Supporting Information

Total Syntheses of Macleanine and Lycoposerramine-S

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General Remarks

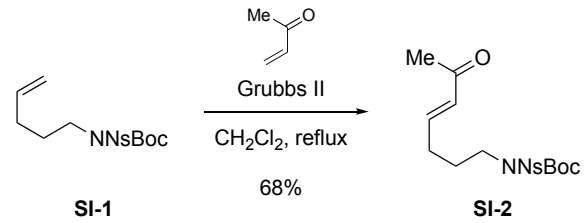
Dehydrated tetrahydrofuran, dichloromethane, methanol, ethanol and chloroform were purchased from FUJIFILM Wako Pure Chemical Co.. *N*,*N*-Dimethylformamide, diethyl ether and toluene were purchased from FUJIFILM Wako Pure Chemical Co. and stored over activated MS4A. Acetonitrile was purchased from FUJIFILM Wako Pure Chemical Co. and stored over activated MS3A. *tert*-Butyl ((4-nitrophenyl)sulfonyl)(pent-4-en-1-yl)carbamate (**SI-1**),[1] (*R*)-2-iodo-5-methylcyclohex-2-en-1-one (**SI-3**),[2] and *S*-*p*-tolyl *p*-toluenethiosulfonate[3] were prepared according to the literature. All other solvents and reagents were purchased at the commercial grade and were used as received, without further purification.

Reactions were performed in oven-dried glassware under a slight positive pressure of argon unless otherwise noted. Reactions that require heating were conducted in an oil bath unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel 60 F254. Preparative TLC separations were performed on Merck analytical plates (0.25 or 0.50 mm thick) precoated with silica gel 60 F254. Flash chromatography separations were performed on KANTO CHEMICAL Silica Gel 60 (spherical, 40-100 mesh) unless otherwise noted. Flash chromatography separations using neutral silica gel were performed on KANTO CHEMICAL Silica Gel 60 (neutral, spherical, 40-50 mesh). Flash chromatography separations using NH_2 silica gel were performed on CHROMATOREX NH-DU3050 purchased from FUJI SILYSIA CHEMICAL. LTD.

Optical rotations were measured on a JASCO P-2200 Polarimeter at room temperature using the sodium D line. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 Fourier Transform Infrared Spectrophotometer and were reported in wavenumbers (cm^{-1}). Nuclear magnetic resonance (NMR) spectra were determined on JEOL-ECS400 or JEOL-ECZ400 instrument unless otherwise noted. Chemical shifts for ^1H NMR are reported in parts per million relative to the line of a singlet at 7.26 ppm for residual chloroform in deuteriochloroform and coupling constants were reported as *J* values in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, m = multiplet, brs = broad singlet. Chemical shifts for ^{13}C NMR were reported in ppm to the center line of a triplet at 77.00 ppm for $CDCl_3$. High resolution mass spectra (HRMS) were obtained on a Bruker Daltonics compact in positive electrospray ionization (ESI) method using ESI tuning mix as the internal standard.

Experimental Section

Compound SI-2



SI-1 **SI-2**

To a stirred solution of **SI-1** (45.3 g, 0.122 mol) [1] and methyl vinyl ketone (19.9 mL, 0.244 mol) dissolved in dichloromethane (244 mL) was added (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium (Grubbs II, 518 mg, 0.610 mmol) at room temperature. After stirring for 2 hours at reflux, the resulting mixture was concentrated. The residue was purified by flash silica gel column chromatography (EtOAc: *n*-hexane = 1:3 then 1:2) to give **SI-2** (34.3 g, 83.2 mmol, 68%) as an orange oil.

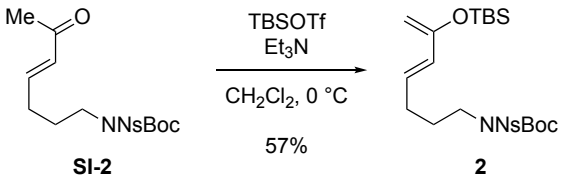
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.30-8.25 (m, 1H), 7.77-7.70 (m, 3H), 6.81 (dt, *J* = 16.0, 6.9 Hz, 1H), 6.12 (dt, *J* = 16.0, 1.4 Hz, 1H), 3.79 (t, *J* = 7.3 Hz, 2H), 2.32 (tdd, *J* = 6.9, 6.8, 1.4 Hz, 2H), 2.24 (s, 3H), 1.92 (tt, *J* = 7.6, 7.3 Hz, 2H), 1.33 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.5 (C), 150.2 (C), 147.5 (C), 146.6 (CH), 134.2 (CH), 133.3 (C), 133.2 (CH), 131.7 (2CH), 124.3 (CH), 85.2 (C), 47.3 (CH_2), 29.4 (CH_2), 28.4 (CH_2), 27.8 ($3CH_3$), 26.9 (CH_3).

IR (cm^{-1}) 1731, 1674, 1545, 1366, 1285, 1255, 1153, 977, 775, 742, 570.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{24}N_2NaO_7S^+$ 435.1196; Found 435.1195.

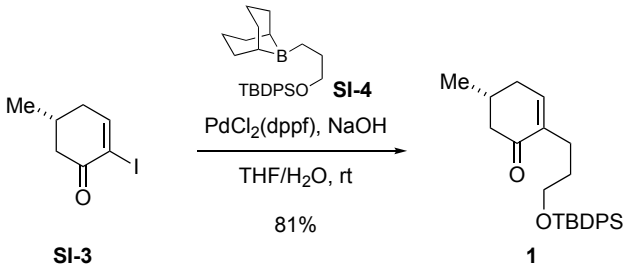
Compound 2



SI-2 **2**

The transformation of **SI-2** into **2** was conducted according to a reported procedure.[4] To a stirred solution of **SI-2** (37.2 g, 90.2 mmol) and triethylamine (15.1 mL, 108 mmol) dissolved in dichloromethane (270 mL) was added *tert*-butyldimethylsilyl trifluoromethanesulfonate (25 g, 95 mmol) at 0 °C. After stirring for 80 minutes at the same temperature, to the reaction mixture was added saturated aqueous sodium bicarbonate. The mixture was extracted with dichloromethane four times. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash silica gel column chromatography (EtOAc: *n*-hexane = 1:6) using NH_2 silica gel to give **2** (26.9 g, 51.1 mmol, 57%) as a yellow oil. Spectroscopic data of **2** were identical to those of the reported compound.[4]

Compound 1



To a solution of allyloxy(*tert*-butyl)diphenylsilane (19.7 g, 66.4 mmol) in tetrahydrofuran (100 mL) was added 9-BBN (200 mL, 100 mmol, 0.5 M in tetrahydrofuran) at room temperature. After heating at 65 °C for 90 minutes, the reaction mixture was cooled down to room temperature. In another flask were placed **SI-3** (13.1 g, 55.5 mmol)[2] and $PdCl_2$(dppf) (2.03 g, 2.77 mmol), and were dissolved in tetrahydrofuran (100 mL) and 1 M aqueous NaOH (100 mL) at room temperature. To this solution was then added the above solution containing the boron reagent **SI-4** via a cannula and the resultant mixture was stirred at room temperature for 30 minutes. After dilution with diethyl ether, the reaction was quenched with aqueous ammonium chloride. After separation the phases, the aqueous phase was extracted three times with diethyl ether. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography (EtOAc: *n*-hexane = 1:20) to afford **1** (18.4 g, 45.2 mmol, 81%) as a pale-yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (dd, *J* = 8.0, 1.6 Hz, 4H), 7.45-7.35 (m, 6H), 6.62 (m, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.46 (dd, *J* = 13.7, 2.3 Hz, 1H), 2.35 (dd, *J* = 17.9, 4.1 Hz, 1H), 2.27 (t, *J* = 7.6 Hz, 2H), 2.10 (m, 1H), 2.08 (d, *J* = 15.6 Hz, 1H), 1.98 (m, 1H), 1.67 (tt, *J* = 7.4, 6.4 Hz, 2H), 1.05 (s, 9H), 1.03 (d, *J* = 6.4 Hz, 3H) .

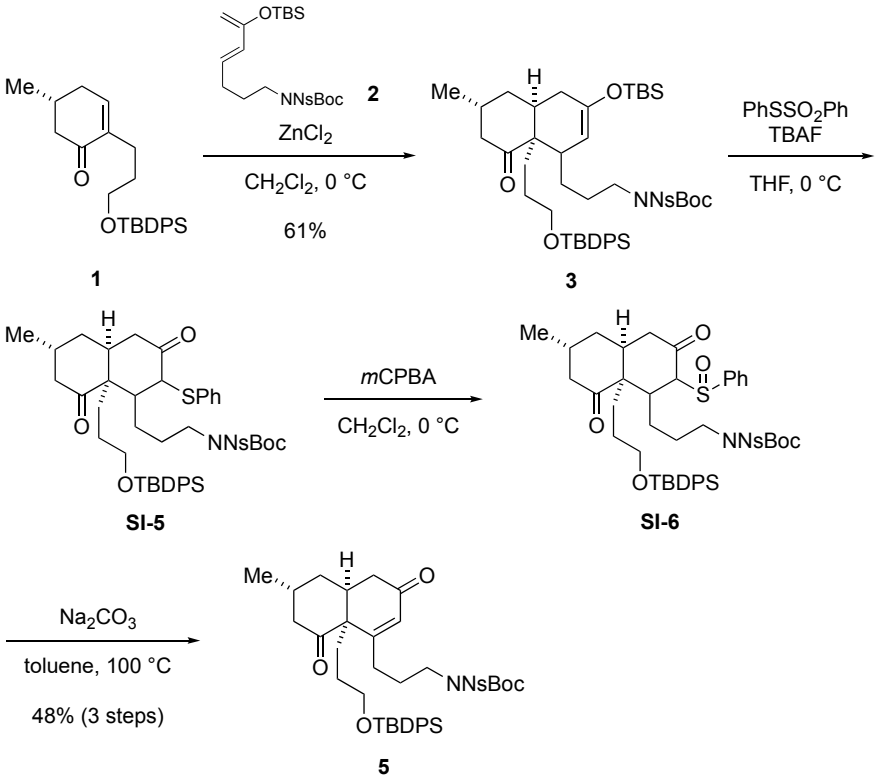
^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.7 (C), 144.5 (CH), 138.9 (C), 135.6 (4CH), 134.0 (2C), 129.5 (2CH), 127.6 (4CH), 63.2 (CH_2), 46.7 (CH_2), 34.3 (CH_2), 31.2 (CH_2), 30.6 (CH), 26.8 ($3CH_3$), 25.7 (CH_2), 21.2 (CH_3), 19.2 (C).

IR (cm^{-1}) 1675, 1472, 1428, 1381, 1110, 823, 741, 703, 613, 505.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{26}H_{34}NaO_2Si^+$ 429.2220; Found 429.2220.

$[\alpha]_D^{19}$ = –29° (*c* 1.06, $CHCl_3$).

Compounds 3 and 5



To a solution of zinc chloride (2.62 g, 19.2 mmol, dried by heating with a heat gun for 5 min under reduced pressure prior to use) in dichloromethane (154 mL) was added a mixture of **1** (7.80 g, 19.2 mmol) and **2** (15.1 g, 28.7 mmol) in dichloromethane (77 mL) at 0 °C. After stirring for 15 minutes at the same temperature, the reaction was quenched with saturated aqueous sodium bicarbonate. The mixture was extracted three times with dichloromethane. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash silica gel column chromatography (EtOAc: *n*-hexane = 1:3) to afford **3** (11.0 g, 11.8 mmol, 61%, based on **1**) as a white foam.

To a stirred solution of **3** (7.50 g, 8.04 mmol) and *S*-*p*-tolyl *p*-toluenethiosulfonate (2.32 g, 9.27 mmol)[3] dissolved in tetrahydrofuran (89 mL) was added a solution of tetrabutylammonium fluoride (8.0 mL, 1.0 M in tetrahydrofuran, 8.04 mmol) at 0 °C. After stirring for 15 minutes at the same temperature, to the reaction mixture was added saturated aqueous ammonium chloride. The mixture was extracted three times with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash silica gel column chromatography (EtOAc: *n*-hexane = 1:2) to afford 6.22 g of **SI-5** which contained inseparable byproducts, and it was used for the next reaction without further purification.

To a stirred solution of **SI-5** (6.22 g, containing inseparable byproducts) dissolved in dichloromethane (134 mL) was added *m*-chloroperbenzoic acid (1.65 g, 70% purity, 6.71 mmol) at 0 °C. After stirring for 45 minutes at the same temperature, to the reaction mixture was added aqueous $Na_2S_2O_3$. The mixture was extracted three times with dichloromethane. The combined organic phases were dried over Na_2SO_4, filtered and concentrated. The crude product was utilized in the next step without further purification.

To a solution of the material obtained above dissolved in toluene (219 mL) was added sodium carbonate (0.70

g, 6.60 mmol) at room temperature. After heating at 100 °C for 7 hours, to the reaction mixture was added water. The mixture was extracted with diethyl ether three times. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash silica gel column chromatography (EtOAc: *n*-hexane = 1:2 then 2:3) to afford **5** (3.12 g, 3.82 mmol, 48% for three steps, based on **3**) as a white foam.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.31-8.24 (m, 1H), 7.76-7.69 (m, 3H), 7.68-7.60 (m, 4H), 7.46-7.33 (m, 6H), 6.04 (s, 1H), 3.78 (t, *J* = 7.3 Hz, 2H), 3.70 (m, 2H), 2.66 (m, 1H), 2.42-2.09 (m, 8H), 2.09-1.81 (m, 2H), 1.76-1.54 (m, 5H), 1.35 (s, 9H), 1.07 (s, 9H), 1.01 (d, *J* = 6.4 Hz, 3H).

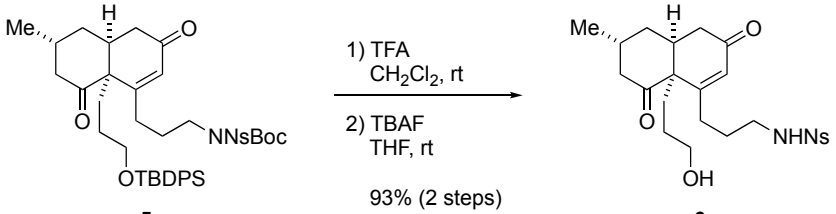
^{13}C NMR ($CDCl_3$, 100 MHz) δ 211.2 (C), 197.8 (C), 163.7 (C), 150.2 (C), 147.6 (C), 135.5 (4CH), 134.1 (CH), 133.7 (C), 133.6 (C), 133.4 (C), 133.3 (CH), 131.7 (CH), 129.7 (2CH), 127.7 (4CH), 126.6 (CH), 124.3 (CH), 85.2 (C), 63.6 (CH_2), 58.1 (C), 47.5 (CH_2), 46.7 (CH_2), 40.0 (CH_2), 36.6 (CH), 34.1 (CH_2), 29.8 (CH), 29.7 (CH_2), 29.0 (CH_2), 27.8 ($3CH_3$), 27.6 (CH_2), 27.4 (CH_2), 26.9 ($3CH_3$), 20.7 (CH_3), 19.2 (C).

IR (cm^{-1}) 1731, 1674, 1544, 1365, 1281, 1151, 1112, 780, 738, 706, 616, 576.

HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{44}H_{56}N_2NaO_9SSi^+$ 839.3368; Found 839.3368.

$[\alpha]_D^{25} = -16°$ (*c* 1.65, $CHCl_3$).

Compound 6



5 **6**

To a stirred solution of **5** (2.78 g, 3.40 mmol) dissolved in dichloromethane (68.0 mL) was added trifluoroacetic acid (34.0 mL) at room temperature. After stirring for 50 minutes at the same temperature, to the reaction mixture was added toluene (70 mL). The resulting mixture was concentrated. The residue was dissolved in tetrahydrofuran (68.0 mL), and to this mixture was added a solution of tetrabutylammonium fluoride (10.2 mL, 1.0 M in tetrahydrofuran, 10 mmol) at room temperature. After stirring for 25 minutes at the same temperature, to the reaction mixture was added saturated ammonium chloride and brine. The mixture was extracted three times with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash silica gel column chromatography (EtOAc: *n*-hexane = 1:1 then 7:1) using neutral silica gel to give **6** (1.52 g, 3.40 mmol, 93% for two steps, based on **5**) as a white foam.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.11 (m, 1H), 7.84 (m, 1H), 7.80–7.68 (m, 2H), 5.92 (s, 1H), 5.76 (brs, 1H), 3.73 (m, 1H), 3.66 (m, 1H), 3.25–3.08 (m, 2H), 2.70 (m, 1H), 2.41–2.16 (m, 9H), 1.94 (brs, 1H), 1.91–1.58 (m, 5H), 1.35 (m, 1H), 1.04 (d, *J* = 6.4 Hz, 3H).

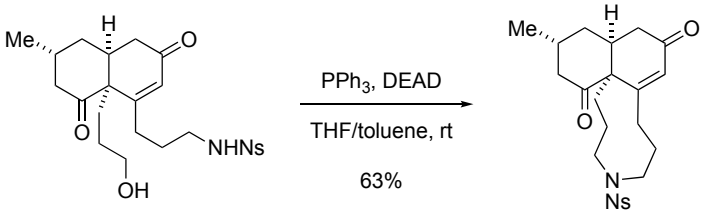
^{13}C NMR ($CDCl_3$, 100 MHz) δ 212.1 (C), 197.8 (C), 163.5 (C), 148.0 (C), 133.7 (C), 133.6 (CH), 132.8 (CH), 131.0 (CH), 127.0 (CH), 125.4 (CH), 62.2 (CH_2), 58.3 (C), 46.7 (CH_2), 42.7 (CH_2), 40.0 (CH_2), 37.0 (CH), 34.2 (CH_2), 29.9 (CH), 29.0 (CH_2), 28.6 (CH_2), 27.4 (CH_2), 26.8 (CH_2), 20.9 (CH_3).

IR (cm^{-1}) 3340, 1699, 1664, 1541, 1363, 1340, 1165, 1059, 753, 655, 589.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{23}H_{30}N_2NaO_7S^+$ 501.1666; Found 501.1667.

$[\alpha]_D^{24} = -44°$ (*c* 0.43, $CHCl_3$).

Compound 7



6 **7**

To a stirred solution of **6** (1.52 g, 3.18 mmol) and triphenylphosphine (1.25 g, 4.77 mmol) dissolved in a mixture of toluene (80 mL) and tetrahydrofuran (80 mL) was added a solution of diethyl azodicarboxylate (2.16 mL, 2.2 M in toluene, 4.75 mmol) at room temperature. After stirring for 30 minutes at the same temperature, the reaction mixture was concentrated. The crude product was roughly purified by flash silica gel column chromatography (EtOAc:dichloromethane = 1:3) using neutral silica gel to give a mixture of **7** and impurities. This mixture was further purified by flash silica gel column chromatography (EtOAc: *n*-hexane = 1:2 then 3:1) using neutral silica gel to give **7** (925 mg, 2.01 mmol, 63%) as a white foam.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (m, 1H), 7.74–7.64 (m, 2H), 7.58 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.23 (s, 1H), 3.58 (ddd, *J* = 12.8, 12.8, 3.7 Hz, 1H), 3.36 (dd, *J* = 15.6, 5.0 Hz, 1H), 2.87–2.77 (m, 2H), 2.61–2.27 (m, 9H), 2.23 (dd, *J* = 15.6, 3.7 Hz, 1H), 2.14 (m, 1H), 1.93 (m, 1H), 1.88–1.77 (m, 2H), 1.61 (m, 1H), 1.33 (m, 1H), 1.08 (d, *J* = 6.4 Hz, 3H).

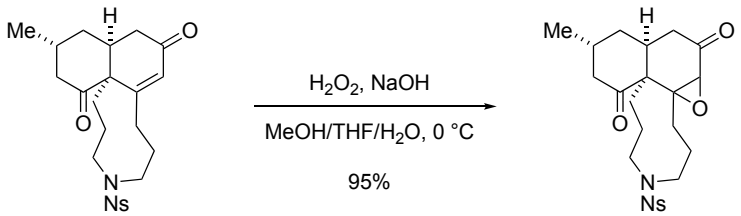
^{13}C NMR ($CDCl_3$, 100 MHz) δ 211.0 (C), 197.8 (C), 165.7 (C), 148.6 (C), 133.8 (CH), 131.3 (CH), 130.7 (CH+C, overlapped), 130.1 (CH), 123.9 (CH), 60.2 (C), 49.5 (CH_2), 46.5 (CH_2), 44.1 (CH_2), 40.1 (CH_2), 39.1 (CH), 34.9 (CH_2), 30.3 (CH), 28.0 (CH_2), 27.3 (CH_2), 25.7 (CH_2), 21.7 (CH_3), 21.4 (CH_2).

IR (cm^{-1}) 1699, 1668, 1545, 1372, 1343, 1170, 954, 747, 579.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{23}H_{28}N_2NaO_6S^+$ 483.1560; Found 483.1559.

$[\alpha]_D^{25} = -94°$ (*c* 0.82, $CHCl_3$).

Compound 8



7 **8**

To a stirred solution of **7** (907 mg, 1.97 mmol) dissolved in a mixed solvent of methanol (50 mL) and tetrahydrofuran (50 mL) were added aqueous hydrogen peroxide (1.12 mL, 30%) and 15% aqueous sodium hydroxide (0.99 mL) at 0 °C. After stirring for 20 minutes at the same temperature, to the reaction mixture was added aqueous sodium thiosulfate and sodium chloride. The mixture was extracted three times with

EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash silica gel column chromatography (EtOAc: *n*-hexane = 1:1 then 3:1) using neutral silica gel to give **8** (896 mg, 1.88 mmol, 95% yield) as a white foam.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (dd, *J* = 7.2, 1.7 Hz, 1H), 7.71 (ddd, *J* = 7.2, 7.2, 1.7 Hz, 1H), 7.67 (ddd, *J* = 7.2, 7.2, 1.7 Hz, 1H), 7.57 (dd, *J* = 7.2, 1.7 Hz, 1H), 3.60 (ddd, *J* = 12.7, 12.7, 3.8 Hz, 1H), 3.45 (ddd, *J* = 6.9, 6.9, 3.4 Hz, 1H), 3.26 (s, 1H), 3.10–2.96 (m, 2H), 2.90 (dd, *J* = 13.0, 13.0 Hz, 1H), 2.73 (m, 1H), 2.59 (dd, *J* = 14.0, 3.4 Hz, 1H), 2.34 (m, 1H), 2.25 (ddd, *J* = 15.1, 6.5, 3.0 Hz, 1H), 2.20–1.94 (m, 5H), 1.85 (m, 1H), 1.77–1.47 (m, 5H), 0.98 (d, *J* = 6.0 Hz, 3H).

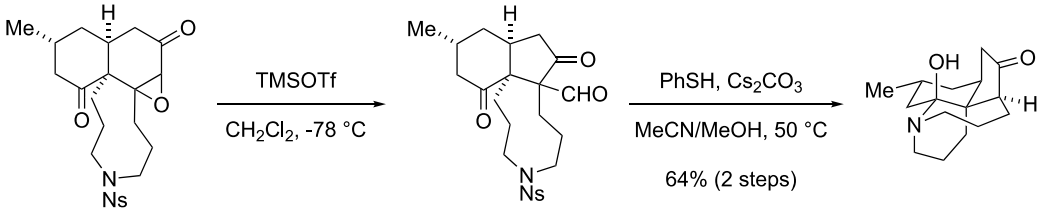
^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.4 (C), 207.4 (C), 148.4 (C), 133.7 (CH), 131.5 (CH), 131.4 (C), 130.7 (CH), 124.0 (CH), 72.5 (C), 60.8 (CH), 56.2 (C), 48.9 (CH_2), 46.8 (CH_2), 46.7 (CH_2), 41.9 (CH), 40.1 (CH_2), 36.6 (CH_2), 29.7 (CH_2), 28.2 (CH_2), 27.4 (CH), 26.2 (CH_2), 22.8 (CH_2), 21.5 (CH_3).

IR (cm^{-1}) 1702, 1544, 1373, 1343, 1224, 1167, 960, 750, 578.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{23}H_{28}N_2NaO_7S^+$ 499.1509; Found 499.1509.

$[\alpha]_D^{25}$ = –39° (*c* 0.41, $CHCl_3$).

Fawcettimine



To a stirred solution of **8** (893 mg, 1.87 mmol) dissolved in dichloromethane (94 mL) was added trimethylsilyl trifluoromethanesulfonate (1.72 mL, 9.35 mmol) at –78 °C dropwise over 3 min. After stirring for 20 minutes at the same temperature, to the reaction mixture was added aqueous sodium bicarbonate. The mixture was extracted three times with dichloromethane. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was dissolved in a mixed solvent of acetonitrile (76 mL) and methanol (19 mL), and to this solution were added cesium carbonate (1.83 g, 5.62 mmol) and thiophenol (0.382 mL, 3.74 mmol) at room temperature. After stirring for 13 hours at 50 °C, the reaction mixture was cooled to room temperature. To the cooled reaction mixture was added 1 M hydrochloric acid. After washing with hexane, sodium carbonate was added to basify the mixture. The mixture was extracted three times with dichloromethane. The combined organic phases were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash silica gel column chromatography (*n*-hexane, then methanol: dichloromethane = 1:15) using NH_2 silica gel to give fawcettimine (316 mg, 1.20 mmol, 64% for two steps, based on **8**) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.39 (ddd, *J* = 14.0, 8.9, 4.6 Hz, 1H), 3.20 (td, *J* = 14.2, 3.6 Hz, 1H), 2.85 (dd, *J* = 14.6, 5.0Hz, 1H), 2.68 (dt, *J* = 14.6, 4.8 Hz, 1H), 2.60 (dd, *J* = 17.9, 13.8 Hz, 1H), 2.28–1.97 (m, 7H), 1.96–1.74 (m, 4H), 1.59 (m, 1H), 1.54–1.31 (m, 3H), 1.15 (m, 1H), 0.92 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 220.6 (C), 60.2 (CH), 53.3 (CH_2), 49.9 (CH_2), 48.2 (C), 44.3 (CH_2), 43.2

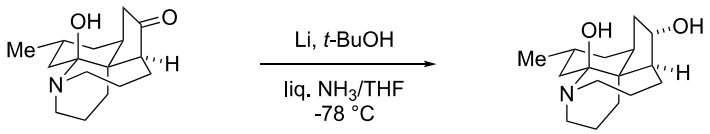
(CH), 41.9 (CH_2), 35.9 (CH_2), 31.9 (CH_2), 28.9 (CH_2), 28.2 (CH_2), 23.6 (CH), 22.6 (CH_2), 21.8 (CH_3).

