4, 9.5, 2.9 Hz, 2H)
8	2.26 (2H, m)	2.24 (bs, 2H)	2.18-2.22 (m, 2H)	2.17 (m, 2H)	2.17 (dq, 7.1, 3.7, 3.3 Hz, 2H)
9	1.96 (1H, brs) 1.94 (1H, brs) 1.86 (2H, brd, 12.7) 1.80 (4H, m)		1.85-1.89 (m, 2H)	1.86-1.78 (m, 2H)	1.84 (dp, 13.2, 2.1 Hz, 2H)
10	1.74 (2H, m)	1.90 – 1.60 (m, 12H)	1.75-1.81 (m, 2H)	1.78-1.66 (m, 3H)	1.75 (ddt, 13.0, 10.0, 3.1 Hz, 2H)
11			1.68-1.72 (m, 1H)		1.70– 1.64 (m, 1H)
12	1.67 (4H, m)		1.53-1.64 (m, 5H)	1.62-1.53 (m, 5H)	1.64 – 1.55 (m, 6H, including N<u>H</u>)
13	1.53 (1H, dd, 4.8, 12.1) 1.51 (1H, dd, 4.8, 12.1)				1.52 (ddd, 12.0, 3.8, 1.7 Hz, 1H, N<u>H</u>)
14	1.43 (2H, dt, 3.9, 13.0)	1.51 – 1.39 (m, 4H)	1.21-1.49 (m, 10H)	1.46-1.18 (m, 10H)	1.42 (tt, 12.5, 3.9 Hz, 2H)
15	1.29 (2H, m)	1.38 – 1.13 (m, 6H)			1.38 – 1.16 (m, 8H)
16	0.86 (6H, d, 6.4)	0.86 (d, 6.0, 6H)	0.86 (d, 6.4 Hz, 3H)	0.84 (d, 6.2 Hz, 3H)	0.83 (d, 6.3 Hz, 3H)
17			0.85 (d, 6.4 Hz, 3H)	0.82 (d, 6.0 Hz, 3H)	0.82 (d, 6.3 Hz, 3H)

Table S2. ^{13}C NMR Data Comparison of Natural (Kobayashi's[5]) and Synthetic (Sarpong's,[6] Siegel's,[7] Tsukano's,[8a] and ours) Complanadine A (**1**) (CD_3OD, ppm)

entry	**Kobayashi's**	**Sarpong's**	**Siegel's**	**Hirama/Tsukano's**	**Ours**
1	160.31	160.3	160.5	160.5	160.5
2	160.09	160.0	159.9	160.0	159.9
3	154.21	154.0	153.7	153.8	153.7
4	147.15	146.8	146.1	146.2	146.1
5	135.25		137.6	137.4	137.7
6	134.78		136.6	136.3	136.7
7	134.17	135.4	135.9	135.9	135.9
8	133.08	134.8	135.0	135.0	135.1
9	132.70	133.2	133.7	133.6	133.7
10	120.49	120.4	120.4	120.5	120.5
11	60.47	59.8	57.9	58.1	57.9
12	60.23	59.6	57.8,	58.0	57.8
13	50.13	50.4	51.7	51.6	51.7
14	49.96	50.3	51.6	51.5	51.6
15	43.76	44.3	44.9	44.8	44.9
16	43.61	44.2	44.8	44.7	44.8
17	42.11	42.0	44.7	44.6	44.7
18	42.05	41.9	42.1	42.1	42.1
19	35.95	36.0	36.2	36.1	36.2
20	35.46	35.5	35.7	35.7	35.7
21	34.48	34.5	34.9	34.9	34.9
22	34.43	34.4	34.8	34.8	34.8
23	27.11, 27.08	27.1, 27.0	27.7	27.5	27.7
24	26.23, 26.12	26.7, 26.5	27.3	27.2	27.3
25	25.93, 25.65	26.3, 26.0	27.1	27.1	27.1
26	22.06	22.1	22.4	22.4	22.41
27				22.3	22.38

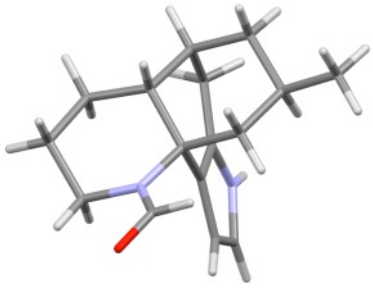
Table S3. ^{1}H NMR Data Comparison of Synthetic (Tsukano's,[8b] Takayama's,[9] Siegel's,[7] and ours) Lycodine (**3**) [CD_3OD (ppm, Hz, Amount of Proton)]

entry	**Tsukano's**	**Takayama's**	**Siegel's**	**Ours**
1	8.31 (dd, 4.9, 1.5 Hz, 1H)	8.30 (dd, 4.9, 1.6 Hz, 1H)	8.31 (dd, J = 1.6, 4.8 Hz, 1H)	8.30 (dd, 4.9, 1.6 Hz, 1H)
2	7.90 (dd, 8.0, 1.5Hz, 1H)	7.91 (dd, 8.1, 1.8 Hz, 1H)	7.89 (dd, 1.6 8.0 Hz, 1H)	7.91 (dd, 7.9, 1.6 Hz, 1H)
3	7.29 (dd, 8.0, 4.9 Hz, 1H)	7.28 (dd, 7.9, 4.9 Hz, 1H)	7.29 (dd, 4.8, 8.0 Hz, 1H)	7.28 (dd, 7.9, 4.8 Hz, 1H)
4	3.16 (d, 7.0 Hz, 1H)	3.15 (dd, 18.9, 7.1 Hz, 1H)	3.15 (dd, 7.2 Hz, 1H)	3.15 (dd, 18.8, 7.2 Hz, 1H)
5	2.76 (ddd, 12.7,3.7, 2.0 Hz, 1H)	2.75 (dddd, 12.6, 3.9, 2.0, 2.0 Hz, 1H)	2.75−2.80 (m, 1H)	2.75 (ddt, 12.6, 4.1, 1.9 Hz, 1H)
6	2.68 (d, 18.8 Hz, 1H)	2.68 (d, 18.7 Hz, 1H)	2.68 (d, 18.8 Hz, 1H)	2.68 (d, 18.8 Hz, 1H)
7	2.44 (ddd, 12.3, 12.3, 3.3 Hz, 1H)	2.42 (td, 12.4, 2.9 Hz, 1H)	2.45 (dt, 3.6, 12.8 Hz, 1H)	2.43 (td, 12.5, 3.0 Hz, 1H)
8	2.14 (ddd, 6.8, 6.7, 3.1 Hz, 1H)	2.12 (td, 6.6, 3.2 Hz, 1H)	2.11−2.15 (m, 1H)	2.13 (dq, 6.9, 3.4 Hz, 1H)
9	1.81 (ddd, 13.3, 5.1, 1.8 Hz, 1H)	1.80 (m, 1H)	1.78−1.84 (m, 1H)	1.81 (ddt, 13.2, 4.6, 2.2 Hz, 1H)
10	1.73 (ddd, 12.7, 3.1, 2.8 Hz, 1H)	1.71 (dt, 12.8, 2.9 Hz, 1H)	1.73 (dt, 3.6, 12.8 Hz, 1H)	1.72 (dt, 12.9, 3.3 Hz, 1H)
11	1.65 (ddd, 13.3, 4.3, 3.9 Hz, 1H)	1.65 (dt, 13.0, 4.3 Hz, 1H)	1.66 (dt, 3.6, 12.8 Hz, 1H)	1.65 (dt, 12.7, 3.9 Hz, 1H)
12	1.62-1.55 (m, 3H)	1.59-1.54 (m, 2H)	1.56−1.61 (m, 2H),	1.62 – 1.53 (m, 2H)
13	1.50 (ddd, 12.1, 3.9, 1.6 Hz, 1H)	1.48 (ddd, 12.1, 3.7, 1.7 Hz, 1H)	1.49 (ddd, 2.0, 3.6, 12.0 Hz, 1H)	1.48 (ddd, 12.2, 4.1, 1.8 Hz, 1H)
14	1.41 (ddd, 13.1, 12.5, 3.0 Hz, 1H)	1.39 (td, 12.6, 3.8 Hz, 1H)	1.36−1.43 (m, 1H)	1.44 – 1.35 (m, 1H)
15	1.32 (t, 11.9 Hz, 1H)	1.31 (t, 11.9 Hz, 1H)	1.32 (m, 2H)	1.35 – 1.26 (m, 2H)
16	1.16 (m, 2H)	1.21-1.09 (m, 2H)	1.10−1.21 (m, 2H)	1.22 – 1.10 (m, 2H)
17	0.81 (d, 6.3 Hz, 3H)	0.80 (d, 6.6 Hz, 3H)	0.81 (d, 6.4 Hz, 3H)	0.81 (d, 6.4 Hz, 3H)

Table S4. ^{13}C NMR Data Comparison of Synthetic (Tsukano's,[8b] Takayama's,[9] Siegel's,[7] and ours) Lycodine (**3**) (CD_3OD, ppm)

entry	**Tsukano's**	**Takayama's**	**Siegel's**	**Ours**
1	156.61	159.6	159.6	159.6
2	147.47	147.4	147.6	147.4
3	137.47	137.7	137.3	137.7
4	135.36	135.4	135.3	135.4
5	123.33	123.3	123.3	123.3
6	57.86	57.7	58.0	57.7
7	51.52	51.6	51.5	51.6
8	44.74	44.8	44.7	44.8
9	44.49	44.6	44.5	44.6
10	41.99	42.0	42.0	42.0
11	35.70	35.7	35.7	35.7
12	34.72	34.8	34.7	34.8
13	27.48	27.6	27.4	27.6
14	27.11	27.2	27.1	27.2
15	27.02	27.0	27.0	27.0
16	22.34	22.4	22.3	22.4

4. X-ray Structure and Analysis Data of 36



X-ray Structure of **36**

Solid Structure of **36**. A brown plate shaped crystal of **36** for X-ray diffraction was obtained by slow evaporation of a hexanes/ethyl acetate solution of **36**. The data were collected at 150(2) K on a Bruker AXS D8 Quest CMOS diffractometer with Mo sealed tube and curved triumph monochromator with a 10 cm x 10 cm Photon-100 detector and fixed chi angle. The supplementary crystallographic data was deposited in The Cambridge Crystallographic Data Centre (CCDC 2101755).

X-ray analysis data:

Bond precision: C-C = 0.0031 A Wavelength=1.54178
Cell: a=9.245(3) b=45.546(7) c=9.284(3)
alpha=90 beta=91.33(2) gamma=90
Temperature: 150 K Calculated Reported
Volume 3908.2(19) 3908.1(17)
Space group P 21 P 21
Hall group P 2yb P 2yb
Moiety formula 5(C16 H22 N2 O), C4 H8 O2 5(C16 H22 N2 O), C4 H8 O2
Sum formula C84 H118 N10 O7 C84 H118 N10 O7
Mr 1379.88 1379.88
Dx,g cm-3 1.173 1.173
Z 2 2
Mu (mm-1) 0.588 0.588
F000 1496.0 1496.0
F000' 1500.09
h,k,lmax 11,58,11 11,55,11
Nref 16992[8605] 15393
Tmin,Tmax 0.884,0.916 0.677,0.754
Tmin' 0.884
Correction method= # Reported T Limits: Tmin=0.677
Tmax=0.754 AbsCorr = MULTI-SCAN
Data completeness= 1.79/0.91 Theta(max)= 79.613
R(reflections)= 0.0322(15094) wR2(reflections)= 0.0858(15393)
S = 1.015 Npar= 975

