Supporting Information Available

I) Experimental Section

II) Abbreviations

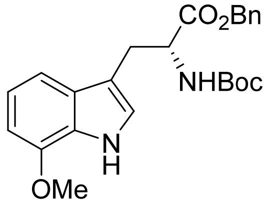
III) References

IV) ^{1}H and ^{13}C NMR Spectra of Compounds

I) Experimental Section

Experimental Data for Compounds

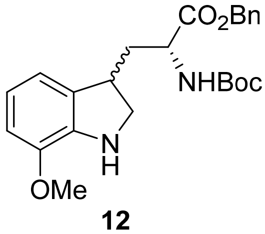
General Procedures. All reactions were carried out under a nitrogen or argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), pentane, diethyl ether (Et_2O), 1,2-dimethoxyethane (DME), 1,4-dioxane, methylene chloride (CH_2Cl_2), toluene and triethylamine (Et_3N) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Methanol (MeOH), benzene and dimethyl sulfoxide (DMSO) were purchased in anhydrous form and used without further purification. Water, ethyl acetate (EtOAc), diethyl ether (Et_2O), methylene chloride (CH_2Cl_2), acetone and hexanes were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thinlayer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of ammonium molybdate, anisaldehyde, and heat as developing agents. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on a Bruker AV-400 instrument and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, pent = pentet, hex = hexet, br = broad. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. Melting points (m.p.) are uncorrected, and recorded on a Buchi B-540 melting point apparatus. High-resolution mass spectra (HRMS) were recorded on an Agilent ESI TOF (time of flight) mass spectrometer at 3500 V emitter voltage.



11

Benzyl ester 11: To a stirred solution of **9**[1] (33.42 g, 100.0 mmol) in DMF (150 mL) at room temperature were added K_2CO_3 (27.64 g, 200.0 mmol) followed by BnBr (14.25 ml, 120.0 mmol). The resulting mixture was stirred for 0.5 h before it was quenched with H_2O (150 mL). The mixture was extracted with Et_2O (3 × 200 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded benzyl ester **11** (38.16 g, 90%) as a yellow amorphous solid. **11**: $R_f = 0.32$ (hexanes:EtOAc 2:1); $[\alpha]_D^{20} = +3.5$ ($c = 1.0$, $CHCl_3$); IR (film) ν_{max} 3348, 3103, 2969, 2891, 2757, 1741, 1711, 1612, 1573, 1491, 1358, 1246, 1138, 1031, 846, 758, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.27$ (d, $J = 20.7$ Hz, 1 H), 7.31–7.23 (m, 3 H), 7.21–7.14 (m, 2 H), 7.10 (dd, *J* = 8.0, 2.6 Hz, 1 H), 7.00–6.93 (m, 1 H), 6.70 (s, 1 H), 6.57 (d, *J* = 7.7 Hz, 1 H), 5.03 (q, *J* = 12.1 Hz, 3 H), 4.65 (s, 1 H), 3.87 (s, 3 H), 3.27–3.13 (m, 2 H), 1.37 ppm (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.2, 155.3, 146.2, 135.4, 129.1, 128.5 (2C), 128.4 (2C), 128.3, 126.7, 122.5, 120.1, 111.6, 110.3, 101.9, 79.8, 67.1, 55.3, 54.4, 28.3 (3C), 28.1 ppm; HRMS (ESI): calcd for $C_{24}H_{29}N_2O_5^+$ [M + H$^+$] 425.2071, found 425.2074.

Indoline 12: To a stirred solution of benzyl ester **11** (21.20 g, 50.0 mmol) in AcOH (100 mL) at 0 °C was added $NaBH_3CN$ (6.20 g, 100.0 mmol). The resulting mixture was stirred at room temperature for 24 h before it was concentrated *in vacuo* and quenched with $NaHCO_3$ (100 mL, sat. aq.). The aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, CH_2Cl_2:EtOAc 20:1) afforded indoline **12** (17.89 g, 84%, ca. 1.2:1 mixture of diastereomers by ^{1}H NMR) as a colorless oil.

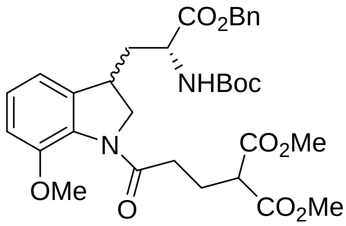


12

12a: R_f = 0.25 (hexanes:EtOAc 3:1); $[\alpha]_D^{20}$ = –31.8 (*c* = 0.5, $CHCl_3$); IR (film) ν_{max} 3326, 3084, 2971, 2856, 2713, 1739, 1713, 1610, 1582, 1501, 1366, 1238, 1140, 1027, 851, 760, 723 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (s, 5 H), 6.74–6.63 (m, 3 H), 5.22–5.06 (m, 3 H), 4.45 (td, *J* = 9.2, 4.5 Hz, 1 H), 3.81 (s, 3 H), 3.77 (d, *J* = 8.5 Hz, 1 H), 3.45–3.36 (m, 1 H), 3.36–3.26 (m, 1 H), 2.07 (td, *J* = 10.4, 9.7, 4.3 Hz, 2 H), 1.45 ppm (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 155.5, 145.5, 140.2, 135.2, 132.7, 128.6 (3C), 128.4, 128.3, 119.3, 116.1, 109.7, 80.1, 67.2, 55.3, 53.5, 52.2, 39.4, 37.4, 28.3 ppm (3C); HRMS (ESI): calcd for $C_{24}H_{31}N_2O_5^+$ [M + H$^+$] 427.2227, found

427.2225.

12b: R_f = 0.20 (hexanes:EtOAc 3:1); $[\alpha]_D^{20}$ = +28.1 (*c* = 0.4, $CHCl_3$); IR (film) ν_{max} 3332, 3092, 2969, 2857, 2721, 1735, 1721, 1611, 1583, 1505, 1370, 1240, 1142, 1030, 853, 764, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 (s, 5 H), 6.82–6.64 (m, 3 H), 5.16 (d, *J* = 2.8 Hz, 3 H), 4.54–4.41 (m, 1 H), 3.81 (s, 3 H), 3.71 (t, *J* = 8.7 Hz, 1 H), 3.44–3.34 (m, 1 H), 3.23 (dd, *J* = 8.8, 7.0 Hz, 1 H), 2.37–2.25 (m, 1 H), 1.87 (m, *J* = 14.0, 8.2 Hz, 1 H), 1.45 ppm (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.6, 155.2, 145.5, 140.1, 135.2, 132.6, 128.6 (3C), 128.4, 128.3, 119.4, 116.5, 109.7, 80.1, 67.1, 55.3, 53.9, 52.5, 39.6, 37.3, 28.3 ppm (3C); HRMS (ESI): calcd for $C_{24}H_{31}N_2O_5^+$ [M + H^+] 427.2227, found 427.2232.



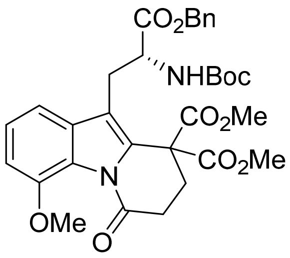
8

Indoline ester 8: To a stirred solution of indoline **12** (4.05 g, 9.5 mmol) in CH_2Cl_2 (15 mL) at room temperature were added Et_3N (2.65 mL, 19.0 mmol) followed by a solution of acyl chloride **10**[2] (4.20 g, 19.0 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred for 1 h before it was quenched with NH_4Cl (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded indoline ester **8** (5.12 g, 88%, ca. 1.2:1 mixture of diastereomers by ^1H NMR) as a colorless oil.

8a: R_f = 0.25 (hexanes:EtOAc 2:1); $[\alpha]_D^{20}$ = –31.3 (*c* = 0.7, $CHCl_3$); IR (film) ν_{max} 3357, 3105, 2967, 2867, 2769, 1741, 1703, 1651, 1523, 1483, 1358, 1246, 1158, 1031, 864, 756, 712 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 5 H), 7.05 (t, *J* = 7.8 Hz, 1 H), 6.80 (dd, *J* = 7.7, 3.9 Hz, 2 H), 5.15 (dd, *J* = 19.5, 7.2 Hz, 3 H), 4.48–4.28 (m, 2 H), 3.84 (s, 4 H), 3.71–3.60 (m, 6 H), 3.52 (t, *J* = 7.5 Hz, 1 H), 3.20 (s, 1 H), 2.54 (t, *J* = 7.1 Hz, 2 H), 2.33–2.20 (m, 2 H), 2.07–1.88 (m, 2 H), 1.43 ppm (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.2, 169.7, 169.6 (2C), 155.3, 149.1, 139.9, 135.1, 130.6, 128.6 (3C), 128.5, 128.3, 126.2, 116.5, 111.7, 80.2, 67.3, 56.9, 55.6, 52.3, 52.3, 52.2, 50.7, 38.1, 36.4, 31.8, 28.2 (3C), 24.6 ppm; HRMS (ESI): calcd for $C_{32}H_{41}N_2O_{10}^+$ [M + H$^+$] 613.2756, found 613.2750.

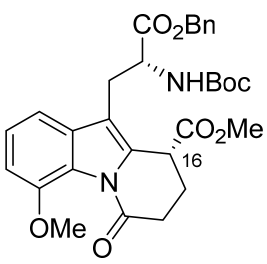
8b: R_f = 0.22 (hexanes:EtOAc 2:1); $[\alpha]_D^{20}$ = +7.2 (*c* = 0.7, $CHCl_3$); IR (film) ν_{max} 3358, 3075, 2981, 2847, 2769, 1729, 1701, 1656, 1519, 1479, 1362, 1258, 1164, 1045, 866 752, 706 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 5 H), 7.08 (t, *J* = 7.9 Hz, 1 H), 6.92 (d, *J* = 6.8 Hz, 1 H), 6.82 (d, *J* = 8.3 Hz, 1 H), 5.22–5.11 (m, 3 H), 4.53–4.43 (m, 1 H), 4.25 (dd, *J* = 11.1, 7.7 Hz, 1 H), 3.92 (dd, *J* = 11.3, 5.3 Hz, 1 H), 3.84 (s, 3 H), 3.66 (s, 3 H), 3.63 (s, 3 H), 3.51 (t, *J* = 7.5 Hz, 1 H), 3.25–3.16 (m, 1 H), 2.63–2.43 (m, 2 H), 2.32–2.16 (m, 3 H), 1.78 (dt, *J* = 14.1, 8.3 Hz, 1 H), 1.45 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.3, 169.7, 169.6 (2C), 155.3, 148.9, 140.1, 135.1, 130.4, 128.6 (3C), 128.5, 128.4, 126.3, 117.1, 111.7, 80.2, 67.3, 57.1, 55.6, 52.5, 52.4, 52.3, 50.7, 38.1, 36.4, 31.7, 28.3 (3C), 24.6 ppm; HRMS (ESI): calcd for $C_{32}H_{41}N_2O_{10}^+$ [M + H$^+$] 613.2756, found 613.2762.

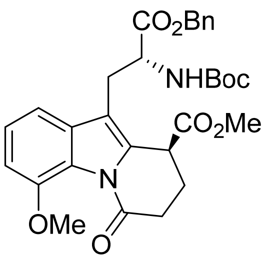
***δ*-Lactamindole 7**: To a solution of indoline ester **8** (6.12 g, 10.0 mmol) in AcOH (100 mL) were added CAN (550 mg, 1.0 mmol) and NaOAc (1.64 g, 20.0 mmol). The reaction vessel was exposed to air through a $CaCl_2$ tube. The resulting mixture was


7

stirred at 110 °C for 12 h before it was cooled down to room temperature and concentrated *in vacuo*. The residue was diluted with H_2O (100 mL), neutralized with $NaHCO_3$ (200 mL, sat. aq.) and extracted with EtOAc (3 × 200 mL). The combined organic layers were washed with brine (400 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 1:1) afforded *δ*-lactamindole **7** (5.05g, 83%) as a white amorphous solid. **7**: $R_f = 0.35$ (hexanes:EtOAc 1:1); $[\alpha]_D^{20} = -8.6$ ($c = 0.7$, $CHCl_3$); IR (film) ν_{max} 3413, 3095, 2967, 1744, 1709, 1513, 1458, 1362, 1246, 1172, 1047, 1010, 918, 761, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.20 (m, 7 H), 6.95–6.90 (m, 1 H), 5.51 (d, J = 6.8 Hz, 1 H), 5.13 (s, 2 H), 4.75 (dd, J = 11.2, 5.4 Hz, 1 H), 3.97 (s, 3 H), 3.80 (s, 3 H), 3.73 (s, 3 H), 3.09 (dd, J = 14.9, 5.6 Hz, 1 H), 2.97–2.82 (m, 3 H), 2.79–2.63 (m, 2 H), 1.34 ppm (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.4, 169.4, 169.2, 165.1, 155.3, 149.1, 135.5, 133.3, 131.8, 128.4 (2C), 128.2, 128.1 (2C), 125.6, 124.3, 117.2, 112.1, 109.3, 79.7, 67.1, 56.5, 55.9, 53.9, 53.6, 52.9, 31.1, 29.4, 28.2 (3C), 27.1 ppm; HRMS (ESI): calcd for $C_{32}H_{37}N_2O_{10}^+$ [M + H^+] 609.2443, found 609.2450.

Monoester 13: To a stirred solution of *δ*-lactamindole **7** (1.82 g, 3.0 mmol) in DMSO (20 mL) were added LiCl (1.26 g, 30 mmol) and H_2O (0.54 mL, 30.0 mmol). The resulting mixture was stirred at 65 °C for 8 h before it was quenched with ice water (40 mL, sat. aq.) and extracted with Et_2O (3 × 50 mL). The combined organic


13a (C16α-isomer)

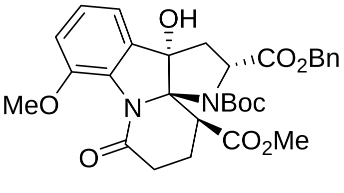

13b (C16β-isomer)

layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, CH_2Cl_2:Et_2O 20:1) afforded monoesters **13a** and **13b** (1.35 g，82% ca. 1:1 mixture of diastereomers by ^{1}H NMR) as a colorless oil.

13a: R_f = 0.20 (CH_2Cl_2:Et_2O 20:1); $[\alpha]_D^{20}$ = –21.8 (*c* = 2.0, $CHCl_3$); IR (film) ν_{max} 3412, 3358, 3096, 2976, 1705, 1523, 1462, 1298, 1230, 1168, 1048, 986, 753, 714 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (s, 3 H), 7.22 (d, *J* = 7.8 Hz, 1 H), 7.20–7.06 (m, 3 H), 6.89 (d, *J* = 8.0 Hz, 1 H), 5.09 (dd, *J* = 21.1, 8.5 Hz, 2 H), 4.97 (d, *J* = 12.1 Hz, 1 H), 4.68–4.56 (m, 1 H), 4.11 (s, 1 H), 3.97 (s, 3 H), 3.67 (s, 3 H), 3.29–3.11 (m, 2 H), 3.07–2.92 (m, 1 H), 2.76 (d, *J* = 17.0 Hz, 1 H), 2.44 (d, *J* = 12.6 Hz, 1 H), 2.13 (s, 1 H), 1.40 ppm (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.8, 171.3, 166.4, 155.1, 149.1, 134.9, 134.2, 133.3, 128.5 (3C), 128.4, 128.1, 125.2, 124.5, 114.4, 111.7, 109.1, 80.1, 67.3, 56.7, 53.6, 52.6, 37.9, 31.7, 28.2 (3C), 27.3, 24.5 ppm; HRMS (ESI): calcd for $C_{30}H_{35}N_2O_8^+$ [M + H$^+$] 551.2388, found 551.2384.

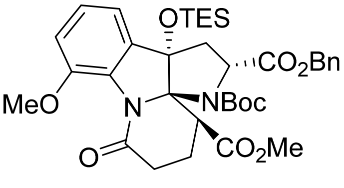
13b: R_f = 0.20 (CH_2Cl_2:Et_2O 20:1); $[\alpha]_D^{20}$ = +6.0 (*c* = 1.2, $CHCl_3$); IR (film) ν_{max} 3400, 3365, 3090, 2976, 1701, 1515, 1456, 1370, 1250, 1168, 1071, 978, 748, 710 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.27 (m, 3 H), 7.24 (d, *J* = 7.9 Hz, 1 H), 7.13 (dd, *J* = 10.1, 5.8 Hz, 3 H), 6.90 (d, *J* = 7.9 Hz, 1 H), 5.23 (d, *J* = 7.1 Hz, 1 H), 5.05 (d, *J* = 3.2 Hz, 2 H), 4.72 (d, *J* = 7.1 Hz, 1 H), 4.09 (s, 1 H), 3.98 (s, 3 H), 3.68 (s, 3 H), 3.24–2.93 (m, 3 H), 2.82–2.70 (m, 1 H), 2.45 (ddt, *J* = 13.5, 5.3, 2.6 Hz, 1 H), 2.13–1.98 (m, 1 H), 1.38 ppm (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.1, 171.3, 166.3, 155.1, 149.2, 135.1, 134.1, 132.9, 128.5 (3C), 128.3, 127.9, 125.3, 124.5, 114.1, 111.4, 109.1, 80.1, 67.1, 56.7, 53.1, 52.7, 37.8, 31.7, 28.2(3C), 27.6, 24.1 ppm; HRMS (ESI): calcd for $C_{30}H_{35}N_2O_8^+$ [M + H$^+$] 551.2388, found 551.2392.

Pyrroloindole 6': To a stirred solution of monoesters **13a** and **13b** (5.50 g, 10.0 mmol) in acetone (100 mL) at 0 °C was added $NaHCO_3$ (100 mL, sat. aq.). The resulting mixture was stirred for 0.5 h before it was added oxone (12.28 g, 20.0 mmol). The reaction mixture was stirred at 0 °C for an additional 2 h before it was diluted with H_2O (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layers were washed with brine (300 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 1:3) afforded pyrroloindole **6'** (3.86 g, 68%) as a white amorphous solid. **6'**: *R*f = 0.23 (hexanes:EtOAc 3:1); $[\alpha]_D^{20}$ = +8.0 (*c* = 1.0, MeOH); IR (film) ν_{max} 3412, 3368, 2984, 2924, 2877, 1701, 1680, 1634, 1596, 1370, 1243, 1160,1041, 912, 758, 724 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (q, *J* = 7.2 Hz, 5 H), 7.19 (t, *J* = 7.8 Hz, 1 H), 7.04 (d, *J* = 7.4 Hz, 1 H), 6.94 (d, *J* = 6.6 Hz, 1 H), 5.16 (d, *J* = 12.0 Hz, 1 H), 5.02 (d, *J* = 12.3 Hz, 1 H), 4.24 (s, 1 H), 3.76 (s, 6 H), 3.61 (s, 1 H), 3.37 (dd, *J* = 13.8, 3.4 Hz, 1 H), 3.23 (s, 1 H), 2.97 (s, 1 H), 2.69 (dd, *J* = 12.4, 7.4 Hz, 1 H), 2.59–2.31 (m, 2 H), 2.10–1.87 (m, 1 H), 1.33 ppm (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 167.9, 161.4, 158.7, 151.5, 135.5, 135.2, 135.1, 129.9, 128.5 (3C), 128.4, 128.2, 127.6, 115.7, 88.3, 86.9, 82.1, 66.7, 58.2, 53.1, 45.7, 30.9, 29.7, 29.3, 27.9 (3C), 20.1 ppm; HRMS (ESI): calcd for $C_{30}H_{35}N_2O_9^+$ [M + H$^+$] 567.2337, found 567.2335.



6'

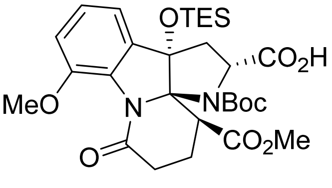
Silyl ether 15: To a stirred solution of pyrroloindole **6'** (1.13 g, 2.0 mmol) in CH_2Cl_2



15

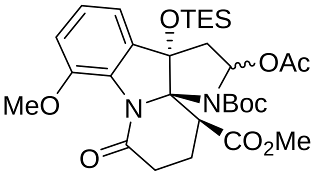
(20 mL) at room temperature were added DMAP (2.44g, 20.0 mmol) and TESOTf (1.35 mL, 6.0 mmol). The resulting mixture was stirred for 1 h before it was quenched with $NaHCO_3$ (35 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine (40 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded silyl ether **15** (1.16 g, 85%) as a colorless oil. **15**: $R_f = 0.40$ (hexanes:EtOAc 3:1); $[\alpha]_D^{20} = -12.0$ ($c = 0.5$, $CHCl_3$); IR (film) ν_{max} 3551, 3434, 2957, 2861, 2334, 1746, 1671, 1483, 1236, 1138, 1021, 760, 723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.31$ (s, 5 H), 7.17 (t, $J = 7.9$ Hz, 1 H), 6.95 (dd, $J = 26.9, 7.5$ Hz, 2 H), 5.24–4.99 (m, 2 H), 3.88–3.65 (m, 6 H), 3.64–3.36 (m, 2 H), 3.22–2.75 (m, 2 H), 2.69–2.54 (m, 2 H), 2.34 (ddd, $J = 18.6, 11.8, 6.9$ Hz, 1 H), 2.04–1.91 (m, 1 H), 1.46 (s, 6 H), 1.17 (s, 3 H), 0.82 (t, $J = 7.9$ Hz, 9 H), 0.56–0.40 ppm (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.7$, 170.2, 168.1, 153.7, 152.3, 136.2, 135.8, 130.3, 128.4, 128.1, 127.3, 126.9, 116.8, 115.7, 115.2, 114.1, 89.4, 86.6, 82.1, 66.6, 58.7, 55.7, 52.2, 44.3, 34.8, 30.7, 28.1 (3C), 21.4, 6.7 (3C), 6.1 ppm (3C); HRMS (ESI): calcd for $C_{36}H_{49}N_2O_9Si^+$ [M + H^+] 681.3202, found 681.3208.

Acid 16: To a stirred solution of silyl ether **15** (0.68 g, 1.0 mmol) in CH_2Cl_2 (20 mL) was added Pd/C (10 % wt/wt, 0.07 g) and bubbled with H_2 over 3 h before it was filtered through a short pad of celite. The filtrate was concentrated *in vacuo*. Flash column chromatography (silica gel, CH_2Cl_2:MeOH 20:1) afforded acid **16** (0.51 g, 86%) as a



16

colorless oil. **16**: R_f = 0.50 (CH_2Cl_2:MeOH 20:1); $[\alpha]_D^{20}$ = +42.7 (*c* = 0.8, $CHCl_3$); IR (film) ν_{max} 3584, 3431, 2974, 2852, 2371, 1746, 1710, 1681, 1463, 1326, 1249, 1123, 1034, 923, 749, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.20 (t, *J* = 7.8 Hz, 1 H), 7.04–6.95 (m, 2 H), 3.79 (d, *J* = 6.1 Hz, 6 H), 3.53 (s, 1 H), 3.35 (s, 1 H), 2.92 (s, 2 H), 2.71 (dd, *J* = 12.3, 6.5 Hz, 1 H), 2.58–2.14 (m, 2 H), 2.02 (s, 1 H), 1.34 (s, 9 H), 0.81 (t, *J* = 7.9 Hz, 9 H), 0.45 ppm (q, *J* = 7.9 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 171.8, 167.6, 152.0 (2C), 130.6, 127.2 (3C), 115.8, 89.7, 86.4, 83.0, 60.9, 56.5, 54.6, 52.9, 44.1, 31.3, 27.7 (3C), 22.8, 6.6 (3C), 6.00 ppm (3C); HRMS (ESI): calcd for $C_{29}H_{43}N_2O_9Si^+$ [M + H^+] 591.2732., found 591.2734.

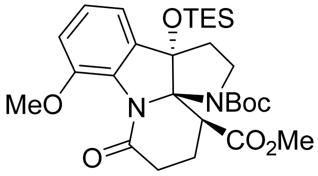


17

Acetate 17: To a stirred solution of acid **16** (0.59 g, 1.0 mmol) in CH_2Cl_2 (10 mL) at room temperature were added iodine (0.16 g, 0.5 mmol) followed by $PhI(OAc)_2$ (0.62 g, 2.0 mmol). The resulting mixture was stirred for 3 h before it was quenched with $NaHCO_3$ (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded acetate **17** (0.50 g, 83%) as a colorless oil. **17**: R_f = 0.42 (hexanes:EtOAc 3:1); $[\alpha]_D^{20}$ = +36.0 (*c* = 1.0, $CHCl_3$); IR (film) ν_{max} 3572, 3428, 2965, 2849, 2342, 1736, 1669, 1453, 1232, 1140, 1051, 756, 719 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.18–7.10 (m, 1 H), 7.00 (d, *J* = 7.9 Hz, 1 H), 6.95 (d, *J* = 7.5 Hz, 1 H), 6.08 (d, *J* = 5.3 Hz, 1 H), 3.82 (s, 3 H), 3.73 (s, 3 H), 3.50–3.40 (m, 1 H), 3.01 (s, 2 H), 2.55–2.37 (m, 3 H), 2.05–1.93 (m, 1 H), 1.57 (s, 3

H), 1.36 (s, 9 H), 0.81 (t, J = 7.9 Hz, 9 H), 0.46 ppm (q, J = 7.9 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.9, 169.7, 168.3, 167.6, 152.5, 152.1, 136.7, 131.1, 126.1, 117.2, 114.2, 89.7, 85.8, 81.6, 57.1, 52.1, 43.2, 30.9, 29.7, 28.1 (3C), 23.1, 20.6, 6.6 (3C), 6.1 ppm (3C); HRMS (ESI): calcd for $C_{30}H_{45}N_2O_9Si^+$ [M + H^+] 605.2889, found 605.2885.

Pyrroloindole 18: To a stirred solution of acid **16** (1.18 g, 2.0 mmol) in CH_2Cl_2 (20 mL) at room temperature were added iodine (0.32 g, 1.0 mmol) followed by $PhI(OAc)_2$ (1.23 g, 4.0 mmol). The resulting mixture was stirred for 3 h before it was added $NaBH_3CN$ (1.24 g, 20.0 mmol). The resulting mixture was stirred for further 1 h before it was quenched with $NaHCO_3$ (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded pyrroloindole **18** (0.95 g, 76%) as a yellow oil. **18**: R_f = 0.44 (hexanes:EtOAc 3:1); $[\alpha]_D^{20}$ = +49.0 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3581, 3432, 2988, 2835, 2359, 1741, 1681, 1468, 1229, 1126, 1053, 764, 726 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (t, J = 7.9 Hz, 1 H), 6.95 (dd, J = 14.9, 7.9 Hz, 2 H), 3.86 (s, 2 H), 3.73 (s, 3 H), 3.49–3.36 (m, 1 H), 3.21 (t, J = 10.1 Hz, 2 H), 2.99–2.65 (m, 3 H), 2.34 (dq, J = 43.1, 11.3 Hz, 3 H), 2.02–1.90 (m, 1 H), 1.38 (d, J = 48.1 Hz, 9 H), 0.82 (t, J = 7.9 Hz, 9 H), 0.47 ppm (d, J = 7.9 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.9, 167.8, 153.7, 152.2, 136.5, 130.7, 126.8, 115.4, 114.4, 88.4, 87.2, 81.0, 55.9, 52.1, 44.9, 43.3, 30.9, 30.3, 28.1 (3C), 22.4, 6.7 (3C), 6.1 ppm (3C); HRMS (ESI):



18

calcd for $C_{28}H_{43}N_2O_7Si^+$ [M + H$^+$] 547.2834, found 547.2836.

Alternatively, pyrroloindole **18** can also be obtained from acetate **17** through the following procedure:

To a stirred solution of acetate **17** (121 mg, 0.2 mmol) in CH_2Cl_2 (5 mL) at room temperature was added $NaBH_3CN$ (124 mg, 2.0 mmol). The resulting mixture was stirred for 1 h before it was quenched with $NaHCO_3$ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo.* Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded pyrroloindole **18** (97 mg, 90%) as a yellow oil.