IR (cm^{-1}) 3289, 1730, 1457, 1337, 1251, 1145, 1024, 753.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{16}H_{25}NaNO_2^+$ 286.1777; Found 286.1780.

$[\alpha]_D^{24}$ = +101° (*c* 1.07, CH_3OH).

Compound (±)-10



(±)-fawcettimine 85% (±)-**10**

(±)-Fawcettimine was prepared via the same procedure starting from (±)-**SI-3**. To a stirred solution of (±)-fawcettimine (323 mg, 1.23 mol) and *t*-BuOH (584 μL, 6.15 mmol) in a mixed solvent of THF (7.5 mL) and liquid ammonia (30 mL) was added lithium wire (85 mg, 12 mmol) at −78 ºC. After stirring for 1 hour at the same temperature brine was added, and the mixture was warmed to room temperature. The mixture was extracted four times with $CHCl_3$, and the combined organic phase was dried over Na_2SO_4. After filtration, removal of the solvent under reduced pressure gave a crude material, which was purified by column chromatography (NH_2 silica gel, dichloromethane: methanol = 15 : 1) to afford (±)-**10** (277 mg, 1.04 mmol, 85%) as a colorless oil.

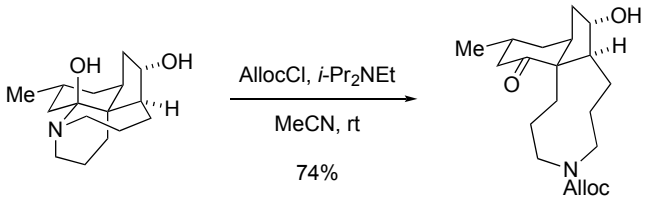
^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.99 (dd, *J* = 6.3, 2.5 Hz, 1H), 3.46 (ddd, *J* = 14.6, 11.6, 3.7 Hz, 1H), 3.18 (ddd, *J* = 14.7, 14.0, 4.1 Hz, 1 H), 2.90 (dd, *J* = 14.7, 5.0 Hz, 1 H), 2.74 (ddd, *J* = 14.6, 3.8, 3.8 Hz, 1 H), 2.34 (ddd, *J* = 13.5, 12.6, 6.5 Hz, 1 H), 2.20-1.97 (m, 6H), 1.95-1.61 (m, 4H), 1.56 (d, *J* = 14.2 Hz, 1H), 1.48-1.39 (m, 2H), 1.35 (dd, *J* = 12.6, 6.7 Hz, 1H), 1.26 (m, 1H), 1.14 (m, 1H), 0.91 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 81.2 (CH), 61.5 (CH), 52.9 (CH_2), 50.0 (CH_2), 49.6 (C), 49.6 (C), 47.4 (CH), 45.2 (CH_2), 39.9 (CH_2), 37.3 (CH_2), 32.6 (CH_2), 32.4 (CH_2), 30.2 (CH_2), 24.8 (CH), 23.4 (CH_2), 22.2 (CH_3).

IR (cm^{-1}): 3317, 2947, 2914, 2865, 2359, 1456, 1255, 1118, 1019, 917.

HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{16}H_{28}NO_2^+$ 266.2115; Found 266.2117.

Compound (±)-11



(±)-**10** (±)-**11**

To a stirred solution of (±)-**10** (254 mg, 0.957 mol) in MeCN (19 mL) were added *N*,*N*-diisopropylethylamine (503 μL, 2.88 mmol) and allyl chloroformate (151 μL, 1.44 mmol) at room temperature. After stirring for 10 minutes at the same temperature, 1 M hydrochloric acid was added. The resulting mixture was stirred for a few minutes, neutralized with sodium bicarbonate and extracted four times with dichloromethane. The combined organic phase was dried over Na_2SO_4 and filtered. Removal of the solvent under reduced pressure

gave a crude material, which was purified by column chromatography (*n*-hexane: EtOAc = 1:1) to afford (±)-**11** (246 mg, 0.704 mmol, 74%) as a colorless oil.

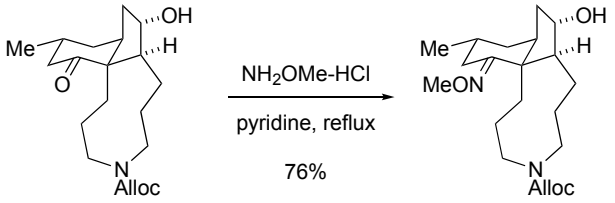
^{1}H NMR ($CDCl_3$, 400 MHz, mixture of rotamers) δ 5.90 (dddd, *J* = 16.8, 11.2, 5.6, 5.6 Hz, 1H), 5.32-5.20 (m, 1H), 5.20-5.10 (m, 1H), 4.64-4.46 (m, 2H), 3.81 (m, 1H), 3.73-3.45 (m, 2H), 3.14-2.91 (m, 2H), 2.44-2.09 (m, 3H), 2.08-1.36 (m, 14H), 0.95 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz, mixture of rotamers) δ 216.4 (C), 216.3 (C), 157.0 (C), 156.2 (C), 133.1 (CH), 117.3 (CH_2), 117.2 (CH_2), 77.8 (CH), 77.4 (CH), 65.9 (CH_2), 65.8 (CH_2), 59.1 (C), 58.8 (C), 54.3 (CH), 50.4 (CH_2), 50.0 (CH_2), 49.6 (CH_2), 48.5 (CH_2), 47.8 (CH_2), 47.7 (CH_2), 43.5 (CH), 43.2 (CH), 36.2 (CH_2), 36.2 (CH_2), 32.2 (CH_2), 32.2 (CH_2), 31.5 (CH_2), 30.7 (CH_2), 30.0 (CH), 29.6 (CH), 27.8 (CH_2), 27.1 (CH_2), 26.7 (CH_2), 22.2 (CH_3), 21.7 (CH_2), 20.7 (CH_2).

IR (cm^{-1}): 3444, 2950, 2927, 2870, 1697, 1475, 1418, 1273, 1216, 1121.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{31}NNaO_4^+$ 372.2145; Found 372.2138.

Compound (±)-12



(±)-**11** (±)-**12**

To a stirred solution of (±)-**11** (42.1 mg, 0.120 mmol) in pyridine (1.2 mL) was added methoxylamine hydrochloride (240 mg, 2.87 mmol) at room temperature. Then the mixture was heated at reflux for 6 hours. After removal of volatile materials under reduced pressure, water was added, and the resulting mixture was extracted four times with EtOAc. The combined organic phase was dried over Na_2SO_4 and filtered. Removal of the solvent under reduced pressure gave a crude material, which was purified by preparative TLC (*n*-hexane: EtOAc = 1:1) to afford (±)-**12** (34.5 mg, 91.1 μmol, 76%) as a colorless oil.

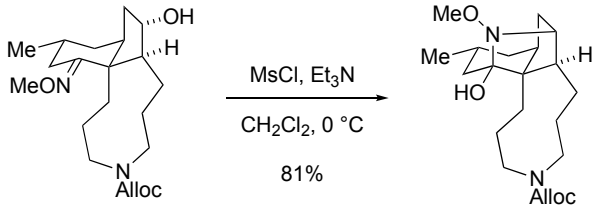
^{1}H NMR ($CDCl_3$, 400 MHz, mixture of rotamers) δ 6.04-5.88 (m, 1H), 5.31 (ddd, *J* = 17.4, 7.3, 1.4 Hz, 1H), 5.20 (d, *J* = 10.5 Hz, 1H), 4.70-4.51 (m, 2H), 4.13 (m, 1H), [3.77 (s), 3.77 (s), *all sum to* 3H], 3.71-3.50 (m, 2H), 3.20-2.96 (m, 3H), 2.38-2.12 (m, 2H), 2.09-1.41 (m, 12H), 1.37-1.20 (m, 2H), 0.93 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz, mixture of rotamers) δ 161.6 (C), 157.2 (C), 156.4 (C), 133.3 (CH), 117.2 (CH_2), 117.2 (CH_2), 78.9 (CH), 78.4 (CH), 65.9 (CH_2), 65.7 (CH_2), 61.2 (CH_3), 61.2 (CH_3), 56.4 (CH), 56.1 (CH), 51.9 (C), 51.7 (C), 50.7 (CH_2), 50.3 (CH_2), 49.8 (CH_2), 49.0 (CH_2), 43.8 (CH), 43.5 (CH), 36.3 (CH_2), 36.1 (CH_2), 32.5 (CH_2), 32.4 (CH_2), 31.7 (CH_2), 31.4 (CH_2), 29.4 (CH_2), 28.5 (CH_2), 27.7 (CH), 27.6 (CH_2), 27.4 (CH), 27.3 (CH_2), 22.3 (CH_3), 21.6 (CH_2), 20.8 (CH_2).

IR (cm^{-1}): 3428, 2947, 1694, 1473, 1445, 1418, 1272, 1215, 1047, 868.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{34}N_2NaO_4^+$ 401.2411; Found 401.2408.

Compound (±)-15



(±)-**12** (±)-**15**

To a stirred solution of (±)-**12** (20.9 mg, 55.2 μmol) in dichloromethane (1.1 mL) were added triethylamine (77 μL, 0.55 mmol) and methanesulfonyl chloride (21 μL, 0.27 mmol) at 0 °C. After stirring for 30 minutes at the same temperature, aqueous sodium bicarbonate was added and the mixture was extracted three times with EtOAc. The combined organic phase was dried over Na_2SO_4 and filtered. Removal of the solvent under reduced pressure gave a crude material, which was purified by preparative TLC (*n*-hexane: EtOAc = 1:1) to afford (±)-**15** (16.9 mg, 44.6 μmol, 81%) as a colorless oil.

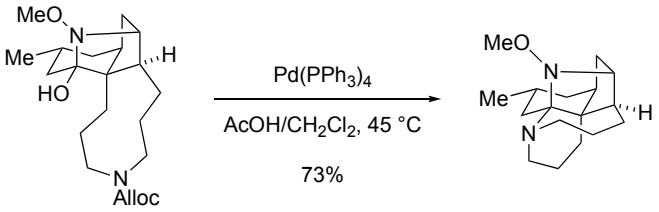
^{1}H NMR ($CDCl_3$, 400 MHz, mixture of rotamers, and an equilibrium between keto-amine and hemiaminal also exists.) δ 6.04-5.85 (m, 1H), 5.38-5.25 (m, 1H), 5.19 (d, J = 10.1 Hz, 1H), 4.75-4.60 (m, 1H), 4.60-4.48 (m, 1H), 3.77-3.42 (m, 5H), 3.30 (s, 1H), 3.22-3.00 (m, 2H), 2.20-1.18 (m, 15H), 1.17-0.91 (m, 2H), 0.86 (d, J = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz, mixture of rotamers, and an equilibrium between keto-amine and hemiaminal also exists.) δ 156.6 (C), 133.3 (CH), 117.3 (CH_2), 117.1 (CH_2), 65.7 (CH_2), 65.6 (CH_2), 63.2 (CH_3), 52.9 (C), 52.9 (C), 51.5 (CH_2), 51.5 (CH_2), 50.3 (CH_2), 49.1 (CH_2), 48.7 (CH_2), 47.9 (CH_2), 47.7 (CH_2), 36.4 (CH), 31.7 (CH_2), 29.7 (CH_2), 27.4 (CH_2), 27.1 (CH_2), 26.2 (CH_2), 25.7 (CH_2), 25.2 (CH_2), 24.8 (CH_2), 23.5 (CH), 23.5 (CH), 22.1 (CH_3), 21.5 (CH_2), 20.7 (CH_2).

IR (cm^{-1}): 2948, 2929, 2867, 1697, 1455, 1337, 1270, 1047, 864, 754.

HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{34}N_2NaO_4^+$ 401.2411; Found 401.2427.

Compound (±)-16



(±)-**15** (±)-**16**

To a stirred solution of (±)-**15** (4.7 mg, 12 μmol) in a mixed solvent of acetic acid (0.2 mL) and dichloromethane (0.2 mL) was added tetrakis(triphenylphosphine)palladium(0) (4.7 mg, 4.1 μmol) at room temperature. Then the mixture was heated at 45 °C for 1.5 hours. The mixture was neutralized with aqueous sodium bicarbonate and extracted three times with EtOAc. The combined organic phase was dried over Na_2SO_4 and filtered. Removal of the solvent under reduced pressure gave a crude material, which was purified by preparative TLC (NH_2 silica gel, *n*-hexane: EtOAc = 1:2) to afford (±)-**16** (2.5 mg, 9.0 μmol, 73%) as a colorless oil.

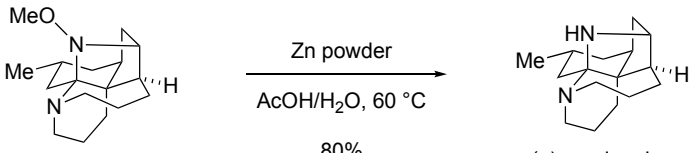
^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.82 (ddd, *J* = 14.6, 7.5, 4.5 Hz, 1H), 3.57 (s, 3H), 3.35 (s, 1H), 3.17 (m, 1H), 2.78 (m, 1H), 2.63 (ddd, *J* = 14.6, 7.3, 7.3 Hz, 1H), 2.18 (dddd, *J* = 14.8, 11.3, 7.3, 4.5 Hz, 1H), 2.09-1.32 (m, 14H), 1.25 (m, 1H), 1.02 (ddd, *J* = 12.8, 12.8, 3.2 Hz, 1H), 0.87 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 78.5 (C), 64.4 (CH), 61.6 (CH_3), 52.4 (CH_2), 50.8 (CH_2), 50.2 (CH), 47.8 (C), 41.9 (CH), 35.1 (CH_2), 32.2 (CH_2), 27.8 (CH_2), 27.5 (CH_2), 26.2 (CH_2), 26.0 (CH_2), 23.9 (CH), 22.5 (CH_3), 20.8 (CH_2).

IR (cm^{-1}): 2925, 2853, 1727, 1455, 1281, 1147, 1124, 1068, 1057, 1006.

HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{29}N_2O^+$ 277.2274; Found 277.2274.

(±)-**Macleanine**



To a stirred solution of (±)-**16** (1.1 mg, 4.0 μmol) in a mixed solvent of acetic acid (0.3 mL) and water (0.15 mL) was added zinc powder (120 mg, 1.8 mmol) at room temperature. Then the mixture was heated at 60 °C for 19 hours. The mixture was filtered through a pad of celite and the filter cake was washed with acetic acid and dichloromethane. The combined filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (NH_2 silica gel, dichloromethane: methanol = 15:1) to afford (±)-macleanine (0.8 mg, 3 μmol, 80%) as a colorless oil.

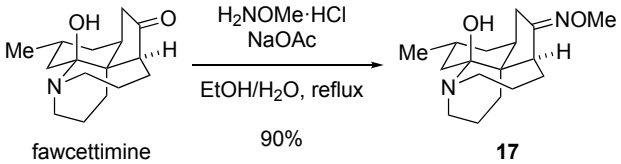
^{1}H NMR ($CDCl_3$, 400 MHz, + 1 equiv of trifluoroacetic acid) δ 10.90 (bs, 1H), 4.14 (m, 1H), 3.46 (ddd, *J* = 14.0, 14.0, 3.2 Hz, 1H), 3.23 (bs, 1H), 3.12 (m, 1H), 2.82 (ddd, *J* = 14.3, 9.7, 5.4 Hz, 1H), 2.54 (dddd, *J* = 20.2, 10.1, 9.7, 5.1 Hz, 1H), 2.27 (dd, *J* = 13.5, 3.0 Hz, 1H), 2.18-2.02 (m, 2H), 2.01-1.60 (m, 10H), 1.47 (d, J = 13.3 Hz, 1H), 1.23 (m, 1H), 1.13 (ddd, *J* = 13.3, 13.3, 3.7 Hz, 1H), 0.99 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz, + 1 equiv of trifluooroacetic acid) δ 84.5 (C), 58.9 (CH), 52.7 (CH_2), 52.6 (CH), 50.1 (CH_2), 47.8 (C), 41.4 (CH), 37.0 (CH_2), 35.6 (CH_2), 31.9 (CH_2), 25.6 (CH_2), 23.1 (CH), 22.9 (CH_2), 22.3 (CH_2), 21.1 (CH_3), 17.9 (CH_2).

IR (cm^{-1}): 2925, 2865, 1729, 1455, 1293, 1284, 1152, 1121, 1076, 1043.

HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{16}H_{27}N_2^+$ 247.2169; Found 247.2169.

Compound 17



To a stirred solution of fawcettimine (30.0 mg, 0.114 mmol) in EtOH (0.84 mL) and H_2O (0.42 mL) were added NaOAc (112 mg, 1.37 mmol) and $H_2NOMe·HCl$ (95.2 mg, 1.14 mmol) at room temperature. After stirring for 12 hours at reflux, to the reaction mixture was added saturated aqueous $NaHCO_3$. The organic materials were extracted five times with a 4:1 mixture of $CHCl_3$ and *i*-PrOH, dried over anhydrous Na_2SO_4,

and concentrated in vacuo after filtration. The residue was purified by preparative TLC (NH_2 silica gel, dichloromethane: methanol = 30:1) to afford ca. 6:1 E/Z mixture of **17** (30.0 mg, 0.103 mmol, 90%) as a white solid. Peaks for the major isomer is described.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 3.43 (ddd, *J* = 14.8, 11.2, 3.6 Hz, 1H), 3.20 (td, *J* = 14.0, 4.0 Hz, 1H), 2.89 (dd, *J* = 14.8, 5.2 Hz, 1H), 2.73 (dt, *J* = 14.8, 4.0 Hz, 1H), 2.53 (dd, *J* = 14.0, 5.2 Hz, 1H), 2.52 (dd, *J* = 13.2, 8.4 Hz, 1H), 2.24-1.78 (m, 9H), 1.70-1.62 (m, 1H), 1.58 (d, *J* = 15.2 Hz, 1H), 1.41 (dd, *J* = 13.2, 4.8 Hz, 1H), 1.36 (dd, *J* = 12.8, 5.2 Hz, 1H), 1.32-1.22 (m, 1H), 1.09 (d, *J* = 20.8, 10.8 Hz, 1H), 0.91 (d, *J* = 6.0 Hz, 3H).

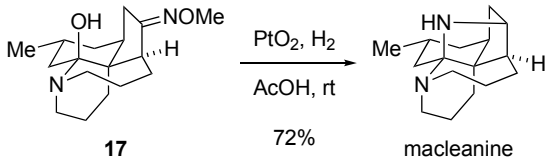
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1 (C), 88.6 (C)*, 61.2 (CH_3), 53.7 (CH), 53.2 (CH_2), 49.9 (CH_2), 48.7 (C), 46.1 (CH), 45.2 (CH_2), 36.4 (CH_2), 32.5 (CH_2), 32.4 (CH_2), 32.1 (CH_2), 29.7 (CH_2), 24.0 (CH), 23.2 (CH_2), 22.0 (CH_3). *This signal was detected in ^{1}H-detected multi-bond heteronuclear multiple quantum coherence spectrum (HMBC).

IR (cm^{-1}) 3314, 2947, 2919, 2864, 2815, 1648, 1457, 1339, 1260, 1217, 1181, 1143, 1091, 1051, 862.

HRMS (ESI) *m/z*: $[M+H]^+$ Calculated for $C_{17}H_{29}N_2O_2^+$ 293.2224; Found 293.2217.

$[\alpha]_D^{24}$ = +59.1º (*c* 1.5, $CHCl_3$).

Macleanine



Oxime ether **17** (10.0 mg, 34 μmmol) and PtO_2 (14.4 mg, 63 μmol) were suspended in AcOH (1.9 mL) under a hydrogen atmosphere. After stirring for 5 hours, the mixture was filtered through a pad of celite and the filter cake was washed with dichloromethane. The combined filtrate was concentrated under reduced pressure, and was added saturated aqueous $NaHCO_3$. The organic materials were extracted five times with a 4:1 mixture of $CHCl_3$ and *i*-PrOH, dried over anhydrous Na_2SO_4, and concentrated in vacuo after filtration. The residue was purified by preparative TLC (NH_2 silica gel, dichloromethane: methanol = 20:1) to afford macleanine (6.1 mg, 25 μmol, 72%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (ddd, *J* = 14.4, 7.2, 5.2 Hz, 1H), 3.15 (tt, *J* = 11.2, 4.0 Hz, 1H), 3.06 (brs, 1H), 2.77 (dd, *J* = 14.8, 4.8 Hz, 1H), 2.55 (dt, *J* = 14.0, 8.0 Hz, 1H), 2.19-2.07 (m, 1H), 2.00-1.60 (m, 13H), 1.36 (d, *J* = 12.0 Hz, 1H), 12.9-1.25 (m, 1H), 1.13 (dd, *J* = 12.0, 3.6 Hz, 1H), 0.94 (d, *J* = 5.6 Hz, 3H).

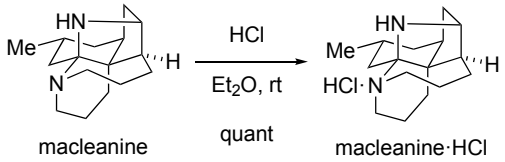
^{13}C NMR (100 MHz, $CDCl_3$) δ 75.5 (C), 58.4 (CH), 53.9 (CH), 51.3 (CH_2), 49.9 (CH_2), 47.9 (C), 41.4 (CH), 38.4 (CH_2), 38.1 (CH_2), 32.5 (CH_2), 26.6 (CH_2), 26.1 (CH), 25.0 (CH_2), 23.5 (CH_2), 21.9 (CH_3), 21.3 (CH_2).

IR (cm^{-1}) 2923, 1735, 1515, 1456, 1379, 1244, 716.

HRMS (ESI) *m/z*: $[M+H]^+$ Calculated for $C_{16}H_{27}N_2^+$: 247.2169; Found: 247.2160.

$[\alpha]_D^{24}$ = +45.8º (*c* 0.20, $CHCl_3$), $[\alpha]_D$ = +12.5º (*c* 0.24, $CHCl_3$, reported[5]).

Macleanine·HCl



macleanine macleanine·HCl

To a stirred solution of macleanine (4.7 mg, 19 μmol) in Et_2O (6.0 mL), HCl in Et_2O (1.0 M, 19 μL, 19 μmol) was added. After stirring for 30 minutes, the reaction mixture was concentrated under reduced pressure to afford macleanine·HCl (5.0 mg, 19 μmol).

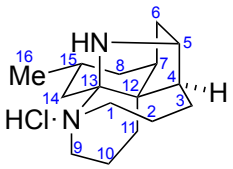
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.9 (brs, 1H), 4.28 (ddd, *J* = 19.2, 12.0, 6.0 Hz, 1H), 3.44 (tt, *J* = 14.0, 3.6 Hz, 1H), 3.23 (brs, 1H), 3.00 (d, *J* = 14.0 Hz), 2.77 (m, 1H), 2.63 (d, *J* = 13.2 Hz, 1H), 2.57 (m, 1H), 2.09 (m, 2H), 1.95 (m, 2H), 1.89 (m, 2H), 1.86 (m, 1H), 1.80 (m, 2H), 1.75 (m, 2H), 1.69 (dd, *J* = 12.4, 6.4 Hz, 1H), 1.47 (d, *J* = 13.6 Hz, 1H), 1.22 (m, 1H), 1.13 (td, *J* =13.6, 3.6 Hz, 1H), 1.00 (d, *J* = 6.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 84.9 (C), 58.8 (CH), 53.2 (CH_2), 52.6 (CH), 50.3 (CH_2), 47.9 (C), 41.4 (CH), 37.0 (CH_2), 35.9 (CH_2), 32.0 (CH_2), 25.7 (CH_2), 23.1 (CH), 22.8 (CH_2), 22.2 (CH_2), 21.2 (CH_3), 17.7 (CH_2).

IR (cm^{-1}) 3258, 2960, 2925, 2856, 1455, 1413, 1261, 1092, 1022, 862, 801, 728, 696.

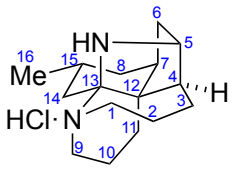
HRMS (ESI) *m/z*: $[M+H]^+$ Calculated for $C_{16}H_{27}N_2^+$: 247.2169; Found: 247.2167.

$[\alpha]_D^{24}$ = +16.4º (*c* 0.25, $CHCl_3$).



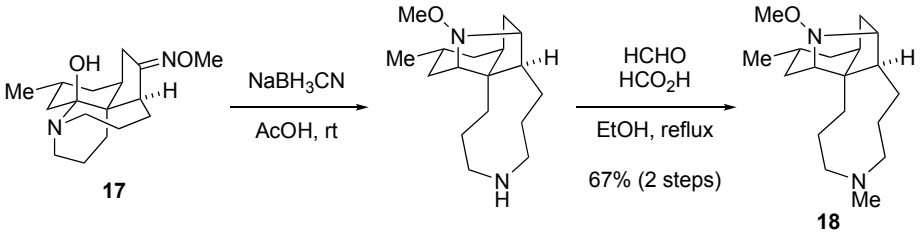
Position	Natural δ_H (ppm) [5]	Synthetic δ_H (ppm)	Δ (δ_{nat}-δ_{syn})
1	4.30	4.28	+0.02
1	2.75	2.77	-0.02
2	2.55	2.57	-0.02
2	1.75*	1.75*	0
3	2.10*	2.09*	+0.01
3	1.90*	1.89*	+0.01
4	1.80*	1.80*	0
5	3.20	3.23	-0.03
6	1.20	1.22	-0.02
6	1.85*	1.86*	-0.01
7	1.90*	1.89*	+0.01
8	1.10	1.13	-0.02
8	1.45	1.47	-0.02
9	3.40	3.44	-0.04
9	2.95	3.00	-0.05
10	2.10*	2.09*	+0.01
10	1.80*	1.80*	0
11	1.95*	1.95*	0
11	1.95*	1.95*	0
14	2.60	2.63	-0.03
14	1.70	1.69	+0.01
15	1.75*	1.75*	0
16	0.99	1.00	-0.01
NH	10.95	10.88	+0.07

*An asterisk denotes overlapping signals.