5. References

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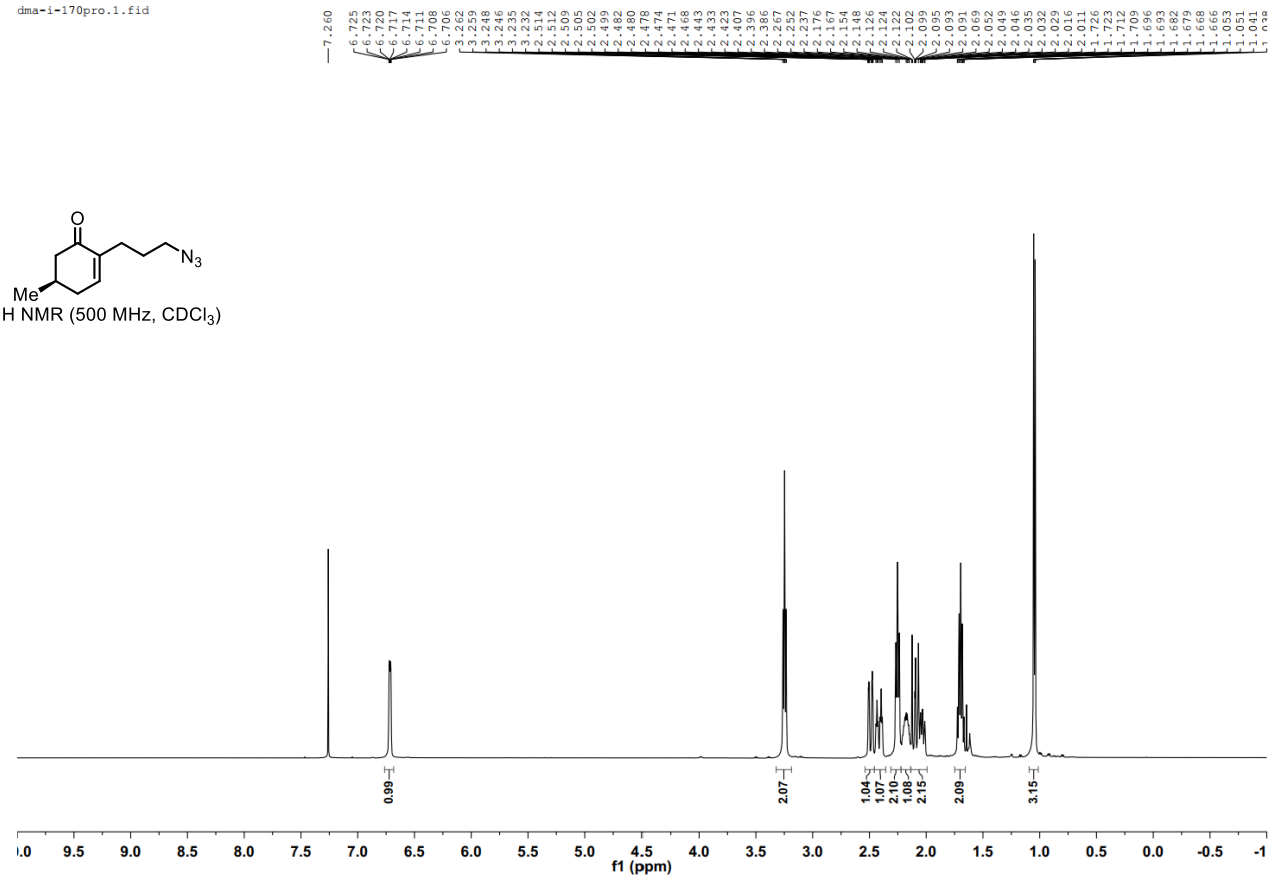
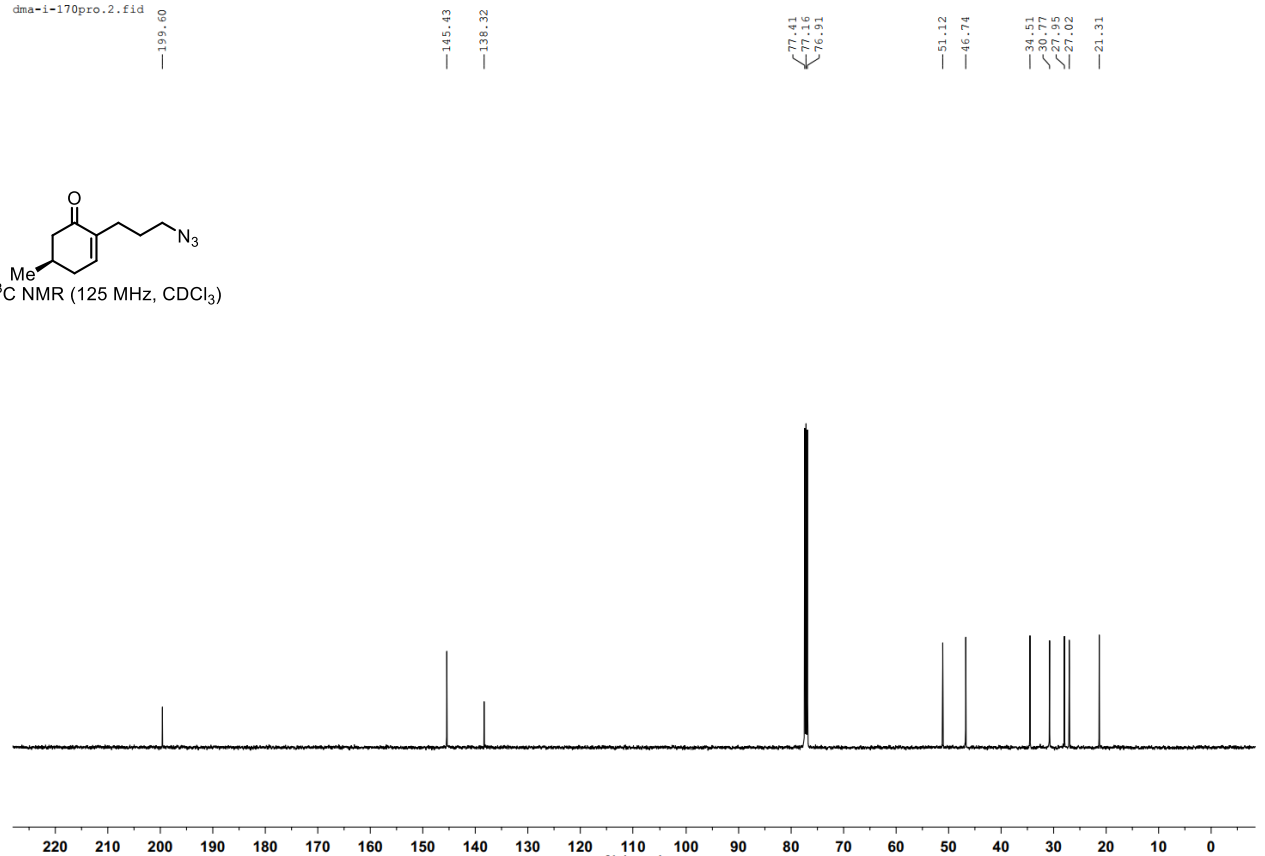
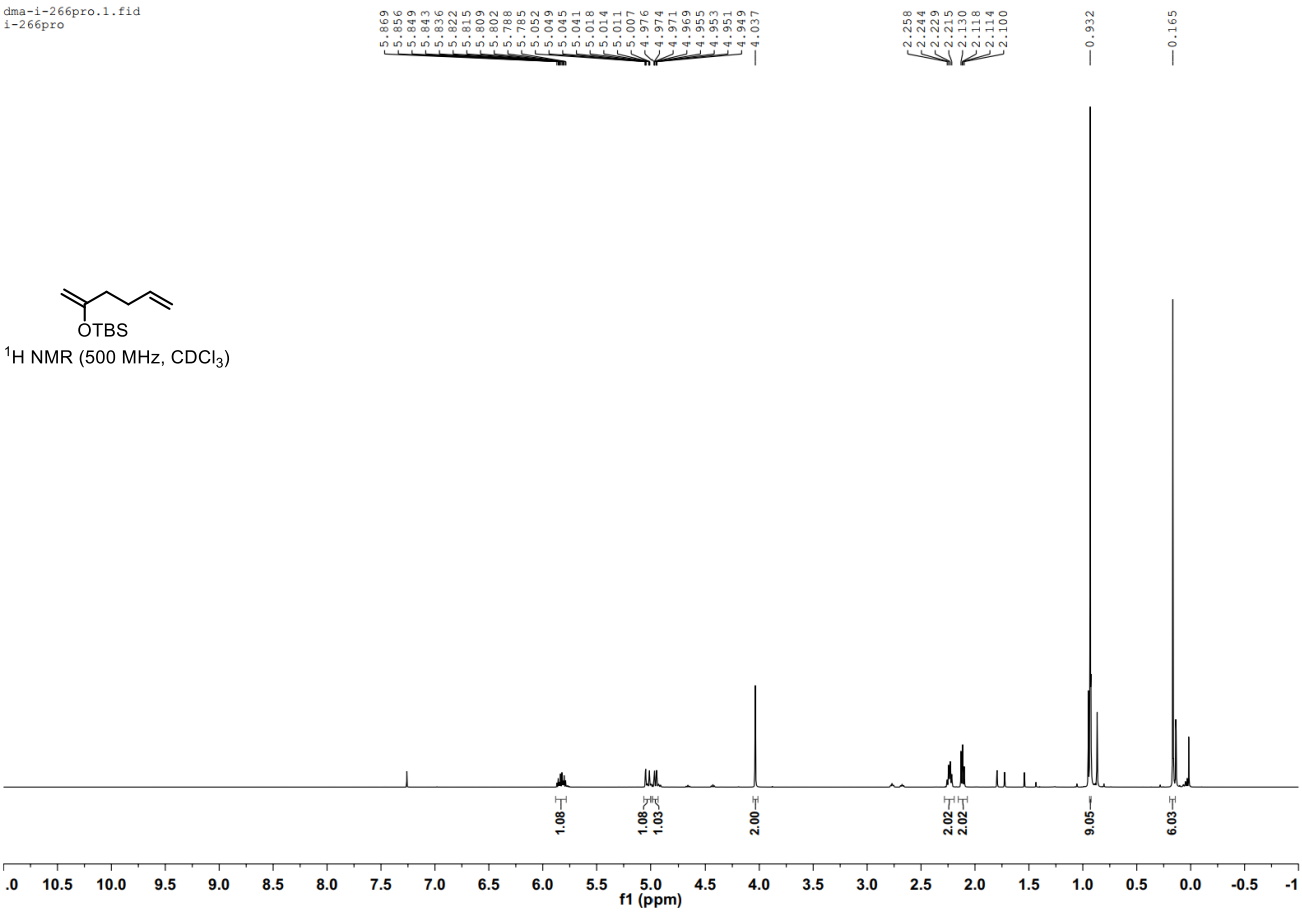
6. ^{1}H, and ^{13}C NMR Spectra



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5.849
5.843
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5.802
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5.049
5.045
5.041
5.018
5.014
5.011
5.007
4.976
4.974
4.971
4.969
4.955
4.953
4.951
4.949
4.037
2.258
2.244
2.229
2.215
2.130
2.118
2.114
2.100
0.932
0.165
OTBS
1H NMR (500 MHz, CDCl3)
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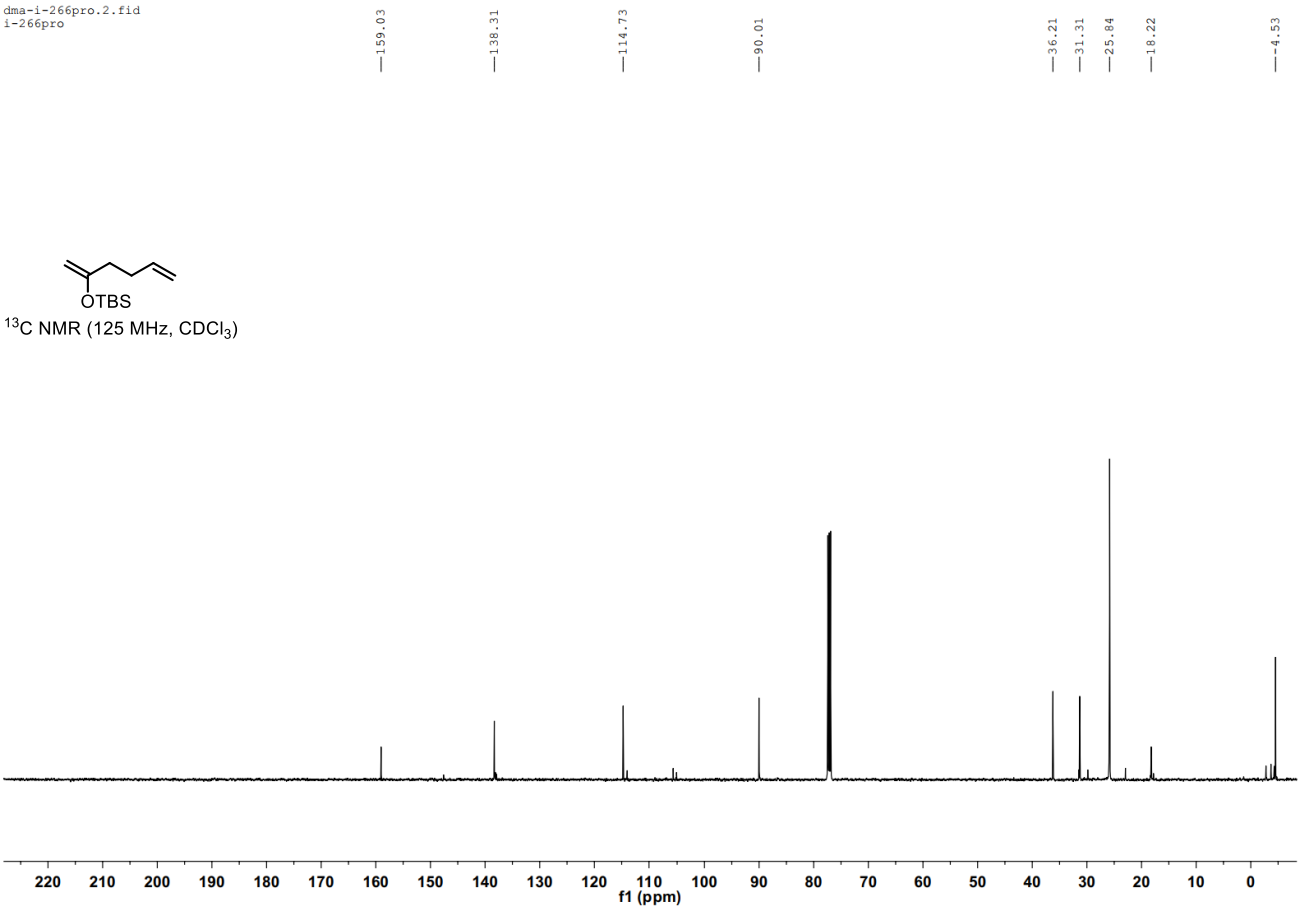
1.08
1.03
2.00
2.02
2.02
9.05
6.03
f1 (ppm)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36.21
31.31
25.84
18.22
-4.53
OTBS
13C NMR (125 MHz, CDCl3)
f1 (ppm)