Synthesis of pyrroloindole 18 through reductive decarboxylation of Barton ester:

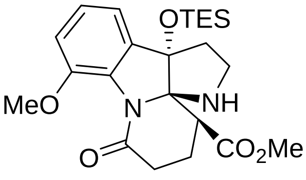
To a stirred solution of acid **16** (59 mg, 0.10 mmol) in THF (5 mL) at room temperature were added Et_3N (56 μL, 0.40 mmol), DMAP (6 mg, 0.05 mmol) and HOTT[3] (56 mg, 0.15 mmol). The resulting mixture was stirred in the dark for 2 h before it was added *t*-dodecanethiol (41 mg, 0.20 mmol). The resulting mixture was stirred at 65 °C for further 12 h before it was cooled to room temperature and diluted with H_2O (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo.* Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded pyrroloindole **18** (23 mg, 43%) as a yellow oil.

Synthesis of pyrroloindole 18 through reductive decarboxylation of selenoester:

To a stirred solution of acid **16** (59 mg, 0.10 mmol) in CH_2Cl_2 (5 mL) at 0 °C were added PhSeSePh (47 mg, 0.15 mmol) and *n*-Bu_3P (76 μL, 0.30 mmol). The resulting mixture was stirred at room temperature for 12 h before it was diluted with EtOAc (5 mL) and washed with H_2O (5 mL). The organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 5:1) afforded crude selenoester (68 mg, 83%) as a yellow solid, which was subjected immediately into the next step.

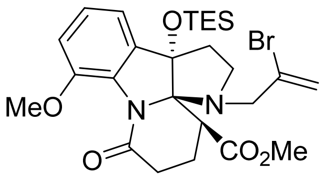
To a stirred solution of the selenoester (crude, obtained above) in benzene (8 mL) were added AIBN (8 mg, 0.05 mmol) and $(TMS)_3SiH$ (138 μL, 0.40 mmol). The resulting mixture was stirred at 80 °C for 24 h before it was cooled to room temperature and concentrated *in vacuo.* Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded pyrroloindole **18** (29 mg, 54%) as a yellow oil.

Amine 19: To a stirred solution of pyrroloindole **18** (1.09 g, 2.0 mmol) in CH_2Cl_2 (9 mL) at 0 °C was added CF_3CO_2H (3 ml). The resulting mixture was stirred at room temperature for 1 h before it was quenched with $NaHCO_3$ (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine (40 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 1:1) afforded amine **19** (0.80 g, 90%) as a colorless oil. **19**: $R_f = 0.33$ (hexanes:EtOAc 1:2); $[\alpha]_D^{20} = +28.0$ ($c = 0.8$, $CHCl_3$); IR (film) ν_{max} 3572, 3423, 2974, 2812, 2364, 1738, 1668, 1474, 1239, 1126, 1031, 986, 768, 724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.17 (t, *J* = 7.9 Hz, 1 H), 7.01–6.97 (m, 1 H), 6.94 (d, *J* = 7.9 Hz, 1 H), 3.88 (s, 3 H), 3.73 (s, 3 H), 3.10



19

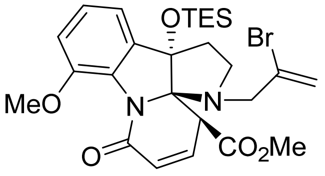
(dd, *J* = 13.1, 2.8 Hz, 1 H), 2.91 (t, *J* = 9.1 Hz, 1 H), 2.83 (ddd, *J* = 17.8, 6.6, 1.4 Hz, 1 H), 2.50–2.15 (m, 6 H), 2.08 (ddd, *J* = 4.9, 2.8, 1.4 Hz, 1 H), 0.82 (t, *J* = 7.9 Hz, 9 H), 0.45 ppm (m, *J* = 8.4, 4.4 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 167.1, 151.3, 136.9, 130.9, 126.5, 116.1, 113.8, 92.1, 88.3, 56.1, 51.7, 44.6, 43.8, 37.2, 32.1, 21.6, 6.7 (3C), 6.1 ppm (3C); HRMS (ESI): calcd for $C_{23}H_{35}N_2O_5Si^+$ $[M + H^+]$ 447.2310, found 447.2312.



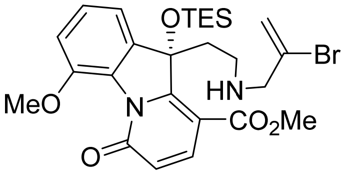
21

Vinyl bromide 21: To a stirred solution of amine **19** (580 mg, 1.3 mmol) in MeCN (10 mL) were added allyl iodide **20** (642 mg, 2.6 mmol) and K_2CO_3 (542 mg, 3.9 mmol). The resulting mixture was stirred at 50 °C for 12 h before it was cooled to room temperature and filtered through a short pad of celite. The filtrate was diluted with EtOAc (15 mL) and washed with brine (15 mL). The organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 3:1) afforded vinyl bromide **21** (623 mg, 85%) as a colorless oil. **21**: R_f = 0.40 (hexanes:EtOAc 3:1); $[\alpha]_D^{20}$ = +64.5 (*c* = 1.0, $CHCl_3$); IR (film) ν_{max} 2972, 2874, 2831, 2370, 1729, 1667, 1478, 1379, 1253, 1166, 1017, 775, 735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (s, 1 H), 7.00–6.94 (m, 2 H), 5.87 (d, *J* = 1.4 Hz, 1 H), 5.46–5.41 (m, 1 H), 3.93 (d, *J* = 15.5 Hz, 4 H), 3.72 (s, 3 H), 3.20 (dd, *J* = 12.7, 3.3 Hz, 1 H), 3.04 (t, *J* = 8.2 Hz , 1 H), 2.88 (ddd, *J* = 17.7, 6.1, 2.2 Hz, 1 H), 2.73 (d, *J* = 16.8 Hz, 1 H), 2.53–2.36 (m, 2 H), 2.35–2.23 (m, 2 H), 2.11–2.02 (m, 1 H), 1.78 (ddd, *J* = 11.2, 8.5, 6.4 Hz, 1 H), 0.82 (t, 9 H), 0.48 ppm (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.6, 168.4, 151.5, 137.5, 131.2, 130.7, 127.1, 116.9, 115.6, 114.1, 92.2, 87.7, 59.9, 56.3, 51.5, 50.8, 45.9, 34.1, 31.5, 20.6, 6.7 (3C), 6.1 ppm (3C); HRMS (ESI): calcd for $C_{26}H_{38}BrN_2O_5Si^+$ [M + H^+] 565.1728, found 565.1730.

Enone *ent*-5 and Amine 22: To a stirred solution of vinyl bromide **21** (620 mg, 1.1 mmol) in THF (10 mL) at –78 °C was added LiHMDS (1.0 M in THF, 1.65 mL, 1.65 mmol). The resulting mixture was stirred for 0.5 h before it was added a solution of PhSeCl (316 mg, 1.65mmol) in THF (10 ml). The resulting mixture was stirred at –78 °C for further 0.5 h before it was diluted with EtOAc (15 mL) and quenched with $NaHCO_3$ (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 5:1) afforded crude selenide (750 mg, 95%), which was subjected immediately into the next step.



ent-**5**



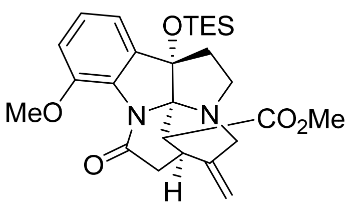
22

To a stirred solution of the selenide (crude, obtained above) in THF (10 mL) at room temperature was added H_2O_2 (30% wt/wt in H_2O, 0.34 mL, 3.0 mmol). The resulting mixture was stirred for 0.5 h before it was diluted with Et_2O (5 mL) and quenched with $Na_2S_2O_3$ (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 5:1) afforded enone *ent*-**5** (56 mg, 10%) as a colorless oil, along with amine **22** (365 mg, 65%) as a colorless oil.

ent-**5**: R_f = 0.32 (hexanes:EtOAc 5:1); $[\alpha]_D^{20}$ = +45.6 (*c* = 1.0, $CHCl_3$); IR (film) ν_{max} 2971, 2868, 2816, 2371, 1735, 1671, 1476, 1379, 1238, 1173, 1133, 1015, 741, 713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.20 (t, *J* = 7.9 Hz, 1 H), 7.05–6.95 (m, 2 H), 6.81 (dd, *J* = 10.1, 2.1 Hz, 1 H), 6.12 (dd, *J* = 10.1, 3.2 Hz, 1 H), 5.45 (s, 1 H), 5.35 (s, 1 H), 4.39–4.34 (m, 1 H), 3.93 (s, 3 H), 3.78 (s, 3 H), 3.75–3.65 (m, 1 H), 3.13 (d, *J* = 15.5 Hz, 1 H), 2.85 (t, *J* = 8.0 Hz, 1 H), 2.68–2.57 (m, 1 H), 2.23 (dd, *J* = 11.6, 5.5 Hz, 1 H), 1.88–1.78 (m, 1 H), 0.82 (t, *J* = 7.9 Hz, 9 H), 0.54–0.42 ppm (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 160.6, 150.8, 137.8, 136.8, 130.5, 129.8, 126.9, 123.3, 117.9, 115.9, 114.4, 90.8, 88.5, 57.9, 56.4, 52.1, 49.1, 46.5, 35.7, 6.7 (3C), 6.2 ppm (3C); HRMS (ESI): calcd for $C_{26}H_{36}BrN_2O_5Si^+$ [M + H$^+$] 563.1571, found 563.1575.

22: R_f = 0.22 (hexanes:EtOAc 2:1); $[\alpha]_D^{20}$ = –31.2 (*c* = 1.0, $CHCl_3$); IR (film) ν_{max} 3351, 2968, 2874, 2843, 2372, 1671, 1552, 1485, 1248, 1099, 1033, 964, 768, 732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 9.6 Hz, 1 H), 7.32 (t, *J* = 7.9 Hz, 1 H), 7.08 (dd, *J* = 7.9, 3.6 Hz, 2 H), 6.56 (d, *J* = 9.6 Hz, 1 H), 5.54 (d, *J* = 1.3 Hz, 1 H), 5.38 (d, *J* = 1.6 Hz, 1 H), 3.99 (s, 3H), 3.88 (s, 3 H), 3.30–3.20 (m, 1 H), 3.17 (s, 2 H), 2.42–2.32 (m, 1 H), 2.08 (t, *J* = 7.4 Hz, 2 H), 0.72 (t, *J* = 7.9 Hz, 9 H), 0.20 ppm (q, *J* = 8.0 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 159.3, 158.1, 149.3, 138.8, 138.7, 132.9, 128.4, 127.6, 120.9, 117.3, 116.1, 115.8, 109.3, 83.2, 57.1, 56.8, 52.1, 42.5, 41.5, 6.6 (3C), 5.5 ppm (3C); HRMS (ESI): calcd for $C_{26}H_{36}BrN_2O_5Si^+$ [M + H$^+$] 563.1571, found 563.1573.

Tetracycle C16-*epi*-*ent*-4: To a stirred solution of amine **22** (303 mg, 0.54 mmol) in toluene (10 mL) at –78 °C were added *n*-Bu_3SnH (0.17 mL, 0.64 mmol) and Et_3B (57



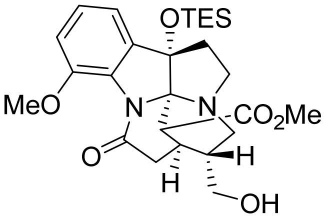
C16-*epi*-*ent*-**4**

μL, 0.54 mmol). The resulting mixture was stirred for 0.5 h before it was warmed to 0 °C and stirred for an additional 2 h. The solvent was removed, and flash column chromatography (silica gel, hexanes:EtOAc 1:1) afforded tetracycle C16-*epi*-*ent*-**4** (183 mg, 70%) as a white amorphous solid. C16-*epi*-*ent*-**4**: $R_f = 0.23$ (hexanes:EtOAc 3:1); $[\alpha]_D^{20} = +126.5$ ($c = 1.0$, $CHCl_3$); IR (film) ν_{max} 2971, 2868, 2822, 2361, 1741, 1683, 1485, 1395, 1237, 1135, 1012, 761, 729 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.13$ (t, $J = 7.9$ Hz, 1 H), 6.99 (d, $J = 7.5$ Hz, 1 H), 6.91 (d, $J = 8.2$ Hz, 1 H), 4.82 (d, $J = 10.7$ Hz, 2 H), 3.87 (s, 3 H), 3.66 (s, 4 H), 3.36 (d, $J = 13.1$ Hz, 1 H), 3.25–3.19 (m, 1 H), 2.98–2.88 (m, 2 H), 2.79 (d, $J = 1.7$ Hz, 1 H), 2.73–2.62 (m, 2 H), 2.22–2.13 (m, 1 H), 2.09 (dd, $J = 10.6, 4.3$ Hz, 1 H), 0.82 (t, $J = 7.9$ Hz, 9 H), 0.47 ppm (q, $J = 7.8$ Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 169.7$, 166.6, 149.8, 143.3, 136.6, 130.7, 126.1, 116.6, 114.3, 111.1, 89.9, 89.2, 56.3, 51.3, 49.01, 48.5, 47.5, 40.5, 40.2, 40.1, 6.8 (3C), 6.3 ppm (3C); HRMS (ESI): calcd for $C_{26}H_{37}N_2O_5Si^+$ $[M + H^+]$ 485.2466, found 485.2467.

Alternatively, tetracycle C16-*epi*-*ent*-**4** can also be obtained from enone *ent*-**5** through the following procedure:

To a stirred solution of enone *ent*-**5** (264 mg, 0.47 mmol) and AIBN (77 mg, 0.47 mmol) in benzene (5 mL) at 80 °C were added *n*-Bu_3SnH (253 μL, 0.94 mmol). The resulting mixture was stirred for 0.5 h before it was cooled to room temperature and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 1:1) afforded tetracycle C16-*epi*-*ent*-**4** (186 mg, 82%) as a white amorphous solid.

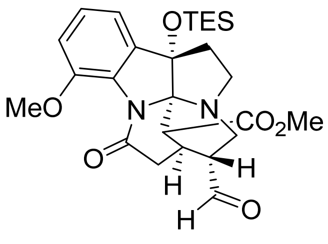
Alcohol 24: To a stirred solution of tetracycle C16-*epi*-*ent*-**4** (126 mg, 0.26 mmol) and



24

$Rh(PPh_3)_3Cl$ (120 mg, 0.13 mmol) in THF (5 mL) at 0 °C was added catecholborane (140 µL, 1.32 mmol). The resulting mixture was warmed to room temperature and stirred for 2 h before it was added NaOH (3 M aq., 0.43 mL, 1.3 mmol) and H_2O_2 (30% wt/wt in H_2O, 0.15 mL, 1.3 mmol). The resulting mixture was stirred for 1 h before it was quenched with $NaHCO_3$ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, EtOAc) afforded alcohol **24** (109 mg, 84%) as a white amorphous solid. **24**: $R_f = 0.40$ (EtOAc); $[\alpha]_D^{20} = +95.3$ ($c = 1.2$, $CHCl_3$); IR (film) ν_{max} 2970, 2858, 2831, 2358, 1736, 1679, 1474, 1386, 1246, 1138, 1017, 971, 758, 732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.11 (m, 1 H), 6.99 (dd, J = 7.5, 0.9 Hz, 1 H), 6.92 (dd, J = 8.2, 0.6 Hz, 1 H), 3.90 (s, 3 H), 3.70 (s, 3 H), 3.64–3.56 (m, 1 H), 3.17 (dd, J = 11.9, 4.4 Hz, 1 H), 2.97 (dd, J = 18.1, 8.0 Hz, 1 H), 2.89–2.81 (m, 3 H), 2.81–2.74 (m, 1 H), 2.66 (dd, J = 9.7, 8.3 Hz, 2 H), 2.17–2.06 (m, 2 H), 1.80 (s, 2 H), 1.62 (s, 1 H), 0.82 (t, J = 7.9 Hz, 9 H), 0.51–0.42 ppm (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 166.8, 149.7, 136.9, 130.5, 126.1, 116.5, 114.2, 90.3, 89.1, 64.7, 56.3, 51.4, 49.4, 45.4, 44.0, 42.9, 42.1, 39.6, 33.1, 6.8 (3C), 6.3 ppm (3C); HRMS (ESI): calcd for $C_{26}H_{39}N_2O_6Si^+$ $[M + H^+]$ 503.2572, found 503.2576.

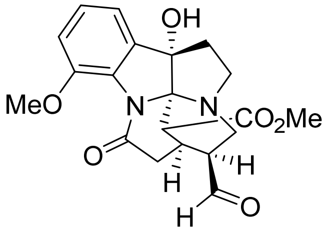
Aldehyde 25: To a stirred solution of alcohol **24** (50 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) at room temperature were added $NaHCO_3$ (50 mg, 0.6 mmol) and Dess–Martin



25

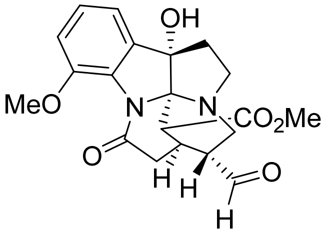
periodinane (46 mg, 0.11 mmol). The resulting mixture was stirred for 0.5 h before it was diluted with CH_2Cl_2 (10 mL) and quenched with $Na_2S_2O_3$ (5 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, EtOAc) afforded aldehyde **25** (44 mg, 88%) as a white amorphous solid. **25**: $R_f = 0.65$ (EtOAc); $[\alpha]_D^{20} = +112.4$ ($c = 0.7$, $CHCl_3$); IR (film) ν_{max} 2983, 2976, 2820, 2353, 1730, 1661, 1468, 1429, 1386, 1249, 1178, 1024, 754, 714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.62$ (s, 1 H), 7.15 (t, $J = 7.9$ Hz, 1 H), 7.01–6.96 (m, 1 H), 6.93 (d, $J = 8.1$ Hz, 1 H), 3.90 (s, 3 H), 3.64 (s, 3 H), 3.41–3.30 (m, 3 H), 3.00 (ddd, $J = 14.8$, 13.1, 7.6 Hz, 2 H), 2.75–2.59 (m, 3 H), 2.20–2.02 (m, 3 H), 0.81 (t, $J = 7.9$ Hz, 9 H), 0.54–0.41 ppm (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 203.1$, 170.1, 166.3, 149.7, 136.4, 130.5, 126.2, 116.6, 114.2, 89.6, 89.1, 56.2, 51.5, 51.2, 49.2, 44.7, 42.2, 40.2, 39.9, 31.5, 6.8 (3C), 6.3 ppm (3C); HRMS (ESI): calcd for $C_{26}H_{37}N_2O_6Si^+$ $[M + H^+]$ 501.2415, found 501.2417.

Aldehyde 27: To a stirred solution of aldehyde **25** (80 mg, 0.16 mmol) in MeCN (5 mL) at room temperature was added HF·py (0.73 mL, 8.0 mmol). The resulting mixture was stirred for 12 h before it was quenched with $NaHCO_3$ (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (5 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel,



27

CH_2Cl_2:MeOH 10:1) afforded aldehyde **27** (53 mg, 86%) as a white amorphous solid. **27**: $R_f = 0.59$ (CH_2Cl_2:MeOH 10:1); $[\alpha]_D^{20} = +25.6$ ($c = 0.8$, $CHCl_3$); IR (film) ν_{max} 3391, 3306, 2983, 2835, 2348, 1809, 1732, 1652, 1482, 1424, 1393, 1271, 1168, 1130, 1021, 924, 756, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.72$ (s, 1 H), 7.19 (t, $J = 7.8$ Hz, 1 H), 7.08–7.04 (m, 1 H), 6.92 (d, $J = 8.0$ Hz, 1 H), 5.21 (s, 1 H), ,3.89 (s, 3 H), 3.87 (s, 3 H), 3.47–3.41 (m, 1 H), 3.18–3.09 (m, 2 H), 3.07–2.98 (m, 2 H), 2.78–2.54 (m, 3 H), 2.45–2.34 (m, 1 H), 2.12–1.99 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 201.4$, 171.8, 166.2, 149.2, 136.2, 129.8, 126.9, 115.9, 113.9, 89.1, 88.7, 56.2, 53.1, 49.4, 48.2, 47.7, 42.6, 40.6, 34.8, 29.3 ppm; HRMS (ESI): calcd for $C_{20}H_{23}N_2O_6^+$ [M + H^+] 387.1551, found 387.1554.

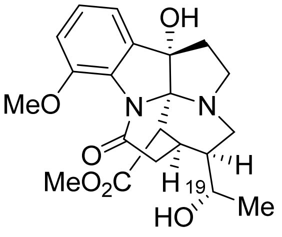


26

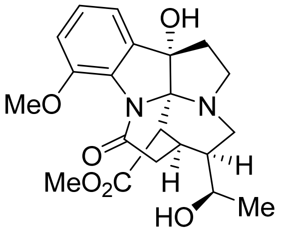
Aldehyde 26: To a stirred solution of aldehyde **25** (100 mg, 0.2 mmol) in MeCN (5 mL) at room temperature were added HF·py (0.91 mL, 10.0 mmol). The resulting mixture was stirred for 6 h before it was quenched with $NaHCO_3$ (20 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (5 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash column chromatography (silica gel, CH_2Cl_2:MeOH 10:1) afforded both aldehydes **26** (41 mg, 53%) and **27** (29 mg, 38%) as white amorphous solids. **26**: $R_f = 0.62$ (CH_2Cl_2:MeOH 10:1); $[\alpha]_D^{20} = +108.3$ ($c = 0.5$, $CHCl_3$); IR (film) ν_{max} 3389, 3301, 2969, 2835, 2349, 1816, 1723, 1648, 1469, 1441, 1362, 1264, 1157, 1138, 1028, 931, 744, 718 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.62$ (s, 1 H), 7.21 (t, $J = 7.8$ Hz, 1 H), 7.06 (dd, $J = 7.5$, 0.8 Hz, 1 H), 6.94 (d, $J =$

8.1 Hz, 1 H), 5.07 (s, 1 H), 3.91 (s, 3 H), 3.73 (s, 3 H), 3.45 (d, *J* = 12.0 Hz, 1 H), 3.37 (dd, *J* = 6.8, 5.3 Hz, 1 H), 3.15 (dd, *J* = 12.0, 4.8 Hz, 1 H), 2.95 (d, *J* = 2.0 Hz, 1 H), 2.83 (dd, *J* = 8.5, 6.4 Hz, 1 H), 2.79–2.67 (m, 2 H), 2.40 (d, *J* = 6.5 Hz, 1 H), 2.24 (d, *J* = 4.8 Hz, 1 H), 2.13–1.96 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) :δ = 200.7, 171.5, 166.2, 149.3, 136.6, 129.7, 127.1, 116.1, 113.8, 88.6, 88.4, 56.2, 52.3, 51.3, 48.5, 46.7, 41.2, 40.6, 40.1, 30.3 ppm; HRMS (ESI): calcd for $C_{20}H_{23}N_2O_6^+$ [M + H$^+$] 387.1551, found 387.1552.

(+)-Asmaphorzaine E (*ent*-3) and C19-*epi*-*ent*-3: To a stirred solution of aldehyde **27** (40 mg, 0.10 mmol) in THF (2 mL) at –78 °C was added MeMgBr (3.0 M in Et_2O, 0.17 mL, 0.52 mmol). The resulting mixture was stirred for 0.5 h before it was quenched with $NaHCO_3$ (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (4 × 5 mL). The combined organic layers were washed with brine (5 mL), dried (Na_2SO_4) and concentrated *in vacuo* to afford the crude alcohol (38 mg，90%, ca. 3:1 mixture of inseparable diastereomers by ^{1}H NMR) as a colorless oil, which was used directly in the next step.



(+)-asmaphorzaine E (*ent*-**3**)



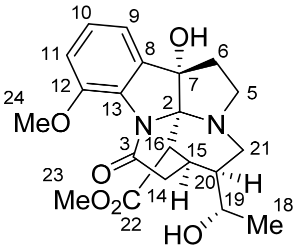
C19-*epi*-*ent*-**3**

To a stirred solution of the alcohol (crude, obtained above) in toluene (2 mL) at 90 °C was added DBU (74 μL, 0.52 mmol). The resulting mixture was stirred for 16 h before it was diluted with EtOAc (10 mL) and quenched with $NaHCO_3$ (10 mL, sat. aq.). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*.

Flash column chromatography (silica gel, EtOAc) afforded (+)-asmaphorzaine E (*ent*-**3**) (26 mg, 68%) as a white solid, along with C19-*epi*-*ent*-**3** (8 mg, 20%) as a white solid. ***ent*-3**: R_f = 0.12 (EtOAc); m.p. 257–259 °C (EtOAc/hexanes); $[\alpha]_\mathrm{D}^{20}$ = +35.8 (*c* = 0.4, MeOH); Lit. $[\alpha]_\mathrm{D}^{20}$ = +26 (*c* = 0.1, MeOH);[4] IR (film) ν_max 3383, 2985, 2808, 1588, 1462, 1437, 1382, 1317, 1206, 1021, 910, 756, 712 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD): δ = 7.22 (t, *J* = 7.8 Hz, 1 H), 7.04 (d, *J* = 7.7 Hz, 1 H), 7.00 (d, *J* = 8.2 Hz, 1 H), 3.85 (s, 3 H), 3.69 (dq, *J* = 9.5, 6.1 Hz, 1 H), 3.60 (s, 3 H), 3.06 (d, *J* = 2.8 Hz, 1 H), 3.04–2.97 (m, 1 H), 2.85 (dd, *J* = 11.6, 4.9 Hz, 1 H), 2.78 (d, *J* = 18.8 Hz, 1 H), 2.74 (dd, *J* = 8.7, 6.5 Hz, 1 H), 2.61 (dd, *J* = 11.6, 11.5 Hz, 1 H), 2.37 (dd, *J* = 18.8, 8.5 Hz, 1 H), 2.27–2.19 (m, 1 H), 2.09–2.00 (m, 1 H), 1.94 (dd, *J* = 11.2, 3.8 Hz, 1 H), 1.90–1.84 (m, 1 H), 1.24 ppm (d, *J* = 6.1 Hz, 3 H); ^{13}C NMR (125 MHz, CD_3OD): δ = 173.7, 171.5, 150.8, 138.7, 131.7, 128.0, 117.1, 115.2, 89.2, 88.8, 66.7, 56.7, 52.2, 49.6, 48.9, 48.7, 45.9, 43.3, 32.3, 31.8, 22.3 ppm; HRMS (ESI): calcd for $C_{21}H_{27}N_2O_6^+$ [M + H$^+$] 403.1864, found 403.1864.

C19-*epi*-*ent*-3: R_f = 0.10 (EtOAc); m.p. 236–238 °C; $[\alpha]_\mathrm{D}^{20}$ = +52.8 (*c* = 0.5, MeOH); IR (film) ν_max 3386, 2954, 2821, 1583, 1452, 1421, 1401, 1322, 1208, 1122, 1032, 910, 754, 716 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD): δ = 7.26–7.19 (m, 1 H), 7.03 (ddd, *J* = 13.6, 7.9, 0.9 Hz, 2 H), 3.86 (s, 3 H), 3.74–3.67 (m, 1 H), 3.60 (s, 3 H), 3.23 (dd, *J* = 11.9, 4.8 Hz, 1 H), 3.11–3.05 (m, 1 H), 2.79–2.64 (m, 4 H), 2.37 (dd, *J* = 18.7, 8.5 Hz, 1 H), 2.24 (td, *J* = 11.0, 6.4 Hz, 1 H), 2.06 (ddd, *J* = 10.8, 8.8, 4.0 Hz, 1 H), 1.94 (dd, *J* = 11.3, 3.8 Hz, 1 H), 1.91–1.81 (m, 1 H), 1.24 ppm (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (100 MHz, CD_3OD): δ = 173.5, 171.1, 150.7, 138.6, 131.6, 128.0, 117.0, 115.2, 89.3, 88.8, 68.5, 56.6, 52.2, 49.7, 48.8, 48.6, 46.1, 43.3, 33.8, 31.6, 21.8 ppm; HRMS (ESI): calcd for $C_{21}H_{27}N_2O_6^+$ [M + H^+] 403.1864, found 403.1863.