Position	Natural δ_C (ppm) [5]	Synthetic δ_C (ppm)	Δ (δ_{nat}-δ_{syn})
1	53.2	53.2	0
2	22.2	22.2	0
3	25.8	25.7	+0.1
4	52.7	52.6	+0.1
5	58.9	58.8	+0.1
6	37.1	37.0	+0.1
7	41.5	41.4	+0.1
8	32.1	32.0	+0.1
9	50.3	50.3	0
10	17.8	17.7	+0.1
11	22.3	22.8	-0.5
12	47.9	47.9	0
13	84.9	84.9	0
14	35.9	35.9	0
15	23.2	23.1	+0.1
16	21.2	21.2	0

Compound 18



To a stirred solution of oxime ether **17** (15.0 mg, 0.051 mmol) in AcOH (1.5 mL) and were added $NaBH_3CN$ (32.2 mg, 0.513 mmol) at room temperature. After stirring for 5 hours, to the reaction mixture was added aqueous 2 M NaOH at 0 ºC. The organic materials were extracted three times with EtOAc, dried over anhydrous Na_2SO_4, and concentrated in vacuo after filtration. The residue was dissolved in EtOH (3.0 mL), and to this solution were added HCO_2H (77 μL, 2.04 mmol) and HCHO (37% in H_2O, 77 μL, 1.02 mmol). After stirring for 5 hours, to the reaction mixture was added aqueous 2 M NaOH at 0 ºC. The reaction mixture was added EtOAc and saturated aqueous $NaHCO_3$. The organic materials were extracted three times with EtOAc, dried over anhydrous Na_2SO_4, and concentrated in vacuo after filtration. The residue was purified by preparative TLC (NH_2 silica gel, EtOAc: *n*-hexane = 1:15) to afford **18** (10.0 mg, 0.034 mmol, 67%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.47 (s, 3H), 3.28 (d, *J* = 3.6 Hz, 1H), 3.00 (brs, 1H), 2.70 (td, *J* = 13.2, 4.4 Hz, 1H), 2.37 (dt, *J* = 12.0, 2.8 Hz, 1H), 2.28-2.21 (m, 1H), 2.25 (s, 3H), 1.96 (ddd, *J* = 13.6, 4.8, 2.4 Hz, 1H), 1.84-1.73 (m, 4H), 1.71-1.60 (m, 4H), 1.55-1.46 (m, 3H), 1.34-1.26 (m, 2H), 1.20-1.10 (m, 2H), 1.04-0.94 (m, 2H), 0.86 (d, *J* = 6.0 Hz, 3H).

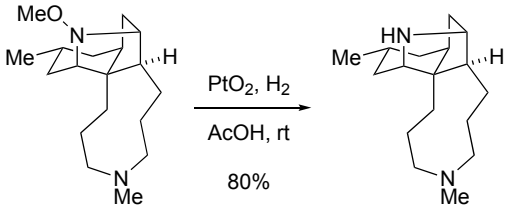
^{13}C NMR (100 MHz, $CDCl_3$) δ 72.2 (CH), 67.4 (CH), 61.2 (CH_3), 56.4 (CH_2), 51.1 (CH), 51.0 (C), 48.4 (CH_2), 44.3 (CH_3), 33.8 (CH), 33.7 (CH_2), 33.2 (CH_2), 32.2 (CH_2), 27.0 (CH_2), 22.2 (CH_2), 22.0 (CH_2), 21.7 (CH), 21.2 (CH_2), 20.0 (CH_2).

IR (cm^{-1}) 2931, 2841, 2781, 1453, 1370, 1267, 1048, 1012, 957.

HRMS (ESI) *m/z*: $[M+H]^+$ Calculated for $C_{18}H_{33}N_2O^+$: 293.2587; Found: 293.2583.

$[\alpha]_D^{24}$ = –351º (*c* 0.3, $CHCl_3$).

Lycoposerramine-S



Tetracyclic amine **18** (6.0 mg, 0.021 mmol) and PtO_2 (12.0 mg, 53 mol) were suspended in AcOH (1.8 mL) under a hydrogen atmosphere. After stirring for 8 hours, the mixture was filtered through a pad of celite and the filter cake was washed with dichloromethane. The combined filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (NH_2 silica gel, dichloromethane: methanol = 20:1) to afford lycoposerramine-S (4.3 mg, 0.016 mmol, 80%) as a colorless oil.

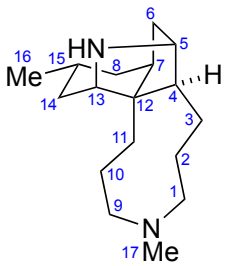
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.99 (d, *J* = 2.4, 1H), 2.96 (d, *J* = 2.8 Hz, 1H), 2.71 (ddd, *J* = 13.6, 13.6, 3.6 Hz, 1H), 2.36 (m, 1H), 2.26 (s, 3H), 2.21 (m, 1H), 2.02 (ddd, *J* = 14.0, 4.8, 2.0, 1H), 1.95 (m, 1H), 1.87 (m, 1H), 1.74 (m, 2H), 1.69 (m, 2H), 1.58 (m, 1H), 1.49 (m, 1H), 1.48 (m, 1H), 1.43 (m, 2H), 1.34 (m, 3H), 1.22 (m, 1H), 1.07 (ddd, *J* = 13.2, 13.2, 3.6 Hz, 1H), 1.01 (ddd, *J* = 13.0, 13.0, 2.8 Hz, 1H), 0.90 (d, *J* = 6.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 60.1 (CH), 58.8 (CH), 56.7 (CH_2), 50.4 (CH), 49.3 (C), 49.0 (CH_2), 44.4 (CH_3), 35.6 (CH_2), 34.8 (CH), 33.6 (CH_2), 32.9 (CH_2), 26.5 (CH_2), 22.0 (CH_3), 21.9 (CH_2), 21.3 (CH_2), 20.6 (CH), 19.4 (CH_2).

IR (cm^{-1}) 2924, 2848, 2781, 1560, 1452, 1403, 1370.

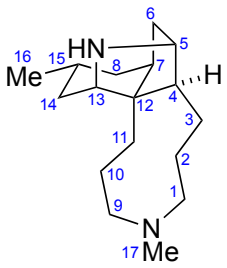
HRMS (ESI) *m/z*: $[M+H]^+$ Calculated for $C_{18}H_{33}N_2O^+$: 263.2482; Found: 263.2486.

$[\alpha]_D^{24}$ = –58.1º (*c* 0.24, methanol), $[\alpha]_D$ = –37.8º (*c* 0.2, methanol, reported[6]).



Position	Natural δ_H (ppm) [6]	Synthetic δ_H (ppm)	Δ (δ_{nat}-δ_{syn})
1	2.68	2.71	-0.05
1	2.01	2.02	-0.01
2	1.69*	1.69*	0
2	1.20*	1.22*	-0.02
3	1.75*	1.74*	+0.01
3	1.34*	1.34*	0
4	1.57*	1.58*	-0.01
5	3.00	2.99	-0.01
6	1.75*	1.74*	+0.01
6	1.34*	1.34*	0
7	1.94	1.95	-0.01
8	1.43*	1.43*	0
8	1.05*	1.07*	-0.02
9	2.36	2.36	0
9	2.21	2.21	0
10	1.48*	1.48*	0
10	1.34*	1.34*	0
11	1.49*	1.49*	0
11	1.43*	1.43*	0
13	2.97	2.96	+0.01
14	1.69*	1.69*	0
14	1.00	1.01	-0.01
15	1.87*	1.87*	0
16	0.88	0.90	+0.02
17	2.24	2.26	-0.02

*An asterisk denotes overlapping signals.



Position	Natural δ_C (ppm) [6]	Synthetic δ_C (ppm)	Δ (δ_{nat}-δ_{syn})
1	49.1	49.0	+0.1
2	26.6	26.5	+0.1
3	19.6	19.4	+0.2
4	50.5	50.4	+0.1
5	60.2	60.1	+0.1
6	35.6	35.6	0
7	35.0	34.8	+0.2
8	33.0	32.9	+0.1
9	56.8	56.7	+0.1
10	22.0	21.9	+0.1
11	21.4	21.3	+0.1
12	49.5	49.3	+0.2
13	59.0	58.8	+0.2
14	33.7	33.6	+0.1
15	20.7	20.6	+0.1
16	22.1	22.0	+0.1
17	44.5	44.4	+0.1

References for Supporting Information

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2. Zeng, X.; Jia, Z.; Qiu, F. G. *Tetrahedron Lett.,* **2020**, *61*, 152329-152332.
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5. Ayer, W. A.; Ma, Y.-T.; Liu, J.-S.; Huang, M.-F.; Schultz, L. W.; Glardy, J. *Can. J. Chem.*, **1994**, *72*, 128-130.
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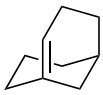
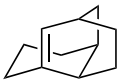
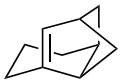
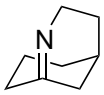
Procedure for calculations. The geometries of the stationary points were optimized using B3PW91 and the 6-311+G(d,p) basis set with Spartan ’16. The vibrational frequencies were calculated at the same level of theory.

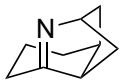

19a


19b

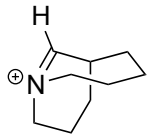

19c



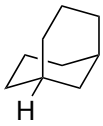
20a



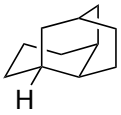
20c



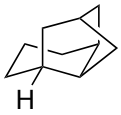
20d



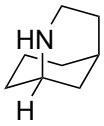
19A



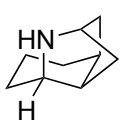
19B



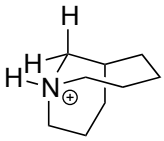
19C



20A



20C



20D

compound	*H*° / au (298.15 K)	compound	*H*° / au (298.15 K)
19a	-351.099395	**19A**	-352.330901
19b	-428.478629	**19B**	-429.705428
19c	-389.193699	**19C**	-390.420068
20a	-367.155663	**20A**	-368.369726
20c	-405.254608	**20C**	-406.461786
20d	-406.786091	**20D**	-408.010383
hydrogen	-1.16521658		

Cartesian coordinates

19a

C	0.222848	0.361017	-1.230254
C	0.227769	1.451362	-0.198981
H	-0.577623	2.174317	-0.359211
H	1.171288	2.003495	-0.168031
C	-0.001239	0.648816	1.098715
C	2.132855	-0.388095	0.041344
H	2.824110	-1.230919	0.122383
H	2.751118	0.517615	0.016300
C	1.240375	-0.510335	-1.159804
H	1.231654	-1.432544	-1.737279
C	-1.156963	-0.049173	-1.639952
H	-1.163413	-0.762949	-2.469383
H	-1.779817	0.807231	-1.923040
C	-1.700510	-0.740416	-0.354297
H	-1.227638	-1.727979	-0.308870
H	-2.781009	-0.911473	-0.433169
C	-1.410203	0.019084	0.959816
H	-2.132530	0.840875	1.053333
H	-1.608047	-0.651956	1.804146
H	-0.030787	1.323583	1.962749
C	1.189283	-0.336175	1.284103
H	0.811611	-1.348152	1.466911
H	1.766868	-0.057230	2.172469

19b

C	-0.826682	0.651720	0.607034
H	-1.373430	1.588892	0.773445
C	-0.462478	0.522579	-0.893326
H	-1.378282	0.484604	-1.493242
C	0.245821	-0.805664	-0.896457
C	-0.671111	-1.986252	-0.896840
H	-0.142910	-2.937151	-1.017516
H	-1.432933	-1.918478	-1.682295
C	-1.318966	-1.922637	0.516102
H	-0.561586	-2.275619	1.225217
H	-2.165038	-2.616712	0.587164
C	-1.788161	-0.513703	0.937073
H	-2.014030	-0.523047	2.010113
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H	0.538303	-0.079227	2.166892
H	0.604908	1.660980	1.925476
C	1.723946	0.512211	0.433080
H	2.657313	0.473104	1.001076
C	1.745503	1.686214	-0.556371
H	2.611809	1.594442	-1.217405
C	1.433811	-0.785306	-0.273590

H	1.985412	-1.691759	-0.034466
H	1.862321	2.625788	-0.004897
C	0.431398	1.674263	-1.364599
H	-0.111401	2.619225	-1.251125
H	0.634430	1.554605	-2.432713

19c

C	-0.532944	0.895650	0.593402
H	-0.938454	1.881773	0.848880
C	-0.106051	0.882024	-0.906789
H	-0.871745	1.248511	-1.594372
C	0.304084	-0.565133	-1.076317
C	-0.779654	-1.588261	-1.115077
H	-0.403152	-2.588997	-1.347435
H	-1.549071	-1.339180	-1.855664
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H	-2.296257	-2.148512	0.365396
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H	-1.872868	-0.195795	1.914285
H	-2.552515	0.237545	0.360494
C	0.844270	0.723139	1.309172
H	0.888040	-0.163491	1.948103
H	1.064010	1.591759	1.938990
C	1.867379	0.622441	0.118536
H	2.908037	0.788884	0.400473
C	1.240096	1.604052	-0.880189
H	1.744075	1.599297	-1.850364
H	1.174555	2.628716	-0.499711
C	1.521491	-0.701164	-0.524289
H	2.007505	-1.642186	-0.284249

20a

C	-0.423630	0.985480	0.532811
H	-0.915403	1.899067	0.884349
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H	0.223186	1.842804	-1.387410
H	-1.331593	0.992162	-1.468568
C	0.372692	-0.322238	-1.208215
C	-0.545348	-1.503343	-1.230641
H	-0.029589	-2.422126	-1.516370
H	-1.412969	-1.352755	-1.880402
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H	-1.788220	-2.274163	0.410409
C	-1.330345	-0.214486	0.905673
H	-1.365989	-0.332107	1.994824
H	-2.349703	0.051016	0.596110
C	1.031871	0.952247	1.076507
H	1.136858	0.166092	1.831291

H	1.275213	1.898830	1.569929
N	1.570647	-0.483201	-0.788518
C	2.058075	0.675490	-0.056315
H	3.043826	0.452953	0.358314
H	2.169746	1.569924	-0.685934

20c

C	-0.458026	0.830935	0.614766
H	-0.857979	1.807081	0.909867
C	-0.067807	0.866933	-0.899932
H	-0.853431	1.219941	-1.568953
C	0.373300	-0.570739	-1.052910
C	-0.665898	-1.633224	-1.132104
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C	1.898991	0.528290	0.049839
H	2.960507	0.604419	0.282873
C	1.288955	1.563525	-0.899873
H	1.768763	1.569711	-1.882428
H	1.266047	2.577198	-0.489639

20d

C	-0.646496	0.852002	-1.259084
C	0.662141	-0.034216	-1.580181
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C	-1.916657	0.018008	-1.137084
H	-2.092071	-0.520139	-2.071996
C	1.912280	-0.059685	-0.629582
H	2.426584	0.908117	-0.651733
H	2.604353	-0.750611	-1.118932
C	1.779819	-0.542122	0.836893
H	1.291795	-1.523243	0.862438
H	2.786419	-0.696741	1.237672
C	1.039180	0.418550	1.782445
H	1.568085	1.369333	1.891128
H	0.867959	0.001480	2.774350
C	-1.819920	-0.963734	0.030324
H	-2.785411	-1.443340	0.206924
H	-1.116750	-1.768970	-0.203736
C	-1.381860	-0.272733	1.316806

H	-2.195606	0.317310	1.748571
H	-1.066354	-0.992908	2.071570
N	-0.258991	0.675355	1.113852
H	-2.768390	0.692570	-1.000954
H	0.300403	-1.060534	-1.681986
H	-0.740575	1.644016	-2.001340
C	-0.132493	1.347840	0.017225
H	0.659025	2.093147	0.003594

19A

C	1.247404	-0.000000	0.670353
H	2.140802	-0.000002	1.307677
C	-0.000000	-0.000000	1.559586
H	0.000001	0.881450	2.213192
H	-0.000001	-0.881450	2.213191
C	-1.247404	0.000000	0.670353
C	-1.279657	-1.299119	-0.153271
H	-2.146500	-1.299503	-0.824913
H	-1.439282	-2.127390	0.550293
C	-0.000002	-1.574056	-0.955440
H	-0.000005	-0.976676	-1.870626
H	-0.000002	-2.618184	-1.289148
C	1.279656	-1.299118	-0.153275
H	2.146497	-1.299496	-0.824921
H	1.439286	-2.127391	0.550285
C	1.279657	1.299120	-0.153270
H	2.146500	1.299503	-0.824912
H	1.439282	2.127391	0.550294
C	0.000002	1.574055	-0.955440
H	0.000005	0.976674	-1.870625
H	0.000002	2.618183	-1.289150
C	-1.279656	1.299118	-0.153275
H	-2.140802	0.000002	1.307677
H	-1.439285	2.127392	0.550286
H	-2.146497	1.299497	-0.824920

19B

C	0.385192	1.246948	-0.238020
H	0.953348	2.134928	0.064955
C	1.165275	0.000001	0.214464
H	2.152427	0.000002	-0.265316
C	0.385193	-1.246947	-0.238021
C	0.261583	-1.266501	-1.767533
H	-0.299867	-2.153268	-2.086150
H	1.267717	-1.364697	-2.197700
C	-0.397892	0.000002	-2.317153
H	-1.465319	0.000006	-2.064800
H	-0.354542	0.000003	-3.411834
C	0.261589	1.266502	-1.767532
H	-0.299853	2.153271	-2.086154

H	1.267726	1.364689	-2.197694
C	-0.991044	1.254779	0.486479
H	-1.808823	1.302373	-0.241693
H	-1.087265	2.147904	1.113596
C	-1.144870	-0.000001	1.356781
H	-2.130478	-0.000002	1.835527
C	-0.047580	0.000001	2.428305
H	-0.161543	-0.877814	3.073457
C	-0.991040	-1.254782	0.486482
H	0.953354	-2.134925	0.064951
H	-1.087257	-2.147907	1.113600
H	-1.808820	-1.302380	-0.241690
H	-0.161543	0.877819	3.073453
C	1.338582	0.000000	1.736694
H	1.922875	0.877152	2.036273
H	1.922874	-0.877153	2.036272

19C

C	-0.441163	-1.256068	-0.019931
H	-1.036144	-2.138818	0.241148
C	-1.180979	0.000001	0.493373
H	-2.249044	0.000002	0.257489
C	-0.441162	1.256068	-0.019930
C	-0.225007	1.260317	-1.534389
H	0.339562	2.153724	-1.826976
H	-1.203403	1.339154	-2.027946
C	0.482345	0.000001	-2.029035
H	1.522765	0.000002	-1.682607
H	0.531054	0.000000	-3.123315
C	-0.225003	-1.260316	-1.534390
H	0.339569	-2.153722	-1.826973
H	-1.203399	-1.339159	-2.027948
C	0.861552	-1.249755	0.843204
H	1.771190	-1.210219	0.235051
H	0.925621	-2.154575	1.455696
C	0.704133	-0.000000	1.727391
H	1.343932	-0.000000	2.613134
C	-0.813093	0.000001	1.982378
H	-1.162776	0.890854	2.514738
H	-1.162778	-0.890852	2.514738
C	0.861554	1.249754	0.843204
H	-1.036143	2.138818	0.241152
H	0.925626	2.154574	1.455695
H	1.771192	1.210215	0.235050

20A

C	0.028316	1.219295	0.640923
H	0.099660	2.134310	1.241493
C	-0.111500	0.011987	1.571787
H	-0.996496	0.114692	2.207692

H	0.764446	-0.073962	2.224856
C	-0.245656	-1.242966	0.710536
C	1.061541	-1.454854	-0.082360
H	0.966108	-2.333801	-0.731308
H	1.846726	-1.698408	0.646656
C	1.498152	-0.236943	-0.909798
H	0.932085	-0.205712	-1.843894
H	2.545964	-0.356667	-1.207987
C	1.336047	1.093628	-0.159045
H	1.430530	1.928577	-0.863376
H	2.164837	1.201052	0.553236
C	-1.253683	1.324296	-0.201718
H	-1.175623	2.143438	-0.925508
H	-2.075386	1.577123	0.478943
C	-1.615765	0.033792	-0.940552
H	-1.016141	-0.043711	-1.859907
H	-2.661316	0.090814	-1.263624
N	-1.483033	-1.129992	-0.066524
H	-1.658652	-1.982694	-0.583828
H	-0.381164	-2.113292	1.363307

20C

C	-0.604289	0.884921	0.691777
H	-1.003287	1.866657	0.970925
C	-0.174128	0.933415	-0.795405
H	-0.916222	1.384204	-1.458581
C	0.238061	-0.492162	-1.223646
C	-0.828338	-1.551086	-0.951263
H	-0.446231	-2.534310	-1.246906
H	-1.695081	-1.342389	-1.594305
C	-1.256971	-1.565965	0.512687
H	-0.418632	-1.927931	1.116889
H	-2.079368	-2.274038	0.660415
C	-1.673692	-0.171542	0.979207
H	-1.902466	-0.181369	2.051588
H	-2.602339	0.119080	0.468837
C	0.760183	0.656044	1.417720
H	0.774460	-0.257604	2.016233
H	1.006757	1.495657	2.074831
C	1.751177	0.560791	0.250666
H	2.801289	0.642700	0.537289
C	1.193675	1.620770	-0.715226
H	1.723853	1.653639	-1.672611
H	1.149323	2.628733	-0.290432
N	1.486672	-0.720417	-0.437805
H	2.252860	-0.938161	-1.063636
H	0.462735	-0.489637	-2.299249

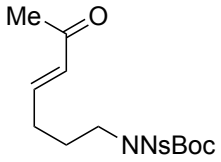
20D

C	-0.459338	1.291309	0.664723

C	0.787688	1.716196	-0.159067
H	1.120877	2.692225	0.203729
C	-1.720594	1.159388	-0.200886
H	-1.845588	2.057320	-0.810715
C	1.999030	0.783863	-0.173420
H	2.428946	0.679814	0.830739
H	2.777859	1.270649	-0.767381
C	1.744204	-0.599609	-0.776248
H	1.199141	-0.514561	-1.721024
H	2.704033	-1.058982	-1.037286
C	1.084173	-1.608581	0.145187
H	1.710402	-1.768890	1.027935
H	0.956266	-2.572601	-0.353753
C	-1.645676	-0.075861	-1.092804
H	-2.577567	-0.207505	-1.650095
H	-0.859377	0.033550	-1.844066
C	-1.438768	-1.339039	-0.274737
H	-2.320708	-1.530203	0.344000
H	-1.261864	-2.219692	-0.895001
N	-0.279776	-1.252221	0.701534
H	-2.606746	1.095847	0.442649
H	0.479047	1.886490	-1.196498
H	-0.649736	2.074538	1.406057
C	-0.304823	0.031030	1.509181
H	0.601086	0.032717	2.117635
H	-1.163092	-0.062551	2.180660
H	-0.459098	-1.994637	1.378954

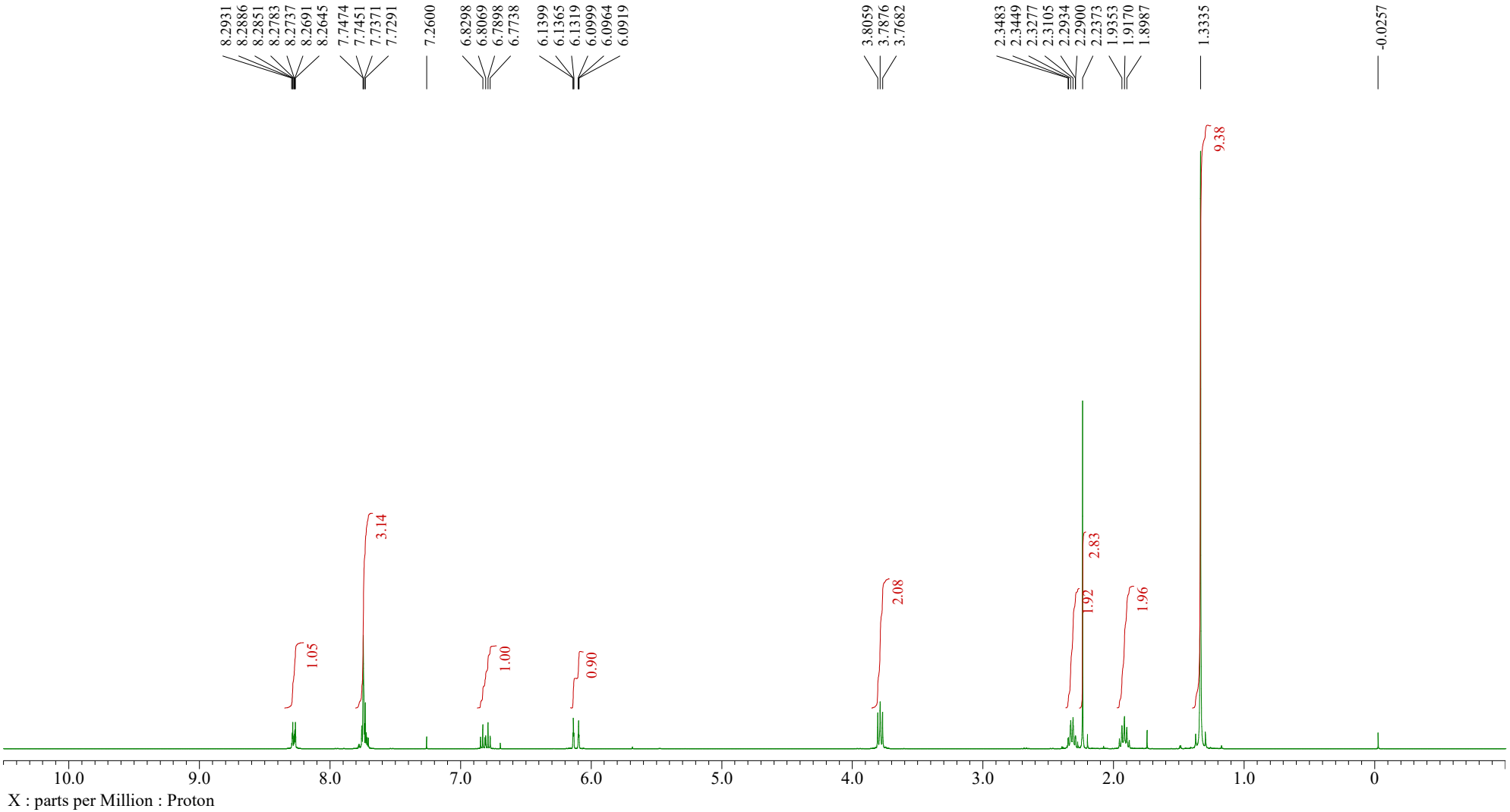
hydrogen

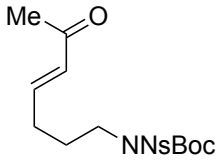
H	0.000000	0.000000	0.372722
H	0.000000	0.000000	-0.372722



SI-2

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





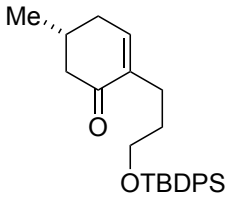
SI-2

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

198.5182
150.1684
147.4605
146.5834
134.2265
133.3303
133.1873
131.7189
124.3297
85.1807
77.3146
77.0000
76.6854
47.3379
29.4034
28.4213
27.7730
26.8672