dma-i-267pro.1.fid
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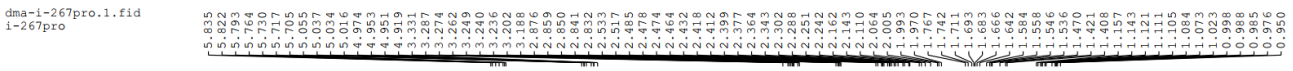

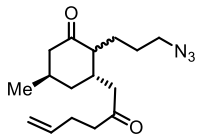

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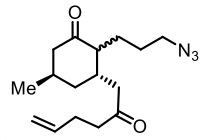

^{13}C NMR (125 MHz, $CDCl_3$)

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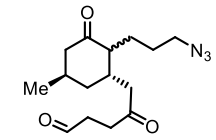
i-275pro



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

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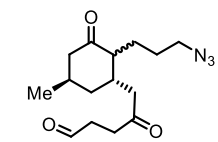
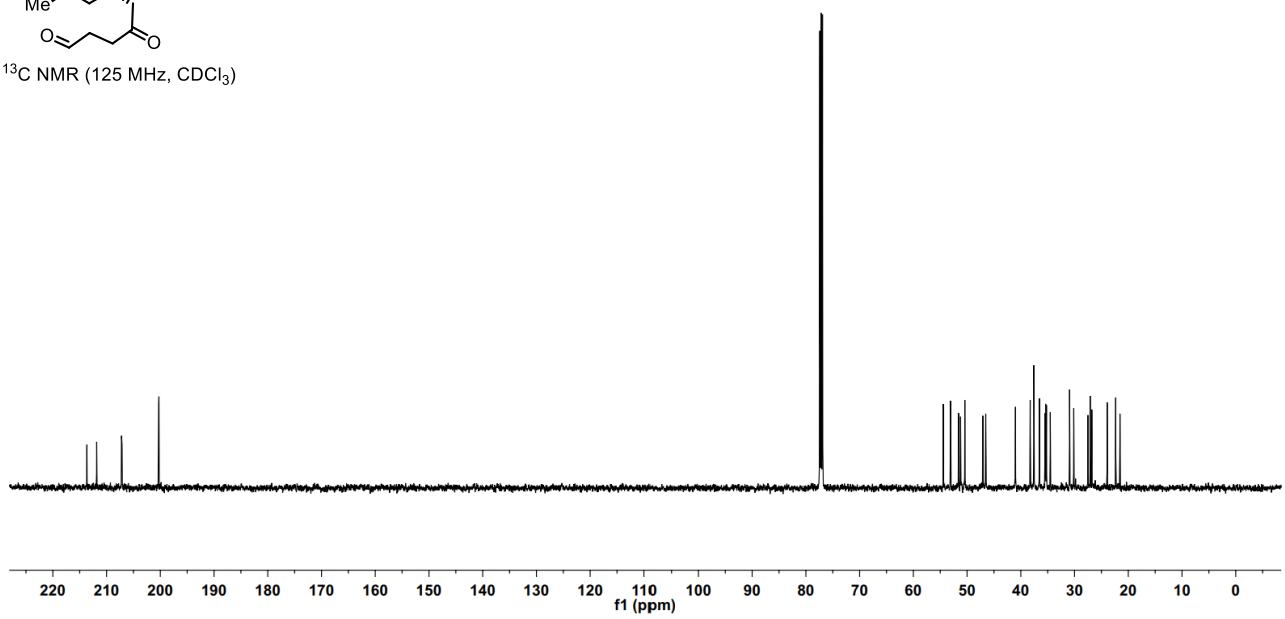


^{13}C NMR (125 MHz, $CDCl_3$)



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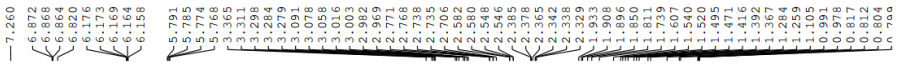
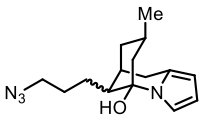
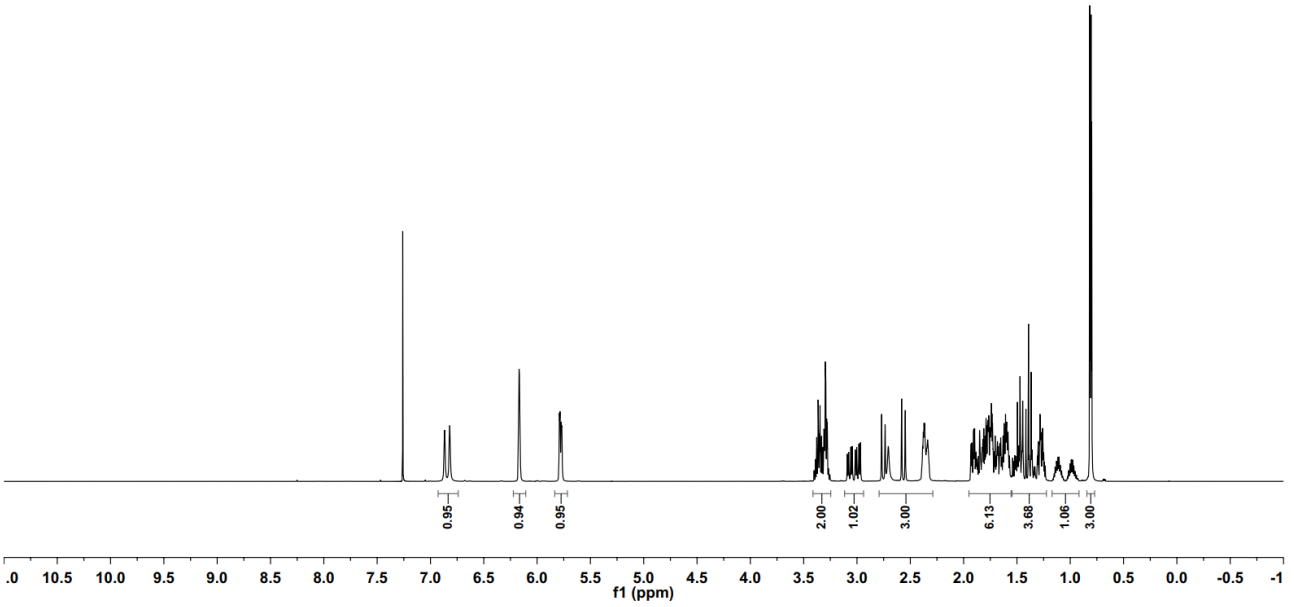




^{1}H NMR (500 MHz, $CDCl_3$)



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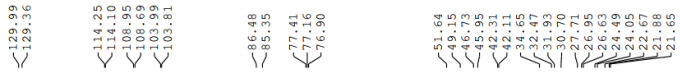
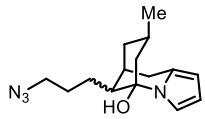
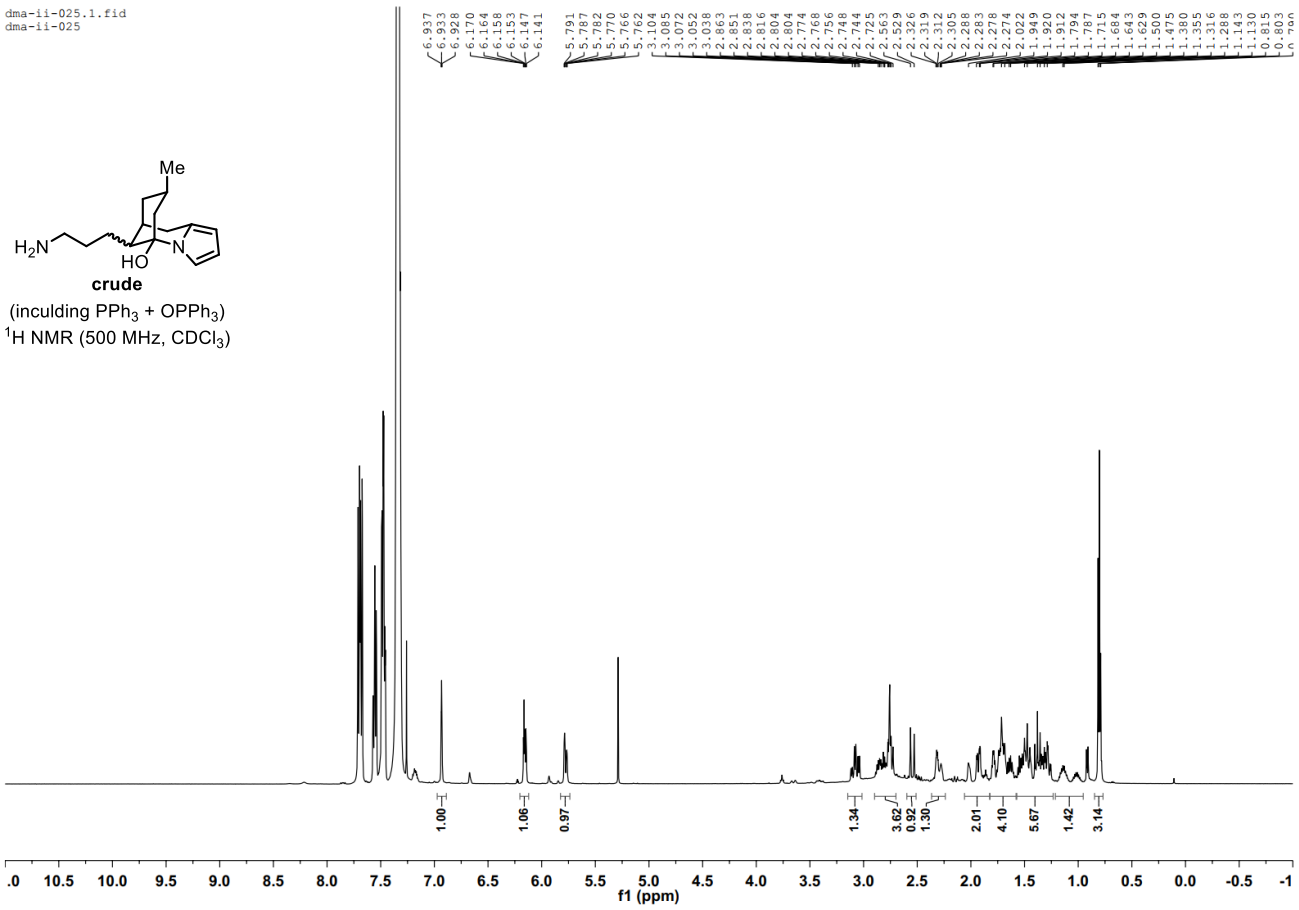