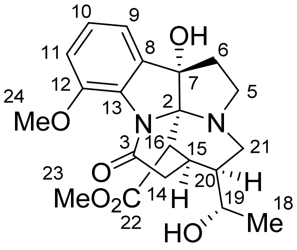
Table 1. ^{1}H NMR Spectroscopic (CD$_3$OD, 25 °C) Comparison of Synthetic and Natural (+)-Alsmaphorazine E (*ent*-**3**)[4]



(+)-asmaphorzaine E (*ent*-**3**)

No.	**Natural**[4] δ ^{1}H [ppm, mult, *J* (Hz)]	**Synthetic** δ ^{1}H [ppm, mult, *J* (Hz)]
2		
3		
5a	2.75 (dd, *J* = 8.7, 6.5 Hz)	2.74 (dd, *J* = 8.7, 6.5 Hz)
5b	2.04 (m)	2.09–2.00 (m)
6a	2.23 (m)	2.27–2.19 (m)
6b	1.93 (dd, *J* = 11.5, 3.8 Hz)	1.93 (dd, *J* = 11.2, 3.8 Hz)
7		
8		
9	7.03 (d, *J* = 7.7Hz)	7.04 (d, *J* = 7.7Hz)
10	7.22 (dd, *J* = 8.0, 7.7 Hz)	7.22 (dd, *J* = 7.8, 7.8 Hz)
11	7.00 (d, *J* = 8.0 Hz)	7.00 (d, *J* = 8.2 Hz)
12		
13		
14a	2.76 (d, *J* = 18.8 Hz)	2.78 (d, *J* = 18.8 Hz)
14b	2.37 (dd, *J* = 18.8, 8.5 Hz)	2.37 (dd, *J* = 18.8, 8.5 Hz)
15	3.00 (m)	3.04–2.97 (m)
16	3.05 (d, *J* = 2.8 Hz)	3.05 (d, *J* = 2.8 Hz)
18	1.24 (d, *J* = 6.1 Hz)	1.24 (d, *J* = 6.1 Hz)
19	3.68 (dq, *J* = 9.5, 6.1 Hz)	3.69 (dq, *J* = 9.5, 6.1 Hz)
20	1.88 (m)	1.90–1.84 (m)
21a	2.85 (dd, *J* = 11.5, 3.8 Hz)	2.85 (dd, *J* = 11.6, 4.9 Hz)
21b	2.61 (dd, *J* = 11.6, 11.5 Hz)	2.61 (dd, *J* = 11.6, 11.5 Hz)
22		
23	3.60 (s)	3.60 (s)
24	3.85 (s)	3.85 (s)

Table 2. ^{13}C NMR Spectroscopic (CD$_3$OD, 25 °C) Comparison of Synthetic and Natural (+)-alsmaphorazine E (***ent*-3**)[4]



(+)-asmaphorzaine E (*ent*-**3**)

No.	**Natural**[4]	**Synthetic**
	δ ^{13}C (ppm)	δ ^{13}C (ppm)
2	89.1	89.2
3	171.3	171.5
5a	48.8	48.7
5b		
6a	43.3	43.3
6b		
7	88.8	88.8
8	138.8	138.7
9	117.1	117.1
10	128.0	128.0
11	115.3	115.2
12	150.9	150.8
13	131.7	131.7
14a	31.8	31.8
14b		
15	32.4	32.3
16	49.7	49.6
18		
19	66.7	66.7
20	48.9	48.9
21a	45.9	45.9
21b		
22	173.8	173.7
23	52.2	52.2
24	56.7	56.7

II) Abbreviations

AIBN	2,2’-azobis(2-methylpropionitrile)
CAN	cerium ammonium nitrate
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMAP	*N*,*N*-Dimethylpyridin-4-amine
DMF	*N,N*-Dimethylformamide
HOTT	*S*-(1-oxido-2-pyridinyl) 1,1,3,3-tetramethylthiouronium hexafluorophosphate
LiHMDS	lithium bis(trimethylsilyl)amide
py	pyridine
TESOTf	triethylsilyltrifluoromethanesulfonate

III) References

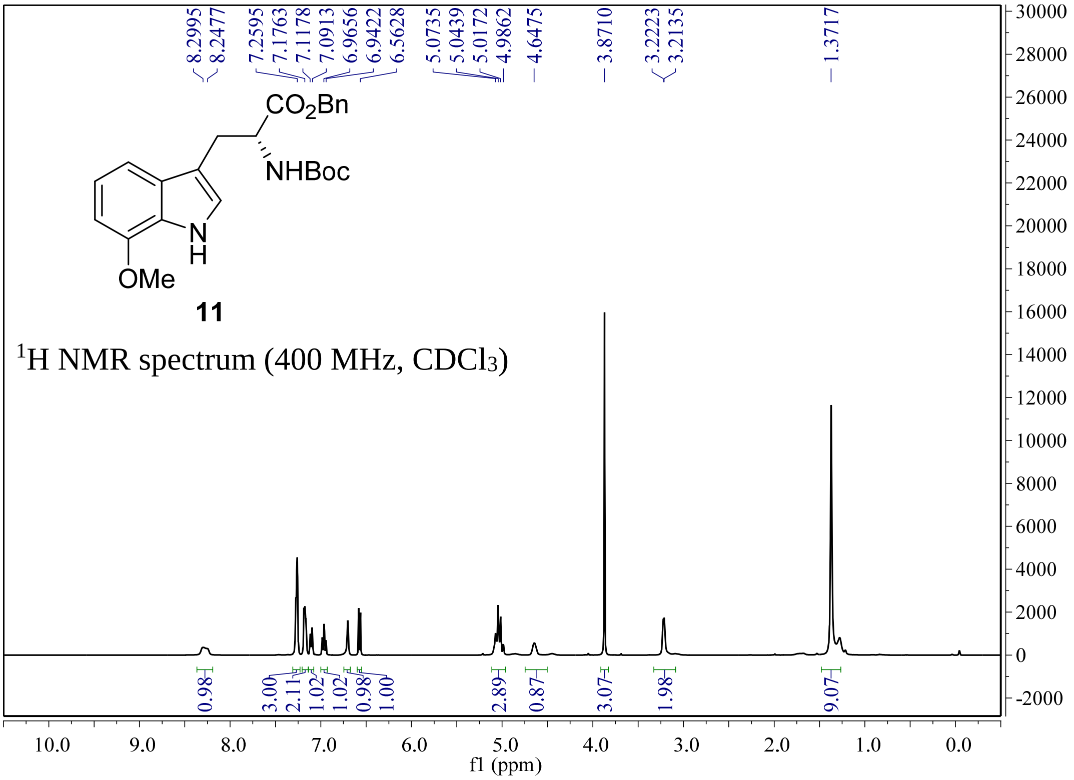
1 For its preparation, see: (*a*) C. Ma, X. Liu, X. Li, J. Flippen-Anderson, S. Yu and J. M. Cook, *J. Org. Chem.*, 2001, **66**, 4525; (*b*) H. Zhou, X. Liao, W. Yin, J. Ma and J. M. Cook, *J. Org. Chem.*, 2006, **71**, 251.

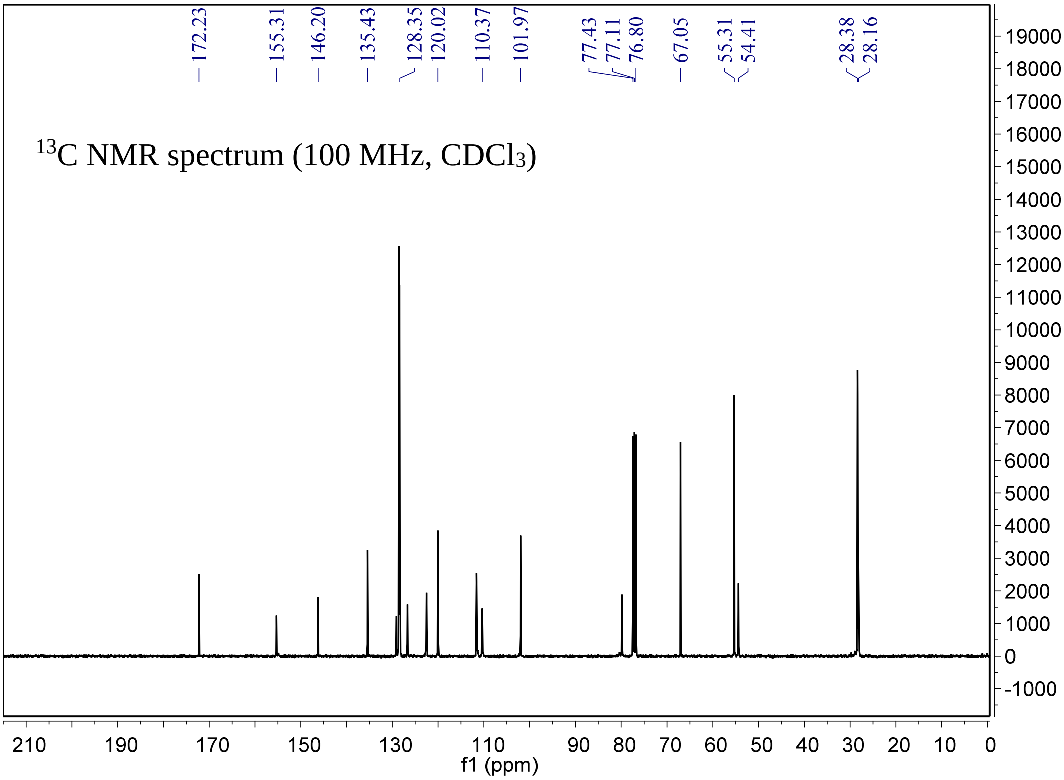
2 K. R. Prabhu, N. Pillarsetty, H. Gali and K. V. Katti, *J. Am. Chem. Soc.*, 2000, **122,** 1554.

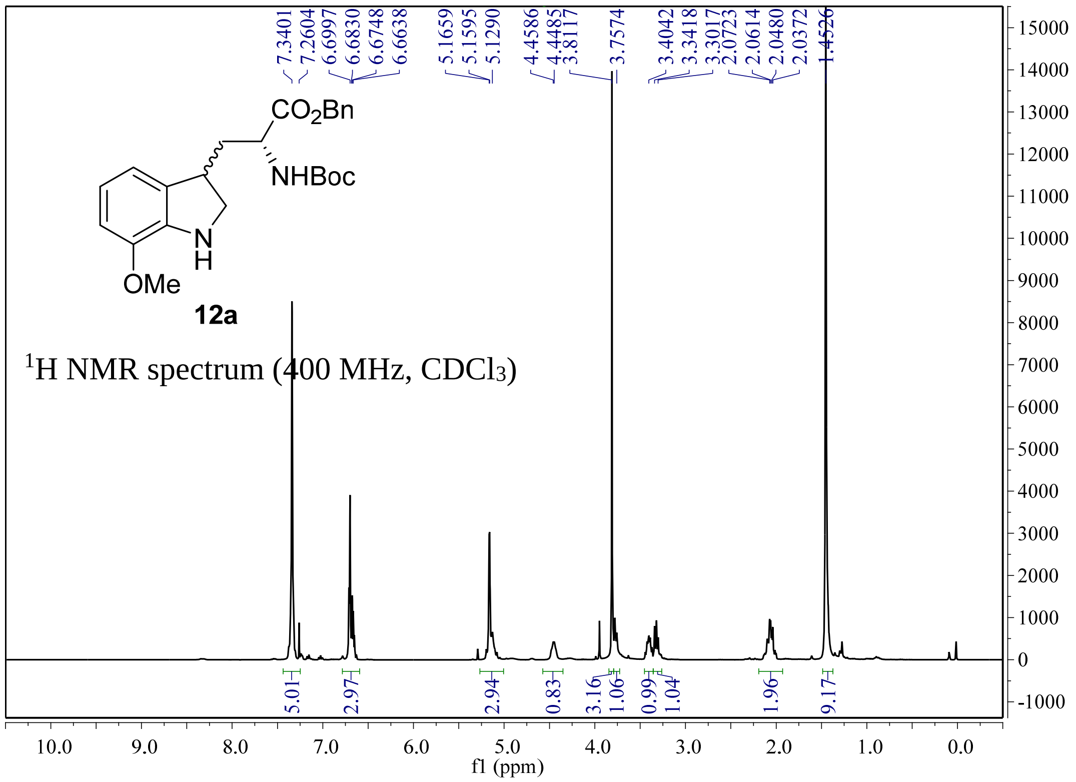
3 P. Garner, J. T. Anderson, S. Dey, W. J. Youngs and K. Galat, *J. Org. Chem.*, 1998, **63**, 5732.

4 K. Koyama, Y. Hirasawa, A. E. Nugroho, T. Kaneda, T. C. Hoe, K.-L. Chan and H. Morita, *Tetrahedron*, 2012, **68**, 1502.

IV) ^{1}H and ^{13}C NMR Spectra of Compounds



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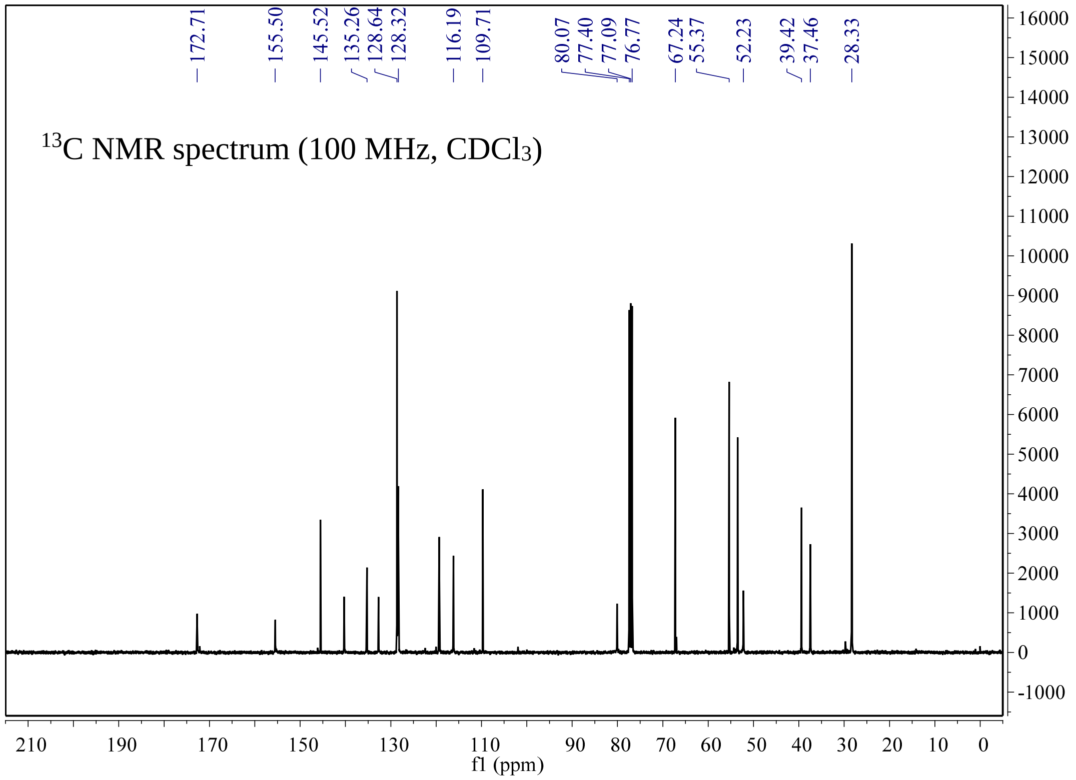
3.8117
3.7574
3.4042
3.3418
3.3017
2.0723
2.0614
2.0480
2.0372
1.4526
CO2Bn
NHBoc
N
H
OMe
12a
1H NMR spectrum (400 MHz, CDCl3)
5.01
2.97
2.94
0.83
3.16
1.06
0.99
1.04
1.96
9.17
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


172.71
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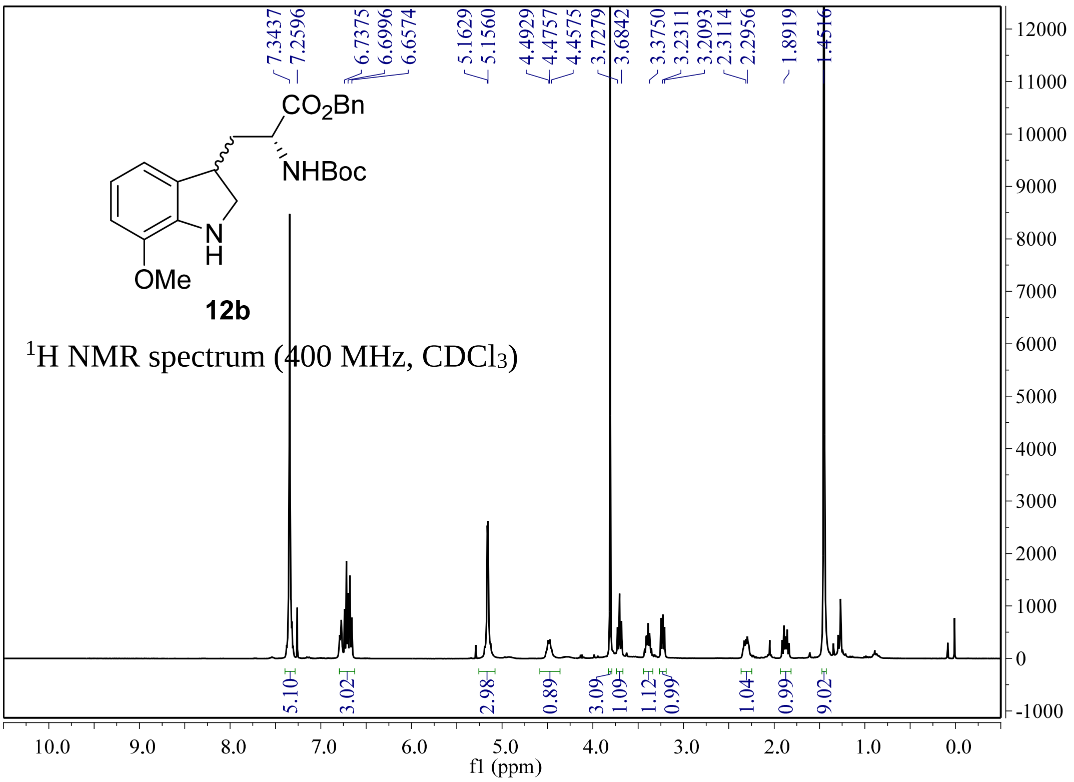
135.26
128.64
128.32
116.19
109.71
80.07
77.40
77.09
76.77
67.24
55.37
52.23
39.42
37.46
28.33
13C NMR spectrum (100 MHz, CDCl3)
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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3.6842
3.3750
3.2311
3.2093
2.3114
2.2956
1.8919
1.4516
CO2Bn
NHBoc
N
H
OMe
12b
1H NMR spectrum (400 MHz, CDCl3)
5.10
3.02
2.98
0.89
3.09
1.09
1.12
0.99
1.04
0.99
9.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
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10000
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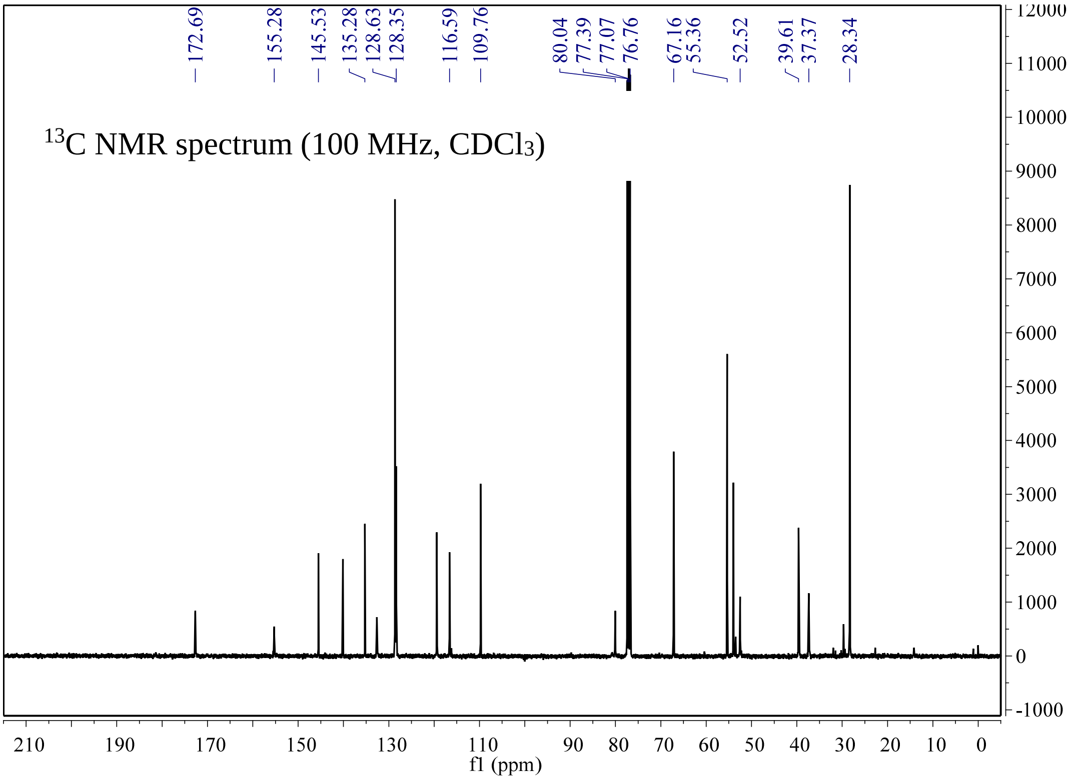
7000
6000
5000
4000
3000
2000
1000
0
-1000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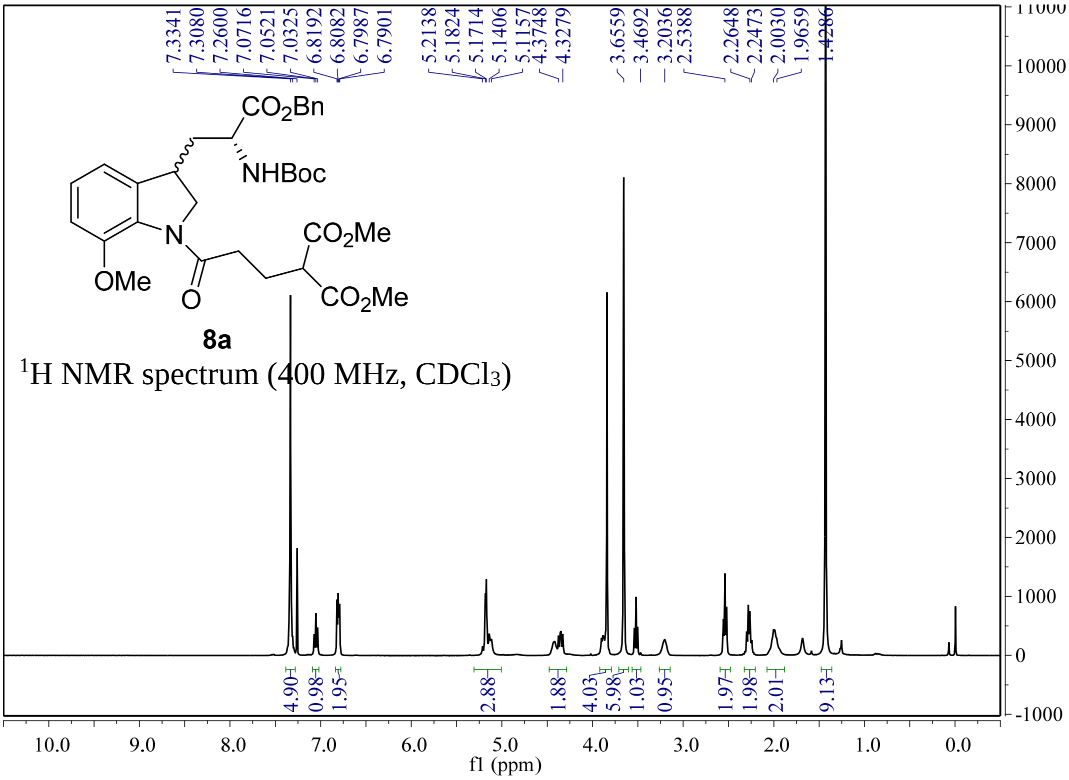
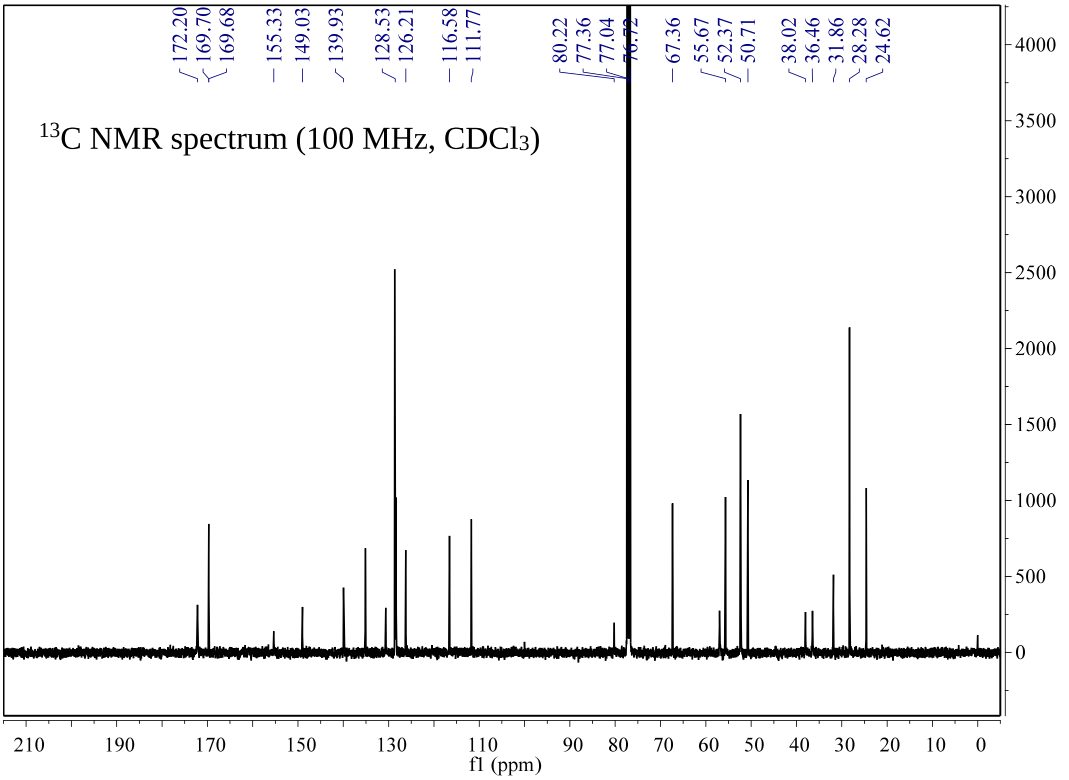
128.35
116.59
109.76
80.04
77.39
77.07
76.76
67.16
55.36
52.52
39.61
37.37
28.34
13C NMR spectrum (100 MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