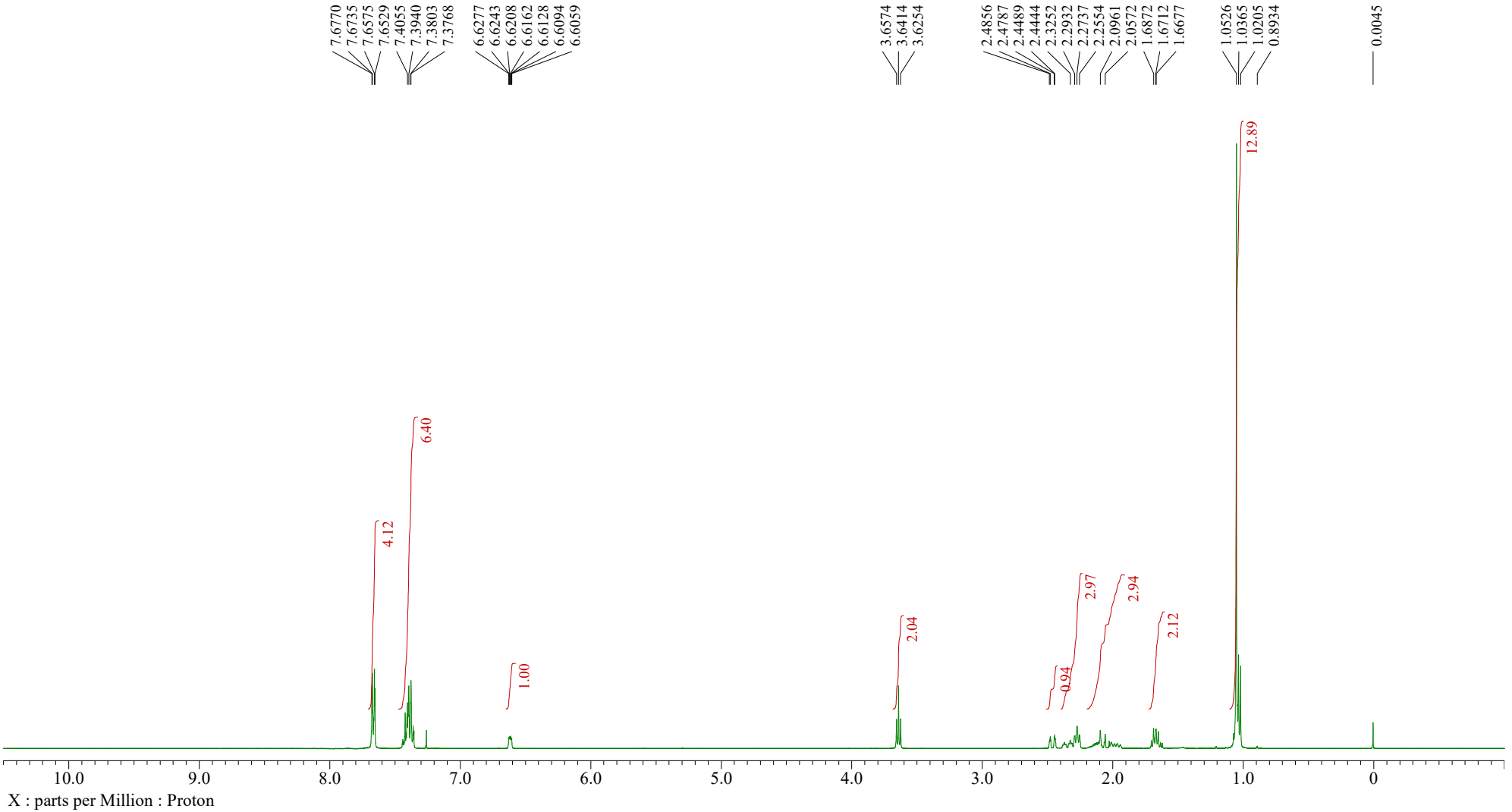
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

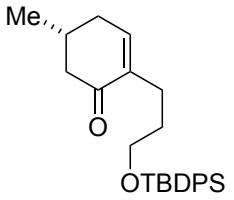
X : parts per Million : Carbon13



1

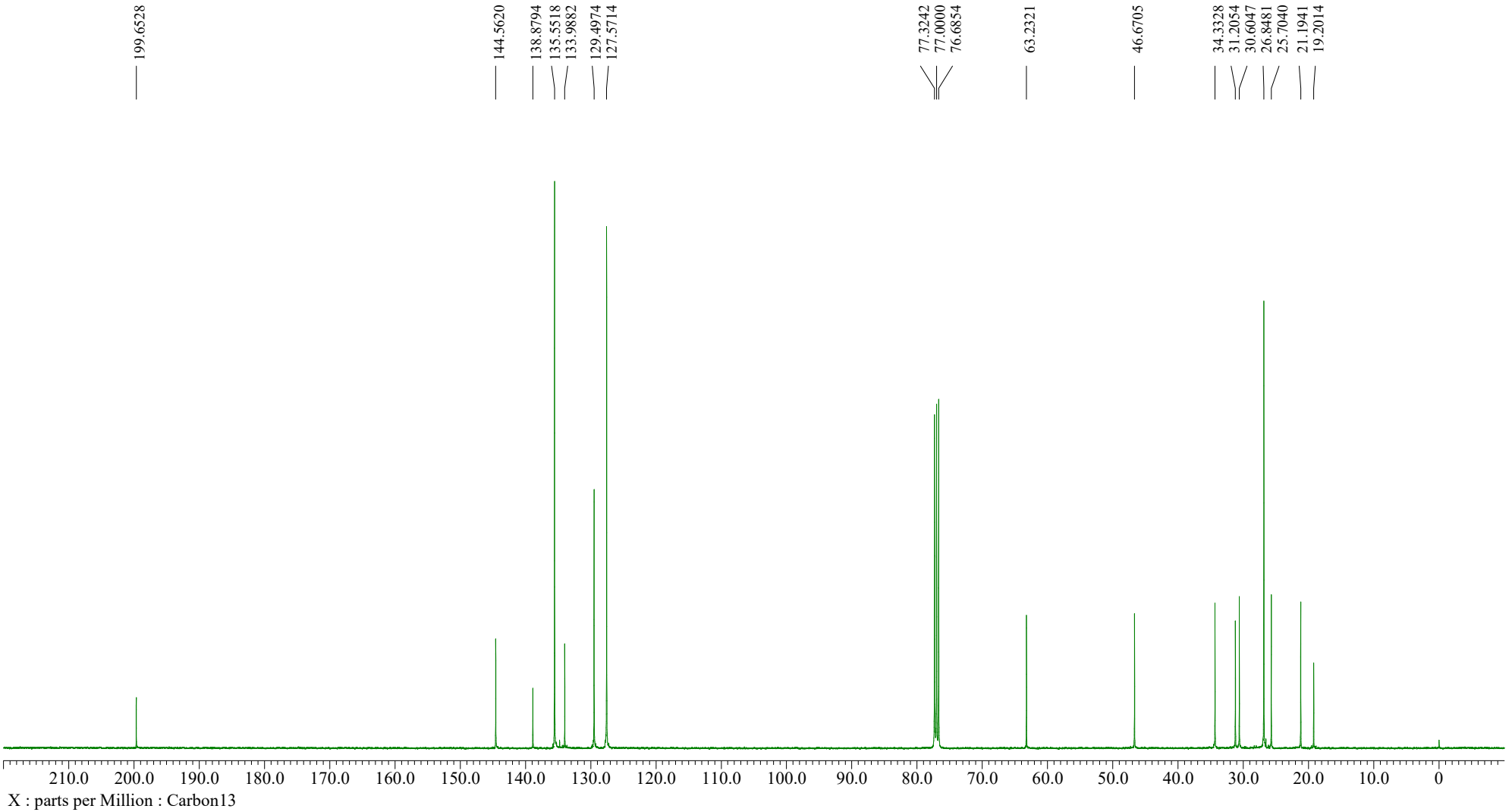
^{1}H NMR (400 MHz, $CDCl_3$)

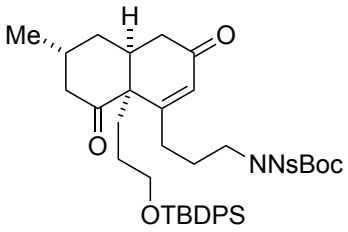




1

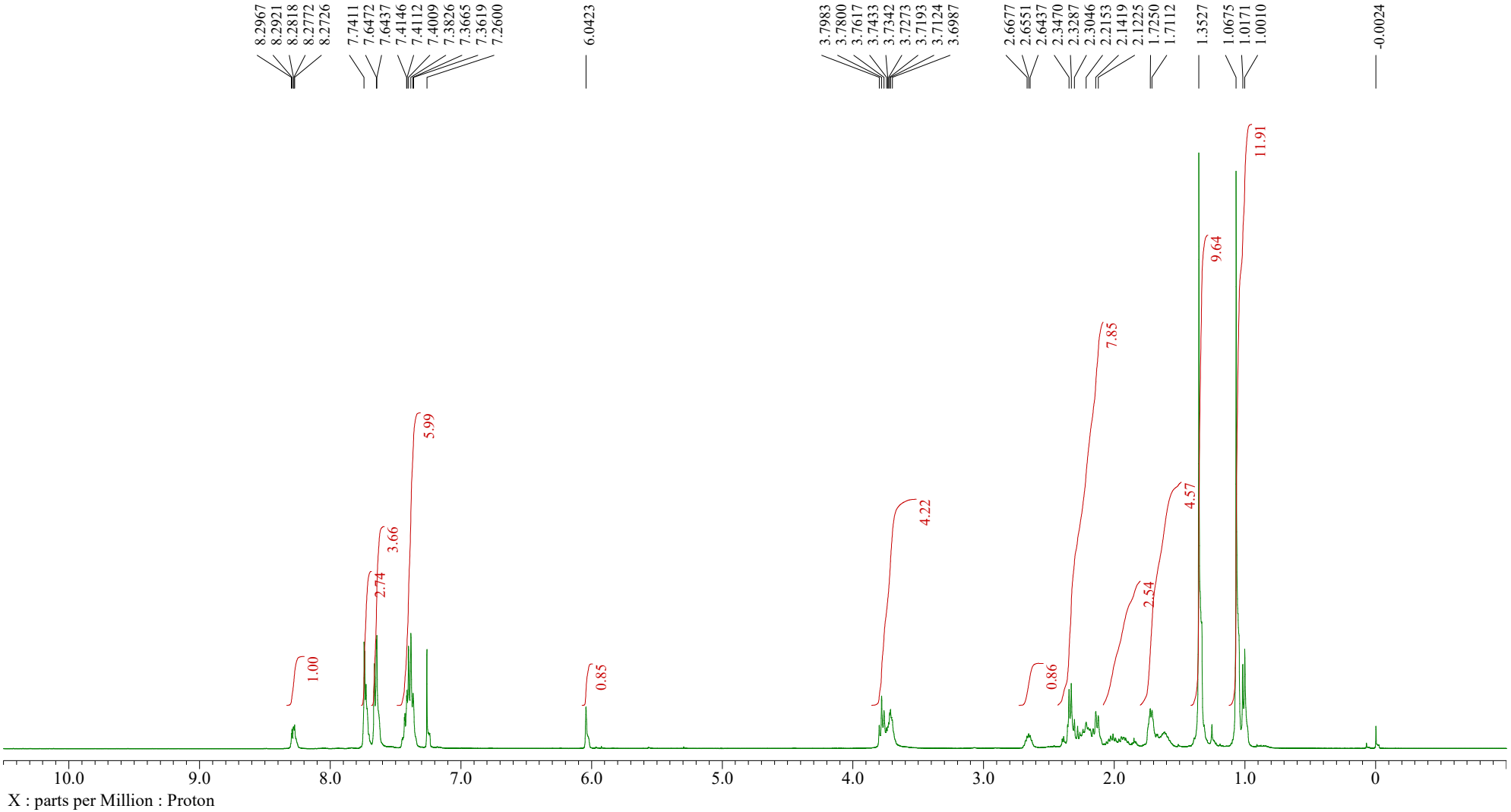
^{13}C NMR (100 MHz, $CDCl_3$)

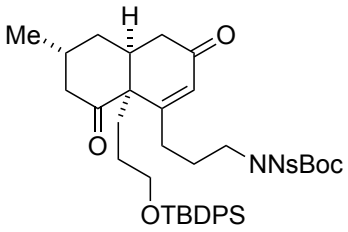




5

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





5

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

211.2183
197.8127
163.7265
150.2065
147.5559
135.5423
134.1026
133.6545
133.6354
133.4352
133.2826
131.6808
129.6881
127.6763
126.6275
124.3106
85.1521
77.3146
77.0000
76.6758
63.5848
58.1215
47.4523
46.7277
39.9868
36.5543
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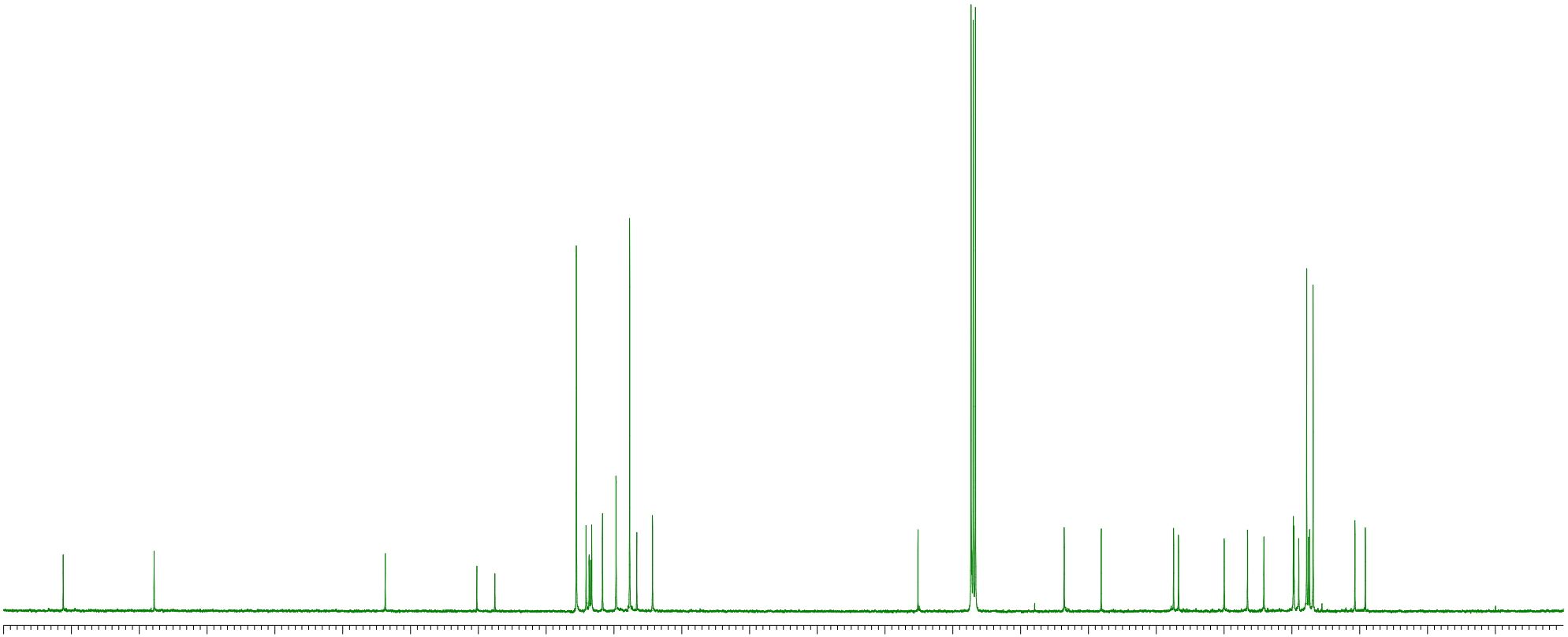
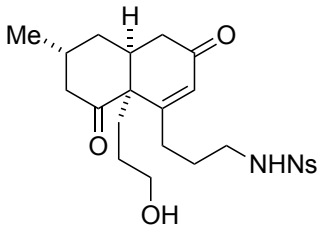
27.5823
27.3820
26.8672
20.7078
19.1632

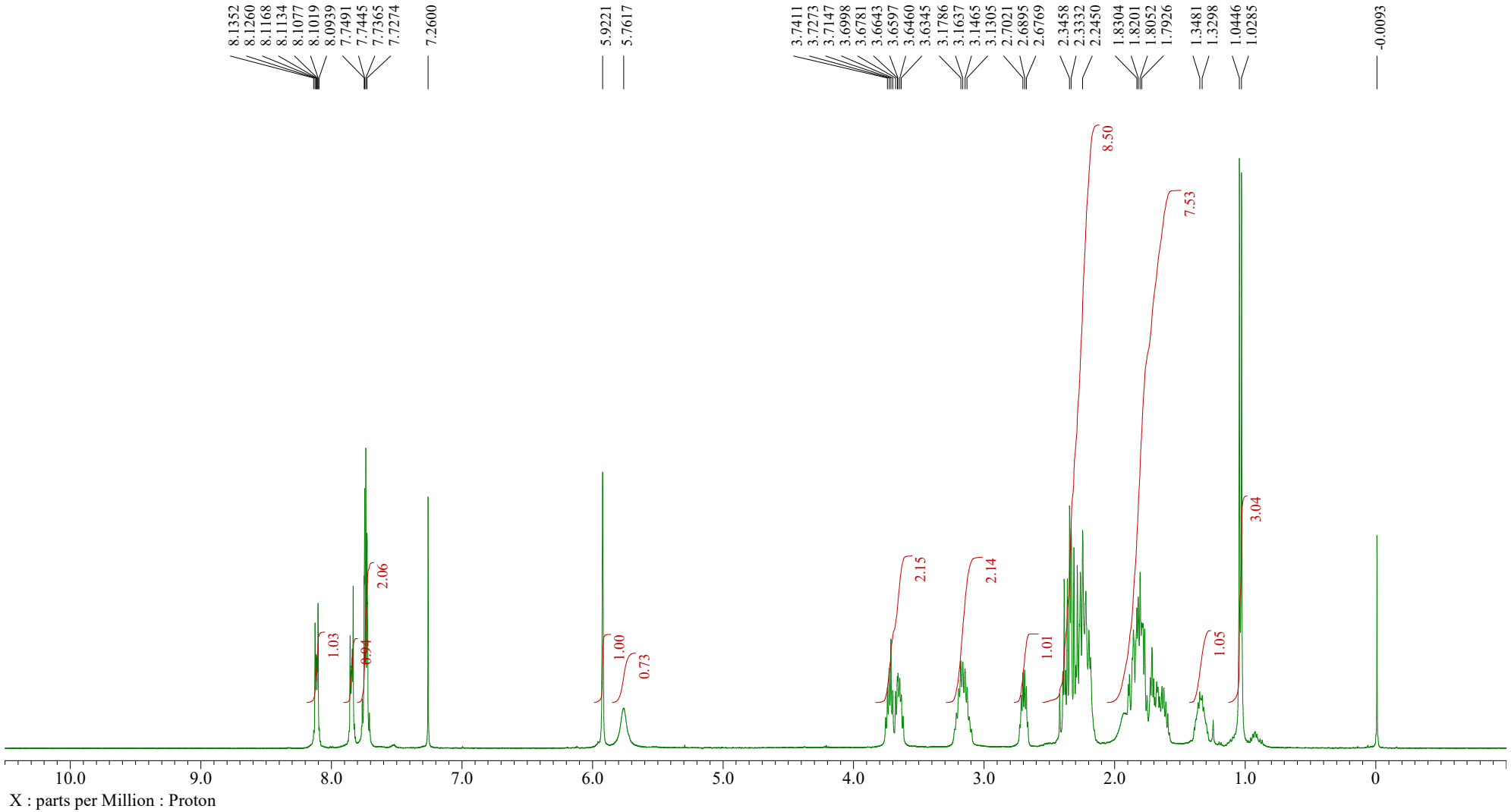


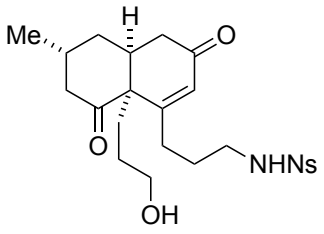
X : parts per Million : Carbon13



6

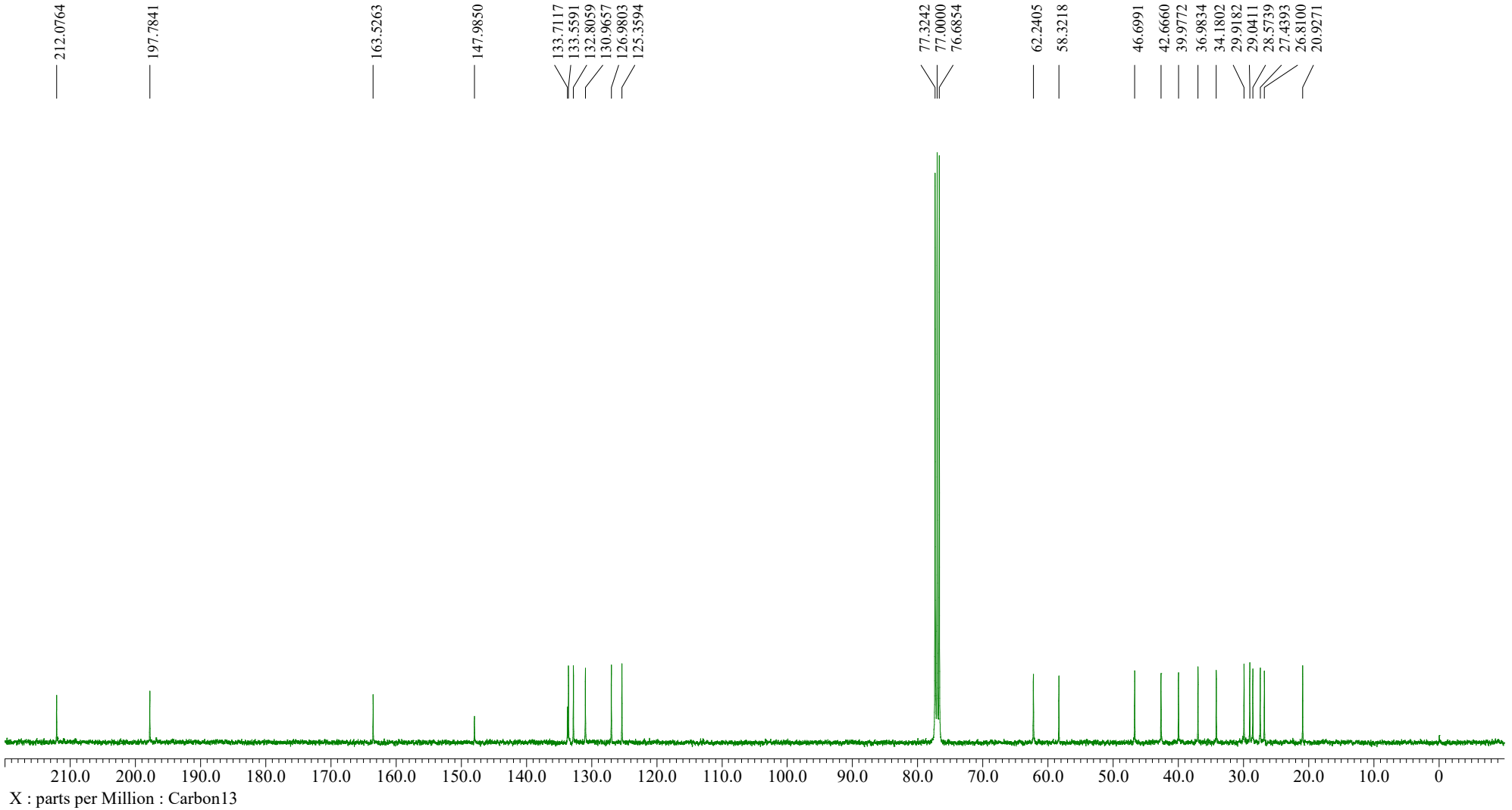
^{1}H NMR (400 MHz, $CDCl_3$)

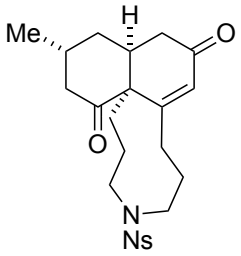




6

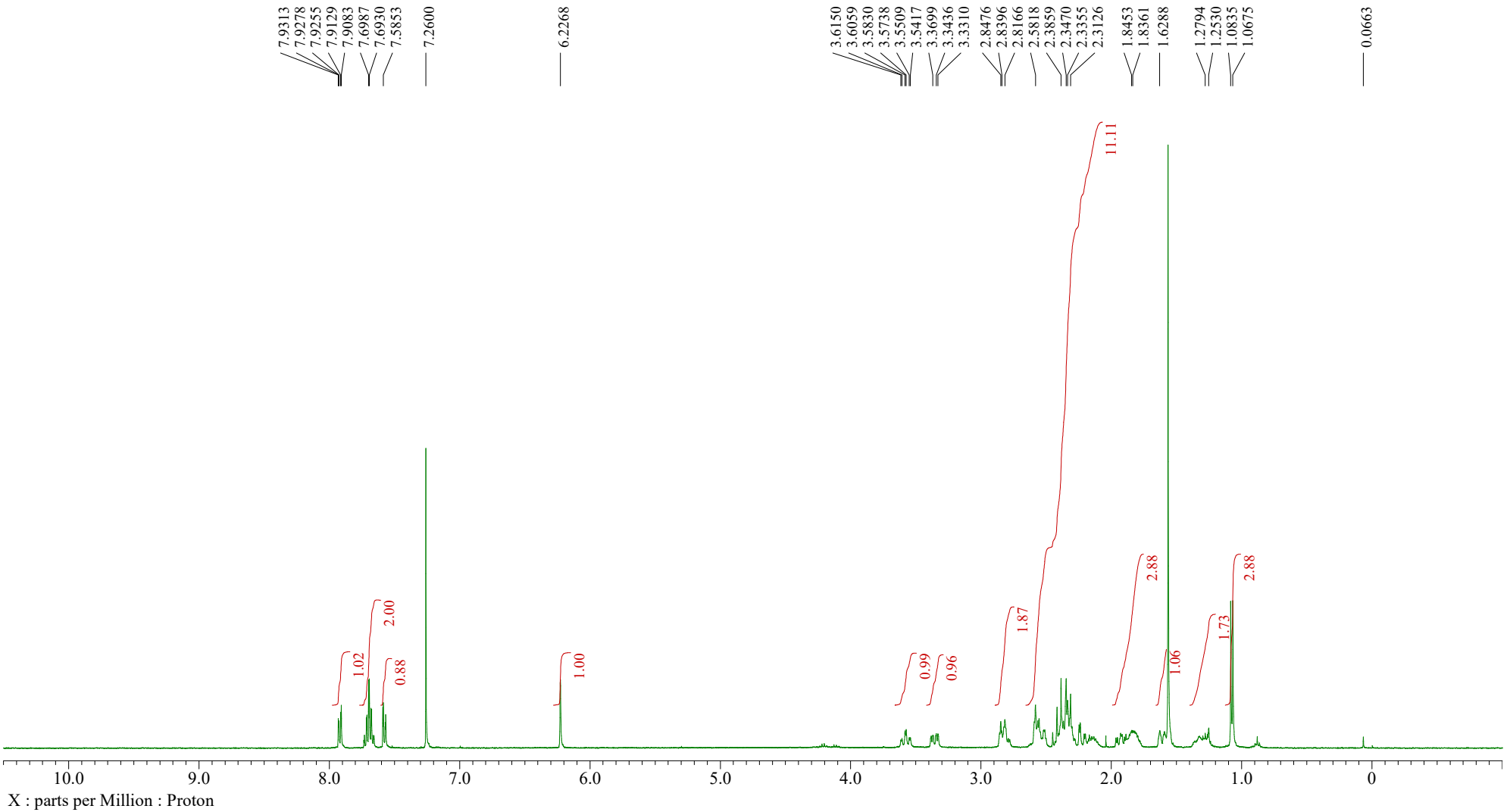
^{13}C NMR (100 MHz, $CDCl_3$)