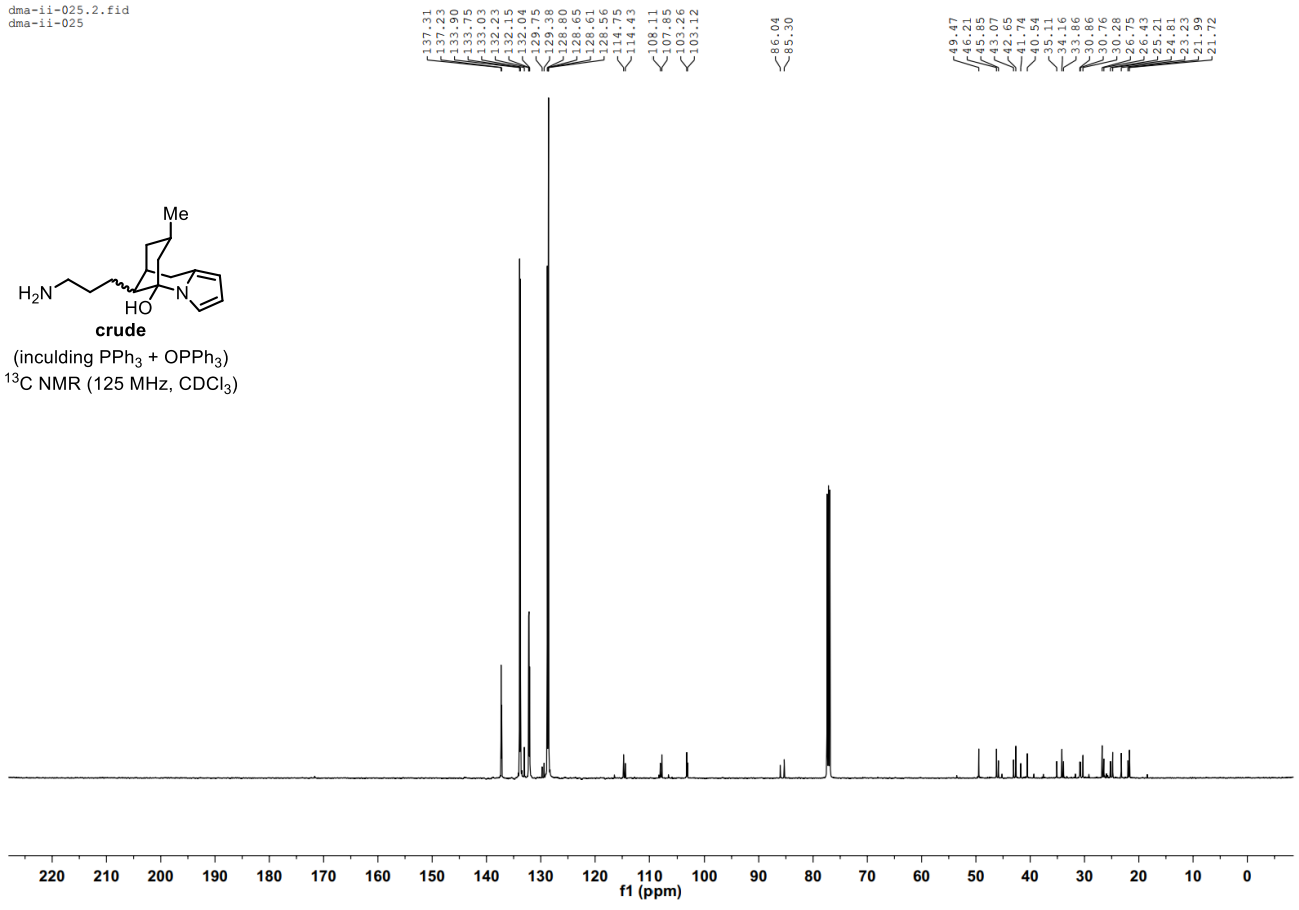
^{13}C NMR (125 MHz, $CDCl_3$)



crude

(inculding PPh_3 + $OPPh_3$)

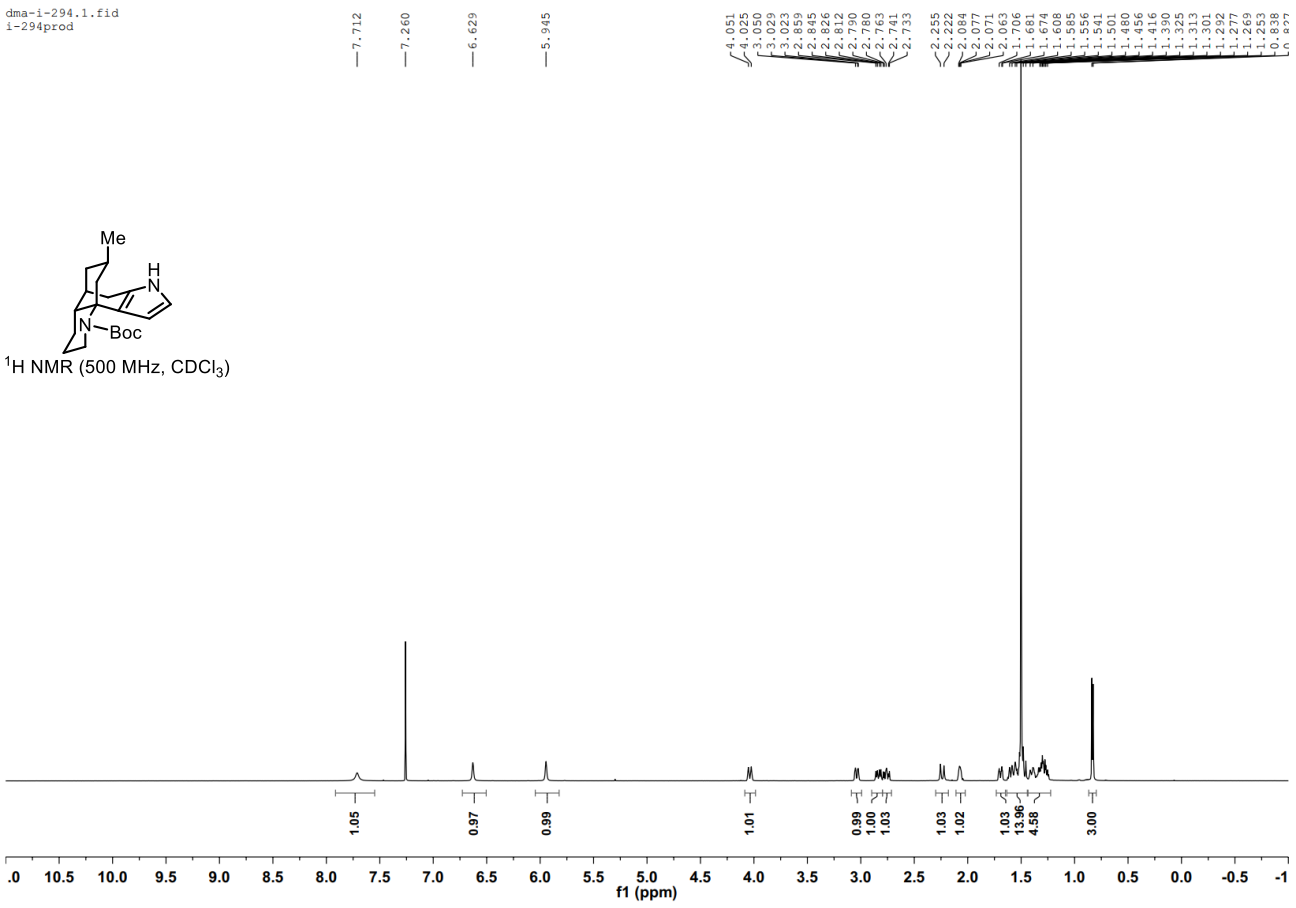
^1H NMR (500 MHz, $CDCl_3$)



crude

(inculding PPh_3 + $OPPh_3$)

^{13}C NMR (125 MHz, $CDCl_3$)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N
Boc
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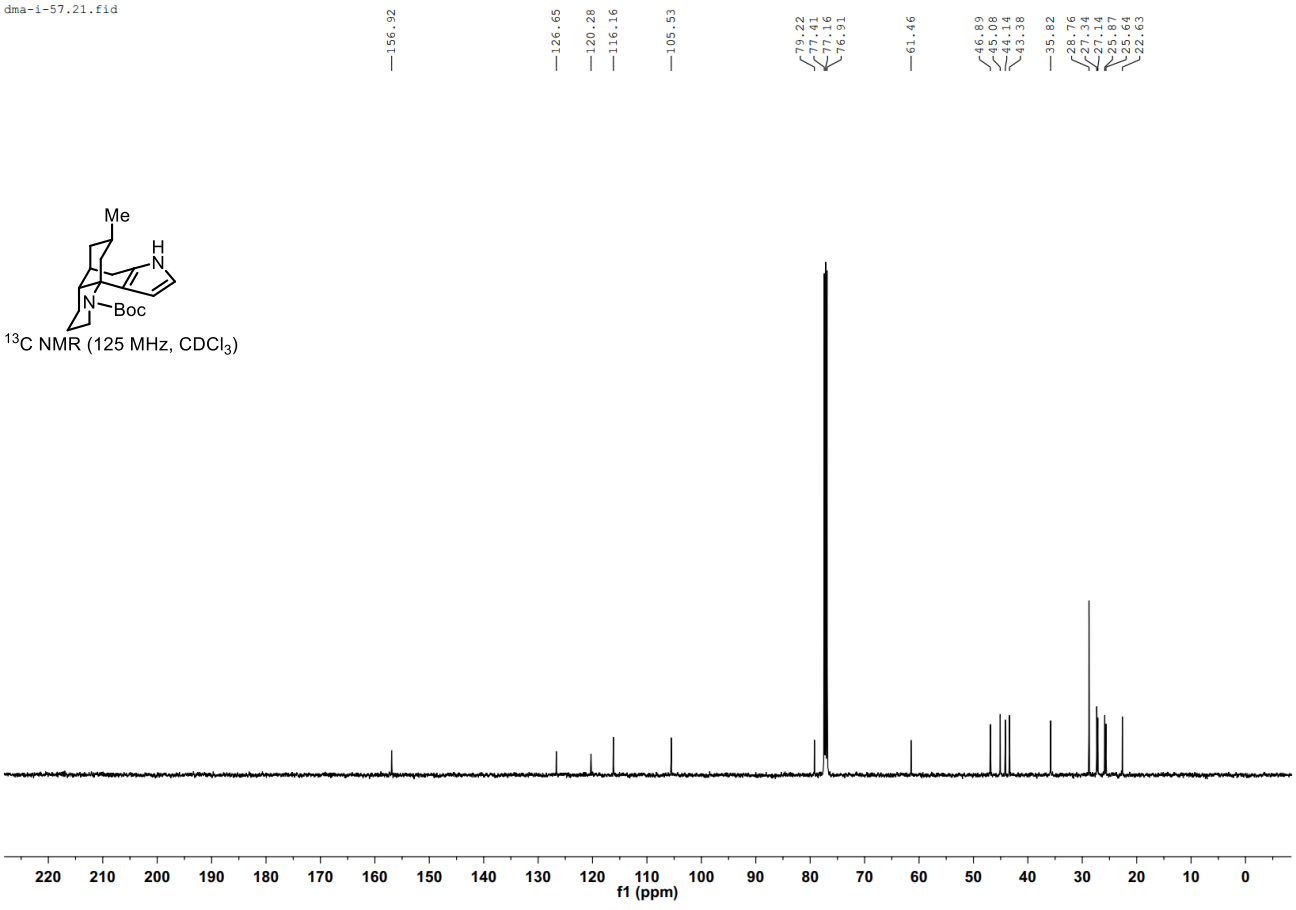
f1 (ppm)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13C NMR (125 MHz, CDCl3)
f1 (ppm)

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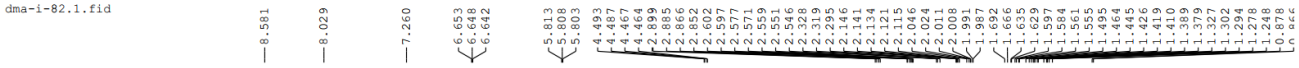

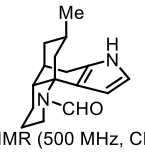

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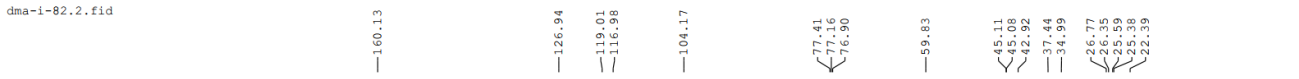