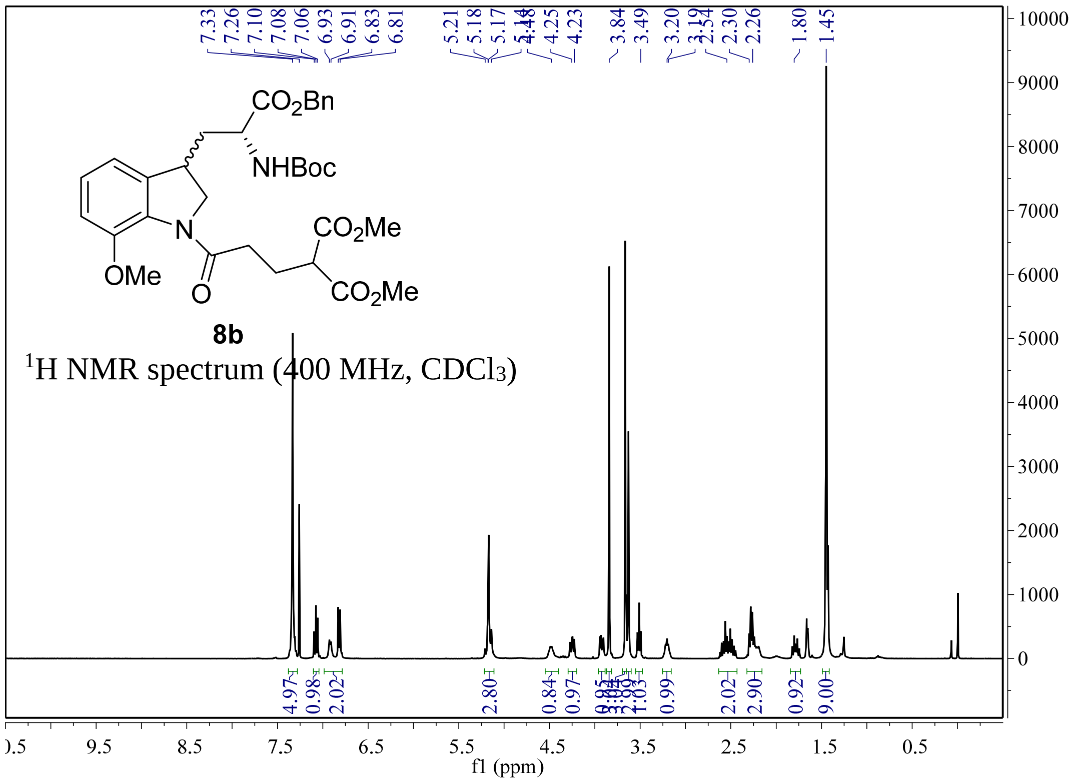


8a

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

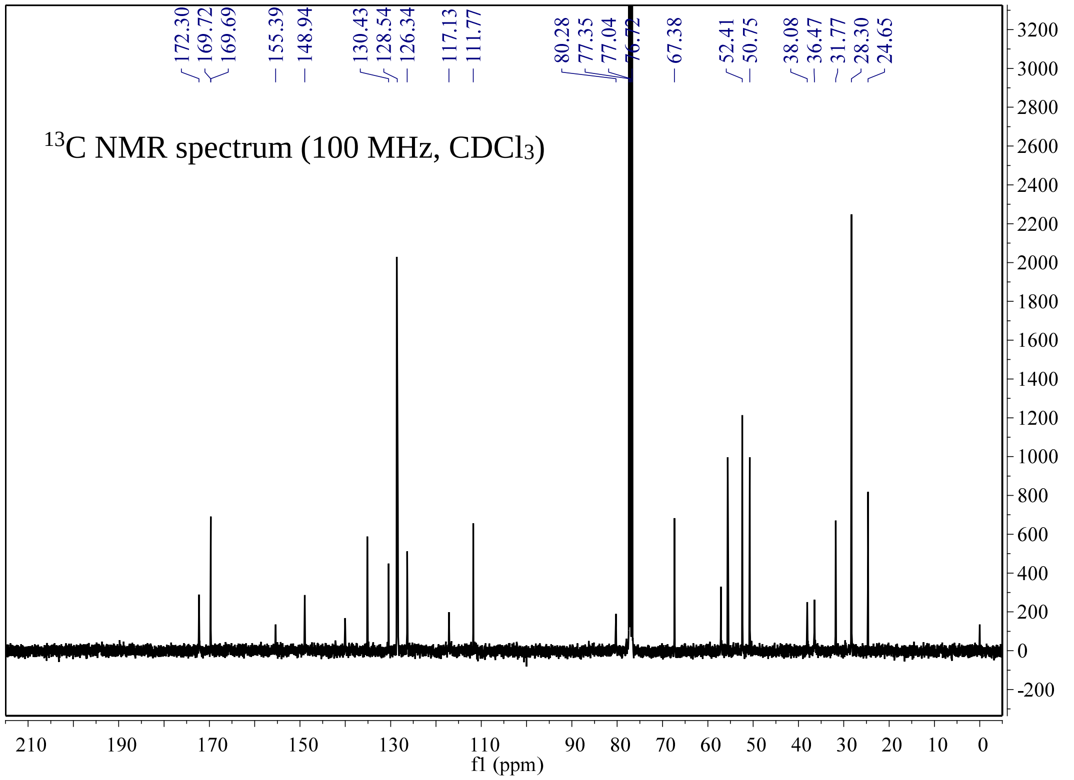


^{13}C NMR spectrum (100 MHz, $CDCl_3$)

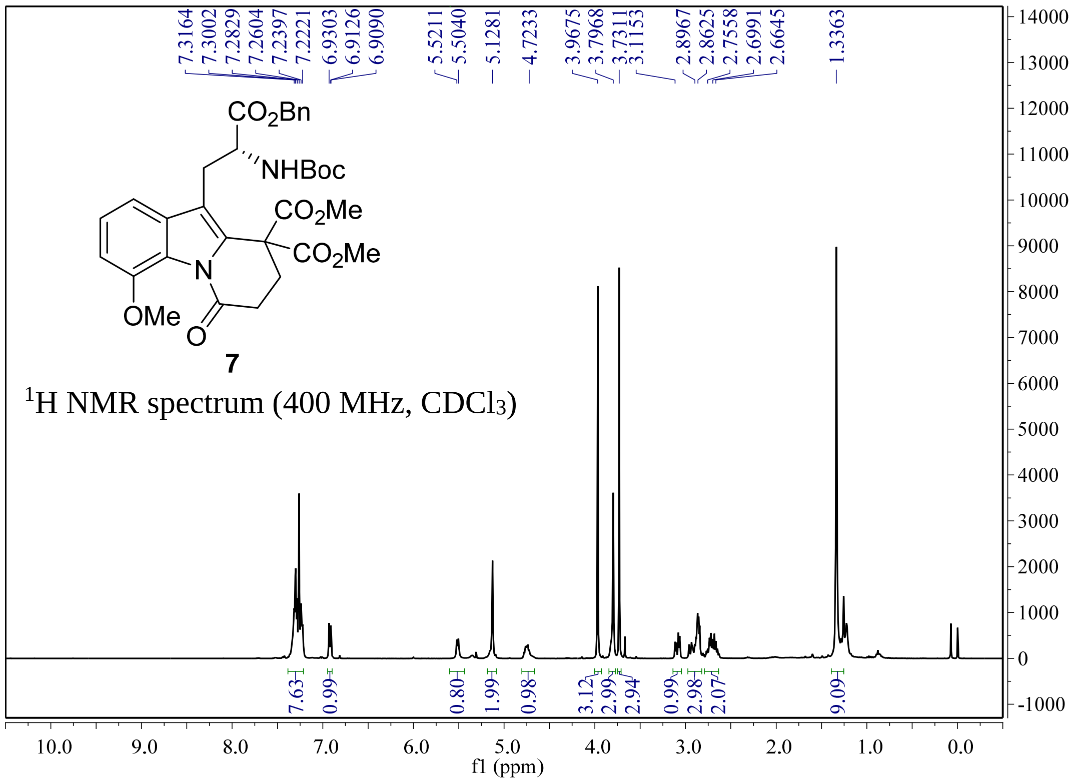


8b

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



^{13}C NMR spectrum (100 MHz, $CDCl_3$)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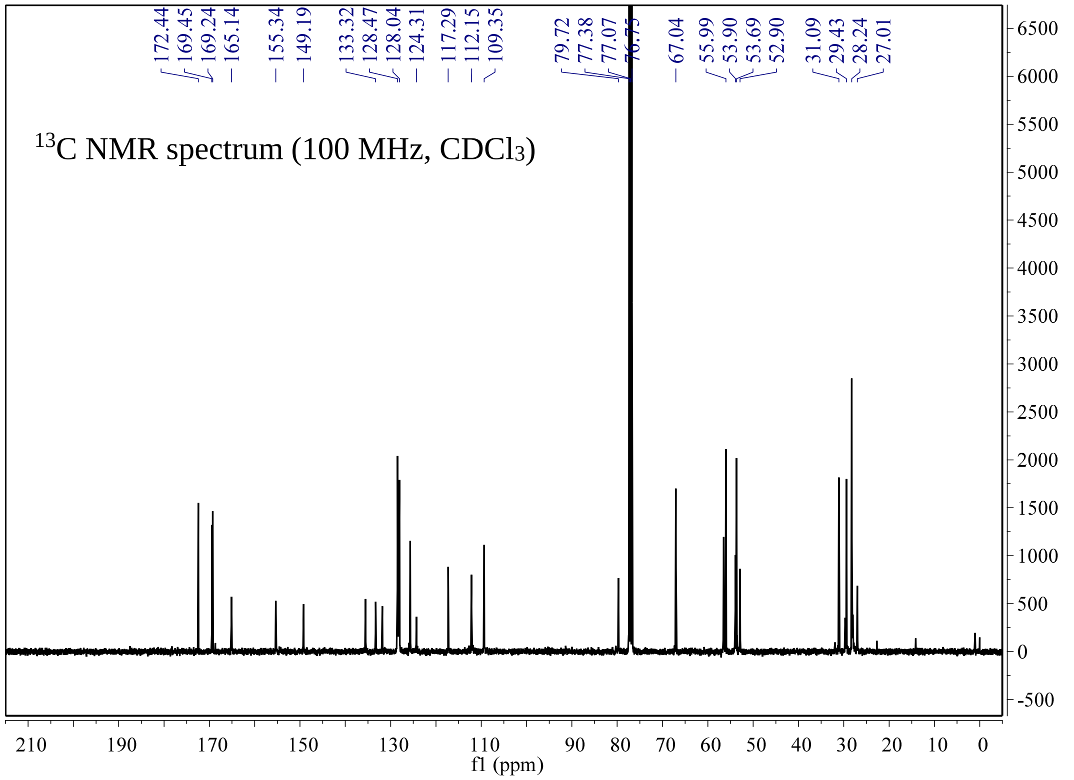
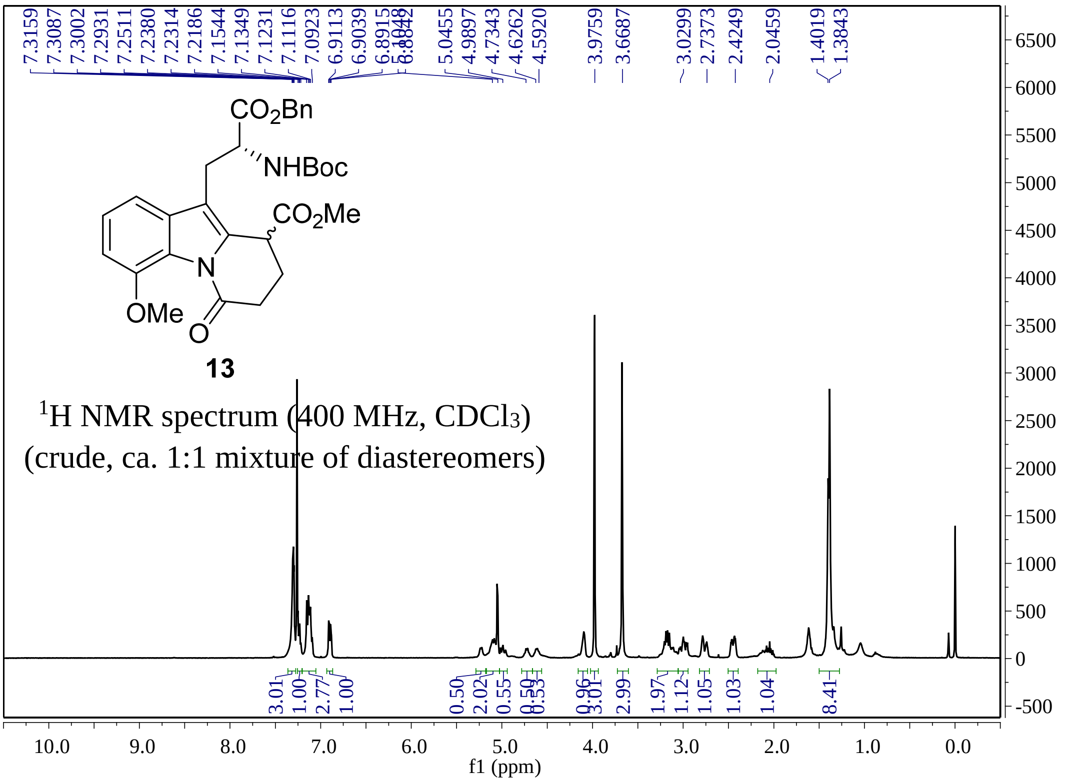
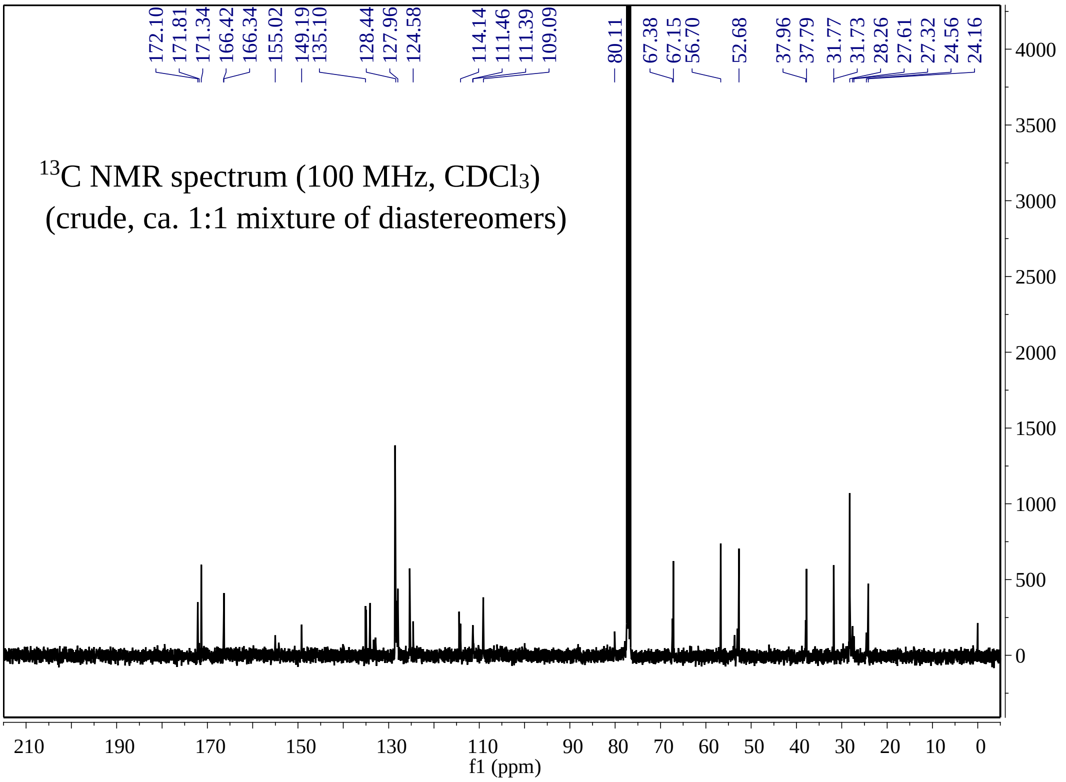
3.1153
2.8967
2.8625
2.7558
2.6991
2.6645
1.3363
CO2Bn
NHBoc
CO2Me
CO2Me
N
OMe
O
7
1H NMR spectrum (400 MHz, CDCl3)
7.63
0.99
0.80
1.99
0.98
3.12
2.99
2.94
0.99
2.98
2.07
9.09
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


172.44
169.45
169.24
165.14
155.34
149.19
133.32
128.47
128.04
124.31
117.29
112.15
109.35
79.72
77.38
77.07
76.75
67.04
55.99
53.90
53.69
52.90
31.09
29.43
28.24
27.01
13C NMR spectrum (100 MHz, CDCl3)
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

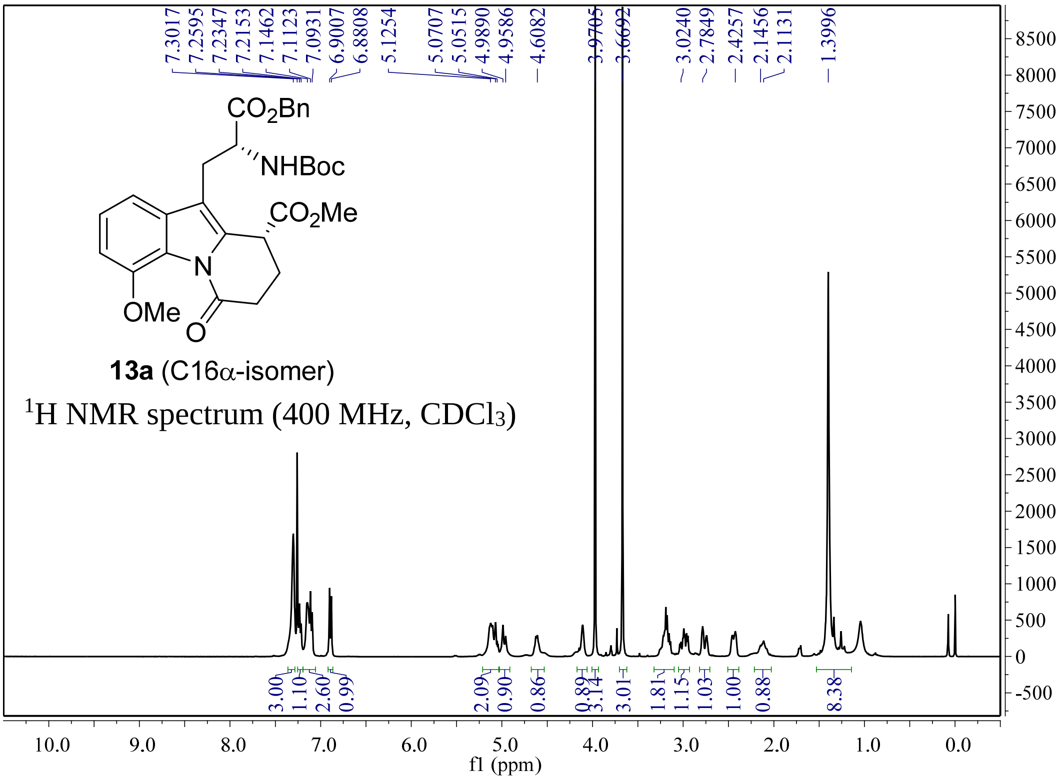


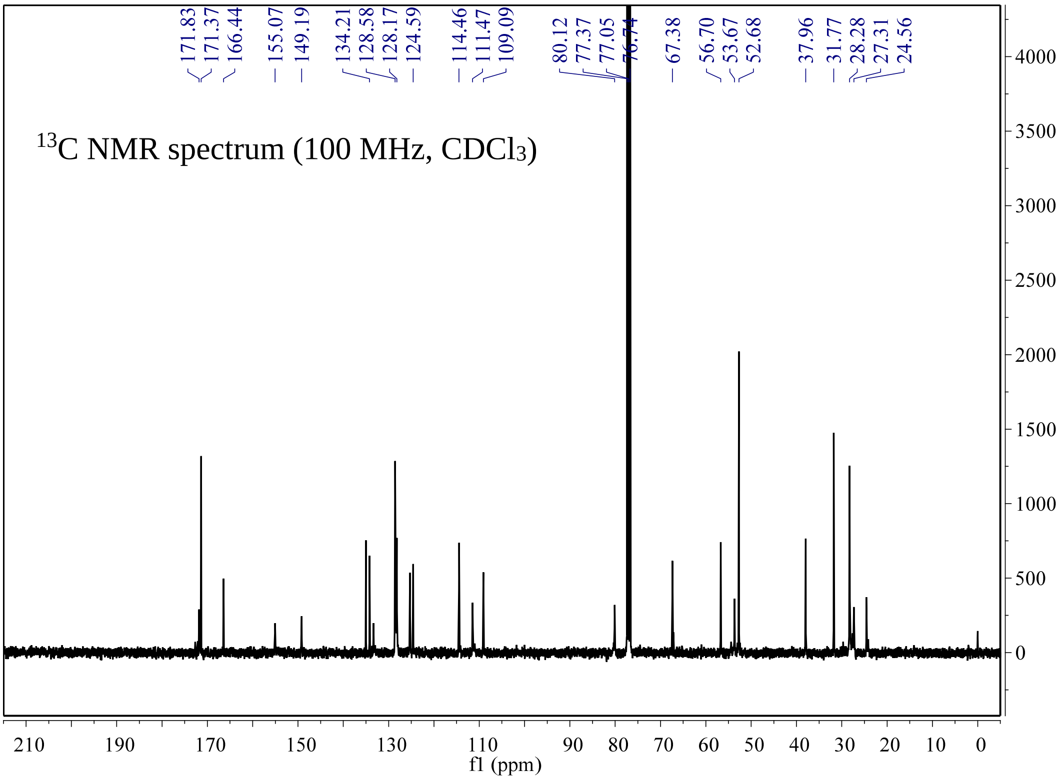
13

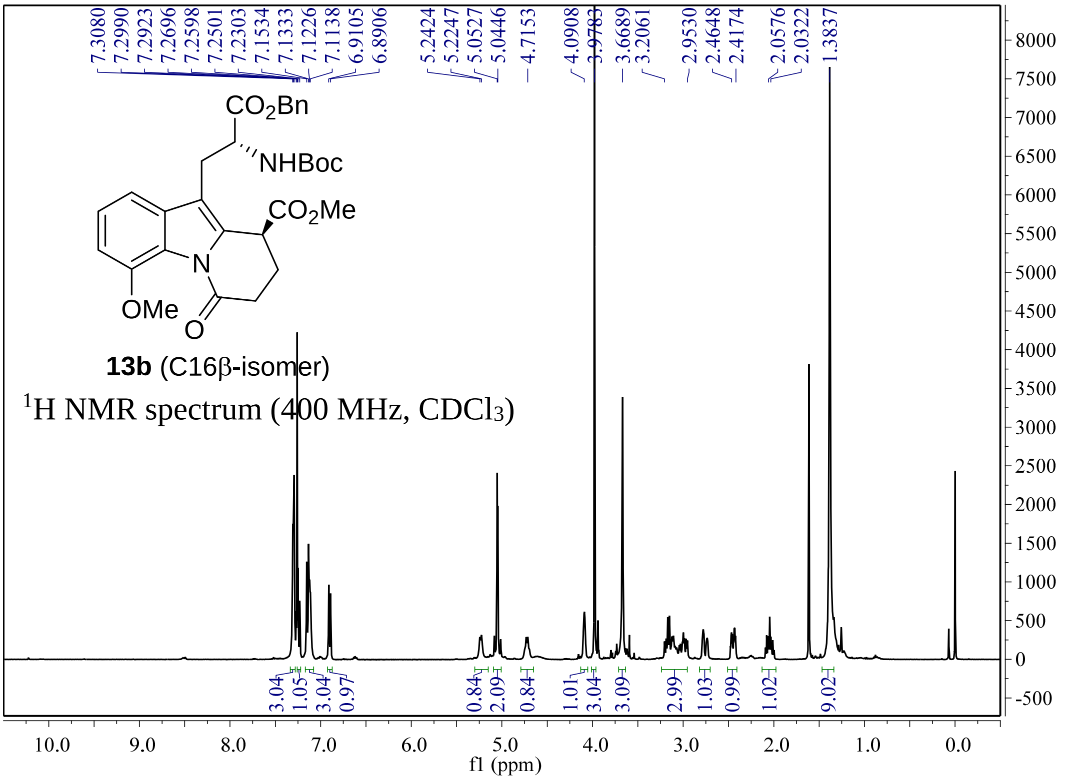
^{1}H NMR spectrum (400 MHz, $CDCl_3$)
(crude, ca. 1:1 mixture of diastereomers)



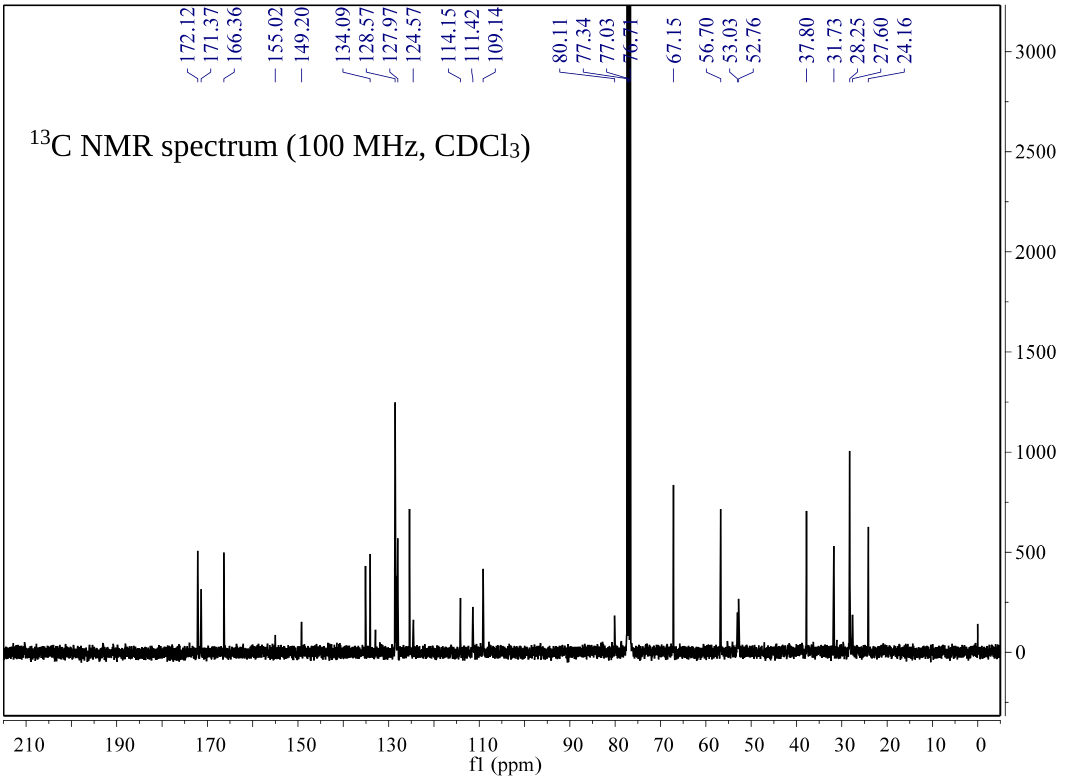
^{13}C NMR spectrum (100 MHz, $CDCl_3$)
(crude, ca. 1:1 mixture of diastereomers)

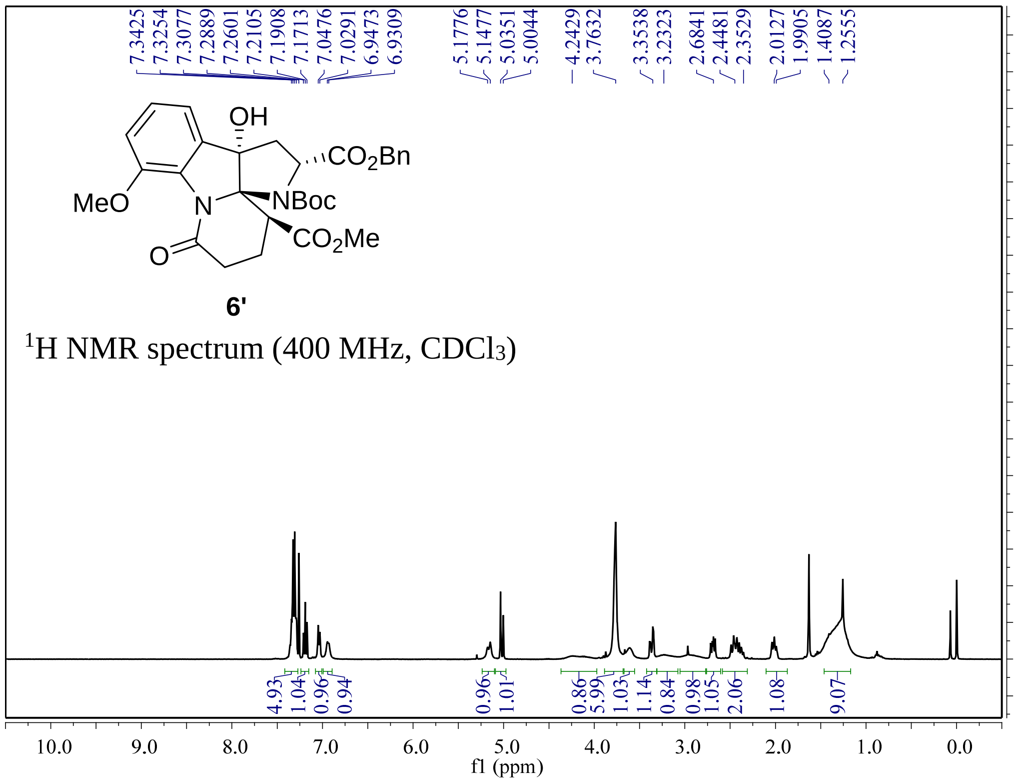

7.3017
7.2595
7.2347
7.2153
7.1462
7.1123
7.0931
6.9007
6.8808
5.1254
5.0707
5.0515
4.9890
4.9586
4.6082
3.9705
3.6692
3.0240
2.7849
2.4257
2.1456
2.1131
1.3996
CO2Bn
NHBoc
CO2Me
N
OMe
O
13a (C16α-isomer)
1H NMR spectrum (400 MHz, CDCl3)
3.00
1.10
2.60
0.99
2.09
0.90
0.86
0.89
3.14
3.01
1.81
1.15
1.03
1.00
0.88
8.38
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