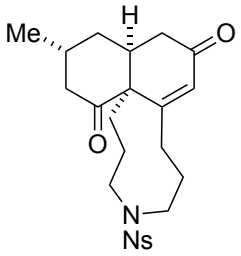




7

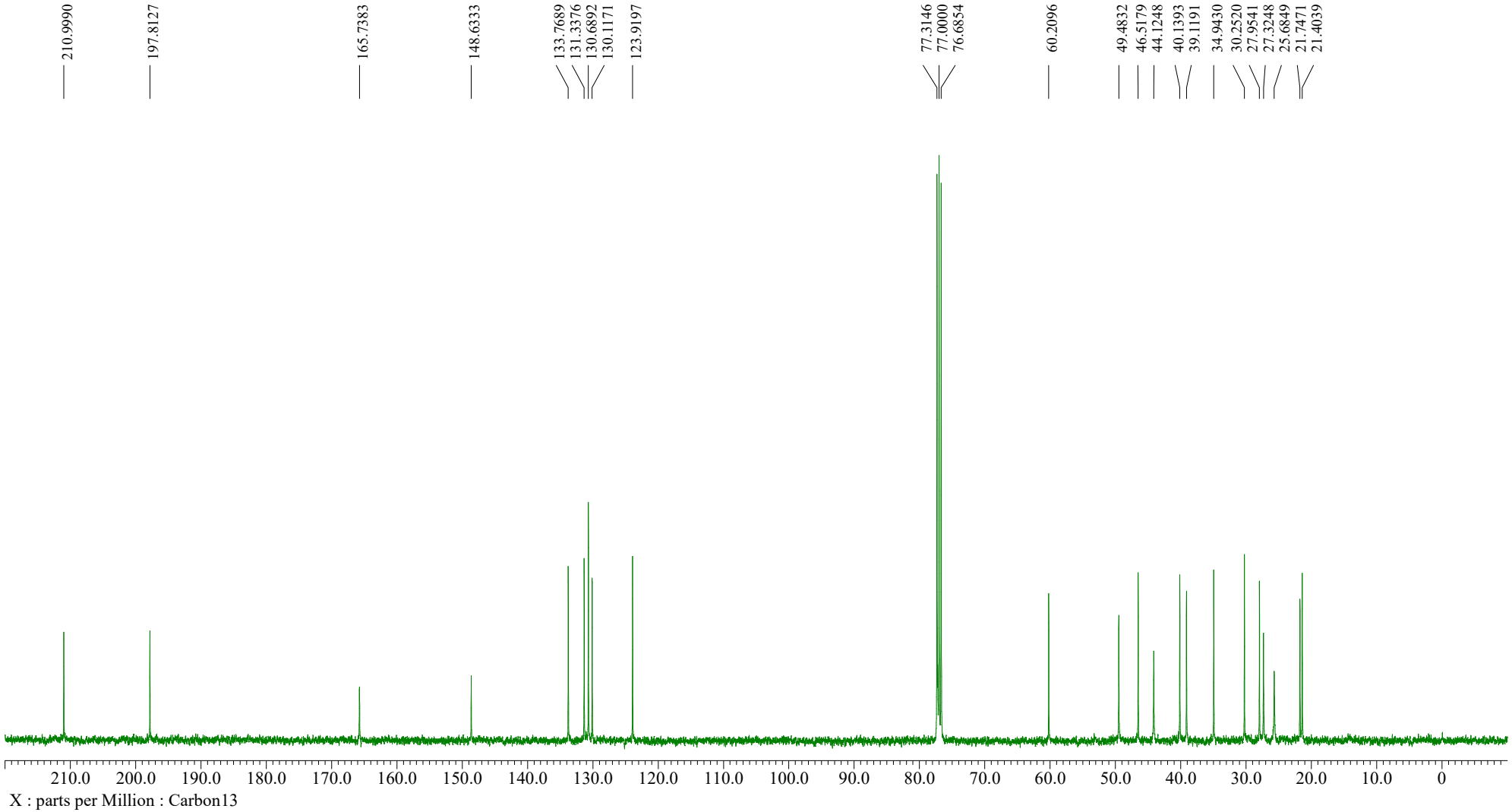
^{1}H NMR (400 MHz, $CDCl_3$)

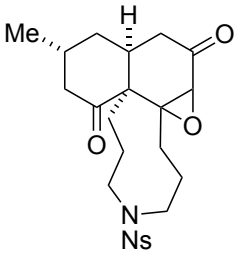




7

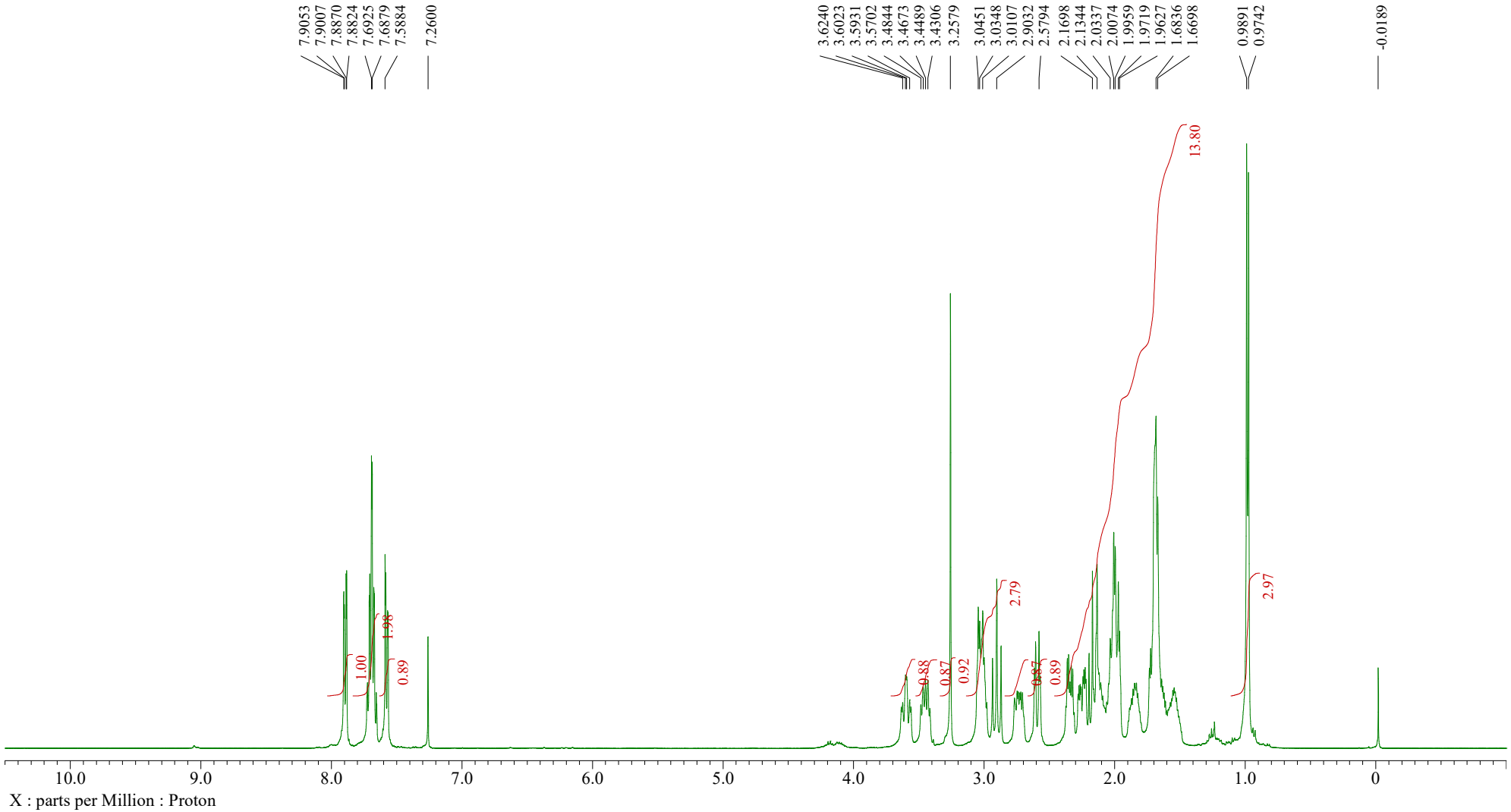
^{13}C NMR (100 MHz, $CDCl_3$)

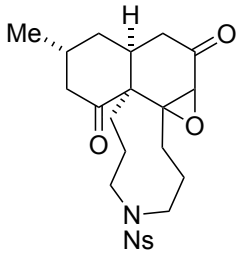




8

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

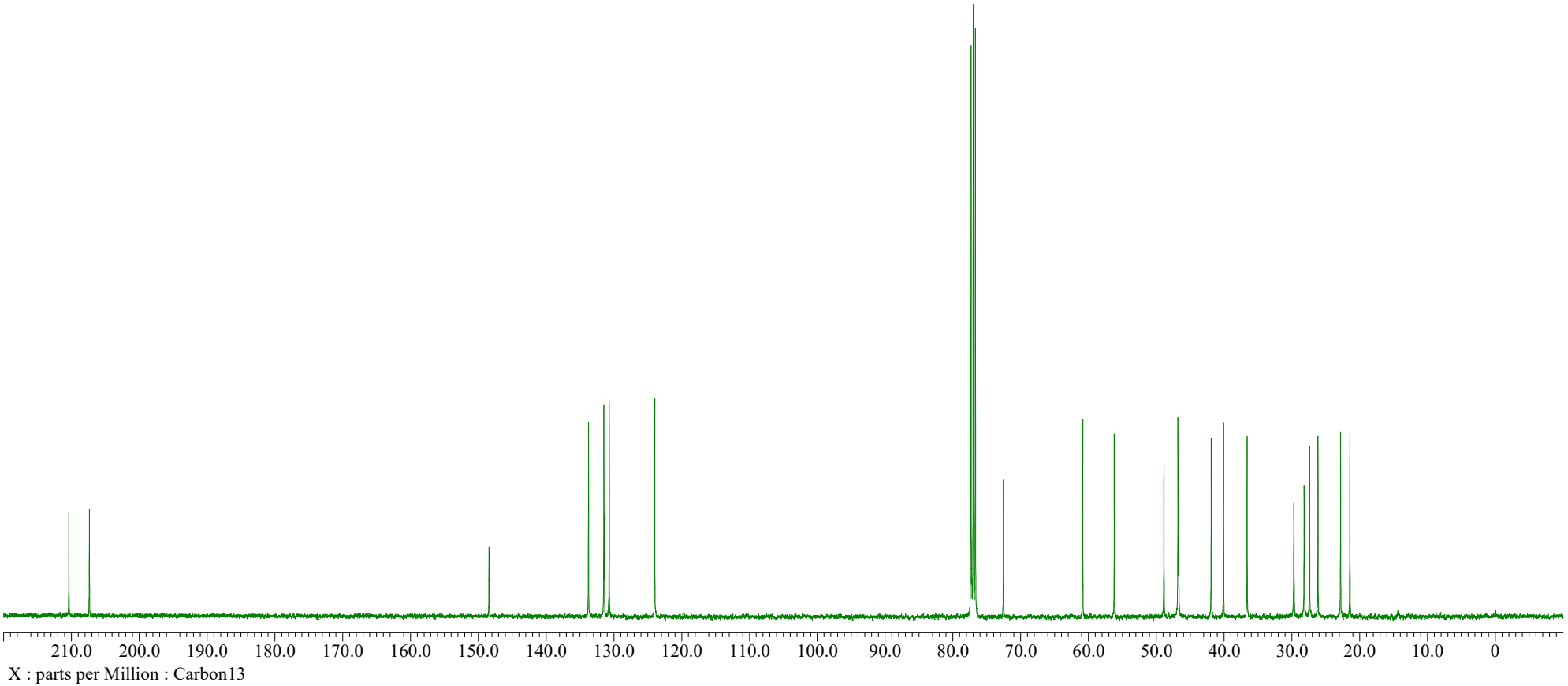


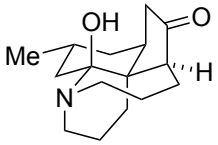


8

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

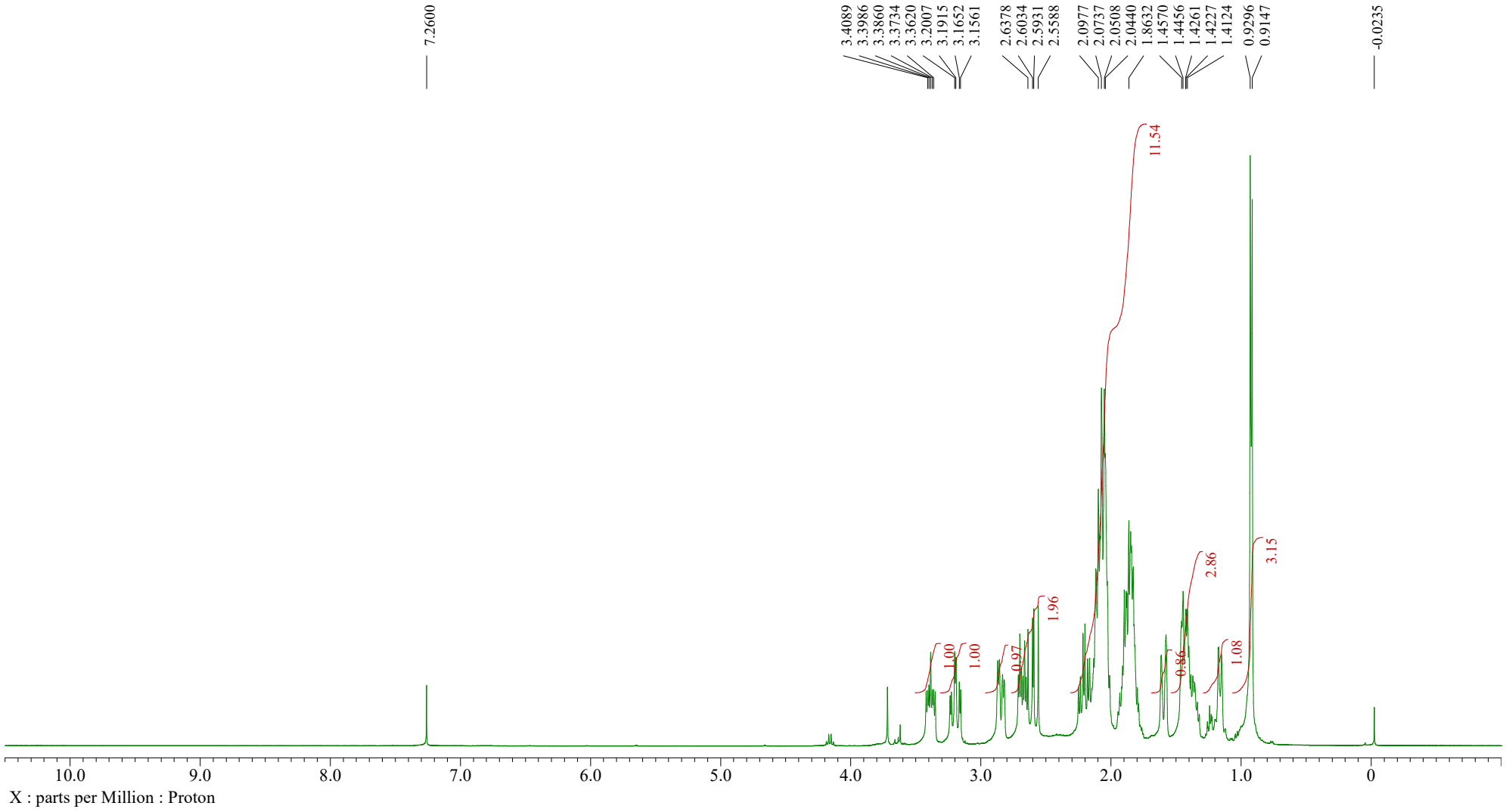
210.3697
207.3568
148.4140
133.7403
131.4901
131.4043
130.6892
123.9769
77.3146
77.0000
76.6854
72.5378
60.8484
56.2051
48.8730
46.8135
46.6991
41.9032
40.0821
36.6115
29.7085
28.1925
27.3916
26.1521
22.8150
21.4515

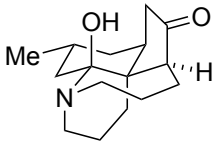




^{1}H NMR (400 MHz, $CDCl_3$)

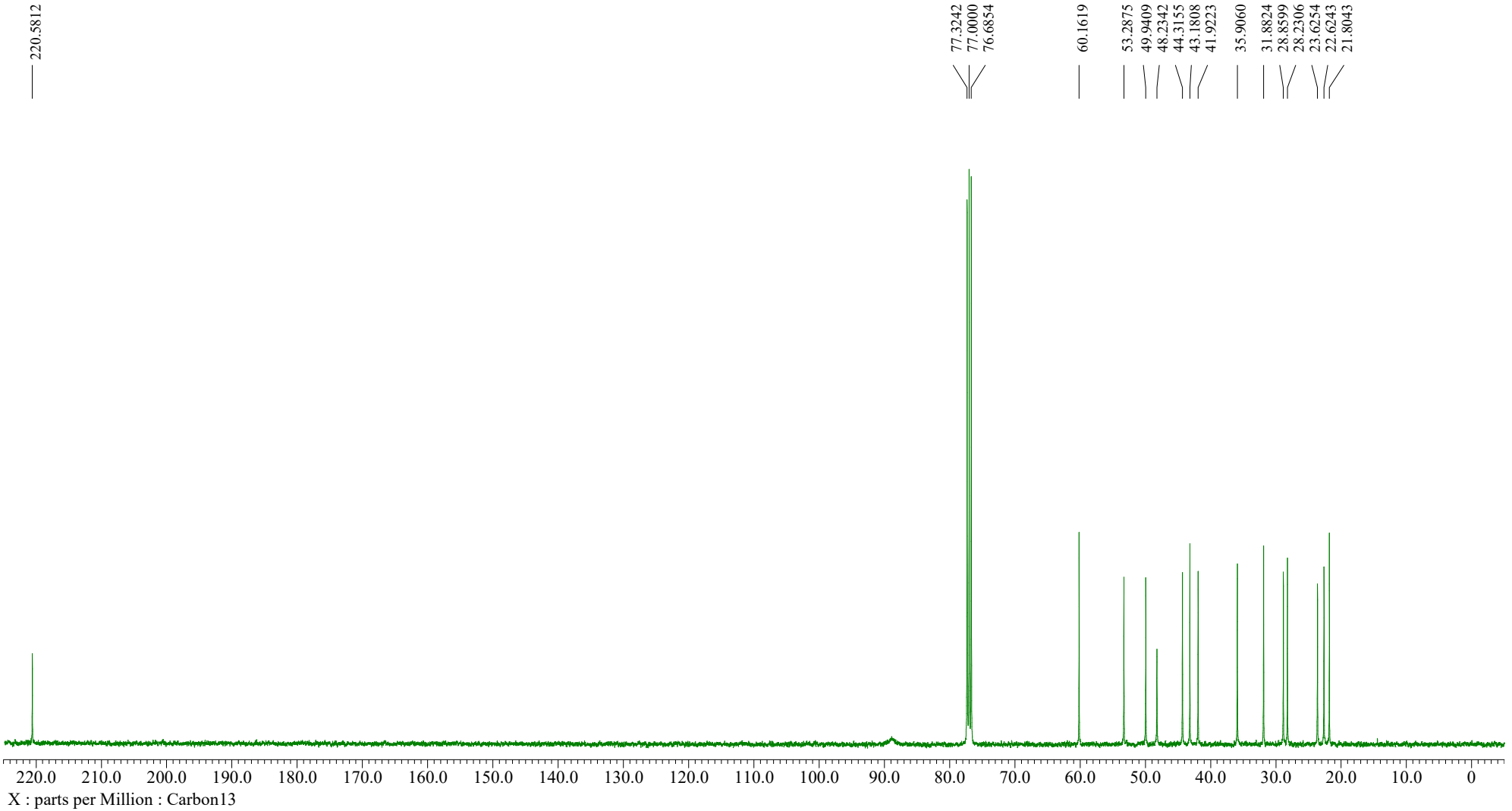
fawcettimine

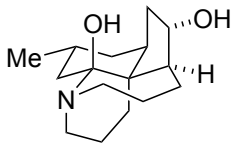




^{13}C NMR (100 MHz, $CDCl_3$)

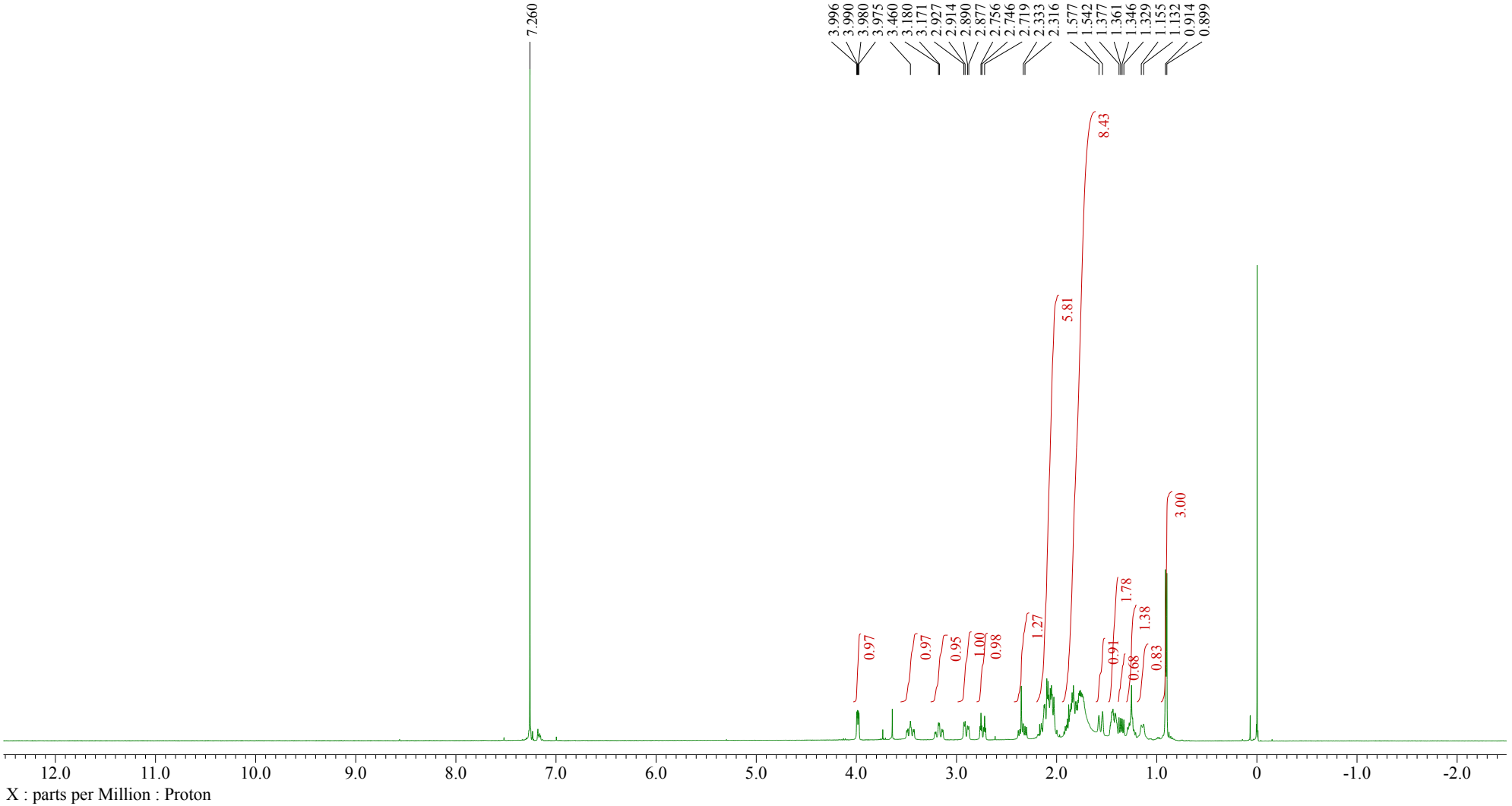
fawcettimine

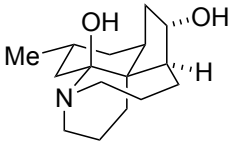




(±)-**10**

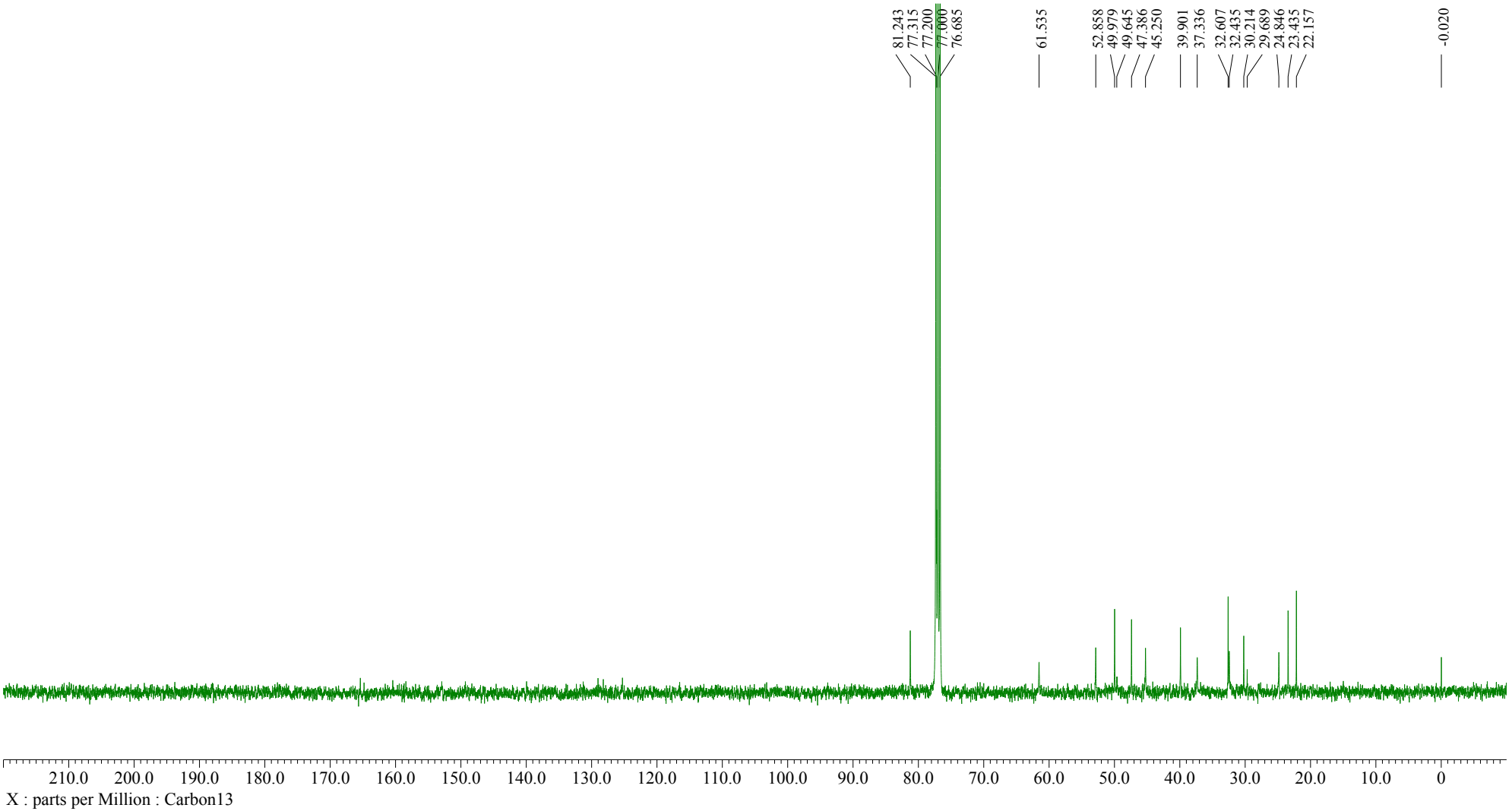
^{1}H NMR (400 MHz, $CDCl_3$)