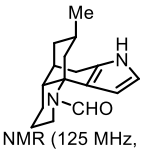

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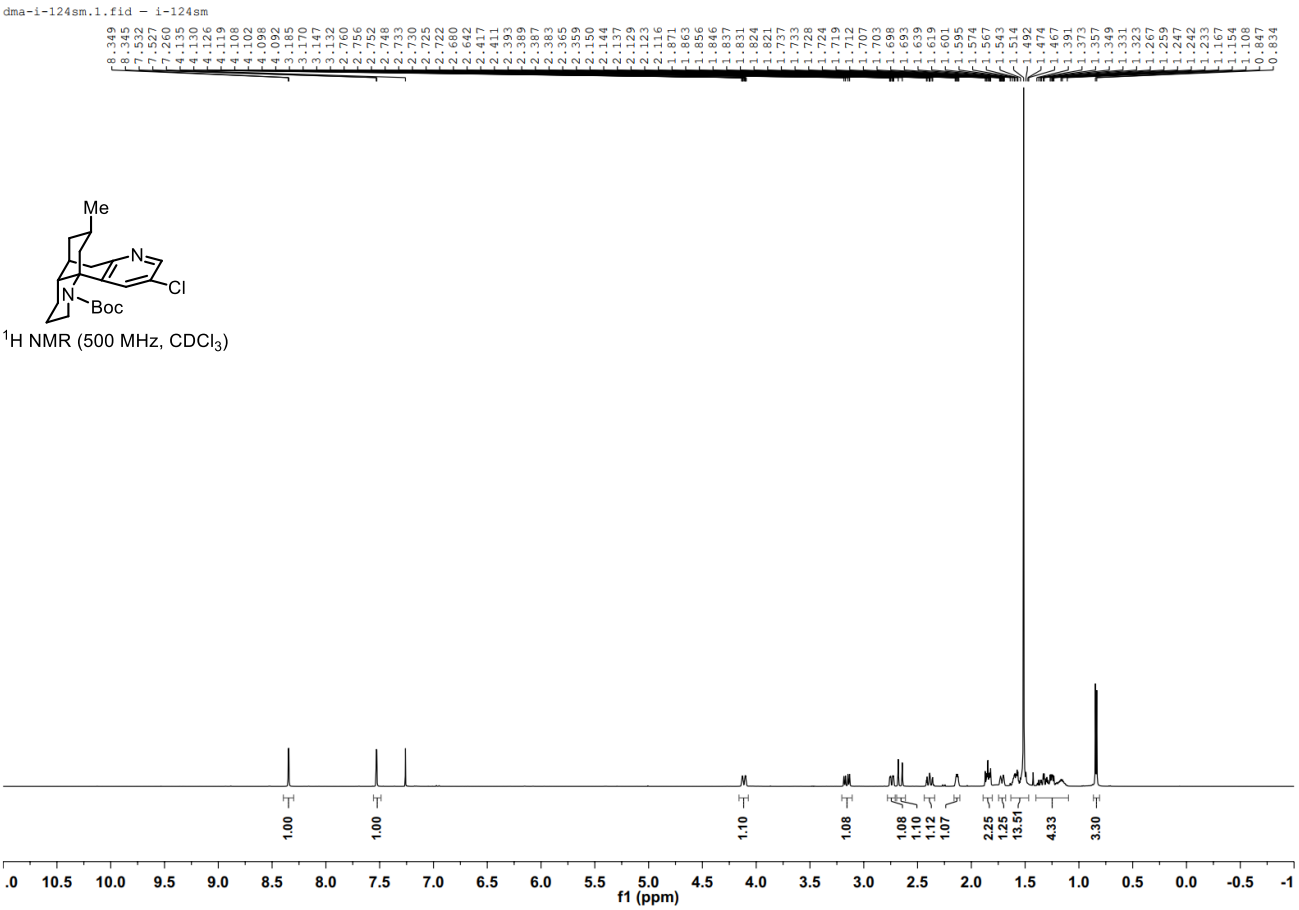

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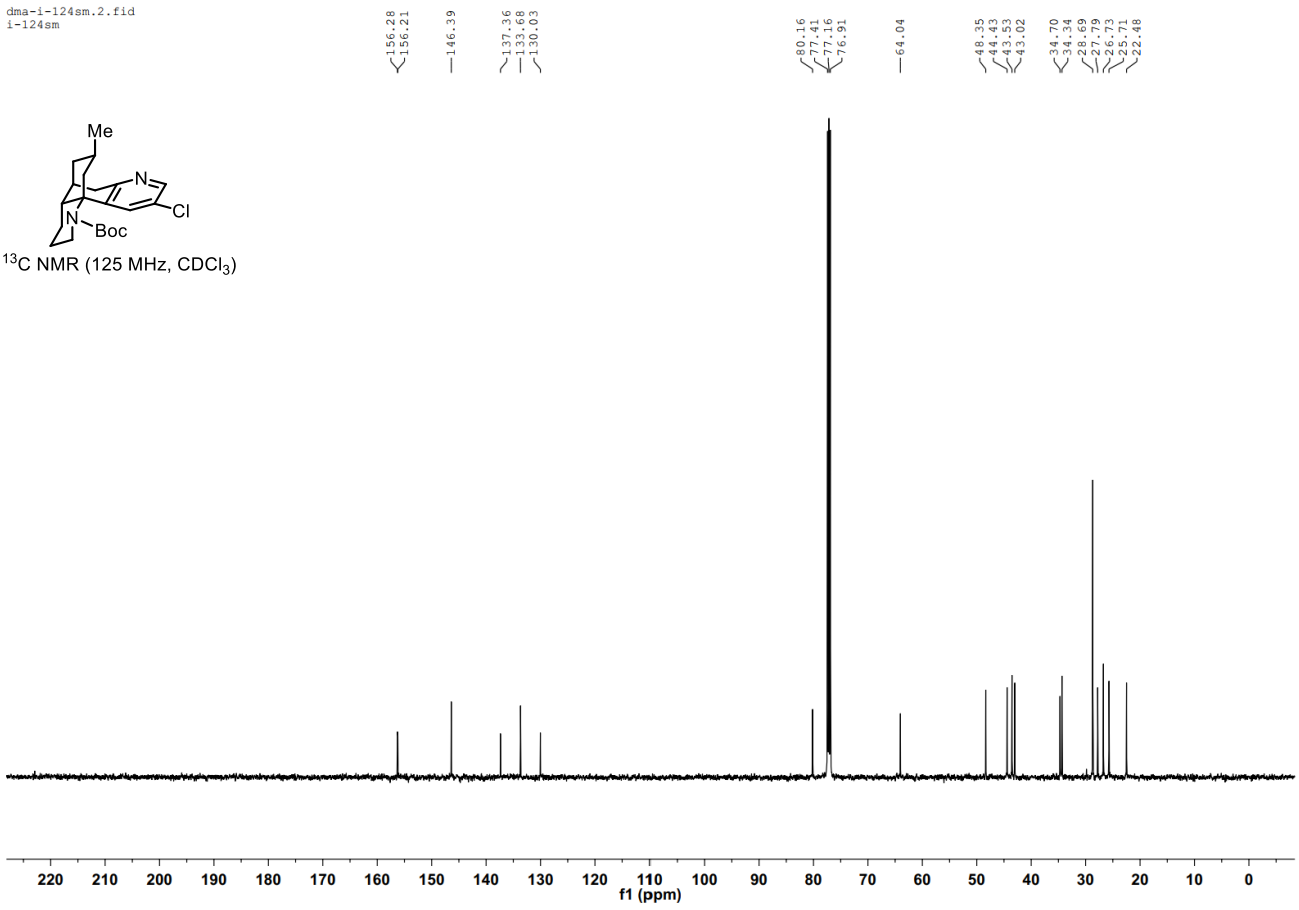

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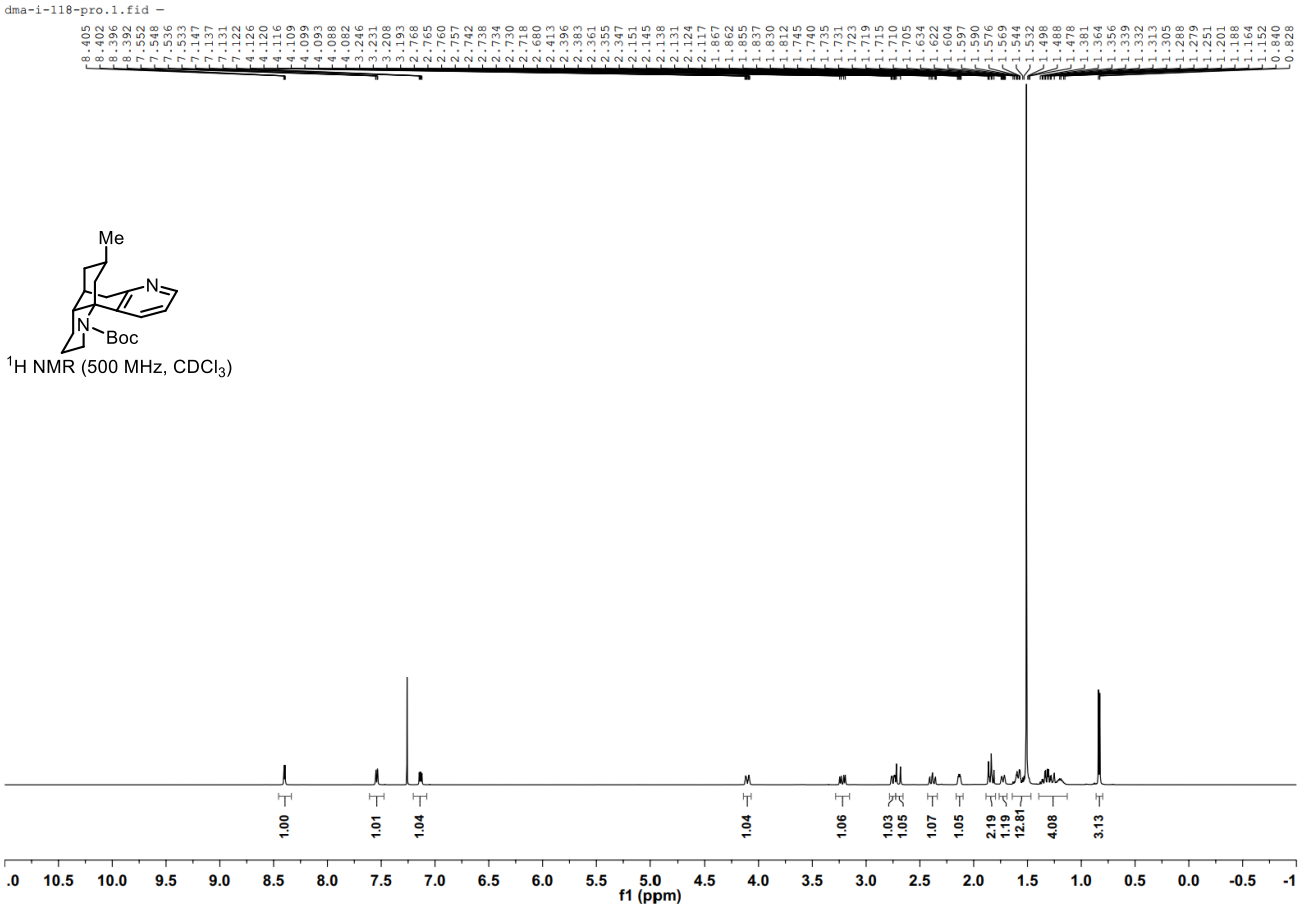