171.83
171.37
166.44
155.07
149.19
134.21
128.58
128.17
124.59
114.46
111.47
109.09
80.12
77.37
77.05
76.74
67.38
56.70
53.67
52.68
37.96
31.77
28.28
27.31
24.56
13C NMR spectrum (100 MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0


13b (C16β-isomer)

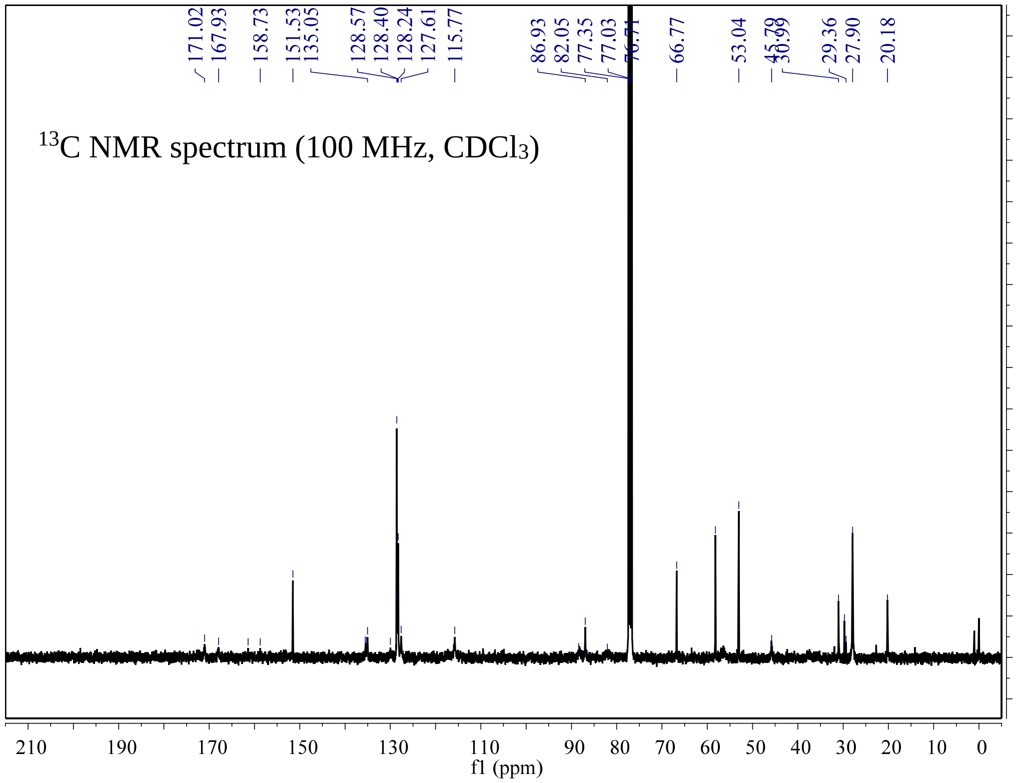
^{1}H NMR spectrum (400 MHz, CDCl$_3$)


^{13}C NMR spectrum (100 MHz, CDCl$_3$)

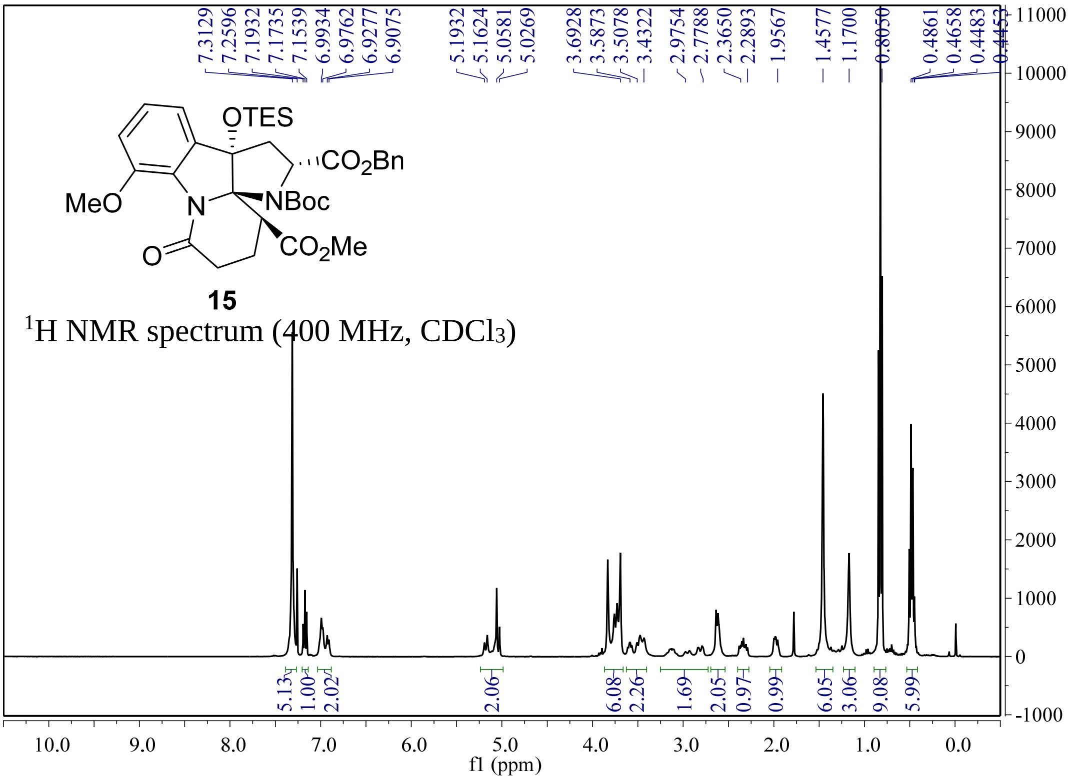


6'

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

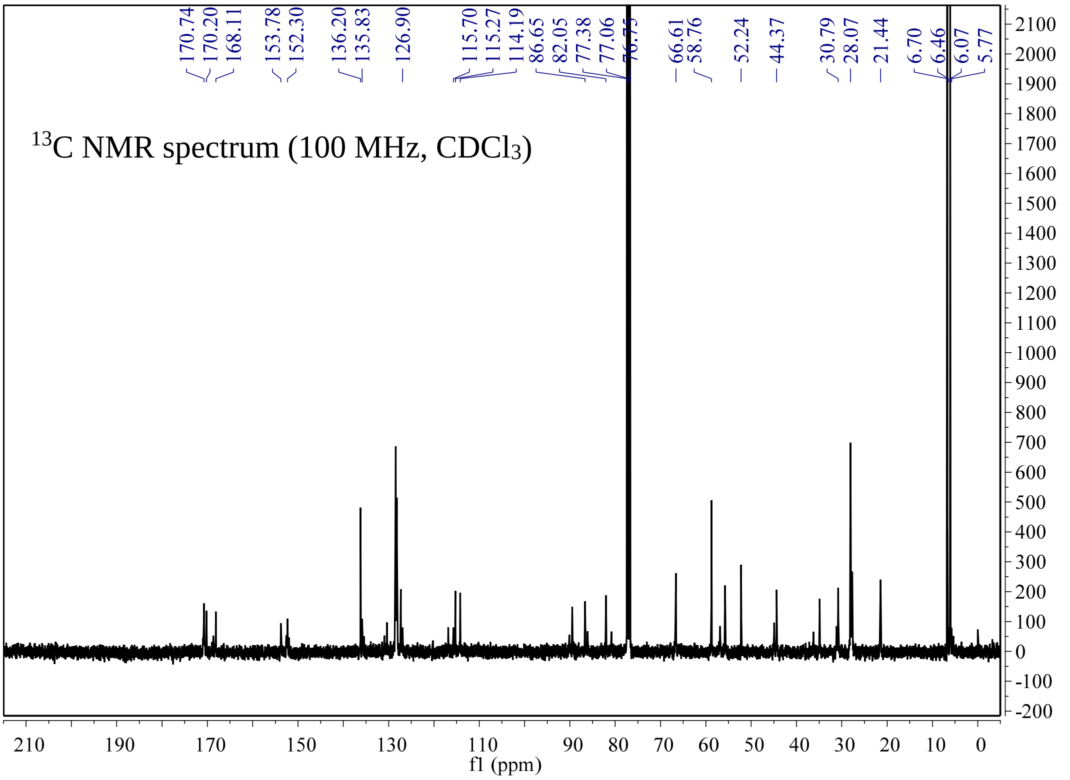


^{13}C NMR spectrum (100 MHz, $CDCl_3$)

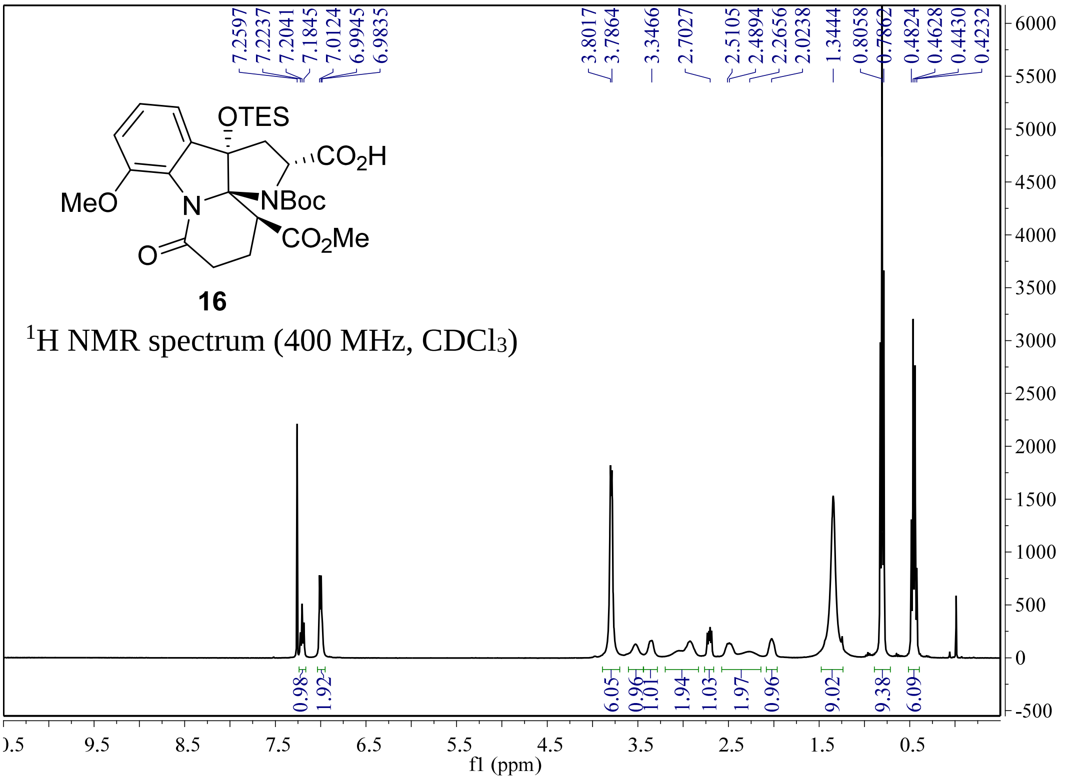


15

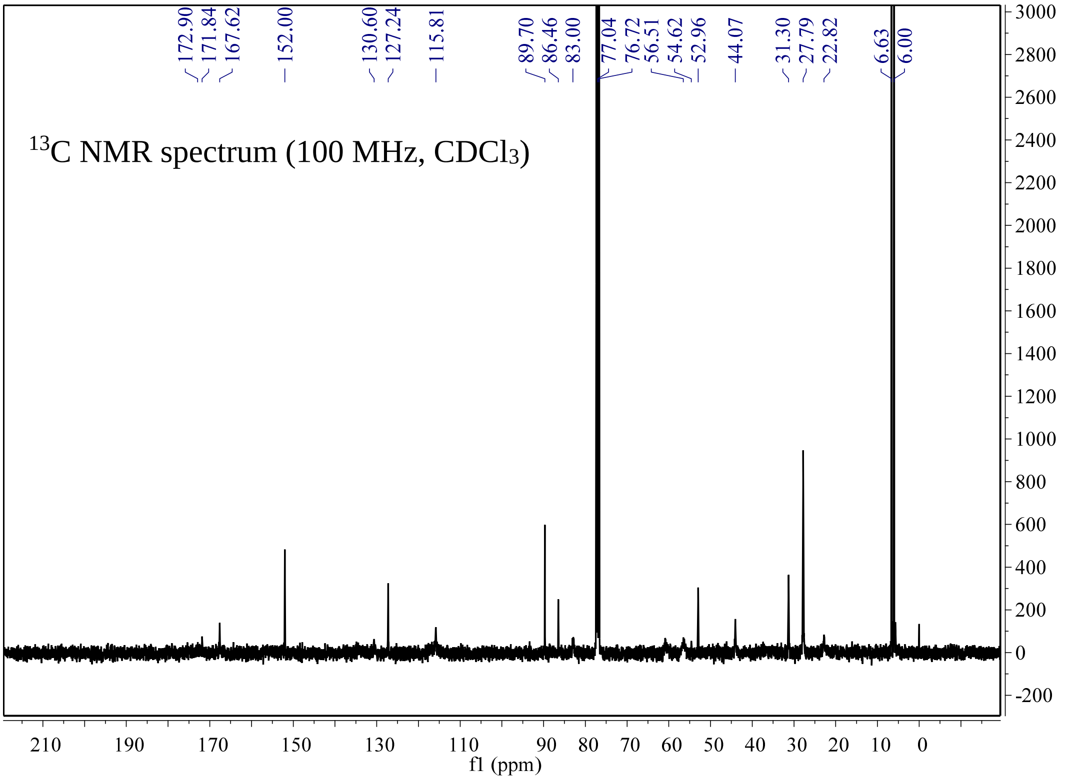
^{1}H NMR spectrum (400 MHz, CDCl$_3$)



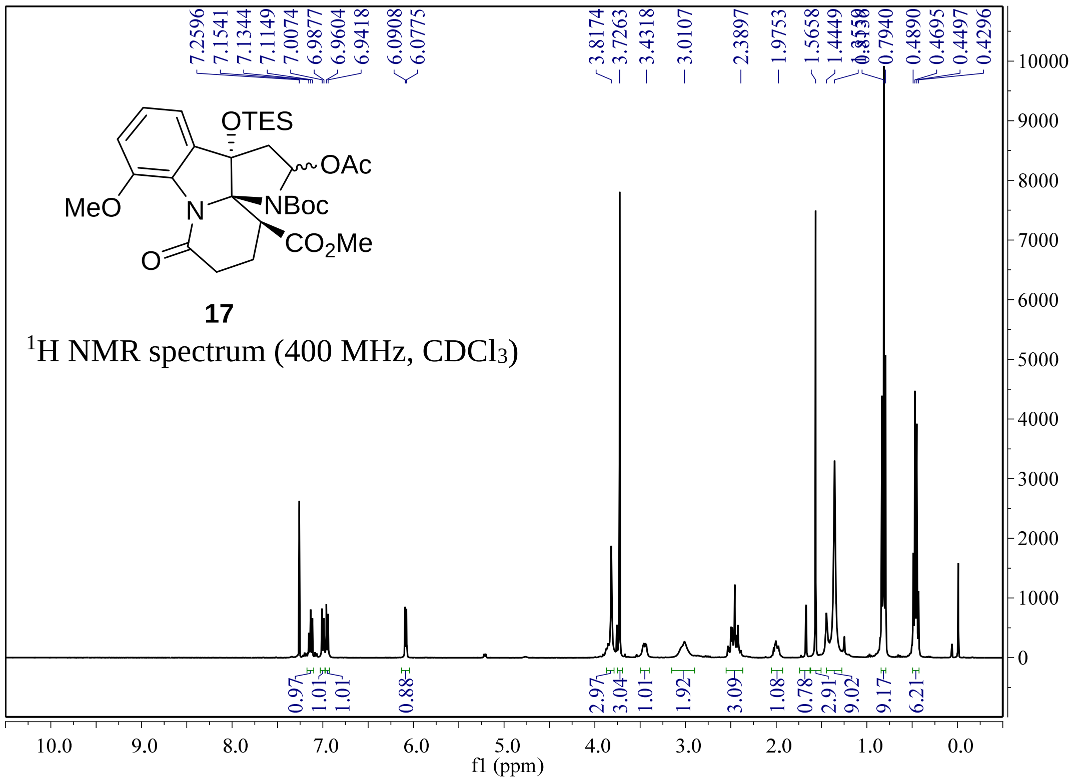
^{13}C NMR spectrum (100 MHz, CDCl$_3$)



^{1}H NMR spectrum (400 MHz, CDCl$_3$)

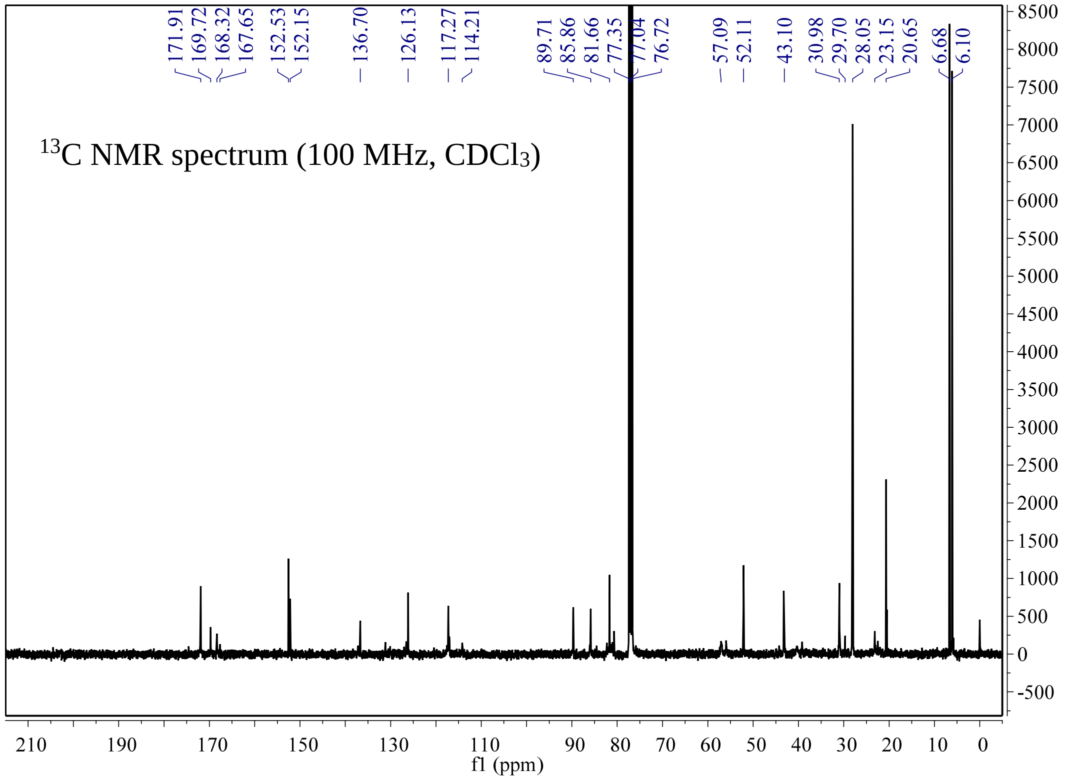


^{13}C NMR spectrum (100 MHz, CDCl$_3$)

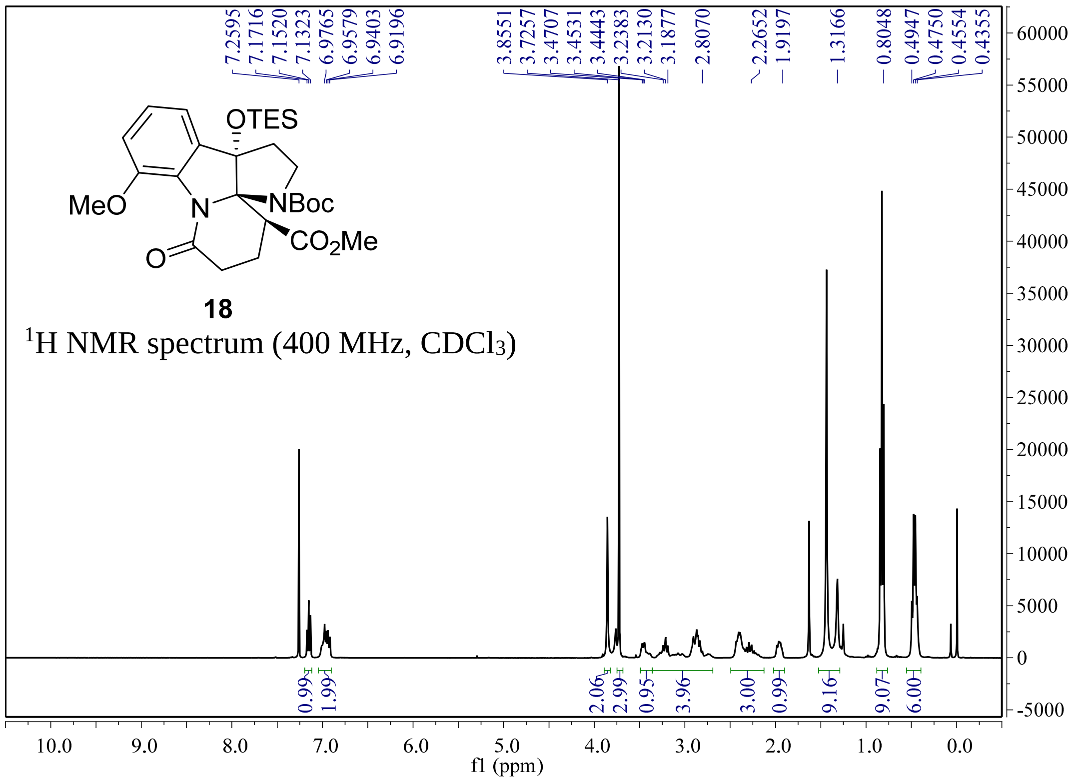


17

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

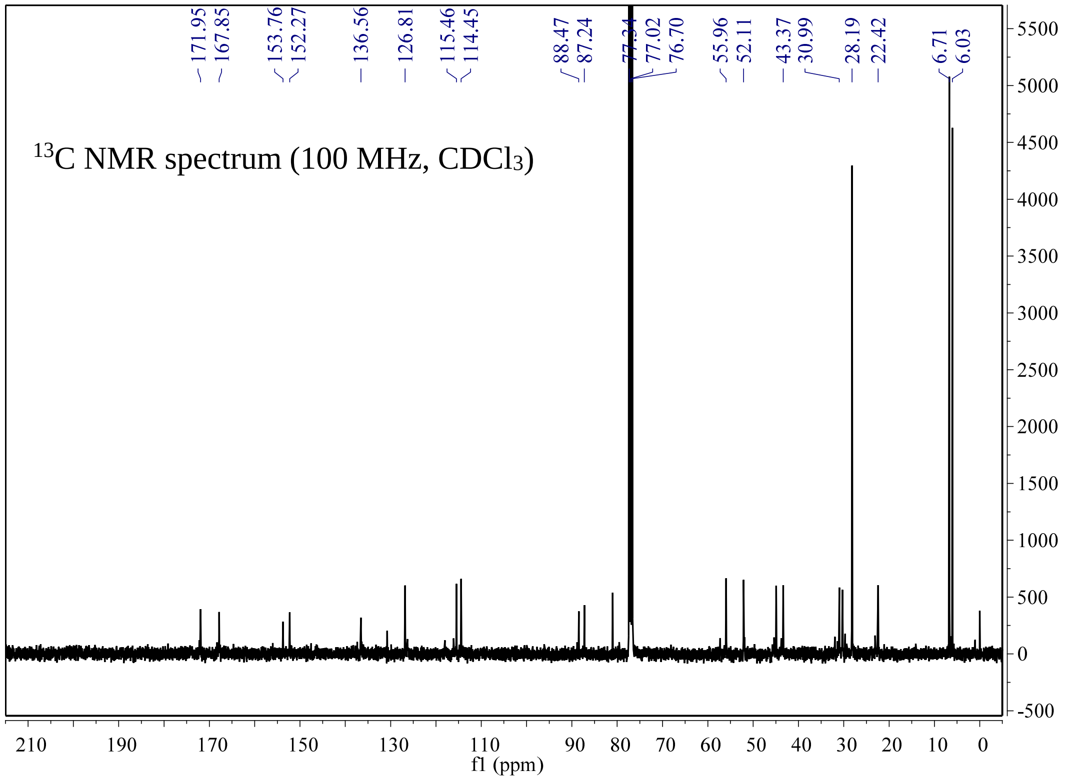


^{13}C NMR spectrum (100 MHz, $CDCl_3$)

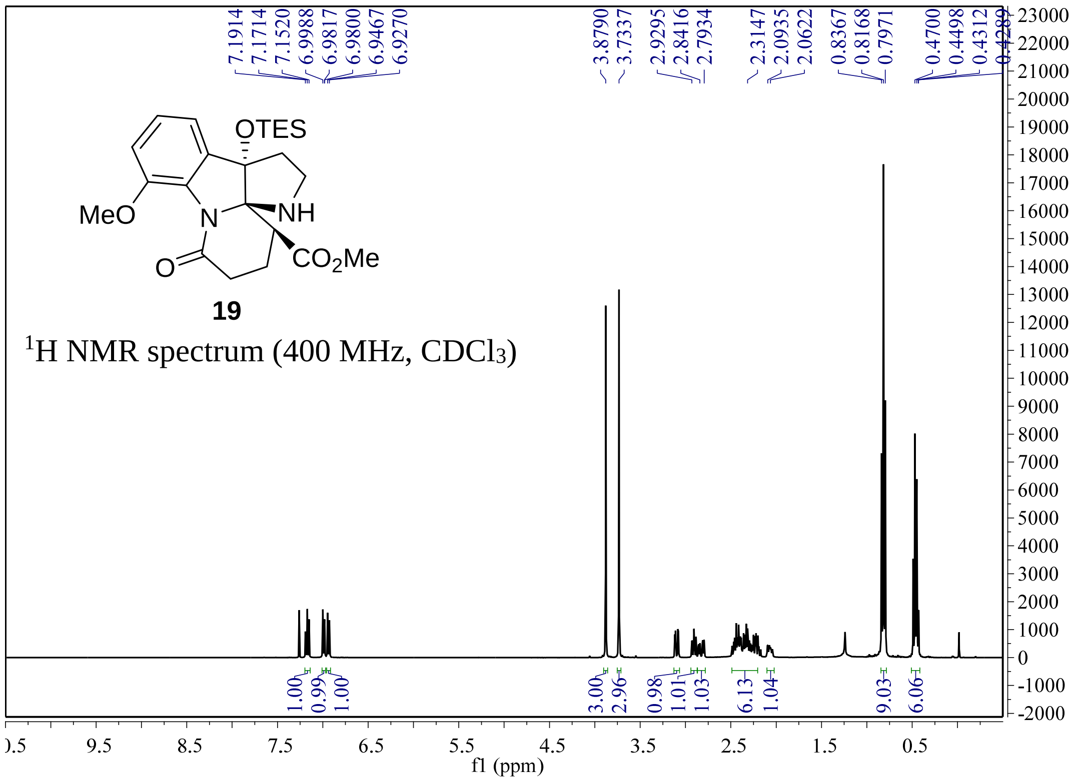


18

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



^{13}C NMR spectrum (100 MHz, $CDCl_3$)