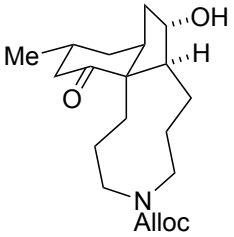




(±)-**10**

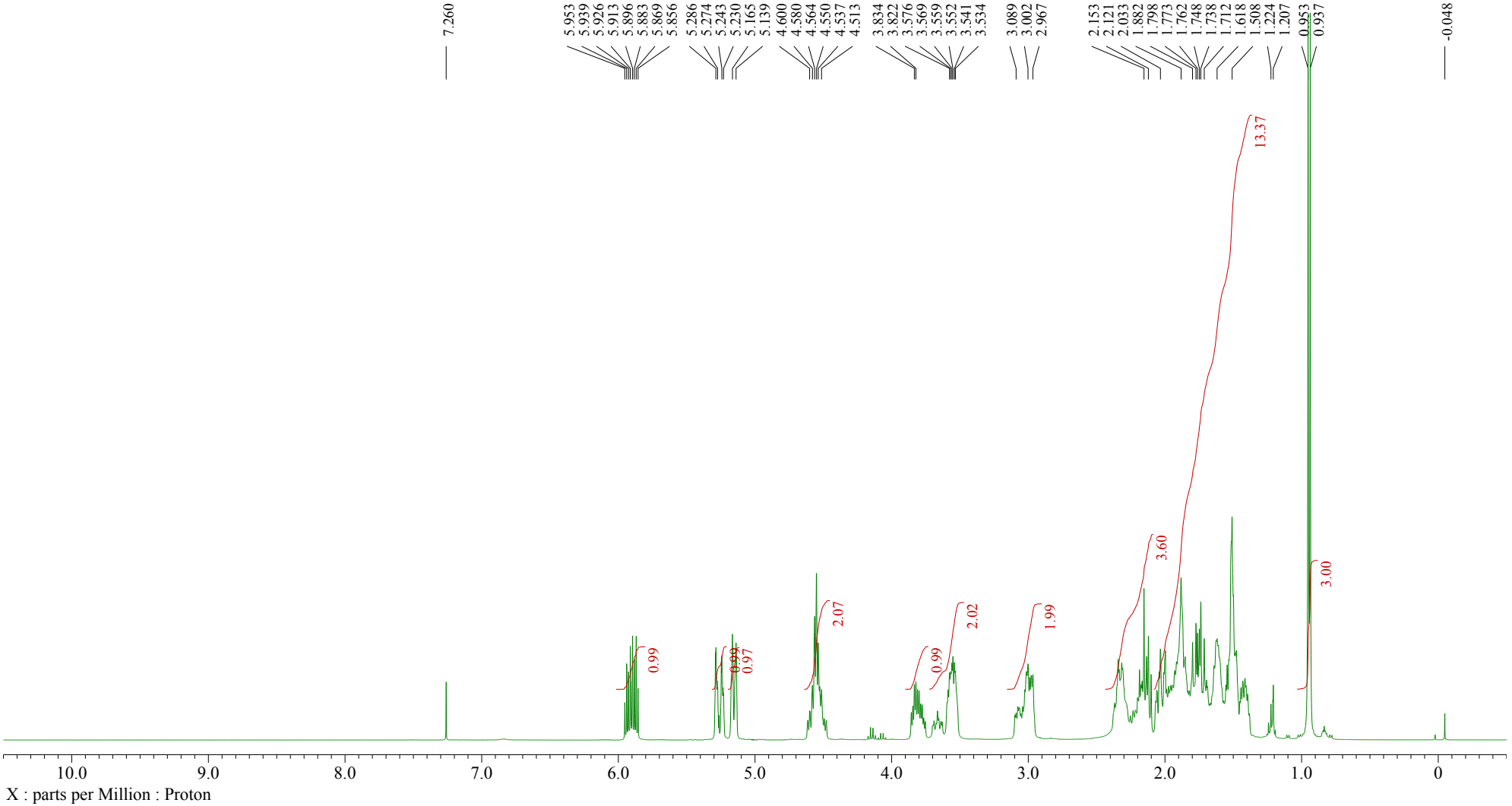
^{13}C NMR (100 MHz, $CDCl_3$)

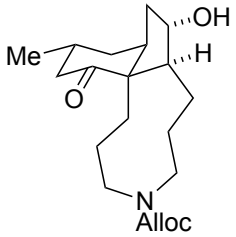




(±)-**11**

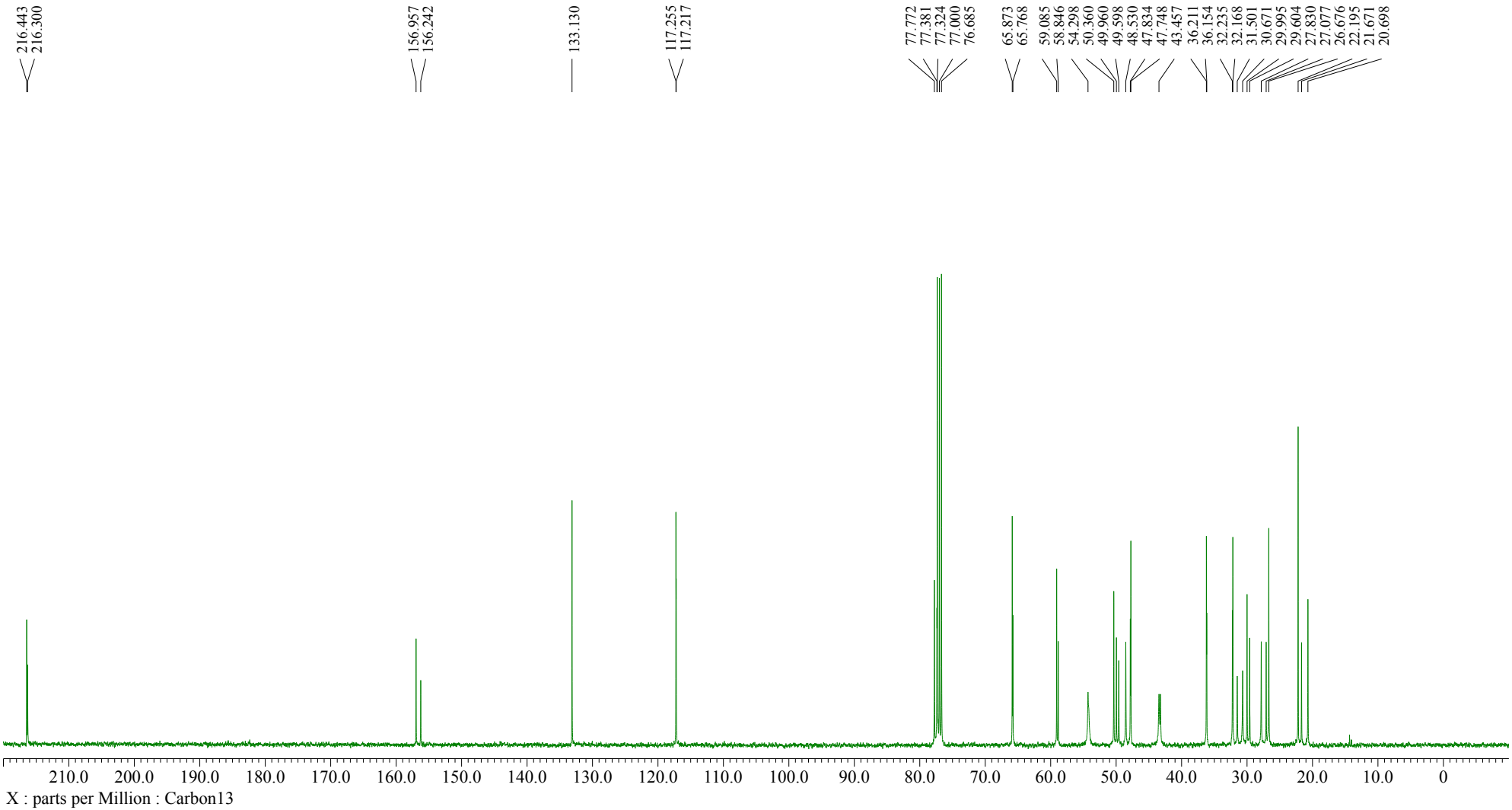
^{1}H NMR (400 MHz, $CDCl_3$)

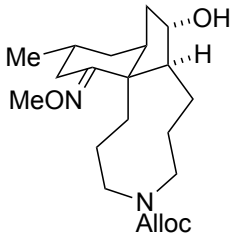




(±)-**11**

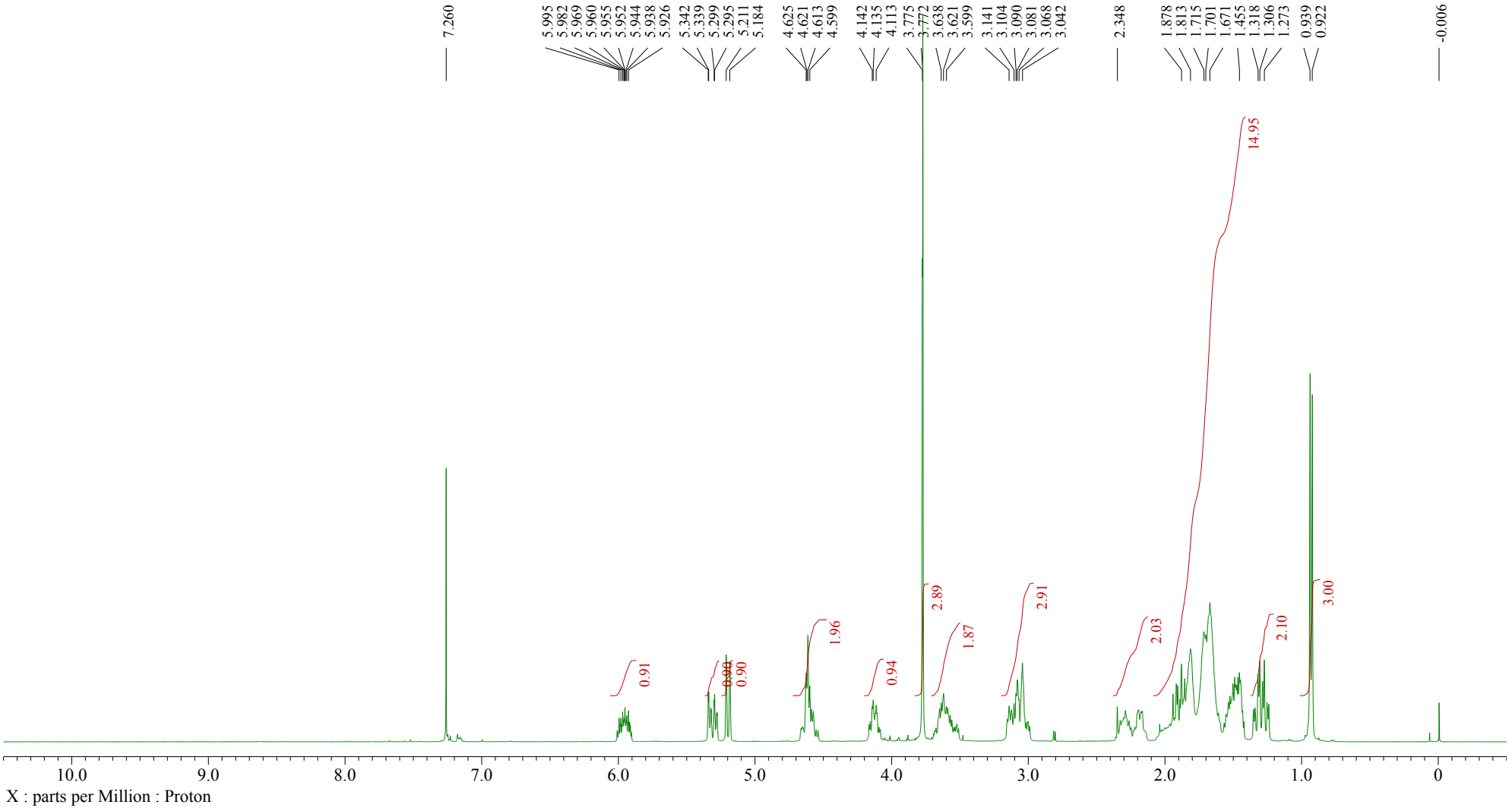
^{13}C NMR (100 MHz, $CDCl_3$)

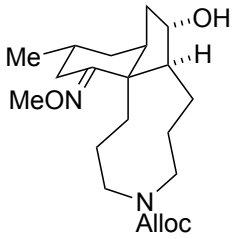




(±)-**12**

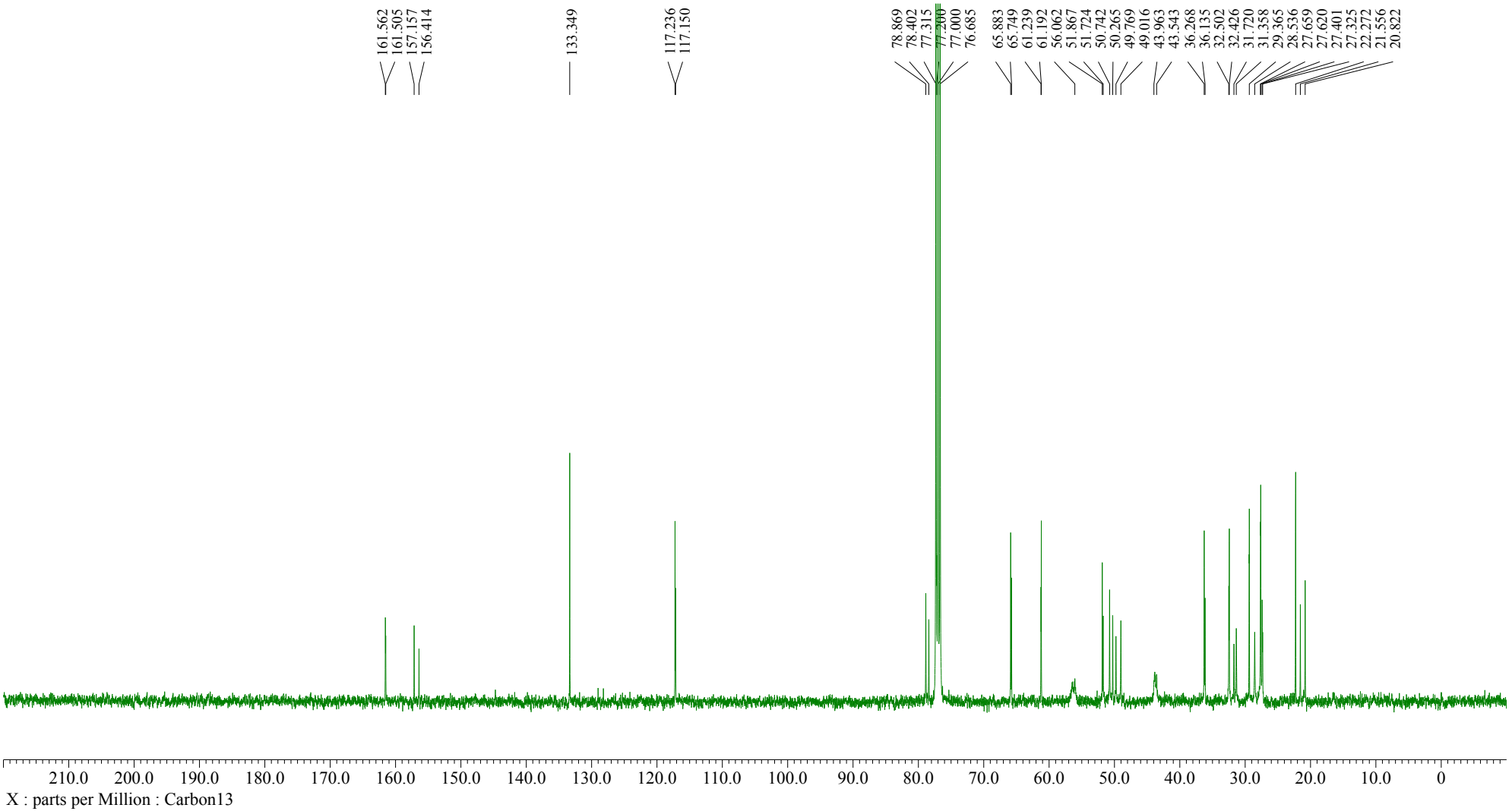
^{1}H NMR (400 MHz, $CDCl_3$)

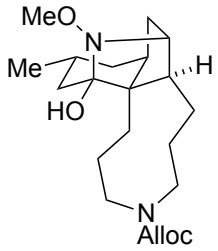




(±)-**12**

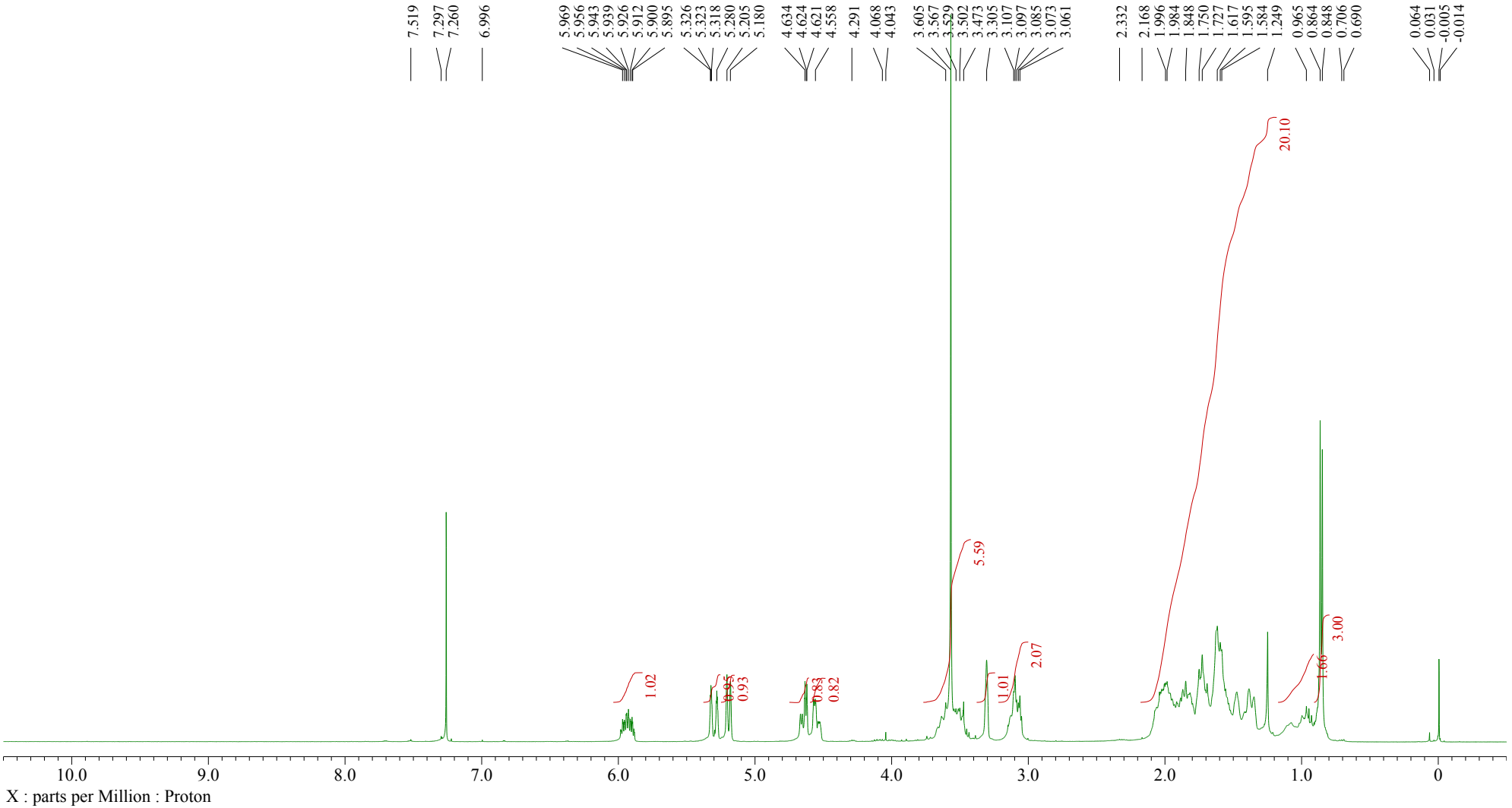
^{13}C NMR (100 MHz, $CDCl_3$)

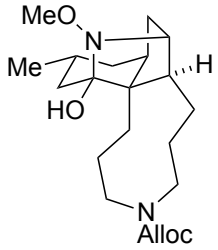




(±)-**15**

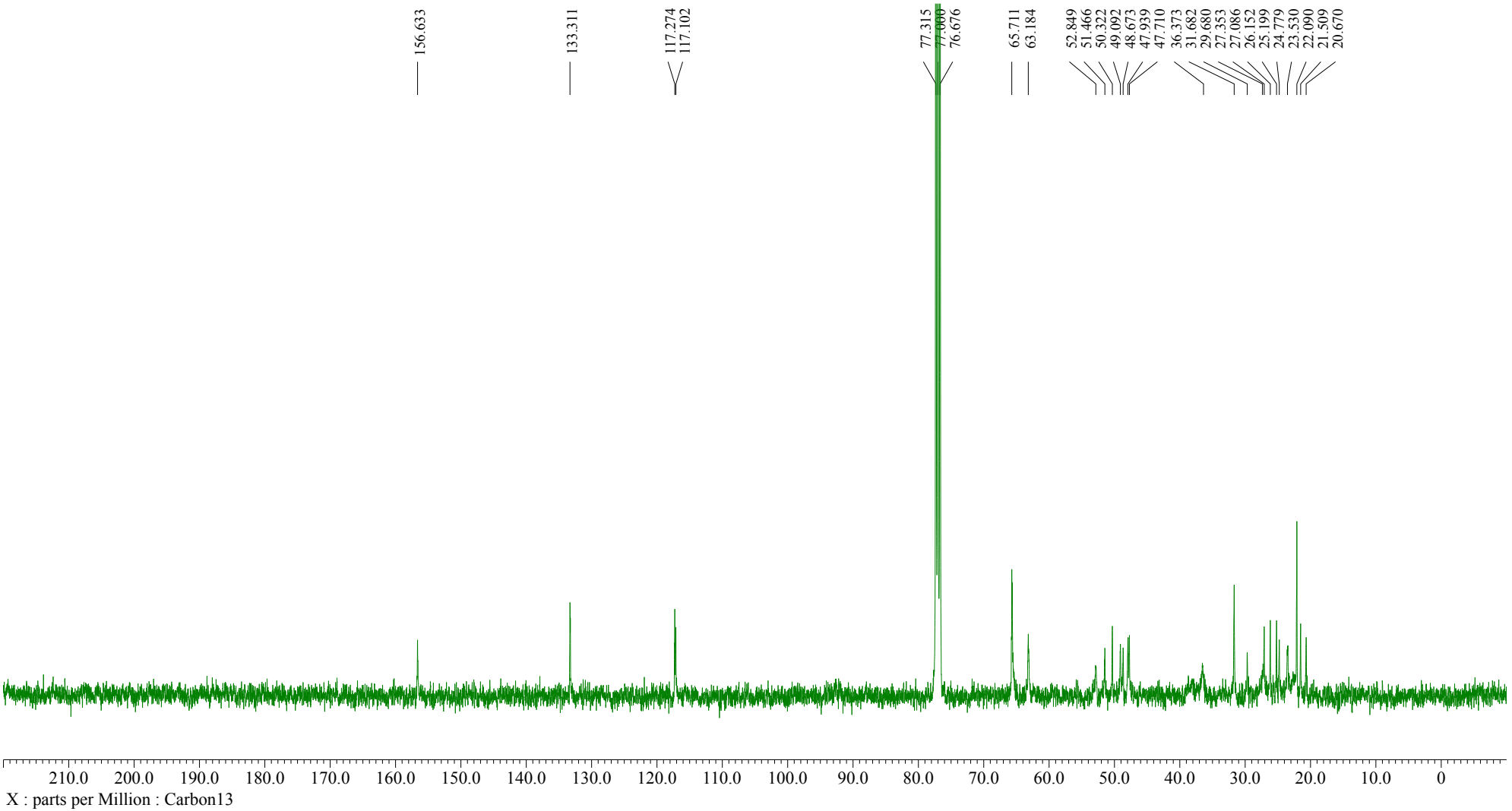
^{1}H NMR (400 MHz, $CDCl_3$)