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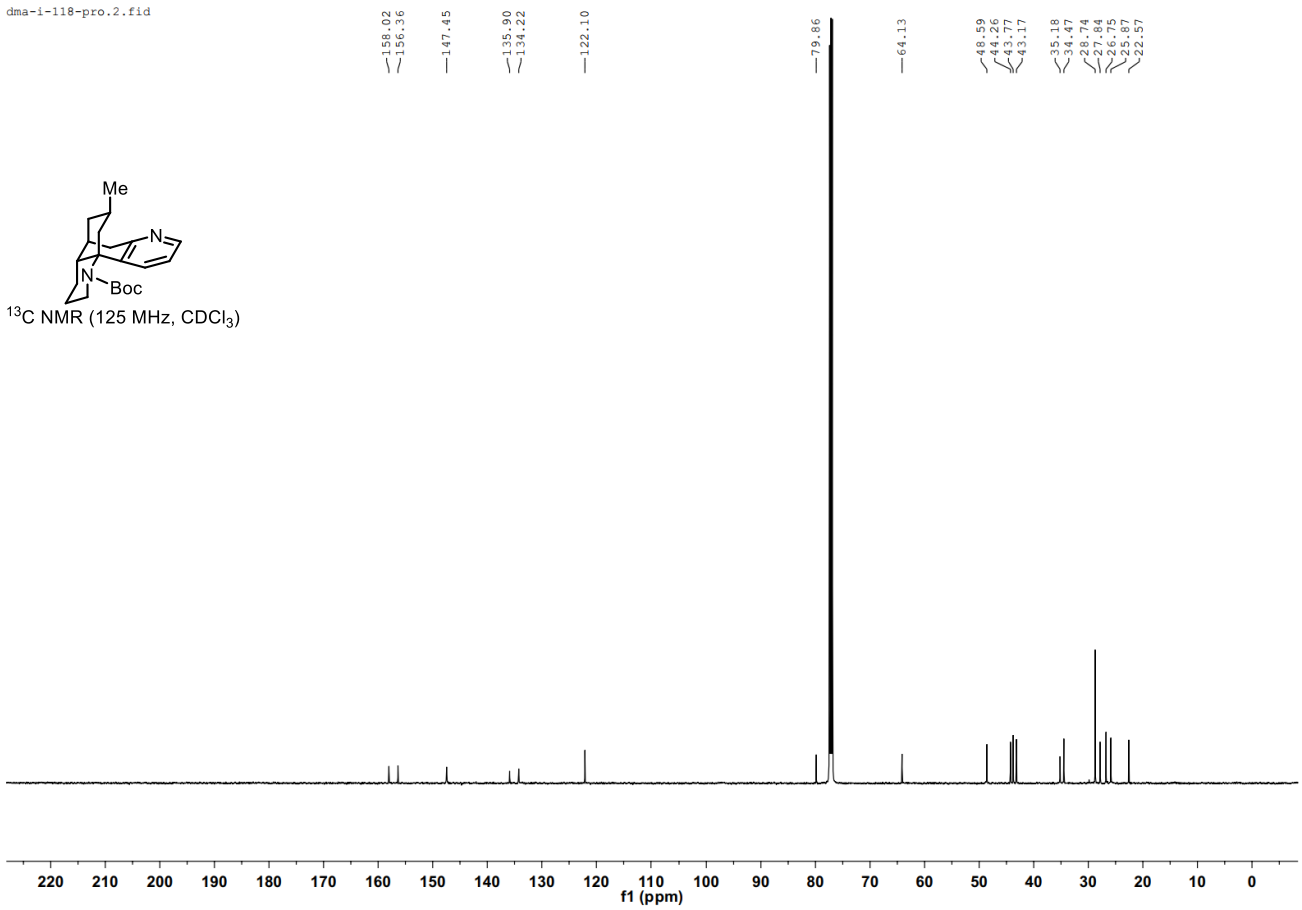

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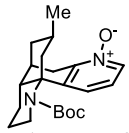

^{1}H NMR (500 MHz, $CDCl_3$)

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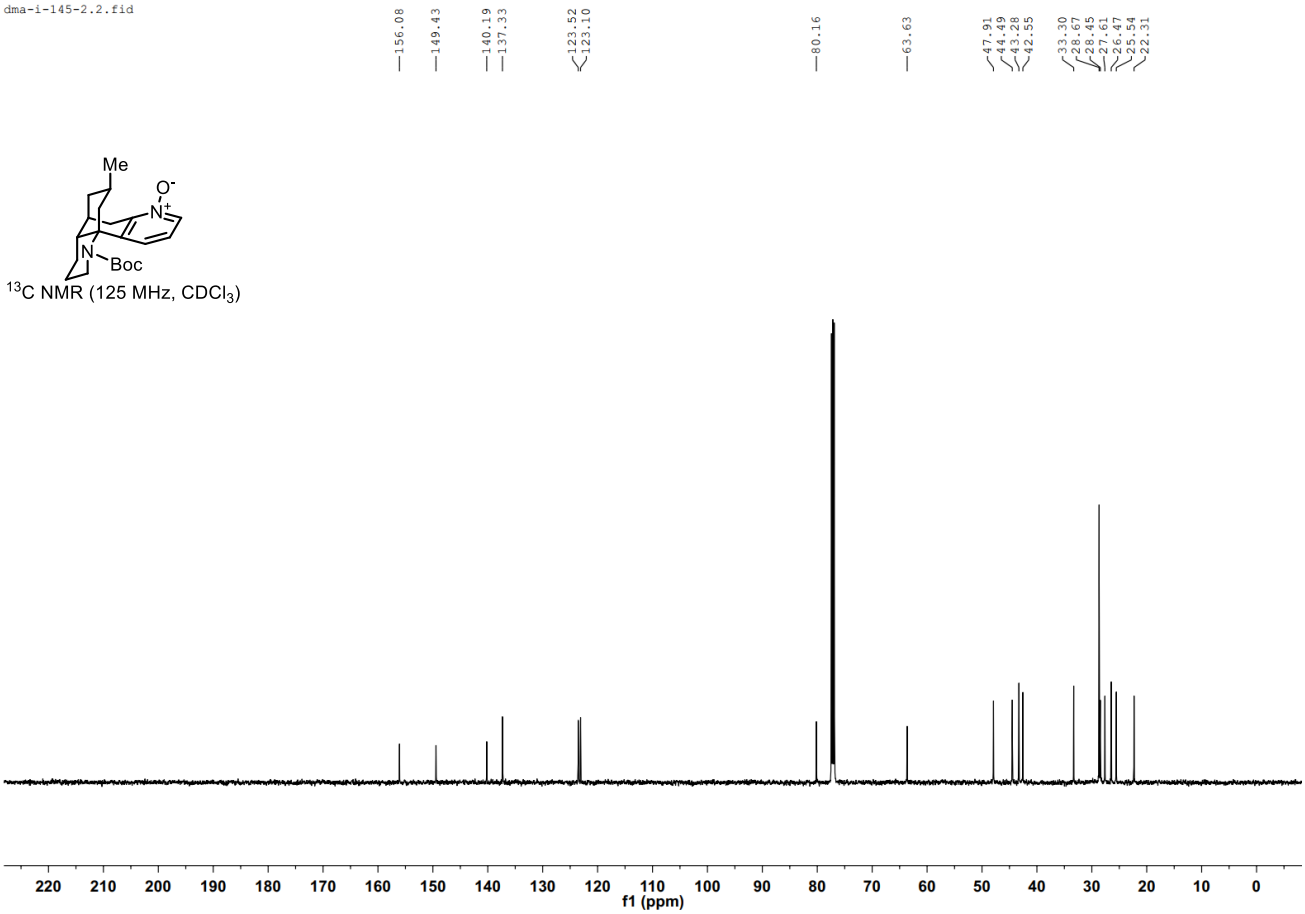

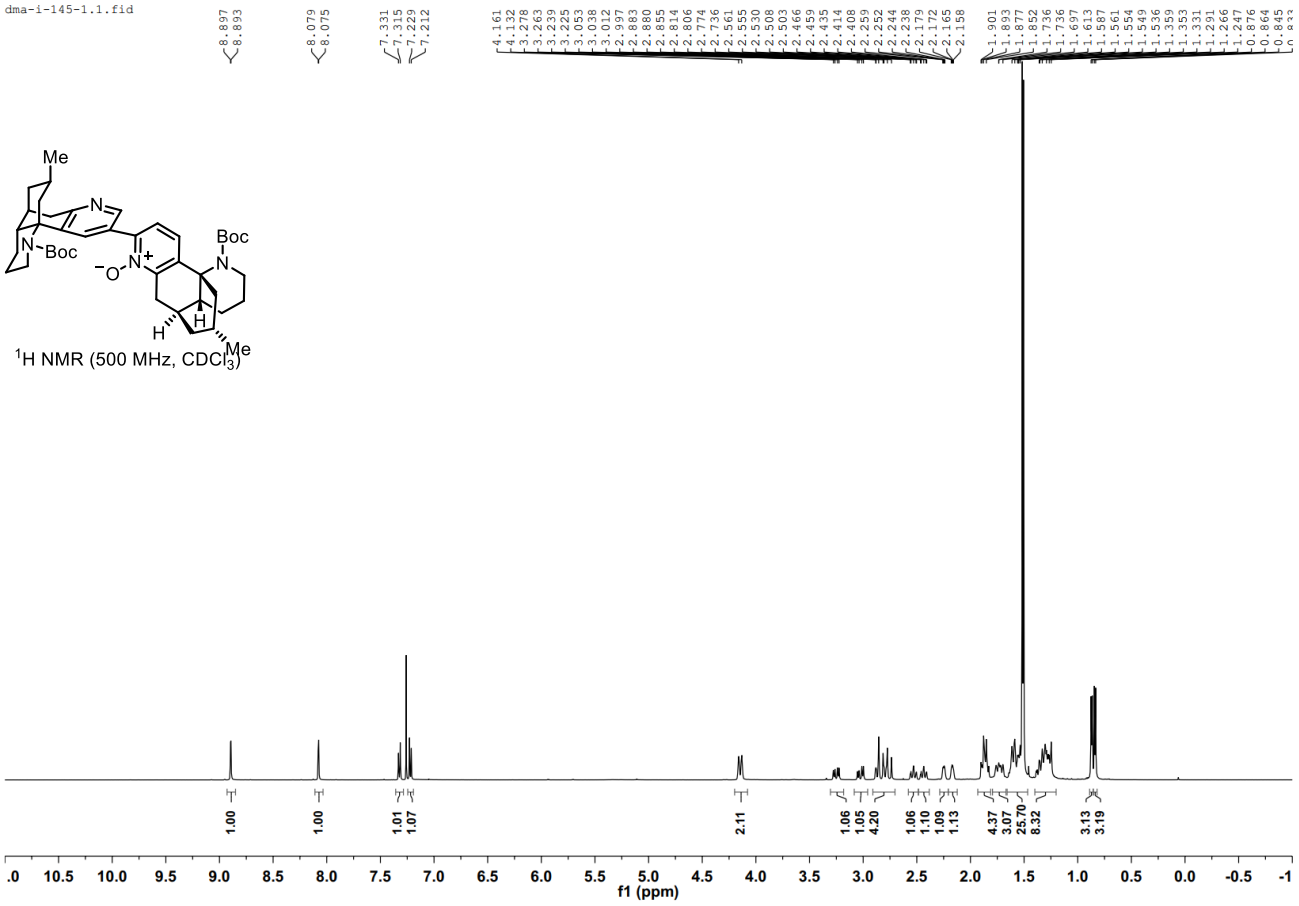
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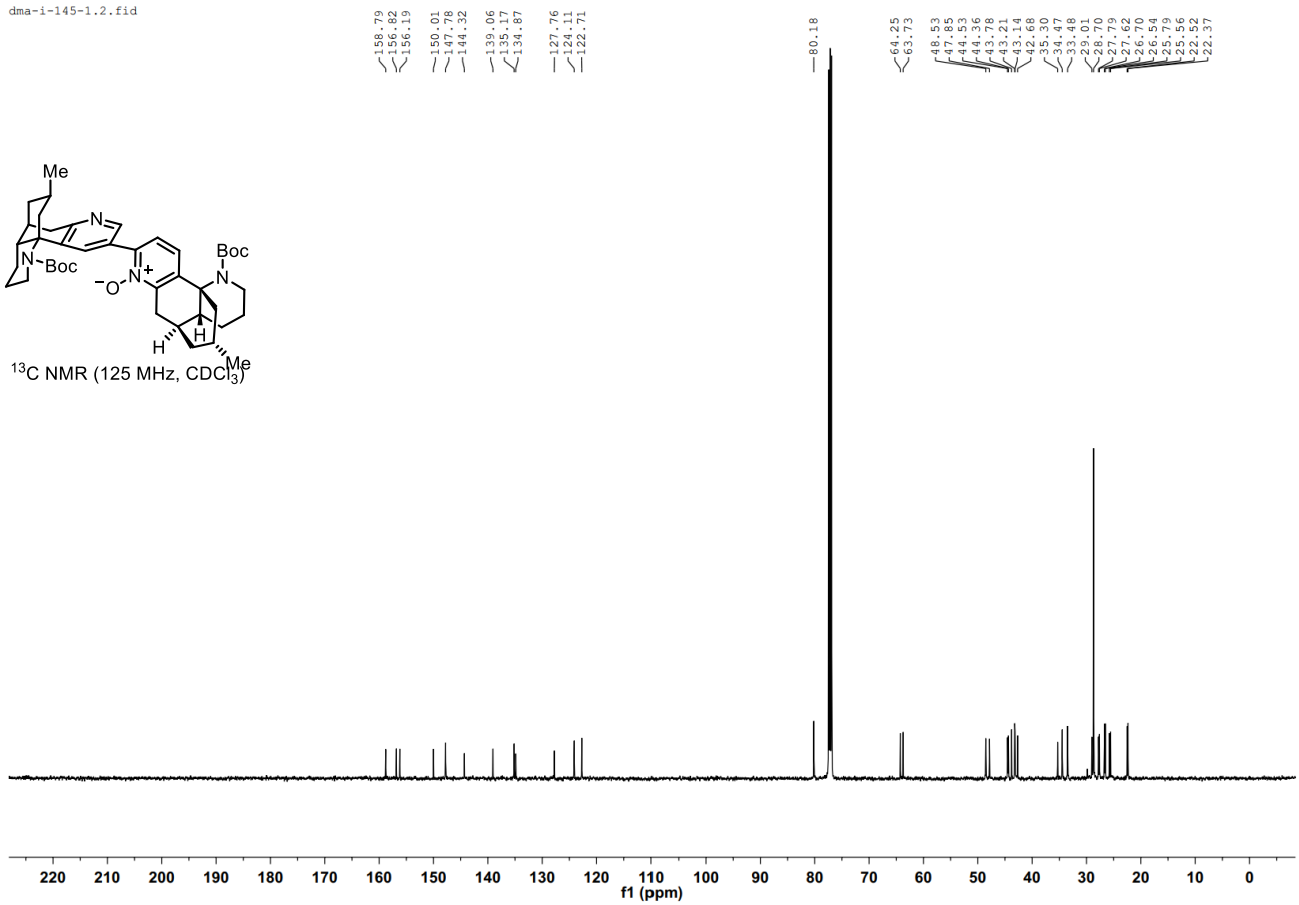
Me
N
N
Boc
Boc
N
O
H
H
Me
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)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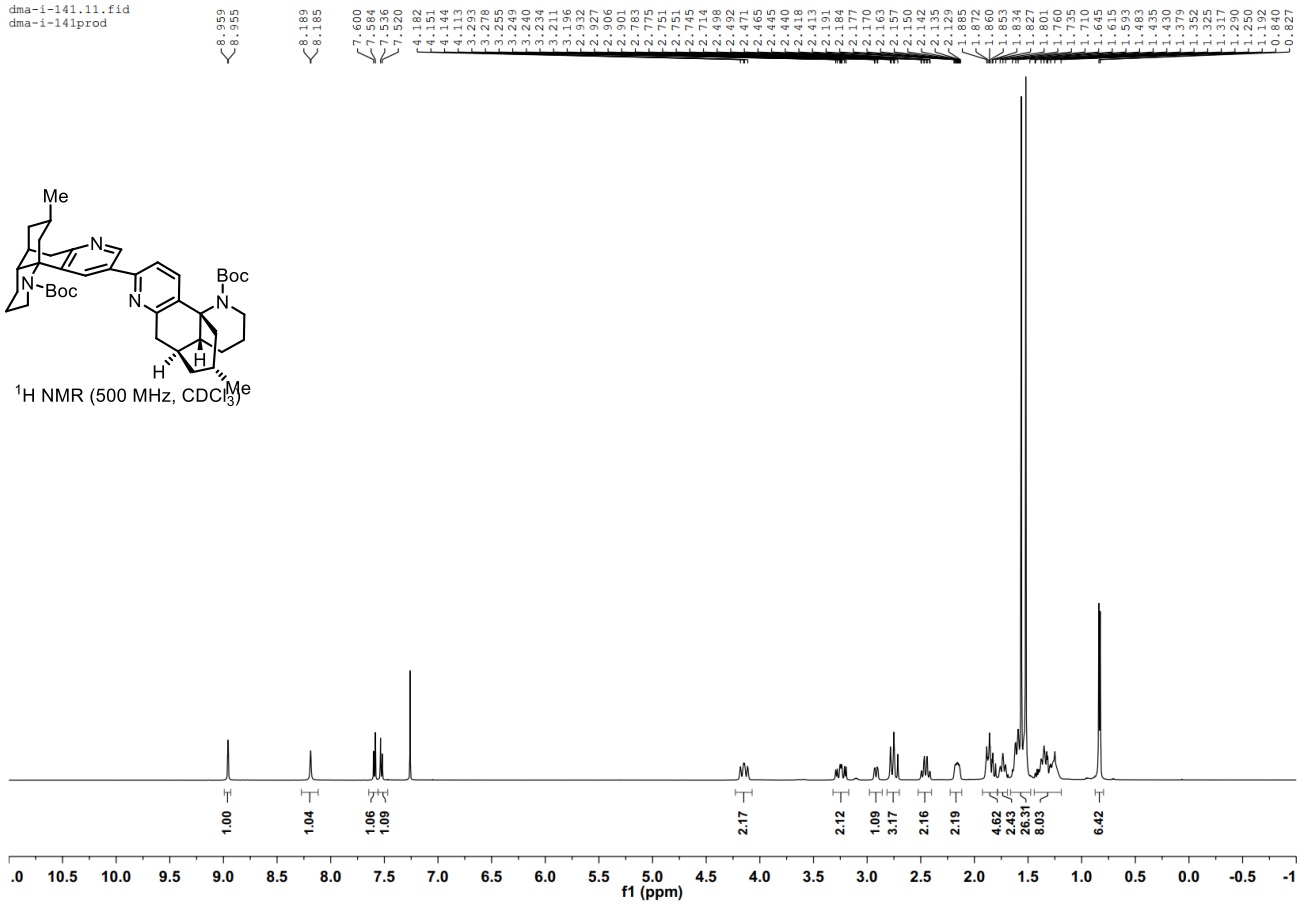
Boc
Boc
N
O
H
H
Me
^{13}C NMR (125 MHz, CDCl$_3$)
f1 (ppm)