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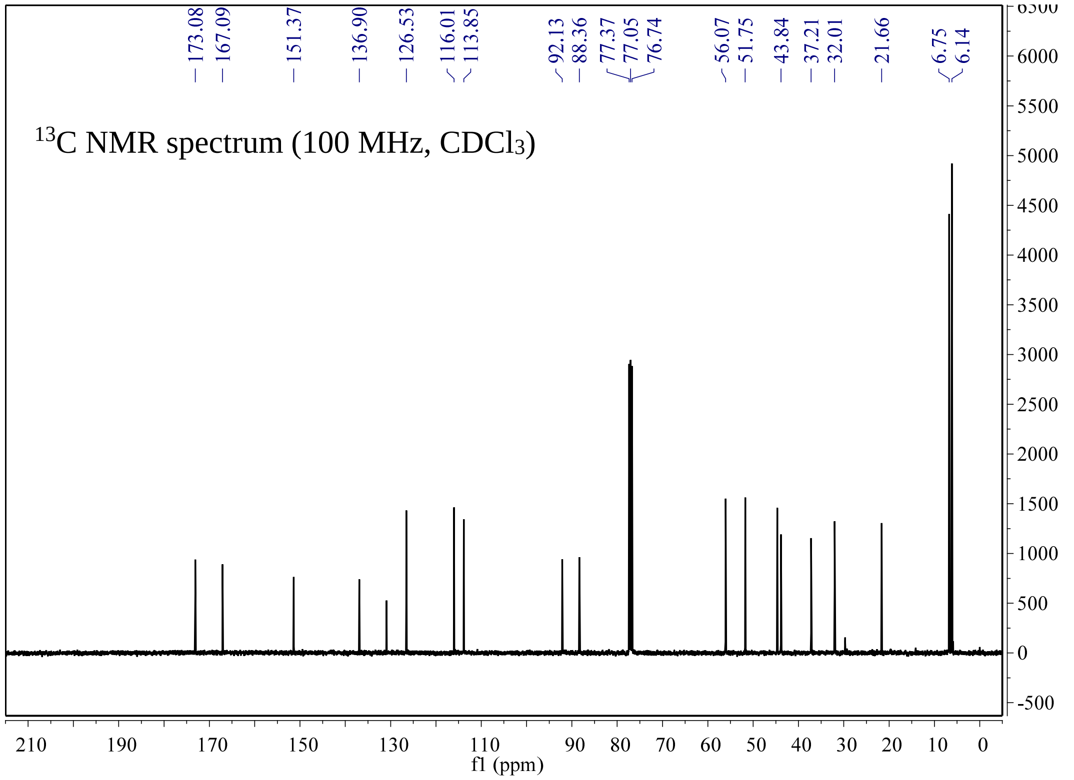
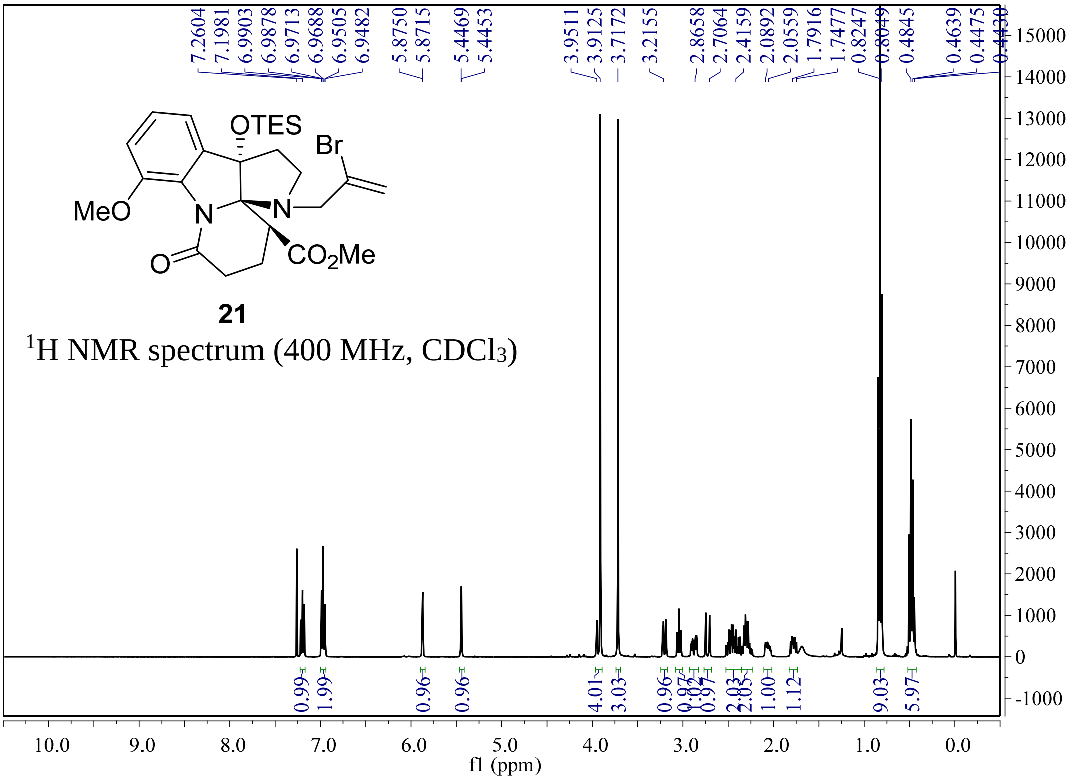
^{1}H NMR spectrum (400 MHz, CDCl$_3$)



^{13}C NMR spectrum (100 MHz, CDCl$_3$)



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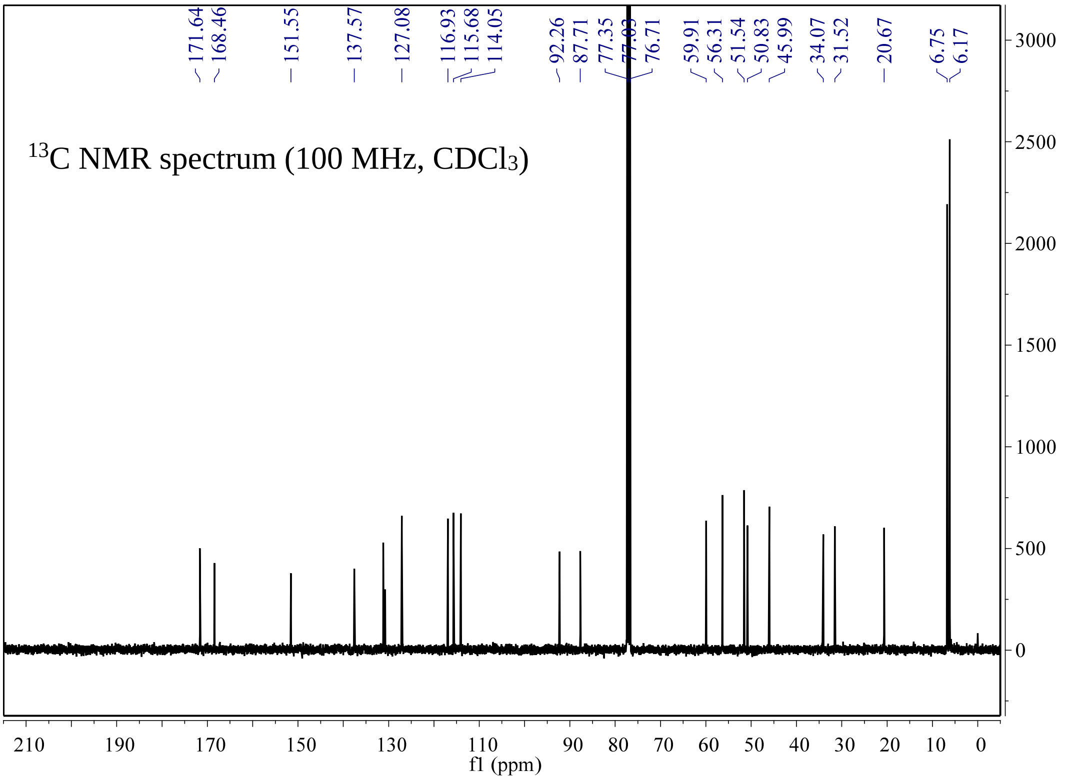
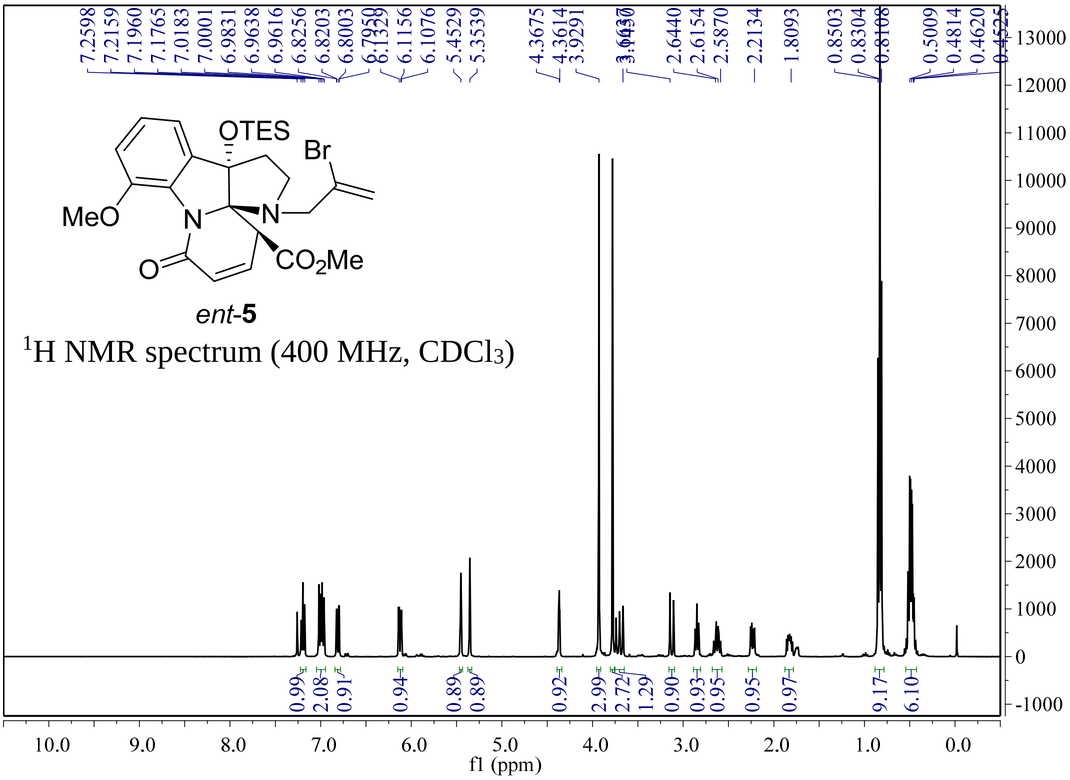
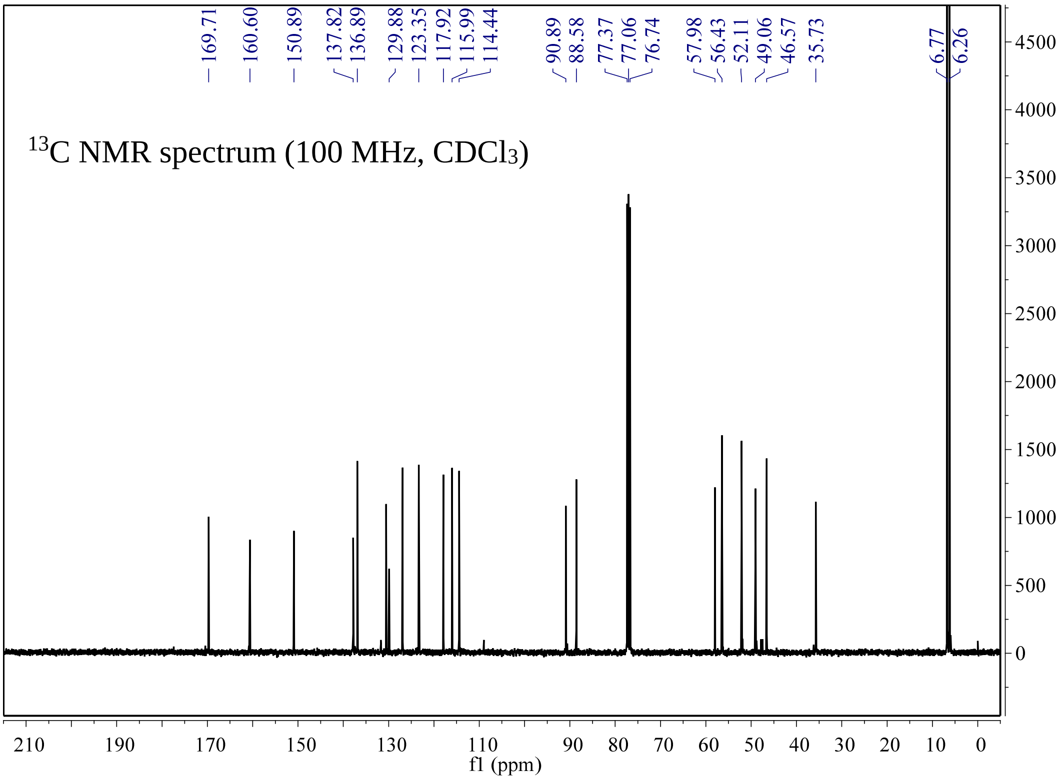
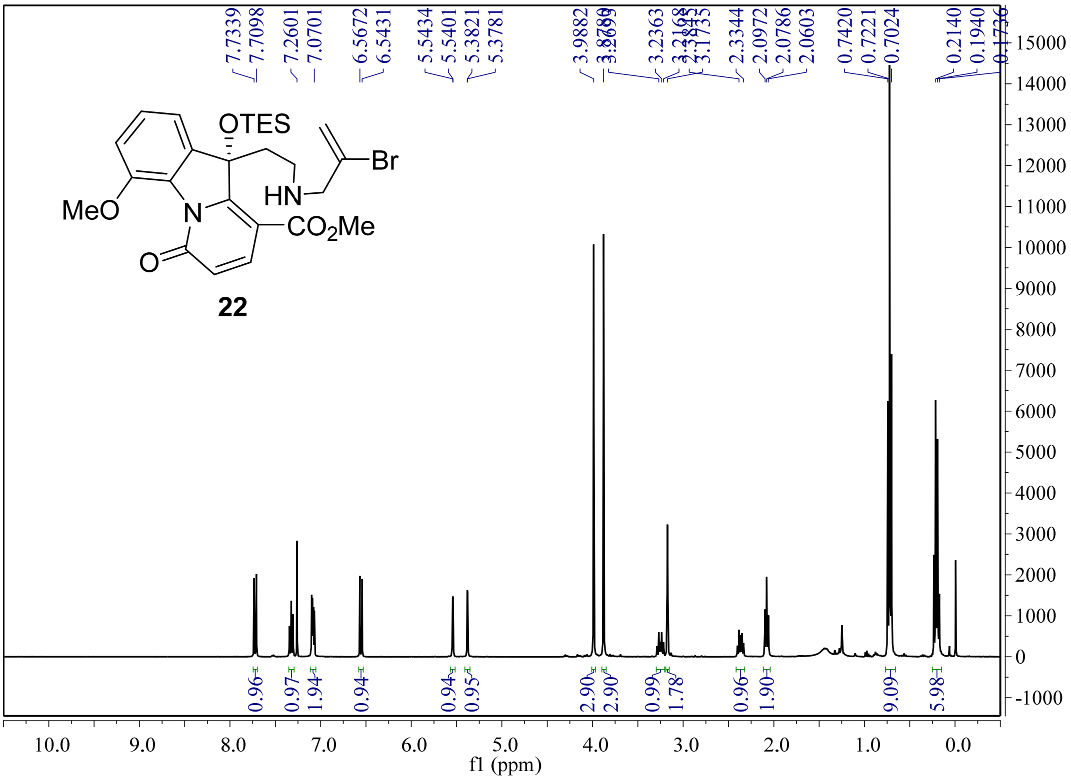
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



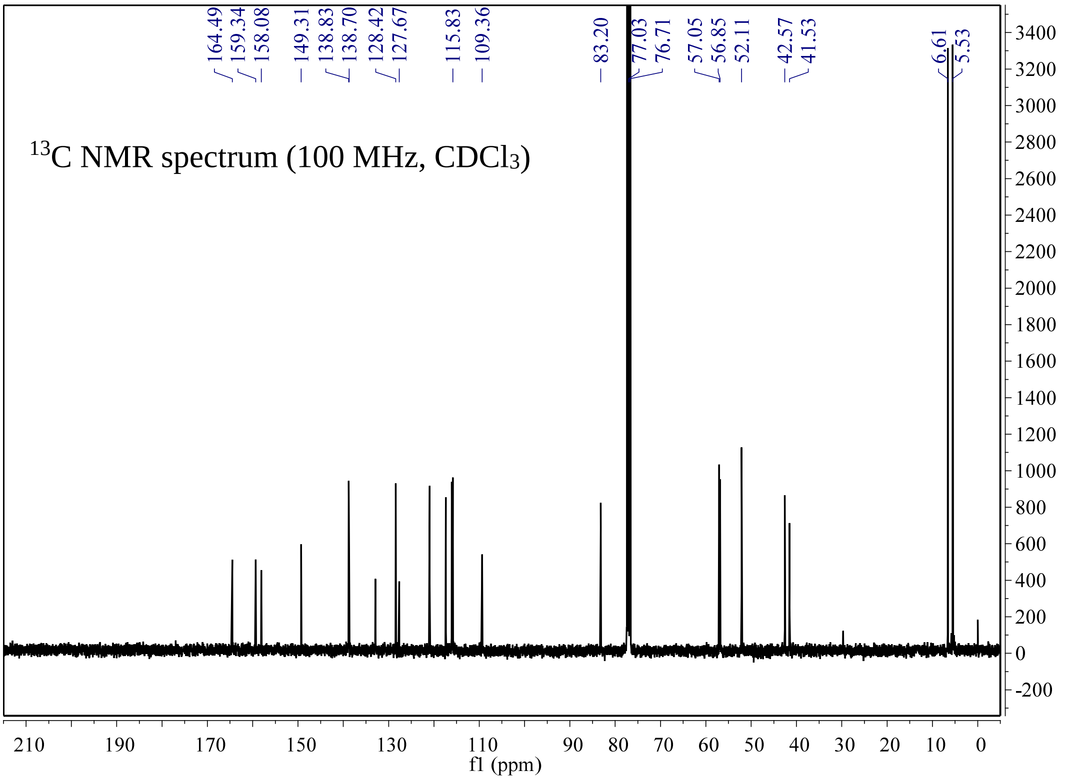
^{13}C NMR spectrum (100 MHz, $CDCl_3$)


OTES
Br
MeO
N
N
O
CO2Me
ent-5
1H NMR spectrum (400 MHz, CDCl3)
7.2598
7.2159
7.1960
7.1765
7.0183
7.0001
6.9831
6.9638
6.9616
6.8256
6.8203
6.8003
6.1329
6.1156
6.1076
5.4529
5.3539
4.3675
4.3614
3.9291
2.6440
2.6154
2.5870
2.2134
1.8093
0.8503
0.8304
0.8108
0.5009
0.4814
0.4620
0.99
2.08
0.91
0.94
0.89
0.89
0.92
2.99
2.72
1.29
0.90
0.93
0.95
0.95
0.97
9.17
6.10
f1 (ppm)

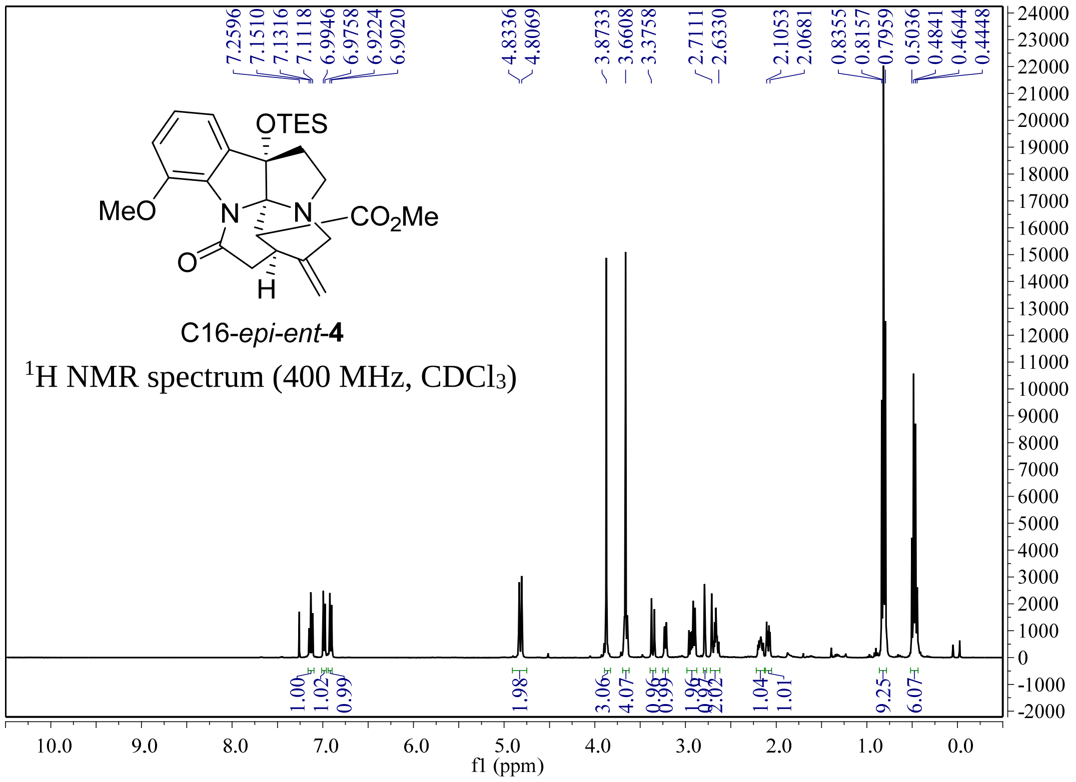

13C NMR spectrum (100 MHz, CDCl3)
169.71
160.60
150.89
137.82
136.89
129.88
123.35
117.92
115.99
114.44
90.89
88.58
77.37
77.06
76.74
57.98
56.43
52.11
49.06
46.57
35.73
6.77
6.26
f1 (ppm)



7.7339
7.7098
7.2601
7.0701
6.5672
6.5431
5.5434
5.5401
5.3821
5.3781
3.9882
3.2363
3.1735
2.3344
2.0972
2.0786
2.0603
0.7420
0.7221
0.7024
0.2140
0.1940
0.96
0.97
1.94
0.94
0.94
0.95
2.90
2.90
0.99
1.78
0.96
1.90
9.09
5.98
OTES
Br
HN
MeO
N
CO2Me
O
22
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

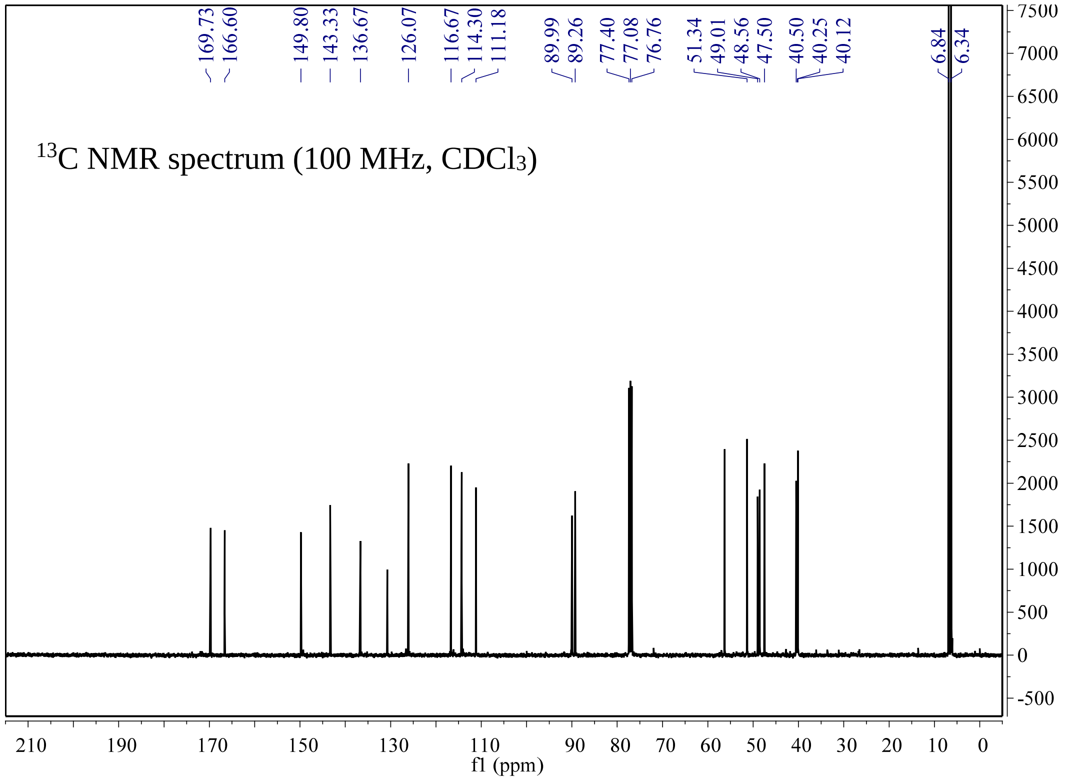


164.49
159.34
158.08
149.31
138.83
138.70
128.42
127.67
115.83
109.36
83.20
77.03
76.71
57.05
56.85
52.11
42.57
41.53
6.61
5.53
13C NMR spectrum (100 MHz, CDCl3)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