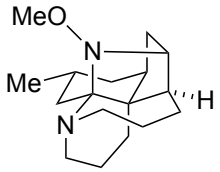




(±)-**15**

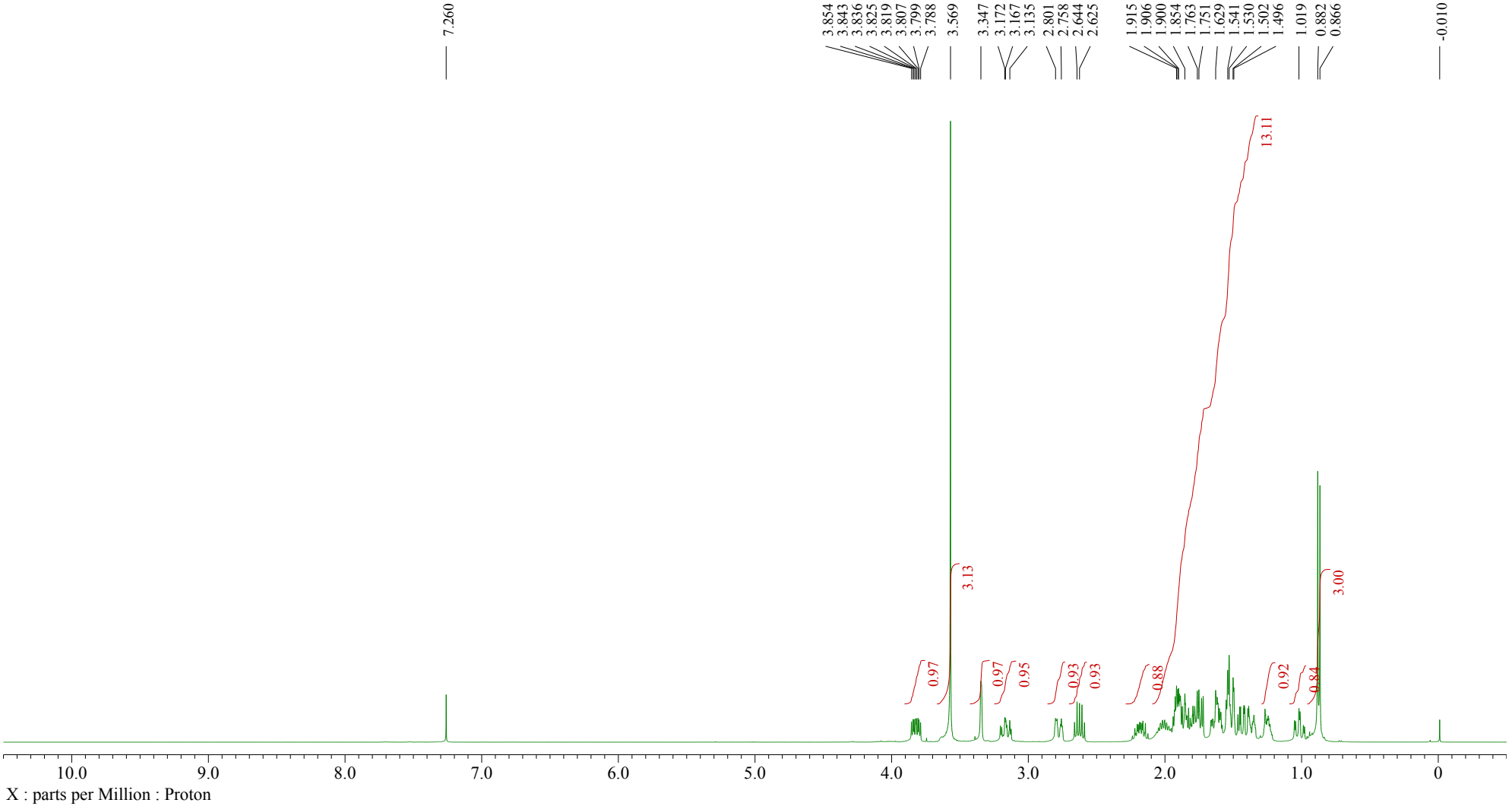
^{13}C NMR (100 MHz, $CDCl_3$)

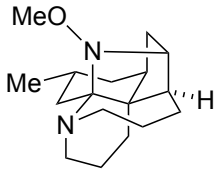




^{1}H NMR (400 MHz, $CDCl_3$)

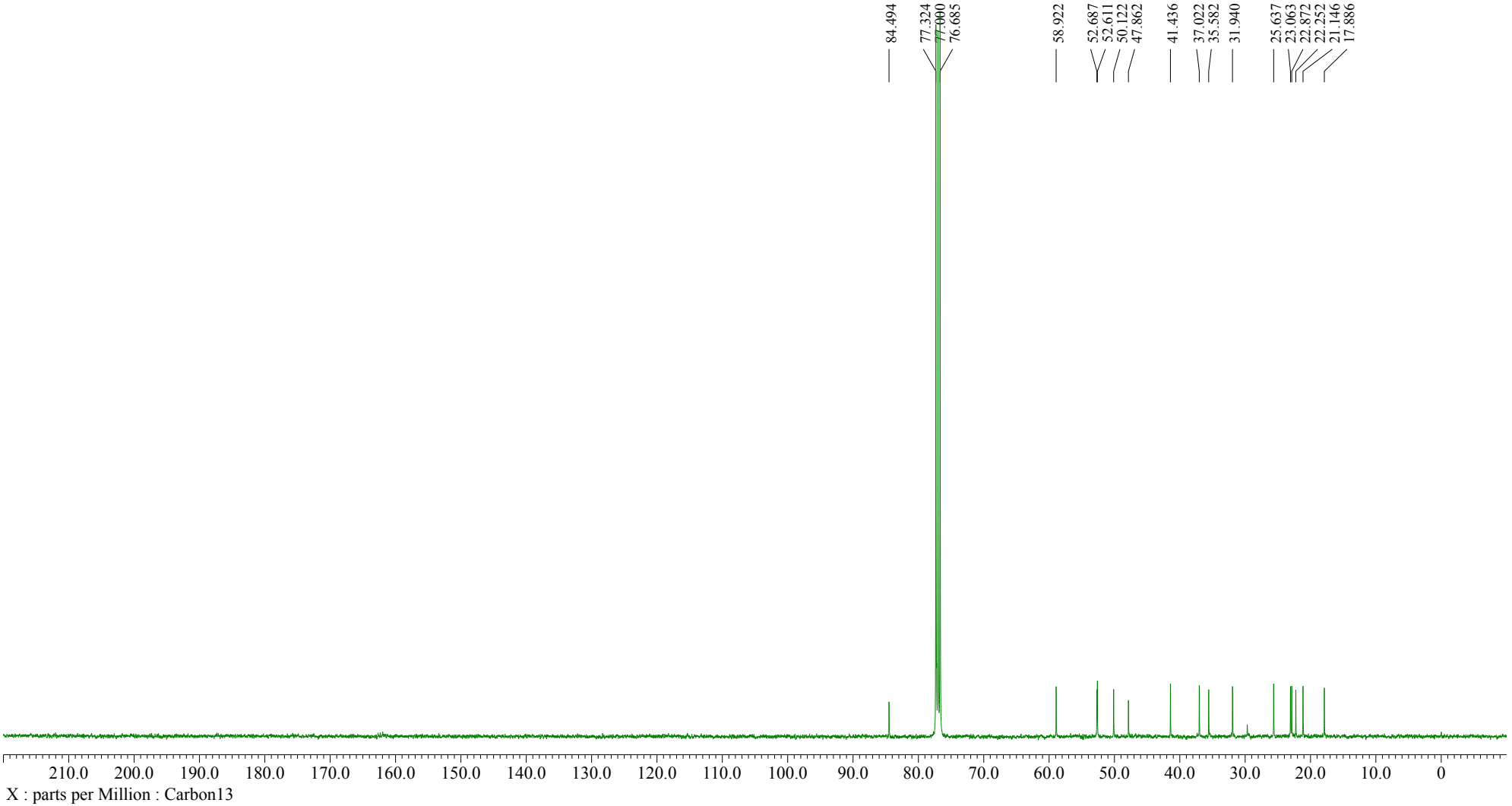
(±)-**16**

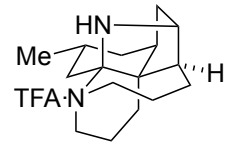




^{13}C NMR (100 MHz, $CDCl_3$)

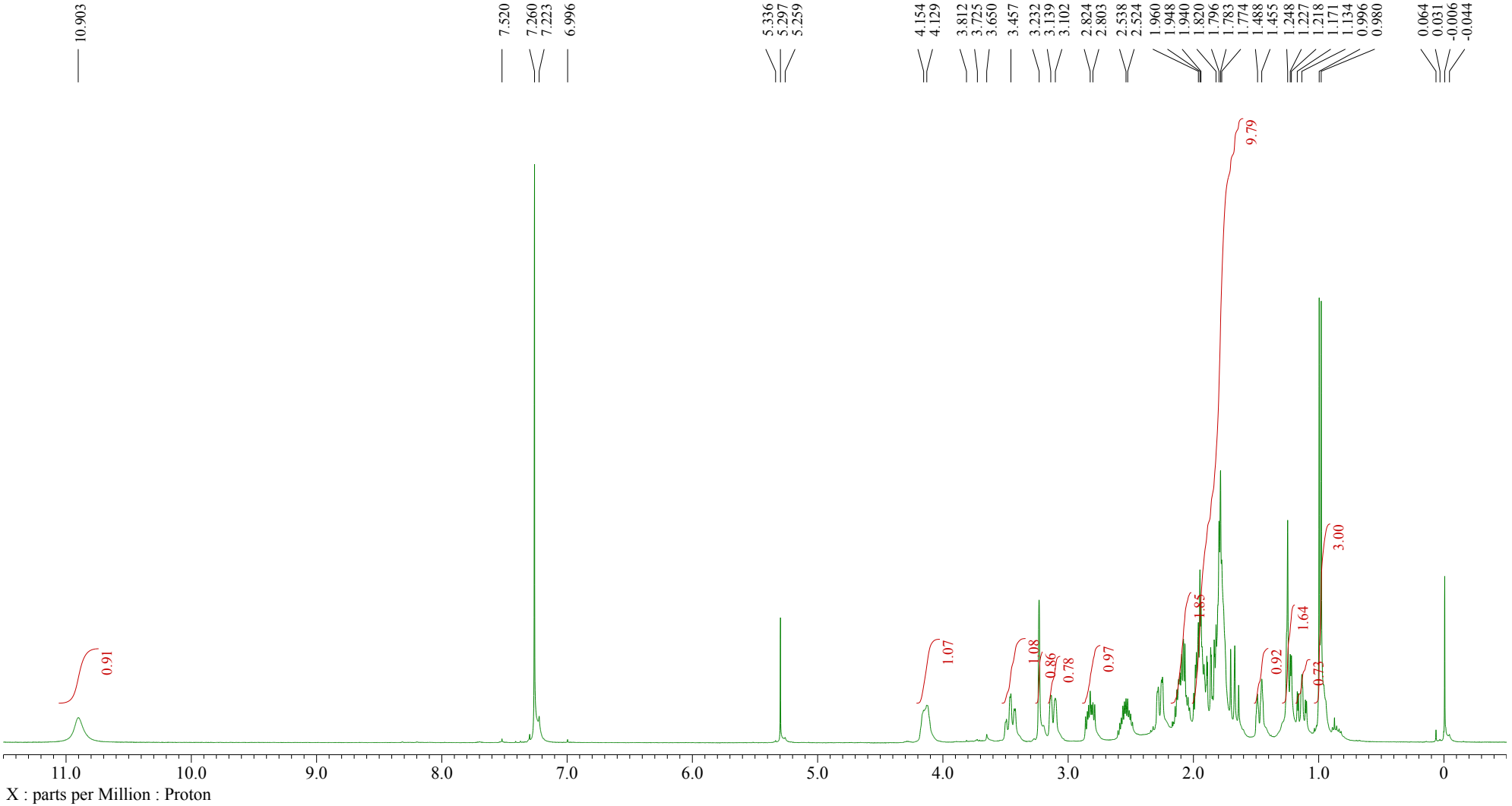
(±)-**16**

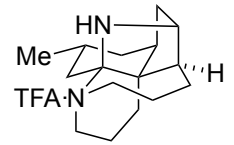




(±)-macleanine·TFA

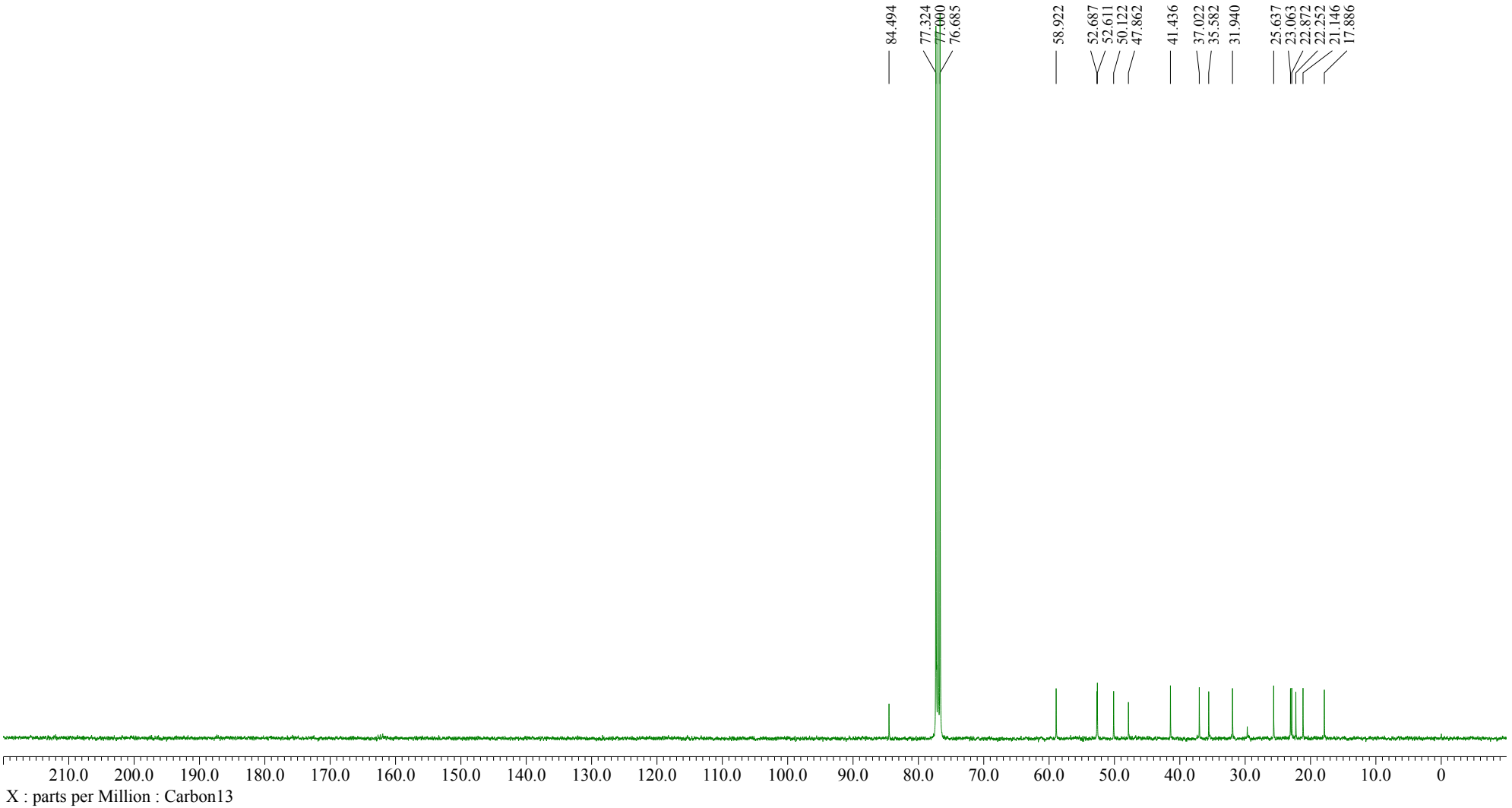
^{1}H NMR (400 MHz, $CDCl_3$)

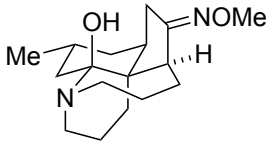




(±)-macleanine·TFA

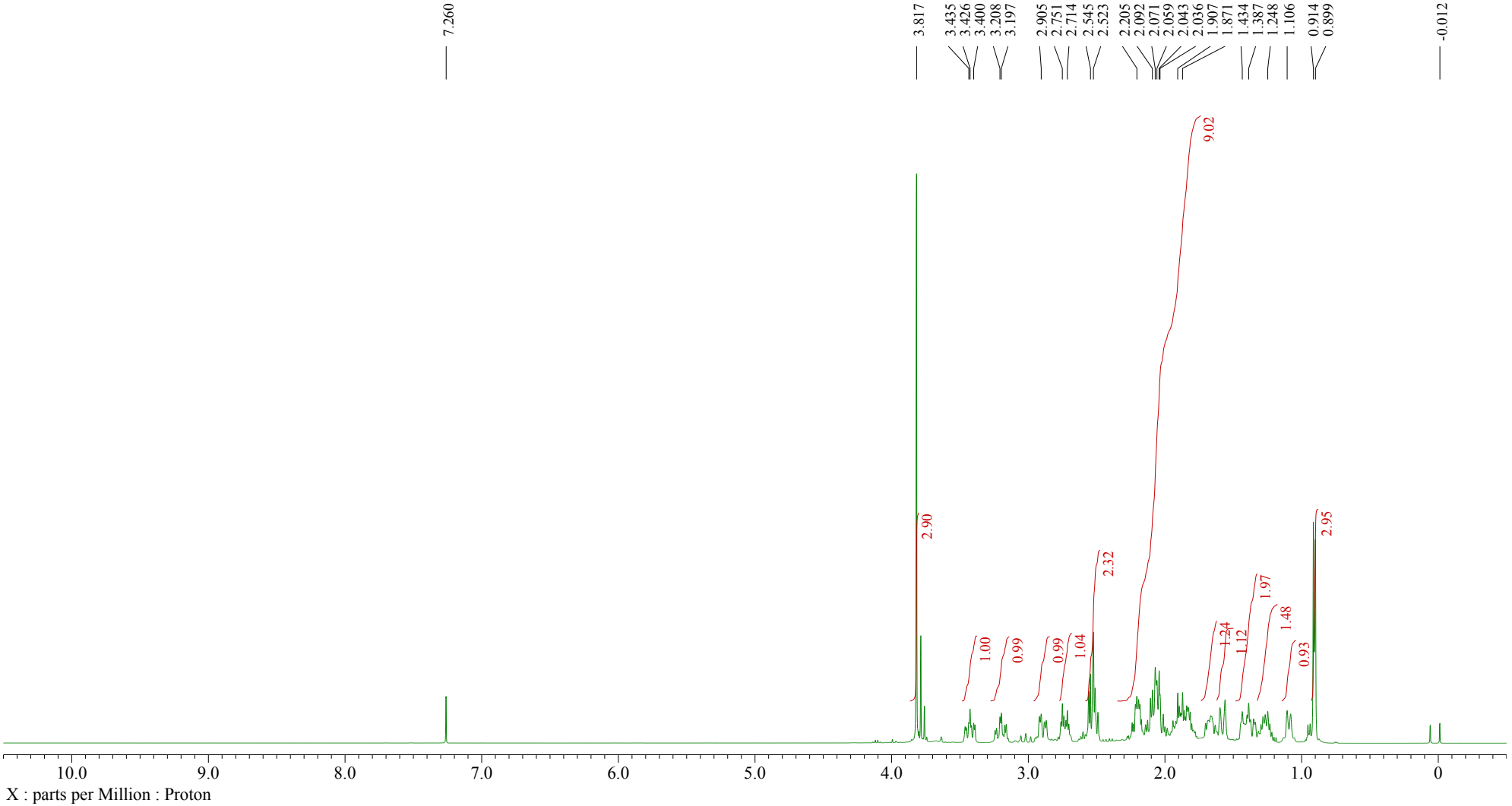
^{13}C NMR (100 MHz, $CDCl_3$)

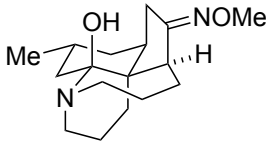




17

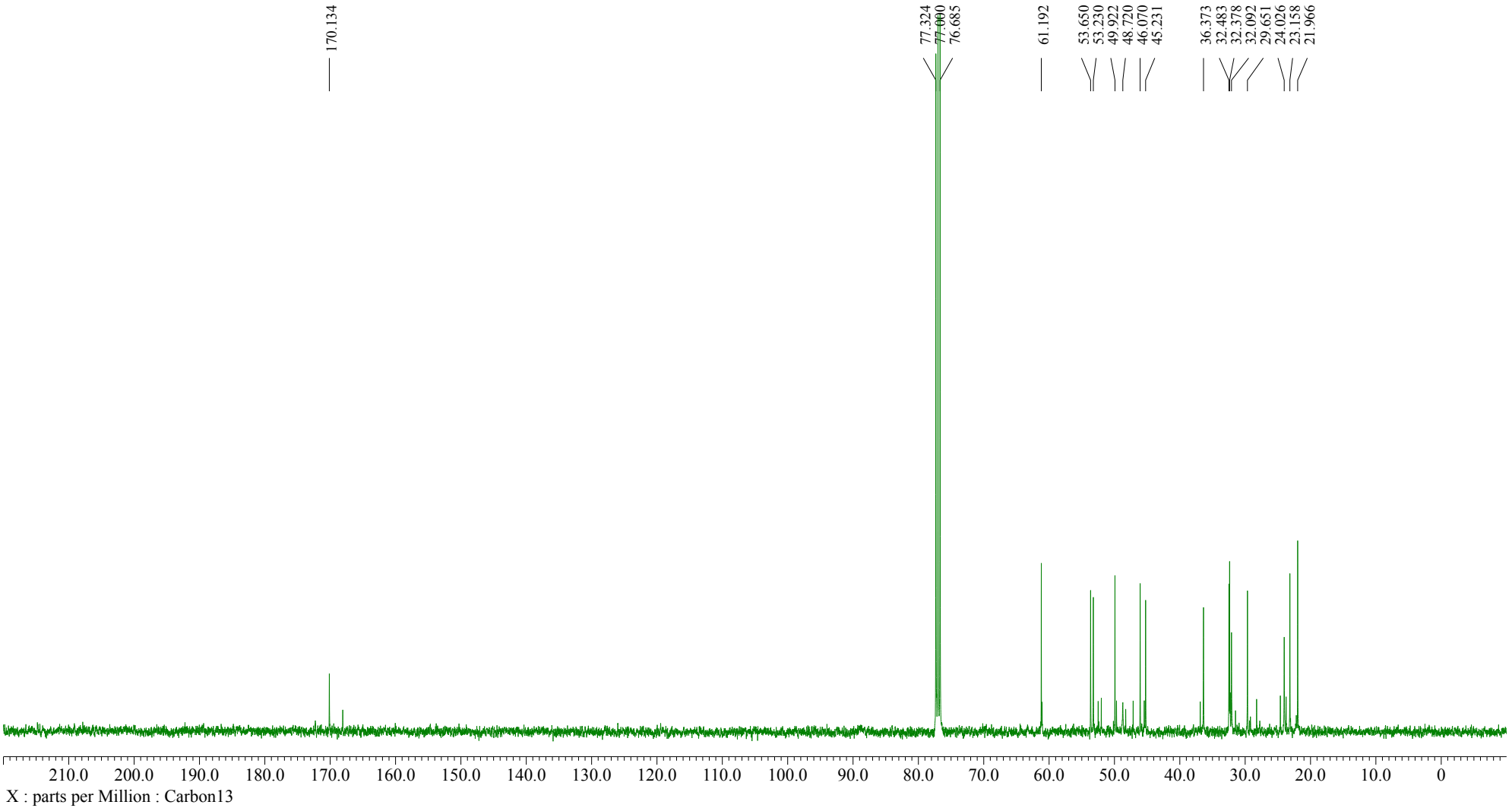
^{1}H NMR (400 MHz, $CDCl_3$)