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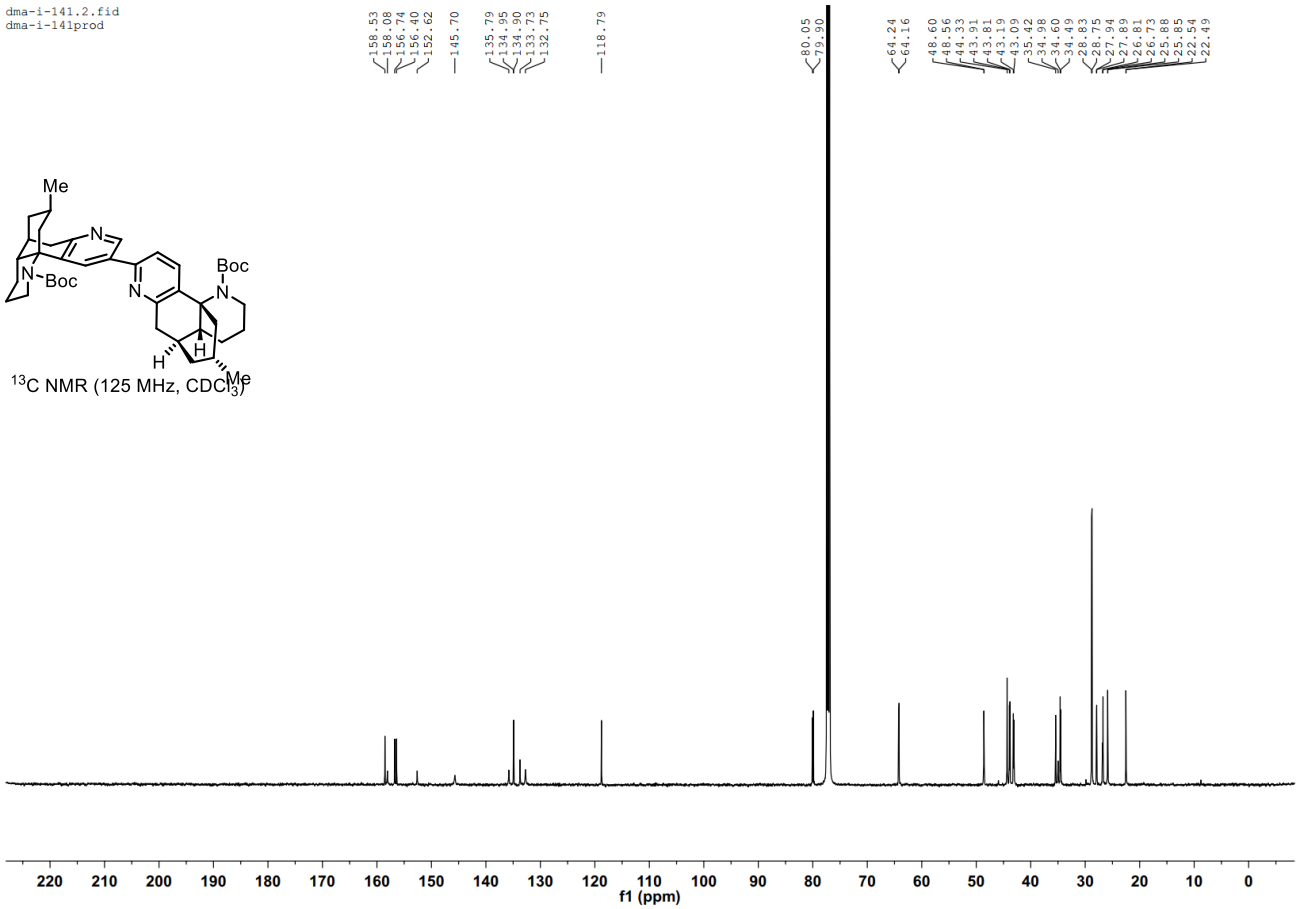