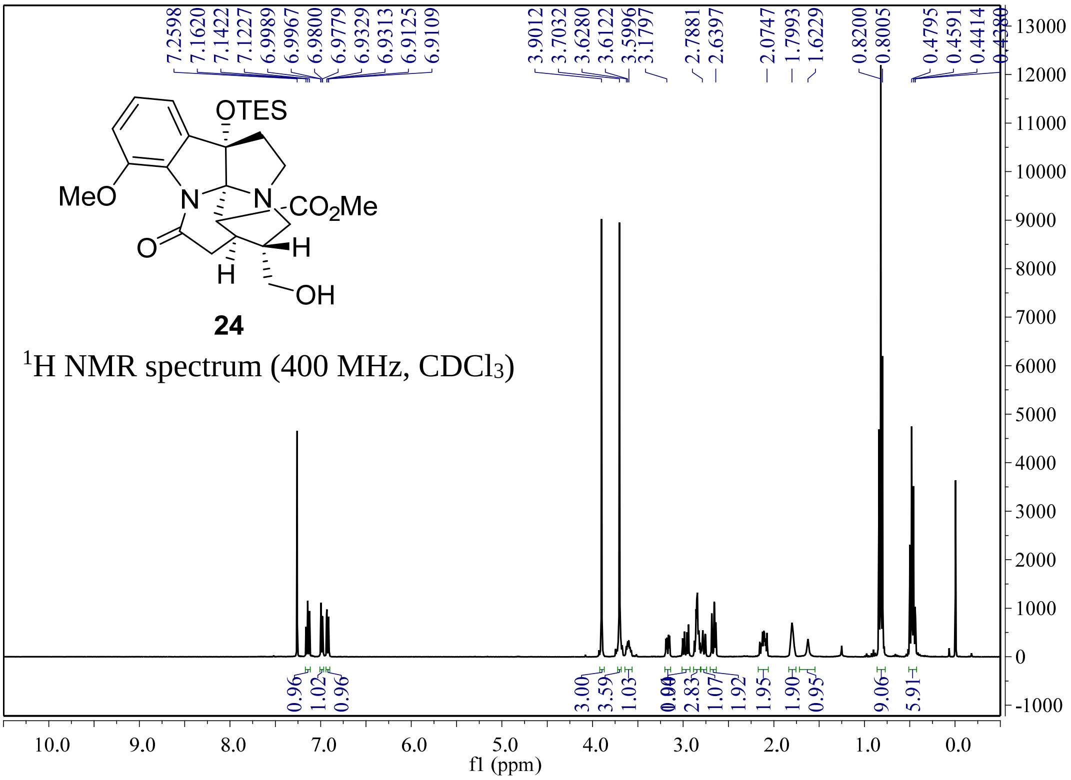


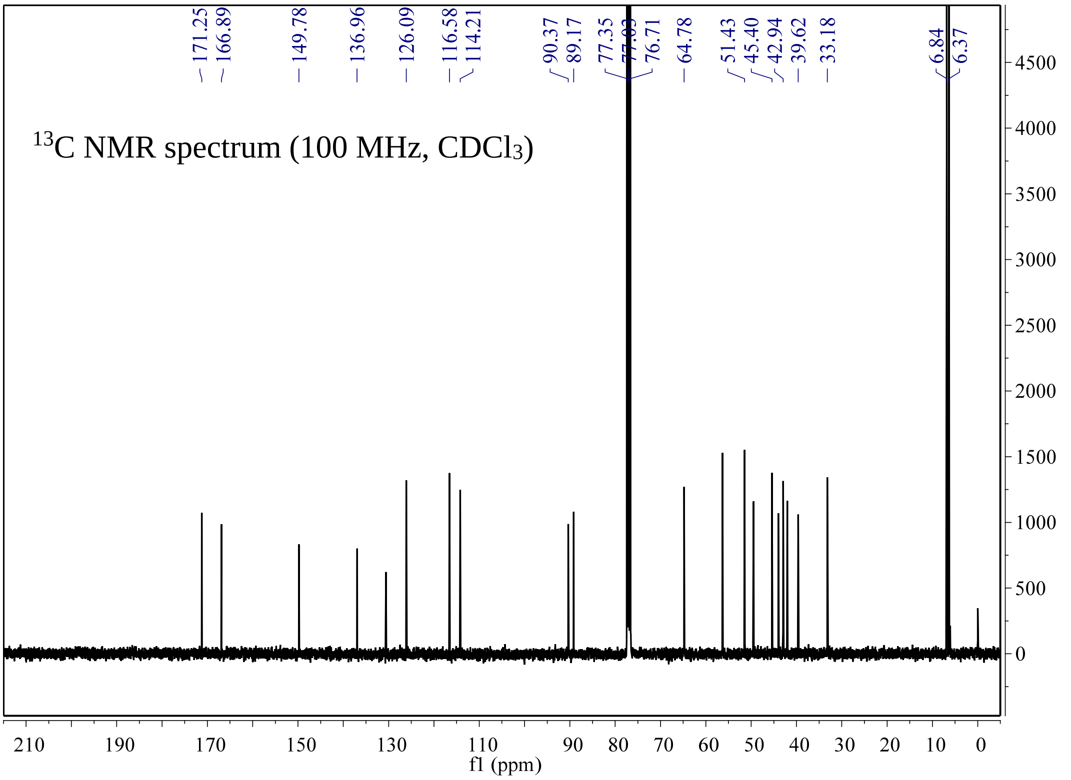
C16-*epi*-*ent*-**4**

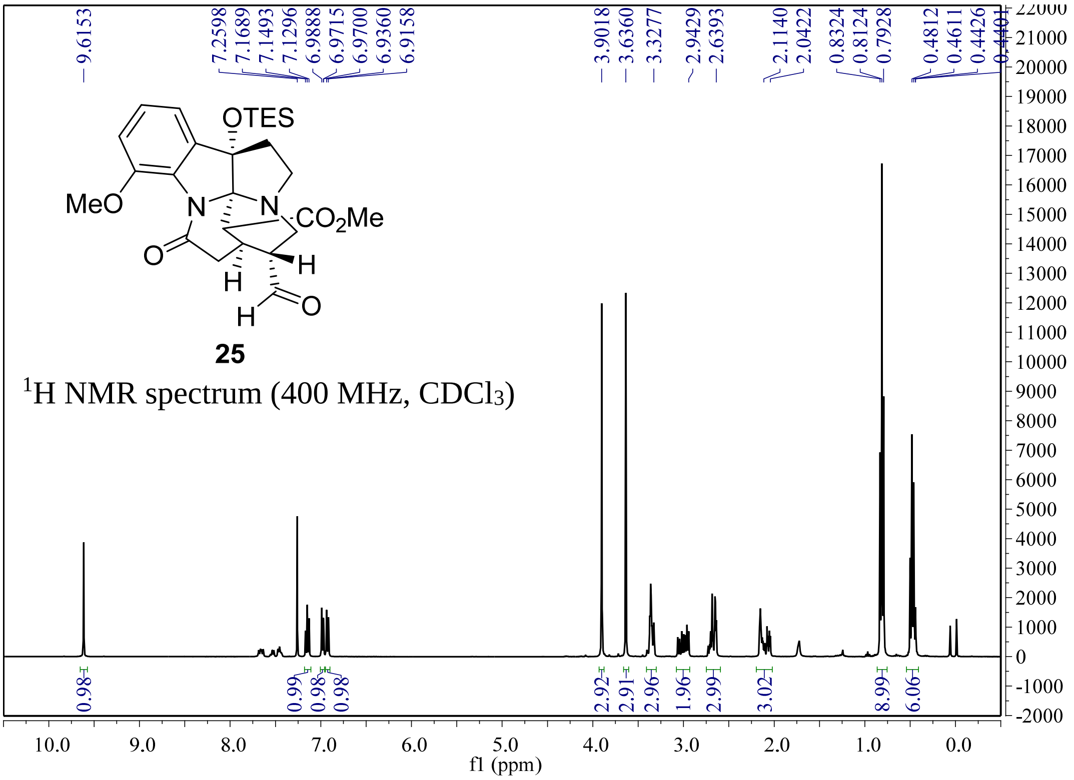
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

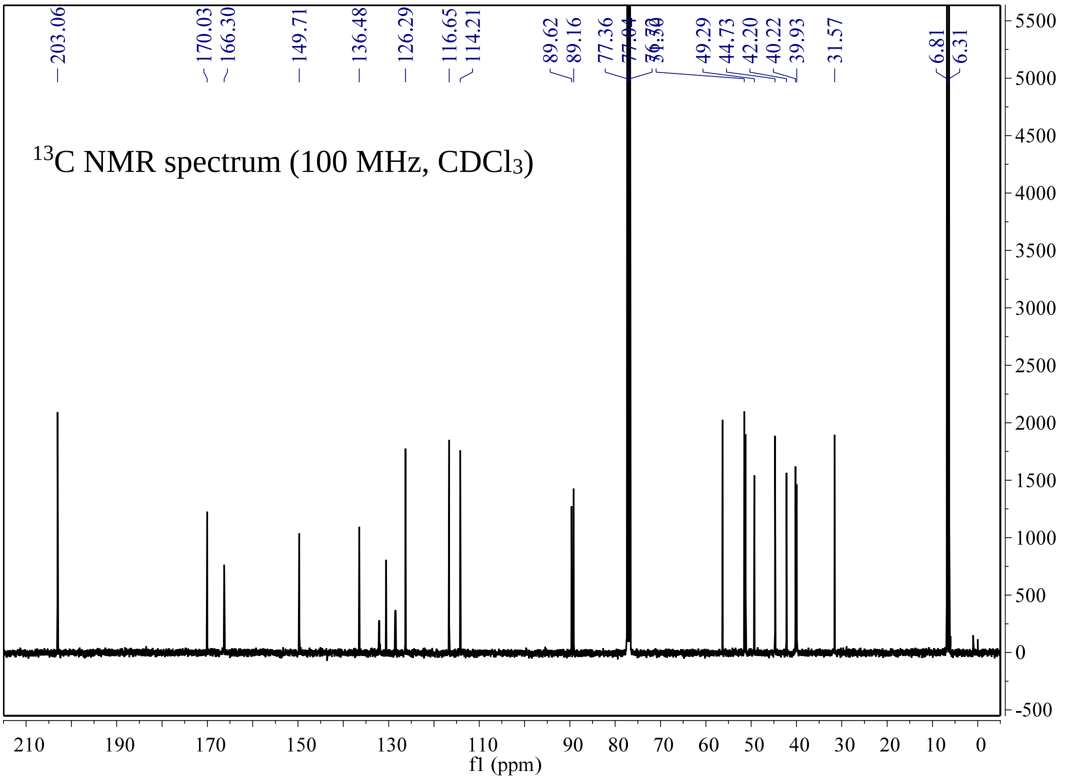


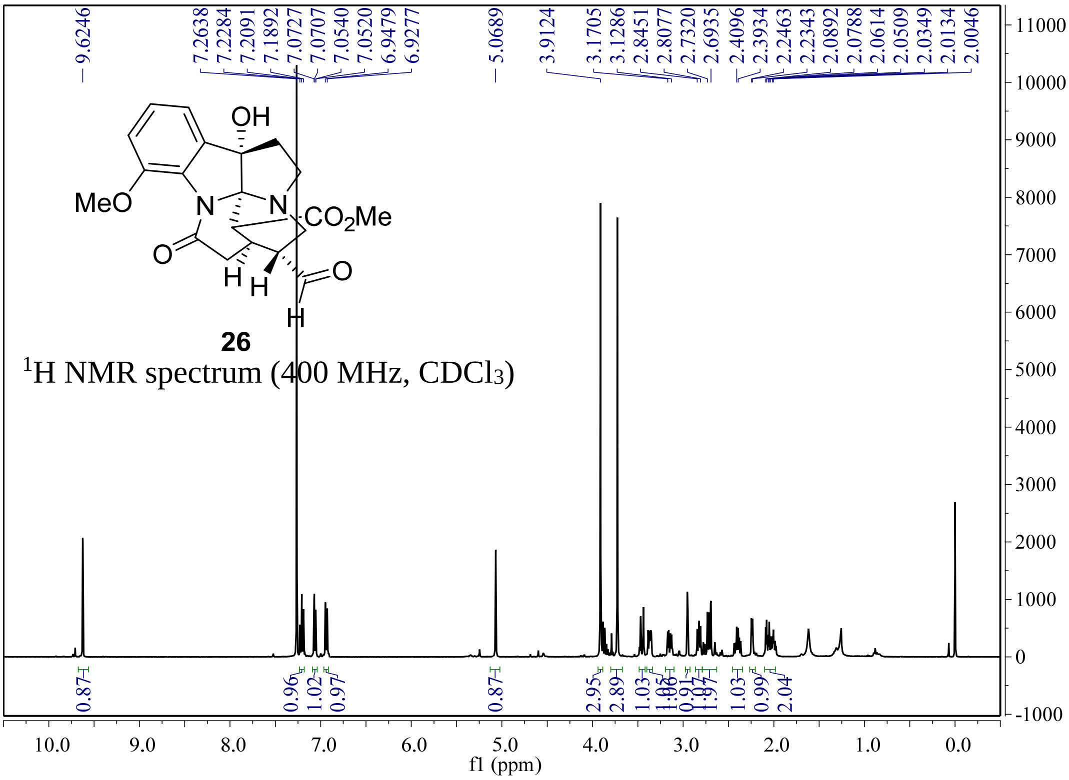
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

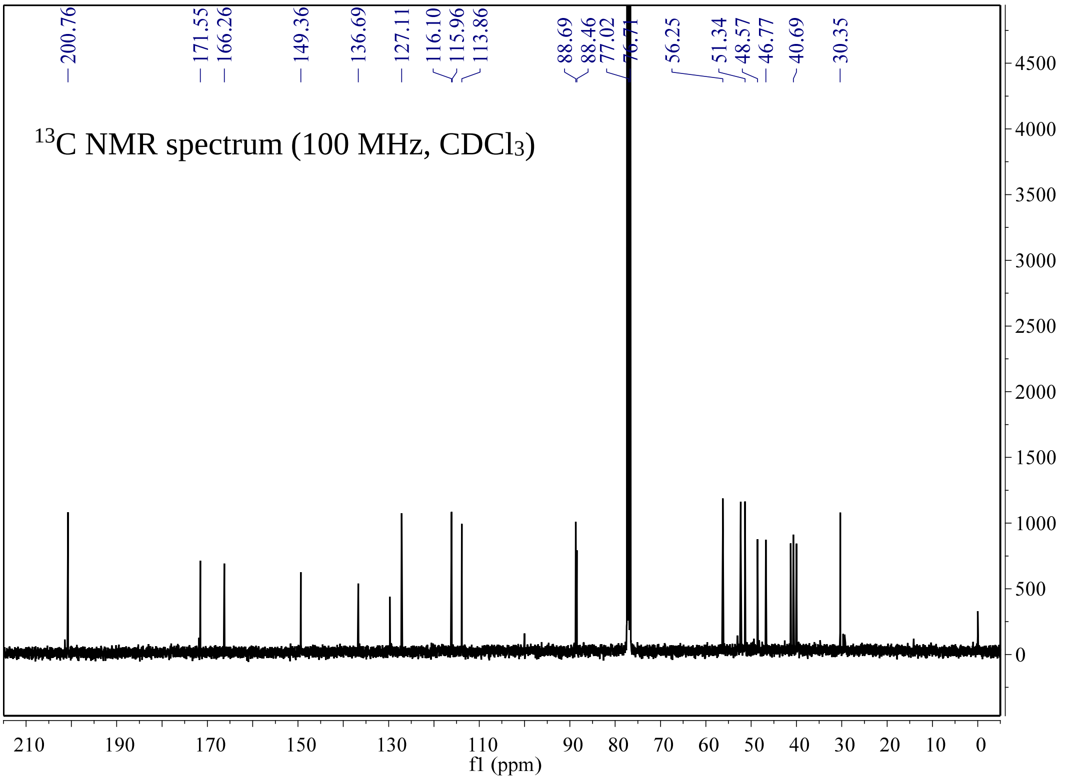

7.2598
7.1620
7.1422
7.1227
6.9989
6.9967
6.9800
6.9779
6.9329
6.9313
6.9125
6.9109
3.9012
3.7032
3.6280
3.6122
3.5996
3.1797
2.7881
2.6397
2.0747
1.7993
1.6229
0.8200
0.8005
0.4795
0.4591
0.4414
0.4380
OTES
MeO
N
N
CO2Me
O
H
H
OH
24
1H NMR spectrum (400 MHz, CDCl3)
0.96
1.02
0.96
3.00
3.59
1.03
0.99
2.83
1.07
1.92
1.95
1.90
0.95
9.06
5.91
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

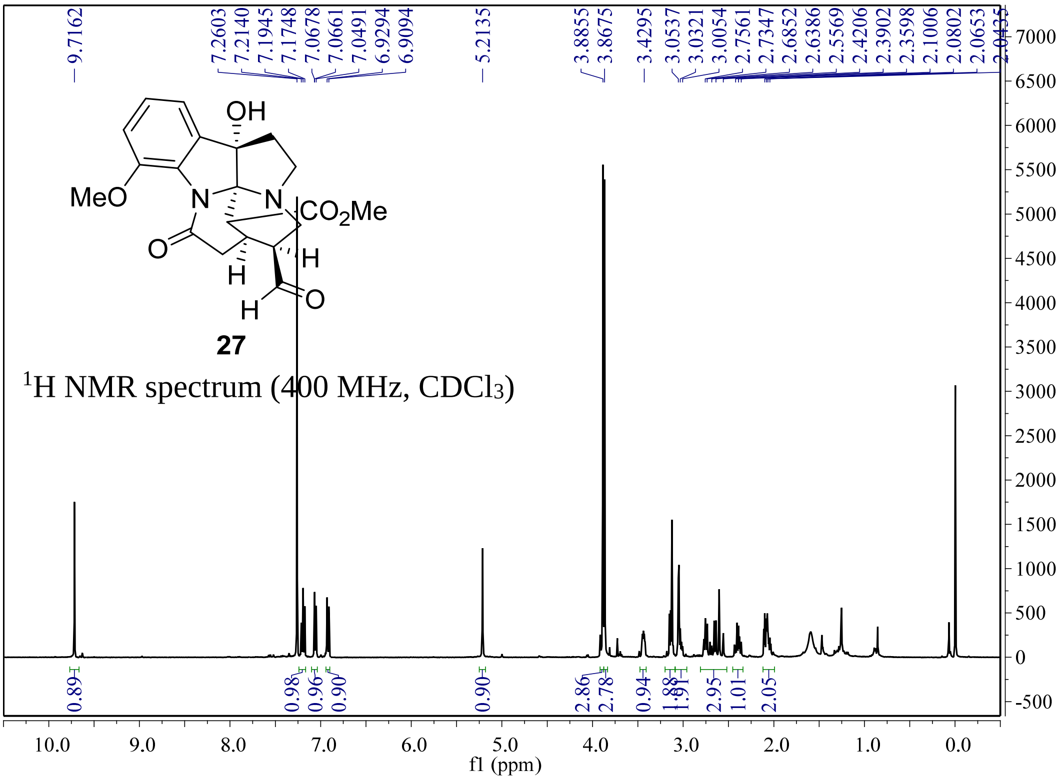

171.25
166.89
149.78
136.96
126.09
116.58
114.21
90.37
89.17
77.35
77.03
76.71
64.78
51.43
45.40
42.94
39.62
33.18
6.84
6.37
13C NMR spectrum (100 MHz, CDCl3)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

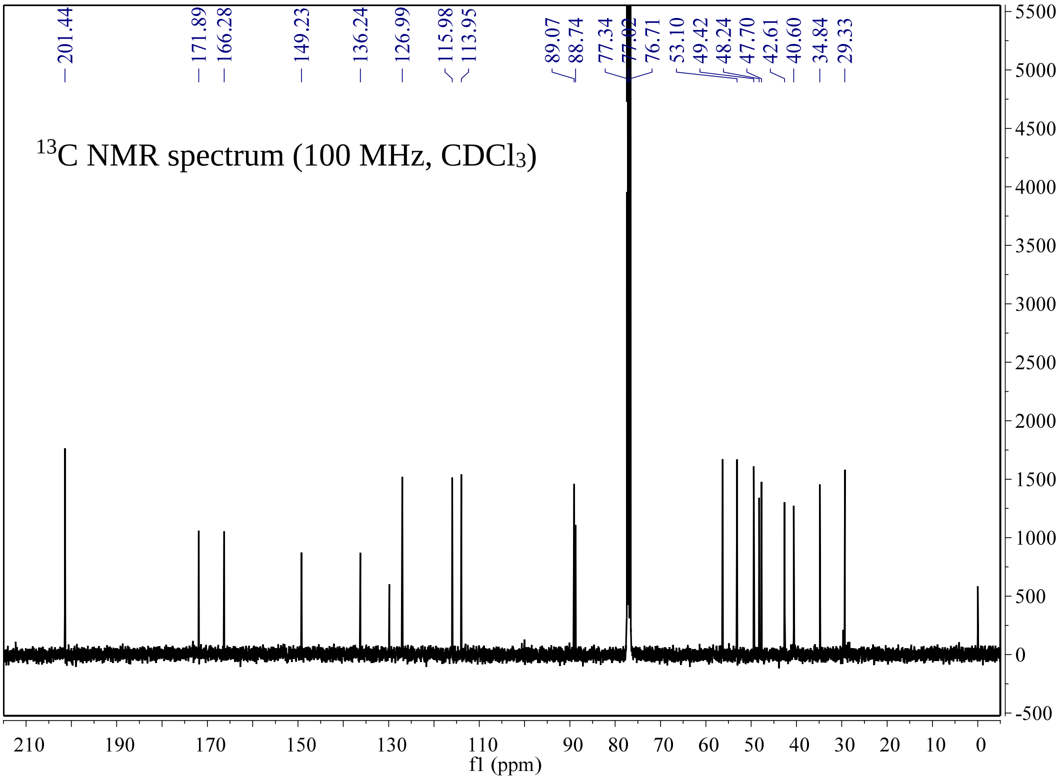

9.6153
7.2598
7.1689
7.1493
7.1296
6.9888
6.9715
6.9700
6.9360
6.9158
3.9018
3.6360
3.3277
2.9429
2.6393
2.1140
2.0422
0.8324
0.8124
0.7928
0.4812
0.4611
0.4426
0.4401
OTES
MeO
N
N
CO2Me
O
H
H
H
O
25
1H NMR spectrum (400 MHz, CDCl3)
0.98
0.99
0.98
0.98
2.92
2.91
2.96
1.96
2.99
3.02
8.99
6.06
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

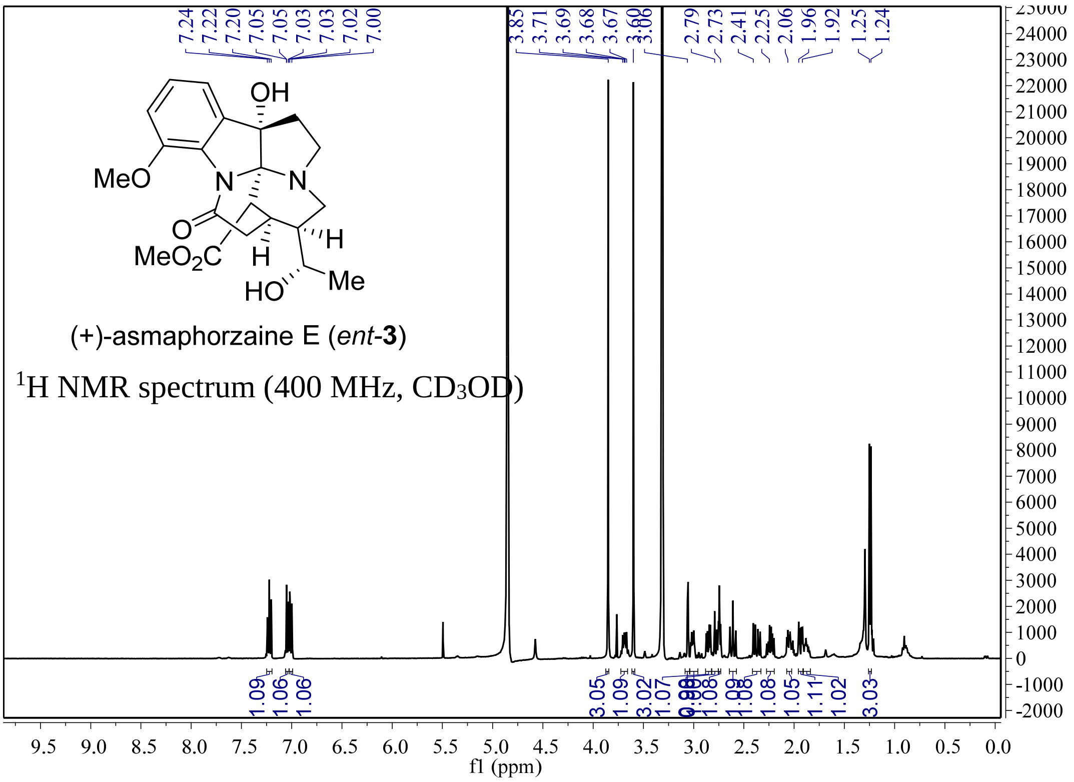

203.06
170.03
166.30
149.71
136.48
126.29
116.65
114.21
89.62
89.16
77.36
77.04
76.72
51.50
49.29
44.73
42.20
40.22
39.93
31.57
6.81
6.31
13C NMR spectrum (100 MHz, CDCl3)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.6246
7.2638
7.2284
7.2091
7.1892
7.0727
7.0707
7.0540
7.0520
6.9479
6.9277
5.0689
3.9124
3.1705
3.1286
2.8451
2.8077
2.7320
2.6935
2.4096
2.3934
2.2463
2.2343
2.0892
2.0788
2.0614
2.0509
2.0349
2.0134
2.0046
OH
MeO
N
N
CO2Me
O
H
H
O
H
26
1H NMR spectrum (400 MHz, CDCl3)
0.87
0.96
1.02
0.97
0.87
2.95
2.89
1.03
1.05
1.06
0.91
1.07
1.97
1.03
0.99
2.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


200.76
171.55
166.26
149.36
136.69
127.11
116.10
115.96
113.86
88.69
88.46
77.02
76.71
56.25
51.34
48.57
46.77
40.69
30.35
13C NMR spectrum (100 MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0

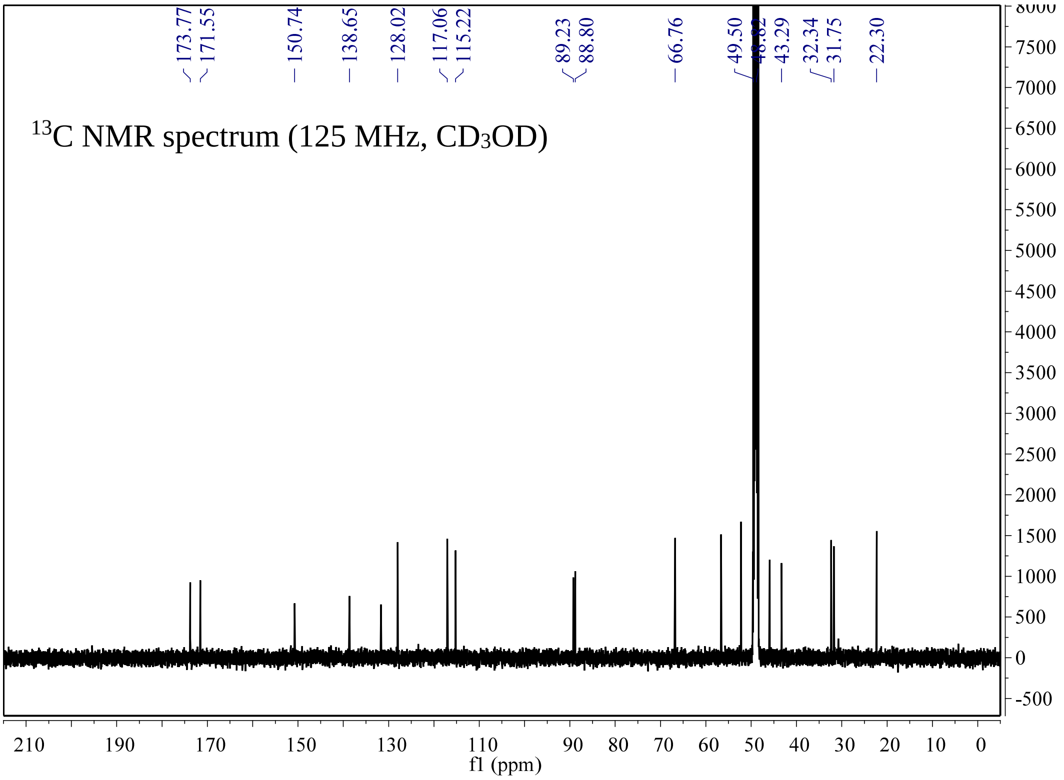

9.7162
7.2603
7.2140
7.1945
7.1748
7.0678
7.0661
7.0491
6.9294
6.9094
5.2135
3.8855
3.8675
3.4295
3.0537
3.0321
3.0054
2.7561
2.7347
2.6852
2.6386
2.5569
2.4206
2.3902
2.3598
2.1006
2.0802
2.0653
2.0435
OH
MeO
N
N
CO2Me
O
H
H
H
O
27
1H NMR spectrum (400 MHz, CDCl3)
0.89
0.98
0.96
0.90
0.90
2.86
2.78
0.94
1.88
1.91
2.95
1.01
2.05
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


201.44
171.89
166.28
149.23
136.24
126.99
115.98
113.95
89.07
88.74
77.34
77.02
76.71
53.10
49.42
48.24
47.70
42.61
40.60
34.84
29.33
13C NMR spectrum (100 MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