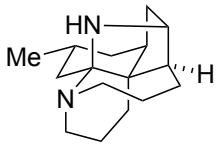




17

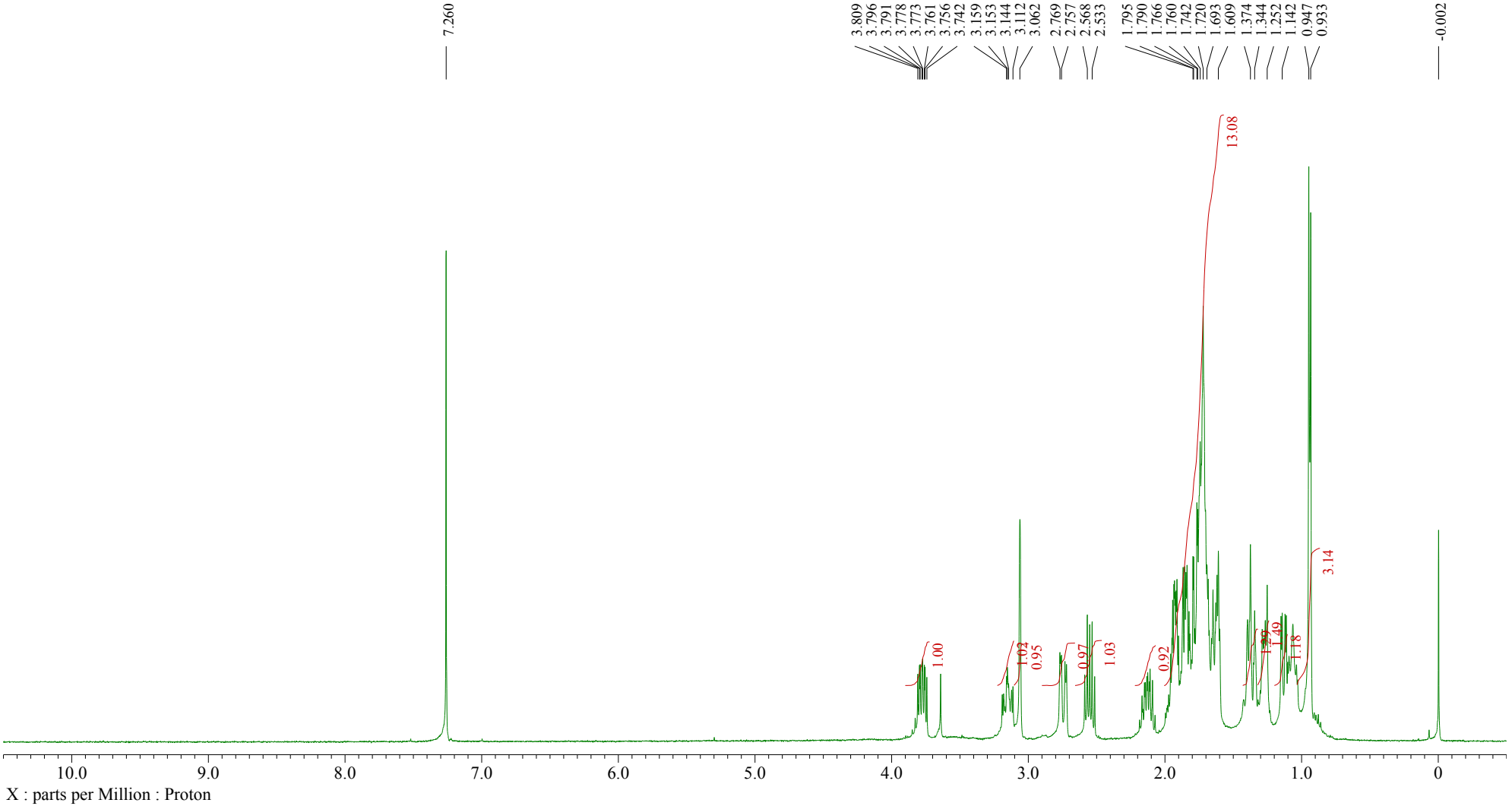
^{13}C NMR (100 MHz, $CDCl_3$)

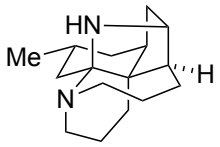




macleanine

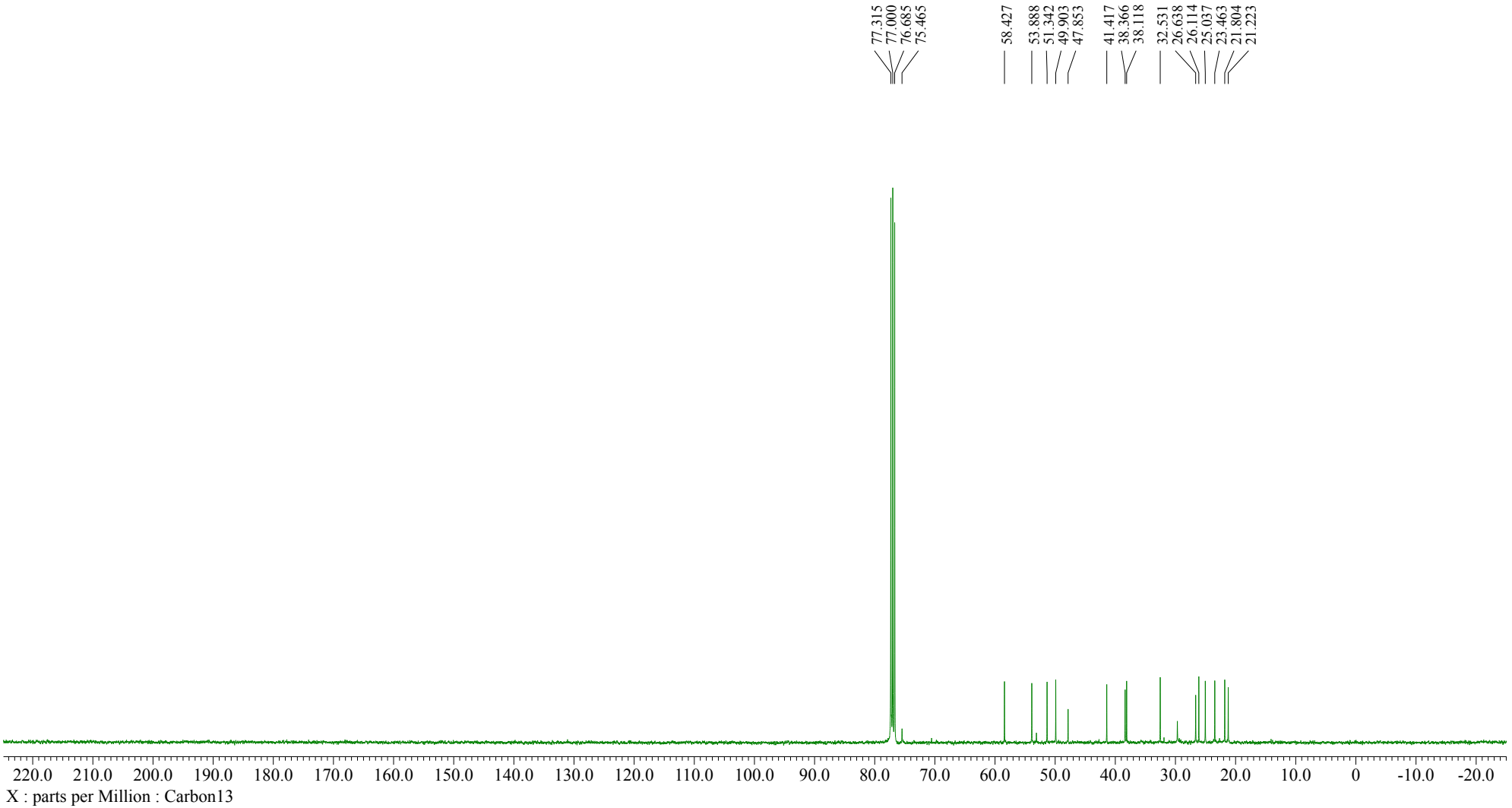
^{1}H NMR (400 MHz, $CDCl_3$)

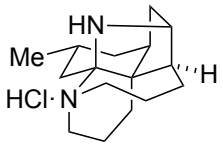




macleanine

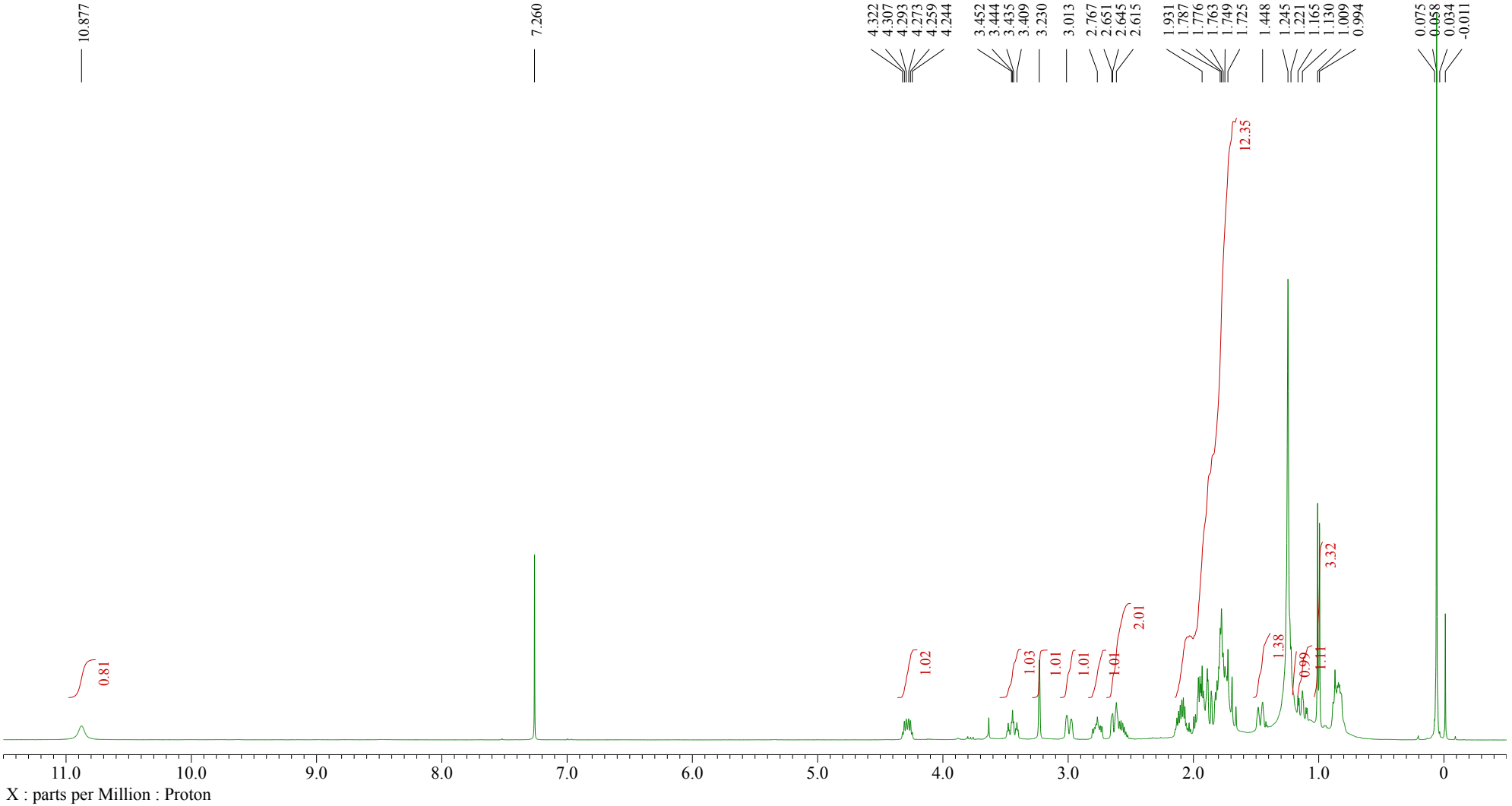
^{13}C NMR (100 MHz, $CDCl_3$)

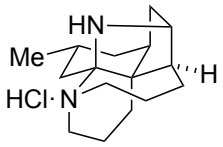




macleanine·HCl

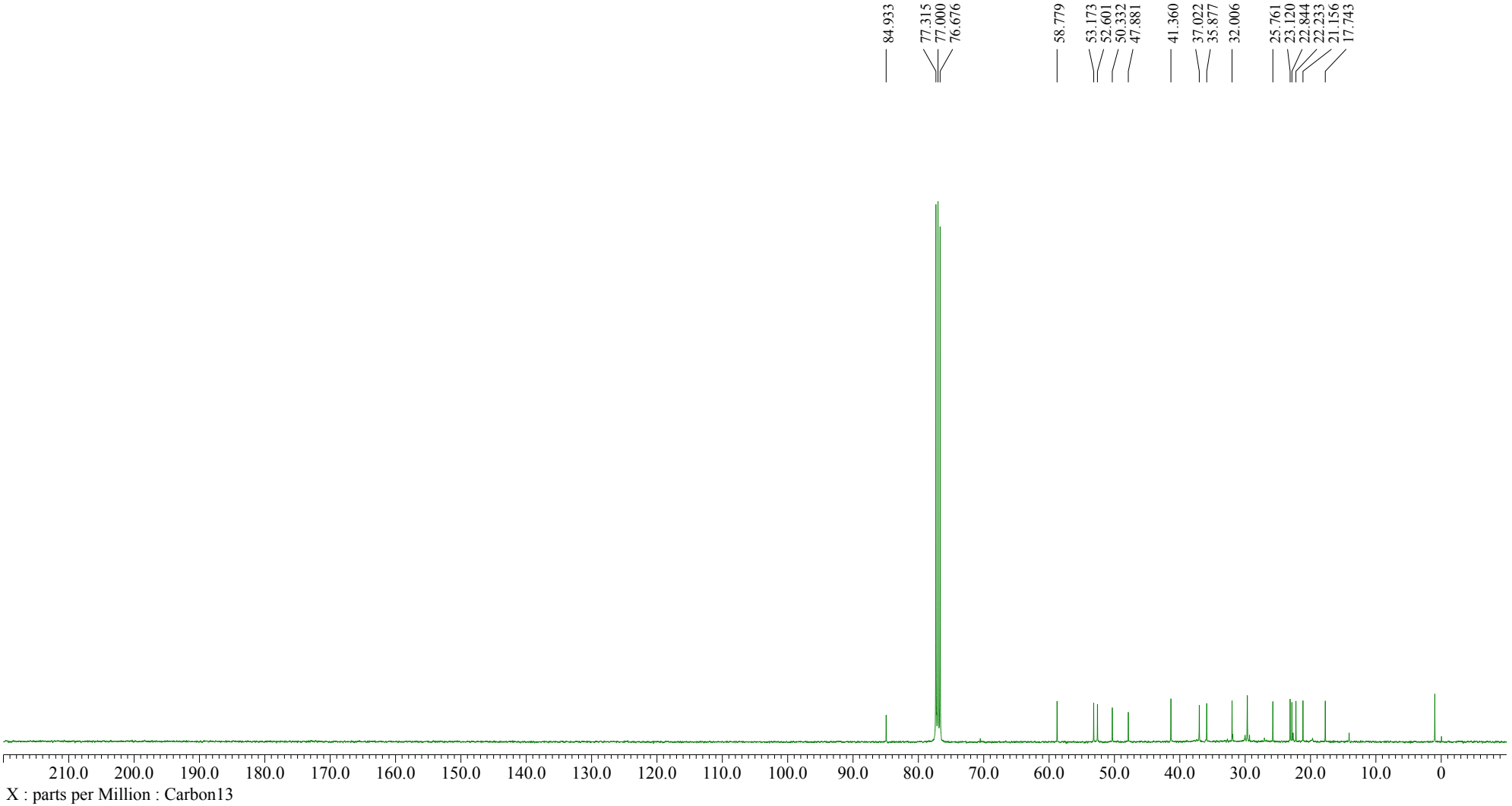
^{1}H NMR (400 MHz, $CDCl_3$)

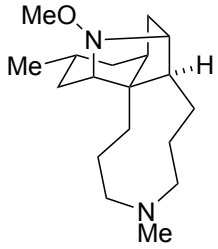




macleanine·HCl

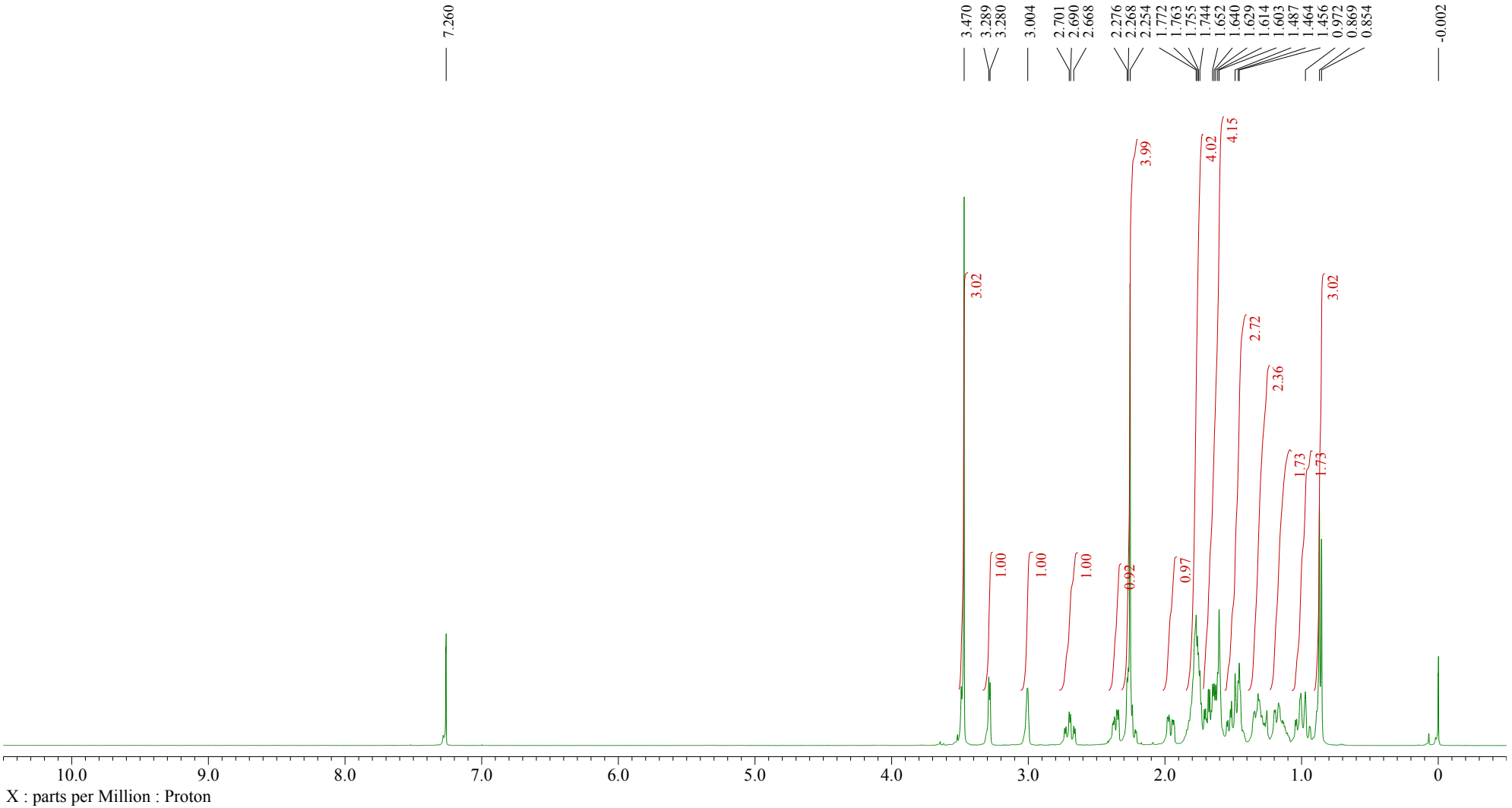
^{13}C NMR (100 MHz, $CDCl_3$)

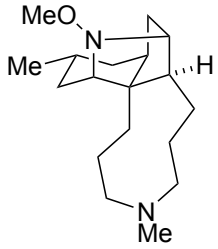




18

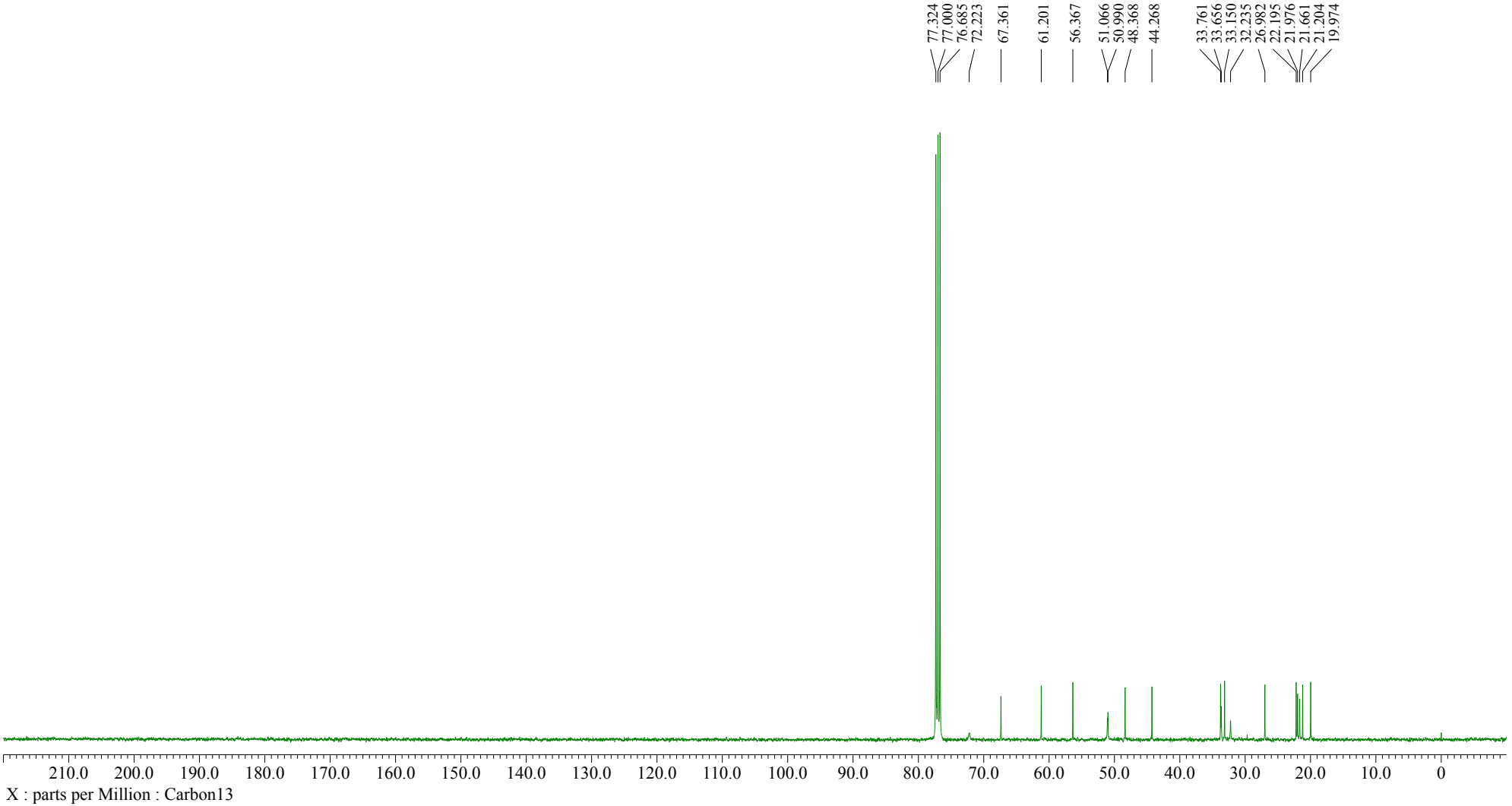
^{1}H NMR (400 MHz, $CDCl_3$)

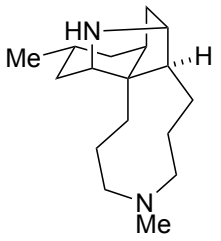




18

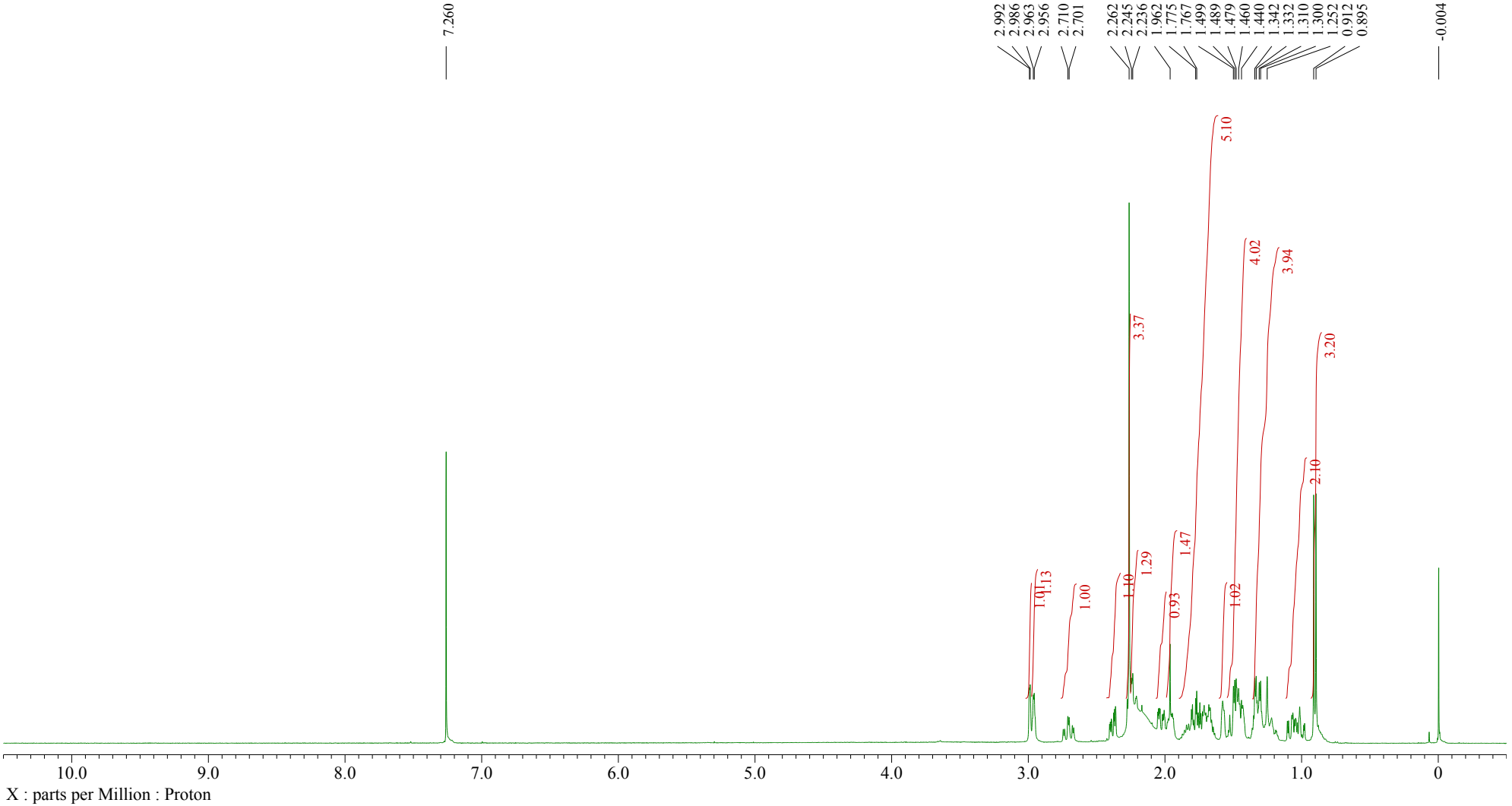
^{13}C NMR (100 MHz, $CDCl_3$)

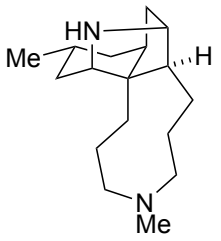




lycoposerramine-S

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





lycoposerramine-S

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