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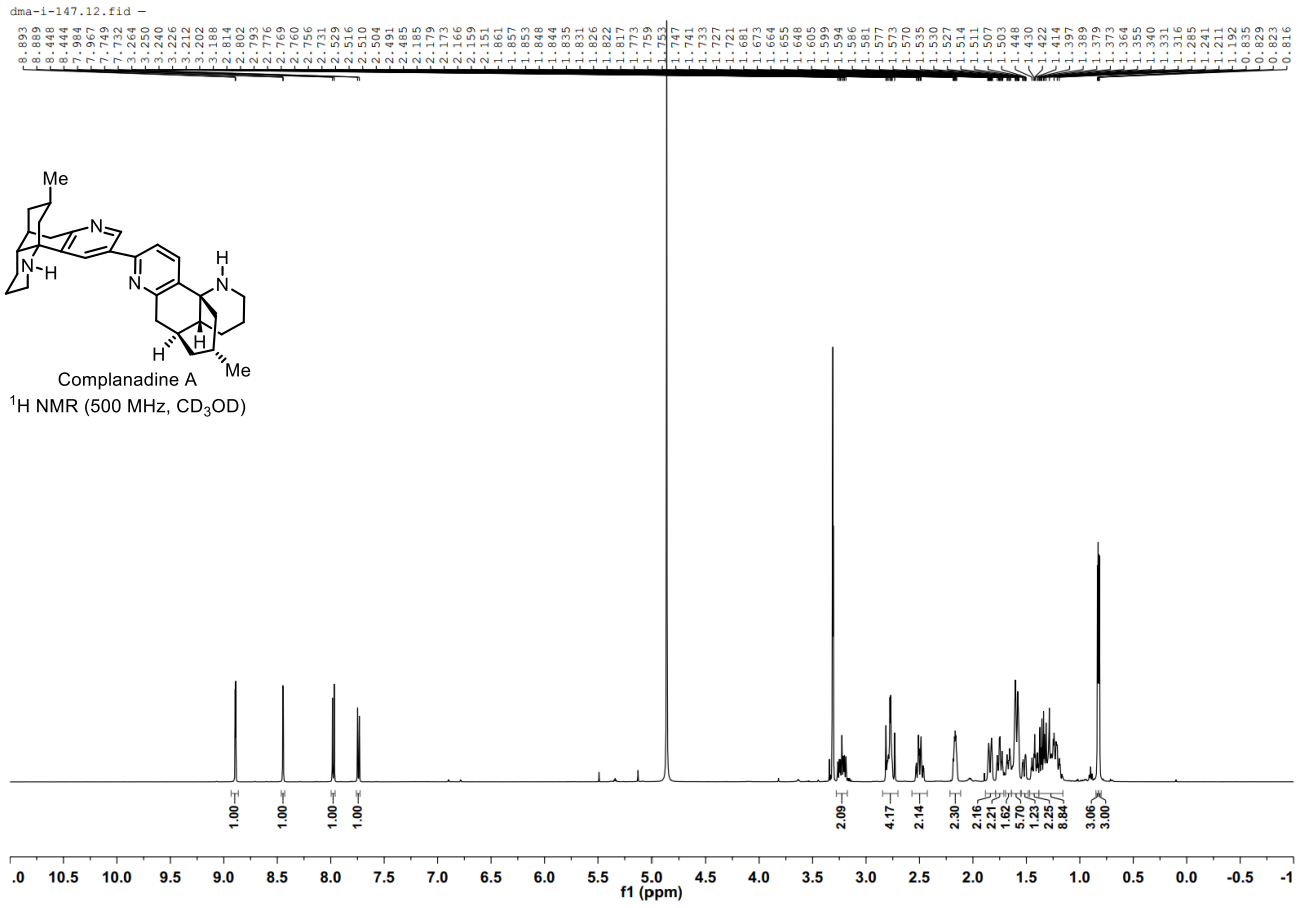
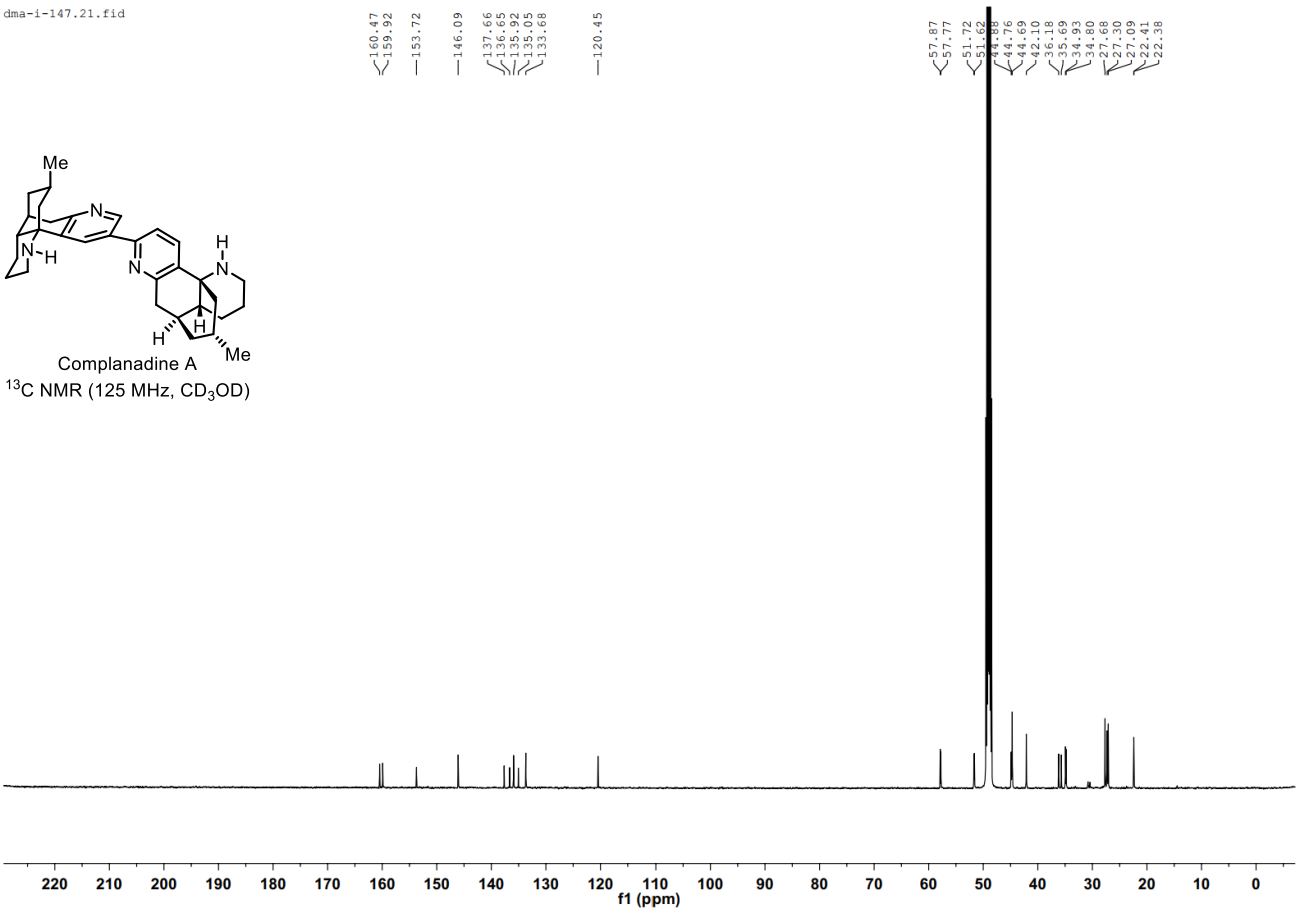


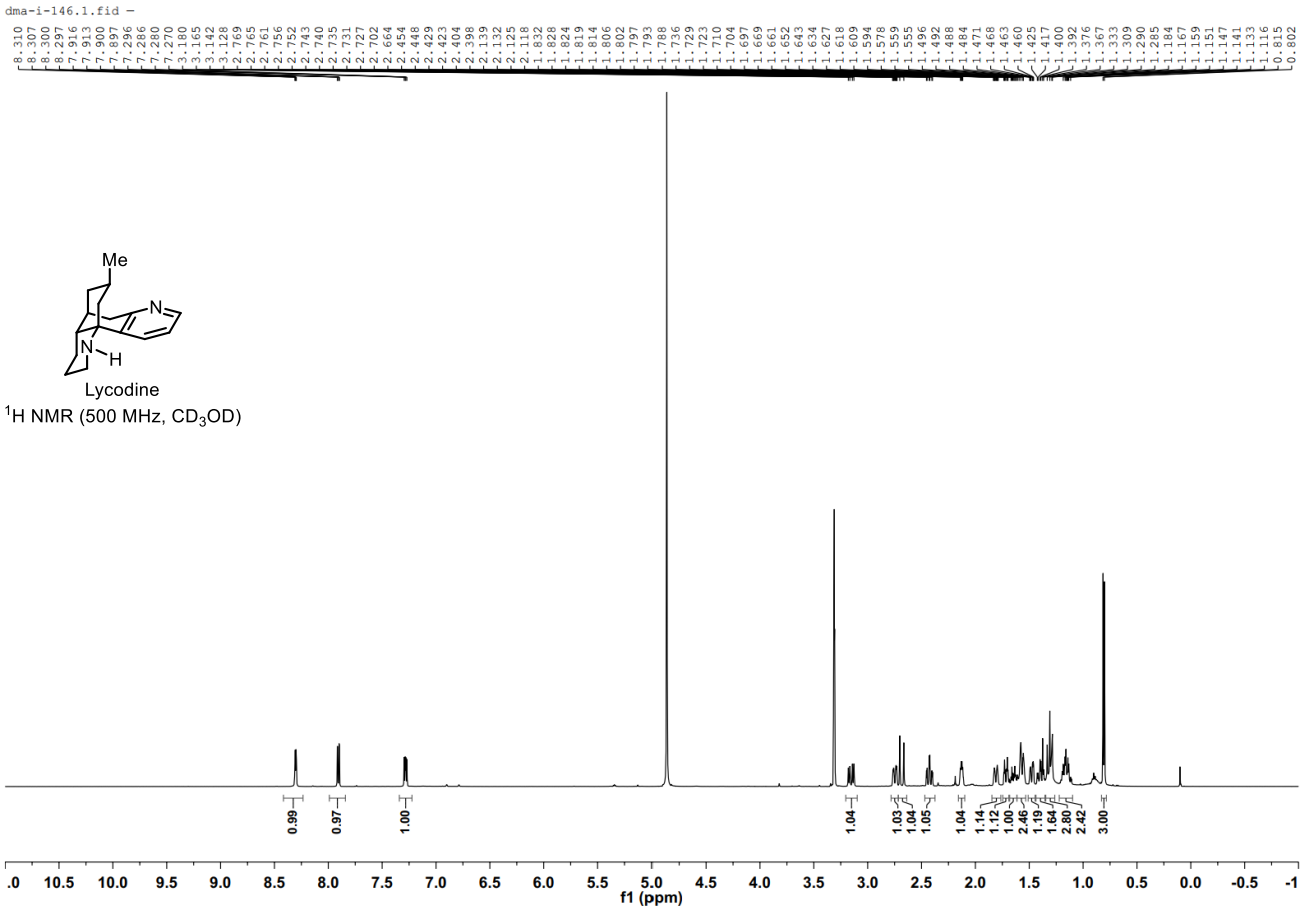
Complanadine A

^{1}H NMR (500 MHz, CD_3OD)



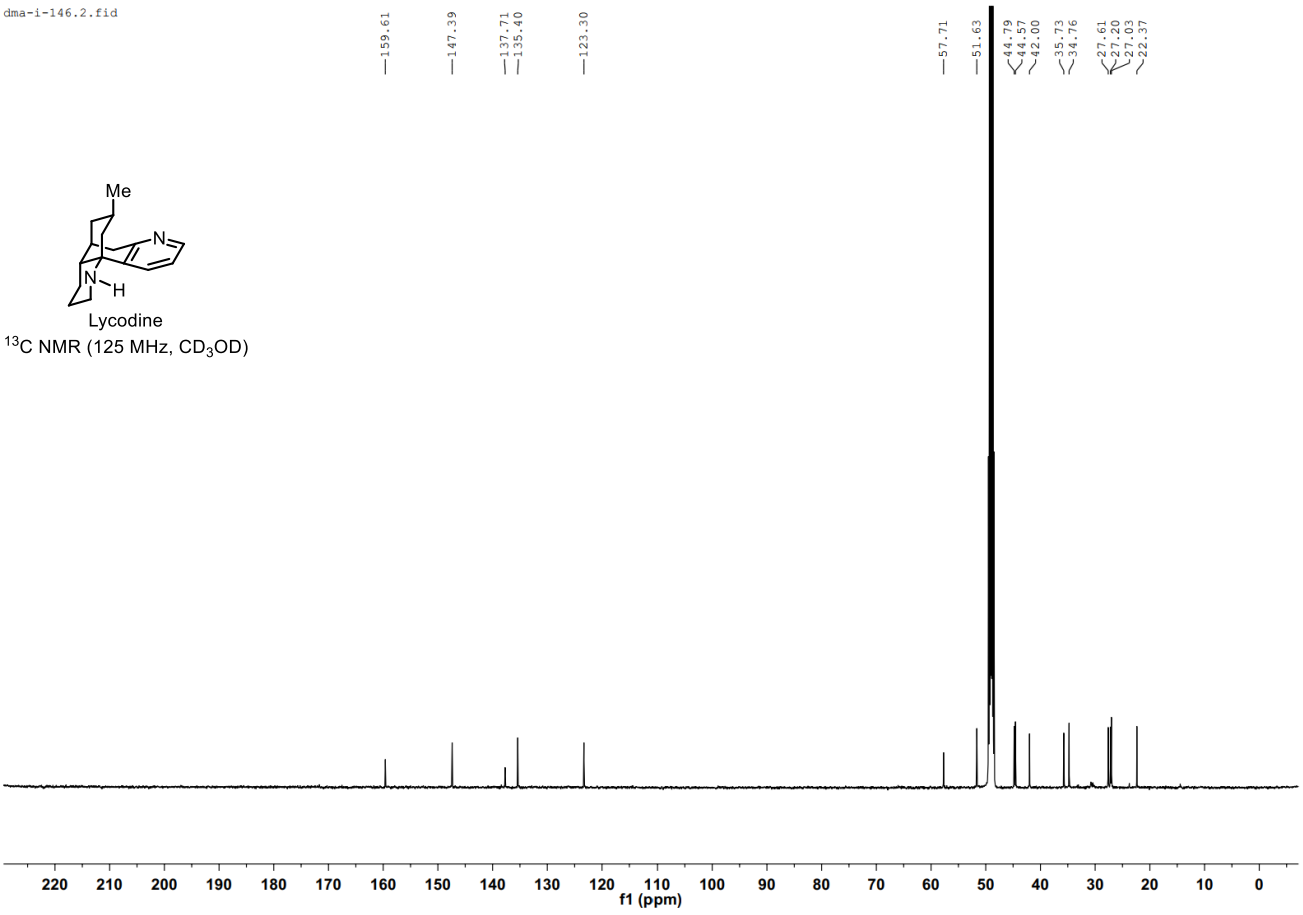
Complanadine A

^{13}C NMR (125 MHz, CD_3OD)



Lycodine

^{1}H NMR (500 MHz, CD_3OD)



Lycodine

^{13}C NMR (125 MHz, CD_3OD)