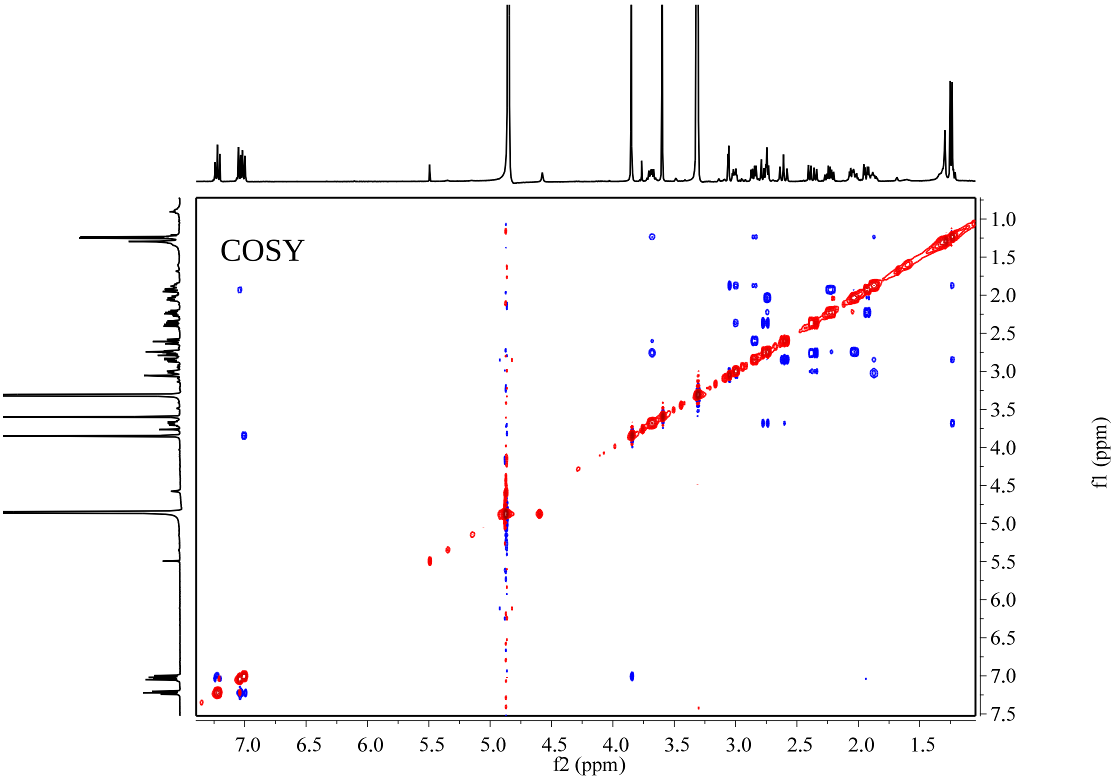


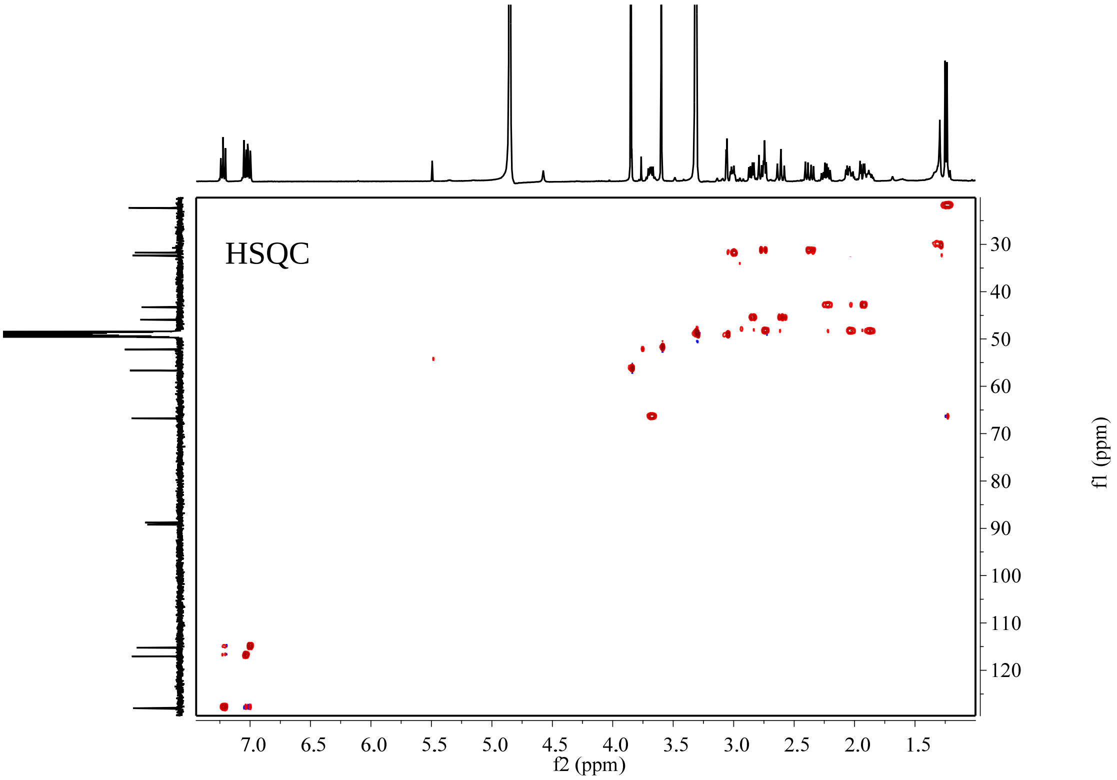
(+)-asmaphorzaine E (*ent*-**3**)

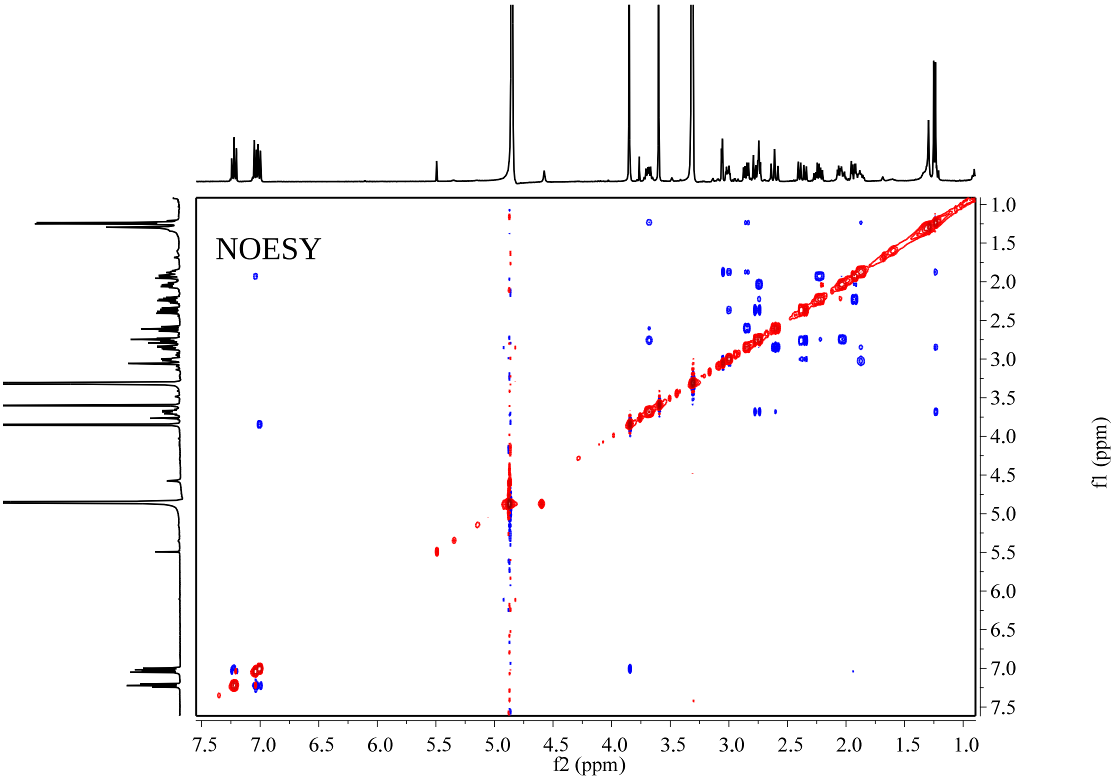
^{1}H NMR spectrum (400 MHz, CD$_3$OD)

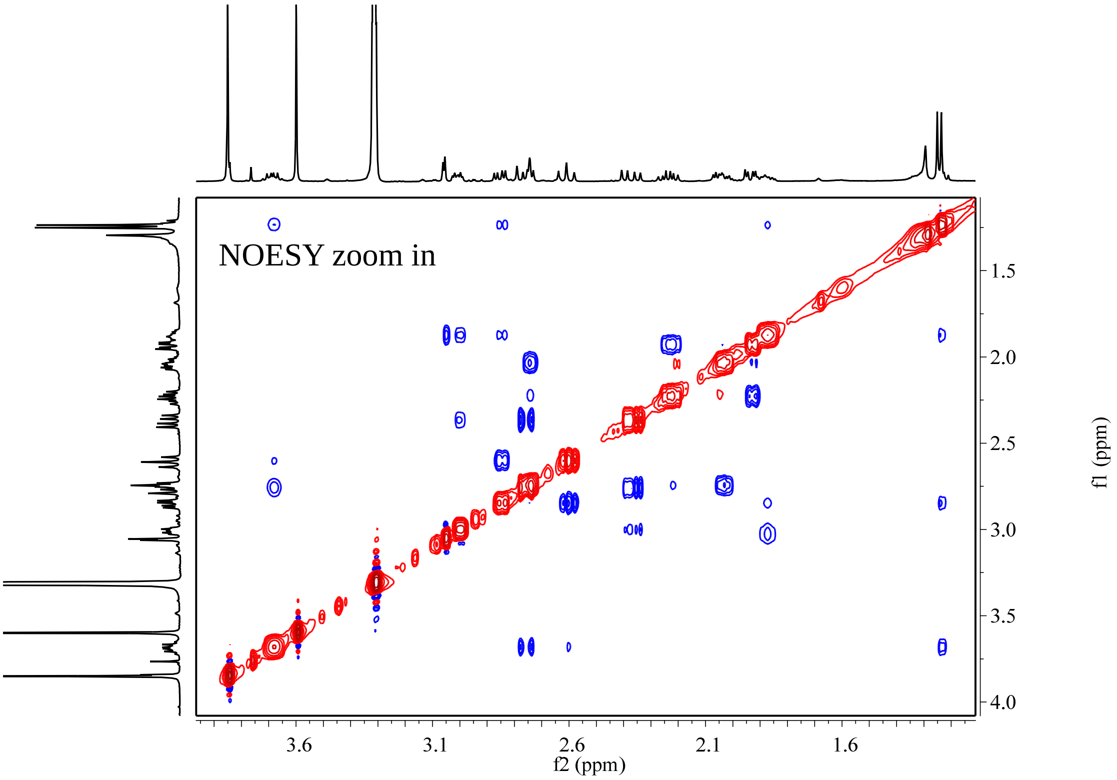


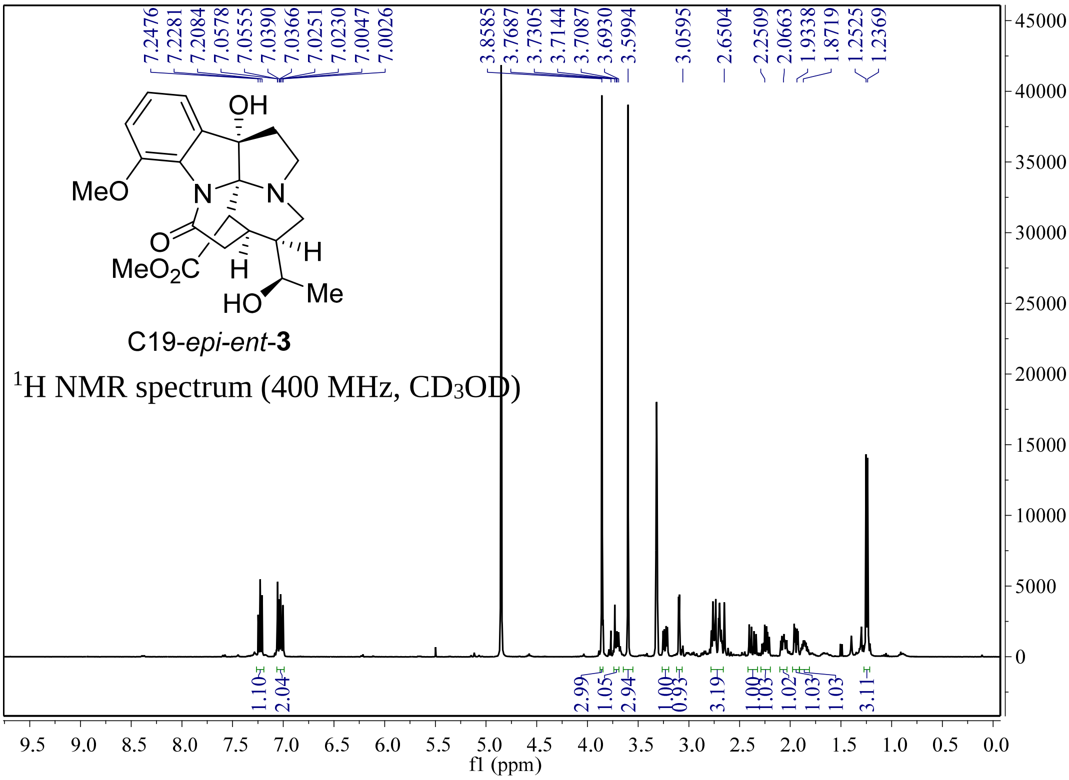
^{13}C NMR spectrum (125 MHz, CD$_3$OD)


COSY
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)


HSQC
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
30
40
50
60
70
80
90
100
110
120
f1 (ppm)

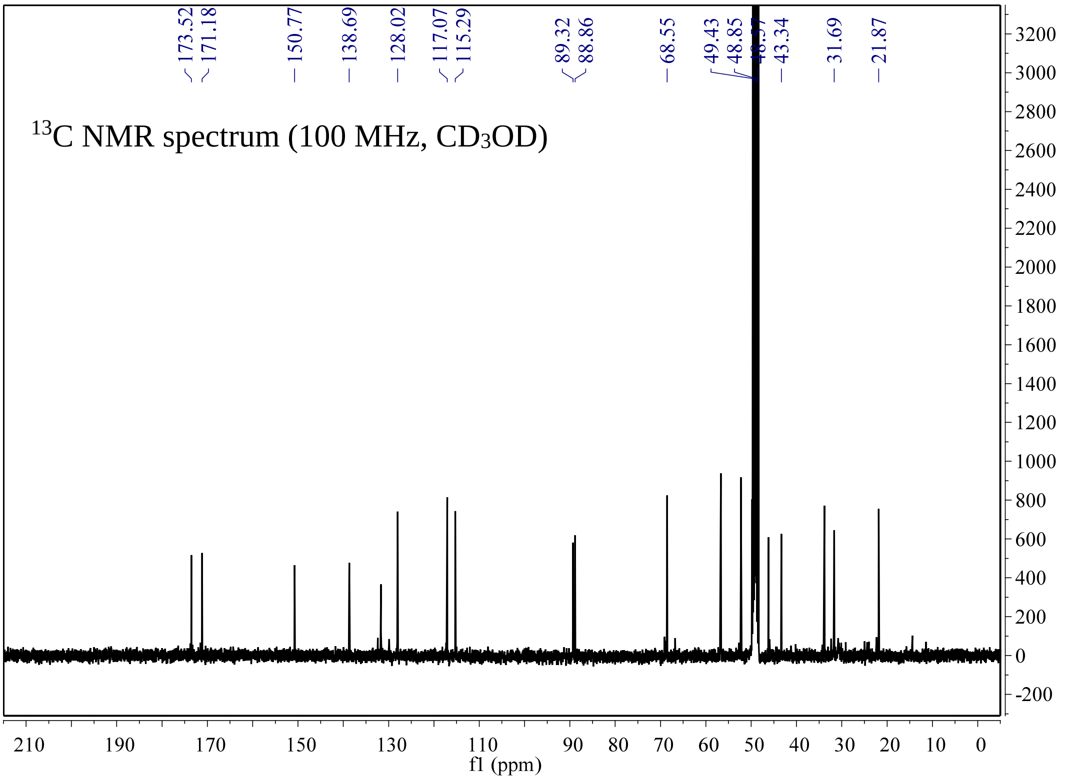

NOESY
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
f1 (ppm)


NOESY zoom in
3.6
3.1
2.6
2.1
1.6
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
f1 (ppm)

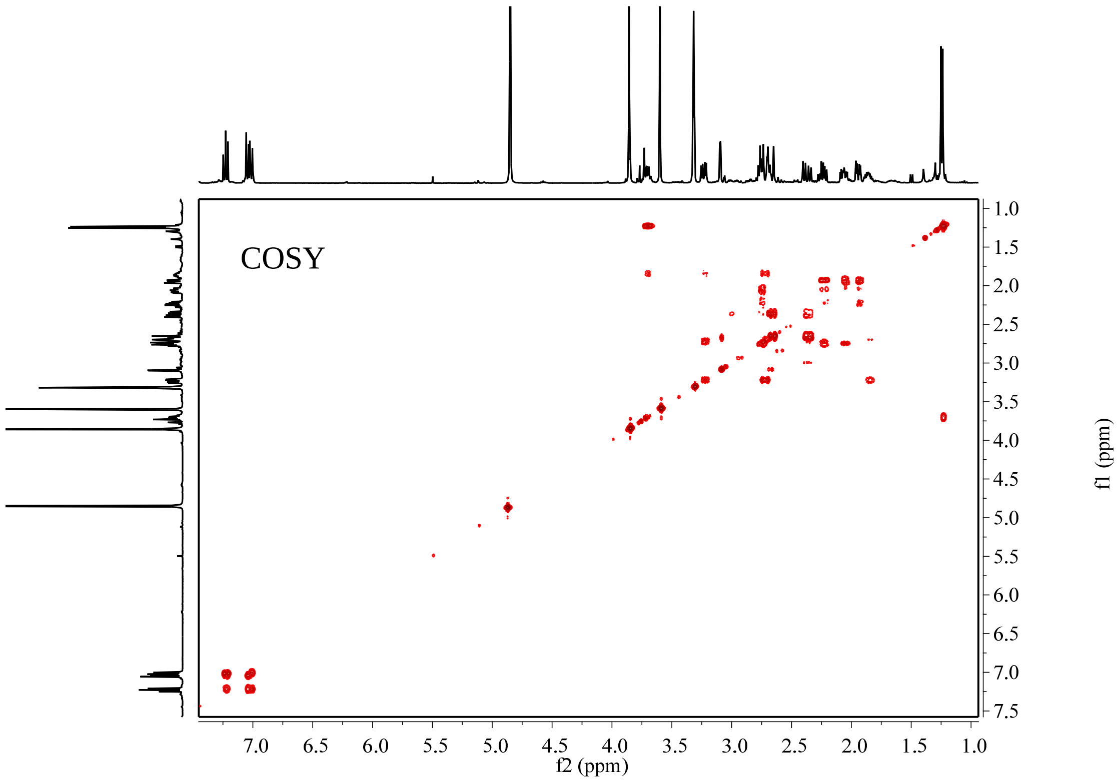


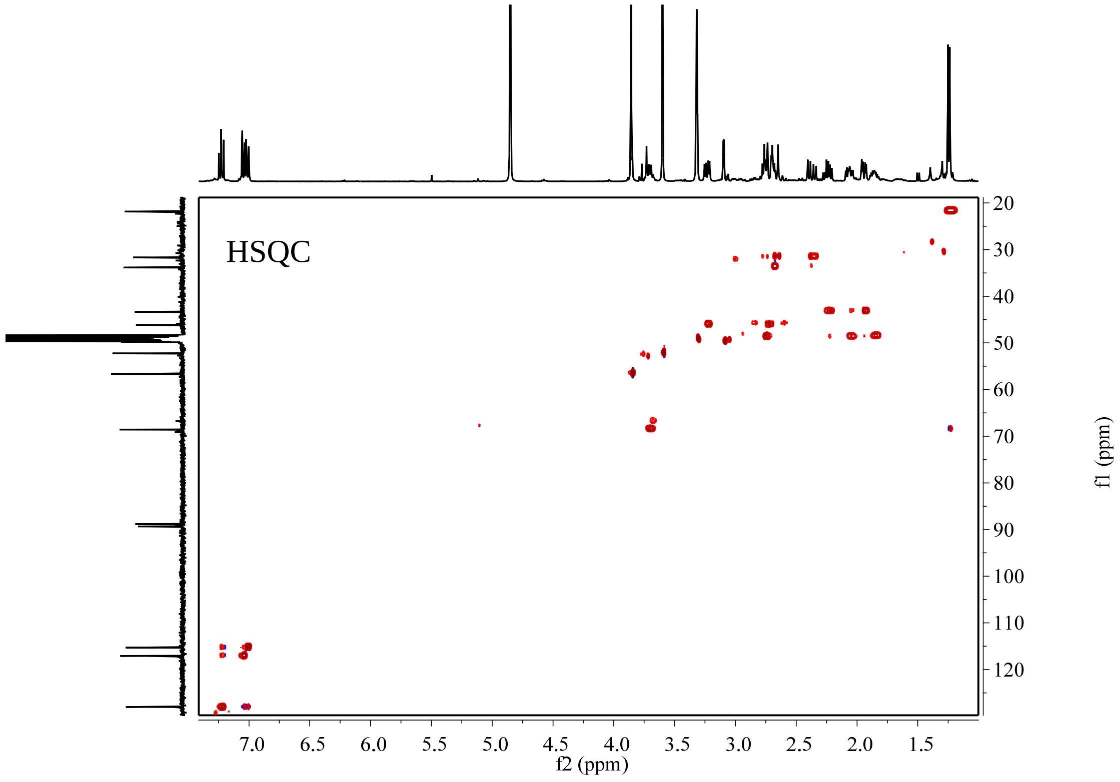
C19-*epi*-*ent*-**3**

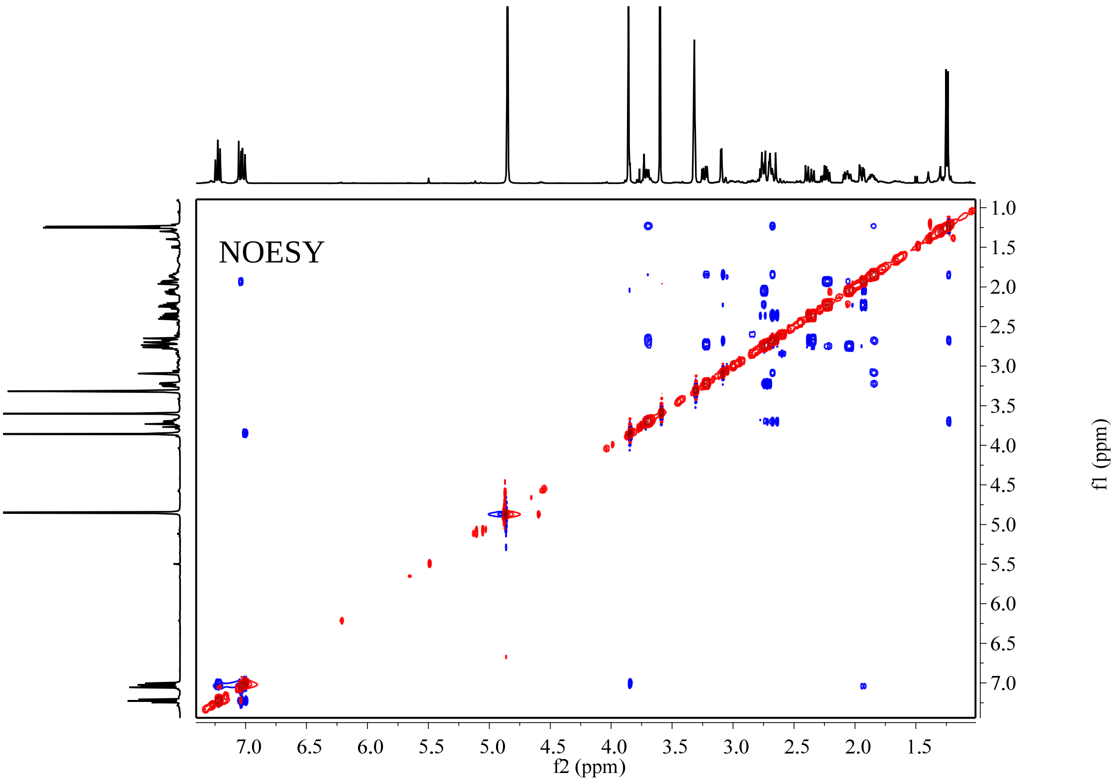
^{1}H NMR spectrum (400 MHz, CD_3OD)

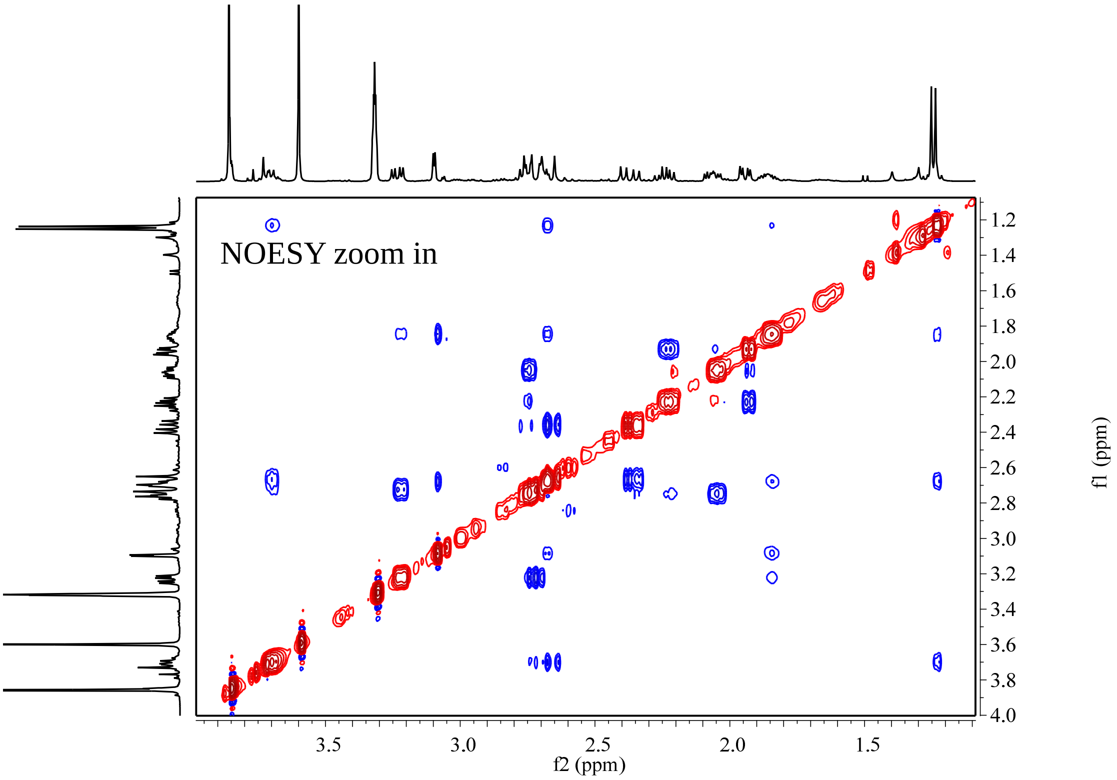


^{13}C NMR spectrum (100 MHz, CD_3OD)


COSY
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)
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
f2 (ppm)


HSQC
20
30
40
50
60
70
80
90
100
110
120
f1 (ppm)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)


NOESY
f2 (ppm)
f1 (ppm)
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


NOESY zoom in
f2 (ppm)
f1 (ppm)
3.5
3.0
2.5
2.0
1.5
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0